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PHASE EQUILIBRIA
IN
SULPHONIC ACID-WATER SYSTEMS

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Doctor of Philosophy

by

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INTRODUCTION.

Little, if anything, appears to have been published previously about sulphonic acid-water systems apart from the fact that the acids form a number of hydrates. Evidence in the literature regarding these hydrates is conflicting. R. Otto(1) has stated that benzene sulphonic acid can be obtained as a $1\frac{1}{2}$ hydrate melting at $43-4^{\circ}\text{C}$, and Hübner(2) declares that a dehydrate can be obtained. Heilbron's Dictionary gives the melting point, when dried over concentrated sulphuric acid, as $43-4^{\circ}\text{C}$, and the melting point of the anhydrous acid as $65-6^{\circ}\text{C}$, or alternatively, $50-1^{\circ}\text{C}$.

The sulphonic acids of the present investigation are strong acids and may be compared with sulphuric acid, in which case stable monohydrates may well be expected, as well as a number of higher hydrates.

For the monohydrates of sulphuric and perchloric acids, the structures $\text{HSO}_4^- \text{H}_3\text{O}^+$, and $\text{ClO}_4^- \text{H}_3\text{O}^+$ have been proposed(3), and the occurrence of somewhat similar structures in sulphonic acid monohydrates would confer some degree of stability with congruent melting points and low dissociation pressures. Similar "ionic structures" have also been proposed for oxalic acid dihydrate, potassium pentaborate tetrahydrate, and the dehydrate of boron fluoride(4).

Phase equilibria were first treated in a rigorous thermodynamic/

thermodynamic manner by J. Willard Gibbs(5), and deductions from his equations have been given by Morey(6). The latter has shown, for example, that for solid-liquid-vapour equilibria in binary systems,

$$\frac{dp}{dt} = \frac{(S^V - S^L)}{(V^V - V^L)} - \frac{(X^V - X^L)}{(X^S - X^L)} \frac{(S^S - S^L)}{(V^S - V^L)}$$

where V = specific volume

S = specific entropy

X = weight fraction of solid component

p = pressure

t = temperature

The superscripts v, l and s denote vapour, liquid and solid respectively.

A similar equation expressing the change in composition with temperature may also be deduced, but neither can be applied in more than a qualitative manner owing to the several unknown quantities which are difficult to determine. In view of this, several attempts have been made to derive simpler relationships, which, although lacking the rigour of Gibb's equations, can be applied quantitatively to the three phase line.

One such simple relationship was deduced by Kume (7), who states that for a number of salts the following relationship exists between the solubility in water and the vapour pressure of the saturated solution:-

$$\frac{p_x - p}{p} = K \cdot \frac{X}{1 - X}$$

where p = vapour pressure of the saturated solution,
 p_w = vapour pressure of pure water,
 x = molar fraction of salt in the saturated solution.

The constant K is stated by Kume to be independent of temperature, and to have a definite value for each salt.

This statement has been examined by Dingemans(8) who came to the conclusion that in many cases it did not hold good. Dingemans and his collaborators(9) have gone on to deduce from theoretical considerations based on Raoult's Law the following equations regarding the pressure maximumⁱⁿ the three phase line.

The composition of the melt at the maximum is given by the equation,

$$\frac{1}{x_{\max}} = \left(1 + \frac{Q_f}{Q_v}\right) \frac{1 + W_2/Q_f}{1 - W_1/Q_v}$$

where x = mole fraction for the salt in the solution,

Q_f = molal heat of fusion of salt,

Q_v = molal heat of evaporation of water,

W_1 = the difference between the partial molal enthalpies of the components in the solution,

W_2 = the difference between the partial molal enthalpies of the pure components.

The temperature corresponding to the pressure maximum is given by,

$$\frac{1}{T_{\max}} - \frac{1}{T_f} = \left(\frac{R}{Q_f}\right) \ln \left(1 + \frac{Q_f}{Q_v}\right) \frac{1 + W_2/Q_f}{1 - W_1/Q_v} - \left(\frac{R}{Q_f}\right) \ln f_2$$

where/

where T_f = temperature of fusion of salt,

R = Gas Constant,

T_{max} = temperature of maximum,

f_2 = the activity coefficient of the salt referred to the pure super-cooled molten salt as the standard state.

If now the logarithm is expanded in a series and only the first term of it is taken, this gives, (with $Q_v = 9.45 \text{ k.cal/mol}$ for water between $50^\circ - 200^\circ \text{C}$), the formula,

$$\frac{1}{T_{max}} - \frac{1}{T_f} = \frac{R}{Q_v} = .00021$$

For a large number of inorganic salts, Dingemans found that the values calculated by means of these formulae agreed fairly well with the experimental values.

An interesting point which Dingemans also noted was that, if the ratio of the vapour pressure of the saturated solution to the vapour pressure of pure water at the same temperature is plotted against temperature, a straight line is obtained in many cases.

Using this observation, he has deduced several formulae for the calculation of the heat of transition of an inorganic salt from one crystalline modification to another.

Application of these ideas in the present work is dealt with in the Discussion Section, but it may be stated here that the Dingemans' treatment has proved/

proved much less satisfactory than when applied to inorganic salts.

Solid-Vapour equilibria such as the dissociation of salt hydrates can in general be treated adequately by the well known Clausius-Clapeyron equation, from which heats of dissociation may be calculated. In the present work, much difficulty has been encountered in measuring dissociation pressures, and accordingly, the method of Pedersen(10) has been employed. Here, the dissociation pressure is calculated from a knowledge of the solubilities, and of the vapour pressures of saturated solutions of the two hydrates, with the assumption that the vapour pressure is a linear function of the solubility over the temperature range involved. His equation is as follows;

$$(n - m) \log p_{m,n} = (n + 1 - k) \log p_n - (m + 1 - k) \log p_m + k \cdot \log \frac{X_n}{X_m}$$

where, n = number of molecules of water per molecule of involatile substance S for hydrate S_n ,

m = number of molecules of water per molecule of involatile substance S for hydrate S_m ,

$\log p_n$ = log. of vapour pressure of a saturated solution of S_n ,

$\log p_m$ = log. of vapour pressure of a saturated solution of S_m ,

$\log p_{mn}$ = log. of vapour pressure of a mixture of S_n and S_m ,

X_n = mole fraction of S in saturated solution of S_n ,

X_m = mole fraction of S in saturated solution of S_m ,

$$k = \frac{P_m - P_n}{X_n P_m - X_m P_n}$$

It is noteworthy that these calculations, approximate as they must be, have yielded reasonable values for the heats of dissociation of the 2.5 hydrates of the halogen substituted sulphonic acids.

An alternative approach to the calculation of heats of dissociation from a knowledge of the vapour pressures of saturated solutions is outlined in the Discussion. This is based on the equation,

$$\frac{dP}{dT} = \frac{\Delta H}{T \Delta V}$$

where, ΔH = the change of heat content accompanying the formation of the given solution from the solid solute and the vapour of the solvent, and

ΔV = the corresponding volume change.

This is a development of the Dingemans' treatment for the calculation of heats of transition between polymorphs. Again, values of the correct order of magnitude have been obtained for the heats of dissociation of the 2.5 hydrates of the halogen substituted sulphonic acids.

An important development from phase equilibria measurements is the determination of heats of solution from vapour pressure and solubility measurements. This is of special interest since direct calorimetric measurement of this quantity in saturated or nearly saturated solutions may be difficult owing to the slow/

slow rate of dissolution or crystallisation of the solid phase. Williamson(11) has directed attention to this problem recently by the derivation from rigorous thermodynamics of the equation,

$$\Delta H_{sol.} = (X - \frac{55.51}{m})RT^2(\frac{dm}{dT})_{sat.} (\frac{\partial \ln a_1}{\partial m})_T,$$

where, $\Delta H_{sol.}$ = heat absorbed per mole of solute dissolved in the nearly saturated solution, or the heat evolved per mole on crystallisation.

- X = number of molecules of water of crystallisation,
- m = molality = moles of solute per 1000grams of water,
- R = gas constant,
- T = absolute temperature,
- a_1 = activity of the solvent.

The successful application of this equation demands, above all, accurate data, owing to the sensitivity of the various terms to small variations in m and p. In applying the equation in the present work, therefore, careful attention has been paid to accuracy of measurement at all stages, and to assessing the probable error in the ultimate $\Delta H_{sol.}$ values.

An interesting point in connection with heats of solution is the calculation by Falkenhagen(12) of heats of hydration of ions in the case of some alkali halides. He has expressed the heat of solution of the halide as the difference between its lattice energy and the heat of hydration of the two ions. Lattice energies were obtained from Haber-Born(13) cycle/

cycle calculations, and with calorimetrically measured heats of solution, values of the expected order were obtained for heats of hydration of the ions.

A very qualitative application of these ideas has been made to the sulphonic acid monohydrates, and it is of note that the treatment gives a relative order for the heats of solution which is substantially the same as the experimental order.

It will be of interest now to consider what influence, if any, substituents, in the benzene nucleus of the sulphonic acids, may have on the phase equilibria in general. The series of acids investigated include benzene, o- and p-toluene, p-fluoro, p-chloro, p-bromo, and p-nitro-benzene sulphonic acids, a series which was chosen specifically with substituent effects in mind.

In organic compounds in general, increase in molecular weight frequently leads to increase in melting point and decrease in solubility, and in this respect, benzene sulphonic acid may be expected to differ from the substituted acids. Of greater interest, however, is the influence which the inductive, mesomeric and hyperconjugation effects of the substituents may have.

The current theories regarding the structure of benzene demand the existence of six electrons of more than ordinary mobility. These mobile electrons endow compounds of benzene with their special aromatic character/

character. The concentration of these electrons, sometimes called the electron density can be affected by the replacement of hydrogen by another radical or group. This takes place by two main methods, viz:-

- a) the inductive effect,
- b) the mesomeric effect (electromeric, resonance effect).

The inductive effect is a measure of the electronegativity of the group relative to hydrogen. If it is more electronegative it will attract electrons, and if it is less electronegative it will repel electrons.

The mesomeric effect comes into play when the group forms part of a conjugated system, as frequently happens when the group is attached to benzene. If the group possesses any lone pairs of electrons, these may become conjugated with the electrons of the benzene ring, and result in a displacement of electrons from one bond to another.

The results of these two effects may be summarised thus:-

<u>Group</u>	<u>Inductive</u>	<u>Mesomeric</u>
MeO, HO	Withdraws electrons	Releases electrons
Halogens	"	"
NO ₂	"	Withdraws
Alkyl	Releases	No lone pairs
		∴ No effect

In addition to the inductive and resonance effects/

effects of substituents, there is now strong evidence in favour of what has been termed hyperconjugation(14), particularly in the case of a methyl group. When a methyl group is attached to a conjugated system, the pair of electrons forming one of the C-H bonds in the methyl group are appreciably less localised than those in, for example, a similarly situated C-C bond. Hence a methyl group, attached to the requisite system, permits electron release by what is essentially a type of mesomeric effect,

This effect acts in addition to, and in the same direction as, the inductive effect.

Of importance also is the phenomenon known as the ortho effect. The view has been expressed(15) that many of the special ortho effects recorded in the literature may be due to chelation, to steric inhibition of resonance, to the short distances from which the inductive effects operate, and to the circumstance that the direction of the group dipole is different from that which it would have in the meta or para positions. Hughes(15) considers that the last two factors may possibly account for some comparatively small ortho effects, but that the first two are of more general importance where large effects are concerned. A group in the ortho position to a sulphonic group would thus be expected to have a different effect from that of the same group in the meta/

meta or para positions.

The fact that substituents can affect acid strength is well illustrated by thermodynamic dissociation constants of substituted aromatic carboxylic acids(16).

Relative to benzoic acid, a p-methyl group decreases the value of K and p-halogen groups increase the value of K. It is interesting to note that the p-bromo group has a greater effect than the p-chloro which in turn has a greater effect than the p-fluoro.

Table

<u>X</u>	<u>$10^5 K$</u>	<u>$X.C_6H_4.COOH$</u>
p -CH ₃	4.24	
H	6.27	
p-F	7.22	
p-Cl	10.55	
p-Br	10.7	

A similar effect may be expected with sulphonic acids, though the relative effect of substituents must necessarily be much smaller owing to the strongly acid character of the sulphonic group to begin with.

These substituent effects may in general be revealed in the characteristics of the solubility curves. It must however be emphasised that transmission of electronic effects to a sulphonic group and the relative magnitude of inductive and resonance effects of substituents may be somewhat different/

different from those occurring in the aromatic carboxylic acids, owing to the difference in the electronegativities of carbon and sulphur and to the different configurations of the sulphonic and carboxylic groups. Nevertheless, that important effects do in fact occur, has been clearly indicated by the differing characteristics of the acid hydrates as described in later sections.

Over the past fifty or sixty years, a considerable number and variety of phase equilibria investigations have been carried out, and various techniques have been evolved for dealing with the different types of equilibria. The latter may be conveniently divided into four main classes:-

1. Solid-Liquid.
2. Solid-Vapour.
3. Liquid-Vapour.
4. Solid-Liquid-Vapour.

In the present investigation dealing with benzene and substituted benzene sulphonic acid-water systems, measurements in all four of these classes have been carried out to illustrate the essential features of each system, and to evaluate the heats of solution and dissociation of certain of the solid phases.

The selection of the techniques employed here has been conditioned by four main factors:-

a)/

- a) the very high solubility of the sulphonic acids in water with attendant high solution viscosities,
- b) the relatively low aqueous vapour pressures encountered,
- c) the long times required to establish equilibria, and
- d) the limited quantities available of some of the sulphonic acids.

Clearly, in measurements of solid-liquid equilibria, methods based on thermal analysis (as for alloy systems) or quenching procedures (as for silicate systems) are not applicable here. Furthermore, analytical procedures, in which solutions are stirred to equilibrium in presence of excess solid phase at a known temperature, require relatively large amounts of solutes for average scale work when solubilities are high. The most suitable method in the present case is a variant of the thaw point - melting point method introduced by Rheinboldt(17), in which mixtures of known composition are heated, preferably in sealed vessels, and the temperature at which the last crystal of solid phase disappears determined. When applied to aqueous systems, this is known as the synthetic method, and is most successful when change in solubility with temperature is not small and when solid-liquid equilibrium is established relatively quickly. The former condition holds good in all the systems here investigated, and the latter is one which received special attention as detailed in the Experimental Section.

For measurements of solid-vapour and liquid-vapour equilibria the methods may, in general, be classed either as (1) static, in which equilibrium is usually established in some form of tensimeter, or as (2) dynamic, in which bulk movement of the equilibrated vapour phase is achieved, either by some form of transpiration process or, for liquid systems, in an equilibrium still of the Othmer type(18). Variants of these procedures such as the dew point method and the isopiestic method have been developed and have proved extremely valuable in the determination, for example, of activities in aqueous solutions.

In the present work, only the solvent is volatile in the temperature range studied, and consequently, a static procedure involving a type of tensimeter, which may be evacuated at will and has an attached water reservoir, has proved satisfactory.

Previous workers(19) have shown that the main difficulty in tensimeter work is the complete removal of all foreign gases from the tensimeter, and this has been achieved by a flushing out and evacuation procedure described later.

Application of isopiestic technique to solid-vapour equilibria for hydrates has been briefly explored but the slowness with which equilibrium with the balancing solution (70%-80% sulphuric acid) was attained rendered the method of little use.

EXPERIMENTAL.

Preparation and Purification

In view of the adverse influence of impurities, both organic and inorganic, in solubility and vapour pressure determinations(20), all the sulphonic acids used were of high purity. In particular, since much use was made of the synthetic method in the solubility measurements, it was essential that the acids should contain no inorganic material which would give precipitates of relatively insoluble metallic sulphonates. The purification, and in certain cases the preparation also, of the various acids was carried out as follows.

a) Benzene Sulphonic Acid.

The starting material here was B.D.H. 32% w/v aqueous solution as supplied in brown bottles. Experience soon showed that this acid, whether in solution or in the solid state, must be protected from bright light as far as ever possible, otherwise considerable darkening with the formation of free sulphuric acid occurs. At all stages therefore, this acid was stored in the dark and used only in subdued light.

Preliminary tests on the 32% solution indicated that iron was the main impurity and this was separated as ferric benzene sulphonate from the free sulphonic acid by a fractional crystallisation process. The solution/

solution was allowed to stand over phosphorus pentoxide in a vacuum desiccator at room temperature until appreciable crystallisation had occurred. This first crop of crystals were in the form of light green plates and were filtered off. On analysis, the iron content of these green plates was found to be close to that required by ferric benzene sulphonate. This crystallisation process required several days and could not be accelerated by heating without considerable darkening of the solution occurring. The mother liquor was now diluted to its original volume with distilled water and the crystallisation process repeated. A three or four fold repetition of this process gave a mother liquor which contained only traces of iron as indicated by testing with ammonium thiocyanate solution; and the resulting liquor was then taken completely to dryness. During the whole process, approximately one fourth of the sulphonic acid initially present was thrown down along with the impurities.

The acid thus obtained was in the form of well crystallised white deliquescent plates, which dissolved completely in distilled water. Tests showed the absence of sulphate, chloride, nitrate, sodium, potassium, calcium, barium, iron, copper and nickel. A sulphated ash determination gave no measurable inorganic residue.

The/

The equivalent was determined and was found to correspond to the monohydrate:-

Weight of weighing bottle empty	=	12.2840g.
Weight of weighing bottle + acid	=	12.8274g.
∴ Weight of acid	=	0.5434g.
Titre of 0.05726 N baryta	=	53.87 mls.
∴ Equivalent	=	176.1
Equivalent of $C_6H_5SO_3H.H_2O$	=	176.2

This substance melted sharply at $52.5^{\circ}C$ (lit. (21) $1\frac{1}{2}$ H_2O m.p. $43-4^{\circ}C$)

b) p-Toluene Sulphonic Acid.

This was obtained from B.D.H. as a solid, of the appearance of prisms, which dissolved completely in water.

Tests with ammonium thiocyanate indicated only traces of iron. Further tests showed the absence of sulphate, chloride, nitrate, sodium, potassium, calcium, barium, copper and nickel. A sulphated ash determination gave a negligible residue of inorganic matter.

Its equivalent was determined and found to correspond to the monohydrate:-

Weight of weighing bottle empty	=	15.9055g.
Weight of weighing bottle + acid	=	16.3553g.
∴ Weight of acid	=	0.4498g.
Titre of 0.05726 N baryta	=	41.31 mls.
∴ Equivalent	=	190.1

Equivalent/

Equivalent of $\text{CH}_3.\text{C}_6\text{H}_4.\text{SO}_3\text{H}.\text{H}_2\text{O}$ = 190.2

This substance melted sharply at $104.8^\circ\text{C}.$ (lit. (22) $104-5^\circ$)

Repeated crystallisation of this acid from aqueous solution did not give a better product and the acid from the bottle was adjudged to be sufficiently pure for solubility and vapour pressure work.

c) o-Toluene Sulphonic Acid.

This was supplied as a solid by B.D.H. It had the appearance of prisms and dissolved completely in water.

No trace of iron could be found on testing with ammonium thiocyanate.

Further tests showed the absence of sulphate, chloride, nitrate, sodium, potassium, calcium, barium, copper or nickel.

A sulphated ash gave no residue whatever.

The equivalent was determined and found to correspond to the dihydrate:-

Weight of weighing bottle empty	= 17.1674g.
Weight of weighing bottle + acid	= 17.8500g.
Weight of acid	= 0.6826g.
Titre of 0.09613 N baryta	= 34.12 mls.
Equivalent	= 208.1

Equivalent of $\text{CH}_3.\text{C}_6\text{H}_4.\text{SO}_3\text{H}.\text{2H}_2\text{O}$ = 208.2

The substance melted sharply at 62.1°C

Repeated crystallisation from water did not alter this melting point. The acid as obtained from B.D.H./

B.D.H. was judged pure enough for solubility and vapour pressure work.

d) p-Nitrobenzene Sulphonic Acid.

This acid was prepared by the action of sodium disulphide on p-chloronitrobenzene and oxidation of the 4:4'-dinitrodiphenyl disulphide with fuming nitric acid(23)(24)(25).

