

Thermodynamics of Dilute Solutions

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By far the most important application of thermodynamics in chemistry is to the study of chemical reactions and, in particular, to the determination of the equilibrium conditions for balanced reactions. This is facilitated by the construction and use of tables of *standard thermodynamic properties* of substances, and a primary object in any introductory course in chemical thermodynamics should be to teach the student how such tables are constructed from calorimetric and related measurements and how they are used to predict equilibrium conditions. The standard thermodynamic properties are those of the substances in their *standard states*. Misconceptions concerning the definitions of these standard states are widespread and a number of articles in THIS JOURNAL (1-3) have referred to some of these. The situation is particularly bad when the substance under consideration is a solute. Robbins (2) found that only three of the twenty-four textbooks he reviewed used the correct definition of the standard state when discussing standard electromotive force. The problem is exacerbated by the ambiguities concerning the definitions of a number of related concepts, in particular those of the "ideal solution" and "ideal dilute solution," and by the confusion arising from the use of several activity coefficients and two osmotic coefficients in the application of thermodynamics to dilute solutions.

Dilute Solution

In discussing phases containing more than one substance it is often convenient to make a distinction between a *mixture* and a *solution*. A *mixture* is a gaseous, liquid, or solid phase in which the substances are all treated the same way. A *solution* is a liquid or solid phase in which one of the substances (or sometimes a mixture of some of the substances), which is called the *solvent*, is treated differently from the other substances, which are called *solutes*. There is nothing fundamental in this distinction between a mixture and a solution: it is a matter of convenience. When the total amount of solute is small compared with the total amount of solvent, the solution is called a *dilute solution*.

Our object is to look at principles applicable to all dilute solutions and, to simplify the discussion, we will consider a liquid, binary dilute solution, at temperature T and pressure p , in which an amount n_2 of a (non-dissociating) solute 2 (of molar mass M_2) is dissolved in an amount n_1 of a solvent 1 (of molar mass M_1). The measures of solute composition [mole fraction $x_2 = n_2/(n_1 + n_2)$, molality $m_2 = n_2/n_1M_1$, concentration (molarity) $c_2 = n_2\rho/(n_1M_1 + n_2M_2)$] are related by the equations

$$M_1m_2 = x_2/(1 - x_2) = M_1c_2/(\rho - M_2c_2) \quad (1)$$

where ρ is the density of the solution, a function of T , p , and composition. In the limit of infinite dilution, defined as $n_2 \rightarrow 0$, eqn. (1) reduces to

$$M_1m_2 = x_2 = M_1c_2/\rho_1^\circ \quad (2)$$

in which ρ_1° is the density of the pure solvent at T and p .

(Throughout this paper the superscript $^\circ$ will be used only in association with the properties of pure substances.) Equation (2) expresses the fact that the various measures of solute composition are directly proportional to one another in the infinite dilution limit. The fact that c_2 , in contrast to x_2 and m_2 , is temperature dependent is widely used as an argument against the use of the concentration scale. It is seldom pointed out that in certain circumstances (for example, when the solvent is a mixture of substances) some ambiguity may arise in the definitions of molality and mole fraction. [Ben-Naim (4) has argued in favor of using the concentration scale in dealing with dilute solutions.]

Gibbs-Duhem Equation

A binary phase (components 1 and 2) possesses three degrees of freedom and, consequently, its thermodynamic state can be determined by specifying T , p , and the composition of one of the components. (In this paper we will not usually include the functional dependencies of the various thermodynamic properties in our equations, but will specify these in the text and/or in tabular form.) The chemical potentials of 1 and 2, μ_1 and μ_2 , are related by the Gibbs-Duhem equation,

$$x_1d\mu_1 + x_2d\mu_2 = 0 \quad (\text{constant } T, p) \quad (3)$$

This equation can be rearranged to give

$$d\mu_1 = -\frac{x_2}{(1-x_2)} \left(\frac{\partial\mu_2}{\partial x_2} \right)_{T,p} dx_2 \quad (4)$$

