CVII.—*The Influence of Position on the Solubilities of the Substituted Benzoic Acids.*

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It has already been shown (Sidgwick, Spurrell, and Davies, T., 1915, **107**, 1202) that whereas in most di-derivatives of benzene the position of the substituents has little influence on the solubilities in the liquid state, in others, in which the substituents may be presumed to react with one another, this is not the case, and the ortho-compounds behave quite unlike the meta- and para-. The same was found to hold with the vapour pressure of the compounds, either in the pure state, or on distillation with steam (Sidgwick, *ibid.*, 1920, **117**, 389, 396). Substances of the former class were described as normal, those of the latter as abnormal.

Among the substituted benzoic acids, the toluic are strictly normal, while the hydroxybenzoic are markedly abnormal in their vapour pressure, and also, so far as is known, in their solubilities. The object of the present investigation was to examine the solubilities of these and other derivatives of benzoic acid in detail, in a variety of solvents. The acids examined were the hydroxybenzoic, hydroxytoluic, nitrobenzoic, and chlorobenzoic (ortho-, meta-, and para- in each case); the solvents were in all cases water and benzene, and with several acids ethyl and butyl alcohols, and *n*-heptane. For comparison with the mono-substitution products, the solubilities in water and benzene of benzoic, phenylacetic, and β -phenylpropionic acids were also measured.

The solubility of *o*-hydroxybenzoic acid in water has been measured by Alexejeff (*Wied. Ann.*, 1886, **28**, 305), and that of the hydroxy-, nitro-, and chloro-benzoic acids in water by Flaschner and Rankin (*Sitzungsber. K. Akad. Wiss. Wien*, 1909, **118**, IIb, 695). We were not aware of the latter work until our own was partly finished. Our results with the first two groups are in substantial agreement with theirs; the chloro-acids we did not examine in water. Numerous measurements have been made of the solubilities of these acids at lower temperatures, such as 25°, which do not immediately concern us. One paper, however, by Walker and Wood (T., 1898, **73**, 618), on the hydroxy-acids, although the measurements do not extend beyond 75°, contains results of unusual interest, which are discussed at the conclusion of this paper.

FIG. 1.

Solubility of hydroxybenzoic acids in benzene and heptane.

Ortho — ○ Full curves — benzene.
 Meta — + Dotted curves - - - heptane.
 Para — ×

EXPERIMENTAL.

Purification of Materials.

The methods by which the acids were prepared and purified have already been described (T., 1920, 117, 401). Their melting points were as follows :

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Benzoic, 122.7°; phenylacetic, 76.7°; β -phenylpropionic, 48.6°.
 Hydroxybenzoic: ortho-, 159.0°; meta-, 201.5°; para-, 213.0°.
 Hydroxytoluic (it is convenient to arrange the substituents in the order of their influence on the properties under discussion):

$\text{CO}_2\text{H}:\text{OH}:\text{CH}_3$: 1:2:3 1:2:4 1:2:5 1:3:4 1:4:3

Melting point: 167.0° 177.8° 152.5° 208.5°* 172.4°

Nitrobenzoic: ortho-, 146.8°;† meta-, 141.4°; para-, 242.4°.

Chlorobenzoic: ortho-, 140.3°; meta-, 154.5°; para-, 241.5°.

FIG. 2.

Solubility of hydroxytoluic acids in water.

* The melting point obtained for this acid depends on the conditions of experiment, as it begins to decompose above 200°. In a capillary tube, immersed suddenly in an already heated bath, it melts at 208.5°. In the previous paper (*loc. cit.*, p. 402) the melting points of the 1:3:4- and 1:4:3-acids were unfortunately transposed.

† Goldschmidt (*Zeitsch. physikal. Chem.*, 1898, 25, 91) finds the melting point of this acid to be 144.0°, in opposition to the usually accepted value, 147°. We find it to melt sharply at 146.8°.

Of the solvents used, the benzene was freed from thiophen by treatment with sulphuric acid, and frozen out seven times; the ethyl alcohol had been distilled over calcium oxide, and its strength,

FIG. 3.

Solubility of hydroxytoluic acids in benzene and heptane.

1 : 2 : 3 — ○ —	Full curves — benzene.
1 : 2 : 4 — ⊕ —	Dotted curves - - - heptane.
1 : 2 : 5 — ⊗ —	
1 : 3 : 4 — + —	
1 : 4 : 3 — × —

as measured by the density, was 99.0 per cent.; the *n*-butyl alcohol was repeatedly fractionated, and distilled within 0.1°; the heptane was a specimen from *Pinus sabiniana*, which had been purified

by the method of Thorpe (T., 1879, 35, 296), by treatment with sulphuric and nitric acids, and distillation.

FIG. 4.

Method of Measurement. Solubility of nitrobenzoic acids in benzene and heptane.

The solubilities were determined synthetically. Weighed quantities of the acid and the solvent were enclosed in bulbs, which were then sealed and heated in a suitable bath. With solvents other than water, a correction was made at higher temperatures for the amount present as vapour in the bulb; for this purpose, the vapour pressure of the saturated solution was assumed to be half that of the pure solvent at the same temperature: a direct measurement of the vapour pressure of a saturated solution of *m*-hydroxybenzoic acid in benzene showed that between 160° and 210° this assumption is sufficiently near the truth. The thermometers had been compared with a standard instrument, and all readings were corrected for the emergent stem. The concentrations are expressed in grams of acid to 100 grams of solution.

Ortho — ○ — Full curves — benzene.
Meta — + — Dotted curves - - - heptane.
Para — × —

The results are given in Table I, and plotted on Figs. 1—6. One or two points may be added.

p-Hydroxybenzoic acid crystallises with a molecule of water (the concentrations, of course, refer to the anhydrous acid). The transition point was determined in a dilatometer with water, and

was found to be 62.0° . The solubility values confirm this result; a distinct break is to be observed in the curve at this temperature.

1:4:3-Hydroxytoluic acid also forms a hydrate, with half a

FIG. 5.