To a boiling solution of p-chloronitrobenzene (250g.) in alcohol (600 c.c) was added in portions the product obtained by fusing crystalline sodium sulphide (200g.) and sulphur (35g.). The mixture was heated for 30 minutes and then cooled to about 50°C. The solid product, after being washed with alcohol, water, and again with alcohol, was boiled with acetic acid (500 c.c) cooled, filtered, dried and divided into 40g. batches. Each batch was added to fuming nitric acid (10c.c) and the solution was warmed for 1 hour, diluted with water (500c.c) and filtered. The combined filtrates were evaporated almost to dryness, and the evaporation repeated after the addition of more water. The residue was neutralised with dilute aqueous ammonia, and ammonium p-nitrobenzene-sulphonate obtained in large crystals. This ammonium salt (78g.) was heated with chlorosulphonic acid (100c.c) at 100°C for 1 hour and the cooled solution poured on to ice. The precipitate was collected.

collected rapidly, dried and crystallised from benzene-light petroleum, from which p-nitrobenzene-sulphonyl chloride separated in large prisms (7 g.) m.p. 77°C (lit.(24) 77°C). Since the yield was poor, the conversion of the ammonium salt to the sulphonyl chloride by use of phosphorus pentachloride was attempted. The product obtained was exactly similar (m.p. 77°C), but the yield was not improved. This sulphonyl chloride could not be vacuum distilled without appreciable decomposition taking place. The sulphonyl chloride was hydrolysed by heating with an equal weight of distilled water on a water bath. Two layers were obtained, the top one of water and the bottom of the almost colourless liquid sulphonyl chloride. The hydrolysis was known to be complete when the bottom layer disappeared. It was found that the best results from the point of view of time and quality of product were obtained by hydrolysing successive small quantities of sulphonyl chloride rather than one large quantity. The solution containing sulphonic acid and hydrochloric acid was then evaporated to dryness over potassium hydroxide in an evacuated desiccator at room temperature. If the temperature is raised to assist evaporation, hydrolysis of the sulphonic group occurs, particularly in the later stages when the concentration of hydrochloric acid is relatively high, and the product may be/

be contaminated with nitrobenzene or some other decomposition product.

At the low pressure at which the evaporation was carried out, it was found that the hydrochloric acid was removed in a few days. When the solid sulphonic acid appeared, it was redissolved in pure distilled water and the process repeated. This process was continued until no trace of hydrochloric acid was left. Usually three evaporations were enough. If yield is unimportant, it is possible to filter off the first crop of solid sulphonic acid, redissolve in distilled water, and then only one further evaporation is required for complete elimination of hydrochloric acid.

The solid acid dissolved completely in water and was found to be free from chloride, nitrate and sulphate.

A sulphated ash determination gave a negligible residue of inorganic matter.

Its equivalent was found to correspond to the dihydrate:-

Weight of weighing bottle empty	=	12.0570 g.
Weight of weighing bottle + acid	=	12.6810 g.
∴ Weight of acid	=	0.6240 g.
Titre of 0.08522N baryta	=	30.60 mls.
∴ Equivalent	=	239.3
Equivalent of $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H} \cdot 2\text{H}_2\text{O}$	=	239.2

The substance melted sharply at 110.2°C . (lit (26) m.p. 95°C)

e) p-Fluorobenzene Sulphonic Acid.

This/

This acid was prepared by two methods. The first method was by the sulphonation of fluorobenzene in the cold with 10% oleum.

The second method was by the diazotisation of the sodium salt of sulphanilic acid in a large excess of hydrofluoric acid followed by the decomposition of the diazonium fluoride.

Method 1. The bulk of the material was prepared by this method.

The fluorobenzene was obtained by a method adapted from that of Balz and Schiemann (27), reported in Organic Synthesis and summarised below.

Aniline is diazotised in hydrochloric acid solution and the resulting diazonium salt is combined with fluoboric acid to form the borofluoride complex which is then decomposed by heat to form fluorobenzene and boron trifluoride.

A mixture of 135 mls. of water and 165 mls. concentrated hydrochloric acid (specific gravity 1.19) was placed in a glass jar and stirred mechanically while strongly cooled by an ice salt mixture. When the temperature of the acid reached 5°C or below, 207 gms. of aniline hydrochloride were added and diazotisation begun by the slow addition of a solution of 120 gms. sodium/

sodium nitrite in 150 mls. of water.

The temperature was held below 7°C and the diazotisation was stopped when a positive test for free nitrous acid was obtained with starch-iodide paper.

Fluoboric acid was made concurrently with the diazotisation by the addition in small amounts of 100 gms. of boric acid to 215 gms. of 60% hydrofluoric acid. The addition was carried out in flasks coated with wax, the temperature being kept below 20°C. Both the diazonium solution and the fluoboric acid were cooled to below 0°C and the fluoboric acid was then added rapidly to the diazonium solution. The temperature was kept below 10°C.

The resulting thick magma was stirred for 30 minutes and then filtered. The yellowish crystalline solid was washed with iced water, methyl alcohol and commercial ethyl ether. Great care was taken to dry the solid as it decomposes if left moist.

It was spread out on absorbent paper overnight in a current of air and then placed in a flask. The flask was connected through a long wide condenser to three Erlenmeyer flasks arranged in series and immersed in ice-salt mixtures. The last flask was fitted with an exit tube leading to a good hood, to carry off the voluminous fumes of boron trifluoride. The complex was decomposed by gentle heat, the flame being used only when the reaction was not proceeding spontaneously/

spontaneously. At the last, the flask was heated until no more fumes of boron trifluoride were evolved. The fluorobenzene distilled over into the receiving flasks.

The combined distillate was washed with 10% sodium hydroxide solution to free it from phenol, then with water to remove the sodium hydroxide and finally dried by shaking it with crushed calcium chloride. It was distilled from a flask through a short column at a rapid rate.

The yield of colourless liquid, with an odour resembling that of benzene, and boiling at 84.5°C was 66 gms. = 44%

At the next stage, fluorobenzene (24 gms.) and sulphuric acid (100 gms.) containing 10% of the anhydride were cautiously stirred in a closed vessel kept below 0°C . The reaction proceeded quite rapidly, the upper layer of fluorobenzene having disappeared in about 45 minutes.

The resulting liquid was then carefully poured into a large excess of cold water and neutralised with pure barium carbonate. The barium salt of p-fluorobenzene sulphonic acid has a solubility of 5% (28) at room temperature. Thus it can easily be separated from the precipitate of barium sulphate by hot filtration.

The filtrate was evaporated to dryness and the barium/

The filtrate was evaporated to dryness and the barium sulphonate dried thoroughly on a water bath. The solid was reduced to powder and mixed with one and a half times its weight of phosphorus pentachloride. No visual effects were noticed, but the mixture became very hot. After the evolution of heat had abated, the flask was heated on the water bath for one hour. The product was then poured carefully and slowly into a beaker containing 200 gms. of crushed ice and allowed to stand for an hour.

The mixture was extracted with ether and the ether removed on a water bath. The resulting sulphonyl chloride was distilled under high vacuum, a pure white solid of melting point 33.7°C being obtained. (lit. (28) 36°C).

Method 2.

Into a waxed beaker was placed 2.5 g. of sodium carbonate in 100 ccs. of water. 10 gms. of sulphanilic acid was now dissolved in the carbonate solution, and a solution of 3.5 gms. of sodium nitrite in 20 ccs. of water added. The mixture was cooled in ice and a solution of hydrofluoric acid gradually added. After diazotisation had been completed, the diazonium salt solution was warmed up and the diazonium group was replaced by fluorine.

A/

A large number of byproducts were produced including a considerable amount of an orange to rose-red dyestuff of unknown constitution. The smell of phenol was also noticeable from the reaction mixture. The sulphonic acid was separated from the hydrofluoric acid by the hot filtration of their calcium salts. Calcium p-fluorobenzene sulphonate is slightly soluble in hot water, but calcium fluoride is almost insoluble.

The calcium sulphonate was converted into the sulphonyl chloride with phosphorus pentachloride as before, and the resulting product extracted with ether and purified by distillation under high vacuum, a pure white solid being obtained.

This product was compared with the one obtained by the sulphonation of fluorobenzene.

1. Melting point of sulphonyl chloride from sulphonation of fluorobenzene = 33.7°C .
2. Melting point of sulphonyl chloride from diazotisation of sulphanilic acid = 33.6°C (lit.(29) 36°C)
3. Melting point of mixture of sulphonyl chlorides = 33.9°C .

Two crystals of sulphonyl chloride, one prepared by each method were examined under the microscope and, as far as could be determined, belonged to the same crystal class, and had the same crystallographic properties.

The/

The sulphonyl chloride was now hydrolysed by heating on the water bath with an equal weight of distilled water until the sulphonyl chloride layer disappeared. The resulting mixture of free sulphonic acid and hydrochloric acid was separated in exactly the same manner as in the preparation of p-nitrobenzene sulphonic acid. Yield = 42 gms.

The p-fluorobenzene sulphonic acid was obtained as a white crystalline solid which dissolved completely in water.

No trace of sodium, potassium, calcium, barium, iron, copper, nickel, sulphate, chloride or nitrate could be found.

A sulphated ash determination gave no measurable amount of inorganic material.

Its equivalent was determined and found to correspond to the monohydrate:-

Weight of weighing bottle empty	= 12.7531 g.
Weight of weighing bottle + acid	= 13.2790 g.
Weight of acid	= 0.5259 g.
Titre of 0.09610 N baryta	= 28.21 mls.
Equivalent	= 194.0
Equivalent of $F.C_6H_4.SO_3H.H_2O$	= 194.2

The acid melted sharply at $85.8^{\circ}C$.

It is noteworthy that a third method for the preparation of this acid was attempted. It was thought that it could be prepared directly by way of the/

the borofluoride complex in the same manner as fluorobenzene itself. Thus the sodium salt of sulphanilic acid was diazotised as described previously and to the diazonium salt was added an ice cold solution of fluoboric acid. The temperature throughout was kept below 0°C .

The complex formed quite readily, but unfortunately was more soluble than that formed from aniline and a much smaller yield was obtained.

The next step, that of decomposing the complex to form the sulphonic acid, was however found to be impossible.

It was dried in the same manner as described under the preparation of fluorobenzene and then heated up slowly in a flask on an oil bath. No reaction at all occurred until a temperature of 130°C was reached, when the whole mass reacted with some violence and the production of charred material from which no sulphonic acid could be extracted.

Various procedures were used to try and decompose the complex gently.

It was heated on a water bath for several hours under vacuum with no result.

It was subjected to a sudden hot flame at a small spot on the flask in the hope that this would initiate a spontaneous reaction. This also was without success.

Finally/

Finally, the complex was again prepared, but after filtering, a solution of caustic soda was poured through the filter to ensure that every sulphonic group would be protected as a sodium salt.

The sodium salt, so formed, was dried and its decomposition into the sodium salt of p-fluorobenzene sulphonic acid was attempted by the three methods given above. This also was a failure, and the method had to be abandoned.

f) p-Chlorobenzene Sulphonic Acid.

This acid was prepared by the sulphonation of chlorobenzene with excess fuming sulphuric acid in the cold. The method is analogous to that of the preparation of p-fluorobenzene sulphonic acid and will be given in outline only.

Chlorobenzene (30 gms.) and sulphuric acid (100 gms.) containing 10% of the anhydride were cautiously stirred in a closed vessel, the temperature of which was kept below 0°C. The reaction proceeded much more slowly than in the case of fluorobenzene, but the upper layer of chlorobenzene disappeared in six days. The sulphonic acid was then separated from the sulphuric acid by hot filtration of their barium salts, and the sulphonyl chloride was prepared by means of phosphorus pentachloride.

This substance melted at 48°C. (lit. (30) m.p. 53.3°C)

The low melting point is probably due to it being contaminated/

contaminated with the ortho isomer.

The impure substance was distilled in high vacuum into three fractions. The melting point of the last fraction was 52°C . This last fraction was redistilled and a fraction of melting point $53-4^{\circ}\text{C}$ was obtained. This was considered to be pure p-chloro-benzene sulphonyl chloride.

The other fractions were worked up to obtain the maximum yield of the substance melting at $53-4^{\circ}\text{C}$.

Yield = 20 gms.

It is noteworthy that chromatography on alumina, eluting with benzene in order to separate the pure para compound was tried but without success.

The free acid was obtained as a white crystalline solid from the sulphonyl chloride by hydrolysis with distilled water as described in the preparation of p-nitrobenzene sulphonic acid.

The resulting acid was completely soluble in water and free from sodium, potassium, calcium, barium, nickel, copper, iron, sulphate, chloride and nitrate. A sulphated ash determination gave no residue of inorganic material.

The equivalent was determined and found to correspond to the monohydrate:-

Weight of weighing bottle empty = 12.7539 g.

Weight of weighing bottle + acid = 13.4513 g.

Weight of acid = 0.6974 g.

Titre/

Titre of .09610 N baryta	= 34.50 mls.
∴ Equivalent	= 210.3
Equivalent of $\text{Cl.C}_6\text{H}_4.\text{SO}_3\text{H.H}_2\text{O}$	= 210.6

The acid melted sharply at 100.3°C (lit.(31)m.p. 68°C)

g) p-Bromobenzene Sulphonic Acid.

This was prepared by the hydrolysis of the corresponding sulphonyl chloride which was obtained from B.D.H. as a solid melting sharply at 75.5°C . (lit.(32)m.p. 75.5°C)

This substance was hydrolysed by heating with an equal weight of distilled water on a water bath and subsequent evaporation of the hydrochloric acid, exactly as described in the hydrolysis of p-nitro-benzene sulphonyl chloride. The free acid was obtained as a white crystalline solid which dissolved completely in water and was free from sodium, potassium, calcium, barium, nickel, copper, iron, sulphate, chloride and nitrate. A sulphated ash gave a negligible residue of inorganic material.

Its equivalent was determined and corresponded to the monohydrate:-

Weight of weighing bottle	= 14.5291 g.
Weight of weighing bottle + acid	= 15.5016 g.
∴ Weight of acid	= 0.9725 g.
Titre of 0.09610 N baryta	= 39.63 mls.
∴ Equivalent	= 255.4
Equivalent of $\text{Br.C}_6\text{H}_4.\text{SO}_3\text{H.H}_2\text{O}$	= 255.1

The acid melted sharply at 90.2°C . (lit.(33)m.p. $102-3^\circ\text{C}$)

Solid-Liquid Equilibria Determinations.

In general, there are two methods which are usually employed in determining the solubility curve of a fairly soluble substance.

In the first method, a mixture of the two components is stirred to equilibrium at a fixed temperature, the mixture being so chosen that there is excess of the solute. At equilibrium, the liquid phase is sampled and analysed. Thus the temperature is chosen and the composition afterwards determined. This is known as the analytical method.

The second method is the opposite. The mixture of the two components is made up to a predetermined composition and the temperature at which the last crystal of the solid phase disappears is determined. Thus the composition is chosen and the temperature afterwards determined. This is known as the synthetic method.

This second method has certain advantages over the first. There is no need whatever to know the approximate solubility curve as is required in the first method, as there we must ensure an excess of the solute. Again, since careful attention must be paid to the disappearance of the last crystal, differences in crystal habit which may denote a change in solid phase are more readily noticed. Furthermore, when dealing with very soluble substances, the solubility curve/

curve can be determined using less material than would be required in the analytical method.

The synthetic method was, with some modifications, the one employed throughout the determination of these solubility curves.

The chief difficulties which had to be surmounted were,

(a) the long interval of time required for the solid and liquid phases to come to equilibrium, and

(b) the dehydration of the mono- and dihydrates which, as has been explained in the previous chapter, were the normal forms in which these acids were obtained and could be most readily kept at room temperature and atmospheric pressure.

The process of determining a point on the solubility curve by the synthetic method in the case of these acids can be divided into three operations.

In the first operation, the mixture is made up as near as possible to the desired composition. It is difficult to make up these mixtures exactly to a predetermined composition because of the small quantities used, and the deliquescence of the acids. The second operation is that of determining the exact temperature at which the last crystal disappears.

These two operations are described more fully below. The third operation is to determine exactly the percentage acid present in the mixture. A method/

method must be used which is not rendered invalid by the deliquescent nature of the acid. The solution to this problem is to make use of the fact that they are strong acids, monobasic and comparable in strength to sulphuric acid. They can readily be titrated against baryta or caustic soda.

Baryta was prepared by the method of Cumming and Kay(34) and standardised against potassium hydrogen phthalate and oxalic acid using phenolphthalein as indicator, the colour at the end-point persisting for one minute. The normality obtained from both agreed quite well, but that of potassium hydrogen phthalate was preferred as the fact that oxalic acid is a "dihydrate" makes it difficult to be absolutely certain of its molecular weight.

It was found that if the container was protected with soda lime towers, the baryta could be kept practically indefinitely without change of normality.

Normality on 4th Jan. = 0.09594

Normality on 15th March = 0.09592

Change in normality after 4 months = Nil

Sodium hydroxide was used initially, but was rejected on account of the fact that it was more difficult to obtain it free and keep it free from carbonate. The end-points were therefore less sharp.

Preparation of Mixtures

Firstly, a weighed quantity of the stock acid was titrated/

titrated with standard baryta and the exact percentage composition determined.

A small test tube of soda glass measuring 3" x $\frac{3}{8}$ " was weighed empty (W_1).

About 0.5 gms. of the acid was added to the test tube and the whole weighed again (W_2).

Freshly distilled water was then added from a 1ml. pipette to give the desired composition, and the tube sealed off by means of a pin-hole burner, great care being taken to avoid decomposing any of the acid solution.

Finally, the test tube + acid + water was weighed again (W_3). The temperature at which the last crystal dissolved was then determined (by a method to be described later), and afterwards the tube was opened and the acid titrated with standard baryta.

The difference in weights ($W_3 - W_1$) gave the total weight of solution present. The titre gave the weight of anhydrous acid present. From this knowledge, the percentage composition could be calculated. W_2 is only of use in making up the mixture to approximately the desired composition. A specimen calculation is shown below.

Weight of test tube empty (W_1)	=	2.5482 g.
Weight of test tube + benzene sulphonic acid (W_2)	=	2.9636 g.
Weight of test tube + acid + water (W_3)	=	3.4191 g.
Weight/		

Weight of solution = 0.8709 g.
Titre of 0.05741 N baryta = 43.20 mls.
% composition = 45.06%

Determination of Temperature at which the last crystal
disappeared.

After the mixture had been prepared to the approximate composition, it was necessary to determine the temperature of complete solution.

Attention was paid to four main points.

1. Rate of Heating.

This was very important as equilibrium between the solid and liquid phases was established only very slowly.

The procedure was to raise the temperature by 1°C per unit of time and note the point of complete solution. Then the rate of heating was halved and the temperature of complete solution again noted. This procedure was continued until the temperature remained constant.

The maximum permissible rate of heating was then employed throughout the range of temperature for which the experiment was valid. At higher temperatures equilibrium was reached more quickly as is to be expected. In general, it was also found that where the solubility curve was steeper, equilibrium could be reached faster but the difference was not very great.

Thus/

Thus for all temperatures below $+10^{\circ}\text{C}$ the temperature was raised at the rate of 1°C every four hours. The test tube containing the mixture was suspended in a five litre beaker containing ethyl alcohol, the beaker being well lagged, and the temperature was controlled by the manual addition of powdered solid carbon dioxide. By this means, the temperature could be kept constant to $\pm 0.1^{\circ}\text{C}$.

Between 10°C and 50°C , the ethyl alcohol was replaced by water, the lagging was removed and the temperature was raised by heating with a micro bunsen. The rate of heating was raised to a rate of 1°C per hour.

Above 50°C , the rate of heating could be as much as 1°C per 30 minutes.

For the temperature range of -5°C to 105°C , a mercury N.P.L. thermometer, graduated in fifths was used. For temperatures below -5°C , one mercury thermometer, graduated in fifths, and two pentane thermometers, graduated in degrees were used. For temperatures above 105°C , a third mercury thermometer, graduated in fifths, was used.

2. Size of Crystals.

The crystal size is very important as large crystals take a much longer time to dissolve than small crystals. Accordingly, each tube was heated until it became completely homogeneous, and then was suddenly crystallised out at a temperature much below its/

its true solubility point. This ensured the production of very small crystals. This method of crystallising out the hydrate from the solution gave, in general, the phase which was stable at this particular composition. There are two exceptions.

Firstly, at the ice-acid eutectic, it sometimes happened that if the temperature of crystallisation was very low, ice was obtained as the solid phase at compositions where it was metastable.

Secondly, in several cases, such as the $4H_2O$ -hydrate of p-toluene sulphonic acid, the hydrate could crystallise out in two crystallographic modifications. In this case also, if the temperature of crystallisation was very low, the metastable form of the hydrate was obtained.

In either case, the procedure was the same; the temperature at which the last crystal of the metastable solid phase dissolved was noted. The temperature was then raised two or three degrees and the tube wall was touched with a small piece of solid carbon dioxide. This usually resulted in the production of the stable phase.

3. Source of Light.

A beam of light was shone from directly behind the tube from a 150 watt lamp and the crystals could be seen very easily. As this caused a certain amount of eyestrain, another method was tried in which/

which the light was shone from behind the operator's head through the tube on to a dark background. This was not as successful as the first method.

4. Agitation.

A brass frame was constructed and connected to a crank with an eccentric drive. The crank was driven at a slow rate from shafting. On the frame about twelve tubes could be accommodated and a high degree of agitation could be obtained.

Attempts were made to determine the temperature at which the first crystal appeared by slowly cooling down the mixtures, but these experiments had to be abandoned owing to the fact that supercooling, often as much as twenty or thirty degrees, below the real solubility point, took place.

For each mixture, the temperature at which the last crystal disappeared was determined twice. In addition, several experiments were performed to check the reliability of the method as a whole including the/

the thermometers.

For example, the melting point of a tube, half filled with freshly distilled water was found to be 0°C. Experiments were also performed to determine various points on the solubility curve of pure potassium chloride and it was found that the results were in agreement with those of Barnes and Maas(35) who determined the solubility curve very accurately by another method:-

Results.