which upon integration becomes

$$\mu_1 = k(T, p) - \int \frac{x_2}{(1-x_2)} \left(\frac{\partial\mu_2}{\partial x_2} \right)_{T,p} dx_2 \quad (5)$$

in which $k(T, p)$ is an integration constant. In those cases where the range of compositions of the binary phase extends to pure component 1, eqn. (5) can be expressed in the form

$$\mu_1(T, p, x_2) = \mu_1^\circ(T, p) - \int_0^{x_2} \frac{x_2}{(1-x_2)} \left(\frac{\partial\mu_2}{\partial x_2} \right)_{T,p} dx_2 \quad (6)$$

in which μ_1° is the chemical potential (molar Gibbs function) of pure 1 at T , p .

Reference Systems

In the application of thermodynamics to pure gases, mixtures, and solutions it is usual to introduce what we will refer to as *reference systems*. The definitions of these systems are based on experimental information, concerning, in particular, the behavior of real systems under certain limiting conditions, or, less frequently, on statistical mechanical information. The reference systems are hypothetical systems, the behavior of any real system deviating to a greater or lesser extent from the behavior of a corresponding reference system. They are used in two ways: (1) As approximations to real systems. In those cases where more than one reference system has been used for a real system (as is the case with dilute solutions), the question arises as to which of the reference systems most closely approximates the behavior of the real system. A recent article in THIS JOURNAL (5) has discussed this question with respect to the Debye-Hückel theory. (2) As references against which to describe the behavior of real systems; one discusses the real

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Table 1. Pure Gases, Gaseous Mixtures, Liquid Mixtures

Reference System	Definition	
Perfect (or ideal) gas	$\mu(pg) = \mu^{pg} + RT \ln(p/p^\ominus)$	
Perfect gaseous mixture	$\mu_i(pgm) = \mu_i^{pg} + RT \ln(p_i/p^\ominus) \quad (i = 1, 2)$	
Ideal mixture	$\mu_i(im) = \mu_i^o RT \ln x_i \quad (i = 1, 2)$	
Real System	Definition of Fugacities and Activity Coefficients	
Pure gas	$\mu = \mu^{pg} + RT \ln(f/p^\ominus); \quad \lim_{p \rightarrow 0} (f/p) = 1$	
Gaseous mixture	$\mu_i = \mu_i^{pg} RT \ln(f_i/p^\ominus); \quad \lim_{p \rightarrow 0} (f_i/p_i) = 1 \quad (i = 1, 2)$	
Liquid mixture	$\mu_i = \mu_i^o + RT \ln x_i \gamma_i^{lm}; \quad \lim_{x_i \rightarrow 1} \gamma_i^{lm} = 1$	
Symbol	Functional Dependence	
μ^{pg}	Chemical potential of perfect gas at T and p^\ominus	T
μ_i^{pg}	Chemical potential of pure perfect gas i at T and p^\ominus	T
μ_i^o	Chemical potential of pure liquid i at T and p	T, p
p_i	Partial pressure of i	p , composition
f	Fugacity of pure gas	T, p
f_i	Fugacity of i in gaseous mixture	T, p , composition
γ_i^{lm}	Activity coefficient of i in liquid mixture	T, p , composition

system in terms of the deviations of its properties from those of a corresponding reference system. (Our use of the adjective "reference" emphasizes this application.)

Pure Gases and Gaseous Mixtures

For pure gases and gaseous mixtures the reference systems are the *perfect (or ideal) gas* and *perfect gaseous mixture*, respectively, which can be defined by the chemical potential expressions in Table 1. In this table p^\ominus represents an arbitrarily chosen standard pressure which is usually, though not necessarily, 101.325 kPa (i.e., exactly 1 atm). We will later use m^\ominus and c^\ominus to represent an arbitrarily chosen standard molality and standard concentration which are usually 1 mol kg⁻¹ and 1 mol dm⁻³, respectively. The behavior of real gases and real gaseous mixtures is discussed in terms of fugacities (defined in Table 1) or the parameters of some equation of state.

