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

The Partial Pressure of Hydrogen Chloride from its Solutions in Some Aprotic Solvents and the Calculation of the Heat and Entropy of Solution[1a]

BY S. JAMES O'BRIEN[1b]

In continuing a study of the partial pressure of hydrogen halides from their solutions in various solvents[2] it seemed desirable to provide more data that could be utilized in calculating thermodynamic quantities for these solutions. The only work of this kind for hydrogen halide solutions seems to be that of Hamai[3] on hydrogen chloride in halogenated aliphatic hydrocarbons, and that of Kapustinskii and Mal'tsev[4] on hydrogen bromide solutions in benzene. It is, then, the purpose of this paper to report additional measurements of the partial pressure of hydrogen chloride from its solutions in benzene, chlorobenzene and nitrobenzene in the temperature range 20 to 40°.

These determinations were employed in the calculation of the change in heat content and entropy of the solute. It was hoped that such information might furnish a connection between work of this kind and infrared absorption studies, both of which seem to indicate the occurrence of complex formation between the solute and solvent in some hydrogen chloride solutions. The results at hand point to a relationship between the infrared absorption and entropy of solution, and it is chiefly from this point of view that the data are discussed.

Experimental

Apparatus and Method.—The apparatus and method were again essentially the same as those described by Saylor[5] with the modifications adopted in the earlier work.[2] However, the data already reported for benzene solutions[5] at 30° and for nitrobenzene solutions[2a] at 25° were found to be inconsistent with those at other temperatures. For all of the other systems so far considered the average deviation from the mean of the Henry law constant is less than ±5% and the maximum deviation in all except one instance is under ±10%. Since results reliable to within ±5% might be expected from this method, and since the data for these two systems deviated from the trend of those at other temperatures by more than the usual maximum deviation, it was decided to make new measurements. Results were obtained which agreed fairly well with one another as well as with those taken at the other temperatures. Since it seems likely that these new data are more accurate than those reported before, they have been included in this paper and used in the subsequent calculations.

Materials.—The benzene had been stored over sodium for several weeks from which it was distilled before using. Its m. p. was 5.48 ± 0.02°.

Commercial nitrobenzene was shaken with a mixture containing 5% sodium sulfate and 5% sodium hydroxide.[6] After settling, the nitrobenzene was separated from the aqueous layer and placed over phosphorus pentoxide from which it was distilled as needed. The m. p. of the product so obtained was 5.72 ± 0.02°.

Chlorobenzene of good quality was distilled after stand-

TABLE I

THE PARTIAL PRESSURE OF HYDROGEN CHLORIDE FROM ITS SOLUTIONS IN SOME APROTIC SOLVENTS

m	*p*, mm.	*k*
I. In Chlorobenzene at 30°		
0.0726	253	4.76
.0449	156	4.58
.0312	103	4.30
.0311	113	4.78
.0069	23.9	4.59
.0058	22.7	5.16
	Mean	4.65 ± 0.20
II. In Chlorobenzene at 40°		
0.0470	203	5.68
.0314	139	5.82
.0291	118	5.34
.0170	75.2	5.82
.0093	38.8	5.48
	Mean	5.71 ± 0.18
III. In Benzene at 30°		
0.263	463	2.31
.252	438	2.29
.145	246	2.23
.0396	72	2.39
.0364	65	2.34
.0255	47	2.43
	Mean	2.33 ± 0.06
IV. In Benzene at 40°		
0.107	247	3.05
.076	159	2.76
.046	108	3.09
.0284	56.2	2.60
.0221	48.8	2.90
.0204	46.7	3.01
.0110	22.4	2.68
.0074	17.0	3.03
.0061	12.3	2.65
.0026	5.8	2.92
	Mean	2.91 ± 0.14
V. In Nitrobenzene at 20°		
0.249	305	1.46
.239	288	1.52
.1310	160	1.63
.0896	111	1.60
.0549	64	1.59
.0507	56	1.61
	Mean	1.59 ± 0.04
VI. In Nitrobenzene at 25°		
0.134	171	1.68
.126	173	1.81
.092	127	1.83
.075	102	1.81
.0332	45.1	1.79
.0319	42.4	1.75
	Mean	1.77 ± 0.05
VII. In Nitrobenzene at 30°		
0.253	402	2.09
.203	318	2.06
.157	248	2.06
.132	214	2.14
.093	144	2.02
.063	99	2.07
.047	74.8	2.08
.0156	24.1	2.03
.0140	20.7	1.95
	Mean	2.08 ± 0.04
VIII. In Nitrobenzene at 40°		
0.201	391	2.56
.169	351	2.72
.0500	95.8	2.52
.0490	90.6	2.44
.0038	7.5	2.59
.0023	4.1	2.25
	Mean	2.51 ± 0.12

[1a] Most of the experimental work reported in this paper was done with the assistance of Mr. R. J. Fuxa, to whom the thanks of the author are due.

