Thermodynamics of Binary and Ternary Solutions Containing One Interstitial Solute

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The activity of a very dilute interstitial component is proportional to the ratio of filled to unfilled interstitial sites. In a liquid solution in which solvent and solute atoms are strongly bonded to form in effect molecules of a solute AB_b, each solvent atom is regarded as providing b sites for B atoms. The activity of the solute and other properties of the solution are treated by the same equations as those describing the interstitial solution. Concentrations are stated in terms of the ratios $y_i = n_i/(n_1 + n_2)$ where components 1 and 2 are lattice atoms and i represents any component. The activity coefficient of the interstitial component is defined as $\Psi_3 = a_3/z_3$ where $z_3 = y_3/(1 - y_3/b)$. Henry's law for the solute at great dilution is $\Psi_3 = $ constant. Examples are cited in which log Ψ_3 is a linear function of y_3 or in other cases of z_3. A simple form of the Gibbs-Duhem relation for ternary solutions is used to deduce the effects of an interstitial solute on the activities of the individual lattice components.

CONSIDERABLE progress has been made in understanding the properties of interstitial solutions and experimental data are accumulating rapidly on both binary and ternary alloys. Recent years have brought forth a number of studies of the behavior of nonmetallic solutes in binary liquid metallic solvents, aimed principally at predicting the activity of the solute, for example oxygen, in the mixture from a knowledge of the three binary systems concerned, for example Fe-O, Mn-O, and Fe-Mn. The more limited purpose of this paper is to examine the equations for activities of the components in interstitial solutions and in liquid metallic solutions in which the solute is strongly bonded to the solvent metals. The latter include not only nonmetallic solutes such as sulfur or oxygen in iron or nitrogen in Fe-Cr alloys, but also certain intermetallic pairs which combine with large evolution of heat, for example sodium in mercury or lead. It will be of interest to see what can be learned about such systems from thermodynamics without recourse to quasichemical theory.

In expressing the thermodynamic properties of a ternary solution in which component 3 is interstitial, it is convenient to adopt as concentration variables the atom ratios:

$$y_1 = \frac{n_1}{n_1 + n_2}; \quad y_2 = \frac{n_2}{n_1 + n_2}; \quad y_3 = \frac{n_3}{n_1 + n_2} \qquad [1]$$

Here y_1 and y_2 are the atom fractions in the base 1-2 binary and y_3 the ratio of interstitial to lattice atoms. The variable y_3 is useful in moderately dilute solutions, for example where less than half of the interstitial sites are occupied.

The Gibbs-Duhem equation may be written:

$$y_1 d\overline{G}_1 + y_2 d\overline{G}_2 + y_3 d\overline{G}_3 = 0 \qquad [2]$$

The molar value of G must be taken per mole of lattice atoms, G^L rather than the more familiar G^M per

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mole of solution. It may be noted that, where both terms refer to the ternary solution:

$$G^L = G^M(1 + y_3) \qquad [3]$$

and, in terms of the relative partial molar properties,

$$G^L = y_1 \overline{G}_1 + y_2 \overline{G}_2 + y_3 \overline{G}_3 \qquad [4]$$

Similar equations may be written for the enthalpy, excess free energy, and entropy.

Certain features of the use of the atom ratio, rather than the atom fraction of the interstitial component, lead to differences in the equations relating the partial molar properties. Simple relations between the two variables x_3 and y_3 for the interstitial solute include: $y_3 = x_3/(1 - x_3)$; $x_3 = y_3/(1 + y_3)$; $(1 - x_3)(1 + y_3) = 1$; $dx_3 = dy_3/(1 + y_3)^2$; $dy_3 = dx_3/(1 - x_3)^2$. The general relation which is the basis for the "tangent intercept" method for evaluating partial properties in a binary solution may be applied to a quasibinary of constant x_2/x_1 thus:

$$\overline{G}_3 = G^M + (1 - x_3)\left(\frac{\partial G^M}{\partial x_3}\right)_{x_2/x_1} \qquad [5]$$

By means of Eq. [3] and the simple relations mentioned above, this becomes

$$\overline{G}_3 = \left(\frac{\partial G^L}{\partial y_3}\right)_{y_2} \qquad [6]$$

Equations for the partial molar properties of the substitutional components are more complex.

THE IDEAL DILUTE INTERSTITIAL SOLUTION

An ideal binary solution may be defined as one having the following properties. The lattice atoms are arranged on a perfect lattice. The interstitial component is randomly distributed on the available interstitial sites. The partial molar energy and volume of the components are independent of concentration. It has been shown that in such a solution the activity of the interstitial component is proportional to the ratio of filled to unfilled interstitial sites. Thus, for an ideal solution of hydrogen in a "good absorber" M at a fixed temperature, Fowler and Guggenheim[1] derive

the expression, in which N is the number of atoms of either kind and b is the number of interstitial sites per lattice atom:

$$\frac{N_H}{bN_M - N_H} = a_H \times \text{const} \qquad [7]$$

A similar equation was derived by Gurney[2] for carbon in fcc iron. Dünwald and Wagner[3] tested the equation for carbon in austenite and cited earlier references to its derivation. Their experimental results showed substantial deviations which they ascribed to a more rapid decrease in the number of available sites than in the denominator of the fraction $[N_C/(bN_{Fe} - N_C)]$. Such a decrease has been the basis for the more recent "blocking models". Many of the equations which have been derived by statistical thermodynamics for the activity of carbon in iron reduce to this simple ratio at infinite dilution, and most of the proposed models are concerned with deviations from the ideal.