Liquid Mixtures

The reference system is the *ideal mixture* which can be defined by the chemical potential expression in Table 1. Assuming that the vapor phase in equilibrium with an ideal mixture is a perfect gaseous mixture, it can be shown (6) that

$$\ln(p_i/p_i^o) = \ln x_i + \frac{1}{RT} \int_{p_i^o}^p V_{mi} dp \quad (i = 1, 2) \quad (7)$$

in which p_i^o is the vapor pressure of pure liquid i at T , and V_{mi}^o is the molar volume of pure liquid i at T and p . As the integral in eqn. (7) usually makes only a small contribution, it is nor-

mally neglected and eqn. (7) reduces to Raoult's law:

$$p_i = p_i^o x_i \quad (i = 1, 2) \quad (8)$$

[If the perfect gaseous mixture approximation is not assumed, the pressures on the left-hand side of eqn. (7) and those in eqn. (8) must be replaced by the corresponding fugacities.] The behavior of real liquid mixtures is discussed in terms of activity coefficients (defined in Table 1) or excess thermodynamic properties. (Sometimes activities are used as well as activity coefficients. In this paper we will consider only the latter.)

Dilute Solutions

In dealing with dilute solutions several reference systems have been used. It is sufficient in defining these to specify the chemical potential of the solute, that of the solvent being determined by eqn. (6). These definitions are given in Table 2; the meanings of the symbols used in this table are given in Table 4. Also given in Table 2 are the corresponding expressions for the solvent chemical potentials, obtained using eqn. (6), and for the partial pressures of the solute and solvent. In obtaining these partial pressures the perfect gaseous mixture assumption is invoked and, in the cases of the solvent partial pressures and the solute partial pressure for an ideal mixture, it is further assumed that an integral of the form of that given in eqn. (7) is negligible. The solute chemical potentials and solute partial pressures for the various reference systems are shown schematically in Figures 1 and 2. (These figures have been based on the following: $M_1 = 100$ g mol⁻¹, $M_2 = 200$ g mol⁻¹, $\rho = \rho_1^o = 0.7$ g cm⁻³, $T = 298$ K. The solute chemical potentials have been plotted as solid lines over a composition range corresponding to $m_2 = 1 \times 10^{-2}$ to 10 mol kg⁻¹. The solute partial pressures have been plotted as solid lines up to a composition corresponding to $m_2 = 10$ mol kg⁻¹. The vertical scales are the same for each of the diagrams in Figure 1 and in Figure 2.)

The reference systems used for dilute solutions fall into two groups; the ideal mixture, which is the reference system used for liquid mixtures, and those based on the behavior of the solute in an infinitely dilute solution. Considering a real dilute solution, it is physically obvious that in the limit of infinite dilution

$$p_2 \propto n_2 \quad (9)$$

(We are assuming perfect gaseous mixture behavior.) This proportionality can, under the appropriate conditions, be consistent with each of the following:

$$p_2 \propto x_2 \quad (10)$$

$$p_2 \propto m_2 \quad (11)$$

$$p_2 \propto c_2 \quad (12)$$

In the limit of infinite dilution, eqn. (2) requires that eqns. (10) to (12) are equivalent. As we go to finite solute compositions, none of the proportionalities, eqns. (10) to (12), will be exact, but they may be, and all in fact have been, used for reference

Table 2. Reference Systems Used for Dilute Solutions

Label	Definition	Solvent Chemical Potential	Solute	Partial Pressures Solvent
im	$\mu_2(im) = \mu_2^o + RT \ln x_2$	$\mu_1(im) = \mu_1^o + RT \ln x_1$	$p_2^o x_2$	$p_1^o x_1$
I	$\mu_2(I) = \mu_2^o + RT \ln x_2$	$\mu_1(I) = \mu_1^o + RT \ln x_1$	$K_2^o x_2$	$p_1^o x_1$
II	$\mu_2(II) = \mu_2^{ } + RT \ln(m_2/m^\ominus)$	$\mu_1(II) = \mu_1^o - RTM_1 m_2$	$K_2^{ } m_2$	$p_1 \exp(-M_1 m_2)$
III	$\mu_2(III) = \mu_2^{ } + RT \ln(c_2/c^\ominus)$	$\mu_1(III) = \mu_1^o - RTM_1 \int_0^{c_2} \frac{1}{\rho - M_2 c_2} dc_2$ $= \mu_1^o + RT(M_1/M_2) \ln[(\rho_1^o - M_2 c_2)/\rho_1^o]^a$	$K_2^{ } c_2$	$= p_1^o x_1 (1 - \frac{1}{2} x_2^2 + \dots)$ $p_1^o (1 - M_2 c_2 / \rho_1^o)^{M_1/M_2 a}$ $= p_1^o x_1 [1 - \frac{1}{2} (1 - M_2/M_1) x_2^2 + \dots]^a$

