Chapter 8: The Fundamental Equation

Chapter 8: The Fundamental Equation ............................................................ 74
8.1 Introduction: The Isolated System ............................................................. 74
    8.1.1 The natural coordinates ................................................................. 75
    8.1.2 The conditions of equilibrium and stability ................................. 75
    8.1.3 The fundamental equation ............................................................. 75
    8.1.4 Alternate forms of the fundamental equation ............................... 77
8.2 The Energy Minimum Principle ............................................................... 78
    8.2.1 Derivation ...................................................................................... 78
    8.2.2 The conditions of equilibrium and stability ................................. 79
    8.2.3 Applications .................................................................................. 80
8.3 The Energy Function .................................................................................. 81
8.4 The Integrated Form of the Fundamental Equation .................................. 82
8.5 The Gibbs-Duhem Equation ..................................................................... 83
8.6 The Energy Density .................................................................................. 85
    8.6.1 Volumetric Densities ................................................................. 85
    8.6.2 Molar or Mass Densities .............................................................. 86
8.7 Internal Equilibrium .................................................................................. 88
    8.7.1 Thermochemical equilibrium in the absence of external fields .... 89
    8.7.2 Thermochemical Equilibrium in an External Field ....................... 91
    8.7.3 Homogeneous Systems .................................................................. 93
8.8 Global Equilibrium ................................................................................... 94
    8.8.1 Experimentally controllable variables ....................................... 94
    8.8.2 The Legendre Transform ............................................................ 96
    8.8.3 The fundamental equation of an interacting system ................. 97
    8.8.4 The conditions of equilibrium in an interacting system .......... 98
8.9 Thermodynamic Potentials .................................................................... 101
    8.9.1 Diathermal walls: the Helmholtz free energy ................................ 102
    8.9.2 Deformable walls: the enthalpy .................................................... 103
    8.9.3 Diathermal, deformable walls: the Gibbs free energy .............. 103
    8.9.4 Open walls: the work function .................................................... 104
    8.9.5 Hybrid walls: hybrid potentials .................................................. 105
    8.9.6 Massieu functions ........................................................................ 105
    8.9.7 Densities of the thermodynamic potentials ............................ 107
8.10 Maximum Work ....................................................................................... 109
8.11 Relations between the Thermodynamic Potentials ............................... 110

8.1 INTRODUCTION: THE ISOLATED SYSTEM

Most of the important applications of thermodynamics to materials science are based on the conditions of equilibrium and stability, and on the properties of the fundamental equation that is derived from them. The conditions of equilibrium for an isolated system were derived in Chapter 5. It is worth reviewing them briefly here.
8.1.1 The natural coordinates

When a system is isolated the constitutive variables that can be controlled experimentally are the geometric coordinates that represent the content of the system, such as the energy, volume and chemical content. The values of these quantities can be adjusted before the system is isolated, but then remain the same so long as the isolation is maintained. It follows that the geometric coordinates are the natural coordinates for an isolated system.

8.1.2 The conditions of equilibrium and stability

The conditions of equilibrium and stability that govern the isolated system were discussed in Chapter 5. They derive from the entropy maximum principle, which asserts that an equilibrium state of the system has higher entropy than any hypothetical state that could be achieved by redistributing the content of the system without changing its total value. The conditions of equilibrium follow from it, and are phrased in three statements. The global condition of equilibrium,

\[(\Delta S)_E,\{q\},\{N\} < 0\]  \hspace{1cm} 8.1

is satisfied if every possible reconfiguration of the system causes its entropy to decrease, and is, hence, necessary and sufficient to insure that the system is stable with respect to any possible change of state. The local condition of equilibrium,

\[(\delta S)_E,\{q\},\{N\} \leq 0\]  \hspace{1cm} 8.2

is necessary (but not sufficient) for equilibrium with respect to all infinitesimal changes of state; it insures that the entropy of the system has an extreme value with respect to infinitesimal reconfigurations of its content, but does not guarantee that the extremum is a maximum. The local condition of stability,

\[(\delta^2 S)_E,\{q\},\{N\} < 0\]  \hspace{1cm} 8.3

is a sufficient condition for the system to be stable with respect to small perturbations. It ensures that the local extremum is a maximum. However, the local condition of stability does not guarantee global equilibrium; even when a state of the system is stable with respect to small perturbations, more substantial reconfigurations may still lead to states of higher entropy. Such states are called metastable equilibrium states.

8.1.3 The fundamental equation

The equilibrium states of a system define its fundamental equation. To each possible set of values of the constitutive coordinates, E, \{q\} and \{N\}, there is a value of S that corresponds to the maximum attainable entropy and defines the global equilibrium state. The maximum values of S are, then, given by the fundamental equation,
The fundamental equation has three important characteristics: (1) its natural variables are the variables that can be controlled experimentally in the isolated system; (2) its values are the entropy maxima that pertain to the equilibrium states of the isolated system; (3) the constitutive equations that govern the forces and equilibrium properties can be obtained from it by differentiation, as discussed in Chapter 5. In this sense the fundamental equation contains all of the equilibrium thermodynamics of the system.

Strictly, there is a unique fundamental equation for a given system. Its values are the entropies of the global equilibrium states. However, most systems have metastable equilibria as well, and can be maintained in metastable equilibrium for arbitrarily long times. If we focus our attention on a particular local maximum of the entropy function, this maximum will ordinarily be retained for some range of values of the constitutive coordinates. Over part of this range it may be the greatest maximum, and correspond to the global equilibrium state. Over another part of its range the local maximum may be metastable; however, the fact that it is metastable is not determined by its own local behavior, but by the behavior of the system in some very different configuration. It is, therefore, often useful to define a separate fundamental equation for each state of the system that is at least metastable. Since there will ordinarily be several of these, we label each of them with an index, \( \alpha \), that denotes which locally stable state we are talking about, and write

\[
S = S_\alpha(E,\{q\},\{N\}) \tag{8.5}
\]

When the \( \alpha \)th metastable state is homogeneous, that is, is physically the same everywhere in the system, we call it the \( \alpha \)th phase of the system.

The fundamental equation of a system is the upper envelope of the fundamental equations of each of its phases. That is, for any given values of \( E, \{q\} \) and \( \{N\} \) the global equilibrium state is determined by the function, \( S_\alpha \), that provides the highest value of the entropy. While the fundamental equation of the system is defined for all admissible values of the constitutive coordinates, the fundamental equations of the metastable states need not be. The \( \alpha \)th phase is ordinarily stable for only a restricted range of the constitutive coordinates, and does not exist outside this range.

The thermodynamic forces that are applied to the system when it is in the \( \alpha \)th phase are determined by the differentials of the fundamental equation of that state. For example, when the system has total content \( E, \{q\} \) and \( \{N\} \) and is in the \( \alpha \)th metastable state, its reciprocal temperature is

\[
\frac{1}{T_\alpha} = \left[ \frac{\partial S_\alpha}{\partial E} \right] \tag{8.6}
\]

which will ordinarily differ from the value the temperature would have if the system were in some other phase. The values of the partial derivatives of the fundamental equations of
the various phases determine the possible values of the thermodynamic forces for given $E$, \{q\}, \{N\}.

### 8.1.4 Alternate forms of the fundamental equation

Since any thermodynamic system can be made into an isolated system by including its environment, the fundamental equation of an isolated system (8.4) is sufficient to treat all solvable problems in equilibrium thermodynamics. However, this approach is often inconvenient, for two reasons.

First, the system of interest is usually not isolated. It can be always be made isolated by incorporating its environment, but this has the consequence that the fundamental equation applies to the composite system. The thermodynamic properties of the environment are usually unknown and almost never of interest. It would be useful to rephrase the fundamental equation so that it is directly applicable to the real, interacting system one wishes to treat.

Second, the thermodynamic forces that are defined by the differentials of equation 8.1 are combinations of those that are normally used to describe physical phenomena. For example, the partial derivative with respect to the $k^{th}$ mechanical coordinate,

\[
\left[ \frac{\partial \tilde{S}}{\partial q_k} \right] = - \frac{p_k}{T}
\]

yields a constitutive equation for the quotient of the mechanical force and the temperature, rather than the force itself. It would be useful to rephrase the fundamental equation in a form that provides the constitutive equations for the mechanical and chemical forces directly.

The material included in this chapter accomplishes both of those objectives. We shall first show that the energy function,

\[
E = \tilde{E}(S,\{q\},\{N\})
\]

is also a form of the Fundamental Equation. It governs the equilibrium of isentropic systems and equilibrium in the limit of low temperature. Its partial derivatives are the constitutive equations for the mechanical and chemical forces. It is also a convenient starting point for the derivation of a number of important results, including the integrated form of the fundamental equation, the Gibbs-Duhem relation, and the internal conditions of equilibrium.