It is convenient to consider the thermodynamic properties per mole of lattice atoms and for this purpose the fraction of Eq. [7] is multiplied by b to define a "lattice ratio", which, for the solution 1-3 is:

$$z_3 \equiv \frac{n_3}{n_1 - n_3/b} \qquad [8]$$

which ideally is proportional to the activity, a_3. The constant of proportionality includes b and a factor which depends upon the standard state adopted. Thus in an ideal interstitial solution:

$$a_3 = kz_3 = \frac{ky_3}{1 - y_3/b} \qquad [9]$$

In a ternary solution containing two types of lattice atoms, components 1 and 2, the usual condition for ideality must be imposed on the lattice itself, and at infinite dilution with respect to the third component, $a_1 = n_1/(n_1 + n_2)$. The interstitial component 3 behaves in the same way as before, provided the number of interstitial sites is unaltered, and, for a fixed atom fraction in the binary lattice,

$$a_3 = kz_3 = kn_3/(n_1 + n_2 - n_3/b) = ky_3/(1 - y_3/b) \qquad [10]$$

It is possible to visualize a partially ideal ternary solution in which the interstitial component forms an ideal solution in a nonideal lattice of fixed composition. In such a case the relation between a_3 and z_3 may become a complex function of the lattice composition.

The use of z_i as a concentration parameter and the application of Eqs. [9] and [10] as limiting equations in certain dilute liquid metallic solutions such as Fe-S, Fe-Cr-C, and Hg-Na has been suggested.[4-6] These are solutions in which the solute element is strongly bonded to the solvent metallic element. This application may be justified by the following argument. Consider the solute B strongly bonded to the solvent A. The AB bonds are very much stronger than the AA bonds while at great dilution the BB bonds are unimportant. Belton and Tankins[7] suggested the formation of molecular species such as FeO, thus reviving the molecular theory of solutes in a new form. More recently Jacob and Jeffes[8] have proposed a model based on the formation of possible species of the type of X_2O. Several were considered by Jacob and Alcock,[9] who discarded the concept of a constant coordination number for the atoms X, Y, and O and found most satis-

factory results when O was assigned a coordination of 4. These authors have been interested in predicting the activity of the solute in the mixed X-Y solution from data on the X-O, Y-O, and X-Y solutions. The present objective is the more limited one of correlating activity and composition in a system which has been studied experimentally.

All of these developments are based on the idea that each solvent atom provides a number of sites for solute atoms, and consequently the situation in this kind of liquid solution is analogous to that in the solid interstitial solution. Hoch[10] has applied the statistical mechanics of interstitial solutions to carbon and oxygen in liquid iron and has concluded that the liquid has the bcc ferrite structure. A somewhat different view has been developed[11] with the aid of equations of the present paper.

For the kind of liquid solution in question, we may say that each atom of solvent provides on the average b interstitial sites. There is no geometrical guide to the value of b and values that have been cited or implied in the foregoing discussion are integers or fractions not far from unity. If we have n_1 moles of solvent and n_3 moles of solute, there are bn_1 sites, of which n_3 are filled. The entropy of random mixing of n_3 filled sites and $bn_1 - n_3$ vacant sites is

$$\Delta S = \frac{-R}{bn_1}\left[(bn_1 - n_3) \ln \frac{bn_1 - n_3}{bn_1} + n_3 \ln \frac{n_3}{bn_1}\right] \qquad [11]$$

which by differentiation gives the partial molar configurational entropy of component 3

$$\overline{S}_3^C = \left(\frac{\partial S}{\partial n_3}\right)_{n_1} = -R \ln \frac{n_3}{bn_1 - n_3} \qquad [12]$$

In the ideal case the partial heat of mixing is constant and the partial molar free energy is

$$\overline{G}_3 = \overline{H}_3^\circ + RT \ln \frac{n_3}{bn_1 - n_3} \qquad [13]$$

And the activity is

$$a_3 = \frac{n_3}{bn_1 - n_3} \times \text{const} = kz_3 \qquad [14]$$

which is identical with that of the ideal interstitial solute, Eq. [7].

