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On the Fusion Surfaces of the System Naphthalene-Chlorobenzene-Phenol, and the Molecular Association of Phenol.

By

H. Hirobe, *Rigakushi.*

With 2 plates.

Introduction.

There is a rather large number of ternary systems, whose fusion surfaces have been investigated. But they have been studied mostly in the light of the phase rule, which is avowedly qualitative; and the chief weight has been laid on the determination of the composition and the stability range of the solid phases. The chemical reactions which take place in the liquid phases (excepting dilute solutions) have hitherto been studied only qualitatively, though it is quite clear that more exact knowledge is essential to the elucidation of the quantitative relations of the heterogeneous equilibria. This is doubtless due to the difficulty of getting more precise insight into the state of homogeneous equilibrium in concentrated solutions.

When the liquid phase is a dilute solution, the quantitative relations of the heterogeneous equilibria can be calculated with great precision, provided the chemical reactions in the solution be known. And conversely, when the quantitative relations of the heterogeneous equilibria are given, the state of chemical equilibrium in the solution can be determined. Such in short is the essential feature of the theory of dilute solution in its manifold applications. And this is possible because the chemical potential of each chemical species in the dilute solution is a simple function of the concentration, and its variation with temperature and pressure can be readily calculated. If the chemical potential in a solution of any concentration were as well known, the general quantitative theory of heterogeneous equilibrium could be developed with equal ease. This is at present by no means the case. But in the solutions, whose component chemical species fulfill the conditions of the ideal solution, the chemical potential has the simple form, whatever may be the relative amount of the various substances. *Therefore, when the liquid phase in a ternary system is such a solution, it should be possible to express the fusion surfaces in terms of the heat and the temperature of fusion of the solid phases and the equilibrium constants and the heat of reaction of the reversible chemical changes in the liquid phase. And on the other hand it should be possible to deduce the equilibrium constants etc. of the chemical reaction in the liquid phase from the study of the fusion surfaces.*

In the majority of the ternary systems hitherto investigated, the chemical reactions involved appear to be too complex to lend themselves readily to mathematical treatment. At least it appears premature to attack them without due preparation. Moreover, the temperature has in general not been measured with sufficient accuracy, simply because it has not been necessary for the purpose of the investigators. Hence in order to be able to test the foregoing thesis, I had to study experimentally a comparatively simple case. I chose the system consisting of naphthalene, chlorobenzene, and phenol. The two former components are known to be normal or unassociated substances; and the melting point of naphthalene is such that the temperatures of fusion fall mostly within the range in which exact measurement can be made with comparative ease. Phenol is chosen as the third component as it is known to be highly associated. As all the chemical species of the system are aromatic compounds and hence of allied chemical nature, it is probable that the conditions of ideal solutions are fulfilled with tolerable approximation. Chemical combination between the components appears to be excluded, so that the only chemical reaction which takes place in the solution is the polymerisation and depolymerisation of phenol.

The determination of the molecular complexity of substances in the liquid state is a very important subject, but the methods hitherto employed for the purpose are rather one sided and not very accurate. Of these the method of EÖTVÖS, and RAMSAY and SHIELD alone is applicable to pure liquids. But there is some doubt about the mode of calculation involved. Other methods are applicable only to solutes in dilute solutions; particularly the cryoscopic method and that of the partition coefficient have been employed with success. In cases like the present, these methods of heterogeneous equilibrium can be employed over a very wide range of concentration.

BECKMANN(1) demonstrated for the first time by the cryoscopic method that phenol is polymerised in its solutions. NERNST(2) arrived at the same conclusion by the method of partition co-

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1) Zeits. f. physik. Chem., 2, (1888), 715.
2) Zeits. f. physik. Chem., 8, (1891), 116.

efficient. T. YAMAMOTO[1] has lately studied the fusion curve of naphthalene in the system naphthalene-phenol, and concluded from his data that the reaction is

$$3\,(C_6H_6O) \rightleftarrows (C_6H_6O)_3.$$

But as there could be only one concentration corresponding to each temperature in the system studied by him, he was unable to study the isothermal relations.

In the present study the fusion surfaces with naphthalene and phenol as solid phases have been determined, necessary precautions being observed in the measurement of the temperatures of equilibrium. From the data so obtained the polymerisation of phenol in the solution has been deduced.

The partition of phenol between water and chlorobenzene in relatively concentrated solution has also been studied, and the results are compared with those obtained in the foregoing investigation.

I. The Fusion Surface of the ternary System, Naphthalene-Chlorobenzene-Phenol.

1. EXPERIMENTAL.

A. The Materials.

Naphthalene was first distilled, and then the portion with a constant boiling point was recrystallised from a large quantity

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[1] See the foregoing paper.

of ordinary alcohol. After the alcohol had been removed, it was dried in a vacuum desiccator over concentrated sulphuric acid. Its melting point was 79.88°–79.89°.

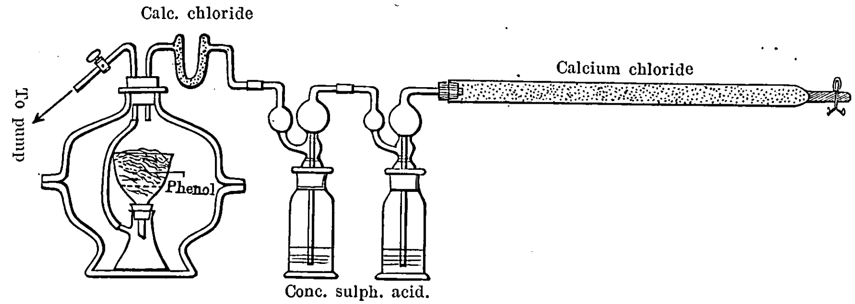


Fig. 1.

Phenol in loose crystals obtained from Kahlbaum, was first distilled, and then crystallised from petroleum-ether (b. p. ca. 60°), from which it separated as fine pure white needles. It was difficult to get rid of the petroleum-ether which adhered to the crystals, because phenol is so hygroscopic that it can not be handled on the suction filter. The apparatus shown in the annexed diagram was therefore set up, and after two days of suction in dry atmosphere with a slow but steady current of air, the sample was placed in a desiccator over phosphoric pentoxide. The melting point was not quite constant but fluctuated between 40.27° and 40.42°, perhaps on account of the different degrees of humidity of the atmosphere and of the vessels at the time of observation.

Chlorobenzene, also from Kahlbaum, was sufficiently pure without further treatment. On distillation the boiling point was quite constant at 132.00°.

B. The Measurement of Temperature.

All temperatures were measured with a thermo-element of iron and nickeline. The fixed temperature was maintained by a thermostat at 25°.

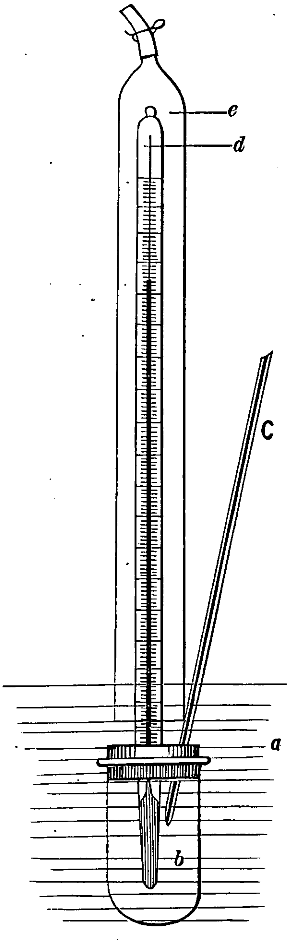


Fig. 2.

The temperature of a thermostat is subject to irregular local fluctuations, which are not usually indicated by the thermometer placed in it, because an ordinary mercury thermometer reacts too slowly. But this may affect the thermo-element whose indication is much quicker. As the disturbance is due to the current of water it can be easily removed. Fig. 2 *b* is a glass vessel with a cork, through two holes in which the thermometer *d* and one of the junctions *c* of the thermo-element are inserted, *e* is a wide glass tube put around the thermometer. The water of the thermostat is sucked up into it and kept at the proper level by means of a pinch cock. In this way the water circulates by convection, and it may be assumed that the whole mercury thread of the thermometer is at the temperature of the thermostat. The glass vessel dipped in the thermostat hinders the communication of the water with the outside and the small local variation in the temperature of the thermostat has little influence upon the interior of the vessel. Thus the fixed temperature was safely constant up to 0.01° during the whole period of observation. The thermometer in the thermostat was corrected by comparison with a thermometer standardised at the Reichsanstalt.

The electromotive force of the thermo-element was compensated by a Weston standard cell of a very large capacity. The cell-liquid contained no crystal of cadmium sulphate to eliminate temperature influence.

Since the regular compensation apparatus was not at hand, we used the ordinary resistance box, and the mode of compensation was as shown in the diagram (Fig. 3).

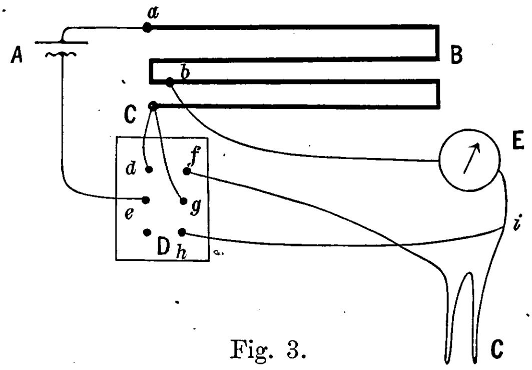


Fig. 3.

A = standard cell.
B = resistance box.
C = thermo-element.
E = mirror galvanometer.
D = commutator made of a paraffine block.

Between *a* and *b* 20000 ohms were inserted, while the necessary resistance for compensating the thermo-electricity was put between *b* and *c*. On closing *d*, *e* and *f*, *g* we have the thermo-electricity compensated by the fraction of the electromotive force of the standard cell. On opening them and closing *g*, *h* we have a circuit from which both the thermo-element and the Weston cell are excluded, and we obtain the zero point of the galvanometer, and even if very little thermo-electricity occurs, on account of some inequality in the distribution of temperature in the circuit, it may be thus eliminated by reading the zero point after every observation. The smallest resistance in B was 0.1 ohm, and by means of the deflection of the galvanometer one hundredth of one ohm could easily be read. Since the sensibility of the galvanometer depends upon the resistance in the circuit, we calculated the relation between the resistance between b and c and the deflection of the galvanometer for the excess of one ohm between the same points, by means of the following equation :

$$y = 89 \times \frac{4.70}{89+12.5+x},$$

where y = the deflection for an excess of one ohm.
89 = the resistance of the galvanometer.
12.5 = the resistance of the thermo-element.
x = the resistance between b and c.
4.70 = the deflection for an excess of one ohm between b and c without the thermo-junctions.

