

THE INTERNATIONAL
ENCYCLOPEDIA
OF PHYSICAL CHEMISTRY
AND CHEMICAL PHYSICS

SOLID-LIQUID EQUILIBRIUM

BY

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Volume 1
SOLID-LIQUID EQUILIBRIUM

BY

R. HAASE AND H. SCHÖNERT

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INTRODUCTION

THE International Encyclopedia of Physical Chemistry and Chemical Physics is a comprehensive and modern account of all aspects of the domain of science between chemistry and physics, and is written primarily for the graduate and research worker. The Editors-in-Chief, Professor D. D. ELEY, Professor J. E. MAYER and Professor F. C. TOMPKINS, have grouped the subject matter in some twenty groups (General Topics), each having its own editor. The complete work consists of about one hundred volumes, each volume being restricted to around two hundred pages and having a large measure of independence. Particular importance has been given to the exposition of the fundamental bases of each topic and to the development of the theoretical aspects; experimental details of an essentially practical nature are not emphasized, although the theoretical background of techniques and procedures is fully developed.

The Encyclopedia is written throughout in English and the recommendations of the International Union of Pure and Applied Chemistry on notation and cognate matters in physical chemistry are adopted. Abbreviations for names of journals are in accordance with *The World List of Scientific Periodicals*.

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CHAPTER 1

BASIC PRINCIPLES

1.1. Introduction

A solid-liquid equilibrium is a heterogeneous equilibrium involving the coexistence of solid and liquid phases. The solids and liquids may be pure substances or mixtures. We shall assume isotropic media throughout and shall ignore external force fields (gravity, centrifugal force, electromagnetic field) as well as surface phenomena. The properties of each phase of a heterogeneous system will then be determined by the temperature, the pressure, and the concentrations of the various substances which constitute the phase. Should the amount of a phase be of interest, the total mass, the total amount of substance, or the volume must also be known.

We start with a summary (Chapter 1) of the most important thermodynamic equations which we shall need.‡ This is followed by a discussion of the determination of molecular weights and activity coefficients from solid-liquid equilibria in order to give the reader easy access to these subjects which constitute a major interest of research workers in the modern literature (Chapter 2).

Chapter 3 is the beginning of the systematic treatment of solid-liquid equilibria based on the classic investigations of Gibbs, van der Waals, van Rijn van Alkemade, and Schreinemakers, and on Gibbs's graphical derivation of phase diagrams from Gibbs function curves or surfaces. These elegant and powerful methods which we are trying to present here in the modern idiom, have so far hardly appeared even in recent textbooks.

The systematic treatment of solid-liquid equilibria is confined for reasons of practicability to one-component systems (Chapter 3), two-component systems (Chapter 4), and three-component systems (Chapter 5). § 2.7 and Chapter 6 are devoted to a brief description of experimental methods.

‡ For the derivation of the basic equations cf. R. Haase, *Thermodynamik der Mischphasen*, Springer-Verlag, Berlin-Göttingen-Heidelberg, 1956.

1.2. Conditions for Equilibrium

According to classical thermodynamics the conditions for the co-existence of several phases (denoted by \prime , $\prime\prime$, \dots , ϕ) with contiguous natural boundaries are:[‡]

$$T' = T'' = \dots = T^\phi = T, \quad (1.2.1)$$

$$P' = P'' = \dots = P^\phi = P, \quad (1.2.2)$$

$$\mu'_i = \mu''_i = \dots = \mu^\phi_i = \mu_i, \quad (1.2.3)$$

where T is the thermodynamic temperature, P the pressure, and μ_i the chemical potential of the molecular species i . Equation (3) applies to all the molecular species capable of penetrating the relevant phase boundaries.

If a chemical reaction can occur within a phase α the condition for homogeneous chemical equilibrium is

$$\sum_i \nu_i \mu_i = 0, \quad (1.2.4)$$

where ν_i is the stoichiometric number for the molecular species i in the chemical equation for the reaction (positive when the species i appears on the right-hand side of the equation and negative when it is on the left). The condition for the heterogeneous chemical equilibrium is found from the combination of eqns. (3) and (4).