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[2] (a) S. J. O'Brien, C. L. Kenny and R. A. Zuercher, THIS JOURNAL, **61**, 2504 (1939); (b) O'Brien and J. B. Byrne, *ibid.*, **62**, 2063 (1940).

[3] S. Hamai, *Bull. Chem. Soc. Japan*, **10**, 5, 207 (1935).

[4] A. F. Kapustinskii and V. A. Mal'tsev, *J. Phys. Chem.* (U. S. S. R.), **14**, 105 (1940).

[5] J. Saylor, THIS JOURNAL, **59**, 1712 (1937).

[6] S. Insozemstev, *Org. Chem. Ind.* (U. S. S. R.), **2**, 151 (1936).

ing over calcium chloride for several weeks. The refractive index n^{20}_D of this material was 1.5420.

Results

The results of the experiments made are given in Table I. The first column of each section of this table gives the molalities of the solutions; the second gives the vapor pressure of hydrogen chloride from the solutions in mm. of mercury; and the third gives the Henry law constant ($k = p/m$) expressed in atm. per mole per 1000 g. of solvent.

From the data of this and other papers,[2,7] mole fraction solubilities of hydrogen chloride under a partial pressure of 1 atm. at 20, 25, 30 and 40° were calculated for these three solvents. The results of these calculations are indicated in Fig. 1, which contains a plot of $-\log N$ against $1/T$, N being the calculated mole fraction of the saturated solution.

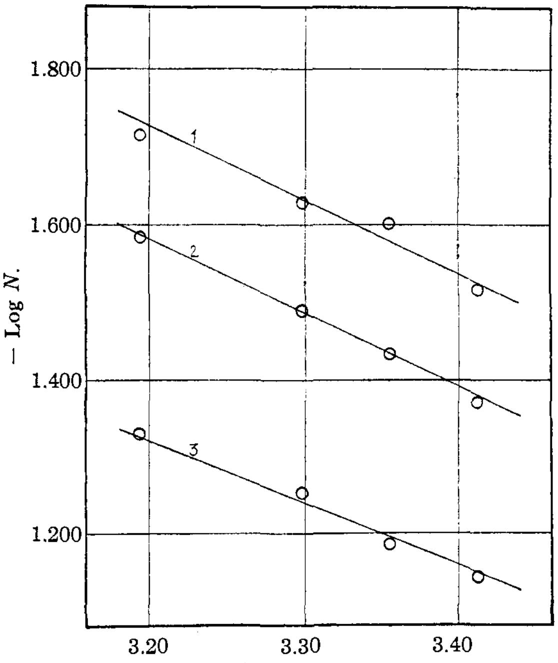

Fig. 1.—A plot of $-\log N$ against $1/T$ for hydrogen chloride solutions in (1) chlorobenzene, (2) benzene and (3) nitrobenzene.

Discussion

It is evident from Fig. 1 that in the temperature range considered the data are in accord with the equation

$$-\log N = A/T + B$$

where A and B are constants which can be identified with $\Delta H/2.3R$ and $-\Delta S/2.3R$, respectively, ΔH and ΔS being the differential heat and entropy of solution of gaseous hydrogen chloride. Values for the heats and entropies obtained by application of least square methods to the data are given in Table II. For comparison, the data reported by Hamai[3] for the heat of solution of hydrogen chloride in some halogenated hydrocarbons are included in the table. The entropy values for these solutions were calculated from his data.

TABLE II

THE HEAT AND ENTROPY OF SOLUTION OF HYDROGEN CHLORIDE

Solvent	$-\Delta H$, cal.	$-\Delta S$, cal./deg.
Chlorobenzene	4000	20.7
Benzene	4300	20.9
Nitrobenzene	4000	18.9
s-Tetrachloroethane	3300	18.4
Carbon tetrachloride	6100[a]	29.2[a]
Ethylene chloride	3500	18.4
Ethylene bromide	3200	17.4
Pentachloroethane	2200	15.0
Trichloroethane	3600	19.2

[a] This value apparently is in error. See discussion below.

It is interesting to compare the heats of solution so obtained with the heat of vaporization of hydrogen chloride, *i. e.*, 3860 cal./mole at its boiling point.[8] From the heat of solution of the vapor and the heat of vaporization, the differential heat of solution of the pure liquid solute is obtained. It is seen that this may be either positive or negative in the solutions listed above, and is, in general, small. It is evident at once that the large difference in the solubility of hydrogen chloride in these solvents is largely due to the difference in the entropy of solution. These solutions are neither ideal nor regular. Consequently, they provide exceptions to the general rules for heats of solution and deviations from the law of Raoult as stated by Hildebrand.[9] This is well illustrated by chlorobenzene solutions in which the deviation of the solute from the law of Raoult is positive[2b] and the heat of solution is also positive.