Solubility of chlorobenzoic acids in benzene and heptane.

Ortho — ○ — Full curves — benzene.
Meta — + — Dotted curves - - - heptane.
Para — × —

molecule of water. The transition point, as shown by the solubility curve, is 99.5° .

In heptane, the acids the solubility of which is small, appeared to decompose very little above their triple points, and so the curves were not carried further.

The determinations with benzoic acid and water were only intended to supplement the results of Alexejeff (*loc. cit.*). As will

FIG. 6.

Solubility of benzoic, phenylacetic, and β -phenylpropionic acids in water and benzene.

Benzoic acid : Alexejeff — $\otimes$ — Full curves — water.
 S. and E. — $\circ$ — Dotted curves - - - benzene.
 Phenylacetic acid — + —
 β -Phenylpropionic acid — $\times$ —

be seen from Fig. 6, our results agree with his as regards the critical solution temperature, but we find the triple point to be 95.0° , and not, as he states, 98° .

TABLE I.

(All solubilities are expressed in grams of acid to 100 grams of solution).

A. *Hydroxybenzoic Acids.*

Solubility in Water.

Ortho-.			Meta-.		Para-.	
Sol ^y .	Temp. (Solid).	Temp. (Liquid.)	Sol ^y .	Temp.	Sol ^y .	Temp.
100·0	159·0°		100·0	201·3°	100·0	213·0°
89·75	131·8		70·80	134·0	85·20	167·0
80·00	119·5		49·85	109·8	71·30	137·5
65·40	109·5	67·0°	33·85	98·3	51·95	114·0
48·18	107·2	86·4	25·22	93·3	46·60	109·5
34·02	106·7	89·1	14·70	84·6	29·47	97·0
16·82	105·6	87·2	9·85	79·6	19·66	89·6
8·02	101·4	77·3	6·11	69·0	11·85	80·1
5·27	97·9				9·28	75·7
2·026	80·0				6·07	68·2
0·717	56·0				5·22	65·1
0·557	50·0				4·75	63·0
Critical solution					4·20	60·2
temp.		89·5°			3·20	56·0
					2·38	50·9
					Transition point of hydrated acid ...	62·0°

Solubility in Ethyl Alcohol (99.0%).

100.0	159.0	100.0	201.3	100.0	213.0
81.2	125.2	81.7	169.0	82.9	184.0
60.4	85.2	61.3	132.0	60.9	136.5
40.6	41.0	39.6	65.0	38.75	67.0

Solubility in *n*-Butyl Alcohol.

79.2	121.6	84.7	180.3	85.5	193.8
48.9	85.6	59.2	151.2	62.4	167.0
28.88	38.0	40.8	115.0	39.45	116.1
24.36	24.0	20.7	36.5	25.08	62.0
				19.50	32.5

Solubility in Benzene.

100.0	159.0	100.0	201.3	100.0	213.0
81.3	140.0	83.3	192.5	83.0	206.0
64.5	131.5	62.3	185.5	61.3	198.8
41.1	114.5	41.6	182.5	40.6	195.7
20.8	98.5	22.4	173.0	21.0	191.5
5.27	65.0	10.54	162.0	10.3	178.0
1.92	44.3	5.16	154.5	4.30	165.3
		2.95	141.0	3.03	156.9
		1.23	122.5	1.04	132.2

Solubility in *n*-Heptane.

81.4	149.5	2.00	197.0(liq.)	1.80	208.5(liq.)
60.2	145.5	0.86	176.0	1.06	197.0
41.6	142.0	Triple point 197.0°		Triple point 208.5°	
20.15	134.3				
10.25	124.7				
5.37	112.4				
2.09	92.2				

TABLE I. (continued).

B. Hydroxytoluic Acids.

(Points at which a second liquid layer separates are marked L.)

Solubility in Water.									
CO ₂ H : OH : CH ₃ 1 : 2 : 3		CO ₂ H : OH : CH ₃ 1 : 2 : 4		CO ₂ H : OH : CH ₃ 1 : 2 : 5		CO ₂ H : OH : CH ₃ 1 : 3 : 4		CO ₂ H : OH : CH ₃ 1 : 4 : 3	
Solv.	Temp.	Solv.	Temp.	Solv.	Temp.	Solv.	Temp.	Solv.	Temp.
100-0	167-0°	100-0	177-8°	100-0	152-5°	100-0	208-5°	100-0	172-4°
90-07	147-5	89-68	147-8	89-71	126-4	76-98	154-0	84-12	146-8
80-50	134-5	79-68	138-3	79-66	112-0	66-07	143-0	65-52	132-4
79-68	134-1	67-68	132-6	77-05	109-5	48-67	131-4	47-57	124-1
69-52	120-8	54-40	139-4(L)	69-29	117-7(L)	30-23	124-2	30-87	118-8
	120-3(L)	41-46	144-6(L)	67-91	120-2(L)	10-33	113-1	9-61	109-0
59-73	148-0(L)	19-89	144-6(L)	59-85	131-5(L)	4-03	98-8	6-52	105-8
50-51	151-3(L)	9-75	138-4(L)	55-16	135-0(L)			5-77	103-4
29-81	153-3(L)	5-53	129-4	38-85	142-0(L)			5-01	99-5
10-18	149-3(L)		125-3(L)	24-55	142-5(L)			3-70	96-6
5-07	131-8(L)	0-412	80-7	10-21	138-5(L)			2-77	92-6
2-20	119-1			4-53	117-5(L)			1-83	84-4
0-364	80-7			3-16	107-0				
					106-8(L)				
				0-92	85-0				
				0-73	80-7				
Triple point	129-2°		131-0°		107-8°			Transition point	
Critical solution temp.	153-5°		145-2°		142-8°			of hydrate	99-5°
Solubility in Benzene.									
90-33	155-4	91-6	167-6	91-10	142-0	91-7	202-5	90-7	166-0
69-92	138-3	71-7	150-3	70-36	124-7	72-7	192-0	71-7	152-8
49-18	123-0	50-7	135-1	52-05	110-6	50-0	183-7	52-6	145-0
29-96	107-2	29-33	117-6	29-98	93-3	29-8	176-5	29-8	139-5
9-67	79-1	9-74	90-2	10-53	68-0	9-80	160-5	10-11	126-2
5-23	62-4	4-96	71-7	4-73	48-8	4-87	147-4	4-78	116-7
2-01	45-2	2-02	48-8	1-76	30-0	2-18	131-6	2-78	109-5
Solubility in n-Heptane.									
100-0	167-0	100-0	177-8	100-0	152-5	100-0	207-0	100-0	172-4
88-95	154-3	79-29	166-7	89-9	145-9	0-94	180	1-40	163-8
70-04	146-6	61-03	162-2	69-9	138-7				156-0(L)
52-08	141-9	36-28	156-6	50-9	135-5			1-02	157-3
47-63	140-9	20-15	147-1	30-38	131-1				135-0(L)
24-77	132-9	10-00	135-6	10-42	116-2				
9-95	119-0	4-51	116-7	4-59	97-1				
4-86	101-0	2-12	100-6	1-84	79-0				
1-89	81-0								
						Triple point	202°	Triple point	168°

