5. The results are interpreted as indicating that the reaction takes place around N_2^+ and N^+ ions. H_2^+ ions, neutral atoms, and excited molecules are relatively inactive.

6. A method of calculating the rate of ion formation, as well as the distribution of ions between the nitrogen and hydrogen, is presented.

7. A ratio of $M/N_2^+ \sim 2$ is obtained below 23 volts (24.5 volts when corrected for contact p. d.). A ratio for $M/N^+ \sim 1$ seems the most probable for the monatomic ion.

8. It is suggested that the reaction goes to completion in a cluster of hydrogen molecules around the nitrogen ions.

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VAPOR PRESSURES AND LATENT HEATS FOR THE SYSTEM: BaCl₂·8NH₃–BaCl₂–NH₃

BY LOUIS J. GILLESPIE AND ELI LURIE

Introduction

In the experimental study of the thermodynamic properties of ammonia in gaseous solutions of ammonia and nitrogen[1] the substances BaCl₂·8NH₃ and BaCl₂ were chosen as the materials to be used to avoid the necessity of a semipermeable membrane, because the high ammonia content of the octammine, the high decomposition pressures at temperatures below 50°, as well as the formation by barium chloride of only one ammine, are very desirable properties from an experimental standpoint.

Hüttig and Martin[2] had studied the 0° isotherm of barium chloride and ammonia, and had shown that barium chloride forms only one ammine, the octammine. They also determined the decomposition pressures of the octammine in the temperature range between 0 and −15.5°.

The large deviations of ammonia from the ideal gas law make the equilibrium an interesting one to study, and we have determined the pressures of ammonia in equilibrium with barium chloride and its octammine from 0 to 50°. One of us has recently discussed equations for representing, as a function of the temperature, the decomposition pressure of solid compounds capable of evolving a gas that deviates from the ideal gas law;[3] we have applied to our data the new equations for the pressures and the latent heats.

[1] Lurie and Gillespie, THIS JOURNAL, 49, 1146 (1927).

[2] Hüttig and Martin, Z. anorg. Chem., 125, 269 (1922).

[3] Gillespie, Proc. Am. Acad. Arts Sci., 66 (No. 3), 153 (1930).

Preparation of Materials.—Liquid ammonia was treated with metallic sodium in a steel vessel. After it had been standing for several months, during which time gas was occasionally drawn off, ammonia was withdrawn and was fractionally distilled three times. After each distillation the ammonia was frozen by means of liquid air and any permanent gas removed by evacuation with a mercury diffusion pump backed with an oil pump. The middle fraction from the distillation was stored in a steel bomb as liquid ammonia.

"C. P." barium chloride was recrystallized from distilled water three times and dried at 110°.

Experimental Procedure and Measurements.—For the determination of the decomposition pressures above three atmospheres an all-steel apparatus was used. About one gram of dry barium chloride was placed in the steel reaction bomb and the entire system was evacuated. The reaction bomb was then connected through the proper steel stopcocks with a liquid ammonia reservoir and the ammine was prepared by causing ammonia to distil over into the reaction bomb. Before measuring the pressure, some ammonia gas was removed from the reaction bomb—enough to insure the presence of barium chloride as one of the phases. The pressures were measured by a piston gage and the temperatures by a platinum resistance thermometer.

The measurements at the lower temperatures and pressures were made using an all-glass apparatus and a mercury manometer. A thermostat of rather large dimensions was necessary in order to keep the temperature constant day and night.

In all cases the temperatures were constant to 0.02°.

The data were taken in three groups, the octammine being prepared separately (though from the same stock of barium chloride) in the three reaction vessels used at 0°, from 7.48 to 19.92°, and from 38.28 to 49.95°. The decomposition pressures are given in Table I in atmospheres, together with those (listed as "calcd. A") calculated by means of the simple equation

$$\text{Log } p = -1998.04/T + 7.13333 \tag{1}$$

where p is the pressure in atmospheres, T is the absolute temperature ($t + 273.13$), and the logarithm is to the base ten. The percentage deviation is the observed minus calculated, divided by the observed, and multiplied by 100. The average percentage deviation without respect to sign is 0.21%.

In Table II are the decomposition pressures in millimeters of mercury obtained by Hüttig and Martin compared with the results from the same equation. Although the agreement at 0° is good, the divergence at lower temperatures is large, though irregular.

The Smoothing of the Pressures and the Calculation of the Heats.— As is well known, the linear relation between log p and $1/T$ shown in equation (1) can be justified theoretically if we assume that the gas is an

ideal gas, that the change of heat capacity attending the reaction is zero, and that the volume of the solids can be neglected. Gibbs[4] and others have given an equation for the case that the gas is ideal, and the change of heat capacity is not zero (though constant), and the volume of the solids is not zero (though constant). This equation is

$$\log p = \text{A} - \text{B} \log T - \text{c}/T \qquad (2)$$

In the present case the gas is ammonia, which deviates greatly from the ideal gas law, and the pressure rises above eight atmospheres. In such a case the deviation from the ideal gas law should probably be taken into account in the smoothing of the pressures, and is certainly important in the calculation of the heat absorbed in the decomposition of the ammine.