The calibration of the thermo-element was done as shown in the " physiko-chemishe Messungen " by OSTWALD and LUTHER (p. 445). For fixed temperatures we selected the freezing points of water, benzene and acetic acid, and the boiling points of carbon bisulphide, chloroform and benzene, compared with the temperature of the thermostat. All the temperatures were measured with the normal thermometer itself or the thermometer corrected by the former, and could be relied upon up to 0.02°. The deviations from the linear equation,

$$\Delta t = \beta r.$$

where $\Delta t = 25.00° -$ Observed temperature,
r = resistance in b and c,
β = coefficient,

were traced in the curve (Fig. 4).

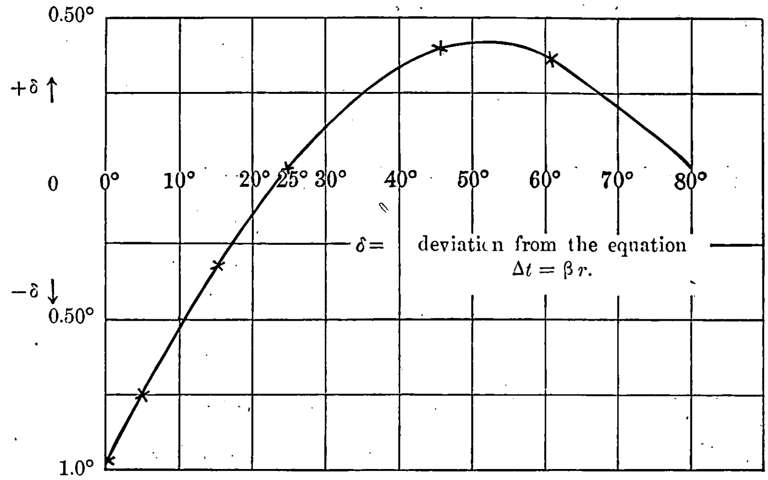


Fig. 4.

C. The Heat Capacity of the Solutions.

In the case of dilute solutions the quantity of crystals which separates out is negligible in the determination of the concentration, but in concentrated solutions this must be taken into account. For this purpose it is necessary to know the heat capacity of the solution, the vessels, etc., and the degree of supercooling. Before proceeding to the observation of the fusion points, the heat capacity was determined in the following manner. Electric energy was converted into heat, and the rise of temperature was read, from which the specific heat could be calculated by the equation,

$$\text{Specific heat} = \frac{R \times \frac{Q^2}{t} \times 0.238}{\text{weight of liquid} \times \text{temperature increase}},$$

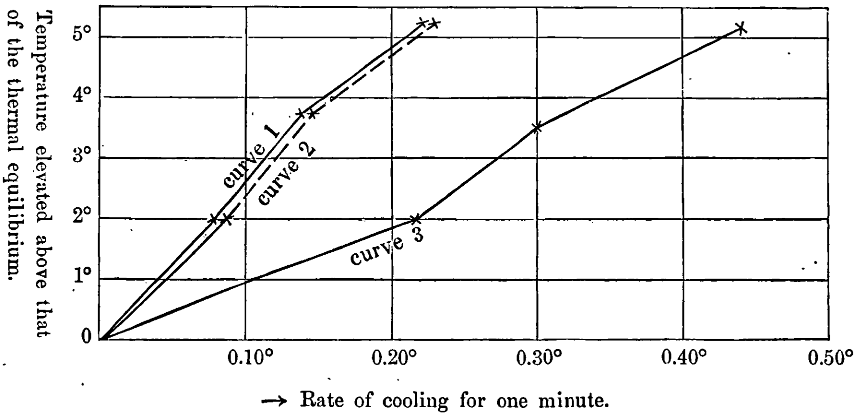
where

R = the resistance of the manganine wire for heating the liquid,

Q = the quantity of electricity passed,
t = the time during which the current was passed,
0.238 = the electric equivalent of the heat.

Q was determined by means of the iodine voltameter,[1] and the time was read to a second with an ordinary watch.

The apparatus employed for the determination was the same as that described later on. In such an arrangement the cooling effect is considerable and must of course be taken into account. In Fig. 5 the relation between the temperature elevation above that of thermal equilibrium and the rate of cooling for one minute is given for water and chlorobenzene. As is to be seen from curves 1 and 2 (Fig. 5) the rapidity of cooling is almost independent of the quantity of the liquid. This is perhaps due to the fact that the greater the amount of the liquid, the greater is the surface exposed. By comparing the curves for chloro-



Curve 1. 20 c.c. water.
Curve 2. 40 c.c. water.
Curve 3. 20 c.c. chlorbenzene.

Fig. 5.

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1) Phys. Zeit, **6**, 579-581, (1905).

benzene and water we see that the former has a rapidity of cooling twice as great as the latter. The heat capacity of the vessel etc. was 3.5 while the heat capacity of 20 c.c. chlorobenzene was 22×0.33 (see below). Hence the total heat capacity was:

$$22 \times 0.33 + 3.5 = 10.8.$$

The total heat capacity of the vessel with 20 c.c. of water was:

$$20 \times 1 + 3.5 = 23.5.$$

The ratio of these heat capacities is:

$$\frac{23.5}{10.8} = 2.17.$$

As might be expected the heat capacity is inversely proportional to the rate of cooling, other conditions being equal. We therefore calculated the loss of heat during observation according to this conclusion. We determined in the first place the heat capacity of the vessel, the stirrer, etc. The result was as follows:

t	Δt	v	$H.Q$	$h.q$	$H.C$
45°C.	2.77°	19.9	65.4	55.4	3.8
70°C.	1.20°	19.9	27.1	24.0	3.3
45°C.	1.83°	2×19.9	83.5	73.2	6.0
45°C.	1.77°	2×19.9	81.0	70.8	6.0

where

t = the temperature at which the determination was made,

Δt = the temperature elevation due to the electric current, + the cooling during the observation,

v = the volume of water to be warmed,

$H.Q$ = the heat quantity determined by means of the iodine-voltameter,

$h.q$ = the heat quantity necessary to warm the water only, calculated from its volume,

$H.C$ = the heat capacity of the vessel etc.

As can be seen from the foregoing table the heat capacity of the vessel, etc. depends upon the volume of the liquid contained in the vessel. We represented graphically the heat capacities of the latter, using those for 20 c.c. and 40 c.c. of the liquid contained in it. In the next place, with the help of the values thus found, we determined the specific heat of naphthalene etc. The results are given in the following table and compared with those of former observers.

t	Substance and its weight.		$s.h$ found.	$s.h$ by former observers.
40°	C_6H_5Cl	21.9 gr.	0.328	0.325 Schiff
60°	„	„	0.326	
90°	$C_{10}H_8$	16.3 gr.	0.381	0.396 Batteli
65°	C_6H_6O	21.1 gr.	0.594	0.561 Schlamp
80°	„	„	0.607	

From these values we calculated the heat capacities of various solutions, on the assumption that the heat capacity is an additive quantity.

The heat capacity enters into the calculation as a term of correction in the determination of the fusion point. If it is reliable up to 10% we can in almost all cases calculate the composition of a solution to 1‰.

The rate of cooling depends not only on the temperature of the bath, but also on the difference between this temperature and that of the room, for heat may radiate into the space above. Hence we observed the rate of cooling immediately before making observations on the fusion points.

D. The Fusion Surface of Naphthalene.

The arrangement employed is shown in Fig. 6. *B* is a glass tube (17 cm. in height, 4 cm. in diameter), within which

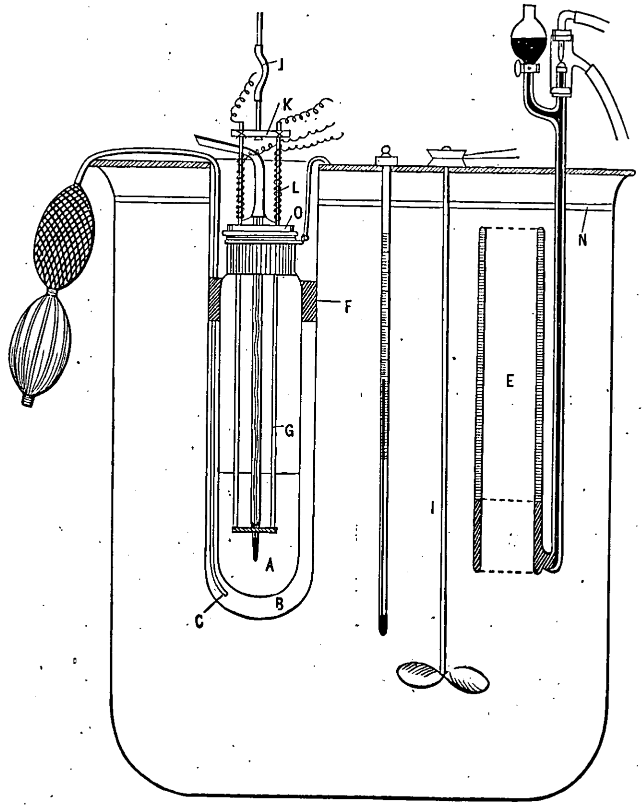

Fig. 6.

a smaller tube *A* (height 13 cm., diameter 3 cm.) is placed. The larger tube is fastened to the wooden cover of the bath. The smaller tube has a hollow glass stopper, the inside of which is filled with a cork. The latter is provided with four holes, two of which serve to admit the stirring rods, the third for the insertion of the thermo-junction, and the fourth for adding phenol or chlorobenzene to the solution. *D* is a hand-bellows which is used to force in air in order to cool the inner tube. *F* is a piece of thick felt and serves to keep the inner tube in position. *L* is thin insulated manganine-wire wound round the stirring rods, through which an electric current is passed to prevent the cooling of the rods from the outside.

