The technique of such radioactive investigations has been improved with a view to giving greater constancy of experimental conditions.

The reaction has been shown to be one of the first order, in agreement with a theory developed, whereby the velocity of formation of hydrochloric acid should be proportional to the energy employed and to the chlorine concentration, inversely proportional to the oxygen concentration.

The analogy between the photochemical reaction and the reaction studied has been emphasized and the bearing of the experimental results on the problem of the photochemical and Röntgen ray reactions has been discussed.

The experimental work of the preceding paper was carried out in the Koenigliche Technische Hochschule zu Hannover. To Professor Max Bodenstein, at whose suggestion the research was undertaken, the author wishes to express his deep indebtedness, as well for the generous advice and kindly interest as for the many details of experimental technique which made the work possible.

PRINCETON, N. J.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF COLUMBIA UNIVERSITY, No. 242.]

THE DENSITIES AND DEGREES OF DISSOCIATION OF THE SATURATED VAPORS OF THE AMMONIUM HALIDES, AND THE RELATED THERMAL DATA.

BY ALEXANDER SMITH AND ROBERT H. LOMBARD.

Received November 13, 1914.

In the case of solids undergoing thermal dissociation the data which possess the greatest chemical significance are those relating to the *saturated* vapors, in which the components of the vapor are in equilibrium with each other and with the solid. Yet, in regard to the great majority of even the most familiar of such substances, as, for example, phosphorus pentachloride and the ammonium halides, definite, quantitative information in this direction has been absolutely lacking. The vapor (dissociation) pressures have been determined, sometimes repeatedly, but for the most part the densities of the unsaturated vapors (namely, at atmospheric pressure) have alone been measured. Of the very few systems involving saturated vapors which have been subjected to exact study, those of the sulfides of ammonium (Isambert and others) and calomel (Smith and Menzies[1]) may be mentioned.

As regards the ammonium halides, their dissociation pressures had not been determined with the requisite degree of accuracy. To secure consistent values for use in the present investigation, these pressures have

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[1] THIS JOURNAL, 32, 1541 (1910); *Z. physik. Chem.*, 76, 251.

been redetermined by Smith and Calvert,[1] using a thermometer identical with that employed in the present work, a bath similarly jacketted but smaller, and the same samples of the ammonium halides.

As regards the vapor densities of the ammonium halides, it is commonly assumed by chemists that the dissociation is complete, and that the densities correspond with this assumption. Only the comparatively easily measured densities of the *unsaturated* vapors have been determined, however, and the results of the present work show that this assumption is very far from being correct. In the present research the densities of the saturated vapors of the ammonium halides have been investigated. The results, together with the corresponding dissociation pressures of Smith and Calvert, have made it possible now to ascertain by calculation, and to give for these substances the values of the degrees of dissociation, the dissociation constants, the partial pressures of the dissociation products, the heats of dissociation, and the latent heats of vaporization.

Previous Determinations of the Vapor Densities.—In Table I the results of previous determinations are given. The methods used (Col. 2) are indicated thus: D. (Dumas), H. (Hofmann), V. M. (V. Meyer). The temperature (Col. 3) is the value assumed by the observer. The heating was effected by the vapor of the substance indicated in Col. 4, boiling (save in one instance) under the existing atmospheric pressure. The actual temperatures obtainable with the vapors of these substances vary considerably with the existing atmospheric pressure, yet Ramsay and Young are the only observers who corrected the boiling point of the bath liquid on this account. The actual temperatures obtainable vary still more (5° to 8° or more) according as much, little, or no jacketing is used. None of the observers mention jacketing and presumably they used none. The recorded temperatures must therefore be, for the most part, considerably higher than those actually attained.

For the purpose of comparison, the observed vapor densities (Col. 5), originally given on such scales as air = 1, hydrogen = 1, or mols per liter, have all been re-calculated to weights of 1 cc. at 0° and 760 mm. The calculated values for the density, assuming no dissociation (δ) are given for each substance after its name. The per cent. dissociated (Col. 6) has been calculated from the values of δ, and of Δ (Col. 5).

Discussion of Previous Determinations.[2]—Where the Dumas method is used, the temperatures, for the reason already given, are only approximate. Then, at 357° the dissociation pressure of ammonium chloride is about 1150 mm., so that, at 760 mm. in the open Dumas bulb at this temperature, the vapor has reached a highly unsaturated condition,

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[1] This Journal, **36**, 1364 (1914).

[2] For a summary of previous work see Abegg, *Handb. anorg. Chem.*, Band III, 252, 265, 271.

TABLE I.—PREVIOUS DETERMINATIONS.

Observer.	Date and method.	Temp.	Method of heating.	Vapor dens. obsd. Δ.	Per cent. dissocd.
	AMMONIUM CHLORIDE (δ = 0.00238).				
Deville and Troost[1]	1859	350°	Mercury	0.00131	82
	D.	1040°	Zinc	0.00129	85
Ramsay and Young[2]	1887	280°	Bromo-naphtha-	0.00133	79
	H.		lene, 752.3 mm.	0.00137	74
Pullinger and Gardner[3]	1891	Mod. red		...	...
	V. M.	heat		0.00120	98
	V. M.	448°	Sulfur	0.00127	87
	V. M.	448°	Sulfur	0.00121	97
	V. M.	360°	Anthracene	0.00122	95
	V. M.	300°	α-Naphthylamine	0.00127	87
	V. M.	300°	α-Naphthylamine	0.00127	87
	V. M.	300°	α-Naphthylamine	0.00127	87
Neuberg[4]	1891	254°	Diphenyl	0.00146	63
	V. M. (25 mm.)	254°	Diphenyl	0.00155	55
Baker[5]	1894	350°	Mercury	0.00119	100
	D.	350°	Mercury	0.00125	91
Gutmann[6]	1898	380°	Anthraquinone	0.00122	95
	V. M.				
Johnson and Abegg[7] (see below)	1908	323°	Air bath	0.00120	98
	AMMONIUM BROMIDE (δ = 0.00438).				
Deville and Troost[8]	1863	440°	Sulfur	0.00216	100
	D.	860°	Cadmium	0.00221	98
	AMMONIUM IODIDE (δ = 0.00648).				
Deville and Troost[8]	1863	440°	Sulfur	0.00335	94
	D.	860°	Cadmium	0.00360	80

and dissociation has been favored. The fact, therefore, that values indicating 91–100% dissociation are thus obtained, does not prove that the vapor when saturated is dissociated to this extent. Similarly, in the case of ammonium bromide, a dissociation pressure of 760 mm. is reached at 394.6°, and at 445° the pressure is over 2 atmos. With ammonium iodide 760 mm. pressure is reached at 405°, and at 445° the pressure is about 2 atmos. These vapors were therefore also under greatly reduced

[1] Deville and Troost, *Ann. chim. phys.*, [3] **58**, 257 (1860); *Compt. rend.*, **49**, 242 (1859).

[2] Ramsay and Young, *Phil. Trans.*, **177**, 99 (1886).

[3] Pullinger and Gardner, *Proc. Chem. Soc.*, **7**, 2 (1891).

[4] Neuberg, *Ber.*, **24**, 2543 (1891).

[5] Baker, *J. Chem. Soc.*, **65**, 615 (1894).

[6] Gutmann, *Ann.*, **299**, 282 (1898).

Three other observations with progressive drying of the salt (intended to delay dissociation) gave, as might be expected, higher and higher values for the density. The percentages dissociated were then 91, 79, and 61, respectively.

[7] F. M. G. Johnson, *Z. physik. Chem.*, **61**, 462 (1908).

[8] Deville and Troost, *Compt. rend.*, **56**, 895 (1863).

pressure, and the observations afford no information in regard to their degree of dissociation when saturated.

Where the Victor Meyer method was used there were two possibilities. In the first four observations of Pullinger and Gardner, in the observations of Neuberg (made under 25 mm. pressure) and in those of Gutmann, the temperature was such that the substance exercised a dissociation pressure greatly exceeding that finally existing in the apparatus. In these instances, therefore, the vapor became highly unsaturated and dissociation was favored. In the last three observations of P. and G. the dissociation pressure at 300° (252.5 mm.) was not sufficient to permit rapid vaporization and free displacement of the air (at 760 mm.). Here, therefore, the vaporization would proceed largely by diffusion of the gases into the air contained in the apparatus. Naturally, dissociation was promoted by this process of diffusion, and the displacement of air could stop only when dissociation was complete. Strictly speaking, the same thing is true of all determinations by the V. Meyer method. Every substance capable of dissociating, no matter how slightly, would be bound by this method to yield a value for the density corresponding to complete dissociation. If these observations had shown 100% dissociation, they would only have proved that the laws of equilibrium were at work, and would have given no new information about the properties of ammonium chloride.[1] Since the P. and G. determinations, for example, gave only 87% dissociation, what they did prove was that the method was inaccurate (densities 7% too low) under these conditions. The results by these two methods, apart from the obvious crudeness of the measurements, are therefore valueless for a study of the state of equilibrium in the system, because the conditions are wholly indefinite.

In the method used by F. M. G. Johnson and Abegg, the solid salt was contained in the smaller of two connected bulbs, both of which were completely evacuated. The bulbs were heated in an air bath, the larger bulb was then sealed off, and its volume and content of ammonium chloride determined. This method would have given the density of the saturated vapor, if both bulbs had been at the same temperature. But that containing the solid was intentionally kept at a temperature about 22° below that of the bulb containing the vapor. Hence, this result also applies to the unsaturated vapor, and no information about the density of the saturated vapor is obtainable from the data.

Finally, the observations of Ramsay and Young were made by the Hofmann method. They made nine determinations at 280° with pres-

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[1] The fact that the facile V. Meyer method is applicable indeed to the detection of the existence of dissociation (if this has not been detected otherwise already), but is valueless for the study of the extent of such dissociation, seems to have been too generally overlooked.

sures varying from 127.3 mm. to 134.9 mm. The values quoted in the table are those obtained at these two pressures, respectively. Now the dissociation pressure at 280° is 135.0 mm., so that the last observation does yield a value for the saturated vapor. Furthermore, the observations are fairly consistent, and clearly are not in error to the extent of 20%. This observation alone, therefore, of all the published results, affords rather definite information about the density of ammonium chloride vapor in the saturated condition, and indicates that the vapor is far from being completely dissociated.

An examination of the degrees of dissociation, showing that nearly all approach 100%, within the rather wide limits of error of the methods, explains the fact that chemists have very generally accepted the erroneous conclusion that the ammonium halides are completely dissociated, and have used this incorrect assumption, for example, in calculating the heats of vaporization[1] to form saturated vapor.

Method and Apparatus.

