
LIQUID METALS

CHEMISTRY AND PHYSICS

Edited by

SYLVAN Z. BEER

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PREFACE

Historically, activity in a science reflects commercial interests and needs. Liquid metals are, in general, an intermediate stage in the commercial utilization of most metals. In the liquid state they are rarely articles of commerce. Therein lies one reason why to so large an extent the research activity in liquid metals for many years lagged behind that of solid-state studies. Familiarity with its form, going back to the primitive metal age, had, perhaps, to some extent dulled Man's curiosity over it. And perhaps also there may have been a sense of disappointment experienced by his lack of ability to find a relationship between the properties of commercial alloys in their solid state and in their liquid phase. Thus, the difficulties of liquid state theory itself and the uncertainties in the relationship between the relatively well understood electron theory of metals and the corresponding nature of liquid metals have deterred many from entering an uncharted field. And to all this, one does not need to dwell on the experimental difficulties often encountered because of the increased reactivity of these materials at their working temperatures.

Within the last two decades the situation has changed, and the liquid state of metals has emerged as an important field of scientific endeavor. The field is no longer underdeveloped or underpopulated, but the papers and other reported work in this field are scattered among a great variety of publications and in many languages. But now as the field approaches maturity, a time arrives for a comprehensive review of its status. In this way, those who approach this field with no background can have an overview of what has been accomplished and what remains undone. The expert in the field would have the benefit of relating his work to the body of existing knowledge. Such reviews have often in the past precipitated a new thrust into still unconquered territory. Herein rest my hopes for this book.

For the reasons given, these articles are presented here largely in the form of summaries of the work done on liquid metals. However, they are not

purely review papers. They were written with the intent of combining reviews with original contributions and critical comment on various selected aspects of a very large field.

Quite obviously not every aspect could be covered, nor every point of view. The reader bemoaning the absence of his favorite subject may take solace in that some of mine are missing also. Here as in other matters, one cannot escape the difficult decisions caused by time and space limitations.

For the convenience of the reader, a separate Systems Index has been included along with the Author and Subject Indexes. This Index has been organized in order of complexity, from Unary to Quaternary, with each section in alphabetical order. It is hoped that this arrangement will be of use in seeking out specific information.

This is the last opportunity I have to thank the authors for their cooperative spirit.

Sylvan Beer
Syracuse, New York

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Chapter 1

ON THE THERMODYNAMIC FORMALISM OF METALLIC SOLUTIONS

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I. INTRODUCTION

Progress in a given field develops formalisms best adapted to the practical and theoretical characteristics of this field. However, this may also hinder the flow of information between investigators of different but related fields. In particular, physicists and chemists may not be very familiar with the formalism most commonly used by metallurgists in their study of the thermodynamic properties of metallic solutions. The goal of the present contribution is to outline this formalism and explain some of its characteristics.

Most fundamental equations in thermodynamics introduce the chemical potential $\mu_i^{(\alpha)}$ of a component i in a phase α . Practically, it is imperative that the relation of $\mu_i^{(\alpha)}$ to the composition of the phase α be known. The

formalism mentioned above is designed to facilitate the study of this composition dependence for metallic solutions. It is valid for both solid and liquid alloys, although it is in liquid alloys that it has found its most extensive applications.

II. THE ACTIVITY AND ACTIVITY COEFFICIENT FUNCTIONS

When the concentration of i (e.g., its mole fraction X_i) becomes very small, μ_i becomes very negative. Mathematically, it is very inconvenient to handle a function which tends toward $-\infty$ and we introduce a new function which is better behaved, the activity a_i . It is defined by the equation

$$\mu_i = \mu_i^0(P, T) + RT \ln a_i \quad (1)$$

μ_i^0 is a reference value for the calculation of a_i . It depends only on the temperature and the pressure of the phase under consideration and is the value of μ_i in a standard state which is entirely arbitrary. For convenience, we shall adopt here the convention that μ_i^0 is the value of μ_i when the element i is pure and when it has the same structure as that of the solution under study (e.g., a liquid). The activity function a_i is then a positive function which is equal to 0 when $X_i = 0$ and to 1 when $X_i = 1$.

