We wish to thank Mr. Roy Overstreet for assistance with the experimental work.

Summary

The heat capacity of solid and liquid nitrous oxide has been determined over their respective ranges from 14°K. to the boiling point. The melting and boiling points were found to be 182.26 and 184.59°K., respectively.

The heat of fusion is 1563 cal./mole. The heat of vaporization at the boiling point is 3958 cal./mole.

The vapor pressure of solid and liquid nitrous oxide has been measured. The data have been represented by the equations: solid nitrous oxide 148.48 to 182.26°K., $\log_{10} P$ (int. cm. Hg) $= -(1286/T) + 9.13061 - 0.0014038T$; liquid nitrous oxide 182.26 to 185.85°K., $\log_{10} P$ (int. cm. Hg) $= -(893.56/T) + 6.72158$. The experimental data have been used to calculate the molal entropy of the gas at the boiling point. The value found, 47.36 ± 0.1 E. U., is 1.14 entropy units less than the value 48.501 E. U., calculated from spectroscopic data.

This difference is in good agreement with a similar discrepancy found by Clusius. The result indicates that NNO enters its crystal lattice without much discrimination between its ends. The similar case of carbon monoxide led Clayton and Giauque to predict that this situation was to be expected with molecules of low polarity and rather similar ends. The maximum discrepancy for two interchangeable atoms or groups is $R \ln 2 = 1.377$ E. U. The molal entropy of nitrous oxide at 298.1°K. and one atmosphere was found to be 52.581 E. U. (without nuclear spin entropy); the absolute entropy is 56.947 E. U. Each of the above values is based on band spectra data.

BERKELEY, CALIF. RECEIVED MARCH 25, 1935

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 48]

Ammines of Thorium Bromide

BY RALPH C. YOUNG

In a study of some reactions of thorium bromide it was noted that the halide combined with a relatively large amount of ammonia and further that even at room temperature the pressure of ammonia above a solid which had an approximate composition of an octammine was only a few millimeters of mercury. It seemed to be of interest to study the system of thorium bromide and ammonia, at 0° and at 25° up to pressures approximating two atmospheres, and to compare the data with those obtained by Chauvenet for thorium chloride. Chauvenet found[1] the following equilibrium to exist

$$\mathrm{ThCl_4{\cdot}18NH_3} \rightleftharpoons \mathrm{ThCl_4{\cdot}12NH_3} + \mathrm{6NH_3}$$

the decomposition pressure of the higher ammine being 1030.5 mm. at 0.1° and 1630.2 mm. at 8.1°.

The tensimetric method was employed, the apparatus resembling in general that used by Kraus[2] in the study of the vapor pressure of the system calcium and ammonia. It differed, however, in that a ground glass joint was used to connect the bulb containing the thorium bromide to a small glass spiral which led to the manometer and to a calibrated exhaustible tube with a reservoir of mercury by means of which a known amount of ammonia could be removed from the system. The glass spiral allowed the contents of the bulb to be agitated.

The preparation and purification of anhydrous thorium bromide has been previously described.[3] About 11 g. (0.02 mole) was introduced in the bulb, the bottom of which was flat allowing the salt to form a thin layer, and after ammonia had been condensed on the solid, which greatly increased in volume, it was allowed to stand for twenty-four hours. The liquid was then permitted to evaporate, a bath of ethyl chloride being used during the evaporation of the last of the ammonia. During this entire procedure the bulb was attached through the ground glass joint to the rest of the apparatus, a stopcock in which allowed the ammonia to escape. The ethyl chloride was replaced by an ice-bath and ammonia was allowed to issue until the pressure was approximately 1180 mm., a value that preliminary experiments had indicated as being the decomposition pressure

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[1] Chauvenet, *Ann. chim. phys.*, **23**, 275 (1911).

[2] Kraus, THIS JOURNAL, **30**, 661 (1908).

[3] Young, *ibid.*, **56**, 29 (1934).

of an ammine containing 20 moles of ammonia. The amount of ammonia corresponding to 2.74 moles based on the amount of thorium bromide used was next removed. The system was then allowed to come to that state, the pressure being read daily, in which there was a change of less than 0.5 mm. of mercury in twenty-four hours. This required about twelve days. In obtaining subsequent points it was customary to remove approximately 0.5 mole of ammonia. In the region of composition where compound formation was indicated, readings were also taken after the bulb had been warmed so that the pressure had been increased by 20 to 30% above that obtained by approaching equilibrium from below. Equilibrium was obtained in a much shorter time by this method of approaching it from above.

