culated in this manner from the extrapolated slopes at zero concentration of poly-soap are designated as p_0 in Table V.

These values of p_0 in Table V are of the same order of magnitude as the values reported by Phillips and Mysels[18] for sodium lauryl sulfate, based on a similar calculation. However our values of p_0—calculated from the slopes—are much higher than the values of p_1 and p_2 calculated on the basis of eq. 1. This discrepancy cannot be accounted for by assuming that the molecules are aggregated, since this assumption would affect the value of p_0 almost as much as the values of p_1 and p_2. Thus, in the experiment with poly-soap R in 0.00391 M KCl, the assumption of aggregation to the extent of an aggregate weight of 2,000,000 would increase p_0 to 128, while increasing p_1 to only 29.4.

Unfortunately the value of p has no direct significance in terms of measurements other than by light scattering. The internal discrepancy between the values of p calculated from the same data by two different methods must cast some doubt on the validity of the theory on which these calculations were based.

We also have attempted to interpret the present data according to the theory of Doty and Steiner.[19] This theory, however, predicts a dissymmetry coefficient $z_{45} < 1$, while in all our experiments we have found z_{45} between 1.0 and 1.2.

Conclusions

From the theoretical standpoint, it appears that the data obtained in aqueous salt solutions cannot be adequately interpreted by either of the theories considered; while the theories proposed for soap in the absence of salt do not permit direct experimental verification.

From a practical standpoint, the present data indicate that molecular weights of soap micelles, estimated from light scattering measurements in aqueous solutions, may be too low by a factor from 2 to 5.

Insofar as the present data can be applied to ordinary soaps and other micelle-forming substances,

(19) P. Doty and R. F. Steiner, *J. Chem. Phys.*, **20**, 85 (1952).

the data obtained in dilute salt solutions indicate that in the presence of an electrolyte in the range 0.01–0.1 N, micelle molecular weights within 30% of the correct value will be obtained. Extrapolation to the critical micelle concentration, as recommended by Debye[20] and Mysels[16] should give molecular weights of this order of accuracy, with soaps of fairly high critical concentration such as sodium laurate or sodium lauryl sulfate. However, with soaps of critical concentration much below 0.01 M, this procedure may give somewhat more erroneous results.

The data obtained in salt solutions of higher concentration (0.2–0.4 M) indicate that association of the poly-soap does take place. It is likely that association or enlargement of ordinary soap micelles would also take place at these salt concentrations. However, the addition of salt to bring the total electrolyte concentration (including unmicellized soap) up to 0.01–0.1 M would seem a safe practice.

Any effects arising from hydrolysis of the poly-soaps do not prevent transfer of the conclusions drawn from the poly-soap systems to ordinary soap systems, since hydrolysis should be comparable in both systems. Furthermore, the extent of hydrolysis must be comparatively small, since poly-soap solutions of 0.34–1% concentration (0.008–0.025 M) have a pH of 9.5. The present data should thus have some bearing on the behavior of detergents such as sodium lauryl sulfate, etc. A sulfate ester type of poly-soap has been prepared in this Laboratory, but we have not had the opportunity to study its light scattering behavior.

(20) P. Debye, *J. Phys. Colloid Chem.*, **53**, 18 (1949); P. Debye and E. W. Anacker, *ibid.*, **55**, 644 (1951).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

The Thermodynamic Properties of Ammonium Fluoride: Heat Capacity from 6 to 309°K., the Entropy, Enthalpy and Free Energy Function[1]

BY EDWIN BENJAMINS AND EDGAR F. WESTRUM, JR.

Measurements of the heat capacity of NH$_4$F have been made by adiabatic calorimetry over the range 6 to 309°K. In contrast with the reports by others of a hump in the heat capacity near 240°K., no thermal anomaly was found in the entire range of measurement. The molal heat capacity and the derived molal entropy and enthalpy at 298.16°K. are 15.60 ± 0.02 cal./deg., 17.20 ± 0.02 cal./deg., and 2655 ± 3 cal., respectively.

