[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE UNIVERSITY[1]]

The Free Energy and Entropy of Dissociation of Methylammonium Chloride from 276 to 313° K. The Barrier Hindering Internal Rotation[2]

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The equilibrium pressures of hydrogen chloride and methylamine above solid methylammonium chloride have been determined from 0 to 40° from cell measurements in anhydrous alcohol. The free energies and entropies of dissociation of solid methylammonium chloride and the absolute entropies of methylamine have been determined over the same range. The entropies of methylamine thus determined have been compared with the ones determined from $\Delta F°$ and $\Delta H°$ and from the spectroscopic data. The barrier hindering internal rotation is 1900 ± 400 cal. mole^{-1} in agreement with the value recently found from the microwave spectrum and not inconsistent with the calorimetric value. The ordered arrangement of methylammonium chloride at 0°K. has been confirmed.

Introduction

The entropy of methylamine has been determined from heat capacity data and the third law of thermodynamics.[3] The value obtained by the third law at the normal boiling point is about 0.5 e.u. below that calculated from the spectroscopic data using the observed product of moments and an observed infra-red band to get the barrier hindering internal rotation.[4] This could be attributed to lack of equilibrium in the third law values or to a wrong assignment of the infrared band at 270 cm.$^{-1}$ to the rotation. The former is possible because hysteresis was observed in the solid. It was decided to attempt to get a value for the entropy of methylamine by measuring the entropy difference in the reaction.

$$CH_3NH_3Cl(s) = CH_3NH_2(g) + HCl(g) \qquad (A)$$

The general method of doing this from cell measurements has already been outlined.[5] The present paper presents the details of the measurements and results leading to a barrier hindering internal rotation in methylamine of 1900 cal. mole^{-1} whereas the band at 270 cm.$^{-1}$ corresponds to 1520 cal. mole^{-1}. The choice between them will be discussed later.

Experimental

Preliminary Considerations.—The electromotive force of the cell

$$H_2(g),\ CH_3NH_2(g),\ CH_3NH_3Cl(s),\ HgCl(s)\ Hg(s)$$

in absolute ethyl alcohol together with the partial pressures of methylamine and hydrogen over the alcohol will yield the partial pressure of hydrogen chloride since the auxiliary data are available. An accuracy of 0.2 mv. in the cell measurements and 1% in measuring the partial pressure of the methylamine were necessary, since each of these corresponds to about 5 cal. in ΔF. Values of ΔS can then be obtained from temperature coefficients over a 40° range to a probable accuracy of between 0.1 and 0.2 e.u., provided that the auxiliary thermodynamic data are equally good. The difficulties encountered due to impurities in the alcohol have already been mentioned.[5]

Materials.—The methylamine was prepared by the method previously described.[3] It was bubbled into the alcohol to make a stock solution. The methylammonium chloride was prepared from pure methylamine as outlined before.[6]

The spiral oxide–silver electrolytic silver chloride electrodes were prepared by the method of Harned.[7]

The alcohol was prepared by first distilling from sodium and ethyl phthalate to which had been added silver nitrate and finally distilling from dry silver oxide. All materials were transferred and solutions made up in a dry-box in a nitrogen atmosphere. The hydrogen was prepared electrolytically and had less than 0.02 mole per cent. of other gases in it, as determined by thermal conductivity.

The hydrogen electrodes were of 0.6 mm. dia. platinum wire, 5 cm. long coiled in a spiral and prepared by the method that Ellis[8] used on platinum foil.

The Cell and Electromotive Force Measurements.—The silver silver–chloride electrode chamber was about 13 cm. long. The chamber containing the hydrogen electrode was filled with the alcoholic solution of methylamine saturated with methylammonium chloride and excess methylammonium chloride added. Electrodes were sealed in by ground joints. The connecting arm had a sealed-in fritted disc as separator.

The chamber containing the silver silver–chloride electrode was then filled with the same alcoholic solution of methylamine saturated with methylammonium chloride so that after excess methylammonium chloride and dry silver chloride had been added its final level was slightly lower than that in the hydrogen electrode chamber.

