unit area $(-S^s/a)$. Those investigators point out that surface heat content per unit area is a constant and independent of temperature, if the temperature coefficient of surface tension is constant for the molten salts. The present authors hoped to test the applicability of this concept to the lead molybdate–bismuth molybdate system. However, they are unable to use the concept because the temperature coefficient of surface tension is not invariant for some of the mixtures of their system.

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Vapor Pressure of Ammonium Nitrate

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FEICK(1) determined the vapor pressure of liquid ammonium nitrate from 190° to 270° C. using a modified boiling point apparatus. He showed that, at these temperatures, ammonium nitrate vaporizes by dissociation:

$$NH4NO_3(l) \rightleftarrows NH_3(g) + HNO_3(g)$$

The object of this investigation was to extend the work of Feick on liquid ammonium nitrate to lower temperatures and to determine the vapor pressure of the solid.

EXPERIMENTAL

The vapor pressure was measured by a transpiration method based on the relationship first derived by Regnault (5).

$$p = Pv/V$$

where p is the vapor pressure in millimeters, P the barometric pressure in millimeters, v the volume in liters of ammonia and nitric acid produced by the dissociation of ammonium nitrate, and V the total gas volume in liters.

A known volume of dry gas (air or nitrogen) was passed slowly over the heated sample (10 to 30 grams) of C.P. ammonium nitrate, then through an air-cooled condensation trap filled with glass wool, and successively through a solid carbon dioxide trap and a wet-test meter. Experiments were of 1 to 120 hours' duration. The temperature of the furnace was controlled by means of a Thermocap relay. The sample temperature was separately measured by a Chromel-Alumel thermocouple placed directly over the sample.

Repeated runs at different flow rates produced only small differences in vapor pressure and no consistent pattern in these differences other than that of experimental error. Calculations indicated that the carrier gas became saturated with ammonium nitrate in a fraction of a second. For solid ammonium nitrate, the gain in weight of the condensation trap (after the contents had been dried in vacuo at room temperature) was essentially equal to the weight loss of the sample, which was taken as the weight of vaporized ammonium nitrate. For liquid ammonium nitrate the weight gain in the condensation trap was less than the sample weight loss, this difference in weight being taken as the amount decomposed. The loss due to decomposition ranged from 0.12% of a 15-gram sample in 6 hours at 170° C. to 15% of the sample in 40 minutes at 240° C. With liquid ammonium nitrate virtually all of the water vapor resulting from the decomposition was retained by the system, part by the condensed ammonium nitrate, and the remainder by the solid carbon dioxide trap. Since this water vapor also made up part of the gas volume above the ammonium nitrate and was not measured by the wet-test meter, its volume was calculated from the amount of decomposed ammonium nitrate and used to correct the vapor pressure calculations. In addition, a method of iteration was used to correct for the period of time the sample was warming to temperature. The vapor pressures were calculated on the assumption that the ammonium nitrate dissociated completely to nitric acid and ammonia

Table I. Vapor Pressure of Solid and Liquid Ammonium Nitrate

State	Temp., ° C.	Vapor Pressure, Mm. Hg	No. of Expts.
Solid	76	0.0024	14
	98	0.0133	12
	100	0.0154	13
	109	0.0283	6
	111	0.0368	4
	123	0.0738	13
	130	0.126	8
	138	0.219	4
	143	0.289	4
	148	0.448	11
	160	0.958	2
	165	1.17	2
Liquid	170	1.40	2
	180	2.51	2
	190	3.69	2
	200	6.31	2
	210	9.05	2
	220	12.3	2
	230	22.1	2
	240	33.4	7

on vaporizing and that only nitrous oxide and water were produced when the salt decomposed.

DISCUSSION OF RESULTS

The vapor pressures averaged for the several experiments run at each temperature are given in Table I. In Figure 1, the points were drawn as two straight lines, one covering the liquid phase and the other the three solid phases of ammonium nitrate covered by this study. The application of the method of least squares to the data yielded the following equations:

$$\text{Solid.}\quad \log p\ (\text{mm.}) = 10.708 - 4670/T$$

$$\text{Liquid.}\quad \log p\ (\text{mm.}) = 9.981 - 4360/T$$

with an estimated standard deviation of 0.031 in each case. Heats of vaporization calculated from the slopes are 42.7 and 39.9 kcal. per mole, respectively, for the solid and the liquid, the latter being in agreement with Feick's work. These may be compared with the values for the heats of dissociation of solid and liquid ammonium nitrate calculated from the published heats of formation at 25° C. for $NH_3(g)$ (*4*), $HNO_3(g)$ (*2*), and $NH_4NO_3(IV)$ (*4*). From the foregoing and heat capacity and heat of transition data published by Kelley (*3*), the following values were calculated for the heats of dissociation:

42.1 kcal. per mole for solid at 115° C.

39.0 kcal. per mole for liquid at 200° C.

The above temperatures are the mid-points of the data for the solid and liquid, respectively.

The agreement between experimental heats of vaporization calculated from vapor pressures and literature values from thermodynamic data on heats of dissociation supports the assumption that the solid also vaporizes by dissociation into ammonia and nitric acid. A further confirmation of this mechanism was demonstrated by passing ammonia with nitrogen through a sample of ammonium nitrate in the apparatus described. When this was done, with both solid and liquid ammonium nitrate, the weight loss per liter of nitrogen passed through the sample was reduced to a fraction of its magnitude in the absence of ammonia. In several runs at 220° to 260° C., nitric acid vapor was passed through liquid ammonium nitrate. Again vaporization was suppressed, judging by the weight of ammonium nitrate recovered in the trap; however, nitric acid accelerated the irreversible decomposition reaction.

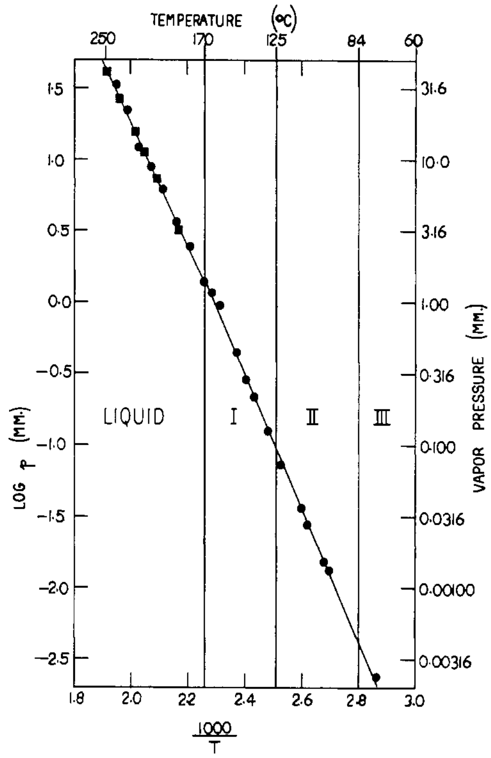

Figure 1. Vapor pressure of ammonium nitrate as a function of temperature

● Experimental data

■ Feick's data

T. ° K.

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