TABLE II

	Ml. M_1^a	Solvent	Solvent, ml.	Base	G. of base	Reacn. temp., °C.	Time, hr.	Resid. P(p.s.i.)	At temp. °C.	% Na or K
1	10	Alcohol	50	KOH	2.13	194, 220, 246	93	680	5	22.2
2	10	Alc.-H_2O	50-55	KOH	2.44	200	106	655	6	24.2
3	20	Ether	30	KOH^b	10	200	11	160	15	33.4
4	20	Ether	35	KOH	4	190	73.5	110	12	36.5
5^c	15	Benzene	50	KOH	3	190	118	200	24	30.8
6	50	M_2	...	KOH	5	190	61.5	290	24	35.7
7	50	M_2	...	KOH^b	5.5	185	43	440	24	..^{d}
8^c	65	M_2	...	NaOH	5	150	46.5	<100	24	31.1
9	50	M_2	...	NaOH	5	190	120	<100	24	38.3

^{a} M_2 = hexamethyldisiloxane. ^{b} KOH not fused. ^{c} Platinum thimble used as liner to collect precipitate. ^{d} Solid hydrolyzed to yield trimethylsilanol.

of metallic sodium with trimethylsilanol. Hydrolysis of a sample of the solid from reaction 9 was carried out with cold water in a small test-tube to yield hexamethyldisiloxane. The infrared spectrogram of this liquid was identical with that obtained from a pure sample of hexamethyldisiloxane. The refractive index at 20° was 1.3772 (reported in the literature, 1.3774[6] and 1.3772[3]).

Summary

The action of sodium and potassium hydroxides

(6) Burkhard, Rochow, Booth and Hartt, *Chem. Revs.*, **41**, 127 (1947).

on hexamethyldisiloxane in various solvents has been investigated. In hydroxyl-containing solvents at elevated temperatures the fission of methyl groups as methane appears to be the principal reaction, but in suitable aprotic solvents the formation of methane may be suppressed to favor the formation of alkali-metal salts of trimethylsilanol.

Thermodynamic Properties of Concentrated Polystyrene Solutions[1]

BY MARTIN J. SCHICK,[2] PAUL DOTY* AND BRUNO H. ZIMM

Thermodynamic investigations in which the heat and entropy of dilution are determined as a function of composition are still insufficient to allow detailed comparison with statistical thermodynamic theories.[3-10] These properties have been determined in very dilute solutions for several cases[11-15] and in the rubber–benzene sys-

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(1) This paper is based upon the dissertation presented by M. J. Schick in the partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Polytechnic Institute of Brooklyn in 1948. It has been presented in part at the 115th Meeting of the American Chemical Society in San Francisco, California.

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(3) P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942); **13**, 453 (1945).

(4) M. L. Huggins, *ibid.*, **46**, 151 (1942); *Ind. Eng. Chem.*, **35**, 216 (1943).

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

(6) W. J. C. Orr, *Trans. Faraday Soc.*, **40**, 320 (1944); **43**, 12 (1947).

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

(8) R. L. Scott and M. Magat, *ibid.*, **13**, 172 (1945).

(9) B. H. Zimm, *ibid.*, **14**, 164 (1946).

(10) A. R. Miller, "Theory of Solutions of High Polymers," Oxford University Press, 1948.

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

(12) E. Wolff, *ibid.*, **23**, 439 (1940).

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

(14) P. Doty and E. Mischuck, THIS JOURNAL, **69**, 1631 (1947).

(15) P. Doty, M. Brownstein and W. Schlener, *J. Phys. Colloid Chem.*, **53**, 213 (1949).

tem[13,16,17] further measurements cover the range from 0.12 to 0.86 volume fraction of rubber. However no measurements exist in the range of concentrated solutions, *i. e.*, 1 to 10% polymer and at still higher concentrations data have been obtained only on one system. Yet in the comparison of theory and experiment the largest differences appear to fall in the concentrated solution region where only interpolated experimental values are available. Indeed our entire knowledge of this system below 12% concentration rests on the measurement at two temperatures of the osmotic pressures of three dilute solutions. Moreover data in the dilute solution region for some other systems are incompatible with present theories. This disagreement appeared to be particularly striking for some polystyrene solutions.[15] For this reason and in view of the absence of data on any concentrated polymer solutions the osmotic pressure of polystyrene solutions at different temperatures has been determined in the range of 0.002 to 0.10 volume fraction. Four different solvents were studied.

