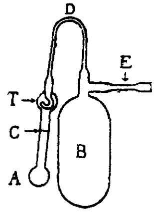
CCCLXXXVI.—*Determination of the Pressure and Density of Moist, Saturated Ammonium Bromide Vapour.*

By ANDREAS SMITS and RONALD PURCELL.

THIS investigation originated in the intention to apply the densitensimeter (this vol., p. 2409) to a study of the influence of intensive drying on the vapour pressure and density of ammonium bromide. The moist material was first reinvestigated in this apparatus, which enables the pressure and density to be determined simultaneously, and thus avoids a source of error occurring in experiments where the pressure is measured first and the density subsequently in a separate apparatus. For example, the method used by Smith and Lombard

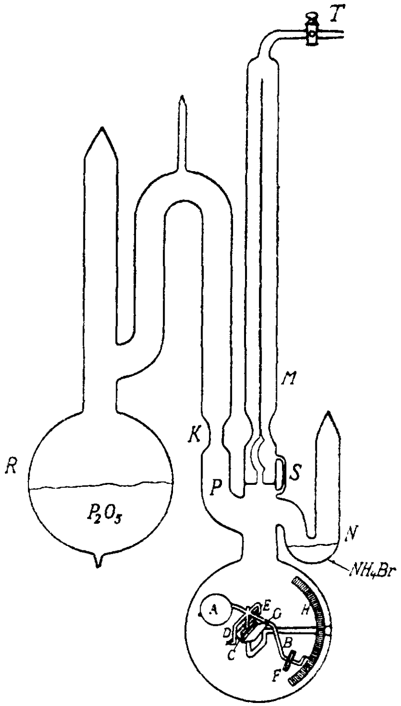
(*J. Amer. Chem. Soc.*, 1915, **37**, 38) is open to criticism unless it is certain that the large bulb, B (Fig. 1), was never at a lower temperature than the small one, A, while the apparatus was attaining the temperature of the bath; but since, in order to hold the apparatus firmly in the bath, the bulb was wired to an iron rod protected with asbestos paper, it is probable that when the capillary, D, was sealed some solid as well as vapour was in the bulb B. Any adsorption of vapour on the walls will introduce an error in the same direction, *i.e.*, giving too high a vapour density.

FIG. 1.



With the densi-tensimeter, it is possible to prevent solid being deposited on the surface of the baroscope by taking readings after the apparatus is cooled from a higher to a lower temperature. During the cooling, the silica baroscope is a little warmer than the outer glass wall of the flask, and consequently all salt sublimes on to the latter. Moreover, the newest baroscopes are so constructed that the error caused by adsorption is negligible.

FIG. 2.



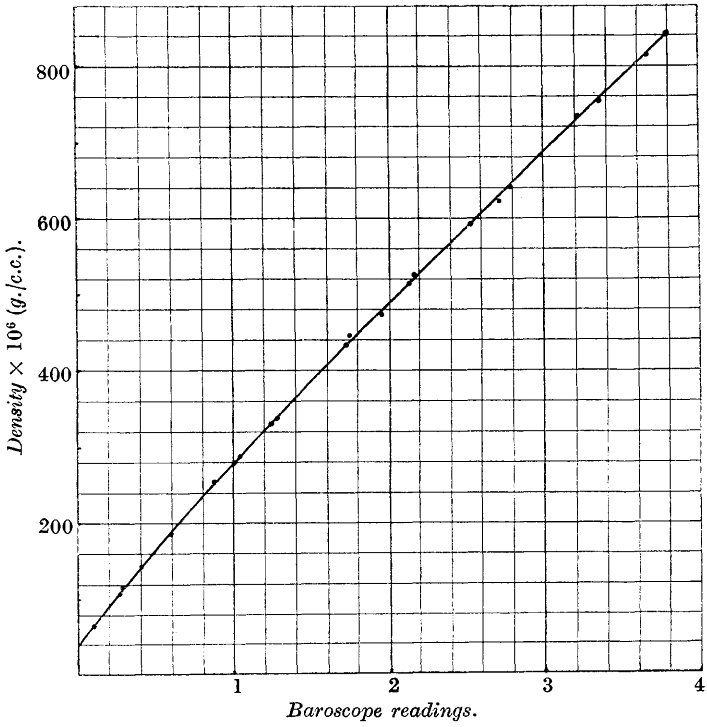
EXPERIMENTAL.

