ACTIVITY AND RELATED THERMODYNAMIC QUANTITIES; THEIR DEFINITION, AND VARIATION WITH TEMPERATURE AND PRESSURE

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The behavior of chemical systems can be simply expressed in terms of a thermodynamic quantity called chemical potential; in theory as well as in practice[1] the chemical potential is of great utility, a large number of the laws of physical chemistry depending directly or indirectly on relations involving this quantity, as shown in detail by Gibbs (6). In the application of the relations to actual measurements there have appeared to be certain difficulties in computation and presentation. Especially in very dilute solutions, or in gases at low pressures, the chemical potential may be inconvenient to tabulate, and the results do not easily give a clear picture of the change in properties of the solution as the concentration varies. Presumably for this reason various substitutes for chemical potential have been proposed and widely used, notably activity, activity coefficient, and osmotic coefficient. These are functions of the chemical potential (or of the partial molal free energy) and are readily obtained from it. For most concentrated solutions it has seemed to some investigators that the advantage of these derived quantities is questionable. The writer in some recent work (2) on the properties of solutions and systems under high pressures, involving much computation of thermodynamic data, came to the conclusion (1) that for such purposes the chemical potential was as convenient as any other function.

On the other hand, we should not lose sight of two important considerations, first, that the introduction of the function, activity, proved a powerful stimulus to the use of thermodynamics by physical chemists, and second, that today activity and related quantities, rather than chemical potential and partial molal free energy, serve as the usual medium for expressing the results of thermodynamic measurements on solutions. This is strikingly evident from a survey of current articles on the subject in

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[1] For example, in the determination of solubility curves in systems under pressure by graphical analysis of the chemical potential of a given component in the various phases.

various journals. If, for example, we count the pertinent entries in the index of *Chemical Abstracts* for 1934 (the most recent available at the time this is written) we shall find references to one hundred and three papers. The number of entries for activity is eleven, for activity coefficient forty-three, for chemical potential three, for thermodynamic potential one, and for free energy forty-five. Of the one hundred and three papers, sixty-one are concerned with solutions, eight using chemical potential or partial molal free energy, and fifty-three activity or activity coefficient.

But whether in the study of solutions we prefer to deal with the classical chemical potential (partial free energy), or with the newer functions such as activity, or whether we number ourselves among the very few who do not object to using the one or the other as occasion may arise, it is important to have the interrelations in unambiguous form and to be able to avoid uncertainties in the interpretation of thermodynamic data expressed in any of the commonly accepted units.

The writer's attention was directed toward this subject in utilizing some measurements on solutions for determining the effect of pressure on activity coefficient. Now that the experimental methods for such measurements have been developed, much interesting information will probably be obtained, allowing us to observe how the various well-known solution laws apply to solutions confined at pressures of 10,000 atmospheres or more. It has seemed worthwhile to reëxamine critically the definition of activity (as well as other related quantities) and to put it in an equivalent form that is more amenable to the common mathematical operations such as differentiation. This, together with a correlation of the temperature and pressure coefficients of five related thermodynamic functions, is the object of the present communication.

DEFINITIONS

Activity

The activity of a pure substance, or of a specified component in a solution, is commonly defined (13, 15) in either of two ways: (1) in terms of the previously defined[2] fugacity (12, 16), the activity of the material or component being the ratio of its fugacity in the given state to that in some "standard state"; or (2) by the relation

$$\bar{F}_2 - \bar{F}_2^0 = RT \ln a_2 \tag{1}$$

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[2] For a critique of Lewis' definition of fugacity see G. Tunell (J. Phys. Chem. **35**, 2885–913 (1931)), who showed that the fugacity as used by Lewis and Randall (15) is rigorously defined by their equation 14 (Chap. XVII, p. 195), whereas it cannot be defined mathematically by their equation 2 (Chap. XVII, p. 191) and the equations $P^* = f^*$ when $P^* = 0$ (Chap. XVII, p. 193).

in which a_2 denotes the activity of component 2, T the absolute temperature, R the gas constant, $\bar{F}_2$ the partial molal free energy (i.e., the chemical potential per mole), and $\bar{F}_2^0$ the value of $\bar{F}_2$ in the "standard state." Equation 1 is also applicable to a pure substance, the subscripts then merely identifying the material. While $\bar{F}_2$ and a_2 are functions of temperature, pressure, and concentration, $\bar{F}_2^0$ is by definition a function only of T. It may be noted that for the standard state, $\bar{F}_2 = \bar{F}_2^0$ and by equation 1 $a_2 = 1$. ($\bar{F}_2^0$ is considered further in the following paragraph.) It is also important to note that the numerical value of $\bar{F}_2$ involves an arbitrary molecular weight or formula weight. The assumed molecular weight is a part of the definition of activity; in order to avoid ambiguity we should write

$$\bar{F}_2 = M_2\mu_2 \tag{2}$$

M_2 being the value taken for the molecular weight, and μ_2 being the chemical potential per gram.

The definition of activity is usually completed by giving more particulars concerning the state designated as "standard." This may be done in a number of ways; for example, by letting this state refer to such a concentration that the ratio of activity to molality approaches unity as the solution becomes more and more dilute. That is,

$$\lim_{m \to 0} \frac{a_2}{m} = 1 \tag{3a}$$

in which m denotes the molality (moles per 1000 grams of solvent). By definition this relation holds at any temperature but only at $P = 1$. It should be noted, however, that an activity may be defined (22) in such a way that the above limit turns out to be unity at all pressures.

Let us suppose that an arbitrary value of $\bar{F}_2^0$ be inserted in equation 1, and that from the a_2 so obtained the value of the limit in equation 3a is taken. Then if the limit turns out to be finite, although not unity, it can be readily made equal to unity by an appropriate change in $\bar{F}_2^0$. But it is important to note at this point that *a priori* there is no necessity for the limit ever to have a finite value; whether it is finite or not is a matter to be decided by experiment or analogy. Lest this seem to be an item of no consequence we may observe that unless one particular value is assigned to the formula weight, M_2 (for a given solute), the limiting value of a_2/m will either vanish or be infinitely great.

In order to demonstrate that the limit can be finite, it is sufficient to show that the limiting ratio of $e^{(\bar{F}_2 - k)/RT}$ to m is finite (k being a constant). For solutes that do not dissociate Gibbs (7) gave an equation for the approximate relation in dilute solutions between the potential and the concentration (i.e., the mass, $\mathbf{m}_2$, of component 2 divided by the total volume, V). The later form of the equation, in which Gibbs utilized a generalization due to van't Hoff, is as follows:

$$M_2\mu_2 - \text{const.} = RT \ln \frac{\mathbf{m}_2}{V} \tag{4}$$

and this equation has been verified by experiment. At low concentrations $\mathbf{m}_2/V$ is nearly proportional to m. Therefore, since $M_2\mu_2 = \bar{F}_2$, the ratio of $e^{(\bar{F}_2-k)/RT}$ to m has a finite limiting value; and consequently the limit in equation 3a is also finite.

But although for a large variety of solutes there can be found a concentration for the standard state such that equation 3a will hold, it will be observed in the case of dissociable substances, such as strong electrolytes, that equation 3a in the form given will not hold with any possible "standard state." The equation must then be modified by raising m to the power, ν, thus,

$$\lim_{m \to 0} \frac{a_2}{Bm^\nu} = 1 \tag{3b}$$

ν being the number of parts or ions into which one molecule of the substance is assumed to dissociate. The factor, B, which is a constant for the given substance, is inserted arbitrarily for a reason explained in a later section; it is defined by the relation

$$B = (\nu_+)^{\nu_+}(\nu_-)^{\nu_-} \tag{5}$$

in which ν_+ and ν_- are the number of the two kinds of ions. Activities based on mole fractions, $(a_2)_X$, and on volume concentrations, $(a_2)_C$, have also been used, and may be evaluated by substituting X_2, the mole fraction of component 2, or C, the number of moles of component 2 per 1000 cc. of solution, for m in equation 3b. The relation between a_2 and $(a_2)_X$ is obviously,

$$\frac{(a_2)_X}{a_2} = \frac{1}{N_1^\nu} \tag{6a}$$

N_1 being the number of moles in 1000 grams of component 1 (solvent).