We shall then consider the behavior of interacting systems, and define the thermodynamic potentials that express the fundamental equation of an interacting system in terms of the variables that can be controlled experimentally in its actual situation. The thermodynamic potentials include the familiar ones that are used in the thermodynamics of simple
fluids, such as the enthalpy, the Helmholtz and Gibbs free energies, and the work function. As we shall see, useful thermodynamic potentials can be defined for arbitrary materials and experimental circumstances in a systematic way.

8.2 THE ENERGY MINIMUM PRINCIPLE

8.2.1 Derivation

The entropy maximum principle can be written in an alternate form that governs changes in the energy at constant entropy. The result is the Energy Minimum Principle:

An equilibrium state has the least value of the energy that is consistent with its entropy and the values of its geometric coordinates.

![Diagram](image)

Fig. 8.1: Sequence of state changes showing that if $E$ can be decreased at constant $S$, $S$ can be increased at constant $E$.

To prove this statement let the system be referred to the coordinates $(S, \{q\},\{N\})$, so that the constitutive equation for the energy is the energy function

$$E = \hat{E}(S,\{q\},\{N\})$$  \hspace{1cm} \text{(8.9)}

Let the system be initially in equilibrium, and assume that there is some way to decrease its energy at constant values of the coordinates, for example, by manipulating internal constraints. Let the energy be decreased in this way, and then let it be increased to its original value by adding energy isometrically. The sequence of transitions is diagrammed in Fig. 8.1. Since

$$\left[ \frac{\partial \hat{E}}{\partial S} \right] = T > 0$$  \hspace{1cm} \text{(8.10)}
the second step increases the entropy. The two-step transition is equivalent to the transition shown by the arrow in Fig. 8.1, in which the entropy is increased at constant values of the energy and the geometric coordinates. But in this transition

\[(\Delta S)_{E,(q),\{N\}} > 0 \quad 8.11\]

Hence the transition would occur spontaneously and the original state could not have been in equilibrium. If it is possible to decrease the energy of a system without changing its entropy or the values of its geometric coordinates the system cannot be in equilibrium, which establishes the Energy Minimum Principle.

The argument given above proves that if the Energy Minimum Principle is violated, the Entropy Maximum Principle is violated as well. However, the argument can be read in reverse by simply interchanging the order of the transitions diagrammed in Fig. 8.1. It then shows that if the entropy is not a maximum for given energy, the energy can be decreased at given entropy. It follows that the Entropy Maximum and Energy Minimum Principles are mathematically equivalent; if one holds, the other must. We can therefore employ the Energy Minimum Principle in place of the Entropy Maximum Principle whenever it is convenient to do so.

**8.2.2 The conditions of equilibrium and stability**

The Energy Minimum Principle provides conditions of equilibrium and stability that parallel those derived from the Entropy Maximum. The condition for global equilibrium is

\[(\Delta E)_{S,(q),\{N\}} > 0 \quad 8.12\]

The necessary condition for local equilibrium is

\[(\delta E)_{S,(q),\{N\}} \geq 0 \quad 8.13\]

and the condition for local stability is

\[(\delta^2 E)_{S,(q),\{N\}} > 0 \quad 8.14\]

These conditions are mathematically equivalent to those expressed in equations 8.1 to 8.3 and can be interchanged with them whenever it is convenient. It follows that the energy function, eq. 8.9, is just the function that assigns the minimum possible value of the energy to each independent set of values of the constitutive variables, \(S\), \(\{q\}\) and \(\{N\}\).

According to equation 8.14, the metastable states of the system are those states for which the energy has a minimum value with respect to small perturbations that redistribute \(S\), \(\{q\}\) and \(\{N\}\) while keeping their total values constant. Since the energy minimum and entropy maximum principles are mathematically equivalent, the metastable states identified by 8.14 are the same as those identified by the condition 8.3. The thermodynamic behavior of the \(\alpha\)th phase is described by the energy function.
\[ E = \tilde{E}^\alpha(S,\{q\},\{N\}) \]

\( \tilde{E}^\alpha \) is the fundamental equation for the \( \alpha \)th state. Its partial derivatives specify the values of the thermodynamic forces when the system is in that state. The fundamental equation of the system is the lower envelope of the functions, \( \tilde{E}^\alpha \). It determines the minimum possible value of the energy for given values of \( S, \{q\} \) and \( \{N\} \).

### 8.2.3 Applications

The utility of the Minimum Energy Principle lies in the fact that the internal energy is a familiar concept, is easily measured, and is readily computed from atomistic models. It hence provides the most convenient formulation of the conditions of equilibrium for most theoretical purposes. Its value for the analysis of experiments is less obvious; the entropy is not a controllable variable in most experimental situations. However, there are two important physical situations in which the entropy is a controlled variable and the Minimum Energy Principle is directly applicable: when the transitions of interest are quasi-static and adiabatic, and when the temperature is near zero. We have already discussed the use of the energy function to describe quasi-static adiabatic transitions. The low-temperature application is important in physics, since it has the consequence that a material always assumes the state of minimum possible energy as the temperature approaches zero.

The Third Law justifies the Energy Minimum Principle as it is ordinarily used in physics to identify the preferred low-temperature states. The state that has the minimum possible energy is always preferred.

Consider a system that is unconstrained or has fixed constraints. As the temperature approaches zero the entropy becomes constant and independent of the values of the geometric coordinates. The value of the entropy is uniquely set by the fact of zero temperature and is, therefore, one of the controlled variables for hypothetical changes of state at \( T=0 \). The equilibrium state is that which minimizes the energy over all possible choices. For example, if the system can, hypothetically, exist in any of a number of ordered phases at \( T=0 \), the preferred phase has the lowest energy.

In the limit of zero temperature the minimum-energy state of the unconstrained system is preferred to that of the same system with internal constraints. When the system is constrained its entropy asymptotes to the value \( S_0 \geq 0 \). Let \( S_0 \) be positive, and let the constraints be relaxed without interaction with any other system. The resulting state has an entropy \( S' \geq S_0 \), a temperature \( T' > 0 \), and an energy \( E(S') \), which is equal to the energy, \( E(S_0) \), it had in the constrained state at zero \( T \). Its energy is necessarily greater than the value, \( E(0) \), of the equilibrium state at \( T = 0 \), since

\[ E(S') = E(S_0) = E(0) + \int_0^{S'} TdS \geq E(0) \]

\[ 8.16 \]
Hence, the preferred state of an isolated system in the limit $T=0$ is the minimum energy state.

The procedure that is usually followed to compute the properties of a material from an atomistic model is to find the minimum energy state from among all possible ways of arranging the atoms in static configurations. If the energy associated with the zero-point lattice vibrations can be neglected, as it usually can, this procedure identifies the preferred state at zero temperature. The influence of temperature is then treated (if at all) as a perturbation on the lowest-energy state.

### 8.3 The Energy Function

The energy function

$$E = 	ilde{E}(\{u\}) = 	ilde{E}(S,\{q\},\{N\})$$  \hspace{1cm} 8.17

can be obtained from the entropy function, $\tilde{S}(E,\{q\},\{N\})$, by solving for the internal energy. It follows that the energy function contains all of the information that is present in the entropy function and is a form of the fundamental equation. Its natural coordinates show that it is the fundamental equation of an *isentropic system*, which is a somewhat unnatural system (except at zero T) whose controlled variables are the entropy and the deformation coordinates.

To show that the energy function has the properties of the fundamental equation consider a hypothetical system whose controlled variables are $S$, $\{q\}$, $\{N\}$; for example, an adiabatic system with fixed walls whose transitions are restricted to be quasi-static. Then the natural variables of the energy function are the controllable variables of the system. The equilibrium states of the system are determined by the minima of the energy function. The first partial derivatives of $\tilde{E}$ yield the constitutive equations for the thermodynamic forces:

$$\left[ \frac{\partial \tilde{E}}{\partial S} \right] = T \hspace{1cm} 8.18$$

$$\left[ \frac{\partial \tilde{E}}{\partial q_k} \right] = p_k \hspace{1cm} 8.19$$

$$\left[ \frac{\partial \tilde{E}}{\partial N_k} \right] = \mu_k \hspace{1cm} 8.20$$

The second partial derivatives are the thermodynamic properties that govern how the forces change with the geometric coordinates, and have the form

$$C_{ij} = \left[ \frac{\partial \tilde{p}_i}{\partial q_j} \right] = \left[ \frac{\partial^2 \tilde{E}}{\partial q_i \partial q_j} \right] = \hat{C}_{ij}(S,\{q\},\{N\})$$  \hspace{1cm} 8.21
The higher derivatives of $\tilde{E}(\{u\})$ provide constitutive equations for the material properties that govern the change in the $C_{ij}$ with infinitesimal changes in state.

Besides sharing the properties of the entropy function, the energy function has an important additional property that was discussed in another context in Chapter 6. If the system is changed by relaxing internal constraints isometrically, the maximum work that can be extracted is equal to the change in the energy function (the isentropic work):

$$\Delta E_{S,(q),(N)} = w_{\text{max}}$$  \hspace{1cm} 8.22

### 8.4 THE INTEGRATED FORM OF THE FUNDAMENTAL EQUATION

The entropy, $S$, energy, $E$, and mole numbers, $\{N\}$, are additive quantities whose values increase linearly with the size of the system; if a system is doubled in size its energy, entropy, and molar contents are doubled as well. We shall require that the mechanical coordinates, $\{q\}$, are defined so that they have the same additive property.

