The two types of phase equilibria, the normal unconstrained one and the constrained one, and their thermodynamics are discussed. The concepts of potential and phase rule, which have recently been discussed in the literature, are reconsidered, and their formal definitions are analyzed in some detail. It is realized that in the unconstrained equilibrium system, the properly defined chemical potentials of all components must be constant across the phase interface in both the hydrostatically and nonhydrostatically stressed systems. It is demonstrated that in a constrained equilibrium system, e.g. with a coherent equilibrium or paraequilibrium, the discussion of the phase rule is rather meaningless even though it is possible to find a relationship between the number of independent potentials and phases. On the other hand, a constrained equilibrium system may be treated as a normal equilibrium by describing its equilibrium features with a different definition of the system.

1. Introduction

As demonstrated, phase equilibria in crystalline solids, which are often nonhydrostatically stressed, may differ remarkably from the phase equilibria in fluid systems.\(^1\)\(^-\)\(^8\) Also, the Gibbs phase rule, originally derived for a fluid system under uniform pressure, i.e. hydrostatic stress,\(^1\) may need to be modified in the nonhydrostatically stressed system, particularly in a coherent system.\(^7\)\(^-\)\(^10\) Unfortunately, these observations have led to a less clear meaning of fundamental thermodynamic concepts, like thermodynamic potential and the Gibbs phase rule.

Before more detail is presented, an important point should be emphasized. As soon as the system and its components have been defined, and there are not yet any restrictions on the possible reactions inside the system, a normal unconstrained equilibrium may be established. If the system is constrained, certain types of reactions are prohibited, and one can define only a constrained equilibrium. However, this distinction is somewhat arbitrary. A mixture of the species H\(_2\), O\(_2\), and H\(_2\)O may be considered as a two-component system because the third species may form by a reaction between the other two, a three-component system if temperature is such that the reaction rate is negligible, or even a one-component system if H\(_2\) and O\(_2\) are allowed to transfer between the system and the surrounding only in the proportions defined by H\(_2\)O. There are thus cases where a constrained equilibrium may be treated as a normal equilibrium if a special definition of the system is used.

In thermodynamics, there are two kinds of variables, potentials and extensive variables. The potentials are intensive variables that have constant value in the equilibrium system. By dividing any extensive variable by the size of the system or a phase in the system, one obtains another kind of intensive variables, usually called molar or specific variables. Its value usually varies from phase to phase.

On the other hand, Johnson and Schmalzried\(^1\)\(^1\) used the terms of thermodynamic field and thermodynamic density, introduced by Griffiths and Wheeler,\(^1\)\(^2\) in discussion of Gibbs phase rule. In their work, the thermodynamic variables that are constant in a system at equilibrium are defined as thermodynamic fields, and their conjugate variables are thermodynamic densities. In their definition, a thermodynamic variable could be either a thermodynamic field or a thermodynamic density depending upon how the system is constrained. For example, the strain components are usually considered as specific variable or thermodynamic density in unstressed equilibrium systems. But some of them will be thermodynamic fields in a coherent equilibrium system, and some stress components will then be thermodynamic densities. It was claimed that by simply replacing the thermodynamic potentials with thermodynamic fields in fundamental thermodynamics, the unconstrained and constrained systems can be treated in precisely the same way.

Furthermore, following their definition of thermodynamic fields (or rather potentials) and considering the partitionless transformation and paraequilibrium,\(^1\)\(^3\)\(^,\)\(^4\) one would have to accept that the compositions are thermodynamic fields, and their chemical potentials are thermodynamic densities. This kind of treatment does not reflect the physical behavior of the system. Note also that the equality of potentials in various phases at equilibrium is a property of potentials, but not the definition of them, as potentials can be well defined in a one-phase system.

In addition, in older literature, some thermodynamic state functions, e.g. the Gibbs energy and the Helmholtz energy, have names containing the word potential even though it is...
clear that the function itself is not a potential. For example, see Ref. 15.

The present report analyzes the fundamental concepts of potential and equilibrium. Some thermodynamic aspects of unconstrained and constrained equilibria are discussed aiming to present a less complicated picture. Partitionless transformation, paraequilibrium, and coherent equilibrium also are considered, and it is demonstrated that caution must be taken when examining the Gibbs phase rule in such constrained systems since the Gibbs phase rule expresses the number of potentials that can be varied independently from the outside of a system without forming a new phase or losing an old phase as emphasized by Hillert. In the following, the term equilibrium is simply used for normal unconstrained equilibrium.