% age Comp.	Observed	Barnes and Maas
10.03	4.8°C	4.7°C
9.78	4.7°C	4.8°C

Thirdly, the melting points of various organic compounds which are known to melt without decomposition were also determined. The compounds were either obtained pure or were recrystallised from a suitable solvent. The results were in all cases in agreement with the known values.

Results.

Compound.	Observed.	Literature.
Diphenyl	70.8°C	70.5°C(36)
Naphthalene	80.2°C	80.2°C(37)
Acenaphthalene	94.6°C	95°C(38)
p-Dichlorobenzene	53.3°C	53.2°C(39)

The method just described was used for the determination of all the points from 0% acid to the position of the mono- or dihydrate (whichever was the/

the hydrate of the stock acid) at points of approximately one per cent apart. It will hereafter be referred to as "Method 1".

It suffers, however, from three disadvantages.

Firstly, it is not possible to prepare with certainty a mixture of a composition correct to 0.1% of the desired composition, owing to the deliquescence of the acids.

Secondly, to complete a solubility curve by this method about 50 grams of stock acid were required.

Thirdly, it is useless for making up mixtures with an acid concentration greater than that of the stock acid.

At eutectic points, incongruent melting points and in certain cases where metastable phases appeared, it was very desirable that the mixture should be made up with a concentration accuracy of at least 0.1%. The need for this was accentuated by the frequent steepness of the solubility curves. Accordingly, the following procedure was followed and will be designated "Method 2".

A weighing bottle was weighed empty (W_1).

It was then half-filled with stock acid and weighed again (W_2).

About 0.5 gms. were transferred to a beaker and titrated with standard baryta (T_1).

The weighing bottle was weighed again (W_3).

The/

The difference in weights ($W_2 - W_3$) and the titre (T_1) gave the exact percentage composition of the stock acid. Freshly distilled water was now added by means of a finely drawn out glass tube until the exact weight of water corresponding to the desired composition had been added. The weighing bottle was weighed again (W_4) and then gently warmed until the acid had completely dissolved. A sample was pipetted off and titrated (T_2) great care being taken to wash the pipette thoroughly. The weighing bottle was weighed again (W_5). The titre (T_2) gave the exact weight of anhydrous acid present and the difference between the weights ($W_4 - W_5$) gave the weight of solution in which the anhydrous acid was dissolved. Thus a mixture could be made up to within 0.1% of the composition desired.

A further quantity was pipetted into a test tube measuring 3" x $\frac{1}{8}$ ", the tube was sealed, and the point at which the last crystal dissolved was determined. A specimen calculation is given below for benzene sulphonie acid:

Weight of weighing bottle empty (W_1)	= 16.5953g.
Weight of weighing bottle + acid (W_2)	= 21.6965g.
Weight of weighing bottle less a little of the acid just put in (W_3)	= 20.8050g.
Titre of 0.05739 N baryta	= 91.20mls.
∴ %age composition of acid	= 92.90%
Weight of weighing bottle + acid + water Weight/ (W_4)	= 21.4164g.

Weight of weighing bottle - a little
solution(W_5) = 20.9170 g.

Titre of 0.05739 N baryta = 44.60 mls.

$\therefore$ %age composition of solution = 81.08%

In certain cases, rather small quantities of sulphonic acid were available, and it was therefore necessary to determine several solubility points on the temperature - composition curve with only one sample of acid. This procedure was permissible, of course, only with the more stable of the sulphonic acids.

For this, the following piece of apparatus was used:-

It consisted simply of a small bulb D with an AlO cone joint, and a tap B with an AlO cone at one end and an AlO socket at the other.

The apparatus with the joint A and the tap B greased, and the joint C clean and dry, was evacuated. The tap B was now closed and the apparatus weighed (W_1). A solution of the desired acid of known composition was now added to the bulb D and the latter rejoined to A. The bulb was now frozen in solid carbon dioxide, and the apparatus evacuated. The tap B was/

was closed, the bulb allowed to come up to room temperature and the apparatus weighed again (W_2).

The solid phase was now frozen out as described in Method 1, the apparatus immersed in the thermostat bath and the temperature of complete solution noted. The apparatus was now removed from the thermostat, dried thoroughly and weighed (W_3). It was now connected to the apparatus shown below.

This was connected to the oil pump and thoroughly evacuated. Tap T was now closed and tap B opened for a short time. A little water was distilled over from the solution to the phosphorus pentoxide trap F. The tap B was closed, the tap E opened to break the vacuum and the apparatus removed. The joint C was thoroughly cleaned and dried, and the apparatus was weighed again (W_4).

The temperature at which the last crystal disappeared was noted again.

This procedure was repeated several times, and then/

then the acid in D finally titrated.

The titre gives the exact weight of anhydrous acid present at each determination. The difference in the weights ($W_2 - W_1$) gives the weight of solution in which the anhydrous acid was dissolved at the first determination.

This figure minus the difference ($W_3 - W_4$) gives the weight of solution for the second determination.

This method, hereafter referred to as "Method 3", has several disadvantages compared with the first method, but it proved useful for its particular purpose. The main disadvantage was the difficulty of predetermining the composition of any mixture accurately.

A specimen calculation is given below.

Acid. p-Chlorobenzene Sulphonic Acid.

Weight of apparatus (W_1)	= 51.7698 g.
Weight of apparatus + p-chlorobenzene sulphonic acid solution (W_2)	= 55.5303 g.
Temperature of complete solution	= -12.5°C .
Weight of apparatus + solution after drying (W_3)	= 55.5254 g.
Weight of apparatus + solution - quantity of water vapour (W_4)	= 55.3731 g.
Temperature of complete solution	= -14.0°C
Titre of 0.08494 N baryta	= 100.85 mls.

Points on solubility curve are:-

1.	2.
43.76%	45.28%
-12.5°C	-14.0°C

Compositions/

Compositions which contain less water than the stock acid require water to be removed instead of added. In general, this dehydration was dependent on two factors;

- (1) the stability of the anhydrous acid, and
- (2) the dissociation pressures of the stock acid.

Benzene sulphonic acid is so unstable that attempts to keep it above room temperature for a period of longer than two hours inevitably resulted in its decomposition. The solid acid darkened with the formation of a black oily sludge in which free sulphuric acid could be detected.

However, the dissociation pressure of the monohydrate is sufficiently great to permit of dehydration at ordinary temperatures. It was kept in an evacuated desiccator over phosphorus pentoxide at room temperature, anhydrous acid being obtained after six weeks. Mixtures ^{could} ~~xxx~~ therefore be made up in the usual way using this as stock acid.

o-Toluene sulphonic acid dihydrate is relatively stable and melts at the comparatively low temperature of 62.1°C. Consequently, individual samples could be dehydrated as follows.

A small test tube (3" x $\frac{3}{8}$ ") was weighed empty (W_1), half-filled with acid and weighed again (W_2). The tube was then connected to the oil pump via a phosphorus pentoxide trap and cautiously evacuated. It/

It was found that on heating to 70°C , water could be quite readily removed. Approximately one molecule of water per molecule of acid present could be removed in 30 minutes.

The rate at which the water was being removed could be followed by periodically disconnecting the test tube and quickly weighing it. When the desired composition was reached, the test tube was sealed off and weighed again (W_3).

The temperature of complete solution was then determined as before, after which the tube was opened and the acid titrated.

The percentage composition was found from the difference in weights ($W_3 - W_1$) and the titre as shown below.

Weight of test tube empty (W_1)	= 2.5060 g.
Weight of test tube + o-toluene sulphonic acid dihydrate (W_2)	= 3.1047 g.
Weight of test tube + acid - quantity of water	= 3.0095 g.
$\therefore$ Weight of mixture	= 0.5035 g.
Titre of 0.09607 N baryta	= 28.40 mls.
$\therefore$ %age composition	= 93.30%

In case any acidic vapours were being evolved, a liquid oxygen trap was inserted in several experiments between the test tube and the oil pump, but only water was condensed. This shows that at 70°C , the concentration of acid in the vapour phase above a liquid of composition 90%-100% is not measurable.

p/ The monohydrates of p-fluoro-, p-chloro-, and

p-bromobenzene sulphonic acid were dehydrated in the manner described above. They were stable enough to be liquified without decomposition, and had sufficiently high vapour pressures to ensure their complete dehydration within an hour.

p-Toluene sulphonic acid monohydrate is not so unstable on heating as benzene sulphonic acid, but it is extraordinarily difficult to dehydrate. The apparatus described in Method 3 was used, and the procedure was exactly the same except that the stock acid was placed in bulb D and dehydration carried out at 35°C.

A specimen calculation is shown below.

Weight of apparatus		= 80.7594 g.
Weight of apparatus + p-toluene sulphonic acid monohydrate		= 86.4051 g.
∴ Weight of acid monohydrate		= 5.6457 g.
Temp. 35°C		Date.
Weight of apparatus	acid = 86.4051 g.	14th Dec.
" "	" = 86.3605 g.	16th "
" "	" = 86.3340 g.	20th "
" "	" = 86.3148 g.	24th "
" "	" = 86.2686 g.	28th "
" "	" = 86.2160 g.	4th Jan.
" "	" = 86.1620 g.	8th "
" "	" = 86.0978 g.	12th "
" "	" = 86.0710 g.	16th "
" "	" = 86.0624 g.	20th "

Acid/

Acid made up to 250 mls. and 25 ml. portions titrated.

Average titre = 58.50 mls.

Normality of baryta = 0.05030 N.

∴ Weight of anhydrous acid present = 5.067 g.

∴ Composition on 20th Jan. = 95.57%

Melting point = 88.6°C

The dehydration was exceedingly slow, but after six months a sample of acid 99.97% was prepared.

A fresh sample had to be used for each determination as heating to a temperature above 40°C resulted in decomposition beginning. This decomposition seemed to proceed very slowly at the start, so that one melting point could be taken fairly readily, but a second reliable melting point on the same sample was not possible. This decomposition is probably due to hydrolysis to form sulphuric acid, which then attacks the remaining sulphonic acid producing charring and blackening.

The p-nitrobenzene sulphonic acid dihydrate was extremely easily dehydrated, a sample being completely dehydrated using the apparatus of Method 3 in 24 hours at 55°C. It could also be dehydrated in test tubes in the same manner as for o-toluene sulphonic acid dihydrate.

However, the acid is not stable at temperatures above 100°C and since the melting point of the dihydrate is 110.2°C, an accurate solubility curve between the dihydrate and the anhydrous acid could not be determined. Only a few approximate points showing that the dihydrate had a congruent melting point could be obtained.

SOLUBILITY CURVE OF BENZENE SULPHONIC ACID

Table No.1

Solubility Data for Benzene Sulphonic Acid.

T°C	% Acid by wt.	Solid Phase	T°C	% Acid by wt.	Solid Phase
-1.5	10.42	Ice	15.1	80.52	Dihydrate
-4.9	21.30	"	21.3	81.10	Monohydrate
-7.8	27.36	"	22.0	81.28	"
-11.5	33.90	"	25.7	81.64	"
-16.0	39.80	"	26.3	81.83	"
-22.0	45.06	"	27.2	81.93	"
-27.0	48.14	"	28.3	82.13	"
-27.2	48.41	"	31.0	82.66	"
-29.8	50.23	"	33.4	83.16	"
-32.0	50.83	"	34.3	83.20	"
-37.5	53.70	"	35.8	83.43	"
-40.4	54.49	"	37.5	83.77	"
-40.8	55.91	Trihydrate	39.5	84.39	"
-39.5	56.04	"	42.4	84.96	"
-34.5	57.94	"	44.6	85.51	"
-29.0	59.96	"	47.0	86.26	"
-26.0	60.98	"	48.6	86.96	"
-18.5	64.18	"	49.0	87.05	"
-10.0	68.87	"	51.9	88.47	"
-8.0	70.13	"	52.2	89.23	"
-5.9	72.14	"	52.4	89.60	"
-4.7	74.44	"	50.7	91.26	"
-4.0	74.87	2.5-hydrate	49.0	92.15	"
-3.3	75.82	"	45.5	93.30	"
-2.5	76.40	"	42.8	93.85	"
-2.3	77.61	"	41.3	93.93	"
2.2	77.61	Dihydrate	39.8	94.04	"
3.0	77.82	"	39.4	94.12	"
4.5	77.99	"	35.0	94.60	"
4.7	78.02	"	32.6	95.35	"
7.5	78.54	"	31.4	95.51	Anhydrous acid
9.3	79.12	"	39.0	96.10	"
13.3	79.79	"	42.6	96.74	"
13.6	79.93	"	49.0	97.45	"
13.7	80.04	"	56.0	98.42	"
13.9	80.07	"	57.4	99.02	"
14.5	80.25	"	61.3	99.56	"
14.6	80.37	"			

SOLUBILITY CURVE FOR p-TOLUENE SULPHONIC ACID.

Table No.2

Solubility Data for p-Toluene Sulphonic Acid.

T°C	% Acid by wt.	Solid Phase	T°C	% Acid by wt.	Solid Phase.
- 1.0	6.14	Ice	-14.4	60.70	4-hydrate (meta- stable)
- 2.0	9.67	"	-11.8	62.56	"
- 2.5	15.26	"	-10.5	63.60	"
- 4.0	19.63	"	- 9.5	64.16	"
- 5.0	22.87	"	- 9.2	64.86	"
- 5.5	24.00	"	-8.5	65.00	"
- 7.5	29.45	"	-8.3	65.21	"
- 8.5	32.74	"	-8.1	65.36	"
- 9.5	37.15	"	-8.0	65.43	"
-13.5	41.74	"	-8.0	65.50	"
-15.0	43.52	"	-7.8	66.33	"
-17.5	45.78	"	-7.4	66.68	"
-19.0	48.08	"	-7.0	66.80	"
-19.5	48.17	"	-6.5	66.89	Monohydrate
-23.0	50.72	"	-1.5	67.58	(metastable)
-23.5	50.97	"	1.5	68.06	Monohydrate
-24.5	51.40	Ice (meta- stable)	18.4	70.10	"
-25.0	51.82	"	20.1	70.20	"
-25.5	52.00	"	38.8	72.50	"
-25.6	52.14	"	55.2	75.23	"
-18.5	54.37	4-hydrate	69.0	77.76	"
- 5.9	62.56	"	69.8	77.85	"
- 3.4	64.49	"	73.5	79.03	"
- 3.2	68.86	"	78.4	79.55	"
- 2.6	65.21	"	85.9	81.75	"
- 2.4	65.43	"	86.4	87.92	"
- 2.2	65.59	"	89.9	82.38	"
- 1.6	66.30	"	93.6	84.24	"
- 1.4	66.68	"	98.6	85.86	"
- 1.0	66.90	"	101.1	86.98	"
-27.0	53.20	4-hydrate (metastable)	104.8	90.53	"
-26.0	54.09	"	102.9	92.39	"
-25.5	54.82	"	89.1	95.37	"
-23.0	55.72	"	73.9	97.36	"
-21.0	56.88	"	45.3	99.02	"
-20.5	57.36	"	36.5	99.73	Anhydrous acid
-19.5	57.79	"	40.5	99.87	"
-16.5	59.48	"	42.5	99.97	"

SOLUBILITY CURVE OF o-TOLUENE SULPHONIC ACID.

Table No.3

Solubility Data for o-Toluene Sulphonic Acid.

T°C	% Acid by wt.	Solid Phase	T°C	% Acid by wt.	Solid Phase
- 0.7	10.26	Ice	56.0	77.07	Dihydrate
- 3.4	19.56	"	58.2	78.38	"
- 7.2	30.42	"	61.2	80.90	"
-12.8	40.38	"	61.9	81.49	"
-25.0	51.37	"	62.0	83.07	"
-30.5	53.56	"	61.6	83.97	"
-33.3	54.81	Ice(meta- stable)	60.4	85.07	"
-37.0	56.10	"	60.0	85.49	"
-37.4	56.31	"	58.6	86.06	"
-39.4	57.12	"	55.4	87.38	"
-40.4	58.37	"	54.0	87.64	"
-44.5	59.16	"	53.2	87.70	"
-25.0	55.69	Dihydrate	52.6	88.00	"
-17.0	57.33	"	51.7	88.54	"
-13.0	58.51	"	48.2	89.23	"
- 4.2	60.39	"	48.5	89.32	Monohydrate
0.8	61.17	"	49.0	89.87	"
7.0	62.34	"	49.2	90.44	"
11.0	63.45	"	49.4	90.52	"
16.8	64.95	"	49.6	90.84	"
25.2	66.84	"	49.6	91.11	"
25.6	66.94	"	49.3	91.56	"
31.2	68.58	"	48.6	92.05	"
37.2	70.25	"	48.5	92.06	"
40.0	71.09	"	45.7	93.30	"
44.0	72.26	"	38.6	94.66	"
47.0	73.38	"	36.8	95.07	"
50.0	74.78	"	32.5	95.65	"

SOLUBILITY CURVE OF p-NITROBENZENE SULPHONIC ACID.

Table No.4.

Solubility Data for p-Nitrobenzene Sulphonic Acid.

T°C	% Acid by wt.	Solid Phase	T°C	% Acid by wt.	Solid Phase
- 3.0	18.88	Ice	19.0	58.76	4-hydrate
- 3.3	19.85	"	23.4	61.25	"
- 4.5	27.09	"	26.3	63.33	"
- 5.1	30.04	"	36.6	66.31	Dihydrate
- 6.0	33.52	"	45.8	68.34	"
- 7.2	37.70	"	49.2	68.69	"
- 8.5	39.74	"	56.6	69.88	"
- 8.3	41.22	4-hydrate	62.5	71.22	"
- 4.7	43.53	"	75.5	73.47	"
- 1.0	46.06	"	79.2	74.74	"
4.5	49.62	"	90.2	77.27	"
6.7	50.97	"	110.2	84.92	"
9.1	52.50	"	106.8	86.50	"
10.8	53.94	"	X 100.5	90.83	Probably anhydrous
13.9	55.29	"	X 105.0	96.13	"
16.0	56.92	"	X 110.0	100.0	Anhydrous

X Decompose on heating

∴ probably inaccurate

SOLUBILITY CURVE OF p-FLUOROBENZENE SULPHONIC ACID.

Table No.5

Solubility Data for p-Fluorobenzene Sulphonic Acid.

T°C	% Acid by wt.	Solid Phase	T°C	% Acid by wt.	Solid Phase
-4.9	19.77	Ice	-15.5	69.15	2.5-hydrate
-15.0	39.81	"	-3.9	71.22	"
-17.8	43.51	"	1.0	72.02	"
-19.0	44.56	"	6.5	73.16	"
-20.5	45.79	"	10.1	74.03	"
-22.4	47.25	"	15.2	75.26	"
-24.0	48.51	"	21.3	76.95	"
-22.5	49.53	"	22.1	77.14	Monohydrate
-28.5	51.84	"	35.4	78.38	"
-32.5	53.94	"	48.1	80.26	"
-33.5	54.42	"	48.5	80.34	"
-36.4	55.63	"	54.2	81.06	"
-38.5	56.45	"	62.4	82.33	"
-43.0	58.34	Ice(meta- stable)	71.2	84.33	"
-38.0	57.42	4-hydrate	71.9	84.59	"
-35.4	58.34	"	76.3	85.86	"
-34.4	59.21	"	80.0	86.72	"
-32.5	60.53	"	81.6	87.72	"
-30.5	61.38	"	83.4	88.24	"
-29.5	62.38	4-hydrate (metastable)	84.9	89.35	"
-27.9	63.36	"	85.5	90.07	"
-26.4	64.54	"	85.2	91.64	"
-25.0	65.25	"	83.5	93.09	"
-24.0	66.25	"	81.0	94.06	"
-21.4	64.54	Trihydrate	78.2	94.52	"
-18.5	65.25	"	77.0	94.64	"
-13.0	67.56	"	74.5	95.01	"
-7.4	69.71	"	54.3	97.24	"
-22.5	66.25	Trihydrate (metastable)	46.4	97.70	"
-19.5	67.56	"	41.4	98.03	"
-17.9	68.13	"			

SOLUBILITY CURVE OF p-CHLOROBENZENE SULPHONIC ACID.

Table No.6

Solubility Data for p-Chlorobenzene Sulphonic Acid.

T°C	% Acid by wt.	Solid Phase	T°C	% Acid by wt.	Solid Phase
- 3.0	19.08	Ice	14.8	70.68	2-5-hydrate
- 6.5	31.96	"	18.6	72.06	"
-12.5	43.76	"	22.9	73.60	"
-14.0	45.28	"	23.5	73.72	"
-16.5	47.95	"	26.0	75.32	"
-19.5	50.04	"	27.6	75.98	"
-20.8	51.27	"	30.8	78.75	2.5-hydrate
-22.0	52.30	"			(meta-stable)
-23.5	53.07	"	41.0	78.75	Monohydrate
-26.0	54.59	"	45.8	79.18	"
-27.5	55.44	"	51.9	79.80	"
-30.0	56.47	Ice (meta- :stable)	59.0	80.81	"
-26.0	56.47	2.5-hydrate	70.1	82.54	"
-22.0	57.71	"	80.4	84.55	"
-20.0	58.49	"	88.8	86.12	"
-17.0	59.43	"	93.1	89.50-??	"
-11.0	61.71	"	99.9	90.90	"
- 8.5	62.49	"	100.2	91.94	"
- 4.5	63.75	"	96.7	93.78	"
- 2.2	64.71	"	89.0	95.83	"
5.0	66.97	"	73.3	97.68	"
7.8	68.08	"	59.8	98.31	"
10.6	69.34	"	59.0	99.02	Anhydrous Acid
			62.4	99.54	"

SOLUBILITY CURVE OF p-BROMOBENZENE SULPHONIC ACID.

