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Thermodynamics of Dilute Solutions of High Polymers¹

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Whereas extensive efforts have been directed recently toward improving the mathematical exactness of the statistical mechanical theory of polymer solutions, fundamental limitations set by the nature of the physical approximations have not received adequate attention. A careful comparison between theory and experiment in dilute solutions reveals a large discrepancy between the calculated and the observed departures from the ideal entropy of dilution. The assumption of random occupancy of lattice sites by polymer segments, which is employed in previous treatments, is at fault. In very dilute solutions of high polymers the solution is microscopically discontinuous. Two regions of the volume can be distinguished: one is totally unoccupied by segments of polymer molecules; the other consists of regions encompassed by the irregularly coiled polymer molecules. In the latter the concentration of lattice cells occupied by polymer segments is determined

by the configuration of the polymer molecule, being independent of the over-all average concentration.

The above concepts have been employed in the formulation of a new statistical mechanical theory of the thermodynamic properties of very dilute high polymer solutions. The deviation from ideality, e.g., the slope of the osmotic pressure: concentration ratio plotted against concentration, is related to the "effective volume ratio" of the irregularly coiled solute molecule. This ratio, or "swelling factor," can be estimated from the intrinsic viscosity of the polymer. Satisfactory agreement between theory and experiment is obtained in this way. The comparatively small deviations from ideality which are observed for protein molecules, not extremely dissymmetric in shape, receive semi-quantitative interpretation under the present theory. The failure, of the van Laar expression to account for heats of mixing in polymer solutions at all concentrations is a necessary consequence of the discontinuities in the dilute region.

INTRODUCTION

THE striking "abnormalities" in the equilibrium properties of high polymer solutions are known to arise from "non-ideal" entropies, which in turn are a consequence of the extreme dissimilarity in the sizes of the molecules of solvent and solute.^{2,3} Recent statistical mechanical treatments of these mixtures⁴⁻⁸ have

met with a noteworthy degree of success in accounting for their osmotic behavior, vapor pressures, and solubility relationships. Nevertheless, definite limitations on these theories become apparent on close examination of their foundations and of their correlation with the available experimental data. The present paper is concerned with these limitations. In particular, it is concerned with the shortcomings of the existing statistical mechanical treatments in the region of low concentrations of polymer, where discrepancies between theory and experiment are greatest.

¹ Presented before the Division of Physical and Inorganic Chemistry at the 106th meeting of the American Chemical Society, Pittsburgh, Pennsylvania, September 1943.

² K. H. Meyer, *Zeits. f. physik. Chemie* **B44**, 383 (1939); K. H. Meyer and A. J. A. van der Wyk, *Helv. Chim. Acta* **23**, 488 (1940); K. H. Meyer, *Natural and Synthetic Polymers* (Interscience Publishers, Inc., New York, 1942), p. 582.

³ E. Hückel, *Zeits. f. Elektrochemie* **42**, 753 (1936).

⁴ M. L. Huggins, *J. Chem. Phys.* **9**, 440 (1941); *J. Phys. Chem.* **46**, 151 (1942); *Ann. N. Y. Acad. Sci.* **43**, 1 (1942).

⁵ P. J. Flory, *J. Chem. Phys.* **9**, 666 (1941); **10**, 51 (1942).

⁶ A. R. Miller, *Proc. Camb. Phil. Soc.* **39**, 54, 131 (1943).

⁷ W. J. C. Orr, *Trans. Faraday Soc.* **40**, 320 (1944).

⁸ E. A. Guggenheim, *Proc. Roy. Soc.* **183**, 203, 213 (1944).

COMPARISON OF THEORETICALLY DERIVED PARTIAL MOLAL ENTROPIES

The various current theoretical treatments of polymer solutions⁴⁻⁷ are based on the same idealized model, which consists of a pseudo-lattice each cell of which may be occupied either by a molecule of solvent or by an element of the chain molecule (solute) equal in size to the solvent molecule. This element will be referred to here as a segment. The chain molecule consists of a sequence of x segments, which necessarily must occupy a sequence of x consecutively adjacent cells of the lattice. It is ordinarily assumed that the segments are flexibly connected so that the $(i+1)$ th segment of the chain is free to occupy any of the z cells (where z is the coordination number of the lattice) surrounding the cell occupied by the i th segment of the chain, the one occupied by the $(i-1)$ th segment excepted of course. This assumption is unimportant in determining the thermodynamic properties of *solutions*, so long as the degree of flexibility is independent of concentration;⁴ the same equations are derived even for stiff rods totally devoid of flexibility.⁶

For the statistical treatment of the problem it is convenient to consider that the polymer molecules are successively added to the empty lattice; solvent molecules may then occupy the remaining vacant cells. The expected number of configurations available to the j th polymer molecule to be added is obtained by taking the product of the following factors: the number of locations available to the first segment of the chain, which number will be equal to the number of vacant cells in the lattice; the expected number of vacancies among the z cells⁹ surrounding a given vacant cell, which gives the expected number of cells available to the second segment; the expected number of vacant cells available to the third segment, the second having been assigned a definite location in the lattice; etc. The writer⁵ introduced the simplifying approximation that the average occupancy of the cells surrounding the cell assigned to the i th segment (and therefore known to have been a vacant cell) will be the same as the over-all concentration of polymer

segments in the entire lattice. In other words, the fact that the cell to which the i th segment is to be assigned is known to be vacant was assumed as an approximation to have no effect on the expected number of vacancies in the immediately surrounding cells. The total number of configurations of the system as a whole was obtained as the product of these expected numbers of configurations available to each successively added polymer molecule.

In this way the following equation was derived for the entropy of mixing N moles of randomly disoriented polymer molecules with n moles of solvent⁵

$$\Delta S = -R[n \ln v_1 + N \ln v_2], \quad (1)$$

where v_1 and v_2 are volume fractions of solvent and solute, respectively, i.e.,

$$v_1 = 1 - v_2 = n / (n + xN). \quad (2)$$

In accordance with previous definition x is equal to the ratio of the molar volumes of solute and solvent. The partial molal entropy of the solvent $\Delta \bar{S}_1$ is obtained by differentiating Eq. (1) with respect to n , keeping in mind that v_1 and v_2 are functions of n as given by Eq. (2).

$$\Delta \bar{S}_1 = -R[\ln(1 - v_2) + (1 - 1/x)v_2], \quad (3)$$

or

$$\Delta \bar{S}_1 = Rv_2(1/x + v_2/2 + v_2^2/3 + \cdots). \quad (3')$$

Huggins⁴ in his treatment of the problem took into account two factors admittedly neglected by the writer:⁵ (a) the exclusion of those impossible configurations in which two segments of the same chain would occupy the same cell of the lattice; and (b) the departure of the frequency of occurrence of polymer segments in cells surrounding a given cell known to be vacant (i.e., unoccupied by a polymer segment) from the over-all average concentration of polymer segments. Thus, if a given cell is known to be vacant, there is a better than average chance that a specified adjacent cell is vacant also; conversely, if a cell is known to be occupied by a polymer segment, then a neighboring cell has an enhanced probability of being likewise occupied by a polymer segment, which may belong to the same or to a different polymer molecule. With these two factors taken into account, Huggins obtained for the partial