When, for example, sodium chloride in the crystalline state (phase \prime) coexists with an aqueous solution (phase $\prime\prime$), eqn. (3) becomes:

$$\mu'_{\text{NaCl}} = \mu''_{\text{NaCl}}.$$

According to eqn. (4)

$$\mu''_{\text{NaCl}} = \mu''_{\text{Na}^+} + \mu''_{\text{Cl}^-} \text{ (dissociation equilibrium).}$$

Combination of these two equations gives

$$\mu'_{\text{NaCl}} = \mu''_{\text{Na}^+} + \mu''_{\text{Cl}^-} \text{ (heterogeneous chemical equilibrium).}$$

The quantity μ''_{NaCl} can be regarded either as the chemical potential of the molecular species NaCl (undissociated sodium chloride) in the solution or as the chemical potential of the “component” NaCl. Only

[‡] A discussion of semi-permeable walls and osmotic equilibria is excluded.

the latter interpretation makes sense in the case of complete dissociation.

It is often convenient to describe a system by the number of components in it rather than by the number of molecular species. This results in a reduction in the number of independent equilibrium conditions. The number of molecular species N^* is related to the number of components N by

$$N = N^* - B, \quad (1.2.5)$$

where B is the number of independent relations between the temperature, the pressure, and the concentrations of the substances involved. These relations may involve, for example, the existence of chemical equilibria or electrical neutrality in mixtures containing ions.

Taking an aqueous sodium chloride solution as an example, we neglect the dissociation of water and thus have four kinds of particles: H_2O , NaCl , Na^+ , Cl^- . The dissociation equilibrium



and the condition of electrical neutrality

$$c_{\text{Na}^+} = c_{\text{Cl}^-}$$

(c_i = molarity of species i) give two independent relations between the concentrations, i.e. $B = 2$. According to eqn. (5) we therefore have two components ($N = 2$, binary system). We shall obviously choose water and sodium chloride as the components of the liquid phase.

We thus have, in the component representation, N equilibrium conditions instead of N^* equations of type (3). μ_i now denotes the chemical potential of component i , and eqn. (4) no longer appears explicitly.

Systems with 1, 2, 3, 4, etc., components are called one-component systems, binary, ternary, quaternary, etc. systems.

In order to represent heterogeneous equilibria graphically, it is convenient to start with the molar Gibbs function[‡] \bar{G}^α of a phase α . Ignoring for the moment the phase index α , we denote the (stoichiometric) mole fraction of component i in the relevant phase by x_i and use the identity

$$\sum_{i=1}^N x_i = 1 \quad (1.2.6)$$

[‡]Let us denote any extensive property by Z . Then, by definition, the molar quantity Z is

$$Z \equiv Z/n,$$

where n is the total amount of substance in the phase considered.

to eliminate x_N , the mole fraction of component N , as a dependent quantity:

$$\bar{G} = \bar{G}(T, P, x_1, x_2, \dots, x_{N-1}) = \sum_{i=1}^N x_i \mu_i, \quad (1.2.7)$$

$$\left(\frac{\partial \bar{G}}{\partial T} \right)_{P, x_i} = -\bar{S}, \quad (1.2.8)$$

$$\left(\frac{\partial \bar{G}}{\partial P} \right)_{T, x_i} = \bar{V}, \quad (1.2.9)$$

$$\left(\frac{\partial \bar{G}}{\partial x_i} \right)_{T, P, x_j} = \mu_i - \mu_N \quad (i, j = 1, 2, \dots, N-1; i \neq j). \quad (1.2.10)$$

\bar{S} is the molar entropy, \bar{V} the molar volume of the phase.

From eqns. (6), (7), and (10) it follows that

$$\bar{G} - \sum_{i=1}^{N-1} x_i \left(\frac{\partial \bar{G}}{\partial x_i} \right)_{T, P, x_j} = \mu_N. \quad (1.2.11)$$

The N equilibrium conditions for two coexisting phases (denoted by ' and ")

$$\mu'_i = \mu''_i \quad (i = 1, 2, \dots, N), \quad (1.2.12)$$

which arise from eqn. (3), can be formulated by means of eqns. (10) and (11) as follows:

$$\left(\frac{\partial \bar{G}}{\partial x_i} \right)' = \left(\frac{\partial \bar{G}}{\partial x_i} \right)'' \quad (i = 1, 2, \dots, N-1), \quad (1.2.13)$$

$$\bar{G}' - \sum_{i=1}^{N-1} x'_i \left(\frac{\partial \bar{G}}{\partial x_i} \right)' = \bar{G}'' - \sum_{i=1}^{N-1} x''_i \left(\frac{\partial \bar{G}}{\partial x_i} \right)''. \quad (1.2.14)$$

We shall see later that the equilibrium conditions in this form have a simple geometric significance in relation to the function $\bar{G}(x_1, x_2, \dots, x_{N-1})$, $T = \text{const.}$, $P = \text{const.}$

In the case of one-component systems, the relation

$$\bar{G}' = \bar{G}'' \quad (1.2.15)$$

replaces eqns. (13) and (14) and the molar Gibbs function \bar{G} is identical with the chemical potential μ .

