equation 1 is combined with the free surface energy as

$$h = \gamma + Q = \gamma - T(\partial\gamma/\partial T) \qquad (2)$$

From reference to equation 1 it is seen that the entropy of surface formation is equal to the negative temperature coefficient of the surface tension, and since the values of this property are tabulated as the b factors for the n-alkanes in Table I, the data necessary to calculate Q and h are available. The temperature–latent heat relations for the n-alkanes take the form of the linear equation, $Q = c + dt$. The Q values, together with the c and d factors of the least squares equations, are tabulated in Table II.

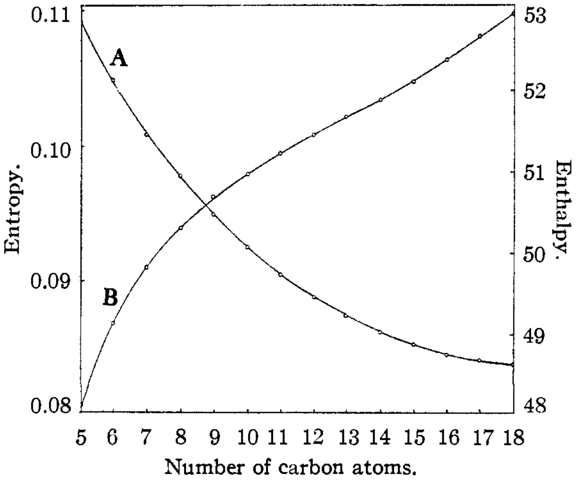

Fig. 1.—A, the entropies of surface formation; B, the enthalpies of surface formation as a function of the number of carbon atoms per molecule.

The least squares equation relating the entropy and the number of carbon atoms per molecule, n, is given by the following power series

$$s = 0.14024 - 0.007921n + 0.0003674n^2 - 0.00000568n^3$$

The plot of the entropies calculated from this equation are shown in Fig. 1a, and the enthalpies are shown in Fig. 1b.

From reference to the tables it is evident that while γ decreases and Q increases with the temperature for each of the compounds, h, the sum of these, and s, which is (Q/T), are independent of the temperature. The curves (a) and (b) of Fig. 1 show that the enthalpies increase and the entropies decrease with increasing molecular weights of the compounds, and that the latter appears to be approaching a limiting value of about 0.0830.

DETROIT, MICH.

[JOINT CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, DUKE UNIVERSITY AND CORNELL UNIVERSITY]

Statistical Mechanics of Dilute Polymer Solutions. V. Evaluation of Thermodynamic Interaction Parameters from Dilute Solution Measurements[1]

BY W. R. KRIGBAUM AND P. J. FLORY

RECEIVED MAY 28, 1953

Accurate osmotic pressure measurements are reported for benzene solutions of four well-fractionated polyisobutylene samples, varying in molecular weight from 102,000 to 720,000, at three temperatures in the vicinity of the Θ temperature at which the second virial coefficient in the expansion of the osmotic pressure vanishes. As evaluated from these data, $\Theta = 297.5$°K., independent of the molecular weight. The entropy of dilution parameter ψ_1, calculated from the change in the second virial coefficient with temperature at $T = \Theta$, is 0.34 ± 0.02. Further examination of the values obtained from the second coefficient reaffirms the previous observation that the theoretical pair interaction function $F(X)$ derived in a recent treatment of dilute polymer solutions varies too slowly with X (which depends on the segment–solvent interaction, and the molecular configuration.) The parameters Θ and ψ_1 for polyisobutylene in benzene have been evaluated independently from measurement of the critical consolute temperatures, T_c, for four fractions. The Θ values deduced by the two methods are in excellent agreement; however, ψ_1 obtained by the precipitation temperature method is twice that deduced from A_2. On the other hand, the ψ_1 value reported for the same system by Fox and Flory from intrinsic viscosity measurements is only half that calculated from the second virial coefficient.

Introduction

According to the statistical treatment of dilute polymer solutions,[2,3] the second coefficient, A_2, in the virial expression for the osmotic pressure

$$\pi = RT[A_1c + A_2c^2 + A_3c^3 + \ldots] \qquad (1)$$

takes the form

$$A_2 = (\bar{v}^2/V_1)(1 - \Theta/T)\psi_1F(X) \qquad (2)$$

where $\bar{v}$ and V_1 are the partial specific volume of polymer and the molar volume of solvent, respectively. The standard state entropy of formation of a polymer–solvent contact pair is given by $k(\psi_1 - {}^1/_2)$, k being Boltzmann's constant, and Θ is the critical temperature for which the second coefficient vanishes. The segment–solvent contact-pair heat parameter, κ_1, is given in terms of the foregoing by $\psi_1\Theta/T$.[4] As given by theory, the function $F(X)$ appearing in equation 2 is equal to unity for all molecular weights at the unique temperature Θ, but under all other conditions varies with molecular weight, temperature and the thermodynamic parameters characterizing the polymer–solvent interaction.

