[CONTRIBUTION FROM THE RESEARCH LABORATORY, UNITED STATES STEEL CORPORATION OF DELAWARE, KEARNY, NEW JERSEY]

Application of the Gibbs-Duhem Equation to Ternary and Multicomponent Systems

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The literature contains very few data on the thermodynamics of isotherms of ternary or multicomponent solutions. Likewise, little is to be found on the theoretical treatment of such solutions, except for regions limited to the vicinity of a pure solvent. This paper deals with an isothermal isobaric section of a ternary system in which section there is but one phase region—that of the single phase solution. With the aid of no extra-thermodynamic assumption other than the assumption of Henry's law as a limiting law at infinite dilution, it is demonstrated that it is possible to calculate the molal free energy, hence the partial molal free energies of the other two components, from an experimental knowledge of the partial molal free energy of one component at all compositions. The same method may readily be extended to systems of more than three components and to functions other than the free energy.

As a preliminary step let us consider the applicability to a ternary system of the well known relation, $\overline{G}_i = G + (1 - N_i)(\mathrm{d}G/\mathrm{d}N_i)$, valid under isothermal isobaric conditions for binary solutions; this relation follows from the generalized Gibbs–Duhem equation. Here, G represents the molal value of any extensive property, $\overline{G}_i$ the corresponding partial molal quantity for the ith component and N_i the mole fraction of the ith component. Since any solution, no matter how many components it contains, may be regarded as binary if we arbitrarily limit composition changes to those corresponding to addition or removal of only one component, it follows that the foregoing equation applies to a multicomponent solution, provided that the derivative $\mathrm{d}G/\mathrm{d}N_i$ be interpreted as a partial derivative, all ratios of mole fractions except those involving N_i being constant. For a ternary system, focusing our attention upon component 2 which is here regarded as the component whose partial molal quantity is experimentally known, we may then write[1]

$$\overline{G}_2 = G + (1 - N_2)\left(\frac{\partial G}{\partial N_2}\right)_{N_1/N_3} \tag{1}$$

By rearranging terms and dividing by $(1 - N_2)^2$, this expression may also be written

$$\left(\frac{\partial \dfrac{G}{1 - N_2}}{\partial N_2}\right)_{N_1/N_3} = \frac{\overline{G}_2}{(1 - N_2)^2} \tag{2}$$

Integration from $N_2 = 1$ to N_2 gives

$$G - (1 - N_2) \lim_{N_2 \to 1} \frac{G}{1 - N_2} = (1 - N_2)\int_1^{N_2} \frac{\overline{G}_2}{(1 - N_2)^2}\,\mathrm{d}N_2 \tag{3}$$

the integration and limit to be taken at constant value of N_1/N_3.[1a]

Let us now apply this relation to the excess molal free energy of mixing F^{xs} which is defined as $F^{xs} = F - F^i$ where F^i is the ideal contribution to the free energy — $\overline{F}_2^{xs} = \overline{F}_2 - \overline{F}_2^{i} = RT\ln\gamma_2$ where γ_2 is the activity coefficient of component 2. Equation 3 now becomes

$$F^{xs} - (1 - N_2) \lim_{N_2 \to 1} \left(\frac{F^{xs}}{1 - N_2}\right) = (1 - N_2)\int_1^{N_2} \frac{\overline{F}_2^{xs}}{(1 - N_2)^2}\,\mathrm{d}N_2 \tag{3a}$$

it being understood that the integration and limit are to be carried out at constant N_1/N_3; in the usual triangular method of representing composition, the integral is taken along a straight line connecting the point of interest to the corner corresponding to pure component 2, as in Fig. 1.

The limit in Eq. 3a is an indeterminate form which may be evaluated by aid of l'Hopital's theorem whereby

$$\lim_{N_2 \to 1} \left(\frac{F^{xs}}{1 - N_2}\right) = - \lim_{N_2 \to 1} \left(\frac{\partial F^{xs}}{\partial N_2}\right)_{N_1/N_3}$$

which by Eq. 1 becomes

$$\lim_{N_2 \to 1} \left(\frac{F^{xs}}{1 - N_2}\right) = - \lim_{N_2 \to 1} \left(\frac{\overline{F}_2^{xs} - F^{xs}}{1 - N_2}\right)$$

and by virtue of the relations $F^{xs} = N_1\overline{F}_1^{xs} + N_2\overline{F}_2^{xs} + N_3F_3^{xs}$, $N_1 = \dfrac{1 - N_2}{1 + \dfrac{N_3}{N_1}}$ and $N_3 = \dfrac{1 - N_2}{1 + \dfrac{N_1}{N_3}}$,

