189. *The Hydrates of Naphthalene-β-sulphonic Acid.*

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The complete phase data for the system naphthalene-β-sulphonic acid–water are presented. Four hydrates of the β-acid exist, a mono-, a tri-, a penta-, and an octa-hydrate, of which only the first two have previously been described. An exact thermodynamic relationship has been applied to the pressure–temperature curves.

DURING work on the vapour pressure of naphthalene-β-sulphonic acid hydrates a penta-hydrate was discovered. It was then decided to undertake a complete phase-rule study of the system naphthalene-β-sulphonic acid–water. The solubility data are shown in Fig. 1, and the co-ordinates of the invariant points and melting points are given in Table 1 which includes the corresponding vapour-pressure data taken from the *P–T* curve of Figs. 2, 2A, and 2B.

FIG. 1. *Temperature-composition diagram.*

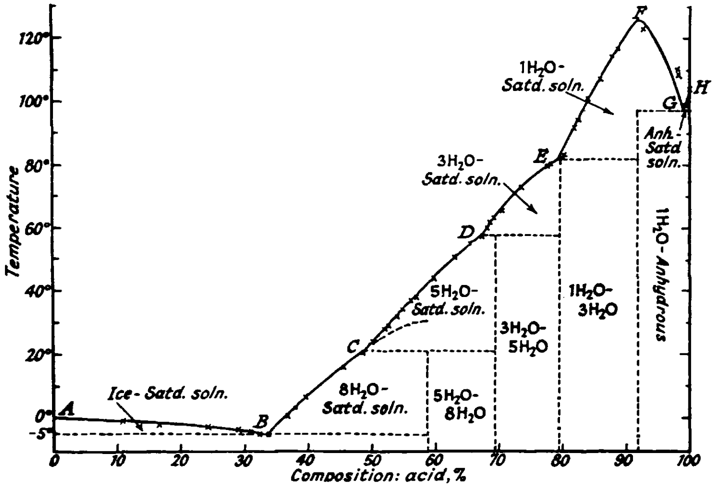


TABLE 1. *Invariant points and melting points in the naphthalene-β-sulphonic acid–water system.*

	Invariant points	*P*, mm. Hg.	*T*	Acid, % (*x*)
A	Triple point of water	4·58	0·008°	0·0
B	Eutectic : ice, octahydrate, satd. soln., vap.	2·35	−5·02	33·5
C	Transition point : octahydrate, pentahydrate, satd. soln., vap.	15·80	20·5	48·5
D	Transition point : pentahydrate, trihydrate, satd. soln., vap.	96	57·8	67·4
E	Transition point : trihydrate, monohydrate, satd. soln., vap.	168	81·4	78·9
F	Melting point of monohydrate	207	125·9	92·02
G	Eutectic : monohydrate, anhydrous acid, satd. soln., vap.	10·0	97	98·8
H	Melting point of anhydrous acid	—	104	100·0

The only recorded solubility data are those of Masson (*J.*, 1912, **101**, 103) who gives a value corresponding to 56·9 g./100 g. of saturated solution at 30°. This value is not in good agreement with our value of 53 g./100 g. of solution for the pentahydrate but could represent the metastable equilibrium of the octahydrate at 30°. The m. p. of the anhydrous acid is 104°; Kraft and Roos's (*Ber.*, 1893, **26**, 2823) value of 100—102° is in fair agreement with this. Witt (*Ber.*, 1915, **48**, 758), however, gives a value of 90·5—91° obtained by drying the monohydrate in a stream of dry air at 110° until the requisite loss in weight was obtained. Since 110° is well above the m. p. of the anhydrous acid (it can be seen from Fig. 1 that material containing approximately 96% of acid melts at 110°) the material must have been in the molten state for some considerable time before the requisite loss in weight took place. It is our experience that such solutions readily partially hydrolyse into naphthalene (detected by its smell) and sulphuric acid, with a certain amount of darkening in colour, and it is therefore possible that Witt's material was not pure anhydrous naphthalene-β-sulphonic acid. Euwes (*Rec. Trav. chim.*, 1909, **28**, 298) dried the monohydrate at 90°/20 mm. for 8 hours and found the dried acid still contained 3% of water and had a m. p. of 119°, which, from our results, corresponds to 5·6% of water.