The hydrogen gas first passed through concentrated sulfuric acid and then over activated alumina and finally through a solution of methylamine saturated with methylammonium chloride identical with that in both chambers of the cell. The total volume of this solution in the presaturator was about 35 cc., and that in the cell about 200 cc. The hydrogen entered the cell through a fritted disc.

The cell vessel and presaturator were immersed in a thermostat whose temperature was held constant to 0.005° as read on a platinum resistance thermometer. All the connecting lines were of glass or specially treated rubber tubing. The lines leaving the cell were wrapped with heaters to avoid condensation.

The electromotive force was read on a calibrated Leeds and Northrup type K-2 potentiometer with a galvanometer having a sensitivity of 1.3 microvolts per mm. The unsaturated Weston standard cell was frequently checked against the laboratory group of saturated Weston standard cells. The instrument was also used in conjunction with a 10 ohm standard resistor to read the platinum resistance thermometer with a current of about 1 milliamp. All of the hydrogen and silver–silver chloride electrodes were tested before and after use in aqueous hydrogen chloride, by comparing the electromotive force of pairs against values computed from the data of Harned and Ehlers.[7b] The value of the average of all pairs was 0.3 millivolt[5] lower than the values of Harned and Ehlers[7c] but the average deviation from the mean of the sixty-one pairs used was 0.08 millivolt.

Cells were made to come to equilibrium from the high side as well as the low by electrolysis. In all cases the agree-

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[3] J. G. Aston, C. W. Siller and G. H. Messerly, THIS JOURNAL, **59**, 1744 (1937).

[4] J. G. Aston and Paul M. Doty, *J. Chem. Phys.*, **8**, 743 (1940).

[5] J. G. Aston, K. H. Hu and F. L. Gittler, THIS JOURNAL, **76**, 4492 (1954).

[6] J. G. Aston and C. Ziemer, *ibid.*, **68**, 1405 (1946).

[7] (a) H. S. Harned, *ibid.*, **51**, 416 (1929); (b) see also M. Randall and L. E. Young, *ibid.*, **50**, 989 (1928); (c) H. S. Harned and R. Ehlers, *ibid.*, **54**, 1350 (1932); **55**, 2179 (1933).

[8] James H. Ellis, *ibid.*, **38**, 737 (1916).

ment was within a few tenths of a millivolt. Any cell was constant to a few tenths of a millivolt for days after the equilibrium period of less than one hr. Two hydrogen electrodes and two silver chloride electrodes were used in each cell.

The Pressures of Hydrogen and Methylamine.—The hydrogen leaving the cell was passed first through a weighed sulfuric acid absorber and then through two weighed finely divided alumina absorbers. The sulfuric acid absorber contained 10 cc. of standard 0.2 N acid. Between the adsorbers and the cell was a differential manometer which, in conjunction with a mercury barometer allowed the pressure of hydrogen at the electrode to be read to about 0.1 mm. of mercury. After weighing all absorbers, the sulfuric acid bulb was back titrated with 0.1 N sodium hydroxide to determine the excess acid using a micro-buret readable to 0.002 cc. and an indicator consisting of an alcoholic mixture of methyl red and methylene blue. The end-point was good to 0.005 cc. of 0.1 N sodium hydroxide. Thus the estimation of the amount of amine was accurate to about 0.1%. The volume of hydrogen passed (about 1.5 l.) was measured to 0.5% by a calibrated wet test meter.

The total increase in weight of the absorbers gave the amount of alcohol plus amine coming over with the hydrogen. With the number of moles of amine known, all the partial pressures could then be calculated.