Introduction

Although recent thermodynamic, spectroscopic and diffractional studies have contributed much to

the interpretation of the mechanism of the pseudorotational transitions in ammonium chloride, bromide and iodide, the treatment of the fluoride has been less decisive. Simon, Simson and Ruhemann[2] determined the low temperature heat capacities

(2) F. Simon, Cl. von Simson and M. Ruhemann, *Z. physik. Chem.* **129**, 339 (1927).

of NH_4F and the other ammonium halides and reported thermal anomalies of varying magnitude in all of them in the vicinity of 245°K. Since the anomaly claimed near 241°K. in ammonium fluoride was rather smaller than that in the other halides, they reached no conclusion as to its cause. Shulvas-Sorokina and Evdokimov[3] investigated the temperature dependence of the dielectric constant of ammonium chloride and ammonium fluoride and thereby confirmed the reported transformation in the chloride and claimed that the fluoride also undergoes a transformation at 246°K. Some authors of recent papers, monographs and texts concur in the view that ammonium fluoride would not be expected to undergo a transformation similar to that of the other halides because of its relatively strong hydrogen bonding and the stability of its wurtzite-type lattice[4]; however, confusion continues to exist.

In the other ammonium halides, each NH_4^+ ion is surrounded by an octet of anions, and the phase transitions occur as a consequence of the disordering of the equilibrium orientation of the ammonium ions. A different explanation must be sought to explain a phase change in NH_4F, if genuine, since only four tetrahedrally disposed nearest neighbors occur in its hexagonal structure.[5] Plumb and Hornig have noted that the infrared spectrum is "consistent with a phase change and may indicate a certain amount of disordering in the room-temperature phase."[5] Their X-ray diffractional studies, however, showed a structure at room temperature which is similar to that deduced from their infrared spectrum at −195°.

The present work was undertaken as part of an extensive study of the thermodynamic properties of hydrogen-bonded substances to ascertain the reality of the reported transition in pure ammonium fluoride.

Experimental

Preparation of Anhydrous Ammonium Fluoride (NH_4F).— A stoichiometric excess of 48% aqueous reagent hydrofluoric acid was added to solid reagent ammonium carbonate in a large silver beaker, and the solution was boiled vigorously to expel carbon dioxide. Gaseous ammonia was bubbled into the solution until pH 8 was achieved. Gradual cooling yielded acicular crystals of NH_4F which were separated from the mother liquor by filtration through a polyethylene Büchner-type funnel and washed with methanol saturated with ammonia. To avoid the dissociation of wet ammonium fluoride into ammonia and ammonium monohydrogen difluoride,[6] the crystals were dried in a polyethylene train under infrared radiation by streaming anhydrous ammonia over them for more than 24 hours. The dried salt was transferred to stoppered polyethylene bottles in a dry-box and stored under an atmosphere of anhydrous ammonia in a desiccator charged with anhydrous calcium oxide; it was highly evacuated to remove excess ammonia prior to weighing.

Spectrochemical analysis revealed the absence of silicon and other metallic contaminants; less than 1 p.p.m. of silver was detected. Volumetric analysis of the product using the Willard and Winter method[7] for fluoride and the distillation procedure of a Kjeldahl nitrogen determination gave the following results: fluoride (as HF), 51.46 ± 0.15%; ammonia, 48.78 ± 0.10% (theoretical, 51.29 and 48.71%,

respectively). Titration of the free acid using a pH meter indicated less than 0.05% excess HF. The absence of any abnormality in the heat capacity measurements near the ice point is probably evidence that the sample was anhydrous. Although direct combinations of anhydrous ammonia with anhydrous HF and with crystalline NH_4HF_2 were also attempted, neither yielded a crystalline product as suitable for thermodynamic measurement as the aqueous method described.

