

Fig. 2.—Plot of the OZ intercepts  $I^{-1}(0)$  vs.  $\Delta T$ .

techniques used in these experiments, we feel that the deviations are real and throw some doubt on the universal validity of the OZ and Debye theories. This conclusion stands in contrast to that of Münster and Schneeweiss,<sup>11</sup> who feel that a general conclusion as to the failure of the OZ theory cannot be drawn from the available evidence.

In spite of the observed deviations, the Debye theory furnishes a very good approximation, and allows the calculation of meaningful parameters, namely the "radius of action of intermolecular forces"  $l$  and the correlation length  $L$ . The former may be calculated from eq. 1. of ref. 2b, and the latter from

$$L^2 = \frac{l^2 T_c}{\Delta T} \quad (1)$$

(11) A. Münster and Ch. Schneeweiss, *Z. physik. Chem.*, **37**, 369 (1963).

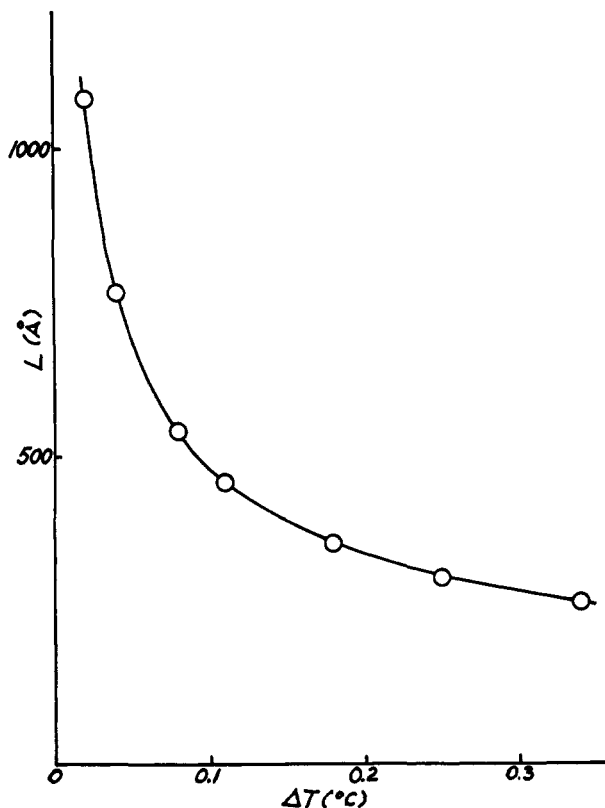


Fig. 3.—Plot of the correlation length  $L$  vs.  $\Delta T$ .

An average  $l$  value of  $8.7 \pm 1.0 \text{ \AA}$ . is obtained from the seven temperature runs of Fig. 1.  $L$  is shown as a function of  $\Delta T$  in Fig. 3.

The suggestion that the deviations from the Debye and OZ theories occur for systems with abnormally flat consolute curves does not seem to hold.<sup>11</sup> A more likely situation is that the OZ curves are not in fact linear except over a relatively narrow range of  $\sin(\theta/2)/\lambda$ ; this is supported by our X-ray and light scattering observation for the nitrobenzene-*n*-heptane system,<sup>6,7</sup> and also by observations reported by Debye.<sup>12</sup>

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(12) P. Debye, ref. 6, pp. 393-401

## COMMUNICATIONS TO THE EDITOR

### Thermodynamic Properties of Nonpolar Mixtures of Small Molecules

Sir:

The treatment of *n*-paraffin hydrocarbons and their mixtures presented elsewhere in this issue<sup>1,2</sup> (these papers will be referred to as I and II, respectively) can be recast in a form<sup>3</sup> which appears to be generally

(1) P. J. Flory, R. A. Orwoll, and A. Vrij, *J. Am. Chem. Soc.*, **86**, 3507 (1964).

(2) P. J. Flory, R. A. Orwoll, and A. Vrij, *ibid.*, **86**, 3515 (1964).

(3) P. J. Flory, to be published.

applicable to liquid solutions, irrespective of the size and shape of the molecular species, provided that they are not hydrogen bonded or highly polar. Here we present a preliminary comparison of theory with experiment for several representative binary mixtures of small, approximately spherical molecules.