Eq. [9] or its equivalent Eq. [14] will be taken as the limiting law at great dilution, the proper form of Henry's law for interstitial and strongly-bonded liquid solutions. The corresponding form of Raoult's law in the binary solution 1-3 is found by integration of the Gibbs-Duhem equation:

$$\ln a_1 = - \int_0^{y_3} y_3 d \ln a_3 = b \ln (1 - y_3/b) \qquad [15]$$

These equations are applicable only at great dilution. For finite concentrations deviations will occur. It is to be expected that the deviations from a correct limiting law will be simpler than the deviations from an incorrect one.

The activity of an ideal interstitial solute, component 3 in the binary 1-3 is shown in Fig. 1 as a function of x_3 the atom fraction, y_3 the atom ratio, and z_3 the lattice ratio. The value of b is taken as one. The relations in the ideal ternary 1-2-3 are illustrated in Fig. 2, where compositions are expressed in atom ratios as defined in Eq. [1].
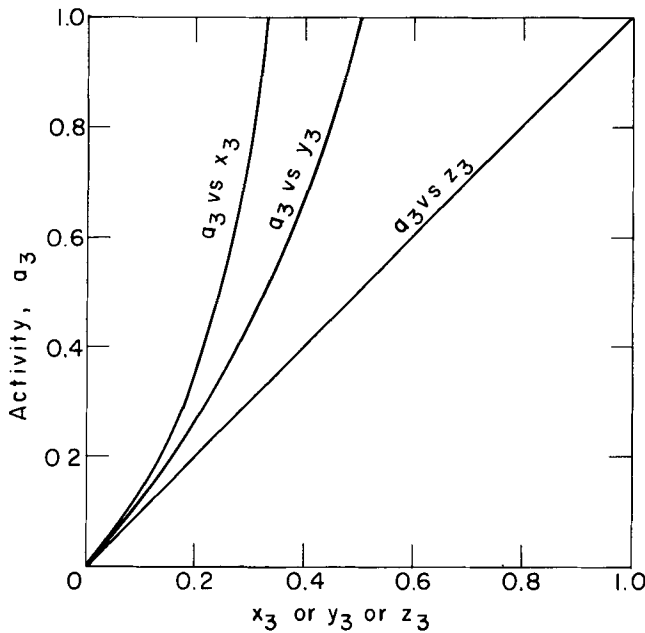
Fig. 1—Activity of an ideal interstitial solute as a function of its atom fraction x_3, atom ratio y_3, or lattice ratio z_3.

DEVIATIONS FROM HENRY'S LAW

In the nonideal solution $a_3 \neq kz_3$, and the ratio a_3/z_3 $\equiv \Psi_3$ approaches a constant limiting value Ψ_3° at infinite dilution with respect to component 3 in an alloy of fixed y_2. In the binary interstitial solutions, as well as in liquid solutions containing strongly-bonded solutes, the deviations from the ideal of Eqs. [10] and [14] are adequately represented by an empirical linear relation, for example in the system 1-3:

$$\ln \Psi_3 = \ln a_3/z_3 = \ln \Psi_3^\circ + \theta_3 y_3 \qquad [16]$$

where θ_3 is an interaction coefficient which is constant at constant temperature. This is illustrated in the following examples. In the interstitial solution, austenite, the activity of carbon has been measured by a number of observers, the widest range of concentration being that covered by Ban-ya, Elliott, and Chipman[12] at 1150°C. Their results are shown in Fig. 3 in the form of a plot of log $K'(z)$ vs y_C where $K'(z)$ is the equilibrium value of $p_{CO}^2/(p_{CO_2} \cdot z_C)$ and log $K' = \log a_C/z_C$ + constant. The linear relation fits the data within experimental errors and has the advantage that it is readily interpreted in terms of some of the proposed statistical models. Their equation describing the activity coefficient is a simple one, graphite being the standard state, and the temperature 1423 K:

$$\log \Psi_C = \log a_C/z_C = 0.685 + 2.76y_C \qquad [17]$$

STANDARD STATE

If it be desired to employ the reference state of infinite dilution, the standard state then becomes a hypothetical state in which $z_C = 1$ and all other properties of the solution correspond to infinite dilution. This is a point at $z_C = 1$ on the imaginary line $a'_C = z_C$. For a solution so dilute that Henry's law is valid, the concentration being z_C^*, the activity referred to graphite is $a_C = \Psi_C^\circ z_C^*$. The activity referred to infinite dilution is $a'_C = z_C^*$. The ratio of the two is $a_C/a'_C = \Psi_C^\circ$. Thus,
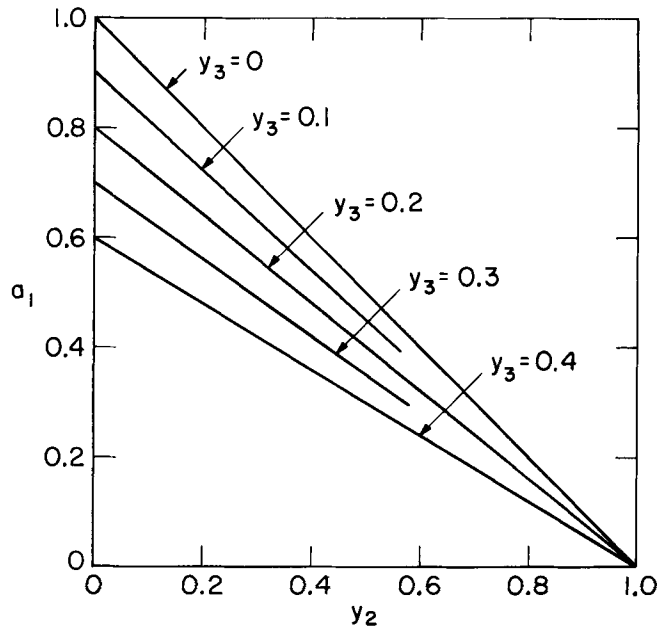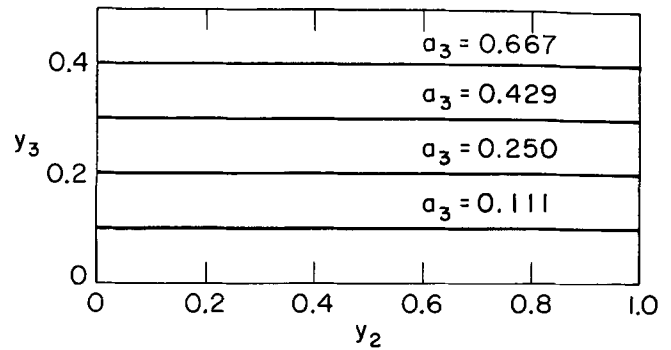

Fig. 2—Activities in an ideal interstitial solution. The activity of the interstitial component increases more rapidly than its concentration.

log $a_C - \log a'_C = \log \Psi_C^\circ$ and the standard free energy of transfer between the two standard states is

$$G_C^\circ(\text{gr}) - \bar{G}_C^\circ(\text{inf. dil.}) = -RT \ln \Psi_C^\circ \qquad [18]$$

It is noted that this hypothetical standard state corresponds to a filling ratio of $1/(b + 1)$ of the interstitial sites or a ratio of filled to unfilled sites of $1/b$. By reference to Eq. [17] the free energy change between the two standard states is

$$C(\text{gr}) = \underline{C}(\gamma, \text{ inf. dil.});$$
$$\Delta G_{1423}^\circ = 2.3RT \cdot 0.685 = 4460 \text{ cal} \qquad [19]$$

and

$$\log a'_C = 2.76y_C + \log z_C \qquad [20]$$

LIQUID SOLUTIONS

An example of the use of z_i in liquid solutions is found in the work of Ban-ya and Chipman[13] on activities in Fe-S solutions. They measured the equilibrium ratio defined as $K'(z) = p_{H_2S}/(p_{H_2} \cdot z_S)$ which is obviously proportional to the activity coefficient Ψ_S. In the absence of any geometrical criterion the value of b was assumed to be one. The values of log $K'(z)$ were plotted against z_S as shown in Fig. 4 and a straight line relation was found. There is no theoretical reason for
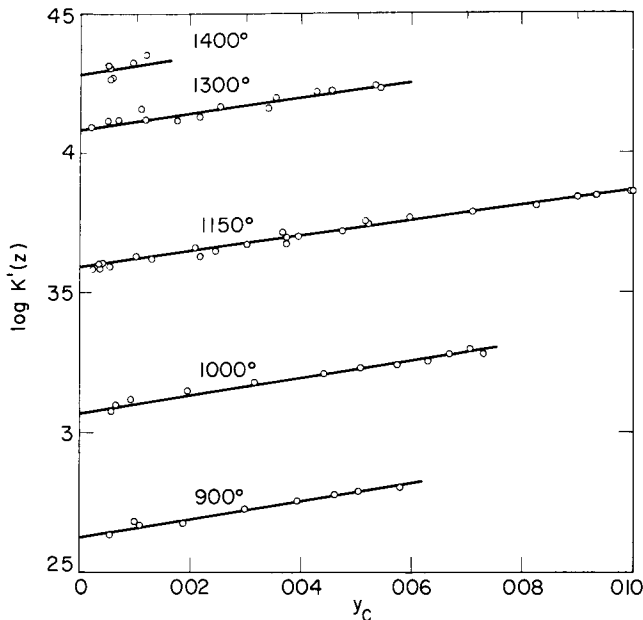
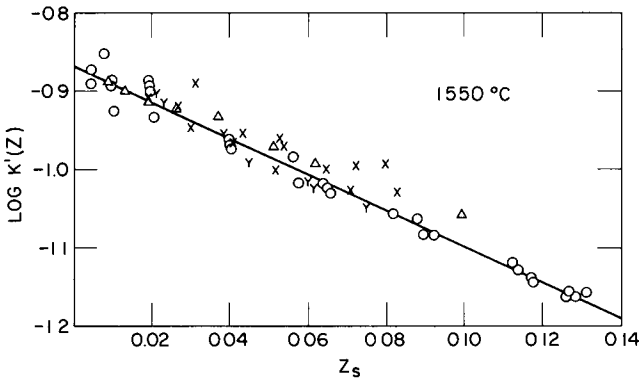Fig. 3—Equilibrium ratio $K'(z) = p_{CO}^2/p_{CO_2} \cdot z_C$ as a function of y_C in austenite (Ref. 12).