Cryostat and Calorimeter.—The Mark I liquid helium cryostat employed in these measurements was similar to one described by Westrum, Hatcher and Osborne[8] and is detailed elsewhere.[9] The adiabatic manner of operation employed in making heat capacity measurements, the determination of the temperature scale above 10°K. by the National Bureau of Standards,[10] the provisional scale employed below 10°K., and confirmation of the accuracy of the calorimeter with benzoic acid also have been described.[9]

The gold-plated copper calorimeter (laboratory designation W-6) is 3.8 cm. in diameter and 7.7 cm. in length. It is quite similar in general design to one already described,[11] except that to facilitate loading and sealing thermally unstable compounds, the diameter of the copper cover was reduced to 1.9 cm. and removed from the main portion of the calorimeter by a short tube of Monel of 0.28 mm. thickness which provides a thermal dam during the sealing operation with Cerroseal (50% tin and 50% indium) solder. This "cupola" does not interfere with the establishment of thermal equilibrium in the cryostat, yet avoids appreciable heating of calorimeter and sample on sealing and opening the calorimeter. The thickness of the copper shell is 0.37 mm. A copper cone provides thermal contact with the adiabatic shield for cooling the calorimeter. Eight radial vanes of 0.062 mm. copper foil aid the rapid achievement of thermal equilibrium. Pure helium gas, at a pressure of one atmosphere at 25°, is used to provide thermal conductivity between the calorimeter and the sample. A small hole drilled in the end of a thin-wall Monel stud permits evacuation, filling with helium and sealing with solder.

An axial re-entrant well contains a 25-ohm capsule-type platinum resistance thermometer with a cylindrical copper heater sleeve wound bifilarly with 160 ohms of No. 40 B. & S. gage double Fibreglas-insulated constantan wire cemented with baked Formvar in conforming double thread grooves. The glass head through which the thermometer leads are sealed is entirely within an enlarged portion of the well. Lead wires to both thermometer and heater are brought to temperature equilibrium with the outside of the calorimeter by a small copper spool around which the leads are cemented with Formvar. The spool is bolted in place over the end of the well with 00–90 brass cap screws. A copper–constantan differential thermocouple junction coated with baked Formvar makes a snug fit in a small tube soldered to the side of the calorimeter. Lubriseal stopcock grease is used to establish thermal contact between the calorimeter, thermometer, heater, spool and thermocouple. The weights of grease and solder are maintained constant for the measurements on the empty and loaded calorimeter. The mass of the empty calorimeter including thermometer, heater, spool solder and grease is 87.0 g. Two independent sets of determinations on the heat capacity of the empty calorimeter were made.

Heat Capacity Measurements.—A 26.711-g. sample (vacuo) of anhydrous ammonium fluoride was weighed into calorimeter W-6 in a dry-box. Corrections for buoyancy were based on a crystallographic density of 1.0092 g./cc.[12] The initial cooling of the sample at an average rate of 0.5°/ min. revealed no indication of a thermal anomaly. The subsequent heat capacity measurements of Series I also failed to reveal any trace of the previously reported hump. After very slow cooling at an average rate of 0.03°/min. the redeterminations of Series II confirmed the absence of any anomalous behavior.

(3) R. D. Shulvas-Sorokina and V. G. Evdokimov, Acta Physicochim. URSS, 11, 291 (1939).

(4) W. Zachariasen, Z. physik. Chem., 127, 218 (1927).

(5) R. C. Plumb and D. F. Hornig, J. Chem. Phys., 23, 947 (1955).

(6) A. C. Shead and G. F. Smith, THIS JOURNAL, 53, 483 (1931).

(7) H. H. Willard and O. B. Winter, Ind. Eng. Chem., Anal. Ed., 5, 7 (1933).

(8) E. F. Westrum, Jr., J. B. Hatcher and D. W. Osborne, J. Chem. Phys., 21, 419 (1953).

(9) E. F. Westrum, Jr., and A. F. Beale, Jr., to be published.

(10) H. J. Hoge and F. G. Brickwedde, J. Research Natl. Bur. Standards, 22, 351 (1939).

(11) D. W. Osborne and E. F. Westrum, Jr., J. Chem. Phys., 21, 1884 (1953).

(12) P. Wulff and H. K. Cameron, Z. physik. Chem., Abt. B, 10, 347 (1930).

Results and Discussion

The individual results of the heat capacity determinations are presented in chronological order in Table I. The approximate temperature increment of each measurement can be inferred from the adjacent mean temperature values. The heat capacities are computed on the basis of a molecular weight of 37.04 g., the defined thermochemical calorie equal to 4.1840 absolute joules, and an ice point of 273.16°K.

