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Theory of Solutions. I[1]

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By the use of suitable partition functions, an exact but formal theory of solutions is developed which yields directly thermodynamic functions expressed in a particularly practical form. For example, for a binary solution (the case considered in the present paper), the chemical potentials and partial molal volumes, entropies and heat contents can be written as power series in the molality or mole fraction of the solute, with coefficients which depend on properties of the solvent (and small sets of solute molecules) at the same pressure and temperature as the solution. An interesting feature of these expansions is their formal identity with the series of Mayer's imperfect gas theory. Three introductory examples are worked out to illustrate the equations.

I. Introduction

Rigorous statistical mechanical theories of solutions have been developed by McMillan and Mayer[3] and by Kirkwood and Buff.[4] The analysis is based in both cases on the grand canonical ensemble and distribution functions. The natural composition variable is the molar concentration, since the system is at constant volume. The McMillan–Mayer theory is especially natural for osmotic systems.

The above-mentioned theories are formally exact and necessarily equivalent through suitable thermodynamic manipulations. In the present paper we introduce an alternative, rigorous solution theory designed to yield directly thermodynamic functions expressed in a particularly practical form. For example, for a binary solution, the chemical potentials and partial molal volumes, entropies and heat contents can be developed as power series in the molality or mole fraction of the solute, with coefficients which depend on properties of the solvent (and small sets of solute molecules) at the same pressure and temperature as the solution. The pressure (instead of the volume) is held fixed at the outset and hence molality and mole fraction are the natural composition variables. An interesting feature of these series expansions is their formal identity[5] with the series of Mayer's imperfect gas theory.

Thus the present theory appears to provide the most direct possible molecular interpretation, through statistical mechanics, of solution thermodynamic data expressed as power series in the molality or mole fraction of the solute (or solutes). Of course the relations presented here, though exact, are formal, but no more so than the formulation of the McMillan–Mayer and Kirkwood–Buff solution theories in terms of (generally unknown) distribution functions. (Incidentally, distribution functions do not appear here in the first instance.) These equations do, however, provide a rigorous starting point for approximate theories or models.

This first paper is restricted to a discussion of certain topics for a binary solution. The subject will be developed further along rather obvious lines[1] in a second paper.

II. Molality as Composition Variable

In order to obtain the desired independent variables, we use an ensemble[6,7] apparently first introduced by Stockmayer (in a study of the relation between light scattering and composition fluctuations). We label the solvent as component 1 and the solute as component 2. Then

$$\Gamma(N_1,p,T,\mu_2) = e^{-N_1\mu_1/kT} = \sum_{N_2 \geq 0} e^{N_2\mu_2/kT}\, \Delta_{N_2}(N_1,p,T) \qquad (1)$$

where

$$\Delta_{N_2} = \sum_V e^{-pV/kT}\, Q(N_1,N_2,V,T) \qquad (2)$$

The μ's are chemical potentials, Q is the canonical ensemble partition function, and Δ_{N_2} is the isothermal-isobaric partition function.[8] The right-hand side of eq. 1 is seen to be a power series in the absolute activity of the solute, $\lambda_2 = e^{\mu_2/kT}$, with coefficients which depend on the solvent (N_1,p,T) containing small numbers (N_2) of solute molecules.

Chemical Potentials.—For convenience, we replace the absolute activity λ_2 by a more practical activity a_2, proportional to λ_2, but defined in such a way that (as will be seen below) $a_2 \rightarrow m_2$ as $m_2 \rightarrow 0$, where $m_2 = \bar{N}_2/N_1$. We shall refer to m_2 as the "molality" of the solute, though this differs from the conventional molality, $1000\ m_2/M_1$, by a constant, where M_1 is the molecular weight of the solvent.[9]

The substitution of a_2 for λ_2 in eq. 1 gives, after dividing by the leading term, Δ_0

$$\Gamma/\Delta_0 = 1 + \sum_{N \geq 1} X_N a_2^N \qquad (3)$$

where

$$X_N = \Delta_N \Delta_0^{N-1} N_1^N / \Delta_1^N \qquad (4)$$

$$a_2 = \Delta_1\lambda_2 / N_1\Delta_0 \qquad (5)$$

We note that $X_1 = N_1$. The logarithm of the quotient

$$\Delta_N\Delta_0^{N-1}/\Delta_1^N = e^{-\Delta F_N/kT} \qquad (6)$$

in eq. 4 has the physical significance of a Gibbs free energy change, as indicated, since $F = -kT \ln \Delta$ in general.[8] ΔF_N in eq. 6 is the free energy

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[1] A preliminary note has been published elsewhere: T. L. Hill, *J. Chem. Phys.*, **25**, 955 (1957).

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[3] W. G. McMillan and J. E. Mayer, *J. Chem. Phys.*, **13**, 276 (1945).

[4] J. G. Kirkwood and F. P. Buff, *ibid.*, **19**, 774 (1951). See also F. P. Buff and R. Brout, *ibid.*, **23**, 458 (1955).

[5] T. L. Hill, *ibid.*, in press.

[6] W. H. Stockmayer, *ibid.*, **18**, 58 (1950).

[7] T. L. Hill, "Statistical Mechanics," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 73.

[8] Reference 7, p. 66.

