

Mats Hillert

Phase Equilibria, Phase Diagrams and Phase Transformations

Their Thermodynamic Basis

Second Edition

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Phase Equilibria, Phase Diagrams and Phase Transformations

Second Edition

Thermodynamic principles are central to understanding material behaviour, particularly as the application of these concepts underpins phase equilibrium, transformation and state. While this is a complex and challenging area, the use of computational tools has allowed the materials scientist to model and analyse increasingly convoluted systems more readily. In order to use and interpret such models and computed results accurately, a strong understanding of the basic thermodynamics is required.

This fully revised and updated edition covers the fundamentals of thermodynamics, with a view to modern computer applications. The theoretical basis of chemical equilibria and chemical changes is covered with an emphasis on the properties of phase diagrams. Starting with the basic principles, discussion moves to systems involving multiple phases. New chapters cover irreversible thermodynamics, extremum principles and the thermodynamics of surfaces and interfaces. Theoretical descriptions of equilibrium conditions, the state of systems at equilibrium and the changes as equilibrium is reached, are all demonstrated graphically. With illustrative examples – many computer calculated – and exercises with solutions, this textbook is a valuable resource for advanced undergraduate and graduate students in materials science and engineering.

Additional information on this title, including further exercises and solutions, is available at www.cambridge.org/9780521853514. The commercial thermodynamic package ‘Thermo-Calc’ is used throughout the book for computer applications; a link to a limited free of charge version can be found at the above website and can be used to solve the further exercises. In principle, however, a similar thermodynamic package can be used.

MATS HILLERT is a Professor Emeritus at KTH (Royal Institute of Technology) in Stockholm.

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Their Thermodynamic Basis

Second Edition

MATS HILLERT

Department of Materials Science and Engineering KTH, Stockholm



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Preface to second edition

The requirement of the second law that the internal entropy production must be positive for all spontaneous changes of a system results in the equilibrium condition that the entropy production must be zero for all conceivable internal processes. Most thermodynamic textbooks are based on this condition but do not discuss the magnitude of the entropy production for processes. In the first edition the entropy production was retained in the equations as far as possible, usually in the form of $Dd\xi$ where D is the driving force for an isothermal process and ξ is its extent. It was thus possible to discuss the magnitude of the driving force for a change and to illustrate it graphically in molar Gibbs energy diagrams. In other words, the driving force for irreversible processes was an important feature of the first edition. Two chapters have now been added in order to include the theoretical treatment of how the driving force determines the rate of a process and how simultaneous processes can affect each other. This field is usually defined as irreversible thermodynamics. The mathematical description of diffusion is an important application for materials science and is given special attention in those two new chapters. Extremum principles are also discussed.

A third new chapter is devoted to the thermodynamics of surfaces and interfaces. The different roles of surface energy and surface stress in solids are explained in detail, including a treatment of critical nuclei. The thermodynamic effects of different types of coherency stresses are outlined and the effect of segregated atoms on the migration of interfaces, so-called solute drag, is discussed using a general treatment applicable to grain boundaries and phase interfaces.

The three new chapters are the results of long and intensive discussions and collaboration with Professor John Ågren and could not have been written without that input. Thanks are also due to several researchers in his department who have been extremely open to discussions and even collaboration. In particular, thanks are due to Dr Malin Selleby who has again given invaluable input by providing the large number of computer-calculated diagrams. They are easily recognized by the triangular *Thermo-Calc* logotype. Those diagrams demonstrate that thermodynamic equations can be directly applied without any new programming. The author hopes that the present textbook will inspire scientists and engineers, professors and students to more frequent use of thermodynamics to solve problems in materials science.

A large number of solved exercises are also available online from the Cambridge University Press website (www.cambridge.org/9780521853514). In addition, the website contains a considerable number of exercises to be solved by the reader using a link to a limited free-of-charge version of the commercial thermodynamic package Thermo-Calc. In principle, they could be solved on a similar thermodynamic package.

Preface to first edition

Thermodynamics is an extremely powerful tool applicable to a wide range of science and technology. However, its full potential has been utilized by relatively few experts and the practical application of thermodynamics has often been based simply on dilute solutions and the law of mass action. In materials science the main use of thermodynamics has taken place indirectly through phase diagrams. These are based on thermodynamic principles but, traditionally, their determination and construction have not made use of thermodynamic calculations, nor have they been used fully in solving practical problems. It is my impression that the role of thermodynamics in the teaching of science and technology has been declining in many faculties during the last few decades, and for good reasons. The students experience thermodynamics as an abstract and difficult subject and very few of them expect to put it to practical use in their future career.

Today we see a drastic change of this situation which should result in a dramatic increase of the use of thermodynamics in many fields. It may result in thermodynamics regaining its traditional role in teaching. The new situation is caused by the development both of computer-operated programs for sophisticated equilibrium calculations and extensive databases containing assessed thermodynamic parameter values for individual phases from which all thermodynamic properties can be calculated. Experts are needed to develop the mathematical models and to derive the numerical values of all the model parameters from experimental information. However, once the fundamental equations are available, it will be possible for engineers with limited experience to make full use of thermodynamic calculations in solving a variety of complicated technical problems. In order to do this, it will not be necessary to remember much from a traditional course in thermodynamics. Nevertheless, in order to use the full potential of the new facilities and to avoid making mistakes, it is still desirable to have a good understanding of the basic principles of thermodynamics. The present book has been written with this new situation in mind. It does not provide the reader with much background in numerical calculation but should give him/her a solid basis for an understanding of the thermodynamic principles behind a problem, help him/her to present the problem to the computer and allow him/her to interpret the computer results.

The principles of thermodynamics were developed in an admirably logical way by Gibbs but he only considered equilibria. It has since been demonstrated, e.g. by Prigogine and Defay, that classical thermodynamics can also be applied to systems not at equilibrium whereby the affinity (or driving force) for an internal process is evaluated as an ordinary thermodynamic quantity. I have followed that approach by introducing a


clear distinction between external variables and internal variables referring to entropy-producing internal processes. The entropy production is retained when the first and second laws are combined and the driving force for internal processes then plays a central role throughout the development of the thermodynamic principles. In this way, the driving force appears as a natural part of the thermodynamic application ‘tool’.

Computerized calculations of equilibria can easily be directed to yield various types of diagram, and phase diagrams are among the most useful. The computer provides the user with considerable freedom of choice of axis variables and in the sectioning and projection of a multicomponent system, which is necessary for producing a two-dimensional diagram. In order to make good use of this facility, one should be familiar with the general principles of phase diagrams. Thus, a considerable part of the present book is devoted to the inter-relations between thermodynamics and phase diagrams. Phase diagrams are also used to illustrate the character of various types of phase transformations. My ambition has been to demonstrate the important role played by thermodynamics in the study of phase transformations.

I have tried to develop thermodynamics without involving the special properties of particular kinds of phases, but have found it necessary sometimes to use the ideal gas or the regular solution to illustrate principles. However, even though thermodynamic models and derived model parameters are already stored in databases, and can be used without the need to inspect them, it is advantageous to have some understanding of thermodynamic modelling. The last few chapters are thus devoted to this subject. Simple models are discussed, not because they are the most useful or popular, but rather as illustrations of how modelling is performed.

Many sections may give the reader little stimulation but may be valuable as reference material for later parts of the book or for future work involving thermodynamic applications. The reader is advised to peruse such sections very quickly, but to remember that this material is available for future consultation.

Practically every section ends with at least one exercise and the accompanying solution. These exercises often contain material that could have been included in the text, but would have made the text too massive. The reader is advised not to study such exercises until a more thorough understanding of the content of a particular section is required.

This book is the result of a long period of research and teaching, centred on thermodynamic applications in materials science. It could not have been written without the inspiration and help received through contacts with numerous students and colleagues. Special thanks are due to my former students, Professor Bo Sundman and Docent Bo Jansson, whose development of the Thermo-Calc data bank system has inspired me to penetrate the underlying thermodynamic principles and has made me aware of many important questions. Thanks are also due to Dr Malin Selleby for producing a large number of diagrams by skilful operation of Thermo-Calc. All her diagrams in this book can be identified by the use of the Thermo-Calc logotype, .

Mats Hillert
Stockholm

1 Basic concepts of thermodynamics

1.1 External state variables

Thermodynamics is concerned with the state of a system when left alone, and when interacting with the surroundings. By ‘system’ we shall mean any portion of the world that can be defined for consideration of the changes that may occur under varying conditions. The system may be separated from the surroundings by a real or imaginary wall. The properties of the wall determine how the system may interact with the surroundings. The wall itself will not usually be regarded as part of the system but rather as part of the surroundings. We shall first consider two kinds of interactions, thermal and mechanical, and we may regard the name ‘thermodynamics’ as an indication that these interactions are of main interest. Secondly, we shall introduce interactions by exchange of matter in the form of chemical species. The name ‘thermochemistry’ is sometimes used as an indication of such applications. The term ‘thermophysical properties’ is sometimes used for thermodynamic properties which do not primarily involve changes in the content of various chemical species, e.g. heat capacity, thermal expansivity and compressibility.

One might imagine that the content of matter in the system could be varied in a number of ways equal to the number of species. However, species may react with each other inside the system. It is thus convenient instead to define a set of **independent components**, the change of which can accomplish all possible variations of the content. By denoting the number of independent components as c and also considering thermal and mechanical interactions with the surroundings, we find by definition that the state of the system may vary in $c + 2$ independent ways. For metallic systems it is usually most convenient to regard the elements as the independent components. For systems with covalent bonds it may sometimes be convenient to regard a very stable molecular species as a component. For systems with a strongly ionic character it may be convenient to select the independent components from the neutral compounds rather than from the ions.

By waiting for the system to come to rest after making a variation we may hope to establish a **state of equilibrium**. A criterion that a state is actually a state of equilibrium would be that the same state would spontaneously be established from different starting points. After a system has reached a state of equilibrium we can, in principle, measure the values of many quantities which are uniquely defined by the state and independent of the history of the system. Examples are temperature T , pressure P , volume V and content of each component N_i . We may call such quantities **state variables** or **state functions**, depending upon the context. It is possible to identify a particular state of equilibrium by

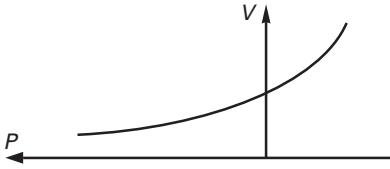


Figure 1.1 Property diagram for a constant amount of a solid material at a constant temperature showing volume as a function of pressure. Notice that P has here been plotted in the negative direction. The reason will be explained later.

giving the values of a number of state variables under which it is established. As might be expected, $c + 2$ variables must be given. The values of all other variables are fixed, provided that equilibrium has really been established. There are thus $c + 2$ independent variables and, after they have been selected and equilibrium has been established, the rest are dependent variables. As we shall see, there are many ways to select the set of independent variables. For each application a certain set is usually most convenient. For any selection of independent variables it is possible to change the value of each one, independent of the others, but only if the wall containing the system is open for exchange of $c + 2$ kinds, i.e. exchanges of mechanical work, heat and c components.

The equilibrium state of a system can be represented by a point in a $c + 2$ dimensional diagram. In principle, all points in such a diagram represent possible states of equilibrium although there may be practical difficulties in establishing the states represented by some region. One can use the diagram to define a state by specifying a point or a series of states by specifying a line. Such a diagram may be regarded as a **state diagram**. It does not give any information on the properties of the system under consideration unless such information is added to the diagram. We shall later see that some vital information on the properties can be included in the state diagram but in order to show the value of some dependent variable a new axis must be added. For convenience of illustration we shall now decrease the number of axes in the $c + 2$ dimensional state diagram by sectioning at constant values of $c + 1$ of the independent variables. All the states to be considered will thus be situated along a single axis, which may now be regarded as the state diagram. We may then plot a dependent variable by introducing a second axis. That property is thus represented by a line. We may call such a diagram a **property diagram**. An example is shown in Fig. 1.1. Of course, we may arbitrarily choose to consider any one of the two axes as the independent variable. The shape of the line is independent of that choice and it is thus the line itself that represents the property of the system.

In many cases the content of matter in a system is kept constant and the wall is only open for exchange of mechanical work and heat. Such a system is often called a **closed** system and we shall start by discussing the properties of such a system. In other cases the content of matter may change and, in particular, the **composition** of the system by which we mean the relative amounts of the various components independent of the size of the system. In materials science such an **open** system is called an ‘alloy system’ and its behaviour as a function of composition is often shown in so-called **phase diagrams**,

which are state diagrams with some additional information on what phases are present in various regions. We shall later discuss the properties of phase diagrams in considerable detail.

The state variables are of two kinds, which we shall call **intensive** and **extensive**. Temperature T and pressure P are intensive variables because they can be defined at each point of the system. As we shall see later, T must have the same value at all points in a system at equilibrium. An intensive variable with this property will be called **potential**. We shall later meet intensive variables, which may have different values at different parts of the system. They will not be regarded as potentials.

Volume V is an extensive variable because its value for a system is equal to the sum of its values of all parts of the system. The content of component i , usually denoted by n_i or N_i , is also an extensive variable. Such quantities obey the **law of additivity**. For a homogeneous system their values are proportional to the size of the system.

One can imagine variables, which depend upon the size of the system but do not always obey the law of additivity. The use of such variables is complicated and will not be much considered. The law of additivity will be further discussed in Section 3.4.

If the system is contained inside a wall that is rigid, thermally insulating and impermeable to matter, then all the interactions mentioned are prevented and the system may be regarded as completely closed to interactions with the surroundings. It is left ‘completely alone’. It is often called an **isolated** system. By changing the properties of the wall we can open the system to exchanges of mechanical work, heat or matter. A system open to all these exchanges may be regarded as a completely open system. We may thus control the values of $c + 2$ variables by interactions with the surroundings and we may regard them as **external variables** because their values can be changed by interaction with the external world through the surroundings.

1.2 Internal state variables

After some or all of the $c + 2$ independent variables have been changed to new values and before the system has come to rest at equilibrium, it is also possible to describe the state of the system, at least in principle. For that description additional variables are required. We may call them **internal variables** because they will change due to internal processes as the system approaches the state of equilibrium under the new values of the $c + 2$ external variables.

An internal variable ξ (pronounced ‘xeye’) is illustrated in Fig. 1.2(a) where $c + 1$ of the independent variables are again kept constant in order to obtain a two-dimensional diagram. The equilibrium value of ξ for various values of the remaining independent variable T is represented by a curve. In that respect, the diagram is a property diagram. On the other hand, by a rapid change of the independent variable T the system may be brought to a point away from the curve. Any such point represents a possible non-equilibrium state and in that sense the diagram is a state diagram. In order to define such a point one must give the value of the internal variable in addition to T . The quantity ξ is thus an independent variable for states of non-equilibrium.

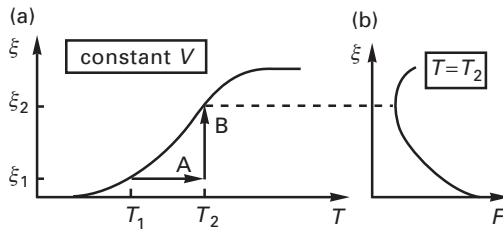


Figure 1.2 (a) Property diagram showing the equilibrium value of an internal variable, ξ , as a function of temperature. Arrow A represents a sudden change of temperature and arrow B the gradual approach to a new state of equilibrium. (b) Property diagram for non-equilibrium states at T_2 , showing the change of Helmholtz energy F as a function of the internal variable, ξ . There will be a spontaneous change with decreasing F and a stable state will eventually be reached at the minimum of F .

For such states of non-equilibrium one may plot any other property versus the value of the internal variable. An example of such a property diagram is given in Fig. 1.2(b). In this particular case we have chosen to show a property called Helmholtz energy F which will decrease by all spontaneous changes at constant T and V . Given sufficient time the system will approach the minimum of F which corresponds to point B on the curve to the left. That curve is the locus of all points of minimum of F , each one obtained under its own constant value of T . Any state of equilibrium can thus be defined by giving T and the proper ξ value or by giving T and the requirement of equilibrium. Under equilibrium ξ is a dependent variable and does not need to be given.

It is sometimes possible to imagine that a non-equilibrium state can be ‘frozen-in’ (see Section 1.4), i.e. by the temperature being so low that the non-equilibrium state does not change markedly during the time it takes to measure an internal variable. Under the given restrictions such a state may be regarded as a state of equilibrium with regard to some internal variable, but the values of the frozen-in variables must be given in the definition of the equilibrium. There is a particular type of internal variable, which can be controlled from outside the system under such restrictions. Such a variable can then be treated as an external variable. It can for instance be the number of O_3 molecules in a system, the rest of which is O_2 . At high temperature the chemical reaction between these species will be rapid and the amount of O_3 may be regarded as a dependent variable. In order to define a state of equilibrium at high temperature it is sufficient to give the amount of oxygen as O or O_2 . At a lower temperature the reaction may be frozen-in and the system has two independent variables, the amounts of O_2 and O_3 which can both be controlled from the outside.

Exercise 1.1

Consider a box of fixed volume containing a small amount of a liquid, which fills the box only partly. Some of the liquid thus evaporates. The equilibrium vapour pressure of the liquid varies with temperature, $P = k \exp(-b/T)$ and we could use as an internal

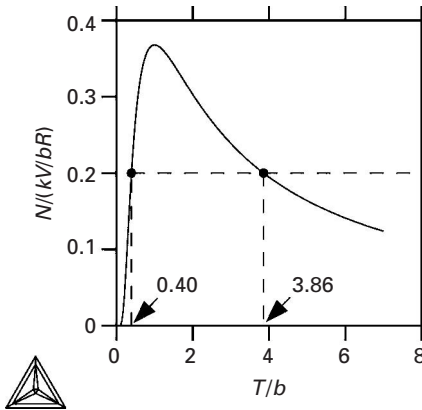


Figure 1.3 Solution to Exercise 1.1.

variable the number of gas molecules which is related to the pressure by the ideal gas law, $NRT = PV$. Calculate and show with a property diagram how N varies as a function of T .

Hint

In order to simplify the calculations, neglect the volume of the liquid in comparison with the volume of the box.

Solution

At equilibrium $N = PV/RT = (kV/RT) \exp(-b/T)$.

Let us introduce dimensionless variables, $N/(kV/bR) = (b/T) \exp(-b/T)$.

This function has a maximum at $T/b = 1$.

If the low temperature is chosen as $T/b = 0.4$, then the diagram shows that N will increase if the higher temperature is below $T/b = 3.86$ but decrease if it is above.

1.3 The first law of thermodynamics

The development of thermodynamics starts by the definition of Q , the amount of heat flow into a closed system, and W , the amount of work done on the system. The concept of work may be regarded as a useful device to avoid having to define what actually happens to the surroundings as a result of certain changes made in the system. The first law of thermodynamics is related to the law of conservation of energy, which says that energy cannot be created, nor destroyed. As a consequence, if a system receives an amount of heat, Q , and the work W is done on the system, then the energy of the system must have increased by $Q + W$. This must hold quite independent of what happened to the energy

inside the system. In order to avoid such discussions, the concept of internal energy U has been invented, and the first law of thermodynamics is formulated as

$$\Delta U = Q + W. \quad (1.1)$$

In differential form we have

$$dU = dQ + dW. \quad (1.2)$$

It is rather evident that the internal energy of the system is uniquely determined by the state of the system and independent of by what processes it has been established. U is a state variable. It should be emphasized that Q and W are not properties of the system but define different ways of interaction with the surroundings. Thus, they could not be state variables. A system can be brought from one state to another by different combinations of heat and work. It is possible to bring the system from one state to another by some route and then let it return to the initial state by a different route. It would thus be possible to get mechanical work out of the system by supplying heat and without any net change of the system. An examination of how efficient such a process can be resulted in the formulation of the second law of thermodynamics. It will be discussed in Sections 1.5 and 1.6.

The internal energy U is a variable, which is not easy to vary experimentally in a controlled fashion. Thus, we shall often regard U as a state function rather than a state variable. At equilibrium it may, for instance, be convenient to consider U as a function of temperature and pressure because those variables may be more easily controlled in the laboratory

$$U = U(T, P). \quad (1.3)$$

However, we shall soon find that there are two more natural variables for U . It is evident that U is an extensive property and obeys the law of additivity. The total value of U of a system is equal to the sum of U of the various parts of the system. Its value does not depend upon how the additional energy, due to added heat and work, is distributed within the system.

It should be emphasized that the absolute value of U is not defined through the first law, but only *changes* of U . Thus, there is no natural zero point for the internal energy. One can only consider changes in internal energy. For practical purposes one often chooses a point of reference, an arbitrary zero point.

For compression work on a system under a hydrostatic pressure P we have

$$dW = P(-dV) = -PdV \quad (1.4)$$

$$dU = dQ - PdV. \quad (1.5)$$

So far, the discussion is limited to cases where the system is closed and the work done on the system is hydrostatic. The treatment will always be applicable to gases and liquids which cannot support shear stresses. It should be emphasized that a complete treatment of the thermodynamics of solid materials requires a consideration of non-hydrostatic stresses. We shall neglect such problems when considering solids.

Mechanical work against a hydrostatic pressure is so important that it is convenient to define a special state function called enthalpy H in the following way, $H = U + PV$. The first law can then be written as

$$dH = dU + PdV + VdP = dQ + VdP. \quad (1.6)$$

In addition, the internal energy must depend on the content of matter, N , and for an open system subjected to compression we should be able to write,

$$dU = dQ - PdV + KdN. \quad (1.7)$$

In order to identify the nature of K we shall consider a system that is part of a larger, homogeneous system for which both T and P are uniform. U may then be evaluated by starting with an infinitesimal system and extending its boundaries until it encloses the volume V . Since there are no real changes in the system $dQ = 0$ and P and K are constant, we can integrate from the initial value of $U = 0$ where the system has no volume, obtaining

$$U = -PV + KN \quad (1.8)$$

$$H = KN. \quad (1.9)$$

By measuring the content of matter in units of mole, we obtain

$$K = H/N = H_m. \quad (1.10)$$

H_m is the molar enthalpy. Molar quantities will be discussed in Section 3.2. The first law in Eq. (1.2) can thus be written as

$$dU = dQ + dW + H_m dN. \quad (1.11)$$

It should be mentioned that there is an alternative way of writing the first law for an open system. It is based on including in the heat the enthalpy carried by the added matter. This new 'kind' of heat would thus be

$$dQ^* = dQ + H_m dN. \quad (1.12)$$

The first law for the open system in Eq. (1.11) would then be very similar to Eq. (1.2) for a closed system,

$$dU = dQ^* + dW = dQ^* - PdV. \quad (1.13)$$

This definition of heat is less useful in treatments of heat conduction and we shall not use it.

Exercise 1.2

One mole of a gas at pressure P_1 is contained in a cylinder of volume V_1 which has a piston. The volume is changed rapidly to V_2 , without time for heat conduction to or from the surroundings.

- (a) Evaluate the change in internal energy of the gas if it behaves as an ideal classical gas for which $PV = RT$ and $U = A + BT$.
- (b) Then evaluate the amount of heat flow until the temperature has returned to its initial value, assuming that the piston is locked in the new position, V_2 .

Hint

The internal energy can change due to mechanical work and heat conduction. The first step is with mechanical work only; the second step with heat conduction only.

Solution

- (a) Without heat conduction $dU = -PdV$ but we also know that $dU = BdT$. This yields $BdT = -PdV$.

Elimination of P using $PV = RT$ gives $BdT/RT = -dV/V$ and by integration we then find $(B/R) \ln(T_2/T_1) = -\ln(V_2/V_1) = \ln(V_1/V_2)$ and $T_2 = T_1(V_1/V_2)^{R/B}$, where T_1 is the initial temperature, $T_1 = P_1 V_1/R$.

Thus: $\Delta U_a = B(T_2 - T_1) = (B P_1 V_1/R)[(V_1/V_2)^{R/B} - 1]$.

- (b) By heat conduction the system returns to the initial temperature and thus to the initial value of U , since U in this case depends only on T . Since the piston is now locked, there will be no mechanical work this time, so that $dU_b = dQ_b$ and, by integration, $\Delta U_b = Q_b$. Considering both steps we find because U depends only upon T :

$$0 = \Delta U_a + \Delta U_b = \Delta U_a + Q_b; \quad Q_b = -\Delta U_a = -(B P_1 V_1/R)[(V_1/V_2)^{R/B} - 1].$$

Exercise 1.3

Two completely isolated containers are each filled with one mole of gas. They are at different temperatures but at the same pressure. The containers are then connected and can exchange heat and molecules freely but do not change their volumes. Evaluate the final temperature and pressure. Suppose that the gas is classical ideal for which $U = A + BT$ and $PV = RT$ if one considers one mole.

Hint

Of course, T and P must finally be uniform in the whole system, say T_3 and P_3 . Use the fact that the containers are still completely isolated from the surroundings. Thus, the total internal energy has not changed.

Solution

$$V = V_1 + V_2 = RT_1/P_1 + RT_2/P_1 = R(T_1 + T_2)/P_1; \quad A + BT_1 + A + BT_2 = U = 2A + 2BT_3; \quad T_3 = (T_1 + T_2)/2; \quad P_3 = 2RT_3/V = R(T_1 + T_2)/[R(T_1 + T_2)/P_1] = P_1.$$

1.4 Freezing-in conditions

As a continuation of our discussion on internal variables we may now consider heat absorption under two different conditions.

We shall first consider an increase in temperature slow enough to allow an internal process to adjust continuously to the changing conditions. If the heating is made under conditions where we can keep the volume constant, we may regard T and V as the independent variables and write

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV. \quad (1.14)$$

By combination with $dU = dQ - PdV$ we find

$$dQ = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV. \quad (1.15)$$

We thus define a quantity called heat capacity and under constant V it is given by

$$C_V \equiv \left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V. \quad (1.16)$$

Secondly, we shall consider an increase in temperature so rapid that an internal process is practically inhibited. Then we must count the internal variable as an additional independent variable which is kept constant. Denoting the internal variable as ξ we obtain

$$dU = \left(\frac{\partial U}{\partial T}\right)_{V,\xi} dT + \left(\frac{\partial U}{\partial V}\right)_{T,\xi} dV + \left(\frac{\partial U}{\partial \xi}\right)_{T,V} d\xi \quad (1.17)$$

$$dQ = \left(\frac{\partial U}{\partial T}\right)_{V,\xi} dT + \left[\left(\frac{\partial U}{\partial V}\right)_{T,\xi} + P\right] dV + \left(\frac{\partial U}{\partial \xi}\right)_{T,V} d\xi. \quad (1.18)$$

Under constant V and ξ we now obtain the following expression for the heat capacity

$$C_{V,\xi} \equiv \left(\frac{\partial Q}{\partial T}\right)_{V,\xi} = \left(\frac{\partial U}{\partial T}\right)_{V,\xi}. \quad (1.19)$$

Experimental conditions under which an internal variable ξ does not change will be called *freezing-in* conditions and an internal variable that does not change due to such conditions will be regarded as being *frozen-in*. We can find a relation between the two heat capacities by comparing the two expressions for dU at constant V ,

$$\left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_{V,\xi} + \left(\frac{\partial U}{\partial \xi}\right)_{T,V} \left(\frac{\partial \xi}{\partial T}\right)_V \quad (1.20)$$

$$C_V = C_{V,\xi} + \left(\frac{\partial U}{\partial \xi}\right)_{T,V} \left(\frac{\partial \xi}{\partial T}\right)_V. \quad (1.21)$$

The two heat capacities will thus be different unless either $(\partial U/\partial \xi)_{T,V}$ or $(\partial \xi/\partial T)_V$ is zero, which may rarely be the case.

It is instructive to note that Eq. (1.18) allows the heat of the internal process to be expressed in state variables,

$$\left(\frac{\partial Q}{\partial \xi}\right)_{T,V} = \left(\frac{\partial U}{\partial \xi}\right)_{T,V}. \quad (1.22)$$

Exercise 1.4

Suppose there is an internal reaction by which a system can adjust to a new equilibrium if the conditions change. There is a complete adjustment if the change is very slow and for a slow increase of T one measures $C_{V,\text{slow}}$. For a very rapid change there will be practically no reaction and one measures $C_{V,\text{rapid}}$. What value of C_V would one find if the change is intermediate and the reaction at each temperature has proceeded to halfway between the initial value and the equilibrium value.

Hint

$$C_V = (\partial Q/\partial T)_{\text{expt.cond.}} = (\partial U/\partial T)_{V,\xi} + (\partial U/\partial \xi)_{T,V} \cdot (\partial \xi/\partial T)_{\text{expt.cond.}} \text{ and} \\ (\partial \xi/\partial T)_{\text{expt.cond.}} = (\partial \xi/\partial T)_{\text{eq.}}$$

Solution

$C_{V,\text{rapid}} = (\partial U/\partial T)_{V,\xi}$; $C_{V,\text{slow}} = (\partial U/\partial T)_{V,\xi} + (\partial U/\partial \xi)_{T,V}(\partial \xi/\partial T)_{\text{eq.}}$; $C_{V,\text{interm.}} = (\partial U/\partial T)_{V,\xi} + (\partial U/\partial \xi)_{T,V}0.5(\partial \xi/\partial T)_{\text{eq.}} = (C_{V,\text{rapid}} + C_{V,\text{slow}})/2$. It should be noticed that the value of $(\partial U/\partial \xi)_{T,V}$ may depend on ξ as well as T . It may thus change during heating and in different ways depending on how ξ changes. The last step in the derivation is thus strictly valid only at the starting point.

1.5 Reversible and irreversible processes

Consider a cylinder filled with a gas and with a frictionless piston which exerts a pressure P on the gas in the cylinder. By gradually increasing P we can compress the gas and perform the work $W = -\int P dV$ on the gas. If the cylinder is thermally insulated from the surroundings, the temperature will rise because $\Delta U = Q + W = -\int P dV > 0$. By then decreasing P we can make the gas expand again and perform the same work on the surroundings through the piston. The initial situation has thus been restored without any net exchange of work or heat with the surroundings and no change of temperature or pressure of the gas. The whole process and any part of it are regarded as **reversible**.

The process would be different if the gas were not thermally insulated. Suppose it were instead in thermal equilibrium with the surroundings during the compression. For an ideal gas the internal energy only varies with the temperature and would thus stay constant during the compression if the surroundings could be kept at a constant temperature. Heat would flow out of the system during that process. By then decreasing P we could make the gas expand and, as it returns to the initial state, it would give back the work

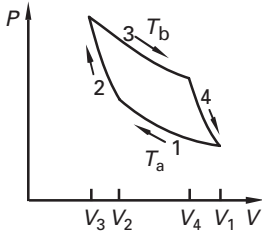


Figure 1.4 Schematic diagram of Carnot's cycle.

to the surroundings and take back the heat. Again there would be no net exchange with the surroundings. This process is also regarded as reversible and it may be described as a reversible **isothermal** process. The previous case may be described as a reversible **adiabatic** process.

By combination of the above processes and with the use of two heat reservoirs of constant temperatures, T_a and T_b , one can make the system go through a cycle which may be defined as reversible because all the steps are reversible. Figure 1.4 illustrates a case with four steps where $T_b > T_a$.

- (1) Isothermal compression from V_1 to V_2 at a constant temperature T_a . The surroundings perform the work W_1 on the system and the system gives away heat, $-Q_1$, to the surroundings, i.e. to the colder heat reservoir, T_a . The heat received by the system, Q_1 , is negative.
- (2) Adiabatic compression from V_2 to V_3 under an increase of the temperature inside the cylinder from T_a to T_b . The surroundings perform the work W_2 on the system but there is no heat exchange, $Q_2 = 0$.
- (3) Isothermal expansion from V_3 to V_4 after the cylinder has been brought into contact with a warmer heat reservoir, T_b . The system now gives back some work to the surroundings; W_3 is negative whereas Q_3 is positive. The warm heat reservoir, T_b , thus gives away this heat to the system.
- (4) Adiabatic expansion from V_4 back to V_1 under a decrease of temperature inside the cylinder from T_b to T_a ; W_4 is negative and $Q_4 = 0$.

The system has thus received a net heat of $Q = Q_1 + Q_3$ but it has returned to the initial state and for the whole process we obtain $Q + W = \Delta U = 0$ and $-W = Q = Q_1 + Q_3$ where W is the net work done on the system. According to Fig. 1.4 the inscribed area is positive and mathematically it corresponds to $\int P dV$. The net work, W , is equal to $-\int P dV$ and it is thus negative and the system has performed work on the surroundings. The net heat, Q , is positive and the system has thus received energy by heating. The system has performed work on the surroundings, $-W$, by transforming into mechanical energy some of the thermal energy, Q_3 , received from the warm heat reservoir. The remaining part of Q_3 is given off to the cold heat reservoir, $-Q_1 < Q_3$. This cycle may thus be used for the construction of a heat engine that can produce mechanical energy from thermal energy. It was first discussed by Carnot [1] and is called Carnot's cycle. From a practical point of view the important question is how efficient that engine would

be. The efficiency may be defined as the ratio between the mechanical work produced, $-W$, and the heat drawn from the warm heat reservoir, Q_3 .

$$\eta = \frac{-W}{Q_3} = \frac{Q_1 + Q_3}{Q_3} = 1 + \frac{Q_1}{Q_3}. \quad (1.23)$$

This is less than unity because Q_1 is negative and its absolute value is smaller than Q_3 .

We can let the engine run in the reverse direction. It would then draw heat from the cold reservoir and deposit it in the warm reservoir by means of some mechanical work. It would thus operate as a heat pump or refrigerator.

Before continuing the discussion, let us consider the flow of heat through a wall separating two heat reservoirs. There is no method by which we could reverse this process. Heat can never flow from a cold reservoir to a warmer one. Heat conduction is an **irreversible** process.

Let us then go back to the Carnot cycle and examine it in more detail. It is clear that in reality it must have some irreversible character. The flow of heat in steps (1) and (3) cannot occur unless there is a temperature difference between the system and the heat reservoir. The irreversible character of the heat flow may be decreased by making the temperature difference smaller but then the process will take more time. A completely reversible heat transfer could, in principle, be accomplished by decreasing the temperature difference to zero but then the process would take an infinite time. A completely reversible process is always an idealization of reality which can never be attained. However, it is an extremely useful concept because it defines the theoretical limit. Much of thermodynamics is concerned with reversible processes.

We may expect that the efficiency would increase if the irreversible character of the engine could be decreased. However, it may also seem conceivable that the efficiency of a completely reversible engine could depend on the choice of temperatures of the two heat reservoirs and on the choice of fluid (gas or liquid) in the system. These matters will be considered in the [next section](#).

Exercise 1.5

Discuss by what physical mechanisms the adiabatic steps of the Carnot cycle can get an irreversible character.

Solution

There may be heat conduction through the wall of the cylinder also during the adiabatic step, i.e. it would not be completely adiabatic. That effect would be less if the compression is very fast. However, for a very fast compression it is possible that there would be violent motions or oscillations inside the system. The damping of them would be an irreversible process.

1.6 Second law of thermodynamics

Let us now compare the efficiency of two heat engines which are so close to the ideal case that they may be regarded as reversible. Let them operate between the same two heat reservoirs, T_a and T_b . Suppose one engine has a lower efficiency than the other and let it operate in the reverse direction, i.e. as a heat pump. Build the heat pump of such a size that it will give to the warm reservoir the same amount of heat as the heat engine will take. Thanks to its higher efficiency the heat engine will produce more work than needed to run the heat pump. The difference can be used for some useful purpose and the equivalent amount of thermal energy must come from the cold reservoir because the warm reservoir is not affected and could be disposed of.

The above arrangement would be a kind of perpetuum mobile. It would for ever produce mechanical work by drawing thermal energy from the surroundings without using a warmer heat source. This does not seem reasonable and one has thus formulated the second law of thermodynamics which states that this is not possible. It then follows that the efficiency of all reversible heat engines must be the same if they operate between the same two heat reservoirs. From the expression for the efficiency η it follows that the ratio Q_1/Q_3 can only be a function of T_a and T_b and the same function for all choices of fluid in the cylinder.

A heat engine, which is not reversible, will have a lower efficiency but, when used in the reverse direction, it will have different properties because it is not reversible. Its efficiency will thus be different in the reverse direction and it could not be used to make a perpetuum mobile.

It remains to examine how high the efficiency is for a reversible heat engine and how it depends on the temperatures of the two heat reservoirs. The answer could be obtained by studying any well-defined engine, for instance an engine built on the Carnot cycle using an ideal classical gas. The result is

$$\eta = \frac{-W}{Q_3} = \frac{T_b - T_a}{T_b}. \quad (1.24)$$

We must now accept that this result is quite general and independent of the choice of fluid. Actually, it would also hold for a solid medium. In line with Carnot's ideas, we can give a more general derivation by first considering the production of work when a body of mass ΔM is moved from a higher level to a lower one, i.e. from a higher gravitational potential, g_b , to a lower one, g_a .

$$-W = \Delta M \cdot (g_b - g_a). \quad (1.25)$$

The minus sign is added because $+W$ should be defined as mechanical energy received by the system (the body). With this case in mind, let us assume that the work produced by a reversible heat engine could be obtained by considering some appropriate thermal quantity which would play a similar role as mass. That quantity is now called entropy and denoted by S . When a certain amount of that quantity is moved from a higher thermal

potential (temperature T_b) to a lower one (temperature T_a) the production of work should be given in analogy to the above equation,

$$-W = \Delta S \cdot (T_b - T_a). \quad (1.26)$$

However, we already know that $-W$ is the sum of Q_1 and Q_3 ,

$$\Delta S \cdot T_b - \Delta S \cdot T_a = Q_3 + Q_1. \quad (1.27)$$

We can find an appropriate quantity S to satisfy this equation by defining S as a state function, the change of which in a system is related to the heat received,

$$\Delta S = Q/T. \quad (1.28)$$

The amount of S received by the system from the warm heat reservoir would then be

$$\Delta S = Q_3/T_b. \quad (1.29)$$

The amount of S given by the system to the cold reservoir would be

$$\Delta S = -Q_1/T_a. \quad (1.30)$$

The equation is satisfied and we also find

$$\frac{Q_1}{Q_3} = \frac{-\Delta S \cdot T_a}{\Delta S \cdot T_b} = -\frac{T_a}{T_b}. \quad (1.31)$$

$$\eta = \frac{-W}{Q_3} = 1 + \frac{Q_1}{Q_3} = \frac{T_b - T_a}{T_b}, \quad (1.32)$$

in agreement with the previous examination of the Carnot cycle.

Let us now look at entropy and temperature in a more general way. By adding a small amount of heat to a system by a reversible process we would increase its entropy by

$$dS = dQ/T. \quad (1.33)$$

For a series of reversible changes that brings the system back to the initial state

$$\int dQ/T = \Delta S = 0. \quad (1.34)$$

This can be demonstrated with the Carnot cycle. By comparing Eqs (1.29) and (1.30) we find

$$Q_1/T_a + Q_3/T_b = 0. \quad (1.35)$$

The quantity T is a measure of temperature but it remains to be discussed exactly how to define T . It is immediately evident that the zero point must be defined in a unique way because T_a/T_b would change if the zero point is changed. That is not allowed because it must be equal to $-Q_1/Q_3$. The quantity T is thus measured relative to an absolute zero point and one can say that T measures the absolute temperature.

It has already been demonstrated that by using an ideal classical gas as the fluid in the Carnot engine, one can derive the correct expression for the efficiency, $\eta = (T_b - T_a)/T_b$. One can thus define the absolute temperature as the temperature scale used in the ideal gas law and one can measure the absolute temperature with a gas thermometer. When

this was done it was decided to express the difference between the boiling and freezing point of water at 1 atm as 100 units, in agreement with the Celsius scale. This unit is now called kelvin (K).

Let us now return to the irreversible process of heat conduction from a warm reservoir to a cold one. By transferring an amount dQ one would decrease the entropy of the warm reservoir by dQ/T_b and increase the entropy of the cold one by dQ/T_a . The net change of the entropy would thus be

$$dS = -dQ/T_b + dQ/T_a = dQ \cdot (T_b - T_a)/T_b T_a. \quad (1.36)$$

This irreversible process thus produces entropy. One talks about **internal entropy production**

$$d_{ip}S > 0. \quad (1.37)$$

The subscript 'ip' indicates that this change of the entropy of the system is due to an internal process. This is the second law of thermodynamics and it should be noted that it concerns what happens inside a system, whereas the first law concerns interactions with the surroundings. As we have seen, the transfer of heat to the system, dQ , will increase the entropy by dQ/T and, by also considering the effect of additional matter, dN , in an open system we can write the second law as

$$dS = dQ/T + S_m dN + d_{ip}S > dQ/T + S_m dN. \quad (1.38)$$

S_m is the molar entropy of the added material and can be derived exactly as H_m in the first law was derived in Section 1.3. With the alternative definition of heat in Eq. (1.12) we would obtain

$$\begin{aligned} dS &= dQ^*/T - (H_m/T - S_m)dN + d_{ip}S = dQ^*/T - ((H_m - TS_m)/T)dN \\ &+ d_{ip}S > dQ^*/T - ((H_m - TS_m)/T)dN. \end{aligned} \quad (1.39)$$

When a spontaneous process proceeds, it is in a direction that can be predicted from the above criterion. A spontaneous process is always an irreversible process, otherwise it would have no preferred direction and it would be reversible. A reversible process is a hypothetical construction and can be defined by either one of the following criteria,

$$d_{ip}S = 0 \quad (1.40)$$

$$dS = dQ/T + S_m dN. \quad (1.41)$$

Exercise 1.6

Suppose a simple model for an internal reaction yields the following expression for the internal production of entropy under conditions of constant T , V and N , $\Delta_{ip}S = -\xi K/T - R[\xi \ln \xi - (1 + \xi) \ln(1 + \xi)]$, where ξ is a measure of the progress of the reaction going from 0 to 1. Find the equilibrium value of ξ , i.e. the value of ξ for which the reaction cannot proceed spontaneously.

Hint

The spontaneous reaction will stop when $d_{ip}S$ is no longer positive, i.e. when $d_{ip}S/d\xi = 0$.

Solution

$$d_{ip}S/d\xi = d(\Delta_{ip}S)/d\xi = -K/T - R[1 + \ln \xi - 1 - \ln(1 + \xi)] = 0; \quad \xi/(1 + \xi) = \exp(-K/RT); \quad \xi = 1/[\exp(K/RT) - 1].$$

Exercise 1.7

Find a state function from which one could evaluate the heat flow out of the system when a homogeneous material is compressed isothermally.

Hint

Heat is not a state function of a system. In order to solve the problem we must know how the change was made. Let us first assume that it was reversible.

Solution

For reversible conditions $Q = \int T dS = T_1 \int dS = T_1(S_2 - S_1)$ and the heat extraction $-Q = T_1(S_1 - S_2)$. For irreversible conditions $dQ < T dS$; $Q < T_1(S_2 - S_1)$ and the extracted heat is $-Q > T_1(S_1 - S_2)$, i.e. larger than before. However, if the final state is the same, ΔU must be the same because it is a state function and the higher value of $-Q$ must be compensated by a higher value of the work of compression W than during reversible compression. How much higher $-Q$ and W will be cannot be calculated without detailed information on the factor making the compression irreversible.

Exercise 1.8

Consider a Carnot cycle with a non-ideal gas and suppose that the process is somewhat irreversible. Use the second law to derive an expression for the efficiency.

Hint

For each complete cycle we have $\Sigma \Delta U = 0$ and $\Sigma \Delta S = 0$ because U and S are both state functions.

Solution

$\Sigma \Delta U = W + Q_1 + Q_3 = 0$; $\Sigma \Delta S = Q_1/T_a + Q_3/T_b + \Delta_{ip}S = 0$ where W and $\Delta_{ip}S$ are the sums over the cycle. We seek $\eta = -W/Q_3$ and should thus eliminate Q_1 by combining these equations: $-Q_1 = Q_3 T_a/T_b + \Delta_{ip}S \cdot T_a$; $-W = Q_1 + Q_3 = -Q_3 T_a/T_b - \Delta_{ip}S \cdot T_a + Q_3 = Q_3(T_b - T_a)/T_b - \Delta_{ip}S \cdot T_a$ and thus $\eta = -W/Q_3 = (T_b - T_a)/T_b - \Delta_{ip}S \cdot T_a/Q_3 < (T_b - T_a)/T_b$ because $\Delta_{ip}S$, T_a and Q_3 are all positive.

1.7 Condition of internal equilibrium

The second law states that an internal process may continue spontaneously as long as $d_{ip}S$ is positive. It must stop when for a continued process one would have

$$d_{ip}S \leq 0. \quad (1.42)$$

This is the condition for equilibrium in a system. By integrating $d_{ip}S$ we may obtain a measure of the total production of entropy by the process, $\Delta_{ip}S$. It has its maximum value at equilibrium. The maximum may be smooth, $d_{ip}S = 0$, or sharp, $d_{ip}S < 0$, but the possibility of that alternative will usually be neglected.

As an example of the first case, Fig. 1.5 shows a diagram for the formation of vacancies in a pure metal. The internal variable, generally denoted by ξ , is here the number of vacancies per mole of the metal.

As an example of the second case, Fig. 1.6 shows a diagram for the solid state reaction between two phases, graphite and $Cr_{0.7}C_{0.3}$, by which a new phase $Cr_{0.6}C_{0.4}$ is formed. The internal variable here represents the amount of $Cr_{0.6}C_{0.4}$. The curve only exists up to a point of maximum where one or both of the reactants have been consumed (in this case $Cr_{0.7}C_{0.3}$). From the point of maximum the reaction can only go in the reverse direction and that would give $d_{ip}S < 0$ which is not permitted for a spontaneous reaction. The sharp point of maximum thus represents a state of equilibrium. This case is often neglected and one usually treats equilibrium with the equality sign only, $d_{ip}S = 0$.

If $d_{ip}S = 0$ it is possible that the system is in a state of minimum $\Delta_{ip}S$ instead of maximum. By a small, finite change the system could then be brought into a state where $d_{ip}S > 0$ for a continued change. Such a system is thus at an **unstable equilibrium**. As a consequence, for a stable equilibrium we require that either $d_{ip}S < 0$, or $d_{ip}S = 0$ but then its second derivative must be negative.

It should be mentioned that instead of introducing the internal entropy production, $d_{ip}S$, one has sometimes introduced dQ'/T where dQ' is called '**uncompensated heat**'. It represents the extra heat, which must be added to the system if the same change of the system were accomplished by a reversible process. Under the actual, irreversible conditions one has $dS = dQ/T + d_{ip}S$. Under the hypothetical, reversible conditions one has $dS = (dQ + dQ')/T$. Thus, $dQ' = T d_{ip}S$. In the actual process $d_{ip}S$ is produced without the system being compensated by such a heat flow from the surroundings.

If the reversible process could be carried out and the system thus received the extra heat dQ' , as compared to the actual process, then the system must also have delivered the corresponding amount of work to the surroundings in view of the first law. Because of the irreversible nature of the process, this work will not be delivered and that is why one sometimes talks about the '**loss of work**' in the actual process which is irreversible and produces some entropy instead of work, $dW = dQ' = T d_{ip}S$.

Exercise 1.9

Check the loss of work in a cyclic process working with a high-temperature heat source of T_b and a low-temperature heat sink of T_a and having some internal entropy production.

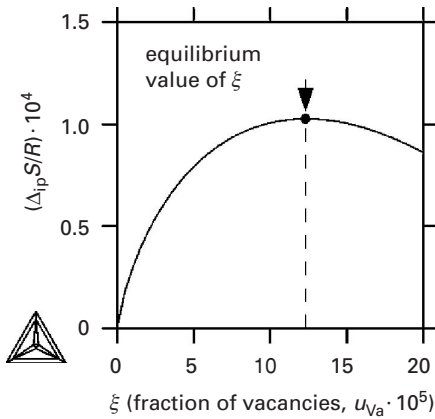


Figure 1.5 The internal entropy production due to the formation of thermal vacancies in 1 mole of a pure element at a temperature where the energy of formation of a vacancy is $9kT$, k being the Boltzmann constant. The initial state is a pure element without any vacancies. The internal variable is here the number of vacancies expressed as moles of vacancies per mole of metal, u_{Va} .

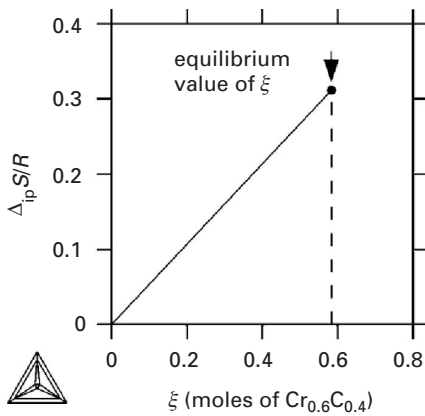


Figure 1.6 The internal entropy production due to the solid state phase transformation $C + Cr_{0.7}C_{0.3} \rightarrow Cr_{0.6}C_{0.4}$ at 1500 K and 1 bar. The initial state is 0.5 mole each of C(graphite) and $Cr_{0.7}C_{0.3}$. The internal variable here represents the amount of $Cr_{0.6}C_{0.4}$.

Hint

In Exercise 1.8 we found $-W = Q_3(T_b - T_a)/T_b - \Delta_{ip}S \cdot T_a$. From this result we can calculate the ‘loss of work’, e.g. if the amount of heat extracted from the heat source is the same in the irreversible case as in the reversible one. Give this loss per heat extracted from the heat source, and give it per heat given to the colder heat sink, Q_1 .

Solution

For a reversible cycle one would have $-W = Q_3(T_b - T_a)/T_b$. The ‘loss of work’ per extracted heat is thus $\Delta_{ip}S \cdot T_a/Q_3$.

For the second case we should eliminate Q_3 from the two equations in the solution of Exercise 1.8: $-Q_3 = \Delta_{ip}S \cdot T_b + Q_1 T_b/T_a$; $-W = Q_1 + Q_3 = -Q_1(T_b - T_a)/T_a - \Delta_{ip}S \cdot T_b$.

The ‘loss of work’ per received heat is thus $\Delta_{ip}S \cdot T_b/(-Q_1)$. The two results are equal in the reversible limit where $Q_3/T_b = -Q_1/T_a$ according to Eq. (1.35).

1.8 Driving force

Let the internal variable ξ represent the extent of a certain internal process. The internal entropy production can then be regarded as a function of this variable and we may define its derivative $d_{ip}S/d\xi$ as a new state variable. It may also be regarded as a state function because it may be expressed as a function of a set of state variables, including ξ , which define the state. For convenience, we shall multiply by T under isothermal conditions to obtain a new state variable,

$$D \equiv T \frac{d_{ip}S}{d\xi}. \quad (1.43)$$

One may use $D = 0$ as the condition of equilibrium. This quantity was introduced by De Donder [2] when considering chemical reactions between molecules and it was thus called **affinity**. However, it has a much wider applicability and will here be regarded as the **driving force** for any internal process. The symbol D , chosen here, may either be regarded as an abbreviation of driving force or as an honour to De Donder. It is usually convenient to define ξ by a variable that is an extensive property, subject to the law of additivity. The driving force D will then be an intensive variable.

If a system is not in a state of equilibrium, there may be a spontaneous internal process for which the second law gives $d_{ip}S > 0$ and thus

$$T d_{ip}S = D d\xi > 0. \quad (1.44)$$

It is evident that $d\xi$ and D must have the same sign in order for the process to proceed. By convention, $d\xi$ is given a positive value in the direction one wants to examine and D must then be positive for a spontaneous process in that direction. In many applications one even attempts to predict the rate of a process from the magnitude of D . Simple models often predict proportionality. This will be further discussed in Chapter 5.

If $D > 0$ for some internal process, then the system is not in a state of equilibrium. The process may proceed and it will eventually approach a state of equilibrium where $D = 0$. The equilibrium value of the variable ξ can, in principle, be evaluated from the condition $D = 0$, which is usually more directly applicable than the basic condition $d_{ip}S = 0$.

In the preceding section we connected an internal entropy production with the progress of an internal process. However, we can now see that it is possible, in principle, to change an internal variable without any entropy production. This can be done by changing the external variables in such a way that the driving force D is always zero. Since D is zero at equilibrium only, it is necessary to change the external variables so slowly that ξ can all the time adjust itself to the new value required by equilibrium. In practice, this cannot be

completely achieved because the rate of the process should be zero if its driving force is zero. An infinitely slow change is thus necessary. Such an idealized change is identical to the reversible process mentioned in the preceding section and it is sometimes described as an ‘equilibrium reaction’. It would take the system through a series of equilibrium states.

It may be convenient to consider a reversible process if one knows a state of equilibrium for a system and wants to find other states of equilibrium under some different conditions. This is the reason why one often applies ‘reversible conditions’. As an example we may consider the heating of a system under constant volume, discussed in Section 1.4. The heat capacity under such conditions, C_V , was found to be different under slow and rapid changes. Both of these cases may be regarded as reversible because the internal entropy production is negligible when D is small for a very slow change and also when $d\xi$ is small for a frozen-in internal process. For both cases we may thus use $dS = dQ/T$ and we obtain two different quantities,

$$C_V \equiv \left(\frac{\partial Q}{\partial T} \right)_V = T \left(\frac{\partial S}{\partial T} \right)_V \quad (1.45)$$

$$C_{V,\xi} \equiv \left(\frac{\partial Q}{\partial T} \right)_{V,\xi} = T \left(\frac{\partial S}{\partial T} \right)_{V,\xi}. \quad (1.46)$$

These expressions are equivalent to those given in Section 1.4 in terms of U . For intermediate cases, which are not reversible, one should consider U and not S , i.e. use the first law and not the second law.

Exercise 1.10

Consider an internal reaction which gives an entropy production under isothermal conditions, $\Delta_{\text{ip}}S = -\xi K/T - R[\xi \ln \xi - (1 + \xi) \ln(1 + \xi)]$. Derive the stability at equilibrium, defined as $B = -T \cdot d_{\text{ip}}^2 S/d\xi^2 = -T \cdot dD/d\xi$. (See Section 6.1.)

Hint

In Exercise 1.6 we have already calculated $d_{\text{ip}}S/d\xi$ and ξ at equilibrium.

Solution

$$d_{\text{ip}}S/d\xi = -K/T - R[\ln \xi - \ln(1 + \xi)]; \quad d_{\text{ip}}^2 S/d\xi^2 = -R[1/\xi - 1/(1 + \xi)].$$

However, at equilibrium $1/\xi = \exp(K/RT) - 1$; $1/(1 + \xi) = [\exp(K/RT) - 1]/\exp(K/RT)$.

$$\text{Thus, } B = +RT[1/\xi - 1/(1 + \xi)] = RT[1 - \exp(K/RT)]^2/\exp(K/RT).$$

This is always positive. The state of equilibrium must be stable.

1.9 Combined first and second law

Combination of the first and second laws, Eqs (1.11) and (1.38) yield by elimination of dQ ,

$$\begin{aligned} dS &= dQ/T + S_m dN + d_{ip}S + (dU - dQ - dW - H_m dN)/T \\ &= dU/T + (S_m - H_m/T)dN - dW/T + d_{ip}S. \end{aligned} \quad (1.47)$$

Denoting $H_m - TS_m$ by G_m , a symbol that will be explained in Section 3.2, and introducing $Dd\xi/T$ for $d_{ip}S$ from Eq. (1.43) and only considering compression work, we obtain

$$dS = (1/T)dU + (P/T)dV - (G_m/T)dN + Dd\xi/T. \quad (1.48)$$

It should be noted that the alternative definition of heat, Eq. (1.12), would yield the same result by eliminating dQ^* between Eqs (1.13) and (1.39). The combination of the two laws is due to Gibbs [3] and Eq. (1.48), without the last term is often called Gibbs' equation or relation. We shall simply refer to Eq. (1.48) as the **combined law** and it can be written in many different forms, expressing one state variable as a function of the others. Such a function, based on the combined law, is regarded as a **characteristic state function** for the set of variables occurring on the right-hand side. The variables in that set are regarded as the **natural variables** for the quantity appearing on the left-hand side.

It is more common to write the combined law in the following form

$$dU = TdS - PdV + G_m dN - Dd\xi. \quad (1.49)$$

Here, U is the characteristic state function and its natural variables are S , V and N . One usually regards S as an external variable although its value is also influenced by internal processes and it is not possible to control its value by actions from the outside without an intimate knowledge of the properties of the system.

When there are i internal processes, one should replace $Dd\xi$ by $\Sigma D^i d\xi^i$. For the sake of simplicity this will be done only when we actually consider more than one process. By grouping together the products of the external variables in Eq. (1.49) we write

$$dU = \Sigma Y^a dX^a - Dd\xi, \quad (1.50)$$

where Y^a represents potentials like T . It is evident that the pressure should be expressed as $-P$ in order to be comparable with other potentials. As a consequence, we shall plot P in the negative direction in many diagrams (see, for instance, Fig. 1.1). X^a represents extensive quantities like S and V . The pair of one potential and one extensive quantity, Y^a and X^a , is called a pair of **conjugate variables**, for instance T , S or $-P$, V . Other pairs of conjugate variables may be included through the first law by considering other types of work, for instance gravitational work. It is important to notice that the change in U is given in terms of the changes in variables all of which are extensive like S and V and all of them are subject to the law of additivity.

Since U is a state variable which is a function of all the external variables, X^a , X^b , etc., and the internal ξ variables, we have

$$Y^b = \left(\frac{\partial U}{\partial X^b} \right)_{X^c, \xi}, \quad (1.51)$$

where X^c represents all the X variables except for X^b . It is interesting to note that all the Y variables are obtained as partial derivatives of an energy with respect to an extensive variable. That is why they are regarded as potentials. One may also regard $-D$ and ξ as a pair of conjugate variables where $-D$ is the potential and is obtained as

$$-D = \left(\frac{\partial U}{\partial \xi} \right)_{X^a}, \quad (1.52)$$

where X^a represents all the X variables. It should be emphasized that the Y potentials have here been defined for a frozen-in state because ξ was treated as an independent variable that is kept constant. Under conditions of maintained equilibrium one should treat ξ as a dependent variable and the potentials are defined as

$$Y^b = \left(\frac{\partial U}{\partial X^b} \right)_{X^c}. \quad (1.53)$$

We will soon see that for equilibrium states the two definitions of Y^b give the same result.

In the following discussions we do not want to be limited to frozen-in states ($d\xi = 0$), nor to equilibrium states or reversible changes ($D = 0$) and we will thus retain the $Dd\xi$ term in the combined law. It should again be emphasized that there are those two different cases for which the term $Dd\xi$ is zero and can be omitted.

The combined law can be expressed in several alternative forms depending upon the choice of independent external variables. These forms make use of new state functions which will be discussed soon.

Exercise 1.11

Try to include the effect of electrical work in the combined law.

Hint

There are two cases. First, consider the addition of an extra charge to the system. Second, consider the case where the system is made part of an electrical circuit.

Solution

In the first case, the first law gives $dU = dQ + dW + dW_{el}$ where we may write $dW_{el} = E \cdot d(\text{charge}) = -E\mathcal{F}dn_e$, where \mathcal{F} is the Faraday constant (the negative of the charge of one mole of electrons) and n_e is the number of extra electrons (in mole). E is the electrical potential. The combined law becomes $dU = TdS - PdV - E\mathcal{F}dn_e - Dd\xi$. However, E increases very rapidly with n_e and reaches extremely high values before n_e is large enough to have a chemical effect. This form is thus of little practical interest.

Let us now consider a system that is part of an electrical circuit. It is evident that the charge entering a system through one lead must be practically equal to the charge leaving the system from the other lead, i.e. $dn_{e1} = -dn_{e2}$. The first law becomes $dU = dQ + dW + dW_{e1} = dQ + dW - E_1 \mathcal{F}dn_{e1} - E_2 \mathcal{F}dn_{e2} = dQ + dW - (E_1 - E_2) \mathcal{F}dn_{e1}$, and the combined law becomes $dU = TdS - PdV - (E_1 - E_2) \mathcal{F}dn_{e1} - Dd\xi$. E_1 and E_2 are the electrical potentials on the two sides of the system. At this time we do not need to speculate on what happens inside the system.

1.10 General conditions of equilibrium

A system is in a state of equilibrium if the driving forces for all possible internal processes are zero. Many kinds of internal processes can be imagined in various types of systems but there is one class of internal process that should always be considered, the transfer of a quantity of an extensive variable from one part of the system, i.e. a subsystem, to another subsystem. In this section we shall examine the equilibrium condition for such a process.

Let us first examine an internal process taking place in a system under constant values of the external extensive variables S and V , here collectively denoted by X^a , and let us not be concerned about the experimental difficulties encountered in performing such an experiment. We could then turn to the combined first and second law in terms of dU , which is reduced as follows

$$dU = \Sigma Y^a dX^a - Dd\xi = -Dd\xi. \quad (1.54)$$

The driving force for the internal process will be

$$D = -(\partial U / \partial \xi) X^a. \quad (1.55)$$

The process can occur spontaneously and proceed until U has reached a minimum. The state of minimum in U at constant S and V is thus a state of equilibrium.

The internal process we shall now consider is the transfer of dX^b from one subsystem (') to the other (''), keeping the remaining X s constant at different values in the two subsystems. It is convenient to measure the extent of this internal process by identifying $d\xi$ with $-dX^b$ for the first subsystem and $+dX^b$ for the second. We thus obtain, by applying the law of additivity to D ,

$$-D = \left(\frac{\partial U}{\partial \xi} \right)_{X^a} = \left(\frac{\partial U}{\partial (-X^b)} \right)'_{X^c} + \left(\frac{\partial U}{\partial X^b} \right)''_{X^c} = - \left(\frac{\partial U}{\partial X^b} \right)'_{X^c} + \left(\frac{\partial U}{\partial X^b} \right)''_{X^c}. \quad (1.56)$$

The derivative $\partial U / \partial X^b$ is identical to the conjugate potential Y^b and we thus find

$$D = Y^{b'} - Y^{b''}. \quad (1.57)$$

The driving force for this process will be zero and the system will be in equilibrium with respect to the process if the potential Y^b has the same value in the two subsystems. We have thus proved that each potential must have the same value in the whole system at

equilibrium. This applies to T , and to P with an exception to be treated in Chapter 16. It also applies to chemical potentials μ_i , which have not yet been introduced.

Exercise 1.12

One may derive a term $-E\mathcal{F}dn_e$ for the electrical contribution to dU . Here E is the electrical potential and $-\mathcal{F}dn_e$ the electrical charge because dn_e is the number of moles of extra electrons and $-\mathcal{F}$ is the charge of one mole of electrons. Evaluate the driving force for the transfer of electrons from one half of the system to the other if their electrical potentials are E' and E'' and can be kept constant. Define $d\xi$ as dn_e .

Solution

$-D = (\partial U/\partial \xi) = -(\partial U/\partial n_e)' + (\partial U/\partial n_e)'' = E'\mathcal{F} - E''\mathcal{F}$; $D = (E'' - E')\mathcal{F}$. In practice, the big question is whether the charge transfer will change the potential difference or whether there is a device for keeping it constant.

1.11 Characteristic state functions

Under experimental conditions of constant S , V and N it is most convenient to use the combined law in the form given by Eq. (1.49) because then it yields simply

$$dU = -Dd\xi. \quad (1.58)$$

At equilibrium, $D = 0$, we obtain

$$D = -(\partial U/\partial \xi)_{S,V,N} = 0 \quad (1.59)$$

for the internal process. If instead $D > 0$, then the internal process may proceed spontaneously and the internal energy will decrease and eventually approach a minimum under constant S , V and N .

From an experimental point of view it is not very easy to control S but relatively easy to control T . A change of independent variable may thus be desirable and it can be performed by subtracting $d(TS)$ which is equal to $TdS + SdT$. The combined law in Eq. (1.49) is thus modified to

$$d(U - TS) = -SdT - PdV + G_m dN - Dd\xi. \quad (1.60)$$

We may regard this as the combined law for the variables T , V and N and the combination $U - TS$ is regarded as the characteristic state function for these variables, whereas U is regarded as the characteristic state function for the variables S and V . The new function

$(U - TS)$ has been given its own name and symbol, Helmholtz energy, F ,

$$F = U - TS. \quad (1.61)$$

Under experimental conditions of constant T , V and N we obtain

$$dF = -Dd\xi. \quad (1.62)$$

The equilibrium condition can then be written as

$$D = -(\partial F/\partial \xi)_{T,V,N} = 0. \quad (1.63)$$

In an experiment under constant T , V and N there may be spontaneous changes until F has approached a minimum.

In the same way we may introduce a state variable $H = U + PV$ obtaining

$$dH = d(U + PV) = TdS + VdP + G_m dN - Dd\xi. \quad (1.64)$$

This may be regarded as the combined law for the variables S , P and N . The new variable H is regarded as the characteristic state function for these variables and it is called enthalpy. In fact, it has already been introduced in connection to the first law in Section 1.3. The equilibrium condition under constant S , P and N is

$$D = -(\partial H/\partial \xi)_{S,P,N} = 0. \quad (1.65)$$

In an experiment under constant S and P there may be spontaneous internal changes until H has approached a minimum.

By applying both modifications we can define $U - TS + PV$ as a new state variable, G , obtaining

$$dG = d(U - TS + PV) = -SdT + VdP + G_m dN - Dd\xi. \quad (1.66)$$

This may be regarded as the combined law for the variables T , P and N and the characteristic state function for these variables is called Gibbs energy, G . This characteristic state function is of particular interest because T and P are the variables, which are most easily controlled experimentally and they are both potentials. G may decrease spontaneously to a minimum under constant T , P and N and the equilibrium condition is

$$D = -(\partial G/\partial \xi)_{P,T,N} = 0. \quad (1.67)$$

It may be mentioned that the mathematical operation, we have used in order to introduce a potential instead of an extensive variable, is called **Legendre transformation**. An important aspect is that no information is lost during such a transformation, as will be discussed in Section 2.1.

Exercise 1.13

Suppose that it would be practically possible to keep H , P and N constant during an internal reaction in a system. What state function should then be used in order to predict the state of equilibrium?

Hint

Find a form of the combined law which has dH , dP and dN on the right-hand side.

Solution

$dH = TdS + VdP + G_m dN - Dd\xi$; $TdS = dH - VdP - G_m dN + Dd\xi$. We thus obtain $D = T(\partial S/\partial \xi)_{H,P,N} > 0$ for spontaneous reactions. Equilibrium is where $S(\xi)$ has its maximum.

Exercise 1.14

In Exercise 1.6 we considered an internal reaction in a closed system giving the following internal production of entropy under isothermal conditions. $\Delta_{ip}S = -\xi K/T - R[\xi \ln \xi - (1 + \xi) \ln(1 + \xi)]$. Now, suppose the heat of reaction under constant T , V and N is $Q = \xi K$. Derive an expression for Helmholtz energy F and use it to calculate the equilibrium value of ξ . Compare with the previous result obtained by maximizing the internal production of entropy.

Hint

Use $\Delta F = \Delta U - \Delta(TS)$, where ΔU is obtained from the first law and ΔS from the second law.

Solution

Under constant T , V and N , the heat of reaction must be compensated by heat flow from the surroundings, $Q = \xi K$. Since the volume is constant $\Delta U = Q = \xi K$.

The total increase of entropy is $\Delta S = Q/T + \Delta_{ip}S = \xi K/T + \Delta_{ip}S = -R[\xi \ln \xi - (1 + \xi) \ln(1 + \xi)]$ and thus $\Delta F = \Delta U - \Delta(TS) = \xi K + RT[\xi \ln \xi - (1 + \xi) \ln(1 + \xi)]$.

This is identical to $-T\Delta_{ip}S$. For this particular system, we thus get the same result if we minimize ΔF or maximize $\Delta_{ip}S$ under constant T , V and N .

1.12 Entropy

Before finishing the present discussion of basic concepts of thermodynamics, a few words regarding entropy should be added. No attempt will here be made to explain the nature of entropy. However, it is important to realize that there is a fundamental difference between entropy and volume in spite of the fact that these two extensive state variables appear in equivalent places in many thermodynamic equations, for instance in the forms of the combined law defining dU or dG . For volume there is a natural zero point and

one can give absolute values of V . As a consequence, the change of G due to a variation of P , $(\partial G/\partial P)_{T,N}$, is a well defined quantity because it is equal to V . One may thus compare the values of G of two systems at different pressures.

For internal energy or enthalpy there is no natural zero point but in practical applications it may be convenient to choose a point of reference for numerical values. The same is true for entropy although it is quite common to put $S = 0$ for a well-crystallized substance at absolute zero. That is only a convention and it does not alter the fact that the change of the Gibbs energy G due to a variation of T , $(\partial G/\partial T)_{P,N}$, cannot be given an absolute value because it is equal to $-S$. As a consequence, it makes no sense to compare the values of G of two systems at the same pressure but different temperatures. The interaction between such systems must be based upon kinetic considerations, not upon the difference in G values. The same is true for the Helmholtz energy F because $(\partial F/\partial T)_{V,N}$ is also equal to $-S$.

The convention to put $S = 0$ at absolute zero is useful because the entropy difference between two crystalline states of a system of fixed composition goes to zero there according to Nernst's heat theorem, sometimes called the **third law**. It should be emphasized that the third law defined in this way only applies to states, which are not frozen in a disordered arrangement.

Statistical thermodynamics can provide answers to some questions, which are beyond classical thermodynamics. It is based upon the Boltzmann relation

$$S = k \ln W, \quad (1.68)$$

where k is the Boltzmann constant ($= R/N^A$, where N^A is Avogadro's number) and W is the number of different ways in which one can arrange a state of given energy. $1/W$ is thus a measure of the probability that a system in this state will actually be arranged in a particular way. Boltzmann's relation is a very useful tool in developing thermodynamic models for various types of phases and it will be used extensively in Chapters 19–22. It will there be applied to one physical phenomenon at a time. The contribution to the entropy from such a phenomenon will be denoted by ΔS or more specifically by ΔS_i and we can write Boltzmann's relation as

$$\Delta S_i = k \ln W_i, \quad (1.69)$$

where W_i and ΔS_i are evaluated for this phenomenon alone. Such a separation of the effects of various phenomena is permitted because $W = W_1 \cdot W_2 \cdot W_3 \cdot \dots$

$$\begin{aligned} S &= k \ln W = k \ln(W_1 \cdot W_2 \cdot W_3 \cdot \dots) = k(\ln W_1 + \ln W_2 + \ln W_3 + \dots) \\ &= \Delta S_1 + \Delta S_2 + \Delta S_3 + \dots \end{aligned} \quad (1.70)$$

Finally, we should mention here the possibility of writing the combined law in a form which treats entropy as a characteristic state function, although this will be discussed in much more detail in Chapters 3 and 6. From Eq. (1.63) we get

$$-dS = -(1/T)dU - (P/T)dV + (G_m/T)dN - (D/T)d\xi. \quad (1.71)$$

This formalism is sometimes called the **entropy scheme** and the formalism based upon dU is then called the **energy scheme**. See Section 3.5 for further discussion. With the entropy scheme we have here introduced new pairs of conjugate variables, $(-1/T, U)$, $(-P/T, V)$ and $(G_m/T, N)$. We may also introduce H into this formalism by the use of $dU = dH - VdP$,

$$dS = -(1/T)dH + (V/T)dP + (G_m/T)dN - (D/T)d\xi. \quad (1.72)$$

Two more pairs of conjugate variables appear here, $(-1/T, H)$ and $(-P, V/T)$. It is evident that S is the characteristic state function for H , P and N as well as for U , V and N . By subtracting dS from $d(H/T)$ we further obtain

$$d(H/T - S) = Hd(1/T) + (V/T)dP + (G_m/T)dN - (D/T)d\xi. \quad (1.73)$$

This is equal to $d(G/T)$ because $G = U - TS + PV = H - TS$. This form of the combined law has the interesting property that it yields directly the following useful expression for the enthalpy,

$$H = \left(\frac{\partial(G/T)}{\partial(1/T)} \right)_{P,N}. \quad (1.74)$$

Exercise 1.15

Equation (1.66) shows that S can be calculated from G as $-(\partial G/\partial T)_{P,N}$. It may be tempting to try to derive this relation as follows: $G = H - TS$; $\partial G/\partial T = -S$. However, that derivation is not very satisfactory. Show that a correction should be added and then prove that the correction is zero under some conditions.

Hint

Remember that H and S may depend upon T .

Solution

$G = H - TS$ gives strictly $(\partial G/\partial T)_{P,N} = (\partial H/\partial T)_{P,N} - T(\partial S/\partial T)_{P,N} - S$. However, the sum of the first two terms (the contributions from the T -dependence of H and S) is zero under reversible conditions and constant P and N because then $dH = TdS + VdP + G_m dN - Dd\xi = TdS$ according to Eq. (1.64).

Exercise 1.16

We have discussed the consequences for G and F of the fact that S has no natural zero point. Actually, nor does U . Find a quantity for which this fact has a similar consequence.

Hint

Look for a form of the combined law which has U as a coefficient just as S is a coefficient in $dG = -SdT + VdP + G_m dN - Dd\xi$.

Solution

Equation (1.71) gives $dS = (1/T)dU + (P/T)dV - (G_m/T)dN + (D/T)d\xi$;
 $d(-F/T) = d(S - U/T) = dS - (1/T)dU - Ud(1/T) = -Ud(1/T) + (P/T)dV - (G_m/T)dN + (D/T)d\xi$; $(\partial[F/T]/\partial[1/T])_{V,N,\xi} = U$.

Thus, one cannot compare the values of F/T at different temperatures.

2 Manipulation of thermodynamic quantities

2.1 Evaluation of one characteristic state function from another

For the sake of simplicity we shall only consider closed systems in this chapter and thus omit terms in dN . In the first chapter we have defined some characteristic state functions, U, F, H and G in addition to S . Each one was introduced through a particular form of the combined law. The independent variables in each form may be regarded as the natural variables for the corresponding characteristic state function. In integrated form these functions can thus be written as

$$U = U(S, V, \xi) \quad (2.1)$$

$$H = H(S, P, \xi) \quad (2.2)$$

$$F = F(T, V, \xi) \quad (2.3)$$

$$G = G(T, P, \xi). \quad (2.4)$$

All these expressions are regarded as **fundamental equations** because all thermodynamic properties of a substance can be evaluated from any one of them. This is because the combined law in its various forms shows how the values of all the dependent variables can be calculated for any given set of values of the independent variables. As an example, from the combined law for the variables S, V and ξ , Eq. (1.49), we get

$$T = (\partial U / \partial S)_{V, \xi} \quad (2.5)$$

$$-P = (\partial U / \partial V)_{S, \xi} \quad (2.6)$$

$$-D = (\partial U / \partial \xi)_{S, V}. \quad (2.7)$$

As a consequence, we can now calculate the value for any other of the characteristic state functions at a given set of values of S, V and ξ , for instance

$$G = U - TS + PV = U - S(\partial U / \partial S)_{V, \xi} - V(\partial U / \partial V)_{S, \xi}. \quad (2.8)$$

It should be noted that the calculation of the value of G from U is only possible because one knows an expression for U as a function of its natural variables. As a consequence of the same principle, even if G can thus be obtained as an analytical expression from $U(S, V, \xi)$ by the use of the above relation, the result is not a fundamental equation because $G(S, V, \xi)$ does not allow the dependent variables to be calculated. They can only be calculated from G as $G(T, P, \xi)$ through $S = -(\partial G / \partial T)_{P, \xi}$ and $V = (\partial G / \partial P)_{T, \xi}$. It is

thus necessary first to replace S and V by T and $-P$ as a new set of independent variables, which is seldom possible to do analytically. If that replacement is not done, then some information has been lost in the calculation of G from U .

It should again be emphasized that an expression for a characteristic state function will be a fundamental equation only if expressed as a function of its natural variables.

Exercise 2.1

Show that $G = (\partial[H/S]/\partial[1/S])_P$.

Hint

Evidently, no internal reaction is considered. The natural variables of H are S and P . It should thus be possible to express G in terms of H and its derivatives.

Solution

Without any internal reaction we have for a closed system from Eq. (1.64): $dH = T dS + V dP$; $T = (\partial H/\partial S)_P$.

We get $(\partial[H/S]/\partial[1/S])_P = H + (1/S)(\partial H/\partial[1/S])_P = H - S(\partial H/\partial S)_P = U + PV - ST = G$.

2.2 Internal variables at equilibrium

We have already emphasized that ξ is a dependent variable if the system is to remain in internal equilibrium. Since $D = 0$ in such a state, the equilibrium value of ξ can be evaluated from a fundamental equation for any one of the characteristic state functions, for instance $U(S, V, \xi)$ from Eq. (1.49),

$$-D = (\partial U/\partial \xi)_{S,V} = 0. \quad (2.9)$$

By applying this to the equation for U one obtains a relation for the equilibrium value of ξ for the prescribed values of S and V ,

$$\xi = \xi(S, V), \quad (2.10)$$

where ξ has thus become a dependent variable since we now consider states of equilibrium. Equation (2.10) can be used to eliminate ξ from the equation for $U(S, V, \xi)$ to yield an equation for states of internal equilibrium. This may be inserted in $U(S, V, \xi)$ in order to yield

$$U = U(S, V). \quad (2.11)$$

It may be of practical importance to calculate the values of various state variables at equilibrium. That would be straightforward if a fundamental equation under equilibrium conditions is available. If only a fundamental equation containing ξ is available, then one

should first apply the equilibrium condition to find how the equilibrium value of ξ varies with the other independent variables. We have just seen how one, in principle, can use that information to eliminate ξ and obtain the wanted fundamental equation. In practice that may be difficult or even impossible to do analytically. In that case one can evaluate the corresponding derivative as a function of ξ from the fundamental equation available and insert the equilibrium value of ξ . We shall now see that this method will give the correct value.

The proof is based on the equilibrium condition for the relevant characteristic state function $\Phi(v', v'', \dots, \xi)$, where v', v'' etc. are the natural variables for Φ and

$$\left(\frac{\partial \Phi}{\partial \xi}\right)_{v^a} = 0. \quad (2.12)$$

The subscript v^a indicates that all the natural variables v', v'' etc. are kept constant. Any derivative of the function for equilibrium states with respect to one of the natural variables, v^b , can be expressed through derivatives of the initial function containing ξ as an independent variable,

$$\left(\frac{\partial \Phi}{\partial v^b}\right)_{v^c} = \left(\frac{\partial \Phi}{\partial v^b}\right)_{v^c, \xi} + \left(\frac{\partial \Phi}{\partial \xi}\right)_{v^a} \left(\frac{\partial \xi}{\partial v^b}\right)_{v^c} = \left(\frac{\partial \Phi}{\partial v^b}\right)_{v^c, \xi} \quad (2.13)$$

when ξ has its equilibrium value. The subscript v^c indicates that all natural variables except v^b are kept constant. This proof depends on the use of Eq. (2.12) which is valid only when the variables v^a that are kept constant are the natural variables of Φ . As an example

$$\left(\frac{\partial U}{\partial \xi}\right)_{T, V} \neq 0, \quad (2.14)$$

because the natural variables of U are S and V . That is why C_V , the heat capacity at constant volume, is different when ξ is frozen-in and when ξ has time to adjust to internal equilibrium (see Eq. (1.21)).

Furthermore, it should be emphasized that this method of calculation can only be applied to the first derivatives of the characteristic state function, and not to higher-order derivatives, since, in general

$$\frac{\partial^2 U}{\partial X^b \partial \xi} \neq 0. \quad (2.15)$$

Exercise 2.2

A very simple model for the magnetic disordering of a ferromagnetic element gives the following expression at a constant pressure, $\Delta G = \xi(1 - \xi)K + RT[\xi \ln \xi + (1 - \xi) \ln(1 - \xi)]$ where K is a constant and ξ is the fraction of spins being disordered. The degree of magnetic disorder varies with T , $\xi = \xi(T)$. Derive an expression for the contribution to the enthalpy due to magnetic disordering, ΔH . Then calculate, at the temperature where $\xi = 1/4$, the corresponding contribution to the heat capacity at constant P which is defined as $\Delta C_P = (\partial \Delta H / \partial T)_P$.

Hint

A magnetic state cannot be frozen-in. ξ will always have its equilibrium value. It can be found from $(\partial \Delta G / \partial \xi)_{T,P} = 0$, which yields $(1 - 2\xi)K + RT \ln[\xi / (1 - \xi)] = 0$. Unfortunately, this does not give ξ as an analytical function of T and we cannot replace ξ by T in ΔG . Thus, it is convenient to make use of the fact that $(\partial \Delta G / \partial \xi)_{T,P} = 0$ at equilibrium, which gives $-\Delta S = (\partial \Delta G / \partial T)_P = (\partial \Delta G / \partial T)_{P,\xi}$ according to Eq. (2.13). We can then evaluate ΔH from $\Delta G + T \Delta S$.

Solution

$\Delta S = -(\partial \Delta G / \partial T)_{P,\xi} = -R[\xi \ln \xi + (1 - \xi) \ln(1 - \xi)]$; $\Delta H = \Delta G + T \Delta S = \xi(1 - \xi)K + RT[\xi \ln \xi + (1 - \xi) \ln(1 - \xi)] - RT[\xi \ln \xi + (1 - \xi) \ln(1 - \xi)] = \xi(1 - \xi)K$; $(\partial \Delta H / \partial T)_{P,\xi} = 0$. It is evident that ΔC_P cannot be evaluated in this way. The reason is that $(\partial \Delta H / \partial \xi)_{T,P} \neq 0$. The natural variables for H are not T and P but S and P . Thus, we must use the basic form of Eq. (2.13), $\Delta C_P \equiv (\partial \Delta H / \partial T)_P = (\partial \Delta H / \partial T)_{P,\xi} + (\partial \Delta H / \partial \xi)_{T,P} (\partial \xi / \partial T)_P$.

From the relation between ξ and T at equilibrium, given in the hint, we get: $(\partial T / \partial \xi)_P = -(K/R)\{-2 / \ln[\xi / (1 - \xi)] - (1 - 2\xi)[1/\xi + 1/(1 - \xi)] / (\ln[\xi / (1 - \xi)])^2\}$; $\Delta C_P = 0 + (1 - 2\xi)KR/K \{2 / \ln[\xi / (1 - \xi)] + (1 - 2\xi)/\xi(1 - \xi)(\ln[\xi / (1 - \xi)])^2\} = 1.29R$ for $\xi = 1/4$.

2.3 Equations of state

If a characteristic state function for a particular substance is given with a different set of variables than the natural one, then it describes some of the properties but not all of them. Such an equation is often regarded as a state equation and not a fundamental equation. As an example,

$$U = U(T, P)$$

is often called the **caloric** equation of state. Some of the quantities which are usually regarded as variables may also be represented with an equation between other variables, for instance,

$$V = V(T, P).$$

This is sometimes called the **thermal** equation of state. The practical importance of some state equations stems from the fact that they can be evaluated fairly directly from measurable quantities and can thus be used to rationalize the results of measurements on a particular substance. As an example, the derivatives of V with respect to T and P can be obtained by measuring the thermal expansivity and the isothermal compressibility, respectively. It is much more laborious to evaluate the fundamental equation for a substance.

A major problem in the evaluation of the fundamental equation or an equation of state is the choice of mathematical form. The form is not specified by thermodynamics but must be chosen from a knowledge of the physical character of the particular substance under consideration. A considerable part of the present text will be concerned with the modelling of the fundamental equation for various types of substances.

Exercise 2.3

An ideal classical gas is defined by two equations of state. For one mole, they are $PV = RT$ and $U = A + BT$ where A and B are two constants. Try to derive a fundamental equation.

Hint

Try to find $F(T, V)$. Use $U = F + TS = F - T(\partial F/\partial T)_V$ which yields $(\partial U/\partial T)_V = -T(\partial^2 F/\partial T^2)_V$. Also use $P = -(\partial F/\partial V)_T$.

Solution

$$(\partial^2 F/\partial T^2)_V = -(\partial U/\partial T)_V/T = B/T.$$

Integration yields $(\partial F/\partial T)_V = -B \ln T + K_1$; $F = -BT \ln T + K_1 T + K_2$, where K_1 and K_2 are independent of T but may depend upon V . That dependency is obtained from $RT/V = P = -(\partial F/\partial V)_T = -T(\partial K_1/\partial V)_T - (\partial K_2/\partial V)_T$.

Thus, $(\partial K_2/\partial V)_T = 0$ and $(\partial K_1/\partial V)_T = -R/V$. K_2 is independent of V and $K_1 = -R \ln V + K_3$.

We get $F = -BT \ln T - RT \ln V + K_3 T + K_2$.

To determine K_2 : $A + BT = U = F + TS = F - T(\partial F/\partial T)_V = BT + K_2$. We thus find $K_2 = A$. We cannot determine K_3 from the information given. Our result is $F = A + K_3 T - BT \ln T - RT \ln V$ which is a fundamental equation, $F(T, V)$. We can also derive the Gibbs energy $G = F + PV = F - V(\partial F/\partial V)_T = F + RT$ but in order to have a fundamental equation in G we must obtain $G(T, P)$ by replacing V with P and T which is possible in the present case where $V = RT/P$. We thus get $G = A + (K_3 + R - R \ln R)T - (B + R)T \ln T + RT \ln P$.

2.4 Experimental conditions

By experimental conditions we here mean the way an experiment is controlled from the outside. It primarily concerns variables which we may regard as external. Let us first consider the pair of conjugate variables $-P$ and V . Either one of them can be controlled from the outside without any knowledge of the properties of the system. In the pair of conjugate variables T and S , one can control the value of T from the outside but the control of S requires knowledge of the properties of the system or extremely slow changes. In practice, it may even be difficult to keep S constant when another variable is changed.

On the other hand, one can control the change in two other state variables, U and H , by controlling the heat flow

$$dU = dQ - PdV \quad (2.16)$$

$$dH = dU + d(PV) = dQ + VdP. \quad (2.17)$$

For some isothermal processes $dQ/d\xi$ is independent of the extent of the process, e.g. melting of a pure substance. It is then convenient to define ξ as the amount of melt formed, expressed in moles, and the **heat of reaction** per mole under constant P is obtained as

$$\frac{Q}{N} = \int_0^1 \left(\frac{\partial Q}{\partial \xi} \right)_{T,P} d\xi = \left(\frac{\partial Q}{\partial \xi} \right)_{T,P}. \quad (2.18)$$

A negative value implies that the process gives off heat to the surroundings under isothermal conditions. Such processes are called **exothermic**. Processes absorbing heat from the surroundings are called **endothermic**. Equations (2.16) and (2.17) show that the heat of reaction may be regarded as the energy or enthalpy of reaction, depending on whether V or P is kept constant. It should be noted that the definition of heat of reaction, which is based on treating Q in the first law as positive when the system receives heat from the surroundings, results in the heat of reaction being negative when heat is ‘generated’ by the reaction, i.e. given off. That is opposite to common sense but may be accepted for the sake of consistency.

Of course, Q itself is not a state variable, because it does not concern the system itself but its interaction with another system, usually the so-called surroundings. An important experimental technique is to keep the system thermally insulated from the surroundings, i.e. to make $dQ = 0$, which is called **adiabatic** conditions. Experimental conditions under which various state variables are kept constant are often given special names,

constant P	isobaric
constant V	isochoric
constant T	isothermal
constant P and T	isobarothermal
constant H	isenthalpic
constant S	isentropic
constant U	isoenergetic
constant composition	isoplethal
constant potential	equipotential

From the above equations for dU and dH , it is evident that an isenthalpic reaction can be accomplished under a combination of isobaric and adiabatic conditions and an isoenergetic reaction can be realized under a combination of isochoric and adiabatic conditions.

Let us now turn to the internal variables, which we have represented by the general symbol ξ . At equilibrium ξ has reached a value where the driving force for its change, D , is zero. If the conditions are changed very slowly by an action from the outside, ξ may vary slowly but all the time be very close to its momentary equilibrium value. In

Section 1.8 we have already concluded that D is then very low and the internal entropy production,

$$d_{\text{ip}}S = Dd\xi / T, \quad (2.19)$$

is very low. In the limit, one talks about a reversible reaction where $d_{\text{ip}}S = 0$. In view of the relation

$$TdS = dQ + Dd\xi, \quad (2.20)$$

we see that a reversible reaction, $D = 0$, which is carried out under adiabatic conditions, $dQ = 0$, is isentropic. By examining the combined law in the variables T and V we see that a reversible reaction, which is carried out under isothermal and isochoric conditions, takes place under constant F . If it is carried out under isothermal and isobaric conditions, it takes place under constant G . It is usual to consider such conditions and they may be called isobarothermal conditions.

The heat flow into a system on heating is often studied experimentally under conditions that may not approach reversible ones. The heat capacity is defined as follows, independent of the reversible or irreversible character of the process.

$$C = dQ/dT. \quad (2.21)$$

For isochoric conditions

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V \quad (2.22)$$

because dU is always equal to $dQ - PdV$ according to the first law. For isobaric conditions we obtain

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P \quad (2.23)$$

because dH is always equal to $dQ + VdP$ according to the first law.

We have already seen that for heat capacity the result will be different if ξ is kept at a constant value or is allowed to be adjusted to its equilibrium value which varies with T . In many experiments with molecular species, their amounts are frozen-in at reasonably low temperatures and ξ is thus kept constant. At higher temperatures, the amounts may be adjusted by molecular reactions and ξ may thus be adjusted to its equilibrium value. When discussing C_P and C_V it may sometimes be wise to specify the conditions regarding ξ . Usually it is assumed that the ξ values for all possible internal processes are adjusted to their equilibrium values but it is not unusual to consider some process as frozen-in.

Exercise 2.4

The isothermal compressibility κ_T is defined as $-(\partial V/\partial P)_T/V$, where the derivative is evaluated under reversible, isothermal conditions, i.e. a very slow compression, $D = 0$. Show a similar way of defining the adiabatic compressibility.

Hint

Suppose the adiabatic compression is so rapid that there can be no internal process, i.e. $d\xi = 0$.

Solution

The second law gives $TdS = dQ + Dd\xi$ and both terms are now zero. We thus have $dS = 0$ and can define the adiabatic compressibility as $-(\partial V/\partial P)_S/V$. This is why this quantity is usually denoted by κ_S . Note that this is justified only if the compression is much faster than all internal reactions, including heat conduction.

2.5 Notation for partial derivatives

Since there are many alternative sets of independent variables it is necessary to indicate which variables are to be kept constant in the evaluation of a particular partial derivative. In order to simplify the notation for characteristic state functions, we can omit this information when we use the natural variables, i.e. the particular set of independent variables characteristic of the state function under consideration. Since G is the characteristic state function for T, P we could then write $\partial G/\partial T$ instead of $(\partial G/\partial T)_P$. Furthermore, we may introduce a shorthand notation for these derivatives, say G_T . Second-order derivatives can be denoted by two subscripts and G_{TP} would thus mean

$$G_{TP} = \left(\frac{\partial}{\partial T} \left(\frac{\partial G}{\partial P} \right)_T \right)_P = \left(\frac{\partial}{\partial P} \left(\frac{\partial G}{\partial T} \right)_P \right)_T = G_{PT}. \quad (2.24)$$

Full information must be given as soon as a set of variables, different from the natural one, is used.

The shorthand notation can be used for frozen-in conditions, $d\xi = 0$, and for equilibrium conditions where ξ is regarded as a dependent variable. When there is any doubt as to what conditions are considered, such information should be given.

Exercise 2.5

How should H_{TT} be interpreted?

Hint

Study the combined law in the form $dH = TdS + VdP - Dd\xi$.

Solution

The natural variables of H are S and P . Thus H_{TT} is an illegal notation because T is not one of the natural variables of H . We conclude that H_{TT} should not be used.

2.6 Use of various derivatives

Of course, C_P and C_V can both be related to any one of the characteristic state functions but in each case a certain choice gives a shorter derivation. C_P is defined with T and P as independent variables and we should thus use G , which has T and P as its natural variables. The fundamental equation $G = G(T, P)$ gives $S = -(\partial G/\partial T)_P$ and thus

$$H(T, P) = G + TS = G - T(\partial G/\partial T)_P = (\partial[G/T]/\partial[1/T])_P \quad (2.25)$$

$$C_P = (\partial H/\partial T)_P = -T(\partial^2 G/\partial T^2)_P = T(\partial S/\partial T)_P. \quad (2.26)$$

For C_V we should use $F(T, V)$ and, since $S = -(\partial F/\partial T)_V$, we find in an analogous way

$$C_V = (\partial U/\partial T)_V = -T(\partial^2 F/\partial T^2)_V = T(\partial S/\partial T)_V. \quad (2.27)$$

However, we may wish to compare the two heat capacities and must then be prepared to derive both from the same characteristic state function, say G . For C_P we already have an expression $-TG_{TT}$, and C_V will now be derived from U through G as a function of T and P .

$$U = G + TS - PV = G - TG_T - PG_P \quad (2.28)$$

$$\begin{aligned} dU &= (G_T - G_T - TG_{TT} - PG_{PT})dT + (G_P - TG_{TP} - G_P - PG_{PP})dP \\ &= -(TG_{TT} + PG_{PT})dT - (TG_{TP} + PG_{PP})dP. \end{aligned} \quad (2.29)$$

However, in order to evaluate C_V which is equal to $(\partial U/\partial T)_V$ we must know U as a function of T and V instead of T and P . We need a relation between dV , dT and dP . Starting with $V = (\partial G/\partial P)_T = G_P$ we obtain

$$dV = G_{PT}dT + G_{PP}dP \quad (2.30)$$

$$dP = dV/G_{PP} - G_{PT}dT/G_{PP}. \quad (2.31)$$

This gives dP as a function of dV and dT which can be inserted in the above equation

$$dU = -(TG_{TT} + PG_{PT})dT - (TG_{TP} + PG_{PP})(dV/G_{PP} - G_{PT}dT/G_{PP}). \quad (2.32)$$

Remembering that G_{PT} is identical to G_{TP} , we thus obtain

$$\begin{aligned} C_V &= (\partial U/\partial T)_V = -TG_{TT} - PG_{TP} + T(G_{TP})^2/G_{PP} + PG_{TP} \\ &= T(G_{TP})^2/G_{PP} - TG_{TT} \end{aligned} \quad (2.33)$$

so that

$$C_V = C_P + T(G_{TP})^2/G_{PP}. \quad (2.34)$$

Using the same method we can derive an expression for any quantity in terms of the derivatives of G with respect to T and P .

It should be pointed out that, by tradition, one instead relates various quantities in terms of the following three quantities which are directly measurable.

$$\text{Heat capacity at constant pressure } C_P = (\partial H/\partial T)_P = -T G_{TT} \quad (2.35)$$

$$\text{Thermal expansivity } \alpha = (\partial V/\partial T)_P/V = G_{TP}/G_P \quad (2.36)$$

$$\text{Isothermal compressibility } \kappa_T = -(\partial V/\partial P)_T/V = -G_{PP}/G_P. \quad (2.37)$$

These three quantities are thus closely related to the three second-order derivatives G_{TT} , G_{TP} and G_{PP} . The two schemes of relating quantities can easily be translated into each other. It is interesting to note that through experimental information on the three quantities C_P , α , and κ_T one has information on all the second-order derivatives of G .

Together, they thus form a good basis for an evaluation of the fundamental equation $G(T, P)$.

Exercise 2.6

Derive an expression for C_V for a substance with $G = a + bT + cT \ln T + dT^2 + eP^2 + fTP + gP^2$.

Hint

Use either one of the equations given for C_V but remember first to make sure that the proper variables are used.

Solution

Let us use $C_V = T(\partial S/\partial T)_V$ but then we must evaluate $S(T, V)$ from G . First, we get $-S(T, P) = (\partial G/\partial T)_P = b + c + c \ln T + 2dT + fP$.

In order to replace P by V we need $V = (\partial G/\partial P)_T = e + fT + 2gP$, which gives $-S = b + c + c \ln T + 2dT + f(V - e - fT)/2g$; $C_V = T(\partial S/\partial T)_V = -T(c/T + 2d - f^2/2g) = -c - T(2d - f^2/2g)$.

Exercise 2.7

Show how one can calculate the heat absorption on reversible isothermal compression from easily measured quantities.

Hint

Since T and P are most easily controlled experimentally, we should use these variables. In Exercise 1.7 we obtained the result $Q = T_1(S_2 - S_1)$ which could be very convenient but only if the properties of the substance have already been evaluated from the experimental information

Solution

Under reversible, isothermal conditions: $dQ = TdS = T(\partial S/\partial P)_T dP = -T(\partial^2 G/\partial T\partial P)dP = -T(\partial V/\partial T)_P dP = -TV\alpha dP$; $Q = -T \int V\alpha dP$, where $\alpha = (\partial V/\partial T)_P/V$.

2.7 Comparison between C_V and C_P

Let us now examine the relation between C_V and C_P in more detail. It is usually given in the following form

$$C_P = C_V(1 + \gamma\alpha T), \quad (2.38)$$

where γ is a dimensionless quantity called Grüneisen's constant. By comparison with the relation between C_V and C_P given by Eq. (2.35) we can express γ in terms of the directly measurable quantities

$$\gamma = -(G_{TP})^2/\alpha C_V G_{PP} = V\alpha/\kappa_T C_V, \quad (2.39)$$

where κ_T and C_V are both positive and, with few exceptions, α is also positive and it is never strongly negative. The γ quantity often has a value of about 2. Note that C_P is always larger than C_V , independent of the sign of α , because $\gamma\alpha$ is equal to $V\alpha^2/\kappa_T C_V$, which is always positive.

The quantity γ can be expressed in many ways, some of which are given here without proof

$$\gamma = \frac{1}{T} \cdot \frac{G_P G_{TP}}{G_{TT} G_{PP} - G_{TP}^2} = \frac{V}{T} \cdot \frac{F_{TV}}{F_{TT}} = \frac{V}{C_V} \left(\frac{\partial S}{\partial V} \right)_T = V \left(\frac{\partial P}{\partial U} \right)_V. \quad (2.40)$$

In all these forms γ is proportional to V , which in turn varies with T if P is kept constant. It is evident that one cannot discuss how γ for a particular substance varies with T without specifying if P or V is kept constant. If $C_V(T)$ is evaluated from $C_P(T)$ using values of γ and α measured at 1 bar, then the resulting values hold for different volumes at different temperatures. C_V may be regarded either as a function of T , V or T , P and it is evident that the functions $C_V(T, V_0)$ and $C_V(T, P_0)$ are different. A comparison of the two functions, evaluated from $C_P(T, P_0)$ for tungsten is given in Fig. 2.1. It should be emphasized that all other quantities, such as α and κ_T , can also be treated as functions of either T , V or T , P .

Exercise 2.8

Express F_{TT} and F_{TV} in terms of G_{TT} and G_{TP} . Then show that the second and third members of Eq. (2.40) actually are equal.

Hint

$$F_T = -S = G_T \text{ and } V = G_P.$$

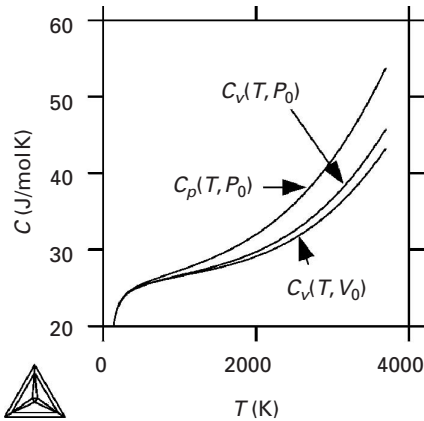


Figure 2.1 The heat capacity of tungsten evaluated in three different ways. Even though C_V is defined as the heat capacity at constant V , it may be regarded as a function of T, V or T, P . At each temperature $C_V(T, P_0)$ is evaluated at the volume given by the actual temperature and a selected constant pressure P_0 .

Solution

In order to change from variables T and P to T and V , we calculate from $V = G_P$; $dV = G_{PT}dT + G_{PP}dP$; $dP = dV/G_{PP} - G_{PT}dV/G_{PP}$.

From the hint: $dF_T = F_{TT}dT + F_{TV}dV = G_{TT}dT + G_{TP}dP = (G_{TT} - G_{TP}^2/G_{PP})dT + G_{TP}dV/G_{PP}$.

Compare terms in these expressions: $F_{TT} = G_{TT} - G_{TP}^2/G_{PP}$; $F_{TV} = G_{TP}/G_{PP}$.

Third member: $(VG_{TP}/G_{PP})/T(G_{TT} - G_{TP}^2/G_{PP}) = G_P G_{TP}/T(G_{TT}G_{PP} - G_{TP}^2)$, which is the second member.

2.8 Change of independent variables

One often wants to change the set of independent variables. An example was given in Section 2.6 where C_V was first given as $(\partial U/\partial T)_V$ and was then evaluated as a function of the derivatives of G with respect to T and P . Such changes can be made by the following automatic procedure, which is based upon the properties of Jacobians. It is here given without mathematical proof. We start by a definition of the Jacobian

$$\frac{\partial(u, v)}{\partial(x, y)} \equiv \begin{vmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} \\ \frac{\partial v}{\partial x} & \frac{\partial v}{\partial y} \end{vmatrix}. \quad (2.41)$$

It should be emphasized that the derivatives in the determinant are partial derivatives, either under constant y or x . It obeys the following rule

$$\frac{\partial(u, v)}{\partial(x, y)} = \frac{\partial(u, v)}{\partial(r, s)} \bigg/ \frac{\partial(x, y)}{\partial(r, s)}. \quad (2.42)$$

We can thus introduce r and s as new independent variables instead of x and y .

The derivative of a thermodynamic quantity can be expressed by a Jacobian because

$$\frac{\partial(u, y)}{\partial(x, y)} = \begin{vmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} \\ \frac{\partial y}{\partial x} & \frac{\partial y}{\partial y} \end{vmatrix} = \begin{vmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} \\ 0 & 1 \end{vmatrix} = \left(\frac{\partial u}{\partial x} \right)_y, \quad (2.43)$$

and the new independent variables, r and s , can thus be introduced in the following way

$$\left(\frac{\partial u}{\partial x} \right)_y = \frac{\partial(u, y)}{\partial(x, y)} = \frac{\partial(u, y)}{\partial(r, s)} \bigg/ \frac{\partial(x, y)}{\partial(r, s)} = \begin{vmatrix} \frac{\partial u}{\partial r} & \frac{\partial u}{\partial s} \\ \frac{\partial y}{\partial r} & \frac{\partial y}{\partial s} \end{vmatrix} \bigg/ \begin{vmatrix} \frac{\partial x}{\partial r} & \frac{\partial x}{\partial s} \\ \frac{\partial y}{\partial r} & \frac{\partial y}{\partial s} \end{vmatrix}. \quad (2.44)$$

It should be realized that $\partial u/\partial x$ actually means $(\partial u/\partial x)_y$ and $\partial u/\partial r$ means $(\partial u/\partial r)_s$. This equation contains the following relations as special cases. They can of course be proved in a much simpler way:

$$\left(\frac{\partial u}{\partial x} \right)_y = 1 \bigg/ \left(\frac{\partial x}{\partial u} \right)_y \quad (2.45)$$

$$\left(\frac{\partial u}{\partial x} \right)_y = - \left(\frac{\partial y}{\partial x} \right)_u \bigg/ \left(\frac{\partial y}{\partial u} \right)_x. \quad (2.46)$$

Exercise 2.9

Express $(\partial G/\partial T)_V$ in terms of functions usually measured and tabulated.

Hint

Most measurements are made by controlling T and P . Change to these variables. Remember that $\partial x/\partial r$ and $\partial x/\partial s$ in Eq. (2.44) mean $(\partial x/\partial r)_s$ and $(\partial x/\partial s)_r$.

Solution

$$\begin{aligned} (\partial G/\partial T)_V &= \begin{vmatrix} \partial G/\partial T & \partial G/\partial P \\ \partial V/\partial T & \partial V/\partial P \end{vmatrix} \bigg/ \begin{vmatrix} \partial T/\partial T & \partial T/\partial P \\ \partial V/\partial T & \partial V/\partial P \end{vmatrix} \\ &= (\partial G/\partial T)_P - (\partial G/\partial P)_T (\partial V/\partial T)_P / (\partial V/\partial P)_T = -S + V\alpha\kappa_T. \end{aligned}$$

Exercise 2.10

A condensed phase is compressed adiabatically and reversibly from a pressure 0 to P . Derive an equation for the temperature change in terms of easily measured quantities.

Hint

Adiabatic and reversible conditions are also isentropic. We want $(\partial T/\partial P)_S$. Change the variables to T and P .

Solution

$$\begin{aligned} (\partial T/\partial P)_S &= \left| \begin{array}{cc} \partial T/\partial T & \partial T/\partial P \\ \partial S/\partial T & \partial S/\partial P \end{array} \right| \bigg/ \left| \begin{array}{cc} \partial P/\partial T & \partial P/\partial P \\ \partial S/\partial T & \partial S/\partial P \end{array} \right| \\ &= -(\partial S/\partial P)_T / (\partial S/\partial T)_P = -G_{TP} / G_{TT} = -V\alpha / (-C_P/T) = TV\alpha / C_P. \end{aligned}$$

We thus get $dT = (TV\alpha/C_P)dP$. The result does not depend on the compressibility which may seem surprising. How could there be compression caused heating if the phase is incompressible? The answer is that the thermal expansivity, α , is zero if the compressibility is zero.

2.9 Maxwell relations

Some partial derivatives can be transformed in a very special way. The requirement is that the variable to be kept constant is a conjugate variable to one of the numerators in the derivative. The method may be illustrated by the following example:

$$dG = -SdT + VdP; \quad -S = (\partial G/\partial T)_P; \quad V = (\partial G/\partial P)_T \quad (2.47)$$

$$\left(\frac{\partial V}{\partial T} \right)_P = \left(\frac{\partial(\partial G/\partial P)_T}{\partial T} \right)_P = \frac{\partial^2 G}{\partial P \partial T} = \frac{\partial^2 G}{\partial T \partial P} = \left(\frac{\partial(\partial G/\partial T)_P}{\partial P} \right)_T = - \left(\frac{\partial S}{\partial P} \right)_T \quad (2.48)$$

or by the shorthand notation

$$\left(\frac{\partial V}{\partial T} \right)_P = G_{PT} = G_{TP} = - \left(\frac{\partial S}{\partial P} \right)_T. \quad (2.49)$$

The relations obtained in this way are called Maxwell relations. We can use any form of the combined law and thus obtain a large number of such relations. It should be noticed that all derivatives related by Maxwell relations are constructed in such a way that the variable to be kept constant is conjugate to the quantity in the numerator but the relations may be inverted, of course.

Exercise 2.11

Transform $(\partial V/\partial T)_S$ using a Maxwell relation.

Hint

Use the inverse quantity, $(\partial T/\partial V)_S$ in order to place the conjugate quantities, T and S , in the right positions. Use the characteristic state function with V and S as natural variables, i.e. U .

Solution

$$(\partial V/\partial T)_S = 1/(\partial T/\partial V)_S = 1/(\partial^2 U/\partial V \partial S) = -1/(\partial P/\partial S)_V = -(\partial S/\partial P)_V.$$

Exercise 2.12

Prove the identity $T(\partial^2 P/\partial T^2)_V = (\partial C_V/\partial V)_T$.

Hint

Since T and V are the variables, it is convenient to base the solution on F and its derivatives. $dF = -SdT - PdV$ gives the following Maxwell relation: $(\partial S/\partial V)_T = (\partial P/\partial T)_V$. Also, use $C_V = T(\partial S/\partial T)_V$ from Eq. (2.27).

Solution

Using the Maxwell relation we get $T(\partial^2 P/\partial T^2)_V = T(\partial(\partial P/\partial T)_V/\partial T)_V = T(\partial(\partial S/\partial V)_T/\partial T)_V = T\partial^2 S/\partial V \partial T$. From $C_V = T(\partial S/\partial T)_V$ we get $(\partial C_V/\partial V)_T = T\partial^2 S/\partial T \partial V$ which is the same result.

3 Systems with variable composition

3.1 Chemical potential

In Chapter 1 we were concerned mainly with closed systems but have also considered the addition of more matter through terms with dN . Without explicitly stating it, it was presumed that the properties of the system were not affected by this addition. That would hold for a one-component system and also if the added matter has the same composition as the initial system. We shall now take changes of composition into account by generalizing $G_m dN$ to $\sum \mu_i dN_i$ where the subscript i identifies different components.

$$dU = TdS - PdV + \sum \mu_i dN_i - Dd\xi. \quad (3.1)$$

The μ_i quantity is a potential just like T , $-P$ and $-D$. It was first introduced by Gibbs [3] and is called **chemical potential**. Its close relation to G_m will be explained in Section 4.1. μ_i and N_i are conjugate variables and the terms $\mu_i dN_i$ may thus be included in $\sum Y^a dX^a$ in the generalized form of the combined law, introduced in Section 1.9. For any component j of the system the chemical potential may be defined from Eq. (3.1) as

$$\mu_j = (\partial U / \partial N_j)_{S, V, N_k, \xi}. \quad (3.2)$$

The subscript ' N_k ' indicates that all N_i are kept constant except for N_j . At equilibrium with respect to the internal process, where ξ is a dependent variable, we have

$$\mu_j = (\partial U / \partial N_j)_{S, V, N_k}. \quad (3.3)$$

The summation $\sum \mu_i dN_i$ is taken over all components in a chosen set of independent components. In chemical thermodynamics one often takes the summation over all molecular species but then one must also define a set of independent reactions. That procedure is less general and will be avoided in the present text.

From the new, more general form of the combined law introduced above, it is evident that the number of external variables which can be varied independently of each other under equilibrium conditions is $c + 2$, if there are c independent components. In general, μ_j is a function of S , V , N_i and ξ and we can write

$$\mu_j = \mu_j(S, V, N_i, \xi), \quad (3.4)$$

or under conditions of internal equilibrium

$$\mu_j = \mu_j(S, V, N_i). \quad (3.5)$$

This is another equation of state but it is not a fundamental equation and, thus, it does not contain all the properties.

When considering systems with variable composition it is useful to define many new quantities. A large part of the present chapter is devoted to discussions of such quantities.

Exercise 3.1

Show how μ_j can be evaluated from a derivative of S instead of U .

Hint

Use the entropy scheme.

Solution

$-dS = (-1/T)dU + (-P/T)dV + \Sigma(\mu_i/T)dN_i - (D/T)d\xi$ yields:
 $(\partial S/\partial N_j)_{U,V,N_k,\xi} = -\mu_j/T$.

3.2 Molar and integral quantities

Let us consider a homogeneous system at equilibrium and define a part of it as a subsystem. The size of the subsystem may be expressed by the value of any extensive variable. The most natural way may be to use the content of matter because from the experimental point of view it is easier to control the content of matter than the volume or entropy. One usually uses the total content of matter, N , defined by

$$N = \Sigma N_i. \quad (3.6)$$

Sometimes we shall use the content of a particular component, N_j , instead of the total content of matter, N .

As a measure of the content of matter Gibbs used the mass, but today it is more common to use the number of atoms or species. We shall use the latter method but it should be emphasized that it is often necessary to specify what species are considered, which Gibbs did not have to do. On the other hand, thermodynamic models of special kinds of substances are often based upon considerations of atoms and it is then convenient to interpret N and N_j as the number of atoms (or groups of atoms). The number is usually expressed in units of moles, i.e. approximately 6×10^{23} pieces (Avogadro's number, N^A).

The volume V is proportional to N in a homogeneous system and we may define a new quantity, the molar volume

$$V_m = V/N. \quad (3.7)$$

This quantity has a defined value at each point of a system. It is thus an **intensive** variable like T , $-P$ and μ_i . However, its properties are quite different, a fact which becomes evident if we consider a system consisting of more than one phase, i.e. regions

exhibiting different properties. In each homogeneous phase V_m has a different, constant value but T , $-P$ and μ_i must have the same value in the whole system at equilibrium (with one exception which we shall deal with later). This is the property of a potential as noted in Section 1.10 and we may conclude that V_m is not a potential. It is very important to distinguish between two kinds of intensive variables, **potentials** and **molar quantities**. One should try to avoid using the words ‘intensive variable’ and when using them one should specify what kind one is considering.

In the same way we may define the molar quantity for any extensive property obeying the law of additivity, e.g. the **molar content** of component i . Usually, it is denoted by x_i and is called mole fraction

$$x_i = N_i/N. \quad (3.8)$$

However, it is sometimes essential to stress its close relation to other molar quantities. ‘Molar content’ is thus preferable.

The molar quantities have been defined for a homogeneous system or for a homogeneous part of a system. The definition may very well be extended to the whole of a system with more than one phase but such a molar quantity is not strictly an intensive quantity and may be regarded as an average of an intensive quantity.

Let us return to a homogeneous system at equilibrium, i.e. with $D = 0$, and define a very small subsystem enclosed inside an imaginary wall. We shall let the subsystem grow in size by expanding the wall but without making any real changes in the system, i.e. without changing P , T or composition. For this process we have

$$dS = S_m dN \quad (3.9)$$

$$dV = V_m dN \quad (3.10)$$

$$dN_i = x_i dN. \quad (3.11)$$

However, $d\xi = 0$ because no internal process is going on. We may thus evaluate the change in U as follows

$$dU = TdS - PdV + \sum \mu_i dN_i = (TS_m - PV_m + \sum \mu_i x_i) dN. \quad (3.12)$$

The value of the expression in parentheses is constant. By integrating over the expansion we obtain

$$U = (TS_m - PV_m + \sum \mu_i x_i) N = TS - PV + \sum \mu_i N_i \quad (3.13)$$

$$U/N = U_m = TS_m - PV_m + \sum \mu_i x_i. \quad (3.14)$$

Using the definition of Gibbs energy in Section 1.11 we get

$$G \equiv U - TS + PV = \sum \mu_i N_i. \quad (3.15)$$

G_m , which was introduced as a notation for $H_m - TS_m$ in Eq. (1.48), is thus identical to the molar Gibbs energy,

$$G_m \equiv U_m - TS_m + PV_m = H_m - TS_m. \quad (3.16)$$

In Section 1.11 we did not recognize changes in composition. For that case Eqs (3.15) and (3.16) would yield

$$G = \sum \mu_i N_i \quad (3.17)$$

$$G_m = \sum \mu_i x_i. \quad (3.18)$$

It may be noted that for a pure substance $x_i = 1$ and G_m will thus be equal to the chemical potential of the substance.

Extensive quantities like U are sometimes called **integral quantities** in order to be distinguished from molar quantities. When defining N as the mass, as Gibbs did, one usually calls the quantities, obtained by dividing with N , **specific** instead of molar. Most of the thermodynamic relations are valid independent of how N is defined.

In many cases it is convenient to consider one mole of formula units or groups of atoms and the molar quantities are then defined by dividing with the number of formula units or groups of atoms, expressed as moles, i.e. units of approximately 6×10^{23} .

It can be easily shown that all the relations between integral quantities also apply to molar quantities, e.g.

$$S_m = \frac{1}{N} S = \frac{-1}{N} \left(\frac{\partial G}{\partial T} \right)_{P, N_i} = \frac{-1}{N} \left(\frac{\partial N G_m}{\partial T} \right)_{P, N_i} = - \left(\frac{\partial G_m}{\partial T} \right)_{P, N_i} = - \left(\frac{\partial G_m}{\partial T} \right)_{P, x_i}. \quad (3.19)$$

because all x_i are constant if all N_i are kept constant.

Exercise 3.2

Cuprous oxide has a density of 6000 kg/m^3 . Give its molar volume in two different ways and also its specific volume.

Hint

The atomic mass is for Cu 63.546 and for O 15.9994.

Solution

The mass of one mole of the formula unit Cu_2O is 143.09 g or 0.14309 kg and the molar volume is thus $0.14309/6000 = 24 \times 10^{-6} \text{ m}^3$ per mole of Cu_2O or $8 \times 10^{-6} \text{ m}^3$ per mole of atoms, i.e. moles of $\text{Cu}_{0.67}\text{O}_{0.33}$. The specific volume is $1/6000 = 167 \times 10^{-6} \text{ m}^3/\text{kg}$, whether one considers Cu_2O or $\text{Cu}_{0.67}\text{O}_{0.33}$.

3.3 More about characteristic state functions

We have seen that

$$U = TS - PV + \sum \mu_i N_i \quad (3.20)$$

in a multicomponent system. It is evident that we get the following relation for the Gibbs energy

$$G = U - TS + PV = \sum \mu_i N_i. \quad (3.21)$$

The relations between the characteristic state functions can be summarized as follows

$$\sum \mu_i N_i = G = H - TS = U + PV - TS = F + PV \quad (3.22)$$

$$\sum \mu_i x_i = G_m = H_m - TS_m = U_m + PV_m - TS_m = F_m + PV_m. \quad (3.23)$$

In Section 1.11 we discussed various forms of the combined law obtained by changing from S to T and from V to P in the set of independent variables. We can now generalize them as follows:

$$dU = TdS - PdV + \sum \mu_i dN_i - Dd\xi \quad (3.24)$$

$$d(U - TS) = dF = -SdT - PdV + \sum \mu_i dN_i - Dd\xi \quad (3.25)$$

$$d(U + PV) = dH = TdS + VdP + \sum \mu_i dN_i - Dd\xi \quad (3.26)$$

$$d(U - TS + PV) = dG = -SdT + VdP + \sum \mu_i dN_i - Dd\xi. \quad (3.27)$$

It is evident that the chemical potentials for a substance can be evaluated from any one of these characteristic state functions if it is given in terms of its natural variables

$$\mu_j = (\partial U / \partial N_j)_{S, V, N_k, \xi} = (\partial F / \partial N_j)_{T, V, N_k, \xi} = (\partial H / \partial N_j)_{S, P, N_k, \xi} = (\partial G / \partial N_j)_{T, P, N_k, \xi}. \quad (3.28)$$

We may consider ξ as a dependent variable under equilibrium conditions but, in view of Section 2.2, that fact does not change the value of a partial derivative. We could thus omit ξ and write

$$\mu_j = (\partial U / \partial N_j)_{S, V, N_k} = (\partial F / \partial N_j)_{T, V, N_k} = (\partial H / \partial N_j)_{S, P, N_k} = (\partial G / \partial N_j)_{T, P, N_k}. \quad (3.29)$$

The remaining extensive variables, N_i , can also be replaced by their conjugate potentials, μ_i , and we can get four new forms of the combined law

$$d(U - \sum \mu_i N_i) = d(TS - PV) = TdS - PdV - \sum N_i d\mu_i - Dd\xi \quad (3.30)$$

$$d(U - TS - \sum \mu_i N_i) = d(-PV) = -SdT - PdV - \sum N_i d\mu_i - Dd\xi \quad (3.31)$$

$$d(U - PV - \sum \mu_i N_i) = d(TS) = TdS + VdP - \sum N_i d\mu_i - Dd\xi \quad (3.32)$$

$$d(U - TS + PV - \sum \mu_i N_i) = 0 = -SdT + VdP - \sum N_i d\mu_i - Dd\xi. \quad (3.33)$$

The first three forms define new characteristic state functions. The fourth form is unique because it defines a function which is identically equal to zero since $U - TS - PV = \sum \mu_i N_i$. For reversible conditions, $D = 0$, or in the absence of internal processes, $d\xi = 0$, it yields a direct relation between the $c + 2$ potentials, the so-called **Gibbs–Duhem relation**. Consequently, one of the potentials is no longer an independent variable.

$$SdT - VdP + \sum N_i d\mu_i = 0. \quad (3.34)$$

This relation is often given in terms of molar quantities

$$S_m dT - V_m dP + \sum x_i d\mu_i = 0 \quad (3.35)$$

For a pure substance $x_i = 1$ and the chemical potential is identical to the molar Gibbs energy, G_m , as noted after Eq. (3.18). The Gibbs–Duhem relation thus simplifies to

$$S_m dT - V_m dP + dG_m = 0. \quad (3.36)$$

Equation (3.31) gives a characteristic state function which is equal to $(-PV)$ and is particularly interesting in statistical thermodynamics. This characteristic state function is sometimes denoted by Ω and is called ‘grand potential’. It can be evaluated from the so-called grand partition function, Ξ ,

$$\Omega = -kT \ln \Xi. \quad (3.37)$$

The grand partition function is defined for a so-called grand canonical ensemble for which T , V and μ_i are the independent variables and $\Omega = \Omega(T, V, \mu_i)$. It is sometimes useful in calculations of equilibrium states because it may yield relatively simple relationships. The fact that it applies under constant values of μ_i , which may be difficult to control experimentally, does not limit its usefulness in such calculations.

In this connection it may be mentioned that the ordinary partition function Z is defined for an ordinary canonical ensemble for which T , V and N_i are the independent variables. It can be used to evaluate the Helmholtz energy

$$F = -kT \ln Z. \quad (3.38)$$

Furthermore, for a microcanonical ensemble one keeps U , V and N_i constant and can evaluate $S(U, V, N_i)$.

The remaining two new forms of the combined law and their characteristic state functions have not found much direct use. However, in the [next section](#) they will prove useful in some thermodynamic derivations. It should finally be emphasized that a large number of additional forms may be derived by selecting some of the N_i and some of the μ_i as independent variables. We shall discuss one such example in Section 14.5.

Exercise 3.3

Prove the well-known equality $(\partial G/\partial N_A)_{T,P,N_j} = (\partial F/\partial N_A)_{T,V,N_j}$ from Eq. (3.29) by changing variables using Jacobians.

Hint

T and all N_j are not to be changed. Simplify the notation by omitting them from the subscripts. Change from N_A, P to N_A, V . Then express all derivatives of G in terms of F using $P = -(\partial F/\partial V)_{T,N_i} = -F_V$ and $G = F + PV = F - VF_V$.

Solution

$$\left(\frac{\partial G}{\partial N_A}\right)_P = \left| \begin{array}{cc} \partial G/\partial N_A & \partial G/\partial V \\ \partial P/\partial N_A & \partial P/\partial V \end{array} \right| \bigg/ \left| \begin{array}{cc} \partial N_A/\partial N_A & \partial N_A/\partial V \\ \partial P/\partial N_A & \partial P/\partial V \end{array} \right|$$

$$= (\partial G/\partial N_A)_V - (\partial G/\partial V)_{N_A} (\partial P/\partial N_A)_V / (\partial P/\partial V)_{N_A}$$

But, $(\partial G/\partial N_A)_V = F_{N_A} - VF_{VN_A}$; $(\partial G/\partial V)_{N_A} = F_V - F_V - VF_{VV} = -VF_{VV}$;
 $(\partial P/\partial N_A)_V = -F_{VN_A}$; $(\partial P/\partial V)_{N_A} = -F_{VV}$. Inserting these we get $(\partial G/\partial N_A)_P =$
 $(F_{N_A} - VF_{VN_A} - (-VF_{VV})(-F_{VN_A})/(-F_{VV})) = F_{N_A} = (\partial F/\partial N_A)_V$.

3.4 Additivity of extensive quantities. Free energy and exergy

The extensive quantities that were primarily defined in Chapter 1 are additive with no restrictions. The values of V , U , S and N of a composite system are always equal to the sum of the values for the subsystems. This is also true for the contents of all components N_i . In Eqs (3.31) and (3.32) we defined quantities that are equal to $-PV$ and TS . They are also extensive but it is evident that they are additive only if the potentials P and T have the same values in the subsystems. The same is true for F , H and G because they are defined by subtracting TS or adding PV . As a consequence, it was mentioned in Section 1.12 that one cannot compare Gibbs energy values for states at different temperatures.

The problem can sometimes be solved by accepting that T and P in the definition $G = U - TS + PV$ are the values in the surroundings. Then one can add the Gibbs energy for two subsystems that are kept at different T and P ,

$$G_1 + G_2 = U_1(T_1, P_1) - TS_1(T_1, P_1) + PV_1(T_1, P_1) + U_2(T_2, P_2)$$

$$- TS_2(T_2, P_2) + PV_2(T_2, P_2) = U_1(T_1, P_1) + U_2(T_2, P_2) - T[S_1(T_1, P_1)$$

$$+ S_2(T_2, P_2)] + P[V_1(T_1, P_1) + V_2(T_2, P_2)] = U_{1+2} - TS_{1+2} + PV_{1+2} = G_{1+2}.$$
(3.39)

because U , S and V are all additive. It should thus be realized that one could add Gibbs energies of two subsystems at different T or P from tabulated values only by first breaking them down into U , S and V values. Then one must decide on the relevant T and P for the whole system. It would normally be T and P of the surroundings which appears natural if only one subsystem has contact with the surroundings and the other one is an inclusion. If each subsystem has its own surroundings, then there is probably no good reason to try to compare or add their G values.

A particularly interesting case is found when a homogeneous system has different T or P than the surroundings. One may then be interested in predicting the maximum amount of work that can be extracted from the system when it moves towards equilibrium with the surroundings. Since the surroundings are always regarded as a homogeneous, infinite reservoir, its T and P are constant and a process under constant T and P should of course be treated with the Gibbs energy function. Equation (3.27) gives, if there is no exchange of matter,

$$dG = -SdT + VdP + \sum \mu_i dN_i - Dd\xi = -Dd\xi. \quad (3.40)$$

For a spontaneous process $Dd\xi$ is positive and $Dd\xi/T$ is equal to the internal production of entropy. If there were a mechanism by which one could extract another kind of work than through a volume change, PdV , then it should have been included in W in the first definition of the first law, Eqs (1.1) and (1.2), and it would have been considered all through the derivations and appear in Eq. (3.40). Of course, extracted work should be given with a minus sign. Equation (3.40) would thus have been modified

$$dG = -dW_{\text{extr}} - Dd\xi. \quad (3.41)$$

For a reversible process one obtains

$$dW_{\text{extr}} = -dG; \quad \Delta W_{\text{extr}} = G(\text{initial}) - G(\text{final}). \quad (3.42)$$

This gives the maximum work that can be extracted. It is clear that $G(\text{final})$ is evaluated for T and P of the surroundings. It is also evident that $G(\text{initial})$ must be given as

$$G(\text{initial}) = U(T_{\text{in}}, P_{\text{in}}) - TS(T_{\text{in}}, P_{\text{in}}) + PV(T_{\text{in}}, P_{\text{in}}), \quad (3.43)$$

because any two extensive quantities can only be compared if the law of additivity applies.

The quantity ΔW_{extr} can be regarded as the part of the energy of the initial system that is free to be transformed into useful work. That is why Gibbs energy was initially called Gibbs free energy. If the surroundings are instead a reservoir of constant T and V then one should repeat the derivation starting from the Helmholtz energy and that is the reason why it was initially called Helmholtz free energy. Often one extracts work by allowing the system to react with a chemical compound in the surroundings, usually O_2 used for burning a fuel. In that case, the appropriate free energy function would be found by considering a reservoir with constant T , P and μ_O ,

$$d\Phi = d(G - N_O\mu_O) = -SdT + VdP + \sum \mu_j dN_j - N_O d\mu_O - dW_{\text{extr}} - Dd\xi. \quad (3.44)$$

For a reversible process under constant P , T , N_j and μ_O , we find

$$\Delta W_{\text{extr}} = G(\text{initial}) - G(\text{final}) - \mu_O[N_O(\text{initial}) - N_O(\text{final})], \quad (3.45)$$

where $N_O(\text{final})$ is the total content of O after the system has received enough O_2 from the surroundings to burn the fuel.

It is evident that, what has here been called **free energy**, must be defined in different ways depending on the surroundings or on how the system reacts with the surroundings. In mechanical engineering it is often called **exergy**.

3.5 Various forms of the combined law

In Section 3.3 the discussion was based on the energy scheme, which starts from the combined law in the form

$$dU = TdS - PdV + \sum \mu_i dN_i - Dd\xi, \quad (3.46)$$

where all the independent variables are extensive ones. It defines the following set of conjugate pairs of variables (T, S) , $(-P, V)$ and (μ_i, N_i) . However, there are many more

possibilities to express the combined law in terms of only extensive quantities as independent variables. Using the new characteristic state functions, obtained in Section 3.3, we can change variables in the combined law. For example, let us replace S by $(TS - PV)/T + PV/T$, obtaining

$$dS = d[(TS - PV)/T] + (P/T)dV + Vd(P/T). \quad (3.47)$$

By inserting this expression we get

$$\begin{aligned} dU &= Td[(TS - PV)/T] + PdV + TVd(P/T) - PdV + \sum \mu_i dN_i - Dd\xi \\ &= Td[(TS - PV)/T] + TVd(P/T) + \sum \mu_i dN_i - Dd\xi. \end{aligned} \quad (3.48)$$

By subtracting $(P/T) \cdot TV$ (which is equal to PV) from U , we can form a new characteristic state function with only extensive quantities as independent variables

$$\begin{aligned} d(U - PV) &= d[U - (P/T) \cdot TV] \\ &= Td[(TS - PV)/T] - (P/T)d(TV) + \sum \mu_i dN_i - Dd\xi. \end{aligned} \quad (3.49)$$

This form of the combined law defines a new set of conjugate pairs, $\{T, [(TS - PV)/T]\}$, $(-P/T, TV)$ and (μ_i, N_i) .

We may instead replace V by $[(PV - TS)/P + TS/P]$ and after some manipulations we obtain a new characteristic state function with only extensive variables as independent variables

$$\begin{aligned} d(U + TS) &= d[U + (T/P) \cdot PS] \\ &= -Pd[(PV - TS)/P] + (T/P)d(PS) + \sum \mu_i dN_i - Dd\xi. \end{aligned} \quad (3.50)$$

which yields a new set of conjugate pairs.

We may also rearrange the terms in the combined law before introducing new functions. The entropy scheme uses

$$-dS = -(1/T)dU - (P/T)dV + \sum (\mu_i/T)dN_i - (D/T)d\xi. \quad (3.51)$$

It immediately defines a new set of conjugate pairs and two more alternatives are obtained by replacing U or V in the way demonstrated above. One may also rearrange the terms in the combined law as follows

$$dV = (T/P)dS - (1/P)dU + \sum (\mu_i/P)dN_i - (D/P)d\xi. \quad (3.52)$$

This may be called the **volume scheme** and it yields three more alternatives. We have thus obtained the sets of conjugate pairs of variables given in Table 3.1. In each pair the potential is given first and between them one can formulate a Gibbs–Duhem relation. In each case the characteristic state function for the extensive variables is given to the left.

We may also define a number of **content schemes** by the following arrangement of terms, but they will probably have very limited use and will not be discussed further.

$$-dN_j = (T/\mu_j)dS - (1/\mu_j)dU - (P/\mu_j)dV + \sum_k (\mu_k/\mu_j)dN_k - (D/\mu_j)d\xi. \quad (3.53)$$

Table 3.1 Some sets of conjugate pairs of state variables

From the energy scheme			
U :	T, S	$-P, V$	μ_i, N_i
$U - PV$:	$T, (S - PV/T)$	$-P/T, TV$	μ_i, N_i
$U + TS$:	$T/P, PS$	$-P, (V - TS/P)$	μ_i, N_i
From the entropy scheme			
$-S$:	$-1/T, U$	$-P/T, V$	$(\mu_i/T), N_i$
$-S - PV/T$:	$-1/T, H$	$-P, V/T$	$(\mu_i/T), N_i$
$-S - U/T$:	$-P/T, H/P$	$-1/P, PU/T$	$(\mu_i/T), N_i$
From the volume scheme			
V :	$T/P, S$	$-1/P, U$	$(\mu_i/P), N_i$
$V - U/P$:	$-1/T, TU/P$	$-T/P, F/T$	$(\mu_i/P), N_i$
$V + TS/P$:	$T, S/P$	$-1/P, F$	$(\mu_i/P), N_i$

Exercise 3.4

Suppose one would like to consider U as an independent variable. What would be its conjugate potential?

Solution

From the entropy scheme we find $-1/T$ and from the volume scheme $-1/P$. Evidently, the choice depends on what other conjugate pairs one would like to consider at the same time.

Exercise 3.5

In Sections 9.1 and 10.7 we will find that the two axes in a phase diagram should be taken from the same set of conjugate pairs. Suppose one would like to use U , F or G as one of the axes in a unary system. How should the other axis be chosen?

Solution

From the entropy scheme we find that U could be combined with $-P/T$ (which may not be very practical) or V . From the volume scheme we find that U could be combined with T/P (which again may not be very practical) or S . We find F in the volume scheme only, and it can be combined with T or S/P (which is not very practical). We do not find G in any scheme except in the form of μ_i for a unary system.

3.6 Calculation of equilibrium

In calculations of equilibrium it is often assumed that the temperature and composition can be kept constant. Instead of using the basic condition of equilibrium, $d_{ip}S = 0$, it is

then more convenient to use $D = 0$, where D is the driving force for the internal process and is equal to $T d_{\text{ip}}S/d\xi$. However, D may be evaluated in a large number of ways, e.g. the following ones, which are based on the energy scheme.

$$\begin{aligned} -D &= (\partial U/\partial \xi)_{S,V,N_i} = (\partial F/\partial \xi)_{T,V,N_i} = (\partial H/\partial \xi)_{S,P,N_i} \\ &= (\partial G/\partial \xi)_{T,P,N_i} = (\partial \Omega/\partial \xi)_{T,V,\mu_i}. \end{aligned} \quad (3.54)$$

In fact, any of these methods could be used and they must all give the same answer to the question whether the system is in equilibrium. The choice simply depends on what fundamental equation is available. In most cases the Gibbs energy is used because a fundamental equation of the form $G = G(T, P, N_i, \xi)$ is available.

Suppose one finds that $D \neq 0$ then the system is not in equilibrium and one may instead like to know what state of equilibrium the system would eventually approach, i.e. the equilibrium value of ξ . Then it is essential to know the experimental conditions because one wants to find a state of equilibrium under the initial values of a particular set of external variables. Suppose one is going to keep T and V constant during the experiment. Then one would primarily like to use $F = F(T, V, N_i, \xi)$, derive an expression for $-D = (\partial F/\partial \xi)_{T,V,N_i} = 0$ and solve for the equilibrium value of ξ .

However, suppose that one has only $G = G(T, P, N_i, \xi)$ but the experimental conditions will keep T and V constant. The calculation is then carried out by iteration, starting with the prescribed T value and evaluating the equilibrium value of ξ from $(\partial G/\partial \xi)_{T,P,N_i} = 0$ for a first choice of value for P . Using the equilibrium value of ξ one can evaluate V from $(\partial G/\partial P)_{T,P,N_i,\xi}$ and compare with the prescribed V value and then obtain a better P value by iteration.

Suppose the initial state is known and the experimental conditions are adiabatic, yielding $dU = dQ - PdV = 0$ or $dH = dQ + VdP = 0$, depending on whether one keeps V or P constant. If P were kept constant then H would also be constant and could be obtained from any fundamental equation. In order then to calculate the equilibrium value of ξ one should prefer a function with P and H as independent variables. By rearranging the terms in $dH = TdS + VdP - Dd\xi$ we find

$$dS = (-1/T)dH + (V/T)dP + \Sigma(\mu_i/T)dN_i - (D/T)d\xi. \quad (3.55)$$

It is evident that $S(H, P, N_i, \xi)$ is the characteristic function for which one should like to have an equation. If instead another fundamental equation is available, one has to use iteration as just described.

When a thermodynamic model for a certain kind of system is based on basic physical properties, it may result in an explicit expression for the grand potential $\Omega(T, V, \mu_i, \xi)$ and not $G(T, P, N_i, \xi)$ or $F(T, V, N_i, \xi)$. The grand potential can then be used to find the equilibrium under prescribed values of N_i by iteration.

Finally, consider an $\alpha + \beta$ two-phase system where the relative amounts and compositions of the phases can vary but not the content of the whole system. The internal variable can be defined as $\xi = N^\alpha = N - N^\beta$, where N is the total content, but it is not immediately evident how the equilibrium compositions of α and β can be related to ξ . However, in a binary system the compositions can be calculated directly from the two-phase

equilibrium if T and P of the equilibrium state are known, using $G_m^\alpha = G_m^\alpha(T, P, N_i^\alpha)$ and $G_m^\beta = G_m^\beta(T, P, N_i^\beta)$. Finally, ξ can be calculated from a mass balance. In a higher order system one must use iteration. If instead the equilibrium values of T and V are known, then the fundamental equation $F_m^\alpha = F_m^\alpha(T, V_m^\alpha, N_i^\alpha)$ and $F_m^\beta = F_m^\beta(T, V_m^\beta, N_i^\beta)$ would be of little use because the molar volumes of the phases are not known until P and the phase compositions have been calculated. One would have to guess the final P value, carry out a calculation based on G_m^α and G_m^β as already described, and finally evaluate the total volume V and compare with the required value. By iteration one could eventually find the P value that gives the correct V value. For the calculation of a phase equilibrium it is evident that $G_m^\alpha = G_m^\alpha(T, P, N_i^\alpha)$ is the most useful fundamental equation for all experimental conditions.

Exercise 3.6

Examine what would be the most convenient way of calculating a two-phase equilibrium under given values of T and V in a pure element.

Hint

We have already seen that it is not practical to use $F_m^\alpha = F_m^\alpha(T, V_m^\alpha)$ and $F_m^\beta = F_m^\beta(T, V_m^\beta)$ for a two-phase equilibrium at given T and V because V_m^α and V_m^β are not defined directly by the experimental conditions.

Solution

Using the molar Gibbs energy for each phase we get for the whole system $G(T, P, \xi) = \xi G_m^\alpha(T, P) + (N - \xi)G_m^\beta(T, P)$ where $\xi = N^\alpha = N - N^\beta$. Equilibrium requires that $-D = (\partial G / \partial \xi)_{T, P} = G_m^\alpha(T, P) - G_m^\beta(T, P) = 0$. In this particular case we may thus calculate P for the two-phase equilibrium at a given T without iteration and without involving ξ , which only describes the amounts of the phases. Then we can calculate $V_m^\alpha = (\partial G_m^\alpha / \partial P)_T$ and $V_m^\beta = (\partial G_m^\beta / \partial P)_T$ for these T and P values. Finally, we calculate the ξ value satisfying $\xi V_m^\alpha + (N - \xi)V_m^\beta = V$.

3.7 Evaluation of the driving force

In the preceding section we discussed the calculation of the equilibrium value of an internal variable, ξ , under various conditions. The calculation of the driving force for the corresponding reaction is simpler because the system does not ‘feel’ which variables are to be kept constant until the reaction is under way. One could use $-D = (\partial G / \partial \xi)_{T, P, N_i}$ as well as any other expression for D . On the other hand, as the reaction gets under way there will be changes in the variables that are not controlled and the result will depend upon the experimental conditions. Then one must either use the appropriate fundamental equation or an iteration technique similar to the one described in the preceding section.

For example, when using $G(T, P, N_i, \xi)$ for an experiment under constant T and V , one can make a series of calculations along the reaction path by selecting a number of ξ values. For each value one can use iteration to evaluate the P value yielding the experimental value of $V = (\partial G/\partial P)_{T, N_i, \xi}$. Using that pair of ξ, P values one can calculate $-D$ from $(\partial G/\partial \xi)_{T, P, N_i}$.

There are many cases where one knows the initial and final states for a process but does not know or is not interested in the ‘**reaction path**’ in detail. In such cases it may be interesting to evaluate the total production of entropy due to internal processes

$$\Delta_{\text{ip}}S = \int d_{\text{ip}}S = \int (D/T)d\xi. \quad (3.56)$$

For isothermal reactions T is constant and

$$\Delta_{\text{ip}}S = (1/T) \int Dd\xi. \quad (3.57)$$

The quantity $\int Dd\xi$ could be called the **integrated driving force** but unfortunately it is often called simply ‘driving force’. It could also be identified with the integrated value of the ‘loss of work’ discussed in Section 1.7. Anyway, it should only be applied to isothermal reactions because T initially appears in the integrand.

Under constant T, P and N_i we obtain, using the combined law expressed for G ,

$$Dd\xi = -SdT + VdP + \sum \mu_i dN_i - dG = -dG. \quad (3.58)$$

Under these conditions, the integrated driving force is thus equal to the decrease in Gibbs energy,

$$\int Dd\xi = -\Delta G. \quad (3.59)$$

Since G is a state function it is evident that ΔG is here independent of the reaction path and so is the integrated driving force, as long as the final state is the same. The driving force D defined by the derivative of G in Eq. (3.54) at any value of ξ along the path, i.e. at any stage of the reaction, depends critically upon the reaction path.

If the reaction occurs under other conditions, the integrated driving force will be given by the change in the characteristic state function for which the natural variables are constant during the reaction. For instance, under constant T, V and composition, $\int Dd\xi = -\Delta F$. However, suppose $G(T, P, N_i, \xi)$ is the only fundamental equation available, then one must first find the final equilibrium by iteration, as described in the preceding section. Then one can use $G(T, P, N_i, \xi)$ to evaluate

$$\int Dd\xi = -\Delta F = -\Delta[G - P(\partial G/\partial P)_{T, N_i, \xi}]. \quad (3.60)$$

Exercise 3.7

Consider a binary system at constant T, V, N_B and μ_A . It is in a metastable state of β .

Show how one can calculate the integrated driving force for the transformation to a more stable phase α .

Hint

$Dd\xi$ is present in all forms of the combined law. In the present case it is most convenient to use the form where T , V , N_B and μ_A are the independent variables.

Solution

Choose $d(-PV) = -SdT - PdV - +\mu_B dN_B - N_A d\mu_B - Dd\xi$. In our case $d(-PV) = -Dd\xi$; $\int Dd\xi = \int d(PV) = (PV)_2 - (PV)_1 = V(P_2 - P_1)$. It is evident that P must increase during the spontaneous transformation. It should be noticed that the content N_A is not constant under these experimental conditions.

3.8 Driving force for molecular reactions

Many kinds of system contain aggregates of atoms, e.g. molecules. Even though there may be reactions between the molecular species (often called ‘chemical reactions’) the individual molecule often has a long lifetime, not only inside a phase but also with respect to exchange of matter between phases or between a system and the surroundings.

When studying the rate of a molecular reaction, it may be interesting to evaluate its driving force. Let the extent of reaction be ξ , expressed per mole of reaction formula. The driving force will then be

$$D^j = - \left(\frac{\partial G}{\partial \xi^j} \right)_{T,P,\xi^k} = - \sum_i \left(\frac{\partial G}{\partial N_i^j} \right)_{T,P,\xi^l} \cdot \frac{dN_i^j}{d\xi^j} = - \sum_i \mu_i v_i^j. \quad (3.61)$$

The reaction coefficients are thus defined as

$$v_i^j = dN_i^j / d\xi_j. \quad (3.62)$$

The equilibrium condition for a single process is given by

$$D = - \sum_i v_i \mu_i = 0. \quad (3.63)$$

As an example, for an ideal gas mixture one can write the chemical potential as a function of the partial pressure

$$\mu_i = {}^\circ\mu_i + RT \ln P_i. \quad (3.64)$$

By inserting this in the equilibrium condition we get

$$\Pi(P_i)_{\text{eq.}}^{v_i} = \exp \left(- \sum (v_i {}^\circ\mu_i / RT) \right). \quad (3.65)$$

This is the law of mass action. The value of the right-hand side is regarded as the equilibrium constant and may be denoted by K . When the left-hand side is not equal to K , then the system is not in equilibrium and the driving force for the reaction is

$$D = - \sum_i v_i \mu_i = RT \ln(K / \Pi(P_i)^{v_i}). \quad (3.66)$$

Exercise 3.8

For dilute, condensed solutions one can express the chemical potential with Henry's law, $\mu_i = {}^\circ\mu_i + RT \ln f_i + RT \ln x_i$, where x_i is the molar content of component i and f_i is the activity coefficient. Show how one can express the equilibrium with a pure compound having the stoichiometric coefficients ν_i . Derive an expression for the driving force for the dissolution of the compound in the solution.

Hint

Suppose the chemical potential of the compound in the other phase is μ_c . The reaction would be: compound $\rightarrow \Sigma \nu_i I$.

Solution

$D = 1 \cdot {}^\circ\mu_c - \Sigma \nu_i \mu_i = {}^\circ\mu_c - \Sigma \nu_i {}^\circ\mu_i - RT \ln(\Pi(f_i)^{\nu_i}) - RT \ln(\Pi(x_i)^{\nu_i}) = RT \ln[\exp(\Delta_f^\circ G_c / RT) / \Pi(f_i)^{\nu_i} \Pi(x_i)^{\nu_i}]$ where $\Delta_f^\circ G_c$ denotes Gibbs energy of formation of the compound from the elements in their reference states. Of course, one may define $(\Delta_f^\circ G_c / RT) \Pi(f_i)^{\nu_i}$ as an equilibrium constant K . From equilibrium, where $D = 0$, one would then have $K = \Pi(x_i)_{\text{eq}}^{\nu_i}$ and in general $D = RT \ln(K / \Pi(x_i)^{\nu_i})$.

3.9 Evaluation of integrated driving force as function of T or P

According to Section 3.7, the integrated driving force for an $\alpha \rightarrow \beta$ phase transformation, which takes place under constant T, P and N_i , should be equal to $-\Delta G = G^\alpha - G^\beta$. One is sometimes interested in evaluating the variation of $-\Delta G$ with T or P . The following procedure can be used close to equilibrium.

For constant P it is convenient to evaluate the effect of a change of T on the relative stability of the two phases by starting from the following equation, obtained by applying $G = H - TS$ to both phases under the same T ,

$$\Delta G(T) = \Delta H - T \Delta S. \quad (3.67)$$

If the two phases are in equilibrium with each other at T_0 for the P value under consideration, we have

$$0 = \Delta H - T_0 \Delta S. \quad (3.68)$$

Suppose the difference $T - T_0$ is so small that ΔH and ΔS have practically the same values at both temperatures. By eliminating ΔS or ΔH we obtain

$$\int D d\xi = -\Delta G = \Delta H(T - T_0) / T_0 = \Delta S(T - T_0). \quad (3.69)$$

For constant T it is convenient to evaluate the effect of a change of P by starting from the following equation

$$\Delta G(P) = \Delta F + P \Delta V. \quad (3.70)$$

By the same procedure we now obtain

$$\int Dd\xi = -\Delta G = \Delta F(P - P_0)/P_0 = \Delta V(P_0 - P). \quad (3.71)$$

Again, this equation can only be used so close to P_0 that the variation of ΔF and ΔV with P is negligible.

Exercise 3.9

Consider two phases of pure A, α and L, which are in equilibrium at T_0, P_0 . At $T = T_0 + \Delta T$ and $P = P_0$ there is a driving force for the transformation $\alpha \rightarrow L$. How much should P be changed in order to restore the equilibrium? To get a numerical value, use the ‘typical’ values $\Delta S_m = R$ and $\Delta V_m = 0.2 \times 10^{-6} \text{ m}^3/\text{mol}$.

Hint

The driving forces due to the two changes must eliminate each other.

Solution

$$\Delta S(T - T_0) + \Delta V(P_0 - P) = 0; \quad (P - P_0)/(T - T_0) = \Delta S/\Delta V = \Delta S_m/\Delta V_m = R/\Delta V_m = 8.3/(0.2 \times 10^{-6}) \text{ Pa/K} = 400 \text{ bar/K}.$$

3.10 Effective driving force

When a phase transformation occurs under diffusion it often happens that the processes occurring at the phase interfaces are rapid compared to the rate of diffusion. The transformation will then be diffusion controlled and the boundary conditions governing the rate of diffusion can be evaluated by assuming that, whenever two phases meet at an interface, their compositions right at the interface are very close to those required by equilibrium. This is called the **local equilibrium** approximation. That approximation will be used in the following, except when other conditions are clearly defined.

So far, we have chosen to regard $T \cdot d_{ip}S/d\xi$ as the driving force for the process, the progress of which is measured by ξ , and it thus seemed natural to assume that the rate of the process is proportional to $D = T \cdot d_{ip}S/d\xi$, at least as a first approximation, yielding $d\xi/dt = KD$ where K is a constant of proportionality. However, one should be aware of the possibility that a process may be accompanied by an entropy production that does not contribute to the rate of the process. This possibility may be best explained by an example from a very simple type of transformation.

Let us first consider particles of pure solid A immersed in liquid B. The component A may dissolve in the liquid to a small but measurable extent, but B does not dissolve in

the solid. It is well known that smaller particles will dissolve and larger ones will grow, so-called coarsening or ‘Ostwald ripening’. The driving force comes from the increased pressure inside the smaller particles due to the surface tension. Next, suppose that B can dissolve in solid A but the temperature is so low that diffusion can be neglected. We would still expect that the pressure difference makes the smaller particles go into solution and the larger ones grow. However, the growing layer of a large particle should now be a solid solution of B in A and the net process could be written as: solid A (from small particle) + liquid B (with low A content) \rightarrow solid A – B alloy (in growing layer). The chemical driving force for such a reaction can be evaluated from $-\Delta G_m$, assuming that all the phases are under the same pressure, and it should be added to the effect of the pressure difference. It would seem that the chemical driving force should give a drastic increase of the net driving force for the process and make it possible even without the pressure effect, at least after the process has started. Such a process has actually been observed in sintering in the presence of a liquid.

However, in this description of the process we did not consider the local equilibrium conditions at the surface of the smaller particle. Even though the rate of diffusion inside solid A is negligible, the rate of transfer of atoms between solid and liquid at the interface may be appreciable. Under ordinary conditions the net rate of any reaction is believed to be the difference between opposite fluxes that are much larger. We should thus recognize that there is a very localized reaction at the interface by which a monolayer of an A–B solid solution forms. The chemical driving force will drive that reaction but it will soon slow down if B does not diffuse into the interior of the smaller particle. Only the pressure difference may remain and cause material from the monolayer to go into solution and diffuse to the larger, growing particle. B from the liquid will then again react with the fresh A in the smaller particle and the monolayer will be healed. It may thus seem that much if not all the chemical driving force will be lost.

This example has demonstrated that there may be a Gibbs energy dissipation caused by a process, which does not actually drive the process. One might say that even if a Gibbs energy dissipation depends on the progress of a process, the process does not necessarily make use of that Gibbs energy dissipation. The effective driving force, from which one may estimate the rate of reaction, has to come from another source, in our example from the pressure difference due to the surface tension.

In the above example, it was fairly easy to identify the various steps in the whole process and thus to identify what part of the total driving force actually contributes to the rate. The example gets more complicated if we replace the liquid by a grain boundary which has contact with a B-rich reservoir outside the A material. Even in that case it has been observed experimentally that an A – B solid solution can grow at the expense of pure A, a phenomenon called DIGM (diffusion-induced grain boundary migration). Cahn *et al.* [4] argued that the chemical driving force does not contribute at all and they proposed that the effective driving force comes from the process of diffusion of B down the grain boundary. Later, it was proposed that a part of the chemical driving force is not dissipated, as described above, thanks to the action of coherency stresses, and that

this undissipated part is able to drive the main process. This will be further discussed in Sections 16.11 and 16.12.

This kind of complication is often neglected and it will not be further considered in this book. We shall regard chemical driving forces as forces actually contributing to the rate of processes but the local-equilibrium approximation will be applied in most cases in order to evaluate it.

4 Practical handling of multicomponent systems

4.1 Partial quantities

It is common to keep T and P constant but vary the amount of some component, N_j . It is interesting to examine what happens to various thermodynamic quantities under such conditions and we shall thus define a new kind of quantity called **partial quantity** for any extensive quantity A .

$$\text{partial quantity of } j: A_j \equiv (\partial A / \partial N_j)_{T, P, N_k}. \quad (4.1)$$

Such partial quantities appear in the expression for the differential of $A(T, P, N_i)$

$$dA = (\partial A / \partial T)_{P, N_i} dT + (\partial A / \partial P)_{T, N_i} dP + \sum A_i dN_i. \quad (4.2)$$

From Eq. (3.29) we saw that the chemical potential μ_j can be derived as a partial derivative of any one of the characteristic state functions U , F , H and G . However, it is important to notice that only one of these partial derivatives is a partial quantity with the definition used here, $(\partial G / \partial N_j)_{T, P, N_k}$, because it is evaluated under constant T and P . We can thus write

$$\mu_j = (\partial G / \partial N_j)_{T, P, N_k} = G_j. \quad (4.3)$$

With the shorthand notation introduced for partial derivatives in Section 2.5, this quantity could also be denoted by G_{N_j} .

Since the chemical potential μ_j is identical to the partial Gibbs energy G_j one may wonder if both names or symbols are necessary. However, we shall find it useful sometimes to use one and sometimes the other. When we are interested in the variation of properties of a homogeneous system consisting of a single phase with variable composition, and employ an analytical function $G_m(T, P, x_i)$, then G_j is the most natural term to use. When we are concerned with a more complex system, where G_j of a small part cannot be defined because the composition of that part cannot vary gradually, then μ_j is the most natural term to use.

In order to distinguish the notation for a partial quantity A_j at any composition from the notation for the same quantity in pure j , the latter one will be identified by a small superscript circle in front, ${}^{\circ}A_j$. It should be noticed that ${}^{\circ}A_j$ is actually identical to A_m

of pure j , because for a system with one component we have $N_j = N$ and obtain from Eq. (4.1),

$${}^{\circ}A_j = (\partial A / \partial N_j)_{T,P,N_k} = (\partial A / \partial N)_{T,P} = A/N = A_m \quad (4.4)$$

It is evident that A_j is also an intensive quantity and this can be demonstrated by the fact that it is related to the intensive quantity A_m and can be calculated from it. Using the following relations: $N = \sum N_i$; $x_j = N_j / \sum N_i$; $\partial x_j / \partial N_j = (N - N_j) / N^2 = (1 - x_j) / N$; $x_k = N_k / \sum N_i$; $\partial x_k / \partial N_j = -N_k / N^2 = -x_k / N$, we obtain

$$\begin{aligned} A_j &= \left(\frac{\partial A}{\partial N_j} \right)_{N_i} = \left(\frac{\partial (N A_m)}{\partial N_j} \right)_{N_i} \\ &= 1 \cdot A_m + N \cdot \left(\frac{\partial A_m}{\partial x_j} \right)_{x_l} \left(\frac{\partial x_j}{\partial N_j} \right)_{N_i} + N \cdot \sum_{k \neq j} \left(\frac{\partial A_m}{\partial x_k} \right)_{x_l} \left(\frac{\partial x_k}{\partial N_j} \right)_{N_i} \\ &= A_m + (1 - x_j) \left(\frac{\partial A_m}{\partial x_j} \right)_{x_l} - \sum_{k \neq j} x_k \left(\frac{\partial A_m}{\partial x_k} \right)_{x_l}. \end{aligned} \quad (4.5)$$

All the partial derivatives of A_m are here taken under constant T and P and molar contents of the other components; x_j is excluded from the summation. We can modify the equation by including x_j in the summation

$$A_j = A_m + \left(\frac{\partial A_m}{\partial x_j} \right)_{x_l} - \sum_{i=1}^c x_i \left(\frac{\partial A_m}{\partial x_i} \right)_{x_l}. \quad (4.6)$$

When evaluating each derivative in Eq. (4.6) from an expression of A as a function of all x_i , one will keep all the other x_l constant, including x_1 although it is really a dependent variable. Since this is physically incorrect, these derivatives cannot be used alone. On the other hand, one may transform Eq. (4.6) by replacing x_l in the first term of the summation using $\sum x_i = 1$, obtaining

$$A_j = A_m + \left(\frac{\partial A_m}{\partial x_j} \right)_{x_l} - \left(\frac{\partial A_m}{\partial x_1} \right)_{x_l} - \sum_{i=2}^c x_i \left[\left(\frac{\partial A_m}{\partial x_i} \right)_{x_l} - \left(\frac{\partial A_m}{\partial x_1} \right)_{x_l} \right]. \quad (4.7)$$

The differences of derivatives appearing here can be interpreted physically. They are actually identical to the derivative of A_m with respect to the particular x_j when x_1 has been selected as the dependent variable. Equation (4.7) is thus the mathematically correct way of evaluating A_j but Eq. (4.6) offers a more convenient way. Furthermore, when Eq. (4.6) is applied to Gibbs energy and the difference is taken between components j and 1, one obtains

$$G_j - G_k = \left(\frac{\partial G_m}{\partial x_j} \right)_{x_l} - \left(\frac{\partial G_m}{\partial x_k} \right)_{x_l}. \quad (4.8)$$

This is the driving force for diffusion of component j in exchange for component 1, sometimes called **diffusion potential**. The diffusion potential for exchange with the major component is thus obtained as the derivative of G_m with respect to the component if the major component has been selected as the dependent one.

Equation (4.6) is frequently used for calculating chemical potentials as partial Gibbs energies. For a binary 1–2 system one can regard $G(T, P, x_1, x_2)$ as $G(T, P, x_2)$ because $x_1 + x_2 = 1$. This yields

$$\mu_1 = G_1 = G_m - x_2 \frac{dG_m}{dx_2} \quad (4.9)$$

$$\mu_2 = G_2 = G_m + (1 - x_2) \frac{dG_m}{dx_2} \quad (4.10)$$

Exercise 4.1

For substitutional solutions one often defines an activity coefficient for a component i as $\gamma_i = \exp[(G_i - {}^\circ G_i - RT \ln x_i)/RT]$. Show that for low contents of B and C in A one has the following approximate relation under constant T and P , if x_A is not included in the set of independent composition variables, $\partial \ln \gamma_B / \partial x_C = \partial \ln \gamma_C / \partial x_B$.

Hint

Start from a Maxwell relation $\partial G_B / \partial N_C = \partial^2 G / \partial N_C \partial N_B = \partial G_C / \partial N_B$. Then go from derivatives with respect to N_i to derivatives with respect to x_i by using $x_i = N_i/N$; $\partial x_i / \partial N_i = (N - N_i)/N^2 = (1 - x_i)/N$; $\partial x_i / \partial N_j = -N_i/N^2 = -x_i/N$.

Solution

$G_i = {}^\circ G_i + RT \ln x_i + RT \ln \gamma_i$; $\partial G_B / \partial N_C = RT[(1/x_B)(-x_B/N) + (\partial \ln \gamma_B / \partial N_C)] = \partial G_C / \partial N_B = RT[(1/x_C)(-x_C/N) + \partial \ln \gamma_C / \partial N_B]$ and thus $\partial \ln \gamma_B / \partial N_C = \partial \ln \gamma_C / \partial N_B$, exactly. However, we should examine derivatives with respect to x_i and not N_i . Notice that we should choose an analytical expression for γ_B containing x_B and x_C as independent variables. For small x_B and x_C we get approximately

$$\begin{aligned} \partial \ln \gamma_B / \partial N_C &= (\partial \ln \gamma_B / \partial x_B)(-x_B)/N + (\partial \ln \gamma_B / \partial x_C)(1 - x_C)/N \\ &\cong (\partial \ln \gamma_B / \partial x_C)/N \end{aligned}$$

$$\begin{aligned} \partial \ln \gamma_C / \partial N_B &= (\partial \ln \gamma_C / \partial x_B)(1 - x_B)/N + (\partial \ln \gamma_C / \partial x_C)(-x_C)/N \\ &\cong (\partial \ln \gamma_C / \partial x_B)/N. \end{aligned}$$

Thus, $\partial \ln \gamma_B / \partial x_C \cong \partial \ln \gamma_C / \partial x_B$.

4.2 Relations for partial quantities

In Section 3.2 we saw how an expression for the integral internal energy could be derived by integration over a homogeneous system. It will now be demonstrated that the same method can be applied to any other extensive quantity, A . Consider a homogeneous system with constant T , P and x_i . Then all the partial quantities A_i are also constant. We select an infinitely small subsystem and allow it to grow by simply extending its

imaginary wall. The growth in size may be represented by dN and the increase of the i content is obtained as

$$dN_i = x_i dN. \quad (4.11)$$

By integrating the differential of A under constant T and P and remembering that all A_i and x_i are constant, we obtain from the definition of A_i , Eq. (4.2),

$$\begin{aligned} A &= \int dA = \int \Sigma A_i dN_i = \int \Sigma A_i x_i dN = \Sigma A_i x_i \int dN \\ &= \Sigma A_i x_i N = \Sigma A_i N_i \end{aligned} \quad (4.12)$$

$$A_m \equiv A/N = \Sigma A_i x_i. \quad (4.13)$$

It may again be emphasized that the partial quantities are always defined with T and P as independent variables. If we were to define a corresponding quantity under constant T and V , for instance, it would not have the same properties because V is an extensive variable.

By differentiating $A = \Sigma A_i N_i$ we obtain

$$dA = \Sigma A_i dN_i + \Sigma N_i dA_i. \quad (4.14)$$

Comparison with the expression for dA in Eq. (4.2), yields

$$\Sigma N_i dA_i - (\partial A/\partial T)_{P, N_i} dT - (\partial A/\partial P)_{T, N_i} dP = 0. \quad (4.15)$$

This expression is most useful when applied to the Gibbs energy, giving

$$\Sigma N_i dG_i + SdT - VdP = 0. \quad (4.16)$$

This is identical to the Gibbs–Duhem relation, Eq. (3.34), since G_i is identical to μ_i . For other quantities it may be most useful under conditions of constant T and P . As an example, for volume we would obtain, under constant T and P ,

$$\Sigma N_i dV_i = 0 \quad \text{or} \quad \Sigma x_i dV_i = 0. \quad (4.17)$$

Since all the partial quantities are defined as the partial derivatives with respect to some content under constant T and P , it is evident that the following relations hold between them

$$\mu_j = G_i = H_i - TS_i = U_i + PV_i - TS_i = F_i + PV_i. \quad (4.18)$$

It is also evident that the expressions for other extensive state variables as derivatives of the characteristic state functions can be applied to partial quantities as well. As an example, we can start from an expression for S in terms of G and derive a similar expression for S_j in terms of G_j ,

$$S = - \left(\frac{\partial G}{\partial T} \right)_{P, N_i} \quad (4.19)$$

$$\begin{aligned} S_j &= \left(\frac{\partial S}{\partial N_j} \right)_{T, P, N_i} = - \left(\frac{\partial}{\partial N_j} \left(\frac{\partial G}{\partial T} \right)_{P, N_i} \right)_{T, P, N_i} \\ &= - \left(\frac{\partial}{\partial T} \left(\frac{\partial G}{\partial N_j} \right)_{T, P, N_i} \right)_{P, N_i} = - \left(\frac{\partial G_j}{\partial T} \right)_{P, N_i} = - \left(\frac{\partial \mu_j}{\partial T} \right)_{P, N_i}. \end{aligned} \quad (4.20)$$

Furthermore, from the Gibbs–Duhem relation, Eq. (3.34), we obtain by taking the derivative with respect to N_j ,

$$V_j dP - S_j dT = d\mu_j + \sum_i N_i \frac{\partial \mu_i}{\partial N_j} = d\mu_j + \sum_i N_i \frac{\partial^2 G}{\partial N_i \partial N_j}. \quad (4.21)$$

It should be emphasized that the summation of terms cannot be omitted. As a consequence, it is not possible to derive a Gibbs–Duhem relation for the partial quantities. Finally, by applying Eqs (4.11) and (4.13) to Eqs (1.11) and (1.38) we can write the first and second laws in the following forms

$$dU = dQ + dW + \sum H_i dN_i \quad (4.22)$$

$$dS = dQ/T + \sum S_i dN_i + d_{ip}S. \quad (4.23)$$

Exercise 4.2

Derive the relation $H_j = (\partial(\mu_j/T)/\partial(1/T))_{P,N_i}$ from $H = (\partial(G/T)/\partial(1/T))_{P,N_i}$ in Eq. (2.25).

Solution

$$\begin{aligned} H_j &= (\partial H/\partial N_j)_{T,P,N_k} = (\partial(\partial(G/T)/\partial(1/T))_{P,N_i}/\partial N_j)_{T,P,N_k} \\ &= (\partial(\partial(G/T)/\partial N_j)_{T,P,N_k}/\partial(1/T))_{P,N_i} \\ &= (\partial(G_j/T)/\partial(1/T))_{P,N_i} = (\partial(\mu_j/T)/\partial(1/T))_{P,N_i}. \end{aligned}$$

4.3 Alternative variables for composition

By composition we mean the *relative* amounts of various components, preferably the set of molar contents, x_i . We shall now examine different ways of expressing the molar contents in a ternary system. The same methods may be applied in higher-order systems. In order to distinguish the methods we shall use a number of different notations.

- (i) $x_j = N_j/N = N_j/\sum N_i$
- (ii) $z_j = N_j/N_1 = x_j/x_1$
- (iii) $u_j = N_j/(N_1 + N_2 + \dots + N_k) = N_j/(\sum N - N_{k+1} - \dots) = x_j/(1 - x_{k+1} - \dots)$.