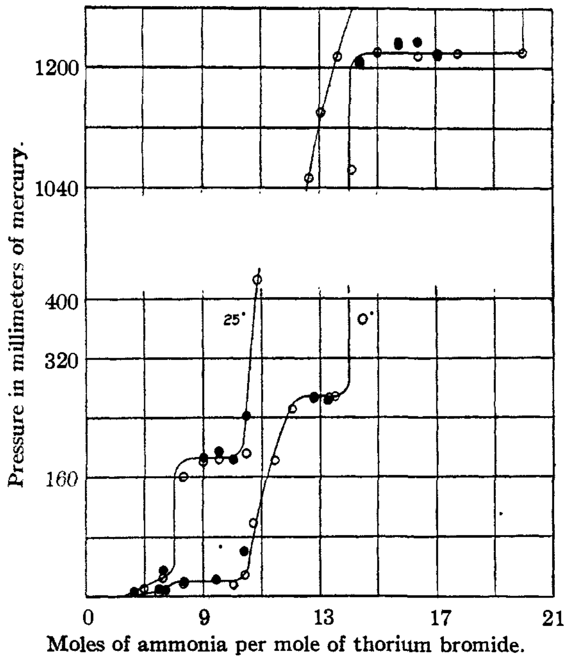

Fig. 1.—Pressure–composition diagram of the system thorium bromide and ammonia at 0° and at 25°. Dark circles represent equilibrium points obtained by approaching equilibrium from "above;" white circles from "below."

By removing the bulb and weighing, it was possible to know the composition of the contents exactly. A thermostat which kept the temperature within 0.01° was used for the work at 25°, the latter temperature being recorded by a standard thermometer. The general procedure was the same as that at 0°. In Table I are given the composition and pressures in mm. of mercury reduced to 0°. Figure 1 is a pressure–composition diagram, the equilibrium pressures obtained by approaching equilibrium from below and above having been used in its construction.

TABLE I

Compn. in moles of ammonia per mole of thorium bromide	Equilibrium pressures at 25° in mm. of mercury approached from		Compn. in moles of ammonia per mole of thorium bromide	Equilibrium pressures at 0° in mm. of mercury approached from	
	Below	Above		Below	Above
13.62	1177.4		17.78	1182.5	
13.12	1102.5		17.09	1178.2	1181.9
12.72	1013.9		16.41	1178.3	1198.1
12.31	913.3		15.75	1192.5	1197.4
11.78	824.8		15.00	1182.0	
11.35	690.4		14.40	1169.9	1168.7
10.91	426.5		14.15	1024.9	
10.47	192.6	242.6	14.05	700.5	
9.99	183.8	183.8	13.56	268.7	
9.53	184.4	196.1	13.36	268.6	265.7
8.99	182.5	187.8	12.80	268.5	267.7
8.30	162.1		12.08	252.5	
7.61	25.2	35.1	11.41	183.9	
7.40	18.6		10.72	99.9	
6.98	11.7		10.44	29.3	62.6
6.93		5.0	10.06	15.3	24.0
6.61	3.9	3.8	9.48	23.9	23.9
			8.36	18.9	19.9
			7.82	9.2	9.3
			7.54	7.3	9.3
			6.55	< 0.2	< 0.2

The data obtained at 0° indicate an equilibrium: $ThBr_4 \cdot 20NH_3 \rightleftharpoons ThBr_4 \cdot 14NH_3 + 6NH_3$. The point representing $ThBr_4 \cdot 20NH_3$ was obtained in a separate experiment at 0° by allowing ammonia to escape against a pressure of 1180 mm. After ammonia had ceased to be evolved, the resulting solid was analyzed; 19.96 moles of ammonia were found per mole of thorium bromide. The compound $ThBr_4 \cdot 14NH_3$ was formed only at the lower temperature. Below a composition corresponding to 12 moles of ammonia, the curves obtained at both temperatures show similar trends, the compound $ThBr_4 \cdot 10NH_3$ being formed at each temperature. The sharp breaks at a composition $ThBr_4 \cdot 8NH_3$ at both temperatures indicate that such a compound may be formed although the slopes of the curves below this composition do not justify making this view positive. Below are given the ammines that were found to be formed and their approximate decomposition pressures as determined graphically from the pressure–composition diagram: at 0°, $ThBr_4 \cdot 20NH_3$, 1180 mm., $ThBr_4 \cdot 14NH_3$, 268 mm.; $ThBr_4 \cdot 10NH_3$, 22 mm.; at 25°, $ThBr_4 \cdot 10NH_3$, 184 mm.