When the ideal gas law is used to calculate the molal volume of ammonia at the temperature and the corresponding vapor pressure of the ammine system, the errors are about 0.9, 2.7 and 7.6% at 0, 25 and 50°, respectively. In the calculation of the latent heat from the Clapeyron equation the error introduced by the use of the ideal gas law for computing the change of volume will be nearly as large. In the use of an equation which assumes the ideal gas law for smoothing the pressures and thus obtaining dp/dT there will be an error, which may be significant even when the linear equation (1) happens to appear satisfactory for the calculation of the pressures.[5]

These considerations apply with more force to the present data than to probably any previous data. Higher decomposition pressures have previously been measured, but not for a gas deviating so greatly from the ideal gas law as ammonia.

As a result of these considerations one of us has recently given general thermodynamic equations for the vapor pressures and latent heats as functions of the temperature, as well as special equations for the case of solids which can evolve a gas.[3] The approximate equations are

$$\log p = \log p_0 - \frac{M(C_p - \bar{c})}{R} \left[\frac{1}{M} \log \frac{T_0}{T} + 1 - \frac{T_0}{T} \right] +$$

$$\frac{M\lambda_0}{R} \left[\frac{1}{T_0} - \frac{1}{T} \right] + M \left[\frac{\bar{v} - B_0}{RT} + \frac{A_0}{R^2 T^2} + \frac{c}{RT^4} \right] (p - p_0) \qquad (3)$$

$$\lambda = T\lambda_0/T_0 + \frac{T}{M}(C_p - \bar{c}) \log \frac{T}{T_0} - \frac{RT}{M} \log \frac{p}{p_0} - Q \left[\frac{A_0}{RT} + \frac{3c}{T^3} \right] (p - p_0) \qquad (4)$$

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[4] Gibbs, "Scientific Papers. I. Thermodynamics," Longmans, Green and Co., New York, 1906 and 1928, footnote beginning on page 152.

[5] This statement would not be true, were we dealing with data of infinite precision. But when the precision of the data is limited and can only be judged by their consistency we can find more than one function, which will represent the body of data with practically the same average precision, though they will not represent any given datum with the same precision and the derivatives of the functions will in general differ at any given point. In such a practical case, we need what help can be obtained from rational equations.

In these equations T_0 is an arbitrary standard temperature, in the present case 0°C., p_0 is the corresponding vapor pressure (obtained from a preliminary smoothing of the data in any convenient manner), and λ_0 is the latent heat at the same temperature and pressure. M is the modulus of logarithms, common logarithms being denoted by log. The constants A_0, B_0 and c are the constants of principal importance in the Beattie–Bridgeman equation of state[6] and have for ammonia the values 2.3930, 0.03415 and 476.87 $\times$ 10^4, respectively, the units being liters per mole, atmospheres and degrees centigrade absolute ($T = t + 273.13$).[7] Q is the conversion factor: 24.2122 cal$_{15}$/liter-atm.[8] T, p and λ are the variable temperature, vapor pressure, and corresponding value of the latent heat, respectively. C_p is the molal heat capacity of the gas and $\bar{c}$ is the partial molal heat capacity of ammonia in the solids (equal to one-eighth of the excess of the molal heat capacity of the octammine over that of the barium chloride),[3] both at the constant pressure p_0. $\bar{v}$ is the partial volume of ammonia in the solids (equal to one-eighth of the excess of the molal volume of the octammine over that of the barium chloride). When equation (3) is applied to data in the manner previously discussed, λ_0 and $C_p - \bar{c}$ will be found in liter-atmospheres, and may be converted into calories by multiplication by Q. In the use of equation (4) it will be convenient to take the heats and heat capacities in calories, and for R the value 1.9869 cal$_{15}$, except when R occurs in the denominator of a fraction containing a constant of the equation of state, when it should be taken as 0.08206.[9]

Equations (3) and (4) are based on the following assumptions: (1) the equation of state used for the gas is the Beattie–Bridgeman equation in the volume form;[10] (2) the difference of heat capacities $C_p - \bar{c}$ is constant at the pressure p_0; (3) the partial molal volume of ammonia in the solids $\bar{v}$ is constant; and (4) terms involving squares and cubes of the pressures p and p_0, arising from the equation of state but not appearing in equations (3) and (4), are negligible. Such terms were found to affect the pressure by not more than 0.03% in any instance and to have a negligible effect on the latent heats.

Equation (3) looks more complicated than equation (2), but the difference is largely due to the fact that equation (2) is not in a form suitable for the graphic treatment of data when the coefficient B is unknown.

Equation (3) was applied to our data. The quantity $\bar{v}$ was known as

[6] Beattie and Bridgeman, *Proc. Am. Acad. Arts Sci.*, **63**, 229 (1928); THIS JOURNAL, **50**, 3133 (1928).

[7] Beattie and Lawrence, THIS JOURNAL, **52**, 6 (1930); Beattie and Bridgeman, *Z. Physik*, **62**, 95 (1930).

[8] "International Critical Tables," **1926**, Vol. I, p. 24.