The size of the system is thus measured by N , N_1 and $(N_1 + N_2 + \dots + N_k)$, respectively.

The characteristics of the three methods for a ternary system (with $k = 2$ in the third method) are compared in Fig. 4.1, where the regular triangle introduced by Gibbs is shown in Fig. 4.1(a). Isopleths (lines along which some composition variable is held constant) according to the other schemes are shown in Fig. 4.1(b) and (c). It should be noticed that the isopleths for u_2 are also isopleths for u_1 , since $u_1 + u_2 = 1$. In Fig. 4.1(c) it should be noticed that $z_1 = 1$ everywhere. The three diagrams are redrawn with linear scales for each kind of variable in Fig. 4.2. Here, the isopleths with arrows extend to

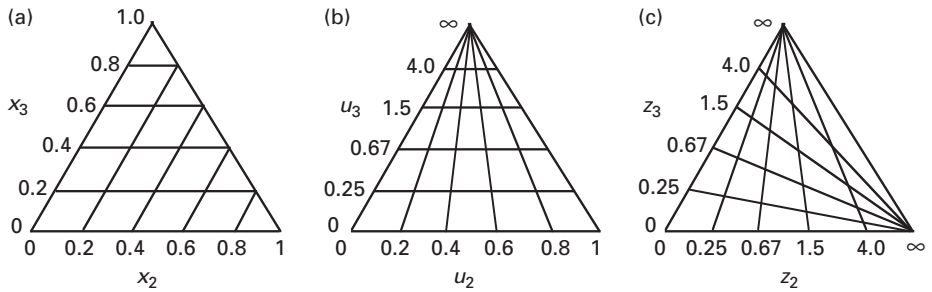


Figure 4.1 The Gibbs triangle showing three different methods of representing composition. The corners represent pure component 1, 2 and 3, respectively.

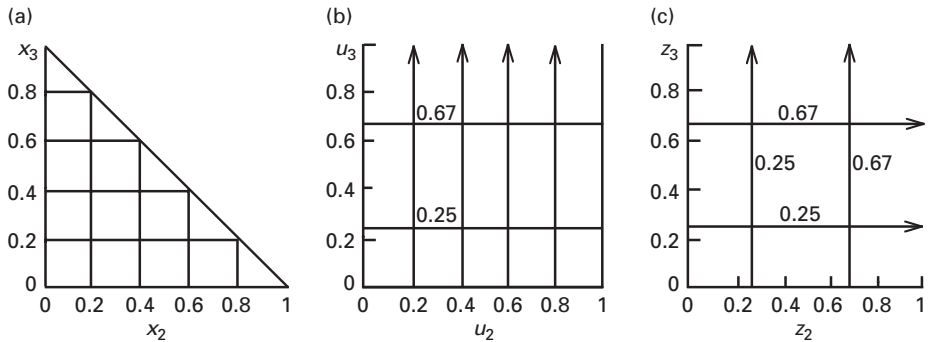


Figure 4.2 The diagrams from Fig. 4.1 drawn with linear scales for the actual composition variables. The arrows indicate that the component is situated at infinity and parallel lines with an arrow pointing to the same pure component at infinity.

infinity. It should be emphasized that any line, which is straight in the Gibbs triangle, is still a straight line in these modified diagrams.

When these new composition variables are used, the calculation of partial quantities is changed. Before turning to these calculations, it should be realized that the definition of all the molar quantities to be used in one context should be modified in the same way. Taking the Gibbs energy as an example, its molar quantity should be defined as G/N_1 when discussed in connection with z_i (case (ii)) and $G/(N_1 + N_2)$ when discussed in connection with u_i (case (iii)) if $k = 2$. We shall denote these molar quantities by G_{m1} and G_{m12} .

With the method used in deriving an expression for A_j in Section 4.1 we obtain, for case (ii),

$$G = N_1 G_{m1}(z_1, z_2, z_3) \text{ with } z_1 = 1 \quad (4.24)$$

$$\mu_1 \equiv G_1 = G_{m1} - z_2 \left(\frac{\partial G_{m1}}{\partial z_2} \right)_{z_3} - z_3 \left(\frac{\partial G_{m1}}{\partial z_3} \right)_{z_2} \quad (4.25)$$

$$\mu_2 \equiv G_2 = z_2 \left(\frac{\partial G_{m1}}{\partial z_2} \right)_{z_3} \quad (4.26)$$

$$\mu_3 \equiv G_3 = z_3 \left(\frac{\partial G_{m1}}{\partial z_3} \right)_{z_2} \quad (4.27)$$

For case (iii) we have

$$G = (N_1 + N_2)G_{m12}(u_1, u_2, u_3) \text{ with } u_1 + u_2 = 1 \quad (4.28)$$

$$\mu_1 \equiv G_1 = G_{m12} + \left(\frac{\partial G_{m12}}{\partial u_1} \right)_{u_i} - \sum u_i \left(\frac{\partial G_{m12}}{\partial u_i} \right)_{u_i} \quad (4.29)$$

$$\mu_2 \equiv G_2 = G_{m12} + \left(\frac{\partial G_{m12}}{\partial u_2} \right)_{u_i} - \sum u_i \left(\frac{\partial G_{m12}}{\partial u_i} \right)_{u_i} \quad (4.30)$$

$$\mu_3 \equiv G_3 = \left(\frac{\partial G_{m12}}{\partial u_3} \right)_{u_i} . \quad (4.31)$$

On the other hand, it should be emphasized that many equations derived with the ordinary way of expressing the size of the system, will hold without further modification, if one simply replaces all molar contents x by the corresponding z or u and all other molar quantities by the corresponding molar quantities which may be denoted by A_{m1} or A_{m12} . The following relations are useful

$$u_j = N_j/(N_1 + N_2) = x_j/(x_1 + x_2) \quad (4.32)$$

$$A_{m12} = A/(N_1 + N_2) = A/N(x_1 + x_2) = A_m/(x_1 + x_2) \quad (4.33)$$

$$A_{m12} = A/(N_1 + N_2) = \Sigma N_i A_i/(N_1 + N_2) = \Sigma u_i A_i \quad (4.34)$$

$$z_j = N_j/N_1 = x_j/x_1 \quad (4.35)$$

$$A_{m1} = A/N_1 = A/Nx_1 = A_m/x_1 \quad (4.36)$$

$$A_{m1} = A/N_1 = \Sigma N_i A_i/N_1 = \Sigma z_i A_i = A_1 + z_2 A_2 + z_3 A_3. \quad (4.37)$$

It should be observed that A_i is the usual partial quantity $(\partial A/\partial N_i)_{T,P,N_j}$.

Sometimes it may be convenient to use the notations A_m and x_i for all these quantities. It is then necessary always to specify how one mole is defined, i.e. whether one considers one mole of 1, one mole of 1 + 2 or one mole total. In higher-order systems one may measure the size of the system in several ways. It may be convenient to use the notations $u_{i(1\dots k)}$ and $A_{m(1\dots k)}$ where $1 \dots k$ are the components used to measure the size.

Exercise 4.3

Show that $\mu_2 = G_m + (1 - x_2)(\partial G_m/\partial x_2)_{x_3/x_1}$ in a ternary system.

Hint

Replace variables N , N_2 and N_3 using $x_2(= N_2/N)$, $x_3/x_1(= N_3/N_1)$ and $N(= N_1 + N_2 + N_3)$.

Solution

Let G_m be a function of x_2 and x_3/x_1 : $G = NG_m(x_2, x_3/x_1)$; $\mu_2 = (\partial G/\partial N_2)_{N_1, N_3} = G_m + N(\partial G_m/\partial x_2)_{x_3/x_1}(\partial x_2/\partial N_2)_{N_1, N_3} + N(\partial G_m/\partial(x_3/x_1))_{x_2}(\partial(x_3/x_1)/\partial N_2)_{N_1, N_3} = G_m + N(\partial G_m/\partial x_2)_{x_3/x_1}(N - N_2)/N^2 + N(\partial G_m/\partial(x_3/x_1))_{x_2} \cdot 0 = G_m + (1 - x_2)(\partial G_m/\partial x_2)_{x_3/x_1}$.

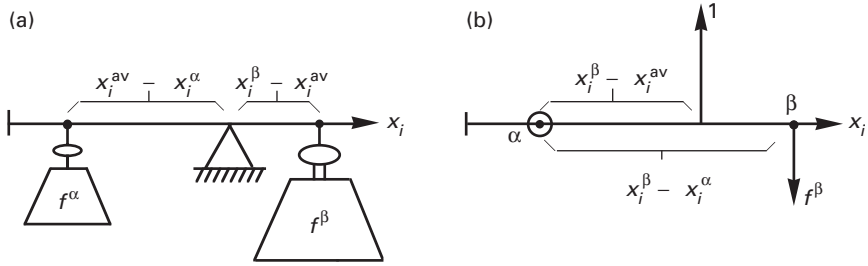


Figure 4.3 Two ways of applying the lever rule.

4.4 The lever rule

Let us consider some molar quantity A_m in two homogeneous subsystems (phases), α and β , with different properties, and then evaluate the average of the molar quantity, A_m^{av} , in the total system. By definition we have

$$A_m^\alpha = A^\alpha / N^\alpha \quad (4.38)$$

$$A_m^\beta = A^\beta / N^\beta. \quad (4.39)$$

Using the law of additivity we obtain

$$A_m^{\text{av}} \equiv (A^\alpha + A^\beta) / (N^\alpha + N^\beta) = A_m^\alpha \cdot \frac{N^\alpha}{N^\alpha + N^\beta} + A_m^\beta \cdot \frac{N^\beta}{N^\alpha + N^\beta} = f^\alpha A_m^\alpha + f^\beta A_m^\beta. \quad (4.40)$$

The fractions of atoms present in each subsystem, i.e. the relative sizes of the two subsystems, are denoted by f^α and f^β . The terms can be rearranged because $f^\alpha + f^\beta = 1$.

$$f^\alpha (A_m^{\text{av}} - A_m^\alpha) = f^\beta (A_m^\beta - A_m^{\text{av}}). \quad (4.41)$$

This is often called the **lever rule** and is often used when A_m is a molar content x_i . That case is illustrated in Fig. 4.3(a).

The terms can be rearranged in another way

$$(A_m^{\text{av}} - A_m^\alpha) = f^\beta (A_m^\beta - A_m^\alpha). \quad (4.42)$$

This equation can be illustrated by two balancing forces, each of which tries to turn the lever around the point representing the α subsystem (see Fig. 4.3(b)).

The lever rule can be extended to more subsystems. It is easy to see that

$$A_m^{\text{av}} = f^\alpha A_m^\alpha + f^\beta A_m^\beta + f^\gamma A_m^\gamma + \dots \quad (4.43)$$

For three subsystems in a diagram with two molar quantities one obtains a triangle and the total system will be represented by a point placed at its centre of gravity. This case is illustrated in Fig. 4.4.

When the positions of the three subsystems and the total system are known, then one can evaluate the fractions by several graphical methods, as illustrated in Fig. 4.5.

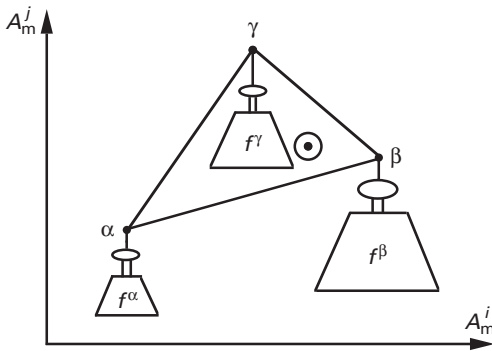


Figure 4.4 The lever rule applied to a system with three subsystems α , β and γ . The triangle is regarded as capable of rotating around the point representing the whole system.

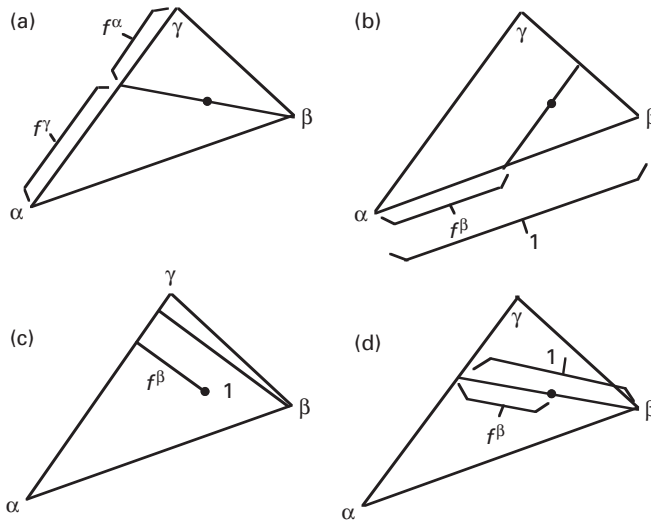


Figure 4.5 (a)–(d) Four methods of evaluating the fractions of a subsystem, f^β , or the ratio of fractions of two subsystems, f^α/f^γ .

4.5 The tie-line rule

It is evident from Fig. 4.4 that a mixture of only two subsystems will fall on the straight line between them, which is called **tie-line** or **conode**. This we shall call the **tie-line rule**. It must be realized that it holds only if the same measure of size is used for both quantities. In most applications we shall use the total number of moles or moles of a specific element. An example is shown in Fig. 4.6. Both V_m and x_B were defined by dividing V or N_B by N . The value of V_m for the composition x'_B is an average between the end-points of the tangent. They represent the partial molar volumes, V_A and V_B , for the same composition.

$$V_m(x'_B) = x'_A V_A(x'_B) + x'_B V_B(x'_B). \quad (4.44)$$

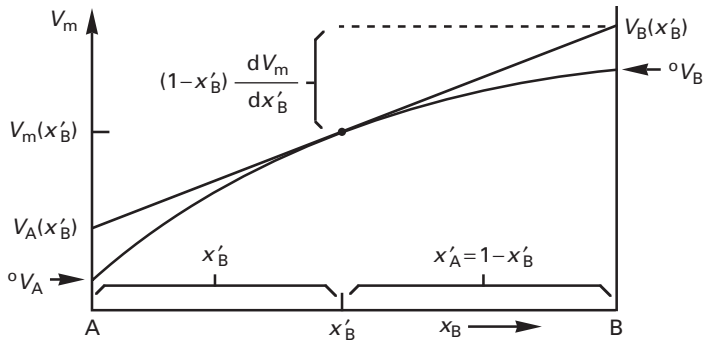


Figure 4.6 Property diagram for a binary system showing the molar volume as a function of composition at constant T and P . The intercepts made by the tangent give the partial quantities.

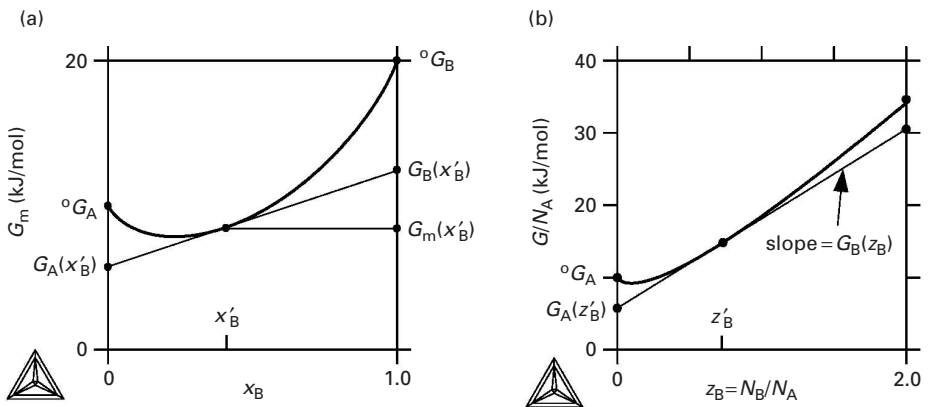


Figure 4.7 Property diagram for a binary system showing the molar Gibbs energy as a function of composition at constant T and P , using the total content of atoms, N , as a measure of size (a) or N_A (b).

The fact that the end-points of the tangent give the partial quantities can be shown with Eq. (4.6). If x_B is regarded as the only variable by treating x_A as $1 - x_B$, we obtain

$$V_B = V_m + \frac{dV_m}{dx_B} - x_B \frac{dV_m}{dx_B} = V_m + (1 - x_B) \frac{dV_m}{dx_B}. \quad (4.45)$$

Two methods of measuring the size are compared in Figs. 4.7(a) and 4.7(b). The tie-line rule applies to both. The rule does not apply to Fig. 4.8 because different measures of size have there been used for the Cr and C contents. The straight lines in (a) have no physical meaning but the curved lines in (b) are the true tie-lines. Other examples of inconvenient choices will be given in Section 10.7.

The tie-line rule also holds in three dimensions. As an example, Fig. 4.9 shows a molar Gibbs energy diagram for a ternary system and the intercepts of the tangent plane

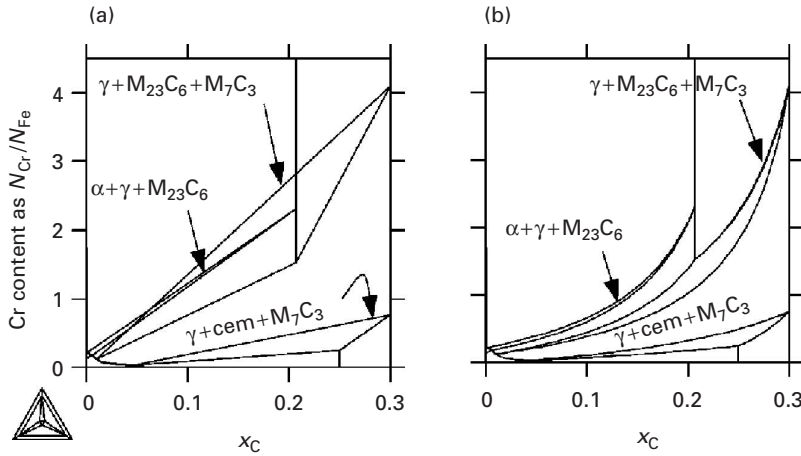


Figure 4.8 z_{Cr} , x_C diagram for Fe–Cr–C at 1 bar and 1200 K. (a) is drawn under the incorrect assumption that the tie-line rule applies; (b) is correct.

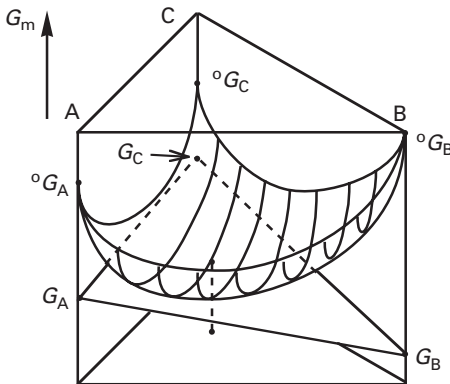


Figure 4.9 Molar Gibbs energy diagram for a ternary solution.

on the component axes represent the partial Gibbs energies. According to the tie-line rule, the molar Gibbs energy of the alloy falls on the plane through these points. This is also in accordance with Eq. (3.18), $G_m = \sum x_i \mu_i$, where μ_i is identical to G_i (see Equation (4.13)).

Exercise 4.4

Suppose one has measured the lattice parameter a of face-centred cubic (fcc)-Fe as a function of the carbon content. What composition variable should be most convenient in a diagram showing the volume of the unit cell, a^3 ?

Hint

It would be most convenient if the tie-line rule could be applied. Then one could, for instance, see immediately if the volume of a system would be different when carbon is distributed uniformly or non-uniformly. Use the fact that carbon dissolves interstitially in fcc-Fe.

Solution

The unit cell contains a fixed number of Fe atoms and a variable number of C atoms. The volume of the unit cell is thus proportional to V/N_{Fe} , i.e. V_m/x_{Fe} . The composition should thus be expressed as $N_{\text{C}}/N_{\text{Fe}}$, i.e. $x_{\text{C}}/x_{\text{Fe}}$.

4.6 Different sets of components

When considering a system open to exchange of matter with the surroundings in Section 3.1, we introduced the terms $\sum \mu_i dN_i$ in the expression for dU . These terms were subsequently carried over into the expression for dG and a chemical potential for any component j can thus be defined as

$$\mu_j = \left(\frac{\partial G}{\partial N_j} \right)_{T, P, N_i, \xi} \quad (4.46)$$

The quantity N_j represents the amount of component j . The quantities N_i and N are often measured as the number of atoms or groups of atoms, whether the corresponding molecule exists or not. However, the set of independent components can be chosen in different ways and it is self-evident that whatever choice is made it cannot be allowed to affect the total value of $dG = \sum \mu_i dN_i$. As a consequence, there is a relation between the chemical potentials defined for different sets of components. Let us compare two sets. As the first set we shall take the elements i, j, k , etc., and as the second set we shall take formula units denoted by d, e, f , etc. Let a_i^d be the number of i atoms in a formula unit of d . It is interesting to note that the set of a_i^d values for a new component d defines its position in the i, j, k compositional space. If the formula unit of d is defined for one mole of atoms then a_i^d is equal to the molar contents of the elements in the new component, x_i^d . Further, let N_d be the total number of formula units of the new component d . The total number of i atoms in the system is then obtained by a summation over all the new components.

$$N_i = \sum_d a_i^d N_d \quad (4.47)$$

We thus obtain

$$\sum \mu_i dN_i = \sum_i \mu_i \left(\sum_d a_i^d dN_d \right) = \sum_d \left(\sum_i a_i^d \mu_i \right) dN_d \quad (4.48)$$

This result can be inserted into the expression for dG instead of $\sum \mu_i dN_i$ and we thus find for the chemical potential of component d ,

$$\mu_d = \left(\frac{\partial G}{\partial N_d} \right)_{T,P,N_e} = \sum_i a_i^d \mu_i. \quad (4.49)$$

It is interesting to note that the final expression for μ_d is independent of how the other components in the new set were selected. The expression can thus be used to calculate the chemical potential of any compound or species or combination of atoms, whether it is used in a set of independent variables or not. Actually, one can define a component with the same composition as the whole system. The chemical potential of such a component is equal to G_m and was used in the combined law in Section 1.9.

Exercise 4.5

Consider a solution phase with two sublattices and the same number of sites on each. If A and B can occupy the first one and C and D the second one, then we can use the chemical formula $(A_x B_{1-x})_1 (C_y D_{1-y})_1$. It may seem reasonable to use the following expressions for the properties in a simple case where all the ternary solutions behave as ideal solutions between two compounds each, e.g. $(A_x B_{1-x})_1 C_1$ as $x A_1 C_1$ and $(1-x) B_1 C_1$ yielding $\mu_{AC} = {}^\circ G_{AC} + RT \ln(xy)$ and $\mu_{AD} = {}^\circ G_{AD} + RT \ln[x(1-y)]$, etc. However, this would be reasonable only under an additional condition. Accept the expressions given here and find the condition.

Hint

The four μ s are related.

Solution

By definition $\mu_{AC} = \mu_A + \mu_C$, etc.

Thus, $\mu_{AC} + \mu_{BD} - \mu_{AD} - \mu_{BC} = 0$ and ${}^\circ G_{AC} + RT \ln(xy) + {}^\circ G_{BD} + RT \ln[(1-x)(1-y)] - {}^\circ G_{AD} - RT \ln[x(1-y)] - {}^\circ G_{BC} - RT \ln[(1-x)y] = 0$ and thus ${}^\circ G_{AC} + {}^\circ G_{BD} = {}^\circ G_{AD} + {}^\circ G_{BC}$. This requires that the pair AC + DB has the same stability as AD + BC, which must be an unusual case.

4.7 Constitution and constituents

The composition of a system together with the condition of equilibrium defines the state of the system but it gives no direct information on how the atoms are arranged. In order to understand the properties and to make a realistic model of the thermodynamic properties as a function of composition, it is necessary to have some idea about the arrangement of the atoms. The modelling should be based on the **constitution** of the system, i.e. the detailed description of the distribution of the atoms. The occurrence

of regions of different structures and compositions, so-called **phases**, is of primary importance. The distribution of atoms within each phase may also be important, for instance their distribution on different sublattices or in groups like molecules, ions or complexes. Groups of atoms, including ions and single atoms, are often called **species**. They may be so stable that they can be transferred from one phase to another and even from the system to the surroundings.

Another useful concept is **constituent** by which one understands a certain kind of species on a certain sublattice in a certain phase. In the following discussion of constituents we shall only consider single atoms. However, the results can be generalized easily to molecular or ionic species.

Let us consider a phase with several sublattices in a higher-order system. The sublattices may be identified by superscripts, s, t, u , etc., their numbers of sites may be denoted by a^s, a^t, a^u , etc., the number of j atoms in the t sublattice by N_j^t and the corresponding **site fraction** by y_j^t . By definition

$$y_j^t = N_j^t / \sum_i N_i^t. \quad (4.50)$$

The site fraction is thus a kind of molar content (mole fraction), evaluated for each sublattice separately. The molar contents in the whole phase can be evaluated from the site fractions

$$x_j = a^t y_j^t / \sum_s a^s, \quad (4.51)$$

where t represents the sublattice in which j resides. In simple cases the relation can be inverted and the site fractions can be evaluated from the composition of the phase

$$y_j^t = x_j \sum_s a^t y_j^t / \sum_s a^s. \quad (4.52)$$

However, in the general case an element may enter into more than one sublattice. One can still evaluate the composition from the site fractions

$$x_j = \sum_t a^t y_j^t / \sum_s a^s, \quad (4.53)$$

but it is not certain that this relation can be inverted, i.e. that the site fractions can be evaluated from the composition. Instead there may now be one or more internal variables, describing the distribution of the elements on the various sublattices. Such internal variables will be discussed further in Chapter 20. Together with the external x_j parameters they define the state of the phase. An alternative way of defining the state is by only giving the site fractions. A site fraction may thus have a mixed character of internal and external variable.

The total number of formula units can be obtained by considering any sublattice or the whole phase,

$$N = \sum_i N_i^t / a^t = \sum_i N_i^u / a^u = \dots = \sum_s \sum_i N_i^s / \sum_s a^s. \quad (4.54)$$

Exercise 4.6

For $(A, B)_a(C, D)_c$, prove that $G_m = y_C \mu_{B_a C_c} + y_A \mu_{A_a D_c} + (y_D - y_A) \mu_{B_a D_c}$.

Hint

Use $\mu_{B_a C_c} = a \mu_B + c \mu_C$ etc., $x_A = a y_A / (a + c)$, etc., and $y_A + y_B = 1 = y_C + y_D$.

Solution

$y_C \mu_{B_a C_c} + y_A \mu_{A_a D_c} + (y_D - y_A) \mu_{B_a D_c} = y_C a \mu_B + y_C c \mu_C + (y_D - y_A) a \mu_B + (y_D - y_A) c \mu_D = y_C c \mu_C + y_A a \mu_A + y_D c \mu_D + (y_C + y_D - y_A) a \mu_B = y_C c \mu_C + y_A a \mu_A + y_D c \mu_D + y_B a \mu_B = (a + c)(x_C \mu_C + x_A \mu_A + x_D \mu_D + x_B \mu_B) = G_m$ for one mole of formula units.

4.8 Chemical potentials in a phase with sublattices

When trying to evaluate a chemical potential of a component in a phase with two or more sublattices, we run into difficulties because we cannot vary the content of one component alone unless it is present in all sublattices. The reason is the fixed total amount of atoms in each sublattice relative to the total amounts in the other sublattices. This kind of restriction on the contents of a phase may be called **stoichiometric constraint** and this kind of phase is called a **stoichiometric compound**. The word stoichiometric actually means that the coefficients in the chemical formula are small integers but the word is often used to mean ‘fixed composition’. Usually, one follows from the other.

If we were to neglect the difficulty with the stoichiometric constraint and calculate the chemical potential of a constituent j in sublattice s with the method used in Section 4.1, we should get the following formal result

$$\mu_j^s = G_m + \frac{1}{a^s} \cdot \left[\left(\frac{\partial G_m}{\partial y_j^s} \right)_{y_i^s} - \sum_i y_i^s \left(\frac{\partial G_m}{\partial y_i^s} \right)_{y_j^s} \right]. \quad (4.55)$$

where G_m is defined for 1 mole of atoms and $\Sigma a^s = 1$. The factor $1/a^s$ comes from the fact that $\Sigma N_i^s = a^s N$. It must be emphasized that the expression for μ_j^s cannot be used alone. It can only be used in combinations obeying the stoichiometric constraint. Two methods of obeying the constraint should be considered. In the first method one considers the addition of balanced amounts of atoms to all sublattices, corresponding to the addition of a compound $j_{a^t} k_{a^u} l_{a^v}$. For the chemical potential of that compound we obtain

$$\begin{aligned} \mu_{j_{a^t} k_{a^u} l_{a^v}} &= a^t \mu_j^t + a^u \mu_k^u + a^v \mu_l^v \\ &= G_m + \left(\frac{\partial G_m}{\partial y_j^t} \right)_{y_i^t} + \left(\frac{\partial G_m}{\partial y_j^u} \right)_{y_i^u} + \left(\frac{\partial G_m}{\partial y_j^v} \right)_{y_i^v} - \sum_s \sum_i y_i^s \left(\frac{\partial G_m}{\partial y_i^s} \right)_{y_j^s}. \end{aligned} \quad (4.56)$$

It is evident that we can here drop the restriction $\Sigma a^s = 1$ and redefine G_m to hold for 1 mole of formula units.

If an element A appears in all sublattices, then one could consider a compound which is a form of the pure element A and with $\Sigma a^s = 1$ its chemical potential would be

$$\begin{aligned}\mu_A &= a^t \mu_A^t + a^u \mu_A^u + a^v \mu_A^v \\ &= G_m + \left(\frac{\partial G_m}{\partial y_A^t} \right)_{y_i^s} + \left(\frac{\partial G_m}{\partial y_A^u} \right)_{y_i^s} + \left(\frac{\partial G_m}{\partial y_A^v} \right)_{y_i^s} - \sum_s \sum_i y_i^s \left(\frac{\partial G_m}{\partial y_i^s} \right)_{y_i^s}.\end{aligned}\quad (4.57)$$

This calculation can be performed only if the element is present in all sublattices. Otherwise, μ_A by itself has no unique physical meaning for such a phase.

The other method of obeying the stoichiometric constraint is to substitute an element for another one in a certain sublattice. The result will be

$$\mu_j - \mu_k = \mu_j^t - \mu_k^t = \frac{1}{a^t} \left[\left(\frac{\partial G_m}{\partial y_j^t} \right)_{y_i^s} - \left(\frac{\partial G_m}{\partial y_k^t} \right)_{y_i^s} \right]. \quad (4.58)$$

The difference $\mu_j - \mu_k$ is the diffusion potential derived in Section 4.1 where it was denoted $G_j - G_k$.

For a system in internal equilibrium the calculation of $\mu_j - \mu_k$ must give the same result independent of what sublattice is used in the calculation. Otherwise there would be a driving force for an exchange of atoms between the sublattices. Thus,

$$\mu_j^t - \mu_k^t = \mu_j^u - \mu_k^u. \quad (4.59)$$

If there are vacancies in one of the sublattices, then one can evaluate the chemical potential of any element present in that sublattice at equilibrium because the vacancies may be treated as an additional element with a chemical potential μ_{va} , which can be defined as zero at equilibrium. It would also be possible to calculate the chemical potential of an element not present in that sublattice but present in all the other ones.

It should again be emphasized that the quantities μ_j^t etc., which refer to a specified sublattice, in general have no unique meaning by themselves and they do not have the same value in different sublattices, not even at equilibrium. There may be several methods of calculating the μ_j^t quantities and they may give different results. But in the combinations obeying the stoichiometric constraint the results must be the same. This question is connected with the fact that one cannot add just one element to a phase with a stoichiometric constraint. It follows that the set of independent components contains less components than there are elements. In such a case one may define the set of components by using compounds and talk about **component compounds**. On the other hand, there may also be too many possible component compounds and for the set of independent components one must make a selection.

Exercise 4.7

We have seen that the chemical potential of an element A in a system with more than one sublattice can be evaluated under two different conditions. In one case the element is present in all sublattices and in the other case it is present in a sublattice t , which has vacancies. In the latter case, consider another element B which is only present in a second sublattice, u , that has no vacancies. Can its chemical potential also be evaluated?

Hint

Use the fact that the chemical potential of the first element, A, can be evaluated.

Solution

Using the second sublattice we can evaluate $\mu_A - \mu_B = \mu_A^u - \mu_B^u$ but only under internal equilibrium conditions. But μ_A is known from the first sublattice $\mu_A = \mu_A^t - \mu_{\text{Va}}^t = \mu_A^t$ and thus $\mu_B = \mu_A^t - (\mu_A^u - \mu_B^u)$.

5 Thermodynamics of processes

5.1 Thermodynamic treatment of kinetics of internal processes

In Chapter 1 we considered spontaneous processes inside a system when discussing the second law but later in that chapter we only considered equilibria. We shall now discuss the thermodynamic treatment of the kinetics of such processes. This field of thermodynamics is often called irreversible thermodynamics but the full term should rather be thermodynamics of irreversible processes. The word irreversible is often replaced by the word spontaneous. A process occurring inside a system may be caused by a change imposed upon the system by some external action, but it will here be regarded as a spontaneous result of the new conditions inside the system. All processes inside a system that actually occur will thus be regarded as spontaneous. It would really be unnecessary to use either of the terms irreversible and spontaneous processes if it were not for the need to distinguish them from the limiting case of a cyclic process, e.g. the Carnot cycle, when it is carried out in such a way that the internal processes it gives rise to produce a negligible amount of entropy. Since a cyclic process is controlled by actions from the outside and they could be performed in the reverse direction, it is possible to run the cycle in the reverse direction. All the internal processes it gives rise to will also reverse and if their entropy production is again negligible the two cases will be identical in the limit, except for the sign. In the limit, such processes are regarded as reversible.

An internal process at any given moment could not spontaneously proceed in either direction except for cases of so-called unstable equilibrium. That would require that the driving force is the same in both directions and must thus be zero and the process must be infinitely slow. A reversible process is thus a hypothetical construction but of considerable theoretical interest as a limiting case.

As a first approximate treatment of the kinetics of processes one assumes that the rate of a process, often called flux and denoted by J , is proportional to a thermodynamic force, X . A positive value of the force implies that it drives the process in a predetermined direction. Counting the flux as positive in the same direction one writes

$$J = LX. \quad (5.1)$$

The kinetic coefficient L is thus positive by definition. If ξ denotes the extent of the process, then the flux is defined as

$$J = \frac{d\xi}{dt}. \quad (5.2)$$

The rate of entropy production can be written as

$$\sigma \equiv \frac{d_{\text{ip}}S}{dt} = \frac{d_{\text{ip}}S}{d\xi} \frac{d\xi}{dt}. \quad (5.3)$$

The definition of the thermodynamic force is given as

$$X = \frac{d_{\text{ip}}S}{d\xi}. \quad (5.4)$$

Combination with Eq. (5.1) yields for the rate of entropy production

$$\sigma = JX = LX^2 > 0. \quad (5.5)$$

Since L is positive by definition, this is in agreement with the second law requiring that a spontaneous process produces entropy.

If there are simultaneous processes, they may all contribute to the entropy production

$$d_{\text{ip}}S = \sum \left(\frac{\partial_{\text{ip}}S}{\partial \xi_i} \right) d\xi_i = \sum X_i d\xi_i \quad (5.6)$$

$$\sigma \equiv \frac{d_{\text{ip}}S}{dt} = \sum \left(\frac{\partial_{\text{ip}}S}{\partial \xi_i} \right) \frac{d\xi_i}{dt} = \sum X_i J_i. \quad (5.7)$$

One should then generalize the linear kinetic equation, Eq. (5.1) by taking into account the possibility that simultaneous processes may interact.

$$J_j = \sum_k L_{jk} X_k = L_{jj} X_j + \sum_{k \neq j} L_{jk} X_k. \quad (5.8)$$

This is usually called **phenomenological equation** because it is not based on any physical model.

The flux and force for an individual process j are defined by Eqs (5.2) and (5.4), using the extent of the process, ξ_j . They are thus related to each other and are regarded as a pair of **conjugated** quantities. Their product gives the entropy production for that process, σ_j , but it should be realized that the second law is derived only for the whole system,

$$\sigma = \sum \sigma_i = \sum_i \left(L_{ii} X_i + \sum_{k \neq i} L_{ik} X_k \right) \cdot X_i > 0. \quad (5.9)$$

On the other hand, the entropy production for an individual process could be negative if there are simultaneous processes. When this happens, it is caused by the **cross coefficients**, L_{jk} , in Eq. (5.8). That possibility can be demonstrated by starting with a situation where $X_j = 0$ and the other forces have such values that $\sum L_{jk} X_k > 0$ for the actual set of L_{jk} values. Then

$$\sigma_j = J_j X_j = \left(L_{jj} X_j + \sum_{k \neq j} L_{jk} X_k \right) X_j = 0, \quad (5.10)$$

even when J_j , as calculated from Eq. (5.8), is not zero. By changing to a slightly negative value of X_j one obtains

$$\sigma_j = J_j X_j = L_{jj} X_j^2 + \sum_{k \neq j} L_{jk} X_k X_j \cong \left(\sum_{k \neq j} L_{jk} X_k \right) \cdot X_j < 0. \quad (5.11)$$

We have here neglected the first term that contains the small quantity X_j squared. The negative value of Eq. (5.11) is caused by the cross coefficients L_{jk} . According to the second law, the negative value must be compensated by the other processes yielding positive values. That puts a special requirement on the relation between the L coefficients. The L matrix must be positive definite and for a system with two processes that means that

$$4L_{11}L_{22} > (L_{12} + L_{21})^2, \quad (5.12)$$

in addition to the requirement that all L_{ii} must be positive, which has already been discussed. Those coefficients may be described as diagonal coefficients.

It is an interesting question whether the change of X_j , which made σ_j negative, as a compensation increased the entropy production from another process. For the simple case of two processes Eq. (5.11) yields,

$$\sigma_j = L_{jj}X_j^2 + L_{jk}X_kX_j \quad (5.13)$$

$$\sigma_k = L_{kj}X_jX_k + L_{kk}X_k^2 \quad (5.14)$$

and σ_j can turn negative only by the action of the cross term $L_{jk}X_kX_j$ in Eq. (5.13) and it is thus necessary that it is negative. Provided that L_{jk} and L_{kj} have the same sign, $L_{kj}X_jX_k$ in Eq. (5.14) will also be negative and both σ_j and σ_k will decrease by the coupling between the two processes. In fact, Onsager [5] has demonstrated that L_{jk} and L_{kj} do not only have the same sign but even the same value. This is called the **reciprocal relation** and can only be applied to a pair of kinetic equations containing conjugate pairs of flux and force. Onsager's derivation was based on the assumption of microscopic reversibility and the assumption that macroscopic processes obey the same kinetic law as the decay of the corresponding microscopic fluctuations. Objections have been raised regarding assumptions not stated explicitly by Onsager, e.g. by Truesdell [6] but the validity of the reciprocal relationship is widely accepted.

Exercise 5.1

Can a process occur, i.e. $J_1 \neq 0$, without producing entropy?

Solution

Yes! The entropy production is equal to J_1X_1 and will vanish if $X_1 = 0$ even if $J_1 = L_{11}X_1 + L_{12}X_2 = L_{12}X_2 \neq 0$.

Exercise 5.2

The material in a living organism can get more ordered, implying that the entropy decreases. Does the second law not hold for living organisms?

Solution

The living organism cannot do this by itself, i.e., if it is completely isolated. It can do it by receiving light energy from the sun, a case, which should be treated with an appropriate

form of the combined law. It can also do it by being a subsystem in a bigger system and its internal processes can then be coupled to processes in the other subsystem.

5.2 Transformation of the set of processes

It is possible to change the formal description of what happens in a system with simultaneous processes without affecting what actually happens. There may be different reasons for such a change to a new set of processes. One reason could be an advantage in the physical interpretation of the processes. Another reason could be that one is looking for a set of phenomenological equations with negligible cross terms in order to simplify numerical calculations.

Of course, one requirement for such a transformation is that the entropy production is the same in both descriptions. For simplicity, we shall limit the present discussion to two simultaneous processes. Let the primary phenomenological equations be

$$J_1 = L_{11}X_1 + L_{12}X_2 \quad (5.15a)$$

$$J_2 = L_{21}X_1 + L_{22}X_2. \quad (5.15b)$$

Introduce a new set of fluxes by linear combinations

$$J_1^* = \alpha_{11}J_1 + \alpha_{12}J_2 \quad (5.16a)$$

$$J_2^* = \alpha_{21}J_1 + \alpha_{22}J_2. \quad (5.16b)$$

The entropy requirement gives

$$\sigma = J_1X_1 + J_2X_2 = J_1^*X_1^* + J_2^*X_2^* = \alpha_{11}J_1X_1^* + \alpha_{12}J_2X_1^* + \alpha_{21}J_1X_2^* + \alpha_{22}J_2X_2^*. \quad (5.17)$$

Comparing terms in first J_1 and then J_2 we find that it is necessary to choose

$$X_1 = \alpha_{11}X_1^* + \alpha_{21}X_2^* \quad (5.18a)$$

$$X_2 = \alpha_{12}X_1^* + \alpha_{22}X_2^*. \quad (5.18b)$$

The fluxes and forces for the primary set of processes can be eliminated by first inserting Eqs. (5.15) and then Eqs (5.18) into Eqs (5.16),

$$\begin{aligned} J_1^* &= \alpha_{11}L_{11}X_1 + \alpha_{11}L_{12}X_2 + \alpha_{12}L_{21}X_1 + \alpha_{12}L_{22}X_2 \\ &= (\alpha_{11}L_{11} + \alpha_{12}L_{21})(\alpha_{11}X_1^* + \alpha_{21}X_2^*) \\ &\quad + (\alpha_{11}L_{12} + \alpha_{12}L_{22})(\alpha_{12}X_1^* + \alpha_{22}X_2^*) = L_{11}^*X_1^* + L_{12}^*X_2^* \end{aligned} \quad (5.19a)$$

$$\begin{aligned} J_2^* &= \alpha_{21}L_{11}X_1 + \alpha_{21}L_{12}X_2 + \alpha_{22}L_{21}X_1 + \alpha_{22}L_{22}X_2 \\ &= (\alpha_{21}L_{11} + \alpha_{22}L_{21})(\alpha_{11}X_1^* + \alpha_{21}X_2^*) \\ &\quad + (\alpha_{21}L_{12} + \alpha_{22}L_{22})(\alpha_{12}X_1^* + \alpha_{22}X_2^*) = L_{21}^*X_1^* + L_{22}^*X_2^*. \end{aligned} \quad (5.19b)$$

where

$$L_{11}^* = \alpha_{11}^2 L_{11} + \alpha_{11}\alpha_{12}L_{21} + \alpha_{11}\alpha_{12}L_{12} + \alpha_{12}^2 L_{22} \quad (5.20a)$$

$$L_{12}^* = \alpha_{11}\alpha_{21}L_{11} + \alpha_{12}\alpha_{21}L_{21} + \alpha_{11}\alpha_{22}L_{12} + \alpha_{12}\alpha_{22}L_{22} \quad (5.20b)$$

$$L_{21}^* = \alpha_{21}\alpha_{11}L_{11} + \alpha_{22}\alpha_{11}L_{21} + \alpha_{21}\alpha_{12}L_{12} + \alpha_{22}\alpha_{12}L_{22} \quad (5.20c)$$

$$L_{22}^* = \alpha_{21}^2 L_{11} + \alpha_{22}\alpha_{21}L_{21} + \alpha_{21}\alpha_{22}L_{12} + \alpha_{22}^2 L_{22}. \quad (5.20d)$$

This derivation of the new coefficients can easily be generalized, resulting in

$$L_{sr}^* = \sum_i \sum_k \alpha_{si}\alpha_{rk}L_{ik}. \quad (5.21)$$

The description has thus been changed to a new set of processes and it is immediately evident that for the new cross coefficients one finds $L_{12}^* = L_{21}^*$ if $L_{12} = L_{21}$. Onsager's reciprocal relation is still valid. It should further be emphasized that the new processes appear to be coupled even if the initial processes were not. According to Eqs (5.20b and c), the following cross coefficients appear if one starts with processes without coupling,

$$\begin{aligned} L_{12} &= L_{21} = 0 \\ L_{12}^* &= \alpha_{11}\alpha_{21}L_{11} + \alpha_{12}\alpha_{22}L_{22} = L_{21}^*. \end{aligned} \quad (5.22)$$

It is interesting to note that for this case the reciprocal relation is a mathematical consequence and there is no need to use a derivation based on physical arguments in order to explain that the reciprocal relation is preserved.

Of course, it is also possible to apply a transformation in order to eliminate the cross coefficients. Starting with $L_{12} = L_{21} \neq 0$ one can change to two new processes for which $L_{12}^* = L_{21}^* = 0$. According to Eqs (5.20b and c), the requirement is that one has chosen the α_{ij} coefficients to satisfy

$$\alpha_{11}\alpha_{21}L_{11} + (\alpha_{12}\alpha_{21} + \alpha_{11}\alpha_{22})L_{12} + \alpha_{12}\alpha_{22}L_{22} = 0. \quad (5.23)$$

However, there are an infinite number of ways to accomplish this even though one can immediately eliminate many of them as trivial variations because σ_j in Eq. (5.7) would not be affected if one of the conjugate pairs of flux and force is redefined by multiplying the flux with a factor and dividing the force with the same factor. One can eliminate this kind of freedom by choosing $\alpha_{11} = 1 = \alpha_{22}$ but the requirement is still satisfied as soon as the following relation between α_{12} and α_{21} is obeyed.

$$\alpha_{21}L_{11} + (1 + \alpha_{12}\alpha_{21})L_{12} + \alpha_{12}L_{22} = 0 \quad (5.24)$$

$$\alpha_{12} = -\frac{L_{12} + \alpha_{21}L_{11}}{L_{22} + \alpha_{21}L_{12}}. \quad (5.25)$$

On the other hand, with the present understanding of principles there is no guarantee that the set of processes that actually occur on a microscale, when Eq. (5.25) is satisfied, should not be coupled in any way. However, there are several cases where two processes could be expected not to be coupled by a physical mechanism. Examples are processes that occur in different subsystems or reactions between molecules in a gas, which occur in contact with one catalyst each. Prigogine [7] has mentioned the case of heat flowing

through a system where a homogeneous molecular reaction takes place, suggesting that the two processes could not be coupled. It is an interesting question whether one would always find that there is no coupling if one could really identify the actual processes on the microscale. If that is the case, then the reciprocal relation should always be a mathematical consequence of a different choice of processes.

Exercise 5.3

Show how Eq. (5.21) can be derived.

Hint

Start with Eq. (5.16a) and insert in turn Eqs (5.15a) and (5.18).

Solution

$$J_s^* = \sum_i \alpha_{si} J_i = \sum_i \alpha_{si} \sum_k L_{ik} X_k = \sum_i \alpha_{si} \sum_k L_{ik} \sum_r \alpha_{rk} X_r^*;$$

$$L_{sr}^* = \sum_i \alpha_{si} \sum_k L_{ik} \alpha_{rk} = \sum_i \sum_k \alpha_{si} \alpha_{rk} L_{ik}.$$

5.3 Alternative methods of transformation

So far, we have introduced a new set of processes by expressing the new fluxes as linear combinations of the initial ones. One could just as well express the new forces as linear combinations of the initial forces

$$X_1^* = \beta_{11} X_1 + \beta_{12} X_2 \quad (5.26a)$$

$$X_2^* = \beta_{21} X_1 + \beta_{22} X_2. \quad (5.26b)$$

The initial processes are still defined by Eqs (5.15) but we shall invert them to make them consistent with the new way of defining the new processes

$$X_1 = R_{11} J_1 + R_{12} J_2 \quad (5.27a)$$

$$X_2 = R_{21} J_1 + R_{22} J_2. \quad (5.27b)$$

The R coefficients can be obtained from the L coefficients in Eqs (5.15) by standard methods. With a similar procedure as before, one now obtains

$$X_s^* = \sum_r R_{sr}^* J_r^* \quad (5.28)$$

$$R_{sr}^* = \sum_i \sum_k \beta_{si} \beta_{rk} R_{ik}. \quad (5.29)$$

The L^* coefficients can be evaluated by inverting Eq. (5.28).

One may also like to prescribe both flux and force for one process and not make any prescription for the other process

$$J_1^* = \alpha_{11}J_1 + \alpha_{12}J_2 \quad (5.30)$$

$$X_1^* = \beta_{11}X_1 + \beta_{12}X_2. \quad (5.31)$$

One should then express J_2^* and X_2^* using the four coefficients defined by these equations. In general, a complete set of β coefficients can be expressed in terms of the α coefficients by inverting Eqs (5.18)

$$\alpha_{11}/\beta_{22} = -\alpha_{12}/\beta_{21} = -\alpha_{21}/\beta_{12} = \alpha_{22}/\beta_{11} = \alpha_{11}\alpha_{22} - \alpha_{12}\alpha_{21}. \quad (5.32)$$

For the second process one could thus write

$$J_2^* = \alpha_{21}J_1 + \alpha_{22}J_2 = \alpha_{22} \left(\frac{\alpha_{21}}{\alpha_{22}}J_1 + J_2 \right) = \alpha_{22} \left(-\frac{\beta_{12}}{\beta_{11}}J_1 + J_2 \right) \quad (5.33)$$

$$X_2^* = \beta_{21}X_1 + \beta_{22}X_2 = \beta_{22} \left(-\frac{\alpha_{12}}{\alpha_{11}}X_1 + X_2 \right) = \frac{\alpha_{11}\beta_{11}}{\alpha_{22}} \left(-\frac{\beta_{12}}{\beta_{11}}X_1 + X_2 \right). \quad (5.34)$$

In these expressions only α_{22} was not given by Eqs (5.30) and (5.31). However, α_{22} is eliminated in the product $J_2^*X_2^*$ and, as in the discussion following Eq. (5.23), it may thus be regarded as a trivial factor for the second new process. It may thus be concluded that in order for a new process, defined by its flux and force, to be part of a new set of conjugate processes it must be combined with a unique partner defined by Eqs (5.33) and (5.34).

Finally, it may happen that for some particular reason one would like to prescribe the flux for a new process but the force for the other process.

$$X_1^* = \beta_{11}X_1 + \beta_{12}X_2 \quad (5.35)$$

$$J_2^* = \alpha_{21}J_1 + \alpha_{22}J_2. \quad (5.36)$$

Again, the α and β coefficients are related by Eq. (5.32) but this time only three of the coefficients given by the initial equations are independent. Let α_{21} be the dependent one. Eq. (5.32) yields

$$\alpha_{21} = -\alpha_{22}\beta_{12}/\beta_{11}. \quad (5.37)$$

This must be satisfied when the initial equations, Eqs (5.35) and (5.36) are formulated. As a compensation, there is a degree of freedom when evaluating the remaining four coefficients. Lets us choose α_{11} as the arbitrary parameter. Eq. (5.32) would then yield

$$\beta_{22} = \frac{\alpha_{11}}{\alpha_{22}}\beta_{11} \quad (5.38)$$

$$\alpha_{12} = \frac{1}{\alpha_{21}} \left(\alpha_{11}\alpha_{22} - \frac{\alpha_{22}}{\beta_{11}} \right) = \frac{\alpha_{22}}{\alpha_{21}\beta_{11}} (\alpha_{11}\beta_{11} - 1) \quad (5.39)$$

$$\beta_{21} = -\frac{\alpha_{12}\beta_{11}}{\alpha_{22}} = -\frac{\alpha_{22}\beta_{11}}{\alpha_{21}\beta_{11}\alpha_{22}} (\alpha_{11}\beta_{11} - 1) = -\frac{1}{\alpha_{21}} (\alpha_{11}\beta_{11} - 1). \quad (5.40)$$

An application of this kind of transformation will be given in Section 17.5.

So far, we have always transformed the initial set of processes into the same number of new processes. However, there are cases where the new set will contain one process more or one less. When transforming the phenomenological equations for diffusion in order to change the frame of reference, one often introduces a set with one process less. That case will be discussed in Section 5.8. A case with an increase of the number of processes will now be described.

It may happen that one describes the development of a system with a set of processes that one is convinced are those that actually take place on a microscale. Nevertheless, experimental measurements have yielded cross coefficients. There is thus a coupling between the processes but it is possible that it may be caused by an additional process that was not considered primarily because it was formally possible to represent the experimental information without using it. By introducing the phenomenological equation for that process into the representation of experimental information, it is possible that the cross coefficients decrease in value or even become negligible. If several additional processes seem possible, one may decide to use the one giving the lowest cross coefficients. That one would then be regarded as the coupling process.

Suppose one has studied two processes finding that they are coupled as described by $L_{12} = L_{21} \neq 0$ in their phenomenological equations,

$$J_1 = L_{11}X_1 + L_{12}X_2 \quad (5.41a)$$

$$J_2 = L_{21}X_1 + L_{22}X_2. \quad (5.41b)$$

With these equations one has thus been able to give an adequate description of how the system develops. However, one is convinced that the two processes actually occur in the system and feels that they should be independent of each other if it were not for the presence of a third process that is responsible for the coupling. Assuming that there should be no cross terms if the system is represented by all three processes one would write

$$J_1^* = L_1^*X_1^* \quad (5.42a)$$

$$J_2^* = L_2^*X_2^* \quad (5.42b)$$

$$J_3^* = L_3^*X_3^*. \quad (5.42c)$$

It should be noticed that it is necessary to redefine the fluxes of the two initial processes when the third one is introduced even though those processes are the same as before and should still have the same forces.

$$X_1^* = X_1 \quad (5.43a)$$

$$X_2^* = X_2. \quad (5.43b)$$

Of course, there should be some relation between the third process and the initial ones because an adequate description of the system can be given already by the initial ones. Suppose the relation is

$$X_3^* = kX_1 + lX_2 = kX_1^* + lX_2^*. \quad (5.44)$$

The entropy production must be the same in both descriptions. By eliminating X_3^* one obtains

$$\begin{aligned}\sigma &= J_1^* X_1^* + J_2^* X_2^* + J_3^* X_3^* = (J_1^* + kJ_3^*)X_1^* + (J_2^* + lJ_3^*)X_2^* \\ &= J_1 X_1 + J_2 X_2.\end{aligned}\quad (5.45)$$

By inserting Eqs (5.43) one can identify the relations between the two sets of processes by comparing terms.

$$J_1 = J_1^* + kJ_3^* \quad (5.46a)$$

$$J_2 = J_2^* + lJ_3^*. \quad (5.46b)$$

Introducing the phenomenological equations for the three new processes from Eqs (5.42) one obtains,

$$J_1 = J_1^* + kJ_3^* = L_1^* X_1^* + kL_3^* (kX_1^* + lX_2^*) = (L_1^* + k^2 L_3^*)X_1^* + klL_3^* X_2^*. \quad (5.47a)$$

$$J_2 = J_2^* + lJ_3^* = L_2^* X_2^* + lL_3^* (kX_1^* + lX_2^*) = klL_3^* X_1^* + (L_2^* + l^2 L_3^*)X_2^*. \quad (5.47b)$$

It is satisfactory to see that the reciprocal relation is obeyed. Comparison with Eqs (5.41) yields

$$L_{11} = L_1^* + k^2 L_3^*, L_{12} = klL_3^* = L_{21}; L_{22} = L_2^* + l^2 L_3^* \quad (5.48)$$

or inverted,

$$L_3^* = L_{12}/kl = L_{21}/kl \quad (5.49a)$$

$$L_2^* = L_{22} - l^2 L_{12}/kl = L_{22} - L_{12}l/k \quad (5.49b)$$

$$L_1^* = L_{11} - k^2 L_{12}/kl = L_{11} - L_{12}k/l. \quad (5.49c)$$

The introduction of a third, coupling process is thus another way of describing the development of the system without any cross terms. The advantage of this method is that the initial processes will be part of the final description. That may be desirable if they have a strong physical basis.

The fact that it is always possible to introduce a set of processes without cross terms may be of theoretical interest even without trying to identify their physical background, as demonstrated by the following example. It may seem self-evident that there could be no spontaneous processes in a system without any entropy being produced. $\sigma = 0$ for the whole system should thus be a condition of equilibrium for the whole system and for all parts of it. However, it has been argued that one process having $\sigma_j > 0$ and another one having $\sigma_k < 0$ could together yield $\sigma = 0$. On the other hand, the fact that one can always describe what happens in the system with a set of processes without coupling proves that there is no basis for that argument. Each one of those processes will only be driven by its own thermodynamic force because all cross coefficients are zero. All those processes will have to give positive contributions to the entropy production if they progress. One could thus apply the second law to the individual processes if they are

not coupled. One may conclude that there can be no spontaneous changes in a system if $\sigma = 0$ for the whole system.

Exercise 5.4

In an attempt to eliminate the cross terms in two processes one introduces a third process by requiring that (1) $J_1 = J_1^* + J_3^*$ and (2) $J_2 = J_2^* - J_3^*$. Evaluate the L^* coefficients if this is possible.

Hint

Start by finding the condition for preserving the rate of entropy production.

Solution

$\sigma = J_1^* X_1^* + J_2^* X_2^* + J_3^* X_3^* = J_1 X_1 + J_2 X_2 = (J_1^* + J_3^*) X_1 + (J_2^* - J_3^*) X_2 = J_1^* X_1 + J_2^* X_2 + J_3^* (X_1 - X_2)$, which yields $X_1^* = X_1$; $X_2^* = X_2$; $X_3^* = X_1 - X_2$.

Insert Eqs (5.42) in Eq. (1) or (2): $J_1 = J_1^* + J_3^* = L_1^* X_1^* + L_3^* X_3^* = L_1^* X_1 + L_3^* (X_1 - X_2) = (L_1^* + L_3^*) X_1 - L_3^* X_2$; $J_2 = J_2^* - J_3^* = L_2^* X_2^* - L_3^* X_3^* = L_2^* X_2 - L_3^* (X_1 - X_2) = -L_3^* X_1 + (L_2^* + L_3^*) X_2$.

Comparison with Eqs (5.41) yields $L_{11} = L_1^* + L_3^*$; $L_{12} = -L_3^* = L_{21}$; $L_{22} = L_2^* + L_3^*$ or inverted: $L_3^* = -L_{12} = -L_{21}$; $L_2^* = L_{22} - L_3^* = L_{22} + L_{12}$; $L_1^* = L_{11} - L_3^* = L_{11} + L_{12}$.

5.4 Basic thermodynamic considerations for processes

In order to apply thermodynamics to the kinetics of processes, one must be aware of some fundamental principles and new assumptions must be made. For inhomogeneous systems the basic extensive quantities, N_i , U , V and S are obtained by integration of the local value of the corresponding intensive property, usually expressed by the molar quantity. It is thus necessary to assume that one can define the local value of those quantities. The molar quantity is not just an average over a larger system. It is an intensive quantity and depends on the local values of T , P and composition and also on the arrangement of the atoms. However, it may also depend on the gradient of those quantities. There are no gradient effects in a homogeneous system and in the present work they will be neglected for inhomogeneous systems unless specifically stated. An exception is the treatment of a phenomenon called spinodal decomposition for which important restrictions are described by including the effect of composition gradients on the Gibbs energy. See Section 15.4.

N_i , U and V obey the law of additivity and their values in a system are conserved quantities in the sense that they can only change by interaction with the surroundings. Their values for the whole system are thus conserved if there is no exchange of heat, work or volume with the surroundings. The entropy, S , can change by internal processes but

$S - \Delta_{\text{ip}}S$ is a conserved quantity if $\Delta_{\text{ip}}S$ is defined as the internally produced entropy. Other extensive quantities are derived from the primary ones by adding or subtracting terms containing P , T and μ_i , e.g. the terms PV and TS . The law of additivity applies to such quantities only under special precautions as discussed in Section 3.4.

Finally, it should be noted that, when applying thermodynamics to systems with internal processes, one assumes that thermodynamic properties, evaluated under equilibrium or frozen-in conditions, apply not only to stable and metastable systems but also to unstable systems undergoing changes. In the present work that assumption will be applied as an approximation without further discussion. We shall for instance evaluate thermodynamic properties by assuming that any momentary situation is frozen-in.

Most of the applications in this chapter are based on the combined law in the form

$$dS = (1/T)dU + (P/T)dV - \sum(\mu_i/T)dN_i + d_{\text{ip}}S, \quad (5.50)$$

where $d_{\text{ip}}S$ is the entropy production which must be positive for a system undergoing spontaneous changes. We shall first consider cases where $d_{\text{ip}}S$ is caused by homogeneous processes that will not disturb the uniformity of a system which is uniform from the beginning. Transport processes require a quite different approach. They concern quantities that can be exchanged with the surroundings and in the limit they could sometimes establish a stationary state of flow through the system. Even though such processes may concern quantities already present in the combined law, it should be realized that in the combined law they represent direct exchanges with the surroundings and not processes of flow inside the system. The discussion of transport processes will thus be preceded by considering a discontinuous system composed of two subsystems and with transport between them.

Starting with processes in homogeneous systems we shall presume that all thermodynamic properties are uniform. Internal processes may tend to change some properties but the processes must progress uniformly in the whole system in order not to change the homogeneous character. In a system that is not completely isolated there may be complications, e.g. due to the heat of reaction leaking out to the surroundings and causing heat flow from the interior of the system to its surface. In a system open for heat transfer to a reservoir of constant temperature it is common to assume that the temperature is kept constant although there must be temperature gradients in order for the heat of reaction to leave the system. Evidently, one assumes that those gradients and the corresponding thermodynamic forces for the heat flow are so small that their production of entropy is negligible. That will now be our assumption.

It may often be more convenient to use the combined law in the form based on Gibbs energy if T and P are kept constant. By further assuming that there is no exchange of matter with the surroundings we get for spontaneous changes of the state,

$$dG = VdP - SdT + \sum\mu_i dN_i - Td_{\text{ip}}S = -Td_{\text{ip}}S = -\sum D_j d\xi_j < 0. \quad (5.51)$$

D_j is the driving force for process j . It is defined as a generalization of the driving force, D , in Section 1.8.

$$D_j \equiv T \frac{\partial_{\text{ip}}S}{\partial \xi_j} = -\frac{\partial G}{\partial \xi_j}. \quad (5.52)$$

Introducing the flux of process j , $J_j = d\xi_j/dt$, we get for the time derivative

$$-\dot{G} = T \frac{d_{ip}S}{dt} = T\sigma = \sum D_j J_j > 0. \quad (5.53)$$

The rate of entropy production, σ , was defined by Eq. (5.3) and the second law requires that it is positive. That explains why dG in Eq. (5.51) was stated as negative. It should be emphasized that the driving force is only defined for constant T and is then related to the more generally applicable thermodynamic force X_j by

$$D_j = TX_j. \quad (5.54)$$

That is shown by comparison with Eq. (5.7). The term driving force for D_j is here used in an attempt to avoid confusion with the thermodynamic force, X_j .

The internal production of entropy, σ , is a well defined quantity and $T\sigma$ is regarded as the dissipation of Gibbs energy. It is thus connected to the internal processes. On the other hand, $-\dot{G}$ in Eq. (5.53) describes the change of the properties of the system with no regard to how the change occurred. The equality of the two may seem self-evident but is extremely useful and may be illustrated in diagrams of the molar Gibbs energy versus molar content. Then it is necessary to express both the dissipation and the change of Gibbs energy in the same dimensions as the diagram, i.e. J/mol. Equation (5.53) is expressed in J/s and it would thus be necessary to divide the whole equation by some flux, J_0 , measured as mol/s. One would then obtain the change of Gibbs energy per mole of the flux,

$$-\Delta G_m = -\dot{G}/J_0 = \sum f_j D_j, \quad (5.55)$$

where $f_j \equiv J_j/J_0$. For simple case with just one process, J_0 will normally be defined as the flux of that process and $-\Delta G_m$ will be equal to D_j . One can then evaluate the driving force D_j from $-\Delta G_m$ and it is even common to regard it as the driving force itself. For more complicated cases one may even regard it as the total driving force. However, it should be remembered that $-\Delta G_m$ is the change of the properties of the system and D_j or $f_j D_j$ represents dissipation.

There are many kinds of homogeneous processes, some of which can be described as a change of order, e.g., short-range order of the atoms relative to each other and even the transition to a state of long-range order if it occurs by a so-called second-order transition, which is homogeneous. An extreme case of order among the atoms is the formation of molecules by so-called chemical reactions. They will be treated separately in the next section.

Exercise 5.5

Suppose T and V are kept constant. What form of the combined law should it then be natural to use? How would the time derivative of that characteristic state function be related to the rate of entropy production if there is no exchange of matter?

Solution

Using Helmholtz energy, the combined law is written as $dF = -VdP - SdT + \sum \mu_i dN_i - Td_{ip}S = -Td_{ip}S = -\sum D_j d\xi_j < 0$. The time derivative of Helmholtz energy is the same as of Gibbs energy but the conditions are different $-\dot{F} = Td_{ip}S/dt = T\sigma = \sum D_j J_j > 0$.

5.5 Homogeneous chemical reactions

The combined law for dG contains the terms $\sum \mu_j dN_j$ where the summation includes a set of c components. Each one is regarded as independent if it cannot be formed by a reaction between the other ones. Basically, the set should only contain the c independent components. For homogeneous chemical reactions one sometimes includes more components. One may then choose which ones should be regarded as independent. The other ones will be regarded as dependent and each one of them can be formed by a reaction between the independent ones. Those reactions are regarded as independent reactions but many more reactions could occur between the components. If one considers s components altogether, there will be $(s - c)$ dependent components and the same number of independent reactions. That number will be represented by $r = s - c$.

A component could be a pure element but could also be a molecule or some hypothetical aggregate of atoms. Let us express the chemical composition of component j by the letter J and write

$$J = \sum_{i=1}^c a_i^j I, \quad (5.56)$$

where a_i^j represents the **stoichiometric coefficients** and I represents a pure element or the composition of any other basic unit used for representing the composition of the components. Let these units be the independent components and J be a dependent component. It is evident that Eq. (5.56) should then be the reaction formula for the formation of J if it is turned around.

$$\sum_{i=1}^c a_i^j I = J. \quad (5.57)$$

We could thus regard the a_i^j coefficients as the **reaction coefficients** for the reaction between J and the c independent components. They have here been normalized by making the coefficient for J equal to 1. There will be such a reaction for each dependent component, i.e. r reactions. They may be chosen as the r independent reactions among the many more possible reactions between the s components.

One reason to include dependent components in $\sum \mu_j dN_j$ is that it may facilitate the modelling of the thermodynamic properties, e.g. for a gas containing several kinds of molecules. A related reason is that one may like to consider frozen-in states where the rates of internal reactions are negligible. In that case one may add some amount of any component without having to consider its possible reactions with other components

inside the system. The dependent components can then be treated as independent and we may define the chemical potential of any component

$$\mu_i = \left(\frac{\partial G}{\partial N_i} \right)_{T, P, N_i} \quad (5.58)$$

Even though the system is frozen-in, we may evaluate the driving force for the r reactions by which each one of the r additional components could react with the independent ones. It may be derived as follows.

Considering the changes of all the s components, both independent and dependent ones, we may write the combined law as

$$dG = VdP - SdT + \sum_{i=1}^s \mu_i dN_i \quad (5.59)$$

We would now like to introduce the extent of the internal reactions, ξ^j , in this equation. One may define the reactions in such a way that each reaction represents the formation of a single dependent component from the set of independent ones, but without the other dependent components being involved. In a closed system, the change of an independent component may be given by the loss caused by several reactions, and may thus be related to the increase of several dependent components.

$$dN_i = - \sum_{j=1}^r a_i^j dN_j \quad (5.60)$$

For the dependent components dN_j is only caused by their own independent reactions. The combined law for a closed isobarothermal system will thus be

$$\begin{aligned} dG &= VdP - SdT + \sum_{i=1}^c \mu_i \left(- \sum_{j=1}^r a_i^j dN_j \right) + \sum_{j=1}^r \mu_j dN_j \\ &= VdP - SdT - \sum_{j=1}^r D^j d\xi^j \end{aligned} \quad (5.61)$$

The driving force for the formation of the dependent component j is here defined as

$$D^j = \sum_{i=1}^c (a_i^j \mu_i) - \mu_j \quad (5.62)$$

The combined law for an open system could thus be written

$$dG = VdP - SdT + \sum_{i=1}^c \mu_i dN_i + \sum_{j=1}^r \mu_j dN_j - \sum_{j=1}^r D^j d\xi^j \quad (5.63)$$

It should be emphasized that dN_i and dN_j here represent only the amounts received from the surroundings. The changes due to all internal reactions are included in $d\xi^j$. Under freezing-in conditions one should omit $\sum D^j d\xi^j$. When the internal reactions are very fast, there is almost internal equilibrium and the driving forces necessary for maintaining

equilibrium are so small that $\Sigma D^j d\xi^j$ can again be omitted. Then

$$\mu_j = \sum_{i=1}^c a_i^j \mu_i \quad (5.64)$$

$$dG = VdP - SdT + \sum_{i=1}^c \mu_i \left(dN_i + \sum_{j=1}^r a_i^j dN_j \right). \quad (5.65)$$

Again, dN_i and dN_j represent only the amounts received from the surroundings. When treating intermediate cases one should take into account the rate of all reactions, starting with the r reactions by which the r dependent components can form from the independent ones and then adding those in which two or more of the dependent ones take part. We shall now consider the very simplest case where there are one independent component and two dependent ones. The dependent components will be denoted by 1 and 2 and their reactions will also be identified by 1 and 2. For consistency with the derivations in Section 5.4 the superscripts used for D and ξ in the above equations will now be given as subscripts. Without any coupling between the first two reactions their rates will thus be given as

$$J_1^* = \frac{d\xi_1}{dt} = L_1^* X_1^* = K_1^* D_1^* \quad (5.66)$$

$$J_2^* = \frac{d\xi_2}{dt} = L_2^* X_2^* = K_2^* D_2^*, \quad (5.67)$$

where $D_i^* = TX_i^*$ according to Eq. (5.54) and $K_i^* = L_i^*/T$. For the additional reaction, where both dependent components take part, we write

$$J_3^* = \frac{d\xi_3}{dt} = L_3^* X_3^* = K_3^* D_3^*. \quad (5.68)$$

Suppose this reaction produces component 1 and consumes component 2. Then we know that its driving force must be

$$D_3^* = D_1^* - D_2^*. \quad (5.69)$$

By direct measurements of the amounts of the two dependent components one would not get any direct information on the third reaction but one can represent the experimental information using the phenomenological equations for those reactions.

$$J_1 = K_{11}D_1 + K_{12}D_2 \quad (5.70a)$$

$$J_2 = K_{21}D_1 + K_{22}D_2. \quad (5.70b)$$

The goal is to evaluate the kinetic coefficients in the three processes, assumed to have no cross terms, from the experimentally determined coefficients in Eqs (5.70a and b). This problem was discussed in more general terms in Section 5.2. By comparing the relations between the driving forces given by Eqs (5.44) and (5.69) we find that the present case corresponds to $k = 1$ and $l = -1$. From Eq. (5.49) we thus find

$$K_3^* = -K_{12} = -K_{21}; \quad K_2^* = K_{22} + K_{12}; \quad K_1^* = K_{11} + K_{12} \quad (5.71)$$

We have thus been able to eliminate the cross terms in Eqs (5.70) by introducing an additional reaction.

Exercise 5.6

Demonstrate that Onsager's reciprocal relation applies to the reactions between CO, CO₂ and O₂ in a gas in contact with pure C as solid graphite.

Hint

Among the four components there are four possible reactions obtained by omitting one component at a time. We should accept that all four actually occur. There will only be two independent components and we may choose C and O₂. First one should decide how many independent reactions there are. There are four species, CO, CO₂, O₂ and C, but only two components. There will thus be two independent reactions. Start by defining them. Denote their driving forces by D_1 and D_2 . Then define as many dependent reactions as possible but express their driving forces in terms of D_1 and D_2 .

Solution

We may choose the following reactions as independent, $\text{CO}_2 \rightarrow \text{C} + \text{O}_2$ (1) and $2\text{CO} \rightarrow 2\text{C} + \text{O}_2$ (2). Then $2\text{CO} - \text{CO}_2 \rightarrow \text{C}$ (3) and $2\text{CO}_2 - 2\text{CO} \rightarrow \text{O}_2$ (4) are dependent reactions. Reaction (1) can be obtained from (3) + (4) and its driving force will be $D_1 = D_3 + D_4$. Reaction (2) can be obtained from 2(3) + (4) with $D_2 = 2D_3 + D_4$. The rates of formation of C and O₂, respectively, will be $J_{\text{C}}^{\text{total}} = K_1 D_1 + 2K_2 D_2 + K_3 D_3 = K_1(D_3 + D_4) + 2K_2(2D_3 + D_4) + K_3 D_3 = (K_1 + 4K_2 + K_3)D_3 + (K_1 + 2K_2)D_4$ and $J_{\text{O}_2}^{\text{total}} = K_1 D_1 + K_2 D_2 + K_4 D_4 = K_1(D_3 + D_4) + K_2(2D_3 + D_4) + K_4 D_4 = (K_1 + 2K_2)D_3 + (K_1 + K_2 + K_4)D_4$. Both cross coefficients are equal to $K_1 + 2K_2$.

5.6 Transport processes in discontinuous systems

We shall now consider the simultaneous transportation of heat and matter within a system. Those quantities are included in the second law, Eq. (1.38), which will now be generalized to several components,

$$dS = dQ/T - \sum S_k dN_k + d_{\text{ip}}S. \quad (5.72)$$

First we shall consider a system completely isolated from the surroundings in which Eq. (5.72) reduces to $dS = d_{\text{ip}}S$ and, introducing the contributions from various internal processes from Eq. (5.6), we write

$$dS = d_{\text{ip}}S = \sum X_i d\xi_i \quad (5.73)$$

We shall not use the second law expressed through dG because the temperature is not the same in the whole system. In the second law heat and matter represent exchanges with

the surroundings. In order to make them take part in an internal transportation process we shall now consider a system with a sharp discontinuity separating two subsystems. For each subsystem it is as if there were exchanges with its surroundings when heat and matter are transported between them. The subsystems will be regarded as homogeneous and it will be assumed that the equilibration within each subsystem is very efficient. It only requires a low thermodynamic force and will thus produce a negligible amount of entropy. We can then evaluate the entropy production due to transportation between the subsystems by simply comparing the total entropy content before and after the exchanges. However, we cannot apply the concept of heat to the state of a system and shall instead apply the combined law in the form of Eq. (1.72), generalized to several components to the two equilibrium states. Under constant P the difference in entropy of the whole system will be

$$d_{\text{ip}}S = dS' + dS'' = (1/T')dH' - \sum(\mu'_k/T')dN'_k + (1/T'')dH'' - \sum(\mu''_k/T'')dN''_k. \quad (5.74)$$

The subsystems are identified by (') and (''). The total values of U and N_k will be maintained in a completely isolated system and that is the choice made by most authors. However, instead of keeping V constant, as for a completely isolated system, we prefer to keep P constant because that is a more common experimental condition. Thus, H and N_k will be conserved in the system,

$$dH = dH' + dH'' = 0 \quad (5.75)$$

$$dN_k = dN'_k + dN''_k = 0 \quad (5.76)$$

The transport of internal energy and matter between the subsystems will be regarded as simultaneous internal processes in the system and their extents will be expressed by the amounts received by the second subsystem (''). Their production of entropy will be given by Eq. (5.74),

$$d_{\text{ip}}S = \left(\frac{1}{T''} - \frac{1}{T'} \right) dH'' - \sum \left(\frac{\mu''_k}{T''} - \frac{\mu'_k}{T'} \right) dN''_k \quad (5.77)$$

We may thus introduce two fluxes, $J_H = dH''/dt$ and $J_k = dN''_k/dt$, and two forces,

$$X_H = \left(\frac{1}{T''} - \frac{1}{T'} \right) = \Delta \left(\frac{1}{T} \right) \quad (5.78)$$

$$X_k = - \left(\frac{\mu''_k}{T''} - \frac{\mu'_k}{T'} \right) = -\Delta \left(\frac{\mu_k}{T} \right) \quad (5.79)$$

$$\sigma \equiv \frac{\partial_{\text{ip}}S}{\partial t} = \sum X_i J_i = \Delta \left(\frac{1}{T} \right) \frac{dH''}{dt} - \sum \Delta \left(\frac{\mu_k}{T} \right) \frac{dN''_k}{dt} \quad (5.80)$$

For small differences in T and composition we can approximate

$$X_H = \Delta \left(\frac{1}{T} \right) = \frac{-1}{T^2} \Delta T \quad (5.81)$$

$$X_k = -\Delta \left(\frac{\mu_k}{T} \right) = \frac{-1}{T} \Delta \mu_k + \frac{\mu_k}{T^2} \Delta T \quad (5.82)$$

The phenomenological equations would be

$$J_H = L_{HH} \Delta \left(\frac{1}{T} \right) - \sum L_{Hj} \Delta \left(\frac{\mu_j}{T} \right) \quad (5.83)$$

$$J_k = L_{kH} \Delta \left(\frac{1}{T} \right) - \sum L_{kj} \Delta \left(\frac{\mu_j}{T} \right) \quad (5.84)$$

According to the reciprocal relation we know $L_{Hk} = L_{kH}$. However, by transforming $-\Delta(\mu_k/T)$ according to Eq. (5.82) we find after rearranging terms

$$J_H = \left(\frac{1}{T^2} \right) \left(-L_{HH} + \sum L_{Hj} \mu_j \right) \Delta T - \left(\frac{1}{T} \right) \sum L_{Hj} \Delta \mu_j \quad (5.85)$$

$$J_k = \left(\frac{1}{T^2} \right) \left(-L_{kH} + \sum \mu_j L_{kj} \right) \Delta T - \left(\frac{1}{T} \right) \sum L_{kj} \Delta \mu_j. \quad (5.86)$$

It is interesting to note that the cross coefficients are no longer equal when we regard ΔT and $\Delta \mu_j$ as the forces. This is a demonstration of the fact that the reciprocal relation holds only when the fluxes and forces have been selected as conjugate pairs, each of which contributes with $X_i J_i$ to the entropy production.

If the discontinuity separating the subsystems is a wall with a hole, one may like to regard the pressure difference between the subsystems as the force for transport of matter through the hole. If there is only one component, its chemical potential is identical to the molar Gibbs energy and it can vary with T and P according to Eq. (3.35),

$$\Delta G_m = V_m \Delta P - S_m \Delta T. \quad (5.87)$$

By also using $G_m = H_m - T S_m$ one can transform X_k in Eq. (5.82) and obtain for a pure element,

$$\begin{aligned} X_k &= -\Delta \left(\frac{G_m}{T} \right) = -G_m \Delta \left(\frac{1}{T} \right) - \frac{1}{T} \Delta G_m \\ &= \frac{G_m}{T^2} \Delta T - \frac{V_m}{T} \Delta P + \frac{S_m}{T} \Delta T = \frac{H_m}{T^2} \Delta T - \frac{V_m}{T} \Delta P. \end{aligned} \quad (5.88)$$

Exercise 5.7

Examine if the reciprocal relation applies to the phenomenological equations for J_H and J_k if expressed with ΔT and ΔP as forces.

Hint

The forces can be replaced by the two new forces, ΔT and ΔP , only for a pure element where there are only two forces to start with. For that case, insert $\Delta(G_m/T)$ from Eq. (5.88) as $\Delta(\mu_j/T)$ into Eqs (5.83) and (5.84).

Solution

We obtain $J_H = -((L_{HH} - L_{Hk}H_m)/T^2)\Delta T - (L_{Hk}V_m/T)\Delta P$ and $J_k = -((L_{kH} - L_{kk}H_m)/T^2)\Delta T - (L_{kk}V_k/T)\Delta P$. The reciprocal relation does not apply.

5.7 Transport processes in continuous systems

It is evident that the kinetic coefficients in Eqs (5.83) and (5.84) do not represent properties of the two subsystems because it was assumed that the equilibration within each subsystem is very efficient and the corresponding production of entropy should be negligible. The kinetic coefficients must represent properties of the discontinuity separating the subsystems and the production of entropy occurs inside the discontinuity. It could be a membrane or wall separating the two subsystems or a phase interface between crystals of two different phases or between two liquids. It could even be an impermeable wall with a small hole through which matter can diffuse as from a Knudsen cell. At the same time, the wall could conduct heat. That could be a case of negligible coupling, i.e., negligible cross coefficients.

In the preceding section there was no discussion of what happens inside the discontinuity but in order to give the kinetic coefficients any physical interpretation it is necessary to give the discontinuity some width and assume a model for its properties. With the very rough approximation that the discontinuity consists of a wall of homogeneous material it would make sense to define an average gradient $\Delta(1/T)/\Delta z$ inside the discontinuity if Δz is its width. Equation (5.80) would thus change to

$$\sigma = \frac{d_p S}{dt} = \left[\frac{\Delta(1/T)}{\Delta z} J_H - \sum \frac{\Delta(\mu_k/T)}{\Delta z} J_k \right] \cdot \Delta z. \quad (5.89)$$

In order to remove the assumption that the discontinuity consists of a layer of a homogeneous material, we shall now consider a thin slice of the material separating the two subsystems. The rate of entropy production in that slice would be

$$\frac{d\sigma}{dz} = \frac{d(1/T)}{dz} J_H - \sum \frac{d(\mu_k/T)}{dz} J_k. \quad (5.90)$$

The local values of the force in a one-dimensional inhomogeneous system are defined as

$$\nabla X_H \equiv \frac{dX_H}{dz} = \frac{d(1/T)}{dz} = \frac{-1}{T^2} \frac{dT}{dz} \quad (5.91)$$

$$\nabla X_k \equiv \frac{dX_k}{dz} = -\frac{d(\mu_k/T)}{dz} = \frac{-1}{T} \frac{d\mu_k}{dz} + \frac{\mu_k}{T^2} \frac{dT}{dz}. \quad (5.92)$$

By integrating over the whole width we obtain

$$\sigma = \int d\sigma = \int \sum J_i \nabla X_i dz. \quad (5.93)$$

As an example, for isothermal diffusion of a number of components we get for the dissipation of Gibbs energy, $-\Delta G$,

$$-\Delta G = T \int d\sigma = - \int \sum J_k (d\mu_k/dz) dz. \quad (5.94)$$

The phenomenological equations, Eqs (5.83) and (5.84), would change to

$$J_H = L_{HH}\nabla(1/T) - \sum L_{Hk}\nabla(\mu_k/T) \quad (5.95)$$

$$J_k = L_{kH}\nabla(1/T) - \sum L_{kj}\nabla(\mu_j/T). \quad (5.96)$$

As already emphasized, heat is not a state variable and one cannot define the content of heat in a system. Instead, it is connected to a particular way of exchanging energy with the surroundings. The popular concept of heat content is actually the amount of energy that can be extracted from the system in that way. Heat capacity is the capacity to receive energy in that way with a given increase of its temperature. By studying how heat has to be fed into a system at one end and extracted from the other end in order to maintain a certain temperature difference, one can study heat conduction, usually denoted by λ . That heat is supposed to flow through the system and it is only in that sense that heat exists inside the system.

In contrast, enthalpy is a property of the system and there is no mechanism operating directly on enthalpy by which it can move between the system and the surroundings. For the same reason, there is no mechanism operating directly on enthalpy that can make it flow through the system. Nevertheless, we have managed to derive the thermodynamic force for enthalpy flow, which is valid in a formal sense. It should now be used to derive the thermodynamic force for the flow of heat, which should be of more fundamental nature. It can be obtained by realizing that the flow of enthalpy depends not only on heat flow but also on the flow of matter, which carries enthalpy with it. We may thus evaluate the flux of heat by subtracting the contribution from the flux of matter from the flux of enthalpy,

$$J_Q^* = J_H - \sum H_k J_k. \quad (5.97)$$

We may retain the flux of matter in the new set of fluxes,

$$J_k^* = J_k. \quad (5.98)$$

It is easy to see that, in order not to change the entropy production, we must use the following forces,

$$\nabla X_Q^* = \nabla X_H = \nabla(1/T) \quad (5.99)$$

$$\nabla X_k^* = \nabla X_k + H_k \nabla X_H = -\nabla(\mu_k/T) + H_k \nabla(1/T). \quad (5.100)$$

It is interesting to note that we thus find the same driving force for heat as for enthalpy but it should be realized that it is to some part the result of how we defined the other process in the new set of processes. Furthermore, since we have a physical understanding for these two processes, the flow of heat and matter, it seems reasonable to start by defining the phenomenological equations for them. By neglecting the possible coupling between them and considering only one diffusing species, we write

$$J_Q^* = L_{QQ}^* \nabla X_Q^* \quad (5.101)$$

$$J_k^* = L_{kk}^* \nabla X_k^*. \quad (5.102)$$

In passing, we may note that comparison of Fourier's law for heat conduction, $J_Q = -\lambda dT/dz$, and Eq. (5.101) with the force from Eq. (5.99) inserted, gives the relation

$L_{QQ}^* = \lambda T^2$, which is particularly interesting since it has been found experimentally that λ is often rather independent of T . It seems that L_{QQ}^* depends strongly on T .

Combining Eqs (5.97) to (5.102) we can relate the phenomenological coefficients in the two formalism,

$$\begin{aligned} J_H &= J_Q^* + H_k J_k^* = L_{QQ}^* \nabla X_Q^* + H_k L_{kk}^* \nabla X_k^* \\ &= L_{QQ}^* \nabla X_H + H_k L_{kk}^* (\nabla X_k + H_k \nabla X_H) \end{aligned} \quad (5.103)$$

$$J_k = J_k^* = L_{kk}^* \nabla X_k^* = L_{kk}^* (\nabla X_k + H_k \nabla X_H). \quad (5.104)$$

The phenomenological coefficients for the set of processes defined by flow of heat together with enthalpy and appearing in Eqs (5.95) and (5.96) would thus be

$$L_{HH} = L_{QQ}^* + H_k^2 L_{kk}^* \quad (5.105)$$

$$L_{Hk} = H_k L_{kk}^* = L_{kH} \quad (5.106)$$

$$L_{kk} = L_{kk}^*. \quad (5.107)$$

In this way it is thus possible to get numerical values for the flow of enthalpy although such flow does not occur physically. It is worth noting that the main information is obtained already from experimental information on diffusion and heat conduction obtained without both processes being present simultaneously and it results in a prediction of cross coefficients for the enthalpy formalism.

Another choice of forces can be obtained from Eq. (5.100) using the same transformation as in Eq. (5.88). It only applies to pure elements or species and yields

$$\nabla X_k^* = -\frac{V_m}{T} \frac{dP}{dz}. \quad (5.108)$$

It is interesting that the thermodynamic force driving the flux of matter due to a pressure gradient is thus independent of the temperature gradient if one considers heat flux as the other flux rather than the flux of internal energy. In principle, this simple expression does not hold in a system with more than one component. However, when a gas or liquid is subjected to a pressure gradient then it will flow as if it were a pure substance and Eq. (5.108) can be applied.

Exercise 5.8

Prove that the entropy production is not changed if the new set of processes, defined by Eqs (5.97) to (5.100), are applied instead of J_H and J_k .

Solution

The procedure in Section 5.2 yields $J_H \nabla X_H + \sum J_k \nabla X_k = \nabla \sigma = J_Q^* \nabla X_Q^* + \sum J_k^* \nabla X_k^* = (J_H - \sum H_k J_k) \nabla X_H + \sum J_k (\nabla X_k + H_k \nabla X_H) = J_H \nabla X_H - \sum H_k J_k \cdot \nabla X_H + \sum J_k \nabla X_k + \sum H_k J_k \cdot \nabla X_H = J_H \nabla X_H + \sum J_k \nabla X_k$.

5.8 Substitutional diffusion

The flux of any transport process must be given relative to some frame of reference. For heat conduction in a solid material it is natural to fix the frame to the material itself because it will not be much affected by the process. However, there may be some heat expansion of the material and the formal description may thus be simplified if distances in the frame are measured as atomic distances. In a crystalline material the frame of reference will thus be fixed to the crystalline lattice. In metallic solutions diffusion normally occurs by atoms jumping into neighbouring vacant sites in the lattice. From a fundamental point of view it may thus seem natural to describe diffusion in a lattice-fixed frame. For diffusion of atoms dissolved interstitially in a host lattice the situation would be somewhat similar to the case of heat conduction if one had chosen a frame fixed to the host lattice. However, there may be a small effect due to the interstitial atoms expanding the host lattice and it would again be an advantage to measure distances in atomic distances.

The situation is different in a substitutional solution where the solute atoms occupy the same kind of lattice sites as the host atoms. A lattice-fixed frame may thus expand or contract locally if the solute atoms diffuse with a different rate to that of the solvent atoms. Experimentally, it may be easiest to study substitutional diffusion in a volume-fixed frame. If the solute atoms diffuse faster and by a vacancy mechanism, there would be a net flow of atoms in one direction and of vacancies in the other relative to the lattice. Vacancies would thus have to be generated in some places and condense in other places, resulting in local creation or disappearance of lattice sites. There could be a considerable difference between the lattice-fixed and volume-fixed frames. It is of considerable practical importance to be able to transform diffusion data from one frame to another and that is done by defining different sets of processes in different frames and to transform between them. We shall first discuss this for a simple binary system and transform from the lattice-fixed frame to a number-fixed frame, which is identical to the volume-fixed frame if the molar volume is constant. A more general treatment will then be given, which could easily be extended to the volume-fixed frame.

Primarily we shall describe diffusion of individual components relative to the lattice-fixed frame. The diffusing atoms will transport volume with a rate $\sum V_i J_i$, where V_i is the partial molar volume and that transport can be studied experimentally by placing small inert markers in the material. They are called Kirkendall markers and can be assumed to be fixed to the lattice. They will thus move with a velocity $v = -\sum V_i J_i$ relative to the volume-fixed frame. Expressed as mol/s m² the Kirkendall shift will thus be represented by the flux

$$J_K^* = v/V_m = -\sum_{i=1}^n a_i J_i, \quad (5.109)$$

where $a_i = V_i/V_m$ and $\sum x_i a_i = 1$. Let the flux of a component j be J_j^* in the volume-fixed frame. If the lattice-fixed frame moves with a velocity v relative to the volume-fixed frame, e.g. measured by the Kirkendall shift, then the flux in the lattice-fixed frame will be

$$J_j = J_j^* - x_j v/V_m. \quad (5.110)$$

Combination with Eq. (5.109) yields

$$J_j^* = J_j + x_j v / V_m = J_j - x_j \sum_{i=1}^n a_i J_i = \sum_{i=1}^n (\delta_{ji} - a_i x_j) J_i, \quad (5.111)$$

where δ_{ij} is the Kronecker symbol and it is equal to 1 for $i = j$ but 0 otherwise. By definition of the volume-fixed frame we have a relation between the new fluxes,

$$\sum_{j=1}^n a_j J_j^* = 0 \quad (5.112)$$

$$J_n^* = -\frac{1}{a_n} \sum_{j=1}^{n-1} a_j J_j^*. \quad (5.113)$$

We can thus eliminate J_n^* and instead include the Kirkendall shift, J_K^* , from Eq. (5.109) in the new set of independent processes. Introducing the new set of processes through a generalized version of Eqs (5.16) we write

$$J_j^* = \sum_{i=1}^n \alpha_{ji} J_i \quad (5.114)$$

Comparing with Eq. (5.111) we find $\alpha_{ji} = \delta_{ji} - a_i x_j$ for $j = 1$ to $n - 1$. For $j = n$, comparison with Eq. (5.109) yields $\alpha_{ni} = -a_i$. The coefficients in the phenomenological equations for the new set of processes are now obtained directly from Eq. (5.21).

$$L_{sr}^* = \sum_{i=1}^n \sum_{k=1}^n (\delta_{ij} - a_i x_s)(\delta_{rk} - a_k x_r) L_{ik} \quad (5.115)$$

$$L_{sK}^* = \sum_{i=1}^n \sum_{k=1}^n (\delta_{si} - a_i x_s)(-a_k) L_{ik} \quad (5.116)$$

$$L_{Kr}^* = \sum_{i=1}^n \sum_{k=1}^n (-a_i)(\delta_{rk} - a_k x_r) L_{ik} \quad (5.117)$$

$$L_{KK}^* = \sum_{i=1}^n \sum_{k=1}^n (-a_i)(-a_k) L_{ik}. \quad (5.118)$$

The relations of the new thermodynamic forces to the initial ones are obtained from a generalization of Eqs (5.18) by inserting the expressions for α_{ij} ,

$$\nabla X_j = \sum_{i=1}^n \alpha_{ij} \nabla X_i^* = \nabla X_j^* - a_j \sum_{i=1}^{n-1} x_i \nabla X_i^* - a_j \nabla X_K^* \quad \text{for } j = 1 \text{ to } n - 1 \quad (5.119)$$

$$\nabla X_n = -a_n \sum_{i=1}^{n-1} x_i \nabla X_i^* - a_n \nabla X_K^*. \quad (5.120)$$

Comparing these equations we find

$$\nabla X_j^* = \nabla X_j - (a_j/a_n) \nabla X_n. \quad (5.121)$$

For the number-fixed frame all $a_i = 1$ and Eq. (5.121) is simplified to

$$\nabla X_j^* = \nabla X_j - \nabla X_n. \quad (5.122)$$

This is the gradient of the diffusion potential and it applies to interdiffusion under exchange of atoms with those of a selected type, n , usually identified as the solvent. Inserting Eq. (5.121) in Eq. (5.120) we obtain the thermodynamic force for the Kirkendall shift

$$\begin{aligned}\nabla X_K^* &= -\nabla X_n/a_n - \sum_{i=1}^{n-1} x_i(\nabla X_i - (a_i/a_n)\nabla X_n) \\ &= -\nabla X_n/a_n - \sum_{i=1}^n x_i\nabla X_i + x_n\nabla X_n + (\nabla X_n/a_n) \sum_{i=1}^n x_i a_i - x_n(a_n/a_n)\nabla X_n \\ &= -\sum_{i=1}^n x_i\nabla X_i.\end{aligned}\quad (5.123)$$

We here made use of $\sum x_i a_i = 1$. The result is equal to 0 because $\nabla X_i = -d(\mu_i/T)dz$, where T is the local temperature, and $\sum x_i d\mu_i = 0$ due to the Gibbs–Duhem relation under isobarothermal conditions. Consequently, the Kirkendall migration will not produce any entropy. That is a natural conclusion because the markers are fixed to the lattice and do not move in a physical sense. It is thus possible to completely neglect the Kirkendall migration when transforming the diffusion equations from the lattice-fixed frame to another frame. This is the case where the number of independent processes is decreased, which was mentioned in the discussion following Eq. (5.40). The description of diffusion of all the components relative to each other will still be complete but the Kirkendall migration will be forgotten. It should be emphasized that the Gibbs–Duhem relation does not apply to diffusion across a phase interface with its discontinuous jumps in properties and composition. The full treatment given here is thus necessary for diffusional phase transformations with a discontinuous jump in composition at the interface. That will be further discussed in Sections 17.5 and 17.6. It will also be useful for diffusion inside a phase with appreciable differences in composition between neighbouring atomic planes, e.g. in ordered alloys or in steep composition spikes close to an interface.

Realizing that the Kirkendall shift should not produce any entropy and its driving force should thus be zero, we could have transformed the diffusion equations from the lattice-fixed frame to the number-fixed frame in an easier way, in particular for a binary system. For diffusion by exchange of A and B atoms the force should be

$$\nabla X_1^* = \nabla X_A - \nabla X_B. \quad (5.124)$$

where the forces in the lattice-fixed frame are $\nabla X_j = -d\mu_j/dz$. For the Kirkendall shift we have

$$J_2^* = -J_A - J_B. \quad (5.125)$$

This case was defined by Eqs (5.35) and (5.36) and now $\alpha_{21} = -1$, $\alpha_{22} = -1$, $\beta_{11} = 1$ and $\beta_{21} = -1$. Equations (5.38) to (5.40) show that in order not to change the entropy production we must have

$$J_1^* = \alpha_{11}J_A + \alpha_{12}J_B = \alpha_{11}J_A - (1 - \alpha_{11})J_B \quad (5.126)$$

$$\nabla X_2^* = \beta_{21}\nabla X_A + \beta_{22}\nabla X_B = -(1 - \alpha_{11})\nabla X_A - \alpha_{11}\nabla X_B. \quad (5.127)$$

It can easily be checked that $\sum J_j \nabla X_j = \sigma = \sum J_i^* \nabla X_i^*$. The α_{11} parameter is arbitrary but with the choice $\alpha_{11} = x_B$ and $1 - \alpha_{11} = x_A$ one finds that $\nabla X_2^* = 0$ due to the Gibbs–Duhem relation. That choice will thus give the same result as the previous derivation. Other alternatives are less useful.

Exercise 5.9

Express the flux of a component in the number-fixed frame in terms of those in the lattice-fixed frame.

Hint

Use Eq. (5.114) and remember that all $a_i = 1$ for the number-fixed frame.

Solution

$$J_k^* = \sum_{i=1}^n (\delta_{ki} - x_k) J_i = J_k - \sum_{i=1}^n x_k J_i = J_k \sum_{i \neq k} x_i - x_k \sum_{i \neq k} J_i.$$

For a binary system, $J_A^* = x_B J_A - x_A J_B$ and $J_B^* = x_A J_B - x_B J_A = -J_A^*$.

5.9 Onsager's extremum principle

When a system is initially in a state of non-equilibrium, it is of practical interest to be able to predict how the state will change with time as a result of internal processes. Normally, this is done by using kinetic equations, e.g. the linear phenomenological equations. An alternative method will now be described but it should be emphasized that it will result in the same predictions as the linear phenomenological equations. As a consequence, it cannot be used outside the linear range. In fact, it may be regarded as a method of deriving the linear phenomenological equations for the processes involved, a method that sometimes may be a convenient way of formulating those equations.

The alternative method is based on the 'dissipation function' defined by Onsager [5]. His function originates from the rate of entropy production of the system, which was derived in Section 5.1. According to the second law, spontaneous processes in a system result in an entropy production and the rate will be

$$\sigma \equiv \sum X_j J_j \geq 0. \quad (5.128)$$

With a linear kinetic equation for each process we have

$$J_j = \sum_k L_{jk} X_k. \quad (5.129)$$

The rate of entropy production would then be

$$\sigma = \sum_j \sum_k L_{jk} X_j X_k. \quad (5.130)$$

One could just as well invert the kinetic equation, Eq. (5.129), obtaining

$$X_j = \sum_k R_{jk} J_k \quad (5.131)$$

$$\sigma \equiv \sum_j J_j X_j = \sum_j J_j \sum_k R_{jk} J_k = \sum_j \sum_k R_{jk} J_j J_k. \quad (5.132)$$

The new kinetic coefficients represent the resistance or friction of the processes whereas the L coefficients represent their mobilities. The set of R coefficients are directly obtainable from the set of L coefficients. If there were no cross coefficients one would simply get

$$\sigma = \sum_j (1/L_{jj}) J_j^2. \quad (5.133)$$

The right-hand side of Eq. (5.132) could have been formulated directly by assuming that the rate of entropy production is a function of the fluxes and developing that function in a Taylor series. Evidently, the first term in the series can be omitted because there can be no entropy production without a flux. The second term can also be omitted in view of the second law because that term is linear in the fluxes and would make the entropy production change sign if the direction is reversed, which is not allowed since the entropy production of spontaneous processes must be positive. The right-hand side of Eq. (5.132) represents the third term except for a factor $1/2$. Onsager thus defined a function

$$\Phi(J, J) \equiv \frac{1}{2} \sum_j \sum_k R_{jk} J_j J_k. \quad (5.134)$$

He called it dissipation function because 2Φ is not only equal to the rate of entropy production, σ . Under isobarothermal conditions $2T\Phi$ actually represents the rate of Gibbs energy dissipation. Without any physical argument, Onsager then formulated a new function, $\Psi = \sigma - \Phi$ and examined under what conditions its value is maximized. For a system with gradual variations of the local state he found the answer by variation analysis. We shall avoid this complication by limiting the derivation to a small volume with approximately uniform conditions or to a system with more than one homogeneous region.

Comparison of Eq. (5.132) and first part of Eq. (5.134) demonstrate that Φ is equal to $\sigma/2$. However, they represent different functions. This is best understood by multiplying them with T . According to Eq. (5.53), $T d_{ip} S$ is equal to the decrease in Gibbs energy of the system if it is completely isolated, and $-T\sigma$ is the time derivative of Gibbs energy, \dot{G} . The quantity σ thus represents a rate of change of the state of the system. On the other hand, $T\Phi$ with Φ defined by Eq. (5.134) shows how the Gibbs energy is being dissipated by friction. The new function is thus defined as

$$\Psi = \sigma - \Phi = \sum_j X_j J_j - \frac{1}{2} \sum_j \sum_k R_{jk} J_j J_k. \quad (5.135)$$

We shall now consider a purely hypothetical case where the fluxes can vary under fixed forces and the coefficients, if they are not constant, vary with the forces but not with the

fluxes. Then we obtain the following conditions, under which Ψ has an extremum,

$$\frac{\partial \Psi}{\partial J_j} = X_j - \frac{1}{2} \sum_k (R_{jk} + R_{kj}) J_k = 0 \quad (5.136)$$

$$\frac{\partial \Psi}{\partial J_k} = X_k - \frac{1}{2} \sum_j (R_{kj} + R_{jk}) J_j = 0. \quad (5.137)$$

It is evident that this is a way of reproducing the kinetic equation, Eq. (5.131), if Onsager's reciprocal relation applies. On the other hand, comparison between Eqs (5.136) and (5.137) demonstrates that this new method of deriving the kinetic equations results in the reciprocal coefficients being equal because $\frac{1}{2}(R_{jk} + R_{kj})$ is equal to $\frac{1}{2}(R_{kj} + R_{jk})$. However, this cannot be taken as a proof for Onsager's reciprocal relation because there is no physical principle behind his extremum principle. It should be regarded simply as a mathematical tool for formulating the linear kinetic equations.

Onsager showed that if there is an extremum it has to be a maximum. However, it should be emphasized that the value of the maximum is of no interest, nor the fact that it is a maximum. His principle has thus been called Onsager's extremum principle. It should further be emphasized that the extremum is an extremum only in comparison with the results of non-linear kinetic equations because it is found by keeping the force constant while varying the flux, i.e., by not requiring the linear law between force and flux.

However, it is difficult to see how the expression for $\Phi(J, J)$ in Eq. (5.134) could be created by combining Eq. (5.128) with a non-linear kinetic equation.

Most practical applications of Onsager's extremum principle might concern systems under constant T and P and it is thus convenient to use Gibbs energy instead of entropy and we know that $\dot{G} = -\sigma T$, e.g. from Eq. (5.53). We could thus write Eq. (5.135) as

$$T\Psi = -\dot{G} - T\Phi. \quad (5.138)$$

One should first model Gibbs energy as a function of various internal variables, ξ_j , and take its time derivative to form \dot{G} as a function of all the fluxes J_j , being defined as $d\xi_j/dt$. One has thus identified some internal processes and from their phenomenological equations one could express the contribution to the dissipation of Gibbs energy from each one,

$$\phi_i = T \sum_k R_{ik} J_i J_k, \quad (5.139)$$

where T , being constant, is usually not shown explicitly but is incorporated into the R coefficient. In addition, there could be other processes that are not identified as easily. Their contributions should also be evaluated in the same way and included in the dissipation function

$$T\Phi = \frac{1}{2} \sum \phi_i. \quad (5.140)$$

Onsager's extremum principle states that the kinetic equations are obtained from

$$T \frac{\partial \Psi}{\partial J_j} = -\frac{\partial \dot{G}}{\partial J_j} - \frac{1}{2} \sum_i \frac{\partial \phi_i}{\partial J_j} = 0. \quad (5.141)$$

By solving this set of equations one can thus calculate how the system develops with time. In order to succeed it is necessary to express all the ϕ_i functions as functions of the same fluxes that describe the change of Gibbs energy, \dot{G} . An example will be given in Section 17.4. A special advantage of this method is that one may use a model of the properties that includes some dependent variables and apply mathematical expressions for their dependencies as auxiliary conditions by using Lagrange multipliers when deriving the conditions for an extremum of Onsager's Ψ function.

It should finally be emphasized that Onsager's extremum principle was derived under the condition that the phenomenological coefficients are constant. It will be discussed again in Section 17.3.

Exercise 5.10

Onsager's principle is sometimes regarded as a principle of extremum or maximum entropy production. Examine if the condition of an extremum for the rate of entropy production, σ , gives the same result as an extremum of Onsager's function Ψ .

Hint

Use $\Phi = \sigma/2$ from Eq. (5.134) as an auxiliary condition by introducing a Lagrange multiplier.

Solution

$L = \sigma + \lambda(\Phi - \sigma/2)$; $\partial L/\partial J_j = X_j + \lambda(\frac{1}{2}\Sigma(R_{jk} + R_{kj})J_k - X_j/2) = 0$. Applying Onsager's reciprocal relation, multiplying by J_j and adding the equations for all j , yields $\Sigma X_j J_j + \lambda(\Sigma \Sigma R_{jk} J_k J_j - \frac{1}{2}\Sigma X_j J_j) = 0$ or $\sigma + \lambda(2\Phi - \frac{1}{2}\sigma)$. With $\Phi = \sigma/2$ this shows that $\lambda = -2$, yielding the kinetic equations as $\partial L/\partial J_j = 2X_j - \Sigma(R_{jk} + R_{kj})J_k = 0$. This is in complete agreement with Eq. (5.136).

6 Stability

6.1 Introduction

For a spontaneous internal process $Dd\xi$ must be positive according to the second law. A positive D value would thus require that $d\xi$ is positive. The process would proceed forward. Negative D values would reverse the direction. At equilibrium we have $D = 0$ by definition but it is then of interest to examine if it is a stable or unstable equilibrium. We should thus examine the consequence of a small fluctuation $d\xi$ that brings the system away from the state of equilibrium. Since D is zero, it is then necessary to consider a higher term in Eq. (1.44)

$$Td_{ip}S = Dd\xi + \frac{1}{2}(dD/d\xi)(d\xi)^2 = \frac{1}{2}(dD/d\xi)(d\xi)^2. \quad (6.1)$$

When $dD/d\xi$ is positive, $Td_{ip}S$ would increase further if $d\xi$ increases further. That would thus happen spontaneously whether the fluctuation is positive or negative. Any small fluctuation would grow and the system is unstable. The quantity $-dD/d\xi$ may be regarded as the stability and will be denoted by B .

As an introduction to a more detailed discussion of stability it may be instructive to compare with the mechanical analogues in Fig. 6.1. It shows two bodies with different cross-sections and in contact with a flat floor. Their potential energy varies with the angle θ .

Only very slow changes will be considered, and it will be assumed that any release of potential energy goes into frictional losses. Kinetic energy will thus be neglected. The extent of the process, ξ , will be expressed by the angle θ and the potential energy will be denoted by E .

The variation of E , D and B with θ is illustrated in Fig. 6.2 for the body with an elliptical profile. It has an energy minimum at $\theta = 0$ and a maximum at $\theta = \pi/2$. In both these positions the driving force for a further rotation is zero, $D = -dE/d\theta = 0$, and they both represent equilibria. The quantity $d^2E/d\theta^2 = -dD/d\theta$ may there be regarded as the stability and the lower part of the diagram shows that for $\theta = 0$ it is positive and the equilibrium is thus a stable one. For $\theta = \pi/2$ it is negative and the equilibrium is unstable. A small fluctuation of θ away from $\pi/2$ in any direction will here give a force for a further growth of the fluctuation.

Figure 6.3 is for the body with a rectangular cross-section. It also has two equilibria, at $\theta = 0$ and $\pi/2$, which are both stable because a small fluctuation of θ will give a force for rotation back to the initial position. This case corresponds to Fig. 1.6 where $\Delta_{ip}S$ has

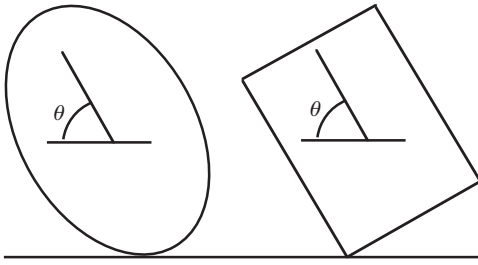


Figure 6.1 Mechanical analogues of two cases of thermodynamic systems.

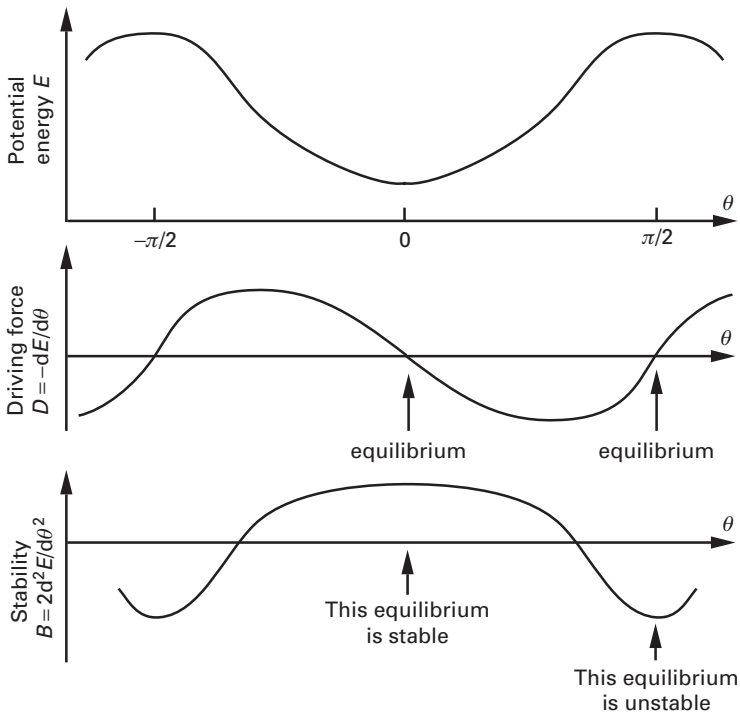


Figure 6.2 The energy, driving force and stability for the elliptical body in Fig. 6.1 as function of the angle of rotation.

a sharp maximum. In order to decide whether such an equilibrium is stable it is not only unnecessary but even incorrect to look at the value of $d^2E/d\theta^2$ because it represents the stability *only when the driving force is zero*, $D = -dE/d\theta = 0$, which is not the case for $\theta = 0$ or $\pi/2$. Figure 6.3 demonstrates that $d^2E/d\theta^2$ would give an incorrect prediction for these two equilibria. On the other hand, there is a third equilibrium which has $D = -dE/d\theta = 0$ at some angle between 0 and $\pi/2$ and there $d^2E/d\theta^2 < 0$ and will correctly predict that the equilibrium is unstable.

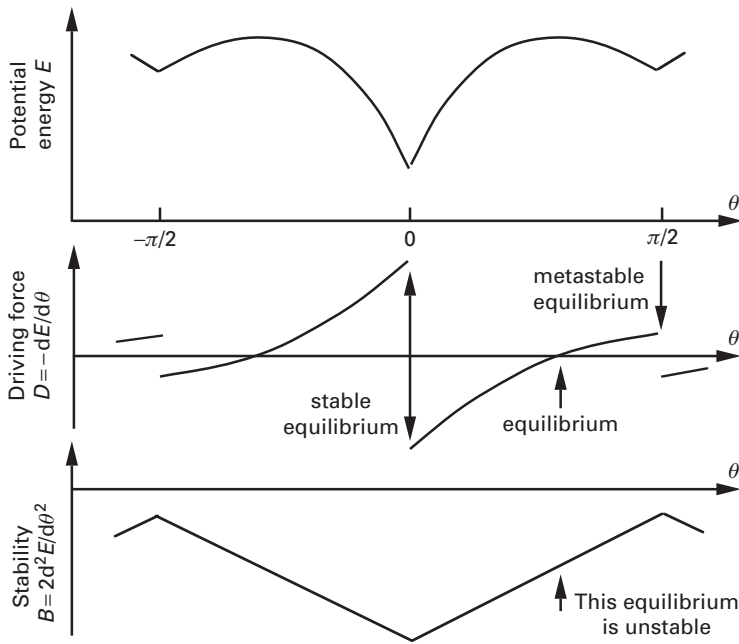


Figure 6.3 The energy, driving force and stability for the rectangular body in Fig. 6.1 as function of the angle of rotation.

Of the two stable equilibria, one ($\theta = \pi/2$) has a higher energy than the other ($\theta = 0$). For thermodynamic systems such a state is called **metastable**.

6.2 Some necessary conditions of stability

In the discussion of general conditions of equilibrium in Section 1.10 we saw that a system is in a state of internal equilibrium with respect to the extensive variables if each one of the potentials has the same value in the whole system. It remains to be tested if it is a stable or unstable equilibrium. We thus return to the combined law according to the energy scheme and apply dU to the whole system, but we replace $Dd\xi$ in Eq. (1.54) by $-1/2B(d\xi)^2$ because we shall only consider a state of equilibrium where $D = 0$.

$$dU = \Sigma Y^a dX^a + 1/2B(d\xi)^2. \quad (6.2)$$

First we shall consider only one internal process at a time, the transfer of dX^b from one half of the system, denoted by $'$, to the other, denoted by $''$, $d\xi = dX^{b''} = -dX^{b'}$. On the other hand, we shall limit the discussion to systems with no exchanges with the

surroundings. All the dX^a of the total system are zero and Eq. (6.2) simplifies to

$$dU = \frac{1}{2}B(d\xi)^2 \quad (6.3)$$

$$B = \frac{\partial^2 U}{\partial \xi^2} = \left(\frac{\partial^2 U}{(\partial X^b)^2} \right)'_{X^c} + \left(\frac{\partial^2 U}{(\partial X^b)^2} \right)''_{X^c}. \quad (6.4)$$

Here we have used the fact that the change of U in the total system must be equal to the sum of the changes in the two subsystems. The two terms are equal if the system consists of a homogeneous substance at equilibrium. By introducing the potential $Y^b = (\partial U / \partial X^b)_{X^c}$ we then obtain

$$B = \frac{\partial^2 U}{\partial \xi^2} = 2 \left(\frac{\partial^2 U}{(\partial X^b)^2} \right)'_{X^c} = 2 \left(\frac{\partial Y^b}{\partial X^b} \right)'_{X^c}. \quad (6.5)$$

The value of this derivative depends upon the size of the system. It should be evaluated for half of the system but the stability condition, $B > 0$, is not affected by the size. The derivative may thus be evaluated for a system of any given size in the formulation of the stability condition. It can be written as

$$\left(\frac{\partial^2 U}{(\partial X^b)^2} \right)'_{X^c} > 0 \quad \text{or} \quad \left(\frac{\partial Y^b}{\partial X^b} \right)'_{X^c} > 0 \quad \text{or} \quad U_{X^b X^b} > 0. \quad (6.6)$$

The last form uses the shorthand notation for derivatives of characteristic state functions, introduced in Section 2.5.

From Eq. (6.6) we may conclude that in order for a substance to be stable it is necessary that it has such properties that any pair of conjugate variables must change in the same direction if all the other extensive variables are kept constant. Actually, so far we have proved this only for conjugate pairs appearing on the energy scheme, i.e., (T, S) , $(-P, V)$ and (μ_i, N_i) . For them the stability conditions could be written as

$$U_{SS} > 0; \quad U_{VV} > 0; \quad U_{N_i N_i} > 0. \quad (6.7)$$

As an example, in a stable system the chemical potential of a component, μ_i , cannot decrease when the content of the same component, N_i , increases under constant S and V . As another example, when the temperature of a substance is increased at a constant volume, the entropy must also increase in order for the system to be stable.

$$U_{SS} \equiv \left(\frac{\partial T}{\partial S} \right)_{V, N_i} > 0. \quad (6.8)$$

Using Eq. (2.27) we can write this stability condition as

$$T/C_V > 0. \quad (6.9)$$

In combination with the fact that the absolute temperature T is always positive, this implies that the heat capacity under constant volume, C_V , must be positive

$$C_V = T(\partial S / \partial T)_{V, N_i} = T / (\partial T / \partial S)_{V, N_i} > 0. \quad (6.10)$$

However, in order to indicate where the limit of stability is, one should stick to the condition as obtained directly from Eq. (6.8), i.e. Eq. (6.9), or since T is positive,

$$1/C_V > 0. \quad (6.11)$$

The limit of stability occurs as $1/C_V$ goes to zero, i.e., as C_V goes to infinity. Similar considerations can be based upon the entropy scheme, where we have

$$-dS = (-1/T)dU + (-P/T)dV + \Sigma(\mu_i/T)dN_i - (D/T)d\xi. \quad (6.12)$$

By again replacing $Dd\xi$ at equilibrium by $-1/2B(d\xi)^2$ we obtain under constant U , V and N_i ,

$$-dS = 1/2 \frac{B}{T} (d\xi)^2 \quad (6.13)$$

$$\frac{B}{T} = \left(\frac{\partial^2(-S)}{\partial \xi^2} \right) = \left(\frac{\partial^2(-S)}{\partial (X^b)^2} \right)'_{X^c} + \left(\frac{\partial^2(-S)}{\partial (X^b)^2} \right)''_{X^c} = 2 \left(\frac{\partial Y^b}{\partial X^b} \right)'_{X^c}. \quad (6.14)$$

Since T is never negative, we find

$$\left(\frac{\partial Y^b}{\partial X^b} \right)'_{X^c} > 0, \quad (6.15)$$

where X^b , Y^b is any pair of conjugate variables appearing in the entropy scheme, i.e. $(-1/T, U)$, $(-P/T, V)$ and $(\mu_i/T, N_i)$. As an alternative we could have defined the stability by replacing $(D/T)d\xi$ with $-1/2B(d\xi)^2$. Then T would not have appeared in Eqs (6.9) and (6.10). Similar considerations can also be based on the volume scheme introduced in Section 3.5,

$$dV = (T/P)dS - (1/P)dU + \Sigma(\mu_i/P)dN_i - (D/P)d\xi. \quad (6.16)$$

At equilibrium under constant S , U and N_i it yields

$$\frac{B}{P} = 2 \left(\frac{\partial Y^b}{\partial X^b} \right)'_{X^c}. \quad (6.17)$$

The conjugate pairs of variables are here $(T/P, S)$, $(-1/P, U)$ and $(\mu_i/P, N_i)$.

Exercise 6.1

In Section 2.7 we saw that Grüneisen's constant can be evaluated from $\gamma = V(\partial P/\partial U)_V$ and it often has a value of about 2. Is this a quantity that is always positive for a stable system?

Solution

γ concerns the variation of P with U but they are not conjugate variables in any of the schemes presented in Table 3.1. Thus, we cannot prove that γ is always positive. On the contrary, it may be negative because α may be negative in rare cases and $\gamma = V\alpha/\kappa_T C_V$.

6.3 Sufficient conditions of stability

So far we have discussed stability with respect to one internal process at a time. In Chapter 5 we considered more than one simultaneous process, expressing $d_{ip}S$ as $\sum X_i d\xi_i$ or $T d_{ip}S$ as $\sum D_i d\xi_i$. At equilibrium the forces are zero and we need the next higher-order terms. Instead of Eq. (6.1) we should write

$$T d_{ip}S = \sum D_i d\xi_i - 1/2 \sum_i \sum_j B_{ij} d\xi_i d\xi_j = -1/2 \sum_i \sum_j B_{ij} d\xi_i d\xi_j. \quad (6.18)$$

We should thus generalize Eq. (6.2) and by arranging the $Y^a dX^a$ terms in a special order we write the combined law as

$$dU = T dS - P dV + \mu_2 dN_2 + \cdots + \mu_c dN_c + \mu_1 dN_1 + 1/2 \sum_i \sum_j B_{ij} d\xi_i d\xi_j. \quad (6.19)$$

We shall again keep all the extensive variables for the whole system constant and consider the transfer of some amounts of the extensive quantities, here $S, V, N_2, N_3, \dots, N_c, N_1$, between the two subsystems. In order for the system to be in a stable equilibrium all the stability conditions given in Eq. (6.7) must be satisfied. However, in Chapter 5 we found that cross terms could be very important for the kinetics and it is also true here. It is an interesting question if it is then necessary to stipulate that all the B_{ij} stabilities are positive in order to ensure that the system will be stable. In fact, it will now be shown that it is sufficient to ensure that a smaller set of conditions are satisfied if the members of that set are chosen in a particular way. For the present set we have the definition

$$B_{ij} = \frac{\partial^2 U}{\partial \xi_i \partial \xi_j} = \frac{\partial^2 U}{\partial X^a \partial X^b} = \left(\frac{\partial Y^a}{\partial X^b} \right)_{X^c} \quad (6.20)$$

According to Section 2.5, B_{ij} could be denoted $U_{X^a X^b}$ because the set of extensive variables are the natural variables of the U .

By first considering the transfer of only some amount of one of the extensive variables, there will be no cross effects and taking the first extensive variable we write

$$U_{SS} \equiv \left(\frac{\partial T}{\partial S} \right)_{V, N_2, \dots, N_c, N_1} > 0, \quad (6.21)$$

as a condition of stability. Next, consider the transfer of dV but also of some S . However, it is possible to eliminate the cross effect between them by the use of the combined law after subtracting $d(TS)$,

$$dF = d(U - TS) = -SdT - PdV + \mu_2 dN_2 + \cdots + \mu_c dN_c + \mu_1 dN_1 + 1/2 \sum_i \sum_j B_{ij} d\xi_i d\xi_j. \quad (6.22)$$

Instead of prescribing the amount dS to be transferred we shall consider the amount that keeps T constant. The value of T , being a potential, must be uniform in the system

at equilibrium and there can be no cross terms between a potential and an extensive quantity. The new stability condition will simply be

$$F_{VV} = \left(\frac{\partial(-P)}{\partial V} \right)_{T, N_2, \dots, N_c, N_1} > 0. \quad (6.23)$$

Next we shall add $d(PV)$ obtaining dG and when considering the transfer of dN_2 the next stability condition in the set will be

$$G_{N_2 N_2} = \left(\frac{\partial \mu_2}{\partial N_2} \right)_{T, P, N_3, \dots, N_c, N_1} > 0. \quad (6.24)$$

Then we subtract $d(\mu_2 N_2)$ obtaining a characteristic state function applied in Eq. (3.44),

$$\begin{aligned} d(G - \mu_2 N_2) = & -SdT + VdP - N_2 d\mu_2 + \mu_3 dN_3 + \dots \\ & + \mu_c dN_c + \mu_1 dN_1 + 1/2 \sum_i \sum_j B_{ij} d\xi_i d\xi_j. \end{aligned} \quad (6.25)$$

When considering the transfer of dN_3 we obtain the stability condition

$$(G - \mu_2 N_2)_{N_3 N_3} = \left(\frac{\partial \mu_3}{\partial N_3} \right)_{T, P, \mu_2, N_4, \dots, N_c, N_1} > 0. \quad (6.26)$$

By proceeding in the same way we obtain conditions involving all the components from 2 to c and each time with one more potential among the variables that are kept constant. Finally we obtain

$$\left(\frac{\partial \mu_c}{\partial N_c} \right)_{T, P, \mu_2, \dots, \mu_{c-1}, N_1} > 0. \quad (6.27)$$

It would seem that there is one more derivative in this series, $(\partial \mu_1 / \partial N_1)_{T, P, \mu_2, \dots, \mu_c}$, where all the variables to be kept constant are potentials. However, that derivative is always equal to zero in view of the Gibbs–Duhem relation between the potentials. It says that μ_1 cannot vary if all the other potentials are constant. The final derivative thus yields a trivial condition, which will not be included in the set of stability conditions.

We have thus been able to derive a set of $c + 1$ stability conditions without involving any cross terms. As explained in more detail in Chapter 8, at equilibrium there are $c + 1$ degrees of freedom in a one-phase system with c components. The set of $c + 1$ stability conditions can thus ensure that the system with its $c + 1$ degrees of freedom is stable against all possible fluctuations that can utilize the $c + 1$ degrees of freedom. We have thus obtained a **sufficient set of stability conditions**. Naturally, one could form a number of such sets by rearranging the extensive variables in a different order. It should be emphasized that if all the conditions in a sufficient set are satisfied, then all other stability conditions are automatically satisfied. It may be mentioned that the variable, put last among all the extensive variables, was thus chosen to express the size of the system. For that purpose Gibbs used the volume V . Of course, any extensive variable could be used.

Finally, it should be emphasized that a set of stability conditions can only be sufficient with respect to the particular kinds of freedom that are considered. In addition to those considered so far, there could be degrees of freedom concerning the homogeneous state

of the system, e.g., the mutual order among different atoms and the crystalline structure. Such a case will be discussed in Section 6.7.

Exercise 6.2

What would be the last stability condition if we use the combined law written according to the basic entropy scheme?

Hint

Consult Table 3.1. Select the content of component 1 to define the size of the system.

Solution

We get $(\partial(\mu_c/T)/\partial N_c)_{1/T, P/T, \mu_2/T, \dots, \mu_{c-1}/T, N_i} > 0$ but since $1/T$ is kept constant, T is also kept constant and because T is always positive we could just as well write this condition as $(\partial\mu_c/\partial N_c)_{T, P, \mu_2, \dots, \mu_{c-1}, N_i} > 0$, which we recognize.

6.4 Summary of stability conditions

We have seen that stability conditions are defined through the derivative of a potential with respect to its conjugate extensive variable. In Section 6.2, all the remaining extensive variables in the same set of conjugate pairs were kept constant. In Section 6.3 it was shown that a stability condition is also obtained if one or more of the potentials are kept constant instead, i.e.

$$\left(\frac{\partial Y^b}{\partial X^b}\right)_{Y^c, X^d} > 0. \quad (6.28)$$

However, it must be emphasized that all the independent variables appearing in a stability condition must come one from each pair in a set of conjugate pairs. One cannot use a mixture of variables from different sets. Nine possible sets were listed in Table 3.1 and they can all be used for this purpose. Each one yields its own form of the Gibbs–Duhem relation and eight stability conditions, not counting those where a mixture of μ_i and N_i are used. This makes 72 stability conditions, but few of them are really useful.

Exercise 6.3

Find a stability condition concerned with C_P .

Hint

Remember that $C_P = T(\partial S/\partial T)_{P, N_i}$.

Solution

It is evident that we should look for a stability condition involving $(\partial T/\partial S)_{P,N_i}$. We find the combination of variables in line 1 of Table 3.1 listing pairs of conjugate variables. The combined law with S , P and N_i as independent variables is obtained as $dU + d(PV) = dH = TdS + Vd(P) + \sum \mu_i dN_i$, where $T = (\partial H/\partial S)_{P,N_i}$. We get the stability condition $H_{SS} \equiv (\partial^2 H/\partial S^2)_{P,N_i} = (\partial T/\partial S)_{P,N_i} > 0$ and thus $T/C_P > 0$.

6.5 Limit of stability

Let us now compare the stability conditions occurring in a given set of sufficient conditions. Suppose we are inside a stable region and want to know which one will first turn negative as we move into a region of instability. We can find this by first examining which derivative is the smallest one inside the stable region. Let us start by comparing any two conditions, which differ only by the choice of variable in a conjugate pair to be kept constant, the extensive variable or the potential. Using the ability of Jacobians to change the independent variable from Y^c to X^c we find

$$\left(\frac{\partial Y^b}{\partial X^b}\right)_{Y^c} = \left(\frac{\partial Y^b}{\partial X^b}\right)_{X^c} - \left(\frac{\partial Y^b}{\partial X^c}\right)_{X^b} \left(\frac{\partial Y^c}{\partial X^b}\right)_{X^c} / \left(\frac{\partial Y^c}{\partial X^c}\right)_{X^b}. \quad (6.29)$$

In view of a Maxwell relation, $(\partial Y^b/\partial X^c)_{X^b}$ and $(\partial Y^c/\partial X^b)_{X^c}$ are equal and $(\partial Y^c/\partial X^c)_{X^b}$ cannot be negative for a stable system. Thus, the last term with its minus sign cannot be positive and we find

$$\left(\frac{\partial Y^b}{\partial X^b}\right)_{Y^c} \leq \left(\frac{\partial Y^b}{\partial X^b}\right)_{X^c}. \quad (6.30)$$

It is evident that each time a potential is introduced among the variables to be kept constant, the stability condition gets more restrictive. The most severe condition is the one where only one extensive variable is kept constant, the one chosen to represent the size of the system. Consequently, this derivative must be the first one to go to zero and that happens on the limit of stability. Of course, it is possible that one or several of the other derivatives also go to zero at the same time. However, we can always find the limit of stability by considering the last condition in the set if we know that we *start the search from inside a stable region*.

Let us now consider what happens to the last derivative in a different set of stability conditions. We can write the condition for the limit of stability according to the first set of necessary conditions in the following general form

$$\left(\frac{\partial Y^b}{\partial X^b}\right)_{Y^c, N_1} = 0, \quad (6.31)$$

where Y^c indicates that all potentials except for Y^b and Y^1 are kept constant during the derivation. However, in this situation where the derivative is zero, Y^b is also constant and, according to the Gibbs–Duhem relation, the only remaining potential, Y^1 , must also be constant. We thus find that, in this situation, it is possible to change the value of an

extensive variable, X^b , without affecting any potential, nor the value of the extensive variable chosen to express the size of the system. However, the other extensive variables will change with X^b , because they are dependent variables, and it would be possible to accomplish the same change of the system by prescribing how any one of them should change. The above relation thus holds for any conjugate pair of variables. We thus find that the last stability condition, obtained in each set of stability conditions, are all zero at the same time. Anyone of them could be used to find the limit of stability if one starts from inside a stable region.

It should be emphasized that inside a region of instability the above conditions may again turn positive when other conditions have become negative. In the general case it is thus necessary to apply a whole set of stability conditions. It is only when one is able to start from a point inside a stable region that one can identify the limit by applying a single condition.

Exercise 6.4

Show for a unary system that $(\partial(-P)/\partial V)_T$ and $(\partial T/\partial S)_P$ go to zero at the same time, as they should because only one extensive variable, N , is kept constant (and it is omitted from the notation in the case of a substance with fixed composition).

Hint

In order to compare them, they must be expressed in the same set of independent variables, which can be done using Jacobians. Take S and V , for instance.

Solution

We obtain $(\partial(-P)/\partial V)_T = U_{VV} - (U_{SV})^2/U_{SS}$ and $(\partial T/\partial S)_P = U_{SS} - (U_{SV})^2/U_{VV} = (\partial(-P)/\partial V)_T \cdot U_{SS}/U_{VV}$. If one expression goes to zero when U_{SS} and U_{VV} are still > 0 , then the other expression also does. The two quantities can be expressed as $1/V\kappa_T$ and T/C_P . It is interesting to note that κ_T and C_P both go to infinity at the limit of stability.

6.6 Limit of stability against fluctuations in composition

Experimentally and in practice it is most common that temperature and pressure are approximately constant. The question of stability then concerns only fluctuations in composition. We can omit T and P from the notation and give the limit of stability as

$$\left(\frac{\partial \mu_c}{\partial N_c} \right)_{\mu_2, \dots, \mu_{c-1}, N_1} = 0. \quad (6.32)$$

Usually the experimental information is available as fundamental equations of Gibbs energy. It would thus be convenient to express Eq. (6.32) in terms of Gibbs energy. This can be done by the use of Jacobians of a higher order than discussed before. The result

is conveniently written with the notation G_{kl} for $(\partial\mu_k/\partial N_l)_{N_j}$ which is also equal to $\partial^2 G/\partial N_k \partial N_l$. One has thus obtained the following (see [8]),

$$\left(\frac{\partial\mu_c}{\partial N_c}\right)_{\mu_2,\dots,\mu_{c-1},N_1} = \left| \begin{array}{cccc} G_{22} & \cdot & \cdot & G_{2c} \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ G_{c2} & \cdot & \cdot & G_{cc} \end{array} \right| / \left| \begin{array}{ccc} G_{22} & \cdot & G_{2,c-1} \\ \cdot & \cdot & \cdot \\ G_{c-1,2} & \cdot & G_{c-1,c-1} \end{array} \right|. \quad (6.33)$$

The second determinant can be related to the derivative for the preceding component,

$$\left(\frac{\partial\mu_{c-1}}{\partial N_{c-1}}\right)_{\mu_2,\dots,\mu_{c-2},N_c,N_1} = \left| \begin{array}{ccc} G_{22} & \cdot & G_{2,c-1} \\ \cdot & \cdot & \cdot \\ G_{c-1,2} & \cdot & G_{c-1,c-1} \end{array} \right| / \left| \begin{array}{cc} G_{22} & G_{2,c-2} \\ G_{c-2,2} & G_{c-2,c-2} \end{array} \right|. \quad (6.34)$$

Again, the second determinant can be related to the derivative for the preceding component, etc. Finally we obtain by eliminating all lower-order determinants

$$\left(\frac{\partial\mu_c}{\partial N_c}\right) \left(\frac{\partial\mu_{c-1}}{\partial N_{c-1}}\right) \cdots \left(\frac{\partial\mu_2}{\partial N_2}\right) = \left| \begin{array}{cccc} G_{22} & \cdot & \cdot & G_{2c} \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ G_{c2} & \cdot & \cdot & G_{cc} \end{array} \right|. \quad (6.35)$$

For convenience, we have here omitted the indices for the derivatives. In a stable region all these derivatives are positive. No derivative can decrease its value to zero before the first one. The criterion of limit of stability can thus be given simply as

$$\left| \begin{array}{cccc} G_{22} & \cdot & \cdot & G_{2c} \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ G_{c2} & \cdot & \cdot & G_{cc} \end{array} \right| = 0. \quad (6.36)$$

However, this is still not the most practical way of writing the criterion because the Gibbs energy is usually given as a function of the composition, x_2, x_3, \dots and the size of the system is expressed by the total number of atoms, N , rather than N_1 . Thus,

$$G = N \cdot G_m(x_2, x_3, \dots). \quad (6.37)$$

It should thus be most practical to express the criterion for the limit of stability in terms of the derivatives of G_m . We should introduce dx_i and dN in the expression for dG . Using $x_1 = 1 - x_2 - x_3 - \dots$ because we have chosen x_1 as the dependent composition variable, we find

$$N_i = Nx_i \quad (6.38)$$

$$dN_i = Ndx_i + x_i dN. \quad (6.39)$$

$$\sum_i \mu_i dN_i = N \sum_{i=1} \mu_i dx_i + dN \sum_{i=1} \mu_i x_i = N \sum_{i=2} (\mu_i - \mu_1) dx_i + G_m dN \quad (6.40)$$

$$dG = -SdT + VdP + N \sum_{i=2} (\mu_i - \mu_1) dx_i + G_m dN - \sum D^i d\xi^i. \quad (6.41)$$

We may proceed as before because we can keep x_j of a whole system constant and transfer dx_j between two halves and the same amount of component 1 in the other direction. The limit of stability will now be given by

$$\left(\frac{\partial(\mu_c - \mu_1)}{\partial x_c} \right)_{\mu_2 - \mu_1, \dots, \mu_{c-1} - \mu_1, N} = 0. \quad (6.42)$$

Again we shall change the variables to be kept constant by using Jacobians. The final expression will then contain derivatives of the type $(\partial(\mu_k - \mu_1)/\partial x_l)_{x_j, N}$ and they can be expressed as $(\partial^2 G_m / \partial x_k \partial x_l)_{x_j}$, which we shall abbreviate as g_{kl} . We shall also use the notation

$$\mu_k - \mu_1 = \left(\frac{\partial G_m}{\partial x_k} \right)_{x_j} \equiv g_k, \quad (6.43)$$

where x_1 is a dependent variable. This was shown in Section 4.1 in which it was mentioned that $\mu_j - \mu_k$ is regarded as the diffusion potential between j and k . The difference from Eq. (4.8) is caused by the molar Gibbs energy G_m here being treated as a function of T , P and all x_i except for x_1 , which is chosen as a dependent variable. In that case $dx_1 = -\sum dx_k$. By introducing the notation g_k for first-order derivatives of G_m and g_{kl} for second-order derivatives, we obtain the following convenient form of the limit of stability

$$\begin{vmatrix} g_{22} & \cdot & \cdot & g_{2c} \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ g_{c2} & \cdot & \cdot & g_{cc} \end{vmatrix} = 0. \quad (6.44)$$

It should be noted that Eq. (6.42) could have been written as

$$\left(\frac{\partial g_c}{\partial x_c} \right)_{g_2, \dots, g_{c-1}, N} = 0. \quad (6.45)$$

It should again be emphasized that g_k and g_{kl} are defined with x_1 as dependent variable.

For a binary system, the condition for the limit of stability reduces to $g_{22} = 0$. Although the limit of stability of a solution is exactly defined by the condition just given, there have been attempts to modify this expression in order to get a function which is more suitable for representing the properties of a solution in its stable range as well. In particular, the determinant in Eq. (6.44) goes to infinity at the sides of an alloy system, an effect which can be removed by multiplication with $x_1 x_2 \dots x_c$. One may further make the expression dimensionless by dividing by RT to the proper power. For a binary system one has thus defined the **stability function** $x_1 x_2 g_{22} / RT$, which is unity over the whole range of composition for an ideal solution and goes to zero at the limit of stability.

Exercise 6.5

Show that the stability function, just defined, is unity over the whole system for an ideal A–B–C solution.

Hint

An ideal solution has $G_m = \sum x_i ({}^\circ G_i + RT \ln x_i)$. Take the derivatives of G_m remembering that $x_1 = 1 - x_2 - x_3$.

Solution

$g_2 = dG_m/dx_2 = {}^\circ G_2 - {}^\circ G_1 + RT(\ln x_2 - \ln x_1)$; $g_{22} = RT(1/x_2 + 1/x_1)$; $g_{23} = RT(1/x_1) = g_{32}$; $g_{33} = RT(1/x_3 + 1/x_1)$. We thus get

$$x_1 x_2 x_3 \begin{vmatrix} g_{22} & g_{32} \\ g_{23} & g_{33} \end{vmatrix} / RT = x_1 x_2 x_3 \left(\frac{1}{x_2 x_3} + \frac{1}{x_2 x_1} + \frac{1}{x_1 x_3} + \frac{1}{x_1 x_1} - \left(\frac{1}{x_1} \right)^2 \right) = x_1 + x_2 + x_3 = 1.$$

Exercise 6.6

Use a Jacobian transformation to show that the limit of stability in a ternary system is

$$\begin{vmatrix} g_{22} & g_{23} \\ g_{32} & g_{33} \end{vmatrix} = 0.$$

Hint

By omitting the variables that are kept constant, the stability condition in Eq. (6.42) can be written as $\left(\frac{\partial(\mu_3 - \mu_1)}{\partial x_3} \right)_{\mu_2 - \mu_1} = 0$.

Solution

$$\begin{aligned} \left(\frac{\partial(\mu_3 - \mu_1)}{\partial x_3} \right)_{\mu_2 - \mu_1} &= \begin{vmatrix} \frac{\partial(\mu_3 - \mu_1)}{\partial x_3} & \frac{\partial(\mu_3 - \mu_1)}{\partial x_2} \\ \frac{\partial(\mu_2 - \mu_1)}{\partial x_3} & \frac{\partial(\mu_2 - \mu_1)}{\partial x_2} \end{vmatrix} / \begin{vmatrix} \frac{\partial x_3}{\partial x_3} & \frac{\partial x_3}{\partial x_2} \\ \frac{\partial(\mu_2 - \mu_1)}{\partial x_3} & \frac{\partial(\mu_2 - \mu_1)}{\partial x_2} \end{vmatrix} \\ &= \begin{vmatrix} \frac{\partial^2 G_m}{\partial x_3 \partial x_3} & \frac{\partial^2 G_m}{\partial x_3 \partial x_2} \\ \frac{\partial^2 G_m}{\partial x_2 \partial x_3} & \frac{\partial^2 G_m}{\partial x_2 \partial x_2} \end{vmatrix} / \frac{\partial^2 G_m}{\partial x_3 \partial x_2} = \begin{vmatrix} g_{22} & g_{23} \\ g_{32} & g_{33} \end{vmatrix} / g_{22} = 0. \end{aligned}$$

However, $g_{22} > 0$ in the stable region and it does not reach $g_{22} = 0$ before our condition is satisfied. Our condition can thus be written as $\begin{vmatrix} g_{22} & g_{23} \\ g_{32} & g_{33} \end{vmatrix} = 0$.

6.7 Chemical capacitance

The diagonal elements in the G_{cc} determinant can be written as $(\partial \mu_j / \partial N_j)_{T,P,N_k}$ and they must all be positive because they are stability conditions according to Section 6.2. In addition, the inverse quantities are sometimes regarded as the chemical capacitance

of the component j [9],

$$\Omega_{jj} = \left(\frac{\partial N_j}{\partial \mu_j} \right)_{T,P,N_k} = 1/G_{jj}. \quad (6.46)$$

This quantity may be of practical importance because it is often of considerable interest to be able to increase the amount of a component j in a system without increasing the chemical potential of the same component too much. A system with a high capacity is said to be well buffered.

An off-diagonal term in the G_{cc} determinant cannot by itself form a stability condition because it concerns variables that do not make a conjugate pair. It may thus be positive or negative in the stable region. Nevertheless, its inverse quantity may also be used as a kind of chemical capacitance. The following relation holds between them,

$$1/\Omega_{jk} = \frac{\partial \mu_j}{\partial N_k} = \frac{\partial^2 G}{\partial N_j \partial N_k} = \frac{\partial \mu_k}{\partial N_j} = 1/\Omega_{kj} \quad (6.47)$$

Exercise 6.7

What gas mixture is best buffered for oxygen: (a) 1 mol of Ar and 10^{-6} mol of O_2 at 1 bar and 1550 K; or (b) 0.99 mol of CO_2 and 0.01 mol of CO at 1 bar and 1550 K?

Hint

The conditions were chosen in such a way that the equilibrium partial pressure of oxygen is very close to 10^{-6} in case (b) as well as in case (a). Accept this information.

Solution

- (a) $P_{O_2} \cong 1 \cdot N_{O_2}/N_{Ar} \cong N_{O_2}$; $\mu_{O_2} = {}^o\mu_{O_2} + RT \ln P_{O_2} = {}^o\mu_{O_2} + RT \ln N_{O_2}$;
 $1/\Omega_{O_2O_2} = \partial \mu_{O_2}/\partial N_{O_2} = RT/N_{O_2} = RT/10^{-6}$.
- (b) If we add N_{O_2} , most of it will react by $O_2 + 2CO \rightarrow 2CO_2$ yielding $N_{CO} = 0.01 - 2N_{O_2}$ and $N_{CO_2} = 0.99 + 2N_{O_2}$. We get, using the equilibrium constant K : $P_{O_2} = K(P_{CO_2}/P_{CO})^2 \cong K[(0.99 + 2N_{O_2})/(0.01 - 2N_{O_2})]^2$; $1/\Omega_{O_2O_2} = \partial \mu_{O_2}/\partial N_{O_2} = 2RT[2/(0.99 + 2N_{O_2}) - (-2)/(0.01 - 2N_{O_2})] \cong 4RT/0.01$. Thus, $(\Omega_{O_2O_2})^b \gg (\Omega_{O_2O_2})^a$.

6.8 Limit of stability against fluctuations of internal variables

As mentioned in Section 6.3 there are $c + 1$ degrees of freedom with respect to fluctuations resulting in differences between various regions of the system and $c - 1$ of them are connected to fluctuations in composition. All these degrees of freedom are related to the extensive variables that were originally defined from interactions with the surroundings. Thus, they can also be used to represent exchanges between various regions of the system, regarded as subsystems. There is another kind of variable that can only describe changes within a homogeneous system and without involving any interaction with the surroundings. They give rise to internal degrees of freedom in addition to those already

discussed. The problem of stability also applies to such variables. As an example we shall now consider a crystalline system with more than one sublattice. In order to describe the constitution in such cases, the concept site fraction was introduced through Eq. (4.50).

$$y_j^s = N_j^s / \sum N_i^s. \quad (6.48)$$

The sum of site fractions in a sublattice is equal to 1. The superscript s identifies a particular sublattice. If N is now the number of moles of formula units, we have

$$G = N \cdot G_m(y_j^s), \quad (6.49)$$

where G_m is the Gibbs energy for one mole of formula units. We now want to express dG in terms of all the dy_j^s and dN . We obtain

$$dG = -SdT + VdP + \sum_s \sum_j \phi_j^s dy_j^s + G_m dN - \sum D^i d\xi^i. \quad (6.50)$$

The summation for each sublattice starts from the second constituent present in that sublattice, the first constituent being chosen as the dependent one. ϕ_j^s is the conjugate variable to y_j^s just as $g_k = \mu_k - \mu_1$ from Eq. (6.43) is the conjugate variable to x_k .

$$\phi_j^s = \left(\frac{\partial G}{\partial y_j^s} \right)_{T,P,y_i^s,y_k^s,N} = N \left(\frac{\partial G_m}{\partial y_j^s} \right)_{T,P,y_i^s,y_k^s}, \quad (6.51)$$

where y_k^s denotes the site fractions of all the other independent constituents on the same sublattice and y_i^s denotes the site fractions of all the independent constituents on other sublattices. By proceeding as before we obtain for the limit of stability

$$\left(\frac{\partial \phi_c^r}{\partial y_c^r} \right)_{T,P,\phi_2^r,\dots,\phi_c^r,\phi_2^s,\dots,\phi_{c-1}^s,N} = 0, \quad (6.52)$$

and, after changing the variables to be kept constant using Jacobians,

$$\begin{vmatrix} g_{11} & \cdot & g_{1k} \\ \cdot & \cdot & \cdot \\ g_{k1} & \cdot & g_{kk} \end{vmatrix} = 0. \quad (6.53)$$

As before, g_{ij} denotes the partial derivatives of G_m but, for convenience, we have now numbered all the independent constituents in all the sublattices from 1 to k . It should be noted that k could be equal to, smaller than or larger than c , the number of components in the system. It should be emphasized that any internal variable, ξ^i , can be included in the k variables if it is an extensive quantity divided by the size of the system. In a ferromagnetic alloy it could be the number of atoms per mole with magnetic spins in a certain direction. A particularly simple case is obtained in a pure element if there is only one interval variable. The stability condition is then

$$B = \frac{\partial^2 G_m}{(\partial \xi^i)^2} > 0. \quad (6.54)$$

Finally, it should be remembered that a criterion of stability can only be applied to a state of equilibrium and all the elements of the determinant, being partial derivatives of G_m , must be evaluated for that state before the value of the determinant can be calculated. It is thus necessary first to calculate the equilibrium values of all the internal variables.

Exercise 6.8

At low T , β -brass has two sublattices and could be represented by the formula $(\text{Cu}, \text{Zn})_1(\text{Zn}, \text{Cu})_1$. The major constituent in each sublattice is given first. All the sites are equivalent and the system will disorder above a certain temperature. Calculate the critical temperature if $G_m = x_A {}^\circ G_A + x_B {}^\circ G_B + 0.5RT(y'_A \ln y'_A + y'_B \ln y'_B + y''_A \ln y''_A + y''_B \ln y''_B) + K(y'_A y''_B + y'_B y''_A)$. K is a negative constant and ' and '' identify the sublattices.

Hint

There are two independent variables in addition to T and P , namely the alloy composition and the degree of order. To simplify the calculations it may be convenient instead to treat y'_A and y''_A as the independent variables. Then $y'_B = 1 - y'_A$; $y''_B = 1 - y''_A$; $x_A = (y'_A + y''_A)/2$; $x_B = (y'_B + y''_B)/2$. Treat T and P as constant. For the disordered state $y'_A = y''_A = x_A$.

Solution

Let y'_A be variable 1 and y''_A be variable 2. We find $g_1 = {}^\circ G_A/2 - {}^\circ G_B/2 + 0.5RT(\ln y'_A - \ln y'_B) + K(y''_B - y''_A)$; $g_2 = {}^\circ G_A/2 - {}^\circ G_B/2 + 0.5RT(\ln y''_A - \ln y''_B) + K(-y'_A + y'_B)$; $g_{12} = K(-1 - 1) = g_{21}$; $g_{11} = 0.5RT(1/y'_A + 1/y'_B) = 0.5RT/y'_A y'_B$; $g_{22} = 0.5RT(1/y''_A + 1/y''_B) = 0.5RT/y''_A y''_B$. The criterion for the limit of stability gives $g_{11}g_{22} - g_{12}g_{21} = 0$; $(0.5RT)^2/y'_A y'_B y''_A y''_B = (-2K)^2$. The critical temperature for ordering in a disordered alloy of composition x_A, x_B is thus $T = 4(-K)x_A x_B/R$.

6.9 Le Chatelier's principle

When discussing the limit of stability we compared the values of two derivatives, which differed only by one of the variables to be kept constant. Using the same method of calculation we can also compare the effect of changing an external variable under a frozen-in internal variable ξ and under a gradual adjustment of ξ according to equilibrium, i.e. $D = 0$. It should be remembered that ξ may be treated as an extensive variable and $-D$ could be regarded as its conjugate potential. We obtain

$$\left(\frac{\partial Y^b}{\partial X^b}\right)_{D=0} = \left(\frac{\partial Y^b}{\partial X^b}\right)_{\xi} - \left(\frac{\partial Y^b}{\partial \xi}\right)_{X^b} \left(\frac{\partial(-D)}{\partial X^b}\right)_{\xi} / \left(\frac{\partial(-D)}{\partial \xi}\right)_{X^b}. \quad (6.55)$$

For simplicity, the variables that have been kept constant in all the derivatives have been omitted from the subscripts but any set of potentials and extensive variables presented in Table 3.1 can be used. $(\partial Y^b/\partial \xi)_{X^b}$ and $(\partial(-D)/\partial X^b)_{\xi}$ are equal due to a Maxwell relation and $(\partial(-D)/\partial \xi)_{X^b}$ is equal to the stability B at equilibrium. For a stable system, B is positive and the second term on the right-hand side with its minus sign cannot be

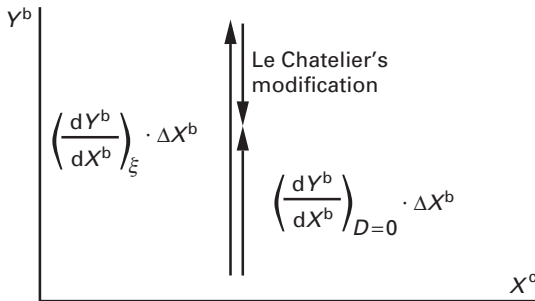


Figure 6.4 Illustration of Le Chatelier's principle. The extensive variable X^b is changed by an amount ΔX^b by an external action. An internal process is first frozen in, $d\xi = 0$, but then proceeds to a new equilibrium, $D = 0$. The initial effect on Y^b is thus partly reversed. During the whole process either the potential or the extensive variable of the other pairs of conjugate variables is kept constant (here represented by X^c on the abscissa).

positive. We thus obtain from Eq. (6.48)

$$0 \leq \left(\frac{\partial Y^b}{\partial X^b} \right)_{D=0} \leq \left(\frac{\partial Y^b}{\partial X^b} \right)_{\xi}. \quad (6.56)$$

This relation is quite general. It has here been derived using the energy scheme. It can also be derived using the other schemes.

Suppose the equilibrium inside a system is disturbed by an action from the outside. For instance, X^b is changed quickly by an amount ΔX^b and there is not enough time for an internal reaction, i.e. ξ is kept constant. Thus, the potential Y^b is changed according to the term appearing on the right-hand side of the inequality and first on the right-hand side of Eq. (6.55) (see the left-hand arrow in Fig. 6.4). After a sufficiently long time the internal reaction will occur and ξ will change to a new state of equilibrium, $D = 0$, and the net change of the two stages may thus be calculated from the term appearing in the middle part of the inequality and on the left-hand side of Eq. (6.55) (see the right-hand arrow pointing upward in the figure). It represents the change of Y^b due to a slow change ΔX^b . The difference between the two changes of Y^b represents the change due to the internal reaction, the so-called Le Chatelier modification. The inequality shows that the change in Y^b will thus be partly reversed during the second stage (see the arrow pointing downward in the figure). This principle was formulated by Le Chatelier [10] but in a less exact manner. It should be emphasized that it concerns two conjugate variables, X^b and Y^b . It should further be emphasized that the extensive variable must be regarded as the primary variable. If, instead, the potential variable is regarded as the primary one, then the opposite result is obtained

$$\left(\frac{\partial X^b}{\partial Y^b} \right)_{D=0} \geq \left(\frac{\partial X^b}{\partial Y^b} \right)_{\xi} \geq 0. \quad (6.57)$$

The derivation of Le Chatelier's principle is based on derivatives and it has thus been proved only for infinitesimal disturbances. There is no guarantee that it always applies to large disturbances.

Exercise 6.9

Test Le Chatelier's principle on the change of temperature and pressure when an amount of heat is added to a two-phase system of water vapour and liquid water under constant volume. Suppose that evaporation is initially very slow due to a thin film of oil.

Hint

Remember that $dU = dQ - PdV$. At constant V we thus have $dU = dQ$ and could choose U as the variable that is changed by an action from the outside. Its conjugate variable is $-1/T$. The internal variable ξ may be identified with the amount of vapour.

Solution

Identify U with X^b and $-1/T$ with Y^b . For a stable system we get, at constant ξ , i.e. before any change of the amount of vapour, $0 < (\partial(-1/T)/\partial U)_\xi$. This means that $-1/T$, and thus also T , has increased due to the increase of U .

At the higher temperature the equilibrium vapour pressure will be higher. In a second stage of the process there will thus be evaporation and the temperature will decrease in agreement with Le Chatelier's principle, $0 < (\partial(-1/T)/\partial U)_{D=0} < (\partial(-1/T)/\partial U)_\xi$.

On the other hand, the pressure has increased during the first stage due to the heating of the vapour present from the beginning. During the second stage, the pressure will increase further, in apparent contradiction to Le Chatelier's principle. However, pressure is not conjugate to U , which was the variable that was changed to a new value in the experiment.

The result is far from trivial because there would be further evaporation during the second stage only if the increase in pressure of the initial vapour due to its heating is smaller than the increase of the equilibrium vapour pressure due to the heating of the water. By relying upon Le Chatelier's principle we may thus conclude that the heating of the vapour gives a smaller increase of the pressure than the heating of the water would increase the equilibrium vapour pressure.

7 Applications of molar Gibbs energy diagrams

7.1 Molar Gibbs energy diagrams for binary systems

In this chapter we shall derive some useful thermodynamic relations relating to phase equilibria under constant temperature and pressure, sometimes in exact form but sometimes using approximations in order to bring the final expressions into a suitable form. We shall see how property diagrams for the molar Gibbs energy can be used in such derivations. Most of the applications will make use of the tie-line rule (see Section 4.5).

As an introduction, some basic properties of solutions must be discussed and, in the present section, a simple solution model will be described. A more thorough discussion will be given in Chapter 20.

Let us first consider a case where a solution phase α can vary in composition over a whole binary system from pure A to pure B. It is then convenient to compare the G_m value at any composition with the value one can read on the straight line between the two end-points, sometimes called the **end-members** of the solution. The difference is often called the **Gibbs energy of mixing** and is denoted with a superscript M. It is illustrated in Fig. 7.1. It is defined by the following equation

$$G_m^\alpha = x_A {}^\circ G_A^\alpha + x_B {}^\circ G_B^\alpha + {}^M G_m^\alpha. \quad (7.1)$$

A warning should be issued regarding the interpretation of ${}^M G_m$. Usually it is defined with reference to the straight line between points representing the pure components in the same state as the phase under consideration, i.e. the end-members of the solution. However, sometimes it is defined with reference to a different state for one of the components, for instance the state which is most stable at the temperature under consideration. This is illustrated in Fig. 7.1(b) where pure B is more stable as β than as α .

The Gibbs energy diagram gives information on the partial molar Gibbs energies for the two components, i.e. the chemical potentials. For a single phase one can use the construction explained for V_m in Fig. 4.6 and illustrated for G_m in Fig. 4.7. It is now demonstrated again in Fig. 7.2(a) and is in agreement with the following relations, which are examples of the more general expression for all partial quantities, derived in Section 4.1.

$$G_B^\alpha = G_m^\alpha + (1 - x_B) dG_m^\alpha / dx_B = G_m^\alpha + x_A dG_m^\alpha / dx_B \quad (7.2)$$

$$G_B^\alpha - G_A^\alpha = dG_m^\alpha / dx_B. \quad (7.3)$$

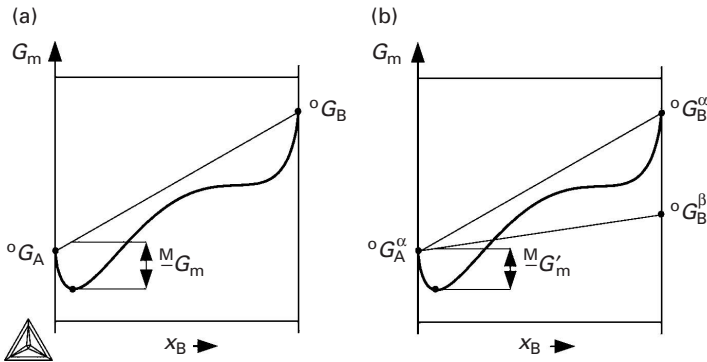


Figure 7.1 Molar Gibbs energy diagram for a binary system illustrating the definition of the Gibbs energy of mixing. The end-members of the solution are used as references in (a) but a more stable state of B is used in (b).

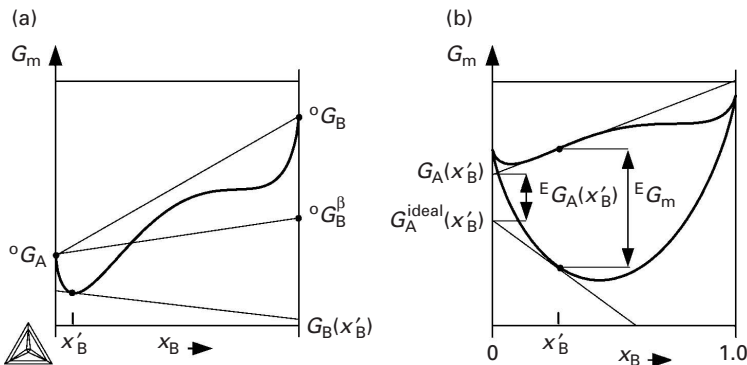


Figure 7.2 (a) Tangent construction to obtain a chemical potential. (b) Definitions of excess quantities for an alloy of composition x'_B .

An important contribution to the Gibbs energy of mixing comes from the entropy of mixing of the two kinds of atoms. In Section 19.8 we shall consider the case where they are distributed at random and shall find that the entropy of mixing of one mole of atoms will then be $-R(x_A \ln x_A + x_B \ln x_B)$. A solution with only this contribution to the Gibbs energy of mixing is regarded as an ideal solution

$$G_m^{\text{ideal}\alpha} = x_A {}^0G_A^\alpha + x_B {}^0G_B^\alpha + RT(x_A \ln x_A + x_B \ln x_B). \quad (7.4)$$

Using Eq. (4.5) relating partial quantities to molar quantities we obtain

$$G_B^{\text{ideal}\alpha} = {}^0G_B^\alpha + RT \ln x_B. \quad (7.5)$$

A comparison with the ideal solution is given in Fig. 7.2(b). The curve for G_m^{ideal} shows that the term $RT(x_A \ln x_A + x_B \ln x_B)$ is negative and makes the G_m curve look like a hanging rope. It is the main cause of the stability of solutions.

It is common to summarize all other contributions to the Gibbs energy with a term called the **excess Gibbs energy** and denoted by ${}^E G_m^\alpha$.

$$G_m^\alpha = G_m^{\text{ideal}} + {}^E G_m^\alpha = x_A {}^\circ G_A^\alpha + x_B {}^\circ G_B^\alpha + RT(x_A \ln x_A + x_B \ln x_B) + {}^E G_m^\alpha. \quad (7.6)$$

This is also illustrated in Fig. 7.2(b). In the same way we may define the mixing and excess quantities for the partial Gibbs energies,

$$G_B^\alpha = G_B^{\text{ideal}} + {}^E G_B^\alpha = {}^\circ G_B^\alpha + RT \ln x_B + {}^E G_B^\alpha. \quad (7.7)$$

$${}^M G_B^\alpha = RT \ln x_B + {}^E G_B^\alpha. \quad (7.8)$$

It is evident that the mixing and excess quantities can be calculated directly in the same way as G_B^α .

$${}^M G_B^\alpha = {}^M G_m^\alpha + (1 - x_B) d{}^M G_m^\alpha / dx_B = {}^M G_m^\alpha - x_A d{}^M G_m^\alpha / dx_A \quad (7.9)$$

$${}^E G_B^\alpha = {}^E G_m^\alpha + (1 - x_B) d{}^E G_m^\alpha / dx_B = {}^E G_m^\alpha - x_A d{}^E G_m^\alpha / dx_A. \quad (7.10)$$

It should be emphasized that one cannot give an absolute numerical value to the partial Gibbs energies, ${}^\circ G_B^\alpha$ or ${}^\circ G_A^\alpha$, because there is no natural zero point for Gibbs energy. Numerical values can be given only to differences in Gibbs energy between two states. Thus we can give a value to $G_B^\alpha - {}^\circ G_B^\alpha$, and another value to $G_B^\alpha - {}^\circ G_B^\beta$, where pure α -B and pure β -B are regarded as two different choices of **reference states** for B. Such a value gives the vertical distance between two points (see the B-axis in Fig. 7.2(a)). For alloys, a numerical value can be given only to differences between two states of the *same composition*. The two lines representing ${}^M G_m$ and ${}^M G'_m$ in Fig. 7.1(a) and (b), respectively, are thus vertical. This stems from the fact that one cannot compare the Gibbs energies for A and B. When starting to construct such a diagram one can give the ${}^\circ G_A^\alpha - {}^\circ G_B^\beta$ line any convenient slope.

If one has chosen the end-members of an A–B solution to define the reference states, ${}^\circ G_A$ and ${}^\circ G_B$, then it is evident that the excess Gibbs energy is zero at the two sides of the system where G_m is equal to ${}^\circ G_A$ or ${}^\circ G_B$. For a dilute solution of B in A we may thus try to approximate ${}^E G_m$ as $Lx_A x_B$, an expression that goes to zero on both sides. This is the regular solution approximation, and using the equation relating G_B to G_m we find

$$G_B^\alpha = {}^\circ G_B^\alpha + RT \ln x_B + {}^E G_B^\alpha = {}^\circ G_B^\alpha + RT \ln x_B + L^\alpha x_A^2. \quad (7.11)$$

It is common to introduce the **chemical activity**, a_B , through the expression

$$G_B^\alpha = {}^\circ G_B^\alpha + RT \ln a_B = {}^\circ G_B^\alpha + RT \ln x_B + RT \ln f_B, \quad (7.12)$$

where

$$a_B = f_B x_B, \quad (7.13)$$

and f_B is called the **activity coefficient** of B. The activity is thus defined as

$$a_B = \exp[(G_B^\alpha - {}^\circ G_B^\alpha) / RT]. \quad (7.14)$$

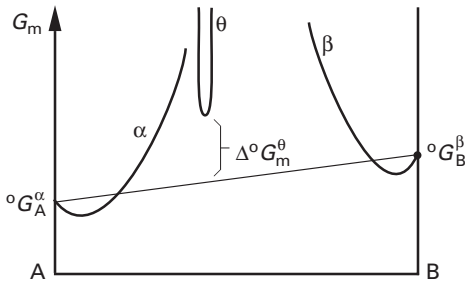


Figure 7.3 Molar Gibbs energy diagram illustrating the definition of the standard Gibbs energy of formation, $\Delta^\circ G_m^\theta$, of a compound θ .