The Vapor Density Bulbs.[2]—The vapor densities were determined in bulbs of the type shown in Fig. 1. A weighed amount of the substance was placed in the small bulb, A, which was then sealed on to the large bulb, B, at C. The whole was then evacuated to less than 0.01 mm. on a mercury pump, and sealed off from the pump at E. The evacuated bulb was next wired to a long iron rod, and then plunged into a well stirred bath having the desired temperature. Local cooling and cracking of the

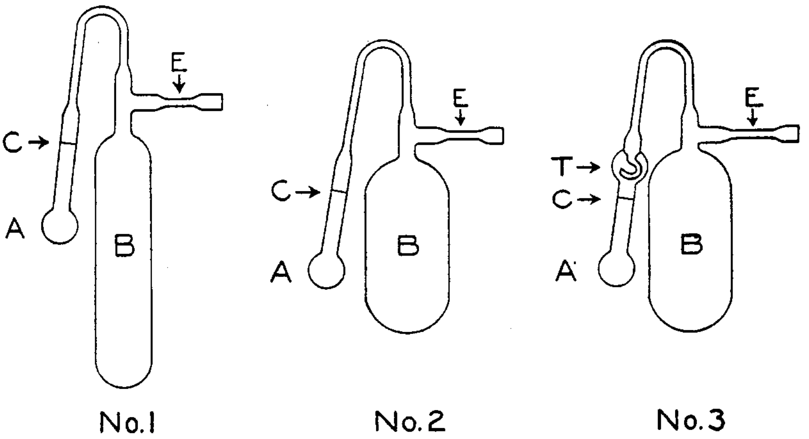

Fig. 1.—Vapor density bulbs.

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[1] F. M. G. Johnson, *Z. physik. Chem.*, **65**, 38 (1908–9); Horstmann, *Ber.*, **2**, 137 (1869).

[2] Essentially the same method has been previously used by Smith and Menzies (THIS JOURNAL, **32**, 1550 (1910)) for determining the density of saturated calomel vapor.

bulb by contact with the cold iron rod were prevented by wrapping the latter with several layers of asbestos paper. When equilibrium had been reached, the large and small bulbs were sealed and separated by raising the bulb until the arched capillary just appeared above the surface of the bath and applying the blow pipe flame to it. The amount of substance which had vaporized into the large bulb was given by the difference between the amount remaining in the small bulb. and that originally put into it. The volume of the large bulb, at the temperature at which the vapor density was measured, was determined by weighing it, first evacuated and then full of water of known temperature, and finally correcting for the expansion of the glass by using the coefficient of cubical expansion, 0.000031.

Bulb No. 1 was the first type tried, and was used for determining the vapor density of ammonium chloride. The results obtained with it had an accuracy of only ±2–3%. Hence, in the case of ammonium bromide, the vapor density of which was next measured, a more compact form of bulb, No. 2, was used, it being thought that there would be less possibility of a difference in temperature between the extreme parts of the bulb. This change, however, did not very much increase the uniformity of the results. With ammonium iodide, Bulb No. 2, gave results so erratic as to be of almost no value. The particles of the salt had a tendency to jump about, and the irregularities were in part due to the carrying over into the large bulb of solid particles of the salt by the ammonium iodide vapor when vaporization first began. To minimize this possibility, Bulb No. 3, which contained a trap T placed between the large and small bulbs, was designed. Glass wool inserted at the same place would also serve the purpose, but would necessitate determining the amount of substance in the large bulb by analysis. The results obtained with ammonium iodide with this trap were very much less erratic than without it. It may be said here that, to determine vapor densities of solids with moderate accuracy, extreme care must be exercised. Even with such care, an erratic and unaccountable result is occasionally obtained, as the results given later will show.

The Bath.—The bath was a pressed steel "oyster bucket," 18 cm. in diameter and 23 cm. deep, filled with a 50% mixture of fused sodium and potassium nitrates. Its sides were lagged by a two-inch thickness of shredded asbestos pipe-covering, and the top was covered by a sheet of $^1/_2$" asbestos board with openings in it for the vapor-density bulb, stirrers, and thermometer. The temperature of the bath, which was heated by a Vulcan gas burner, was kept constant within ±0.2–0.3° by the constant manipulation of a screw clamp on the gas supply tube. Two stirrers of the type described by Smith and Menzies[1] were used, each rapidly

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[1] Smith and Menzies, This Journal, **32**, 1421 (1910).

driven by an electric motor. The vapor-density bulb was in the center of the bath, the stirrers on diameterically opposite sides of the bulb, and the thermometer directly behind the bulb.

Measurement of the Temperature.—The temperature of the bath was measured by a fused quartz, platinum resistance thermometer of the Heraeus type[1] without compensating leads. The resistance of the thermometer was measured by a dial Wheatstone bridge (5 dials), and a D'Arsonval galvanometer, both manufactured by the Leeds & Northrup Co.

The thermometer was calibrated, by the method recommended by Waidner and Burgess,[2] at the melting point of ice, and at the boiling points of water and of sulfur (444.7°). The steam point was determined in a glass tube 5 cm. in diameter, and 46 cm. long, heated by a Vulcan gas burner, and lagged by a conical asbestos jacket 2 cm. thick at the top, 6 cm. thick at the bottom, and 32 cm. high. The depth of water in the tube was about 10–12 cm., the bottom of the thermometer was about 4 cm. above the surface of the water, and glass beads were used to prevent bumping. An aluminum radiation shield, of the type recommended by Waidner and Burgess, was used. The sulfur boiling point tube was of brass, 4.7 cm. in diameter, and 47 cm. long. A depth of 10–12 cm. of sulfur were used, and the end of the thermometer was placed about 4 cm. above the surface of the boiling sulfur. Two mica windows at the top of the tube made it possible to observe the point of condensation of the sulfur vapor. This was kept about half way between the top of the tube and the top of the jacket. The asbestos insulating jacket and aluminum radiation shield described above were used.

In order to test the accuracy of the calibration, the boiling point of napthalene was determined several times. The results were usually about 0.2° higher than the value given by Waidner and Burgess.[3] This is probably as good a result as could be expected without using compensating leads. The constants of the thermometer increased gradually during the investigation, but the change was followed closely, and new values were adopted as soon as the difference became great enough to cause an error of as much as 0.1–0.2° in the temperature measurement. The accuracy and constancy of the temperature of the bath is estimated to have been about ±0.2–0.3°.

Ammonium Chloride.

The Data.—The ammonium chloride was recrystallized once from distilled water, dried at 110°, finely ground, and kept in a desiccator over

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[1] Waidner and Burgess, "The Measurement of High Temperatures" (Wiley, 3rd ed.) 205.

[2] Waidner and Burgess, *Bull. Bur. Standards*, **6**, 150 (1910).

[3] *Ibid.*, **7**, 4 (1910).

phosphorus pentoxide. The vapor density was determined at ten-degree intervals from 280° to 330°, the first temperature being that at which the vapor density becomes large enough to be accurately measured, and the second that at which the dissociation pressure becomes almost equal to atmospheric pressure. The pressure of the ammonium chloride vapor in the bulb must not be allowed to become greater than atmospheric because, if it did, the capillary tube between the large and small bulbs would blow out instead of collapsing, when the two bulbs were sealed apart.

In order to obtain a final, mean result which was sufficiently accurate, it was necessary to make a number of determinations at each temperature. In order that the degree of accuracy of the measurements may be clearly seen, the results of all the determinations made are given (Table II). The volumes (Col. 3 of the table) are at the temperature at which the vapor density determination was made. The column entitled "deviation from mean" contains the difference between the average value of the vapor density and the individual measurements. Occasionally a vapor density would be obtained which was so far from the average value that we have felt justified in rejecting it. Such values are printed in italics. The precision of the average value at each temperature was obtained by averaging the "deviations from the mean," and then dividing the average by the square root of the number of observations. It will be seen that the final results usually have an accuracy of about ±2–3%.

TABLE II.—DENSITIES OF NH_4Cl VAPOR (SATURATED)—DATA.

Temp.	G. NH_4Cl in large bulb.	Vol. (cc.) of large bulb.	Vapor dens. g. per cc.	Deviation from mean.	Minutes in bath.
280°	0.0081	54.71	0.000148	+13	15
	0.0068	61.80	0.000110	—25	15
	0.0088	64.65	0.000136	+ 1	15
	0.0073	59.39	0.000123	—12	21
	0.0084	55.46	0.000151	+16	20
	0.0099	66.21	0.000150	+15	20
	0.0075	53.16	0.000141	+ 6	20
	0.0079	61.21	0.000129	— 6	20
	0.0076	61.39	0.000124	—11	20
Average vapor density.............			0.000135	±4, or ±2.9%	
290°	0.0098	64.67	0.000152	—17	15
	0.0102	65.48	0.000156	—13	15
	0.0095	61.05	0.000156	—13	15
	0.0110	63.15	0.000174	+ 6	15
	0.0103	60.87	0.000169	00	20
	0.0110	63.97	0.000173	+ 4	20
	0.0132	67.27	0.000196	+27	20
	0.0110	66.05	0.000167	— 2	20
	0.0116	67.21	0.000177	+ 8	20
	0.0111	64.66	0.000172	+ 3	20
Average vapor density............			0.000169	±3, or ±1.8%	

TABLE II.—DENSITIES OF NH_4Cl VAPOR (SATURATED)—DATA (*continued*).