2. Definition of Thermodynamic Potentials

In the definition of chemical potentials, Gibbs considered “the energy of a homogeneous mass as a function of its entropy, its volume, and the quantities of the various substances composing it. Then the potential for one of these substances is defined as the differential coefficient of the energy taken with respect to the variable expressing the quantity of that substance.”

In the spirit of Gibbs, the authors define the potential in a more general way. Let \( q_i \) be a set of scalar variables that express the amounts of some extensive quantities that may be added to the system from the outside. In addition, all the \( q_i \) can be varied independently. There may be more than one way to define a set of independent variables, \( q_i \). An independent set is defined in such a way that the change of the system accomplished by varying one of the variables may not be accomplished by varying a combination of the others. Assume that the different \( q_i \) have been fixed, and the system has come to rest at equilibrium. The internal energy \( U \) of the system then has a well-defined value, which depends on the external conditions, i.e.:

\[
U = U(q_1, q_2, \ldots) \quad \text{(Eq 1)}
\]

To each \( q_i \), there is a conjugate potential \( \psi_i \) defined as:

\[
\psi_i = \left( \frac{\partial U}{\partial q_i} \right)_{q_{i-1}} \quad \text{(Eq 2)}
\]

The derivative is taken while keeping all the other \( q_i \) constant. From the extensive character of \( U \) and \( q_i \), it follows that:

\[
U = \sum_i q_i \psi_i \quad \text{(Eq 3)}
\]

where the summation is taken over all \( i \). The combination of the first and second laws of thermodynamics is, for a system in equilibrium,

\[
dU = \sum_i \psi_i dq_i \quad \text{(Eq 4)}
\]

A new state function may be defined by moving one or several terms in the summation to the left-hand side of the equation. For example, by moving the term \(-PV\), the enthalpy, \( H \), is obtained, and by moving also the term \( TS \), the Gibbs energy, \( G \), is obtained, etc. In fact, to each subset of combinations of \( q_i \), there exists a thermodynamic state function,

\[
\Phi_j = \sum_{i \in j} \psi_i q_i \quad \text{(Eq 5)}
\]

where \( i \in j \) means the summation of the \( i \) in the subset of \( j \). For a system that is not at equilibrium, the internal energy will vary also with some internal variables \( \xi_i \), i.e. \( U = U(q_1, q_2, \ldots, \xi_1, \xi_2, \ldots) \). In this connection, it may be convenient to regard the \( q_i \) as external extensive variables. If all of them are kept fixed, the internal variables \( \xi_i \) will take such values at equilibrium that the internal energy \( U \) is minimized. If one or several of the potentials are fixed rather than the conjugate \( q_i \), the corresponding \( \Phi_j \) must be minimized in order to find the equilibrium state.

Note that the \( q_i \) are extensive external variables; i.e. their values may be directly controlled from outside the system. The conjugate potentials are thus properties of the system as a whole. If the system is divided into two subsystems and the redistribution of \( q_i \) is considered an internal variable of the whole system but an external variable of the subsystems, then, at equilibrium, the conjugate potential to \( q_i \), i.e. \( \psi_i \), must have the same value in the two subsystems.

The above equations also hold locally in inhomogeneous systems when sufficiently small regions can be approximated as homogeneous. However, it is usually more convenient to introduce the energy density in an inhomogeneous system and replace the \( q_i \) with the corresponding densities, i.e. molar or specific quantities.

3. Equilibrium in Inhomogeneous Systems

A thorough treatment of equilibrium conditions in an inhomogeneous system was carried out by Larché and Cahn in which purely elastic problems were first solved and the composition distribution was then calculated from the solution of the elastic problem. However, their papers contain some heavy algebra and are difficult to follow. The present authors attempt a simpler approach.

As elastic problems are often difficult to solve, consider a very simple situation, namely the influence of gravity on the internal equilibrium in a vertical tube considered by Gibbs. Gibbs found the following chemical equilibrium condition under constant temperature and volume:

\[
\mu_i + M_i gh = \text{constant} \quad \text{(Eq 6)}
\]

The left side of Eq 6 may be defined as a new chemico-gravitational potential of component \( i \), which is constant through the system. \( \mu_i \) is the normal chemical potential of component \( i \); i.e. it is “entirely determined at any point in the mass by the nature and state of the mass about that point.” \( M_i \) is the molar mass, \( h \) is the height, and \( g \) is the acceleration of gravity. In Gibbs’ original equation, \( \mu_i \) was expressed per unit of mass, and \( M_i \)