The activity coefficient is obtained through

$$RT \ln f_B = {}^E G_B^\alpha. \quad (7.15)$$

For a dilute solution, i.e. low x_B , we may thus write

$$RT \ln f_B = {}^E G_B^\alpha = L^\alpha x_A^2 \cong L^\alpha \quad \text{or} \quad f_B \cong \exp(L^\alpha/RT). \quad (7.16)$$

With this approximation, the activity is proportional to the content. This is called Henry's law. We also find for low x_B ,

$$RT \ln f_A = {}^E G_A^\alpha + (1 - x_A)d^E G_m^\alpha / dx_A = L^\alpha x_B^2 \cong 0. \quad (7.17)$$

The value of f_A is thus unity close to the A side. This is called Raoult's law. When Henry's law holds for B and Raoult's law holds for A, then we obtain

$$dG_m^\alpha / dx_B = G_B^\alpha - G_A^\alpha = {}^\circ G_B^\alpha + RT \ln x_B + L^\alpha - {}^\circ G_A^\alpha - RT \ln x_A \quad (7.18)$$

$$d^2 G_m^\alpha / dx_B^2 = RT/x_B + RT/x_A = RT(x_A + x_B)/x_A x_B = RT/x_A x_B \cong RT/x_B. \quad (7.19)$$

For an intermediary phase, which does not extend to the pure components, one must always refer the Gibbs energy to the values of the components in selected states, usually their stable states. For a phase with a well-defined composition one often talks about the **standard Gibbs energy of formation** (see Fig. 7.3). From that diagram we obtain

$$\Delta^\circ G_m^\theta = {}^\circ G_m^\theta - x_A {}^\circ G_A^\alpha - x_B {}^\circ G_B^\beta. \quad (7.20)$$

This quantity is often denoted by $\Delta_f G_m^\theta$ or $\Delta_f^\circ G_m^\theta$. It is important to mention the reference states to which it refers and also the amount of material being considered, for instance 1 mole of atoms or 1 mole of formula units (like, e.g., Cr_{23}C_6).

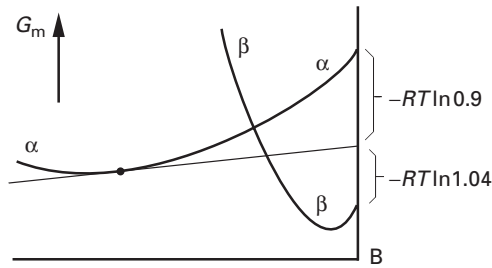


Figure 7.4 Solution to Exercise 7.1.

Exercise 7.1

An α solution in the A–B system has $a_B = 0.9$ at 1000 K when pure α -B is used as reference state. Calculate a_B referred to another state of B, called β -B, which is more stable than α -B by 1200 J/mol. Illustrate with a G_m diagram.

Hint

The position of the point on the B-axis representing G_B^α does not depend upon the choice of reference state. We can thus equate any two expressions for G_B^α .

Solution

$a_B^{\text{ref}\alpha} = 0.9$; ${}^\circ G_B^\alpha + RT \ln(a_B^{\text{ref}\alpha}) = G_B^\alpha = {}^\circ G_B^\alpha + RT \ln(a_B^{\text{ref}\beta})$;
 $a_B^{\text{ref}\beta} = a_B^{\text{ref}\alpha} \exp[({}^\circ G_B^\alpha - {}^\circ G_B^\beta)/RT] = 0.9 \times \exp(1200/8.3145 \times 1000) = 1.04$. Since this is > 1 , the α solution is supersaturated with B in comparison with the stable β state of B (see Fig. 7.4).

Exercise 7.2

Fe_3C is metastable at all temperatures and could thus decompose into an Fe-rich phase and graphite. At 1169 K the stable Fe phase (γ) dissolves about 1.24 mass% C. Measurements have shown that the Gibbs energy of formation of Fe_3C at 1169 K is negative (-1620 J/mole of formula units). Explain how this can be reconciled with the fact that Fe_3C is not stable by sketching a G_m, x_C diagram.

Solution

Fe_3C falls 1620 J/mol below the line of reference between pure Fe and pure graphite (dashed line in Fig. 7.5) but it falls above the common tangent representing the $\gamma +$ graphite equilibrium. Thus, Fe_3C is more stable than a mixture of the pure elements but less stable than a mixture of an Fe–C solution and pure C.

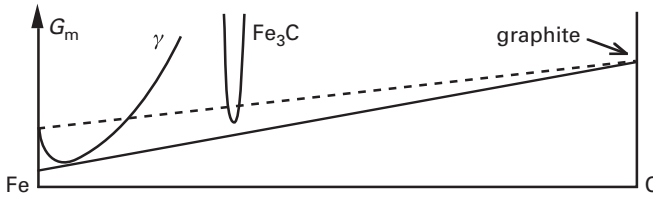


Figure 7.5 Solution to Exercise 7.2.

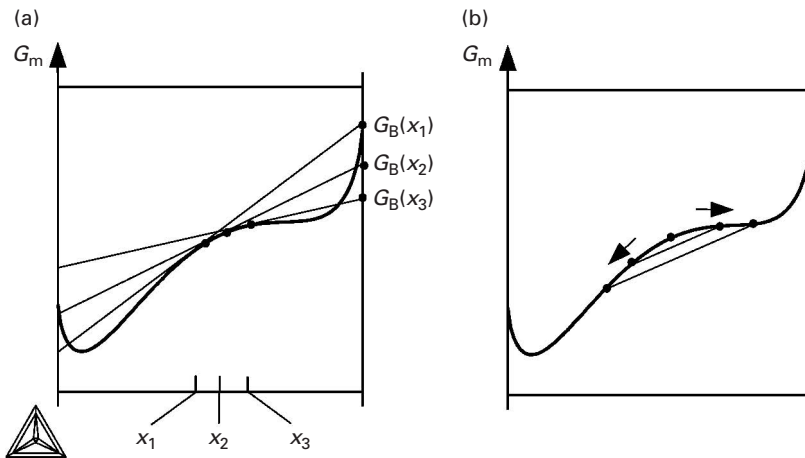


Figure 7.6 (a) Construction showing that a negative curvature results in a decrease of G_B when x_B is increased. (b) Demonstration that a system between the points of inflexion is unstable. A small difference in composition will increase spontaneously.

7.2 Instability of binary solutions

In Figs 7.1 and 7.2 we have sketched molar Gibbs energy curves, each with two minima and a central region where $\partial^2 G_m / \partial x_B^2$ is negative. This region falls between two points of inflexion and according to Section 6.6 they should define the limit of stability. In Fig. 7.6(a) tangents have been drawn at some compositions between the points of inflexion and it can be seen that G_B decreases when x_B increases. According to Eq. (6.27) this is also a violation of the condition of stability.

The change in the total Gibbs energy of the system, when one half of the system grows richer in A and the other one in B, is illustrated in Fig. 7.6(b). The tie-line rule requires that the total Gibbs energy of a mixture is represented by a point on the line connecting the points representing the two parts. Since the overall composition is not changed, the total Gibbs energy moves down along a vertical line at the alloy composition (not shown here). Such a system is thus unstable against fluctuations in composition.

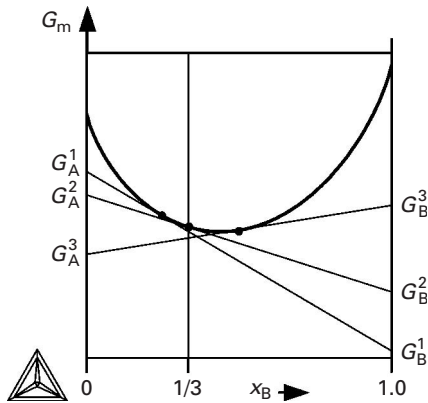


Figure 7.7 Solution to Exercise 7.3.

Exercise 7.3

In a binary solution one usually discusses two activities, a_A and a_B , and for a stable system each of them increases monotonously with the content of the same component. However, one may define the activity of an intermediary species, e.g. A_2B . Prove that a_{A_2B} also increases as the content of A_2B increases in a stable system and thus has a maximum at the very composition of A_2B .

Hint

Instead of the chemical activity, a_{A_2B} , let us consider the chemical potential μ_{A_2B} , which is equal to $2\mu_A + \mu_B$, i.e. $2G_A + G_B$, or, even better, $\mu_{A_2/3B_{1/3}}$, i.e. $(2G_A + G_B)/3$. It may be studied in a G_m, x_B diagram.

Solution

For any alloy the tangent in the G_m, x_B diagram gives G_A and G_B on the two sides and the intersection of the tangent with a vertical line at $x_B = 1/3$ thus gives $(2G_A + G_B)/3$. By inspection it is evident that the intersection has its highest position for the alloy $x_B = 1/3$ (see Fig. 7.7). Otherwise, the G_m curve must have a negative curvature somewhere.

7.3 Illustration of the Gibbs–Duhem relation

The molar Gibbs energy diagram in Fig. 7.8(a) shows a stoichiometric compound, θ , with a well-defined composition A_aB_b , possibly because it is a crystalline phase with two sublattices. Often, the composition of such a phase cannot vary appreciably without a very steep increase of the Gibbs energy. It is thus practically impossible to vary N_A and keep N_B constant and the definition of partial Gibbs energy, given in Section 4.1,

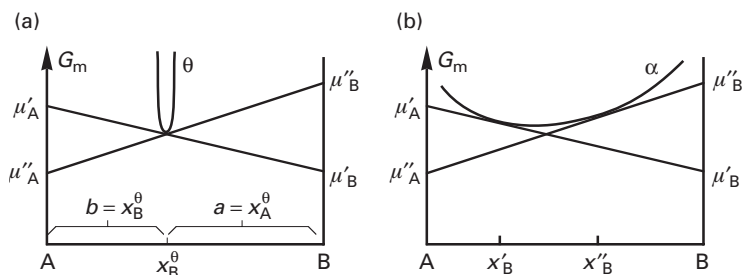


Figure 7.8 Molar Gibbs energy diagram for (a) a binary stoichiometric phase θ and (b) a binary solution phase α . If μ_A is controlled by some method, then the value of μ_B is given in both cases.

cannot be used. However, the tangent construction in Fig. 7.2 can still be used. For this case we shall prefer to talk about chemical potentials and use the notations μ_A and μ_B . The situation is not drastically different for a phase with variable composition (see Fig. 7.8(b)). For both types of phase one may select the value of μ_A and the value of μ_B will then be fixed. One could also talk about the chemical potential of the compound, $\mu_{A_aB_b}$. From Section 4.8 we get

$$G_{A_aB_b} = \mu_{A_aB_b} = \sum a_i^s \mu_i = a\mu_A + b\mu_B; \quad \mu_B = (\mu_{A_aB_b} - a\mu_A)/b. \quad (7.21)$$

By comparing the values defined by two different tangents we find for a stoichiometric compound, because $\mu_{A_aB_b}$ is fixed,

$$x_A(\mu''_A - \mu'_A) + x_B(\mu''_B - \mu'_B) = 0, \quad (7.22)$$

where $a = x_A$ and $b = x_B$ if $a + b$ is chosen as 1. This may be regarded as the Gibbs–Duhem relation integrated for a phase with constant composition.

For a phase with variable composition one may also select the value for μ_A , and the value for μ_B will then be fixed by the expression for the molar Gibbs energy,

$$G_m = x_A\mu_A + x_B\mu_B; \quad \mu_B = (G_m - x_A\mu_A)/x_B, \quad (7.23)$$

but here G_m varies with the composition and the composition varies with the choice of μ_A , as demonstrated for a solution phase α in Fig. 7.8(b). The Gibbs–Duhem relation holds

$$x_A d\mu_A + x_B d\mu_B = 0, \quad (7.24)$$

but not in the integrated form given for the stoichiometric compound, because the tangents do not intersect in a point on the G_m curve.

In a ternary system one may have a solution between two binary stoichiometric phases if they are isomorphous (have the same structure). Figure 7.9 shows a Gibbs energy diagram for such a case. The composition can now be varied with one degree of freedom and we may consider two components or end-members A_aC_c and B_aC_c .

This kind of solution may be represented by the formula $(A, B)_aC_c$ and the composition may be represented by molar contents defined as

$$x_{B_aC_c} = N_{B_aC_c}/(N_{A_aC_c} + N_{B_aC_c}), \quad (7.25)$$

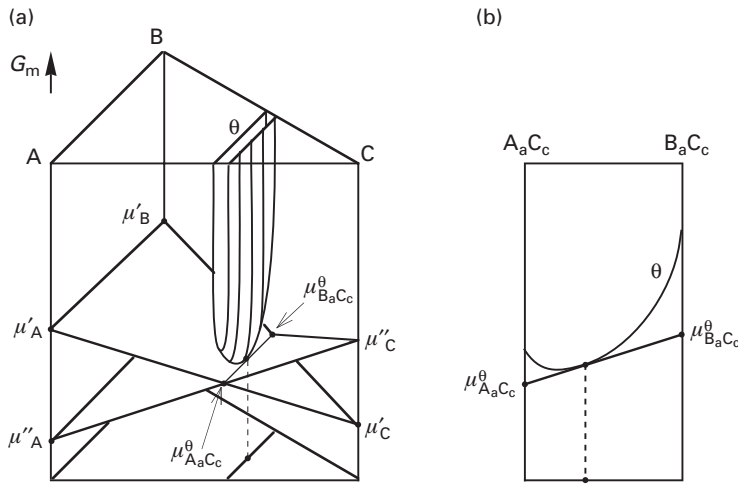


Figure 7.9 Molar Gibbs energy diagram for a ternary solution between two binary stoichiometric phases.

where the two N s represent the moles of formula units. Another method of representation is based on the molar contents evaluated for each sublattice, the so-called site fractions which were discussed in Section 4.7.

From Fig. 7.9 it is evident that the molar Gibbs energy for this kind of solution phase can be expressed in the following ways if $a + c = 1$.

$$G_m = x_A\mu_A + x_B\mu_B + x_C\mu_C = y_A\mu_{A_aC_c} + y_B\mu_{B_aC_c}. \quad (7.26)$$

The diagram in Fig. 7.9(a) with two possible tangent planes shows that the values of $\mu_{A_aC_c}$ and $\mu_{B_aC_c}$ are well defined by the composition but μ_A , μ_B and μ_C are not.

Exercise 7.4

Consider the chemical potential of Fe_3C in a solution phase of Fe, C and Mn, using basic principles. Show that it is actually equal to $3\mu_{\text{Fe}} + \mu_{\text{C}}$ by making a calculation using Section 4.6.

Hint

In the Fe–C–Mn system we usually use Fe, C and Mn as the components but now we should change to a new set of components. Fe_3C is one component and the others could be C and Mn. Notice that $dG = \sum \mu_i dN_i$ cannot change its value just because we change the set of components to be considered.

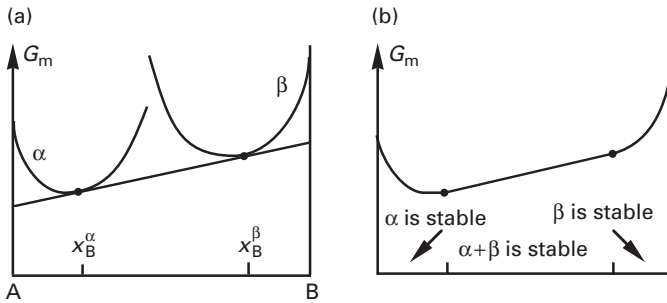


Figure 7.10 The common-tangent construction for finding the compositions of two phases in equilibrium at given T and P .

Solution

Let the amounts of the components be N_{Fe} , N_{C} and N_{Mn} in the old description and $N'_{\text{Fe}_3\text{C}}$, N'_C and N'_{Mn} in the new one. Denote the chemical potentials in the new description with μ'_i . The mass balance for each element gives $N_{\text{Mn}} = N'_{\text{Mn}}$, $N_{\text{Fe}} = 3N'_{\text{Fe}_3\text{C}}$ and $N_{\text{C}} = N'_C + N'_{\text{Fe}_3\text{C}}$.

We thus get $\sum \mu'_i dN'_i = \sum \mu_i dN_i = \mu_{\text{Fe}} dN_{\text{Fe}} + \mu_{\text{Mn}} dN_{\text{Mn}} + \mu_{\text{C}} dN_{\text{C}} = \mu_{\text{Fe}} \cdot 3dN'_{\text{Fe}_3\text{C}} + \mu_{\text{Mn}} dN'_{\text{Mn}} + \mu_{\text{C}} dN'_C + \mu_{\text{C}} dN'_{\text{Fe}_3\text{C}} = (3\mu_{\text{Fe}} + \mu_{\text{C}}) dN'_{\text{Fe}_3\text{C}} + \mu_{\text{C}} dN'_C + \mu_{\text{Mn}} dN'_{\text{Mn}}$.

Thus, $\mu'_C = \mu_C$, $\mu'_{\text{Mn}} = \mu_{\text{Mn}}$ and $\mu'_{\text{Fe}_3\text{C}} = 3\mu_{\text{Fe}} + \mu_{\text{C}}$.

7.4 Two-phase equilibria in binary systems

In a two-phase equilibrium we have the following two conditions at constant T and P because the chemical potential for each component must be the same in the two phases.

$$G_{\text{B}}^{\alpha} = \mu_{\text{B}} = G_{\text{B}}^{\beta} \quad (7.27)$$

$$G_{\text{A}}^{\alpha} = \mu_{\text{A}} = G_{\text{A}}^{\beta}. \quad (7.28)$$

It is evident that these conditions can be satisfied only by a **common tangent**, as illustrated in Fig. 7.10(a). The lowest possible G_{m} for each composition is shown in Fig. 7.10(b) and it is evident that some mixture of $\alpha + \beta$ represents the stable state for an alloy between the two tangent points.

For a stoichiometric phase with its well-defined composition, it is not possible to define the chemical potentials since one can draw different tangents without changing the composition of the point of tangency markedly. On the other hand, the chemical potentials of a phase can be defined by equilibrium with a second phase. Figure 7.11(a) illustrates this case when the second phase is a solution phase or (b) another stoichiometric phase. When it is a solution phase, we obtain

$$G_{\text{m}}^{\beta} = x_{\text{A}}^{\theta} \cdot G_{\text{A}}^{\beta}(x_{\text{B}}^{\beta}) + x_{\text{B}}^{\theta} \cdot G_{\text{B}}^{\beta}(x_{\text{B}}^{\beta}). \quad (7.29)$$

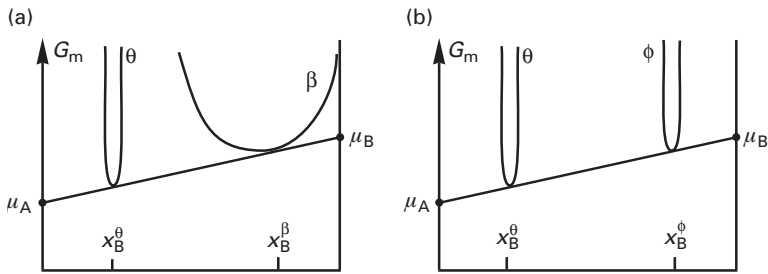


Figure 7.11 Molar Gibbs energy diagram showing the equilibrium between (a) a stoichiometric phase and a solution phase and (b) between two stoichiometric phases.

By solving this equation, one can determine the composition of the solution phase, β , and from the known properties of β one can then calculate μ_A and μ_B . In Fig. 7.11(b) both phases, θ and ϕ , are stoichiometric phases, and we obtain the following relations

$$G_m^\theta = x_A^\theta \mu_A + x_B^\theta \mu_B; \quad \mu_A = \frac{x_B^\theta G_m^\phi - x_B^\phi G_m^\theta}{x_B^\theta - x_B^\phi} \quad (7.30)$$

$$G_m^\phi = x_A^\phi \mu_A + x_B^\phi \mu_B; \quad \mu_B = \frac{x_A^\theta G_m^\phi - x_A^\phi G_m^\theta}{x_A^\theta - x_A^\phi}. \quad (7.31)$$

These equations also apply to the equilibrium between two solution phases if the G_m^θ and G_m^ϕ are evaluated for the equilibrium compositions.

Exercise 7.5

In a binary system, where the mutual solubilities are very small, there are two stable stoichiometric phases α (A_3B_2) and β (AB_3). Calculate the chemical potential of B in a 50 : 50 alloy in terms of the quantities G_m^α and G_m^β . Base the calculation on a construction in the G_m diagram.

Hint

Remember that the Gibbs energy of a two-phase state falls on the common tangent. Start by drawing a solid line representing all stable states. It should show that both stoichiometric phases are stable.

Solution

Evidently, the alloy is $\alpha + \beta$ (see Fig. 7.12). With $x_A^\alpha = 0.6$ and $x_A^\beta = 0.25$ the construction gives $\mu_B = \mu_B^{\alpha+\beta} = G_m^\alpha + (G_m^\beta - G_m^\alpha) \cdot (x_A^\alpha - 0)/(x_A^\alpha - x_A^\beta) = G_m^\alpha + (G_m^\beta - G_m^\alpha) \cdot 60/(60 - 25) = (60/35)G_m^\beta - (25/35)G_m^\alpha$.

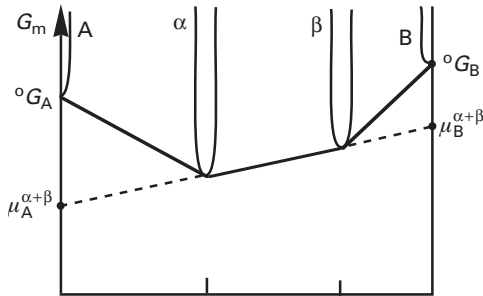


Figure 7.12 Solution to Exercise 7.5.

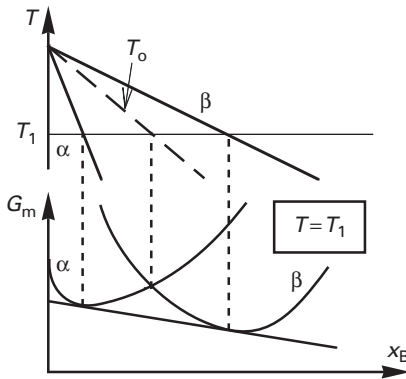


Figure 7.13 The relation between Gibbs energy curves of two phases and their two-phase fields in the phase diagram. The dashed line is the so-called T_0 line or allotropic phase boundary.

7.5 Allotropic phase boundaries

One can sometimes draw a line inside a two-phase region to show where the two phases would have the same Gibbs energy value if they had the same composition. It is the critical limit for a hypothetical diffusionless phase transformation. Such a transformation is very similar to an allotropic transformation in a pure element and the line, sometimes called the **allotropic phase boundary**, is often denoted by T_0 . This name is derived from the word ‘allotropy’, i.e. the property of a substance of being found in two or more forms. Figure 7.13 illustrates the relation between the allotropic phase boundary and the molar Gibbs energy diagram.

Exercise 7.6

Consider a binary system with three phases of variable compositions and in a eutectic equilibrium (see Section 12.5) with each other. Show reasonable positions of the three allotropic phase boundaries. Extrapolate all of them below the eutectic temperature.

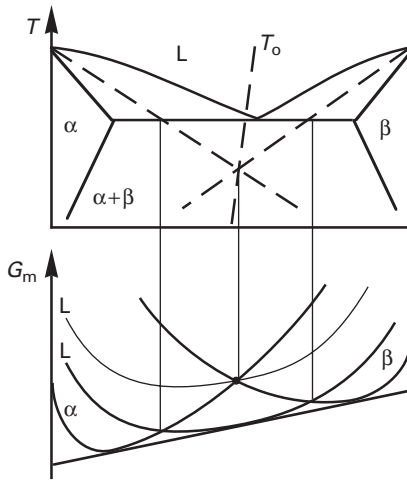


Figure 7.14 Solution to Exercise 7.6.

Hint

Consider in particular how the three allotropic phase boundaries intersect each other when extrapolated. Will there be one or three points of intersection? It may be instructive to sketch a molar Gibbs energy diagram.

Solution

It is evident that $T_0^{\alpha+L}$ and $T_0^{L+\beta}$ will intersect inside the $\alpha + \beta$ phase field. Consider a G_m diagram (Fig. 7.14) at the eutectic temperature, showing one G_m curve for each phase (thick lines in the lower portion of the figure). Each one of the three intersections is a point on a T_0 line. When the temperature is decreased, the L curve is lifted (see thin line) relative to the other two until all three curves finally intersect in one point. There the three T_0 lines will intersect. In the phase diagram (upper portion) we should thus draw the $T_0^{\alpha+\beta}$ line through the intersection of the other two.

7.6 Effect of a pressure difference on a two-phase equilibrium

In order to illustrate the effect of pressure, we shall consider an incompressible phase, β . The application of a hydrostatic pressure will lift up its Gibbs energy curve by the amount $P^\beta V_m^\beta$. This is illustrated in Fig. 7.15(a). Since V_m^β is usually dependent on the composition, the curve will be somewhat deformed. The construction with a tangent will yield $P^\beta V_A^\beta$ and $P^\beta V_B^\beta$ where V_A^β and V_B^β are defined from V_m^β in the same way as G_A^β and G_B^β are defined from G_m^β (see Fig. 4.6).

The relative position of the Gibbs energy curves for different phases can change with pressure due to differences in the molar volumes. The equilibrium conditions can thus be modified by the application of a hydrostatic pressure. This effect is even stronger if the pressure is applied to one of the phases only, which may happen due to the effect

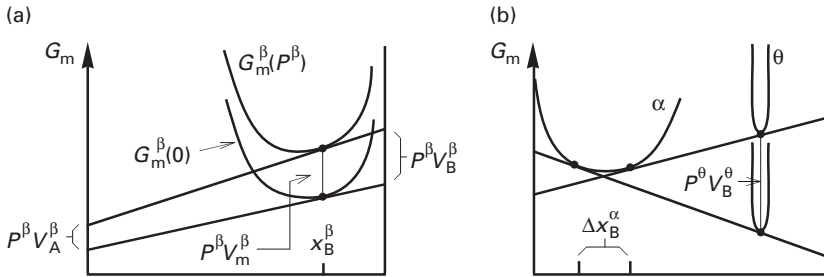


Figure 7.15 (a) Effect of a hydrostatic pressure on the molar Gibbs energy of a single phase. The phase is assumed to be incompressible. (b) The effect of pressure in a stoichiometric phase on the equilibrium composition of a coexisting phase not under pressure.

of surface energy in a curved interface. In Fig. 7.15(b) the phase under pressure is a stoichiometric phase and its molar Gibbs energy is increased by $P^\theta V_m^\theta$. We may, for instance, imagine that the phases are contained in a cylinder where the balance of surface energies, σ , at the wall of the cylinder gives a constant radius of curvature $\rho = 2\sigma/P^\theta$. The diagram illustrates that the solubility of θ in α is increased due to the pressure in θ , assuming ordinary pressure in α . It should be emphasized that this case must be treated with care because the two phases are under different pressures and the law of additivity does not apply to the Gibbs energy unless special precautions are taken. This was mentioned in Section 3.4 and will be discussed in Section 16.7. However, in applying the common-tangent construction we have only made use of the definition of the chemical potentials.

The effect on the solubility can be estimated if one knows the curvature of the G_m^α curve. The difference in slope between the two tangents can be estimated as $[x_B^{\alpha/\theta}(P^\theta) - x_B^{\alpha/\theta}(0)] \cdot d^2 G_m^\alpha / dx_B^2$ if the change in composition is small. If the distance between the two phases is reasonably constant, we obtain, by multiplying with that distance,

$$P^\theta V_m^\theta = (x_B^\theta - x_B^\alpha) [x_B^{\alpha/\theta}(P^\theta) - x_B^{\alpha/\theta}(0)] \cdot d^2 G_m^\alpha / dx_B^2 \quad (7.32)$$

$$x_B^{\alpha/\theta}(P^\theta) - x_B^{\alpha/\theta}(0) = P^\theta V_m^\theta / (x_B^\theta - x_B^\alpha) d^2 G_m^\alpha / dx_B^2. \quad (7.33)$$

When α is a dilute solution we may approximate $d^2 G_m^\alpha / dx_B^2$ with $RT/x_B^{\alpha/\theta}$ according to Eq. (7.19) and obtain

$$x_B^{\alpha/\theta}(P^\theta) - x_B^{\alpha/\theta}(0) = P^\theta V_m^\theta x_B^{\alpha/\theta} / RT (x_B^\theta - x_B^\alpha). \quad (7.34)$$

This equation is often applied to a spherical interface and $2\sigma/r$ is then substituted for P^θ . In that form it is known as the Gibbs–Thomson equation. For large changes in solubility one should integrate over the pressure increase and allow $x_B^{\alpha/\theta}$ on the right-hand side to vary during the integration. For an infinitesimal increase in P^θ we get

$$dx_B^{\alpha/\theta} / x_B^{\alpha/\theta} = [V_m^\theta / RT (x_B^\theta - x_B^\alpha)] \cdot dP^\theta. \quad (7.35)$$

For the case where $(x_B^\theta - x_B^\alpha)$ is reasonably constant integration yields

$$\ln [x_B^{\alpha/\theta}(P^\theta) / x_B^{\alpha/\theta}(0)] = P^\theta V_m^\theta / RT (x_B^\theta - x_B^\alpha). \quad (7.36)$$

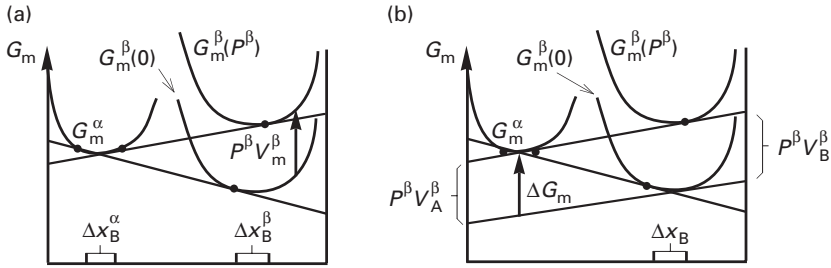


Figure 7.16 Molar Gibbs energy diagram illustrating the change in composition of a phase, β , under pressure when in equilibrium with another phase, α .

If the phase under pressure can also vary in composition, its equilibrium composition will also change. This case is illustrated in Fig. 7.16. The change in composition of the phase under pressure can be evaluated from Fig. 7.16(b) where a tangent to the initial G_m^β curve has been drawn for the β composition of the new equilibrium. The diagram defines a quantity ΔG_m which is given as

$$\Delta G_m = P^\beta (x_A^\alpha V_A^\beta + x_B^\alpha V_B^\beta), \quad (7.37)$$

but also as

$$\Delta G_m = (x_B^\beta - x_B^\alpha) \cdot d^2 G_m^\beta / dx_B^2 \cdot [x_B^{\beta/\alpha}(P^\beta) - x_B^{\beta/\alpha}(0)], \quad (7.38)$$

if $d^2 G_m^\beta / dx_B^2$ is reasonably constant. By equating the two expressions we obtain

$$x_B^{\beta/\alpha}(P^\beta) - x_B^{\beta/\alpha}(0) = P^\beta (x_A^\alpha V_A^\beta + x_B^\alpha V_B^\beta) / [(x_B^\beta - x_B^\alpha) \cdot d^2 G_m^\beta / dx_B^2]. \quad (7.39)$$

If the β phase is a dilute solution of B in A, then $x_A^\alpha V_A^\beta + x_B^\alpha V_B^\beta$ is approximately equal to the molar volume for pure A in the β state, which we shall simply denote by V_m^β , and $d^2 G_m^\beta / dx_B^2$ can be approximated by RT/x_B^β according to Eq. (7.19), yielding

$$dx_B^{\beta/\alpha} / x_B^{\beta/\alpha} = [V_m^\beta / RT (x_B^\beta - x_B^\alpha)] \cdot dP^\beta. \quad (7.40)$$

We can take into account the effect of P^β on both phases if they are both dilute solutions of B in A but then we cannot treat $x_B^\beta - x_B^\alpha$ as a constant. However, the expressions for $dx_B^{\alpha/\beta} / x_B^{\alpha/\beta}$ and $dx_B^{\beta/\alpha} / x_B^{\beta/\alpha}$ are identical for two dilute solutions,

$$dx_B^{\alpha/\beta} / x_B^{\alpha/\beta} = dx_B^{\beta/\alpha} / x_B^{\beta/\alpha}. \quad (7.41)$$

Integration yields

$$x_B^{\alpha/\beta}(P^\beta) / x_B^{\alpha/\beta}(0) = x_B^{\beta/\alpha}(P^\beta) / x_B^{\beta/\alpha}(0) \quad (7.42)$$

$$\frac{x_B^{\beta/\alpha}(P^\beta) - x_B^{\alpha/\beta}(P^\beta)}{x_B^{\beta/\alpha}(P^\beta)} = \frac{x_B^{\beta/\alpha}(0) - x_B^{\alpha/\beta}(0)}{x_B^{\beta/\alpha}(0)}. \quad (7.43)$$

The quantity on the left-hand side appears in the equation for $dx_B^{\beta/\alpha}$ with a slightly different notation, $(x_B^\beta - x_B^\alpha)/x_B^\beta$. This ratio can thus be treated as a constant during the integration of $dx_B^{\beta/\alpha}$, yielding

$$x_B^{\beta/\alpha}(P^\beta) - x_B^{\beta/\alpha}(0) = (P^\beta V_m^\beta / RT) \cdot x_B^{\beta/\alpha} / (x_B^\beta - x_B^\alpha) \quad (7.44)$$

$$x_B^{\alpha/\beta}(P^\beta) - x_B^{\alpha/\beta}(0) = (P^\beta V_m^\beta / RT) \cdot x_B^{\alpha/\beta} / (x_B^\beta - x_B^\alpha). \quad (7.45)$$

It should again be emphasized that the equations in the present section were derived only for an incompressible phase.

Exercise 7.7

The precipitation of Sn from a supersaturated solid solution of Sn in Pb sometimes results in a lamellar aggregate of a Sn phase with very little Pb and a Pb phase with less Sn. The aggregate, comprising alternate layers, grows into a Pb-rich matrix of the original composition. Experimental studies have been made of the coarseness of such a structure in terms of a quantity w , the combined width of one lamella of each phase. When discussing theoretical predictions the measured w is compared with the critical value w^* which would completely stop the growth of the Sn phase because, due to the effect of surface energy, it would put this phase under such a high pressure that it would be in equilibrium with the original Pb matrix in spite of its supersaturation. This pressure can be calculated from the effect of surface energy. In one study an alloy with $x_{Sn} = 0.112$ was investigated at a temperature where the equilibrium value was 0.06. The investigators assumed that the new phase had the equilibrium composition, $x_{Sn} = 0.06$, and using the Gibbs–Thomson equation for large changes they calculated w^* from $w^* = 2\sigma V_m / RT \ln(0.112/0.06)$. They found that the observed w was about 100 times larger than w^* instead of twice according to a simple theory. Check their calculation.

Hint

Make a careful analysis of what pressure the surface energy will impose on the Sn phase under the simplifying assumption that the Pb lamellae are not under an increased pressure.

Solution

The pressure in the Sn phase will balance the surface energy, which gives a force of $2\sigma L$ if L is the length of the lamella. The area of the edge is $f w^* L$ if f is the fraction of the Sn phase. Thus, $P^* f w^* L = 2\sigma L$. The lever rule gives $f = (0.112 - 0.06)/(1 - 0.06) = 0.055$. Now relate the pressure to the change in solubility, $\ln(0.112/0.06) = P^* V_m / RT (1 - 0.112) \cong P^* V_m / RT$. Combining these equations yields $w^* = 2\sigma / P^* f = 2\sigma V_m / f RT \ln(0.112/0.06)$. The investigators missed the factor $f (= 0.055)$ which explains most of the discrepancy.

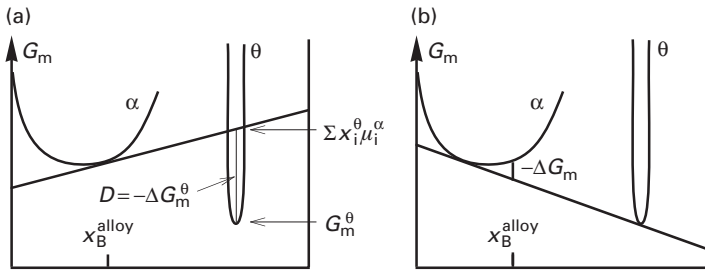


Figure 7.17 (a) Molar Gibbs energy diagram. (b) Method for evaluation of the driving force for the formation of a new phase θ from a supersaturated β solution.

7.7 Driving force for the formation of a new phase

When we take some A and B away from a large quantity of a solution phase, α , it is like taking them from one reservoir each, with the chemical potentials equal to G_A^α and G_B^α , respectively. As long as the amount of the α phase is large, we can take A and B in any proportion without changing the values of G_A^α and G_B^α . We can thus form a small amount of a new phase, θ , of any composition without changing the Gibbs energy of the whole system, provided that the new phase falls on the α tangent. If the new phase falls below the tangent, the decrease counted per mole of atoms in the new phase is obtained as

$$-\Delta G_m^\theta = x_A^\theta \cdot G_A^\alpha(x_B^\alpha) + x_B^\theta \cdot G_B^\alpha(x_B^\alpha) - G_m^\theta(x_B^\theta). \quad (7.46)$$

This is illustrated in the molar Gibbs energy diagram in Fig. 7.17(a). By convention, the change of Gibbs energy accompanying a reaction is defined as $\Delta G_m = G_m^{\text{products}} - G_m^{\text{reactants}}$. It is evident that the decrease in Gibbs energy, $-\Delta G_m$, is equal to the driving force for the precipitation of the θ phase from a supersaturated β solution, counted per mole of θ , if the extent of the reaction, ξ , is expressed as the number of moles of θ , N^θ ,

$$D = -\left(\frac{\partial G}{\partial \xi}\right)_{T,P,N_i} = -\left(\frac{\partial G}{\partial N^\theta}\right)_{T,P,N_i} = -\Delta G_m^\theta. \quad (7.47)$$

The magnitude of the driving force for the precipitation of θ from a supersaturated α solution, counted per mole of θ , can be estimated from the supersaturation Δx_B^α in almost the same way as the effect of pressure on solubility was evaluated. By comparing Fig. 7.17(a) with Fig. 7.15(b) we obtain from Eq. (7.32)

$$D = -\Delta G_m^\theta = P^\theta V_m^\theta = \Delta x_B^\alpha \cdot d^2 G_m^\alpha / dx_B^2 \cdot (x_B^\theta - x_B^\alpha). \quad (7.48)$$

This is the driving force at the start of the precipitation of θ . As the process continues, the supersaturation will decrease gradually and so will the driving force. It may thus be interesting to evaluate the integrated driving force which should represent an average value for the whole process. The method of evaluation is illustrated in Fig. 7.17(b). One usually evaluates the integrated driving force for the transformation of the whole system, i.e. the difference in Gibbs energy between the final $\alpha + \theta$ mixture and the initial supersaturated α . It is simply given by the short vertical line in Fig. 7.17(b).

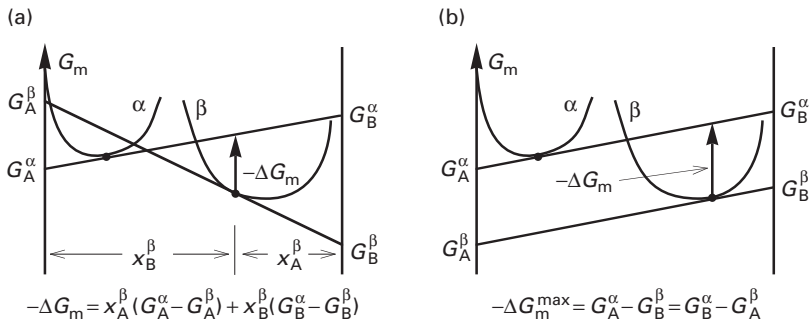


Figure 7.18 Solution to Exercise 7.8.

Exercise 7.8

Consider the formation of a small amount of β from a large reservoir of α under conditions such that the reservoir has the potentials G_A^α and G_B^α and the new phase has G_A^β and G_B^β (accepting that such conditions can somehow be realized). (a) Construct a reasonable molar Gibbs energy diagram and use it for deriving an expression for the driving force per mole of β phase. Express the result in terms of the potentials and the compositions of the two phases. (b) Suppose the composition of α has been decided. How should one choose the composition of β in order to get the largest driving force?

Hint

(a) Using the given potentials one can draw the tangents to the two Gibbs energy curves. Evaluate the distance between them at the proper composition. (b) In this exercise, the tangent to the α curve is given. The question is how we can find the point on the β curve which lies as low as possible relative to the α tangent. In principle, it can be found without drawing the corresponding β tangent but it would be most helpful to do so, so long as one draws that tangent correctly.

Solution

(a) See Fig. 7.18(a). (b) One should choose the composition obtained from a parallel tangent construction (see Fig. 7.18(b)).

Exercise 7.9

Show with the construction in Fig. 7.17(b) the magnitude of the integrated driving force counted per mole of the θ phase formed.

Hint

The magnitude is $-\Delta G_m/f^\theta$ if f^θ is the final fraction of θ in the alloy. The question is how to find this by construction. Notice that f^θ can be found graphically using the lever rule.

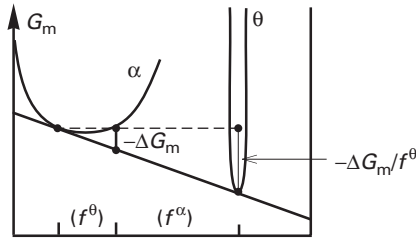


Figure 7.19 Solution to Exercise 7.9.

Solution

Draw a straight line joining the final α and the initial α (Fig. 7.19). Extend the line to the composition of θ . Also use the tangent to the final α point shown in Fig. 7.17(b). Read the distance between intersections on the θ composition.

7.8 Partitionless transformation under local equilibrium

So far, we have mainly considered stationary states and for a state with more than one phase we have assumed equilibrium between the phases, which is a reasonable approximation after a long enough time at a high enough temperature. The situation is quite different during a phase transformation but it is still common to assume that full equilibrium is established locally at the phase interface even when it is migrating through the material. This was introduced in Section 3.10 and is called the local-equilibrium approximation and will now be our starting point for an examination of **partitionless transformations**. The local conditions at migrating interfaces will be further discussed in Chapter 14.

When a $\beta \rightarrow \alpha$ transformation occurs in an alloy without any difference in composition between the reactant phase (also called parent phase) and the product phase (also called daughter phase or growing phase), it is regarded as a partitionless transformation. The two phases will fall on the same vertical line in the molar Gibbs energy diagram. Figure 7.20(a) shows the construction for a binary system. Under constant T and P , the driving force is given by the vertical distance between two points representing the initial β and the growing α

$$D = G_m^\beta - G_m^\alpha = -\Delta G_m. \quad (7.49)$$

It is evident that the partitionless transformation cannot possibly occur under local equilibrium unless the composition of the phases falls on the left-hand side of the point of intersection between the two G_m curves.

Whether or not a transformation can actually occur under the conditions illustrated in Fig. 7.20(a) will be discussed in Section 14.4. An attractive possibility is illustrated in Fig. 7.20(b). It is based on the assumption of local equilibrium at the interface and that is why the common-tangent construction is used here. This illustration presumes that the parent phase is so supersaturated that its composition falls on the equilibrium composition

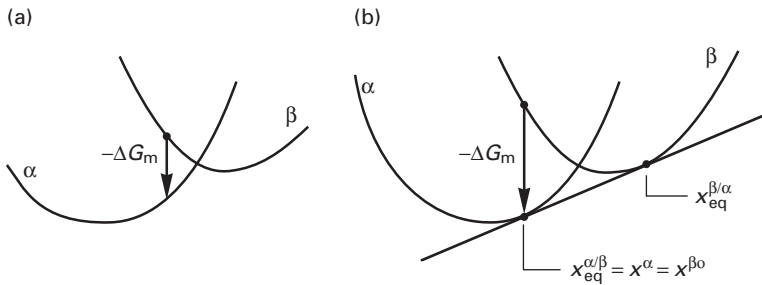


Figure 7.20 (a) Change in Gibbs energy for a partitionless $\beta \rightarrow \alpha$ transformation. (b) A partitionless transformation under local equilibrium. Here the whole decrease in Gibbs energy drives the diffusion in the matrix phase, β . The quantity x^{β_0} is the initial composition of the β alloy and also the equilibrium composition of α .

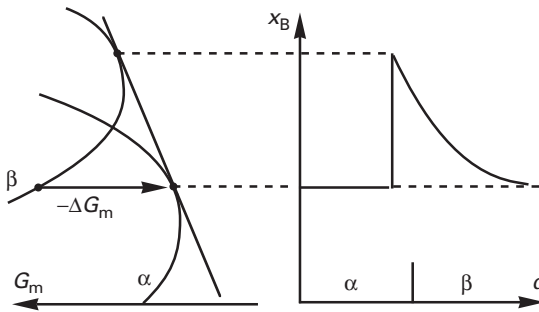


Figure 7.21 Use of the common-tangent construction to find the boundary conditions for the diffusion process.

of the growing phase. It should be realized that the local-equilibrium assumption implies that there is a gradient within the parent phase, as illustrated in Fig. 7.21. There the composition axis has been turned vertically in order to demonstrate how the molar Gibbs energy diagram can yield the boundary conditions for diffusion.

Figure 7.21 demonstrates that the local-equilibrium assumption implies that there is a pile-up of one of the components in front of the migrating interface. After an induction period during which this pile-up is being built, one could expect a steady-state process in which the rate of migration and the composition profile stay constant. As the interface migrates through the system and pushes the pile-up forward, it makes material of the initial alloy composition move up on the pile-up and on the top it will be deposited on the growing phase, the composition of which is here assumed to be equal to the initial one. During this process the material passes through regions of higher and higher alloy content. In each such region the chemical potentials can be described by the end-points of the tangent to the G_m curve at the local composition. The value of G_m for the material we consider will be found on that tangent and at the initial composition. It is thus evident that the material will gradually decrease its Gibbs energy by an amount $-\Delta G_m$ corresponding to the arrow in the G_m diagram. The length of the arrow represents the

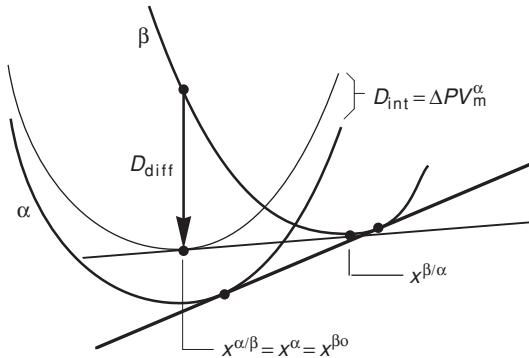


Figure 7.22 Partitionless $\beta \rightarrow \alpha$ transformation under local equilibrium and under a pressure difference, respectively.

integrated driving force dissipated by diffusion in the pile-up. Under our assumptions, all the driving force is used to drive the diffusion and the transformation is completely diffusion controlled.

In rapid transformations an appreciable driving force may be required in order to make the phase interface move with the high speed. A driving force may also be required in order to balance the pressure difference across a curved phase interface, caused by its surface energy, $2\sigma/\rho$. The total driving force on the interface, D_{int} , may actually be regarded as a pressure difference $\Delta P = D_{\text{int}}/V_m$. In a very crude but useful approach it is assumed that the rate of migration, v , of an interface is proportional to the net pressure difference,

$$v = M \cdot \Delta P_{\text{net}} = M \cdot (D_{\text{int}}/V_m - 2\sigma/\rho), \quad (7.50)$$

where M is the mobility of the interface, σ is the specific surface energy and ρ is the radius of curvature, assuming a spherical shape.

The part of the driving force acting on the interface, D_{int} , has an effect on the local equilibrium between the two phases, as illustrated in Fig. 7.22. The G_m curve for the growing phase is lifted by an amount D_{int} relative to the curve for the parent phase as if there actually were a pressure difference D_{int}/V_m . Due to this construction, the equilibrium composition of the growing phase is displaced and the local-equilibrium assumption now requires that the parent phase is initially even more supersaturated and falls on the other side of the equilibrium composition of the growing phase, i.e. inside its one-phase field. The amount of driving force dissipated by diffusion will in general be higher than before.

Exercise 7.10

Consider the partitionless growth of α into a small spherical β particle of radius ρ in a binary alloy. Suppose there is local equilibrium at the interface and no driving force is required in order to make the interface move at a velocity v . Make a reasonable

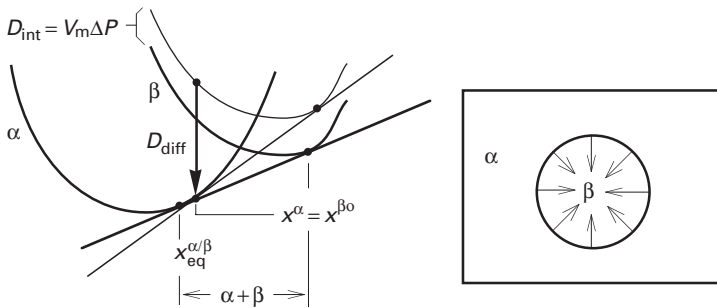


Figure 7.23 Solution to Exercise 7.10.

construction in a G_m diagram illustrating that this could occur at an alloy composition inside the $\alpha + \beta$ two-phase region.

Hint

The surface energy, σ , may lift the G_m curve for β .

Solution

The solution is presented in Fig. 7.23.

7.9 Activation energy for a fluctuation

Sometimes one is interested in the formation of a fluctuation for which the driving force is negative. In such cases one instead talks about the **activation energy**. For the moment, we shall make two assumptions: (i) the fluctuation is only in composition, not in structure; and (ii) the size will not be prescribed. We have already demonstrated that a system is not stable against fluctuations in composition if d^2G_m/dx^2 is negative. We shall now consider the case of a positive curvature, Fig. 7.24. The activation energy per mole of atoms in a fluctuation Δx_B is represented by ΔG_m in the diagram. By introducing the curvature of the G_m^α curve we directly obtain an approximate expression if both Henry's and Raoult's laws hold,

$$\begin{aligned}\Delta G_m &\cong \frac{1}{2} (\Delta x_B^\alpha)^2 \cdot d^2 G_m^\alpha / dx_B^2 \cong \frac{1}{2} (\Delta x_B^\alpha)^2 \cdot RT / x_A^\alpha x_B^\alpha \\ &\cong \frac{1}{2} (\Delta x_B^\alpha)^2 \cdot RT / x_B^\alpha.\end{aligned}\quad (7.51)$$

However, in this case we should examine the validity of the approximation by also carrying out an exact calculation. By comparing with the evaluation of the driving force for the precipitation of a new phase we find without any approximation

$$\Delta G_m = G_m^f - x_A^f G_A^\alpha - x_B^f G_B^\alpha = x_A^f (G_A^f - G_A^\alpha) + x_B^f (G_B^f - G_B^\alpha), \quad (7.52)$$

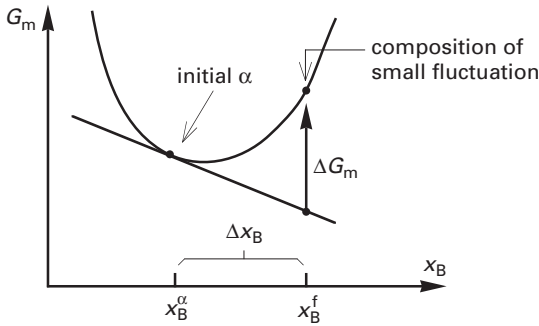


Figure 7.24 Molar Gibbs energy diagram for a fluctuation in composition.

where the superscript *f* denotes the fluctuation. Henry's and Raoult's laws yield

$$\Delta G_m \cong RT [x_A^f \ln(x_A^f/x_A^\alpha) + x_B^f \ln(x_B^f/x_B^\alpha)]. \quad (7.53)$$

For $|x_B^f - x_B^\alpha| \ll x_B^\alpha \ll 1$ we obtain approximately

$$\Delta G_m \cong \frac{1}{2}RT(x_B^\alpha - x_B^f)^2/x_B^\alpha. \quad (7.54)$$

This is in agreement with the previous approximation, Eq. (7.51).

Exercise 7.11

Consider a binary liquid with 0.1% of B in A at 1273 K. Evaluate the activation energy for the formation of fluctuations with 0.05 and 0.15% of B, respectively. Express the results as joule per mole of atoms in the fluctuations.

Hint

It might be justified to use a dilute solution approximation but not the special approximation for $|x_B^f - x_B^\alpha| \ll x_B^\alpha$.

Solution

- (a) $\Delta G_m = RT[0.9995 \ln(0.9995/0.9990) + 0.0005 \ln(0.0005/0.0010)] = 1.625 RT$.
 (b) $\Delta G_m = RT[0.9985 \ln(0.9985/0.9990) + 0.0015 \ln(0.0015/0.0010)] = 1.147 RT$.

Notice that the approximate equation would have given:

- (a) $\Delta G_m = 0.5RT(0.0010 - 0.0005)^2/0.0005 = 2.646 RT$.
 (b) $\Delta G_m = 0.5RT(0.0010 - 0.0015)^2/0.0015 = 0.882 RT$.

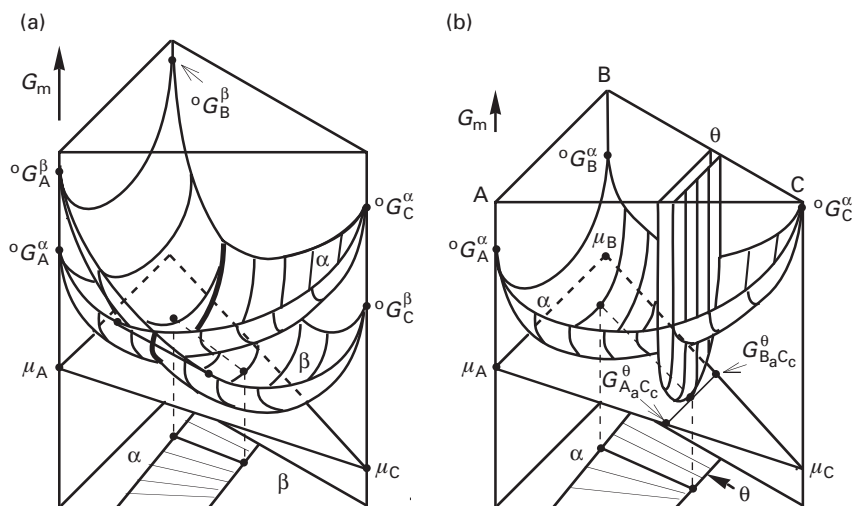


Figure 7.25 Molar Gibbs energy diagram for a two-phase equilibrium in a ternary system. The two-phase field is created by the common tangent-plane rolling under the two surfaces. (a) Two ordinary solution phases. (b) One ordinary solution phase, α , and one solution between two compounds.

7.10 Ternary systems

The property diagram for G_m at constant T and P as function of the molar content in a ternary phase is a three-dimensional diagram with a surface like a canopy. It can be shown that for a stable phase it is everywhere convex downwards and Fig. 4.9 was drawn in accordance with that fact. In that diagram the tangent plane to an alloy was also drawn, the intersections of which give the partial Gibbs energies in the alloy, i.e. the chemical potentials. We shall now apply such diagrams to various cases of phase equilibria.

Equilibrium between two phases requires that they have the same value for the chemical potential of each component. In a binary system this leads to the common-tangent construction where the intersections with the sides represent the chemical potentials. In a ternary system it leads to a common tangent-plane construction where the intersections with the three edges represent the chemical potentials. With the two Gibbs energy surfaces given, one can allow this tangent plane to roll under them and thus describe a series of possible equilibrium situations, each one represented by a tie-line between the two tangent points in the plane. The result will be a two-phase field, formed by projection on the compositional triangle (see Fig. 7.25(a) where one tie-line is projected).

The general equilibrium condition in a ternary system is of course $G_A^\alpha = \mu_A = G_A^\beta$, $G_B^\alpha = \mu_B = G_B^\beta$ and $G_C^\alpha = \mu_C = G_C^\beta$. These three equations leave one degree of freedom for the two-phase equilibrium since each phase can vary its composition by two degrees of freedom. The two-phase region in a ternary phase diagram will thus be an area covered by tie-lines. Each tie-line connects two points, representing the coexisting phases in a

possible state of equilibrium. This conclusion still holds even if there is a restriction to the variation in composition of one of the phases but the equilibrium equations will then be modified, as we shall now see.

Let us first consider the equilibrium between a solution of compounds and an ordinary solution phase. It can be illustrated with the molar Gibbs energy diagram in Fig. 7.25(b). It should be noticed that here $a + c = 1$ because the diagram is for one mole of atoms. The construction shows that the equilibrium condition can be derived by considering two of the sides of the triangular tangent plane

$$G_{A_a C_c}^{\theta} = a\mu_A + c\mu_C = aG_A^{\alpha} + cG_C^{\alpha} \quad (7.55a)$$

$$G_{B_a C_c}^{\theta} = a\mu_B + c\mu_C = aG_B^{\alpha} + cG_C^{\alpha}. \quad (7.55b)$$

These equilibrium conditions leave one degree of freedom because there are two equations and three possible variations in composition, one for the solution of compounds and two for the ordinary solution phase. By taking the difference between the equations we find that

$$(G_{A_a C_c}^{\theta} - G_{B_a C_c}^{\theta})/a = G_A^{\alpha} - G_B^{\alpha}. \quad (7.56)$$

Let us next consider the equilibrium between two solutions of compounds, θ and ϕ , with the formulas $(A, B)_a C_c$ and $(A, B)_b C_d$, where $a + c = 1 = b + d$. The previous type of equation applies to each one of these phases although the chemical potentials on the right-hand side cannot be referred to any one of the phases but are simply the chemical potentials of the two-phase equilibrium.

$$G_{A_a C_c}^{\theta} = a\mu_A + c\mu_C$$

$$G_{B_a C_c}^{\theta} = a\mu_B + c\mu_C$$

$$G_{A_b C_d}^{\phi} = b\mu_A + d\mu_C$$

$$G_{B_b C_d}^{\phi} = b\mu_B + d\mu_C.$$

By eliminating the unknown potentials we find a single equilibrium condition

$$(G_{A_a C_c}^{\theta} - G_{B_a C_c}^{\theta})/a = \mu_A - \mu_B = (G_{A_b C_d}^{\phi} - G_{B_b C_d}^{\phi})/b. \quad (7.57)$$

We have thus found that there will again be one degree of freedom because now there are two possible variations in composition, one for each line compound. If one selects a composition for one phase, the composition of the other one is given by this equation. The result will be similar but mathematically more complicated if the two solution phases are formed by the mixing of a different pair of components.

Exercise 7.12

Consider the equilibrium between a solution phase $(A, B)_a C_c$ and a stoichiometric compound $A_l B_m C_n$ in a ternary system. Show how the chemical potential of the element C can be calculated.

Hint

For the stoichiometric compound, ϕ , there is only one relation. For the solution phase, θ , there are two. Find a combination of G s that eliminates μ_A and μ_B .

Solution

${}^\circ G_m^\phi = l\mu_A + m\mu_B + n\mu_C$; $G_{A_aC_c}^\theta = a\mu_A + c\mu_C$; $G_{B_bC_c}^\theta = b\mu_B + c\mu_C$. Eliminate μ_A and μ_B by taking $a{}^\circ G_m^\phi - lG_{A_aC_c}^\theta - mG_{B_bC_c}^\theta$, which is found to be equal to $(an - cl - cm)\mu_C$. We obtain $\mu_C = (a{}^\circ G_m^\phi - lG_{A_aC_c}^\theta - mG_{B_bC_c}^\theta)/(an - cl - cm)$.

7.11 Solubility product

According to Eq. (3.18) the Gibbs energy of a phase ϕ is always related to the chemical potentials μ_i by the following relation

$$G_m^\phi = \sum x_i^\phi \mu_i, \quad (7.58)$$

where x_i^ϕ represents the composition of the phase. When the phase is a compound, the composition is constant and it is described by the indices in the formula, e.g. l, m, n in $A_lB_mC_n$. For one mole of formula units we have, if $l + m + n = 1$,

$${}^\circ G_m^\phi = l\mu_A + m\mu_B + n\mu_C. \quad (7.59)$$

The superscript $^\circ$ is used in order to indicate that the value refers to the compound itself, the ‘pure compound’, and not to a compound phase, diluted by other components being dissolved in it.

Figure 7.26 illustrates the equilibrium between a compound ϕ and a solution phase, α . There is only one equilibrium condition and it is obtained by inserting the partial Gibbs energies of the solution phase instead of the chemical potentials in the last equation. So,

$${}^\circ G_m^\phi = lG_A^\alpha + mG_B^\alpha + nG_C^\alpha \quad (7.60)$$

Let us consider the solubility curve of ϕ in α close to the A corner and introduce activities instead of chemical potentials. The activity a_i is defined through the equation

$$G_i = {}^\circ G_i + RT \ln a_i, \quad (7.61)$$

where ${}^\circ G_i$ is the molar Gibbs energy of some reference state for i . Eq. (7.59) yields

$$\left({}^\circ G_m^\phi - l{}^\circ G_A - m{}^\circ G_B - n{}^\circ G_C \right) / RT = l \cdot \ln a_A + m \cdot \ln a_B + n \cdot \ln a_C. \quad (7.62)$$

Using the standard Gibbs energy of formation of the ϕ phase from the pure components in their reference states, which is equal to the expression in parentheses, we get

$$\exp \left(\Delta {}^\circ G_m^\phi / RT \right) = (a_A)^l (a_B)^m (a_C)^n. \quad (7.63)$$

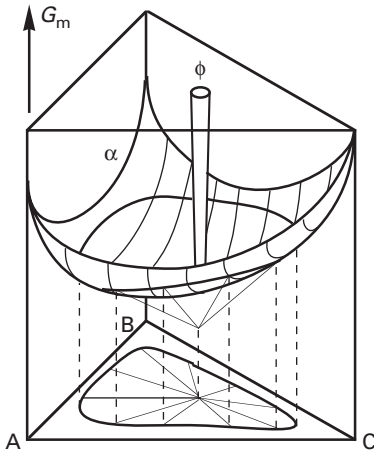


Figure 7.26 Molar Gibbs energy diagram for a ternary system with an ordinary solution phase, α , and a ternary stoichiometric phase, ϕ .

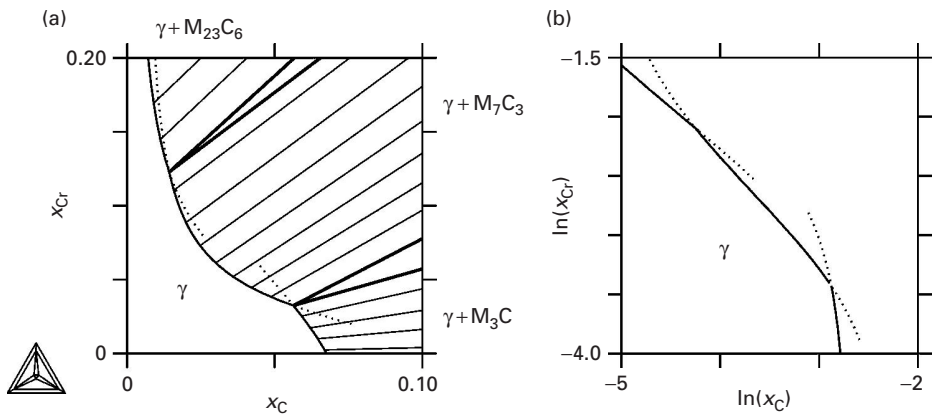


Figure 7.27 Isothermal and isobaric section of the Fe–Cr–C phase diagram near the Fe corner. The solubility curves for strictly stoichiometric compounds would have been straight lines in the logarithmic diagram (b) and hyperbolic in the linear diagram (a).

In a dilute solution the activity of minor components is approximately proportional to the content expressed, for instance, as the molar content. The activity of the major component is approximately unity and can thus be omitted from the equations. Thus,

$$\exp(\Delta^\circ G_m^\phi/RT) = (a_B)^m (a_C)^n. \quad (7.64)$$

The left-hand side is often denoted by K and is regarded as the solubility product. The solubility curve for a compound in a terminal solution may thus be approximated by a

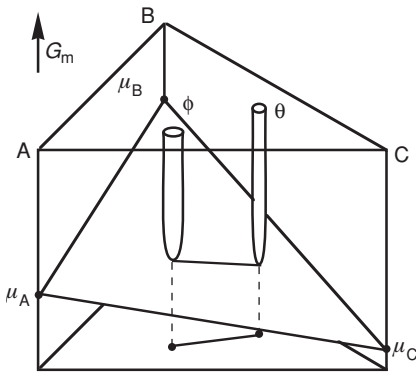


Figure 7.28 Solution to Exercise 7.13.

hyperbolic curve in a linear phase diagram and with a straight line in a logarithmic phase diagram. As an example, in Fig. 7.27 an isobarothermal section of the phase diagram Fe–Cr–C is presented. The diagram shows the solubilities of three carbides in γ . In the logarithmic diagram the solubility lines are almost straight although the compositions of the carbides are not quite constant.

Exercise 7.13

Consider the equilibrium between two ternary stoichiometric phases. Even though the compositions are fixed, there is a degree of freedom from a thermodynamic point of view because there must be three chemical potentials. After a value has been chosen for one of them, the other two are fixed. Derive equations for their calculation.

Hint

There are only two equations relating the three potentials, one for each phase. Choose one of the potentials as the independent one and eliminate one of the other two.

Solution

Write the two conditions as ${}^{\circ}G_m^{\theta} = a\mu_A + b\mu_B + c\mu_C$ and ${}^{\circ}G_m^{\phi} = l\mu_A + m\mu_B + n\mu_C$. A Gibbs energy diagram demonstrates that there is indeed one degree of freedom (Fig. 7.28). We can thus take any value of μ_C , for instance, and then express the other two in μ_C . After eliminating μ_B by multiplying the first equation with m and the other with b and subtracting, we get $\mu_A = [m{}^{\circ}G_m^{\theta} - b{}^{\circ}G_m^{\phi} + (bn - cm)\mu_C]/(am - bl)$ and in the same way $\mu_B = [l{}^{\circ}G_m^{\theta} - a{}^{\circ}G_m^{\phi} + (an - cl)\mu_C]/(bl - am)$.

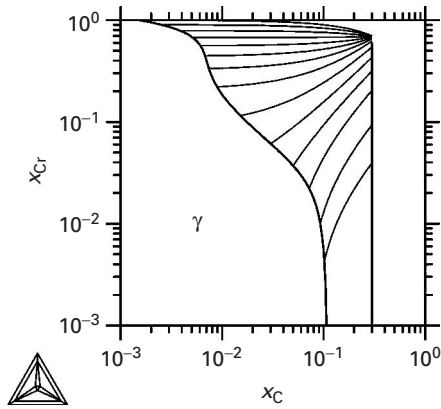


Figure 7.29 Solution to Exercise 7.14.

Exercise 7.14

Sketch the whole $\gamma + M_7C_3$ two-phase field in Fig. 7.27 and include a series of tie-lines.

Hint

Tie-lines are straight lines in diagrams with linear scales. When the scales are changed to logarithmic, only those tie-lines remain straight that are horizontal or vertical or have a slope of unity.

Solution

The solution is given in Fig. 7.29.

8 Phase equilibria and potential phase diagrams

8.1 Gibbs' phase rule

We saw in Section 3.1 that the internal energy of a c -component system is a function of $c + 2$ independent, extensive state variables, with the possible addition of internal variables, and the fact is that the equilibrium state of the system is completely determined by the $c + 2$ variables. Consequently, if the state of a system is known, one may calculate the change of internal energy U by specifying the change of these variables, assuming that there is no entropy-producing process inside the system. So, for a reversible change we have

$$dU = TdS - PdV + \sum \mu_i dN_i, \quad (8.1)$$

where T , $-P$ and μ_i are potentials. We have also seen that one can instead introduce other independent variables, for instance the potentials T and $-P$, obtaining

$$dG = d(U - ST + VP) = -SdT - Vd(-P) + \sum \mu_i dN_i. \quad (8.2)$$

The state of the system is still determined by $c + 2$ independent variables. However, when we further introduced all the chemical potentials μ_i as variables in Section 3.3, we obtained a relation between the $c + 2$ variables which did not involve any other state function,

$$0 = d(G - \sum N_i \mu_i) = -SdT + VdP - \sum N_i d\mu_i. \quad (8.3)$$

Instead, this equation gave a relation between the $c + 2$ potential variables. As mentioned in Section 3.3 it is usually called the Gibbs–Duhem relation. As a consequence, only $c + 1$ of the potentials, T , $-P$ and μ_i are independent and any one of them may be regarded as the dependent potential. In order to define the state of a system completely it is thus necessary to use at least one extensive variable and that is for the purpose of defining the size of the system. It is convenient to use the total content of matter, N , for this purpose or the content of one of the components, N_j . If one is only interested in the properties of a substance, one may disregard the size of the system and regard the state as completely defined by $c + 1$ potentials. In order to represent all the states we then need a diagram with $r = c + 1$ axes, a state diagram according to Section 1.1. We shall call r the **dimensionality** of that diagram. In the following, when we talk about the properties of a system, we shall disregard its size.

If μ_1 is chosen as the dependent potential, then it is convenient to divide by N_1 and thus introduce molar quantities per mole of component 1.

$$d\mu_1 = -S_{m1}dT - V_{m1}d(-P) - \sum_2^c z_i d\mu_i. \quad (8.4)$$

In this connection it may again be emphasized that one should always specify how the formula unit is defined for molar quantities like S_m and V_m . In Section 4.3 the molar quantities, obtained by dividing by N_1 , were identified with the subscript 'm1' and N_i/N_1 was denoted by z_i . For clarity this notation is adopted in the present discussion.

When considering more than one phase in mutual equilibrium, one has a relation of the above type for each phase and every such relation should be obeyed simultaneously if the phases are to stay in equilibrium during the change. Of course, T must have the same value in all the phases and the same holds for all μ_i . Neglecting the effect of surface energy, the same holds for P . The Gibbs–Duhem relations for all phases will thus contain the same changes of the potentials. For each new phase, added to the equilibrium, there will thus be one more relation between the changes of the potentials and the number of independent variables will decrease by one. This is expressed by Gibbs' phase rule, Eq. (8.5).

$$v = c + 2 - p, \quad (8.5)$$

where v is called the **variance** or the **number of degrees of freedom** for the equilibrium with p phases.

The independent variables in Gibbs' phase rule are primarily the potentials because the derivation of the expression for the variance is based upon the Gibbs–Duhem relation, which concerns the change of potentials. An extensive quantity must be included in the set of independent variables in order to define the size of the system but that feature is not covered by Gibbs' phase rule and will not be further discussed here. On the other hand, instead of a potential one may alternatively use one of the molar quantities S_{m1}^α , V_{m1}^α and z_i^α for any phases α , because they are intensive variables and are strictly related to T , $-P$ and μ_i . However, it may again be emphasized that the molar quantities are not potentials like T , $-P$ and μ_i although they are intensive quantities. They will generally have different values in the individual phases.

It should be emphasized that c is the number of independent components. In an alloy system it is usually the number of elements but in a system with molecules it may not be immediately evident how many species should be included in the set of independent components because it is affected by stoichiometric constraints. In a complicated system it may be difficult to identify the number of stoichiometric constraints. We shall return to this problem in Chapter 13.

We may encounter even more complicated cases in systems with molecules of restricted capability to react with each other. In order to describe such cases with Gibbs' phase rule one sometimes includes all molecules or 'chemical substances' and then subtracts a term for the number of 'independent reactions' in order to obtain the number of components. However, the problem remains and is now focused on defining the number of independent reactions. This problem was discussed in Section 5.5. As a consequence,

we shall not modify Gibbs' phase rule in this way. By components we shall understand a set of chemical substances necessary and sufficient for defining the over-all composition of every phase, taking due notice of all the chemical reactions which can occur and also of all stoichiometric constraints.

In the remainder of the present chapter we shall discuss the consequences of Gibbs' phase rule for a kind of diagram which will be introduced soon, the so-called phase diagrams.

Exercise 8.1

Consider as a system the content of an expandable vessel. In the vessel one has enclosed a certain amount of water. Then one varies T and P by actions from the outside and studies what happens to V in an attempt to decide whether the system behaves as a unary system. Due to its larger volume, it is easy to see when a gas phase forms. Discuss what one would expect to happen. Suppose the wall of the vessel acts as a catalyst for the dissociation of H_2O into H_2 and $\frac{1}{2} \text{O}_2$.

Hint

The discussion should be based upon Gibbs' phase rule written as $c = v - 2 + p$.

Solution

The vapour pressure of H_2O depends on T . At any arbitrary external P there will be a unique T where water and vapour can coexist. To choose P arbitrarily is the only freedom, which yields $c = v - 2 + p = 1 - 2 + 2 = 1$. This system behaves as a unary. It would start to behave as a binary if some hydrogen can leak out through the wall of the vessel. Then water and gas can coexist over a range of T although very small.

8.2 Fundamental property diagram

Let us first discuss a T, P diagram for a substance with one component, A , and one phase, α . According to Gibbs' phase rule the state is completely determined by giving the values of T and P , i.e. by giving a point in the T, P diagram. In this sense we may thus regard the T, P diagram as a state diagram according to Section 1.1. The value of μ_A for the substance can be calculated and plotted as a surface above the T, P state diagram, yielding a three-dimensional diagram, see Fig. 8.1. This type of diagram we may regard as a property diagram for the particular substance under consideration. Actually, this diagram can be looked at from any direction and any one of T, P and μ_A may be regarded as the dependent variable. The state may be defined by a point on any side of the property diagram. As a state diagram one may thus use a diagram formed by any two of the potentials.

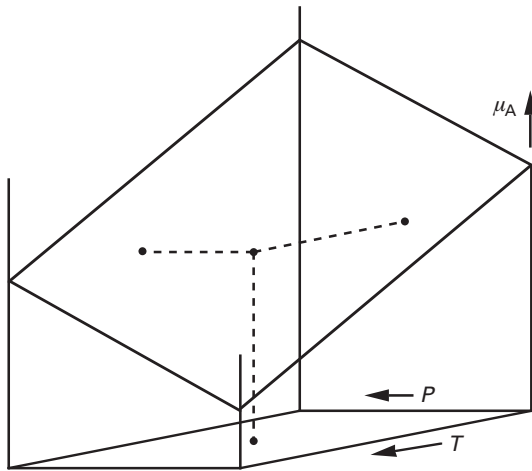


Figure 8.1 Fundamental property diagram for a unary system with one phase. Any one of the three potentials can be chosen as the dependent variable (property). The potential P has been plotted in the negative direction because $-P$ appears naturally in thermodynamic equations.

This kind of property diagram is of special interest because it is composed of a complete set of potentials. We shall call it the **fundamental property diagram** and it has the axes T , P and one μ_i for each component. In a unary system μ_A is identical to G_m and the surface in the diagram thus represents a fundamental equation, $G_m(T, P)$.

For a higher-order system it represents a fundamental equation $\mu_1(T, P, \mu_2, \mu_3, \dots)$ which is of a type we have not defined before. In principle, we could calculate a point on the surface from any one of the fundamental equations, if it is available. One can then follow the surface by applying the Gibbs–Duhem relation. For a unary system we get

$$SdT - VdP + N_A d\mu_A = 0. \quad (8.6)$$

The direction of the surface is given by the relations

$$\left(\frac{\partial \mu_A}{\partial (-P)} \right)_T = -\frac{V}{N_A} < 0; \quad \left(\frac{\partial \mu_A}{\partial T} \right)_P = -\frac{S}{N_A}; \quad \left(\frac{\partial (-P)}{\partial T} \right)_{\mu_A} = -\frac{S}{V}. \quad (8.7)$$

As many times before, we take $-P$ as a potential rather than $+P$. The numerical values of the last two ratios depend on what reference we choose for the entropy. If we accept the common choice of $S = 0$ at $T = 0$ K, then S and all the ratios are positive at $T > 0$ and all the derivatives are negative. Figure 8.1 was constructed accordingly. Similar expressions can be derived for a system with several components and we can summarize all the expressions in a general form

$$\left(\frac{\partial Y^a}{\partial Y^b} \right)_{Y^c} = -\frac{X^b}{X^a} < 0, \quad (8.8)$$

where Y^c represents all the potentials except Y^a and Y^b .

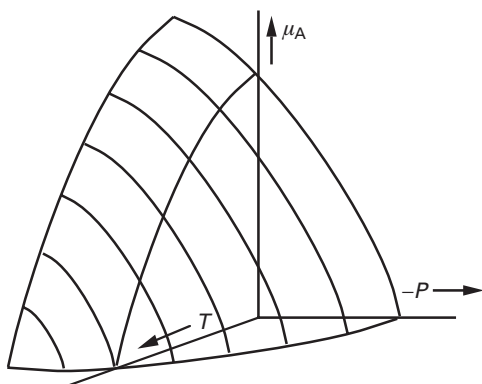


Figure 8.2 Fundamental property diagram for a unary phase. The surface is everywhere convex. The property surface is here shown for negative pressures, which is not unrealistic for solid substances.

Since a point on any side of the T, P, μ_A diagram defines the state, we can use the third axis for the representation of some other property. We may, for instance, represent the refractive index r as a function of T and P but that would not be a fundamental property diagram. However, knowing a point on the surface, we may follow the surface by applying an equation similar to the Gibbs–Duhem relation.

$$dr = \left(\frac{\partial r}{\partial T} \right)_P dT + \left(\frac{\partial r}{\partial P} \right)_T dP. \quad (8.9)$$

The surface in Fig. 8.1 was given as a plane for the sake of simplicity. That would require that V/N_A and S/N_A are constant for the α phase, independent of T and P . In reality, they are not constant and the surface would be curved. We shall now examine in what direction it will be curved. The fundamental property diagram is independent of the size of the system since only potentials are concerned. However, we have the right to consider a system of a constant size and to define that size by any extensive variable. If we take X^a as that variable, and keep it constant when we evaluate the curvature in a section of constant Y^c from the derivative of Eq. (8.8), we obtain

$$\left(\frac{\partial^2 Y^a}{\partial (Y^b)^2} \right)_{Y^c, X^a} = \left(\frac{\partial(-X^b/X^a)}{\partial Y^b} \right)_{Y^c, X^a} = -\frac{1}{X^a} \left(\frac{\partial X^b}{\partial Y^b} \right)_{Y^c, X^a} = -\frac{1}{X^a} \left/ \left(\frac{\partial Y^b}{\partial X^b} \right)_{Y^c, X^a} \right. < 0. \quad (8.10)$$

in view of the stability condition Eq. (6.28). The result is illustrated in Fig. 8.2 for an element A with the choice of $\mu_A > 0$ at $T = 0$ and $P = 0$. The surface looks like part of a dome and is everywhere convex, as seen from the origin. A different choice of reference for μ_A will simply displace the whole surface vertically.

Let us return to the simple picture in Fig. 8.1. Suppose that we make a similar diagram for the same substance in another possible structure (phase), β , and plot the two surfaces

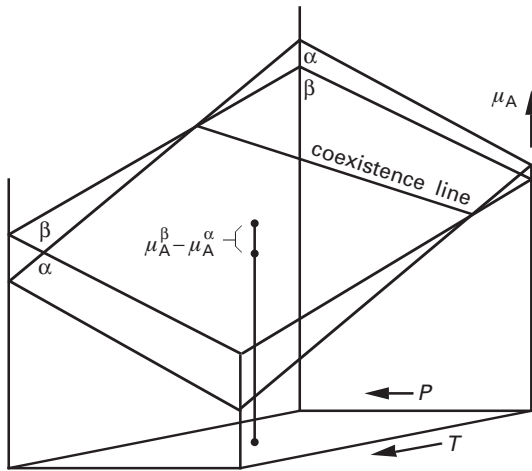


Figure 8.3 Fundamental property diagram for a unary system with two phases. One may regard $\mu_A^\beta - \mu_A^\alpha$ as the integrated driving force for transformation from β to α at the given values of T and P .

in the same coordinate frame. We can then compare the two phases at the same T and P , for instance, and evaluate the difference in μ_A , see Fig. 8.3.

Let us consider a possible transition from phase β to phase α at the fixed values of T and P . We cannot evaluate the driving force for that transition without knowing the detailed mechanism, i.e. the reaction path. However, we can evaluate the integrated driving force for the transition, $\int Dd\xi$. We should then use the form of the combined law having T , $-P$ and μ_A as the variables:

$$0 = -SdT - Vd(-P) - N_A d\mu_A - Dd\xi, \quad (8.11)$$

in which T and P must be regarded as independent variables if they are kept constant. The third potential, μ_A , must then be regarded as a dependent variable. In addition, we may choose one of the extensive variables as independent in order to define the size of the system and it must come from the conjugate pair, which has not yet been used to define an independent variable. It must thus be N_A . For a system at constant T , $-P$ and N_A we obtain

$$\int Dd\xi = - \int N_A d\mu_A = -N_A (\mu_A^\alpha - \mu_A^\beta) = N_A (\mu_A^\beta - \mu_A^\alpha). \quad (8.12)$$

It is evident that the phase with the lower μ_A value will be the more stable phase. At the combination of T and P , marked in Fig. 8.3, α is thus the more stable phase. Furthermore, the line of intersection of the two surfaces must be a line of coexistence because on that line there is no driving force for a change. This line is shown in Fig. 8.3. In the figure the α phase is stable in front of the coexistence line and the β phase behind it. It is evident that the coexistence line represents a ridge on the composite surface representing the stable states. We may generalize this observation and conclude that the surface representing stable states in a system with several phases is composed of pieces, one for each stable

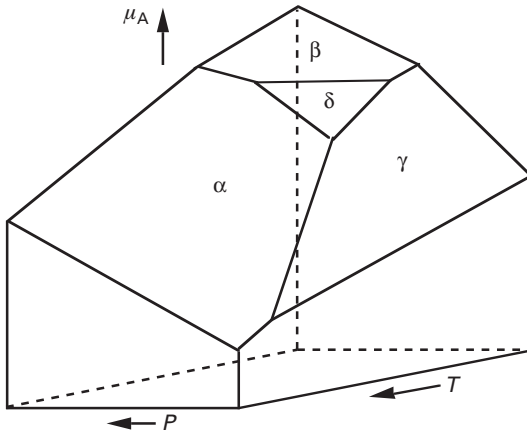


Figure 8.4 Fundamental property diagram for a substance having four different structures (phases). The two-phase lines are all ridges. There are no re-entrant angles.

phase, and joined by coexistence lines which are all ridges. An example with four phases is shown in Fig. 8.4. If we combine this with the previous conclusion that the surface for each single phase is convex, we may conclude that the composite surface is also convex.

Exercise 8.2

Using the criterion that the more stable phase in a unary system under constant T and P has the lower chemical potential, it is possible to obtain a so-called phase diagram from Fig. 8.3. (This will be demonstrated in Fig. 8.5.) Suppose that one would instead like to choose μ_A and T as the independent variables and construct a phase diagram with these axes. What criterion could then be used for deciding where each phase is stable?

Hint

The answer can be found by again considering the combined law in the form of Eq. (8.12). What extensive variable should be regarded as independent when μ_A and T are chosen as independent potentials?

Solution

We must choose V as the independent extensive variable. By keeping V constant together with T and μ_A we should obtain $\int Dd\xi = \int VdP = \int V(P^\alpha - P^\beta) > 0$ if α is the more stable phase. It is evident that the phase with the highest P will be the more stable phase.

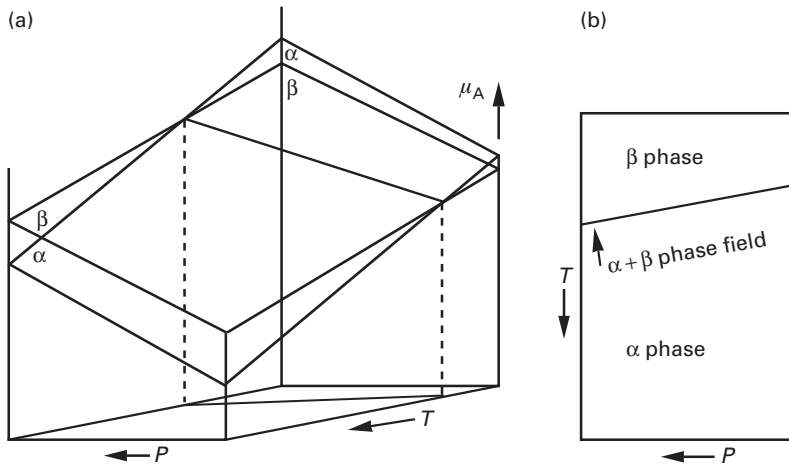


Figure 8.5 Projection of the fundamental property diagram onto the T, P state diagram, yielding a potential phase diagram.

8.3 Topology of potential phase diagrams

A coexistence line in the fundamental property diagram can be projected onto any side of the diagram, for instance the T, P side (see Fig. 8.5). In that T, P diagram (Fig. 8.5(b)) we may indicate on which side of the line each phase is stable, i.e. has a lower μ_A value than the other phase. We may further indicate that the coexistence line represents the $\alpha + \beta$ equilibrium. Such a diagram is called a phase diagram and it is actually a state diagram used for plotting coexistence lines. In this chapter we shall mainly be concerned with phase diagrams. In order to emphasize the character of the axis variables we may call the present diagram a **potential phase diagram**. It is worth remembering that it is actually a projection of the fundamental property diagram. When $T, -P, \mu_A$ is used as the complete set of potentials, one usually projects in the direction of μ_A and presents the T, P phase diagram. However, it should be remembered that in Section 3.5 it was shown that there are at least nine ways of writing the Gibbs–Duhem relation and there are thus at least nine sets of potentials that can be used in the construction of potential phase diagrams.

Knowing one point on the coexistence line in the fundamental property diagram we can determine the direction of the line by applying the Gibbs–Duhem relation to both phases using the fact that dT, dP and $d\mu_A$ must be the same in both phases if they still coexist

$$d\mu_A = -S_m^\alpha dT + V_m^\alpha dP \quad (8.13)$$

$$d\mu_A = -S_m^\beta dT + V_m^\beta dP. \quad (8.14)$$

This system of equations defines the direction of the $\alpha + \beta$ coexistence line in the fundamental property diagram. The direction of the projected line in the T, P phase

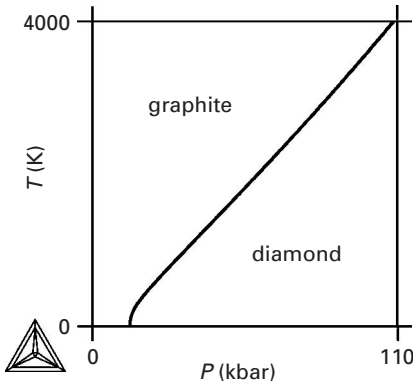


Figure 8.6 The T, P phase diagram for carbon, according to a thermodynamic assessment.

diagram, i.e. the $\alpha + \beta$ phase field, is obtained by eliminating $d\mu_A$ from the Gibbs–Duhem relations

$$\frac{dP}{dT} = \frac{S_m^\alpha - S_m^\beta}{V_m^\alpha - V_m^\beta}. \quad (8.15)$$

As an example Fig. 8.6 shows the equilibrium between graphite and diamond in a T, P phase diagram for carbon. Except for low temperatures the equilibrium line is almost a straight line because the differences in S_m and V_m stay rather constant. At low temperature the line becomes parallel to the T axis because the difference in S_m goes to zero at absolute zero in agreement with the third law of thermodynamics.

Using the alternative form of the Gibbs–Duhem relation, obtained from line 5 in Table 3.1, we may introduce $(H_m^\alpha - H_m^\beta)/T$ instead of $(S_m^\alpha - S_m^\beta)$.

$$\frac{d(-P)}{d(-1/T)} = -\frac{H^\alpha - H^\beta}{(V^\alpha - V^\beta)/T} \quad (8.16)$$

$$\frac{dP}{dT} = -\frac{(H^\alpha - H^\beta)/T}{V^\alpha - V^\beta}. \quad (8.17)$$

This is known as Clapeyron's relation. It should be realized that the molar volumes of condensed phases are so small that pressures of about 1 bar have an effect on the equilibrium temperature which is negligible for many purposes.

Suppose there is a third possible phase. We shall then have a third surface in the property diagram. There will be three coexistence lines and one point of intersection, a triple point, and by projection they will all show up on the phase diagram (see Fig. 8.7).

It is immediately evident that all the angles between the three intersecting lines in the phase diagram are less than 180° . We have thus found the 180° rule which says that the corners of a one-phase field must have angles less than 180° . The dashed lines in Fig. 8.7 represent metastable extrapolations of the two-phase coexistence lines and they fall inside the one-phase field of the third phase. The geometrical elements of the potential phase diagram are called **phase fields** and they are listed here.

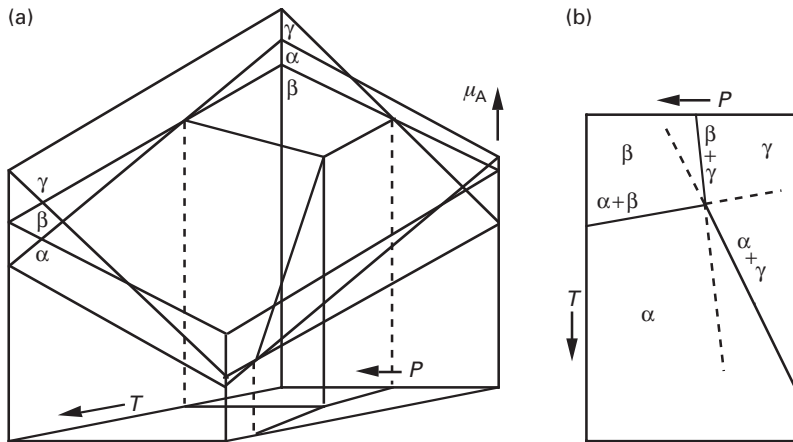


Figure 8.7 Projection of a property diagram (a) onto the T, P state diagram, yielding a phase diagram (b) with three univariant and one invariant phase equilibria. Metastable equilibria are shown with dashed lines.

- (a) Points where three phases are in equilibrium. We cannot change any variable without changing the kind of equilibrium. We call this an invariant equilibrium or a zero-dimensional phase field.
- (b) Lines where two phases are in equilibrium. We can change only one variable independently without leaving the line. We call this a univariant equilibrium or a one-dimensional phase field.
- (c) Surfaces where a single phase exists. We can change two independent variables without leaving this kind of phase field. We call this a divariant equilibrium or a two-dimensional phase field.

The dimensionality of a phase field in the potential phase diagram is thus equal to the variance of the corresponding phase equilibrium. We shall denote the dimensionality by d and can calculate it from Gibbs' phase rule. With one component it yields

$$d = v = c + 2 - p = 3 - p. \quad (8.18)$$

A three-phase equilibrium thus has a variance of 0 and appears as a point ($d = 0$). A single phase has a variance of 2 and it thus requires a surface ($d = 2$) to be represented.

More phases can be added but there will be no new kind of geometrical element. The probability of more than three surfaces meeting in a point in a property diagram is negligible for any real system. As an example of a more complex phase diagram, Fig. 8.8 reproduces the Fe phase diagram. Most of the lines are fairly straight similar to the line in Fig. 8.6. An exception is the two branches of the bcc + fcc line because they can be joined by a curve looking as a parabola by extrapolating them to negative P values. Clapeyron's relation shows that the heat of transformation has different signs for the two branches and must go through zero at some intermediate temperature, i.e. at a negative pressure. The reason is a magnetic transition in the bcc phase.

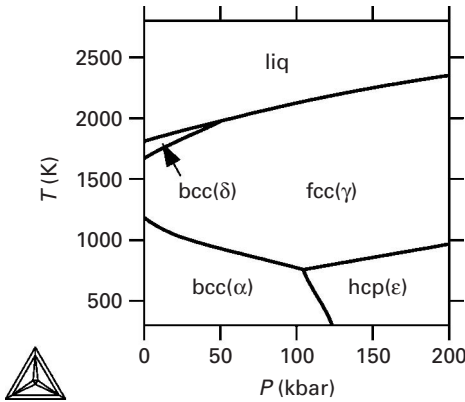


Figure 8.8 T, P phase diagram of Fe according to an assessment of experimental information.

Exercise 8.3

Derive an equation for the $\alpha + \beta$ line in a unary T, P phase diagram under the conditions that ΔH_m and ΔV_m can be regarded as constant.

Hint

Start with Clapeyron's relation, Eq. (8.17).

Solution

$dP = (\Delta H_m / \Delta V_m)(dT/T)$ and $P - P_0 = (\Delta H_m / \Delta V_m) \ln(T/T_0)$ under constant ΔH_m and ΔV_m . In addition, a point on the line, T_0, P_0 , must be known. It should be noticed that it is sometimes more convenient to approximate ΔS_m as constant than ΔH_m . The result is then a straight line in a linear T, P phase diagram. When one of the phases is a gas, one may approximate ΔV_m by RT/P and integration yields, if ΔH_m is constant, $\ln P = K \exp(-\Delta H_m/T)$.

Exercise 8.4

A T, P phase diagram for a unary system (pure A) is given in Fig. 8.9. It shows four phases. Construct a reasonable T, μ_A property diagram at P_1 . It should show all the stable and metastable two-phase equilibria at P_1 .

Hint

The T values for all the two-phase equilibria at P_1 are easily found by extrapolation. Approximate all the T, μ_A lines by straight lines, intersecting at the two-phase equilibria.

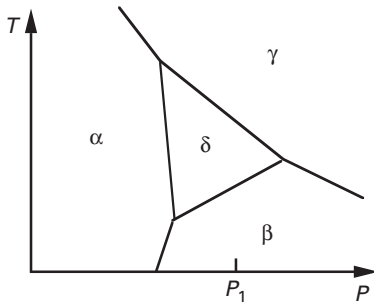


Figure 8.9 See Exercise 8.4.

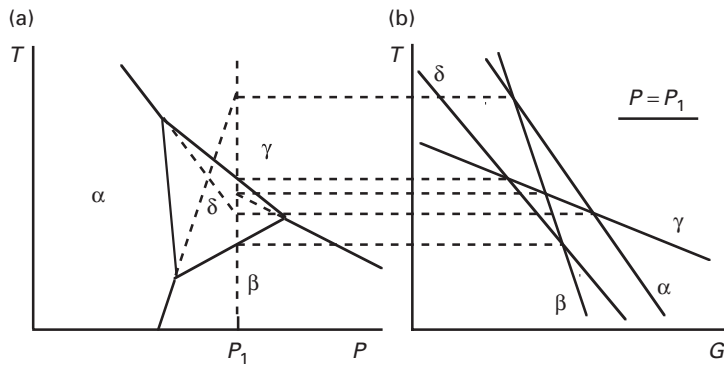


Figure 8.10 Solution to Exercise 8.4.

Solution

The solution is given in Fig. 8.10. The convex polygon close to the origin represents the stable equilibria.

8.4 Potential phase diagrams in binary and multinary systems

So far we have discussed a system with one component, a unary system. In a binary system we have two components and four potentials, T , $-P$, μ_A and μ_B . The fundamental property diagram will be four-dimensional and cannot be visualized. The phase diagram will be three-dimensional and it will be composed of four geometrical elements as illustrated in Fig. 8.11. They are all phase fields.

- Points where four phases are in equilibrium. We cannot change any variable without changing the kind of equilibrium.
- Lines where three phases are in equilibrium. We can change only one variable independently without leaving the line.

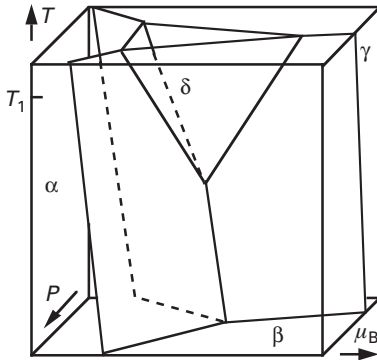


Figure 8.11 T, P, μ_B phase diagram for a binary system with four phases.

- (c) Surfaces where two phases are in equilibrium. We can change two independent variables without leaving this phase field.
- (d) Volumes where a single phase exists. We can change three independent variables without leaving this kind of phase field. Its equilibrium is trivariant.

For higher-order systems, ternary, quaternary, quinary, etc., the principles will be the same. The phase diagram will have $c + 1$ axes, where c is the number of components. The geometrical elements will be points, lines, surfaces, volumes, hypervolumes, etc., and they will represent phase equilibria which have a variance of zero, one, two, three, four, etc., in accordance with Gibbs' phase rule.

Suppose one wants to calculate a state of equilibrium under the requirement that it must consist of p specified phases. Then one must, in addition, specify the values of v independent variables, where v is given by Gibbs' phase rule, $v = c + 2 - p$. On the other hand, suppose one wants to calculate a state of equilibrium without specifying any phase. Then one must specify the values of v independent variables, where v is equal to $c + 1$ because the phase diagram will have $c + 1$ axes. That corresponds to the case of one specified phase. This does not violate Gibbs' phase rule because one will always fall inside a one-phase field, $p = 1$. In practice one will never be able to hit exactly on the other types of geometrical elements.

Figure 8.3 illustrated the integrated driving force for a transition from β to α . The same situation cannot be illustrated for a higher-order system but the integrated driving force can be derived in the same way under conditions where T, P and all the chemical potentials except for μ_1 are kept constant. The combined law yields

$$N_1 d\mu_1 = -SdT + VdP - \sum_2^c N_k d\mu_k - Dd\xi = -Dd\xi \quad (8.19)$$

$$\int Dd\xi = -N_1(\mu_1^\alpha - \mu_1^\beta) = N_1(\mu_1^\beta - \mu_1^\alpha). \quad (8.20)$$

It is thus necessary that μ_1 is lowest in the stable phase if all the other potentials are kept constant.

In the above integration it was assumed that N_1 is kept constant which was the way to define the size of the system. However, it must be noted that the content of all the other components will most probably change during a transition carried out under the conditions considered here. It may be of more practical interest to derive the integrated driving force for a transition under constant T , P and composition. It can be obtained from the combined law expressed in terms of Gibbs energy,

$$dG = -SdT + VdP + \sum \mu_i dN_i - Dd\xi = -Dd\xi \quad (8.21)$$

$$\int Dd\xi = G^\beta - G^\alpha. \quad (8.22)$$

Exercise 8.5

Try to formulate the equivalence of the 180° rule for a point where four phases coexist in a binary three-dimensional phase diagram.

Solution

All such points must be on pointed tips. The four adjoining three-phase lines must fall on ridges.

8.5 Sections of potential phase diagrams

In order to visualize a higher-order potential phase diagram one may decrease the number of dimensions by making a **section** at a constant value of some potential, an equipotential section. It will show exactly the same geometrical elements as a potential phase diagram for a system with one component less. One may section several times and thus decrease the dimensions of a higher-order phase diagram until it can be plotted as a two-dimensional diagram. It is common first to keep P constant and then T . One may then continue and keep the chemical potential of some component constant.

At each sectioning one will lose the geometrical element of the lowest dimensionality. This is demonstrated in Fig. 8.12 which was obtained by taking a horizontal ($T = T_1$) section through the potential phase diagram in Fig. 8.11. The chance of hitting the four-phase point is negligible and no four-phase point should be included in this type of diagram. The topology of a diagram will thus be the same whether the number of dimensions is decreased by sectioning at a constant value of a potential or by reducing the number of components by one. In order to distinguish the two cases, one may call the diagram with axes for all the independent potentials a **complete potential phase diagram**. It has $c + 1$ axes.

In Section 8.3 we called the geometrical elements phase fields. In the complete potential phase diagram a phase field has the dimensions given by Gibbs' phase rule. However,

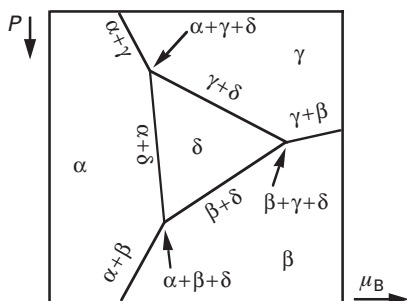


Figure 8.12 Equipotential (isothermal) section of the potential phase diagram in Fig. 8.11 at $T = T_1$.

its dimensionality decreases by one unit for each sectioning and we obtain

$$d = \nu - n_s = c + 2 - p - n_s, \quad (8.23)$$

where n_s is the number of sectionings. In order to avoid confusion with the variance of a phase equilibrium, which is given by Gibbs' phase rule and is independent of what kind of diagram is used, this will be called the **phase field rule**. The number of axes in the diagram, r , which initially is $c + 1$, will also decrease by sectioning, $r = c + 1 - n_s$, and we can thus write the phase field rule as

$$d = r + 1 - p. \quad (8.24)$$

Phase fields for which $d < 0$ will normally not show up in the final diagram, as demonstrated by the negligible chance of hitting the four-phase point in the above case.

It is evident from the second form of the phase field rule that a diagram with r axes has the same topology independent of how many sectionings of potential axes have been used to obtain it. By inspecting a diagram without knowing the number of components, it is thus impossible to tell if it is a section or not.

Exercise 8.6

Consider the equilibrium $\text{Fe} + \text{S}(\text{gas}) \leftrightarrow \text{FeS}$ under a constant P . Can it exist in a range of T ?

Solution

We have two components, Fe and S, i.e. $c = 2$, and three phases, Fe, gas and FeS, i.e. $p = 3$. If we section at some pressure, we have $n_s = 1$. Thus $d = c + 2 - p - n_s = 2 + 2 - 3 - 1 = 0$. Under these conditions the equilibrium can exist only at a particular T .

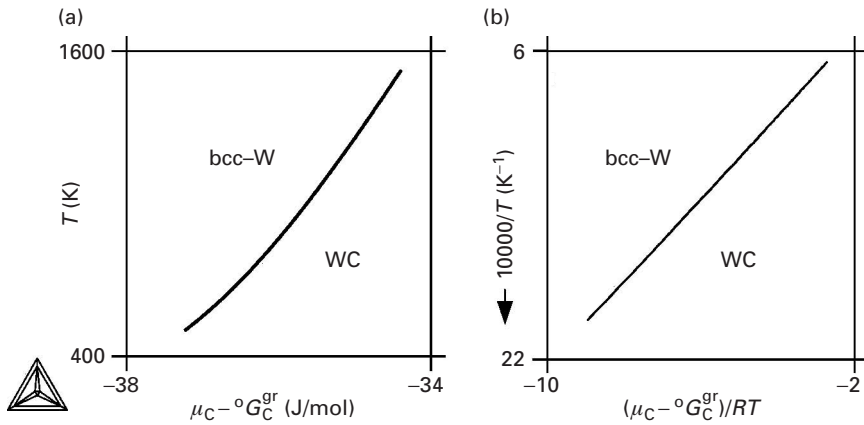


Figure 8.13 Isobaric section at 1 bar of the W–C phase diagram with two potential axes, drawn in two alternative ways. $1/T$ has been plotted in the negative direction because $-1/T$ appears naturally as a potential in thermodynamic equations.

8.6 Binary systems

As an example of a sectioned phase diagram, Fig. 8.13 shows the bcc–W and WC phases in the W–C phase diagram at 1 bar. Two different sets of axes are used. Since a chemical potential has no natural zero point, a reference must be chosen. In this case graphite at 1 bar and the actual temperature was chosen for carbon.

It is interesting to note that the univariant two-phase field approximates very well to a straight line in Fig. 8.13(b). Its slope is obtained from the Gibbs–Duhem relation for constant P , applied to each one of the phases. In order to calculate the slope of the line in Fig. 8.13(b) we shall apply the Gibbs–Duhem relation in an alternative form obtained from the fifth line of Table 3.1 after dividing all the extensive quantities by N_W .

$$d(\mu_W/T) = H_{m1}^W d(1/T) - z_C^W d(\mu_C/T) \quad (8.25)$$

$$d(\mu_W/T) = H_{m1}^{WC} d(1/T) - z_C^{WC} d(\mu_C/T). \quad (8.26)$$

On the line of coexistence the change of each potential must be the same in both phases. We may thus eliminate $d(\mu_W/T)$ by subtracting one equation from the other, to obtain

$$\frac{d(\mu_C/T)}{d(1/T)} = \frac{H_{m1}^{WC} - H_{m1}^W}{z_C^{WC} - z_C^W}. \quad (8.27)$$

Here, $z_C^W = 0$ and $z_C^{WC} = 1$. Since the solubility of carbon in bcc–W is very low, we can approximate H_{m1}^W with the enthalpy of pure bcc–W, ${}^{\circ}H_W^{bcc}$, to obtain

$$\frac{d(\mu_C/T)}{d(1/T)} = H_{m1}^{WC} - {}^{\circ}H_W^{bcc}. \quad (8.28)$$

However, in order to define a numerical value for the right-hand side, it is necessary to choose a state of reference for carbon. By introducing graphite as the state of reference

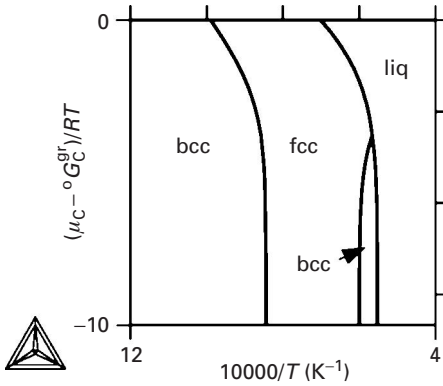


Figure 8.14 The Fe–C phase diagram at 1 bar, plotted with two potential axes.

for carbon, we obtain

$$\frac{d((\mu_C - {}^\circ G_C^{\text{gr}})/T)}{d(1/T)} = H_{\text{ml}}^{\text{WC}} - {}^\circ H_{\text{W}}^{\text{bcc}} - {}^\circ H_{\text{C}}^{\text{gr}}, \quad (8.29)$$

because $d({}^\circ G_C^{\text{gr}}/T)/d(1/T) = {}^\circ H_{\text{C}}^{\text{gr}}$. The right-hand side is the heat of formation of one mole of WC units from the pure elements, a quantity we may denote by $\Delta_{\text{f}}^{\circ} H_{\text{WC}}$. The fact that the curve in Fig. 8.13(b) is almost straight, indicates that the heat of formation is approximately constant. By definition $\mu_C - {}^\circ G_C^{\text{gr}}$ is equal to $RT \ln a_C$ where a_C is the carbon activity, referred to graphite, and Eq. (8.29) can be written as

$$\frac{Rd \ln a_C}{d(1/T)} = \Delta_{\text{f}}^{\circ} H_{\text{WC}}, \quad (8.30)$$

and we could have plotted $R \ln a_C$ as the abscissa and still have the almost straight line.

In Fig. 8.13(a) the potentials T and $\mu_C - {}^\circ G_C^{\text{gr}}$ have been used on the axes and with the usual form of the Gibbs–Duhem relation we obtain

$$\frac{d(\mu_C - {}^\circ G_C^{\text{gr}})}{dT} = -S_{\text{ml}}^{\text{WC}} + {}^\circ S_{\text{W}}^{\text{bcc}} + {}^\circ S_{\text{C}}^{\text{gr}} = \Delta_{\text{f}}^{\circ} S_{\text{WC}}. \quad (8.31)$$

The abscissa could have been interpreted as $RT \ln a_C$. From the fact that the slope is reasonably constant we may conclude that the entropy of formation of WC is approximately constant, but not as constant as the heat of formation.

The situation will be more complicated if one or both phases can vary in composition. As an example, a complete Fe–C phase diagram at a constant pressure is presented in Fig. 8.14, using the axes $1/T$ and $(\mu_C - {}^\circ G_C^{\text{gr}})/T$. The strong curvatures are caused by the strong variation in composition of the fcc and liquid phases. All the lines turn vertical at low values of μ_C . That is where the C content goes to zero and all phases become pure Fe. The difference in composition thus goes to zero.

For reactions involving oxygen it is natural to use an O_2 gas of 1 bar as reference. However, we may also express the oxygen potential by the ratio of the partial pressures of CO_2 and CO in an ideal gas and use as a reference a gas where these partial pressures are equal. Figure 8.15 gives an example of such a diagram with information from a large

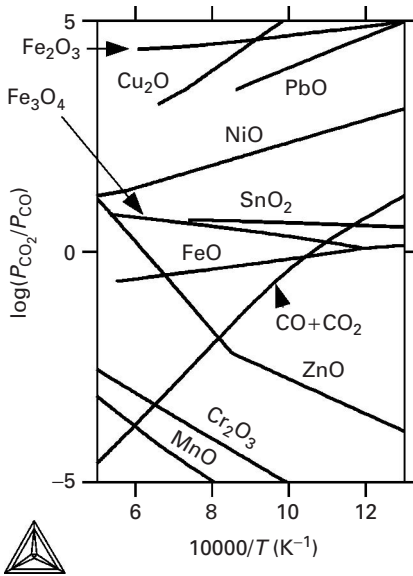


Figure 8.15 Combination of isobaric phase diagrams for many M–O systems at 1 bar. The oxygen potential is represented by $P_{\text{CO}_2}/P_{\text{CO}}$ in a hypothetical gas which is not present, except for the line CO + CO₂.

number of M–O systems. An oxide is stable above each line. Below the line the stable state is either the pure metal or a lower oxide. The diagram is calculated for 1 bar and the state for pure Zn above the boiling point is thus Zn gas of 1 bar because the O₂ pressure is low enough to be neglected. This diagram is often called the Ellingham diagram. It should be emphasized that the effect of pressure is so small that this diagram could be used for any pressure down to zero and up to many bars, except for (i) the line CO + CO₂ which holds only for $P_{\text{CO}} + P_{\text{CO}_2} = 1$ bar and (ii) the line for gaseous Zn.

Exercise 8.7

Consider a system with graphite in a vessel under a pressure of 1 bar and a temperature of 1000 °C. The vessel can expand and accommodate a gas. What would be the partial pressures in the gas if a small amount of oxygen is introduced?

Hint

In this case the ordinate axis in Fig. 8.15 expresses not only the oxygen potential but also gives the actual value of $P_{\text{CO}_2}/P_{\text{CO}}$.

Solution

The system would place itself on the CO + CO₂ line and from Fig. 8.15 we read for 1000 °C: $\log(P_{\text{CO}_2}/P_{\text{CO}}) = -2$ which together with $P_{\text{CO}_2} + P_{\text{CO}} = 1$ bar yields $P_{\text{CO}_2} = 0.01$ bar and $P_{\text{CO}} = 0.99$ bar.

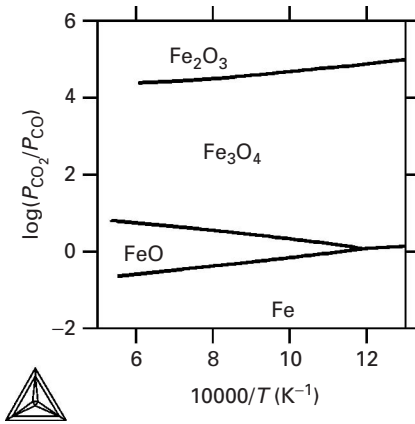


Figure 8.16 Solution to Exercise 8.8.

Exercise 8.8

From the information given in Fig. 8.15 construct an Fe–O potential phase diagram at a constant pressure of 1 bar.

Hint

It is not necessary to change the axes. The liquid phase cannot be included due to lack of information.

Solution

The phase diagram is shown in Fig. 8.16.

8.7 Ternary systems

For a ternary system one may obtain a two-dimensional phase diagram by sectioning at constant T and P . Figure 8.17 shows such a diagram for the Ti–O–Cl system and the axes represent μ_{O}/RT and μ_{Cl}/RT , expressed by the logarithm of the partial pressures of O_2 and Cl_2 in an imagined ideal gas that would be in equilibrium with the system.

Again we find that the univariant phase equilibria are represented by lines which look straight, a fact that can again be illustrated by application of the Gibbs–Duhem relation. For constant T and P we get by applying the Gibbs–Duhem relation in its ordinary form, Eq. (3.84), and dividing all the extensive quantities by N_{Ti} and thus introducing z_i ,

$$d\mu_{\text{Ti}} = -z_{\text{O}}^{\alpha}d\mu_{\text{O}} - z_{\text{Cl}}^{\alpha}d\mu_{\text{Cl}} \quad (8.32)$$

$$d\mu_{\text{Ti}} = -z_{\text{O}}^{\beta}d\mu_{\text{O}} - z_{\text{Cl}}^{\beta}d\mu_{\text{Cl}} \quad (8.33)$$

$$\frac{d\mu_{\text{Cl}}}{d\mu_{\text{O}}} = -\frac{z_{\text{O}}^{\alpha} - z_{\text{O}}^{\beta}}{z_{\text{Cl}}^{\alpha} - z_{\text{Cl}}^{\beta}}. \quad (8.34)$$

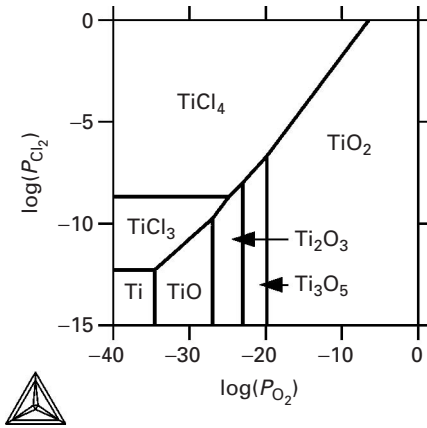


Figure 8.17 The Ti–O–Cl phase diagram at 1 bar and 1273 K, plotted with two potential axes. The potentials are expressed in terms of the partial pressures (in bar) in an ideal gas which is not present.

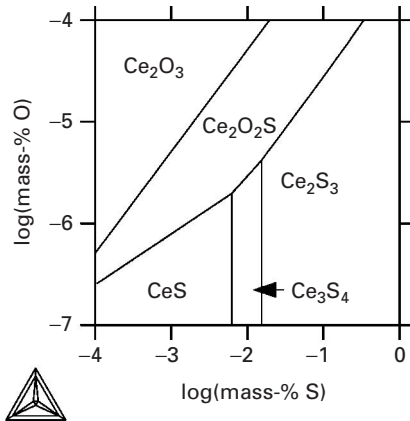


Figure 8.18 The Ce–O–S phase diagram at 1 bar and 1273 K, plotted with two potential axes. The potentials are expressed in terms of the contents in liquid iron which is not present.

It is interesting to note that the slope can be calculated directly from the compositions involved.

A sectioned potential diagram like Fig. 8.17 is sometimes called a Kellogg diagram. It must be emphasized that here the gas phase is not considered in the phase equilibria. The partial pressure is simply a popular means of expressing the chemical potential of volatile elements. It may be expressed in bar and the reference states are chosen as an ideal gas with a partial pressure for O_2 or Cl_2 of 1 bar. Thus we have, for instance,

$$2(\mu_O - {}^\circ G_O^{\text{ref}})/RT = \ln P_{O_2}. \quad (8.35)$$

Alternatively, one may express chemical potentials through the content in any other phase that happens to be present or could be present. As an example, Fig. 8.18 shows a case

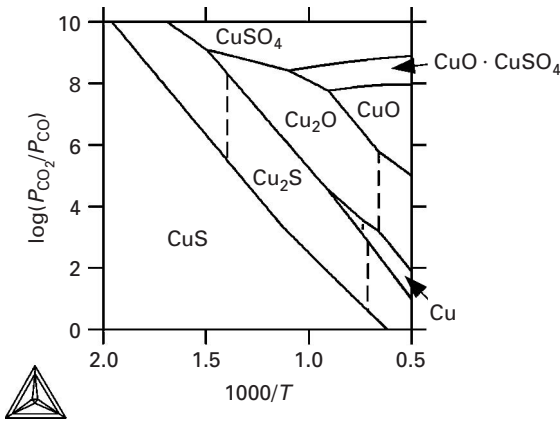


Figure 8.19 The Cu–O–S phase diagram sectioned at 1 bar and a potential of SO_2 equal to the potential of pure SO_2 gas of 1 bar.

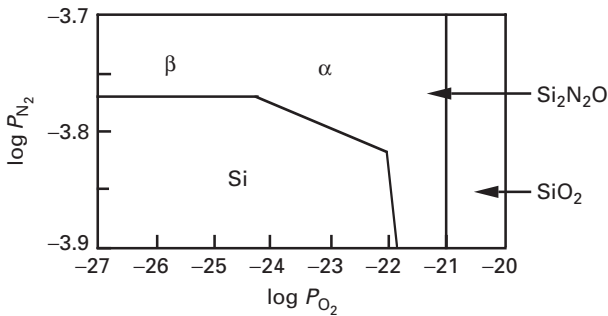


Figure 8.20 See Exercise 8.9.

where the logarithm of the contents of O and S in liquid iron are used for representing the Ce–O–S phase diagram at constant temperature and pressure. With these axes one can directly see what cerium compound should form first from liquid iron if the cerium content is gradually increased. However, the diagram does not reveal what cerium contents are required in the liquid iron phase.

One may also section a ternary phase diagram at some value of a chemical potential and keep the temperature as an axis. Figure 8.19 shows such a case sectioned at a constant value of $\mu_S + 2\mu_O$ and plotted with μ_O/RT versus $1/T$. Here μ_O/RT is expressed by the ratio of the partial pressures of CO_2 and CO in an ideal gas.

Exercise 8.9

Figure 8.20 shows at what O_2 and N_2 pressures three nitrides can form from pure Si at 1840 K. (a) Use the slopes in order to evaluate the O content in α and β , both of which are usually considered to be Si_3N_4 . (b) Their coexistence lines are missing in the phase diagram. Calculate their slopes.

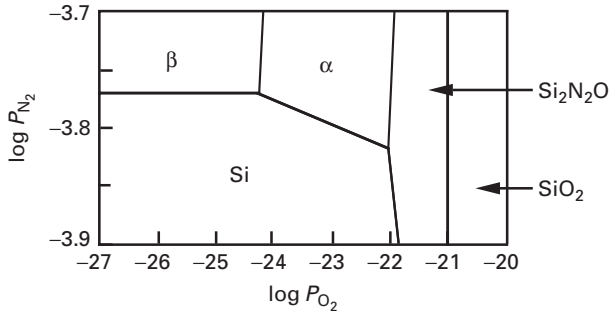


Figure 8.21 Solution to Exercise 8.9.

Hint

The axes may be regarded as potential axes for O and N because T is constant. We can thus apply the relation $d\mu_O/d\mu_N = -(z_N^\gamma - z_N^\delta)/(z_O^\gamma - z_O^\delta)$, similar to Eq. (8.34). The Si phase does not dissolve noticeable amounts of O or N. In all the oxides and oxynitrides we can assume the following valencies: +4 for Si, -2 for O, -3 for N.

Solution

(a) z_i is here defined as N_i/N_{Si} . For α/Si we read $d\mu_O/d\mu_N = -45 = -(z_N^\alpha - 0)/(z_O^\alpha - 0) = -z_N^\alpha/z_O^\alpha$. Applying electroneutrality, $4 = 2z_O^\alpha + 3z_N^\alpha = 2z_O^\alpha + 45 \cdot 3z_O^\alpha = 137z_O^\alpha$; $z_O^\alpha = 0.0292$; $z_N^\alpha = 45 \cdot 0.0292 = 1.3139$. Figure 8.21 thus predicts that the formula for the α phase is $Si_1N_{1.3139}O_{0.0292}$ or $Si_{2.978}Va_{0.022}N_{3.913}O_{0.087}$.

For β/Si we read $d\mu_O/d\mu_N = \infty = -(z_N^\beta - 0)/(z_O^\beta - 0)$; $z_O^\beta = 0$. The formula for β is Si_3N_4 .

(b) For α/β we then get: $d\mu_O/d\mu_N = -(1.313 - 1.3333)/(0.0292 - 0) = 0.664$. For α/Si_2N_2O we get: $d\mu_O/d\mu_N = -(1.3139 - 1)/(0.0292 - 0.5) = 0.667$. The two new coexistence lines will thus be parallel and almost vertical in Fig. 8.21 because of the very enlarged scale for $\log P_{N_2}$.

Exercise 8.10

For the invariant equilibrium $TiCl_4 + TiO_2 + Ti_3O_5$ in Fig. 8.17 it has been found that the partial pressure of Ti is 5×10^{-22} bar. Construct a reasonable $\log P_{O_2}$, $\log a_{Ti}$ diagram for these three phases at the constant values of T and P .

Hint

Evidently, the potential diagram in Fig. 8.17 was obtained from the fundamental property diagram by first sectioning twice (at constant T and P) and then projecting in the μ_{Ti} direction. Now we are asked instead to project in the μ_{Cl} direction. Start by plotting the point for the three-phase equilibrium at $\log P_{Ti} = -21.3$ and a value of $\log P_{O_2}$ obtained from Fig. 8.17. Then we can calculate the slopes of invariant equilibria in terms of the

compositions involved. When one obtains an indeterminate value one should go back to the derivation of the equation used.

Solution

At constant T, P we have a three-dimensional property diagram looking like Fig. 8.7(a) but with $\mu_{\text{Ti}}, \mu_{\text{O}}$ and μ_{Cl} on the axes. Figure 8.17 is the projection on the $\mu_{\text{O}}, \mu_{\text{Cl}}$ side. Now we want the projection on the $\mu_{\text{O}}, \mu_{\text{Ti}}$ side. Then we must project in the μ_{Cl} direction and define z_i as N_i/N_{Cl} . For TiO_2 and Ti_3O_5 we get z_{O} and z_{Ti} equal to infinity. We should thus go back to the Gibbs–Duhem relation for two phases, α and β , and get $x_{\text{Ti}}^\alpha d\mu_{\text{Ti}} + x_{\text{O}}^\alpha d\mu_{\text{O}} + x_{\text{Cl}}^\alpha d\mu_{\text{Cl}} = 0$ and $x_{\text{Ti}}^\beta d\mu_{\text{Ti}} + x_{\text{O}}^\beta d\mu_{\text{O}} + x_{\text{Cl}}^\beta d\mu_{\text{Cl}} = 0$.

For $\text{TiO}_2/\text{TiCl}_4$: $x_{\text{Cl}}^\alpha = 0$ and already the first equation yields $d\mu_{\text{Ti}}/d\mu_{\text{O}} = -x_{\text{O}}^\alpha/x_{\text{Ti}}^\alpha = -2$ and $d \ln a_{\text{Ti}}/d \ln P_{\text{O}_2} = 0.5d\mu_{\text{Ti}}/d\mu_{\text{O}} = -1$.

For $\text{Ti}_3\text{O}_5/\text{TiCl}_4$: $x_{\text{Cl}}^\alpha = 0$ and already the first equation yields $d\mu_{\text{Ti}}/d\mu_{\text{O}} = -x_{\text{O}}^\alpha/x_{\text{Ti}}^\alpha = -5/3$ and $d \ln a_{\text{Ti}}/d \ln P_{\text{O}_2} = 0.5d\mu_{\text{Ti}}/d\mu_{\text{O}} = -5/6$.

For $\text{TiO}_2/\text{Ti}_3\text{O}_5$: $x_{\text{Cl}}^\alpha = x_{\text{Cl}}^\beta = 0$ and the only solution to the two equations is $d\mu_{\text{Ti}} = 0$ and $d\mu_{\text{O}} = 0$. This two-phase equilibrium will thus occur in one point only (see Fig. 8.22). The reason is that we have projected the property diagram in the direction of the $\text{TiO}_2 + \text{Ti}_3\text{O}_5$ coexistence line.

In a two-dimensional potential phase diagram we normally expect to see two-dimensional phase fields for single phases and one-dimensional phase fields for two phases in equilibrium. As expected, the phase field for TiCl_4 is two-dimensional but not the one for TiO_2 or Ti_3O_5 . However, since TiO_2 and Ti_3O_5 do not dissolve any Cl, their properties are not affected by μ_{Cl} . The μ_{Cl} axis in the fundamental property diagram is thus parallel to the property surface of both phases and hence parallel to the line representing their intersection. In the μ_{Cl} projection these surfaces will become lines and their intersection, representing a two-phase equilibrium, will become a point. Compare Fig. 8.7 and let μ_{Ti} correspond to μ_{A} , let μ_{O} correspond to $-P$ and μ_{Cl} correspond to T . Rotate all the surfaces slightly until the $\beta + \gamma$ coexistence line is parallel to the T axis. It will then appear as a point in the T projection.

8.8 Direction of phase fields in potential phase diagrams

In the discussions of two-dimensional phase diagrams we have several times derived equations for the slope of two-dimensional phase fields. We shall now give a more general treatment. The direction of phase fields is governed by the Gibbs–Duhem relation, which applies to each one of the p phases in an equilibrium, e.g. for the phase α :

$$-S_{\text{m}}^\alpha dT + V_{\text{m}}^\alpha dP - \sum x_i^\alpha d\mu_i = 0. \quad (8.36)$$

If all the phases stay in equilibrium with each other when some variation is made, each of $d\mu_i, dT$ and dP must have the same value for all phases. By combining the Gibbs–Duhem relation for all phases one obtains a system of equations for the coexistence of the phases in the fundamental property diagram. With p phases we have p Gibbs–Duhem relations

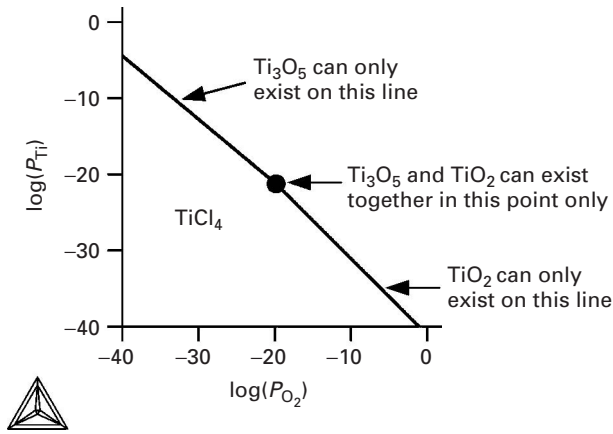


Figure 8.22 Solution to Exercise 8.10.

and can thus eliminate $p - 1$ of the variables. If we would choose to eliminate μ_i for i from 1 to $p - 1$, we should multiply each equation by a factor that we can represent by a determinant. For example, the equation for the α phase should be multiplied by a factor

$$\begin{vmatrix} x_1^\beta & x_2^\beta & \dots & x_{p-1}^\beta \\ x_1^\gamma & x_2^\gamma & \dots & x_{p-1}^\gamma \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ x_1^\epsilon & x_2^\epsilon & \dots & x_{p-1}^\epsilon \end{vmatrix}.$$

As a shorthand notation such a determinant will be written by giving the diagonal elements $|x_1^\beta \ x_2^\gamma \ \dots \ x_{p-1}^\epsilon|$. By adding the equations for all the phases, we obtain

$$- \left| S_m^\alpha x_1^\beta x_2^\gamma \ \dots \ x_{p-1}^\epsilon \right| dT + \left| V_m^\alpha x_1^\beta x_2^\gamma \ \dots \ x_{p-1}^\epsilon \right| dP - \sum \left| x_i^\alpha x_1^\beta x_2^\gamma \ \dots \ x_{p-1}^\epsilon \right| d\mu_i = 0. \quad (8.37)$$

Using an alternative form of the Gibbs–Duhem relation found from line 5 in Table 3.1 we instead obtain

$$\begin{aligned} & \left| H_m^\alpha \ x_1^\beta \ x_2^\gamma \ \dots \ x_{p-1}^\epsilon \right| d(1/T) + \left(V_m^\alpha / T \right) \left| x_1^\beta \ x_2^\gamma \ \dots \ x_{p-1}^\epsilon \right| dP \\ & - \sum \left| x_i^\alpha x_1^\beta x_2^\gamma \ \dots \ x_{p-1}^\epsilon \right| d(\mu_i / T) = 0. \end{aligned} \quad (8.38)$$

The factors in front of $d\mu_i$ or $d(\mu_i/T)$ for i from 1 to $p - 1$ are zero because two columns have the same elements. For instance, with $i = p - 1$ the first and last columns in the last determinant are identical. It should be emphasized that the equation can be formulated in many ways by including different μ_i in the set of eliminated variables. All such alternative equations apply simultaneously and together they give the direction of the phase field. We shall now consider various cases by considering different values of $p - c$ and in some cases different values of p .

For $\mathbf{p} = \mathbf{c} + \mathbf{1}$ we have a univariant equilibrium according to Gibbs' phase rule, $\nu = 1$, and shall thus obtain a linear phase field in the potential phase diagram. All the $d\mu_i$ or $d(\mu_i/T)$ can be eliminated mathematically because $c = p - 1$. Furthermore, in this case each column in each determinant contains all the x_i in a phase and we can make use of $\sum x_i = 1$ in the remaining terms,

$$\left| \begin{array}{cccc} H_m^\alpha & 1 & x_2^\gamma & \dots & x_c^\epsilon \end{array} \right| d(1/T) + \left| \begin{array}{cccc} V_m^\alpha & 1 & x_2^\gamma & \dots & x_c^\epsilon \end{array} \right| dP/T = 0. \quad (8.39)$$

This gives the direction of the phase field in a $(1/T)$, P phase diagram produced by projection of the complete phase diagram. As an example, for a binary system with three phases the equation gives

$$\left| \begin{array}{ccc} H_m^\alpha & 1 & x_2^\gamma \end{array} \right| d(1/T) + \left| \begin{array}{ccc} V_m^\alpha & 1 & x_2^\gamma \end{array} \right| dP/T = 0. \quad (8.40)$$

This gives the slope of the phase field for a univariant phase equilibrium in a projection onto the $(1/T)$, P side of the phase diagram. It can also be written as follows,

$$\frac{dP}{dT} = \frac{(x_2^\gamma - x_2^\beta)H_m^\alpha + (x_2^\alpha - x_2^\gamma)H_m^\beta + (x_2^\beta - x_2^\alpha)H_m^\gamma}{(x_2^\gamma - x_2^\beta)V_m^\alpha + (x_2^\alpha - x_2^\gamma)V_m^\beta + (x_2^\beta - x_2^\alpha)V_m^\gamma} \cdot \frac{1}{T}. \quad (8.41)$$

In Section 13.2 we shall see that the equation can be reduced to a much simpler form. In fact, the numerator is equal to the heat of the three-phase reaction between α , β and γ and is thus independent of the choice of reference states chosen for the H values. The denominator is equal to the change in volume. Thus, the value of dP/dT is independent of the choice of references, as it should be, and Eq. (8.41) is a generalization of Eq. (8.17).

If we had eliminated $d(\mu_1/T)$ and dP instead of $d(\mu_1/T)$ and $d(\mu_2/T)$ we would have obtained

$$\frac{d(\mu_2/T)}{d(1/T)} = \frac{(V_m^\gamma - V_m^\beta)H_m^\alpha + (V_m^\alpha - V_m^\gamma)H_m^\beta + (V_m^\beta - V_m^\alpha)H_m^\gamma}{(V_m^\gamma - V_m^\beta)x_2^\alpha + (V_m^\alpha - V_m^\gamma)x_2^\beta + (V_m^\beta - V_m^\alpha)x_2^\gamma}. \quad (8.42)$$

This is the slope of the phase field for a univariant phase equilibrium in a projection onto the (μ_2/T) , $(1/T)$ side of the complete phase diagram. The value of the numerator here depends upon the choice of reference states for the H values and that choice will thus affect the value of $d(\mu_2/T)/d(1/T)$.

For $\mathbf{p} = \mathbf{c}$ we have a divariant equilibrium, $\nu = 2$, and the corresponding phase field will form a surface in the phase diagram. We can, for instance, eliminate all $d(\mu_i/T)$ terms except for $d(\mu_c/T)$ and obtain a relation between $d(1/T)$, dP and $d(\mu_c/T)$, representing the direction of the two-dimensional phase field in a three-dimensional projection of the complete phase diagram:

$$\begin{aligned} & \left| \begin{array}{cccc} H_m^\alpha & x_1^\beta & x_2^\gamma & \dots & x_{c-1}^\epsilon \end{array} \right| d(1/T) + \left| \begin{array}{cccc} (V_m^\alpha/T) & x_1^\beta & x_2^\gamma & \dots & x_{c-1}^\epsilon \end{array} \right| dP \\ & = \left| \begin{array}{cccc} x_c^\alpha & x_1^\beta & x_2^\gamma & \dots & x_{c-1}^\epsilon \end{array} \right| d(\mu_c/T). \end{aligned} \quad (8.43)$$

Under isobaric conditions we obtain a one-dimensional phase field, the slope of which is given by

$$\left| x_1^\alpha \quad x_2^\beta \quad \dots \quad x_{c-1}^\delta \quad H_m^\varepsilon \right| d(1/T) = \left| x_1^\alpha \quad x_2^\beta \quad \dots \quad x_{c-1}^\delta \quad x_c^\varepsilon \right| d(\mu_c/T). \quad (8.44)$$

For $p = c - 1$ we obtain a similar equation but now two terms will remain of the summations in Eqs (8.38) and (8.39) since both c and $c - 1$ will be larger than $p - 1$. Under isobarothermal conditions it simplifies to

$$\left| x_{c-1}^\alpha x_1^\beta \quad \dots \quad x_{c-2}^\varepsilon \right| d\mu_{c-1} + \left| x_c^\alpha x_1^\beta \quad \dots \quad x_{c-2}^\varepsilon \right| d\mu_c = 0. \quad (8.45)$$

We may thus evaluate the slope $d\mu_c/d\mu_{c-1}$ for the one-dimensional phase field in the constant T and P section of the phase diagram. We can see that it is completely defined by the ratio of two subdeterminants of the complete composition determinant.

For a two-phase equilibrium in a ternary system at constant T and P , the equation reduces to

$$\frac{d\mu_2}{d\mu_3} = -\frac{x_3^\alpha x_1^\varepsilon - x_1^\alpha x_3^\varepsilon}{x_2^\alpha x_1^\varepsilon - x_1^\alpha x_2^\varepsilon} = -\frac{z_3^\alpha - z_3^\varepsilon}{z_2^\alpha - z_2^\varepsilon}. \quad (8.46)$$

This is an example where the final result is simplified by introducing the z variables defined as $z_i = x_i/x_1$. This equation was derived in a more direct way when ternary systems were discussed in Section 8.7. We could apply the present method to two-phase equilibria in general, obtaining

$$\sum_2^c (z_i^\alpha - z_i^\beta) d\mu_i = -(S_{m1}^\alpha - S_{m1}^\beta) dT + (V_{m1}^\alpha - V_{m1}^\beta) dP \quad (8.47)$$

$$\sum_2^c (z_i^\alpha - z_i^\beta) d(\mu_i/T) = (H_{m1}^\alpha - H_{m1}^\beta) d(1/T) + (V_{m1}^\alpha - V_{m1}^\beta) dP/T. \quad (8.48)$$

Exercise 8.11

Calculate the change of μ_O for the Al + Al₂O₃ two-phase equilibrium when the pressure is increased. The densities of the phases are 2.7 and 3.5 g/cm³, respectively.

Hint

Since $p = 2$ and also $c = 2$, we have the case $p = c$ and there is a relation between $d(\mu_c/T)$, $d(1/T)$ and dP . It is thus necessary to define the problem better. Let us assume that the intention was to keep T constant.

Solution

Let Al be α : $V_m^\alpha = (1/2.7) \cdot 27 = 10 \text{ cm}^3/\text{mole}$ of atoms. Let Al₂O₃ be β : $V_m^\beta = (1/3.5) \cdot (102/5) = 5.8 \text{ cm}^3/\text{mole}$ of atoms. $(\partial(\mu_O/T)/\partial P)_T = (x_1^\alpha V_m^\beta - x_1^\beta V_m^\alpha) / T(x_1^\alpha x_2^\beta - x_1^\beta x_2^\alpha) = (1 \cdot 5.8 - 0.4 \cdot 10) / T(1 \cdot 0.6 - 0) = 3/T \text{ cm}^3/\text{mol K}$.

Since $T = \text{constant}$, $J = \text{Nm}$ and $\text{Pa} = \text{N/m}^2$ we get $(\partial\mu_O/\partial P)_T = 3 \times 10^{-6} \text{ J/molPa}$.

8.9 Extremum in temperature and pressure

For convenience we shall now use the relation derived from the Gibbs–Duhem relation in its ordinary form, i.e. we shall use S instead of H .

For $p = c$ we obtain, by rearranging the terms in the determinants,

$$\begin{aligned} & - \begin{vmatrix} x_1^\alpha & x_2^\beta & \dots & x_{c-1}^\delta & S_m^\epsilon \end{vmatrix} dT + \begin{vmatrix} x_1^\alpha & x_2^\beta & \dots & x_{c-1}^\delta & V_m^\epsilon \end{vmatrix} dP \\ & = \begin{vmatrix} x_1^\alpha & x_2^\beta & \dots & x_{c-1}^\delta & x_c^\epsilon \end{vmatrix} d\mu_c. \end{aligned} \quad (8.49)$$

Suppose the composition determinant on the right-hand side is zero, i.e., suppose

$$\begin{vmatrix} x_1^\alpha & x_2^\beta & \dots & x_{c-1}^\delta & x_c^\epsilon \end{vmatrix} = 0. \quad (8.50)$$

Under isobaric conditions this would yield $dT/d\mu_c = 0$ for the linear phase field obtained in the μ_c, T phase diagram and the phase field must go through a temperature extremum. Equation (8.50) is thus the requirement for an extremum to occur and it can also be written in the following form because $\sum x_i = 1$ in each phase,

$$\begin{vmatrix} 1 & x_2^\beta & \dots & x_{c-1}^\delta & x_c^\epsilon \end{vmatrix} = 0. \quad (8.51)$$

This is a well-known equation from the theory of determinants and shows that the phases fall on the same point (i.e. have the same composition) for $c = p = 2$, they fall on a straight line for $c = p = 3$, on a plane surface for $c = p = 4$, etc. The first two cases are described by Konovalov's and von Alkemade's rules, respectively (see Sections 10.8 and 10.9). Furthermore, if one knows that there is such a temperature extremum under isobaric conditions, then one can conclude that the composition determinant must be zero and the equation shows that there will also be a pressure extremum under isothermal conditions. For a binary case, $c = p = 2$, this is illustrated in Fig. 8.23.

For $p = c - 1$ we obtain

$$\begin{aligned} & - \begin{vmatrix} x_1^\alpha & x_2^\beta & \dots & x_{c-2}^\delta & S_m^\epsilon \end{vmatrix} dT + \begin{vmatrix} x_1^\alpha & x_2^\beta & \dots & x_{c-2}^\delta & V_m^\epsilon \end{vmatrix} dP \\ & = \begin{vmatrix} x_1^\alpha & x_2^\beta & \dots & x_{c-2}^\delta & x_{c-1}^\epsilon \end{vmatrix} d\mu_{c-1} + \begin{vmatrix} x_1^\alpha & x_2^\beta & \dots & x_{c-2}^\delta & x_c^\epsilon \end{vmatrix} d\mu_c. \end{aligned} \quad (8.52)$$

In order to obtain an extremum in T at constant P (and thus in P at constant T), it is now necessary that two determinants are zero,

$$\begin{vmatrix} x_1^\alpha & x_2^\beta & \dots & x_{c-2}^\delta & x_{c-1}^\epsilon \end{vmatrix} = 0 \quad (8.53)$$

$$\begin{vmatrix} x_1^\alpha & x_2^\beta & \dots & x_{c-2}^\delta & x_c^\epsilon \end{vmatrix} = 0. \quad (8.54)$$

For a binary system this condition has no meaning because $p = 1$. For $p = 2$ and $c = 3$ it implies that the two phases fall on the same point in the composition plane (in agreement with a generalization of Konovalov's rule), for $p = 3$ and $c = 4$ it implies that the three phases fall on a straight line in the composition volume (in agreement with a generalization of Alkemade's rule), etc. For a ternary system this can be demonstrated

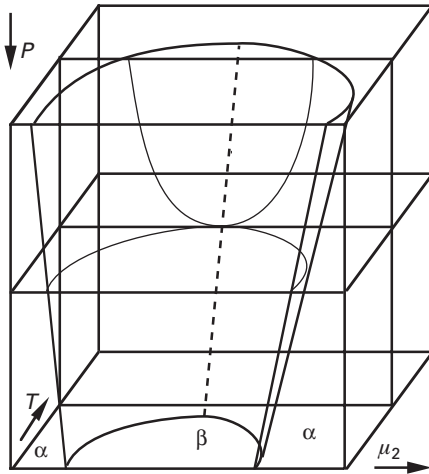


Figure 8.23 Potential phase diagram for a binary system showing a divariant phase field having a T extremum in an isobaric section (see thin horizontal curve). It follows that an isothermal section will show a P extremum (see thin vertical curve).

easily

$$\begin{vmatrix} x_1^\alpha & x_2^\beta \end{vmatrix} = 0 \quad (8.55)$$

$$\begin{vmatrix} x_1^\alpha & x_3^\beta \end{vmatrix} = 0. \quad (8.56)$$

By adding the two equations we get

$$0 = \begin{vmatrix} x_1^\alpha & (x_2^\beta + x_3^\beta) \end{vmatrix} = |x_1^\alpha 1| = x_1^\alpha - x_1^\beta. \quad (8.57)$$

or $x_1^\alpha = x_1^\beta$. By inserting this in the Eqs (8.55) and (8.56) we get $x_2^\alpha = x_2^\beta$ and $x_3^\alpha = x_3^\beta$ and, consequently, also $\begin{vmatrix} x_2^\alpha & x_3^\beta \end{vmatrix} = 0$. This case is illustrated in Fig. 8.24 which may be regarded as a diagram corresponding to the P section through the diagram in Fig. 8.23 but with one more axis due to the third element. It follows from Eq. (8.52) that here will also be an extremum in P under isothermal conditions but we would need four dimensions to show a diagram corresponding to the whole diagram in Fig. 8.23.

For $p = c - 2$ the conditions for an extremum in T at constant P (and thus in P for constant T) is obtained as a set of three determinants equal to zero and this means that the compositions of the phases fall on the same point for $p = 2$ and $c = 4$, same line for $p = 3$ and $c = 5$, same plane for $p = 4$ and $c = 2$, etc.

Exercise 8.12

Consider a three-phase equilibrium at 1 bar in a ternary system between pure A, a compound B_1C_1 and a third phase with variable composition. Can this equilibrium go through a T maximum? Under what conditions?

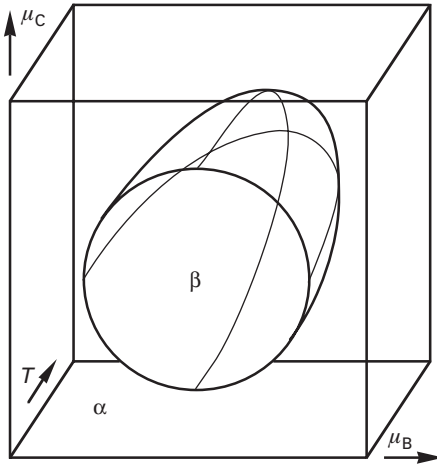


Figure 8.24 Potential phase diagram showing a divariant phase field with a T extremum at a certain combination μ_B, μ_C . The complete phase diagram has been sectioned at a constant P .

Hint

Notice that $p = 3$ and $c = 3$ and thus $c = p$.

Solution

$$0 = \begin{vmatrix} x_1^\alpha & x_2^\alpha & x_3^\alpha \\ x_1^\beta & x_2^\beta & x_3^\beta \\ x_1^\gamma & x_2^\gamma & x_3^\gamma \end{vmatrix} = \begin{vmatrix} 1 & x_2^\alpha & x_3^\alpha \\ 1 & x_2^\beta & x_3^\beta \\ 1 & x_2^\gamma & x_3^\gamma \end{vmatrix} = \begin{vmatrix} 1 & 0 & 0 \\ 1 & 0.5 & 0.5 \\ 1 & x_2^\gamma & x_3^\gamma \end{vmatrix} = 0.5x_C^\gamma - 0.5x_B^\gamma,$$

or $x_B^\gamma = x_C^\gamma$. The variable phase must fall on the straight line between A and B_1C_1 in order for a T extremum to occur. However, we cannot tell if it will be a T maximum or minimum.

Exercise 8.13

Consider a ternary system where the potential of the third component is kept constant (by means of a high diffusivity and equilibrium with an external reservoir). The pressure is also kept constant. Suppose one will thus find that there is a maximum temperature for a certain $\alpha + \beta$ equilibrium. What conclusion can be drawn regarding the compositions of the two phases? What would be the most convenient composition variable to use in such a case?

Hint

$p = c - 1$. Equation (8.52) was derived for that case. Under constant P and μ_c it yields

$$\begin{vmatrix} x_1^\alpha & x_2^\beta & \dots & x_{c-2}^\delta & x_{c-1}^\epsilon \end{vmatrix} d\mu_{c-1} = - \begin{vmatrix} x_1^\alpha & x_2^\beta & \dots & x_{c-2}^\delta & S_m^\epsilon \end{vmatrix} dT.$$

Solution

At the T maximum, the equation yields $|x_1^\alpha \ x_2^\beta \ \dots \ x_{c-2}^\delta \ x_{c-1}^\epsilon| = 0$ and for a ternary system $|x_1^\alpha \ x_2^\beta| = 0$ or $x_1^\alpha/x_2^\alpha = x_1^\beta/x_2^\beta$. The ratio of components 1 and 2 is thus the same in the two phases. The most convenient composition variable in this case is $u_i = x_i/(1 - x_c)$ since $u_1 + u_2 + \dots + u_{c-1} = 1$ and we find

$$|u_1^\alpha \ u_2^\beta \ \dots \ u_{c-2}^\delta \ u_{c-1}^\epsilon| = |1 \ u_2^\beta \ \dots \ u_{c-2}^\delta \ u_{c-1}^\epsilon| = 0.$$

For a ternary system we get $|1 \ u_2^\beta| = u_2^\alpha - u_2^\beta = 0$.

9 Molar phase diagrams

9.1 Molar axes

If one starts from a potential phase diagram, one may decide to replace one of the potentials by its conjugate variable. However, the potential phase diagram has no information on the size of the system and one should thus accept introducing a molar quantity rather than its extensive variable. By replacing all the potentials with their conjugate molar variables, one gets a molar diagram. One would like to retain the diagram's character of a true phase diagram, which means that there should be a unique answer as to which phase or phases are stable at each location. In this chapter we shall examine the properties of molar diagrams and we shall find under what conditions they are true phase diagrams. Only then may they be called **molar phase diagrams**. However, we shall start with a simple demonstration of how a diagram changes when molar axes are introduced.

Figure 9.1(a)–(d) demonstrates what happens to a part of the T, P potential phase diagram for Fe when S_m and V_m axes are introduced. Initially the P axis is plotted in the negative direction because V is conjugate to $-P$. It can be seen that the one-phase fields separate and leave room for a two-phase field. It can be filled with tie-lines connecting the points representing the individual phases in the two-phase equilibrium. It is self-evident how to draw them when one axis is still a potential but they yield additional information when all axes are molar (Fig. 9.1(d)).

Figure 9.2(a)–(d) is a similar demonstration using a part of the Fe phase diagram with a three-phase equilibrium, a triple point. It forms a tie-triangle when both potentials have been replaced (Fig. 9.2(d)). All the phase fields are then two-dimensional. One may also notice that each one-phase field from the potential diagram maintains its general shape. Their corners still have angles less than 180° (see the 180° rule formulated in Section 8.3).

It should be emphasized that the phase fields never overlap in these diagrams. They may all be classified as true phase diagrams because each point represents one and only one phase equilibrium. Three requirements must be fulfilled in order for this to happen. Firstly, the two one-phase fields meeting at a two-phase line in a potential phase diagram must move away from each other and leave room for an extended two-phase field, when a molar axis is introduced. Secondly, the one-phase field extending from the two-phase field in the direction of increasing values of a potential must also extend to increasing values of the conjugate molar variable that is introduced. If it goes the other way, it would overlap the two-phase region. The other one-phase field must extend in the other

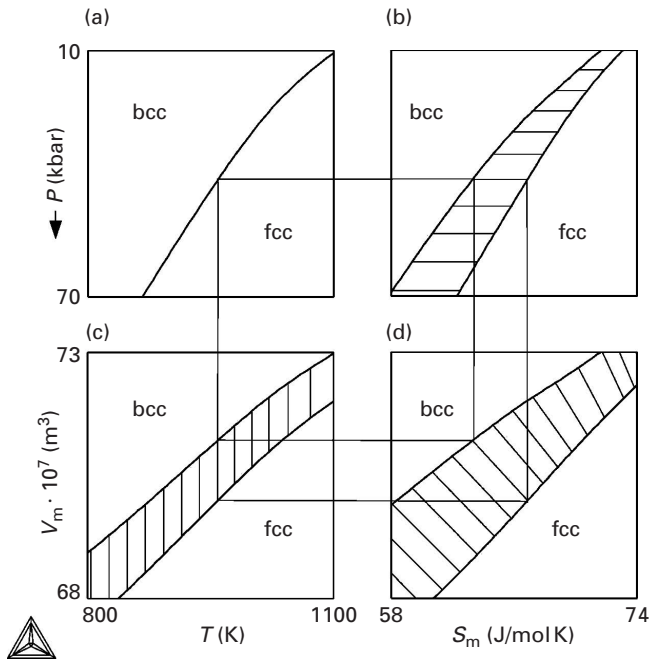


Figure 9.1 Introduction of molar axes instead of potential axes in a part of the unary phase diagram for Fe with two phases.

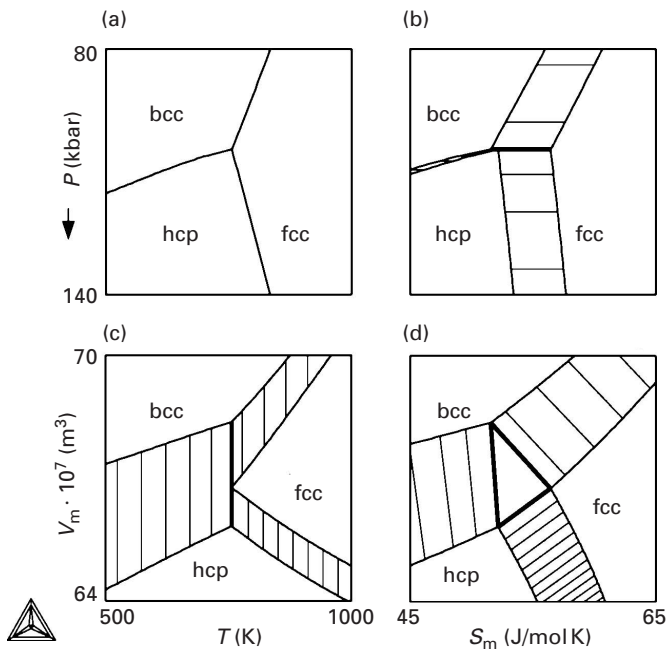


Figure 9.2 Introduction of molar axes instead of potential axes in a part of the unary phase diagram for Fe with three phases. All phase fields here become two-dimensional.

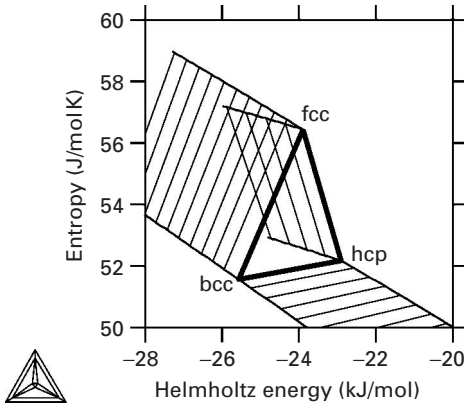


Figure 9.3 S, H diagram for Fe. This is not a true phase diagram because S and H never appear in the same set of conjugate variables.

direction, before as well as after replacing the potential with the conjugate molar variable. Thirdly, a one-phase field is nowhere allowed to fold over itself.

The last two requirements are fulfilled if the system is everywhere stable because of the stability condition from Eq. (6.28),

$$\left(\frac{\partial Y^b}{\partial X^b} \right)_{Y^c, X^d} > 0. \quad (9.1)$$

The potential Y^b and its conjugate variable X^b thus increase in the same direction. However, as already emphasized, this stability condition requires that all the variables to be kept constant, here represented by Y^c, X^d , come from the same set of conjugate pairs as Y^b and X^b . Nine such sets were presented in Table 3.1 but it is necessary to examine what happens to them when the size of the system is measured in different ways. This will be discussed in the next section. Figure 9.3 is an example of what can happen if one uses two molar variables which do not appear in the same set of conjugate variables, S and H . It is not a true phase diagram according to the definition given at the very beginning of this section. Other cases will be discussed in Section 10.7.

The first requirement can be tested as follows, using the form of the Gibbs–Duhem relation with molar quantities introduced in Eq. (8.4),

$$d\mu_1 = -S_{m1}dT + V_{m1}dP - \sum_2^c z_i d\mu_i = - \sum_2^{c+2} X_{m1}^j dY^j. \quad (9.2)$$

Consider two phases, α and β , which are initially in equilibrium with each other. The system is then moved away from equilibrium by changing the value of one potential, Y^j , keeping the other independent potentials in the summation constant. Applying the Gibbs–Duhem relation to each of the two phases and taking the difference, we obtain

$$d(\mu_1^\beta - \mu_1^\alpha) = (X_{m1}^{j\alpha} - X_{m1}^{j\beta})dY^j. \quad (9.3)$$

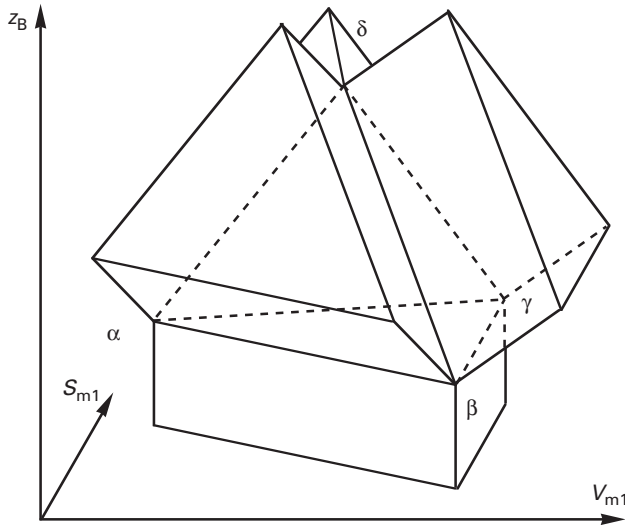


Figure 9.4 Four-phase equilibrium in a phase diagram with three molar axes. The four-phase field is tetrahedral and is covered by triangular prisms representing three-phase equilibria. The two- and one-phase fields are not outlined but they are also three-dimensional.

Suppose α is the phase favoured by the increased Y^j value. Then μ_1^α must be smaller than μ_1^β as demonstrated by Fig. 8.3. We thus obtain

$$X_{m1}^{j\alpha} - X_{m1}^{j\beta} = \frac{d(\mu_1^\beta - \mu_1^\alpha)}{dY^j} > 0. \quad (9.4)$$

It is thus evident that the two one-phase fields will move apart by a positive distance $X_{m1}^{j\alpha} - X_{m1}^{j\beta}$ when X_{m1}^j is introduced as an axis instead of Y^j . The one-phase fields will separate and give room for the two-phase field in between, $X_{m1}^{j\alpha} - X_{m1}^{j\beta}$ being the length of the tie-line.

In a binary system there are three independent potential axes. If they are all replaced by molar axes, all the phase fields become three-dimensional and the invariant four-phase equilibrium expands into a tetrahedron. This is demonstrated by Fig. 9.4 which corresponds to the central region of Fig. 8.11.

It was emphasized that the topology of potential phase diagrams is very simple and each geometrical element is a phase field. A phase diagram with only molar axes has a relatively simple topology. All the phase fields have the same dimensionality as the diagram itself. For the unary system in Fig. 9.2 all the phase fields have two dimensions and for the binary system in Fig. 9.4 they have three dimensions.

Exercise 9.1

Suppose one studies the total vapour pressure of a liquid mixture of two metals, A and B, at a constant temperature. One finds that the total vapour pressure increases if more B is added to the mixture. Show whether the vapour or the liquid is richer in B.

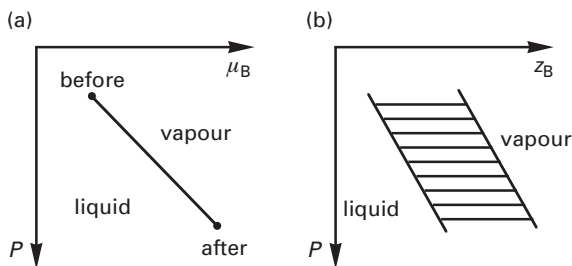


Figure 9.5 Solution to Exercise 9.1.

Hint

At constant T , the P , μ_B potential phase diagram will be two-dimensional. Sketch it using μ_A as the dependent potential variable. Remember that the conjugate composition variable to μ_B would then be $z_B = N_B/N_A$. High pressure should favour the liquid, being much denser than the vapour.

Solution

The construction (Fig. 9.5) shows that the vapour would be richer in B than the liquid if measured relative to A.

9.2 Sets of conjugate pairs containing molar variables

A molar variable can easily be introduced in the stability condition, Eq. (6.28), by dividing X^b with the quantity used to define the size of the system because that quantity is kept constant. Expressing the size by N , we get for instance,

$$\left(\frac{\partial Y^b}{\partial X_m^b} \right)_{Y^c, X_m^d} = N \cdot \left(\frac{\partial Y^b}{\partial X^b} \right)_{Y^c, X^d} > 0. \quad (9.5)$$

However, with this measure of size the Gibbs–Duhem relation gives

$$S_m dT - V_m dP + \sum x_i d\mu_i = 0, \quad (9.6)$$

where one of the x_i is dependent on the others because $\sum x_i = 1$. Choosing x_1 as the dependent one, we obtain $x_1 = 1 - \sum_2 x_i$,

$$-d\mu_1 = S_m dT - V_m dP + \sum_2 x_i d(\mu_i - \mu_1). \quad (9.7)$$

Then it is logical to regard μ_1 as the dependent potential but the consequence is that the conjugate variable to x_i is no longer μ_i but $(\mu_i - \mu_1)$.

If we instead measure the size with the amount of a certain component, N_1 , then we obtain the form given by Eq. (9.2),

$$-d\mu_1 = S_{m1} dT - V_{m1} dP + \sum_2 z_i d\mu_i. \quad (9.8)$$

Table 9.1 Sets of conjugate pairs of independent state variables using molar quantities defined by dividing with $\sum N_i$

T, S_m	$-P, V_m$	$\sum_2 (\mu_i - \mu_1), x_i$
$T, (TS_m - PV_m)/T$	$-P/T, TV_m$	$\sum_2 (\mu_i - \mu_1), x_i$
$T/P, PS_m$	$P, (TS_m - PV_m)/P$	$\sum_2 (\mu_i - \mu_1), x_i$
$-1/T, U_m$	$-P/T, V_m$	$\sum_2 (\mu_i - \mu_1)/T, x_i$
$-1/T, H_m$	$-P, V_m/T$	$\sum_2 (\mu_i - \mu_1)/T, x_i$
$-P/T, H_m/P$	$-1/P, PU_m/T$	$\sum_2 (\mu_i - \mu_1)/T, x_i$
$T/P, S_m$	$-1/P, U_m$	$\sum_2 (\mu_i - \mu_1)/P, x_i$
$-1/T, TU_m/P$	$-T/P, F_m/T$	$\sum_2 (\mu_i - \mu_1)/P, x_i$
$T, S_m/P$	$-1/P, F_m$	$\sum_2 (\mu_i - \mu_1)/P, x_i$

In this way one may keep μ_i but its conjugate variable is $z_i = N_i/N_j$ and S_{m1} and V_{m1} are also defined by dividing with N_1 .

Sometimes it is convenient to measure the size as the total content of more than one component, e.g. of those which do not easily evaporate. Suppose they are the first k components. Using $u_1 = 1 - \sum_2^k u_i$ we obtain

$$S_{m(1\dots k)}dT - V_{m(1\dots k)}dP + \sum_2^c u_{i(1\dots k)}d\mu_i = 0 \quad (9.9)$$

$$-d\mu_1 = S_{m(1\dots k)}dT - V_{m(1\dots k)}dP + \sum_2^k u_{i(1\dots k)}d(\mu_i - \mu_1) + \sum_{k+1}^c u_{i(1\dots k)}d\mu_i = 0. \quad (9.10)$$

where the S , V and u variables are defined in Section 4.3.

These three methods of measuring the size of the system can be applied to all the rows in Table 3.1. We may thus construct Tables 9.1, 9.2 and 9.3 for the sets of conjugate potentials and molar variables. Each row defines a set of conjugate variables and each pair can be used to construct a stability condition if the variables to be kept constant are taken from the same set. There is an important difference from Table 3.1 which gave sets of conjugate pairs related by the Gibbs–Duhem relation. A dependent potential has now been eliminated using the Gibbs–Duhem relation and the new tables contain one pair less and give sets of pairs of independent variables.

Table 9.2 Sets of conjugate pairs of independent state variables using molar quantities defined by dividing with N_1

T, S_{m1}	$-P, V_{m1}$	$\sum_2 \mu_i, z_i$
$T, (TS_{m1} - PV_{m1})/T$	$-P/T, TV_{m1}$	$\sum_2 \mu_i, z_i$
$T/P, PS_{m1}$	$P, (TS_{m1} - PV_{m1})/P$	$\sum_2 \mu_i, z_i$
$-1/T, U_{m1}$	$-P/T, V_{m1}$	$\sum_2 \mu_i/T, z_i$
$-1/T, H_{m1}$	$-P, V_{m1}/T$	$\sum_2 \mu_i/T, z_i$
$-P/T, H_{m1}/P$	$-1/P, PU_{m1}/T$	$\sum_2 \mu_i/T, z_i$
$T/P, S_{m1}$	$-1/P, U_{m1}$	$\sum_2 \mu_i/P, z_i$
$-1/T, TU_{m1}/P$	$-T/P, F_{m1}/T$	$\sum_2 \mu_i/P, z_i$
$T, S_{m1}/P$	$-1/P, F_{m1}$	$\sum_2 \mu_i/P, z_i$

Table 9.3 Sets of conjugate pairs of independent state variables using molar quantities defined by dividing with $N_1 + N_2$

T, S_{m12}	$-P, V_{m12}$	$(\mu_2 - \mu_1), u_{i(12)}$	$\sum_3 \mu_i, u_{i(12)}$
$T, (TS_{m12} - PV_{m12})/T$	$-P/T, TV_{m12}$	$(\mu_2 - \mu_1), u_{i(12)}$	$\sum_3 \mu_i, u_{i(12)}$
$T/P, PS_{m12}$	$P, (TS_{m12} - PV_{m12})/P$	$(\mu_2 - \mu_1), u_{i(12)}$	$\sum_3 \mu_i, u_{i(12)}$
$-1/T, U_{m12}$	$-P/T, V_{m12}$	$(\mu_2 - \mu_1)/T, u_{i(12)}$	$\sum_3 \mu_i/T, u_{i(12)}$
$-1/T, H_{m12}$	$-P, V_{m12}/T$	$(\mu_2 - \mu_1)/T, u_{i(12)}$	$\sum_3 \mu_i/T, u_{i(12)}$
$-P/T, H_{m12}/P$	$-1/P, PU_{m12}/T$	$(\mu_2 - \mu_1)/T, u_{i(12)}$	$\sum_3 \mu_i/T, u_{i(12)}$
$T/P, S_{m12}$	$-1/P, U_{m12}$	$(\mu_2 - \mu_1)/P, u_{i(12)}$	$\sum_3 \mu_i/P, u_{i(12)}$
$-1/T, TU_{m12}/P$	$-T/P, F_{m12}/T$	$(\mu_2 - \mu_1)/P, u_{i(12)}$	$\sum_3 \mu_i/P, u_{i(12)}$
$T, S_{m12}/P$	$-1/P, F_{m12}$	$(\mu_2 - \mu_1)/P, u_{i(12)}$	$\sum_3 \mu_i/P, u_{i(12)}$

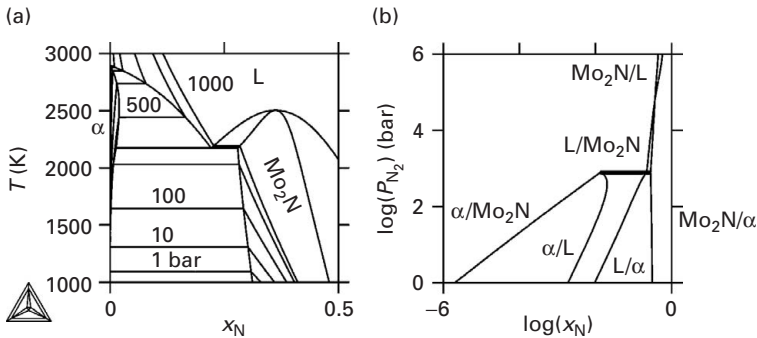


Figure 9.6 See Exercise 9.3.