When this precaution is not observed, the naphthalene is apt at higher temperatures to sublime round the rods; and moreover it is difficult to maintain the state of superfusion before stirring the liquid, since naphthalene crystalises rapidly round the cold copper rods. *K* is an ebonite piece. *J* is a caoutchouc tubing connecting the stirrer and the rod hanging from an excentric wheel which is kept in motion by an electric motor. The caoutchouc tube proved to be very useful, since by shortening or elongating it we could very easily adjust the height to which the stirrer was to be lifted; so that it might correspond to the amount of liquid contained in the tube. *I* is the stirrer of the bath kept rotating by a hot air engine. *E* is a temperature regulator with a hollow cylindrical reservoir containing toluene in the space between its double walls, so that the surface exposed to the liquid of the thermostat is large in comparison to the capacity of the reservoir. The temperature of the bath must be varied from time to time as the fusion point descends, and it was absolutely necessary to have a sensitive and rapidly adjustable regulator to economise time. The shape given to the regulator was found to answer the purpose very well. It required only two or three minutes before we could be assured that the toluene within it had attained the temperature of the bath, and there was no fear of breaking the thin rubber cover[1] by closing the stop-cock too early. *N* is the layer of paraffine oil floating upon the water to prevent evaporation.

In order to make observations on the fusion surface of naphthalene, about 10 gramme of it was placed in the inner tube, and phenol or a mixture of phenol and chlorobenzene was added in successive portions by means of the pipette shown in Fig. 7. After each addition the bath was cooled a few degrees below the supposed fusion point, and forcing in cold air by means of the hand-bellows the fusion point was roughly observed. Then the temperature of the bath was raised to just within 0.1°–0.5° of the fusion point. The crystal which had separated out was dissolved by passing an electric current through the ring of wire attached to the stirrer, and on opening the circuit the rate of cooling was observed for one minute. Then cold air was blown in, the temperature in the inner tube fell 0.1°–0.2° below the fusion point. The stirrer was again set in motion, the minimum temperature was observed, and the time was recorded. In a short time crystals made their appearance in abundance, the maximum temperature and the time were noted. The cooling during the observation of the fusion point was calculated from the rate of cooling already observed, assuming it to be proportional to the temperature difference between the solution and the bath. In this way the quantity

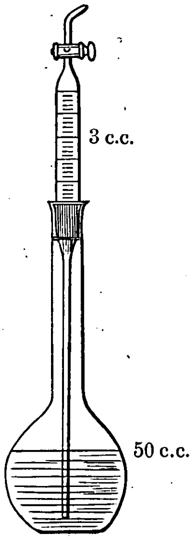

Fig. 7.

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[1] In order to prevent the mercury from coming into direct contact with the gas, a thin rubber cover is stretched over the top of the tube containing the mercury and communicating below with the reservoir. This device, the invention of an English chemist, proved very advantageous when a very exact regulation of temperature was needed.

of the crystals separated out was calculated, and the composition of the solution was corrected accordingly. The maximum temperature was constant for from 20 seconds to 2 minutes according to the rate of cooling.

The results of our determinations are given in the following tables.

TABLE 1.

Fusion Curve No. 8.

Naphthalene-chlorobenzene. Solid phase : naphthalene.

No.	t	c	Δt	X	n	C	N	C_A	Q
1	79.88	0.000	—	—	—	—	—	1.0000	(4650)
2	72.88	1.285	0.58	0.13	10.47	.01142	.08179	0.8775	4530
3	65.67	2.815	0.47	0.11	10.49	.02502	.08196	0.7662	4450
4	59.46	4.464	0.80	0.20	10.40	.03968	.08125	0.6720	4535
5	53.66	6.193	0.73	0.20	10.40	.05505	.08125	0.5964	4515
6	47.73	8.209	0.62	0.20	10.40	.07300	.08125	0.5269	4480
7	42.69	10.259	0.63	0.23	10.37	.0913	.08102	0.4700	4490
8	35.01	13.701	0.80	0.20	10.30	.1228	.08047	0.3980	4420
9	25.58	19.142	0.78	0.34	10.26	.1701	.08017	0.3205	4390

t is the fusion temperature in centigrade,

c is the weight of chlorobenzene added,

Δt is the degrees of supercooling + degrees of cooling during observation,

X is the quantity of the crystals separated out, calculated from Δt and the heat capacity of the solution, the vessel, etc.,

n is the weight of naphthalene in the solution at the moment of equilibrium,

C_A is the molar fraction of naphthalene in the same solution,

Q is the value calculated from the equation,

$$\ln C_A = \frac{Q}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right),$$

where $T_0 =$ the absolute fusion point of pure naphthalene,
$T =$ the absolute fusion point of the solution,
(4650) is the value experimentally obtained by ALLUARD.[1]

The values of Q in No. 2 and No. 3 are not reliable, because $(T_0 - T)$ and $\ln C_A$ have too small values and an error may effect even the second figure of Q.

At any rate the values decrease regularly with a decreasing temperature, or with an increasing concentration of chlorobenzene. This is doubtless due to the inequality of the specific heats of liquid and solid naphthalene. But it may also be due to the insufficient fulfillment of the conditions of the ideal solution by naphthalene and chlorobenzene. This point will be discussed further on.

TABLE 2.

Fusion Curve No. 1.

Naphthalene-phenol. Solid phase: naphthalene.

No.	t	p	Δt	X	n	P	N	x
1	79.87°	0.000	—	—	—	—	—	1.0000
2	72.87°	1.355	0.81	0.18	9.90	.01441	.07734	0.8433
3	67.98°	2.807	1.16	0.29	9.79	.02986	.07648	0.7190
4	63.58°	4.684	0.68	0.20	9.88	.04983	.07719	0.6083
5	59.11°	7.010	1.35	0.45	9.63	.07458	.07523	0.5002
6	54.64°	9.708	0.33	0.13	9.95	.1033	.07773	0.4294

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[1] Ann. de chim. et de phys. (3), **57**, 471, (1859).

7	51.02°	12.757	0.58	0.26	9.82	.1358	.07672	0.3610
8	45.59°	17.310	0.91	0.48	9.60	.1842	.07500	0.2894
9	40.20°	22.846	0.55	0.35	9.73	.2431	.07602	0.2382
10	34.59°	29.295	0.59	0.45	9.63	.3117	.07524	0.1947
11	29.60°	37.345	0.09	0.09	9.99	.3974	.07805	0.1641
12	29.27°	—	—	—	—	—	—	(0.162)

where

p is the weight of phenol added,

P is the number of phenol molecules calculated as C_6H_6O,

N is the number of naphthalene molecules,

x is the empirical molar fraction of naphthalene calculated with phenol as C_6H_6O,

t, Δt, X, n have the same meaning as table 1.

The fusion curve observed by T. YAMAMOTO[1] coincides fairly with ours except at a few points.

The data in the two foregoing tables give the boundary curves for the fusion surface with naphthalene as the solid phase.

TABLE 3.

Fusion Curve No. 2.

Naphthalene-chlorobenzene-phenol. Solid phase: naphthalene.

No.	t	m	Δt	X	n	$P+C$	N	x
1	(79.88°)	—	—	—	—	—	—	1.0000
2	72.49°	1.336	0.18	0.04	9.94	.01400	.07766	0.8472
3	67.76°	2.749	0.83	0.21	9.77	.02880	.07633	0.7263
4	63.97°	4.177	0.48	0.13	9.85	.04376	.07695	0.6375
5	59.55°	6.193	0.52	0.16	9.82	.06488	.07672	0.5418

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[1] See the foregoing article.

6	54.76°	8.908	0.62	0.22	9.76	.09333	.07624	0.4496
7	49.32°	12.636	0.40	0.15	9.83	.1324	.07696	0.3675
8	42.38°	18.15	0.49	0.26	9.72	.1902	.07694	0.2854
9	37.31°	23.22	0.34	0.20	9.78	.2433	.07640	0.2390
10	31.55°	29.70	0.60	0.43	9.55	.3112	.07461	0.1943
11	27.02°	36.10	0.78	0.67	9.31	.3782	.07273	0.1613

The fusion point of pure naphthalene was not observed, since the same sample was used as in fusion curves No. 1 and No. 8.

In the above table m is the mixture of phenol and chlorobenzene in the ratio of 40.248 gramme: 4.135 gramme.

$$\frac{P}{P+C} : \frac{C}{P+C} = .9209 : .0791$$

x is the empirical molar fraction of naphthalene calculated with the mean molecular weight of the mixture of phenol and chlorobenzene = 95.45.

TABLE 4.

Fusion Curve No. 3.

Naphthalene-chlorobenzene-phenol. Solid phase: naphthalene.

No.	t	m	Δt	X	n	$P+C$	N	x
1	(79.88°)	0.000	—	—	—	—	—	1.0000
2	71.81°	1.474	0.54	0.12	10.02	.01499	.07828	0.8395
3	67.05°	2.710	0.87	0.21	9.93	.02756	.07757	0.7381
4	60.30°	5.036	0.96	0.27	9.87	.05122	.07711	0.6010
5	56.15°	6.807	0.78	0.24	9.90	.06923	.07734	0.5276
6	51.57°	9.136	0.49	0.17	9.97	.09294	.07789	0.4560
7	46.82°	11.84	0.30	0.12	10.02	.1204	.07828	0.3940
8	41.38°	15.59	0.62	0.28	9.86	.1585	.07704	0.3271

9	35.76°	20.12	0.60	0.32	9.82	.2046	.07672	0.2727
10	30.13°	25.64	0.27	0.20	9.94	.2606	.07766	0.2296
11	25.25°	31.42	0.48	0.32	9.82	.3198	.07672	0.1935

where m is the amount of the mixture in the ratio:

24.102 gramme (phenol): 8.967 gramme (chlorobenzene),

i. e. $$\frac{P}{P+C} : \frac{C}{P+C} = .7628 : .2372 ;$$

the mean molecular weight of the mixture is 98.33.

TABLE 5.

Fusion Curve No. 4.

Naphthalene-chlorobenzene-phenol. Solid phase: naphthalene.