Temp.	G. NH_4Cl in large bulb.	Vol. (cc.) of large bulb.	Vapor dens. g. per cc.	Deviation from mean.	Minutes in bath.
300°	0.0160	65.09	0.000246	+16	11
	0.0153	63.43	0.000242	+12	11
	0.0146	64.75	0.000226	— 6	12
	0.0122	59.83	0.000204	—26	13
	0.0113	65.84	*0.000172*	..	13
	0.0167	74.23	0.000225	— 5	10
	0.0150	62.55	0.000240	+10	13
	Average vapor density.............		0.000230	±5, or 2.2%	
310°	0.0229	71.19	0.000322	+15	13
	0.0161	62.70	*0.000257*	..	10
	0.0217	70.44	0.000308	+ 1	12
	0.0203	62.45	0.000325	+18	11
	0.0169	62.09	*0.000272*	..	13
	0.0186	59.66	0.000312	+ 5	12
	0.0185	63.68	0.000291	—16	12
	0.0182	56.26	0.000324	+17	13
	0.0194	66.37	0.000292	—15	12
	0.0166	54.40	0.000305	— 2	11
	0.0200	70.93	0.000282	—25	12
	Average vapor density.............		0.000307	±4, or ±1.3%	
320°	0.0255	61.94	0.000413	+ 7	11
	0.0248	60.51	0.000410	+ 4	12
	0.0282	71.66	0.000394	—12	12
	0.0274	67.33	0.000407	+ 1	11
	Average vapor density.............		0.000406	±3, or ±0.7%	
330°	0.0330	66.93	0.000493	—38	20
	0.0330	70.07	*0.000471*	..	15
	0.0387	68.77	0.000563	+32	18
	0.0424	74.63	0.000568	+37	17
	0.0321	65.25	0.000492	—39	17
	0.0291	63.87	*0.000456*	..	12
	0.0348	63.50	0.000548	+17	11
	0.0302	56.66	0.000533	+ 2	13
	0.0345	62.65	0.000551	+20	13
	0.0366	68.16	0.000537	+ 6	11
	0.0297	66.64	*0.000446*	..	11
	0.0343	66.68	0.000514	—17	11
	0.0271	53.75	0.000504	—27	12
	0.0323	59.94	0.000539	+ 8	11
	Average vapor density.............		0.000531	±6, or ±1.3%	

In Table III are summarized the vapor density results in the form in which they were used in the calculations. The vapor pressures given in this table are those determined by Smith and Calvert.[1] The method for, and the purpose of determining the "interpolated" values given in the fifth column will be explained when the calculation of the dissociation

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[1] Smith and Calvert, THIS JOURNAL, **36**, 1373 (1914).

constants is discussed. The densities, δ_m, which the vapor would have if it were undissociated (expressed in mols per liter), and yet gave the measured dissociation pressures were calculated by the formula

$$\delta_m = \frac{1}{22.4} \cdot \frac{273}{T} \cdot \frac{P}{760}.$$

These values are given in the column headed, "undissociated.". In the column headed, "completely dissociated," are the densities which the vapor would have if it were wholly dissociated and gave the measured dissociation pressure. These values are just one-half of the corresponding "undissociated" vapor densities.

In order to show the relation between the measured vapor density and the density of the vapor if it were completely dissociated, and if undissociated, these values have been plotted in Fig. 2. The fact that the experimentally determined values lie between the "undissociated" and the "completely dissociated" densities, shows conclusively that saturated ammonium chloride vapor is not completely dissociated. If it were completely dissociated, the measured values would lie, at least approximately, on the "completely dissociated" curve.

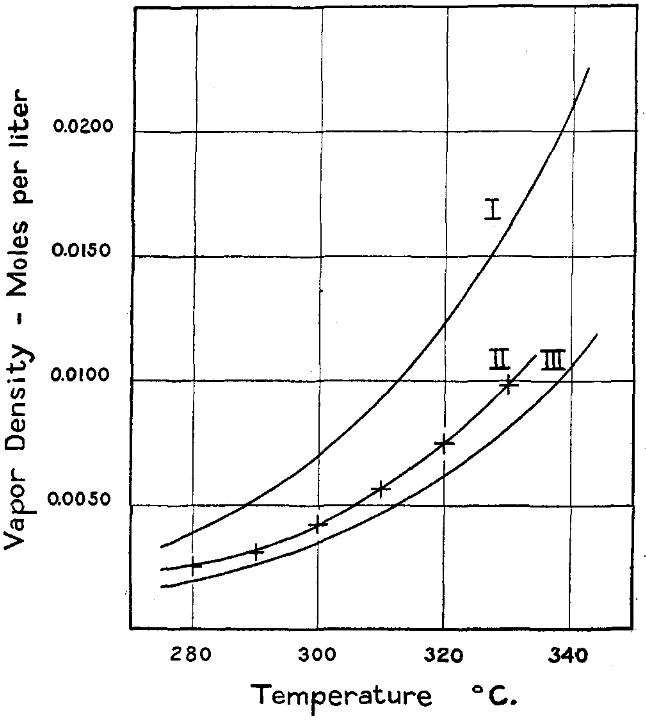

Fig. 2.—Vapor densities of ammonium chloride: Curve I—Undissociated (calculated); Curve II—Observed; Curve III—Completely dissociated (calculated).

Table III.—Densities of NH_4Cl Vapor (Saturated)—Summary.

		Vapor density.					
Temp.		Observed.		Calculated.			
C.	Abs.	G. per cc.	Mols per l. Δm.	Interpol. Mols per l. Δmi.	Undissoc. Mols per l. δm.	Compl. dissoc. Mols per l.	Total press. Mm.
280	553	0.000135	0.00252	0.00235	0.00392	0.00196	135.0
290	563	0.000169	0.00316	0.00318	0.00528	0.00264	185.3
300	573	0.000230	0.00430	0.00428	0.00707	0.00354	252.5
310	583	0.000307	0.00573	0.00571	0.00939	0.00470	341.3
320	593	0.000406	0.00759	0.00757	0.01239	0.00620	458.1
330	603	0.000531	0.00993	0.00998	0.01624	0.00812	610.6
340	613	......	.....	.....	0.02114	0.01067	808.2

The Degrees of Dissociation.—In calculating the degree of dissociation of ammonium chloride vapor, it was assumed that the equilibrium present in the vapor is represented by the equation

$$NH_4Cl \text{ (gas)} \rightleftarrows NH_3 + HCl,$$

and that the gases follow the laws of perfect gases. If so, the degree of dissociation α is given by the formula

$$\alpha = \frac{\delta_m - \Delta_m}{\Delta_m}.$$

In this formula, δ_m, and Δ_m, are respectively the "undissociated," and the observed molar vapor densities (Table III). The degrees of dissociation thus calculated are given in Table IV (Col. 2).

Table IV.—NH_4Cl—Degrees of Dissociation.

Temp. C.	Percentage dissociation.		Deviation of α from straight line.		% error in α. (Calcd.)
	Obsd.	Interpol.	Actual.	%.	
280	55.5	66.8	...	...	...
290	67.1	66.0	+1.1	+1.7	±4.5
300	64.2	65.2	—1.0	—1.5	±5.5
310	63.8	64.4	—0.6	—0.93	±3.5
320	63.3	63.6	—0.3	—0.47	±1.8
330	63.6	62.8	+0.8	+1.3	±3.3

Inasmuch as the measured results are somewhat irregular,[1] the relation between the degree of dissociation and the temperature is seen best from the graphic representation of the results given by Fig. 3, Curve I. This curve shows that between 280° and 330°, saturated ammonium chloride vapor is 67–63% dissociated; and that, although the degree of dissociation is very nearly constant, it apparently decreases slightly and, as nearly

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[1] The irregularities in our results might be attributed to adsorption of the vapors by the surface of the bulbs, or might be connected with the existence of transition points for ammonium chloride and bromide at 159° and 109°, respectively (Wallace, *Chem. Zentr.*, 81, 727 (1910)). In view of the fact that our measurements were made at relatively high temperatures, usually 300° and above, these explanations must be discarded.

as can be judged, linearly with the temperature. In view of the irregularity of the measured values of α, we shall use hereafter in any calculations which involve α, values interpolated from Curve I in Fig. 3. These values are given in the third column of Table IV.

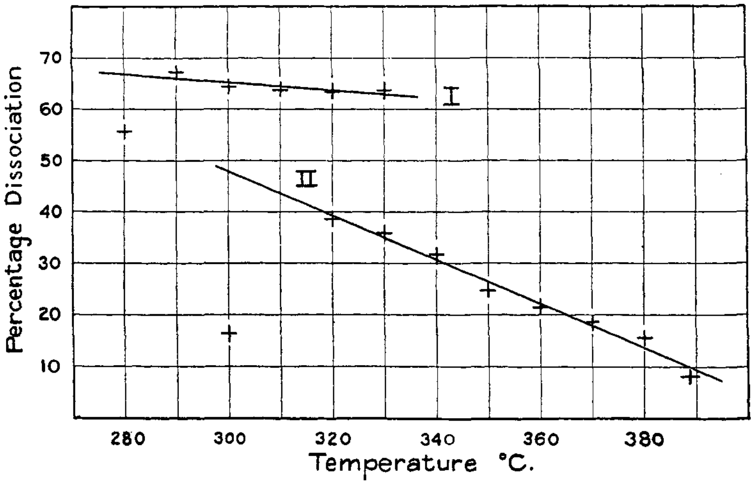

Fig. 3.—Percentage dissociation of saturated ammonium chloride and bromide vapors: Curve I—Ammonium chloride; Curve II—Ammonium bromide.

The irregularity of α is not, however, more than might be expected, because the relation between α and Δ_m is of such a nature than an error in Δ_m is multiplied several times in α. To illustrate this, we give the errors in the values of α which might be expected, and compare these with the actual errors. The error in α which would be caused by an error in Δ_m may be calculated as follows: If $d\Delta_m$ is the error in Δ_m, the error in α, will be,

$$\frac{\partial\alpha}{\partial\Delta_m} d\Delta_m = \frac{\partial}{\partial\Delta_m}\left[\frac{\delta_m - \Delta_m}{\Delta_m}\right] d\Delta_m = -\frac{\delta_m}{\Delta^2_m} d\Delta_m,$$

and the percentage error in α will be,

$$\frac{\partial\alpha/\partial\Delta_m\, d\Delta_m}{\alpha} = \frac{-\delta_m/\Delta^2_m\, d\Delta_m}{\delta_m - \Delta_m/\Delta_m} = -\frac{\delta_m}{\delta_m - \Delta_m}\frac{d\Delta_m}{\Delta_m}$$

But $\frac{d\Delta_m}{\Delta_m}$ is the percentage error in Δ_m. Therefore,

$$(\% \text{ error in } \alpha) = -(\% \text{ error in } \Delta_m)\frac{\delta_m}{\delta_m - \Delta_m}.$$

In the sixth column of Table IV are given the percentage errors in α, calculated by this equation, which would result from the percentage errors in Δ_m which are given in Table II. The actual errors in α, *i. e.*, the deviation of the observed values of α from the average values, are given by the difference between the observed values of α and the value interpolated from the straight line. These differences are given in the fourth column of Table IV, and the fifth column contains these differences expressed as percentages of the observed value of α. Comparison of Columns 5 and 6 shows that the percentage deviation of α from a straight line is much less than might be expected to result from the errors in Δ_m. Therefore, a straight line represents the relation between the degree of dissociation and the temperature within the experimental error of the observations. The value of α at 280°, which is obviously too low, was not considered when the best representative straight line was drawn.

The fact that the vapor density increases and that the degree of dissociation *diminishes* with rising temperature, is at first sight anomalous. It must be remembered, however, that the results are not obtained with constant total pressure (as in the Dumas and V. Meyer methods) but with rapidly rising total pressure (vapor pressure). Thus between 290° and 330° the partial pressure of free ammonia (or HCl, see Table XV) rises from 73.7 mm. to 234.5 mm., while the total pressure increases from 185.3 mm. to 610.6 mm., or almost in the same proportion. If we calculate the change in partial pressure of free ammonia which would occur between the same limits of temperature if the total pressure were kept constantly at 185.3 mm., we find that this partial pressure would rise from 73.7 to 83.6 mm. Thus at a constant pressure of 185.3 mm., the density would diminish and the degree of dissociation would *increase* from 66% to 82%.

