[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BOSTON UNIVERSITY]

The Heat Capacity, Entropy and Heat Content of Sodium Amide from 15 to 300°K. The Thermodynamics of Amide Ion in Liquid Ammonia[1]

BY L. V. COULTER, J. R. SINCLAIR, A. G. COLE AND G. C. ROPER

RECEIVED OCTOBER 8, 1958

The heat capacity of sodium amide has been determined from 15 to 300°K. in an adiabatically operated calorimeter. At 298.15°K. the heat capacity, entropy and enthalpy were found to be 15.81 cal. deg.$^{-1}$ mole^{-1}, 18.38 cal. deg.$^{-1}$ mole^{-1} and 2841.6 cal. mole^{-1}, respectively. At 240° K. the standard free energy of formation of ammonous amide ion in the hypothetical 1 molal ammonia solution is 30.5 kcal. and the partial molal entropy of amide ion is -19.3 cal. deg.$^{-1}$ mole^{-1} relative to $\bar{S}_{240}\,[H^{+}{}_{(am)}] = 0.0$. In comparison with other negative ions the observed entropy of the amide ion in liquid ammonia appears qualitatively correct for a freely rotating ion. For the reaction: $NH_3(l) = H^{+}{}_{(am)} + NH_2{}^{-}{}_{(am)}$ the ionization constant $K = 3.2 \times 10^{-33}$ at 240°K. At 298.15°K., $\Delta F^0{}_f[NH_2{}^{-}{}_{(am)}] = 35.0$ kcal.; $\bar{S}^0[NH_2{}^{-}{}_{(am)}] = -14.7$ cal. deg.$^{-1}$ mole^{-1} and $K = 2.2 \times 10^{-28}$ for the ionization of liquid ammonia.

The lack of entropy data for sodium amide has precluded an accurate thermodynamic description of this simple and important compound. Although a heat of formation has been reported,[2] estimates of the entropy have heretofore been utilized in calculating the free energy of formation which is of practical interest for liquid ammonia solution chemistry as well as for reactions involving the solid amide. Accordingly, the low temperature heat capacity of sodium amide has been measured over the temperature range of 15 to 300°K. from which the entropy and heat content functions have been calculated. In addition, with the aid of other thermodynamic data, the partial molal ionic entropy and the free energy of formation of ammonous amide ion have been calculated at 240°K. (vicinity of the normal boiling point of ammonia) and 298.15°K.

Preparation of Sodium Amide.—The sodium amide employed in the heat capacity measurements was prepared by the reaction of gaseous ammonia with molten sodium as described by Dennis and Browne.[3] Prior to the synthesis, oxide free molten sodium was injected into the reaction chamber in a manner described by Kraus.[4] The capillary exit of the glass injector apparatus[4] extended through the entrance tube ($5'' \times {}^{7}/_{32}''$ i.d.) of the reaction chamber[3] and delivered the molten sodium metal, devoid of oxide, directly into the nickel reaction crucible. Following the introduction of the sodium the capillary was withdrawn, and in its place a stainless steel ammonia inlet tube was inserted within a few millimeters of the bottom of the crucible holding the molten sodium metal. At all times the sodium metal or sodium amide product was protected by an atmosphere of dry helium or sodium-dried ammonia gas. As a precautionary measure,[5] the introduction of ammonia gas was continued for several hours beyond the recommended time. Upon completion of the reaction, the apparatus was filled with ammonia gas above atmospheric pressure and transferred directly to a dry box in which the filling of the calorimeter and sample bulbs for analyses was completed in an inert atmosphere. On the basis of total base content the amide was 99.91% pure; and on the basis of ammonia content the amide was 99.77% pure. Although it is likely that sodium hydride comprised the impurity,[5] no attempt has been made to correct the heat capacity data. Anhydrous ammonia, dried with sodium, and reagent grade sodium metal were used in the synthesis.