No.	t	m	Δt	X	n	$P+C$	N	x
1	79.88°	0.000	—	—	—	—	—	1.0000
2	72.36°	1.326	0.48	0.11	10.10	.01320	.07891	0.8566
3	67.53°	2.485	0.73	0.10	10.11	.02473	.07898	0.7616
4	62.33°	4.018	0.16	0.04	10.17	.03999	.07945	0.6653
5	57.88°	5.536	0.47	0.14	10.07	.05510	.07867	0.5880
6	53.46°	7.364	0.74	0.24	9.97	.07328	.07789	0.5152
7	48.76°	9.623	0.47	0.17	10.04	.09576	.07844	0.4503
8	42.78°	12.90	0.37	0.16	10.05	.1284	.07852	0.3795
9	35.82°	17.60	0.50	0.25	9.96	.1751	.07781	0.3149
10	28.48°	24.13	0.48	0.30	9.91	.2391	.07742	0.2446

Phenol : chlorobenzene = 12.555 gramme : 9.319 gramme,

i. e. $$\frac{P}{P+C} : \frac{C}{P+C} = .6482 : .3518 ;$$

the mean molecular weight of the mixture is 100.5.

TABLE 6.

Fusion Curve No. 5.

Naphthalene-chlorobenzene-phenol. Solid phase: naphthalene.

No.	t	m	Δt	X	n	$P+C$	N	x
1	(79.88°)	—	—	—	—	—	—	1.0000
2	67.01°	2.496	0.44	0.10	10.08	.02428	.07876	0.7644
3	61.92°	3.823	0.35	0.09	10.09	.03718	.07876	0.6795
4	57.13°	5.403	0.45	0.13	10.05	.05254	.07852	0.5990
5	51.98°	7.393	0.34	0.11	10.07	.07190	.07867	0.5224
6	47.52°	9.308	0.58	0.21	9.97	.09055	.07790	0.4626
7	43.43°	11.298	0.44	0.17	10.01	.1099	.07820	0.4157
8	39.88°	13.31	0.18	0.07	10.10	.1295	0.7891	0.3786
9	35.22°	16.23	0.21	0.10	10.08	.1578	.07876	0.3329
10	30.58°	19.76	0.21	0.11	10.07	.1922	.07867	0.2904
11	24.70°	24.58	0.34	0.17	10.01	.2390	.07820	0.2466

Phenol: chlorobenzene 16.47 gramme: 18.07 gramme,

i. e. $$\frac{P}{P+C}:\frac{C}{P+C} = .5218:.4782;$$

the mean molecular weight of mixture is 102.8.

TABLE 7.

Fusion Curve No. 6.

Naphthalene-chlorobenzene-phenol. Solid phase: naphthalene.

No.	t	m	Δt	X	n	$P+C$	N	x
1	(79.88°)	—	—	—	—	—	—	1.0000
2	73.01°	1.243	0.24	0.06	10.54	.01179	.08234	0.8748
3	67.35°	2.486	0.56	0.14	10.46	.02357	.08171	0.7761
4	62.54°	3.710	0.33	0.09	10.51	.03517	.08211	0.7000

5	57.67°	5.181	0.33	0.12	10.48	.04911	.08188	0.6250
6	52.88°	6.791	0.30	0.09	10.50	.06437	.08203	0.5604
7	48.03°	8.645	0.50	0.17	10.43	.08196	.08149	0.4985
8	42.89°	10.94	0.36	0.17	10.43	.1037	.08149	0.4401
9	37.37°	13.78	0.56	0.23	10.36	.1306	.08095	0.3827
10	31.56°	17.31	0.50	0.23	10.36	.1641	.08095	0.3304
11	25.23°	21.92	0.50	0.27	10.33	.2078	.08071	0.2798

Phenol : chlorobenzene = 8.073 gramme : 15.785 gramme,

i. e. $$\frac{P}{P+C} : \frac{C}{P+C} = .3796 : .6204 ;$$

the mean molecular weight of the mixture is 105.5.

TABLE 8.

Fusion Curve No. 7.

Naphthalene-chlorobenzene-phenol. Solid phase : naphthalene.

No.	t	m	Δt	X	n	$P+C$	N	x
1	(79.88°)	—	—	—	—	—	—	1.0000
2	73.71°	1.061	0.42	0.09	9.96	.00991	.07782	0.8870
3	68.21°	2.114	0.26	0.06	9.99	.01975	.07805	0.7982
4	63.31°	3.241	0.58	0.14	9.91	.03028	.07743	0.7190
5	58.53°	4.503	0.41	0.11	9.94	.04207	.07766	0.6488
6	53.69°	5.959	0.44	0.13	9.92	.05568	.07750	0.5815
7	49.42°	7.410	0.60	0.18	9.87	.06923	.07711	0.5269
8	44.71°	9.160	0.57	0.19	9.86	.08560	.07704	0.4738
9	40.29°	11.09	0.57	0.20	9.85	.1036	.07695	0.4261
10	36.12°	13.14	0.51	0.19	9.86	.1228	.07704	0.3856
11	31.58°	15.70	0.44	0.18	9.87	.1467	.07711	0.3445
12	23.41°	21.34	0.35	0.16	9.89	.1994	.07727	.02792

Phenol : chlorobenzene = 7.000 gramme : 10.052 gramme,

i. e. $$\frac{P}{P+C} : \frac{C}{P+C} = .2940 : .7058\,;$$

the mean molecular weight of the mixture is 107.0.

These eight curves are reproduced in Plate I, with the empirical molar fraction of naphthalene x as abscissa and the temperature t as ordinate. $1-x$ is the sum of the molar fractions of phenol and chlorobenzene, which have a fixed ratio in each curve. It is advantageous to represent the relative amount of these two components again in the form of the molar fraction:

$$Y = \frac{P}{P+C}.$$

Curve 8, in which $Y=0$, has a form approximating to that of the ideal fusion curve, while in Curve 1, in which $Y=1$, the deviation is enormous. All the other curves find their positions between these two boundary curves according to the value of Y. The curves with Y larger than 0.5 have inflexion points, while the other curves are concave throughout. These curves should properly be erected on the triangular diagram representing the composition, and the curved surface passing through these eight curves is the fusion surface of naphthalene.

The isothermal curves in the triangular diagram (Plate II) are obtained in the following manner. In this diagram N stands for naphthalene, C for chlorobenzene, and P for phenol. The points corresponding to the different values of Y are taken on the line PC, and these points are united with the apex N by straight lines. These straight lines are the projection of the fusion curves on the plane of composition. Drawing straight lines parallel to the axis of x in Plate I, the points of intersection give the values of x on the fusion curves at constant temperatures. In the next place the points having these values of x (the empirical molar fraction of naphthalene) are taken on the corresponding straight lines in the triangular diagram of Plate II, and connecting all the points of the same temperatures we get the isotherms.

These are shown in the figure and are all convex towards N. The diagram thus obtained is the horizontal projection of the fusion surface. Suppose these isothermal curves to be elevated to proper heights according to the temperature, and imagine a surface passing through all these isothermal curves, then we get the fusion surface under consideration. The surface on the whole has a negative curvature, only a small portion near the apex and next the line NP has a positive curvature being convex towards the corner N.

E. The Fusion Surface of Phenol.

The fusion surface of phenol was determined in a similar manner, and the experimental data are given in the following five tables.

TABLE 9.

Fusion Curve A.

Naphthalene-phenol. Solid phase: phenol.

No.	t	n	Δt	X	p	N	P	x'
1	40.29°	—	—	—	—	—	—	1.0000
2	35.79°	1.004	0.41	0.13	10.74	.00784	.1143	0.9357
3	32.26°	1.957	0.68	0.23	10.64	.01529	.1132	0.8809
4	30.05°	2.577	0.87	0.31	10.56	.02014	.1123	0.8485
5	29.42°	—	—	—	—	—	—	(0.838)

x' is the empirical molar fraction of phenol calculated as C_6H_6O.

All the other symbols in this table have the same meanings as those in the foregoing tables. Naphthalene was added in the pressed form. The curve coincides fairly well with that observed by T. YAMAMOTO.[1]

The eutectic point is 0.15° higher than that in the curve with naphthalene as the solid phase, this is due to the moisture absorbed, since in the former case the observations took two days, while in the present case they were completed in only a few hours.

TABLE 10.

Fusion Curve B.

Naphthalene-chlorobenzene-phenol. Solid phase: phenol.

No.	t	Δt	X	p	n	c	N	C	P	x'
1	40.42°	—	—	—	—	—	—	—	—	1.0000
2	37.27°	0.32	0.09	12.54	0.698	0.084	.00545	.00075	.1334	0.9556
3	32.15°	0.26	0.07	12.56	1.736	0.507	.01356	.00451	.1336	0.8808
4	28.24°	0.34	0.11	12.52	2.817	0.797	.02201	.00709	.1332	0.8207

Since naphthalene and chlorobenzene in such proportions as are given in Table 10 do not form solutions at ordinary temperatures, naphthalene was first added in compressed form and then a corresponding quantity of chlorobenzene by means of a thin graduated pipette.

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1) See the foregoing article.

TABLE 11.

Fusion Curve C.

Naphthalene-chlorobenzene-phenol. Solid phase : phenol.

No.	t	Δt	X	p	n	c	N	C	P	x'
1	40.37°	—	—	—	—	—	—	—	—	1.0000
2	38.32°	0.49	0.18	12.87	0.279	0.241	.00218	.00214	.1358	0.9692
3	34.18°	0.69	0.27	12.78	0.938	0.716	.00735	.00637	.1360	0.9083
4	29.83°	0.58	0.23	12.82	1.661	1.392	.01298	.01237	.1364	0.8433
5	24.64°	0.69	0.30	12.65	2.526	2.577	.01970	.02290	.1346	0.7595
6	20.39°	0.51	0.24	12.81	3.621	3.662	.02830	.03260	.1363	0.6911

TABLE 12.

Fusion Curve D.

Naphthalene-chlorobenzene-phenol. Solid phase : phenol.

No.	t	m	Δt	X	p	$N+C$	P	x'
1	40.33°	—	—	—	—	—	—	1.0000
2	38.49°	0.459	0.16	0.06	13.64	.00396	.1451	0.9732
3	35.75°	1.178	0.44	0.18	13.53	.01015	.1439	0.9338
4	32.20°	2.239	0.27	0.11	13.59	.01929	.1446	0.8822
5	28.05°	3.697	0.47	0.21	13.50	.03185	.1436	0.8182
6	24.02°	5.813	0.23	0.11	14.13	.05009	.1503	0.7501
7	19.93°	8.044	0.35	0.18	14.06	.06931	.1496	0.6834
8	16.59°	10.418	0.42	0.23	14.01	.08977	.1490	0.6242
9	12.83°	13.817	0.93	0.57	13.67	.11905	.1454	0.5499
10	9.38°	17.18	0.35	0.23	14.01	.1480	.1490	0.5017
11	6.50°	20.48	0.23	0.16	14.08	.1765	.1498	0.4591

where

m is the mixture of naphthalene and chlorobenzene in the proportion :

1.473 gramme (naphthalene) : 4.322 gramme (chlorobenzene)

i. e. $$\frac{N}{N+C} : \frac{C}{N+C} = .2305 : 7695$$

the mean molecular weight of the mixture is 116.1.