Consider a composite system that is composed of $\alpha$ identical subsystems that are in free communication with each other across open boundaries. Since the subsystems are identical, each of them has the same value, $u_k$, of each of the coordinates in $\{u\}$. The composite system is a simple system that can also be referred to the coordinates $\{u\}$, which have the values

$$u'_k = \alpha u_k$$  \hspace{1cm} 8.23

for each $u_k$ in $\{u\}$.

The composite system obeys the same fundamental equation that governs the subsystems,

$$E = \tilde{E}(\{u\}) = \tilde{E}(S,\{q\},\{N\})$$  \hspace{1cm} 8.24

since the composite system can be made from the subsystem by simply replacing the values $\{u\}$ by the values $\{\alpha u\}$. But if this substitution is made in equation 8.24 the result must be the energy of the composite system, for which $E = \alpha E$. Hence

$$\tilde{E}(\alpha S,\{\alpha q\},\{\alpha N\}) = \alpha E$$  \hspace{1cm} 8.25

An equation that has the property 8.25, that multiplying each of the independent variables by a constant multiplies the dependent variable by the same constant, is said to be a homogeneous equation of first order. A homogeneous equation of first order can be written in a simple integrated form. To find the integrated form let $\alpha$ be a continuous variable and differentiate equation 8.25 with respect to it. The result is
\[ E = \left[ \frac{\partial \tilde{E}}{\partial (\alpha S)} \right] S + \sum_k \left[ \frac{\partial \tilde{E}}{\partial (\alpha q_k)} \right] q_k + \sum_k \left[ \frac{\partial \tilde{E}}{\partial (\alpha N_k)} \right] N_k \] \tag{8.26}

Since equation 8.26 is true for any value of the parameter \( \alpha \), it holds for the particular value \( \alpha = 1 \). Hence

\[ E = \left[ \frac{\partial \tilde{E}}{\partial S} \right] S + \sum_k \left[ \frac{\partial \tilde{E}}{\partial q_k} \right] q_k + \sum_k \left[ \frac{\partial \tilde{E}}{\partial N_k} \right] N_k \] \tag{8.27}

or

\[ E = TS + \sum_k p_k q_k + \sum_k \mu_k N_k \] \tag{8.28}

Equation 8.28 is the integrated form of the fundamental equation.

### 8.5 THE GIBBS-DUHEM EQUATION

The differential of the integrated form of the energy function is

\[ dE = TdS + SdT + \sum_k p_k dq_k + \sum_k q_k dp_k + \sum_k \mu_k dN_k + \sum_k N_k d\mu_k \] \tag{8.29}

Since the total differential of the energy is

\[ dE = TdS + \sum_k p_k dq_k + \sum_k \mu_k dN_k \] \tag{8.30}

equation 8.29 establishes the Gibbs-Duhem Equation:

\[ SdT + \sum_k q_k dp_k + \sum_k N_k d\mu_k = 0 \] \tag{8.31}

The Gibbs-Duhem equation shows that there is a mutual dependence between the thermodynamic forces. If there are \( n \) constitutive coordinates, there are only \( n-1 \) independent thermodynamic forces. This result should not be surprising since one of the properties that is measured by the constitutive coordinates is the size of the system. The forces do not depend on the system size and hence cannot be used to measure it. If equation 8.31 is divided through by a measure of system size, such as the volume, the coefficients are volumetric densities that are also independent of system size and the size disappears completely from the equation. A degree of freedom is hence lost in the translation from equation 8.29 to 8.31, and the number of independent variables decreases accordingly.
The Gibbs-Duhem equation, 8.31, can be solved for any one of the forces and integrated, yielding equations such as

\[ T = \tilde{T}(\{p\},\{\mu\}) \]  

Equation 8.32 can be easily shown to be a restricted form of the fundamental equation. Its partial derivatives

\[
\left[ \frac{\partial \tilde{T}}{\partial p_k} \right] = -\frac{q_k}{S} \quad \text{8.33}
\]

\[
\left[ \frac{\partial \tilde{T}}{\partial \mu_k} \right] = -\frac{N_k}{S} \quad \text{8.34}
\]

regenerate the geometric coordinates, but in such a way that the size of the system is lost.

This result is most clear in the case of the n-component fluid, which is characterized by the coordinates \{S,V,\{N\}\}. The negative of the hydrostatic pressure, \(P\), is the force conjugate to the volume, \(V\). The Gibbs-Duhem equation can then be written

\[
dP = \left[ \frac{S}{V} \right] dT + \sum_k \left[ \frac{N_k}{V} \right] d\mu_k \quad \text{8.35}
\]

which integrates to the function

\[
P = \tilde{P}(T,\{\mu\}) \quad \text{8.36}
\]

which determines the pressure as a function of the temperature and the chemical potentials. Its partial derivatives are

\[
\left[ \frac{\partial \tilde{P}}{\partial T} \right] = \frac{S}{V} = S_v \quad \text{8.37}
\]

\[
\left[ \frac{\partial \tilde{P}}{\partial \mu_k} \right] = \frac{N_k}{V} = n_k \quad \text{8.38}
\]

The former is just the entropy per unit volume, the latter is the molar density of the \(k^{th}\) component. The volume cannot be recovered.
8.6 THE ENERGY DENSITY

Since the energy and entropy increase linearly with the size of the system it is often useful to express them as densities so that the size of the system can be left arbitrary. These densities are also the coefficients in the Gibbs-Duhem equation. Three different forms of the density are commonly used, based alternately on the volume, V, the mole or atom content, N, and the mass, m, as measures of system size.

8.6.1 Volumetric Densities

When the total volume, V, is used as a reference the mechanical coordinates (let there be r of them) are chosen so that V is one of them (the r\textsuperscript{th}) whether or not the material is a fluid. When the system contains no internal partitions that restrict mechanical behavior the force conjugate to the volume is the negative of the hydrostatic pressure

\[ p_r = -P \]  \hspace{1cm} 8.39

When the system contains mechanical partitions (rigid walls or interfaces with mechanical properties of their own) the force conjugate to the volume is the negative of the hydrostatic pressure (P\textsubscript{s}) in one homogeneous subvolume that is chosen as a reference

\[ p_r = -P_s \]  \hspace{1cm} 8.40

The volumetric densities of the constitutive coordinates are

\[ E_v = \frac{E}{V} \hspace{1cm} S_v = \frac{S}{V} \]

\[ q_v^k = \mu_k = \frac{q_k}{V} \hspace{1cm} n_k = \frac{N_k}{V} \hspace{1cm} \rho_k = \frac{m_k}{V} \]  \hspace{1cm} (k = 1,\ldots,r-1)  \hspace{1cm} 8.41

where m\textsubscript{k} is the total mass of the k\textsuperscript{th} component, and the symbol, \( \mu_k \), is used for the volume density of the k\textsuperscript{th} mechanical coordinate for convenience.

The energy function can be written in terms of the volumetric densities by simply dividing its integrated form, equation 8.28, by the volume V. The result is

\[ E_v = T S_v + \sum_{k=1}^{r-1} p_k \mu_k + \sum_k \mu_k n_k - P \]  \hspace{1cm} 8.42

where the first summation is over the (r-1) residual mechanical densities. With this notation the Gibbs-Duhem equation is
\[ dP = S_v dT + \sum_k \nu_k d\rho_k + \sum_k n_k d\mu_k \quad 8.43 \]

and the differential of the energy is

\[ dE_v = TdS_v + \sum_k p_k d\nu_k + \sum_k \mu_k d\pi_k \quad 8.44 \]

It follows that the energy density is given by the function

\[ E_v = \tilde{E}_v(S_v,\{\nu\},\{n\}) \quad 8.45 \]

whose derivatives are

\[
\left[ \frac{\partial \tilde{E}_v}{\partial S_v} \right] = T \quad 8.46
\]

\[
\left[ \frac{\partial \tilde{E}_v}{\partial \nu_k} \right] = p_k \quad (k = 1,\ldots,r-1) \quad 8.47
\]

\[
\left[ \frac{\partial \tilde{E}_v}{\partial \pi_k} \right] = \mu_k \quad 8.48
\]

Note that the energy density requires one less constitutive coordinate than the energy itself. Equation 8.45 is a form of the fundamental equation, but is a restricted form in that the volume of the system is left arbitrary.

It follows from equation 8.43 that the pressure is given by the function

\[ P = \tilde{P}(T,\{p'\},\{\mu\}) \quad 8.49 \]

where the set \( \{p'\} \) does not contain the pressure. In general, the value of the pressure depends on the other mechanical forces as well as on the temperature and the chemical potentials.