Experimental Details

Osmometers.—Two glass osmometers, each having a capacity of 3 cc., were used. The type employed to measure pressures up to 4 g./sq. cm. was that described by

(16) J. Ferry, G. Gee and L. R. G. Treloar, *Trans. Faraday Soc.*, **41**, 340 (1945).

(17) G. Gee and W. J. C. Orr, *ibid.*, **42**, 507 (1946).

Zimm and Meyerson.[18] Higher osmotic pressures were measured in a modification illustrated in Fig. 1. In this arrangement a high pressure, glass stopcock is used to close the filling tube which is joined to the solution capillary tube by a ground-glass joint. The stopcocks and joint were greased with a silicone lubricant (Dow Corning Co.) which was insoluble in the solvents used. In the high pressure measurements end-plates having a large number of small holes were required in order to support the membrane properly. Denitrated cellulose nitrate membranes were employed. They were conditioned by a stepwise transfer through a series of liquids of decreasing polarity, finally remaining at least one week in the solvent for which they were being conditioned.

Manipulation.—In the osmotic pressure range below 4 g./sq. cm. the procedure already described[18] was followed. The osmometer was mounted within a cylinder containing the solvent. The cylinder was stoppered with a cork wrapped in aluminum foil and carrying a long glass tube which served as a reflux condenser for the solvent. The apparatus is mounted in a thermostat having a temperature control of 0.01°. The static method of observation was used here. The difference in height of the menisci in the solution and capillary tubes became constant within a few hours. This equilibrium height was then corrected by the difference in menisci observed when only solvent was present in the apparatus—a correction of only a few tenths of a millimeter at most. The osmotic pressure was obtained by multiplying the corrected menisci difference by the density of the solution at the temperature of the measurement. The blank correction was redetermined after every fifth osmotic pressure determination. Each time the osmometer was refilled it was rinsed first with solvent and then three times with the next solution to be measured.

For osmotic pressures above 4 g./sq. cm. a different procedure was developed using the modified osmometer. In this case the osmotic pressure is equal to the sum of the corrected menisci difference multiplied by the solution density at the bath temperature and the product of the mercury manometer head and the density of mercury at the manometer temperature. The determination is carried out as follows. After a pressure-tight seal is made at the ball joint the external pressure is adjusted by opening stopcock 1 and raising the mercury level in the bulb. As the pressure increases, the mercury level is raised to keep the solution level within the capillary section. Stopcock 2 permits the regulation of the air volume between the solution and the mercury. The equilibrium pressure was determined by a dynamic procedure. First the approximate value was found by noting the mercury pressure at which the reading in the solution capillary remained nearly constant. The mercury pressure was then raised somewhat above this approximate value and the height of the solution meniscus followed as a function of time. Similar observations were made with the mercury pressure adjusted to a lower value than the approximate value. A constant value of the half sums for such a series of measurements defined the equilibrium value. No effects of diffusion through the membrane were observed and no visible opalescence could be detected when solvent taken from the osmometer following a measurement was dropped into methanol.

Materials.—The solvents used were of chemically pure grade and before use were refractionated by withdrawing the center fraction from a distillation in a helices-packed fractionation column. The solvents exhibited the correct densities and refractive indices.

The polystyrene was prepared by emulsion polymerization in a manner already described[19] using persulfate catalyst at a temperature of 63°. During purification of the polymer by repeated solution in butanone and precipitation by the addition of methanol 10% of the polymer was removed. It is expected that this removal occurred pre-

(18) B. H. Zimm and I. Meyerson, THIS JOURNAL, **68**, 911 (1946).
(19) A. I. Goldberg, W. P. Hohenstein and H. Mark, *J. Polymer Sci.*, **2**, 503 (1947).
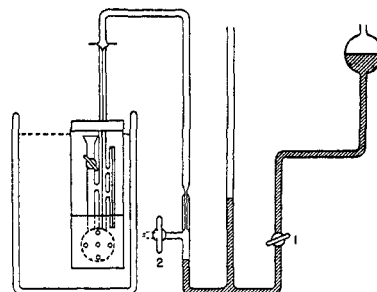

Fig. 1.—Osmometer assembly.

dominantly on the low side of the molecular weight distribution, thus removing the species most likely to diffuse through the membrane in later measurements. The purified sample, after prolonged vacuum drying at 45°, had an intrinsic viscosity in toluene at 26.0° of 220 cu. cm./g. Osmotic pressure measurements on dilute butanone solutions recorded in the next section showed the number average molecular weight to be 540,000.