Earlier statistical treatments,[5,6] which disre-

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[1] The experimental work reported in this paper was carried out at Cornell University under sponsorship of the Government Research Program on Synthetic Rubber, Synthetic Rubber Division, Reconstruction Finance Corporation.

[2] P. J. Flory, *J. Chem. Phys.*, **17**, 1347 (1949).

[3] (a) P. J. Flory and W. R. Krigbaum, *ibid.*, **18**, 1086 (1950); (b) W. R. Krigbaum and P. J. Flory, *ibid.*, **20**, 873 (1952).

[4] These parameters are discussed more fully in ref. 3a; see also, "Thermodynamics of High Polymer Solutions," by P. J. Flory and W. R. Krigbaum, a chapter in the "Annual Review of Physical Chemistry," Vol. 2, 1951; published by Annual Reviews, Inc., Stanford, California.

[5] M. L. Huggins, *J. Phys. Chem.*, **46**, 151 (1942); *Ann. N. Y. Acad. Sci.*, **43**, 1 (1942).

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

garded the essential discontinuous nature of very dilute solutions of high polymers, led to an expression for the second virial coefficient which differs from equation 2 through omission of the factor $F(X)$. The second virial coefficient then appeared to be independent of molecular weight, and of molecular weight heterogeneity as well. Osmotic pressure measurements at two temperatures (for any molecular weight whatsoever) would suffice to evaluate the desired thermodynamic parameters ψ_1 and Θ in equation 2, if the factor $F(X)$ could be omitted.

The determination of thermodynamic parameters according to the dilute solution theory is complicated by the implicit dependence of the factor $F(X)$ on these same parameters. ψ_1 and Θ might be deduced by a method of successive approximations, making literal application of the theoretical relationship for $F(X)$; however, the previous investigation[7] has revealed a discrepancy between the theoretical and the observed $F(X)$ functions. Thus, while the second coefficients, A_2, for polystyrene in toluene and for polyisobutylene in cyclohexane (both good solvents for the respective polymers) have been observed[7] to decrease with molecular weight, as is required by the dilute solution theory, the changes are more rapid than the theoretical $F(X)$ would predict. A predicted increase in A_2 with molecular weight heterogeneity was confirmed by results reported in the previous paper.[7]

Evaluation of the thermodynamic parameters is greatly simplified in a poor solvent at the Θ temperature, where $F(X)$ must necessarily equal unity. The entropy parameter, ψ_1, may then be determined without relying on the form of the function $F(X)$, as will be seen from equation 2. The present paper reports osmotic measurements on dilute benzene solutions of polyisobutylene fractions carried out at three temperatures, 20, 30 and 40°, in the vicinity of the Θ temperature, 297.5°K. Once Θ is known, and ψ_1 has been determined by interpolating $A_2/(\bar{v}^2/V_1)(1 - \Theta/T)$ to $T = \Theta$, the experimental A_2 values furnish a further test of the theoretical $F(X)$ function.

Experimental

Four polyisobutylene fractions were selected from those obtained by a large scale fractionation described elsewhere.[7] The solvent was freshly distilled reagent grade benzene ($\rho_{20} = 0.879$, $\rho_{30} = 0.868$, $\rho_{40} = 0.857$). Details of construction of the osmometers appeared in a previous paper[7] of this series. The membranes employed were Sylvania No. 300 regenerated cellophane. At 30° the permeability of this type of membrane to benzene was such that one hour was required for the difference in heights of the liquid columns to decrease to half its initial value when both cells were filled with solvent. The rate of solvent permeation exhibited a considerable positive temperature coefficient. The differences in heights of the liquid columns were measured with a cathetometer reading directly to 0.001 cm. The temperatures of the three water-baths, operated at 20, 30 and 40°, were controlled to within ±0.01° by means of thyratron relays and mercury control switches.

Since values of the second virial coefficient for polyisobutylene in benzene are considerably smaller than those encountered in the preceding investigation, the present measurements were extended to higher concentrations to ensure reliable evaluation of the second coefficient. In order to minimize the amount of polymer required, successive measurements were performed on each solution at the three temperatures. There were disadvantages to this procedure, however. The series of observations for a single solution required five to six days; furthermore, cycling the osmometers between the three temperatures appeared to shorten materially the useful life of the membranes. The average difference, ±0.02 g./cm.,^{2} between the measured values for π and those calculated from the smoothed π/c *vs.* c relationship fitted as described below was almost three times the corresponding difference experienced in the previous isothermal investigation.[7] Comparison of the experimental and the smoothed (π/c) ratios is probably more significant, considering the different concentration ranges covered in the two sets of measurements. On this basis the average deviation, ±0.02, in (π/c) for the present measurements compares more favorably with ±0.015 realized previously.

