274. *Relative Vapour Pressure and Aqueous Solubility of the Solid-solution System β-Naphthol–Naphthalene.*

By Robert Wright and Nelson E. Wallace.

Naphthalene when fused with β-naphthol yields a continuous series of solid solutions (Rudolphi, *Z. physikal. Chem.*, 1909, **66**, 717), from which water removes only the β-naphthol. Küster (*ibid.*, 1895, **17**, 357) investigated the aqueous solubility of the series at 25° and found increasing solubility with increasing β-naphthol content, reaching a maximum when the amount of β-naphthol in the solid solution was about 50 mols. %, the solubility of such a solid solution being greater than that of pure β-naphthol. With higher concentration of β-naphthol the solubility of the solid solution fell, and was in all cases equal to that of pure β-naphthol.

According to Küster, the explanation of this phenomenon is that a molecular compound is formed (though there is no evidence of the existence of such a compound from the thermal diagram), that this compound has a solution pressure greater than that of pure β-naphthol, and hence we get a maximum solubility with the 50% mixture. An aqueous solution in equilibrium with this compound is, however, supersaturated with regard to β-naphthol, and hence at higher concentrations, when excess of β-naphthol is present, the solubility falls to that of the pure substance.

In order to test Küster's theory, we investigated the solubility of the system at higher temperatures (this solubility, if a compound exists, should always show a maximum value near the 50% mixture) and also determined the vapour pressure of the series at different temperatures, since compound formation might be expected to affect the form of the vapour pressure–composition curve.

The data obtained are shown in the table. The solubilities at 25° are comparable, though not identical, with those of Küster, showing a maximum solubility for the 50% mixture which is greater than that of pure β-naphthol. At higher temperatures (65° and 78°), there is no longer a maximum at 50%, but the solubility rises with β-naphthol content until, when the latter is about 80%, it suddenly rises to that of pure β-naphthol.

The results for relative vapour pressure, *i.e.*, the ratio of the vapour pressure of naphthalene in the solid solution to that of pure naphthalene, show that at the higher temperatures (65° and 78°) the vapour pressure of the solid solution increases continuously with the naphthalene content, though even at 78° the relation is not linear. At lower temperatures (30° and 55°), the vapour pressure remains constant over a definite composition range, *viz.*, 50—80% at 30° and 60—70% at 55°, showing that two solid phases are present for certain compositions of the system. The simplest explanation of the results would seem to be that the continuous solubility in the solid state which exists at temperatures in the neighbourhood of the m. p.'s of the constituents, breaks down at lower temperatures, giving two solid solutions in which the solubility is limited. Change of physical nature of a solid binary system with fall of temperature has often been noted with alloys; the peculiarity of the present case is that the change takes place so close to the melting-point region. If the view that two solid solutions are formed with fall of temperature is admitted, the thermal diagram for the system should be modified as shown in Fig. 1.

FIG. 1.

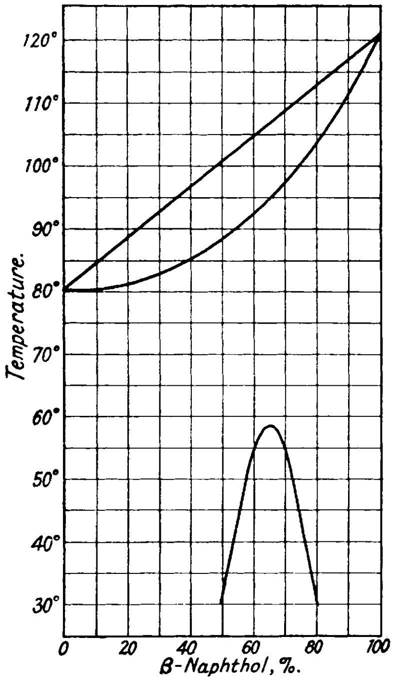
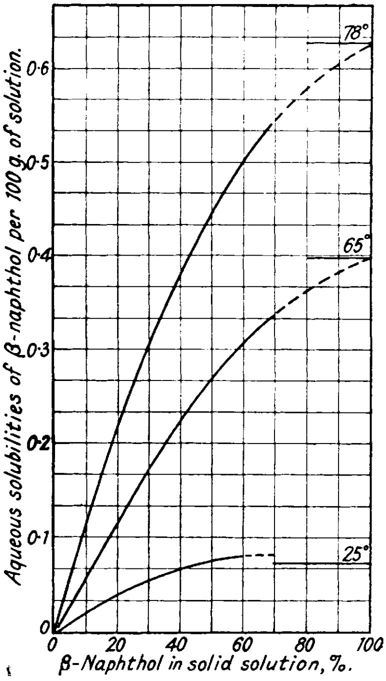


FIG. 2.