While Gordy and Stanford[10] have recently compared heats of mixing of chloroform in various solvents with the change in wave length of the OD vibrational band of heavy methyl alcohol produced by these solvents, finding a rough linear relationship between them, from the data avail-

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

[8] W. F. Giauque and R. Wiebe, THIS JOURNAL, **50**, 101 (1928).

[9] J. H. Hildebrand, "Solubility of Non-electrolytes," 2nd ed., Reinhold Publishing Co., New York, N. Y., 1936, p. 57.

[10] W. Gordy and S. C. Stanford, *J. Chem. Phys.*, **9**, 214 (1941).

able for hydrogen chloride solutions it seems that the shift of the 3.46 μ vibrational band of the solute is more closely related to its change in entropy than to its change in heat content. This is shown in Fig. 2 (open circles) in which the change in wave length of the infrared band[11] is plotted against the entropy of solution for benzene, chlorobenzene and nitrobenzene solutions. The line in this figure has been arbitrarily drawn, consequently no significance is to be attached to the fact that a number of points fall on it exactly. The black circles in the figure indicate three instances in which this arbitrary line has been used to obtain entropy values from the spectroscopic data, the entropy values in turn being used to calculate with fair success the solubility of hydrogen chloride in diethyl ether and in bromobenzene and the heat of solution of hydrogen chloride in carbon tetrachloride. They serve only as indirect confirmation of the straight line relationship intimated by the limited data from which the graph was constructed. In addition, data being collected for hydrogen chloride solutions in five other ethers and in *m*-nitrotoluene which will be ready for presentation in the near future lend additional support to the relationship in general, but they are not yet sufficiently complete to determine how closely they will agree with the line in Fig. 2. Indications are that the deviations will be small.

In calculating the solubility of hydrogen chloride in diethyl ether, data in the literature[12] in the temperature range of 15 to 25° where a plot of log N against $1/T$ shows the heat of solution to be very nearly constant, are used together with the infrared data of Gordy[11] and the equation

$$-2.303RT \log N = \Delta F = \Delta H - T\Delta S \qquad (1)$$

to obtain the heat of solution. The calculations are summarized in Table III.

TABLE III

THE SOLUBILITY OF HYDROGEN CHLORIDE IN DIETHYL ETHER

Temp., °C.	N (calcd.)	N ("I. C. T.")
15	0.440	0.437
20	(.405)	.405
25	.366	.367

(ΔH = −3840 cal.)

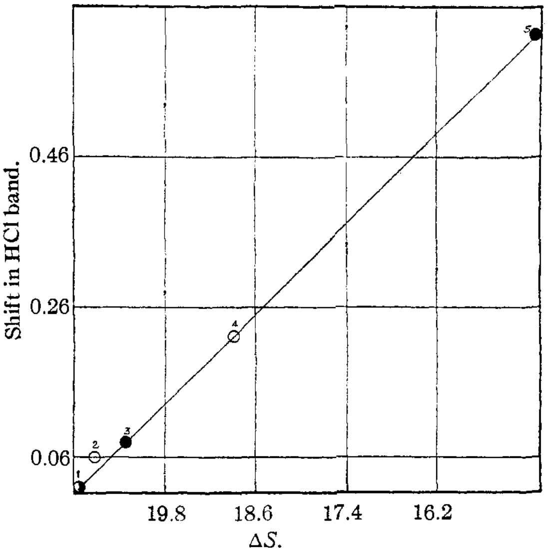

Fig. 2.—A plot of the shift in the 3.46 μ vibrational band of hydrogen chloride against its change in entropy for solutions in (1) benzene and bromobenzene, (2) chlorobenzene, (3) carbon tetrachloride, (4) nitrobenzene and (5) diethyl ether.

The heat of solution of hydrogen chloride in carbon tetrachloride was calculated to be 3610 cal. using equation (1), the Raman spectra data of West and Arthur[13] and the solubility obtained by Bell[7] at 20°. This value corresponds with the calorimetric determination of Noyes and Tuley[14] amounting to 3680 cal., and is a further indication that the value obtained by Hamai from solubility measurements, which is included in Table II, is in error.[15]

In the calculation of the solubility of hydrogen chloride in bromobenzene, the entropy of solution was obtained indirectly from the shift of the 4.0 μ band of heavy methyl alcohol produced by this solvent.[11,16] Using equation (1) and the solubility[7] at 20°, the heat of solution was found to be 4100 cal. Then, the mole fraction solubility at 25° was calculated to be 0.026 in comparison with an experimental value[2b] of 0.029.