Precipitation temperature measurements were performed on benzene solutions of four polyisobutylene fractions having molecular weights 2.5×10^5, 9×10^5, 3×10^6 and 6×10^6. Owing to the slight difference in refractive indices, the first appearance of the second phase in finely divided form did not give rise to a detectable turbidity. It was therefore necessary to lower the temperature stepwise, maintaining the solution at each temperature for a period of several hours in order to allow any droplets which might be present to coalesce and settle to form a distinct second phase.

Results

Osmotic Pressure–Concentration Relationship.—The osmotic pressure data for the four polyisobutylene fractions in benzene at 20, 30 and 40° were fitted to the equation

$$\pi/c = (\pi/c)_0[1 + \Gamma_2 c + g(\Gamma_2 c)^2] \quad (3)$$

using the procedure described by Fox, Flory and Bueche.[8] Since the temperatures of interest are near $T = \Theta$, plots of π/c against c shown in Fig. 1 exhibit negligible curvature, except those for fraction PABIF (highest molecular weight). However, for the sake of consistency the factor g relating the third and second coefficients was estimated for each molecular weight and temperature according to the calculation of Stockmayer and Casassa,[9] making use of values for the molecular expansion factor α deduced from the intrinsic viscosity data of Fox and Flory.[10] From the highest to the lowest molecular weights, g values so calculated varied from −0.098 to −0.032 at 20°, and from 0.151 to 0.072 at 40°.

The logarithms of the measured (π/c) ratios were plotted against the logarithm of the polymer concentration, as shown in Fig. 2. Each experimental curve was fitted to the corresponding standard curve obtained by plotting the quantity in square brackets in equation 3, using the appropriate value for g, against $\Gamma_2 c$ on a log–log scale. $(\pi/c)_0$ and Γ_2 were evaluated from the displacements of the axes of the two graphs. In Table I are given the values so deduced for $(\pi/c)_0$ and A_2, equal to $(\pi/c)_0\Gamma_2/RT$ according to equations 1 and 3.

(π/c) ratios calculated according to equation 3, using the fitted values for $(\pi/c)_0$ and Γ_2, are compared with the observed ratios in Fig. 1.

Thermodynamic Parameters for Polyisobutylene in Benzene Calculated from the Second Virial Coefficient.—Values of A_2 given in Table I for these

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[7] W. R. Krigbaum and P. J. Flory, THIS JOURNAL, **75**, 1775 (1953).

[8] T. G Fox, Jr., P. J. Flory and A. M. Bueche, *ibid.*, **73**, 285 (1951); see also, W. R. Krigbaum and P. J. Flory, *J. Polymer Sci.*, **9**, 503 (1952).

[9] W. H. Stockmayer and E. F. Casassa, *J. Chem. Phys.*, **20**, 1560 (1952).

[10] T. G Fox, Jr., and P. J. Flory, THIS JOURNAL, **73**, 1909 (1951).

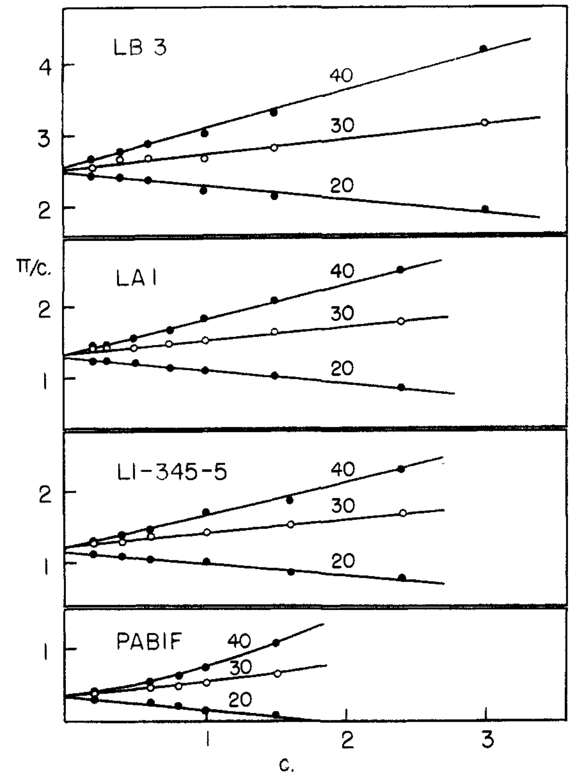

Fig. 1.—(π/c) plotted against polymer concentration for four polyisobutylene fractions in benzene at 20, 30 and 40°. Circles designate the experimental points; the full curves represent (π/c) ratios calculated according to equation 3 using values for the parameters taken from Table I.