^a Assuming that the density of the dilute solution is equal to that of the pure solvent at the same T, p .

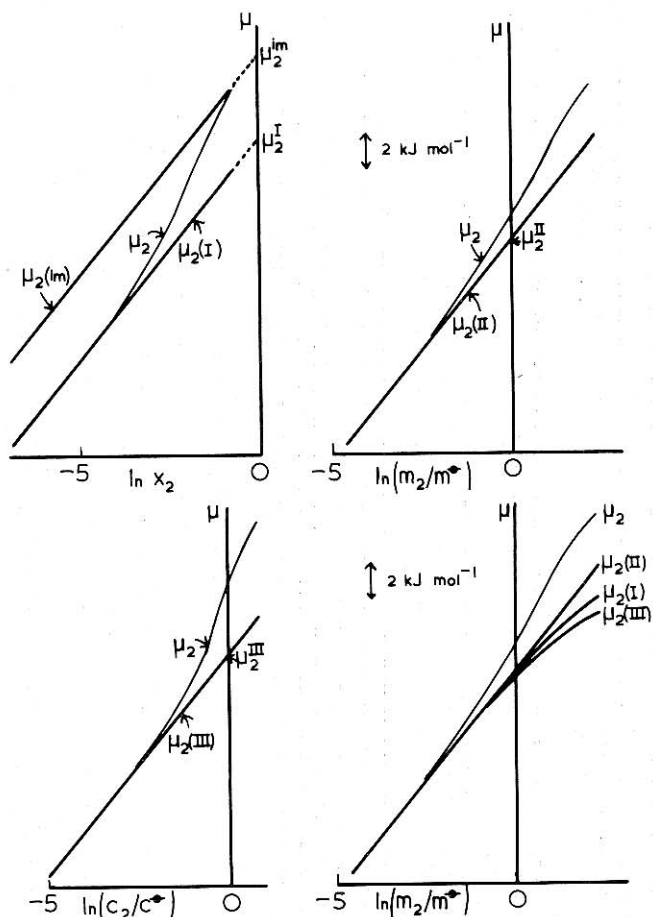


Figure 1. Solute chemical potentials at T and p for the various dilute solution reference systems and for a real dilute solution.

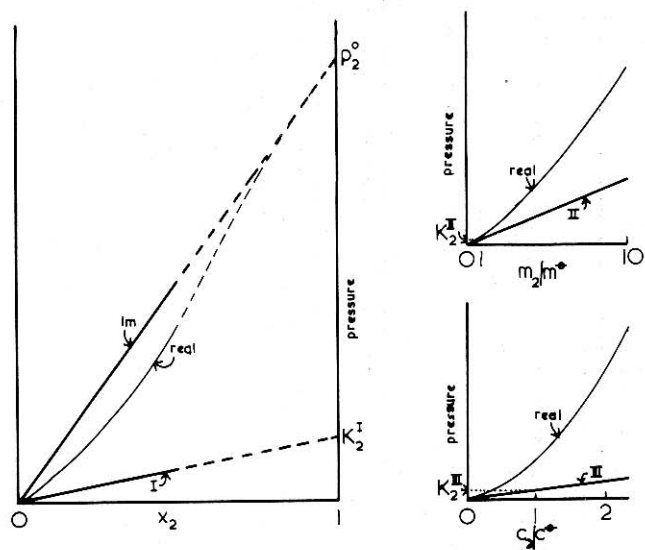


Figure 2. Solute partial pressures at T for the various dilute solution reference systems and for a real dilute solution.

purposes. As can be seen in Table 2, the reference systems I, II, and III correspond to the proportionalities in eqns. (10), (11), and (12), respectively.