The Latent Heat of Vaporization.—Several determinations of the latent heat of vaporization of ammonium chloride have previously been attempted, but none of them gives the true latent heat of vaporization, namely, the heat-change involved when ammonium chloride vaporizes in equilibrium with the products of its vaporization. These previous determinations are summarized in Table V.

TABLE V.—NH_4Cl—LATENT HEATS OF VAPORIZATION (Kg. cal. per mol).

Observer.	Date.	Temp.	L. Kg. cal.
Marignac[1]	1869	420–500	37.8
Horstmann[2]	1869	340	37.4
Horstmann	1869	300	39.5
Horstmann	1869	260	41.4
Horstmann	1869	220	43.9
F. M. G. Johnson[3]	1909	245–345	37.8

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[1] Marignac, Liebig's *Ann.*, **149,** 351 (1869).

[2] Horstmann, *Ber.*, **2,** 137 (1869).

[3] F. M. G. Johnson, *Z. physik. Chem.*, **65,** 38 (1908–9); Favre and Silberman (*Ann. chim. phys.*, [3] **37,** 422 (1853)), and J. Thomsen (*Thermochem. Untersuch.*, Leipzig, Band II, 73–75 (1889)) have found the values 39.7 and 41.3, respectively, for the heat of reaction between ammonia and hydrogen chloride

Horstmann and F. M. G. Johnson calculated the latent heat of vaporization from their respective vapor pressure data, the former using the Clausius-Clapeyron equation, and the latter the relation, $d \ln p/dT = Q/2RT^2$. Both, however, made the incorrect assumption that saturated ammonium chloride vapor is completely dissociated. Hence, their results must be larger than the correct values.

Marignac's experimental method was admittedly rather inaccurate, the measurements were made at atmospheric pressure, and the value for the latent heat of vaporization given in Table V is the mean of two extreme values, 33.0 and 43.8. Since his measurements were not made under equilibrium conditions, the results have little quantitative significance.

Previous observers have, therefore, failed to obtain correct values for the latent heat of vaporization of ammonium chloride, either because they have not worked under equilibrium conditions, or because, in the absence of data in regard to the densities of the saturated vapor, they have uncritically assumed complete dissociation.

Neither of these objections, however, applies to the method which we have used, because we have calculated the molar latent heat of vaporization from the dissociation pressures and the saturated vapor densities, using the Clausius-Clapeyron equation, $L = T\ \partial P/\partial T\ (V - v)$. In this equation, v, the molar volume of the solid, is negligible; and the molar volume of the vapor V is equal to $1/\Delta_{mi}$. The value of $\partial P/\partial T$ was found from the Kirchoff-Rankin-Dupré equation

$$\log P = -A/T + B \log T + C,$$

in which the constants, A, B, and C have been evaluated for the ammonium halides by Smith and Calvert.[1] When this equation is solved for P, and the resulting value of P is differentiated with respect to T, it is found that,

$$\frac{\partial P}{\partial T} = P\left[\frac{A}{0.4343\ T^2} + \frac{B}{T}\right].$$

Substituting now in the Clausius-Clapeyron equation these **expressions** for V, and $\partial P/\partial T$ gives

$$L = T\frac{P}{760}\left[\frac{A}{0.4343\ T^2} + \frac{B}{T}\right]\frac{0.02419}{\Delta_{mi}}\ \text{Kg. cal.}$$

P is the dissociation pressure of ammonium chloride in mm. of mercury, and Δ_{mi} is the interpolated molar vapor density, both as given in Table III. $A = 1920$, and $B = 9.779$.

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at room temperature. Johnson incorrectly quotes these data as heats of vaporization, and compares his values of the latent heat of vaporization with them.

[1] Smith and Calvert, This Journal, **36**, 1368, 1371, 1373 (1914).

Using this formula, the following values of the molar latent heats of vaporization between 280° and 330° were obtained:

NH_4Cl—Latent Heats of Vaporization (Kg. cal. per mol).

280°	290°	300°	310°	320°	330°
32.5	32.7	32.9	33.0	33.2	33.3

Average value....... 32.9

Since the extreme values differ only by about 1% from the average value, it may be assumed that the latent heat of vaporization of ammonium chloride between 280° and 330° is constant within the experimental error. That the average value is smaller than the older values given in Table V is to be expected, because, as explained above, the latter were obtained by methods which would necessarily yield results larger than the correct value.

The Dissociation Constant.—For calculating the heats of dissociation, it is necessary to determine the dissociation constants of ammonium chloride at different temperatures. The dissociation constant K_c is given by the equation

$$K_c = \frac{\alpha^2}{1-\alpha} \Delta_{mi}.$$

First, a series of values of K_c was calculated, using the observed molar vapor densities Δ_m (Table III), and the observed values of α (Table IV). The values of the dissociation constant thus determined are the "observed" values given in Table VI, and they are represented graphically by the points which lie on either side of the curve in Fig. 4. They are, of course, somewhat irregular because of the experimental errors in Δ_m and, especially, in α. In order to get a smooth, average set of values of K_c, a second series of values was calculated,

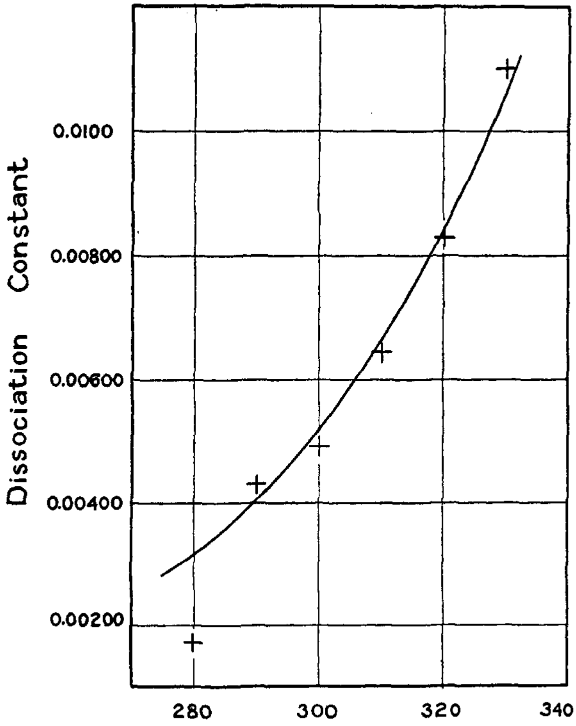

Fig. 4.—Dissociation constants of saturated ammonium chloride vapor.

using the interpolated values of α, given in Table IV, and the "interpolated" vapor densities, Δ_{mi} (Table III). Δ_{mi} was calculated by the formula

$$\Delta_{mi} = \frac{\delta}{1 + \alpha_{interpol.}},$$

and is simply the density which the saturated vapor would have if it gave the interpolated values of α instead of the measured values. This second series of values of K_c is that entitled "average" in Table VI, and they lie directly on the curve in Fig. 4.

TABLE VI.—NH_4Cl—DISSOCIATION CONSTANTS—K_c.

Temp.	280°.	290°.	300°.	310°.	320°.	330°.
Observed................	0.00174	0.00432	0.00496	0.00644	0.00828	0.0110
Average..................	0.00316	0.00407	0.00523	0.00665	0.00842	0.0106

The difference between the observed and the "average" values of K_c is, in some cases, rather large, but not greater than would be expected from the nature of the relation between K_c and α, and the error in α. Fig. 4 shows that the "average" values of K_c, as represented by the curve, are the best possible average of the observed values. These "average" values of K_c will be used in calculating the heat of dissociation rather than the observed values.

The Heat of Dissociation—General.—The fundamental relation bebetween the heat evolved during dissociation, and the dissociation constant is expressed by the van't Hoff equation

$$\frac{d \ln K_c}{dT} = -\frac{U}{RT^2}.$$

U is the heat which would be *evolved* if one mol of substance, *e. g.*, ammonium chloride vapor, dissociated isothermally, without performing external work. In order to integrate this equation it is necessary to decide upon the nature of the relation between U and T. The exact relation not being known, it has been customary to employ an interpolation formula of the type

$$U = A + BT + CT^2 + DT^3 + \ldots\ldots \qquad \text{(I)}$$

where A, B, C, D, ... are constants. Lundén,[1] in the calculation of heats of ionization, has used the condensed form,

$$U = A + BT, \qquad \text{(II)}$$

disregarding powers of T higher than the first. This, however, is not in agreement with Nernst's heat theorem, which postulates the relation,

$$dU_0/dT = \text{zero.} \quad (U_0 = U \text{ at absolute zero.})$$

The equation used by Lundén gives $dU_0/dT = B$. Hence, it is evident that in Equation I above, B = zero.

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[1] Lundén, *J. chim. phys.*, **5**, 593 (1907).

The representation of U in expanding powers of T has recently been studied by Arrhenius.[1] We have, from the second law of thermodynamics,

$$U = A - TdA/dT \quad (A = \text{free energy}).$$

Hence, if we assume A represented in expanding powers of T, *i. e.*,

$$A = A_0 + BT + CT^2 + DT^3 + \dots\dots$$

we have also,

$$T\,dA/dT = BT + 2CT^2 + 3DT^3 + \dots\dots$$

and consequently, by subtraction,

$$U = A_0 - CT^2 - 2DT^3 - \dots\dots \qquad \text{(III)}$$

Now Arrhenius has shown that in this equation, if we do not consider very high temperatures, all powers of T above the second may be disregarded. The resultant equation,

$$U = A_0 - CT^2$$

is very widely applicable, and has been proved to hold for many different types of reactions through large ranges of temperature. Nevertheless, it must always be carefully borne in mind that the equation is, in the end, only an approximation, being a condensed form of the expanding series shown in (III), and breaking down if its limits are overstepped. Strictly speaking, the equation is also dependent upon the gas laws, and should be applied only if they hold exactly. The practical range, however, is much wider, and it can be used with success in many cases where the gas laws do not even approximately apply. In such instances it must be considered to be merely an interpolation formula, and in this character it may be employed in the present investigation. Examination of our experimental results shows that, for them, the equation used by Lundén does not hold. With the equation of Arrhenius, however, satisfactory agreement can be obtained, in the case of ammonium chloride, throughout the available temperature range.

The Heat of Dissociation of NH_4Cl.—The heat of dissociation of ammonium chloride vapor has not been determined previously because the values of the dissociation constant at different temperatures are necessary for its calculation, and they have never been determined.