Results

The electromotive force of the cell together with $E°$ in abs. volts for the cell

$$H_2(g), HCl(g), AgCl(s)\ Ag(s)$$

gives at once the partial pressure of HCl in atmospheres. In the calculation $RTF^{-1}\ln 10$ was taken equal to 0.059156 abs. volt eqt.$^{-1}$ at 25° (298.16°K.). The value of $E°$ used was −0.1508 abs. volt[9] at 25°. This was directly measured using hydrogen chloride in acetic acid water mixtures, as discussed in the next paper. From this and the entropies, values of $E°$ were deduced at the other temperatures.[9]

The values of pressures of methylamine hydrogen and hydrogen chloride are given in Table I along with the reciprocal of the equilibrium constant and the standard free energy of reaction A. The defined calorie was taken equal to 4.18674 abs. joules and R equal to 1.98719 cal. deg.$^{-1}$mole^{-1}. From the free energy data, equation 1 was deduced by the method of least squares

$$\Delta F° = -4.3880252 \times 10^4 - 7.1602640 \times 10\,T + 3.3678870 \times 10^{-3}\,T^2 \quad (1)$$

The last column of Table I gives the values of $\Delta F°$ deduced from this equation. The root mean square deviation of $\Delta F°$ from the equation is 13 cal. The maximum deviation is 25 cal. at 301.16°K. The standard deviation of the constants in equation 1 is 12 cal. for the constant term and 0.13 cal. deg.$^{-1}$ for the linear term.

Combining the value of $\Delta F°$ at 298.16°K. with the value of $\Delta H°$ at 298.16° for this reaction, the value of $\Delta S°$ can be obtained and thus the value of $S°$ for methylamine. Table II tabulates the data used along with references and the derived values of ΔS of reaction A and the entropy of methylamine. The errors given are the so called "standard errors of estimate." The calculation of the entropies of methylamine by differentiation of equation 1 is summarized in Table III for temperatures given in

TABLE I

THE FREE ENERGY OF REACTION (A) AT CERTAIN TEMPERATURES

0°C. = 273.16°K., 1 cal. = 4.18674 abs. joules.

T, °K.	$P_{CH_3NH_2}$, 10^3 atm.	P_{H_2}, atm.	P_{HCl},[a] 10^{17} atm.	$(1/K) \times 10^{-15}$ $(P_{H_2}P_{HCl}/P_{CH_3NH_2})^{-1}$	$\Delta F°$, cal. Found	Calcd eq. 1
276.16	0.8990	0.9336	5.627	19060	24383	24363
276.16	.8990	.9336	5.637	19060	24382	24363
276.16	.8990	.9336	5.653	19060	24380	24363
276.16	.8990	.9336	5.646	19060	24381	24363
276.16	.9271	.9343	5.628	19060	24366	24363
276.16	.9271	.9343	5.637	19060	24365	24363
276.16	.9271	.9343	5.653	19060	24363	24363
276.16	.9271	.9343	5.644	19060	24363	24363
282.16	2.076	.9364	14.29	3521	23923	23945
282.16	2.076	.9364	14.32	3521	23922	23945
282.16	2.076	.9364	14.28	3521	23924	23924
282.16	2.076	.9364	14.14	3521	23930	23924
295.16	2.723	.9032	323.5	114.5	23034	23039
295.16	2.723	.9032	322.5	114.5	23036	23039
295.16	2.723	.9032	317.9	114.5	23043	23039
295.16	2.723	.9032	319.0	114.5	23042	23039
298.16	4.150	.8927	434.9	54.26	22844	22831
298.16	4.150	.8927	439.6	54.26	22837	22831
298.16	4.150	.8927	446.2	54.26	22828	22831
298.16	4.150	.8927	442.8	54.26	22833	22831
301.16	3.222	.8866	1206	26.81	22597	22622
301.16	3.222	.8866	1188	26.81	22617	22622
301.16	3.222	.8866	1168	26.81	22607	22622
301.16	3.222	.8866	1193	26.81	22608	22622
308.16	4.071	.8636	4845	4.990	22144	22135
308.16	4.071	.8636	4828	4.990	22147	22135
308.16	4.071	.8636	4775	4.990	22153	22135
308.16	4.071	.8636	4884	4.990	22140	22135
313.16	8.653	.8474	7157	1.604	21792	21788
313.16	8.653	.8474	7209	1.604	21788	21788

[a] Calculated from $E° - E = RTF^{-1}\ln(P_{HCl}/P_{H_2})$.