TABLE 13.

Fusion Curve E.

Chlorobenzene-phenol. Solid phase: phenol.

No.	t	c	Δt	X	p	C	P	x'
1	40.24°	—	—	—	—	—	—	1.0000
2	38.46°	0.477	0.29	0.12	14.25	.00424	.1516	0.9730
3	34.69°	1.509	0.36	0.15	14.22	.01340	.1513	0.9185
4	30.87°	2.723	0.55	0.24	14.13	.02421	.1503	0.8614
5	27.54°	3.986	0.34	0.16	14.21	.03542	.1512	0.8101
6	21.76°	6.231	0.54	0.25	13.18	.05539	.1402	0.7168
7	18.89°	7.982	0.49	0.24	13.19	.07095	.1403	0.6642
8	14.88°	10.461	0.51	0.11	13.32	.09298	.1417	0.6038
9	11.09°	13.60	0.42	0.24	13.19	.1209	.1403	0.5372
10	6.12°	18.94	0.40	0.26	13.17	.1684	.1401	0.4542

In the fusion curves D and E the different temperatures below 20°C. were maintained by dropping ice-cold water into the bath at different rates of rapidity.

These five curves reproduced on the left side of Plate I coincide almost exactly. But at lower temperatures the deviation between the curves D and E exceeds the limits of experimental error. The curves are nearly straight lines being only very slightly convex towards the axis of temperature. Of some of these curves only short sections have been observed owing to the appearance of the eutectic points. Were the observations extended to lower temperatures, doubtless the curves would become concave.

As the curves $(t. x)$ coincide so closely, the isothermals are nearly straight lines parallel to the line NC. From the deviation between the curves D and E we are led to the conclusion that the isothermal must be slightly concave toward P.

The fusion surface of phenol is therefore almost a plane, having a very small negative curvature, being slightly concave in the horizontal and convex in the vertical direction in the region observed.

As the melting point of chlorobenzene is too low for convenient measurement, its fusion surface has not been determined.

F. The Eutectic Curve.

Of the three eutectic curves of the system only one has been studied, i.e. the line of intersection of the fusion surfaces of naphthalene and phenol. On this curve six points have been determined. The binary eutectic point is already given in Tables 2 and 9. Two other points have been determined by following up the fusion curves of naphthalene, and the other three by following up those of phenol.

In the observation of a point on the eutectic line the temperature of the bath was kept some ten degrees below the fusion point of the solution, which was steadily stirred in order to have the liquid and the crystals in a state of equilibrium. The temperature sank continuously while the crystals separated out more and more. At a certain point $t-\Delta t$ the temperature began to rise owing to the separation of the other component as the solid phase, reached the maximum point t in a short time, and fell again slowly. This maximum temperature was read, and the composition of the liquid phase corresponding to it was calculated in the following manner.

To make the procedure clear let us suppose that the eutectic point, or more properly the point on the eutectic line, had been reached by cooling along the fusion curve of naphthalene. The projection of this curve on the plane of composition is represented by a straight line passing through the apex N and the point

$$Y = \frac{P}{P+C},$$

on the line CP. But the fusion curve was displaced somewhat owing to the separation of a small quantity of phenol as the second solid phase. In order to estimate this amount ΔP it is necessary to know the quantity of heat required to heat the system from $t-\Delta t$ to t, and also the heat lost by radiation during the rise of temperature. The latter can be estimated from the rate of cooling, which for this duration amounted to $\Delta t'$. The former amount of heat is again the sum of two heat quantities, viz., first the heat required simply to elevate the temperature of the system; and second the heat absorbed by the dissolution of a small amount of naphthalene, because with the rise of temperature the concentration of naphthalene in the solution must again increase. Now the quantity so dissolved is

$$\begin{aligned} \Delta N &= (N+P+C)\frac{dx}{dt}\Delta t, \\ &= \frac{P+C}{1-x}\,\frac{dx}{dt}\Delta t. \end{aligned}$$

The value of x and $\frac{dx}{dt}$ at t can be determined from the fusion curve, if necessary by exterpolation; hence ΔN can be estimated in this way. If we express the heat capacity of the system by H, and the molecular heat of fusion of naphthalene and phenol by Q_N and Q_P respectively, then the quantity of phenol crystalised out is:

$$\varDelta P = \frac{\varDelta N \,.\, Q_N + (\varDelta t + \varDelta t')\, H}{Q_P},$$

and
$$Y = \frac{P - \varDelta P}{P - \varDelta P + C}.$$

The composition of the eutectic point is to be found in the diagram of Plate II at the intersection of the projection of the fusion curve so displaced and the isothermal curve of the fusion surface of phenol for the temperature t. As both these curves are straight lines the composition is found readily by this graphical method.

Quite the same method of calculation applies to the cases in which the fusion curves of phenol were followed up, where

$$\varDelta N = \frac{\varDelta P\, Q_P + (\varDelta t + \varDelta t')\, H}{Q_N},$$

and
$$Z = \frac{N - \varDelta N}{N - \varDelta N + C}.$$

On following up the fusion curves of phenol were observed,

t	$\varDelta t$	$\varDelta t'$	n	$\varDelta n$	c	Z
26.21°	.13	.06	2.77	.06	.802	.748
19.47°	.08	.14	2.74	.24	2.54	.465
12.26°	.04	.12	2.74	.22	4.63	.323

On following up the fusion curves of naphthalene,

t	$\varDelta t$	$\varDelta t'$	p	$\varDelta p$	c	Y
25.18°	.02	.16	32.74	.23	3.36	.915
17.00°	.13	.26	22.93	.56	8.51	.745

n, c, p are the weights of naphthalene, chlorobenzene and phenol in grammes.

The coordinates of the points are,

	Molar fraction of		
t	naphthalene	chlorobenzene	phenol.
29.00°	.162	.000	.838
26.21°	.160	.057	.783
25.18°	.159	.073	.768
19.47°	.150	.177	.673
17.00°	.150	.217	.633
12.26°	.141	.309	.550

The projection of the eutectic curve on the plane of composition is nearly a straight line; and as the fusion surface of phenol is almost a plane, the curve itself must be nearly a straight line, so far as it has been observed. This does not hold for lower temperatures, but the projection must have the course indicated by the dotted line.

2. THEORETICAL.

In order to facilitate a general survey, the fusion surfaces (in projection on the plane of composition) are reproduced with their isothermal curves. The parts which have not been experimentally determined are supplemented from analogical considerations. This can be done in this case without much danger of falling into gross errors, because the relations of symmetry are so simple and clear.

As we have seen the isotherms of the fusion surface of phenol are nearly straight lines parallel to the line NC. This means that phenol stands to chlorobenzene in exactly the same relation as to naphthalene. Naphthalene can be replaced in the solution mol for mol by chlorobenzene without causing any change in the concentration of the phenol which is in equilibrium with the solid phase.

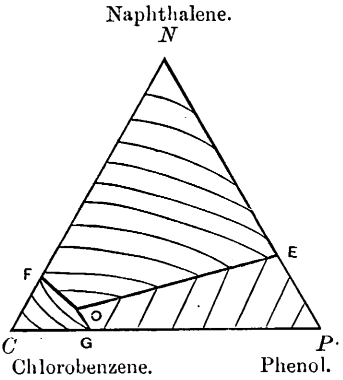

Fig. 8.

The isotherms of the fusion furface of naphthalene are concave towards the line CP, and the empiricial molar fraction of naphthalene decreases with the increasing proportion of phenol. The fusion surface of chlorobenzene lies of course much lower than the other two, but it must have a form quite similar to that of naphthalene, and the isotherms must lie as shown in the figure.

The eutectic curve E O must be the longest of the three, being the line of intersection of the fusion surfaces of the two components with the highest melting points. The other two eutectic curves F O and GO would be relatively undeveloped.

So much can be supplemented from the symmetry relations of the three components. These relations can be readily comprehended, when we consider that naphthalene and chlorobenzene are normal, undissociated substances fulfilling the conditions of the ideal solution with respect to each other, while phenol is an associated substance. That the isotherms of the fusion surface of naphthalene are concave to the axis CP at least in the region where the molar fraction of phenol is not very large, is also to be expected.[1] But in order to account quantitatively for the

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[1] See Art. 10 of this volume.

special form assumed by the fusion surface, we must have more detailed knowledge about the association of phenol.

Nothing certain is as yet known about the polymerisation of phenol in solution. NERNST has concluded from the study of the partition coefficient, that phenol dissolved in benzene is associated to double molecule.[1] But it can not be ascertained whether all of the phenol is associated to such a degree, since in the more dilute solutions it must be considered to be dissociated to a great extent.[2] On the other hand YAMAMOTO[3] has concluded from his study on the fusion curve of naphthalene and phenol, which has also been confirmed in the course of the present investigation, that phenol must be considered to contain more complex molecules, at least $(C_6H_6O)_3$. It is plain that the degree of association depends upon the concentration, as well as on the temperature. The following two equations may be assumed to represent these relations:

$$\mathfrak{K} = \frac{c_1^n}{c_n},$$

$$ln\,\mathfrak{K} = \frac{\mathfrak{Q}}{R}\left(\frac{1}{\mathfrak{T}} - \frac{1}{T}\right).$$

Where

c_1 = the molar fraction of the simple molecule C_6H_6O,

c_n = the molar fraction of $(C_6H_6O)_n$,

$\mathfrak{Q}$ = the heat of dissociation,

$\mathfrak{T}$ = the temperature at which $ln\,\mathfrak{K}$ vanishes,

T = the temperature under consideration.

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[1] Zeit. phys. Chem., **8**, p. 116, (1891).

[2] BECKMANN: Zeit. phys. Chem., **2**, 715, (1888).
AUWERS: Zeit. phys. Chem., **18**, 599, (1895).

[3] Loc. cit.

