gested that these bands result from the NH and NH_2 radicals, respectively. In connection with the suggestion that NH_2 radicals are present in the blue material, we have failed to find any trace of hydrazine in the warmed up product and have concluded that if NH_2 radicals are present, it can be present only in very minute concentration.

Originally[2] we thought that hydrazoic acid underwent a primary decomposition according to the equation $HN_3 \rightarrow N_2 + NH$ and much of the NH reached the color finger and was frozen either as a monomer, a polymer or a mixture of these. The ammonium azide was supposed to be formed at the transition temperature of the blue material since ammonium azide may be written $(NH)_4$. More recent work in this Laboratory on mass balances indicates that the NH radical builds up to ammonia in the furnace and the ammonia on reaching the cold finger combines with undecomposed hydrazoic acid to form ammonium azide. The stoichiometry of the decomposition is in agreement with this supposition so that the substance giving the blue color can be present in only small amount. Both Mador and Williams,[9] as well as Becker, Pimentel and Van Thiel,[8] observed that the amount of ammonium azide present did not increase on warming.

To sum up, we do not yet even after some ten years of intensive work have any proof of the constitution of the blue material. We have even examined the possibility that electrons might be trapped in the ammonium azide and that we might have a phenomenon analogous to f-centers,[10] but we could find no evidence for this.

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Thermodynamics of Polymer Solutions. The Polystyrene–Cyclohexane System near the Flory Theta Temperature

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Solvent activities for the polystyrene–cyclohexane system were obtained over the entire concentration range by combining osmotic pressure, isothermal distillation and differential vapor pressure measurements. Three fractionated polymer samples were examined, and data were obtained at three temperatures. At the theta temperature the solutions behave more ideally than would be expected from the Flory lattice model equation, hence a minimum of two χ parameters is required to represent the activity, even at low polymer concentrations. Both the second and third virial coefficients vanish at theta, since $\chi_2 = {}^1/_2$ and $\chi_3 = {}^1/_3$ at this temperature. The ribbon model treated by Tompa furnishes a reasonable representation of the observed entropies of dilution for volume fractions up to 0.35. At higher concentrations both the heat and entropy of dilution increase rapidly, the latter exceeding the values computed according to the Flory lattice model for $v_2 > 0.6$, while the free energy of dilution follows a more normal course.

During the past fifteen years a growing interest has developed in the application of statistical mechanics to the problem of the thermodynamic behavior of polymer solutions. Paralleling this interest in obtaining a satisfactory theoretical description of polymer solution thermodynamics, there has been a continuing effort to obtain reliable activity measurements for polymeric systems. Although the majority of these studies have been concerned with dilute solutions, activity measurements covering a considerable portion of the concentration range have been obtained in several instances.[1-10] Most of the systems investigated have involved thermodynamically good solvents for the polymer. In the low concentration region one anticipates systematic deviations from the behavior predicted by the lattice model treatments due to the appearance of excluded volume effects. On the other hand, activity measurements performed under Flory theta conditions[11] would allow a test of the treatments based upon the lattice model over the entire concentration range. In addition, such measurements would provide information concerning the behavior of the higher virial coefficients which would be useful as a check on the validity of the theoretical treatments of dilute solutions.

With these objectives in mind, we have undertaken a study of the polystyrene–cyclohexane system in the vicinity of the theta temperature. The entire concentration range was covered by combining osmotic pressure, isothermal distillation and differential vapor pressure measurements. Since the inception of this work, papers have appeared by Bawn and Patel,[5,6] and Flory and Daoust[9] which, when combined, furnish fairly complete activity data for the polyisobutylene–benzene system at the theta temperature. The vapor pressure measurements of Jessup[10] give activities for the same system a few degrees above the theta temperature. In addition, Kabayami and Daoust[12] have reported calorimetric data for the

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(11) P. J. Flory, "Principles of Polymer Chemistry," Cornell Univ. Press, Ithaca, N. Y., 1953, Chapter 12.

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polyisobutylene–benzene system. Finally, Schmoll and Jenckel[7] have presented vapor pressure measurements for the polystyrene–cyclohexane system for $v_2 > 0.5$. These were performed at several temperatures, though not at the theta temperature.

Experimental

Osmotic Pressure.—The solvent activity was determined osmotically for solutions having concentrations less than 25% polymer. Undried Avisco No. 300 cellophane membranes were employed. Brass block osmometers described elsewhere[13] were used without modification for osmotic pressures below 10 g./cm.^{2}. For the higher polymer concentrations additional pressure was applied through the capillary tube on the solution side. This was done by slipping a piece of Tygon tubing over the capillary and attaching the other end of the tubing to a thermostated one liter flask which, in turn, was connected to a tank of oxygen. The pressure in the flask could be adjusted manually and was read on a mercury manometer. A combination of the dynamic and static methods was used for the higher pressures. The rate of change of the difference between the solution and solvent levels was observed for a certain applied pressure. These observations were then repeated for other applied pressures. A plot of this rate of change *vs.* the total pressure forms a straight line, which could be interpolated to yield an estimate of the osmotic pressure. The total pressure was adjusted to this value and subsequent readings were obtained by the static method. Although the solution inside the osmometer was not stirred, final equilibrium was attained within 24 hr. for nearly all of the solutions. The difference in heights was converted to a pressure difference using the measured solution densities.

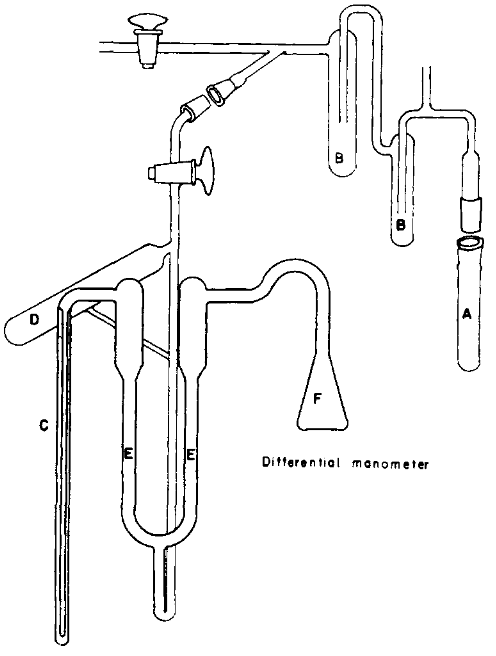

Fig. 1.—Diagram of the differential manometer.

An upper concentration limit for the osmotic measurements was not imposed by the slowness of diffusion near the membrane, as one might have supposed, but by the viscosity of the solution. In filling the osmometer the solution had to be forced through a small orifice in a needle valve, and the filling time therefore became the limiting factor.

Isothermal Distillation.—In the intermediate concentration range isothermal distillation measurements were performed at 34 and 44° upon three polymer fractions. The apparatus consisted of a glass vacuum desiccator partially filled with mercury upon which were floated three glass Petrie dishes. Polymer solution was placed in one dish, a reference solution of triphenylmethane in cyclohexane occupied the second dish, and either a polymer solution with a different concentration or a reference solution having a different concentration was placed in the third dish. The third dish served as a check on the attainment of equilibrium. Only those results were retained in which the two similar solutions reached the same concentration. After filling the dishes, the desiccator was closed and most of the air was removed. The desiccator joints were coated with paraffin and the desiccator was sunk into a thermostated bath whose temperature was maintained to within ±0.02°. The pool of mercury served both to increase the heat capacity of the system and as a heat transfer agent. Equilibrium was reached in three days at 44° and in nine days at 34°. At the end of the experiment the desiccator was removed from the bath, quickly dried and opened, and the dishes were capped. The concentrations were determined gravimetrically. It might be noted that aluminum dishes could not be used due to their rapid corrosion by the triphenylmethane solutions.