A total sample weight of 75.282 g. *in vacuo* (1.9296 moles based on a formula weight of 39.015) was used in the heat capacity measurements.

Heat Capacity Measurements.—The heat capacity measurements were made in the adiabatically controlled cryostat constructed, previously used and described by Yost.[6]

A gold plated copper calorimeter of conventional[6] design was used for the heat capacity measurements. The calorimeter was constructed from 1.5″ diameter copper tubing and had an internal volume of 108 ml. The total weight of the calorimeter including the thermometer heater unit was 106 g.

To facilitate sealing the calorimeter with a minimum risk of decomposing heat sensitive compounds, one end of the calorimeter was provided with a protruding loading port consisting of a metal collar ${}^{1}/_{4}''$ wide $\times$ ${}^{1}/_{4}''$ diameter. The latter was provided with a platinum lid attached by a soft solder seal.

At the opposite end of the calorimeter a thermometer–heater unit of the capsule type was held in a re-entrant tube[5] (0.3″ i.d.) extending approximately $3{}^{1}/_{8}''$ into the calorimeter along the cylinder axis. Eight radial vanes soldered to the wall of the re-entrant tube and extending to the internal wall of the calorimeter facilitated rapid attainment of thermal equilibrium. The calorimeter was filled with one atmosphere of helium at room temperature to assist in heat transfer.

The platinum resistance thermometer (B.U.I.; $R_0 = 40.52583$ ohms) employed in the heat capacity measurements was constructed according to the specifications of Meyers[7] and the National Bureau of Standards and was enclosed in a glass sealed platinum cylinder ${}^{5}/_{16}''$ o.d. $\times$ 8 cm., along with a constantan heater (260 ohms) which was also mounted on the mica support cross.[7] Two sets of platinum leads from both the thermometer and the heater extended through the glass seal and were firmly attached to the external surface of the glass seal.

The thermometer was calibrated by comparison[8] at appropriate intervals from 12 to 300°K. with a platinum resistance thermometer (B.U. II; $R_0 = 33.94601$ ohms) calibrated by the National Bureau of Standards. The latter thermometer unaccompanied by a heater was similarly contained in a sealed platinum container ${}^{5}/_{16}''$ o.d. $\times$ 3.4 cm. The thermometers were mounted in a copper block which occupied the normal calorimeter position within the cryostat. From the resistance comparison data the usual deviation plot and temperature resistance table were prepared.[8] The data were smoothed to third differences by a least squares method[9] using an I.B.M. type 650 computer.

The heat capacity measurements were made in the usual manner[10] employing a modified double White potentiometer and a matched galvanometer. The energy input was corrected for the energy loss in the volt box circuit and for the energy gain from the leads between the heater–thermometer unit and the adiabatic shield walls. When necessary, corrections of very small magnitude were made for incomplete adiabaticity. Time measurements were made with a frequently calibrated stopwatch. The over-all accuracy of

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(1) This research was supported in part by the Callery Chemical Company under a contract from the Bureau of Aeronautics, Department of the Navy.

(2) R. Juza, K. Fasold and C. Haeberle, *Z. anorg. allgem. Chem.*, **234**, 74 (1937).

(3) L. M. Dennis and A. N. Browne, "Inorganic Syntheses," Vol. 1, McGraw–Hill Book Co., Inc., New York, N. Y., 1939, p. 74.

(4) C. A. Kraus, THIS JOURNAL, **30**, 1197 (1908).

(5) R. Levine and W. C. Fernelius, *Chem. Revs.*, **54**, 449 (1954).

(6) D. M. Yost, C. S. Garner, D. W. Osborne, T. R. Rubin and H. Russell, Jr., THIS JOURNAL, **63**, 3488 (1941).

(7) C. H. Meyers, *J. Research Natl. Bur. Standards*, **9**, 807 (1932).

(8) H. J. Hoge and F. G. Brickwedde, *ibid.*, **22**, 351 (1939).