Table No.7

Solubility Data for p-Bromobenzene Sulphonic Acid.

T°C	% Acid by wt.	Solid Phase	T°C	% Acid by wt.	Solid Phase
- 1.9	14.96	Ice	25.7	78.43	2.5-hydrate
- 4.5	30.21	"	27.6	79.16	"
- 9.0	45.07	"	33.5	82.28	"
-11.5	49.07	"	34.6	83.49	"
-12.5	50.74	"	43.8	84.78	Monohydrate
-14.0	52.38	"	52.0	85.65	"
-15.0	53.10	"	60.2	86.72	"
-15.2	53.52	"	64.8	87.18	"
-16.0	54.03	"	65.9	87.30	"
-17.8	55.63	"	67.3	87.46	"
-18.0	55.77	"	71.2	87.92	"
-19.5	56.94	"	72.5	88.24	"
-23.5	59.36	"	74.0	88.59	"
-24.5	60.06	"	76.4	88.92	"
-26.5	61.28	"	79.7	89.43	"
-29.5	62.46	Ice (meta- stable)	80.3	89.78	"
-30.5	62.85	"	81.6	89.86	"
-31.5	63.39	"	82.1	90.20	"
-31.5	63.39	"	86.2	91.05	"
-33.0	65.21	"	87.5	91.70	"
-21.0	63.41	2.5-hydrate	88.7	92.19	"
-16.5	64.25	"	90.2	92.99	"
-10.5	65.97	"	88.8	94.34	"
- 7.5	66.92	"	87.2	94.75	"
- 3.5	68.00	"	84.8	95.35	"
0.0	68.95	"	78.5	96.18	"
3.0	70.13	"	76.6	96.43	"
5.2	70.87	"	82.3	97.21	Anhydrous acid
12.5	72.97	"	83.1	97.29	"
15.9	74.15	"	88.2	97.88	"
16.5	74.23	"	89.6	98.00	"
17.8	75.09	"	89.3	98.06	"
19.9	75.25	"	93.1	98.45	"
			93.8	98.51	"
			97.6	98.90	"

Analysis of Higher Hydrates.

These sulphonic acids formed hydrates other than the monohydrates, and since these, with the exceptions of the dihydrates of o-toluene sulphonic acid and p-nitrobenzene sulphonic acid, melted incongruently, the number of molecules of water of crystallisation could not be determined from the solubility curves. Such hydrates were therefore analysed as follows.

They all formed well defined crystals which by careful adjustment of temperature could be grown to a fair size. These could be filtered easily, the mother liquor removed almost entirely, and then they could be weighed and titrated. Thus there was no need for the employment of any tracer technique(40).

The procedure employed for hydrates stable only below 10°C was as follows.

A tall sintered glass (No.1 porosity) crucible was fitted to a conical flask by a two-holed rubber stopper as shown in the accompanying sketch. The second/

second connection from the flask led via a phosphorus pentoxide trap to the oil pump. Air, dried by passing through a calcium chloride tower, could be passed through the apparatus. This apparatus was immersed in a well lagged five litre beaker containing ethyl alcohol which could be adjusted to the required temperature by the manual addition of powdered solid carbon dioxide.

From the solubility curve, a composition was chosen which lay well within the range of stability of the hydrate under examination. A mixture was made up in a test tube (6" x $\frac{1}{2}$ ") by the Method 2 described previously. The composition was known accurately and so the temperature at which the last crystal disappeared could be approached closely. When the last crystal had almost disappeared, the temperature was noted and compared with that given by the solubility curve. In this way, the presence of the required hydrate could be ensured.

The agitator was now stopped and the crystal allowed to sink to the bottom of the liquid in the test tube. The temperature was now lowered very slowly, ensuring the growth of large crystals. The temperature of the ethyl alcohol in the beaker was held a few degrees below the temperature of complete solution of the mixture.

When a sufficient number of large crystals had been/

been formed, the tube was quickly removed from the bath, broken open, and the mixture poured into the sintered glass crucible. As has been stated previously, the solid and liquid phases do not come to equilibrium quickly at these low temperatures, and therefore this operation could be performed without dissolving the solid hydrate.

The supply of dry air was now connected to the sintered glass crucible and the pump turned on. The temperature of the beaker was now raised to 1 Centigrade degree below the transition point of the hydrate and kept there for 60 minutes.

A suitably shaped nickel spatula, together with two pairs of nickel forceps and several filter papers were meantime placed in a metal container, containing calcium chloride beneath a pad of cotton wool. The container was tightly corked and placed in the solid carbon dioxide container for one hour.

After the elapse of this time, the crystals were scooped out by means of the cold dry nickel spatula, pressed once between the cold filter papers held by the forceps, and then brushed quickly into a weighing bottle and weighed.

The/

The crystals were then dissolved in distilled water and titrated against standard baryta, thus giving the number of molecules of water of crystallisation.

A specimen calculation is shown below.

Results.

It is required to determine the hydrate ~~xxxxx~~^{of} p-fluorobenzene sulphonic acid stable between compositions 61.25%-71.0% and temperatures -31.0° and -7.0°C .

%age composition of mixture	= 68.11%
Melting point	= -12.0°C
Weight of weighing bottle empty	= 15.0703 g.
Weight of weighing bottle + crystals	= 16.1275 g.
$\therefore$ Weight of crystals	= 1.0572 g.
Titre of 0.08494 N baryta	= 53.72 mls.
$\therefore$ %age composition	= 76.07%
No. of molecules of water of crystallisation	= 3.089
	= 3.

For hydrates which are stable above 10°C , the method was essentially the same, but the precautions taken to avoid decomposing the hydrate by a rise in temperature were not so stringent and the ethyl alcohol in the beaker was replaced by water.

This method gave sufficiently accurate to give reproducible results and was employed throughout.

A table of the hydrates is given on the following page.

The hydrates of the sulphonic acids are conveniently summarised in the following table.

Table No.8.

Acid	Mols. of water	Temperature Range	Composition Range	Stability	Congruency	M.P.	Appearance
Benzene Sulphonic Acid	3	-44°C to -4.5°C	55.25% to 74.5%	Stable	Incongruent	-	Prisms
Benzene Sulphonic Acid	2.5	-4.5°C to -2.3°C	74.5% to 77.6%	Stable	Incongruent	-	Plates
Benzene Sulphonic Acid	2	-2.3°C to 15.5°C	77.6% to 81.6%	Stable	Incongruent	-	Plates
Benzene Sulphonic Acid	1	15.5°C to 52.5°C	81.6% to 95.4%	Stable	Congruent	52.5°C	Prisms
p-Toluene Sulphonic Acid	4	-24.5°C to -0.7°C	51.0% to 67.75%	Stable	Incongruent	-	Plates
p-Toluene Sulphonic Acid	4	-0.7°C to -6.9°C	67.75% to 66.9%	Meta-stable	Incongruent	-	Prisms
p-Toluene Sulphonic Acid	1	-6.9°C to 104.8°C	67.75% to 99.6%	Stable	Congruent	104.8°C	Prisms
o-Toluene Sulphonic Acid	2	-34°C to 62.2°C	54.0% to 89.0%	Stable	Congruent	62.2°C	Prisms
o-Toluene Sulphonic Acid	1	49.9°C to unknown temp.	89.0% to unknown composition	Stable	Congruent	49.9°C	Prisms
p-Nitrobenzene Sulphonic Acid	4	-9°C to 29°C	41% to 65%	Stable	Incongruent	-	Prisms
p-Nitrobenzene Sulphonic Acid	2	29°C to 110.2°C	65% to unknown comp.	Stable	Congruent	110.2°C	Prisms
p-Fluorobenzene Sulphonic Acid	4	-39°C to -28.5°C	56.6% to 63%	Stable	Incongruent	-	Prisms
p-Fluorobenzene Sulphonic Acid	3	-28.5°C to -5.5°C	63% to 71%	Stable	Incongruent	-	Plates
p-Fluorobenzene Sulphonic Acid	3	-5.5°C to -17°C	71% to 69%	Meta-stable	Incongruent	-	Prisms
p-Fluorobenzene Sulphonic Acid	2.5	-17°C to 21.5°C	69% to 77%	Stable	Incongruent	-	Prisms
p-Fluorobenzene Sulphonic Acid	1	21.5°C to 85.7°C	77% to unknown comp.	Stable	Congruent	85.7°C	Needles

Table 8 (Cont'd)

Acid	Mols. of water	Temperature Range	Composition Range	Stability	Congruency	M.P.	Appearance
p-Chloro- :benzene	2.5	-28.5°C to 29.0°C	56% to 73.6%	Stable	Incongru- :ent	-	Prisms
Sulph: :onic Acid	1	29.0°C to 100.4°C	73.6% to 97.5%	Stable	Congruent	100.4°C	Needles
p-Bromo- :benzene	2.5	-29.0°C to 34.8°C	62.0% to 83.9%	Stable	Incongru- :ent	-	Prisms
	1	34.8°C to 90.3°C	83.9% to 96.4%	Stable	Congruent	90.3°C	Needles

Solid-Liquid-Vapour Equilibria Determinations.

The vapour pressure (i.e. the water vapour pressure since only water is present in the vapour phase) along the solubility curve where all three phases - solid hydrate, saturated solution and water vapour - can exist together in equilibrium was determined using the simple apparatus shown above.

Basically, it consists of a mercury manometer which is evacuated completely on one side and exposed to the vapour pressure of the saturated solution on the other.

The mercury manometer A was 31 cms. long, the two limbs being interconnected by the tap B. The reaction vessel C was simply a glass tube connected by a B.34 joint. The glass spiral E enabled the reaction vessel to be slightly shaken. Attached to the reaction vessel/

vessel on the other side was a water reservoir F, kept outside the thermostat and cut off from the reaction vessel by the tap D which was inside the thermostat. The connecting arm G led off via a phosphorus pent-oxide trap to an oil pump. A McLeod gauge was also included in the external system. The mercury levels in A were read from outside the thermostat by means of a travelling microscope reading to 0.02mm.

The procedure for any one vapour pressure determination was as follows.

The apparatus was cleaned with hot concentrated nitric acid, rinsed with distilled water and dried in an oven at 100°C. It was then assembled on a brass stand, all joints and taps being greased with Dow Corning Silicone high vacuum grease. The stand was now lowered into the thermostat and connected to the vacuum system by means of quickfit joints cemented with Picien black wax.

The travelling microscope was next set up outside the thermostat on a sheet of plate glass and carefully levelled by means of levelling screws and a spirit level. The microscope was then focussed on a plumb line in the thermostat near the manometer, and the levelling was further adjusted to ensure that the microscope cross-wires did not depart from the plumb line throughout the entire height of the thermostat.

The mercury for A was cleaned by,

a)/

- a) running it through a column of 5% nitric acid twelve times,
- b) running it through a column of acetone twice, and, finally,
- c) running it through a column of distilled water.

It was then heated to a temperature of 110°C for 30 minutes in a fume cupboard to dry and degas it, and finally distilled in vacuo.

It was introduced into A via a funnel so that it did not come into contact with any tap grease. Freshly distilled water, boiled down to one quarter bulk to remove dissolved gases was introduced into the water reservoir by means of the opening L which was then sealed off.

The water was frozen in solid carbon dioxide to a temperature of approximately -80°C , all the taps opened, and the apparatus evacuated until the McLeod gauge showed a reading of .001mm. of mercury or less. Tap D was then closed and the water allowed to warm up to room temperature. Any gas which may have still remained dissolved was thus allowed to distil out. The water was again cooled to -80°C and the tap D again opened to the vacuum. This sequence of operations was repeated five times. The tap D was finally closed and then the vacuum in the remainder of the apparatus was released. The apparatus was then disconnected from the vacuum line and removed from the thermostat.

A/

A solution of the acid whose pressure-temperature curve was being determined was made up so as to be slightly unsaturated at the desired starting temperature. The apparatus was replaced in the thermostat and reconnected to the vacuum line. The tap M was now closed and the main vacuum line plus the McLeod gauge was evacuated to a pressure of .001 mm. of mercury or less. The pump was now shut off, and after making sure that tap B was open, tap M was opened to equalise the pressures in the vacuum line and the apparatus. Then tap M was closed and the vacuum line re-evacuated. This was repeated until it was found that the reading on the McLeod gauge did not alter on opening tap M. This proved that all the air had been removed from the system. By this process, in which the system is in effect washed out by a stream of water vapour from the solution, it was found that air could be entirely removed in a relatively short time.

Removal of water vapour was continued until crystals began to appear in the solution. As these crystals were prepared in an out-gassed solution it was assumed that they contained no enclosed permanent gases. Tap B was now closed, and the right hand limb of A evacuated completely.

The vapour pressure of the solution could now be read by means of the difference in the mercury levels. It was found that after approximately 24 hours the difference/

difference became constant showing that equilibrium was established.

Tap B was now opened momentarily to the vacuum, then closed and a second reading of the equilibrium vapour pressure taken.

Generally, it was found that agitation reduced the time required for the solution to register its equilibrium vapour pressure. Suitable agitation was achieved by placing a glass marble in the reaction vessel C. As the latter was shaken, the marble moved across the flattened bottom of the vessel, stirring up the solution.

After equilibrium had been established for a second time, the temperature of the water in the reservoir F was adjusted so that the pressure of the water was one to one and a half mm. above that of the saturated solution. The tap D was opened and the pressure in C allowed to rise. The tap D was then closed and it was found that the pressure fell to the equilibrium value of the saturated solution in about one hour and thereafter remained constant.

The vapour pressure was thus checked by these two methods, agreement being within the experimental error in reading the microscope.

The temperature was now raised and the determinations continued at a higher temperature. In order to maintain the presence of the solid phase, water vapour/

vapour had thus frequently to be removed from C via the main vacuum line, and thus any traces of foreign gases which may have accumulated were removed.

When moving past a transition point, the lower hydrate was usually produced in the system without any difficulty. Experiments were also performed in which the higher hydrate was produced in the system from a lower hydrate, by a lowering of the thermostat temperature and the results were found to be identical with those obtained when the higher hydrate was produced in C directly.

Previously, the apparatus had been tested in the following way. It was completely evacuated, all the taps were closed and it was left for three days. Then the mercury levels were read and found not to have changed. This proved that no foreign gases were evolved from the grease or the mercury and showed the absence of leaks.

Secondly, conductivity water was introduced into the reaction vessel and the vapour pressure measured in the manner already described. The results agreed with those of International Critical Tables(41), to within the experimental error in reading the microscope.

Results.

Error in reading of microscope $\pm .04$ mm.

<u>T°C</u>	<u>Observed</u>	<u>Tables</u>
25.18	23.95 mm.	24.01 mm.
22.15	20.04 mm.	20.01 mm.
20.14/		

Results(Cont'd)

<u>T°C</u>	<u>Observed</u>	<u>Tables.</u>
20.14	17.65 mm.	17.67 mm.
19.20	16.66 mm.	16.68 mm.
17.82	15.34 mm.	15.30 mm.
16.82	14.38 mm.	14.36 mm.

For these experiments, accurate control of temperature was required and was obtained as follows.

The thermostat consisted of a copper tank with glass windows on opposite sides and which was thoroughly lagged with asbestos boards. Heating was provided by means of 250 watt immersion heaters, controlled by a mercury-toluene regulator and electronic relay.

In general, there were three separate ranges of temperature to be considered:

- (1) below room temperature,
- (2) between room temperature and 80°C, and
- (3) above 80°C.

For temperatures below room temperature, water in a slow stream was run through a copper spiral immersed in a refrigerating tank and thence through a second spiral immersed in the thermostat. The refrigerating tank was held at 0°C by a mercury toluene regulator and electronic relay.

Only one immersion heater, connected in series with an adjustable resistance, was required, and by careful adjustment of the resistance the temperature could be kept constant to within $\pm 0.02^{\circ}\text{C}$.

Between/

Between room temperature and 80°C , the flow of cold water was dispensed with and several heaters were connected up, either for continuous running or for intermittent use with the relay as the situation demanded.

Above 40°C , the water in the thermostat was covered by a layer of liquid paraffin to prevent excessive evaporation. A constant level device was also incorporated in the thermostat.

In the range 18°C to 65°C the temperature accuracy was $\pm 0.02^{\circ}\text{C}$ and from 65°C to 80°C was $\pm 0.05^{\circ}\text{C}$.

For temperatures above 80°C , a replica of the apparatus, small enough to be accommodated in a five litre beaker, was used, the thermostat liquid being dibutyl phthalate. The specific heat of this liquid is much lower than that of water, and so accurate temperature control is more difficult.

The vessel required to be well lagged to reduce heat losses, and the current supplied to the heaters was carefully adjusted to prevent overheating.

The dibutyl phthalate was quite successful up to temperatures of 97°C , but above this it seeped in through the joints and taps to fill the reaction vessel and so the experiments above 97°C had to be abandoned.

Two further points deserve mention.

It was usually found advantageous to use only small quantities (0.5 gms.) of material in the reaction chamber, as the solutions then tended to come/

come to equilibrium more quickly.

Also the most satisfactory illumination of the mercury manometer was provided by a 150 watt lamp shining through a ground glass plate arranged behind the thermostat.

In this way, the three phase lines between 9°C and 97°C were determined. Measurements below 9°C were not feasible owing to the very long time required to establish equilibrium.

VAPOUR PRESSURES OF SATURATED SOLUTIONS OF BENZENE SULPHONIC ACID (GRAPH 1)

Table No.9.

Vapour Pressure of Saturated Solutions of
Benzene Sulphonic Acid. (Graph I).

No.	Temperature T°C	Pressure mm. of Hg.	Solid Phase
1.	50.0	5.91	Monohydrate
2.	49.1	5.94	"
3.	48.0	5.98	"
4.	47.0	5.93	"
5.	46.0	5.90	"
6.	44.95	5.87	"
7.	43.0	5.69	"
8.	41.0	5.41	"
9.	39.0	5.14	"
10.	36.95	4.88	"
11.	35.0	4.53	"
12.	32.95	4.23	"
13.	31.0	3.94	"
14.	28.9	3.57	"
15.	26.9	3.32	"
16.	25.0	2.99	"
17.	23.05	2.69	"
18.	21.0	2.42	"
19.	18.95	2.12	"
20.	18.0	2.05	"

VAPOUR PRESSURES OF SATURATED SOLUTIONS OF BENZENE SULPHONIC
ACID (GRAPH 2)

Table No.10.

Vapour Pressure of Saturated Solutions of
Benzene Sulphonic Acid (Graph II).

No.	Temperature T°C	Pressure mm. of Hg	Solid Phase
1.	9.0	1.24	Dihydrate
2.	13.0	1.65	"
3.	15.0	1.86	"
4.	16.0	1.95	"
5.	17.1	2.02	"
6.	18.0	2.05	"
7.	18.95	2.12	Monohydrate
8.	21.0	2.42	"
9.	23.05	2.69	"
10.	25.0	2.99	"
11.	26.9	3.32	"

VAPOUR PRESSURES OF SATURATED SOLUTIONS OF o-TOLUENE SULPHONIC ACID.

Table No.11.

Vapour Pressure of Saturated Solutions of
o-Toluene Sulphonic Acid.

No.	Temperature T°C	Pressure mm. of Hg.	Solid Phase
1.	25.0	12.55	Dihydrate
2.	30.0	16.08	"
3.	35.0	20.32	"
4.	40.0	24.97	"
5.	45.0	30.09	"
6.	50.0	35.86	"
7.	55.0	39.85	"
8.	57.0	40.66	"
9.	58.0	41.03	"
10.	58.5	41.05	"
11.	59.0	41.03	"
12.	60.0	40.90	"

VAPOUR PRESSURES OF SATURATED SOLUTIONS OF p-NITROBENZENE
SULPHONIC ACID (GRAPH I)

Table No.12

Vapour Pressure of Saturated Solutions of
p-Nitrobenzene Sulphonic Acid (Graph I).

No.	Temperature T°C	Pressure mm. of Hg.	Solid Phase
1.	30.0	19.32	Dihydrate
2.	40.0	31.75	"
3.	50.0	49.58	"
4.	65.0	91.64	"
5.	79.0	143.4	"

VAPOUR PRESSURES OF SATURATED SOLUTIONS OF p-NITROBENZENE
SULPHONIC ACID (GRAPH 2)

Table No.13.

Vapour Pressure of Saturated Solutions of
p-Nitrobenzene Sulphonic Acid (Graph II).

