CCCLXXXVII.—*Determination of the Pressure and Density of Moist, Saturated Ammonium Chloride Vapour.*

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IN the course of our study of the influence of intensive drying on the pressure and density of saturated ammonium chloride vapour by means of the densi-tensimeter (this vol., p. 2409), we required, as in the case of ammonium bromide (Smits and Purcell, preceding paper), accurate data for the moist material, and as Braune and Knoke (*Z. physikal. Chem.*, 1928, **135**, 49) have recently described experiments on this subject, we thought it desirable to publish this part of our study at once.

For the solution of the " ammonium chloride problem," it was necessary to determine the vapour pressure of the solid and the density of the saturated vapour simultaneously, and this is rendered possible by our densi-tensimeter. In previous determinations of the density of the saturated vapour, the vapour pressure of the solid was measured first, and the density was subsequently found either by sealing off a bulb of the same apparatus (Johnson, *ibid.*, 1908, **61**, 457), or by use of a separate apparatus, care being taken that the apparatus was filled with the saturated vapour (Smith and Lombard, *J. Amer. Chem. Soc.*, 1915, **37**, 38). As already explained (Smits and Purcell, *loc. cit.*), however, the possibilities of error in such determinations are considerable, for the density bulb which must be sealed off may never have been at a lower temperature than the bulb with the solid ammonium chloride. Johnson intentionally kept the density bulb at a slightly higher temperature than the solid substance. On the other hand, Smith and Lombard wished to determine the density of the completely saturated vapour, and therefore tried to keep the bulb containing solid ammonium chloride and the density bulb at exactly the same temperature; Smits and Purcell, however, adduced a reason why these authors did not succeed in the case of ammonium bromide, and it is now shown that their results for ammonium chloride also are incorrect, probably for a similar reason. Braune and Knoke tried to avoid the difficulty. They first determined the pressure of the saturated vapour in an apparatus of known volume, and after the solid substance had disappeared and the vapour had become unsaturated, they continued the pressure reading at different temperatures. Then all the salt was condensed in a bulb which was sealed off, and the quantity of salt was thus determined. They therefore found the density of almost saturated and of less saturated vapour.*

Our purpose was to find the density of the completely *saturated* vapour by the two different methods described by Smits and Purcell (*loc. cit.*).

In the second method (the " extrapolation method "), it was shown that any error introduced by adsorption of vapour on the wall of the density bulb could be detected and an appropriate correction made in the density.

Experiments with the Densi-tensimeter.

We used two baroscopes, A and B, which correspond respectively to Figs. 2 and 3 given in the description of this apparatus (this vol., p. 2409), and the method by which they are sealed to the

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* Braune and Knoke did not use the glass-spring indicator, the zero position of which, as we stated long ago, is independent of temperature, but they used a glass spiral, of which the position is influenced by temperature, so they were obliged to apply a correction.

The vapour pressures indicated in their tables as " Dissoziations-drucke " are much too low.

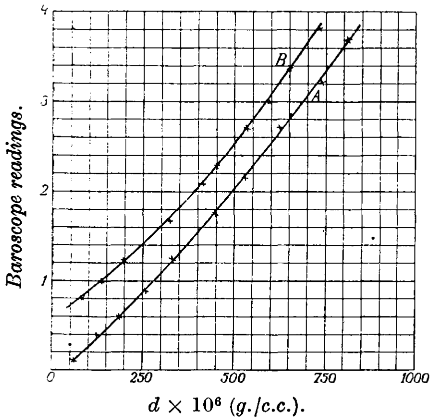
vapour-pressure apparatus with the glass-spring indicator is shown in the paper of Smits and Purcell (Fig. 2), where details of the method of using the apparatus are also to be found.