A range of constant solubility corresponding to that of constant vapour pressure is to be expected; but constant solubility from 80% upwards is found for the temperatures 65° and 78°, at which the vapour pressure–composition curves are continuous, while at the lower temperature, 25°, constant solubility is obtained over the range 50—100% of β-naphthol. In order to explain this behaviour, it is suggested that solid solutions of high β-naphthol content may give a solubility almost or quite identical with that of pure β-naphthol owing to the following causes: (1) decomposition of the solid solution into its constituents by the action of water, (2) loss of naphthalene by volatilisation during the process of grinding preparatory to solubility determination. Both of these causes would result in the production of pure β-naphthol, and as the solubility of this substance is small, a very slight disintegration of the solid solution would supply enough β-naphthol to produce a saturated aqueous solution.

Disintegration of the solid solutions would explain the constant solubility of the 80—100% systems at 65° and 78°. At the lower temperature (25°), on the assumption that the system consists of two solid solutions, one of high and the other of low β-naphthol content, we would get the same constant solubility over a more extended range.

The fact that at 25° the solubility of the 50% mixture is greater than that of pure β-naphthol may be explained by the assumption that at this composition the system consists of a single solid solution supersaturated with β-naphthol and therefore metastable; such a solution would have a higher β-naphthol solution pressure than that of the pure substance, and in consequence would give an enhanced solubility. Similar behaviour is obtained when water is brought into equilibrium with a supersaturated solution of benzoic acid in benzene; the solution pressure of the benzoic acid in the supersaturated benzene solution being greater than that of the pure solid, the resulting aqueous solution also becomes supersaturated with the acid.

Limited solubility in the solid state between β-naphthol and naphthalene at room temperature would seem to offer the simplest explanation of the peculiar behaviour of the system with regard to solubility and vapour pressure. The evidence cannot, however, be regarded as conclusive, and it would be of interest to examine the system by *X*-ray or optical methods.

Solid solution system β-naphthol–naphthalene.

β-Naphthol.		Solubility of β-naphthol, g./100 g. of solution.				Relative v. p. of naphthalene.			
		25°.							
Wt. %.	Mols. %.	Küster.	Authors.	65°.	78°.	30°.	55°.	65°.	78°.
0	0	0	0	0	0	1	1	1	1
10	8·9	0·0261	0·0157	0·049	0·115	0·92	0·92	0·91	0·90
20	18·2	0·0461	0·0325	0·106	0·21	0·82	0·83	0·85	0·86
30	27·6	0·0595	0·0483	0·175	0·30	0·76	0·76	0·80	0·81
40	37·2	0·0670	0·0670	0·22	0·38	0·72	0·72	0·76	0·76
50	47·1	0·0768	0·0720	0·28	0·46	0·70	0·62	0·70	0·70
60	57·0	0·0785	0·0740	0·31	0·50	0·70	0·59	0·64	0·60
70	67·5	0·0743	0·0723	0·34	0·54	0·70	0·59	0·57	0·43
80	78·0	0·0742	0·0725	0·39	0·65	0·69	0·57	0·47	0·30
90	89·0	0·0742	0·0724	0·38	0·66	0·34	0·44	0·27	0·13
100	100	0·0741	0·0723	0·40	0·66	0	0	0	0

EXPERIMENTAL.

Preparation.—The materials used were the purest that could be obtained from B.D.H., the m. p.'s being: naphthalene 80°, β-naphthol 121·5°. The solid solutions were prepared by weighing out the constituents in a test-tube, evacuating and sealing it, and melting the contents. In the earlier experiments the solid solution was annealed for 3 days at 78°, but, in view of the probable changes which take place in the nature of the system on cooling, in later experiments the melt was slowly solidified (3 hours). On account of the possible loss of naphthalene by volatilisation, the solidified mass was not ground until just before a vapour-pressure or solubility determination.

Vapour Pressure.—For the determination of vapour pressure the air-current method was employed. This method is open to three objections: (1) solubility of air in the solution, with consequent lowering of vapour pressure; (2) increase in volume of air as it passes along the absorbing train owing to the pressure gradient; (3) slowness with which the air becomes saturated with vapour. Since we are dealing with the volatility of a solid, we may neglect the effect due to (1), but errors due to causes (2) and (3) remain; hence the values obtained should only be regarded as comparative.