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[1] A more detailed derivation of Eq. 1 for a ternary system is: the relation

$$G = N_1\overline{G}_1 + N_2\overline{G}_2 + N_3\overline{G}_3$$

is differentiated partially with respect to N_2 at constant N_1/N_3, giving

$$\left(\frac{\partial G}{\partial N_2}\right)_{N_1/N_3} = N_1\left(\frac{\partial \overline{G}_1}{\partial N_2}\right)_{N_1/N_3} - \frac{N_1}{1 - N_2}\overline{G}_1 + N_2\left(\frac{\partial \overline{G}_2}{\partial N_2}\right)_{N_1/N_3} + \overline{G}_2 + N_3\left(\frac{\partial \overline{G}_3}{\partial N_2}\right)_{N_1/N_3} - \frac{N_3}{1 - N_2}\overline{G}_3$$

By virtue of the Gibbs–Duhem equation ($N_1\mathrm{d}\overline{G}_1 + N_2\mathrm{d}\overline{G}_2 + N_3\mathrm{d}\overline{G}_3 = 0$) the sum of the first, third and fifth terms is zero, whence

$$\left(\frac{\partial G}{\partial N_2}\right)_{N_1/N_3} = -\frac{N_1}{1 - N_2}\overline{G}_1 + \overline{G}_2 - \frac{N_3}{1 - N_2}\overline{G}_3 = \frac{\overline{G}_2 - N_1\overline{G}_1 - N_2\overline{G}_2 - N_3\overline{G}_3}{1 - N_2} = \frac{\overline{G}_2 - G}{1 - N_2}$$

Rearrangement of terms gives Eq. 1.

[1a] Integration of Eq. 2 from $N_2 = 0$ to N_2 leads to

$$G = (1 - N_2)\left[G_{N_2=0} + \int_0^{N_2} \frac{\overline{G}_2}{(1 - N_2)^2}\,\mathrm{d}N_2\right]$$

thus providing a method of determining G for a ternary composition from a knowledge of (1) $\overline{G}_2$ for ternary compositions of constant N_1/N_3 and (2) G for the binary system with the same ratio N_1/N_3.

$$\lim_{N_2\to 1}\left(\frac{F^{xs}}{1-N_2}\right) = \left[\bar{F}_2^{xs} + \frac{1}{1+\frac{N_3}{N_1}}\,\bar{F}_1^{xs} + \frac{1}{1+\frac{N_1}{N_3}}\,\bar{F}_3^{xs}\right]_{N_2=1} \qquad (4)$$

If the standard state be so chosen for each component that $\bar{F}_i^{xs} = 0$ (*i.e.*, so that $\gamma_i = 1$) at $N_2 = 1$ then the above limit is zero, and Eq. 3a becomes

$$F^{xs\prime} = (1 - N_2)\int_1^{N_2} \frac{\bar{F}_2^{xs}}{(1-N_2)^2}\,dN_2 \qquad (5)$$

a prime being used to indicate this particular choice of standard state. If, however, the standard state be chosen as pure component in each case (*i.e.*, $\bar{F}_i^{xs} = 0$ at $N_i = 1$) then the limit becomes

$$\lim_{N_2\to 1}\left(\frac{F^{xs}}{1-N_2}\right) = \frac{1}{1+\frac{N_3}{N_1}}\,(\bar{F}_1^{xs})_{N_2=1} + \frac{1}{1+\frac{N_1}{N_3}}\,(\bar{F}_3^{xs})_{N_2=1} \qquad (4a)$$

All further treatment in this paper is based on this second choice of standard state. Eq. 3a becomes, on noting again that

$$N_1 = \frac{1-N_2}{1+\frac{N_3}{N_1}} \text{ and } N_3 = \frac{1-N_2}{1+\frac{N_1}{N_3}}$$

$$F^{xs} = (1-N_2)\int_1^{N_2}\frac{\bar{F}_2^{xs}}{(1-N_2)^2}\,dN_2 + N_1\,[\bar{F}_1^{xs}]_{N_2=1} + N_3\,[\bar{F}_3^{xs}]_{N_2=1} \qquad (5a)$$

The two constants $[\bar{F}_1^{xs}]_{N_2=1}$ and $[\bar{F}_3^{xs}]_{N_2=1}$ are determinable from measurements on the two binary systems 1–2 and 2–3, respectively. If $\bar{F}_2^{xs}$ is regarded as the experimentally determined quantity, these two constants may be expressed in terms thereof by application of the Gibbs–Duhem equation to each of these two binary systems.