Exercise 9.2

At the end of Section 6.6 we found that the stability limit in a binary solution is $g_{22} = 0$. Show how this condition can be obtained from the list of conjugate variables presented in Table 9.1.

Hint

The index 2 in g_{22} indicates a derivative with respect to x_2 , with x_1 as a dependent variable. Thus, one should use a set of conjugate variables containing x_2 .

Solution

From the first row of Table 9.1 we can formulate the condition $(\partial(\mu_2 - \mu_1)/\partial x_2)_{T,P,N} = 0$. However, x_1 is a dependent variable and $\mu_2 - \mu_1 = \partial G_m/\partial x_2$ and our stability condition can be expressed as $\partial^2 G_m/\partial x_2^2 = 0$ and g_{22} is the notation for that derivative.

Exercise 9.3

Two diagrams of the Mo-N system are presented in Fig. 9.6. How would you interpret them?

Hint

In diagram (a) notice that the phase field for the gas is not included but isobars for the N_2 gas are given. In order to interpret diagram (b) it is helpful first to construct a $T, \log P_{\text{N}_2}$ diagram and then replace the T axis with a $\log x_N$ axis.

Solution

Diagram (a) above is a T, x_N diagram at 1 bar. The lines for various N_2 pressures should be understood as isoactivity lines for N expressed as P_{N_2} of a gas which is not present.

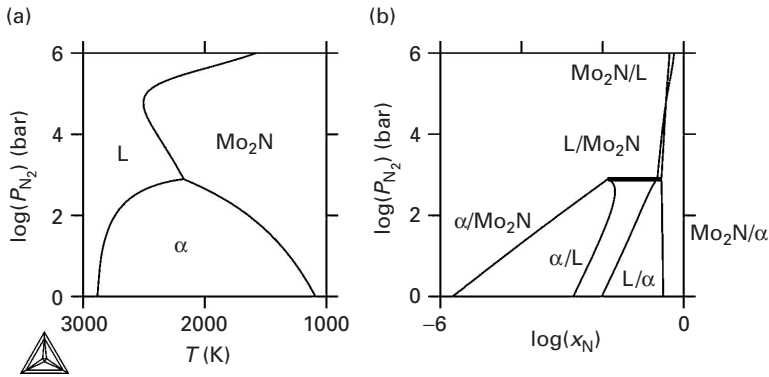


Figure 9.7 Solution to Exercise 9.3.

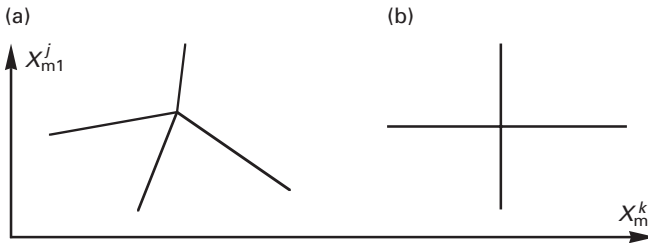


Figure 9.8 (a) Elementary unit of a phase diagram with two molar axes. (b) Topological equivalence.

Using these values of P_{N_2} it is easy to construct a $T, \log P_{N_2}$ diagram (see Fig. 9.7(a)). For convenience, we shall make T the abscissa. Next we shall introduce x_N (with a logarithmic scale) instead of T , i.e. a molar quantity instead of a potential. The two-phase fields will open up but there may be overlapping because the new variable, x_N , is not conjugate to the old one, T . As an example, the $\alpha + L$ field falls inside the $\alpha + Mo_2N$ field.

9.3 Phase boundaries

Since all the phase fields in a molar diagram have the same dimensionality as the diagram has axes, it is evident that all other geometrical elements, surfaces, line and points in a three-dimensional diagram, are not phase fields. They separate phase fields and may be called **phase boundaries**. When discussing the topology of a molar phase diagram in terms of the phase boundaries, it is possible and convenient to choose a smaller elementary unit than a phase field. A smaller unit is shown in Fig. 9.8(a) and it is composed of four linear phase boundaries meeting at a point. Topologically it may be represented by two intersecting lines as shown in Fig. 9.8(b). Any complicated two-dimensional phase diagram with molar axes is composed of such units.

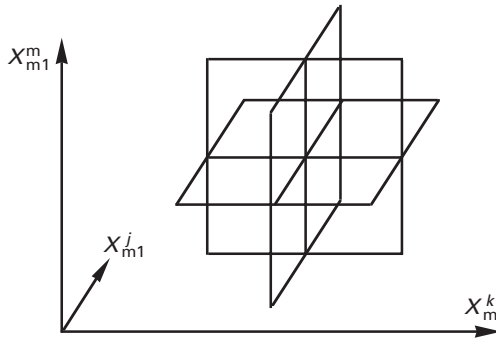


Figure 9.9 Elementary unit of a phase diagram with three molar axes.

It can be seen by inspection of the three-dimensional diagram in Fig. 9.4, that it is possible to divide it into four topologically identical, elementary units, each one composed of a point where eight phase fields meet, although only four of them are shown. Six linear phase boundaries radiate from these points. They are all shown for the β and δ points. Topologically, this elementary unit can be represented by three intersecting planes as shown in Fig. 9.9. Evidently, the topology of a complicated three-dimensional molar diagram can be represented by a system of intersecting surfaces.

When studying two-dimensional molar diagrams, Masing [11] observed that the number of phases in the phase fields changes by one unit when one crosses a linear phase boundary. This is easily verified by inspection of Fig. 9.2(d). Masing's rule was later generalized by Palatnik and Landau [12] who gave it the following form

$$D^+ + D^- = r - b, \quad (9.11)$$

where D^+ and D^- are the number of phases that appear and disappear, respectively, as one crosses a phase boundary of dimensionality b , and r is the number of axes in the molar diagram. This rule may be referred to as the **MPL boundary rule**, after Masing, Palatnik and Landau.

It may be added that phase boundaries sometimes have special names. The boundary between a liquid phase and a liquid + solid phase field is called the **liquidus** and the corresponding boundary for the coexisting solid phase is called the **solidus**. The boundary between a solid and the two-phase field with another solid is sometimes called the **solvus**.

Exercise 9.4

In the central region of Fig. 9.4 there is a tetrahedron, representing a four-phase field. Apply the MPL rule in order to find how many phases there are outside the $\alpha - \beta$ line and outside the β point.

Hint

There are only four phases in the system and D^+ must be zero when we move out from the four-phase field because there is no new phase that can be added.

Solution

This is a three-dimensional diagram, $r = 3$, and the dimensionality of the $\alpha - \beta$ line is one, $b = 1$. We get $D^- = r - b = 3 - 1 = 2$. The number of phases has decreased from 4 to 2. We have moved into the $\alpha + \beta$ two-phase region by crossing the $\alpha - \beta$ line. The dimensionality of the β point is zero, $b = 0$, and we get $D^- = r - b = 3 - 0 = 3$. The number of phases has decreased from 4 to 1. We have moved into the β one-phase region by crossing the β point.

9.4 Sections of molar phase diagrams

A diagram with a full set of molar axes may be called a **complete molar phase diagram**. For practical reasons one often likes to reduce the number of axes. A popular method is to section at a constant value of a potential, e.g. P or T . The resulting diagram looks just like a complete molar phase diagram for a system with one component less. Another method is to section at a constant value of a molar variable, a so-called **isoplethal section** or an **isopleth**.

Since all phase fields in a molar phase diagram have the same dimensionality as the phase diagram has axes, all kinds of phase fields may show up in that kind of section whereas a phase field with the maximum number of phases (i.e. for an invariant equilibrium) will disappear in an equipotential section because the section cannot be expected to go exactly through a given point. The topology of a molar section is simplified if it is again accepted that it will not be possible to place a section exactly through a point. All two-dimensional sections with molar axes will be composed of the elementary unit shown in Fig. 9.8 and all three-dimensional sections will be composed of the elementary unit shown in Fig. 9.9, independent of how many potential or molar axes have been sectioned. Of course, if one adds a component, one must section once more in order to keep the number of dimensions. As an example, two sections through Fig. 9.4 are indicated in Fig. 9.10. In each case, the section gives the same arrangement of lines as in Fig. 9.8(a). Furthermore, the MPL boundary rule applies to the sections, since the value of $r - b$ does not change by sectioning.

Inspection of the two sections in Fig. 9.10 reveals that one shows an intersection between phase fields of 2, 3, 3 and 4 phases and the other 1, 2, 2 and 3 phases. We may thus give the general picture shown in Fig. 9.11. For the sections shown in Fig. 9.10 we have $e = 3$ and 4, respectively, where e is the highest number of phases in any of the two adjoining phase fields. In fact, the maximum value of e in a two-dimensional diagram, which is also the maximum number of phases in a phase field, depends upon the number of sectioned molar axes, n_{ms} ,

$$e_{\max} = 3 + n_{ms}. \quad (9.12)$$

Exercise 9.5

On the right-hand side of the tetrahedron in Fig. 9.10 there is a triangular prism. Make a section through that prism parallel to the side of the tetrahedron. Make a sketch of the

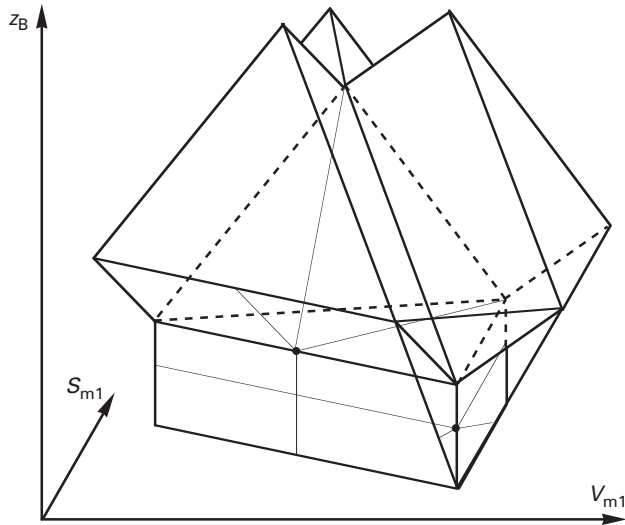


Figure 9.10 Two sections through the molar phase diagram of Fig. 9.4. The sections are shown with thin lines.

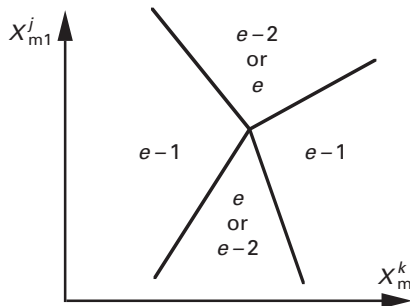


Figure 9.11 Elementary unit of a molar phase diagram, sectioned a sufficient number of times to make it two-dimensional. The diagram may have units with different e values from 3 up to a maximum, determined by the number of sectionings.

intersection obtained at the front edge of the prism. Indicate the number of phases in the four adjoining phase fields.

Hint

It may be useful to go back to the Exercise 9.4.

Solution

The solution is given in Fig. 9.12.

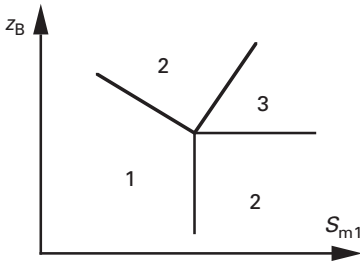


Figure 9.12 Solution to Exercise 9.5.

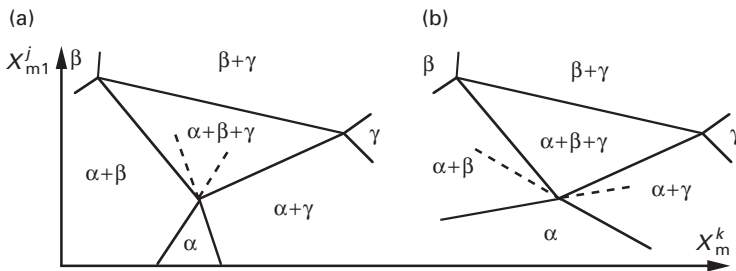


Figure 9.13 Elementary unit of a phase diagram with two molar axes. Two of the phase boundaries of the one-phase field are shown.

9.5 Schreinemakers' rule

When studying isobarothermal sections of ternary diagrams Schreinemakers [13] found that the extrapolations of the boundaries of the one-phase field in the elementary unit must either both fall inside the three-phase fields or one inside each of the two two-phase fields. This is illustrated in Fig. 9.13 and is called Schreinemakers' rule. It can be generalized in the following way [14].

Let us examine if Schreinemakers' rule applies to different e values and start by considering a complete phase diagram constructed with molar axes only. A discussion of thermodynamic properties should then be based upon the internal energy. For reversible changes we obtain

$$dU = TdS - PdV + \sum_1^c \mu_i dN_i. \quad (9.13)$$

In Section 4.6 we saw that it is always possible to introduce a new set of components instead of the old one by combining the components in a new way as long as we get a complete set of independent components and do not change the value of the sum, $\sum \mu_i dN_i$. We can do so by selecting c points in the compositional space and make sure that they can be used to define a new set of independent components by checking that three of them never fall on a line, four of them never fall on a plane, etc. We shall use this method of changing to a new set of components but we shall then consider entropy and

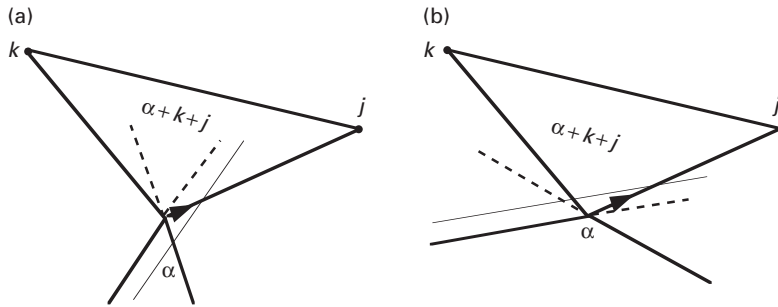


Figure 9.14 General proof of Schreinemakers' rule.

volume as components, whose amounts are expressed by S and V , and whose chemical potentials are T and $-P$, respectively. The introduction of $c + 2$ new components instead of the old ones will now be effected by selecting $c + 2$ points in the state diagram. They will each be identified by an index d .

We can follow the procedure outlined in Section 4.6 and obtain

$$dU = \sum_1^{c+2} \mu_i dN_i = \sum_1^{c+2} \mu_d dN_d, \quad (9.14)$$

where $\mu_d = \sum_i a_i^d \mu_i$ and $N_i = \sum_d a_i^d N_d$. For these generalized chemical potentials, the following Maxwell relation is obtained

$$\left(\frac{\partial \mu_j}{\partial N_k} \right)_{N_j} = \frac{\partial^2 U}{\partial N_k \partial N_j} = \left(\frac{\partial \mu_k}{\partial N_j} \right)_{N_k}. \quad (9.15)$$

When considering the cases in Fig. 9.13 with a tie-triangle in the section, we shall include the β and γ corners in the set of new components. In a more general case we shall denote them by k and j (see Fig. 9.14).

At the point under consideration, one of the two boundaries, the extrapolations of which we discuss, represents equilibrium with k , and is thus an equipotential line for k in α . If it extrapolates outside the $\alpha - k - j$ triangle, the potential of k must increase on moving closer to the point j , because this path intersects equipotential lines for k in α situated closer to the point k , i.e.

$$\frac{\partial \mu_k}{\partial N_j} > 0 \quad (9.16)$$

(see thin line in Fig. 9.14(b)). Then, from the Maxwell relation,

$$\frac{\partial \mu_j}{\partial N_k} > 0 \quad (9.17)$$

It follows that the second boundary must also extrapolate outside the $\alpha - k - j$ triangle. On the other hand, if the k boundary extrapolates into the triangle, a movement towards the point j will intersect equipotential lines for k further away from the point k (see thin line in Fig. 9.14(a)). Both derivatives must then be negative, and both boundaries must

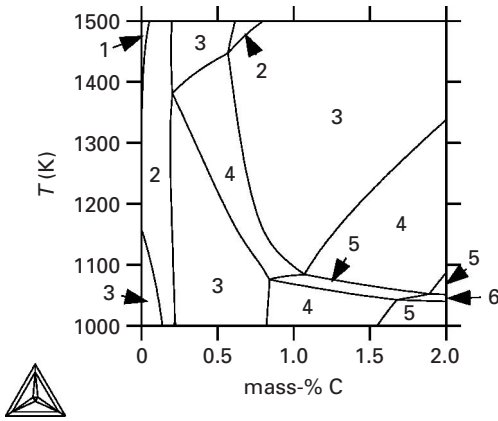


Figure 9.15 Calculated phase diagram for system with seven components. The complete phase diagram has two potential axes and six molar axes and has been sectioned at one constant potential, P , and five constant molar quantities, x_i . Schreinemakers' rule holds at all intersections. Numbers given are number of phases in each phase field.

extrapolate into the triangle. It has thus been shown that the extrapolations of both phase boundaries under consideration must fall either outside the highest-order phase field or inside it, in agreement with Schreinemakers' rule. It may be emphasized that the rule also holds for equipotential sections. In order to prove it in such a case, one must use a Maxwell relation based on a thermodynamic function which allows the corresponding potentials to be kept constant, for instance G in the case actually considered by Schreinemakers, constant T and P .

In the derivation of Schreinemakers' rule it is essential that the two boundaries of the highest-order phase field of those considered are straight lines. That this happens in the ternary case under isobarothermal conditions is self-evident because then the tie-triangle is situated in the plane of the diagram. In a quaternary system the sides of a four-phase equilibrium will be planar and the intersections shown in a two-dimensional section will be straight lines. The components k and j then represent two-phase mixtures situated in the section. On the other hand, a three-phase equilibrium will not be bounded by planar sides and its boundaries in the two-dimensional section will not be straight lines. Then the boundaries of the one-phase field will not be equipotential lines for any components k and j chosen in the section. It may be concluded that the proof, given above, is not rigorous except when an equilibrium of the highest order allowed in the section is involved. However, experience shows that Schreinemakers' rule is obeyed in most cases, and it may be used as a convenient guide when other information is lacking. As an example, the result of a computer-operated calculation of a section through a seven-component system is presented in Fig. 9.15. The rule is satisfied at all the intersections in this diagram.

Figure 9.16 shows an apparent violation of Schreinemakers' rule at the corner of the bct phase field. However, this is not a true phase diagram because S_m and z_i never appear in the same set of conjugate variables in Table 9.2.

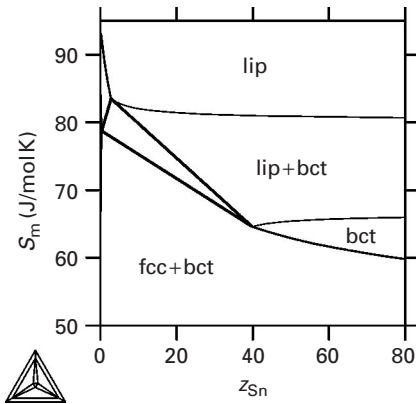


Figure 9.16 S_m , z_{Sn} diagram for Pb–Sn at 1 bar. It shows an apparent violation of Schreinemakers' rule but is not a true phase diagram.

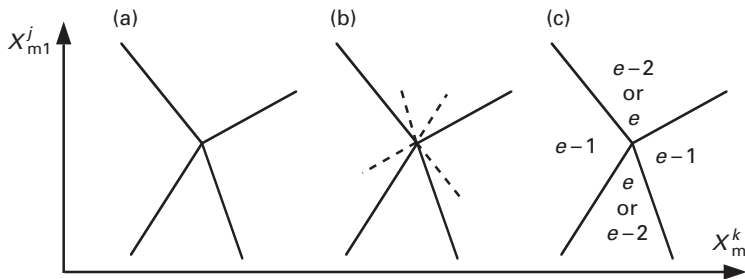


Figure 9.17 Use of Schreinemakers' rule to decide which phase fields have equal number of phases.

Usually, Schreinemakers' rule is used to predict the directions of phase boundaries. On the other hand, if the phase boundaries are given, for instance from calculation or experiment, then the rule can help to give the number of phases in the various phase fields. Suppose the arrangement in Fig. 9.17(a) is given, but the numbers of phases in the four adjoining phase fields are not known. One should then extrapolate all the lines, as shown in Fig. 9.17(b). Two of the phase fields will contain one extrapolation each, and these phase fields will be opposite to one another. According to Schreinemakers' rule, these will be the phase fields with the same number of phases, $e - 1$ in Fig. 9.17(c). Of the two remaining phase fields, one will contain two extrapolations and the other none. These phase fields will contain one phase more and one phase less than the others, respectively. However, the rule does not allow us to tell which has more and which less. It would be possible to predict the number of phases in all the phase fields of Fig. 9.15 by this method, if it were known that the phase field in the upper left corner has one phase.

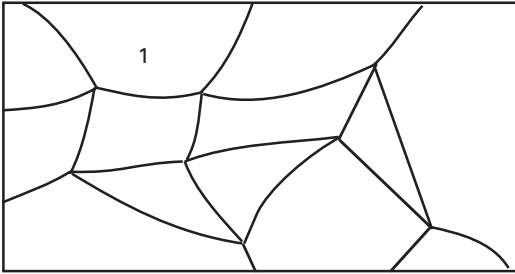


Figure 9.18 See Exercise 9.6.

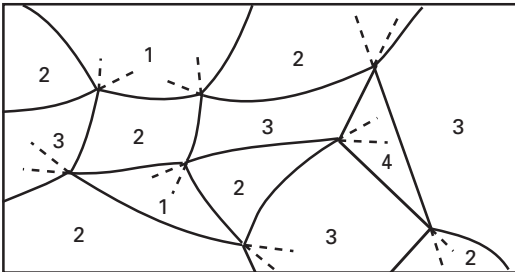


Figure 9.19 Solution to Exercise 9.6.

Exercise 9.6

A diagram for a multicomponent system is given in Fig. 9.18 but the numbers of phases have been left out except for one phase field. Try to decide the numbers of phases in all the other phase fields.

Hint

Discuss first what kind of phase diagram it is.

Solution

It looks like a molar diagram because at each point of intersection there are four lines. It may thus be reasonable to use Schreinemakers' rule. The result is shown in Fig. 9.19.

9.6 Topology of sectioned molar diagrams

Before leaving the discussion of sections of molar phase diagrams we should further consider the topology of diagrams with several phases. Figure 9.8 showed the elementary unit of a two-dimensional molar diagram. The result of sectioning can vary depending upon the direction of sectioning and the regularity of the diagram before sectioning. However, topologically the whole section can be regarded as composed of intersecting

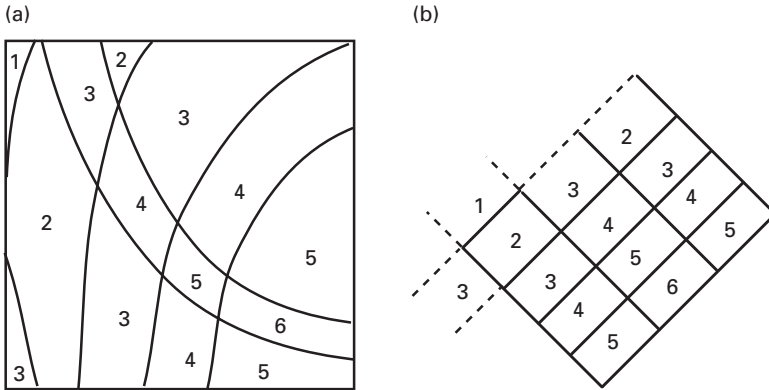


Figure 9.20 Two diagrams topologically equivalent to the sectioned molar phase diagram of Fig. 9.15.

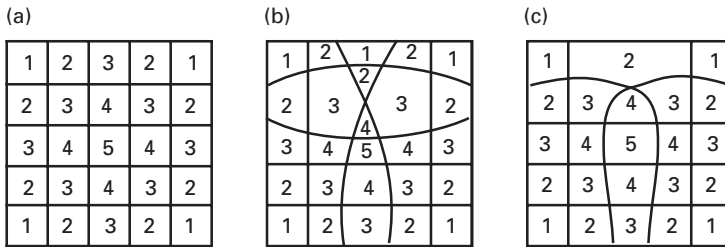


Figure 9.21 Some possibilities for the topology of a sectioned molar phase diagram with several phases. Both axes are molar axes.

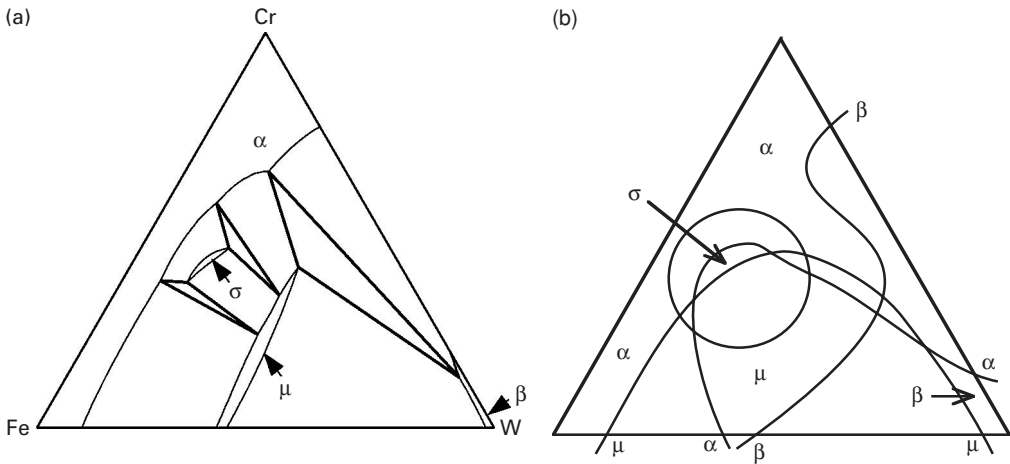


Figure 9.22 (a) The Fe–W–Cr phase diagram at 1 bar and 1673 K. α and β are both bcc but do not mix completely. μ and σ are intermetallic phases. (b) Topologically equivalent diagram but drawn with lines without any sharp points. These lines represent the limit of existence for one phase each, as given by the letters outside the triangle. The circle is the limit for σ .

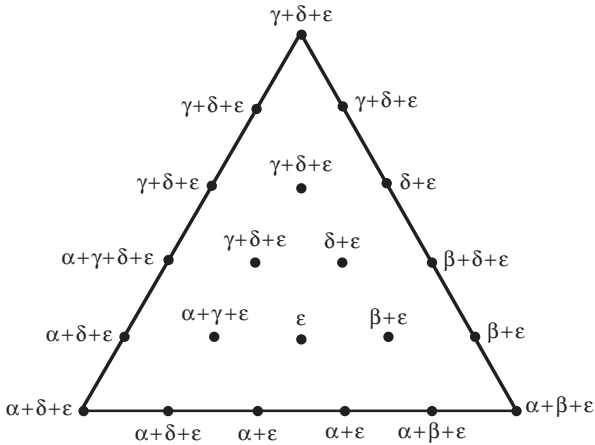


Figure 9.23 See Exercise 9.7.

lines, and the elementary unit will be the same as in Fig. 9.8(b). By the same reasoning, a three-dimensional diagram will have elementary units like the one in Fig. 9.9 and will give units like the one in Fig. 9.8(b) after sectioning. A many-dimensional molar phase diagram, after being sectioned a sufficient number of times, may look something like the one illustrated in Fig. 9.20(a). It was constructed to be topologically equivalent to the phase diagram in Fig. 9.15. In Fig. 9.20(b) it has been further simplified but it still has the same topology. This is an unusually simple case. The lines may very well intersect in a more complicated manner, as illustrated in Fig. 9.21.

The observation by Masing can be generalized. For each one of the lines in a two-dimensional section of a molar phase diagram there is a phase which ceases to exist on the line. It is illustrated for a complicated case in Fig. 9.22(a), using the topologically equivalent diagram in Fig. 9.22(b). These lines running through a complicated phase diagram have been called ‘zero-phase-fraction’ lines by Gupta, Morral and Nowotny [15] and they can be used as a valuable tool for identifying the phase fields and even for constructing a phase diagram from experimental information. The same principle applies to the surfaces in three-dimensional sections of molar phase diagrams.

Exercise 9.7

In order to investigate the phase relations in a quinary system Gupta, Morral and Nowotny established equilibrium in 21 alloys by isothermal treatment at 1400 K and 1 bar. All alloys had the same molar content of two components. The phases found in the various alloys could thus be shown in a composition triangle (see Fig. 9.23, where the compositions are represented by the relative fractions of the three remaining components). Draw a reasonable phase diagram.

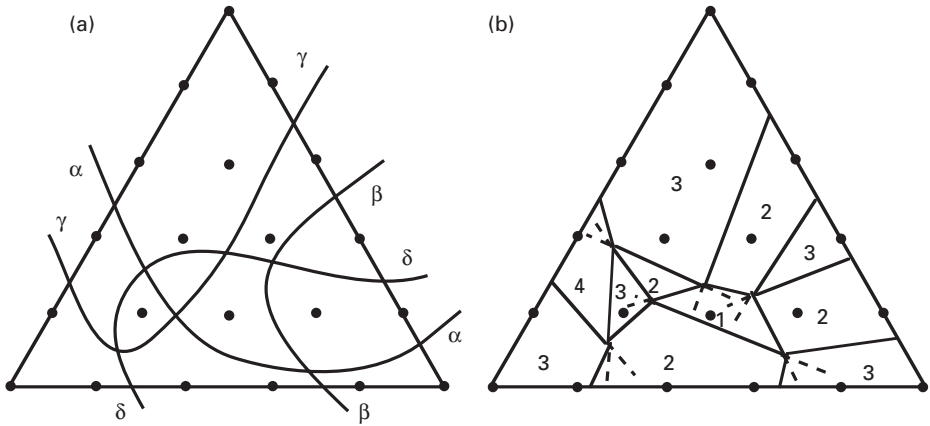


Figure 9.24 Solution to Exercise 9.7.

Hint

The diagram is a molar phase diagram. Start by drawing lines showing the limit of existence of each phase (zero-phase-fraction lines). Improve the diagram by making the various phase boundaries reasonably straight. Phase boundaries for invariant equilibria must be quite straight. Improve the diagram further by applying Schreinemakers' rule.

Solution

At constant T and P the maximum number of phases in a quinary system is five. None of the alloys falls in such a phase field. All the phase boundaries may thus be curved but we may find that it is possible to use straight lines which is preferable when we do not know in which direction a line should be curved. Figure 9.24 shows a possible solution.

10 Projected and mixed phase diagrams

10.1 Schreinemakers' projection of potential phase diagrams

Another method of reducing the number of axes is based on projection. By projecting all the features onto one side of the phase diagram, one will retain all the features, but the features of the highest dimensionality will no longer be visible because the dimensionality of a geometrical element will decrease by one unit by projection and they may thus overlap each other and also overlap features of the next-higher dimensionality. As an example, Fig. 10.1(b) shows a P, T diagram obtained by projection of Fig. 8.11 (shown again as Fig. 10.1(a)) in the μ_B direction. Such a P, T diagram is called Schreinemakers' projection [16]. In a system with c components it is obtained by projecting in the directions of $c - 1$ μ_i axes. It will show invariant equilibria with $c + 2$ phases as points, univariant equilibria with $c + 1$ phases as lines and in the angles between them there will be surfaces representing divariant equilibria with c phases. Using a short-hand notation developed by Schreinemakers, the coexistence lines for $c - 1$ phases are here identified also by giving in parentheses the phases from the invariant equilibrium which do *not take part*. For example, the (α) curve represents the α -absent equilibrium, i.e. $\beta + \gamma + \delta$. By comparison with Fig. 10.1(a) it can be seen that the angle between (α) and (β) is covered by the $\gamma + \delta$ surface but also by the $\alpha + \delta$ surface which extends to the (γ) line and by the $\beta + \gamma$ surface which extends to the (δ) line. The α one-phase field covers the whole diagram and the other one-phase fields each cover part of it.

Suppose we have a binary system with five phases, denoted 1, 2, 3, 4 and 5. An invariant equilibrium would have four phases. Suppose the system shows two such equilibria and by giving the absent phase they may be denoted (1) and (5). The complete phase diagram would have three dimensions (same as for a one-phase field). Projection would give just one of the diagrams shown in Fig. 10.2 but by presenting two diagrams obtained by projection in slightly different directions as a stereographic pair one can preserve the three-dimensional information. It is thus evident that the apparent intersection between the lines (1, 4) and (5, 3) is not an intersection in three dimensions. Therefore, it does not represent an invariant equilibrium.

T, P diagrams obtained by projection are particularly useful for multinary systems and are obtained by projecting in the direction of all the independent chemical potentials. We shall return to such diagrams in Section 10.5 but first we shall consider simpler cases.

In a projected diagram one sometimes includes a series of parallel sections drawn with thinner lines. Such lines may be called equipotentials (or isotherms or isobars when

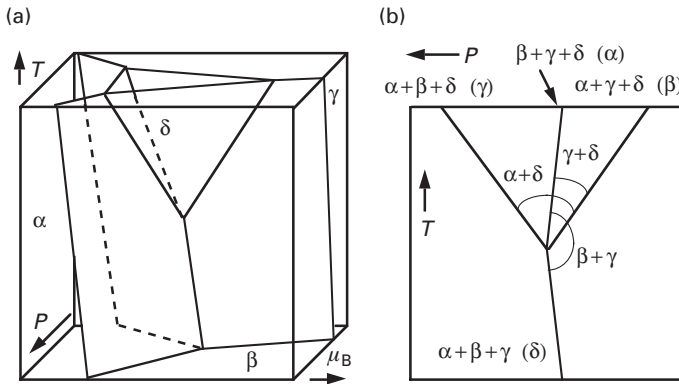


Figure 10.1 (a) The binary potential phase diagram of Fig. 8.11 reproduced to illustrate the projection in the μ_B direction. (b) The diagram obtained by projection. The positions of some of the two-phase surfaces are shown.

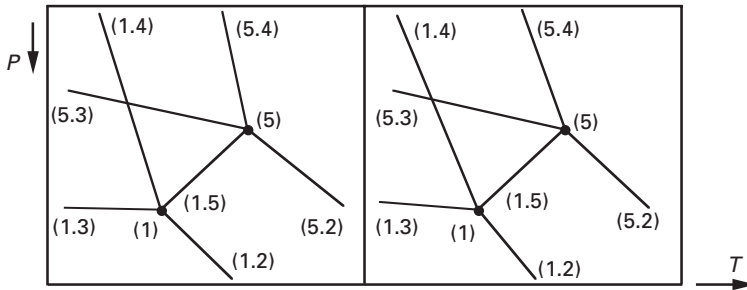


Figure 10.2 Stereographic pair of Schreinemaker's projection of a binary system, showing the three-dimensional shape. The phases not taking part in an equilibrium are given in parentheses. It can be seen that lines (1.4) and (5.3) do not intersect.

appropriate). Such a section was presented in Fig. 8.12. Figure 10.3(b) shows a diagram with several parallel sections. In order to simplify this picture, only the equilibria with the δ phase are shown here. Arrows within the figure show the direction of decreasing temperature.

Sometimes one uses both projecting and equipotential sectioning in order to reduce the number of axes. One may be interested in the changes of various phase equilibria with T and the chemical potential of some volatile component, e.g. oxygen, and one is willing to limit the information by making an equipotential section at $P = 1$ bar. Figure 10.4 gives an illustration from a quaternary system. According to Gibbs' phase rule an invariant equilibrium is obtained with $c + 2 = 6$ phases for $c = 4$, and six univariant equilibria should radiate from it. Let us denote the phases by 1 to 6. A section at $P = P_1$ will cut through the lines (1), (2) and (3). They will thus appear as points in the right-hand part where one of the projected axes, μ_{O_2} , is now shown. The surfaces extending between the lines in the T, P diagram (see Fig. 10.1(b)) will appear as lines in

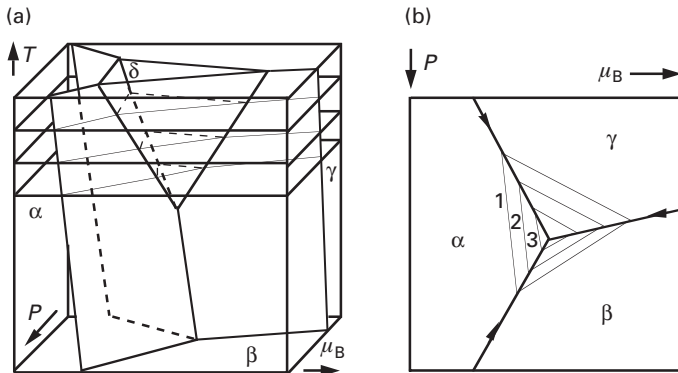


Figure 10.3 (a) Equipotential sections inserted in the potential phase diagram of Fig. 8.11. (b) The projection of the same potential phase diagram with inserted equipotential sections of the two-phase surfaces involving the δ phase.

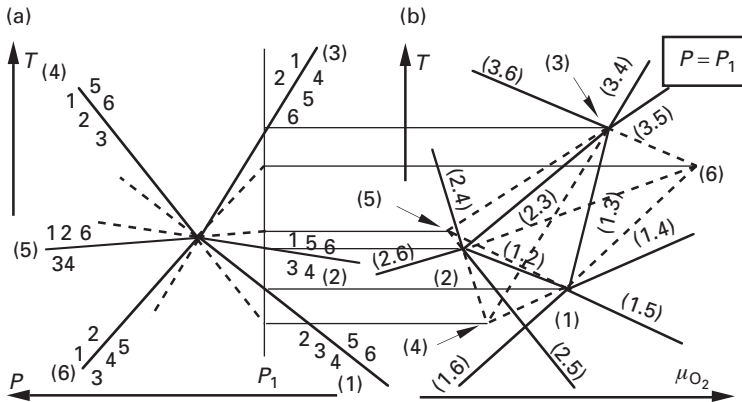


Figure 10.4 (a) Schreinemakers' projection of a quaternary system. (b) Section at $P = P_1$. The new axis, μ_{O_2} , is one of those projected in the T, P diagram.

the section. A major difference between the two diagrams is that in (a) all other potentials were projected but in (b) one of them, P , was sectioned.

Exercise 10.1

Find the section of the $2 + 4 + 5 + 6$ equilibrium in the T, μ_{O_2} diagram of Fig. 10.4. Then, find its surface in the T, P diagram.

Hint

How would that equilibrium be denoted using the absent phases?

Solution

It would be (1.3). In the T, μ_{O_2} diagram it is represented by a line between the points (1) and (3). In the T, P diagram its surface covers the angle between the (1) and (3) lines.

Exercise 10.2

A series of Fe–Cr alloys are heat treated together in a flowing gas of constant C and N potentials. After heat treatment for a long time at 1273 K, it is sometimes found that four phases are present but not all in the same specimen. The experiment is repeated several times with different C and N potentials and in some of those experiments the four phases are again found. It may be assumed that Cr is not transferred between the alloys. Is it possible that the four phases are found in more than one experiment, i.e. at different combinations of C and N potentials?

Hint

We may treat T and P as constant in addition to the potentials of C and N. With four components we thus have the same situation as in a binary system at variable P and T . We may use Fig. 10.1(b) and identify μ_{B} with μ_{Cr} , T with μ_{C} and $-P$ with μ_{N} .

Solution

It is thus useful to look at a $\mu_{\text{N}}, \mu_{\text{C}}$ diagram obtained by projection in the μ_{Cr} direction. Each experiment should be represented by a point in that diagram but individual specimens would fall on different positions along the projected μ_{Cr} axis, which may also be regarded as a projection along the conjugate molar axis, z_{Cr} according to Table 9.2. Such a diagram is given in Fig. 10.1(b). We can see that all experiments falling between lines (α) and (β) may cut through three two-phase surfaces, together involving all four phases. With all such combinations of μ_{C} and μ_{N} we will cut through all four one-phase fields in Fig. 10.1(a). Four phases can thus be found in several of the experiments with different values of μ_{C} and μ_{N} .

10.2 The phase field rule and projected diagrams

In Section 8.5 we derived the phase field rule for equipotential sections. Expressed in terms of the number of components, c , it was given by Eq. (8.23) and in terms of the number of axes in the diagram, r , by Eq. (8.24) by the use of $r = c + 1 - n_{\text{s}}$. The rule will now be extended to include projections as well. The dimensionality of phase fields with a large number of phases will not change their dimensionality by projecting. For example, the phase field for an invariant equilibrium will still be a point, Eq. (8.23) would still hold,

$$d = c + 2 - p - n_{\text{s}}. \quad (10.1)$$

On the other hand, the dimensionality of the diagram would decrease by each projection, yielding the following relation,

$$r = c + 1 - n_s - n_{\text{pr}}. \quad (10.2)$$

Inserting this in Eq. (8.23), here reproduced as Eq. (10.1), we obtain instead of Eq. (8.24),

$$d = v - n_s = c + 2 - p - n_s = 1 + r - p + n_{\text{pr}}. \quad (10.3)$$

The dimensionality of the diagram after a number of projections may have decreased to the dimensionality of a phase field, i.e. to $r = d$, and that happens when $n_{\text{pr}} = p - 1$ as demonstrated by Eq. (10.3). Each further projection will decrease the dimensionalities of the diagram and the phase field by one unit because a feature in the diagram can never have a higher dimensionality than the diagram itself. We thus find that

$$d = r = c + 1 - n_s - n_{\text{pr}} \text{ for } n_{\text{pr}} \geq p - 1. \quad (10.4)$$

whereas Eq. (10.3) holds for $n_{\text{pr}} \leq p - 1$.

A practical example is given in Fig. 10.5, concerning the Fe–O–S system. Since there are four lines radiating from each point we may conclude that the invariant equilibria concern four phases. The phase field rule in Eq. (10.3) gives, for large p ,

$$\begin{aligned} 0 &= c + 2 - p - n_s \\ &= 3 + 2 - 4 - n_s \\ &= r + 1 - p + n_{\text{pr}} \\ &= 2 + 1 - 4 + n_{\text{pr}} \\ n_s &= 1; \quad n_{\text{pr}} = 1. \end{aligned}$$

It is evident that one has sectioned at a constant value of some potential, probably P at 1 bar. Then one has projected once, in the direction of μ_s or μ_{Fe} . However, it must be remembered that the complete phase diagram was first obtained from the fundamental property diagram by projecting in the direction of some μ_i , the one which was considered as the dependent variable. Figure 10.5 has thus been obtained from the fundamental property diagram by projecting twice, and sectioning once, and it does not matter which projection was made first, μ_s or μ_{Fe} . It should be emphasized that n_{pr} represents the number of projections of the complete phase diagram. The first projection of the fundamental property diagram is not included in n_{pr} .

It is interesting to note that the two three-phase lines h (FeO + Fe₃O₄ + L) and f (Fe + FeO + L) stop inside the diagram. They stop at invariant three-phase points in the binary Fe–O system which overlaps the diagram. In principle, the whole surface of the diagram is covered by the binary Fe–O diagram which may be regarded as the bottom plate of the three-dimensional phase diagram, where $\mu_s = -\infty$, assuming that the fundamental property diagram was first projected in the μ_{Fe} direction to give a phase diagram. On the bottom plate, there is no S and the number of components c is thus 2 instead of 3. Three-phase equilibria would thus appear as points and two-phase equilibria as lines. That bottom plate is shown in (b) but was not included in (a) because

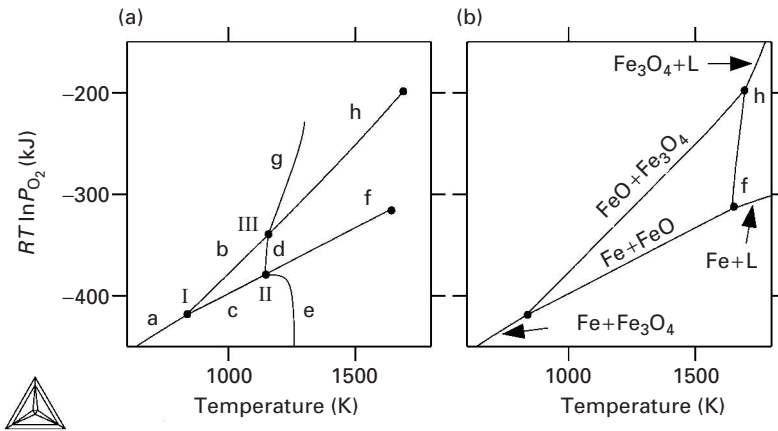


Figure 10.5 (a) Projected and sectioned ($P = 1$ bar) phase diagram for the Fe–O–S system. (a) Fe + Fe₃O₄ + FeS; (b) FeO + Fe₃O₄ + FeS; (c) Fe + FeO + FeS; (d) FeO + FeS + L; (e) Fe + FeS + L; (f) Fe + FeO + L; (g) Fe₃O₄ + FeS + L; (h) FeO + Fe₃O₄ + L. The invariant four-phase equilibria are (I) Fe + FeO + Fe₃O₄ + FeS; (II) Fe + FeO + FeS + L; (III) FeO + Fe₃O₄ + FeS + L. (b) The Fe–O bottom plate.

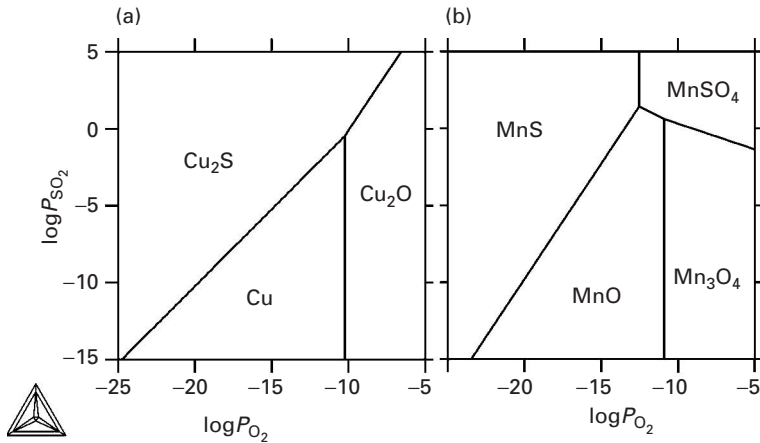


Figure 10.6 Potential phase diagram for (a) Cu–O–S and (b) Mn–O–S at 1 bar and 1000 K. These phase diagrams are two-dimensional and are not projections.

it would have made the diagram difficult to interpret. Only the binary end-points for FeO + Fe₃O₄ + L and Fe + FeO + L were marked.

In many cases one should consider the top plate as well as the bottom plate. A $\log P_{\text{SO}_2}$, $\log P_{\text{O}_2}$ diagram of the Cu–Mn–O–S system under $P = 1$ bar and $T = 1000$ K would be an example. The top and bottom would represent the Cu–O–S and Mn–O–S systems, respectively, if the projected axis is taken as $(\mu_{\text{Cu}} - \mu_{\text{Mn}})$. These diagrams are given in Fig. 10.6.

The solubilities of Cu in the Mn phases and of Mn in the Cu phases are all very low. The equilibria between the Cu–O–S phases will not be affected by the presence

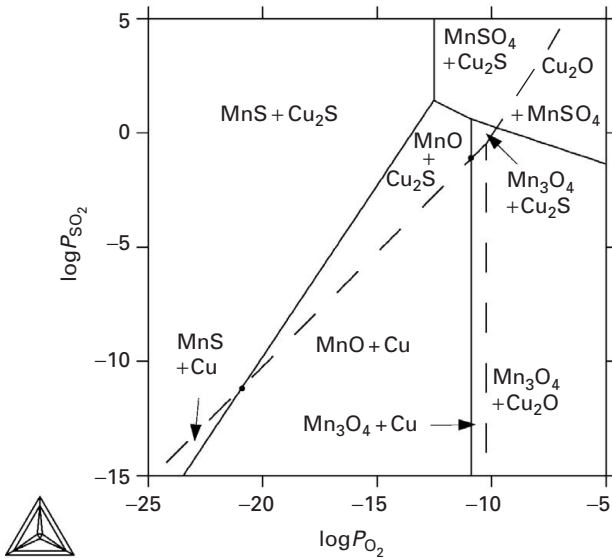


Figure 10.7 Projected phase diagram for Cu–Mn–O–S at 1 bar and 1000 K. For clarity, all the lines from the Cu–O–S side are presented with dashed lines here.

of Mn, nor the Mn–O–S phases by Cu. Both diagrams can thus be plotted in the same $RT \ln P_{\text{SO}_2}$, $RT \ln P_{\text{O}_2}$ coordinate frame to form the Cu–Mn–O–S diagram (Fig. 10.7). The lines in the ternary systems can be copied into the quaternary system and they become surfaces in the projected direction and they still appear as lines in the Cu–Mn–O–S diagram. New two-phase surfaces form between the previous one-phase fields and they are identified in the diagram.

An interesting question is the choice of projected axis in Fig. 10.7. In order to treat Cu and Mn in a symmetric way, it is convenient to consider $(\mu_{\text{Cu}} + \mu_{\text{Mn}})$ as the projected axis to give a phase diagram from the fundamental property diagram and then $(\mu_{\text{Cu}} - \mu_{\text{Mn}})$ as the axis used for projection of the phase diagram to reduce the number of axes to two.

Exercise 10.3

Only three lines intersect at the invariant equilibrium I in Fig. 10.5. What line is not shown and why not?

Hint

The fourth line should be the one without FeS.

Solution

The Fe + FeO + Fe₃O₄ line is not shown because one has projected the diagram exactly in its direction and the line thus appears as a point. The reason is that the projection has

been made in the μ_S direction and S does not dissolve in any one of these three phases. Thus, the equilibrium $\text{Fe} + \text{FeO} + \text{Fe}_3\text{O}_4$ is not affected by S and its line goes exactly in the μ_S direction. It exists at a certain T, P_{O_2} , only, and it is shown in the binary Fe–O diagram in Fig. 10.5(b).

Exercise 10.4

At 1000 K one measures the emf of an electrolytic cell where one electrode is a mixture of MnS, MnO, Cu₂S and Cu and the other is a mixture of Cu₂O and Cu. The electrolyte is solid zirconia stabilized with calcia. Use Fig. 10.7 to estimate the resulting emf.

Hint

The electrical current can pass through this electrolyte mainly by the diffusion of O^{2-} ions. The emf will thus be an expression of the difference in oxygen potential between the two electrodes and it can be estimated from the difference in $RT \ln P_{\text{O}_2}$ for two points in the diagram representing the electrodes.

Solution

The point for Cu₂O + Cu can be taken anywhere on the corresponding line yielding $\log P_{\text{O}_2} = -10.2$ in Fig. 10.6(a) (also dashed line in Fig. 10.7). The other point is obtained as the intersection between two lines in the lower left part of Fig. 10.7 and yields $\log P_{\text{O}_2} = -21.2$. We get $\Delta\mu_{\text{O}} = 0.5\Delta\mu_{\text{O}_2} = 0.5RT (1 \ln P'_{\text{O}_2} - 1 \ln P''_{\text{O}_2}) = 0.5RT \ln 10 \cdot (-10.2 + 21.2) = 12.7 RT$. Remembering that the O ion is divalent we get $E \cdot 27 = \Delta\mu_{\text{O}}$ where 7 is Faraday's constant (96 486 coulomb/mole) and thus $E = 0.547 \text{ V}$.

10.3 Relation between molar diagrams and Schreinemakers' projected diagrams

As demonstrated by Figs. 8.7 and 8.11, the elementary units of potential diagrams are very simple from the topological point of view. In this sense, the projections of such diagrams are more interesting. This is evident if one considers the dashed extrapolations shown in the projected diagram in Fig. 10.8(b). Between the lines there are two extrapolations in one case, one extrapolation in two cases, and no extrapolation in one case. In fact, this is the only way to draw four lines in different directions if the 180° rule is to be obeyed. It is evident that, in the projected direction, the four phases are related to each other in a special way. This phenomenon will now be examined. In order to simplify the discussion the method of identifying a univariant line by giving within parentheses the absent phase is used in Fig. 10.8(b).

If potential axes are chosen for plotting the complete, three-dimensional phase diagram of a binary system, the four phases of an invariant equilibrium will fall on one point. If

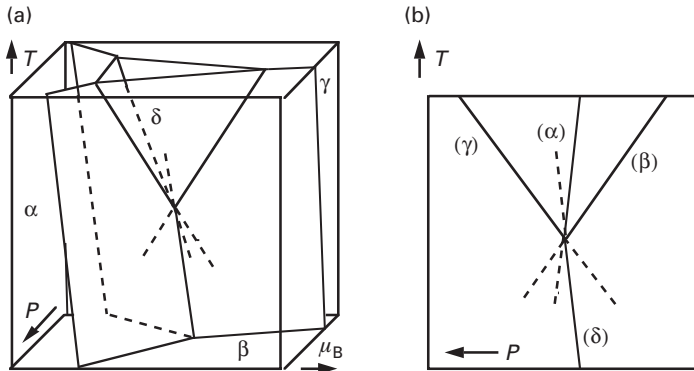


Figure 10.8 (a) Binary phase diagram and (b) projection in the μ_B direction, taken from Fig. 10.1. The extrapolations of the three-phase lines are marked with dashed lines.

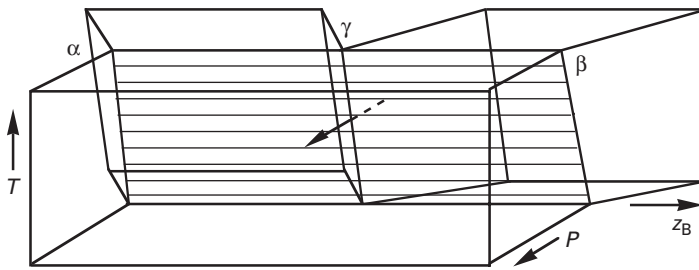


Figure 10.9 Introduction of a molar axis into the potential diagram of Fig. 10.8. Only the lower half of that diagram is used here. The surface marked with horizontal tie-lines represents the $\alpha + \beta + \gamma$ equilibrium.

one molar quantity is introduced, say, instead of Y^j , then the four phases will fall on a line, just as the three phases in the three-phase equilibrium in Fig. 9.2(a) fall on a line in Fig. 9.2(b). In that case, it is easy to see the order in which the phases are arranged along the line. The hcp phase must be placed between bcc and fcc. Otherwise, there would be some overlapping of the one-phase fields which is not allowed according to Section 9.1. Using the same reasoning, it is easy to see the order in which the four phases of Fig. 10.8 will be arranged when a molar quantity is introduced. One simply looks at the direction of the two-phase surfaces. Each one will turn into a two-phase volume when z_B is introduced instead of the μ_B axis. In Fig. 10.9 these volumes are demonstrated for the three surfaces between α , β and γ . It is evident that γ must fall between α and β along the z_B axis.

When the phase diagram of Fig. 10.8(a) is projected in the μ_B direction and Fig. 10.8(b) is formed, much information is lost. However, the information regarding the order of arrangement along the projected direction, obtained when the molar quantity is introduced, is not lost. This is because some conclusions can still be drawn regarding the directions of the two-phase surfaces. They are situated between the three-phase lines.

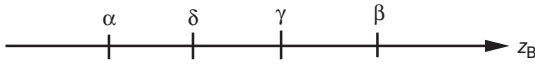


Figure 10.10 One-dimensional molar phase diagram at constant T and P , showing the relative position of four phases along the z_B axis, introduced instead of a μ_B axis, through the invariant equilibrium in Fig. 10.8(a). The composition is here expressed with the z_B variable because it is the conjugate variable to μ_B according to Table 9.2. The relative positions of all the four phases along a z_B axis, going through the invariant phase equilibrium are demonstrated schematically in Fig. 10.3.

This was demonstrated in Fig. 10.1(a). It is thus possible to get an impression of the relative positions of the six surfaces and thus of the relative positions of the phases along the molar axis of the projection.

The simplest method to interpret an experimental diagram like Fig. 10.8(b) is to draw the four extrapolations and then turn the diagram in the same way as Fig. 10.8(b) with respect to the dashed extrapolations. The compositions of the phases will then be arranged in the order given by Fig. 10.10 or in the completely reverse order. A more logical method will be described in the following section.

Exercise 10.5

In Exercise 10.2 we considered a heat treatment of several Fe–Cr specimens under carburizing and nitriding conditions at constant T and P . It had been found that four phases could be present in some experiments but not in the same specimen. Now try to find what is the maximum number of phases in any one specimen.

Hint

As already explained, we can use Fig. 10.1(b) because our quaternary system at constant T and P behaves like a binary system at variable T and P . In our case the two axes should be μ_C and μ_N and the projection has been made in the direction of μ_{Cr} , which is the same as the direction of z_{Cr} .

Solution

In Exercise 10.2 we saw that four phases can be present if μ_C and μ_N fall between the lines (α) and (β) in Fig. 10.1. The specimens fall on different positions along the projected axis. Most of them may fall between the surfaces representing two phases and they will thus have only one phase. What is the chance that some fall on the two-phase surface? Since the specimens are defined by their contents of Cr we should regard the projected molar axis rather than the potential axis. The two-phase surface in the potential diagram has a thickness when the molar axis has been introduced. There is thus definite chance that a specimen falls within the two-phase region.

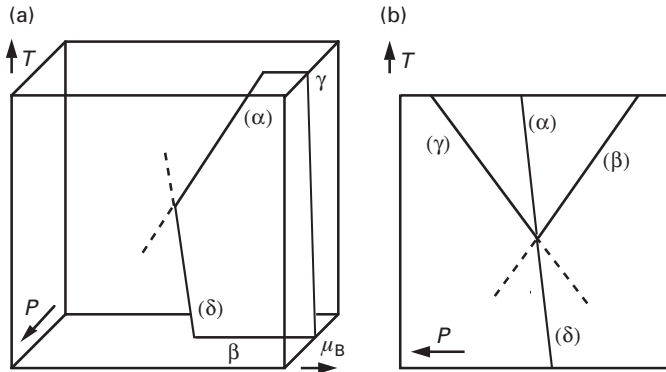


Figure 10.11 Modification of Fig. 10.8 by rotation of the $\beta + \gamma$ surface until it is parallel to the μ_B axis. In the μ_B projection the $\beta + \gamma + \delta(\alpha)$ and $\alpha + \beta + \gamma + (\delta)$ lines will now coincide and their extrapolations will not be visible.

On the other hand, if predetermined amounts of C and N are added to a set of specimens in a capsule, then one could not use Fig. 10.1(b) directly. For each specimen one should rather consider a molar diagram like Fig. 9.4 and it is evident that the four phases could occur in the same specimen and this could even happen in more than one specimen in the same experiment.

10.4 Coincidence of projected surfaces

The method to determine the relative compositions of phases, now to be described, can be used in higher-order systems as demonstrated in the next section, but a binary system will be considered first.

Suppose one could gradually change the properties of the system in such a way that the $\beta + \gamma$ surface in Fig. 10.8 would rotate around an axis roughly parallel to the T axis. One could thus make the two lines (α) and (δ) in the projection approach each other without changing the topology of the projected diagram. At the moment of coincidence, one has a situation such as that illustrated in Fig. 10.11.

The $\beta + \gamma$ surface is now parallel to the direction of projection, μ_B , and a continued rotation would put the $\beta + \gamma$ surface on the other side of the (α) and (δ) lines. Thus, β and γ would be transposed in Fig. 10.10. It is possible to conclude that the β and γ phases have the same value of z_B if the μ_B projections of the (δ) and (α) lines coincide when they meet at the four-phase point. Evidently, before the gradual rotation the β and γ phases must have been neighbours along the z_B line in Fig. 10.10. When the lines coincide, the phases fall on the same point on the z_B axis. This rule of coincidence is closely related to Konovalov's rule which will be discussed in Section 10.8. The relative positions of the phases for the various cases of coincidence are shown in Fig. 10.12. Other cases of coincidence may occur but not until at least one of these has occurred. Before any rotation, the phases must have been arranged along the z_B axis as shown in Fig. 10.10 or in the completely reverse order.

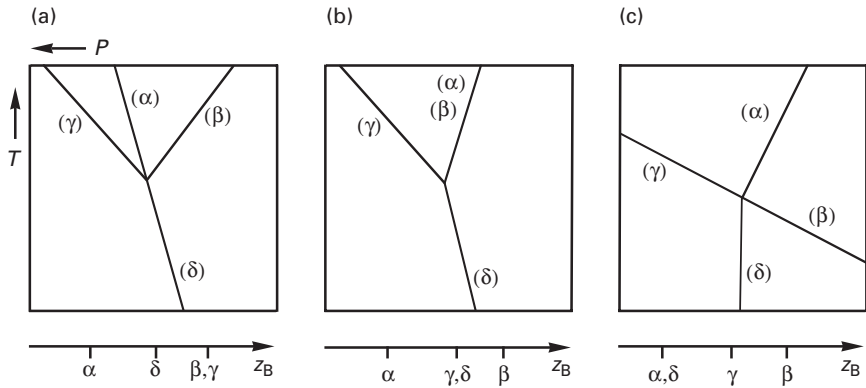


Figure 10.12 Three cases of coincidence of three-phase lines in a projected potential phase diagram obtained by modifying Fig. 10.8.

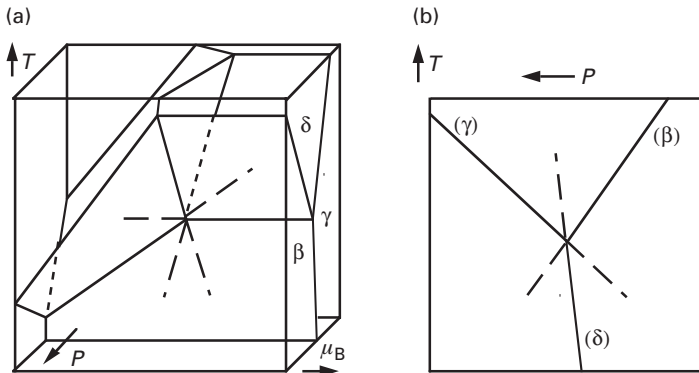


Figure 10.13 (a) Modification of Fig. 10.8 by rotation of the entire diagram until the $\beta + \gamma + \delta(\alpha)$ is parallel to the μ_B axis. All three surfaces, $\beta + \gamma$, $\gamma + \delta$ and $\delta + \beta$, are then parallel to the μ_B axis. In the μ_B projection (b), $\beta + \gamma + \delta(\alpha)$ degenerates to a point and will thus coincide with all the other lines without them coinciding with one another.

It is interesting to note from Fig. 10.8 that it should be possible to rotate the $\alpha + \beta$ surface in such a way that the (γ) and (δ) lines approach each other and finally coincide. However, the 180° rule prevents this from happening before there is another coincidence.

What happens if three of the four phases β , γ and δ , have the same z_B value will now be investigated. The three surfaces representing $\beta + \gamma$, $\beta + \delta$, $\gamma + \delta$ must all be parallel to the μ_B axis and the $\beta + \gamma + \delta(\alpha)$ line must point in the μ_B direction. It thus degenerates to a point. This case is illustrated in Fig. 10.13.

Exercise 10.6

Prove mathematically that the compositions of β and γ must coincide when the μ_B axis in a binary system is parallel to the $\beta + \gamma$ surface, as in Fig. 10.11.

Hint

Apply Eq. (8.47) to the binary case.

Solution

For a binary system we get $(z_B^\beta - z_B^\gamma)d\mu_B = -(S_{m1}^\beta - S_{m1}^\gamma)dT + (V_{m1}^\beta - V_{m1}^\gamma)dP$. When the $\beta + \gamma$ surface is parallel to μ_B , then we can change μ_B and stay on the surface without changing T or P , i.e. with $dT = 0$ and $dP = 0$. The coefficient of $d\mu_B$ must thus be zero, i.e. $z_B^\beta = z_B^\gamma$.

Exercise 10.7

Suppose one has measured μ_C as function of T at 1 bar for a ternary A–B–C system. What conclusion could be drawn if the diagram looks like Fig. 10.11(b) with μ_C inserted instead of P ?

Hint

Compared to Fig. 10.11 we have one component more but the dimensionality has been reduced to the same by keeping P constant. In both cases μ_A and μ_B are the potentials that are not shown in the projection, i.e. those used to reduce the number of axes by projection from the four-dimensional fundamental property diagram.

Solution

One of μ_A and μ_B is the dependent variable and the final projection has been made in the direction of the other one. From the coincidence of the (α) and (δ) lines we may conclude that $z_B^\beta = z_B^\gamma$ if μ_A is the dependent variable and $z_A^\beta = z_A^\gamma$ if μ_B is the dependent one. These two results are identical since $z_B = N_B/N_A = 1/z_A$.

10.5 Projection of higher-order invariant equilibria

The topological examination may be extended to higher-order invariant equilibria and adjoining univariant equilibria, although the visibility is then lost. However, it has been shown by analytical methods [17–19] that the same principles, which have been derived here by inspection, apply. Three components will yield a four-dimensional phase diagram and it must be projected twice in order to yield a two-dimensional picture. It may show an invariant five-phase equilibrium and five adjoining four-phase lines. If no lines coincide, they can arrange themselves in three different ways, as illustrated in Fig. 10.14.

For a closer discussion of the compositions of the phases taking part in the five-phase equilibrium, the two potentials on the axes will be kept constant at the values of the invariant equilibrium, while the two projected potentials will be replaced by their

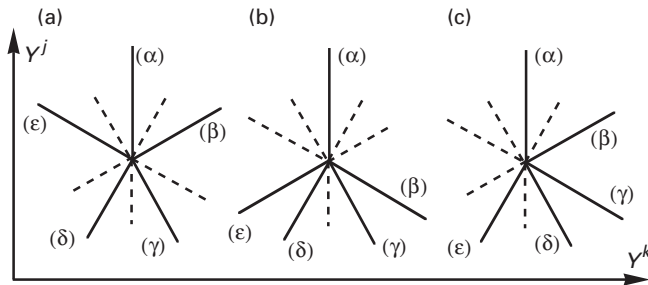


Figure 10.14 Possible Schreinemaker's projections for a ternary system obtained by projecting the Y^j , Y^k , Y^m , Y^n phase diagram in the Y^m and Y^n directions. Points represent invariant five-phase equilibria. The five lines radiating from each point represent four-phase equilibria and are identified by giving the absent phase in parentheses. Dashed lines are metastable extrapolations.

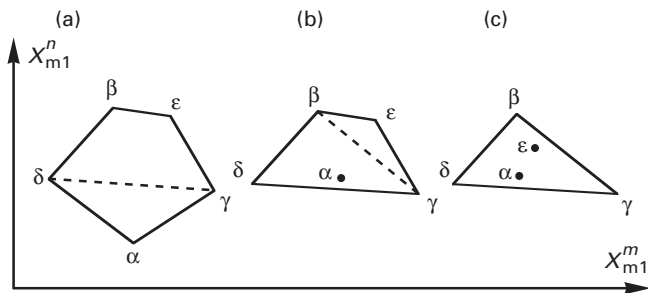


Figure 10.15 Molar phase diagrams at constant Y^j and Y^k showing the relative positions of the five phases in the invariant equilibria in Fig. 10.14. The change occurring when lines (ϵ) and (β) in case (a) are rotated to approach each other can be illustrated by moving point α towards the straight line between δ and γ . Case (b) is obtained by letting the (ϵ) and (β) lines pass one another, thus making point α cross the $\delta - \gamma$ tie-line. Case (c) is obtained by letting the (α) and (δ) lines rotate and pass one another, whereupon ϵ will cross the $\beta - \gamma$ line.

conjugate molar quantities. The five phases will fall on different points on the plane formed by the two molar quantities, and Fig. 10.15 illustrates the arrangement of the phases in the three different cases. Three phases may here be regarded as neighbours if their points can be connected to form a triangle with no other point inside and if the triangle can be changed into a line without any one of its points first moving inside any other such triangle. If two lines in the projected potential phase diagram coincide, then the three phases they have in common will fall on a straight line in the molar diagram.

Four components yield a five-dimensional phase diagram and it must be projected three times in order to yield a two-dimensional picture. A six-phase equilibrium will be invariant and represented by a point from which six lines will radiate, representing univariant equilibria with one phase absent in each. The relative positions of the six lines will reveal how the six phases are arranged in the three-dimensional compositional space formed by three molar quantities. However, this is not easy to visualize. The rule relating

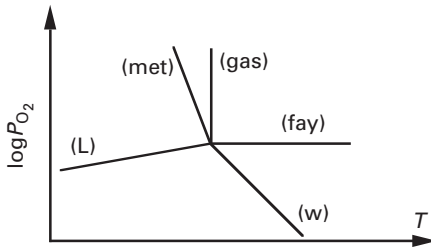


Figure 10.16 See Exercise 10.8.

the coincidence of lines in a projected potential phase diagram to the positions of the common phases in the space formed by the molar quantities has been called the ‘coincidence theorem’ [19]. The theorem can be generalized as demonstrated by the following example. Suppose that two of the points, α and δ , in the left-hand picture of Fig. 10.15 coincide. Then δ , α and γ fall on a line, and lines (β) and (ϵ) in Fig. 10.14 should coincide. However, β , δ and α would also fall on a line, and lines (γ) and (ϵ) in Fig. 10.14 should also coincide. As a consequence all three lines, (β) , (γ) and (ϵ) , should coincide. It is thus possible to generalize the coincidence theorem as follows. Consider a two-dimensional projection of an r -dimensional potential diagram. It may have an invariant equilibrium involving $r + 1$ phases. From this point, $r + 1$ univariant equilibria, each with r phases, radiate. The theorem concerns the positions of the phases in the $(r - 2)$ -dimensional space formed by the molar quantities conjugate to the projected potentials. If t of the phases fall in a $(t - 2)$ -dimensional section through that space, then all the univariant equilibria, which contain the t phases, coincide in the two-dimensional projection. There would be $r + 1 - t$ such equilibria.

Exercise 10.8

Figure 10.16 is part of the potential phase diagram for the Fe–Si–O system, showing the five-phase equilibrium, metallic melt (met), liquid melt (L), wüstite (w), fayalite (fay) and gas (gas). Use the information in the diagram to decide how the composition of L falls relative to the other phases.

Hint

By extrapolating the lines we find that our case corresponds to case (b) in Fig. 10.14 with L identified as α . Our diagram can be regarded as obtained by projecting the fundamental potential diagram in the directions of P , μ_{Fe} and μ_{Si} , leaving T and μ_{O} as axes in our diagram. The first projection produces a complete potential phase diagram and, since we are interested in comparing compositions, we shall regard P as subjected to the first projection. We should thus write the Gibbs–Duhem relation as $dP = (S/V)dT + \Sigma(N_i/V)d\mu_i$. The conjugate variable to the next two potentials to be projected would thus be N_{Fe}/V and N_{Si}/V . They should appear in our diagram as in Fig. 10.15(b).

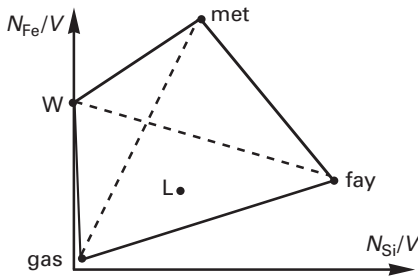


Figure 10.17 Solution to Exercise 10.8.

Solution

Since L is identified as α , it will have to form within the quadrangle formed by the other four phases. Fayalite is $2\text{FeO} \cdot \text{SiO}_2$, wüstite is approximately FeO and the metallic melt is mainly Fe. The gas has a very large volume and will thus fall close to the origin in the diagram. Since the extension of the (L) line in our potential phase diagram falls between (gas) and (fay), corresponding to (γ) and (δ), its composition falls close to the gas + fay join, corresponding to $\gamma + \delta$ join, as illustrated in Fig. 10.17.

10.6 The phase field rule and mixed diagrams

The number of axes in a complete phase diagram, whether a potential one or a molar one, is $r = c + 1$. For a closed system one has fixed the composition and has actually sectioned at $c - 1$ molar axes. The number of remaining axes is $r = c + 1 - (c - 1) = 2$. For a closed system the equilibrium state is thus uniquely defined by choosing values for T and P or their conjugate variables independent of how many phases it has. This is called **Duhem's theorem**.

In the most common type of phase diagram there is a temperature axis and a composition axis. It is thus an example of phase diagrams with a mixture of potential and molar axes. Such diagrams are more complicated and due to the large variety no general description will be given. However, it is worth discussing how the phase field rule can be generalized to such diagrams but first it should be emphasized that the discussion only concerns true phase diagrams, i.e. diagrams obtained from a single set of conjugate pairs of variables. The nine possibilities were discussed in Section 3.5 and they resulted in 27 sets when molar variables were introduced in Section 9.2. As a consequence, all the variables in a mixed diagram, including those that have been projected or sectioned, must come from one of the 27 sets in Tables 9.1, 9.2 and 9.3.

Figures 8.1 and 8.2 give the impression that the degrees of freedom increase by one unit for each molar axis that is introduced instead of its conjugate potential axis. However, it should be remembered that Gibbs' phase rule was derived by considering potentials and not molar quantities. The freedom to vary the amounts of the phases by moving along a tie-line without varying the compositions of the individual phases is

not regarded as a degree of freedom in Gibbs' phase rule because the potentials do not vary. Instead of redefining Gibbs' phase rule we have thus decided to also to work with a parallel concept, the dimensionality of a phase field. That was the main reason why the phase field rule was introduced in Section 8.5. The effect of molar axes on Eq. (8.23) yields

$$d = v - n_s + n_m = c + 2 - p - n_s + n_m, \quad (10.5)$$

where n_s is the total number of sectioned quantities, potentials as well as molar quantities, and n_m is the total number of molar quantities used, i.e. sectioned molar quantities, n_{ms} , as well as molar axes in the final diagram, n_{ma} . Of course, $n_m = n_{ms} + n_{ma}$. On the other hand, *if we project a phase diagram in the direction of an axis, then it does not matter what kind of variable was chosen on that axis, a potential or its conjugate molar quantity.* The projected phase diagram will look the same and all the projections will thus have the same effect on the phase field rule. The number of projected molar quantities should not be included in n_m .

As before, the number of axes in the phase diagram will be given by Eq. (10.2), $r = c + 1 - n_s - n_{pr}$, and Eq. (10.5) can thus be written as

$$d = c + 2 - p - n_s + n_m = 1 + r - p + n_{pr} + n_m \text{ for } p \geq 1 + n_{pr} + n_m. \quad (10.6)$$

This expression is valid only as long as $p \geq 1 + n_{pr} + n_m$ because it yields $d = r$ for $p = 1 + n_{pr} + n_m$. This is a critical value because when the number of projections or molar axes is increased further Eq. (10.6) would yield $d > r$ which is impossible. For each one of further projections and molar axes both the phase field and the diagram will lose one dimension and retain the relation $d = r$. For less phases we obtain instead of Eq. (10.4),

$$d = r = c + 1 - n_{pr} - n_s \text{ for } p \leq 1 + n_{pr} + n_m. \quad (10.7)$$

A few more considerations of the properties of mixed diagrams should be added. The lowest possible dimensionality of a phase field will occur for the maximum number of phases. In a potential phase diagram that dimensionality will be zero but it is evident from the preceding discussion that it will increase by one unit for each molar axis and the lowest possible dimensionality will thus be equal to the number of molar axes in the final diagram, n_{ma} , and this will occur at the maximum number of phases. By inserting $n_{ms} + n_{ma} = n_m$ we obtain

$$\begin{aligned} n_{ma} = d_{\min} &= c + 2 - p_{\max} - n_s + n_{ma} + n_{ms} \\ &= r + 1 - p_{\max} + n_{pr} + n_{ma} + n_{ms} \end{aligned} \quad (10.8)$$

$$p_{\max} = c + 2 - n_s + n_{ms} = r + 1 + n_{pr} + n_{ms}. \quad (10.9)$$

The MPL boundary rule can be applied to mixed diagrams but only with caution. It is important first to distinguish between phase fields and phase boundaries. The rule concerns two adjoining phase fields separated by a phase boundary. As an example, we may examine the case illustrated in Fig. 9.2(c). It is reproduced in Fig. 10.18 without tie-lines and with the three-phase field $bcc + fcc + hcp$ marked with a thick line. All the other lines are phase boundaries. The MPL rule cannot be applied to the contact between

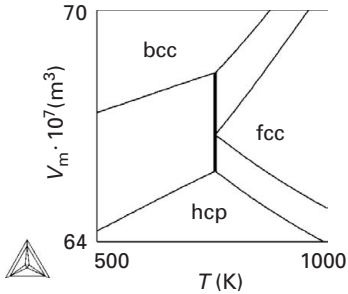


Figure 10.18 Mixed phase diagram from Fig. 9.2(c), reproduced without tie-lines. The thick line represents the three-phase field. All other lines are phase boundaries.

fcc and bcc + hcp phase fields because they are not connected by a phase boundary but separated by the three-phase field bcc + fcc + hcp. For the contact between fcc and bcc + fcc + hcp the rule gives

$$b = r - D^+ - D^- = 2 - 2 - 0 = 0,$$

in agreement with the fact that these two phase fields meet at a point, only. For the contact between bcc + hcp and bcc + fcc the rule gives

$$b = r - D^+ - D^- = 2 - 1 - 1 = 0.$$

This is also correct because these two phase fields do not make contact along the thick horizontal line, where they are separated by the bcc + fcc + hcp phase field. They only make contact at the upper end-point of the thick line. Cases like this can be easily analyzed by imagining that the one-dimensional phase field is a very thin triangle [12]. That method is also helpful if one wants to draw zero-phase-fraction lines. Each one-dimensional phase field will have one such line on each side.

Exercise 10.9

The T , %C phase diagram (Fig. 10.19) is for a quaternary A–B–C–D system at 20% B and 20% D and at 1 bar. Test it with the phase field rule.

Solution

There are four components, $c = 4$. The complete phase diagram has been sectioned three times, $n_s = 3$, but two of the sections were for the molar quantities %B and %D, $n_{ms} = 2$. In the final diagram there is one molar axis, $n_{ma} = 1$. There is no projection, $n_{pr} = 0$. In the diagram we can see a horizontal line. Let us test if it is a phase field or just a boundary between two-dimensional phase fields. A line has the dimensionality 1 and it thus gives $1 = d = c + 2 - p - n_s + n_{ma} + n_{ms} = 4 + 2 - p - 3 + 1 + 2 = 6 - p$; $p = 5$. If the horizontal line is a phase field, it should have five phases. From the neighbouring phase fields we find $\alpha + \beta + \gamma + \delta + L$. We may conclude that this

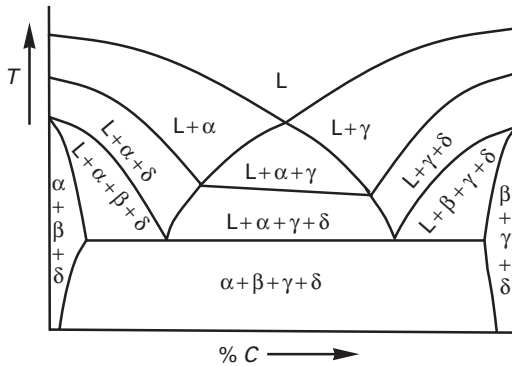


Figure 10.19 See Exercise 10.9.

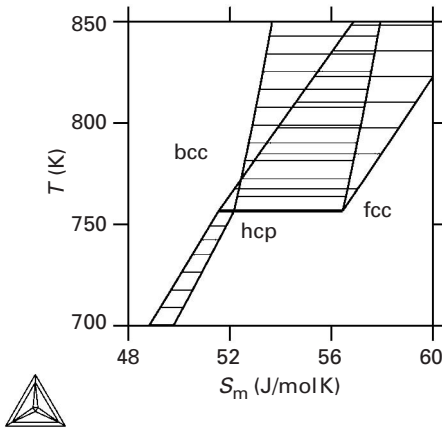


Figure 10.20 T, S_m diagram for Fe. This is not a true phase diagram.

line is a phase field. The diagram is two-dimensional, $r = 2$. Let us now check for what number of phases a field should be two-dimensional, $p \leq 1 + n_{pr} + n_{ma} + n_{ms} = 1 + 0 + 1 + 2 = 4$. This is also confirmed by the diagram.

10.7 Selection of axes in mixed diagrams

For mixed diagrams it is particularly important to pay attention to how the axes are selected. As already emphasized, they must all come from a set of conjugate pairs of variables and one from each conjugate pair. The various possibilities are listed in Tables 9.1, 9.2 and 9.3. A number of examples will now be given in order to demonstrate what could otherwise happen.

Figure 10.20 shows part of the T, S_m diagram for Fe. Two two-phase fields overlap which is made possible by the fact that T and S_m do not represent different conjugate pairs in any of the sets in the tables. This is not a true phase diagram.

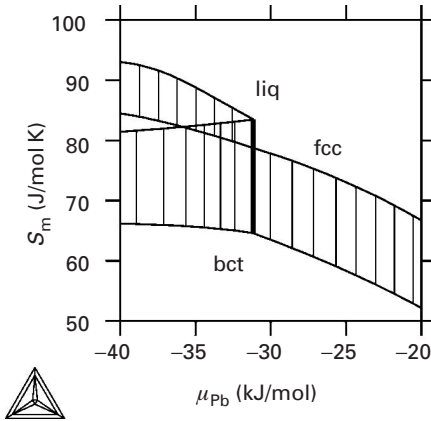


Figure 10.21 S_m , μ_{Pb} diagram for Pb–Sn. This is not a true phase diagram.

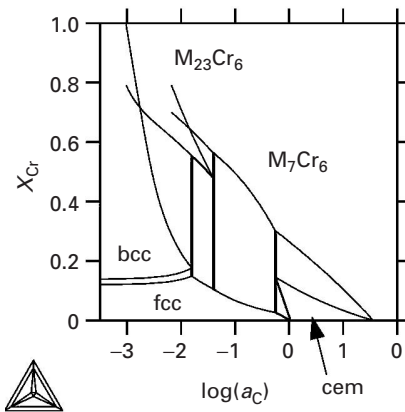


Figure 10.22 x_{Cr} , a_C diagram for Fe–Cr–C. This is not a true phase diagram.

Figure 10.21 shows the S_m , μ_{Pb} diagram for the Pb–Sn system at 1 bar. Two two-phase fields overlap because S_m and μ_{Pb} do not come from the same set of conjugate pairs. This is not a true phase diagram. One should have combined S_m with $\mu_{Pb} - \mu_{Sn}$ or S_{m1} with μ_{Pb} .

Figure 10.22 shows the x_{Cr} , a_C diagram for Fe–Cr–C at 1 bar and 1200 K. The intersecting phase boundaries in the upper left corner, forming two ‘swallow-tails’, indicate that this is not a true phase diagram. The activity a_C can be regarded as an expression for μ_C/T and should have been combined with u_{Cr} or z_{Cr} but not x_{Cr} .

Figure 10.23 shows the T , x_{Cr} diagram for Fe–Cr–C at 1 bar and $a_C = 0.3$, relative to graphite. The two intersecting phase boundaries on the right-hand side indicate that this is not a true phase diagram. The two axes, T and x_{Cr} , do belong to the same set of conjugate variables but one must also consider the sectioned axes. In this case one has sectioned at constant P and a_C , i.e. μ_C/T . However, μ_C/T and x_{Cr} do not belong to the same set.

Figure 10.24(a) shows the H_{m1} , a_C diagram for Fe–C at 1 bar. This is not a true phase diagram although H_{m1} and μ_C/T , here represented by a_C , come from the same set of

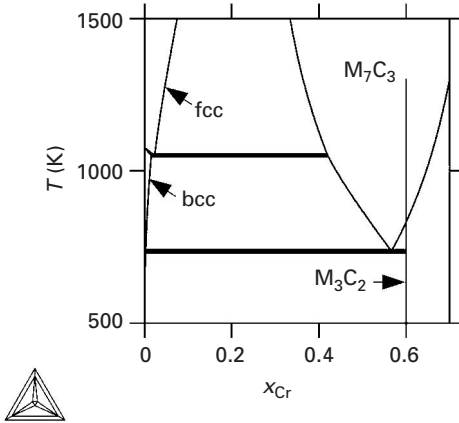


Figure 10.23 T, x_C diagram for Fe–Cr–C at 1 bar and $a_C = 0.3$. This is not a true phase diagram.

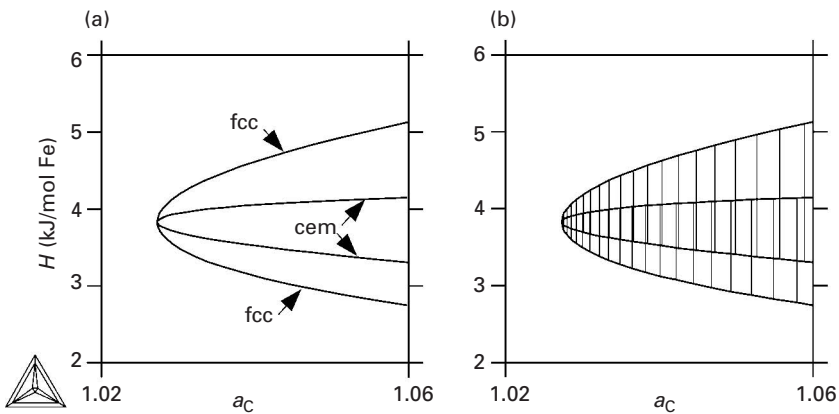


Figure 10.24 H_{m1}, a_C diagram for Fe–C at 1 bar. This is not a true phase diagram as revealed by the overlapping two-phase fields, shown when the tie-lines are included in (b).

conjugate variables. That is revealed by the tie-lines which are included in Fig. 10.24(b). The reason is that the numerical values used for H_{m1} refer to reference states of Fe and C at 298 K but a_C refers to graphite at the actual temperatures. It is evident that one should also be careful when representing the oxygen potential with P_{O_2} . It is only under isothermal conditions that it should be combined with an axis for a molar quantity given relative to references at 298 K. It should be noted that the diagrams in Figs 8.13 and 8.14 used $\mu_C - {}^\circ G_C^{gr}$ or $(\mu_C - {}^\circ G_C^{gr})/T$ as an axis and ${}^\circ G_C^{gr}$ was defined at the actual temperature which varied. That did not cause any problem because there was no molar axis in those diagrams.

Exercise 10.10

Figure 10.23 showed an incorrect selection of axes. If one really wanted to section at a constant value of a_C , what composition axis should one have used?

Hint

Consult the Tables 9.1, 9.2 and 9.3.

Solution

a_C represents μ_C/T which may be combined with $-1/T$, $-P$, and z_{Cr} (according to fifth row in Table 9.2) or u_{Cr} (according to fifth row in Table 9.3). Of course, $-1/T$ could be replaced by T .

10.8 Konovalov's rule

The rule that two one-phase fields are separated from each other by a positive distance, when the proper molar quantity is introduced instead of a potential, was described in Section 9.1. That rule is not as trivial as it may appear. It was discovered experimentally by Konovalov [20] when measuring the vapour pressure of liquid solutions of water and various organic substances under isothermal conditions. He established that, compared with the solution, the vapour contains a higher relative content of that component which, when added to the solution, increases the total vapour pressure. In addition, he found two cases with a pressure maximum and realized that the liquid and vapour must have the same composition at such a point. A case of this type is shown in Fig. 10.25, and it is evident that it is simply due to the fact that the molar quantity which is used, here z_B , replaces a potential whose axis happens to be parallel to a *line* tangential to the linear two-phase field in the potential diagram. Except for that, the system has no unique properties at this point. The point is sometimes called a **singular point** and the equilibrium under this special condition is called **singular equilibrium**.

Figure 10.26(a) shows a three-dimensional diagram for the same kind of system but including both temperature and pressure axes. It was presented in Fig. 8.23 and it was then concluded that an extremum in P at constant T must lead to an extremum in T at constant P . The corresponding diagram, where z_B has been introduced instead of μ_B , is shown in Fig. 10.26(b) and it confirms that the two phases have the same composition at the point of extremum considered. In fact, there is a whole series of such points, marked as a dotted line. This is the locus of points of tangency for tangents parallel to the μ_B or z_B axis. That line represents a singular equilibrium and could be included in the T , P diagram, obtained by projecting in the μ_B (i.e. z_B) direction, Schreinemakers' projection. The line representing singular equilibrium is called a **singular curve**. Singular equilibria will be further discussed in Sections 12.6 and 13.7 to 13.9.

A major difference between univariant lines and singular curves should be noted. A univariant line shows exactly where a particular univariant equilibrium occurs. A singular curve shows the maximum extension of a divariant equilibrium which is otherwise not shown in the diagram. It would thus be wise to indicate on what side of a singular curve the particular equilibrium exists. This is done in Fig. 10.27, which is a projection of Fig. 10.26.

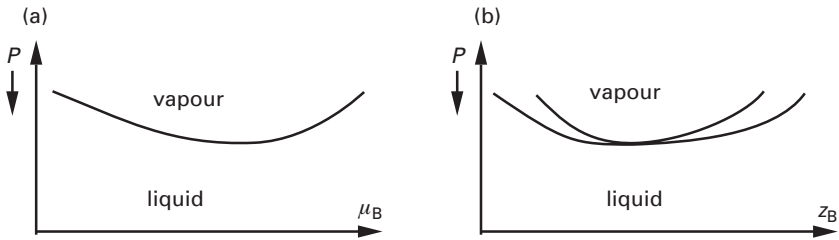


Figure 10.25 An isothermal section of a binary diagram with a singular point for two phases illustrating Kononov's rule.

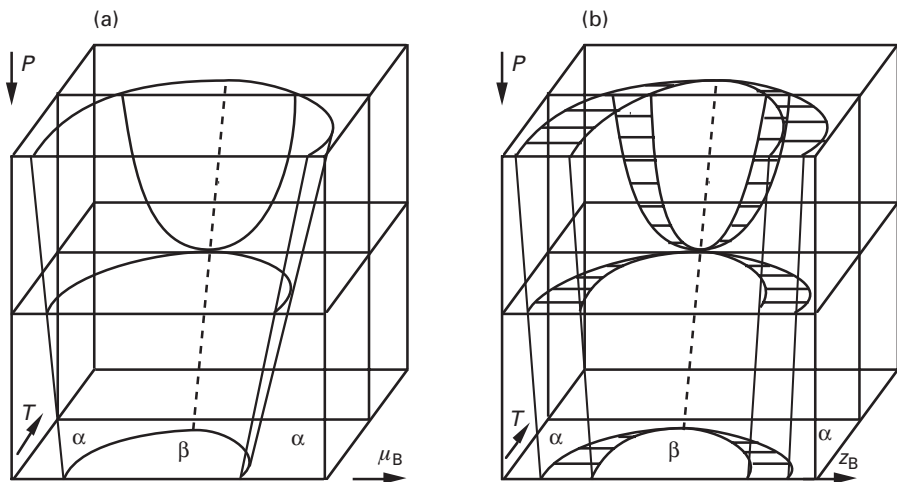


Figure 10.26 (a) A two-phase equilibrium in a binary system illustrated with the complete three-dimensional potential phase diagram. Points of tangency for lines parallel to the μ_B axis are marked with a dotted line. (b) After μ_B has been replaced by its conjugate molar quantity, z_B , the phases still coincide along the dotted line where the two phases have the same composition, expressed through z_B .

Points of extremum in P and T were discussed in Section 8.9 and Kononov's rule was actually derived there in an analytical way, using the ordinary molar quantities, S_m , V_m and x_i . In Chapter 8 and the present one we have mainly used molar quantities defined by dividing the integral quantities with the content of a certain component, N_A for instance. We denote these quantities with S_{m1} , V_{m1} and z_i . However, if all the molar quantities we are interested in are molar contents, then the results look the same in both notations. As an example, the insertion of $x_i = x_1 z_i$ in the result for $p = c$ in Section 8.9 yields

$$\begin{aligned}
 0 &= \begin{vmatrix} 1 & x_2^\beta & \dots & x_c^\beta \\ & & & x_c^\beta \end{vmatrix} = \begin{vmatrix} x_1^\alpha & x_2^\beta & \dots & x_c^\beta \\ & & & x_c^\beta \end{vmatrix} \\
 &= \begin{vmatrix} 1 & z_2^\beta & \dots & z_c^\beta \\ & & & z_c^\beta \end{vmatrix} \cdot x_1^\alpha x_1^\beta \dots x_1^\epsilon
 \end{aligned} \tag{10.10}$$

$$0 = \begin{vmatrix} 1 & z_2^\beta & \dots & z_c^\beta \end{vmatrix} \tag{10.11}$$

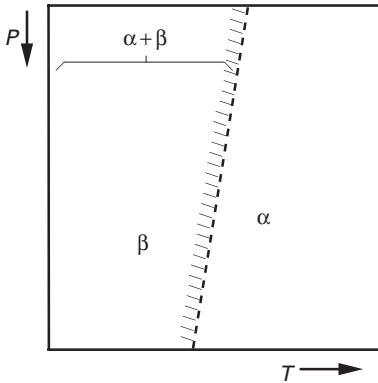


Figure 10.27 Singular curve showing the maximum extension of the $\alpha + \beta$ equilibrium in Fig. 10.25. Projected in the z_B direction. The $\alpha + \beta$ surface is folded and to the left of the curve one would intersect that surface twice by moving in the projected direction, i.e., perpendicular to the picture.

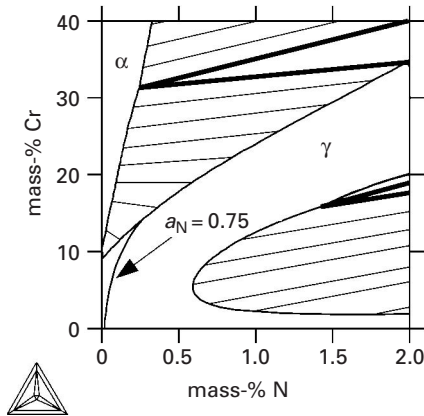


Figure 10.28 See Exercise 10.11.

We shall continue to use z_i but it should be remembered that the results hold for x_i as well.

The importance of Konovalov's rule stems from the fact that composition is often used as an experimental variable. A system with a composition at a point of maximum or minimum undergoes an azeotropic or congruent transformation on passing through it and such a point is often given a special name, **azeotropic** (actually meaning 'boiling unchanged') or **congruent**.

Exercise 10.11

The phase diagram (Fig. 10.28) is an isobarothermal section at 1273 K and 1 bar of the Fe–Cr–N phase diagram under conditions where N_2 gas does not form. An isoactivity

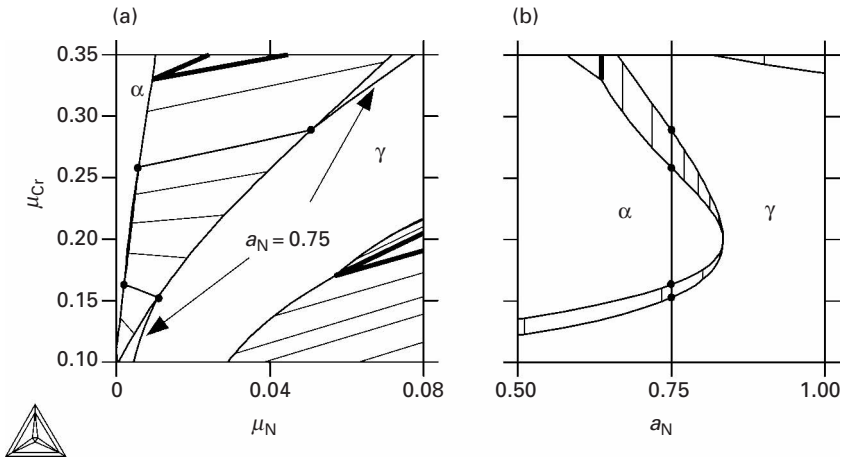


Figure 10.29 Solution to Exercise 10.11.

line for N has been drawn in the γ phase field. Show a reasonable continuation of it after first sketching the corresponding μ_{Cr} , a_N phase diagram.

Hint

Notice that there is a tie-line for which the α and γ phases have the same Cr content. It should be a point of extremum for the N potential (or N activity).

Solution

The solution is given in Fig. 10.29.

10.9 General rule for singular equilibria

It is evident that Konovalov's rule does not only apply to composition. It may thus be generalized. Suppose that a linear two-phase field in a Y^k, Y^j diagram, determined at constant values of all the other potentials except Y^l , which is chosen as the dependent potential, shows a Y^j maximum or minimum. At the point of extremum the two phases must have the same value of X_{m-1}^k . Furthermore, if Y^j is kept constant and another potential is allowed to vary, it will also have an extremum at the same value of X_{m-1}^k .

Let us now consider a two-phase equilibrium in an isobaric potential diagram for a ternary system, which is three-dimensional. Thus, $p = c - 1$. Suppose there is a point of tangency for a *plane* parallel to the μ_B, μ_C plane (i.e. an isothermal plane) as shown in Fig. 10.30(a) which is a reproduction of Fig. 8.24. As demonstrated in Fig. 10.30(b), the two phases thus have the same composition and the point of extremum is a congruent transformation point. This was already proved in Section 8.9 using an analytical method.

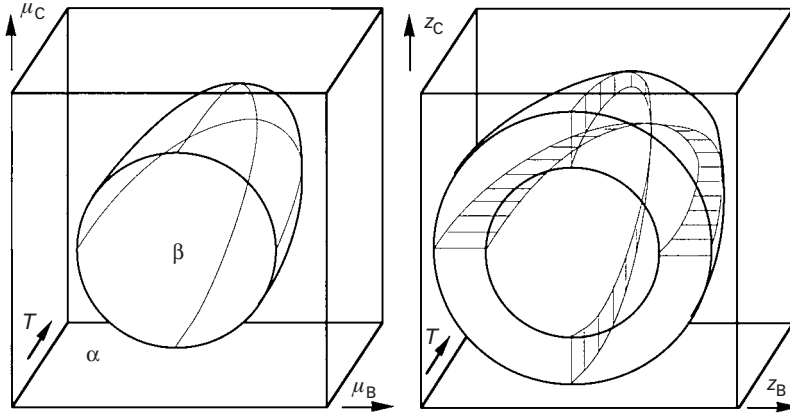


Figure 10.30 (a) Isobaric potential phase diagram of a ternary system with a doubly singular point on a divariant phase field. Thin lines represent points of tangency for lines parallel to the μ_B or μ_C axis. Their intersection is a point of tangency on a μ_B, μ_C plane. It gives an extremum of T . (b) By replacing μ_B and μ_C with their conjugate molar quantities, z_B and z_C , it is shown that the two phases in the point of T extremum must have the same z_B and the same z_C value. The point of extremum thus defines the composition of an alloy which can transform congruently between the two phases.

The point of extremum in Fig. 10.30 may be characterized as a doubly singular point. It would also appear in a diagram with a P axis under a constant value of T equal to the extreme value. In order to show in one diagram that this point is an extremum for P as well as T , one would need a fourth dimension. It is evident that the doubly singular point in Fig. 10.30 would fall at a different T value if the constant P value was different and in a P, T projection all such points would form a line, a **doubly singular curve**.

From Section 8.9 it is evident that Konovalov's rule is just a special case of a more general rule. In fact, for the ternary case, $p = c = 3$, it was formulated by von Alkemade [21]. His rule was originally formulated for a liquid which solidifies to two solid phases and P is regarded as constant. It may be stated as follows, 'The direction of falling temperature of the liquid in equilibrium with two solid phases is always away from the tie-line between the solid phases. If the liquid falls on the tie-line, then the three-phase equilibrium is at a temperature maximum.' Figure 10.31 illustrates von Alkemade's rule. It is evident that Alkemade neglected the possibility of having a temperature minimum.

The reasoning applied to Konovalov's rule can also be applied to von Alkemade's rule. If T is kept constant at the extreme value and P is varied with the three phases present, then one will find that P also has an extremum. At a different constant value of P , the T extremum would occur at a different value. The locus of these three-phase equilibria would also give a line in Schreinemaker's projection, a singular curve.

From the mathematical study of conditions of extrema given in Section 8.9 it is evident that Konovalov's rule can be applied to two-phase equilibria and von Alkemade's rule to three-phase equilibria in systems with $c > p$, although they were originally formulated for $c = p$. Konovalov's rule: T at constant P and P at constant T have extreme values for a

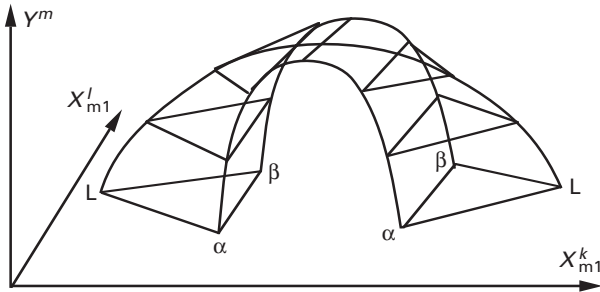


Figure 10.31 Ternary phase diagram at constant P and with two molar axes showing a three-phase equilibrium with an extremum of T (here represented by Y^m), illustrating von Alkemade's rule. The triangles are parallel to the X_{m1}^k, X_{m1}^l plane.

two-phase equilibrium if the two phases have the same composition, i.e. fall on the same point; von Alkemade's rule: T at constant P and P at constant T have extreme values for a three-phase equilibrium if the compositions of the three phases fall on a straight line. We can combine these cases into a general **rule for singular equilibria**: T at constant P and P at constant T have extreme values for an equilibrium between p phases if their compositions fall on a point for $p = 2$ (Konovalov's rule), on a line for $p = 3$ (von Alkemade's rule), on a plane for $p = 4$, etc. In all these cases a curve representing the locus of these equilibria can be plotted in the T, P diagram obtained by Schreinemaker's projection. For $p = c$ such a line is called a singular line, for $p = c - 1$ a doubly singular line, etc. The connection between such lines will be demonstrated in Fig. 12.15.

Finally, it may be instructive to apply the phase field rule to the diagram in Fig. 10.25(b). For the two-phase field liquid + vapour we get

$$d = c = +2 - p - n_s + n_m = 2 + 2 - 2 - 1 + 1 = 2,$$

because we have sectioned once, $n_s = 1$, by keeping temperature, which is a potential, constant. There is one molar variable, used as axis in the P, z_B diagram, $n_m = 1$. The result agrees with the diagram because it shows a two-dimensional phase field for the two phases. However, if we section once more, at a constant value of z_B , then $n_s = 2$ and we get $d = 2 + 2 - 2 - 2 + 1 = 1$. The phase diagram is now just a vertical line and in general it will show that the two-phase field extends over a range of P values in agreement with the calculated $d = 1$. However, the special section, going through the point of extremum (the singular point), will show the two phases coexisting at a point, and one should thus have expected to obtain $d = 0$. It is evident that one should exercise special care when applying the phase field rule to systems with singular points. This problem will be discussed further in Chapter 13.

Exercise 10.12

Try to construct a diagram similar to Fig. 10.31 for a case where α falls between L and β at the maximum.

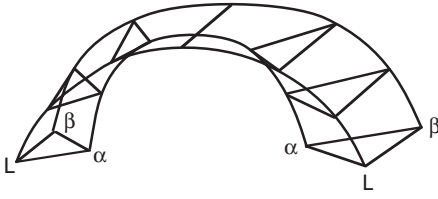


Figure 10.32 Solution to Exercise 10.12.

Solution

The solution is given in Fig. 10.32.

11 Direction of phase boundaries

11.1 Use of distribution coefficient

In this chapter we shall examine in more detail the direction of phase boundaries in molar and mixed phase diagrams. As an introduction we shall first discuss some approximate calculations based upon the use of the distribution coefficient of a component between two phases but later we shall use a more general method.

In multinary systems one is often interested in the distribution of a particular component between two phases. One may for instance define a distribution coefficient (also called partition coefficient) which can be used to represent experimental data and to carry out calculations of phase boundaries and changes in chemical potentials.

Let us consider the equilibrium between two solution phases, α and β , which exist already without an element B. On adding B one finds that it partitions between the two phases in a characteristic manner, which can be derived from the equilibrium condition $G_B^\alpha = G_B^\beta$. By applying a general model for a solution phase we obtain

$${}^\circ G_B^\alpha + RT \ln x_B^\alpha + {}^E G_B^\alpha = {}^\circ G_B^\beta + RT \ln x_B^\beta + {}^E G_B^\beta, \quad (11.1)$$

in which ${}^E G_B^\alpha$ and ${}^E G_B^\beta$ represent the deviation from ideal solution behaviour. We may define a distribution coefficient $K_B^{\alpha/\beta}$ as

$$K_B^{\alpha/\beta} = x_B^{\alpha/\beta} / x_B^{\beta/\alpha} = \exp \left[\frac{1}{RT} ({}^\circ G_B^\beta - {}^\circ G_B^\alpha + {}^E G_B^\beta - {}^E G_B^\alpha) \right]. \quad (11.2)$$

In many cases the distribution coefficient is relatively independent of composition. This occurs when the composition dependence of the partial Gibbs energy of each phase is mainly given by the $RT \ln x$ term. In such cases the distribution coefficient may be a useful tool. As an example we may consider the case where both phases are dilute solutions in a major component A. The excess Gibbs energy terms may then be approximated by a regular solution parameter L and we find, for low B contents,

$$K_B^{\alpha/\beta} = \exp(\Delta G_B / RT) \text{ where } \Delta G_B = {}^\circ G_B^\beta - {}^\circ G_B^\alpha + L^\beta - L^\alpha, \quad (11.3)$$

It should be emphasized that ΔG_B , being a Gibbs energy, may be represented as $\Delta H_B - T \Delta S_B$ and we thus obtain

$$K_B^{\alpha/\beta} = K_o \exp(\Delta H_B / RT), \quad (11.4)$$

in which K_0 and ΔH_B are often approximated as constant. When there are several minor components, we can define a distribution coefficient for each one

$$x_j^\alpha/x_j^\beta \equiv K_j^{\alpha/\beta}. \quad (11.5)$$

For the major component we obtain, from $G_A^\alpha = G_A^\beta$,

$${}^oG_A^\alpha + RT \ln x_A^\alpha + {}^E G_A^\alpha = {}^oG_A^\beta + RT \ln x_A^\beta + {}^E G_A^\beta, \quad (11.6)$$

but it is not useful to define a distribution coefficient for this component. Instead we can apply another approximation if the total content of alloying elements is small,

$$\ln x_A = \ln(1 - \sum x_j) \cong -\sum x_j. \quad (11.7)$$

For dilute solutions we may neglect the excess Gibbs energy for this component, obtaining

$$\sum x_j^\beta - \sum x_j^\alpha = ({}^oG_A^\beta - {}^oG_A^\alpha)/RT. \quad (11.8)$$

For a binary system we thus have two equations derived from the equilibrium conditions for the two components. For any temperature and pressure we can calculate two unknown quantities, i.e. the compositions of the two phases. The temperature dependence of the various parameters will give the directions of the two phase boundaries in a T, x diagram. In an isobarothermal section of a ternary system there will be three equations and each of the two phase boundaries will be represented by a line. With the approximations used here we have been able to simplify all the equilibrium equations to linear equations and the phase boundaries will thus be approximately straight lines as far as the dilute solution approximation is valid. It is thus possible to construct the A-rich corner of a ternary diagram from the binary diagrams by simply using a ruler. Two examples are given in Fig. 11.1 and it should be noticed that the construction of the second one is based upon an extrapolation of the phase boundaries in one of the binary systems to negative compositions. This is non-physical but in accordance with the form of the mathematical equations.

Exercise 11.1

Fe has two allotropic modifications, γ (fcc) and α (bcc). At 1423 K γ is more stable by 71 J/mol but α can be stabilized by alloying with 5 atom % Si. Estimate how much Si is required if the alloy also contains 0.5 atom % Ni, which has a distribution coefficient between γ and α of 1.3.

Hint

First evaluate the distribution coefficient for Si from the information.

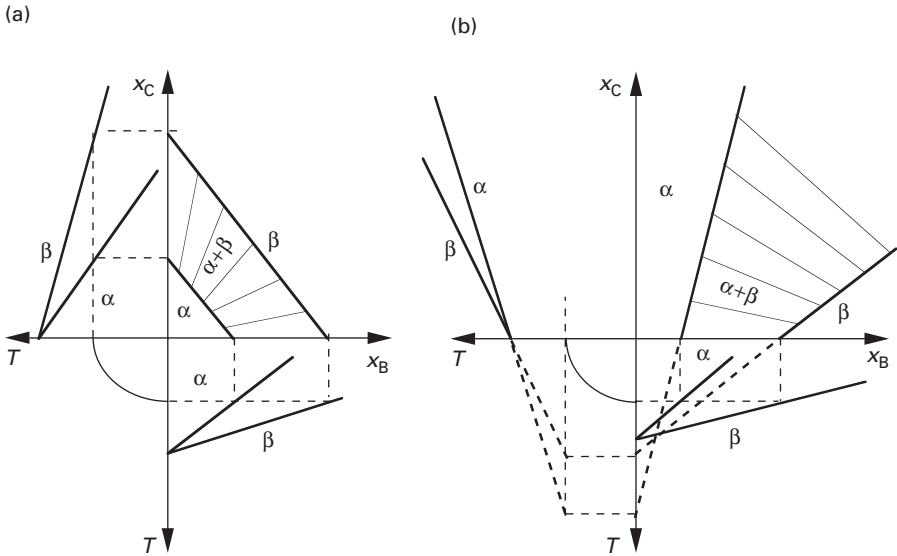


Figure 11.1 Isobarothermal section of ternary phase diagram showing equilibrium between two phases, both with the same major component.

Solution

$\Sigma x_j^\gamma - \Sigma x_j^\alpha = ({}^{\circ}G_{\text{Fe}}^\gamma - {}^{\circ}G_{\text{Fe}}^\alpha)/RT = -71/8.3145 \cdot 1423 = -0.006$; For the binary Fe–Si system: $-0.006 = x_{\text{Si}}^\gamma - x_{\text{Si}}^\alpha = x_{\text{Si}}^\alpha(K_{\text{Si}}^{\gamma/\alpha} - 1) = 0.05(K_{\text{Si}}^{\gamma/\alpha} - 1)$; $K_{\text{Si}}^{\gamma/\alpha} = 1 - 0.12 = 0.88$.

For Fe–Si–Ni alloy: $-0.006 = x_{\text{Si}}^\alpha(K_{\text{Si}}^{\gamma/\alpha} - 1) + x_{\text{Ni}}^\alpha(K_{\text{Ni}}^{\gamma/\alpha} - 1) = x_{\text{Si}}^\alpha \cdot (0.88 - 1) + 0.005 \cdot (1.3 - 1) = -0.12x_{\text{Si}}^\alpha + 0.0015$; $x_{\text{Si}}^\alpha = 0.0075/0.12 = 0.0625$.

11.2 Calculation of allotropic phase boundaries

On an allotropic phase boundary the two phases have the same composition (see Section 7.5). When comparing two phases we get the following expression by definition if we apply the regular solution model to both phases (${}^E G_m = x_A x_B L$, see Section 7.1) because the ideal entropy term will be the same for two solution phases of the same compositions and will thus drop out.

$$G_m^\beta - G_m^\alpha = x_A({}^{\circ}G_A^\beta - {}^{\circ}G_A^\alpha) + x_B({}^{\circ}G_B^\beta - {}^{\circ}G_B^\alpha) + x_A x_B(L^\beta - L^\alpha). \quad (11.9)$$

For low B contents it may be convenient to rearrange the equation as

$$G_m^\beta - G_m^\alpha = {}^{\circ}G_A^\beta - {}^{\circ}G_A^\alpha + x_B({}^{\circ}G_B^\beta - {}^{\circ}G_B^\alpha - {}^{\circ}G_A^\beta + {}^{\circ}G_A^\alpha + L^\beta - L^\alpha) - x_B^2(L^\beta - L^\alpha). \quad (11.10)$$

At sufficiently low B contents we can neglect the last square term. Close to the temperature

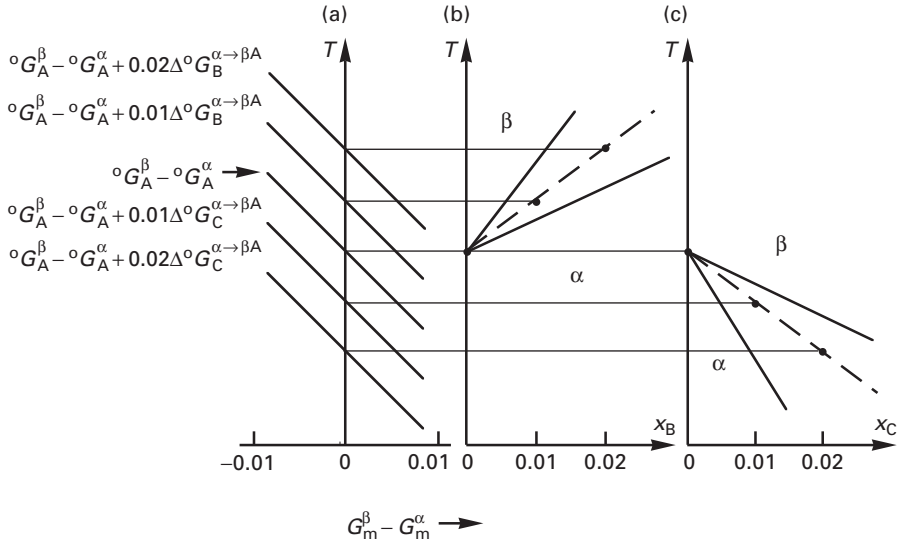


Figure 11.2 The effects of two types of alloying elements on the allotropic phase boundary. The equilibrium phase boundaries (solid lines) fall one on each side of the allotropic phase boundary (dashed lines). The diagrams are calculated with $\Delta^\circ G_B^{\alpha \rightarrow \beta A} = RT \ln 2$ and $\Delta^\circ G_C^{\alpha \rightarrow \beta A} = -RT \ln 2$.

of the allotropic phase transformation for pure A we can neglect the term ${}^\circ G_A^\beta - {}^\circ G_A^\alpha$ in the bracket, which is there close to zero, and we thus get

$$G_m^\beta - G_m^\alpha \cong {}^\circ G_A^\beta - {}^\circ G_A^\alpha + x_B \cdot \Delta^\circ G_B^{\alpha \rightarrow \beta A}, \quad (11.11)$$

where we have introduced the following notation

$$\Delta^\circ G_B^{\alpha \rightarrow \beta A} = {}^\circ G_B^\beta - {}^\circ G_B^\alpha + L^\beta - L^\alpha. \quad (11.12)$$

We have already seen that the distribution coefficient of B between α and β can be approximated by an expression for low B contents

$$K_B^{\alpha/\beta} = \exp(\Delta^\circ G_B^{\alpha \rightarrow \beta A} / RT) = \exp[({}^\circ G_B^\beta - {}^\circ G_B^\alpha + L^\beta - L^\alpha) / RT]. \quad (11.13)$$

We thus find the following relation between the parameters used in the calculation of allotropic boundaries as well as ordinary phase boundaries

$$\Delta^\circ G_B^{\alpha \rightarrow \beta A} = RT \ln K_B^{\alpha/\beta}. \quad (11.14)$$

Within a narrow range of temperature and composition, it is reasonable to assume that $\Delta^\circ G_B^{\alpha \rightarrow \beta A}$ is constant and we can then describe the effect of the alloying element as a parallel displacement of the curve for ${}^\circ G_A^\beta - {}^\circ G_A^\alpha$ by the amount $x_A \cdot \Delta^\circ G_B^{\alpha \rightarrow \beta A}$. We shall thus get two types of alloying effect, which are demonstrated by B and C in Fig. 11.2. There it is assumed that ${}^\circ G_A^\beta - {}^\circ G_A^\alpha$ varies linearly with temperature.

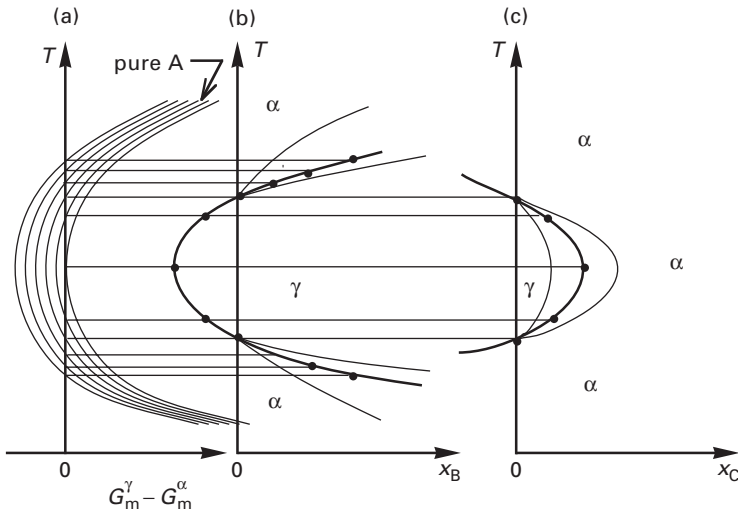


Figure 11.3 The effects of two types of alloying elements on the allotropic phase boundary (thick lines) when the low-temperature phase comes back at high temperatures. The phase boundaries are here given with thin lines.

We can obtain an equation for the allotropic phase boundary by inserting $G_m^\beta - G_m^\alpha = 0$ in Eq. (11.11).

$$x_B^{\text{allot}} = -(G_A^\beta - G_A^\alpha) / \Delta G_B^{\alpha \rightarrow \beta A} = -(G_A^\beta - G_A^\alpha) / RT \ln K_B^{\alpha/\beta}. \quad (11.15)$$

Close to the transition point T_0 for pure A we obtain

$$x_B^{\text{allot}} = -(T - T_0)(H_A^\beta - H_A^\alpha) / T_0 \Delta G_B^{\alpha \rightarrow \beta A}. \quad (11.16)$$

This type of construction is especially interesting for iron because its high-temperature phase δ is identical to its low-temperature phase α . As a consequence, the allotropic phase boundary must be strongly curved as demonstrated in Fig. 11.3. It should be noticed that one can extrapolate all phase boundaries mathematically, even to negative alloy contents if one avoids the use of mathematical expressions containing $\ln x_B$. The two types of alloying effects on iron, the stabilization of austenite (γ) by element B and ferrite (α) by element C, thus look like each other's mirror images. It should finally be emphasized that the approximate equations derived in this section are valid only up to a few atomic per cent of the alloying element.

Exercise 11.2

Suppose pure A has an α/β transition at 1000 K. An alloying element B, which itself has the α structure at all temperatures, has been found first to expand the range of the β phase to lower temperatures but at higher B contents the α phase will win. Find the congruent point for the α/β equilibrium from the following kind of expression for

both phases: $G_m = x_A^\alpha G_A + x_B^\alpha G_B + RT(x_A \ln x_A + x_B \ln x_B) + L x_A x_B$, where ${}^\circ G_A^\alpha - {}^\circ G_A^\beta = R(T - 1000)$; ${}^\circ G_B^\alpha - {}^\circ G_B^\beta = -RT$; $L^\alpha = 200R$ and $L^\beta = -1000R$.

Hint

At a point of extremum, where the ordinary phase boundaries are horizontal, the allotropic phase boundary coincides with them and is also horizontal. It is much easier to calculate this point from the allotropic phase boundary than from the ordinary ones. It is given by $G_m^\alpha - G_m^\beta = 0$.

Solution

$$G_m^\alpha - G_m^\beta = x_A({}^\circ G_A^\alpha - {}^\circ G_A^\beta) + x_B({}^\circ G_B^\alpha - {}^\circ G_B^\beta) + (L^\alpha - L^\beta)x_A x_B; \quad x_A R(T - 1000) + x_B(-RT) + (200 + 1000)R x_A x_B = 0; \quad RT(x_A - x_B) - 1000R x_A + 1200R x_A x_B = 0; \quad T = (1000x_A - 1200x_A x_B)/(x_A - x_B) = 1000(1 - 2.2x_B + 1.2x_B^2)/(1 - 2x_B); \quad dT/dx_B = 1000[(1 - 2x_B)(-2.2 + 2.4x_B) - (1 - 2.2x_B + 1.2x_B^2)(-2)]/(1 - 2x_B)^2 = 0; \quad x_B = 0.092; \quad T = 990K.$$

11.3 Variation of a chemical potential in a two-phase field

We shall now consider the effect of a ternary alloying addition on a two-phase equilibrium which exists already in a binary system. The effect of the minor binary component on the chemical potential can be estimated rather accurately from the distribution coefficient of the alloying element between the two phases without using any information on the direction of the phase boundaries in the ternary system. In Section 8.8 we considered the effect of any small change in composition of phases in a ternary system by combining two Gibbs–Duhem relations at constant T and P . We can easily introduce a distribution coefficient in Eq. (8.46).

$$d\mu_C = -\frac{x_B^\alpha x_A^\beta - x_B^\beta x_A^\alpha}{x_A^\beta x_C^\alpha - x_A^\alpha x_C^\beta} \cdot d\mu_B = x_B^\alpha x_A^\beta \cdot \frac{1 - K_{BA}^{\beta/\alpha}}{x_A^\alpha x_C^\beta - x_A^\beta x_C^\alpha} \cdot d\mu_B. \quad (11.17)$$

By dividing through with $(x_A^\alpha + x_B^\alpha) \cdot (x_A^\beta + x_B^\beta)$, which is equal to 1, we can change from the x composition to u (see Section 4.3). The distribution coefficient for B and A between the two phases can be defined with both types of variable

$$K_{BA}^{\beta/\alpha} = x_B^\beta x_A^\alpha / x_A^\beta x_B^\alpha = u_B^\beta u_A^\alpha / u_A^\beta u_B^\alpha. \quad (11.18)$$

At low contents of B in both phases we can approximate u_A^α and u_A^β with unity and we can apply Henry's law to B in the α phase in the following form if the C content in α is also low,

$$\mu_B = G_B^\alpha = {}^\circ G_B^\alpha + RT \ln f_B^\alpha + RT \ln u_B^\alpha \quad (11.19)$$

$$d\mu_B = (RT/u_B^\alpha) \cdot du_B^\alpha. \quad (11.20)$$

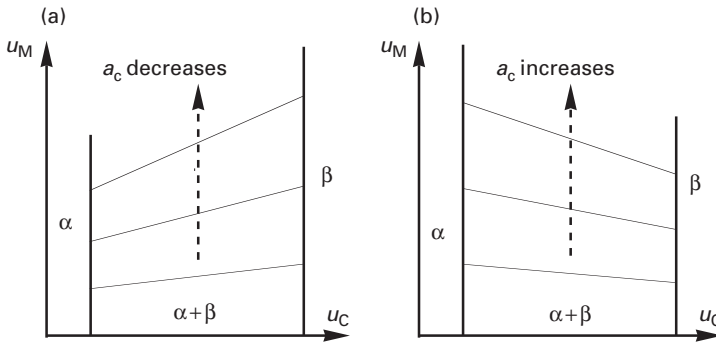


Figure 11.4 The effect of the slope of tie-lines on the activity of a component in a two-phase field.

The equation is thus simplified to

$$\frac{d\mu_C}{du_B^\alpha} = RT \cdot \frac{1 - K_{BA}^{\beta/\alpha}}{u_C^\beta - u_C^\alpha}. \quad (11.21)$$

By approximating the right-hand side with its value close to the binary A–C side of the system, we can easily integrate and obtain

$$\mu_C^{\text{ternary}} - \mu_C^{\text{binary}} = RT \cdot \frac{1 - K_{BA}^{\beta/\alpha}}{u_C^\beta - u_C^\alpha} \cdot u_B^\alpha, \quad (11.22)$$

where u_B^α is the B content of α in the ternary alloy. By introducing the activity for C we instead obtain

$$\ln \frac{a_C^{\text{ternary}}}{a_C^{\text{binary}}} = \frac{1 - K_{BA}^{\beta/\alpha}}{u_C^\beta - u_C^\alpha} \cdot u_B^\alpha. \quad (11.23)$$

This is a useful equation for rough calculations. It demonstrates that an alloying element which concentrates to the phase which is richest in C, i.e. which has $K_{BA}^{\beta/\alpha} > 1$ if β is the C-rich phase, will decrease the C activity for the two-phase equilibrium $\alpha + \beta$. An alloying element that concentrates to the C-poor phase will increase the C activity. From the derivation it is evident that this effect is additive for several alloying elements if evaluated for μ_C or $\ln a_C$.

The value of $K_{BA}^{\beta/\alpha}$ is directly related to the slope of the tie-lines in the u_C , u_M phase diagram. We can thus illustrate the two cases with the phase diagrams in Fig. 11.4 where the u parameters are used. The alloying element will have no effect on the C activity of the two-phase equilibrium if the tie-lines are horizontal, i.e. if they are directed towards the C corner which is situated infinitely far away in a diagram with the u variable.

The equation shows that μ_C does not change in a two-phase field where $K = 1$, i.e. where the two phases have the same content of B relative to A. This is thus a point of extremum and the present result is in complete agreement with Kononov's rule. Compare with Exercise 10.11 where N plays the role of C and Cr the role of B.

The chemical potential of a two-phase equilibrium can also be strongly affected by a difference in pressure, caused by the surface energy in a curved phase interface. The complete form of the Gibbs–Duhem equation is the following:

$$x_A d\mu_A + x_B d\mu_B + x_C d\mu_C = V_m dP - S_m dT. \quad (11.24)$$

Now we shall let the pressure vary in the β phase but keep the temperature constant. Equation (11.17) will thus have one more term, which can be written as

$$\frac{x_A^\alpha V_m^\beta dP^\beta}{x_A^\alpha x_C^\beta - x_A^\beta x_C^\alpha} \quad \text{or} \quad \frac{u_A^\alpha dP^\beta}{u_A^\alpha u_C^\beta - u_A^\beta u_C^\alpha} \cdot \frac{V_m^\beta}{1 - x_C^\beta}. \quad (11.25)$$

For low B contents we can thus write

$$d\mu_C = k \cdot d\mu_B^\alpha + l \cdot dP^\beta, \quad (11.26)$$

where $k = RT(1 - K_{BA}^{\beta/\alpha})/(u_C^\beta - u_C^\alpha)$ and $l = V_m^\beta/(1 - x_C^\beta)(u_C^\beta - u_C^\alpha)$.

Exercise 11.3

Low-carbon steels are sometimes carburized in order to increase the surface hardness. This is done at a temperature where γ (fcc) is the stable phase. A hard and brittle carbide called cementite, Fe_3C , may form if one uses a high carbon activity in the gas. In the binary system it has a carbon activity of 1.04 when in equilibrium with γ at 1173 K. What would be the highest carbon activity to be used if one wants to avoid cementite for a steel with 1.5 atom % Cr and 3 atom % Ni. They can both replace Fe in cementite and the distribution coefficient $K_{\text{MFe}}^{\text{cementite}/\gamma}$ is 6 for Cr and 0.1 for Ni.

Hint

The effects of two alloying elements on μ_C or $\ln a_C$ are additive. The alloy contents given are for the initial low-carbon steel and we should evaluate the u variable because it does not change when C is added due to its definition. We obtain $u_{\text{Cr}}^\gamma = 0.015$ and $u_{\text{Ni}}^\gamma = 0.03$. For cementite $u_C = 1/3$ and for γ in equilibrium with cementite at 1173 K we have 1.23 mass % C which gives $u_C = 0.059$.

Solution

$\ln(a_C^{\text{alloy}}/a_C^{\text{binary}}) = [(1 - 6) \cdot 0.015 + (1 - 0.1) \cdot 0.03]/[(1/3) - 0.059] = -0.17$;
 $a_C^{\text{alloy}} = a_C^{\text{binary}} \cdot \exp(-0.17) = 1.04 \cdot 0.84 = 0.88$. This is the highest value one should use.

11.4 Direction of phase boundaries

So far, we have discussed the direction of phase boundaries in some simple cases. For the general case we need a more powerful method and we should then turn to the Gibbs–Duhem relation. In fact, we have already calculated the directions of phase fields in

potential phase diagrams by the application of the Gibbs–Duhem relation. However, in order to calculate the directions of the phase boundaries in molar phase diagrams we must introduce the molar quantities instead of the potentials as variables in the Gibbs–Duhem relation. No general treatment can be given here in view of the large variety that can occur in mixed phase diagrams. Only the special case will be treated where T and P are retained but all the chemical potentials are replaced by molar contents.

The fact that the molar quantities of two phases in equilibrium are generally different, although the potentials are equal, makes it necessary to choose one of the phases, for instance α , and express the potentials through its molar quantities. If T and P are retained, then it is convenient to express the changes of the chemical potentials μ_i through the composition dependence of the partial Gibbs energies in the α phase, G_i^α . In order to make the enthalpy appear in the final expression instead of the entropy we shall use the potentials occurring in the special form of the Gibbs–Duhem relation containing enthalpy. It is obtained from the fifth line in Table 3.1.

$$H_m^\beta d(1/T) + (V_m^\beta/T) dP - \sum_{i=1}^c x_i^\beta d(\mu_i/T) = 0. \quad (11.27)$$

We shall now introduce the properties of the chosen phase α by using $\mu_i = G_i^\alpha$ and with $1/T$, P and x_j^α for $j > 1$ as the independent variables, treating x_1^α as the dependent composition variable. We can then eliminate $d(\mu_i/T)$ using

$$d(\mu_i/T) = \frac{\partial G_i^\alpha}{\partial(1/T)} d(1/T) + \frac{\partial G_i^\alpha}{\partial P} dP/T + \sum_{j=2}^c \frac{\partial G_i^\alpha}{\partial x_j^\alpha} dx_j^\alpha/T. \quad (11.28)$$

We can insert

$$\partial(G_i^\alpha/T)/\partial(1/T) = H_i^\alpha \quad (11.29)$$

$$\partial G_i^\alpha/\partial P = V_i^\alpha. \quad (11.30)$$

Applying Eq. (4.7) to the Gibbs energy we obtain by selecting component 1 as the dependent one,

$$G_i^\alpha = G_m^\alpha + \partial G_m^\alpha/\partial x_i^\alpha - \sum_{l=2}^c x_l^\alpha \partial G_m^\alpha/\partial x_l^\alpha. \quad (11.31)$$

Using the notation of second derivatives of G_m when component 1 is the dependent one, which was introduced in Section 6.6, we obtain,

$$\partial G_i^\alpha/\partial x_j^\alpha = g_{ij}^\alpha - \sum_{l=2}^c x_l^\alpha g_{jl}^\alpha. \quad (11.32)$$

It should be noted that g_{1j}^α does not exist since component 1 is the dependent one. When inserting these expressions in Eq. (11.27) we shall also replace H_m^β by $\sum x_i^\beta H_i^\beta$ and V_m^β by $\sum x_i^\beta V_i^\beta$.

$$\begin{aligned} & \sum x_i^\beta H_i^\beta d(1/T) + \sum x_i^\beta V_i^\beta dP/T \\ & - \sum x_i^\beta \left[H_i^\alpha d(1/T) + V_i^\alpha dP/T + \sum_{j=2}^c \left(g_{ij}^\alpha - \sum_{l=2}^c x_l^\alpha g_{jl}^\alpha \right) dx_j^\alpha/T \right] = 0. \quad (11.33) \end{aligned}$$

However,

$$\sum_{i=1}^c x_i^\beta \left(g_{ij}^\alpha - \sum_{l=2}^c x_l^\alpha g_{jl}^\alpha \right) = \sum_{i=2}^c x_i^\beta g_{ji}^\alpha - 1 \cdot \sum_{l=2}^c x_l^\alpha g_{jl}^\alpha = \sum_{i=2}^c (x_i^\beta - x_i^\alpha) g_{ji}^\alpha, \quad (11.34)$$

since g_{ij} for $i = 1$ does not exist and the terms in the summation over index l are independent of index i . We obtain, because $d(1/T) = -dT/T^2$

$$\sum_{i=2}^c \sum_{j=2}^c (x_i^\beta - x_i^\alpha) g_{ji}^\alpha dx_j^\alpha + \sum_{i=1}^c x_i^\beta (H_i^\beta - H_i^\alpha) dT/T - \sum_{i=1}^c x_i^\beta (V_i^\beta - V_i^\alpha) dP = 0. \quad (11.35)$$

This is the desired relation. Contrary to the Gibbs–Duhem relation this equation always concerns two phases, and all the terms become zero when applied to the phase which was chosen for expressing the chemical potentials. When applied to more than two phases it yields a system of equations and some variables can then be eliminated with the method used for calculating the direction of phase fields from the Gibbs–Duhem relation. The elements of the determinants will then be $\Sigma(x_i^\beta - x_i^\alpha)g_{ij}^\alpha$ instead of x_i^β . However, we shall apply the equation to equilibria concerning two coexisting phases and the equation can then be applied directly.

For a binary system under isobaric conditions we get for the phase boundaries

$$\left(\frac{\partial x_2^\alpha}{\partial T} \right)_{\text{coex}} = \frac{x_1^\beta (H_1^\alpha - H_1^\beta) + x_2^\beta (H_2^\alpha - H_2^\beta)}{(x_2^\beta - x_2^\alpha) g_{22}^\alpha T} = \frac{\Delta H_m^{\beta\text{in}\alpha}}{(x_2^\beta - x_2^\alpha) g_{22}^\alpha T} \quad (11.36)$$

$$\left(\frac{\partial x_2^\beta}{\partial T} \right)_{\text{coex}} = \frac{x_1^\alpha (H_1^\beta - H_1^\alpha) + x_2^\alpha (H_2^\beta - H_2^\alpha)}{(x_2^\alpha - x_2^\beta) g_{22}^\beta T} = \frac{\Delta H_m^{\alpha\text{in}\beta}}{(x_2^\alpha - x_2^\beta) g_{22}^\beta T} \quad (11.37)$$

The numerator is equal to the heat of solution of the other phase (α or β) in the phase being considered (β or α). The phase boundary will be vertical if the heat of solution is zero. Figure 11.3(c) shows a case where both boundaries turn vertical at almost the same temperature and then lean the other way. Both phases were rich in one component, 1, and the heat of solution mainly depended on the terms with $(H_1^\alpha - H_1^\beta)$, a quantity that went through zero in that temperature range.

Either of these two equations can be used to evaluate the slope of a phase boundary but also to calculate the width of a two-phase field if the slope is known.

$$x_2^\beta - x_2^\alpha = \frac{\Delta H_m^{\beta\text{in}\alpha}}{g_{22}^\alpha T (dx_2^\alpha/dT)_{\text{coex}}} = - \frac{\Delta H_m^{\alpha\text{in}\beta}}{g_{22}^\beta T (dx_2^\beta/dT)_{\text{coex}}}. \quad (11.38)$$

Exercise 11.4

Derive an equation for the solubility of pure component 2 in a phase α which is almost pure component 1.

Hint

Section 7.1 gives $g_{22}^{\alpha} \equiv d^2 G_m^{\alpha} / d(x_2^{\alpha})^2 \cong RT/x_2^{\alpha}$ if x_2^{α} is small. Also use $x_2^{\beta} - x_2^{\alpha} \cong 1$.

Solution

$dx_2^{\alpha}/dT = \Delta H_m / (RT^2/x_2^{\alpha})$; $d(\ln x_2^{\alpha})/d(1/T) = \Delta H_m/R$; $x_2^{\alpha} = K \cdot \exp(\Delta H_m/RT)$. Usually, ΔH_m is replaced by $-L$, where L is the heat given off by the dissolution of β .

Exercise 11.5

Apply Eq. (11.35) to a binary case at constant P . Then consider the $\alpha/\alpha + \beta$ phase boundary in the T, x phase diagram in a system where α is almost pure A and β is a bcc phase close to the 50–50 composition. Suppose β has a sharp transformation at T_0 from a perfectly ordered to a perfectly disordered state (which would never happen). Calculate the angle of the $\alpha/(\alpha + \beta)$ phase boundary at T_0 (or, more precisely, the difference in direction, dx/dT , of this phase boundary just below and just above T_0).

Hint

At constant P : $[x_1^{\beta}(H_1^{\alpha} - H_1^{\beta}) + x_2^{\beta}(H_2^{\alpha} - H_2^{\beta})]dT = (x_2^{\beta} - x_2^{\alpha})g_{22}^{\alpha}Tdx_2^{\alpha}$. Notice that $x_1^{\beta}H_1^{\beta} + x_2^{\beta}H_2^{\beta} = H_m^{\beta}$ and that the entropy of disordering is $-R(x_1 \ln x_1 + x_2 \ln x_2) = R \ln 2$ for $x_1 = x_2 = 0.5$. For the dilute solution of component 2 in α we may use $g_{22}^{\alpha} = RT/x_1^{\alpha}x_2^{\alpha}$.

Solution

$x_1^{\beta} = x_2^{\beta} = 0.5$ gives $dx_2^{\alpha}/dT = 0.5(H_1^{\alpha} - H_1^{\beta} + H_2^{\alpha} - H_2^{\beta})/(0.5 - 0)g_{22}^{\alpha}T$. By taking the difference between just below and just above the transition, we eliminate H_1^{α} and H_2^{α} and thus get $\Delta(dx_2^{\alpha}/dT) = (H_m^{\beta} - H_m^{\beta'})/0.5g_{22}^{\alpha}T_0$. But $H_m^{\beta} - H_m^{\beta'} = \Delta H_m^{\text{ordering}}$ and at the transition point the two states have the same Gibbs energy and thus $\Delta H_m^{\text{ord}} - T_0 \Delta S_m^{\text{ord}} = 0$; $\Delta(dx_2^{\alpha}/dT) = T_0 \Delta S_m^{\text{ord}}/0.5g_{22}^{\alpha}T_0 = R \ln 2 / (0.5RT_0/x_2^{\alpha}) = 2x_2^{\alpha} \ln 2 / T_0$.

Exercise 11.6

When adding a third component C to a certain binary system A–B under constant P , one found that the depression of the freezing point of a stoichiometric phase A_aB_b only depended upon the molar content x_C and was independent of whether one kept x_A, x_B or x_A/x_B constant. Examine if this result can be expected in general. Suppose the pressure is constant.

Hint

Apply the general equation for the direction of phase boundaries, Eq. (11.35), to the ternary case, making C the dependent component 1. Remember that g_2 is the derivative of G_m with respect to x_2 , keeping x_3 constant, i.e. with $dx_1 = -dx_2$. Writing G_m as $\sum x_i ({}^\circ G_i + RT \ln x_i) + {}^E G_m(x_2, x_3)$ we get: $g_2 = {}^\circ G_2 - {}^\circ G_1 + RT(\ln x_2 - \ln x_1) + \partial^E G_m / \partial x_2$ and $g_{22} = RT(1/x_2 + 1/x_1) + \partial^{2E} G_m / \partial x_2^2$, etc. Look for the predominating term when x_1 is small. Furthermore, the liquid composition is close to that of $A_a B_b$.

Solution

For $x_C \equiv x_1 \rightarrow 0$ we get $[(x_2^\beta - x_2^L)g_{22}^L + (x_3^\beta - x_3^L)g_{23}^L]dx_2^L + [(x_2^\beta - x_2^L)g_{32}^L + (x_3^\beta - x_3^L)g_{33}^L]dx_3^L = -[x_2^L(H_2^\beta - H_2^L) + x_3^L(H_3^\beta - H_3^L)]dT/T$ under constant P . The predominating term in g_{22} is RT/x_1 and all the other second derivatives of g have the same predominating term. By neglecting other terms we get $[(x_2^\beta - x_2^L + x_3^\beta - x_3^L) \cdot RT/x_1^L] dx_2^L + [(x_2^\beta - x_2^L + x_3^\beta - x_3^L) \cdot RT/x_1^L] dx_3^L = [(x_2^\beta - x_2^L + x_3^\beta - x_3^L) \cdot RT/x_1^L](dx_2^L + dx_3^L) = -[x_2^L(H_2^\beta - H_2^L) + x_3^L(H_3^\beta - H_3^L)]dT/T$. The depression of the freezing point thus depends on $dx_2^L + dx_3^L$ which is equal to $-dx_C^L$ whether one keeps x_A, x_B or x_A/x_B constant.

11.5 Congruent melting points

It is immediately clear from our equations for dx/dT that for a congruent transformation point in a binary system, e.g. for $x_2^\beta = x_2^L$, the phase boundaries must be horizontal and such a point must be a point of temperature extremum. This is also in agreement with Konovalov's rule (see also [22]). However, at the side of the system where x_2^L approaches zero, g_{22}^L approaches infinity as RT/x_2^L and the whole denominator in Eq. (11.37), with L instead of β , approaches $RT^2(x_2^\alpha/x_2^L - 1)$ which is not zero. Thus, the phase boundaries do not turn horizontal on the sides of the system. The two cases are demonstrated in Fig. 11.5.

The slopes of the phase boundaries at the left-hand side of the binary system in Fig. 11.5 can be evaluated from the limiting value of g_{22}^α which is RT/x_2^α when $x_2^\alpha \rightarrow 0$ (see Section 7.1).

$$\left(\frac{\partial x_2^\alpha}{\partial T}\right)_{\text{coex}} = \frac{1}{x_2^\beta - x_2^\alpha} \cdot \frac{{}^\circ H_1^\alpha - {}^\circ H_1^\beta}{(RT/x_2^\alpha)T} = \frac{K_2^{\alpha/\beta}}{1 - K_2^{\alpha/\beta}} \cdot \frac{{}^\circ H_1^\alpha - {}^\circ H_1^\beta}{RT^2} \quad (11.39)$$

$$\left(\frac{\partial x_2^\beta}{\partial T}\right)_{\text{coex}} = \frac{1}{x_2^\alpha - x_2^\beta} \cdot \frac{{}^\circ H_1^\beta - {}^\circ H_1^\alpha}{(RT/x_2^\beta)T} = \frac{1}{1 - K_2^{\alpha/\beta}} \cdot \frac{{}^\circ H_1^\alpha - {}^\circ H_1^\beta}{RT^2} \quad (11.40)$$

The width of the two-phase field at some temperature T below the transformation point T_0 for pure component 1 is obtained from the difference,

$$\frac{{}^\circ H_1^\beta - {}^\circ H_1^\alpha}{RT^2} = \frac{\partial(x_2^\beta - x_2^\alpha)}{\partial T} \cong \frac{x_2^\beta - x_2^\alpha}{T_0 - T} \quad (11.41)$$

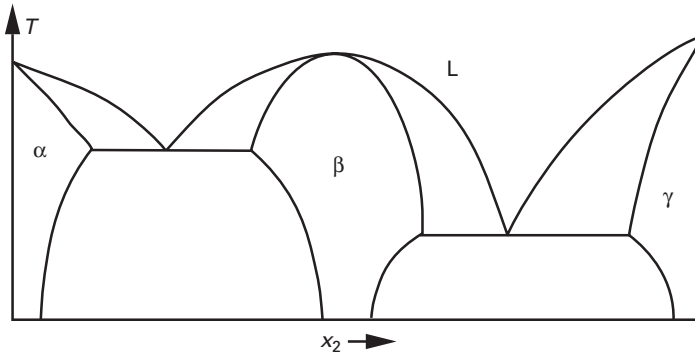


Figure 11.5 Binary T, x phase diagram at 1 bar. The point of congruent melting of β must have horizontal phase boundaries. At the melting points of the two components the phase boundaries are not horizontal.

If one of the phases is liquid, one can often neglect the solubility in the solid phase and one thus obtains a simple expression for the freezing-point depression,

$$T_0 - T = x_2^L \cdot RT^2 / ({}^{\circ}H_m^L - {}^{\circ}H_m^{\alpha}). \quad (11.42)$$

It should be emphasized that it would be difficult to see the horizontal part of a phase boundary at a congruent transformation point if the properties of the phase change so rapidly that g_{22} is very large. An obvious case is the $\beta/(\beta + L)$ boundary when β is almost stoichiometric, i.e. the composition of β does not vary noticeably. The phase boundary of the surrounding phase, in our case $L/(L + \beta)$ can also be very sharp if the properties of the liquid change rapidly with composition at the particular composition of the congruent transformation. For such cases it may be interesting to evaluate the curvatures of the two phase boundaries. At the congruent point we have $x_2^{\alpha} = x_2^{\beta}$ and the heat of solution of each phase in the other one is simply the heat of transformation of the other phase into the phase under consideration.

$$\frac{dx_2^{\beta}}{dx_2^{\alpha}} = \frac{dx_2^{\beta}/dT}{dx_2^{\alpha}/dT} = \frac{(H_m^{\beta} - H_m^{\alpha})(x_2^{\beta} - x_2^{\alpha})g_{22}^{\alpha}T}{(H_m^{\alpha} - H_m^{\beta})(x_2^{\alpha} - x_2^{\beta})g_{22}^{\beta}T} = \frac{g_{22}^{\alpha}}{g_{22}^{\beta}} \quad (11.43)$$

$$\frac{d^2T}{d(x_2^{\alpha})^2} = \frac{g_{22}^{\alpha}T}{H_m^{\alpha} - H_m^{\beta}} \left(\frac{dx_2^{\beta}}{dx_2^{\alpha}} - 1 \right) = \frac{g_{22}^{\alpha}T}{H_m^{\alpha} - H_m^{\beta}} \left(\frac{g_{22}^{\alpha}}{g_{22}^{\beta}} - 1 \right) \quad (11.44)$$

$$\frac{d^2T}{d(x_2^{\beta})^2} = \frac{g_{22}^{\beta}T}{H_m^{\beta} - H_m^{\alpha}} \left(\frac{dx_2^{\alpha}}{dx_2^{\beta}} - 1 \right) = \frac{g_{22}^{\beta}T}{H_m^{\beta} - H_m^{\alpha}} \left(\frac{g_{22}^{\beta}}{g_{22}^{\alpha}} - 1 \right) = \frac{d^2T}{d(x_2^{\alpha})^2} \left(\frac{g_{22}^{\alpha}}{g_{22}^{\beta}} \right)^2. \quad (11.45)$$

For an almost stoichiometric phase, g_{22}^{β} would be very large and for the liquid at a congruent melting point we then get

$$\frac{d^2T}{d(x_2^L)^2} = \frac{g_{22}^L T}{H_m^{\beta} - H_m^L}. \quad (11.46)$$

It should be noted that $H_m^{\beta} - H_m^L$ is negative and so is $d^2T/d(x_2^L)^2$.

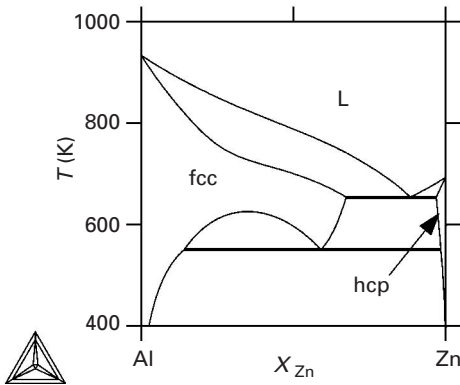


Figure 11.6 See Exercise 11.7.

It should be emphasized that another possibility of finding a horizontal phase boundary is by having g_{22}^{α} approach zero, i.e. a limit of stability.

Exercise 11.7

The T, x phase diagram of Al–Zn shows an unusual feature (Fig. 11.6). The solidus line turns almost horizontal in the centre of the system but the liquidus does not. It thus seems to be due to some property of the solid phase rather than the interaction between the two phases. Examine the possible explanation by inspecting the equation for the slope of a phase boundary. If a conclusion is reached, try to test it by examining other features of the diagram.

Hint

If the explanation is to be found in the G_m function of the solid, then the same factor may have consequences for other phase equilibria with the solid.

Solution

The equation suggests that g_{22}^{α} is very small at the centre of the system. We may thus be close to a limit of stability of the α phase where g_{22}^{α} goes through zero to turn negative. Indeed, at lower temperatures one can see the top of a miscibility gap in the α phase where a homogeneous fcc alloy starts to decompose in regions of two different compositions.

Exercise 11.8

In elementary textbooks one can sometimes see a series of sketched phase diagrams as shown in Fig. 11.7. Criticize it.

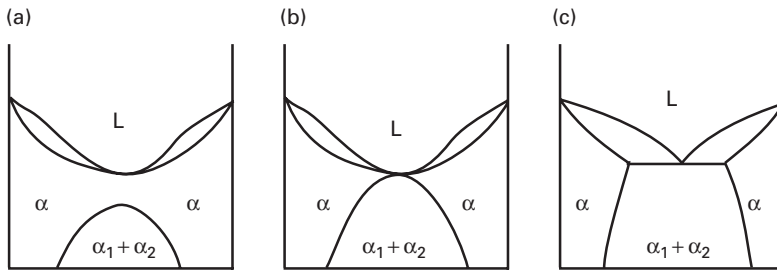


Figure 11.7 See Exercise 11.8.

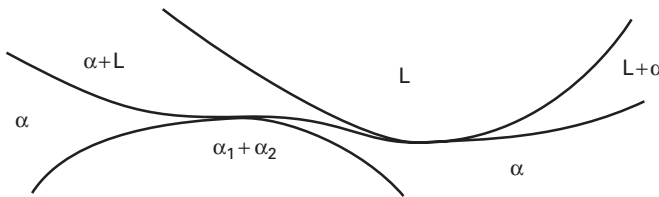


Figure 11.8 Solution to Exercise 11.8.

Hint

The author may not have remembered that there are two different effects which can make a phase boundary horizontal.

Solution

In diagram (a) the two phase boundaries at the minimum are horizontal because it is a congruent transformation point. It is an effect of the combined properties of the two phases. The top of the miscibility gap, $\alpha_1 + \alpha_2$, is horizontal because $g_{22}^{\alpha} = 0$ and that is a property of the α phase alone. It would be highly unlikely that these two phenomena should occur at the same composition, as indicated in diagram (b). Figure 11.8 gives an idea of how the two phase boundaries may meet. Compare with the phase diagram to Exercise 11.7.

Exercise 11.9

Calculate what value of g_{22}^L would give the melting point of a stoichiometric phase such a strong curvature that it looks sharp. Compare with the value for an ideal solution.

Hint

Suppose Richard's rule can be applied, $\Delta H_m = H_m^{\alpha} - H_m^L \cong -RT$. The maximum may look sharp if the radius of curvature $-1/(d^2T/dx^2)$ is less than $0.005/T$.

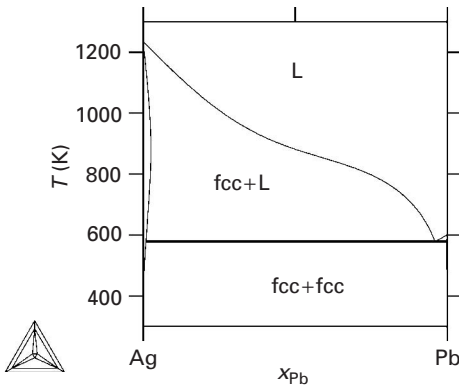


Figure 11.9 The T, x phase diagram for Ag–Pb. The solidus of the Ag phase is retrograde.

Solution

Equation (11.46) yields $-d^2T/dx^2 = -g_{22}T/(-RT) > T/0.005$; $g_{22} > 200RT$. If the solution is ideal we have $g_{22} = RT/x_1x_2$, which is generally very much lower.

11.6 Vertical phase boundaries

It is also interesting to discuss the possibility of finding a vertical phase boundary. This requires that the numerator is zero, i.e. that the heat of reaction, when β is dissolved in α , is zero. An example is given in Fig. 11.9 showing a so-called retrograde solidus line.

As another example we may take the well-known case of the so-called γ loop in binary iron diagrams with α -stabilizing alloying elements (see Fig. 11.3(c)). Here both phases are rich in iron and we can approximate the numerator in Eq. (11.36) for α with $H_{\text{Fe}}^\alpha - H_{\text{Fe}}^\gamma$ and for γ with $H_{\text{Fe}}^\gamma - H_{\text{Fe}}^\alpha$ since the alloy contents are low. The characteristic γ loop thus depends upon the fact that the enthalpy difference between α -Fe and γ -Fe changes sign and goes through zero in this range of temperature.

Exercise 11.10

From the detail of the Fe–O phase diagram (Fig. 11.10), what can be said about the heat of solution of γ -Fe in the wüstite phase?

Hint

Examine the boundary representing the solubility of γ -Fe in wüstite (W).

Solution

Since the γ phase is almost pure Fe, the numerator in the expression for $dx_{\text{O}}^{\text{W}}/dT$, obtained from Eq. (11.37), is $x_{\text{Fe}}^\gamma(H_{\text{Fe}}^{\text{W}} - H_{\text{Fe}}^\gamma) + x_{\text{O}}^\gamma(H_{\text{O}}^{\text{W}} - H_{\text{O}}^\gamma) \cong H_{\text{Fe}}^{\text{W}} - H_{\text{Fe}}^\gamma$, i.e. the heat of solution of γ -Fe in wüstite. This quantity is thus close to zero over a wide range of temperature because the boundary is almost vertical.

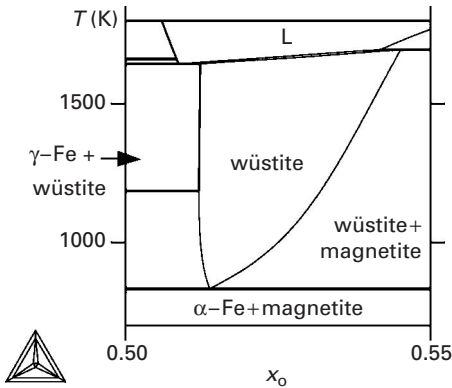


Figure 11.10 See Exercise 11.10.

11.7 Slope of phase boundaries in isothermal sections

For a ternary system under isobarothermal conditions we get

$$[(x_2^\beta - x_2^\alpha)g_{22}^\alpha + (x_3^\beta - x_3^\alpha)g_{32}^\alpha]dx_2^\alpha + [(x_2^\beta - x_2^\alpha)g_{23}^\alpha + (x_3^\beta - x_3^\alpha)g_{33}^\alpha]dx_3^\alpha = 0. \quad (11.47)$$

We can here introduce the slope of the $\alpha + \beta$ tie-line,

$$n = (x_3^\beta - x_3^\alpha)/(x_2^\beta - x_2^\alpha) \quad (11.48)$$

$$\frac{dx_3^\alpha}{dx_2^\alpha} = -\frac{g_{22}^\alpha + ng_{32}^\alpha}{g_{23}^\alpha + ng_{33}^\alpha}. \quad (11.49)$$

As an application we shall examine when the $\alpha/(\alpha + \beta)$ phase boundary is parallel to the x_2 axis, i.e. when $dx_3^\alpha/dx_2^\alpha = 0$. We find the condition

$$g_{22}^\alpha/g_{32}^\alpha = -n. \quad (11.50)$$

When the α phase is a dilute solution of components 2 and 3 in 1, the leading term in g_{22}^α/RT is $1/x_2^\alpha$ and it may be more convenient to recast the result into one of the following forms by inserting $g_{22}^\alpha/RT - 1/x_2^\alpha + 1/x_2^\alpha$ instead of g_{22}^α/RT .

$$x_2^\alpha = -\frac{1}{g_{22}^\alpha/RT - 1/x_2^\alpha + ng_{32}^\alpha/RT} \quad (11.51)$$

$$x_2^\alpha = -\frac{x_2^\beta}{(x_2^\beta - x_2^\alpha)(g_{22}^\alpha/RT - 1/x_2^\alpha) + (x_3^\beta - x_3^\alpha)g_{32}^\alpha/RT - 1}. \quad (11.52)$$

The latter equation can be rearranged into a form which is even more convenient because the ideal entropy of mixing gives a contribution of RT/x_1^α to both g_{22}^α and g_{23}^α ,

$$x_2^\alpha = \frac{x_2^\beta}{(x_2^\beta - x_2^\alpha)(1/x_1^\alpha + 1/x_2^\alpha - g_{22}^\alpha/RT) + (x_3^\beta - x_3^\alpha)(1/x_1^\alpha - g_{32}^\alpha/RT) + x_1^\beta/x_1^\alpha}. \quad (11.53)$$

We have thus made the first term in the denominator so small that it can often be neglected. One could then write

$$x_2^\alpha \cong \frac{x_2^\beta}{(x_3^\beta - x_3^\alpha) (1/x_1^\alpha - g_{32}^\alpha/RT) + x_1^\beta/x_1^\alpha} \quad (11.54)$$

It is common to introduce Wagner's interaction parameter ε_2^3 which will be discussed in Section 20.7. It yields

$$x_2^\alpha = -\frac{x_2^\beta}{\varepsilon_2^3(x_3^\beta - x_3^\alpha) - x_1^\beta/x_1^\alpha} \cong -\frac{x_2^\beta}{\varepsilon_2^3(x_3^\beta - x_3^\alpha)} \quad (11.55)$$

Exercise 11.11

According to Schreinemakers' rule the phase boundary $\alpha/(\alpha + \gamma)$ in an isobarothermal section of a ternary phase diagram must be directed towards the β point if $\alpha/(\alpha + \beta)$ is directed towards the γ point. Prove this using Eq. (11.49).

Hint

Denote the slope of the $\alpha + \gamma$ tie-line by $n^{\alpha/\gamma}$ and the slope of the $\alpha + \beta$ tie-line by $n^{\alpha/\beta}$.

Solution

$n^{\alpha/\gamma} = (dx_3/dx_2)^{\alpha/\beta} = -(g_{22}^\alpha + n^{\alpha/\beta}g_{32}^\alpha)/(g_{23}^\alpha + n^{\alpha/\beta}g_{33}^\alpha)$. Thus, $-g_{22}^\alpha - n^{\alpha/\beta}g_{32}^\alpha = n^{\alpha/\gamma}g_{23}^\alpha + n^{\alpha/\gamma}n^{\alpha/\beta}g_{33}^\alpha$. By rearranging the terms we get $-g_{22}^\alpha - n^{\alpha/\gamma}g_{23}^\alpha = n^{\alpha/\beta}g_{32}^\alpha + n^{\alpha/\beta}n^{\alpha/\gamma}g_{33}^\alpha$ and we can form $n^{\alpha/\beta} = -(g_{22}^\alpha + n^{\alpha/\gamma}g_{23}^\alpha)/(g_{32}^\alpha + n^{\alpha/\gamma}g_{33}^\alpha)$ which is equal to $(dx_3/dx_2)^{\alpha/\gamma}$ since $g_{23}^\alpha = g_{32}^\alpha$.

Exercise 11.12

Figure 11.11 shows the solubilities of the three oxides in liquid Fe at 1823 K according to an experimental study. All curves show minima. Use this information in order to estimate the Cr content of the two spinels.

Hint

Start by evaluating $\varepsilon_{\text{Cr}}^{\text{O}}$ from the minimum for the phase with a known composition, Cr_3O_4 . Knowing $\varepsilon_{\text{Cr}}^{\text{O}}$ one can then calculate the Cr content for another oxide from its minimum. Both spinels can be represented by the general formula $(\text{Fe,Cr})_3\text{O}_4$. Considering the limited accuracy of the data it is justified to approximate mass fraction Cr in liquid Fe as molar content Cr.

Solution

Let $\beta = \text{oxide}$; $\alpha = \text{liquid}$; 2 = Cr; 3 = O. Then $x_3^\beta = x_{\text{O}}^{\text{oxide}} = 4/7$ for all these oxides and $x_3^\alpha = x_{\text{O}}^{\text{L}} \cong 0$.

From the known composition of Cr_3O_4 : $0.1 = x_{\text{Cr}}^{\text{L}} = x_2^\alpha = -x_2^\beta/\varepsilon(x_3^\beta - x_3^\alpha) = -(3/7)/\varepsilon(4/7)$; $\varepsilon = -3/4 \cdot 0.1 = -7.5$.

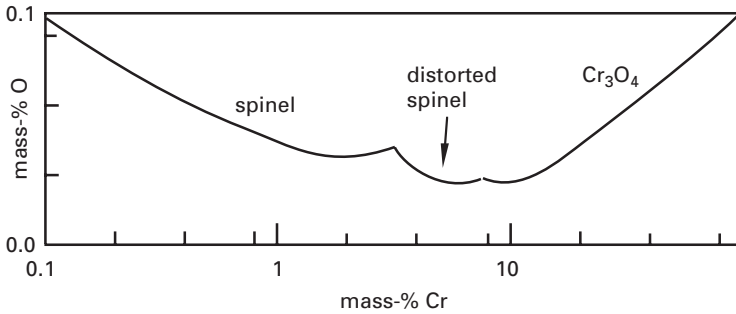


Figure 11.11 See Exercise 11.12.

Using this value we find: For an undistorted spinel: $0.02 = -x_{\text{Cr}}^{\text{oxide}}/(-7.5)(4/7)$; $x_{\text{Cr}}^{\text{oxide}} = 0.6/7$. The formula is $\text{Fe}_{2.4} \text{Cr}_{0.6} \text{O}_4$.

For distorted spinel: $0.06 = -x_{\text{Cr}}^{\text{oxide}}/(-7.5)(4/7)$; $x_{\text{Cr}}^{\text{oxide}} = 1.8/7$. The formula is $\text{Fe}_{1.2} \text{Cr}_{1.8} \text{O}_4$.

11.8 The effect of a pressure difference between two phases

In Section 11.4 we derived an expression for the change in composition of an α phase in equilibrium with a β phase caused by changes in T and P . It was then assumed that T and P had always the same values in both phases. The derivation of Eq. (11.35) can be carried out even if P changes in different ways in the two phases. This will occur when they are separated by a curved interface. In Section 16.2 we will find the equilibrium condition $P^\beta = P^\alpha + 2\sigma/r$. Now we shall simply assume that α and β can be in equilibrium even at a difference in pressure. The result will then be

$$\sum_{i=2}^c \sum_{j=2}^c (x_i^\beta - x_i^\alpha) g_{ij}^\alpha dx_j^\alpha = \sum_{i=1}^c x_i^\beta (V_i^\beta dP^\beta - V_i^\alpha dP^\alpha) - \sum_{i=1}^c x_i^\beta (H_i^\beta - H_i^\alpha) dT/T. \quad (11.56)$$

Let us now apply this equation to a binary case in which $dP^\alpha = 0$ and $dT = 0$. Using $V_m^\beta = x_1^\beta V_1^\beta + x_2^\beta V_2^\beta$ we get

$$dx_2^\alpha = \frac{V_m^\beta dP^\beta}{(x_2^\beta - x_2^\alpha) g_{22}^\alpha}. \quad (11.57)$$

An expression for the simultaneous change in the β phase can be obtained by first exchanging α and β in Eq. (11.56) and then applying it to the case $dP^\alpha = 0$ and $dT = 0$,

$$(x_2^\beta - x_2^\alpha) g_{22}^\beta dx_2^\beta = (x_1^\alpha V_1^\beta + x_2^\alpha V_2^\beta) dP^\beta \quad (11.58)$$

$$dx_2^\beta = \frac{(x_1^\alpha V_1^\beta + x_2^\alpha V_2^\beta) dP^\beta}{(x_2^\beta - x_2^\alpha) g_{22}^\beta}. \quad (11.59)$$

It is interesting to see that α and β change their composition in the same direction.

It should be noted that these equations were actually derived graphically by means of molar Gibbs energy diagrams in Figs 7.15 and 7.16.

Exercise 11.13

For the α/β equilibrium in a ternary system at constant T and P^α one obtains $(V_m^\beta/RT)dP^\beta = h^\alpha dx_2^\beta + k^\alpha dx_3^\alpha$. Show that $h^\alpha = x_2^\beta/x_2^\alpha - x_1^\beta/x_1^\alpha$ and $k^\alpha = x_3^\beta/x_3^\alpha - x_1^\beta/x_1^\alpha$ if α and β are ideal solutions.

Hint

The right-hand side of Eq. (11.56) again yields $V_m^\beta dP^\beta$. For an ideal solution $g_{22}/RT = 1/x_1 + 1/x_2$; $g_{23} = g_{32} = RT/x_1$; $g_{33}/RT = 1/x_1 + 1/x_3$.

Solution

The dx_2^α coefficient for $(V_m^\beta/RT)dP^\beta$, obtained from the left-hand side of Eq. (11.56) for $j = 1$, is $(x_2^\beta - x_2^\alpha)g_{22}^\alpha/RT + (x_3^\beta - x_3^\alpha)g_{32}^\alpha/RT = (x_2^\beta - x_2^\alpha)(x_1^\alpha + x_2^\alpha)/x_1^\alpha x_2^\alpha + (-x_2^\beta - x_1^\beta + x_2^\alpha + x_1^\alpha)/x_1^\alpha = (x_2^\beta x_1^\alpha + x_2^\beta x_2^\alpha - x_2^\alpha x_1^\alpha - x_2^\alpha x_2^\alpha - x_2^\beta x_2^\alpha - x_1^\beta x_2^\alpha + x_2^\alpha x_2^\alpha + x_1^\alpha x_2^\alpha)/x_1^\alpha x_2^\alpha = (x_2^\beta x_1^\alpha - x_1^\beta x_2^\alpha)/x_1^\alpha x_2^\alpha = x_2^\beta/x_2^\alpha - x_1^\beta/x_1^\alpha = h^\alpha$. The dx_3^α coefficient is obtained in the same way.