[9] If we were to use the conventional molality, we would redefine a_2 and X_N as

$$a_2 = 1000\ \Delta_1\lambda_2/N_1\Delta_0M_1$$

$$X_N = \frac{\Delta_N\Delta_0^{N-1}}{\Delta_1^N}\left(\frac{N_1M_1}{1000}\right)^N$$

change (non-pV work done by the surroundings) for the process

$$N \text{ systems with } N_1,N_2 = 1,p,T \rightarrow \begin{cases} 1 \text{ system with } N_1,N_2 = N,p,T \\ \quad + \\ N-1 \text{ (solvent) systems with } N_1,N_2 = 0,p,T \end{cases}$$

As has been shown elsewhere,[5] eq. 3 can be manipulated in exactly the same way as can the grand partition function for a one-component imperfect gas, considered a power series in the activity of the gas. We first note that

$$N_1\mu_1(p,T,0) = -kT \ln \Delta_0$$

where $\mu_1(p,T,0)$ is the chemical potential of the pure solvent. Then if we define

$$\mu'_1(p,T,m_2) = \mu_1(p,T,m_2) - \mu_1(p,T,0)$$

we have[5]

$$-\frac{\mu'_1(p,T,a_2)}{kT} = \frac{1}{N_1} \ln \frac{\Gamma}{\Delta_0} = \sum_{j \geqslant 1} \theta_j(p,T)a_2^j \tag{7}$$

where

$$N\theta_1 = X_1 = N_1$$
$$N_1\theta_2 = X_2 - \frac{1}{2}X_1^2 \tag{8}$$
$$N_1\theta_3 = X_3 - X_1X_2 + \frac{1}{3}X_1^3$$

etc. Or

$$\theta_1 = 1$$
$$\theta_2 = N_1\left(e^{-\Delta F_2/kT} - \frac{1}{2}\right) \tag{9}$$
$$\theta_3 = N_1^2\left(e^{-\Delta F_3/kT} - e^{-\Delta F_2/kT} + \frac{1}{3}\right)$$

etc. From eq. 7 and 9 we see that $\theta_j = O(1)$, $e^{-\Delta F_N/kT} = O(1)$, while the quantity in parentheses in the expression for θ_j (*i.e.*, θ_j/N_1^{j-1}) must be of order $1/N_1^{j-1}$. This situation is of course completely analogous with the imperfect gas case. For example (using convential notation), in the equation

$$b_2 = V\left(\frac{Z_2}{2V^2} - \frac{1}{2}\right)$$

$Z_2/2V^2 = O(1)$ but ( ) $= O(1/\bar{N})$. The θ_j are intensive properties of the solvent (containing small sets of solute molecules) and are functions of p and T only.

From the Gibbs-Duhem equation

$$a_2\left(\frac{\partial(-\mu'_1/kT)}{\partial a_2}\right)_{p,T} = m_2 \tag{10}$$

we have

$$m_2(p,T,a_2) = \sum_{j > 1} j\theta_j(p,T)a_2^j \tag{11}$$

The inverse of eq. 11, that is, a_2 as a power series in m_2, is easily obtained. The logarithmic form is more convenient, however

$$\ln \gamma_2(p,T,m_2) = -\sum_{k \geqslant 1} \delta_k(p,T)m_2^k \tag{12}$$

where γ_2 (the solute activity coefficient) $= a_2/m_2$ and

$$\delta_1 = 2\theta_2$$
$$\delta_2 = 3\theta_3 - 6\theta_2^2 \tag{13}$$

etc. General expressions for the θ_j and δ_k in terms of the X_N and θ_j, respectively, are available elsewhere.[5] Finally, if we replace a_2 by m_2 as independent variable in eq. 7, by use of eq. 12, we find

$$-\frac{\mu'_1(p,T,m_2)}{kT} = m_2 - \sum_{k \geqslant 1} \frac{k}{k+1}\delta_k(p,T)m_2^{k+1} \tag{14}$$

$$= m_2 + \sum_{n \geqslant 2} C_n(p,T)m_2^n \tag{15}$$

where

$$C_n = -\frac{n-1}{n}\delta_{n-1} \tag{16}$$

Eq. 15 is the formal equivalent of the virial expansion of an imperfect gas.[5] Thus eq. 12 and 15 give essentially the desired expansions of the two chemical potentials in powers of the molality.

It should, perhaps, be pointed out that the relations indicated above between the θ_j, δ_k and C_n are basically of thermodynamic origin and that these relations should be satisfied when experimental data are expressed as power series in the molality. Of course this remark does not apply to eq. 9 which is extra-thermodynamic (molecular) in origin.

Dilute Solution.—In a dilute solution $\gamma_2 \rightarrow 1$ and $a_2 \rightarrow m_2$, according to eq. 12. Hence, from eq. 5

$$\mu_2 = kT \ln (N_1\Delta_0/\Delta_1) + kT \ln m_2 \quad (m_2 \rightarrow 0) \tag{17}$$