Fig. 4—Equilibrium ratio $K'(z) = p_{H_2S}^2/p_{H_2} \cdot z_C$ as a function of z_S in liquid iron (Ref. 13).

supposing that a plot of log Ψ_i vs z_i should be more nearly linear than a plot of log Ψ_i vs y_i. In austenite, the linearity of log Ψ_C vs y_C appears in some of the more acceptable statistical treatments (models II and XI of Ref. 12) and its possible application to liquid solutions needs further investigation. The simplicity of the mathematical treatment presented here would tend to encourage the use of y_i. The following treatment is based on the constancy of θ_3 in Eq. [16].

REAL TERNARY SOLUTIONS

In the ternary solution the values of Ψ_3° and of θ_3 are functions of the base composition y_2. They are designated $[\Psi_3^\circ]_{y_2}$ and $[\theta_3]_{y_2}$ and the equation is

$$\ln \Psi_3^{(123)} = [\ln \Psi_3^\circ]_{y_2} + [\theta_3]_{y_2} y_3 \qquad [21]$$

The activities of components 1 and 2 in the binary solutions 1-3 and 2-3 are found by substituting $a_3 = \Psi_3 z_3$ from Eq. [16] and integrating as in Eq. [15] to obtain

$$\ln a_1^{(13)} = -\tfrac{1}{2}\theta_3^{(13)} y_3^2 + b \ln (1 - y_3/b) \qquad [22]$$

and a corresponding equation for $\ln a_2^{(23)}$.
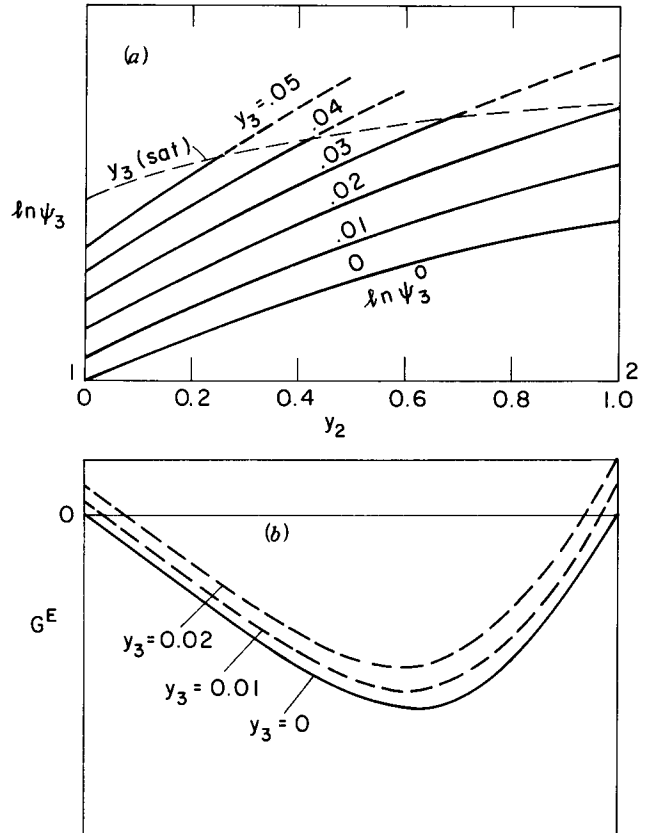
In determining a_1 in the ternary solution, the inte-

gration of Eq. [15] has as its lower limit not pure 1, but the binary 1-2 of composition y_1 in which the ideal activity is y_1. Hence, in the ideal ternary solution

$$\ln a_1^{(id)} = \ln y_1 + b \ln (1 - y_3/b) \qquad [23]$$

It is noted that for values of b not far from unity and for the small values of y_3 encountered in most interstitial solutions, the last term is approximately equal to $\ln (1 - y_3)$. Now if we define the activity coefficient as the ratio of the activity to its ideal value, we may define Ψ_1 as

$$\Psi_1 \equiv a_1/y_1(1 - y_3/b)^b \approx a_1/y_1(1 - y_3) \qquad [24]$$

and a corresponding definition for Ψ_2.