Fig. 2 shows the bulb containing the baroscope sealed to the glass-spring indicator. The figure also shows, however, a bulb with phosphoric oxide, which was not present in these experiments with the moist substance—in this case tube P was sealed off at K. This apparatus was cleaned with boiling nitric–chromic acid mixture, washed, steamed, and dried. The baroscope was then calibrated at 100°, 306°, and 394° by altering the pressure of the air in the instrument and reading the position of the pointer of the baroscope. The density (g./c.c.) of the air was then calculated and plotted against the baroscope readings, thus giving a calibration curve (see Table I and Fig. 3).

TABLE I.

Temp. 100°.		306°.		394°.	
Baroscope reading.	$d \times 10^6$.	Baroscope reading.	$d \times 10^6$.	Baroscope reading.	$d \times 10^6$.
3·80	845	3·72	820	3·68	819
3·22	737	2·71	624	3·36	756
2·52	596	1·95	476	2·78	642
2·16	527	1·28	336	2·13	517
1·75	447	1·04	288	1·72	439
1·25	330	0·60	184	1·42	372
1·01	280	0·40	142	0·88	257
0·27	108	0·10	61	0·28	114

FIG. 3.



After calibration, the apparatus was heated to near the softening point of the glass in a stream of dry oxygen. The ammonium bromide was introduced into the bend of the tube N (Fig. 2), which was then resealed, and the apparatus connected to the high-vacuum pump through tap T. After exhaustion, this tap was closed, and the thin tube, S (called the bridge), sealed off. The apparatus was placed vertically, and the zero position of the glass-spring indicator ascertained in the usual manner.

The apparatus was then placed in a bath of fused potassium and sodium nitrates contained in a 4-litre Pyrex-glass beaker. With suitable illumination, the position of the needle of the baroscope could be read with the aid of a small telescope. The beaker was placed over a large double-ring gas burner and surrounded by an asbestos hood, in which two holes were made to permit baroscope readings to be taken. Two large Bunsen burners, for regulation of the temperature, also passed through this hood.

The top of the hood was covered with asbestos board, through which passed the mantle of the densi-tensimeter, a resistance thermometer, and a stirrer. It was possible to detect a change of 0·005° with the thermometer, and the bath could be readily kept constant to within 0·1° during a reading by means of a specially designed stirrer with ball bearings, which was driven at 800 r.p.m. A number of simultaneous readings of the vapour pressure (p in cm. Hg) and baroscope positions were then made at temperatures between 330° and 400°. The results of these are given in Table II. The densities, d, were read from the calibration curve, and the vapour densities, $D(=\frac{1}{2}M)$, calculated from this, on the assumption that the gas laws were obeyed :

$$D = 22\cdot4 \times d \times T \times 760/(2 \times 273 \times p).$$

TABLE II.

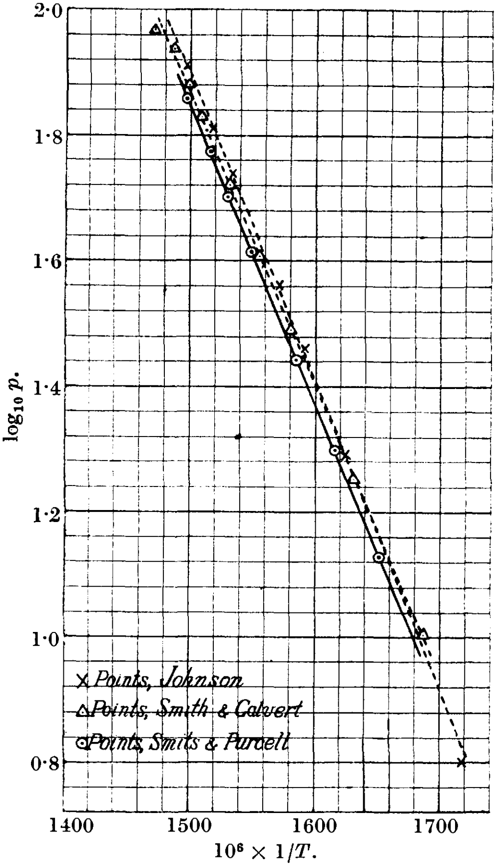
Results with damp ammonium bromide.