This is essentially Henry's law. In conventional notation

$$\mu_2 = \mu_2^0(T) + kT \ln f_2 \tag{18}$$
$$= \mu_2^0(T) + kT \ln k_2(p,T)x_2 \quad (x_2 \rightarrow 0) \tag{19}$$

where f_2 = fugacity of solute, x_2 = mole fraction of solute, k_2 = Henry's law constant and μ_2^0 = chemical potential of solute gas at unit fugacity. Since $x_2 \rightarrow m_2$ as $m_2 \rightarrow 0$, comparison of eq. 17 and 19 yields, for the Henry's law constant

$$k_2 = N_1\Delta_0 e^{-\mu_2^0/kT}/\Delta_1 \tag{20}$$

If we write

$$k_2/N_1 = \Delta_0 e^{-\mu_2^0/kT}/\Delta_1 = e^{-\Delta F/kT} \tag{21}$$

then ΔF is the Gibbs free energy change for the process

$$\text{system with } N_1,N_2 = 1,p,T \rightarrow \begin{cases} \text{system (solvent) with } N_1,N_2 = 0,p,T \\ \quad + \\ 1 \text{ molecule of solute in gas at } f_2 = 1 \end{cases}$$

Of course, when the solution is not dilute, $f_2 = k_2m_2\gamma_2$ in eq. 18, and m_2 is replaced by $m_2\gamma_2$ in eq. 17.

For the solvent, we have in general

$$-\mu'_1/kT = -\ln (f_1/f_1^0) \tag{22}$$

where f_1^0 is the fugacity of the pure solvent. For a dilute solution (Raoult's law)

$$-\mu'_1/kT = -\ln(1 - x_2) \rightarrow x_2 \rightarrow m_2 \tag{23}$$

in agreement with eq. 14 and 15.

Free Energy.—From eq. 12 and 15, we obtain for the Gibbs free energy

$$\frac{F}{N_1kT} = \frac{\mu_1}{kT} + m_2\frac{\mu_2}{kT} \tag{24}$$

$$= \frac{\mu_1(p,T,0)}{kT} + m_2 \ln f + m_2 \ln m_2 - m_2 + \sum_{n > 2} \frac{1}{n-1} C_n m_2^n \tag{25}$$

where

$$f(p,T) = N_1\Delta_0/\Delta_1 = k_2e^{\mu_2^0/kT} \qquad (26)$$

Volume.—From the thermodynamic relation

$$\left(\frac{\partial\mu'_1}{\partial p}\right)_{T,m_2} = \bar{v}_1 - v_1$$

and eq. 15, we find

$$\bar{v}_1(p,T,m_2) = v_1(p,T) - kT\sum_{n\geqslant 2}\left(\frac{\partial C_n}{\partial p}\right)_T m_2^n \qquad (27)$$

Similarly, from eq. 12, we have

$$\bar{v}_2(p,T,m_2) = \bar{v}_2^0(p,T) - kT\sum_{k\geqslant 1}\left(\frac{\partial \delta_k}{\partial p}\right)_T m_2^k \qquad (28)$$

where

$$\frac{\bar{v}_2^0}{kT} = \left(\frac{\partial \ln f}{\partial p}\right)_T \qquad (29)$$

For the volume we deduce

$$\frac{V}{N_1} = \frac{1}{\rho_1} = \bar{v}_1 + m_2\bar{v}_2 = v_1 + m_2\bar{v}_2^0 + kT\sum_{n\geqslant 2}\frac{1}{n-1}\left(\frac{\partial C_n}{\partial p}\right)_T m_2^n \qquad (30)$$

The pressure derivatives of C_n (or δ_k) and f above may be obtained most easily in applications simply by differentiation of the particular C_n and f found for the given problem. However, we give here general expressions which may be of some interest. We make use of the relation[8]

$$\bar{V}_N = -kT\left(\frac{\partial \ln \Delta_N}{\partial p}\right)_{N_1,T} = \frac{1}{\Delta_N}\sum_V Ve^{-pV/kT}\,Q(N_1,N,V,T) \qquad (31)$$

where $\bar{V}_N$ is the mean volume of the system with $N_1,N_2 = N,p,T$. Then, on differentiating either side of eq. 6

$$\left(\frac{\partial \ln e^{-\Delta F_N/kT}}{\partial p}\right)_{N_1,T} = -\frac{\Delta V_N}{kT} \qquad (32)$$

where ΔV_N is the volume change for the process following eq. 6. Thus, from eq. 9, 13 and 16, we have

$$kT\left(\frac{\partial C_2}{\partial p}\right)_T = N_1e^{-\Delta F_2/kT}\,\Delta V_2 \qquad (33)$$

$$kT\left(\frac{\partial C_3}{\partial p}\right)_T = 2N_1^2[e^{-\Delta F_3/kT}\Delta V_3 + e^{-\Delta F_2/kT}\Delta V_2(1 - 4e^{-\Delta F_2/kT})]$$

etc.

From eq. 29 and 31

$$\bar{v}_2^0 = \bar{V}_1 - \bar{V}_0 \qquad (34)$$

as might have been anticipated. Also

$$\bar{V}_N - \bar{V}_{N-1} = (\bar{V}_1 - \bar{V}_0) + \Delta V_N - \Delta V_{N-1} \qquad (35)$$

In the above equations, since $kT\ \partial C_n/\partial p$ is of order v (volume per molecule), we see that ΔV_N is of order v/N_1, while [ ] in eq. 33 must be of order v/N_1^2. The difference $\Delta V_N - \Delta V_{N-1}$ in eq. 35 is of order v/N_1.