⁹ In the present paper the more widely accepted symbol " z " has been used for the coordination number of the lattice, in place of the " γ " previously used by the writer.

molal entropy of the solvent

$$\Delta\bar{S}_1 = -R[\ln(1-v_2) - (1-1/x)(z'/2) \ln(1-2v_2/z')], \quad (4)$$

where z' is a corrected "coordination number" given when x is large by

$$z' = (z - 2f_0)/(1 - f_0), \quad (5)$$

where f_0 is the probability that a given cell adjacent to the cell occupied by the i th segment (i large) is occupied by a preceding segment of the same chain. Huggins estimated that f_0 should have a value of the order of 0.05. Hence, z' will not differ very much from z . Since z is to be employed as a semi-arbitrary parameter, it will be permissible to replace z' with z in Eq. (4), which on series expansion then becomes

$$\Delta\bar{S}_1 = Rv_2\{1/x + v_2[1 - 2(1-1/x)/z]/2 + v_2^2[1 - 4(1-1/x)/z^2]/3 + \dots\}. \quad (4')$$

When x is large no significant error is introduced by dropping higher terms in x ; hence,

$$\Delta\bar{S}_1 = Rv_2\{1/x + v_2(1-2/z)/2 + v_2^2(1-4/z^2)/3 + \dots\}. \quad (4'')$$

Miller⁶ arrived at a partial molal entropy expression practically equivalent to (4) by applying the Bethe first-order approximation method.

Recently Orr⁷ has taken into account the effect of a non-zero energy of interaction between neighboring solvent molecules and polymer segments on the thermodynamic functions for the solution. His equation for $\Delta\bar{S}_1$ consists of two terms.¹⁰ The first of these is equivalent to Huggins' Eq. (4), with z' replaced by z . The second consists of a power series in $(2w/zRT)$ where w represents the energy of interaction. In the first and dominant term of the series this quantity occurs as the square. Hence, the departures from random local mixing caused by positive as well as negative heats of mixing *increase* the entropy of dilution according to Orr's results. In the more common case where $w > 0$, corresponding to endothermic mixing, it is found (letting $z=6$) that when w is sufficiently large to make the second term in Orr's equation exceed about 10 percent of the first term (Eq. (4)), immiscibility is encountered owing to the magnitude attained by the *heat* of dilution. For

physically realizable mixtures of polymer and solvent Orr's correction for non-random local order in general is well within other limitations on the above theories (cf. seq.). Equations (1) and (4'') will therefore be employed to represent the essential results of all theories previously derived from the lattice model.¹¹

When x is large the influence of x on the partial molal entropy is appreciable only in dilute solutions. At high dilutions the $1/x$ term in each of the series expansion forms of the above equations becomes dominant, and at infinite dilution

$$(\Delta\bar{S}_1/v_2)_{v_2=0} = R/x, \quad (6)$$

which is a necessary result required of any acceptable thermodynamic function regardless of the model assumed for the mixture.

For the purpose of comparing experimental results with theory it is desirable to deduct the $1/x$ term from the above equations, since x is characteristic only of the particular polymer employed. Also, since partial molal entropy values cover such a wide range when all concentrations are to be included, for graphical representations it is preferable to employ a suitable function of the partial molal entropy rather than the partial molal entropy itself. For this purpose, therefore, we shall employ a "reduced partial molal entropy," or "RPME," defined as follows:

$$RPME = \Delta\bar{S}_1/v_2 - (\Delta\bar{S}_1/v_2)_0, \quad (7)$$

where $(\Delta\bar{S}_1/v_2)_0$ denotes the limiting value of the ratio at $v_2=0$. Substituting from Eq. (6)

$$RPME = \Delta\bar{S}_1/v_2 - R/x. \quad (7')$$

Substituting from Eq. (3)

$$RPME = -R[(1/v_2) \ln(1-v_2) + 1], \quad (8)$$

or

$$RPME = R[v_2/2 + v_2^2/3 + v_2^3/4 + \dots]. \quad (8')$$

The Huggins expression (4), with z' replaced by z , yields

$$RPME = -R[(1/v_2) \ln(1-v_2) - (1-1/x)(z/2v_2) \ln(1-2v_2/z) + 1/x], \quad (9)$$

¹¹ If z is made sufficiently large the Huggins, Miller, and Orr expressions reduce eventually to Eq. (3). This is evident from their series expansions. Contrary to statements occurring in Orr's paper, in the derivation of Eq. (3) z was not assumed to be infinite. Under the approximations there employed, z does not appear in the entropy of mixing expression; it occupies a prominent place in the entropy of disorientation function, however.

¹⁰ See Eq. (26b) of reference 7.

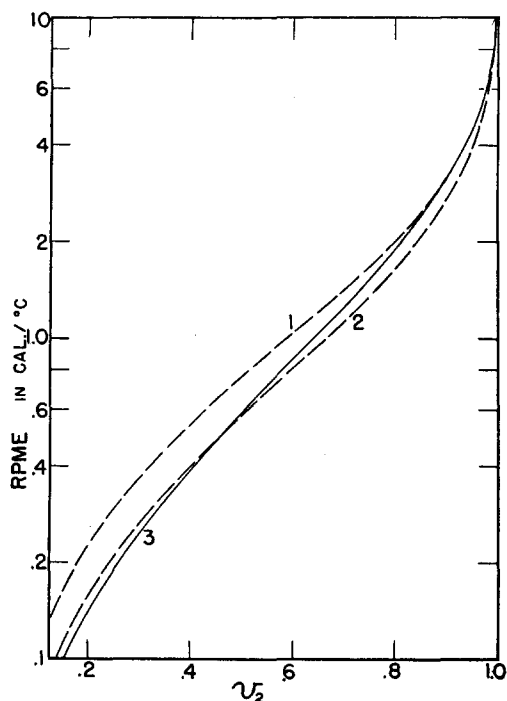


FIG. 1. Reduced partial molal entropy (log scale) vs. volume fraction of polymer for concentrated solutions. Curve 1, as calculated from (8); 2, as calculated from (9) with $z=6$; 3, experimental results for rubber in benzene.

which, in common with Miller's equation, can be expanded for large values of x to the form

$$RPME = R[v_2(1 - 2/z)/2 + v_2^2(1 - 4/z^2)/3 + \dots], \quad (9')$$

which again is independent of x .