(9) F. Hildebrand, "Introduction to Numerical Analysis," McGraw–Hill Book Company, New York, N. Y., 1956, p. 296.

(10) J. C. Southard and F. G. Brickwedde, THIS JOURNAL, **55**, 4378 (1933).

measurement is believed to be 0.1 to 0.2% above 40°K. and about 1% at 20°K. The heating periods varied from 5 minutes at low temperatures to 14 minutes at room temperature. No temperature interval was omitted in the measurements.

The absolute temperature of the ice point was taken to be 273.15°K. and one defined calorie was taken to be 4.184 abs. joules.

Heat Capacity of Sodium Amide and the Torsional Oscillation of the Amide Ion.—The experimental heat capacities are listed in Table I. No discontinuities in the heat capacity curve were observed which is consistent with the observation by Zalkin and Templeton[11] who found no structural change at −120° and 160° relative to the room temperature structure and who also concluded on the basis of the structure of the solid amide that free rotation of the amide ion is impossible.

In general, temperature equilibrium was more slowly attained in the heat capacity measurements than is usually found to be the case and probably accounts for the somewhat larger than normal scattering of the data in the 200 to 250°K. range.

TABLE I

EXPERIMENTAL MOLAR HEAT CAPACITY OF SODIUM AMIDE

T, °K.	C_p, cal. deg.$^{-1}$	T, °K.	C_p, cal. deg.$^{-1}$	T, °K.	C_p, cal. deg.$^{-1}$
14.49	0.335	59.89	4.087	172.32	12.03
15.52	.280	65.63	4.619	178.88	12.31
16.66	.329	70.64	5.096	185.59	12.61
18.16	.520	75.63	5.546	192.14	12.92
19.93	.668	80.85	6.027	198.61	13.09
21.56	.785	86.04	6.508	203.33	13.35
23.46	.934	92.43	7.056	209.18	13.47
25.78	1.131	99.52	7.616	214.19	13.63
28.08	1.300	106.98	8.149	220.43	13.86
30.50	1.492	110.33	8.410	227.75	13.95
33.38	1.708	116.80	8.885	234.16	14.38
36.44	1.977	122.96	9.297	240.84	14.42
39.17	2.337	129.15	9.720	247.72	14.62
43.99	2.642	135.37	10.09	254.49	14.81
47.28	2.913	141.25	10.47	261.16	15.00
50.96	3.249	147.56	10.80	274.05	15.26
54.77	3.610	154.23	11.13	280.96	15.39
58.00	3.869	160.35	11.48	287.79	15.56
55.58	3.682	166.24	11.76	294.55	15.74
				301.45	15.87

The experimental heat capacities in the 18–45°K. temperature interval are accurately described by the combination of a six degree Debye heat capacity function and a one degree Einstein heat capacity function, $C_v = 6D^\circ(404/T) + E^0(84/T)$, with which the thermodynamic functions for the 0–15.85° interval were calculated. Presumably, each of two three degree Debye functions with θ's = 404° describe the lattice vibrations of the sodium and amide ions, and the one degree Einstein function with $\theta = 84°$ is to be associated with a single torsional oscillation or librational motion of the amide ion with a frequency ν = 58 cm.$^{-1}$. Between 45 and 300°K. the experimental heat capacities are accounted for approximately by the expression, $C_v = 6D^0(404/T) + E^0(84/T) + E^0(825/T) + E^0(875/T)$.

Although the foregoing heat capacity analysis is admittedly qualitative in nature, it is consistent with the orientation of amide ions in sodium amide recently suggested by Zalkin and Templeton.[11] For this structure, it would appear that at low temperatures significant excitation of only one degree of torsional oscillation in the HNH plane of the amide ion is possible in which only a grazing approach of the hydrogens to neighboring groups results for a substantial angular displacement of the amide ion from its equilibrium position. This mode of libration with relatively low repulsion we associate with ν = 58 cm.$^{-1}$, whereas the two remaining modes of oscillation involving direct approaches between the hydrogens and neighboring groups are expected to be higher frequency modes corresponding to the two higher Einstein θ's.