Heat Content and Entropy.—From

$$\left(\frac{\partial \mu_i/kT}{\partial T}\right)_{p,m_2} = -\frac{\bar{\mathrm{H}}_1}{kT^2} \qquad (i = 1,2)$$

we find

$$\bar{\mathrm{H}}_1 = \mathrm{H}_1 + kT^2\sum_{n\geqslant 2}\left(\frac{\partial C_n}{\partial T}\right)_p m_2^n \qquad (36)$$

Differentiation of eq. 17 leads to

$$\left(\frac{\partial \ln f}{\partial T}\right)_p = -\frac{\bar{\mathrm{H}}_2^0}{kT^2} \qquad (37)$$

Hence, from eq. 12

$$\bar{\mathrm{H}}_2 = \bar{\mathrm{H}}_2^0 + kT^2\sum_{k\geqslant 1}\left(\frac{\partial \delta_k}{\partial T}\right)_p m_2^k \qquad (38)$$

Then

$$\frac{H}{N_1kT} = \frac{\bar{\mathrm{H}}_1 + m_2\bar{\mathrm{H}}_2}{kT} = \frac{\mathrm{H}_1 + m_2\bar{\mathrm{H}}_2^0}{kT} - \sum_{n\geqslant 2}\frac{1}{n-1}\,T\left(\frac{\partial C_n}{\partial T}\right)_p m_2^n \qquad (39)$$

The entropy expressions follow from the free energy and heat content

$$\frac{\bar{s}_1}{k} = \frac{s_1}{k} + m_2 + \sum_{n\geqslant 2}\left(C_n + T\frac{\partial C_n}{\partial T}\right)m_2^n \qquad (40)$$

$$\frac{\bar{s}_2}{k} = \frac{\bar{s}_2(m_2 \to 0)}{k} + \sum_{k\geqslant 1}\left(\delta_k + T\frac{\partial \delta_k}{\partial T}\right)m_2^k \qquad (41)$$

$$\frac{S}{N_1k} = \frac{s_1 + m_2\bar{s}_2(m_2 \to 0)}{k} + m_2 - \sum_{n\geqslant 2}\frac{1}{n-1}\left(C_n + T\frac{\partial C_n}{\partial T}\right)m_2^n \qquad (42)$$

where

$$T\bar{s}_2(m_2 \to 0) = \bar{\mathrm{H}}_2^0 - kT\ln fm_2 \qquad (43)$$

Using (compare eq. 31)

$$\bar{H}_N = \bar{E}_N + p\bar{V}_N = kT^2\left(\frac{\partial \ln \Delta_N}{\partial T}\right)_{N_1,p} \qquad (44)$$

we obtain easily

$$kT^2\left(\frac{\partial C_2}{\partial T}\right)_p = -N_1e^{-\Delta F_2/kT}\,\Delta H_2 \qquad (45)$$

$$kT^2\left(\frac{\partial C_3}{\partial T}\right)_p = -2N_1^2[e^{-\Delta F_3/kT}\,\Delta H_3 + e^{-\Delta F_2/kT}\,\Delta H_2(1 - 4e^{-\Delta F_2/kT})]$$

etc., and

$$\bar{\mathrm{H}}_2^0 = \bar{H}_1 - \bar{H}_0 \qquad (46)$$

The relation

$$\left(\frac{\partial \bar{\mathrm{G}}_1}{\partial m_2}\right)_{p,T} = -m_2\left(\frac{\partial \bar{\mathrm{G}}_2}{\partial m_2}\right)_{p,T} \qquad (47)$$

which holds for any pair of partial molal quantities, can be used to check the self-consistency of the above series expansions of the partial molal free energies, volumes, heat contents and entropies.

Osmotic Pressure.—Suppose we have osmotic equilibrium between the solution at p,T,m_2 and the pure solvent at $p - \pi$, T

$$\mu_1(p,T,m_2) = \mu_1(p - \pi,T,0) \qquad (48)$$

But

$$\mu_1(p,T,0) - \mu_1(p - \pi,T,0) = \int_{p-\pi}^{p} v_1(p,T)\,\mathrm{d}p \qquad (49)$$

Therefore, from eq. 15, 48 and 49

$$\frac{1}{kT}\int_{p-\pi}^{p} v_1(p,T)\,\mathrm{d}p = m_2 + \sum_{n\geqslant 2} C_n(p,T)m_2^n \qquad (50)$$

This equation determines π as a function of p, T and m_2. If the pure solvent is incompressible, the left-hand side becomes $\pi v_1/kT$.

McMillan–Mayer Theory.—McMillan and Mayer[3] point out that their equations can be manipulated in such a way as to obtain a relation between the activities of solute and solvent for a solution at the same pressure and temperature as the pure solvent (in their analysis, V is the same for solution and solvent but $\bar{N}_1$ is different). In the present notation and that of reference 7, p. 277, McMillan and Mayer's eq. 92 can be put in the form of eq. 7, with, for example

$$\theta_2 = \frac{1}{2} + \frac{\bar{N}_1{}^0}{2V^2}(Z^*_{20} + Z^*_{02} - 2Z^*_{11}) \qquad (51)$$

where $\bar{N}_1{}^0$ is the mean number of solvent molecules in the pure solvent, and the Z^*'s refer to solvent–solvent, solute–solute and solvent–solute pairs in the pure solvent, respectively. Equation 51 has been checked against the three examples in Section IV. In evaluating the Z^*'s, care must be taken with terms of order $V^2/\bar{N}_1{}^0$.