12 Sharp and gradual phase transformations

12.1 Experimental conditions

There will be a driving force for a phase transformation if the conditions of a system are changed in such a way that the system moves from one phase field into another in the phase diagram. In this chapter we shall examine the character of such phase transformations and we shall find that they depend upon the experimental method of controlling and changing the conditions. It is important first to realize that the possibility of efficiently controlling the various state variables is very different. For gaseous and liquid phases it is comparatively easy to control the pressure. It can be kept constant or it can be changed gradually according to an experimental programme. At any moment it is very uniform in the system apart from effects due to the surface energy of curved phase interfaces. For solid systems it is more difficult to control the pressure, in particular during a phase transformation resulting in a volume change. This may give rise to local deformation and internal stresses. On the other hand, solid phases are usually so dense and rigid that the thermodynamic effect of pressure differences and stresses can often be ignored. From a practical point of view we may often regard the pressure as an experimental variable which can be reasonably well maintained at a low enough level to have a negligible effect.

The temperature can often be kept relatively constant but in a large piece of material it may be difficult to change the temperature according to an experimental programme. This is due to the limited rate of heat conduction. As a consequence, in a well-controlled experiment the required change of temperature must be slow enough. Another way to change the temperature is to control the flow of heat to the system. If the pressure is kept constant we have

$$dH = dU + d(PV) = dU + PdV + VdP = dQ + VdP = dQ. \quad (12.1)$$

and this is therefore a way of controlling the enthalpy rather than the temperature. Again, the rate of heat conduction may be a limiting factor and in order for an experiment to be well controlled it can only involve slow internal changes or small specimens. Furthermore, the heat content will change locally if there is a spontaneous phase transformation. Only slow phase transformations or small specimens can thus be studied if one wants to have at least approximately isothermal conditions.

If the chemical potential of an element is changed gradually by changing its value in the surroundings, considerable potential differences within the system will normally

prevail for a long time unless the change is extremely slow. This is because equilibration of the chemical potential requires a change of the local composition, which can only be accomplished by diffusion or convection. Diffusion is usually many orders of magnitude slower than heat conduction.

There are cases where a particular component is much more mobile than the other components. This may occur for elements with small atoms when dissolved interstitially in solid phases. An example of some practical importance is carbon in steel. An even better example is hydrogen in most metals and alloys. In such cases one may have some success in controlling the chemical potential of that particular component.

A phase transformation may itself give rise to severe difficulties in the control of the experimental conditions. Under the given values of the potential variables the new phase will most probably have different values for all the molar quantities and there will be a tendency for their conjugate potential variables to change locally during a phase transformation, independent of what potential is being changed experimentally. In practice, the difficulties in carrying out a well-controlled experiment may be the same whatever potential one has decided to change. As an example, if the changed conditions give rise to a phase transformation, then the transformation may in turn give rise to a redistribution of the components by diffusion, heat flow by conduction and material transport by plastic and elastic deformation.

Due to the complications caused by a phase transformation in a solid material it may be somewhat easier to carry out a well-controlled experiment under constant values of some extensive variables rather than potentials. However, that will affect the character of the phase transformation. This will be evident from the discussion in this chapter.

Exercise 12.1

A solid substance is kept at its melting point T_1 under a certain high pressure P_1 . Discuss what happens if the pressure is suddenly released. Suppose that the liquid form of the substance is less dense.

Hint

The solid phase with its higher density was favoured by the high pressure. T_1 being the melting point at P_1 is thus above the melting point at $P = 0$.

Solution

Melting will most probably start somewhere. The melt will instantaneously be at the new melting point which is lower than T_1 . Heat will thus start to flow into the melted region from the remaining solid which may thus cool down to the new melting point. Thus, a mixture of the two phases may be established and its temperature will be at the new melting point. However, this may cause heat flow into the system from the surroundings if they are kept at T_1 . The whole system will thus melt eventually. On the other hand, if

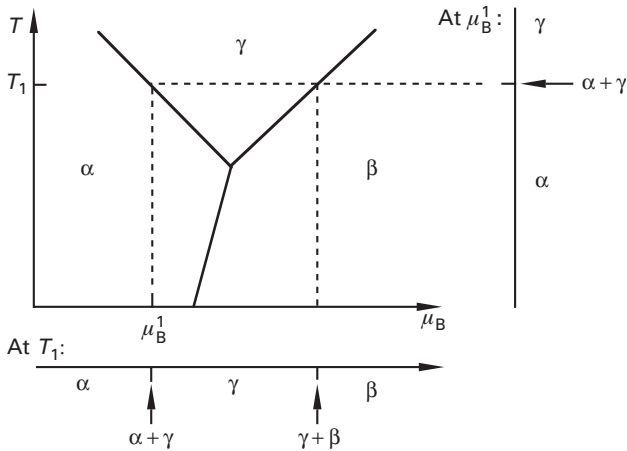


Figure 12.1 Illustration of the conditions for a sharp phase transformation in a simple case where all external variables to be kept constant are potentials.

the new melting point is very low compared to T_1 , then the whole system may melt even before any heat has flown into the system. See Exercise 14.2.

12.2 Characterization of phase transformations

In this section we shall neglect the difficulties mentioned in Section 12.1 regarding the control of the variables. We shall limit the discussion to cases where we have selected one variable to be varied in a controlled fashion, keeping all the others constant. Thus, we shall not consider any projections here. The present question is not how we look at the system but how we control it. From the phase diagram point of view this means that c of the $c + 1$ independent variables in a set of external state variables will be sectioned, $n_s = c$, and the selected variable can be represented on the resulting one-dimensional phase diagram, $r = 1$.

When the selected variable is changed gradually, the system may move from one phase field into another and a phase transformation may thus occur. It can be represented by a reaction formula obtained by combining the names of the phase fields. For instance, when moving from an α phase field into a γ phase field we expect the transformation $\alpha \rightarrow \gamma$. In doing so we must pass an $\alpha + \gamma$ phase field and one may characterize the transformation as a **sharp** one if the $\alpha + \gamma$ phase field has no extension in the one-dimensional phase diagram we are using. The phase field rule, Eq. (10.6), must yield $d = 0$. Otherwise, it may be characterized as a **gradual** transformation and has $d \geq 1$. These cases may be illustrated by starting with two-dimensional phase diagrams. The main part of Fig. 12.1 is a two-dimensional diagram obtained by starting with only potential variables, $c - 1$ of which have then been sectioned, $n_s = c - 1$, (here an isobaric section of a binary system). A further sectioning (making $n_s = c$) could be made at $T = T_1$, giving the one-dimensional phase diagram in the lower part of the figure. The phase field rule yields for

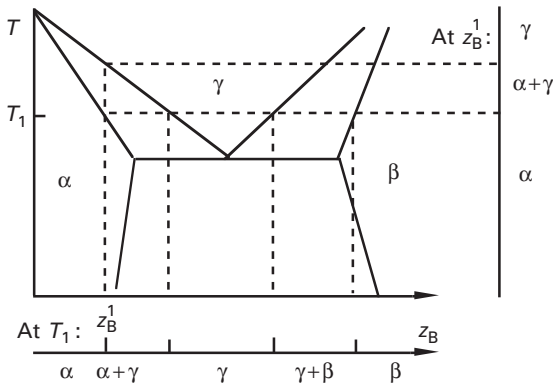


Figure 12.2 Illustration of the conditions for a gradual phase transformation in the simple case where one molar variable is used.

$\alpha + \gamma$: $d = c + 2 - p - n_s + n_m = c + 2 - 2 - c + 0 = 0$ and confirms that the phase transformation $\alpha \rightarrow \gamma$ should be a sharp one if μ_B is increased gradually. A similar result would be obtained if one could keep μ_B constant at μ_B^1 and gradually increase T (see the right-hand part of Fig. 12.1).

Figure 12.2 shows the diagram for the same system when the chemical potential has been replaced by the conjugate variable, z_B . By sectioning at $T = T_1$ one obtains the one-dimensional diagram in the lower part. Compared to the lower part of Fig. 12.1, the two-phase fields have opened up and the $\alpha \rightarrow \gamma$ transformation will be gradual if z_B is increased gradually. It is evident that *a transformation can never be sharp if it occurs under a gradual increase of a molar quantity* because all phase fields have some extension in the direction of a molar quantity. The result would be the same if one instead worked with the ordinary molar content, x_B , which is the conjugate variable to $\mu_B - \mu_A$.

A section at $z_B = z_B^1$ is shown to the right of Fig. 12.2. It also shows a gradual transformation when T is changed gradually but that result cannot be predicted without inspecting the phase diagram or applying the phase field rule. In this case $c = 2$, $p = 2$, $n_s = 2$ (P and z_B) and $n_m = 1$ (z_B), yielding $d = c + 2 - p - n_s + n_m = c + 2 - 2 - c + 1 = 1$.

Let us now return to the case of a sharp transformation in Fig. 12.1. If the gradual change of μ_B at $T = T_1$ is continued, then the sharp transformation $\alpha \rightarrow \gamma$ will be followed by another sharp transformation $\gamma \rightarrow \beta$ at a higher value of μ_B . It is then interesting to discuss what would happen if the section were made exactly at the temperature of the three-phase equilibrium. The lower part of the figure would show a point for the $\alpha + \beta + \gamma$ equilibrium instead of two points for $\alpha + \gamma$ and $\gamma + \beta$. However, with $p = 3$ the phase field rule would yield $d = c + 2 - p - n_s + n_m = c + 2 - 3 - 0 + 0 = -1$. Since $d = 0$ represents a point, one may conclude that $d = -1$ represents a phase field which should not show up at all in the one-dimensional diagram and the reason is that it is practically impossible to place the section exactly through the three-phase equilibrium. Let us for a while neglect that practical difficulty and suppose that the section actually goes right through the three-phase equilibrium. What phase transformation would one

then observe on gradually increasing μ_B ? One could expect to observe the sharp transformation $\alpha \rightarrow \gamma$, followed by $\gamma \rightarrow \beta$ but also a direct transformation $\alpha \rightarrow \beta$. We may regard this as a case of **overlapping sharp transformations**.

Let us next replace μ_B by z_B and still assume that T can be chosen and controlled in such a way that the section goes right through the three-phase equilibrium, in this case right through the three-phase horizontal in Fig. 12.2. The lower part of that figure would then show an $\alpha + \beta + \gamma$ region instead of the three regions, $\alpha + \gamma$, γ and $\gamma + \beta$. For three phases the phase field rule would now give $d = c + 2 - p - n_s + n_m = c + 2 - 3 - c + 1 = 0$ yielding the incorrect prediction of a three-phase point instead of an extended region.

In order to understand this puzzling result one should remember that a transformation can never be sharp when taking place under a gradual change of a molar quantity. If the phase field rule gives $d = 0$ for a molar axis, the interpretation must be that it is practically impossible to carry out such an experiment. It thus corresponds to the improbable case of $d = -1$ for a potential axis. We may conclude that, if a molar quantity is varied, $d = 0$ predicts **overlapping gradual transformations** (in the present case $\alpha \rightarrow \beta$ or $\alpha \rightarrow \gamma$ followed by $\gamma \rightarrow \beta$). However, it is as unlikely as the case of overlapping sharp transformations for $d = -1$.

It is evident that the only way to get a sharp transformation is to vary a potential. Usually this is T and one keeps P and the composition constant, $n_s = c$ and $n_m = c - 1$. Using Eq. (10.6) we find that the sharp transformation will then occur when $0 = d = c + 2 - p - n_s + n_m = c + 2 - p - c + (c - 1) = c + 1 - p$, i.e. $p = c + 1$.

If $p = c + 2$ under the same conditions, one would obtain $d = -1$, i.e. overlapping sharp transformations. The present discussion thus results in two schemes for the character of phase transformations. When a potential is varied gradually we obtain

- for $d = +1$: gradual transformation
- for $d = 0$: sharp transformation
- for $d = -1$: overlapping sharp transformations.

When a molar quantity is varied gradually, we obtain

- for $d = +1$: gradual transformation
- for $d = 0$: overlapping gradual transformations.

In a sharp transformation (i.e., $d = 0$ and a potential is varied) the fractions of the phases (i.e. the extent of the transformation) are not fixed by the value of the changing variable. This is why the corresponding state of phase equilibrium is sometimes called ‘indifferent’ [23]. On the other hand, the compositions of all the phases are fixed. This is why any sharp transformation is sometimes called ‘azeotropic’ although that term is usually reserved for the case with an extremum discussed in connection with Konovalov’s rule in Section 10.8. Cases with an extremum have been neglected in the present discussion but will be further discussed in Sections 13.7 to 13.9.

In addition, overlapping sharp transformations (i.e., $d = -1$ and a potential is varied) are sometimes called ‘indifferent’, because the extent of transformation is not fixed. In that case, however, there is more than one transformation and their relative progress is also not fixed.

Before leaving this topic, it should be emphasized that the present discussion is based on considerations of equilibrium. In practice, there are many kinetic obstacles and it is not impossible to observe overlapping transformations (often regarded as competing reactions) if the experimental conditions come close to the improbable ones, for which the phase field rule predicts overlapping transformations.

Exercise 12.2

Consider an A–B system with two solid phases, A-rich and B-rich, and liquid and gas. What type of transformation should one expect between these phases if T is changed gradually for a system with constant composition and pressure?

Hint

If needed, assume that A has a higher vapour pressure than B.

Solution

$c = 2$, $p = 4$ and Gibbs' phase rule yields $\nu = c + 2 - p = 2 + 2 - 4 = 0$. This equilibrium would thus show up as a point in the complete potential phase diagram. Under the present experimental conditions, $n_m = c - 1$ (constant overall composition), and $n_s = c$ (constant overall composition and pressure), the phase field rule in Eq. (10.6) predicts $d = c + 2 - p - n_s + n_m = 2 + 2 - 4 - c + (c - 1) = -1$. The chance of observing the corresponding phase transformation would be negligible since it would require that a particular value of P could be chosen and kept constant. If we were to succeed in doing this, the system could transform with all four phases present but it would be a case of overlapping sharp transformations. They could be $A + B \rightarrow \text{liq.}$, $A + B \rightarrow \text{vapour}$, $A + \text{liq.} \rightarrow \text{vapour}$, $\text{liq.} \rightarrow B + \text{vapour}$.

Exercise 12.3

Consider the same system as in Exercise 12.2 but suppose that the system is heated gradually.

Hint

As before, $n_s = c$, but instead of a gradually changing temperature, we should now consider a gradually changing enthalpy. Thus $n_m = c - 1 + 1 = c$.

Solution

Under the new experimental conditions $d = c + 2 - p - n_s + n_m = 2 + 2 - 4 - c + c = 0$. We would observe the same overlapping transformations but they would now be gradual.

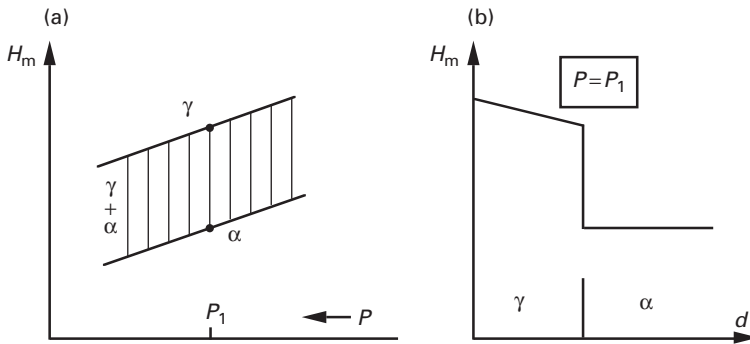


Figure 12.3 Phase transformation $\alpha \rightarrow \beta$ is a unary system under pressure P_1 and heating through the surface. d is the distance from the surface.

12.3 Microstructural character

We shall now discuss how the phases will be distributed within a system as a result of a phase transformation. With most materials one needs a microscope in order to study the distribution of the phases, thus the term **microstructure**.

During a gradual transformation the new product will only occupy some fraction of the volume. If there are many nuclei, the result may be an intimate mixture of the old and new phases, with a gradual change of the fractions and of the compositions of the phases. Such a transformation may be regarded as **microstructurally gradual**. On the other hand, in a sharp phase transformation the new phase or phases will completely replace the old ones but it may still be interesting to discuss the microstructural appearance during the transformation because it is never instantaneous, due to kinetic restrictions. Thus, let us first consider the effect of the limited rate of heat conduction when heating a pure element with two solid phases, α and β .

Whether one regards T or H_m (enthalpy per mole of the system) as the controlling variable, heat supplied from the surroundings must normally flow into the system through the surface layer. If there is no other kinetic restriction, then the phase transformation should start at the surface where the temperature must be at least slightly higher than in the interior. After some time there will be a massive surface layer of the new β phase. It will form with a sharp interface to the old α phase in the interior. Thus, the phase transformation will be **microstructurally sharp** in both cases. Figure 12.3 illustrates the variation of the local value of the molar enthalpy as a function of the distance from the surface, assuming that the whole system was initially in a state of α at the temperature of equilibrium with β . The P axis has been added to Fig. 12.3(a) in order to illustrate that P is kept constant. The difference between the two cases is that with T as the controlling variable the process will not stop until the microstructurally sharp transformation has proceeded through the entire system. With H_m as the controlling variable, the process will stop when the average value of H_m has reached the prescribed value.

On the other hand, suppose that the phase transformation is so slow due to kinetic reasons that it would be possible to increase H_m of the initial α phase to a value falling

inside the $\alpha + \beta$ phase field and, thus, to increase T to a value falling inside the β phase field before the phase transformation starts. Wherever there are β nuclei, they could then grow and an $\alpha + \beta$ mixture would develop, the final fractions of α and β being controlled by the lever rule applied to the prescribed H_m value. The kinetics may be so slow that α and β are not in equilibrium, not even at the α/β interfaces, until the fraction of β has approached its final value. In that case the progressing phase transformation may look similar to the microstructurally gradual transformation.

We have here considered a phase transformation which is sharp when a potential is varied. We have found that in order to predict its microscopic appearance one must first examine if the transformation is slow due to other kinetic restrictions. If that is the case, the transformation may be microstructurally gradual. If the transformation is fast enough to follow the changes of the controlling variable, then it may be microstructurally sharp. In both cases the result will be the same whether one varies the potential or its conjugate molar quantity. However, in the remainder of the present chapter we shall always use a potential as the variable.

Exercise 12.4

Is it possible to solidify a pure liquid substance by increasing P to a new value if the solid form is denser? If so, will the solidification be complete or only partial? Will it be microscopically sharp or not?

Hint

It all depends upon what other variable is controlled. One will probably try to keep some variable constant. Consider two conditions, isothermal (very slow) and adiabatic (very rapid). It may be helpful to sketch the appropriate phase diagrams.

Solution

We get complete solidification if T is kept constant. Adiabatic conditions are more difficult to discuss, because they give, according to the first law, $dQ = dU + PdV = 0$ and $dQ = dH - VdP = 0$. Neither U nor H is thus constant when P is changed. In order to find a state function which is constant, we must assume reversible conditions, and, using the second law, we then get $dQ = TdS - Dd\xi = TdS = 0$. For this case we should thus use an S_m, P diagram. We could then see that the solidification may be partial or complete depending upon how large the P change is. This conclusion may not change if there is some internal entropy production due to the transformation.

When considering the microstructural character we may first examine the adiabatic case and accept that the change of P is more rapid than the transformation. Then many nuclei distributed over the whole system may form and give the transformation a gradual appearance. In the slow isothermal case we may assume that the transformation starts at the surface or very close to it. The transformation will then be microstructurally sharp if the phase field rule predicts that the dimensionality of the $\alpha + L$ phase field should be zero. For a unary system Eq. (10.6) yields $d = c + 2 - p - n_s + n_m = 1 + 2 - 2 - 1 + 0 = 0$.

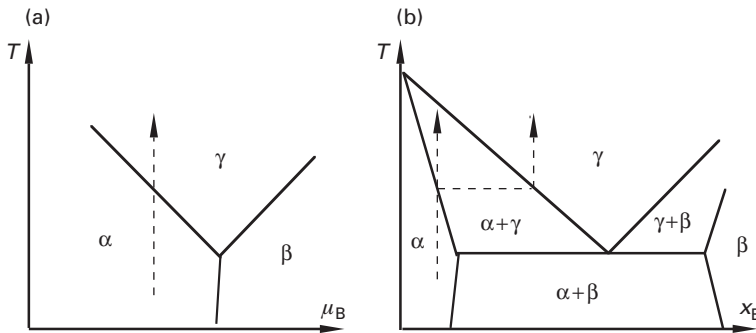


Figure 12.4 Illustration of difficulty for a phase transformation in a binary system to occur under constant μ_B when T is increased under constant P .

12.4 Phase transformations in alloys

Diffusion is usually much slower than heat conduction and may thus give a very severe kinetic restriction on the phase transformations in alloys. This is true even if we would decide to control the experimental conditions by keeping all the potentials constant except for T , which is varied gradually. The complications are not immediately evident from the T, μ_B phase diagram but are clearly demonstrated by the T, x_B phase diagram at constant P in Fig. 12.4.

If we could keep μ_B constant during an increase of T , we would move through the T, x_B phase diagram according to the broken arrow in Fig. 12.4(b). This corresponds to the straight arrow in the T, μ_B phase diagram of Fig. 12.4(a) and represents a sharp transformation $\alpha \rightarrow \gamma$. However, this would require an exchange of atoms with the surroundings and, due to the low rate of diffusion compared to heat conduction, the system would rather move along the straight arrow in the T, x_B phase diagram of Fig. 12.4(b), when T is increased, and the composition rather than the chemical potential would stay constant if the time of the experiment is not very long. One would not manage to keep μ_B constant except in very special cases. The composition would not have time to change much and the system would move into the $\alpha + \gamma$ two-phase field. A gradual phase transformation would result. The transformation would be microstructurally gradual and the system would show a mixture of α and γ and the fraction of γ would gradually increase on increasing T .

The effect of slow diffusion discussed here is the reason why most experimental conditions can be approximated by assuming that the composition is constant during a change of T (or P).

Exercise 12.5

Suppose the temperature is increased gradually under constant pressure. Consider a phase transformation which would be sharp if a particular chemical potential were kept constant. However, due to slow diffusion it is difficult to study a phase transformation under a constant chemical potential. Instead, one keeps the molar content of the same component constant. Is it thus possible to minimize the role played by diffusion?

Hint

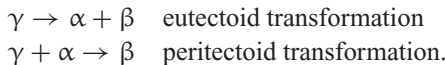
If $d = 0$ when the particular chemical potential is kept constant, then $d = 1$ if instead the corresponding molar content is kept constant because n_m in Eq. (10.6) increases by one unit. The transformation may thus be classified as gradual.

Solution

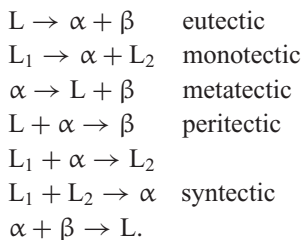
Since this transformation is now gradual, there will be a gradual change of the fractions of various phases. One will thus get a mixture of phases. If they have different compositions, diffusion is required over distances related to the coarseness of the microstructure. However, such diffusion distances will normally be much shorter than those which are necessary under conditions of constant potential.

12.5 Classification of sharp phase transformations

Sharp phase transformations in alloys at constant P involving few phases have been classified into various groups. For unary systems there is only one type, $\alpha \rightarrow \beta$, and it is called an **allotropic** transformation; melting may be regarded as a special case. In binary systems there are two main types,



The $\alpha + \beta$ mixture resulting from the first transformation is often called a eutectoid structure or simply a eutectoid. In order to identify a particular eutectoid it is sometimes denoted by the name of the parent phase. In the present case it would thus be called γ -eutectoid. In addition there are special names depending upon the role played by the liquid phase. The following names refer to transformations occurring on cooling but, in addition, the same names are often applied to the corresponding features in the phase diagram and even to the phase diagrams with such features.



The first transformation to be given a name was the eutectic transformation $L \rightarrow \alpha + \beta$. The word ‘eutectic’ is taken from Aristotle who used it as meaning ‘beautifully or easily melted’ and that was the definition when first used by Guthrie [24]. He was not yet aware of the regular microstructure usually formed in such alloys on solidification, a lamellar example of which is sketched in Fig. 12.5. Today, when we speak of a ‘eutectic’ we tend to imply this type of microstructure. The eutectoid transformation has come to mean

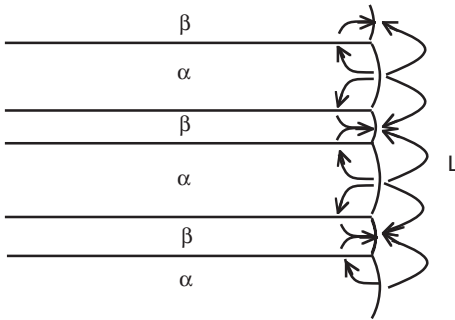


Figure 12.5 Cooperative growth of two phases in a eutectic transformation. The arrows indicate possible diffusion paths.

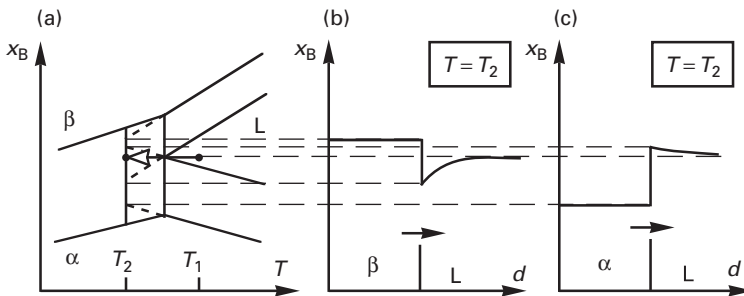


Figure 12.6 Conditions of a eutectic transformation, $L \rightarrow \alpha + \beta$, in a binary system at constant P and a constant overall composition. The temperature was decreased from T_1 to T_2 .

$\gamma \rightarrow \alpha + \beta$ independent of whether it occurs on heating or cooling or under isothermal conditions and independent of how the phase diagram looks. It is interesting to note that the eutectic type of microstructure can form on partial melting of an intermetallic phase from a peritectic phase diagram.

The growth conditions for a eutectic transformation are illustrated by Fig. 12.6, where two two-phase regions have been extrapolated to a transformation temperature below the equilibrium temperature for $L + \alpha + \beta$. Figures 12.6(b) and (c) show the variation of composition within the parent phase, L , in front of β and α , respectively. Diffusion of B may thus occur inside the L phase from the α interface to the β interface and growth is thus made possible. As illustrated by the arrows in Fig. 12.5, diffusion may also occur inside the two growing phases, α and β , when they grow side by side, but that diffusion is generally much slower than diffusion in the liquid.

It is interesting to note that eutectoid transformations often result in a rather regular arrangement of the two new phases. The reason is that such arrangements give short diffusion paths. It is called cooperative growth.

The peritectoid transformations derive their name from the peritectic transformation, $L + \alpha \rightarrow \beta$, which occurs on solidification. The name ‘peritectic’ means that a phase formed by such a reaction grows along the interface, i.e. along the periphery of the primary solid phase as illustrated in the sketched microstructure of Fig. 12.7.

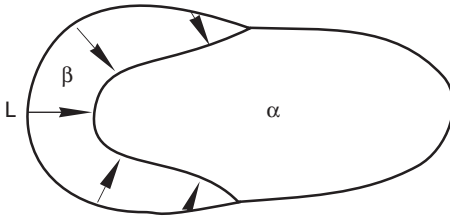


Figure 12.7 Geometric arrangement of the growing β phase during a peritectic transformation, obtained by growth along the previous phase interface, L/α , and by subsequent thickening.

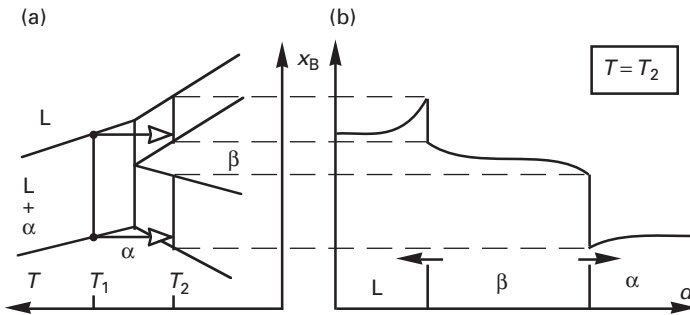


Figure 12.8 Conditions for an $L + \alpha \rightarrow \beta$ transformation in a binary system at constant P and a constant overall composition. The temperature was changed from T_1 to T_2 . The arrows above diagram (b) indicate the migration of the new phase interfaces during thickening.

Normally, all peritectoid transformations give the same type of geometric arrangement. The growth conditions during a transformation can be illustrated by Fig. 12.8.

The diffusion distance is shortest close to the β tip advancing along the L/α interface in Fig. 12.7. That growth process is thus rapid. The subsequent thickening of β , can occur only by diffusion through β itself. It grows slower the thicker it gets and a peritectoid reaction seldom goes to completion. On continued cooling, β can also grow into the matrix phase as an ordinary primary precipitation but it is common that some of the primary solid phase, α , remains.

In ternary systems there are three kinds of sharp phase transformations.

- $\alpha \rightarrow \beta + \gamma + \delta$ Four-phase eutectoid transformation or class I four-phase transformation
- $\alpha + \beta \rightarrow \gamma + \delta$ Four-phase peritectoid transformation or class II four-phase transformation
- $\alpha + \beta + \gamma \rightarrow \delta$ Class III four-phase transformation.

The four-phase transformations are illustrated in Fig. 12.9.

Exercise 12.6

Vertical sections through two different ternary T, x_B, x_C diagrams at constant P are reproduced in Fig. 12.10. Discuss what type of sharp four-phase transformations the

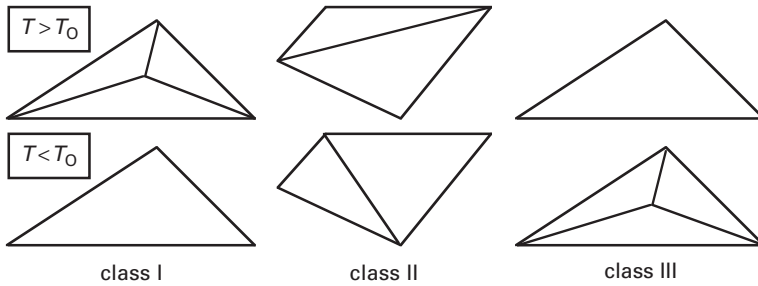


Figure 12.9 Different types of four-phase reactions in a ternary system, represented in a compositional coordinate system.

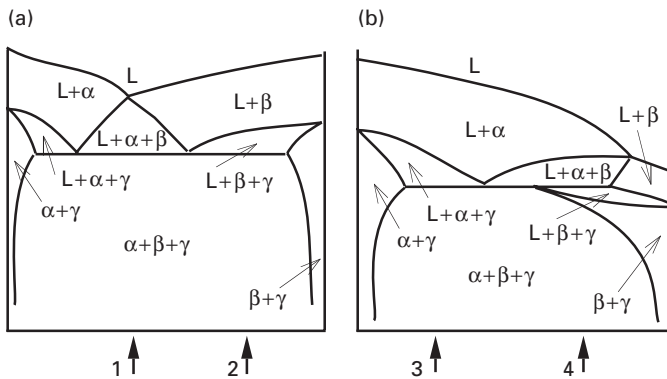


Figure 12.10 See Exercise 12.6.

four alloys, indicated by arrows, go through on cooling. Show projections of the four-phase planes and draw lines representing the two sections.

Hint

In both diagrams all four three-phase fields connected to the invariant four-phase field are shown in the section. It is thus possible to know the type of transformation. In diagram (a), three of the four fall above the invariant one and these three all contain liquid. It is evident that this is a four-phase eutectic transformation. Both the alloys, 1 and 2, give $L \rightarrow \alpha + \beta + \gamma$ and the parts of these alloys, already solidified, remain unchanged. In diagram (b) there are two three-phase fields on each side of the four-phase horizontal. This must be a class II transformation and both alloys, 3 and 4, give $L + \alpha \rightarrow \beta + \gamma$.

Solution

The solution is shown in Fig. 12.11.

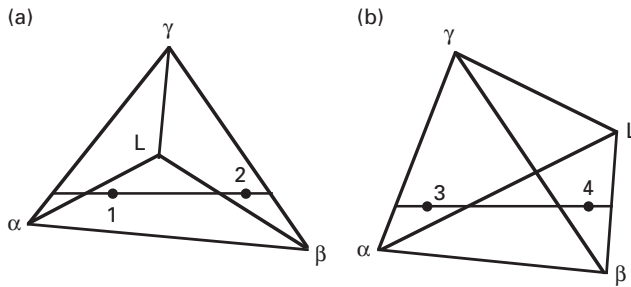


Figure 12.11 Solution to Exercise 12.6.

12.6 Applications of Schreinemakers' projection

Schreinemakers' T, P diagram, introduced in Section 10.1, can be very useful in a discussion of phase transformations, in particular for higher-order systems where all other methods of reducing the number of axes to two would yield much more complicated pictures. As an introduction, consider the diagram in Fig. 10.1(b). It shows that there are three two-phase surfaces covering the angle between the (α) and (β) lines. By keeping P and T constant at values within that angle and varying μ_B we could expect the transformations $\alpha \leftrightarrow \delta$, $\gamma \leftrightarrow \delta$ and $\beta \leftrightarrow \gamma$. Of course, they should occur one after the other and only two reaction sequences are possible, $\beta \rightarrow \gamma \rightarrow \delta \rightarrow \alpha$ or the reverse. By this consideration we can immediately conclude that the phases are arranged in this order along the composition axis, z_B . This is confirmed by Fig. 10.10. Similar considerations based on the other angles will give less complete answers. Unfortunately, this very simple way of deciding the relative compositions of the phases taking part in an invariant equilibrium gets much more complicated in higher-order systems. The method based on coincidence, described in Section 10.4, may be more powerful.

Next, let us consider a transformation occurring by changing T or P and keeping the other constant. If the composition is also constant, then the phase field rule from Eq. (10.6) would yield

$$d = c + 2 - p - n_s + n_m = c + 2 - p - c + c - 1 = c + 1 - p$$

because $n_s = 1 + c - 1 = c$ and $n_m = c - 1$. A sharp transformation should be obtained for $d = 0$, i.e. $p = c + 1$, and should thus occur if the system would cross a univariant line (for which $p = c + 1$, see Section 10.1). This can be accomplished by a suitable choice of composition. For illustration, see the arrow in Fig. 10.9. Then the question is, what type of sharp transformation will it be. From the projection in Fig. 10.1(b) we would only know that the (δ) line should give a transformation between α , β and γ . However, the following method can be used to give more detailed information.

Since δ does not exist along the (δ) line, it can only exist on the other side of the invariant point. It will thus exist on the upper sides of the other univariant lines but not on their lower sides (see Fig. 12.12(a)). Using the same kind of information from

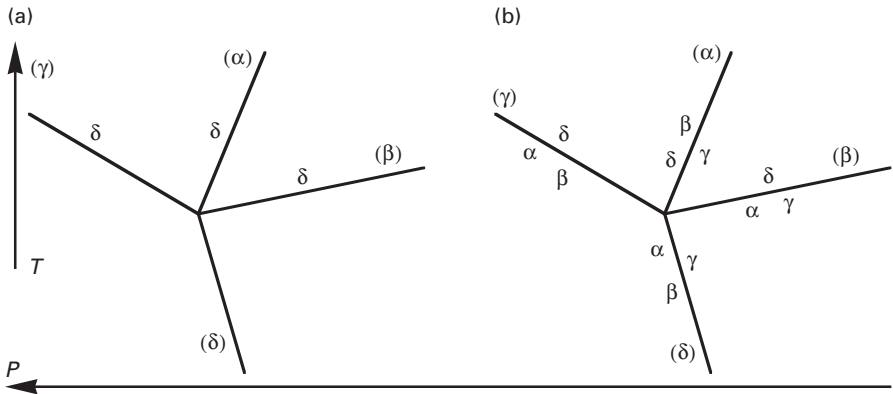


Figure 12.12 Method to decide the type of transformation. For instance, the δ phase only exists on the other side of the invariant point, counted from the δ -absent line, here denoted (δ) . The arrow in Fig. 10.9, which is an expansion of the lower part of the present figure in the z_B direction, illustrates the $\gamma \rightarrow \alpha + \beta$ transformation.

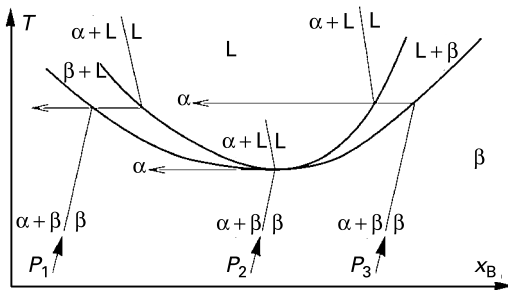


Figure 12.13 Detail of binary T, x phase diagram with a point of minimum for the $\beta + L$ equilibrium. There the transformation $\beta \rightarrow L$ will be congruent. Three sets of lines representing equilibrium with α at different P are given.

the other lines we get the results shown in Fig. 12.12(b). By crossing the (δ) line from left to right, i.e. by decreasing P , under a suitable constant value of z_B , we thus get the transformation $\alpha + \beta \rightarrow \gamma$. It should be emphasized that the transformations described by the positions of the Greek letters in Fig. 12.12 only occur when a line is crossed in the plane of the projected diagram. It gives no information on the transformations in any other direction.

In Section 10.8 it was concluded that one can include in Schreinemakers' projection a curve showing where an equilibrium with $p = c$ phases degenerates by the phases falling on the same point for a binary system, on the same line for a ternary system, etc. An example was shown in Fig. 10.27. Such a singular curve may originate from a univariant line, as demonstrated in Figs 12.13 and 12.14, using a binary system for illustration.

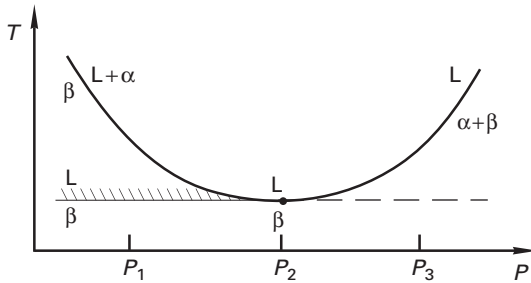


Figure 12.14 Schreinemakers' P, T diagram corresponding to Fig. 12.13. The univariant line changes character at the black point. That is where the singular curve originates and there is a compositional degeneracy in that point. The α phase does not take part in the reaction there.

In order to simplify the construction, it was here assumed that the $\beta + L$ equilibrium is not affected by P but an increased P will increase the stability of α . Lines for equilibrium with α are presented for three P values. With the lowest P value, P_1 , the $\alpha + \beta + L$ equilibrium is of the peritectic type. With the highest P value, P_3 , it is of the eutectic type and the intermediate P value, P_2 , shows the transition where α does not take part in the transformation of L to β . That will give a singular point on the univariant line for $\alpha + \beta + L$ in Fig. 12.14 and that is where the singular curve for $\beta + L$ starts.

At low P (to the left of the transition point in Fig. 12.14) an alloy of suitable composition would transform by $L + \alpha \rightarrow \beta$ on the univariant line if its composition is such that it reaches the three-phase horizontal in Fig. 12.13 on cooling. Otherwise, it would transform by $L \rightarrow \beta$ at lower T . That would happen if the composition is to the right of the L point for P_1 in Fig. 12.13. In any case, the transformation $L \rightarrow \beta$ would be completed at or before the point of minimum in Fig. 12.13, i.e. the singular curve in Fig. 12.14. At high P (to the right of the transition point) an alloy of suitable composition would transform by $L \rightarrow \alpha + \beta$ on the univariant line. That would happen for compositions on both sides of the L point for P_3 in Fig. 12.13, but usually after a proeutectic precipitation of α or β . If the liquid alloy can be undercooled by α not nucleating, it may solidify by $L \rightarrow \beta$ according to the part of the $L + \beta$ phase field below the eutectic temperature. The lowest temperature of solidification by $L \rightarrow \beta$ according to the phase diagram is again the minimum. However, this part of the $L + \beta$ phase field is only metastable at P_3 . That is why the singular curve in Fig. 12.14 has been drawn with a dashed line to the right of the transition point.

Figure 10.3 illustrated a congruent point in a ternary system and it was concluded that the position of such points could also be illustrated by a line in Schreinemakers' projection. The name 'doubly singular' was proposed. Such a curve can originate from a transition point on a singular curve, much in the same way as the singular curve originates from a univariant line. This is illustrated in Fig. 12.15 where an invariant equilibrium is also included. The $L + \beta + \gamma$ surface covers the area between the (α) and (δ) lines. However, to the left of the singular point $L/(\beta + \gamma)$ that surface, when coming from the (α) line, will overshoot the (δ) line, reach the singular curve and then bend back and end up on the (δ) line. If the composition is suitable, then the alloy will not transform by

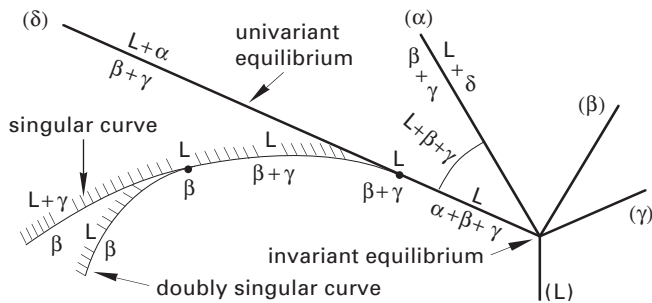


Figure 12.15 Schematic Schreinemakers' projection of a ternary system, illustrating a possible arrangement of a univariant line, a singular curve and a doubly singular curve.

$L + \alpha \rightarrow \beta + \gamma$ on the univariant line because there will be no α present. Such an alloy will solidify by $L \rightarrow \beta + \gamma$ below the univariant line but in any case not later than on the singular curve. However, if there is a transition point on the singular curve, to the left of which the solidification reaction is $L + \gamma \rightarrow \beta$, then the solidification can only occur by $L \rightarrow \beta$ if there is no γ present. The alloy may then pass the singular curve on cooling but in any case it should have solidified before passing the doubly singular curve.

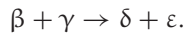
Exercise 12.7

What transformation would occur on crossing the (α) line in Fig. 10.14(b) by increasing the value of Y^k at constant values of Y^j , X_{m1}^m and X_{m1}^n ?

Hint

Use the method illustrated by Fig. 12.12.

Solution



Exercise 12.8

Use the three-phase reactions indicated by Fig. 12.12(b) to decide on the relative compositions of the four phases.

Hint

The reactions on decreasing T are $\delta \rightarrow \alpha + \beta$, $\beta + \delta \rightarrow \gamma$, $\delta \rightarrow \alpha + \gamma$ and $\gamma \rightarrow \alpha + \beta$.

Solution

δ must fall between α and β , γ between β and δ , δ between α and γ and finally γ between α and β . They must be arranged in the order $\beta, \gamma, \delta, \alpha$ or in the opposite direction.

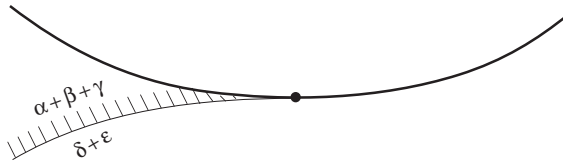


Figure 12.16 See Exercise 12.9.

Exercise 12.9

Figure 12.16 gives a detail of Schreinemaker's projection of a quinary system. It shows a univariant line for the $\alpha + \beta + \gamma + \delta + \epsilon + \phi$ equilibrium and a singular curve for the $\alpha + \beta + \gamma + \delta + \epsilon$ singular equilibrium. What transformation can be expected when the univariant line is crossed?

Hint

Use the fact that the singular curve is stable only on the indicated side of the singular point.

Solution

To the left of the transition point one can avoid the univariant reaction and reach the singular curve if ϕ is not present before the univariant line is reached. Thus, ϕ does not form by the univariant reaction but would be consumed if it were present. The reaction must be $\alpha + \beta + \gamma + \phi \rightarrow \delta + \epsilon$. To the right of the transition point, the univariant reaction cannot be suppressed, not even if ϕ is absent, and the reaction must be $\alpha + \beta + \gamma \rightarrow \delta + \epsilon + \phi$.

12.7 Scheil's reaction diagram

In many types of systems, P has a negligible effect and without any loss of information one can section at $P = 1$ bar. For a binary system one will thus get the usual T, x diagram. For a ternary system there is one dimension more but one could project in the T direction and use x_B and x_C as axes. Such diagrams are useful but tend to be overloaded with phase boundaries if many phases are solutions because there will be lines showing the compositional changes of all those phases. A simpler diagram would be obtained by using μ_B and μ_C (or a_B and a_C) as axes. However, much information would be missing. Using the method illustrated in Fig. 12.12 one could easily find what transformation would occur on crossing a univariant line but that would be of limited use. In order to hit the line one must now work with a constant heat content because the projected axis is T . Furthermore, one would have to vary μ_B or μ_C which is rarely very practical.

A rather useful method was proposed by Scheil [25] for ternary systems. His reaction diagram shows how the lines representing three-phase equilibria are connected to form

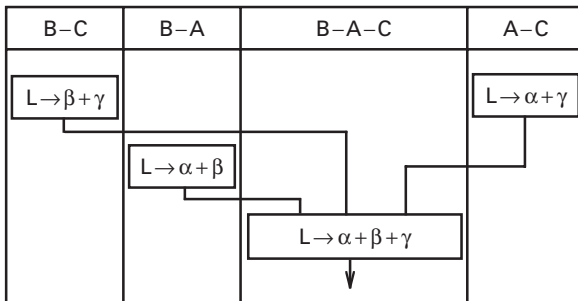


Figure 12.17 Scheil's reaction scheme for a simple ternary system with eutectic reactions.

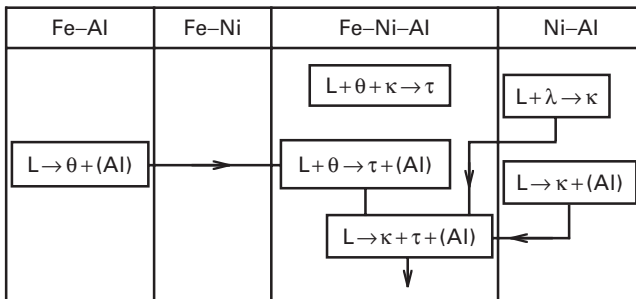


Figure 12.18 See Exercise 12.10.

four-phase equilibria as a function of T but with no regard for composition. His diagram also shows what three-phase equilibria originate from the binary sides. In addition, the reactions occurring on cooling through the four-phase equilibria are given explicitly in boxes. The diagram for a simple eutectic system is presented in Fig. 12.17. Of course, similar diagrams can be constructed for quaternary systems, showing four- and five-phase equilibria.

Exercise 12.10

Part of Scheil's diagram for the Al-Fe-Ni system is shown in Fig. 12.18, reproduced from a publication. A mistake was made by joining the binary $(L + \lambda \rightarrow \kappa)$ with $(L \rightarrow \kappa + \tau + (Al))$. Try to correct it.

Hint

What phases are common for the four-phase equilibria? What one-dimensional equilibria should connect them?

Solution

The solution is shown in Fig. 12.19.

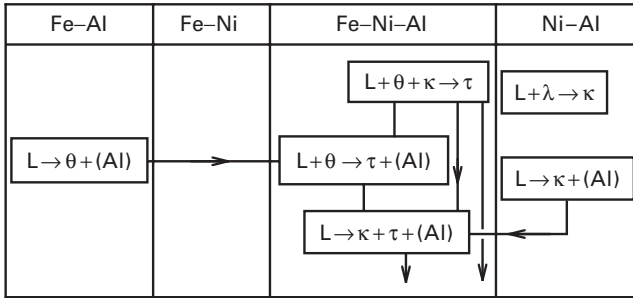


Figure 12.19 Solution to Exercise 12.10.

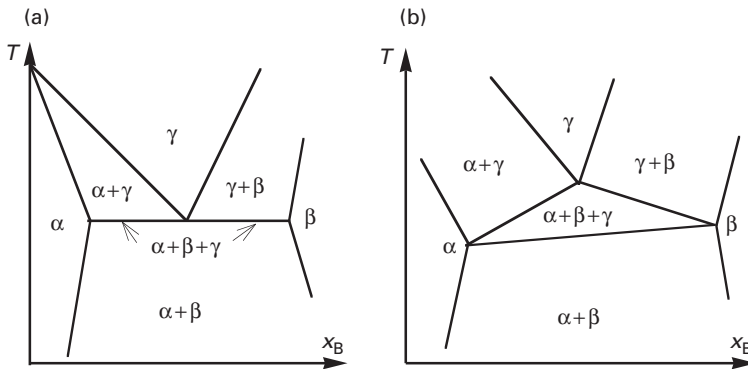


Figure 12.20 A section at constant P and x_C through a ternary phase diagram in (b), compared with a binary diagram in (a).

12.8 Gradual phase transformations at fixed composition

If a new component is added to a system where a sharp transformation with $p = c + 1$ has been found at constant P (see Fig. 12.20(a)), then the value of c increases by one unit and for the same transformation one will now have $p = c$. The dimensionality of the corresponding phase field will thus increase by one unit. This case may be illustrated by an x_C section at a low value of x_C (see Fig. 12.20(b)).

It is evident that the phase transformation between γ and $\alpha + \beta$, occurring when T is changed, can no longer be sharp but is somewhat gradual. However, if the addition of the new component is small, its effect on the actual phase transformation should also be small and one may still recognize its characteristic features, for instance in the resulting eutectic microstructure illustrated in Fig. 12.5, in particular if the temperature has been changed enough to move the system from the γ phase field to the $\alpha + \beta$ phase field before the transformation has started. The transformation may thus appear as sharp even though it is classified as a gradual transformation on thermodynamic grounds. As an example, we shall now examine a case involving three phases and three components. Figure 12.21 shows the T projection of such a phase diagram under constant P .

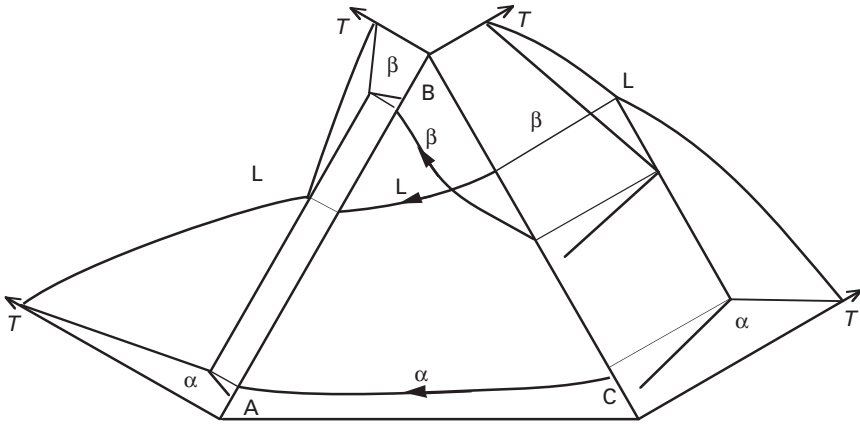


Figure 12.21 Temperature projection of the isobaric A–B–C phase diagram.

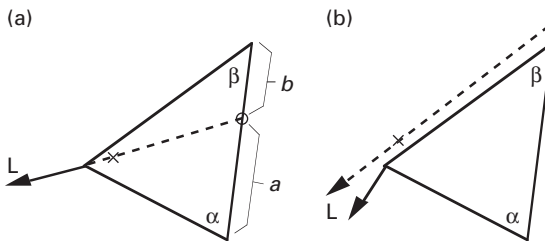


Figure 12.22 Conditions for (a) a eutectic transformation and (b) a peritectic transformation in a ternary system under constant pressure and a gradual decrease of the temperature.

In this particular case the same three-phase equilibrium occurs in two of the binary systems but it has different character, being eutectic on one side and peritectic on the other. Evidently, there must be a transition between the two types somewhere inside the ternary system. In order to decide where the transition is situated we must first examine how we can recognize the two types when the compositions of the phases change during the transformation. This is fairly easy if we consider a system which consists of an L phase only and if it has the correct composition for equilibrium with the α and β phases. As the temperature is lowered slightly, the three-phase triangle moves and covers the composition of the system (see the cross in Fig. 12.22(a)). Evidently, we should expect the reaction $L \rightarrow L + \alpha + \beta$. Here we have included the L phase on both sides because it has different compositions and it would be impossible to satisfy the mass balance condition if that is not taken into account.

The dashed line in Fig. 12.22(a) is the extrapolation of the direction in which the L phase is moving. It goes through the L corner of the triangle and the average composition of the system, and it intersects the opposite side, a and b being the intercepts. From Fig. 4.5 it is easy to see that the α and β phases must form in the proportion $b:a$ and this will be the ratio between them in the microstructure. As far as α and β are concerned they have formed from material corresponding to the circle. It may not be very important that

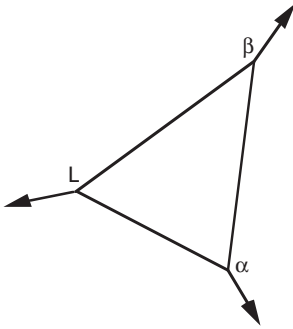


Figure 12.23 See Exercise 12.11.

this material has been drawn from a phase with a different composition. From this point of view, the reaction is clearly of the eutectic type. The result will be quite different if the extrapolation does not intersect the opposite side. An example is given in Fig. 12.22(b). The composition of the system will then fall outside the new three-phase triangle and inside a two-phase field, $L + \beta$. The reaction will simply be $L \rightarrow L + \beta$ and L will not move in the direction of the L line in the phase diagram (solid arrow) but straight away from the β phase (dashed arrow). L will no longer be in equilibrium with α .

The limiting case is found when the extrapolation, i.e. the solid arrow, is directed away from the β corner. Using that criterion one could find the point of transition in the phase diagram in Fig. 12.21 if it were equipped with a series of three-phase triangles for slightly different temperatures. Even though the criterion was derived by considering an alloy composed of an L phase only, it is more general because, in practice, it may often be justified to neglect the diffusion inside the solidified material in comparison with the rapid diffusion in the liquid phase. The progress of the reaction at each stage is thus mainly determined by the momentary composition of the L phase and in which direction it is moving. For a reaction, where three solid phases are involved, it may be necessary to make a detailed analysis of the diffusion of all the elements in all the phases. In the next section we shall consider a special case where one component diffuses much faster than the others.

Exercise 12.11

The sketched detail of an isobarothermal section of a ternary phase diagram (Fig. 12.23) shows how all the phases in a three-phase equilibrium change on cooling.

- Test how a melted specimen with the composition of the L corner will react on cooling. Give a reaction formula.
- Test how a β phase specimen with the composition of the β corner will react on cooling. Give a reaction formula.
- Compare the two results. Discuss anything that may seem surprising.

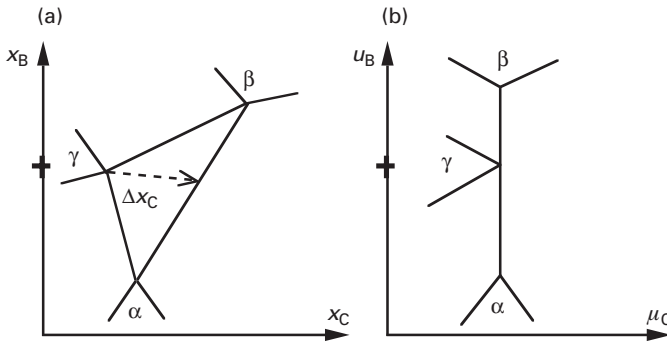


Figure 12.24 Conditions of a transformation under changing the content or chemical potential of C in a ternary system. T and P are kept constant. The arrow in (a) points towards the C corner. In (b) it would be horizontal.

Solution

(a) $L \rightarrow \alpha + \beta(+L)$; (b) $\beta \rightarrow L + \alpha(+\beta)$; (c) The first reaction looks like a eutectic reaction and the second one like a metatectic one although the phase diagram is the same. The reason is that this is not a sharp transformation and the concepts developed for sharp transformations cannot be strictly applied.

12.9 Phase transformations controlled by a chemical potential

It is sometimes possible to contain a system inside a wall, which allows some components to penetrate but not others. In alloy systems it sometimes happens that one component diffuses much faster than the others. In other cases, one or a few components are volatile and can easily be exchanged with the surroundings. In these cases it is possible to produce a phase transformation by gradually changing the chemical potential of the mobile component but keeping constant the content of all the other components and also T and P . The conditions may be illustrated by the pair of x_C, x_B and μ_C, u_B phase diagrams in Fig. 12.24(a) and (b), respectively, for a case where $p = c$ and the mobile component is denoted by C. The arrow in Fig. 12.24(a) represents a discontinuous change of the C content and is pointing towards the C corner. The u_B variable in Fig. 12.24(b) is explained in Section 4.3.

It is evident that the binary A–B alloy represented by a cross will eventually undergo a phase transformation $\gamma \rightarrow \alpha + \beta$ if the C content is gradually increased. This may be indicated in the following way using a reaction formula, $\gamma + C(\text{source}) \rightarrow \alpha + \beta$.

The μ_C, u_B diagram demonstrates that the transformation will be sharp if the μ_C potential can be controlled experimentally and there are no kinetic restrictions. In fact, the result of such a transformation would be very similar to the result of the well-known pearlite transformation taking place on a gradual change of temperature in an iron–carbon alloy. As a consequence, one should expect γ to transform to an intimate mixture

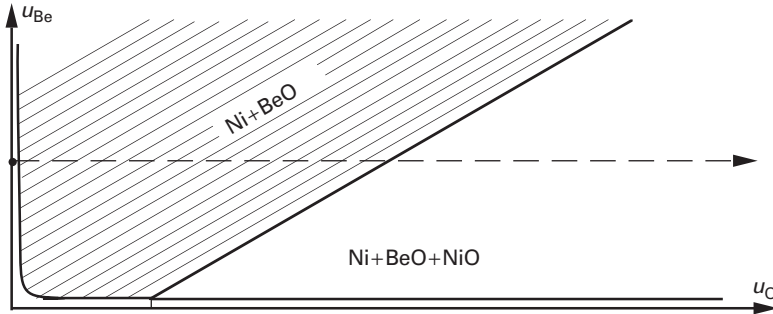


Figure 12.25 See Exercise 12.12.

of the two new phases, α and β , a so-called eutectoid microstructure. This has actually been observed in many carbon-containing alloyed steels when carburized.

As demonstrated by Fig. 12.24(a), the same transformation is predicted to be gradual if the C content is increased. However, when the supply of C comes from the surroundings, there must be a chemical potential difference driving the diffusion of C. A growing surface layer of $\alpha + \beta$ will thus form and the transformation will behave as a microscopically sharp one. A region has either transformed completely to $\alpha + \beta$ or is still pure γ .

Exercise 12.12

Figure 12.25 shows a very rough sketch of the Ni–O–Be phase diagram at 1623 K and 1 bar. The hyperbolic solubility curve for BeO in the Ni-rich phase approaches the Ni corner very closely. It is known that pure Ni oxidizes to NiO in air at 1623 K. Construct a reasonable profile for the O content from the surface and into the interior of the Ni–Be alloy denoted by the filled circle on the u_{Be} axis, after some time in air at 1623 K.

Hint

The composition of all layers must lie on the horizontal line through the initial alloy composition because the u_{Be} axis has been used and the diffusion of Be is slow compared to that of O. Remember that the inward diffusion of O requires a continuous decrease of the O potential or, more conveniently in the present case, a continuous decrease of the O content of the Ni phase close to the corner of the diagram (because its Be content is too low to affect the O potential).

Solution

Suppose an oxide scale of NiO + BeO will form on the surface and also an inner layer of Ni + BeO. Between them there will be a sharp interface because a three-phase layer of Ni + NiO + BeO could not exist in a potential gradient. It can exist at a particular O potential, only, that of the three-phase equilibrium. Furthermore, the average O content

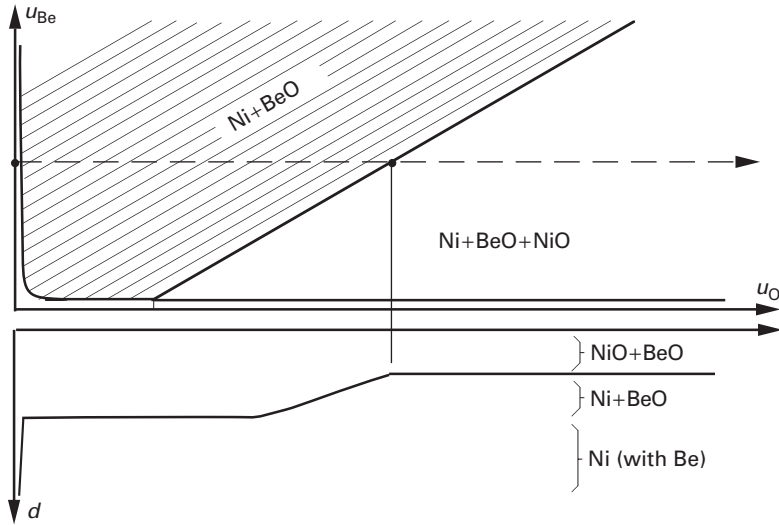


Figure 12.26 Solution to Exercise 12.12.

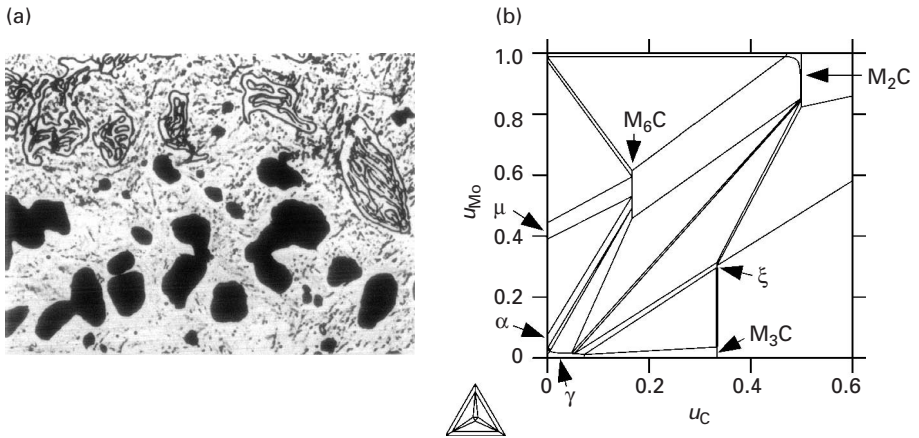


Figure 12.27 See Exercise 12.13.

in the layer of Ni + BeO varies quickly close to its inner side where the O solubility in the Ni phase is low and the solubility line is almost vertical in the phase diagram (Fig. 12.26). Otherwise, practically no O could diffuse through that part.

Exercise 12.13

The micrograph (Fig. 12.27) shows the structure of an Fe–20 mass% Mo–1 mass% C alloy at a magnification of 500 \times , which has been carburized further at 1273 K and then quenched. The lower part shows the original structure of M_6C particles (black) in a matrix of γ (now martensite after quenching) and the upper part the new structure. The

surface is above this picture. Explain the microstructure using the phase diagram which is for the same temperature.

Hint

From the composition given we calculate $u_{\text{Mo}} = 0.13$ and $u_{\text{C}} = 0.05$. The value of u_{Mo} does not change when we add more carbon. The alloy will thus move along a horizontal line to the right in the phase diagram.

Solution

The alloy is initially in the $\gamma + \text{M}_6\text{C}$ phase field. Moving to the right in the phase diagram the alloy may enter the three-phase triangle $\gamma + \text{M}_6\text{C} + \text{M}_2\text{C}$ and approach the $\gamma + \text{M}_2\text{C}$ phase field. We can thus understand that M_6C must transform. A horizontal line from the M_6C corner to the $\gamma + \text{M}_2\text{C}$ side of the triangle would illustrate the reaction $\text{M}_6\text{C} + \text{carbon} \rightarrow \text{M}_2\text{C} + \gamma$. This may be regarded as a eutectoid transformation where carbon plays the role usually played by heat. The conclusion is confirmed by the upper part of the picture showing regions of a eutectic-like two-phase mixture, evidently $\text{M}_2\text{C} + \gamma$ formed from previous M_6C particles by the above reaction formula.

13 Transformations in closed systems

13.1 The phase field rule at constant composition

Most of the discussion in the preceding chapter concerned transformations in systems of constant composition, so-called closed systems. We shall now examine that case in more detail.

To keep a variable constant means that the phase diagram is sectioned at that value of the variable. Constant composition means that $c - 1$ molar axes have been sectioned and thus $n_m = c - 1 = n_s$. This can be inserted in the phase field rule which is given by Eqs (10.6) and (10.7). They hold one on each side of a critical p value. Without any projection the critical value will be

$$p = 1 + n_{pr} + n_m = 1 + 0 + (c - 1) = c. \quad (13.1)$$

Equation (10.7) will then apply to all $p \leq c$, yielding

$$d = r = c + 1 - n_s - n_{pr} = c + 1 - (c - 1) - 0 = 2. \quad (13.2)$$

The two variables are T and P . Equation (10.6) will apply to all $p \geq c$, yielding

$$d = c + 2 - p - n_s + n_m = c + 2 - p. \quad (13.3)$$

This expression resembles Gibbs' phase rule but it should be emphasized that it applies to systems with constant composition only for $p \geq c$, and in all such cases we obtain $d \leq 2$.

In Sections 13.8 and 13.9 it will be shown that one must take special account of the presence of congruent transformations. They were neglected when the phase field rule was derived.

Exercise 13.1

Consider the equilibrium $\text{CH}_4 \leftrightarrow \text{C}(\text{gr}) + 2\text{H}_2$ at a constant pressure of 1 bar. Can it exist at one temperature only or in a range of temperatures?

Hint

Graphite is solid C, CH_4 and H_2 are both gaseous but there can be only one gas phase which is thus a mixture of them.

Solution

We have two components, C and H, $c = 2$. We have two phases, graphite and gas, $p = 2$, and thus $p = c$ and $d = c + 2 - p = 2 + 2 - 2 = 2$. We may vary P and T , i.e. under any value chosen for P we can still vary T .

Exercise 13.2

Consider the equilibrium $\text{CaCO}_3 \leftrightarrow \text{CaO} + \text{CO}_2$ in an atmosphere, initially composed of pure N_2 . Can the equilibrium exist in a range of temperature if the pressure is kept constant at 1 bar?

Hint

CaCO_3 and CaO are two different solid phases. If CO_2 forms, it will go into the gas and may form several species, CO_2 , CO and O_2 , mixed with N_2 , but there will still be only one gas phase.

Solution

We have four components, Ca, C, O and N, $c = 4$. We have three phases, CaCO_3 , CaO and gas, $p = 3$. Thus $p < c$ and the phase field rule gives $d = 2$. For any chosen value of P we can still vary T . It should be emphasized that without N_2 we could not vary T at a chosen P .

13.2 Reaction coefficients in sharp transformations for $p = c + 1$

Keeping P constant in a closed system, i.e. in a system with constant composition, we have $n_m = c - 1$ but $n_s = c$. Instead of Eq. (13.3) we obtain

$$d = c + 2 - p - n_s + n_m = c + 2 - p - c + (c + 1) = c + 1 - p. \quad (13.4)$$

With $p = c + 1$ phases, we will thus get a sharp transformation ($d = 0$) by changing T . The result would be the same by keeping T constant and varying P . This is why we shall now discuss the case $p = c + 1$ in more detail.

Figure 13.1 shows conditions for a sharp transformation in (a) a binary and (b) a ternary system. For the binary case ($c = 2$, $p = 3$) we can write the reaction formula for the sharp transformation as follows if we omit any part of an initial phase that remains when the reaction is completed.



This is independent of whether one passes from $\alpha + \beta$ to $\alpha + \gamma$ or from $\alpha + \beta$ to $\gamma + \beta$, i.e. independent of whether some α or β will remain.

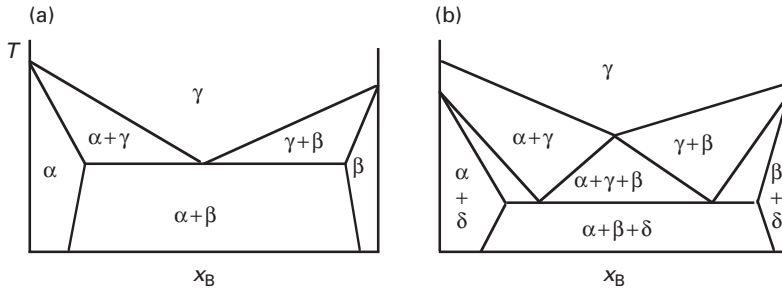


Figure 13.1 Conditions for (a) a three-phase transformation in a binary system and (b) a four-phase transformation in a ternary system at a low constant value of x_C . P is constant in both cases.

It is common to write chemical reaction formulas with **reaction coefficients**, ν . Accepting this procedure we can modify the reaction formula for the phase transformation and make it more quantitative,

$$\nu^\alpha \alpha + \nu^\beta \beta = \nu^\gamma \gamma. \tag{13.6}$$

It expresses the fact that ν^α moles of the α phase react with ν^β moles of the β phase to form ν^γ moles of the γ phase. As an example we may consider the oxidation of solid Ag by gaseous O_2



In this simple case the reaction coefficients can be given as small integers. In the general case this is not possible since the phases are not always stoichiometric.

By making the reaction coefficients negative for all the reactants and positive for all the products we can simply write the formula as $\sum \nu^j J = 0$. The ν^j values will represent the relative amounts of the phases taking part in the reaction, for instance expressed as formula units. Naturally, the ν^j values must be such that mass balance is fulfilled for each component i ,

$$\sum_j \nu^j a_i^j = 0 \quad \text{for each component } i, \tag{13.8}$$

where a_i^j is the number of i atoms per formula unit of phase j . We are considering a sharp phase transformation with $p = c + 1$ and we thus have a system of c equations with $p = c + 1$ coefficients each and in the form of a $(c + 1) \times c$ matrix. By excluding the j th column of coefficients one obtains a $c \times c$ determinant and the value of each ν^j is given by such a determinant.

$$\nu^j = (-1)^{j-1} \begin{vmatrix} a_1^\alpha & \dots & a_{j-1}^{j-1} & a_j^{j+1} & \dots & a_c^\epsilon \end{vmatrix}. \tag{13.9}$$

It is easy to see that the above condition is fulfilled by this expression because we find

$$\begin{aligned} \sum_j a_i^j v^j &= a_i^\alpha \left| a_1^\beta \quad a_2^\gamma \quad \dots \quad a_c^\epsilon \right| - a_i^\beta \left| a_1^\alpha \quad a_2^\gamma \quad \dots \quad a_c^\epsilon \right| + \dots \\ &= \left| a_i^\alpha \quad a_1^\beta \quad a_2^\gamma \quad \dots \quad a_c^\epsilon \right| = 0. \end{aligned} \quad (13.10)$$

The reason is that two columns in Eq. (13.10) have identical elements because i is one of the numbers 1 to c . It should be noticed that in the calculation of v^j one makes no distinction between reactants and products. Some of the v values will turn out positive and others negative and one may thus identify the members of each group. If the value for a selected phase turns out with the wrong sign, according to the direction chosen for the reaction, then one should simply change all the signs.

When non-stoichiometric phases are involved it may be convenient to identify the a_i coefficients with the molar contents x_i . We get, for instance,

$$v^\alpha = (-1)^{1-1} \left| x_1^\beta \quad x_2^\gamma \quad \dots \quad x_c^\epsilon \right| = \left| x_1^\beta \quad x_2^\gamma \quad \dots \quad x_c^\epsilon \right|. \quad (13.11)$$

The reaction coefficients of a sharp phase transformation can be used for evaluating the change of any molar quantity, X_m , during the transformation. We obtain

$$\Delta X_m = \sum X_m^j v^j = \left| X_m^\alpha \quad a_1^\beta \quad a_2^\gamma \quad \dots \quad a_c^\epsilon \right|. \quad (13.12)$$

This value refers to 1 mole of the reaction formula, as defined by the reaction coefficients.

It must be emphasized that the present discussion only applies to phase equilibria with $p = c + 1$, i.e. phase equilibria which are univariant in the complete phase diagram. That is exactly the case considered in Section 8.8. There Eq. (8.39) was derived which can be written as

$$\left| H_m^\alpha \quad x_1^\beta \quad x_2^\gamma \quad \dots \quad x_c^\epsilon \right| dT/T = \left| V_m^\alpha \quad x_1^\beta \quad x_2^\gamma \quad \dots \quad x_c^\epsilon \right| dP. \quad (13.13)$$

It can now be transformed into the simpler form

$$\frac{dP}{dT} = \frac{\Delta H_m/T}{\Delta V_m}. \quad (13.14)$$

Consequently, this simple expression holds for any univariant equilibrium and not only for the two-phase equilibrium considered initially in Section 8.3.

Exercise 13.3

Prove Kirchhoff's law for a reaction between well-defined substances, $(\partial \Delta H / \partial T)_P = \Delta C_P$.

Hint

For well defined substances all v^j are fixed. Express ΔH in terms of H_m for the various substances and the reaction coefficients.

Solution

$\Delta H = \sum v^j H_m^j$; $(\partial \Delta H / \partial T)_P = (\partial \sum v^j H_m^j / \partial T)_P = \sum v^j (\partial H_m^j / \partial T)_P = \sum v^j C_P^j = \Delta C_P$ but only because $(\partial v^j / \partial T)_P = 0$ for well-defined substances.

Exercise 13.4

From dilatometric measurements on the pearlite transformation in the Fe–C system at 1 bar we know $T = 1000$ K and $\Delta V_m = 0.047$ cm³/mol and from calorimetric measurements we know that $\Delta H_m = -4540$ J/mol. Calculate the pressure dependence of the transformation temperature.

Hint

The pearlite transformation is $\gamma \rightarrow \alpha + \text{Fe}_3\text{C}$. First check how many degrees of freedom this equilibrium has in a binary system. Then use an equation derived for that particular case.

Solution

We have $p = 3$ and $c = 2$ and, thus, $p = c + 1$, i.e. a sharp transformation at constant P . For that case we get the slope $dT/dP = T \Delta V_m / \Delta H_m = 1000 \times 0.047 \times 10^{-6} / (-4540) = -1.04 \times 10^{-8}$ K/Pa = -10^{-3} K/bar.

13.3 Graphical evaluation of reaction coefficients

The reaction coefficients for a sharp transformation in a closed system can also be evaluated graphically using the lever rule. For $c = 2$, $p = 3$ one of the phases transforms into a mixture of the other two. The composition of the first phase is thus equal to the average composition of the other two and the lever rule can be applied directly. For $c = 3$, $p = 4$ there are three different cases as illustrated by Fig. 12.9. In class I and class III reactions one of the phases may transform into a mixture of the other three and, again, the composition of the first phase is equal to the average composition of the others. If the reaction coefficient of the first phase is taken as -1 , the coefficients of the other phases are obtained as the fractions of the subsystems using one of the methods described in Fig. 4.5.

Class II can be handled by considering that a mixture of two phases will transform into a mixture of the remaining two phases. Evidently, the compositions of the two mixtures must be equal and should thus fall on the point of intersection between the two diagonals, point 'i' in Fig. 13.2.

If the average composition of the system does not coincide with the first phase discussed for classes I and III, then it falls inside one of the three smaller triangles (see the diagram for $\delta \rightarrow \alpha + \beta + \gamma$ in Fig. 13.3(a)). The composition of δ will be adjusted

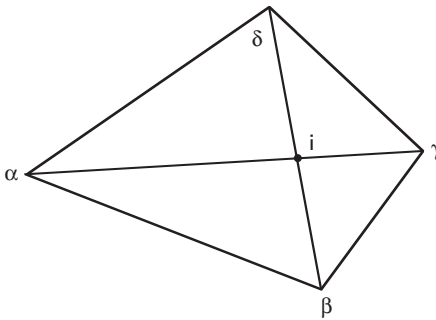


Figure 13.2 Compositions of phases in a class II reaction in a ternary system. The weighted average of the two reacting phases, say α and γ , must fall on the intersection between the diagonals and so must the weighted average of the two product phases, say β and δ .

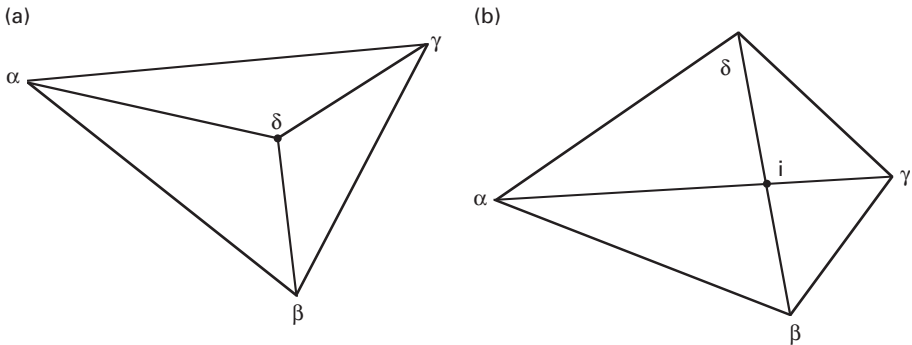


Figure 13.3 Relations between phase compositions in (a) a class I or III transformation and in (b) a class II transformation.

by precipitation of first one and later two of the other phases in the small triangle as the temperature of the four-phase plane is approached. There the rest of it will fall on the δ point in the diagram and will transform to a mixture of the other three phases. The microstructure will show a matrix with a characteristic pattern of the three-phase mixture in which one can see imbedded one-phase regions of the first phase to precipitate and eutectoid regions of the two co-precipitated phases. If the average composition falls outside the triangular four-phase plane, then the δ phase will never reach the four-phase plane.

For class II there are four alternatives and it is interesting to note that the range of existence of each one of the four phases extends to both sides of the four-phase plane. In Fig. 13.3(b) the three-phase fields $\alpha + \beta + \delta$ and $\beta + \delta + \gamma$ extend to one side and $\alpha + \beta + \gamma$ and $\alpha + \gamma + \delta$ extend to the other side. If a specimen with an average composition falling inside the $\alpha - \beta - i$ triangle is approaching the four-phase plane from the first side, then it will contain a mixture of $\alpha + \beta + \delta$ when reaching the four-phase plane. From a mass balance point of view it may be regarded as a mixture of $\beta + \delta$ falling on point i and some extra amounts of α and β . The mixture of $\beta + \delta$ will

transform to $\alpha + \gamma$ when the system crosses the four-phase plane. However, since the extra amount of β is present in the $\beta + \delta$ mixture over the whole specimen, there are no particular β regions predestined not to take part in the $\beta + \delta \rightarrow \alpha + \gamma$ transformation. The progress of the transformation will determine which parts of β will not transform and, afterwards, they will be found scattered all over the specimen. The α , present before the four-phase reaction, may indirectly take part in the reaction by providing favourable sites for the precipitation of α .

Exercise 13.5

Suppose the δ phase in Fig. 13.3(b) is a liquid and that the average composition of the system is such that the liquid will be just about consumed by the four-phase reaction. What phases will the system contain at a temperature just below the four-phase plane.

Hint

Suppose there is full equilibrium at each temperature. Remember that the amount of a phase in a three-phase assemblage is given by the position in the three-phase triangle.

Solution

At an earlier stage the composition may fall inside the $\alpha + \beta + \delta(L)$ or $\beta + \gamma + \delta(L)$ triangle. If a very slight amount of liquid should remain below the four-phase temperature then the system would be in the $\alpha + \beta + \delta(L)$ triangle. If the liquid would be just about consumed then the system, should fall on the $\alpha + \gamma$ line.

13.4 Reaction coefficients in gradual transformations for $p = c$

Let us now consider a gradual transformation in a closed system with $p = c$ by keeping pressure constant and changing the temperature. In order to write a reaction formula with the mass balance conserved it is now necessary also to include the change in composition of regions not taking part directly in the phase transformation. As a simple example of $p = c = 2$, consider the precipitation of Al_2Cu from α phase, a solution of Cu in fcc-Al. The solubility decreases with decreasing temperature at constant pressure and there will thus be a gradual precipitation of Al_2Cu . One way of writing this reaction would be



The reaction coefficients can then be evaluated with the same method used for sharp transformations with $p = c + 1$ but with the extra supply of Cu introduced instead of the missing phase $c + 1$. However, it should be emphasized that this way of writing the transformation is not unique. Another possibility would be



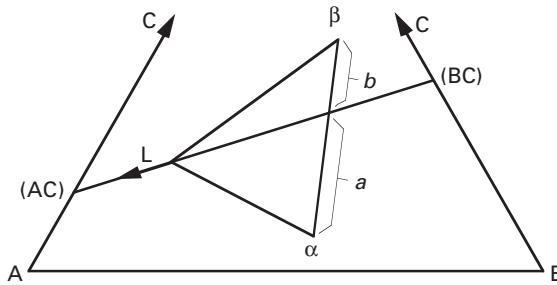


Figure 13.4 Gradual three-phase transformation in a ternary system. The arrow shows the direction of change in composition of the L phase.

In order to define a unique way one would have to specify some special criterion. If one is interested in the mechanism of the transformation, then one should consider exchange of both Cu and Al but in proportions balanced according to their rates of diffusion in the α phase.

A three-phase transformation in a ternary system is another case of gradual transformation, now with $p = c = 3$. An example was given in Fig. 12.22 but in Fig. 13.4 it is reproduced with the composition triangle included. Two of the ways of writing this transformation are



where (BC) and (AC) represent the compositions one can read on the two sides of the composition triangle. In each case one can calculate the reaction coefficients by including (BC) or (AC) instead of the missing phase $c + 1$. The ratio between α and β will indeed be independent of whether one includes (BC) or (AC). It will be b/a according to the lever rule.

Exercise 13.6

In an Al–Cu–Si specimen at 1 bar and 803 K one finds that the phases have the following compositions at equilibrium: $\alpha(0.025\text{Cu}; 0.006\text{Si}) + L(0.16\text{Cu}; 0.05\text{Si}) + \text{Al}_2\text{Cu}$. When the temperature is decreased, L changes in the direction away from the point 0.83Al;0.17Cu. Calculate the relative amounts of α and Al_2Cu in the eutectic structure formed by $L \rightarrow \alpha + \text{Al}_2\text{Cu}$ on further cooling. (The numbers given above are molar contents.)

Hint

We have $c = 3$ and $p = 3$ but we should write the transformation in a way resembling a sharp transformation for $p = c + 1$. The relative amounts of the two phases are then obtained as the ratio of their reaction coefficients.

Solution

Write the reaction as $L + (0.83\text{Al}; 0.17\text{Cu}) \rightarrow \alpha + \text{Al}_2\text{Cu}$. Eq. (13.11) yields

$$v^\alpha = (-1)^{3-1} \begin{vmatrix} \text{Al} & \text{Cu} & \text{Si} \\ -0.79 & -0.16 & -0.05 \\ -0.83 & -0.17 & 0 \\ 2 & 1 & 0 \end{vmatrix} = +0.0245$$

$$v^{\text{Al}_2\text{Cu}} = (-1)^{4-1} \begin{vmatrix} \text{Al} & \text{Cu} & \text{Si} \\ -0.79 & -0.16 & -0.05 \\ -0.83 & -0.17 & 0 \\ 0.969 & 0.025 & 0.006 \end{vmatrix} = +0.00719$$

$$v^{\text{Al}_2\text{Cu}}/v^\alpha = 0.00719/0.0245 = 0.2935 = 0.23 : 0.77.$$

13.5 Driving force for sharp phase transformations

The driving force for the precipitation of a new phase under a gradual transformation in a closed system was discussed in Section 7.7. As an introduction to a discussion of the driving force for a sharp transformation we shall now consider a eutectoid transformation in a binary alloy. We have seen that it usually gives rise to an intimate mixture of the two new phases, illustrated by Fig. 12.5. It may give the material advantageous properties. The most famous example is pearlite, the eutectoid formed from the austenite phase in steel.

Because the rate of transformation is controlled by slow diffusion and evolution of the heat of transformation will thus be slow, it is often possible to control the temperature and it makes sense to discuss the transformation under isothermal conditions, for instance at T_2 in Fig. 12.6. The character of the transformation as sharp is evident from its progress. A region has either been completely transformed or is not at all affected. The transformation occurs by the growth of colonies composed of an intimate mixture of the two new phases and, under isothermal conditions, the growth continues until the whole system has transformed.

It is well known that the mixture will be the finer, the lower the temperature of formation is. The reason is that the interfaces in the mixture have surface energy and cannot form without the supply of a corresponding amount of driving force. According to an approximate treatment, one-half of the available driving force goes into surface energy and the other half is used for driving the diffusion.

The conditions for cooperative growth of the two new phases can be illustrated by extrapolating the phase boundaries in the T, x_B phase diagram as shown in Fig. 12.6. This kind of construction is given again in Fig. 13.5(a) but a solid phase, γ , has been substituted for the liquid phase and the diagram has been rotated. The transformation temperature is now denoted by T_1 . The diagram shows how one can evaluate the composition difference driving the diffusion in each one of the phases if there is local equilibrium with the γ phase (see the arrows in Fig. 12.5).

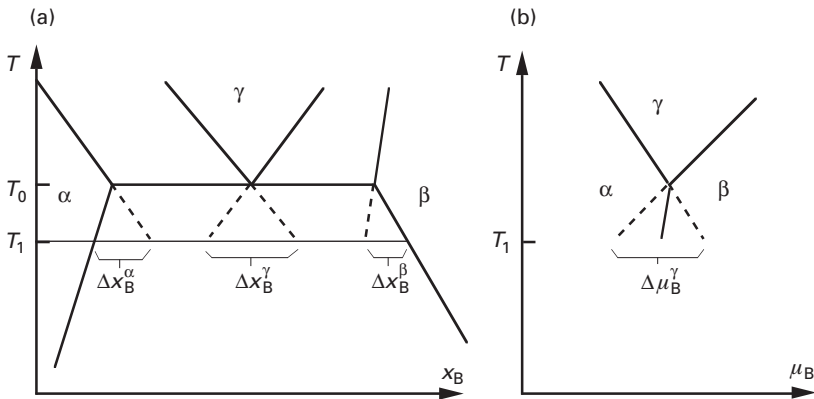


Figure 13.5 Evaluation of the differences in composition (a) and chemical potential (b) driving the diffusion in a three-phase transformation in a binary system.

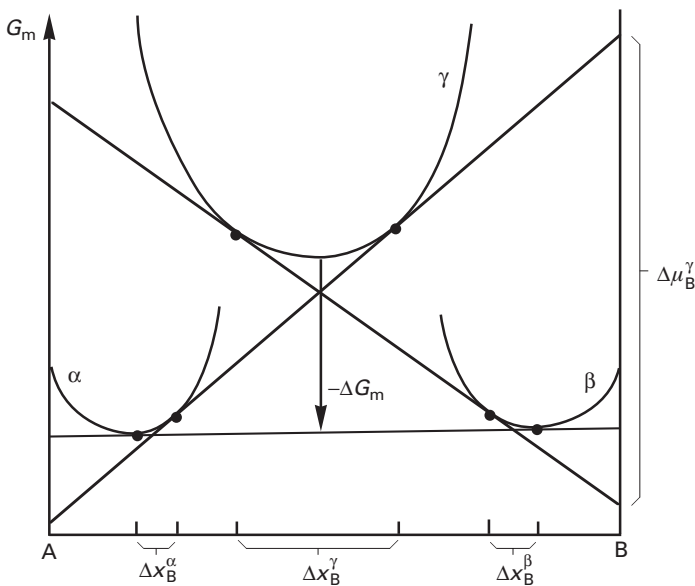


Figure 13.6 Gibbs energy diagram illustrating the eutectoid transformation $\gamma \rightarrow \alpha + \beta$ at T_1 in Fig. 13.5.

A similar construction in the T , μ_B phase diagram in Fig. 13.5(b) yields a difference in chemical potential of B, $\Delta \mu_B^\gamma$, which may be used in a treatment of the rate of diffusion of B in γ , although the composition difference is usually used for that purpose. The conditions for the eutectoid reaction $\gamma \rightarrow \alpha + \beta$ may also be illustrated with a molar Gibbs energy diagram at T_1 (see Fig. 13.6).

As explained in Section 7.7, the driving force for the precipitation of a new phase in a gradual transformation decreases during its growth but for the whole reaction one can define and evaluate an integrated driving force along the reaction path. This problem is

absent if the phase transformation is a sharp one because the parent phase which has not yet transformed has not changed at all. Under constant T and P the driving force is thus constant and the integrated driving force is equal to the momentary driving force if they are both expressed per mole of the transformed structure. Under constant T and P we obtain, by identifying the extent of the transformation, ξ , with the number of moles of the products which is also equal to the number of moles of transformed reactants,

$$D = - \left(\frac{\partial G}{\partial \xi} \right)_{T,P,N_i} = -G_m(\text{products}) + G_m(\text{reactants}). \quad (13.19)$$

This quantity is illustrated in Fig. 13.6 for a eutectoid transformation $\gamma \rightarrow \alpha + \beta$ in a binary system.

The value of the driving force may be calculated using the reaction coefficients for a sharp phase transformation at fixed composition. Per mole of the reactant, γ , we obtain from Eq. (13.12),

$$D = -\Delta G_m = - \sum G_m^j \nu^j / (-\nu^\gamma) = - \left| G_m^\alpha \quad x_1^\beta \quad x_2^\gamma \right| / \left| x_1^\alpha \quad x_2^\beta \right|. \quad (13.20)$$

Even though this expression looks quite simple, it may sometimes be difficult to evaluate all the molar contents to be inserted. A useful approximation would be to assume that all the phases have the same compositions they have at the equilibrium temperature. If it is further assumed that the resulting value of ΔG_m varies linearly with temperature, we could use the method introduced in Section 3.9 for a transformation that we now recognize as a sharp one. Since D stays constant for a sharp transformation, we get

$$\Delta S(T_1 - T_0) = \Delta H(T_1 - T_0)/T_0 = -\Delta G = \int D d\xi = D \int d\xi = D \Delta \xi. \quad (13.21)$$

Let $\Delta \xi$ be the number of moles transformed. The driving force for the transformation of one mole is thus

$$D = \Delta S_m(T_1 - T_0) = \Delta H_m(T_1 - T_0)/T_0. \quad (13.22)$$

Here, T_0 is the equilibrium temperature and T_1 is the actual temperature of the transformation. For small ΔT the heat of transformation may be taken as the value at T_0 . It may be available from direct measurements. For larger undercoolings one may have to consider variations of ΔH_m with temperature, for instance due to changes of the compositions of various phases.

Let us now examine the situation below the equilibrium temperature in more detail. Figure 13.6 demonstrates the complexity found in a eutectoid transformation in a binary system. Each one of the phases is in contact with the other two phases and two different compositions are thus defined for each phase. Figure 13.5 shows how they are obtained from the phase diagram by extrapolating the phase boundaries to the temperature of transformation T_1 under the assumption of local equilibrium at all the two-phase interfaces.

The situation gets even more complicated if one tries to analyze how the driving force is consumed during the transformation. This is illustrated in Fig. 13.7. This diagram demonstrates several complications. Firstly, α and β grow under an increased pressure

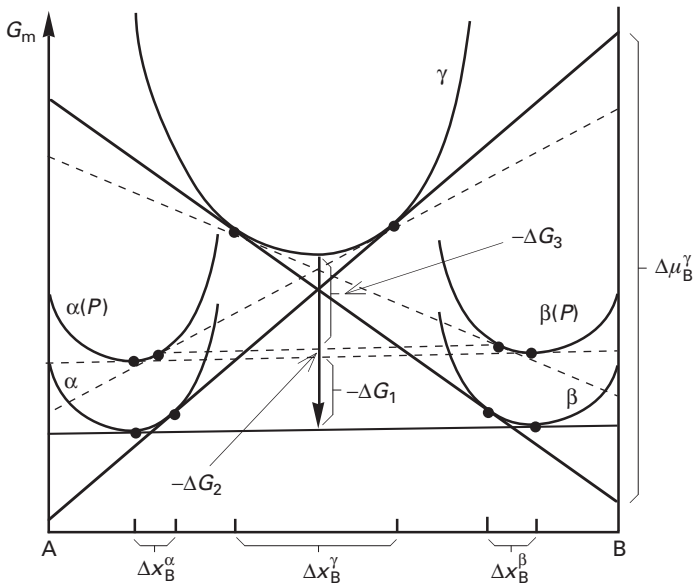


Figure 13.7 Molar Gibbs energy diagram for a binary system with a eutectoid transformation, showing three dissipations of the driving force, ΔG_1 , ΔG_2 and ΔG_3 .

because the interfaces to the parent γ are curved (as illustrated in Fig. 12.5). The corresponding $-\Delta G_1$ is consumed by the creation of all the α/β interfaces in the eutectoid structure. Secondly, the two new phases are not formed with their final compositions, which are governed by the α/β equilibrium, because they grow from the γ phase. The corresponding $-\Delta G_2$ is consumed by diffusion from the interior of α to the interior of β behind the reaction front. The remaining part of the driving force, $-\Delta G_3$, is consumed by diffusion at the reaction front.

As already mentioned, according to an approximate treatment of the rate of transformation, the highest growth rate is obtained when one-half of the total driving force goes into the surface energy of all the α/β interfaces.

Exercise 13.7

The difference in chemical potential of B driving the diffusion in the γ phase during the eutectoid transformation, shown in Fig. 12.5, was identified in Fig. 13.5(b). Find the corresponding differences for α and for β . How are the three related?

Solution

$\Delta\mu_B^\alpha$ is found between the lines for γ/α and β/α and $\Delta\mu_B^\beta$ is found between the lines for β/α and β/γ . Evidently, $\Delta\mu_B^\gamma = \Delta\mu_B^\alpha + \Delta\mu_B^\beta$.

Exercise 13.8

The heat of formation of pearlite from austenite is $\Delta H_m = -4.5$ kJ/mol and the equilibrium temperature is $T_o = 1000$ K. Estimate the coarseness of pearlite formed at $T_1 = 950$ K, assuming that all the driving force goes into interfacial energy between the two phases of pearlite. Suppose that the interfacial energy is approximately $\sigma = 1$ J/m² and the molar volumes of all the phases are approximately $V_m = 7 \times 10^{-6}$ m³/mol. Compare with an experimental value of the coarseness, $w = 0.14$ μ m.

Hint

w is the total thickness of one lamella of each phase in pearlite. One mole of pearlite then contains an area of $2V_m/w$ of interfaces.

Solution

The total interfacial energy is $2\sigma V_m/w$ J/mol. The driving force is $(\Delta H_m/T_o)(T_1 - T_o)$. Thus, $2\sigma V_m/w = (\Delta H_m/T_o)(T_1 - T_o)$; $w = 2\sigma V_m T_o / (-\Delta H_m)(T_o - T) = 2 \times 1 \times 7 \times 10^{-6} \times 1000 / 4500 \times 50 = 6 \times 10^{-8}$ m = 0.06 μ m.

The observed value is about twice as large, which is expected if only one-half of the driving force should go into interfacial energy.

13.6 Driving force under constant chemical potential

In the preceding section it was shown how the driving force for a sharp transformation can be estimated from the undercooling ΔT at which the transformation occurs. In the same way, the driving force for a γ -eutectoid transformation in a ternary A–B–C system, controlled by the chemical potential of a mobile component C under constant T and P , should depend upon the difference in chemical potential of C during the transformation and at equilibrium, $\Delta\mu_C$. We can illustrate the conditions by extrapolations in the μ_C , u_B phase diagram in Fig. 12.24 or in the corresponding μ_C , μ_B phase diagram (see Fig. 13.8 where the diagram has been rotated in order to emphasize the similarity with the binary case in Fig. 13.5).

Since μ_C is assumed to be constant instead of N_C , we must evaluate the driving force from a new alternative of the combined first and second law,

$$\begin{aligned} Dd\xi &= VdP - SdT + \sum_{j \neq C} \mu_j dN_j + \mu_C dN_C - dG + N_C d\mu_C - N_C d\mu_C \\ &= VdP - SdT + \sum_{j \neq C} \mu_j dN_j - N_C d\mu_C - d(G - N_C \mu_C) \end{aligned} \quad (13.23)$$

where $G - N_C \mu_C$ is a new characteristic state function. At constant T , P , N_j and μ_C we get

$$Dd\xi = -d(G - N_C \mu_C). \quad (13.24)$$

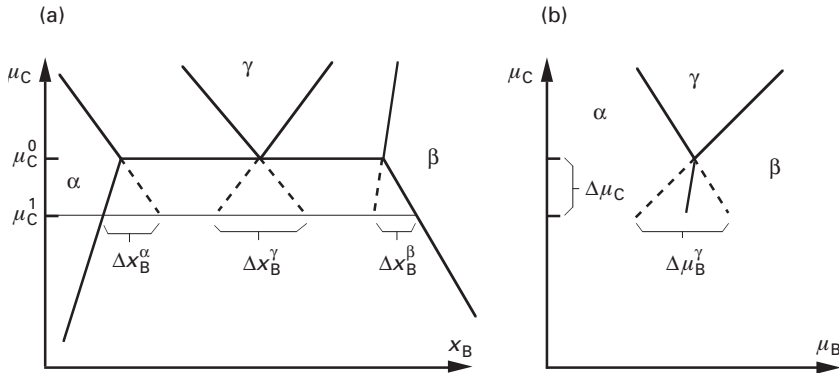


Figure 13.8 Evaluation of the driving force, $\Delta\mu_C$, for an isobarothermal transformation under changing C content in a ternary system.

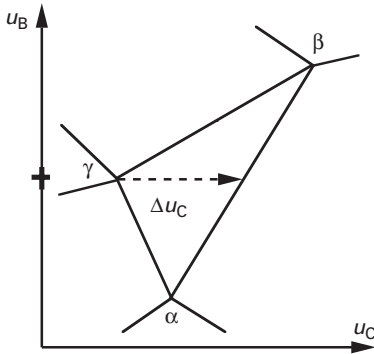


Figure 13.9 Sharp transformation $\gamma \rightarrow \alpha + \beta$ in a ternary system with a mobile component, C. The increase of the C content can be read directly.

However, by identifying the extent of the transformation, ξ , with the increased content of C, N_C , we return to more well known quantities,

$$D = -(\partial G/\partial N_C)_{T,P,N_j} + \mu_C = -{}^0\mu_C + \mu_C = \Delta\mu_C. \quad (13.25)$$

By definition, the first term is the chemical potential of C at equilibrium. Therefore,

$$D = \mu_C - {}^0\mu_C = \Delta\mu_C. \quad (13.26)$$

This is the driving force per mole of C added to the system. It should be multiplied by the amount of C required by the transformation. That quantity is conveniently expressed in terms of the u_C fraction, the amount of C per mole of A + B. Figure 13.9 demonstrates how the increase Δu_C can be evaluated graphically and the driving force for the transformation $\gamma \rightarrow \alpha + \beta$ expressed per mole of A + B is given by

$$D = \Delta u_C \times \Delta\mu_C.$$

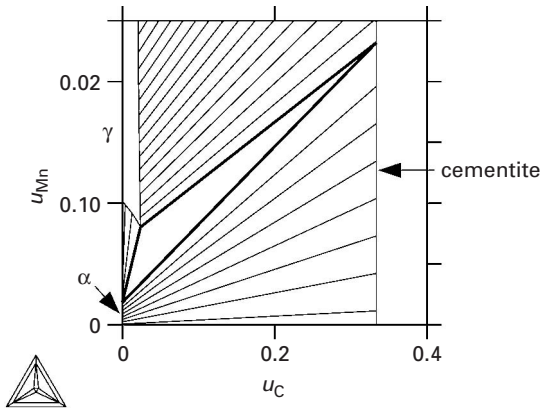


Figure 13.10 See Exercise 13.9.

Figure 13.9 resembles Fig. 12.24 but the choice of u axis makes the arrow horizontal. The analytical evaluation of Δu_C is described in the next section.

Exercise 13.9

In the Fe–C system the γ phase exists above 1000 K and at lower temperatures it transforms to a lamellar aggregate of α and cementite (Fe_3C) that is called pearlite. The phase diagram (Fig. 13.10) for 923 K shows that it is possible to stabilize γ by the addition of Mn. Consider an alloy composed of γ with a composition falling exactly on the γ corner of the $\alpha + \gamma + \text{cementite}$ triangle at 923 K. That alloy must have a C activity of 0.7. By carburizing such an alloy one can form a surface layer of pearlite. Estimate its coarseness if one carburizes with an atmosphere having a carbon activity of 0.9. Use the values $V_m = 7 \times 10^{-6} \text{ m}^3/\text{mol}$ and surface energy $\sigma = 1 \text{ J/m}^2$.

Hint

It should first be realized that we do not know how much of the difference in carbon activity is lost by driving the diffusion of carbon through the carburized layer. In order to get a numerical result, let us assume that all the driving force acts at the reaction front.

The increase of the C content is obtained from a horizontal construction in the three-phase triangle. The increase in C potential is obtained from the activity through $\mu_C = {}^\circ\mu_C + RT \ln a_C$. Assume that half of the driving force goes into surface energy. Express the coarseness with w , the total width of one lamella of α and one of cementite. The area of $\alpha/\text{cementite}$ interfaces is then $2V_m/w$ per mole of the material and we thus get the relation $2V_m\sigma/w = 0.5 \times \Delta u_C \Delta \mu_C$.

Solution

By measuring the horizontal distance of the γ point from the $\alpha + \text{cementite}$ side of the triangle we get $\Delta \mu_C = 0.08$. By comparing the C activities we get $\Delta \mu_C =$

$RT \ln(0.9/0.7) = 1930 \text{ J/mol}$ and using half of this we find $w = 2V_m\sigma/0.5\Delta u_C\Delta\mu_C = 2 \times 7 \times 10^{-6} \times 1/0.5 \times 0.08 \times 1930 = 2 \times 10^{-7} \text{ m} = 0.2 \text{ }\mu\text{m}$.

13.7 Reaction coefficients at constant chemical potential

In Section 13.2 we were able to calculate the fractions of the various phases taking part in a sharp transformation in a system of constant composition because p was equal to $c + 1$. Now we shall consider the case $p = c$ where one of the components is very mobile and is controlled through its potential. The total contents of all the other components in the system will be kept constant, i.e. $n_m = c - 2$. Together with the constant potential and pressure we have $n_s = c - 2 + 1 + 1 = c$ and instead of Eq. (13.3) we now obtain $d = c + 2 - p - n_s + n_m = c + 2 - c - c + (c - 2) = 0$. This will also be a sharp transformation. The mobile component will be denoted C and will be given the number c . By not considering that component we get the same condition as before but must now express the molar contents without regard for the mobile component. Thus we must use the u variable instead of the ordinary molar content x , and we obtain for instance

$$v^\gamma = \begin{vmatrix} u_1^\alpha & u_2^\beta & u_3^\delta & \dots & u_{c-1}^\epsilon \end{vmatrix}. \quad (13.27)$$

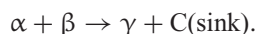
The mobile component is not included in the determinant. The amount of the γ phase taking part in the reaction, v^γ , is here expressed without regard for the mobile component. The change in content of the mobile component can be evaluated just like the change of any other molar quantity using Eq. (13.12).

$$\Delta u_C = \begin{vmatrix} u_C^\alpha & u_1^\beta & u_2^\gamma & \dots & u_{c-1}^\epsilon \end{vmatrix}. \quad (13.28)$$

This is the increase of C per mole of units of the reaction formula as given by the v^j values. If γ is the only reactant and all the other phases are products, it is interesting to evaluate Δu_C per mole of all the other components in γ . It is obtained by dividing with $-v^\gamma$.

$$\Delta u_C = \begin{vmatrix} u_C^\alpha & u_1^\beta & u_2^\gamma & \dots & u_{c-1}^\epsilon \end{vmatrix} / \begin{vmatrix} u_1^\alpha & u_2^\beta & u_3^\delta & \dots & u_{c-1}^\epsilon \end{vmatrix}. \quad (13.29)$$

If a mixture of α and β in the ternary A–B–C system is treated under conditions of a lower chemical potential for C, the system will move from right to left in Fig. 13.9 and one should expect the reverse transformation



This is a peritectoid transformation and one should primarily expect the new γ to form at the α/β interfaces. If the transformation is not inhibited due to slow diffusion of the two sluggish elements, it will look almost as a sharp phase transformation.

Exercise 13.10

The equation for Δu_C , the addition of a mobile component C consumed by a sharp transformation, can be applied to the reaction $\gamma + \text{C(source)} \rightarrow \alpha + \beta$ in a ternary system at constant T and P and the result will be $\Delta u_C/v^\gamma = |u_C^\alpha u_1^\beta u_2^\gamma|/|u_1^\alpha u_2^\beta|$. Show

that the same result is obtained if $C(\text{source})$ is regarded as a phase taking part in the transformation.

Hint

According to the text we really have $p = c = 3$ but now we shall insert $p = c + 1 = 4$ which is the condition for a sharp transformation. We can then use the ordinary equations expressed in terms of x fractions. We can calculate the amount of the 'phase' C , taking part in the reaction, as ν^C . The amount per mole of metal in γ is $\nu^C/\nu^\gamma(1 - x_C^\gamma)$.

Solution

Let $C(\text{source})$ be the fourth phase and let C be the third component. Then, $\nu^C = -|x_1^\alpha \ x_2^\beta \ x_C^\gamma| = -|x_C^\alpha \ x_1^\beta \ x_2^\gamma|$ and $\nu^\gamma = -|x_1^\alpha \ x_2^\beta \ x_C^C| = -|x_1^\alpha \ x_2^\beta|$ since $x_C^C \equiv x_3^C = 1$ and $x_1^C = 0 = x_2^C$. Thus, $\nu^C/\nu^\gamma(1 - x_C^\gamma) = -|x_C^\alpha \ x_1^\beta \ x_2^\gamma|/|x_1^\alpha \ x_2^\beta|(1 - x_C^\gamma) = -|u_C^\alpha \ u_1^\beta \ u_2^\gamma|/|u_1^\alpha \ u_2^\beta|$. The minus sign is due to the fact that $C(\text{source})$ must lose C in order for the mixture of the other phases to gain C .

13.8 Compositional degeneracies for $p = c$

Let us now return to transformations in closed systems, i.e. systems of constant composition. In Chapter 11 we saw that a transformation involving $c + 1$ phases will be sharp if P and the composition are kept constant and T is varied gradually (or T is kept constant and P is changed gradually). In Section 13.2 we then saw how one can calculate the reaction coefficients for each phase in a sharp transformation from the determinant obtained by omitting the corresponding column from the composition matrix. A phase transformation involving less than $c + 1$ phases will normally be gradual. It will extend over a range of T at constant P and the compositions of non-stoichiometric phases will normally change gradually. However, it sometimes happens that such a transformation is sharp even for $p < c + 1$. This possibility will now be examined.

Let us start with the case $p = c$, which normally yields a gradual transformation. We saw in Section 13.4 that the reaction coefficients in such a case can be calculated by treating the exchange of components with the remaining parts of the system as a reaction with a hypothetical phase $c + 1$. The amount of that exchange is thus obtained as

$$\nu^{c+1} = (-1)^c \begin{vmatrix} x_1^\alpha & x_2^\beta & \dots & x_c^\epsilon \end{vmatrix}. \quad (13.30)$$

If this coefficient happens to be zero, then there is no exchange with the real parts of the system and the transformation between them is sharp in spite of the fact that $p = c$ and not $c + 1$. The condition for having a sharp transformation with $p = c$ is thus that the composition determinant involving the real phases is zero:

$$\begin{vmatrix} x_1^\alpha & x_2^\beta & \dots & x_c^\epsilon \end{vmatrix} = 0. \quad (13.31)$$

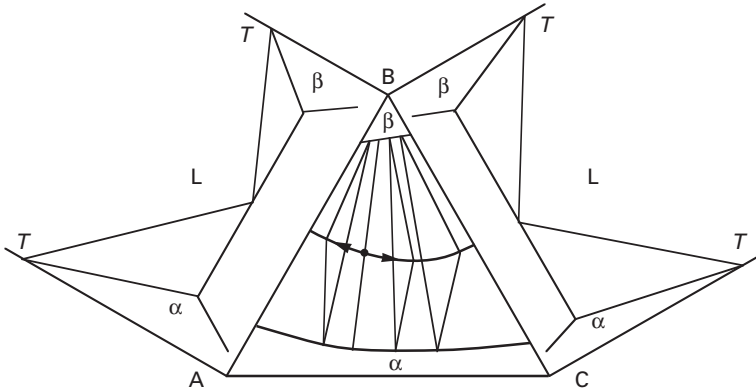


Figure 13.11 Projection of a ternary phase diagram at $P = 1$ bar, showing a temperature maximum for a three-phase equilibrium.

This means that the real phases fall on a point, line, plane, etc., when $p = c = 2, 3, 4$, etc. This was shown in Chapter 9 in connection with Konovalov's and von Alkemade's rules. As an illustration, Fig. 13.11 presents a three-phase equilibrium in a ternary system with a temperature maximum. A liquid with the composition represented by the point will thus solidify by a sharp transformation. A three-dimensional illustration of the same situation was given in Fig. 10.31.

In many cases of $p = c$, where the composition determinant is zero, all the phases are stoichiometric. The reason may be that their compositions are governed by the valency of the elements. This puts a constraint on the compositions of the phases which is manifested mathematically by the composition determinant being equal to zero. This phenomenon may thus be called stoichiometric constraint. However, Fig. 13.11 demonstrates that it may happen even if the phases are not stoichiometric and we shall thus use the more general term **compositional degeneracy**. We can formulate the following rule: 'A transformation involving $p = c$ phases will be sharp when T or P is varied if there is one compositional degeneracy' and that may be tested with Eq. (13.31). In Section 10.8 we called the corresponding phase equilibrium singular.

In order to evaluate the reaction coefficients in sharp transformations where $p = c$, we can make any convenient assumption regarding the composition of the additional phase because it does not take part in the reaction anyway. If we assume that the additional phase is pure component 1 we obtain

$$\nu^\alpha = \begin{vmatrix} x_1^\beta & x_2^\beta & x_3^\beta & \dots & x_c^\beta \\ x_1^\gamma & x_2^\gamma & x_3^\gamma & \dots & x_c^\gamma \\ \cdot & \cdot & \cdot & \dots & \cdot \\ \cdot & \cdot & \cdot & \dots & \cdot \\ x_1^\varepsilon & x_2^\varepsilon & x_3^\varepsilon & \dots & x_c^\varepsilon \\ 1 & 0 & 0 & 0 & 0 \end{vmatrix} = \begin{vmatrix} x_2^\beta & x_3^\beta & \dots & x_c^\beta \\ x_2^\gamma & x_3^\gamma & \dots & x_c^\gamma \\ \cdot & \cdot & \dots & \cdot \\ \cdot & \cdot & \dots & \cdot \\ x_2^\varepsilon & x_3^\varepsilon & \dots & x_c^\varepsilon \end{vmatrix}, \quad (13.32)$$

$$\nu^\beta = - \begin{vmatrix} x_2^\alpha & x_3^\alpha & \dots & x_c^\alpha \\ x_2^\gamma & x_3^\gamma & \dots & x_c^\gamma \\ \cdot & \cdot & \dots & \cdot \\ \cdot & \cdot & \dots & \cdot \\ x_2^\varepsilon & x_3^\varepsilon & \dots & x_c^\varepsilon \end{vmatrix}, \quad (13.33)$$

etc.

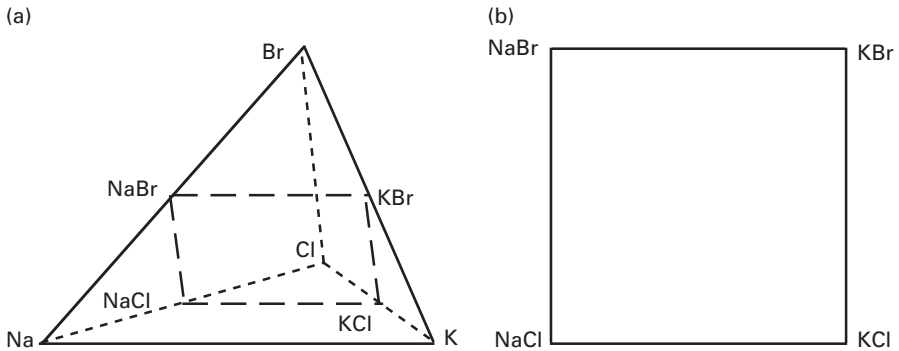


Figure 13.12 The composition space for a quaternary, reciprocal system reduced to a plane due to a stoichiometric constraint, common to all the phases.

The mass balance is satisfied because for each component i from 2 to c we find,

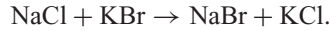
$$\begin{aligned} \sum_j x_i^j v^j &= x_i^\alpha \begin{vmatrix} x_2^\beta & x_3^\gamma & \dots & x_c^\epsilon \end{vmatrix} - x_i^\beta \begin{vmatrix} x_2^\alpha & x_3^\gamma & \dots & x_c^\epsilon \end{vmatrix} + \dots \\ &= \begin{vmatrix} x_i^\alpha & x_2^\beta & x_3^\gamma & \dots & x_c^\epsilon \end{vmatrix} = 0. \end{aligned} \quad (13.34)$$

This is zero because there are two identical columns, since i has a value from 2 to c .

In this example, the first column of elements in the composition matrix dropped out because the additional phase was taken as pure component 1. For a different choice, another column would have dropped out. We may summarize the result of this section as follows: If the composition determinant for a phase transformation with $p = c$ is equal to zero, then it is a sharp transformation and there is a compositional degeneracy. The reaction coefficients can be calculated from the determinants obtained by first omitting any column from the composition matrix and then, in turn, the row corresponding to each phase. In addition, a minus sign must be added for the second, fourth, etc., phase.

Figure 13.11 illustrates a case where a compositional degeneracy occurs only in a particular place in the phase diagram where the phases happen to fall on a line. There is another very important case where the compositions of several phases are subject to a stoichiometric constraint that results in a compositional degeneracy for equilibrium between those phases in an extended portion of the phase diagram. An example is an ionic system where each element has a fixed valency (see Fig. 13.12 which gives the composition space for the Na–K–Cl–Br system). It is evident that all possible mixtures of the ionic phases will fall on a plane inside the three-dimensional space. The phase relations can thus be plotted in a diagram with one dimension less. Such a diagram is called a **quasi-ternary** diagram. In the same way, a ternary system can sometimes be represented with a **quasi-binary** diagram. In practice, one often uses the word quasi-binary to describe an isopleth section of a ternary diagram when many or the most important tie-lines fall in or close to the section even without full stoichiometric constraints. In the present case a composition square can be used and, except for the different outer shape, the diagram would have the same properties as a triangular diagram for a ternary system.

This is often called a **reciprocal system** because the amounts of the four components are not independent but are related by a reciprocal reaction



All ionic phases in a reciprocal system will fall in the composition square and the composition of each phase can only move inside the square. As an example, the liquid phase may cover the whole square at high temperatures and each solid covers a small area close to its corner at low temperatures. However, it should be realized that the chemical system under consideration may contain other phases which are not subject to the same constraint. In the present case there may be metallic phases of Na and K and a gas phase composed mainly of Cl_2 and Br_2 . They fall outside the plane and they can be shown only by the use of the three-dimensional quaternary diagram in Fig. 13.12(a).

The results of this section may be summarized as follows. When there is a compositional degeneracy for the phases taking part in a certain transformation, it is possible to define the compositions of the phases with a new set of components having one member less but at least one of the components in the new set cannot be a member of the initial set. If c still represents the initial number of components, one should modify Gibbs' phase rule to

$$v = c - n_{\text{cd}} + 2 - p, \quad (13.35)$$

where n_{cd} is the number of compositional degeneracies. In the section through the phases, taking part in the transformation, the phase diagram has the properties of a system with $c - n_{\text{cd}}$ components. Normally, it is interesting to calculate such a section only if the degeneracies are caused by stoichiometric constraints. If there are other phases in the system, not subjected to the same stoichiometric constraints, it may be inconvenient to apply a new set of components for the equilibria containing only some of the phases. It may be more convenient to introduce an additional component into the calculation with a compositional constraint. The amount of that component will automatically come out as zero.

Exercise 13.11

Suppose we have a computer program for the calculation of phase equilibria. When trying to calculate the equilibrium temperature for $\text{SiO}_2 + \text{Al}_2\text{SiO}_5 + \text{Al}_2\text{O}_3$ at a pressure of 1 bar we get the message, 'cannot calculate because degrees of freedom not zero'. What action could we take?

Hint

Evidently, the program can only deliver a unique answer and there is a unique temperature for the equilibrium only if it is invariant at the given pressure, i.e., monovariant according to the Gibbs' phase rule. The program may require $p = c + 1$. We should start by checking if our transformation is sharp, although $p = c$. Otherwise, we have a gradual transformation or overlapping transformations and cannot expect to calculate a unique value of T .

Solution

The composition determinant is

$$\begin{array}{c} \text{Si} \quad \text{O} \quad \text{Al} \\ \text{SiO}_2 \\ \text{Al}_2\text{SiO}_5 \\ \text{Al}_2\text{O}_3 \end{array} \left| \begin{array}{ccc} 1 & 2 & 0 \\ 1 & 5 & 2 \\ 0 & 3 & 2 \end{array} \right| = 10 - 4 - 6 = 0.$$

This transformation thus has a compositional degeneracy and is sharp. The reason is that all the c phases fall on the straight line going from SiO_2 to Al_2O_3 . It is thus possible to calculate a unique transformation temperature. Our program seems to need $p = c + 1$ phases. We can solve the problem by introducing a fourth phase in the Al–O–Si system, which is outside the straight line, e.g. pure Al. It will not affect the equilibrium between the initial phases.

Exercise 13.12

We have seen the following. For $p = c + 1$ we get a sharp transformation by gradually changing T , keeping the composition and P constant. For $p = c$ we get a sharp transformation by gradually changing μ for a mobile component, keeping the composition constant except for the mobile component, and keeping P and T constant.

Then we saw that for $p = c$ it may happen that one gets a sharp transformation by gradually changing T and keeping the composition and P constant. Discuss whether it is possible also to get a sharp transformation in a system where $p = c - 1$ by gradually changing μ for a mobile component, keeping the composition constant, except for the mobile component, and keeping P and T constant. If so, what should be the expression for the reaction coefficients, ν^α , etc.

Hint

Accept that equations for the case of a mobile component are obtained by using u_i instead of x_i .

Solution

For $p = c$ we can get a sharp transformation in the ordinary case by gradually changing T if $|x_1^\alpha \quad x_2^\beta \quad \dots \quad x_c^\epsilon| = 0$ for constant P . For $p = c - 1$ we would get a sharp transformation by gradually changing μ_C if $|u_1^\alpha \quad u_2^\beta \quad \dots \quad u_{c-1}^\epsilon| = 0$ for constant P and T .

13.9 Effect of two compositional degeneracies for $p = c - 1$

Let us now consider whether there can be a sharp transformation in a closed system if $p = c - 1$. By comparison with Section 13.8 it may be suggested that we need two

compositional degeneracies in order to get a sharp transformation at constant composition and pressure or temperature. If this is correct, we could treat this case by introducing two additional phases, c and $c + 1$, and then require that their reaction coefficients are both zero. We can try this suggestion by first letting phase c be pure component 1. The requirement for phase $c + 1$ to represent a degeneracy would be

$$\nu^{c+1} = (-1)^c \begin{vmatrix} x_1^\alpha & x_2^\alpha & x_3^\alpha & \cdot & \cdot & x_c^\alpha \\ x_1^\beta & x_2^\beta & x_3^\beta & \cdot & \cdot & x_c^\beta \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ x_1^\varepsilon & x_2^\varepsilon & x_3^\varepsilon & \cdot & \cdot & x_c^\varepsilon \\ 1 & 0 & 0 & 0 & 0 & 0 \end{vmatrix} = (-1)^c \begin{vmatrix} x_2^\alpha & x_3^\alpha & \cdot & \cdot & x_c^\alpha \\ x_2^\beta & x_3^\beta & \cdot & \cdot & x_c^\beta \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ x_2^\varepsilon & x_3^\varepsilon & \cdot & \cdot & x_c^\varepsilon \end{vmatrix} = 0. \quad (13.36)$$

By letting phase $c + 1$ be pure component 2, the requirement for phase c to represent a degeneracy would be

$$\nu^c = (-1)^{c-1} \begin{vmatrix} x_1^\alpha & x_3^\alpha & \cdot & \cdot & x_c^\alpha \\ x_1^\beta & x_3^\beta & \cdot & \cdot & x_c^\beta \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ x_1^\varepsilon & x_3^\varepsilon & \cdot & \cdot & x_c^\varepsilon \end{vmatrix} = 0. \quad (13.37)$$

We have thus found that two compositional degeneracies can be defined for a system, which has a sharp transformation between $c - 1$ phases in a closed system when P or T is varied. In Section 10.9 we called the corresponding equilibrium doubly singular. The conditions of the two compositional degeneracies may be obtained by forming two determinants from the composition matrix by omitting first one column and then another, irrespectively of which ones, and putting to zero the two determinants thus obtained. Such a set of two equations was obtained in Section 8.9 when extrema in both T and P were discussed and it was concluded that they imply that the compositions of the phases fall on the same point for $p = 2$, same line for $p = 3$, etc. The same is true here, of course.

We may also look at the situation from the other side and conclude that there is a sharp transformation at constant composition and pressure in the case $p = c - 1$ if there are two compositional degeneracies. Then we may evaluate the reaction coefficients from the determinants obtained by omitting two columns from the composition matrix and then the row corresponding to each phase, one at a time

$$\nu^\alpha = \begin{vmatrix} x_1^\beta & x_2^\beta & x_3^\beta & \cdot & \cdot & x_c^\beta \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ x_1^\varepsilon & x_2^\varepsilon & x_3^\varepsilon & \cdot & \cdot & x_c^\varepsilon \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \end{vmatrix} = \begin{vmatrix} x_3^\beta & x_4^\beta & \cdot & \cdot & x_c^\beta \\ x_3^\varepsilon & x_4^\varepsilon & \cdot & \cdot & x_c^\varepsilon \end{vmatrix}. \quad (13.38)$$

We may summarize the result of this section as follows: If the composition determinants, obtained in a case of $p = c - 1$ by excluding one column at a time, are equal to zero, one will get a sharp transformation when T or P is varied. The reaction coefficients can be calculated from the determinants obtained by excluding any two columns from the

composition matrix and, in turn, the row corresponding to each phase. In addition, a minus sign must be added for the second, fourth, etc. phase. A sharp transformation at constant composition and constant T or P thus requires that there are $n_{\text{cd}} = c + 1 - p$ composition degeneracies.

We may generalize the above result. A transformation involving p phases in a system with c components will be sharp if the composition determinants, obtained by omitting $c - p$ columns from the composition matrix, are all zero. The reaction coefficients can then be evaluated from the determinants obtained by omitting $c + 1 - p$ columns and then omitting in turn the row corresponding to each phase.

When a chemical reaction involving compounds and species is written in the form $\sum \nu^j J = 0$, it is implied that all the compounds and species with negative ν^j disappear completely by the reaction and all with positive ν^j appear suddenly. This is equivalent to assuming that there is a sharp transformation and the rule for calculating the reaction coefficients, derived here, applies if each compound and species is regarded as a phase.

Exercise 13.13

Suppose we have a computer program for the calculation of phase equilibria. When trying to calculate the equilibrium temperature at 1 bar for the equilibrium between Ca_2SiO_4 , $\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$ and $\text{Ca}_5\text{Mg}(\text{SiO}_4)_3$, we get the message, ‘cannot calculate because degrees of freedom not zero’. What action should one take?

Hint

We would expect an equilibrium temperature if there is a sharp transformation and for a closed system we normally need $p = c + 1$ phases but we have $p = 3$ and $c = 4$, i.e., $p = c - 1$. However, the number of phases will decrease by 1 for each degeneracy. Start by checking for degeneracies.

Solution

The composition matrix is

	Ca	Mg	Si	O
Ca_2SiO_4	2	0	1	4
$\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$	3	1	2	8
$\text{Ca}_5\text{Mg}(\text{SiO}_4)_3$	5	1	3	12

By omitting one column at a time we find

$$\begin{vmatrix} 0 & 1 & 4 \\ 1 & 2 & 8 \\ 1 & 3 & 12 \end{vmatrix} = 0 \text{ and } \begin{vmatrix} 2 & 1 & 4 \\ 3 & 2 & 8 \\ 5 & 3 & 12 \end{vmatrix} = 0.$$

We may conclude that there are two compositional degeneracies and the transformation is sharp when T is varied for any chosen value of P . In fact, the determinants obtained by omitting any of the other columns are also zero. The solution to the computational problem would be to add two new phases, e.g., O and Mg.

14 Partitionless transformations

14.1 Deviation from local equilibrium

As discussed in Section 7.8 it is common to assume that the rate of a phase transformation in an alloy is controlled by the rate of diffusion. The local compositions at the phase interfaces are then used as boundary conditions for the diffusion problem and they are evaluated by assuming local equilibrium at the interfaces. That is a very useful approximation but there are important exceptions. It is necessary to realize that the exceptions are of two different types and they have opposite effects. The first type of exception is caused by a limited mobility of the interface. In order to keep pace with the diffusion, the interface requires a driving force which is subtracted from the total driving force and decreases the driving force for the diffusion process. Due to this effect, a partitionless transformation, which would otherwise be completely diffusion-controlled but rapid due to a very short diffusion distance, requires an increased supersaturation of the parent phase, as shown in Section 7.8. Formally, this case was treated by assuming a pressure difference between the two phases as if the interface were curved more than it actually is, and the local equilibrium assumption was modified to this case.

The other type of exception will instead decrease the driving force needed by decreasing the need for diffusion and will thus result in a higher rate of transformation and make it possible for an alloy with a lower supersaturation to transform. It is primarily caused by a low atomic mobility in the migrating interface. The present chapter will discuss such cases but also related cases of full local equilibrium. Naturally, such phenomena cannot be described by assuming local equilibrium under a pressure difference which would increase the driving force needed. Instead, the local equilibrium seems to be constrained in some way. Sometimes one talks about partial equilibrium or deviation from local equilibrium.

In general, the rate of migration of an interface during a phase transformation is limited by the mobility of the interface itself and by the transport of various extensive quantities, i.e., contents of various components by diffusion, enthalpy by heat conduction and volume by elastic and plastic flow. We shall not consider the latter problem but presume that there is some efficient mechanism for the accommodation of changes in volume. However, there are many interesting thermodynamic features that could have been discussed. In general, we shall also neglect the need for heat conduction and assume that isothermal conditions can be maintained in spite of the heat of transformation. We

shall start with that problem because it has much in common with diffusion and may be used to demonstrate important principles.

14.2 Adiabatic phase transformation

For a process taking place under adiabatic and isobaric conditions, $dQ = 0$ and $dP = 0$, we have from the first law

$$dH = d(U + PV) = dU + PdV + VdP = dQ + VdP = 0. \quad (14.1)$$

For a system which is closed to exchange of matter as well as heat we also have $dN_i = 0$ and it is convenient to use the combined law in the following form obtained from Eqs (14.1) and a generalized form of Eq. (1.72)

$$T \cdot d_{ip}S = TdS + VdP + \sum \mu_i dN_i - dH = TdS. \quad (14.2)$$

It should be emphasized that here we have not represented $T \cdot d_{ip}S$ with the driving force $Dd\xi$ because the reaction is not isothermal. The condition for a reversible reaction is $d_{ip}S = 0$ and thus $dS = 0$. In order for the reaction to proceed with a measurable rate it is necessary that $d_{ip}S > 0$ and thus $dS > 0$.

A homogeneous reaction (e.g. a spontaneous reaction between molecules in a gas) occurs gradually in the whole system and one can usually presume that it has proceeded to the same extent ξ in all parts of the system. It is evident that such a reaction can occur under adiabatic and isobaric conditions. The situation is different for a heterogeneous reaction which takes place by nucleation and growth. Let us examine the simple case of a sharp phase transformation which goes to completion instantaneously at any point as an interface passes by. The extent of reaction can be measured as the fraction of the system which has undergone the transformation. Thus, ξ would go from 0 to 1. Alternatively, ξ can be given as the number of atoms in the transformed part. Let us suppose that this reaction can occur under adiabatic conditions. Due to the heat of transformation, this should mean that the transformed part of the system is at a different temperature than the rest and heat would thus flow between the different parts unless the transformation is extremely rapid and leaves no time for the flow of heat. Such high transformation rates are not very common. An explosion may come close. We may thus conclude that the transformation in a material cannot normally be truly adiabatic even if it occurs inside a thermally insulated system. Before considering the effect of the heat transfer we shall nevertheless examine the conditions for a hypothetical transformation which is truly adiabatic. Since we realize that the transformation will cause a change of temperature we must start by defining the thermal properties.

Let us consider a unary system with two phases, α and β , and let us suppose that the difference in their heat capacities, ΔC_p , is independent of temperature. Then the differences in molar enthalpy ΔH_m and in entropy ΔS_m at any temperature are independent of temperature but may vary with pressure. The equilibrium temperature at a given pressure will be $T^e = \Delta H_m / \Delta S_m$. Schematic T, P and H_m, P phase diagrams are given in Fig. 14.1. The boundary between α and $\alpha + \beta$ is denoted α/β because it represents α in equilibrium

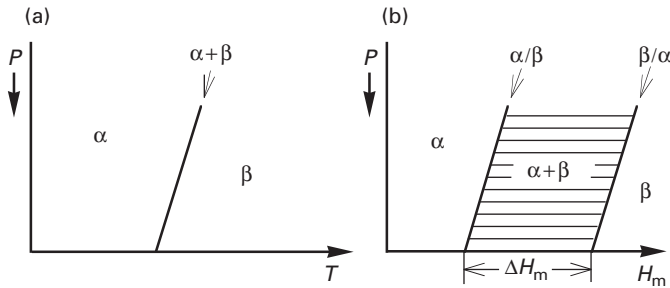


Figure 14.1 Ordinary phase diagram for a unary system.

with β . We have here taken β as the high-temperature phase and it is evident from the H_m, P diagram that $\Delta H_m = H_m^\beta - H_m^\alpha$ is positive and then $\Delta S_m = S_m^\beta - S_m^\alpha$ must also be positive because T^e is positive.

On the other hand, if the two phases are at different temperatures we get

$$\Delta H = \Delta H_m + C_P(T^\beta - T^\alpha) \quad (14.3)$$

$$\Delta S = \Delta S_m + C_P \ln(T^\beta / T^\alpha). \quad (14.4)$$

Suppose it were possible to transform β of T^β to α of T^α under adiabatic and reversible conditions, i.e. under isentropic conditions, $\Delta S = 0$. If the pressure is also kept constant, then $\Delta H = 0$ and we have two equations from which we can evaluate T^α and T^β ,

$$T^\beta = T^e \cdot \frac{\Delta S_m / C_P}{\exp(\Delta S_m / C_P) - 1} \cong T^e - \Delta H_m / 2C_P \quad (14.5)$$

$$T^\alpha = T^e \cdot \frac{\Delta S_m / C_P}{1 - \exp(-\Delta S_m / C_P)} \cong T^e + \Delta H_m / 2C_P, \quad (14.6)$$

where the approximation is justified for $\Delta S_m \ll C_P$, only. These results are plotted in two new diagrams, see Fig. 14.2. In this case there is only one line in the P, H_m diagram and it shows where α and β have equal values of H_m and also equal values of S_m . This results in the α and β one-phase fields overlapping in the T, P diagram. The interpretation is that, on cooling under these conditions, a β phase would not transform to α of the same temperature when cooled to the equilibrium temperature T^e , but it would transform at $T^\beta = T^e - \Delta H_m / 2C_P$ and the α phase would be at a higher temperature $T^\alpha = T^e + \Delta H_m / 2C_P$ when it forms. The two-phase boundaries in the T, P diagram have thus separated by $T^\alpha - T^\beta = \Delta H_m / C_P$. This diagram would predict that β , if super-cooled to reach the $(\alpha + \beta)_H$ line, could transform instantaneously and completely to α if there were no kinetic obstacles. It would be a sharp transformation at the constant H_m value. It has been speculated that this kind of reaction could occur in solidification of very rapidly cooled liquid droplets.

However, there are two major objections. First, the reaction must be extremely fast in order to prevent heat flowing from the warmer, growing α into the colder parent β , $T^\alpha - T^\beta$ being positive (equal to $\Delta H_m / C_P$). Secondly, even if α of the temperature T^α

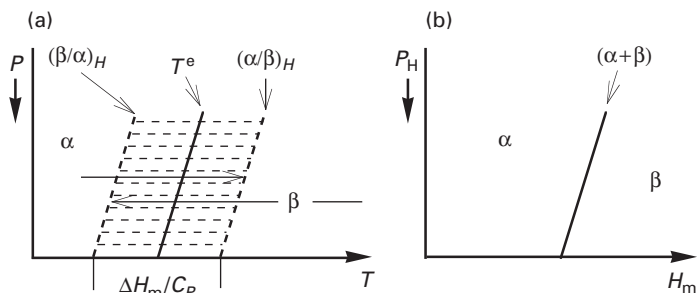


Figure 14.2 Phase diagram for isobaric and adiabatic conditions in a unary system. Notice that the α and β one-phase fields in the P, T diagram overlap in a region around the equilibrium temperature.

could form, it would not be stable because it is inside the stable one-phase field for β according to the T, P diagram in Fig. 14.1. Part of α could thus transform back to β . In the next section we shall examine a more realistic model.

Exercise 14.1

Estimate the internal entropy production when 1 mole of a pure substance transforms adiabatically from α to β when the temperature of α is ΔT above the value where there is no entropy production.

Hint

Of the two conditions used in the text, only one holds here, $\Delta H = 0$, but $\Delta_{ip}S$ is still equal to ΔS and can be calculated from $\Delta S_m + C_P \ln(T^\beta / T^\alpha)$, if C_P is constant and equal in the two phases.

Solution

$$T^\alpha = T^e + \Delta H_m / 2C_P + \Delta T = T^e + T^e \Delta S_m / 2C_P + \Delta T.$$

$$\begin{aligned} \text{From } 0 = \Delta H = \Delta H_m + C_P(T^\beta - T^\alpha) = T^e \Delta S_m + C_P(T^\beta - T^\alpha) \text{ we get } T^\beta &= \\ T^\alpha - T^e \Delta S_m / C_P = T^e - T^e \Delta S_m / 2C_P + \Delta T; \quad \Delta_{ip}S = \Delta S_m - C_P \ln(T^\beta / T^\alpha) &= \\ \Delta S_m - C_P \ln\left\{ [1 - T^e(\Delta S_m / 2C_P) / (T^e + \Delta T)] / [1 - T^e(\Delta S_m / 2C_P) / (T^e + \Delta T)] \right\} &\cong \\ \Delta S_m - C_P T^e (\Delta S_m / C_P) (T^e + \Delta T) &\cong \Delta S_m \Delta T / T^e. \end{aligned}$$

14.3 Quasi-adiabatic phase transformation

Let us now examine if there are conditions under which the transformation can occur by a steady-state process, i.e. without a gradual change of the conditions at the migrating

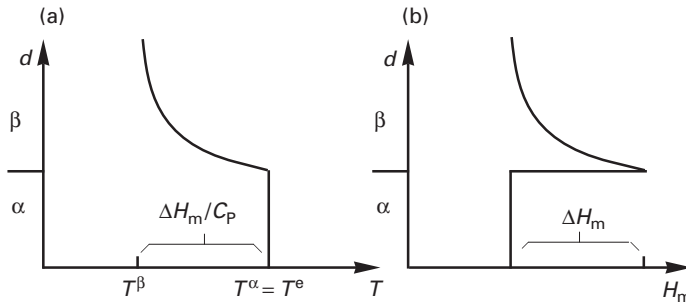


Figure 14.3 Steady-state conditions for a quasi-adiabatic $\beta \rightarrow \alpha$ transformation under constant P . The growing α has the same enthalpy as the initial β .

interface. The growing α should then have a uniform temperature, T^α , but the temperature may vary inside the parent β . The temperature profile can be illustrated by Fig. 14.3(a) which has been drawn under the assumption of local equilibrium at the interface. All of the α phase must be at the equilibrium temperature, T^e . In order for this to be a steady-state process it is necessary that α has the same enthalpy as the bulk of the β phase. This is illustrated in Fig. 14.3(b) and the following equations are obtained if the heat capacity can be approximated as constant and the same in both phases.

$$\Delta H = \Delta H_m + C_P(T^\beta - T^\alpha) = 0 \quad (14.7)$$

$$T^\beta = T^\alpha - \Delta H_m / C_P = T^e - \Delta H_m / C_P. \quad (14.8)$$

The reaction can thus be essentially adiabatic if it is possible to change the temperature of the whole β system to $T^e - \Delta H_m / C_P$ before the nucleation of α occurs. This model thus requires twice as large a ΔT as the truly adiabatic model. This is a demonstration of the fact that a deviation from local equilibrium results in less need of driving force. After a transient period, during which an enthalpy spike of height ΔH_m will develop in the β phase at the migrating interface, steady-state conditions will be established and then maintained towards the end of the reaction. The duration of the transient period and the width of the temperature spike in the parent phase will depend upon the rate of transformation and the rate of heat flow. We can use the phase diagrams, given below, for a summary of our conclusions (see Fig. 14.4).

Point 1 in Fig. 14.4 is the isothermal transformation temperature for β . A β phase cooled just below that point could start to transform to α but the progress of the transformation would be directly controlled by the further extraction of heat from the system. The growing α phase will be at point 2. If a β phase could be cooled to point 3 before the transformation starts, then the transformation could, in principle, occur very quickly and adiabatically and the α phase would be at point 4. However, if the phase interface does not move with an extremely high velocity, there will be heat conduction into the remaining β phase and it will no longer be able to transform adiabatically but would depend upon further heat extraction. Finally, if a β phase could be cooled to point 5 before the transformation starts, then the transformation could occur without any further heat extraction even if there is time for heat conduction. All of the α formed would be

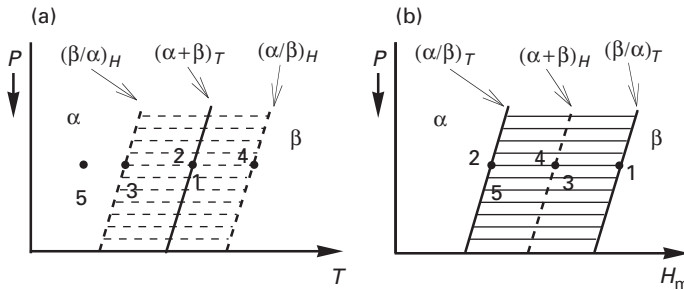


Figure 14.4 Phase diagram illustrating the conditions for a quasi-adiabatic transformation in a unary system. Subscript T indicates isothermal conditions. Subscript H indicates adiabatic conditions because P is kept constant.

at point 2 and β at the interface would be at point 1. The transformation could occur in a steady-state fashion where the growing α phase forms at T^e . The initial β is at a lower temperature (compare point 2 in the P, T phase diagram with point 5) but has the same enthalpy (compare point 2 in the P, H_m phase diagram with point 5). This type of reaction could be called a quasi-adiabatic transformation. It is interesting to note that it occurs when the parent phase, by cooling, is entering into the field for the new phase in the P, H_m diagram.

It is usually assumed that a transformation starts from a stationary nucleus and picks up speed during an initial transient period. It would then be natural to expect a situation somewhat similar to Fig. 14.3 to be established after some short time. It is an interesting question whether it could later develop into a truly adiabatic mechanism. The requirement would be that the speed becomes so fast that the temperature spike in the parent phase becomes so thin that it disappears between the atoms. A simple calculation would show that the thickness should be less than about \mathcal{D}/ν , where \mathcal{D} is the diffusion coefficient of heat and ν is the growth rate. This transition turns out to be very unlikely.

Exercise 14.2

Figure 14.5 gives the relations between S_m and H_m for bcc and liquid W. The melting point is marked with an asterisk for each phase. Evaluate the change of entropy during quasi-adiabatic melting and solidification.

Hint

The growing phase must be stable in contact with the parent phase at the interface, i.e., it must grow at the melting temperature. The bulk of the parent phase must be at a different temperature in order to have the same enthalpy as the growing phase.

Solution

The melting point on the liquid curve (the asterisk) represents the growing liquid and the bulk of the parent bcc is situated exactly below it. The change of entropy can be read

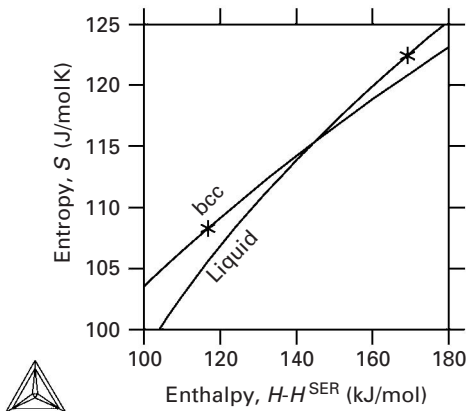


Figure 14.5 See Exercise 14.2.

as $+1.5 \text{ J/mol, K}$ and for solidification as $+2.8 \text{ J/mol, K}$. In both cases the entropy is produced in the thermal spike in front of the interface.

Exercise 14.3

Estimate how fast a transformation should be in order to reach truly adiabatic conditions.

Hint

The diffusion coefficient D for heat conduction is about $10^{-5} \text{ m}^2/\text{s}$. The atomic distances are about 10^{-10} m .

Solution

$D/v < 10^{-8}$ yields $v > 10^{-5}/10^{-10} = 10^5 \text{ m/s}$. This is higher than the speed of sound.

14.4 Partitionless transformations in binary system

We shall now examine a partitionless transformation, i.e., a transformation where the components do not partition between the parent phase and the product, and we shall find striking similarities with the adiabatic case. We shall use the combined law from Eq. (3.27) because temperature and pressure will be kept constant in addition to composition.

$$Dd\xi = -SdT + VdP + \sum \mu_i dN_i - dG = -dG. \quad (14.9)$$

In this case G plays the same role as S from Eq. (14.2) under adiabatic conditions. The driving force for the reaction is $D = -dG/d\xi$ and for $D = 0$ we would have a reversible reaction which would occur without a change of the Gibbs energy but infinitely slowly. The reaction could proceed with a measurable rate if $D > 0$, i.e. $dG < 0$. Partitionless

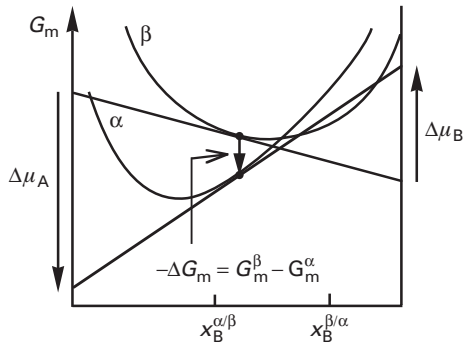


Figure 14.6 Conditions for a true diffusionless transformation.

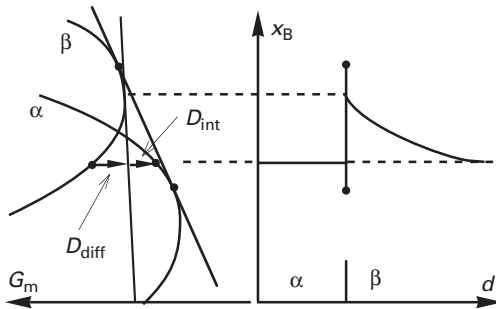


Figure 14.7 Crude model for deviation from local equilibrium under a quasi-diffusionless transformation.

transformations were discussed in Section 7.8. We shall now examine such a reaction in more detail and discuss two limiting cases depending on whether any diffusion is involved. In principle, it could be completely **diffusionless**, a case that is illustrated in Fig. 14.6. However, there could also be some diffusion, e.g. in a thin pile-up of a component which is pushed forward in front of the advancing interface. It is illustrated in Fig. 14.7 and resembles the quasi-adiabatic case in Fig. 14.3 and may be regarded as **quasi-diffusionless**. Both cases are illustrated in Fig. 14.8 which can be compared with Fig. 14.4 for the adiabatic cases. The dashed line in the T, x_B diagram, denoted by T_0 , corresponds to the dashed line in the P, H_m diagram, which showed where α and β have equal values of H_m . On the T_0 line, α and β have equal values of x_B and equal values of G_m , i.e., a true diffusionless transformation. The other limiting case is found when there is full local equilibrium at the migrating interface, according to the full lines in Fig. 14.8(b), similar to the quasi-adiabatic case in Fig. 14.4(b). It is the limiting case of a quasi-diffusionless transformation and could be called local-equilibrium partitionless transformation or simply **LE-partitionless** transformation. It was discussed in Section 7.8 and illustrated in Fig. 7.21.

The true diffusionless transformation is easy to understand. If a β alloy is cooled below the T_0 line, where α of the same composition has the same G_m value, then G_m may

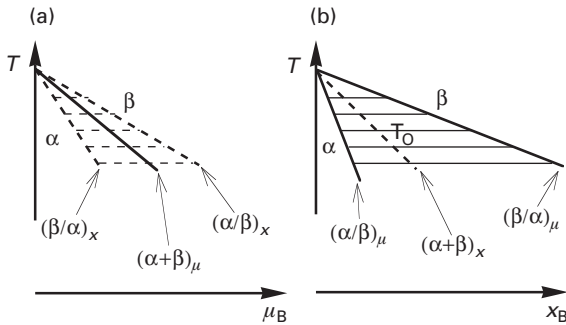


Figure 14.8 Phase diagram for a binary system illustrating the conditions for diffusionless and LE-partitionless transformations. The full lines show the phase boundaries under equilibrium (constant T , P and μ_i). The dashed lines hold if there is no diffusion.

decrease by the $\beta \rightarrow \alpha$ transformation even without any change of the composition. The molar Gibbs energy diagram in Fig. 14.6 demonstrates that μ_B will increase by that transformation, which corresponds to the increase of T during the true adiabatic transformation.

In practice, it is seldom possible to avoid diffusion completely. It would be necessary that the mathematical width of the pile-up in Fig. 14.7 is below atomic dimensions. The growth rate should be of the order of \mathcal{D}/d or higher. \mathcal{D} is the diffusion coefficient and d is about 10^{-10} m. Otherwise, the transformation could not be regarded as diffusionless. On the other hand, at diffusion-controlled transformations the growth rate may often be low enough to make the LE-partitionless transformation a reasonably good approximation. Figure 14.7 demonstrates a more general case where there is some deviation from local equilibrium at the interface and the compositions at the interface do not fall on the points of tangency for the common tangent.

In metallic materials there are two well-known partitionless transformations called ‘martensitic’ and ‘massive’. The martensitic transformation is usually very rapid and comes close to the true diffusionless case but its interface migrates with an atomic mechanism that creates strong stresses which require a high driving force. This type of transformation can very well occur far inside the $\alpha + \beta$ two-phase field but only at a considerable distance below the T_0 line due to the necessity of a driving force. The massive transformation is rapid but not extremely rapid. There may be time for individual atoms to diffuse across the interface and maybe even for a pile-up to form. This transformation may thus fall well between the two limiting cases.

An interesting problem may be mentioned in this connection. Figure 14.6 demonstrates that the chemical potential of B increases as it crosses the interface and moves from β to α . One should ask what forces the B atoms to move against their driving force. In the LE-partitionless transformation the problem is solved by the presence of the pile-up. As it moves in front of the migrating interface, it gradually lifts the B atoms to higher potential as illustrated in Fig. 14.7. For the martensitic transformation the explanation must be that all atoms cross the interface with some kind of a cooperative mechanism. For a rapid massive transformation there may not be a sufficiently well developed pile-up

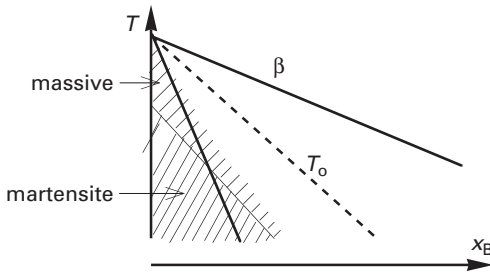


Figure 14.9 Solution to Exercise 14.4.

and the mechanism of transfer of atoms across the interface must be partly cooperative. This will be further discussed in Chapters 16 and 17.

Exercise 14.4

Given the phase diagram in Fig. 14.6, mark the regions where one could expect the massive or the martensitic transformations $\beta \rightarrow \alpha$. Suppose that the martensitic transformation requires an undercooling below T_0 which is independent of the composition and that the massive transformation occurs with some small deviation from equilibrium.

Hint

Martensite will normally grow much faster because it requires no diffusion. Martensite would thus predominate in a region where both types of transformation could occur, in principle.

Solution

The solution is given in Fig. 14.9.

14.5 Partial chemical equilibrium

In a ternary alloy it could very well happen that one of the elements diffuses very much faster than the other two, for example if it is an interstitial solute. It is then possible that a new phase forms with a different content of the mobile element but without a change of the relative contents of the other two. Such a transformation would be partly partitionless. Hultgren [26] proposed that it could even occur without any diffusion of the latter two elements and used the term **paraequilibrium** to describe the local equilibrium at the phase interface under such a transformation. We shall now examine that kind of local equilibrium. Hultgren studied systems with Fe, C and a metallic solute which we shall denote by M. We shall keep those symbols but Fe could represent any element, C any mobile element and M any element as sluggish as Fe.

Under full local equilibrium at a phase interface, there is no driving force on the interface as shown by the following form of the combined law Eq. (3.33),

$$Dd\xi = -SdT + VdP - \sum N_i d\mu_i = 0, \quad (14.10)$$

because T , P and all μ_i have the same values on both sides of the interface. When a transformation occurs under paraequilibrium, μ_C has the same value on both sides because C is very mobile, but μ_{Fe} and μ_M have different values. Instead, u_{Fe} and u_M have the same values if u_i is defined as $N_i/(N_{Fe} + N_M)$. It is thus useful to consider the combined law in a new form which can be derived as follows,

$$Dd\xi = -SdT + VdP - \sum N_i d\mu_i \quad (14.11)$$

$$\begin{aligned} Dd\xi/(N_{Fe} + N_M) &= -S_{m12}dT + V_{m12}dP - \sum u_i d\mu_i \pm (\mu_{Fe}du_{Fe} + \mu_M du_M) \\ &= -S_{m12}dT + V_{m12}dP - \sum u_C d\mu_C + \mu_{Fe}du_{Fe} + \mu_M du_M - d(u_{Fe}\mu_{Fe} + u_M\mu_M). \end{aligned} \quad (14.12)$$

The subscript 'm12' is explained in Section 4.3. Under paraequilibrium $dT = dP = d\mu_C = du_{Fe} = du_M = 0$ and we find

$$Dd\xi/(N_{Fe} + N_M) = -d(u_{Fe}\mu_{Fe} + u_M\mu_M) = 0. \quad (14.13)$$

The driving force has here been put to zero for a transformation occurring under paraequilibrium conditions because, ideally, paraequilibrium is supposed to be a kind of local equilibrium. It is thus necessary that $u_{Fe}\mu_{Fe} + u_M\mu_M$ has the same value on both sides of the interface. Of course, T , P and μ_C must also have the same values on both sides. The new quantity that must have the same value in both phases is simply an average value for Fe and M, as if they together have formed a new element. The quantity can be written in various ways because $G_{m12} = \sum u_i \mu_i$,

$$u_{Fe}\mu_{Fe} + u_M\mu_M = G_{m12} - u_C\mu_C = \frac{G_m - x_C\mu_C}{1 - x_C}. \quad (14.14)$$

Suppose the three elements can form a compound θ of the formula $(Fe, M)_a C_c$ with $a + c = 1$. For paraequilibrium between θ and a solution phase, γ , we find

$$\left(\frac{G_m - c\mu_C}{a}\right)^\theta = \left(\frac{G_m - x_C\mu_C}{1 - x_C}\right)^\gamma. \quad (14.15)$$

It should be noted that $u_{Fe}\mu_{Fe} + u_M\mu_M$ is a characteristic state function. It was actually derived in Section 13.6 in a slightly different way and written as $G - N_C\mu_C$.

In a molar Gibbs energy diagram the tie-line between the two phases in paraequilibrium is directed towards the C corner. It falls on a common tangent line to the two Gibbs energy surfaces but not on the common tangent plane. Figure 14.10 demonstrates that the common tangent line for paraequilibrium, which must go through the C axis, is situated above the common tangent plane that holds for full equilibrium. The chemical potential of C will thus be slightly different.

Figure 14.11(a)–(d) gives various versions of the phase diagram showing the equilibrium between two solution phases, α and γ , at some convenient T and P values. Instead of using the chemical potentials, μ_C and μ_M , as axes the chemical activities, a_C and a_M , have been used in order to make the diagram show low contents of C and M where the chemical potentials would approach negative infinity. It is interesting to note that

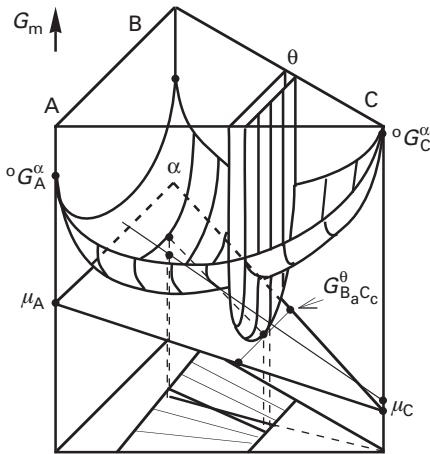


Figure 14.10 Molar Gibbs energy diagram for a ternary system illustrating the paraequilibrium conditions. The common tangent line from the C axis is situated above the common tangent plane.

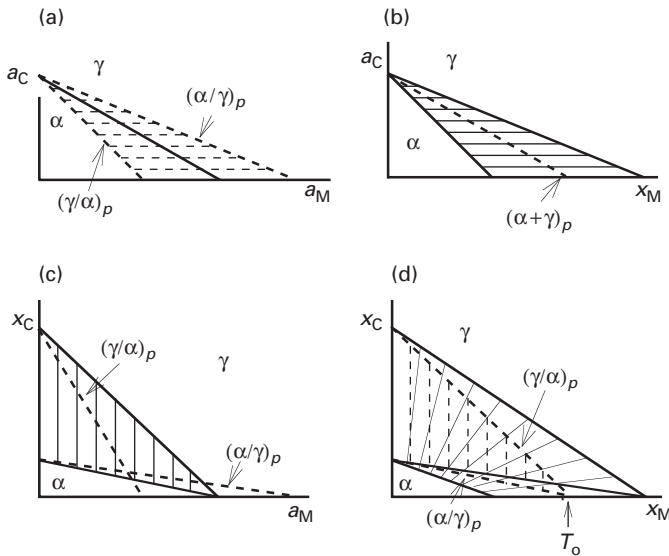


Figure 14.11 The phase diagram for a ternary system at constant T and P , drawn with different sets of axes in order to illustrate the paraequilibrium conditions (dashed lines), assuming that C is the only mobile component.

Figs 14.11(a) and (b) are very similar to Fig. 14.6 but T has been replaced by a_C . In fact, the two reactions are very similar because the additional component in the present case is compensated by the temperature being kept constant.

The point of equal Gibbs energy of α and γ on the binary Fe–M side has been marked as T_o in Fig. 14.11(d) because it belongs to the T_o line in the binary T, x_M diagram. It is important to note that the two paraequilibrium phase boundaries fall inside the full equilibrium two-phase field. This is a general rule.

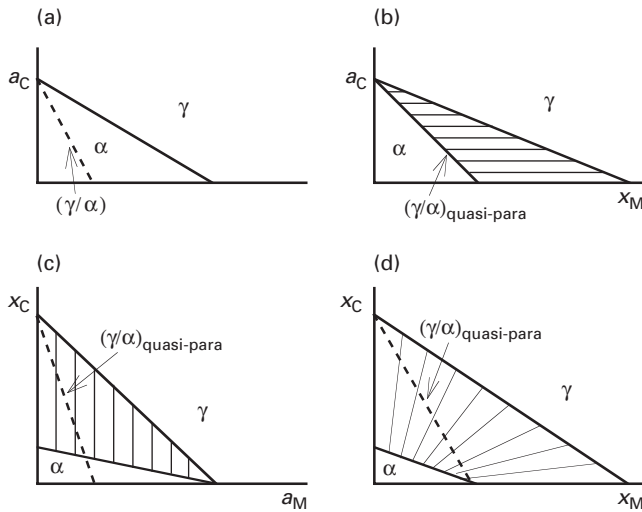


Figure 14.12 Dashed lines show the conditions for quasi-paratransformation $\gamma \rightarrow \alpha$ in a ternary system with a very mobile component C.

As in the binary case, discussed in the preceding section, we should also examine the possibility of obtaining a partitionless (here of Fe and M) transformation under full local equilibrium. That should be possible if there is a composition spike in front of the migrating interface. The critical limit for a $\gamma \rightarrow \alpha$ transformation to take place under such **quasi-paraequilibrium** conditions is that the initial γ phase falls on the α phase boundary in the a_C, x_M phase diagram (see Fig. 14.12(b)). Again the conclusions are very similar to the previous case. However, in the present case it is more common to use an x_C, x_M phase diagram (see Fig. 14.12(d)). It should be noticed that the critical limit for a quasi-paratransformation will not fall on the α phase boundary in such a diagram because γ and α must have the same μ_C (i.e. a_C) and that requires different x_C .

Finally, we may compare the critical limit for the two partitionless kinds of growth by means of Fig. 14.13. It is interesting to note that paraequilibrium with its deviation from full local equilibrium requires less supersaturation of the parent γ . This is in agreement with a more general principle mentioned in Section 14.1. In practice, one should expect something between quasi-paraequilibrium and paraequilibrium depending on the mobilities of Fe and M, especially inside the interface, relative to the rate of migration of the interface. In the next section we shall give a more detailed account of some phase transformations assuming that they take place under quasi-paraequilibrium.

Exercise 14.5

In Fig. 14.11 there are two diagrams with dashed tie-lines. They hold for paraequilibrium. In the other two diagrams the corresponding tie-lines have not been drawn. Indicate where they should fall.

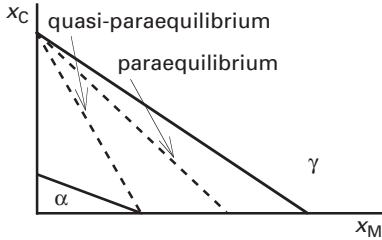


Figure 14.13 Comparison of two partitionless growth conditions for the $\gamma \rightarrow \alpha$ transformation in a ternary system with a very mobile component C.

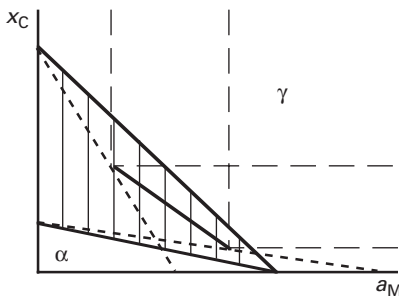


Figure 14.14 Solution to Exercise 14.5.

Hint

Find tie-lines in Fig. 14.11(c) by projection from Fig. 14.11(a) and (d).

Solution

The $\alpha + \gamma$ two-phase field under paraequilibrium is a line in Fig. 14.11(b) and there are no tie-lines. A tie-line in Fig. 14.11(c) is shown in Fig. 14.14.

14.6 Transformations in steel under quasi-paraequilibrium

In a steel with carbon and some substitutional alloying elements it often happens that a new phase forms with the same alloy content as the parent phase but with a different carbon content. Such a phase transformation may occur under local paraequilibrium at the migrating interface, or under quasi-paraequilibrium, or in between. In this section we shall examine the quasi-paraequilibrium case, using results from the preceding section. As a simple example we shall first discuss the $\gamma \rightarrow \alpha$ transformation. In a u_M, u_C phase diagram all products of a paratransformation or a quasi-paratransformation will fall on the same horizontal line as the parent phase. In the phase diagram we can easily find a point representing the composition of a growing phase, because it must fall on the correct level of alloy content but also on the appropriate phase boundary, the α/γ phase

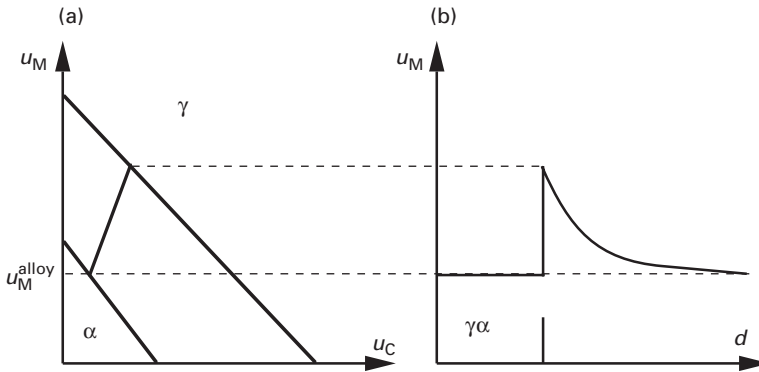


Figure 14.15 Construction yielding the conditions at the phase interface for a quasi-paratransformation $\gamma \rightarrow \alpha$ in a ternary system with a mobile component C.

boundary in the present case. Having located that intersection we have found a tie-line representing the local equilibrium conditions at the migrating α/γ interface. We can thus construct a composition profile for the alloying element. In order to do this we shall plot u_M on the ordinate axis (see Fig. 14.15).

From the composition profile we may conclude that there is a thin spike of the alloying element in front of the migrating interface. This is similar to the quasi-diffusionless case in a binary alloy. According to the mathematics of diffusion, we can estimate the width of the spike to \mathcal{D}_M/ν , where ν is the rate of migration of the interface and \mathcal{D}_M is the diffusion coefficient of the alloying element M relative to Fe. The width is usually extremely small and the alloy content in the spike originates from a transient stage of growth at a very early time.

One may normally expect that the rate is governed by the rate of long-range diffusion of carbon. In order for the transformation to proceed, carbon must diffuse from the α/γ interface and into the interior of the γ phase because the growing α phase has less carbon than γ . It is thus necessary that the carbon potential is higher at the interface than in the interior of the γ phase. The critical limit for the position of the initial γ phase is thus found on the intersection of the level of alloy content, u_M^{alloy} , and the isoactivity line for carbon in γ which goes through the γ end-point of the tie-line. This construction is shown in Fig. 14.16. Naturally, this isoactivity line must be extrapolated below the $\gamma/(\alpha + \gamma)$ boundary. The critical limit is represented by a circle in the diagrams and falls on the line for quasi-paraequilibrium in Fig. 14.13. The rapid, quasi-paratransformation can only occur on the left-hand side of that critical line, i.e. in this case below the line.

Suppose the carbon activity for a γ phase is initially lower than for the isoactivity line in Fig. 14.16. The $\gamma \rightarrow \alpha$ transformation can then start in the way described above. However, during the growth of α , the γ phase will accumulate more and more carbon. Its carbon activity will increase and eventually reach the value for the isoactivity line in Fig. 14.16. The rapid growth will then stop and the transformation can only continue at a much slower rate which permits the sluggish alloying element M to be redistributed

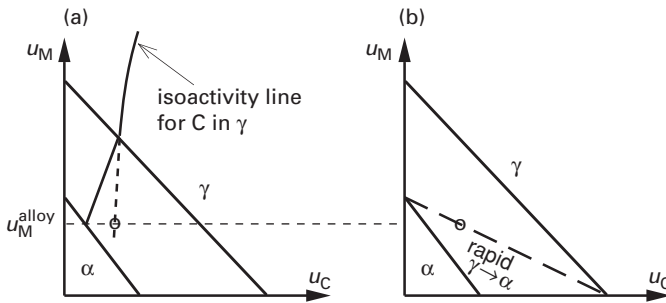


Figure 14.16 Construction yielding the critical limit for a quasi-paratransformation $\gamma \rightarrow \alpha$ in a ternary alloy with a mobile component C.

