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THE general problem of the thermodynamics of linearly associated systems has received much attention in recent years in connection with the properties of solutions of stable linear polymers.[1-4] The problem of equilibrium size distribution for reversible polymerization-depolymerization has also been treated.[5-7] It is the purpose of this note to indicate the possible applicability of these lattice model methods for the treatment of general thermodynamic problems of reversible association. As example of the types of systems under discussion we may include associated liquids, such as the alcohols, and solutions of associated materials in non-associated liquids, such as the system ethyl alcohol-toluene.

The partition function for a system of the latter kind can be written as

$$Z = f_0{}^{n_0} f_1{}^N \frac{1}{\sigma^{\Sigma n_x}} \left\{ \frac{(n_0+N)!}{n_0!\Pi n_x!} \left(\frac{\gamma}{n_0+N} \right)^{\Sigma(x-1)n_x} \right\}$$

$$\times b^{n_0+\Sigma n_x} a^{\Sigma(x-1)n_x}$$

$$\times \exp\left[\frac{\Sigma(x-1)n_x P}{kT} \right] \exp\left[-\mu \frac{n_0 N}{n_0+N} \right], \quad (1)$$

where n_0 is the number of unassociated solvent molecules, n_x is the number of x-mers of the associated solute, N is the total number of monomeric units of the associated solute including those incorporated as segments of the x-mers, σ is the symmetry number of the solute molecules, γ is the coordination number of the space lattice, P is the heat of association,* f_0 and f_1

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[1] M. L. Huggins, J. Phys. Chem. **46**, 151 (1942); Ann. N. Y. Acad. Sci. **43**, 1 (1942); J. Am. Chem. Soc. **64**, 1712 (1942).
[2] P. J. Flory, J. Chem. Phys. **10**, 51 (1942); **12**, 425 (1944).
[3] A. R. Miller, Proc. Camb. Phil. Soc. **39**, 54 (1943).
[4] R. L. Scott and M. Magat, J. Chem. Phys. **13**, 172 (1945).
[5] A. V. Tobolsky, J. Chem. Phys. **12**, 402 (1944).
[6] P. J. Flory, J. Chem. Phys. **12**, 425 (1944).
[7] P. J. Blatz and A. V. Tobolsky, J. Phys. Chem. **49**, 77 (1945).

* It appears to us that Flory's criticism (reference 6) of the use of P in reference 5 arises from a misunderstanding of the partition function method.

are the vibrational partition functions for each solvent molecule and for each segment (monomeric unit) of solute respectively, μ is a constant characterizing the Van Laar heat of mixing of solvent and solute, and a and b are constants to be discussed later. The factor in Eq. (1) enclosed in curly brackets is the approximate number of distinguishable configurations available to the system for the size distribution specified by the numbers n_0, n_1, $n_2 \cdots n_x$, etc., on the basis of the lattice model.[2,3] A very straightforward intuitive method for deriving this factor is given below, although the counting formula must be regarded as approximate.

If every associated solute molecule were broken down into its monomeric segments and if all segments and solvent molecules were distinguishable, the number of configurations on the lattice would be $(n_0+N)!$ In the case of the mixing of associated and non-associated molecules, every solvent molecule and every monomeric solute molecule can go into the lattice in exactly as many ways as previously. Similarly the first segment of every polymeric solute molecule can enter the lattice in exactly as many ways as if it were a monomeric unit. On the other hand the second, third, and higher segments of each polymeric solute molecule has, at most, γ-sites available to it because of being bonded to the immediately preceding segment. Assuming that the number of the γ-sites available to a bonded segment is cut down by the occupancy of previous solvent molecules and segments in the same ratio as is the total number of available sites, each of these bonded segments (second, third, etc.) has exactly γ/n_0+N times as many ways of entering the lattice as if it were a free monomeric unit. The total number of $(n_0+N)!$ configurations available to n_0+N distinguishable monomeric segments is therefore cut down by the factor $(\gamma/n_0+N)^{\Sigma(x-1)n_x}$. The denominator $n_0!\Pi n_x!$ appearing within the curly brackets arises from the necessity of excluding

configurations which are identical save for the interchange of indistinguishable molecules.