TABLE I

OSMOTIC PARAMETERS FOR POLYISOBUTYLENE–BENZENE

Fraction	→	LB3	LA1	L1-5	PAB1F
$\bar{M}n$	→	101,000	191,000	206,000	710,000
$(\pi/c)_0{}^a$	$T = 293$	2.45	1.28	1.17	0.330
	$T = 303$	2.52	1.34	1.25	.365
	$T = 313$	2.60	1.37	1.28	.379
10^5A_2	$T = 293$	−7.18	−7.14	−6.67	−7.03
	$T = 303$	8.33	7.78	7.21	7.04
	$T = 313$	19.4	17.3	15.9	15.1
$\psi_1F(X)$ (Θ = 297.5°)	$T = 293$	0.37	0.36	0.34	0.36
	$T = 303$	.34	.32	.30	.29
	$T = 313$	.29	.26	.24	.23

[a] π, in g./cm.^{2} and c in g./100 cc.

four fractions appear plotted against the absolute temperature in Fig. 3. From this figure the temperature Θ at which the second virial coefficient vanishes is 297.5°K. for each of these polyisobutylene–benzene systems. In accord with theory, Θ exhibits no dependence on molecular weight over the sevenfold range investigated. The $\psi_1F(X)$ products calculated from the A_2's according to equation 2 appear at the foot of Table I. For this calculation we have assigned Θ = 297.5°K. and, corresponding to the temperatures 293, 303 and 313°K., the respective values: V_1 = 88.86, 89.99 and 91.14 cc./mole and $\bar{v}$ = 1.063, 1.097 and 1.104 cc./g. (the latter were obtained by extrapolating the volume-temperature relation reported by Fox and Flory[11] for bulk polyisobutylene). These $\psi_1F(X)$ products appear plotted against the absolute temperature in Fig. 4. Since $F(X)$ must necessarily equal unity at the unique temperature Θ, the data shown in Fig. 4 lead to the conclusion that ψ_1 = 0.34 ± 0.02 for each of the four fractions.

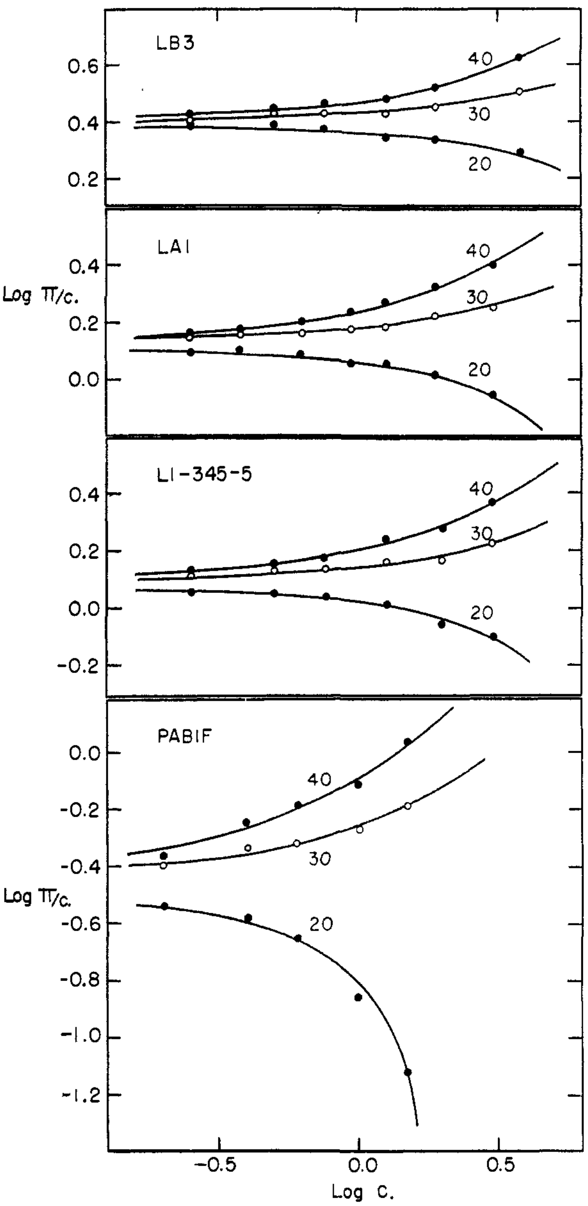

Fig. 2.—log (π/c) plotted against log c for the polyisobutylene fractions shown in Fig. 1.