Vapor Pressures.—The differential manometer shown in Fig. 1 was used for the static measurement of vapor pressures of concentrated solutions (50–100% polymer). Flask F contained a known weight of polymer (*ca.* one gram). Degassed solvent was placed in tube A, which was packed with broken glass. Two sublimations transferred the solvent to the upper tube labeled B, and a final sublimation transferred the cyclohexane to the calibrated Trubore capillary tube C, which served as a solvent reservoir. The manometer stopcock was closed and the manometer was tilted to pour mercury from reservoir D into the manometer arms E. The mercury level could be lowered at will, permitting the distillation of solvent between capillary tube C and solution flask F. The direction of distillation could be controlled by chilling either the flask or the capillary. Concentrations were calculated by observing the solvent level in capillary C with a cathetometer and applying a correction for the solvent in the vapor space. After each solvent transfer the manometer was maintained in a thermostated water-bath for 1–3 days before beginning readings.

Materials.—The polymerization and fractionation of the polystyrene has been described elsewhere.[13] The number average molecular weights obtained from the osmotic measurements were: I, 25,100; II, 72,000; III, 440,000.

The solvent was Eastman white label cyclohexane, further purified by distillation from sodium, passing through a column of alumina, and four fractional crystallizations. The vapor pressure of the solvent was 144.4 mm. at 34.00°, which compares favorably with the value 144.38 reported by the National Bureau of Standards.[14] The freezing point was 6.11°. This represents 0.18 mole % impurity, most of which is probably methylcyclopentane.

The triphenylmethane used as a reference solute for the isothermal distillation measurements was Eastman white labeled grade, purified by two recrystallizations from ethanol. The melting point, 92.0–92.5°, stands in good agreement with the literature value, 92.5°.

Results

Theoretical Relations.—Historically, the earliest statistical mechanical treatments of polymer solutions were based upon the lattice model. These were presented by Flory,[15] Huggins,[16] Miller,[17] Orr[18] and Guggenheim.[19] The treatment of this model was extended by Staverman[20] and Tompa,[21] who considered the effect of multiply connected sites. The lattice model approach furnishes relatively simple expressions for the chemical potentials in closed form. It has successfully demon-

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[14] N. B. S. Circular C461, U. S. Government Printing Office, Washington, D. C., 1947.

[15] P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942); **12**, 425 (1944).

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strated the effects of molecular size and molecular structure upon the configurational entropy.

On the other hand, it is now recognized that the above lattice model treatments have serious shortcomings. Firstly, they assume that the expectancy of finding a site occupied is uniform throughout the solution. As pointed out many years ago by Flory,[22] this condition will not obtain for dilute solutions in which excluded volume effects are operative. Numerous papers[23-36] have appeared in which very dilute polymer solutions are treated by the methods developed for imperfect gases. Further shortcomings of the lattice model are its failure to take into account volume changes on mixing and a possible concentration dependence of the potential of mean force. These difficulties are inherent in the lattice model and can only be overcome by rejecting this model. Prigogine[37] has achieved some success in this direction by making use of the Lennard-Jones potential and the theorem of corresponding states to deduce an expression for the average potential of mean force in a mixture of two components.

One should, perhaps, test the simplest theoretical expression first. This is obtained on combining the lattice model entropy of mixing as calculated by Flory[15] with a single term of the van Laar form representing the free energy contribution arising from local pair interactions. The expression so obtained for the Helmholtz free energy change on mixing N_1 moles of solvent with N_2 moles of polymer is

$$\Delta A_M = RT[N_1 \ln v_1 + N_2 \ln v_2 + N_2 r\chi_1 v_1] \quad (1)$$

Here v_1 and v_2 are the volume fractions of solvent and polymer, respectively, r represents the ratio, V_2/V_1 of the molar volumes of polymer and solvent, and χ_1 as a free energy parameter.[38] The corresponding expression for the partial molar free energy of dilution is

$$\Delta\bar{A}_1 = RT[\ln(1 - v_2) + (1 - 1/r)v_2 + \chi_1 v_2^2] \quad (2)$$

Upon expanding the logarithmic term there is obtained a series form applicable for v_2 small

$$\Delta\bar{A}_1 = RT[-v_2/r - (^1/_2 - \chi_1)v_2^2 - v_2^3/3 - \ldots] \quad (3)$$

The osmotic pressure π of a dilute solution may be expressed in virial form

$$\pi/c = RT[\mathbf{A}_1 + \mathbf{A}_2 c + \mathbf{A}_3 c^2 + \ldots] \quad (4)$$

where the first coefficient, $\mathbf{A}_1$, is just $1/\bar{M}_n$. If it is assumed that there is no volume change on mixing, so that $\Delta\bar{F}_1 = \Delta\bar{A}_1$, then upon comparing equations 3 and 4 there is obtained according to the lattice model treatment

$$\mathbf{A}_2 = (\bar{v}^2/V_1)(^1/_2 - \chi_1) \quad (5a)$$

where $\bar{v}$ is the partial specific volume of the polymer. If the free energy parameter χ_1 is further resolved into an energy component, $\psi_1\,\Theta/T$ and an entropy component, $(\psi_1 - {}^1/_2)$, where Θ is the Flory theta temperature, then (5a) may be rewritten as

$$\mathbf{A}_2 = (\bar{v}^2/V_1)\psi_1(1 - \Theta/T) \quad (6a)$$

The third and higher coefficients are of the form

$$\mathbf{A}_i = (\bar{v}^i/V_1^i)(1/i) \quad (i > 2) \quad (7a)$$

Thus, the Flory lattice model treatment predicts that $\mathbf{A}_2$ will be a function of temperature, vanishing at $T = \Theta$, but will be independent of molecular weight. The third and higher coefficients are predicted to be independent of both temperature and molecular weight.

The treatment of Flory makes the assumption, as do the more refined treatments of the lattice model, that the polymer segments are uniformly distributed throughout the solution. As mentioned above, this assumption is unrealistic for dilute solutions whenever excluded volume effects are operative. The dilute solution treatment of Flory and Krigbaum[24] assumed, instead, that the expectancy of finding a segment of a given polymer molecule in a small volume element within that molecule can be considered uniform. In view of the low segment densities involved, the chemical potential was represented by the first two terms on the right-hand side of (3). Making use of procedures developed for treating imperfect gases, the following expression was derived for the second virial coefficient

$$\mathbf{A}_2 = (\bar{v}^2/V_1)(^1/_2 - \chi_1)F(X) \quad (5b)$$

Equation 5b differs from (5a) based on the lattice model treatment through the factor $F(X)$. Since $F(X) = 1$ when $T = \Theta$, the expressions for the second virial coefficient given by the two types of treatment coincide when the excluded volume vanishes. At other temperatures the factor $F(X)$ introduces a dependence of $\mathbf{A}_2$ upon molecular weight, as well as further implicit dependences upon temperature and the thermodynamic parameters ψ_1 and Θ.