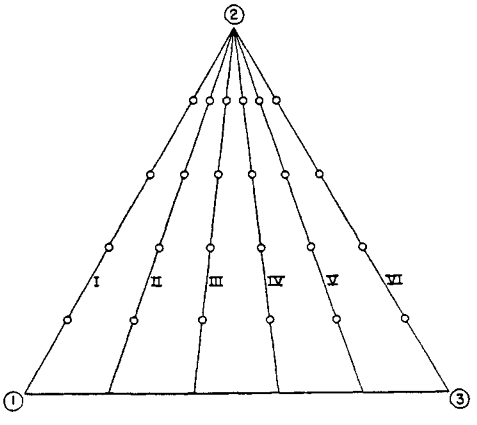

Fig. 1.—Illustration on triangular coördinates of compositions to be investigated in ternary system for proposed method of obtaining F^{xs} for binary system 1–3.

$$[\bar{F}_1^{xs}]_{N_2=1} = -\left[\int_1^0 \frac{\bar{F}_2^{xs}}{(1-N_2)^2}\,dN_2\right]_{N_3=0}$$

$$[\bar{F}_3^{xs}]_{N_2=1} = -\left[\int_1^0 \frac{\bar{F}_2^{xs}}{(1-N_2)^2}\,dN_2\right]_{N_1=0}$$

These two expressions may also be obtained from Eq. 5a by setting $N_3 = 0$ and $N_1 = 0$ respectively, N_2 being set zero in both cases. Substituting for these two constants in Eq. 5a

$$F^{xs} = (1-N_2)\left[\int_1^{N_2}\frac{\bar{F}_2^{xs}}{(1-N_2)^2}\,dN_2\right]_{N_1/N_3} - N_1\left[\int_1^0 \frac{\bar{F}_2^{xs}}{(1-N_2)^2}\,dN_2\right]_{N_3=0} - N_3\left[\int_1^0 \frac{\bar{F}_2^{xs}}{(1-N_2)^2}\,dN_2\right]_{N_1=0} \qquad (6)$$

This is the final equation expressing the excess molal free energy of a ternary solution in terms of the partial molal excess free energy of only one component. As noted previously, the standard state for each component is chosen as that pure component. It will be noted that in general the integrations may be performed, and F^{xs} thus evaluated, only if there are no miscibility gaps intersecting the lines along which the integrations are to be performed.

If, for a particular system, F^{xs} be so determined at all compositions then $\bar{F}_1^{xs}$ and $\bar{F}_3^{xs}$ may be determined, if desired, by the usual methods. For example Eq. 2 may be put in the following forms

$$\bar{F}_1^{xs} = (1-N_1)^2\left(\frac{\partial \frac{F^{xs}}{1-N_1}}{\partial N_1}\right)_{N_2/N_3}$$

$$\bar{F}_3^{xs} = (1-N_3)^2\left(\frac{\partial \frac{F^{xs}}{1-N_3}}{\partial N_3}\right)_{N_1/N_2}$$

Thus $\bar{F}_{xs}$, $\bar{F}_1^{xs}$ and $\bar{F}_3^{xs}$ may be evaluated at all compositions provided $\bar{F}_2^{xs}$ is known at all compositions.

A Method of Determining the Free Energy of Binary Systems.—Let us suppose that it is desired to determine experimentally the excess free energy of mixing of a binary solution (components designated 1 and 3) but that the usual methods do not seem practical for this particular case. For example, the vapor pressures may be too small for application of the vapor pressure method. However, it would frequently be possible to find another substance (designated component 2) which is volatile and is miscible in all proportions with components 1 and 3 and all mixtures thereof. In such a case it would be relatively easy to determine the vapor pressure of component 2 and hence $\bar{F}_2^{xs}$ in the ternary system. Similarly, it may be difficult to apply the e. m. f. method to a series of binary liquid metallic solutions; but perhaps another metal miscible with the other two, could be found. If, further, this other metal behaves reversibly (usually by virtue of lower electronegativity) in the cell, then its excess partial molal free energy may readily be determined.

In such cases Equation (6) may be applied to determine F^{xs} for the binary system. The binary system 1–3 is obviously a limiting case of the ternary system 1–2–3 in which $N_2 = 0$. Setting $N_2 = 0$ in Eq. 6 we find

$$F^{xs}_{(\text{binary system 1-3})} = \left[\int_1^0 \frac{\bar{F}_2{}^{xs}}{(1-N_2)^2}\,\mathrm{d}N_2\right]_{N_1/N_3} - N_1\left[\int_1^0 \frac{\bar{F}_2{}^{xs}}{(1-N_2)^2}\,\mathrm{d}N_2\right]_{N_3=0} - N_3\left[\int_1^0 \frac{\bar{F}_2{}^{xs}}{(1-N_2)^2}\,\mathrm{d}N_2\right]_{N_1=0} \quad (7)$$

Thus the free energy of formation of the binary solution 1–3, may be obtained by this indirect method. Although many more experimental measurements are required, this indirect method may be of occasional use in cases such as that discussed above in which direct measurements for the binary system are impractical.