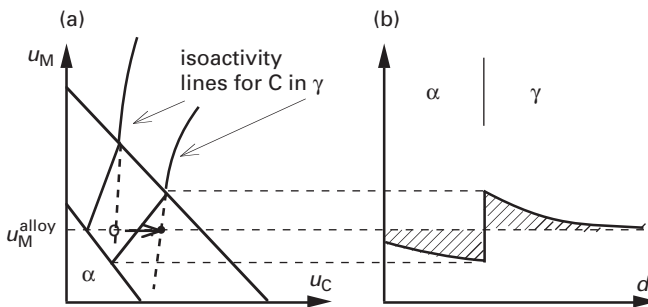


Figure 14.17 Growth conditions of α from γ at a stage where diffusion of the sluggish alloying element M is required.

relative to Fe. During this stage of slow growth there will be sufficient time for the mobile carbon to equilibrate inside the system and at each moment all the γ phase present may fall practically on a common isoactivity line for carbon in γ . If we know the momentary composition of the interior of the γ phase we can easily find the γ end-point of a tie-line representing the equilibrium conditions on the migrating α/γ interface. We can thus construct the composition profile for the alloying element M during any stage of very slow growth; see Fig. 14.17 in which the filled circle represents the present composition of the interior of the γ phase and the arrow indicates that its carbon content is gradually increasing during this growth. In the composition profile the spike has now widened to a considerable thickness, which may be evaluated by using the fact that the two shaded areas represent the same amount of M. The rate of growth is now governed by diffusion of the alloying element down the spike.

Let us now examine the more complicated case where the γ phase transforms to the eutectoid mixture of α and cementite, $(\text{Fe},\text{M})_3\text{C}$, which is called pearlite. In order for that reaction to be governed by the rate of carbon diffusion it is necessary for both α and cementite to inherit the alloy content of the parent γ . Each one of the two growing phases must fall on the correct side of its critical line. We shall first illustrate this by two separate phase diagrams in Fig. 14.18(a) showing the α/γ equilibrium and (b) showing the

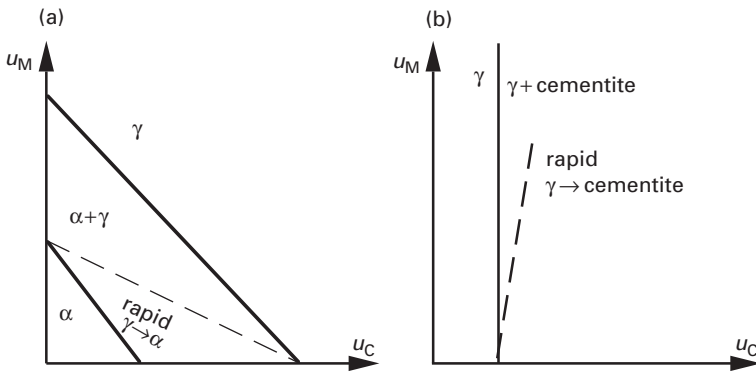


Figure 14.18 The critical limit for the quasi-paratransformation of γ to (a) α ; and (b) cementite in an Fe–M–C alloy.

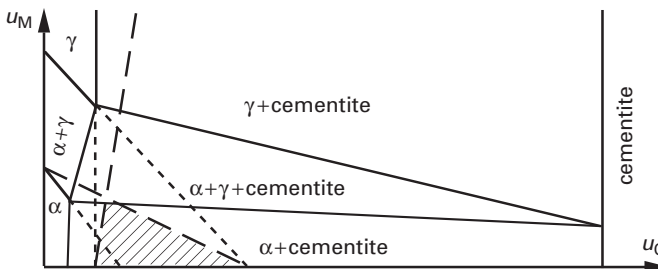


Figure 14.19 Phase diagram for an Fe–M–C system, illustrating the conditions for a rapid formation of α + cementite (so-called pearlite) under quasi-paraequilibrium (see shaded triangle).

γ /cementite equilibrium. The position of the region for rapid precipitation of cementite, relative to the full equilibrium phase boundary, has been drawn in agreement with the general rule that the paraequilibrium phase boundaries lie inside the full equilibrium two-phase field.

If the alloy is at a temperature where the $\gamma \rightarrow \alpha$ + cementite transformation is possible, the two two-phase regions $\alpha + \gamma$ and $\gamma + \text{cementite}$ must overlap to some degree and there must be a three-phase $\alpha + \gamma + \text{cementite}$ region, as illustrated in Fig. 14.19.

This phase diagram resembles the Fe–Ni–C phase diagram because Ni prefers to dissolve in γ rather than in α or cementite. The metastable parts of the phase boundaries have been drawn with dotted lines. The two critical lines form a small triangular region which we may regard as a critical triangle. Rapidly growing quasi-parapearlite can be expected to form from a γ phase situated inside the critical triangle. A γ phase situated to the left of the triangle should first precipitate so-called proeutectoid α and thus move into the triangle where pearlite can start forming. A γ phase situated to the right of the triangle should first precipitate proeutectoid cementite and then pearlite. However, a requirement is that the level of alloy content falls below the top of the triangle. Otherwise,

the rapid, proeutectoid precipitation will stop at its critical line. The transformation can continue only by the slow rate of diffusion of the alloying element into the interior of the austenite because both α and cementite must dispose of nickel into the parent γ . That should normally be a very slow reaction and pearlite formed under such conditions has not been reported. In solidification, the growth conditions for a eutectic may be similar but the rate of diffusion in the liquid phase is so rapid that the eutectic reaction is not inhibited above the triangle for the rapid eutectic transformation.

Exercise 14.6

An Fe–Ni alloy with $u_{\text{Ni}} = 0.01$ is first in the state of γ (fcc) at 1273 K but then it is carburized and cementite (Fe_3C) forms isothermally. Suppose one would like to try to produce homogeneous cementite with $u_{\text{Ni}} = 0.01$. Estimate what carbon activity is required during the carburization. It is known that the $\gamma + \text{cementite}$ equilibrium in the binary Fe–C system is 1.01 at 1273 K. It is also known that the distribution coefficient for Ni between cementite and γ is $K_{\text{Ni}}^{\text{cementite}/\gamma} = 0.26$.

Hint

Inspiration can be obtained from Fig. 14.18(b) because formation of cementite with the initial Ni content can only occur under a rapid reaction. However, in order to calculate the necessary carbon activity we can go to Section 11.3. The carbon content of cementite is $u_{\text{C}} = 1/3$ and for γ it is about 0.073.

Solution

If the growing cementite has $u_{\text{Ni}} = 0.01$ and there is local equilibrium (quasi-paraconditions) then the adjoining γ has $u_{\text{Ni}} = 0.01/0.26 = 0.038$. Equation (11.23) gives $\ln(a_{\text{C}}/a_{\text{C}}^{\text{binary}}) = (1 - 0.26)/[(1/3) - 0.073] \times 0.038 = 0.108$; $a_{\text{C}} = 1.01 \times 1.114 = 1.125$. The carbon activity must be higher than this value.

14.7 Transformations in steel under partitioning of alloying elements

In the preceding section we concluded for Fe–Ni–C that, for Ni contents falling above the top of the critical triangle, pearlite could grow only by nickel diffusing into the remaining γ because both growing phases, α and cementite, require that the nickel content is lower than in the adjoining γ . The situation will be quite different if one of the phases, α or cementite, can grow with a higher alloy content than the adjoining γ . Then it would be sufficient that the alloying element diffuses side-wise and distributes itself between the two growing phases. This process can take place with an observable speed by diffusion inside the pearlite/ γ interface. Interfacial diffusion can be orders of magnitude faster than volume diffusion.

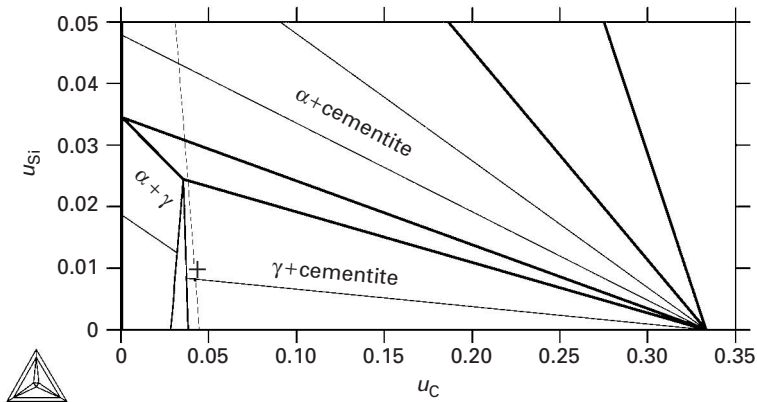


Figure 14.20 See Exercise 14.7.

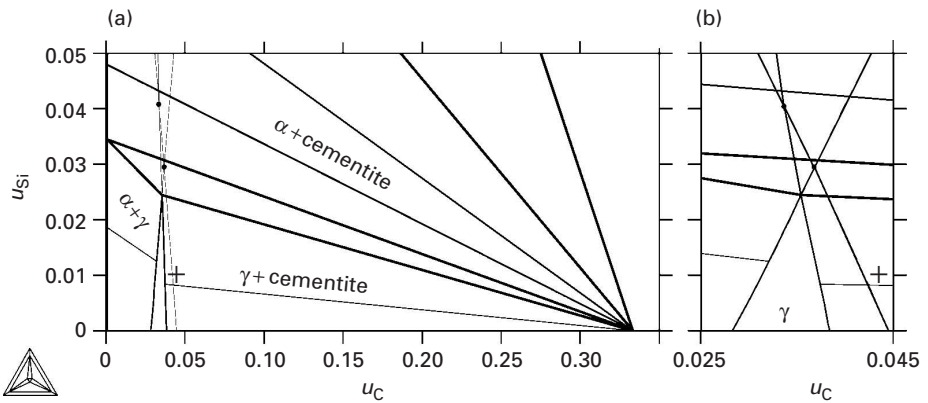


Figure 14.21 Solution to Exercise 14.7.

Examples of alloying elements allowing pearlite to grow under partitioning between α and cementite are manganese and silicon. Cementite will attract manganese and α will attract silicon.

Exercise 14.7

Suppose a steel is first transformed to homogeneous γ at a high temperature and then cooled to 1023 K where it is represented by the cross in the Fe–Si–C phase diagram (Fig. 14.20). The thin line is an isoactivity line for γ going through the cross. Examine if there would be a positive difference in Si content inside γ , $\Delta u_{\text{Si}}^{\gamma}$, to drive the redistribution of Si between α and cementite and thus allow γ to transform to pearlite. If that is the case, evaluate the fractions of α and cementite in that pearlite.

Hint

First find the intersections with the isoactivity line and the extrapolated phase boundaries for γ . Then try to find the other end-points on the corresponding tie-lines.

Solution

The construction is shown in Fig. 14.21(a) and again, with an expanded u_C scale, in (b). The intersection of the isoactivity line with the two phase boundaries will give the compositions of γ at the interfaces to α and cementite if there is full local equilibrium. The difference $\Delta u_{\text{Si}}^\gamma = u_{\text{Si}}^{\gamma/\text{cementite}} - u_{\text{Si}}^{\gamma/\alpha}$ is positive and will thus make silicon diffuse away from cementite to α . Pearlite can thus grow but it must have the same average Si content as the initial γ , $u_{\text{Si}} = 0.01$. Since cementite has practically no Si and α has about 0.035, we find that the fraction of α is $0.01/0.035 = 0.3$. The fraction of cementite is thus 0.7 and the carbon content of this pearlite is extremely high. It requires a large supply of carbon to be drawn from the interior of the γ phase.

15 Limit of stability and critical phenomena

15.1 Transformations and transitions

In Chapter 12 we were mainly concerned with the question whether a transformation is sharp or gradual. The difference between those cases is very practical and straightforward. It is based on a one-dimensional phase diagram where the only axis represents the quantity that is being varied. If that diagram shows a two-phase field of some extension between the two one-phase fields, then the transformation between the two phases will be gradual. If the two-phase field has no extension, then the transformation will be sharp. For a unary system with a transformation this will happen if one varies a potential, e.g. T . The Gibbs energy is a continuous function of T across the sharp transformation but its derivatives, yielding S and V , show discontinuous jumps. This is why the phase boundaries separate when a molar axis is introduced (see Figs 9.1 and 9.2). In other cases there is no such separation because the first-order derivatives are zero. A typical example is found in a ferromagnetic substance, which gradually loses its magnetization as the temperature is increased. At the Curie temperature it reaches zero and the substance has thus become paramagnetic. There is no temperature where ferromagnetic and paramagnetic regions coexist in a pure substance, not even if one varies a molar quantity. As a consequence, there is not really a two-phase field between the two one-phase fields and this fact is indicated by the use of a dashed line to separate the one-phase fields (see Fig. 15.1 where the two phases are denoted by β and β' in order to emphasize their close relationship). If there is no discontinuous jump in the first-order derivatives but there is one in the second-order derivatives, then one calls this a second-order transition as distinguished from a first-order transition when there is a jump in the first-order derivatives.

When considering a T, P diagram and calculating the locus of a sharp transformation between two phases in Section 8.3, we applied the Gibbs–Duhem relation to each of the phases, obtaining two equations for $d\mu_A$. By requiring that μ_A must change in the same way for the two phases along their line of coexistence, it was possible to calculate the slope of that line, (see Fig. 8.6). In this way dP/dT was obtained as a function of discontinuous jumps in the two first-order derivatives, ΔS and ΔV . This method does not work in the present case because the two equations become identical on the line we want to calculate, and ΔS and ΔV both go to zero there. This problem was solved by Ehrenfest [27] who instead used the fact that on the line there is no difference between

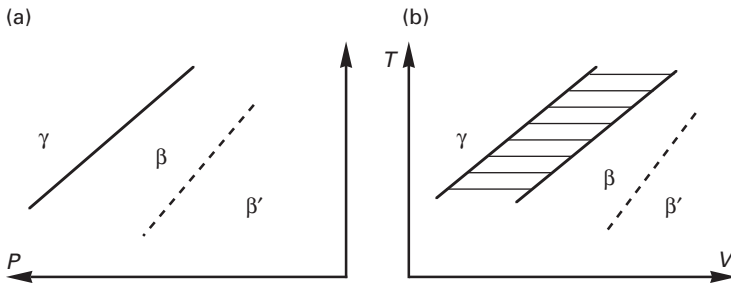


Figure 15.1 Characteristics of a second-order transition $\beta \leftrightarrow \beta'$. The $\gamma \leftrightarrow \beta$ transition is first order.

V of the two states. The expression for dV ,

$$dV = \left(\frac{\partial V}{\partial T} \right)_P dT + \left(\frac{\partial V}{\partial P} \right)_T dP = V\alpha dT - V\kappa_T dP, \quad (15.1)$$

must give the same value in both states. Because V itself also has the same value in both states but α and κ_T do not, we get, by taking the difference between the two states,

$$\frac{dP}{dT} = \frac{\Delta\alpha}{\Delta\kappa_T} \quad (15.2)$$

It is also possible that the discontinuous jumps first occur in the third-order derivatives of G and the corresponding transition would be of third order, etc. In practice, it is often difficult to decide by experimental measurements whether $\Delta\alpha$ and $\Delta\kappa_T$ differ from zero, as they should for a second-order transition. Sometimes the individual values of the second-order derivatives appear to go to infinity at the transition point and it is not meaningful to try to evaluate their difference. Ehrenfest's expression for dP/dT is then of little practical use. Of course, it can be used when one investigates a particular model that gives definite values for second-order derivatives. In view of these complications, it is common to call all transitions with continuous first-order derivatives, second order.

It should be emphasized that nothing really happens in a system when it passes a second-order transition point. It does not really transform. The only difference is that it starts behaving in a new way. The real changes in the system occur gradually as the system moves away from the point of transition. In that sense, the second-order transition is just the start of a gradual transformation. Figure 15.2 illustrates different possibilities for a pure substance at constant pressure. The internal variable ξ is some measure of the arrangements of the atoms or electrons. Curve (a) with its discontinuous jump represents a first-order transition. Curve (b) shows a discontinuous jump but also a gradual change. In curve (c) the jump has disappeared but the curve is horizontal at the break point. In curve (d) the curve never turns horizontal.

The words transformation and transition are often used as synonyms. One word is favoured by the experts in some fields and the other word in other fields. There is a need for two words with different meanings. For our purposes, it would seem most natural to use transition in much the same way as above but use transformation to describe the

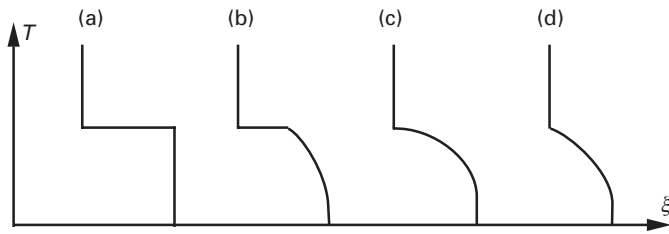


Figure 15.2 Different cases of transitions and transformations. (a) A first-order transition that occurs with a sharp transformation. (b) A first-order transition where the transformation is partly sharp, partly gradual. (c) and (d) Second-order transitions with completely gradual transformations.

progress of the real changes occurring in a system. The break points in all the curves in Fig. 15.2 would thus be regarded as the transition point and the transition is the change occurring at the transition point, whether it is a real change or a change in behaviour that will reveal itself as the system moves away from the transition point. In curve (a) the first-order transition yields a sharp transformation if T , being a potential, is varied. In curve (b) part of the transformation would be sharp and occur at the transition point, and another part would be gradual and occur below the transition point. In curves (c) and (d) the transformation would be completely gradual and start as the transition point is crossed. Thus, a transition point yielding a transformation that is at least partly sharp, would be of first order. Otherwise, it would be of second order. It should be emphasized, however, that there are many cases where the concept of first- and second-order transition does not appear to be very useful. This will be demonstrated in Section 15.4.

The strict difference between first-order and second-order transitions is of considerable theoretical interest but from a practical point of view it may sometimes be of less importance whether there is a small discontinuous jump or no jump at all.

In the previous chapters, only the word transformation has been used. From now on, an attempt will be made to apply both terms and with the definitions given here. In view of the conclusion drawn in Section 12.2, a sharp transformation, which must always be a first-order transition, will turn gradual when the variable is changed from a potential to a molar quantity. From the theoretical point of view this is a trivial effect and should not affect the classification of the transition. The theoretical study of phase transitions is thus carried out without involving any molar quantity.

A phase transition is often caused by a tendency of an ordered arrangement to disorder. Such transitions are called **order–disorder transitions** and the driving force comes primarily from the increasing configurational entropy. In other cases, the cause may be the lowering of the energy by deformation of the structure, e.g. by decreasing the tetragonality, without changing the configurational entropy. Such transitions are called **displacive transitions**. Of course, the characteristics of order–disorder and displacive can be applied to the corresponding transformation, as well. In both cases, the progress of the change can be expressed by some internal variable, e.g. the degree of long-range order or the tetragonality. For simplicity, all such variables are sometimes called ‘order parameters’ and, in principle, all internal variables could play this role.

Another method of classifying phase transitions is based on what happens to the atoms during the transition. A **reconstructive** transition involves a reorganization of the atomic arrangement with the breaking of atomic bonds and the formation of new bonds. The opposite case would be a displacive transition which involves only small adjustments of the atomic positions without the atoms ever losing contact with their initial neighbours. This classification thus depends on the nature of the interface migrating through the parent crystal. If the two crystal structures are closely related, one could imagine an interface so highly coherent that the atoms find their positions in the new crystal (phase) with only small adjustments of their positions relative to each other. However, it is possible in the same material that another interface is incoherent and one could not predict exactly where an atom from the parent crystal will end up in the growing crystal. The transition would then be regarded as reconstructive even if the structures of the two crystals (phases) are identical. That is the case in ordinary grain growth where large crystals consume small ones of the same phase and composition.

Furthermore, we may define a **partitional** transition as a transition in an alloy where the new phase has a different composition and can grow only under long-range diffusion. The solute atoms have partitioned between the parent phase and the new phase, which requires diffusion and may be regarded as a **diffusional** transition. The opposite case is a **partitionless** transition which would be the result if there is no diffusion. However, the result could be partitionless even if there is some local diffusion during the transition. We shall apply the term **diffusionless** only to cases where there is not even any short-range diffusion. Evidently, a diffusional transition can at the same time be reconstructive or displacive. It can even be an order–disorder transition.

Exercise 15.1

Derive an expression for dP/dT for a second-order transition by considering the variation of S along the transition line.

Hint

A Maxwell relation can be used to transform the result into well-known parameters.

Solution

$$dS = (\partial S/\partial T)_P dT + (\partial S/\partial P)_T dP = (C_P/T)dT - V\alpha dP \text{ since } (\partial S/\partial P)_T = -(\partial V/\partial T)_P.$$

On the transition line, where $\Delta(dS) = 0$, we get $dP/dT = \Delta C_P / VT \Delta\alpha$.

15.2 Order–disorder transitions

Let us consider an ordering phenomenon in a phase with a crystal symmetry such that the properties can be expressed as even functions of the order parameter ξ . As demonstrated

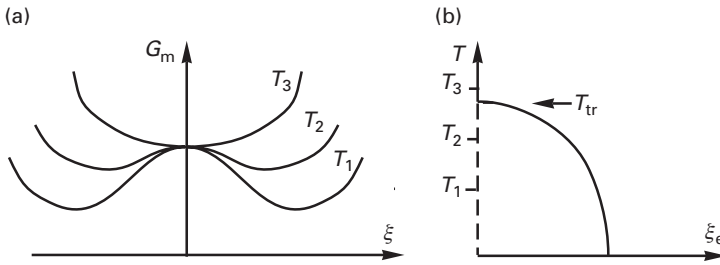


Figure 15.3 Molar Gibbs energy diagram illustrating the properties of a substance showing a second-order transition. The dashed line in (b) represents unstable states, shown as points of maximum in (a).

by Landau and Lifshitz [28] the simplest form of the Gibbs energy expansion in the neighbourhood of the transition from disordered to ordered state would be

$$G_m = g_0 + \frac{1}{2}g_{\xi\xi}\xi^2 + \frac{1}{24}g_{\xi\xi\xi\xi}\xi^4, \quad (15.3)$$

where $g_{\xi\xi} = \partial^2 G_m / \partial \xi^2$, etc., and g_0 , $g_{\xi\xi}$ and $g_{\xi\xi\xi\xi}$ may vary with temperature and composition although variations in composition will not be considered yet. In order to place the minimum of G_m in the region close to $\xi = 0$, where the G_m expression is supposed to hold, it is necessary to make $g_{\xi\xi\xi\xi} > 0$. In order to predict an ordered state at low temperatures but not at high, it is necessary to assume that $g_{\xi\xi}$ is negative at low temperatures and positive at high. The equilibrium value ξ_e can be found from

$$dG_m/d\xi = g_{\xi\xi}\xi + \frac{1}{6}g_{\xi\xi\xi\xi}\xi^3 = 0. \quad (15.4)$$

The disordered, high-temperature state is described by $\xi_e = 0$. At low temperature there are two other solutions

$$\xi_e = \pm(-6g_{\xi\xi}/g_{\xi\xi\xi\xi})^{1/2}. \quad (15.5)$$

By symmetry these two solutions are physically equivalent. They only exist as long as $g_{\xi\xi} < 0$ and they approach $\xi_e = 0$ as $g_{\xi\xi}$ approaches 0. The transition point would thus be given by $g_{\xi\xi} = 0$. Below the temperature where this occurs, the solution $\xi_e = 0$, representing a disordered state, would give a G_m maximum and the disordered state would thus be unstable here. Figure 15.3(a) demonstrates the shape of G_m at temperatures above and below the transition point, T_{tr} . Figure 15.3(b) shows how ξ_e , obtained from the minima, varies with temperature.

Let us now examine how we can calculate the limit of stability for the disordered state. The condition would be simply

$$\left(\frac{\partial^2 G_m}{\partial \xi^2}\right)_{T,P,\text{comp.},N_i} = 0, \quad (15.6)$$

since we have decided not to consider variations in composition yet. We get directly

$$g_{\xi\xi} + 1/2g_{\xi\xi\xi\xi}\xi^2 = 0, \quad (15.7)$$

but the stability condition can only be applied to states of equilibrium. Thus, we must insert the equilibrium value, which is $\xi_e = 0$ for the disordered state, yielding the limit of stability at $g_{\xi\xi} = 0$ for the disordered state when cooled from a high temperature. This limit of stability thus falls on the transition point. When inserting the expression for ξ_e in the ordered state we find

$$g_{\xi\xi} = -1/2g_{\xi\xi\xi\xi}\xi_e^2 = 3g_{\xi\xi}. \quad \text{Thus, } g_{\xi\xi} = 0. \quad (15.8)$$

The limit of stability for the ordered state when heated from a low temperature also falls on the transition point. That is typical of second-order transitions.

It is interesting to insert the equilibrium value ξ_e in Eq. (15.3) for G_m and thus to obtain Gibbs energy expressions at equilibrium for ξ .

$$G_m^{\text{dis}} = g_o \text{ in disordered state} \quad (15.9)$$

$$G_m^{\text{ord}} = g_o - \frac{3}{2}g_{\xi\xi}^2/g_{\xi\xi\xi\xi\xi\xi} \text{ in ordered state.} \quad (15.10)$$

At the transition point $G_m^{\text{dis}} = G_m^{\text{ord}}$ and $dG_m^{\text{dis}}/dT = dG_m^{\text{ord}}/dT$ because $g_{\xi\xi} = 0$ there, but the second-order derivatives are different, confirming that this transition is of second-order.

In order to model a first-order transition one can either remove the symmetry by introducing a ξ^3 term or one can keep the symmetry but introduce a ξ^6 term. With the latter alternative we obtain

$$G_m = g_o + \frac{1}{2}g_{\xi\xi}\xi^2 + \frac{1}{24}g_{\xi\xi\xi\xi}\xi^4 + \frac{1}{720}g_{\xi\xi\xi\xi\xi\xi}\xi^6. \quad (15.11)$$

In this case we must take $g_{\xi\xi\xi\xi\xi\xi} > 0$ and $g_{\xi\xi\xi\xi} < 0$. Equilibrium requires that

$$dG_m/d\xi = g_{\xi\xi}\xi + \frac{1}{6}g_{\xi\xi\xi\xi}\xi^3 + \frac{1}{120}g_{\xi\xi\xi\xi\xi\xi}\xi^5 = 0. \quad (15.12)$$

One solution is the disordered, high-temperature state, $\xi_e = 0$, but one also finds low-temperature states

$$\xi_e^2 = -10g_{\xi\xi\xi\xi}/g_{\xi\xi\xi\xi\xi\xi} \pm [100(g_{\xi\xi\xi\xi}/g_{\xi\xi\xi\xi\xi\xi})^2 - 120g_{\xi\xi}/g_{\xi\xi\xi\xi\xi\xi}]^{1/2}. \quad (15.13)$$

The ‘+’ sign gives a new minimum and the ‘-’ sign gives a maximum in between. Figure 15.4 illustrates how G_m varies with ξ above and below a temperature of equilibrium between the two states, the transition temperature, T_t , where the minima fall on the same level.

It is evident that the low-temperature minimum exists only as long as

$$100(g_{\xi\xi\xi\xi}/g_{\xi\xi\xi\xi\xi\xi})^2 - 120g_{\xi\xi}/g_{\xi\xi\xi\xi\xi\xi} \geq 0 \quad (15.14)$$

$$g_{\xi\xi} \leq g_{\xi\xi\xi\xi}^2/1.2g_{\xi\xi\xi\xi\xi\xi}, \quad (15.15)$$

and ξ_e does not approach zero at any temperature. Wherever the transition occurs, it must occur with a discontinuous jump in ξ and will thus be of first order. The ordered state can exist as a metastable state above the point of transition. The limit of stability for the

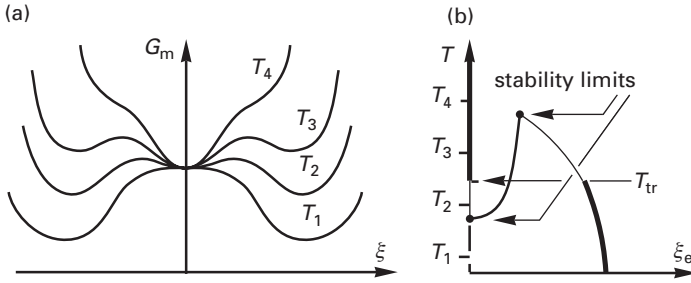


Figure 15.4 Molar Gibbs energy diagram illustrating the properties of a substance showing a first-order transition. The black dots in (b) represent the two limits of stability. Metastable states (exhibiting a minimum with a higher G_m value than another minimum at the same temperature) are represented by thin lines, and unstable states (shown as points of maximum) by a dashed line.

ordered state is obtained from

$$d^2 G_m / d\xi^2 = g_{\xi\xi} + \frac{1}{2} g_{\xi\xi\xi\xi} \xi^2 + \frac{1}{24} g_{\xi\xi\xi\xi\xi\xi} \xi^4 = 0. \tag{15.16}$$

By inserting the equilibrium value ξ_e for the ordered state from Eq. (15.5) and solving for $g_{\xi\xi}$ we find the limit of stability at the temperature where

$$g_{\xi\xi} = g_{\xi\xi\xi\xi}^2 / 1.2 g_{\xi\xi\xi\xi\xi\xi}. \tag{15.17}$$

As expected, the limit of stability occurs when the low-temperature minimum disappears by merging with the maximum and forming a point of inflexion.

By inserting the equilibrium value of ξ for the disordered state, $\xi_e = 0$, we find another limit

$$d^2 G_m / d\xi^2 = g_{\xi\xi} = 0. \tag{15.18}$$

The disordered state thus becomes unstable at the point where $g_{\xi\xi}$ turns negative. Between the two limits, $g_{\xi\xi} = 0$ and $g_{\xi\xi} = g_{\xi\xi\xi\xi}^2 / 1.2 g_{\xi\xi\xi\xi\xi\xi}$, one of the states is stable and the other is metastable. The first-order transition between the states occurs where they change roles. The exact position can be evaluated from the condition that G_m has the same value for the two states, somewhere between T_2 and T_3 in Fig. 15.4. On the other hand, in a system showing a second-order transition, a state is never metastable on the wrong side of the transition point because that is also the limit of stability and there is only one such limit.

It is worth emphasizing that for a second-order transition Landau's approach is not a special model because it only applies at small ξ values and it says nothing about the temperature dependencies of the coefficients. Any analytical model can be represented by a Taylor series expansion near the transition point and will thus predict the temperature dependencies. If $g_{\xi} = g_{\xi\xi\xi} = 0$ and $g_{\xi\xi\xi\xi} > 0$ at all T , and if $g_{\xi\xi}$ goes through zero at some value of T , then the model predicts a second-order transition and all the results for transition obtained from Landau's approach apply. On the other hand, if $g_{\xi\xi\xi\xi} < 0$ then

the model does not predict a second-order transition but maybe a first-order transition. However, in that case the characteristics of the transition are not given completely by the properties at low values of ξ . In order to examine an analytical model of this kind, it is not enough to retain just one more term, ξ^6 , in the series expansion and the result obtained above does not apply in all its details. For a first-order transition, Landau's approach with the choice of only three terms, ξ^2 , ξ^4 and ξ^6 , represents a special model and should be regarded just as a means of demonstrating schematically the characteristics of such a transition.

Exercise 15.2

Use the mathematical description of the first-order transition and calculate exactly where the transition point falls. Show that it falls between the two limits.

Hint

The two minima must have the same G_m value at the transition.

Solution

Equations (15.11) and (15.12) yield $g_o = g_o + (1/2)g_{\xi\xi}\xi^2 + (1/24)g_{\xi\xi\xi\xi}\xi^4 + (1/720)g_{\xi\xi\xi\xi\xi\xi}\xi^6$ and $g_{\xi\xi}\xi + (1/6)g_{\xi\xi\xi\xi}\xi^3 + (1/120)g_{\xi\xi\xi\xi\xi}\xi^5 = 0$.

The most important variables are $g_{\xi\xi}$, which may go through zero, and ξ .

Elimination of $g_{\xi\xi}$ between the two equations yields $\xi^2 = -15g_{\xi\xi\xi\xi}/g_{\xi\xi\xi\xi\xi\xi}$.

Insertion of ξ_e from Eq. (15.5) into Eq. (15.12) yields $g_{\xi\xi} = (1/6)g_{\xi\xi\xi\xi} \cdot (-15g_{\xi\xi\xi\xi}/g_{\xi\xi\xi\xi\xi\xi}) + (1/120)g_{\xi\xi\xi\xi\xi\xi} \cdot (-15g_{\xi\xi\xi\xi}/g_{\xi\xi\xi\xi\xi\xi})^2 = g_{\xi\xi\xi\xi}^2/1.6g_{\xi\xi\xi\xi\xi\xi}$.

This occurs at a temperature between those for the two limits of stability according to Eqs (15.17) and (15.18).

Exercise 15.3

Try to describe a second-order transition with the asymmetric expression $G_m = g_o + (1/2)g_{\xi\xi}\xi^2 + (1/6)g_{\xi\xi\xi}\xi^3 + (1/24)g_{\xi\xi\xi\xi}\xi^4$.

Hint

Calculate the equilibrium value of ξ for the ordered state and examine if it can approach zero gradually.

Solution

The equilibrium value is obtained from $dG_m/d\xi = g_{\xi\xi}\xi + (1/2)g_{\xi\xi\xi}\xi^2 + (1/6)g_{\xi\xi\xi\xi}\xi^3 = 0$.

For the ordered state we get $\xi_e = -(3/2)g_{\xi\xi\xi}/g_{\xi\xi\xi\xi} \pm [(9/4)(g_{\xi\xi\xi}/g_{\xi\xi\xi\xi})^2 - 6g_{\xi\xi}/g_{\xi\xi\xi\xi}]^{1/2}$.

It is evident that ξ_e cannot approach zero gradually unless $g_{\xi\xi\xi} = 0$ which would make G_m symmetric. The asymmetric G_m expression can only describe a first-order transition.

We can conclude that to describe a second-order transition we need a symmetric G_m function. On the other hand, a symmetric G_m function can describe a second-order or a first-order transition, as demonstrated above.

15.3 Miscibility gaps

It sometimes happens that a two-phase coexistence line in the T, P phase diagram ends at a critical point and this always happens for the liquid–vapour line. Above the critical point one can move continuously from a high density, characteristic of a liquid, to a low density, characteristic of a vapour (see Fig. 15.5). A similar phenomenon can occur in binary systems under constant pressure (see Fig. 15.6). Such phase fields are often called miscibility gaps and the top, which is a critical point, is called **consolute point**.

In the binary case the condition for the stability limit would be $(\partial^2 G_m / \partial x_B^2)_{T,P} \equiv g_{BB} = 0$. However, for most compositions this would give a point falling inside the miscibility gap where the homogeneous state is not the most stable one. As explained in Section 7.2, the stability condition here defines inflexion points and Fig. 15.7 gives G_m curves for a series of temperatures demonstrating that the two inflexion points move together to a point at the top of the miscibility gap. The consolute point can thus be found by combining the stability condition already given with a new condition,

$$\left(\frac{\partial^3 G_m}{\partial x_B^3} \right)_{T,P} = 0. \quad (15.19)$$

We thus have two equations and can evaluate two unknowns, the temperature and the composition of the consolute point. For the miscibility gap in a unary system the top can be found in two ways because the limit of stability can be expressed in two ways,

$$F_{VV} = - \left(\frac{\partial P}{\partial V} \right)_T = \frac{1}{V\kappa_T} = 0 \text{ and } F_{VVV} = 0 \quad (15.20)$$

$$H_{SS} = - \left(\frac{\partial T}{\partial S} \right)_P = \frac{T}{C_P} = 0 \text{ and } H_{SSS} = 0. \quad (15.21)$$

The thin line in Fig. 15.6(b) is the locus of points representing the stability limit and the diagram confirms that it touches the top of the miscibility gap. The consolute point is thus the only point where the stability limit can be reached by a stable system. It is regarded as a **critical point** because two coexisting states become identical there. For all other compositions the homogeneous system turns metastable on cooling before reaching the stability limit. It should be noted that the transition point for a second-order

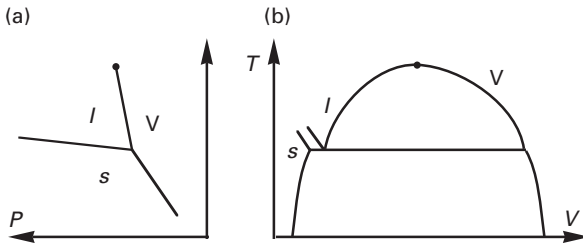


Figure 15.5 Phase diagram for a unary system showing the liquid + vapour miscibility gap.

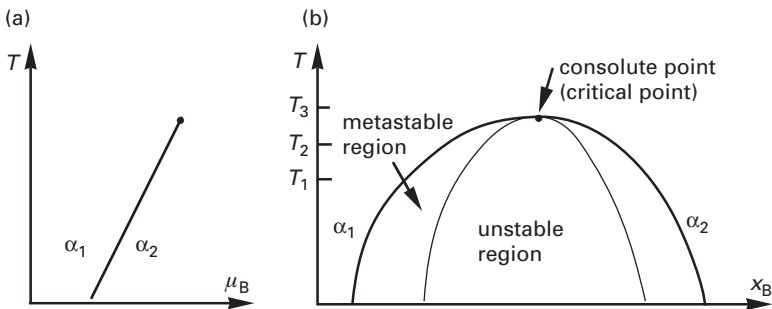


Figure 15.6 Phase diagram for a binary system at constant P , showing a solid miscibility gap.

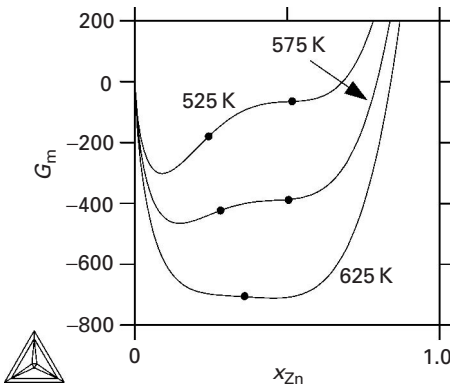


Figure 15.7 Gibbs energy curves at a series of temperatures through the fcc miscibility gap in the Al–Zn system at constant P . The inflexion points are marked with black dots. They represent the spinodal. Just below 625 K they coincide and form a critical point.

transition is not a critical point in this sense because the ordered and the disordered states never coexist as two different phases if the transition is second-order.

The line representing the stability limit in a miscibility gap is called a **spinodal curve** or simply a spinodal or a spinode because it falls on a sharp point (*spine* meaning *thorn*) in property diagrams with potential axes. An example is shown in Fig. 15.8.

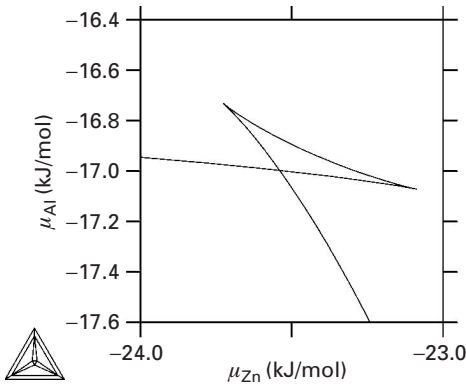


Figure 15.8 Property diagram at constant T and P for a binary system with a miscibility gap, the fcc phase in Al–Zn at 525 K.

In this connection it is common to call the phase boundary of the miscibility gap a **binodal**.

The critical point on a miscibility gap extends into a line when a third component is added, into a surface when a fourth component is added, etc. According to Section 6.6 the limit of stability of a multicomponent system, i.e. the spinodal, is defined by

$$\left(\frac{\partial g_c}{\partial x_c} \right)_{T, P, g_2, \dots, g_{c-1}, N} = 0. \quad (15.22)$$

The critical point is found by also applying the condition

$$\left(\frac{\partial^2 g_c}{\partial x_c^2} \right)_{T, P, g_2, \dots, g_{c-1}, N} = 0. \quad (15.23)$$

It should be remembered that g_c is the notation for $(\partial G_m / \partial x_c)_{x_2, x_3, \dots, x_{c-1}}$. In Section 6.6 it was shown that the stability condition can be transformed into such quantities, using the Jacobian method. For a ternary system the result can be written as

$$\begin{vmatrix} g_{22} & g_{23} \\ g_{32} & g_{33} \end{vmatrix} / g_{22} = g_{33} - (g_{23})^2 / g_{22} = 0. \quad (15.24)$$

Using the same technique the condition for a critical point can be transformed, but the result will be more complicated (see, for instance, [29]). In the ternary case it can be written as

$$g_{33} - 3g_{233}(g_{23}/g_{22}) + 3g_{223}(g_{23}/g_{22})^2 - g_{222}(g_{23}/g_{22})^3 = 0. \quad (15.25)$$

Equation (15.25) can be modified in several ways using $g_{33}/g_{23} = g_{23}/g_{22}$ which holds on the spinodal. For the binary case the result is simply $g_{222} = 0$, which is just a notation for $\partial^3 G_m / \partial x_2^3 = 0$ when x_3 is treated as the independent variable that is kept constant.

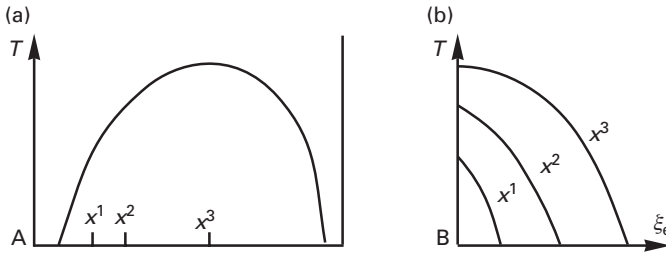


Figure 15.9 Progress of reaction in a miscibility gap for a series of compositions, demonstrating that this is a gradual transformation for all compositions, but it is not a second-order transition.

The reason why one cannot find the critical point in a ternary case by applying $g_{222} = 0$ and $g_{333} = 0$ is that the most dangerous fluctuation may not be parallel to any of the two composition axes. It should be noted that this is the reason why the condition for the stability limit is primarily given under constant potentials, not extensive or molar quantities.

For the binary miscibility gap it may be instructive to introduce an internal variable in order to describe the progress of the reaction as a function of temperature in a system with fixed composition. We can define an internal variable having the following equilibrium value

$$\xi_e(T) = [x^\beta(T) - x^0][x^0 - x^\alpha(T)], \quad (15.26)$$

where $x^\beta(T)$ and $x^\alpha(T)$ are the equilibrium compositions on the two sides of the miscibility gap and x^0 is the average composition. In Fig. 15.9 this variable is plotted against temperature for three values of the average composition, x^0 , equal to x^1 , x^2 and x^3 , respectively. Figure 15.9(b) can be compared with Figs 15.2(c) and 15.2(d). It is evident that this will be a gradual transformation for all compositions.

Exercise 15.4

Consider a unary system with a liquid(l) + vapour(v) miscibility gap in the T, V_m phase diagram. Within the gap there is a spinodal curve, representing the limit of stability. Examine what happens to the spinodal in the diagram if P is introduced instead of V_m . Furthermore, sketch a μ_A, P property diagram at constant T .

Hint

The spinodal, has two branches. Denote the stability limit of liquid by S_l and of vapour S_v . Each one represents the end of a metastable range and should thus be situated on the ‘wrong’ side of the line of coexistence in the P, T diagram.

In the property diagram each phase is represented by a line and they intersect in such a way that the stable phase always has the lowest μ_A value. They only extend to their limits of stability.

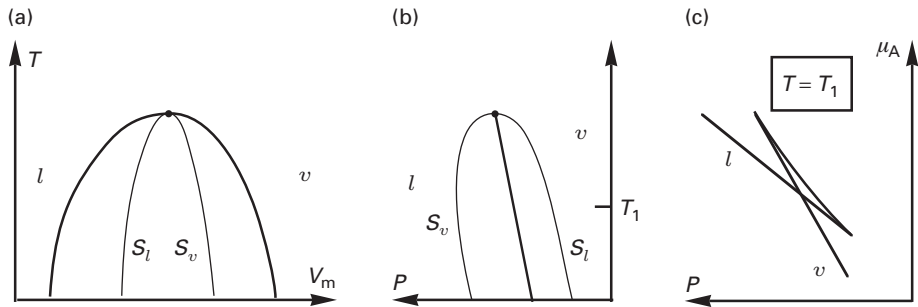


Figure 15.10 Solution to Exercise 15.4.

Solution

The solution is presented in Fig. 15.10.

Exercise 15.5

Transform the condition for a critical point in a ternary system, $(\partial^2 g_3 / \partial x_3^2)_{g_2} = 0$, to the variables x_2 and x_3 using Jacobians and confirm Eq. (15.25).

Hint

The derivative should first be expressed as $\left(\frac{\partial}{\partial x_3} \left(\frac{\partial g_3}{\partial x_3} \right)_{g_2} \right)_{g_2}$. Use a method similar to the one applied when showing that $\left(\frac{\partial g_3}{\partial x_3} \right)_{g_2} = \begin{vmatrix} g_{33} & g_{23} \\ g_{32} & g_{22} \end{vmatrix} / g_{22} = g_{33} - (g_{23})^2 / g_{22}$ in Exercise 6.6.

Solution

$$\begin{aligned} \left(\frac{\partial}{\partial x_3} \left(\frac{\partial g_3}{\partial x_3} \right)_{g_2} \right)_{g_2} &= \begin{vmatrix} \frac{\partial(g_{33} - (g_{23})^2 / g_{22})}{\partial x_3} & \frac{\partial(g_{33} - (g_{23})^2 / g_{22})}{\partial x_2} \\ \frac{\partial g_2}{\partial x_3} & \frac{\partial g_2}{\partial x_2} \end{vmatrix} = \begin{vmatrix} \frac{\partial x_3}{\partial x_3} & \frac{\partial x_3}{\partial x_2} \\ \frac{\partial g_2}{\partial x_3} & \frac{\partial g_2}{\partial x_2} \end{vmatrix} \\ &= [g_{22}g_{333} - g_{22} \cdot 2g_{23}g_{233} / g_{22} + g_{22} \cdot (g_{23})^2 g_{223} / (g_{22})^2 - g_{23}g_{233} + g_{23} \cdot 2g_{23}g_{223} / g_{22} - g_{23} \cdot (g_{23})^2 g_{222} / (g_{22})^2] / g_{22} = g_{333} - 3g_{233}(g_{23} / g_{22}) + 3g_{223}(g_{23} / g_{22})^2 - g_{222}(g_{23} / g_{22})^3 = 0. \end{aligned}$$

15.4 Spinodal decomposition

Thermodynamically, a system inside the spinodal is unstable with respect to compositional fluctuations and one could expect the system to decompose to a mixture of

regions with the two stable compositions, one on each side of the miscibility gap. This process is called **spinodal decomposition**. However, a fluctuation will be surrounded by a matrix of a different composition and the interfacial region where the composition varies will add some extra energy to the system. It is sometimes described as a *gradient energy*. As a result, the driving force for the process will be diminished by some amount and there may not even be a positive driving force if the fluctuation is too localized. The interfacial area-to-volume ratio must not be too large. In order to simplify the mathematics one may consider sinusoidal fluctuations in composition and then one will find a critical wavelength above which the driving force is positive. The rate of reaction will have its maximum somewhere above the critical wavelength but not very much above because the longer the wavelength, the longer the diffusion distances will be.

A mathematical treatment of this phenomenon is based on the condition for the stability limit $d^2G_m/dx^2 = 0$. As demonstrated in Section 7.7, d^2G_m/dx^2 appears in the expression for the diffusion coefficient. Thus, inside the spinodal, where d^2G_m/dx^2 is negative, the diffusion should go in the wrong direction and small fluctuations should grow. This is called up-hill diffusion. However, we should also include the contribution from the gradient energy. For small fluctuations in composition one may use the following simple approach,

$$G_m = G_m(x) + K \cdot (dx/dy)^2, \quad (15.27)$$

where y is the length coordinate and dx/dy is the composition gradient. As shown by Cahn [30], this yields the following expression to be inserted in Fick's first law and a related expression for the second law,

$$\frac{d^2G_m}{dx^2} = \frac{d^2G_m(x)}{dx^2} - 2K \cdot \frac{d^3x/dy^3}{dx/dy}. \quad (15.28)$$

If the composition x varies proportional to $\sin(ky)$, the limit of stability would be found where

$$\frac{d^2G_m}{dx^2} = \frac{d^2G_m(x)}{dx^2} - 2K \cdot k^2 = 0. \quad (15.29)$$

A sinusoidal fluctuation could thus grow in amplitude if its wavelength $\lambda(=2\pi/k)$ is longer than a critical value

$$\lambda_{\text{crit.}} = 8\pi^2 K \left/ \left(-\frac{d^2G_m(x)}{dx^2} \right) \right. . \quad (15.30)$$

Shorter wavelengths could not grow in amplitude but would shrink.

In reality, one should expect some random fluctuation in composition throughout the whole system. It is possible to describe it with a spectrum of wavelengths. In view of the above result, one could expect those that are longer than the critical wavelength to grow in amplitude and one could guess that the fastest growth may occur at about twice the critical wavelength. This value would then be what one could expect to find in early observations of spinodal decomposition. At longer times, one could expect a continuous coarsening.

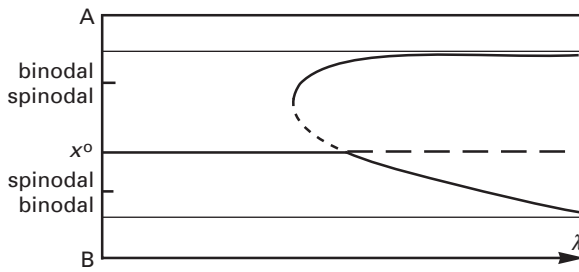


Figure 15.11 Stable (full lines) and unstable (dashed lines) equilibrium states with a periodic variation in composition. T and P are constant and the average composition is inside the spinodal.

Any sinusoidal fluctuation with a wavelength longer than the critical value would spontaneously grow in amplitude and approach a stable state which would still be periodic but no longer sinusoidal. The maxima and minima would be much flatter and could be expected to fall close to the two equilibrium compositions of the miscibility gap. Hillert [31] showed how such states of equilibrium can be calculated by applying the equilibrium condition to each point in the system. If the gradient energy is included and only one direction is considered, then one will find solutions represented by a periodic variation of composition, characterized by a wavelength and an amplitude but not necessarily sinusoidal. As an example, Fig. 15.11 illustrates schematically all the solutions for a system inside the spinodal.

It may be noted that there is a critical value of the wavelength and the homogeneous state is stable against fluctuations of a lower wavelength. Above the critical wavelength two new solutions appear and the homogeneous state is not stable against such fluctuations. The critical point is thus a typical bifurcation point. It may be mentioned that the diagram is quite symmetric for the 50/50 alloy composition.

The critical wavelength will approach infinity as the average composition is chosen closer and closer to the spinodal. Outside the spinodal the homogeneous system will be metastable. All small fluctuations in composition will increase the Gibbs energy as illustrated by the molar Gibbs energy diagram in Fig. 15.12. It is constructed without considering the gradient energy that would increase the Gibbs energy of the fluctuations even more.

Figure 15.13 illustrates schematically the effect of the gradient energy for the same case. The inverse of the wavelength, $1/\lambda$, is used here in order to include an infinite wavelength ($1/\lambda = 0$) in the diagram. The end-points at infinite wavelength are particularly interesting. The upper one is close to the binodal and represents the stable state where all the surplus of the minor component is concentrated in a single, local enrichment surrounded by a diffuse interface. It represents a system with a precipitated second-phase particle. The other point falls on the line for unstable equilibria and represents a system with a local critical fluctuation, termed a ‘critical nucleus’.

An additional factor of importance to spinodal decomposition in crystalline phases should be mentioned. The lattice parameter of a crystalline structure usually varies with

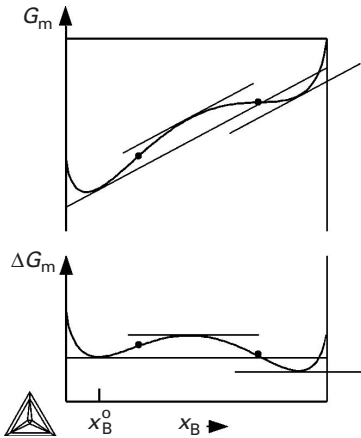


Figure 15.12 Illustration of the fact that small fluctuations in composition are not stable and would disappear if the average composition, x_B^0 , is outside the spinodal (marked with black dots). The diagram is easier to read when the tangent to x_B^0 is turned horizontal, as in the (lower) ΔG_m versus x_B diagram.

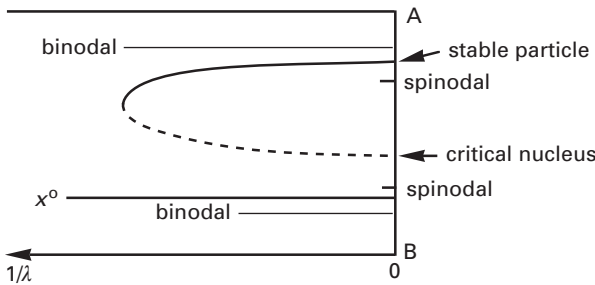


Figure 15.13 Same as Fig. 15.11 but for an average composition outside the spinodal and plotted versus the inverse wave-length.

composition. Fluctuations in composition will thus give rise to internal stresses (So-called coherency stresses, see Section 16.10) and these will increase the energy of a fluctuation. As long as the crystal is fully coherent, this effect is independent of the wavelength. The effect will be denoted by a constant C and should be added to $d^2 G_m/dx^2$ yielding

$$\frac{d^2 G_m}{dx^2} = \frac{d^2 G_m(x)}{dx^2} - 2K \cdot k^2 + C = 0, \tag{15.31}$$

for the limit of stability. C is always positive and will thus act to stabilize the homogeneous state. It will displace the spinodal to lower temperatures. In this connection one talks about two spinodals, the coherent one, and the incoherent (or chemical) spinodal (see Fig. 15.14). In practice, the region of metastability will thus be extended.

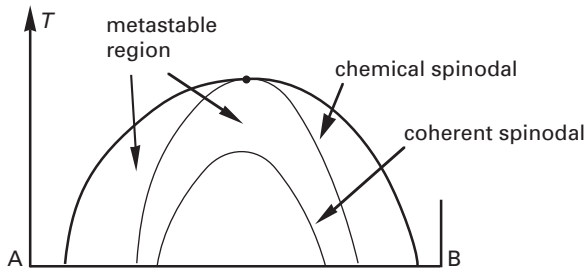


Figure 15.14 A solid-phase miscibility gap showing two spinodals.

Exercise 15.6

Au and Ni both have the simple fcc structure. The Au–Ni system has a miscibility gap in the fcc phase with a consolute point at 1083 K. A homogeneous alloy of the consolute composition, cooled from 1150 to 900 K, will decompose by a microscopically sharp eutectoid-like transformation $\text{fcc}_0 \rightarrow \text{fcc}_1 + \text{fcc}_2$ and not by spinodal decomposition. Suggest an explanation.

Solution

The Au atoms are much larger than the Ni atoms. The molar volumes of pure Au and Ni are 10.2 and $6.59 \text{ cm}^3/\text{mol}$, respectively. Fluctuations in composition will thus give rise to high coherency stresses. The coherent spinodal will be depressed to lower temperatures by several hundred kelvin.

15.5 Tri-critical points

In the discussion of order–disorder transitions we only considered a single composition but it is self-evident that one can represent the points for a second-order transition at all compositions in a binary system by a line. For a second-order transition, which is known to occur in one of the components, e.g. a magnetic transition, we would expect a diagram like the one in Fig. 15.15(a). However, now we should also consider the possibility of obtaining a miscibility gap by separation into regions of different compositions. In order to explore this possibility we can use Landau's simple mathematical model, discussed in Section 15.2, where all the parameters may be functions of T and x . In the disordered state $G_m = g_o$ and we shall assume that g_o does not contain any factor favouring the formation of a miscibility gap. Then there would be no spinodal inside the region for the disordered state, i.e. above the transition line. In the ordered state we have from before

$$G_m^{\text{ord}} = g_o - \frac{3}{2}(g_{\xi\xi})^2/g_{\xi\xi\xi\xi}, \quad (15.32)$$

and we should consider the possibility of a spinodal reaching the transition line from below. Remembering that $g_{\xi\xi} = 0$ on the transition line, we find there

$$\partial^2 G_m^{\text{ord}}/\partial x^2 = \partial^2 g_o/\partial x^2 - 3(g_{\xi\xi x})^2/g_{\xi\xi\xi\xi}. \quad (15.33)$$

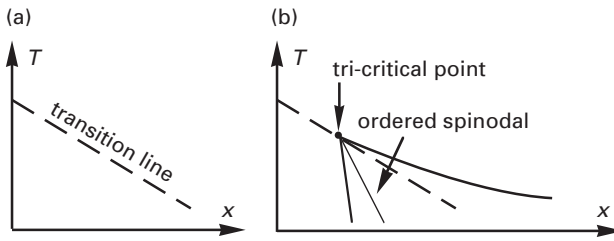


Figure 15.15 The formation of a miscibility gap around the line for a second-order transition.

There would thus be a miscibility gap with its consolute point on the transition line if this expression is zero which could very well happen. The temperature and composition of the consolute point would be found by combination with $g_{\xi\xi} = 0$. The resulting phase diagram would look like the diagram in Fig. 15.15(b). This consolute point is regarded as a **tri-critical point** which is an unfortunate name. It may remind us of a triple point between three phases in a T, μ_B diagram but it has that shape only in a T, x diagram. In the T, μ_B diagram it would just be a point on a line.

It should be emphasized that we here have two internal variables or ‘order parameters’, one describing the ordering and the other describing the separation into different compositions. We could thus test the stability with respect to variations in one or the other. When testing for variations in ordering we found the transition line. However, the test of the real stability limit must take into account simultaneous variations in both internal variables. That would be the most severe test. We should look for the possibility that a system encounters the real stability limit and transforms *before* reaching the transition line. We could then find one spinodal on each side of the transition line but it would be quite a different case from that illustrated in Fig. 15.2. That case concerned a first-order transition where a system may cross the transition line and reach a limit of stability *on the other side*.

Figure 15.15(b) shows a spinodal below the transition line and it applies to homogeneous, ordered states coming from lower temperatures. We should also look for a spinodal above the transition line, applicable to the disordered state, cooled from a high temperature. It should be given by

$$\partial^2 G_m^{\text{dis}} / \partial x^2 = \partial^2 g_o / \partial x^2 = 0, \quad (15.34)$$

because $\xi = 0$. As a consequence, our model which yields this relation cannot predict such a spinodal unless g_o contains a factor promoting a miscibility gap. Otherwise, $\partial^2 g_o / \partial x^2 > 0$. That is why Fig. 15.15 was constructed without a disordered spinodal. The transition line itself acts as the limit of stability for disordered systems coming from higher temperatures. However, it is not the same type of spinodal as the lower one because it does not represent the limit of stability against compositional fluctuations. On the other hand, as soon as the system starts to order, it will find that it is above the spinodal for ordered states and is no longer stable against compositional fluctuations. It may thus be regarded as a **conditional spinodal**.

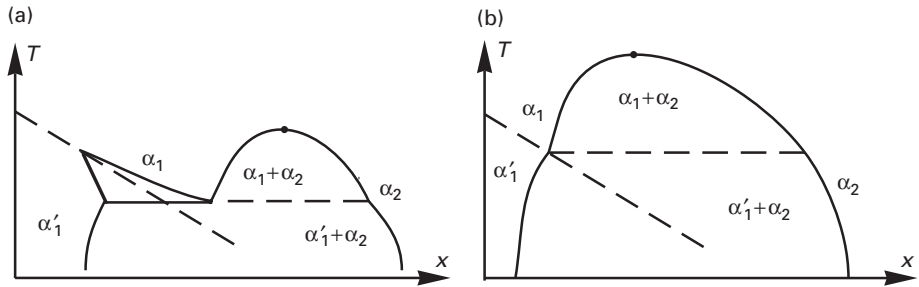


Figure 15.16 Different types of interaction between an ordering transition and a usual miscibility gap.

When looking for spinodals and trying to find the tri-critical point, we have here applied the condition of stability limit to the function $G_m(T, x)$ obtained with the equilibrium value of ξ inserted in $G_m(T, x, \xi)$. We could instead have used $G_m(T, x, \xi)$ directly by applying the stability condition from Section 6.7, reduced to two variables

$$\begin{vmatrix} g_{11} & g_{12} \\ g_{21} & g_{22} \end{vmatrix} = 0; \quad g_{11}g_{22} - (g_{12})^2 = 0. \quad (15.35)$$

Identify Δx with variable 1 and ξ with variable 2. Then G_m from Eq. (15.3) gives

$$\left(\partial^2 g_o / \partial x^2 + \frac{1}{2} g_{\xi\xi xx} \xi^2 + \frac{1}{24} g_{\xi\xi\xi\xi xx} \xi^4 \right) \left(g_{\xi\xi} + \frac{1}{2} g_{\xi\xi\xi\xi} \xi^2 \right) - \left(g_{\xi\xi x} \xi + \frac{1}{6} g_{\xi\xi\xi\xi x} \xi^3 \right)^2 = 0. \quad (15.36)$$

This relation should be applied to the equilibrium value of ξ which is equal to $(-6g_{\xi\xi}/g_{\xi\xi\xi\xi})^{1/2}$ in the ordered region according to Eq. (15.5). Neglecting the ξ^2 and ξ^4 terms in comparison to $\partial^2 g_o / \partial x^2$, and $g_{\xi\xi\xi\xi} \xi^2$ in comparison to $6g_{\xi\xi x}$ close to the transition line, we get

$$\partial^2 g_o / \partial x^2 = (g_{\xi\xi x})^2 / \left(g_{\xi\xi} / \xi^2 + \frac{1}{2} g_{\xi\xi\xi\xi} \right) = 3(g_{\xi\xi x})^2 / g_{\xi\xi\xi\xi}. \quad (15.37)$$

in full agreement with the previous result.

In the disordered region the equilibrium value is $\xi_e = 0$ and we find

$$\partial^2 g_o / \partial x^2 \cdot g_{\xi\xi} = 0. \quad (15.38)$$

Above the transition line $g_{\xi\xi} > 0$ and we would find a spinodal only if $\partial^2 g_o / \partial x^2$ turns negative before the transition line is approached on cooling. That would yield a usual miscibility gap, which would interact with the one formed due to the tendency of ordering. This is illustrated in Fig. 15.16(a).

If the usual miscibility gap is larger, it may cover the other one, as illustrated in Fig. 15.16(b). At the intersection with the transition line the phase boundary shows an angle. The reason is that g_{22} appears in the denominator of the expression for $(dx_2^\alpha/dT)_{\text{coex}}$, given in Section 11.4, and the phase boundary will thus be less steep (smaller dT/dx) below the transition line because g_{22} (i.e. $\partial^2 G_m / \partial x_2^2$) is smaller in the ordered region.

In our first calculation of the tri-critical point we started with a function $G_m(T, x, \xi)$ where ξ is an internal variable. An expression for its equilibrium value was then inserted and a function $G_m(T, x)$ was obtained which had different expressions above and below the transition line. They were then used in the calculation. Of course, one could just as well have used the results of experimental measurements in such a calculation. As a demonstration, let us suppose the contribution G_m^p to the Gibbs energy from an ordering reaction has been measured across the transition line, including the effects of short- as well as long-range order. Suppose further that this effect is found to be approximately the same function of $T - T_{tr}$ for all compositions and the transition temperature, T_{tr} , varies linearly with composition. Then

$$\frac{\partial G_m^p}{\partial x} = \frac{\partial G_m^p}{\partial T_{tr}} \cdot \frac{dT_{tr}}{dx} = -\frac{\partial G_m^p}{\partial T} \cdot \frac{dT_{tr}}{dx} \quad (15.39)$$

and

$$\frac{\partial^2 G_m^p}{\partial x^2} = \frac{\partial^2 G_m^p}{\partial T^2} \cdot \left(\frac{dT_{tr}}{dx}\right)^2 = -\frac{C_P^p}{T} \cdot \left(\frac{\partial T_{tr}}{\partial x}\right)^2, \quad (15.40)$$

where C_P^p is the effect of the ordering reaction on the heat capacity. Suppose the solution is otherwise ideal, $\partial^2 G_m^{\text{ideal}}/\partial x^2 = RT_{tr}/x(1-x)$. The intersection of a spinodal with the transition line is found where

$$\frac{\partial^2 G_m}{\partial x^2} = \frac{RT_{tr}}{x(1-x)} - \frac{C_P^p}{T_{tr}} \cdot \left(\frac{\partial T_{tr}}{\partial x}\right)^2 = 0 \quad (15.41)$$

$$x(1-x) = (RT_{tr}^2/C_P^p) \cdot \left(\frac{dx}{dT_{tr}}\right)^2. \quad (15.42)$$

This would be a tri-critical point. It is thus demonstrated that the tri-critical point will be closer to the T axis of the system, the larger the heat effect is. This is an expected result but the direct role played by C_P is very interesting in view of the many measurements indicating that C_P goes to very high values close to T_{tr} and theoretical models of ordering predicting that C_P actually should approach infinity at T_{tr} . The tri-critical point would thus approach the T axis of the binary system but the miscibility gap would there be extremely thin. It is also worth noting that C_P may approach different values on the two sides of T_{tr} . The spinodals on the two sides may thus intersect the transition line at different points. The point of intersection for the upper spinodal could fall much below the other one but would move up along the transition line if there is short-range order in the disordered state above the transition line. However, it could not reach the point of intersection for the lower spinodal because the heat effect of long-range order is larger.

It is also interesting to note the role of the slope of the transition line, dT_{tr}/dx . Its effect is demonstrated in Fig. 15.17(a) which shows an ordering reaction that does not occur in the pure components but has its ideal composition in the middle of the system. Miscibility gaps with tri-critical points may appear on both sides where the transition line is steep enough. It should be emphasized that this case is not related to the case of a first-order transition which forms a complete two-phase field in a binary

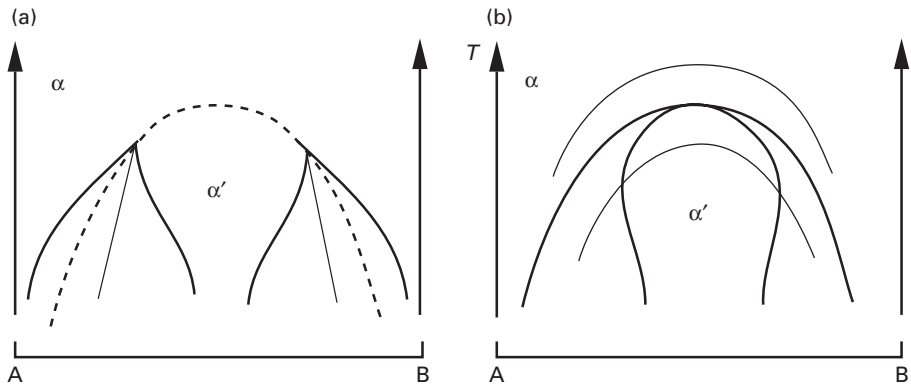


Figure 15.17 Two types of ordering miscibility gaps. (a) The ordering transition is of second order and the dashed line is the transition line. The spinodals are drawn with thin lines. (b) The transition is of first order and the thin lines represent stability limits calculated for a superheated or supercooled homogeneous system and without considering compositional fluctuations.

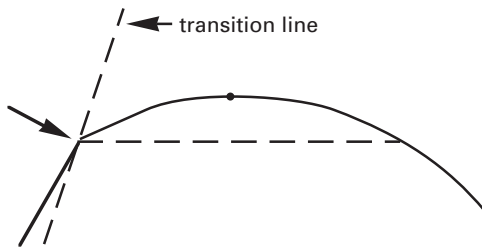


Figure 15.18 See Exercise 15.7.

diagram (see Fig. 15.17(b)). This two-phase field can be regarded as two connected miscibility gaps but there is no ordinary consolute point. Instead, the point of maximum is here a congruent point where the ordered phase can transform into the disordered phase by a first-order transition as it would do if the two phases were not related structurally.

The two points representing the limit of stability for an ordering reaction of first-order, indicated in Fig. 15.4(b), also extend into lines and they also demonstrate that the congruent point is not a critical point. The disordered state is metastable well below and the ordered state is metastable well above the temperature where the ordered and disordered states of the same composition have the same Gibbs energy. However, in order to find the real limits of stability, the spinodals, one should also consider the simultaneous variation in composition. That would make no difference when cooling the disordered state because g_{12} , which is defined as $\partial^2 G_m / \partial x \partial \xi$, is zero for $\xi = 0$. On the other hand, when heating the ordered state, one may encounter a spinodal before the limit of stability calculated without considering fluctuations in composition. This possibility is not indicated in Fig. 15.17(b).

Exercise 15.7

Figure 15.18 looks like a violation of the 180° rule. Try to find an explanation.

Hint

Compare with Fig. 15.16(b) and apply the same type of argument to the present case.

Solution

In the present case, the lower part of the binodal is situated *above* the transition line. In both diagrams, the binodal is steeper above the transition lines than below and the explanation is the same.

16 Interfaces

16.1 Surface energy and surface stress

By cutting a piece of material in two one can create two fresh surfaces and it is evident that they represent an increase of the energy of the system because bonds between atoms or molecules have been broken. Admittedly, the energy may then decrease somewhat by relaxation in the surface layer. The net effect can be defined as the surface energy or rather surface free energy or surface Gibbs energy under the usual isobarothermal conditions. We shall simply use the term surface energy and apply the same term to real surfaces as well as interfaces. Specific surface energy, i.e. the energy per surface area, will be denoted by σ .

However, the energy of the system may decrease further by minimizing the surface area. Primarily, there would be a tendency of the two new pieces to minimize the surface area by a shape change of the material and for an isotropic material the final shape would be spherical. That could happen quickly if the material is liquid but it could be an extremely slow process for a piece of solid material. The decrease of energy during the shape change is easily calculated for an isotropic material because its specific surface energy, σ , the energy per area, is constant.

Secondarily, the surface could contract further without a shape change by compressing the material in the sphere. It will thus be put under an increased pressure, formally caused by a stress in the surface. For a sphere one would get

$$\Delta P = 2f/r, \tag{16.1}$$

where r is the radius and f is the surface stress. For a liquid phase it seems reasonable to assume that the structure of the surface is reorganized as it contracts and is thus able always to maintain the same structure and the same specific surface energy. The tendency to contract would thus be directly connected to the energy decrease by the decrease of surface area. The surface stress f would then be equal to the specific surface energy σ .

The situation is different for a crystalline material where the surface layer is coherent with the material in the interior. Not only the area of the surface layer but also its structure will contract in order to fit into the structure of the compressed material. It is not even evident that the energy of the surface will decrease at all by such a contraction. In reality one may expect some decrease because there was probably a tendency of relaxation in the surface layer when first formed but it was prevented by the coherency. Some stress

was thus built into the surface layer and probably a compressive stress because the atoms or molecules in the surface layer may tend to attract each other more when losing their neighbours outside the surface. Very little is known about the magnitude of surface stress but it seems evident that it should be lower than the specific surface energy, $f < \sigma$.

What has here been said about surfaces applies as well to interfaces and it is then important to distinguish interfaces between two fluids, for which $f = \sigma$, from those where at least one of the phases is crystalline. For them $f < \sigma$.

Three materials can be in contact with each other along a line. In a section perpendicular to that line one can measure three contact angles and they can be calculated by minimizing the surface energy of the system. They are thus controlled by the three specific surface energies and the result is the same as if they were regarded as three balancing surface tensions. It is thus common to regard the specific surface energy as a surface tension, which is equal to σ . It is important not to confuse surface tension with surface stress, which is the quantity that gives rise to the increased pressure according to Eq. (16.1). The term surface tension should be avoided as much as possible.

The effect of surface energy is particularly pronounced for liquids inside the thin holes of capillaries and this whole field is often referred to as capillarity.

16.2 Phase equilibrium at curved interfaces

We shall start with a general method of finding equilibrium conditions by maximizing the entropy under constant energy, volume and content of matter. It is based on the use of Lagrange's multipliers. We shall apply the method to a system with a spherical β phase in an α matrix. We have $V^\beta = (4\pi/3)r^3$ and the surface energy will be $4\pi r^2\sigma = 4\pi\sigma(3V^\beta/4\pi)^{2/3}$.

For a completely closed (isolated) system with $dN_i = dV = dQ = 0$, and thus $dU = 0$, the combined law yields, e.g., after rearranging the terms in Eq. (3.1),

$$dS = (1/T)dU + (P/T)dV - \sum (\mu_i/T)dN_i + (D/T)d\xi = (D/T)d\xi. \quad (16.2)$$

The condition of equilibrium is thus obtained from the maximum of S for the total system but we must find that maximum under the constant values of U , V and N_i

$$U^\alpha + U^\beta = U(\text{constant}) \quad (16.3)$$

$$V^\alpha + V^\beta = V(\text{constant}) \quad (16.4)$$

$$N_i^\alpha + N_i^\beta = N_i(\text{constant}). \quad (16.5)$$

According to Lagrange's method we should form a new function which must have its maximum at the same time because the additional terms are always zero.

$$L = S^\alpha + S^\beta + \lambda[U - U^\alpha - U^\beta - 4\pi\sigma(3V^\beta/4\pi)^{2/3}] \\ + \nu(V - V^\alpha - V^\beta) + \sum \eta_i(N_i - N_i^\alpha - N_i^\beta). \quad (16.6)$$

Here, λ , ν and η_i are Lagrange multipliers and their values will be determined by maximizing L . When searching for the maximum, we get six conditions,

$$\partial L/\partial U^\alpha = \partial S^\alpha/\partial U^\alpha - \lambda = 0 \quad (16.7)$$

$$\partial L/\partial U^\beta = \partial S^\beta/\partial U^\beta - \lambda = 0 \quad (16.8)$$

$$\partial L/\partial V^\beta = \partial S^\beta/\partial V^\beta - \lambda\sigma(32\pi/3V^\beta)^{1/3} - \nu = 0 \quad (16.9)$$

$$\partial L/\partial V^\alpha = \partial S^\alpha/\partial V^\alpha - \nu = 0 \quad (16.10)$$

$$\partial L/\partial N_i^\alpha = \partial S^\alpha/\partial N_i^\alpha - \eta_i = 0 \quad (16.11)$$

$$\partial L/\partial N_i^\beta = \partial S^\beta/\partial N_i^\beta - \eta_i = 0. \quad (16.12)$$

All the derivatives of S are well known from the combined law applied to one phase at a time. We obtain

$$1/T^\alpha = \partial S^\alpha/\partial U^\alpha = \lambda = \partial S^\beta/\partial U^\beta = 1/T^\beta \quad (16.13)$$

$$\mu_i^\alpha/T^\alpha = -\partial S^\alpha/\partial N_i^\alpha = -\eta_i = -\partial S^\beta/\partial N_i^\beta = \mu_i^\beta/T^\beta. \quad (16.14)$$

We have thus derived the well-known conditions of equilibrium, $T^\alpha = T^\beta$, and $\mu_i^\alpha = \mu_i^\beta$. The remaining two equations give

$$\begin{aligned} P^\alpha/T^\alpha &= \partial S^\alpha/\partial S^\alpha = \nu = \partial S^\beta/\partial V^\beta - \lambda\sigma(32\pi/3V^\beta)^{1/3} \\ &= P^\beta/T^\beta - \lambda\sigma(32\pi/3V^\beta)^{1/3} \end{aligned} \quad (16.15)$$

$$P^\beta - P^\alpha = \sigma(32\pi/3V^\beta)^{1/3} = 2\sigma/r \quad (16.16)$$

This is a well-known expression for the pressure difference for fluid/fluid interfaces but we have not been able to take into account the possibility that the pressure difference should instead be given by Eq. (16.1) with f instead of σ if the β phase were a crystalline substance. Furthermore, we found $P^\alpha \neq P^\beta$ and it is evident that the ordinary equilibrium condition, Eq. (16.14) or $\mu_i^\alpha = \mu_i^\beta$ when $T^\alpha = T^\beta$, here applies to two phases under different pressures. For clarity it should thus be written

$$\mu_i^\alpha(P^\alpha) = \mu_i^\beta(P^\beta). \quad (16.17)$$

This is a famous relation derived by Gibbs [3]. It remains to be discussed whether this relation applies to the local situation at any spherical piece of interface where r is the radius of curvature or only when there is a full sphere. In the next section we shall thus examine the problem in more detail.

16.3 Phase equilibrium at fluid/fluid interfaces

The effect of capillarity on the equilibrium between the two phases separated by an interface can be treated with any characteristic state function and we shall now use the Gibbs energy because its natural variables are those that are usually kept constant

experimentally, P , T and content of matter. The total Gibbs energy of an $\alpha + \beta$ system with an α/β interface can be given as

$$G = G^\alpha + G^\beta + G^\sigma. \quad (16.18)$$

The α phase will be chosen as the matrix phase and it will be under the same pressure as the surroundings, P . The β phase will be an inclusion under a higher pressure due the surface stress, $P^\beta > P$, and it will depend on the size of the β inclusion through Eq. (16.1). The amounts of the various components in the β phase will be regarded as internal variables because they can vary by exchanges with the α phase, which is part of the system. We shall later study the effect on G of a transfer of a small amount of a single component j to β from α , dN_j^β , but we shall first consider an exchange of balanced amounts of all components, i.e., the composition of the β inclusion will be fixed and given by x_i^β and thus $dN_i^\beta = x_i^\beta dN^\beta$. The independent variable will thus be N^β , and P^β is a dependent variable through Eq. (16.1) because the radius r depends on N^β .

According to Section 3.4 the Gibbs energy of β must be expressed in the following way using the values of T and P in the surroundings,

$$G^\beta = N^\beta [U_m^\beta(P^\beta, T^\beta) - TS_m^\beta(P^\beta, T^\beta) + PV_m^\beta(P^\beta, T^\beta)]. \quad (16.19a)$$

The reason is that U , S and V are additive properties but G is not unless T and P have the same values in all the subsystems. In the present case, which is isothermal we get

$$\begin{aligned} G^\beta &= N^\beta [U_m^\beta(P^\beta) - TS_m^\beta(P^\beta) + PV_m^\beta(P^\beta)] \\ &= G^\beta(P^\beta) - (P^\beta - P)V^\beta(P^\beta). \end{aligned} \quad (16.19b)$$

$G^\beta(P^\beta)$ is a Gibbs energy function defined for a β phase in the hypothetical case where the pressure of P^β applies to the surroundings as well as the β phase itself. We shall now take the derivative of Eq. (16.18) with respect to the only independent variable, N^β , whereas P^β is a variable dependent on the size of the β particle through Eq. (16.1), i.e. on N^β . However, we would like to use the quantity $G_m^\beta(P^\beta)$, which is defined as $(\partial G^\beta / \partial N^\beta)_{P^\beta}$ where P^β is treated as an independent variable. Then, we must also take into account the partial derivative with respect to P^β .

$$\begin{aligned} \frac{dG}{dN^\beta} &= \frac{dG^\alpha}{dN^\beta} + \left(\frac{\partial G^\beta}{\partial N^\beta} \right)_{P^\beta} + \left(\frac{\partial G^\beta}{\partial P^\beta} \right)_{N^\beta} \\ &\quad \times \frac{dP^\beta}{dN^\beta} - \frac{dP^\beta}{dN^\beta} \times V^\beta(P^\beta) - (P^\beta - P) \times \frac{dV^\beta}{dN^\beta} + \frac{dG^\sigma}{dN^\beta}. \end{aligned} \quad (16.20)$$

The third and fourth terms on the right-hand side eliminate each other because $\partial G / \partial P = V$ and it is thus unnecessary to discuss the interpretation of dP^β / dN^β .

$$dG/dN^\beta = - \sum x_i^\beta \mu_i^\alpha(P) + G_m^\beta(P^\beta) - (P^\beta - P) \times dV^\beta/dN^\beta + dG^\sigma/dN^\beta. \quad (16.21)$$

Equation (16.21) will now be applied to a spherical β particle in a fluid/fluid system. The surface energy, G^σ , is equal to $A^\beta \cdot \sigma$ and $dA^\beta = 8\pi r dr = (2/r)dV^\beta$. The specific

surface energy can be regarded as independent of size except for nano-sized particles, yielding

$$dG^\sigma/dN^\beta = \sigma \times dA^\beta/dN^\beta = (2\sigma/r) \times dV^\beta/dN^\beta \quad (16.22)$$

According to Eq. (16.1) we can express $P^\beta - P$ as $2\sigma/r$ since $f = \sigma$ for a fluid/fluid system. The last two terms in Eq. (16.21) thus eliminate each other, leaving

$$dG/dN^\beta = - \sum x_i^\beta \mu_i^\alpha(P) + G_m^\beta(P^\beta). \quad (16.23)$$

At this time it is thus unnecessary to discuss the interpretation of dV^β/dN^β as well as dP^β/dN^β . At equilibrium with respect to growth of the β inclusion dG/dN^β must be zero and we thus obtain the following equilibrium condition,

$$\sum x_i^\beta \mu_i^\alpha(P) = G_m^\beta(P_e^\beta). \quad (16.24)$$

The subscript 'e' has been added in order to emphasize that this is the increased pressure in β required for equilibrium with the α phase of its given composition. It is important to notice that the properties of each phase must here be evaluated at its own pressure. It is more convenient to compare them at the same pressure. We may thus like to introduce $G_m^\beta(P)$. That can be done using the following relations obtained with a constant compressibility κ of the liquid β phase,

$$V_m^\beta(P^\beta) = V_m^\beta(P)(1 - \kappa(P^\beta - P)) \quad (16.25)$$

$$\begin{aligned} G_m^\beta(P^\beta) - G_m^\beta(P) &= \int_P^{P^\beta} V_m^\beta(P^\beta) dP^\beta = V_m^\beta(P) (P^\beta - P - \frac{1}{2}\kappa(P^\beta - P)^2) \\ &= V_m^\beta(P)(P^\beta - P)(1 - \kappa\sigma/r). \end{aligned} \quad (16.26)$$

We can now introduce the driving force for precipitation of β from the α matrix and using the equilibrium condition Eq. (16.24) we find,

$$\begin{aligned} -\Delta G_m &\equiv \sum x_i^\beta \mu_i^\alpha(P) - G_m^\beta(P) = G_m^\beta(P_e^\beta) - G_m^\beta(P) \\ &= V_m^\beta(P)(P_e^\beta - P)(1 - \kappa\sigma/r_e). \end{aligned} \quad (16.27)$$

$(1 - \kappa\sigma/r_e)$ can be regarded as a correction factor to the result for an incompressible β phase. It is close to unity and is thus of minor importance.

Expressing $P_e^\beta - P$ as $2\sigma/r_e$ we can write the equilibrium condition, Eq. (16.24), as

$$\sum x_i^\beta \mu_i^\alpha(P) - G_m^\beta(P) = -\Delta G_m = (2\sigma/r_e)V_m^\beta(P)(1 - \kappa\sigma/r_e). \quad (16.28)$$

The equilibrium size of a spherical droplet is thus

$$r_e = 2\sigma(1 - \kappa\sigma/r_e)/(-\Delta G_m/V_m^\beta(P)). \quad (16.29)$$

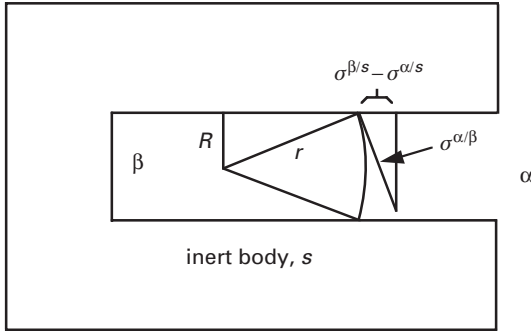


Figure 16.1 The use of a cylindrical hole in an inert body to achieve a constant pressure P^β in an included phase.

Of course, $-\Delta G_m$ is a positive quantity if there is a tendency to form β from the α phase.

For a gas bubble one has $P V_m = RT$ and obtains

$$\int V_m^\beta dP = RT \ln (P_e^\beta / P) \quad (16.30)$$

$$-\Delta G_m = \sum x_i^\beta \mu_i^\alpha(P) - G_m^\beta(P) = RT \ln (P_e^\beta / P) \quad (16.31)$$

$$P_e^\beta = P \exp(-\Delta G_m / RT) \quad (16.32)$$

$$r_e = 2\sigma / (P_e^\beta - P) = 2\sigma / P [\exp(-\Delta G_m / RT) - 1]. \quad (16.33)$$

When the β particle grows, its internal pressure decreases and one may wonder if that fact should not affect the equilibrium condition. It should thus be interesting also to consider a case where P^β does not vary with the size of the β phase. That could be realized with the arrangement in Fig. 16.1. When β is growing, the spherical α/β interface moves a distance dl without any change of shape. The change of surface energy will depend on the changes of the interfaces to the wall of the container, $(\sigma^{\beta/s} - \sigma^{\alpha/s}) \times 2\pi R dl$. However, that difference controls the contact angle of the α/β interface to the surface of the container through an energy balance and thus its curvature. Figure 16.1 yields

$$dG^\sigma = 2\pi R(\sigma^{\beta/s} - \sigma^{\alpha/s})dl = \pi R^2(2\sigma^{\alpha/\beta}/r)dl. \quad (16.34)$$

In the following we shall drop the superscript in $\sigma^{\alpha/\beta}$. Introduction of the change of volume, $dV^\beta = \pi R^2 dl$, yields

$$dG^\sigma = (2\sigma/r)dV^\beta. \quad (16.35)$$

This is the same result as for the spherical particle. We may conclude that the effect of surface energy can be applied locally to any piece of a fluid/fluid interface. An explanation why a possible change of P^β during growth has no effect on the equilibrium conditions is provided by the fact that the two terms containing the derivative dP^β/dN^β in Eq. (16.20) eliminated each other. Furthermore, according to Eq. (16.22) there are two terms in Eq. (16.21) with the derivative dV^β/dN^β , which actually contains dP^β/dN^β , in the same way as the full derivative dG^β/dN^β was represented by two terms in Eq. (16.20)

containing dP^β/dN^β . They also eliminated each other. Finally, it may here be mentioned without giving the proof that for a non-spherical interface one should replace $2/r$ by an expression using the principal radii of curvature, $1/\rho_1 + 1/\rho_2$.

Exercise 16.1

Evaluate the equilibrium size of a bubble if the supersaturation of the matrix, expressed as $-\Delta G_m$, is very low.

Hint

$$\ln(1 + \varepsilon) \cong \varepsilon$$

Solution

Equation (16.32) gives for small $(P^\beta - P)/P$: $-\Delta G_m = RT \ln(P^\beta/P) = RT \ln(1 + (P^\beta - P)/P) \cong RT((P^\beta - P)/P) = (2\sigma/r)V_m^\beta(P)$. In this limit there is full agreement with an incompressible liquid according to Eq. (16.29).

16.4 Size stability for spherical inclusions

We have derived an equilibrium condition for a spherical particle in a fluid/fluid system but should now examine if it is a stable or unstable equilibrium. According to Chapter 6 we could examine the stability through the second derivative of G . We shall thus evaluate the derivative of Eq. (16.23). The α phase gives no contribution since its chemical potentials are not affected by the size and the stability is obtained as

$$\frac{d^2G}{d(N^\beta)^2} = \frac{dG_m^\beta}{dP^\beta} \cdot \frac{dP^\beta}{dN^\beta} = V_m^\beta \cdot \frac{dP^\beta}{dN^\beta}. \quad (16.36)$$

This will be zero when P^β is kept constant, as in Fig. 16.1. That can be compared to the case in the left-hand part of Fig. 6.1 for a circular cross-section. All positions are equivalent.

If the hole in Fig. 16.1 is slightly conical, r could either increase or decrease during growth. If the hole is narrowing to the right, r will decrease and the pressure will increase as the β phase grows. The stability will be positive and there is a stable situation at the position where the equilibrium condition, Eq. (16.29), is satisfied. If it is widening to the right, the stability will be negative and the situation will be unstable. The β phase would either grow out of the hole or shrink.

It is evident that for a spherical particle the instability will be even larger. The pressure will decrease during growth. There would be a critical size satisfying the equilibrium condition, Eq. (16.29). If the β particle were just a little smaller, it would shrink and disappear. If it were just a little larger, it would grow even larger. If the reservoir of α phase were not infinite, the supersaturation would decrease gradually during growth and

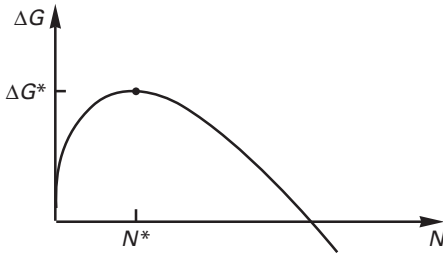


Figure 16.2 The Gibbs energy increase as a function of the size of a spherical particle of a liquid phase. N^* is the size of a critical nucleus and ΔG^* is its activation energy.

the growth would eventually stop. If there were a large number of β particles, they would be smaller when growth stops. On the other hand, not even such an ensemble would be stable. A small fluctuation in size would make the slightly larger particles grow at the expense of the smaller ones because the composition of the α matrix in local equilibrium with a particle would differ depending on the size, according to the equilibrium condition Eq. (16.28). There would thus be diffusion of material through the α matrix from the smaller particles to the larger ones. This phenomenon is called Ostwald ripening.

16.5 Nucleation

For a system with a spherical β particle included in an α matrix we can formulate the total Gibbs energy from Eq. (16.18), e.g. by inserting Eq. (16.19). The result will depend on the size N^β .

$$G(N^\beta) = \sum (N_i^\circ - N_i^\beta) \mu_i^\alpha(P) + G^\beta(P^\beta) - (P^\beta - P)V^\beta(P^\beta) + A\sigma, \quad (16.37)$$

where N_i° is the initial i content in the α matrix. For a spherical β particle the last term can be expressed as $3\sigma V/r$ and we can express $P^\beta - P$ as $2f/r$ according to Eq. (16.1). The change of Gibbs energy from the initial homogeneous α matrix will be

$$\begin{aligned} \Delta G(N^\beta) &= G(N^\beta) - G(0) \\ &= - \sum N_i^\beta \mu_i^\alpha(P) + G^\beta(P^\beta) - (2f/r)V^\beta(P^\beta) + (3\sigma/r)V^\beta(P^\beta). \end{aligned} \quad (16.38)$$

For a liquid β phase $f = \sigma$ and Eq. (16.37) simplifies to

$$\Delta G(N^\beta) = N^\beta \left[- \sum x_i^\beta \mu_i^\alpha(P) + G_m^\beta(P^\beta) + (\sigma/r)V_m^\beta(P^\beta) \right]. \quad (16.39)$$

Since r is proportional to $(N^\beta)^{1/3}$, the function will look as illustrated in Fig. 16.2. It is evident that the formation of β cannot start spontaneously from a zero size. There is a barrier of height ΔG^* , which must be overcome by some kind of activated process. A β particle of a critical size N^* is in an unstable equilibrium. However, at both types

of equilibrium the first two terms in Eq. (16.39) eliminate each other according to the equilibrium condition in Eq. (16.24). Using $P_e^\beta - P = 2\sigma/r_e$ we obtain

$$\begin{aligned}\Delta G^* &= N^* \cdot (\sigma/r_e) V_m^\beta(P_e^\beta) = \frac{1}{2} N^* \times (P_e^\beta - P) V_m^\beta(P_e^\beta) = \frac{4}{3} \pi \sigma (r_e)^2 \\ &= \frac{16\pi\sigma^3}{3(P_e^\beta - P)^2}.\end{aligned}\quad (16.40)$$

This is the energy, which must be supplied by some kind of activated process in order for the β phase to form. It is regarded as the **activation energy**. A particle of this size can either grow or shrink by a small fluctuation in size. It is regarded as a **critical nucleus**. Equation (16.40) expresses the activation energy in the most general way but in order to apply it to a particular case one must relate it to the driving force, $-\Delta G_m$. It is then necessary to define the compressibility of the β phase. For a compressible liquid one can use Eq. (16.27), obtaining

$$\begin{aligned}\Delta G^* &= \frac{16\pi\sigma^3}{3(-\Delta G_m/V_m^\beta(P))^2} (1 - \kappa\sigma/r_e)^2 \\ &\cong \frac{16\pi\sigma^3}{3(-\Delta G_m/V_m^\beta(P))^2} (1 - 2\kappa\sigma/r_e).\end{aligned}\quad (16.41)$$

Equation (16.40) is still valid for a bubble of an ideal gas but one should insert Eq. (16.32) instead of Eq. (16.27),

$$\Delta G^* = \frac{16\pi\sigma^3}{3P^2[\exp(-\Delta G_m/RT) - 1]^2}.\quad (16.42)$$

Finally, we should discuss the fact that a supersaturated solution can be unstable with respect to two quite different kinds of fluctuations. Here we have considered a critical nucleus being a fluctuation small in extent but large in composition (and structure). In Chapter 15 we discussed spinodal decomposition, which can start spontaneously without any activation barrier, i.e. without any critical nucleus. However, that treatment also describes critical nuclei when the composition is moved outside the spinodal. Right on the spinodal the critical nucleus is represented by a point at $1/\lambda = 0$ and of composition x^0 . In principle, it is thus an infinitely extended fluctuation with an infinitely small change of composition. With an initial composition further outside the spinodal, the change in composition grows and an arrow in Fig. 15.13 illustrates such a case. A detailed calculation would show that the critical fluctuation, i.e. nucleus, becomes more localized and starts to resemble the kind of critical nucleus described in the present chapter. The explanation why the two treatments give different results is that a constant σ was used here whereas it decreases with decreasing difference in composition between fluctuation and matrix in the spinodal treatment. The use of a constant σ in the present case can be justified by assuming that it mainly depends on the difference in structure between the two phases. In the spinodal treatment there is only a difference in composition.

Exercise 16.2

In textbooks one often finds the following simple treatment of nucleation. The increase of the Gibbs energy of a system due to a nucleus is given as $\Delta G = (4\pi/3)r^3(\Delta G_m/V_m) + 4\pi r^2\sigma$ which yields: $\partial\Delta G/\partial r = 4\pi r^2(\Delta G_m/V_m) + 8\pi r\sigma = 0$; $r^* = 2\sigma/(-\Delta G_m/V_m)$; $\Delta G^* = (4\pi/3)r^{*3}(\Delta G_m/V_m) + 2\pi r^{*2}\sigma = (2\pi/3)r^{*3}(-\Delta G_m/V_m) = (16\pi/3)\sigma^3/(-\Delta G_m/V_m)^2$. Compare this result with the correct result given by Eq. (16.42) when applied to the nucleation of a gas bubble at a temperature above the boiling point of a liquid composed of only one species.

Hint

Approximate the gas as ideal. The vapour pressure of the liquid matrix, corresponding to P^β in our treatment, must be larger than the pressure on the liquid from the surroundings, P .

Solution

Equation (16.32) reduces to the textbook result for small $-\Delta G_m/RT$: $\Delta G^* \cong (16\pi/3)\sigma^3/[-\Delta G_m P/RT]^2 = (16\pi/3)\sigma^3/(-\Delta G_m/V_m)^2$. However, small $-\Delta G_m/RT$ means small $\ln(P^\beta/P)$. Large values of P^β/P can easily be obtained by superheating of a liquid or when the gas is dissolved in a liquid or solid. The textbook treatment holds strictly for incompressible phases, only.

16.6 Phase equilibrium at crystal/fluid interface

If one of the phases is crystalline, the derivations will be more complicated because $f \neq \sigma$. There will be even more complications if the crystalline phase is the matrix phase because it may build up internal stresses in the matrix during a growth process. We shall thus limit the discussion to cases with a crystalline phase included in a fluid matrix.

Equation (16.21) was derived without any particular requirement about the nature of the interface but was then applied to a fluid/fluid interface. It will now be applied to a crystalline/fluid interface. When expressing the pressure difference, we shall thus retain the surface stress, f from Eq. (16.1). On the other hand, the specific surface energy, σ , should still appear when expressing the surface energy term, G^σ . However, there one must notice an important difference. It has already been mentioned that a fluid/fluid interface will reorganize its structure if expanded or contracted and the surface energy is always proportional to the actual area, i.e., σ is constant in the expression $G^\sigma = A\sigma$. With full coherency to the interior, the surface of a crystalline phase will not change its structure if the bulk is expanded or compressed. It may thus seem reasonable to approximate the surface energy as $A_P\sigma_P$, evaluated at the pressure in the surroundings,

P . Furthermore, in the case where the matrix is a condensed fluid, i.e. a liquid, one may argue that the structure on that side of the interface should relax to some degree. However, that possibility will be neglected whereas the consequences of the above approximation will be examined.

The surface energy will be described with $G^\sigma = A_P \sigma_P$ where σ_P is measured at a planar interface and will be treated as independent of P^β . Eq. (16.22) will give

$$\frac{dG^\sigma}{dN^\beta} = \frac{dA_P}{dN^\beta} \cdot \sigma_P = \frac{2\sigma_P}{r_P} \cdot \frac{dV^\beta(P)}{dN^\beta} = \frac{2\sigma_P}{r_P} \cdot V_m^\beta(P). \quad (16.43)$$

The radius r_P is also measured at the pressure P .

In analogy to the description of G^σ we may introduce f_P/r_P in Eq. (16.1) obtaining

$$\begin{aligned} dP^\beta &= (-2f_P/r_P^2)dr_P = (-2f_P/r_P^2) \cdot r_P dV^\beta(P)/3V^\beta(P) \\ &= (-2f_P/3r_P V^\beta(P)) \cdot V_m^\beta(P) dN^\beta, \end{aligned} \quad (16.44)$$

since $3dr/r = dV/V$. This time we must study how to interpret dV^β/dN^β in Eq. (16.21), considering the dependent variable P^β . Inserting $(\partial V^\beta/\partial P^\beta)_{N^\beta}$ from Eq. (16.25) and dP^β/dN^β from Eq. (16.44) we obtain

$$\begin{aligned} dV^\beta/dN^\beta &= (\partial V^\beta/\partial N^\beta)_{P^\beta} + (\partial V^\beta/\partial P^\beta)_{N^\beta} \cdot dP^\beta/dN^\beta \\ &= V_m^\beta(P^\beta) - \kappa V^\beta(P) \cdot (-2f_P V_m^\beta(P)/3r_P V^\beta(P)) \\ &= V_m^\beta(P)(1 - 2\kappa f_P/r_P + 2\kappa f_P/3r_P) \\ &= V_m^\beta(P)(1 - 4\kappa f_P/3r_P). \end{aligned} \quad (16.45)$$

From Eq. (16.26) we find

$$G_m^\beta(P^\beta) = G_m^\beta(P) + (P^\beta - P)V_m^\beta(P)(1 - \kappa f_P/r_P). \quad (16.46)$$

Inserting Eqs (16.45) and (16.46) and the definition of ΔG_m from Eq. (16.27) in Eq. (16.21) we obtain

$$\begin{aligned} dG/dN^\beta &= - \sum x_i^\beta \mu_i^\alpha(P) + G_m^\beta(P) \\ &\quad - (P^\beta - P)dV_m^\beta(1 - \kappa f_P/r_P - 1 + 4\kappa f_P/3r_P) \\ &= \Delta G_m + [(2f_P/r_P)(\kappa f_P/3r_P) + (2\sigma_P/r_P)] V_m^\beta(P). \end{aligned} \quad (16.47)$$

In Eq. (16.21) the third and fourth terms eliminated each other because $f = \sigma$. That is not the case here and it was thus necessary this time to interpret dV^β/dN^β and the result depended on the compressibility, κ . It is interesting to note that for an incompressible β phase the third term in Eq. (16.21) would be eliminated by a term appearing in Eq. (16.46) when $G_m^\beta(P)$ was introduced. Only a correction term proportional to κ remained when the compressibility was considered. In practice, P^β would probably be unknown because of lack of information on the surface stress, f_P , and one would be dealing with $G_m^\beta(P)$. It is evident that the surface stress is not of much practical importance and the compressibility will cause only a small correction term.

Putting dG/dN^β to zero in Eq. (16.47) we obtain the equilibrium condition for crystalline/fluid interfaces.

$$-\Delta G_m = \left[(2\sigma_P/r_{Pe}) + (2\kappa/3)(f_P/r_{Pe})^2 \right] V_m^\beta(P) \quad (16.48)$$

$$r_{Pe} = 2\sigma_P / \left[-\Delta G_m / V_m^\beta(P) - (2\kappa/3)(f_P/r_{Pe})^2 \right]. \quad (16.49)$$

It may be added that the actual radius at equilibrium is obtained as

$$r_e = r_{Pe} \left(1 - \kappa(P^\beta - P) \right)^{1/3} \cong r_{Pe} \left(1 - \frac{2}{3}\kappa f_P/r_{Pe} \right). \quad (16.50)$$

The important conclusion to be drawn from Eq. (16.48) is that the effect of surface energy is the same for solid and liquid inclusions. The Gibbs energy of both kinds of phases is increased by $2\sigma V_m/r$ which is equal to $V_m\Delta P$ only for liquids. It is common to neglect this fact and to express $2\sigma/r$ as ΔP also for solids, a procedure that does not cause any erroneous results. There are several equations in the present textbook where $V_m\Delta P$ is used without explicit mention that it should be interpreted as $2\sigma V_m/r$ for solids.

By modifying Eq. (16.38) for the present case we obtain for the increase of Gibbs energy due to the precipitation of a β inclusion,

$$\begin{aligned} \Delta G(N^\beta) &= N^\beta \left[-\sum x_i^\beta \mu_i^\alpha + G_m^\beta(P^\beta) - (P^\beta - P)V_m^\beta(P^\beta) + (3\sigma_P/r_P)V_m^\beta(P) \right] \\ &= N^\beta \left[\Delta G_m + (P^\beta - P)V_m^\beta(P)(1 - \kappa f_P/r_P) - (P^\beta - P)V_m^\beta(P)(1 - 2\kappa f_P/r_P) \right. \\ &\quad \left. + (3\sigma_P/r_P)V_m^\beta(P) \right] = N^\beta \left[\Delta G_m + (2f_P/r_P)V_m^\beta(P)(\kappa f_P/r_P) + (3\sigma_P/r_P)V_m^\beta(P) \right]. \end{aligned} \quad (16.51)$$

Inserting ΔG_m from Eq. (16.48) we obtain for equilibrium of a spherical crystalline inclusion

$$\begin{aligned} \Delta G^* &= N^* V_m^\beta(P) \left[-2\sigma_P/r_{Pe} - (2\kappa/3)(f_P/r_{Pe})^2 + 2\kappa(f_P/r_{Pe})^2 + 3\sigma_P/r_{Pe} \right] \\ &= \frac{4}{3}\pi r_{Pe}^3 \cdot (\sigma_P/r_{Pe}) (1 + 4\kappa f_{Pe}^2/3\sigma_P r_{Pe}) = \frac{16\pi\sigma_P^3 (1 + 4\kappa f_P^2/3\sigma_P r_{Pe})}{3 \left[-\Delta G_m / V_m^\beta(P) - (2\kappa/3)(f_P/r_{Pe})^2 \right]}. \end{aligned} \quad (16.52)$$

Again we find that the surface stress is of minor importance and enters only in corrections, depending on the compressibility. For incompressible crystalline solids the result is identical to the result for incompressible liquids obtained from Eq. (16.41).

Exercise 16.3

Consider two solid (β) spherical particles of a pure element, floating in a melt of the same element. Derive an equation for the difference in temperature between them if they have different radii, r_1 and r_2 . Which one will grow as a result of the heat flow between them?

Hint

Simplify the problem by assuming incompressibility. Two phases at an interface might have the same T , yielding $\Delta G_m = \Delta H_m - T\Delta S_m$. At the melting point T_0 , $\Delta G_m = 0$

and we get $\Delta G_m = (T_o - T)\Delta S_m$. For solidification we define ΔG_m and ΔS_m as negative.

Solution

Equation (16.48) yields $(2\sigma V_m^\beta/r) = -\Delta G_m = (T_o - T)(-\Delta S_m)$. Compare two particles: $2\sigma V_m^\beta(1/r_1 - 1/r_2) = (T_2 - T_1)(-\Delta S_m)$. Suppose $r_2 > r_1$. Then $T_2 > T_1$. Heat will flow from the larger one and the heat of solidification can thus leave that region. The larger particle will thus grow at the expense of the smaller one if the system is thermally insulated. This is an example of Ostwald ripening.

16.7 Equilibrium at curved interfaces with regard to composition

So far we have only considered the equilibrium with respect to the transfer of balanced amounts of the various components. Now we shall study the transfer of a single component, dN_j^β , by again regarding only two variables, the independent variable N_j^β and the dependent variable P^β . Instead of Eqs (16.20) and (16.21) we now obtain

$$\begin{aligned} \frac{dG}{dN_j^\beta} &= -\mu_j^\alpha(P) + \mu_j^\beta(P^\beta) + \left(\frac{\partial G^\beta}{\partial P^\beta} \right)_{N_j^\beta} \frac{dP^\beta}{dN_j^\beta} - \frac{dP^\beta}{dN_j^\beta} \cdot V^\beta(P^\beta) \\ &\quad - (P^\beta - P) \cdot \frac{dV^\beta}{dN_j^\beta} + \frac{dG^\sigma}{dN_j^\beta} = -\mu_j^\alpha(P) + \mu_j^\beta(P^\beta) - (2f/r)dV^\beta/dN_j^\beta \\ &\quad + (2\sigma/r)dV^\beta/dN_j^\beta. \end{aligned} \quad (16.53)$$

For a fluid/fluid interface we have $f = \sigma$ and the last two terms eliminate each other. At equilibrium $dG/dN_j^\beta = 0$ and the equilibrium condition would then be

$$\mu_j^\alpha(P) = \mu_j^\beta(P_e^\beta). \quad (16.54)$$

We have again derived Gibbs' famous relation. However, he did not have to introduce the limitation that σ is independent of composition because he considered a β phase with only one component. His result is a special case of Eq. (16.24).

When replacing P^β by P we must know how the partial molar volume, V_j^β varies with P^β . For simplicity we shall assume that the same compressibility applies to the partial volumes as to the integral volume. By integration we obtain similar to Eq. (16.26),

$$\int V_j^\beta dP = V_j^\beta(P)(P^\beta - P)(1 - \kappa\sigma/r). \quad (16.55)$$

We can thus write the equilibrium condition, Eq. (16.54), as

$$\mu_j^\alpha(P) = \mu_j^\beta(P) + (2\sigma/r_e)V_j^\beta(P)(1 - \kappa\sigma/r_e). \quad (16.56)$$

By summing this over all the components, we can recreate Eq. (16.28). Equation (16.56) describes the equilibrium for all the components whereas Eq. (16.28) is a necessary but

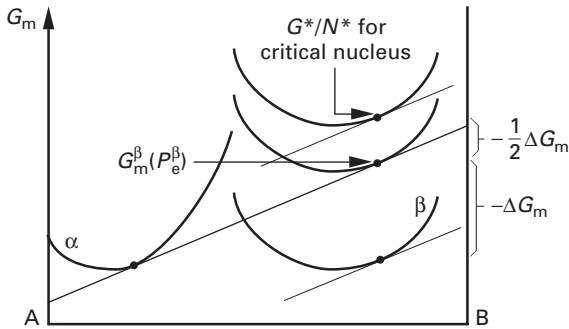


Figure 16.3 Molar Gibbs energy diagram for nucleation of β from a supersaturated α solution.

not sufficient condition. The equilibrium size, r_e , was then expressed in terms of ΔG_m in Eq. (16.29). It can now be inserted into Eq. (16.56) yielding for the equilibrium condition

$$\mu_j^\alpha(P) = \mu_j^\beta(P) - \Delta G_m \cdot V_j^\beta / V_m^\beta. \quad (16.57)$$

From its definition in Eq. (16.27) one can evaluate the driving force, $-\Delta G_m$, provided that one knows the critical composition of the β phase. However, the driving force and the composition can both be determined graphically for any given supersaturated α matrix. One should draw the tangent to the α curve for the composition of the matrix and then lower it until it becomes a tangent to the G_m^β curve. That should be done by a parallel displacement if all $V_j = V_m$ and the magnitude of the displacement gives the driving force, $-\Delta G_m$. This means that one has made a parallel tangent construction. If $V_j \neq V_m$ then Eq. (16.57) requires that one rotates the tangent slightly to make sure that the displacements on the component axes are proportional to the V_j values. If all $V_j = V_m$ then one could instead lift the G_m^β curve until it touches the α tangent. That would be a common tangent construction. See Fig. 16.3.

For the critical nucleus, including the contribution from the surface energy, one can give a point representing its Gibbs energy divided by N^* . It is obtained by adding the activation energy, ΔG^* , divided by N^* to the G_m value of β on the common tangent. $\Delta G^*/N^*$ is obtained from the first part of Eq. (16.40) by inserting σ/r_e from Eq. (16.28). We find $\Delta G^*/N^* = -\Delta G_m/2$, a value that applies even for a compressible β phase. In Fig. 16.3 the whole G_m^β curve has been lifted by $-\Delta G_m/2$. However, tangents to that curve do not have the usual properties because the curve is defined for a certain pressure, which is given by the size. When adding some A or B atoms, one should move to a curve for a slightly larger particle, i.e., for a slightly lower pressure. It is illustrated with a thin curve in Fig. 16.4. The chemical potentials of A and B are thus obtained from the intersection of the thin straight lines with the component axes and they will actually coincide with the intersections of the common tangent.

The effect of a pressure difference on the composition of the two phases was examined already in Section 7.6. We shall now base a derivation on Eq. (16.54) by first applying the Gibbs–Duhem relation to each one of the phases. Starting from the equilibrium at a

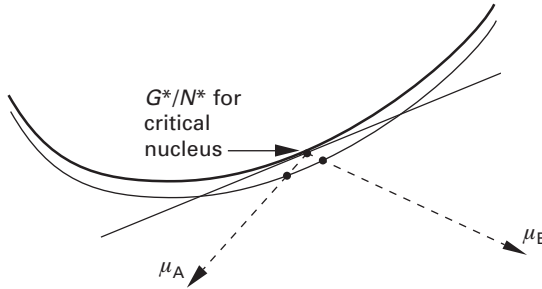


Figure 16.4 Enlarged detail of Fig. 16.3, illustrating that the critical nucleus has the correct values of the chemical potentials.

planar interface and introducing a small curvature that will give rise to a small difference in pressure, dP^β , we obtain

$$\sum x_i^\beta d\mu_i^\beta = V_m^\beta dP^\beta. \quad (16.58)$$

For the α phase there is no change of pressure and, whatever changes there will be in composition, they also must obey the Gibbs–Duhem relation which now gives

$$\sum x_i^\alpha d\mu_i^\alpha = 0. \quad (16.59)$$

From Eq. (16.54) we can see that maintained equilibrium requires that $d\mu_i^\beta = d\mu_i^\alpha$ even though the pressure inside β is increasing. We can thus reformulate Eq. (16.58),

$$\sum x_i^\beta d\mu_i^\alpha = V_m^\beta dP^\beta. \quad (16.60)$$

Combination of Eqs (16.59) and (16.60) will yield a unique answer only for a binary system, which yields, after eliminating $d\mu_A^\alpha$,

$$(x_A^\alpha x_B^\beta - x_A^\beta x_B^\alpha) d\mu_B^\alpha = x_A^\alpha V_m^\beta dP^\beta \quad (16.61)$$

$$d\mu_B^\alpha = \frac{x_A^\alpha V_m^\beta}{x_B^\beta - x_B^\alpha} \cdot dP^\beta \quad (16.62)$$

$$\mu_B^\alpha(r) - \mu_B^\alpha(\infty) \cong \frac{x_A^\alpha V_m^\beta}{x_B^\beta - x_B^\alpha} \cdot \frac{2\sigma}{r}. \quad (16.63)$$

Any solution model can be applied to the α phase to evaluate its change in composition. Using Eq. (16.54) we get for the β phase,

$$\begin{aligned} \mu_B^\alpha(r) - \mu_B^\alpha(\infty) &= \mu_B^\beta(r, P^\beta) - \mu_B^\beta(\infty, P^\beta) = \mu_B^\beta(r) + \int V_B^\beta(r) dP^\beta \\ &- \mu_B^\beta(\infty) - \int V_B^\beta(\infty) dP^\beta \cong \mu_B^\beta(r) - \mu_B^\beta(\infty) \cong \frac{x_A^\alpha V_m^\beta}{x_B^\beta - x_B^\alpha} \cdot \frac{2\sigma}{r}. \end{aligned} \quad (16.64)$$

The result is thus the same for both phases when expressed as the change in chemical potential. It is interesting to note that this final result is independent of the partial molar volume for the component although it appears in Eq. (16.57). It may be concluded that

the partial molar volumes have a negligible effect on the composition as well as on the activation energy of a critical nucleus.

Exercise 16.4

A liquid substance A in an inert atmosphere of 1 bar has an equilibrium vapour pressure of P_A° . What would be the vapour pressure of a droplet of the same substance if its radius is (a) 1 μm or (b) 1 nm and the surface energy is 1 J/m²? Suppose the molar volume is $5 \times 10^{-6} \text{ m}^3$ and the temperature is 25°C and use the ideal gas law. First, assume that the substance is incompressible. Would the pressure in case (b) be higher or lower if A is compressible?

Solution

Equation (16.56) yields (a): $\mu_j^\alpha(P) = \mu_j^\beta(P) + (2\sigma/r)V_j^\beta = \mu_j^\beta(P) + (2 \times 1/10^{-6}) \times 5 \times 10^{-6} = \mu_j^\beta(P) + 10$; $P_A(1 \mu\text{m}) = P_A^\circ \exp(10/8.3145 \times 298) = 1.004P_A^\circ$ and (b): $P_A(1 \text{ nm}) = P_A^\circ \exp[(2 \times 1/10^{-9}) \times 5 \times 10^{-6}/8.3145 \times 298] = 57P_A^\circ$. For a compressible liquid the effect would be lower.

16.8 Equilibrium for crystalline inclusions with regard to composition

For a crystalline inclusion in a fluid matrix we shall start with Eq. (16.43), giving the effect of the surface energy, and with a similar equation for the effect of surface stress. When applying Eq. (16.53) we obtain

$$\frac{\partial G}{\partial N_j^\beta} = -\mu_j^\alpha(P) + \mu_j^\beta(P^\beta) - (2f_P/r_P)dV^\beta/dN_j^\beta + (2\sigma_P/r_P)dV^\beta/dN_j^\beta. \quad (16.65)$$

We shall again assume that the same compressibility applies to the partial volumes as the integral volume. We shall thus modify Eqs (16.45) and (16.46) to partial quantities.

$$dV^\beta/dN_j^\beta = V_j^\beta(P)(1 - 4\kappa f_P/3r_P) \quad (16.66)$$

$$\mu_j^\beta(P^\beta) = \mu_j^\beta(P) + (P^\beta - P)V_m^\beta(P)(1 - \kappa f_P/r_e) \quad (16.67)$$

Introducing these results into Eq. (16.65) we obtain, similar to Eq. (16.48),

$$\mu_j^\alpha(P) = \mu_j^\beta(P) + [(2\sigma_P/r_P) + (2\kappa/3)(f_P/r_P)^2]V_j^\beta(P). \quad (16.68)$$

When applying Eq. (16.53) to an interstitial component, k , we shall accept that it does not affect the surface energy even if it increases the volume somewhat. On the other hand, the effect of surface stress will be given by the same expression as for substitutional components because it depends primarily on the effect on the volume. Instead of Eq. (16.68) we thus obtain

$$\mu_k^\alpha(P) = \mu_k^\beta(P) + (2\kappa/3)(f_P/r_P)^2V_k^\beta(P). \quad (16.69)$$

It is interesting to note that $\mu_k^\beta(P)$ could be approximated by $\mu_k^\alpha(P)$ for an interstitial component if its partial molar volume were negligible.

When now summing this over all the components we do not recreate Eq. (16.48). It seems that, when accepting Eq. (16.69) for an interstitial component, we should introduce a correction to the second term in Eq. (16.68) for the substitutional components.

$$\mu_j^\alpha(P) = \mu_j^\beta(P) + (2\sigma_P/r_P)[V_j^\beta(P) + x_k V_k^\beta/(1 - x_k^\beta)] + (2\kappa/3)(f_P/r_P)^2 V_j^\beta(P). \quad (16.70)$$

The equilibrium conditions are obtained by inserting r_{Pe} instead of r_P in Eqs (16.69) and (16.70).

Finally, we shall evaluate the effect on the compositions from the Gibbs–Duhem relation. Then we need a relation between $d\mu_i^\alpha$ and $d\mu_i^\beta$. For simplicity we shall limit this discussion to incompressible β phases. Equations (16.67) and (16.70) yield

$$d\mu_k^\alpha(P) = d\mu_k^\beta(P^\beta) - V_k^\beta(P^\beta)dP^\beta \quad (16.71)$$

$$d\mu_j^\alpha(P) = d\mu_j^\beta(P^\beta) - V_j^\beta(P^\beta)dP^\beta + [V_j^\beta(P) + x_k^\beta V_k^\beta/(1 - x_k^\beta)]d(2\sigma_P/r_P). \quad (16.72)$$

Inserting this in Eq. (16.58) we obtain

$$\begin{aligned} V_m^\beta dP^\beta = \sum x_i^\beta d\mu_i^\beta &= \sum x_i^\beta d\mu_i^\alpha + \sum x_i^\beta V_i^\beta dP^\beta - \sum x_j^\beta [V_j^\beta(P) \\ &+ x_k^\beta V_k^\beta/(1 - x_k^\beta)]d(2\sigma_P/r_P) = \sum x_i^\beta d\mu_i^\alpha + \sum V_m^\beta dP^\beta - d(2\sigma_P/r_P) \end{aligned} \quad (16.73)$$

$$\sum x_i^\beta d\mu_j^\alpha = V_m^\beta d(2\sigma_P/r_P). \quad (16.74)$$

For a binary system we get instead of Eq. (16.62)

$$d\mu_B^\alpha = \frac{x_A^\alpha V_m^\beta}{x_B^\beta - x_B^\alpha} \cdot d(2\sigma_P/r_P). \quad (16.75)$$

The final result will be identical to Eq. (16.63) except for the slightly different interpretation of σ and r : Equation (16.63) can thus be applied to all kinds of interfaces.

Exercise 16.5

Somebody has derived the following equilibrium condition for the case where the partial molar volume of an interstitial component is small but not negligible, $\mu_i^\alpha(P) = \mu_i^\beta(P) + (2f/r)V_j^\beta$. Give a physical argument for or against this relation.

Hint

Even if we do not consider compressibility, Eq. (16.68) shows that it is wrong. It may thus be easier to find an argument against it.

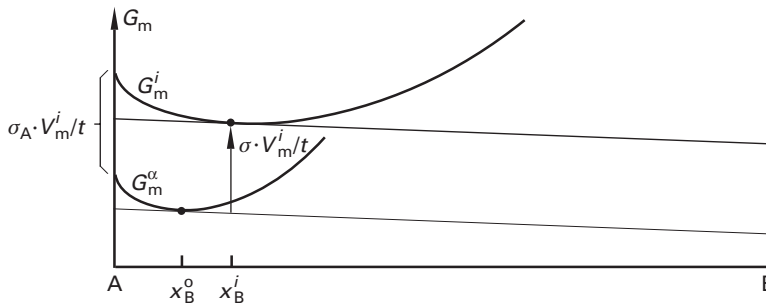


Figure 16.5 The parallel tangent construction to find the interface composition.

Solution

For an incompressible phase it is not reasonable that the surface stress has any effect because the phase is not affected. The last term should thus contain the compressibility as a factor.

Exercise 16.6

The partial molar volume for an interstitial component is small and is sometimes approximated as zero. Accepting that approximation, how should one formulate the equilibrium for the interstitial component in a compressible β phase?

Solution

For $V_k^\beta = 0$, Eq. (16.67) gives directly $\mu_k^\alpha(P) = \mu_k^\beta(P)$. The internal pressure has no effect in this case.

16.9 Surface segregation

Another important aspect is segregation of the components to or from the surface or interface. In order to describe this phenomenon we shall use a very crude model. It applies to surfaces as well as interfaces and in the formulation of the model it will be sufficient to consider the properties of one of the phases at an interface because it is assumed that the whole system is in equilibrium. Suppose the interface can be approximated as a thin layer of a homogeneous phase of constant thickness and with its own Gibbs energy function. We shall also assume that the partial molar volumes of all the phases, including the interfacial phase, are independent of composition. It is then easy to see that the composition of the material in the interface can be found by a parallel tangent construction when the volume of the interface is constant. Then we cannot consider the addition of N_A to the interface but the exchange of N_A for N_B . Thus, it is the slopes of the tangents that must be equal, not their intersections with the component axes. Figure 16.5 shows a reasonable molar Gibbs energy diagram for a one-phase material with an interface between two crystals, a so-called grain boundary. The distance between the two

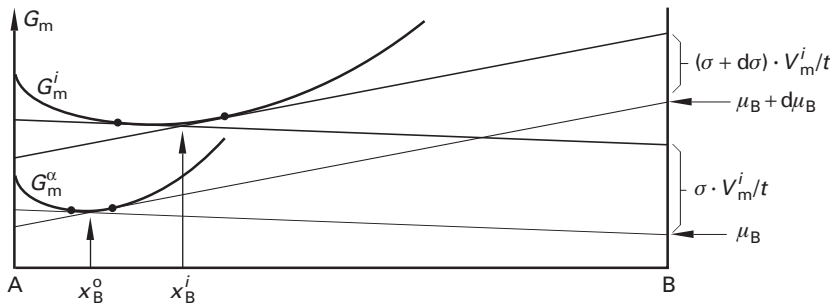


Figure 16.6 Derivation of Gibbs' adsorption equation.

curves on the left-hand side is equal to $\sigma_A \cdot V_m^i/t$ where σ_A is the specific interfacial energy of pure A, V_m^i is the molar volume of the interfacial phase and t is its thickness. Now, suppose the material has the composition x_B^0 . The composition of the interface material, x_B^i , is obtained from the parallel tangent construction and the length of the vertical arrow is equal to $\sigma_A \cdot V_m^i/t$ because it is the energy required for the formation of an interface of composition x_B^i from an α reservoir of composition x_B^0 .

Let us now vary the composition of the material and, thus, its chemical potential for B from μ_B to $\mu_B + d\mu_B$. By comparing triangles in Fig. 16.6 one can derive an equation, called Gibbs' adsorption equation,

$$-d\sigma = \frac{x_B^i - x_B^0}{1 - x_B^0} \cdot \frac{t}{V_m^i} \cdot d\mu_B. \quad (16.76)$$

Exercise 16.7

Apply the regular solution model and use the parallel tangent construction to calculate the composition of a grain boundary. Examine what factor can give strong segregation.

Hint

The regular solution model gives $G_m^\alpha = x_A^\alpha G_A^\alpha + x_B^\alpha G_B^\alpha + RT(x_A^\alpha \ln x_A^\alpha + x_B^\alpha \ln x_B^\alpha) + L^\alpha x_A^\alpha x_B^\alpha$. We should apply the same type of model to the interface. Remember that ${}^\circ G_A^i - {}^\circ G_A^\alpha = \sigma_A V_m^i/t$ and ${}^\circ G_B^i - {}^\circ G_B^\alpha = \sigma_B V_m^i/t$. The tangent construction gives $G_A^\alpha - G_B^\alpha = G_A^i - G_B^i$.

Solution

$$dG_m/x_A^\alpha = {}^\circ G_B^\alpha - {}^\circ G_A^\alpha + RT \ln(x_B^\alpha/x_A^\alpha) + L^\alpha(x_A^\alpha - x_B^\alpha) = {}^\circ G_B^i - {}^\circ G_A^i + RT \ln(x_B^i/x_A^i) + L^i(x_A^i - x_B^i); \quad RT \ln(x_A^\alpha x_B^i/x_B^\alpha x_A^i) = (\sigma_A - \sigma_B)V_m^i/t + L^\alpha(x_B^\alpha - x_A^\alpha) - L^i(x_B^i - x_A^i).$$

For ordinary metals $\sigma \cong 1\text{J/m}^2$, $V_m \cong 7\text{cm}^3/\text{mol}$, $t \cong 10^{-7}\text{cm}$.

At $T = 1000\text{K}$ the first term on the right-hand side will be less than RT even if $\sigma_B = 0$. Strong segregation must be due to the L terms and, in particular, to a large negative value of L^i , i.e. to the tendency of A and B to mix in the interface. However, the L^i term will go to zero at $x_B^i = 0$. Thus, the regular solution model predicts that

$x_B^i < 0$ even for the strongest segregation. The strongest segregation is thus predicted to give not much more than what corresponds to a monolayer.

Exercise 16.8

Gibbs' adsorption equation is usually written as $-d\sigma = \Gamma_{B(A)} \cdot d\mu_B$ where $\Gamma_{B(A)}$ is a notation for $\Gamma_B - \Gamma_A x_B^0 / (1 - x_B^0)$ and Γ_B and Γ_A are the excess amounts of B and A per unit area, due to segregation. Show that it gives the same result as the equation derived graphically.

Hint

Remember that we assumed that the volume of the interfacial phase is constant. Thus, $-\Gamma_A = \Gamma_B$.

Solution

$-\Gamma_A = \Gamma_B = (x_B^i - x_B^0) \cdot t / V_m^i$; $\Gamma_{B(A)} = (x_B^i - x_B^0) / (1 - x_B^0) \cdot t / V_m^i$ in full agreement with our result.

16.10 Coherency within a phase

The lattice parameter of a phase usually varies with the composition. The composition differences in a surface layer obtained by diffusion through the surface may thus result in internal stresses that could be partially relieved by the formation of dislocations. However, if the composition gradient is very strong, the affected surface layer could be so thin that it is difficult for dislocations to form. We shall now assume that no dislocations form and the surface layer will then be stressed to the same lattice parameter as the bulk in the planes parallel to the surface. Suppose the lattice parameter is a_1 in a binary phase of composition x_1 . In the unstressed condition the lattice parameter in a thin surface layer of a slightly different composition would be $a = a_1 + (x - x_1)da/dx$. The stresses in the plane parallel to the surface in an isotropic material would have to be

$$\sigma_1 = \sigma_2 = \frac{E}{1 - \nu} \frac{d \ln a}{dx} (x_1 - x). \quad (16.77)$$

They will allow the surface layer to be coherent with the bulk. E is the elastic modulus and ν is Poisson's ratio. The elastic energy per mole of the material in the thin layer would be

$$W = \frac{E V_m}{1 - \nu} \left(\frac{d \ln a}{dx} \right)^2 (x_1 - x)^2 = M(x_1 - x)^2. \quad (16.78)$$

The coefficient M is introduced for convenience. The composition may vary gradually with the distance from the surface but we shall apply Eq. (16.78) to the outermost layer and x will thus be the composition of the surface. We shall now examine how the equilibrium composition in a surrounding liquid solution will be affected by the coherency stresses.

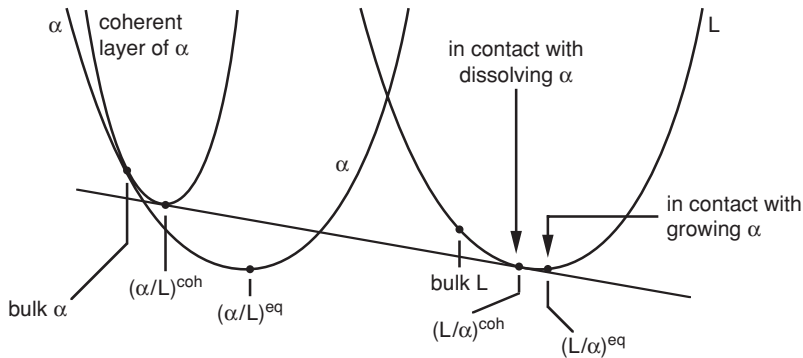


Figure 16.7 Equilibrium between a supersaturated liquid, initially x_1^L , and a crystalline α phase, initially x_1^α . The composition of the surface layer, x^{coh} , will not reach the equilibrium composition because it is coherent with a bulk of a different composition.

Introducing the elastic energy in the Gibbs energy of a surface layer coherent with an α layer of composition x_1 , we obtain

$$G_m^{\text{coh}}(x) = G_m^\alpha(x) + M(x_1 - x)^2. \quad (16.79)$$

Fig. 16.7 illustrates the situation where the bulk of the α phase is within the $\alpha + L$ two-phase field but the liquid has a composition within the $\alpha + L$ two-phase field and should thus have a tendency to precipitate α . The diagram demonstrates that the coherent surface layer will not reach the solubility limit, $x_{\text{eq}}^{\alpha/L}$, and the composition of the liquid in contact with α will still be within the $\alpha + L$ two-phase field.

When a supersaturated solid solution precipitates a new phase, it happens that the new phase grows together with a new grain of the parent phase and both phases are in contact with the supersaturated solution. Such observations are made at fairly low temperatures where volume diffusion is slow. The precipitated phase has received its alloy content by boundary diffusion along the grain boundary between the new, growing grain of the parent phase and the adjoining supersaturated parent grain. It was long a mystery what force made the new grain grow into the supersaturated grain of the same phase. Evidently, there is a force because the growing grain has been observed to be bowing out and is thus growing against the action of surface energy. The explanation is given by Fig. 16.8. In contact with the grain boundary the supersaturated α grain will be less supersaturated because of loss by grain boundary diffusion. However, due to coherency stresses the outermost surface layer will have a higher Gibbs energy than normal. See the point marked on the curve for $G_m^\alpha + W$. It can thus be in local equilibrium with a growing grain but subject to an effect we shall represent by $\Delta P = 2\sigma/r$. The common tangent shows that there can still be a driving force for the precipitation of the new phase.

This phenomenon is usually called discontinuous precipitation because the supersaturation drops discontinuously to a lower level represented by the new growing α grain. It usually develops into a lamellar aggregate of the new phase mixed with a depleted grain of the parent phase. Sometimes, the new phase develops as more massive particles and the depleted grain of the parent phase bows out from the initial grain boundary to pick up the alloying element and feed it to the particles. That is the normal case when the

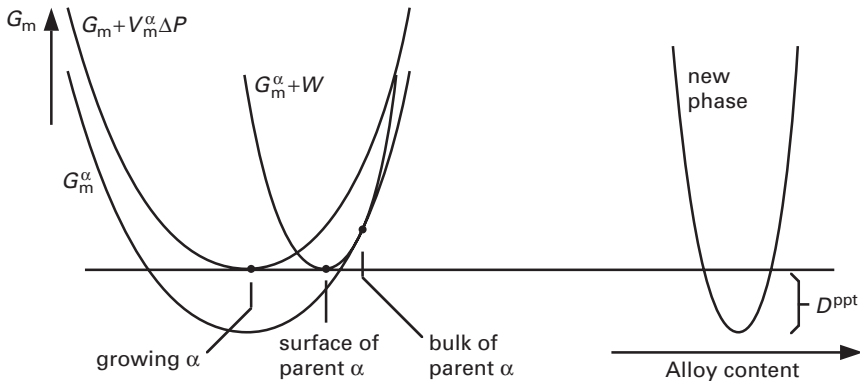


Figure 16.8 Illustration of grain boundary migration induced by grain boundary diffusion. In discontinuous precipitation the new phase is usually a solid phase but could also be liquid. In DIGM it is the atmosphere.

new phase is liquid. A related phenomenon has been observed where the alloy content diffuses through the grain boundary and is disposed of into the atmosphere instead of a new phase. It has been called DIGM for Diffusion Induced Grain boundary Migration. Both phenomena should be described as ‘grain boundary migration induced by grain boundary diffusion’. It should be mentioned that DIGM occurs also when the alloying element diffuses into the grain boundary and could thus be a mechanism of alloying a surface layer at a temperature where volume diffusion is too slow.

Exercise 16.9

When a liquid film of Cu has penetrated a grain boundary in pure Ni due to wetting, there will be a tendency of Cu to dissolve in Ni. One has observed that this has resulted in one of the Ni grains growing into the other one while the liquid film is migrating between them. The new parts of the growing grain will be alloyed with Cu that comes from the liquid reservoir but its Ni must come from the other grain. This is why that grain shrinks. This phenomenon looks very similar to discontinuous precipitation and DIGM and is called LFM for Liquid Film Migration. Explain why Ni should diffuse across the liquid film.

Hint

Once a grain has started to grow, the alloyed layer is thick enough to be less affected by the bulk. The shrinking grain will not have time to build up a thick surface layer alloyed with Cu because it will constantly be dissolved. Its alloyed surface layer will thus be more affected by coherency.

Solution

Figure 16.7 can be used to illustrate this case as well but the new phase, which may be an atmosphere in the case of DIGM, must here be replaced by the liquid reservoir. The

new Cu is provided by fresh liquid being sucked in between the Ni grains instead of by grain boundary diffusion but that difference does not affect the diagram. The L phase in the diagram is rich in Cu. It will thus have a higher Ni content in contact to the coherent layer than to the growing grain. Ni will thus diffuse to that grain.

16.11 Coherency between two phases

When a new phase precipitates from a supersaturated solid solution, it is common that many small particles form with such an orientation that they fit well into the parent phase acting as a matrix. The two crystalline lattices are then coherent with each other and structurally the phase interface is regarded as a coherent interface. This is favourable, particularly during the nucleation stage, because the coherent interface has a lower surface energy than an incoherent interface. As the new particles grow larger they may gradually lose coherency by the formation of interface dislocations. However, we shall neglect that possibility and examine the effect of coherency from the overall volume fractions of the phases. To simplify the discussion we shall also neglect the ordinary surface energy.

In general, the dimensions of the two lattices are not perfect for an exact fit to each other. There will thus be coherency stresses. In the previous section we discussed coherency stresses present in a thin surface layer when coherent with the bulk. In the present case we shall assume that they will apply to the whole phase. We shall assume that each phase is homogeneous with respect to composition as well as stresses. The coherency stresses in a thin precipitated plate will deform it to fit into the matrix, which is deformed very little. The elastic energy per mole of the new phase can depend on several factors. The present discussion will be limited to cases where the misfit between the two lattices is independent of composition and depends solely on the two crystal structures. M in Eq. (16.78) will thus be constant. It is defined per mole of the deformed phase and the energy increase, ΔG_m , will thus be $f^\beta W$ per mole of the material as a whole. f^β is the mole fraction of the new phase. However, a correction must be introduced to make the elastic energy go to zero as f^β goes to unity. The following equation seems reasonable if the phases have the same mechanical properties.

$$\Delta G_m = f^\alpha f^\beta W. \quad (16.80)$$

The Gibbs energy for a binary alloy can be written as

$$G_m = f^\alpha G_m^\alpha + f^\beta G_m^\beta + \Delta G_m(f^\beta). \quad (16.81)$$

The state of equilibrium for a material of average composition x_B^0 is found by minimizing G_m with respect to the independent variables, which should be x^α , x^β and x^0 . The phase fractions are dependent variables through the mass balance

$$x^0 - f^\alpha x^\alpha - f^\beta x^\beta = 0. \quad (16.82)$$

We could thus eliminate the phase fractions but Liu and Ågren [32] have demonstrated that the calculations can be simplified by keeping the phase fractions and use Eq. (16.82)

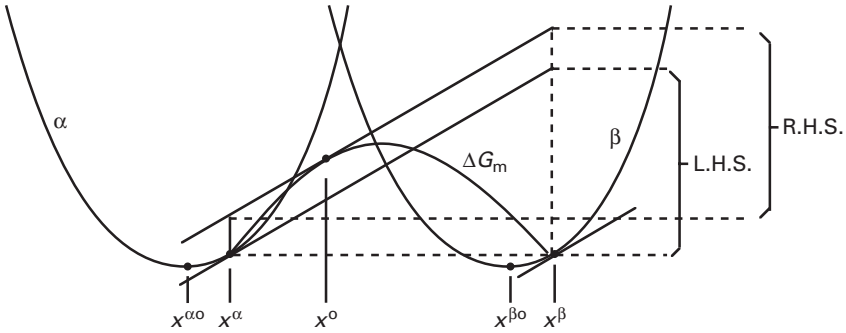


Figure 16.9 Conditions for coherent $\alpha + \beta$ equilibrium. $x^{\alpha\alpha}$ and $x^{\beta o}$ are the ordinary equilibrium compositions. x^α and x^β represent a possible coherent equilibrium. The lever rule can be applied to the $x^\alpha - x^\beta$ tie-line using the average composition x^o . The parabola between x^α and x^β represent the elastic energy caused by coherency. The tangents through x^α and x^β are parallel. The tangent through x^o is at least approximately parallel to the other two.

as an auxiliary condition. Applying a Lagrange multiplier, λ , we shall thus minimize the function

$$L = G_m + \lambda(x^o - f^\alpha x^\alpha - f^\beta x^\beta) \quad (16.83)$$

$$\frac{\partial L}{\partial x^\alpha} = f^\alpha \frac{dG_m^\alpha}{dx^\alpha} + \lambda(-f^\alpha) = 0 \quad (16.84)$$

$$\frac{\partial L}{\partial x^\beta} = f^\beta \frac{dG_m^\beta}{dx^\beta} + \lambda(-f^\beta) = 0 \quad (16.85)$$

$$\frac{\partial L}{\partial f^\beta} = -G_m^\alpha(x^\alpha) + G_m^\beta(x^\beta) + \frac{\partial \Delta G_m}{\partial f^\beta} + \lambda(x^\alpha - x^\beta) = 0. \quad (16.86)$$

Equations (16.84) and (16.85) yield

$$\frac{dG_m^\alpha}{dx^\alpha} = \lambda = \frac{dG_m^\beta}{dx^\beta}. \quad (16.87)$$

Graphically the compositions of the two phases are thus related by a parallel tangent construction (see Fig. 16.9). $\partial \Delta G_m / \partial f^\beta$ in Eq. (16.86) can be expressed as $\partial \Delta G_m / \partial x^o \cdot \partial x^o / \partial f^\beta$ and Eq. (16.82) yields $\partial x^o / \partial f^\beta = -x^\alpha + x^o$. We can thus write $\partial \Delta G_m / \partial f^\beta$ as $(x^\beta - x^\alpha) \partial \Delta G_m / \partial x^o$ where $\partial \Delta G_m / \partial x^o$ is the slope of the ΔG_m curve at the composition x^o . By further inserting the expression for λ from Eq. (16.87) into Eq. (16.86) we obtain

$$G_m^\alpha(x^\alpha) + (x^\beta - x^\alpha) \frac{dG_m^\alpha}{dx^\alpha} - G_m^\beta(x^\beta) = (x^\beta - x^\alpha) \frac{d\Delta G_m}{dx^o}. \quad (16.88)$$

The left-hand side represents the driving force for further formation of β from the α reservoir. Equation (16.88) requires that it is equal to the right-hand side, which represents the rate of increase of the elastic energy. Figure 16.9 demonstrates this relation. That diagram is based on $G_m^\alpha(x^\alpha)$ and $G_m^\beta(x^\beta)$ having the same shape and the frame of reference was chosen to make the common tangent horizontal. Both phases will thus have the same G_m value when x^α and x^β yield the same slope, which is required by Eq. (16.88).

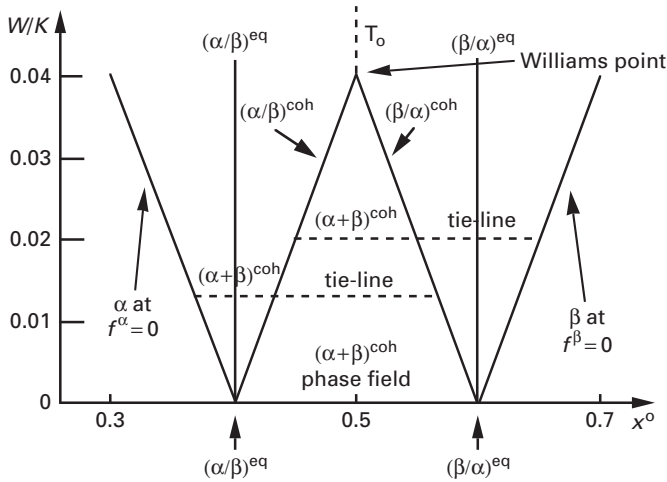


Figure 16.10 Binary phase diagram with coherent phase boundaries. The point where two coherent phase boundaries and the T_o -line meet is a Williams point. The boundaries of the coherent $\alpha + \beta$ two-phase field fall inside the ordinary $\alpha + \beta$ two-phase field. The lines representing compositions of a new phase forming at a coherent phase boundary or the last portion of the initial phase to disappear fall within the respective one-phase field.

In that case the tangent to the ΔG_m curve must also have the same slope. For any phase fraction f^β one knows the point on the ΔG_m curve. The slope of the three parallel tangents is thus known and one can easily find x^α , x^β and x^o . When the G_m curves have different shapes, the parallel tangent construction may still be used as an approximation.

For an analytical calculation one must give the exact shapes and for simplicity we shall assume parabolic shapes, which is always good enough in a small range of composition except for close to a pure component. Equation (16.81) will thus become

$$G_m = f^\alpha K^\alpha (x^\alpha - x^{\alpha o})^2 + f^\beta K^\beta (x^\beta - x^{\beta o})^2 + f^\alpha f^\beta W, \quad (16.89)$$

where $x^{\alpha o}$ and $x^{\beta o}$ are the equilibrium compositions of the two phases and G_m is given relative to the state of equilibrium and the common tangent is used as a line of reference. It was thus drawn horizontally in Fig. 16.9. Equations (16.86) and (16.87) yield

$$2K^\alpha (x^\alpha - x^{\alpha o}) = 2K^\beta (x^\beta - x^{\beta o}) \quad (16.90)$$

$$\begin{aligned} K^\alpha (x^\alpha - x^{\alpha o})^2 + (x^\beta - x^\alpha) \cdot 2K^\beta (x^\beta - x^{\beta o}) - K^\beta (x^\beta - x^{\beta o})^2 \\ = (1 - 2f^\beta)W. \end{aligned} \quad (16.91)$$

Equations (16.82), (16.90) and (16.91) can be used for calculating x^β , x^o and f^β for a series of x^α values at a given set of $x^{\alpha o}$, $x^{\beta o}$, K^α , K^β and W . These calculations will apply to the coherent $\alpha + \beta$ equilibrium and intuitively one could expect it to extend between the compositions where $x^o = x^\alpha$ and $x^o = x^\beta$, i.e., between $f^\beta = 0$ and $f^\alpha = 0$. This is indeed so for the symmetric case where $K^\alpha = K^\beta = K$ and it is interesting to note that the boundaries of the coherent $\alpha + \beta$ phase field fall within the ordinary $\alpha + \beta$ phase field. The result varies with the W value as illustrated in Fig. 16.10, which would be a classical T - x phase diagram if W/K varies linearly with T .

The coherent $\alpha + \beta$ two-phase field coincides with the ordinary $\alpha + \beta$ field if $W = 0$ because there are no stresses although the phases are coherent with each other. They fit together perfectly. As W/K is increased, the coherent $\alpha + \beta$ two-phase field will shrink and the two phase boundaries will finally meet in a point. A coherent $\alpha + \beta$ mixture cannot be stable above that point. The dashed line starting from that point is the well-known equal Gibbs energy curve (T_0) where, in principle, α and β could transform into each other without diffusion. Usually, such a transformation is difficult to study because the system could easily start to transform by diffusion. It may now be concluded that diffusional formation of coherent particles can be prevented if the coherency effect is strong enough. The point where the T_0 line meets the two coherent phase boundaries is called Williams point after the person who first predicted such points [33]. The Williams point may be an important feature of coherent phase diagrams. The physical factor behind the Williams point is easy to understand. If the coherency effect is increased by magnifying the ΔG_m curve in Fig. 16.9 until it finally intersects the point where the two Gibbs energy curves cross. A coherent $\alpha + \beta$ mixture can be stable only when part of the ΔG_m curve falls below both Gibbs energy curves.

It should be emphasized that the lever rule cannot be applied to the two boundaries of a coherent $\alpha + \beta$ phase field because they do not represent the compositions of coexisting phases. It is evident from Fig. 16.9 that the coexisting phases must be represented by the two end-points of the parabolic ΔG_m curve because the elastic energy is evaluated from them. Due to the parallel tangent construction x^β must fall inside the ordinary β phase field if x^α falls inside the ordinary $\alpha + \beta$ phase field. The compositions of minute amounts of coherent α or β are represented by lines extending into the respective one-phase field in Fig. 16.10. The lever rule can be applied to the tie-lines between the two kinds of coherent boundaries. This is better demonstrated in Fig. 16.11 showing what should happen if one could gradually increase the average alloy content of the system. Starting from the lower left corner the system is in the α one-phase field and $x^\alpha = x^0$. At $x^0 = 0.4$ the ordinary solubility limit is reached and β should start to form if there were no coherency effect. See the horizontal line at $x^\alpha = 0.4$ which is marked with 0. If there is an effect of the strength $100 W/K = 1.2$ then coherent precipitation of β could not start until $x^0 = 0.43$. A minute amount of β with composition $x^\beta = 0.63$ could form. As the average alloy content is rising further, the amount of β will grow and the alloy content of both phases will decrease gradually. The composition of the α phase will cross the ordinary phase boundary, $x^\alpha = 0.4$, when the β phase takes over the role of majority phase above $x^0 = 0.5$ and most of the elastic energy will then be stored in the α phase.

If the coherency effect has the strength $100W/K = 4$, the α one-phase state will remain until the Williams point is reached at $x^0 = 0.5$. On passing that point α will be fully transformed into β by a sharp transformation. However, it will occur gradually in time because the first portion of β is stable only with the composition $x^\beta = 0.7$ and the transformation will thus be rate controlled by diffusion. The alloy content of β can decrease only as the α matrix decreases its alloy content.

The result will be different for an asymmetric system, $K^\alpha \neq K^\beta$. Figure 16.12 is part of a diagram like Fig. 16.11 but calculated for $K^\alpha = 2K^\beta$. The result is shown only for $100 W = 3K^\alpha$. As the average composition x^0 is increased, minute amounts of β could start forming at $x^0 = 0.465$. Due to precipitation of the solute-rich β phase, the solute

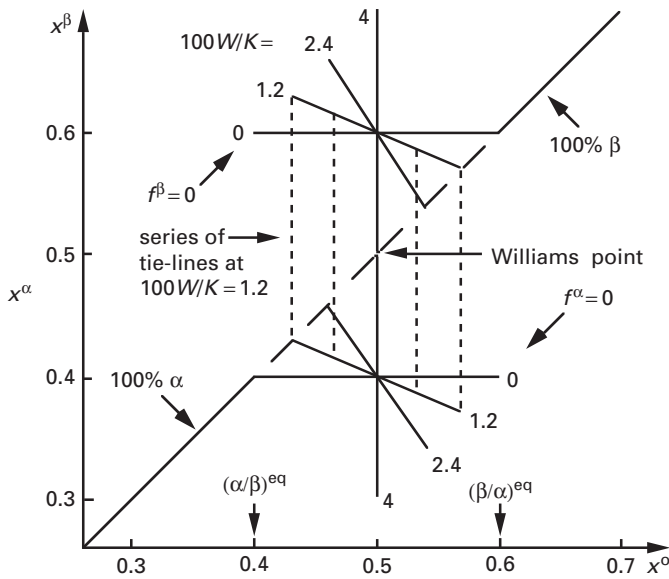


Figure 16.11 The change in composition of two coherent phases as the average composition is varied. The effect of different strengths of the coherency effect is examined.

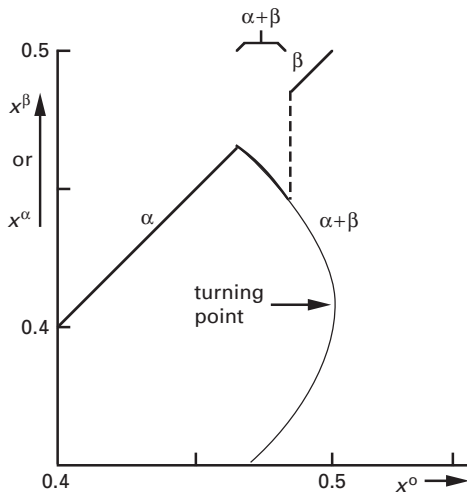


Figure 16.12 Part of a diagram like Fig. 16.11 but for an asymmetric system. According to this equilibrium diagram, the disappearance of the α phase should here be discontinuous and occur along the dashed line. In reality it may be more probable that it will happen at the point where the $\alpha + \beta$ curve turns back.

content of α will decrease as in Fig. 16.11. However, due to the asymmetry of the system, the coherent $\alpha + \beta$ mixture will soon be less stable than pure β . Thermodynamically one could expect a discontinuous change into pure β as indicated by the vertical dashed line. The phase boundary in a coherent phase diagram should thus fall on the composition of that line. Kinetically, one should expect the process to be impossible because it is difficult

to imagine a continuous path between the two states without involving intermediate states of higher energy. In practice, the system should rather follow the curve for coherent $\alpha + \beta$, which is getting steeper and finally even turns back. At higher alloy contents there is no stable $\alpha + \beta$ mixture and it has been proposed that the discontinuous change into pure β will occur spontaneously at the turning point of the $\alpha + \beta$ curve. Fig. 16.12 could as well be used to illustrate the process when one starts from pure β at the upper right corner.

It has been emphasized that the present discussion of coherent phase equilibria is based on a very simple model. Complications of large practical importance could be that the mechanical properties are anisotropic and different in the two phases and the elastic energy could depend on the composition difference. However, the existence of Williams points and discontinuous changes of the phase fractions are probably typical of coherent phase diagrams.

As another simple case one could assume that the elastic energy only depends on the difference in composition as described by Eq. (16.78) and not on a structural difference. However, then it would be logical to allow the interface to lower the elastic energy by spreading out into a diffuse transition zone between the two phases. That is actually how the theory of spinodal decomposition is constructed. As mentioned in Section 15.4 it also results in the prediction that the coherent miscibility gap is more limited than the ordinary one and the coherent spinodal thus falls inside the ordinary one.

Exercise 16.10

Sketch a diagram like Fig. 16.9 but showing the situation exactly when the coherent phase boundary is reached.

Hint

The compositions x^α and x^β should then coincide.

Solution

Accepting the parallel tangent construction, the two tangents should coincide. Figure 16.13 illustrates the only possibility for that.

16.12 Solute drag

In Section 16.9 we discussed the segregation of solute atoms to a stationary grain boundary. If the boundary starts moving, there would be a tendency of the segregated atoms to stay inside the boundary. They would thus have to diffuse with the migrating boundary and that process would dissipate Gibbs energy and consume some of the driving force for the grain boundary migration. The rate of migration would be lower than in a pure material. An alternative approach would be to consider the force that makes the segregated

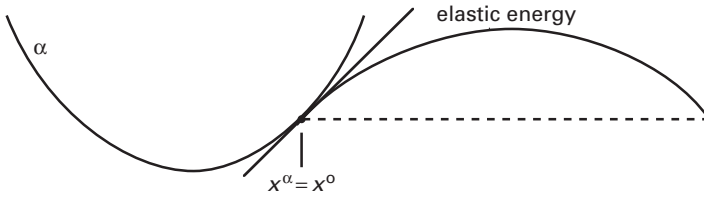


Figure 16.13 Solution to Exercise 16.10.

atoms diffuse with the boundary. It could be concluded that those atoms exert an opposite mechanical force on the grain boundary, a force that should be subtracted from the force driving the boundary migration. That approach gave rise to the term ‘solute drag’ for this phenomenon.

The driving force for grain boundary migration in so-called grain growth, by which the average grain size increases, derives from the surface energy of the curved grain boundary. It will thus be denoted P^σ and for a spherical boundary we have $P^\sigma = 2\sigma/r$. In a pure material this driving force will be balanced by friction connected to the grain boundary migration and also in an alloy, where the solute drag will be added.

$$P^\sigma = P^{\text{fric}} + P^{\text{s.d.}} \quad (16.92)$$

In the thermodynamic approach to a $\beta \rightarrow \alpha$ phase transformation one first evaluates the chemical driving force acting over the interface under steady state conditions, which means that the new phase grows with a constant composition, inherited from the initial composition of the parent phase, x_i^0 . When the interface is passing by, material of that composition will move to lower chemical potentials and the net effect on the interface will be

$$D^{\text{chem}} = \sum x_i^0 (\mu_i^{\beta/\text{int}} - \mu_i^{\alpha/\text{int}}), \quad (16.93)$$

where $\mu_i^{\beta/\text{int}}$ and $\mu_i^{\alpha/\text{int}}$ are the chemical potentials of component i in the two phases on the sides of the interface. Together with the effect of surface energy of a curved interface, the chemical driving force will pay for the dissipation of Gibbs energy caused by friction and by diffusion of the segregated atoms. The balance of Gibbs energy will yield

$$D^{\text{chem}} + P^\sigma V_m = P^{\text{fric}} V_m + \Delta G^{\text{diff}}. \quad (16.94)$$

Two of the pressures in Eq. (16.92) appear here but multiplied by V_m in order to express the change of Gibbs energy per mole of material passed by the migrating interface. Comparison of Eqs (16.91) and (16.93) shows that the two approaches would yield the same result if

$$D^{\text{chem}} = \Delta G^{\text{diff}} - P^{\text{s.d.}} V_m. \quad (16.95)$$

There is no reason why both models should not apply to migration of grain boundaries as well as phase interfaces. When modelling ΔG^{diff} and $P^{\text{s.d.}}$ one should thus make sure that Eq. (16.95) is satisfied.

When evaluating the dissipation by diffusion inside the interface we should integrate over the width of the interface, say from $z = 0$ to δ . At each position, the segregated amount of component i is defined as $x_i - x_i^0$ and the driving force on them will be $-\mathrm{d}\mu_i/\mathrm{d}z$ under isobarothermal conditions. The flux relative to the migrating interface will be $x_i - x_i^0$ per mole of material the interface is passing through. Equation (5.94) will thus yield

$$\Delta G^{\text{diff}} = - \int_0^{\delta} \sum (x_i - x_i^0) \frac{\mathrm{d}\mu_i}{\mathrm{d}z} \mathrm{d}z. \quad (16.96)$$

When evaluating the solute drag we shall also integrate over the width of the interface but we shall now consider the forces acting on all the atoms. The force on the atoms is the same as before and the opposite force on the interface will have the same magnitude but opposite direction. The solute drag will thus be

$$P^{\text{s.d.}} = \frac{-1}{V_m} \int_0^{\delta} \sum x_i \frac{\mathrm{d}\mu_i}{\mathrm{d}z} \mathrm{d}z. \quad (16.97)$$

Inserting Eqs (16.96) and (16.97) into (16.95) we find

$$\begin{aligned} D^{\text{chem}} &= \Delta G^{\text{diff}} - P^{\text{s.d.}} V_m = \int_0^{\delta} \sum x_i^0 \frac{\mathrm{d}\mu_i}{\mathrm{d}z} \mathrm{d}z \\ &= \sum x_i^0 \int_0^{\delta} \mathrm{d}\mu_i = \sum x_i^0 (\mu_i^{\beta/\text{int}} - \mu_i^{\alpha/\text{int}}) = D^{\text{chem}}. \end{aligned} \quad (16.98)$$

We may conclude that the two approaches are indeed equivalent. It may be argued that the force on the interface should only include the part of μ_i which originates from how the structure varies through the interface because that is what attracts atoms to remain inside the interface. One should thus exclude from μ_i all parts that originate from the variation of the composition. However, for those parts the Gibbs–Duhem relation yields $\sum x_i \mathrm{d}\mu_i = 0$. The only contribution to the summation in Eq. (16.97) comes from factors that depend on position and not composition. It is thus permitted and indeed convenient to evaluate the solute drag by interpreting $\mathrm{d}\mu_i/\mathrm{d}z$ as the derivative of the energy of atoms with respect to position without counting interactions from other atoms. In practice, one must first calculate how the composition varies through the interface taking all contributions to μ_i into account. It will not be very important how the solute drag is then evaluated.

It may be informative to represent the equations with molar Gibbs energy diagrams. For the mechanical approach that is done by simply dividing G_m with V_m . See Fig. 16.14(a), where the arrow representing P^σ points upwards because it is the force driving the process. The Gibbs energy for the parent grain has been lifted a distance $P^\sigma V_m$ because it is under the influence of the surface energy as compared to the new grain. The corresponding diagram for the thermodynamic approach is more complicated (see Fig. 16.14(b)). The curves for the two grains are the same as before and their distance

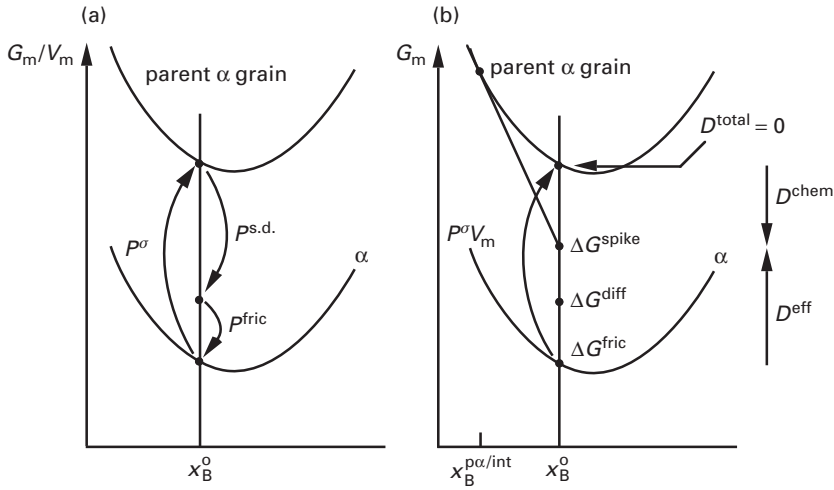


Figure 16.14 Illustration of the effect of diffusion inside a migrating grain boundary. (a) This is based on the solute drag approach and considers mechanical forces. (b) This is based on dissipation of Gibbs energy. It illustrates that a negative chemical driving force, D^{chem} , is acting on the boundary. As the boundary migrates, the material of composition x_B^0 moves down the vertical line, starting from the interior of the parent grain. It first moves through the spike and then crosses the boundary.

is given by $P^\sigma V_m$. The dissipation by friction is also directly related to the corresponding force, $\Delta G^{\text{fric}} = P^{\text{fric}} V_m$, but the solute drag in Fig. 16.14(a) now corresponds to two dissipations. According to Eq. (16.95), $P^{\text{s.d.}} V_m$ should correspond to $\Delta G^{\text{diff}} - D^{\text{chem}}$, where D^{chem} is a driving force, not a dissipation. However, for grain growth there is no chemical driving force for the process because the new grain has the same structure as the parent grain and inherits its initial composition (see Fig. 16.14(b)). On the other hand, if the solute atoms are attracted to the grain boundary during its migration, then there must be a deficit of solute atoms just in front of the boundary, a negative spike. Diffusion in that spike will dissipate Gibbs energy, ΔG^{spike} . The chemical potentials on the forward side of the boundary, $\mu_i^{\beta/\text{int}}$ in Eq. (16.93), will have to be evaluated from the local composition of the parent grain, i.e., from the bottom of the negative spike. That will result in a negative driving force, D^{chem} . It can be shown that under steady state conditions it will be equal to the dissipation in the spike. The driving force for the migration, which is given by the left-hand side of Eq. (16.94), is thus lower than $P^\sigma V_m$ because D^{chem} is negative. We could write

$$D^{\text{chem}} + P^\sigma V_m = D^{\text{eff}} = \Delta G^{\text{fric}} + \Delta G^{\text{diff}}. \quad (16.99)$$

The two diagrams give equivalent results but the thermodynamic one gives a more complete picture of the process. The mechanical diagram neglects the existence of the negative spike.

Figure 16.15(a) and (b) illustrate the two approaches applied to a $\beta \rightarrow \alpha$ phase transformation. Again the thermodynamic diagram gives the more complete picture. As for grain growth in Figs 16.14(a) and (b), the new diagrams are constructed for a partitionless

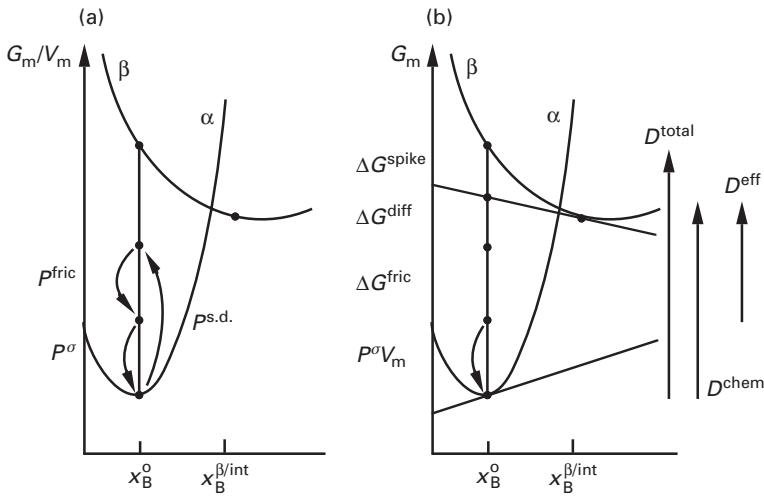


Figure 16.15 Illustration of the effect of diffusion inside a migrating phase interface. (a) This is based on the solute drag approach and considers mechanical forces. It illustrates that the so-called solute drag can act as a driving force because $P^{s.d.}$ points upwards here but downwards in Fig. 16.14(a). (b) This is based on dissipation of Gibbs energy and shows that the chemical driving force is here positive, pointing upwards. For grain growth in Fig. 16.14(b) it was negative, pointing downwards.

reaction, i.e., the new phase inherits the initial composition of the parent phase. Again there is dissipation in a spike but now there is a positive chemical driving force for the whole reaction, $D^{total} > 0$, and it is more than sufficient to balance the dissipation in the spike. There will thus be a positive chemical driving force on the interface, represented by the arrow for D^{chem} pointing upwards in Fig. 16.15(b), in contrast to grain growth where it was pointing downwards in Fig. 16.14(b). Now it is thus possible for the interface to migrate against the action of a negative curvature. The growing α phase may thus bow out into the parent β phase. To illustrate this possibility, the arrow representing $P^\sigma V_m$ is pointing downwards in Fig. 16.15(b).

When applying Eq. (16.99) to grain growth we found that D^{chem} was negative and the effective driving force was thus less than $P^\sigma V_m$. For a phase transformation $P^\sigma V_m$ may be positive or negative depending on how the interface is curved. In any case, the effective driving force must be equal to $\Delta G^{fric} + \Delta G^{diff}$ but how it is divided between the two depends on the detailed model of the interface, which will not be discussed here.

When applying Eq. (16.92) to a partitionless phase transformation we could rearrange the terms to make them all positive,

$$-P^{s.d.} = P^{fric} - P^\sigma. \quad (16.100)$$

This is illustrated in Fig. 16.15(a) and it is particularly interesting that the definition of the solute drag through Eq. (16.97) can make it negative. It has then become a *driving force instead of a drag*. Of course, the tendency of segregated atoms to stay inside the migrating interface will still act against the migration but how that is accomplished can only be explained by the thermodynamic diagram in Fig. 16.15(b).

The fact that the solute drag can turn negative and become a driving force for the migration suggests a new possibility of providing a driving force for DIGM, which is a kind of grain growth. DIGM was discussed in Section 16.10 and it was there explained that it may be driven by coherency stresses.

For low rates of migration, the segregated solute atoms can diffuse with the interface under a low dissipation of Gibbs energy. At very high rates of migration they may not be able to keep pace with the interface and the amount of segregated atoms will decrease and approach zero. After having reached a maximum at some intermediate rate, the dissipation will thus decrease and almost vanish if the remaining resistance to migration, mainly friction at high rates, is not too large. With increasing driving force, whether by a decreasing initial grain size or an increasing supersaturation, there may be a discontinuous jump from a region of low rates to a region of high rates on the other side of the maximum.

