

CIV.—*Molecular Weight of β -Naphthol in Solution in Solid Naphthalene.*

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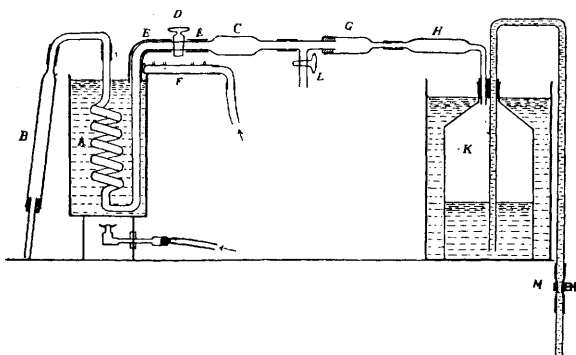
PREVIOUS work on this subject has been carried out by Küster (*Zeitsch. physikal. Chem.*, 1895, 17, 357) and Speranski (*ibid.*, 1903, 46, 70); it was thought, however, that their results needed confirmation and extension, and we consequently undertook to measure the vapour pressure of solid naphthalene and of solid solutions of β -naphthol in naphthalene by another method, namely, by passing a current of air over solid naphthalene or the naphthalene solution, and finding by loss of weight the quantity of naphthalene carried off.

Apparatus and Method.—The naphthalene or naphthalene solution was broken into very small fragments and placed in a spiral glass tube *A*, about 1 metre in length (if unwound) and 5 mm. in diameter. The spiral was supported in a thermostat maintained at 70°. This temperature is near the melting point of naphthalene, and was chosen in order to obtain as high a vapour pressure as possible.

The air-current first entered the soda-lime tube *B*, which deprived it of moisture and of carbon dioxide. It then passed into the spiral, where it became saturated with naphthalene vapour; from the spiral it passed through the stopcock *D* into the wide tube *C*, where the main part of the naphthalene condensed. In order to prevent condensation in the tube *EE*, it was heated above the temperature of the bath by a row of small gas-burners, *F*. The glass tube was protected from the flame by two brass tubes, each being split into two lengthwise; the parts were held together by a wire during an experiment.

The air passed from *C* through a calcium chloride tube *G* and a tube *H* containing wet sponge into a large aspirator *K*, which stood in a vessel of water.

The method of conducting an experiment was as follows. The spiral being filled with the solid and in position, air was drawn through it for some hours (this was necessary only for the first experiment with a given sample). The stopcock *D* was then turned off and the condensed naphthalene was removed from *C* by heating it and drawing air through it by means of a capillary tube. The tubes *EE* were removed, and the spiral was taken out of the bath and allowed to cool; it was then disconnected from *B* and the end stoppered. The spiral was cleaned from the oil of the thermostat by immersing it successively in two jars of light petroleum and wiping thoroughly. It was then carefully weighed, replaced in the thermostat, and connected as before. The tubes *EE* were heated, and the stopcock *L* was opened



a few moments in order to ensure that the pressure inside *C* was that of the atmosphere before beginning the aspiration. The stopcock *D* was then opened and the aspiration begun, the water being run into a graduated flask.

To bring the experiment to an end, the water stream was stopped by the clip *M*, and the tap *D* turned a few moments later. The spiral was then removed, cleaned, and weighed exactly as before.

The loss of weight gave the weight of naphthalene drawn off by the air-current. The barometric height and the temperature of the aspirator were read at the end of the experiment.

Vapour Pressure of Naphthalene at 70°.—Experiments were made to discover whether the glass spiral lost weight on continued heating in the bath (water covered with oil). It was found that during the first six hours it lost 0.5 milligram, but during the next twelve hours it lost only 0.2 milligram. As the times of heating during the deter-

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mination of vapour pressure were much less than this, no correction for such loss of weight was made.

To ensure saturation of the air with naphthalene vapour the air was passed through at a very slow rate, and the rate was varied in order to discover whether such variation has any effect on the vapour pressure.

The results are here tabulated :

w = weight of naphthalene drawn off, in grams.

P = barometric height, mm.

V = volume of air at temperature and pressure of aspirator, litres.

p = pressure of air in aspirator (corrected for moisture).

