XLII.—*The Vapour Density and Pressure of Ammonium Iodide.*

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THE first determinations of the vapour density of ammonium iodide vapour were carried out by Deville and Troost (*Compt. rend.*, 1859, **49**, 255; 1863, **56**, 891), who found that the unsaturated vapour was 96% dissociated at 440° and 80% at 860°. No further values were available until Smith and Lombard (*J. Amer. Chem. Soc.*, 1915, **37**, 2055) determined the density of the saturated vapour between 300° and 380°. Their figures indicate that there is only slight dissociation above 340°, and that there is actually association below this temperature. Similar work for ammonium chloride and bromide has been shown to be inaccurate (Braune and Knoke, *Z. physikal. Chem.*, 1928, **135**, 49; Smits and Purcell, J., 1928, 2936; Smits and de Lange, *ibid.*, p. 2944), and since trustworthy values were required in connexion with the work on intensive drying it was thought necessary to redetermine the vapour densities.

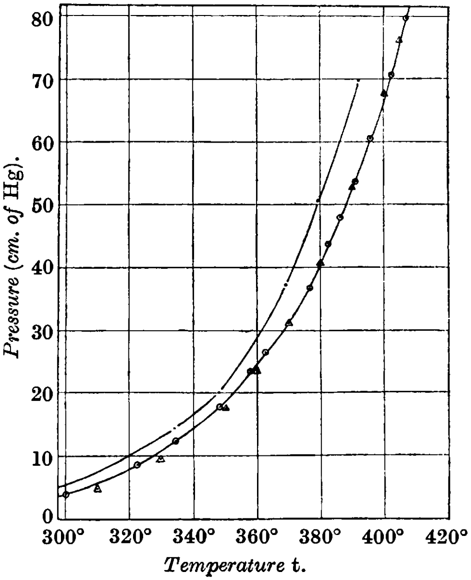
The vapour pressure of ammonium iodide has been determined by Johnson (*Z. physikal. Chem.*, 1908, **65**, 36) and by Smith and Calvert (*J. Amer. Chem. Soc.*, 1914, **36**, 1363). The differences in the values they recorded were considerable, amounting to more than 12 cm. at the higher temperatures. Smith and Calvert attributed this to the use of a sealed apparatus by Johnson, which, they maintained, would cause the further dissociation, $2HI = H_2 + I_2$, to affect his measurements. Johnson had, however, shown that the rate of formation of iodine was small compared with his rate of working. The results described subsequently agree very well with those of Smith and Calvert, but were obtained in a sealed apparatus. Consequently, it is more probable that the difference was due to some impurity in the sample of salt used by Johnson.

The experimental method used in this research was identical with the second one used by Smits and his co-workers (*locc. cit.*) for ammonium bromide and chloride. The ammonium iodide used was a sample of the purest salt supplied by E. de Häen. It was further purified by sublimation in high vacuum. If the salt was heated to 200° in an electric furnace and was thoroughly dry, there was hardly any decomposition, as was shown by the fact that only a trace of iodine collected in the liquid-air trap. The product was powdered and stored over solid potash.

Preliminary experiments, carried out with an excess of salt, showed that the rate of decomposition of hydrogen iodide was negligible if the apparatus had been carefully cleaned and the water removed from the glass walls, prior to filling, by heating to dull redness in a stream of dry oxygen. Consequently, this precaution was always taken. The salt was weighed in through a side tube in a counter-stream of dry gas, and the tube melted off, the apparatus re-evacuated, and finally sealed off from the pumps (for details, see Smits and Purcell, *loc. cit.*).

