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Thermodynamics of High Polymer Solutions¹

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A statistical mechanical treatment of high polymer solutions has been carried out on the basis of an idealized model, originally proposed by Meyer, which is analogous to the one ordinarily assumed in the derivation of the "ideal" solution laws for molecules of equal size. There is obtained for the entropy of mixing of n solvent and N linear polymer molecules (originally disoriented), $\Delta S = -k[(n/\beta) \ln v_1 + N \ln v_2]$ where v_1 and v_2 are volume fractions and β is the number of solvent molecules replaceable by a freely orienting segment of the polymer chain. This expression is similar in form to the classical expression for equal-sized molecules, mole fractions having been replaced by volume fractions. When the disparity between the sizes of the two components is great, this expression gives entropies differing widely from the

classical values, which accounts for the large deviations of high polymer solutions from "ideal" behavior. The entropy of disorientation of a perfectly arranged linear polymer is found to be of the order of R cal. per chain segment. After introducing a suitable heat of mixing term, partial molal free energies are computed, and the calculations are compared with experimental data for all concentrations. Phase equilibria have been calculated in the region of partial miscibility. The theory predicts, in agreement with experiment, that the critical composition for partial miscibility lies at a low concentration of polymer. Low intrinsic viscosities of polymers dissolved in poor solvents are attributed to the tendency for the molecule to assume a more compact configuration in such an environment.

INTRODUCTION

IT is customary to correlate the thermodynamic properties of binary liquid systems with the so-called "ideal" solution laws. These rest fundamentally on an entropy of mixing given by

$$\Delta S_{\text{mixing}} = -R(n_1 \ln X_1 + n_2 \ln X_2), \quad (1)$$

where n_1 and n_2 are the numbers of moles of the two components, and X_1 and X_2 are their mole fractions in the mixture. Partial differentiation of (1) with respect to n_1 yields for the partial molal entropy of dilution

$$\Delta \bar{S}_1 = -R \ln X_1. \quad (2)$$

Although (1) and (2) frequently have been applied indiscriminately, at finite concentrations they can be justified theoretically only when molecules of the two species are equivalent in size and shape, i.e., when molecules of the two species are interchangeable in the liquid. The importance of this limitation has been emphasized by a number of authors during recent years.²⁻⁴

Meyer and co-workers^{5, 6} have found that $\Delta \bar{S}_1$ for solutions of long chain compounds dissolved in simple solvents, e.g., for carbon tetrachloride solutions of long chain esters, is much greater than Eq. (2) would predict. In other words, they have found strong negative deviations from Raoult's law, even when $\Delta \bar{H}_1 = 0$. Meyer and Lühdemann⁵ suggested that this abnormal entropy effect was due to the ability of sections of a long chain solute molecule to act more or less independently of one another as kinetic units. Thus, the effective mole fraction should be greater than the actual mole fraction. An equivalent explanation has been advanced recently by Powell, Clark and Eyring.⁷ Apparently they were unaware of the serious criticisms of this point of view advanced by Hückel,² principally on the grounds that it inherently assumes primary validity of the ideal solution laws when applied to mixtures of molecules differing greatly in size. Hückel has also pointed out that the kinetic units cannot be truly independent, nor are they independently interchangeable in the liquid as applicability of (1) or (2) would require. Finally, in order to explain experimental results,

¹ Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society, at the Atlantic City Meeting, September 11, 1941.

² E. Hückel, *Zeits. f. Elektrochemie* **42**, 753 (1936).

³ E. A. Guggenheim, *Trans. Faraday Soc.* **33**, 151 (1937).

⁴ R. H. Fowler and G. S. Rushbrooke, *Trans. Faraday Soc.* **33**, 1272 (1937).

⁵ K. H. Meyer and R. Lühdemann, *Helv. Chim. Acta* **18**, 307 (1935).

⁶ Ch. G. Boissonnas, *Helv. Chim. Acta* **20**, 768 (1937).

⁷ R. E. Powell, C. R. Clark, and H. Eyring, *J. Chem. Phys.* **9**, 268 (1941).

it is necessary to assume a size for the kinetic unit, which, though equal to the entire solute molecule at infinite dilution, decreases rapidly with increasing concentration, approaching a limiting size of some 15 to 30 chain atoms^{5,7} at high concentrations.

Recently Meyer⁸ has provided a more plausible explanation of the "abnormalities" of solutions of long chain, or polymeric, molecules. He has suggested an idealized model for such solutions, which consists of a quasi-solid lattice, not unlike that customarily used in the derivation of (1) for the case of a mixture of equal-sized molecules. A cell of the hypothetical lattice may be occupied either by a solvent molecule or by a segment of the polymer (solute). The segments of a given polymer chain must occupy a continuous sequence of adjacent cells, which, however, may meander irregularly through the lattice. There will be many such sequences emanating from a given cell, and the polymer molecule may conform to any one of them through suitable rotations about the valence bonds of the chain skeleton. According to Meyer, entropies of mixing in excess of "ideal" values given by (1) are the result of these numerous configurations available to the polymer molecules.

Meyer has discussed his model in qualitative terms only. Recently quantitative statistical mechanical treatments⁹⁻¹¹ of this model have been carried out independently by Huggins and the writer. On the basis of the preliminary accounts which have been published concerning these investigations, the results appear to be in substantial agreement. In this paper the writer's treatment of the problem will be presented in full, with particular emphasis on an extension of the model and applications to hitherto unexplained characteristics of polymer solutions.

DERIVATION OF THE ENTROPY OF MIXING

Throughout this paper polymer molecules which are linear, i.e., consist of a single linear sequence of structural units, are under con-

sideration. Somewhat arbitrarily, the symmetry number of these molecules is taken to be two, due to (assumed) indistinguishability of the two ends of the molecule. Concurrently with the derivation of the fundamental relationships, special prominence will be given to the assumptions involved.