Mole Fraction and Molarity.—Any of the above series in m_2 can be converted easily into series in x_2 by the substitution

$$m_2 = \frac{x_2}{1 - x_2} = x_2 + x_2{}^2 + x_2{}^3 + \ldots \qquad (52)$$

However, more direct and fundamental equations for the mole fraction are derived in the next section.

To obtain series in $\rho_2 = \bar{N}_2/V$ (which is essentially the molarity of solute), one can rewrite eq. 30 as

$$\rho_2 = m_2\rho_1 = \frac{m_2}{v_1}\left[1 + m_2\frac{\overline{v_2}^0}{v_1} + \frac{kT}{v_1}\sum_{n \geqslant 2}\frac{1}{n-1}\left(\frac{\partial C_n}{\partial p}\right)_T m_2{}^n\right]^{-1} \qquad (53)$$

This gives the series $\rho_2(m_2)$. Inversion to provide $m_2(\rho_2)$ and finally substitution in the m_2-series for the various thermodynamic functions completes the program, which we do not carry out here.

III. Mole Fraction as Composition Variable

We give a more condensed discussion in this section since the argument is very similar to that in Section II.

We choose the partition function[10] in such a way that the independent variables (for a binary solution) p, T and x_2 replace p, T and m_2. Specifically, the partition function is

$$Y(B,p,T,\mu_2 - \mu_1) = e^{-B\mu_1/kT} = \sum_{N_2 = 0}^{B} e^{N_2(\mu_2 - \mu_1)/kT}\,\Delta'_{N_2}(B,p,T) \qquad (54)$$

where (compare Eq. (2))

$$\Delta'_{N_2} = \sum_V e^{-pV/kT}\,Q(N_1 = B - N_2, N_2, V, T) \qquad (55)$$

That is, in the sum in eq. 54, the total number of molecules in the solution, $B = N_1 + N_2$, is held fixed,[11] instead of N_1 as in eq. 1. Δ'_{N_2} is an isothermal-isobaric partition function[8]; the prime is inserted as a reminder that $N_1 + N_2$ is constant.

An advantage of Y over Γ is that Y is a *polynomial* (in λ_2/λ_1). Hence the zeros of the partition function[12] can be used, for example, in a discussion of phase transitions. Equation 54 can be rewritten as

$$Y/\Delta'_0 = 1 + \sum_{N = 1}^{B} X'_N w^N \qquad (56)$$

where

$$X'_N = \Delta'_N\,\Delta'_0{}^{N-1}\,B^N/\Delta'_1{}^N \qquad (57)$$

$$w = \Delta'_1\lambda_2/B\Delta'_0\lambda_1 \qquad (58)$$

In the equation

$$\Delta'_N\,\Delta'_0{}^{N-1}/\Delta'_1{}^N = e^{-\Delta F'_N/kT} \qquad (59)$$

$\Delta F'_N$ is the Gibbs free energy change for the process

$$N \text{ systems with } N_1 = B - 1,\ N_2 = 1,p,T \rightarrow \begin{cases} 1 \text{ system with } N_1 = B - N, N_2 = N,p,T \\ \qquad + \\ N - 1\text{(solvent) systems with } N_1 = B, N_2 = 0,p,T \end{cases}$$

Then

$$B\mu_1(p,T,0) = -kT\ln\Delta'_0 \qquad (60)$$

$$\mu'_1(p,T,x_2) = \mu_1(p,T,x_2) - \mu_1(p,T,0) \qquad (61)$$

$$-\frac{\mu'_1(p,T,w)}{kT} = \frac{1}{B}\ln\frac{Y}{\Delta'_0} = \sum_{j \geqslant 1}\theta'_j(p,T)w^j \qquad (62)$$

where

$$B\theta'_1 = X'_1 = B,\ \theta'_1 = 1 \qquad (63)$$

$$B\theta'_2 = X'_2 - \frac{1}{2}X'_1{}^2,\ \theta'_2 = B\left(e^{-\Delta F'_2/kT} - \frac{1}{2}\right)$$

etc. Further

$$x_2(p,T,w) = \sum_{j \geqslant 1} j\theta'_j(p,T)w^j \qquad (64)$$

and

$$\ln\frac{w}{x_2} = -\sum_{k \geqslant 1}\delta'_k(p,T)x_2{}^k \qquad (65)$$

where the δ'_k are related to the θ'_j by eq. 13. We see here that $w \rightarrow x_2$ as $x_2 \rightarrow 0$. Finally

$$-\frac{\mu'_1(p,T,x_2)}{kT} = x_2 + \sum_{n \geqslant 2} C'_n(p,T)x_2{}^n \qquad (66)$$

where the δ'_k and C'_n are related by eq. 16.