Stockmayer and Casassa[25] have carried the dilute solution treatment one step further to obtain, after some approximations

$$\mathbf{A}_3 = gM\mathbf{A}_2^2 \quad (7b)$$

Here g is a function depending upon molecular weight, temperature and the thermodynamic parameters; furthermore, g vanishes at $T = \Theta$. Hence, according to the dilute solution treatment both $\mathbf{A}_2$ and $\mathbf{A}_3$ depend upon temperature and molecular weight, and both vanish at the Flory theta temperature. On the other hand, the lattice model treatment predicts that the third and higher coefficients should remain positive at all temperatures. We see, therefore, that although

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(31) A. Isihara and R. Koyama, *ibid.*, **25**, 712 (1956); R. Koyama, *ibid.*, **27**, 234 (1957).

(32) T. A. Orofino and P. J. Flory, *ibid.*, **26**, 1067 (1957).

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(34) A. C. Albrecht, *ibid.*, **27**, 1002 (1957).

(35) D. K. Carpenter and W. R. Krigbaum, *ibid.*, **28**, 513 (1958).

(36) M. Kurata, H. Yamakawa and F. Teramoto, *ibid.*, **28**, 785 (1958).

(37) I. Prigogine, "The Molecular Theory of Solutions," Interscience Publishers, Inc., New York, N. Y., 1957.

(38) P. J. Flory and W. R. Krigbaum, "Annual Review of Physical Chemistry," Vol. II, Annual Reviews, Inc., Stanford, California, 1951, p. 383.

the two types of treatment might be expected to give the same result in the absence of excluded volume effects, the coincidence at $T = \Theta$ does not extend beyond the second virial coefficient.

One may question whether the single term involving χ_1 in equation 1 suffices to represent the free energy contribution from local interactions. The more refined lattice model treatments of Huggins,[16] Miller,[17] Orr[18] and Guggenheim[19] require the replacement of equation 2 by

$$\Delta\bar{A}_1 = RT[\ln(1 - v_2) + (1 - 1/r)v_2 + \sum_{i=2} \chi_{i-1} v_2^i] \quad (2')$$

Kirkwood and Buff[39] derived a similar expression by a method making use of radial distribution functions. The latter approach is, of course, free from the objections mentioned above concerning the lattice model. In addition, Tompa[40] has pointed out that the introduction of a second χ parameter results in improved agreement with the observed phase diagrams for polymer–solvent systems. According to (2′) the second virial coefficient is again given by (5a); however, in place of (7a) the higher coefficients are now of the form

$$A_i = (\bar{v}^i/V_1)(1/i - \chi_{i-1}) \quad (i > 2) \qquad (7a')$$

Hence the higher coefficients given by this revised treatment are temperature dependent.

Now it is evident that a satisfactory theoretical treatment must predict the magnitudes of all the χ parameters required to fit the observed free energies. It should be pointed out that the χ_i in equation 2′ may consist in part of corrections to the *configurational* entropy as calculated by Flory. This possibility is evident upon comparing the latter in expanded form

$$\Delta\bar{S}_1 = R\left[v_2/r + \sum_{i=2} v_2^i/i\right] \qquad (8)$$

with the expression for the total partial molar entropy of dilution obtained on including the entropy components, $(\psi_{i-1} - 1/i)$, of the various χ_{i-1}

$$\Delta\bar{S}_1 = -R\left[v_2/r + \sum_{i=2} \psi_{i-1} v_2^i\right] \qquad (8')$$

Flory and Orofino[32] have recently repeated the earlier dilute solution treatment, representing the chemical potential of solvent in a volume element within an isolated molecule by

$$\Delta\bar{A}_1 - RT[-v_2/r - (1/2 - \chi_1)v_2^2 - (1/3 - \chi_2)v_2^3] \quad (3')$$

Thus, this refinement consists of retaining the next higher term and the introduction of a second χ parameter. For thermodynamically poor solvents their final result may be expanded to yield

$$A_2 = \frac{\bar{v}^2}{V_1}[(1/2 - \chi_1) + a(1/3 - \chi_2) + \ldots] \quad (5b')$$

where $a = (3^4/2^{5/2}\pi^{3/2})\ \bar{v}M/\mathbf{N}(\bar{r}^2)^{3/2}$, $\bar{r}^2$ being the mean-square distance between chain ends and $\mathbf{N}$ representing Avogadro's number. These authors treat χ_1 and χ_2 as adjustable parameters. Upon replacing χ_i by $1/(i+1) - \psi_i + \psi_i\,\Theta_i/T$ there is obtained

$$A_2 = \frac{\bar{v}^2}{V_1}[\psi_1(1 - \Theta_1/T) + a\psi_2(1 - \Theta_2/T) + \ldots] \quad (6b')$$

Since the factor a is non-vanishing for finite M, one sees that the temperature at which the second virial coefficient vanishes is no longer related by theory to either Θ_1 or Θ_2. This is in contrast to equation 3′, which predicts a vanishing second virial coefficient when $T = \Theta_1$. In addition, one suspects that the further refinement of the dilute solution treatment by the retention of still higher terms in (3′) would result in their appearance in the A_2 as well. Thus, the Flory–Orofino treatment casts serious doubt upon the entire concept of a unique theta temperature for a given polymer–solvent system. Also in question, of course, is the procedure previously used[41] to evaluate the parameter ψ_1 from measurements performed in the vicinity of the theta temperature. Since the Flory–Orofino treatment attaches no physical significance to the χ parameters, these questions can only be answered by recourse to experiment.

Osmotic Pressure Data.—The π/RTc ratios obtained for the three fractions appear in Table I. Measurements were performed only at 34° for fraction I. Although the membrane retains this polymer when π is small, thus permitting the determination of $\bar{M}_n$, the downward curvature of the data for this fraction at higher concentrations shows that some polymer diffuses through the membrane when external pressure is applied to the solution. Measurements were performed at 24, 34 and 44° for fraction II and at 34 and 44° for fractions III (this polymer precipitates at 24°).

TABLE I

OSMOTIC PRESSURE DATA[a] FOR POLYSTYRENE IN CYCLOHEXANE

t (°C.)	v_2	c(g./ml.)	$10^6\pi/RTc$	t (°C.)	v_2	c(g./ml.)	$10^6\pi/RTc$
Fraction I, M_n = 25,100				Fraction II, M_n = 72,000			
34°	0.00187	0.00201	39.9	24°	0.090	0.0976	8.0
	.0187	.0199	39.5		.168	.182	6.0
	....	.0524	(37.2)		.241	.259	8.7
	....	.0745	(35.2)				
Fraction III, M_n = 440,000							
				34°	.0077	.0081	13.3
34°	0.0145	0.0156	2.46		.0187	.0201	14.2
	.0450	.0482	2.24		.090	.0964	14.2
	.085	.0911	3.42		.167	.180	18.7
	.118	.126	4.96		.210	.257	26.2
	.130	.139	6.65				
				44°	.090	.0959	18.6
44°	.0148	.0178	5.50		.166	.178	28.1
	.117	.125	11.0		.239	.255	40.0
	.130	.138	13.2				

[a] π in atm. and c in g./ml. solution.

The first two virial coefficients were evaluated in the usual manner from a plot of $(\pi/c)^{1/2}$ *vs.* c. The third coefficient, A_3, was assigned the value calculated according to the relation of Stockmayer and Casassa,[25] while A_4 was chosen to fit the data at higher concentrations. The resulting values are collected in Table II. The π/RTc ratios calculated using these virial coefficients are compared with the observed ratios in Fig. 2. The agreement is within 3%, which is the estimated experimental error. This corresponds to an average error in π of 1 g./cm.^{2}, with the largest errors occurring

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(41) W. R. Krigbaum and P. J. Flory, THIS JOURNAL, **75**, 1775 (1953); W. R. Krigbaum, *ibid.*, **76**, 3758 (1954).