[9] This exception was unfortunately not mentioned in the previous discussion, page 163 of reference 3.

[10] Beattie, *Proc. Nat. Acad. Sci.*, **16**, 14 (1930).

21.53 cc./mole at 25°.[11] The quantities λ_0 and $C_p - \bar{c}$ were treated as adjustable constants and were determined by drawing a straight line as explained in reference 3. The value found for $C_p - \bar{c}$ is -7.050 cal., which corresponds to a value of $\bar{c}$ of about 16 calories per mole of ammonia in the solids. This appears to be a reasonable value, judging by the value $\bar{c} = 11$ calories per mole found for the system $AlCl_3 + AlCl_3 \cdot 6NH_3$, the only value obtainable from data for ammines reported in "International Critical Tables."[12] The value for λ_0 is 9074.0 cal$_{15}$ per mole of ammonia, which may be compared with 9141, the value according to the simple equation (1).

The pressures thus calculated are entered as "calcd. (B)" in Table I. The average percentage deviation is 0.15. This may not seem to be a great improvement over equation (1), but the deviation for every point is less by equation (3) than by equation (1), provided that we do not count three cases in which equation (1) is closer by a negligible amount, 0.03% or less. A deviation plot shows that equation (1) fails to represent the slope at the higher temperatures, whereas equation (3) gives much improvement. Hence the latent heats calculated from equation (3) (by means of equation (4) should be much better than those calculable from equation (1), even if in the latter case an exact value of the volume change is computed for use in the Clapeyron equation.

As regards the data obtained by Hüttig and Martin for lower tempera-

TABLE I

OBSERVED DECOMPOSITION PRESSURES IN ATMOSPHERES AND THOSE CALCULATED (A) BY EQUATION 1 AND THOSE CALCULATED (B) BY EQUATION 3. THE PERCENTAGE DEVIATION = 100 (OBS. − CALCD.)/OBS.

t	Obs.	Calcd. (A)	% Dev.	Calcd. (B)	% Dev
0	0.6576	0.6576	0.00	0.6576	0.00
7.48	1.031	1.030	.00	1.031	.00
9.28	1.148	1.144	.35	1.144	.35
11.95	1.337	1.332	.37	1.333	.30
14.95	1.574	1.576	−.13	1.576	−.13
19.92	2.063	2.066	−.15	2.066	−.15
38.28	5.195	5.215	−.38	5.205	−.19
40.40	5.747	5.762	−.26	5.753	−.10
42.10	6.209	6.237	−.45	6.228	−.31
44.00	6.797	6.807	−.15	6.800	−.04
46.00	7.471	7.455	.21	7.453	.24
46.52	7.637	7.632	.07	7.630	.09
46.78	7.726	7.721	.06	7.722	.05
48.07	8.200	8.181	.23	8.187	.16
49.95	8.916	8.891	.28	8.905	.12

The average percentage deviations are (A) 0.21, and (B) 0.15.

[11] Gillespie and Gerry (unpublished).
[12] "International Critical Tables," 1929, Vol. V, p. 95.

tures, reference to Table II shows that equations (1) and (3) are in practical agreement at these temperatures. The distribution of the percentage deviations is such as to suggest that the fault lies in the experimental values. At lower temperatures it appears more difficult to obtain equilibrium. This interpretation is suggested also by the deviation plots of our own data.

TABLE II

OBSERVED DECOMPOSITION PRESSURES IN MILLIMETERS OF MERCURY AT LOWER TEMPERATURES (HÜTTIG AND MARTIN) AND THOSE CALCULATED (A) BY EQUATION 1, AND THOSE CALCULATED (B) BY EQUATION 3.   EQUATIONS 1 AND 3 GIVE 499.8 MM. AT 0°

t	Obs.	Calcd. (A)	% Dev.	Calcd. (B)	% Dev.
0	500	500	0	500	0
−10.8	287	250	13	249	13
−15.0	193	188	3	187	3
−15.5	189	181	4	180	5

In Table III are given values of the decomposition pressures and the latent heats for every ten degrees from 0 to 50° centigrade, as well as for 25°, as calculated from equations (3) and (4). The calculations of the heats were checked by the method already outlined.[3]

TABLE III

DECOMPOSITION PRESSURES IN ATMOSPHERES AND LATENT HEATS IN 15° CALORIES, CALCULATED FROM THE DATA BY MEANS OF EQUATIONS 3 AND 4

t..............	0	10	20	25	30	40	50
Pressure.........	0.658	1.193	2.074	2.696	3.476	5.646	8.925
Heat............	9074	8990	8901	8853	8804	8696	8575

Summary

The decomposition pressures of the system $BaCl_2 \cdot 8NH_3$–$BaCl_2$–NH_3, were measured from 0 to 50° with an average precision of about 0.2%. The results were interpreted by means of a vapor pressure equation previously derived,[3] which can be regarded as the equation $\log p = A - B \log T - c/T$ with added terms for the deviation of ammonia gas from the ideal gas law.

Interpolated values for the pressure and calculated values of the corresponding latent heat of decomposition are given in Table III.

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