XXXIX.—*The Maximum Pressure of Naphthalene Vapour.*

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THE formation of naphthalene during the carbonisation of coal in gas works is a source of much trouble to gas engineers, for the naphthalene, finding its way into the pipes, forms deposits which obstruct the passage of the gas. The systematic study of the causes and means of prevention of such deposits necessitates an exact knowledge of the amount of naphthalene required to saturate a given volume of any gas at various temperatures and consequently of the maximum pressure of naphthalene vapour at such temperatures. The only measurements of the maximum vapour pressure of naphthalene hitherto carried out are those by Naumann (*Ber.*, 1871, 4, 647) which are as follows :

At 15° vapour pressure =	2	mm.
At 78° vapour pressure =	9	„
At 100° vapour pressure =	20·5	„

The absence of decimals (other than the 5) suggests that they are only approximations, and they were, in fact, determined in the ordinary barometric vacuum without any special precautions; the tube was jacketed for a few centimetres only below the top of the mercury column, and no method of direct comparison with a standard barometer was employed. Moreover, the value 2 mm. for the vapour pressure at 15° is improbable, for any substance having that vapour pressure at 15° would soon disappear if freely exposed to the air, whereas a small piece of naphthalene so treated shows little diminution in size, even after many weeks. That Naumann was satisfied with an approximation is not to be wondered at, since, except from the point of view of the coal gas industry, a knowledge of the maximum pressure of naphthalene vapour does not appear to be of much importance. Ramsay and Young (*Phil. Trans.*, 1884, Part I, xxxvii, 461) applied the apparatus they devised for measuring the influence of pressure on the temperature of volatilisation of solids to the measurement of the vapour pressures of benzene, water, acetic acid, and camphor, but the preliminary observations they made with naphthalene led to no result, and were abandoned owing to the low vapour pressure of the hydrocarbon (9 mm.) at its melting point (97.6°), and to the want of data regarding its vapour pressure at low temperatures; it may therefore be assumed that the method is inapplicable to naphthalene at the ordinary temperature.

The vapour pressure of naphthalene at the ordinary temperature being very small, the ordinary method of measurement in the barometric vacuum was at first deemed unsuitable. Among other methods, that of evaporation, which has been occasionally employed in the case of liquids, seemed to offer decided advantages. In it, as is well known, a given volume of an indifferent gas at a definite temperature is passed over a weighed quantity of the substance whose vapour pressure is to be measured, and the loss in weight of the latter estimated; this loss represents the weight, and hence the volume, of the vapour required to saturate the given volume of the gas at the given temperature and pressure, and a simple calculation yields the value of the vapour pressure at that temperature. The method is based on the assumption which was proved to be legitimate by the experiments of Regnault and Magnus, that the vapour pressure of a volatile liquid in a space filled with an indifferent gas is very nearly equal to the vapour pressure in a vacuum, and the more nearly is it so the smaller the pressure of the vapour. J. Walker (*Zeit. physikal. Chem.*, 1888, 2, 602) measured the relative vapour pressures of aqueous solutions of various inorganic salts, and Wall and Bredig (*Ber.*, 1889, 22, 1084) those of various alcoholic solutions by this method and obtained very good results. The process being unlimited as regards the length of

time for which the gas is passed, the slowness of the operation, and the volume of the gas employed, it seemed capable of great delicacy and exactness, and hence especially well adapted for measuring the low vapour pressures of such solids as naphthalene. Some pure naphthalene was accordingly first prepared by digesting a commercial sample alternately with sulphuric acid and caustic potash several times and washing repeatedly with water between each digestion; in this way, most of the phenols and hydrocarbons were removed. The purified sample was then three times distilled with steam; finally, it was drained free from water, melted, powdered, and set to dry for several weeks in a large bell jar over concentrated sulphuric acid. It then melted at 79.6° and gave only a slight pink coloration on boiling with strong sulphuric acid; hence it might be considered pure. This dry, powdered naphthalene was then filled into light U-tubes, above the powder a little cotton wool was placed to prevent any of it being carried over mechanically, and dry corks, provided with glass outlet tubes, were fitted into the tubes and rendered air-

FIG. 1.