Similarly the relation between a_2 and $(a_2)_C$ is

$$\frac{(a_2)_C}{a_2} = \rho_0^\nu \tag{6b}$$

ρ_0 being the density of pure liquid 1. Concentrations have been expressed (9) in terms of the "modified mole fraction," Y_2, calculated on the basis of the solute being completely dissociated. We may also define an activity, $(a_2)_Y$, in terms of Y_2, and we have

$$\frac{(a_2)_Y}{(a_2)_X} = \nu^\nu \tag{6c}$$

If we were to concern ourselves only with solutions of components miscible in all proportions, the definition of activity could be made much simpler; for in that event the "standard state" (in this instance the concentration to which $\bar{F}_2^0$ pertains) could be—but does not need to be—taken as the pure component under consideration. In mixtures of water and ethyl alcohol, for example, the activity of the alcohol could be evaluated by using the pure alcohol as the fiduciary, or standard, state; equations 3a and 3b and the limiting behavior in dilute solutions would not then be involved in the definition.

The majority of solutions for which thermodynamic data exist show limited miscibility, and even in those that show complete miscibility it may be preferred to reckon always from one end of the diagram. In general, therefore, the definition of activity has required two equations, for example 1 and 3a. It is obvious that a single equation would be more convenient for mathematical treatment.

Now equation 1 defines a_2 except for an arbitrary multiplicative constant and equation 3 defines the constant. This circumstance led to the following single equation for defining activity.

$$a_2 = \lim_{m' \to 0} \frac{m'}{e^{(\bar{F}_2' - \bar{F}_2)/RT}} \tag{7a}$$

For simplicity we have taken first the special case of a solute that does not dissociate. The equation is applied (at a given temperature and pressure) by choosing any concentration, m, and determining $\bar{F}_2' - \bar{F}_2$, for a series of concentrations, m', keeping m, and consequently $\bar{F}_2$, constant, and then finding by graphical or other means the limiting value toward which the ratio on the right hand of the equation tends as m' approaches zero. Substituting this limiting value in equation 7a we find a_2 at the concentration m. Here $\bar{F}_2'$ pertains to a fixed pressure, that is, $P = 1$. This is equivalent to the statement that $\bar{F}_2^0$ is always to be taken at $P = 1$. It may be noted that although Lewis and Randall specify that the standard state of a pure liquid, and also that of a solute, is always taken at unit pressure, a similar definite statement is not made for the solute. The assumption here made is that the activities of solute and solvent are to be defined on the same basis.

The operation of evaluating the limit as m approaches zero is analogous to the operation of evaluating a definite integral. Here m' and $\bar{F}_2'$ play the part of variables, and m (or $\bar{F}_2$) is a parameter corresponding to one of the limits of the integral. Moreover, the determination of the limit in equation 7a is implied by, and presupposed in, Lewis' definition; and the evaluation of the limit has in effect been carried out whenever a_2 has been determined. In applying this equation at various temperatures and pressures (if it is to conform to Lewis' definition of activity) we must observe that $\bar{F}_2$ is a function of T and P, and that $\bar{F}_2'$ is a function of T but not of P.

That equation 7a is equivalent to the two equations, 1 and 3a, which have previously been used to define activity, may be readily shown. We may write equation 7a in the form,

$$a_2 = e^{\bar{F}_2/RT} \lim_{m' \to 0} \frac{m'}{e^{\bar{F}_2'/RT}} \tag{8}$$

Then for any a_2 (the limit itself being constant) we have, after taking logarithms,

$$RT \ln a_2 = \bar{F}_2 - \text{const.} = \bar{F}_2 - \bar{F}_2^0$$

since $\bar{F}_2^0$ is the value of the constant for which $a_2 = 1$. Equation 7a thus leads to an equation identical with equation 1. Furthermore, by dividing equation 7a by m and taking the limit as m approaches zero, we have (at $P = 1$, since in that event one limit is the reciprocal of the other),

$$\lim_{m \to 0} \frac{a_2}{m} = \left(\lim_{m \to 0} \frac{e^{\bar{F}_2/RT}}{m} \right) \left(\lim_{m' \to 0} \frac{m'}{e^{\bar{F}_2'/RT}} \right) = 1$$

which is identical with equation 3a.

Equation 7a may readily be put in the more general form applicable to all classes of solutes. Thus

$$a_2 = B \lim_{m' \to 0} \frac{(m')^{\nu}}{e^{(\bar{F}_2' - \bar{F}_2)/RT}} \tag{7b}$$

in which, as before, $B = \nu_+^{\nu_+} \cdot \nu_-^{\nu_-}$. By following the same procedure as for equation 7a it may be readily shown that equation 7b is equivalent to the two equations (1 and 3b) used in the general definition of activity. Here, also, $\bar{F}_2$ is a function of T and P, and $\bar{F}_2'$ is a function of T but not of P. For purposes of this definition ν may be regarded as that number which will give a finite value for the limit. With a larger number the limit is zero and with a smaller number it is infinite. Experimentally it will be found that ν is a small positive integer, and is usually in agreement with the number of parts into which, from other considerations, the component is known to dissociate.

In many instances the quantity directly measured is the difference between $\bar{F}_2$ at a concentration m, and $\bar{F}_2''$ at some fixed arbitrary reference concentration. Equation 7b may be put in a slightly different form, which is more directly applicable to the data from which a_2 is usually determined. Inserting $e^{(F_2''-F_2'')/RT}$ (= 1) in equation 7b, and making use of the fact that (at $P = 1$) the value of the limit involving only $\bar{F}_2'$ and m' as variables is the same as that of the limit involving only $\bar{F}_2$ and m as variables, we have

$$a_2^{1/\nu} = B^{1/\nu} \frac{e^{(\bar{F}_2-\bar{F}_2'')/\nu RT}}{\lim\limits_{m\to 0} \dfrac{e^{(\bar{F}_2-\bar{F}_2'')/\nu RT}}{m}} \tag{9}$$

In determining the value of the limit by graphical means it is convenient in the case of strong electrolytes to plot the ratio (whose limit is sought) against $\sqrt{m}$, because at low concentrations a nearly straight line will be obtained. This equation is primarily suitable for calculating a_2 at some fixed temperature and at one atmosphere pressure. For variations in T and P, the quantity $\bar{F}_2''$, *and also the quantities determining the limit,* must be taken at the given temperature but at a fixed pressure.

If it is desired to work with logarithms rather than exponentials, we can alter equation 9 by taking the logarithms of both sides. But it should be noted that a limiting *ratio* is often less troublesome to work with than the limiting *difference* that occurs in the altered equation. In order to define $(a_2)_X$, the activity based on mole fractions, X_2 or X_2' may be substituted for m or m' respectively, in equations 7, 8, and 9; similarly, $(a_2)_C$ may be defined by the equations after substituting C and C' for m and m'.