COMPARISON OF CALCULATED AND OBSERVED PARTIAL MOLAL QUANTITIES

Entropies

The $RPME$'s calculated from Eq. (8) and from (9) with $z=6$ are plotted on a log scale against composition in Figs. 1 and 2. Experimental results of Gee and Treloar¹² on the rubber: benzene system are shown by the solid curves numbered "3" in each figure. This curve has been computed from the smoothed out partial molal entropies as given in Table VI of their paper, these being converted to calories per gram and substituted into Eq. (7). The R/x term, which is significant only at very low concentrations, has been ob-

¹² G. Gee and L. R. G. Treloar, *Trans. Faraday Soc.* **38**, 147 (1942).

tained from extrapolation of their osmotic pressure results (cf. seq.). At high concentrations the agreement with Eq. (8), based on the writer's simpler Eqs. (1) and (3), is good; at intermediate concentrations the observed entropies depart from Eq. (8), but the $RPME$ calculated from Eq. (9) with $z=6$ coincides with them fairly well; at low concentrations both calculated curves are too high. A smaller value of z would of course improve the fit at low concentrations, but only at the expense of the agreement reached at higher concentrations. Furthermore, a smaller coordination number would be unreasonable for the assumed lattice structure.

Thus, while either of Eqs. (8) or (9) has its merits at higher concentrations, neither appears to be satisfactory in dilute solutions. In the rubber: benzene system deviations from perfect random local order should be expected since the heat of mixing is appreciable, and positive. However, the resulting correction according to Orr's⁷ treatment should not be large, and if applied would actually raise the calculated curve ($z=6$), thus increasing the discrepancy. The approximate estimate of this correction for dilute solutions published recently by Doty and Alfrey¹³ likewise raises the theoretical curve farther from the observed results.

The logarithmic plots of Figs. 1 and 2 are unsatisfactory for very dilute solutions, i.e., in

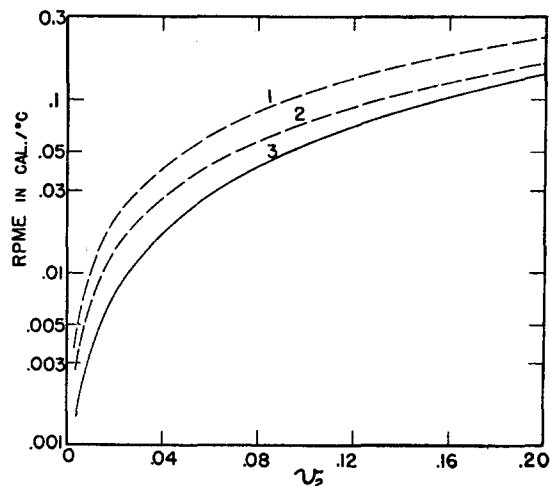


FIG. 2. Reduced partial molal entropy (log scale) vs. volume fraction of polymer for dilute solutions. Numeration of curves corresponds to Fig. 1.

¹³ P. M. Doty and T. Alfrey, *J. Chem. Phys.* **13**, 77 (1945).

the region where osmotic pressure methods are commonly employed. Here it is customary to plot an osmotic pressure:concentration ratio against concentration. In Fig. 3 the function $T(RPME)$ is plotted against concentration (v_2), this function being related to a "reduced osmotic pressure," and to the π/v_2 ratio, as follows:

$$\begin{aligned} T(RPME) &\equiv T[(\Delta\bar{S}_1/v_2) - (\Delta\bar{S}_1/v_2)_0] \\ &= -[(\Delta\bar{F}_1/v_2) - (\Delta\bar{F}_1/v_2)_0] \\ &\quad + \Delta\bar{H}_1/v_2 \\ &= V_1[(\pi/v_2) - (\pi/v_2)_0] + \Delta\bar{H}_1/v_2, \quad (10) \end{aligned}$$

where π is the osmotic pressure and V_1 is the molar volume of the solvent. The first term on the right side of (10) will be referred to as the reduced osmotic pressure. As in Figs. 1 and 2, curves 1 and 2 of Fig. 3 represent $T(RPME)$'s calculated, respectively, from Eq. (8), or (8'), and Eq. (9), or (9'), with $z=6$.

Experimental results for the following four polymer:solvent pairs are shown in Fig. 3: rubber in benzene (Gee and Treloar¹²), rubber in toluene (Meyer, Wolff, and Boissonnas¹⁴),¹⁵ polyisobutylene in cyclohexane (Flory¹⁶), and polystyrene in toluene (Schulz¹⁷).¹⁸ These particular pairs have been selected because they represent cases where either the heat of dilution term has been estimated experimentally from temperature coefficients, or the chemical similarity of solvent and solute lead to the conclusion that the heat term must be very small.

For the purpose of computing the function expressed in Eq. (10), it has been necessary first of all to assign values to $(\pi/v_2)_0$. The precise form of the π/v_2 vs. v_2 extrapolation to zero concentration has been subject to controversy. Thus, Meyer¹⁴ and co-workers draw a straight line.

¹⁴ K. H. Meyer, E. Wolff, and C. G. Boissonnas, *Helv. Chim. Acta* **23**, 430 (1940).

¹⁵ H. Staudinger and K. Fischer, *J. prakt. Chem.* **157**, 19 (1940), obtained osmotic results for toluene solutions of rubber which agree with, but apparently are less accurate than, those of Meyer and co-workers.

¹⁶ P. J. Flory, *J. Am. Chem. Soc.* **65**, 372 (1943).

¹⁷ G. V. Schulz, *Zeits. f. physik. Chemie* **A176**, 317 (1936).

¹⁸ T. Alfrey, A. Bartovics, and H. Mark, *J. Am. Chem. Soc.* **65**, 2319 (1943), carried out more extensive osmotic pressure measurements on dilute solutions of polystyrene in toluene. While their results for the dependence of π/v_2 on concentration are generally similar to those of Schulz, they concluded that the shape and slope of the π/v_2 vs. v_2 curve depended somewhat on the temperature of preparation of the polymer. The set of data given here has been chosen arbitrarily from the work of Schulz.

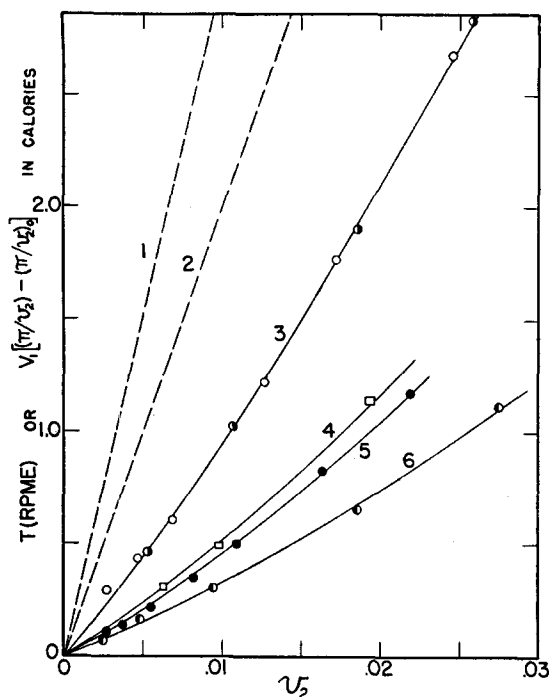


FIG. 3. $T(RPME)$, or the reduced osmotic pressure, vs. concentration in the very dilute region. Curve 1, $T(RPME)$ calculated from Eq. (8'); curve 2, calculated from Eq. (9') with $z=6$. Curve 3, $T(RPME)$ for rubber in toluene (Gee and Treloar, see reference 12): \circ 55/45 fraction, \bullet intermediate fraction. Curve 4, \square reduced osmotic pressures for rubber in toluene (Meyer, Wolff, and Boissonnas, see reference 17). Curve 5, \bullet reduced osmotic pressures for polyisobutylene in cyclohexane (Flory, see reference 16). Curve 6, \bullet reduced osmotic pressures for polystyrene in toluene (Schulz, see reference 17).

