616. *Phase Equilibria in Sulphonic Acid–Water Systems.*

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Solubility and vapour-pressure relations for the systems $X{\cdot}C_6H_4{\cdot}SO_3H$–$H_2O$, where X = H, *o*-Me, *p*-Me, *p*-NO_2, *p*-F, *p*-Cl, *p*-Br, have been measured, 20 hydrates identified, and several heats of solution and of dissociation calculated. Dingemans's treatment of three-phase data at transition points of anhydrous polymorphs has been extended to inter-hydrate transitions, thus providing heats of dissociation independently of dissociation pressures. The results indicate a greater stability of monohydrates relatively to higher hydrates, in agreement with probable ionic structures for the former.

Williamson (*Trans. Faraday Soc.*, 1944, **40**, 421), in calculating heats of solution from solubility and activity data, took his examples largely from inorganic compounds. The same applies to the work of Dingemans and his co-workers (*Rec. Trav. chim.*, 1943, **62**, 625, 653) on three-phase equilibria in two-component systems and that of Pedersen (*Acta Chem. Scand.*, 1949, **3**, 65) on the calculation of hydrate dissociation pressures from saturated-solution vapour pressures. The following investigation involving benzene-, toluene-*o*- and -*p*-, and *p*-nitro-, *p*-fluoro-, *p*-chloro-, and *p*-bromo-benzene-sulphonic acids was carried out as a specific application, and in certain cases test, of the above theoretical work in aqueous systems of highly soluble organic compounds. It was desired first to establish from solubility measurements which hydrates were formed, and then to determine vapour-pressure data for both saturated and unsaturated solutions to allow (1) calculation of heats of solution by Williamson's procedure, (2) comparison of the observed temperatures of pressure maxima on the three-phase curves with those calculated from an equation of Dingemans *et al.*, and (3) calculation of hydrate dissociation pressures, and hence heats of dissociation, from Pedersen's equations. It was also proposed to extend Dingemans's calculations of heats of transition of polymorphs, using three-phase data, to include the case of inter-hydrate transitions. Heats of dissociation would thus be available without the need for solid–vapour equilibrium data, which are difficult to determine, or metastable equilibrium data as required in Pedersen's calculation. Furthermore, in view of a possible analogy with sulphuric and perchloric acids, for whose monohydrates ionic structures have been proposed (Volmer, *Annalen*, 1924, **440**, 200; Richards and Smith, *Trans. Faraday Soc.*, 1951, **47**, 1261), direct determinations of monohydrate dissociation pressures were planned to confirm their expected high stability. Little appears to have been published about $X{\cdot}C_6H_4{\cdot}SO_3H$–$H_2O$ systems apart from the melting points of some doubtful hydrates (Heilbron and Bunbury, "Dictionary of Organic Compounds," Eyre and Spottiswoode, 1943).

Experimental

Preparation and Purification of Sulphonic Acids.—Benzenesulphonic acid. The B.D.H. 32% w/v solution was caused to crystallise fractionally at room temperature over phosphoric oxide in a vacuum-desiccator, the main impurity being iron which readily separated as the ferric salt from early fractions. Four-fold crystallisation gave the free acid as colourless deliquescent plates, m. p. 52·5°, whose equivalent by titration with standard barium hydroxide corresponded exactly to the monohydrate. Owing to darkening in bright daylight, the acid was stored in the dark and used only in subdued light.

*Toluene-*o*- and -*p*-sulphonic acids.* Tests showed that the B.D.H. products could be used satisfactorily without further purification. The *p*-acid had m. p. 104·8° and its equivalent corresponded exactly to the monohydrate; the *o*-acid had m. p. 62·1°, with equivalent exactly that of the dihydrate. Repeated crystallisation from water did not give better products or significantly alter certain check solubility results.