The entropy and heat content functions for 298.15°K. and selected temperatures were calculated graphically from plots of C_p *versus* ln T and T, respectively. These results along with smoothed values of the heat capacity are listed in Table II.

TABLE II

SMOOTHED VALUES OF THE THERMODYNAMIC FUNCTIONS FOR SODIUM AMIDE AT SELECTED TEMPERATURES

T, °K.	Cp, cal. deg.$^{-1}$ mole^{-1}	S^0, cal. deg.$^{-1}$ mole^{-1}	$(H^0 - H_0^0)$, cal. mole^{-1}
16	0.324	0.085	1.104
20	0.673	.196	3.117
25	1.066	.386	7.424
30	1.452	.615	13.712
35	1.846	.867	21.932
40	2.293	1.143	32.287
45	2.723	1.439	44.846
50	3.160	1.748	59.513
60	4.083	2.415	95.78
70	5.035	3.105	141.45
80	5.946	3.837	196.34
90	6.844	4.590	260.30
100	7.642	5.354	332.74
110	8.405	6.119	412.95
120	9.10	6.880	500.56
130	9.77	7.635	594.93
140	10.37	8.381	695.69
150	10.92	9.116	802.16
160	11.45	9.837	913.97
170	11.93	10.546	1030.9
180	12.35	11.240	1152.4
190	12.81	11.920	1278.3
200	13.18	12.587	1408.3
210	13.51	13.238	1541.6
220	13.83	13.874	1678.4
230	14.13	14.495	1818.4
240	14.40	15.101	1961.2
250	14.68	15.695	2106.6
260	14.96	16.276	2254.8
270	15.18	16.844	2405.6
280	15.38	17.400	2558.4
290	15.61	17.944	2713.4
300	15.86	18.477	2870.8
298.15	15.81	18.380	2841.6

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(11) A. Zalkin and D. H. Templeton, *J. Phys. Chem.*, **60**, 821 (1956); also see R. Juza, H. Weber and K. Opp, *Z. anorg. allgem. Chem.*, **284**, 73 (1956).

It has been assumed in this research that perfection of the sodium amide crystal at very low temperatures prevails, *i.e.*, $S_{T=0} = 0$. The lack of thermodynamic information for other paths leading to an independent value for the entropy of sodium amide precludes the possibility of testing this assumption at the present. Although hydrogen bonding has been eliminated[11] as a significant factor in the structure of sodium amide (minimum $d_{N-N} = 3.81$ Å. to be compared with $d_{N-N} = 3.38$ Å. in solid ammonia),[11] the orderliness of the amide ion arrangement is still unsettled and the entropy values must, therefore, be regarded as tentative values.

The Free Energy of Formation of Sodium Amide.—For the formation of sodium amide from the elements at 298.15°K., $\Delta H_f^0 = -28.4$ kcal.[2] and $\Delta S_f^0 = S^0[\mathrm{NaNH_{2(c)}}] - S^0[\mathrm{Na_{(c)}}] - {}^1/_2\, S^0[\mathrm{N_{2(g)}}] - S^0[\mathrm{H_{2(g)}}] = 18.38^{12} - 12.25^{13} - 22.88^{13} - 31.21^{13} = -47.96$ cal. deg.$^{-1}$ mole^{-1}. We then calculate $\Delta F_f^0 = -14.1$ kcal. per mole at 298.15°K. For the heat of formation of sodium amide at 240°K., $\Delta H_f^0 = -28.3$ kcal.[14]; $\Delta S_f^0 = 15.10^{12} - 10.83^{13} - 22.14^{15} - 29.88^{15} = -47.75$ cal. deg.$^{-1}$ mole^{-1} and $\Delta F_f^0\,[\mathrm{NaNH_{2(c)}}] = -16.84$ kcal. at 240°K.