Assumption 1: the mixture of polymer and solvent molecules is assumed to conform to Meyer's model. This involves assumption of (a) a quasi-solid lattice in the liquid, (b) interchangeability of segments (not necessarily identical with the polymer structural units) of the polymer chain with solvent molecules in the lattice cells and (c) independence of lattice constants on composition. Although these assumptions obviously are quite artificial, there is some consolation in the fact that analogous ones are inherent in the model from which Eq. (1) is derived for mixtures of small molecules of equal size.

Assumption 2: all polymer molecules are assumed to be of the same size.

Assumption 3: the average concentration of polymer segments in cells adjacent to cells unoccupied by the polymeric solute is taken to be equal to the over-all average concentration.

Let n_0 = the total number of cells in the lattice.

N = the number of polymer molecules, each composed of x segments, any one of which may replace a solvent molecule in the lattice.

γ = a coordination number for the lattice, i.e., the number of "first neighbor" cells in the lattice available to the next consecutive segment of the polymer chain.

In order to determine the total number of possible non-identical configurations, let us first consider the process of successive addition of polymer molecules to the empty lattice containing n_0 cells. After N polymer molecules have been added, there will be $n_0 - xN$ cells which may be occupied by the terminal segment of the next polymer molecule to enter the lattice. According to assumption 3, the expected number of available unoccupied cells immediately adjacent to the cell occupied by the terminal segment of this polymer chain will be $\gamma(n_0 - xN)/n_0$. For the third segment the expected number of available cells will be given by $\alpha = (\gamma - 1)(n_0 - xN)/n_0$, since the cell occupied by the terminal segment eliminates one of the neighboring cells.

Assumption 4: the expected number of avail-

⁸ K. H. Meyer, *Zeits. f. physik. Chemie* **B44**, 383 (1939); *Helv. Chim. Acta* **23**, 1063 (1940).

⁹ M. L. Huggins, *J. Chem. Phys.* **9**, 440 (1941).

¹⁰ Paper presented by Dr. Huggins before the Wilder D. Bancroft Colloid Symposium, Ithaca, New York, June 20, 1941.

¹¹ P. J. Flory, *J. Chem. Phys.* **9**, 660 (1941).

able positions for each successive segment is taken to be equal to $\alpha \equiv (\gamma - 1)(n_0 - xN)/n_0$. This is of the nature of an approximation, as it fails to exclude impossible configurations in which two segments, separated by two or more intervening segments but belonging to the same chain, occupy the same cell. Use of this "assumption" obviously will lead to computation of too many configurations.

For the expected number of configurations which the particular chain may assume without shifting the terminal group we have

$$[\gamma/(\gamma - 1)]\alpha^{x-1} \quad (3)$$

and for the expected total number of configurations for the chain in the entire lattice

$$\nu_{N+1} = \frac{1}{2}(n_0 - xN)[\gamma/(\gamma - 1)]\alpha^{x-1}, \quad (4)$$

$$\cong \frac{1}{2}(n_0 - xN)^x(\gamma - 1)^{x-1}, n_0^{1-x}, \quad (4.1)$$

where the factor $\frac{1}{2}$ has been included in order to eliminate redundancy of configurations due to the indistinguishability of the ends of the polymer chain.

The total number of possible configurations for the system consisting of N polymer and n solvent molecules in a lattice composed of $n_0 = n + xN$ cells is given by

$$W = (1/N!) \prod_{N=1}^N \nu_N, \quad (5)$$

where the factor $1/N!$ eliminates redundant configurations which differ only by an interchange of one or more pairs of polymer molecules. Substituting (4.1) in (5) we obtain by suitable rearrangement

$$W = \left(\frac{\gamma - 1}{n_0}\right)^{(x-1)N} \left(\frac{x^{xN}}{2^N N!}\right) \left[\frac{(n_0/x)!}{(n_0/x - N)!}\right]^x.$$

Replacing factorials by Stirling's approximation, $N! = (N/e)^N$

$$W = \left(\frac{\gamma - 1}{e}\right)^{(x-1)N} (1/2)^N \frac{(n + xN)^{n+N}}{n^n N^N}. \quad (6)$$

For the entropy of mixing, according to the well-known Boltzmann relationship $S = k \ln W$, where

k is Boltzmann's constant, we obtain¹¹

$$\Delta S_{\text{mixing}} = -k \left[n \ln \left(\frac{n}{n + xN} \right) + N \ln \left(\frac{N}{n + xN} \right) \right] + k(x-1)N[\ln(\gamma - 1) - 1] - kN \ln 2. \quad (7)$$

This expression refers to the entropy change in the process of mixing n pure solvent and N perfectly arranged (or oriented) polymer molecules, subject, of course, to the assumptions introduced above concerning the nature of the solution. When $x = 1$, (7) reduces to the classical expression (1), except for the symmetry term.

A few remarks should be made concerning the use in the above derivation of "expected values" for the numbers of configurations, since actual values in many cases may deviate enormously from expectancy. When α is greater than unity (i.e., when the concentration of polymer is not too great) the expected number of available configurations which extend from a given site in the lattice, is, according to Eq. (3), a very large number. (We consider x to be at least of the order of 100.) But the actual number of configurations may be zero; for example, there might be only one cell available for the second segment and none for the third. On the other hand, for a more favorably located initial cell, the number of available configurations may be an exceedingly large number. Since the total number of sites available to the terminal segment of the N th polymer molecule to be added to the lattice is very large when $\alpha > 1$, the actual total number of configurations available to the particular molecule will deviate negligibly from the expected number calculated from (4).