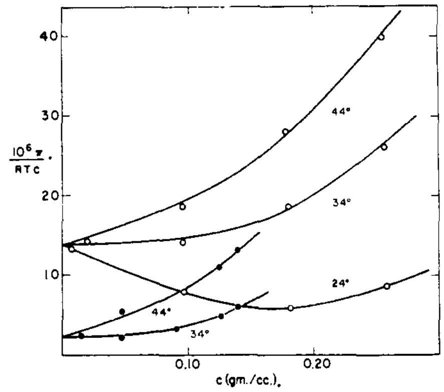

Fig. 2.—Osmotic pressures plotted as π/RTc *vs.* concentration for polystyrene fractions II (○) and III (●) in cyclohexane.

at the higher pressures, which run up to 260 g./cm.^{2}

From the A_2 values for fraction II at 24 and 44° we obtain $\Theta = 307.2$–307.9°K., the latter being an upper bound obtained by linear interpolation. This stands in good agreement with $\Theta = 307.6$°K.

TABLE II

VIRIAL COEFFICIENTS FOR POLYSTYRENE FRACTIONS IN CYCLOHEXANE

Fraction	t(°C.)	10^5A_1	10^5A_2	10^6A_3	10^5A_4
I	34	3.86	...	...	..
II	24	1.39	−6.7	−1	74
	34	1.39	0	0	76
	44	1.39	5.0	0.5	80
III	34	0.227	0	0	140
	44	0.227	4.5	5.6	130

obtained by one of the authors from osmotic measurements[41] performed upon very dilute solutions, and with 307.2°K. reported by Shultz and Flory[42] from precipitation measurements. From the same osmotic data there are obtained $\psi_1 F(X) = 0.25$ and 0.20 at 24 and 44°, respectively, so that $\psi_1 = 0.23$. This is to be compared with $\psi_1 = 0.36$ previously obtained[41] from osmotic measurements for concentrations up to 0.02 g./cc. Although A_2 cannot be determined as accurately from the present data, this difference in ψ_1 values is still surprising.

The A_3 values found in Table II are small, and the contribution of the third term is therefore relatively small over the concentration range of these measurements. On the other hand A_4 as evaluated in the manner just described is large, positive and essentially independent of temperature. For comparison, equation 7a deduced from the Flory lattice model treatment gives $A_4 = 170 \times 10^{-5}$, independent of temperature and molecular weight. Although $(\pi/c)/(\pi/c)_0 = 3$ was the maximum value of this ratio observed for fraction II at 44°, at this point the contributions from the first, second and fourth terms were approximately equal. The magnitudes of A_4 are quite insensitive to the values assigned A_3, since the latter are so small. We recognize, however, that the A_4 values listed in Table II are uncertain due to the neglect of still higher terms in the virial expansion.

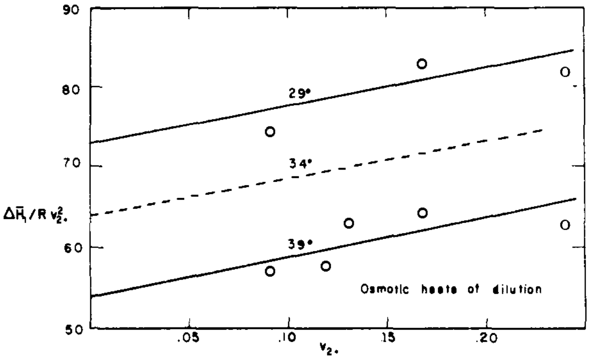

Fig. 3.—Partial molar heats of dilution obtained from the osmotic data.

Figure 3 shows the partial molar heats of dilution calculated from the osmotic data at 24, 34 and 44°. If we assume no volume change on mixing and utilize equation 6a, which omits the factor F(X), then from the intercept, $\psi_1\Theta$, there is obtained $\psi_1 = 0.21$. The positive slopes of these lines indicate a positive enthalpy contribution to the third virial coefficient. As will be demonstrated more clearly below, A_3 vanishes at $T = \Theta$. Hence, at this temperature there must be an equal and compensating entropy contribution. Upon rewriting $(1/3 - \chi_2)$ in equation 3′ as $\psi_2(1 - \Theta_2/T)$ and setting $\Theta_2 = \Theta_1$ as required to reduce A_3 to zero at Θ_1, we obtain $\psi_2 = 0.15$.

The vertical displacement of the 29 and 39° lines in Fig. 3 indicates a partial molal heat capacity of the solvent. According to the lattice model treatment this quantity should be zero, whereas the dilute solution treatments predict a temperature dependence of $\Delta\bar{E}_1$ which enters through the factor $F(X)$. As calculated from the Flory–Krigbaum dilute solution treatment,[24] $(\Delta\bar{C}_v)_1/Rv_2^2 = -0.6$, while from the activity data $(\Delta\bar{C}_p)_1/Rv_2^2$ is -1.9. This may be taken as additional evidence that the theoretical $F(X)$ function does not vary sufficiently rapidly with X.[41]

Isothermal Distillation.—Prior to the isothermal distillation measurements the activity of cyclohexane was measured in solutions of the standard solute, triphenylmethane. This was determined cryoscopically and by manometric measurements at 34 and 47.5°. The freezing point depression appears plotted against the mole fraction of triphenylmethane in Fig. 4. The manometric data were quite reproducible, and no consistent differences were observed between the ascending and descend-

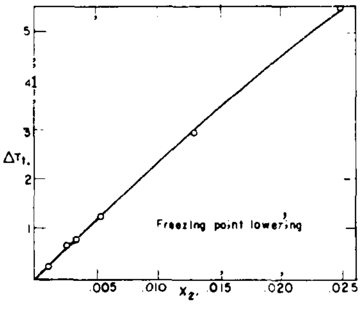

Fig. 4.—Freezing point depression of cyclohexane plotted against the mole fraction of triphenylmethane.

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(42) A. R. Shultz and P. J. Flory, THIS JOURNAL, **76**, 3758 (1954).

ing concentration branches. The vapor pressure lowerings observed at the two temperatures appear plotted against the mole fraction of triphenylmethane in Fig. 5. The dashed curves represent Raoult's law behavior at the two temperatures. The horizontal portion of the experimental 34° curve is due to the fact that the highest concentration exceeded the solubility limit at this temperature. Fortunately, the solubility of triphenylmethane in cyclohexane was sufficiently large so that this was not a limiting factor in the isothermal distillation measurements.

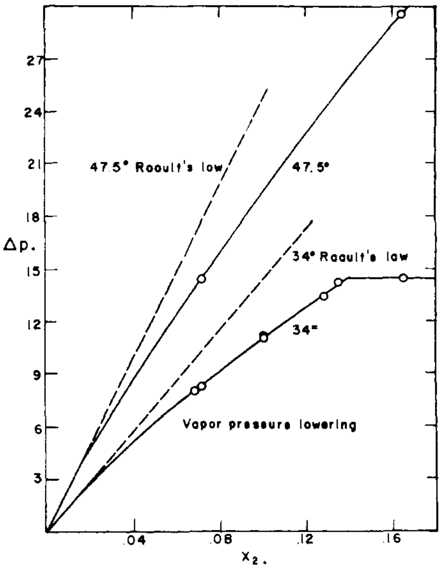

Fig. 5.—Vapor pressure lowering of cyclohexane at 34 and 47.5° *vs.* mole fraction triphenylmethane.