The values of Boyer and Spencer[20] were used for the density of polystyrene in the solutions. The thermal expansion coefficients of the solvents were measured over the temperature range here studied and were found to be: butanone 0.00125, cyclohexane 0.0123, ethyl acetate 0.00139 and toluene 0.00112. The agreement between calculated and measured solution densities was better than one part in ten thousand in all cases thereby justifying the use of molar volume in place of partial molar volume. At 27.00° the solvent densities were found to be: butanone 0.7976, cyclohexane 0.7736, ethyl acetate 0.8919 and toluene 0.8592.

Results and Calculations

The osmotic pressure data obtained, using four different solvents at various temperatures, are recorded in Table I. For the calculation of the heats and entropies of dilution the experimental points were replaced by smooth curves that were considered to fit the data best. In order to characterize the curves that were used, the value of the reduced osmotic pressures read from these curves are entered in Tables I and II. The concentrations are expressed in grams of polystyrene per cc. at the temperature of measurement and osmotic pressure is in units of grams (force)/sq. cm. The data for cyclohexanone at 37.15° was not used in calculations. The limited range covered in this case was due to the proximity of the phase separation conditions.

As an illustration of the scope and precision of the data a plot is given in Fig. 2 of the reduced osmotic pressure for some of the toluene solutions at the two temperatures and the butanone solutions at one temperature. The uppermost curve represents the behavior expected at 69.2° for toluene on the basis of the 27° measurements if the heat of dilution had been zero. The difference between this curve and the experimental points at this temperature is a measure of the accuracy with which the heat of dilution can be estimated.

The data can be approximately represented by evaluating the virial coefficients B_n in the equation

$$\pi = RT\Sigma_n B_n c^n$$

(20) R. F. Boyer and R. S. Spencer, *ibid.*, **2**, 97 (1948).

TABLE I
OSMOTIC PRESSURE DATA

100 c g./cc.	$\pi/100\,c$ obsd.	smoothed	100 c g./cc.	$\pi/100\,c$ obsd.	smoothed	100 c g./cc.	$\pi/100\,c$ obsd.	smoothed	100 c g./cc.	$\pi/100\,c$ obsd.	smoothed	100 c g./cc.	$\pi/100\,c$ obsd.	smoothed
Toluene, 27.00°			Toluene, 69.20°			Butanone, 27.00°						Butanone, 49.05°		
0.496	1.21	1.15	0.474	1.12	1.12	0.0954	0.502	0.51	0.0927	0.501	0.58	5.230	2.46	2.68
1.031	1.86	1.95	.578	1.22	1.25	.2379	.570	.57	.3062	.582	.64	5.356	2.62	2.75
1.681	2.87	2.87	.985	1.85	1.85	.3153	.618	.60	.429	.697	.69	6.158	3.10	3.10
1.681	2.78	2.87	1.526	2.67	2.73	.481	.707	.67	.467	.714	.71	7.240	3.73	3.62
2.084	3.74	3.74	2.421	4.62	4.50	.786	.793	.77	.747	.790	.80	8.188	4.44	4.13
2.534	4.60	4.60	3.008	5.51	5.77	.943	.861	.84	.915	.878	.87	9.034	4.73	4.68
3.137	5.81	5.81	3.541	7.52	7.10	1.596	1.08	1.08	1.513	1.10	1.10	10.034	5.34	5.55
3.702	7.06	7.05	4.575	9.89	9.80	2.362	1.38	1.40	1.804	1.21	1.21	10.261	5.77	5.77
4.790	9.75	9.75	6.244	14.77	14.80	3.780	2.05	2.05	2.971	1.73	1.70	11.539	7.22	..
6.530	14.63	14.32	8.209	21.58	21.55	5.431	2.85	2.86	4.220	2.17	2.25			
8.572	19.65	19.80	10.001	28.03	28.00	7.021	3.65	3.65						
10.446	24.94	24.94				9.008	4.72	4.67						