The two baroscopes were calibrated at different temperatures as already described. The data for baroscope A are those already given; those for B are in Table I, and the two calibration curves are shown in Fig. 1. The vapour densities are calculated from the densities (d; in g./c.c.) read from the calibration curves by the formula :

$$D = \tfrac{1}{2}M = 224 \times 76dT/2 \times 273p = 31{\cdot}18dT/p.$$

After the necessary preliminary operations, a number of simultaneous readings were made at temperatures between 254° and 353°. The densities were read from the calibration curve and the vapour densities calculated. A few of the results are shown in Table II, where p is given in cm. of mercury; the other points are included in Figs. 2 and 3. Both baroscopes give identical results, and since the theoretical value for complete dissociation is $\frac{1}{4} \times 53{\cdot}5 = 13{\cdot}4$, it follows that the saturated vapour in the temperature range 280—340° is completely dissociated.

FIG. 1.



When $\log p$ is plotted against $1/T$, the points marked ⊙ in Fig. 2 are obtained. These points lie on a straight line, which shows that Q_{SG} is not a temperature function within the range investigated. This result is in complete agreement with the density

TABLE I.

Baroscope B.

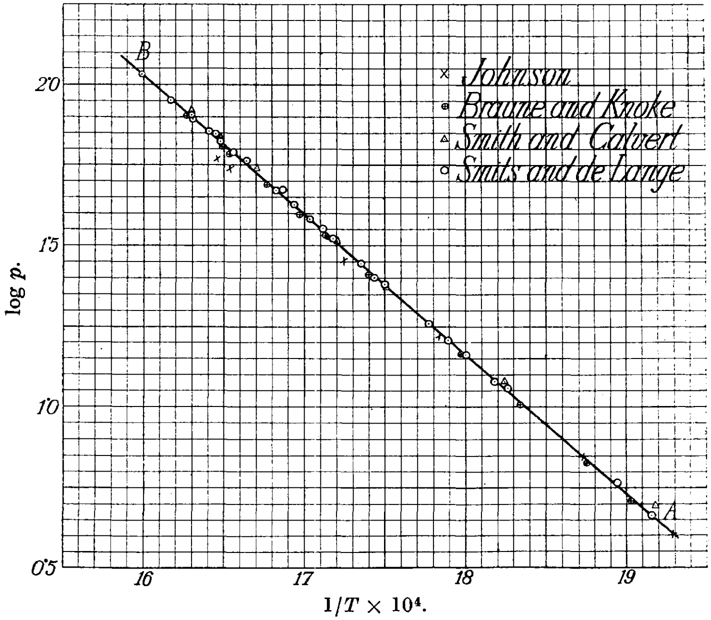
Temp. 100°.		265°.		311°.	
Baroscope reading.	$d \times 10^6$.	Baroscope reading.	$d \times 10^6$.	Baroscope reading.	$d \times 10^6$.
3·72	702	3·81	732	3·36	651
2·95	581	3·00	597	3·11	608
2·70	533	2·59	520	2·61	524
2·08	415	1·78	335	2·28	450
1·73	335	1·23	196	1·67	321
0·99	135	1·01	130	1·14	173
0·91	116	0·91	113	0·80	83

TABLE II.

Vapour densities of damp ammonium chloride.

Temp.	T.	$10^6/T$.	p.	$\log_{10} p$.	Baroscope reading.	$d \times 10^6$.	D.
			Baroscope A.				
254·9°	527·9	1894	5·87	0·769	—	—	—
303·4	576·4	1735	27·95	1·446	—	—	—
311·5	584·5	1711	35·84	1·554	0·91	269	13·6
320·2	593·2	1686	47·10	1·673	1·29	347	13·5
328·5	601·5	1663	58·00	1·763	1·62	414	13·3
335·4	608·4	1644	70·18	1·846	2·04	500	13·4
341·0	614·0	1629	80·43	1·905	2·38	570	13·5
352·6	625·6	1598	108·13	2·034	—	—	—
			Baroscope B.				
277·0	550·0	1818	12·02	1·080	—	—	—
282·4	555·4	1800	14·58	1·164	0·94	116	13·7
289·8	562·8	1777	18·22	1·261	1·02	141	13·5
300·7	573·7	1743	25·29	1·403	1·19	189	13·3
314·1	587·1	1703	38·16	1·582	1·55	284	13·5
346·0	619·0	1616	89·25	1·951	—	—	—
						Mean	13·48

