

Outline

- Solid solution
- Gibbs free energy of binary solutions
- Ideal solution
- Chemical potential of an ideal solution
- Regular solutions
- Activity of a component
- Real solutions
- Equilibrium in heterogeneous systems

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Solid Solutions

The same concepts apply to solid phases:





Solid Solutions

Solid solutions are made of a host (the **solvent** or matrix) which dissolves the minor component (solute). The ability to dissolve is called solubility.

✓ Solvent: the element or compound that presents in greater amount in a solution

✓ Solute: the element or compound that presents in lesser amount in a solution.

✓ Solid Solution:

- homogeneous
- maintains crystal structure
- contains randomly dispersed impurities (substitutional or *interstitial*)

Solubility Limit of a component in a phase is the maximum amount of the component that can be dissolved in the phase (e.g. alcohol has

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Solid Solutions

If the solubility limit is exceeded a second phase (compound or another solution) starts forming.

U Whether the addition of impurities results in formation of solid solution or second phase depends on the nature of the impurities, their concentration, temperature, pressure, etc..

Real materials are almost always mixtures of different elements rather than pure substances: in addition to T and P, composition is also a variable.

□ To understand conditions for equilibrium and phase diagrams we have to understand how the Gibbs free energy of a given phase depends on composition, temperature and pressure.

Since many real experiments are performed at fixed pressure of 1 atm, we will focus on G(T, composition).

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Gibbs Free Energy of a Binary Solution

Let us consider a binary solution of A and B atoms that have the **same crystal structures** in their pure states and can be mixed in any proportions - form a solid solution with the same crystal structure (unlimited solid solubility). *Example:* Cu and Ni.

1 mole of homogeneous solid solution contains X_A mole of A and X_B mole of B. X_A and X_B are the mole fractions of A and B in the alloy.

$$X_A + X_B =$$

Let's consider two steps of mixing: 1. Bring together X_A mol of pure A and X_B mol of pure B

2. Mix A and B to make a homogeneous solution G^{\uparrow}

After step 1, the free energy of the system is: $G_{step1} = X_A G_A + X_B G_B$

ergy G_{A} G_{step1} G_{B} G_{B} G_{B} G_{B} G_{A} G_{B} $G_{$

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A A A A A

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 $X_AG_A = X_BG_B$



Gibbs Free Energy of a Binary Solution

Step 2: Mix A and B to make a homogeneous solution

After step 2 the free energy of the system is

 $G_{step2} = G_{step1} + \Delta G_{mix}$



Where ΔG_{mix} is the change of the Gibbs free energy caused by the mixing.

 $\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$

 $\Delta H_{mix} = H_{step2} - H_{step1}$

Heat of mixing of the components (*heat of formation of a solution*)

 $\Delta S_{mix} = S_{step2} - S_{step1}$

The difference in entropy between mixed and unmixed states (*entropy of formation of a solution*)

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Ideal Solution

Let us first consider an <u>ideal</u> solution where the interactions between atoms A-A, B-B and A-B are identical, and $\Delta H_{mix} = 0$. The free energy change upon mixing is only due to the change in entropy:

$$\Delta \mathbf{G}_{\mathrm{mix}}^{\mathrm{id}}=\!-\mathrm{T}\Delta\,\mathbf{S}_{\mathrm{mix}}$$

$$\Delta S_{mix} = S_{step2} - S_{step1}$$

Since there is only one way the atoms can be arranged before mixing

$$\therefore$$
 S_{step1} = k_B ln1 = 0

$$\therefore \Delta S_{mix} = S_{step2}$$



is:

Entropy of Formation of an Ideal Solution

Statistical definition of entropy: $S = k_B \ln \Omega$

From statistical mechanics, if we have N_t objects and N_s of them are special or different, the number of ways the objects can be arranged (*number of*)



$$\Omega = \frac{N_t!}{N_s!(N_t - N_s)!}$$

For mixing of N_A atoms of type A with N_B atoms of type B:

$$\begin{split} \Omega = & \frac{(N_A + N_B)!}{N_B! N_A!} \\ \Delta S_{mix} = & k_B \ln \Omega = k_B \ln \frac{(N_A + N_B)!}{N_B! N_A!} \\ \Delta S_{mix} = & k_B [\ln (N_A + N_B)! - \ln N_A! - \ln N_B!] \end{split}$$