An examination of Table I shows that evaluation of these data according to the earlier theories, which omit the factor $F(X)$, would yield *apparent* values for the entropy parameter ψ_1 varying from 0.23 to 0.37, depending on the temperature and molecular weight. As the critical temperature is approached, $F(X) \to 1$ and the two theories converge; therefore the apparent value is equal to the true value only at this unique temperature.

A Further Test of the Dilute Solution Treatment.—The function $F(X)$ appearing in equation 2 is given according to theory by the series

$$F(X) = 1 - X/2!2^{3/2} + X^2/3!3^{3/2} - \dots \qquad (4)$$

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[11] T. G Fox, Jr., and P. J. Flory, *J. Phys. Colloid Chem.*, **55**, 221 (1951).

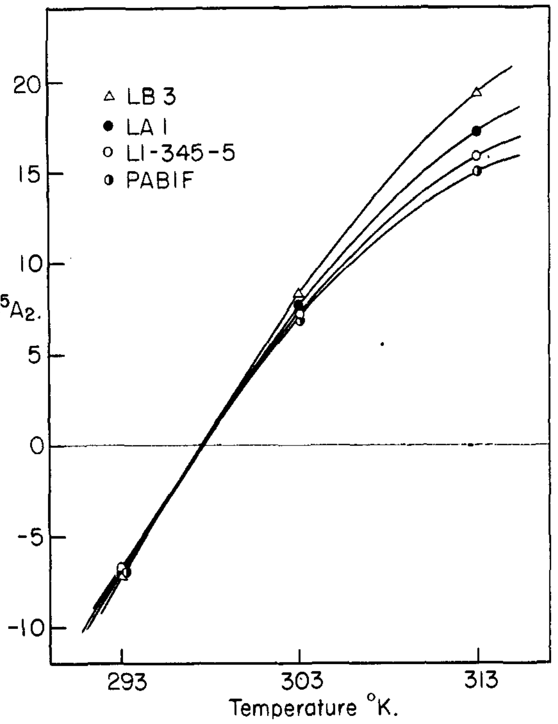

Fig. 3.—Fitted values for $A_2 \times 10^5$ plotted against the absolute temperature.

for small values of X.[12] This function has been evaluated numerically[3a] for larger values of the argument X, which is given by

$$X = 4C_M\psi_1(1 - \Theta/T)M^{1/2}/\alpha^3 \qquad (5)$$

where

$$C_M = (3^3/2^{5/2}\pi^{3/2})(\bar{v}^2/\mathbf{N}V_1)(\overline{r_0^2}/M)^{-3/2} \qquad (6)$$

Here **N** is Avogadro's number, M is the molecular weight of the polymer, and $\overline{r_0^2}$ is its mean-square end-to-end distance in the *unperturbed state* which prevails in a poor solvent at $T = \Theta$. The ratio $(\overline{r_0^2}/M)$ is a constant for a given series of polymer homologs characteristic of the chain structure, but is *dependent on the temperature.* This important ratio may be deduced from the intrinsic viscosity $[\eta]_\Theta$ measured in a Θ solvent according to the semi-empirical relationship[13]

$$[\eta]_\Theta/M^{1/2} = \Phi(\overline{r_0^2}/M)^{3/2} \qquad (7)$$

where Φ is a universal parameter which present estimates[13] indicate to be about 2.1×10^{21} with $(\overline{r_0^2})^{1/2}$ expresses in cm., M in molecular weight units, and $[\eta]_\Theta$ in the conventional deciliters/g. Inasmuch as the average unperturbed molecular configuration generally depends on the temperature, it is essential that viscosity measurements be performed for a series of Θ solvents (or mixtures), thus to evaluate $\overline{r_0^2}/M$ as a function of temperature. Since the other quantities appearing in equation 6 are readily determined, C_M may be computed for each temperature; it should depend on the solvent only through its molar volume, V_1.