C. Nitrobenzoic Acids.

Solubility in Water.					
Ortho-.		Meta-.		Para-.	
Solv.	Temp.	Solv.	Temp.	Solv.	Temp.
100-0	146-8°	100-0	141-4°	100-0	242-4°
90-38	110-4	89-76	104-8	79-22	184-8
79-32	90-5	79-52	85-4	59-21	168-6
59-85	79-5	60-85	97-7(L)	38-30	163-5
39-92	78-0	40-31	108-4(L)	18-50	158-8
19-24	77-5	19-85	107-8(L)	9-17	153-0
9-48	75-3	9-90	99-3(L)	0-88	177-0
1-85	49-5	4-57	79-3(L)		
		Triple point	76-8°		
		Critical solution temp.	109-0°		

TABLE I. (*continued*).

Solubility in Benzene.					
Sol ^y .	Temp.	Sol ^y .	Temp.	Sol ^y .	Temp.
100.0	146.8	100.0	141.4	100.0	242.4
81.00	128.3	79.6	121.0	82.1	222.0
50.25	113.0	55.5	105.0	54.8	201.6
28.32	105.8	30.54	89.5	33.42	196.5
10.00	90.5	9.87	65.2	21.10	183.4
5.03	78.6	4.95	48.0	9.45	164.5
2.10	63.0	1.95	33.0		
Solubility in Heptane.					
1.37	135.0	2.07	123.4	1.04	179.0
„	130.5(L)	1.03	103.0		
Triple point	139.6°		135°		234.0°

D. *Chlorobenzoic Acids.*

Solubility in Benzene.					
Ortho.-		Meta.-		Para.-	
100.0	140.3	100.0	154.5	100.0	241.5
90.9	129.5	90.2	142.5	92.2	232.5
70.4	113.9	71.15	125.3	72.9	212.7
50.08	99.6	49.0	108.0	52.5	194.0
29.81	82.7	30.1	93.7	30.5	172.5
9.91	57.7	9.67	65.5	10.30	137.4
5.15	44.8	4.96	51.2	5.30	119.4
1.98	26.0	2.25	35.8	1.98	93.6

Solubility in *n*-Heptane.

88.68	134.7	89.82	147.7	76.86	227.6
68.76	129.8	70.05	140.1	51.30	218.3
51.90	128.0	50.06	134.2	31.23	207.2
36.89	126.0	30.60	128.1	10.09	180.9
12.55	112.8	9.98	105.8	4.96	165.3
10.42	108.8	4.48	89.6	1.69	136.1
4.61	94.8	1.92	72.2		
2.57	79.0				

E. *Benzoic Acid.* F. *Phenylacetic Acid.* G. β -*Phenylpropionic Acid.*

Solubility in Water.					
Sol ^y .	Temp.	Sol ^y .	Temp.	Sol ^y .	Temp.
100.0	122.7°	100.0	76.7°	100.0	48.6°
89.40	103.5	80.96	48.5	94.92	38.5
80.36	98.0	61.94	94.8(L)	80.30	101.5(L)
„	77.8(L)	39.69	106.8(L)	60.16	143.5(L)
30.78	116.2(L)	20.00	108.0(L)	39.31	150.0(L)
		5.65	84.7(L)	19.31	149.2(L)
				5.00	119.9(L)
Triple point	95.0°		45.5°		34.0°
Critical solu- tion temp.	115.5°		108.0°		150.0°

TABLE I. (*continued*).

Solubility in Benzene (Points where benzene separates marked B).					
Sol ^l .	Temp.	Sol ^l .	Temp.	Sol ^l .	Temp.
100·0	122·7	100·0	76·7	100·0	48·6
80·5	103·0	81·03	59·0	78·87	28·0
59·70	84·4	61·28	42·0	60·43	+12·8
40·12	66·7	42·98	29·0	40·20	-3·1
20·08	43·5	28·00	13·0	31·26	-1·8(B)
9·40	23·0	19·93	3·0	19·65	+1·5(B)
4·92	6·5	16·30	2·2(B)	0·0	+5·5(B)
		13·04	3·2(B)		
		6·22	4·6(B)		
		0·0	5·5(B)		

Interpretation of Results.