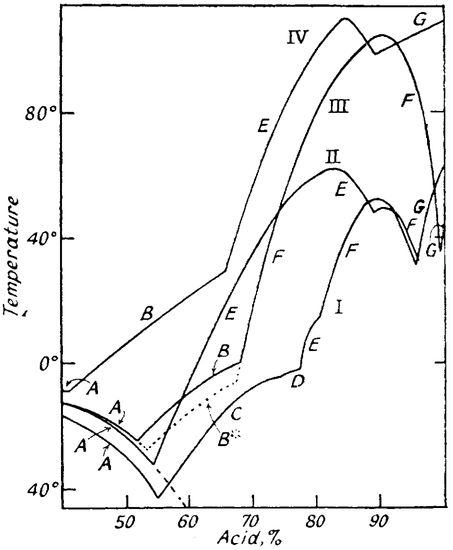
p-*Nitrobenzenesulphonic acid.* Bell's method (*J.*, 1928, 2776) was used and the acid obtained in the pure state *via* the sulphonyl chloride. The latter was crystallised to a sharp m. p. of 77° and then hydrolysed with distilled water, and the resulting solution was evaporated at room temperature over solid potassium hydroxide in a vacuum-desiccator till hydrogen chloride was undetectable. The free acid melted sharply at 110·2° and its equivalent was exactly that of the dihydrate.

p-*Fluorobenzenesulphonic acid.* Fluorobenzene, prepared by Balz and Schiemann's method (*Org. Synth.*, 1939, **13**, 46), was sulphonated in the cold with 10% oleum. Treatment with barium carbonate followed by phosphorus pentachloride gave the sulphonyl chloride, which was vacuum distilled; it had m. p. 33·7°, and a mixed m. p. with a sample of pure *p*-fluorobenzenesulphonyl chloride 33·9°. The free acid, obtained by hydrolysis in the same manner as the *p*-nitro-acid, melted at 85·8°, and its equivalent corresponded exactly to the monohydrate.

p-*Chlorobenzenesulphonic acid.* This acid was prepared from chlorobenzene in a similar manner to the fluoro-acid. The intermediate sulphonyl chloride melted at 53°, and the free acid at 100·3° (Found : equiv., 210·3. Calc. for $C_6H_5O_3ClS,H_2O$: equiv., 210·6).

p-*Bromobenzenesulphonic acid.* The B.D.H. sulphonyl chloride, m. p. 75·5°, was hydrolysed and the free acid obtained as for the *p*-nitro-acid; m. p. 90·2° (Found : equiv., 255·4. Calc. for $C_6H_5O_3BrS,H_2O$: equiv., 255·1).

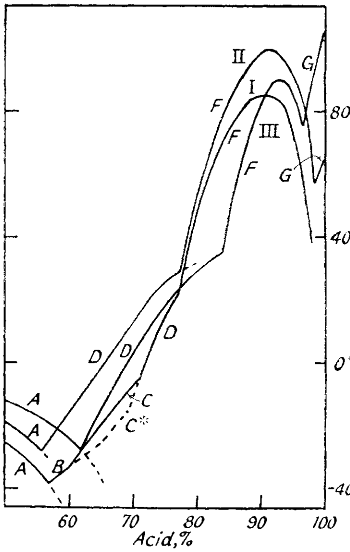
FIG. 1. *Solubility of sulphonic acids.*



*I, Benzene-. II, Toluene-*o-. *III, Toluene-*p-. *IV,* p-*Nitrobenzene-.*

*Solid phases : A = ice, B = tetrahydrate, C = trihydrate, D = 2·5-hydrate, E = dihydrate, F = monohydrate, G = anhydrous acid, * = metastable form.*

FIG. 2. *Solubility of* p-*halogen-substituted benzenesulphonic acids.*



I, Fluoro-. II, Chloro-. III, Bromo-.

Solid phases as in Fig. 1.

All the above sulphonic acids dissolved completely in water and contained no inorganic matter, as shown by negligible residues in sulphated ash tests. For some of the solubility measurements, sulphonic acids containing less water than the above hydrates were required. In the cases of the *o*-Me, *p*-F-, *p*-Cl-, and *p*-Br-acids, dehydration was effected rapidly without decomposition by heating *in vacuo* just above the m. p. of the initial hydrate. The *p*-NO_2-acid dihydrate was completely dehydrated in 24 hours at 55° *in vacuo* over phosphoric oxide, benzenesulphonic acid monohydrate required 6 weeks at room temperature, and the *p*-Me acid monohydrate required 6 months at 35°. Higher temperatures for periods of more than a few hours were precluded owing to slight decomposition.