The value of X depends on the cube of the molecular expansion factor α which relates the root-mean-square end-to-end distance $(\overline{r^2})^{1/2}$ in a given solvent to the unperturbed value $(\overline{r_0^2})^{1/2}$ at the same temperature. The expansion factor α which applies for given conditions of solvent and temperature may be determined from the ratio of the intrinsic viscosity measured at the specified conditions to that in a Θ solvent at the same temperature according to the relation

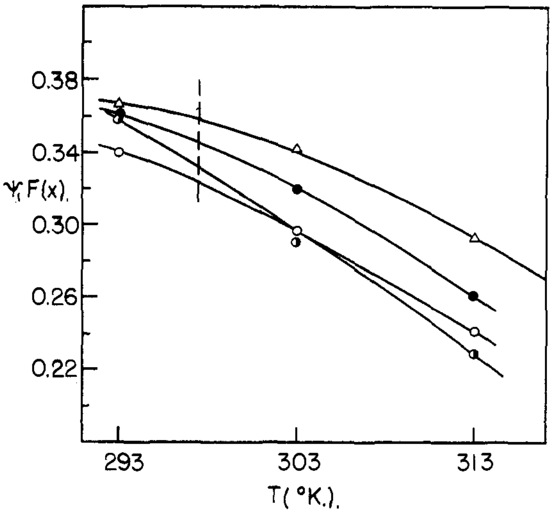

Fig. 4.—Experimental values for $\psi_1F(X)$ products plotted against absolute temperature. The symbols have the same significance as in Fig. 3.

$$\alpha^3 = [\eta]/[\eta]_\Theta \qquad (8)$$

Thus all the quantities occurring in equation 5, other than the molecular weight and the thermodynamic parameters, are determinable from independent measurements. It is particularly noteworthy that $F(X)$, and therefore A_2 also, depends not only on the thermodynamic parameters, but also on the molecular configuration as expressed by the quantities α^3 and $\overline{r_0^2}/M$.

Once ψ_1 has been evaluated, experimental $F(X)$ values may be obtained from the $\psi_1F(X)$ products found at the foot of Table I. These experimental $F(X)$ values are shown in Fig. 5 plotted against X, the latter having been calculated according to equation 5 as described above, using $\psi_1 = 0.34$ and the intrinsic viscosity data of Fox and Flory.[10] For comparison, theoretical $F(X)$ values calculated according to equation 4 are represented by the solid curve in Fig. 5. Although the experimental points are uncertain to some extent, due to the extreme sensitivity of $F(X)$ calculated in this manner to the precise value assigned to Θ, the trend of these data clearly indicates that the theoretical $F(X)$ as given by equation 4 varies too slowly with X. The difference between the experimental and calculated $F(X)$ curves is even more pronounced if X is calculated using ψ_1 obtained by the intrinsic viscosity method (*cf. seq.*). A similar conclusion was reached from comparison of calculated and observed molecular weight dependences of the second virial coefficient for polystyrene in toluene and for polyisobutylene in cyclohexane reported in the preceding paper.[7] Such defects in $F(X)$ should not, of course, affect values for the thermodynamic parameters de-

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[12] X is used here to represent the quantity $J\xi^3$ appearing in earlier notation. See refs. 3a and 4.

[13] T. G Fox, Jr., and P. J. Flory, *J. Polymer Sci.*, **5**, 745 (1950); THIS JOURNAL, **73**, 1915 (1951).

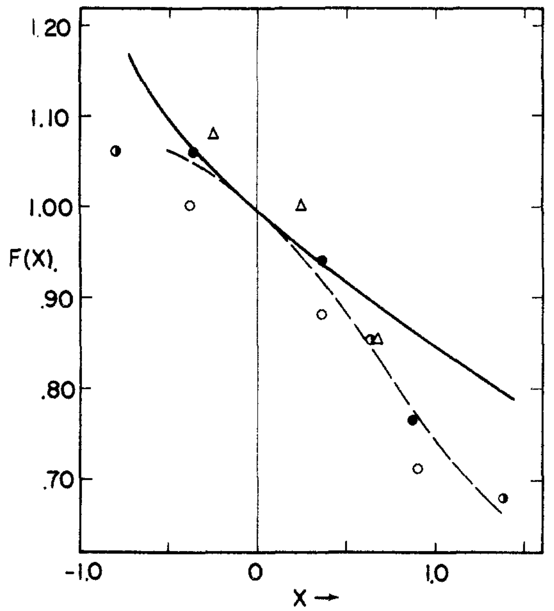

Fig. 5.—Values for $F(X)$ required to fit the observed temperature dependence of the second virial coefficient for polyisobutylene plotted against X. The symbols have the same significance as in Fig. 3. The theoretical $F(X)$ function is represented by the full curve; the dashed curve represents the trend of the observed $F(X)$ values.

duced as described above from measurement of the second virial coefficient near the Θ temperature.