By combining Arrhenius' formula with the van't Hoff equation, there is obtained

$$d \ln K_c = -\frac{A_0}{RT^2}\,dt + \frac{C}{R}\,dT$$

and integration of this equation yields,

$$4.571\,\frac{\log K_{c_1} - \log K_{c_2}}{T_1 - T_2} = -\frac{A_0}{T_1T_2} + C. \qquad \text{(IV)}$$

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[1] Arrhenius, "Energieverhältnisse bei Dampfbildung und bei elektrolytischer Dissoziation," *Meddel. från K. Vet. Akads. Nobelinstitut*, Band 2, No. 8.

From Equation IV the values of A_0 and of C may be found by solving the two simultaneous equations obtainable from the values of K_c at any three different temperatures; but we have used the following graphic method which is more general and more accurate. If Equation IV is written in the form,

$$y = -A_0x + C,$$

it is evident that it is the equation of a straight line. From each pair of values of K_c which is available from the data, and the corresponding temperatures, a value of both y and x may be obtained. If these values of y and x are plotted they will lie on a straight line, providing Equation IV represents the correct relation between U and T. The slope of this line will be A_0, and its intercept on the y-axis will be C. From the fifteen possible pairs of the "average" values of K_c given in Table VI, we calculated fifteen values of x and y. These were then plotted, and the best

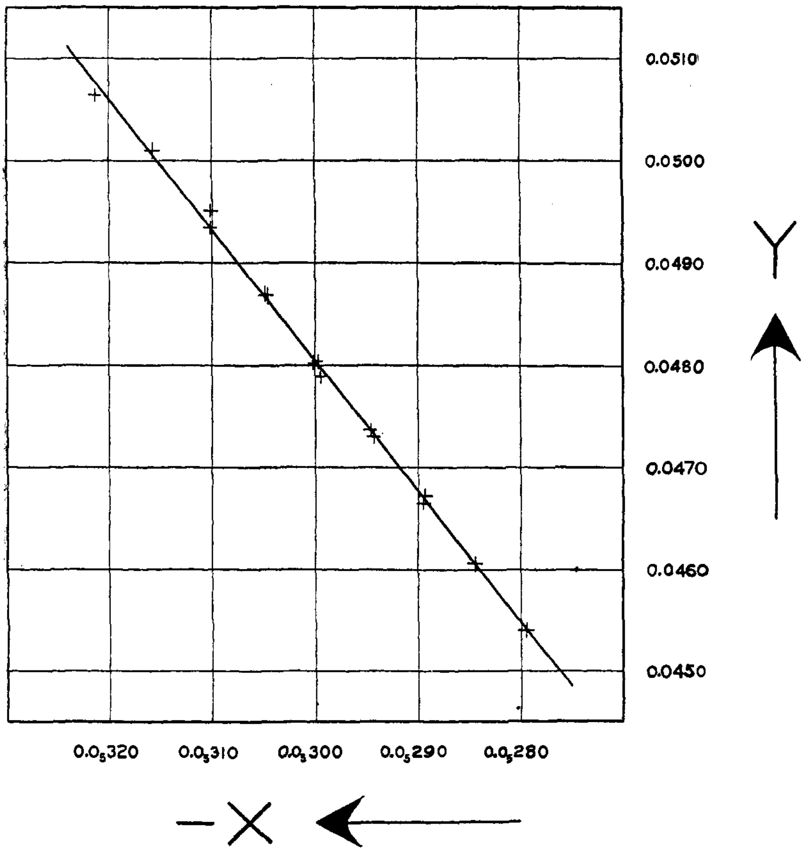

Fig. 5.—Calculation of the heat of dissociation of saturated ammonium chloride vapor. Plot of the equation, $y = - A_0\ x + C$.

representative straight line was drawn through them, as shown in Fig. 5. A_0, the slope of this line, was found to be —12800, and C, the intercept on the y-axis had the value 0.00967, whence,

$$U = -12800 - 0.00967T^2 \text{ gram calories per mol.}$$

The fact that the results lie so well along a straight line shows that the van't Hoff equation, in conjunction with Arrhenius' relation between U and T, correctly represents the facts in the case of ammonium chloride. It is also to be noticed that the heat absorbed during dissociation increases as the temperature increases. This indicates that the molar heat of ammonium chloride vapor is less than the sum of the molar heats of its products of dissociation, and this conclusion is in accordance with the kinetic theory of gases.

Ammonium Bromide.

The Data.—The densities of saturated ammonium bromide vapor were determined between 300° and 388°, the range of temperature being determined by the same factors as in the case of ammonium chloride. Vapor density bulbs of type No. 2 (Fig. 1) were used, except at 300° and 388°. At these temperatures the "trap bulb," Fig. 1, No. 3, was employed. The ammonium bromide was recrystallized once from distilled water, then sublimed in a large evacuated glass tube, and finely pulverized.

TABLE VII.—DENSITIES OF NH_4Br VAPOR (SATURATED)—DATA.

Temp.	G. NH_4Br in large bulb	Vol. (cc.) of large bulb.	Vapor dens. g. per cc.	Deviation from mean.	Minutes in bath.
300°	0.0102	78.51	0.000130	0	30
	0.0105	81.49	0.000129	— 1	30
	0.0102	78.04	0.000131	+ 1	30
	0.0096	72.83	0.000132	+ 2	30
	0.0087	68.64	0.000127	— 3	30
	0.0104	79.23	0.000131	+ 1	30
Average vapor density.............			0.000130	± 0.5, or ±0.4%	
320°	0.0134	72.18	0.000186	— 6	60
	0.0155	81.71	0.000190	— 2	60
	0.0135	67.27	0.000201	+ 9	60
	0.0141	73.18	0.000192	0	60
Average vapor density.............			0.000192	± 2, or ±1.0%	
330°	0.0190	65.06	0.000292	+33	60
	0.0256	68.61	*0.000373*	..	60
	0.0173	69.79	0.000248	—11	60
	0.0159	67.17	0.000237	—22	60
	0.0214	71.62	0.000299	+40	60
	0.0179	71.37	0.000251	— 8	60
	0.0189	75.17	0.000252	— 7	60
	0.0248	76.83	*0.000323*	..	60
	0.0182	78.00	0.000233	—26	60
	0.0181	70.31	0.000258	— 1	60
Average vapor density.............			0.000259	± 6, or ±2.3%	

TABLE VII.—DENSITIES OF NH_4Br VAPOR (SATURATED)—DATA (*continued*).

Temp.	G. NH_4Br in large bulb.	Vol. (cc.) of large bulb.	Vapor dens. g. per cc.	Deviation from mean.	Minutes in bath.
340°	0.0256	66.97	0.000382	+34	60
	0.0205	60.46	0.000339	— 9	60
	0.0228	66.74	0.000342	— 6	60
	0.0338	78.72	*0.000429*	..	60
	0.0255	74.87	0.000341	— 7	60
	0.0295	71.81	*0.000411*	..	60
	0.0256	78.02	0.000328	—20	60
	0.0238	66.44	0.000358	+10	60
Average vapor density.............			0.000348	± 6, or ±1.7%	
350°	0.0429	81.96	*0.000524*	..	60
	0.0334	66.74	0.000496	+18	60
	0.0359	73.32	0.000490	+12	60
	0.0335	71.81	0.000466	—12	60
	0.0349	72.51	0.000481	+ 3	60
	0.0321	69.90	0.000459	—19	60
Average vapor density.............			0.000478	± 6, or ±1.2%	
360°	0.0435	66.65	0.000653	+20	60
	0.0388	62.70	0.000619	—14	60
	0.0522	65.54	*0.000797*	..	60
	0.0473	77.71	0.000609	—24	60
	0.0530	80.54	0.000658	+25	60
	0.0419	66.99	0.000626	— 7	60
	0.0378	68.72	*0.000550*	..	60
	0.0469	74.08	0.000633	00	60
Average vapor density.............			0.000633	± 6, or ±1.0%	
370°	0.0565	68.63	0.000823	—13	60
	0.0512	60.53	0.000846	+10	60
	0.0758	74.68	*0.00102*	..	60
	0.0566	67.59	0.000837	+ 1	60
	0.0705	74.77	*0.000943*	..	60
	0.0366	72.31	*0.000506*	..	60
Average vapor density.............			0.000836	± 5, or ±0.6%	
380°	0.0783	77.43	0.00101	— 9	60
	0.0725	61.53	0.00118	+ 8	60
	0.0724	64.92	0.00112	+ 2	60
	0.0837	77.41	0.00108	— 2	60
Average vapor density.............			0.00110	± 3, or ±2.7%	
388°	0.0946	68.72	0.00138	— 4	30
	0.0987	66.36	0.00149	+ 7	30
	0.1044	74.11	0.00141	— 1	30
	0.0996	71.95	0.00139	— 3	30
	0.1030	71.47	0.00144	+ 2	30
	0.1135	80.33	0.00141	— 1	30
Average vapor density.............			0.00142	± 1.2, or ±0.9%	

The data of the individual vapor density determinations are presented in Table VII. For an explanation of this table see the discussion that precedes Table II (ammonium chloride), which is identical in form. The accuracy of the ammonium bromide data is the same as in the case of the ammonium chloride, namely, about ±2%.

In Table VIII are given the densities of saturated ammonium bromide vapor in the form in which they were used in the calculations. This table corresponds to Table III (ammonium chloride), and the explanation which precedes Table III applies also to it.

In order to facilitate the comparison of the observed vapor densities with the "completely dissociated" and the "undissociated" vapor densities, these have been plotted in Fig. 6.

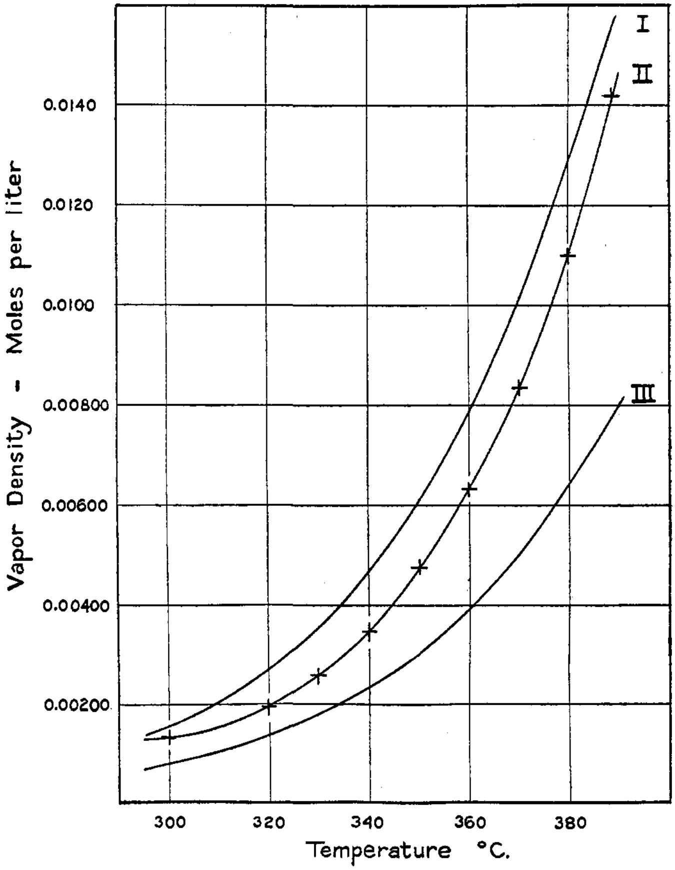

Fig. 6.—Vapor densities of ammonium bromide: Curve I—Undissociated (calculated); Curve II—Observed; Curve III—Completely dissociated (calculated).