Before considering real dilute solutions it is appropriate to draw attention to a number of points concerning the dilute solution reference systems: (a) As we approach the pure liquid solute, $m_2 \rightarrow \infty$ and, consequently, the equations for reference

system II in Table 2 become untenable; they predict, for example, an infinite value for p_2^0 . In dealing with dilute solutions, however, we are not concerned with conditions approaching pure liquid solute and, consequently, such problems do not arise.

(b) μ_2^0 and p_2^0 are properties of the pure liquid solute. In dealing with dilute solutions this is usually a hypothetical state, being a supercooled liquid in those cases where the solute is a solid at T, p and a superheated liquid in those cases where it is a gas.

(c) As can be seen in Table 2, the solvent partial pressures for reference systems II and III deviate from Raoult's law, defined by eqn. (8), although usually to only a very small extent. It is often stated that, as a consequence of the Gibbs-Duhem equation, if the solvent obeys Raoult's law over some composition range, the solute must obey Henry's law over the same composition range, and vice versa. Except in the limit of infinite dilution, this statement is rigorously correct only if Henry's law is expressed in terms of x_2 [i.e., by eqn. (10)], a restriction that is by no means clear in many treatments of the subject.

(d) Reference systems I, II, and III represent different (hypothetical) systems, the properties of which converge with one another, and with those of a real dilute solution, in the limit of infinite dilution (Fig. 1).

Real Dilute Solutions

Solute

The behavior of the solute in a real dilute solution has been referred to each of the reference systems in Table 2 by the introduction of corresponding solute activity coefficients (or solute activities). In the case of the ideal mixture (im) reference system the solute activity coefficient, γ_2^{im} , is defined as in Table 1. For the other reference systems we consider firstly the general case of a reference system α ($\alpha = \text{I, II, III}$) defined, as in Table 2, in terms of a (dimensionless) measure of solute composition $\chi_2^\alpha (= x_2, m_2/m^\ominus, c_2/c^\ominus)$. We define a solute activity coefficient, γ_2^α , a function of T, p , and the composition, by the equations

$$\mu_2 = k^\alpha(T, p) + RT \ln \chi_2^\alpha \gamma_2^\alpha (\alpha = \text{I, II, III}) \quad (13)$$

$$\lim_{\chi_2^\alpha \rightarrow 0} \gamma_2^\alpha = 1 \quad (14)$$

in which μ_2 is the chemical potential of the solute in the real dilute solution. These equations define both γ_2^α and $k^\alpha(T, p)$. The physical significance of the latter can be established as follows. According to eqns. (13) and (14),

$$k^\alpha(T, p) = \lim_{\chi_2^\alpha \rightarrow 0} (\mu_2 - RT \ln \chi_2^\alpha) (\alpha = \text{I, II, III}) \quad (15)$$

The reference system α was defined (Table 2) such that $\mu_2(\alpha) - RT \ln \chi_2^\alpha$ was independent of χ_2^α for finite values of χ_2^α . Therefore,

$$k^\alpha(T, p) = \mu_2(\alpha) - RT \ln \chi_2^\alpha (\alpha = \text{I, II, III}) \quad (16)$$

$$= \mu_2(\alpha) (\chi_2^\alpha = 1) = \mu_2^\alpha (\alpha = \text{I, II, III}) \quad (17)$$

The meanings of μ_2^α ($\alpha = \text{I, II, III}$) are exactly the same as in Table 3; these are given in Table 4. Miconceptions concerning the physical significance of the composition independent term in eqn. (13) are widespread. The definitions of the solute activity coefficients and the corresponding equations for the solute partial pressure (again assuming perfect gaseous mixture behavior) are given in Table 3; the meanings of the symbols used in this table are given in Table 4. The solute chemical potential and solute partial pressure of a real dilute solution are compared schematically with these properties for the various reference systems in Figures 1 and 2.