No.	Temp.	$10^6 \times 1/T$.	p.	$\text{Log}_{10}\, p$.	Baroscope readings.	$d \times 10^6$.	D.
1	331·8°	1651	13·4	1·1271			
2	345·6	1617	19·9	1·2987	0·88	250	24·2
4	357·7	1585	27·8	1·4442	1·29	340	24·0
5	364·3	1569	33·1	1·5195	1·52	394	23·7
6	372·1	1550	41·1	1·6137	1·91(?)	474	23·2(?)
7	380·7	1530	50·5	1·7021	2·52	590	23·8
8	386·7	1516	59·7	1·7759	2·95	680	23·4
9	395·0	1497	72·7	1·8613	3·67	820	23·5
						Average	23·7

When log p is plotted against $1/T$ (the reciprocal of the absolute temperature), the points on Fig. 4 are obtained. It will be seen that they lie on a straight line, thus showing that the heat of evaporation is not a function of temperature within the range investigated. This result is in agreement with the values of the densities in the last column, which correspond closely with complete dissociation, the calculated value being 24·5. It will be noticed, however, that the values found are even lower than this. An error in this direction will be introduced if there is any adsorption on the bulb of the baroscope, and, as shown later, there is sufficient adsorption to give such an error, but when this is eliminated, the result corresponds exactly with complete dissociation.

The above results are represented graphically in Fig. 5, where the vapour pressures are plotted against the temperature, the determinations by Smith and Calvert (*J. Amer. Chem. Soc.*, 1914, **36**, 1368) and by Johnson (*Z. physikal. Chem.*, 1908, **56**, 39) being inserted for reference. It will be noted that our values are slightly below those of the earlier workers. The vapour densities have been determined by Deville and Troost and by Smith and Lombard (*loc. cit.*). The former found complete dissociation at 440° and 860°, whilst the latter found a *change from* 48% *dissociation at* 300° *to* 10% *at* 390°. The measurements of Smith and his co-workers would seem to be beyond criticism, but closer consideration shows that an error must have been introduced, for when the logarithms of their vapour pressures are plotted against $1/T$ a straight line is obtained (see Fig. 4). This indicates that the heat of evaporation is *not* a temperature function, and hence that the degree of dissociation cannot change appreciably unless the heat of dissociation is very small; but since this is known not to be the case, most probably the dissociation is complete. Hence it was thought that Smith and Lombard's density determinations were incorrect, and an independent method of checking the results was sought.

FIG. 4.



We therefore determined the vapour density in yet another way, namely, by what we called the "extrapolation method." A vapour-pressure apparatus of known volume was filled with a known weight of ammonium bromide, highly evacuated, and the bridge sealed off. The vapour density could be determined by measuring first the pressure curve of the saturated vapour and then the Boyle–Gay-Lussac line or the curve of the unsaturated vapour, since, from the point of intersection of the lines obtained by plotting log p against $1/T$, the vapour density of the just-saturated vapour is readily calculated. Table III gives the results obtained with a glass apparatus and two other experiments with glass and quartz apparatus gave similar results. These three experiments carried out in this manner, with an apparatus of Durobax glass and quartz, gave the results in Table IV, in which the pressure and temperature refer to the points of intersection. These points had to be found by extending the two lines mentioned above, since experimentally we

FIG. 5.