In terms of activities, Eq. [4] may be written

$$G^L/RT = y_1 \ln a_1 + y_2 \ln a_2 + y_3 \ln a_3' \qquad [25]$$

where a_3' is based on infinite dilution and is defined as $a_3' \equiv (\Psi_3/\Psi_3^\circ) z_3$ and Ψ_3 and Ψ_3° are for a specified value of y_2. The ideal free energy is:

$$G^{L\,(id)}/RT = y_1 \ln [y_1(1 - y_3)] + y_2 \ln [y_2(1 - y_3)]$$
$$+ y_3 \ln z_3 \qquad [26]$$

The excess free energy above that of an ideal ternary in terms of the activity coefficients defined in Eqs. [16] and [24] is found by subtracting the above to give:

$$G^E/RT = y_1 \ln \Psi_1 + y_2 \ln \Psi_2 + [y_3 \ln \Psi_3/\Psi_3^\circ]_{y_2} \qquad [27]$$

The situation is illustrated in Fig. 5 where the upper portion A represents hypothetical determinations of the activity coefficient of a solute at several concentrations in the binary solvent. The excess free energy

Fig. 5—Schematic representation of the activity coefficient of a solute and its effect on the excess free energy of the solution.

of the solution is shown in the lower portion, *B*. One would like to be able to compute the curves of *B* from the data shown in *A*, but thermodynamics does not offer a method for doing this. It is possible, however, given the data of *A* and the curve for the excess free energy of the binary, to calculate the corresponding values for the ternary solution. This may not be done by the simple addition of $RT \ln \Psi_3/\Psi_3^\circ$ to the values for the binary. The addition of component 3 alters the values of Ψ_1 and Ψ_2 and, therefore, the construction of the broken curves of *B* requires the application of some form of ternary Gibbs-Duhem equation.

ACTIVITIES OF THE SOLVENT COMPONENTS

In his original treatment of the application of the Gibbs-Duhem equation to ternary solutions, Darken[14] showed that the thermodynamic properties of the solvent components can be calculated from that of a third component provided the latter is known at all compositions of the ternary. This method obviously is not applicable in the present context since y_3 approaches infinity as x_3 approaches unity. Darken showed further that in the case of a dilute solution of the third component the activities of the solvent components can be estimated with a reasonable degree of certainty provided a mathematical model of the binary is available. Several examples were cited and chemical intuition was sustained. More recent attempts to apply regular solution theory[15] or a quasichemical model[16,9] or hidden assumptions of a model[17] have yielded only qualified success, but have not obtained quantitative confirmation. It would appear impossible to solve this problem by thermodynamics alone.

Wagner[18] has discussed the applications of the Gibbs-Duhem equation to ternary systems and has deduced a number of useful equations which may be simplified somewhat by using y_3 rather than x_3 and substituting some of the relations mentioned above. It should be remembered that Wagner's third component (in our sense) was numbered 2 and his binary, like Darken's, was system 1-3. Rewritten in our notation his Eq. [1-72] becomes:

$$\left(\frac{\partial \overline{G}_1}{\partial y_3}\right) = -y_2\left(\frac{\partial \overline{G}_3}{\partial y_2}\right) - y_3\left(\frac{\partial \overline{G}_3}{\partial y_3}\right) \qquad [28]$$

This and the corresponding equation for $\partial \overline{G}_2/\partial y_3$ are regarded by Wagner as the most profitable forms for a ternary system. The introduction of y_3, however, limits their use to compositions in which x_3 is substantially less than unity and the above equation cannot be used for the full integration.

If the thermodynamic functions of the binary system are known, the equation may be integrated with $y_3 = 0$ as the lower limit to find the effect of component 3 on the partial molar properties of each of the other components. In terms of excess properties, Wagner's Eq. [1-80] reduces to:

$$G_1^E(y_2, y_3) = G_1^E(y_2, y_3 = 0) + \left\{\int_0^{y_3}\left[G_3^E - y_2\frac{\partial G_3^E}{\partial y_2}\right]\right.$$
$$\left. \times dy_3 - y_3 G_3^E\right\}_{y_2} \qquad [29]$$

The quantity in brackets may be evaluated as the ordinate intercept of the tangent lines for stated values

of y_3 on a plot of G_3^E vs y_2 at a particular value of y_2.

On the other hand, if the activity coefficient Ψ_3 has been expressed as an algebraic function of y_2 and y_3 an analytical solution may be obtained for the effect of component 3 on the activities of the other components. As an example, the recent data of Wada, Wada, Elliott, and Chipman[19] on the activity coefficient of carbon in Fe-Ni alloys up to $y_{Ni} = 0.25$ at 1000°C are expressed by the equation:

$$\log \Psi_C = 0.887 + 1.87 y_{Ni} + 3.03 y_C \qquad [30]$$

and $\log \Psi_C^\circ$ is the value of the above at $y_C = 0$. Eq. [29] is rearranged and applied to the activity coefficient Ψ_C/Ψ_C° and is then solved for the increment $\delta \log \Psi_{Fe}$:

$$\log \Psi_{Fe}(y_{Ni} y_C) - \log \Psi_{Fe}(y_{Ni}, y_C = 0) \equiv \delta \log \Psi_{Fe}$$
$$= \left\{\int_0^{y_C}\left[\log \frac{\Psi_C}{\Psi_C^\circ} - y_{Ni}\frac{\partial \log \Psi_C/\Psi_C^\circ}{\partial y_{Ni}}\right]dy_C - y_C \log \frac{\Psi_C}{\Psi_C^\circ}\right\}_{y_{Ni}}$$
$$[31]$$