Making use of the facts that, in the limit of infinite dilution, the measures of solute composition are related by eqn. (2) and

the chemical potentials of reference systems I, II, and III converge, it is readily shown that

$$\mu_2^I = \mu_2^{II} - RT \ln (M_1 m^\ominus) = \mu_2^{III} + RT \ln (\rho_1^\ominus / M_1 c^\ominus) \quad (18)$$

Combining eqns. (1) and (18) with the definitions of the solute activity coefficients in Table 3, it can be shown that

$$\gamma_2^I = \gamma_2^{II} (1 + m_2 M_1) = \gamma_2^{III} [\rho + c_2 (M_1 - M_2)] / \rho_1^\ominus \quad (19)$$

(The activity coefficients γ_2^I and γ_2^{II} are sometimes called the *rational* and *practical* activity coefficients, respectively. The symbols f_2 , γ_2 , and y_2 have been used for γ_2^I , γ_2^{II} and γ_2^{III} , respectively.)

Solvent

The behavior of the solvent in a real dilute solution has been referred to the ideal mixture and reference system I (Tables 1, 2), these being equivalent as far as the solvent is concerned, by the introduction of a solvent activity coefficient, $\gamma_1^{im} (= \gamma_1^I)$, and an osmotic coefficient, g (the *rational* osmotic coefficient), and to reference system II by the introduction of an osmotic coefficient, ϕ (the *practical* osmotic coefficient). These three properties, each of which is a function of T , p and the composition, are defined in Table 3. The corresponding equations for the solvent partial pressure, obtained by assuming perfect gaseous mixture behavior and neglecting an integral of the form of that given in eqn. (7), are included in Table 3.

It follows from the Gibbs-Duhem equation, eqn. (3), that in dilute solutions the deviation of $\gamma_1^{im} (= \gamma_1^I)$ from unity is much less than that of γ_2^{im} or γ_2^I . From Table 3 it follows that

$$g - 1 = \ln \gamma_1^{im} / \ln x_1 \approx (1 - \gamma_1^{im}) / x_2 \quad (20)$$

Table 3. Activity Coefficients and Osmotic Coefficients used for Dilute Solutions

Reference System	Definition	Partial Pressure
Solute		
im	$\mu_2 = \mu_2^\ominus + RT \ln x_2 \gamma_2^{im}; \lim_{x_2 \rightarrow 1} \gamma_2^{im} = 1$	$p_2^\ominus x_2 \gamma_2^{im}$
I	$\mu_2 = \mu_2^I + RT \ln x_2 \gamma_2^I; \lim_{x_2 \rightarrow 0} \gamma_2^I = 1$	$K_2^I x_2 \gamma_2^I$
II	$\mu_2 = \mu_2^{II} + RT \ln (m_2 \gamma_2^{II} / m^\ominus); \lim_{m_2 \rightarrow 0} \gamma_2^{II} = 1$	$K_2^{II} m_2 \gamma_2^{II}$
III	$\mu_2 = \mu_2^{III} + RT \ln (c_2 \gamma_2^{III} / c^\ominus); \lim_{c_2 \rightarrow 0} \gamma_2^{III} = 1$	$K_2^{III} c_2 \gamma_2^{III}$
Solvent		
im, I	$\mu_1 = \mu_1^\ominus + RT \ln x_1 \gamma_1^{im}; \lim_{x_1 \rightarrow 1} \gamma_1^{im} = 1$	$p_1^\ominus x_1 \gamma_1^{im}$
im, I	$\mu_1 = \mu_1^\ominus + gRT \ln x_1; \lim_{x_1 \rightarrow 1} g = 1$	$p_1^\ominus x_1^g$
II	$\mu_1 = \mu_1^\ominus - \phi RT M_1 m_2; \lim_{m_2 \rightarrow 0} \phi = 1$	$p_1^\ominus \times \exp(-\phi M_1 m_2)$