It will be seen that the observed vapor densities lie between the "completely dissociated" and the "undissociated" densities throughout the range of temperatures studied. This fact indicates that ammonium bromide vapor is dissociated, although not completely. Furthermore, the measured vapor densities of ammonium bromide lie much nearer to the "undissociated" curve than do the measured densities of ammonium chloride (Fig. 2), so that ammonium bromide vapor is less dissociated than is ammonium chloride vapor.

TABLE VIII.—DENSITIES OF NH_4Br VAPOR (SATURATED)—SUMMARY.

Temp.		Vapor Density.					Pressure.
		Observed.		Calculated.			
C.	Abs.	G. per cc.	Mols per l. Δm.	Interpol. Mols per l. Δmi.	Undissoc. Mols per l. δm.	Comp. dissoc. Mols per l.	Total mm.
300	573	0.000130	0.00133	0.00104	0.00154	0.00077	55.0
310	583	....	.....	0.00143	0.00205	0.00103	74.6
320	593	0.000192	0.00196	0.00195	0.00272	0.00136	100.6
330	603	0.000259	0.00264	0.00266	0.00358	0.00179	134.7
340	613	0.000348	0.00356	0.00358	0.00468	0.00234	178.8
350	623	0.000478	0.00488	0.00482	0.00609	0.00305	236.6
360	633	0.000633	0.00646	0.00645	0.00786	0.00393	310.4
370	643	0.000836	0.00853	0.00858	0.01010	0.00505	404.8
380	653	0.00110	0.0112	0.0114	0.01290	0.00645	525.5
388	661	0.00142	0.0145	0.0142	0.01564	0.00782	644.4

The Degrees of Dissociation.—The degrees of dissociation of ammonium bromide vapor are calculated by the same method as were those of ammonium chloride. The results are presented in Table IX and are plotted in Fig. 3. The quantities in the several columns of Table IX have the same significance as those in the corresponding columns of Table IV (ammonium chloride).

TABLE IX.—NH_4Br—DEGREES OF DISSOCIATION.

Temp. C.	Percentage dissociation.		Deviation of α from straight line.		% error in α. (Calcd.)
	Obsd.	Interpol.	Actual.	%.	
300°	16.1	47.9	—31.8	..	..
310°	..	43.6	..	..	..
320°	38.7	39.3	— 0.6	1.5	4.3
330°	35.7	34.9	+ 0.8	2.3	9.8
340°	31.6	30.6	+ 1.0	3.3	7.1
350°	24.7	26.3	— 1.6	6.1	6.5
360°	21.7	22.0	— 0.3	1.4	5.4
370°	18.4	17.7	+ 0.7	4.0	3.7
380°	15.3	13.4	+ 1.9	14	18
388°	8.0	10.0	— 2.0	20	12

Inspection of Table IX and of Fig. 3 will show that at 320° ammonium bromide vapor is about 39% dissociated and, as the temperature increases, the degree of dissociation *decreases* regularly until at 388° it is only about 8–10%. As was the case with ammonium chloride, a straight line represents the results within the experimental error of the observations.

As will be seen from Table IX, the deviations of the measured values of α from a straight line are, with one or two exceptions, less than the deviations calculated from the known experimental error in the observed vapor densities.

The exact degree of dissociation at temperatures below 320° is somewhat in doubt. If, below 320°, the degree of dissociation continued to vary linearly with the temperature, as it does above 320°, it should have a value of about 48% at 300°, with a corresponding vapor density of 0.000102 g. per cc. We first used bulbs of type No. 2 (Fig. 1), and obtained a set of nine densities with the average value 0.000135 ± 3.1% (not given in the table), corresponding to a dissociation of 11.1%. Later, we repeated the determination using the trap bulb, No. 3 (Fig. 1), and obtained the value cited above, namely 0.000130 g. per cc. (16.1% dissociation).[1] The mean of the two values 0.0001325, differs from each of the values by less than 2%. Since at this temperature the vapor pressure is very low, the total weight of the vapor filling the large bulb is only 8–10 mg. The agreement of the two sets within 4% is therefore better than one would expect under the conditions. On the other hand, it seems improbable that the real value was 0.000102, and that the errors in the two sets were as great as 25% and 30%, respectively. Speaking conservatively, all that can be said is, that the measurements indicate that the degree of dissociation of ammonium bromide vapor passes through a maximum near 320°, but that this inference depends entirely upon the vapor density at 300°, which is the one most subject to error in the series.

As already pointed out, the measurements are not made at constant pressure, but at pressures which rise rapidly with rising temperature. Thus between 330° and 380° the total pressure of all components increases from 134.7 mm. to 644.4 mm., while the partial pressure of free ammonia (or HBr, see Table XV) increases from 34.6 mm. to 57.8 mm. only. Calculation shows that if the total pressure were to be kept constant at 134.7 mm. then the partial pressure of ammonia would change from 34.6 mm. to 23.5 mm. Hence, the degree of dissociation would decrease from 35% to 21% only. Thus the decrease shown in Table IX is greatly exaggerated by the effect of increasing total pressure. Ammonium bromide vapor is apparently the only dissociating gas whose degree of dissociation at constant pressure is known to decrease with increasing temperature.

In this connection attention should be called to the fact that this behavior is not unique, in the sense that many, and therefore possibly all

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[1] This case illustrates very strikingly the way in which a moderate error in the observed density gives rise to a very large error in the degree of dissociation calculated therefrom. Here the higher of the two values obtained for the density exceeded the lower by 4%, while one of the corresponding, calculated values of α is no less than 45% greater than the other (see p. 49).

other substances are *known* to show the opposite behavior. If this were true, the isolated nature of the phenomenon would enjoin extreme caution before acceptance. The situation is, rather, that we lack information in regard to almost all the other dissociating substances, and do not know what their behavior in this respect is. For example, the vapor density of ammonium bromide was previously investigated by Deville and Troost by the Dumas method, and the results did give a slightly greater (2%) density (and therefore less dissociation) at the higher temperature (Table I). But this difference was quite naturally attributed to error, due to the inadequacy of the method when applied to such substances. The data thus far obtained in regard to the vapor densities of solids dissociating at high temperatures simply have not usually been such as would enable us to distinguish with certainty between cases in which, with rising temperature, the dissociation increased, and those in which it decreased.

The Latent Heat of Vaporization.—The only previous attempt to determine the molar latent heat of vaporization of ammonium bromide is that of F. M. G. Johnson,[1] who, by using the equation $d \ln P/dT = Q/2RT^2$, in conjunction with his measurements of the vapor pressures of ammonium bromide, found the value 45.4 kg. cal. at 297–394°. Since this equation involves the assumption that ammonium bromide vapor is completely dissociated, Johnson's value is larger than the correct value, and does not represent the heat absorbed when one mol of ammonium bromide vaporizes in equilibrium with its saturated vapor.

We have calculated the molar latent heat of vaporization from the following equation, which was derived and explained when the latent heat of vaporization of ammonium chloride was discussed, namely,

$$L = T\frac{P}{760}\left[\frac{A}{0.4343\,T^2} + \frac{B}{T}\right]\frac{0.02419}{\Delta_{mi}}\ \text{kg. cal.}$$

For ammonium bromide, $A = 2057$, and $B = 9.540$.[2]

The values of the latent heat of vaporization thus obtained are given in Table X.

TABLE X.—NH_4Br—LATENT HEATS OF VAPORIZATION (Kg. cal. per mol).

300°	320°	330°	340°	350°	360°	370°	380°	388°
23.5	28.7	28.1	27.4	26.8	26.1	25.4	24.7	24.1

These values of the latent heat of vaporization are less than those of Johnson, as would be expected from the nature of the error in his determinations. The fact that above 320° the latent heat of vaporization decreases is not unusual. If the vapor of a solid or a liquid does not dissociate, the latent heat of vaporization will, in general, decrease with increasing temperature, because the specific heat of the solid or liquid is greater than that of its

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[1] F. M. G. Johnson, *Z. physik. Chem.*, **65**, 38 (1908–9).

[2] Smith and Calvert, THIS JOURNAL, **36**, 1368 (1914).

saturated vapor. Ammonium bromide, therefore, behaves in this respect exactly like a normal, nondissociated substance. It must consequently be concluded that the disturbing influences upon the heat of vaporization (*e. g.*, the heat involved in the dissociation of the vapor) are insufficient to affect the general run of the results, or are approximately constant throughout the temperature range considered.

The Dissociation Constants and the Heat of Dissociation.—The dissociation constants of ammonium bromide vapor were calculated from the data in Table VIII by the same relation which was used in the case of ammonium chloride, namely,

$$K_c = \frac{\alpha^2}{1 - \alpha} \Delta_{mi}.$$

As under ammonium chloride, two series of values of K_c were determined, one by using the observed values of α and the second by using the "interpolated" values of α. The latter series represents the best average of the measured dissociation constants. These observed and "average" dissociation constants are given in Table XI; and they are plotted in Fig. 7. The "average" values are represented by the curve, and the observed values by the points which lie on either side of the curve.

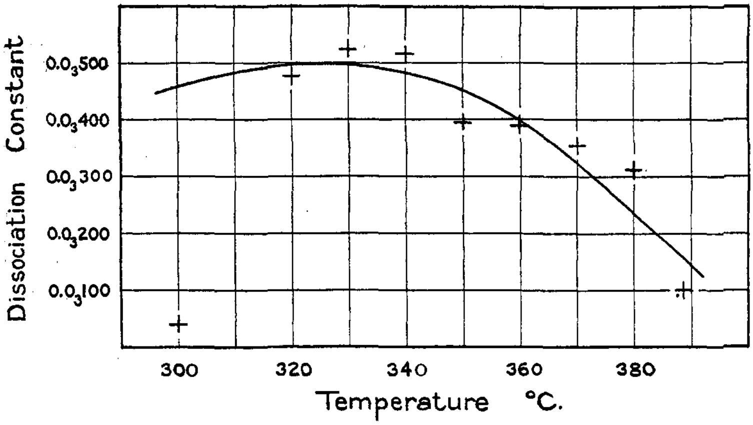

Fig. 7.—Dissociation constants of saturated ammonium bromide vapor.