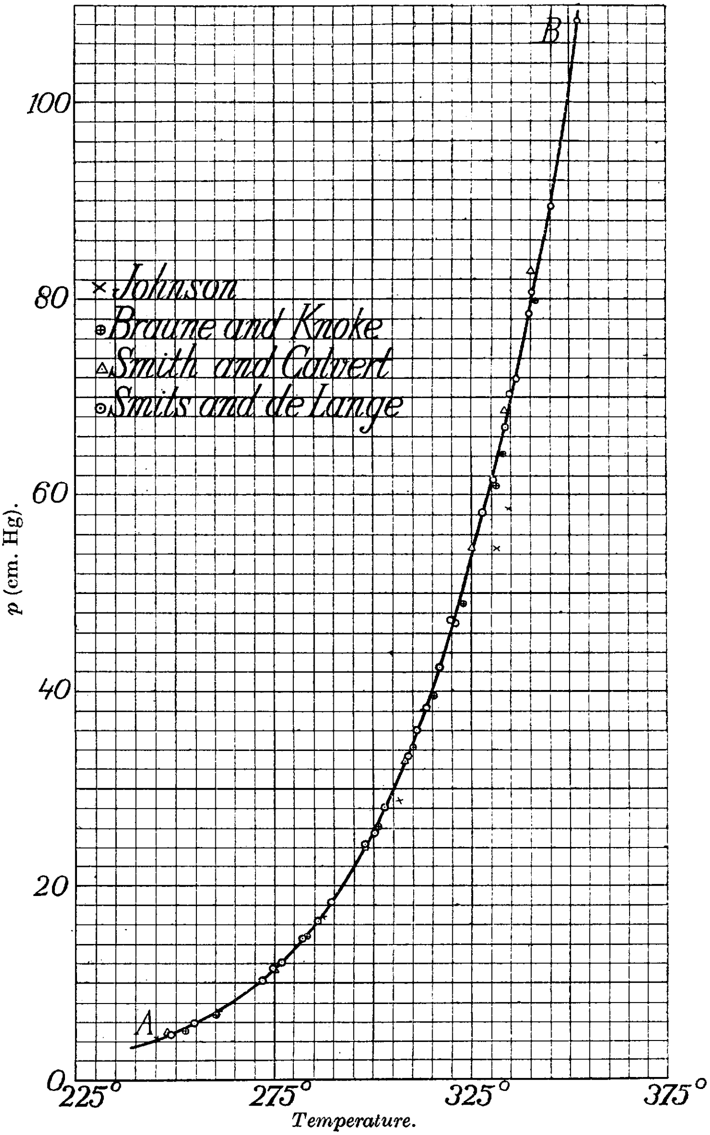
FIG. 2.



determinations, corresponding with practically total dissociation. In Fig. 3 the vapour pressure is plotted against the temperature, again marked ⊙.

The extrapolation method for the determination of the vapour density was then used in order to find whether adsorption occurred, and if so, to what extent. A vapour-pressure apparatus of known

FIG. 3.



volume was therefore filled with a known weight of ammonium chloride, highly evacuated, and the bridge sealed off. The pressure of the saturated vapour was measured first and then the Boyle-Gay-Lussac line, or the curve of the unsaturated vapour. The point of intersection of the lines obtained by plotting log p against $1/T$ enables the vapour density of the just-saturated vapour to be calculated.