TABLE I

MOLAL HEAT CAPACITY OF AMMONIUM FLUORIDE

T, °K.	C_p cal. deg.$^{-1}$	T, °K.	C_p cal. deg.$^{-1}$	T, °K.	C_p, cal. deg.$^{-1}$
(Series 1)		(Series 2)		(Series 3)	
111.19	7.539	54.83	3.487	6.01	0.051
120.93	8.158	62.07	4.009	7.25	.028
129.55	8.674	69.27	4.559	9.41	.079
137.81	9.157	76.69	5.124	11.41	.138
145.96	9.623	84.64	5.730	13.10	.210
154.13	10.06	93.38	6.348	14.38	.283
162.37	10.48	102.34	6.950	15.59	.363
171.18	10.90	111.01	7.531	16.89	.460
180.18	11.33	119.33	8.061	18.30	.555
189.28	11.73	230.44	13.36	19.99	.688
198.55	12.12	238.97	13.68	22.07	.863
206.70	12.46	247.34	13.97	24.58	1.078
215.25	12.80	255.57	14.25	27.45	1.323
223.77	13.12	263.67	14.51	30.59	1.589
232.64	13.45	271.64	14.79	33.85	1.853
241.54	13.80	279.50	15.02	37.22	2.119
250.28	14.11			40.83	2.380
259.00	14.37			44.79	2.691
267.75	14.67			49.24	3.027
276.65	14.95			54.24	3.407
285.79	15.23				
295.05	15.51				
304.36	15.79				

Corrections have been applied to the heat capacity values for curvature (*i.e.*, for the finite temperature increments employed in the measurements) and for the slight differences between the amounts of helium gas in the loaded and empty calorimeter. The precision of the data above 40°K. is of the order of 0.03%

The molal thermodynamic functions $S°$ and $H° - H_0°$ were computed by numerical quadrature of C_p *versus* log T and T, respectively; however, all values were obtained from a single plot of C_p *versus* log T. These functions, together with the free energy function and values of the molal heat capacity read from the smooth curve through the experimental points, are tabulated at selected temperatures in Table II. These heat capacity values are considered to have a probable error of 0.1% above 25°K.; at 10°K. the probable error may be 1%, and at 5°K. it may be 5% as a consequence of the decreased sensitivity of the resistance thermometer and the provisional nature of the temperature scale below 10°K. Entropies and enthalpies at 10°K. are calculated by extrapolation of the heat capacity to 0°K. using a T-cubed dependence and assuming $S_0°$ to be zero.

The expectation of no residual (zero-point) en-

TABLE II

MOLAL THERMODYNAMIC FUNCTIONS OF AMMONIUM FLUORIDE

T, °K.	C_p, cal. deg.$^{-1}$	$S°$, cal. deg.$^{-1}$	$H° - H_0°$, cal.	$-(F° - H_0°)/T$, cal. deg.$^{-1}$
10	0.094	0.0312	0.234	0.0078
15	.323	.1053	1.189	.0260
20	.689	.2465	3.688	.0621
25	1.114	.4456	8.189	.1180
30	1.540	.6866	14.829	.1923
35	1.942	0.9545	23.546	.2817
40	2.316	1.2381	34.184	.3835
45	2.707	1.5335	46.745	.4947
50	3.086	1.8383	61.22	.6138
60	3.848	2.4679	95.88	.8098
70	4.616	3.1188	138.20	1.1445
80	5.374	3.7847	188.15	1.4328
90	6.108	4.4603	245.59	1.7315
100	6.802	5.1404	310.19	2.0385
110	7.465	5.8199	381.54	2.3514
120	8.100	6.4968	459.38	2.6686
130	8.700	7.1691	543.4	2.9890
140	9.282	7.8353	633.3	3.3116
150	9.837	8.4948	728.9	3.6353
160	10.36	9.1464	829.9	3.9594
170	10.85	9.7893	936.0	4.2836
180	11.33	10.423	1046.9	4.607
190	11.76	11.047	1162.3	4.930
200	12.18	11.661	1282.0	5.251
210	12.59	12.265	1405.9	5.570
220	12.98	12.860	1533.8	5.888
230	13.35	13.445	1665.4	6.204
240	13.71	14.021	1800.7	6.518
250	14.06	14.588	1939.6	6.829
260	14.40	15.146	2082.0	7.138
270	14.73	15.696	2227.6	7.445
280	15.05	16.238	2376.6	7.750
290	15.36	16.771	2528.6	8.052
300	15.65	17.297	2683.7	8.351
273.16	14.84	15.868	2274.4	7.542
298.16	15.60 ± 0.02	17.201 ± 0.02	2654.9 ± 3	8.297 ± 0.01