Solubility Determinations.—Since these covered a wide range of temperatures and compositions, the synthetic method was used. Sulphonic acid–water mixtures were prepared by weight in small test-tubes which were then sealed and attached to a simple wire framework. The latter was gently rocked, and thermostatic control was provided by manually operated solid carbon dioxide–ethanol, water, or dibutyl phthalate baths according to the temperature required. Supercooling was very pronounced in all cases, and accordingly, mixtures were first completely melted, then cooled and frozen out rapidly by touching the tube with solid carbon dioxide to produce small crystals, and the temperature of complete solution approached from below with careful attention to the rate of heating, after which the contents of the tubes were titrated with standard barium hydroxide to give the exact composition. The maximum permissible rates were 0·25° per hour below 10°, 1° per hour between 10° and 50°, and 2° per hour above 50°, calibrated thermometers being used throughout. Mixtures were heated above room temperature for the minimum length of time, in which circumstances no decomposition with the formation of sulphuric acid occurred. Where metastable crystals were encountered, the temperature of the initial freezing out was selected so as to produce the desired solid phase. For economy reasons in a few cases, several solution points were determined with the same sample of acid in a bulb of one-inch diameter, to which known amounts of water could be added with a pipette *via* a ground-glass joint and tap. For those parts of the curves between the m. p.s of congruent hydrates and 100% acid, it was frequently more convenient to start with the hydrate in the test-tube or bulb and remove water by evacuation than to prepare mixtures from anhydrous acid and water. For toluene-*o*-sulphonic acid, mixtures in the range 95·7—100% acid could not be induced to crystallise under any conditions, cooling merely producing a glass, and the same applies to the 98—100% range for the fluoro-acid. From Figs. 1 and 2 only the congruent mono- and di-hydrates can be identified directly. The composition of all other hydrates, both stable and metastable, was determined by direct titration: samples were isolated by filtration through sintered-glass filters previously cooled to the appropriate temperature and drying with filter-paper cooled to the same temperature. The number of molecules of water of crystallisation always corresponded very closely to whole numbers or to 2·5, and no results were obtained which were not in harmony both with the solubility curves and with neighbouring hydrates. Results are given in Table 1. In general, Figs. 1 and 2 confirm the expected high stability of monohydrates relatively to higher hydrates.

Vapour-pressure Determinations.—The vapour pressures of saturated and unsaturated solutions were measured by a static procedure. The apparatus consisted of a flat-bottomed reaction vessel attached *via* taps and glass sprials to a water reservoir and a wide-bore 15-cm.