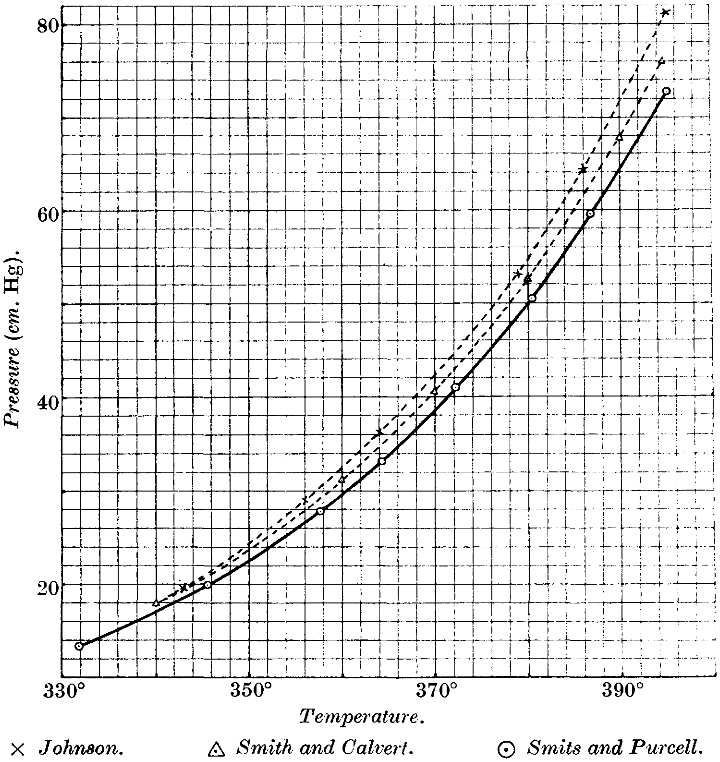


TABLE III.

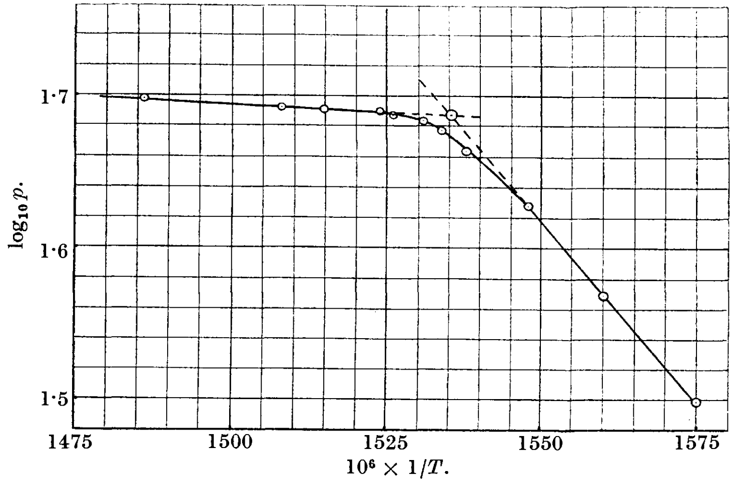
Vapour pressures and temperatures (Expt. 1; glass apparatus).

Temp.	p.	$10^6/T$.	$\text{Log}_{10}\,p$.	Temp.	p.	$10^6/T$.	$\text{Log}_{10}\,p$.
362·0°	31·5	1575	1·4983	381·5°	48·7	1526	1·6875
367·8	37·1	1560	1·5691	383·2	49·0	1524	1·6902
373·2	42·4	1548	1·6274	387·0	49·1	1515	1·6911
376·7	46·1	1538	1·6637	390·4	49·3	1508	1·6928
378·9	47·5	1534	1·6767	399·6	49·9	1486	1·6981
379·9	48·3	1531	1·6839				

TABLE IV.

Apparatus.	Glass, I.	Glass, II.	Quartz, III.
Weight of NH_4Br, g.	0·3404	0·2108	0·1376
Volume of bulb, c.c.	580·3	303·9	310·0
Temp.	379·0°	385·0°	369·0°
Pressure, p	48·7	58·0	36·5
D	24·6	24·5	24·4

FIG. 6.



Intersection point : $\log p = 1{\cdot}6875$. $1/T = 0{\cdot}001535$.
$p = 48{\cdot}7$ *cm.* Hg. $t = 379°$.

did not find an intersection but a continuous change of one line into the other (see Fig. 6).