FIG. 2. *Vapour pressure–temperature diagram.*

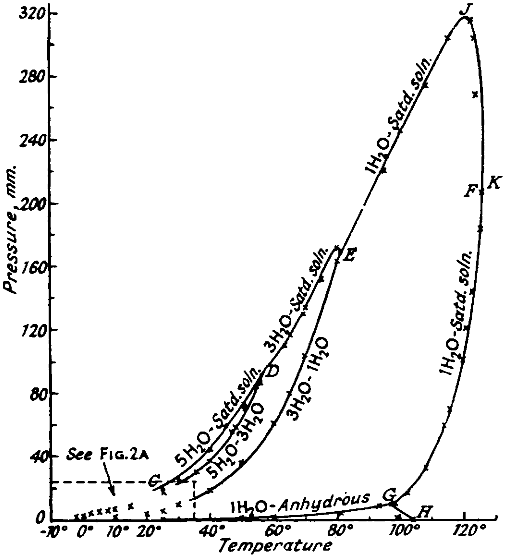


FIG. 2B. *P–T relationships at the trihydrate transition point.*

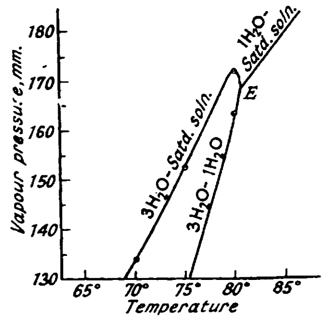


FIG. 2A. *P–T relationships at low temperatures.*

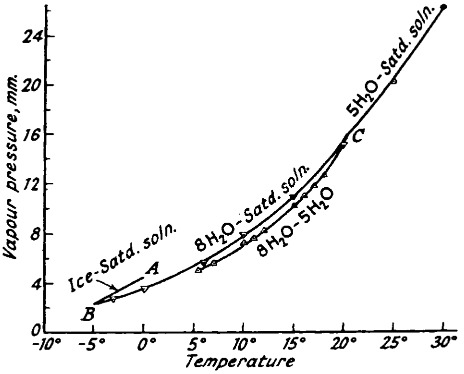
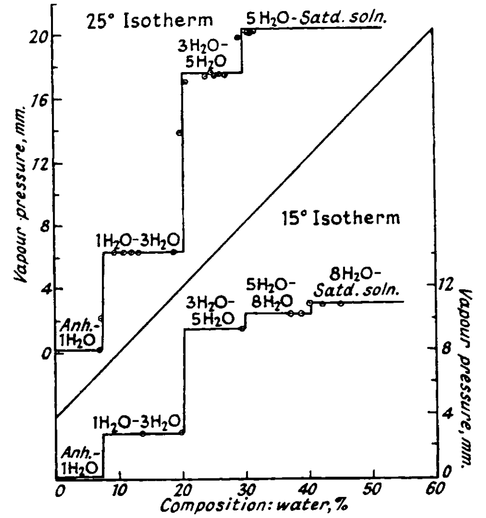


FIG. 3. *Vapour pressure–composition diagram.*



The values obtained for the m. p. of the monohydrate by Kraft and Roos (124—125°) and by Witt (124°) are in close agreement with that obtained in this work, *viz.*, 125·9°.

Witt's value of 83° for the m. p. of the trihydrate is in reasonable agreement with our value of 81·4°, which is not, however, a congruent m. p. but a transition point from the tri- to the mono-hydrate.

The pentahydrate was discovered by hydrating the mixed mono- and tri-hydrates (the stable mixture under normal atmospheric conditions) at 25°. The results are shown as a "step" diagram in Fig. 3, where the steps corresponding to the dissociation pressure of the mono- and tri-hydrates are shown in addition to that of the pentahydrate. The values of these dissociation pressures are shown in Table 2. The solubility curve (Fig. 1) shows a definite break at *D* corresponding to the phase change from tri- to penta-hydrate, and a further change in slope in the neighbourhood of point *C* which corresponds to the separation of a solid hydrate containing more water of crystallisation. This was shown to be an octahydrate, and the composition of the pentahydrate was confirmed by using a " tracer " technique (see p. 917). The dissociation pressure of the octahydrate at 15° is shown in a " step " diagram in Fig. 3 and the values are quoted in Table 2. The 25° isotherm in Fig. 3 does not reveal the presence of the octahydrate, as the transition point is at 20·5°.

