CHEMISTRY OF TITANIUM COMPOUNDS IN CONCENTRATED SULPHURIC ACID SOLUTION

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ABSTRACT

The reactions of titanium compounds with sulphuric acid have been reviewed, and the general behaviour of oxides, hydroxides, salts and other compounds in sulphuric acid solution has been discussed. The apparent solubilities of titanium dioxide and titanyl sulphate in sulphuric acid were determined. Some titanium sulphate complexes were isolated and analysed, and an X-ray study of these compounds was attempted. Ultra-violet spectroscopic investigations were carried out on the solutions of titanium sulphate in sulphuric acid. For conductivity and cryoscopic determinations, solutions of titanium sulphate in sulphuric acid were prepared from titanium tetrachloride and isopropyl titanate. The electrical conductivity and cryoscopic measurements were undertaken to determine as fully as possible the nature of the sulphate complex present in the solution, and its mode of ionisation. The experimental results are discussed with reference to the probable constitution of solutions of titanium sulphate in c concentrated sulphuric acid.

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(a) Sulphates of Titanium.

Titanium is often grouped with the rare elements but it is more abundant in the lithosphere than copper, lead or zinc(1). However, concentrated deposits of titanium are scarce. Titanium is nearly always a constituent of igneous rocks, and it is very widespread in small amounts, so that almost every soil contains detectable amounts (over 0.5% on the average). The commonest method of manufacturing titanium oxide, which is a very important pigment, is by treating ilmenite ($FeTiO_3$) with sulphuric acid and then hydrolysing the solution(2). In view of the importance of this process, it is noteworthy that the reactions of titanium compounds with sulphuric acid have never been extensively studied.

A study of the phase relations in concentrated sulphuric acid at 100°C(3,4), shows the existence of the following as solid phases:

TiO_2,SO_3,H_2O

$2TiO_2,3SO_3,5H_2O$

$TiO_2,4SO_3,4.5H_2O$

$TiO_2,4SO_3,2H_2O$

$TiO_2,4SO_3$.

$TiO_2,4SO_3$ is the stable, soluble solid phase near the concentration range of concentrated sulphuric acid. The solubility of titanium dioxide is quite low (ranging up to $\sim$ 0.6%, but frequently much less) even at 100°C. There are some solubility data for titanium compounds in sulphate solution, but most of these data relate to dilute sulphuric acid(5).

There are other known sulphates, e.g. $TiOSO_4$, titanyl sulphate, which is formed when titanium dioxide is "fumed down" with sulphuric acid (6). There are also sulphates of bivalent and tervalent titanium, which are of little interest in the present study. Titanium monosulphate, $TiSO_4$, is reported to be formed under certain conditions by the evaporation of a solution of titanium in sulphuric acid(7). Titanous sulphate, $Ti_2(SO_4)_3$, is also said to be formed by dissolving titanium metal in cold sulphuric acid(2). Neutral titanium sulphate, $Ti(SO_4)_2$, is not known with certainty, but Hayek and Engelbrecht(8), and Chukhlantsev(9), claimed that anhydrous $Ti(SO_4)_2$ can be prepared from titanium tetrachloride and sulphur trioxide in sulphuryl chloride solution.

The pioneer workers on titanium and sulphuric acid have prepared a number of alleged sulphates of titanium by various methods and a list of these is given in Table I.

Table I.

	Compounds	References
Glatzel (1876)	$Ti_2(SO_4)_3.8H_2O$	10
	$Ti(SO_4)_2.3H_2O$	
Ebelmen (1846)	Violet crystals of a titanium sulphate	11
Wöhler and Deville (1858)	Violet crystals	12
Stähler and Wirthwein (1905)	$3Ti_2(SO_4)_3.H_2SO_4.25H_2O$	7
Blondel (1899)	$Ti_2O(SO_4)_3.3H_2O$	13
	$TiOSO_4$	
Berzelius (1825)	$TiOSO_4.H_2O$	14
Rose (1823)	$TiOSO_4.H_2O$	15
Ditte (1887)	$TiOSO_4.2H_2O$	16
Blondel (1899)	$TiOSO_4.2H_2O$	13
Rosenheim and Schütte (1901)	$TiOSO_4.5H_2O$	17

There is still controversy as to the existence of some of the above compounds.

(b) General Behaviour of Oxides and Hydroxides in Sulphuric Acid.

When an oxide or a hydroxide is dissolved in sulphuric acid, there is generally a tendency to form

	X_2O_3	$XO(OH)$	$X_2O(OH)_4$	$X(OH)_3$
	$X_2O_2(SO_4)$	$X_2O_2(OH)(HSO_4)$	$X_2O(OH)_3(HSO_4)$	
SO_3 ↓	$X_2O(SO_4)_2$	$XO(HSO_4)$	$X_2O(OH)_2(HSO_4)$	$X(OH)_2(HSO_4)$
	$X_2(SO_4)_3$	$X_2O(SO_4)(HSO_4)_2$	$X_2O(OH)(HSO_4)_3$	
		$XSO_4(HSO_4)$	$X_2O(HSO_4)_4$	$X(OH)(HSO_4)_2$
			$X_2SO_4(HSO_4)_4$	
				$X(HSO_4)_3$

H_2O →

	YO_2	$YO(OH)_2$	$Y(OH)_4$
SO_3 ↓	$YO(SO_4)$	$YO(OH)(HSO_4)$	$Y(OH_3)(HSO_4)$
	$Y(SO_4)_2$	$YO(HSO_4)_2$	$Y(OH)_2(HSO_4)_2$
		$YSO_4)HSO_4)_2$	$Y(OH)(HSO_4)_3$
			$Y(HSO_4)_4$

H_2O →

Fig. 1. Oxy-, hydroxy-, sulphato-, and hydrogen sulphato-derivatives of a trivalent element X and a tetravalent element Y.

a sulphate or hydrogen sulphate, with the elimination of water, but the extent to which this occurs varies widely from one element to another. In general, a wide variety of compounds intermediate between the sulphates and hydrogen sulphates of the sulphuric acid system may be formed. This is illustrated empirically in Fig. I but the formulae do not represent the actual molecular constitution of the compounds, because some may be ionized either completely or partially and some may polymerise.

In Fig. I, moving from top to bottom corresponds to the addition of sulphur trioxide, from left to right across the diagram to the addition of water, and diagonally from upper left to lower right to the addition of sulphuric acid. The compounds in the top row belong entirely to the water solvent-system and those in the bottom ~~diagonally~~ belong to the sulphuric acid solvent-system(18).

(c) "Acids" Characteristic of Aqueous Solutions, in Sulphuric Acid.

The chemistry of solutions in sulphuric acid is interesting because a great variety of different cations are known, many of which cannot exist in aqueous solutions. Many compounds which behave as electrolytes are unfamiliar and cannot be obtained at all in aqueous solution, whereas many compounds which behave as electrolytes in aqueous solution are unstable in sulphuric acid. Most of the "acids" characteristic of aqueous solution chemistry do not behave as acids at all in sulphuric acid solution; they form bases of various types, e.g.:

$$CH_3CO_2H + H_2SO_4 = CH_3CO_2H_2^+ + HSO_4^-$$

$$H_3PO_4 + H_2SO_4 = H_4PO_4^+ + HSO_4^-$$

$$HNO_3 + 2H_2SO_4 = NO_2^+ + H_3O^+ + 2HSO_4^-$$

$$H_3BO_3 + 6H_2SO_4 = 3H_3O^+ + B(HSO_4)_4^- + 2HSO_4^-$$

$$H_2SO_3 + H_2SO_4 = SO_2 + H_3O^+ + HSO_4^-$$

$$HF + 2H_2SO_4 = HSO_3F + H_3O^+ + HSO_4^-$$

Hydrogen chloride is very sparingly soluble in sulphuric acid and hydrogen bromide and iodide are oxidised to bromine and iodine, respectively. Usually perchloric acid is regarded as the strongest known acid, but in sulphuric acid it shows little or no acid properties.

(d) Resemblance of Sulphuric Acid and Water.

Sulphuric acid resembles water as a solvent in many ways. It is an amphoteric solvent and proton transfer between solvent molecules (autoprotolysis) occurs as it does in water; one molecule acts as an acid and the other as a base, as in the following reactions:

$$2H_2O \quad = \quad H_3O^+ + OH^-$$

$$2NH_3 \quad = \quad NH_4^+ + NH_2^-$$

$$2H_2SO_4 \quad = \quad H_3SO_4^+ + HSO_4^-.$$

However, there are also other self-dissociation processes in sulphuric acid. The primary self-dissociation reaction in the concentrated acid is

$$2H_2SO_4 \quad = \quad H_2O + H_2S_2O_7;$$

both the products are further ionised, water extensively and disulphuric acid partially, according to the following equations

$$H_2O + H_2SO_4 \quad = \quad H_3O^+ + HSO_4^-;$$

$$H_2S_2O_7 + H_2SO_4 \quad = \quad H_3SO_4^+ + HS_2O_7^-.$$

The very high electrical conductivity of sulphuric acid is due to the abnormally high mobilities of the HSO_4^- or $H_3SO_4^+$ ions formed by the autoprotolysis and self dehydration reactions; it is again analogous to the high mobilities of H_3O^+ and OH^- in water.

The alkali-metal and some other metal hydrogen sulphates are strong bases in sulphuric acid and are analogous to the hydroxides in water, e.g.

$$KHSO_4 \quad = \quad K^+ + HSO_4^-$$

$$KOH \quad = \quad K^+ + OH^-.$$

The corresponding normal sulphates are completely converted to the hydrogen sulphates, and they are analogous to the metal oxides in water, e.g.

$$K_2SO_4 + H_2SO_4 = 2K^+ + 2HSO_4^-$$

$$K_2O + H_2O = 2K^+ + 2OH^-.$$

(e) Acids and Bases in Sulphuric Acid.

In the sulphuric acid system an acid is any substance that gives rise to the sulphuric acidium ion, $H_3SO_4^+$; a base is any substance which gives hydrogen sulphate ion HSO_4^-. Simple monoprotic acids and bases will ionise according to the equations

$$HA + H_2SO_4 = H_3SO_4^+ + A^-$$

and $$B + H_2SO_4 = BH^+ + HSO_4^-.$$

Reaction between an acid and a base occurs according to the equation

$$H_3SO_4^+ + HSO_4^- = 2H_2SO_4.$$

Although sulphuric acid is an extremely weakly basic solvent a few substances are known which show acidic behaviour. These substances and their acid dissociation constants are given in Table 2(19).

Table 2.

Compounds	Ka, Acid Dissociation constants at 25°C
$HB(HSO_4)_4$	2×10^{-1}
$H_2S_3O_{10}$ etc.	Moderately strong
$H_2S_2O_7$	1.4×10^{-2}
$H_2Pb(HSO_4)_6$	1.1×10^{-2}
HSO_3F	2.3×10^{-3}
$HPb(HSO_4)_6^-$	1.8×10^{-3}
$HAs(HSO_4)_4$	1.5×10^{-3}
HSO_3Cl	9×10^{-4}
$HClO_4$	Very weak
H_2SO_4	2.4×10^{-5}

(f) Inorganic Salts in Sulphuric Acid.