tight with a coating of cement. In order that the temperature of the experiment might be kept perfectly under control, a large zinc water-bath three feet long, two feet six inches high, and two feet three inches wide was constructed. It had six air compartments running lengthwise through it, arranged in two tiers of three each, each compartment being six inches high and four inches wide. The water could circulate freely round each compartment, and was kept well stirred by a large iron stirrer working up and down and driven by a water engine at any desired speed. The temperature of the water was controlled by means of a mercury thermostat, to which was attached a non-atmospheric burner capable of very delicate adjustment. The bath was fitted with a close lid which had three small holes, one in the centre for the rod of the stirrer, and two close together at one end and in the middle line, one being for the thermostat, the other for the thermometers, which were all divided to tenths of a degree. By these means, the temperature could be kept constant throughout the bath to 0.1° for 24 hours. Fig. 1 shows the arrangement for one compartment: the gas, entering through the wash-

bottle into the safety tube, A, inserted to measure the pressure in the apparatus and prevent it exceeding that of the atmosphere, was partially dried by passage up a cylinder, B, filled with beads moistened with concentrated sulphuric acid. After being further dried and raised to the temperature of the bath by passage through the sulphuric acid bulb, C, and the calcium chloride tube, D, the gas was passed through the weighed tube of naphthalene, E. In the succeeding sulphuric acid tube, F, most of the naphthalene carried over was re-absorbed and thus prevented from condensing in the tubes outside the bath and blocking them up. The tube G is connected with an aspirator by means of which the gas is drawn through the system of tubes. The several aspirators had slightly different capacities, but as each experiment was concluded the pressure and temperature of the atmosphere were observed, and due correction being also applied for the water vapour saturating the gas in the aspirator, the weight of naphthalene carried over in the given time by 36 litres of dry gas at 15° and 760 mm. pressure was calculated from the observed values. Thus the figures given in the third column of Tables I, II, III, and IV are strictly comparable. The ends of each air compartment were carefully closed, as shown in Fig. 1, by stoppers made of triple layers

TABLE I

Gas employed. Temp. 30°.	Duration of ex- periment.	Weight of naphthalene carried over.
Air	2½ hours	0·0318 gram
"	3¼ "	0·0319 "
"	4 "	0·0320 "
"	7 "	0·0322 "
"	9½ "	0·0324 "
"	11 "	0·0327 "
"	17 "	0·0330 "
"	30 "	0·0332 "
"	39 "	0·0335 "
"	135 "	0·0340 "
Hydrogen	1½ "	0·0312 "
"	4½ "	0·0313 "
"	6½ "	0·0315 "
"	14 "	0·0330 "
"	24 "	0·0337 "
"	110 "	0·0342 "
Coal gas	3 "	0·0315 "
"	6 "	0·0320 "
"	15 "	0·0322 "
"	20 "	0·0325 "
"	55 "	0·0339 "

of wood, each layer being covered by flannel and separated with cork from the adjoining one. In this way, air currents were prevented, and the temperature in a compartment ensured as being that of the water of the bath. The temperature of the bath having been raised in the first place exactly to 30° , and the various tubes arranged as described, the gas was passed at various speeds through the weighed tubes of naphthalene, and the loss in weight of the tubes observed; from this the weight of naphthalene required to saturate 36 litres of dry gas measured at 15° and 760 mm. was calculated. It remains to be mentioned that, in addition to air, hydrogen and coal gas were employed in these experiments, as it was deemed better not to rely on results obtained by one gas only: when these gases were employed, the U-tubes of naphthalene were always swept clear of them before weighing by blowing a small quantity (about 50 c.c.) of dry air through them; trial showed that the extra loss of naphthalene due to this precaution was quite negligible. In Table I (p. 403) are given the observed results.

It is noticeable that the weight of naphthalene carried over increases slightly as the rate at which the gas is passed over diminishes. The nature, however, of the gas into which the naphthalene diffuses seems to exercise no influence on the rapidity of the diffusion; the values in Tables II and III confirm this. From the above figures, it would appear that practically complete saturation was attained in the slowest experiments; owing, however, to the obvious difficulty of keeping a large bulk of water at a constant temperature much higher than that of the surrounding air for days at a time, and inasmuch as 97 per cent. saturation was obtained in the 24 and 30 hours experiments, it was decided to limit future experiments to about 24 hours, and allow an extra 3 per cent. on the observed values in order to obtain the true saturation or "limit" value. Tables II, III, and IV contain the results of experiments conducted at other temperatures. As previously, due corrections have been made in each experiment for temperature and pressure, and for the hygrometric state of the gas in the aspirators, the values given being those for 36 litres of dry air at 15° and 760 mm. pressure.

TABLE II.

Gas employed. Temp. 45° .	Duration of ex- periment.	Weight of naphthalene carried off.
Air	$1\frac{1}{2}$ hours	0.1192 gram
"	$2\frac{1}{4}$ "	0.1222 "
"	$2\frac{3}{4}$ "	0.1224 "
"	5 "	0.1232 "
"	9 "	0.1250 "
"	21 "	0.1260 "

TABLE II.—(continued).