Thermodynamic Parameters from Precipitation Temperatures.—In order to compare the thermodynamic parameters for polyisobutylene in benzene obtained from the second virial coefficient with those deduced from the dependence of the critical consolute temperature T_c on the molecular weight, critical temperatures were determined for benzene solutions of four polyisobutylene fractions varying in molecular weight from 2.5 × 10^5 to 6 × 10^6. According to theory,[6a,14] T_c is given by

$$1/T_c = (1/\Theta)[1 + (1/\psi_1)(1/x^{1/2} + 1/2x)] \quad (9)$$

where x is the ratio of the molar volumes of the polymer and the solvent. The results of these measurements are shown in Fig. 6, where $1/T_c$ appears plotted against $(1/x^{1/2} + 1/2x)$. As shown in Table II, the intercept of the straight line drawn in Fig. 6 corresponds to Θ = 298°K., which agrees satisfactorily with the value 297°K. estimated previously[10] from precipitation measurements without precise extrapolation to infinite molecular weight. It also agrees very well with the value obtained from the behavior of the second virial coefficient.

TABLE II

COMPARISON OF THERMODYNAMIC PARAMETERS FOR POLYISOBUTYLENE IN BENZENE

Method of measurement	Θ	ψ_1
Virial coefficient	297.5°K.	0.34
Precipitation temperature	298	.65
Intrinsic viscosity[10]		.15

The precipitation method involving measurements on a series of fractions covering a wide molecular weight range (as illustrated in Fig. 6) has been used most frequently in the past to determine the important parameter Θ. However, measurements of the osmotic pressure, or turbidity, at a series of temperatures offers the advantage that a single unfractionated polymer sample suffices.

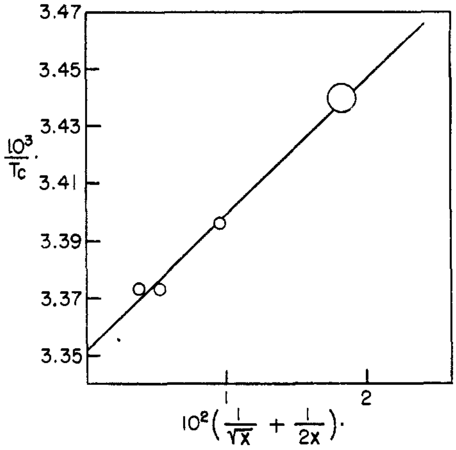

Fig. 6.—The reciprocal of the critical consolute temperature plotted against $(1/x^{1/2} + 1/2x)$ for four polyisobutylene fractions in benzene.

The value of the entropy parameter deduced from the slope of the line drawn in Fig. 6 is twice that obtained from the foregoing analysis of the second virial coefficients. The reason for this discrepancy is not immediately evident. The second virial coefficient A_2 is, of course, a property of the infinitely dilute solution; *i.e.*, it represents the initial slope of the plot of π/RTc against c. The value here obtained for ψ_1 is derived from the value of the ratio $A_2/(1 - \Theta/T)$ in the limit $T = \Theta$. The precipitation method depends on measurements at the critical precipitation point which occurs at substantially higher concentrations, generally from 1 to 5%, depending on the molecular weight. A variation in the parameters (ψ_1 and $\kappa_1 = \psi_1\Theta/T$) with concentration seems indicated,[15] although the basis for such variation is not clear. The validity of the precipitation method was previously questioned by Shultz and Flory[14] on the ground that critical conditions for phase separation should be sensitive to small variations in the thermodynamic parameters with concentration. Further work[16] has shown, however, that the entropy and energy parameters for several polymer–solvent systems obtained by the precipitation method stand in agreement with results for solutions of simple molecule analogs of the polymers. The discrepancy between the results obtained by the two methods cannot be resolved within the scope of present theories.

Parameters from Intrinsic Viscosities.—The expansion factor α by which the polymer is swollen due to the osmotic action of the solvent on the molecule at high dilution may be deduced from the intrinsic viscosity through use of equation 8. The value of α depends of course on the thermodynamic interaction between polymer segments and the solvent, and it may be related to the same thermodynamic parameters used in the theory of the sec-

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(14) A. R. Shultz and P. J. Flory, THIS JOURNAL, **74**, 4760 (1952).

(15) See in this connection H. Tompa, "Comptes Rendus 2nd Réunion de Chimie Physique," Paris, 1952, p. 163.

(16) A. R. Shultz and P. J. Flory, to be published.

ond virial coefficient. Thus, the following relationship has been derived[17]

$$\alpha^5 - \alpha^3 = 2C_M\psi_1(1 - \Theta/T)M^{1/2} \qquad (10)$$

where C_M is defined according to equation 6. ψ_1 may therefore be computed from the intrinsic viscosity measurements yielding α^3, provided C_M (at the temperature T; see above), Θ, and M are known. If Θ is not known, viscosity measurements at two temperatures suffice for resolution of the quantity $\psi_1(1 - \Theta/T)$. As shown in Table II, the ψ_1 value obtained in this manner for the polyisobutylene–benzene system is about half that obtained from the second virial coefficient. Application of the intrinsic viscosity method to other systems yields similar or smaller ψ_1 values; hence, the result for polyisobutylene–benzene is not exceptional.