The mole fraction activity coefficient, $\gamma_1 = a_1/x_1$, was calculated from the cryoscopic data through use of the relation[14]:

$$-\ln \gamma_1 = 4.11 \times 10^{-3} \Delta t(1 + 7.2 \times 10^{-4} \Delta t) + \ln(1 - x_2)$$

and from the vapor pressure lowering by

$$\gamma_1 = (1 - \Delta p/p_1^0)/(1 - x_2)$$

These values appear in Fig. 6 plotted as $(\gamma_1 - 1)/x_2^2$ *vs.* x_2. Expressions for the activity coefficient of cyclohexane in triphenylmethane solution obtained from these data are

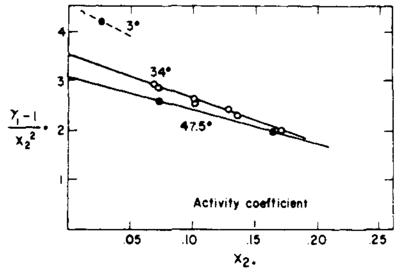

Fig. 6.—Mole fraction activity coefficient of cyclohexane in solutions of triphenylmethane at three temperatures.

$$\gamma_1 = 1 + 5x_2^2 \quad (3°)$$
$$\gamma_1 = 1 + 3.50x_2^2 - 8.8x_2^2 \quad (34°)$$
$$\gamma_1 = 1 + 3.07x_2^2 - 6.6x_2^3 \quad (47.5°)$$

By interpolation, we obtain for the activity coefficient of the solvent at 44°

$$\gamma_1 = 1 + 3.18x_2^2 - 7.2x_2^3 \quad (44°)$$

Isothermal distillation data obtained for the three polymer fractions at 34 and 44° appear in Table III. The fourth column represents the

TABLE III
ISOTHERMAL DISTILLATION DATA FOR POLYSTYRENE IN CYCLOHEXANE

Fraction	t(°C.)	v_2	$10^2(x_2)_{\text{TPM}}$	$-\Delta\bar{F}_1/RT$
I	34	0.248	0.21	0.0021
		.300	0.316	.00316
		.446	1.40	.0140
	44	.625	7.64	.0644
II	34	.341	0.392	.00392
		.51	2.42	.0225
		.546	3.10	.0284
	44	.372	0.82	.0080
		.660	11.2	.087
III	34	.285	0.23	.0023
		.348	.406	.00406
		.400	.77	.0075
		.554	3.90	.0346
		.600	5.97	.0509
	44	.355	0.466	.00466
		.409	1.16	.0112
		.480	4.62	.0412
		.517	4.80	.0422

TABLE IV
MANOMETRIC DATA FOR POLYSTYRENE IN CYCLOHEXANE

t (°C.)	v_2	Δp (mm.)	$-\Delta\bar{F}_1/RT$
Fraction I ($\bar{M}_n$ = 25,900)			
24	0.434[a]	1.0	0.011
	.442	1.0	.011
	.625[a]	4.2	.046
	.733	8.7	.087
	.771[a]	12.7	.146
	.843[a]	18.8	.226
	.897[a]	29.4	.378
34	.343[a]	0.6	.004
	.344	0.4	.0029
	.388[a]	0.6	.0042
	.426[a]	1.4	.010
	.435[a]	1.8	.013
	.441	1.5	.0102
	.443	1.7	.012
	.485	2.4	.018
	.489[a]	2.2	.0156
	.543[a]	3.4	.024
	.629[a]	7.9	.056
	.637[a]	8.8	.063
	.640	6.3	.045
	.673	11.4	.082
	.690[a]	12.3	.089
	.738	16.5	.121
	.766[a]	20.4	.152
	.768	20.2	.151
	.780[a]	22.1	.166
	.801[a]	26.6	.203
	.804	31.7	.247
	.818[a]	29.8	.232
	.849[a]	34.6	.273
	.871[a]	46.1	.384
	.896	44.5	.368
	.902[a]	53.3	.460
	.905	41.1	.335
	.954	43.4	.357
	.954	63.5	.580
	.979	93.9	1.05
	.983[a]	93.1	1.036
	.989	126.0	2.06
	.993	138.6	3.2
	.994	85.7	0.899
44	.434[a]	3.00	.0139
	.442	3.4	.0160
	.444	3.02	.0140
	.491[a]	5.9	.0274
	.556	8.83	.0416
	.633[a]	15.0	.072
	.676	21.7	.105
	.743	30.0	.150
	.789[a]	39.6	.202
	.810	55.8	.298
	.855[a]	59.8	.323
	.907[a]	88.7	.528
	.909	89.5	.534
	.955	130.1	.919
Fraction III ($\bar{M}_n$ = 440,000)			
34	0.389	0.3	0.002
	.483[a]	2.6	.0182
	.485	2.6	.0182
	.568[a]	6.3	.0446
	.661[a]	10.9	.0785
	.671	11.6	.0837
	.758[a]	27.1	.166
	.802[a]	29.6	.229
	.828	35.5	.281
	.859[a]	48.4	.408
44	.392	1.8	.0083
	.537[a]	7.4	.0347
	.593[a]	11.5	.0547
	.731[a]	27.1	.134
	.827[a]	51.2	.269
	.882[a]	78.1	.448

[a] Data taken upon increasing concentration.

mole fraction of triphenylmethane in the reference solution at equilibrium. Diffusion was too slow at 24° to allow the use of this procedure. Column five lists values of $-\Delta\bar{F}_1/RT$, where $\Delta\bar{F}_1$ is the (Gibbs) partial molar free energy.

Vapor Pressure Measurements.—The data obtained using the differential manometer for fractions I and III at the three temperatures are given in Table IV. The values for fraction I represent two independent sets of measurements. As shown in Fig. 7, the data for the two fractions fall on the same curve, despite the twenty-fold difference in molecular weight. The glass temperature of the solution exceeds 34° for volume fractions of polymer above $v_2 = 0.88$. At higher concentrations the ascending and descending branches of the 34° curve diverge due to the slowness of diffusion. Unfortunately, this difficulty is inherent in the system at hand. The ascending branch is probably more reliable in this region, since the solvent concentration is higher while reaching a given composition by desorption, and the rate of diffusion increases approximately exponentially with solvent concentration in this range.

Schmoll and Jenckel[7] have reported vapor pressure measurements for the polystyrene–cyclohexane system which cover the concentration range $v_2 = 0.5 - 0.8$. Their measurements were performed at several temperatures, though not at Θ. Due to the different temperatures studied the two sets of vapor pressure data cannot be compared directly; however, they are at least compatible. As will be indicated below, the heats of dilution derived from our manometric data stand in good agreement with those reported by Schmoll and Jenckel.

Discussion

It is difficult to choose a function which allows the representation of activity data covering a wide concentration range. One function which satisfies this criterion is shown in Fig. 8, where all of the data obtained at 34° by the three types of measurement appear plotted as $\Delta\bar{F}_1/RT \ln v_1$ *vs.* v_2 using a semi-logarithmic scale. At infinite dilution this function must approach a constant, $1/r$, where r is the ratio of the molar volumes of polymer and solvent. At the other end of the concentration range $\Delta\bar{F}_1/RT \ln v_1$ must attain a limiting value of unity. There is good agreement between the isothermal distillation and vapor pressure data in the region where the two types of measurement overlap. Although the isothermal distillation and osmotic data do not overlap, Fig. 8 shows that the two sets of data can be connected reasonably well by a smooth curve.