This remarkable fact proves that there is a perceptible adsorption, caused by the glass wall. So long as there is an excess of solid substance, this adsorption does not exert any influence on the vapour pressure, but when the solid substance has apparently just disappeared there is still a small quantity adsorbed by the wall of the vessel, which is gradually liberated at higher temperatures. The effect is that with rising temperature the curve of the saturated vapour pressures is left at too low a temperature and the Boyle–Gay-Lussac line is reached at too high a temperature. Between these two the pressure is abnormally low. Both glass and quartz behaved in the same way. This phenomenon, which has also been found with mercuric iodide (Rinse, this vol., p. 1442), interested us, since it explained the slightly low values of vapour densities determined with our baroscope. The adsorption per sq. cm. of silica surface of the apparatus can be calculated, and from this result we find that the weight of adsorbed material on the baroscope is just sufficient to account for the low values. Though the differences are rather small, Smits thought it advisable to change the construction of the baroscope once more, in order to eliminate the error, and this was effected by having equal silica surfaces on each side (this vol., p. 2410).

Finally, the value of the heat of evaporation can be calculated from our results. From the formula, $d \log_e p/dT = Q/RT^2$, it follows that $d \log_e p/d\left(\frac{1}{T}\right) = Q/R$. Now it has been shown that $\log_{10} p$ is a linear function of $1/T$, which proves that Q is not a temperature function. In agreement with this, the vapour-density determinations showed that the dissociation of ammonium bromide in the vapour state from 330—400° is complete. Consequently we can write $2{\cdot}303 \log_{10} p = -Q/RT + C$. From Fig. 4, using Briggsian logarithms, we read,

for $1/T_1 = 0{\cdot}001651, \log_{10} p_1 = 1{\cdot}1271,$

and for $1/T_2 = 0{\cdot}001497, \log_{10} p_2 = 1{\cdot}8613,$

hence $$Q/R = \frac{2{\cdot}303(1{\cdot}8613 - 1{\cdot}1271)}{1651 \times 10^{-6} - 1497 \times 10^{-6}} = 10980$$

or $Q = 22 \times 10^3$ cals. This value refers to 1 g.-mol. of vapour, and since the salt is completely dissociated, it corresponds to 1/2 g.-mol. of ammonium bromide; thus $(Q_{SG})_{NH_4Br} = 44 \times 10^3$ cals. The value given by Johnson, *viz.*, $45{\cdot}4 \times 10^3$ cals., differs somewhat from this.

The value of C follows from

$$C = \frac{2{\cdot}303(T_2 \log p_2 - T_1 \log p_1)}{T_2 - T_1} = 20{\cdot}8$$

so that $$\log_e p = -\frac{10980}{T} + 20{\cdot}8.$$

Summary.

Using a new apparatus, the " densi-tensimeter " (see Smits, this vol., p. 2409), we have measured simultaneously the vapour pressures and vapour densities of ammonium bromide. When $\log p$ was plotted against $1/T$, a straight line was obtained, from which it follows that the latent heat of evaporation between 300° and 400° is

not a function of temperature. This result indicated that most probably the vapour would be completely dissociated, and the density determinations with the baroscope showed, in fact, a total dissociation.

The cause of the discrepancy between this result and that of Smith and his co-workers is discussed, and a possible source of error in their work is indicated.

In order to check the density determinations, the authors applied the "extrapolation method," measuring the pressure of the saturated and of the unsaturated vapour of a weighed quantity of salt in a known volume. The plot of log p against $1/T$ gave two straight lines, and when these were produced, their point of intersection gave the pressure and temperature of the just-saturated vapour, from which it was calculated that the corresponding vapour density agreed with complete dissociation.

The two straight lines did not actually intersect, however, but curved and merged into one another, thus indicating a perceptible adsorption on the wall of the apparatus.

Calculation indicated that if the baroscope reading was corrected for this adsorption the result agreed with that obtained by the second method.

The heat of evaporation of ammonium bromide was calculated from the experimental data and found to be 44,000 cals.

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