TABLE 1. *Solubility of substituted benzenesulphonic acids in water.*

$C_6H_5{\cdot}SO_3H$		*o*-$C_6H_4Me{\cdot}SO_3H$		*p*-$C_6H_4Me{\cdot}SO_3H$		*p*-$NO_2{\cdot}C_6H_4{\cdot}SO_3H$	
Temp.	Acid, %	Temp.	Acid, %	Temp.	Acid, %	Temp.	Acid, %
−1·5°	10·42*a*	−0·7°	10·26*a*	−2·0°	9·67*a*	−3·0°	18·88*a*
−4·9	21·30*a*	−3·4	19·56*a*	−4·0	19·63*a*	−5·1	30·04*a*
−11·5	33·9*a*	−7·2	30·42*a*	−7·5	29·45*a*	−8·5	39·74*a*
−22·0	45·06*a*	−12·8	40·38*a*	−13·5	41·74*a*	−8·3	41·22*b*
−29·8	50·23*a*	−25·0	51·37*a*	−23·0	50·72*a*	−1·0	46·06*b*
−40·4	54·49*a*	−30·5	53·56*a*	−23·5	50·97*a*	10·8	53·94*b*
−40·8	55·91*c*	−33·3	54·81*a* ‡	−24·5	51·40*a* ‡	16·0	56·92*b*
−29·0	59·96*c*	−37·0	56·10*a* ‡	−25·0	51·82*a* ‡	26·3	63·33*b*
−18·5	64·18*c*	−39·4	57·12*a* ‡	−25·5	52·00*a* ‡	36·6	66·31*e*
−10·0	68·87*c*	−44·5	59·16*a* ‡	−25·6	52·14*a* ‡	56·6	69·88*e*
−5·9	72·14*c*	−25·0	55·69*e*	−18·5	54·87*b*	75·5	73·47*e*
−4·7	74·44*c*	−13·0	58·51*e*	−5·9	62·56*b*	90·2	77·27*e*
−4·0	74·87*d*	0·8	61·17*e*	−3·4	64·49*b*	110·2	84·92*e*
−3·3	75·82*d*	16·8	64·95*e*	−2·2	65·59*b*	106·8	86·50*e*
−2·5	76·40*d*	31·2	68·58*e*	−1·0	66·90*b*	100·5 †	90·83*g*
−2·3	77·61*d*	50·0	74·78*e*	−27·0	53·20*b* *	105·0 †	96·13*g*
2·2	77·61*e*	56·0	77·07*e*	−26·0	54·09*b* *	110·0 †	100·0*g*
7·5	78·54*e*	61·2	80·90*e*	−16·5	59·48*b* *		
13·7	80·04*e*	62·0	83·07*e*	−10·5	63·60*b* *		
15·1	80·52*e*	60·4	85·07*e*	−8·5	65·0*b* *		
21·3	81·10*f*	54·0	87·64*e*	−7·0	66·80*b* *		
31·0	82·66*f*	48·2	89·23*e*	−6·5	66·89*f* ‡		
39·5	84·39*f*	48·5	89·32*f*	−1·5	67·58*f* ‡		
49·0	87·05*f*	49·0	89·87*f*	1·5	68·06*f*		
52·4	89·60*f*	49·6	91·11*f*	20·1	70·20*f*		
49·0	92·15f	48·6	92·05*f*	38·8	72·50*f*		
39·8	94·04*f*	45·7	93·30*f*	55·2	75·23*f*		
32·6	95·35*f*	38·6	94·66*f*	78·4	79·55*f*		
31·4	95·51*g*	32·5	95·65*f*	89·9	82·38*f*		
42·6	96·74*g*			101·1	86·98*f*		
56·0	98·42*g*			104·8	90·53*f*		
61·3	99·56*g*			102·9	92·39*f*		
				89·1	95·37*f*		
				73·9	97·36*f*		
				45·3	99·02*f*		
				36·5	99·73*g*		
				40·5	99·87*g*		
				42·5	99·97*g*		

TABLE 1 (*continued*).

p-$C_6H_4F{\cdot}SO_3H$		p-$C_6H_4Cl{\cdot}SO_3H$		p-$C_6H_4Br{\cdot}SO_3H$	
Temp.	Acid, %	Temp.	Acid, %	Temp.	Acid, %
− 4·9°	19·77*a*	− 3·0°	19·08*a*	− 1·9°	14·96*a*
−15·0	39·81*a*	− 6·5	31·96*a*	− 4·5	30·21*a*
−20·5	45·79*a*	−12·5	43·76*a*	− 9·0	45·07*a*
−28·5	51·84*a*	−19·5	50·04*a*	−12·5	50·74*a*
−36·4	55·63*a*	−23·5	53·07*a*	−16·0	54·03*a*
−38·5	56·45*a*	−27·5	55·44*a*	−19·5	56·94*a*
−43·0	58·34*a* ‡	−30·0	56·47*a* ‡	−26·5	61·28*a*
−38·0	57·42*b*	−26·0	56·47*d*	−29·5	62·46*a* ‡
−35·4	58·34*b*	−20·0	58·49*d*	−31·5	63·39*a* ‡
−34·4	59·21*b*	−11·0	61·71*d*	−38·0	65·21*a* ‡
−32·5	60·53*b* ‡	− 2·2	64·71*d*	−21·0	63·41*d*
−30·5	61·38*b* ‡	10·6	69·34*d*	−10·5	65·97*d*
−26·4	64·54*b* ‡	22·9	73·60*d*	0·0	68·95*d*
−24·0	66·25*b* ‡	27·6	75·98*d*	12·5	72·97*d*
−21·4	64·54*c*	30·8	78·75*d* ‡	19·9	75·25*d*
−18·5	65·25*c*	41·0	78·75*f*	27·6	79·16*d*
−13·0	67·56*c*	51·9	79·80*f*	34·6	83·49*d*
− 7·4	69·71*c*	70·1	82·54*f*	43·8	84·78*f*
−22·5	66·25*c* *	80·4	84·55*f*	60·2	86·72*f*
−19·5	67·56*c* *	88·8	86·12*f*	71·2	67·92*f*
−17·9	68·13*c* *	99·9	90·90*f*	80·3	89·78*f*
−15·5	69·15*d*	100·2	91·94*f*	86·2	91·05*f*
− 3·9	71·22*d*	96·7	93·78*f*	90·2	92·99*f*
1·0	72·02*d*	89·0	95·83*f*	87·2	94·75*f*
10·1	74·03*d*	73·3	97·68*f*	78·5	96·18*f*
21·3	76·95*d*	59·8	98·31*f*	76·6	96·43*f*
22·1	77·14*f*	59·0	99·02*g*	82·3	97·21*g*
35·4	78·38*f*	62·4	99·54*g*	89·6	98·00*g*
54·2	81·06*f*			93·1	98·45*g*
71·2	84·33*f*			97·6	98·90*g*
80·0	86·72*f*				
85·5	90·07*f*				
85·2	91·64*f*				
81·0	94·06*f*				
74·5	95·01*f*				
54·3	97·24*f*				
41·4	98·03*f*				