In carrying out a vapour-pressure determination, the solid was ground to a fine powder and packed in a glass tube 10 cm. long and of 4 mm. diameter, the powder being held in position by means of plugs of cotton-wool. The pure naphthalene was contained in a second similar tube, the two tubes were joined by rubber and also joined to a third tube of the same diameter and about 40 cm. long. The three tubes were then suspended by a cork inside a tube, about 80 cm. long, mounted vertically in a heating bath; at the lower temperatures this bath was a deep thermostat, and at the higher temperatures a vapour bath of methyl or ethyl alcohol (see Wright, J., 1915, **107**, 1527) was employed. A stream of dry carbon dioxide-free air was led over the solid solution and naphthalene at a rate of about 500 c.c. per hour. After ½ hour the tubes were removed and weighed, the object of this preliminary heating being to remove traces of moisture from the cotton-wool. The tubes were now replaced, and the air allowed to pass till a sufficient quantity of naphthalene had been removed; the time of flow was 2 days for the determinations at 30° and 3 hours for those at 78°. A second weighing gave the loss of naphthalene from each of the tubes, and from these losses the relative vapour pressure could be calculated.

In a control experiment where both tubes were filled with naphthalene a loss of 10% of the total was obtained from the second tube, indicating that the air was not completely saturated on leaving the first tube. In order to compare the solid solution and naphthalene under identical conditions, they should both be in the position of the first tube; it was therefore considered necessary to deduct 10% from the total loss of weight in fixing the weight corresponding to the vapour pressure of the pure naphthalene—this correction does not affect the existence of the flat portion of the vapour-pressure curve.

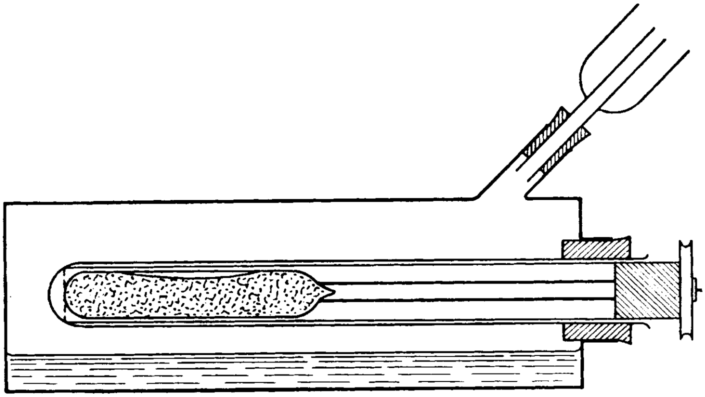


FIG. 3.

Solubility.—The determination of β-naphthol in solution was carried out by titration with *N*/100-iodine, which reacts with the β-naphthol according to the equation $I_2 + C_{10}H_7{\cdot}OH = C_{10}H_6I{\cdot}OH + HI$. The titration was carried out at ordinary temperature with starch as indicator, excess of sodium bicarbonate being added to neutralise the hydriodic acid. The method was tested on a solution containing 0·0300 g. of β-naphthol, and 0·0301 g. was found on titration.

The saturated solutions at 25° were prepared by shaking the solid solution with water in bottles in a thermostat for 4 hours; the solution was then filtered, and the β-naphthol estimated. At the higher temperatures the solutions had to be prepared in a sealed vessel so as to avoid loss of naphthalene and consequent production of free β-naphthol.

The apparatus used is shown in Fig. 3. The water with excess solid solution was sealed in a thin-walled test-tube, which was then slipped into a brass tube about 20 cm. long and having a perforated brass plate brazed on to one end; the other end of the brass tube was closed with a cork carrying a driving wheel, and a piece of stout rubber tubing was introduced between the cork and the sealed tube so that the latter was kept pressed against the perforated end of the brass tube. The brass tube was now placed inside a glass boiling-tube held horizontally in a copper heater, which contained boiling methyl or ethyl alcohol, and the side arm which was connected with the condenser made an angle of 45° with the body of the heater. The upper end of the condenser was connected to a manostat so that the temperature of the boiling liquid could be kept exactly at 65° or 78°. This temperature was adjusted by a thermometer placed in the boiling-tube before the introduction of the brass tube. After the introduction of the brass tube a driving belt was placed over the driving wheel and a stop held against the latter to keep the tube in position; the tube was then rotated for 4 hours to produce a saturated solution. The driving belt was now removed, the heater brought into a vertical position by rotating round the joint between the heater and the condenser, the cork and rubber tube were removed from the brass tube, and the sealed glass tube fractured by striking it with a previously heated brass rod; during the fracturing the brass tube must be held firmly slightly above the bottom of the boiling-tube to avoid breaking the latter. The brass tube containing fragments of glass was then removed, leaving the saturated solution with excess of solid in the boiling-tube which was still maintained at the temperature of the boiling alcohol. A heated filtering tube, consisting of a glass tube with its constricted end closed with a plug of cotton-wool, was then introduced, and the saturated solution drawn into it by suction. The solution was removed from the filter tube by a warmed pipette, and quickly transferred to a weighing bottle which was at once stoppered, cooled, and weighed. The contents of the bottle were then washed out into a basin, dissolved in excess of water, and titrated with *N*/100-iodine.

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