It has already been pointed out that the properties of a crystalline substance are due to two causes : those depending on the molecule itself, and those which arise from the crystalline forces ; and that quite small differences in structure (such as those between the isomerides of a normal group), which have practically no effect on the behaviour of the fused or dissolved substance, may lead to a large difference in any property in which the solid phase is concerned. If, therefore, we are to discover the effect of position on the properties of the molecule, we must eliminate the influence of the crystalline forces, by considering the solubility in the liquid state. This is best characterised by the critical solution temperature (the temperature at which the fused substance and the solvent become infinitely miscible), whenever this can be determined. In many cases the L_1 — L_2 equilibrium is stable, and the critical solution temperature can be observed directly, if it is not too high. With other substances, this curve is wholly metastable : it lies entirely below the S — L curve ; but if it is not too far below, it may be possible to realise it experimentally, as happens with salicylic acid, where the solution, supersaturated with respect to the solid acid, separates into two liquid layers before crystallisation begins. With other substances, however, the L_1 — L_2 area lies too low for this, and crystallisation always sets in before it can be reached. An ingenious method has been devised by Flaschner and Rankin (*loc. cit.*) for dealing with such cases. A third substance, miscible with the acid rather than with the solvent, is added to a mixture containing about 40 per cent. of the acid (this is roughly the composition at the critical solution point) ; this raises the temperature of the L_1 — L_2 curve, until finally the two-liquid system can be realised. If several measurements are made with different quantities of the third substance, and these quantities plotted against the temperatures of separation, they are found

to give nearly a straight line, at least when the amount of the third substance is small; and from this by extrapolation the temperature for no addition—the critical solution temperature for acid and solvent—can be obtained. This method gives only approximate results, and is naturally less accurate the larger the extrapolation required; but it is of considerable value. Flaschner and Rankin employed it in a series of instances in aqueous solution, using chiefly naphthalene, but also benzil, benzophenone, and camphor, as the third substance. We find that where the solvent is water, sodium chloride can be used as the third substance. Thus with *p*-nitrobenzoic acid in water, Flaschner and Rankin, using benzophenone, obtained the following values, which extrapolate to 118° for the critical solution temperature (the third line, dt/dw , gives the quotient of rise of temperature above the extrapolated point by weight per cent. added, and its constancy shows the closeness with which the results approach to a straight line):

Benzophenone per cent.	10.9	7.9	6.7	5.8	(0.0)
Separation temp.....	172°	157°	151°	147°	(118°)
dt/dw	5.0°	4.9°	4.9°	5.0°	—

Our own results with sodium chloride extrapolated to practically the same point :

Salt per cent.	7.99	7.04	6.03	(0.0)
Separation temp.....	179.5°	173.5°	164.4°	(118°)
dt/dw	7.7°	7.9°	7.7°	—

When the solvent is benzene, it is not easy to select a suitable third substance, which should be readily miscible with one component, and little, if at all, with the other. Unexpectedly good results were, however, obtained with water, as is shown below (the values of dt/dw are calculated back from the extrapolated value of the critical solution temperature):

o-Hydroxybenzoic acid in benzene :

Water per cent.	6.97	6.21	4.98	(0.0)
Separation temp.....	121.5°	110.5°	91.6°	(+17°)
dt/dw	15.0°	15.1°	15.0°	—

m-Hydroxybenzoic acid in benzene :

Water per cent.	(9.20)	6.25	4.10	(0.0)
Separation temp.....	(189.0°)	169.8°	152.0°	(119°)
dt/dw	(7.6°)	8.0°	8.0°	—

p-Hydroxybenzoic acid in benzene :

Water per cent.	5.46	4.11	3.36	(0.0)
Separation temp.....	187.0°	177.5°	172.5°	(150°)
dt/dw	6.8°	6.7°	6.7°	—

m-Nitrobenzoic acid in benzene :

Water per cent.	6.72	4.86	3.12	(0.0)
Separation temp.....	118.0°	82.0°	50.0°	(-9°)
dt/dw	18.9°	18.7°	18.9°	—

In heptane, with *o*-hydroxybenzoic acid, less satisfactory results were obtained :

Water per cent.	4.14	2.00	1.47	0.96	(0.0)
Separation temp.....	189.5°	154.0°	141.0°	124.0°	(90°)
dt/dw	24°	32°	35°	35°	—

The zero value of 90° was got from the two lowest observations ; it gives an upper limit for the critical solution temperature.

When the critical solution temperature cannot be obtained in this way, another, less accurate, method may be used, depending on the slope of the *S*—*L* solubility curve. It is obvious that the middle part of this is flatter, the nearer it lies to the *L*₁—*L*₂ curve. In aqueous solutions (and in one or two cases in other solvents also), Flaschner and Rankin found that if the slope of this curve (increase in weight per cent. for 1° rise of temperature) at 40 per cent. solute is multiplied by the difference in temperature at this concentration between the *S*—*L* and the *L*₁—*L*₂ curves, it gives a number (*E*) which is approximately constant. For eleven substituted benzoic acids in water they found values of *E* varying from 520 to 189 (mostly between 250 and 360), with a mean value of 330. With benzene or heptane as solvents, we have obtained the following values (the first column gives the slope of the *S*—*L* curve, the second the difference in temperature between the two curves at 40 per cent. acid, the third, *E*, the product of these two) :

	dc/dt	<i>Dt</i>	<i>E</i>
Hydroxybenzoic acid, ortho- in benzene	1.62	98.8°	160
" " meta- " 	2.76	57.3	157
" " para- " 	5.78	45.5	263
" " ortho- in heptane ...	3.72	52.0	193
Nitrobenzoic acid, ortho- in benzene	3.21	130.8	[420]
" " meta- " 	1.70	106.0	180

Mean 190

It will be seen that the values obtained in non-dissociating solvents agree about as closely as those in water, and give a distinctly lower mean.* It is difficult to see any quantitative theoretical basis for this rule, but the agreement is close enough for it to be worth while examining the results got by applying it to cases where the two-liquid curve lies too low to be reached even by salting out; and they have therefore been calculated in such cases, using the mean value 330 for *E* in water, and 190 in benzene and heptane. In Table II, all the values of the critical solution temperatures obtained by any of the three methods are collected, the method employed in each case being indicated. It is obvious that little weight can be attached to the absolute magnitude of the temperatures obtained

* The value for *o*-nitrobenzoic acid is excluded in calculating the mean.

TABLE II.

Critical Solution Temperatures.

(Obs.=by direct observation. S.O.=by method of salting out.