For a dilute solution, we put $w = x_2$ and $\mu_1 = \mu_1(0)$ in eq. 58 and obtain

$$\frac{\mu_2}{kT} = \frac{\mu_1(0)}{kT} + \ln\frac{B\Delta'_0}{\Delta'_1} + \ln x_2 \qquad (67)$$

Then from eq. 19

$$k_2 = \frac{B\Delta'_0}{\Delta'_1}\,e^{\mu_1(0)/kT}e^{-\mu_2{}^0/kT} \qquad (68)$$

If we define $\Delta F'$ by $k_2/B = e^{-\Delta F'/kT}$, then $\Delta F'$ refers to the process

$$\left.\begin{array}{l} \text{system with } N_1 = B - 1,\ N_2 = 1,p,T \\ \qquad + \\ 1 \text{ molecule of solvent in pure solvent at } p,T \end{array}\right\} \rightarrow \begin{cases} \text{system(solvent) with } N_1 = B,\ N_2 = 0,p,T \\ \qquad + \\ 1 \text{ molecule of solute in gas at } f_2 = 1 \end{cases}$$

If we define the activity coefficient γ'_2 by

$$\frac{\mu_2}{kT} = \frac{\mu_2{}^0}{kT} + \ln k_2x_2\gamma'_2 \qquad (69)$$

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(10) Compare the closely related partition function in reference 7, pp. 293–294.

(11) The partition function Γ is physically appropriate (*e.g.*, in a study of fluctuations) for a solution at constant p and T which is open with respect to component 2. Y is physically appropriate for a solution at constant p and T which can *exchange* one molecule for another with the surroundings. Other partition functions might be devised which would perhaps be useful in electrolyte theory in automatically maintaining neutrality: (a) exchange of ions with the same charge; (b) system open with respect to neutral pairs or groups of ions.

(12) Reference 7, pp. 169–178.

we find from eq. 58 and 67–69

$$\ln \gamma'_2(p,T,x_2) = \ln \frac{w}{x_2} + \frac{\mu'_1}{kT}$$

$$= -(1+\delta'_1)x_2 + \sum_{k \geqslant 2} \left(\frac{k-1}{k}\delta'_{k-1} - \delta'_k\right)x_2^k \quad (70)$$

Of course $x_2\gamma'_2 = m_2\gamma_2$.

For the free energy, we have

$$\frac{F}{BkT} = \frac{\mu_1(0)}{kT} + x_2 \ln f' + x_2 \ln x_2 - x_2 + \sum_{n \geqslant 2} \frac{1}{n-1} C'_n x_2^n \quad (71)$$

$$f'(p,T) = B\Delta'_0/\Delta'_1 = k_2 e^{-\mu_1(0)/kT} e^{\mu_2^0/kT} \quad (72)$$

and, for the volume

$$\bar{v}_1 = v_1 - kT \sum_{n \geqslant 2} \left(\frac{\partial C'_n}{\partial p}\right)_T x_2^n \quad (73)$$

$$\bar{v}_2 = \bar{v}_2^0 - kT\left(\frac{\partial \delta'_1}{\partial p}\right)_T x_2 + kT \sum_{k \geqslant 2} \left[\frac{k-1}{k}\left(\frac{\partial \delta'_{k-1}}{\partial p}\right)_T - \left(\frac{\partial \delta'_k}{\partial p}\right)_T\right] x_2^k \quad (74)$$

$$\bar{v}_2^0 = v_1 + kT\left(\frac{\partial \ln f'}{\partial p}\right)_T = v_1 + \bar{V}_1' - \bar{V}_0' \quad (75)$$

$$\frac{V}{B} = (1-x_2)v_1 + x_2\bar{v}_2^0 + kT \sum_{n \geqslant 2} \frac{1}{n-1}\left(\frac{\partial C'_n}{\partial p}\right)_T x_2^n \quad (76)$$

$$kT\left(\frac{\partial C'_2}{\partial p}\right)_T = Be^{-\Delta F'_2/kT}\,\Delta V'_2 \quad (77)$$

etc.

Similarly, for the heat content and entropy

$$\bar{\mathrm{H}}_1 = \mathrm{H}_1 + kT^2 \sum_{n \geqslant 2} \left(\frac{\partial C'_n}{\partial T}\right)_p x_2^n \quad (78)$$

$$\bar{\mathrm{H}}_2 = \bar{\mathrm{H}}_2^0 + kT^2\left(\frac{\partial \delta'_1}{\partial T}\right)_p x_2 - kT^2 \sum_{k \geqslant 2} \left[\frac{k-1}{k}\left(\frac{\partial \delta'_{k-1}}{\partial T}\right)_p - \left(\frac{\partial \delta'_k}{\partial T}\right)\right] x_2^k \quad (79)$$

$$\bar{\mathrm{H}}_2^0 = \mathrm{H}_1 - kT^2\left(\frac{\partial \ln f'}{\partial T}\right)_p = \mathrm{H}_1 + \bar{H}'_1 - \bar{H}'_0 \quad (80)$$

$$\frac{H}{BkT} = \frac{(1-x_2)\mathrm{H}_1 + x_2\bar{\mathrm{H}}_2^0}{kT} - \sum_{n \geqslant 2} \frac{1}{n-1}\, T\left(\frac{\partial C'_n}{\partial T}\right)_p x_2^n \quad (81)$$

$$\frac{\bar{s}_1}{k} = \frac{s_1}{k} + x_2 + \sum_{n \geqslant 2} \left(C'_n + T\frac{\partial C'_n}{\partial T}\right) x_2^n \quad (82)$$

$$\frac{\bar{s}_2}{k} = \frac{\bar{s}_2(x_2 \rightarrow 0)}{k} + \left(1 + \delta'_1 + T\frac{\partial \delta'_1}{\partial T}\right) x_2 - \sum_{k \geqslant 2} \left[\frac{k-1}{k}\left(\delta'_{k-1} + T\frac{\partial \delta'_{k-1}}{\partial T}\right) - \left(\delta'_k + T\frac{\partial \delta'_k}{\partial T}\right)\right] x_2^k \quad (83)$$

$$T\bar{s}_2(x_2 \rightarrow 0) = \bar{\mathrm{H}}_2^0 - \mu_1(0) - kT \ln f' x_2 \quad (84)$$

$$\frac{S}{Bk} = \frac{(1-x_2)s_1 + x_2\bar{s}_2(x_2 \rightarrow 0)}{k} + x_2 - \sum_{n \geqslant 2} \frac{1}{n-1}\left(C'_n + T\frac{\partial C'_n}{\partial T}\right) x_2^n \quad (85)$$