When α is appreciably less than unity, i.e., at high concentrations of polymer, the expected number of configurations (Eq. (3)) extending from a given site will be very much less than unity. If α is sufficiently small, e.g., of the order of 0.5, then ν_N also may be extremely small (for large x). That is, at high polymer concentrations the expected number of configurations available for an additional polymer molecule is much less than unity. Of all the possible configurations for the $N - 1$ polymer molecules in the lattice, only a small fraction (not exactly equal to ν_N) possess one or more continuous sequences of x vacant cells any place in the entire lattice. According to

this interpretation, ν_N is the average "yield" of such sequences of unoccupied cells per configuration of the $N-1$ polymer molecules in the lattice. Thus, after a certain concentration is exceeded, addition of more polymer molecules to the lattice (possessing a fixed number of cells) decreases the total number of configurations for the system.^{12a} In spite of the use of expected values from which actual deviations may be large, Eq. (6) for the total number of configurations should be a valid approximation at all concentrations, subject only to the original assumptions.

THE ENTROPY OF DISORIENTATION

The "configurational" entropy of a lattice filled with N polymer molecules in the absence of solvent, which is obtained by setting $n=0$ in (7), is¹¹

$$\Delta S^* = kN \ln (x/2) + kN(x-1)[\ln (\gamma-1) - 1]. \quad (8)$$

When x is large

$$\Delta S^*/Nx \cong k \ln [(\gamma-1)/e]. \quad (9)$$

That is, the entropy change per mole of segments is of the order of R .^{12b} These relationships express the entropy change for the transformation of N polymer molecules from a state of perfect orientation and arrangement in the lattice to the state of random entanglement. This probably is the source of an appreciable portion of the entropy of fusion of polymer crystallites (e.g., in rubber, polyesters, etc.). Obviously, other terms arising from change in the lattice constants and in the arrangements and motions within the segments when fusion occurs also contribute to the total entropy of fusion.

It can be shown that the lattice "saturated" with polymer molecules will contain a few vacant cells, equivalent to the "holes"¹³ in simple liquids. From the point of view of the equations used

^{12a} Alternatively, one may consider that the polymer molecules are continually diffusing in the lattice, i.e., the system is continually changing from one configuration to another. Then ν_N is the time average number of available sequences of x units.

^{12b} H. Mark, J. App. Phys. **12**, 41 (1941), using the statistical theory of the internal configurations of polymer molecules, has arrived at a similar value for the entropy of disorientation *per chain bond* about which there is free rotation.

¹³ H. Eyring, J. Chem. Phys. **4**, 283 (1936); H. Eyring and J. O. Hirschfelder, J. Phys. Chem. **41**, 249 (1937).

above, these vacant cells should be treated as molecules of a second component. However, their concentration is so small that no significant error has been committed in setting $n=0$ in the derivation of (8).

The entropy change on mixing n solvent with N randomly entangled (liquid state) polymer molecules is

$$\begin{aligned} \Delta S_{\text{mixing}} &= \Delta S_{\text{mixing}} - \Delta S^* \\ &= -k \left[n \ln \left(\frac{n}{n+xN} \right) \right. \\ &\quad \left. + N \ln \left(\frac{xN}{n+xN} \right) \right]. \quad (10) \end{aligned}$$

Or

$$\Delta S_{\text{mixing}} = -k[n \ln v_1 + N \ln v_2], \quad (10.1)$$

where v_1 and v_2 are volume fractions of solvent and polymer, respectively. The pure liquid polymer (disoriented) will be chosen as the standard state for the solute, as is customary for binary liquid mixtures. Equation (10) will serve as the starting point for the derivation of the thermodynamic relationships discussed below.

It is interesting to note that (10.1) is so similar in form to (1); replacement of volume fractions by mole fractions in the logarithms of the former yields the latter. The entropy of mixing of polymer and solvent is greater than (1) would predict, but less than that for mixing the completely dissociated polymer segments with solvent. Meyer's⁸ qualitative discussion of the problem leads to the same conclusion.

PARTIAL MOLAL FUNCTIONS

Differentiating (10) with respect to n , there is obtained for the partial molal entropy of the solvent

$$\Delta \bar{S}_1 = -R \ln (1-v_2) - R(1-1/x)v_2 \quad (11)$$

$$= Rv_2(1/x + v_2/2 + v_2^2/3 + \dots). \quad (11.1)$$

Similarly,

$$\Delta \bar{S}_2 = -R \ln (1-v_1) + R(x-1)v_1. \quad (12)$$

Inasmuch as the forces acting between two polymer molecules, or between a polymer and a simple molecule, obviously are of the same sort as those operating between pairs of simple molecules, the heat of interaction between a polymer

molecule and its environment should vary linearly with the composition. Consequently, the heat of mixing can be represented by a relationship used by Scatchard¹⁴ for simple molecules

$$\Delta H = BV_1V_2nN/(nV_1 + NV_2), \quad (13)$$

where B is a constant for a given pair of liquids and V_1 and V_2 are the molar volumes of solvent and polymeric solute, respectively. According to the model considered here, $V_2 = xV_1$.

The partial molal heat contents are, according to (13)

$$\Delta \bar{H}_1 = BV_1v_2^2 \quad (14)$$

and

$$\Delta \bar{H}_2 = BV_2v_1^2 = BxV_1v_1^2. \quad (15)$$

Combining these equations with (11) and (12), there is obtained for the partial molal free energy of the solvent

$$\begin{aligned} \Delta \bar{F}_1 &= RT \ln (1 - v_2) \\ &\quad + RT(1 - 1/x)v_2 + BV_1v_2^2 \quad (16) \\ &= -RTv_2[1/x + (1 - K)v_2/2 \\ &\quad + v_2^2/3 + \dots], \quad (16.1) \end{aligned}$$

where

$$K = 2BV_1/RT$$

and for the partial molal free energy of the solute

$$\begin{aligned} \Delta \bar{F}_2 &= RT \ln (1 - v_1) - RT(x - 1)v_1 \\ &\quad + BV_1xv_1^2. \quad (17) \end{aligned}$$

