

Statistical Mechanics of Linear Association Equilibria

Paul J. Flory

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zero the scatter increases but is always less than 0.2 percent. This may be attributed to more accurate temperature control during the determinations at the higher temperatures.

4. COMPARISON WITH PREVIOUS DETERMINATIONS

Paternò and Mazzucchelli1 give an equation based on experiments over the range -15.4°C to +59.9°C which is about 0.6 percent above the present data at 20 C and gives a slightly lower coefficient of expansion.

Atkinson, Heycock, and Pope² found still higher densities and exceed the latest figures by about 1.2 percent.

Germann³ only did determinations at 0°C and 25°C and agrees closely with Paternò and Mazzucchelli.

Figures given by Emmerling and Lengvel⁴ and Beckmann⁵ are fairly close to Atkinson, Heycock, and Pope.

All these determinations may be compared with the present findings (see Fig. 1). It is significant that the older values are high which suggests that the presence of carbon tetrachloride might explain the discrepancies. About 6 percent would raise the density of phosgene by 1 percent and the deviation would tend to increase with rise of temperature as is observed in the case of the Italian data. It is probable that dissolved chlorine would also raise the density. The results of Atkinson, Heycock, and Pope were obtained by chemical estimation of the phosgene instead of direct weighing. It is not possible to draw any conclusions from the methods of manufacture of the phosgene since various processes have been used and no correlation with the observed densities is apparent.

5. SUMMARY

A determination of the density and thermal expansion of liquid phospene over the range -20° C to $+60^{\circ}$ C is described. The density in this range is given by the following equation:

$$\rho = 1.42014 - 0.0023120t - 0.000002872t^2.$$

6. ACKNOWLEDGMENT

These experiments were carried out in a Ministry of Supply Research Establishment and the results are published by permission of the Director General of Scientific Research and Development.

- Paternò and Mazzucchelli, Gazzetta [1] 50, 30 (1920).
- ² Atkinson, Heycock, and Pope, J. Chem. Soc. Trans. **2**, 1410 (1920). ³ Germann, J. Phys. Chem. **29**, 138 (1925). ⁴ Emmerling and Lengyel, Ann. Suppl. **7**, 106 (1870); Berichte **2**, 6 (1960).
- 546 (1869).

 ⁵ Beckmann, Zeits. f. Ann. Chem. **55**, 371 (1907).

Statistical Mechanics of Linear Association Equilibria

PAUL J. FLORY Research Laboratory, The Goodyear Tire and Rubber Company, Akron, Ohio November 21, 1945

N a recently published paper Tobolsky and Blatz¹ have discussed the "possible application" of the lattice model for mixtures of linear polymers with small molecules to reversible associations of liquids such as the alcohols and their solutions in non-associated solvents.

It appears that they were unaware that this particular problem can be treated by previously derived relationships pertaining to heterogeneous polymer-solvent mixtures.2 Their paper contains the unfounded and misleading statement, "... whereas Florv2 was considering stable polymer molecules which did not change their size distribution when diluted, we are here concerned with the problem of reversible association. . . . " It is the writer's purpose to emphasize here the generality of the previously derived thermodynamic functions as applied to equilibria involving transformations between various polymeric species.

In applying the methods of thermodynamics, or statistical mechanics, to chemical equilibrium problems the character of the bonds, or intermolecular forces, subject to equilibration need not be specified. The treatment, previously presented, of equilibria involving polymer molecules is completely general, and although secondary valence polymers were not mentioned, it should have been clear that it is also applicable to these as well, provided that the "polymers" consist predominantly of linear sequences of structural units. This treatment led to the conclusion that the equilibrium constant for processes involving polymeric substances assumes the same form as that for the analogous reaction between monomeric species; the relationship of the equilibrium constant to the standard state free energy change is the same in the two cases. Thus, no modifications in the formulation of equilibrium constants are occasioned by the configurational randomness of the polymeric reacting species.

For the purpose of applying this principle to associative equilibria specifically, consider a solution containing N_0 associating units per unit volume, each of which is capable of entering into two "bonds" to form linear polymers. If each of these bonds forms independently of the presence or absence of other bonds attached to the adjoining units, then an equilibrium constant governing the associative process can be written

$$K = p/(1-p)^2 N_0, \tag{1}$$

where p (equivalent to the "y" of Tobolsky and Blatz) is the "degree of association," i.e., N_0p represents the concentration of association bonds at equilibrium. Also from the above assumptions and the nature of the dependence of partial molal free energies on concentrations, it follows that the molecular size distribution is given by

$$N_x = N_0(1-p)^2 p^{x-1},$$
 (2)3,4

where N_x represents the molar concentration of x-mers; the number average degree of polymerization, according to (2), is given by

$$\bar{x}_n = 1/(1-p),$$
 (3)

the partial molal free energy of the solvent in this system is obtained directly by substituting (3) into Eq. (17) of reference 2, giving

$$\Delta \bar{F}_1 = RT[\ln (1 - v_2) + v_2 p + \mu v_2^2], \tag{4}$$

where v_2 is the volume fraction of solute including all species, and μ is a semi-empirical parameter^{5, 6} in which is included the heat of dilution term. Equation (4) is identical with Tobolsky and Blatz's Eq. (5), which is merely a special case of the more general equation, namely that in which the molecular size distribution of the solute is given by (2). Similarly, if desired, partial molal free energies for any of the various solute species can be derived by appropriately substituting Eqs. (2) and (3) into Eqs. (18) and (19) of reference 2. The resulting expressions differ from Tobolsky and Blatz's (6) and (7), which latter contain the intractable quantity y' and refer to the ambiguous standard state consisting of "pure mixed" solute molecules.

Whereas Tobolsky and Blatz prefer to include the factors controlling p, the extent of association (or reaction), in the partition function, the writer has preferred to relate p separately to an equilibrium constant. The procedures are fundamentally equivalent, the writer's being generally more easily applied.

The factor $b^n 0 + \sum n_x$ introduced into their intuitively derived partition function to account for mixing of molecules with holes in the lattice appears to be both unnecessary and incorrect. Tobolsky and Blatz1 include the entropy of bond formation $(k \ln a[\Sigma(x-1)N_x])$, which had been omitted by Tobolsky⁷ previously. Hence, their definition of P as the heat of association is correct, but in the previous paper P must be considered to represent a standard state free energy change, as previously pointed out.2

In conclusion it should be emphasized that the previously derived thermodynamic relationships are general, and a new derivation of the partition function for each application to a specific problem would seem to be unnecessary.

¹ A. V. Tobolsky and P. J. Blatz, J. Chem. Phys. 13, 379 (1945).

² P. J. Flory, J. Chem. Phys. 12, 425 (1944).

³ P. J. Flory, J. Am. Chem. Soc. 58, 1877 (1936); *ibid.* 64, 2205 (1942).

⁴ K. H. Meyer and A. van der Wyk, Helv. Chim. Acta 20, 1321 (1937), derived Eq. (2) for association processes in which the free energy change for each successive monomer added to the micell is assumed to be the

same.

⁵ M. L. Huggins, J. Phys. Chem. 46, 15 (1942); Ann. N. Y. Acad. Sci.

43, 1 (1942); *ibid.* 44, 431 (1943); J. Am. Chem. Soc. 64, 1712 (1942).

⁶ P. J. Flory, J. Chem. Phys. 13, 453 (1945).

⁷ A. V. Tobolsky, J. Chem. Phys. 12, 402 (1944).