calories per degree per mole is only correct if the potential function is sinusoidal with three equal minima.

Using $\delta_1 = 950$ cm.$^{-1}$ and $V = 3870$ for the restricting potential, tables of S, F/T and H/T can be compiled which are not in error by more than a few tenths of a calorie per degree per mole up to 1500°K.[17] It is important to realize that the small error is due to the fact that the potential was chosen to give the best fit with the experimental data and not to the accuracy of the molecular data.

Acknowledgment.—We wish to thank the Standard Oil Development Company, without whose aid this work would not have been possible. Dr. G. H. Messerly kindly helped with the experimental work on the thermal data. The extremely pure sample of isobutane was prepared by Dr. R. B. Greenburg and Mr. R. E. Meyer.

Summary

1. The heat capacity of isobutane has been determined from 12°K. to the normal boiling point.

2. The melting point of isobutane is 113.74°K. (−159.42°C.) and the boiling point is 261.44°K. (−11.72°C.).

3. The heats of fusion and vaporization at the boiling point are 1085.4 calories/mole and 5089.6 calories/mole, respectively.

4. The vapor pressure of isobutane from 200°K. to the boiling point is given by the equation:

$$\text{Log } P_{\text{mm.}} = -1716.687/T - 6.38879 \log T + 0.0024132\,T + 24.260325$$

5. The molal entropy of the liquid at the boiling point is 47.94 ± 0.10 e. u. The molal entropy of the ideal gas at the boiling point calculated from the experimental data is 67.52 ± 0.10 e. u.

6. The molal entropy of the liquid at 298.16°K. extrapolated from the experimental data is 52.09 ± 0.10 e. u. The molal entropy of the ideal gas from the experimental data at 298.16°K. is 70.43 ± 0.15 e. u.

7. In order to make the entropy calculated from the spectroscopic and molecular data agree with the experimental value at the boiling point it is necessary to assume that the potential hindering internal rotation of the methyl groups is 3870 cal.

8. The results of this investigation seem to indicate errors in existing heat capacity data on the gas.

STATE COLLEGE, PENNA. RECEIVED JUNE 5, 1940

[17] See Aston and Messerly, THIS JOURNAL, **62**, 1917 (1940), for a discussion of the cancellation of errors in this type of calculation.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE CREIGHTON UNIVERSITY]

The Partial Pressure of Hydrogen Chloride from its Solutions in the Mono-halobenzenes at 25°

BY S. JAMES O'BRIEN AND JOSEPH B. BYRNE

In previous papers[1,2] measurements of the partial pressure of hydrogen chloride from its solutions in a number of solvents were reported. Since work of this kind provides information which may be of assistance in studying the nature of acid–base reactions and the bonding present between solvent molecules, similar determinations are being made in other solvents. In this paper measurements of the vapor pressure of hydrogen chloride from its solutions in the four monohalobenzenes at 25° are reported. These measurements were undertaken since conclusions concerning the basicity of chlorobenzene derived from measurements of the solubility of hydrogen chloride at one atmosphere[3] disagree with those obtained from the shift of the 3.46 μ absorption band of hydrogen chloride.[4,5] The shift of the infrared band indicates a proton-attracting tendency for chlorobenzene that is approximately the same as that of benzene. A negative deviation of hydrogen chloride from the law of Raoult in chlorobenzene solutions of about the same magnitude as that shown in benzene solutions[1] might, then, be expected. The solubility measurements of Bell,[3] however, indicate a rather large positive deviation. Measurements were made to determine whether such a deviation persists at lower pressures and whether such a deviation is to be

[1] S. J. O'Brien, C. L. Kenny and R. A. Zuercher, THIS JOURNAL, **61**, 2504 (1939).

[2] S. J. O'Brien and C. L. Kenny, *ibid.*, **62**, 1189 (1940).

[3] R. P. Bell, *J. Chem. Soc.*, 1371 (1931).

[4] D. Williams, *Phys. Rev.*, **50**, 719 (1936).

[5] W. Gordy and P. C. Martin, *J. Chem. Phys.*, **7**, 99 (1939).

found in hydrogen chloride solutions in fluorobenzene and iodobenzene, the measurements of Bell indicating that a positive deviation from the law is also found in bromobenzene solutions. It is the purpose of this paper to report the results of these experiments.