Salts of inorganic acids often undergo complete solvolysis, e.g.:

$$NaCl + H_2SO_4 = Na^+ + HSO_4^- + HCl$$

$$NH_4ClO_4 + H_2SO_4 = NH_4^+ + HSO_4^- + HClO_4$$

$$Na_3PO_4 + 3H_2SO_4 = 3Na^+ + 3HSO_4^- + H_3PO_4$$

$$KNO_3 + H_2SO_4 = K^+ + HSO_4^- + HNO_3$$

(some of the acids formed undergo further reaction). In other cases the salts are insoluble at ordinary temperatures, e.g. AgCl, $CuBr_2$, $AlCl_3$ and $AlPO_4$.

(g) Hydrogen Sulphates in Sulphuric Acid.

Anhydrides in sulphuric acid may be converted into hydrogen sulphates, e.g.(20,21)

$$(CH_3)_3SiOSi(CH_3)_3 + 3H_2SO_4 = 2(CH_3)_3SiSO_4H + H_3O^+ + HSO_4^-$$

The hydrogen sulphates may (a) remain stable; (b) exhibit basic properties, undergoing further ionisation; or (c) behave as acids. For example, under (a) $(CH_3)_3SiSO_4H$ is a stable non-electrolyte. Under (b), nitronium and nitrosonium hydrogen sulphate formed from nitric acid, dinitrogen pentoxide, dinitrogen tetroxide, and dinitrogen trioxide ionize to form nitronium and nitrosonium ions, e.g.(22)

$$NO_2.HSO_4 = NO_2^+ + HSO_4^-$$
$$NO.HSO_4 = NO^+ + HSO_4^-$$

The following equations represent the complete reactions of the other solutes:

$$HNO_3 + 2H_2SO_4 = NO_2^+ + H_3O^+ + 2HSO_4^-$$
$$N_2O_5 + 3H_2SO_4 = 2NO_2^+ + H_3O^+ + 3HSO_4^-$$
$$N_2O_4 + 3H_2SO_4 = NO_2^+ + NO^+ + H_3O^+ + 3HSO_4^-$$
$$N_2O_3 + 3H_2SO_4 = 2NO^+ + H_3O^+ + 3HSO_4^-$$

Some alkyl hydrogen sulphates formed from the reactions of aliphatic alcohols and sulphuric acid undergo ionization according to the following equations:(23)

$$ROH + 2H_2SO_4 = RHSO_4 + H_3O^+ + HSO_4^-$$
$$RHSO_4 + H_2SO_4 = RSO_4H_2^+ + HSO_4^-$$
or $$RHSO_4 = R^+ + HSO_4^-.$$

e.g. $$C_2H_5OH + 2H_2SO_4 = C_2H_5HSO_4 + H_3O^+ + HSO_4^-$$
$$C_2H_5HSO_4 + H_2SO_4 = C_2H_5SO_4H_2^+ + HSO_4^-$$

$$CH_3OH + 2H_2SO_4 = CH_3HSO_4 + H_3O^+ + HSO_4^-$$
$$CH_3HSO_4 = CH_3^+ + HSO_4^-$$

Under category (c) above, boric acid is converted into boron tri(hydrogen sulphate), in sulphuric acid

e.g. $B(OH)_3 + 6H_2SO_4 = 3B(SO_4H)_3 + 3H_3O^+ + 3HSO_4^-$, but the boron tri(hydrogen sulphate) formed is itself an acid and it reacts with hydrogen sulphate ion,

$$B(SO_4H)_3 + HSO_4^- = B(SO_4H)_4^- .$$

One third of the hydrogen sulphate formed is neutralised; nevertheless the overall reaction of the boric acid is still basic,(16)

$$B(OH)_3 + 6H_2SO_4 = 3H_3O^+ + B(HSO_4)^- + 2HSO_4^-.$$

(h) Hydroxy-compounds in Sulphuric Acid.

Some hydroxy-compounds are converted into anhydrides in sulphuric acid

e.g. $$2HOCl + H_2SO_4 = Cl_2O + H_3O^+ + HSO_4^-$$
$$H_2SO_3 + H_2SO_4 = SO_2 + H_3O^+ + HSO_4^-.$$

(i) Experimental Methods.

Sulphuric acid solutions have been studied generally by cryoscopic and conductivity measurements, and examination of Raman, infra-red and ultra-violet absorption spectra. By cryoscopic measurements, the number of moles (ν) of particles (ions and molecules) produced by one mole of any solute may be determined. From conductivity measurements, the number of moles (γ) of hydrogen sulphate ions produced by one mole of the solute can be calculated. The acids in the sulphuric acid system may be titrated with bases such as potassium hydrogen sulphate, benzoic acid, and some nitro-compounds, and the neutralization reactions can be conveniently followed by measuring the electrical conductivity of the solutions.

Knowledge of the values of ν and γ often allows the mode of ionization of the solute to be determined. Some examples are given in Table 3.

The identification and the measurement of the approximate concentrations of the various ionic or molecular species in sulphuric acid have been carried out by study of Raman spectra. For example, nitronium ion NO_2^+ and nitrosonium ion NO^+ were identified and their concentrations were estimated(25,26,27,45).

Table 3.

Examples of Values of ν and γ for some Solutes in Sulphuric Acid Solutions.

System	ν	γ	Ref.
$C_6H_4(NH_2)_2 + 2H_2SO_4$ $= C_6H_4(NH_3)_2^{++} + 2HSO_4^-$	3	2	23
$Ph_3COH + 2H_2SO_4$ $= Ph_3C^+ + H_3O^+ + 2HSO_4^-$	4	2	23
$KMnO_4 + 3H_2SO_4$ $= K^+ + H_3O^+ + MnO_3^+ + 3HSO_4^-$	6	3	28
$B_2O_3 + 9H_2SO_4$ $= 3H_3O^+ + 2B(HSO_4)_4^- + HSO_4^-$	6	1	24
$Sn(OAc)_4 + 10H_2SO_4$ $= H_2Sn(HSO_4)_6 + 4AcOH_2^+ + 4HSO_4^-$	9	4	18

The degrees of ionization of weak bases (such as nitro-compounds)(29) in oleum and also those of some other bases have been determined from their visible and untra-violet absorption spectra(30,31,32).

(j) More Complicated Reactions in Sulphuric Acid.

1. Boron Compounds.

Boric acid and boric oxide dissolve in sulphuric acid according to the following equations(24):

$$H_3BO_3 + 6H_2SO_4 = B(HSO_4)_4^- + 3H_3O^+ + 2HSO_4^-$$

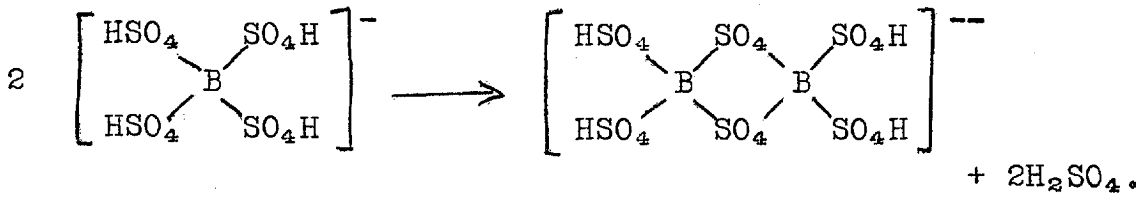
$$B_2O_3 + 9H_2SO_4 = 2B(HSO_4)_4^- + 3H_3O^+ + HSO_4^-.$$

The formation of the boron tetra(hydrogen sulphate) ion indicates that the corresponding acid $HB(HSO_4)_4$ must be a strong acid in the sulphuric acid solvent system. A solution of the free acid is prepared by dissolving boric oxide or boric acid in oleum:

$$H_3BO_3 + 3H_2S_2O_7 = H_3SO_4^+ + B(HSO_4)_4^- + H_2SO_4$$

$$B_2O_3 + 3H_2S_2O_7 + 4H_2SO_4 = 2H_3SO_4^+ + 2B(HSO_4)_4^-.$$

Attempts to prepare the simple salts of the acid $HB(HSO_4)_4$ have not been successful. The crystallised salts of sodium, potassium, ammonium and strontium contain sulphate and boron in the ratio of less than four. They evidently contain polymeric ions formed from the boron tetra(hydrogen sulphate) anion by the elimination of sulphuric acid; e.g.(18) the dimer ion will be



There are many such possibilities for the formation of complex anions from compounds intermediate in composition between $B(HSO_4)_3$ and $B_2(SO_4)_3$. In this respect there is an analogy with the behaviour of the borate ion, which has the formula $B(OH)_4^-$ (33) in the dilute aqueous solution, although there are many solid borates containing complex anions such as $B_4O_7^{--}$ and $B_6O_{11}^{4-}$.

2. Silicon Compounds.

Cryoscopic and conductivity measurements on solutions of methyltriethoxysilane in sulphuric acid over the concentration range 0.015-0.055 m give $\nu = 8.0 - 7.7$ and $\gamma = 2.6 - 2.2$(18). If the reaction is according to the following equation:

$$CH_3Si(OEt)_3 + 9H_2SO_4 = CH_3Si(SO_4H)_3 + 3EtHSO_4 + 3H_3O^+ + 3HSO_4^-$$

then $\nu = 10$ and $\gamma = 3$ should be obtained. It appears therefore that conversion to the sulphate derivative is not complete. The formation of the compound $(SO_4H)_2CH_3SiOSiCH_3(SO_4H)_2$ would give $\nu = 8.5$ and $\gamma = 2.5$.

$$2CH_3(Si(OEt)_3 + 15H_2SO_4 = (SO_4H)_2CH_3.SiOSi.CH_3(SO_4H)_2 + 6EtSO_4H + 5H_3O^+ + 5HSO_4^-.$$

The smaller experimental values of ν and γ show that a mixture of higher polymers is formed. The compounds $Si(OEt)_4$, $Ph_3Si(OH)$, $Ph_2Si(OH)_2$, $Si(OAc)_4$ and $(naphthyl)_3SiOH$ may react with sulphuric acid to form insoluble polymers because they appear to be insoluble in sulphuric acid.

3. Tin Compounds.

Stannic acid and stannic sulphate are very sparingly soluble in sulphuric acid, but salts of sulphate-stannic acid, $H_2Sn(SO_4)_3$,

e.g. $Rb_2Sn(SO_4)_3$
$K_2Sn(SO_4)_3$
$Ag_2Sn(SO_4)_3,3H_2O$
$CaSn(SO_4)_3,3H_2O$
$PbSn(SO_4)3,3H_2O$ have been prepared by evaporating mixtures of stannic oxide, a metal sulphate and sulphuric acid (34,35,36).