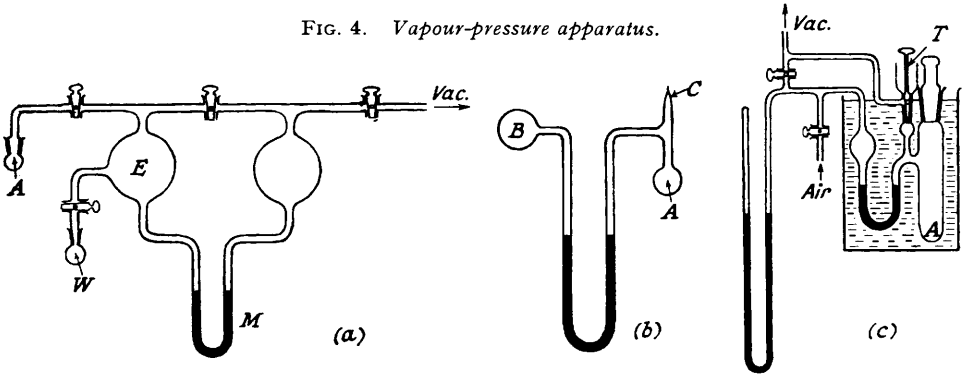
TABLE 2. *Dissociation pressures of hydrates (mm.* Hg).

	Hydrate			
Temp.	$1H_2O$	$3H_2O$	$5H_2O$	$8H_2O$
15°	—	2·90	9·36	10·35
25	0·18	6·34	17·50	—

EXPERIMENTAL

The naphthalene-β-sulphonic acid was prepared according to Witt (*Ber.*, 1915, **48**, 743). Several different preparations had slightly different properties, probably caused by traces of impurities. One sample gave an anhydrous acid which charred very rapidly near its m. p.; this was thought to be due to a trace of sulphuric acid. All the samples contained a small amount of water-insoluble material, probably the sulphone, which was sufficient to give an opalescence in relatively dilute solutions but disappeared in more concentrated solutions.

FIG. 4. *Vapour-pressure apparatus.*



Determination of Solubility.—Most of the points on the three-phase boundary curve were determined by Pounder and Masson's modification of the thaw-melt method (*J.*, 1934, 1357). About 0·5 g. of a mixture of acid and water was contained in a glass tube of 4 mm. internal diameter attached to the bulb of a calibrated thermometer and immersed in a liquid bath. The mixture in the tube was stirred with a 1-mm. diameter glass rod. The bath was heated slowly and the temperature at which the last trace of solid went into solution was noted. The tube was then cooled quickly, the bottom end containing the mixture broken off and weighed, and the mixture analysed by titration with standard alkali.

The results are given in Table 3 and the temperature–composition diagram is shown in Fig. 1. Points on the portion *AB* of the curve (Fig. 1), where ice is the solid phase, were obtained by the

TABLE 3. T–x *Data for the system naphthalene-*β*-sulphonic acid–water.*

Sol. pt.*	Solid phase	Acid, % (x)	Sol. pt.*	Solid phase	Acid, % (x)	Sol. pt.*	Solid phase	Acid, % (x)	Sol. pt.*	Solid phase	Acid, % (x)
0°	Ice	0	16·0°	$8H_2O$	45·5	55·2°	$5H_2O$	65·6	92·0°	$1H_2O$	81·8
−1·23	,,	11·00	20·5	$8H_2O$	48·8	57·6	$3H_2O$	67·3	94·4	$1H_2O$	82·5
−1·97	,,	16·68	24·0	$5H_2O$	50·2	59·8	$3H_2O$	68·2	101·4	$1H_2O$	84·1
−2·84	,,	24·36	28·0	$5H_2O$	52·1	61·9	$3H_2O$	68·6	107·2	$1H_2O$	86·2
−3·68	,,	29·04	29·3	$5H_2O$	52·7	63·4	$3H_2O$	69·3	114·5	$1H_2O$	87·7
−4·34	,,	31·02	32·2	$5H_2O$	54·0	65·7	$3H_2O$	70·5	116·8	$1H_2O$	88·7
−4·70	,,	32·62	34·5	$5H_2O$	55·0	73·2	$3H_2O$	73·6	123·0	$1H_2O$	92·6
−4·97	$8H_2O$	33·78	37·2	$5H_2O$	56·3	79·9	$3H_2O$	77·6	110·0	$1H_2O$	98·0
+0·07	$8H_2O$	36·61	38·1	$5H_2O$	57·1	80·1	$3H_2O$	78·1	108·4	$1H_2O$	98·1
3·2	$8H_2O$	37·9	43·8	$5H_2O$	59·9	82·5	$1H_2O$	79·9	99·0	†	99·4
6·2	$8H_2O$	39·6	50·7	$5H_2O$	63·0	83·3	$1H_2O$	80·1	104·0	†	100·0

* Sol. pt. = solubility point. † = Anhydrous acid.

usual cryoscopic method for the determination of molecular weights. The point *H* (the m. p. of the anhydrous acid) and the one point on the curve *GH* were obtained by a separate technique described later. These two points are represented by the last two values in Table 3.