Equations (16.1) and (11.1) reduce to the "ideal" solution relationships at infinite dilution. This is virtually a necessary consequence³ of the Gibbs-Duhem relationship

$$\partial \Delta \bar{F}_1 / \partial \ln X_1 = \partial \Delta \bar{F}_2 / \partial \ln X_2.$$

Since for any acceptable model for the system the activity a_2 of the solute must be proportional to the concentration at infinite dilution

$$\begin{aligned} \partial \ln a_2 / \partial \ln X_2 &\equiv (1/RT) \partial \Delta \bar{F}_2 / \partial \ln X_2 = 1 \\ \partial \Delta \bar{F}_1 / \partial \ln X_1 &= RT. \end{aligned}$$

Or

$$\Delta \bar{F}_1 = RT \ln X_1$$

which at infinite dilution may be replaced by

$$\Delta \bar{F}_1 = -RTX_2 = -RTv_2/x, \quad (16.2)$$

which is identical with (16.1) as v_2 approaches zero.

¹⁴ G. Scatchard, Chem. Rev. **8**, 321 (1931).

THE EFFECT OF SEGMENT SIZE

It has been assumed that a section of the polymer chain which occupies a volume equal to that of one solvent molecule is equally free to occupy any one of $\gamma - 1$ cells, entirely independent of the configuration of preceding segments of the chain. If the solvent molecule is very small, or if there are limitations, perhaps steric in nature, on the tortuosity which the chain may comfortably assume, then the size of the section of the chain which is free to orient itself at random, irrespective of the orientation of the preceding sections, may be equivalent to the volume occupied by several solvent molecules. In this situation, we may construct a new lattice in which one cell will accommodate either β solvent molecules or one segment of the polymer chain.

The entropy of mixing according to this revised model will be given by either of the Eqs. (7) or (10), provided that n is replaced by $n' = n/\beta$; x likewise has been decreased by the same factor, but a modified symbol is unnecessary. Differentiating the resulting expression with respect to n (not n')¹¹

$$\Delta \bar{S}_1 = -(R/\beta)[\ln (1 - v_2) + (1 - 1/x)v_2] \quad (18)$$

$$= (Rv_2/\beta)(1/x + v_2/2 + v_2^2/3 + \dots), \quad (18.1)$$

and

$$\begin{aligned} \Delta \bar{F}_1 &= (RT/\beta)[\ln (1 - v_2) \\ &\quad + (1 - 1/x)v_2 + Kv_2^2/2] \quad (19) \end{aligned}$$

$$= -(RTv_2/\beta)[1/x + (1 - K)v_2/2 + v_2^2/3 + \dots], \quad (19.1)$$

where K is re-defined as $2\beta BV_1/RT$. Equation (19.1) reduces to $\Delta \bar{F}_1 = -RTX_2$ at infinite dilution, as is required. Equation (12) for the partial molal entropy of the solute can be applied intact when $\beta > 1$, except that x must be taken equal to the number of re-defined segments per chain. Consequently, Eq. (17) can be written

$$\begin{aligned} \Delta \bar{F}_2 &= RT[\ln (1 - v_1) \\ &\quad - (x - 1)v_1 + Kxv_1^2/2]. \quad (17.1) \end{aligned}$$

COMPARISONS WITH EXPERIMENTAL DATA

Osmotic pressures of dilute polymer solutions have been investigated quite extensively,¹⁵⁻¹⁹ as a

¹⁵ H. Staudinger and G. V. Schulz, Ber. **68**, 2320, 2336 (1935); G. V. Schulz, Zeits. f. physik. Chemie **A176**, 317 (1936).

means for determination of molecular weight. Strong deviation from Van't Hoff's law, i.e., from "ideality," are invariably observed at low concentrations, necessitating a frequently precarious extrapolation to infinite dilution. Experimental results for a number of dilute polymer solutions^{15,16,19,20} support the simple relationship between osmotic pressure π and concentration c of polymer (in grams per cc)

$$\pi = RTc/\bar{M}_n + bc^2, \quad (20)$$

where \bar{M}_n is the number average molecular weight of the polymer and b is a constant, independent of \bar{M}_n ,^{15,19} representing the degree of departure from ideality.

For dilute solutions Eq. (19.1) yields

$$\pi = -\Delta\bar{F}_1/V_1 \cong RTv_2/V_1\beta x + RT(1-K)v_2^2/2V_1\beta$$

which reduces at once to (20);²¹ overlooking the difference between volume and weight concentration in the second term

$$b \cong RT(1-K)/2V_1\beta. \quad (21)$$

Huggins^{9,10} has reported a similar deduction of (20) for the case $K=0$, $\beta=1$.

When various solvents or solvent mixtures are considered, according to (21) the greater the heat of mixing the smaller will be the value of b at a given temperature, since K depends directly on the heat of mixing constant B . As K approaches unity b approaches zero, and the solution approaches classical "ideality." When K becomes but slightly greater than unity, (x large), the region of partial miscibility is reached and the polymer will no longer dissolve to an appreciable concentration (cf. *seq.*). Thus, a dilute high polymer solution should be most nearly "ideal" when it is approximately on the verge of precipitation. Osmotic pressure measurements on rubber dissolved in benzene-alcohol mixtures²²

and on solutions of polyvinyl chloride in tetrahydrofuran, a good solvent, and in dioxane, a poor solvent,²³ confirm this deduction.²⁴ However, to conclude, as Gee²² has done, that a better extrapolation to infinite dilution is obtained in the presence of alcohol is not necessarily correct; higher terms in the series expansion of (19) must be included if the extrapolation is to be improved.