These equations may be easily applied by an appropriate choice of subscripts to any component in a solution, the limiting composition, and its distinguishing sign, corresponding to one of the pure (liquid) components; and the equations readily take the simpler form that suffices for defining the activity of a component, when the component itself in pure liquid form is chosen as the limiting state (10). If we write the analog of equation 7a or 7b with X_1' in place of m', the limit being taken as X_1' approaches one, and note that here $\bar{F}_1'$ has the finite limiting value $\bar{F}_1^*$ (the value of $\bar{F}_1$ for pure component 1) we obtain an equation, similar to equation 1,

$$a_1 = e^{(\bar{F}_1-\bar{F}_1^*)/RT} \tag{10}$$

for completely defining the activity in this instance. The above equations may be made more general by using a generalized subscript instead of the numerals 1 and 2, which have been used above in order to emphasize the fact that more care is needed in the definition and evaluation of the activity of the solute than in the case of the solvent. A more general form of definition than equation 7b is,

$$a_i = B \lim_{X_i' \to K} \frac{(X_i')^{\nu}}{e^{(\bar{F}_i' - \bar{F}_i)/RT}} \qquad (7c)$$

The question sometimes arises as to whether, in the case of electrolytes, the activity, a_2, refers to the undissociated solute or to the dissociated part, or to something else. In order to avoid confusion it should be carefully noted that, inasmuch as a_2 (at a fixed T and P) is proportional to e^{μ_2}, and inasmuch as μ_2 is simply the chemical potential of one gram of the solute, then a_2 for, say, sodium chloride, as commonly used and as defined above, may be regarded as merely the activity of a solute whose condition is not qualified except by the statement that its gross composition (in this instance) corresponds to the formula NaCl. It may be noted, however, that a_2 is equal to, or proportional to, the activity of the undissociated part, and to the geometric mean of the ion activities.

Activity coefficient

As usually defined, the activity coefficient, γ, of a given solute (at $P = 1$) bears the following relation to the activity, a_2, of the same component,

$$\gamma = \frac{a_2^{1/\nu}}{B^{1/\nu} m} \qquad \text{(at } P = 1\text{)} \qquad (11)$$

From equation 3b it is evident that γ, defined in this way, approaches 1 as a limit, as m approaches zero. Instead of defining γ in terms of the previously defined a_2, we may define it directly in terms of $\bar{F}_2$. Upon combining equations 7b and 11, we have

$$m\gamma = \lim_{m' \to 0} \frac{m'}{e^{(\bar{F}_2 - \bar{F}_2)/\nu RT}} \qquad (12)$$

Since this was obtained from equation 10 (with $\bar{F}_2'$ having the meaning specified in equation 7b), γ, by equation 3b, approaches 1 as a limit only at $P = 1$. Now, from the pressure coefficient of a_2 (see below) it is evident that a more general form of equation 3b is

$$\lim_{m \to 0} \frac{a_2^{1/\nu}}{B^{1/\nu} m} = e^{I/\nu RT} \qquad \text{(at any } P\text{)} \qquad (13)$$

in which I is written for the integral $\int_1^P \bar{V}_2^* dP$, $\bar{V}_2^*$ being the limiting value of the partial molal volume of component 2. Since we wish to have γ

approach 1 at all pressures, we therefore divide the right-hand side of equation 12 by $e^{I/\nu RT}$. This is equivalent to adding $I/\nu RT$ to $\bar{F}'_2$, which originally was always at $P = 1$, and thus changing $\bar{F}'_2$ to the value it would have at the given pressure. Hence in order to define γ so that for any pressure it approaches 1 as m approaches zero, we merely specify that in equation 12 $\bar{F}'_2$, as well as $\bar{F}_2$, is a function of P. That is, $\bar{F}_2$ and $\bar{F}'_2$ are both taken at the given pressure and temperature.

For actual calculation of γ a somewhat more convenient form is obtained by combining equations 9 and 11. Thus,

$$\gamma = \frac{\dfrac{e^{(\bar{F}_2 - \bar{F}''_2)/\nu RT}}{m}}{\lim\limits_{m \to 0} \dfrac{e^{(\bar{F}_2 - \bar{F}''_2)/\nu RT}}{m}} \tag{14}$$

By reasoning similar to that employed in connection with equation 11 it follows that here $\bar{F}_2$ and $\bar{F}''_2$ are both functions of T and P. Of the two equations, equation 12 is the simpler, but equation 14 is the more generally useful; it is directly applicable to measurements of $\bar{F}_2 - \bar{F}''_2$, such as those obtained from the E.M.F.'s of concentration cells without liquid junctions, by use of the well-known relation, $\bar{F}_2 - \bar{F}''_2 = n\mathbf{F}\mathbf{E}$, in which $\mathbf{E}$ is the E.M.F. of the cell in volts, $\mathbf{F}$ is the number of energy units (e.g., calories) per volt equivalent, and n is the number of equivalents associated with the particular formula weight, M_2, that is used in connection with $\bar{F}_2$. The sign of $\bar{F}_2 - \bar{F}''_2$ can be kept correct by recalling that $\bar{F}_2$ always increases algebraically with the concentration of component 2.

The operation of finding the value of the limit in equation 14 is analogous to that used by Lewis and Randall (17) in connection with their equation XXVI-15 for calculating γ from $\mathbf{E}$. If we take the natural logarithm of the limit and multiply by $-\nu RT/n\mathbf{F}$ we obtain the quantity designated as $\mathbf{E}^0$ by Lewis and Randall.

Other kinds of activity coefficient of the solute, such as

$$\gamma_{X_2}\ (= (a_2)_X^{1/\nu}/B^{1/\nu}X_2)$$

based on mole fractions, or γ_C $(= (a_2)_C^{1/\nu}/B^{1/\nu}C)$, based on volume concentration, have been used, and can be defined by substituting X_2 or C, respectively, for m in the above equations. The interrelations of these various activity coefficients may be readily obtained. If the analog of equation 12, containing X_2 in place of m, and γ_{X_2} in place of γ, be written, and the one equation divided by the other, we obtain

$$\frac{X_2\gamma_{X_2}}{m\gamma} = \lim_{\substack{X'_2 \to 0 \\ m' \to 0}} \frac{X'_2}{m'} = \frac{1}{N_1} \tag{15}$$

(N_1 being the number of moles of solute in 1000 grams). Thence,

$$\gamma_{X_2} = \gamma\left(1 + \frac{m}{N_1}\right) = \frac{\gamma}{X_1} \tag{16a}$$

Similarly, it follows directly that

$$\gamma_C = \gamma \frac{m}{C} \rho_0 = \gamma \frac{\rho_0}{x_1} \tag{16b}$$

in which ρ and ρ_0 are the densities of solution and solute and x_1 is the weight fraction of the solvent. We may also define γ_{Y_2} ($= (a_2)_Y^{1/\nu}/B^{1/\nu}\ Y_2$) by substituting Y_2 for m in equation 12, and we have,

$$\gamma_{Y_2} = \gamma_{X_2}\nu \frac{X_2}{Y_2} \tag{16c}$$

Although it is the activity coefficient of the dilute component (solute) that is the most useful one in actual practice, the activity coefficient of the solvent (or in general the activity coefficient of any component in a solution) may be similarly defined in terms of the activity of the component and its concentration. If component 1 is the solvent, then both X_1 and a_1, as defined by equation 10, approach unity in dilute solution. Therefore any power of a_1, divided by any power of X_1, might be chosen as the activity coefficient, for example of water in an aqueous solution. The natural choice would seem to be a_1/X_1, and this coefficient is the one commonly used (11). But it should be noted that in general $(a_2)_X$ becomes nearly equal to X_2^ν in dilute solution; whence by the well-known relation connecting a_1 and a_2 it follows that in dilute solution a_1 is more nearly proportional to X_1^ν than to X_1. Accordingly the activity coefficient, γ_{X_1}, of the solvent will be defined by the equation,

$$\gamma_{X_1} = \frac{a_1^{1/\nu}}{X_1} = \frac{e^{(\bar{F}_1 - F_1^{\bullet})/\nu RT}}{X_1} \tag{17}$$

This of course includes the special case for which $\nu = 1$. It may seem strange that the definition of the activity coefficient of the solvent should involve the factor ν, which is entirely a property of the solute. But as a matter of fact the definition does not need to involve ν; putting in the ν as indicated in equation 17 merely makes the γ_{X_1}, so defined, more nearly equal to unity (as a rule), and causes the relations between γ_{X_1} and other quantities such as osmotic coefficient (see below) to be more simple than they otherwise would be.