Determination of the Composition of the Solid Phases.—The solid phases listed in Table 1 include two hydrates, the octahydrate and the pentahydrate, which have not previously been described. The mono- and tri-hydrate were described by Witt (*loc. cit.*) and by Kraft and Roos (*loc. cit.*), and their existence was verified by the isothermal pressure–composition (*P–x*) diagrams (Fig. 3) which are described later. These diagrams also show the existence of a penta- and an octa-hydrate, the compositions of which were confirmed by analysis. That of the *octahydrate* was determined by stirring a complex of solid and saturated solution, to which a small amount of hydrochloric acid had been added as solution indicator, at 0° until equilibrium was attained. The solution and wet solid were separated by filtration and analysed for total chloride and acid. From these analyses the compositions of the solid and liquid phases were calculated. The composition of the *pentahydrate* at 30° was determined in a similar manner. The theoretical and experimental values for the solid phases are :

	Naphthalene-β-sulphonic acid, %				Naphthalene-β-sulphonic acid, %	
Temperature	Found		Required	Temperature	Found	Required
0° (octahydrate)	59·2	58·6	59·1	30° (pentahydrate)	68·9	69·8

Determination of the T–x *Co-ordinates of Invariant Points.*—As can be seen from Fig. 1, the binary system contains five invariant points : *B* and *G* are eutectic points, *C*, *D*, and *E* are solid-phase transition points, and *F* is a congruent m. p. The composition of the ice eutectic (*B*) was obtained with sufficient precision from the intersection of the two relevant portions of the saturated solution boundary curve; its temperature was determined more exactly as the lowest obtainable by adding alternately small portions of water and hydrated β-acid to a cooled mixture of approximately the eutectic composition without causing complete solidification. In this way the composition of the eutectic was " straddled." The composition of the anhydrous acid–monohydrate eutectic (*G*) was similarly determined although, owing to the hygroscopic nature of the anhydrous acid, not with the same precision as for the ice eutectic. Its temperature was determined by evaporating known amounts of water vapour from mixtures of the tri- and the mono-hydrate by a technique similar to that used for the determination of pressure–composition data. The mixed hydrates were dehydrated at 90° until their compositions were between those of the monohydrate and the anhydrous acid, and were then sealed in small glass tubes, and the temperature was slowly raised until the first signs of softening were observed. This method located the eutectic point to within $\pm 0{\cdot}5°$. By weighing one such sealed tube and analysing the contents, one point on the anhydrous acid solubility curve, *GH*, was obtained.

Owing to the slight change in slope of the solubility curve at the transition points *C*, *D*, and *E*, the *T–x* co-ordinates could be determined only approximately from the points of intersection of the two relevant portions of the curve. Thermal analysis proved satisfactory for determining accurately the temperatures of the penta–tri-hydrate (point *D*) and tri–mono-hydrate (point *E*) transitions but failed in the case of the octa–penta-hydrate transition point (*C*) presumably because of the small heat of transition. However, the temperature of the latter transition was determined by means of a sensitive dilatometer with a precision of $\pm 0{\cdot}5°$.

The m. p. of the monohydrate (*F*) was determined by heating a sample of the monohydrate, obtained by dehydrating the normal material, under a partial water-vapour pressure somewhat greater than its vapour pressure at the m. p. in order to prevent dissociation of the monohydrate.

The complete co-ordinates of the invariant points are given in Table 1.

Determination of the Melting Point of Anhydrous Naphthalene-β-sulphonic Acid.—Anhydrous β-acid was obtained by evacuating a small glass bulb containing a mixture of the mono- and the tri-hydrate to a pressure of 4×10^{-3} mm. and maintaining this vacuum whilst slowly heating (1 hour) the sample to 90° : there was no softening of the material. Finally, the temperature was again raised and a sharp m. p. was observed at 103·5—104°. This procedure was repeated several times and the reproducibility and sharpness of the m. p. justify the conclusion that the material was anhydrous. The liquid β-acid was practically colourless.