Summary

Tensimetric measurements of the system thorium bromide and ammonia, in mm. of mercury at 0° and at pressures up to 1190 mm. indicate that the equilibrium $ThBr_4 \cdot 20NH_3 \rightleftarrows ThBr_4 \cdot 14NH_3 + 6NH_3$, exists and that the pressure of the higher ammine is 1180 mm. The decomposition pressure of $ThBr_4 \cdot 14NH_3$ is 268 mm. and that of $ThBr_4 \cdot 10NH_3$ is 22 mm. At 25° the decomposition pressure of $ThBr_4 \cdot 10NH_3$ is 184 mm.

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

The Halochromism of Ketones. II[1]

BY LEIGH C. ANDERSON AND C. M. GOODING

Absorption spectra data which have been reported from this Laboratory[2] show that although benzophenone dissolves in ether to give colorless and in sulfuric acid to give colored solutions, the same absorption bands are obtained in each case. The band associated with the carbonyl group was found to be much more intense in the acid solution and the yellow color of the solution was caused by the widening of the base of this band until it extended into the visible region. Since the carbonyl band was intensified and no new bands appeared, we concluded that the colored solute had been produced through the reactivity of the carbonyl group. The fact that the same bands appear in both the colorless and colored solutions is evidence that this is a case of true halochromism as originally defined by Baeyer.[3] This paper presents additional data which constitute conclusive evidence: first, that in the ketones we have studied the reactivity of the carbonyl group alone is responsible for the color in those cases where we find true halochromism; second, that the addition compounds produced with reagents like sulfuric acid and stannic chloride in the presence of hydrogen chloride do not involve the loss of the carbonyl group by addition to the carbonyl double bond; third, that some ketones give a colored solution in sulfuric acid and in addition to the enhancement of the carbonyl band, new bands are produced which we believe to be due to quinoidation, thereby showing two effects which can contribute to the formation of color. In the case of the ketone chlorides, the absorption spectra of their colored solutions with stannic chloride or sulfuric acid are entirely different from those of the corresponding ethylene dichloride solutions. We believe that the color in these solutions is due to quinoidation and not to halochromism. These cases will be discussed later in the paper.

Comparisons of the absorption spectra of sulfuric acid solutions of 4-phenyl- and 4,4′-diphenylbenzophenone with corresponding ethylene dichloride solutions show that these are cases of true halochromism (Figs. 1 and 2). Solutions of these compounds, as well as benzophenone (Fig. 3), in mixtures of ethylene dichloride and stannic chloride give absorption curves which are very similar to those obtained for the corresponding ketone in sulfuric acid. The principal differences noted are that with stannic chloride the band having a maximum in the carbonyl region is displaced toward longer wave lengths (Table I) and is not quite as intense. In these cases, therefore, true halochromism is produced by either stannic chloride or sulfuric acid.

In all ketones that have been studied the absorption spectra of their colored solutions, whether the color is caused by sulfuric acid or stannic chloride, show marked enhancement of the absorption band which occurs in the carbonyl region of the spectrum and a shift of this band toward longer wave lengths. In order to see whether these changes were due to the rearrangement of an aromatic ring with formation of a new chromophore as, for example, the quinonoid nucleus, solutions of a number of aliphatic ketones were separately prepared in ethylene dichloride and sulfuric acid and the absorption spectra determined. The data show that the absorption

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[1] The material in this paper comprises a portion of a thesis presented by C. M. Gooding to the Graduate School of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1934.

[2] Anderson, THIS JOURNAL, 55, 2094 (1933).

[3] In the discussion that follows we shall define as examples of true halochromism those solutions where the absorption spectra show that the color is produced through enhancement of the carbonyl absorption band without the production of new bands.