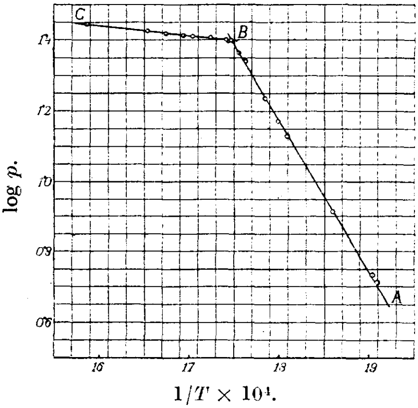
Two series of experiments were carried out with a quartz-apparatus with both rising and falling temperatures, and readings were recorded only after the vapour pressure at any one temperature had been constant for an hour. The results are in Table III.

TABLE III.

Temp.	T.	$10^6/T$.	p.	$\log_{10} p$.	Temp.	T.	$10^6/T$.	p.	$\log_{10} p$.
251·0°	524·0	1909	5·20	0·716	280·2°	553·2	1808	13·51	1·131
264·9	537·9	1859	8·26	0·917	300·6	573·6	1743	24·96	1·397
317·5	590·5	1693	25·96	1·414	314·3	587·3	1703	25·72	1·410
331·9	604·9	1653	26·68	1·426	300·5	573·5	1745	25·14	1·400
357·4	630·4	1586	27·89	1·445	294·6	267·6	1762	21·95	1·341
324·8	597·8	1673	26·22	1·419	287·6	560·6	1784	17·81	1·236
307·5	380·5	1723	25·57	1·408	296·6	569·6	1755	23·10	1·364
					301·5	574·5	1741	25·18	1·401
					283·2	556·2	1798	14·87	1·172
					252·3	525·3	1904	5·46	0·787

When log p is plotted against $1/T$, two straight lines (Fig. 4) are obtained; these intersect in a point such that log $p = 1·399$ and $1/T = 0·001746$, *i.e.*, $p = 25·06$ cm. and $T = 572·7$. Since the volume of the apparatus was 314·7 c.c. and the weight of ammonium chloride 59·6 mg., the density is *13·4*, which is just the theoretical value for complete dissociation, whereas the densi-tensimeter gave *13·48*.

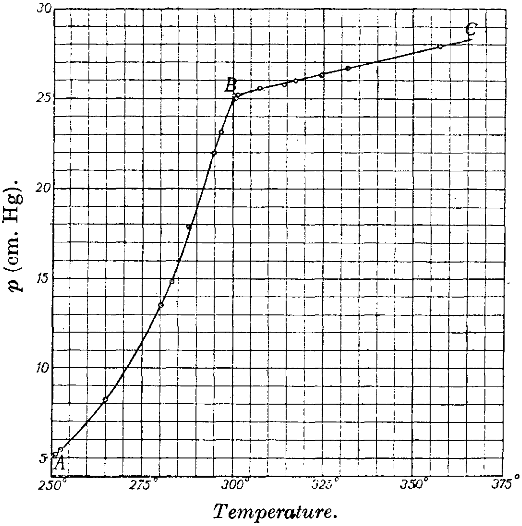
FIG. 4.



These determinations were also important in deciding whether there was any perceptible adsorption by the quartz wall, as in the case of ammonium bromide. From Fig. 4, and also from Fig. 5, in which p is plotted against temperature, it is seen that if a continuous change of one line into the other exists at all it can only occur over an exceedingly small range of temperature, and hence, unlike the bromide, ammonium chloride is not perceptibly adsorbed by the quartz wall, and the same remarks apply to glass. This explains why both forms of the baroscope (A and B) gave exactly the same results (Table II).

The points derived from other workers' determinations of the vapour pressure have been inserted in Figs. 2 and 3. It will be noted that the values of Johnson are not very correct; those of Smith and Calvert (*J. Amer. Chem. Soc.*, 1914, **36**, 1363) and of Braune and Knoke are much better. If Smith and Calvert had plotted a curve as in Fig. 2, they would have found that their points lie on a straight line, and hence that the heat of evaporation is not a temperature function and the degree of dissociation could not change appreciably, unless the heat of dissociation were very small, which is known not to be the case. Consequently, before we started our vapour-density determinations it was already almost certain that practically complete dissociation would be found. Smith and Lombard (*loc. cit.*), however, found a dissociation varying from 55·5 to 63·6% in the temperature range 280—333°.