Mark and co-workers¹⁸ find the relationship to be linear when the polystyrene has been prepared above 100°, but curved upwards when prepared at 60°C. Schulz¹⁷ used his specific co-volume equation which leads to opposite curvature at very low concentrations. Gee and Treloar¹² and the writer¹⁶ find upward curvature.

For present purposes the various experimental π/v_2 values were re-plotted against v_2 , and curves were drawn through the points with an admitted predisposition favoring the postulate that the curves for all of these solutions, when experimental errors are properly eliminated, should possess similar shapes. Since the balance of the evidence favors upward curvature, all have been drawn in this fashion. The limiting values of π/v_2 obtained in this way are given in Table I, where they are compared with the author's values. The corresponding molecular weights computed from

TABLE I.

System	Source	Author's values				Values employed here				
		$(\pi/v_2)_0$ atmos.	$V_1(\pi/v_2)_0$ cal.	\bar{M}_n $\times 10^{-5}$	α cal./ mole	$(\pi/v_2)_0$ atmos.	$V_1(\pi/v_2)_0$ cal.	\bar{M}_n $\times 10^{-5}$	π $\times 10^{-3}$	α cal./ mole
Rubber:benzene (55/45 fraction)	Gee and Treloar ¹²	0.148	0.321	1.5		0.100	0.217	2.2	2.75	58
Rubber:benzene (Intermediate fraction)	Gee and Treloar ¹²	.080	.173	2.8	58 \pm 15	.050	.108	4.4	5.50	58
Rubber:toluene	Meyer, Wolff, and Boissonnas ¹⁴	.082	.212	2.7	20 \pm 10	.105	.27	2.1	2.2	Neg- lected 0
Polyisobutylene: cyclohexane	Flory ¹⁶			See Table II of reference 15						
Polystyrene:toluene (Fraction II, pre- pared at 135°)	Schulz ¹⁷	.115	.30	2.2	—	.127	.33	2.0	1.9	0

these $(\pi/v_2)_0$'s are also given. The curvature assigned to these plots is less than Gee and Treloar assumed at very low concentrations; hence our $(\pi/v_2)_0$'s are lower, and average molecular weights are higher, than theirs. In other cases assignment of upward curvature has raised $(\pi/v_2)_0$ somewhat, thus lowering \bar{N}_n . The precise value of $(\pi/v_2)_0$ is only of secondary importance here; a change in its value would merely shift the ordinate for each point of a given set in Fig. 3 by the same amount.

Except in the case of the rubber in benzene results, the quantity $V_1[(\pi/v_2) - (\pi/v_2)_0]$, obtained by deducting the $(\pi/v_2)_0$ values of Table I from observed (π/v_2) 's, is plotted directly in Fig. 3. In other words the $\Delta\bar{H}_1/v_2$ term of Eq. (10) has been neglected. Hence, curves 4, 5, and 6 are representative of the conventional π/v_2 vs. v_2 plots except that $(\pi/v_2)_0$ has been deducted from each ordinate, bringing the intercepts for all curves to the origin. This neglect of $\Delta\bar{H}_1$ assuredly is well justified for the polyisobutylene-cyclohexane and the polystyrene-toluene solutions, in consideration of the equivalence of cohesive energies of solvent and solute for each pair. Measurements of the temperature coefficient of osmotic pressures of rubber:toluene solutions by Meyer and co-workers¹⁴ yield approximate heats of dilution, which when substituted in the van Laar expression

$$\Delta\bar{H}_1 = \alpha v_2^2, \quad (11)$$

lead to an α which is roughly equal to 20 cal. per mole (see Table I). If the $\Delta\bar{H}_1/v_2$ term of Eq. (10) had been included, with $\Delta\bar{H}_1 = 20v_2^2$, curve 4

would have been raised to a position between curves 3 and that now occupied by curve 4.

Results of Wolff¹⁹ and of Staudinger and Fischer¹⁵ on dilute solutions of gutta-percha in toluene agree in placing the reduced osmotic pressure curve very slightly above curve 4 of Fig. 3. Gutta-percha, being a configurational isomer of rubber hydrocarbon, would be expected to mix with toluene with the same heat effect. However, Wolff¹⁹ concluded from the temperature coefficients of the osmotic pressure that the heat of mixing is approximately zero; i.e., $\alpha = 0 \pm 10$ cal. Hence, the $T(RPME)$ curve for gutta-percha is indicated to lie close to curve 4. The difference between the indicated values of α for rubber and for gutta-percha in toluene is not beyond the combined experimental errors, and it is possible that the $T(RPME)$ curves for both isomeric polymers lie near curve 4, or at any rate not far above it.²⁰

The points along curve 3 of Fig. 3, depicting Gee and Treloar's¹² osmotic pressure results for rubber in benzene, represent $T(RPME)$'s computed in accordance with (10) from observed reduced osmotic pressures and a heat term calculated from the value of α (Table I) indicated by the temperature coefficient of osmotic pressure. Considering the experimental error in these

¹⁹ E. Wolff, *Helv. Chim. Acta* **23**, 439 (1940).

²⁰ According to the results of Staudinger and Fischer (see reference 15), the π/v_2 vs. v_2 curves for toluene solutions of a series of polybutadienes ranging from 54,000 to 440,000 in molecular weight are substantially parallel. When $(\pi/v_2)_0$ values are deducted, these results fall very near to curve 4 of Fig. 3. If the reasonable assumption is made that the heat of dilution is negligible, curve 4 can be considered to represent $T(RPME)$ for the polybutadiene:toluene system also.

heats of dilution it is evident that the position of curve 3 for rubber:benzene is subject to at least as much uncertainty as are curves 5 and 6 for polyisobutylene:cyclohexane and polystyrene:toluene where no experimental estimates of α are available, but where chemical similarity of solvent and solute leads to the expectation of an α very nearly zero.

The most striking feature of Fig. 3 is the decidedly lower slopes of the experimental curves as compared with those calculated from theory. Comparing initial slopes, that for the rubber:benzene curve 3 is less than half the slope of calculated curve 2 ($z=6$); the other slopes are from four to six times lower than this calculated slope. To bring about approximate agreement between Eq. (9') and curve 3 it would be necessary to reduce z to a value less than three; for the other solutions z would have to assume values less than 2.5. A lattice coordination number so low is inconceivable. If a value of this magnitude is accepted, the basic concept of a lattice composed of an array of cells is undermined.

The apparent curvature of these plots is also a significant, though much less disturbing, discrepancy. The above theory predicts a relationship which is very nearly linear, aside from the minor contribution of higher terms in the series expansion (see Eqs. (8') and (9')).