Calc.=calculated by the formula of Flaschner and Rankin from the slope of the *S*—*L* curve, using *E*=330 for water, and 190 for benzene and heptane.)

Acid	Solvent.	Ortho-.	Meta-	Para-		
Hydroxybenzoic	water	89.5° Obs.	—122° Calc.	—229° Calc.		
	ethyl alcohol }	v. low	v. low	v. low		
	butyl alcohol }					
	benzene					
	heptane	+17° S.O. (—6° Calc.)	119° S.O. (114° Calc.)	150° S.O. (162° Calc.)		
heptane	90° S.O. (91° Calc.)	v. high	v. high			
Nitrobenzoic	water	52° S.O.* —21° S.O.	109.0 Obs. —9° S.O.	118° S.O.		
	benzene	(+53° Calc.)	(—16° Calc.)	+84° Calc.		
	heptane	v. high	v. high	v. high		
Chlorobenzoic	water	126.2° Obs.*	142.8° Obs.*	167.0° Obs.*		
	benzene	—52° Calc.	—36° Calc.	—13° Calc.		
	heptane	+99° Calc.	+75° Calc.	+123° Calc.		
Hydroxytoluic (CO ₂ H:OH:CH ₃)	Solvent.	1:2:3-	1:2:4-	1:2:5-	1:3:4-	1:4:3-
	water	153.5° Obs.	145.2° Obs.	142.8° Obs.	+9° Calc.	+17° Calc.
	benzene	—33° Calc.	—16° Calc.	—47° Calc.	+117° Calc.	+98° Calc.
	heptane	+84° Calc.	+111° Calc.	+107° Calc.	v. high	v. high
Solvent.	Benzoic acid.	Phenylacetic acid		β-Phenylpropionic acid.		
Water	116.2° Obs.	108.0° Obs.		150.0° Obs.		
Benzene	v. low	v. low		v. low		

by the third method—indeed, with the alcohols they come below the absolute zero—but they show on the whole a remarkable regularity, and indicate that there is some definite relation between the slope of the solid solubility curve and its distance from the two-liquid curve, although the exact form of the function is not yet known.

Nominal Heats of Solution.

In solvents other than water, the critical solution temperatures usually cannot be determined, except by large interpolations with uncertain formulæ, and we have to rely on the solid solubility curves alone. The differences between these are much less easy to detect. The curves seem to be governed by the melting points and heats of fusion of the solid acids (properties depending mainly on the crystalline forces) and it is not easy to see how far their course departs from the normal. A much clearer view is afforded by plotting the heats of solution against the concentration. As van't Hoff has shown,† it is possible, if we know the solubility of a solid in a solvent at two temperatures, to calculate the mean

* These observations are due to Flaschner and Rankin, *loc. cit.*† See also Schröder, *Zeitsch. physikal. Chem.* 1893, 11, 449.

heat of solution (in the saturated solution) by means of the equation :

$$\log_e \frac{S}{S_1} = \frac{Q}{1.985} \times \frac{T_1 - T}{TT_1},$$

where S , S_1 are the solubilities (expressed as molecular concentrations) at the absolute temperature T , T_1 , and Q is the heat of solution. This equation was applied by interpolating values of the temperature on the solubility curves for every 10 (molecular) per cent., calculating the heats of solution between each successive pair, and plotting the results against the concentration. The values so obtained are given in tables III and IV, and those in benzene plotted on Fig. 7.

It must be noticed that this equation only holds on two assumptions : (1) that the solutions obey the gas laws, and (2) that no changes of molecular weight occur with change of concentration. As neither of these assumptions can be supposed to hold throughout, the results do not really represent the heat of solution, and we have therefore called them the nominal heats of solution. They are, however, of considerable importance as affording an expression of the total departure of the liquid system from the behaviour of an ideal solution. With such a solution, the solubility curve is entirely determined by the melting point and heat of fusion of the solid, and is independent of the solvent. In this case the curve gives the real (and not merely the nominal) heat of solution, which is the sum of the heat of fusion of the solid and the heat of mixture of the resulting liquid with the solvent. For ideal components which give a straight line vapour pressure curve the heat of mixture is zero (Bose, *Zeitsch. physikal. Chem.*, 1907, **58**, 621), and hence the value obtained is that of the heat of fusion. This varies with the temperature, its coefficient being equal to the difference between the specific heats of the liquid and solid. It was shown by van't Hoff (Boltzmann, *Festschrift*, 1904, 233) that the specific heat of a substance is always less in the solid state than when it is melted ; and this has subsequently been recognised as a necessary consequence of Nernst's theorem. The difference, however, is usually small. From the list of thirteen organic substances * given by van't Hoff (most of which are taken from the results of Bruner, *Ber.*, 1894, **27**, 2102), it appears that the difference is nearly always less than 0.02 kgr.-cal. per gram-molecule per degree ; its mean value is 0.013. This means that the heat of fusion will always fall with

* To these may be added anthracene and triphenylmethane, for which the differences are 0.009 and 0.016 kgr.-cal. per molecule per degree respectively (Hildebrand, Derschak, Foster, and Beebe, *J. Amer. Chem. Soc.*, 1917, **39**, 2293).

the temperature, but that 50° below the melting point it will have diminished on the average by not more than 0.65 kgr.-cal., and only in exceptional cases by as much as 1 kgr.-cal. The influence of this factor is also regular; it will cause a small continuous fall of the heat curve. For example, the specific heat of solid benzoic

FIG. 7.

Heats of solution in benzene.