The first exponential factor in Eq. (1) involving the heat of association P obviously arises from the assumption of a constant heat of association per bond between segments of the associating solute. The total number of bonds is clearly $\Sigma(x-1)n_x$. The second exponential factor comes from the Van Laar heat of mixing expression.

The factors involving the constants a and b represent a very simplified attempt to account for and characterize entropy changes due to bond formation and due to mixing of holes and molecules, respectively. It is assumed that the formation of each intermolecular bond between the solute segments gives rise to an entropy $k \ln a$ and the mixing of each solute and each solvent molecules with the holes of the liquid gives rise to an entropy $k \ln b$ (if b is equal to e, the base of natural logarithms, this assumption is equivalent to the use of communal entropy).

For simplicity Eq. (1) can be re-written as follows:

$$Z = f_0'^{n_0} f_1'^N \frac{(n_0+N)!}{n_0! \Pi n_x!} \left(\frac{\delta}{N+n_0}\right)^{\Sigma(x-1)n_x}$$

$$\times \exp\left[-\mu(n_0 N/(n_0+N))\right], \quad (2)$$

where $f_0' = f_0 b$ and $f_1' = f_1 b/\sigma$ and $\delta = \beta' e^{P/kT}$ where $\beta' = \gamma \sigma a/b$.

Equations (1) and (2) are the partition function for a system of n_0 solvent molecules and a definite distribution in sizes of associated solute molecules specified by a given set of n_x's. The macrostate corresponding to equilibrium which is characterized by an equilibrium distribution in the n_x's can be calculated by minimizing the free energy obtained from the expression (2). The result of this calculation for the equilibrium distribution gives:

$$n_x = N y^{x-1}(1-y)^2 \quad (3)$$

where

$$y/(1-y)^2 = v_p \delta$$

and

$$v_p = N/(n_0+N).$$

Substituting expression (3) in expression (2) will give the partition function of the macrostate

corresponding to equilibrium. The free energy can be obtained as follows:

$$F \cong A = -kT \ln Z. \quad (4)$$

Of particular interest are the partial molar free energies of solute and solvent with respect to the standard states of pure solvent and pure solute, respectively. These differ from the Eqs. (17)–(19) previously given by Flory[6] in that, whereas Flory was considering stable polymer molecules which did not change their size distribution when diluted, we are here concerned with the problem of reversible association which changes with dilution and temperature.

The partial molar free energy of the solvent with respect to the pure solvent as reference state is given by

$$\bar{F}_0 - \bar{F}_{0,N=0} = kT\left[\ln v_0 + v_p y + \mu v_p^2\right], \quad (5)$$

where v_0 is the volume fraction of solvent, and v_p the volume fraction of solute. The symbol y appearing in Eq. (4) is the same as defined in Eq. (3).

The partial molar free energies of the solute species with respect to the pure mixed disoriented solute molecules as the standard state is given by the expression

$$F_1 - F_{1,\,n_0=0} = kT\left[\ln v_p + \ln \frac{(1-y)^2}{(1-y')^2}\right.$$

$$\left. + v_p y - y' + \mu v_0^2\right],$$

$$(6)$$

$$\bar{F}_x - \bar{F}_{x,\,n_0=0} = kT\left[\ln \frac{y^{x-1}(1-y)^2}{y'^{x-1}(1-y')^2} + xv_p y\right.$$

$$\left. - xy' + \ln v_p + \mu x v_0^2\right],$$

where

$$y/(1-y)^2 = v_p \delta; \quad y'/(1-y')^2 = \delta. \quad (7)$$

Other reference states, such as the hypothetical pure monomeric solute, are also of interest. Numerical analysis of vapor pressure data and other thermodynamic data are in progress to evaluate the applicability of these ideas to linearly associated systems of the types discussed.