Using Stirling formula for big numbers: $\ln N! \approx N \ln N - N$

$$\begin{split} \Delta S_{mix} &= k_B [(N_A + N_B) \ln(N_A + N_B) - (N_A + N_B) - N_A \ln N_A + N_A - N_B \ln N_B + N_B] \\ &= -k_B \Biggl[N_A \ln \Biggl(\frac{N_A}{N_A + N_B} \Biggr) + N_B \ln \Biggl(\frac{N_B}{N_A + N_B} \Biggr) \Biggr] \end{split}$$

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Entropy of Formation of an Ideal Solution

$$X_{A} = \frac{N_{A}}{N_{A} + N_{B}} \qquad \qquad X_{B} = \frac{N_{B}}{N_{A} + N_{B}}$$

If the total amount of material is $l \mod N_A + N_B = Avogadro's$ number (N_a), and N_A = X_AN_a, N_B = X_BN_a, N_ak_B = R.

$$\begin{split} \Delta S_{mix} &= -k_{B} \Bigg[N_{A} ln \Bigg(\frac{N_{A}}{N_{A} + N_{B}} \Bigg) + N_{B} ln \Bigg(\frac{N_{B}}{N_{A} + N_{B}} \Bigg) \Bigg] = \\ &= -R \left[X_{A} ln X_{A} + X_{B} ln X_{B} \right] \\ \Delta G_{mix}^{id} &= -T \Delta S_{mix} = RT [X_{A} ln X_{A} + X_{B} ln X_{B}] \end{split}$$

For the total Gibbs free energy of an ideal solution:

$$G^{id} = G_{step2} = G_{step1} + \Delta G^{id}_{mix}$$
 $G_{step1} = X_A G_A + X_B G_B$

 $\Rightarrow G^{id} = X_A G_A + X_B G_B + RT [X_A ln X_A + X_B ln X_B]$

For a non-ideal solution we have to take into account heat of formation ΔH_{mix} : $\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$

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Gibbs Free Energy of an Ideal Solutions

$$\Delta G_{mix}^{id} = -T\Delta S_{mix} = RT[X_A lnX_A + X_B lnX_B]$$

$$G^{id} = X_A G_A + X_B G_B + RT [X_A lnX_A + X_B lnX_B]$$

$$T_2 > T_1$$

$$T_2 > T_1$$

$$T_3 = T_1$$

$$T_2 = T_1$$

$$T_3 = T_1$$

$$T_4 = T_1$$

$$T_2 = T_1$$

$$T_3 = T_1$$

$$T_4 = T_1$$

$$T_2 = T_1$$

$$T_2 = T_1$$

$$T_3 = T_1$$

$$T_4 = T_1$$

$$T_2 = T_1$$

$$T_2 = T_1$$

$$T_3 = T_2$$

$$T_4 = T_1$$

$$T_4 = T_1$$

$$T_5 = T_1$$

$$T_1 = T_2$$

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Chemical Potential of an Ideal Solution

Remember the definition of the chemical potential of the species *i*:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j,\dots}$$

$$dG = -SdT + VdP + \sum_{i=1}^{i=k} \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_i,\dots} dn_i$$

For a binary solution at constant P and T: $dG = \mu_A dn_A + \mu_B dn_B$

Addition of X_A mole of atoms A and X_B mole of atoms B (i.e. $dn_A/dn_B = X_A/X_B$) will increase the size of the system by 1 mol without changing composition and, therefore without changing μ_A and μ_B . \rightarrow The Gibbs free energy of an ideal solution will increase, in this case, by the molar Gibbs free energy G:

$$G = \mu_A X_A + \mu_B X_B [J/mol]$$

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Solid Solutions

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$$G = \mu_A X_A + \mu_B X_B [J/mol]$$

Since $X_A + X_B = 1 \Rightarrow G = \mu_A + (\mu_B - \mu_A)X_B \Rightarrow \frac{\partial G}{\partial X_B} = \mu_B - \mu_A$
Also, $G^{id} = X_A G_A + X_B G_B + RT (X_A \ln X_A + X_B \ln X_B)$



Therefore, for an ideal solution:



 μ_A and μ_B depend on the composition of the phase.

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<u>G(T, composition).</u>





Regular Solutions: Heat of Formation of a Solution

For a non-ideal solution we have to take into account heat of formation $\Delta H_{mix} \neq 0$: $\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$

$\Delta H_{mix} > 0$	mixing is	(heat absorbed)
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 $\Delta H_{mix} < 0$ mixing is (heat released)

We need to account for the heat of formation. $\Delta H_{mix} \neq 0$ using a simple model called statistical or quasi-chemical model. In this model the heat of mixing is only related to the bond energies between adjacent atoms.