Nitrobenzoic	Ortho	— ○ —	Hydroxybenzoic	Ortho	-- ○ --
	Meta	— + —		Meta	-- + --
	Para	— × —		Para	-- × --
Chlorobenzoic	Ortho	-- ○ --	Hydroxytoluic	1:2:3	— ○ —
	Meta	-- + --		1:2:4	— ⊕ —
	Para	-- × --		1:2:5	— ⊗ —
Benzoic		— ○ —		1:3:4	— + —
Phenylacetic		— + —		1:4:3	— × —
β-Phenylpropionic		— × —

acid is 0.27 cal. per gram, and that of the liquid 0.37 (van't Hoff); this corresponds with a fall of 0.0122 kgr.-cal. per gram-molecule per degree. The solubility in benzene was measured from the melting point (122.7°) down to $+6^{\circ}$. The heat of fusion at the melting point being 4.83 kgr.-cals., it will have fallen at 6° to 3.41. With phenylacetic acid, the fall is from 4.3 at the melting point to

2.7 at the lowest temperature ($+3^{\circ}$) at which the solubility was measured.

The heat of solution for an ideal pair of components will therefore approximate to a horizontal straight line. Such a pair can, of course, never separate into two layers. At the other extreme, we have those substances which "melt under the solvent," where the two-liquid area is stable, and cuts across the $S-L$ curve. The latter then runs horizontally between the two triple points, and over this range the nominal heat of solution is infinite. The cases which in practice it is important to distinguish are the intermediate ones, in which the $S-L$ curve shows a certain amount of flattening, indicating that there is an unstable two-liquid area some way below it. Any such flattening is represented on the heat curve by a large increase, and the departures from the normal become much more conspicuous. The value of this method of representation is well shown by comparing the solubility curves of the nitro- and chloro-benzoic acids in benzene (figs. 4, 5) with the corresponding curves (Fig. 7) for their nominal heats of solution. The former do not indicate clearly whether the behaviour of the isomerides in either case is similar or not, whilst from the heat curves it is at once apparent that the chloro-acids are normal and the nitro-acids abnormal.

This method of treatment * is based on the same principles as the calculation of the critical solution temperatures from the slope of the $S-L$ curve, but it has a firmer theoretical basis, and avoids the somewhat arbitrary selection of a particular concentration. Both methods ultimately depend on the variation of the vapour pressure of one component in the solution with the concentration.

Vapour Pressure of the Liquid Acids.

The vapour pressures of these acids have been determined by means of their volatility in steam (Sidgwick, T., 1920, 117, 396). This gives the partial pressure of the acid in the vapour from the saturated aqueous solution at 100° , that solution being in equilibrium either with the solid acid or with a second liquid phase, according as the triple point is above or below 100° . In order to compare the properties of the liquid substances, we require to know the vapour pressures of the pure liquid acids, and therefore to eliminate the effect upon them of their dilution by the solvent. When the solid acid is present, the vapour pressure measured is that of the solid; and from this we can calculate that of the pure liquid at

* For a further discussion of solubility from the point of view of the heat relations, see Hildebrand, *J. Amer. Chem. Soc.*, 1916, 38, 1451, 2297.

TABLE III.

Nominal Heats of Solution in Benzene (Kgr.-cals. per gram-mol.)

Mean mol. per cent. of acid.	Hydroxybenzoic acids.			Hydroxytoluic acids.					
	Ortho-.	Meta-.	Para-.	1 : 2 : 3-.	1 : 2 : 4-.	1 : 2 : 5-.	1 : 3 : 4-.	1 : 4 : 3-.	
95	5.01	14.3	19.0	7.17	6.71	6.00	12.6	10.9	
85	6.51	15.7	21.1	7.50	7.62	6.79	13.5	11.2	
75	8.67	17.0	23.6	8.41	8.40	7.74	16.4	11.2	
65	10.8	20.0	27.0	8.68	9.43	8.39	19.2	12.7	
55	11.5	28.5	31.5	10.1	10.8	8.90	19.6	13.2	
45	12.5	71.9	39.7	10.5	11.0	9.08	23.6	19.8	
35	11.7	79.9	84.6	10.4	11.3	10.2	48.0	40.3	
25	13.0	66.9	88.8	11.4	12.2	10.6	37.0	40.0	
15	12.8	24.1	49.7	12.7	14.2	12.4	29.1	31.0	
Heat of Fusion.....	4.2	11.5	(18.2)	7.0	6.2	5.6	7.26*	10.6	

Mean mol. per cent. of acid.	Nitrobenzoic acids.			Chlorobenzoic acids.			Benzoic acid.	Phenyl- acetic acid.	β -Phenyl- propionic acid.
	Ortho-.	Meta-.	Para-.	Ortho-.	Meta-.	Para-.			
95	5.18	5.44	5.99	4.88	5.15	8.68	4.59	4.34	3.60
85	7.42	6.71	9.70	6.91	6.46	9.17	4.75	4.40	3.87
75	9.27	8.31	15.0	8.41	7.11	9.95	5.34	4.43	3.90
65	10.9	9.36	19.7	8.60	8.10	9.90	5.61	4.70	4.46
55	12.6	9.12	26.4	9.22	8.60	11.0	5.81	5.16	4.33
45	14.4	11.0	30.9	9.62	8.94	11.2	6.32	5.72	4.84
35	21.8	12.3	24.6	10.2	10.1	12.9	6.72	7.21	5.02
25	28.8	13.9	20.4	10.1	11.4	13.1	6.87	5.45	—
17.5	30.5	13.9	17.3	10.3	12.5	12.3	7.34	5.51	—
12.5	27.2	14.2	16.9	10.2	11.6	12.3	7.60	6.90	—
Heat of Fusion.....	7.34*	5.11*	(5.0)	3.8	4.2	(8.4)	4.83*	4.3	3.5

TABLE IV.

Nominal Heats of Solution in Heptane.