Table 4. Meanings of the Symbols used in Tables 2 and 3

Symbol		Functional Dependence
$\mu_i (i = 1, 2)$	Chemical potential of i in a real dilute solution	$T, p, \text{composition}$
$\mu_i^\ominus (\alpha) (i = 1, 2) (\alpha = \text{im, I, II, III})$	Chemical potential of i in reference system α	$T, p, \text{composition}$
$\mu_i^I (i = 1, 2)$	Chemical potential of pure liquid i at T, p	T, p
μ_2^I	Chemical potential of solute in reference system I at $x_2 = 1$ and T, p	T, p
μ_2^{II}	Chemical potential of solute in reference system II at $m_2 = m^\ominus$ and T, p	T, p
μ_2^{III}	Chemical potential of solute in reference system III at $c_2 = c^\ominus$ and T, p	T, p
$\gamma_2^\alpha (\alpha = \text{im, I, II, III})$	Activity coefficient of solute defined with respect to reference system α	$T, p, \text{composition}$
γ_1^{im}	Activity coefficient of solvent defined with respect to reference system im (or I)	$T, p, \text{composition}$
$p_i^\ominus (i = 1, 2)$	Vapor pressure of pure liquid i at T	T
K_2^I	$p^\ominus \exp[(\mu_2^I - \mu_2^{II}) / RT]$	T, p
K_2^{II}	$(p^\ominus / m^\ominus) \exp[(\mu_2^{II} - \mu_2^{III}) / RT]$	T, p
K_2^{III}	$(p^\ominus / c^\ominus) \exp[(\mu_2^{III} - \mu_2^{II}) / RT]$	T, p

The osmotic coefficient g therefore provides a more sensitive measure of the deviation of the solvent from ideal mixture or reference system I behavior than does $\gamma_1^{im} (= \gamma_1^I)$. As can be seen by comparing the definition of the osmotic coefficient ϕ (Table 3) with the expression for the solvent chemical potential in reference system II (Table 2), ϕ provides a direct measure of the extent to which the solvent deviates from reference system II behavior. Combining equations in Table 3 it can be shown that the two osmotic coefficients are related by the equation

$$\phi = - \frac{\ln x_1}{M_1 m_2} g = [1 + M_1 m_2 / 2 + (M_1 m_2)^2 / 3 + \dots] g \quad (21)$$

Terminology

In the preceding discussion we have omitted some of the terminology usually associated with the thermodynamics of dilute solutions; in particular, we have not used the expressions "ideality," "ideal solution," or "ideal dilute solution." This we have done deliberately because, as we will now discuss, such terms are not uniquely defined, and this situation has sometimes led to confusion. A perusal of textbooks on physical chemistry and thermodynamics shows that an *ideal solution* has been defined in two ways.

(1) An ideal solution is defined as one for which the chemical potential of each component is given by

$$\mu_i = \mu_i^*(T, p) + RT \ln x_i \quad (i = 1, 2) \quad (22)$$

The physical significance of $\mu_i^*(T, p)$ depends upon the composition range over which eqn. (22) applies. Two cases arise: (a) Eqn. (22) holds at all compositions; $\mu_i^*(T, p) = \mu_i^\ominus(T, p)$ and we have the *ideal mixture* defined in Table 1. This case has also been referred to as a *perfect solution* (7). (b) Eqn. (22) holds only for dilute solutions; $\mu_1^*(T, p) = \mu_1^\ominus(T, p)$, $\mu_2^*(T, p) = \mu_2^\ominus(T, p)$ and we have reference system I defined in Table 2. This case has also been referred to as an *ideal dilute solution* (7). The definition of an ideal solution by eqn. (22) therefore includes both the ideal mixture and reference system I depending upon the composition range over which the equation is applicable.

(2) An ideal solution is defined in the same way as an ideal mixture (Table 1). To within the approximations mentioned above, this is equivalent to the definition, familiar in many elementary textbooks, that an ideal solution is one in which all components obey Raoult's law, eqn. (8). In recent IUPAC sponsored articles (8, 9) and elsewhere (10) the *ideal dilute solution* has been defined as in the case of reference system II in Table 2. It has, however, also been defined as in the cases of reference system I (7) and reference system III (4). The term *dilute solution* has been used for reference system I (11).

This is by no means a complete picture. It is sufficient, however, to make clear the necessity of stating unambiguously

what definition is being adopted whenever terms such as "ideality," "ideal solution" and "ideal dilute solution" are being used.