The Free Energy of Formation and the Relative Partial Molal Entropy of $\mathrm{NH_2^-}_{(am)}$.—For the calculation of the thermodynamic properties of amide ion in liquid ammonia, it has been assumed that ammonous sodium amide is the stable phase in equilibrium with the saturated solution at 240°K.

$$\mathrm{NaNH_2(c)} \rightleftarrows \mathrm{Na^+}_{(am)} + \mathrm{NH_2^-}_{(am)}$$

For the solution reaction to give the hypothetical one molal solution at 240°K. $\Delta F° = -RT \ln (\gamma_\pm M_\pm)^2$ where $\gamma_\pm$ is the mean activity coefficient of sodium amide in liquid ammonia at saturation and $M_\pm = 0.026$,[16] the concentration of the saturated solution at 240°K.

Since no activity coefficient data have been reported for sodium amide in liquid ammonia, we have estimated the activity coefficient with the help of experimental data for ammonia solutions of NaCl,[17] KCl[17] and $\mathrm{NH_4Cl}$.[18] At saturation, 0.026 M, we estimate $\gamma_\pm = 0.30 \pm 0.05$ for ammonous sodium amide and calculate $\Delta F_s^0 = -240R \ln (0.3 \times 0.026)^2 = 4.63$ kcal. ± 0.3 kcal. and $\Delta F_f^0[\mathrm{NH_2^-}_{(am)}] = -\Delta F_f^0[\mathrm{Na^+}_{(am)}]^{14} + \Delta F_f^0[\mathrm{NaNH_{2(c)}}] + \Delta F^0(\text{solution}) = 42.7^{19} - 16.8^{12} + 4.6 = 30.5$ kcal. at 240°*K*.

At 298.15°K., $M = 0.0434$, $\gamma_\pm = 0.25$, $\Delta F_s^0 = 5.35$ kcal.; and $\Delta F_f^0[\mathrm{NH_2^-}_{(am)}] = 35.0$ kcal.

The heat of formation of $\mathrm{NH_2^-}_{(am)}$ at 240°K. may be calculated from the reactions:

$$\mathrm{NH_2^-}_{(am)} + \mathrm{H^+}_{(am)} = \mathrm{NH_3(l)} \text{ and}$$

$$\mathrm{KNH_{2(c)}} = \mathrm{K^+}_{(am)} + \mathrm{NH_2^-}_{(am)}$$

for which the heats of reaction have been measured.[20] For the first, $\Delta H^0 = -26.1$ kcal.^{20} $= \Delta H_f^0[\mathrm{NH_3(l)}]^{21} - \Delta H_f^0[\mathrm{H^+}_{(am)}]^{22} - \Delta H_f^0[\mathrm{NH_2^-}_{(am)}]$, and $\Delta H_f^0[\mathrm{NH_2^-}_{(am)}] = 9.8 \pm 0.3$ kcal. For the second reaction $\Delta H^0 = -2.3 \pm .3$ kcal.,[20] $\Delta H_f^0[\mathrm{K^+}_{(am)}] = -39.7$ kcal.[19] and $\Delta H_f^0[\mathrm{KNH_{2(c)}}] = -28.2$ kcal.[13,14] from which we calculate $\Delta H_f^0[\mathrm{NH_2^-}_{(am)}] = 9.2$ kcal. in fair agreement with the heat of formation of $\mathrm{NH_2^-}$ based on the neutralization reaction.