Gas employed. Temp. 45°.	Duration of ex- periment.	Weight of naphthalene carried off.
Hydrogen	1½ hours	0·1194 gram
„	3 „	0·1214 „
„	6 „	0·1236 „
„	8½ „	0·1252 „
„	24 „	0·1272 „
Coal gas	2½ „	0·1204 „
„	5 „	0·1224 „
„	5 „	0·1228 „
„	18 „	0·1260 „
„	22 „	0·1270 „

$$\begin{aligned}\text{Limit value} &= (0·1272 + 3 \text{ per cent.}) \text{ gram.} \\ &= 0·1310 \text{ gram.}\end{aligned}$$

which is taken to be the true weight of naphthalene required at 45° to saturate 36 litres of dry air measured at 760 mm. and 15°.

TABLE III.

Gas employed. Temp. 60°.	Duration of ex- periment.	Weight of naphthalene carried off.
Air	2½ hours	0·3784 gram
„	5 „	0·4010 „
„	15 „	0·4498 „
Hydrogen	2 „	0·3818 „
„	3½ „	0·3972 „
„	4½ „	0·4043 „
„	15 „	0·4445 „
„	30 „	0·4515 „
Coal gas	1¾ „	0·3728 „
„	3¾ „	0·4016 „
„	19 „	0·4509 „

$$\begin{aligned}\text{Limit value} &= (0·4515 + 3 \text{ per cent.}) \text{ gram.} \\ &= 0·4650 \text{ gram.}\end{aligned}$$

TABLE IV.

Temperature of air.	Duration of experiment.	Weight of naphthalene carried off.
15°	2½ hours	0·0165 gram
15	4 "	0·0168 "
15	10 "	0·0168 "
15	93 "	0·0170 "
75	2½ "	1·165 "
75	3 "	1·180 "
75	3½ "	1·191 "

It was found impossible to keep the water in the bath constant at 75° for more than 3—4 hours, hence the limit value for 75° cannot be ascertained with certainty; but assuming that the rate of increase in weight of naphthalene carried over as the length of experiment becomes greater is in the same proportion as at 60°, we may deduce it as follows: Mean weight carried over at 60° in 3½ hours = 0·399 gram — limit assumed = 0·465 gram, or an increase of 17 per cent. Now increase the weight carried over at 75° in 3½ hours, that is, 1·191 grams by 17 per cent., and a limit value of 1·395 grams is obtained.

From these limit values, the vapour pressure of the naphthalene may be easily deduced by means of Ostwald's formula ("Physico-Chemical Measurements," p. 114)

$$p = \frac{62290}{m} \frac{gT}{v} \text{ mm.}$$

where g = weight in grams of the substance carried off.

T = absolute temperature of room.

m = molecular weight of the body.

v = volume of gas passed over the solid.

Substituting the following values in the above equation, we get the results set forth in Table V.

g = weight of naphthalene carried over given in column 2.

$T = 273 + 15 = 288^\circ$.

$m = 128$ and $v = 36000$ c.c.

TABLE V.

Temperature.	Limit weight of naphthalene carried over.	Corresponding vapour pressure.
15°	0·0170 gram	0·066 mm.
30	0·0345 "	0·135 "
45	0·1312 "	0·51 "
60	0·4650 "	1·81 "
75	1·395 "	5·43 "