An activity coefficient of the solvent based on Y_1, the "modified mole fraction," has also been used (9, see also 8). The Y_1 is calculated from the known weight of the constituents by taking the (mean) molecular weight of the solute as $1/\nu$ of the formula weight used in calculating X_1. The activity coefficient γ_{Y1} is then defined as

$$\gamma_{Y1} = \frac{a_1}{Y_1} \tag{18}$$

When X_1 is nearly equal to 1, X_1^ν is approximately equal to Y_1; from which it may be shown that γ_{X1}^ν and γ_{Y1} have nearly the same numerical values for dilute solutions, although they differ appreciably for higher concentrations. The exact and approximate relations between these two varieties of activity coefficient of the solvent are as follows:

$$\frac{\gamma_{X1}^\nu}{\gamma_{Y1}} = \frac{Y_1}{X_1^\nu} \doteq 1 + \frac{\nu(\nu-1)}{2}\left(\frac{X_2}{X_1}\right)^2 - \frac{\nu(\nu^2-1)}{3}\left(\frac{X_2}{X_1}\right)^3 \tag{19}$$

Alternate definition of activity

By Lewis' definition of activity a_2/m^ν does not in general approach unity as a limit as m approaches zero, even at $P = 1$; it does so only for di-ionic electrolytes or non-dissociable substances (ν equal to 1 or 2). This is because Lewis, for strong electrolytes, writes $a_+^{\nu_+} \cdot a_-^{\nu_-}/a_2$ as an equilibrium constant involving the activities of the individual ions and adopts the arbitrary convention (20) that the equilibrium constant is equal to 1. Now, the activities of the individual ions may be taken as sensibly equal to $\nu_+ m$ and $\nu_- m$, respectively, at high dilutions, and therefore $a_+^{\nu_+} \cdot a_-^{\nu_-}$ at atmospheric pressure will approach Bm^ν as a limit as m approaches zero. Hence, by the above convention as to equilibrium constant, a_2 approaches Bm^ν as a limit (which is in accord with equation 3b); and the factor B thus enters into the definition of a_2.

But it would be better for many purposes to define an activity in such a way that the factor B would be omitted. This could be done by adopting the convention that $a_+^{\nu_+} \cdot a_-^{\nu_-}/a_2$ equals B rather than 1. If this were done, a_2 at high dilutions would approach the limit Bm^ν/B, or m^ν. That is,

$$\lim_{m \to 0} \frac{[a_2]}{m^\nu} = 1 \qquad (\text{at } P = 1) \tag{20}$$

in which we put $[a_2]$ for the quantity that bears a simple relation to a_2, the activity as ordinarily defined (being identical with a_2 when ν is 1 or 2). Since $[a_2] = Ba_2$, we may now omit the B in the fundamental definition of activity, and write

$$[a_2] = \lim_{m' \to 0} \frac{(m')^\nu}{e^{(\overline{F}_2' - \overline{F}_2)/RT}} \tag{21}$$

by analogy with equation 7a. Here, as before, $\bar{F}_2$ is a function of P and T, and $\bar{F}_2'$ a function of T but not of P. It is thus possible to define a useful variety of solute activity, in terms of measurable quantities, without any reference to the activities or properties of individual ions, ν as stated above being merely that number which gives the limit a finite value. The only disadvantage of the alternate definition is that $[a_2]$ is less simply related to the activities of the individual ions, and this is offset by the greater simplicity of the relation between $[a_2]$ and γ.

As is evident from equation 11, γ *may be defined independently of any convention regarding* a_2; hence the value of γ is not affected by the suggested change in the definition of activity.

We have, moreover,

$$[a_2^{1/\nu}] = m\gamma, \quad [a_2^{1/\nu}]_X = X_2\gamma_{X_2}, \quad [a_2^{1/\nu}]_C = C\gamma_C, \quad [a_2^{1/\nu}]_Y = Y_2\gamma_{Y_2} \tag{22}$$

(at $P = 1$), and instead of the usual equation,

$$\bar{F}_2 - \bar{F}_2^0 = \nu RT \ln (m\gamma) + RT \ln B \tag{23}$$

we have the simpler equation,

$$\bar{F}_2 - [\bar{F}_2^0] = \nu RT \ln (m\gamma) \tag{24}$$

in which $[\bar{F}_2^0]$ pertains to a "standard state" for which not only $[a_2]$ but also $m\gamma$ is equal to 1.

Osmotic coefficient

A now familiar thermodynamic function is the osmotic coefficient, introduced by Bjerrum (3) and originally defined in terms of osmotic pressure. For any solution, f_P, the osmotic coefficient of the solute, may be defined as the ratio of π, the osmotic pressure of the solution, to what the osmotic pressure would be if the solution followed some ideal-solution law; that is,

$$f_P = \frac{\pi}{\pi_{id}} \tag{25}$$

The numerical value of f_P thus depends on the particular ideal law that is chosen.

Osmotic pressure and chemical potential (partial free energy) are connected by the well-known exact relation,

$$\Delta\bar{F}_1 = \bar{F}_1 - \bar{F}_1^* = -(\bar{V}_1)_0\pi + I_v \tag{26}$$

in which $\bar{F}_1$ and $\bar{F}_1^*$ are the partial molal free energies (at atmospheric pressure) of component 1 and of pure liquid 1, respectively, $(\bar{V}_1)_0$ is the fictive volume per mole of component 1 in the given solution at atmospheric pressure, and I_v is given by

$$I_v = -\int_1^{\pi} \Delta_P \bar{V}_1 \, dP$$

$\Delta_P \bar{V}_1$ being the difference between the value of $\bar{V}_1$ at any pressure P and that at atmospheric pressure.[3] From equation 26 it is evident that the ideal-solution law employed to determine π_{id} also determines $(\Delta\bar{F}_1)_{id}$, the value of $\Delta\bar{F}_1$ in the hypothetical solution that follows the chosen ideal law. We have, then,

$$(\Delta\bar{F}_1)_{id} = -(\bar{V}_1)_0\pi_{id} + (I_v) \tag{27}$$

in which (I_v) is written for the integral taken between the limits 1 and π_{id}.

From equations 25, 26, and 27 it follows that

$$f_P = \frac{-\Delta\bar{F}_1 + I_v}{-(\Delta\bar{F}_1)_{id} + (I_v)} \tag{28}$$

The osmotic coefficient, f_P, can thus be defined in terms of measurable quantities and an arbitrary assumption as to the course of either π or $\Delta\bar{F}_1$ in an ideal solution. Therefore in order to complete the definition of f_P, we may choose an ideal law for $\Delta\bar{F}_1$.

For the sake of convenience it is preferable to have a "law" that does not deviate too much from the actual measurements, and it is necessary that in dilute solution $(\Delta\bar{F}_1)_{id}$ should approach $\Delta\bar{F}_1$ if the limiting value of f_P is to be 1. Although there are a number of relations that may serve the purpose, there appears to be no simple relation that is entirely satisfactory for all classes of solutions. The most convenient one for many purposes is,

$$(\Delta\bar{F}_1)'_{id} = -\nu RT \frac{m}{N_1} \tag{29}$$

The well-known expression that includes Raoult's law and puts $\Delta\bar{F}_1$ equal to $RT \ln X_1$ is not even approximately true for solutions of electrolytes, dilute or concentrated; but a slight modification makes it more generally applicable. Thus, if we write

$$(\Delta\bar{F}_1)''_{id} = \nu RT \ln X_1 \tag{30}$$

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[3] For the special case of constant compressibility, or more exactly, of linear variation of $\bar{V}_1$ with P, the term $(\bar{V}_1)_0\pi - I_v$ becomes equal to π times the value of V_1 at $P/2$. See reference 11, pp. 109, 120.

the equation conforms fairly well to the actual course of $\bar{F}_1$ in very dilute solutions of electrolytes; and for non-electrolytes (ν then being equal to 1) it reduces to the familiar form. Another expression nearly equivalent to equation 30 in dilute solutions is

$$(\Delta\bar{F}_1)^{\cdots}_{id} = RT \ln Y_1 \tag{31}$$

Y_1 being the "modified" mole fraction (see above).