No.	Temperature T°C	Pressure mm. of Hg.	Solid Phase
1.	21.0	12.93	4-hydrate
2.	22.1	13.65	"
3.	23.0	14.25	"
4.	23.9	14.84	"
5.	25.0	15.60	"
6.	26.0	16.29	"
7.	27.0	16.87	"
8.	28.0	17.55	"
9.	29.05	18.44	Dihydrate
10.	30.0	19.32	"
11.	31.0	20.41	"
12.	32.0	21.57	"
13.	33.0	22.66	"
14.	34.0	23.89	"
15.	36.0	26.24	"
16.	38.0	28.84	"
17.	40.0	31.75	"

VAPOUR PRESSURES OF SATURATED SOLUTIONS OF p-FLUOROBENZENE
SULPHONIC ACID (GRAPH 1)

Table No.14.

Vapour Pressure of Saturated Solutions of

p-Fluorobenzene Sulphonic Acid (Graph I).

No.	Temperature T°C	Pressure mm. of Hg.	Solid Phase
1.	25.0	5.95	Monohydrate
2.	35.0	9.80 -	"
3.	44.95	15.25	"
4.	55.0	22.65 -	"
5.	65.0	32.56	"
6.	70.0	38.06 -	"
7.	74.0	41.22	"
8.	75.0	42.01 -	"
9.	76.0	42.58	"
10.	77.1	43.03 -	"
11.	78.0	43.29	"
12.	79.0	43.72 -	"
13.	80.0	43.74 -	"
14.	80.95	43.38	"
15.	83.1	41.37 -	"

VAPOUR PRESSURES OF SATURATED SOLUTIONS OF p-FLUOROBENZENE
SULPHONIC ACID (GRAPH 2)

Table No.15

Vapour Pressure of Saturated Solutions of
p-Fluorobenzene Sulphonic Acid (Graph II).

No.	Temperature T ^o C	Pressure mm. of Hg.	Solid Phase
1.	12.0	3.21 -	2.5-hydrate
2.	13.0	3.37	"
3.	14.0	3.49 -	"
4.	15.0	3.68	"
5.	16.0	3.84 -	"
6.	17.0	4.02	"
7.	18.0	4.16 -	"
8.	19.0	4.39	"
9.	20.0	4.54 -	"
10.	21.0	4.64	Monohydrate
11.	22.0	4.98 -	"
12.	23.0	5.28	"
13.	24.0	5.62 -	"
14.	25.0	5.90	"
15.	26.0	6.19	"
16.	27.0	6.50	"
17.	28.0	6.91 -	"
18.	35.0	9.80 -	"

VAPOUR PRESSURES OF SATURATED SOLUTIONS OF p-CHLOROBENZENE
SULPHONIC ACID (GRAPH I)

Table No.16

Vapour Pressure of Saturated Solutions of
p-Chlorobenzene Sulphonic Acid (Graph I).

No.	Temperature T °C	Pressure mm. of Hg.	Solid Phase
1.	39.8	16.22 -	Monohydrate
2.	49.9	25.61	"
3.	60.0	38.19 -	"
4.	69.7	54.76	"
5.	80.1	73.30 -	"
6.	88.9	85.59 -	"
7.	89.9	86.60	"
8.	91.0	87.48 -	"
9.	92.2	87.94	"
10.	93.4	88.41 -	"
11.	94.3	88.24 -	"
12.	95.1	87.50	"
13.	96.2	87.00 -	"

VAPOUR PRESSURES OF SATURATED SOLUTIONS OF p-CHLOROBENZENE
SULPHONIC ACID (GRAPH 2)

Table No.17

Vapour Pressure of Saturated Solutions of
p-Chlorobenzene Sulphonic Acid (Graph II)

No.	Temperature T°C	Pressure mm. of Hg.	Solid Phase
1.	22.0	6.62	2.5-hydrate
2.	23.0	7.05	"
3.	24.0	7.43	"
4.	25.0	7.80	"
5.	26.0	8.26	"
6.	27.0	8.71	"
7.	28.0	9.15	"
8.	29.0	9.59	"
9.	30.0	10.13	Monohydrate
10.	31.0	10.68	"
11.	32.0	11.28	"
12.	33.0	11.88	"
13.	34.0	12.43	"
14.	35.0	13.09	"
15.	36.0	13.75	"
16.	37.0	14.50	"
17.	38.0	15.09	"

VAPOUR PRESSURES OF SATURATED SOLUTIONS OF p-BROMOBENZENE
SULFONIC ACID (GRAFT 1).

Table No.18

Vapour Pressure of Saturated Solutions of
p-Bromobenzene Sulphonic Acid (Graph I)

No.	Temperature °C	Pressure mm. of Hg.	Solid Phase
1.	50.0	20.27 -	Monohydrate
2.	60.0	29.32 -	"
3.	70.0	39.60 -	"
4.	80.1	52.25 -	"
5.	82.1	53.43	"
6.	83.2	53.79	"
7.	83.9	53.89 -	"
8.	84.4	53.91 -	"
9.	84.95	53.89 -	"
10.	85.8	53.35 -	"

VAPOUR PRESSURE OF SATURATED SOLUTIONS OF p-BROMOBENZENE
SULPHONIC ACID (GRAPH 2)

Table No.19

Vapour Pressure of Saturated Solutions of
p-Bromobenzene Sulphonic Acid (Graph II)

No.	Temperature T°C	Pressure mm. of Hg.	Solid Phase
1.	20.1	4.74 -	2.5-hydrate
2.	25.0	6.24	"
3.	26.0	6.63 -	"
4.	27.0	7.03	"
5.	28.0	7.39 -	"
6.	29.0	7.80	"
7.	30.0	8.20 -	"
8.	31.0	8.61	"
9.	32.0	9.02 -	"
10.	33.0	9.50 2.5	Monohydrate ?
11.	34.0	10.02 2.5	" ?
12.	35.0	10.51 -	Mono "
13.	36.0	11.03	"
14.	37.0	11.54	"
15.	38.0	12.10 -	"
16.	39.0	12.63	"
17.	40.0	13.24 -	"

Liquid-Vapour Equilibria.

Determination of the Heats of Solution.

To determine heats of solution, it is possible to use either a direct calorimetric method or to evaluate them from solubility and vapour pressure data using the equation of Williamson(11). In this case they were obtained by the latter method.

The determination of the solubility data has already been described, and the other data required is a knowledge of the vapour pressures of unsaturated solutions of known concentration, determined at the temperature at which the heat of solution is being measured.

These vapour pressures were measured in the same apparatus as was used for determining the three phase lines. As it was proposed to compare the heats of solution principally of the monohydrates, it was necessary to choose from the solubility curves a temperature which would be within the stability range of all the monohydrates. Unfortunately, this was not possible, but the temperature of 50°C was chosen, as this enables the determination for five of the acids to be carried out; viz:- the monohydrates of benzene, p-toluene, p-fluoro-, p-chloro- and p-bromobenzene sulphonic acids. The temperature also provides for the dihydrates of o-toluene and p-nitrobenzene sulphonic acid.

In any case, the monohydrate of p-nitrobenzene sulphonic/

sulphonic acid, if it exists at all, would probably not be stable over any range at which the others could be measured, and the o-toluene sulphonic acid monohydrate is stable over so short a range of temperature and composition and is in such close proximity to the dihydrate that it would be very difficult to measure its heat of solution by this method.

The thermostat was therefore set at 50°C and the apparatus set up as described previously.

The solutions were made up from crystals, which had been crystallised out of aqueous solution in vacuo, and freshly distilled water boiled down to one quarter bulk. The unsaturated solution, containing about 1gm. of anhydrous acid, was placed in the bottom of the reaction chamber and the air expelled in the manner described in the previous chapter. From the three phase curves, the vapour pressures of the saturated solutions are known at this temperature. Water was therefore gradually removed until the vapour pressure was about one mm. higher than that of the saturated solution. The apparatus was now left for the pressure to come to equilibrium which usually took about 24 hrs. As before, agitation by means of a glass marble speeded up the attainment of equilibrium.

Then, keeping the tap B closed, air was gradually allowed into the right hand limb of the manometer. This was continued to the limit of the mercury column. The/

Then tap B was opened, the vacuum completely broken, and the apparatus removed from the thermostat. The reaction vessel was quickly removed from the apparatus, a portion of the solution rapidly pipetted into a weighing bottle, weighed and titrated. The composition of the solution was thus obtained.

A specimen result is shown below.

Acid p-Fluorobenzene Sulphonic Acid.

Weight of weighing bottle empty (W_1)	= 14.5500g.
Weight of weighing bottle + sulphonic acid solution (W_2)	= 15.0361g.
Titre of 0.08494 N baryta	= 26.12mls.
Microscope readings	Molality
157.16 mm.	
<u>137.53 mm.</u>	
<u>19.63 mm.</u>	23.27 m.

The object of allowing air into the evacuated side of the apparatus was to prevent any flow of water vapour to the phosphorus pentoxide (which would mean a change in composition of the solution), by providing an air current into the reaction chamber in the opposite direction. In this way, the percentage composition would probably not alter significantly in the time interval while the vacuum was broken and the solution sampled.

The experiment was now repeated using another sample and a pressure adjusted to one mm. more than the previous one. About seven determinations were carried out for each of the seven acids, and the results were plotted as molality against vapour pressure/

pressure. The composition of each saturated solution was taken from the appropriate solubility curve, and the vapour pressure of the saturated solution from the three phase curve.

The thermostat, although set at 50.00°C was found to vary over the range $\pm 0.02^{\circ}\text{C}$. This is as good as can be expected from the apparatus employed, but it did cause a slight variation in the mercury levels of the order of 0.10 mm.

This is partly attributable to the expansion and contraction of the vapour phase as the temperature changes, and partly to change of vapour pressure with change of temperature. The second effect is probably the more important since the thermal conductivity of water vapour is low and the actual pressure change is greater than that which application of the gas laws would demand.

The indicator light on the sunvic relay was carefully observed, and the pressure was read immediately the light went on and immediately it went off. The temperature was also taken at the same instant. Both were noted and the average was taken.

A difficulty is that of "bumping" during evacuation. This can be greatly reduced by reducing the pressure very gradually. In this way, and using a sufficiently large reaction vessel, splashing could be reduced to a level which caused no serious trouble. A subsidiary use of the spiral in these experiments was to protect the mercury manometer from any contamination by sulphonic acid solution.

SOLUBILITY DATA FOR BENZENE SULPHONIC ACID (TABLE NO.20).

Table No.20

Solubility Data for Benzene Sulphonic Acid
(Molalities for Heat of Solution)

No.	Temperature °C	Composition molality (m)
1.	35.8	31.84
2.	37.5	32.63
3.	42.4	35.72
4.	47.1	39.82
5.	48.4	41.86
6.	49.1	42.52
7.	51.9	48.51
8.	52.1	52.26

At 50.0°C

from graph (1) $m = 43.65$ and (2) $\frac{dm}{dt} = \frac{17.35}{11.15} = \underline{1.556}$.

VAPOUR PRESSURES OF UNSATURATED SOLUTIONS OF BENZENE SULPHONIC ACID (TABLE 21).

TABLE NO.21.

Vapour Pressure of Unsaturated Solutions of
Benzene Sulphonic Acid at Constant Temperature
(50.0°C)

No.	Pressure mm. of Hg.	Composition molality. (m)
1.	14.23	27.23
2.	11.53	30.18
3.	9.11	33.36
4.	8.34	34.18
5.	7.15	38.07
6.	6.37	40.16
7.	6.18	41.78
8.	5.88	42.24
9.	5.91	43.65 (Saturated)

From graph $\frac{1}{P} \times \frac{dP}{dm} = -\frac{1}{5.91} \left(-\frac{1.82}{20.4} \right) = -0.01955$

$x(\text{molecules of water of crystallisation}) = 1$

$$\begin{aligned} \Delta H_{sol} &= \left(x - \frac{55.51}{m} \right) R T^2 \left(\frac{dm}{dt} \right)_{sat.} \left(\frac{\partial \ln a}{\partial m} \right)_T \\ &= \left(1 - \frac{55.51}{43.65} \right) \times 1.987 \times (323.1)^2 \times 1.556 \times (-0.01955) \\ &= 1.71 \text{ kg.cals./mole.} \end{aligned}$$

SOLUBILITY DATA FOR p-TOLUENE SULPHONIC ACID (TABLE NO.22).

TABLE NO.22

Solubility Data for p-Toluene Sulphonic Acid

(Molalities for Heat of Solution)

No.	Temperature °C	Composition molality (m)
1.	18.4	13.61
2.	20.1	13.18
3.	38.8	15.31
4.	55.2	17.64
5.	69.0	20.30
6.	69.8	20.41

At 50.0°C

From graph (1) $m = 16.83$ and (2) $\frac{dm}{dt} = \frac{7.215}{46.9} = 0.1538$

VAPOUR PRESSURES OF UNSATURATED SOLUTIONS OF p-TOLUENE SULPHONIC
ACID (TABLE NO. 23).

TABLE NO.23.

Vapour Pressure of Unsaturated Solutions of
p-Toluene Sulphonic Acid at Constant Temperature
(50.0°C)

No.	Pressure mm. of Hg	Composition molality (m)
1.	46.44	13.03
2.	44.92	13.60
3.	43.86	14.01
4.	41.44	14.69
5.	39.37	15.45
6.	37.38	16.12
7.	36.87	16.29
8.	35.90	16.60
9.	35.33	16.83 (saturated)

$$\text{From graph } \frac{1}{P} \frac{dP}{dm} = \frac{1}{35.33} \left(-\frac{11.62}{3.91} \right) = -0.08410$$

$$x(\text{molecules of water of crystallisation}) = 1$$

$$\begin{aligned} \Delta H_{\text{sol}} &= \left(x - \frac{55.51}{m} \right) R T^2 \left(\frac{dm}{dt} \right)_{\text{sat.}} \left(\frac{\partial \ln \gamma}{\partial m} \right)_T \\ &= \left(1 - \frac{55.51}{16.83} \right) \times 1.987 \times (323.1)^2 \times (0.1538) \times (-0.08410) \\ &= 6.18 \text{ kg.cals./mole.} \end{aligned}$$

SOLUBILITY DATA FOR o-TOLUENE SULPHONIC ACID (TABLE NO.24).

TABLE NO.24.

Solubility Data for o-Toluene Sulphonic Acid.

(Molalities for Heat of Solution)

No.	Temperature °C	Composition molality (m)
1.	40.0	14.28
2.	44.0	15.13
3.	47.0	16.01
4.	50.0	17.22
5.	58.2	21.05
6.	61.2	24.60

At 50.0°C

From graph (1) $m = 17.22$ and (2) $\frac{dm}{dt} = \frac{8.45}{20.9} = 0.4044.$

VAPOUR PRESSURES OF UNSATURATED SOLUTIONS OF o-TOLUENE
SULPHONIC ACID (TABLE NO.25).

TABLE NO.25.

Vapour Pressure of Unsaturated Solutions of

o-Toluene Sulphonic Acid at Constant Temperature
(50.0°C)

No.	Pressure mm. of Hg.	Composition molality (m)
1.	42.89	14.38
2.	40.89	15.02
3.	39.99	15.27
4.	38.48	15.80
5.	37.87	16.14
6.	36.56	16.85
7.	36.11	17.11
8.	35.86	17.22(saturated)

$$\text{From graph } \frac{1}{P} \times \frac{dP}{dm} = \frac{1}{35.86} \left(-\frac{5.64}{3.325} \right)$$

$$= -0.04732$$

$$x(\text{molecules of water of crystallisation}) = 2$$

$$\Delta H_{sol} = (x - \frac{55.51}{m}) R T^2 \left(\frac{dm}{dT} \right)_{sat.} \left(\frac{\partial \ln a}{\partial m} \right)_T$$

$$= (2 - \frac{55.51}{17.22}) \times 1.987 \times (323.1)^2 \times 0.4044 \times (-0.04732)$$

$$= 4.86 \text{ kg.cals./mole.}$$

SOLUBILITY DATA FOR p-NITROBENZENE SULPHONIC ACID (TABLE NO.26)

TABLE NO.26

Solubility Data for p-Nitrobenzene Sulphonic Acid
(Molalities for Heat of Solution)

No.	Temperature °C	Composition molality (m)
1.	36.6	9.69
2.	45.8	10.63
3.	49.2	10.80
4.	56.6	11.12
5.	62.5	12.18
6.	75.5	13.62
7.	79.2	14.56
8.	90.2	16.23

At 50°C

From graph (1) $m = 10.90$ and (2) $\frac{dm}{dt} = \frac{5.17}{54} = 0.09574$.

VAPOUR PRESSURES OF UNSATURATED SOLUTIONS OF p-NITROBENZENE
SULPHONIC ACID (TABLE NO. 27)

TABLE NO.27

Vapour Pressure of Unsaturated Solutions of
p-Nitrobenzene Sulphonic Acid at Constant Temperature
(50.0°C)

No. 66	Pressure mm.of Hg.	Composition molality (m)
1.	61.02	8.312
2.	57.50	8.991
3.	54.93	9.543
4.	53.99	9.831
5.	53.56	9.959
6.	52.55	10.22
7.	50.82	10.58
8.	50.43	10.66
9.	49.66	10.90(saturated)

From graph $\frac{1}{P} \times \frac{dp}{dm} = \frac{1}{49.66} \left\{ - \frac{10.27}{2.95} \right\} = 0.07015.$

$x(\text{molecules of water of crystallisation}) = 2.$

$$\begin{aligned} \Delta H_{sol} &= (x - \frac{55.51}{m}) R T^2 \left(\frac{dm}{dT} \right)_{\text{sat.}} \left(\frac{\partial \ln a}{\partial m} \right)_T \\ &= (2 - \frac{55.51}{10.9}) \times 1.987 \times (323.1)^2 \times 0.09574 \times (-0.07015) \\ &= 4.30 \text{ kg.cal./mole.} \end{aligned}$$

SOLUBILITY DATA FOR p-FLUOROBENZENE SULPHONIC ACID (TABLE 28)

TABLE NO.28

Solubility Data for p-Fluorobenzene Sulphonic Acid
(Molalities for Heat of Solution)

No.	Temperature °C	Composition molality (m)
1.	35.4	20.58
2.	48.1	23.09
3.	48.5	23.19
4.	54.2	24.30
5.	62.4	26.52

At 50.0°C

From graph (1) $m = 23.45$ and (2) $\frac{dm}{dt} = \frac{5.75}{27.7} = 0.2076$

VAPOUR PRESSURES OF UNSATURATED SOLUTIONS OF p-FLUOROBENZENE
SULPHONIC ACID (TABLE NO. 29)

TABLE NO.29

Vapour Pressure of Unsaturated Solutions of
p-Fluorobenzene Sulphonic Acid at Constant Temperature
(50.0°C)

No.	Pressure mm. of Hg.	Composition molality (m)
1.	24.96	20.03
2.	23.48	20.55
3.	22.61	20.88
4.	22.04	21.30
5.	21.51	21.72
6.	20.50	22.21
7.	19.42	23.07
8.	18.63	23.45(saturated)

From graph $\frac{1}{P} \times \frac{dp}{dm} = \frac{1}{18.63} \left(-\frac{5.45}{3.90} \right) = -0.07504.$

$x(\text{molecules of water of crystallisation}) = 1$

$$\begin{aligned} \Delta H_{sol} &= \left(x - \frac{55.51}{m} \right) R T^2 \left(\frac{dm}{dT} \right)_{sat.} \left(\frac{\partial \ln a}{\partial m} \right)_T \\ &= \left(1 - \frac{55.51}{23.45} \right) \times 1.987 \times (323.1)^2 \times 0.2076 \times (-0.07504) \\ &= 4.41 \text{ kg.cal./mole.} \end{aligned}$$

SOLUBILITY DATA FOR p-CHLOROBENZENE SULPHONIC ACID (TABLE NO.30)

TABLE NO.30

Solubility Data for p-Chlorobenzene Sulphonic Acid
(Molalities for Heat of Solution)

No.	Temperature °C	Composition molality (m)
1.	41.0	19.24
2.	45.8	19.74
3.	51.9	20.50
4.	59.0	21.87
5.	70.1	24.55

At 50.0°C

From graph (1) $m = 20.24$ and (2) $\frac{dm}{dt} = \frac{2.925}{22.4} = 0.1306$

VAPOUR PRESSURES OF UNSATURATED SOLUTIONS OF p-CHLOROBENZENE
SULPHONIC ACID (TABLE NO.31)

TABLE NO.31.