Heats of Dilution

If it is assumed that only interactions between nearest neighbors are important, then, as Orr⁷ has shown most convincingly, the lattice theory leads to a heat of mixing of the van Laar form. The partial molal heat of dilution, consequently, should conform with Eq. (11). Gee and Treloar¹² found, however, that the observed partial molal heats of dilution could not be reconciled with (11) at all concentrations. Their values of $\Delta\bar{H}_1$, and the α 's calculated from them, are given in Table II. Although the uncertainty in any single determination is relatively large, a much greater discrepancy between the indicated α 's for low and for high concentrations is well established by these results.

Partial Molal Free Energies

Combining the lattice theory Eqs. (4) and (11) for the partial molal entropy and heat of dilution,

respectively, there is obtained for the partial molal free energy

$$\Delta\bar{F}_1 = RT[\ln(1-v_2) - (1-1/x)(z/2) \ln(1-2v_2/z)] + \alpha v_2^2.$$

Expanding the second logarithm in series and discarding terms beyond the second, Huggins⁴ simplified this equation to

$$\Delta\bar{F}_1 = RT[\ln(1-v_2) - (1-1/x)v_2 + \mu v_2^2], \quad (12)$$

where

$$\mu = 1/z + \alpha/RT. \quad (13)$$

Equation (12) is also obtained directly from Eqs. (3) and (11), except that μ is then to be redefined omitting the $1/z$ term of (13).

Huggins^{4,21-23} has shown that published data on solutions of high polymers agree quite well with Eq. (12) when suitable values of μ are chosen. Only in the case of the rubber:benzene solutions do the available data extend beyond the dilute, or moderately dilute, region. The partial molal free energies¹² of benzene in this system for $v_2 > 0.02$ lead to μ values of 0.40 ± 0.03 , the variation being not greater than the probable experimental error. At very low concentrations ($v_2 < 0.02$), an increase in μ is indicated by the experimental data.²⁴ The above value of μ is very nearly equal to α/RT at high concentrations (see Table II), the contribution of $1/z$ in Eq. (13) being negligible. This is merely a reiteration of the previously noted agreement of the simpler

TABLE II. Heats of dilution for rubber:benzene solutions. (From Gee and Treloar.¹²)

v_2	$\Delta\bar{H}_1$ (cal./mole)	α
0.0127	$1.25 (\pm 0.6) \times 10^{-2}$	78
0.0172	$1.8 (\pm 0.4) \times 10^{-2}$	61
0.0210	$2.3 (\pm 0.8) \times 10^{-2}$	52
0.0245	$3.1 (\pm 1.5) \times 10^{-2}$	52
0.77	$150 (\pm 80)$	250
0.915	$190 (\pm 80)$	230
0.95	$210 (\pm 80)$	230
0.99 to 1.00	$390 (\pm 80)$	390

²¹ M. L. Huggins, J. Am. Chem. Soc. **64**, 1712 (1942); Ann. N. Y. Acad. Sci. **44**, 431 (1943).

²² M. L. Huggins, Ind. Eng. Chem. **35**, 216 (1943).

²³ M. L. Huggins, Ind. Eng. Chem. **35**, 980 (1943).

²⁴ It is unnecessary to include here a detailed analysis of the agreement between Eq. (12) and various sets of experimental results. This has been thoroughly covered by Huggins (see references 21, 22, and 23). See in particular Fig. 9 of reference 22.

theoretical Eq. (3) with experimental partial molal entropies at high concentrations. At lower concentrations α diminishes, according to the results quoted in Table II, but μ remains approximately constant. Hence, it is necessary to re-formulate μ as follows:

$$\mu = \beta + \alpha/RT, \quad (14)$$

where β is an empirical quantity which, in common with α , varies with composition; α retains the definition inherent in Eq. (11). Thus, in spite of the failure of both the theoretical entropy and heat functions separately, when combined in the free energy function a surprisingly close approximation to the observed results for rubber in benzene is obtained. This agreement is attained, however, by assigning to μ an arbitrary value which at lower concentrations does not accord with the theoretically derived μ of Eq. (13).

In other polymer:solvent systems it is likewise necessary to throw the burden of μ on β in dilute solutions. If the mixture is more nearly athermal than the rubber:benzene solution, α will be small at all concentrations, and a marked decrease in μ with increasing concentration can be expected. Further experimental data covering a wide range of concentrations are needed to clarify this point.

A NEW THEORY FOR DILUTE SOLUTIONS

In the derivation of Eq. (3) it was assumed⁵ that, with respect to any given polymer molecule to be added to the lattice, those previously added occupy a random distribution of occupied sites. In Huggins' derivation⁴ of Eq. (4) this random distribution was appropriately modified only

insofar as immediate lattice neighbors are concerned (see (b) on page 454). That is, in seeking the number of available sequences of x sites in the lattice which remain vacant and hence could be occupied by the molecule in question, it has been assumed that segments of the molecules previously added are distributed essentially at random, rather than in continuous sequences of x consecutively adjacent cells. In sufficiently concentrated solutions the molecules will be intertwined to such an extent that no long range departures from this assumed random distribution of occupied sites are to be expected. Hence, the above assumption, inherent in the theories examined above, should be inconsequential here.

In very dilute solutions this assumption is totally invalid for solutes composed of very long (large x) flexible molecules. Each polymer molecule occupies a sequence of x sites in the same locality. Between these regions all sites are vacant. The very dilute solution, therefore, consists of two regions, one completely unoccupied by solute and the other possessing an average "concentration" of occupied sites determined by the statistical configuration of the polymer chain and independent of the over-all average concentration of polymer. As the concentration is increased the extent of the former region is decreased and the latter is increased.

This concept of a dilute solution of randomly coiled polymer molecules is illustrated in Fig. 4. The actual domain pervaded by a polymer chain is not sharply defined. For the purpose of carrying out an approximate treatment, it will be assumed that each molecule is distributed within an effective volume of radius A . All molecules are assumed to be of the same size. As a convenient approximation it is assumed further that within the sphere of radius A the average concentration of polymer segments is radially uniform, i.e., independent of the distance from the center. Then if the swelling factor s is defined as the ratio of lattice cells within the sphere of radius A to the number x of polymer segments

$$(4/3)\pi A^3 = sxV_1$$

where V_1 is the molecular volume of the solvent, the volume fraction of polymer within the sphere is $1/s$. For a large, randomly coiled

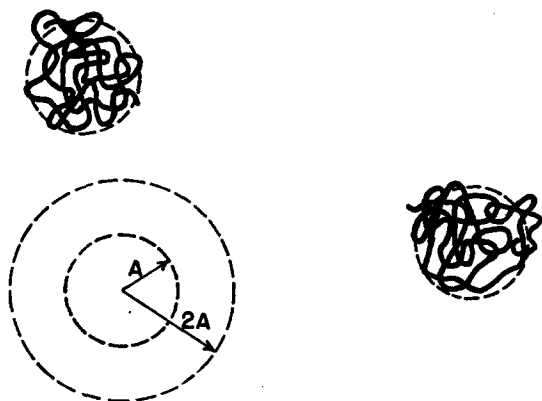


FIG. 4. Diagrammatic representation of an extremely dilute solution of an irregularly coiled long chain polymer.

polymer molecule $1/s$ will be small—of the order of .05 or less.