tropy in NH_4F is confirmed by the determination of the equilibrium dissociation pressures over the system $NH_4F–NH_4HF_2$ together with a determination of the phase diagram of the binary system between these compositions and other related data.[13]

A comparison of the data obtained in this study with those of Simon, Simson and Ruhemann[2] is presented in Fig. 1. No evidence of a hump is pres-
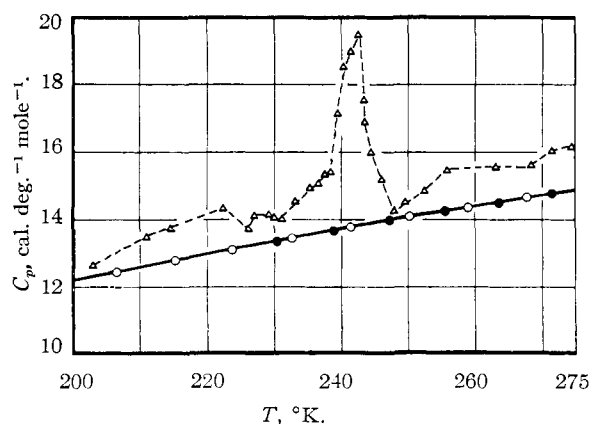

Fig. 1.—The molal heat capacity of ammonium fluoride near 240°K. The triangles indicate the data of Simon, Simson and Ruhemann; the open and solid circles represent, respectively, series I and II of this work.

(13) E. Benjamins and E. F. Westrum, Jr., to be published.

ent in our measurements, and the heat capacity data show the typical sigmoid curve anticipated in the absence of anomalous behavior. The heat capacity hump and the dielectric constant anomaly previously reported by others may be attributable to the presence of water or other impurities in their preparations. This hypothesis is consistent with the preparative methods described, but cannot be tested further because of the scant analytical data provided. Although thermal analysis[14] of the NH_4F-H_2O system indicated simple eutectic behavior with a eutectic temperature of 246°K. involving the phases NH_4F and NH_4F-H_2O, more

recent studies by Zaromb and Brill[15] have indicated that solid solutions exist in the water-rich region of the system. No corresponding examination of the ammonium fluoride-rich region of the phase diagram has been published.

(14) V. S. Yatlov and E. M. Polyakova, *J. Gen. Chem. USSR*, **15**, 724 (1945).

(15) S. Zaromb and R. Brill, *J. Chem. Phys.*, **24**, 895 (1956).

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Photochemical Studies. LII. The Nitrous Oxide–Ethane System[1]

BY GEORGE A. CASTELLION AND W. ALBERT NOYES, JR.

The ratio of nitrogen formed photochemically at about 1900 Å. in pure nitrous oxide to that formed under identical conditions in a nitrous oxide–ethane mixture is 1.4. This indicates that the primary photochemical process is probably $N_2O = N_2 + O$ and that oxygen atoms react much more rapidly with ethane than with nitrous oxide. Several products are formed including ethylene, butane, carbon monoxide, hydrogen, methane and probably ethanol and acetaldehyde. A complete elucidation of the mechanism is not possible, due to the fact that oxygen atoms seem to react more rapidly with one or more of the products than they do with ethane itself. More ethylene is formed than one would expect from the amount of butane. Due to secondary reactions which must involve the initially formed products it has not been possible to obtain precise information about the reactions of oxygen atoms and of hydroxyl radicals.