### 8.6.2 Molar or Mass Densities

The total chemical content of the system is also a useful measure of the system size. The chemical content can be expressed in terms of the total mass, \( m \), or the total molar or atom content, \( N \). Since the two cases are similar we shall present only the molar form.

The total molar (or atom) content is
\[ N = \sum_k N_k \]  

The molar densities of the geometric coordinates are written:

\[ e = \frac{E}{N}, \quad s = \frac{S}{N} \]

\[ q_k^n = \frac{q_k}{N}, \quad x_k = \frac{N_k}{N} \]  

where the \( n \) quantities \( x_k \) are the concentrations of the independent components present (the mass concentrations are usually written \( c_k = m_k/m \), otherwise the notation is the same). Only \( n - 1 \) of the concentration variables are independent since

\[ \sum_k x_k = 1 \]  

If the integrated form of the energy function 8.28 is divided through by \( N \) the result is

\[ e = Ts + \sum_k p_k q_k^n + \sum_k \mu_k x_k \]  

Let one of the chemical components, the \( n^{th} \) be used as a reference. The reference component would normally be the solvent in the case of a solution, and is often most conveniently taken to be the number of lattice sites in the case of a crystalline solid, where lattice vacancies are also a component. Using equation 8.52 in 8.53,

\[ e = Ts + \sum_k p_k q_k^n + \sum_{k=1}^{n-1} \mu_k x_k + \mu_n \]  

where \( \bar{\mu}_k \) is the relative chemical potential

\[ \bar{\mu}_k = \mu_k - \mu_n \]  

and the summation over concentrations on the right hand side of equation 8.54 contains only \( n - 1 \) terms. The Gibbs-Duhem equation is

\[ \sum_k q_k^n dP_k + \sum_{k=1}^{n-1} x_k d\bar{\mu}_k + d\mu_n = 0 \]  

The differential of the molar energy density is
\[ de = Tds + \sum_{k} p_k dq_k^n + \sum_{k=1}^{n-1} \mu_k dx_k \] 8.57

where the last summation on the right is over the \( n - 1 \) independent concentrations in the set \( \{x\} \). Equation 8.57 integrates to the form

\[ e = \tilde{e}(s, \{q^n\}, \{x\}) \] 8.58

where

\[
\left[ \frac{\partial \tilde{e}}{\partial s} \right] = T \] 8.59

\[
\left[ \frac{\partial \tilde{e}}{\partial q_k^n} \right] = p_k \] 8.60

\[
\left[ \frac{\partial \tilde{e}}{\partial x_k} \right] = \bar{\mu}_k \] 8.61

Note equation 8.61, which is presented in a confusing way in some of the literature. The differential of the energy density with respect to the concentration of the \( k \)th component is the relative chemical potential, \( \bar{\mu}_k \), not the chemical potential itself. The reference potential, \( \mu_n \), cannot be found by differentiating with respect to the composition.

A second common confusion arises from the fact that the same symbol, \( \mu_k \), is commonly used for the chemical potential whether it is defined in terms of the molar or the mass content. Since

\[
\left[ \frac{\partial \tilde{E}}{\partial N_k} \right] = M_k \left[ \frac{\partial \tilde{E}}{\partial m_k} \right] \] 8.62

where \( M_k \) is the molar weight, the two definitions are not the same. The relative chemical potentials, \( [\partial e/\partial x_k] \) and \( [\partial e/\partial c_k] \), are not even simply proportional to one another. It is therefore important to be clear whether the mass or molar form is used. We shall ordinarily use the molar form, but it is occasionally more convenient to use the mass as a reference, as Gibbs does throughout.

### 8.7 INTERNAL EQUILIBRIUM

The fundamental equation can be used to phrase necessary conditions for thermal and chemical equilibrium within a system whose parts are in thermal and chemical contact.
with one another. The system may contain a number of distinct materials or phases. However, to keep the derivation simple we shall ignore the properties of the interfaces that separate these. We shall show later that the presence of interfaces does not change the result. The conditions of mechanical equilibrium depend on the particular set of mechanical coordinates that are used and will be discussed at a later point when we treat the properties of specific classes of materials. The conditions of chemical equilibrium change slightly when potential fields, such as gravitational, centrifugal, or electric fields, influence the system to a measurable extent. We shall neglect potential fields at first, since they are negligible in typical applications, and then show how the conditions of chemical equilibrium are altered when they are present.

8.7.1 Thermochemical equilibrium in the absence of external fields

Consider a simple system in the absence of external potential fields. The condition of equilibrium is

\[
(\delta E)_{(u)} \geq 0
\]

that is, the energy can only increase in any change that leaves the total entropy, mechanical and chemical contents the same. As discussed in Chapter 5, the states to which the condition 8.63 applies are alternate equilibrium states of the system that could be created and brought to equilibrium by imposing suitable constraints. One class of alternate states are those that involve a spatial redistribution of the entropy and the chemical constituents through the system. To examine these test states let the system be divided into elementary subvolumes, dV. A redistribution of the entropy and chemical content can be accomplished by letting the subvolumes be separated by isolating partitions and allocating the total entropy and chemical contents among them. The equilibrium state of the unconstrained system must provide a value of the energy that satisfies the condition 8.63 with respect to any infinitesimal redistribution of this type.

To phrase this condition mathematically let the different subvolumes be identified by their spatial positions, \( R \), in some coordinate frame. Then the energy may be regarded as a function of the quantities \( S_v(R) \) and \( \{n(R)\} \):

\[
E = \tilde{E}(\{S_v(R)\},\{\{n(R)\}\},\{q\})
\]

The total quantities of the energy, the entropy and the components are given by the integrals

\[
E = \int_V [E_v(R)] \, dV
\]

\[
S = \int_V [S_v(R)] \, dV
\]

\[
N_k = \int_V [n_k(R)] \, dV
\]
and the condition of equilibrium becomes

\[ \delta E_{\{u\}} = \int_V [\delta E_v(R)] \, dV \geq 0 \quad 8.68 \]

where \( \delta E_v(R) \) is the variation of the energy of the volume element located at \( R \). The volume elements may be regarded as fixed since the mechanical coordinates, \( \{q\} \), are unchanged in the variations we are considering, but the local variations of the energy are related to one another since they must not change the total quantities of \( S \) and \( \{N\} \), that is, the values of the integrals 8.66 and 8.67.

There are at least two ways in which the constraints 8.66 and 8.67 can be incorporated into the integral variation of the total energy. The first is by choosing one subvolume (say the one at \( R_0 \)) as a reference volume and using equations 8.66 and 8.67 to eliminate it from the equation. However, this approach is impractical when \( dV \) is arbitrarily small. The second approach is the technique of Lagrange multipliers. This method relies on the following theorem, which is stated here without proof:

*If the function \( \phi(x_1,\ldots,x_n) \) has an extremum at the values \( x'_1,\ldots,x'_n \) when the variables are subject to the \( r \) constraints

\[ h_k(x_1,\ldots,x_n) = 0 \quad (k = 1,\ldots,r) \]

then the function

\[ \Omega(x_1,\ldots,x_n) = \phi - \sum_k \lambda_k h_k \]

where the \( \lambda_k \) are constants, has an extremum at the same values \( x'_1,\ldots,x'_n \) when the \( x_i \) are varied without constraint.*

The constants \( \lambda_k \) are called Lagrange multipliers.

Consider the function

\[ \xi = E - \theta S - \sum_k \gamma_k N_k \quad 8.69 \]

where \( \theta \) and the \( \{\gamma\} \) are Lagrange multipliers. This quantity may be written as a function of the variables \( \{S_v(R)\} \) and \( \{n(R)\} \). The Lagrange theorem states that if \( E \) has an extremum for values of these variables that satisfy the constraints 8.66 and 8.67 then \( \xi \) has an extremum for the same values of these variables when they are imagined to be completely independent. We must then have

\[ \delta \xi = \delta \left[ \int_V (E_v) \, dV \right] - \theta \delta \left[ \int_V (S_v) \, dV \right] \]
\[- \sum_k \gamma_k \delta \left[ \int_V (n_k) \, dV \right] \]

\[= \int_V \left[ \delta E_V - \theta \delta S_V - \sum_k \gamma_k \delta n_k \right] dV \geq 0 \quad 8.70\]

for arbitrary choices of the individual \( \delta S_V(R) \) and \( \delta n_k(R) \). Substituting equation 8.44 at constant values of the mechanical coordinates gives

\[\delta \xi = \int_V \left[ (T - \theta) \delta S_V + \sum_k (\mu_k - \gamma_k) \delta n_k \right] dV \geq 0 \quad 8.71\]

The condition 8.71 must be satisfied for arbitrary positive or negative choices of the variations \( \delta S_V \) and \( \delta n_k \) in the differential subvolume at any position, \( R \). This is only possible if

\[T = \theta \quad 8.72\]

\[\mu_k = \gamma_k \quad 8.73\]

that is, if the temperature and the chemical potentials of all the components are constant throughout. Equations 8.72 and 8.73 are the thermal and chemical conditions of equilibrium. They are necessary conditions that must be satisfied if the system is to be at equilibrium with respect to spontaneous redistributions of its entropy and chemical constituents.