It can be shown as follows that the molecules will tend to avoid overlapping in spite of the fact that the concentration of segments $1/s$ is small within the domain of radius A occupied by a molecule. The probability that an arbitrarily chosen sequence of j vacant sites ($j \leq s$) exists within a sphere occupied by a molecule, and hence is available for occupancy by j segments of another molecule, is $(1 - 1/s)^j$. Although $1/s$ may be quite small, the above factor becomes small when j exceeds s . Since s is generally much smaller than x , it is clear that a considerable degree of overlapping, corresponding to a j value which is a considerable fraction of x , will be discouraged by the adverse statistical factor given above. Hence, to a first approximation the molecule will not overlap so long as unoccupied space is available elsewhere in the lattice. In the treatment which follows overlapping nevertheless is taken into account in an approximate manner.

If N polymer molecules have been added to the lattice previously, then the number of configurations, ν_{N+1} , available to the next molecule to be added can be expressed in two separate terms: the number ν'_{N+1} of available configurations in which the domain of the $(N+1)$ th molecule does not overlap that of any other, and the ν''_{N+1} available configurations in which some degree of overlapping does occur. Each of the N molecules blocks out a volume of radius $2A$ in which the center of another molecule cannot be placed without encountering overlapping. The total volume blocked out by N molecules poses a difficult geometrical problem owing to the fact that the regions distant A to $2A$ from the centers of different molecules may overlap freely. Here we neglect this factor and simply express the volume (more accurately, the number of lattice cells) which the center of the $(N+1)$ th molecule may not enter without introducing overlapping of its domain (radius A) with that of another previously added molecule as

$$4\pi(2A)^3 N/3 = 8sxN. \quad (15)^{26}$$

²⁶ A somewhat better approximation probably is obtained by setting the blocked out volume equal to

$$8sxN[1 - q(1 - q/8)sxN/n_0]$$

where q is the ratio of the total volume to the actual volume

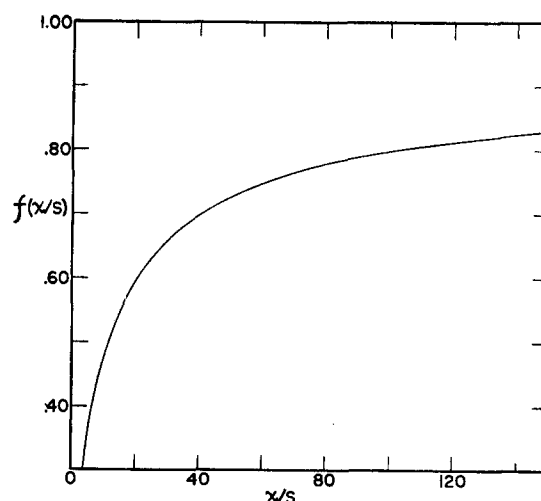


FIG. 5. The function $f(x/s)$ as computed from (19).

Since there will be $n_0 - 8sxN$ lattice sites available to the center of the $(N+1)$ th molecule such that no overlapping will occur,

$$\nu'_{N+1} = (n_0 - 8sxN)(z-1)^{x-1}. \quad (16)^{26}$$

If the center of the $(N+1)$ th molecule falls on one of the $8sxN$ (according to the above assumption) lattice sites which lies at a distance $a < 2A$ from the center of a previously added molecule, the two molecules will jointly occupy a volume

$$V_J = (sxV_1)(y^3 - 3y + 2)/2, \quad (17)$$

where $y = a/2A$. Within this region of joint occupancy the expected number of sites available to each consecutive segment of the $(N+1)$ th molecule is reduced to $(1 - 1/s)(z-1)$ owing to the concentration $1/s$ of segments of the other molecule; for segments falling outside this region the factor is of course $(z-1)$. Hence

$$\nu''_{N+1} = N \sum_{8sx \text{ cells}} [(z-1)^{x-1} (1 - 1/s)^{(x-1)V_J/sxV_1}].$$

Replacing the summation by an integral and

of close packed, non-interpenetrating spheres. Thus, when the concentration of polymer is extremely small the above function is equivalent to (15). In contrast to (15), however, the blocked out volume according to this expression does not reach the total volume, represented by the total number of cells n_0 , until $sxN = n_0/q$. The value of q should be 1.35 to 2.0.

Substitution of this expression in place of Eq. (15) does not appear to alter the essential character of the results obtained. Only the second and higher terms of the series in Eq. (22') are lowered somewhat.

²⁶ The symmetry factor, $\frac{1}{2}$, to account for the twofold symmetry of the linear polymer molecule is here omitted.

substituting from Eq. (17)

$$\nu''_{N+1} = 8sxN(z-1)^{z-1}[1-f(x/s)], \quad (18)$$

where

$$f(x/s) = 1 - \int_0^1 (1-1/s)^{(x-1)(y^3-3y+2)/2} 3y^2 dy$$

which for large values of s reduces, approximately, to

$$f(x/s) = 1 - \int_0^1 [\exp(-x/2s)]^{(y^3-3y+2)/2} 3y^2 dy. \quad (19)$$

In Fig. 5 $f(x/s)$, computed by graphical integration of (19) for various values of x/s , is plotted against x/s . An asymptotic increase toward unity is indicated.

Combining Eqs. (16) and (18)

$$\nu_{N+1} = \nu'_{N+1} + \nu''_{N+1} = (z-1)^{z-1}(n_0 - gxN), \quad (20)$$

where $g = 8sf(x/s)$. The total number of configurations for N polymer molecules in the lattice composed of n_0 cells is given by

$$\begin{aligned} W &= (1/N!) \prod_{N=1}^N \nu_N \\ &= (1/N!)(gx)^N (z-1)^{N(z-1)} \prod_{N=1}^N \left[\frac{n_0}{gx} - (N-1) \right] \\ &= (1/N!)(gx)^N (z-1)^{N(z-1)} \\ &\quad \times (n_0/gx)! / [(n_0/gx) - N]!. \end{aligned}$$

Introducing the Boltzmann relationship $\Delta S/R = \ln W$ and replacing factorial terms with their Stirling approximations

$$\begin{aligned} \Delta S/R &= N[\ln(gx/N) + (x-1)\ln(z-1)] \\ &\quad + (n_0/gx)\ln(n_0/gx) \\ &\quad - [(n_0/gx) - N]\ln[(n_0/gx) - N]. \quad (21) \end{aligned}$$

If n_0 is replaced by its equivalent $n + xN$ in the above expression for the entropy of mixing, which is then differentiated with respect to n , there is obtained for the partial molal free energy

$$\begin{aligned} \Delta \bar{S}_1/R &= -(1/gx)\ln[1 - gxN/(n + xN)] \\ &= -(1/gx)\ln(1 - g\nu_2) \\ &= \nu_2[1/x + (4sf/x)\nu_2 \\ &\quad + (64s^2f^2/3x)\nu_2^2 + \dots]. \quad (22') \end{aligned} \quad (22)$$