Standard States

The information required to calculate the yield of a chemical reaction is made available in thermodynamic tables. McGlashan (10) has divided these into primary thermodynamic tables, which contain the information needed to calculate values of the (standard) equilibrium constant $K^\ominus(T)$, and secondary thermodynamic tables, which contain the additional information (e.g., virial coefficients, fugacities, activity coefficients, osmotic coefficients) required to calculate the yield of a reaction from $K^\ominus(T)$. He has pointed out that, while primary thermodynamic tables are sufficiently extensive to be useful (the U.S. National Bureau of Standards' Circular 500, superseded by the parts of Technical Note 270, being the best-known), there is a paucity of secondary thermodynamic tables.

Primary thermodynamic tables contain values of the standard thermodynamic properties of substances, and sums and differences of these. Such properties are those of the substances in their standard states. While, as McGlashan (10) points out, an algebraic definition of the standard chemical potential avoids any difficulties associated with the definition of a standard state, the use of standard states is widespread and, we believe, advantageous in an introductory chemical thermodynamics course. The selection of a standard state for a substance is a matter of convenience and will depend on the problem under consideration. The choice must be clearly stated and, in using thermodynamics tables, care must be taken to ascertain which standard states have been employed.

In Technical Note 270 and in many other thermodynamic tables, the standard states for solutes in solution (and for gases) are states of what we have called reference systems. For a solute in a nonaqueous solution the standard state is reference system I at $x_2 = 1$, p^\ominus , and T . For a solute in aqueous solution the standard state is reference system II at $m_2 = m^\ominus$, p^\ominus , and T . For a solvent in any liquid solution the standard state is pure, liquid solvent at p^\ominus and T . The definitions of all standard states involve an arbitrarily chosen standard pressure p^\ominus and, in the case of aqueous solutions, an arbitrarily chosen standard molality m^\ominus ; the temperature is not defined (1). Consequently, the standard thermodynamic properties are functions only of temperature. While values of the standard thermodynamic properties, and the sums and differences of these, are frequently tabulated at a particular temperature, usually 298.15 K, those at other temperatures can be calculated using thermodynamic relations.

Reference Systems and Reality

The use of reference systems as approximations to real systems is commonplace, the former possessing the obvious advantages of being mathematically tractable and, at least in some cases, physically simple. In many, but by no means all,

situations such approximations are adequate. For dilute solutions several reference systems have been defined (Table 2) and the question therefore arises as to whether one of these best approximates a real dilute solution. This question was raised with respect to the Debye-Hückel theory in a recent article in THIS JOURNAL (5). Contrary to the approach used in that paper, we contend that such a question can be answered only on the basis of experimental and/or statistical mechanical considerations. It is readily concluded from experimental evidence that the ideal mixture is a much less reasonable approximation to a dilute solution than are reference systems I, II, and III. It is much more difficult, however, to decide which, if any, of these three "infinite dilution" reference systems best approximates the behavior of some real dilute solution. In those cases where the solute is a non-electrolyte of molar volume similar to that of the solvent, all are usually reasonable approximations; the experimental evidence does not generally point to any one as being "best" and the statistical mechanical evidence is equivocal as it depends on the theory being used. In those cases when the solute is an electrolyte or when there is a substantial size difference between the solvent and solute molecules, none of the reference systems (I, II, III) is a reasonable approximation except at very low solute compositions. For dilute polymer solutions the experimental and statistical mechanical evidence suggests that a reference system based on a volume fraction (or, what is virtually equivalent, a concentration) scale will best approximate the real system (12). In the Debye-Hückel theory of electrolyte solutions it is assumed that the solute chemical potential can be divided into two contributions: a non-electrolyte contribution, this being the solute chemical potential if the ions were uncharged species, and an electrical contribution arising from the charges on the ions. Debye and Hückel estimated the former using reference system I but, subsequently, reference systems II and III have also been used. From what we have said above concerning non-electrolyte solutions, the choice is a matter of convenience and, accordingly, we cannot accept Morel's (5) conclusion that the Debye-Hückel theory gives γ_2^I rather than γ_2^{II} or γ_2^{III} .

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