The general relation between the Gibbs function G , the enthalpy H , and the entropy S of any phase is given by

$$G = H - TS. \quad (1.2.16)$$

We therefore have

$$\tilde{G} = \tilde{H} - T\tilde{S} \quad (1.2.17)$$

and

$$\mu_i = H_i - TS_i, \quad (1.2.18)$$

where \tilde{H} is the molar enthalpy, and H_i and S_i are the partial molar enthalpy and partial molar entropy of component i . Equations (15) and (17) give, for a two-phase equilibrium in a one-component system,

$$\tilde{H}'' - \tilde{H}' = T(\tilde{S}'' - \tilde{S}'). \quad (1.2.19)$$

For a two-phase equilibrium in a multicomponent system eqns. (12) and (18) give

$$H_i'' - H_i' = T(S_i'' - S_i'). \quad (1.2.20)$$

1.3. Phase Rule

The simplest way to deduce Gibbs's phase rule is to start from the concept of components introduced in § 1.2. The equilibrium state of a heterogeneous system can then be defined by the temperature T , the pressure P , and $\phi(N-1)$ independent composition variables (e.g. stoichiometric mole fractions) where ϕ is the number of phases and N the number of components. There will be $N(\phi-1)$ equations of type (1.2.3) connecting the $\phi(N-1)+2$ intensive variables of state. Furthermore, there may be other conditions such as, for instance, the requirement that a certain selected phase shall coexist with another phase not included in the discussion; or that, for a two-component system, only states of the same composition (azeotropic mixtures) are to be discussed. If the number of these additional equilibrium conditions is B' there will be a total of

$$N(\phi-1) + B'$$

independent equations connecting the $\phi(N-1)+2$ variables. The number of "degrees of freedom", i.e. the number of independent intensive variables is called the *variance* v of the system. It is represented by:

$$v = N + 2 - \phi - B'. \quad (1.3.1)$$

Usually there are no additional conditions, i.e. $B' = 0$, and we obtain the common expression of Gibbs's phase rule:

$$v = N + 2 - \phi. \quad (1.3.2)$$

However, problems involving azeotropic points, critical points, etc., require the application of the general eqn. (1).

Equation (1) or (2) can also be used when some components do not occur in certain phases, e.g. the binary two-phase system NaCl (solid) + aqueous solution of NaCl where the component H_2O is absent from the solid phase. The number of concentrations and the number of equilibrium conditions of type (1.2.3) are then correspondingly reduced.

Equilibria are called:

invariant when	$v = 0$	$(\phi = N + 2),$
univariant when	$v = 1$	$(\phi = N + 1),$
bivariant when	$v = 2$	$(\phi = N),$
multivariant when	$v > 2$	$(\phi > N).$

The relations in parentheses assume the validity of eqn. (2), i.e. $B' = 0$.

Many solid-liquid equilibria which are investigated are systems consisting of solid and liquid phases in open containers and thus in contact with air at atmospheric pressure. If the air is either insoluble or practically insoluble in the condensed phases such a heterogeneous system can be treated as an isobaric condensed system without a vapour phase. The air is regarded simply as a piston which exerts atmospheric pressure on the condensed phases. When applying the phase rule (1) or (2), it must be remembered that there is no gas phase, that the constituents of the air are not components of the system, and that pressure is no longer a degree of freedom. Thus the ice point (equilibrium of ice + liquid water at atmospheric pressure, the water being saturated with air) is a fixed point (invariant point) in the same way as the triple point of water (equilibrium of ice + liquid water + water vapour, air being excluded). The influence of pressure on the equilibrium between condensed phases is small. For the above two fixed points for water we have ($K = \text{kelvin}$):

Ice point: 0°C or 273.15K ($1 \text{ atm} = 760 \text{ torr}$)

Triple point: 0.01°C or 273.16K (4.579 torr).

Thus when we later fail to specify the pressure in isobaric equilibrium diagrams it can be assumed that the pressure is about 1 atm.