Vapour Pressure of Unsaturated Solutions of

p-Chlorobenzene Sulphonic Acid at Constant Temperature
(50.0°C)

No.	Pressure mm. of Hg.	Composition molality (m)
1.	33.23	16.54
2.	31.56	17.48
3.	30.09	18.06
4.	29.23	18.45
5.	28.21	18.96
6.	27.55	19.27
7.	26.63	19.74
8.	25.57	20.24(saturated)

$$\text{From graph } \frac{1}{P} \times \frac{dp}{dm} = \frac{1}{25.57} \left(-\frac{9.04}{4.5} \right) = -0.07857$$

x(molecules of water of crystallisation) = 1

$$\begin{aligned} \Delta H_{sol} &= \left(x - \frac{55.51}{m} \right) R T^2 \left(\frac{dm}{dt} \right)_{sat} \left(\frac{\partial \ln a}{\partial m} \right)_T \\ &= \left(1 - \frac{55.51}{20.24} \right) \times 1.987 \times (323.1)^2 \times 0.1306 \times (-0.07857) \\ &= 3.70 \text{ kg.cal./mole.} \end{aligned}$$

SOLUBILITY DATA FOR p-BROMOBENZENE SULPHONIC ACID (TABLE NO.32)

TABLE NO.32

Solubility Data for p-Bromobenzene Sulphonic Acid
(Molalities for Heat of Solution)

No.	Temperature °C	Composition molality (m)
1.	43.8	23.50
2.	52.0	25.05
3.	60.2	27.54
4.	64.8	28.68
5.	65.9	28.99
6.	67.3	29.42
7.	72.5	31.65

At 50.0°C

From graph (1) $m = 24.73$ and (2) $\frac{dm}{dt} = \frac{7.98}{36} = 0.2217$

VAPOUR PRESSURES OF UNSATURATED SOLUTIONS OF p-BROMOBENZENE
SULPHONIC ACID (TABLE NO.33)

TABLE NO.33

Vapour Pressure of Unsaturated Solutions of
p-Bromobenzene Sulphonic Acid at Constant Temperature
(50.0°C)

No.	Pressure mm. of Hg.	Composition molality (m)
1.	24.90	20.61
2.	22.25	22.21
3.	21.85	22.58
4.	21.41	23.09
5.	20.91	23.64
6.	20.21	24.73(saturated)

From graph $\frac{1}{P} \times \frac{dp}{dm} = \frac{1}{20.21} \left\{ \frac{-2.73}{4.5} \right\} = -0.03002.$

$x(\text{molecules of water of crystallisation}) = 1$

$\Delta H_{sol} = (x - \frac{55.51}{m}) R T^2 \left(\frac{dm}{dt} \right)_{sat.} \left(\frac{\partial \ln a}{\partial m} \right)_T$

$= (1 - \frac{55.51}{24.73}) \times 1.987 \times (323.1)^2 \times 0.2217 \times (-0.03002)$
 $= 1.72 \text{ kg.cals./mole.}$

Heats of Solution.

TABLE NO.34

Acid	Hydrate	H
Benzene Sulphonic Acid	Monohydrate	1.7 kg.cal/mol.
p-Toluene Sulphonic Acid	Monohydrate	6.2 kg.cal/mol.
o-Toluene Sulphonic Acid	Dihydrate	4.9 kg.cal/mol.
p-Nitrobenzene Sulphonic Acid	Dihydrate	4.3 kg.cal/mol.
p-Fluorobenzene Sulphonic Acid	Monohydrate	4.4 kg.cal/mol.
p-Chlorobenzene Sulphonic Acid	Monohydrate	3.7 kg.cal/mol.
p-Bromobenzene Sulphonic Acid	Monohydrate	1.7 kg.cal/mol.

Solid-Vapour Equilibria Determinations.

Attempts were made to measure the solid-vapour equilibria of the dissociating system,

monohydrate $\rightleftharpoons$ anhydrous acid + water vapour
at temperatures below the relevant eutectic point.

Samples of air-free monohydrate crystals were prepared and about one gm. placed in the same apparatus as was used for the measurement of solution vapour pressures. The apparatus was then pumped out for several hours at room temperature to ensure that the system was gas free. The reaction chamber was now heated to a sufficient temperature to melt the monohydrate and the pumping continued for about five minutes. The time of pumping varied according to the acid. The aim was to produce roughly equal quantities of monohydrate and anhydrous acid. The loss of water with time at the temperature used to melt the monohydrate was roughly known from the solubility experiments. After this mixture of monohydrate and anhydrous acid had been prepared, tap B was closed and the system allowed to approach equilibrium. This unfortunately frequently required many weeks and the procedure was therefore of little use.

Attempts were made to approach equilibrium from a pressure initially greater than the dissociation pressure.

As the latter are small, being seldom more than 2 mm./

2 mm., the water in the reservoir had to be frozen to about -5°C before opening tap D and allowing water vapour to enter the system. At this point, an unusual result was obtained. The pressure fell rapidly to a certain value within about 30 minutes and remained constant at this value for several hours. After this however, the pressure rose and reached a new constant value, usually about three times as great, after about four days. The pressure now remained constant for approximately another four days, and then began to rise very slowly. If the experiment was now repeated on the same sample, by simply allowing a further quantity of water vapour to enter the system, these results could be repeated, but the time lag was much shorter. The first equilibrium pressure was usually slightly higher, and the time during which this low pressure value remained constant was usually only one hour. Pressure-Time graphs for these two experiments would be approximately as follows.

Successive experiments on the same samples smoothed out the minimum on this curve, and the points could be reproduced quite accurately on different samples.

The main work was done with p-bromobenzene sulphonic acid for which the eutectic point is 76°C .
At/

At temperatures near 50°C , the solid-vapour equilibria could be measured quite well, but the low value of the dissociation pressure and the long time required to establish equilibrium caused much difficulty. For temperatures below 50°C the time involved ran into months, while above 50°C , one or two weeks were required. Dissociation pressures above 55°C were however unreliable owing to perceptible decomposition of the sulphonic acid with the formation of free sulphuric acid.

In view of these difficulties, attempts were made to use simple tensimeters for temperatures below 50°C . These were constructed as shown

They consisted of a mercury manometer and attached to one limb was a bulb, large enough to contain about one gram of the sample. Above the other limb was a compartment large enough to contain all the mercury.

These tensimeters were thoroughly cleaned. Into the bulb A was introduced a mixture of approximately equal amounts of the monohydrate and the anhydrous acid, and the inlet tube then sealed off.

Freshly/

Freshly distilled mercury, previously cleaned with nitric acid, acetone and distilled water was placed in the reservoir B and the apparatus adjusted so that it was horizontal. By means of a quickfit joint the tensimeter was connected to an oil pump with a McLeod gauge in the system. The bulb containing the acid was immersed in a solid carbon dioxide-ethyl alcohol freezing mixture to prevent loss of water. The pressure was reduced to .001mm. of mercury or less, and the mercury in B gently heated with a small flame to expel any dissolved water vapour or gases. This evacuation was continued for 30 minutes and then the tensimeter was rotated at the joint L. The apparatus was now vertical and the mercury ran into the U-tube sealing off the acid. The tensimeter was now sealed off under vacuum at D and then erected vertically in a thermostat at the desired temperature. Unfortunately, the dissociation pressure results obtained by this method were not reproducible and consequently were of little value. It is thought that this was due either to dissolved air in the crystal lattice being released over a long period of time, or to diffusion of water vapour through the mercury into the other limb of the tensimeter.

Attempts were also made to measure the dissociation pressure at the higher temperatures by an isopiestic method. The balancing liquid employed was a solution of sulphuric acid. This method was thought to have great/

great possibilities since if the sulphonic acid decomposed slightly, into bromobenzene and sulphuric acid for example, then, provided the decomposition was small, the equilibrium would not be affected, and the experiment would still be valid. Furthermore, if any air was enclosed in the sulphonic acid crystal lattice and diffused out, the experiment would still not be affected. Neither would there be any difficulty of reading mercury levels. Also the apparatus could be left for a long time completely immersed in a thermostat without attention. The usual objection to isopiestic methods, namely bumping and splashing, would not operate in this case as we are here dealing with a solid and a very concentrated solution of sulphuric acid. The apparatus was very simple. Glass tubing ($\frac{1}{2}$ " internal diameter) was made up in the form of an H, and into one limb was placed the mixture of monohydrate and anhydrous acid, and the limb sealed. Into the other was placed a solution of sulphuric acid of known concentration. The apparatus is shown below.

The quantities of each were adjusted so that equilibrium could be attained without complete dehydration of the monohydrate. The apparatus was now evacuated by means of an oil pump and during the evacuation, both the limbs were frozen in solid carbon dioxide to prevent loss of water by evaporation. The apparatus was/

was now sealed off under vacuum and left for several weeks in a thermostat. After this time the sulphuric acid was sampled as follows:-

A weighing bottle was half-filled with distilled water and weighed (W_1). The apparatus was now removed from the thermostat, broken open, and two drops of sulphuric acid removed by means of a dry, clean pipette. The two drops were pipetted into the weighing bottle which was now weighed again (W_2). The purpose of the water was to dilute the acid and so allow it to be weighed without introduction of errors due to its deliquescence. The contents of the weighing bottle were washed into a beaker and titrated. From these results, the concentration of sulphuric acid solution was calculated, and from the percentage composition the vapour pressure could be found from International Critical Tables.

The results were promising but hereagain the experiments had to be abandoned owing to the very long time required to establish equilibrium.

From these various experiments on solid-vapour equilibria, two partial curves have been obtained - one for benzene sulphonic acid and the other for p-bromobenzene sulphonic acid.

SOLID-VAPOUR DATA FOR BENZENE SULPHONIC ACID MONOHYDRATE $\rightleftharpoons$
 ANHYDROUS ACID + WATER VAPOUR

Log $p / \frac{1}{T}$

380

170

0

0

9 .71 .73 .75 .77 .79 .81 .83 .85 .87 .89 .91 .93 .95 .97 .99 1.01 1.03 1.05

$\log p \times (-1)$

Table No.35.

Solid-Vapour Equilibria for the system Benzene Sulphonic Acid Monohydrate $\rightleftharpoons$ Anhydrous acid + Water Vapour	
T °C	P mm. of Hg.
29.85	0.200
29.10	0.175
27.90	0.155
26.85	0.140
25.90	0.120
24.90	0.105
24.00	0.096
20.00	0.080

These pressures are each the average of 10 readings.

$$\text{From the graph } \frac{d(\log P)}{d\left(\frac{1}{T}\right)} = -4,922$$

$$\begin{aligned} \text{Heat of Dissociation } Q &= -R \times 2.303 \times -4,922 \\ &= -1.987 \times 2.303 \times -4,922 \\ &= 22.53 \text{ kg.cals./mole of water} \\ &\quad \text{vapour} \end{aligned}$$

SOLID-VAPOUR DATA FOR p-BROMOBENZENE SULPHONIC ACID MONOHYDRATE $\uparrow$
 ANHYDROUS ACID + WATER VAPOUR

Table No.36

Solid-Vapour Equilibria for the system p-Bromobenzene Sulphonic Acid Monohydrate $\rightleftharpoons$ Anhydrous Acid + Water Vapour	
T °C	P mm. of Hg.
40.0 °C	0.75
50.0 °C	1.54
54.8 °C	2.11

These pressures are the average of 10 readings.

From the graph $\frac{d(\log_{10}P)}{d(\frac{1}{T})} = -3.087$

Heat of Dissociation $Q = -1.987 \times 2.303 \times -3.087$
 $= 14.13 \text{ kg.cals./mole of}$
 water vapour

Table No.37

Values obtained in attempted measurement of solid-vapour equilibria by an isopiestic method for the system

p-Bromobenzene Sulphonic Acid Monohydrate $\rightleftharpoons$ Anhydrous

Acid + Water Vapour

using aqueous solutions of sulphuric acid as the balancing solution at 50.0°C.

The vapour pressures of sulphuric acid-water mixtures were taken from International Critical Tables.

Initial Sulphonic Acid	Initial Sulphuric Acid	Time T	%age Sulphuric Acid after Time T	Corresponding Vapour Pressure
3g.monohydrate slightly dehydrated	0.5g. of 90.0%	21 Days	81.83%	0.50 mm.
2g.monohydrate slightly dehydrated	0.5g. of 84.47%	14 Days	77.14%	1.45 mm.
2g.monohydrate slightly dehydrated	0.5g. of 81.5%	34 Days	76.38%	1.60 mm.
3g.monohydrate fully dehydrated	0.5g. of 70.1%	19 Days	72.73%	3.30 mm.

Table No.38

Series of minimum pressures of water vapour on mixture of p-bromobenzene sulphonic acid monohydrate and the anhydrous acid.

Temperature		Adsorption Pressure	
30°C	$\frac{1}{F}$ 0.0033	0.12 mm.	$\log_{10} p$ 7.0792 - 0.9208
41°C	3184	0.26 mm.	7.4150 - 0.5850
45°C	3144	0.34 mm.	7.5315 - 0.4685
50°C	3095	0.54 mm.	7.7324 - 0.2676
55.1°C	3047	0.86 mm.	7.9345 - 0.0655
60.9°C	2994	1.21 mm.	8.0828
65.2°C	2956	1.84 mm.	0.2648
67.0°C	2940	2.11 mm.	0.3243
69.9°C	2915	2.44 mm.	0.3874
72.04°C	2878	2.84 mm.	0.4533

DISCUSSION

Preparation and Purification.

In the measurement of solubilities and vapour pressures in sulphonic-acid water systems, it is essential that the acids should be pure, and, in particular, free from inorganic salts. The adverse effect of the latter impurities is in almost all cases very large, especially when using the synthetic method for solubility determinations. Another impurity which must be eliminated is free sulphuric acid. This appeared liable to initiate a very rapid decomposition, probably hydrolytic in nature, with the production of more sulphuric acid, such that eventual blackening and charring of the sulphonic acid took place, particularly at higher temperatures. For these reasons, the acids were rigorously purified as required, to ensure the absence of sodium, potassium, calcium, barium, copper, nickel, iron, sulphate, chloride and nitrate. In every case an ash determination was performed. The absence of any residue was held to be a good indication that no inorganic matter was present.

Of equal importance, is the absence of organic impurities, and in particular, of isomeric sulphonic acids. A brief discussion follows of the purification procedures employed.

Iron was present in the benzene sulphonic acid and the p-toluene sulphonic acid supplied by B.D.H.
It/

It was removed as far as possible, but could never be completely eliminated. However, its concentration was reduced to such an extent that only a faint coloration could be obtained with ammonium thiocyanate. As the concentration limit of this reagent is 1 per 200,000 (Sensitivity 0.25 μ g.) it was decided that solubility and vapour pressure measurements would not be affected to any measureable extent.

The o-toluene sulphonic acid was exceedingly pure when supplied and did not need any further treatment. The four other acids were all prepared via the sulphonyl chlorides, which were recrystallised from ether. This ensures the absence of inorganic material.

The second consideration is the possible presence of isomers.

The p-bromobenzene sulphonic acid was supplied as a sulphonyl chloride, whose melting point agreed exactly with the value reported in the literature. It was therefore considered to be free from isomers.

The p-fluorobenzene sulphonic acid could conceivably be contaminated with the ortho, or, less likely, the meta form, or both, but that is considered unlikely for the following reasons.

The sulphonyl chloride prepared from sulphanilic acid is certain to be the para form. It is by essentially the same method that para compounds are prepared by the Sandmeyer reaction. Furthermore, migrations/

migrations of substituents usually take place towards the para position and not away from it.

This sulphonyl chloride had the same melting point as the sulphonyl chloride prepared by the sulphonation of fluorobenzene and the mixture of both produced no depression of melting point. The two sulphonyl chlorides both crystallised out in rhombs, and both gave symmetrical extinction under crossed nicols.

Also, it has been found that in the nitration of fluorobenzene, if a large excess of the nitrating agent is present, and the reaction is carried out in the cold, only the para compound is formed.

The melting point of the sulphonyl chloride was 2°C lower than that reported in the literature. Repeated crystallisation from various solvents and high vacuum distillation could not raise the melting point. The higher value was reported in 1879 and it is thought that our value is more reliable.

One of the points on the solubility curve was determined using acid which had been obtained from sulphanilic acid. This point fitted perfectly into the rest of the curve which was determined using acid from the sulphonation of fluorobenzene.

For these reasons, the acid was considered to be pure.

With the exception of the point on the solubility curve referred to, all the solubilities and vapour pressure/

pressure measurements were performed on acid prepared from the sulphonation of fluorobenzene, since the latter gave the better yield.

The best method would have been from sulphanilic acid via the borofluoride complex, but unfortunately this was not possible.

The p-chlorobenzene sulphonic acid was prepared by the sulphonation of chlorobenzene. The figure of 53°C for the melting point of the sulphonyl chloride is well established, and when, by vacuum distillation a sample melting at this point was obtained, it was considered pure.

The p-nitrobenzene sulphonic acid was prepared by a method which leaves no doubt that it is purely a para compound. There are two figures reported in the literature for the melting point of the sulphonyl chloride.

77° by Demeny, Rec. trav. chim., 1929, 48, 1145

80° by Bell, J. Chem. Soc., 1928, 2776.

The figure obtained in this investigation was 77°C .

It could not be raised by recrystallisation from various solvents or vacuum distillation.

The yield obtained was not good. The main losses occurred in the conversion of the ammonium salt to the sulphonyl chloride. The reagents used were in one case chlorosulphonic acid and in the other phosphorus pentachloride. Chlorosulphonic acid gave the better yield/

yield, but neither were very good.

The p-toluene sulphonic acid and the o-toluene sulphonic acid supplied by B.D.H. could conceivably be contaminated with one another, but this is considered unlikely for the following reasons. As can be seen from the solubility curves, the form in which the p-toluene sulphonic acid is most stable under normal conditions prevailing in the laboratory is the monohydrate, and for the o-toluene sulphonic acid it is the dihydrate. These have different solubilities and should thus be capable of being separated by fractional crystallisation. Both of these acids were recrystallised five times from water without change in melting point. Also solutions of p-toluene sulphonic acid were saturated with hydrogen chloride and the sulphonic acid thus precipitated from the solution. It was found that the melting point was unaltered by this procedure. Furthermore, the acid was mixed with a known quantity of water, and the temperature of complete solution determined. In three separate cases, it was found that solutions made up from uncrystallised acid and solutions from recrystallised acid gave the same solubility point. In all cases, the acids dissolved completely in distilled water and the presence of organic impurities such as sulphones was therefore considered highly unlikely. For these reasons the acids were considered pure.

Solid-Liquid Equilibria Determinations.

The solubility curves were thought to be reliable because of the success of the tests of the method employed. As has been stated in the Experimental section, three tests were successfully performed.

Firstly, the melting point of a tube filled with conductivity water was found to be 0°C .

Secondly, the experiments of Barnes and Maas on the solubility of pure potassium chloride-water mixtures were repeated and the same results obtained.

Thirdly, the melting points of various organic compounds were measured by this method and found to be in agreement with the values reported in the literature.

As far as estimating the percentage compositions was concerned, it was felt that the weighings and titrations could be performed to give an accuracy of 0.05%.

The rate of heating was sufficiently slow to allow the solid and liquid phases to come to equilibrium.

One test of accuracy lies in the curves themselves. The points all lie on smooth curves and do not vary from the best line which can be drawn through all of them by more than $\pm 0.05\%$. This proves that any error must be a systematic one. This could be either impure material, inaccurately standardised baryta or inaccurate weights.

The first consideration has already been discussed/

discussed in the preceding chapter.

The baryta was standardised against Analar potassium hydrogen phthalate three times without deviation. It was also standardised against oxalic acid.

The weights were certified correct.

Furthermore, the maximum temperature would not have been realised at a composition corresponding exactly to that of the monohydrate in the case of congruent monohydrates if either of the two latter considerations had been in error.

For these reasons, the solubility curves are considered accurate.

Analysis of Hydrates.

The method of analysing the hydrates may seem at first sight to be approximate because of two factors.

Firstly, it is possible that the dissociation pressure of the hydrate might be such that the process of filtration would cause so much dry air to be drawn over the hydrate as to cause its decomposition into a lower hydrate plus water vapour.

Secondly, it is possible that the process of filtration might be inefficient in separating the hydrate from the solution giving a wet solid and consequently a lower percentage composition.

In considering these points we must differentiate between the hydrates which were stable at room temperature or approximately room temperature and those which/

which were stable only at much lower temperatures.

The hydrates stable at room temperature were only filtered for several minutes. They were then pressed between filter paper several times until the crystals looked perfectly dry. Several determinations gave the same results as is shown below for the case of p-bromobenzene sulphonic acid.

Results: a) Solution A of initial concentration 80.01% yielded on filtration at 21°C crystals of composition 83.99% corresponding to 2.507 molecules of water.

b) Solution B of initial concentration 81.10% yielded on filtration at 25°C crystals of composition 84.03% corresponding to 2.501 molecules of water.

The hydrates only stable at temperatures much below room temperature were filtered for thirty to sixty minutes. The vapour pressures of the saturated solutions at these temperatures is of the order of one or two mm. and the dissociation pressures of the hydrates will be even smaller. Thus it is felt that the process of filtration for the time stated will not decompose the hydrates.

As far as the second factor is concerned, it must be stated that it is very difficult to filter and obtain perfectly dry crystals. It was for this reason that the crystals were pressed between filter papers. This was found to result in crystals of a very dry appearance and which gave on analysis compositions close to probable hydrates.

As/

As can be seen from the solubility curves no result was obtained which was not in harmony both with the solubility curve and with neighbouring hydrates.

These solubility curves display certain interesting points.

From these curves, it is possible to divide the acids into two groups.

In the first group, we have benzene sulphonic acid, p-toluene sulphonic acid and p-fluorobenzene, p-chlorobenzene and p-bromobenzene sulphonic acids. These all possess monohydrates of congruent melting point. Relative to the rest of the curve, in each case these monohydrates are very stable, and this indicates that their structures are in some way different from the higher hydrates and the anhydrous acids. A significant point is the slope of the solubility curves for the monohydrates. In almost every case, they are of steeper gradient than the solubility curves for the higher hydrates. We will now consider them individually. The benzene sulphonic acid monohydrate is the least stable of the monohydrates. It has a fairly low melting point (52.5°C) and does not extend over a very great range of temperature or composition (15.5°C to 52.5°C and 87.6% to 95.55%).