The assumption is that the **interatomic distances** and **bond energies** are *independent* of composition.



3 types of bonds: A - A bond (energy E_{AA}) A - B bond (energy E_{AB}) B - B bond (energy E_{BB})

If P_{AA} , P_{BB} , P_{AB} are the number of bonds of each type, the internal energy of the solution is:

 $\mathbf{E} = \mathbf{P}_{AA}\mathbf{E}_{AA} + \mathbf{P}_{BB}\mathbf{E}_{BB} + \mathbf{P}_{AB}\mathbf{E}_{AB}$

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Regular Solutions: Heat of Formation of a Solution

We can calculate the internal energy of the solution as:

$$\mathbf{E} = \mathbf{P}_{AA}\mathbf{E}_{AA} + \mathbf{P}_{BB}\mathbf{E}_{BB} + \mathbf{P}_{AB}\mathbf{E}_{AB}$$

If z is the coordination number of an atom in a crystal, then the number of atoms N_A and N_B are related to the number of bonds as:

$$\begin{array}{c} N_{A}z = 2P_{AA} + P_{AB} \\ N_{B}z = 2P_{BB} + P_{AB} \end{array} \end{array} \right\} \qquad \begin{array}{c} P_{AA} = \frac{N_{A}z}{2} - \frac{P_{AB}}{2} \\ P_{BB} = \frac{N_{B}z}{2} - \frac{P_{AB}}{2} \end{array}$$

Using these expressions for P_{AA} and P_{BB} in the expression for energy, we have $(N_{AZ} - P_{AB}) = (N_{BZ} - P_{AB})$

$$E = \left(\frac{N_{A}Z}{2} - \frac{P_{AB}}{2}\right)E_{AA} + \left(\frac{N_{B}Z}{2} - \frac{P_{AB}}{2}\right)E_{BB} + P_{AB}E_{AB} = \frac{N_{A}Z}{2}E_{AA} + \frac{N_{B}Z}{2}E_{BB} + P_{AB}\left(E_{AB} - \frac{E_{AA} + E_{BB}}{2}\right)E_{AA} + \frac{N_{B}Z}{2}E_{AA} + \frac{N_{B}Z}{2}E_{AB} + \frac{N_{B$$

Therefore, the energy of mixing (*heat of formation* ΔH_{mix}) is

$$\Delta H_{mix} = H_{step2} - H_{step1} \approx \Delta E_{mix} = P_{AB} \left(E_{AB} - \frac{E_{AA} + E_{BB}}{2} \right)_{MECH6661 \text{ lectures } 6/15}$$

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Regular Solutions: Heat of Formation of a Solution

The energy of mixing (*heat of formation*; ΔH_{mix}) calculated within statistical or quasi-chemical model is:

$$\Delta H_{\rm mix} = P_{\rm AB} \left(E_{\rm AB} - \frac{E_{\rm AA} + E_{\rm BB}}{2} \right)$$

If
$$E_{AB} = \frac{E_{AA} + E_{BB}}{2}$$

the solution is
$$\rightarrow \Delta H_{mix} = 0$$

$$f \quad E_{AB} > \frac{E_{AA} + E_{BB}}{2}$$

 $\Delta H_{mix} > 0 \rightarrow$ atoms will tend to be surrounded by atoms of the same type

f
$$E_{AB} < \frac{E_{AA} + E_{BB}}{2}$$

 $\Delta H_{mix} < 0 \rightarrow$ atoms will tend to be surrounded by atoms of different type

T



Regular Solutions: Heat of Formation of a Solution

But for small differences between E_{AB} and $(E_{AA}+E_{BB})/2$ (and for high T) we can still consider a random arrangement of atoms in a solution (such solutions are called solutions). Then

 $P_{AB} = z N_{tot} X_A X_B$ and $\Delta H_{mix} = \Omega X_A X_B$ where $\Delta H_{mix} = P_{AB} \left(E_{AB} - \frac{E_{AA} + E_{BB}}{2} \right) \qquad \Omega = \begin{bmatrix} a + bX_B \end{bmatrix} + cX_B^2 + \dots \\ solution$ $P_{AB} = zN_{tot}X_A X_B$ Since $\Omega = \Delta H_{mix}/X_A X_B$, $\Delta H_{mix} \qquad \Omega > 0$ Since $\Omega = \Delta H_{mix} / X_A X_B$, $\rightarrow \Omega = zN_{tot} \left(E_{AB} - \frac{E_{AA} + E_{BB}}{2} \right)$ X MECH6661 lectures 6/17 Mech. Eng. Dept. - Concordia University Dr. M. Medraj