For solutions of components which are not too dissimilar in character, it is experimentally observed that a_i is approximately equal to the mole fraction X_i . These observations have led to the concept of an ideal solution; it is thermodynamically defined by the equation

$$a_i = X_i \quad (2)$$

At first, it may seem strange to define the behavior of a solution by the behavior of only one of its components. However, although other definitions of an ideal solution are possible, this one is perfectly satisfactory, as it is an easy matter to demonstrate (through the use of the Gibbs-Duhem equation) that if Eq. (2) is valid for one solute, then the activity of any other solute is also equal to its mole fraction.

Real solutions do not behave ideally. To account for these deviations, large or small, a correction factor is entered in the relation (2) by means of the activity coefficient γ_i . It is defined by the equality

$$\gamma_i = \frac{a_i}{X_i} \quad (3)$$

For an ideal solution, γ_i is identical to 1.

Thus, the problem of the composition dependence of μ_i has now been transferred to the problem of the composition dependence of γ_i . A mathematical formalism often implies certain assumptions and it must rely on some experimental observations. The formalism that is developed below is based on the experimental behavior of γ_i in dilute solutions.

III. PRESENTATION AND DISCUSSION OF RAOULT'S AND HENRY'S LAWS

Raoult's and Henry's laws concern, respectively, the behavior of the solvent and the solute in dilute solutions. The observations which led to Raoult's law showed that the activity of the solvent is approximately equal to its mole fraction; those which led to Henry's law also showed that the activity of the solute is approximately proportional to its mole fraction. Henry published his results in 1803 [1]* and Raoult in 1887 [2]. At these dates, the concept of an activity function was of course unknown, but today these laws must be given a rigorous definition in terms of functions of current usage if they are to be considered as laws rather than approximations. Too often, in the literature, even modern versions of the historical formulations are imprecise and may lead to some confusion as to their significance. Because they are relevant to the foundation of any formalism describing mixing properties, they will be presented and discussed here in some detail.

In the case of a binary solution, it is often stated [3-5] that the solvent 1 follows Raoult's law in a given range of concentration including the pure element 1, if, in this range, the activity curve of 1 is the line of ideal mixing:

$$a_1 = X_1$$

*Henry's law may be found in the following statement: "The absorption of gas ... is exactly proportional to the density of the gas, considered abstractly from any other gas with which it may accidentally be mixed." [1], p. 274.

This statement, however, only yields a different name to the phenomenon of ideal mixing. The interesting feature in the concept of Raoult's law is that the solvent approaches the ideal behavior when its concentration approaches unity, i. e., the slope of its activity curve at the point $X_1 = 1$ is the line of ideal mixing:

$$\left(\frac{da_1}{dX_1} \right)_{X_1 \rightarrow 1} = 1 \quad (4)$$

or, in terms of the activity coefficient γ_1 [see Eq. (3)]:

$$\left[\frac{d(\ln \gamma_1)}{dX_2} \right]_{X_1 \rightarrow 1} = 0 \quad (5)$$

Quite similarly, a common definition of Henry's law [4, 5] states that the activity of the solute 2 becomes proportional to its concentration when it is very dilute. Clearly, this proportionality exists only as an approximation, i. e., it is only within the experimental scatter that the activity curve may be replaced by its tangent at the point of infinite dilution. The argument that both Raoult's and Henry's laws are properly statements about limiting slopes may seem evident; indeed, it is often implicit in the presentation of these laws. That it should be made explicit will become more apparent in the following discussion.