T = temperature of aspirator (absolute).

t = duration of experiment (minutes).

w .	P .	V .	p .	T .	t .	$V.P.$
0.1461	758.5	5.530	746.2	287.4	300	3.742
0.1466	755.1	5.530	742.5	287.7	240	3.760
0.1462	749.3	5.530	736.6	287.9	310	3.754
0.1456	765.2	5.530	751.9	288.6	422	3.749
Mean.....						3.751

Here no connexion can be traced between the vapour pressure and the rate of the air-current, so that the air was evidently saturated with the vapour.

A somewhat similar method was used by Allen (Trans., 1900, 77, 400), who found 3.80 at this temperature (read from his curve). Allen's experiments do not seem entirely satisfactory, as he did not cause the air to be saturated with the vapour, but found the saturation pressure by a method of extrapolation. Speranski, using a differential tensimeter, obtained the value 2.917 at the same temperature, but this we believe to be erroneous.

Vapour Pressure of β -Naphthol.—This was measured in exactly the same way as the vapour pressure of naphthalene. The following results were obtained :

w .	P .	V .	p .	T .	t .	$V.P.$
0.0050	759.2	5.530	748.0	286.0	305	0.1135
0.0050	758.1	5.530	747.2	285.5	285	0.1133
Mean						0.1134

The vapour pressure was less than 3 per cent. of that of naphthalene. This would cause only a slight error in the dilute solutions employed. An approximate correction has, however, been introduced by reckoning the vapour pressure of the β -naphthol in the solid solution to bear the same ratio to the vapour pressure of the pure substance as the quantity of β -naphthol present bore to the total mass of the mixture.

Vapour Pressure of Solid Solutions of β -Naphthol in Naphthalene.
—The solutions were made by melting together the required propor-

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tions of the substances in a sealed tube and allowing to cool. The solid mass was then broken into small fragments and the spiral was filled with them. It was refilled after every two experiments. The following are the results :

C = concentration, parts of β -naphthol to 100 parts of naphthalene.

C .	w .	P .	V .	p .	T .	t .	$V.P.$
5	0.1379	763.9	5.530	748.8	290.6	285	3.585
5	0.1383	761.3	5.530	746.1	290.7	325	3.597
5	0.1385	759.3	5.530	744.5	290.3	265	3.595
10	0.1357	768.4	5.530	755.4	288.2	255	3.489
10	0.1356	766.1	5.530	752.3	289.2	260	3.459
10	0.1334	767.4	5.530	752.9	290.0	310	3.457
10	0.1350	763.7	5.530	749.2	290.0	295	3.500
15	0.1303	770.7	5.530	756.6	289.5	240	3.383
15	0.1306	770.2	5.530	755.8	289.9	285	3.384
15	0.1300	765.9	5.530	751.3	290.1	255	3.372

The vapour pressures of the solutions and the molecular weights calculated from them are here tabulated :

C .	Mean $V.P.$	Mean $V.P.$ of β -naphthol.	$M.W.$ (from uncorrected $V.P.$).	$M.W.$ (from corrected $V.P.$).
5	3.592	3.587	151.0	146.4
10	3.476	3.466	174.6	168.5
15	3.380	3.365	194.1	186.5

Summary.—Since the normal molecular weight of β -naphthol is 144, it appears from these experiments that in dilute solid solutions β -naphthol has the same molecular weight as in the gaseous state, whilst it associates in more concentrated solutions. These results agree approximately with those of Speranski (*loc. cit.*), who obtained the following numbers :

Number of mols. β -naphthol to 100 mols. mixture	14.6	17.3	17.4	24.6	33.6
$M.W.$	198	249	245	257	255

They are somewhat in opposition to those of Küster, whose conclusion was that the molecular weights in the crystalline state were 288 and 256 respectively, and that in isomorphous mixtures a compound, $C_{10}H_8, C_{10}H_7 \cdot OH$, was formed, but the experiments leading to this result do not seem very convincing.

In calculating the molecular weights, it has to be assumed that the lowering of vapour pressure follows the same laws as in the case of liquids ; theoretically this appears to be correct, and the reasonableness of the results obtained may be considered a practical confirmation of their applicability.

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