If we choose equation 29 for our ideal-solution law, then by equations 25, 26, and 28 we have

$$f_P = \frac{(\bar{V}_1)_0\pi}{\nu RTm/N_1 + (I_v)} = \frac{-\Delta F_1 + I_v}{\nu RTm/N_1 + (I_v)} \tag{32}$$

Other choices of ideal law would, of course, lead to different expressions and to different numerical values of f_P.

Now, I_v is usually small in comparison with the terms to which it is added. For example, $-\Delta\bar{F}_1$ for a 4.277 molal solution of sodium chloride in water at 25°C. is 103.8 cal., $\nu RTm/N_1$ is 91.3 cal., π is 243.8 bars (calculated from $\Delta\bar{F}_1$), and I_v is 0.6 cal. The fact that I_v is small suggests that another variety of osmotic coefficient[4] might be defined by the equation,

$$f_r = \frac{-\Delta\bar{F}_1}{\nu RTm/N_1} \tag{33}$$

It is evident that when, as is approximately so in sufficiently dilute solutions, equation 29 represents the variation of $\Delta\bar{F}_1$ with m, f_r will be 1. For the purpose of defining f_r, the factor ν may be regarded as that number (usually an integer) which will make f_r tend toward unity in dilute solution.

Since I_v and (I_v) are nearly proportional to π^2 and π_{id}^2, respectively, an approximate relation between f_r and f_P may be obtained by combining equations 32 and 33. Thus,

$$f_P \doteq f_r + \frac{I_v}{-\Delta\bar{F}_1}(f_r - 1) \tag{34}$$

For π less than 1000 bars the difference between f_P and f_r is less than can be determined by any method that has been used for measuring $\Delta\bar{F}_1$. The two coefficients, f_P and f_r, become strictly identical for an incompressible solution ($I_v = 0$). Moreover, if not only $I_v = 0$, but $\bar{V}_1 = v_1$, the molal volume of the pure solvent, and if the ideal-solution law is

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[4] Called the "osmotic coefficient for the chemical potential" by Scatchard and Prentiss (J. Am. Chem. Soc. **56**, 1486–92 (1934)).

equation 29, then it follows that $[\pi_{id}]'$, the osmotic pressure under the specified conditions, would be

$$[\pi_{id}]'V = \nu N_2RT \tag{35}$$

in which V denotes the total volume of the solution and N_2 denotes the total number of moles of solute. This is the van't Hoff equation in more general form (5) on account of the inclusion of the factor ν, and indicates that if an osmotic coefficient were defined as $\pi V/\nu N_2RT$ this coefficient would, under the assumed restriction (incompressibility and no volume change on mixing), be identical with f_r.

Equation 30 suggests the definition of a third well-known kind of osmotic coefficient, thus,

$$f_X = \frac{\Delta \bar{F}_1}{\nu RT \ln X_1} \tag{36}$$

By combining equations 34 and 36 and expanding ln X_1, the relation between f_r and f_X may be expressed as follows,

$$\frac{f_r}{f_X} = \frac{-\ln X_1}{m/N_1} = 1 - \frac{m}{2N_1} + \frac{m^2}{3N_1^2} - \cdots \tag{37}$$

Again, a coefficient f_Y may be defined by the equation,

$$f_Y = \frac{\Delta \bar{F}_1}{RT \ln Y_1} \tag{38}$$

and we have,

$$\frac{f_r}{f_Y} = 1 - \frac{\nu m}{2N_1} + \frac{\nu^2 m^2}{3N_1^2} - \cdots \tag{39}$$

Still another common way of defining an osmotic coefficient[5] is in terms of the freezing-point depression, which by well-known thermodynamic equations is directly related to the osmotic pressure of the solution. Let us define f by

$$f = \frac{\vartheta}{\vartheta_{id}} \tag{40}$$

in which $\vartheta \equiv T_0 - T'$ (T_0 being the freezing point of the pure solvent and T' that of the solution), and ϑ_{id} is determined by some ideal-solution law.

[5] We might also define an osmotic coefficient in terms of C, the volume concentration or molality, by substituting C for m in equation 33.

The familiar equation for freezing-point lowering in a dilute solution may be expressed as follows,

$$\lim_{m \to 0} - \frac{\mathrm{d}T'}{\mathrm{d}m} = \nu \frac{RT_0^2}{N_1 \Delta H_0} = \nu\lambda \tag{41}$$

in which R is the gas constant, N_1 as before is the number of moles of solvent in 1000 grams, ΔH_0 is the heat *absorbed* in the melting of one mole of solvent at T_0, and λ is a factor defined by the second part of the equation ($\lambda = 1.858$ for aqueous solutions). Now, ϑ_{id} is conveniently defined as $m(\mathrm{d}T/\mathrm{d}m)_0$, that is, $\nu\lambda m$; whence

$$f = \frac{\vartheta}{\nu\lambda m} = \frac{\vartheta \Delta H_0}{\nu R T_0^2 m / N_1} \tag{42}$$

In order to write an expression for the exact relation between f and one of the other osmotic coefficients, we first note the equation given by Lewis and Randall (18) for connecting $\Delta\bar{F}_1$ and ϑ. This is

$$-(\Delta F_1)' = \vartheta\left(\frac{\Delta H_0}{T_0} - \vartheta \frac{\Delta C_P}{2T_0} - \vartheta^2 \frac{\Delta C_P}{6T_2^0}\right) \tag{43}$$

which is equivalent to

$$- \ln (a_1)' = \frac{1}{N_1\lambda} \vartheta + b\vartheta^2 + c\vartheta^3 + \cdots \tag{44}$$

Here

$$b = \left(\frac{\Delta H_0}{T_0} - \frac{\Delta C_P}{2}\right)\Big/RT_0^2, \qquad c = \left(\frac{\Delta H_0}{T_0} - \frac{2\Delta C_P}{3}\right)\Big/RT_0^3$$

and ΔC_P (assumed constant) is the molal heat capacity of the pure liquid solvent minus that of the solid. For aqueous solutions, $\Delta H_0/T_0 = 1438$ cal. per degree, $\Delta C_P = 9$, $b = 5.16 \times 10^{-6}$, $c = 1.8 \times 10^{-8}$.

When ϑ for a given concentration has been determined, equations 43 and 44 give $\Delta\bar{F}_1$ and a_1 for that concentration *and at a temperature equal to the freezing point of the particular solution.* The $\Delta\bar{F}_1$'s obtained in this way from a series of ϑ's thus pertain to various temperatures. Now, f_r may be calculated from $\Delta\bar{F}_1$ by equation 33, which involves also the temperature T, and we designate by the symbols $(f_r)'$, $(\Delta F_1)'$, and $(a_1)'$ those values pertaining not to a single fixed temperature but to a temperature that for each concentration is T' ($= T_0 - \vartheta$). We have, then, by equations 33 and 43,

$$(f_r)' = \frac{\vartheta\left(\frac{\Delta H_0}{T_0} - \vartheta \frac{\Delta C_P}{2T_0} - \vartheta^2 \frac{\Delta C_P}{6T_0^2}\right)}{\nu R T m / N_1} \tag{45}$$

and by equation 42

$$\frac{(f_r)'}{f} = \frac{T_0}{T'}\left(1 - \frac{\Delta C_P}{2\Delta H_0}\vartheta - \frac{\Delta C_P}{6T_0\Delta H_0}\vartheta^2\right) \qquad (46)$$

Noting that $T_0/T' = 1/(1 - \vartheta/T_0)$, expanding and neglecting terms containing ϑ^3 and higher powers of ϑ, we obtain finally

$$\frac{(f_r)'}{f} = 1 + bN_1\lambda^2\nu fm + cN_1\lambda^3\nu^2 f^2 m^2 \qquad (47)$$

The last term in this equation can usually be neglected, and we then have for aqueous solutions,

$$\frac{(f_r)'}{f} = 1 + 0.00099\,\nu fm \qquad (47a)$$

Equation 47a is practically the same as that given by Scatchard and Prentiss (21). Equation 47 can be put in the following form,

$$f = (f_r)' - \frac{bN_1\vartheta^2}{\nu m} - \frac{cN_1\vartheta^3}{\nu m} \qquad (48)$$

In order to pass from $(f_r)'$ to f_r we may make use of the equation given below for calculating the variation of f_r with temperature. It should be noted that whereas f_r, f_X, f_Y, and f_P are functions of T, f and $(f_r)'$ are not. All six of these quantities (by definition) approach 1 as a limit as the concentration of the solute decreases. At $m = 0.01$ they are practically identical, but at higher concentrations they differ appreciably among themselves. For example, f for a 4.277 molal sodium chloride solution in water is 1.042, $(f_r)'$ is 1.051, and at 25°C., f_r, f_X, f_Y, and f_P are respectively 1.137, 1.180, 1.223, and 1.138.