### 8.7.2 Thermochemical Equilibrium in an External Field

Now let the system be subject to a force derived from a scalar potential field, \( \phi(R) \). The common potential fields are the gravitational field, the electric field, and the centrifugal field.

The gravitational field affects every system that has mass. The gravitational potential of a unit mass that is located at the vector position \( R \) is

\[\phi = g(R \cdot e_z) = gh \quad 8.74\]

where \( g \) is the acceleration due to gravity, \( e_z \) is a unit vector in the vertical direction, and \( h \) is scalar height above an arbitrary plane perpendicular to \( e_z \) that is chosen for reference. The gravitational potential of the quantity of component \( k \) located in the unit volume \( dV \) at position \( R \) is then

\[\phi_k(R) = \rho_k \phi(R) = n_k M_k \phi(R) \quad 8.75\]

or

\[\phi_k(R) = n_k \phi_k(R) \quad 8.76\]
where

\[ \phi_k(\mathbf{R}) = M_k \phi(\mathbf{R}) \]  

8.77

The electric field only affects species that are charged. The potential of an elementary charge, \( q \), that is located at the vector position, \( \mathbf{R} \), in a constant electric field, \( \mathbf{E} \), is

\[ \phi(\mathbf{R}) = -q(\mathbf{E} \cdot \mathbf{R}) \]  

8.78

The electric potential per mole of a specie, \( k \), that carries the charge, \( z_q \), is

\[ \phi_k(\mathbf{R}) = -z_q N_0 (\mathbf{E} \cdot \mathbf{R}) \]  

8.79

where \( N_0 \) is Avogadro's number. The electric potential of the quantity of component \( k \) that is located in the volume \( dV \) at \( \mathbf{R} \) is

\[ \phi_k(\mathbf{R}) = n_k \phi_k(\mathbf{R}) = \left[ \frac{\rho_k}{M_k} \right] \phi_k(\mathbf{R}) \]  

8.80

The centrifugal field acts on the mass of a component. The potential of a unit mass located at a distance, \( r \), from the axis of rotation of a system that rotates with the angular velocity \( \omega \) is

\[ \phi(r) = - (\omega r)^2 \]  

8.81

from which the potential energy of a component, \( \phi_k(\mathbf{R}) \), can be derived.

When the system has potential as well as internal energy the First Law applies to its total energy, \( \mathcal{H} = E + \Phi \), and the condition of equilibrium is

\[ (\delta H)_{S_r \{q\} \{N\}} \geq 0 \]  

8.82

The total potential energy is

\[ \Phi = \sum_k \phi_k = \sum_k \left[ \int_V [n_k \phi_k(\mathbf{R})] \, dV \right] \]  

8.83

and its variation is

\[ \delta \Phi = \sum_k \left[ \int_V [\phi_k(\mathbf{R})] \delta n_k \, dV \right] \]  

8.84
The appropriate integral form of the condition 8.82 can be obtained from equation 8.70 by simply adding equation 8.84 to it. The result is to replace the condition 8.71 by the condition

\[ \int_V [(T - \theta)\delta S_V + \sum_k (\mu_k + \phi_k - \gamma_k) \delta n_k] \, dV \geq 0 \]  

8.85

The inequality 8.85 yields two necessary conditions for equilibrium:

\[ T = \theta \]  

8.86

\[ \mu_k + \phi_k = \gamma_k \]  

8.87

The condition of thermal equilibrium is unaffected by the presence of a scalar field. The condition of chemical equilibrium is, however, altered to state that the sum \( \mu_k + \phi_k \) is constant. The chemical potential of a component in an external field changes monotonically to accommodate the change in the potential of the field.

### 8.7.3 Homogeneous Systems

The conditions of thermochemical equilibrium do not determine the equilibrium of the mechanical forces in general, but do when the system is homogeneous.

Consider a system that is homogeneous in the sense that its local state is the same at every point. Such a system evidently cannot be at equilibrium in the presence of external fields, but can exist when the external fields are negligible, when they do not interact with the system, or when they vary so slowly over the dimensions of the system that they can be assumed constant. This situation often exists in practice.

A homogeneous system can be conveniently referred to coordinates that are volumetric densities. Let the mechanical coordinates be chosen to be the set

\[ \{q\} = \{V,\{u\}\} \]  

8.88

where the \( \{u\} \) are independent of the volume (for example, in an elastic solid the \( u \) are the elastic strains). Then the energy density is

\[ E_V = TS_V + \sum_k p_k u_k + \sum_k \mu_k n_k - P \]

\[ = \tilde{E}_V[S_V,\{u\},\{n\}] \]  

8.89

where \(-P\) is the pressure, conjugate to the volume, and homogeneity implies that the coordinates \( S_V, \{u\}, \{n\} \) have the same values for every volume element in the system. It can easily be shown that if the volumetric densities are constant throughout the system.
then the thermodynamic forces are as well. The partial derivatives of equation 8.89 yield the constitutive equations:

\[
T = \left[ \frac{\partial \tilde{E}_V}{\partial S_V} \right] = T^\dagger [S_V, \{v\}, \{n\}] \quad 8.90
\]

\[
p_k = \left[ \frac{\partial \tilde{E}_V}{\partial v_k} \right] = p_k^\dagger [S_V, \{v\}, \{n\}] \quad 8.91
\]

\[
\mu_k = \left[ \frac{\partial \tilde{E}_V}{\partial n_k} \right] = \mu_k^\dagger [S_V, \{v\}, \{n\}] \quad 8.92
\]

since the constitutive variables have the same values everywhere in the system the thermodynamic forces conjugate to those variables are everywhere the same. The thermodynamic pressure is also constant since the Gibbs-Duhem equation is

\[
P = \tilde{P}[T, \{p\}', \{\mu\}] \quad 8.93
\]

from which it follows that the energy density, \(E_v\), also has a constant value.

A homogeneous state satisfies the internal conditions of thermal and chemical equilibrium (we shall show later that it satisfies mechanical equilibrium as well), and has constant values of all thermodynamic forces.

### 8.8 GLOBAL EQUILIBRIUM

#### 8.8.1 Experimentally controllable variables

The fundamental equation for the isolated system, \(\tilde{S}(E,\{q\},\{N\})\), is sufficient for any experimental situation, since any system can be regarded as a subpart of an isolated system that includes its relevant environment. The overall, or "global" equilibrium of the system is determined by the condition that the entropy of the composite system have a maximum value with respect to all changes that do not disturb its isolation. However, the detailed thermodynamic properties of the environment are usually unknown and almost always uninteresting. In order to apply thermodynamics to practical situations it is essential to rephrase the fundamental equation and conditions of equilibrium so that they relate to the system alone.

To accomplish this we let the system be surrounded by walls that govern its interaction with the environment, and let the environment act only as a reservoir that fixes the values of the thermodynamic forces conjugate to the thermodynamic quantities that can be exchanged through the wall. This viewpoint is consistent with experimental practice. The statement that an experiment was done at constant temperature, for example, has the impli-
cation that the system was diathermally enclosed and was in contact with some other system that behaved as a thermal reservoir, such as the air mass in the laboratory or a furnace equipped with a temperature controller. The statement that a property was measured as a function of the stress at constant temperature and composition implies that the system was enclosed in a membrane that was deformable, diothermal and impermeable, and was in contact with a thermal reservoir that also fixed the traction on its boundary. An example is a room temperature tension test that is done under stress control at a rate that is sufficiently slow that vibration and adiabatic heating can be ignored. The laboratory air mass is the thermal reservoir, the mechanical testing machine is the mechanical reservoir, and the surface of the sample is the membrane. The conditions of equilibrium for the isolated system that contains the test sample, the machine and the air mass show that, at equilibrium, the temperature is fixed by that of the air mass, the traction is fixed by the machine, and the composition is fixed by the initial composition of the specimen.

To treat this kind of experiment it is necessary to express the fundamental equation in terms of the variables that are actually controlled and determine conditions of equilibrium that pertain to the specimen alone. This requires the definition of new thermodynamic potentials; one cannot simply re-express the energy and entropy as functions of the controllable variables.

Consider, for example, an experiment in which the system is a fluid and the controlled variables are $T$, $V$, $\{N\}$, that is, the system is in contact with a thermal reservoir across a rigid, impermeable, diothermal wall. If the internal energy of the system is measured as a function of the operational variables the result is

$$E = E^\dagger[T,V,\{N\}]$$

which is the caloric equation of state, not the fundamental equation. Moreover, the equilibria of the system are not characterized by the minima of its energy (or maxima of its entropy). Since the system is in diothermal contact with its environment, it is the combined energy of the system and environment that must be minimized, and the energy minima of the composite system cannot be found from the thermodynamic properties of the system alone.