The vapour pressure was first determined in an apparatus of approximately 30 c.c. capacity containing an excess of ammonium iodide. The results of these measurements are given in Table I and plotted in Fig. 1, and they are seen to be in good agreement with those of Smith and Calvert. The pressures, at the lower temperatures, obtained at the end of the experiment agree with those taken at the beginning, thus showing that there was no appreciable formation of iodine. Also the experiment was carried out in a fused-salt bath in a 4-litre Pyrex beaker so that any iodine vapour could have been readily seen; actually, none was observed. Hence the slight difference between our values and those of Smith and Calvert at lower temperatures cannot be ascribed to this cause. The log p–$1/T$ curve is shown in Fig. 2. It will be seen that the points lie on a straight line, indicating that the molecular complexity does not change with temperature.

Fig. 1.



• *Johnson.* △ *Smith and Calvert.*
⊙ *Present authors.*

In the tables, the pressure p is given in cm. of mercury, t is the temperature (in °C.), and T the absolute temperature.

TABLE I.

p.	*t.*	*p.*	*t.*	*p.*	*t.*	*p.*	*t.*
4·0	299·1°	36·4	376·8°	70·5	402·5°	20·4	352·3°
5·8	310·3	43·6	382·6	60·4	395·8	12·3	334·5
13·8	339·2	48·6	386·4	47·9	386·4	8·5	322·4
17·8	348·5	53·6	399·1	42·8	381·6	6·1	311·2
23·4	357·9	60·7	395·8	26·3	362·6		

A series of determinations of the vapour density of the saturated vapour between 340° and 400° was then carried out. The results of these experiments are given in Tables II—VI. The volume, V, of the apparatus and the weight, W, of the ammonium iodide introduced are also recorded. The volume was obtained by weighing the apparatus dry and also when full of water, and is correct to 0·1 c.c.

TABLE II.

p.	t.	$\log p$.	$1/T \cdot 10^6$.	p.	t.	$\log p$.	$1/T \cdot 10^6$.
8·3	323·1°	0·919	1678	13·9	351·4°	1·143	1602
9·6	325·7	0·982	1670	13·8	347·8	1·140	1611
10·8	332·1	1·033	1653	13·7	342·0	1·137	1626
13·9	347·8	1·143	1611	13·4	337·6	1·127	1638
14·2	356·2	1·152	1589	10·4	328·9	1·017	1661

(V = 314·7 c.c.; W = 0·0809 g.)

TABLE III.

p.	t.	$\log p$.	$1/T \cdot 10^6$.	p.	t.	$\log p$.	$1/T \cdot 10^6$.
11·8	334·6°	1·075	1646	26·1	375·9°	1·417	1541
17·4	348·3	1·241	1610	25·6	366·4	1·408	1564
24·2	359·3	1·384	1581	25·6	364·9	1·408	1568
26·6	385·4	1·425	1519	25·5	363·1	1·407	1572
27·1	394·0	1·433	1499	21·7	355·9	1·336	1590
27·3	402·9	1·436	1480	14·7	342·0	1·167	1626

(V = 310·0 c.c.; W = 0·1467 g.)

TABLE IV.

p.	t.	$\log p$.	$1/T \cdot 10^6$.	p.	t.	$\log p$.	$1/T \cdot 10^6$.
25·1	361·4°	1·400	1576	41·5	408·8°	1·618	1467
30·2	367·7	1·480	1561	40·9	399·6	1·612	1487
39·8	385·4	1·600	1519	39·8	380·2	1·600	1531
40·6	395·8	1·609	1495	37·7	376·6	1·576	1539
41·1	405·7	1·614	1473	18·3	348·9	1·262	1608

(V = 579·7 c.c.; W = 0·4083 g.)

TABLE V.

p.	t.	$\log p$.	$1/T \cdot 10^6$.	p.	t.	$\log p$.	$1/T \cdot 10^6$.
66·6	410·0°	1·823	1464	61·8	397·0°	1·791	1493
67·6	419·6	1·830	1444	55·6	392·2	1·745	1503
65·2	399·7	1·814	1487				

(V = 314·7 c.c.; W = 0·3575 g.)