According to Eq. [30] the value of $\log \Psi_C/\Psi_C^\circ$ is independent of y_{Ni} and is equal to $3.03 y_C$. Substitution in Eq. [31] gives

$$\delta \log \Psi_{Fe} = \int_0^{y_C} 3.03 y_C\, dy_C - 3.03 y_C^2 = -1.51 y_C^2 \qquad [32]$$

Thus, the effect of carbon on the activity coefficient of iron is independent of y_{Ni} up to $y_{Ni} = 0.25$. Because of the decreased solubility of graphite the maximum effect of carbon decreases sharply with increasing nickel content. In the binary Fe-C the solubility of graphite is $y_C = 0.0725$ while at $y_{Ni} = 0.25$ it is reduced to $y_C = 0.030$. Maximum values for $\delta \log \Psi_{Fe}$ are respectively −0.0080 and −0.0014. It is to be remembered that these are only the incremental effects of carbon, to which must be added the value of Ψ_{Fe} for the activity coefficient in the Fe-Ni binary.

Schuhmann's[20] method of integration is especially designed for use with triangular coordinates and is not readily applicable to the kinds of systems considered here. An alternative method which, like Schuhmann's, utilizes isoactivity lines and is applicable to systems such as a gas in a metal pair or carbon in a binary iron alloy is developed as follows. For simplicity the equations will apply to a solution in which $b = 1$.

Eq. [4] is differentiated with respect to y_2 keeping $\overline{G}_3$ constant.

$$\left(\frac{\partial G^L}{\partial y_2}\right)_{\overline{G}_3} = y_1\left(\frac{\partial \overline{G}_1}{\partial y_2}\right)_{\overline{G}_3} - \overline{G}_1 + y_2\left(\frac{\partial \overline{G}_2}{\partial y_2}\right)_{\overline{G}_3} + \overline{G}_2$$
$$+ \overline{G}_3\left(\frac{\partial y_3}{\partial y_2}\right)_{\overline{G}_3} \qquad [33]$$

Eq. [2] is divided by dy_2 again keeping $\overline{G}_3$ constant

$$y_1\left(\frac{\partial \overline{G}_1}{\partial y_2}\right)_{\overline{G}_3} + y_2\left(\frac{\partial \overline{G}_2}{\partial y_2}\right)_{\overline{G}_3} = 0 \qquad [34]$$

Subtracting the above

$$\left(\frac{\partial G^L}{\partial y_2}\right)_{\overline{G}_3} = \overline{G}_2 - \overline{G}_1 + \overline{G}_3\left(\frac{\partial y_3}{\partial y_2}\right)_{\overline{G}_3} \qquad [35]$$

which is combined with Eq. [4] and rearranged to give

$$\bar{G}_2 = G^L - y_3\bar{G}_3 + y_1 \left(\frac{\partial (G^L - y_3\bar{G}_3)}{\partial y_2} \right)_{\bar{G}_3} \qquad [36]$$

Now if the value of $(G^L - y_3\bar{G}_3)$ for a specific constant value of the chemical potential $\bar{G}_3$ of component 3 is plotted against y_2 and a tangent is drawn at any value of y_2, the intercept at $y_2 = 1$ is $\bar{G}_2$ and the intercept at $y_1 = 1$ is $\bar{G}_1$.

In order to calculate the activities of components 1 and 2 by means of Eq. [36], it is necessary to know the free energy of the whole solution, G^L containing 1 mole of the lattice elements and y_3 moles of the interstitial. If G^M, the molar free energy, is known for all compositions of the base-binary 1-2, the value of G^L for any quasibinary of fixed y_2 is by Eq. [6]

$$G^L = G^M + \int_0^{y_3} (\bar{G}_3 \, \partial y_3)_{y_2} \qquad [37]$$

Since $\bar{G}_3$ is a function of y_3 the integral of Eq. [37] may be replaced by $[y_3\bar{G}_3 - \int_0^{y_3}(y_3 \, d\bar{G}_3)_{y_2}]$. This is substituted in Eq. [36] to yield Eq. [38] which applies to a series of values of y_2:

$$\bar{G}_2 = G^M - \int_0^{y_3} (y_3 \, \partial \bar{G})_{y_2} + y_1 \frac{\partial}{\partial y_2} \left[G^M - \int_0^{y_3} (y_3 \, \partial \bar{G}_3)_{y_2} \right]_{\bar{G}_3}$$
$$[38]$$

This equation is based on thermodynamics alone and may be solved when sufficient data are available without recourse to models or empirical equations. However, sufficient data are rarely available and empirical equations may be very helpful.