Although the solubility curve is steep, that of the dihydrate is almost equally steep. Also, the melting point of the anhydrous acid is higher than that of the monohydrate.

The/

The p-toluene sulphonic acid monohydrate is the most stable. Its melting point is high (104.8°C) and it is stable over a very large range of temperature and composition (-0.7°C to 104.8°C and 67.6% to 99.5%).

This monohydrate is the only one to exist as a phase, stable in contact with solutions, below 0°C . A further point of interest is the fact that the monohydrate-anhydrous acid eutectic point is at 99.5% and 38°C . The anhydrous melts far below the monohydrate at 43°C .

The three p-halogen benzene sulphonic acids are all of comparable stability as judged from the solubility curves. All melt fairly high and are protected by steep curves. The solubility curve of p-fluorobenzene sulphonic acid was not continued beyond 98% (%age acid by weight). This was because the mixtures became difficult to crystallise. This point will be discussed later, but it is thought that it may possibly indicate a low melting point for the anhydrous acid. This would mean that the composition at the eutectic point was near to the pure anhydrous acid.

The monohydrate-anhydrous acid eutectic point for p-chlorobenzene sulphonic acid is near the anhydrous acid (98.5% and 55°C approximately) while the melting point of the anhydrous acid is at 64°C . This is 36°C below that of the monohydrate.

The composition and temperature of the monohydrate-anhydrous/

anhydrous acid eutectic point for p-bromobenzene sulphonic acid is 96.5% and 76°C respectively. The melting point of the anhydrous acid is 104°C .

Although it cannot be stated definitely, owing to the uncertainty regarding the p-fluorobenzene sulphonic acid, it seems on the evidence that there is a rise in melting point for the anhydrous acids from p-fluorobenzene sulphonic acid to p-chlorobenzene sulphonic acid, and to p-bromobenzene sulphonic acid. This is what might be expected. In consequence of this rise in melting point of the anhydrous acids, the eutectic point temperatures also increase in the same order. The composition at the eutectic points decreases from fluoro to bromo. This is a consequence of the fact that the monohydrates are all of comparable melting point and % composition.

A further characteristic of all members of this group of acids, with the exception of p-toluene sulphonic acid, is the presence of the 2.5-hydrate. The absence of the 2.5-hydrate in p-toluene sulphonic acid may be due to the over-riding stability of the monohydrate. The reason for this 2.5 hydrate is not known. These hydrates are very easily dehydrated to the monohydrate so presumably the water is not strongly held. None of them are of congruent melting point.

A point of interest is that the steepness of the solubility curve falls off as we proceed from p-fluoro- to p-chloro- and to p-bromo-, and the transition point rises/

rises from 21°C for p-fluoro-, to 29°C for p-chloro- and to 34.7°C for p-bromobenzene sulphonic acid.

The 2.5-hydrate for benzene sulphonic acid is the most unstable. It extends over a very short range of temperature and composition (-4.5°C to -2.3°C and 74.4% to 77.6%) and the corresponding solubility curve has only a small gradient. This instability is in keeping with the properties of the other hydrates of this acid.

The p-chloro- and p-bromobenzene sulphonic acids form only the two hydrates, namely, the monohydrate and the 2.5-hydrate. Benzene sulphonic acid and p-fluorobenzene sulphonic acid each form four hydrates, namely, a trihydrate, a 2.5-hydrate, a dihydrate and a monohydrate for benzene sulphonic acid, and a 4 hydrate, a trihydrate existing in two forms, a 2.5-hydrate and a monohydrate for p-fluorobenzene sulphonic acid.

The p-toluene sulphonic acid forms only two hydrates, the monohydrate already described and a 4-hydrate existing in two forms, both forms being easily dehydrated and having a solubility curve of slight gradient.

It would therefore seem that aromatic sulphonic acids with no substituent or only a small substituent such as fluorine are more capable of forming a range of hydrates than aromatic sulphonic acids with a fairly large substituent.

The second group of acids contains the o-toluene sulphonic acid and p-nitrobenzene sulphonic acid. These two/

two acids have only one thing in common, namely the fact that they both form stable dihydrates of congruent melting points. Otherwise, they differ considerably. The o-toluene sulphonic acid forms a monohydrate of congruent melting point. The p-nitrobenzene sulphon-ic acid seems to require the two molecules of water of crystallisation to form a stable crystal. Attempts to determine the solubility curve between the compositions of the dihydrate and the anhydrous acid gave only a series of approximate points since the acid decomposed on heating to temperatures above 100°C. In comparison with the o-toluene sulphonic acid, however, it must be said that the temperatures there were much lower, being less than 62°C.

Another difference is that whereas the o-toluene sulphonic acid forms no hydrate higher than the dihydrate, the p-nitrobenzene sulphonic acid forms a 4-hydrate, possessing a solubility curve of slight gradient, and which on exposure to air loses water to form the dihydrate. The p-nitrobenzene sulphonic acid differs from the rest of the acids in hydrate formation.

This may be due to the fact that the nitro group is a group which severely drains the benzene ring of electrons. On the other hand, it may be due to the fairly large size of the NO₂ group. In any case, it must be emphasised that the presence of two molecules of water results in the formation of a very stable crystal/

crystal. The anhydrous acid, prepared by dehydration at 55°C , gains moisture, on exposure to the atmosphere, to form the dihydrate and the 4-hydrate loses water to form the dihydrate. This acid also differs from the other acids in the temperature and composition of the ice-acid eutectic.

In the other acids, this eutectic lies at a temperature of $-35^{\circ}\text{C} \pm 8^{\circ}\text{C}$ and a composition of $57\% \pm 5\%$. p-Nitrobenzene sulphonic acid has an ice-acid eutectic at -8°C and composition 40%.

Apart from the p-nitrobenzene sulphonic acid, these ice-acid eutectic points lie at a fairly high concentration of acid. This is a consequence of the formation of low hydrates, and the fact that the monohydrate solubility curves are very steep.

Two of the acids form hydrates which crystallise in two crystallographic modifications. These are p-toluene sulphonic acid 4-hydrate and p-fluorobenzene sulphonic acid trihydrate. In each case the two different modifications differ considerably in appearance and can be easily recognised. In the case of the p-toluene sulphonic acid 4-hydrate, over the range of composition 53% to 62.5% except for the point (54.87%, -18.5°C) only the metastable 4-hydrate could be crystallised out. There is a general rule that if a substance can crystallise in two modifications, then the metastable form will crystallise out first/

first, then transitioning to the stable phase. At the low temperatures here prevailing, the rate of transition is probably very slow.

A curious phenomenon was the appearance in certain concentration ranges of mixtures which were very difficult to crystallise. One such range was the o-toluene sulphonic acid near the ice-acid eutectic point. In this case the ice phase could be crystallised out as a metastable phase at a fairly low temperature and the temperature of disappearance of the last crystal taken in a fairly fluid solution. When it was attempted to crystallise out the dihydrate, only a glassy solution could be obtained at compositions 55% to 60%. On seeding with a crystal of dihydrate, the acid slowly crystallised out, but taking the point at which the last crystal disappeared was difficult, as the solutions were very viscous.

Two other portions of the curves at which this difficulty was encountered were the range 95% to 100% for o-toluene sulphonic acid and the range 98% to 100% for p-fluorobenzene sulphonic acid. This failure to crystallise is thought to be due to the high viscosity. It is thought that it indicates a low eutectic, probably very close in composition to 100% and an anhydrous acid of low melting point. It may be that the eutectic point and the melting point of the anhydrous acid lie below room temperature, since mixtures/

mixtures of these acids of composition greater than 98% were kept in a vacuum system at room temperature in contact with phosphorus pentoxide for eighteen months without a sign of crystallisation.

In conclusion, it can be stated, that, in the majority of cases, the stable monohydrate, which, from theoretical considerations would be expected to have a crystal lattice possessing a degree of ionic character with the possible tendency to form entities H_3O^+ and RSO_3^- , has been obtained. With the exception of the dihydrates of o-toluene sulphonic acid and p-nitrobenzene sulphonic acid, the higher hydrates are much less stable and more easily dehydrated, indicating that the extra water is not bound up in the crystal lattice in the same manner as in the monohydrate.

Solid-Liquid-Vapour Equilibria.

The accuracy of the vapour pressure readings along the line of univariant equilibrium (involatile acid hydrate-saturated solution - water vapour) depends mainly on five factors.

Firstly, it is necessary to have pure compounds.

Secondly, there must be no foreign gases present.

Thirdly, there must be a means of maintaining accurate temperature control.

Fourthly, it is essential to have a means of measuring the pressure accurately.

Fifthly, the system must be in equilibrium.

The acids were pure initially, as described in previous chapters. The time during which they were kept in the reaction chamber varied with the temperature owing to the different times required to establish equilibrium. In the great majority of cases, the concentration of the solutions was very high and accordingly rather long times were required. No determination was considered reliable unless the solution at the conclusion of the measurements showed complete absence of free sulphuric acid. Slight decomposition in some cases was indicated by the vapour pressure showing a continued slight rise. This behaviour, particularly at the higher temperatures, required the frequent renewal of the solutions. It was also found that recognisable breaks occurred in the/

the curves at the same temperature as in the solubility curves. There was no tendency for the higher hydrates to exist above the transition points, showing that the water is fairly easily removed from the higher hydrate crystal lattice.

No pressures were obtained at temperatures above 98°C because of the difficulty of finding a satisfactory thermostat liquid. This liquid must not corrode the metal heaters, must be involatile, must be transparent, have a fairly high boiling point and have a fairly high specific heat. Silicone oil would have been suitable, but there were not sufficient supplies available. Dibutyl phthalate was tried, but it was found that it infiltrated through the ground glass surfaces of the joints and traps into the reaction vessel.

The solid was crystallised out in the reaction chamber in vacuo to ensure that no air was trapped in the crystals. The method of preparing the reaction chamber, described in the Experimental Section, is regarded as certain to drive out any foreign gases, and if the compound does not decompose, then no foreign gases can be produced from it during the course of an experiment. It was found by experiment that the grease by itself does not produce any foreign gases.

The temperature control of the bath was found to be accurate to $\pm 0.02^\circ\text{C}$ at temperatures below 65°C and/

and accurate to $\pm 0.05^{\circ}\text{C}$ at temperature above 65°C . This caused a variation in pressure as described in the Experimental Section, but the method of averaging out the results gave the correct pressure at the temperature desired.

The pressure was measured by reading the difference in two mercury levels. The clean mercury in the wide tubes ($\frac{1}{8}$ " internal diameter) was found not to "tail" or stick. If the levels were read, the tubes smartly tapped to cause a disturbance of the mercury and then read after a settling down period, the results were found to be identical with the previous ones. The accuracy of the microscope and its ability to read correctly the mercury levels in a thermostat when mounted on a glass plate was demonstrated by the experiment of measuring accurately the difference between two points on the standard rule.

The measurement of the vapour pressure of conductivity water was held to be proof of the reliability of the method of reading the pressures and of the fact that silicone grease in contact with water vapour did not produce any foreign gases.

At a temperature at which previous experiments had demonstrated that there was no decomposition, the pressure was read at frequent intervals for three days. It was found that it remained constant after twenty four hours. Furthermore, experiments during which/

which the vapour pressure decreased from a higher value gave the same result at the same temperature. These were held to indicate that the system was in equilibrium at the value obtained by both methods.

It was found that the points lie on smooth curves. As before, in the discussion on the solubility curves, it was felt that this implied that any error must be a systematic one. The measurement of the vapour pressure of water and the other reasons here argued are held to support the view that a systematic error is unlikely.

The variation in vapour pressure with temperature can be considered qualitatively as follows. As we proceed along the three phase curve in the direction of rising temperature, the vapour pressure will be influenced in two ways: the rising temperature will tend to increase the vapour pressure while the rise in concentration will tend to reduce the vapour pressure. Thus not infrequently the vapour pressure-temperature curve shows a maximum at some intermediate temperature below the melting point of the solute. A steeply rising solubility curve, on a graph in which temperature is plotted as the ordinate and composition as the abscissa, entails a small change in composition over a large range of temperature, in which case the appearance of the pressure maximum will, in general, be displaced towards higher temperatures, while a less/

less steeply rising curve will lead to the early appearance of the maximum. For the present monohydrates the maxima occur only a few degrees less than the melting point temperatures, and it is of interest to note that the curve, where the benzene sulphonic acid dihydrate is the stable solid phase, also shows a maximum.

These features of the vapour pressures can be derived theoretically. The first comprehensive treatment of heterogeneous equilibria was given by Gibbs. His treatment was rigorously based on fundamental principles.

From his fundamental equation for each of the phases

$$Vdp = Sdt + m_1 d\mu_1 + m_2 d\mu_2 + \dots + m_n d\mu_n$$

where p = pressure

t = temperature

$m_1 m_2 \dots m_n$ = the quantities present of the independent components of the phase considered

V = volume of the phase considered

S = entropy of the phase considered

μ = chemical potential

Morey has deduced the equation

$$\frac{dp}{dt} = \frac{(s^v - s^l) - \left\{ \frac{x^v}{x^s} - \frac{x^l}{x^l} \right\} (s^s - s^l)}{(v^v - v^l) - \left\{ \frac{x^v}{x^s} - \frac{x^l}{x^l} \right\} (v^s - v^l)}$$

where v = specific volume

s = specific entropy

x = weight fraction of solute, and

superscripts v , l and s refer to vapour, liquid and solid/

solid respectively, and the equation

$$\frac{dt}{dx''} = \frac{-1}{(1-x'')} \frac{\partial \ln 2}{\partial x''} \frac{\Delta v^{32}(x' - x'') - \Delta v^{12}(x''' - x'')}{\Delta v^{32} \Delta s^{12} - \Delta v^{12} \Delta s^{32}}$$

$$\text{where } \Delta v^{12} = (v' - v'' - (x' - x'') \frac{\partial v''}{\partial x''})$$

$$\Delta s^{12} = (s' - s'' - (x' - x'') \frac{\partial s''}{\partial x''})$$

and the single, double and triple accents refer to the three co-existing phases.

This latter is a general equation which applies to any three phase equilibrium in a two component system.

The first equation may be used to predict the general trend of the vapour pressure results.

In the numerator of the R.H.S. we have the entropy differences $(s^v - s^l)$ and $(s^s - s^l)$. The entropy of the vapour is greater than that of the liquid by the entropy of vapourisation. Thus $(s^v - s^l)$ is the dominant term in the numerator which is therefore positive. In the denominator, the dominant term is the volume difference $(v^v - v^l)$ which is large and positive. As the temperature increases, the specific entropy of the vapour continually decreases, and consequently the numerator decreases. Furthermore, the increasing vapour pressure increases the density of the vapour hence decreasing its specific volume. The denominator therefore decreases.

At low temperatures the relative rates of decrease are such that $\frac{dp}{dt}$ increases and the vapour pressure curves are concave downwards.

The/

The sulphonic acid content of the liquid increases with temperature, and there comes a point at which the ratio $\frac{(x^v - x^l)}{(x^s - x^l)}$ becomes such that the entire second term in the numerator equals the first term. At this point $\frac{dp}{dt} = 0$ and we have the maxima in the vapour pressure curves.

On further increase in temperature, x^l continues to increase and the numerator thus becomes negative. The denominator is still positive so the pressure-temperature curve has a negative gradient.

As the water content decreases, the coefficient $\frac{(x^v - x^l)}{(x^s - x^l)}$ of the second term of the denominator increases rapidly, the denominator approaches zero and the gradient of the pressure temperature curve $\frac{dp}{dt}$ becomes infinite. This occurs when $x^s = x^l$ i.e. at the melting point. The vapour pressure curves of the monohydrates should thus have vertical tangents at the respective melting points. This is not reached in any of the present graphs owing to the fact that with so little water present temperatures are relatively high, and it was impossible to reach equilibrium before significant decomposition had occurred.

On application of Morey's second equation to the three phase system it is clear that the term $\frac{1}{1 - x''}$ is necessarily positive. It has been shown by Gibbs that $\frac{\delta \mu_2}{\delta m_2}$ is always positive and therefore it follows/

follows that $\frac{\delta \Delta}{\delta x}$ must be positive also.

In the denominator Δv^{sl} is usually negative, Δs^{sl} always positive and therefore the first term is usually negative. In the second term, Δv^{vl} is positive, Δs^{sl} is negative, making the second term always negative. Since Δv^{vl} is the preponderant factor, the second term is greater than the first, and, since this term has a negative sign, the denominator is positive.

On considering the numerator, Δv^{sl} is usually negative and $(x^v - x^l)$ negative, so the first term is positive in the usual case. The quantity Δv^{vl} is dominant in the numerator also: its product with the term $(x^s - x^l)$ is always positive, but as it bears a negative sign, the numerator is usually negative.

This makes $\frac{dt}{dx}$ positive and the temperature-composition curve has usually a positive slope.

As in the case of the pressure-temperature curve, a point is reached at which the algebraic sum of the terms of the numerator is zero, and the curve has a maximum. This is, in the present cases, the melting points of the congruent hydrates.

In the case of the hydrates of incongruent melting point, this composition is not reached.

The difficulties involved in the solution of these rigorous equations have lead to attempts to deduce other simpler equations, which, though lacking the/

the rigour of Gibb's treatment have the advantage of being applicable in a quantitative manner to experimental data.

One such attempt has been that of Dingemans and his collaborators. They have deduced, from consideration of their data regarding the vapour pressures of saturated aqueous solutions of inorganic salts and by calculations based on Raoult's law, a series of equations which deal with the composition, vapour pressure and temperature at the maxima in the three phase curves.

The solution of the equations for composition and vapour pressure involve terms, such as the heat of fusion, which for these sulphonic acids are unknown. However, the equation deduced by Dingemans and Korvezee for the temperature of the maxima can be applied to these sulphonic acid-water systems.

Temperature is given by

$$\frac{1}{T_{\max}} - \frac{1}{T_f} = \frac{R}{Q_v} = .00021$$

where $T_{\max}$ = temperature of the pressure maximum

T_f = melting point of the solute

R = gas constant

Q_v = latent heat of evaporation of water per mole.

This would mean that the maximum was only dependent on the melting point of the solute.

However, as can be seen from the following table, there is a wide divergence between the observed and the calculated values of $T_{\max}$.

Acid	T calculated	T observed
Benzene sulphonic acid monohydrate	31.7°C	48.0°C
o-Toluene sulphonic acid dihydrate	39.9°C	58.5°C
p-Fluorobenzene sulphon- ic acid monohydrate	60.6°C	80.0°C
p-Chlorobenzene sulphon- ic acid monohydrate	73.2°C	93.4°C
p-Bromobenzene sulphonic acid monohydrate	64.5°C	84.4°C

As has been previously stated, the most outstanding feature of these maxima is that they lie very close to the melting points of the monohydrates.

Heats of Solution

The heats of solution of the monohydrates of benzene sulphonic acid, p-toluene sulphonic acid and p-fluorobenzene, p-chlorobenzene and p-bromobenzene sulphonic acids and the heats of solution of the dihydrates of o-toluene sulphonic acid and p-nitrobenzene sulphonic acid were measured at 50°C from solubility and vapour pressure measurements employing the equation

$$\Delta H_{sol} = \left(x - \frac{55.51}{m} \right) RT^2 \left(\frac{dm}{dT} \right)_{sat.} \left(\frac{\partial \ln a}{\partial m} \right)_T$$

This is a precise thermodynamic equation which can be applied to solutions of any kind, ideal or non-ideal, regular or irregular, electrolytic or non-electrolytic, in equilibrium with hydrated or unhydrated solutes of any sort. The accuracy of the calculation is limited only by the quality of the experimental data.

Activity coefficients at low concentrations are frequently obtained by freezing point or e.m.f. determinations, but at higher concentrations, methods involving directly or indirectly (i.e. isopiestic) the measurement of vapour pressures are often more convenient, and this is the method employed here.

The activity of the solvent is usually given with sufficient accuracy by the equation $a = p/p_0$ where p = the vapour pressure of the solvent over the solution and p_0 = the vapour pressure of the pure solvent at the same temperature.

Strictly speaking, fugacities should be used instead of pressures, but, if the solution is aqueous and the temperature is not too close to the boiling/

point, the vapour behaves in a near-ideal manner and the distinction between fugacity and pressure becomes negligible. With sufficient vapour pressure data it is therefore an easy matter to calculate a as a function of m .

The data required to solve this equation are

- a) the number of molecules of water which the hydrate possesses
- b) the variation of composition with temperature for the saturated solution near to the temperature at which the measurement is taking place
- c) the solubility at the desired temperature and
- d) the variation of the vapour pressure with composition at the temperature at which the measurement is taking place.

The number of molecules of water possessed by the hydrate is in the present work easily determined since all the relevant hydrates were of congruent melting point.

The accuracy of the solubility curves has already been discussed.

The variation of vapour pressure with composition involves firstly a measurement of pressure whose accuracy has already been discussed and an analysis of the solution. The method of measuring the composition involves the same weighing and titrating procedure as in the solubility measurements and reaches the same standard of accuracy.