The enthalpy of mixing can be expressed as follows

$$H^E = N_1 p_1^* v_1^* (\bar{v}_1^{-1} - \bar{v}^{-1}) + N_2 p_2^* v_2^* (\bar{v}_2^{-1} - \bar{v}^{-1}) + (N_1 v_1^* \varphi_2 / \bar{v}) X_{12} \quad (1)$$

TABLE I  
PARAMETERS FOR THE PURE COMPONENTS

	—CCl <sub>4</sub> —		c-C <sub>6</sub> H <sub>12</sub>	C <sub>6</sub> H <sub>6</sub>	C(CH <sub>3</sub> ) <sub>4</sub>
	0°	25°	25°	25°	25°
$v$ , cc. mole <sup>-1</sup>	94.21	97.08	108.75	89.40	118.03
$\alpha \times 10^3$ , deg. <sup>-1</sup>	1.191 <sup>a</sup>	1.229 <sup>a</sup>	1.217 <sup>a</sup>	1.223 <sup>b</sup>	1.811 <sup>c</sup>
$\gamma$ , cal. cc. <sup>-1</sup> deg. <sup>-1</sup>	0.320 <sub>9</sub> <sup>d</sup>	0.272 <sub>7</sub> <sup>e</sup>	0.255 <sub>3</sub> <sup>e</sup>	0.301 <sub>8</sub> <sup>e</sup>	0.185 <sub>2</sub> <sup>d</sup>
$\bar{v}$	1.2660	1.2927	1.2905	1.2916	1.3687
$T^*$ , °K.	4571	4697	4719	4708	3762
$p^*$ , cal. cc. <sup>-1</sup>	140.4	135.8	126.7	150.0	94.7

<sup>a</sup> S. E. Wood and J. A. Gray, *J. Am. Chem. Soc.*, **74**, 3729 (1952).  
<sup>b</sup> S. E. Wood and J. P. Brusie, *ibid.*, **65**, 1891 (1943). <sup>c</sup> American Petroleum Institute compilations, F. D. Rossini, *et al.*, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," API Research Project 44, Carnegie Press, Pittsburgh, Pa., 1953. <sup>d</sup> Calculated from compressibilities reported by J. Jeener, *J. Chem. Phys.*, **25**, 584 (1956). <sup>e</sup> Calculated from compressibilities reported by G. A. Holder and E. Whalley, *Trans. Faraday Soc.*, **58**, 2095 (1962).

TABLE II  
COMPARISON OF CALCULATED AND OBSERVED EXCESS QUANTITIES FOR EQUIMOLAR MIXTURES

	CCl <sub>4</sub> (1)-c-C <sub>6</sub> H <sub>12</sub> (2)		C <sub>6</sub> H <sub>6</sub> (1)-CCl <sub>4</sub> (2)		C <sub>6</sub> H <sub>6</sub> (1)-c-C <sub>6</sub> H <sub>12</sub> (2)		CCl <sub>4</sub> (1)-C(CH <sub>3</sub> ) <sub>4</sub> (2)	
	25°		25°		25°		0°	
	$X_{12}v_1^*/R$ , °K.							
	53		47		253		151	
	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.
$\bar{v}^E$	0.0013	0.0021	0.0011	0.0001	0.0063	0.0085	-0.0095	-0.0062
$H^E/N$ , cal. mole <sup>-1</sup>	29	35	26	26	146	200	75	75
$G^E/N$ , cal. mole <sup>-1</sup>	22	17	19	20	107	78	75	76

In eq. 1  $N_1$  and  $N_2$  are the numbers of moles and  $v_1^*$  and  $v_2^*$  are the characteristic molar volumes of species 1 and 2 ( $v_i^* = x_i v_i^*$  in the notation of I and II)

$$\varphi_2 = N_2 v_2^* / (N_1 v_1^* + N_2 v_2^*)$$

and  $X_{12}$  is the pair interaction parameter (analogous but not equal to  $p_{12}^*$  of eq. II-24) defined formally by

$$X_{12} = s_1(\eta_{11} + \eta_{22} - 2\eta_{12}) / 2(v_1^*)^2 \quad (2)$$

with  $s_1$  interpreted as the number of interaction sites per molecule of 1. We do not, however, make use of this relationship;  $X_{12}$  will be treated as an empirical parameter. Other quantities appearing in eq. 1 and 2 are defined in I and II. For molecules differing considerably in size, the volume fraction  $\varphi_2$  should be replaced in eq. 1 by the corresponding surface (site) fraction; the distinction is unimportant however for the systems considered here.

For spherical molecules of comparable size, the combinatorial term in eq. II-14 for the free energy of mixing may be replaced appropriately by the ideal free energy. On this basis, the excess free energy can be written

$$G^E = 3T \left\{ (N_1 p_1^* v_1^* / T_1^*) \ln [(\bar{v}_1^{1/3} - 1) / (\bar{v}^{1/3} - 1)] + (N_2 p_2^* v_2^* / T_2^*) \ln [(\bar{v}_2^{1/3} - 1) / (\bar{v}^{1/3} - 1)] \right\} + H^E \quad (3)$$

The term in braces represents, of course, the contribution from the excess entropy, and this contribution depends on equation of state properties of the pure components.