In the series expression (22') g has been replaced by $8sf$, with f representing $f(x/s)$. When the heat of mixing can be neglected, the reduced osmotic

pressure function becomes

$$\begin{aligned} V_1[(\pi/\nu_2) - (\pi/\nu_2)_0] &= T(RPME) \\ &= RT[(4sf/x)\nu_2 + (64s^2f^2/3x)\nu_2^2 + \dots]. \quad (23) \end{aligned}$$

From Eq. (22) it is clear that the present treatment is limited to concentrations such that $g\nu_2$ is considerably less than unity, i.e., to dilutions such that only a small fraction of the volume is encompassed by the randomly coiled molecules. Hence, the treatment is essentially limited to the range where higher terms of Eq. (22') are small compared to the first. For athermal solutions this corresponds to the region where π/ν_2 is only fractionally greater than $(\pi/\nu_2)_0$. Here we shall be concerned only with the second term of Eq. (22'), or the first term of Eq. (23), which predicts the initial slope for a π/ν_2 vs. ν_2 plot, or for a plot such as the one shown in Fig. 3. In consideration of the approximate nature of the theory on the one hand and the experimental difficulties attending accurate determination of the shape of the π/ν_2 vs. ν_2 plot in the very dilute region, higher terms will be disregarded.²⁷

COMPARISON OF THE NEW THEORY FOR DILUTE SOLUTIONS WITH EXPERIMENT

Dilute Solutions of Irregularly Coiled Long Chain Polymers

A test of the above equations requires an independent estimate of s , the ratio of the effective to the actual molecular volume. According to Kuhn's²⁸ interpretation of viscosities in dilute polymer solutions, it is possible to estimate an effective volume for the dissolved polymer molecule from the viscosity increment, or intrinsic viscosity, of the solution. Kuhn considers that when the chain length is great²⁹ solvent within the region occupied by the randomly coiled molecule moves with the molecule as a unit. If the rate of shear is not too great, the molecule plus "enclosed" solvent affects the viscosity in much

²⁷ When the somewhat better approximation mentioned in footnote 25 is employed, the first and second term of the series expansion obtained for $\Delta \bar{S}_1/R$ are identical with those of Eq. (22'), while higher terms are reduced. The range of convergence is therefore extended to higher concentrations. This suggests that the first two terms of Eq. (22') may be valid over a somewhat greater concentration range than the above equations alone would indicate.

²⁸ W. Kuhn, *Kolloid Zeits.* **58**, 2 (1934); **49**, 959 (1936).
²⁹ W. Kuhn and H. Kuhn, *Helv. Chim. Acta* **26**, 1394 (1943).

TABLE III. Comparison of observed initial slopes for the $V_1(\pi/v_2)$ vs. v_2 curve with those calculated from the theory for dilute solutions.

Polymer designation	Polyisobutylene in cyclohexane ¹⁸ B (9-13)	Polyisobutylene in cyclohexane ¹⁸ C (4-9)	Polystyrene in toluene; ¹⁷ 135° polymer fraction II
\bar{M}_n	78,000	256,000	200,000
x	780	2560	2000
$[\eta]$	0.70*	1.45*	1.03
s from Eq. (24)	26	54	43
x/s	30	47.5	46.5
$f(x/s)$ from Fig. 5	0.66	0.72	0.72
Slope calc'd.	53	36	37
$RT(4sf/x)$, cal.			
Observed slope, cal.	38	38	31

* The intrinsic viscosities of these samples were not published; the above intrinsic viscosities have been calculated from their molecular weights and the known intrinsic viscosity-molecular weight relationship in cyclohexane.

the same way as would a suspended rigid sphere. Then, according to Einstein's equation

$$\eta_r - 1 = 2.5v_2',$$

where η_r is the relative viscosity and v_2' is the volume fraction of suspended spheres. Setting $v_2' = sv_2$

$$(\eta_r - 1) = 2.5sv_2$$

and converting to intrinsic viscosity

$$[\eta] \equiv [(\eta_r - 1)/c]_{c \rightarrow 0} = 0.025s/\rho, \quad (24)$$

where c is the concentration of polymer in g. per 100 ml and ρ is the density of the polymer. The value of s computed from the intrinsic viscosity using Eq. (24) may not, of course, necessarily correspond to the effective volume ratio of concern here; the former is a kinetically determined quantity while the latter relates to an equilibrium property. Presumably these effective volumes should at least be similar in magnitude, however.

In Table III several examples are given to illustrate the calculation of the π/v_2 vs. v_2 slope term, $4RTsf/x$ according to (23), from the "viscosity" s value. The calculated slopes are in remarkably good agreement with those observed. The differences are scarcely greater than the experimental error on the one hand, and on the other they are well within the limits imposed by the approximations in the development of the theory.

The slope term calculated as above is found to decrease slowly with increase in molecular weight.

This can be shown as follows. Since s is proportional to the intrinsic viscosity and the intrinsic viscosity generally depends on about the two-thirds power of the molecular weight¹⁶ (i.e., $x^{\frac{2}{3}}$), x/s should vary approximately as $x^{\frac{1}{3}}$. In the slope term, $4fs/x$, the change in x/s with x is partially, but not entirely, offset by the increase in f with x/s (see Fig. 5). The net predicted decrease in slope of the π/v_2 vs. v_2 plot with molecular weight is quite small, and, in view of the approximate nature of the theory, may not necessarily be significant. Nevertheless Gee and Treloar¹² have reported a decrease in the slope with molecular weight for the rubber:benzene system, in support of this prediction. The writer¹⁶ failed to observe a change in initial slope with molecular weight for polyisobutylene in cyclohexane, perhaps owing to the failure to extend accurate osmotic pressure-concentration measurements over a sufficiently extended molecular weight range.

The Heat of Dilution in Dilute Solutions

If there were no overlapping of the regions occupied by the polymer molecules there would be virtually no heat change on dilution with additional solvent; $\Delta\bar{H}_1$ would equal zero in the very dilute solution regardless of the nature of the interactions between like and unlike components. Actually some overlapping will occur, and its extent presumably will vary in proportion to the concentration. Where overlapping occurs the number of polymer-to-polymer contacts will be increased while the number of solvent-to-polymer contacts are decreased. Hence, the heat of mixing should assume the form

$$\Delta H = \Delta H_0 - (\text{const.}) \times v_2,$$

where ΔH_0 is the heat of mixing N polymer molecules with an infinite amount of solvent. Upon differentiating with respect to moles of solvent, an expression of the van Laar form, Eq. (11), is obtained for the partial molal heat of dilution. When the concentration is so increased that the molecules necessarily overlap extensively, this derivation no longer holds. Eventually at high polymer concentrations the proportion of polymer:polymer contacts, as compared to polymer:solvent contacts, will approximate that

prevailing in a solution of a monomeric analog of the polymer at the same volume concentration. Here the heat of dilution for the polymer solution may again be expected to follow the van Laar formula, but with a different value of α .