Cryoscopic and conductivity measurements on solutions of tetraphenyl tin, triphenyl tin hydroxide and tin tetraacetate in sulphuric acid show the following modes of ionization:

$$Ph_4Sn + 14H_2SO_4 = H_2Sn(HSO_4)_6 + 4PhSO_3H + 4H_3O^+ + 4HSO_4^-$$
$$Ph_3SnOH + 13H_2SO_4 = H_2Sn(HSO_4)_6 + 3PhSO_3H + 4H_3O^+ + 4HSO_4^-$$
$$Sn(OAc)_4 + 10H_2SO_4 = H_2Sn(HSO_4)_6 + 4AcOH_2^+ + 4HSO_4^-.$$

The values of ν and γ decrease with increasing concentration in each case; this is due to the equilibrium between the free acid, its anions, and hydrogen sulphate ion, (18)

$$H_2Sn(HSO_4)_6 + 2HSO_4^- = HSn(HSO_4)_6^- + HSO_4^- + H_2SO_4$$
$$= Sn(HSO_4)_6^{--} + 2H_2SO_4.$$

4. Lead Compounds.

Lead tetraacetate is the only compound soluble in sulphuric acid that has been studied so far and the reaction is(37)

$$Pb(OAc)_4 + 10H_2SO_4 = H_2Pb(HSO_4)_6 + 4AcOH_2^+ + 4HSO_4^-.$$

From the decrease in values of ν and γ with increasing concentration, the two dissociation constants of the hexa(hydrogen sulphate) plumbic acid are calculated to be $K_1 = 1.1 \times 10^{-2}$ and $K_2 = 1.8 \times 10^{-3}$, corresponding with the reactions:

$$H_2Pb(HSO_4)_6 + H_2SO_4 = HPb(HSO_4)_6^- + H_3SO_4^+$$

$$HPb(HSO_4)_6^- + H_2SO_4 = Pb(HSO_4)_6^{--} + H_3SO_4^+.$$

On warming the solutions of hexa(hydrogen sulphate) plumbic acid, bright yellow plumbic sulphate is deposited. Lead dioxide is insoluble and plumbic sulphate is only sparingly soluble in sulphuric acid. The insolubility of the sulphate is due to the formation of polymers and the structure is illustrated diagramat~~y~~ically in Fig. (3).

The potassium salt of trisulphate plumbic acid, $K_2Pb(SO_4)_3$, has been prepared(38); it is only slightly soluble in sulphuric acid. The actual structure has not been determined, but it is suggested that it is highly polymeric and may be constituted in the way broadly indicated by Fig. (4).

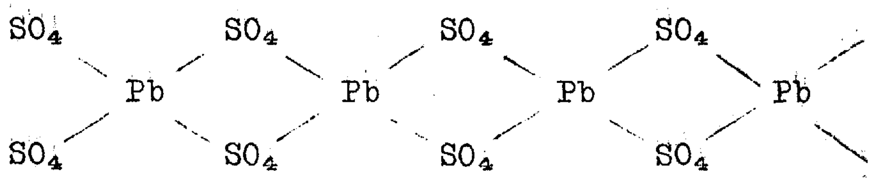

SO_4
SO_4
SO_4
SO_4
Pb
Pb
Pb
Pb
SO_4
SO_4
SO_4
SO_4

Fig. 3.

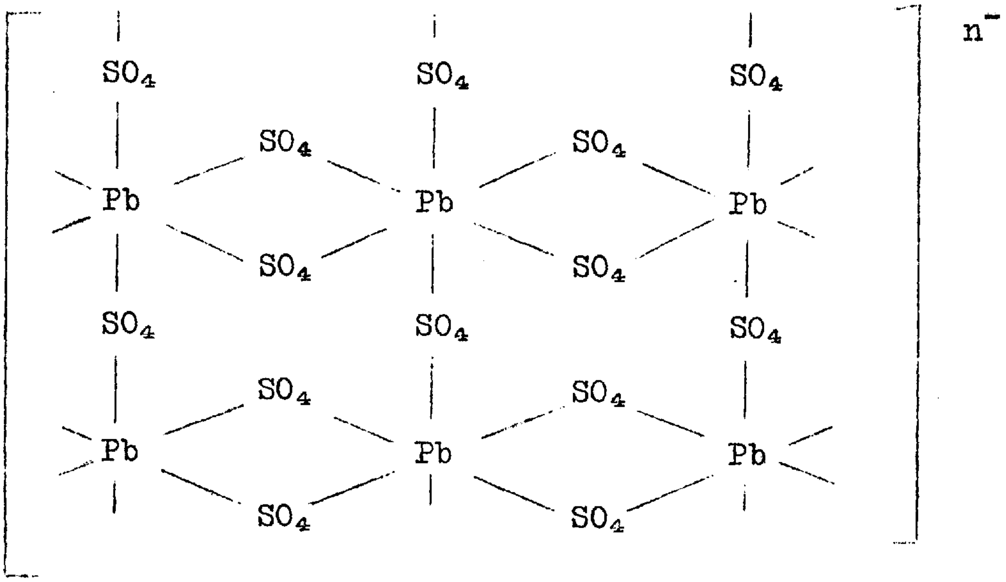

SO_4
SO_4
SO_4
n$^-$
SO_4
SO_4
Pb
Pb
Pb
SO_4
SO_4
SO_4
SO_4
SO_4
SO_4
SO_4
Pb
Pb
Pb
SO_4
SO_4

Fig. 4.

The monomeric complex ion $Pb(HSO_4)_6^{--}$ can exist only in dilute solutions; at higher concentrations it polymerises with elimination of sulphuric acid, forming complex polymeric anions containing sulphate bridges(37).

5. Selenium Compounds.

Selenium dioxide is soluble in anhydrous sulphuric acid to form a bright yellow solution(39,40,41). Recent cryoscopic and conductivity measurements on selenium dioxide(44) show that the values of ν and γ decrease with increasing concentration; in dilute solutions selenium dioxide behaves as a weak base, protonated according to the equation

$$SeO_2 + H_2SO_4 = SeO_2H^+ + HSO_4^-.$$

These solutions also contain polymeric ions or molecules such as $Se_2O_4H^+$ and SeO_2,H_2SO_4; Se_2O_4,H_2SO_4, etc., formed by the un-ionized portion of the selenium dioxide and sulphuric acid. As the concentration of selenium dioxide in sulphuric acid increases, the amount of the dimeric and higher polymeric ions also increases.

6. Variation of ν with Time.

Cryoscopic measurements on higher alcohols show that the value of ν increases with time and also the colours of the solutions become darker.

It is not possible to determine the mode of ionization of these solutes from the ν values because of the complexity of the reactions occurring in solution(23).

(k) Solubilities of Sulphates in Sulphuric Acid.

The solubilities of the metal sulphates in sulphuric acid are given in Table 4. A metal sulphate is more soluble in sulphuric acid when the solid phase in equilibrium with the saturated solution is a hydrogen sulphate solvate; with sparingly soluble sulphates the unsolvated hydrogen sulphate or normal sulphate is the equilibrium solid phase.

Table 4.

Solubilities of Metal Sulphates in Sulphuric Acid at 25°C.

Sulphate	Solubility (mole %)	Solid phase	Ref.
$HgSO_4$	0.02	$HgSO_4$	42
$CuSO_4$	0.08	$CuSO_4$	42
$FeSO_4$	0.17	-	42
$ZnSO_4$	0.17	-	42
$MgSO_4$	0.18	$Mg(HSO_4)_2,2H_2O$	42
Hg_2SO_4	0.78	$Hg_2(HSO_4)_2$	42
$CaSO_4$	5.16	$Ca(HSO_4)_2,2H_2SO_4$	42
Na_2SO_4	5.28	$4NaHSO_4,7H_2SO_4$	43
$BaSO_4$	8.85	$Ba(HSO_4)_2,2H_2SO_4$	42
Ag_2SO_4	9.11	$2AgHSO_4,H2SO_4$	42
K_2SO_4	9.28	$KHSO_4,H_2SO_4$	43
Li_2SO_4	14.28	$2LiHSO_4,H_2SO_4$	43

Sulphuric acid is a poor solvent for non-electrolytes but it is a good solvent for electrolytes. The hydrogen bonding interactions between the sulphuric acid molecules are very strong, and it is difficult to disrupt sufficiently the structure of the acid to make a substance dissolve in it. For a substance to be a solute in sulphuric acid it must be strongly solvated either because it is ionic or because it can form strong hydrogen bonds with sulphuric acid. If a substance is sufficiently basic to form strong hydrogen bonds with sulphuric acid, then there may be at least a small degree of ionization due to some proton transfer along the hydrogen bonds. Therefore for a non-electrolyte to be a solute in sulphuric acid, it must have sufficient basic properties to form strong hydrogen bonds with the solvent, but it must be insufficiently basic to protonate. These conditions are so restrictive that very few solutes behave as non-electrolytes in sulphuric acid.

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Chapter 2.

Determination of Solubility of Titanium Dioxide and Titanium Sulphate in Sulphuric Acid.

Chapter 2. Determination of Solubility of Titanium Dioxide and Titanium Sulphate in Sulphuric Acid.

GENERAL.

It is well known that titanium dioxide, TiO_2, can be rendered soluble by fusion with an alkali bisulphate; it is only with difficulty soluble in concentrated sulphuric acid. When titanium dioxide and concentrated sulphuric acid are heated until no more fumes are evolved, a white powder is formed, which is usually reported to be titanyl sulphate, $TiOSO_4$. This compound is soluble in cold water, but it is decomposed by hot water forming gelatinous, hydrated titanium dioxide(1)

$$TiOSO_4 + H_2O \longrightarrow TiO_2 \text{ (hydrated)} + H_2SO_4 .$$

"Orthotitanic acid", H_4TiO_4, or $TiO_2,2H_2O$, is soluble in cold concentrated sulphuric acid, whereas "metatitanic acid", H_2TiO_3 or TiO_2,H_2O, dissolves only slowly in hot concentrated sulphuric acid. It is probably better to regard the "titanic acids" as hydrated oxides, TiO_2,xH_2O, with an indefinite amount of combined water which varies with the conditions under which the precipitate is formed. The ease with which the hydrated oxide dissolves in sulphuric acid depends on the amount of water of hydration present(2).

Reliable solubility data for titanium as a sulphate in sulphuric acid, at different acid concentrations, were not available. Attempts were therefore made to estimate the equilibrium titanium concentrations in sulphate solutions at varying (but relatively high) sulphuric acid concentrations.

EXPERIMENTAL TECHNIQUES AND RESULTS.

(a) Materials.

The titanium oxide used was a pure material of moderate reactivity, in the rutile form, prepared by oxidation of purified titanium tetrachloride. The titanyl sulphate (containing TiO_2 28.4% and 59.1% of H_2SO_4, by weight) was a pure product prepared in the laboratories of Laporte Titanium Ltd. This company kindly donated a supply of both the oxide and titanyl sulphate.

The sulphuric acid used was of "Analar" quality; its total sulphate content was determined so that an appropriate quantity of oleum could be added, when necessary, in order to obtain exactly 100.0% H_2SO_4. The oleum was of normal quality and contained approximately 20% of sulphur trioxide; its total sulphate content was determined gravimetrically by precipitation of barium sulphate.

(b) Methods of Determination for Titanium and Sulphate in Solutions.

In determinations of titanium dioxide and sulphate concentrations in the solutions, gravimetric methods of precipitation as tannin complex and barium sulphate, respectively, were developed and used. These are described below.

(1) Determination of Titanium by the Tannin Method(3).