A more precise statement of Henry's law is that at the point of infinite dilution of 2 where a_2 is zero, the slope of a_2 versus X_2 ,

$$\left(\frac{da_2}{dX_2} \right)_{X_2 \rightarrow 0} = \left(\gamma_2 + X_2 \frac{d\gamma_2}{dX_2} \right)_{X_2 \rightarrow 0} \quad (6)$$

has a nonzero finite value. By definition of the activity coefficient and by l'Hospital's rule,

$$\gamma_2^0 \equiv (\gamma_2)_{X_2 \rightarrow 0} = \left(\frac{a_2}{X_2} \right)_{X_2 \rightarrow 0} = \left(\frac{da_2}{dX_2} \right)_{X_2 \rightarrow 0} \quad (7)$$

Consequently, γ_2^0 is finite and different from zero. A comparison of Eqs. (6) and (7) yields

$$\left[X_2 \frac{d(\ln \gamma_2)}{dX_2} \right]_{X_2 \rightarrow 0} = 0 \quad (8)$$

Whereas Eq. (8) is a necessary consequence of Henry's law — in the form proposed here — it is not a sufficient condition for it [6]. As a consequence, it is easily seen through the Gibbs-Duhem equation

$$X_1 \frac{d(\ln \gamma_1)}{dX_2} + X_2 \frac{d(\ln \gamma_2)}{dX_2} = 0$$

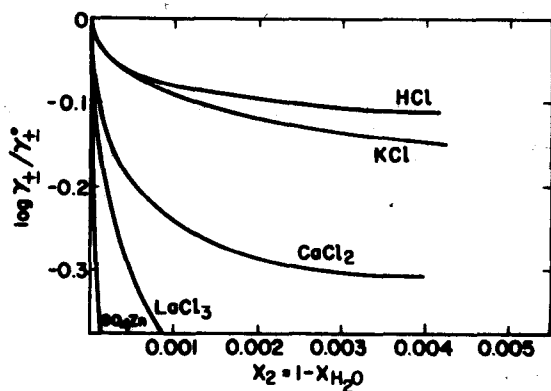
that Raoult's law is a necessary consequence of Henry's law, but not a sufficient condition for it.

This definition of Henry's law implies that it is generally applicable to the ionic species of an electrolytic solution, and consequently, to the mean activity a_{\pm} and activity coefficient γ_{\pm} of an electrolyte [7]. The peculiarity of this case is that, as $\ln \gamma_{\pm}$ varies as $X_2^{1/2}$ in dilute solutions, which is a result of the Debye-Hückel treatment, $d[(\ln \gamma_{\pm})/dX_2]_{X_2 \rightarrow 0}$ is infinite, while $\ln \gamma_{\pm}^0$ is finite and $[X_2 d(\ln \gamma_{\pm})/dX_2]_{X_2 \rightarrow 0} = 0$; from Eq. (6) $(da_{\pm}/dX_2)_{X_2 \rightarrow 0}$ is then seen to be finite. It may easily be checked that the electrolyte itself does not follow Henry's law because $\gamma_2 \rightarrow 0$ when $X_2 \rightarrow 0$.

For nonelectrolytic solutions (and metallic solutions in particular), the applicability of Henry's law is commonly considered to mean that in a small concentration range (0, X_2) the composition dependence of γ_2 may be neglected, thus that $[d(\ln \gamma_2)/dX_2]_{X_2 \rightarrow 0}$ is not infinite. As already shown, this condition is more restrictive than the definition of Henry's law previously adopted, but its range of applicability is wide enough to warrant the title of a "law". Thus, it appears desirable to distinguish between Henry's law as previously defined — or Henry's zeroth-order law — which states the existence of $\ln \gamma_2^0$, and Henry's first-order law, which states the existence of both $\ln \gamma_2^0$ and $[d(\ln \gamma_2)/dX_2]_{X_2 \rightarrow 0}$ (see Fig. 1).