Experimental

The apparatus and method were the same as those previously employed.[1,2,6] The addition of a few drops of capryl alcohol was again found to be advantageous in the analysis of the non-aqueous hydrogen chloride solutions. The time allowed for establishment of equilibrium ranged from two to three days. The constant-temperature bath was regulated at 25.00 ± 0.02°.

The indices of refraction, n^{20}_D, of the liquids used were as follows: fluorobenzene, 1.4650 (1.4646); chlorobenzene, 1.5240 (1.525); bromobenzene, 1.5588 (1.560); iodobenzene, 1.6192, (1.621). The values given in parentheses were taken from "International Critical Tables."[7]

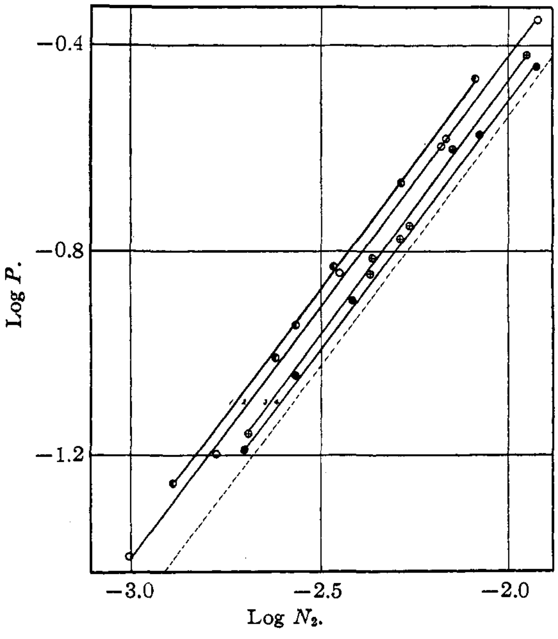

Fig. 1.—The vapor pressure of hydrogen chloride from its solutions in (1) iodobenzene, (2) chlorobenzene, (3) bromobenzene and (4) fluorobenzene. The broken line represents the law of Raoult.

Results

The data obtained are given in Tables I–IV in which the first column contains the molalities of the solutions; the second, the vapor pressure of hydrogen chloride in mm. of mercury; the third, the Henry law constant, $k = p/m$, in atm. per mole per 1000 g. of solvent. The mean value of this constant was obtained as in the previous paper.[2]

The results are also shown graphically in Fig. 1, where the logarithm of the pressure of hydrogen chloride is plotted against the logarithm of its mole fraction (N_2) in the solutions.

Table I

The Partial Pressure of Hydrogen Chloride from its Solutions in Fluorobenzene at 25°

m	p	k
0.121	259	2.82
.085	202	3.10
.0402	95.3	3.12
.0277	69.9	3.32
.0208	48.9	3.09
	Mean	3.02 ± 0.17

Table II

The Partial Pressure of Hydrogen Chloride from its Solutions in Chlorobenzene at 25°

m	p	k
0.1027	340	4.35
.0597	198	4.31
.0578	193	4.39
.0310	108	4.58
.0152	48.0	4.16
.0081	30.1	4.85
	Mean	4.38 ± 0.17

Table III

The Partial Pressure of Hydrogen Chloride from its Solutions in Bromobenzene at 25°

m	p	k
0.0686	290	5.56
.0447	189	5.57
.0346	134	5.11
.0328	128	5.12
.0278	116	5.51
.0272	110	5.30
.0131	53.2	5.35
	Mean	5.40 ± 0.17

Table IV

The Partial Pressure of Hydrogen Chloride from its Solutions in Bromobenzene at 25°

m	p	k
0.0403	262	8.56
.0247	164	8.75
.0168	113	8.82
.0133	85.8	8.48
.0118	71.8	8.47
.0064	41.8	8.56
	Mean	8.58 ± 0.13

Discussion

It is obvious from the figure that the deviation of hydrogen chloride from the law of Raoult in halobenzene solutions at low pressures is positive,

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(6) J. Saylor, This Journal, **59**, 1712 (1937).

(7) "International Critical Tables," McGraw-Hill Book Company, New York, N. Y., 1926, Vol. I, pp. 277–278.

although there may be some doubt in the case of fluorobenzene due to the uncertainty involved in the calculation of the value of the fugacity of pure hydrogen chloride.[1] These results, then, further demonstrate the apparent discrepancy between the conclusions concerning the basicity of chlorobenzene derived from solubility and from infrared absorption studies. Gordy and Stanford,[8] in comparing shifts of the OD vibrational band produced by various solvents with the solubility of monofluorodichloromethane, measured by Copley and co-workers,[9] encounter similar apparent discrepancies. These, however, seem to be adequately explained in terms of steric hindrance or solvent association, although it is difficult to understand why the absorption in a solvent in which complex formation is hindered should be more intense than in solvents in which these effects are not present.