The characteristic temperature  $T^*$  for the mixture is given by

$$1/T^* = (\varphi_1 p_1^* / T_1^* + \varphi_2 p_2^* / T_2^*) (\varphi_1 p_1^* + \varphi_2 p_2^* - \varphi_1 \varphi_2 X_{12})^{-1} \quad (4)$$

Molar volumes  $v$ , thermal expansion coefficients  $\alpha$ , and thermal pressure coefficients  $\gamma = (\partial p / \partial T)_v$  for the pure components whose binary mixtures are considered here are listed in Table I. The reduced volumes  $\bar{v}$ , the characteristic temperatures  $T^*$ , and the characteristic pressures  $p^*$ , all calculated from the aforementioned equation of state parameters as prescribed in I, are given in this table also. Calculation of the excess functions for a given binary mixture according to the foregoing equations requires the single parameter  $X_{12}$  in addition to the quantities characterizing the pure components (Table I). Values chosen for  $X_{12}$  to afford optimum agreement with the observed excess quantities are given in the first row of Table II. In succeeding rows of Table II, the calculated excess quantities for four equimolar mixtures are compared

with experimental results. The latter are from the compilations included by Rowlinson.<sup>4</sup>

Calculations were carried out in the following way. The reduced temperature  $\bar{T} = T/T^*$  for each equimolar mixture listed in Table II was obtained from  $T^*$  calculated according to eq. 4. The corresponding reduced volume  $\bar{v}$  was then computed according to eq. I-18 (see also eq. II-12). Comparison with the additive reduced volume  $\bar{v}^0 = \varphi_1 \bar{v}_1 + \varphi_2 \bar{v}_2$  gives the calculated excess reduced volume  $\bar{v}^E$  (Table II). The excess enthalpies  $H^E/N$  per mole of mixture were computed according to eq. 1, the calculated values of  $\bar{v}$  being used. The excess free energies were computed according to eq. 3, the calculated values of  $H^E/N$  and  $\bar{v}$  being used for this purpose. Thus,  $[(H^E - G^E)/TN]_{\text{calcd}}$  as deduced from Table II represents the calculated excess entropy  $S^E/N$  per mole of mixture.

For two of the systems,  $\bar{v}^E$  is small and positive; for the third it is substantially positive, and for the last it is decidedly negative. Calculated  $\bar{v}^E$  values reproduce these variations fairly well. The significance of this achievement is underscored by the fact that neither the excess enthalpies nor the interaction parameters  $X_{12}$  parallel the excess volumes. It becomes apparent from examination of the relevant equations that a large difference between the characteristic temperatures  $T_1^*$  and  $T_2^*$  favors  $\bar{v}^E < 0$ , a tendency opposed by  $X_{12} > 0$ . The comparisons presented are typical of those for other binary mixtures currently under investigation.

The calculated excess enthalpies match experiment within probable limits of error. It will be apparent from the data in Table II that the calculated excess entropies  $(H^E - G^E)/TN$  are in the direction of those observed.

(4) J. S. Rowlinson, "Liquids and Liquid Mixtures," Butterworths, London, 1959. References to original sources from which the data were obtained are given by Rowlinson.

A full treatment of the subject, including analysis of data for a wider variety of binary systems, will be published in the near future.<sup>5</sup>

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(5) A. Abe and P. J. Flory, in preparation.

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### The Reaction of Organoboranes with Chloramine and with Hydroxylamine-O-sulfonic Acid. A Convenient Synthesis of Amines from Olefins *via* Hydroboration

Sir:

We wish to report that organoboranes, such as are produced in the hydroboration of representative olefins,<sup>1</sup> react readily with either chloramine or with hydroxylamine-O-sulfonic acid to form the corresponding amine. In the majority of cases examined, yields of 60% ( $\pm 5\%$ ) have been realized. Consequently, this procedure permits a simple conversion of olefinic derivatives into the corresponding amine.

In the procedure the olefin in tetrahydrofuran solution is conveniently converted into the corresponding organoborane by treatment with the equivalent quantity of diborane in tetrahydrofuran solution.<sup>2</sup> In the chloramine route, the organoborane, with added alkali, is treated with a freshly prepared solution of chloramine<sup>3</sup> for 1 hr. at room temperature. In the hydroxylamine-O-sulfonic acid procedure the reagent<sup>4</sup> is added directly to the tetrahydrofuran solution and the reaction mixture heated under reflux for 3 hr. In both procedures the solutions are acidified with hydrochloric acid, extracted with ether to remove residual organoboron derivatives, and the amines are then isolated from the acidic aqueous solutions by standard methods.