The heat of formation of $\mathrm{NH_2^-}_{(am)}$ may also be estimated from the temperature dependence of the solubility product[23] of sodium amide. For the heat of solution of sodium amide we calculate $\Delta H^0 = 1.4$ kcal. and $\Delta H_f^0[\mathrm{NH_2^-}_{(am)}] = 11.8$ kcal. which is in poor agreement with the direct thermochemical data. In view of the uncertainties associated with solubility measurements at low concentrations and with the nature of the solid phase in equilibrium with the saturated solution, we choose as the best value $\Delta H_f^0[\mathrm{NH_2^-}_{(am)}] = 9.8$ kcal. corresponding to -0.6 kcal. for the ΔH^0 of solution of sodium amide. For the entropy of solution, $\Delta S^0 = (-600 - 4630)/240 = -21.8$ cal, deg.$^{-1}$ mole^{-1} and $\bar{S}^0[\mathrm{NH_2^-}_{(am)}] = \Delta S^0(\text{solution}) - \bar{S}^0[\mathrm{Na^+}_{(am)}] + S^0[\mathrm{NaNH_{2(c)}}] = -21.8 - 12.6^{19} + 15.10 = -19.3$ cal. deg.$^{-1}$ mole^{-1} at 240°K.

For the solution reaction of sodium amide at 298.15°K., $\Delta H_s^0 = -0.5$ kcal., $\Delta F_s^0 = 5.35$ kcal. and $\Delta S_s^0 = -19.7$ cal. deg.$^{-1}$ mole^{-1}. At 298.15° K., $\bar{S}^0[\mathrm{Na^+}_{(am)}] = 13.4$,[19] $S^0[\mathrm{NaNH_{2(c)}}] = 18.38^{12}$ and $\bar{S}^0[\mathrm{NH_2^-}_{(am)}] = -14.7$ cal. deg.$^{-1}$ mole^{-1}.

The entropy of the ammonous amide ion is appropriately compared with other ions of similar charge and radius in terms of the solvation entropy of the gas ion. For comparison we have chosen the chloride ($r = 1.81$ Å.)[24] and borohydride ($r = 2.03$ Å.)[25] ions for which the relative partial molal entropies are known with some certainty, $\bar{S}^0[\mathrm{Cl^-}_{(am)}] = -31.8$ e.u.[19] and $\bar{S}^0[\mathrm{BH_4^-}_{(am)}] = -18.4$ e.u.[26] for the hypothetical 1 molal solution at 240°K. For the gas ions, $S^0[\mathrm{Cl^-}_{(g)}] = 30.4$ e.u., $S^0[\mathrm{BH_4^-}_{(g)}] = 38.2$ e.u.[27] and $S^0[\mathrm{NH_2^-}_{(g)}] = 38.1$ e.u.[28] at 240°K. and at the same concentration. For the solvation reaction we obtain $\Delta S^0 = -62.2$, -56.6 and -57.4 e.u. for the ammoniation of the chloride, borohydride and amide ions, respectively.

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(12) This research.

(13) F. D. Rossini, *et al.*, N.B.S. Circular 500, "Selected Values of Chemical Thermodynamic Properties," U. S. Govt. Printing Office, Washington, D. C., 1952. N.B.S., "Selected Values of Chemical Thermodynamic Properties," Series III, U. S. Govt. Printing Office, Washington, D. C., 1954.

(14) ΔH_f^0 at 298.15°K. corrected to 240°K.

(15) F. D. Rossini, *et al.*, "Selected Values of Properties of Hydrocarbons," Circular C461 N.B.S., U. S. Govt. Printing Office, Washington, D. C., 1947.

(16) S. Sigetomi, *J. Soc. Chem. Ind. Japan*, **41**, 409 (1938); W. W. Hawes, THIS JOURNAL, **55**, 4422 (1933).

(17) J. Sedlet and T. DeVries, *ibid.*, **73**, 5808 (1951).

(18) V. A. Pleskov and A. M. Monoszon, *J. Phys. Chem.* (*U.S.S.R.*), **6**, 513 (1935).