TABLE II

CALCULATION OF THE ENTROPY OF METHYLAMINE AT 298.16° K. FROM $\Delta H°$ AND $\Delta F°$

	Value	Ref.
$\Delta H°$ reaction,[a] cal.	43,616 ± 54	6 (see note a)
$S°$ of HCl, e.u.	44.62 ± 0	10
$S°$ CH_3NH_3Cl, e.u.	33.13 ± 0.05	6
$\Delta F°$ (reaction A), cal.	22,831 ± 12	
$\Delta S°$ (reaction A), e.u.	69.71 ± 0.18	
$S°$ CH_3NH_2, e.u.	58.22 ± 0.18	

[a] To obtain this value the value in ref. 6 has been modified by using the barrier later derived in this paper to bring the value of heat of vaporization of methylamine to 298.16°K., also one experimental value of the heat of vaporization of methylamine was discarded before taking an average.

TABLE III

THE ENTROPY OF METHYLAMINE DERIVED FROM REACTION (A)

T, °K.	$S°$ Reaction (slope), e.u.	$S°_{CH_3NH_3Cl}$, e.u.	$S°_{HCl}$, e.u.	$S°_{CH_3NH_2}$ (exp.), e.u.	$S°_{CH_3NH_2}$, (spect.) e.u. V = 1520 cal. mole^{-1}	$\Delta H°_0$, cal.
276.16	69.74	31.48	44.09	57.13	57.42	43,550
282.16	69.70	31.94	44.25	57.39	57.70	43,553
295.16	69.61	32.91	44.55	57.97	58.23	43,549
298.16	69.59	33.13	44.62	58.10	58.35	43,559
301.16	69.57	33.55	44.68	58.24	58.48	43,564
308.16	69.53	33.85	44.85	58.53	58.76	43,541
313.16	69.49	34.21	44.96	58.74	58.96	43,532
					Av.	43,550 ± 8
					From $\Delta H°_{298.16}$	43,521

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(9) J. G. Aston and F. L. Gittler, THIS JOURNAL, **77**, 3173 (1955).

col. 1. Column 2 gives the values of ΔS° calculated by differentiating equation 1. The error as estimated from the standard error in the linear coefficient of equation 1 is 0.13 e.u. Columns 3 and 4 give values of the entropies of methylammonium chloride and hydrogen chloride obtained, respectively, by integrating the measured heat capacities for methylammonium chloride and from the tables of Giauque and Overstreet.[10] Column 5 gives the experimental values of the entropy of methylamine derived from these values.

The Thermodynamic Functions of Methylamine from Spectroscopic Data.—The following distances and angles were used: CN, 1.48 Å.; NH, 1.01 Å.; H, 1.093 Å.; HCH, 109°26; HNH, 108°; HCN, 109°26; HNC, 108°. From these the principal moments I_1, I_2 and I_3 deduced were, respectively, 3.68×10^{-39}, 3.84×10^{-39} and 0.817×10^{-39} g. cm.^{2} and the reduced moment for the internal rotation[11] was 1.06×10^{-40} g. cm.^{2}. In computing the thermodynamic functions for the internal rotation Pitzer's method[11] was used with the tables of Pitzer and Gwinn[12] taking the symmetry number as unity for the external rotation and three for the internal rotation. Take the spectroscopic band at 270 cm.$^{-1}$ [13] as due to the hindered rotation, by use of the formula I

$$\nu = \frac{n}{2\pi}\sqrt{\frac{V_0}{2T_{\text{red}}}} \qquad (2)$$

V_0 is found to be 1538 cal. mole^{-1} and this barrier was first used in the calculations. Using the spectroscopic assignment[4] of the infrared data of Owens and Barker[13] and the standard formula for the translational and rotational entropy, the calculation of the thermodynamic quantities was completed. The value for the entropy of methylamine thus computed at 298.16°K. is 58.35 e.u. which agrees with the value found in Table II within the standard error of estimate. Column 6 of Table III gives the necessary values of the entropy, calculated from spectroscopic data, for comparison with the values from the temperature coefficient. Here the agreement is within the maximum error but not within the standard error.