The yields are similar in both procedures. However, the commercial availability of hydroxylamine-O-sulfonic acid avoids the synthesis and standardization of the chloramine solution. Consequently, the use of the hydroxylamine-O-sulfonic acid is preferable in cases where the reagent is available.

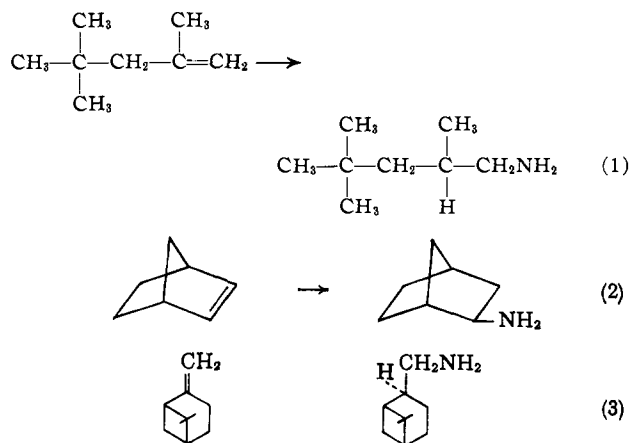
In this way 1-octene has been converted into *n*-octylamine,  $\alpha$ -methylstyrene into 2-phenyl-1-aminopropane, and 2,3,3-trimethyl-1-pentene into 2,3,3-trimethyl-1-aminopentane (1). Similarly, cyclopentene and cyclohexene have been converted into the corresponding amines, and norbornene into *exo*-norbornylamine (2). The mildness of the procedure is indicated by the conversion of  $\beta$ -pinene into *cis*-myrtanylamine (3), without evidence of any rearrangement or alteration of the carbon skeleton.

(1) For a recent summary, see H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

(2) One molar solutions of borane in tetrahydrofuran are now commercially available from Metal Hydrides Incorporated, Beverly, Mass.

(3) The chloramine solution is prepared by treating dilute aqueous ammonia with sodium hypochlorite at 0°. F. Raschig, *Ber.*, **40**, 4586 (1907).

(4) Hydroxylamine-O-sulfonic acid is now commercially available from Allied Chemical Co., Marcus Hook, Pa.



Representative results are summarized in Table I.

TABLE I  
CONVERSION OF OLEFINS INTO AMINES BY THE  
HYDROBORATION-AMINATION REACTION

Olefin	Amine	Yield, %	
		Hydroxylamine-O-sulfonic acid	Chloramine
1-Octene	<i>n</i> -Octylamine	64	
1-Decene	<i>n</i> -Decylamine		51
2-Methyl-1-pentene	2-Methyl-1-aminopentane	59	29
2,4,4-Trimethyl-1-pentene	2,4,4-Trimethyl-1-aminopentane	58	28
$\alpha$ -Methylstyrene	2-Phenyl-1-aminopropane	58	58
1,1-Diphenylethylene	$\beta,\beta$ -Diphenylethylamine	27	
Cyclopentene	Cyclopentylamine	59	50
Cyclohexene	Cyclohexylamine	55	49
1-Methylcyclohexene	<i>trans</i> -2-Methylcyclohexylamine		8.5
Norbornene	<i>exo</i> -Norbornylamine	52	51
$\beta$ -Pinene	<i>cis</i> -Myrtanylamine	55	48
Ethyl undecenoate	11-Aminoundecanoic acid	30	30

The observation that the yields in so many cases were in the range of 55 to 60% suggested the possibility that only two of the three alkyl groups on the organoborane were undergoing reaction. This was confirmed by the isolation of the monoalkylboronic acid from the reaction mixture and the demonstration that the reaction of such boronic acids with the reagents is very slow. The hydroboration of hindered olefins proceeds readily only to the mono- or dialkylborane stage.<sup>1</sup> Consequently, the yields are much lower for such derivatives. In spite of the low yield realized in applying the reaction to 1-methylcyclohexene, it is of considerable theoretical interest that the product produced was pure *trans*-2-methylcyclohexylamine, corresponding to replacement of the boron by the amino group stereospecifically with retention of configuration. Similarly, the isolation of pure *exo*-norbornylamine supports the conclusion that the reaction course is stereochemically similar to that proposed for the oxidation of the organoborane by alkaline hydrogen peroxide.<sup>1</sup>

The following procedures are representative

In a 500-ml. flask was placed 11.8 g. (100 mmoles) of  $\alpha$ -methylstyrene and 30 ml. of tetrahydrofuran.