3. THE FUNDAMENTAL EQUATION

A functional relation between all extensive parameters of a thermodynamic system is called its fundamental equation (Gibbs, 1948). The fundamental equation contains all of the thermodynamic information on the system. Thermodynamic theory does not depend on the knowledge or even the existence of an explicit form of the fundamental equation. If one can, indeed, be formulated, it is bound to be rather complicated in general, because the constitution of the matter of which the thermodynamic system is composed will necessarily be complex. Thus, precious few explicit fundamental equations have been proposed and these all describe particularly simple systems (cf. §§ 12.1, 15.1, and 17.13). It is, nevertheless, crucial to an understanding of thermodynamic theory to examine the formal aspects and properties which characterize any fundamental theory, whether its explicit form is known or not. This is the task of the present chapter.

3.0 Chapter Contents

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3.1 The Entropy and Internal Energy Representations of the Fundamental Equation

The functional relation

\[ f(U, S, \ldots, X_k, \ldots) = 0 \]  \hspace{1cm} (3.1)\textsuperscript{1}

is a first-order homogeneous equation of the extensive parameters of the system. Since \( U \) and \( S \) are the only two extensive parameters that cannot be measured directly (cf. §§ 2.8 and 2.20), we cast Eq.(3.1)\textsuperscript{1} in either of two equivalent forms, explicit either for the internal energy, \( U \), or the entropy, \( S \). In the latter case we have

\[ S = S(U, \ldots, X_k, \ldots) , \]  \hspace{1cm} (3.1)\textsuperscript{2}

and speak of the entropy function, or the fundamental equation in the entropy representation. The extensive variables of state \( U, \ldots, X_k, \ldots \), are called the 'natural' or 'canonical' variables in the entropy representation.
3. THE FUNDAMENTAL EQUATION

Since, by Postulates III and V, the entropy, \( S \), is a continuous, differentiable, monotone non-decreasing function of \( U \), Eq. (3.1) can be inverted to give

\[
U = U(S, \ldots, X_k, \ldots).
\]

Equation (3.1) is called the energy function, or the fundamental equation in the internal energy representation, or simply the energy representation. The extensive variables of state \( S, \ldots, X_k, \ldots \) are called the 'natural' or 'canonical' variables in the energy representation.

The entropy and the energy representations are two different but equivalent ways of representing the same fundamental equation. Other representations will be introduced in Chapter 8. However, the entropy and the energy representations are the only ones whose canonical variables consist exclusively of extensive parameters. The energy function, \( U \), and the entropy function, \( S \), may be called the cardinal functions of equilibrium thermodynamics.

3.2 The Fundamental Surface in Thermodynamic Configuration Space

The fundamental equation defines a surface, the fundamental surface, in thermodynamic configuration space (Gibbs space). The coordinates of this space are the extensive parameters \( S, U, \) and \( X_k \). For the physical simple system these parameters become simply \( S, U, \) and \( V \). Hence, the fundamental equation of this system can be represented by a surface in three-dimensional Euclidean space as shown schematically in Fig. 3.2.

![Fig. 3.2 The surface \( S = S(U, V) \) in \( S, U, V \) – space](image)

3.3 The Intensive Parameters in the Energy Representation

The differential form of the fundamental equation in the energy representation becomes
\[ dU = \frac{\partial U}{\partial S} \bigg|_{X(\neq S)} dS + \sum_{k} \frac{\partial U}{\partial X_k} \bigg|_{X(\neq X_k)} dX_k \]  

(3.3)\textsuperscript{1}

where \( k = 1, 2, \ldots, r, \ldots \). We recognize the first term on the right as the right hand side of Eq.(2.19), and the second term as containing the right hand sides of both Eqs.(2.11) and (2.12).