(19) (a) L. V. Coulter, *ibid.*, **57**, 553 (1953). For $\mathrm{Na^+(am)}$ at 298°K. $\Delta F_f^0 = -43.7$ kcal., $\Delta H_f^0 = -38.7$ kcal. and $\bar{S}^0 = 13.4$ cal. deg.$^{-1}$ mole^{-1}; (b) W. M. Latimer and W. L. Jolly, THIS JOURNAL, **75**, 4147 (1953).

(20) H. D. Mulder and F. C. Schmidt, THIS JOURNAL, **73**, 5575 (1951); $\Delta H_s^0[\mathrm{KNH_2}]$ corrected approximately for infinite dilution.

(21) ΔH_f^0 at 298° corrected to 240°K. gives $\Delta H_f^0 = -16.3$ kcal.

(22) By convention: $\Delta H_f^0[\mathrm{H^+}_{(am)}] = 0$ and for $\mathrm{H^+}_{(am)} + \mathrm{NH_3} = \mathrm{NH_4^+}_{(am)}$, $\Delta H^0 = 0$.

(23) Based on the solubility data of ref. 16 and estimated activity coefficients.

(24) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940.

(25) S. C. Abrahams and J. Kalnajs, *J. Chem. Phys.*, **22**, 434 (1954).

(26) J. R. Sinclair, Ph.D. thesis, Boston University, 1956.

(27) A. P. Altshuller, THIS JOURNAL, **77**, 5455 (1955).

(28) Based on $r_{NH} = 1.01$ Å. and $d_{HH} = 1.6$ Å.

Accurate comparison of the solvation entropies of the amide ion and symmetrical ions of like charge is difficult because of the ambiguity of the amide ionic radius which falls between 2.06 and 1.6 Å. depending on the criterion employed. Assuming the upper limit and freely rotating ions, we note that the solvation entropies of the borohydride and amide ions are in good agreement as should be the case in view of the similarity of charge and radius. Since it is likely, however, that the actual radius displayed by the amide ion is somewhat less than 2.06 Å., which value is based on the NH_2–H_2N distance of neighboring ions with opposed hydrogens, comparison should probably be made with a smaller ion such as the chloride ion for which the solvation entropy is more negative by 5 e.u. In view of present experimental uncertainties, this discrepancy is probably without significance. It is, of course, to be expected that the entropy of solvation of a monatomic ion should not be more negative relative to a polyatomic ion of similar charge and radius since loss of rotational motion of the latter would result in a more negative solvation entropy for the polyatomic ion.

Ionization Constant of Liquid Ammonia.—With the aid of the heat of ionization of liquid ammonia and the entropy of the amide ion determined in this research, the free energy of ionization of ammonia and the equilibrium constant of the reaction: $NH_3(l) = H^+_{(am)} + NH_2^-{}_{(am)}$, can be calculated. At 240°K., $\Delta H^0 = 26.1$[20] kcal.; $\Delta S^0 = \bar{S}^0[H^+] + \bar{S}^0[NH_2^-] - S^0[NH_3(l)] =$ 0.0[29] − 19.3[12] − 20.8[30] = − 40.1 cal. deg.$^{-1}$ mole^{-1}; $\Delta F^0 = 35.7$ kcal. and $K = 3.2 \times 10^{-33}$. Pleskov and Monoszon[31] calculated $K = 1.9 \times 10^{-33}$ from cell potential data at −50°. Correcting their value to 240°K. we obtain 1.3×10^{-31} which differs substantially from the K obtained in this research.

For the ionization of liquid ammonia at 298.15° K., $\Delta S^0 = \bar{S}^0[NH_2^-] + \bar{S}^0[H^+] - S^0[NH_3(l)] =$ − 14.7[12] + 0 − 24.7[32] = − 39.1 cal. deg.$^{-1}$ mole^{-1}; $\Delta F^0 = 37.76$ kcal. and $K = 2.2 \times 10^{-28}$. For comparison with this value we correct K (Pleskov and Monoszon) to 298°K. giving $K = 5.1 \times 10^{-27}$.