TABLE XI.—NH_4Br—DISSOCIATION CONSTANT, K_c.

Temp.	Observed.	Average.	Temp.	Observed.	Average.
300°	0.0_4409	0.0_3458	350°	0.0_3396	0.0_3453
310°	.....	0.0_3481	360°	0.0_3390	0.0_3400
320°	0.0_3478	0.0_3497	370°	0.0_3353	0.0_3327
330°	0.0_3525	0.0_3497	380°	0.0_3311	0.0_3236
340°	0.0_3517	0.0_3483	388°	0.0_4998	0.0_3158

It will be seen that the dissociation constant first increases to a maximum at 320°, and then decreases. If we consider first the decrease, we see that this has an important bearing upon the heat of dissociation. If in the van't Hoff equation, $d \ln K_c/dT = -U/RT^2$, the term $d \ln K_c/dT$ is negative, as it is here above 320°, then U must be *positive*. That is to say, above 320°, heat will be *evolved* by the reaction. Hence, the data show that above 320° the dissociation of ammonium bromide vapor is accompanied by evolution of heat. This result was wholly unexpected. If the decrease had been slight, it might have been explained as due to errors of observations, or to inadequacy of the method, for the measurement of vapor densities at high temperatures is undoubtedly difficult and subject to considerable errors. The decrease is so very rapid, however, the values at the various temperatures are so regular in their decrease, and the estimated errors of observation are relatively so small (see Table VII), that no doubt can exist that the decrease really occurs.

As regards the maximum point, the phenomena are the opposite of those shown by hydrogen iodide, where at low temperatures heat is given out in the dissociation and at higher temperatures is absorbed, so that the dissociation constant passes through a minimum. The cases are not parallel, however, because the decomposition of the hydrogen iodide is accompanied by recombination to form H_2 and I_2, and the case is not one of simple dissociation like that of ammonium bromide. Although the case of ammonium bromide is thus unique among gases, there are analogies among liquids which, to a certain extent, reconcile us to its occurrence. Thus, Lundén[1] has found that with rising temperature the ionic dissociation constants of ammonium hydroxide and of acetic acid pass through maxima. However, the case is not strictly analogous, because the conditions in a system involving two components, such as a solution, are different from those in a system involving only one component like the present one. The analogy is closer in a single ionizing liquid like water. According to Arrhenius' equation $U = A_0 - CT^2$, U being here the heat of ionic dissociation, there must be for each substance some temperature at which the dissociation reaches a maximum. This happens when $U = O$, and therefore $T = \sqrt{A_0/C}$. In the case of water this temperature happens to fall within the experimental range. According to A. A. Noyes[2] U = zero for water between 250° and 275°. According to Arrhenius[3] U = zero for water at 229°. It is therefore quite conceivable that similar relations should exist in dissociating vapors.

An attempt to obtain an expression for the values of the heat of dissociation of ammonium bromide by means of the combined van't Hoff and Arrhenius equations, which served so well in the case of ammonium chloride, was made. It was found, however, that for ammonium bromide this equation does not represent the relation between the dissociation

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[1] Lundén, *J. chim. phys.*, **5**, 598 (1907).

[2] Carnegie Inst. of Washington, Publication No. **63**, 233 (1907).

[3] "Theories of Solutions" **1912**, p. 212.

constants and the heat of dissociation. Arrhenius himself found that his interpolation formula does not always apply where a change in the sign of U occurs. In such cases it can be used with success only where the sign of U passes through zero at a moderate temperature. For example, it does not represent the heat of electrolytic dissociation of water at temperatures much above the boiling point of water, unless powers of T higher than the second are included. Since, in the present instance, the change in sign occurs as high as 320°, the Arrhenius formula could not be expected to hold.

Ammonium Iodide.

The Data.—The densities of saturated ammonium iodide vapor were determined from 300° to 380° by using the "trap" bulb, Fig. 1, No. 3. The bulbs remained in the nitrate bath for thirty minutes each. Ammonium iodide, once recrystallized, and dried at 100° *in vacuo*, was used. The vapor density data are presented in Table XII.

TABLE XII.—DENSITIES OF NH_4I VAPOR (SATURATED)—DATA.

Temp.	G. NH_4I in large bulb.	Vol. (cc.) of large bulb.	Vapor dens. g. per cc.	Deviation from mean.
300°	0.0158	77.88	0.000203	+ 22
	0.0144	75.42	0.000191	+ 10
	0.0114	74.35	0.000153	— 28
	0.0073	68.74	*0.000106*	...
	0.0108	63.94	0.000169	— 12
	0.0137	73.02	0.000188	+ 7
Average vapor density................			0.000181	±7, or ±3.9%
320°	0.0233	73.94	0.000315	+ 8
	0.0227	73.93	0.000307	0
	0.0232	77.07	0.000301	— 6
	0.0262	81.45	0.000322	+ 15
	0.0201	65.78	0.000306	— 1
	0.0213	73.28	0.000291	— 16
Average vapor density................			0.000307	±3, or ±1.0%
340°	0.0233	76.65	*0.000304*	...
	0.0367	68.72	0.000534	+ 46
	0.0425	78.24	0.000543	+ 55
	0.0330	68.64	0.000481	— 7
	0.0278	70.52	0.000394	— 94
	0.0390	71.86	0.000543	+ 55
	0.0280	75.77	0.000370	—118
	0.0367	67.58	0.000543	+ 55
	0.0358	66.05	0.000542	+ 54
	0.0360	80.25	0.000443	— 45
Average vapor density................			0.000488	±19, or ±3.9%
350°	0.0491	72.96	0.000673	+ 26
	0.0470	70.24	0.000669	+ 22
	0.0450	67.50	0.000667	+ 20
	0.0437	74.56	0.000579	— 68
Average vapor density................			0.000647	±17, or ±2.6%

TABLE XII.—DENSITIES OF NH_4I VAPOR (SATURATED)—DATA (*continued*).

Temp.	G. NH_4I in large bulb.	Vol. (cc.) of large bulb.	Vapor dens. g. per cc.	Deviation from mean.
360°	0.0687	82.41	0.000834	− 40
	0.0743	86.80	0.000856	− 18
	0.0699	78.67	0.000889	+ 15
	0.0768	89.39	0.000859	− 15
	0.0749	82.76	0.000905	− 31
	0.0637	69.56	0.000903	+ 29
Average vapor density................			0.000874	±10, or ±1.1%
370°	0.0755	68.83	0.00110	+ 5
	0.0722	69.14	0.00104	− 1
	0.0740	72.53	0.00102	− 3
	0.0696	69.02	0.00101	− 4
	0.0682	66.25	0.00103	− 2
	0.0759	71.32	0.00108	− 3
Average vapor density................			0.00105	±1, or ±1.0%
380°	0.0947	74.92	0.00126	− 3
	0.1001	79.49	0.00126	− 3
	0.1004	78.96	0.00127	− 2
	0.1062	86.88	0.00120	− 9
	0.1088	75.22	0.00143	+ 14
Average vapor density................			0.00129	±3, or ±2.3%

The error in the ammonium iodide vapor densities is, at several of the temperatures, greater than that observed for the chloride and bromide; and the average values of the vapor densities do not lie so smoothly on a curve. This greater irregularity may be due to the slow decomposition of the hydrogen iodide,[1] although no iodine vapor was ever noticed in the hot vapor density bulbs immediately after they were removed from the nitrate bath (see also p. 67).

TABLE XIII.—DENSITIES OF NH_4I VAPOR (SATURATED)—SUMMARY.

Temp.		Vapor density. Observed.		Vapor density. Calculated.			Pressure.
C.	Abs.	G. per cc.	Mols per l. Δm.	Interpol. Mols per l. Δm_i.	Undissoc. Mols per l. δm.	Compl. dissoc. Mols per l.	Total mm.
300	573	0.000181	0.00125	0.00126	0.00095	0.00048	33.9
310	583	....	...	0.00166	0.00133	0.00067	48.5
320	593	0.000307	0.00212	0.00212	0.00185	0.00093	68.4
330	603	....	...	0.00270	0.00253	0.00126	95.0
340	613	0.000488	0.00337	0.00345	0.00341	0.00170	130.3
350	623	0.000647	0.00446	0.00447	0.00454	0.00227	176.3
360	633	0.000874	0.00603	0.00573	0.00597	0.00299	235.7
370	643	0.00105	0.00721	0.00730	0.00777	0.00389	311.5
380	653	0.00129	0.00886	0.00898	0.0100	0.00500	407.3

The vapor density results are summarized in Table XIII, as was done in Table III for ammonium chloride. The dissociation pressures given

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[1] Smith and Calvert, THIS JOURNAL, **36**, 1370 (1914).

in this table are those of Smith and Calvert.[1] The "interpolated" values of the vapor density given in Table XIII were not determined by calculation from the interpolated values of α, as in the case of ammonium chloride, because, as will be seen below, the values of α for ammonium iodide cannot be determined. The "interpolated" values were therefore found by graphical interpolation from the best representative curve which could be drawn through the observed vapor densities. This curve, together with the "undissociated" and "completely dissociated" vapor density curves are given in Fig. 8.

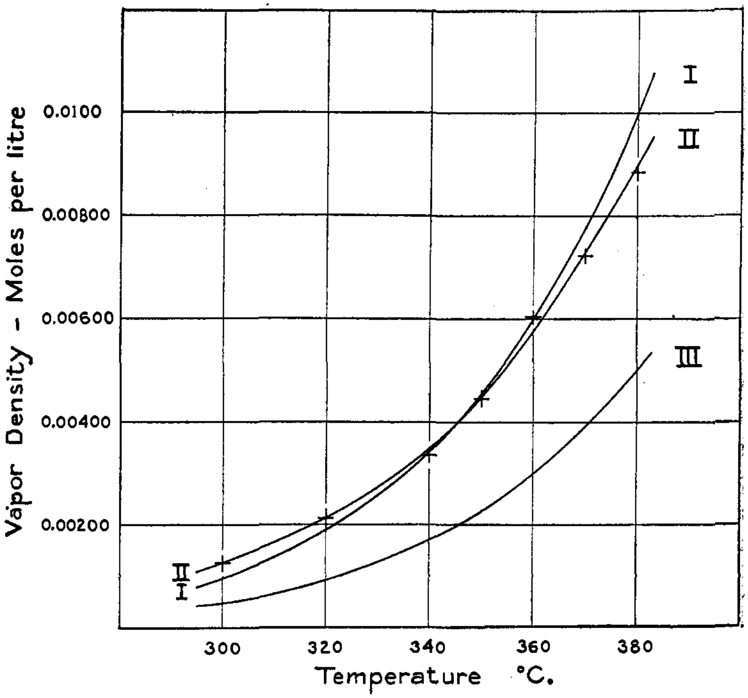

Fig. 8.—Vapor densities of ammonium iodide: Curve I—Undissociated (calculated); Curve II—Observed; Curve III—Completely dissociated (calculated).