In accordance with the factorability of the energy, the first-order partial derivatives in Eq.(3.3)\textsuperscript{1} are recognized as the intensive parameters of the system in the energy representation. We denote the general intensity parameter in this representation by \( Y \), and write

\[ dU = Y_0 dS + \sum_{k} Y_k dX_k, \]  

(3.3)\textsuperscript{2}

where

\[ Y_0 = \frac{\partial U}{\partial S} \bigg|_{X(\neq S)} \]  

(3.3)\textsuperscript{3}

and

\[ Y_k = \frac{\partial U}{\partial X_k} \bigg|_{X(\neq X_k)}. \]  

(3.3)\textsuperscript{4}

The nature of the \( Y_k \) depends on the system considered. When \( k = 1, 2, \ldots, r \), we shall let the \( Y_k dX_k \) represent physical work terms. When \( k = r + 1, \ldots \), the \( Y_k dX_k \) will represent chemical work, i.e., mass action terms.

3.4 The Intensive Parameters in the Entropy Representation

In the entropy representation the differential form of the fundamental equation becomes

\[ dS = \frac{\partial S}{\partial U} \bigg|_{X(\neq U)} dU + \sum_{k} \frac{\partial S}{\partial X_k} \bigg|_{X(\neq X_k)} dX_k. \]  

(3.4)\textsuperscript{1}

where the first-order partial derivatives are the intensive parameters of the system in the entropy representation. We denote them by \( I \), and write

\[ dS = I_0 dU + \sum_{k} I_k dX_k \]  

(3.4)\textsuperscript{2}

where
3. THE FUNDAMENTAL EQUATION

\[ I_0 = \frac{\partial S}{\partial U} \bigg|_{X(\neq U)} \]  
\[ (3.4)_3 \]

and

\[ I_k = \frac{\partial S}{\partial X_k} \bigg|_{X(\neq X_k)} \]  
\[ (3.4)_4 \]

Again, when \( k = 1, 2, \ldots, r \), the \( I_k dX_k \) represent physical work terms, and when \( k = r + 1, \ldots \), they represent chemical work, i.e., mass action terms.

3.5 The Intensity Factor of Heat – The Thermodynamic Temperature

Postulate III established entropy as the capacity factor of heat. In accordance with the factorability of the energy we identify \( Y_0 \) in Eq.\((3.3)_2\) with the thermodynamic temperature, \( T \), the intensity factor of heat. The differential form of the fundamental equation in the energy representation thus becomes

\[ dU = TdS + \sum_k Y_k dX_k \]  
\[ (3.5)_1 \]

where \( TdS \) is the heat term and the remainder are the work terms. The partial derivatives in Eqs.\((2.19)\) and \((2.21)\) are now also recognized to represent the temperature, \( T \).

We note that by Postulate V, i.e. by the monotonic property of the entropy (§ 2.22), the thermodynamic temperature is positive semi-definite.

In an analogous manner the partial derivatives in Eqs.\((2.22)\) and \((3.4)_3\) are seen to be the reciprocal thermodynamic temperature, \( 1/T \). Thus,

\[ I_0 = \frac{1}{T} \quad \text{and} \quad I_k = -\frac{Y_k}{T}, \]  
\[ (3.5)_2 \]

and the differential form of the fundamental equation in the entropy representation thus becomes

\[ dS = \frac{1}{T} dU - \sum_k I_k dX_k \]  
\[ (3.5)_3 \]

where \( dU/T \) is the heat term while the remaining terms are the work terms.

In both representations of the fundamental equation we distinguish the heat terms from the work terms because of the special nature of heat as a form of energy exchange (§ 2.20).
3.6 Conjugate Parameters

The pairs of intensive and extensive parameters \( T \) and \( S \), and \( Y_k \) and \( X_k \) in the energy representation, as well as \( 1/T \) and \( U \), and \( I_k \) and \( X_k \) in the entropy representation, are conjugate parameters. The product of conjugate parameters in the energy representation have the dimensions of energy while that of conjugate parameters in the entropy representation have the dimensions of entropy.