Here n is quite unknown. Moreover various sorts of associated molecules may exist simultaneously in a solution, and the reactions between them take place freely. Hence the actual relation may be so complex that to make a reliable deduction from the data obtained is impossible. Yet we have ventured to make some calculations on the basis of a simple hypothesis. We have assumed that in the temperature range of 80°–20°, only $(C_6H_6O)_3$ and (C_6H_6O) exist, and other molecular associations may be neglected. It is not excluded that in the higher temperature $(C_6H_6O)_2$ may exist also and in the lower $(C_6H_6O)_4$, and even in the temperature range under consideration molecular associations other than $3\,(C_6H_6O) \rightleftarrows (C_6H_6O)_3$ may take place as a side reaction. But we have ignored these to avoid too great a complexity in the calculation.

From the data given in Tables 2–8 $\mathfrak{K}$ has been calculated for each observation, in order to see whether it remains constant for different concentrations at a constant temperature. The calculation was done in the following manner.

For the ideal or quasi-ideal solutions we have:

$$ln\, C_A = \frac{Q}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right).$$

Where the symbols are the same as in the equation in page 17. In the next place put

$\mathfrak{N}$ = the actual number of molecules of phenol,

N = the empirical number of molecules of phenol calculated as (C_6H_6O),

A = the number of molecules of naphthalene,

B = the number of molecules of chlorobenzene,

n_1 = the number of simple molecules of phenol,

n_3 = the number of triple molecules of phenol,

then we have

$$C_A = \frac{A}{A+B+\mathfrak{N}} \quad\ldots\ldots\ldots\ldots\ldots (a)$$

$$\mathfrak{N} = n_1 + n_3 \quad\ldots\ldots\ldots\ldots\ldots (b)$$

$$N = n_1 + 3\, n_3 \quad\ldots\ldots\ldots\ldots\ldots (c)$$

$$c_1 = \frac{n_1}{A+B+\mathfrak{N}} \quad\ldots\ldots\ldots\ldots\ldots (d)$$

$$c_3 = \frac{n_3}{A+B+\mathfrak{N}} \quad\ldots\ldots\ldots\ldots\ldots (e)$$

$$\therefore \quad \mathfrak{K} = \frac{c_1^3}{c_3} = \frac{(3\,\mathfrak{N}-N)^3}{4\,(N-\mathfrak{N})\,(A+B+\mathfrak{N})^2} \quad\ldots\ldots\ldots (f)$$

Where $\mathfrak{N}$ may be obtained from (a) and the equation

$$ln\, C_A = \frac{Q}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right).$$

In the following table are shown the values of $-\log \mathfrak{K}$ at different temperatures for every fusion curve.

TABLE 14.

Values of $-\log \mathfrak{K}$.

	Numbers of the fusion curves.						
Temperature.	1	2	3	4	5	6	7
65°	1.30	1.39	1.29	1.20	1.17	1.17	1.18
60°	1.59	1.50	1.35	1.30	1.30	1.20	1.20
55°	1.75	1.69	1.54	1.49	1.35	1.29	1.29
50°	1.93	1.99	1.70	1.58	1.49	1.31	1.30
45°	2.22	2.18	1.91	1.68	1.56	1.37	1.29
40°	2.45	2.41	2.12	1.85	1.55	1.47	1.32
35°	2.75	2.77	2.49	2.07	1.75	1.52	1.36
30°	3.70	3.45	2.74	2.51	2.12	1.65	1.56

The terms $(3\mathfrak{N}-N)^3$ and $(N-\mathfrak{N})$ are highly sensitive to experimental errors, and the effects are moreover magnified in the calculation according to (f). Hence exact determination of this magnitude is impossible particularly when the concentration of phenol is small. At a constant temperature $\mathfrak{K}$ ought to be independent of the concentration of phenol. This holds true only for curves 1 and 2. For all others $\mathfrak{K}$ diminishes with the decreasing amount of phenol. The deviation is too regular and one-sided to be accounted for by accidental experimental errors. Therefore we must conclude that either this simple hypothesis does not correspond closely enough to the actual state of things; or that the conditions of the ideal solution are not fulfilled with sufficient approximation; or that there is some constant source of error in our measurements.

But in order to test the equation

$$\frac{c_1^3}{c_3} = \mathfrak{K},$$

the values of $\mathfrak{K}$ as determined above are not accurate enough. Hence it would be more rational to represent $\mathfrak{K}$ as a function of temperature, and then calculate x by means of $\mathfrak{K}$. The value of x so found can then be compared with observation.

The constants in the equation

$$ln\,\mathfrak{K} = \frac{\mathfrak{Q}}{R}\left(\frac{1}{\mathfrak{T}} - \frac{1}{T}\right),$$

have been calculated from the values of $\log \mathfrak{K}$ for fusion curve No. 1 and found to be:

$$q = 20940 \text{ calories}, \qquad T_3 = 373.2.^{1)}$$

---

1) These values do not agree very well with those found by YAMAMOTO; for he has calculated $\mathfrak{K}$ under the assumption that the heat of fusion of naphthalene Q is constant for all temperatures. Moreover a very slight discrepancy in the measurement of the fusion curve may give rise to such deviations.

Inversely $\mathfrak{R}$ has been calculated with these constants.

No.	2	3	4	6	7	8	9	10	11
t	72.87°	67.98°	63.58°	54.64°	51.02°	45.59°	40.20°	34.59°	29.60°
$\log \mathfrak{R}$ (obs.)	1.25	1.23	1.33	1.64	1.87	2.22	2.44	2.78	3.97
$\log \mathfrak{R}$ (calc.)	1.01	1.21	1.40	1.59	1.95	2.20	2.46	2.74	3.00

The numbers refer to the points in Table 2. The agreement is tolerable, and it may be said that $\mathfrak{R}$ can be expressed by the logarithmic equation.

We may now proceed to calculate x. Since

$$\mathfrak{R} = \frac{c_1^3}{c_3},$$

$$c_1 = \sqrt[3]{\mathfrak{R}\, c_3};$$

and as the sum of all the molar fractions is unity,

$$c_3 + \sqrt[3]{\mathfrak{R}\, c_3} + C_B + C_A = 1,$$

where C_A = the actual molar fraction of naphthalene,
C_B = the actual molar fraction of chlorobenzene.

Put

$$\frac{C_B}{c_1 + 3\, c_3} = a,$$

i.e. a = the ratio of the number of molecules of chlorobenzene and phenol in the fusion curve.

Hence

$$c_3 + \sqrt[3]{\mathfrak{R}\, c_3} + a\,(c_1 + 3\, c_3) + C_A = 1,$$

$$\therefore \quad (1 + 3\,a)\, c_3 + (1 + a) \sqrt[3]{\mathfrak{R}\, c_3} - (1 - C_A) = 0,$$

or

$$c_3 + \frac{(1 + a)\sqrt[3]{\mathfrak{R}}}{1 + 3\,a} \sqrt[3]{c_3} - \frac{(1 - C_A)}{1 + 3\,a} = 0.$$

$$\therefore \quad \sqrt[3]{c_3} = \sqrt[3]{\frac{(1-C_A)}{2\,(1+3\,a)} - \sqrt{\frac{(1-C_A)^2}{4\,(1+3\,a)^2} + \frac{(1+a)^3\,\mathfrak{K}}{27\,(1+3\,a)^3}}}$$

$$+\sqrt[3]{\frac{(1-C_A)}{2\,(1+3\,a)} + \sqrt{\frac{(1-C_A)}{4\,(1+3\,a)^2} + \frac{(1+a)^3\,\mathfrak{K}}{27\,(1+3\,a)^3}}}.$$

But as

$$x = \frac{C_A}{C_A + C_B + c_1 + 3\,c_3} = \frac{C_A}{1+2\,c_3},$$

if we substitute for $\mathfrak{K}$ and C_A in these equations the functions of temperature given above we get the expression for the fusion surface of naphthalene:

$$x = \frac{e^{\frac{Q}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)}}{1+2\left\{\sqrt[3]{\frac{1-e^{\frac{Q}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)}}{2\,(1+3\,a)} + \sqrt{\frac{1-e^{\frac{Q}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)}}{4\,(1+3\,a)^2} + \frac{(1+a)^3\,e^{\frac{q}{R_0}\left(\frac{1}{T_3}-\frac{1}{T_0}\right)}}{27\,(1+a)^3}}} + \sqrt[3]{\frac{1-e^{\frac{Q}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)}}{2\,(1+3\,a)} - \sqrt{\frac{1-e^{\frac{Q}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)}}{4\,(1+3\,a)^2} + \frac{(1+a)^3\,e^{\frac{q}{R}\left(\frac{1}{T_3}-\frac{1}{T}\right)}}{27\,(1+3\,a)^3}}}\right\}^3}.$$

In the above expression Q is not a constant factor, and as we could not find any rational expression for it, we have traced graphically the relation between the temperature and the values of Q, and obtained the value of Q for given temperatures by interpolation. To compare the values of x calculated from the above equation with those experimentally obtained, we selected the fusion curve No. 5 and the isothermal curve at the temperature 51.04°, because they lie at about the middle of the fusion surface.

Fusion Curve No. 5.

t	67.01°	61.92°	57.13°	51.98°	47.52°
x (calc.)	.7802	.6691	.5872	.5091	.4490
x (obs.)	.7644	.6795	.5990	.5224	.4626
Δx	−.0158	+.0104	+.0118	+.0133	+.0136

t	43.43°	39.88°	35.22°	30.58°	24.70°
x (calc.)	.4004	.3626	.3191	.2813	.2391
x (obs.)	.4157	.3786	.3329	.2904	.2466
Δx	+.0153	+.0160	+.0134	+.0091	+.0075

Isotherm 51.04°.

No. of fus. curve.	1	2	3	4	5	6	7
x (calc.)	.3585	.3875	.4344	.4663	.4981	.5220	.5364
x (obs.)	.359	.391	.448	.482	.509	.536	.547
Δx	.000	+.004	+.014	+.016	+.011	+.014	+.011

In the foregoing table the values of x observed were obtained by graphical interpolation from their respective curves in Plate I and accordingly they are given with only three figures.

On the whole the deviations are one-sided, and seems to be greatest at about the middle of the surface. The limit of error, considering the effects of heat capacity, surpercooling and temperature reading, seems to be 2 or 3 units in the third decimal of x, while the error from vaporisation of the mixture which reached 0.1–0.2 grammes out of 30–40 grammes of the total solution will cause an error of 5–6 units in the third decimal at the lower temperatures, yet this error is constant and common to all the curves including curve No. 1, from which N has been calculated, and will have little influence upon the values of x as compared above. Hence the deviations in the above two tables are too large as well as too regular to be referred to experimental error, and seem to show that our starting supposition is not quite correct, perhaps other molecular associations are not strictly excluded in the temperature range studied.