Solid phases: *a* = ice; *b* = tetrahydrate; *c* = trihydrate; *d* = 2·5 hydrate; *e* = dihydrate; = monohydrate; *g* = anhydrous acid.

* Metastable form. † With decomp. ‡ Metastable.

mercury manometer whose levels were read to ±0·02 mm. with a travelling microscope. The spirals and a glass marble in the reaction vessel allowed gentle agitation of its contents to assist attainment of equilibrium. The system could be evacuated to less than 0·001 mm. of mercury with an oil pump, and was immersed, with the exception of the water reservoir, in a glass-sided water thermostat controlled with electronic relays to better than 0·05°. Below room temperature, a 0° cooling coil was used, and above 80° the water was replaced by dibutyl phthalate. The use of Silicone high-vacuum grease on joints and taps allowed reliable measurements up to 96°. Measurements above this temperature were impracticable owing to slight seepage of dibutyl phthalate into the apparatus, and below 9° because of the very long time to reach equilibrium. Solutions were repeatedly boiled out *in vacuo* to remove dissolved air, compositions being adjusted as desired with de-gassed water from the reservoir. Equilibrium was approached first from below and then from above the equilibrium pressure, and a third time in the case of saturated solutions after a further brief evacuation. The results of these separate experiments, each of which required a maximum of 24 hours, always agreed. Corresponding temperatures and pressures were measured for saturated solutions from beyond the pressure maximum on the mono- or di-hydrate curves, as the case may be, to below the transition to the next highest hydrate.

Measurements at 50° on unsaturated solutions, whose compositions were determined by titration, covered a short composition range up to and including saturation. In no case was more than a minute trace of free sulphuric acid detected in the solutions at the end of an experiment. Previous tests using distilled water gave vapour pressures agreeing within the limits of the microscope with values given in International Critical Tables, **3**, 210, thus confirming the accuracy of the procedure. In Tables 2 and 3 all pressures are given in mm. of mercury corrected to 0°.

TABLE 2. *Vapour pressure (mm.* Hg) *of saturated aqueous solutions of substituted benzenesulphonic acids.*