These values differ so much from those usually given for the vapour pressure of naphthalene, that it was thought that, with due care, they might easily be either confirmed or refuted by the ordinary barometric method. Accordingly, glass tubes $\frac{5}{8}$ -in. in diameter and 3 ft. long were taken, thoroughly cleaned, and drawn out at one end to a fine capillary thread, so that the free end might be connected with the mercury joint of a Sprengel pump. Each tube was then strongly heated to expel all moisture, the capillary end connected with the pump, and the other end dipped into hot, freshly distilled mercury, which was then slowly drawn up by means of the pump. As the mercury rose, it was boiled by means of a large Bunsen burner, finally the mercury was boiled throughout its whole length, and the tubes lowered into the bath till the mercury rose well into the capillary thread, when the tubes were sealed off with the blow-pipe. After several attempts, two tubes were obtained in which the residual air could, with difficulty, be distinguished on inclining the tubes. The heights of the mercury in the two tubes, as read off by the cathetometer (which read with great accuracy to 0.01 mm.), were exactly the same. Having thus obtained two perfect barometer tubes, a small glass bulb blown in a capillary thread was filled with pure melted naphthalene by suction with a pump, and the ends sealed off when the naphthalene had solidified. Before passing this bulb up into one of the barometer tubes, it was cleaned and dried, and the mercury in the trough warmed so as to prevent the introduction of moisture. Notwithstanding all precautions, a small quantity of air was introduced with the bulb, and the mercury stood 1.86 mm. lower than it did in the standard barometer. The naphthalene bulb was then burst by warming the top of the mercury column, and the tube inclined, and clamped in that position, so that, on cooling, the naphthalene with the bulb attached to it solidified in the top of the tube, and so did not interfere with the readings. The two barometers were now lashed together, and delicate thermometers, divided to tenths of a degree, fastened between them. To ascertain whether the depression in the experimental tube, due to the air admitted, amounted exactly to 1.86 mm. at 15° or whether an additional small quantity of air had been enclosed in the bulb with the naphthalene, the two tubes were enclosed in a case with plate glass windows, and surrounded with a freezing mixture. After the temperature had remained constant at -18° for 20 minutes, the heights in the two columns were taken. At the temperature -18° , it was assumed that the naphthalene had practically no vapour pressure; on this assumption the difference of level of the mercury columns A and B was due solely to the air in B. The readings were as follows :

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Barometer = 759.6 mm.

Height of the column in A = 448.04 mm.

"	"	"	B = 446.36	"
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Difference.....	1.68 mm.	= $1.68 \times (1 + 18 \times 0.000179)$
	= 1.68 mm.	of mercury at 0°.

A simple calculation shows that the air, which exerts a pressure of 1.68 mm. at -18° and 759.6 mm., will exert a pressure of 1.90 mm. at 15° and 760 mm. Before bursting the bulb, the difference of level was 1.86 mm., so that the air that had been enclosed with the naphthalene was only sufficient to produce a depression of 0.04 mm. at 15° . The freezing mixture having been removed, and the tubes allowed to take the temperature of the air, they were surrounded with the melting ice. After the temperature of the air space above the ice had remained constant at zero for a considerable time, new readings were taken as follows:

Temperature = 0° Barometer = 759.9 mm.

Height of mercury in column A = 448.34 mm.

"	"	"	B = 446.53	"
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Difference.....	1.81	"
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of which difference $\frac{1.68 \times 273 \times 760}{(273 - 18) \times 759.9}$ mm., or 1.80 mm., are due to air, hence the true vapour pressure at $0^\circ = 0.01$ mm. The case was now removed and next day, after the temperature had been constant at 15.6° for an hour, fresh readings were taken as follows:

Barometer = 758.6 mm.

Height of mercury column in A = 439.08 mm.

"	"	"	B = 437.10	"
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Difference.....	1.98	"
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Subtract $\frac{1.80 \times (273 + 15.6) \times 760}{273 \times 558.6}$ mm. or 1.90 mm. for air and

vapour pressure at $15.6^\circ = 0.08$ mm. of mercury at 0° . The value found by the "evaporation method," 0.068 mm. at 15° , agrees well with this. In order to obtain values at other temperatures, the tubes were jacketed with a Hofmann's density tube, and the vapours of the following substances introduced: ether, carbon disulphide, chloroform, alcohol, benzene, water, acetic acid, isoamyl alcohol, boiling at 39° , 46.8° , 61.8° , 78.4° , 80.4° , 100° , 116° , and 130° respectively, as indicated by the thermometers. The following results were now obtained:

Ether, b. p. 39° . Barometer = 758.1 mm.

Height of mercury column in A = 458.02 mm.

" " " B = 455.66 "

Difference = 2.36 "

Depression due to air,

$$= \frac{1.80 (273 + 39) \times 760}{273 \times 758.1} = 2.06 "$$

Difference = 0.30 " of mercury at 39° .

= 0.30 " of mercury at 0°

Carbon disulphide, b. p. 46.8° . Barometer = 762.5 mm.

Height of mercury column in A = 462.43 mm.

" " " B = 459.59 "

Difference = 2.84

Depression due to air,

$$= \frac{1.80 \times (273 + 46.8) \times 760}{273 \times 762.5} = 2.10 "$$

Hence vapour pressure at 46.8° = 0.74 " of mercury at 46.8°

= 0.73 " of mercury at 0° .

Chloroform, b. p. 61.8° . Barometer = 757.6 mm.

Height of mercury column in A = 457.38 mm.

" " " B = 452.88 "

Difference = 4.50

Depression due to air,

$$= \frac{1.80 \times (273 + 61.8) \times 760}{273 \times 757.6} = 2.21 "$$

Hence vapour pressure at 61.8° = 2.29 " of mercury at 61.8° .