The general scheme of the procedure is illustrated schematically in Figs. 1, 2 and 3. Figure 1 shows the compositions of the solutions along lines of constant ratio N_1/N_3. Figure 2 illustrates schematically the plot of the experimental data. The total area under each curve is then evaluated and plotted (with reversed sign) as indicated by Fig. 3 (top). F^{xs} at each value of N_3 for the binary system 1–3 then corresponds to the departure of the corresponding point from the straight line connecting the termini of the curve; these values of F^{xs} are indicated by the arrows in the top portion of Fig. 3 and are plotted at the bottom thereof. Obvious modification of this procedure is used if it is desired to obtain F^x for ternary compositions.

It seems worth while at this point to call attention to the fact that Equation 7 lends thermodynamic support to the chemists intuition that it is possible to gain some knowledge of the chemistry of a series of binary solutions by investigating the solubility of another substance slightly soluble therein. For example, the solubility of sulfur dioxide gas at 1 atm., in sulfuric acid–water mixtures is a minimum at a composition (86% sulfuric acid) corresponding approximately to the one to one ratio of sulfuric acid to water (84.5% sulfuric acid). This behavior is commonly interpreted as evidence of the existence of a hydrate of sulfuric acid in aqueous solution. Although Eq. 7 cannot be fully applied with this limited amount of information, it would not seem unreasonable to infer that such minimum solubility would be found at higher concentrations of sulfur dioxide also, and hence that the first integral in Eq. 7 would have a minimum value at or near this ratio of sulfuric acid to water. Granting this inference, it follows then from Eq. 7 that the excess free energy F^{xs} of the binary system H_2SO_4–H_2O has a minimum value at this ratio. Thus in a sense, the intuitive reasoning is justified

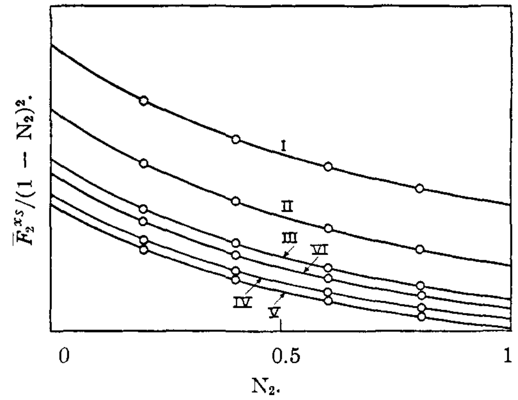

Fig. 2.—Schematic representation of $\frac{\bar{F}_2{}^{xs}}{(1-N_2)^2}$ as functions of N_2 along the lines of Fig. 1.

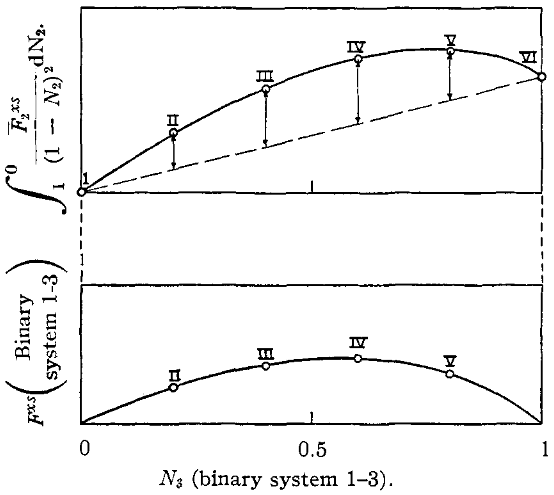

Fig. 3.—Top—the integrals of the curves in Fig. 2 plotted as a function of N_3 for the binary system 1–3. Bottom—replot of the distances indicated by arrows above, which are values of F^{xs} for the binary system 1–3.

—although of course thermodynamics gives no direct support to the idea of hydration or compound formation in solution.