TABLE II
OSMOTIC PRESSURE DATA

100 c g./cc.	$\pi/100\,c$ obsd.	smoothed	100 c g./cc.	$\pi/100\,c$ obsd.	smoothed
Ethyl acetate, 27.00°			Cyclohexane, 37.15°		
0.426	0.523	0.540	0.409	0.447	0.475
.699	.613	.625	.665	.493	.460
.913	.664	.688	.809	.497	.455
1.071	.747	.737			
1.643	.921	.925	Cyclohexane, 49.05°		
1.647	.929	.925	0.259	0.551	0.551
2.193	1.10	1.10	.402	.561	.576
2.867	1.38	1.34	.614	.572	.605
5.199	2.26	2.26	.819	.618	.637
6.514	2.90	2.81	1.234	.734	.717
6.514	2.70	2.81	1.611	.854	.800
8.510	3.77	3.77	2.095	.920	.928
Ethyl acetate 49.05°			Cyclohexane, 60.00°		
0.413	0.639	0.590	0.606	0.723	0.723
.679	.697	.690	0.807	.765	.788
.887	.774	.765	1.217	.953	.938
1.039	.828	.825	1.590	1.089	1.080
1.594	1.05	1.04	2.160	1.315	1.315
2.127	1.26	1.25	3.009	1.693	1.69
2.906	1.49	1.57			
5.044	2.51	2.56			
6.320	3.33	3.19			
8.316	4.15	4.25			

TABLE III
VIRIAL COEFFICIENTS FOR POLYSTYRENE SOLUTIONS

$$\pi = RT\,(B_1c + B_2c^2 + B_3c^3 + \ldots)$$

π in grams (force)/sq. cm., c in grams/cu. cm. and R in gram (force)cm./degree/mole

Solvent	Temp., °C.	$B_2 \times 10^6$ moles/g.²/cm.³	$B_3 \times 10^7$ moles/g.³/cm.⁶
Cyclohexane	49.0	0.4	1.5
	60.0	1.1	1.0
Butanone	27.0	1.4	0.6
	49.0	1.4	0.4
Ethyl acetate	27.0	0.9	1.1
	49.0	1.0	1.1
Toluene	27.0	5.1	5.2
	69.0	3.8	7.2

The first virial coefficient is the reciprocal molecular weight, in this case equal to 1.91×10^{-6} mole/gram. The second and third coefficient have been evaluated and are listed in Table III. The fourth coefficient is zero within probable experimental error except in the case of toluene solutions where a value of about -4×10^{-7} mole-cm.⁹/g.[4] appears to be required. It is interesting to note that in these four cases the third virial coefficient is approximately proportional to the second: in other words, the higher the initial slope of the reduced osmotic pressure plot the greater the curvature.

The free energy of dilution as a function of concentration was calculated from the smoothed curves of reduced osmotic pressure. The heat of dilution was then derived at various concentrations by dividing the difference between $\Delta \bar{F}_1/T$ for the same solution (equal weight fraction concentration) at the two temperatures by the difference of the reciprocal absolute temperatures. The results are shown in Fig. 3 where the heat of dilution in calories divided by the square of the volume fraction of the polymer, at the average of the two temperatures of observation, is plotted against volume fraction. The probable experimental error in $\Delta \bar{H}_1/v_2^2$ is estimated to be ± 20 cal. Within this probable error the results can be represented by straight lines. However, for completeness, the detailed results of our calculations have been given as dashed lines in those cases where they deviated greatly from straight lines. The estimates for $\Delta \bar{H}_1/v_2^2$ from previous work[15] has also been included as circles in Fig. 3. These values are about 25% lower than originally quoted due to the approximate nature of the earlier calculation in which the temperature dependence of concentration was neglected. The agreement is seen to be just within the estimated probable error of the two experiments.