Mean mol. per cent. of acid.	<i>o</i> -Hydroxy- benzoic acid.	Hydroxytoluic acids.			Chlorobenzoic acids.		
		1 : 2 : 3-.	1 : 2 : 4-.	1 : 2 : 5-.	Ortho-.	Meta-.	Para-.
95	7.56	4.05	8.08	7.64	9.57	7.87	11.4
85	11.7	9.52	12.8	11.4	13.9	11.5	13.4
75	22.5	13.6	19.8	11.7	19.9	14.9	17.2
65	31.9	17.5	26.8	20.1	29.4	18.2	21.9
55	45.3	27.5	34.4	32.1	53.3	21.9	29.7
45	51.4	33.3	39.7	49.4	89.2	26.4	29.9
35	39.4	31.4	39.4	52.7	65.3	29.4	26.9
25	35.1	30.6	30.1	37.7	44.0	31.7	23.1
17.5	31.8	25.4	22.7	33.0	31.9	22.1	21.5
12.5	25.3	27.6	22.1	24.1	23.7	14.4	20.0
7.5	18.6	14.0	16.7	15.0	15.7	13.9	20.4

Hydroxybenzoic, meta- and para-
Hydroxytoluic, 1 : 3 : 4- and 1 : 4 : 3-
Nitrobenzoic, ortho-, meta-, para- } Heat infinite (two layers).

Nominal Heats of Solution of Hydroxybenzoic Acids in Alcohols.

Mean mol. per cent. of acid.	in Ethyl alcohol.			in Butyl alcohol.		
	Ortho-.	Meta-.	Para-.	Ortho-.	Meta-.	Para-.
95	6.40	7.74	8.57	6.00	5.64	6.07
85	5.69	6.71	8.18	5.45	5.94	6.72
75	5.21	6.43	7.23	5.08	6.34	7.59
65	4.68	6.26	6.25	5.17	7.22	7.66
55	4.48	5.61	5.61	4.63	7.09	7.62
45	3.88	5.27	4.70	4.12	6.66	5.95
35	3.44	4.92	3.78	3.39	4.63	4.17
25	3.05	2.90	2.75	2.97	2.76	2.54
17.5	1.19	1.54	1.78	—	2.32	2.79

the same temperature if its heat of fusion is known, the two being related by the formula

$$2.3026 \log \frac{p}{p'} = \frac{1000 W}{R} \times \left(\frac{1}{T} - \frac{1}{T_0} \right),$$

where p , p' are the vapour pressures of liquid and solid at T , the absolute temperature of distillation, and W is the heat of fusion in kgr.-cals. per gram-molecule, T_0 being the melting point. When the substance melts in contact with water below 100° and there are two liquid phases present, an approximate correction can be arrived at in this way. At the triple point (which in this case is below 100°), we can calculate the value of p/p' as before, and hence we know how much the vapour pressure of the acid is diminished by the amount of water dissolved in it at this point. Further, we know that the vapour pressure is the same for the conjugate solution at the other triple point on the dilute side. Nearly the same relations hold for temperatures and concentrations lying outside the two-liquid area, but not too far from it. Over this range the vapour pressure changes very slightly with the concentration. The proportion of acid in the saturated liquid at 100° will not be much less than at the triple point; and hence we shall not be far wrong if we assume that the vapour pressure of the pure liquid acid is lowered to the same relative extent by the amount of water dissolved in it at 100° as it is by the amount dissolved at the triple point. The corrected values for the pure fused acid are therefore obtained by multiplying the observed vapour pressures by the ratio $p_{\text{liquid}}/p_{\text{solid}}$ at 100° when the solid acid is present during the distillation, and by the same ratio at the triple point when two liquid phases are present. The results are given, together with the observed vapour pressures, in Table V.

The heats of fusion required for this purpose have been obtained in most cases by extrapolation from the Q -curves in benzene. These give satisfactory values for the acids of the ortho-group, for which these curves are normal. They are less satisfactory with the meta- and para-compounds, for which the Q -curves show a large rise. The acids melting in the neighbourhood of 200° begin to decompose near this temperature, and the observed melting points are too low, which makes the heat of fusion too high; the logarithmic form of the equation exaggerates this error. We have attempted to measure the heats of fusion by the lowering of the melting point on addition of such substances as anthraquinone and benzil; but with the less fusible acids no definite readings could be obtained, owing to incipient decomposition. Where the corrections are for these reasons uncertain, the corrected values,

which are undoubtedly too high, are enclosed in brackets. The values of the heats of fusion employed are given in Table III, those which are obtained by special cryoscopic experiments being marked with an asterisk. The value 4.83 for benzoic acid is taken from Ciamician and Garelli (*Zeitsch. physikal. Chem.*, 1895, **18**, 54); extrapolation of the Q -curves in benzene gave 4.5. From the former value we get at the triple point (95°) $p_{\text{liquid}}/p_{\text{solid}} = 1.59$. The observed vapour pressure by steam distillation was 1.129 mm., so that the corrected value for the pure liquid at 100° would appear to be $1.129 \times 1.59 = 1.79$ mm. Kahlbaum's measurements of the vapour pressure of the liquid acid (*Zeitsch. physikal. Chem.*, 1898, **26**, 603) (by a rather large extrapolation, his lowest value being 10 mm. at 132.5°) give 1.7 mm. at 100° .

TABLE V.

Acid.	Hydroxybenzoic acids.			Hydroxytoluic acids.					
	Ortho-.	Meta-.	Para-.	1:2:3-.	1:2:4-.	1:2:5-.	1:3:4-.	1:4:3-.	
Vap. press. at 100° in mm. $\times 100$...	Obs. 39.7 Corr. 86.2	0.149 (25.7)	0.030 (2.48)	23.5 98.2	12.1 50.7	18.2 46.2	1.76 (15.1)	0.072 0.727	
Critical solution temp. in water...	89.5°	v. low	v. low	153.5°	145.2°	142.8°	(+9°)	(+17°)	
Increase of Q in benzene.....	8.0	65.6	69.2	5.2	7.5	6.4	35.9	29.4	
Increase of Q in heptane.....	43.8	∞	∞	29.2	31.3	45.0	∞	∞	

Acid.	Nitrobenzoic acids.			Chlorobenzoic acids.			Benzol- acid.	Phenyl- acetic acid.	β - Phenyl- propionic acid.
	Ortho-.	Meta-.	Para-.	Ortho-.	Meta-.	Para-.			
Vap. press. at 100° in mm. $\times 100$...	Obs. 2.01 Corr. 6.05	0.70 2.12	0.096 (0.592)	18.0 29.8	19.7 33.3	4.59 (94.0)	112.9 179	29.6 54.1	22.5 29.3
Critical solution temp. in water	52°	109.5°	118°	126°	143°	167°	116.2°	108.0°	150.0°
Increase of Q in benzene	25.3	8.8	24.9	5.4	7.3	4.4	3.0	2.9	1.4
Increase of Q in heptane	∞	∞	∞	79.6	23.8	18.4	—	—	—

The sign of infinity, ∞ , indicates the existence of a stable two-liquid area.