Although the statistical theory presented above predicts the correct form for the osmotic pressure-concentration relationship (20), quantitative correlation with the observed "deviation term" (i.e., bc^2) requires a larger value of β than would be expected from steric considerations regarding chain flexibility. Thus, from osmotic pressure measurements on dilute solutions of rubber in toluene, Meyer, Wolff and Boissonnas found $V_1b=56$ cal. at 298°K. The heat of mixing, deduced from the temperature coefficient of the osmotic pressure, was negligibly positive.²⁵ Taking $K=0$, according to (21) $bV_1=300/\beta$, or $\beta \cong 5.3$, which corresponds to about seven isoprene units, or 28 chain atoms, per segment. A similar value for bV_1 was obtained by Wolff¹⁷ for gutta-percha in toluene.

For the system toluene-polystyrene, according to osmotic pressure measurements by Schulz,¹⁵ $bV_1=39$ cal. at ordinary temperature. Although reliable data concerning the heat of mixing do not appear to have been obtained,²⁶ certainly the heat effect accompanying mixing of two such chemically similar materials is negligible, and it may be assumed that $K=0$. A value of $\beta=8$ is

²³ H. Staudinger and J. Schneiders, *Ann. d. Chemie* **541**, 151 (1939).

²⁴ R. E. Powell, C. R. Clark and H. Eyring, in a paper presented at the Conference on Viscosity sponsored by the New York Academy of Sciences, February 14, 1941, have reached the fantastic conclusion from Gee's results that a benzene-methanol mixture is a better solvent for rubber hydrocarbon than benzene alone. Apparently they have confused the literal meaning of the term "ideal" with its conventional meaning with reference to the so-called "ideal" solution laws. Addition of methanol to the benzene solution of rubber *decreases* $-\Delta\bar{F}_1$, the free energy of dilution, thus decreasing the thermodynamic solvent power. Since $-\Delta\bar{F}_1$ is greater for pure benzene solutions than $-\Delta\bar{F}_1$ for an "ideal" solution, addition of methanol decreases the discrepancy between observed and "ideal" values, but this is another matter.

²⁵ L. Hock and H. Schmidt, *Kautschuk* **10**, 33 (1934), have shown by direct calorimetric measurements that the heat of mixing of benzene and rubber is positive, but very small.

²⁶ See Ch. G. Boissonnas and K. H. Meyer, *Zeits. f. physik. Chemie* **B44**, 392 (1939).

¹⁵ K. H. Meyer, E. Wolff and Ch. G. Boissonnas, *Helv. Chim. Acta* **23**, 430 (1940).

¹⁷ E. Wolff, *Helv. Chim. Acta*, **23**, 439 (1940).

¹⁸ O. Hagger and A. J. A. Van der Wijk, *Helv. Chim. Acta*, **23**, 484 (1940).

¹⁹ See also, H. Mark, *Physical Chemistry of High Polymeric Systems* (Interscience Publishers, Inc., New York, 1940), pp. 228-245.

²⁰ G. Gee, *Trans. Faraday Soc.* **36**, 1161 (1940).

²¹ Actually, the partial molal volume \bar{V}_1 should be used in place of V_1 , but since the difference between them is so small in dilute solutions (see ref. (16)) they need not be distinguished here.

²² G. Gee, *Trans. Faraday Soc.* **36**, 1171 (1940).

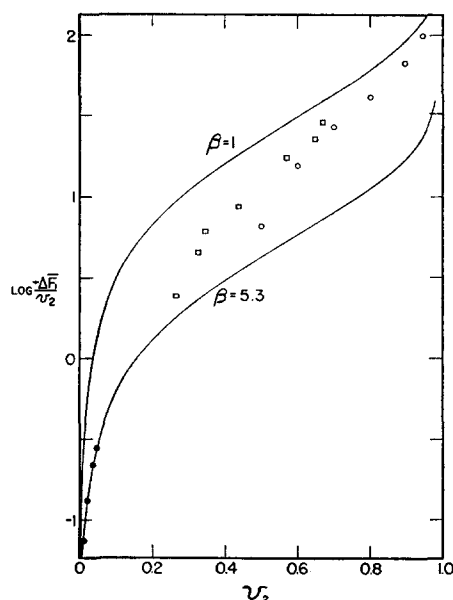


FIG. 1. Partial molal free energy as a function of the volume fraction of polymer for $\beta = 1$ and $\beta = 5.3$. ●—Osmotic pressure results for toluene-rubber, reference 16; ○—results from vapor pressures of toluene-rubber mixtures, reference 16; □—results from vapor pressures of benzene-rubber mixtures, reference 28.

required in order to bring the theoretically derived relationship into agreement with experiment; the corresponding segment contains about 16 chain atoms.

If rotation about each single bond in the chain were completely free, one or two single bonds should be sufficient to allow a new choice of direction of the chain independent of its preceding portions. Allowances for the limitations on the effective available configurations due to the potential restricting rotation about single carbon-carbon bonds and to the steric interferences of side chain substituents, presumably would raise the segment size somewhat. But it is difficult to account for segments of the size indicated by the above analysis on these grounds alone. Oversimplifications inherent in the model which has been postulated, and in particular assumption 4, probably are responsible for a considerable part of the discrepancy. The latter assumption allows too many configurations to be included, thus giving a configurational entropy which is too large.

The segment sizes calculated above are similar to those deduced from the temperature coeffi-

cients of polymer viscosities,²⁷ but the writer is not inclined to consider this as more than a coincidence. Viscous flow is a kinetic phenomenon, whereas the thermodynamic properties of polymer solutions (taking the pure liquids as reference states) depend primarily upon configurational characteristics, according to the premises of this paper. Unless it can be shown that kinetic and configurational segments should be the same, correlation⁷ of these independently estimated segment sizes is likely to be illusory.

In Fig. 1 partial molal free energies calculated from Eq. (19) are compared with experimental values for solutions of rubber in toluene (Meyer, Wolff and Boissonnas¹⁶) and in benzene (Stamberger²⁸). The dilute solution data, which are from those discussed previously, were obtained osmotically. Data at higher concentrations ($v_2 > 0.20$) are based on vapor pressure measurements.²⁹ Stamberger²⁸ found no perceptible differences in the vapor pressure lowering for samples of rubber varying considerably in molecular weight. This is in agreement with Eq. (19) which predicts virtual independence of $\Delta\bar{F}_1$ on x when x is large and the solution is not too dilute.