While solvent association is only one of the factors which might account for the positive deviation from the law of Raoult in the halobenzenes, there seems to be no explanation in terms of other properties as is indicated in Table V. In this table, the second column gives as a measure of the deviation from the law, values for the activity coefficients (a_2/N_2) of hydrogen chloride in the various solutions, a_2 being the activity of hydrogen chloride referred to the pure liquid[10]; the third column gives, as an indication of the internal pressures of the liquids, values for $a^{1/2}/V$, a being the van der Waals constant and V the molar volume; the fourth column gives the dipole moments of the liquids.

TABLE V[a]

Solvent	a_2/N_2	$a^{1/2}/V$	$\mu \times 10^{18}$
Hexane	2.03	7.20	0
Iodobenzene	1.39	9.41	1.30
Chlorobenzene	1.29	9.52	1.56
Bromobenzene	1.14	8.95	1.49
Fluorobenzene	1.04	(8.85)	1.45
Benzene	0.86	9.00	0

[a] Activity coefficients for hexane and benzene were calculated from data given in previous papers.[1,2] Values of $a^{1/2}/V$, with the exception of that for fluorobenzene which was estimated from the boiling point[10] (pp. 101–103), were taken from the table of Hildebrand[10] (pp. 104–105). The dipole moments given are solution values and were taken from the table of H. B. Watson, "Modern Theories of Organic Chemistry," Oxford University Press, London, 1937, p. 31.

Since both solute and solvent are polar in these solutions, it is not surprising that there is no apparent relationship between internal pressure and the deviation from the law of Raoult. That the dipole moment is not the most important factor in explaining the behavior of hydrogen chloride solutions already has been pointed out.[5]

Comparison of calculated with experimental values of the dipole moments of polar liquids has been taken as an indication of the extent of dipole–dipole association,[11] and by this criterion it was shown that the *contra-association* of dipoles in chlorobenzene is considerable. Association of this type might provide an explanation for the positive deviation of hydrogen chloride from the law of Raoult, if such association persists in the presence of this solute. It was pointed out that, apparently, the hydrogen bond association between ethylene glycol molecules is considerably reduced by the presence of hydrogen chloride,[1] while chelate bonds seem to be more stable.[2,12] While dipole–dipole association of the solvent may be the explanation for the fact that the apparent basicity of benzene[1] is reduced by the substitution of halogens into the benzene molecule, further discussion in this connection will be deferred until the results from other studies of this kind can be presented.

Acknowledgment.—To Dr. C. L. Kenny, Head of the Chemistry Department of Creighton University, the sincere thanks of the writers are due for making this work possible and for his continued interest in it.

Summary

1. Measurements are reported of the partial vapor pressure of hydrogen chloride from its solutions in fluoro-, chloro-, bromo- and iodo-benzene, over the concentration ranges, 0.02–0.121, 0.008–0.103, 0.013–0.069, and 0.006–0.040 molal, respectively. Over the concentration ranges studied, hydrogen chloride corresponds with the law of Henry but shows a positive deviation from the law of Raoult.

OMAHA, NEBRASKA RECEIVED MAY 16, 1940

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[8] W. Gordy and S. C. Stanford, *J. Chem. Phys.*, **8**, 170 (1940).

[9] M. J. Copley, G. F. Zellhoefer and C. S. Marvel, THIS JOURNAL, **60**, 1337, 2666, 2714 (1938).

[10] J. H. Hildebrand, "The Solubility of Non-electrolytes," Second Edition, Reinhold Publishing Company, New York, N. Y., 1936, pp. 24–25.

[11] J. N. Wilson, *Chem. Rev.*, **25**, 377 (1939).

[12] In addition to the measurements of the solubility of hydrogen chloride in the ortho and meta isomers of nitrotoluene, some preliminary determinations made in this Laboratory show that hydrogen chloride is much more soluble in benzaldehyde than in salicylaldehyde. This seems to be additional evidence for the stability of chelate bonds in the presence of hydrogen chloride.