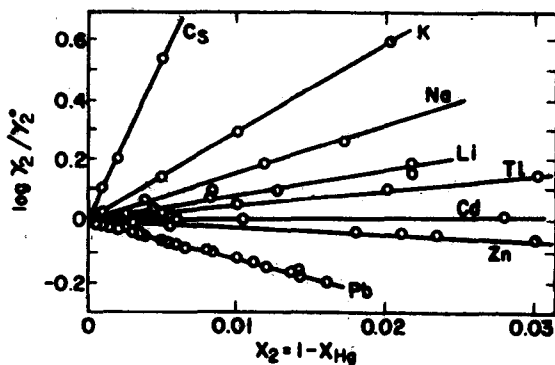
Perhaps the best justification for such a distinction is that obedience to the zeroth-order law may be interpreted in terms of the selection of the species describing the system, and obedience to the first-order law in terms of the short-range effectiveness of the forces in the solution.

As a simple illustration, let us consider the case of nitrogen solubility



(a) Aqueous Solutions
at 25°C.

Data compiled by
S. Glasstone (7)



(b) Liquid Amalgams
at 25°C.

Data compiled by L.S. Dorken
and E.T. Turkdogan (8)

FIG. 1. Henry's zeroth-order law is obeyed in both cases (a) and (b), whereas Henry's first-order law is not obeyed in (a) but obeyed in (b). In (a), the zeroth-order law is obeyed by the ions, not the electrolyte.

in liquid iron. Numerous investigations have shown that the concentration of nitrogen in iron is practically proportional to the square root of the partial pressure of nitrogen (at least under the usual range of pressures). The binary system may be described by the couple of species Fe and N_2 or Fe and N. If we select the species Fe and N_2 , we can write the absorption reaction



and the equilibrium constant

$$K = \frac{a_{N_2}}{p_{N_2}} = \frac{\gamma_{N_2} X_{N_2}}{p_{N_2}}$$

At high dilutions, all measures of concentrations are practically proportional to each other (e. g., $X_{N_2} \simeq \frac{1}{2} X_N$) and it is equivalent to write that the square root of p_{N_2} is proportional to X_{N_2} or to X_N ; thus,

$$p_{N_2}^{1/2} = h X_{N_2} \quad \text{or} \quad p_{N_2} = h^2 X_{N_2}^2$$

Consequently,

$$\gamma_{N_2} = K h^2 X_{N_2}$$

For $X_{N_2} \rightarrow 0$, we see that $\gamma_{N_2}^0 = 0$ or $\ln \gamma_{N_2}^0 = -\infty$; Henry's zeroth-order law is not obeyed. If, on the contrary, we were to select the species Fe and N, we would find by a similar procedure that γ_N^0 is finite and different from zero, i. e., that Henry's zeroth-order law is obeyed.

A converse example may also be given. If we consider the solubility of nitrogen in water, it is found experimentally that the concentration of nitrogen is approximately proportional to the partial pressure of nitrogen. As a consequence, it is easy to show that a description of the system in terms of H_2O and N_2 leads to an applicability of Henry's zeroth-order law ($\ln \gamma_{N_2}^0$ finite) but that a description in terms of H_2O and N results in its violation ($\gamma_N^0 = \infty$). The importance of these considerations is that they indicate that nitrogen is dissociated in liquid iron and is present as atoms, whereas in water it is not dissociated and is present as diatomic molecules. Thus, Henry's zeroth-order law is relevant to a study of the structure of a solution.

Henry's first-order law may give us some information on the interactions in solution. Through various statistical models (similar to those of the free volume [9] or the central atoms [10]), it is possible to see that the derivatives of $\ln \gamma_i$ with respect to composition involve integrals which converge when the net interaction potential between atoms or molecules decreases rapidly with the distance and which diverge when it decreases slowly with the distance (e. g., as $1/r$ between electrical charges). Thus, it is not surprising to find that Henry's first-order law is obeyed by metallic solutions and not by

electrolytic solutions. It should be emphasized that this fact does not prove that the forces between solute atoms in metallic solutions are necessarily short-range; it merely establishes that in most cases the thermodynamic properties of the solution can be adequately described through short-range forces.