All the derivations in this section have concerned interfaces migrating under steady state conditions. The new grain or phase is thus assumed to inherit the initial composition of the parent. However, since the interfaces are extremely thin, compared to ordinary diffusion distances, the equations can also be applied to cases where there is long-range diffusion in the grains or phases. Only one modification must be made. The composition of the material passing through the interface may not be given by x_i^o . In Section 17.5 it will be shown that it depends on the long-range diffusion. For such cases one should substitute x_i^t from Eq. (17.56) for x_i^o in Eqs (16.93), (16.96) and (16.98).

In summary, it may be concluded that, from a practical point of view, it is just a matter of personal taste whether to prefer the mechanical, solute drag approach or the thermodynamic, dissipative approach. On the other hand, from a physical point of view the latter alternative is preferable. In Section 16.8 it was shown that the mechanical driving force for grain growth, $P^\sigma = 2\sigma/r$, is not the pressure difference between the two grains. It cannot be interpreted physically until it is multiplied with a partial molar volume which is done in the dissipation approach.

Exercise 16.11

Apply Eq. (16.96) to a binary system and simplify the expression. Interpret the result physically.

Hint

Use $x_A = 1 - x_B$

Solution

$(x_A - x_A^o)d\mu_A + (x_B - x_B^o)d\mu_B = (x_B - x_B^o)d(\mu_B - \mu_A)$. Even though Eq. (16.96) concerns individual diffusion, the net result for the dissipation is the same as for interdiffusion.

17 Kinetics of transport processes

17.1 Thermal activation

Arrhenius noticed that the velocity of many reactions increases with temperature according to a simple law

$$J = K \exp(-Q/RT). \quad (17.1)$$

He proposed that the reactant molecules must be thermally activated in order to react and Q represents the activation energy. According to Boltzmann statistics, the probability of such an activation is proportional to $\exp(-Q/RT)$. Eyring *et al.* [34] introduced a frequency factor in order to predict an absolute reaction rate, kT/h , where k is Boltzmann's constant and h is Planck's constant. The kinetic coefficient in Eq. (17.1) may thus contain T as a factor. We shall accept this but shall trust experimental information for the estimate of the absolute reaction rate by adding the factor RT to the K coefficient. In general we shall consider a reaction between two states with the driving force D but with a barrier of height Q in the middle between the two states. The driving force will affect the need of activation energy and it will be $Q - D/2$ in the forward direction and $Q + D/2$ in the reverse direction. The net rate of reaction will be the difference between two opposite reactions, each one of which is described with Eq. (17.1). For low driving forces relative to RT we get

$$\begin{aligned} J &= KRT \left[\exp -\frac{Q - D/2}{RT} - \exp -\frac{Q + D/2}{RT} \right] \\ &= KRT \exp(-Q/RT) \cdot 2 \sinh(D/2RT) \cong K \exp(-Q/RT) \cdot D. \end{aligned} \quad (17.2)$$

$K \exp(-Q/RT)$ is a kinetic coefficient and it is common to define it as the mobility M in a linear kinetic equation,

$$J = M \cdot D. \quad (17.3)$$

The first line of Eq. (17.2) shows that without any driving force, the two reactions would balance and the net flux would be zero. This is an example of the **principle of detailed balance**, which is supposed to hold at equilibrium for each mechanism even if there is more than one mechanism for a given reaction.

It should be emphasized that Eq. (17.2) became a linear kinetic law through the approximation of $\sinh(D/2RT)$ as $D/2RT$, which is allowed for low driving forces compared to RT . Without that approximation the model can be applied outside the linear

range. Since the driving force is expressed as D J/mol, the flux J must have the dimension mol/s because the product $J \cdot D$ would then have the dimensions J/s, which is correct for dissipation of Gibbs energy. The mobility, M , would have the dimensions mol²/J s.

Diffusionless migration of a grain boundary. As a first application we shall examine the migration of a grain boundary in a one-component system, i.e. the interface between two crystals of the same material but different orientations. Some kind of unit of the material on one side of the grain boundary may be transferred to the other side by some deformation and rotation or individual atoms may simply jump across the interface. Those two mechanisms will be discussed further in Section 17.6. In any case, there may be an energy barrier, Q , and a driving force, D , e.g. caused by the boundary being curved. We can directly apply Eq. (17.3) with $M = M_0 \exp(-Q/RT)$ but in this case it may be more convenient to express the driving force in Eq. (17.3) as D/V_m which has the dimension J/m³, i.e. N/m². If the flux J is expressed as the velocity v in m/s, then the rate of dissipation of Gibbs energy, obtained from the product of flux and driving force, will have the dimensions J/s m² and the rate of dissipation of Gibbs energy in J/s is obtained by multiplying with the cross-section of the grain boundary, a m². The mobility M would then have the dimensions m⁴/J s.

$$J \equiv v = M \cdot (D/V_m). \quad (17.4)$$

For the dissipation of Gibbs energy we get from Eq. (5.133), considering the cross-section,

$$-\dot{G} = T\sigma = av(D/V_m) = a(1/M)v^2. \quad (17.5)$$

Evidently, these equations can also be applied to the migration of a phase interface in a pure element and in an alloy if the atoms do not move individually with respect to each other, i.e. for so-called diffusionless transformations. However, it must be modified if the new grain or phase has a different composition. See Section 17.5.

Interstitial diffusion. The next application will be diffusion of an interstitial solute C, which can jump between the interstitial sites in a host lattice. During each jump a C atom has to squeeze between the neighbouring host atoms and that gives rise to an energy barrier. The kinetic equation will be very similar to the previous case but this time the rate of the process must depend on how many C atoms take part in the process. Presumably, they all take part but per mole of host atoms there is only a fraction y_C of C atoms. Furthermore, according to Section 5.7 the force for diffusion is $-\nabla(\mu_C/T)$. As T is now constant, we could consider the negative of the chemical potential gradient, $-\nabla\mu_C$, as the driving force. However, we now use a detailed model according to which the atoms exchange positions with vacancies. Their chemical potential should also be considered and also their fraction. We should thus write the kinetic equation for the exchange of positions of an interstitial atom with a vacancy as

$$J_C = -M_C y_C y_{va} \cdot \nabla(\mu_C - \mu_{va}). \quad (17.6)$$

In this case J_C is a real flux expressed in the lattice-fixed frame and has the dimensions mol/s m². If $-\nabla(\mu_C - \mu_{va})$ is accepted as the driving force with its dimensions J/mol m, then the entropy production given by the product would have the dimensions J/s m³,

which is correct for the dissipation of Gibbs energy per volume. The mobility would then have the dimensions $\text{mol}^2/\text{J s m}$.

Substitutional diffusion. Let us consider substitutional diffusion in a binary A–B solution and as a background to a more realistic case we shall now accept the less probable mechanism where atoms diffuse by exchanging positions with each other. In that special case there would be no difference between the lattice- and number-fixed frames. It seems reasonable that the diffusion of A in exchange of B across a certain plane in the system is proportional to the probability that an A and a B atom are in the correct positions on opposite sides of the plane, i.e. proportional to $x_A x_B$. We shall now treat the problem of activation and consider two opposite fluxes. By comparing with Eq. (17.2) it may seem reasonable to write the net flux as

$$\begin{aligned} J &= KRT \left[x'_A x''_B \exp -\frac{Q - D/2}{RT} - x''_A x'_B \exp -\frac{Q + D/2}{RT} \right] \\ &= KRT \exp \frac{-Q}{RT} \left[x'_A x''_B \exp \frac{D}{2RT} - x''_A x'_B \exp -\frac{D}{2RT} \right]. \end{aligned} \quad (17.7)$$

The two sides are identified by (') and (") and the driving force for the exchange of A and B is $D = -\Delta(\mu_A - \mu_B)$. It looks as if the effects of the two opposite fluxes cannot be combined into a sinh function due to the different pre-exponential factors. However, it should be realized that the chemical potentials depend on the mole fractions of A and B, which are also present in the pre-exponential factors. In order to avoid counting their effects twice, one should not let the driving forces include the ideal entropy of mixing, which is $R \ln(x'_A x'_B / x''_A x''_B)$ and $R \ln(x'_A x''_B / x''_A x'_B)$, respectively. We shall thus modify Eq. (17.7),

$$\begin{aligned} J &= KRT \exp \frac{-Q}{RT} \left[x'_A x''_B \exp \frac{D + RT \ln(x''_A x'_B / x'_A x''_B)}{2RT} \right. \\ &\quad \left. - x''_A x'_B \exp -\frac{D + RT \ln(x'_A x''_B / x''_A x'_B)}{2RT} \right] \\ &= KRT \exp(-Q/RT) \sqrt{x'_A x''_B x''_A x'_B} \cdot 2 \sinh(D/2RT) \\ &\cong -KRT \exp(-Q/RT) x_A x_B \cdot \Delta(\mu_A - \mu_B). \end{aligned} \quad (17.8)$$

It is more convenient to express the difference $\Delta(\mu_A - \mu_B)$ between two neighbouring sites by the gradient $\nabla(\mu_A - \mu_B)$ multiplied with the jump distance. Including the latter in the mobility we write

$$J = -M_{AB} x_A x_B \nabla(\mu_A - \mu_B). \quad (17.9)$$

We have here assumed that the difference in composition is very small. The flux and driving force again have the dimensions mol/s m^2 and J/mol m , respectively, and their product has the dimensions J/s m^3 , which is correct for dissipation of Gibbs energy per volume. $M_{AB} x_A x_B$ is the phenomenological coefficient and has the dimensions $\text{mol}^2/\text{J s m}$.

Vacancy mechanism for diffusion. Finally, let us consider the more realistic vacancy mechanism for diffusion in a substitutional solution. The diffusion of an element by exchanging positions with vacancies or with atoms of a second element will be very

similar. We can adopt Eq. (17.6) or (17.9) with very slight modifications. The driving force will now be $-\Delta(\mu_A - \mu_{v_a})$ and the crucial question is what happens to the vacancies. Contrary to vacancies in the interstitial sublattice and to atoms, vacancies in the host lattice can be generated or absorbed at crystalline defects, mainly dislocations. The frame of reference based on the lattice or on the number of atoms will thus make a difference. We shall only discuss the simplest case and assume that the mechanisms of regulating the local number of vacancies are so efficient that equilibrium is maintained everywhere. The possible gradients of μ_{v_a} may thus be neglected and the driving force will simply be $-\Delta\mu_A$. The fraction of vacancies should be retained in Eq. (17.6) but expressed by the ordinary mole fraction x_{v_a} instead of y_{v_a} , which was a site fraction in the interstitial sublattice. In Eq. (17.9) it would replace x_B . However, for practical reasons the equilibrium fraction of vacancies may be incorporated in the M coefficient. For small composition gradients the flux of element A can thus be approximated by

$$J_A = -M_A \sqrt{x'_A x''_A} \cdot \nabla \mu_A \cong -M_A x_A \cdot \nabla \mu_A. \quad (17.10)$$

This flux is given in the lattice-fixed frame and M_A is regarded as the individual mobility of A. Its activation energy, Q , would be the sum of activation for creating vacancies and for atoms jumping into vacant sites. $M_A x_A$ corresponds to the first diagonal coefficient in the phenomenological equation for a lattice-fixed frame, L_{AA} , and again has the dimensions $\text{mol}^2/\text{J s m}$. It is evident that no coupling effects were considered in the present modelling of diffusion of A and B and it should be emphasized that correlation effects were also neglected, i.e., the fact that a reverse jump is always more probable directly after a jump because the atom and the vacancy are in the correct positions for an exchange in the reverse direction.

Diffusion in number-fixed frame. If the net effect of diffusion by the vacancy mechanism is expressed in the number-fixed frame, the net effect will be the same as if atoms exchange positions with each other. It should thus be interesting to change the description of individual diffusion by the vacancy mechanism to the number-fixed frame and compare with predictions based on interdiffusion, i.e. Eq. (17.9).

Equations (5.115) to (5.118) yield the kinetic coefficients after transformation to the number-fixed frame by inserting the value 1 for all the a parameters. By again neglecting cross coefficients in the lattice-fixed frame we obtain for the number-fixed frame in a binary system,

$$\begin{aligned} L_{11}^* &= L_{11}(1 - x_1)^2 + L_{22}x_1^2 = (M_A x_A x_B^2 + M_B x_B x_A^2)/V_m \\ &= x_A x_B (x_B M_A + x_A M_B)/V_m. \end{aligned} \quad (17.11)$$

L_{11} and L_{22} were identified as $M_A x_A$ and $M_B x_B$ using Eq. (17.10). Comparison with Eq. (17.9) shows that the results may indeed be formally identical and the requirement is

$$M_{AB} = x_B M_A + x_A M_B. \quad (17.12)$$

For a formal description of interdiffusion one may thus use the number-fixed frame and from experiments one may evaluate the M_{AB} mobility without specifying or even

knowing the particular diffusion mechanism. If the individual mobilities in the lattice-fixed frame are known experimentally, then M_{AB} can be calculated from Eq. (17.12).

Exercise 17.1

Estimate at what temperature the deviation from the linear law is 100% for solidification of a pure metal.

Hint

This exercise concerns the approximation of \sinh in Eq. (17.2). The entropy of *melting* for ordinary metals can be approximated to $\Delta S_m = R$. The enthalpy of *melting* can be estimated from $\Delta G_m = \Delta H_m - T\Delta S_m = \Delta H_m - T_0\Delta S_m = 0$ at the melting temperature T_0 .

Solution

Assuming that ΔS_m and ΔH_m are independent of temperature, the driving force for *solidification* at T will be $-\Delta G = \Delta H_m - T\Delta S_m = RT_0 - TR = R(T_0 - T)$.

When is $2 \sinh[(T_0 - T)/2T] = 2(T_0 - T)/T$? A table gives $\sinh 2.18 = 4.36$. We find $T = 0.19T_0$.

Exercise 17.2

Evaluate the Kirkendall velocity in the number-fixed frame from Eq. (5.109) for a binary system in terms of the individual mobilities.

Hint

The Gibbs–Duhem relation yields $x_A d\mu_A + x_B d\mu_B = 0$ under isobarothermal conditions.

Solution

$$\begin{aligned} J_K^* &= -J_A - J_B = (M_A x_A / V_m) \cdot d\mu_A / dz + (M_B x_B / V_m) \cdot d\mu_B / dz \\ &= (M_A / V_m) \cdot x_A d\mu_A / dz + (M_B / V_m) \cdot x_B d\mu_B / dz = (1 / V_m)(M_A - M_B) \cdot x_A d\mu_A / dz. \end{aligned}$$

17.2 Diffusion coefficients

In lattice-fixed frame. In experiments on diffusion one usually studies how the composition profiles change with time and from the composition one can in principle evaluate the chemical potentials of the components and their gradients that drive the diffusion. However, it is then necessary to know the thermodynamic properties of the system,

which may not be available. It is thus more practical to regard the composition gradient as the driving force for diffusion. In a binary system there will be only one independent composition variable and only one such driving force, say dx_A/dz , which is equal to $-dx_B/dz$. By not neglecting the cross terms in the basic phenomenological equations in the lattice-fixed frame, we find by using the Gibbs–Duhem relation

$$\begin{aligned} J_A &= L_{AA}X_A + L_{AB}X_B = -L_{AA}\nabla\mu_A - L_{AB}\nabla\mu_B = -(L_{AA} - L_{AB}x_A/x_B)\nabla\mu_A \\ &= -(L_{AA} - L_{AB}x_A/x_B)\frac{d\mu_A}{dx_A}\frac{dx_A}{dz} = -\frac{\mathcal{D}_A}{V_m}\frac{dx_A}{dz}. \end{aligned} \quad (17.13)$$

This defines \mathcal{D}_A , the individual or intrinsic diffusion coefficient of component A. The molar volume, V_m , was introduced in the equation in order to give \mathcal{D}_A the dimensions m^2/s , the same as in an equation based on the gradient of the concentration instead of mole fraction. There is no cross coefficient in Eq. (17.13) in spite of the fact that there are two diffusion coefficients, one each for A and B, the reason being that there is only one driving force. Neglecting the cross coefficient L_{AB} we can identify L_{AA} with M_Ax_A in Eq. (17.10) and express the diffusion coefficient as

$$\frac{\mathcal{D}_A}{V_m} = M_Ax_A\frac{d\mu_A}{dx_A} = M_A\frac{d\mu_A}{d\ln x_A}, \quad (17.14)$$

where $d\mu_A/d\ln x_A$ is called thermodynamic factor. For dilute and ideal solutions it is equal to RT , yielding

$$\mathcal{D}_A = M_AV_mRT. \quad (17.15)$$

It should be noticed that mobility has the dimensions $\text{mol}^2/\text{J s m}$ but it is more common to include V_m in the mobility, which would then have the dimensions $\text{mol m}^2/\text{J s}$.

Many diffusion experiments are made with radioactive isotopes. They may be used as a method of following the diffusion of an element, usually at a very low content and Eq. (17.15) then applies. It is more common to study how the radioactive atoms mix with stable atoms of the same element that are distributed homogeneously in the system. That phenomenon is regarded as self-diffusion and can also be described with Eq. (17.15) because the mixture of isotopes of the same element is extremely close to ideal. This is called a tracer diffusion experiment and the diffusion coefficient is usually denoted by \mathcal{D}_A^* .

Of course, the thermodynamic factor cannot be evaluated without information about the thermodynamic properties and, if one likes to use such information in the analysis of experimental data, it makes no difference in practice if one uses the diffusion coefficient or the mobility. It should be emphasized that most diffusion studies only concern inter-diffusion that will be discussed next. They are not sufficient for evaluating individual diffusivities like \mathcal{D}_A .

In number- or volume-fixed frame. Considering the fact that there will be one independent force less than the number of components due to the Gibbs–Duhem relation, it may be interesting to define diffusion coefficients in the number- or volume-fixed frame where the number of independent diffusional fluxes is also one less. In order to have two independent diffusional fluxes in those frames we shall consider a ternary system with

two independent composition variables, x_A and x_B with $x_C = 1 - x_A - x_B$. The driving force is given by Eq. (5.121) and for a ternary case we obtain

$$\begin{aligned} J_A^* &= L_{AA}^* \nabla X_A^* + L_{AB}^* \nabla X_B^* = -L_{AA}^* \nabla(\mu_A - (a_A/a_C)\mu_C) - L_{AB}^* \nabla(\mu_B - (a_B/a_C)\mu_C) \\ &= - \left[L_{AA}^* \frac{d(\mu_A - (a_A/a_C)\mu_C)}{dx_A} + L_{AB}^* \frac{d(\mu_B - (a_B/a_C)\mu_C)}{dx_A} \right] \frac{dx_A}{dz} \\ &\quad - \left[L_{AA}^* \frac{d(\mu_A - (a_A/a_C)\mu_C)}{dx_B} + L_{AB}^* \frac{d(\mu_B - (a_B/a_C)\mu_C)}{dx_B} \right] \frac{dx_B}{dz}. \end{aligned} \quad (17.16)$$

The L_{ij}^* coefficients are those given by Eq. (5.115) and the asterisk is used to indicate a new set of processes. It should not be mistaken for the asterisk often used for tracer diffusion. We would like to write Eq. (17.16) as

$$J_A^* = - \frac{\mathcal{D}_{AA}}{V_m} \frac{dx_A}{dz} - \frac{\mathcal{D}_{AB}}{V_m} \frac{dx_B}{dz} \quad (17.17)$$

and similarly for J_B^* . \mathcal{D}_{AA} is regarded as the chemical, mutual or interdiffusion coefficient. The value of \mathcal{D}_{AB} is given by the second expression in brackets in Eq. (17.16). A similar expression is obtained for the cross coefficient \mathcal{D}_{BA} but they are not equal. This is another demonstration that Onsager's reciprocal relation applies only to a set of conjugate pairs of flux and force.

For a system with n components we obtain

$$J_i^* = - \sum_{j=1}^{n-1} \sum_{k=1}^{n-1} L_{ik}^* \frac{\partial(\mu_k - (a_k/a_n)\mu_n)}{\partial x_j} \frac{dx_j}{dz} \quad (17.18)$$

$$\frac{\mathcal{D}_{ij}}{V_m} = \sum_{k=1}^{n-1} L_{ik}^* \frac{\partial(\mu_k - (a_k/a_n)\mu_n)}{\partial x_j}. \quad (17.19)$$

It should be noticed that individual diffusion coefficients, \mathcal{D}_A , etc., always refer to the lattice-fixed frame and interdiffusion coefficients, \mathcal{D}_{AA} , etc., always refer to the volume- or number-fixed frame. Furthermore, in order to avoid confusion one could give the dependent component as a superscript, e.g. \mathcal{D}_{AA}^C . For clarity it could also be given in the subscript for the flux, e.g. J_{A-C} because it gives the interdiffusion between A and C.

Exercise 17.3

For a binary A–B system, derive a relation between the interdiffusion coefficient in a number-fixed frame, \mathcal{D}_{AA} , and the individual diffusion coefficients, \mathcal{D}_A and \mathcal{D}_B .

Hint

In the number-fixed frame all $a_i = 1$. Use the Gibbs–Duhem relation to relate $d\mu_B$ and $d(\mu_A - \mu_B)$ to $d\mu_A$.

Solution

$x_B d\mu_B = -x_A d\mu_A$; $d(\mu_A - \mu_B) = (1 + x_A/x_B)d\mu_A = (1/x_B)d\mu_A$. Equations (17.16) and (17.17) yield for a binary system $\mathcal{D}_{AA} = V_m L_{AA}^* d(\mu_A - \mu_B)/dx_A = (V_m L_{AA}^*/x_B) d\mu_A/dx_A$. Insert L_{ii}^* from Eq. (17.8) as L_{AA}^* , take \mathcal{D}_A from Eq. (17.14) and a similar expression for \mathcal{D}_B : $\mathcal{D}_{AA} = (x_B M_A + x_A M_B) \cdot x_A d\mu_A/dx_A = x_B M_A x_A d\mu_A/dx_A + x_A M_B x_B d\mu_B/dx_B = x_B \mathcal{D}_A + x_A \mathcal{D}_B$.

Exercise 17.4

Express the result for the Kirkendall velocity in a binary system, given in Exercise 17.2, in terms of the individual diffusion coefficients.

Solution

$$J_K^* = (M_A/V_m)x_A d\mu_A/dz + (M_B/V_m)x_B d\mu_B/dz = (1/V_m)\mathcal{D}_A dx_A/dz + (1/V_m)\mathcal{D}_B dx_B/dz = (1/V_m)(\mathcal{D}_A - \mathcal{D}_B)dx_A/dz.$$

17.3 Stationary states for transport processes

A state of stationary flow through a system can be established if the system is subjected to different but constant conditions at different parts of its contact with the surroundings. We shall consider the simple case of a cylindrical system of length l where heat and some substance or substances can enter and leave the system through the two flat ends. We shall also assume that other substances cannot leave the system but can diffuse inside it. The phenomenological equations for them must give zero flux in the stationary state and for the other substances the fluxes must become constant but non-zero due to constant actions from the outside. For the case of one substance of each kind we get,

$$J_1 = (L_{11}\Delta X_1 + L_{12}\Delta X_2)/l = C_1 \quad (17.20)$$

$$J_2 = (L_{21}\Delta X_1 + L_{22}\Delta X_2)/l = 0. \quad (17.21)$$

The two ΔX are the potential differences between the ends. ΔX_1 is controlled from the outside and is assumed to be kept constant. ΔX_2 varies with time but approaches a certain value when the stationary state is being established and the J_2 flux stops. ΔX_2 is given by Eq. (17.21).

$$\Delta X_2 = -\Delta X_1 L_{21}/L_{22}. \quad (17.22)$$

Combination with Eq. (17.20) yields

$$J_1 = (L_{11}/l)(1 - L_{12}L_{21}/L_{11}L_{22})\Delta X_1 \quad (17.23)$$

Since $L_{12} = L_{21}$ and L_{11} and L_{22} must be positive, we find that the internal process, that is not directly affected by the external conditions, will decrease the flux of the other process if there is a coupling between them.

Prigogine [7] has proposed that in the stationary state of flow the diffusing substances will distribute themselves in such a way that the flow produces least entropy. This principle of minimum entropy production should apply to all transport processes, e.g. heat conduction and diffusion and can be demonstrated as follows.

Consider the transport of several substances through a cylindrical system of length l . For each substance there is a phenomenological equation

$$J_j = \sum_k L_{jk} \nabla X_k. \quad (17.24)$$

The total entropy production will be obtained by multiplying with the force and integration over the length of the system,

$$\sigma = \int \sum_j J_j \nabla X_j dz = \int \sum_j \sum_k L_{jk} \nabla X_j \nabla X_k dz. \quad (17.25)$$

The integration is carried out between the two sides of the system. According to Euler's equation, which is based on variation analysis, we can evaluate the distributions of all the X_i potentials through the system for which σ has an extremum. The integrand will be denoted by I and it contains the variables X_i , which are functions of z . However, in our case they enter into the integrand only as their derivatives with respect to z . For that case the Euler equation is simply

$$\frac{d}{dz} \left(\frac{dI}{d\nabla X_j} \right) = 0. \quad (17.26)$$

From Eq. (17.25) we find if all the L_{ij} coefficients are constant,

$$\frac{dI}{d\nabla X_j} = 2L_{jj} \nabla X_j + \sum_k (L_{jk} + L_{kj}) \nabla X_k \quad (17.27)$$

$$\frac{d}{dz} \left(\frac{dI}{d\nabla X_j} \right) = 2L_{jj} \frac{d^2 X_j}{dz^2} + \sum_k (L_{jk} + L_{kj}) \frac{d^2 X_k}{dz^2} = 0. \quad (17.28)$$

There is such an equation for each process and the solution to that system of equations is

$$\frac{d^2 X_i}{dz^2} = 0 \quad (17.29)$$

$$\frac{dX_i}{dz} = K_i, \quad (17.30)$$

where K_i is a constant for each process and it can be found by integrating over the whole length of the system. Since K_i is constant we obtain

$$K_i = \frac{dX_i}{dz} = \frac{\Delta X_i}{l}. \quad (17.31)$$

It is evident that this result is identical to the stationary state of flow through the system. Prigogine thus concluded that the stationary state is a state of extremum in the entropy production and, in fact, a minimum because the entropy production can never be negative. It should thus be possible to find the stationary state distribution of the potentials in the system by minimizing the entropy production if one has an analytical expression for the

dissipation of Gibbs energy, which is equal to $T\sigma$. However, it should be noted that the derivation was based on the assumption that all L_{ij} are constant.

It should be emphasized that Prigogine's extremum principle has no similarity with Onsager's, which was discussed in Section 5.9, except for the fact that they both involve a search for an extremum. Onsager's principle can be used to find how a system in a given state will change, Prigogine's principle concerns a final stationary state where there will be no more changes. It is less interesting that they also differ by Onsager's principle dealing with a maximum and Prigogine's with a minimum. The purpose of the principles is not to give information on the entropy production itself but to predict the behaviour of the system.

It has often been emphasized that Prigogine's principle is limited to cases where the phenomenological coefficients are constant. This condition is rarely fulfilled but it has been proposed that his principle could nevertheless be applied if the difference in potential over the system is small enough. This will now be tested with a simple case, that of interstitial diffusion.

For a dilute interstitial solution one may disregard the variations in y_{V_a} and μ_{V_a} and simplify Eq. (17.6),

$$J_C = -M_C y_C \nabla \mu_C, \quad (17.32)$$

where $M_C y_C$ is the phenomenological coefficient and it may vary linearly with composition. However, it is common to introduce the composition gradient using the dilute solution approximation,

$$\nabla \mu_C \equiv \frac{d\mu_C}{dz} = \frac{RT d \ln a_C}{dz} = \frac{RT}{a_C} \frac{da_C}{dz} \approx \frac{RT}{y_C} \frac{dy_C}{dz}. \quad (17.33)$$

We thus obtain

$$J_C = -\mathcal{D}_C \frac{dy_C}{dz}, \quad (17.34)$$

where the diffusion coefficient is equal to RTM_C and may be treated as constant. However, the rate of entropy production is based on the basic phenomenological equation, Eq. (17.32) with its variable coefficient. We obtain for the dissipation

$$T\sigma = \int M_C y_C (\nabla \mu_C)^2 dz = \int M_C y_C \left(\frac{RT}{y_C} \right)^2 \left(\frac{dy_C}{dz} \right)^2 dz = \int \frac{\mathcal{D}RT}{y_C} \left(\frac{dy_C}{dz} \right)^2 dz, \quad (17.35)$$

where $\mathcal{D} = M_C RT$. The integral will be transformed in order to apply Euler's equation

$$\sigma = \int 4\mathcal{D}R \left(\frac{d\sqrt{y_C}}{dz} \right)^2 dz = \int 4\mathcal{D}R (\nabla \sqrt{y_C})^2 dz \quad (17.36)$$

$$\frac{dI}{d(\nabla \sqrt{y_C})} = 8\mathcal{D}R \nabla \sqrt{y_C} \quad (17.37)$$

$$\frac{d}{dz} \left(\frac{dI}{d(\nabla \sqrt{y_C})} \right) = 8\mathcal{D}R \frac{d^2 \sqrt{y_C}}{dz^2} = 0 \quad (17.38)$$

$$\frac{d\sqrt{y_C}}{dz} = K = \frac{\Delta \sqrt{y_C}}{l}. \quad (17.39)$$

From Eq. (17.36) we now obtain

$$\sigma^{\min} = 4DR \int K^2 dz = 4DRK^2l = (4DR/l) \left(\sqrt{y'_C} - \sqrt{y''_C} \right)^2. \quad (17.40)$$

Since it has been proposed that the minimum principle can be applied if the difference across the system is small enough, we shall start by representing the difference with

$$\varepsilon \equiv \sqrt{y''_C/y'_C} - 1 \quad (17.41)$$

$$\sigma^{\min} = \frac{4DRy'_C}{l} \left(\sqrt{y''_C/y'_C} - 1 \right)^2 = \frac{4DRy'_C}{l} \varepsilon^2. \quad (17.42)$$

The stationary state solution yields from Eqs. (17.33) and (17.34)

$$T\sigma^{\text{ss}} = - \int J_C \nabla \mu_C dz = -J_C \int \frac{RT}{y_C} \frac{dy_C}{dz} = \mathcal{D}_C \frac{\Delta y_C}{l} \cdot RT \ln \frac{y''_C}{y'_C} \quad (17.43)$$

$$\begin{aligned} \sigma^{\text{ss}} &= \frac{RD_C y'_C}{l} \left(\frac{y''_C}{y'_C} - 1 \right) \cdot 2 \ln(1 + \varepsilon) = \frac{2RD_C y'_C}{l} ((1 + \varepsilon)^2 - 1)(\varepsilon - \varepsilon^2/2 + \varepsilon^3/3) \\ &= \frac{2RD_C y'_C}{l} (2\varepsilon^2 + \varepsilon^4/6) \end{aligned} \quad (17.44)$$

$$(\sigma^{\min} - \sigma^{\text{ss}})/\sigma^{\text{ss}} = -\varepsilon^2/12 \quad (17.45)$$

The error in the entropy production will indeed be small if ε is small. However, to keep ε small is a very severe restriction for diffusion. The error may be very large if a low content is used at one end of the system.

As already stated, the minimum in entropy production itself is seldom of much interest. It should be more interesting to examine how well the principle of minimum entropy production can predict the stationary state of the system. Equation (17.34) shows that y_C should vary linearly through the system if $\mathcal{D}_C = RTM_C$ is constant but Eq. (17.39) shows that the principle predicts that $\sqrt{y_C}$ should vary linearly. Furthermore, when evaluating the flux one must use the gradient of y_C and the principle would give different results from the two ends of the system. If one could accept an average one could just as well have made an estimate without studying the stationary state but using the two constant boundary conditions directly. It thus seems difficult to use this simple example for justifying the principle when the thermodynamic coefficients are not constant. On the other hand, it may not be sufficient ground for ruling out the principle in more complicated cases. Anyway, there is no justification for using it in cases that do not concern stationary states, i.e., without constant boundary conditions.

Exercise 17.5

Carry out the variation analysis for heat conduction, accepting that the phenomenological coefficient can be given as λT^2 .

Hint

Remember that the force for heat conduction is $d(1/T)/dz$. Introduce $d \ln T = (1/T)dT$.

Solution

$$\begin{aligned} \sigma &= \int L (d(1/T)/dz)^2 dz = \int \lambda T^2 (1/T^4) (dT/dz)^2 dz = \int \lambda (d \ln T/dz)^2 dz; \\ \frac{dI}{d(d \ln T/dz)} &= 2\lambda \frac{d \ln T}{dz}; \quad 2\lambda d^2 \ln T/dz^2 = 0; \quad d \ln T/dz = K = \ln(T_2/T_1)/l; \\ \sigma^{\min} &= \lambda (d \ln T/dz)^2 \cdot l = (\lambda/l) \cdot (\ln T_2/T_1)^2 \text{ and the heat flux would then be } J_Q = \\ &= -\lambda dT/dz = -\lambda T d \ln T/dz = -(\lambda T/l) \ln(T_2/T_1). \end{aligned}$$

17.4 Local volume change

In the following sections we shall examine what happens at the interface during a diffusional phase transformation. The material leaving one phase at the interface must be received by the other phase. The flux of component j transferred across the interface, J_j^{tr} , can thus be given in two ways:

$$J_j^\alpha - \frac{x_j^\alpha v^{\alpha/\beta}}{V_m^\alpha} = J_j^{\text{tr}} = J_j^\beta - \frac{x_j^\beta v^{\beta/\alpha}}{V_m^\beta}, \quad (17.46)$$

where $v^{\alpha/\beta}$ and $v^{\beta/\alpha}$ are the velocities of the lattices of the two phases relative to the interface. They will generally be different because the phases may move relative to each other. All v and J are defined as positive in the same direction, the direction from α to β . It should be emphasized that this equation is quite different from Eq. (5.110). Both are material balances but in Eq. (5.110) v is the velocity of Kirkendall markers (or of any plane in the lattice) relative to the volume-fixed frame. J_j in Eq. (5.110) was given in the lattice-fixed frame and so are J_j^α and J_j^β in Eq. (17.46) but it should be emphasized that they are given relative to the lattice of each phase.

The difference between the two velocities will have little practical consequences in a planar case where the phases are free to move and maintain a stress free contact with each other at the interface. The situation is quite different in a two- or three-dimensional system where a maintained contact will cause stresses, which in turn will deform the material and thus create the required local change of volume. Several deformation mechanisms may be involved and result in very complex situations. They will not be further discussed here but an early treatment of the growth of spherical particles may be mentioned where elastic and plastic deformation was considered, including pressure-induced diffusion as a possible creep mechanism [35]. Here we shall only examine how the processes of ordinary diffusion will give rise to a requirement of local volume changes. Summation of Eq. (17.46) over all the components yields

$$v^{\beta/\alpha}/V_m^\beta - v^{\alpha/\beta}/V_m^\alpha = \sum J_i^\beta - \sum J_i^\alpha. \quad (17.47)$$

By inserting this in Eq. (17.46) we find

$$J_j^\alpha - J_j^\beta = x_j^\alpha v^{\alpha/\beta} / V_m^\alpha - x_j^\beta v^{\beta/\alpha} / V_m^\beta = (x_j^\alpha - x_j^\beta) v^{\alpha/\beta} / V_m^\alpha - x_j^\beta (\Sigma J_i^\beta - \Sigma J_i^\alpha) \quad (17.48)$$

$$v^{\alpha/\beta} / V_m^\alpha = [J_j^\alpha - J_j^\beta - x_j^\beta (\Sigma J_i^\alpha - \Sigma J_i^\beta)] / (x_j^\alpha - x_j^\beta) \quad (17.49)$$

$$v^{\beta/\alpha} / V_m^\beta = [J_j^\alpha - J_j^\beta - x_j^\alpha (\Sigma J_i^\alpha - \Sigma J_i^\beta)] / (x_j^\alpha - x_j^\beta) \quad (17.50)$$

$$\begin{aligned} \Delta v &= v^{\alpha/\beta} - v^{\beta/\alpha} = V_m^\alpha \cdot v^{\alpha/\beta} / V_m^\alpha - V_m^\beta \cdot v^{\beta/\alpha} / V_m^\beta \\ &= [(V_m^\alpha - V_m^\beta)(J_j^\alpha - J_j^\beta) - (V_m^\alpha x_j^\beta - V_m^\beta x_j^\alpha)(\Sigma J_i^\alpha - \Sigma J_i^\beta)] / (x_j^\alpha - x_j^\beta). \end{aligned} \quad (17.51)$$

For a binary system the result will be

$$\Delta v = [(V_m^\alpha x_B^\beta - V_m^\beta x_B^\alpha)(J_A^\alpha - J_A^\beta) - (V_m^\alpha x_A^\beta - V_m^\beta x_A^\alpha)(J_B^\alpha - J_B^\beta)] / (x_A^\alpha - x_A^\beta). \quad (17.52)$$

Δv has the dimensions of a velocity (m/s) and should here be interpreted as the requirement of volume (m^3/s) per area of the interface (m^2) in order to provide room for the concentration of material to the interface.

Exercise 17.6

Pure C as graphite may precipitate on small spherical inclusions in a solution of C in bcc-Fe. Consider the thickening of the layer of graphite. You may approximate the mole fractions of C in graphite and of Fe in bcc as 1.

Hint

Graphite will grow by a supersaturation of C in bcc diffusing to the growing particle. Diffusion in graphite and of Fe in bcc may be neglected.

Solution

Equation (17.52) yields $\Delta v = [(V_m^{\text{graphite}} \cdot 1 - 0)(0 - J_C^{\text{bcc}}) - (0 - 0)(0 - 1)] / (1 - 0) = -J_C^{\text{bcc}} V_m^{\text{graphite}}$ which is positive because the flux of C towards the particle, identified as α , is counted as negative. All the volume of the graphite has to come from deformation of the bcc matrix. When the graphite layer is still very thin, it is almost as a one-dimensional case and growth is easy. When it is much larger than the inclusion, then the graphite is situated in a spherical hole in the bcc matrix that must have been created by severe deformation of the matrix. A corresponding amount of material must have moved far away from the hole either by plastic deformation or elastic compression.

17.5 Composition of material crossing an interface

In order to evaluate the driving force for the migration of an interface through a material, it is necessary to know the composition of the material crossing the interface as a result of the migration. It can be evaluated from Eq. (17.46) as follows. Insert Eq. (17.49) in the first part of Eq. (17.46),

$$\begin{aligned}
 J_j^{\text{tr}} &= J_j^\alpha - x_j^\alpha v^{\alpha/\beta} / V_m^\alpha \\
 &= [(x_j^\alpha - x_j^\beta) J_j^\alpha - x_j^\alpha (J_j^\alpha - J_j^\beta) + x_j^\alpha x_j^\beta (\Sigma J_i^\alpha - \Sigma J_i^\beta)] / (x_j^\alpha - x_j^\beta) \\
 &= [x_j^\alpha (J_j^\beta - x_j^\beta \Sigma J_i^\beta) - x_j^\beta (J_j^\alpha - x_j^\alpha \Sigma J_i^\alpha)] / (x_j^\alpha - x_j^\beta) \\
 &= (x_j^\alpha J_j^{\beta*} - x_j^\beta J_j^{\alpha*}) / (x_j^\alpha - x_j^\beta)
 \end{aligned} \tag{17.53}$$

We have here introduced the fluxes in the number-fixed frame from Eq. (5.111) with $a_i = 1$,

$$J_j^* = J_j - x_j \Sigma J_i \tag{17.54}$$

By instead inserting Eq. (17.49) in Eq. (17.46) after first summing over all the components, we obtain,

$$\begin{aligned}
 \Sigma J_j^{\text{tr}} &= \Sigma J_j^\alpha - v^{\alpha/\beta} / V_m^\alpha \\
 &= [(x_j^\alpha - x_j^\beta) \Sigma J_j^\alpha - (J_j^\alpha - J_j^\beta) + x_j^\beta (\Sigma J_i^\alpha - \Sigma J_i^\beta)] / (x_j^\alpha - x_j^\beta) \\
 &= [(J_j^\beta - x_j^\beta \Sigma J_i^\beta) - (J_j^\alpha - x_j^\alpha \Sigma J_i^\alpha)] / (x_j^\alpha - x_j^\beta) \\
 &= (J_j^{\beta*} - J_j^{\alpha*}) / (x_j^\alpha - x_j^\beta).
 \end{aligned} \tag{17.55}$$

The mole fraction of component j in the transferred material is thus obtained as

$$x_j^{\text{tr}} = J_j^{\text{tr}} / \Sigma J_i^{\text{tr}} = (x_j^\alpha J_j^{\beta*} - x_j^\beta J_j^{\alpha*}) / (J_j^{\beta*} - J_j^{\alpha*}). \tag{17.56}$$

Alternatively, we should express the result in terms of the fluxes in the lattice-fixed frame, J_j . For each phase in a binary system we should then insert a relation obtained from Eq. (17.54),

$$J_j^* = J_j - x_j \Sigma J_i = x_B J_A - x_A J_B. \tag{17.57}$$

It is interesting to note that it was here possible to simplify the expressions by introducing the fluxes in the number-fixed frame, not those in the volume-fixed frame (unless all $V_i = V_m$) although Eq. (17.46) was formulated to account for changes in volume. The reason is that we have considered the flow of material across an interface with only one composition for each phase being involved.

Exercise 17.7

Examine the composition of the material crossing the liquid(α)/solid(β) interface in the following two cases of melting. (1) The dissolution of a solid stoichiometric phase into an undersaturated liquid. (2) The formation of a liquid from a solid, supersaturated with respect to the liquid phase, i.e. superheated.

Solution

In case (1) there is no diffusion in the solid phase. Equation (17.56) yields $x_j^{\text{tr}} = -x_j^{\text{sol}} J_j^{\text{liq}*} / (-J_j^{\text{liq}*}) = x_j^{\text{sol}}$.

In case (2) there is no diffusion in the liquid phase, $x_j^{\text{tr}} = x_j^{\text{liq}} J_j^{\text{sol}*} / J_j^{\text{sol}*} = x_j^{\text{liq}}$.

Comment: These results are self-evident. Equation (17.56) is mainly useful for intermediate cases with diffusion in both phases.

17.6 Mechanisms of interface migration

We shall now examine the role of various mechanisms of migration of a phase interface in an $\alpha \rightarrow \beta$ transformation under isothermal conditions. Fluxes in the direction α to β will be regarded as positive. The deviation from equilibrium at the interface, which provides the driving force for the interface migration, i.e., $\Delta\mu_i$ over the interface, will be defined as $\mu_i^{\beta/\alpha} - \mu_i^{\alpha/\beta}$ and α will be the A rich phase. The basic idea is that the flux of i atoms leaving one phase must enter the other one and is related to the fluxes in the two phases. In that respect it is independent of the mechanism of transfer across the interface. On the other hand, the fluxes across the interface must keep pace with the fluxes in the phases, which can only be accomplished by an effect on $\Delta\mu_i$. That will also have an effect on the fluxes in the two phases. There is thus strong coupling between the fluxes. In order to understand this complex situation we have to consider the role of the mechanisms of material transfer across the interface. In doing so, we shall first assume that there are no cross terms in the phenomenological equations.

In principle, there are two limiting cases, individual diffusion of atoms and a cooperative mechanism, which may be regarded as diffusionless. In reality there may be intermediate cases but we shall instead discuss a combination of the two if occurring simultaneously. It should be noted that the net effect of the two mechanisms of transfer must give the correct composition of the transferred material according to Eq. (17.56).

Let us start by considering individual diffusion of atoms across the interface. We can apply Eq. (17.10) but not use the approximation of almost same composition, which would be a natural approximation for diffusion inside a phase. For a phase interface it would apply only to diffusionless transformations. Furthermore, we shall apply the discontinuity in the chemical potentials, $\Delta\mu_i$. Including the thickness of the interface in its mobility, we write Eq. (17.10) as

$$J_j = M_j \sqrt{x_j^{\alpha/\beta} x_j^{\beta/\alpha}} \cdot (-\Delta\mu_j). \quad (17.58)$$

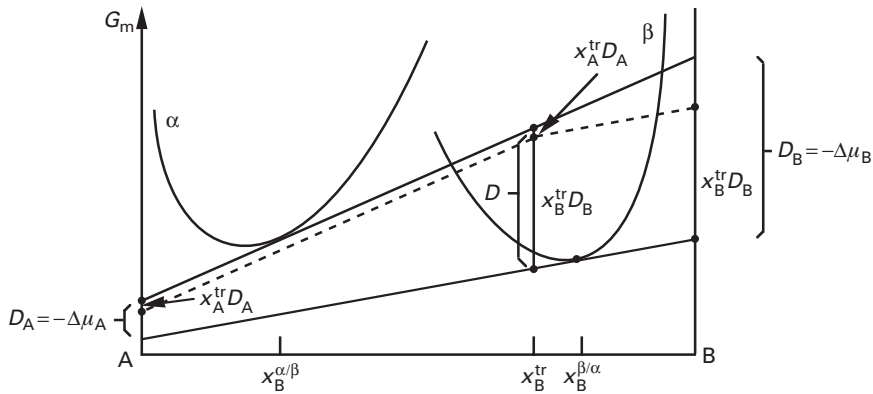


Figure 17.1 Molar Gibbs energy diagram for precipitation of β from α assuming that x_B^{tr} is the composition of the material transferred across the interface. The dissipation by diffusion of each component, counted per mole of precipitated β , is obtained by multiplying its driving force with the ratio of the fluxes, which must be equal to the mole fractions $f_j = J_j / \sum J_i = x_j^{\text{tr}}$. The sum of the dissipations is equal to the total driving force, D .

For a binary system this diffusion-controlled process can be illustrated with a molar Gibbs energy diagram. Figure 17.1 shows how α of composition $x_B^{\alpha/\beta}$ precipitates β of composition $x_B^{\beta/\alpha}$ and the driving forces for diffusion of A and B, $D_A = -\Delta\mu_A$ and $D_B = -\Delta\mu_B$, are given on the two sides of the diagram. The net composition of the material transferred across the interface, x_B^{tr} , depends on diffusion inside the phases as given by Eq. (17.56). The fluxes per mole of transferred material are thus x_A^{tr} and x_B^{tr} and the dissipation for each flux is obtained by multiplying with its driving force, $x_i^{\text{tr}} D_i$. The total driving force per mole, evaluated for the actual fractions of A and B, is

$$D = x_A^{\text{tr}} D_A + x_B^{\text{tr}} D_B. \quad (17.59)$$

It is evident that individual diffusion across an interface cannot describe a transfer of atoms across an interface against their own driving force, a phenomenon that has been observed and is called trapping. One way to describe that phenomenon would be to introduce a cooperative mechanism by which atoms of different components are transformed as a group. A negative driving force for some component could then be compensated by a strong driving force for another component.

As an introduction to the cooperative mechanism it is instructive again to consider the effects of individual diffusion but now expressed through a new set of processes obtained after transforming the primary set of processes. One of the new processes should be the transfer of atoms in the correct amount to equal the total transfer of atoms, $J_2^* = J_A^{\text{tr}} + J_B^{\text{tr}}$. One may regard this process as diffusionless and the diffusion, necessary for giving the correct composition to the transferred material, is achieved by the other process, interdiffusion by the exchange of A and B atoms across the interface. Its driving force could be defined as $D_1^* = D_B - D_A = -\Delta\mu_B + \Delta\mu_A$ or one could use the opposite sign.

This particular way of introducing two new processes was discussed by Eqs (5.35) to (5.40), which contained an arbitrary parameter α_{11} . Those equations were described for thermodynamic forces and can be applied to driving forces under isothermal conditions. From the definitions of forces and fluxes we now have $-\beta_{11} = 1 = \beta_{12}$ and $\alpha_{21} = 1 = \alpha_{22}$ and Eqs (5.38) to (5.40) yield $\beta_{22} = -\alpha_{11}$ and $\alpha_{12} = 1 + \alpha_{11} = \beta_{21}$. We may choose to represent $-\alpha_{11}$ with a composition x_B^* . Comparison with Eqs (5.16) and (5.26), which define the α and β coefficients, gives

$$J_1^* = \alpha_{11} J_A^{\text{tr}} + \alpha_{12} J_B^{\text{tr}} = -x_B^* J_A^{\text{tr}} + (1 - x_B^*) J_B^{\text{tr}} \quad (17.60)$$

$$D_2^* = \beta_{21} D_A + \beta_{22} D_B = (1 - x_B^*) D_A + x_B^* D_B = \sum x_i^* D_i. \quad (17.61)$$

For the dissipation by the interdiffusion process we thus get by using the definition of x_B^{tr} in Eq. (17.56)

$$J_1^* D_1^* = (-x_B^* J_A^{\text{tr}} + x_A^* J_B^{\text{tr}})(D_B - D_A) = (-x_B^* x_A^{\text{tr}} + x_A^* x_B^{\text{tr}})(J_A^{\text{tr}} + J_B^{\text{tr}})(D_B - D_A). \quad (17.62)$$

Per mole of transferred atoms, $J_A^{\text{tr}} + J_B^{\text{tr}} = 1$, this reduces to

$$J_1^* D_1^* = (x_B^{\text{tr}} - x_B^*)(D_B - D_A). \quad (17.63)$$

The dissipation by the diffusionless process will be

$$J_2^* D_2^* = (J_A^{\text{tr}} + J_B^{\text{tr}})(x_A^* D_A + x_B^* D_B). \quad (17.64)$$

Per mole of transferred atoms we thus get

$$J_2^* D_2^* = x_A^* D_A + x_B^* D_B. \quad (17.65)$$

This is illustrated in Fig. 17.2 where the composition of the diffusionless process, x_B^* , has been chosen arbitrarily. With that choice D_2^* is the driving force for the diffusionless process and it is also its dissipation per mole of transferred material. The dissipation by the interdiffusion process is the fraction f_1 of its driving force D_1^* where $f_1 = x_B^{\text{tr}} - x_B^*$. As in Fig. 17.1 the dissipations of the two processes will together balance the total driving force, D , but in a different way. It should again be emphasized that we are free to choose any convenient value of x_B^* because α_{11} is an arbitrary parameter.

We may now examine the cooperative mechanism. It should be recognized that on a microscale the transfer of atoms across the interface goes in both directions and the net result is given by the difference. The problem is that it should seem natural to expect from a cooperative mechanism that each phase should transfer material of its own composition to the other phase. However, the consequence for a stationary interface with no net transfer of atoms would be a net transfer of A atoms in one direction and B atoms in the other. That would not be an acceptable model. It seems necessary to accept that the two opposite fluxes carry material of the same composition. It will be denoted by x_A^{co} , x_B^{co} and it will soon be discussed by what physical factors it may be determined. The driving force for the cooperative mechanism should be given by the same expression as

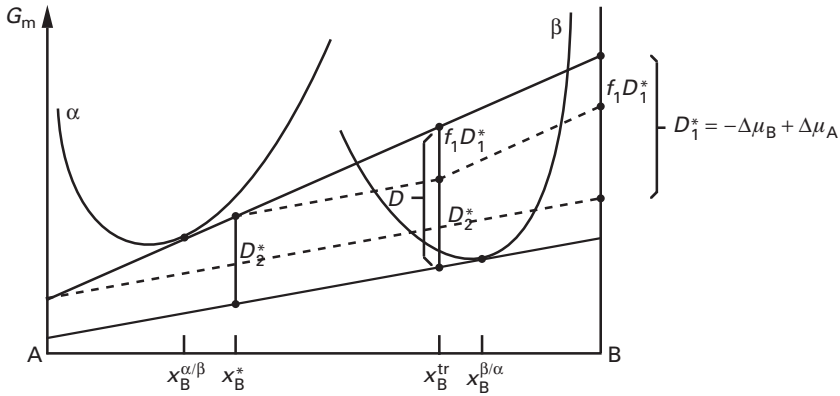


Figure 17.2 The same reaction as in Fig. 17.1 but described with a different set of processes, based on the number-fixed frame. $f_1 = x_B^{tr} - x_B^*$.

for the diffusionless process introduced by transforming the set of individual diffusion processes, Eq. (17.61). The flux would thus be

$$J^{co} = (M^{\alpha/\beta} / V_m) \sum x_i^{co} D_i. \tag{17.66}$$

The cooperative mechanism cannot be the only one unless the two phases have the same composition. In general, it will thus be necessary also to consider interdiffusion. However, it is difficult to imagine a true interdiffusion mechanism by direct exchange of A and B atoms, especially over an interface. It seems more natural to consider interdiffusion occurring by individual diffusion of atoms and those fluxes would hardly be of the same magnitude. It seems that one should combine the cooperative mechanism with individual diffusion mechanisms for A and B. For a binary system that would make three independent mechanisms. That situation is illustrated in Fig. 17.3 and it is demonstrated how the three dissipations add up and balance the total driving force.

In contrast to the diffusionless mechanism in Fig. 17.2, the dissipation by the cooperative mechanism will now be less than its driving force because only a fraction of the atoms are transferred by that mechanism,

$$f^{co} = J^{co} / (J^{co} + \sum J_i). \tag{17.67}$$

The overall process now has a mixed character and f^{co} represents the importance of the cooperative mechanism. It is evident that $f^{co} = 1$ can only be achieved when x_B^{co} coincides with x_B^{tr} .

One may replace the new set of two individual diffusion processes by interdiffusion and diffusionless transformation as demonstrated in Fig. 17.2. The two mechanisms would coincide in the diagram by choosing x_B^* for the new diffusionless mechanism, which is an arbitrary parameter, as x_B^{co} . It would then look much like Fig. 17.2 and, formally, one could represent the interface migration as if there were only two processes but the flux equation for the combined diffusionless and cooperative process would be more complicated than Eq. (17.66).

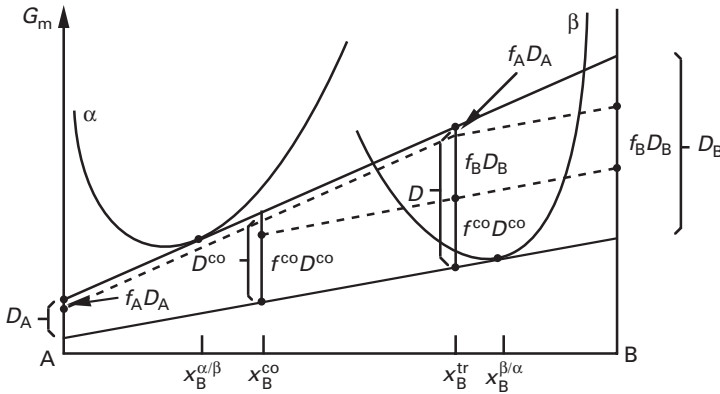


Figure 17.3 Precipitation of β from α by three processes, individual diffusion of A and B and a cooperative mechanism. The dissipations per mole of transferred atoms are obtained from each driving force multiplied by the fraction of its flux, $f_j = J_j / (J^{co} + \sum J_i)$.

An alternative way of reducing the net effect of the three processes to an effect of two may be preferable. One would then divide the cooperative flux on the individual components obtaining $J_j^{co} = x_j^{co} J_j$. For the total flux of component j one would then obtain

$$J_j^{total} = J_j + x_j^{co} J^{co} = \sqrt{x_j^{\alpha/\beta} x_j^{\beta/\alpha}} M_j (-\Delta\mu_j) + x_j^{co} (M^{\alpha:\beta} / V_m) \sum x_i^{co} (-\Delta\mu_i) \quad (17.68)$$

Then one could determine the composition of the cooperative mechanism by inserting Eq. (17.68) into Eq. (17.56), whose right-hand side is given by the fluxes inside the α and β phases.

We can now see from Eq. (17.68) that by adding the cooperative mechanism to the individual diffusion of the components we have actually entered cross terms into the individual phenomenological equations. It may thus seem that one could have obtained the same effect by taking cross terms into account directly without modelling any mechanism. However, there is a major difference. Through the presence of x_j^{co} and x_i^{co} Eq. (17.68), which are related to the fluxes inside the phases through Eq. (17.56), it is possible to make the cross coefficients change automatically as the growth conditions vary during a process. Furthermore, through Eq. (17.68) the cross coefficients of various components are related and the summation in Eq. (17.68) also contains a term for the component under consideration, i.e. for $i = j$, and it will also change with the growth conditions. Finally, it will also be easy to introduce a non-linear kinetic law for the cooperative part of the phase transformation by making the mobility $M^{\alpha:\beta}$ depend on the velocity.

Exercise 17.8

Prove that the introduction of the processes defined by Eqs (17.60) to (17.63) actually kept the rate of entropy production invariant.

Hint

One can add $\left(J_n - x_n \sum_k^n J_k\right) (D_n - D_n)$ which is equal to zero.

Solution

$$\begin{aligned}
 \sum_{i=1}^n J_i^* D_i^* &= \sum_{i=1}^{n-1} \left(J_i - x_i \sum_k^n J_k \right) (D_i - D_n) + \sum_{i=1}^n J_i \sum_k^n x_k D_k \\
 &= \sum_{i=1}^n \left[J_i D_i - J_i D_n - x_i D_i \sum_{k=1}^n J_k + x_i D_n \sum_{k=1}^n J_k \right] + \sum_{k=1}^n J_k \sum_{i=1}^n x_i D_i \\
 &= \sum_{i=1}^n J_i D_i - D_n \sum_{i=1}^n J_i - \sum_{k=1}^n J_k \sum_{i=1}^n x_i D_i \\
 &\quad + D_n \sum_{k=1}^n J_k \sum_{i=1}^n x_i + \sum_{k=1}^n J_k \sum_{i=1}^n x_i D_i = \sum_{i=1}^n J_i D_i.
 \end{aligned}$$

17.7 Balance of forces and dissipation

We shall now examine how the driving forces and dissipations of Gibbs energy are balanced in a simple case of diffusional phase transformation. The equation for diffusion by the vacancy mechanism will be applied. A limited mobility of the interfaces will also be considered. Svoboda *et al.* [36] has emphasized that this is a case where it may be an advantage to apply Onsager's extremum principle from Section 5.9 because one cannot make any *a priori* assumption about the conditions at the migrating interfaces if there is friction in them and those conditions are usually required as boundary conditions for solving the diffusion equations inside the phases. We shall follow that procedure.

We shall consider a binary case where all phases have almost constant compositions and a β phase is being formed from an initial interface between an A-rich α phase and a B-rich γ phase. In α and γ there will be no diffusion. The system is shaped as a rod with a constant cross-section of a and with the $\alpha:\gamma$ interface perpendicular to the length coordinate. Because the β phase has an almost constant composition, the fluxes of A or B can at each moment be approximated as constant through the whole length of β .

First we must find the rate of change of Gibbs energy of the whole system. Gibbs energy per area a of the rod is

$$G/a = \Sigma l^\varphi G_m^\varphi / V_m^\varphi, \quad (17.69)$$

where l^φ is the length of the respective phase. The velocities of the interfaces are obtained from the time derivatives of l^φ and the rate of change of Gibbs energy will be

$$\frac{\dot{G}}{a} = \sum G_m^\varphi \frac{v^\varphi}{V_m^\varphi} = G_m^\alpha \frac{v^{\alpha/\beta}}{V_m^\alpha} - G_m^\beta \frac{v^{\beta/\alpha}}{V_m^\beta} + G_m^\beta \frac{v^{\beta/\gamma}}{V_m^\beta} - G_m^\gamma \frac{v^{\gamma/\beta}}{V_m^\gamma}. \quad (17.70)$$

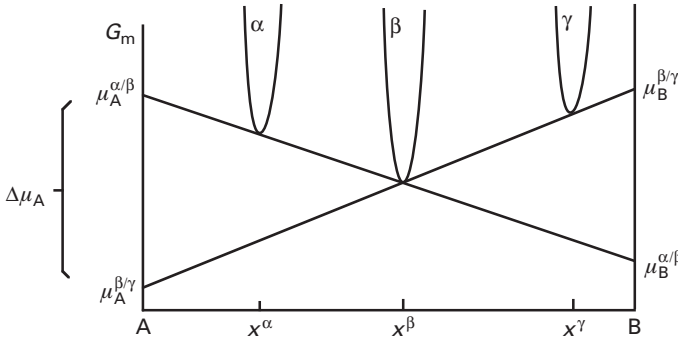


Figure 17.4 Molar Gibbs energy diagram for a system with three phases. A will diffuse from the α/β interface to the β/γ interface and B in the other direction. β will grow into both α and γ .

By inserting the velocities from Eqs (17.49) and (17.50) we can evaluate two driving forces for diffusion through the β phase, $\partial\dot{G}/\partial J_A^\beta$ and $\partial\dot{G}/\partial J_B^\beta$.

$$\frac{1}{a} \frac{\partial\dot{G}}{\partial J_A^\beta} = \frac{-G_m^\alpha x_B^\beta + G_m^\beta x_B^\alpha}{x_A^\alpha - x_A^\beta} + \frac{G_m^\beta x_B^\gamma - G_m^\gamma x_B^\beta}{x_A^\beta - x_A^\gamma}. \quad (17.71)$$

Figure 17.4 illustrates that this result can be expressed as $\Delta\mu_A = \mu_A^{\beta/\gamma} - \mu_A^{\alpha/\beta}$, where the chemical potentials are evaluated for full equilibrium between the phases across the interface, as if there were no losses in the interface. The diagram shows that $\Delta\mu_A$ is negative and we have thus a positive driving force for diffusion of A in the direction from α to γ . On the other hand, $\Delta\mu_B$ will be positive and the driving force for B would thus drive B in the opposite direction.

The rate of dissipation of Gibbs energy for a process is given by Eq. (5.133) if the cross coefficients can be neglected,

$$\phi_i = X_i J_i = (1/L_{ii}) J_i^2. \quad (17.72)$$

We shall first apply this to the two individual diffusion processes. As explained below Eq. (17.6), for diffusion this is the dissipation per volume of the phase. We can easily integrate over the whole length of the β phase because the fluxes can be treated as constant, as already explained. The volume of the β phase is $a \cdot l^\beta$ and the diffusion equation, Eq. (17.10), yields for diffusion of A,

$$\phi_A = a l^\beta J_A^2 / L_{AA} = a l^\beta J_A^2 / M_A^\beta x_A^\beta. \quad (17.73)$$

We shall soon need the derivative with respect to the diffusion fluxes, e.g.,

$$\frac{1}{a} \frac{\partial\phi_A}{\partial J_A^\beta} = \frac{2l^\beta J_A}{M_A^\beta x_A^\beta}. \quad (17.74)$$

The present problem would have been trivial if the two diffusion processes were the only ones to consider. However, we shall also consider friction of the migrating interface caused by a cooperative mechanism. For that process one would perhaps like to apply Eq. (17.4) but there is a problem because, according to Section 17.5, there are two

different velocities depending on what lattice is used as reference. The difference is caused by the two elements having different diffusivities in the β phase. The velocity relative to the lattice of the β phase is affected by the difference resulting in a net transportation of vacancies to or from the interface. However, there is no diffusion in the α phase and the velocity relative to that lattice is caused only by the atoms crossing the interface. We shall thus use $v^{\alpha/\beta}$ from Eq. (17.49). Furthermore, there is a factor V_m on the right-hand side of Eq. (17.4) which may also be different for the two phases. However, it was eliminated in Eq. (17.5) although the choice of V_m in Eq. (17.4) has affected the value of the mobility M . The rate of dissipation of Gibbs energy due to the friction in the interface is thus obtained as

$$T\sigma_{\alpha/\beta} = \phi_{\alpha/\beta} = av^{\alpha/\beta} (-\Delta G_m / V_m^\alpha) = a \frac{1}{M^{\alpha/\beta}} (v^{\alpha/\beta})^2 = a \frac{(V_m^\alpha)^2}{M^{\alpha/\beta}} \left(\frac{v^{\alpha/\beta}}{V_m^\alpha} \right)^2. \quad (17.75)$$

Comparison with Eq. (17.73) shows that the thickness of the interface has been included in the mobility. Using Eq. (17.49) we can evaluate the derivatives with respect to the fluxes,

$$\frac{1}{a} \frac{\partial \phi_{\alpha/\beta}}{\partial J_A^\beta} = \frac{2(V_m^\alpha)^2}{M^{\alpha/\beta}} \frac{v^{\alpha/\beta}}{V_m^\alpha} \frac{-x_B^\beta}{x_A^\alpha - x_A^\beta}. \quad (17.76)$$

We get similar equations for the β/γ interface. The complete dissipation function will be

$$\Phi = \phi_A + \phi_B + \phi_{\alpha/\beta} + \phi_{\beta/\gamma}. \quad (17.77)$$

We can evaluate $\partial \Phi / \partial J_A^\beta$ and $\partial \Phi / \partial J_B^\beta$ and Onsager's extremum principle, Eq. (5.141), yields two kinetic equations,

$$-\frac{\partial \dot{G}}{\partial J_i^\beta} = \frac{1}{2} \frac{\partial \Phi}{\partial J_i^\beta}, \quad (17.78)$$

where i is either A or B. In principle we can thus solve for J_A^β and J_B^β . We can insert the right-hand side of Eq. (17.71), which is equal to $\Delta\mu_A$ according to Fig. 17.4, and of Eq. (17.74). By first omitting the effects of the friction in the interfaces we find

$$-\Delta\mu_A = \frac{l^\beta J_A}{M_A^\beta x_A^\beta}; \quad -\Delta\mu_B = \frac{l^\beta J_B}{M_B^\beta x_B^\beta} \quad (17.79)$$

$$J_A = \frac{M_A^\beta x_A^\beta}{l^\beta} (-\Delta\mu_A); \quad J_B = -\frac{M_B^\beta x_B^\beta}{l^\beta} \Delta\mu_B. \quad (17.80)$$

These are well-known equations obtainable by classical methods. However, the result will be more complicated by including the effects from the interfaces given by Eq. (17.76).

$$-\Delta\mu_A = \frac{l^\beta J_A^\beta}{M_A^\beta x_A^\beta} + \frac{(V_m^\alpha)^2}{M^{\alpha/\beta}} \frac{v^{\alpha/\beta}}{V_m^\alpha} \frac{-x_B^\beta}{x_A^\alpha - x_A^\beta} + \frac{(V_m^\gamma)^2}{M^{\beta/\gamma}} \frac{v^{\gamma/\beta}}{V_m^\gamma} \frac{x_B^\beta}{x_A^\beta - x_A^\gamma}. \quad (17.81)$$

$$J_A = \frac{M_A^\beta x_A^\beta}{l^\beta} \left(-\Delta\mu_A + \frac{(V_m^\alpha)^2}{M^{\alpha/\beta}} \frac{v^{\alpha/\beta}}{V_m^\alpha} \frac{x_B^\beta}{x_A^\alpha - x_A^\beta} - \frac{(V_m^\gamma)^2}{M^{\beta/\gamma}} \frac{v^{\gamma/\beta}}{V_m^\gamma} \frac{x_B^\beta}{x_A^\beta - x_A^\gamma} \right). \quad (17.82)$$

In the present case where β grows into both α and γ , $v^{\alpha/\beta}$ is negative and $v^{\gamma/\beta}$ is positive. Equation (17.82) demonstrates that for weak effects of friction they may both be regarded as negative corrections to the driving force, $-\Delta\mu_A$, caused by deviations from local equilibrium at the interfaces. For stronger effects it may be more natural to regard them as dissipations of Gibbs energy as in Eq. (17.81). There may be a numerical problem because the contributions from the interfaces contain the velocities and they are functions of the fluxes. However, with computerized methods there should be no great problem.

With this example we have demonstrated that even in a case with several processes that dissipate Gibbs energy it may be possible to formulate the kinetic equations directly.

18 Methods of modelling

18.1 General principles

By ‘modelling’ we shall understand the selection of some assumptions from which it is possible to calculate the properties of a system. Sometimes it is possible to obtain a close mathematical expression giving a property as a function of interesting variables. In this chapter and the following ones we shall mainly concern ourselves with such models. However, in many cases the model cannot be expressed in a closed mathematical form but results can also be obtained by numerical calculations using some iterative method. When the iteration in some way resembles the behaviour of a real physical system one talks about ‘simulation’. Such methods are becoming increasingly more powerful thanks to access to more and more powerful computers.

The purpose of modelling is two-fold. From a scientific point of view one likes to learn how nature functions. One way of gaining knowledge is to define some hypothesis resulting in a model and test it by comparing the predictions from the model with experimental information. Then, it does not matter much if the predictions are made by an analytical calculation or by some numerical method. From a more technological point of view one likes to predict the properties of a particular system in order to put it to efficient use in some practical construction or operation. Then it is often most convenient to have a model which yields an analytical expression.

In the simplest case, modelling is just the selection of a mathematical form which has proved useful, whether it is based on some physical model or not. However, experience shows that a model is usually more powerful if it is based upon physically sound principles. With such a model one can hope to make predictions outside the tested range with some confidence.

The first question to discuss is what thermodynamic function to model. That question will be addressed in the next section.

Exercise 18.1

Figure 18.1 shows a P, V diagram for a pure substance at a high temperature where only gas and liquid exist. Above the critical point c there is no sharp difference between the two phases. It is thus tempting to try to apply a single mathematical model for both phases but it would then give values also for one-phase states inside the two-phase field, i.e., below the thick line. Such states would be metastable or unstable. The thermodynamic

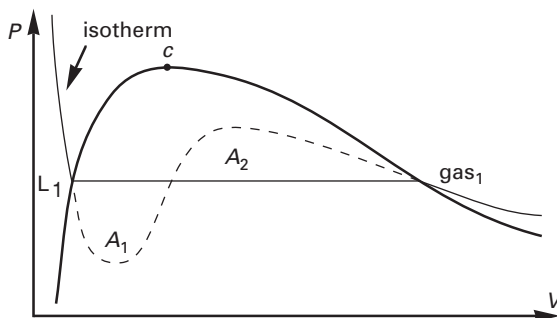


Figure 18.1 See Exercise 18.1.

properties of unstable states may be questioned but it seems reasonable at least to obey basic thermodynamic principles when constructing the model.

The thin line represents an isotherm. Show that the model must be constructed in such a way that the two areas A_1 and A_2 are equal. Actually, this is a way of identifying the equilibrium points, L_1 and gas_1 , on the curve from a model that extends over the whole range (sometimes called Maxwell's construction).

Hint

Evaluate the change in Gibbs energy along the dashed line. It is an isothermal change and thus $dG = VdP - SdT = VdP$. Then remember that the Gibbs energy of L_1 and gas_1 must be equal because they represent two states of the same substance in equilibrium with each other at given values of P and T .

Solution

$G(gas_1) - G(L_1) = \int VdP = A_1 - A_2$. But $G(gas_1) = G(L_1)$. Thus, $A_1 = A_2$. This result demonstrates that satisfactory modelling is more than just choosing a mathematical expression.

18.2 Choice of characteristic state function

From a practical point of view we are most interested in models giving the Gibbs energy which has temperature and pressure as its natural variables. They are usually the most convenient experimental variables. On the other hand, the physical model itself may make a different choice more natural. An example is the effect of thermal vibrations of the atoms. The frequencies depend upon the forces between atoms which in turn, depend upon the atomic distances. In that case it is most straightforward to consider the effect under a constant volume in spite of the fact that the vibrations themselves tend to expand the system. It is thus natural to consider the Helmholtz energy. The formation of thermal vacancies is a very different case. There the physical picture is that an atom is removed

from the interior of a crystal and placed on the surface. The volume is thus increased by one lattice site. If the atomic distances are to be kept constant, it is now necessary to let the volume increase. It will thus be more straightforward to consider this process under a constant pressure and to work with the Gibbs energy. It may be emphasized that one should choose to model the internal energy only for a case where it is natural to consider entropy and volume as constant and that may be very rare. On the other hand, there may be cases where the internal energy and the volume are kept constant and one could then model the entropy.

A different question is how to model the simultaneous effects of two different phenomena. It is true that the law of additivity applies to all the extensive state functions as far as contributions from different parts of the system are concerned. However, it must be remembered that the internal energy, volume or entropy of the whole system is then the sum of the values for the parts, whereas the variables T and P are often the same in all the parts and in the whole system. If there are curved interfaces between different parts then the parts may be under different pressures and it must be remembered that the variable P in the Gibbs energy for the whole system refers to the externally applied pressure. It may then be more straightforward to consider the Helmholtz energy but, even so, one must take into account the effect of the actual pressure inside each part because it affects the molar volume.

The situation is quite different if each one of two phenomena applies to the whole system. Each phenomenon may contribute to the total pressure which may be regarded as the sum of two partial pressures but only if the two phenomena do not interact with each other. On the other hand, the two phenomena in this case refer to the same volume.

In the present chapter the discussion of modelling will simply be limited to the use of Gibbs energy.

Exercise 18.2

What would be the most natural quantity to use in a model of evaporation of a solid?

Hint

Consider which state variables should be kept constant in order to leave the bulk of the solid unaffected by the process of evaporation.

Solution

It is not convenient to require that the volume should stay constant because then one must compress the solid to make room for the vapour. The bulk will be unaffected if the pressure is kept constant. One should thus model the Gibbs energy.

18.3 Reference states

As an introduction to our discussion of the modelling of the Gibbs energy it is instructive to examine some real cases. The Gibbs energy is always given relative to some reference.

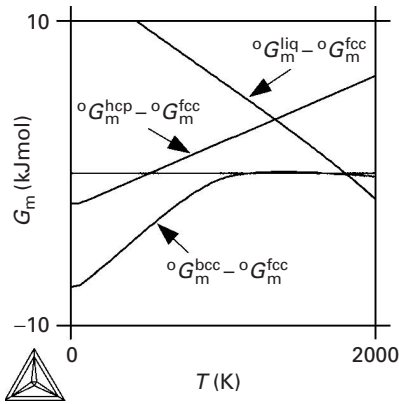


Figure 18.2 The Gibbs energy of various forms of iron, given relative to the fcc form at the same temperature and a pressure of 1 bar.

As an example, if one inquires about the Gibbs energy for the various forms of pure solid iron one may find information on all the other forms relative to the fcc form. Figure 18.2 shows how these Gibbs energy differences vary with temperature at 1 bar. It is a striking feature that such curves are often rather straight but in some regions the curvature is strong.

Since the negative slope of these curves is identical to the entropy difference between the two phases, we may conclude that the entropy difference is often rather constant. In regions of strong curvature there is a strong variation of the entropy difference and this should in turn be due to some special physical effect. The strong curvature in ${}^{\circ}G_{\text{Fe}}^{\text{bcc}} - {}^{\circ}G_{\text{Fe}}^{\text{fcc}}$ above 1000 K is due to the magnetic transition in bcc-Fe with a Curie temperature at 1043 K. It is evident that in order to model this curve one must include a description of the magnetic contribution to the Gibbs energy. Furthermore, all the curves start out parallel to the T axis at absolute zero in accordance with the third law which states that all ordered forms of a substance should approach the same entropy at absolute zero. On heating from absolute zero, a difference in entropy between the various forms develops at fairly low temperatures resulting in strong curvatures. This is due to differences in the vibration frequencies, a factor which evidently must be taken into account in modelling these curves at low temperatures. These two physical factors (magnetic and vibrational) will be discussed in some detail in Chapter 19. Except for such specific physical phenomena the Gibbs energy difference is often described with fairly simple mathematical expressions. The use of a power series in T will be described in the next section.

Before discussing the use of a power series it is useful to examine a different way of choosing the reference for the Gibbs energy. When representing the Gibbs energy for a substance as a function of T , one can use as reference the same substance at some constant T and P . As an example, Fig. 18.3 shows the Gibbs energy of graphite as a function of T at 1 bar, and three different curves are presented because three different references have been used.

It is evident that changing the choice of reference does not always displace the curve vertically; the slope may also be affected. This is due to the fact that Gibbs energy may

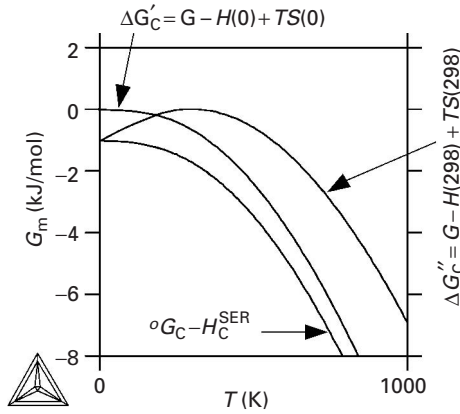


Figure 18.3 The Gibbs energy of graphite, given relative to various references. The pressure is 1 bar.

be regarded as composed of an enthalpy part and an entropy part and neither of these quantities has a natural zero point. In reality, one must define references for both. This can be done by choosing graphite of some temperature, e.g. 0 or 298.15 K. The quantities plotted with these choices are

$$\Delta^{\circ}G'_C = {}^{\circ}G_C(T) - {}^{\circ}H_C(0) + T {}^{\circ}S_C(0) \quad (18.1)$$

$$\Delta^{\circ}G''_C = {}^{\circ}G_C(T) - {}^{\circ}H_C(298) + T {}^{\circ}S_C(298), \quad (18.2)$$

where 298.15 K has been abbreviated as 298. The slope of the curves is obtained as

$$d\Delta^{\circ}G'_C/dT = -{}^{\circ}S_C(T) + {}^{\circ}S_C(0) \quad (18.3)$$

$$d\Delta^{\circ}G''_C/dT = -{}^{\circ}S_C(T) + {}^{\circ}S_C(298). \quad (18.4)$$

These are both satisfactory results.

It is also possible to define the references for H and S using different states. A rather popular choice is the following

$$\Delta^{\circ}G_C = {}^{\circ}G_C(T) - {}^{\circ}H_C(298) + T {}^{\circ}S_C(0). \quad (18.5)$$

It is usually combined with the convention to set ${}^{\circ}S_C(0)$ to zero. The last term is thus omitted. Furthermore, ${}^{\circ}H_C(298)$ is often chosen as the value for the element in its most stable form at 298 K and 1 bar, a quantity which is sometimes denoted by H_C^{SER} for stable element reference. This is why the third curve in Fig. 18.3 is identified as ${}^{\circ}G_C - H_C^{\text{SER}}$. When no reference entropy is given, it means that one has in fact chosen ${}^{\circ}S_i(0)$ and set this quantity to zero. In any case, it is not necessary to decide on the choice of reference until one wants to put in numerical values. In the present text we shall use the notation H_i^{REF} and it mainly serves the purpose of reminding us that for each element one should normally decide on a particular choice and then stick to it. However, it is only after one has started to put in numbers that one must not change the reference.

Before leaving the discussion of reference states we should mention one more alternative. One sometimes uses $G(298)$ as reference for $G(T)$. However, $G(298)$ is just a number and could be interpreted as a reference for enthalpy chosen in such a way that $\Delta^\circ G_C = 0$ at 298 K when ${}^\circ S_C(0) = 0$ is the reference for entropy. This alternative may lead to misunderstandings.

For compounds we shall use the weighted average of H^{REF} for the components,

$$H^{\text{REF}} = \sum v_i H_i^{\text{REF}}, \quad (18.6)$$

and thus plot a quantity ΔG_m which is defined as $G_m - H^{\text{REF}}$. The v_i parameters are the stoichiometric coefficients for the substance, i.e. the number of moles of each component i in one mole of the substance.

Exercise 18.3

Show how one can calculate the change of Gibbs energy on heating a substance from 273 to 373 K under a constant pressure of 1 bar. Assume C_P has a constant value.

Hint

Start by evaluating the changes in H and S separately.

Solution

$$H'' - H' = \int C_P dT = 100C_P; \quad S'' - S' = \int (C_P/T) dT = C_P \ln(373.15/273.15) = 0.312C_P; \quad G'' - G' = H'' - 373.15S'' - H' + 273.15S' = H'' - H' - 373.15(S'' - S') - 100S' = 100C_P - 373.15 \cdot 0.312C_P - 100S' = -16.4C_P - 100S'.$$

We thus find that it is necessary to have a numerical value of S at some temperature. It is not sufficient to be able to calculate the changes in H and S . The change in G also depends upon the choice of reference for S .

18.4 Representation of Gibbs energy of formation

The molar Gibbs energy of formation of a stoichiometric compound θ from the pure elements at any temperature and pressure is obtained by combining expressions for the compound and the component elements, respectively, if they are available,

$$\Delta_f^\circ G_m^\theta = {}^\circ G_m^\theta - \sum v_i {}^\circ G_i^\alpha. \quad (18.7)$$

This quantity is usually regarded as the standard Gibbs energy of formation of θ and was illustrated in Fig. 7.3. The pressure is chosen as 1 bar but any one temperature can be chosen. Often one evaluates this quantity at the actual temperature of interest. ${}^\circ G_m^\theta$ for the compound can be given for any type of formula unit. v_i denotes the stoichiometric coefficients of the compound according to the formula unit chosen and ${}^\circ G_i^\alpha$ usually represents G_m for pure element i in the stable state at 1 bar and the temperature chosen.

The quantity H^{REF} which refers to a particular temperature and pressure does not enter into the equation and one could thus describe experimental information on $\Delta_f^\circ G_m^\theta$ without involving H^{REF} . However, in order to evaluate ${}^\circ G_m^\theta$ from a tabulated value of $\Delta_f^\circ G_m^\theta$ we must introduce H^{REF} through the following modification of Eq. (18.7) by the use of Eq. (18.6),

$${}^\circ G_m^\theta - H^{\text{REF}} = \Delta_f^\circ G_m^\theta + \sum v_i ({}^\circ G_i^\alpha - H_i^{\text{REF}}). \quad (18.8)$$

The temperature dependence of ${}^\circ G_i^\alpha - H_i^{\text{REF}}$ may be known for all the components through mathematical expressions, e.g. power series in T , and stored in that way in a data bank. For the θ compound one may thus store $\Delta_f^\circ G_m^\theta$ and the set of v_i values, or one may store an expression for the temperature dependence of the whole right-hand side of the equation, i.e. of ${}^\circ G_m^\theta - H^{\text{REF}}$. A drawback with the first method is that one must also store information on the particular state α for each element that $\Delta_f^\circ G_m^\theta$ refers to. Furthermore, $\Delta_f^\circ G_m^\theta$ will contain all the peculiarities of the states of the component elements and may thus require a complicated mathematical representation. The second method may thus be more convenient. It may be argued that for many compounds the properties are only known in a narrow range of temperatures and could thus be adequately represented by $\Delta_f^\circ G_m^\theta$ using a few parameters. On the other hand, the representation of ${}^\circ G_m^\theta - H^{\text{REF}}$ provides a better means of extrapolation because it only involves the temperature dependence of the compound itself. It thus seems that this second method should be recommended for general use although the first method may occasionally be used, especially if the experimental information is meagre. One may then use the Neumann–Kopp rule stating that the heat capacity of a substance can be estimated as an average of the values of the components. This leads to the simple expression

$$\Delta_f^\circ G_m^\theta = A + BT. \quad (18.9)$$

In the field of oxides it is common to talk about the Gibbs energy of formation of a complex oxide from its component oxides and apply the same type of expression

$$\Delta_f^\circ G_m^{\text{complexoxide}} = {}^\circ G_m^{\text{complexoxide}} - \sum v_i {}^\circ G_i^{\text{componentoxide}}. \quad (18.10)$$

What has here been said about compounds also applies to various states of a pure element. Using a different notation for this case we can write the equation as,

$${}^\circ G_i^\beta - H_i^{\text{REF}} = \Delta_f^\circ G_i^{\beta/\alpha} + {}^\circ G_i^\alpha - H_i^{\text{REF}}. \quad (18.11)$$

The quantity $\Delta_f^\circ G_i^{\beta/\alpha}$ is the Gibbs energy of formation of β from α and is often called **lattice stability** because it represents the stability of the element in a kind of lattice compared to a reference. In view of the discussion above it is recommended that ${}^\circ G_i^\beta - H_i^{\text{REF}}$ be stored rather than $\Delta_f^\circ G_i^{\beta/\alpha} = {}^\circ G_i^\beta(T) - {}^\circ G_i^\alpha(T)$.

Solution phases differ from stoichiometric phases by having variable composition instead of the constant stoichiometric coefficients v_i . As a consequence, it is not practical to store the properties of solution phases as $G_m - H^{\text{REF}}$. It is more convenient first to compare with the reference states chosen for the components at the same T and P .

Usually one chooses the pure components in the same structure as the solution, the so-called end-members, and the quantity thus defined for the solution is the Gibbs energy of mixing

$${}^M G_m^\alpha(x_i) = G_m^\alpha(x_i) - \sum x_i {}^o G_m^\alpha \quad (18.12)$$

$$G_m^\alpha(x_i) - H^{\text{REF}} = {}^M G_m^\alpha(x_i) + \sum x_i ({}^o G_m^\alpha - H_i^{\text{REF}}). \quad (18.13)$$

Exercise 18.4

From a database using H^{SER} as reference, we get the following Gibbs energy values in J/mole of atoms at 1000 K: For bcc-Cr – 36 694, for C as graphite – 12 659, for Cr_7C_3 – 47 633. Calculate the standard Gibbs energy of formation of Cr_7C_3 at 1000 K.

Hint

We must trust that a database is self-consistent and always uses the same references, whether H^{SER} or another kind. We can thus forget what references this particular database uses.

Solution

$$\Delta_f^o G_m^{\text{Cr}_7\text{C}_3} = {}^o G_m^{\text{Cr}_7\text{C}_3} - 0.7H_{\text{Cr}}^{\text{SER}} - 0.3H_{\text{C}}^{\text{SER}} - 0.7{}^o G_m^{\text{bcc}} + 0.7H_{\text{Cr}}^{\text{SER}} - 0.3{}^o G_{\text{C}}^{\text{graphite}} + 0.3H_{\text{C}}^{\text{SER}} = {}^o G_m^{\text{Cr}_7\text{C}_3} - 0.7{}^o G_m^{\text{bcc}} - 0.3{}^o G_{\text{C}}^{\text{graphite}} = -18150 \text{ J/mol.}$$

18.5 Use of power series in T

Before discussing more sophisticated models for various types of substances, it may be useful to consider the use of a power series in T and P . Let us start with terms in T . Using an ordinary power series we get

$$G_m - H^{\text{REF}} = a + bT + dT^2 + \dots \quad (18.14)$$

$$C_P = -T \partial^2 G_m / \partial T^2 = -2dT + \dots \quad (18.15)$$

Comparison with experimental data shows that this expression for C_P is not very satisfactory and the addition of higher-power terms like T^3 to G_m does not improve the situation much. There are strong experimental indications that one should first of all add a constant term in C_P in order to describe information from well above room temperature. That can be done by adding a term in $T \ln T$ to G_m :

$$G_m - H^{\text{REF}} = a + bT + cT \ln T + dT^2 \quad (18.16)$$

$$S_m = b - c - c \ln T - 2dT \quad (18.17)$$

$$H_m - H^{\text{REF}} = a - cT - dT^2 \quad (18.18)$$

$$C_P = -c - 2dT. \quad (18.19)$$

It could be suggested that we should have written the new term as $cT \ln(T/T_0)$ in order to make the argument dimensionless. However, it is generally agreed to express T and T_0 in kelvin and to include $-cT \ln T_0$ in the bT term.

We may conclude that in the expression for a quantity, representing a contribution to the Gibbs energy, one should normally use $cT \ln T$ as the first term after a and bT . This may simply be regarded as a mathematical model for Gibbs energy which has proved itself useful. It may also be possible to justify the $T \ln T$ term by a physical model predicting that the leading term in the heat capacity should be a constant under some conditions.

When higher-power terms are needed it may seem natural to continue with a T^2 term, possibly followed by even higher powers. However, the coefficients are usually fitted to information from room temperature and up and sometimes one likes to extrapolate to temperatures above the experimental range. Terms in T^2 and T^3 may then give difficulties because they increase rapidly with temperature. For this reason, it is often preferred to use T^{-2} instead of T^2 . Of course, T^{-2} will give the same kind of difficulty in extrapolations below room temperature. However, the power series is already quite inadequate at low temperatures because of the $T \ln T$ term. It is thus necessary to use at least two different mathematical descriptions, one for low temperatures and one for high. The description for low temperatures will be discussed in Chapter 19. For practical reasons, it would often be advantageous to choose 298 K as the break point. It must be noticed that special care must be taken to make H_m , S_m and C_p continuous at the break point.

18.6 Representation of pressure dependence

Let us now define a mathematical model for the pressure dependence by adding terms in P to the power series representation of the Gibbs energy of a substance

$$G_m - H^{\text{REF}} = a + bT + cT \ln T + dT^2 + \dots + eP + fTP + gP^2 + \dots \quad (18.20)$$

It yields the following expressions for other quantities, if the power series is truncated.

$$C_p = -c - 2dT \quad (18.21)$$

$$V_m = e + fT + 2gP \quad (18.22)$$

$$S_m = -b - c - c \ln T - 2dT - fP \quad (18.23)$$

$$H_m - H^{\text{REF}} = a - cT - dT^2 + eP + gP^2 \quad (18.24)$$

$$F_m - H^{\text{REF}} = a + bT + cT \ln T + dT^2 - gP^2 \quad (18.25)$$

$$U_m - H^{\text{REF}} = a - cT - dT^2 - fTP - gP^2 \quad (18.26)$$

$$\alpha = f/V_m = \frac{f}{e + fT + 2gP} \quad (18.27)$$

$$\kappa_T = -2g/V_m = \frac{-2g}{e + fT + 2gP}. \quad (18.28)$$

If we only use G_m terms up to P^2 , we can invert $V_m(P)$ to $P(V_m)$ and thus replace the variable P and express the Helmholtz energy, F_m , as a function of its natural

variables:

$$F_m - H^{\text{REF}} = a + bT + cT \ln T + dT^2 - (e + fT - V_m)^2/4g. \quad (18.29)$$

On the other hand, we cannot replace T by an expression in terms of S_m if we use terms higher than bT . In general, it is thus impossible to get a closed mathematical expression for H_m or U_m as functions of their natural variables, which are (S_m, P) and (S_m, V_m) , respectively.

From F_m we get

$$C_V = -T(\partial^2 F/\partial T^2)_V = -c - 2dT + f^2T/2g. \quad (18.30)$$

The term gP^2 in G_m causes severe difficulties at high P . From the expression for V_m it is evident that g must be negative and V_m will go through zero at some high P , a result which is non-physical. Like the power series in T , a power series in P can thus be used only in a limited range.

As an example of the many alternative models suggested for the representation of the P dependence up to very high P , the following expression may be mentioned for a special reason

$$G_m - H^{\text{REF}} = a + bT + cT \ln T + dT^2 + A[(1 + nPK)^{1-1/n} - 1] \\ \times \exp(\alpha_0 T + 0.5\alpha_1 T^2)/K(n-1). \quad (18.31)$$

It yields the following expression for the molar volume, which is a form of an equation named after Murnaghan [37].

$$V_m(T, P) = A(1 + nPK)^{-1/n} \exp(\alpha_0 T + 0.5\alpha_1 T^2). \quad (18.32)$$

It is evident that the parameter A is formally equal to the molar volume at zero T and P . Furthermore, it can be shown that K is equal to the isothermal compressibility at zero pressure and $\alpha_0 + \alpha_1 T$ can be used to represent the thermal expansivity. This model correctly predicts that the volume should decrease monotonously with increasing pressure but the volume is predicted to approach zero at infinitely high P , which is not realistic. To compensate for this one may add a constant V_0 to the expression for $V_m(T, P)$, which means that one should add a term $V_0 P$ to the G_m expression:

$$G_m - H^{\text{REF}} = a + bT + cT \ln T + dT^2 + V_0 P + [(1 + nPK)^{1-1/n} - 1] \\ \times \exp(\alpha_0 T + 0.5\alpha_1 T^2)/K(n-1). \quad (18.33)$$

The interesting property of Murnaghan's expression for $V_m(T, P)$ is that it can be analytically solved for $P(T, V_m)$,

$$P(T, V_m) = \{A^n(V_m - V_0)^{-n} \exp[n(\alpha_0 T + 0.5\alpha_1 T^2)] - 1\}/nK. \quad (18.34)$$

This is thus a rare case where $F_m(T, V_m)$ can be derived analytically from $G_m(T, P)$,

$$F_m(T, V_m) = G_m - PV_m = H^{\text{SER}} + a + bT + cT \ln T + dT^2 \\ + \frac{A^n(V_m - V_0)^{1-n}}{Kn(n-1)} \cdot \exp[n(\alpha_0 T + 0.5\alpha_1 T^2)] \\ - \frac{A}{K(n-1)} \cdot \exp(\alpha_0 T + 0.5\alpha_1 T^2) + \frac{V_m - V_0}{Kn}. \quad (18.35)$$

Many models for the effect of P are formulated as an equation for P as a function of V_m . Integration yields an expression for the Helmholtz energy. If the equation can give the same P value for two different values of V_m , then it is, in principle, impossible to invert the equation to get $V_m(T, P)$ and to get the Gibbs energy by integration. There are substances which can thus be modelled by the use of the Helmholtz energy but not by using the Gibbs energy which will always give a unique V_m for each P . The critical phenomenon at the gas–liquid transition is a case which cannot be modelled by the use of a Gibbs energy expression.

Exercise 18.5

Show that K in Murnaghan's equation is equal to the isothermal compressibility at zero P .

Hint

Equation (2.37) gives $\kappa_T = -(\partial V/\partial P)_T/V$ which is equal to $-(\partial V_m/\partial P)_T/V_m$ or $-(\partial \ln V_m/\partial P)_T$.

Solution

In $V_m = \ln A - (1/n)\ln(1 + nPK) + \alpha_0 T + 0.5\alpha_1 T^2$; $\kappa_T = (1/n) \cdot 1/(1 + nPK) \cdot nK = K/(1 + nPK)$; $\kappa_T \rightarrow K$ when $P \rightarrow 0$. However, this is no longer true if we add a constant V_0 to V_m .

18.7 Application of physical models

When a particular physical effect can be identified, it could be better described with some special mathematical expression than with a power series. The power series could still be retained for the purpose of describing other effects occurring simultaneously. We may thus divide the molar Gibbs energy into two parts, one due to the special physical effect, G_m^p , and one describing a hypothetical state without that effect, G_m^h ,

$$G_m = G_m^p + G_m^h \quad (18.36)$$

$$G_m - H^{\text{REF}} = G_m^h - H^{\text{REF}} + G_m^p. \quad (18.37)$$

We may apply some special expression for G_m^p and a power series for $G_m^h - H^{\text{REF}}$ and adjust the values of a , b , c , etc., to give a satisfactory representation of the experimental information on $G_m - H^{\text{REF}}$.

In the following chapters we shall examine a large number of different substances or phases and discuss mathematical models based upon some information on their physical or structural properties. The superscript 'p' in G_m^p will sometimes be replaced by letters referring to the particular effect under consideration.

18.8 Ideal gas

In order to demonstrate the principles of modelling, we shall now consider gases. The simplest model of a gaseous element A is defined by the following expression,

$$G_m = {}^\circ G_A(T, P_0) + RT \ln(P/P_0). \quad (18.38)$$

This expression is defined for one mole of gas molecules. ${}^\circ G_A(T, P_0)$ is the value of G_m at any temperature but at a reference pressure usually chosen as $P_0 = 1 \text{ bar} = 100\,000 \text{ Pa}$. ${}^\circ G_A(T, 1 \text{ bar})$ is usually expressed as a power series $K(T)$, including the term $-RT \ln P_0$ which is equal to $-RT \ln 10^5$ if one uses the SI unit, pascal (Pa).

$$G_m - H^{\text{REF}} = K(T) + RT \ln P. \quad (18.39)$$

It should be remembered that one must express P in the term $RT \ln P$ in the same unit that was used in evaluating $K(T)$.

Using the standard procedures we find that this mathematical model yields

$$V_m = RT/P \quad (18.40)$$

$$S_m = -K'(T) - R \ln P \quad (18.41)$$

$$F_m - H^{\text{REF}} = K(T) + RT \ln P - PV_m = K(T) - RT + RT \ln P \quad (18.42)$$

$$\begin{aligned} U_m - H^{\text{REF}} &= K(T) - RT + RT \ln P + TS_m = K(T) - RT \\ &+ RT \ln P - TK'(T) - TR \ln P = K(T) - RT - TK'(T), \end{aligned} \quad (18.43)$$

where $K' = dK/dT$. This is a very useful model because it has been found that many gases have an internal energy which is a function of T but varies very little with P or V under constant T , and they also satisfy the expression for V_m very well. In fact it seems that all gases approach this model at low enough pressures.

This model is regarded as the model for an **ideal gas** and $PV_m = RT$ is called the ideal gas law. It is usually written for N moles of gas molecules (not N moles of atoms),

$$PV = NRT, \quad (18.44)$$

We can easily express the Helmholtz energy as a function of its natural variables

$$F_m - H^{\text{SER}} = K(T) - RT + RT \ln(RT/V_m). \quad (18.45)$$

It is sometimes convenient to express $K(T)$ as a power series in T and from Section 18.5 we remember that it should include a $T \ln T$ term. We may thus write the model for an ideal gas as

$$G_m - H^{\text{REF}} = a + bT + cT \ln T + dT^2 + eT^3 + \dots + RT \ln P. \quad (18.46)$$

and by standard procedures we obtain

$$S_m = -b - c - c \ln T - 2dT - \dots - R \ln P \quad (18.47)$$

$$V_m = RT/P \quad (18.48)$$

$$F_m - H^{\text{REF}} = a + (b - R)T + cT \ln T + dT^2 + eT^3 + \dots + RT \ln P \quad (18.49)$$

$$H_m - H^{\text{REF}} = a - cT - dT^2 - 2eT^3 - \dots \quad (18.50)$$

$$C_P = -c - 2dT - 6eT^2 - \dots \quad (18.51)$$

$$U_m - H^{\text{REF}} = a - (c + R)T - dT^2 - 2eT^3 - \dots \quad (18.52)$$

$$C_V = -c - R - 2dT - 6eT^2 - \dots = C_P - R. \quad (18.53)$$

Sometimes one defines an **ideal classical gas** by further requiring that C_V should be independent of T , which means that d , e and all higher coefficients must be zero.

For monatomic gases the 'ideal classical value' of C_V is $1.5R$ and for diatomic gases it is $2.5R$. Values found experimentally for diatomic gases confirm that they can often be approximated as ideal but not as ideal classical.

Exercise 18.6

A thermally insulated container has two compartments of volumes V_1 and V_2 . A gas is contained in V_1 but V_2 is empty. Suddenly, the wall between the two compartments is removed. Calculate the change in T of the gas when it has come to rest in the whole volume. Assume that the gas is ideal.

Hint

There is no exchange of heat or work with the surroundings.

Solution

The internal energy has not changed because there was no interaction with the surroundings. Since the internal energy is only a function of T and not of P , we realize that T has not changed.

18.9 Real gases

The properties of a real gas can sometimes be approximated by a model obtained by adding a power series in P to the ideal gas model in Eq. (18.39),

$$G_m - H^{\text{REF}} = K(T) + RT \ln P + LP + MP^2 + NP^3 + \dots \quad (18.54)$$

where L , M , N etc., may depend on T . By standard procedures we obtain

$$V_m = RT/P + L + 2MP + 3NP^2 \dots \quad (18.55)$$

$$F_m - H^{\text{REF}} = G_m - H^{\text{REF}} - PV_m = K(T) + RT \ln P - RT - MP^2 - 2NP^3 - \dots \quad (18.56)$$

It is evident that the V_m expression cannot be inverted to $P(V_m)$ and it is thus impossible to derive an analytical expression for $F_m(T, V_m)$. However, by using only the LP term from the power series one obtains an expression for V_m which can be inverted

$$P = RT/(V_m - L). \quad (18.57)$$

We could then express F_m in its natural variables,

$$F_m - H^{\text{REF}} = K(T) - RT + RT \ln \frac{RT}{V_m - L}. \quad (18.58)$$

A gas obeying this model is sometimes called a **slightly imperfect gas**.

It is sometimes convenient to treat real gases by introducing a new quantity f , called **fugacity**, through the expression

$$G_m - H^{\text{SER}} = K^f(T) + RT \ln f, \quad (18.59)$$

where $K^f(T)$ has been chosen in such a way that f approaches P for low P . Using this concept one can temporarily treat any gas as if it were ideal and postpone the introduction of its real properties until later. Sometimes one introduces the **fugacity coefficient**, f/P , and it is evident that it approaches the value 1 at low P . However, if this approach is applied to a gas with molecules, e.g. O_2 , it should be realized that there may be some dissociation into atoms $\text{O}_2 \rightarrow 2\text{O}$ which would increase the pressure. This effect would be more pronounced at low pressures. The concept of fugacity should thus be applied to each gas species separately but it must then be combined with a calculation of the equilibrium contents of the species.

So far we have based the modelling of gases on the Gibbs energy, using T and P as the variables. However, it is sometimes more convenient to use T and V_m as the variables and thus to define the model using the Helmholtz energy. One may for instance define a model with the following expression where $K(T)$ is not the same as before,

$$F_m - H^{\text{REF}} = K(T) + RT[-\ln V_m + B_2/V_m + B_3/2V_m^2 + \dots], \quad (18.60)$$

which gives

$$P = RT[1/V_m + B_2/V_m^2 + B_3/V_m^3 + \dots], \quad (18.61)$$

where B_2, B_3 , etc., are called virial coefficients. There is no exact relation between these coefficients and those introduced through the G_m expression, but in order to compare them we can write the expressions in the following forms

$$PV_m = RT + LP + 2MP^2 + 3NP^3 + \dots \quad (18.62)$$

$$PV_m = RT + RTB_2/V_m + RTB_3/V_m^2 + \dots \quad (18.63)$$

For small values of the coefficients, we may first approximate $1/V_m$ by P/RT . By introducing this in the second term in Eq. (18.63) and dropping the last term we get

$$PV_m = RT + RTB_2P/RT = RT + B_2P. \quad (18.64)$$

We can use

$$1/V_m = 1/(RT/P + B_2) = (P/RT)/(1 + B_2P/RT) \cong P/RT - B_2(P/RT)^2. \quad (18.65)$$

as a better approximation. By introducing this we get

$$PV_m = RT + B_2P + (B_3 - B_2^2)P^2/RT, \quad (18.66)$$

when omitting higher-order terms. Comparing with Eq. (18.62) we may thus approximate L as B_2 and M as $(B_3 - B_2^2)/2RT$.

Another model based on $F_m(T, V_m)$ is the following

$$F_m - H^{\text{REF}} = K(T) - a/V_m - RT \ln(V_m - b). \quad (18.67)$$

It gives

$$P = -a/V_m^2 + RT/(V_m - b), \quad (18.68)$$

which can be rearranged into

$$(P + a/V_m^2)(V_m - b) = RT. \quad (18.69)$$

This expression was proposed by van der Waals. The terms a/V_m^2 and $-b$ may be regarded as corrections to the ideal gas law. This expression correctly predicts that there is a critical point below which a system decomposes into a liquid and a gas. However, it does not describe real systems with any accuracy. Many improvements of the van der Waals equation have been suggested but they will not be discussed here.

Exercise 18.7

Derive an expression for the fugacity of a gas obeying the van der Waals equation of state. Then calculate the fugacity coefficient, f/P .

Hint

$G_m - H^{\text{REF}} = F_m - H^{\text{REF}} + PV_m = K(T) - a/V_m - RT \ln(V_m - b) - a/V_m + RTV_m/(V_m - b)$ should be compared with $G_m - H^{\text{REF}} = K^f(T) + RT \ln f$.

At small P , and thus large V_m , the two expressions should be equal if f is replaced by P .

For large V_m we find that $G_m - H^{\text{REF}}$ goes towards $K(T) - RT \ln RT + RT \ln P + RT$. We should thus identify $K^f(T)$ with $K(T) - RT \ln RT + RT$.

Solution

For any P we can write $K(T) - RT \ln RT + RT + RT \ln f = K(T) - 2a/V_m - RT \ln(V_m - b) + RTV_m/(V_m - b)$ and get $RT \ln f = -RT \ln[(V_m - b)/RT] + RTb/(V_m - b) - 2a/V_m$.

This yields $f = RT/(V_m - b) \cdot \exp[b/(V_m - b) - 2a/RTV_m]$. By dividing with $P = -a/V_m^2 + RT/(V_m - b)$ we finally find $f/P = [1 - a(V_m - b)/RTV_m^2]^{-1} \cdot \exp[b/(V_m - b) - 2a/RTV_m]$.

18.10 Mixtures of gas species

Gases dissolve in each other so readily and with so little interaction that the resulting phase is regarded as a mixture of the component species (free atoms, molecules and ions). In principle, it may also be regarded as a solution. We shall first discuss a mixture of several species, each one of which forms an ideal gas when pure. Let y_k be the fraction of species k and thus $\sum y_k = 1$. Let us consider a mixture of one mole of species. Each gas will fill the complete volume V , but in line with the ideal gas concept we shall assume that there is no interaction between them. We shall thus assume that the ideal gas law applies to the mixture, $PV_m = RT$, and that the chemical potential of a component k , μ_k , has the same value it would have, had it been alone in the same volume V . The pressure of that component would then be $P_k = y_k RT/V = y_k P$ where P is the pressure of the mixture

$$\begin{aligned}\mu_k &= G_m(k) = {}^\circ G_k(T, P_0) + RT \ln P_k \\ &= H_k^{\text{REF}} + K_k(T) + RT \ln P_k = H_k^{\text{REF}} + K_k(T) + RT \ln y_k + RT \ln P,\end{aligned}\quad (18.70)$$

and we get for the mixture

$$\begin{aligned}G_m &= \sum y_i \mu_i = \sum y_i {}^\circ G_i(T, P_0) + RT \sum y_i \ln P_i \\ &= H^{\text{REF}} + \sum y_i K_i(T) + RT \sum y_i \ln y_i + RT \ln P\end{aligned}\quad (18.71)$$

$$G_m - H^{\text{REF}} = \sum y_i K_i(T) + RT \ln P + RT \sum y_i \ln y_i. \quad (18.72)$$

The last term may be regarded as the contribution from the mixing of different molecules. It is proportional to T and is thus of pure entropy character. $-R \sum y_i \ln y_i$ may be regarded as the ideal entropy of mixing.

For a mixture of ideal gases it can be imagined that gas k actually has the pressure P_k in the gas mixture and that the total pressure of the mixture is the sum of the pressures of the individual gases. We have thus used

$$\sum P_i = \sum y_i P = P. \quad (18.73)$$

P_k is regarded as the **partial pressure** of gas k in the mixture. It is interesting to note that the expression for ideal entropy of mixing appears in Eq. (18.72) as a direct result of the model. For real gases it is no longer possible to define the partial pressure in a strict sense but it is common to use this concept and the relation $P_i = y_i P$ even in such cases. As a first attempt to model G_m for a mixture of real gases, one could add the terms for slightly imperfect gases in the form $\sum y_i L_i P_i$ which can be written as $\sum y_i^2 L_i P$. The second power of y_i indicates that these terms describe the interaction of molecules with other molecules of the same kind. It would be natural also to add terms representing interactions between different kinds of molecules, $\sum \sum y_i y_j L_{ij} P$. We thus get

$$G_m - H^{\text{REF}} = \sum y_i K_i(T) + RT \ln P + RT \sum y_i \ln y_i + P \sum \sum y_i y_j L_{ij} \quad (18.74)$$

It is interesting to calculate what pressure, P' , the same amount of gas k would have if it were alone in the same volume. For pure k we get

$${}^\circ G_k - H_k^{\text{REF}} = K_k(T) + RT \ln P' + P' L_{kk}. \quad (18.75)$$

The molar volume would be $RT/P' + L_{kk}$ and the volume of the actual amount y_k would be

$$V = y_k(RT/P' + L_{kk}). \quad (18.76)$$

However, this is supposed to be equal to the molar volume of the mixture,

$$y_k(RT/P' + L_{kk}) = RT/P + \sum \sum y_i y_j L_{ij}. \quad (18.77)$$

We thus find

$$\begin{aligned} 1/P' &= 1/y_k P + (\sum \sum y_i y_j L_{ij} - y_k L_{kk}) / RT y_k \\ &= 1/P_k + (\sum \sum y_i y_j L_{ij} - y_k L_{kk}) / RT y_k. \end{aligned} \quad (18.78)$$

We have here expressed $y_k P$ through the partial pressure and it is evident that it is no longer equal to the pressure of the same amount of pure k , unless all the interactions are zero. The concept of partial pressure is thus less useful for real gas mixtures than for ideal ones. The concept of fugacity is more useful. For a component k in a mixture it is defined from

$$\mu_k - H^{\text{REF}} = K_k(T) + RT \ln f_k, \quad (18.79)$$

where $K_k(T)$ is formulated in such a way that f_k approaches $y_k P$ for low P . In order to evaluate the fugacity from a particular model one must first derive an expression for μ_k from the model. From Eq. (18.74) we get

$$\mu_k - H^{\text{REF}} = K_k(T) + RT \ln(y_k P) + P (2y_k \sum L_{kj} - \sum \sum y_i y_j L_{ij}), \quad (18.80)$$

and for the fugacity coefficient we obtain

$$f_k/P_k = f_k/y_k P = \exp[P(2y_k \sum L_{kj} - \sum \sum y_i y_j L_{ij})/RT]. \quad (18.81)$$

For an ideal gas mixture we get

$$f_k/P_k = f_k/y_k P = 1. \quad (18.82)$$

A similar model based upon the Helmholtz energy is generally written as

$$\begin{aligned} P &= RT [1/V_m + (\sum y_i^2 B_{ii} + \sum \sum y_i y_j B_{ij}) / V_m^2] \\ &= RT [1/V_m + (\sum y_i B_{ii} + \sum \sum y_i y_j (B_{ij} - (B_{ii} + B_{jj})/2)) / V_m^2] \end{aligned} \quad (18.83)$$

and it is often found that $B_{ij} - (B_{ii} + B_{jj})/2$ is small.

Exercise 18.8

Examine a slightly imperfect gas with two kinds of molecules, A and B. Is there any relation between the L coefficients which would make the fugacity coefficients independent of the composition?

Hint

Use Eq. (18.81). For a binary system only one composition variable is independent, say y_B .

Solution

$\ln(f_A/P_A) = (P/RT) \cdot (2y_A L_{AA} + 2y_B L_{AB} - y_A^2 L_{AA} - 2y_A y_B L_{AB} - y_B^2 L_{BB}) = (P/RT) \cdot [L_{AA} - (L_{AA} + L_{BB} - 2L_{AB})y_B^2]$. We thus find that $L_{AA} + L_{BB} - 2L_{AB} = 0$ makes f_A/P_A independent of composition. For symmetry reasons, it also makes f_B/P_B independent of composition.

18.11 Black-body radiation

It is illustrative to compare the ideal gas behaviour with the properties of black-body radiation and with an electron gas. For the former we may start from a result from quantum mechanics saying that the energy of black-body radiation is proportional to the volume and T^4 . The constant of proportionality, a , is called the Stefan constant and it has a value of $8\pi^5 k^4 / 15c^3 h^3 = 7.57 \cdot 10^{-16} \text{ J/m}^3 \text{ K}^4$, where k is Boltzmann's constant, c is the speed of light and h is Planck's constant.

$$U = aT^4 V. \quad (18.84)$$

However, in order to derive other quantities we need $U(S, V)$. By simple manipulations we obtain

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = 4aT^3 V \quad (18.85)$$

$$S = \int_0^T \frac{C_V}{T} dT = \frac{4}{3} aT^3 V; \quad T^3 = 3S/4aV \quad (18.86)$$

$$U(S, V) = a(3S/4aV)^{4/3} V = (3S/4)^{4/3} / (aV)^{1/3}. \quad (18.87)$$

We have thus derived a characteristic state function for black-body radiation and can now calculate any thermodynamic quantity.

$$F = U - ST = -\frac{1}{3} aT^4 V \quad (18.88)$$

$$P = - \left(\frac{\partial U}{\partial V} \right)_S = -(3S/4)^{3/4} \cdot \frac{-1}{3} (aV)^{-4/3} = \frac{1}{3} (3S/4aV)^{4/3} = \frac{1}{3} aT^4 \quad (18.89)$$

$$PV = \frac{1}{3} aT^4 V \quad (18.90)$$

$$G = U + PV - TS = aT^4 V + \frac{1}{3} aT^4 V - \frac{4}{3} aT^4 V = 0. \quad (18.91)$$

The last result may seem surprising but is natural because P and T are not independent variables in the particular case of black-body radiation. Consider a container containing no matter and with its walls kept at a certain temperature T and an external pressure P is applied, then the container will collapse if $P > aT^4/3$ and all the radiation will vanish. If $P < aT^4/3$ then the container will expand indefinitely and new radiation will be created with no limitation as long as the walls are kept at the same temperature.

Exercise 18.9

Derive an expression for the isothermal compressibility of black-body radiation.

Hint

It may be easier to derive $(\partial P/\partial V)_T$ than $(\partial V/\partial P)_T$.

Solution

We get $\kappa_T = -(1/V_m) \cdot (\partial V_m/\partial P)_T = -(1/V) \cdot (\partial V/\partial P)_T$ from the definition. From $P = aT^4/3$ we get $(\partial P/\partial V)_T = 0$ and $(\partial V/\partial P)_T = \infty$ and $\kappa_T = \infty$. This is in complete agreement with the last two sentences in the text.

18.12 Electron gas

The heat capacity for the electron gas in a metal is often given as

$$C_V = \gamma_e T. \quad (18.92)$$

In real metals, the coefficient γ_e has different values at low and high T and a single expression cannot be used for the whole range of T . The low- T value is often about 1.4 times the high- T value. However, γ_e is independent of T in a free electron gas. We shall now examine the properties of such a gas. Its γ_e value depends upon the density which can be expressed through V_m . According to the electron theory, γ_e is actually proportional to $V_m^{2/3}$. For one mole of electrons we obtain

$$U_m = \int_0^T C_V dT = U_m(0K) + \gamma_e T^2/2 \quad (18.93)$$

$$S_m = \int_0^T \frac{C_V}{T} dT = \gamma_e T \quad (18.94)$$

$$F_m = U_m - TS_m = U_m(0K) - \gamma_e T^2/2. \quad (18.95)$$

In order to derive an expression for G_m we must calculate P from F_m as a function of T , V_m . Then we must remember that the electron theory predicts that γ_e is proportional to $V_m^{2/3}$ and we should treat $\gamma_e/V_m^{2/3}$ as a constant

$$F_m = U_m(0\text{K}) - (\gamma_e/V_m^{2/3}) \cdot V_m^{2/3} T^2/2 \quad (18.96)$$

$$P = - \left(\frac{\partial F_m}{\partial V_m} \right)_T = \frac{1}{2} \frac{\gamma_e T^2}{V_m^{2/3}} \cdot \frac{2}{3} V_m^{-1/3} = \frac{1}{3} \gamma_e T^2 / V_m \quad (18.97)$$

$$G_m = F_m + P V_m = U_m(0\text{K}) - \gamma_e T^2/2 + \gamma_e T^2/3 = U_m(0\text{K}) - \gamma_e T^2/6. \quad (18.98)$$

We have neglected to discuss the possible dependence of $U_m(0\text{ K})$ on V_m but that could only contribute a T -independent term in G_m .

If we want to apply the treatment of an electron gas to a metal we should realize that there is a strong interaction between the electrons and the ionized atoms which more or less eliminates the pressure of the electron gas. It is thus common to give their contribution to G_m as $-\gamma_e T^2/2$.

It should be realized that published values of γ_e for metals refer to one mole of atoms, and not electrons. The values of γ_e are relatively small and its contribution to C_V only grows proportional to T . Even though it predominates at very low T it will soon be negligible in comparison with the contribution from thermal vibrations of the atoms which initially increases proportional to T^3 . However, at very high T the latter contribution levels off at the value of $3R$ and the electronic contribution again becomes important.

Exercise 18.10

Estimate the ratio of the electronic contribution to C_V of pure Ni and the contribution from thermal vibrations at the melting point, 1728 K, if $\gamma_e = 54.4 \cdot 10^{-4} \text{ J/mol K}^2$.

Hint

Suppose the temperature is so high that the vibrational contribution can be approximated as $3R$ and the γ_e value may be taken as the tabulated value divided by 1.4.

Solution

$$(54.5 \cdot 10^{-4}/1.4)1728/3 \cdot 8.3145 = 0.27.$$

19 Modelling of disorder

19.1 Introduction

In this chapter we shall model the thermodynamic effect of some physical phenomena. In each case we shall start by defining an internal variable representing the extent of the physical phenomenon to be discussed. We shall proceed by deriving an expression for one of the characteristic state functions in terms of the internal variable together with a set of external variables. The choice of characteristic state function depends upon what set of external variables is most convenient. Then we shall calculate the equilibrium value of the internal variable by putting the driving force for its change equal to zero. Finally, we shall try to eliminate the internal variable by inserting the expression for its equilibrium value in the characteristic state function.

Our derivation of an expression for the characteristic state function will usually be based upon two separate evaluations, one concerned with the entropy due to the disorder created by the physical phenomenon and the other concerned with what may be called the non-configurational contribution. The entropy will be evaluated from Boltzmann's relation which is here preferred because it is felt that it gives a better physical insight than the more general and elegant method of statistical thermodynamics based upon the use of partition functions. The purpose of statistical thermodynamics is to model the thermodynamic properties of various types of systems from statistical considerations on the atomic level. The relation proposed by Boltzmann can be derived from such considerations.

19.2 Thermal vacancies in a crystal

We shall start by considering vacancies in a crystal of a pure element. A convenient internal variable would be the number of vacancies, N_{va} , in a crystal with N atoms. This internal variable is sufficient for defining the contribution of the vacancies to the internal energy if it is assumed that the interaction between the vacancies can be neglected. This may be a reasonable approximation for low contents of vacancies and we shall construct a model from this approximation.

The state with N_{va} vacancies can be realized in a number of ways by placing the vacancies in different arrangements on the lattice sites. The number of different

arrangements is

$$W = \frac{(N + N_{\text{Va}})!}{N!N_{\text{Va}}!}, \quad (19.1)$$

since there must be $N + N_{\text{Va}}$ lattice sites and we cannot distinguish between two atoms, nor between two vacancies. From Boltzmann's relation we can now calculate the contribution to the entropy from the vacancies and we can use the following approximation if we consider a system where N and N_{Va} are both large numbers,

$$\begin{aligned} \Delta S/k &= \ln W = \ln(N + N_{\text{Va}})! - \ln N! - \ln N_{\text{Va}}! \\ &\cong (N + N_{\text{Va}}) \ln(N + N_{\text{Va}}) - N \ln N - N_{\text{Va}} \ln N_{\text{Va}} \\ &= -N \ln \frac{N}{N + N_{\text{Va}}} - N_{\text{Va}} \ln \frac{N_{\text{Va}}}{N + N_{\text{Va}}} \\ &= -N \left(\ln(1 - y_{\text{Va}}) + \frac{y_{\text{Va}}}{1 - y_{\text{Va}}} \ln y_{\text{Va}} \right), \end{aligned} \quad (19.2)$$

where $y_{\text{Va}} = N_{\text{Va}}/(N + N_{\text{Va}})$, the fraction of sites that are vacant.

When choosing a characteristic state function we should realize that it is very awkward to treat the energy of a vacancy, u , as a function of S_{m} and V_{m} or of T and V_{m} because V_{m} is usually defined for one mole of atoms, not lattice sites. Thus V_{m} will naturally increase, or the lattice must be compressed, when a vacancy is introduced by the creation of a new lattice site. It is most convenient to treat u as a function of T and P and we should thus choose G as our characteristic state function. In order to be rigorous in the derivation to follow, we should actually introduce a Gibbs energy of formation of a vacancy, g , instead of the energy, u , and obtain for the contribution due to N_{Va} vacancies, when added to N atoms,

$$\Delta G = N_{\text{Va}}g + kNT \left(\ln \frac{N}{N + N_{\text{Va}}} + \frac{N_{\text{Va}}}{N} \ln \frac{N_{\text{Va}}}{N + N_{\text{Va}}} \right). \quad (19.3)$$

The quantity g may be regarded as the non-configurational Gibbs energy per vacancy. We have thus achieved our first goal. It is worth emphasizing that we managed to derive an expression for ΔG without introducing any further internal variable. Before proceeding it is important to realize that N_{Va} is in fact an internal variable because we do not need an external reservoir from which to take vacancies. Alternatively, we may imagine that we have an external reservoir of vacancies with a chemical potential equal to zero. We may thus regard g as the non-configurational Gibbs energy of formation of a vacancy or of dissolution of a vacancy from an external reservoir.

We have found an expression for the contribution to the Gibbs energy from a given number of vacancies, N_{Va} . It can be used to evaluate the equilibrium number of vacancies under constant T and P . If there is a mechanism, or 'reaction', by which vacancies can form, then there should be a spontaneous change as long as the driving force for change is positive. Assuming that g is independent of N_{Va} under constant T , P and N , we obtain

by expressing the extent of reaction with N_{Va} ,

$$\begin{aligned}
 -D &= (\partial G / \partial \xi)_{T,P,N} \equiv (\partial G / \partial N_{\text{Va}})_{T,P,N} \\
 &= g + kNT \left(\frac{-1}{N + N_{\text{Va}}} + \frac{1}{N} \ln \frac{N_{\text{Va}}}{N + N_{\text{Va}}} + \frac{N_{\text{Va}}}{N} \cdot \frac{1}{N_{\text{Va}}} - \frac{N_{\text{Va}}}{N} \ln \frac{N_{\text{Va}}}{N + N_{\text{Va}}} \right) \\
 &= g + kT \ln \frac{N_{\text{Va}}}{N + N_{\text{Va}}} = g + kT \ln y_{\text{Va}}. \tag{19.4}
 \end{aligned}$$

By putting this equal to zero we obtain, for the equilibrium number of vacancies,

$$y_{\text{Va}}^{\text{eq}} = \exp(-g/kT). \tag{19.5}$$

This is an expression characteristic of so-called Boltzmann statistics. It reveals how the fraction of vacant sites varies with temperature. The higher the temperature, the larger the fraction is. This is why such vacancies are often called **thermal vacancies**.

If we instead focus our interest upon the number of vacancies per mole of atoms we obtain, for its equilibrium value,

$$\frac{y_{\text{Va}}^{\text{eq}}}{1 - y_{\text{Va}}^{\text{eq}}} = \frac{N_{\text{Va}}^{\text{eq}}}{N} = \frac{1}{\exp(g/kT) - 1}. \tag{19.6}$$

This kind of expression is usually connected with the so-called Bose–Einstein statistics.

In the present case it will be possible to eliminate the internal variable at equilibrium and obtain the contribution of thermal vacancies to the Gibbs energy,

$$\begin{aligned}
 \Delta G &= N_{\text{Va}}g + kTN \ln(1 - y_{\text{Va}}^{\text{eq}}) + kTN_{\text{Va}} \ln y_{\text{Va}}^{\text{eq}} \\
 &= N_{\text{Va}}g + kTN \ln(1 - y_{\text{Va}}^{\text{eq}}) + kTN_{\text{Va}}(-g/kT) \\
 &= kTN \ln(1 - y_{\text{Va}}^{\text{eq}}) \cong -kTN y_{\text{Va}}^{\text{eq}}. \tag{19.7}
 \end{aligned}$$

For a system containing one mole of atoms, i.e. with N equal to Avogadro's number, we obtain $\Delta G_{\text{m}} \cong -RT y_{\text{Va}}^{\text{eq}}$, a value that is negligible in most contexts.

For a typical metal we can estimate the value of g from Eq. (19.5) using the information that the fraction of vacant sites is between 10^{-3} and 10^{-4} close to the melting temperature, $T_{\text{m.p.}}$. We thus obtain $g/kT_{\text{m.p.}} = 2.3 \cdot (3 \text{ to } 4) \cong 8$.

The result of Eq. (19.7) is surprisingly simple. It gives the complete information on ΔG at equilibrium as function of T and, if one is only interested in thermodynamic properties at equilibrium, this expression will be sufficient. On the other hand, the number of vacancies may itself be of importance because of effects on other properties like volume or diffusivity. The model can even be applied for evaluating ΔG when the number of vacancies differs from the equilibrium number. In such cases one must use the basic equation of ΔG as a function of T and N_{Va} . One may, for instance, be interested in the process by which the number of vacancies could approach the equilibrium value. There are many possible mechanisms. If the actual number of vacancies is much higher than the equilibrium value, then the driving force could be large enough for the nucleation of a pore. If it is lower, mechanisms involving condensation on dislocations could still operate. For such considerations it is essential to know the driving force. Eliminating g

between Eqs (19.4) and (19.5) we obtain

$$D = kT \ln y_{\text{Va}}^{\text{eq}} - kT \ln y_{\text{Va}} = -kT \ln (y_{\text{Va}}/y_{\text{Va}}^{\text{eq}}) \quad (19.8)$$

This is the driving force for the formation of a new vacancy. The driving force per mole of disappeared vacancies is obtained as

$$D = RT \ln (y_{\text{Va}}/y_{\text{Va}}^{\text{eq}}) \quad (19.9)$$

Exercise 19.1

Consider a pure metal A with an equilibrium amount of vacancies. Derive an expression for the chemical potential of vacancies.

Hint

We need an expression for the total G and should then start from pure A without any vacancies. That G is proportional to N , say Ng_A .

Solution

$G = Ng_A + N_{\text{Va}}g_{\text{Va}} + kNT\{\ln[N/(N + N_{\text{Va}})] + (N_{\text{Va}}/N) \ln[N_{\text{Va}}/(N + N_{\text{Va}})]\}$; μ_{Va}
 $= \partial G/\partial N_{\text{Va}} = g_{\text{Va}} + kNT\{-1/(N + N_{\text{Va}}) + (1/N) \ln[N_{\text{Va}}/(N + N_{\text{Va}})] + (N_{\text{Va}}/N)$
 $(1/N_{\text{Va}}) - (N_{\text{Va}}/N)[1/(N + N_{\text{Va}})]\} = g_{\text{Va}} + kT \ln[N_{\text{Va}}/(N + N_{\text{Va}})] = g_{\text{Va}} + kT \ln y_{\text{Va}}$.
 At equilibrium we get from Eq. (19.5): $\mu_{\text{Va}} = g_{\text{Va}} - g_{\text{Va}} = 0$.

19.3 Topological disorder

Even though the structure of a melt may intuitively be imagined as completely disordered, in reality the short-range arrangement of the atoms in a liquid metal is rather similar to that in the crystalline state. It may thus be useful to describe the liquid as a crystalline phase with so much disorder that all the long-range order has been destroyed. In this connection one talks about **topological disorder**. A very simple and crude model of the topological disorder in a liquid metal is based upon the assumption that the amount of thermal vacancies increases discontinuously during melting. This model can be supported by many semi-quantitative considerations involving such properties as density, compressibility, thermal expansion and diffusivity. X-ray measurements have indicated that the coordination number in liquid metals is about 11, as compared to 12 for the close-packed fcc and hcp structures. This result immediately suggests that the vacancy concentration would be about 1/12, i.e. 8%.

This value compares favourably with a value we obtain by evaluating how many vacancies can form when the heat of melting is added to the solid. According to Richards' rule the entropy of melting is approximately R and the heat of melting is $RT_{\text{m.p.}}$. With

the approximate value of 8 for $g/kT_{m.p.}$ given above, we get

$$N_{Va} = RT_{m.p.}/g = RT_{m.p.}/8kT_{m.p.} = N/8 \quad (19.10)$$

$$y_{Va} = \frac{N_{Va}}{N + N_{Va}} = \frac{1}{9} \cong 11\%. \quad (19.11)$$

It does not compare so nicely with a value obtained from the entropy of melting

$$\Delta S/k = -N \ln \frac{N}{N + N_{Va}} - N_{Va} \ln \frac{N_{Va}}{N + N_{Va}} = R/k = N \quad (19.12)$$

$$\ln(1 - y_{Va}) + \frac{y_{Va}}{1 - y_{Va}} \ln y_{Va} = -1. \quad (19.13)$$

By solving this equation numerically one finds approximately $y_{Va} = 1/3$ or 35%. It is evident that this simple model is too crude to give a quantitative description of melting.

At the melting point of a metal, C_P is often larger in the melt than in the solid. This difference grows for the undercooled melt and the difference in entropy between the two phases will thus decrease with decreasing temperature. Extrapolations have indicated that one may approach a temperature below which the undercooled melt would have lower entropy than the crystalline solid. This is regarded as impossible and is called Kauzmann's paradox [38]. It has instead been suggested that the liquid has turned amorphous on cooling to the temperature where the difference in entropy disappears. Below that critical point the amorphous solid is assumed to have almost the same entropy as the crystalline solid. Experimentally one has observed a so-called glass transition where the liquid turns extremely viscous and it has been related to the temperature defined by equal entropy. According to this picture, the topological disorder in the amorphous solid should be very limited. It is not sufficient to make the phase liquid and it has rather low entropy. On heating above the glass transition temperature a large amount of defects are created. They make the amorphous phase more liquid and contribute to the entropy and heat capacity. An increasing amount of defects are created as the temperature is raised towards the melting point. From the thermodynamic point of view, the melting of the amorphous solid is thus a gradual process which continues to or even continues above the melting point. Figure 19.1 illustrates this behaviour schematically.

Exercise 19.2

Estimate the difference in H at 0 K between the amorphous and crystalline states of a metal from the following simplifying assumptions. The two states have the same entropy at 0 K. Up to T_{glass} the two states have the same C_P . T_{glass} falls at $T_{m.p.}/3$ and above $T_{m.p.}/3$ the difference in C_P is linear in T . Let $\Delta C_P = 0$ at $T_{m.p.}$.

Hint

Estimate the difference in enthalpy and entropy at $T_{m.p.}$ from Richards' rule, $\Delta H_m/T_{m.p.} = \Delta S_m \cong R$. The assumptions give $\Delta S_m = 0$ at $T_{m.p.}/3$.

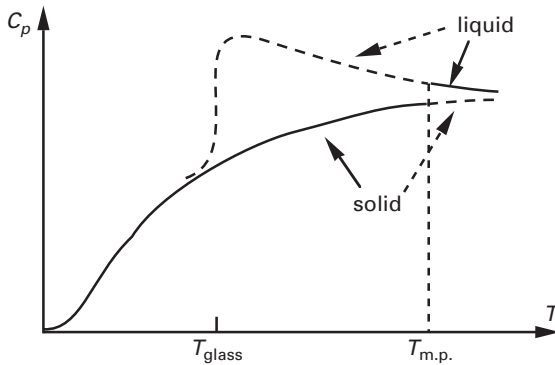


Figure 19.1 Schematic diagram comparing the heat capacities of a crystallized metal and its amorphous state.

Solution

$\Delta C_P = a + bT$ where $a + bT_{m.p.} = 0$. A second relation between a and b is obtained by integrating for the entropy between $T_{m.p.}/3$ and $T_{m.p.}$: $R = \int (\Delta C_P/T) dT = a \ln 3 + (2/3)bT_{m.p.}$; $a = R/(\ln 3 - 2/3) = 2.3R$; $b = -2.3R/T_{m.p.}$. ΔH_m changes between $T_{m.p.}/3$ and $T_{m.p.}$ by $\int \Delta C_P dT = a(T_{m.p.} - T_{m.p.}/3) + 0.5b(T_{m.p.}^2 - T_{m.p.}^2/9) = 2.3RT_{m.p.}(2/3 - 4/9) = 0.51RT_{m.p.}$.

Thus we get, at $T_{m.p.}/3$ as well as at 0 K, $\Delta H_m = RT_{m.p.} - 0.51RT_{m.p.} = 0.49RT_{m.p.}$.

19.4 Heat capacity due to thermal vibrations

According to quantum mechanics, the energy of heating can be added only as quanta. For an harmonic oscillator of frequency ν , the magnitude of the quanta is $h\nu$ where h is Planck's constant. Einstein constructed a simple model of a crystal by assuming that each atom vibrates independent of all the others and has three directions of movement. A crystal with N atoms could thus be regarded as consisting of $3N$ linear oscillators, all of them with a frequency ν . The question, how many quanta such a crystal should have at equilibrium, is closely related to our previous question how many vacancies a crystal should have at equilibrium. If there are n quanta, the energy increase is $\Delta U = nh\nu$ compared to the conditions at absolute zero. In order to evaluate the entropy contribution we must find in how many ways n quanta can distribute themselves on $3N$ oscillators. By numbering the oscillators $a_1 a_2 a_3 \dots a_{3N}$ and the quanta $k_1 k_2 k_3 \dots k_n$ we can describe a particular distribution by first giving the number of a certain oscillator and then the quanta which are placed there, e.g. $a_4 k_3 k_5 a_6 k_2 a_1 k_7 k_9 a_7 a_2 \dots$. If all the permutations of these elements represent possible distributions there should be $(3N + n)!$ different distributions. However, we must start with an oscillator and the first factor should thus be $3N$ instead of $3N + n$. Furthermore, it would be impossible to distinguish between many of the distributions since all the oscillators are identical and so are all the quanta.

The number of distinguishable distributions is thus

$$W = \frac{3N}{3N+n} \frac{(3N+n)!}{(3N)!n!}. \quad (19.14)$$

This is almost identical to the result for thermal vacancies except for the first factor, which is of no importance for large N and n when we take the logarithm, and except for the fact that N has been replaced by $3N$. We can thus use the final result from the previous derivation but this time we shall apply it to the Helmholtz energy because the frequency, and thus the energy $h\nu$, will vary with the distance between the atoms, i.e. the volume. Thus we should like to keep the volume constant. We obtain

$$\Delta F = nh\nu + 3kNT \left(\ln \frac{3N}{3N+n} + \frac{n}{3N} \ln \frac{n}{3N+n} \right). \quad (19.15)$$

The equilibrium number of quanta under constant T and V is obtained from $\partial \Delta F / \partial n = 0$,

$$\frac{n}{3N+n} = \exp(-h\nu/kT). \quad (19.16)$$

Again it will be possible to eliminate the internal variable at equilibrium and we find

$$\Delta F = 3RT \ln[1 - \exp(-h\nu/kT)]. \quad (19.17)$$

By standard methods we can calculate the heat capacity due to thermal vibrations,

$$C_V = -T(\partial^2 \Delta F / \partial T^2)_V = 3R \left(\frac{h\nu}{kT} \right)^2 \cdot \frac{\exp(h\nu/kT)}{[\exp(h\nu/kT) - 1]^2}. \quad (19.18)$$

The only parameter characteristic of the particular material under consideration is the frequency, ν . It always appears in the dimensionless combination $h\nu/kT$. The combination of constants $h\nu/k$ is of the dimension temperature and we can thus introduce a new material constant instead of the frequency, the Einstein temperature $\Theta = h\nu/k$.

$$C_V = 3R(\Theta/T)^2 \cdot \exp(\Theta/T)[\exp(\Theta/T) - 1]^2. \quad (19.19)$$

There have been many attempts to improve Einstein's model by removing the assumption that the atoms vibrate independent of each other. An elegant method was proposed by Debye. If the atoms cooperate when they vibrate, it means that the vibrating units are larger and the frequency should be lower. For each possible frequency, one should be able to apply Einstein's model and by a summation over all the frequencies one may obtain the proper result. Debye considered a whole spectrum of oscillators down to the mechanical vibrations of the crystal. His spectrum thus extends all the way from the high frequency of individual atoms and down to the acoustic range. He further assumed that the number of oscillators is still $3N$ and that they distribute themselves over the range of frequencies proportional to ν^2 . From Debye's model one does not get C_V as an analytical expression of T but C_V is now available in tables using the parameter $x = \Theta/T$ where Θ is equal to $h\nu_{\max}/k$ and ν_{\max} is the maximum frequency, i.e. the vibrational frequency of an atom. One often tabulates not only C_V but also S and U . Debye's model agrees fairly well with measurements for many materials. Θ is evaluated as a material constant to give the best agreement between model and experiment.

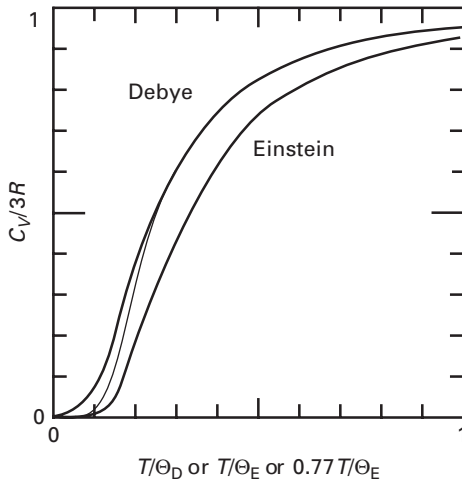


Figure 19.2 Comparison between the Einstein and Debye theories of C_V made at temperatures given relative to the characteristic temperature Θ , as defined in each theory. In addition, the thin line is for Einstein's theory plotted versus $0.77T/\Theta$.

We can calculate C_P from C_V by means of the Grüneisen constant. With the approximate value $\gamma = 2$ we would get from Eq. (2.38)

$$C_P = C_V(1 + 2\alpha T). \quad (19.20)$$

S as a function of T at constant volume is obtained by integrating C_V/T . On the other hand, if one should like to have S as a function of T at constant pressure it could be obtained by integrating C_P/T which yields

$$S = S(x) + 2\alpha U(x), \quad (19.21)$$

if α is a constant. Furthermore, after some manipulations one obtains approximately

$$H = U(x) + (5/2)R\alpha T^2 + (9/8)R\Theta + H_0. \quad (19.22)$$

Notice that H_0 is obtained as an unknown constant of integration, and it represents the cohesive energy. The term $(9/8)R\Theta$ comes from quantum mechanics which says that a linear oscillator of frequency ν has a zero point energy of $h\nu/2$.

A comparison between Einstein's and Debye's models is given in Fig. 19.2. Both models predict a C_V value of $3R$ at very high temperatures but the diagram seems to indicate that the theories give quite different results up to fairly high temperatures. However, if Θ is regarded as an empirical constant, to be evaluated from experimental information, then the two models would work with different Θ values. These empirical constants are called Einstein's and Debye's temperatures. Reasonably good agreement can thus be obtained from high down to fairly low temperatures and for many applications it is reasonable to use the equations derived by Einstein. The value of the Einstein temperature can be estimated from tabulated values of the Debye temperature by multiplication with a factor. The factor is slightly different depending on which quantity one is most interested

in. For heat capacity, internal energy, entropy and Helmholtz energy one should use the values 0.77, 0.73, 0.71 and 0.72, respectively. The thin line in Fig. 19.2 shows how well Einstein's theory agrees with Debye's if the same temperature scale is used but different Θ values. The difference is negligible above $0.3\Theta_D$.

The fact that C_V approaches the same value of $3R$ at high temperatures, independent of the material constant Θ , does not mean that all crystalline substances would have the same stability at high temperatures. For a given element with two possible structures, the structure with the highest S value will increase its relative stability towards high temperatures more than the other one. The S value is the result of integration over C_V/T from absolute zero. S will thus be larger, the faster C_V approaches the asymptotic value of $3R$, i.e. the lower Θ is. A difference in C_V between two structures at low temperatures will be very important at high temperatures because T appears in the denominator of the integrand. A structure with a low Θ will thus have high stability at high temperature. The fact that the S term dominates over the U term in F at high temperatures can be demonstrated by a calculation for some temperature T_1 .

$$\begin{aligned} F &= U - T_1 S = U_0 + \int_0^{T_1} C dT - T_1 \int_0^{T_1} (C/T) dT \\ &= U_0 - \int_0^{T_1} [C(T_1 - T)/T] dT. \end{aligned} \quad (19.23)$$

The integrand is always positive since C and $T_1 - T$ are both positive. We can make a similar calculation for G and obtain a similar result.

At low temperatures where $T \ll \Theta$ one would obtain, according to Einstein

$$C_V = 3R \left(\frac{\Theta}{T} \right)^2 \cdot \exp \left(-\frac{\Theta}{T} \right). \quad (19.24)$$

This would imply that C_V decreases rapidly as one approaches the absolute zero. Experiments showed a slower decrease and that was the reason why one wanted to improve Einstein's theory. Debye's theory instead yields the following expression at low temperature, and it agrees fairly well with experiments if the electronic contribution is subtracted for metallic conductors.

$$C_V = 234R(T/\Theta)^3. \quad (19.25)$$

Exercise 19.3

From Debye's theory, derive the term in H originating from the zero-point energy.

Hint

First neglect the difference between U and H . According to Einstein, the zero-point energy for all oscillators is the same, yielding $\Delta U = 3N(h\nu/2) = 3Nk \cdot \Theta/2 = (3/2)R\Theta$. However, according to Debye there is a distribution of frequencies $z(\nu) = K\nu^2$ and $3N = \int z(\nu) d\nu = \int K\nu^2 d\nu = K\nu_{\max}^3/3$ and thus $K = 9N/\nu_{\max}^3$.

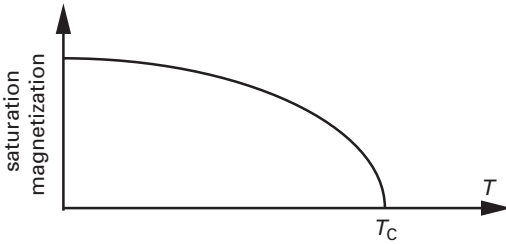


Figure 19.3 Schematic diagram showing the variation of the saturation magnetization as a function of temperature.

Solution

$$\begin{aligned} \Delta H \cong \Delta U &= \int (h\nu/2) \cdot z(\nu) d\nu = \int (h\nu/2) \cdot (9N/\nu_{\max}^3) \cdot \nu^2 d\nu = (9N/\nu_{\max}^3) \cdot \\ &(h\nu_{\max}^4/8) = (9/8) \cdot Nk(h\nu_{\max}/k) = (9/8) \cdot R\Theta_{\text{Debye}}. \end{aligned}$$

19.5 Magnetic contribution to thermodynamic properties

The atoms in a ferromagnetic substance contain unpaired electron spins which give each atom a certain magnetic moment. It can have different directions and will thus give rise to **magnetic disorder**. According to the localized spin model of magnetism, a disordered arrangement gives a contribution to the entropy which can be evaluated from Boltzmann's relation. Due to its simplicity we shall only use this model. W is the number of different arrangements for the whole system. Let w be the number of possible directions for each atom. If the direction of each atom in the disordered state is independent of all the others, we can write $W = w^N$ for one mole of the substance. Thus

$$S = k \ln W = k \ln w^N = kN \ln w = R \ln w. \quad (19.26)$$

According to quantum mechanics,

$$w = \beta + 1 = 2s + 1, \quad (19.27)$$

where β is the number of unpaired electron spins and s is the resulting spin. For a free electron $s = 1/2$.

There is a critical temperature, the Curie temperature T_C , below which the spins will position themselves parallel to each other in a ferromagnetic substance. For a perfectly ordered state, the above contribution to the entropy should disappear completely but, in practice, there will be some disorder left. However, it will disappear as one approaches absolute zero and the saturation magnetization will thus increase (see Fig. 19.3). The degree of magnetic order can be measured by measuring the saturation magnetization. Note that an externally applied magnetic field usually does not change the ordering appreciably. It simply makes the magnetization of the various magnetic domains align along one direction. From the saturation magnetization at low temperatures, one can get direct information on the magnetic moment of the atoms, i.e. the values of s and β .

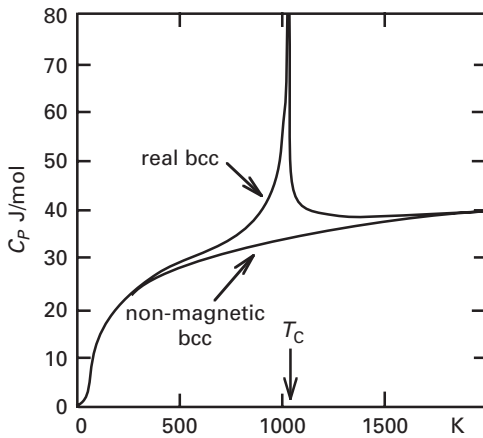


Figure 19.4 Heat capacity (C_p) of bcc-Fe. Notice that a considerable part of the magnetic effect occurs above T_C .

The magnetic moment per atom is usually given in units of Bohr magnetons which is identical to $2s$, i.e. to β according to our simple model. Such measurements indicate that β is seldom an integer. This casts some doubt on the localized spin model and one may wonder if the entropy of magnetic disorder can be evaluated as shown above. Despite this, the method is often used and may be regarded as a convenient approximation.

The disordered state above the Curie temperature is called paramagnetic. It is evident that it has a high entropy and should thus grow even more stable at higher temperatures. The reason why the ferromagnetic state becomes stable below a critical temperature must be a lower energy for that state. When the disorder increases as the temperature is raised, energy must thus be added and the magnetic transformation is revealed in the curve for the heat capacity (see Fig. 19.4).

The curve shows that the transformation occurs gradually up to T_C but a small part of the order still exists at T_C . It does not disappear until well above T_C and it thus yields a contribution to the heat capacity above T_C . We can evaluate the magnetic enthalpy by integrating the abnormal contribution to the curve. As always, the transformation temperature is determined by the balance between enthalpy and entropy. This is best demonstrated by approximating the magnetic transformation (which is actually a second-order transition (see Section 15.1)) with a sharp transformation. For such a transformation we have

$$\Delta G = \Delta H - T \Delta S. \quad (19.28)$$

With $\Delta G = 0$ we find a transformation temperature $T^1 = \Delta H / \Delta S$. The larger the energy gain is at the magnetic ordering, the higher the transformation temperature will be.

Figure 19.5 illustrates the difference in the Gibbs energy between the most stable state at each temperature, G^{eq} , and the completely disordered state. The slope of the curve at low temperature gives the entropy decrease due to complete order of the spins.

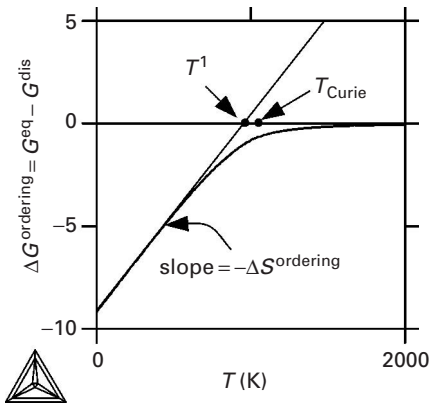


Figure 19.5 The effect of magnetic ordering on the Gibbs energy of bcc-Fe. The reference state is the completely disordered state at each temperature.

The thin line gives the difference between the completely ordered and the completely disordered states at each temperature. The intersection with the abscissa gives the temperature, T^1 , for the hypothetical, sharp transformation. In reality, the ferromagnetic state is stable to a higher temperature, T_C , because it lowers its Gibbs energy by disordering gradually.

Exercise 19.4

Evaluate β for bcc-Fe from an estimate of the magnetic entropy of bcc-Fe using Fig. 18.2.

Hint

The sharp bend in the curve for ${}^{\circ}G_{\text{Fe}}^{\text{bcc}} - {}^{\circ}G_{\text{Fe}}^{\text{fcc}}$ is due to the magnetic entropy of bcc-Fe and is not influenced by the magnetic entropy of fcc-Fe which changes at much lower temperatures.

Solution

The slopes for the paramagnetic and ferromagnetic states can be estimated where the curve is reasonably flat. We obtain $\Delta S = -d({}^{\circ}G_{\text{Fe}}^{\text{param.bcc}} - {}^{\circ}G_{\text{Fe}}^{\text{fcc}})/dT + d({}^{\circ}G_{\text{Fe}}^{\text{ferrom.bcc}} - {}^{\circ}G_{\text{Fe}}^{\text{fcc}})/dT = 2.4 + 9.1 = 11.5 = 1.4R = R \ln(\beta + 1)$; $\beta \cong 3$.

19.6 A simple physical model for the magnetic contribution

The magnetic disorder remaining below the Curie temperature can be treated in about the same way as we treated vacancies. We have already discussed the contribution to the entropy. In order to develop a complete model for the magnetic transformation we must

also formulate the contribution to the enthalpy. The calculations will be especially simple if the magnetic moment of the atoms is $1/2$ since this value gives two possible orientations with a spin difference of 1, according to the requirements of quantum mechanics. Let us suppose that n atoms in a system of totally N atoms have their spins directed opposite to the majority which consists of $N - n$ atoms. We may guess that the extra energy connected with the misorientation of the n atoms can be represented by the following simple expression,

$$\Delta H = K_1 n(N - n) = K_1 x(1 - x)N^2, \quad (19.29)$$

where x represents the fraction of atoms with the wrong orientation, $x = n/N$. This expression gives ΔH a maximum at $x = 1/2$, i.e. for the disordered, demagnetized state. Since $x = 0$ represents the fully magnetized state, we can write

$$\Delta H = x(1 - x) \cdot 4\Delta H^{\text{dis}}, \quad (19.30)$$

where ΔH^{dis} is the enthalpy increase on complete disordering.

Let us now turn to the configurational entropy. The two types of atoms can mix with each other in a number of ways,

$$W = \frac{N!}{n!(N - n)!}. \quad (19.31)$$

Boltzmann's relation will thus yield

$$\begin{aligned} \Delta S/k &= \ln N! - \ln n! - \ln(N - n)! \cong N \ln N - n \ln n - (N - n) \ln(N - n) \\ &= -n \ln \frac{n}{N} - (N - n) \ln \frac{N - n}{N} \end{aligned} \quad (19.32)$$

$$\Delta S/R = -\frac{n}{N} \ln \frac{n}{N} - \frac{N - n}{N} \ln \frac{N - n}{N} = -x \ln x - (1 - x) \ln(1 - x). \quad (19.33)$$

By combination of ΔH and ΔS we obtain for the Gibbs energy of disordering

$$\Delta G = x(1 - x) \cdot 4\Delta H^{\text{dis}} + RT[x \ln x + (1 - x) \ln(1 - x)]. \quad (19.34)$$

We want to determine the equilibrium value of x under constant T and P and shall thus consider a process by which x is increased. By identifying x with an internal variable ξ we obtain, at equilibrium,

$$\begin{aligned} -D &= \left(\frac{\partial G}{\partial \xi} \right)_{T,P} = \frac{d\Delta G}{dx} = (1 - 2x) \cdot 4\Delta H^{\text{dis}} \\ &+ RT \left(\ln x + \frac{x}{x} - \ln(1 - x) - \frac{1 - x}{1 - x} \right) = 0 \end{aligned} \quad (19.35)$$

$$\ln \frac{x}{1 - x} = -(1 - 2x) \cdot 4\Delta H^{\text{dis}} / RT. \quad (19.36)$$

The solutions of Eq. (19.36) are plotted against temperature in Fig. 19.6. Below a critical temperature there are two identical states, $x_2 = 1 - x_1$. They represent ordered states but the degree of order varies from perfect at absolute zero ($x = 0$ or 1) and decreases gradually as the temperature is raised. Finally it disappears completely at

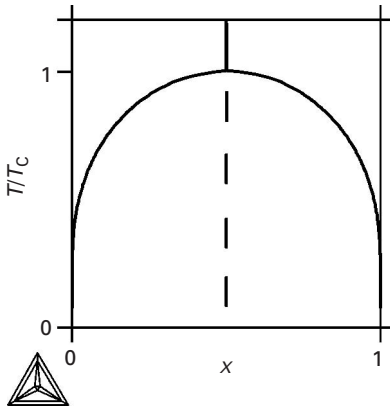


Figure 19.6 Magnetic ordering as a function of temperature according to a simple model. $x = 0.5$ represents the disordered state. The dashed line represents unstable equilibria.

the critical temperature where $x = 0.5$. The states above the critical temperature are disordered because $x = 0.5$. The value of the critical temperature is obtained by inserting the value of $x = 0.5$, which primarily yields $0/0$. The limiting value is obtained as

$$\begin{aligned} T_C &= \frac{4\Delta H^{\text{dis}}}{R} \cdot \frac{2x - 1}{\ln[x/(1-x)]} = \frac{4\Delta H^{\text{dis}}}{R} \cdot \frac{2}{1/x + 1/(1-x)} \\ &= \frac{4\Delta H^{\text{dis}}}{R} \cdot 2x(1-x) = 2\Delta H^{\text{dis}}/R. \end{aligned} \quad (19.37)$$

Above the critical temperature there is only one solution showing that the disordered state ($x = 0.5$) is the stable state. The equation also has the solution $x = 0.5$ below the critical temperature but there it represents an unstable state. That is why it was there drawn with a dashed line. The fact that the disordered state is unstable there, can be tested with a stability condition from Eq. (6.54). We obtain negative values for $x = 0.5$ and $T < T_C = 2\Delta H^{\text{dis}}/R$,

$$\begin{aligned} B &= \left(\frac{\partial^2 G_m}{\partial x^2} \right)_{T,P} = -2 \cdot 4\Delta H^{\text{dis}} + RT[1/x + 1/(1-x)] \\ &= -8\Delta H^{\text{dis}} + 4RT < 0. \end{aligned} \quad (19.38)$$

Let us now assume incorrectly that the magnetic transformation is a sharp one and that a completely disordered state becomes completely ordered at T^1 . The entropy of the completely disordered state is $\Delta S^{\text{dis}} = R \ln 2$ and for a sharp transformation we should thus have expected the following transition temperature,

$$T^1 = \Delta H^{\text{dis}} / \Delta S^{\text{dis}} = \Delta H^{\text{dis}} / R \ln 2 = 1.44\Delta H^{\text{dis}} / R = 0.72T_C. \quad (19.39)$$

The fact that T_C is higher than T^1 was illustrated in Fig. 19.5. That result demonstrates that the possibility for some of the atoms to disorder within the ordered state increases the stability of the ordered state and raises the transformation temperature from the value predicted for a sharp transformation. On the other hand, it should also be pointed out

that the stability of the disordered state is increased by the existence of some short-range order which has not been considered in our model. This is the factor that produces the tail above the C_p maximum which was shown in Fig. 19.4. It makes the difference between T_C and T^1 smaller than indicated by the above model.

The model we have used here for the magnetic order–disorder transformation is based upon the assumption that each individual atom has its own magnetic moment. This is called the localized spin model and is regarded as a rather crude approximation. Magnetism can be treated in a more satisfactory way by the electron band theory. However, it is much more complicated and thus difficult to apply, in particular at high temperature and in alloys.

Exercise 19.5

Use the C_p curve in Fig. 19.4 to evaluate the enthalpy of magnetic disordering. Then estimate the number of unpaired electrons in bcc-Fe.

Hint

The number of unpaired electrons could be estimated from the magnetic entropy which, in turn, could be evaluated from the enthalpy and the estimated transformation temperature for a sharp transformation.

Solution

A rough graphical integration yields $H^{\text{dis}} = 7000 \text{ J/mol}$. We know $T_C = 1043 \text{ K}$ and accepting the result of the simple model we can estimate $T^1 = 0.72T_C$, and thus we get $\Delta S^{\text{dis}} = \Delta H^{\text{dis}}/T^1 = 7000/(0.72 \cdot 1043) = 9.3$; $\ln(\beta + 1) = \Delta S/R = 1.12$; $\beta = 2.1$.

19.7 Random mixture of atoms

Before leaving the discussion of models of disordering phenomena we should mention disorder in solution phases. Actually, most substances can have a variable composition and we shall call such substances solution phases. On the atomic scale they consist of a mixture of different species, in the simplest case atoms. In a crystal the atomic sites are arranged in a regular pattern, a lattice, but the distribution of different kinds of atoms on the sites is generally determined by chance to some extent. This situation is often described as chemical disorder or **configurational disorder**. For a complete description of such a case one needs a model with an internal variable representing the degree of order. Such a model will be further discussed in the Chapters 21 and 22. In order to prepare for that discussion it is convenient now to discuss the entropy of solution phases with the maximum chemical disorder, so called **random mixtures**. The degree of order can be used as an internal variable but will not be introduced until later.

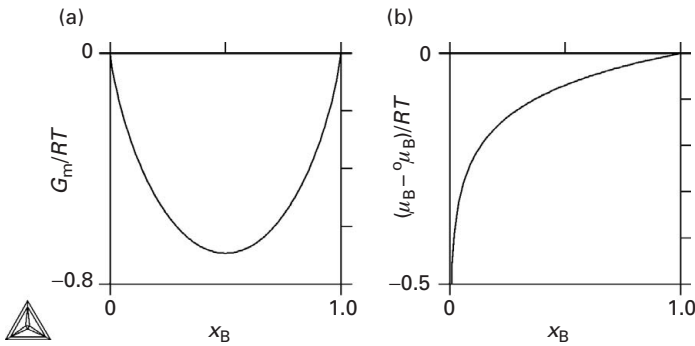


Figure 19.7 (a) Gibbs energy of mixing for an ideal, binary solution. (b) Variation of a chemical potential in the same solution. In both cases the values have been normalized by dividing with RT .

Let us consider a substance where all the sites are equivalent. Since all the various atoms dissolved in the substance can substitute for each other, such a substance is called a substitutional solution. The number of different ways in which N_A atoms of A, N_B atoms of B, N_C atoms of C, etc., can be arranged is

$$W = \frac{N!}{N_A!N_B!N_C!\dots} \quad (19.40)$$

This randomness will give the following contribution to the entropy of the system according to Boltzmann's relation,

$$\begin{aligned} \Delta S/k &= \ln W = \ln N! - \sum \ln N_i! \\ &\cong N \ln N - \sum N_i \ln N_i = -N \sum (N_i/N) \ln(N_i/N) = -N \sum x_i \ln x_i, \end{aligned} \quad (19.41)$$

since N is equal to $\sum N_i$ and $x_i = N_i/N$.

We may construct a model for an ideal substitutional solution by requiring that there is no energy change on mixing the atoms. The only effect on the Gibbs energy would come from the configurational disorder,

$$\Delta G = -T\Delta S = NkT \sum x_i \ln x_i, \quad (19.42)$$

where N is the number of moles of atoms. Let us consider an ideal system with one mole of atoms. Using Eq. (4.6) we obtain

$$\Delta G_m = -T\Delta S = N^A kT \sum x_i \ln x_i = RT \sum x_i \ln x_i \quad (19.43)$$

$$\Delta \mu_j = \Delta G_m + \frac{\partial \Delta G_m}{\partial x_j} - \sum x_i \frac{\partial \Delta G_m}{\partial x_i} = RT \ln x_j. \quad (19.44)$$

Figure 19.7 gives ΔG_m and $\Delta \mu_B$ for an ideal, binary A–B system. It is worth emphasizing that $\Delta \mu_B$ goes to $-\infty$ as x_B goes to 0. As a consequence the ΔG_m curve should be vertical at its end-points. However, this tendency starts to develop so close to the end-points that it is hardly discernible.

In the model for an ideal solution there is no internal variable because the situation has been completely fixed by the assumption of random mixing. The situation will be different if all the arrangements do not have the same energy. The disorder will then be incomplete and one can introduce internal variables describing short- and long-range order. This phenomenon will be described in Section 22.6. However, there is a class of solution phases where all the sites are not equivalent and they may be, at the same time, close to random in one sense and well ordered in another. They will be discussed in the next sections.

Exercise 19.6

An A–B–C alloy is prepared by mixing x_C moles of pure C with $1 - x_C$ moles of an A–B alloy. Calculate (a) the entropy of mixing in $1 - x_C$ moles of the initial A–B alloy, (b) the entropy due to the mixing of C into the A–B alloy and (c) the sum of the two contributions.

Hint

The A content of the initial alloy can be expressed as $x_A/(x_A + x_B)$ if x_A and x_B refer to the final, ternary alloy. The effect of mixing C with a mixture of A + B is the same as the effect of mixing C with a single element which could very well consist of two isotopes. Remember that $x_A + x_B = 1 - x_C$.

Solution

$$\begin{aligned} \Delta S(\text{a}) &= (1 - x_C) \cdot \{x_A/(x_A + x_B) \cdot \ln[x_A/(x_A + x_B)] + x_B/(x_A + x_B) \cdot \ln[x_B/(x_A + x_B)]\} \\ &= x_A \ln x_A + x_B \ln x_B - (x_A + x_B) \ln(x_A + x_B); \quad \Delta S(\text{b}) = x_C \ln x_C + (1 - x_C) \ln(1 - x_C) \\ &= x_C \ln x_C + (x_A + x_B) \ln(x_A + x_B); \quad \Delta S(\text{c}) = x_A \ln x_A + x_B \ln x_B + x_C \ln x_C. \end{aligned}$$

19.8 Restricted random mixture

Many crystalline phases have more than one family of sites. It is convenient to describe such phases with the use of sublattices and the state may be defined by giving the site fractions (see Section 4.8).

$$y_j^t = N_j^t / N^t. \quad (19.45)$$

If the atoms in one sublattice are mixed with each other at random, they give the following contribution to the entropy

$$\Delta S^t = -kN \sum_i \frac{N_i^t}{N^t} \ln \frac{N_i^t}{N^t} = -R \sum_i y_i^t \ln y_i^t. \quad (19.46)$$

Since entropy is an extensive property which obeys the law of additivity, one could add the contributions from the individual sublattices,

$$\Delta S_m = \Sigma \Delta S^s = -R \sum_s a^s \sum_i y_i^s \ln y_i^s. \quad (19.47)$$

This expression holds for one mole of atoms if there are no vacant sites. a^s is then defined as N^s/N , the fraction of all sites belonging to the s sublattice, and Σa^s is unity. One may instead like to consider one mole of formula units where the formula is written with integers for all a^s . Then Σa^s is the number of atoms per formula unit.

This may be regarded as an ideal solution model for the particular type of crystalline structure. If all the elements can go into all the sublattices with the same probability, this model reduces to the previous ideal solution model because y_i^s is then identical to x_i .

Exercise 19.7

Consider a so-called Laves phase with two components each on two sublattices, (A, B)₁(C, D)₂. Calculate the entropy of mixing assuming random mixing within each sublattice for equal amounts of A and B and also for C and D. Compare with the ideal entropy of mixing when all four components are mixed randomly with each other.

Hint

Consider 3 moles of atoms, 0.5 of A, 0.5 of B, 1 of C and 1 of D.

Solution

$$\Delta S/R = -1 \cdot (0.5 \ln 0.5 + 0.5 \ln 0.5) - 2 \cdot (0.5 \ln 0.5 + 0.5 \ln 0.5) = +3 \ln 2 = 2.08.$$

For an ideal solution we get

$$\Delta S/R = 3[(1/6) \ln(1/6) + (1/6) \ln(1/6) + (2/6) \ln(2/6) + (2/6) \ln(2/6)] = 3.99.$$

19.9 Crystals with stoichiometric vacancies

A binary crystal can vary in composition even if each component is restricted to its own sublattice. An example is wüstite which has separate sublattices for Fe and O. The Fe sublattice can have vacant sites and we should thus write the formula as (Fe,Va)₁O₁. We shall call such vacancies **stoichiometric vacancies** because in the simplest case, their number is fixed by the stoichiometric imbalance between the amounts of the elements. The entropy of disorder in a crystal with any kind of vacancies is given by the expression already discussed, if the vacancies are distributed at random on a sublattice. The vacancies are then treated as the atoms of any element and one must define their site fraction, y_{Va}^s . On the other hand, the vacancies are not included in the mole fractions x_i which give

the composition of the crystal. Consequently, when evaluating x from y , one should not include the vacancies in the summation. We can give the equation as

$$x_j = \sum_s a^s y_j^s / \left(\sum_s a^s - \sum_s a^s y_{\text{Va}}^s \right). \quad (19.48)$$

On the other hand, it is not always possible to calculate the y values from the overall composition given by the set of x values. If each element is dissolved in one sublattice only, then we can still evaluate the site fractions from the composition of the crystal provided that there is at least one sublattice without vacancies. First we can identify that sublattice as the one having the largest value of $\sum x_i^s / a^s$. Let us denote that sublattice by r . The site fractions in any sublattice t are then given by

$$y_j^t = x_j a^r / a^t \sum_i x_i^r. \quad (19.49)$$

If $\sum y_j^t$ in any sublattice is less than unity then the difference from unity gives the site fraction of vacancies

$$y_{\text{Va}}^t = 1 - \sum_i y_i^t. \quad (19.50)$$

This relation illustrates why they are called stoichiometric vacancies. The amount of stoichiometric vacancies does not change directly with the temperature but there may be an indirect effect if the phase is in equilibrium with another phase. The composition may then vary by an exchange of atoms between the phases. The amount of vacancies can also vary if the composition of the other phase varies by an action from the outside. A typical example is an oxide in equilibrium with an atmosphere of variable P_{O_2} .