To treat the system we need an alternate thermodynamic potential that is a form of the fundamental equation when it is written as a function of the variables that are actually controlled, and takes an extreme value when the system is in equilibrium with fixed values of them. A general procedure exists for defining the appropriate thermodynamic potential for a particular experimental situation. The method involves the use of the "Legendre transform" to create a new functions that are mathematically equivalent to the energy and entropy functions.
8.8.2 The Legendre Transform

The Legendre transform is a general mathematical method for replacing a variable by its conjugate partial derivative in the list of independent variables without sacrificing information. It is based on the following theorem.

Let $A$ be a function of the $n$ variables, $x_1,\ldots,x_n$

$$A = \tilde{A}(x_1,\ldots,x_n) \quad 8.95$$

and let $y_1,\ldots,y_n$ be the partial derivatives

$$y_k = \left[ \frac{\partial \tilde{A}}{\partial x_k} \right] \quad 8.96$$

Then the $p^{th}$ Legendre transform of $\tilde{A}$,

$$\Phi_p = A - \sum_{k=1}^{p} y_k x_k$$

$$= \tilde{\Phi}_p(y_1,\ldots,y_p,x_{p+1},\ldots,x_n) \quad 8.97$$

is mathematically equivalent to $A$ and has the partial derivatives

$$\left[ \frac{\partial \tilde{\Phi}_p}{\partial y_k} \right] = -x_k \quad (i = 1,\ldots,p) \quad 8.98$$

$$\left[ \frac{\partial \tilde{\Phi}_p}{\partial x_k} \right] = y_k \quad (i = p+1,\ldots,n) \quad 8.99$$

To prove this theorem consider the differential of the function $\tilde{\Phi}_p$:

$$d\Phi_p = dA - \sum_{k=1}^{p} [y_k dx_k + x_k dy_k] \quad 8.100$$

But since $A$ is a function of $x_1,\ldots,x_n$ with partial derivatives $y_1,\ldots,y_n$ equation 8.100 becomes

$$d\Phi_p = - \sum_{k=1}^{p} x_k dy_k + \sum_{k=p+1}^{n} y_k dx_k \quad 8.101$$
which can be integrated to yield the function 8.97 whose partial derivatives are given by 8.98-99. The constant of integration is fixed by the first form of 8.97. It follows that the function $\Phi_p$ contains precisely the same information as the function $A$. The values of the variables, $x_1,\ldots,x_p$, that were replaced by the variables $y_1,\ldots,y_p$ are determined by the partial derivatives of $\Phi_p$ with respect to the $\{y\}$.

### 8.8.3 The fundamental equation of an interacting system

To formulate the fundamental equation of a system that interacts with its environment it is easiest to begin from the energy function, which is the fundamental equation of an isentropic system. The energy function has the form

$$E = \tilde{E}(\{u\})$$

where the $\{u\}$ are the thermodynamic deformation coordinates. Its partial derivatives define the conjugate thermodynamic forces

$$p_k = \left[ \frac{\partial \tilde{E}}{\partial u_k} \right]$$

and its integrated form is

$$E = \sum_k p_k u_k$$

Consider a system that is enclosed by a wall that permits interaction with respect to the coordinates $u_1,\ldots,u_r$ and forbids all others, and is in contact with a reservoir that fixes the values of the forces $p_1,\ldots,p_r$ that are conjugate to the $u_1,\ldots,u_r$. The operational variables of the interacting system are the forces $p_1,\ldots,p_r$ and the quantities $u_{r+1},\ldots,u_n$. The forces $p_1,\ldots,p_r$ can be controlled experimentally by fixing the forces exerted by the reservoir, and the quantities $u_{r+1},\ldots,u_n$ are determined by the amount of each of these that was present in the system at the time it was sealed off by the wall.

It follows from the properties of the Legendre transform that the function

$$\Phi_r = \tilde{E} - \sum_{k=1}^{r} p_k u_k$$

$$= \tilde{\Phi}_r(p_1,\ldots,p_r,u_{r+1},\ldots,u_n)$$

contains precisely the same information as the function $\tilde{E}(\{u\})$. Its natural variables are the controllable variables ($p_1,\ldots,p_r,u_{r+1},\ldots,u_n$). It includes the remaining thermodynamic quantities and forces through the relations.
These results show that

The function $\tilde{\Phi}_r$ is an alternate form of the fundamental equation, and is
the natural form of the fundamental equation when the variables
$(p_1, \ldots, p_r, u_{r+1}, \ldots, u_n)$ are controlled.

It follows from equations 8.104-105 that $\Phi_1$ has the integrated form

$$\Phi_1 = \sum_{k=r+1}^{n} p_k u_k \quad 8.108$$

The functions, $\tilde{\Phi}_r(p_1, \ldots, p_r, u_{r+1}, \ldots, u_n)$, that provide alternate forms of the fundamental
equation are called the thermodynamic potentials.

A case of particular interest is the $n^{th}$ Legendre transform of the energy function

$$\Phi_n = E - \sum_{k=1}^{n} p_k u_k$$

$$= \tilde{\Phi}_n(\{p\}) \quad 8.109$$

By equation 8.106 the partial derivatives of $\tilde{\Phi}_n$ are the negatives of the thermodynamic
quantities $\{u\}$. But, by equation 8.108, the integrated form is

$$\Phi_n = 0 \quad 8.110$$

which has the consequence that only (n-1) of the n forces in the set $\{p\}$ are independent.
The differential of $\Phi_n(\{p\})$ is the Gibbs-Duhem equation.

### 8.8.4 The conditions of equilibrium in an interacting system

To complete the demonstration that the function

$$\Phi_1 = \tilde{\Phi}_r(p_1, \ldots, p_r, u_{r+1}, \ldots, u_n) \quad 8.111$$

is the fundamental equation of a system for which the mixed set of forces and quantities
$(p_1, \ldots, p_r, u_{r+1}, \ldots, u_n)$ are the controllable variables it remains to show that the equilibrium
states are extrema of the quantity, \( \Phi_t \), for given values of the constitutive variables \((p_1, \ldots, p_r, u_{r+1}, \ldots, u_n)\).

To address this point we consider a composite system that includes the system of interest and its environment, which acts as a reservoir. The local condition of equilibrium for the composite system is

\[
(\delta E)\{u\} \geq 0
\]

Since a general transition alters both the system and the reservoir

\[
\delta E_T = \delta E + \delta E_r
\]

where \(E_T\) and \(E_r\) refer to the energy of the composite system and the reservoir, respectively, and \(E\) designates the energy of the system.

An infinitesimal transition in the reservoir can be regarded as the sum of a quasi-static change in its state that is due to an interaction with the system and an internal change in state that does not affect the system. Transitions of the second kind cannot occur if the reservoir is in equilibrium, and are of no interest anyway since they do not affect the system. We therefore ignore them, and require that any changes in the reservoir happen quasi-statically.

The interaction between the reservoir and the system depends on the nature of the wall that separates them. However, the interactions can be divided into three types: thermal, chemical and mechanical (including electromagnetic interactions). The thermal interaction is governed by the entropy, which is a conserved quantity since the total entropy is constant in the variations included in equation 8.112. It follows that, if the wall is diothermal,

\[
\delta S_r = - \delta S
\]

and, since thermal equilibrium requires that \(T_r = T_s = T\),

\[
(\delta E_r)_{\text{thermal}} = T \delta S_r = - T \delta S
\]

A similar relation holds for the chemical interaction of the \(k\)th specie if the wall is permeable to this component. Since the total quantity of the \(k\)th independent component is conserved,

\[
\delta N^r_k = - \delta N_k
\]

Since, moreover, the condition of chemical equilibrium requires that

\[
\mu^r_k = \mu_k
\]
if the wall is permeable to the \( k \)th component (even in the presence of potential fields, since the systems are in contact at the wall),

\[
(\delta E_r)_{\text{chemical}} = \sum_k \left[ \mu_k^r \delta N_k^r \right]
\]

\[
= - \sum_k \mu_k \delta N_k
\]

8.118

where the summation is taken over the components that can pass through the wall.

The mechanical interaction is more complicated. Its detailed form depends on the mechanical coordinates, and is changed if interfaces are present (such as the wall) that have mechanical properties of their own. Assuming that these are negligible (we shall treat interfaces in a later section) we can use the fact that energy is conserved during interactions between the system and the reservoir to state that

\[
\delta E_r = (\delta E_r)_{\text{thermal}} + (\delta E_r)_{\text{chemical}} + \delta W_r
\]

\[
= - \delta E
\]

8.119

from which it follows that

\[
\delta W_r = - \delta W = - \sum_k p_k \delta q_k
\]

8.120

where the mechanical force, \( p_k \), and the coordinates \( q_k \) refer to the system, and the summation is taken over all mechanical coordinates whose variation is permitted by the wall.