The lowest value of subscript \( k \) will always be 1. We shall use subscript \( j \) instead of \( k \) when the lowest value is 0, and \( m \) when the lowest value is 2.

3.7 The Chemical Potential

We call the intensive parameters furnished by the first-order partial derivatives of the internal energy, when taken with respect to the mole numbers,

\[
\left. \frac{\partial U}{\partial N_k} \right|_{X(x,N_k)} = \mu_k, \quad (k = r + 1, \ldots) \tag{3.7}
\]

the chemical potentials. The concept of the chemical potential is again due to Gibbs (1948). The name reflects the fact that the internal energy, \( U \), may be considered a potential for chemical work (cf. § 8.4). Thus, we recognize the \( \mu_k dN_k \) \((k = r + 1, \ldots)\) terms in Eq.(3.3)\(_3\) as the mass action terms or chemical work terms. Just as in the case of the entropy (cf. § 2.13) the chemical potential, \( \mu \), is required by the factorability of the energy as the intensity factor in the product \( \mu N \), the mole number, \( N \), supplying the extensive factor (cf. § 1.5).

Unlike the other intensive parameters, the chemical potential cannot be measured directly. Its relation to measurable physical quantities is in the form of a differential equation [see Eq.(8.22)\(_2\)]. Since the solution of such an equation requires a constant of integration, absolute values of the chemical potential must be defined relative to a judiciously chosen reference state (cf. § 12.12). Generally, however, only the change in chemical potential is of interest.

3.8 Significance of the Chemical Potential

The chemical potential is required by the factorability of the energy (cf. § 1.5) as the intensity parameter of mass action. It is the driving force for any change in the chemical composition of matter as specified by the mole numbers. The introduction of the concept of the chemical potential thus extends the scope of thermodynamics to the treatment of open systems, i.e., to systems which exchange matter with their surroundings, of phase transitions, i.e., transitions between homogeneous subsystems bounded by a surface across which the physical properties change discontinuously (see Chapter 19), and of reactive systems, i.e., to systems in which changes in composition occur as a result of chemical reactions (see Chapter 20).

3.9 The Gibbs Equation

The differential forms of the fundamental equation, Eqs.(3.5)\(_1\) and (3.5)\(_3\), are commonly called the Gibbs equations. For the (multicomponent) simple system these equations become
3. THE FUNDAMENTAL EQUATION

\[ dU = TdS - PdV + \sum_{m} \mu_{m} dN_{m} \]  

(3.9)\textsuperscript{1}

in the energy representation, and

\[ dS = \frac{1}{T} dU + \frac{P}{T} dV - \sum_{m} \frac{\mu_{m}}{T} dN_{m} \]  

(3.9)\textsuperscript{2}

in the entropy representation. In writing these equations we have taken into account that—

for the simple system—pressure-volume work is the only physical work admitted. Thus, \( X_{1} \)

is the volume, \( V \), and \(-Y_{1}\) is the pressure, \( P \), of the simple system.

For a single component simple system the above equations become simply

\[ dU = TdS - PdV + \mu dN \]  

(3.9)\textsuperscript{3}

and

\[ dS = \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu}{T} dN . \]  

(3.9)\textsuperscript{4}

in the energy and entropy representations, respectively.

3.10 The Euler Equation

Since the internal energy is a first-order homogeneous equation of the extensive

variables of the system (Postulate I), we may write

\[ U(\lambda S, \ldots, \lambda X_{k}, \ldots) = \lambda U(S, \ldots, X_{k}, \ldots) \]  

(3.10)\textsuperscript{1}

where \( \lambda \) is a scaling parameter. Differentiating with respect to \( \lambda \) and then letting \( \lambda = 1 \) we

obtain the energy function in the form

\[ U = \sum_{j} Y_{j} X_{j} \]  

(3.10)\textsuperscript{2}

where the \( Y_{j} \) are given by Eqs.(3.3)\textsuperscript{3} and (3.3)\textsuperscript{4}. Equation (3.10)\textsuperscript{2} is called the Euler

equation in the energy representation. It equates the energy function to the (algebraic) sum

of the products formed from the conjugate parameters of the system.