The osmotic pressure $\pi(p,T,x_2)$ is determined by

$$\frac{1}{kT}\int_{p-\pi}^{p} v_1(p,T)\,\mathrm{d}p = x_2 + \sum_{n \geqslant 2} C'_n(p,T)x_2^n \quad (86)$$

IV. Introductory Examples

We confine ourselves here, for brevity, to illustrations of Section II.

Binary Perfect Gas Mixture.—We obtain easily[13]

$$e^{-\Delta F_N/kT} = \frac{1}{N!}\left[\frac{(N_1+N)(N_1+N-1)\ldots(N_1+1)}{(N_1+1)^N}\right] \quad (87)$$

In order to calculate the θ_j up to, say, θ_l, all of the $e^{-\Delta F_N/kT}$ up to $e^{-\Delta F_l/kT}$ have to be evaluated (by expanding [ ] in eq. 87) to terms of order $1/N_1^{l-1}$. For example

$$e^{-\Delta F_2/kT} = \frac{1}{2}(1 + N_1^{-1} - N_1^{-2} + N_1^{-3} + \ldots)$$

$$e^{-\Delta F_3/kT} = \frac{1}{6}(1 + 3N_1^{-1} - N_1^{-2} - N_1^{-3} + \ldots) \quad (88)$$

$$e^{-\Delta F_4/kT} = \frac{1}{24}(1 + 6N_1^{-1} + 5N_1^{-2} - 10N_1^{-3} + \ldots)$$

We then find from eq. 9, 13 and 16

$$\theta_j = 1/j,\ \delta_k = (-1)^{k-1}/k,\ C_n = (-1)^{n-1}/n \quad (89)$$

and

$$-\frac{\mu'_1}{kT} = a_2 + \frac{a_2}{2} + \frac{a_3}{3} + \ldots = -\ln(1-a_2) \quad (90)$$

$$= m_2 - \frac{m_2^2}{2} + \frac{m_2^3}{3} - \ldots = \ln(1+m_2) \quad (91)$$

$$\ln \gamma_2 = -m_2 + \frac{m_2^2}{2} - \frac{m_2^3}{3} + \ldots = -\ln(1+m_2) \quad (92)$$

$$\frac{p}{p-\pi} = \frac{N_1 + \bar{N}_2}{N_1} \quad (93)$$

as expected. The temperature and pressure derivatives of θ_j, δ_k and C_n are equal to zero.

Gas Mixture with Non-interacting Solvent.—Solvent molecules are assumed not to interact with each other or with solute molecules. On the other hand, solute molecules are assumed to interact with each other; these interactions will be characterized by imperfect gas virial coefficients $B_2(T)$, $B_3(T)$, etc.

In notation introduced elsewhere[14]

$$Q(N_1, N_2 = N) = \frac{V^{N_1}Z_N}{N_1!\Lambda_1^{3N_1}N!\Lambda_2^{3N}} \quad (94)$$

where the configuration integral for solute molecules, Z_N, can be written in terms of the virial coefficients

$$\begin{aligned} Z_0 &= 1,\ Z_1 = V \\ Z_2 &= -2VB_2 + V^2 \\ Z_3 &= -3VB_3 + 12VB_2^2 - 6V^2B_2 + V^3 \end{aligned} \quad (95)$$

etc. We substitute eq. 94 in eq. 2 and integrate[13] (the integrals are gamma functions) to obtain the Δ_N. Then we find, for example

$$e^{-\Delta F_2/kT} = \frac{1}{(N_1+1)}\left(\frac{N_1+2}{2} - \frac{B_2 p}{kT}\right) \quad (96)$$

$$e^{-\Delta F_3/kT} = \frac{1}{6(N_1+1)^2}\left[(N_1+3)(N_1+2) - \frac{6B_2 p}{kT}(N_1+2) + (12B_2^2 - 3B_3)\left(\frac{p}{kT}\right)^2\right]$$

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[13] See eq. A3.3 of reference 7 for a derivation of Δ_N.

[14] Reference 7, p. 399.

and

$$C_2 = -\theta_2 = -\frac{1}{2} + \frac{B_2 p}{kT}$$

$$\theta_3 = \frac{1}{3} - \frac{B_2 p}{kT} + \left(2B_2^2 - \frac{B_3}{2}\right)\left(\frac{p}{kT}\right)^2 \qquad (97)$$

$$C_3 = \frac{1}{3} - \frac{2B_2 p}{kT} + B_3\left(\frac{p}{kT}\right)^2$$

Pressure and temperature derivatives of these coefficients follow immediately. It is easy to show that the expression

$$\ln \frac{p}{p - \pi} = -\frac{\mu'_1}{kT} \qquad (98)$$

for the osmotic pressure (using eq. 15 and 97) is equivalent to

$$\frac{p}{kT} = \rho_1 + \frac{\pi}{kT}$$

$$(99)$$

$$\frac{\pi}{kT} = \rho_2 + B_2\rho_2^2 + B_3\rho_3^2 + \dots$$

as would be anticipated from the model.