For a solution of m components, we choose as independent variables the mole fractions of the solutes X_2, X_3, \dots, X_m . The generalization of Raoult's law is straightforward and may be expressed by the following equations:

$$\left[\frac{\partial (\ln a_1)}{\partial X_j} \right]_{X_1 \rightarrow 1} = -1 \quad \text{for } j = 2, 3, \dots, m \quad (9a)$$

or

$$\left[\frac{\partial (\ln \gamma_1)}{\partial X_j} \right]_{X_1 \rightarrow 1} = 0 \quad \text{for } j = 2, 3, \dots, m \quad (9b)$$

Each of the partial derivatives in Eqs. (9a) and (9b) is a binary property (of the binary system 1-j); thus, the generalization of Raoult's law to a multi-component system introduces no new information.

Whereas Raoult's law is necessarily defined at the point $X_1 = 1$, the concept of Henry's law should apply to the behavior of a very dilute element in a solution of any arbitrary composition with respect to the other elements. In other words, for the element i ($i \neq 1$), Henry's law is defined at any point α' where X_i and a_i are zero (see Fig. 2). The law may be expressed by the following equations:

$$\left(\frac{\partial a_i}{\partial X_i} \right)_{\text{at } \alpha'} = \text{finite value different from zero} \quad (10a)$$

and

$$\left(\frac{\partial a_i}{\partial X_j} \right)_{\text{at } \alpha'} = 0 \quad \text{for } j = 2, 3, \dots, m \quad \text{and } j \neq i \quad (10b)$$

In contrast to the case of Raoult's law, the validity of Henry's law in the various binaries $i-1$, $i-j$, does not ensure its validity in the multicomponent system $1-i \dots j$. A geometric interpretation of both Raoult's law and Henry's

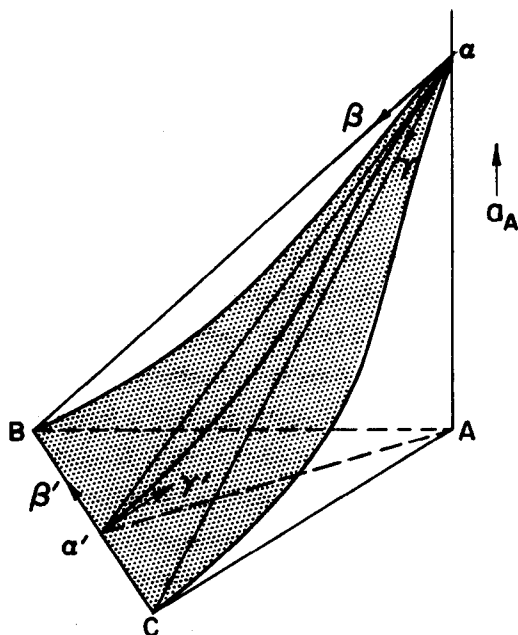


FIG. 2. Illustration of Raoult's and Henry's laws for a ternary system. Raoult's law is defined at the point α by the tangent plane $\alpha\beta\gamma$, which is identical to the plane of ideal mixing αBC . Henry's law is defined at any point α' on BC by the tangent plane $\alpha'\beta'\gamma'$, which contains BC and is neither horizontal nor vertical.

law for a ternary system is given in Fig. 2.

A necessary consequence of Eqs. (10a and (10b) is

$$\left[X_i \frac{\partial (\ln \gamma_i)}{\partial X_j} \right]_{\text{at } \alpha'} = 0 \quad \text{for } j = 2, 3, \dots, i, \dots, m \quad (11)$$

The special case of Henry's first-order law adds the restriction that each derivative $[\partial (\ln \gamma_i) / \partial X_j]_{\text{at } \alpha'}$ is finite.

IV. BASIS OF A POLYNOMIAL FORMALISM FOR DILUTE SOLUTIONS

Our present understanding of metallic solutions does not allow us to derive theoretically analytic forms of much accuracy for the composition dependence of thermodynamic properties. However, the need for analytic