TABLE VI.

p.	t.	$\log p$.	$1/T \cdot 10^6$.	p.	t.	$\log p$.	$1/T \cdot 10^6$.
64·5	397·2°	1·810	1492	88·7	436·1°	1·948	1410
79·7	406·8	1·901	1471	89·2	440·0	1·950	1403
85·3	415·9	1·931	1452	84·1	410·1	1·925	1464
87·0	426·5	1·940	1430				

(V = 314·0 c.c.; W = 0·4495 g.)

When the above values of $\log p$ and $1/T$ are plotted, a straight line is obtained for the points corresponding to saturated vapour which is cut by five other lines which correspond to the unsaturated vapour in the various experiments. From the points of intersection, the temperature and pressure of the just-saturated vapour can be found accurately, and from these the vapour density is calculated from the formula

$$\text{Vapour density} = \tfrac{1}{2}M = \tfrac{1}{2} \times 22{,}400 \times 76WT/273Vp.$$

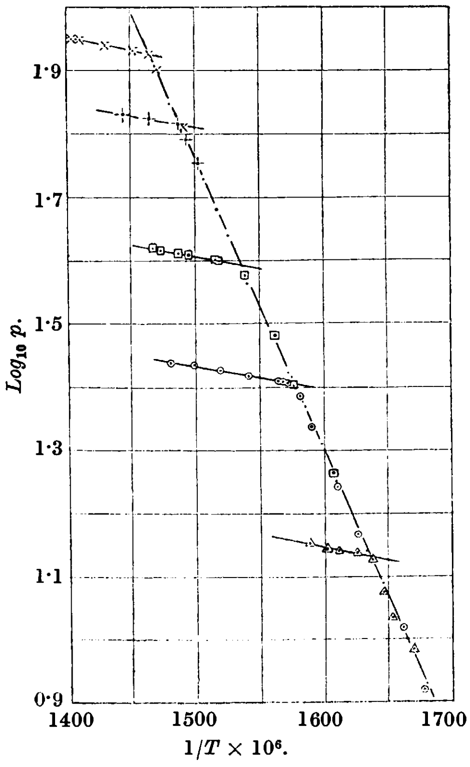
The values calculated from this formula are :

Experiment	II	III	IV	V	VI	
Vapour density	36·1	36·4	36·2	36·5	36·1.	Mean, 36·26.

Calc. for NH_3 + HI, 36·24.

The divergence of the results from the theoretical value required for complete dissociation is very small and within the limits of experimental error. It may consequently be concluded that up to 400° the vapour of ammonium iodide is always completely dissociated.

FIG. 2.



Points from Table II △, *Table III* ⊙, *Table IV* ▣, *Table V* +, *Table VI* ×.

It is of interest to note that no tendency was observed for the ammonium iodide to be adsorbed on the glass walls, as was the case with ammonium bromide. Near the point where the vapour becomes unsaturated there was always a tendency for the vapour pressures to be low owing to the slowness with which the last particles of salt evaporate. In spite of this and of the fact that rather rapid working was desirable at the higher temperatures, none of the points was more than a few mm. below the normal vapour-pressure line.

Since Q is not a temperature function we are justified in applying the well-known thermodynamical relationship, $d\log_e p/dT = Q/RT^2$, or $d\log_e p/d(1/T) = -Q/R$. From Fig. 2 we find that $\log_{10}p = -4616{\cdot}5.1/T + 8{\cdot}67$, and hence $Q/R =$

4616·5 × 2·303, or $Q = 21{\cdot}1 \times 10^3$ cals. for $\frac{1}{2}$ g.-mol. of ammonium iodide. Hence the value per g.-mol. is $42{\cdot}2 \times 10^3$ cals., whereas Johnson obtained the value $43{\cdot}5 \times 10^3$ cals.

Summary.

The pressure and density of saturated ammonium iodide vapour have been redetermined, and it has been shown that the vapour is completely dissociated at all temperatures up to 400°.

In conclusion, the authors wish to thank Professor Smits, in whose laboratory these experiments were carried out, for his kind interest in this work.

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