The entropy function takes the form

\[ S = \sum_{j} I_{j} X_{j} . \]  

(3.10)\textsuperscript{3}
where the $I_j$ are defined by Eqs. (3.4)\_3 and (3.4)\_4. Equation (3.10)\_3 is called the Euler equation in the entropy representation. It equates the entropy function to the (algebraic) sum of the products formed from the conjugate parameters of the system.

For the \textit{(multicomponent) simple system} the cardinal functions become

$$U = TS - PV + \sum_m \mu_m N_m$$  \hspace{1cm} (3.10)\_4$$

in the energy representation, and

$$S = \frac{1}{T} U + \frac{P}{T} V - \sum_m \frac{\mu_m}{T} N_m$$  \hspace{1cm} (3.10)\_5$$

in the entropy representation.

The cardinal functions are connected through the relation

$$U = - TS.$$  \hspace{1cm} (3.10)\_6$$

Indeed, multiplication of Eq. (3.10)\_6 by $- T$ and rearranging leads at once to Eq. (3.10)\_4.

3.11 Equations of State

A functional relation expressing an intensive parameter in terms of the extensive parameters of the system is called an \textit{equation of state}. An equation of state is a zeroth-order homogeneous equation of the extensive parameters of the system.

The equations of state are obtained as the partial derivatives of the Euler equation. In the energy representation they are, therefore,

$$Y_j = Y_j(S, \ldots, X_k, \ldots) = \frac{\partial U}{\partial X_j} \Big|_{X_{i \neq j}}$$  \hspace{1cm} (3.11)\_1$$

and the entropy representation they become

$$I_j = I_j(U, \ldots, X_k, \ldots) = \frac{\partial S}{\partial X_j} \Big|_{X_{i \neq j}}.$$  \hspace{1cm} (3.11)\_2$$

For the \textit{(multicomponent) simple system} we have

$$Y_0 = \frac{\partial U}{\partial S} \Big|_{X_{i=0}} = T$$  \hspace{1cm} (3.11)\_3,1$$
3. THE FUNDAMENTAL EQUATION

\[ Y_1 = \left. \frac{\partial U}{\partial V} \right|_{X, \mu_1} = P \]  
\[ (3.11)_{3.2} \]

and

\[ Y_2 = \left. \frac{\partial U}{\partial N_m} \right|_{X, \mu_2} = \mu_m \]  
\[ (3.11)_{3.3} \]

in the energy representation, and

\[ I_0 = \left. \frac{\partial S}{\partial U} \right|_{X, \mu_0} = \frac{1}{T} \]  
\[ (3.11)_{4.1} \]

\[ I_1 = \left. \frac{\partial S}{\partial V} \right|_{X, \mu_1} = \frac{P}{T} \]  
\[ (3.11)_{4.2} \]

and

\[ I_2 = \left. \frac{\partial S}{\partial N_m} \right|_{X, \mu_2} = \frac{\mu_m}{T} \]  
\[ (3.11)_{4.3} \]

in the entropy representation.

3.12 Relation between the Fundamental Equation and the Equations of State

Equations of state are generally much easier to establish than fundamental equations. However, in contrast to a fundamental equation, an equation of state does not contain complete information on the thermodynamic system. This follows from the fact that the intensive variables are (partial) derivatives of the extensive ones. The differentiation results in a loss of information. Nevertheless, the totality (i.e., the complete set) of the equations of state is equivalent to the fundamental equation. To recover the latter it is only necessary to insert all the state equations into the Euler equation from which were derived (cf. §§ 12.3 and 13.8). Since we thus regain the complete information on the system, this is tantamount to an integration. The Euler equation in either representation is therefore a form of the fundamental equation.