Another way of comparing the results is to use the spectroscopic and molecular data for methylamine with the barrier of 1520 cal. mole^{-1} to calculate values of $(F^\circ - E^\circ)/T$. By combining these with the values for hydrogen chloride[10,14] and methylammonium chloride, obtained by integration using the heat capacity data,[6] values of $\Delta(F^\circ - E^\circ/T)$ are obtained. These values together with $\Delta F^\circ/T$ values deduced from the results of Table II yield values of ΔH_0° which are tabulated in the last column of Table III. There is no meaningful trend in the values. For completeness a value of ΔH_0°, calculated from the value of ΔH° at 298.16 from Table II and $\Delta(H^\circ - E_0^\circ)$ values obtained similarly to those of $\Delta(F^\circ - E^\circ)/T$, is given at the foot of the Table. The agreement is well within the standard error. Essential agreement of the entropy and better consistency in the ΔH_0° values is obtained with a barrier of about 1900 cal. mole. Table IV summarizes the values of the entropy at the same temperatures as Table III (col. 1) calculated with a barrier of 1900 cal. mole^{-1} (col. 2). The agreement with the experimental ones (col. 3) is greatly improved. In the last column of this table are given the values of ΔH_0° calculated on the same basis. The consistency of the ΔH_0° values is, of course, not impaired for this small change in barrier nor is the agreement with ΔH_0° calculated from the value of ΔH° at 298.16 (foot of col. 4).

TABLE IV

THE SPECTROSCOPIC ENTROPIES OF METHYLAMINE BASED ON A BARRIER OF 1900 CAL. MOLE^{-1}

T, °K.	$S^0_{CH_3NH_2}$ exp. (slope), e.u. ± 0.13	$S^0_{CH_3NH_2}$, (spect.), e.u.	ΔH°_0, cal. mole^{-}
276.16	57.13	57.23	43,515
282.16	57.39	57.50	43,515
295.16	57.97	58.03	43,506
298.16	58.10	58.15	43,516
301.16	58.24	58.28	43,509
308.16	58.53	58.55	43,494
313.16	58.74	58.76	43,481
		Av.	43,505
		From $\Delta H^\circ_{298.16}$	43,469 ± 54[a]

[a] This error is based on the experimental error in $\Delta H^\circ_{298.16}$ and in ΔS from the equilibrium data.

Conclusion.—While the probable error in the value of 1900 cal. mole^{-1} is about ±300 cal. mole^{-1}, thus making possible a value agreeing with the barrier of 1520 cal. mole^{-1} which comes from the spectroscopic line, it gives a value of the entropy at the normal boiling point (266.84°K.) of 56.83 e.u., using the value of I_1, I_2 and I_3 calculated from the bond distances. This is in closer agreement with the calorimetric value of 56.42 ± 0.3 e.u. If the value of I_1, I_2 and I_3 of Aston and Doty[4] (derived from the spectroscopic data) be used the spectroscopic entropy at 266.84°K. is 56.74 e.u. which agrees with the experimental value within the claimed error of ±0.3. This error was due to hysteresis in the solid heat capacities. Thus it is reasonable to assume that by reasonably slow cooling no randomness is left in solid methylamine at 0°K.

However, just recently microwave data have given values of the barrier between 1800 and 1940 cal. mole^{-1} [15a,b] so that there now seems little doubt that the barrier is about 1900 cal. mole^{-1}.

It is to be noted that the zero point entropy of methylammonium chloride has been taken as zero in agreement with the X-ray results of Lipscomb.[16]

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