We have not extended the comparison over other fusion curves and isotherms, because it is almost certain that the deviations would not be so great as along the two curves we have chosen.

Yet it is of considerable interest to observe that the fusion surface is expressed within the maximum error of 1.5% in composition and of 1° of temperature over the tempereture range of 50° by the equation thermodynamically deduced starting from only the two boundary curves. Hence it may not be too bold to affirm that within the temperature range given the following reaction mainly takes place in the solutions

$$(C_6H_6O)_3 \rightleftarrows 3\,(C_6H_6O).$$

The next question is " What side reaction can take place besides the above ? " The above calculation as well as the values of $\mathfrak{K}$ in Table 13, shows that the convexity of the fusion surface towards the edge of the naphthalene is too large to be explained by our simple hypothesis (see Plates I and II). Suppose that there exist double molecules besides triple molecules of phenol and let n_2 represent the number of these double molecules. Then

$$N = n_1 + 2\,n_2 + 3\,n_3$$
$$\mathfrak{N} = n_1 + n_2 + n_3$$
$$\therefore\quad 3\,\mathfrak{N} - N = 2\,n_1 + n_2$$
$$2\,\mathfrak{N} - N = n_1 + n_3.$$

Put $(3\,\mathfrak{N} - N) = \alpha, \qquad (2\,\mathfrak{N} - N) = \beta$

then

$$n_2 = \alpha - 2\,n_1$$

$$n_3 = n_1 - \beta$$

$$\therefore\ \frac{n_1^3}{n_1'^3} = \frac{(n_1-\beta)\,(A+B+\mathfrak{N})^2}{(n_1'-\beta')\,(A'+B'+\mathfrak{N}')^2} \text{..............} (1)$$

$$\frac{n_1^2}{n_1'^2} = \frac{(\alpha-2\,n_1)\,(A+B+\mathfrak{N})}{(\alpha'-2\,n_1')\,(A'+B'+\mathfrak{N}')} \text{...........} (2)$$

Where dashed terms refer to a second point of the isothermal under question. We have to solve n_1 and n_1' from the two equations by inspection, but there is the condition that $n_2 > 0$ that is $\alpha > 2\,n_1$. We tried to apply the equations to an isothermal curve in order to obtain n_1 and n_1', but found that they were impossible under condition $n_2 > 0$. Hence it is clear that the deviation can not be explained in that way. In the next place suppose there exist quadleple molecules whose number is n_4, then we have the analogous simultaneous equations for n_1, n_1', and they were found not to be impossible under the condition $n_4 > 0$. But as the simultaneous equations contain the fourth power of n_1 the experimental error is extraordinarily magnified and no conclusive result can be arrived at.

II. Partition Coefficient of Phenol between Water and Chlorobenzene.

The theory of the constant partition coefficient has been developed by NERNST from the theory of the dilute solution, and since that time it has been customary to apply this law only to the study of dilute solutions. But the field of its legitimate application is much wider. The only condition to be fulfilled is the sufficient immiscibility of the two solvents, and the calculability of the chemical potential as a fuction of the composition in one of the solutions. The last condition is fulfilled when the solution is either dilute or approximates sufficiently to the ideal solution.

When one of the solutions is dilute and the other is an ideal or quasi-ideal solution, the relation is particularly simple. Let the spatial concentration of the common chemical species in the dilute solution be c, and the molar fraction of the same in the ideal solution be C. Then the potential of the chemical species is given by

$$\mu = z' + RT\,ln\,c$$

and

$$\mu = z + RT\,ln\,C,$$

in which z' and z are functions of temperature and pressure. Hence at a constant temperature and pressure, we have

$$\frac{c}{C} = \text{constant}.$$

This relation can be employed for the elucidation of the problem of the molecular association of phenol in solution.

NERNST has concluded that phenol in benzene is associated to double molecule, from the partition coefficient of this substance between water and benzene. But his observations were made on dilute solutions, and the concentrations were determined by the depression of the freezing point. Hence the result seems not to be quite reliable. We tried to determine the partition coefficient of phenol between water and chlorobenzene up to a concentration of about 50% in the oily phase, expecting some verification for the conclusion arrived at from the study of the fusion surface. When the concentration of phenol is so large water goes to the chlorobenzene phase in no small quantities, and moreover phenol in the watery phase becomes too large to be treated as a dilute solution. To avoid these difficulties we took the aqueous solution almost saturated with both $NaCl$ and Na_2SO_4. The salt solution contained

8.24%	$NaCl$
18.57%	Na_2SO_4

by weight. It is well known that in such solutions the solubility of the phenol is much less than in pure water.

The concentration of phenol in the aqueous solution was determined by the bromine-water method,[1] and that in chlorobenzene was calculated by difference. The method of determination of phenol has hitherto been worked out chiefly for commercial purposes, and is not very exact. It was therefore found necessary to modify the method somewhat. The chief difficulties lie in the fact, that bromine vaporises during the manupilation and that the precipitation of tribromophenol makes the end reaction very indistinct. These difficulties have been overcome in the following manner. We took a bottle of about 10 litre capacity which was filled with a 0.03 normal solution of bromine (Fig. 9). The reason for using such a capacious bottle was to keep the concentration

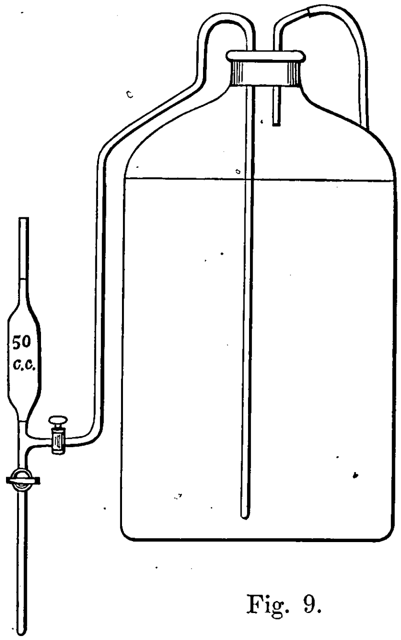

Fig. 9.

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[1] ALLEN's: Commercial Organic Analysis. Vol. II. Part II, p. 244, (1900).

of bromine-water as constant as possible, yet we tested it for the sake of control before and after each observation. It was constant up to about 0.02 c.c. of the sodium thiosulphate solution, of which 40 c.c. was used in each titration. The lower end of the pipette connected with the syphon tube was dipped in the solution containing phenol, while bromine-water was allowed to run into it. This hindered the bromine from evaporating, and consequently made the titration more constant.

The aqueous solution of phenol was first separated by sucking it from under the chlorobenzene, since the salt solution was heavier than the chlorobenzene. 2 c.c. or 5 c.c. of the aqueous solution was taken by means of a pipitte with a cotton wool filter at the end, and put into a bottle of 300 c.c. capacity with a well fitting glass stopper, and 50 c.c. of pure water and 2 c.c. of chlorobenzene or chloroform were added. On admitting bromine-water into the bottle, a white flocky precipitate was produced, which on shaking vigorously dissolved completely in the oil, the greater part of the remaining bromine went to it and there was little fear of losing it by evaporation. After about 15 minutes the necessary quantity of potassium iodide solution was added and well shaken, then the iodine set free was titrated with 0.03 normal solution of sodium thiosulphate; chloroform or chlorobenzene functionating as an indicator. The partition coefficient was observed at three different temperatures 25°, 45°, 65°, the temperatures were maintained in a thermostat and were constant to 0.1° during observation. The most concentrated solution in chlorobenzene contained 50% of phenol. This was made by taking equal quantities by weight. The mixture was diluted with various proportions of chlorobenzene, seven solutions in all being prepared with percentages of phenol varying between 5% and 50%.

20 c.c. of each solution was put into a 50 c.c. bottle with a closely fitting glass stopper, and then 20 c.c. of the salt solution was added. All the seven bottles were placed in the thermostat. After 30 minutes the bottles were shaken until the liquids had become perfectly milky. This was repeated several times at regular intervals. One or two hours after the last shaking, when the liquids had cleared one after another, the aqueous solutions, were sucked out and titrated in the manner described above. In the following tables c is the spatial concentration of phenol in the salt solution, C is the empirical molar fraction of phenol in the oil phase, which was calculated from the quantity of phenol added and that taken up by the water phase. C_1 is the molar fraction of simple phenol molecules (C_6H_6O) in the colorobenzene phase, calculated in the following manner.

$$C = \frac{C_1 + 3\,C_3}{1 + 2\,C_3},$$

$$\mathfrak{R} = \frac{C_1^3}{C_3},$$

$$\therefore \quad C = \frac{\mathfrak{R}_3\, C_1 + 3\,C_1^3}{\mathfrak{R}_3 + 2\,C_1^3},$$

or

$$C_1^3 + \frac{\mathfrak{R}_3}{3-2\,C}\, C_1 + \frac{\mathfrak{R}\, C}{3-2C} = 0$$

$$\therefore \quad C_1 = \sqrt[3]{\frac{\mathfrak{R}\,C}{2\,(3-2\,C)} + \sqrt{\frac{\mathfrak{R}\,C}{4\,(3-2\,C)^2} + \frac{\mathfrak{R}^3}{27\,(3-2\,C)^3}}}$$
$$+ \sqrt[3]{\frac{\mathfrak{R}\,C}{2\,(3-2\,C)} - \sqrt{\frac{\mathfrak{R}\,C}{4\,(3-2\,C)^2} + \frac{\mathfrak{R}^3}{27\,(3-2\,C)^3}}}.$$

In more concentrated solutions or at lower temperatures where $\mathfrak{R}$ is small the value of C_1 is almost equal to

$$\sqrt[3]{\frac{\mathfrak{R}\,C}{3-2\,C}}.$$

Phenol in water is dissociated to simple molecules at least in the more dilute solutions.[1] Hence if phenol in chlorobenzene is all associated to $(C_6H_6O)_3$, then $\frac{c^3}{C}$ must be constant and if $(C_6H_6O)_2$ alone exists in the solution, then $\frac{c^2}{C}$ must be constant. If it be completely dissociated $\frac{c}{C}$ must be constant, while if it be partially dissociated according to the chemical equation

$$(C_6H_6O)_3 \rightleftarrows 3\ C_6H_6O$$

the ratio $\frac{c}{C_1}$ must be unchangeable.