The 25° Pressure–Composition Isotherm.—The *P–x* relationships at 25° for the whole system were determined in the apparatus shown in Fig. 4(*a*). The samples were placed in bulb *A* which was immersed in a thermostat at 25° ± 0·1°. The expansion bulb *E* was of known volume so that the amount of water vapour exerting a measured pressure on the mercury manometer *M* could be calculated. Bulb *W*, which contained solid $Na_2SO_4,10H_2O$, supplied water vapour to the apparatus. Well-defined " steps " were obtained on hydrating and dehydrating the starting material, which is a mixture of the mono- and the tri-hydrate. The results obtained are represented graphically in Fig. 3. All the values are given for the dehydration of the starting material, but when hydrating the anhydrous–monohydrate mixture complete equilibrium was not allowed to take place between all the separate additions of water vapour in order to save time.

The 15° *Pressure–Composition Isotherm.*—After the discovery of the existence of an octahydrate stable up to about 20°, a similar procedure to the above was carried out at 15° to include the dissociation pressure of the octahydrate. Table 4 gives the results obtained, the same apparatus being used as for the 25° isotherm with the sample in a thermostat regulated at 15° ± 0·1°, the hydration technique being used. The dehydration technique was unsuccessful in this case, for the solid separating from saturated solution appeared to be the metastable pentahydrate instead of the octahydrate. The determination of this isotherm, however, is complicated by the fact that the dissociation pressures of the higher hydrates are very similar at this temperature.

TABLE 4. *Hydration of the mixed mono- and tri-hydrates of naphthalene-β-sulphonic acid at* 15°

Vapour pressure (mm. of Hg)	2·90	2·92	9·35	10·33	10·35	10·98	10·95
Water in sample, %	13·3	20·0	29·6	36·9	38·6	40·6	42·1
Moles of H_2O per mole of acid	1·77	2·83	4·86	6·76	7·25	7·90	8·40

The values in Table 4 are plotted in Fig. 3, from a study of which it is obvious that the points themselves are not sufficient evidence for the construction of the complete step-wise graph shown. However, this part of the work was only undertaken to prove that an octahydrate did exist at 15° and there are sufficient points to show this. The other hydrates were already known to exist, and their *P–T* relationships had been established by the methods outlined in the following section.

Pressure–Temperature Relationships.—Three types of apparatus were used for measuring vapour pressure, each type being of all-glass construction and involving the use of a mercury manometer as the pressure indicator. In all cases the mercury levels were read with a cathetometer reading to 0·01 mm. The first type of apparatus, shown in Fig. 4(*a*) has already been discussed. The most useful apparatus for determining *P–T* values is shown in Fig. 4(*b*). It consists essentially of a mercury manometer, which can be made to any required length, with glass bulbs blown on each limb. Before being filled, the tube at *C* is open at the end. Freshly distilled mercury was poured into the clean, dry apparatus so that it was all held in bulb *B*; the sample was then introduced into bulb *A* through a filling tube, and the apparatus connected to the vacuum system at point *C*. The sample in bulb *A* was surrounded by an ethanol–solid carbon dioxide mixture at −80°, and evacuation started with a rotary oil pump. When the pressure was down to about 0·03 mm., the mercury in bulb *B* was warmed gently until it began to boil. After the mercury had cooled, the connection to the pump was closed by means of a tap, and the sample in *A* allowed to warm to room temperature. The sample was then re-cooled to −80° so that any water vapour which came off recondensed on to the sample, leaving behind any air which was originally trapped in the sample. The tap to the vacuum system was opened, any air released from the sample pumped off, and the tube finally sealed off at *C*. The apparatus was then tilted, whilst the sample was still at −80°, so that the mercury ran into the manometer limbs. When in use, the whole apparatus was immersed in a thermostatically-controlled water-bath, and the pressure read directly at various temperatures. The advantages of this type of apparatus are that no taps are used once the apparatus is sealed; hence there is no possibility of leakage, or of condensation of water vapour on the cooler parts of the apparatus since the entire apparatus can readily be immersed in a thermostat and is thus at the same temperature.

The applicability of this instrument was limited by the size of thermostat tank available, and hence for vapour pressures above 200 mm. an isoteniscope method [Fig. 4(*c*)] was used. The air pressure, which is of course equal to the water vapour pressure if both mercury limbs are at the same height, was measured on a 760-mm. closed-end mercury manometer. All parts of the apparatus in contact with water vapour must be at the thermostat temperature, and this involves the use of a tap *T* [Fig. 4(*c*)] working at temperatures up to 130°. Silicone grease was used to lubricate this tap. Even so, it remained leak-proof for only a few hours, which was however long enough to enable measurements on this system to be carried out. The samples, contained in a small tube, were introduced into tube *A*, and the apparatus has the advantage that the samples can be readily changed without dismantling.