An important feature of Fig. 8 is the fact that polystyrene in cyclohexane at the theta temperature behaves ideally up to surprisingly high concentrations. This feature is exhibited more strikingly in Fig. 9, where the same plot of the experimental data for fraction III at 34° is contrasted with the behavior predicted by the Flory lattice model treatment, equation 2, for various values of the interaction parameter χ_1. Since $\chi_1 = {}^1/_2$ at theta, the system is clearly behaving more ideally than would be expected from equation 2. This suggests that some of the higher χ parameters in the revised equation 2′ are positive.

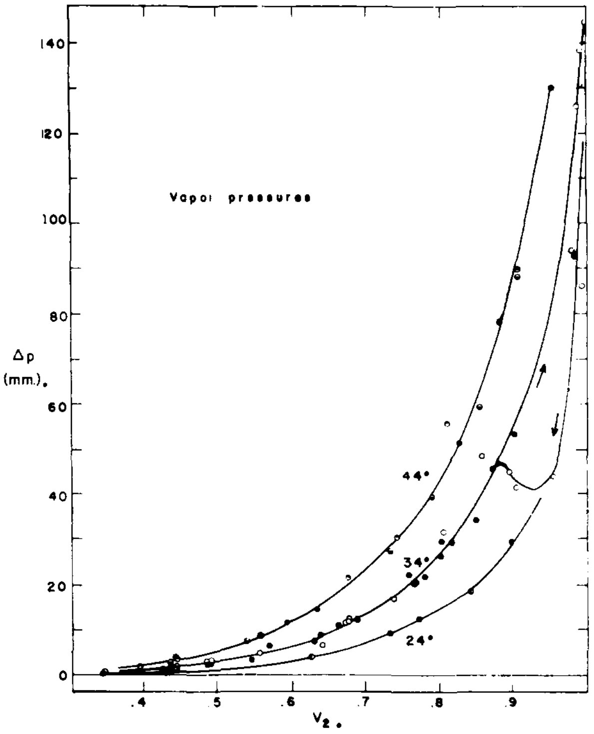

Fig. 7.—Vapor pressure lowering of cyclohexane by polystyrene at 24° (◐, up branch; ◑, down branch); 34° (●, up branch; ○, down branch); and 44° (◒, up branch; ◐, down branch).

Figure 10 shows the values of $\chi - {}^1/_2$ calculated from the experimental $\Delta\bar{F}_1/RT$ at 34° through use of equation 2. If a single term in χ sufficed, this function would be zero at all concentrations. A similar behavior of χ has been observed for the polyisobutylene–benzene system by Bawn and Patel,[6] Jessup,[10] and Flory and Daoust[9] and for the rubber-ethyl acetate system by Booth, Gee and Williamson.[8] From the intercept and initial slope of the curve in Fig. 10, $\chi_1 = {}^1/_2$ and $\chi_2 = {}^1/_3$. Thus both A_2 and A_3 as calculated according to the revised lattice model equation 3′ vanish at Θ_1. After assignment of these χ values a series of similar plots were used to evaluate some of the higher χ parameters. This procedure led to $\chi_3 = 0.07$–0.08, while χ_4 through χ_7 were found to vanish at Θ_1. As is evident from Fig. 10, some of the still higher χ parameters must be large and positive, however.

Partial molar heats of dilution, $\Delta\bar{H}_1$, were calculated from those manometric measurements in which a given concentration was studied at more than one temperature. These are represented by the open circles in Fig. 11, where $\Delta\bar{H}_1/Rv_2^2$ is plotted against v_2. The filled circles are the values calculated from the osmotic data (*cf.* Fig. 3). The points in Fig. 11 would fall on a horizontal line if the heat of dilution were expressible by a single van Laar term. $\Delta\bar{H}_1/Rv_2^2$ is seen to increase slowly with concentration up to $v_2 = 0.4$ and to increase sharply thereafter. The calorimetric data

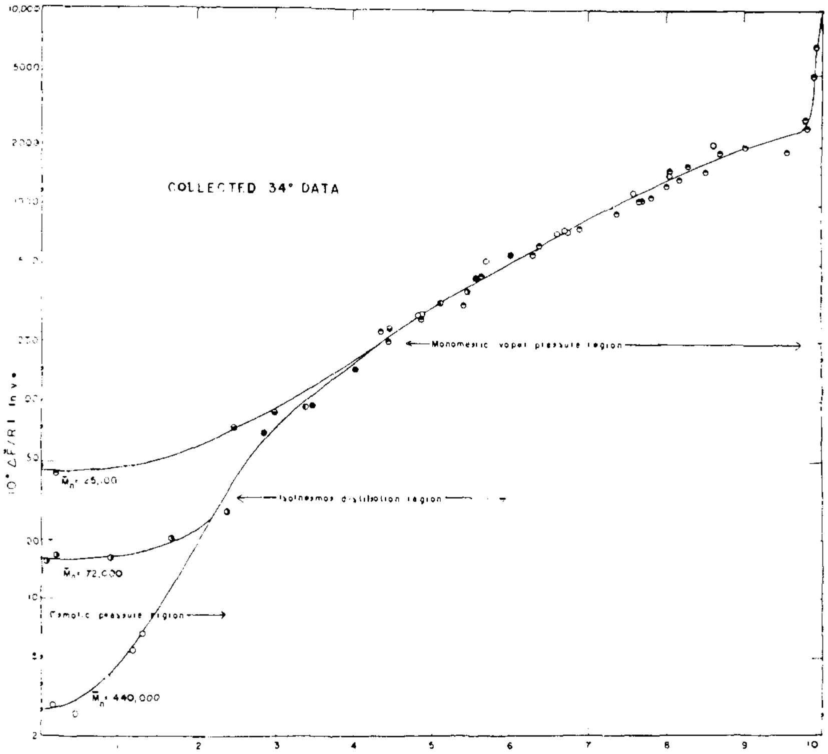

Fig. 8.—Activity data for polystyrene–cyclohexane at 34°. $\bar{M}_n$ = 25,900: ◓, osmotic and manometric; ◒, isothermal distillation; $\bar{M}_n$ = 72,000: ◑, osmotic; ◐, isothermal distillation; $\bar{M}_n$ = 557,000: ○, osmotic and manometric; ●, isothermal distillation.

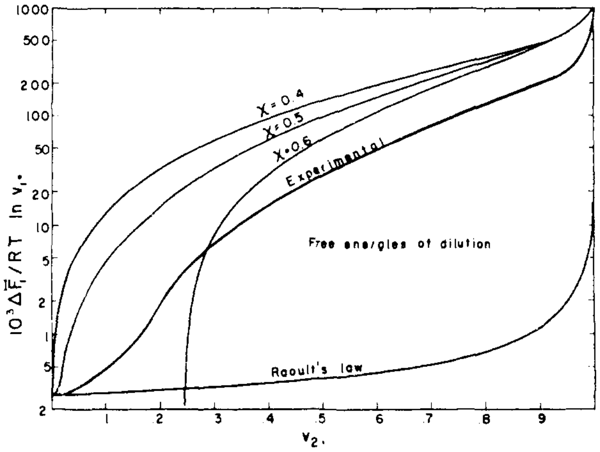

Fig. 9.—Comparison of the experimental free energies of dilution at 34° with Raoult's law and the behavior predicted according to equation 2 for various values of χ_1.

of Tager and Dombek[43] for the polystyrene–benzene system shows a similar sharp increase above $v_2 = 0.5$, and $\Delta\bar{H}_1/Rv_2^2$ increasing with v_2 has been observed by Kabayami and Daoust[12] for polyisobutylene–benzene and by Booth, Gee and Williamson[8] for rubber–ethyl acetate.