10 MINUTES BREAK



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Regular Solutions: Gibbs Free Energy

 $\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} = \Omega X_A X_B + RT(X_A \ln X_A + X_B \ln X_B)$

• For $\Omega < 0, \Delta H_{mix} < 0 \rightarrow$ exothermic solution and mixing is at all T

• For high $|\Omega|$ and low T P_{AB} \rightarrow an ordered alloy could be formed, the assumption of random mixing is <u>not valid</u>, solution is **not** regular, $\Delta H_{mix} \neq \Omega X_A X_B$

• For $\Omega > 0$, $\Delta H_{mix} > 0 \rightarrow$ mixing (formation of A-B pairs) is avoided at low T. • At low T clustering may occur \rightarrow solution is not regular.

 $\Omega < 0$

 ΔH_{mi}

T_{ΔS}

ΔG.

X

• At high T entropy helps to mix.





 $\mu_{\rm B} = G_{\rm B} + \Omega (1 - X_{\rm B})^2 + RT \ln X_{\rm B}$



Regular Solutions: Gibbs Free Energy

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} = \Omega X_A X_B + RT (X_A ln X_A + X_B ln X_B)$$

Addition of a small amount of solute always
leads to the decrease of
$$\Delta G_{mix}$$
 and G.
 $G = X_A G_A + X_B G_B + \Omega X_A X_B + RT[X_A \ln X_A + X_B \ln X_B]$
Or, using definition of chemical potential,
 $G = \mu_A X_A + \mu_B X_B$
where, for regular solution
 $\mu_A = G_A + \Omega(1 - X_A)^2 + RT \ln X_A$
 $\Omega > 0$, low T
 ΔH_{mix}
 $-T\Delta S_{mix}$
 0
 X_B



Regular Solutions: *Gibbs Free Energy*

 $\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} = \Omega X_A X_B + RT(X_A \ln X_A + X_B \ln X_B)$ $G = \mu_A X_A + \mu_B X_B \qquad \begin{array}{l} \mu_A = G_A + \Omega (1 - X_A)^2 + RTln X_A \\ \mu_B = G_B + \Omega (1 - X_B)^2 + RTln X_B \end{array}$

Or we can introduce activities a_A and a_B (effective concentration) of components A and B so that expressions for the chemical potentials would have the same form as for ideal solution:



Regular Solutions: Heat of Formation of a Solution $\ln\left(\frac{a_{A}}{X_{A}}\right) = \frac{\Omega}{RT}(1-X_{A})^{2} \quad \ln\left(\frac{a_{B}}{X_{B}}\right) = \frac{\Omega}{RT}(1-X_{B})^{2}$ For an **ideal** solution $a_A = X_A$ and a_B $a_{B} = X_{B}$. For a **regular** solution

with $\Delta H_{mix} < 0$ activity of the components is than in an ideal solution, for $\Delta H_{mix} > 0 \rightarrow$ than in an ideal solution.



The ratio a_A/X_A is called the activity coefficient γ_A of A.

 $\gamma_{\rm B} = \frac{a_{\rm B}}{X_{\rm D}} \approx const \rightarrow \text{Henry's law} \qquad \gamma_{\rm A} = \frac{a_{\rm A}}{X_{\rm A}} \approx 1 \rightarrow \text{Raoult's law}$

Activity and chemical potential are measures of the tendency of an atom to leave a solution (i.e. if the activity or chemical potential is low "interaction with other atoms is low", the atoms are reluctant to leave the solution).

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Real Solutions

For regular solutions we still assumed a random arrangement of atoms in a solution. For many real materials this is not a valid assumption.



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If $\Omega < 0$ the internal energy is minimized by increasing the number of A-B bonds, this can lead to ordered solution at low T

if $\Omega > 0$ the internal energy is minimized by increasing the number of A-A and B-B bonds, this can lead to clustering at low T



The arrangement of atoms is a result of compromise between the lowest internal energy and highest entropy. Degree of "clustering"

or "ordering" decreases with increasing T since the entropy contribution (-TS) to Gibbs free energy becomes more important.