About 2 g. of the solution of titanium sulphate in sulphuric acid ~~was~~ were weighed out, and diluted to about 100 ml. with water in a beaker. The boiling solution was cautiously neutralised with ammonia until a faint cloudiness appeared, which was at once removed with a minimum quantity of dilute hydrochloric acid. Neutralisation with ammonia was essential because titanium is not precipitated as the tannin complex in free sulphuric acid, even as dilute as 5%(4). Five drops of concentrated hydrochloric acid were added, and the solution was diluted with 100 ml. of saturated ammonium chloride solution and boiled. Freshly prepared 5% tannin solution was added, drop by drop, with continuous stirring of the solution. The solution was allowed to boil for one to two minutes after the addition of the reagent. The weight of tannin added was approximately 20 times that of the titania present. The beaker was transfered to a steam bath and the orange-red titanium-tannin complex allowed to coagulate. At this stage of the determination the colour of the clear liquid in the beaker should be straw yellow; if it was orange, indicating incomplete precipitation of titanium, more tannin was added and the solution was stirred briskly. The beaker was then kept on a steam bath for one hour. The liquid was filtered through a No. 40 Whatman filter paper containing some creamed filter pulp. The precipitate was then returned to the beaker with 100 ml. of hot wash-liquor (5% ammonium chloride solution) and stirred until the clots were broken up. The solution was then filtered through the original paper and the precipitate was washed until free from sulphate (barium chloride test). To test for complete precipitation, all the filtrates were collected and evaporated down to about 300 ml; 10 ml. of 5% tannin solution were added, and the solution was boiled. Ammonia solution (N) was added drop by drop until some precipitate was formed. If this precipitate was dirty white in colour and it dissolved readily on adding one or two drops of N. hydrochloric acid, precipitation was considered complete. On the other hand, if the precipitate was orange, more ammonia was added to complete the precipitation of titanium; the precipitate was collected and washed (as above) and added to the first precipitate. The filtrates were collected and again tested for complete precipitation. The total precipitate was dried under the infra-red lamp, ignited in a porcelain crucible, and weighed as TiO_2.

2. Determination of Total Sulphate as Barium Sulphate.

It proved to be convenient to determine total sulphate in the combined filtrates from a titanium determination performed by the method just described. The filtrates were made up to 500 ml., and the sulphate concentration was determined by the conventional barium sulphate method(5) in a 50-ml. aliquot of the solution.

(c) Results of Analyses.

It was convenient, in view of later interpretation, to express titanium oxide contents of solutions as percentages by weight of TiO_2. Sulphuric acid contents were stated as values of molality, or (where more convenient) as gram-molecules of SO_3 (or, in some cases, of H_2O) in 1000 g. of the solution.

(d) Preparation of Sulphate Solutions for Solubility Measurements.

Solutions for the oxide as starting material were prepared by taking 0.5 g. of titanium dioxide and sulphuric acid, with varying amounts of 20% oleum or water, making up the total volume to 20 ml. The solutions were shaken mechanically for 8 hours. Another set of solutions of titanium oxide in sulphuric acid was made up as described above, but the solutions were heated in an oil bath at about 200°C for 8 hours, instead of being shaken at room temperature.

Solutions were prepared from titanyl sulphate and sulphuric acid in a similar way; 1 g. portions of titanyl sulphate were treated with sulphuric acid and with appropriate proportions of 20% oleum or water, the total volume being made up to 50 ml. One set of solutions was shaken for 8 hr. and another set for 24 hr.

All the solutions after heating or shaking were allowed to stand overnight at laboratory temperature (16°C) and portions of clear solution were sucked off by a "pumpette" and analysed.

(e) Results of Solubility Measurements.

Tables I - IV present the results of the solubility measurements on the four sets of solutions referred to above. Curves 1 and 2 in Fig. 1 represent the solubility data in Tables I and II, respectively; curves 3 and 4 in Fig. 2 represent the data in Tables III and IV.

Table I.

Solubilities in Sulphuric Acid Solutions obtained by shaking Titanium Oxide with Different Concentrations of Sulphuric Acid for 8 Hours.

Molalities of H_2O in sulphuric acid	% TiO_2 in solution
0.02	0.266
0.09	0.345
0.19	0.366
1.45	0.425
3.00	0.602
4.20	0.632
5.72	0.813
6.94	0.910

Table II.

Solubilities in Sulphuric Acid Solutions obtained by heating Titanium Oxide in Different Concentrations of Sulphuric Acid at 200°C for 8 hours.

Molalities of H_2O in sulphuric acid	% TiO_2 in solution
0.02	0.409
1.01	0.548
2.77	0.800
5.28	1.190
9.60	1.440

Table III.

Solubilities in Sulphuric Acid Solutions obtained by shaking Titanyl Sulphate in Sulphuric Acid for 8 Hours.

Molalities in sulphuric acid of H_2O	SO_3	% TiO_2 in solution
0.55	-	0.063
2.54	-	0.069
3.74	-	0.075
6.67	-	0.110
7.43	-	0.147
0.02	-	0.409
-	0.25	0.079
-	0.34	0.152
-	0.26	0.157
-	0.65	0.178
-	1.27	0.310
-	0.38	0.405
-	0.97	0.410
-	0.30	0.460
-	0.47	0.570
-	0.57	0.590
-	0.31	0.739

Table IV.

Solubilities in Sulphuric Acid Solutions obtained by shaking Titanyl Sulphate in Sulphuric Acid for24~~8~~ hours.

Molalities in sulphuric acid of		% TiO_2 in solution
H_2O	SO_3	
0.57	-	0.100
1.01	-	0.100
2.17	-	0.112
0.02	-	0.160
0.18	-	0.180
0.08	-	0.448
-	0.23	0.124
-	0.26	0.157
-	0.54	0.249
-	0.60	0.268
-	1.28	0.356
-	0.80	0.375
-	0.61	0.403
-	0.99	0.424

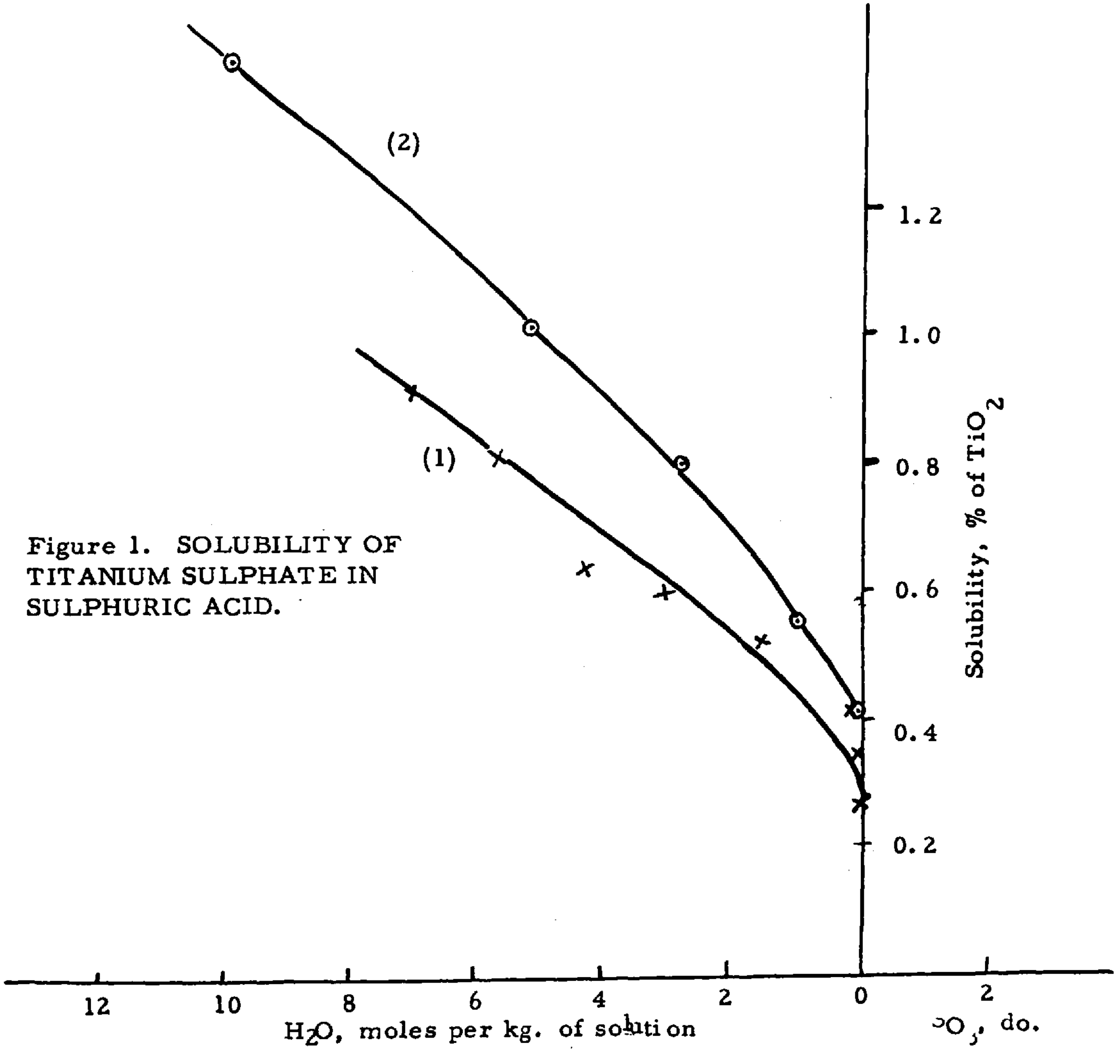
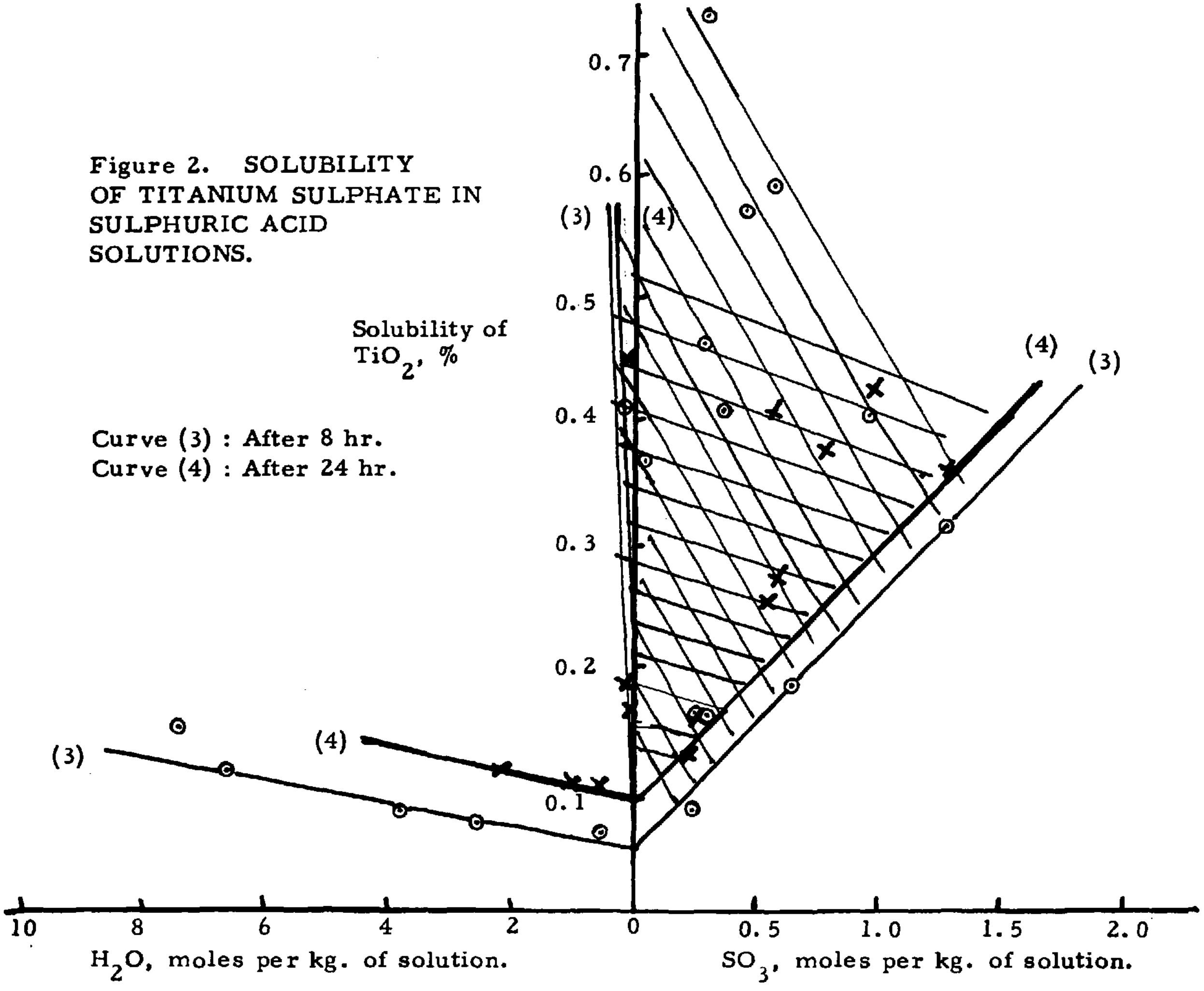