One further example will be given. Liang, Bever and Floe[1b] have measured the solubility of hydrogen gas at 1 atm. pressure in molten iron–silicon alloys. The logarithm of the solubility ($= \bar{F}_2{}^{xs}/2.303RT +$ Const) is shown in Fig. 4. This is perhaps a rather unexpected type of curve exhibiting a near discontinuity in slope near the one to one atom ratio. If we may be permitted to infer that $\bar{F}_2{}^{xs}$ would behave similarly over part of the ternary system, then the first integral of Eq. 7, and hence the excess free energy of the binary system iron–silicon, would exhibit a similar near-discontinuity in slope near the one to one ratio of iron to silicon. The relation may be found more explicitly if we make, for the purpose of illustration, the crude

(1b) H. Liang, M. B. Bever and C. F. Floe, *Trans. Am. Inst. Min. Met. Engrs.*, **167**, 395 (1946).

approximation that $\bar{F}_2^{xs}/(1 - N_2)^2$ is a function of the ratio N_1/N_3 only, hence from Eq. 7

$$F^{xs}_{(\text{Fe-Si System})} = -\bar{F}^{xs}_{2(N_2=0)} + N_1\bar{F}^{xs}_{2(N_1=1)} + N_3\bar{F}^{xs}_{2(N_3=1)}$$

Denoting the low solubility of H_2 as N_2^0 this becomes (approximately)

$$F^{xs}_{(\text{Fe-Si System})} = RT\,[\ln N_2^0 - N_1 \ln N_2^0{}_{(N_1=1)} - N_3 \ln N_2^0{}_{(N_3=1)}]$$

This gives an explicit relation for the excess free energy of the binary system, although a very crude approximation is involved. It is thus seen from this relation that on the basis of this crude assumption the excess free energy of iron–silicon solutions is proportional to the lengths of the arrows in Fig. 4. Crude as this may be it indicates a rather large departure from ideality in the system iron–silicon ($F^{xs} = -7000$ cal. per gram atom); a strong possibility of a rather unusual behavior in this binary system is indicated by the near discontinuity in slope.

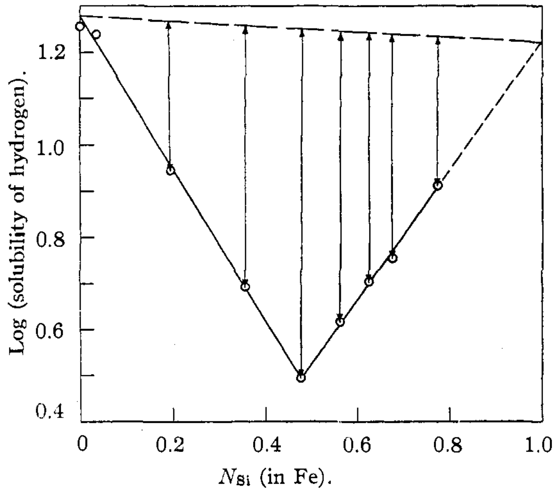

Fig. 4.—Solubility of hydrogen in molten iron–silicon alloys at 1650° (data of Liang, Bever and Floe). Solubility is expressed as cc. NTP of H_2 per gram atom of alloy. Length of arrows indicates crude approximation of $\dfrac{F^{xs}}{2.303RT}$ for binary system Fe–Si.

It is apparent that the method of this section may be extended to find G for an n-component solution by the introduction of an additional miscible component and by measurement of $\bar{G}$ therefore.

Limitations of the Method.—As illustrated in Fig. 2, Eqs. 6 and 7 call for the integration of the function $\bar{F}_2^{xs}/(1 - N_2)^2$ over the entire range of N_2 from zero to one. If the proposed method is to be fruitful, then $\bar{F}_2^{xs}/(1 - N_2)^2$ must be a reasonably well-behaved function. Certainly it would be disastrous if the integrals thereof approached infinite value. It may easily be shown that the integral may be written

$$\int_0^1 \frac{\bar{F}_2^{xs}}{(1 - N_2)^2}\,dN_2 = -\frac{1}{1 + \dfrac{N_1}{N_3}}\left\{\frac{N_1}{N_3}[(\bar{F}_1^{xs})_{N_2=1} - (\bar{F}_1^{xs})_{N_2=0}] + [(\bar{F}_3^{xs})_{N_2=1} - (\bar{F}_3^{xs})_{N_2=0}]\right\}$$

Barring dissociation, all the partial molal excess free energies appearing on the right side are non-infinite[2] (by virtue of Henry's law) and hence it follows that the integral is finite.