Relation between activity coefficients and osmotic coefficients

By equation 23 and the well-known equation connecting $\bar{F}_1$ and $\bar{F}_2$ we have (at constant temperature and pressure),

$$-\frac{N_1}{m}\,\mathrm{d}\bar{F}_1 = \mathrm{d}\bar{F}_2 = \nu RT\,\mathrm{d}\ln(m\gamma) \qquad (49)$$

Then from equation 33 it follows that

$$\mathrm{d}(f_r m) = m\,\mathrm{d}\ln(m\gamma) = m\,\mathrm{d}\ln\gamma + \mathrm{d}m \qquad (50)$$

This equation, in slightly different form, has been given by Bjerrum (4).

Integrating (temperature and pressure being constant), we obtain

$$f_r = 1 + \frac{1}{m}\int_1^{\gamma} m\,\mathrm{d}\ln\gamma = 1 + \ln\gamma - \frac{1}{m}\int_0^{m}\ln\gamma\,\mathrm{d}m \qquad (51)$$

since $f_r = 1$ and $\gamma = 1$, when $m = 0$. This is an exact relation between f_r and γ at any concentration and at a given constant T and P.

An equation resembling equation 51 but involving f rather than f_r may also be written. By equation 49, we have,

$$-\frac{N_1}{m}\,\mathrm{d}\ln a_1 = \mathrm{d}\ln a_2 = \nu\mathrm{d}\ln(m\gamma) \tag{52}$$

and by differentiating equation 44, the last term being neglected, we obtain

$$-\,\mathrm{d}\ln(a_1)' \doteq \frac{1}{N_1\lambda}\,\mathrm{d}\vartheta + 2b\vartheta\mathrm{d}\vartheta \tag{53}$$

Now, equation 52 gives the relation between a_1 and γ *at a fixed temperature.* Nevertheless we may apply the first and last terms to connect $(a_1)'$, which is the activity at the varying temperature T', with a number, $(\gamma)'$, which is not the activity coefficient but becomes equal to it if a_1 is independent of T. Combining this modification of equation 52 with equation 53 and with the differential form of equation 42 we obtain,

$$\mathrm{d}\ln(m\gamma') \doteq \frac{\mathrm{d}(fm)}{m} + \frac{2bN_1\vartheta\mathrm{d}\vartheta}{\nu m} \tag{54}$$

and, by integration,

$$f \doteq 1 + \frac{1}{m}\int_1^{\gamma'} m\,\mathrm{d}\ln(\gamma)' - \frac{bN_1\vartheta^2}{\nu m} \tag{55}$$

A closer approximation can of course be obtained by not neglecting the term containing ϑ^3 in equation 44.

For aqueous solutions bN_1 is equal to 0.000286. Equation 54 is essentially the equation given by Lewis and Randall (19) for connecting $(\gamma)'$ with the function j, which is closely related to f (see below). In general γ differs from $(\gamma)'$,—by an amount that depends on the heat of dilution. In moderately dilute solutions this effect becomes inappreciable and $(\gamma)'$ is then (sensibly) equal to γ. By subtracting equation 48 from equation 55 it may be observed that

$$(f_r)' = 1 + \frac{1}{m}\int_1^{\gamma'} m\,\mathrm{d}\ln(\gamma)' \tag{56}$$

The exact relation between f_X and γ_{X_2} is easily obtained. Since

$$-\frac{X_1}{X_2}\,\mathrm{d}\bar{F}_1 = \mathrm{d}\bar{F}_2 = \nu RT\,\mathrm{d}\ln(X_2\gamma_{X_2}) \tag{57}$$

we have, by applying equation 36,

$$d(f_X \ln X_1) = -\frac{X_2}{X_1} d \ln (X_2 \gamma_{X_2}) \tag{58}$$

or, by integration,

$$f_X = 1 - \frac{1}{\ln X_1} \int_1^{\gamma_{X_2}} \frac{X_2}{X_1} d \ln \gamma_{X_2} \tag{59}$$

Furthermore, the relation between γ_{X_1}, the activity coefficient of the solvent, and its osmotic coefficient, f_X, is obtained by combining equations 17 and 36. Thus

$$\ln \gamma_{X_1} = (f_X - 1) \ln X_1 \tag{60}$$

These and other interrelations between activity coefficients and osmotic coefficients have been given previously, for example by Guggenheim (reference 11, p. 107), who has also pointed out that in dilute solutions the activity coefficient of the solvent differs from unity by a much smaller quantity than does the osmotic coefficient. This is immediately evident from the approximate form of equation 60, obtained by expanding $\ln X_1$:

$$\gamma_{X_1} = 1 + (1 - f_X)X_2 \tag{61}$$

Since in dilute solutions both X_2 and $1 - f_X$ are small quantities, it follows that $\gamma_{X_1} - 1$ has a magnitude that is one order smaller than $1 - f_X$. For example in a 0.01 molal sodium chloride solution at ordinary room temperature f_X is 0.9703 and γ_{X_1} is 1.00000535. In general, for dilute solutions, if $1 - \gamma_{X_2}$ is proportional to $X_2^{\frac{1}{2}}$ or X_2, then $1 - f_X$ is proportional to $X_2^{\frac{1}{2}}$ or X_2, respectively, and $\gamma_{X_1} - 1$ is proportional to $X_2^{\frac{3}{2}}$ or X_2^2, respectively. Moreover, $1 - \gamma_{X_2}$, $1 - f_X$, and $\gamma_{X_1} - 1$ have the same sign (usually positive in dilute solutions for electrolytes and negative for non-electrolytes).

It is of interest to note that the factor ν in the more general definitions of γ_{X_2}, f_X, and γ_{X_1} does not appear in the transformation equations. On the other hand, for the activity coefficient, a_1/X_1, in dilute solutions we have the following approximate relation,

$$\frac{a_1}{X_1} = 1 - (\nu f_X - 1) X_2 \tag{62}$$

The Lewis and Randall function, j

This was devised (14) as an aid in the calculation of activity coefficients from freezing-point measurements. It is defined in terms of ϑ, the freezing-point lowering, as follows:

$$j = 1 - \frac{\vartheta}{\nu \lambda m} \tag{63}$$

(ν being 1 for a non-dissociable solute) and is closely related to one of the several varieties of osmotic coefficients. From equation 42 it is obvious that

$$j = 1 - f \tag{64}$$

This function, like f, readily determines $(\Delta \bar{F}_1)'$ for a given concentration at the temperature T', the freezing point of the particular solution. By the same procedure used with f it follows that, to a sufficient approximation,

$$j \doteq -\frac{1}{m}\int_1^{\gamma'} m \,\mathrm{d} \ln (\gamma)' + \frac{bN_1\vartheta^2}{\nu m} \tag{65}$$

which is one form of Lewis and Randall's equation, and connects j with $(\gamma)'$, the "uncorrected activity coefficient." Since j is uniquely determined by $(\Delta \bar{F}_1)'$, it may properly be called a thermodynamic function.