Figure 1. SOLUBILITY OF TITANIUM SULPHATE IN SULPHURIC ACID.

Figure 2. SOLUBILITY OF TITANIUM SULPHATE IN SULPHURIC ACID SOLUTIONS.



Discussion of the Results.

Curve (1) in Fig. 1 shows that the solubility of titanium sulphate in sulphuric acid at room temperature (16°C) decreases as the concentration of the sulphuric acid increases.

Curve (2) in Fig. 1 shows the solubilities of titanium sulphate in sulphuric acid solutions at 200°C. The solubility values are greater than those in the cold, but the effect of increased temperature is small. Curve (2) also shows that the solubility again decreases with increasing sulphuric acid concentration.

The solubilities of titanium sulphate in solutions obtained by shaking titanyl sulphate in sulphuric acid for 8 hours also decrease with increasing sulphuric acid concentration in the aqueous region; in the sulphur trioxide region the solubility increases with increasing sulphur trioxide concentration. There is a wide spread of the results in this region. The minimum solubility of titanium sulphate is at 100% sulphuric acid (see curve (3), Fig. 2).

When the time of shaking titanyl sulphate in sulphuric acid is increased to 24 hours, the observed solubility increases, but the results give a similar curve and the spreads overlap (see curve (4), Fig. 2). The results show that attainment of equilibrium in these solutions is excessively slow, an observation also recorded by other investigators of this system.

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Chapter 3.

Isolation and Analysis of some Titanium Sulphate Complexes.

X-Ray Study of Solid Compounds.

Chapter 3. Isolation and Analysis of Some Titanium Sulphate Complexes.

X-Ray Study of Solid Compounds.

EXPERIMENTAL TECHNIQUES AND RESULTS.

(a) Materials.

The titanium tetrachloride was redistilled and the fraction boiling at 136°C was collected. The 100% sulphuric acid used was prepared from "Analar" sulphuric acid and 20% oleum.

(b) Experiments and Results.

About 3 g. of titanium tetrachloride ~~was~~ were weighed into a 250-ml. stoppered "Pyrex" flask. 100% sulphuric acid was added drop by drop with constant shaking. When about 1.4 g. of sulphuric acid had been added, a large amount of yellow crystalline substance was formed. It had a very pungent odour. A weighed quantity of this yellow substance was taken and analysed as described below.

(c) Determination of Titanium, Sulphate and Chloride in the Yellow Intermediate Product obtained by the Reaction of 100% Sulphuric Acid with Titanium Tetrachloride.

About 1 g. of the yellow substance was weighed and 100 ml. of water were added. The substance immediately hydrolysed, forming a white precipitate. To complete the hydrolysis, ammonia (N.) was added until the solution was just alkaline. The solution was finally boiled. The precipitate was filtered off, washed, dried under an infra-red lamp, ignited in a platinum crucible, and weighed as TiO_2(1).

The filtrate and washings were made up to 500 ml.; 50 ml. of this solution were taken, and sulphate in it was determined by the conventional barium sulphate method.

Chloride was determined by titrating 25 ml. of the solution with standard silver nitrate solution; potassium chromate was used as indicator(2).

(d) Results of Analysis.

Wt. of substance = 0.9036 g.
Wt. of TiO_2 = 0.2822 g.
Wt. of $BaSO_4$ = 0.7270 g.
Wt. of Cl^- = 0.4282 g.

These values give the percentages recorded below and correspond with theoretical values of $TiCl_4,H_2SO_4$.

	Determined, %	$TiCl_4,H_2SO_4$ requires:
Ti	18.73	16.64
Cl	47.39	49.28
SO_3	27.58	27.82
H_2O (by difference)	6.30	6.26

(e) Further Reaction of Yellow $TiCl_4,H_2SO_4$ with Sulphuric Acid.

When more 100% sulphuric acid is added drop by drop to the yellow substance, hydrogen chloride gas is evolved in a very vigorous reaction, and some of the substance dissolves, forming an orange-coloured solution. A large excess of sulphuric acid (about 25 g.) was added so that all the solid material was totally immersed in acid, and the mixture was left overnight. All the solid then dissolved, and the orange solution turned green. This green solution was heated in an oil bath at 140°C until no more hydrogen chloride was evolved; the solution then became colourless. A few drops of this solution were taken and diluted with water, and a few drops of silver nitrate solution were added. No white precipitate was formed; there was therefore no chloride remaining in the solution. The main bulk of the solution was left overnight to cool. Colourless crystals were deposited. These were found to dissolve very readily in excess acid. It was difficult to obtain the crystals in dry state, but a fairly dry product was obtained by keeping the flask for several hours in a position such that acid drained slowly away from the mass of crystals. A weighed quantity of the crystals was taken and analysed (see below).

(f) Analysis of the Colourless Crystalline Sulphate.

About 1 g. of the crystals was ~~were~~ weighed and titanium and SO_3 were determined by tannin and the conventional barium sulphate methods respectively.

(g) Results of Analysis.

	g.		g.		Mean %	Required for TiO_2, $10SO_3$, $24H_2O$ %
Wt. of substance	1.3151		0.7742			
Wt. of TiO_2	0.0834		0.0482			
% of TiO_2		6.18		6.23	6.20	6.09
Wt. of $BaSO_4$	2.2945		1.7660			
% of SO_3		59.82		60.50	60.16	60.98
% of H_2O (by difference)		34.00		33.27	33.64	32.93

X-Ray Study of Solid Compounds.

The samples (yellow intermediate compound and titanium sulphate complex), sealed into capillary tubes of Lindemann glass, were examined by conventional X-ray powder methods. Nickel-filtered copper radiation was used (50 kV, 10 milliamps), and 30-minute exposures sufficed in 9-cm. Unicam cameras with fairly wide collimators. The photographs obtained showed considerable general scattering, characteristic of solids of poor crystallinity. Both show a diffuse line corresponding with a spacing of 3.08 A, but since this line appears in both photographs it may correspond with a decomposition product common to both materials. The sulphate complex shows an additional line (3.32 A).

It is not infrequently found that highly solvated and unstable materials of this kind appear largely amorphous to X-rays.

References.

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Chapter 4.

Preparation of Titanium Sulphate Solution from Titanium Tetrachloride and Titanium Alkoxide.

Chapter 4. Preparation of Titanium Sulphate Solution from Titanium Tetrachloride and Titanium Alkoxide.

GENERAL.

The general procedure for preparing the solutions for freezing-point or conductivity measurements is to introduce a weighed quantity of the solvent (100% sulphuric acid) into the cell and allow it to remain overnight so that any moisture present is absorbed. Liquid solutes are added, a small quantity at a time, with the aid of a weight-pipette. Granular solids are added by means of a weight-burette with a wide top and a long, wide stem which can be closed with a cap for weighing. Some solids which are difficult to handle are dissolved in this solvent to form a concentrated solution(1).

Titanium oxide and titanyl sulphates are very sparingly soluble in anhydrous sulphuric acid and so solutions prepared directly from these solutes cannot be used effectively for freezing point and conductivity measurements; the change in freezing point or conductivity due to the low concentration of solute is too small to be measured accurately. Attempts were therefore made to prepare titanium sulphate solutions by allowing sulphuric acid to react with titanium tetrachloride or isopropyl titanate.

PROCEDURE.

The procedure for the preparation of titanium sulphate solution from titanium tetrachloride and sulphuric acid is similar to that for the preparation of titanium sulphate complexes (see p.40.), but in this case more sulphuric acid is necessary. About 6 g. of titanium tetrachloride were weighed accurately and put in a 250-ml. stoppered "Pyrex" flask. 100% sulphuric acid was added, drop by drop at first and then small quantities at a time from a weight burette. The total weight of sulphuric acid added was about 50 g. A yellow crystalline intermediate product was formed during this reaction. This yellow substance reacted vigorously with more sulphuric acid and hydrogen chloride gas was given off. The solution was left overnight so that all the yellow substance dissolved in the acid, and it was then heated in an oil bath at about 140°C until no more hydrogen chloride was evolved. The solution was cooled and analysed.

About 1.5 g. of the titanium sulphate solution were weighed accurately, and the TiO_2 content was determined by the tannin method described previously. The amount of sulphate was also determined by the barium sulphate method.

ANALYSIS RESULTS.

Wt. of titanium sulphate solution = 1.4105 g.

Wt. of TiO_2 = 0.0698 g.

Wt. of $BaSO_4$ = 3.1844 g.

$$^{*}\ TiCl_4 + 2H_2SO_4 = Ti(SO_4)_2 + 4HCl$$

$$TiO_2 \equiv Ti(SO_4)_2 \equiv 2BaSO_4$$

$$79.9 \qquad 239.9 \qquad 466.72$$

$$\therefore 0.0698 \text{ g} = 0.2096 \text{ g} = 0.4076 \text{ g.}$$

Total wt. of $BaSO_4$ = 3.1844 g.

Wt. of $BaSO_4$, obtained from $Ti(SO_4)_2$ = 0.4076 g.

$\therefore$ Wt. of $BaSO_4$ from sulphuric acid = 2.7768 g.

2.7768 g $BaSO_4$ $\equiv$ 1.1658 g. H_2SO_4

Wt. of sulphuric acid by analysis = 1.1658 g.

Wt. of $Ti(SO_4)_2$ by analysis = 0.2095 g.

$\therefore$ Total wt. of solution by analysis = 1.3753 g.

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[*] In the calculations even though the simple equation is used, it may not be as simple as that.

Percentages by Weight.