The entropies of dilution have been evaluated in such a manner as to remove the effect of molecular weight. This is done by subtracting the in-
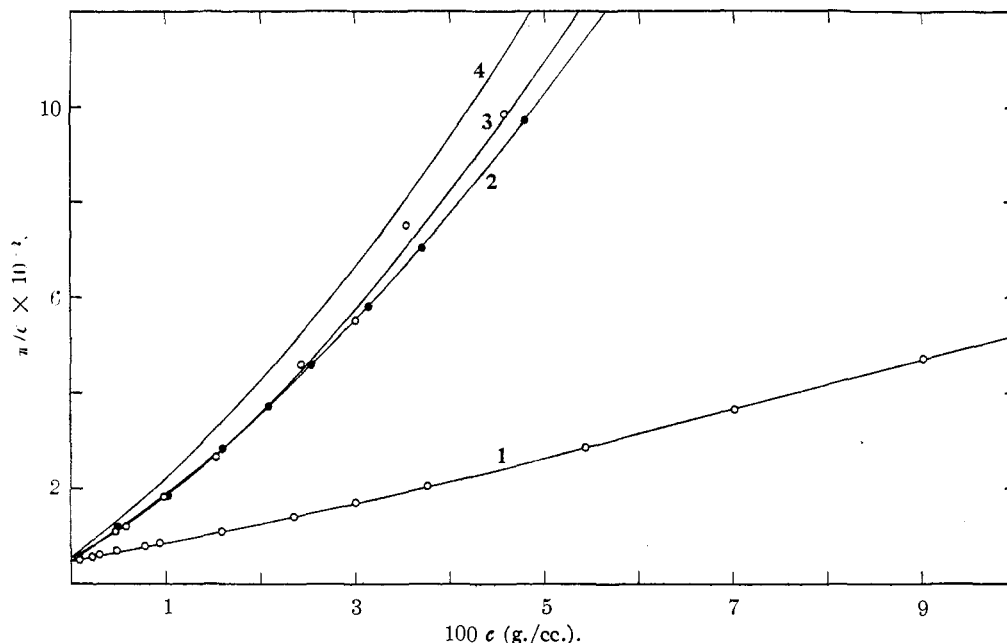
Fig. 2.—Reduced osmotic pressure of polystyrene solutions: curve 1, butanone solutions at 27.0°;   curve 2, toluene solutions at 27 0°;   curve 3, toluene solutions at 69.2°;   curve 4, expected value of curve 3 if heat of dilution were zero.

tercept at $c = 0$ of the reduced osmotic pressure from the value at a given concentration. If the free energy of dilution obtained from this altered osmotic pressure is subtracted from the heat of dilution and the result divided by absolute temperature, $\Delta \bar{S}_1{}^*$, the entropy of dilution corrected
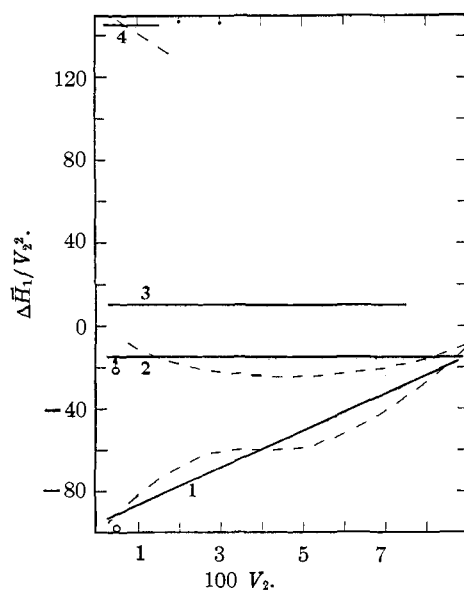

Fig. 3.—Heat of dilution divided by square of volume fraction as a function of volume fraction: curve 1, toluene; curve 2, butanone; curve 3, ethyl acetate; curve 4, cyclohexane. Dashed lines correspond to calculation, full lines to simplest representation of result. Circles express previous determinations. The lower circle should appear at an abscissa value of -125.

to infinite molecular weight of polymer, is obtained. This quantity divided by the square of the volume fraction is shown in Fig. 4. These values are calculated for 27°.
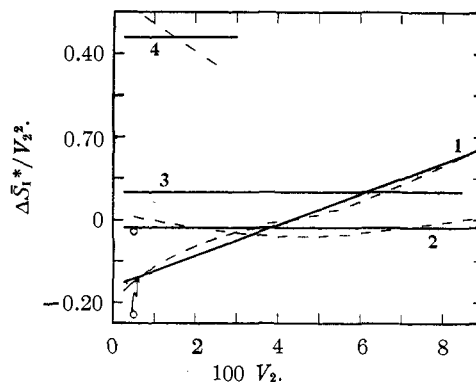
Fig. 4.—Entropy of dilution: curve 1, toluene; curve 2, butanone; curve 3, ethyl acetate; curve 4, cyclohexane. Dashed lines correspond to calculation, full lines to simplest representation of result. Circles express previous determinations.

Although not of direct interest the reduced specific viscosity of toluene, cyclohexane and butanone solutions is shown in Fig. 5. Contrary to the usual correlation between the magnitude of the reduced specific viscosity and the slope of the reduced osmotic pressure in vinyl polymers cyclohexane exhibits unexpectedly large values of specific viscosity as compared with butanone.