= 2.26 " of mercury at 0° .

Ethyl alcohol, b. p. 78.4° . Barometer = 755.5 mm.

Height of mercury column in A = 455.30 mm.

" " " B = 445.86 "

Difference = 9.44 "

Depression due to air,

$$= \frac{1.80 \times (273 + 78.4) \times 760}{273 \times 755.5} = 2.38 "$$

Hence vapour pressure at 78.4° = 7.11 " of mercury at 78.4° .

= 7.01 " of mercury at 0° .

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Benzene, b. p. 80.4° . Barometer = 760 mm.

Height of mercury column in A = 459.82 mm.

"	"	"	B = 449.84	"
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	Difference =	9.98	"
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Depression due to air,

$$= \frac{1.80 \times (273 + 80.4)}{273} = 2.33 \quad "$$

	Hence vapour pressure at 80.4° =	7.65	"	of mercury at 80.4° .
		= 7.54	"	of mercury at 0° .

Water, b. p. 100° . Barometer = 759 mm.

Height of mercury column in A = 459.12 mm.

"	"	"	B = 437.84	"
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	Difference =	21.28	"
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Depression due to air,

$$= \frac{1.80 \times (273 + 100) \times 760}{273 \times 759} = 2.44 \quad "$$

	Hence vapour pressure at 100° =	18.84	"	of mercury at 100° .
		= 18.50	"	of mercury at 0° .

Acetic acid, b. p. 118° . Barometer = 760.4 mm.

Height of mercury column in A = 460.86 mm.

"	"	"	B = 420.60	"
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	Difference =	40.26	"
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Depression due to air

$$= \frac{1.80 \times (273 + 116) \times 760}{273 \times 760.4} = 2.58 \quad "$$

	Hence vapour pressure at 118° =	37.68	"	of mercury at 118°
		= 36.87	"	of mercury at 0°

Isoamyl alcohol, b. p. 130° . Barometer = 761.6 mm.

Height of mercury column in A = 462.66 mm.

"	"	"	B = 396.50	"
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	Difference =	66.16	"
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Depression due to air

$$= \frac{1.80 \times 273 + 138 \times 760}{273 \times 761.6} = 2.70 \quad "$$

	Hence vapour pressure at 130° =	63.46	"	of mercury at 130°
		= 61.95	"	of mercury at 0°

In Table VI are set out the results thus obtained by the barometric method.

TABLE VI.

Temperature.	Corresponding vapour pressure.	Temperature.	Corresponding vapour pressure.
0°	0.01 mm.	78.4°	7.01 mm.
15.6	0.08 "	80.4	7.54 "
39	0.30 "	100	18.50 "
46.8	0.73 "	116	36.87 "
61.8	2.26 "	130	61.95 "

The values obtained by the two methods were then plotted out and a curve constructed.

FIG. 2.

Curve of Vapour Pressures for Naphthalene.

Values obtained by evaporation method are marked ⊕.

Values obtained by barometric method are marked +.

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The agreement between the two sets of values is very close ; from the curve shown on a reduced scale in Fig. 2, the maximum vapour pressures corresponding to every 5° were deduced. These values are given in Table VII.

TABLE VII.

Temperature.	Corresponding vapour pressure.	Temperature.	Corresponding vapour pressure.
0°	0.022 mm.	70°	3.95 mm.
5	0.034 "	75	5.43 "
10	0.047 "	80	7.4 "
15	0.062 "	85	9.8 "
20	0.080 "	90	12.6 "
25	0.103 "	95	15.5 "
30	0.135 "	100	18.5 "
35	0.21 "	105	22.4 "
40	0.32 "	110	27.3 "
45	0.51 "	115	32.4 "
50	0.81 "	120	40.2 "
55	1.26 "	125	49.8 "
60	1.83 "	130	61.9 "
65	2.65 "		

In conclusion, attention may be drawn to the following points :

1. The great advantages that the "evaporation method" has over other methods in measurements of the low vapour pressure of solids at moderate temperatures, both in regard to accuracy and ease of manipulation.

2. The rate of evaporation of the naphthalene into the three gases, hydrogen, air, and coal gas is the same in each case, being independent of the nature of the gas. This is confirmed by other experiments, in which carbon dioxide, acetylene, marsh gas, and air containing the vapours of ether, carbon disulphide, benzene, chloroform, or ethyl alcohol, in quantities insufficient for saturation, were employed instead of the above three gases.

3. The very much lower vapour pressure of naphthalene at moderate temperatures than has been hitherto accepted.

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