In the absence of precise calorimetric data, smoothed values of $\Delta\bar{H}_1$ were taken from the curve in Fig. 11. These indicate the heat of mixing curve to be unsymmetrical, with a maximum of 190 cal./mole at $v_2 = 0.75$. This magnitude agrees perfectly with the value reported by Schnoll and Jenckel from their vapor pressure data at various temperatures. The calorimetric data of Jenckel and Gorke[44] lead to a much higher maximal value for the heat of mixing, 320 cal./mole; however, this must be regarded as approximate due to the difficulties encountered with glassy behavior in the concentration range they studied.

Since the polymer solution treatments based on the lattice model assume no volume change on mixing, the quantities $\Delta\bar{A}_1$, $\Delta\bar{E}_1$ and $(\Delta\bar{S}_1)_v$ are required for a test. We have made use of the relation given by Hildebrand and Scott[45] to estimate the correction for volume change

$$\Delta\bar{F}_1 = \Delta\bar{A}_1$$
$$\Delta\bar{H}_1 = \Delta\bar{E}_1(1 + \alpha_s T) \quad (9)$$

where α_s, the coefficient of cubical expansion for the solution, may be approximated by $\alpha_s = \alpha_1 v_1 + \alpha_2 v_2$. The values assigned were $\alpha_1 = 5.9 \times 10^{-4}$ for cyclohexane and $\alpha_2 = 12.6 \times 10^{-4}$ for polystyrene. Smoothed values for the thermodynamic parameters so derived from the data for fraction III at 34° appear in Table V.

Table V

Smoothed Values of the Thermodynamic Parameters for Polystyrene Fraction III ($\bar{M}_n$ = 440,000) in Cyclohexane at 34°

v_2	$\frac{\Delta\bar{F}_1}{RTv_2^2}$	$\frac{\Delta\bar{H}_1}{RTv_2^2}$	$\frac{\Delta\bar{E}_1}{RTv_2^2}$	$\frac{(\Delta\bar{S}_1)_p}{Rv_2^2}$	$\frac{(\Delta\bar{S}_1)_v}{Rv_2^2}$	$\frac{\Delta\bar{S}_1^*}{Rv_2^2}$
0.01	0.027	0.210	0.152	0.237	0.179	0.530
.02	.014	.212	.153	.226	.167	.527
.05	.0065	.214	.155	.221	.162	.522
.10	.0049	.221	.162	.226	.167	.538
.15	.0062	.228	.168	.234	.174	.558
.20	.0105	.232	.172	.243	.183	.580
.25	.0192	.237	.178	.256	.197	.604
.30	.0289	.251	.190	.280	.219	.633
.40	.0512	.293	.225	.344	.276	.700
.50	.0816	.488	.380	.570	.462	.772
.60	.1283	.846	.669	.974	.797	.878
.70	.2083	1.367	1.101	1.575	1.309	1.031
.80	.3343	1.953	1.603	2.287	1.937	1.266
.90	.5534	2.897	2.414	3.451	2.968	1.728

The $(\Delta\bar{S}_1)_v/Rv_2^2$ values for polystyrene fraction III at Θ_1 appear in column six, while column seven gives the same function of the *configurational* entropy of dilution, $\Delta\bar{S}_1^*$, as calculated according to the Flory treatment of the lattice model

$$\Delta\bar{S}_1^* = -R[\ln v_1 + (1 - 1/r)v_2] \quad (10)$$

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[43] A. Tager and Zh. S. Dombek, *Kolloid Zhur.*, **15**, 69 (1953).

[44] E. Jenckel and K. Gorke, *Z. Elektrochem.*, **60**, 579 (1956).

[45] J. H. Hildebrand and R. L. Scott, "Solubility of Non-Electrolytes," 3rd Ed., Reinhold Publ. Corp., New York, N. Y., 1950.

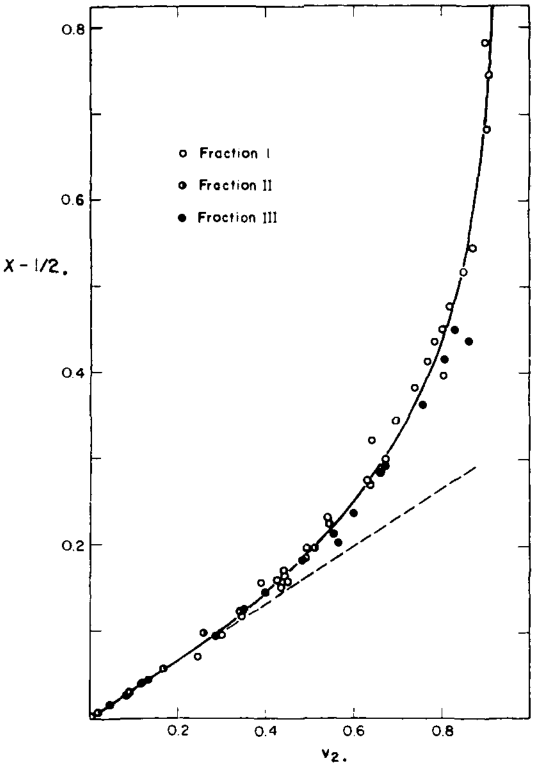

Fig. 10.—Values of $\chi - {}^1/_2$ calculated from the data at 34° according to equation 2. The dashed line has a slope of ${}^1/_3$.

Of course, the $(\Delta\bar{S}_1)_v$ values are only approximate, since they contain errors introduced both through the $\Delta\bar{H}_1$ values and the correction for the volume change on mixing. Nevertheless, the difference between column six and seven is rather striking. If this difference is attributed to the entropy contribution from local interactions, then the latter must be negative at low polymer concentrations and positive at high concentrations. Upon representing $(1/v_2^2) \sum_{i=2} \psi_{i-1}v_2^i$ (see equation (8')) by $\psi(v_2)$, the values of this parameter calculated from the entries in Table V are exhibited by the full curve in Fig. 12. We note that the first few values of ψ_i are less than $1/(i - 1)$, indicating a negative contribution to $(\Delta\bar{S}_1)v$ from local pair interactions, whereas some of the higher ψ_i must clearly be larger than $1/(i - 1)$.

Upon replacing $[1/(i - 1) - \chi_i]$ in equation 3' by $\psi_i(1 - \Theta_i/T)$, there is obtained for the partial molar energy of dilution

$$\Delta\bar{E}_1 = RT \sum_{i=2} (\psi_{i-1}\,\Theta_{i-1}/T)v_2^i \qquad (11)$$

Now if all Θ_i equal Θ_1, then at the temperature Θ_1 $\Delta\bar{E}_1/RTv_2^2$ would be given by the same function, $\psi(v_2)$, mentioned above. Values of $(1/v_2^2) \sum_{i=2} \psi_{i-1}\cdot\Theta_{i-1}v_2^i/\Theta_1$ calculated from the entries in Table V yield the dashed curve shown in Fig. 12. Although the two curves have similar shapes, the dashed curve falls below the full one, indicating that some of the higher Θ_i are less then Θ_1. This is not surprising, since we know that all of the higher virial coefficients do not vanish when T equals Θ_1. The insert to Fig. 12 shows values of the ratio $\sum_{i=2} (\psi_{i-1}\Theta_{i-1}/T)v_2^i / \sum_{i=2} \psi_{i-1}v_2^i$, symbolized by Θ/T. When $T = \Theta_1$ this function is seen to decrease with concentration, ultimately reaching eight-tenths the value exhibited at infinite dilution.