It is interesting to note that the 3.46 μ absorption band of hydrogen chloride in the vapor is shifted to 3.57 μ in the liquid state.[17] According to the line drawn in Fig. 2, this corresponds to an entropy change of 20.0 units which may be compared with the entropy of vaporization amounting to 20.52 cal./deg. at the boiling point.[8] This may be sufficiently close agreement to be

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[11] W. Gordy, *J. Chem. Phys.*, **9**, 215 (1941).

[12] "International Critical Tables," Vol. III, McGraw-Hill Book Co., New York, N. Y., 1928, p. 264.

[13] W. West and P. Arthur, *J. Chem. Phys.*, **2**, 215 (1934).

[14] W. A. Noyes and W. F. Tuley, THIS JOURNAL, **47**, 1338 (1925).

[15] The solubility measurements of Hamai are generally in poor agreement with those of Bell.

[16] W. Gordy, *J. Chem. Phys.*, **7**, 93 (1939).

[17] W. West, *ibid.*, **7**, 795 (1939).

considered as evidence in favor of the relationship between entropy change and band shift.

As far as the hydrogen chloride data go, the proportionality between shift in wave length of the infrared absorption band of the solute and its change in entropy seems to be valid. It must be noted, however, that if this relationship is true its derivation has been somewhat fortuitous because of the limited accuracy of much of the solubility data employed. Relatively small deviations in the solubility determinations may lead to very large deviations in the thermodynamic quantities which depend on them. While additional and more accurate experimental work will be necessary to fully establish the validity and accuracy of this rule, as it now stands, applicable at least approximately to several hydrogen chloride solutions and in solvents of different types, it seems to be more than a coincidence, and may be of some value.

Acknowledgment.—The author wishes to express his sincere thanks to Dr. C. L. Kenny, Head of the Chemistry Department of Creighton University, for his support of this work and for his continued interest in it.

Summary

1. Measurements are reported of the partial vapor pressure of hydrogen chloride from its solutions in benzene and in chlorobenzene at 30 and 40°, and in nitrobenzene at 20, 25, 30 and 40°. These include new measurements for nitrobenzene solutions at 25° and for benzene solutions at 30°.

2. These data together with those already in the literature were used to calculate the change in heat content and in entropy of the solute in the formation of these solutions.

3. A comparison of the derived thermodynamic data with infrared absorption data suggests a straight line relationship between the entropy change of the solute and the shift in its 3.46 μ vibrational band produced by the solvent.

OMAHA, NEBRASKA RECEIVED JULY 14, 1941

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

Adsorption. I. The Effect of Heat Treatment on the Low Temperature Adsorption of Nitrogen by Aluminum Oxide

BY K. A. KRIEGER

In beginning an extended study of the adsorptive properties of aluminum oxide, it has seemed advisable to study first the effect of various methods of cleaning the adsorbent surface. This paper describes a study of the commonly used method where the adsorbent is simultaneously heated and evacuated. The effect of varying temperatures of evacuation upon the surface area and upon the average heat of adsorption of nitrogen in the first layer, as measured by the procedures of Brunauer, Emmett and co-workers,[1] has been ascertained.

Apparatus and Materials

The apparatus was similar to that of Durau[2] but mercury valves replaced all the stopcocks in contact with the gas under investigation except one graphite lubricated and mercury-sealed stopcock which served to isolate the adsorbent from the measuring system. An air thermostat enclosed the entire measuring system and was maintained at 30.00 ± 0.01° by a regulator of the Gouy type.[3] Temperatures were measured with a mercury thermometer calibrated against a Bureau of Standards resistance thermometer.

Pressures were measured with a steel scale and corrected for thermal expansion and for the value of g at Philadelphia. All readings were made with a cathetometer.

The liquid nitrogen used for cooling was not analyzed for purity, but any error thus introduced was eliminated by calibrating the empty apparatus with hydrogen and nitrogen, using several samples of liquid nitrogen. No variation in the properties of these samples was observed. The temperature of the liquid nitrogen was calculated from atmospheric pressure.[4]

High temperatures were measured and regulated by means of a Chromel–Alumel thermocouple calibrated against Bureau of Standards melting point standards, and a pyrometer controller. The temperature variation was approximately ±4°, and the absolute error about the same.

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[1] Brunauer, Emmett and Teller, THIS JOURNAL, **60**, 309 (1938).

[2] Durau, *Z. Physik*, **101**, 27 (1936); see Fig. 3, p. 33.

[3] Sligh, THIS JOURNAL, **42**, 60 (1920). This almost forgotten device has proved exceedingly effective, diminishing the temperature variation of this thermostat to about one-tenth of that observed with the conventional, non-oscillating regulator.

[4] "International Critical Tables," Vol. III, p. 203.