The utility of Eqs. 6 and 7 would be seriously impaired if the function $\bar{F}_2^{xs}/(1 - N_2)^2$ ever approaches infinite value even though its integral does not. The behavior of this function must therefore be investigated, particularly as N_2 approaches one. Modern solution theory and experiment[3] are in accord that for non-electrolytes, $N_1\partial\bar{F}_1^{xs}/\partial N_2$ is proportional to N_1 (or to $1 - N_2$ under the condition considered) at sufficiently low concentration. Using a similar expression for $N_3\partial\bar{F}_3^{xs}/\partial N_2$, it is readily found by aid of the Gibbs–Duhem Equation and d'Hopital's theorem that $\lim\limits_{N_2\to 0} \dfrac{\bar{F}_2^{xs}}{(1 - N_2)^2}$ is not infinite. This matter as well as the further complications involved in the treatment of solutions of electrolytes is discussed by Scatchard and Prentiss.[4]

Attention should be called to the fact that although, for non-electrolytes, the function $f = \bar{F}_2^{xs}/(1 - N_2)^2$ is probably finite at all compositions, the precise evaluation thereof in the vicinity of $N_2 = 1$ requires a very high degree of experimental accuracy. Departures from ideality, and hence $\bar{F}_2^{xs}$ and also $(1 - N_2)^2$, are very small in this vicinity. For the binary metallic systems on which data are available in the literature there is no indication of any anomalous behavior of the function, f, in the vincity of $N_2 = 1$. Hence it seems reasonable to suppose that the best construction of the curve (f against N_2) in the vicinity of $N_2 = 1$ is by smooth extension from the region in which the experimental precision is good, *i.e.*, that discordant points near $N_2 = 1$ should be disregarded in the construction of the curve (Fig. 2). It will be noticed that to obtain equal precision in f over the range of experimental observations, the precision in $\bar{F}_2^{xs}$ must increase markedly with increase in N_2; for example the precision at $N_2 = 0.9$ should be 100 times as great as in the vicinity of $N_2 = 0$. Vapor pressure and e. m. f. methods tend to give greater precision at high values of N_2 but not this much greater. However, attention should be called

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[2] If dissociation occurs, the difficulty of an infinite integral may be avoided by choosing the products of dissociation as components. In metallic systems the chemical elements are chosen as components and this possibility is avoided.

[3] M. Margules, *Sitzber. d. Wien Akad.*, [2] **104**, 1243 (1895); A. W. Porter, *Trans. Far. Soc.*, **16**, 236 (1921); George Scatchard, *Chem. Rev.*, **8**, 321 (1931); J. H. Hildebrand, "Solubility of Non-Electrolytes," Reinhold Publ. Corp., New York, N. Y., 1936; Fowler and Guggenheim, "Statistical Thermodynamics," Cambridge University Press, 1939; W. J. C. Orr, *Trans. Far. Soc.*, **40**, 320 (1944).

[4] George Scatchard and S. S. Prentiss, THIS JOURNAL, **56**, 1486 and 2314 (1934).

to the fact that this demand for greater precision in the vicinity of $N_2 = 1$ is inherent in any method utilizing the Gibbs–Duhem equation. Frequently, it is concealed by the method of treatment. In fact, it is common in experimental investigations to neglect this region entirely, upon the assumption that Raoult's law is rapidly approached and measurement is unnecessary. Although it is true that Raoult's law is here approached rapidly, nevertheless it is the small departures therefrom which are important in determining the partial molal free energy of the other constituent(s) by any method involving the Gibbs–Duhem equation. The present method makes clear this requirement, whereas some other methods of applying the Gibbs–Duhem equation to binary systems do not; this latter fact has contributed to a tendency on the part of some experimental investigators to ignore compositions in the vicinity of the pure component whose partial pressure or activity is being measured.

Application to Other Thermodynamic Functions.—The same method developed here may be applied to the molal values of other extensive thermodynamic functions which have zero value at $N_2 = 1$; such functions are the enthalpy, energy and volume of mixing, and the excess entropy. This is apparent from the consideration that equation (3) and the evaluation of the limit leading to Eq. 4a are perfectly general. From Eq. 4a it is seen that the general form of the limit in Eq. 3 is

$$\lim_{N_2 \to 1} \frac{G}{1 - N_2} = \frac{1}{1 + \frac{N_3}{N_1}} [\overline{G}_1]_{N_2=1} + \frac{1}{1 + \frac{N_1}{N_3}} [\overline{G}_3]_{N_2=1}$$

which is never infinite unless $[\overline{G}_1]_{N_2=1}$ or $[\overline{G}_3]_{N_2=1}$ is, providing as mentioned above that $G = 0$ at $N_2 = 0$. Hence it is apparent that the method is applicable in principle to any molal quantity which has the value zero at $N_2 = 0$ providing that none of the corresponding partial molal quantities become infinite at infinite dilution and providing that $\overline{G}_2$ approaches zero as N_2 approaches unity. The general equation is similar to Eq. 6.

$$G = (1 - N_2)\left[\int_1^{N_2} \frac{\overline{G}_2}{(1 - N_2)^2}\,\mathrm{d}N_2\right]_{N_1/N_3} - N_1\left[\int_1^{0} \frac{\overline{G}_2}{(1 - N_2)^2}\,\mathrm{d}N_2\right]_{N_3=0} - N_3\left[\int_1^{0} \frac{\overline{G}_2}{(1 - N_2)^2}\,\mathrm{d}N_2\right]_{N_1/0} \quad (6a)$$