The upper curve in the figure has been calculated from (19) taking $K=0$, $\beta=1$ and $x=2900$, which corresponds to the average molecular weight, 270,000, obtained by Meyer and co-workers¹⁶ from the limiting value of π/c . For the lower curve a value of $\beta=5.3$ has been chosen in order to obtain agreement with experiment at low concentrations (see above). The value of x has been lowered correspondingly to 550 in order to preserve consistency with the observed molecular weight. With increasing concentration the experimental points depart from the $\beta=5.3$ curve, approaching the $\beta=1$ curve at high concentrations. The comparison of observed and calculated values at high concentrations of polymer is shown more effectively in Table I by a tabulation of observed activities $a_1 = p_1/p_1^0$ and those calculated from (19) and the relationship $\ln a_1 = \Delta\bar{F}_1/RT$, taking $\beta=1$.

²⁷ P. J. Flory, J. Am. Chem. Soc. **62**, 1057 (1940); W. Kauzman and H. Eyring, *ibid.* **62**, 3113 (1940).

²⁸ P. Stamberger, J. Chem. Soc. 2318 (1929).

²⁹ Concentrations for the experimental data actually are in weight fractions, although volume fractions are indicated. The difference is unimportant, however, since the densities of the two components are similar.

The measure of agreement in this range is all that should be expected considering the crudity of the original assumptions.

It would be possible, of course, to improve the agreement between theory and experiment by assuming an appropriate dependence of β on v_2 . However, this apparent variation of β may reflect imperfections in the theory, rather than an actual variation in segment size with concentration.

PHASE EQUILIBRIA

When there is a large heat effect accompanying the mixing of two liquids composed of molecules of ordinary size, the observed entropy of mixing usually deviates considerably from the ideal entropy given by (1), i.e., the solution is not "regular."³⁰ Due to differences in the energies of interaction between neighboring pairs of like and unlike molecules, distribution of the two species is not random, as is assumed in the derivation of (1). Furthermore, if $\Delta H < 0$ the comparatively large solvent solute interactions in the solution are likely to lead to a higher degree of local orientation of neighboring pairs than is found in the pure components, thus decreasing the entropy of mixing; if $\Delta H > 0$, the opposite is likely to be true.

Similarly, in the case of polymer solutions for which ΔH is large in magnitude the entropy of mixing should not be expected to agree with that calculated assuming random distribution of the two species, random configurations for the polymer molecules, and packing and local orientations equivalent to the pure liquid components.¹⁸ "Deviations" should be expected to arise from the same sources discussed above for simple molecules. When $\Delta H > 0$, moreover, compact configurations of the polymer chains should

be preferred, thus decreasing the configurational entropy (cf. *seq.*).

In spite of these additional limitations imposed on the partial molal entropy and free energy Eqs. (18) and (19) when $\Delta H \gg 0$, it is of interest to examine the character of the phase-composition diagram which they predict when ΔH is sufficiently large to cause separation into two phases.

Equilibrium between two phases in a binary system requires that their compositions v_2 and v'_2 shall be such that

$$\Delta\bar{F}_1(v_2) = \Delta\bar{F}_1(v'_2), \quad \Delta\bar{F}_2(v_2) = \Delta\bar{F}_2(v'_2). \quad (22)$$

When $\Delta\bar{H}_1 = 0$, i.e., when $K = 2\beta B V_1/RT = 0$, $\Delta\bar{F}_1$ decreases continuously as v_2 increases from zero to unity. But when K is sufficiently positive, according to (19) the curve for $\Delta\bar{F}_1$ will possess a maximum and a minimum in this range. Differentiating (19) with respect to v_2 and equating to zero

$$Kxv_2^2 - (Kx - x + 1)v_2 + 1 = 0,$$

the solution of which is

$$v_2 = \frac{Kx - (x - 1) \pm [(Kx - x + 1)^2 - 4Kx]^{\frac{1}{2}}}{2Kx}. \quad (23)$$

The critical condition for incipient separation into two phases requires that the maximum and minimum in $\Delta\bar{F}_1$ coincide, i.e., that the two roots of (23) shall be equal. This occurs when¹¹

$$K(\text{critical}) = (1 + \sqrt{x})^2/x. \quad (24)$$

Substituting (24) in (23)

$$v_2(\text{critical}) = 1/(1 + \sqrt{x}). \quad (25)^{11}$$

When x is large the critical value of K is slightly greater than unity, and it approaches unity as x approaches infinity; at larger values of K two phases will co-exist in equilibrium. The critical composition, at which the two phases become identical, according to (25), occurs at a low concentration when x is large. The same relationships could have been derived by setting $\partial\Delta\bar{F}_2/\partial v_2$ equal to zero, since

$$\partial\Delta\bar{F}_2/\partial v_2 = -\left(\frac{\beta x v_1}{v_2}\right)\partial\Delta\bar{F}_1/\partial v_2. \quad (26)$$

In Fig. 2, $-\beta\Delta\bar{F}_1/RT$ calculated from (19) when $x = 1000$ is plotted against v_2 for several

TABLE I.

v_2	a_1 (obs.) ¹⁶	a_1 (calc.)
0.95	0.20	0.13
0.90	0.36	0.25
0.80	0.57	0.45
0.70	0.73	0.60
0.60	0.86	0.73

³⁰ J. H. Hildebrand, *Solubility of Non-Electrolytes* (Chemical Catalog Company, New York, 1936), second edition, p. 65.

values of K in the neighborhood of K (critical) = 1.0644. Two scales have been used in order to cover in a single graph a broader concentration range. The character of the curves changes very rapidly with K . Since K depends inversely on the absolute temperature, these curves may be regarded as representative of a series of temperatures in the vicinity of the critical temperature for total miscibility. The corresponding curves for $-\Delta\bar{F}_2/RT$ show related characteristics, as is required by (26); the occurrence of a maximum in $\Delta\bar{F}_1$ is accompanied by a minimum in $\Delta\bar{F}_2$, and vice versa.