$C_6H_5{\cdot}SO_3H$		o-$C_6H_4Me{\cdot}SO_3H$		p-$NO_2{\cdot}C_6H_4{\cdot}SO_3H$		p-$C_6H_4F{\cdot}SO_3H$		p-$C_6H_4Cl{\cdot}SO_3H$		p-$C_6H_4Br{\cdot}SO_3H$	
Temp.	Mm.	Temp.	Mm.	Temp.	Mm.	Temp.	Mm.	Temp.	Mm.	Temp.	Mm.
9·0°	1·24*e*	25·0°	12·55*e*	21·0°	12·93*b*	12·0°	3·21*d*	22·0°	6·62*d*	20·1°	4·74*d*
13·0	1·65*e*	35·0	20·32*e*	23·0	14·25*b*	14·0	3·49*d*	24·0	7·43*d*	26·0	6·63*d*
15·0	1·86*e*	45·0	30·09*e*	25·0	15·60*b*	16·0	3·84*d*	26·0	8·26*d*	28·0	7·39*d*
16·0	1·95*e*	55·0	39·85*e*	27·0	16·87*b*	18·0	4·16*d*	28·0	9·15*d*	30·0	8·20*d*
17·1	2·02*e*	57·0	40·66*e*	28·0	17·55*b*	20·0	4·54*d*	29·0	9·59*d*	32·0	9·02*d*
18·0	2·05*e*	58·0	41·03*e*	29·05	18·44*e*	22·0	4·98*f*	30·0	10·13*f*	35·0	10·51*f*
18·95	2·12*f*	58·5	41·05*e*	31·0	20·41*e*	24·0	5·62*f*	32·0	11·28*f*	38·0	12·10*f*
23·05	2·69*f*	59·0	41·03*e*	33·0	22·66*e*	28·0	6·91*f*	35·0	13·09*f*	40·0	13·24*f*
31·0	3·94*f*	60·0	40·90*e*	40·0	31·75*e*	35·0	9·80*f*	39·8	16·22*f*	50·0	20·27*f*
39·0	5·14*f*			50·0	49·58*e*	55·0	22·65*f*	60·0	38·19*f*	60·0	29·32*f*
43·0	5·69*f*			65·0	91·64*e*	70·0	38·06*f*	80·1	73·30*f*	70·0	39·60*f*
46·0	5·90*f*			79·0	143·4*e*	75·0	42·01*f*	88·9	85·59*f*	80·1	52·25*f*
48·0	5·98*f*					77·1	43·03*f*	91·0	47·48*f*	83·9	53·89*f*
50·0	5·19*f*					79·0	43·72*f*	93·4	88·41*f*	84·4	53·91*f*
						80·0	43·74*f*	94·3	88·24*f*	84·95	53·89*f*
						83·1	41·37*f*	96·2	87·00*f*	85·8	53·35*f*

Solid phases: As in Table 1.

TABLE 3. *Vapour pressure (mm.* Hg) *of unsaturated aqueous solutions of substituted benzenesulphonic acids at* 50·0°.*

$C_6H_5{\cdot}SO_3H$		o-$C_6H_4Me{\cdot}SO_3H$		p-$C_6H_4Me{\cdot}SO_3H$		p-$NO_2{\cdot}C_6H_4{\cdot}SO_3H$	
Mm.	*m*	Mm.	*m*	Mm.	*m*	Mm.	*m*
14·23	27·23	42·89	14·38	46·44	13·03	61·02	8·312
11·53	30·18	40·89	15·02	44·92	13·60	57·50	8·991
9·11	33·36	39·99	15·27	43·86	14·01	54·93	9·543
8·34	34·18	38·48	15·80	41·44	14·69	53·99	9·831
7·15	38·07	37·87	16·14	39·37	15·45	53·56	9·959
6·37	40·16	36·56	16·85	37·38	16·12	52·55	10·22
6·18	41·78	36·11	17·11	36·87	16·29	50·82	10·58
5·88	42·24	35·86	17·22 †	35·90	16·60	50·43	10·66
5·91	43·65 †			35·33	16·83 †	49·66	10·90 †

p-$C_6H_4F{\cdot}SO_3H$		p-$C_6H_4Cl{\cdot}SO_3H$		p-$C_6H_4Br{\cdot}SO_3H$	
Mm.	*m*	Mm.	*m*	Mm.	*m*
24·96	20·03	33·23	16·54	24·90	20·61
23·48	20·55	31·56	17·48	22·25	22·21
22·61	20·88	30·09	18·06	21·85	22·58
22·04	21·30	29·23	18·45	21·41	23·09
21·51	21·72	28·21	18·96	20·91	23·64
20·50	22·21	27·55	19·27	20·21	24·73 †
19·42	23·07	26·63	19·74		
18·63	23·45 †	25·57	20·24 †		

* m = G.-mole of solute per 1000 g. of water. † Saturated.

Solid phases at saturation: monohydrate for benzene, p-CH_3, p-F, p-Cl, p-Br; dihydrate for o-CH_3 and p-NO_2.

Dissociation Pressure of Monohydrates.—The same apparatus was used as for solution vapour pressures. Monohydrate was crystallised *in vacuo* in the reaction vessel, and approximately half the water of crystallisation removed by prolonged evacuation before allowing the system to come to equilibrium. The times required ran into months and frequently at the end of an experiment traces of free sulphuric acid could be detected. Reliable results were obtained in two cases only.