Exercise 19.8

We know the composition of an oxide by chemical analysis as $x_{\text{U}} = 0.252$, $x_{\text{Pu}} = 0.094$ and $x_{\text{O}} = 0.654$. Calculate the site fractions under the assumption that the oxide is a so-called stoichiometric phase with only a small deviation from stoichiometry.

Hint

Suppose that U and Pu occupy one sublattice and O another. The number of sites can then be estimated from the number of atoms supposing there are no vacancies. Vacancies can then be assumed on one sublattice for stoichiometric reasons.

Solution

$x_{\text{U}} + x_{\text{Pu}} = 0.346$; $x_{\text{O}} / (x_{\text{U}} + x_{\text{Pu}}) = 0.654 / 0.346 = 1.89$. This is close to 2. We may thus assume that the formula is $(\text{U,Pu})_1(\text{O,Va})_2$ and we find $y_{\text{O}} = 0.654 \cdot 1/2 \cdot 0.346 = 0.945$; $y_{\text{Va}} = 0.055$.

19.10 Interstitial solutions

Phases with two or more sublattices are often called compounds or intermediary phases, or intermetallic phases when appropriate. Such compounds may be strictly stoichiometric or may show a deviation from stoichiometry, caused by defects. One such defect is the vacancy. A related case is the interstitial solution where some solute atoms dissolve in a crystalline solvent by going into interstitial sites that are initially empty. These sites form a sublattice. An example is the solution of carbon in the bcc modification of iron, so-called ferrite or α -Fe. The formula can be written as $\text{Fe}_1(\text{Va},\text{C})_3$. The entropy of interstitial solutions can be treated with the method discussed in the preceding sections. A more complicated case occurs when an element goes mainly into ordinary lattice sites but some of its atoms go into interstitial sites.

In Section 4.8 we found that it was possible to derive an expression for the chemical potential of a compound in a stoichiometric phase but not for the chemical potential of an element. The situation is different for a phase with vacancies. For the interstitial solution of C in α -Fe we can by standard methods derive expressions for μ_{FeC_3} and μ_{FeVa_3} . We can thus evaluate μ_{C} from

$$\frac{1}{3}(\mu_{\text{FeC}_3} - \mu_{\text{FeVa}_3}) = \frac{1}{3}\mu_{\text{Fe}} + \mu_{\text{C}} - \frac{1}{3}\mu_{\text{Fe}} - \mu_{\text{Va}} = \mu_{\text{C}} - \mu_{\text{Va}} = \mu_{\text{C}}. \quad (19.51)$$

because we can usually assume that the chemical potential of vacancies is zero. Assuming random mixing of carbon atoms and vacancies we obtain the following contributions to the entropy of mixing, the Gibbs energy of mixing and the chemical potential of carbon

$$\Delta S_{\text{m}} = -3R(y_{\text{Va}} \ln y_{\text{Va}} + y_{\text{C}} \ln y_{\text{C}}) \quad (19.52)$$

$$\Delta G_{\text{m}} = 3RT(y_{\text{Va}} \ln y_{\text{Va}} + y_{\text{C}} \ln y_{\text{C}}) \quad (19.53)$$

$$\begin{aligned} \Delta \mu_{\text{C}} = \mu_{\text{C}} - \mu_{\text{Va}} &= \frac{1}{3} \left(\Delta G_{\text{m}} + \frac{\partial \Delta G_{\text{m}}}{\partial y_{\text{C}}} - \sum y_i \frac{\partial \Delta G_{\text{m}}}{\partial y_i} - \Delta G_{\text{m}} \right. \\ &\quad \left. - \frac{\partial \Delta G_{\text{m}}}{\partial y_{\text{Va}}} + \sum y_i \frac{\partial \Delta G_{\text{m}}}{\partial y_i} \right) = \frac{1}{3} \left(\frac{\partial \Delta G_{\text{m}}}{\partial y_{\text{C}}} - \frac{\partial \Delta G_{\text{m}}}{\partial y_{\text{Va}}} \right) \\ &= \frac{1}{3} \cdot 3RT \ln \frac{y_{\text{C}}}{y_{\text{Va}}} = RT \ln \frac{y_{\text{C}}}{1 - y_{\text{C}}}. \end{aligned} \quad (19.54)$$

Interstitial solutions will be further discussed in Section 21.2.

It is important to notice that the deviation from stoichiometry of a compound may also be caused by some atoms going into sites of the ‘wrong’ sublattice (in that connection called anti-sites) or into interstitial sites.

Exercise 19.9

The interstitial solution of carbon in fcc- and bcc-iron can be represented with the formula $(\text{Fe})_1(\text{Va},\text{C})_1$ and $(\text{Fe})_1(\text{Va},\text{C})_3$, respectively. The martensitic transformation from fcc to bcc is very rapid and carbon is not able to take advantage of the additional interstitial sites. Estimate how much larger the driving force for the martensitic transformation

would have been if carbon could be distributed among all the sites available in bcc-Fe. Make a numerical calculation for an Fe-C alloy with a molar content of 0.02 C.

Hint

For simplicity, suppose that the redistribution of carbon atoms has an effect on the Gibbs energy through the ideal entropy term only. Consider a system with one mole of Fe atoms and thus $z_C = 0.02/0.98 = 0.0204$ moles of C atoms.

Solution

$\Delta G = 3RT[(z_C/3) \ln(z_C/3) + (1 - z_C/3) \ln(1 - z_C/3)] - RT[z_C \ln z_C + (1 - z_C) \ln(1 - z_C)] = RT(-0.1219 + 0.0996) = -0.223RT$. The driving force would increase with $0.223RT$.

20 Mathematical modelling of solution phases

20.1 Ideal solution

The thermodynamic properties of some solutions were illustrated graphically in Section 7.1 and some mathematical expressions were also given. We shall now give a more thorough discussion. In Section 18.7 we mentioned the possibility of modelling a special physical effect, p, in a substance and defining the remaining part of the Gibbs energy as the property of a hypothetical state, h, which does not have that physical effect,

$$G_m = G_m^h + G_m^p. \quad (20.1)$$

This approach can also be applied to solution phases. The most important application is the treatment of the thermodynamic effects of mixing the atoms in a solution. The hypothetical state would then be a so-called mechanical mixture of the pure components at the same temperature and pressure,

$$G_m^h = \sum x_i {}^\circ G_i. \quad (20.2)$$

The physical effect, G_m^p would here be the contribution due to the intimate mixing of the atoms in a solution. It is usually denoted by ${}^M G_m$, which is thus defined by

$$G_m = \sum x_i {}^\circ G_i + {}^M G_m. \quad (20.3)$$

The mechanical mixture may be regarded as a reference for the properties of a solution and ${}^M G_m$ gives the solution behaviour. It is called Gibbs energy of mixing but a better name would have been ‘Gibbs energy of solution’ because it represents the effect of forming a solution from a mechanical mixture. For a binary system the reference is a straight line in the molar Gibbs energy diagram, in a ternary system it is a plane, etc. Earlier, in Fig. 7.1, it was demonstrated that one can use this straight line in a binary system as the line of reference in a molar Gibbs energy diagram and the concept of Gibbs energy of mixing was introduced.

The simplest model for the intimate mixing of atoms in a solution is based on the assumption of random mixing and no particular interactions between atoms of different kinds. For that case we have

$$G_m = \sum x_i {}^\circ G_i - T \cdot {}^M S_m^{\text{ideal}}, \quad (20.4)$$

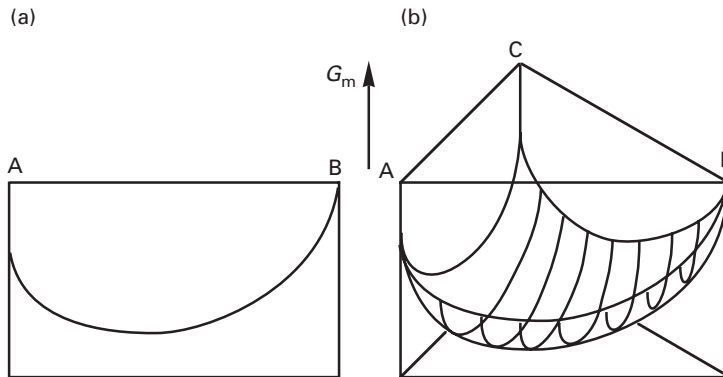


Figure 20.1 Characteristic shapes of the molar Gibbs energy curves in (a) binary and (b) ternary systems, caused by the entropy of mixing.

and expressions for the ideal entropy of mixing in phases with different structures were derived in Sections 19.7 to 19.10. A solution obeying such an equation may be called an ideal solution. For an ideal substitutional solution we have

$${}^M S_m^{\text{ideal}} = -R \sum x_i \ln x_i \quad (20.5)$$

$$G_m = \sum x_i {}^\circ G_i + RT \sum x_i \ln x_i, \quad (20.6)$$

and we may also define a partial ideal entropy of mixing for component I ,

$${}^M S_i^{\text{ideal}} = -R \ln x_i \quad (20.7)$$

Sometimes one explicitly requires that the molar volume of an ideal solution should be equal to a weighted average of the values for the pure components. It is easy to see that Eq. (20.4) satisfies this requirement because the derivative with respect to P yields

$$V_m = \partial G_m / \partial P = \sum x_i \partial {}^\circ G_m / \partial P = \sum x_i {}^\circ V_i. \quad (20.8)$$

The term $-T \cdot {}^M S_m^{\text{ideal}}$ is important even in real, non-ideal solutions and it gives the Gibbs energy its characteristic shape of a hanging rope for a binary system and a canopy for a ternary. This has already been illustrated in a number of diagrams in Sections 7.1 and 7.10 and is again shown in Fig. 20.1.

Exercise 20.1

Suppose one knows that a binary solution is not ideal because the molar volume obeys the relation: $V_m = x_A {}^\circ V_A + x_B {}^\circ V_B + x_A x_B \cdot |{}^\circ V_A - {}^\circ V_B|$. Examine the effect on G_m if ${}^\circ V_A - {}^\circ V_B = 2 \cdot 10^{-6} \text{ m}^3 \text{ mol}$.

Hint

Represent G_m with $x_A {}^\circ G_A + x_B {}^\circ G_B - T \cdot {}^M S_m^{\text{ideal}} + x_A x_B L$ and evaluate the effect on L .

Solution

Compare with $V_m = \partial G_m / \partial P = x_A {}^\circ V_A + x_B {}^\circ V_B + x_A x_B \partial L / \partial P$. Thus, $\partial L / \partial P = ({}^\circ V_A - {}^\circ V_B)$ and, neglecting the pressure dependence of ${}^\circ V_A - {}^\circ V_B$, we find $L = L_o + P \cdot \sum ({}^\circ V_A - {}^\circ V_B)$. At 1 bar (10^5 Pa) this effect would increase L by $10^5 \cdot 2 \cdot 10^{-6} = 0.2$ J mol. This is negligible in most cases.

20.2 Mixing quantities

It is convenient to compare the value of any molar quantity in a solution with the weighted average of the values for the pure components and define a **molar quantity of mixing**, ${}^M A_m$,

$$A_m = \sum x_i {}^\circ A_i + {}^M A_m. \quad (20.9)$$

The additional requirement for an ideal solution, mentioned in the preceding section, may thus be formulated by stating that the volume of mixing, ${}^M V_m$, must be zero.

Partial quantities of mixing can be defined relative to the value for the pure component,

$${}^M A_i = A_i - {}^\circ A_i. \quad (20.10)$$

It is evident that all relations derived for A_m and A_i in Section 4.2 also apply to ${}^M A_m$ and ${}^M A_i$ because the references ${}^\circ A_i$ will drop out from all such relations. We get, for instance,

$${}^M A_m = A_m - \sum x_i {}^\circ A_i = \sum x_i A_i - \sum x_i {}^\circ A_i = \sum x_i (A_i - {}^\circ A_i) = \sum x_i {}^M A_i. \quad (20.11)$$

We find, as for A_m in Section 4.1,

$${}^M A_j = {}^M A_m + \frac{\partial {}^M A_m}{\partial x_j} - \sum x_i \frac{\partial {}^M A_m}{\partial x_i}. \quad (20.12)$$

Exercise 20.2

Show that the partial enthalpy of mixing can be calculated from ${}^M H_j = \partial ({}^M G_j / T) / \partial (1/T)$.

Hint

We know $H_j = \partial (G_j / T) / \partial (1/T)$. Use ${}^M H_j = H_j - {}^\circ H_j$ and ${}^M G_j = G_j - {}^\circ G_j$.

Solution

$$\partial ({}^M G_j / T) \partial (1/T) = \partial (G_j / T) / \partial (1/T) - \partial ({}^\circ G_j / T) / \partial (1/T) = H_j - {}^\circ H_j = {}^M H_j.$$

20.3 Excess quantities

The various mixing quantities were defined relative to the mechanical mixture of the components. In the same way one may define **excess quantities** relative to an ideal solution, e.g.

$$G_m = \sum x_i {}^{\circ}G_i - T \cdot {}^M S_m^{\text{ideal}} + {}^E G_m. \quad (20.13)$$

The excess quantities represent the deviation from ideal behaviour and are thus subject to direct study and modelling. In this chapter we shall examine mathematical models of the excess Gibbs energy and in the next chapter we shall discuss some very simple physical models.

From the excess Gibbs energy one may define partial excess Gibbs energies and obtain, by standard procedures,

$${}^E G_j = {}^E G_m + \partial {}^E G_m / \partial x_j - \sum x_i \partial {}^E G_m / \partial x_i \quad (20.14)$$

$${}^E G_i = G_i - {}^{\circ}G_i + T \cdot {}^M S_i^{\text{ideal}} \quad (20.15)$$

$${}^E G_m = \sum x_i {}^E G_i \quad (20.16)$$

$${}^E S_i = S_i - {}^{\circ}S_i - {}^M S_i^{\text{ideal}} \quad (20.17)$$

$${}^E H_i = H_i - {}^{\circ}H_i = {}^M H_i. \quad (20.18)$$

We note that it is not necessary to introduce the concept of excess enthalpy because all enthalpy of mixing is in excess of the ideal solution behaviour. For a substitutional solution we get

$${}^E G_j = G_j - {}^{\circ}G_j - RT \ln x_j. \quad (20.19)$$

$${}^E S_i = S_i - {}^{\circ}S_i - R \ln x_i \quad (20.20)$$

Exercise 20.3

Using a Maxwell relation at constant T and P we get $\partial G_i / \partial N_j = \partial^2 G / \partial N_i \partial N_j = \partial^2 G / \partial N_j \partial N_i = \partial G / \partial N_i$. Using this relation, show that $\partial {}^E G_i / \partial N_j = \partial {}^E G_j / \partial N_i$.

Hint

$$G_i = {}^{\circ}G_i + RT \ln x_i + {}^E G_i; \quad \partial x_i / \partial N_j = -x_i / N; \quad \partial x_j / \partial N_i = -x_j / N.$$

Solution

$\partial G_i / \partial N_j = RT(1/x_i) \cdot (-x_i/N) + \partial {}^E G_i / \partial N_j = -RT/N + \partial {}^E G_i / \partial N_j$; $\partial G_j / \partial N_i = -RT/N + \partial {}^E G_j / \partial N_i$. If the two left-hand sides are equal, we obtain $\partial {}^E G_i / \partial N_j = \partial {}^E G_j / \partial N_i$.

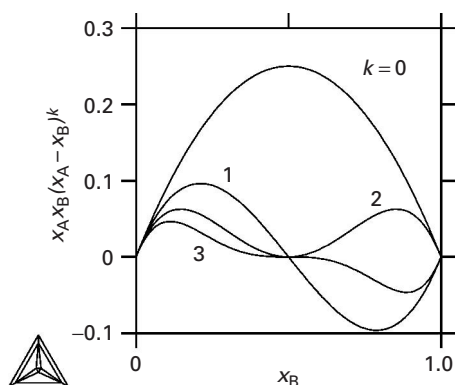


Figure 20.2 Properties of Redlich–Kister terms.

20.4 Empirical approach to substitutional solutions

We shall now discuss an empirical approach to the modelling of the excess Gibbs energy of solution phases. We have already seen that the difference between the properties of a real solution and an ideal solution may be represented by a quantity called the excess Gibbs energy, ${}^E G_m$. For a substitutional solution we can immediately see that it must go to zero for the pure components and a convenient way of representing its composition dependence in a binary system is to introduce the factor $x_A x_B$ which goes to zero for pure A as well as pure B. We shall thus express ${}^E G_m$ as $x_A x_B I$. We shall allow I to be a function of composition. It may for instance be represented by a power series, often called Redlich–Kister polynomial [39]. Figure 20.2 illustrates the properties of the various terms in ${}^E G_m$.

$$I = {}^0L + {}^1L(x_A - x_B) + {}^2L(x_A - x_B)^2 + \dots \quad (20.21)$$

$${}^E G_m = x_A x_B \sum_{k=0}^n {}^kL(x_A - x_B)^k. \quad (20.22)$$

The parameter I may be regarded as a representation of the interaction between the two components. It is convenient to give the two components as an index to I and write it as I_{AB} for an A–B solution. When I is a constant, independent of composition as well as temperature, one talks about a **regular solution** and 0L may thus be called the regular solution parameter. When it appears alone, it is usually denoted by L . 1L may be called the subregular solution parameter and 2L the subsubregular solution parameter. However, it should be mentioned that a regular solution is sometimes defined as a solution where ${}^E G_m$ is independent of temperature but may have any composition dependence. On the other hand, in recent years there is a tendency to call a solution regular as soon as I is independent of composition, whether or not I is independent of temperature.

Positive values of the regular solution parameter result in a tendency of demixing. If not interrupted by other reactions a miscibility gap will form when the temperature is

lowered. It is easy to calculate its spinodal from the condition for the stability limit. For a constant I we get

$$g_B = dG_m/dx_B = (x_A - x_B)^0 L + RT(x_B/x_B + \ln x_B - x_A/x_A - \ln x_A) \quad (20.23)$$

$$g_{BB} = d^2 G_m / dx_B^2 = (-1 - 1)^0 L + RT(1/x_B + 1/x_A) = 0 \quad (20.24)$$

$$T_{sp} = x_A x_B \cdot 2^0 L / R \quad (20.25)$$

$$x_A x_B = RT_{sp} / 2^0 L. \quad (20.26)$$

The spinodal will thus be a parabola in this simple case and its maximum will fall at $x_A = x_B = 0.5$ and be a consolute point.

$$T_{cons} = {}^0 L / 2R \text{ and } x_A x_B = T_{sp} / 4T_{cons}. \quad (20.27)$$

A second equation is required in order to calculate the consolute point if I is not a constant and it is obtained through the condition of a critical point,

$$d^3 G_m / dx_B^3 = 0. \quad (20.28)$$

For further reference it is convenient here to derive expressions for the partial Gibbs energies from the Redlich–Kister polynomial. Using the standard method presented in Section 4.1, we can evaluate the last two terms in the following general expression

$$G_l = {}^0 G_l - T \cdot {}^M S_l^{\text{ideal}} + {}^E G_l. \quad (20.29)$$

With the power series representation of ${}^E G_m$ we first obtain a general expression for the effect of an interaction between two components, l and i ,

$${}^E G_l = {}^0 L_{li} x_i (1 - x_l) + \sum_{k=1}^n {}^k L_{li} x_i (x_l - x_i)^{k-1} [(k+1)(1 - x_l)(x_l - x_i) + kx_i]. \quad (20.30)$$

For a binary A–B system we can replace $1 - x_A$ by x_B and $1 - x_B$ by x_A and obtain

$${}^E G_A = x_B^2 \left\{ {}^0 L_{AB} + \sum_{k=1}^n {}^k L_{AB} (x_A - x_B)^{k-1} [(2k+1)x_A - x_B] \right\} \quad (20.31)$$

$${}^E G_B = x_A^2 \left\{ {}^0 L_{AB} + \sum_{k=1}^n {}^k L_{AB} (x_A - x_B)^{k-1} [x_A - (2k+1)x_B] \right\}. \quad (20.32)$$

It should be noticed that in our notation the sign of ${}^k L_{AB}$ changes for odd k if the order between A and B is reversed. It is also interesting to note that the expression for the partial excess Gibbs energy of one component contains the square of the molar content of the other. The partial excess Gibbs energy of a component will thus go to zero asymptotically as the pure component is approached. In this respect the very dilute solutions are ideal, a result which is usually formulated in Raoult's law. It will be discussed in the next section.

For a solution with more than two components we should consider interactions within each combination of two components and possibly also interactions between more than

two components, so-called ternary, quaternary, etc., interactions. By limiting the present discussion to binary interactions we obtain

$$G_m = \sum x_i^0 G_i + RT \sum x_i \ln x_i + \sum_i \sum_{j>i} x_i x_j I_{ij}, \quad (20.33)$$

and ${}^E G_i$ will be the sum of contributions from all I_{li} but also from other I_{ij} . We obtain

$$\begin{aligned} {}^E G_i = \sum_{i \neq l} \left\{ {}^0 L_{li} x_i (1 - x_l) + \sum_{k=1}^n {}^k L_{li} x_i (x_l - x_i)^{k-1} [(k+1) \right. \\ \left. \times (1 - x_l)(x_l - x_i) + k x_i] \right\} \\ - \sum_{i \neq l} \sum_{j \neq l, > i} x_i x_j \left[{}^0 L_{ij} + \sum_{k=1}^n {}^k L_{ij} (x_i - x_j)^k (k+1) \right]. \quad (20.34) \end{aligned}$$

For a ternary system with constant interaction energies (i.e. for the regular solution model) we can write the result as follows by omitting the superscript 0 in ${}^0 L$,

$$G_A = {}^0 G_A + RT \ln x_A + x_B(x_B + x_C)L_{AB} - x_B x_C L_{BC} + x_C(x_C + x_B)L_{CA} \quad (20.35)$$

$$G_B = {}^0 G_B + RT \ln x_B + x_A(x_A + x_C)L_{AB} + x_C(x_C + x_A)L_{BC} - x_C x_A L_{CA} \quad (20.36)$$

$$G_C = {}^0 G_C + RT \ln x_C - x_A x_B L_{AB} + x_B(x_B + x_A)L_{AB} + x_A(x_A + x_B)L_{CA}. \quad (20.37)$$

Exercise 20.4

Apply the expressions for ${}^E G_A$ and ${}^E G_B$, given by Eqs (20.31) and (20.32), to a binary system and show that $G_m = \sum x_i G_i$.

Hint

We know that for an ideal solution $G_m = \sum x_i G_i$. Now it is thus sufficient to show that ${}^E G_m = \sum x_i {}^E G_i$.

Solution

$$\begin{aligned} \sum x_i {}^E G_i &= x_A x_B^2 \left\{ {}^0 L_{AB} + \sum^k L_{AB} (x_A - x_B)^{k-1} [(2k+1)x_A - x_B] \right\} \\ &\quad + x_B x_A^2 \left\{ {}^0 L_{AB} + \sum^k L_{AB} (x_A - x_B)^{k-1} [x_A - (2k+1)x_B] \right\} \\ &= x_A x_B \left\{ {}^0 L_{AB} (x_A + x_B) + \sum^k L_{AB} (x_A - x_B)^{k-1} \right. \\ &\quad \left. \times [x_B(2k+1)x_A - x_B^2 + x_A^2 - x_A(2k+1)x_B] \right\} \\ &= x_A x_B \left[{}^0 L_{AB} + \sum^k L_{AB} (x_A - x_B)^k \right]. \end{aligned}$$

Exercise 20.5

Mo has the same structure as α -Fe(bcc) and it is thus possible to combine them into the same model, covering the whole range of composition of bcc in the Fe–Mo phase diagram. Determine the G_m expression for this model from the mutual solubilities at 1300°C which are 0.16 Mo in Fe and 0.075 Fe in Mo.

Hint

Since two pieces of information are given, we can determine two parameters. The excess term will thus be written as $x_{\text{Fe}}x_{\text{Mo}}[{}^0L + {}^1L(x_{\text{Fe}} - x_{\text{Mo}})]$ where 0L and 1L will be considered as independent of T . At equilibrium $G_{\text{Fe}} - {}^0G_{\text{Fe}}$, i.e. $RT \ln x_{\text{Fe}} + {}^E G_{\text{Fe}}$ would have the same value in both phases and so would $RT \ln x_{\text{Mo}} + {}^E G_{\text{Mo}}$. For a binary solution we find ${}^E G_{\text{A}} = x_{\text{B}}^2[{}^0L + {}^1L(3x_{\text{A}} - x_{\text{B}})]$ and ${}^E G_{\text{B}} = x_{\text{B}}^2[{}^0L + {}^1L(3x_{\text{A}} - x_{\text{B}})]$.

Solution

$$RT \ln x_{\text{Fe}} + {}^E G_{\text{Fe}} = RT \ln 0.84 + (0.16)^2[{}^0L + {}^1L(3 \cdot 0.84 - 0.16)] = RT \ln 0.075 + (0.925)^2[{}^0L + {}^1L(3 \cdot 0.075 - 0.925)];$$

$$RT \ln x_{\text{Mo}} + {}^E G_{\text{Mo}} = RT \ln 0.16 + (0.84)^2[{}^0L + {}^1L(0.84 - 3 \cdot 0.16)] = RT \ln 0.925 + (0.075)^2[{}^0L + {}^1L(0.075 - 3 \cdot 0.925)].$$

The numerical result is ${}^0L = 34\,500$ and ${}^1L = -4500$ J/mol.

20.5 Real solutions

As discussed already in Section 7.1, one often represents the properties of real solutions with the activity a_i and activity coefficient f_i , defined through

$$\mu_i = \mu_i^{\text{REF}} + RT \ln a_i = \mu_i^{\text{REF}} + RT \ln x_i + RT \ln f_i. \quad (20.38)$$

It is common to choose as reference the state of pure i at the same temperature and pressure as the state under consideration, usually denoted 0G_i or ${}^0\mu_i$.

The activity coefficient is often intended for use in dilute solutions only. It is interesting to examine its variation with composition by applying the regular solution model for a binary substitutional solution. Figure 20.3 shows three curves for the activity obtained with ${}^0L/RT = 2, 0$ or -2 . For high B contents x_{A} is small and the regular solution model yields

$$a_{\text{B}} = x_{\text{B}} \exp({}^0Lx_{\text{A}}^2/RT) \cong x_{\text{B}}; \quad f_{\text{B}} \cong 1. \quad (20.39)$$

As a consequence, all the curves approach asymptotically the diagonal in the diagram. This is **Raoult's law** and its validity is very general. We have already seen that ${}^E G_{\text{B}}$ has the factor x_{A}^2 independent of what power series has been chosen. This factor originates from the factor $x_{\text{A}}x_{\text{B}}$, introduced in order to make ${}^E G_m$ go to zero for pure B and for pure A. For low B contents where x_{A} may be approximated by 1 we obtain

$$a_{\text{B}} = x_{\text{B}} \exp({}^0Lx_{\text{A}}^2/RT) \cong x_{\text{B}} \exp({}^0L/RT); \quad f_{\text{B}} \cong \exp({}^0L/RT). \quad (20.40)$$

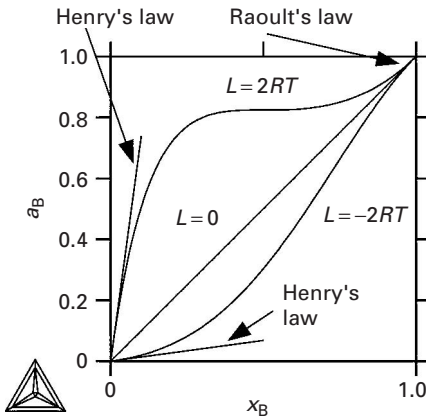


Figure 20.3 The properties of a binary solution according to the regular solution model with three different values of the regular solution parameter.

This gives the slope of the tangent to the curve at the origin. It is self-evident that at low B contents the alloys fall close to this tangent. This is often formulated as **Henry's law**. It must be emphasized that this law says nothing about the slope of the tangent, contrary to Raoult's law. It is interesting to mention that Raoult's law for component A can be derived by applying Henry's law to component B.

A convenient method of studying the properties of a binary solution is based upon the presence of the factor x_A^2 in the expression for the partial excess Gibbs energy of B in the empirical model. We obtain

$$\begin{aligned} {}^0L_{AB} + \sum_{k=1}^n k L_{AB}(x_A - x_B)^{k-1} [x_A - (2k+1)x_B] &= {}^E G_B / x_A^2 \\ &= RT \ln (a_B / x_B) / x_A^2 = RT \ln f_B / x_A^2. \end{aligned} \quad (20.41)$$

If a plot of experimental values of $RT \ln f_B / x_A^2$ versus x_B can be represented by a straight line then the properties can be represented by two parameters, ${}^0L_{AB}$ and ${}^1L_{AB}$. If experimental data are available for both components, then the two-parameter representation requires that one finds two straight lines, one for each component and such that they yield the same set of 0L and 1L values. An example for liquid Fe–Ni at 1852 K is given in Fig. 20.4. In Fig. 20.4(b) the two lines have the same slope, representing ${}^1L_{\text{Fe,Ni}}$, and the same value at $x_{\text{Ni}} = 0.25$ for the Ni line and $x_{\text{Fe}} = 0.25$ for the Fe line, representing ${}^0L_{\text{Fe,Ni}}$. The experimental scatter is considerable in Fig. 20.4(b), especially at low Ni contents for Fe and at low Fe contents for Ni because of the very small values then taken by the factors x_{Ni}^2 and x_{Fe}^2 in the denominators.

It should be emphasized that there are many binary systems where the power series representation is not very convenient. Figure 20.5 shows an example from liquid Bi–Mg at 973 K where a very large number of power terms would be needed for a satisfactory representation of the data. It is evident that some particular physical effect occurs at the centre of the system and it would be difficult to represent such data mathematically

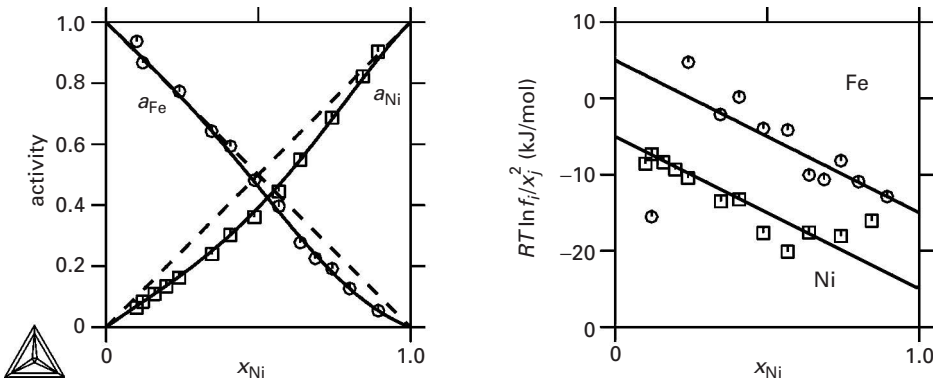


Figure 20.4 The properties of liquid Fe–Ni solutions at 1852 K according to direct measurements and a subregular solution model with ${}^0L_{Fe,Ni} = -10$ and ${}^1L_{Fe,Ni} = 5$ kJ/mol.

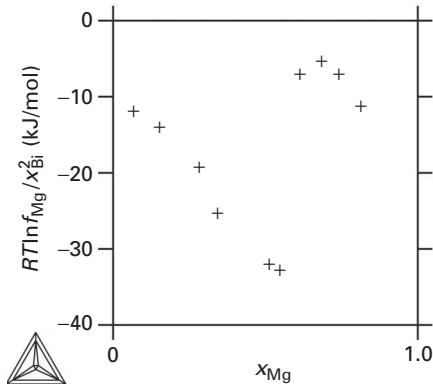


Figure 20.5 Experimental data from liquid Bi–Mg alloys at 973 K. This behaviour cannot be well represented with a power series.

without identifying that effect and representing it with an adequate model. Such models will be described later on.

Exercise 20.6

Consider the gaseous mixture (solution) of H_2 and O_2 at 1 bar and a temperature high enough for the reaction $2H_2 + O_2 \rightarrow 2H_2O$ to go to equilibrium but still low enough to make the formation of H_2O practically complete. Examine how the activity of O_2 would vary across the binary H_2 – O_2 system as a function of x_{O_2} .

Hint

The binary system has two components and it is evident that they are defined as H_2 and O_2 and that x_{O_2} is thus defined with no regard for the formation of H_2O . Suppose that the

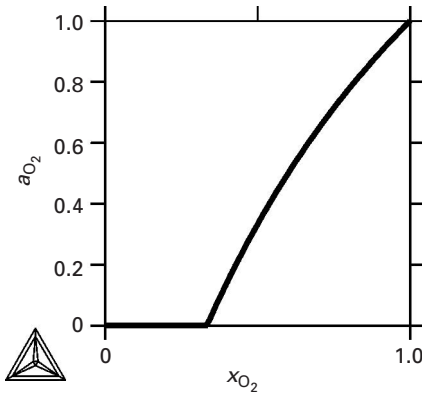


Figure 20.6 Solution to Exercise 20.6.

gas is actually an ideal gas mixture of H_2 , O_2 and H_2O . At constant T and P we then have $RT \ln x_{O_2} = \mu_{O_2} - {}^\circ\mu_{O_2} = RT \ln y_{O_2}$ where the definition of y_{O_2} takes into account the presence of H_2O .

Solution

Between $x_{O_2} = 0$ and $1/3$ there are practically no molecules of O_2 . All oxygen goes into H_2O . Between $x_{O_2} = 1/3$ and 1 there are, for the same reason, practically no H_2 molecules and $y_{H_2O} + y_{O_2} = 1$ and $x_{O_2} = (y_{O_2} + 0.5y_{H_2O})/(y_{O_2} + 1.5y_{H_2O})$ and thus $a_{O_2} = y_{O_2} = (3x_{O_2} - 1)/(x_{O_2} + 1)$. It is evident that it is impossible to describe the deviation of this solution from the ordinary ideal solution with a power series. Any reasonable model must recognize that the interaction between the two components is here so strong that large quantities of a new kind of molecule form (Fig. 20.6).

Exercise 20.7

It is common to define the activity of a component i in a solution with reference to pure i at the same temperature. The chemical potential of i in the solution is then written as $\mu_i = {}^\circ G_i(T) + RT \ln a_i$. Suppose that one would instead like to define an activity by referring to pure i at absolute zero as reference. Derive a relation between the two kinds of activity, a_i^T and a_i^0 .

Hint

The chemical potential of i in the solution, μ_i , is a well defined quantity even though its value can be given only relative to a reference, i.e., as $\mu_i - {}^\circ G_i$.

Solution

μ_i is the same quantity in the two equations: $\mu_i = {}^\circ G_i(T) + RT \ln a_i^T$ and $\mu_i = {}^\circ G_i(0) + RT \ln a_i^0$. Let us take the difference: $0 = {}^\circ G_i(T) - {}^\circ G_i(0) +$

$RT \ln(a_i^T/a_i^0)$; $a_i^0 = a_i^T \exp[(^\circ G_i(T) - ^\circ G_i(0))/RT]$. Thus $a_i^0 < a_i^T$ since $^\circ G_i(0) > ^\circ G_i(T)$.

20.6 Applications of the Gibbs–Duhem relation

At constant T and P the Gibbs–Duhem relation, Eq. (3.34), reduces to

$$\sum x_i dG_i = 0 \text{ or } \sum x_i d \ln a_i = 0. \quad (20.42)$$

We have here chosen the notation G_i instead of μ_i since we shall consider a single solution phase. By introducing partial excess Gibbs energies or activity coefficients through

$$G_i = ^\circ G_i + RT \ln x_i + {}^E G_i = ^\circ G_i + RT \ln x_i + RT \ln f_i, \quad (20.43)$$

we get

$$\sum x_i d {}^E G_i = 0 \text{ or } \sum x_i d \ln f_i = 0, \quad (20.44)$$

because

$$\sum x_i d \ln x_i = \sum x_i dx_i/x_i = \sum dx_i = 0. \quad (20.45)$$

In a binary system it is thus possible to evaluate f_1 from measurements of f_2 by integration from pure 1.

$$\ln f_1 = - \int_0^{x_2} \frac{x_2}{x_1} \cdot \frac{d \ln f_2}{dx_2} dx_2. \quad (20.46)$$

For graphical or numerical integration Wagner [40] suggested that this equation should first be transformed by integration by parts, yielding

$$\ln f_1 = \int_0^{x_2} \frac{\ln f_2}{x_1^2} dx_2 - \frac{x_2 \ln f_2}{x_1}. \quad (20.47)$$

One can also evaluate ${}^E G_m$ from the information on f_2 . The last equation gives

$$x_1 \ln f_1 + x_2 \ln f_2 = x_1 \int_0^{x_2} \frac{\ln f_2}{x_1^2} dx_2, \quad (20.48)$$

and this is identical to ${}^E G_m/RT$.

As an introduction to a discussion of ternary systems, it may be useful to repeat the last derivation by starting from the well-known expression for a binary system in Section 7.1, when x_1 is regarded as a dependent variable.

$${}^E G_2 = {}^E G_m + (1 - x_2)d {}^E G_m/dx_2. \quad (20.49)$$

This can be rearranged into

$${}^E G_2 = (1 - x_2)^2 d [{}^E G_m/(1 - x_2)]/dx_2. \quad (20.50)$$

Integration from $x_2 = 0$ where ${}^E G_m = 0$, yields

$$\begin{aligned} {}^E G_m &= (1 - x_2) \left\{ {}^E G_m(x_2 = 0) + (1 - x_2) \int_0^{x_2} [{}^E G_2 / (1 - x_2)^2] dx_2 \right\} \\ &= (1 - x_2) \int_0^{x_2} [{}^E G_2 / (1 - x_2)^2] dx_2, \end{aligned} \quad (20.51)$$

which is actually identical to the result of Eq. (20.48).

For a ternary system one may derive the same equations if the ratio x_1/x_3 is regarded as the second independent variable. However, when integrating from $x_2 = 0$ one now starts from a binary 1–3 alloy and its ${}^E G_m$ is not zero. We should thus write the result as

$${}^E G_m = (1 - x_2) \left\{ {}^E G_m(x_2 = 0) + \int_0^{x_2} [{}^E G_2 / (1 - x_2)^2] dx_2 \right\}_{x_1/x_3}. \quad (20.52)$$

This equation can be useful if one has measured ${}^E G_2$ (i.e. $RT \ln f_2$) in sections of constant x_1/x_3 .

Exercise 20.8

Show that $G_2 = G_m + (1 - x_2) \cdot (\partial G_m / \partial x_2)_{x_1/x_3}$ in a ternary system by starting from $G = N G_m(x_2, x_1/x_3)$.

Hint

Since $x_1/x_3 = N_1/N_3$ we find $(\partial(x_1/x_3)/\partial N_2)_{N_1, N_3} = 0$.

Solution

$$\begin{aligned} x_2 &= N_2 / (N_1 + N_2 + N_3); \quad (\partial x_2 / \partial N_2)_{N_1, N_3} = (N - N_2) / N^2 = (1 - x_2) / N; \quad G_2 \equiv \\ &(\partial G / \partial N_2)_{N_1, N_3} = G_m + N \cdot (\partial G_m / \partial x_2)_{x_1/x_3} \cdot (\partial x_2 / \partial N_2)_{N_1, N_3} + N \cdot (\partial G_m / \partial (x_1/x_3))_{x_2} \cdot \\ &(\partial(x_1/x_3) / \partial N_2)_{N_1, N_3} = G_m + N \cdot (\partial G_m / \partial x_2)_{x_1/x_3} \cdot (1 - x_2) / N + N \cdot (\partial G_m / \partial (x_1/x_3))_{x_2} \cdot \\ &0 = G_m + (1 - x_2) \cdot (\partial G_m / \partial x_2)_{x_1, x_3} \end{aligned}$$

Exercise 20.9

By studying the ratio of vapour pressures over A–B alloys one can measure how the ratio of activities a_A/a_B varies with composition. Show how one can evaluate a_A and a_B from such information.

Hint

Use the Gibbs–Duhem relation in the form $x_A d \ln a_A + x_B d \ln a_B = 0$. Replace $\ln a_B$ by $\ln(a_B/a_A) + \ln a_A$.

Solution

$$0 = x_A d \ln a_A + x_B d \ln(a_B/a_A) + x_B d \ln a_A = (x_A + x_B) d \ln a_A + x_B d \ln(a_B/a_A) = d \ln a_A + x_B d \ln(a_B/a_A); \quad \ln a_A = - \int x_B d \ln(a_B/a_A)$$

20.7 Dilute solution approximations

When discussing dilute solutions Wagner [40] suggested that one should consider the composition dependence of the activity coefficient. For a dilute solution of B in A he wrote

$$(G_B - {}^\circ G_B)/RT = \ln a_B = \ln f_B + \ln x_B = \ln {}^\circ f_B + \ln x_B + \varepsilon_B x_B \quad (20.53)$$

This may be compared with the expression we obtained for the regular solution model, i.e., Eq. (20.32) with a constant parameter.

$$G_B = {}^\circ G_B + RT \ln x_B + (1 - 2x_B + x_B^2) L_{AB} \quad (20.54)$$

The two formalisms are identical if the second-order term can be neglected, i.e. for dilute solutions. We identify parameters as follows if the same reference is used in both cases.

$$\ln {}^\circ f_B = L_{AB}/RT \quad (20.55)$$

$$\varepsilon_B = -2L_{AB}/RT \quad (20.56)$$

However, a different reference state is often used in the ε formalism. As an example, the infinite-dilution reference state is defined in such a way that it makes $\ln {}^\circ f_B = 0$ and gives the relation

$${}^\circ G_B^{\text{inf.dil.}} = {}^\circ G_B + L_{AB} \quad (20.57)$$

$$G_B = {}^\circ G_B^{\text{inf.dil.}} + RT \ln x_B + (-2x_B + x_B^2) L_{AB} \quad (20.58)$$

For a ternary system, where small amounts of B and C are dissolved in A, Wagner introduced an interaction coefficient between the two solutes, $\varepsilon_B^C = \varepsilon_C^B$, and gave the expressions

$$(G_B - {}^\circ G_B)/RT = \ln a_B = \ln f_B + \ln x_B = \ln {}^\circ f_B + \ln x_B + \varepsilon_B^B x_B + \varepsilon_B^C x_C \quad (20.59)$$

$$(G_C - {}^\circ G_C)/RT = \ln a_C = \ln f_C + \ln x_C = \ln {}^\circ f_C + \ln x_C + \varepsilon_C^B x_B + \varepsilon_C^C x_C. \quad (20.60)$$

This may be compared with the regular solution model yielding Eqs (20.35) to (20.37)

after replacing x_A with $1 - x_B - x_C$,

$$G_A = {}^\circ G_A + RT \ln x_A + (x_B^2 + x_B x_C) L_{AB} + (x_B x_C + x_C^2) L_{AC} - x_B x_C L_{BC} \quad (20.61)$$

$$G_B = {}^\circ G_B + RT \ln x_B + (1 - 2x_B + x_B^2 - x_C + x_B x_C) L_{AB} + (-x_C + x_B x_C + x_C^2) L_{AC} + (x_C - x_B x_C) L_{BC} \quad (20.62)$$

$$G_C = {}^\circ G_C + RT \ln x_C + (-x_B + x_B^2 + x_B x_C) L_{AB} + (1 - x_B + x_B x_C - 2x_C + x_C^2) L_{AC} + (x_B - x_B x_C) L_{BC}. \quad (20.63)$$

The two formalisms are again identical if the second-order terms are neglected and the following relations are obtained by comparing Eqs (20.59) and (20.60) with Eqs (20.62) and (20.63).

$$\varepsilon_B^B = -2L_{AB}/RT \quad (20.64)$$

$$\varepsilon_B^C = (L_{BC} - L_{AB} - L_{AC})/RT = \varepsilon_B^B \quad (20.65)$$

$$\varepsilon_C^C = -2L_{AC}/RT. \quad (20.66)$$

Equation (20.55) is still valid. We note that ε_B^C and ε_C^B must be equal in order to make the two formalisms identical.

Equation (20.61) demonstrated that one needs second-order terms in order to model any deviation from Raoult's law for the solvent, A. There are no such terms in the ε formalism and a related feature is that the expressions for G_A , G_B and G_C obtained from the ε formalism do not satisfy the Gibbs–Duhem relation. Pelton and Bale [41] showed that it can be satisfied by adding a particular term, K , to the expressions for all three G_A , G_B and G_C . Inspection of Eqs (20.62) and (20.63) reveals that the set of second-order terms is the same in all cases and it actually represents the K term,

$$KRT = (x_B^2 + x_B x_C) L_{AB} + (x_C^2 + x_B x_C) L_{AC} - x_B x_C L_{BC}. \quad (20.67)$$

Using the relations (20.64) to (20.66) it could as well be expressed in the form proposed by Pelton and Bale.

$$-K = \frac{1}{2}\varepsilon_B^B x_B^2 + \varepsilon_B^C x_B x_C + \frac{1}{2}\varepsilon_C^C x_C^2. \quad (20.68)$$

Darken [42] noticed that the regular solution model for binary solutions is often very inadequate and showed that it sometimes works well in the A-rich part by using a hypothetical state of reference for the solute. This is called the quadratic formalism and simply means that one substitutes ${}^\circ G_B + M_B$ for ${}^\circ G_B$, which represents the real Gibbs energy of pure B in the same phase. This can be done directly in Eq. (20.62) and similarly for pure C in Eq. (20.63). The values of M_A and M_B are given by a comparison of Eqs (20.59) and (20.60).

$$\ln {}^\circ f_B = (M_B + L_{AB})/RT = M_B/RT - 0.5\varepsilon_B^B \quad (20.69)$$

$$\ln {}^\circ f_C = (M_C + L_{AC})/RT = M_C/RT - 0.5\varepsilon_C^C. \quad (20.70)$$

The corrected ε formalism is completely equivalent to the quadratic formalism and thus offers a convenient way of evaluating the M and L coefficients to fit the experimental information.

Exercise 20.10

Derive the expression for K in Eq. (20.70).

Hint

Apply the Gibbs–Duhem relation in the x_B direction and in the x_C direction, respectively, in a ternary system, after first expressing x_A in terms of x_B and x_C .

Solution

$0 = x_A d \ln a_A + x_B d \ln a_B + x_C d \ln a_C = x_A d(\ln x_A + K) + x_B d(\ln x_B + \varepsilon_B^B x_B + \varepsilon_B^C x_C + K) + x_C d(\ln x_C + \varepsilon_C^B x_B + \varepsilon_C^C x_C + K)$. $\partial/\partial x_B$ of this gives since $x_A = 1 - x_B - x_C$: $0 = x_A(-1/x_A + \partial K/\partial x_B) + x_B(1/x_B + \varepsilon_B^B + \partial K/\partial x_B) + x_C(\varepsilon_C^B + \partial K/\partial x_B)$; $\partial K/\partial x_B = -x_B \varepsilon_B^B - x_C \varepsilon_C^B$. In the same way we find $\partial K/\partial x_C = -x_B \varepsilon_B^C - x_C \varepsilon_C^C$. These conditions are satisfied with $K = -(\varepsilon_B^B x_B^2 + 2\varepsilon_B^C x_B x_C + \varepsilon_C^C x_C^2)/2$.

20.8 Predictions for solutions in higher-order systems

Taking all binary interactions into account we obtain the following expression for the excess Gibbs energy in a multicomponent solution phase.

$${}^E G_m = \sum_i \sum_{j>i} x_i x_j I_{ij}. \quad (20.71)$$

If this model applies, all the I_{ij} coefficients can be determined experimentally on the respective binary systems and the properties of the higher-order system can be predicted by combination. On the other hand, if a composition-dependent I is required in order to represent the experimental information on a binary system, then there is no simple physical model predicting the properties of the higher-order system. It may be stated that a composition-dependent I implies that the interaction energy is not determined completely by the pair-wise interaction of atoms. If I in a binary system is equal to ${}^0L + (x_A - x_B)^1L$, then the excess Gibbs energy is described by

$${}^E G_m = x_A x_B^0L + x_A x_A x_B^1L - x_A x_B x_B^1L. \quad (20.72)$$

The last two terms seem to originate from interactions within groups of three atoms. If that is the case, one should expect similar effects in the higher-order system, for instance an interaction between an A, a B and a C atom given by $x_A x_B x_C I_{ABC}$. Of course, there

is no way by which this interaction can be predicted from the binary systems where that group of atoms does not occur.

When the binary interaction energies depend upon the composition, it should be advisable to introduce I_{ABC} in the description of the ternary system. However, it must be realized that there is no unique way of defining such a parameter because there is no unique way of predicting how the properties of a binary system contribute to the properties of the higher-order system unless I_{AB} is a constant. For variable I_{AB} several expressions are used

$$I_{AB} = {}^0Lx_A^2 + {}^1Lx_Ax_B + {}^2Lx_B^2 \quad (20.73)$$

$$I_{AB} = {}^0L + {}^1Lx_B + {}^2Lx_B^2 \quad (20.74)$$

$$I_{AB} = {}^0L + {}^1L(2x_B - 1) + {}^2L(6x_B^2 - 6x_B + 1) \quad (20.75)$$

$$I_{AB} = {}^0L + {}^1L(x_A - x_B) + {}^2L(x_A^2 - 4x_Ax_B + x_B^2) \quad (20.76)$$

$$I_{AB} = {}^0L + {}^1L(x_A - x_B) + {}^2L(x_A - x_B)^2. \quad (20.77)$$

These expressions are quite equivalent when applied to a binary system because they can be transformed into each other by the use of $x_A + x_B = 1$. When applied to a higher-order system the expressions give different results because $x_A + x_B$ is no longer unity. For practical reasons it may be important to select a particular expression and at present there is a strong preference for the last one. It was first suggested by Redlich and Kister [39] that this particular form, initially intended for binary systems, should be used for representing the binary contributions in a multicomponent system.

The same kind of problem appears when one wants to predict the properties of a quaternary solution from the four ternaries. A general method may be based upon the observation that all the expressions, listed for the binary interaction energy I_{AB} , become identical if x_A is replaced by $x_A + (1 - x_A - x_B)/2$ and x_B by $x_B + (1 - x_A - x_B)/2$. In fact, with this method all second-order expressions can be transformed into expressions identical to the Redlich–Kister polynomial. Generalizing this method we find that x_A should be replaced by $x_A + (1 - x_A - x_B - x_C)/3$, x_B by $x_B + (1 - x_A - x_B - x_C)/3$ and x_C by $x_C + (1 - x_A - x_B - x_C)/3$ in the ternary interaction energy I_{ABC} . This method can easily be extended to higher-order terms [43].

Exercise 20.11

Show that Eqs (20.74) and (20.77) become identical for a binary system if x_B is replaced by $x_B + (1 - x_A - x_B)/2$. Show how the second set of L parameters can be evaluated from the first one.

Hint

The expression by which we shall replace x_B is equal to $1/2 - (x_A - x_B)/2$.

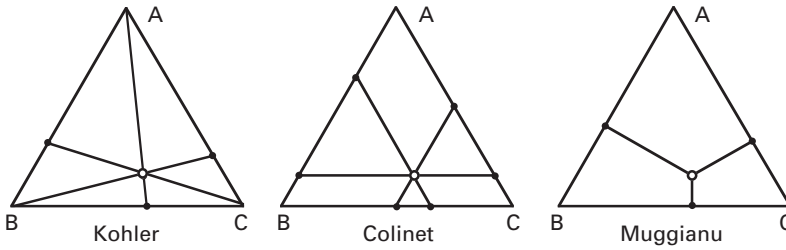


Figure 20.7 Selection of binary alloys (black points) according to three symmetric methods of predicting ternary properties.

Solution

$$I_{AB}(\text{in Eq. (20.74)}) = {}^0L + {}^1L/2 - {}^1L/2 \cdot (x_A - x_B) + {}^2L/4 + {}^2L/4(x_A - x_B)^2 - {}^2L/4 \cdot (x_A - x_B).$$

$$\text{Comparison shows that: } {}^0L (\text{in Eq. (20.77)}) = {}^0L + {}^1L/2 + {}^2L/4; \quad {}^1L (\text{in Eq. (20.77)}) = -({}^1L + {}^2L)/2; \quad {}^2L (\text{in Eq. (20.77)}) = {}^2L/4.$$

20.9 Numerical methods of predictions for higher-order solutions

As an alternative to the analytical methods described in the preceding section, several numerical methods have been suggested. They allow the properties of a ternary solution phase to be estimated from binary solutions without first assessing all the information available in the binary systems. However, it should be emphasized that they are nevertheless based upon some assumptions regarding the properties. The expression for the Gibbs energy of a ternary alloy of the composition x_A , x_B , x_C must contain the terms $x_A {}^0G_A + x_B {}^0G_B + x_C {}^0G_C$ and it is common also to include the ideal entropy of mixing. This leaves only the excess Gibbs energy and the following three symmetric methods have been proposed.

$$\text{Kohler [44]: } {}^E G_m = \sum_i \sum_{j>i} (x_i + x_j)^2 \cdot {}^E G_m^{ij} \left(\frac{x_i}{x_i + x_j}; \frac{x_j}{x_i + x_j} \right). \quad (20.78)$$

$$\text{Colinet [45]: } {}^E G_m = \sum_i \sum_{j>i} \left[\frac{x_j/2}{1-x_i} \cdot {}^E G_m^{ij}(x_i; 1-x_i) + \frac{x_i/2}{1-x_j} \cdot {}^E G_m^{ij}(1-x_j; x_j) \right]. \quad (20.79)$$

$$\begin{aligned} \text{Muggianu [46]: } {}^E G_m &= \sum_i \sum_{j>i} \frac{4x_i x_j}{(1+x_i-x_j)(1+x_j-x_i)} \\ &\times {}^E G_m^{ij}((1+x_i-x_j)/2; (1+x_j-x_i)/2). \end{aligned} \quad (20.80)$$

All the weighting factors have been selected in such a way that the methods correctly reproduce the term $x_i x_j {}^0L_{ij}$. Colinet and Muggianu also reproduce the terms $x_i x_j \cdot {}^1L_{ij}(x_i - x_j)$. In addition, Muggianu reproduces all the higher-power terms if they are written in the form $x_i x_j \cdot {}^kL_{ij}(x_i - x_j)^k$. As a consequence, the numerical method by

Muggianu and the analytical method based upon the Redlich–Kister polynomial give the same result and may be recommended for general use.

These numerical methods were initially defined geometrically as illustrated in Fig. 20.7. It explains how one selected the binary alloys, the Gibbs energies of which were used to estimate the ternary properties. It should be emphasized that these methods only apply to integral excess quantities.

Exercise 20.12

Refer to Fig. 20.7 and show that the binary A–B alloy used in Muggianu’s method has an A content of $(1 + x_A - x_B)/2$.

Hint

Draw lines through the ternary alloy, parallel to sides A–C and B–C. The intercepts on the A–B side have lengths equal to x_B , x_C and x_A .

Solution

The distance of the binary alloy from the B corner is $x_C/2 + x_A$. Using the relation $x_C = 1 - x_A - x_B$ one can transform this expression into $1/2 + x_A/2 - x_B/2$.

21 Solution phases with sublattices

21.1 Sublattice solution phases

In the substitutional solutions discussed in Section 20.4 all lattice sites were equivalent and a solution was formed from a pure substance by substituting new kinds of atoms for the initial one. However, relatively few crystalline phases belong to this class. The great majority have different kinds of lattice sites and can be described by using two or more sublattices. Examples of such phases will be discussed in this chapter. It will be demonstrated that a great variety of such phases can be modelled in a very direct way using an approach often called the compound energy model or formalism. It is a crude model in the sense that it assumes random mixing within each sublattice. The expression for the entropy of such phases is simple and was presented in Section 19.8, ‘Restricted random mixtures’, but the excess Gibbs energy can easily become very complicated. However, it should be realized that actual calculations of equilibria, and even of whole phase diagrams, can now be carried out with sophisticated computer programs which only require that the expression for the molar Gibbs energy of each phase is defined.

Section 19.8 gave the expression for the entropy assuming random mixing of all the components present in each sublattice. The result was expressed in terms of the site fraction variable, y_i , and in Section 19.10 it was then applied to interstitial solutions, which are a special case of solution phases with sublattices. We shall first consider the rather simple case where there is only one component, M, in one sublattice, and a number of components, i, j, \dots , in another sublattice. It is then convenient to consider a formula unit with one mole of atoms in the second sublattice $(M)_b(i, j, \dots)_1$. For 1 mole of such formula units we get

$$S_m^{\text{ideal}} = -R \sum y_i \ln y_i. \quad (21.1)$$

The deviation from ideal solution behaviour may be represented by the interactions between the components in the second sublattice. Using the Redlich–Kister type of power series we have, for the interaction between components i and j , when the first sublattice is filled with M,

$${}^E G_m = y_i y_j \sum_{k=0}^n L_{ij}^M (y_i - y_j)^k. \quad (21.2)$$

For $y_i = 1$ the phase is identical to a compound $M_b i$ and the whole expression of the molar Gibbs energy for 1 mole of formula units will be

$$G_m = \sum_i y_i {}^{\circ}G_{M_b i} + RT \sum_i y_i \ln y_i + \sum_i \sum_{j>i} y_i y_j \sum_{k=0}^n {}^k L_{ij}^M (y_i - y_j)^k. \quad (21.3)$$

It should be noticed that y_j is at the same time the site fraction of j in the second sublattice and the mole fraction of the compound $M_b j$ among all $M_b i$ compounds. From G_m we may thus derive expressions for the partial Gibbs energies of the compounds, using Eq. (4.6) but replacing x fractions with y fractions.

$$\begin{aligned} G_{M_b l} = & {}^{\circ}G_{M_b l} + RT \ln y_l + \sum_{i \neq l} \left\{ {}^0 L_{li}^M y_i (1 - y_l) + \sum_{k=1}^n {}^k L_{li}^M y_i (y_l - y_i)^{k-1} \right. \\ & \left. \cdot [(k+1)(1 - y_l)(y_l - y_i) + k y_i] \right\} \\ & - \sum_{i \neq l} \sum_{j \neq l, > i} y_i y_j \left\{ {}^0 L_{ij}^M + \sum_{k=1}^n {}^k L_{ij}^M (y_i - y_j)^k (k+1) \right\}. \end{aligned} \quad (21.4)$$

The expression is thus analogous to the one for a substitutional solution in Eq. (20.34). A ternary phase of this type would behave as a binary, substitutional phase. It is sometimes called a **quasi-binary** or **pseudo-binary** solution. For the same reason one may call a quaternary phase of this type a quasi-ternary phase.

As already shown in Eq. (4.56) one can generalize Eq. (4.6) to a solution phase with several sublattices, t , u and v , and with several constituents on the sublattices, e.g.,

$$G_{A_a B_b C_c} = G_m + \partial G_m / \partial y_A^t + \partial G_m / \partial y_B^u + \partial G_m / \partial y_C^v - \sum \Sigma y_i^s \partial G_m / \partial y_i^s. \quad (21.5)$$

The last term is a summation over all the constituents, i , in all the sublattices, s . Furthermore,

$$G_{A_a B_b C_c} \equiv \mu_{A_a B_b C_c} = a \mu_A + b \mu_B + c \mu_C. \quad (21.6)$$

Exercise 21.1

High-temperature measurements have shown complete miscibility in the solid phase of $\text{Al}_2\text{O}_3 - \text{Cr}_2\text{O}_3$. Information from lower temperatures is less certain but there is some report of a miscibility gap with a maximum at about $T_{\text{crit}} = 2000$ K. Model this solution phase.

Hint

Introduce a constant regular solution parameter. Express the ideal entropy contribution with regard to the size of the formula unit chosen.

Solution

Define the unit as $M_1O_{1.5}$. Then we get $G_m = y_{Al} {}^\circ G_{AlO_{1.5}} + y_{Cr} {}^\circ G_{CrO_{1.5}} + RT(y_{Al} \ln y_{Al} + y_{Cr} \ln y_{Cr}) + y_{Al} y_{Cr} L$. Because we have chosen a symmetric description, the miscibility gap will be modelled as symmetric. Its maximum will be found at $y_{Al} = y_{Cr} = 0.5$ which yields $0 = d^2 G_m / dy_{Cr}^2 = RT / y_{Al} y_{Cr} - 2L$; $L = 2RT_{crit} = 2R \cdot 2000 = 33\,000 \text{ J/mol}$.

21.2 Interstitial solutions

In Section 19.10 we discussed the ideal entropy of mixing in an interstitial solution. In fact, it may be regarded as the special case of a solution with two sublattices obtained by allowing vacant sites on one of the sublattices. For 1 mole of sites in that sublattice we can write the formula as $(M)_b(Va, i, j, \dots)_1$. All the equations derived for the phase with two sublattices in the preceding section can be applied if the vacancies are included as a component. For a binary M–C system we write the interstitial solution as $M_b(Va, C)_1$ and Eq. (21.3) yields,

$$G_m = y_C {}^\circ G_{M_b C} + y_{Va} {}^\circ G_{M_b Va} + RT(y_C \ln y_C + y_{Va} \ln y_{Va}) + y_C y_{Va} \sum_{k=0}^n {}^k L_{CVa} (y_C - y_{Va})^k \quad (21.7)$$

$$G_{M_b C} = {}^\circ G_{M_b C} + RT \ln y_C + y_{Va}^2 \left\{ {}^0 L_{CVa} + \sum_{k=1}^n {}^k L_{CVa} (y_C - y_{Va})^{k-1} [(2k+1)y_C - y_{Va}] \right\} \quad (21.8)$$

$$G_{M_b Va} = {}^\circ G_{M_b Va} + RT \ln y_{Va} + y_C^2 \left\{ {}^0 L_{CVa} + \sum_{k=1}^n {}^k L_{CVa} (y_C - y_{Va})^{k-1} [y_C - (2k+1)y_{Va}] \right\}. \quad (21.9)$$

Since all the sites in the second sublattice are vacant in the compound $M_b Va$, it is identical to b moles of pure M. G_M is thus obtained by dividing the last equation by b . G_C can be obtained by taking the difference between the two equations because

$$G_{M_b C} - G_{M_b Va} = bG_M + G_C - bG_M - G_{Va} = G_C - G_{Va}, \quad (21.10)$$

and it may be assumed that the chemical potential of vacancies is zero at equilibrium. We thus obtain

$$G_C = G_{M_b C} - G_{M_b Va} = {}^\circ G_{M_b C} - b {}^\circ G_M + RT \ln(y_C / y_{Va}) + {}^0 L_{CVa} (y_{Va} - y_C) + \sum_{k=1}^n {}^k L_{CVa} (y_C - y_{Va})^{k-1} [2ky_C y_{Va} - (y_C - y_{Va})^2]. \quad (21.11)$$

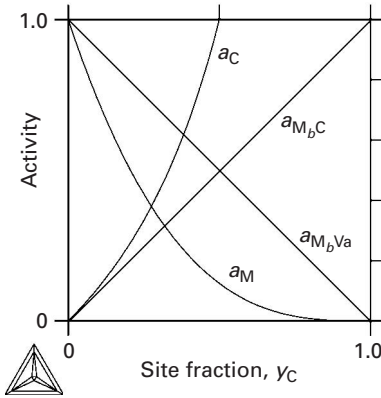


Figure 21.1 Variation of different activities in an ideal interstitial solution of C in M with the formula $M_{1/3}(Va, C)_1$.

Actually, we could have obtained $G_{M_b C} - G_{M_b Va}$ and thus G_C directly from G_m using Eq. (4.8),

$$G_C = G_{M_b C} - G_{M_b Va} = \frac{\partial G_m}{\partial y_C} - \frac{\partial G_m}{\partial y_{Va}} \quad (21.12)$$

It is important to notice that pure C cannot exist in the interstitial sublattice without M in the other sublattice. As a consequence, the reference state for C must be chosen using another phase. If pure C in a form α is chosen and y_{Va} is replaced by $1 - y_C$, then we obtain

$$\begin{aligned} RT \ln a_C &= G_C - {}^0G_C^\alpha = {}^0G_{M_b C} - {}^0G_{M_b Va} - {}^0G_C^\alpha + RT \ln[y_C/(1 - y_C)] \\ &+ {}^0L_{CVa} \cdot (1 - 2y_C) + {}^1L_{CVa} \cdot (-1 + 6y_C - 6y_C^2) \\ &+ {}^2L_{CVa} \cdot (1 - 10y_C + 24y_C^2 - 16y_C^3) + \dots \end{aligned} \quad (21.13)$$

One formula unit of $M_b Va$ is identical to b mole of M. The activity coefficient for very dilute solutions would be given by

$${}^0f_C = \exp[(G_{M_b C} - bG_M - {}^0G_C^\alpha + {}^0L_{CVa} - {}^1L_{CVa} + {}^2L_{CVa} - \dots)/RT]. \quad (21.14)$$

The deviation from Henry's law for less dilute solutions depends strongly upon the choice of composition variable. In order to get a constant activity coefficient for C over the whole system, when all the L parameters are zero, one must use $y_C/(1 - y_C)$ as the composition variable. If y_C is used one will find that a_C goes to infinity at $y_C = 1$. This is demonstrated in Fig. 21.1. On the other hand, in this type of diagram the activities of $M_b Va$ and $M_b C$ show an ideal behaviour when all the parameters are zero. The diagram was drawn for $b = 1/3$ and all L parameters equal to zero.

Exercise 21.2

In the plot of a_M versus y_C for an interstitial solution of C in M it may seem surprising in view of Raoult's law that the curve for a_M does not approach the diagonal close to $y_C = 0$. Find the reason and calculate the initial slope according to Raoult's law.

Hint

Raoult's law says that a_M should approach x_M , i.e. $1 - x_C$, not $1 - y_C$. Evaluate x_M from y_C using the formula $M_b(\text{Va}, \text{C})_1$ with $b = 1/3$ (the value for bcc).

Solution

For a binary interstitial solution we have $x_M = b/(b + y_C) = 1/(1 + y_C/b) \cong 1 - y_C/b = 1 - 3y_C$. The initial slope should be -3 and not -1 .

21.3 Reciprocal solution phases

With a stoichiometric phase one usually means a phase with a constant composition. This may, for instance, be caused by a crystalline structure which is composed of different sublattices, one for each component. An example is cementite, Fe_3C . Such a phase is also described as a compound. When a further component is added, it may go into one of the existing sublattices, an example being manganese-alloyed cementite, $(\text{Fe}, \text{Mn})_3\text{C}$. The composition of such a phase may thus vary along a line in the ternary phase diagram and it is sometimes described as a quasi-binary phase. Such phases were described in Section 21.1. If still another component is added, two alternatives result, examples being $(\text{Fe}, \text{Mn}, \text{Cr})_3\text{C}$ and $(\text{Fe}, \text{Mn})_3(\text{C}, \text{N})_1$. The latter type of phase is sometimes called a reciprocal solution phase because the central alloy can be regarded as a solution between either Fe_3C and Mn_3N or Fe_3N and Mn_3C . Both kinds of phases have the restriction to the variation in composition which we have called stoichiometric constraint. The composition of a reciprocal solution phase is represented by two sets of site fractions, one set for each sublattice, $y_A + y_B = 1$ and $y_C + y_D = 1$.

Accepting the stoichiometric constraint it is logical to consider the binary compounds as the components of the system. They were introduced in Section 4.8 and are called component compounds. Let us discuss the reciprocal case represented by $(\text{A}, \text{B})_b(\text{C}, \text{D})_c$. This is a quaternary phase but its composition can only be varied with two degrees of freedom instead of three due to the stoichiometric constraint. All possible compositions can thus be represented on a plane just like a ternary system. As shown in Fig. 13.12, a square diagram is now the natural shape and each corner is an end-member and represents a component compound. Perpendicular to that plane we may plot the Gibbs energy (see Fig. 21.2).

The diagram demonstrates that it is, in general, impossible to place a plane through the four points representing the Gibbs energy values of the four component compounds. The question is then what surface of reference one should use when giving the Gibbs

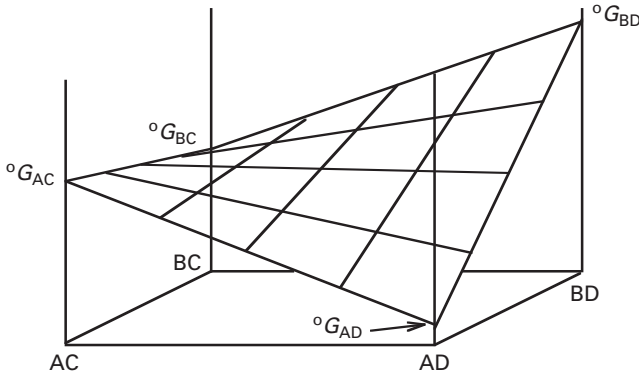


Figure 21.2 Surface of reference for a reciprocal phase.

energy value for a composition inside the system. The most natural choice seems to be the curved surface shown in the diagram and for a simple case that choice may be supported by the random mixing version of the nearest-neighbour bond energy model to be described in the next chapter. This surface of reference is accepted as the basis for the **compound energy formalism** [47] and it yields the following expression for the Gibbs energy.

$$G_m = y_A y_C {}^\circ G_{A_b C_c} + y_A y_D {}^\circ G_{A_b D_c} + y_B y_C {}^\circ G_{B_b C_c} + y_B y_D {}^\circ G_{B_b D_c} + RT[b y_A \ln y_A + b y_B \ln y_B + c y_C \ln y_C + c y_D \ln y_D] + {}^E G_m. \quad (21.15)$$

This expression may be regarded merely as a definition of the excess term ${}^E G_m$ but it becomes very important if one, as a first approximation, neglects the excess term. G_m refers to 1 mole of formula units $M_b N_c$. The simplest type of power series representation of the excess term makes use of the remaining two second-power terms, $y_A y_B$ and $y_C y_D$. However, in order to allow different behaviour on two opposite sides of the composition square we shall not use them but go directly to third-power terms,

$${}^E G_m = y_A y_B y_C I_{AB:C} + y_A y_B y_D I_{AB:D} + y_A y_C y_D I_{A:CD} + y_B y_C y_D I_{B:CD}. \quad (21.16)$$

The colon in the subscript is used to separate sublattices. For any side of the system this expression reduces to the expression discussed in the preceding section and all these interaction energies can thus be evaluated from the properties of the side systems. As an example, for the $A_b C_c$ – $B_b C_c$ side of the system we have $y_D = 0$, $y_C = 1$ and the excess Gibbs energy expression reduces to $y_A y_B I_{AB:C}$.

For more complicated cases one may express each one of the parameters $I_{AB:C}$, etc., with a power series of the Redlich–Kister type using site fractions. We have already done this for the simple case of a phase with sublattices considered previously. In this way we can introduce a large number of higher-power terms but it should be noticed that for each such term all the y_i except for one come from one sublattice and all those coefficients can be evaluated from the side systems. In order to adjust a description to information from inside the composition square we need a term like $y_A y_B y_C y_D I_{AB:CD}$.

In our discussion on constituents in Section 4.8 we saw that the chemical potentials of the compounds can be evaluated from Eq. (4.56) which here yields

$$G_{A_bC_c} = bG_A + cG_C = G_m + \partial G_m / \partial A + \partial G_m / \partial C - \sum y_i \partial G_m / \partial y_i \quad (21.17)$$

We thus obtain, for instance,

$$G_{A_bC_c} = {}^\circ G_{A_bC_c} + y_B y_D \cdot \Delta^\circ G_{AD+BC} + bRT \ln y_A + cRT \ln y_C + {}^E G_{A_bC_c} \quad (21.18)$$

$$G_{B_bC_c} = {}^\circ G_{B_bC_c} - y_A y_D \cdot \Delta^\circ G_{AD+BC} + bRT \ln y_B + cRT \ln y_C + {}^E G_{B_bC_c}. \quad (21.19)$$

where the quantity

$$\Delta^\circ G_{AD+BC} \equiv {}^\circ G_{A_bD_c} + {}^\circ G_{B_bC_c} - {}^\circ G_{A_bC_c} - {}^\circ G_{B_bD_c}, \quad (21.20)$$

is the Gibbs energy for the reciprocal reaction, $A_bC_c + B_bD_c \rightarrow A_bD_c + B_bC_c$. For constant interaction energies, to be denoted by L , we find

$$\begin{aligned} {}^E G_{A_bC_c} &= y_B(y_D y_A + y_B y_C) L_{AB:C} + y_D(y_D y_A + y_B y_C) L_{A:CD} \\ &\quad + y_B y_D (y_D - y_C) L_{B:CD} + y_B y_D (y_B - y_A) L_{AB:D} \end{aligned} \quad (21.21)$$

$$\begin{aligned} {}^E G_{B_bC_c} &= y_A(y_D y_A + y_B y_C) L_{AB:C} + y_D(y_D y_B + y_A y_C) L_{B:CD} \\ &\quad + y_A y_D (y_D - y_C) L_{A:CD} + y_A y_D (y_A - y_B) L_{AB:D}. \end{aligned} \quad (21.22)$$

It should be noticed that the quantity $\Delta^\circ G_{AD+BC}$ is evaluated from information on the four pure component compounds and does not even concern the quasi-binary sides. It often has a dominating influence on the properties of alloys inside the quaternary system. One may regard $\Delta^\circ G_{AD+BC}$ as a representation of the difference in interaction between nearest neighbours, i.e. usually between atoms in different sublattices. The L values, on the other hand, which enter in the excess Gibbs energy and control the behaviour of the quasi-binary sides, represent the interactions between atoms in the same sublattice, i.e. next-nearest neighbours in most cases, and may thus be of secondary importance.

It is worth noting that the partial Gibbs energies of the four component compounds are not independent of each other. From Eq. (4.49) it is evident that

$$\begin{aligned} G_{A_bD_c} + G_{B_bC_c} - G_{A_bC_c} - G_{B_bD_c} &= bG_A + cG_D + bG_B + cG_C \\ &\quad - bG_A - cG_C - bG_B - cG_D = 0. \end{aligned} \quad (21.23)$$

If one, for some reason, wants to consider the partial Gibbs energies of the elements, then it can be done relative to the value of one of them, e.g. G_A ,

$$cG_C = G_{A_bC_c} - bG_A \quad (21.24)$$

$$cG_D = G_{A_bD_c} - bG_A \quad (21.25)$$

$$bG_B = G_{B_bC_c} - G_{A_bC_c} + bG_A = G_{B_bD_c} - G_{A_bD_c} + bG_A. \quad (21.26)$$

However, G_A is indeterminate unless a second phase is present. The same phenomenon is illustrated for binary and ternary systems in Figs. 7.8 and 7.9 but it cannot be easily illustrated for a phase with four components.

One can introduce Redlich–Kister polynomials to describe the composition dependence of the interaction energies. When calculating ${}^E G_{M_b i_c}$ we must then evaluate several

kinds of contributions if there are many components. We find contributions of the following forms from interactions on the second sublattice

$$\begin{aligned} \Delta_1^E G_{M_b i_c} &= {}^0 L_{M:i j} y_j (y_i + y_M - 2y_i y_M) + \sum_{k=1}^n k L_{M:i j} (y_i - y_j)^{k-1} y_j \{(y_i - y_j) \\ &\quad \times [y_M(1+k)(1-y_i) + y_i - y_M y_i] + k y_M y_j\} \end{aligned} \quad (21.27)$$

$$\begin{aligned} \Delta_2^E G_{M_b i_c} &= {}^0 L_{N:i j} y_N y_j (1 - 2y_i) + \sum_{k=1}^n k L_{N:i j} (y_i - y_j)^{k-1} y_N y_j \{(y_i - y_j) \\ &\quad \times [(1+k)(1-y_i) - y_i] + k y_j\} \end{aligned} \quad (21.28)$$

$$\Delta_3^E G_{M_b i_c} = {}^0 L_{M:l j} y_l y_j (1 - 2y_M) + \sum_{k=1}^n k L_{M:l j} (y_l - y_j)^k y_l y_j (1 - 2y_M - k y_M) \quad (21.29)$$

$$\Delta_4^E G_{M_b i_c} = {}^0 L_{N:l j} y_N y_l y_j (-2) + \sum_{k=1}^n k L_{N:l j} (y_l - y_j)^k y_N y_l y_j (-2 - k). \quad (21.30)$$

Equivalent terms would come from the interactions on the first sublattice, $L_{MN:i}$, $L_{MN:j}$, $L_{KN:i}$ and $L_{KN:j}$.

The model for reciprocal phases, which has been discussed here, can be generalized to several sublattices and several components on each one. For three sublattices we find

$$G_m = \Sigma \Sigma \Sigma y_i^1 y_j^2 y_l^3 {}^0 G_{i_a j_b l_c} + RT(a \Sigma y_i \ln y_i + b \Sigma y_j \ln y_j + c \Sigma y_l \ln y_l) + {}^E G_m \quad (21.31)$$

It should be repeated that one can make computer calculations by simply defining the G_m expression. The complicated expressions for partial excess quantities given here are seldom needed.

Exercise 21.3

Examine how $G_{B_b D_c}$ varies along the $A_b C_c - B_b D_c$ diagonal if all the L parameters are zero. Compare with a binary substitutional solution A–B.

Hint

On the diagonal $y_B = y_D$ and $y_A = y_C$.

Solution

The model gives $G_{B_b D_c} = {}^0 G_{B_b D_c} + y_A y_C \Delta^0 G + b RT \ln y_B + c RT \ln y_D = {}^0 G_{B_b D_c} + y_A^2 \Delta^0 G + (b + c) RT \ln y_B$. This holds for one mole of atoms if $b + c = 1$ and it then resembles the regular solution model if ${}^0 L = \Delta^0 G \equiv {}^0 G_{A_b D_c} + {}^0 G_{B_b C_c} - {}^0 G_{A_b C_c} - {}^0 G_{B_b D_c}$.

21.4 Combination of interstitial and substitutional solution

The compound energy model, used to describe a reciprocal phase, can also be used for the case where there are two substitutionally mixed elements and one interstitial element. If we use C to represent the interstitial element then D represents the vacant interstitial sites. A and B represent the two substitutional elements. The compound A_bD_c will thus simply represent b atoms of A and B_bD_c represents b atoms of B. The difference between A_bC_c and A_bD_c or the difference between B_bC_c and B_bD_c can be used to represent c atoms of C. By the methods used in our preceding discussion on interstitial solutions we now obtain

$$G_A = {}^\circ G_A - y_B y_C \Delta^\circ G_{AD+BC}/b + RT \ln y_A + (c/b)RT \ln(1 - y_C) + {}^E G_A \quad (21.32)$$

$$G_B = {}^\circ G_B + y_A y_C \Delta^\circ G_{AD+BC}/b + RT \ln y_B + (c/b)RT \ln(1 - y_C) + {}^E G_B \quad (21.33)$$

$$G_C = y_A ({}^\circ G_{A_bC_c} - {}^\circ G_{A_bD_c})/c + y_B ({}^\circ G_{B_bC_c} - {}^\circ G_{B_bD_c})/c + RT \ln[y_C/(1 - y_C)] + {}^E G_C, \quad (21.34)$$

where

$$b^E G_A = y_B y_C (L_{AB:D} - L_{AB:C} - L_{B:CD} + L_{A:CD}) + y_B^2 L_{AB:D} + y_C^2 L_{A:CD} + 2y_B^2 y_C (L_{AB:C} - L_{AB:D}) + 2y_B y_C^2 (L_{B:CD} - L_{A:CD}) \quad (21.35)$$

$$b^E G_B = y_A y_C (L_{AB:D} - L_{AB:C} + L_{B:CD} - L_{A:CD}) + y_A^2 L_{AB:D} + y_C^2 L_{B:CD} + 2y_A^2 y_C (L_{AB:C} - L_{AB:D}) + 2y_A y_C^2 (L_{A:CD} - L_{B:CD}) \quad (21.36)$$

$$c^E G_C = y_A y_B (L_{AB:C} - L_{AB:D}) + (1 - 2y_C)(y_A L_{A:CD} - y_B L_{B:CD}). \quad (21.37)$$

The expression for G_C has been made symmetric for A and B. Alternatively, we can modify the expression by considering A as the base metal.

Exercise 21.4

By considering the Fe–Mn–S melt as a reciprocal solution $(\text{Fe}, \text{Mn})_1(\text{Va}, \text{S})_1$, estimate the $\varepsilon_S^{\text{Mn}}$ parameter at 1900 K from the following binary information, ${}^\circ G_{\text{MnS}} - {}^\circ G_{\text{Mn}} - {}^\circ G_{\text{S}} = -139.4$ kJ/mol and ${}^\circ G_{\text{FeS}} - {}^\circ G_{\text{Fe}} - {}^\circ G_{\text{S}} = -62.4$ kJ/mol.

Hint

The model is actually the combination of a substitutional and interstitial model. Neglecting binary interaction energies we obtain for S, which in the model plays the role of an interstitial element, $G_S = {}^\circ G_{\text{FeS}} - {}^\circ G_{\text{Fe}} + RT \ln[y_S/(1 - y_S)] + y_{\text{Mn}} \Delta^\circ G$. The $\varepsilon_S^{\text{Mn}}$ parameter is defined from Eq. (20.6): $(G_S - {}^\circ G_S)/RT = \ln^\circ f_S + \ln x_S + \varepsilon_S^{\text{Mn}} x_{\text{Mn}} + \varepsilon_S^{\text{S}} x_{\text{S}}$ but for low Mn and in particular low S contents we may approximate x by y and neglect the last term.

Solution

By comparing the two expressions we find $RT\varepsilon_S^{\text{Mn}} \cong \Delta^\circ G \equiv {}^\circ G_{\text{MnS}} - {}^\circ G_{\text{Mn}} - {}^\circ G_{\text{FeS}} + {}^\circ G_{\text{Fe}} = -139.4 + 62.4 = -77.0 \text{ kJ/mol}$; $\varepsilon_S^{\text{Mn}} = -77000/1900R = -4.9$.

21.5 Phases with variable order

So far we have discussed reciprocal phases where each element can go into one sublattice, only. However, there are many cases where an element can go into two or more sublattices although it energetically prefers a particular one. The distribution on various sublattices will then vary with temperature, with the highest degree of order found at the lowest temperature at which the atoms are still able to move. To illustrate the case we shall consider a phase with the formula $(\text{A},\text{B})_b(\text{B},\text{A})_c$ where A prefers the first sublattice and B the second one. For simplicity we shall choose $b + c = 1$. The four component compounds will be A_bB_c , A_bA_c , B_bB_c and B_bA_c . We can apply all the equations already derived for a reciprocal phase but now the site fractions are not fixed by the composition. However, there is a relation between composition and site fractions and we can write it in two different ways,

$$x_A = by'_A + cy''_A = y'_A y''_A + by'_A y''_B + cy'_B y''_A \quad (21.38)$$

$$x_B = by'_B + cy''_B = y'_B y''_B + by'_B y''_A + cy'_A y''_B. \quad (21.39)$$

These relations can be used to simplify the G_m expression obtained by applying Eq. (21.15) to the present case.

$$\begin{aligned} G_m &= y'_A y''_A {}^\circ G_{\text{A}_b\text{A}_c} + y'_A y''_B {}^\circ G_{\text{A}_b\text{B}_c} + y'_B y''_A {}^\circ G_{\text{B}_b\text{A}_c} + y'_B y''_B {}^\circ G_{\text{B}_b\text{B}_c} \\ &\quad + RT(by'_A \ln y'_A + by'_B \ln y'_B + cy''_A \ln y''_A + cy''_B \ln y''_B) \\ &= x_A {}^\circ G_{\text{A}_b\text{A}_c} + x_B {}^\circ G_{\text{B}_b\text{B}_c} + y'_A y''_B ({}^\circ G_{\text{A}_b\text{B}_c} - b {}^\circ G_{\text{A}_b\text{A}_c} - c {}^\circ G_{\text{B}_b\text{B}_c}) \\ &\quad + y'_B y''_A ({}^\circ G_{\text{B}_b\text{A}_c} - b {}^\circ G_{\text{B}_b\text{B}_c} - c {}^\circ G_{\text{A}_b\text{A}_c}) \\ &\quad + RT(by'_A \ln y'_A + by'_B \ln y'_B + cy''_A \ln y''_A + cy''_B \ln y''_B), \end{aligned} \quad (21.40)$$

where ${}^\circ G_{\text{A}_b\text{A}_c}$ and ${}^\circ G_{\text{B}_b\text{B}_c}$ are the Gibbs energy of 1 mole of A or B in this structure and may be denoted by ${}^\circ G_A$ and ${}^\circ G_B$. We can introduce the following two quantities, which represent the Gibbs energy of formation of the compounds A_bB_c and B_bA_c .

$$\Delta^\circ G_{\text{A}_b\text{B}_c} = {}^\circ G_{\text{A}_b\text{B}_c} - b {}^\circ G_{\text{A}_b\text{A}_c} - c {}^\circ G_{\text{B}_b\text{B}_c} = {}^\circ G_{\text{A}_b\text{B}_c} - b {}^\circ G_A - c {}^\circ G_B \quad (21.41)$$

$$\Delta^\circ G_{\text{B}_b\text{A}_c} = {}^\circ G_{\text{B}_b\text{A}_c} - b {}^\circ G_{\text{B}_b\text{B}_c} - c {}^\circ G_{\text{A}_b\text{A}_c} = {}^\circ G_{\text{B}_b\text{A}_c} - b {}^\circ G_B - c {}^\circ G_A. \quad (21.42)$$

The sum of the two quantities is identical to the Gibbs energy of the reciprocal reaction introduced in Section 21.3,

$$\Delta^\circ G_{\text{A}_b\text{B}_c} + \Delta^\circ G_{\text{B}_b\text{A}_c} = {}^\circ G_{\text{A}_b\text{B}_c} + {}^\circ G_{\text{B}_b\text{A}_c} - {}^\circ G_{\text{B}_b\text{B}_c} - {}^\circ G_{\text{A}_b\text{A}_c} \equiv \Delta^\circ G_{\text{AB}+\text{BA}}. \quad (21.43)$$

We now obtain

$$G_m = x_A^\circ G_A + x_B^\circ G_B + y'_A y''_B \Delta^\circ G_{A_b B_c} + y'_B y''_A \Delta^\circ G_{B_b A_c} \\ + RT(b y'_A \ln y'_A + b y'_B \ln y'_B + c y''_A \ln y''_A + c y''_B \ln y''_B). \quad (21.44)$$

There are only two independent y_i parameters and after fixing the composition there will be only one independent parameter, e.g. y'_A yielding $dy'_B = -dy'_A$ and $dy''_B = -dy''_A = (b/c)dy'_A$. The equilibrium value of y'_A under constant composition and any T is obtained by minimizing G_m .

$$c \cdot \partial G_m / \partial y'_A = (c y''_B + b y'_A) \Delta^\circ G_{A_b B_c} - (c y''_A + b y'_B) \Delta^\circ G_{B_b A_c} \\ + bc \cdot RT(1 + \ln y'_A - 1 - \ln y'_B - 1 - \ln y''_A + 1 + \ln y''_B) = 0. \quad (21.45)$$

It is easiest to solve for T at any chosen value of y'_A ,

$$bcRT = \frac{(c y''_A + b y'_B) \Delta^\circ G_{B_b A_c} - (c y''_B + b y'_A) \Delta^\circ G_{A_b B_c}}{\ln(y'_A y''_B / y'_B y''_A)}. \quad (21.46)$$

When the two sublattices are equivalent, $b = c = 0.5$ and

$$\Delta^\circ G_{A_b B_c} = \Delta^\circ G_{B_b A_c} = 0.5 \Delta^\circ G_{AB+BA}. \quad (21.47)$$

and the equilibrium condition is

$$\frac{RT}{-\Delta^\circ G_{AB+BA}} = \frac{y'_A - y'_B - y''_A + y''_B}{\ln(y'_A y''_B / y'_B y''_A)}, \quad (21.48)$$

where $\Delta^\circ G_{AB+BA}$ is defined by Eq. (21.20). This may be called the symmetric case. The disordered state, $y''_A = y'_A = x_A$, is a solution to the equation at all temperatures and compositions but in order to examine where it is a stable or unstable equilibrium, we must study the second-order derivative,

$$c \cdot \partial^2 G_m / \partial y'^2_A \\ = (b + b + b + b) \cdot 0.5 \Delta^\circ G_{AB+BA} + bRT(c/y'_A + c/y'_B + b/y''_A + b/y''_B) \\ = 2b \Delta^\circ G_{AB+BA} + bRT/x_A x_B. \quad (21.49)$$

For positive values of $\Delta^\circ G_{AB+BA}$ the second derivative is always positive and the disordered state is always the stable state. There is no ordering tendency. For negative values of $\Delta^\circ G_{AB+BA}$ it is positive at higher temperatures and negative at lower and there is a transition temperature where it is zero, corresponding to the criterion $g_{\xi\xi} = 0$ in Eq. (15.18). We find

$$\frac{RT_{tr}}{-\Delta^\circ G_{AB+BA}} = 2x_A x_B. \quad (21.50)$$

The disordered state is thus a state of stable equilibrium above this critical temperature but an unstable equilibrium below. Two new solutions to the equation appear there, representing stable ordered states. This is demonstrated for a composition of $x_A = 0.6$ in Fig. 21.3(b) and the dashed line represents the unstable, disordered state below the transition point. The phase diagram is shown in Fig. 21.3(a). The whole curve is there

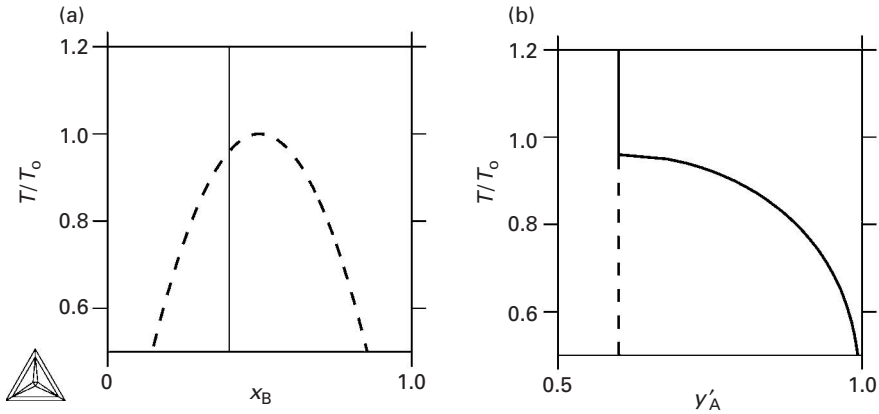


Figure 21.3 Second-order transition in a binary system. (a) Phase diagram. (b) Variation of degree of order with temperature for $x_A = 0.6$.

drawn as a dashed line because it is not a phase boundary but a transition line, the transition being of second order. The site fraction y'_A approaches the x_A value without any jump, as demonstrated in Fig. 21.3(b). We have thus managed again to model the second-order type of ordering transition but this time we have used a model containing parameters of some physical significance. In Section 15.2 we followed Landau's approach and simply worked with coefficients in a power series expansion.

When $\Delta^\circ G_{A_b B_c}$ and $\Delta^\circ G_{B_b A_c}$ are not equal, the result will be quite different. This is demonstrated in Fig. 21.4(a) for $b = c = 0.5$, $x_A = 0.5$, and $\Delta^\circ G_{A_b B_c} - \Delta^\circ G_{B_b A_c} = -0.1 \Delta^\circ G_{AB+BA}$. This may be called the asymmetric case. As soon as the two compound energies differ, the completely disordered state will never be stable and the ordered region in the phase diagram does not show an order–disorder transition. The variation of order with composition is shown at three temperatures in Fig. 21.4(b). The results for $x_A = 0.5$ can be read on the diagonal between the upper left and lower right corners.

Exercise 21.5

Where in Fig. 21.4(a) would a line for $\Delta^\circ G_{A_b B_c} - \Delta^\circ G_{B_b A_c} = +0.1 \Delta^\circ G_{AB+BA}$ fall?

Hint

Do not try to solve this problem by looking at the equations. The answer should be based upon a more basic consideration.

Solution

A change of sign of $\Delta^\circ G_{AB+BA}$ means that the other sublattice will be preferred by the A atoms but otherwise the effects will be the same as before. The effect of $\Delta^\circ G_{AB+BA}$ is to accentuate the order, independent of what sublattice the A atoms prefer. We will

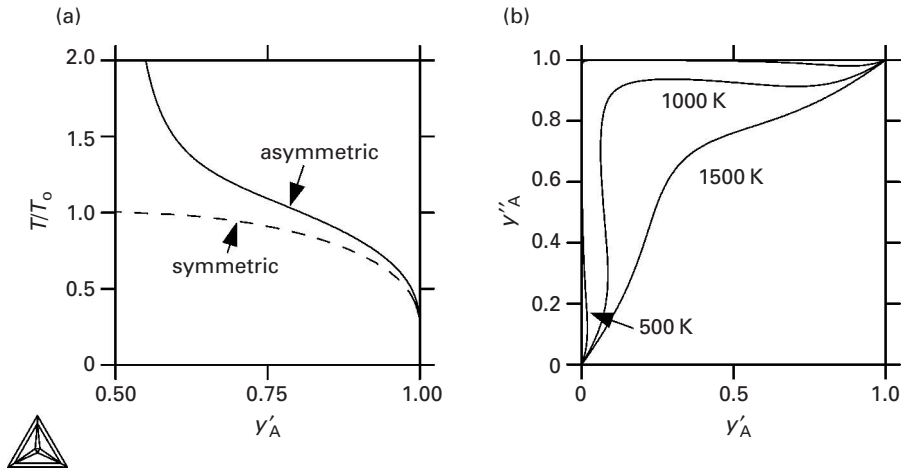


Figure 21.4 Model calculation of an ordered phase without a transition to a completely disordered state at any temperature. (a) Result for $x_A = 0.5$ compared with the result for a symmetric case showing a transition (dashed line). (b) Variation with composition.

thus get the same shape of curve as in Fig. 21.4(a) but starting from $y'_A = 0$ at $T = 0$ and approaching $y'_A = 0.5$ from the left.

21.6 Ionic solid solutions

In this chapter we have modelled various types of phases with sublattices without actually discussing the nature of the atoms (or 'species' to be more general). The compound energy model also applies to ionic substances but there are some complications due to the requirement of electroneutrality which should now be discussed.

Let us first consider solid solutions between NaCl, KCl, NaBr and KBr which all have the same crystalline structure. All the elements are ionized and we could give the formula as $(\text{Na}^{+1}, \text{K}^{+1})_1(\text{Cl}^{-1}, \text{Br}^{-1})_1$. One can vary the composition freely within the composition square because all the ions are univalent and the condition of electroneutrality is automatically fulfilled over the whole square by the fact that the two sublattices have the same number of sites. The compound energy formalism can be applied with no additional complications in this case.

Let us next consider the solution of CaCl_2 in NaCl. A complication is then caused by Ca being divalent and in order to compensate for this some of the cation sites will be vacant. The formula would thus be $(\text{Na}^{+1}, \text{Ca}^{+2}, \text{Va}^0)_1(\text{Cl}^{-1})_1$. This seems to resemble a ternary system with Na_1Cl_1 , Ca_1Cl_1 and Va_1Cl_1 as the components. However, electroneutrality requires that $y_{\text{Ca}} = y_{\text{Va}}$ and one can only vary the composition along a straight line in the composition triangle. In order to model the properties of solutions on this line we shall apply the ordinary expression for the compound energy model but with the additional

condition of electroneutrality. For 1 mole of formula units we get by neglecting the excess Gibbs energy,

$$G_m = y_{\text{Na}} \circ G_{\text{NaCl}} + y_{\text{Ca}} \circ G_{\text{CaCl}} + y_{\text{Va}} \circ G_{\text{VaCl}} + RT \sum y_i \ln y_i. \quad (21.51)$$

Here we have two quantities which cannot be studied experimentally, $\circ G_{\text{CaCl}}$ and $\circ G_{\text{VaCl}}$, because they are defined for charged compounds. However, due to the auxiliary condition $y_{\text{Ca}} = y_{\text{Va}}$, they always appear in the neutral combination, $(\circ G_{\text{CaCl}} + \circ G_{\text{VaCl}})$. The properties of this combination can be studied by studying neutral solutions. Instead of introducing this combination in the equation, it may be recommended to keep the original form and apply the condition of electroneutrality in the final expression one wants to use. When listing the parameter values for an ionic system one could select one of the charged compounds and give all the other charged compounds relative to that one. As an example, one may like to express the chemical potential of CaCl_2 in the solution. It is obtained as

$$\begin{aligned} \mu_{\text{CaCl}_2} &\equiv G_{\text{CaCl}} + G_{\text{VaCl}} = \circ G_{\text{CaCl}} + RT \ln y_{\text{Ca}} + \circ G_{\text{VaCl}} + RT \ln y_{\text{Va}} \\ &= \circ G_{\text{CaCl}} + \circ G_{\text{VaCl}} + 2RT \ln y_{\text{Ca}}, \end{aligned} \quad (21.52)$$

since $y_{\text{Ca}} = y_{\text{Va}}$. The neutral combination $(\circ G_{\text{CaCl}} + \circ G_{\text{VaCl}})$ can be given a numerical value.

Let us now consider the opposite case, the solution of NaCl in CaCl_2 . Electroneutrality may there be satisfied by the formation of vacant sites on the anion sublattice, $(\text{Ca}^{+2}, \text{Na}^{+1})_1(\text{Cl}^{-1}, \text{Va}^0)_2$, and the condition of electroneutrality is now $1 \cdot y_{\text{Na}} = 2 \cdot y_{\text{Va}}$. This is a reciprocal system and the compound energy formalism yields

$$\begin{aligned} G_m &= y_{\text{Ca}} y_{\text{Cl}} \circ G_{\text{CaCl}_2} + y_{\text{Ca}} y_{\text{Va}} \circ G_{\text{CaVa}_2} + y_{\text{Na}} y_{\text{Cl}} \circ G_{\text{NaCl}_2} \\ &\quad + y_{\text{Na}} y_{\text{Va}} \circ G_{\text{NaVa}_2} + RT \sum y_i \ln y_i + {}^E G_m. \end{aligned} \quad (21.53)$$

The chemical potential of NaCl is obtained by applying Eq. (21.19)

$$\begin{aligned} 2\mu_{\text{NaCl}} &= G_{\text{NaCl}_2} + G_{\text{NaVa}_2} = \circ G_{\text{NaCl}_2} - y_{\text{Ca}} y_{\text{Va}} \Delta^\circ G + RT \ln y_{\text{Na}} \\ &\quad + 2RT \ln y_{\text{Cl}} + {}^E G_{\text{NaCl}_2} + \circ G_{\text{NaVa}_2} + y_{\text{Ca}} y_{\text{Cl}} \Delta^\circ G \\ &\quad + RT \ln y_{\text{Na}} + 2RT \ln y_{\text{Va}} + {}^E G_{\text{NaVa}_2} = \circ G_{\text{NaCl}_2} + \circ G_{\text{NaVa}_2} + (1 - y_{\text{Na}})^2 \Delta^\circ G \\ &\quad + 2RT \ln [0.5 y_{\text{Na}}^2 (1 - 0.5 y_{\text{Na}})] + {}^E G_{\text{NaCl}_2} + {}^E G_{\text{NaVa}_2}, \end{aligned} \quad (21.54)$$

where $\circ G_{\text{NaCl}_2} + \circ G_{\text{NaVa}_2}$ and $\Delta^\circ G$ (which is identical to $\circ G_{\text{CaCl}_2} + \circ G_{\text{NaVa}_2} - \circ G_{\text{CaVa}_2} - \circ G_{\text{NaCl}_2}$ and may be written as $\Delta^\circ G_{\text{CaCl} + \text{NaVa}}$) represent neutral combinations and can be given numerical values. Figure 21.5 illustrates the neutral line in the two cases. How the model may describe the properties outside these lines is of no practical consequence.

Many ionic compounds are non-stoichiometric, an example being CeO_2 . It may be modelled by assuming that some of the Ce ions are only trivalent, yielding the formula $(\text{Ce}^{+4}, \text{Ce}^{+3})_1(\text{O}^{-2}, \text{Va}^0)_2$.

$$\begin{aligned} G_m &= y_{\text{Ce}^{+4}} y_{\text{O}} \circ G_{\text{Ce}^{+4}\text{O}_2} + y_{\text{Ce}^{+4}} y_{\text{Va}} \circ G_{\text{Ce}^{+4}\text{Va}_2} + y_{\text{Ce}^{+3}} y_{\text{O}} \circ G_{\text{Ce}^{+3}\text{O}_2} \\ &\quad + y_{\text{Ce}^{+3}} y_{\text{Va}} \circ G_{\text{Ce}^{+3}\text{Va}_2} + RT \sum 2y_i \ln y_i + {}^E G_m. \end{aligned} \quad (21.55)$$

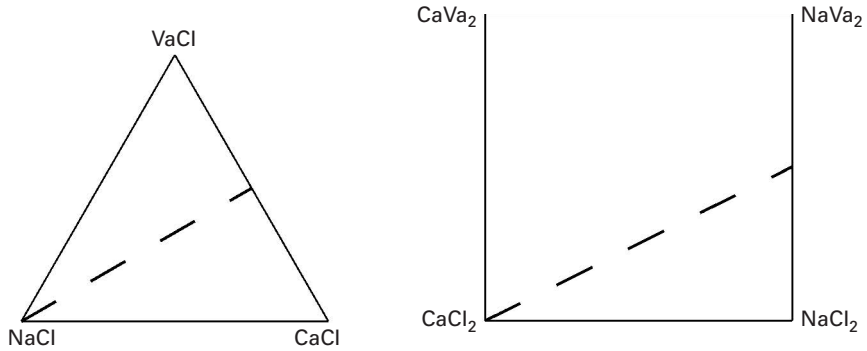
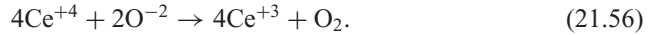
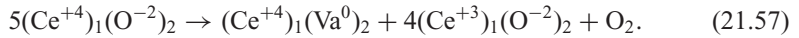


Figure 21.5 Neutral lines for two cases of ionic solutions, the solution of CaCl_2 in NaCl and of NaCl in CaCl_2 .

The deviation from the stoichiometric composition depends upon the oxygen potential in the surroundings. In order to derive an expression for the oxygen potential one must find a reaction formula for the formation of oxygen which balances atoms as well as charges.



Then the reaction formula must be expressed in terms of the component compounds in the model. Instead of 2O^{-2} we thus write $\text{Ce}^{+4}\text{O}_2 - \text{Ce}^{+4}\text{Va}_2$. With all charges shown we write the reaction as



Applying Eq. (3.19) we thus obtain

$$\begin{aligned} 2\mu_{\text{O}} &= \mu_{\text{O}_2} = 5G_{\text{Ce}^{+4}\text{O}_2} - G_{\text{Ce}^{+4}\text{Va}_2} - 4G_{\text{Ce}^{+3}\text{O}_2} \\ &= 5^{\circ}G_{\text{Ce}^{+4}\text{O}_2} + 5y_{\text{Ce}^{+3}}y_{\text{Va}}\Delta^{\circ}G_{\text{Ce}^{+4}\text{Va}+\text{Ce}^{+3}\text{O}} \\ &\quad + 5RT \ln y_{\text{Ce}^{+4}} + 10RT \ln y_{\text{O}} + 5^{\text{E}}G_{\text{Ce}^{+4}\text{O}_2} - {}^{\circ}G_{\text{Ce}^{+4}\text{Va}_2} \\ &\quad + y_{\text{Ce}^{+3}}y_{\text{O}}\Delta^{\circ}G_{\text{Ce}^{+4}\text{Va}+\text{Ce}^{+3}\text{O}} - RT \ln y_{\text{Ce}^{+4}} \\ &\quad - 2RT \ln y_{\text{Va}} - {}^{\text{E}}G_{\text{Ce}^{+4}\text{Va}_2} - 4^{\circ}G_{\text{Ce}^{+3}\text{O}_2} + 4y_{\text{Ce}^{+4}}y_{\text{Va}}\Delta^{\circ}G_{\text{Ce}^{+4}\text{Va}+\text{Ce}^{+3}\text{O}} \\ &\quad - 4RT \ln y_{\text{Ce}^{+3}} - 8RT \ln y_{\text{O}} - 4^{\text{E}}G_{\text{Ce}^{+3}\text{O}_2} = 5^{\circ}G_{\text{Ce}^{+4}\text{O}_2} - {}^{\circ}G_{\text{Ce}^{+4}\text{Va}_2} \\ &\quad - 4^{\circ}G_{\text{Ce}^{+3}\text{O}_2} + RT \ln \left(\frac{y_{\text{Ce}^{+4}}^4 y_{\text{O}}^2}{y_{\text{Ce}^{+3}}^4 y_{\text{Va}}^2} \right) \\ &\quad + (y_{\text{Ce}^{+3}} + 4y_{\text{Va}})\Delta^{\circ}G_{\text{Ce}^{+4}\text{Va}+\text{Ce}^{+3}\text{O}} + 5^{\text{E}}G_{\text{Ce}^{+4}\text{O}_2} \\ &\quad - 4^{\text{E}}G_{\text{Ce}^{+3}\text{O}_2} - {}^{\text{E}}G_{\text{Ce}^{+4}\text{Va}_2}, \end{aligned} \quad (21.58)$$

where the factor $y_{\text{Ce}^{+3}} + 4y_{\text{Va}}$ can be written as $8y_{\text{Va}}$ because the condition of electroneutrality for $(\text{Ce}^{+4}, \text{Ce}^{+3})_1(\text{O}^{-2}, \text{Va}^0)_2$ is

$$1 \cdot [4(1 - y_{\text{Ce}^{+3}}) + 3y_{\text{Ce}^{+3}}] = 2 \cdot 2(1 - y_{\text{Va}}) \text{ or } y_{\text{Ce}^{+3}} = 4y_{\text{Va}}. \quad (21.59)$$

For low deviations from stoichiometry, $y_{\text{Ce}^{+4}} \cong 1$ and $y_{\text{O}} \cong 1$, we may neglect all excess terms, so that

$$\begin{aligned} RT \ln P_{\text{O}_2} &\equiv \mu_{\text{O}_2} - {}^{\circ}\mu_{\text{O}_2} \\ &= 5{}^{\circ}G_{\text{Ce}^{+4}\text{O}_2} - 4{}^{\circ}G_{\text{Ce}^{+3}\text{O}_2} - {}^{\circ}G_{\text{Ce}^{+4}\text{V}_{\text{a}_2}} - {}^{\circ}\mu_{\text{O}_2} - RT \ln (256y_{\text{V}_{\text{a}}}^6). \end{aligned} \quad (21.60)$$

This model will thus predict that the vacancy content is proportional to $P_{\text{O}_2}^{-1/6}$. Experimental data indicate that the true value may rather be $-1/5$ at low values of $y_{\text{V}_{\text{a}}}$. The model may thus require some modification. One possibility is to introduce a strong association between a vacancy and a cation with abnormal valency, in this case Ce^{+3} .

It may again be emphasized that a computer calculation only requires that the G_{m} expression is defined. On the other hand, the complicated expressions derived in this section are needed for the kind of analytical examination of the model presented here.

Exercise 21.6

It is possible to dissolve Al and O in Si_3N_4 . Show in a composition square $\text{Si}_3\text{N}_4 - \text{SiO}_2 - \text{Al}_2\text{O}_3 - \text{AlN}$ where you would expect to find such a solid solution phase.

Hint

Since these materials are strongly covalent, the vacancy concentration is likely to be low. As a first approximation we may thus neglect vacancies. On the other hand, the ordinary condition of electroneutrality may be applied.

Solution

The general formula would be $(\text{Si}^{+4}, \text{Al}^{+3})_3(\text{N}^{-3}, \text{O}^{-2})_4$. The requirement of electroneutrality gives $3[4(1 - y_{\text{Al}}) + 3y_{\text{Al}}] = 4[3(1 - y_{\text{O}}) + 2y_{\text{O}}]$ and thus $3y_{\text{Al}} = 4y_{\text{O}}$.

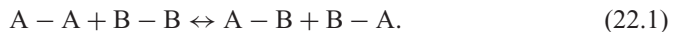
For the highest Al content, $y_{\text{Al}} = 1$, we find $y_{\text{O}} = 0.75$. The solution phase thus falls on the join $\text{Si}_3\text{N}_4 - \text{Al}_3\text{N}_1\text{O}_3$.

How close to $\text{Al}_3\text{N}_1\text{O}_3$ one can actually get experimentally depends on the competition with other phases.

22 Physical solution models

22.1 Concept of nearest-neighbour bond energies

The modelling of solution phases described in Chapters 20 and 21 was based on the proper expression for the ideal entropy of mixing assuming random mixing within each sublattice. The rest of the modelling was purely mathematical and was not related directly to any physical effects. The present chapter is devoted to models based on more physical considerations. In particular, the interaction energies between atoms will be considered. A very simple and useful way of modelling the thermodynamic properties of a binary solution is based upon the assumption that the energy of the whole system is the sum of the bond energies between neighbouring atoms. In the simplest case one only considers the energies of pairs of nearest neighbours. The formation of the solution from the pure components can then be regarded as a chemical reaction between different kinds of bonds, similar to a reaction between molecules



We have here chosen to distinguish between an A–B bond and a B–A bond although they are of course quite equivalent if all the lattice sites are equivalent.

The reaction gives a change of energy which we may denote by $2v$ and regard as an **exchange energy**. Since our aim is to construct an expression for the Gibbs energy of the solution we shall consider the Gibbs energies of the bonds rather than the internal energies. This actually means that we take into account not only the bond energies but also their temperature dependence.

$$2v = g_{AB} + g_{BA} - g_{AA} - g_{BB}. \quad (22.2)$$

In some cases g_{AB} and g_{BA} may be different and it may thus be useful to define two different quantities from the beginning,

$$v_{AB} = g_{AB} - g_{AA}/2 - g_{BB}/2 \quad (22.3)$$

$$v_{BA} = g_{BA} - g_{AA}/2 - g_{BB}/2, \quad (22.4)$$

where $v_{AB} + v_{BA} = 2v$. All bonds of each kind are assumed to have the same energy independent of the local composition. The Gibbs energy contribution from the bond energies can thus be evaluated by counting the number of bonds, N_{AA} , N_{BB} , N_{AB} and N_{BA} .

$$\Delta G = \sum_i \sum_j N_{ij} g_{ij}. \quad (22.5)$$

This is the mathematical definition of the nearest-neighbour bond energy model. In the next section we shall evaluate N_{ij} and add the contribution due to the entropy of configurational disorder.

The counting of the number of bonds of each kind can be done with different degrees of ambition. In the simplest treatment, which is called the Bragg–Williams model, one assumes that the atoms are placed at random on the sites in the crystal and it leads to an expression which is identical to the so-called regular solution model. It may thus be used to justify the regular solution model. In more ambitious treatments one tries to calculate how the ν value influences the number of bonds. A positive ν value indicates that the A and B atoms do not like to mix with each other and, if they have been mixed with each other in a solution, they should at least try to arrange themselves in such a way that there are less A–B bonds than in a random arrangement. A negative ν value, on the other hand, would favour arrangements where the A atoms are surrounded by more B atoms than in a random arrangement. Such effects will be considered later in this chapter using an approximation called the quasi-chemical approach. It is primarily based on a random mixture of the nearest neighbour bonds. In Kikuchi's cluster variation method one considers the random mixture of larger clusters. In principle, one should get an exact description of the configurational entropy by going to clusters of infinite size but that is not practically possible, nor is it necessary. A sufficiently good result is probably obtained by including just a few cluster sizes. It is interesting to note that in the cluster variation method one estimates the energy of a cluster as a sum of its bond energies (also called pair energies), assuming that each kind of pair energy is a constant, independent of the local and global composition.

The concept of nearest neighbour bond energies is closely related to the concept of molecules with a Gibbs energy of formation for each kind of molecule but it is much more difficult to justify. In a substance with molecules the atoms are actually present as groups of atoms bound together tightly and it is often a good approximation to neglect interactions between atoms in different molecules. However, the splitting up of the total energy of a crystal into a large number of bond energies is quite arbitrary and one may, for instance, choose to consider or neglect next-nearest neighbour bonds and to consider bond energies related to pairs of atoms or to larger groups of atoms, i.e. clusters. Even if one decides to consider only pairs of atoms or larger groups of atoms, the energy of the different kinds of bonds is rather arbitrary unless one has information relating to different types of ordering. This being so, it is doubtful whether a rather random distribution of atoms can be described with cluster energies evaluated from ordered arrangements. A very crude but useful way of improving the pair energy model would be to assume that only part of the excess Gibbs energy in a disordered state is of such short-range character that it can affect short- and long-range order. That approach would give an additional adjustable parameter to be used in the description of thermodynamic and configurational information.

The justification of the nearest-neighbour bond energy model has to come from its success in representing experimental facts. It has been found very useful in giving qualitative explanations of many phenomena in alloy systems but less successful in accounting for experimental data in detail. There are many modifications of the basic treatment but we

shall first consider the simplest possible approach, the random mixing model of Bragg and Williams.

Exercise 22.1

Suppose one has found experimentally that ν is a constant across a binary system. This result may be interpreted by assuming that all the bond energies are independent of composition. However, suppose one has some theoretical reason to expect that g_{AA} and g_{BB} should vary linearly across the system. Would it then be possible to explain the same experimental result?

Hint

Let $g_{AA} = g_{AA}^{\circ} + ax_B$ and $g_{BB} = g_{BB}^{\circ} + bx_B$.

Solution

$2\nu = g_{AB} + g_{BA} - g_{AA}^{\circ} - ax_B - g_{BB}^{\circ} - bx_B$. Yes, it is possible to eliminate x_B if $g_{AB} + g_{BA} - ax_B - bx_B = 0$ but there are no good reasons to expect such a relation.

22.2 Random mixing model for a substitutional solution

A solid phase where atoms of different components can substitute for each other, i.e. occupy the same kind of lattice sites, is called a substitutional solution. The composition of such a solution is conveniently described with the molar contents of the atoms, x_A and x_B in a binary solution. In order to describe the arrangement of the atoms relative to each other, it may be convenient to introduce the fractions of bonds, p_{AA} , p_{AB} , p_{BA} and p_{BB} . The notation p is chosen because the fraction of a certain kind of bond is equal to the probability of finding that kind of bond. Of course, $\sum p_{ij} = 1$. The fractions are also related through the composition and for the simple case where all the atoms have the same number of bonds this condition can be written in two ways

$$x_A = p_{AA} + (p_{AB} + p_{BA})/2 \quad (22.6)$$

$$x_B = p_{BB} + (p_{AB} + p_{BA})/2. \quad (22.7)$$

In the case of random mixing we get

$$p_{AA} = x_A^2 \quad (22.8)$$

$$p_{AB} = x_A x_B = p_{BA} \quad (22.9)$$

$$p_{BB} = x_B^2. \quad (22.10)$$

Let us assume that all atoms have the same number of nearest neighbours. We can thus introduce a single z value as the coordination number. The total number of bonds in a system containing one mole of atoms is thus $zN^A/2$ since each bond is shared

between two atoms. N^A is Avogadro's number. One will thus obtain, for instance, $N_{AA} = p_{AA} \cdot zN^A/2$ and for one mole of pure A we obtain

$${}^\circ G_A = g_{AA} \cdot 1 \cdot zN^A/2. \quad (22.11)$$

The Gibbs energy contribution from all the bond energies is

$$\Delta G_m = \sum_i \sum_j N_{ij} g_{ij} = (p_{AA}g_{AA} + p_{AB}g_{AB} + p_{BA}g_{BA} + p_{BB}g_{BB}) \cdot zN^A/2. \quad (22.12)$$

By inserting v_{AB} and v_{BA} we obtain

$$\begin{aligned} \Delta G_m &= [p_{AB}v_{AB} + p_{BA}v_{BA} + g_{AA}(p_{AA} + p_{AB}/2 + p_{BA}/2) \\ &\quad + g_{BB}(p_{BB} + p_{AB}/2 + p_{BA}/2)] \cdot zN^A/2 \\ &= x_A {}^\circ G_A + x_B {}^\circ G_B + [p_{AB}v_{AB} + p_{BA}v_{BA}] \cdot zN^A/2. \end{aligned} \quad (22.13)$$

We shall now add the contribution due to the entropy of mixing by considering random mixing of atoms. We get by substituting $x_A x_B$ for p_{AB} and p_{BA} and inserting $2v = v_{AB} + v_{BA}$,

$$G_m = x_A {}^\circ G_A + x_B {}^\circ G_B + v z N^A x_A x_B + RT(x_A \ln x_A + \ln x_B). \quad (22.14)$$

Exercise 22.2

Compare the final G_m expression for this random mixing model with the corresponding expression according to the regular solution model.

Hint

According to Section 20.4, the regular solution model gives ${}^E G_m = x_A x_B {}^0 L$.

Solution

The random bond energy model yields ${}^E G_m = v z N^A x_A x_B$. The two models are exactly related to each other by ${}^0 L = v z N^A$.

22.3 Deviation from random distribution

In order to describe non-random solutions we shall make extensive use of the bond probabilities, p_{ij} . In order to describe both long- and short-range order we need two independent internal variables and they can be defined in many ways. A convenient choice is the following,

$$K = (p_{AB} + p_{BA})/2 \quad (22.15)$$

$$L = (p_{AB} - p_{BA})/2, \quad (22.16)$$

and it yields

$$p_{AB} = K + L; \quad dp_{AB} = dK + dL \quad (22.17)$$

$$p_{BA} = K - L; \quad dp_{BA} = dK - dL \quad (22.18)$$

$$p_{AA} = x_A - (p_{AB} + p_{BA})/2 = x_A - K; \quad dp_{AA} = dx_A - dK \quad (22.19)$$

$$p_{BB} = x_B - (p_{AB} + p_{BA})/2 = x_B - K; \quad dp_{BB} = -dx_A - dK. \quad (22.20)$$

Long-range order can only be described with the use of two or more sublattices. The situation in an ordered alloy with two sublattices can be described with the site fractions which, in turn, can be expressed through the bond probabilities. Assuming that all the bonds go between atoms in two different sublattices we find

$$y'_A = p_{AA} + p_{AB} = x_A + L; \quad dy'_A = dx_A + dL \quad (22.21)$$

$$y'_B = p_{BB} + p_{BA} = x_B - L; \quad dy'_B = -dx_A - dL \quad (22.22)$$

$$y''_A = p_{AA} + p_{BA} = x_A - L; \quad dy''_A = dx_A - dL \quad (22.23)$$

$$y''_B = p_{BB} + p_{AB} = x_B + L; \quad dy''_B = -dx_A + dL. \quad (22.24)$$

Long-range order means that element A prefers one sublattice and B the other. It is conveniently defined as

$$l.r.o. = y'_A - y''_A = p_{AA} + p_{AB} - p_{AA} - p_{BA} = 2L. \quad (22.25)$$

Short-range order means that the atoms with given site fractions do not arrange themselves at random within each sublattice. Random distribution would yield the following probabilities of finding various bonds between the two sublattices and we shall still assume that there are no bonds within a sublattice.

$$p_{AA} = y'_A y''_A \quad (22.26)$$

$$p_{AB} = y'_A y''_B \quad (22.27)$$

$$p_{BA} = y'_B y''_A \quad (22.28)$$

$$p_{BB} = y'_B y''_B. \quad (22.29)$$

Short-range order may be defined as the deviation from this arrangement

$$\begin{aligned} s.r.o. &= [p_{AB} - y'_A y''_B + p_{BA} - y'_B y''_A]/2 \\ &= [2K - (x_A + L)(x_B + L) - (x_B - L)(x_A - L)]/2 \\ &= K - L^2 - x_A x_B. \end{aligned} \quad (22.30)$$

We know from Section 19.8 that a random distribution within each sublattice would yield the following configurational entropy for 1 mole of atoms,

$$S_m/R = -(y'_A \ln y'_A + y'_B \ln y'_B + y''_A \ln y''_A + y''_B \ln y''_B). \quad (22.31)$$

This does not account for short-range order. In an attempt to treat that case, one could start by considering a random distribution of the bonds,

$$S_m/R = -(z/2)(p_{AA} \ln p_{AA} + p_{AB} \ln p_{AB} + p_{BA} \ln p_{BA} + p_{BB} \ln p_{BB}). \quad (22.32)$$

However, this does not reduce to the previous expression when the random values for the four p_{ij} are inserted. That condition can be satisfied if we divide each p_{ij} under an \ln sign by its random value, which will make the whole expression go to zero for a random case, and then add the previous expression, which should be the correct one for the random case and a good approximation for small deviations from randomness.

$$\begin{aligned}
 -S_m/R &= (z/2)[p_{AA} \ln(p_{AA}/y'_A y''_A) + p_{AB} \ln(p_{AB}/y'_A y''_B) \\
 &\quad + p_{BA} \ln(p_{BA}/y'_B y''_A) + p_{BB} \ln(p_{BB}/y'_B y''_B)] \\
 &\quad + [y'_A \ln y'_A + y'_B \ln y'_B + y''_A \ln y''_A + y''_B \ln y''_B]/2. \quad (22.33)
 \end{aligned}$$

The contribution from the bond energies was given by Eq. (22.13). The complete expression will thus be

$$\begin{aligned}
 G_m &= x_A^\circ G_A + x_B^\circ G_B + [p_{AB} v_{AB} + p_{BA} v_{BA}] \cdot zN^A/2 \\
 &\quad + RT(z/2)[(p_{AA} \ln(p_{AA}/y'_A y''_A) + p_{AB} \ln(p_{AB}/y'_A y''_B) \\
 &\quad + p_{BA} \ln(p_{BA}/y'_B y''_A) + p_{BB} \ln(p_{BB}/y'_B y''_B)] \\
 &\quad + RT[y'_A \ln y'_A + y'_B \ln y'_B + y''_A \ln y''_A + y''_B \ln y''_B]/2. \quad (22.34)
 \end{aligned}$$

We shall now apply this general expression to several special cases. However, it should be remembered that the expression is valid only under the assumption that there are two sublattices, that they contain the same number of bonds and that all bonds go between atoms in different sublattices. The simple bcc structure (A2) can order in this way, yielding B2.

Exercise 22.3

Demonstrate that the general equation for ordering reduces to the model for random mixing in a substitutional solution without short-range order.

Hint

In a substitutional solution without long-range order and thus $y'_A = y''_A = x_A$ and $y'_B = y''_B = x_B$ and without short-range order $p_{ij} = y'_i y''_j = x_A x_B$. Furthermore, v_{AB} and v_{BA} must be equal in order to prevent long-range order.

Solution

The first part of the entropy contribution in Eq. (22.34) reduces to zero and the second one to $RT(x_A \ln x_A + x_B \ln x_B)$. In the energy part $p_{AB} v_{AB} + p_{BA} v_{BA}$ reduces to $2x_A x_B v$. Thus, $\Delta G_m = x_A^\circ G_A + x_B^\circ G_B + zN^A x_A x_B + RT(x_A \ln x_A + x_B \ln x_B)$.

22.4 Short-range order

At a high enough temperature long-range order will disappear if $v_{AB} = v_{BA} = v$ and only short-range order remains. For this case, $y'_A = y''_A = x_A$ and $y'_B = y''_B = x_B$ would yield $L = 0$ and $p_{AB} = p_{BA}$. We obtain from Eq. (22.34)

$$\begin{aligned} G_m = & x_A^0 G_A + x_B^0 G_B + v z N^A p_{AB} + RT(z/2)[p_{AA} \ln(p_{AA}/x_A^2) \\ & + 2p_{AB} \ln(p_{AB}/x_A x_B) + p_{BB} \ln(p_{BB}/x_B^2)] \\ & + RT[x_A \ln x_A + x_B \ln x_B]. \end{aligned} \quad (22.35)$$

We have only one internal variable $K = (p_{AB} + p_{BA})/2 = p_{AB}$. Its equilibrium value under constant composition is obtained from

$$\begin{aligned} (\partial G_m / \partial K)_{L, x_A} = & v z N^A + RT(z/2)[- \ln(p_{AA}/x_A^2) - p_{AA}/p_{AA} + 2 \ln(p_{AB}/x_A x_B) \\ & + 2p_{AB}/p_{AB} - \ln(p_{BB}/x_B^2) - p_{BB}/p_{BB}] \\ = & v z N^A + RT(z/2) \ln(p_{AB}^2/p_{AA} p_{BB}) = 0 \end{aligned} \quad (22.36)$$

$$\frac{p_{AB}^2}{p_{AA} p_{BB}} = \exp(-2v/kT). \quad (22.37)$$

This resembles the law of mass action for a chemical reaction between molecules and this method of correcting the entropy expression is thus called the quasi-chemical method. It should be emphasized that p_{AB} is here defined as half the number of AB bonds because the other half is counted as p_{BA} .

It is worth noting that the quasi-chemical method of correcting the entropy expression is valid only for small deviations from randomness, i.e. for low values of v/kT . It is immediately evident that very large values of v/kT will produce unreasonable results. An infinite value of v/kT will make $p_{AB} = p_{BA} = 0$ and thus $p_{AA} = x_A$ and $p_{BB} = x_B$. This implies a separation of the system into two parts, one containing all the A atoms and the other all the B atoms. The configurational entropy should thus be zero but the entropy part of Eq. (22.35) would yield

$$\begin{aligned} S_m = & -R(z/2)[x_A \ln(1/x_A) + 0 + x_B \ln(1/x_B)] - R[x_A \ln x_A + x_B \ln x_B] \\ = & (z/2 - 1)R[x_A + x_B \ln x_B]. \end{aligned} \quad (22.38)$$

This yields the correct value (zero) for $z = 2$, which applies when all the atoms are arranged in a string (the Ising model). For all realistic z values (e.g. $z = 8$ for bcc and $z = 12$ for fcc) the entropy expression yields large negative values. This result emphasizes that the quasi-chemical method should be used only for low values of v/kT , i.e. for low deviations from the ideal entropy. There one can simplify the expression by series expansions,

$$\exp \varepsilon = 1 + \varepsilon + \varepsilon^2/2 \quad (22.39)$$

$$\sqrt{1 + \varepsilon} = 1 + \varepsilon/2 - \varepsilon^2/8 + \varepsilon^3/16, \quad (22.40)$$

yielding

$$p_{AB} = p_{BA} = x_A x_B [1 - 2x_A x_B v/kT - 2x_A x_B (x_A - x_B)^2 (v/kT)^2]. \quad (22.41)$$

$$G_m = x_A^{\circ} G_A + x_B^{\circ} G_B + RT(x_A \ln x_A + x_B \ln x_B) + v z N^A x_A x_B [1 - x_A x_B v/kT - (2/3)x_A x_B (x_A - x_B)^2 (v/kT)^2]. \quad (22.42)$$

It is self-evident that the Gibbs energy will decrease due to short-range order, otherwise it would not form. The presence of short-range order will thus stabilize the disordered state and depress the temperature for the transition to a state with long-range order. This conclusion holds independent of the sign of v . Positive v will result in a miscibility gap at low temperatures if that reaction is not prevented by other reactions. Already above the miscibility gap a positive v will favour A–A bonds and B–B bonds and result in clusters. This tendency grows very strong as the consolute point is approached on cooling of a system with the correct composition. The tendency to actually separate into two phases will thus decrease and the consolute point of the miscibility gap will be depressed to lower temperatures. Also, the consolute point will be flatter than calculated from the regular solution model because the effect will be strongest close to the consolute point. This effect is quite noticeable in the liquid state where the presence of clusters may give rise to opalescence close to the consolute point. In the solid case the effect is counteracted by coherency stresses due to the difference in atomic sizes.

In order to treat this effect properly it is not enough to consider nearest neighbours. It is not even enough to extend the consideration to larger clusters. It has to be treated with a mathematical technique called the renormalization group approach. The resulting shape of the miscibility gap is non-analytical, especially close to the maximum.

Exercise 22.4

In the [next section](#) we shall find that long-range order is predicted to occur below $T_{tr} = 2x_A x_B (-vz/k)$ if the effect of short-range order is neglected. Evaluate the short-range order in a 50/50 bcc alloy at this temperature in order to test if the neglect of short-range order is serious.

Solution

$p_{AA} p_{BB} = (p_{AB})^2 \exp(2v/kT_{tr}) = (p_{AB})^2 \exp[2v/2x_A x_B (-vz)] = (p_{AB})^2 \exp(-4/z)$;
 Insert p_{AA} and p_{BB} from Eqs (22.6) and (22.7): $(0.5 - p_{AB})^2 = 0.606(p_{AB})^2$; $p_{AB} = 0.2811$; $s.r.o. = K - L^2 - x_A x_B = 0.2811 - 0 - 0.25 = 0.0311$. This is not negligible. The value of T_{tr} given above may be regarded as a rough estimate but short-range order makes the disordered state more stable and it should depress T_{tr} .

22.5 Long-range order

Let us again consider negative exchange energies. There is always a tendency for short-range order but as an introduction to the more general case it may be illustrative first to consider long-range order and neglect short-range order which is done by taking all $p_{ij} = y'_i y''_j$. The general equation then only contains y_i variables. The first part of the entropy contribution reduces to zero and with $\nu_{AB} + \nu_{BA} = 2\nu$ we find

$$G_m = x_A {}^\circ G_A + x_B {}^\circ G_B + (y'_A y''_B + y'_B y''_A) \cdot \nu z N^A / 2 \\ + RT [y'_A \ln y'_A + y'_B \ln y'_B + y''_A \ln y''_A + y''_B \ln y''_B] / 2. \quad (22.43)$$

With a fixed composition there is only one independent internal variable and we may choose any one of the four y_i or the long-range order parameter L . Using the relations between L and the y variables in Eqs (22.19) to (22.24) we thus find the equilibrium from

$$(\partial G_m / \partial L)_{x_A} = (y''_B + y'_A - y''_A - y'_B) \cdot \nu z N^A / 2 + RT [y'_A / y'_A + \ln y'_A \\ - y'_B / y'_B - \ln y'_B - y''_A / y''_A - \ln y''_A + y''_B / y''_B + \ln y''_B] / 2 = 0 \quad (22.44)$$

$$\frac{kT}{-\nu z} = \frac{y'_A + y''_B - y''_A - y'_B}{\ln(y'_A y''_B / y''_A y'_B)}. \quad (22.45)$$

using $R = kN^A$. It is evident that $y'_A = y''_A = x_A$ (and thus $y'_B = y''_B = x_B$) is a solution for all T values and it represents a completely random distribution. However, below a particular T value another kind of solution appears and it represents long-range order. That temperature has to be calculated as the limiting value of T where y'_A and y''_A of the new kind of solution approach x_A since the numerator and denominator are both zero. It is obtained by taking the ratio of their derivatives,

$$\frac{kT_{tr}}{-\nu z} = \frac{1 + 1 + 1 + 1}{1/y'_A + 1/y''_B + 1/y''_A + 1/y'_B} = \frac{4}{2/x_A + 2/x_B} = 2x_A x_B. \quad (22.46)$$

This relation defines the transition line, i.e. the boundary of the ordering region in the T, x_B phase diagram, see Fig. 21.3(a). It has a parabolic shape just as the spinodal curve for positive ν values. Its maximum is found at $x_A = x_B = 0.5$ and $T_{tr}^{\max} = -\nu z / 2k$. The present result is identical to the result of the compound energy formalism in Section 21.5 and the two models are related by $\Delta {}^\circ G_{AB+BA} = \nu z N^A$. The Bragg–Williams model thus provides a physical interpretation of the model parameter in this simple application of the compound energy formalism.

Above the ordering region the present model predicts complete disorder and the expression for G_m degenerates to

$$G_m = x_A {}^\circ G_A + x_B {}^\circ G_B + \nu z N^A x_A x_B + RT(x_A \ln x_A + x_B \ln x_B), \quad (22.47)$$

because $y'_A = y''_A = x_A$ and $y'_B = y''_B = x_B$. This expression was derived in Section 22.2 and it was then emphasized that $\nu z N^A$ is identical to the regular solution parameter 0L . Within the limitations of the nearest-neighbour bond energy model it would thus be possible to predict the ordering behaviour of a binary solution at low temperatures from the value of the regular solution parameter at high temperatures. However, as mentioned

in Section 22.1, it should be realized that part of the energy may be of a more long-range character than nearest-neighbour interactions. It is thus possible that the ordering tendency should be represented by a ν value which is not quite equal to $^0L/zN^A$.

Exercise 22.5

We have derived an expression for the transition line for ordering in a binary system, taking into account a gradual increase of long-range order with decreasing temperature. Now, formulate a more primitive theory by considering only two possible states, complete order and complete disorder. Calculate the transition temperature and compare with the result just obtained for the critical temperature. Limit the calculation to a 50/50 alloy.

Hint

One can directly calculate the Gibbs energy contributions from configurational entropy and bond energies for the two states. Do not introduce the exchange energy ν until the two states are compared.

Solution

In the disordered state the configurational entropy for 1 mole of atoms is $R \ln 2$ and the energy due to bonds is $(x_A^2 g_{AA} + 2x_A x_B g_{AB} + x_B^2 g_{BB}) \cdot zN^A/2 = (g_{AA} + 2g_{AB} + g_{BB}) \cdot zN^A/8$ for $x_A = x_B = 0.5$. In the ordered state there is no configurational entropy and the bonds give an energy of $g_{AB}zN^A/2$. At equilibrium: $-RT \ln 2 + (g_{AA} + 2g_{AB} + g_{BB})zN^A/8 = g_{AB}zN^A/2$; $RT \ln 2 = (g_{AA} - 2g_{AB} + g_{BB})zN^A/8 = -\nu zN^A/4$; $T = -\nu z/4k \ln 2$. This should be compared with $T_{tr} = -\nu z/2k$. The ratio is $T/T_{tr} = 1/2 \ln 2 = 0.72$.

Exercise 22.6

Apply the condition of stability limit and verify that the transition temperature falls at the limit of stability as it should for a second-order transition.

Hint

The stability condition, Eq. (6.54), can here be written as $(\partial^2 G_m / \partial L^2)_{x_A} = 0$. We have already an expression for $(\partial G_m / \partial L)_{x_A}$.

Solution

$(\partial^2 G_m / \partial L^2)_{x_A} = (1 + 1 + 1 + 1)\nu zN^A/2 + RT[1/y'_A + 1/y'_B + 1/y''_A + 1/y''_B]/2$. For the disordered state, $y'_A = y''_A = x_A$, we get $(\partial^2 G_m / \partial L^2)_{x_A} = 2\nu zN^A + RT(1/x_A + 1/x_B) = 2\nu zN^A + RT/x_A x_B = 0$ yielding $T_{limit} = -2\nu z x_A x_B / k$ in agreement with the expression for T_{tr} .

22.6 Long- and short-range order

In the general case there will be both long- and short-range order and the situation will be described with two independent internal variables. We shall use K and L and with the relations of the various y and p quantities to L and K , given by Eqs (22.17) to (22.24), we obtain for equilibrium,

$$\begin{aligned}
 (\partial G_m / \partial K)_L &= (v_{AB} + v_{BA}) \cdot zN^A / 2 + RT(z/2)[- \ln(p_{AA}/y'_A y''_A) - 1 \\
 &\quad + \ln(p_{AB}/y'_A y''_B) + 1 + \ln(p_{BA}/y'_B y''_A) + 1 - \ln(p_{BB}/y'_B y''_B) - 1] = 0
 \end{aligned}
 \tag{22.48}$$

$$\frac{p_{AB} p_{BA}}{p_{AA} p_{BB}} = \exp[-(v_{AB} + v_{BA}) \cdot z / kT]
 \tag{22.49}$$

$$\begin{aligned}
 (\partial G_m / \partial L)_K &= (v_{AB} - v_{BA}) \cdot zN^A / 2 + RT(z/2)[-p_{AA}/y'_A + p_{AA}/y''_A \\
 &\quad + \ln(p_{AB}/y'_A y''_B) + 1 - p_{AB}/y'_A - p_{AB}/y''_B - \ln(p_{BA}/y'_B y''_A) \\
 &\quad - 1 + p_{BA}/y'_B + p_{BA}/y''_A + p_{BB}/y'_B - p_{BB}/y''_B] \\
 &\quad + RT[\ln y'_A + 1 - \ln y'_B - 1 - \ln y''_A - 1 + \ln y''_B + 1] / 2 \\
 &= (zRT/2) \ln(p_{AB}/p_{BA}) + (zR/2k)(v_{AB} - v_{BA}) - (z - 1) \\
 &\quad \times (RT/2) \ln(y'_A y''_B / y'_B y''_A) = 0.
 \end{aligned}
 \tag{22.50}$$

This equation was simplified using $p_{AA} = y'_A - p_{AB} = y''_A - p_{BA}$ and $p_{BB} = y'_B - p_{BA} = y''_B - p_{AB}$ from Eqs (22.21) to (22.24). It is easy to make numerical calculations from Eqs (22.49) and (22.50).

In this chapter we have so far discussed ordering of different kinds of atoms. This phenomenon is often called **chemical ordering** or **configurational ordering**. A completely different kind of ordering occurs when a liquid solidifies and the atoms arrange themselves in a regular pattern, the crystalline structure. In this connection the liquid is said to be topologically disordered. The solid \rightarrow liquid reaction can thus be regarded as an order–disorder transition and, evidently, it is a first-order transition. In the first-order transition, illustrated in Fig. 15.4, the superheated, ordered state reaches a stability limit at some high temperature and the undercooled, disordered state reaches a stability limit at some low temperature. The question whether such limits of stability exist for the solid–liquid transition has attracted some attention. The very simple and crude model described in Section 19.3 may be used to model a continuous transition from solid to liquid and it would predict limits of stability. On the other hand, cooling experiments with liquid alloys have revealed that the high entropy of the liquid state, as compared to the solid, disappears on cooling, and extrapolation of the high-temperature data seems to indicate that it approaches the entropy of the solid at some low temperature. In the same range of temperature the viscosity increases drastically and the liquid transforms into a viscous, amorphous state, which has an entropy similar to the solid. It seems that the amorphous state has only a low topological disorder although it is enough to prevent

the topological long-range order found in crystalline solids. It seems that the topological disorder in the amorphous-liquid phase increases gradually with temperature and never shows a transition point. This is somewhat similar to the behaviour of the asymmetric case of chemical ordering illustrated in Fig. 21.4. From the mechanical point of view, one defines the drastic increase of the viscosity as a glass transition. Thermodynamically, one could define a related point where extrapolated data predict that the entropy of liquid and solid should be equal. However, one should not really expect that the entropy of the liquid reaches that of the crystal and then suddenly starts to follow the value of the crystal. Most probably, there is no sharp thermodynamic transition point between the liquid and the amorphous states.

Due to the topological disorder in a liquid, it would not be possible to observe chemical long-range order in liquid alloys. Nevertheless, there are many cases with very strong chemical ordering in liquids, the most typical case is a molten salt where the electric charges make the cations tend to surround themselves with anions and vice versa. A rather realistic model of a molten salt is thus based on the assumption of two sublattices, one for cations and one for anions. That would be to assume complete long-range order and the effect of short-range order could then be added to the model. A problem with such a model is that the coefficients in the chemical formula (the stoichiometric coefficients) will vary with composition if there are cations of different valencies or anions of different valencies.

Another difficulty appears when one wants to model the change in chemical order in a liquid from a high value at a low temperature and to a low value at a high temperature. As demonstrated in Section 22.4 the quasi-chemical approach to short-range order becomes unrealistic at large degrees of short-range order. It has been proposed that this difficulty can be overcome by using $z = 2$, for which the quasi-chemical approach does not break down at high degrees of short-range order. However, that would make the model less physical. Another possibility would be to use a two-sublattice model of the asymmetric type illustrated in Fig. 21.4(a). It can predict a gradual change from very low to very high degrees of order and without a transition point. A further possibility is to mimic the chemical ordering in a liquid by the formation of molecular-like clusters of atoms, so-called associates. Finally, in an attempt to develop the two-sublattice model to a model applicable to many different types of systems and to intermediate cases, the two-sublattice model with complete long-range order has been manipulated in such a way that it can describe high as well as low degrees of ordering.

Exercise 22.7

Calculate the degree of short-range order when the disordered state is just becoming unstable in a second-order transition.

Hint

There are two internal degrees of freedom, K and L . The limit of stability is thus obtained as $g_{KK} \cdot g_{LL} - g_{KL} \cdot g_{LK} = 0$ according to Eq. (6.53). However, L is still zero at that point,

$y'_A = y''_A = x_A$ and $p_{AB} = p_{BA}$. Then it is easily shown that $g_{KL} = g_{LK} = 0$ and $g_{KK} > 0$. The condition is thus $g_{LL} = 0$.

Solution

From Eq. (22.50) we get, using the relations of dL to dp_{ij} and y_i^s from Eqs (22.17) to (22.24): $g_{LL} = (\partial^2 G_m / \partial L^2)_K = (zRT/2)(1/p_{AB} + 1/p_{BA}) - (z-1)(RT/2)(1/y'_A + 1/y''_B + 1/y''_A + 1/y'_B) = 0$; $p_{AB} = x_A x_B z / (z-1) = p_{BA} = K$ and s.r.o. = $K - L^2 - x_A x_B = x_A x_B [z / (z-1) - 1] = x_A x_B / (z-1)$ since $L = 0$.

22.7 The compound energy formalism with short-range order

In Section 22.2 it was assumed that all atoms have the same z value. In Section 22.3 it was further assumed that all bonds go between atoms in two different sublattices. These assumptions were carried over to the treatment of order in Sections 22.3 to 22.6. However, the treatment can be generalized to cases with different coordination numbers, z' and z'' , if it is still assumed that all bonds go between atoms in two different sublattices but that requires that the number of sites, b and c , are related by $bz' = cz''$. The total number of bonds in a system containing one mole of atoms is $bz'N^A = cz''N^A$ if the sum of b and c is made equal to unity. Thus $N_{AA} = p_{AA} \cdot bz'N^A$ and ${}^\circ G_A = g_{AA} \cdot bz'N^A$ and

$$x_A = p_{AA} + bp_{AB} + cp_{BA}; \quad p_{AA} = x_A - bp_{AB} - cp_{BA} \quad (22.51)$$

$$x_B = p_{BB} + bp_{BA} + cp_{AB}; \quad p_{BB} = x_B - bp_{BA} - cp_{AB}. \quad (22.52)$$

Using these expressions for p_{AA} and p_{BB} we obtain, for the Gibbs energy contribution from all the bond energies,

$$\begin{aligned} \Delta G_m &= \sum_i \sum_j N_{ij} g_{ij} = [p_{AA} g_{AA} + p_{AB} g_{AB} + p_{BA} g_{BA} + p_{BB} g_{BB}] \cdot bz'N^A \\ &= [x_A g_{AA} + x_B g_{BB} + p_{AB}(g_{AB} - bg_{AA} - cg_{BB}) \\ &\quad + p_{BA}(g_{BA} - bg_{BB} - cg_{AA})] \cdot z'bn^A/2. \end{aligned} \quad (22.53)$$

We find, by generalizing the definitions of the v quantities,

$$v_{AB} = g_{AB} - bg_{AA} - cg_{BB} \quad (22.54)$$

$$v_{BA} = g_{BA} - bg_{BB} - cg_{AA} \quad (22.55)$$

$$\Delta G_m = x_A {}^\circ G_A + x_B {}^\circ G_B + bz'N^A \cdot [p_{AB}v_{AB} + p_{BA}v_{BA}]. \quad (22.56)$$

The expression for the configurational entropy in Eq. (22.33) will also be modified by replacing $z/2$ by bz' or cz'' and $1/2$ by b or c , yielding for the total Gibbs energy instead of Eq. (22.34),

$$\begin{aligned} G_m &= x_A {}^\circ G_A + x_B {}^\circ G_B + bz'N^A \cdot [p_{AB}v_{AB} + p_{BA}v_{BA}] + RTbz' [p_{AA} \ln(p_{AA}/y'_A y''_A) \\ &\quad + p_{AB} \ln(p_{AB}/y'_A y''_B) + p_{BA} \ln(p_{BA}/y'_B y''_A) + p_{BB} \ln(p_{BB}/y'_B y''_{BB})] \\ &\quad + RT[b y'_A \ln y'_A + b y''_B \ln y''_B + c y'_A \ln y'_A + c y''_B \ln y''_B]. \end{aligned} \quad (22.57)$$

This may be regarded as a generalization of Eq. (22.34). However, the definitions of v_{AB} and v_{BA} cannot be reconciled with the simple concept of bond energies presented in Section 22.1. The new definition is closely related to the definition of $\Delta^\circ G_{A_bB_c}$ and $\Delta^\circ G_{B_aA_c}$ in the compound energy formalism in Section 21.5, the only difference being the numerical factor $bz'N^A$. However, the compound energy formalism goes one step further. It postulates that phases, with some bonds between atoms in the same sublattice, can be treated with the same formalism. That may not be correct but may be remedied by the use of the I parameters in the excess terms in Section 21.3.

Using Eq. (22.57) one can formally account for the effect of short-range order with the compound energy formalism. The G_m expression in Eq. (21.40) would be modified to

$$\begin{aligned} G_m = & x_A^\circ G_A + x_B^\circ G_B + p_{AB} \Delta^\circ G_{A_bB_c} + p_{BA} \Delta^\circ G_{B_aA_c} \\ & + RTbz' \cdot [p_{AA} \ln(p_{AA}/y'_A y''_A) + p_{AB} \ln(p_{AB}/y'_A y''_B) \\ & + p_{BA} \ln(p_{BA}/y'_B y''_A) + p_{BB} \ln(p_{BB}/y'_B y''_B)] \\ & + RT[by'_A \ln y'_A + by'_B \ln y'_B + cy''_A \ln y''_A + cy''_B \ln y''_B]. \end{aligned} \quad (22.58)$$

For a reciprocal solution, i.e., a quaternary phase where each sublattice dissolves only two of the four elements, we would obtain per mole of formula unit

$$\begin{aligned} G_m = & x_A^\circ G_A + x_B^\circ G_B + x_C^\circ G_C + x_D^\circ G_D + p_{AC} \Delta^\circ G_{A_bC_c} \\ & + p_{AD} \Delta^\circ G_{A_bD_c} + p_{BC} \Delta^\circ G_{B_bC_c} + p_{BD} \Delta^\circ G_{B_bD_c} \\ & + RTbz' \cdot [p_{AC} \ln(p_{AC}/y'_A y''_C) + p_{AD} \ln(p_{AD}/y'_A y''_D) \\ & + p_{BC} \ln(p_{BC}/y'_B y''_C) + p_{BD} \ln(p_{BD}/y'_B y''_D)] \\ & + RT[by'_A \ln y'_A + by'_B \ln y'_B + cy''_C \ln y''_C + cy''_D \ln y''_D]. \end{aligned} \quad (22.59)$$

This would be a case of short-range order at complete long-range order. Again we have four p_{ij} related by $\sum p_{ij} = 1$ but their relation to the composition now yields two independent equations instead of one given by Eqs (22.6) or (22.7). In this case it is most convenient to use the y_i variables which are here fixed by the composition,

$$p_{AC} + p_{AD} = y'_A \quad (22.60)$$

$$p_{AC} + p_{BC} = y''_C. \quad (22.61)$$

Consequently, now there is just one independent internal variable, one of the four p_{ij} , instead of two, and it represents short-range order because the long-range order is here perfect. It may be convenient to define the short-range order in a way similar to Eq. (22.30). However, since each kind of bond can now go in one direction, only, we shall define

$$\text{s.r.o.} = p_{AC} - y'_A y''_C. \quad (22.62)$$

We shall denote this variable by s and by combination with the relations of p_{ij} to the

composition we find

$$p_{AC} = y'_A y''_C + s; \quad dp_{AC} = ds \quad (22.63)$$

$$p_{AD} = y'_A y''_D - s; \quad dp_{AD} = -ds \quad (22.64)$$

$$p_{BC} = y'_B y''_C - s; \quad dp_{BC} = -ds \quad (22.65)$$

$$p_{BD} = y'_B y''_D + s; \quad dp_{BD} = ds. \quad (22.66)$$

The equilibrium value of s is obtained from

$$\begin{aligned} (\partial G_m / \partial s)_{y'_A, y''_C} &= \Delta^\circ G_{A_b C_c} - \Delta^\circ G_{A_b D_c} - \Delta^\circ G_{B_b C_c} + \Delta^\circ G_{B_b D_c} \\ &\quad + RTbz' \cdot [1 + \ln(p_{AC}/y'_A y''_C) - 1 - \ln(p_{AD}/y'_A y''_D) \\ &\quad - 1 - \ln(p_{BC}/y'_B y''_C) + 1 + \ln(p_{BD}/y'_B y''_D)] \\ &= \Delta^\circ G_{AC+BD} + RTbz' \cdot \ln(p_{AC} p_{BD} / p_{AD} p_{BC}) = 0 \end{aligned} \quad (22.67)$$

$$\frac{p_{AC} p_{BD}}{p_{AD} p_{BC}} = \exp(-\Delta^\circ G_{AC+BD} / RTbz'). \quad (22.68)$$

This is a result characteristic of the quasi-chemical approach. The notation $\Delta^\circ G_{AC+BD}$ was introduced in Eq. (21.20) and then used in Section 21.5.

Exercise 22.8

Consider a solution phase defined by the formula $(A, B)_b(C, D)_c$ with $N_A = N_B$ and $N_C = N_D$. Apply the compound energy formalism and estimate how much the short-range order decreases the Gibbs energy if changes in the configurational entropy are neglected. Suppose $z' = 8$, $b = c = 0.5$ and $\Delta^\circ G_{AC+BD} = 8RT$.

Hint

According to the instruction, we should study: $p_{AC} \Delta^\circ G_{A_b C_c} + p_{AD} \Delta^\circ G_{A_b D_c} + p_{BC} \Delta^\circ G_{B_b C_c} + p_{BD} \Delta^\circ G_{B_b D_c}$ which can be changed to $y'_A y''_C \Delta^\circ G_{A_b C_c} + y'_A y''_D \Delta^\circ G_{A_b D_c} + y'_B y''_C \Delta^\circ G_{B_b C_c} + y'_B y''_D \Delta^\circ G_{B_b D_c} + s(\Delta^\circ G_{A_b C_c} - \Delta^\circ G_{A_b D_c} + \Delta^\circ G_{B_b C_c} - \Delta^\circ G_{B_b D_c})$. All site fractions are fixed ($= 0.5$). The change is thus given by the last term and it can be written as $s \cdot \Delta^\circ G_{AC+BD}$.

Solution

$\Delta^\circ G_{AC+BD} / RTbz' = 2$. Inserting Eqs (22.63) to (22.66) in the quasi-chemical equation, Eq. (22.68), yields $(1/4 + s)^2 / (1/4 - s)^2 = \exp(-2)$; $s = -0.1155$; $s \cdot \Delta^\circ G_{AC+BD} = -0.1155 \cdot 8RT = -0.92RT$. This is an appreciable part of $\Delta^\circ G_{AC+BD}$.

22.8 Interstitial ordering

Interstitial solutions can also show ordering. Two effects may be recognized. The first effect is a tendency for the interstitial atoms to avoid occupying sites which are nearest

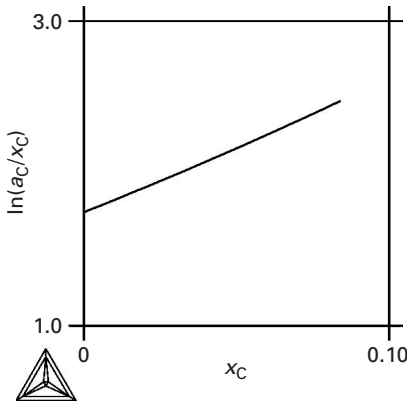


Figure 22.1 The activity coefficient of C in fcc-Fe at 1400 K as function of the C content.

neighbours to each other. In the extreme case, all the sites which are nearest neighbours to an interstitial atom will be excluded from occupancy. ‘Excluded-sites’ models have been developed for this case. As an example, we may consider fcc-Fe where the interstitial sites form their own fcc sublattice. Each interstitial site is surrounded by 12 nearest-neighbour interstitial sites. According to the model, each interstitial atom in a dilute solution excludes its own site and 12 neighbouring interstitial sites from being occupied by other atoms. For dilute solutions the lattice would thus behave as if it should be completely filled at a value of $y_C = 1/13$ where C represents the interstitial component. The partial entropy of C would thus be

$$S_C = -R \ln \frac{y_C}{1 - 13y_C} \cong -R(\ln y_C + 13y_C). \quad (22.69)$$

In the ideal case, i.e. neglecting all other interactions, this model will predict a very strong positive deviation from Henry’s law. Experimental information on the carbon activity in fcc-Fe–C does show a strong positive deviation but not enough to satisfy the excluded-sites model. This is demonstrated by Fig. 22.1 where $\ln(a_C/x_C)$ has been plotted versus x_C . The slope is about 8 but should have been 14 according to the excluded-sites model because $y_C/(1 - 13y_C)$ is equal to $x_C/(1 - 14x_C)$ when $a = 1$ for both sublattices.

In order to obtain better agreement for carbon in fcc-Fe one has to relax the condition of absolute exclusion to one in which a neighbouring site can be occupied at the expense of a certain energy v . Such models are sometimes called statistical models. A treatment can also be based upon the quasi-chemical approach which will formally apply to interactions between atoms in the interstitial sublattice just as well as to the ordinary lattice in a substitutional solution. By substituting y for x in Eq. (22.42) we obtain

$$G_m = y_C^\circ G_{M_b C} + y_{V_a}^\circ G_{M_b V_a} + RT(y_C \ln y_C + y_{V_a} \ln y_{V_a}) + v z N^A y_C y_{V_a} [1 - y_C y_{V_a} v/kT - (2/3)y_C y_{V_a} (y_C - y_{V_a})^2 (v/kT)^2]. \quad (22.70)$$

With the rule of calculation given for G_C in Eq. (21.12) we obtain, for composition-independent v ,

$$\begin{aligned} RT \ln a_C = G_C - {}^0G_C = {}^0G_{M_bC} - b^0G_M - {}^0G_C^\alpha \\ + RT \ln[y_C/(1 - y_C)] + v z N^A (y_{V_a} - y_C) [1 - 2y_C y_{V_a} v/kT \\ + 8y_C y_{V_a} (y_C y_{V_a} - 1/6)(v/kT)^2]. \end{aligned} \quad (22.71)$$

For small y_C the last term can be approximated by $v z N^A \{1 - 2y_C [1 + v/kT + (2/3)(v/kT)^2]\}$. By comparing with the power series treatment of a random interstitial solution in Section 21.2 we see that $v z N^A$ corresponds to ${}^0L_{CV_a}$ if v is independent of composition. For $v/kT = 0$ we thus have complete agreement with that expression. For small v/kT there will be a difference of $-2y_C v z N^A \cdot [v/kT + (2/3)(v/kT)^2]$. This difference is initially negative for positive as well as negative v which is natural because the random mixing model always results in higher Gibbs energies than a model which allows the arrangement of the atoms to be adjusted to minimize the Gibbs energy. For a given value of v , or 0L , the quasi-chemical model will thus predict a slightly weaker deviation from Henry's law.

At high enough values of the interstitial content and of $-v/kT$ there will be long-range order, an example being the γ' phase in the Fe–N system. It has a nitrogen content corresponding to Fe_4N and the Fe atoms have the same arrangement as in fcc-Fe. It may be regarded as an ordered interstitial solution of N in fcc-Fe. It is interesting to note that no N atoms occupy nearest neighbour sites. This phase is thus a perfect example of the excluded-sites principle. The high N content, compared to the limiting value of $y_C = 1/13$ given previously, is due to the fact that each excluded site is now nearest neighbour to not only one interstitial atom but four which does not happen in a dilute solution.

In the Fe–N system there is a two-phase field between the disordered solution of N in fcc-Fe and the ordered Fe_4N phase. That reveals that there is a first-order ordering transition. The situation is different for interstitial solutions in hcp metals where one can sometimes observe that the change from the disordered, dilute solution to an ordered M_2I phase is gradual, i.e., without any kind of transition. The explanation is that the distance between the interstitial sites is shortest in the hexagonal c direction. They are thus arranged in strings and, as mentioned in Section 22.4, the number of nearest neighbors is thus $z = 2$. This is a rare case where the quasi-chemical model is not limited to dilute solutions but applies all the way to a maximum content of M_2I .

Exercise 22.9

What value of ${}^0L_{CV_a}$ in the random mixing model or v/kT in the quasi-chemical model is required in order to explain the slope of 8 in the plot of $\ln(a_C/x_C)$ versus x_C for carbon in fcc-Fe?

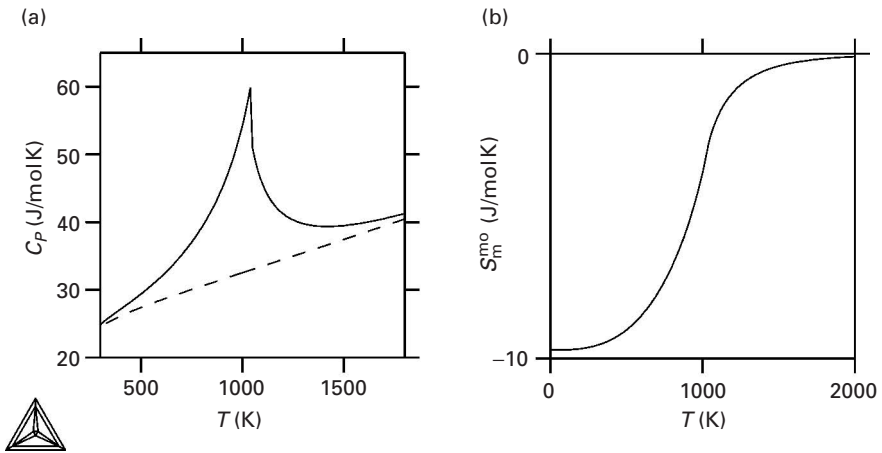


Figure 22.2 The effect of magnetic ordering on the heat capacity and entropy of bcc-Fe.

Hint

The entropy contribution to G_C in Eq. (21.11) gives $\ln[y_C/(1 - y_C)] = \ln[x_C/(1 - 2x_C)] \cong \ln x_C + 2x_C$. Remember $z = 12$.

Solution

The random mixing model for an interstitial solution gives $RT \ln(a_C/x_C) \cong \text{const} + 2RTx_C - {}^0L \cdot 2y_C \cong \text{const} + (2RT - 2{}^0L)x_C$, yielding a slope of $2RT - 2{}^0L = 8RT$; ${}^0L/RT = -3$. The quasi-chemical model gives, for small y_C , $RT \ln(a_C/x_C) \cong \text{const} + 2RTx_C - zvN^A(-2y_C)[1 + (v/kT) + (2/3)(v/kT)^2 + \dots] \cong \text{const} + \{2RT - 2zvN^A[1 + (v/kT) + (2/3)(v/kT)^2]\} \cdot x_C$, yielding a slope of $2RT - 2zvN^A[1 + (v/kT) + (2/3)(v/kT)^2] = 8RT$; $-24(v/kT)[1 + (v/kT) + (2/3)(v/kT)^2] = 8 - 2$; $v/kT = -0.339$, corresponding to ${}^0L/RT = zv/kT = 12 \cdot (-0.342) = -4.07$.

22.9 Composition dependence of physical effects

In Section 18.7 it was suggested that one should sometimes model the effect of a special physical phenomenon separately. A typical example would be the effect of magnetic ordering in a ferromagnetic material. That effect will now be used to demonstrate how the composition dependence of such an effect can be taken into account.

Figure 22.2 shows (a) the magnetic contribution to the heat capacity and (b) the decrease of the magnetic entropy from a disordered state of bcc-Fe at very high temperature. The peak temperature for the heat capacity and the inflexion point for the magnetic entropy represent the Curie temperature, T_C , i.e. the transition point between

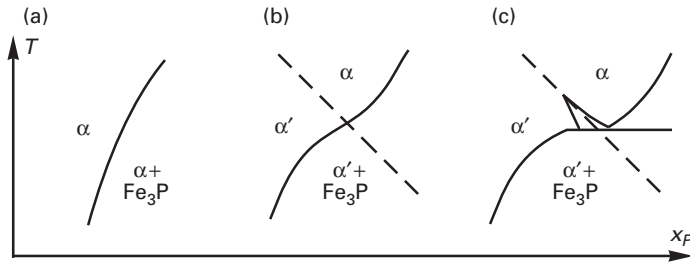


Figure 22.3 Solution to Exercise 22.11.

the high-temperature paramagnetic state which has only magnetic short-range order and the low-temperature state with long-range magnetic order.

A very simple model of magnetic ordering was presented in Section 19.6. It takes into account only long-range order. It would be possible also to include short-range order with a quasi-chemical type of approach. However, it would still be a very primitive model. For reasonably accurate modelling it seems necessary to rely on experimental measurements and some simple assumption of the dependence on composition. There have been several suggestions of mathematical expressions to be used. The first was made by Inden [48] and it is still the most widely used model. He described the heat capacity with a logarithmic expression but in order to derive an analytical expression for the contribution to the Gibbs energy it was later found necessary to use a series expansion. With truncation after the third term it yields the following expressions above and below the Curie temperature.

$$G_m^{\text{mo}} = -RT \ln(\beta + 1) \left(\frac{\tau^{-5}}{10} + \frac{\tau^{-15}}{315} + \frac{\tau^{-25}}{1500} \right) / \left[\frac{518}{1125} + \frac{11692}{15975} \left(\frac{1}{p} - 1 \right) \right] \text{ for } \tau > 1 \quad (22.72)$$

$$G_m^{\text{mo}} = RT \ln(\beta + 1) \left\{ 1 - \left[\frac{79\tau^{-1}}{140p} + \frac{474}{497} \left(\frac{1}{p} - 1 \right) \left(\frac{\tau^3}{6} + \frac{\tau^9}{135} + \frac{\tau^{15}}{600} \right) \right] \right\} / \left[\frac{518}{1125} + \frac{11692}{15975} \left(\frac{1}{p} - 1 \right) \right] \text{ for } \tau < 1, \quad (22.73)$$

where p is a constant defined as the fraction of the total disordering enthalpy which is absorbed above the critical temperature. It was given as 0.28 for fcc metals and 0.40 for bcc metals. τ is a normalized temperature defined as T/T_C . The superscript 'mo' refers to magnetic order. The equations contain two material constants, the Curie temperature T_C and the Bohr magneton number β . The equations could hopefully be applied to solutions by inserting experimental or estimated expressions for their composition dependence.

The two diagrams in Fig. 22.2 were calculated from these equations after an assessment of the magnetic properties of bcc-Fe. However, experimental measurements indicate that C_P goes to infinity at T_C from both sides (see Fig. 19.4) and that result was originally modelled by Inden. It was abandoned for practical reasons when a Gibbs energy expression was derived by integration. This approximation may seem as a bad one from a theoretical point of view but for the calculation of phase equilibria it seems to have a

comparatively small effect. An exception may be the position of the tri-critical point in a binary diagram like Fig. 15.15. According to the crude treatment of the effect of C_p^p , presented in Section 15.5, the tri-critical point should approach the side of the binary system if the magnetic C_p goes to infinity at T_C .

In order to extend the magnetic model to alloys it is necessary to make the model parameters composition-dependent. So far, investigators have studied the effect of composition-dependent β and T_C but kept the p parameter constant.

Exercise 22.10

Use the C_p curve in Fig. 22.2(a) for an estimate of p , the fraction of the total disordering enthalpy which has not yet been absorbed on heating to T_C because of the remaining short-range order.

Hint

Divide the area between the solid and dashed curves into two, one above and one below T_C , and make a crude graphical integration of these two areas.

Solution

The two areas are proportional to the two parts of ΔH . Thus $p = A_1/(A_1 + A_2) = 1/(1 + A_2/A_1) \cong 1/(1 + 1.5) = 0.4$.

Exercise 22.11

Show schematically how the solubility of phosphorus (P) in bcc-Fe can be expected to vary with temperature around the intersection with the magnetic transition line, the Curie line. Consider three different conditions: (a) no magnetic effect; (b) a magnetic effect but no separation into regions of different composition; (c) a magnetic effect and separation into regions of different composition, resulting in a miscibility gap with a tri-critical point.

Hint

Consult Section 15.5 and, in particular, Fig. 15.16 and Exercise 15.7.

Solution

(a) Without a magnetic effect we expect that $\ln(x_p)$ should vary linearly with $1/T$ (see Exercise 11.4). (b). The slope should be smaller where C_p is larger due to the magnetic effect. (c) See Fig. 22.3.

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