The titanium sulphate solution contains 82.65% by weight of sulphuric acid and 14.86% by weight of $Ti(SO_4)_2$. It is convenient to know the percentages by weight for the later calculations.

The solution of titanium sulphate ~~for~~ from isopropyl titanate and sulphuric acid is prepared by added pure isopropyl titanate drop by drop from a weight-burette into a weighed quantity of 100% sulphuric acid. A dark brown solution is formed.

RESULTS.

Wt. of 100% sulphuric acid = 24.63040 g.

Wt. of isopropyl titanate = 5.54208 g.

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Chapter 5.

Spectrophotometric Study of Titanium Sulphate in Sulphuric Acid.

Chapter 5. Ultra-violet Spectroscopic Investigations of Titanium Sulphate in Sulphuric Acid Solutions.

GENERAL.

There have been many papers (e.g. by Millner(1), Molland(2), Hisky and Meloche(3), Bent and French(4), Vosburgh and Cooper(5), Job(6), Moss and Mellon(7), Yoe and Jones(8), Tarbell and Bunnett(9), and Yoe and Harvey(10)) on identification of complexes by spectrophotometric methods based on measuring the absorbancies of mixtures containing varying proportions of the metal and the complexing reagents.

Vosburgh and Cooper(5) have described a quick and simple method called "continuous variation", a modification of the well-known method of Job(6). To identify a complex AB_n formed from the two atoms or groups A and B, by the equation $A + nB \longrightarrow AB_n$, they prepared solutions of A and B of the same concentration and mixed them in varying proportions. The absorption coefficients of these solutions were measured; and the proportion which gave the maximum or minimum absorption corresponded with the composition of the complex. According to Vosburgh and Cooper the "continuous variation" method could be applied to two substances forming more than one complex compound.

Milner(1) studied the compositions of aluminium eriochromecyanine-R complexes. He prepared two sets of solutions, one set containing a fixed amount of aluminium with varying amounts of reagent (eriochromecyanine-R, an orange-red dye) and the other containing a fixed amount of reagent with different amounts of aluminium. He found that the compositions of the complexes formed depended on the proportions of aluminium and reagent in the mixtures.

In the ultra-violet spectroscopic investigation of titanium sulphate in sulphuric acid solutions, which is described below, a modified method of continuous variation was used.

EXPERIMENTAL METHOD AND RESULTS.

Apparatus and Techniques.

1-mm. silica cells were used for holding the solutions and the blanks, and the optical densities were measured in a "Unicam" S.P. 500 Photoelectric Quartz Spectrophotometer. Sulphuric acid is transparent to ultra-violet and visible light.

The solution of titanium sulphate in sulphuric acid was prepared by shaking titanyl sulphate with sulphuric acid (nearly 100%) for 24 hours. The titanium and sulphuric acid contents were determined by the methods described previously. The solubility of titanium sulphate in concentrated sulphuric acid is quite small so solutions of titanium sulphate and sulphuric acid of equal concentration could not be prepared. The solutions proved to be very highly absorbent in the ultraviolet region, but they were transparent to visible light.

The solubility of titanium sulphate in sulphuric acid is equivalent to about 0.3% of TiO_2 by weight. Test solutions were prepared by taking one ml. of titanium sulphate solution in sulphuric acid and diluted to 100 ml. with "Analar" sulphuric acid; 1 ml. of this solution is further diluted to 10 ml. with sulphuric acid of different concentrations. In this way the concentration of titanium was fixed and the sulphuric acid concentration was varied over an appropriate range.

The optical densities of seventeen solutions were measured over the wavelength range 2000 to 3200 A, at 100-A. intervals (at the maximum of optical density at 50-A. intervals). The results are collected in Table I. A curve of optical density against wavelengths was drawn for each solution; Fig. 1 shows three such curves. It was found that the maximum optical density for each curve occurred at the same wavelength, 2550 A.

Table I.

Optical Densities of Solutions of Titanium Sulphate in Sulphuric Acid.

Wavelength	Optical densities of solutions			
A	(1)	(2)	(3)	(4)
2000	-	0.012	0.036	0.053
2100	-	0.027	0.054	0.073
2200	0.009	0.040	0.072	0.098
2300	0.016	0.056	0.099	0.123
2400	0.026	0.074	0.116	0.147
2450	0.027	0.080	0.132	0.168
2500	0.034	0.092	0.146	0.191
2550	0.045	0.101	0.158	0.203
2600	0.056	0.109	0.156	0.196
2650	0.066	0.110	0.152	0.184
2700	0.064	0.105	0.138	0.165
2750	0.052	0.089	0.128	0.150
2800	0.048	0.084	0.114	0.136
2900	0.038	0.067	0.089	0.109
3000	0.026	0.046	0.068	0.083
3100	0.012	0.028	0.046	0.062
3200	0.006	0.009	0.029	0.048

Table I, continued.

Optical Densities of Solutions of Titanium Sulphate in Sulphuric Acid.

Wavelength	Optical densities of solutions			
A	(5)	(6)	(7)	(8)
2000	0.066	0.070	0.069	0.080
2100	0.086	0.088	0.086	0.102
2200	0.112	0.108	0.118	0.128
2300	0.140	0.139	0.155	0.165
2400	0.168	0.179	0.190	0.195
2450	0.190	0.199	0.210	0.216
2500	0.212	0.218	0.229	0.233
2550	0.221	0.227	0.238	0.242
2600	0.217	0.223	0.232	0.236
2650	0.201	0.208	0.216	0.218
2700	0.183	0.189	0.194	0.196
2750	0.160	0.170	0.162	0.180
2800	0.144	0.152	0.151	0.162
2900	0.116	0.121	0.127	0.130
3000	0.091	0.100	0.098	0.104
3100	0.070	0.081	0.077	0.078
3200	-	0.068	0.056	0.060

Table I, continued.

Optical Densities of Solutions of Titanium Sulphate in Sulphuric Acid.

Wavelength A	Optical densities of the solution (9)	(10)	(11)	(12)
2000	0.071	0.063	0.05[illegible]	0.056
2100	0.094	0.092	0.090	0.074
2200	0.125	0.122	0.100	0.093
2300	0.163	0.160	0.118	0.116
2400	0.191	0.189	0.151	0.149
2450	0.212	0.196	0.163	0.160
2500	0.232	0.216	0.178	0.176
2550	0.239	0.225	0.192	0.186
2600	0.236	0.221	0.190	0.186
2650	0.219	0.208	0.179	0.174
2700	0.199	0.179	0.163	0.161
2750	0.176	0.162	0.152	0.140
2800	0.151	0.143	0.138	0.130
2900	0.126	0.124	0.118	0.099
3000	0.098	0.096	0.086	0.072
3100	0.076	0.078	0.063	0.054
3200	0.056	0.052	0.047	0.043

Table I, continued.

Optical Densities of Solutions of Titanium Sulphate in Sulphuric Acid.

Wavelength	Optical densities of solutions				
A	(13)	(14)	(15)	(16)	(17)
2000	0.049	0.042	0.039	0.034	-
2100	0.068	0.058	0.052	0.050	0.004
2200	0.089	0.076	0.069	0.058	0.006
2300	0.114	0.109	0.099	0.089	0.016
2400	0.137	0.136	0.141	0.128	0.024
2450	0.140	0.143	0.149	0.128	0.026
2500	0.155	0.154	0.167	0.137	0.039
2550	0.166	0.160	0.176	0.143	0.059
2600	0.168	0.166	0.176	0.150	0.056
2650	0.166	0.165	0.166	0.153	0.057
2700	0.156	0.152	0.155	0.147	0.044
2750	0.136	0.130	0.124	0.118	0.040
2800	0.124	0.120	0.112	0.106	0.032
2900	0.096	0.089	0.079	0.068	0.024
3000	0.066	0.060	0.053	0.049	0.016
3100	0.049	0.043	0.033	0.029	0.008
3200	0.039	0.029	0.021	-	-

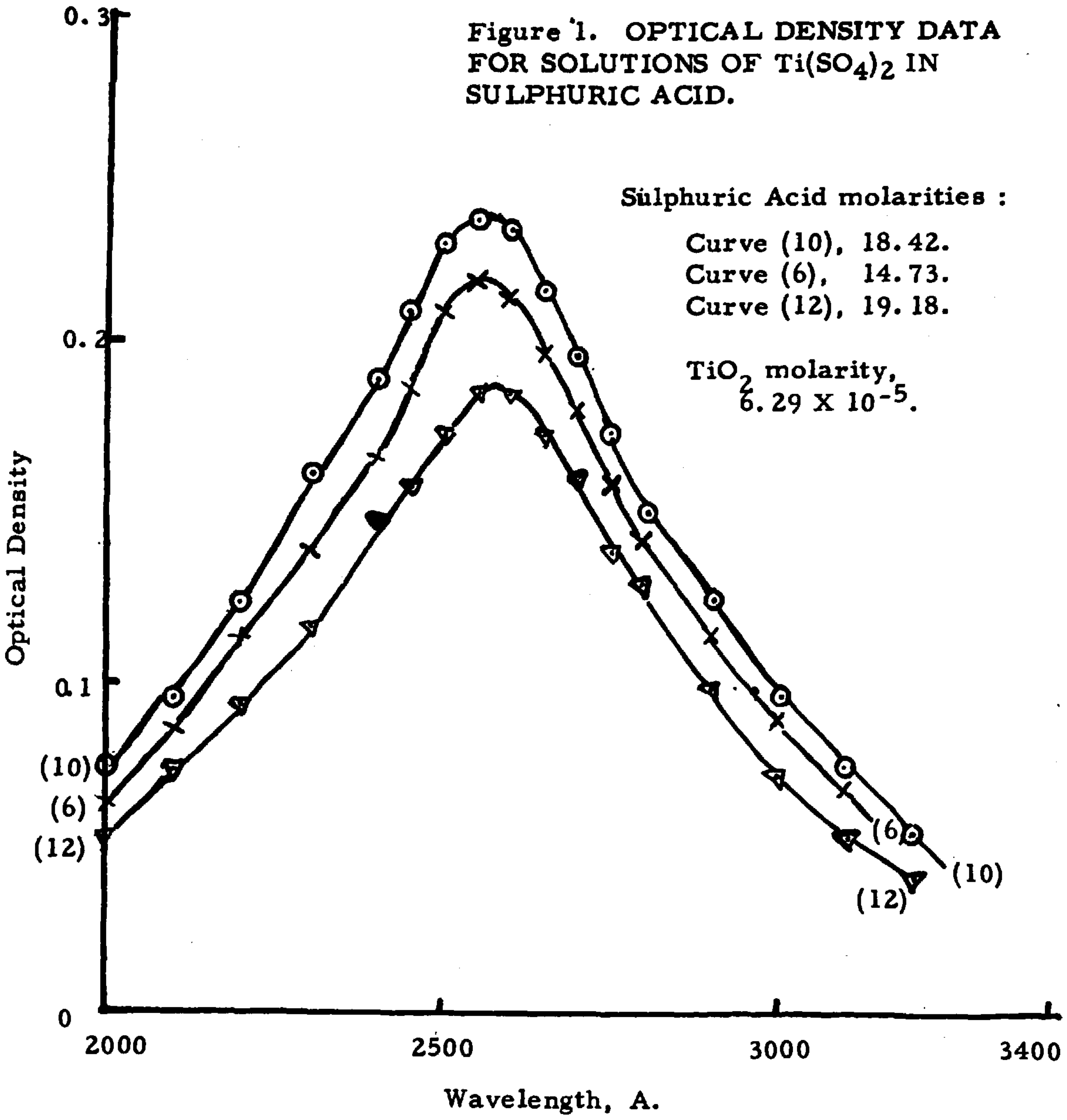

Figure 1. OPTICAL DENSITY DATA FOR SOLUTIONS OF $Ti(SO_4)_2$ IN SULPHURIC ACID.