When K exceeds the critical value, there exists a pair of values v_2 and v'_2 which satisfies the equilibrium conditions (22). The smaller of these (v_2) will lie between zero and the maximum in $-\Delta\bar{F}_1$ plotted against v_2 , as in Fig. 2; the larger (v'_2) will lie at a concentration greater than that at the minimum in $-\Delta\bar{F}_1$. The value of $\Delta\bar{F}_1(v_2) = \Delta\bar{F}_1(v'_2)$ must necessarily be small, since $\Delta\bar{F}_1$ at the maximum in the curve is small. In fact, except when K is very near K (critical), it is permissible to set $\Delta\bar{F}_1(v'_2) = 0$ and to compute v'_2 from K using Eq. (19); $-\partial\Delta\bar{F}_1/\partial v_2$ is so large at v'_2 that the error so introduced is insignificant.

Since (19) can be solved explicitly for K but not for v'_2 , it is more convenient, having set $\Delta\bar{F}_1 = 0$ to compute K for a given value of v'_2 . That is, we may take

$$K = -2[\ln(1-v'_2) + (1-1/x)v'_2]/(v'_2)^2. \quad (27)$$

Substituting (17.1) in the second part of (22)

$$\begin{aligned} (\ln v_2)/x - (1-1/x)(1-v_2) + K(1-v_2)^2/2 \\ = (\ln v'_2)/x - (1-1/x)(1-v'_2) \\ + K(1-v'_2)^2/2, \end{aligned} \quad (28)$$

which can be solved by trial for v_2 using the above values of v'_2 and K . If necessary, a second approximation can be computed by substituting the first approximation values of K and v_2 into (19) to obtain $\Delta\bar{F}_1$, which in combination with v'_2 will yield a second approximation value for K . The second approximation value of v_2 can then be obtained from (28).

In the range where this procedure is applicable v_2 is quite small (assuming a large value of x). Replacing $(1-v_2)$ and $(1-v_2)^2$ by unity in (28), substitution therein of (27) for K , and expansion

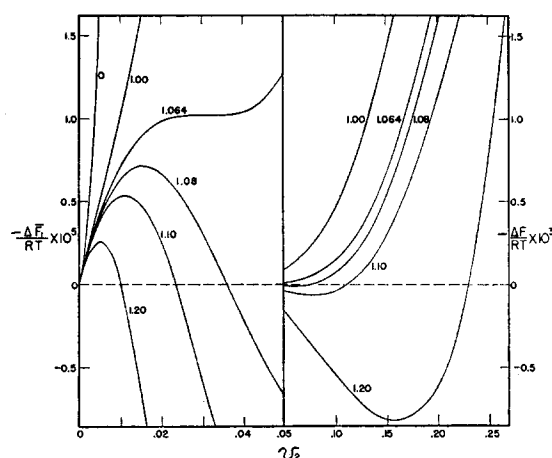


FIG. 2. Partial molal free energies as functions of the volume fraction of polymer for various values of K in the critical region for partial miscibility.

in series gives as an approximate relationship between v_2 and v'_2

$$\begin{aligned} (1/x) \ln(v'_2/v_2) = 2/x + (v'_2)^2/2 \cdot 3 \\ + (v'_2)^3 \cdot 2/3 \cdot 4 + (v'_2)^4 \cdot 3/4 \cdot 5 + \dots \end{aligned} \quad (29)$$

These procedures are unsatisfactory very near the critical point, e.g., for $K < 1.10$ when $x = 1000$. Here it is necessary to solve for K and v_2 by trial.

The curve in Fig. 3, showing v_2 and v'_2 as a function of $1/K$ when $x = 1000$, has been calculated as described above. Since the ordinate is proportional to the absolute temperature, the curve represents the calculated temperature-composition diagram. The concentration (v_2) of polymer in the solvent phase rapidly approaches a negligible value as $1/K$ decreases. This is amplified by the following calculated compositions which extend beyond the range of Fig. 3. See Table II.

Thus, the theory predicts an extremely unsymmetrical phase composition relationship. The solvent is readily soluble in the polymer even at large values of K (e.g., far below the critical temperature for complete miscibility), but the polymer will dissolve perceptibly in the solvent only very near the critical point, and then only to a small extent.¹¹

These deductions are confirmed by the work of Brönsted and Volqvartz³¹ on mixtures of various lauric acid esters with high molecular weight

³¹ J. N. Brönsted and K. Volqvartz, Trans. Faraday Soc. 35, 576 (1939); *ibid.* 36, 619 (1940).

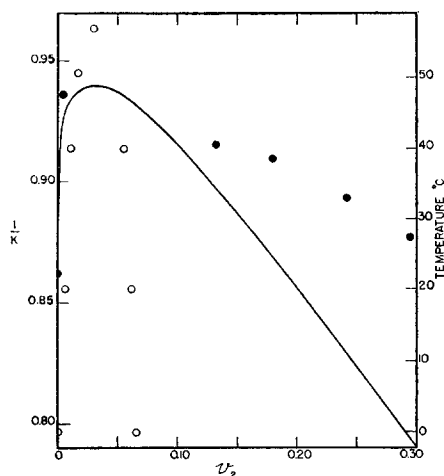


FIG. 3. Phase composition curve calculated for a solution of a polymer composed of 1000 segments. ●—*n*-propyl laurate-polystyrene, reference 31; ○—chloroform-cellulose acetate, reference 32.