1.4. Stability Conditions and Critical Phenomena

Conditions for stability may be described with the aid of the molar Gibbs function \bar{G} of the phase under consideration, a process similar to that applied to equilibrium conditions at the end of § 1.2. \bar{G} is regarded

as a function of temperature T , pressure P , and mole fractions x_1, x_2, \dots, x_{N-1} . Both absolute stability and metastability are here regarded as “stability”; it is thus necessary to define the conditions for which the phase is not absolutely unstable, i.e. not unstable with respect to arbitrarily near neighbouring states. Ignoring, for the moment, stability limits and critical phases, we can formulate the stability conditions in terms of the sign of the second differential coefficients of the molar Gibbs function with respect to its associated variables $T, P, x_1, x_2, \dots, x_{N-1}$:

$$\frac{\partial^2 \bar{G}}{\partial T^2} = -\frac{\bar{C}_P}{T} < 0, \quad (1.4.1)$$

$$\frac{\partial^2 \bar{G}}{\partial P^2} = -\kappa \bar{V} < 0, \quad (1.4.2)$$

$$\frac{\partial^2 \bar{G}}{\partial T^2} \frac{\partial^2 \bar{G}}{\partial P^2} - \left(\frac{\partial^2 \bar{G}}{\partial T \partial P} \right)^2 = \frac{\kappa \bar{V} \bar{C}_V}{T} > 0, \quad (1.4.3)$$

[illegible]

where

$$D = \left| \begin{array}{cccc} \frac{\partial^2 \tilde{G}}{\partial x_1^2} & \frac{\partial^2 \tilde{G}}{\partial x_1 \partial x_2} & \cdots & \frac{\partial^2 \tilde{G}}{\partial x_1 \partial x_{N-1}} \\ \frac{\partial^2 \tilde{G}}{\partial x_2 \partial x_1} & \frac{\partial^2 \tilde{G}}{\partial x_2^2} & \cdots & \frac{\partial^2 \tilde{G}}{\partial x_2 \partial x_{N-1}} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial^2 \tilde{G}}{\partial x_{N-1} \partial x_1} & \frac{\partial^2 \tilde{G}}{\partial x_{N-1} \partial x_2} & \cdots & \frac{\partial^2 \tilde{G}}{\partial x_{N-1}^2} \end{array} \right| \quad (1.4.5)$$

and \bar{V} is the molar volume, \bar{C}_P the molar heat capacity at constant pressure, \bar{C}_V the molar heat capacity at constant volume, and κ the compressibility.†

The inequalities (1) to (3) relate to thermal and mechanical stabilities. The inequalities (4) relate to material stability (stability with respect to the formation of phases of slightly different composition). They state that the determinant D and all its principal minors are positive. We shall show later that statements (1) to (3) have simple geometrical meanings for the function $\bar{G}(T, P)$ and statements (4) for the function $\bar{G}(x_1, x_2, \dots, x_{N-1})$.

The stability limit marks the boundary between regions of stable or metastable states and unstable regions. Apart from the case of one-component systems, in which stability limits are of no interest in connection with solid-liquid equilibria, the general equation for the stability limit is

$$D = 0. \quad (1.4.6)$$

In binary systems ($N = 2$) the relation

$$\frac{\partial^2 \bar{G}}{\partial x_1^2} = 0 \quad (1.4.7)$$

therefore represents the equation for the stability-limit curve.

A critical phase occurs by the merging of two coexisting phases. It occurs at the stability limit. It thus lies on a coexistence curve as well as on a stability-limit curve. It is therefore definable by two independent equations. According to the generalized phase rule (1.3.1) with $B' = 2$ and $\phi = 1$, there are, therefore, $N - 1$ degrees of freedom. Accordingly, one-component systems have a critical point ($v = 0$), binary systems a critical curve ($v = 1$), ternary systems a critical surface ($v = 2$), etc. If we again exclude one-component systems, the two equations which characterize a critical phase are:‡

$$D = 0, \quad D' = 0, \quad (1.4.8)$$

‡ Equation (3) involves the relation

$$\bar{C}_P - \bar{C}_V = \beta^2 T \bar{V} / \kappa,$$

where β is the thermal expansivity.

§ The general equations for critical phases (including one-component systems) are given in R. Haase, *Thermodynamik der Mischphasen*, Springer-Verlag, Berlin-Göttingen-Heidelberg, 1956, p. 177. Cf. also J. S. Rowlinson, *Liquids and Liquid Mixtures*, Butterworths, London, 1959.