For benzenesulphonic acid monohydrate, the dissociation pressures were:

Temp.	24·00°	24·90°	25·90°	26·85°	27·90°	29·10°	29·85°
P, mm. Hg	0·096	0·105	0·120	0·140	0·155	0·175	0·200

Each of these pressures was the average of ten readings. They do not deviate by more than about 3% from the equation $\log_{10} P = -4922/T + 15{\cdot}54$, the heat of dissociation being 22·5 kcal./mole. Results (average of 10 readings) for the p-bromo-acid were:

Temp.	40·0°	50·0°	54·8°
P, mm. Hg	0·75	1·54	2·11

Agreement is better than 1% with the equation $\log_{10} P = -3087/T + 9{\cdot}743$, giving a heat of dissociation of 14·1 kcal./mole. Attempts to approach equilibrium by adding water vapour to a pressure initially greater than the dissociation pressure were vitiated by rapid adsorption on the anhydrous acid phase. For the *p*-bromo-acid, adsorption equilibrium pressures (average of 10 readings) were :

Temp.	41°	45°	50°	55·1°	60·9°	65·2°	67·0°	69·9°	72·04°
P, mm. Hg	0·26	0·34	0·54	0·86	1·21	1·84	2·11	2·44	2·84

They agree closely with the equation $\log_{10} P = -3663/T + 11{\cdot}07$. The pressure remained at the low adsorption value for several hours before very slowly rising to the true dissociation value.

Pressure Maxima on the Three-phase Curves.—Below are given the observed maxima and those calculated from Dingemans's equation $1/T_{\text{max.}} = 1/T_f + 0{\cdot}00021$, where T_f is the m. p. in °K of the stable solid phase. Dingemans has shown (*loc. cit.*) that this equation applies with remarkable success to inorganic compounds where $T_{\text{max.}}$ is 20—30° less than T. In the present work $T_{\text{max.}}$ is close to T_f, and failure is marked :

Acid	T_f, °C	$T_{\text{max.}}$, obs., °C	$T_{\text{max.}}$, calc., °C	Acid	T_f, °C	$T_{\text{max.}}$, obs., °C	$T_{\text{max.}}$, calc., °C
† C_6H_5·	52·5	48·0	31·7	† *p*-Cl·C_6H_4·	100·4	93·4	73·4
* *o*-CH_3·C_6H_4·	62·2	58·5	40·2	† *p*-Br·C_6H_4·	90·3	84·4	64·7
† *p*-F·C_6H_4· ...	85·7	80·8	60·3				

Stable solid phases : * dihydrate, † monohydrate.

Heats of Solution at 50°.—These were calculated from Williamson's equation 49 (*loc. cit.*, Appendix). The data in Table 1 were recalculated in terms of molalities, and $(dm/dT)_{\text{sat.}}$ evaluated graphically. The term $\left(\frac{\partial \ln \alpha}{\partial m}\right)_T = \frac{1}{P}\left(\frac{\partial P}{\partial m}\right)_T$, where α and *P* are respectively the activity and vapour pressure of the solvent, was determined graphically at saturation from the data in Table 3. The heat of solution at saturation is then given by

$$\left(x - \frac{55{\cdot}51}{m}\right)\boldsymbol{R}T^2\left(\frac{dm}{dT}\right)_{\text{sat.}}\frac{1}{P}\left(\frac{\partial P}{\partial m}\right)_T$$

where *x* is the number of molecules of water of crystallisation in the stable solid phase. Results were as follows, in which estimated errors allow only for errors in drawing tangents :

R in C_6H_4R·SO_3H	Heat of soln., kcal./mole	R in C_6H_4R·SO_3H	Heat of soln., kcal./mole	R in C_6H_4R·SO_3H	Heat of soln., kcal./mole
H, $+H_2O$	$1{\cdot}8 \pm 0{\cdot}2$	*p*-NO_2, $+2H_2O$ ...	$4{\cdot}3 \pm 0{\cdot}2$	*p*-Cl, $+H_2O$	$3{\cdot}8 \pm 0{\cdot}2$
o-Me, $+2H_2O$ ...	$5{\cdot}1 \pm 0{\cdot}3$	*p*-F, $+H_2O$	$4{\cdot}3 \pm 0{\cdot}2$	*p*-Br, $+H_2O$	$1{\cdot}7 \pm 0{\cdot}1$
p-Me, $+H_2O$ ...	$6{\cdot}2 \pm 0{\cdot}2$				

Heats of Dissociation of Hydrates Other than Monohydrates.—Full details for the approximate calculation of dissociation pressures from a combination of stable and metastable saturated solution vapour pressures are given by Pedersen (*loc. cit.*). For a selection of hydrates, the calculated pressures and heats of dissociation are given in Table 4. In view of the extrapolation of the data in Table 2 required to give vapour pressures of metastable solutions, and the small differences between these and the pressures of stable solutions, the heat of dissociation values are probably not accurate to better than ±1 kcal.