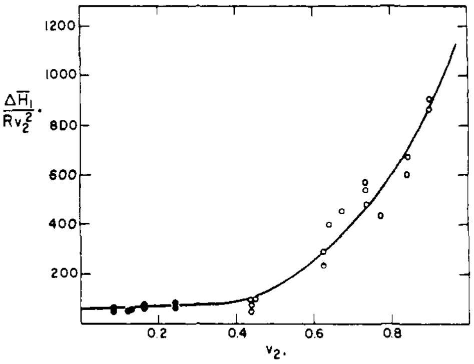

Fig. 11.—Partial molar heats of dilution calculated from the temperature dependence of the osmotic data (●) and manometric data (○).

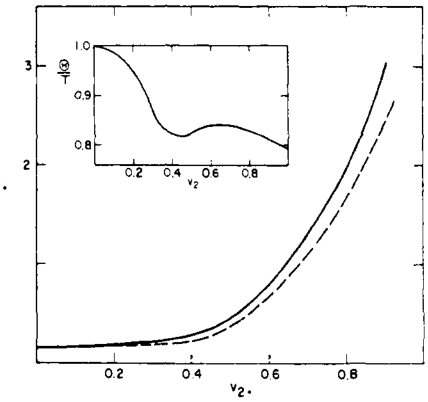

Fig. 12.—Values of ψ calculated from the smoothed $(\Delta\bar{S}_1)$v (full curve) and $\psi\Theta/T$ calculated from the smoothed $\Delta\bar{E}_1$. The insert shows the ratio $(\psi\Theta/T)/\psi$ as a function of v_2.

The minimum in this curve may be fictitious, since this function depends strongly upon the behavior of $\Delta\bar{H}_1/Rv_2^2$ in the region where it begins to increase rapidly (see Fig. 11).

Conclusions

The activity data presented here for the polystyrene–cyclohexane system indicate large deviations from the behavior predicted according to the original lattice model treatment of Flory.[15] At least two χ parameters are required to fit the data at finite concentrations, and the use of two permits a fit to be achieved for the various thermodynamic functions only up to v_2 = 0.1 to 0.2. This confirms the suggestion of Tompa[40] that a second χ parameter is required in the theoretical treatment of polymer–diluent phase equilibria. Concerning the dilute solution treatment of Flory and Orofino,[32] the present data show that both $\mathbf{A}_2$ and $\mathbf{A}_3$ vanish at the same temperature, indicating $\Theta_2 = \Theta_1$. For comparison, Flory and Daoust[9] have reported χ_2 = 0.31 at the theta temperature of the polyisobutylene–benzene system, corresponding to

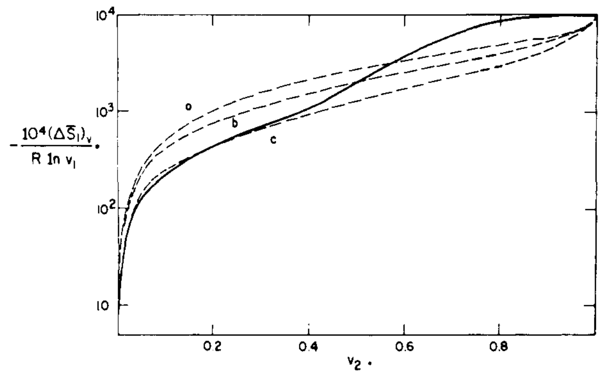

Fig. 13.—Smoothed values of $(\Delta\bar{S}_1)_V$ for polystyrene–cyclohexane (full curve) compared with theoretical values calculated as described in the text.

a very small, but positive, value of $\mathbf{A}_3$. Some of the other questions raised by the Flory–Orofino treatment are still more difficult to answer. We may examine the effect of higher χ parameters upon the procedure previously used[41] to evaluate ψ_1 and Θ_1 from dilute solution measurements. Upon taking $\psi_2 = 0.15$, equation 6b′ predicts a small decrease of the apparent ψ_1 values with molecular weight of about the magnitude actually observed.[41] For molecular weights of the order of that of fraction III, the second term in equation 6b′ would contribute $0.02 - 0.03$ to the apparent ψ_1, which is well within the experimental error of these measurements. On the other hand, had Flory and Orofino retained still higher terms in the expansion of (2′) and if these make a significant contribution to $\mathbf{A}_2$, then $\mathbf{A}_2$ would presumably vanish at a temperature somewhat below Θ_1. As stated previously, this would invalidate the procedure used to deduce ψ_1 and Θ_1 values from dilute solution measurements near Θ_1 by destroying the concept of a unique theta temperature. The only evidence bearing on this point appears to be the good agreement between Θ_1 values deduced from precipitation temperature and virial coefficient measurements, and the fact that χ_1 as evaluated from the revised lattice model equation 3′ exhibits a value of $^1/_2$ at the temperature for which $\mathbf{A}_2$ vanishes, both for the present system and for polyisobutylene–benzene.[9]

The Flory lattice model treatment must be considered incomplete inasmuch as it does not furnish an explicit expression for the χ parameters. One might represent the configurational entropy of dilution by some expression other than (10), on the assumption that the terms in ψ represent corrections to the Flory configurational entropy as suggested by equations 8 and 8′. In Fig. 13 the experimental $(\Delta\bar{S}_1)_V$ values (full curve) are compared with the configurational entropies of dilution as calculated from several lattice model treatments. Dashed curve *a* represents the configurational entropy of dilution as given by equation 10 used above to evaluate ψ and Θ. Curve *b* was calculated according to Guggenheim's treatment,[19] taking $z = 6$ and $w/kT = 0.116$. One could force a fit to the lower concentration region of the experimental curve by assigning to z a number between two and three, but this would not be a physically realistic coördination number. A more satisfactory approach is to consider some of the sites to be multiply connected. Curve *c* is calculated from Tompa's treatment[21] of a ribbonlike molecule two sites wide, with $z = 6$. This provides a good representation of the observed $(\Delta\bar{S}_1)_V$ values up to $v_2 \cong 0.35$. If the structure of the polystyrene molecule requires such a model to fit the data in cyclohexane, the same should be true of this polymer in other solvents as well. This point of view is supported by the observation of Bawn and Wajid[46] that the entropy of dilution for polystyrene in several solvents can only be fitted by the expression of Guggenheim if the coördination number is assigned an unrealistically low value.

The marked increases observed for $\Delta\bar{E}_1$ and $\Delta\bar{S}_1$ at concentrations above $v_2 = 0.35$ still require comment. This type of deviation is not evident in the free energy of dilution, as can be seen upon comparing Figs. 9 and 13. It is particularly disturbing that the experimental values for $(\Delta\bar{S}_1)_V$ fall above curve *a* in Fig. 13. An analysis of the vapor pressure data of Bawn and Patel[6] for polyisobutylene–benzene at 25, 40 and 65° also leads to the conclusion that $(\Delta\bar{S}_1)_V > \Delta\bar{S}_1{}^*$ for $v_2 > 0.6$ at all three temperatures. (It should be mentioned that the values of $\Delta\bar{H}_1$ listed by Bawn and Patel appear to be in error by approximately a constant factor at all concentrations.) This conclusion is not altered by replacing the $\Delta\bar{F}_1$ values taken from Bawn and Patel's data with those deduced from the manometric data of Jessup.[10] Since the refinements of Flory's treatment of the lattice model result in a *diminished* entropy of dilution, one must assume either that order exists in at least one of the pure components of both systems or that there are unusually large volume changes upon forming concentrated solutions of both polymers.

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