When dealing with *P–T* relationships, the complete system naphthalene-β-sulphonic acid–water must be divided into separate smaller systems consisting of two solid hydrates and vapour, or one solid hydrate, saturated solution, and vapour, and each one studied separately. Each separate sample was made up before being introduced into the vapour-pressure apparatus so as to contain as great a proportion of the lower hydrate as conveniently possible. When dealing with solid hydrates, this enabled pressure measurements to be taken beyond the transition point of the higher hydrate, where the system now contained the lower hydrate and saturated solution, and up to the solubility curve of the system where the solution became unsaturated and further pressure measurements were valueless.

In Table 5, *P–T* results are given for each of the ten three-phase systems and the values are plotted in Figs. 2, 2A, and 2B. Fig. 2A is an enlarged portion of the area enclosed by the dotted line in Fig. 2, and Fig. 2B shows the pressure–temperature relationships at the trihydrate transition point (*E*).

TABLE 5. P–T *data for the system naphthalene-β-sulphonic acid–water.*

(*A*) *Monohydrate–anhydrous acid.*

Temp.	25°	50°	60°	81°	93°	97°
Press., mm. ...	0·18	1·00	1·55	4·85	9·0	10·0

(*B*) *Anhydrous acid–saturated solution.*

Temp.	97°	99°	104°
Press., mm. ...	10·0	0·82	*

(*C*) *Trihydrate–monohydrate.*

Temp.	5°	10°	15°	20°	25°	30°	40°	50°	60°	65°	70°	80°
Press., mm. ...	1·13	1·90	2·90	4·19	6·34	9·97	18·84	36·23	60·68	80·24	104·0	163·2

(*D*) *Monohydrate–saturated solution (more water in liquid phase than solid phase).*

Temp.	95°	100°	108°	115°	122°	123°	123·6°	125·9°
Press., mm. ...	220	246	274	304	315	304	268	207

(*E*) *Monohydrate–saturated solution (more water in solid phase than liquid phase).*

Temp.	97°	98°	102°	108°	114°	115·5°	119·5°	120·5°	122·5°	125°	125·9°
Press., mm. ...	10·0	10·9	20·9	33·0	60·0	71·0	102	121	144	184	207

(*F*) *Pentahydrate–trihydrate.*

Temp.	−2·5°	0°	2·5°	5·0°	7·5°	10·0°	15°	25°	36°	40°	47°
Press., mm. ...	2·35	3·00	3·75	4·62	5·68	6·95	9·36	17·50	30·06	37·2	55·5
Temp.	48°	51°	56°								
Press., mm. ...	58·4	71·0	87·0								

(*G*) *Trihydrate–saturated solution.*

Temp.	63·5°	65·0°	69·5°	70·0°	75·0°	80·0°
Press., mm. ...	110·4	117·0	129·5	134·0	152·5	171·8

(*H*) *Octahydrate–pentahydrate.*

Temp.	5·4°	7·0°	10·0°	11·0°	12·0°	15·0°	16·0°	17·0°	18·0°
Press., mm. ...	5·06	5·84	7·27	7·69	8·28	10·35	11·08	11·91	12·71

(*I*) *Pentahydrate–saturated solution.*

Temp.	25°	30°	40°	45°	51°	55°	56·5°
Press., mm. ...	20·3	26·3	44·5	58·7	73·0	84·9	92·0

(*J*) *Octahydrate–saturated solution.*

Temp.	−5°	−3°	0°	6·0°	10·0°	15·0°	20·0°
Press., mm. ...	2·35	2·76	3·59	5·67	7·88	10·95	15·10

* Vapour pressure too small to be measured on mercury manometer.

In general, the measurement of the *P–T* relationship for a solid and its saturated solution presents little difficulty in a closed system such as the apparatus shown in Fig. 4(*b*) even though the volume of the vapour space is large compared with that of the condensed phases. When the vapour pressure increases very rapidly with temperature, as it does along *GJ*, in Fig. 2, then an appreciable amount of water must vaporise when the temperature is increased in order to register the equilibrium pressure. This entails a relatively large change in the ratio of the amounts of the two condensed phases, and it is extremely difficult to prevent the disappearance of one of them. The apparatus shown in Fig. 4(*c*) was therefore modified by attaching to vessel *A* a bulb containing water which could be heated electrically. By this means water vapour could be introduced into the apparatus while it was being heated, and the vapour pressure built up without decomposing completely one of the phases in vessel *A*. When the temperature had become constant, the heated water reservoir was shut off from *A*. In order to check that equilibrium was established, small amounts of water vapour were removed from the system.