FIG. 5.



Earlier workers, *viz.*, Deville and Troost (*Ann. Chim. Phys.*, 1860, **58**, 257; *Compt. rend.*, 1859, **49**, 242), Ramsay and Young (*Phil. Trans.*, 1886, **177**, 99), and Pullinger and Gardner (P., 1891, **7**, 2), applying respectively the methods of Dumas, Hofmann, and Victor Meyer, found degrees of dissociation of 82—98% between 280° and 400°, but Smith thought that the difference between these values and his own was due to the fact that most of the earlier determinations related to unsaturated vapour and that, in consequence of the slow evaporation, the Victor Meyer method did not give exact results, owing to diffusion before the reading could be taken.

Similarly, Smith contended that other high degrees of dissociation (*e.g.* 100% and 91% at 350°, Baker, J., 1894, **65**, 611; 95% at 380°, Gutmann, *Annalen*, 1898, **299**, 282; 98% at 322°, Johnson, *loc. cit.*) were due to the vapour being unsaturated in these cases also. Our determinations, carried out in two different ways, prove, however, that Smith and Lombard's density determinations must have been incorrect for reasons already given (Smits and Purcell, *loc. cit.*), and the measurements of Braune and Knoke, relating to vapours some of which were almost saturated, also indicated complete dissociation.*

Finally, the heat of evaporation and the constant C in the vapour-pressure formula $2{\cdot}303 \log_{10} p = -Q/RT + C$ can be calculated from our results by applying the methods used by Smits and Purcell (*loc. cit.*). From our graph we have

for $1/T_1 = 0{\cdot}001900, \log p_1 = 0{\cdot}735,$

and for $1/T_2 = 0{\cdot}001600, \log p_2 = 2{\cdot}025;$

hence $Q/R = 9903$, or $Q_{SG} = 19{\cdot}8 \times 10^3$ cals. This value refers to 1 g.-mol. of vapour, and since we have found that the vapour is completely dissociated, it corresponds to 0·5 g.-mol. of ammonium chloride, so the value for 1 g.-mol. is $(Q_{SG})_{NH_4Cl} = 39{\cdot}6 \times 10^3$ cals., whereas Johnson found $37{\cdot}8 \times 10^3$ cals. and Braune and Knoke $39{\cdot}4 \times 10^3$ cals.

Also, from the same data, $C = 20{\cdot}5$, and hence the vapour-pressure formula is

$$2{\cdot}303 \log_{10} p = -9903/T + 20{\cdot}5$$

whence the sublimation temperature (for $p = 76$) is $T = 612{\cdot}3°$ (339·3° C.).

Summary.

Using the latest form of the densi-tensimeter and also its immediate predecessor, the authors determined the pressures and densities of moist, saturated ammonium chloride vapour, as a preliminary to studying the influence of intensive drying on these properties.

Vapour-pressure determinations showed that the heat of sublimation is not a temperature function within the range 254—353°, and the density determinations give the explanation of this behaviour, for they show the dissociation of the saturated vapour to be practically complete over the same range of temperature. Similarly, complete dissociation was found by using the extrapolation method previously described.

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* The remarks of Braune and Knoke about the explanation of the behaviour of intensely dried ammonium chloride are incorrect. Our results with the moist material do not affect that explanation at all.

The authors conclude that the results of Smith and his collaborators, giving dissociations of about 60%, must be incorrect—probably for the same reason that their results for the vapour density of ammonium bromide are incorrect. The results of Braune and Knoke are in agreement with those of the authors.

The molecular heat of sublimation for 1 g.-mol. of ammonium chloride is calculated to be 39·6 × 10^3 cals., and from the derived vapour-pressure formula the sublimation temperature is calculated as 339·3°.

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