With the concentration of the titanium constant and the concentration of the sulphuric acid increasing, the optical density at 2550 A at first increased and then decreased. Similar curves were obtained for other wavelengths (e.g. 2450 A. and 2650 A.) and the maximum optical density for all the curves occurred at the same concentration of sulphuric acid. The results are shown in Table II and Fig. 2.

Table II.

Dependence of Optical Density in Titanium Sulphate Solution on Sulphuric Acid Concentration.

Solutions	Sulphuric acid (molarity)	Optical densities at		
		2450A	2550A	2650A
1	11.05	0.027	0.045	0.066
2	11.98	0.080	0.101	0.112
3	12.89	0.132	0.158	0.152
4	13.81	0.168	0.203	0.184
5	14.74	0.190	0.221	0.201
6	15.66	0.199	0.227	0.208
7	16.58	0.210	0.238	0.216
8	17.50	0.216	0.242	0.218
9	18.42	0.212	0.239	0.219
10	18.61	0.196	0.225	0.208
11	18.80	0.163	0.192	0.179
12	18.99	0.160	0.186	0.174
13	19.18	0.140	0.166	0.166
14	19.37	0.143	0.160	0.165
15	19.75	0.149	0.176	0.166
16	19.94	0.128	0.143	0.153
17	20.13	0.026	0.059	0.051

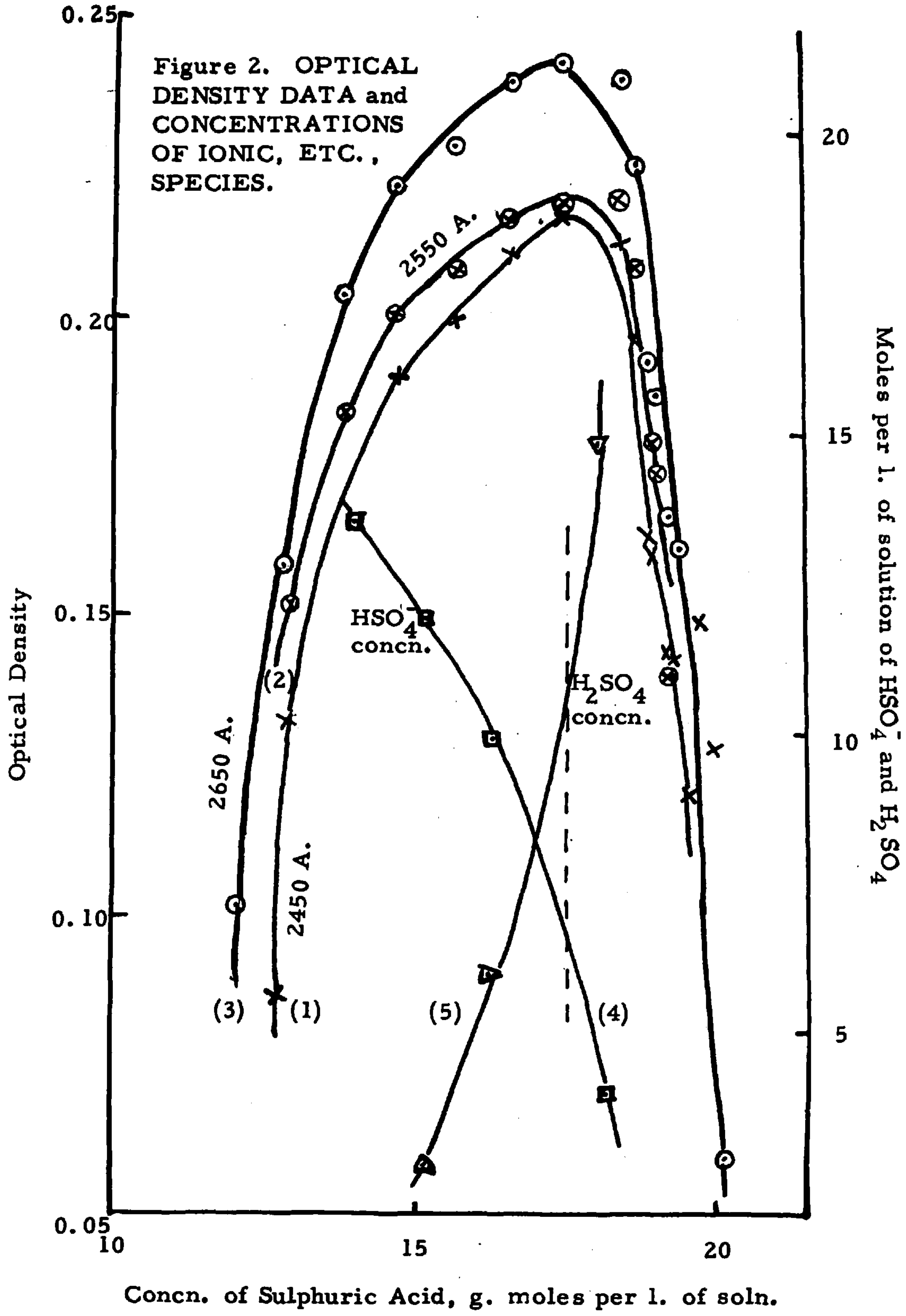

Figure 2. OPTICAL DENSITY DATA and CONCENTRATIONS OF IONIC, ETC., SPECIES.

Discussion of the Results.

Any interpretation of the results summarised in Figs. 1 and 2 will require knowledge of the constitution of sulphuric acid at concentrations near 100% H_2SO_4. Fortunately, the study of the Raman spectrum of the acid has afforded considerable information on the species and concentrations of molecules or ions in it.

When the concentration of the acid exceeds 15 molarity, the SO_4^{2-} ion concentration is negligible(11,12) and undissociated acid and HSO_4^- ions are present. The concentration of H_2SO_4 was determined by subtracting the concentration of HSO_4^- ions from the stoichiometric molality. The determination was difficult because of (1) overlapping of lines, and (2) light absorption in the acid.

In solutions more dilute than 14 molarity, only SO_4^{2-} and HSO_4^- ions are present; the presence of undissociated acid could not be detected from the Raman spectrum. The concentration of SO_4^{-2} ions was determined by measuring the intensity of 980-cm^{-1} line, and the concentration of HSO_4^- ions was calculated by subtracting the SO_4^{2-} concentration from the stoichiometric concentration of the solution. It was verified that the intensity of the 1040-cm^{-1} HSO_4^- line was proportional to the concentration of HSO_4^- ion obtained by difference.

For the solutions more concentrated than 14 molarity, the calculation of concentrations was not so accurate as that for the more dilute solution but the overall agreement was very good(12).

Young et al(12) have calculated the concentrations of HSO_4^- and the undissociated H_2SO_4 in the region of 14 to 18 moles of sulphuric acid per litre of the solution and the results are given in Table III.

Table III. Concentration of Species in Concentrated Sulphuric Acid Solutions.

Concentration of sulphuric acid in molarity	Moles per litre of undissociated	
	HSO_4^-	H_2SO_4
18.1	4	15
16.24	10	6
15.18	12	2.8
13.94	13.6	-

The above results are also plotted in Fig. 2 (see Fig. 2, curves (4) and (5)); the concentrations of HSO_4^- and undissociated H_2SO_4 are found to be equal at 16.9 moles of sulphuric acid per litre of solution.

Curves (1), (2) and (3) in Fig. 2 show that the maximum optical density occurs at 17.5 moles of sulphuric acid per litre of solution, which corresponds closely with the value 16.9. The optical densities decrease sharply on both sides. It is also evident from curves (4) and (5) that above 16.9 molarity, the concentration of HSO_4^- decreases sharply and below 16.9 molarity, the concentration of undissociated H_2SO_4 also decreases sharply. Following the general principle of Job's method, it may be deduced that H_2SO_4 and HSO_4^- groups occur in the light-absorbing complex containing titanium, and that they are present in equimolecular proportions. The actual constitution of the complex will be considered later when other experimental evidence has been examined.

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Chapter 6.

Electrical Conductivity Determinations on Solutions of Titanium Sulphate in Sulphuric Acid.

Chapter 6. Electrical Conductivity Determinations on Solutions of Titanium Sulphate in Sulphuric Acid.

GENERAL.

(a) The Water-sulphur Trioxide System.

There have been numerous papers on conductivity measurements on sulphuric acid with water and sulphur trioxide as solutes. The pioneer work was by Kohlrausch(1), Knietsch(2), Hantzsch(3), Lichty(4) and Bergius(5) published many papers. Hantzsch(3) was the first to make a systematic study of the conductivity and cryoscopy of sulphuric acid with water, sulphur trioxide and other substances as solutes. More recent work has been by Ussanowitsch et al(6), Reinhardt(7), and Kunzler and Giauque(8). Gillespie and Wasif(9) made a very thorough study of the conductivity of the water-sulphur trioxide system with an improved technique for making conductivity measurements, using a modified form of the conductivity cell originally designed by Shedlovsky(10).

All these workers have shown that the conductivity of sulphuric acid increases with addition of water or sulphur trioxide, and the minimum conductivity occurs at or very near the composition of 100% sulphuric acid. But there are disagreements on the actual value of the minimum conductivity and the percentage of sulphuric acid. The various results are summarised in Table I.

Table I.

Conductivity Data for Sulphuric Acid.

	Minimum conductivity of sulphuric acid at 25°C (k in $ohm^{-1}cm^{-1}$)	Composition at the minimum conductivity	
		% of H_2SO_4	% of water
Kohlrausch (1882)	-	99.75	0.25
Knietsch (1901)	-	99.9	0.1
Hantzsch (1907)	0.0098	100	-
Lichty (1908)	0.01041	100	-
Bergius (1910)	0.0097	100	-
Ussananowitsch et al (1939)	0.0106	100	-
Reinhardt (1950)	0.0108	100	-
Kunzler and Giauque (1952	-	99.996	-
Gillespie and Wasif (1953)	0.01033	100	-

Gillespie, Oubridge and Solomons(11) reinvestigated the conductivity of the water-sulphur trioxide system in 1957. They used conductivity cells of a new design and made improvements in the technique. For these very accurate measurements the temperature controls in the thermostat must be accurate to within ±0.003°C. According to these authors the minimum conductivity occurs on the slightly aqueous side of the composition H_2SO_4, at the concentration 0.0019 ± 0.0005 mole of water (as solute) per kg of solution. The minimum conductivity is $(1.0432 \pm 0.0005) \times 10^{-2}$ ohm^{-1} cm^{-1} at 25°C. At 100% sulphuric acid, the conductivity is $(1.0439 \pm 0.0005) \times 10^{-2}$ ohm^{-1} cm^{-1}.