Other functions

The van't Hoff mole number (23) is the ratio of the magnitude of some effect, such as freezing-point depression, osmotic pressure, or vapor-pressure lowering, to the effect expected from an arbitrary ideal-solution or dilute-solution law applied to an undissociated substance with the assumed molecular weight. The effect most commonly used is that involved in equations 41 and 42 with ν equal to 1, namely, $\vartheta = \lambda m$. Accordingly the mole number, i, may be defined by the equation,

$$i = \frac{\vartheta}{\lambda m} \tag{66}$$

It follows that

$$i = \nu f \tag{67}$$

and from equation 55 that

$$i \doteq \nu + \frac{\nu}{m}\int_1^{\gamma'} m \,\mathrm{d} \ln (\gamma)' - \frac{bN_1\vartheta^2}{m} \tag{68}$$

For a solute that does not dissociate i is identical with f; but of course the mole number is ordinarily used only in connection with electrolytes.

It is also worthwhile to include in our list of the thermodynamic functions, frequently employed in the study of solutions, the Arrhenius dissociation factor α. This is the classical "degree of dissociation" and is commonly defined in terms of the mole number i. For a di-ionic electrolyte α is put equal to $i - 1$, and in general is defined by the equation,

$$\alpha = \frac{i - 1}{\nu - 1} \tag{69}$$

From equations 55 and 67 we have an equation connecting α and (γ'),

$$\alpha \doteq 1 + \frac{\nu}{(\nu - 1)m} \int_1^{\gamma'} m \, \mathrm{d} \ln (\gamma)' - \frac{bN_1\vartheta^2}{(\nu - 1)m} \qquad (70)$$

Defined in this way i and α are thermodynamic functions in the same sense and for the same reason that the osmotic coefficient f is a thermodynamic function. For a solution of any specified concentration, the mole number i determines $(\Delta \bar{F}_1)'$ at T' and, if the heat of dilution is known, $\Delta \bar{F}_1$ at any temperature. The same applies to α, which, it may be noted, can not be used if $\nu = 1$. The conductance ratio, also designated sometimes by the symbol α, bears no exact relation to the α here defined, although in many instances the two factors are strikingly similar in magnitude.

It is interesting to compare the four quantities: α, the Arrhenius dissociation factor; i, the van't Hoff mole number; f, (one form of) the Bjerrum osmotic coefficient; and j, the Lewis and Randall function—each of which has played an important part in the development of physical chemistry. Their interrelation may be summarized as follows

$$(\nu - 1)(1 - \alpha) = \nu - i = \nu(1 - f) = \nu j \qquad (71)$$

VARIATION WITH TEMPERATURE

Activity

When once the definition of a quantity has been formulated it is usually a simple matter to differentiate the function with respect to temperature and thus to find its temperature coefficient. An exception to this rule is found in activity as ordinarily defined. If we attempt to find $\mathrm{d}a_2/\mathrm{d}T$ at constant concentration by taking the derivative of equation 1, we at once run into difficulty. This is because $\bar{F}_2^0$ (for the solute), in general, pertains to a different concentration for each temperature. Solutions of the problem have been obtained by utilizing the two equations (1 and 3) of the complete definition of a_2, an essential part of which is a statement concerning the limiting behavior of a_2 in an infinitely dilute solution. Although the correct answer has been given, it appears that the methods used for deriving the expression for the change with temperature of the activity of the solute have proved troublesome for many serious students of the subject.

On the other hand, the single equation (7b) for defining activity is easily amenable to rigorous mathematical treatment. For determining the temperature coefficient of a_2 at constant composition and pressure we note first that the operation of taking the limit is associative with respect to the other common mathematical operations, as illustrated by the well-known rule that "the limit of a product is the product of the limits," and second, the familiar relation between $\bar{F}_2$ and T:

$$\frac{\mathrm{d}(\bar{F}_2/T)}{\mathrm{d}T} = -\frac{\bar{H}_2}{T^2} \qquad \text{(constant } m \text{ and } P\text{)} \qquad (72)$$

$\bar{H}_2$ being the fictive enthalpy (per mole) of component 2 (that is, $(\partial H_2/\partial N_2)_{T,P,N_1}$, H_2 being the enthalpy, or heat content, and N_1 and N_2 the total number of moles of component 1 and 2, respectively). We note also that $\bar{F}_2$ and $\bar{F}_2'$ in equation 7 are functions of T, and that the limit refers to a series of values of m' that may be taken to be the same at all temperatures; m' is not a function of T. Taking the derivative of equation 7b we have

$$\frac{\mathrm{d}a_2}{\mathrm{d}T} = B \lim_{m' \to 0} \frac{(m')^{\nu}(\bar{H}_2' - \bar{H}_2)/RT^2}{e^{(\bar{F}_2'-\bar{F}_2)/RT}}$$

$$= a_2 \lim_{m' \to 0} \frac{\bar{H}_2' - \bar{H}_2}{RT^2}$$

Let the limiting value of $\bar{H}_2$, as m' approaches zero, be $\bar{H}_2^*$. (By experiment it is known that $(\bar{H}_2' - \bar{H}_2)$ has a finite and readily determinable limit.) Then,

$$\frac{\mathrm{d} \ln a_2}{\mathrm{d}T} = -\frac{\bar{H}_2 - \bar{H}_2^*}{RT^2} \qquad \text{(const. } P \text{ and } m\text{)} \qquad (73)$$

It might possibly have been somewhat simpler to take the logarithm of both sides of equation 7b before taking the derivative. The derivative of $\ln(a_2)_X$, of $\ln(a_2)_C$, and of $\ln(a_2)_Y$ will be found to be the same as that of $\ln a_2$. By changing subscripts in equation 73 we obtain $\mathrm{d} \ln a_1/\mathrm{d}T$ (also at constant composition and pressure). The quantity $\bar{H}_1^*$ that occurs here is the molal enthalpy (heat content) of the pure solvent.

Activity coefficient

The variation of γ with temperature offers comparatively little difficulty; it may be obtained in a variety of ways, for example by taking the derivative of equation 12, which yields the expression,

$$\frac{\mathrm{d} \ln \gamma}{\mathrm{d}T} = -\frac{\bar{H}_2 - \bar{H}_2^*}{\nu RT^2} \qquad \text{(const. } P \text{ and } m\text{)} \qquad (74)$$

and the same for $\mathrm{d} \ln \gamma_{X_2}/\mathrm{d}T$, for $\mathrm{d} \ln \gamma_{Y_2}/\mathrm{d}T$, and for $\mathrm{d} \ln \gamma_C/\mathrm{d}T$. Similarly, from equation 17,

$$\frac{\mathrm{d} \ln \gamma_{X_1}}{\mathrm{d}T} = -\frac{\bar{H}_1 - \bar{H}_1^*}{\nu RT^2} \qquad \text{(const. } P \text{ and } m\text{)} \qquad (75)$$

and the same for $\mathrm{d}\ln\gamma_{Y_1}/\mathrm{d}T$, except that the ν is omitted. The "uncorrected" activity coefficient, $(\gamma)'$, can not be considered a function of T.