TABLE 4. *Heats of dissociation.*

		Calculations after Pedersen :			
Acid	Hydrate equilibrium	Temp.	Dissocn. press., mm. Hg	Heat of dissocn., kcal./mole	Heat of dissocn., from ΔH values, kcal./mole
C_6H_5·SO_3H	$2H_2O \rightleftharpoons H_2O$	14·0°	1·47	10·5	10·5
		9·0	1·05		
p-NO_2·C_6H_4·SO_3H ...	$4H_2O \rightleftharpoons 2H_2O$	27·0	15·78	14·7	14·0
		22·0	10·43		
p-C_6H_4F·SO_3H	$2{\cdot}5H_2O \rightleftharpoons H_2O$	20·0	4·43	15·4	11·4
		15·0	3·21		
p-C_6H_4Cl·SO_3H	$2{\cdot}5H_2O \rightleftharpoons H_2O$	27·0	8·70	12·4	9·4
		22·0	6·13		
p-C_6H_4Br·SO_3H	$2{\cdot}5H_2O \rightleftharpoons H_2O$	30·0	8·07	12·1	9·1
		25·0	5·73		

Dingemans's approximate treatment (*loc. cit.*) of heats of transition of polymorphs of anhydrous compounds can be extended to hydrates to give heats of dissociation as follows. In the case of 2·5 hydrate $\rightleftharpoons$ monohydrate equilibria, let 1 mole of saturated solution at the transition point contain x moles of anhydrous acid and $(1 - x)$ moles of water. On isothermal evaporation of the solution at a temperature infinitesimally greater than the transition point,

$$\Delta H_1 + [1/(1 - 2x)] \text{ mole of sat. soln.} \longrightarrow 1 \text{ mole of water vapour} + [x/(1 - 2x)] \text{ mole of monohydrate}$$

where ΔH_1 is the change of heat content accompanying the formation of the saturated solution from solid monohydrate and solvent vapour and may be evaluated from the gradient of the three-phase curve (Glasstone, " Thermodynamics for Chemists," Van Nostrand, 1947, p. 241). Similarly, for crystallisation of the 2·5 hydrate at a temperature infinitesimally lower than the transition point,

$$\Delta H_{2\cdot5} + [1/(1 - 3{\cdot}5x)] \text{ mole of sat. soln.} \longrightarrow 1 \text{ mole of water vapour} + [x/(1 - 3{\cdot}5x)] \text{ mole of 2·5 hydrate.}$$

Rearrangement and subtraction of these two equations gives

$$2/3\{[(1 - 2x)/x]\ \Delta H_1 - [(1 - 3{\cdot}5x)/x]\ \Delta H_{2\cdot5}\} + 2/3 \text{ mole of 2·5 hydrate} \longrightarrow 1 \text{ mole of water vapour} + 2/3 \text{ mole of monohydrate}$$

in which the first term is the heat of dissociation of the 2·5 hydrate at the transition point. The dissociation of benzenesulphonic acid dihydrate and of the *p*-nitro-acid tetrahydrate may be treated similarly. In certain cases, to determine the ΔH value the plot of $\log_{10} P$ against $1/T$ results in two very similar gradients above and below the transition point. This introduces no major error, however, since both ΔH quantities are multiplied by composition factors, and the respective products are appreciably different. The data in Tables 1 and 2 being used, the values in Table 4 were obtained for which an accuracy of not more than ±1 kcal. is claimed. The agreement between these and Pedersen's values is as good as can be expected considering the approximate nature of the treatments. In the case of monohydrates of benzene- and *p*-bromobenzene-sulphonic acids, dissociation pressures are much smaller and heats of dissociation greater than for higher hydrates, thus confirming the higher relative stability of their monohydrates evident from Figs. 1 and 2.

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