This resulted in a fall in pressure which, however, was quickly restored to its previous value, thus ensuring that the measured vapour corresponded to the dissociation pressure of the monohydrate. The maximum temperature point (K) was approached both from the water-rich side, where the saturated solution contains more water than the monohydrate, and the acid-rich side, where the saturated solution contains less water than the monohydrate, *i.e.*, from J and G, respectively.

p–T–V *Relationship*.—Let subscripts 1 and 2 refer respectively to the components water and naphthalene-β-sulphonic acid, and denote the mole-fraction of 2 by x. Then the condition for equilibrium of component 1 between any two phases is that $d\mu_1^V = d\mu_1^L$, where μ is the chemical potential of component 1, the superscripts S (below), L, or V indicating solid, liquid, or vapour phase, respectively. By applying the usual thermodynamic arguments (Guggenheim, "Thermodynamics," North Holland Publ. Co., Amsterdam, 1949) to the equilibrium of components 1 and 2 between the phases V and L and also between S and L it can be shown that

$$T\frac{dp}{dT} = \frac{(x^V - x^L)\Delta H^{SL} - (x^S - x^L)\Delta H^{VL}}{(x^V - x^L)\Delta V^{SL} - (x^S - x^L)\Delta V^{VL}} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

where $\Delta H^{SL} = (\bar{H}_1^L - \bar{H}_1^S)(1 - x^S) + (\bar{H}_2^L - \bar{H}_2^S)x^S$ and so is the enthalpy increase accompanying the transfer of $1 - x^S$ moles of component 1 with x^S moles of component 2 from the solid phase to an infinite amount of the liquid phase. ΔH^{VL}, ΔV^{SL}, and ΔV^{VL} are similarly defined. This expression appears to have been first derived by Smits (*Z. phys. Chem.*, 1912, **78**, 708).

It is easily shown that if 1 mole of liquid phase, *i.e.*, $1 - x^L$ moles of 1, and x^L moles of 2, are formed from the other two phases, then the enthalpy increase accompanying the reaction is given by

$$\Delta H = \frac{x^L - x^V}{x^S - x^V}\Delta H^{SL} - \frac{x^L - x^S}{x^V - x^S}\Delta H^{VL} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

with a similar expression for the volume increase. On insertion of this in equation (1), an equation of the same form as the well known Clausius–Clapeyron equation is obtained, *viz.*,

$$dp/dT = \Delta H/T\Delta V \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

If the volume of 1 mole of any phase is denoted by V with the necessary superscript, and we assume that in our system $x^V = 0$, we find that

$$\Delta V = V^L - V^V(1 - x^L/x^S) - V^S x^L/x^S \quad . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

Usually all volume terms except V^V can be neglected, since it is far greater than any of the others, and so on replacement of V^V by $\boldsymbol{R}T/p$ the expression becomes

$$\Delta V = \boldsymbol{R}T(1 - x^L/x^S)/p \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

This approximation for ΔV is not valid when x^L approaches x^S closely in value.

From equation (1) it can be seen that ΔH consists of a heat of solution and a heat of vaporisation term. We make use of the term $\Delta H_{\text{sol.}}$, defined by Williamson (*Trans. Faraday Soc.*, 1944, **40**, 421) as the enthalpy increase occurring when 1 mole of solid, in this case comprising 1 mole of component 2 and $(1 - x^S)/x^S$ moles of component 1, is dissolved in an infinite amount of nearly saturated solution. A similar term $\Delta H_{\text{vap.}}$ can be introduced for the enthalpy change when 1 mole of vapour evaporates from an infinite amount of the solution. As we assume $x^V = 0$, then the approximate equation can be written

$$d \ln p/d(1/T) = \Delta H/\boldsymbol{R}(1 - x^L/x^S) \quad . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

and

$$\Delta H = x^L\Delta H_{\text{sol.}} - (1 - x^L/x^S)\Delta H_{\text{vap.}} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

Monohydrate–Saturated Solution System.—The pressure–temperature curve of this system has two turning points J and K (Fig. 2), the data for which are as follows :

Turning point	Temp.	Composition of liquid : Acid, %	Composition of liquid : x^L	Press., mm.
$dp/dT = 0$ (J)	120·5°	89·5	0·425	316
$dp/dT = \infty$ (K)	125·9	92·0	0·499	207