It will be noted that for the functions

$$\frac{\overline{H}_2 - H_2^0}{(1 - N_2)^2}, \frac{\overline{S}_2^{xs}}{(1 - N_2)^2}, \text{ and } \frac{\overline{V}_2 - V_2^0}{(1 - N_2)^2}$$

essentially the same considerations as to finite values apply as for $\overline{F}_2^{xs}/(1 - N_2)^2$ this by virtue of the thermodynamic relations between H, S, V and F. For example, since

$$\left\{\frac{\partial\left[\frac{\overline{F}_2^{xs}}{(1 - N_2)^2}\Big/ T\right]}{\partial[1/T]}\right\}_{P,\text{ Comp.}} = \frac{\overline{H}_2 - H_2^0}{(1 - N_2)^2}$$

it is seen that if $\lim_{N_2 \to 1} \frac{\overline{F}_2^{xs}}{(1 - N_2)^2}$ is finite at all temperatures, then in general[5] the derivative and hence $\lim_{N_2 \to 1} \frac{\overline{H}_2 - H_2^0}{(1 - N_2)^2}$ is finite. Similarly, since

$$\left\{\frac{\partial\left[\frac{\overline{F}_2^{xs}}{(1 - N_2)^2}\right]}{\partial T}\right\}_{P.\text{Comp.}} = \frac{\overline{S}_2^{xs}}{(1 - N_2)^2} \text{ and}$$

$$\left\{\frac{\partial\left[\frac{\overline{F}_2^{xs}}{(1 - N_2)^2}\right]}{\partial P}\right\}_{T,\text{Comp.}} = \frac{\overline{V}_2 - V_2^0}{(1 - N_2)^2}$$

it follows in general that the limit of $\overline{S}_2^{xs}/(1 - N_2)^2$ and of $(\overline{V}_2 - V_2^0)/(1 - N_2)$ as $N_2 \to 1$ is also finite.

Extension to Multicomponent Solutions.—The same method is readily extended to systems of more than three components. Equations 1 and 2 hold in identically the same form except that the partial derivatives are to be interpreted as partials at constant ratio of all mole fractions except for ratios involving N_2. Equation 3 is then valid under the condition that the integration and limit are to be taken in this same way. The final equation (6) or (6a) follows in just the same way and with the same limitation as for a ternary system. Thus the excess free energy, or other extensive property meeting the requirements discussed in the preceding section, at all compositions in a multicomponent solution may be derived from a precise knowledge of the corresponding partial molal quantity of any one component at all compositions.

Acknowledgment.—The author wishes to acknowledge the benefit of discussion with George Scatchard (Mass. Inst. of Tech.) who kindly reviewed the fundamental idea of this contribution and offered suggestions for the improvement of the presentation.

Summary

A general method has been developed for determining a molal quantity and the other corresponding partial molal quantities for ternary and multicomponent solutions under isothermal isobaric conditions, from an experimental knowledge of one of the corresponding partial molal quantities, but at all compositions. The general relation is

$$G = (1 - N_2)\left[\int_1^{N_2} \frac{\overline{G}_2}{(1 - N_2)^2}\,\mathrm{d}N_2\right]_{\frac{N_3}{N_1}, \frac{N_4}{N_1}, \ldots} - N_1\left[\int_1^{0} \frac{\overline{G}_2}{(1 - N_2)_2}\,\mathrm{d}N_2\right]_{\frac{N_3}{N_1}, \frac{N_4}{N_1}, \ldots = 0} -$$

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[5] Exceptions may conceivably exist at particular temperatures at which the plot of $\lim_{N_2 \to 1} \frac{\overline{F}_2^{xs}}{(1 - N_2)^2}$ *vs.* $1/T$ may exibit infinite slope.

$$N_3\left[\int_1^0 \frac{\overline{G}_2}{(1 - N_2)^2}\,\mathrm{d}N_2\right]_{\frac{N_1}{N_3},\frac{N_4}{N_3}\ldots = 0} - \ldots$$

The only assumptions involved are: (1) that G is the molal value of an extensive function, and hence that the extended Gibbs–Duhem equation may be applied; G must be so chosen as to have zero value for each pure component; (2) that Henry's law is valid as a limiting law for all components at infinite dilution. The restrictions on the usefulness of the relation are discussed; departures from Henry's law at small finite concentrations must be such that $\overline{G}_2$ is proportional to $(1 - N_2)^2$ in the near vicinity of $N_2 = 1$, in order that the function to be integrated in the above equation be always finite.