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Real Solutions

• If atoms A and B have different sizes, the statistical or quasi-chemical model will underestimate ΔH_{mix} .

• The energy of the elastic strain fields due to the mismatch in atomic sizes should be taken into account.

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• If the size difference is large, the contribution of the strain energy term could be as important as the chemical (bonding) term.

• If the size difference between the atoms is very large. then interstitial solid solutions are energetically favorable.

• In systems with strong chemical bonding between the atoms there is a tendency for formation of intermediate *phases*. The intermediate phases can have a different crystal structure and may be highly ordered.



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Substitutional Solid Solutions

Max solute concentration = 50 at% e.g. Cu-Ni (*unlimited* solid solubility)

Factors for high solubility:

✓ Atomic size factor - atoms need to fit \Rightarrow solute and solvent atomic radii should be within ~ 15% →

✓ Crystal structures of solute and solvent should be the same

 \checkmark Electronegativities of solute and solvent should be comparable (otherwise new intermediate phases are encouraged)

 \checkmark Generally more solute goes into solution when it has higher valency than solvent

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Interstitial Solid Solutions

Normally, max. solute concentration $\leq 10\%$

e.g. ≤ 0.1 at% of C in α -Fe (BCC).



Factors for high solubility:

For fcc, bcc, hcp structures the voids (or interstices) between the host atoms are relatively small \Rightarrow atomic radius of solute should be significantly less than solvent.

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Intermediate Phases

The intermediate phases can have a crystal structure that is different from the one of the pure components, and an additional Gibbs free energy curve for the intermediate phase should be considered.

If an intermediate phase have a specific composition and small deviations from the ideal composition cause a rapid rise in G, the phase is called compound. Compounds typically have a stoichiometric composition (A_nB_m where n and m are integers).



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Intermediate Phases

The structure of intermediate phases is determined by:

> <u>Relative atomic size</u>: $R_A/R_B \sim 1.1-1.6 \Rightarrow$ Laves phases (e.g. MgZn₂, MgNi₂); $R_A >> R_B \Rightarrow$ interstitial compounds, e.g. Fe₃C

Laves phases have composition AB_2 , where the A atoms are ordered as in diamond or a related structure, and the B atoms form tetrahedra around the A atoms

The Mg atoms are located on the sites of the diamond structure.

> <u>Valency</u>: stability of phases depends on the # of valence electrons per unit cell

> <u>Electronegativity</u>: different electronegativity of components leads to charge transfer and formation of strong ionic bonding, e.g. Mg^{2+} + $Sn^{4-} = Mg_2Sn$

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Equilibrium in Heterogeneous Systems

Systems with two or more phases are heterogeneous systems. If pure components A and B have different equilibrium crystal structures, phase α and phase β , we have to consider two Gibbs free energy curves, one for each phase:



For compositions near cross-over of G_{α} and G_{β} , the total Gibbs free energy can be minimized by separation into two phases.

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Equilibrium in Heterogeneous Systems

Let us consider a system with two phases α and β , that have compositions X_B^{α} and X_B^{β} and Gibbs free energies G_{α} and G_{β} .

If the average composition of the system is X_B° , the molar free energy $G^{\alpha+\beta}$ is given by the point on a straight line that connects G_{α} and G_{β} , and the relative number of moles of phases α and β can be found by the lever rule:

 $M^{\alpha} = (X_B^{\beta} - X_B^{0})/(X_B^{\beta} - X_B^{\alpha})$ $M^{\beta} = (X_R^{0} - X_R^{\alpha})/(X_R^{\beta} - X_R^{\alpha})$

 $L_1 = G^{\alpha}$ $L_4 = G^{\beta}$





 $G^{\alpha+\beta}$ is the molar free energy of the phase mixture of α and β , with M_{α} and M_{β} molar fractions.

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Equilibrium in Heterogeneous Systems

For composition X_B° the lowest Gibbs free energy is G_o^{α} for a homogeneous system. The total Gibbs free energy can be additionally decreased by separation into two phases, for example with compositions $X_B^{\alpha 1}$ and $X_B^{\beta 1}$.

The total Gibbs free energy is at minimum if phases α and β have compositions $X_{B}^{\alpha_{eq}}$ and $X_{B}^{\beta_{eq}}$

These are the equilibrium compositions of the phases

In equilibrium tangents to G_{α} and G_{β} curves are the same (lie on a common line). Therefore, the condition for heterogeneous equilibrium is equity of the and of each component in the two phases.





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Next time: Binary Phase Diagrams