When $dp/dT = 0$ the numerator of equation (3) must be zero, *i.e.*, the heat of formation of 1 mole of liquid phase from the other two phases must be zero. Hence by using equation (7) the relative magnitude of $H_{\text{vap.}}$ and $H_{\text{sol.}}$ can be obtained :

$$\Delta H_{\text{sol.}}/\Delta H_{\text{vap.}} = 1/x^L - 1/x^S = 0{\cdot}35$$

When $dp/dT = \infty$ the denominator of equation (3) is zero and the approximate form for ΔV can no longer be used. From equation (4) this turning point occurs when x^L is given by the equation $x^L/x^S = (V^V - V^L)/(V^V - V^S)$. It will be noticed that neither of the turning points occurs when the saturated solution has the same composition as the solid; this would only occur if $\Delta H_{sol.}$ were equal to $\Delta H_{vap.}$, or if the volumes of 1 mole of the liquid and solid phases were equal when x^L was equal to x^S.

Invariant Points.—Congruent m. p.s do not occur with the other three hydrates. However, at point E the composition of the liquid phase is very close to that of the trihydrate, so the condition for a maximum in the p–T curve can possibly occur. The experimental points shown in the enlarged diagram, Fig. 2B, indicate that a maximum does occur, and from considerations of the ΔH values of the three systems in equilibrium at E it can be shown that dp/dT is negative at the transition point.

At any transition point three invariant systems, (X), (Y), and (Z), are in equilibrium, *viz.*, two solid hydrates + vapour (system X), the lower solid hydrate + vapour + saturated solution (system Y), and the higher solid hydrate + vapour + saturated solution (system Z). Naphthalene-β-sulphonic acid being represented by the symbol N, the lower hydrate is written as N,nH_2O, the higher hydrate as $N,(n + y)H_2O$, and the saturated solution as $N,(n + y + z)H_2O$; then the three invariant systems can be represented by the following equations :

$$N,nH_2O\ (s) + yH_2O\ (g) \rightleftharpoons N,(n + y)H_2O\ (s) \qquad . \quad . \quad . \quad . \quad . \quad (X)$$

$$N,(n + y)H_2O\ (s) + zH_2O\ (g) \rightleftharpoons N,(n + y + z)H_2O\ (l) \qquad . \quad . \quad . \quad . \quad . \quad (Y)$$

$$N,nH_2O + (y + z)H_2O\ (g) \rightleftharpoons N,(n + y + z)H_2O\ (l) \qquad . \quad . \quad . \quad . \quad (Z)$$

As the third equation is obtained by summing the other two, then the same relationship will hold for the enthalpy changes, so that if ΔH_x, ΔH_y, and ΔH_z represent the heat of formation of 1 mole of the phase occurring on the right-hand side of each equation then

$$(n + y + 1)\Delta H_x + (n + y + z + 1)\Delta H_y = (n + y + z + 1)\Delta H_z \quad . \quad . \quad . \quad (8)$$

The values of ΔH_x, ΔH_y, and ΔH_z can be obtained from the ln P–$1/T$ curve for each system by using equation (6). These curves are found to be linear, but in the case of any system where x^L approaches x^S very closely in value, then ΔH can decrease to zero and change sign, as occurred in the case of the monohydrate. In system (Y) the liquid-phase composition approaches that of the solid phase more closely than in system (Z), so ΔH_y can be expected to vary rapidly near a transition point where the composition of the saturated solution approaches that of the higher hydrate. In the case of the three transition points, the following ΔH values are obtained for the system (Y) in each case—the experimental value is that obtained from the ln P–$1/T$ curve by use of equation (6), the calculated value being obtained from ΔH_x and ΔH_y by means of equation (8).

Heat of formation of 1 *mole of liquid phase.*

Transition temp.	System	x^S	x^L	ΔH, cal./mole Exptl.	Calc.
20·5°	$N,8H_2O$–Satd. soln.	0·111	0·0752	−3500	−2500
57·8	$N,5H_2O$–Satd. soln.	0·167	0·152	− 830	+ 62
81·4	$N,3H_2O$–Satd. soln.	0·250	0·245	−2540	+3710

The agreement between the experimental and calculated results at the lower transition temperature is within experimental error, but at the highest transition temperature, where x^L and x^S are most nearly equal, the calculated value for ΔH is markedly different from the experimental value and has changed sign, indicating that the p–T curve for this system has a negative slope at the transition point and so must have passed through a maximum in the immediate neighbourhood.

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