It will be convenient to divide Eq. [38] by $2.3RT$ and to introduce the defined term E which can be evaluated for each specific value of y_2:

$$E \equiv G^M/2.3RT - \int_0^{y_3} (y_3 \, \partial \log a_3)_{y_2} \qquad [39]$$

This procedure gives the useful results:

$$\log a_2 = E + y_1 \left(\frac{\partial E}{\partial y_2} \right)_{a_3} \qquad [40]$$

Similarly

$$\log a_1 = E + y_2 \left(\frac{\partial E}{\partial y_1} \right)_{a_3} \qquad [41]$$

If information on the base-binary is lacking, Eqs. [40] and [41] give us only the increment in $\log a_1$ or $\log a_2$ due to the presence of component 3. This increment is designated $\delta \log a_1$ or $\delta \log a_2$. Since the value of G^M is unknown and we are concerned only with incremental values in $\log a_1$ or $\log a_2$, we simply let G^M equal to 0 for all values of y_2. Then, if E is to be used only in an incremental calculation, we may call it E_δ and write

$$E_\delta = - \int_0^{y_3} (y_3 \, \partial \log a_3)_{y_2} \qquad [42]$$

This is to be evaluated from experimental data on a_3 at various values of y_2. The activity a_3 is replaced by $\Psi_3 z_3$.

We now introduce the empirical observation that $\log \Psi_3$ is a linear function of y_3 for a fixed value of y_2,
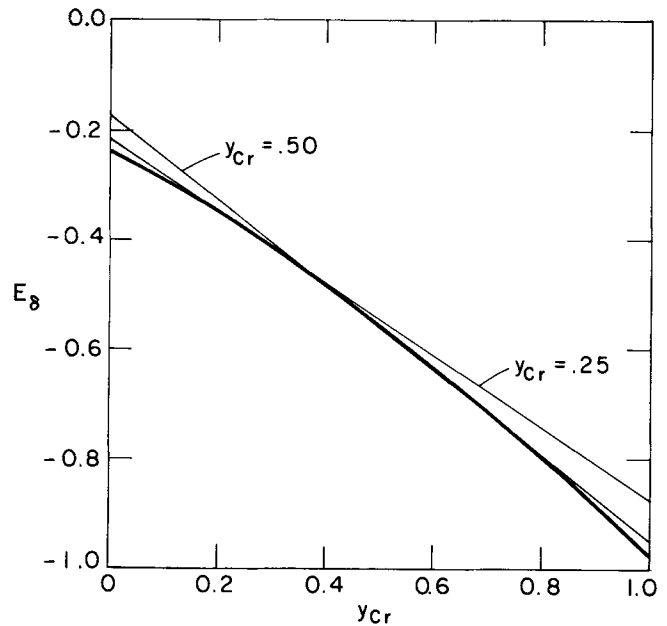

Fig. 6—Determination of the effect of carbon on the individual activities in liquid Fe-Cr solution at 1660°C.

Table I. Effect of Graphite Saturation on the Activities of Iron and Chromium at 1660°C

y_{Cr}	0	0.1	0.25	0.50	0.75 (extrap)	1 0 (extrap)
y_C sat	0.275	0 306	0.355	0.429	0.484	
y_C^2	0.0756	0.094	0.126	0.184	0.234	
$\theta_C/2.303$	2.48	2.68	2.98	3.48	3.99	
$-\frac{1}{2}\theta_C y_C^2/2.3$	-0.094	-0.126	-0.188	-0.320	-0.467	
$\log(1 - y_C)$	-0.140	-0.161	-0.191	-0.243	-0.287	
E_δ	-0.234	-0.287	-0.379	-0.563	-0.754	
$\delta \log a_{Fe}$	-0.234	-0.232	-0.217	-0.17	-0.13	-0.1
$\delta \log a_{Cr}$	-0.75	-0 79	-0.87	-0.95	-0.97	-0.98

Eq. [21]. The integration follows the same course as that used in obtaining Eq. [22] and the result is similar, namely,

$$E_\delta = - \frac{1}{4.6} [\theta_3]_{y_2} y_3^2 + \log (1 - y_3) \qquad [43]$$

The increment in $\log a_2$ attributable to the presence of component 3 at the fixed activity a_3 is:

$$\delta \log a_2 = E_\delta + y_1 \left(\frac{\partial E}{\partial y_2} \right)_{a_3} \qquad [44]$$

As an example, let it be required to find the effect of graphite saturation in the liquid system Fe-Cr-C on the activities of the two metallic components. The activity of carbon has been determined by Richardson and Dennis[21] for a number of quasibinaries while graphite solubilities are interpolated from Griffing, Forgeng, and Healy.[22] Their data, as analyzed by the author,[6] are shown in Table I along with the terms required for solution of Eq. [44]. A plot is shown in Fig. 6 with tangents drawn at the experimental compositions. Their intercepts, tabulated as $\delta \log a_{Fe}$ and $\delta \log a_{Cr}$, represent the effect of graphite saturation on the activities of the two components.

Let it be understood that the methods here suggested are not of broad general usefulness, but are speci-

fically applicable to interstitial solutions and to certain liquid solutions which are found by experiment to conform to Eq. [21].

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