(average ca. 300,000) polystyrene, which had been fractionated to remove low molecular weight constituents. Below the critical temperature for complete miscibility, none of these were observed to dissolve the polymer to an appreciable extent, although the polymer imbibed as much as several times its volume of solvent. Brönsted and Volqvartz concluded that their results were "compatible with the existence of a critical point at which the solubility of solvent in the swelled phase is infinite." Their results are also consistent with a critical value of v_2 slightly greater than zero, which would be in accord with theoretical predictions.

Brönsted and Volqvartz's data for the *n*-propyl laurate-polystyrene system are shown in Fig. 3. The temperature scale, shown on the right, has been related to $1/K$ by an arbitrary proportionality factor (340) so that the absolute temperature is proportional to $1/K$, as the definition of K requires. Results of Papkov, Rogovin, and Kargin³² on the chloroform-cellulose acetate (average molecular weight about 175,000)³³ system are also shown using the same temperature scale.

Quantitative agreement between theory and experiment cannot be expected in view of the

³² S. Papkov, S. Rogovin, and V. Kargin, *Acta Physicochim. U.R.S.S.* **8**, 647 (1938).

³³ This estimated molecular weight is based on a specific viscosity given by the above authors, and the intrinsic viscosity-molecular weight data of E. O. Kraemer, *Ind. Eng. Chem.* **30**, 1200 (1938).

various approximations which have been introduced. But the ability of the theory to predict the two outstanding characteristics of such binary systems, namely, a very low critical composition, and a high swelling capacity accompanied by negligible solubility, is a most gratifying confirmation of the validity of Meyer's model and the statistical treatment of it which has been presented here. Many of the so-called gels composed of polymers saturated with solvent doubtless owe their existence merely to this peculiarity of the temperature-composition curve, rather than to any peculiar colloidal structure, as generally has been assumed.

MOLECULAR CONFIGURATION IN POOR SOLVENTS

Staudinger and Heuer³⁴ observed that the relative viscosity of a dilute solution of polystyrene was less in a poor solvent than in a good one at the same concentration. They also found that the addition of a precipitant, e.g., ethanol, to a solution of polystyrene in a solvent such as toluene reduced the relative viscosity continuously to the point of precipitation. Staudinger and Schneiders²³ found lower viscosities for solutions of polyvinyl chloride in dioxane than in tetrahydrofuran, which their osmotic pressure results showed to be a better solvent. Similar results were obtained by Gee²² on solutions of rubber in various solvents and solvent mixtures.

The diminution of viscosities in poor solvents frequently has been attributed to decreased solvation. If by "solvation" some specific interaction between solute and solvent is meant, it is difficult to conceive of solvation in a toluene solution of polystyrene, where the van der Waals forces between like and unlike components are both similar and small. Furthermore, if solvation does occur, how can it be so markedly decreased

TABLE II.

$1/K$	v_2	v'_2
0.862	1.4×10^{-5}	0.1915
0.833	1.7×10^{-7}	0.2357
0.770	1.3×10^{-13}	0.3300
0.715	1×10^{-21}	0.407
0.625	5×10^{-42}	0.527
0.500	3×10^{-96}	0.683

³⁴ H. Staudinger and W. Heuer, *Zeits. f. physik. Chemie* **A171**, 129 (1934).

by the addition of a few cc of alcohol which has no particular affinity for either component?

When the heat of mixing of polymer and solvent is positive, i.e., in a poor solvent medium, the polymer molecules should tend to prefer more compact configurations where intramolecular contacts are more numerous. As is well known, globular or spherical polymer molecules enhance the viscosity of their solutions relatively little in contrast to the marked effects of uncoiled long polymer chains which assume more or less random configurations. Therefore, the low relative viscosities in poor solvents very probably reflect changes in average configuration of the polymer molecules, dependent upon the solvent medium. Intrinsic viscosities at incipient precipitation are of the order of one-half or less of the values for the same polymers in a good solvent medium.²² This would lead to the conclusion that the polymer molecule at the critical point pervades about the same volume as another molecule of half its chain length in a good solvent.

CONCLUSIONS

Quantitative statistical treatment of Meyer's model accounts for the following hitherto unexplained peculiar properties of high polymer solutions: (a) the shape of the partial molal free energy-composition diagram throughout the composition range (i.e., the large deviation from "ideal" entropies), (b) the virtual independence of partial pressure on molecular weight of the polymer except in dilute solutions, and (c) the extreme dissymmetry of the mutual solubility-temperature diagram and the limited high swelling capacity of linear polymers in certain media. These achievements confirm the correctness of the general point of view regarding these systems. On the other hand, quantitative agreement between calculations and observations is not particularly good, presumably due to imperfections of the model itself and to limitations of the present treatment imposed by assumption 4.

Statistical Mechanics of Nearest Neighbor Systems

II. General Theory and Application to Two-Dimensional Ferromagnets

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This is a continuation of an effort to reduce to the solution of a characteristic value problem the rigorous calculation of thermodynamic properties of systems in which the intermolecular forces are sufficiently short ranged so that practically the entire potential energy of the system results from interactions between nearest neighbors. The partition function of such a system can be expressed in terms of the largest characteristic value of a linear operator equation and finally as the ratio of partition functions of systems with relatively few particles whose potential energy functions differ somewhat from those in the original system. A method of evaluating grand partition functions and one of introducing interactions between more distant neighbors are discussed. The general theory is applied to the calculation of magnetization, internal energy, and specific heat of two-dimensional ferromagnets on the basis of the Ising model. There seems to exist a λ -point phase transition in the change from ferromagnetic to nonferromagnetic states.

I. INTRODUCTION

THE intermolecular forces in many solids are sufficiently short ranged to permit the

total potential energy of the solid to be represented by the sum of the interactions of each molecule with its nearest neighbors. With this approximation the evaluation of the potential energy contribution to the partition function and the thermodynamic properties of a solid can

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