The results are summarised in Table V, which shows (1) the vapour pressure of the acid in hundredths of a mm. at 100° (obtained by steam distillation, T., 1920, **117**, 396); (2) the critical solution temperature in water (values in brackets are calculated from the slope of the curve); (3) the increase of the heat of solution in benzene (difference between the maximum value and that for 95 molecules per cent., which is nearly the heat of fusion); (4) the corresponding increase in heptane.

Among the hydroxy-acids, which are typical abnormal compounds, it will be seen that the solubility relations are reversed as we pass from water to benzene; the isomerides with the lowest critical solution temperature (greatest solubility) in water show the largest

increase in heat of solution (indicating the least solubility) in benzene. Heptane shows the same properties as benzene, but in a more marked degree. The isomerides with the greatest solubility in water invariably have the smallest vapour pressure. The alcohols occupy a peculiar position, the solubilities being abnormally high in every case, as is indicated by the fall in the Q values. Thus at 60° *o*-hydroxybenzoic acid is more than two hundred times as soluble (as measured by the molecular concentrations) in ethyl or butyl alcohol as in water, and more than twenty times as soluble in either as in benzene: with the para-acid, the solubility in the alcohols is thirty to fifty times as great as in water, and upwards of one thousand times as great as in benzene. Walker and Wood's measurements (T., 1898, **73**, 618) show that ether and acetone resemble the alcohols in this respect. In the neighbourhood of 20° the ortho-acid is about six hundred times as soluble in either as in water, and about forty times as soluble as in benzene: the para-acid about one hundred times as soluble as in water, and from three thousand to six thousand times as soluble as in benzene.

A possible explanation may be suggested for this remarkable difference. When a substance forms a compound with the solvent, its solubility is thereby increased, since in addition to the amount present in solution as such, there is the amount present as compound. Examples are quoted at the end of the following paper (for example, nitrophenols in aniline) where the formation of a compound (which can be isolated) determines a large increase in the solubility, and a corresponding fall in the heat of solution. It is therefore possible that these acids form compounds in solution with the alcohols, and these might perhaps be isolated if the solubility curves were carried to a low enough temperature. It must, however, be observed that the results of Pickering (T., 1893, **63**, 1023) with acetic acid in methyl, ethyl, and propyl alcohols do not support this view. He measured the solubility curve of the acid nearly to -80° , and obtained no definite evidence of the existence of a compound with the solvent, although the heats of fusion of the acid calculated from the results show the same diminution that we have observed, and the solubilities of the acid are correspondingly large.

A comparison of the solubilities of the three hydroxybenzoic acids in various solvents at moderate temperatures brings out the remarkable result that the ratio ortho:para, which is very small in water, rises as the dielectric constant of the solvent falls, reaching a maximum in benzene* which is yet far short of the ratio of the vapour pressures. The ratio meta:para, which is very much

* The values in heptane have not been determined, but the ratio would obviously be larger still.

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nearer to unity, tends to rise in the same direction. The values at and near 20° are taken from Walker and Wood.

Solvent.	Water.		Ethyl	Butyl	Ace-	Ether.	Benzene.		Vap. press.
	60°	20°	alcohol. 60°	alcohol. 60°	tone. 23°		60°	20°	
Dielectric const.	80		25	19	21.5	4.3	2.3		1
Ortho/para	0.200	0.388	1.63	0.855	1.46	2.67	127.5	193.4	1320
Meta/para	0.739	1.84	1.03	0.560	1.17	1.03	1.04	2.76	4.53

The ortho-acids behave like non-hydroxylic ("non-polar") compounds, and are more soluble in non-associated solvents of low dielectric power, while the para-, and in a rather smaller degree the meta-, have the opposite character. The alcohols, ether, and acetone have an equally high solvent power for both classes.

The hydroxytoluic acids closely resemble the hydroxybenzoic, and give a good illustration of the difference between normal and abnormal behaviour. The three in which the hydroxyl- and carboxyl-groups are in the ortho-position to one another are almost identical in all these properties: vapour pressure, and solubility in water, benzene, and heptane. A change in the position of the methyl group is practically without effect. When, however, the hydroxyl group is shifted to the meta- (1 : 3 : 4-) or para- (1 : 4 : 3-) position with respect to the carboxyl, these properties are entirely altered.

Of the other groups of acids, the chloro-derivatives are practically normal; their vapour pressures and solubilities are of the same order. The nitro-acids are abnormal, but in a different sense from the hydroxy-acids. The differences in volatility are distinct, although not large; the ortho-compound, as usual, has the highest vapour pressure. But the solubilities, which are very different, are the reverse of what we should expect, the ortho-acid having the lowest and the para- the highest critical solution temperature in water; the meta-, as usual, resembles the para-. In benzene, the solubilities of the ortho- and meta-compounds are in the opposite order to those in water, as we should expect; but the para-compound, although the least soluble in water, is also about as insoluble in benzene as the ortho-. The unusual relation between the slope of the solubility curve and the critical solution temperature in benzene is another anomaly in this group. The nitrobenzoic acids are the only abnormal group hitherto examined which does not contain a phenolic hydroxyl group, and this may explain why this kind of anomaly has not been observed elsewhere.

The mono-substituted acids, benzoic, phenylacetic, and β -phenylpropionic, with their high vapour pressures, somewhat high critical solution temperatures in water, and low heats of solution in benzene,

resemble rather the ortho- than the para-hydroxy-acids, as do also the three chloro-acids.

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