Osmotic coefficient

The variation of f_r with temperature, obtained by taking the derivative of equation 33, may be expressed as follows:

$$\frac{\mathrm{d}f_r}{\mathrm{d}T} = \frac{\bar{H}_1 - \bar{H}_1^*}{\nu RT^2 m/N_1} \qquad \text{(const. } P \text{ and } m) \tag{76}$$

If $\Delta\bar{C}_{P_1}$ is the (constant) difference between the fictive molal heat capacity of the component 1 and the pure solvent, then the integrated form of equation 76 is,

$$\frac{\nu Rm}{N_1}(f_r - (f_r)') = -\left(\frac{\Delta\bar{F}_1}{T} - \frac{(\bar{F}_1)'}{T'}\right) = \left(\frac{(\Delta\bar{H}_1)_T}{T} - \Delta\bar{C}_{P_1}\right)\frac{T - T'}{T'} + \Delta\bar{C}_{P_1}\ln\frac{T}{T'} \doteq \frac{(\Delta\bar{H}_1)_T}{T}\frac{\theta}{T} + \left(\frac{(\Delta\bar{H}_1)_T}{T} - \frac{\Delta\bar{C}_{P_1}}{2}\right)\frac{\theta^2}{T^2} + \left(\frac{(\Delta\bar{H}_1)_T}{T} - \frac{2\,\Delta\bar{C}_{P_1}}{3}\right)\frac{\theta^3}{T^3} \tag{77}$$

in which $\theta = T - T'$ and $(\Delta\bar{H}_1)_T = \bar{H}_1 - \bar{H}_1^*$ at T. Equation 77 is in convenient form for calculating f_r at a fixed temperature T, when $(f_r)'$ at a given temperature T' is known. Incidentally the equation closely resembles equation 44. It may be noted that the determination of γ from f (or from i, j, or α) would involve the calculation of $(f_r)'$ by equation 47 or 48, the calculation of f_r by equation 77, and the calculation of γ by equation 51.

From equation 36 we obtain the expression, similar to that for f_r,

$$\frac{\mathrm{d}f_X}{\mathrm{d}T} = -\frac{\bar{H}_1 - \bar{H}_1^*}{\nu RT^2 \ln X_1} \tag{78}$$

The equation for $\mathrm{d}f_Y/\mathrm{d}T$ is of the same form (without the ν). An expression for $\mathrm{d}f_P/\mathrm{d}T$ can be written, but it is somewhat complicated. The other variety of osmotic coefficient, f, is not a function of temperature; the same applies to i, j, and α.

VARIATION WITH PRESSURE

Activity

The change of a_2 with P (at constant m and T) can be obtained from equation 7, or still more easily from equation 1, since by definition $\bar{F}_2^0$ is not a function of P,—which accounts for the fact that the variation with

P is more simple in form than the corresponding variation with T. We have then (since $\mathrm{d}\bar{F}_2/\mathrm{d}P = \bar{V}_2$),

$$\frac{\mathrm{d}\ln a_2}{\mathrm{d}P} = \frac{\bar{V}_2}{RT} \qquad \text{(const. } m \text{ and } T\text{)} \tag{79}$$

and the same expression for $(a_2)_X$, $(a_2)_C$, or $(a_2)_Y$. The quantity $\bar{V}_2$ is the fictive volume of component 2 (per mole). Similarly, from equation 10 we have,

$$\frac{\mathrm{d}\ln a_1}{\mathrm{d}P} = \frac{\bar{V}_1}{RT} \qquad \text{(const. } X_1 \text{ and } T\text{)} \tag{80}$$

Activity coefficient

From equation 12 we obtain,

$$\frac{\mathrm{d}\ln \gamma}{\mathrm{d}P} = \frac{\bar{V}_2 - \bar{V}_2^*}{\nu RT} \qquad \text{(const. } m \text{ and } T\text{)} \tag{81}$$

This may be put in the integrated form,

$$\ln \gamma = (\ln \gamma)_{P=1} + \frac{1}{\nu RT}\int_1^P \Delta_X \bar{V}_2 \,\mathrm{d}P \tag{82}$$

Here $\bar{V}_2^*$ is the limiting value of $\bar{V}_2$ as m approaches zero, and $\Delta_X\bar{V}_2$ is written for $\bar{V}_2 - \bar{V}_2^*$ at any pressure, P. The same expression is obtained when γ_{X_2}, γ_{Y_2}, or γ_C is substituted for γ.

It is well known that if, as is true for strong electrolytes in dilute solution, $\ln\gamma = -\omega m^{\frac{1}{2}}$ (ω being a function of T and P but not of m) then $\bar{H}_2 - \bar{H}_2^*$ is proportional to $m^{\frac{1}{2}}$ and $\bar{H}_1 - \bar{H}_1^*$ is equal to $-m(\bar{H}_2 - \bar{H}_2^*)/3N_1$. From this it follows that for such solutions $(\partial \ln \gamma/\partial T)_{P,m} = 3(\partial f_r/\partial T)_{P,m}$. This relation is in agreement with, and might have been derived from, the relation shown by Lewis and Randall (reference 15, p. 346) to exist at low concentrations between $\ln \gamma$ and j, which in dilute solutions is approximately equal to $1 - f_r$.

From equation 10 we have also

$$\frac{\mathrm{d}\ln \gamma_{X_1}}{\mathrm{d}P} = \frac{\bar{V}_1 - \bar{V}_1^*}{\nu RT} \qquad \text{(const. } X_1 \text{ and } T\text{)} \tag{83}$$

On the other hand, for the other varieties of activity coefficient (of the solvent), a_1/X_1 and γ_{Y_1}, we have equations similar to equation 83 except that the ν is omitted.

Osmotic coefficient

The change of f_r and of f_X with P is obtained directly from equations 33 and 36, respectively. Thus

$$\frac{\mathrm{d}f_r}{\mathrm{d}P} = -\frac{\bar{V}_1 - \bar{V}_1^*}{\nu RTm/N_1} \qquad \text{(const. } m \text{ and } T) \tag{84}$$

and

$$\frac{\mathrm{d}f_X}{\mathrm{d}P} = \frac{\bar{V}_1 - \bar{V}_1^*}{\nu RT \ln X_1} \qquad \text{(const. } X_1 \text{ and } T) \tag{85}$$

The equation for $\mathrm{d}f_Y/\mathrm{d}P$ is obtained by replacing $\nu \ln X_1$ by $\ln Y_1$.

It may be noted that by experiment it has been found that for all types of solutes the limit of $(\bar{V}_1 - \bar{V}_1^*)/m$, as m approaches zero, is zero. This is in accord with the definition of f_r, by which f_r has the limiting value 1 at all pressures. In dilute solutions of strong electrolytes it is known that $\bar{V}_2 - \bar{V}_2^*$ is proportional to $m^{½}$; whence, $\bar{V}_1 - \bar{V}_1^*$ is equal to $-m(\bar{V}_2 - \bar{V}_2^*)/3N_1$, and $(\partial \ln \gamma/\partial P)_{T,m} = 3(\partial f_r/\partial T)_{T,m}$ for such solutions.

The derivative of f_P with respect to P can not be written, because from the method of defining it f_P can not be considered a function of P. If f_P were defined (more generally) on the basis of an osmotic pressure, π, measured from P as a starting point, then f_P obviously would depend on P, and $\mathrm{d}f_P/\mathrm{d}P$ would have a meaning.

Since f is a function of $(\Delta\bar{F}_1)'$ it is also a function of P—although not of T, because $(\Delta\bar{F}_1)'$ is at a predetermined temperature. An expression for $\mathrm{d}f/\mathrm{d}P$ can be obtained, but the complete equation is rather complicated, and it will suffice, for the present, to note that in dilute solutions, or whenever $\bar{H}_1 - H_1^*$ is negligible, f is nearly equal to f_r and therefore

$$\left(\frac{\partial f}{\partial P}\right)_m \doteq -\frac{\Delta_X \bar{V}_1}{\nu RTm/N_1} \qquad \text{(approx., in dilute solution)} \tag{86}$$

Under the same conditions a similar expression can be written for the variation of i, j, and α with pressure.

SUMMARY

It is shown that activity may be defined by a single equation equivalent to the two equations of the usual definition. This equation is easily amenable to mathematical operations such as differentiation.

It is furthermore suggested that activity be defined so as to omit the factor $\nu_+^{\nu_+} \cdot \nu_-^{\nu_-}$ that appears in the customary definition of the activity of an electrolyte.

Several varieties of activity coefficient, osmotic coefficient, and other related functions are in common use. A number of these are defined and correlated, and their derivatives with respect to temperature and pressure are given.

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