Now assume that the system is enclosed in a wall that permits an interchange of the quantities \( u_1, \ldots, u_r \). The values of the conjugate forces, \( p_1, \ldots, p_r \), are fixed by the reservoir. The reversible change in the energy of the reservoir is then

\[
\delta E_r = - \sum_{k=1}^r p_k \delta u_k
\]

8.121

where the quantities \( u_k \) are the \( r \) geometric coordinates of the system that are affected by the interaction with the reservoir. The total energy change is

\[
\delta E_T = \delta E - \sum_{k=1}^r p_k \delta u_k \geq 0
\]

8.122
if the system is in equilibrium. Note that all of the quantities on the left hand side of the inequality 8.122 refer to the system; the properties of the reservoir no longer appear.

Since the \( r \) forces \( p_k \) are fixed by the reservoir, the condition for equilibrium can be rewritten

\[
\delta E_T = \delta \left[ E - \sum_{k=1}^{r} p_k u_k \right] \geq 0
\]

The quantity in brackets is a Legendre transform of \( \tilde{E} \), and is that particular Legendre transform that reformulates the fundamental equation in terms of the natural variables of the interacting system:

\[
\Phi_k = E - \sum_{k=1}^{r} p_k u_k
\]

\[
\Phi_k(p_1,\ldots,p_r,u_{r+1},\ldots,u_n) \quad 8.124
\]

The condition of equilibrium is, hence,

\[
(\delta \Phi)\{p_1\ldots p_r\}\{u_{r+1}\ldots u_n\} \geq 0
\]

It follows in general that

*if the controlled set of constitutive variables for a system includes the thermodynamic forces \( \{p\}' \) and deformation quantities \( \{u\}' \), then when the system is in equilibrium the thermodynamic potential whose natural variables are \( \{p\}' \) and \( \{u\}' \) has an extreme value with respect to all perturbations that maintain the values of these quantities.*

The appropriate thermodynamic potential is obtained from the energy function by using the Legendre transform to introduce each of the controlled forces, \( p_k \), in place of its conjugate deformation coordinate, \( u_k \).

It is straightforward to generalize these results to obtain the local condition of stability and the global condition of equilibrium, which have the form given in section 8.2 with the potential \( \Phi \) replacing the energy.

### 8.9 THERMODYNAMIC POTENTIALS

The thermodynamic potentials that are most commonly used were originally formulated to treat the thermodynamics of simple fluids. They are the Legendre transforms of the
energy function with respect to the thermal, chemical or mechanical coordinates taken as a set. They are easily generalized to arbitrary sets of coordinates. To define them we start with the integrated form of the energy function:

\[ E = TS + \sum_k p_k q_k + \sum_k \mu_k N_k \]  

where the \( \{q\} \) are the mechanical coordinates and the \( \{N\} \) are the mole or atom numbers of the chemical components.

### 8.9.1 Diathermal walls: the Helmholtz free energy

Let the system be in contact with a thermal reservoir across a rigid, diathermal, impermeable wall. The operational variables are \( T, \{q\}, \) and \( \{N\}. \) The appropriate form of the fundamental equation is

\[ F = E - TS = \sum_k p_k q_k + \sum_k \mu_k N_k \]

\[ = \tilde{F}(T,\{q\},\{N\}) \]  

where the quantity \( F \) is called the **Helmholtz free energy.** The partial derivatives of \( \tilde{F} \) are:

\[ \left[ \frac{\partial \tilde{F}}{\partial T} \right] = -S \]  

\[ \left[ \frac{\partial \tilde{F}}{\partial q_k} \right] = p_k \]  

\[ \left[ \frac{\partial \tilde{F}}{\partial N_k} \right] = \mu_k \]

The condition of equilibrium for the system is that the Helmholtz free energy be a minimum:

\[ (\delta F)_{T,\{q\},\{N\}} \geq 0 \]

The Helmholtz free energy is widely used in the thermodynamics of solids since the temperature is commonly controlled and the forces exerted on solids in typical applications (for example, atmospheric pressure) have so little consequence that the mechanical deformation coordinates can be assumed constant.
8.9.2 Deformable walls: the enthalpy

Let the system be in contact with a mechanical reservoir across an impermeable, adiabatic wall. The reservoir fixes the mechanical forces, \{p\}. If we assume that the system is internally in equilibrium the operational variables are \(S, \{p\}, \{N\}\). The appropriate form of the fundamental equation is:

\[
H = E - \sum_k p_k q_k + TS + \sum_k \mu_k N_k
\]

\[
= \tilde{H}(S, \{p\}, \{N\}) \tag{8.132}
\]

where \(H\) is called the enthalpy. The partial derivatives of the enthalpy function, \(\tilde{H}\), are:

\[
\left[ \frac{\partial \tilde{H}}{\partial S} \right] = T \tag{8.133}
\]

\[
\left[ \frac{\partial \tilde{H}}{\partial p_k} \right] = - q_k \tag{8.134}
\]

\[
\left[ \frac{\partial \tilde{H}}{\partial N_k} \right] = \mu_k \tag{8.135}
\]

The condition of equilibrium for the system is that the enthalpy be a minimum:

\[
(\delta H)_S, \{p\}, \{N\} \geq 0 \tag{8.136}
\]

The enthalpy is rarely used in the thermodynamics of solids, but is often used in the thermodynamics of fluid flow, where mechanical relaxations in the local state of the fluid often take place so rapidly that heat flow can be ignored.

8.9.3 Diathermal, deformable walls: the Gibbs free energy

Let the system be in contact with a thermal and mechanical reservoir across a wall that is diathermal and deformable, but impermeable. The reservoir fixes the temperature and the mechanical forces. The operational variables are hence \(T, \{p\}, \{N\}\). The appropriate form of the fundamental equation is:
where \( G \) is called the Gibbs free energy. The quantity \( G \) is sometimes referred to as the chemical energy function since its integrated value is completely determined by the chemical content and the chemical potentials. The differentials of the Gibbs free energy function, \( G \), are:

\[
\begin{align*}
\left[ \frac{\partial \tilde{G}}{\partial T} \right] & = -S & \text{(8.138)} \\
\left[ \frac{\partial \tilde{G}}{\partial p_k} \right] & = -q_k & \text{(8.139)} \\
\left[ \frac{\partial \tilde{G}}{\partial N_k} \right] & = \mu_k & \text{(8.140)}
\end{align*}
\]

The condition of equilibrium for the system is that its Gibbs free energy be a minimum:

\[
(\delta G)_{T,\{p\},\{N\}} \geq 0 & \quad \text{(8.141)}
\]

The Gibbs free energy is widely used in materials science since the temperature and mechanical forces are often controlled (automatically if the material is in contact with the atmosphere), and since chemical reactions with the environment are often so slow that they can be ignored.

### 8.9.4 Open walls: the work function

Let the system be in contact with a thermal and chemical reservoir across an open boundary (rigid, diathermal, permeable). The temperature and the chemical potentials are fixed by the reservoir. Hence the operational variables are \( T \), \( \{q\} \), and \( \{\mu\} \). The appropriate form of the fundamental equation is

\[
\Omega = E - TS - \sum_k p_k q_k = \sum_k \mu_k N_k
\]

\[
= \tilde{\Omega}(T,\{q\},\{\mu\}) & \quad \text{(8.142)}
\]

where \( \Omega \) is called the work function, because its integrated value is determined by the mechanical variables. The partial derivatives of the work function, \( \Omega \), are:
\[
\left[ \frac{\partial \Omega}{\partial T} \right] = -S \quad 8.143
\]

\[
\left[ \frac{\partial \Omega}{\partial q_k} \right] = p_k \quad 8.144
\]

\[
\left[ \frac{\partial \Omega}{\partial \mu_k} \right] = -N_k \quad 8.145
\]

The condition of equilibrium for the system is that its work function be a minimum:

\[(\delta \Omega)_T,\{q\},\{\mu\} \geq 0 \quad 8.146\]

The work function is often used to treat problems that involve chemical reactions or chemical redistributions within solids.

### 8.9.5 Hybrid walls: hybrid potentials

When there is more than one chemical or mechanical coordinate then it is possible for the system to be contained within walls that permit only a restricted set of chemical or mechanical interactions. These are called hybrid walls, and lead to the definition of hybrid potentials by the appropriate Legendre transformations. A variety of such functions can be defined and may be useful for particular problems. Most of them have no particular names (although, as we shall see, the function that is often called the Gibbs free energy of an elastic solid is a hybrid function).

As one example of a hybrid function, let a system be in contact with a thermal and chemical reservoir across a rigid, semipermeable membrane that will pass only one of its \(n\) components. If this component is designated the \(n^{th}\), the operational variables are \(T\), \(\{q\}\), \(\{N\}'\), and \(\mu_n\), where the set \(\{N\}'\) contains the first \(n-1\) chemical components. The appropriate form of the fundamental equation is

\[
\Omega_n = E - TS - \mu_n N_n = \sum_k p_k q_k + \sum_{k=1}^{n-1} \mu_k N_k
\]

\[
= \Omega_n(T,\{q\},N_1,...,N_{n-1},\mu_n) \quad 8.147
\]

This function is minimum at equilibrium.