Although the difference between the constant obtained by Pleskov and Monoszon and the constant based on the thermodynamic properties of amides previously estimated by Jolly[32] has been narrowed substantially with the use of experimental entropy data for sodium amide, a considerable difference still remains. This difference may be explained, however, by the presence of unknown liquid junction potentials in the cells employed by Pleskov and Monoszon, by an incorrect degree of dissociation of potassium amide assumed for the calculation of their K or by the uncertainty in the free energy of solution of sodium amide employed in this research.

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[29] By convention $\bar{S}^0[H^+{}_{(am)}] = 0.0$.

[30] R. Overstreet and W. F. Giauque, THIS JOURNAL, **59**, 254 (1937).

[31] V. A. Pleskov and A. M. Monoszon, *J. Phys. Chem.*, (*U.S.S.R.*), **6**, 513 (1935).

[32] W. L. Jolly, *Chem. Revs.*, **50**, 351 (1952); U. S. Atomic Energy Commission, UCRL Report No. 2201, May, 1953; ref. 19b.

BOSTON, MASS.

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY, HARVARD UNIVERSITY]

Molecular Addition Compounds of Boron. II. Thiophane–Borane and Related Adducts[1,2]

BY T. D. COYLE,[3] H. D. KAESZ[4] AND F. G. A. STONE

RECEIVED DECEMBER 20, 1958

The addition compounds $(CH_2)_4S \cdot BH_3$, $(CH_2)_4S \cdot BF_3$, $Et_2S \cdot BH_3$ and $Et_3S \cdot BF_3$ have been prepared, and their liquid saturation pressures and dissociations in the gas phase examined. Gas-phase dissociation of the adduct $Me_2S \cdot BH_3$ has been re-investigated. As might be expected, all the complexes are weak. Indeed, only the borane adducts are sufficiently associated in the gas phase to permit reliable determination of thermodynamic constants. Nevertheless, it was clearly demonstrated that borane forms much more stable adducts than does boron trifluoride with the thioethers, whereas the reverse is true with ordinary ethers. Moreover, adducts like $Et_2S \cdot BH_3$ are much more stable than their oxygen analogs. Furthermore, the order of coördination of the thioethers toward borane is $Me_2S \simeq Et_2S > (CH_2)_4S$, in contrast to the order displayed by ethers, *viz.*, $(CH_2)_4O > Me_2O > Et_2O$. It is probable that the thioethers display a similar sequence of coördination toward boron trifluoride but in this case, because of the weakness of the boron trifluoride adducts, experimental evidence is only qualitative.

Introduction

During the period 1942–1951, the gas-phase dissociations of many molecular addition compounds were studied by Brown and his co-workers and by Coates.[5] These addition compounds involved a variety of combinations of different Lewis acids with different Lewis bases, *e.g.*, $(CH_2)_4O \cdot BF_3$, $Me_2S \cdot AlMe_3$, $Me_3N \cdot BMe_3$, $Me_3As \cdot GaMe_3$ and $Me_3P \cdot BF_3$, etc. It was natural that the relative stabilities of these compounds, usually compared in terms of relative heats of gas-phase dissociation, should excite interest. This was especially so on the realization that if one compared all the adducts made by Brown, *et al.*, and by Coates, it was possible to make a generalization. This generalization has been expressed in several different ways by several authors, *e.g.*, (i) "The order of stability of complexes formed by alkyl derivatives of the

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[1] Previous paper, W. A. G. Graham and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, **3**, 164 (1956).

[2] The work described in this paper was made possible by the award of a Grant (G5106) from the National Science Foundation.

[3] Natvar Corporation Fellow at Harvard University, 1958–1959.

[4] Public Health Predoctoral Research Fellow of the National Heart Institute.

[5] For a review of molecular addition compounds of the Group III elements see F. G. A. Stone, *Chem. Revs.*, **58**, 101 (1957).