It is shown that the above equation may be used as the basis of a new method for determining G for an n-component solution; this method involves the introduction of another miscible component and the experimental determination of $\overline{G}$ therefor in the new system of $n + 1$ components.

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Heat Capacities at Low Temperatures and Entropies of Zirconium, Zirconium Nitride, and Zirconium Tetrachloride

BY S. S. TODD[1]

A recent paper of Coughlin and King[2] presents high-temperature heat-content data for zirconium metal and its oxide (ZrO_2), nitride (ZrN), silicate ($ZrSiO_4$), and tetrachloride ($ZrCl_4$). The present paper gives low-temperature heat-capacity values and entropies at 298.16° K. for the metal, nitride, and tetrachloride, thus making possible free-energy calculations for the last two substances. Low-temperature heat-capacity and entropy values for the oxide and silicate have been reported by Kelley.[3,4]

Heat Capacities

The materials used in this investigation were identical with those described by Coughlin and King,[2] and repetition of the methods of preparation and tests of purity appears unnecessary. Correction was made for the hafnium contents, based upon the assumption that corresponding zirconium and hafnium compounds have the same molal heat capacity. This correction increased the measured heat-capacity values by the following amounts: Zr, 1.0%; ZrN, 0.7%; and $ZrCl_4$, 0.35%.

The measurements were made with previously described apparatus.[5] The results, expressed in thermochemical calories[6] (1 cal. = 4.1833 int. joules), are listed in Table I and plotted against

TABLE I

MOLAL HEAT CAPACITIES

T, °K.	Cp, cal./deg.	T, °K.	Cp, cal./deg.	T, °K.	Cp, cal./deg.
		Zr (mol. wt., 91.22)			
53.2	2.418	115.0	4.796	216.4	5.861
56.8	2.640	124.1	4.971	226.2	5.905
60.8	2.873	136.1	5.172	236.4	5.948
65.6	3.134	146.2	5.293	246.0	5.981
70.6	3.383	156.0	5.409	256.7	6.042
75.4	3.609	166.1	5.510	266.4	6.083
79.8	3.789	176.0	5.606	276.4	6.127
84.1	3.945	186.2	5.672	286.6	6.149
94.9	4.296	196.1	5.737	296.8	6.168
104.5	4.562	206.3	5.802	(298.16)	(6.186)
		ZrN (mol. wt., 105.23)			
53.1	1.198	114.9	4.416	216.6	8.048
57.1	1.426	124.8	4.867	226.5	8.287
62.0	1.699	136.2	5.358	236.5	8.516
67.5	2.018	145.9	5.747	246.0	8.714
72.7	2.308	155.9	6.137	256.4	8.954
77.6	2.574	166.2	6.517	266.4	9.127
80.5	2.731	176.7	6.876	276.6	9.325
85.3	2.978	186.2	7.177	286.8	9.482
95.2	3.477	196.4	7.495	296.7	9.613
104.8	3.946	206.7	7.784	(298.16)	(9.655)
		$ZrCl_4$ (mol. wt., 233.05)			
52.6	11.24	114.6	20.24	216.6	26.53
55.9	11.86	124.7	21.21	226.7	26.79
60.0	12.63	136.1	22.23	236.4	27.11
64.9	13.53	146.3	22.97	246.3	27.37
69.3	14.30	156.2	23.66	256.5	27.66
74.0	15.06	166.3	24.25	266.4	27.94
80.0	15.98	176.3	24.87	276.5	28.17
83.9	16.53	186.4	25.33	286.8	28.37
94.8	17.96	196.4	25.75	296.7	28.63
104.6	19.15	206.7	26.15	(298.16)	(28.65)

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(1) Pacific Experiment Station, U. S. Bureau of Mines. Article not copyrighted.

(2) J. P. Coughlin and E. G. King, THIS JOURNAL, **72**, 2262 (1950).

(3) K. K. Kelley, (a) *ibid.*, **63**, 2750 (1941); (b) *Ind. Eng. Chem.*, **36**, 377 (1944).

(4) In this connection, it appears worth-while to record that Kelley's entropy values should be increased slightly to account for the now known hafnium contents of the materials. Recalculation gives $S^0_{298.16}$ = 12.12 ± 0.08 for ZrO_2 (monoclinic) and $S^0_{298.16}$ = 20.2 ± 0.2 for $ZrSiO_4$ (zircon).

(5) K. K. Kelley, B. F. Naylor, and C. H. Shomate, *U. S. Bur. Mines Tech. Paper*, 686 (1946).

(6) E. F. Mueller and F. D. Rossini, *Am. J. Phys.*, **12**, 1 (1944).