It is too much to expect that the present treatments of the second virial coefficient and of the expansion factor α should be quantitatively exact. Experimental measurements[18] of intrinsic viscosities over very wide ranges in molecular weight show equation 10 to be only approximately of the correct form. The ψ_1 value calculated from intrinsic viscosity for this particular system could be brought into agreement with that obtained by one of the other methods by a numerical revision of the right hand member in equation 6; however, in view of the above-noted deficiency in the form of the ($\alpha^5 - \alpha^3$) relation, an improved treatment of intramolecular interactions may be required to remove these discrepancies.

Acknowledgment.—The authors wish to express their gratitude to Miss Norma O'Conner for assistance in performing the osmotic measurements, and to Mrs. Wylan Shultz who carried out the precipitation temperature and viscosity determinations.

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ITHACA, N. Y.

[17] P. J. Flory and T. G Fox, Jr., *J. Polymer Sci.*, **5**, 745 (1950); THIS JOURNAL, **73**, 1904 (1951).

[18] W. R. Krigbaum and P. J. Flory, *J. Polymer Sci.*, **10**, 37 (1953).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA]

Thermodynamic Functions of the Halogenated Methanes[1]

BY EDWARD GELLES AND KENNETH S. PITZER

RECEIVED JUNE 18, 1953

The heat capacity C_p^0, heat content $(H^0 - H_0^0)$, free energy function $-(F^0 - H_0^0)/T$ and entropy S^0 of 39 halogenated methanes have been calculated for 18 temperatures in the range 100–1500°K. to the rigid rotator-harmonic oscillator approximation employing recently revised vibration frequency assignments. The available thermodynamic data on the halogenated methanes are discussed in the light of these calculations.

The vibrational frequency assignments for the halogenated methanes have been examined recently by the authors with the aid of the Substitution Product Rule.[2]

Previous assignments for a number of halogenated methanes have been revised, and the confirmation of other assignments together with recent accurate infrared measurements on the vapors of a number of these compounds has provided a secure basis for the calculation of the vibrational contributions to the thermodynamic functions of the halogenated methanes.

TABLE I

PRODUCTS OF PRINCIPAL MOMENTS OF INERTIA OF HALOGENATED METHANES

$10^{117} \times I_1I_2I_3$ (g.^{3} cm.^{6})

Compound		Compound	
CF_4	3.24×10^3	CH_2I_2	5.69×10^4
CCl_4	1.14×10^5	CF_2Cl_2	2.50×10^4
CBr_4	2.35×10^6	CF_2Br_2	1.60×10^5
CH_3F	5.92	CCl_2Br_2	5.44×10^5
CH_3Cl	17.9	CH_2FCl	4.72×10^2
CH_3Br	44.6	CH_2FBr	1.06×10^3
CH_3I	55.1	CH_2ClBr	4.54×10^3
CHF_3	9.73×10^2	CH_2ClI	8.82×10^3
CF_3Cl	1.03×10^4	CH_2BrI	3.11×10^4
CF_3Br	2.38×10^4	CF_2HCl	3.44×10^3
CF_3I	4.50×10^4	CF_2HBr	8.22×10^3
$CHCl_3$	3.30×10^4	CF_2ClBr	6.08×10^4
CCl_3F	6.22×10^4	CCl_2HF	1.09×10^4
CCl_3Br	2.56×10^5	CCl_2HBr	7.50×10^4
$CHBr_3$	6.10×10^5	CCl_2FBr	1.30×10^5
$CFBr_3$	8.30×10^5	CBr_2HF	8.00×10^4
$CClBr_3$	1.24×10^6	CBr_2HCl	2.11×10^5
CH_2F_2	1.17×10^2	CBr_2FCl	3.22×10^5
CH_2Cl_2	1.87×10^3	$CHFClBr$	2.68×10^4
CH_2Br_2	1.41×10^4		

TABLE II

COMPARISON OF CALCULATED AND EXPERIMENTAL ENTROPY VALUES

(All at 298.16° K. in units of cal./deg. mole.)

Substance	$S_{calc.}$	$S_{expl.}$
CF_4	62.48	62.43[3]
CCl_4	73.94	73.7[4]
CH_3Cl	55.80	55.94[5]
CH_3Br	58.82	58.61[6]
$CFCl_3$	73.96	74.07[7]

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