Inert, Incompressible Solvent.—The solvent in this model is an inert incompressible fluid of volume $V_0 = N_1 v_1$ whose only role is to provide a suspension medium for solute molecules. The solute molecules interact with each other, as in the previous model. The solution, as well as the pure solvent, is assumed incompressible with volume

$$V = V_0 + N_2 v_2$$

For the pure solvent we write

$$Q(N_1, 0, V) = Q_0 \delta(V - V_0)$$

where $\delta(V - V_0)$ is the Dirac δ-function (introduced because of incompressibility). In general

$$Q(N_1, N, V) = \frac{Q_0 \delta[V - (V_0 + Nv_2)] Z_N(V)}{N!\,\Lambda_2^{3N}} \qquad (100)$$

where $Z_N(V)$ is given by eq. 95. Then, from eq. 2

$$\Delta_N = \frac{e^{-p(V_0 + Nv_2)/kT}\, Q_0 Z_N(V_0 + Nv_2)}{N!\,\Lambda_2^{3N}} \qquad (101)$$

and

$$e^{-\Delta F_N/kT} = \frac{Z_N(V_0 + Nv_2)}{N!\,(V_0 + v_2)^N} \qquad (102)$$

For example, to terms in N_1^{-2}

$$e^{-\Delta F_2/kT} = \frac{1}{2}\left[1 + 2\frac{v_2}{V_0} - 2\frac{B_2}{V_0} - \left(\frac{v_2}{V_0}\right)^2 + \dots\right]$$

$$(103)$$

$$e^{-\Delta F_3/kT} = \frac{1}{6}\left[1 + 6\frac{v_2}{V_0} - 6\frac{B_2}{V_0} + 6\left(\frac{v_2}{V_0}\right)^2 + 12\left(\frac{B_2}{V_0}\right)^2 - 18\frac{v_2 B_2}{V_0^2} - 3\frac{B_3}{V_0^2} + \dots\right]$$

and

$$\theta_2 = \frac{v_2}{v_1} - \frac{B_2}{v_1} = -C_2$$

$$\theta_3 = \frac{3}{2}\left(\frac{v_2}{v_1}\right)^2 + 2\left(\frac{B_2}{v_1}\right)^2 - 3\frac{v_2 B_2}{v_1^2} - \frac{1}{2}\frac{B_3}{v_1^2} \qquad (104)$$

$$C_3 = \left(\frac{v_2}{v_1}\right)^2 - 2\left(\frac{v_2 B_2}{v_1^2}\right) + \frac{B_3}{v_1^2}$$

The pressure derivatives of these coefficients vanish, of course. The osmotic pressure is given by (with eq. 15)

$$\frac{\pi v_1}{kT} = -\frac{\mu'_1}{kT} \qquad (105)$$

which can be shown without difficulty to be equivalent to

$$\frac{\pi}{kT} = \rho_2 + B_2\rho_2^2 + B_3\rho_2^3 + \dots \qquad (106)$$

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[CONTRIBUTION FROM MONSANTO CHEMICAL COMPANY, INORGANIC CHEMICALS DIVISION]

Structure and Properties of the Condensed Phosphates. XII. Reorganization Theory and Some Applications

BY J. R. PARKS AND J. R. VAN WAZER

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Reorganization is first treated in terms of equilibria between the various phosphate building units (branches, middles and ends) as well as between them and orthophosphate and unreacted M_2O. Variation of the relative proportions of these units with the M_2O/P_2O_5 mole ratio is discussed in terms of the amount of ionization of the M's in the M_2O–P_2O_5 system. Molecular structures are developed on the basis of statistics. In addition to the random-reorganization distribution function first obtained by Flory, a new distribution function is derived on the basis of Information Theory. The Flory distribution corresponds to flexible chains (un-ionized molecules); whereas the new distribution corresponds to rigid rods (polyelectrolytes). Both of these distribution functions apply only to those values of the M_2O/P_2O_5 ratio at which there is a vanishingly small amount of branching units. The principles presented herein are generally applicable to all systems composed of reorganizing molecular structures, ranging from un-ionized, non-polar molecules to completely ionized polyelectrolytes.

In a previous paper[1] the basic principles of the structure of sodium phosphate glasses were enunciated, and the key difference between these glasses and the condensed phosphoric acids was denoted in a qualitative manner. In the following discussion, we shall extend these principles quantitatively to all amorphous phosphates which are in equilibrium with respect to reorganization of their structures. It should be noted that the distribution theory derived here is of general application to all reorganizing systems—not only phosphates but other systems as well.

Reorganization Theory

Let M stand for an equivalent of any cation or organic radical in a phosphate, which can then be written as $xM_2O \cdot yP_2O_5$. The reorganizing, single-phase (liquid) phosphates can be described in terms of an M_2O/P_2O_5 mole ratio, $R = x/y$. Although in high-temperature melts the oxygens of a given

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[1] J. R. Van Wazer, THIS JOURNAL, 72, 644 (1950).