As/

As can be seen from the graphs (Table No.20 to Table No.33) the points lie on smooth curves. This suggests that if there is an error it is probably a systematic one. The reasons against a systematic error are the same as were discussed in the chapter dealing with the accuracy of the solubility measurements. In this case the important point is that it is a gradient which we are measuring. This will not be greatly affected by a systematic error provided it is not large.

The heats of solution are given in Table No.34.

The errors in the calculation must now be estimated. There are six terms in the equation. Three of them, x , R and T can all be determined accurately. The value of m is taken from the solubility curve. However, it is also required for the determination of the activity coefficient. A value of m which did not give a smooth curve with the other values on the pressure-composition curve would be wrong. Therefore, in practice, the value of m is determined by two different series of measurements, and its value must satisfy both requirements. The margin for error in this case is too small to seriously affect the final figure.

There remains the two gradients. The different gradients which could reasonably be drawn are here listed for the acids and the variation in the final answer which differs for each acid is calculated in kg.cals./mole.

Acid	$\frac{dm}{dt}$	$\frac{1}{p} \frac{dp}{dm}$	Heat of Solution
Benzene sulphonc acid monohydrate	1.556 1.490	0.1955 0.2274	1.64 1.99
p-Toluene sulphonc acid monohydrate	0.1538 0.1582	0.0839 0.0841	6.15 6.35
o-Toluene sulphonc acid dihydrate	0.4044 0.4301	0.04732 0.04976	4.86 5.43
p-Nitrobenzene sulph: ionic acid dihydrate	0.09574 0.09975	0.06635 0.07015	4.07 4.48
p-Fluorobenzene sulph: ionic acid monohydrate	0.2076 0.1992	0.07604 0.07635	4.09 4.49
p-Chlorobenzene sulph: ionic acid monohydrate	0.1306 0.1382	0.07670 0.07857	3.62 3.92
p-Bromobenzene sulph: ionic acid monohydrate	0.2217 0.2145	0.03144 0.03002	1.84 1.66

Consideration will now be given briefly to what the term heat of solution involves.

The nature of the forces involved in these solutions is very complex. Account must be taken of the facts that these sulphonc acids are strong electrolytes and that the solutions concerned are very concentrated. It is highly probable therefore that the great majority of the ions will be paired and their freedom of movement will be much restricted. Also, water is an associated polar liquid whose structure is not yet known with certainty.

The/

The problem may be contrasted with the simple cavity treatment applied to non-electrolytes in non-polar solvents by Hildebrande for measuring heats of dilution.

In this case the heat of transfer of a molecule A from its pure liquid to a solution B is divided into three operations.

1. Removal of the molecule A from its own pure liquid, involving a heat of vapourisation.
2. Formation of a cavity in solution B to accommodate molecule A.
3. Introduction of the molecule A into the cavity.

In simple cases, agreement between theory and experiment is satisfactory. The calculations however become much more difficult when the solute and solvent molecules differ simply in size, and so far no satisfactory treatment has been given for concentrated solutions involving electrolytes and polar solvents.

As has been pointed out in the Introduction, Falkenhagen has made some calculations on the energy relations of infinitely dilute solutions of alkali halides and has concluded that the heat of solution may be expressed as the difference between the lattice energy and the heat of hydration of the separate ions. This treatment can be applied to the present problem only in an extremely qualitative manner owing to the difficulty/

difficulty of assessing lattice energies and heats of hydration, and also since the experimental figures relate to concentrated solutions.

The lattice energies of these sulphonic acids may be placed in the following order from considerations of melting point, gradient of solubility curve and ease of dehydration.

The heats of hydration are influenced by the strength of the acid group, presence of a polar substituent and is dependent on whether two molecules of water or only one are present in the hydrate. General consideration of these factors gives an approximate order of

This would give an approximate order for the heats of solution of

The actual order is

In/

In view of the very qualitative nature of the treatment, closer agreement between the theoretical and experimental orders could^{not}/be expected.

Solid-Vapour Equilibria.

As has been stated in the Experimental Section, dissociation pressures were difficult to measure and have been realised only over very short ranges of temperature for the dissociating system

monohydrate $\rightleftharpoons$ anhydrous acid + water vapour
for benzene sulphonic acid and p-bromobenzene sulphonic acid. The chief difficulty was the length of time required to establish equilibrium. This was possibly due to the fact that there would be in the system only about $\frac{1}{2}$ molecule of water for each molecule of sulphonic acid. From this difficulty another arose. The sulphonic acids decomposed if left at high or moderately high temperatures for a long time. Temperatures which would not produce decomposition meant that equilibrium could be reached only in a prohibitively long time and thus satisfactory results were obtained only over a narrow range of temperature. We will now consider the results of the methods described.

The first method made use of the same apparatus as was used to measure the vapour pressure along the three phase lines. The same precautions were taken to ensure the absence of foreign gases, to maintain accurate temperature control and to read correctly the mercury levels. The sole difference lay in the composition of the water-sulphonic acid mixture in the reaction/

reaction vessel. The main measurements were carried out at 50°C on p-bromobenzene sulphonic acid. This temperature did not appear to cause decomposition, but nevertheless the mixture was frequently renewed. A dissociation pressure of 1.54mm. of mercury was obtained 10 times using a different mixture each time and seems reliable. The same value was obtained when equilibrium was approached either from below or above the true equilibrium pressure. The curious effect in which the pressure goes down to a value of 0.54mm. on first allowing water vapour to enter the system is probably an adsorption effect, the water molecules being held on the sulphonic acid surface and then slowly released as the reaction

monohydrate $\rightleftharpoons$ anhydrous acid + water vapour comes to equilibrium. The effect is quite reproducible and a whole series of such values at temperatures from 30°C to 74°C have been obtained. It was thought at one time that this adsorption effect was associated with decomposition of the sulphonic acid and formation of free sulphuric acid. However, the proved absence of the latter in the mixtures at the conclusion of the experiments and the reproducibility of the effect render this view unlikely.

Other measurements of the true dissociation pressure were taken at 55°C and 40°C and a plot of log P against $\frac{1}{T}$ gave a straight line. A slightly different procedure was occasionally employed in which/

which the value of 1.54mm. of mercury was first obtained at 50°C and then the temperature readjusted to the required point without further disturbance of the system. This was not so successful as was hoped, because it meant that the total time required was twice as long and only one result could be obtained from each sample.

The same procedure was employed in the determination of the equilibrium,

and a series of results have been obtained over the range 20°C - 30°C. These values are very small and consequently cannot be of high accuracy.

Simple tensimeter methods were tried for all the acids at fairly low temperatures (18°C - 25°C). The results could not be accurately reproduced and are of little value. The difficulties were the same - long periods required to achieve equilibrium, difficulty of removing all traces of air and very low dissociation pressures.

The isopiestic method gave promising results, but the time factor was again prohibitive. On the assumption that the value of 1.54mm. for p-bromobenzene sulphonic acid at 50°C was correct, aqueous solutions of sulphuric acid were made up, the vapour pressure being in some cases lower than 1.54mm. and in some cases higher.

From/

From the table of results (Table No.37) it can be seen that both sets are tending to the value of 76% sulphuric acid corresponding to an aqueous vapour pressure of 1.5 - 1.6 mm.

From the $\log P / \frac{1}{T}$ graphs the values of the heats of dissociation have been calculated.

p-bromobenzene sulphonic acid monohydrate $\rightleftharpoons$ anhydrous acid

+ water vapour = 14.1 kg.cals./mole of water vapour.

benzene sulphonic acid monohydrate $\rightleftharpoons$ anhydrous acid

+ water vapour = 22.5 kg.cals/mole of water vapour.

The heat of dissociation is a product of many factors such as the difference in the lattice energies of the monohydrate and anhydrous/acid crystals which is itself influenced by such values as acid strengths and effect of polar substituents. As these values are unknown, little can be deduced from a knowledge of the heats of dissociation alone. It is however evident that heats of dissociation of the monohydrates are fairly high and in keeping with structures of the type $RSO_3^- \cdot H_3O^+$.

We can compare roughly the free energies of the phase reaction for the two acids since these free energies are proportional to the logarithms of the vapour pressures measured at the same temperature. Since the vapour pressures were not measured at the same temperature (the time required to measure the dissociation/

dissociation pressure of the p-bromobenzene sulphonic acid below 40°C being prohibitive) a direct comparison cannot be made, but by extrapolation it is clear that the dissociation pressures of the p-bromobenzene sulphonic acid would be less than those of benzene sulphonic acid at similar temperatures. This coincides with the fact that dehydration of the benzene sulphonic acid monohydrate to the anhydrous acid proceeded at room temperature in an evacuated desiccator, while p-bromobenzene sulphonic acid remained as the monohydrate.

In view of the difficulties discussed above, the method developed by Pedersen(10) for calculating dissociation pressures has been employed in the following systems:-

benzene sulphonic acid dihydrate $\rightleftharpoons$ benzene sulphonic acid monohydrate + water vapour

p-nitrobenzene sulphonic acid 4-hydrate $\rightleftharpoons$ p-nitrobenzene sulphonic acid dihydrate + water vapour

p-fluorobenzene sulphonic acid 2.5-hydrate $\rightleftharpoons$ p-fluorobenzene sulphonic acid monohydrate + water vapour

p-chlorobenzene sulphonic acid 2.5-hydrate $\rightleftharpoons$ p-chlorobenzene sulphonic acid monohydrate + water vapour

p-bromobenzene sulphonic acid 2.5-hydrate $\rightleftharpoons$ p-bromobenzene sulphonic acid + water vapour

Pedersen has derived the equation

$$(m - n) \ln p_{mn} = (n + 1) \ln p_n - (m + 1) \ln p_m - \int_{xm}^{xn} \frac{d \ln p}{x}$$

where/

where m = number of molecules of water associated with the hydrate S_m

n = number of molecules of water associated with the hydrate S_n

p_{mn} = vapour pressure of a mixture of crystals of S_m and S_n

p_n = vapour pressure of a saturated solution of S_n

p_m = vapour pressure of a saturated solution of S_m

x_n = mole fraction of substance S in saturated solution of S_n

x_m = mole fraction of substance S in saturated solution of S_m

An exact solution of the integral cannot be given if p the vapour pressure is not known as a function of x , the mole fraction of S . If the vapour pressures of the unstable solutions in the concentration interval from x_m to x_n have been measured, a numerical value of the integral may be computed. An approximate formula may be deduced from this equation by making the assumption that p , in the interval from x_m to x_n is a linear function of x , viz:-

$$(n - m) \log p_{mn} = (n + 1 - k) \log p_n - (m + 1 - k) \log p_m \quad k \log \frac{x_n}{x_m}$$

$$\text{where } k = \frac{p_m - p_n}{x_n p_m - x_m p_n}$$

By means of this formula, one may calculate an approximate value of the vapour pressure p_{mn} of the mixture of the crystals S_m and S_n when the solubilities of the two hydrates and the vapour pressures of their saturated solutions have been measured.

This equation was applied to the systems previously mentioned. In each case, the solubility and vapour/

vapour pressure data for the higher hydrate of each system were determined directly but the corresponding data for the lower hydrate at the same two temperatures had to be obtained by extrapolation since measurements on solutions where the lower hydrate was metastable were not possible.

The results are given in the following Table.

Acid	Temp.	Vapour Pressure of the mixture of hydrates		Q kg./cal.
		Monohydrate	Dihydrate	
Benzene sulphonic acid	14°C	1.47 mm.		10.50
	9°C	1.05 mm.		
p-Nitrobenzene sulphonic acid	27°C	15.78 mm.		14.70
	22°C	10.43 mm.		
p-Fluorobenzene sulphonic acid	20°C	4.43 mm.		15.40
	15°C	3.21 mm.		
p-Chlorobenzene sulphonic acid	27°C	8.70 mm.		12.40
	22°C	6.13 mm.		
p-Bromobenzene sulphonic acid	30°C	8.07		12.10
	25°C	5.73		

From these vapour pressures of the mixtures of solid hydrates the factor $\frac{d \log p}{d(\frac{1}{T})}$ was obtained and from this the heats of dissociation Q were calculated by the Clausius-Clapeyron equation and are listed in the Table.

An alternative method of calculating heats of dissociation from solubility and vapour pressure data is/

is as follows. It may be shown that the equation

$$\frac{dp}{dT} = \frac{\Delta H}{T \Delta V} \quad (42)$$

applies to the univariant three phase lines in binary systems, where ΔH is the change of heat content accompanying the formation of the saturated solution from the solid solute and the vapour of the solvent and ΔV is the corresponding volume change. Neglecting the volume of the solid and liquid phases in comparison with that of the vapour, ΔH can be evaluated from the gradient of the three phase line. If this calculation is carried out at a transition point (e.g. the 2.5-hydrate-monohydrate transition points for the p-halogenated benzene sulphonic acids),

ΔH can be found for each hydrate and the heat of dissociation calculated knowing the composition of the solution at the transition point.

The argument in the case of the p-halogenated benzene sulphonic acid 2.5-hydrates $\rightleftharpoons$ p-halogenated benzene sulphonic acid monohydrates + water vapour is as follows.

Let 1 mole of saturated solution at the transition point contain X moles of anhydrous acid and (1 - X) moles of water. On isothermally evaporating the solution so that the monohydrate crystallises out:-

1 mole sat. soln. $\rightarrow$ (1-2X) moles water vapour + X moles monohydrate
 or $\Delta H + \left(\frac{1}{1-2X}\right)$ moles sat. soln. $\rightarrow$ 1 mole water vapour + $\left(\frac{X}{1-2X}\right)$ moles monohydrate
 or $\left(\frac{1-2X}{X}\right) \Delta H + \frac{1}{X}$ moles sat. soln. $\rightarrow$ $\left(\frac{1-2X}{X}\right)$ moles water vapour + 1 mole monohydrate
 (Eg.1)

On isothermally evaporating the solution so that the 2.5-hydrate crystallises out:-

$$\begin{aligned}
 &1 \text{ mole sat. soln.} \rightarrow (1-3.5X) \text{ moles water vapour} + X \text{ moles 2.5-hydrate} \\
 \text{or } &\Delta H_{2.5} + \left(\frac{1}{1-3.5X}\right) \text{ moles sat. soln.} \rightarrow 1 \text{ mole water vapour} + \frac{X}{1-3.5X} \text{ moles 2.5-hydrate} \\
 \text{or } &\left(\frac{1-3.5X}{X}\right) \Delta H_{2.5} + \frac{1}{X} \text{ moles sat. soln.} \rightarrow \left(\frac{1-3.5X}{X}\right) \text{ moles water vapour} + 1 \text{ mole 2.5-hydrate} \\
 &\hspace{15em} \text{(Eg. (2))}
 \end{aligned}$$

Eg. (1) - Eg. (2):-

$$\begin{aligned}
 &\left(\frac{1-2X}{X}\right) \Delta H_1 - \left(\frac{1-3.5X}{X}\right) \Delta H_{2.5} \rightarrow \left\{ \left(\frac{1-2X}{X}\right) - \left(\frac{1-3.5X}{X}\right) \right\} \text{ moles water vapour} \\
 &\hspace{15em} + 1 \text{ mole monohydrate} - 1 \text{ mole 2.5-hydrate} \\
 \text{or } &\left(\frac{1-2X}{X}\right) \Delta H_1 - \left(\frac{1-3.5X}{X}\right) \Delta H_{2.5} + 1 \text{ mole 2.5-hydrate} \\
 &\hspace{15em} \rightarrow 1.5 \text{ moles water vapour} + 1 \text{ mole monohydrate} \\
 \text{or } &\frac{2}{3} \left\{ \left(\frac{1-2X}{X}\right) \Delta H_1 - \left(\frac{1-3.5X}{X}\right) \Delta H_{2.5} \right\} + \frac{1}{1.5} \text{ moles 2.5-hydrate} \\
 &\hspace{15em} \rightarrow 1 \text{ mole water vapour} + \frac{1}{1.5} \text{ moles monohydrate}
 \end{aligned}$$

The quantity $\frac{2}{3} \left\{ \left(\frac{1-2X}{X}\right) \Delta H_1 - \left(\frac{1-3.5X}{X}\right) \Delta H_{2.5} \right\}$ is the heat of dissociation of the 2.5-hydrate. Heats of dissociation for benzene sulphonic acid dihydrate and p-nitrobenzene 4-hydrate may be obtained in a similar manner, viz:-

<u>Acid</u>	<u>Heat of Dissociation</u>
Benzene sulphonic acid dihydrate	$\left\{ \left(\frac{1-2X}{X}\right) \Delta H_1 - \left(\frac{1-3X}{X}\right) \Delta H_2 \right\}$
p-nitrobenzene sulphonic acid 4-hydrate	$\frac{1}{2} \left\{ \left(\frac{1-3X}{X}\right) \Delta H_2 - \left(\frac{1-5X}{X}\right) \Delta H_H \right\}$

The detailed calculation in the case of p-fluorobenzene sulphonic acid 2.5-hydrate is given below.

In the graph opposite the vapour pressures along the three/

VAPOUR PRESSURES OF SATURATED SOLUTIONS of p-FLUOROBENZENE
SULPHONIC ACID

three phase lines are plotted as $\log p$ against $\frac{1}{T}$ and the following factors obtained.

$$\frac{d(\log p)}{d(\frac{1}{T})} \text{ (monohydrate)} = - \frac{.183}{.00008}$$

$$\Delta H_1 = 10,470 \text{ cal.}$$

$$\frac{d \log p}{d(\frac{1}{T})} \text{ (2.5-hydrate)} = - \frac{.193}{.000122}$$

$$\Delta H_{2.5} = 7,243 \text{ cal.}$$

The composition at the transition point = 77.0%

$$X_p = 0.255$$

$$\left(\frac{1-2X}{X}\right) = 1.921 \text{ and } \left(\frac{1-3.5X}{X}\right) = 0.4196$$

$$Q = \frac{2}{3} \left\{ \left(\frac{1-2X}{X}\right) \Delta H_1 - \left(\frac{1-3.5X}{X}\right) \Delta H_{2.5} \right\}$$

$$= \frac{2}{3} \left\{ 10,470 \times 1.921 - 7,243 \times .4196 \right\}$$

$$= 11,380 \text{ cal./mole of water vapour.}$$

In certain cases, such as p-bromobenzene sulphonic acid and p-chlorobenzene sulphonic acid, the plot of the logarithm of the vapour pressures against the reciprocal of the absolute temperature gives two gradients which are extremely similar. This introduces no major errors since both ΔH_1 and $\Delta H_{2.5}$ are multiplied by a composition factor, $(1 - \frac{2X}{X})$ and $(1 - \frac{3.5X}{X})$, respectively and the respected products are appreciably different. The dominant factor in the calculation is $\left(\frac{1-2X}{X}\right) \Delta H_1$.

The/

VAPOUR PRESSURES OF SATURATED SOLUTIONS OF p-CHLOROBENZENE
SULPHONIC ACIDS.

The results are tabulated below.

Acid	ΔH		Heat of Dissociation Q
	ΔH_1	ΔH_2	
Benzene sulphonic acid	9,877	2,706	10,500 cal.
p-Nitrobenzene sulphonic acid	ΔH_2 10,350	ΔH_4 6,516	14,000 cal.
p-Fluorobenzene sulphonic acid	ΔH_1 10,470	$\Delta H_{2.5}$ 7,243	11,400 cal.
p-Chlorobenzene sulphonic acid	ΔH_1 9,417	$\Delta H_{2.5}$ 9,417	9,400 cal.
p-Bromobenzene sulphonic acid	ΔH_1 9,303	$\Delta H_{2.5}$ 9,303	9,100 cal.

On comparing these values with those obtained by the Pedersen procedure, it can be seen that only the values of Q for benzene sulphonic acid dihydrate and p-nitrobenzene sulphonic acid 4-hydrate agree closely. As several of the results required to solve Pedersen's formula were obtained by extrapolation and since the formula itself is approximate, it is felt that the values obtained from the difference of the ΔH factors are probably the more accurate. Even so, however, the results are probably not accurate to more than ± 1 Kg.cal.

SUMMARY.

Benzene sulphonic acid and six monosubstituted benzene sulphonic acids have been obtained in a pure state. The solubility curves for each of the seven acids have been determined by the synthetic method. These show that apart from one case, all the acids form stable monohydrates of congruent melting point in keeping with a suggested structure $\text{RSO}_3^- \text{H}_3\text{O}^+$. In two cases, a stable dihydrate of congruent melting point was obtained. Other hydrates were formed which were easily dehydrated and of incongruent melting point.

The vapour pressure along the three phase lines was determined for the most stable hydrate of each acid, and the point of maximum pressure established in the case of five of the acids. In contrast to inorganic compounds, these maxima lie close to the respective melting points, and do not agree with those calculated theoretically from a formula given by Dingemans.

From solubility measurements and activity co-efficients, the latter determined by measurements of vapour pressure of unsaturated solutions, the heat of solution of the most stable hydrate of each acid was calculated at 50°C. Attempts to relate these heats of solution to structure differences were without success.

From/

-liquid-

From solid-vapour equilibria data, the heat of dissociation of certain of the higher hydrates of five of the acids was calculated by two different methods and results of the correct order of magnitude were obtained.

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