### 8.9.6 Massieu functions

The entropy function can be written in the integrated form
\[ S = \beta E - \sum_k (\beta p_k) q_k - \sum_k (\beta \mu_k) N_k \]

\[ = \tilde{S}(E,\{q\},\{N\}) \quad 8.148 \]

where

\[ \beta = \frac{1}{T} \quad 8.149 \]

and

\[ \frac{\partial \tilde{S}}{\partial E} = \beta \quad 8.150 \]

\[ \frac{\partial \tilde{S}}{\partial q_k} = -\beta p_k \quad 8.151 \]

\[ \frac{\partial \tilde{S}}{\partial N_k} = -\beta \mu_k \quad 8.152 \]

This form of the fundamental equation has a more direct physical meaning than the energy function, \( E \), since it is the fundamental equation for the isolated system. The condition for the equilibrium of an isolated system is that \( S \) be a maximum.

The entropy function, \( \tilde{S} \), can be used to define an alternate set of thermodynamic potentials by Legendre transformation with respect to the forces \( \beta, -\beta p_k \), and \( -\beta \mu_k \). These functions are called Massieu functions. They are also examples of the fundamental equation. They are appropriate when their natural variables are controllable, and have maximal values in the equilibrium states.

The common Massieu functions are:

\[ \Psi_1 = S - \beta E = -\beta F \]

\[ = \tilde{\Psi}_1(\beta,\{q\},\{N\}) \quad 8.148 \]

\[ \Psi_2 = S - \beta E + \sum_k \beta p_k q_k = -\beta G \]

\[ = \tilde{\Psi}_2(\beta,\{p\},\{N\}) \quad 8.149 \]

\[ \Psi_3 = S - \beta E + \sum_k \beta \mu_k N_k = -\beta \Omega \]
\[ \Psi_3(\beta, \{q\}, \{\beta \mu\}) \]

8.150

The Massieu functions are not commonly used in classical thermodynamics, but are used widely, albeit implicitly, in statistical thermodynamics. As we shall see, the various partition functions that are defined in statistical thermodynamics are directly related to the Massieu functions.

### 8.9.7 Densities of the thermodynamic potentials

The volume, mass, or molar density of any thermodynamic potential is obtained by simply dividing its integrated form by the appropriate quantity. The most useful measures of system size are the volume, \( V \), and the total molar (N) or mass content (m). To use either, one defines the set of constitutive coordinates so that the measure of size is a member of the set, and then divides it out. To employ volumetric densities the set of mechanical coordinates is taken to be

\[ \{q\} = \{V, \{v\}\} \]

8.151

where the \( \{v\} \) can be varied independently of \( V \). To employ molar (or mass) densities the set of chemical coordinates is taken to be

\[ \{N\} = \{N, \{x\}\} \]

8.152

where \( N \) is the total molar content and the set \( \{x\} \) includes the (n-1) independent concentrations of the n individual species.

This approach is useful when the measure of system size (\( V, N \) or \( M \)) is a member of the natural set of coordinates of the function whose density is to be defined. Since both \( V \) and \( N \) are natural variables for the energy, \( E \), and the Helmholtz free energy, \( F \), both the volumetric densities, \( E_v \) and \( F_v \), and the molar densities, \( e \) and \( f \), are useful thermodynamic densities; each is not only independent of the system size, but has only less independent variable than the potential, \( E \) or \( F \), itself. This is not true of the other thermodynamic potentials. For example, the Gibbs free energy, \( G \), is a natural function of the mole number, \( N \), but is not a natural function of the volume, \( V \). The Gibbs free energy is the relevant thermodynamic potential when the pressure, \( P \), is controlled, and \( P \) can only be controlled by adjusting \( V \), which is necessarily uncontrolled. The work function, \( \Omega \), is a natural function of the volume, \( V \), but is not a natural function of the molar content, since it pertains when the chemical potentials rather than the chemical contents are controlled.

The Gibbs free energy per mole, \( g \), obeys the fundamental equation

\[ g = e - Ts - \sum_k p_k q_k^n = \sum_k \mu_k x_k \]
\[ = g(T,\{p\},\{x\}) \]

and has the partial derivatives

\[
\frac{\partial g}{\partial T} = - s \quad 8.154
\]

\[
\frac{\partial g}{\partial p_k} = - q^p_k \quad 8.155
\]

\[
\frac{\partial g}{\partial x_k} = \mu_k \quad (k = 1,\ldots,n-1) \quad 8.156
\]

where \( \mu_k \) is the relative chemical potential of the \( k^{th} \) component. The number of constitutive coordinates, and conjugate forces, is reduced by one. It is possible to define a Gibbs free energy per unit volume \( (G_v) \), and this is done with surprising frequency in the materials literature. But it makes very little sense to do so, since the volume is not controlled in situations where \( G \) is used. For this reason, the variables that govern \( G_v \) are as numerous as those that govern \( G \) itself.

The Helmholtz free energy per unit volume \( (F_v) \) obeys the fundamental equation:

\[
F_v = E_v - TS_v = \sum_k \mu_k n_k + \sum_k p_k v_k
\]

\[
= \tilde{F}_v(T,\{v\},\{n\}) \quad 8.157
\]

Since the set of volume-independent mechanical coordinates, \( \{v\} \), contains one less variable than the set of mechanical coordinates, \( \{q\} \), the total number of coordinates is reduced by one. The partial derivatives are:

\[
\frac{\partial \tilde{F}_v}{\partial T} = - S_v \quad 8.158
\]

\[
\frac{\partial \tilde{F}_v}{\partial v_k} = p_k \quad 8.159
\]

\[
\frac{\partial \tilde{F}_v}{\partial n_k} = \mu_k \quad 8.160
\]

The densities of the other thermodynamic potentials are defined in a similar way.
8.10 **MAXIMUM WORK**

We found in Chapter 6 that the maximum work that can be done by an adiabatic system in an isometric transition is the change in the energy at constant entropy:

\[
\delta w_{\text{max}} = - \delta W_{\text{max}} = - (\delta E)_{S,\{q\},\{N\}}  
\]

Note that in this case the energy function is the appropriate form of the fundamental equation. In order for the system to do work at all its initial state must not satisfy the global condition of equilibrium, since otherwise the change in the value of the energy function would necessarily be positive. The right-hand side of equation 8.161 measures the progress toward equilibrium in terms of the value of the fundamental function; the same quantity gives the maximum possible work.

This result can be generalized into the following theorem:

*Given an interacting system for which the variables \((p_1, \ldots, p_r, u_{r+1}, \ldots, u_n)\) are controlled, the maximum work that can be done as the system evolves toward equilibrium is

\[
w_{\text{max}} = - \Delta \Phi_r \tag{8.162}
\]

where \(\Phi_r(p_1, \ldots, p_r, u_{r+1}, \ldots, u_n)\) is the governing potential of the system.*

To prove this theorem let the system of interest be joined with the reservoir that fixes the values of \((p_1, \ldots, p_r)\) into a composite system, across a partition that is only permeable to the quantities \((u_1, \ldots, u_r)\). Let the composite system approach equilibrium by changes in the system of interest; the reservoir is of no interest and can be assumed to be in equilibrium throughout. The maximum possible work is

\[
w_{\text{max}} = - (\Delta E_T)_{\{u\}} = - (\Delta E + \Delta E_r)_{\{u\}} \tag{8.163}
\]

where the symbol \(r\) labels the reservoir. The change in energy of the reservoir in an infinitesimal transition is given by equation 8.121. Since the forces are held constant during the transition this equation integrates to

\[
\Delta E_r = - \sum_{k=1}^{r} p_k \Delta u_k \tag{8.164}
\]

where the \(p_k\) and the \(\Delta u_k\) refer to the system. Substituting this result in equation 8.163,

\[
w_{\text{max}} = - (\Delta E - \sum_{k=1}^{r} p_k \Delta u_k)
\]
\[ - \Delta(E - \sum_{k=1}^{r} p_k u_k) = - \Delta \Phi_f \] 8.165

which establishes the theorem.

Among its other implications, this result shows that, since the earth is effectively a T, P reservoir, the useful work that is available to it is the excess of its Gibbs free energy. As we have all come to discover, however, this energy is anything but free.

### 8.11 RELATIONS BETWEEN THE THERMODYNAMIC POTENTIALS

A set of useful relations between the thermodynamic potentials can be found in the following way. Let the function \( \Phi \) be a first Legendre transform of the function \( \Psi \). Then

\[
\Phi = \Psi - pq
\] 8.166

where

\[
q = - \left[ \frac{\partial \Phi}{\partial p} \right]
\] 8.167

Then

\[
\Psi = \Phi - p \left[ \frac{\partial \Phi}{\partial p} \right] = - p^2 \left[ \frac{\partial}{\partial p} \left( \frac{\partial \Phi}{\partial p} \right) \right]
\] 8.168

For example,

\[
E = - T^2 \left[ \frac{\partial}{\partial T} \left( \frac{\Phi}{T} \right) \right]
\] 8.169