TABLE 15.

Temperature 25.41°.

No.	c	C	C_1	$\frac{c}{C}$	$\frac{c^2}{C}$	$\frac{c^3}{C}$	$\frac{c}{C_1}$
1	.0489	.537	.0548	.091	.00445	.000217	.89
2	.0457	.440	.0497	.104	.00377	.000217	.92
3	.0443	.349	.0447	.127	.00446	.000249	.99
4	.0404	.299	.0416	.147	.00592	.000240	.97
5	.0377	.213	.0366	.177	.00666	.000251	1.03
6	.0305	.103	.0279	.302	.00899	.000272	1.09
7	.0209	.0485	.0208	.451	.00942	.000197	1.00

TABLE 16.

Temperature 44.93°.

No.	c	C	C_1	$\frac{c}{C}$	$\frac{c^2}{C}$	$\frac{c^3}{C}$	$\frac{c}{C_1}$
1	.0574	.502	.114	.1143	.00656	.000376	.502
2	.0535	.418	.104	.1280	.00686	.000366	.515

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[1] ARRHENIUS: Zeit. physik. Chem., 2, 491, (1888).

3	.0492	.324	.0931	.1516	.00746	.000367	.529
4	.0454	.256	.0843	.1768	.00803	.000364	.538
5	.0405	.195	.0759	.2070	.00838	.000339	.534
6	.0317	.098	.0588	.3238	.01025	.000325	.539
7	.0185	.0385	.0277	.4820	.00893	.000166	.669

TABLE 17.

Temperature 64.30°.

No.	c	C	C_1	$\frac{c}{C}$	$\frac{c^2}{C}$	$\frac{c^3}{C}$	$\frac{c}{C_1}$
1	.0781	.511	.191	.153	.0119	.000931	.410
2	.0672	.378	.160	.178	.0120	.000805	.419
3	.0620	.342	.154	.182	.0113	.000698	.403
4	.0554	.263	.134	.211	.0117	.000647	.413
5	.0496	.196	.111	.253	.0125	.000621	.446
6	.0358	.099	.0769	.364	.0130	.000466	.466
7	.0213	.0428	.0388	.498	.0106	.000226	.548

On the whole the results obtained accord well with our hypothesis. At lower temperatures where dissociation is small $\frac{c^3}{C}$ is nearly constant, demonstrating that most of the phenol is in the form of $(C_6H_6O)_3$. At 64.30° $\frac{c^3}{C}$ is no longer constant, but decreases with the decreasing concentration of phenol. $\mathfrak{K}$ has a far larger value at this temperature, and the amount of C_6H_6O is not inconsiderable in comparison with that of $(C_6H_6O)_3$. Moreover the degree of dissociation must increase with the decreasing concentration, so that the variation of $\frac{c^3}{C}$ in the sense observed is to be expected.

But the best criterion is the ratio of the concentration of phenol in the aqueous solution and the molar fraction of the chemical species C_6H_6O. If our hypothesis be correct $\frac{c}{C_1}$ must be constant at each temperature. This is approximately the case shown in the last columns of the foregoing tables.

The ratio has indeed the tendency to increase with the decrease of the concentration. In the calculation of C_1 the value of $\mathfrak{K}$ from fusion curve No. 1 was employed and as may be seen from Table 14, $\mathfrak{K}$ increases with the decreasing concentration, so this result corresponds to that deduced from the fusion surface.

The ratio $\frac{c}{C}$ increases rapidly with the decreasing concentration at all temperatures. That the ratio $\frac{c^2}{C}$ is nearly constant at 64.30° must be looked upon as accidental. This demonstrates how dangerous it is to draw theoretical conclusions from observations at a single temperature.

In the foregoing calculations the amount of water taken up by the oily phase has been left out of consideration. In the solutions in which the concentration of phenol is small, this can have no significance; but in the other cases the effect may not be altogether negligible. In order to be able to estimate this disturbing effect, the quantity of water absorbed by the 50% solution of phenol in chlorobenzene was determined in the following manner. A very thin graduated pipette (0.00597 c.c. for 1 division and one drop corresponding to about 2 divisions) was employed to add water to the phenol solution until a slight turbidity occurred. The solution was then shaken with 20 c.c. of the salt solution in the thermostat at 45°. The clear oil was sucked from the bottle and after being cooled, water was again added until turbidity occurred again. The difference of the quantity of water in these two titrations gives the quantity of water absorbed from the salt solution at 45°. 19.90 c.c. of phenol and chlorobenzene mixture was employed and the water absorbed was 0.962 grammes. To apply the proper correction for the quantity of water absorbed is a very difficult matter. On one hand water has a considerable power of dissociating complex molecules, as may be seen from the depression of the freezing point of the aqueous solution of phenol. On the other hand the degree of association of water molecule itself is not known even in dilute solutions. The addition of water decreases the value of C and consequently that of C_1. But since the presence of water promotes the dissociation of phenol, that is increases C_1, the resulting effect can not be very large.

In more dilute solutions the absorption of water must have been much less and the effect must accordingly have been much smaller.

Summary.

1. The fusion surfaces of naphthalene and phenol of the system naphthalene-chlorobenzene-phenol have been determined.

2. The eutectic line between the two fusion surfaces has also been observed.

3. The general forms of the fusion surfaces have been found to be such as would be furnished by two unassociated components and an associated one.

4. An attempt has been made to account quantitatively for the special form of the fusion surface of naphthalene by the hypothesis that in the solution phenol is more or less associated

to triple molecules. It has been found possible to represent the fusion surface approximately by an equation based on this hypothesis and derived from the fusion curves of naphthalene in the binary systems, naphthalene-chlorobenzene and naphthalene-phenol.

5. The partition of phenol between chlorobenzene and an aqueous solution of common salt and sodium sulphate at three different temperatures has been studied, the concentration of phenol in chlorobenzene being in some cases very considerable.

6. The results obtained support on the whole the hypothesis that phenol is associated to triple molecules.

The present study has been undertaken and prosecuted under the kind guidance of Prof. IKEDA to whom my best thanks are due.

August 1907.

Chemical Institute of the Science College,
the Imperial University of Tokyo.

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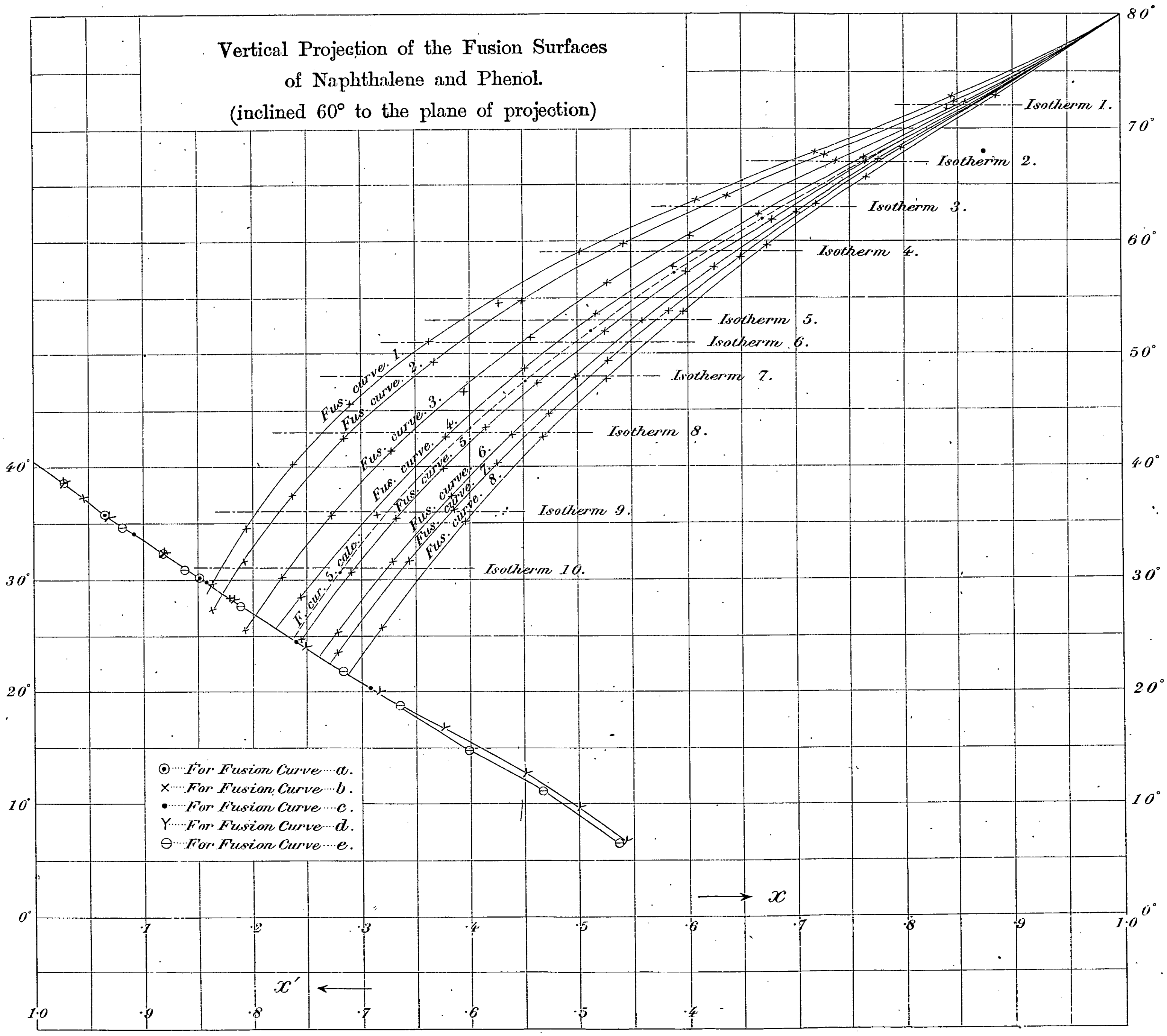

Vertical Projection of the Fusion Surfaces
of Naphthalene and Phenol.
(inclined 60° to the plane of projection)

Jour. Sci. Coll. Vol. XXV. Art. 12. Pl. II.

Horizontal Projection of the Fusion Surfaces.