Discussion

On the basis of the experiments cited in the introduction, especially those of the rubber–benzene

Fig. 5.—Reduced specific viscosity of polystyrene solutions at 50°: curve 1, butanone; curve 2, cyclohexane; curve 3, toluene.

system, the concept has grown that in the absence of specific interaction in polymer solutions $\Delta \bar{H}_1/v_2^2$ is positive to an extent depending on the difference in cohesive energy density between solvent and polymer and increases with increasing concentr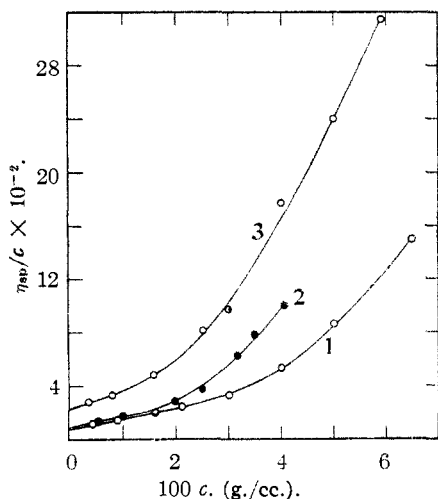ation toward a constant limiting value. The data in Fig. 3 for cyclohexane and ethyl acetate can be fitted into this pattern, but the values for butanone and toluene, being negative below 0.1 volume fraction are in conflict with current views. At higher concentrations it appears that $\Delta \bar{H}_1/v_2^2$ probably becomes positive; consequently the difficulty may exist only at the lower end of the concentration scale. Possible explanations for this anomalous behavior at low concentrations have been offered.[15,22]

The large slopes of the reduced osmotic pressure plots for many polymer solutions have been interpreted,[3] on the assumption that the heat of dilution was negligible, as corresponding to large values of the entropy of dilution. It is generally agreed that the statistical calculations of the entropy of dilution using the lattice model[3-8,10] predict excessively large values but qualitative arguments can be introduced which diminish the original estimates by a factor of about one-half.[3,21] This is sufficient to account for the values of about 0.5 found for $\Delta \bar{S}_1^*/v_2^2$ in dilute benzene solutions of rubber. Similarly the values for cyclohexane solutions in this study can be explained. However, the values of $\Delta \bar{S}_1^*/v_2^2$ for the other three systems cluster about zero. The expectation of this behavior on the basis of earlier osmotic pressure[15] and light scattering[22] studies of dilute toluene solutions is clearly borne out. At this point it is of

(21) A. R. Miller, *Nature*, **163**, 838 (1949).

(22) B. H. Zimm. *J. Chem. Phys.*, **16**, 1099 (1948).

interest to recall that in a similar investigation of dilute polyvinyl chloride solutions[14] abnormally low values of the entropy of dilution were found in cyclohexanone and butanone solutions. This point was not emphasized at the time because of the complicated character of these solutions. But its consideration now in connection with these more extensive measurements on extremely simple systems devoid of any strong specific interactions establishes the point that widely different entropies of dilution are exhibited by different solutions of the same polymer at the same concentration and that, moreover, these entropy values can be many times lower than can be accounted for by current statistical theories.

The establishment of an unique explanation of these thermodynamic data in terms of molecular concepts appears unlikely at present in view of the paucity of detailed molecular knowledge of such systems. The suggestion[15] made previously to account for low entropy of dilution in toluene solutions still appears to be feasible, but its extension to include the wide range of values found in different solvents is admittedly difficult. With respect to this latter point it seems of interest to note that in both the polyvinyl chloride and polystyrene solutions the solvents capable of the least specific interaction with the polymers—dioxane and cyclohexane—gave rise to the highest entropy values. Perhaps the abnormally high reduced specific viscosity of cyclohexane solutions is not an unrelated phenomenon. These observations emphasize the possibility that the solvent molecules may govern to a very large extent the number and character of the configurations that dissolved polymer molecules may display.

Acknowledgment.—The authors appreciate the assistance of Professor F. Eirich during the progress of the work reported herein.

Summary

1. The osmotic pressures of polystyrene solutions have been measured at different temperatures over the concentrated solution range of approximately 0.5 to 11%. Measurements were made in four solvents: toluene, butanone, ethyl acetate and cyclohexane.

2. Heats and entropies of dilution were calculated. Small negative heats of dilution were obtained for toluene and butanone solutions. A trend toward normal positive values was indicated by the results at higher concentrations.

3. The entropy of dilution for cyclohexane solutions was high enough to be within the range predicted by statistical theories. The values in other solutions were very low—in the vicinity of zero—clearly in conflict with theoretical expectation.