Introduction

The absorption spectrum of nitrous oxide probably consists of a continuum extending from about 3000 Å. to shorter wave lengths.[2]

The photochemistry has been studied with radiation directly absorbed by nitrous oxide[3] as well as through mercury sensitization.[4] The reaction products (at least of the unsensitized reaction) are nitrogen, oxygen and nitric oxide. Oxygen atoms must be formed in the primary process.[3b,c,d,e]

One of the great gaps in the interpretation of oxidation reactions of organic molecules lies in the behavior of hydroxyl radicals.[5] The present work was started in the hope that oxygen atoms from nitrous oxide would react with hydrocarbons, such as ethane, to give hydroxyl radicals and that the behavior of the latter could be investigated. This hope has not been realized because oxygen atoms also react rapidly with some of the reaction products. Thus the over-all reaction is complex but certain conclusions about it are possible.

(1) This work was supported in part by Contract with the Office of Naval Research, United States Navy, and with the Office of Air Research, United States Air Force. Further details are available in the Ph.D. Thesis of George Castellion, University of Rochester, 1956. This material may be reproduced by or used in any way by the United States Government.

(2) (a) H. Sponer and L. G. Bonner, *J. Chem. Phys.*, **8**, 33 (1940); (b) A. B. F. Duncan, *ibid.*, **4**, 638 (1936); (c) M. Zelikoff, K. Watanabe and E. Inn, *ibid.*, **21**, 1643 (1953).

(3) (a) J. MacDonald, *J. Chem. Soc.*, 1 (1928); (b) W. A. Noyes, Jr., *J. Chem. Phys.*, **5**, 807 (1937); (c) J. Zabor and W. A. Noyes, Jr., THIS JOURNAL, **62**, 1975 (1940); (d) M. Zelikoff and L. Aschenbrand, *J. Chem. Phys.*, **22**, 1680 (1954); (e) **22**, 1685 (1954).

(4) (a) W. M. Manning and W. A. Noyes, Jr., THIS JOURNAL, **54**, 3907 (1932); (b) R. J. Cvetanović, *J. Chem. Phys.*, **23**, 1203 (1955).

(5) E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, N. Y., 1954, p. 605 *et ff.*

Experimental

An aluminum spark, which gives several intense lines between 1850 and 1990 Å., was used as a source of radiation. The general design of the spark was similar to that developed by Wiig and Kistiakowsky.[6] The transformer has a capacity of 10.4 KVA with a 17600 v. secondary when operated on 115 v. Actually it was operated on 220 v. primary circuit with 0.032 mfd. capacity in parallel with the spark. Air jets played directly on the spark for cooling purposes and to increase steadiness of operation.

The method of focal isolation was used to obtain approximately monochromatic radiation. The change in focal length with wave length of a quartz lens 3 cm. in diameter with a focal length of about 18 cm. was used to isolate radiation of the desired wave length. The center of the lens was blocked off. A camera iris was placed between the focus and the lens and the size of opening adjusted to allow mainly light of wave length below 2000 Å. to pass. The focus was located either by a piece of canary glass (Corning No. 9750) or by a piece of glass "silvered" with mercury. A spectrogram showed that the 1850 Å. line of aluminum did enter the cell.

The portion of the glass vacuum system of the reaction cell and the nitrous oxide and ethane purification, storage and measuring system were kept as free from mercury as possible. High vacuum stopcocks, greased with Apiezon (Type N) grease separated the various parts. Pressures in this part of the system were measured with a click gage.[7] The mercury-free portion of the system was never opened to the rest of the system without at least a Dry Ice bath on a trap connecting the two parts.

Nitrous oxide (Ohio Chemical Company) was distilled between two U-tubes four times with the condensing trap at −183° while the system was continuously open to the mercury diffusion pump. Finally the nitrous oxide was distilled through a trap at −78° to a cold finger attached to a two-liter storage bulb. Only the middle third was retained. The final product showed no impurities at −183° and none not volatile at −112°.

(6) E. O. Wiig and G. B. Kistiakowsky, THIS JOURNAL, **54**, 1806 (1932).

(7) D. F. Smith and N. W. Taylor, *ibid.*, **46**, 1393 (1924).