It is also evident from the above discussion that the proportion of polymer-to-polymer contacts in a dilute polymer solution will be much less dependent on concentration, and hence $\Delta\bar{H}_1$ will be smaller in magnitude, than in the case of a solution containing a monomeric solvent at the same actual volume concentration. Consequently, α should be correspondingly much smaller in dilute polymer solutions. In more concentrated solutions it should assume a value more nearly that to be expected for random mixing of a monomeric solute with solvent. Thus, the large change in the apparent α 's in passing from dilute to concentrated solutions of rubber in benzene¹² (see Table II) is readily explained in the light of the discontinuous character of dilute polymer solutions.

Compact Polymer Molecules (Proteins) in Solution

Results obtained with the ultracentrifuge show that protein molecules are "globular" in solution. In contrast with synthetic high polymers, rubber and cellulose derivatives, the native protein molecules assume a definite, fairly compact form in solution, not highly swollen by solvent (water). Their intrinsic viscosities are small—around 0.05—in harmony with this conclusion. Hence, s should be small, having a value from one to not over three at the most.

When s is small Eq. (22), or (22'), predicts only a very gradual departure from van't Hoff's law with increasing concentration. This is actually observed to be the case for solutions of undenatured proteins near their isoelectric points.^{30,31} In fact, by suitably choosing s values in the range from one to two, the observed osmotic pressures³¹ of hemoglobin, serum albumin, myogen, and casein are well duplicated by Eq. (22), or (23), up

to concentrations of ten or twenty percent. These values of s are precisely in the range to be expected according to the known character of the protein solute. Denaturation, which is believed to involve unfolding of the polypeptide chain, is accompanied both by an increase in intrinsic viscosity and by an increase in the departure from van't Hoff's law,³¹ both corresponding to an increase in s .

Although native protein molecules generally are somewhat ellipsoidal, those mentioned above probably do not depart from sphericity sufficiently to invalidate correlation with the theory here developed. Thus, the character of the deviation from van't Hoff's law can be used as a criterion of the nature of the dissolved protein particle.

Thermodynamics of Highly Swollen Gels

Insoluble polymers having a loose network structure (e.g., a very lightly vulcanized rubber) will swell in suitable solvents to the extent that they become dilute polymer "solutions," although they will not disperse as solutions in the ordinary sense. With low degrees of cross-linking, or branching, the gel at equilibrium with excess solvent may contain no more than two percent polymer. Owing to the permanence of the network structure, the polymer chains are prevented from segregating from one another entirely. Hence, the discontinuities of the dilute polymer solutions previously discussed will be suppressed, although not necessarily entirely eliminated, in swollen network gels. The theories developed previously perhaps may be more appropriately applied to swollen gels³² than to finite (soluble) polymers. In support of this view a value of μ equal to about 0.3 has been indicated for vulcanized butyl rubber (essentially cross-linked polyisobutylene) swollen in cyclohexane,³³ for soluble polyisobutylene in the same solvent¹⁶ $\mu = 0.41$.²³

SUMMARY AND CONCLUSIONS

Previous statistical mechanical treatments of polymer solutions have been compared. All of them stem from similar concepts regarding the

³⁰ See for example the results of G. S. Adair, *Proc. Roy. Soc. 120A*, 573 (1928), on osmotic pressures of aqueous hemoglobin.

³¹ For a summary including other proteins, see *The Chemistry of Amino Acids and Proteins*, edited by C. L. A. Schmidt (C. C. Thomas, Publishers, Springfield, Illinois, 1944), Chapter VIII by D. M. Greenberg.

³² P. J. Flory and J. Rehner, Jr., *J. Chem. Phys.* **11**, 521 (1943).

³³ P. J. Flory, *Chem. Rev.* **35**, 51 (1944).

physical constitution of solutions of long chain molecules; their results consequently are similar. While they predict partial molal entropies in good agreement with observations at high concentrations of polymer, large discrepancies are noted in dilute solutions; the predicted deviations from Raoult's law are several-fold too large at concentrations of several percent or less.

The assumption of random occupancy of lattice sites by polymer segments, which is inherently a part of the previous treatments of polymer solution statistical mechanics, has been shown to be at fault at high dilutions. Here the solution is decidedly discontinuous. Loose clusters of segments, corresponding to individual polymer molecules, occupy separate regions of the volume. Between them the medium consists of pure solvent.

A new theory based on this concept has been developed. The deviation from ideality is found to be a function of the "effective volume ratio" or "swelling factor" s , which represents the ratio of the volume of the solution pervaded by a polymer molecule to its actual molecular volume. For a long, flexible chain molecule in solution, s will be large; it can be estimated from the intrinsic viscosity. Initial slopes of the π/v_2 (osmotic pressure:concentration ratio) *vs.* v_2 plots for hydrocarbon polymers in non-polar solvents calculated from "viscosity" s values in accordance with the new theory for dilute solutions are in remarkably good agreement with experiment. The theory also predicts a very small decrease in this slope with increase in molecular weight.

Solutions of native proteins deviate very slowly from van't Hoff's law with increase in concentration. This is to be expected according to the present theory, owing to the compact form of the protein molecule in solution. Hence a new method for characterizing the form of the protein molecule in solution is suggested. Existing data for proteins such as hemoglobin and serum albumin indicate s values in aqueous solutions between one and two.

The segregation which exists in dilute solutions also affects the partial molal heat of dilution $\Delta\bar{H}_1$. In dilute solutions $\Delta\bar{H}_1$ is smaller than

would be the case for random mixing of the separate segments. A single van Laar heat of mixing expression will not hold for all concentrations.

Unfortunately, the present treatment of entropies of mixing is limited (except for compact solutes such as proteins) to extremely dilute solutions ($sv_2 \ll 1$), and no means for integrating it with the previous theories applicable at higher concentrations is yet apparent. It is obvious, however, that discontinuities in polymer segment occupancy of the cells of the liquid lattice will persist well beyond the concentration at which polymer molecules encompass almost the entire volume (which may occur at concentrations of several percent, depending of course on the intrinsic viscosity). Eventually these discontinuities virtually disappear as the concentration is further increased. At concentrations beyond 20 to 30 percent polymer the previous theories give a reasonably good account of the facts.

Various attempts at improvement of the mathematical exactness of these previous theories have been published⁶⁻⁸ recently. However, in the opinion of the writer it is doubtful that the assumptions inherent in the idealized lattice model warrant these refinements. The simpler theoretical treatment⁵ by means of which the relatively tractable entropy of mixing expression (1) was derived is well within the bounds of these physical approximations in the assumed model.³⁴

In spite of the divergence in dilute solutions from the previously derived partial molal entropy and heat of dilution expressions, when these are combined a free energy function is obtained which, as Huggins²¹⁻²³ has shown, is empirically acceptable through the dilute solution range, and in one instance (rubber in benzene) at all concentrations. The present work serves to clarify to some extent the semi-empirical character of the single parameter μ contained in this free energy function. In spite of the approximate constancy of μ for rubber in benzene at all concentrations, it is unlikely that this condition applies to high polymer solutions generally.

³⁴ See also P. J. Flory, J. Chem. Phys. 12, 425 (1944).