Discussion of Results.—Inspection of Table XIII and of Fig. 8 shows several interesting facts concerning ammonium iodide vapor. It will be noticed that, below 340–350°, the observed densities of the saturated vapor are larger than the densities calculated for no dissociation. This means that ammonium iodide vapor is associated. However, it does not exclude the possibility that part of the vapor is also dissociated at the same time, although it does indicate that the amount of association at lower temperatures is relatively larger than the amount of dissociation. The

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[1] Smith and Calvert, *Loc. cit.*, 1371.

equilibrium in the vapor at any temperature may be represented most simply by the equation,

$$(NH_4I)_2 \rightleftarrows 2(NH_4I) \rightleftarrows 2NH_3 + 2HI. \qquad (I)$$

It will be seen also that, as the temperature increases, the observed vapor densities become first equal to, and then less than the "undissociated" vapor densities. This indicates that the amount of association decreases and the amount of dissociation increases as the temperature of the vapor rises.

The unexpected character of the results suggests the possibility of some secondary reaction. Thus, if the hydrogen iodide itself dissociated, the free iodine might interact with the ammonia to produce free nitrogen and hydrogen iodide. This reaction would result in a diminished partial pressure of ammonia, which in turn would permit further vaporization of the salt, and so give greater apparent densities. A similar reaction might even be imagined to have occurred in the case of the bromide. Such a reaction, however, would have left permanent gases (nitrogen and hydrogen) in the bulb. Now, in all the measurements in this paper, the evacuated bulbs, when opened under water, were filled completely by the liquid. The minute bubble of gas (much less than 1 cc.) which was visible, appeared to come mainly from the atmospheric gases dissolved in the water. Hence no reaction producing a permanent gas can have occurred.

The association of ammonium iodide vapor renders it impossible to make for it many of the calculations which were made for ammonium chloride and bromide. If it is assumed that the equilibrium in the vapor is represented by Equation I above, and if α is the percentage of the total number of NH_4I molecules dissociated, and β the percentage associated at any temperature, then

$$(\alpha - 0.5\,\beta) = \frac{\delta_m - \Delta_m}{\Delta_m}. \qquad (II)$$

This is the only relation between α and β which can be obtained from our data, and therefore, since there is only one equation involving these two unknown quantities, it is impossible to determine either of them. Since α and β are indeterminable, the dissociation constants, the heat of dissociation, and the partial pressures cannot be calculated, because the values of α and β are necessary for the calculation of each of these.

Although it is thus impossible to determine the actual degree of association or of dissociation of the vapor, the maximum and minimum values at any temperature may be estimated. At temperatures below that at which the observed and the "undissociated" vapor density curves cross each other, the minimum value of β may be found by placing α in Equation II equal to zero, and solving for β. The minimum value of α in this temperature region is, of course, zero. At temperatures above the intersection of these two curves, the minimum value of β is zero, and the minimum value of α may be found by assuming β in Equation II to be zero, and solving for α. The maximum values of α and β may be determined by assuming that all of the NH_4I molecules in the vapor have associated and dissociated; *i. e.*, by assuming that $\alpha + \beta = 1.00$, and then solving the simultaneous equations

$$\begin{cases} \alpha - 0.5\beta = \dfrac{\delta_m - \Delta_m}{\Delta_m} \\ \alpha + \beta = 1.00 \end{cases}$$

In this way we have estimated that ammonium iodide vapor at 300° is between 24% and 83% associated, and from 0% to 17% dissociated. At 380°, it is between 0% and 59% associated, and from 11% to 41% dissociated. These estimates are, of course, based upon the assumption that there are no ammonium iodide molecules in the vapor more complex than the type $(NH_4I)_2$, but they give some idea as to the conditions possibly present.

The Latent Heat of Vaporization.—F. M. G. Johnson[1] has found the value 44.5 kg. cal. for the molar latent heat of vaporization of ammonium iodide by the same method which he used for the chloride and bromide. But this method involves the assumption of the complete dissociation of the vapor, and so his result is too large. This is apparently the only estimate of the latent heat of vaporization of ammonium iodide which has thus far been made.

We have computed the molar latent heat of vaporization from the data in Table XIII, by the method we used for ammonium chloride and bromide, the equation for ammonium iodide being

$$L = T\,\frac{P}{760}\left[\frac{7715}{0.4343\,T^2} - \frac{10.04}{T}\right]\frac{0.02419}{\Delta_{mi}}\ \text{kg. cal.}$$

The values obtained are given in Table XIV. Those at 310° and 330° are in italics because they were calculated from purely interpolated data, there being no measured vapor densities of ammonium iodide at these temperatures. In the last line of the table are given the differences between the successive values of the heat of vaporization, in order that its mode of variation with the temperature may be clearly seen.

TABLE XIV.—NH_4I—LATENT HEATS OF VAPORIZATION (Kg. cal. per mol).

300°	310°	320°	330°	340°	350°	360°	370°	380°
18.0	*19.0*	20.4	*21.7*	22.8	23.2	23.6	23.9	24.8
	1.0	1.4	1.3	1.1	0.4	0.3	0.3	0.9

The latent heat of vaporization of ammonium iodide increases as the temperature increases. Since the latent heat of vaporization of substances whose vapors are neither associated or dissociated generally

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[1] F. M. G. Johnson, *Z. physik. Chem.*, **65**, 40 (1908–9).

decreases with a rise of temperature, the above fact makes it probable that heat is absorbed during the dissociation of ammonium iodide vapor, and that the amount of heat absorbed by dissociation increases as the temperature increases. This latter fact would be expected, because it has already been shown that the amount of dissociation of ammonium iodide vapor increases as the temperature rises.

The Partial Pressures of the Ammonium Halides.—The partial pressures for ammonium iodide could not be calculated on account of the association of its vapor. Taking ammonium chloride as an example, and assuming the equilibrium in the vapor to be of the type,

$$NH_4Cl \text{ (gas)} \rightleftarrows NH_3 + HCl,$$

the partial pressures of the three gases in the vapor are given by the formulae

$$p_{NH_4Cl} = P_{Total}\,\frac{2\Delta_{mi} - \delta_m}{\delta_m}, \text{ and } p_{NH_3} = p_{HCl} = \frac{P_{Total} - p_{NH_4Cl}}{2}.$$

P_{Total} is the dissociation pressure of the ammonium halide in question. The data for ammonium chloride and bromide, given in Tables III and VIII, respectively, were used for calculating the partial pressures, and the results are presented in Table XV.[1]

TABLE XV.—NH_4Cl AND NH_4Br—PARTIAL PRESSURES.

	Ammonium chloride.			Ammonium bromide.		
Temp. C.	$P_{Total.}$ Mm.	$p_{NH_4Cl.}$ Mm.	$p_{NH_3} = p_{HCl.}$ Mm.	$P_{Total.}$ Mm.	$P_{NH_4Br.}$ Mm.	$p_{NH_3} = p_{HBr.}$ Mm.
280°	135.0	30.3	52.4	...	...	..
290°	185.3	37.9	73.7	...	...	..
300°	252.5	53.2	99.7	55.0	19.3	17.9
310°	341.3	73.8	133.8	74.6	29.5	22.6
320°	458.1	101.2	178.5	100.6	43.6	28.5
330°	610.6	141.7	234.5	134.7	65.5	34.6
340°	...	...	...	178.8	94.8	42.0
350°	...	...	...	236.6	137.9	49.4
360°	...	...	...	310.4	199.0	55.7
370°	...	...	...	404.8	282.9	61.0
380°	...	...	...	525.5	403.3	61.1
388°	...	...	...	644.4	528.8	57.8

Summary.

Measurements of the densities of the saturated vapors of ammonium chloride (280° to 330°), bromide (300° to 388°), and iodide (300 to 380°) are recorded. With these data, and the previously measured dissociation pressures, a study is made of the degrees of dissociation, dissociation constants, heats of dissociation, latent heats of vaporization, and partial pressures of these substances, with the following results:

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[1] In order to facilitate reference and comparison, we have also given in Table XV the dissociation pressures of ammonium chloride and bromide as measured by Smith and Calvert (*Loc. cit.*).

Ammonium chloride vapor is 67–63% dissociated between 280° and 330°; and although the degree of dissociation is very nearly constant, it decreases slightly between these temperatures. Ammonium bromide vapor is about 39% dissociated at 320°, and above this temperature the percentage dissociation decreases linearly, until, at 388°, it is about 10%. Ammonium iodide vapor is associated, especially at lower temperatures, but the amount of association decreases, and the dissociation increases as the temperature rises. The assumption that the vapors of the ammonium halides are completely dissociated is therefore no longer tenable.

The dissociation constants of ammonium chloride and bromide are calculated. That of ammonium chloride vapor increases steadily with the temperature, whereas that of ammonium bromide vapor passes through a maximum near 320°, and then decreases.

The heat of dissociation of ammonium chloride vapor is computed by the van't Hoff equation, and is represented by the relation, $U = -12800-0.00967T^2$ gram calories (U is heat evolved). The mode of variation of the dissociation constant with the temperature indicates that the dissociation of ammonium bromide vapor above 320° is accompanied by the evolution of heat, but the actual value of the heat of dissociation can not be computed.

The latent heats of vaporization are calculated by the Clausius-Clapeyron equation. That of ammonium chloride is 32.9 kg. cal. between 280° and 330°, and is constant within 1%; that of ammonium bromide is 28.7 kg. cal. at 320°, and decreases to 24.1 at 388°; that of ammonium iodide increases from 18.0 kg. cal., at 300°, to 24.2 at 380°.

The partial pressures of the various components in the ammonium chloride and bromide vapors are computed.

Nichols Laboratories of Inorganic Chemistry,
Columbia University, New York, N. Y.

ON THE RATE OF REDUCTION OF MERCURIC CHLORIDE BY SODIUM FORMATE.

By G. A. Linhart.

Received November 12, 1914.

In a previous paper[1] an investigation of the rate of the reduction of mercuric chloride by phosphorous acid was described. The purpose of this article is to present the results of a similar study of the rate of reduction of mercuric chloride by sodium formate, with special reference to the influence of sodium chloride upon it, which has already been shown to have a great effect on the reduction by phosphorous acid.

Very recently, after the experimental work described below had been

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[1] Linhart, *Am. J. Sci.*, **35**, 353–368 (1913).