(b) High Conductivity of Sulphuric Acid.

For a pure liquid, sulphuric acid has a very high conductivity. This is due to the extensive self-dissociation(12), which is partly an autoprotolysis $2H_2SO_4 = H_3SO_4^+ + HSO_4^-$ and partly a self-dehydration $2H_2SO_4 = H_3O^+ + HS_2O_7^-$.

The mobilities of $H_3SO_4^+$ and HSO_4^- ions are very high, and greater than those of any other ions in the sulphuric acid. This can be clearly seen from the cation transport numbers (t) of many metal hydrogen sulphates, measured by Gillespie and Wasif(13) (see Table II).

Table II.

Cation Transport Numbers for some Electrolytes.

Electrolyte	m	t
$AgHSO_4$	0.249	0.026
$KHSO_4$	0.624	0.030
$NaHSO_4$	0.792	0.021
$LiHSO_4$	0.556	0.013
$Ba(HSO_4)_2$	0.174	0.009
$Sr(HSO_4)_2$	0.211	0.007

The mobilities of the metal ions are very small in sulphuric acid; this is partly because sulphuric acid has a very high viscosity (24.5 centipoises at 25°C, which is about 25 times that of water). Earlier work by Hammett and Lowenhein(14) also showed that the cation transport numbers of barium and strontium are very small in sulphuric acid; they were the first to suggest that the only reasonable way to explain the abnormal mobilities of the HSO_4^- and $H_3SO_4^+$ ions is to assume that the solution conducts almost entirely by a proton-transfer mechanism. The cause would then be analogous to that of the high mobilities of the H_3O^+ and OH^- in water(15). This view was later supported by Gillespie and Wasif(13), who considered that because of the successive transfer of protons the changes of hydrogen sulphate ion and hydroxonium ions are transfered through the solution without the actual movement of any of the ions. This process is represented very diagrammatrically as follows:-

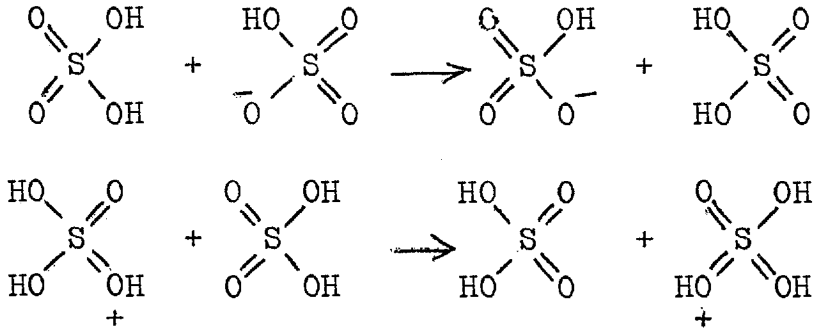

Table III compares the values of the mobilities of $H_3SO_4^+$, HSO_4^-, and other ions in 100% H_2SO_4 and the values for the same ions in water at infinite dilution(16).

Table III.

Ionic Mobilities (λ) in 100% Sulphuric Acid and Water at Infinite Dilution (25°C).

Ion	$\lambda(H_2SO_4)$	$\lambda(H_2O)$
$H_3SO_4^+$	242	-
HSO_4^-	171	-
H_3O^+	$\sim$5	349.8
OH^-	-	198.6
Na^+	$\sim$ 3	50.1
K^+	$\sim$ 5	73.5
Ba^{++}	$\sim$2	33.6

(c) The Number γ.

When substances dissolve in sulphuric acid, and the conductivities of the solutions increase with increasing concentration, it is recognised that the substances ionise in sulphuric acid. The conductivities of solutions of substances which behave as acids or bases in sulphuric acid are determined almost entirely by the concentration of $H_3SO_4^+$ or HSO_4^-, respectively, to which they give rise. All the simple bases which ionise in sulphuric acid to produce one HSO_4^- ion (i.e. hydrogen sulphate of univalent cations) will therefore have very similar molar conductances; bases which give two hydrogen sulphate ions (i.e. hydrogen sulphates of bivalent cations) will have molar conductances approximately twice those of mono hydrogen sulphates at the same concentration. The number, γ, of moles of hydrogen sulphate ions produced by one mole of any solute can thus be determined from the conductivity measurements(17).

Some typical examples of conductivity data for substances in sulphuric acid, determined by Gillespie and Wasif(17), are given in Table IV.

Table IV.

Molar Conductivities at 25°C.

Bases which give rise to one hydrogen sulphate ion

M	NH_4HSO_4	$(CH_3)_2CO$	H_2O	C_2H_5OH	CH_3CO_2H
0.1	158	155	156	156	152
0.2	120	120	115	117	116
0.3	105	102	100	103	99.3
0.4	95.3	92.5	90.3	93.8	89.5
0.6	82.2	80.1	78.3	79.8	77.1
0.8	73.5	72.4	70.0	70.1	67.9
1.0	66.3	63.9	63.2	62.2	59.8

Bases which give rise to two hydrogen sulphate ions

M	HNO_3	o-$C_6H_4(NH_2)_2$	$Ba(HSO_4)_2$
0.05	306	306	304
0.10	229	236	221
0.15	197	201	179
0.20	177	187	150
0.30	155	153	132
0.40	138	130	110
0.50	125	119	95

Base which gives rise to three hydrogen sulphate ions

M	N_2O_4
0.033	453
0.066	336
0.100	296
0.133	268

Base which gives rise to four hydrogen sulphate ions

M	Hexamethylenetetramine
0.025	616
0.050	454
0.075	388
0.100	349

(d) Small Differences in the Conductivities of the Solutions.

Recently Bass et al(18) measured the conductivities of solutions in sulphuric acid of many electrolytes, such as metal sulphates, ketones, and tetra(hydrogen sulphate)boric acid. Also Gillespie and Solomons(19) measured the conductivities of solutions of nitro compounds in sulphuric acid.

Hantzsch(20) first suggested that even the observed small differences in the conductivities of solutions of alkali-metal hydrogen sulphates are too large to be attributed to the small differences between the mobilities of their cations alone. It must therefore be concluded that the mobility of the hydrogen sulphate ion does to some extent depend on the nature of the cation. Gillespie and Wasif(9) also showed that the specific conductivity of alkali and alkaline-earth metal hydrogen sulphates does not increase linearly with concentration, but more slowly (see Fig. 1). This unexpectedly slow increase represents a fall in the equivalent conductivity of the electrolyte; the mobility of the hydrogen sulphate ion decreases with increasing concentration. The differences in the conductivities are more apparent at the higher concentrations. At lower concentrations the

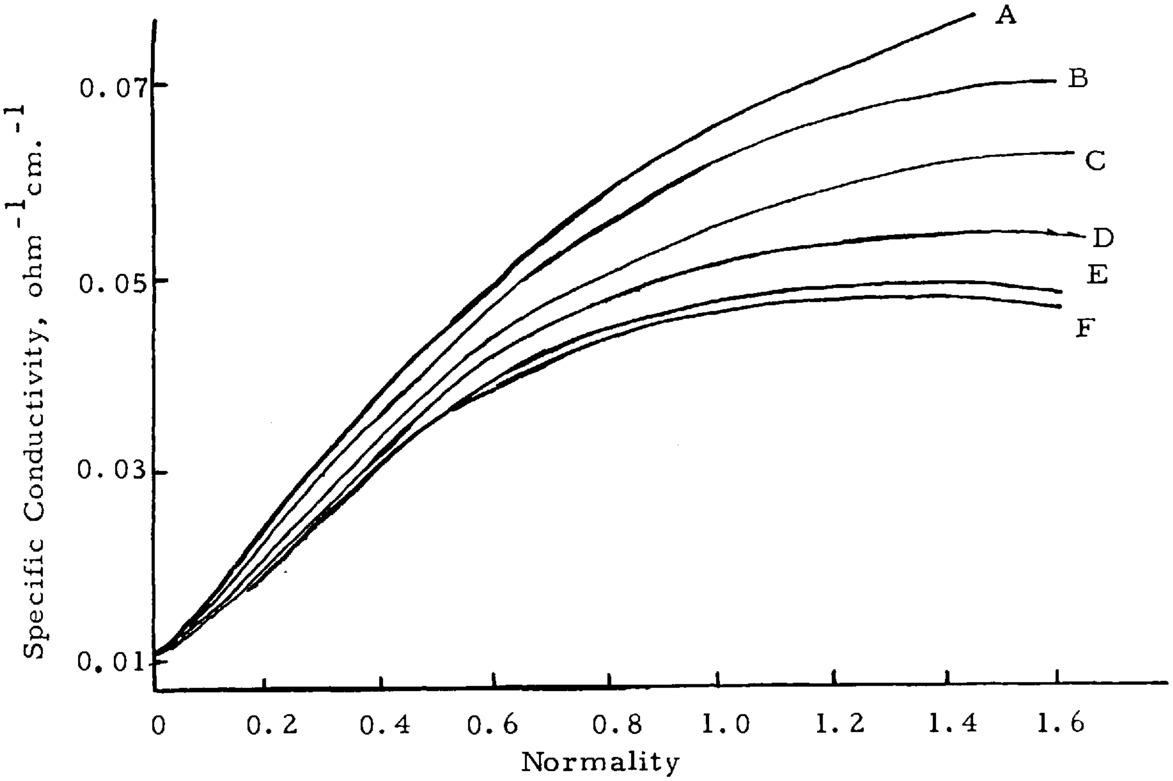

Figure 1. SPECIFIC CONDUCTIVITIES OF SOME ALKALI AND ALKALINE-EARTH METAL HYDROGEN SULPHATES. (Reproduced from Gillespie and Wasif, J.chem. Soc., 1953, p. 224.)

Curve A : NH_4HSO_4.
Curve B : $KHSO_4$.
Curve C : $NaHSO_4$.
Curve D : $LiHSO_4$.
Curve E : $Ba(HSO_4)_2$.
Curve F : $Sr(HSO_4)_2$.

conductivities are nearly the same because the cation transport numbers are small; as indicated earlier, the conductivities are due largely to the HSO_4^- ion, which contributes to the conductivity to an extent almost independent of the nature of the associated cation.

(e) General Behaviour of ~~Electrolytes~~ Solutes in Sulphuric Acid.

Electrolytes.

When substances which behave as electrolytes dissolve in sulphuric acid, the conductivity of the solutions increases with increasing concentration.

Strong bases.

The strong bases can be classified as mono, di, tri, tetra, etc., by the number of hydrogen sulphate ions produced when one molecule of solute is ionised in sulphuric acid.

Weak bases.

When weak bases dissolve in sulphuric acid, the value of γ (the number of hydrogen sulphate ions formed per molecule of solvent) decreases with increasing concentration. This is due to incomplete ionisation.

Acids.

When substances which behave as acids dissolve in sulphuric acid, they give rise to the sulphuric acidium ion, $H_3SO_4^+$. The reaction between an acid and a base occurs according to the equation

$$H_3SO_4^+ + HSO_4^- = 2H_2SO_4 .$$

When a base is added to a solution of an acid, the concentration of $H_3SO_4^+$ decreases and the concentration of HSO_4^- increases. Since the conductivity of the solution is mainly due to $H_3SO_4^+$ and HSO_4^- ions, there will be a decrease in conductivity initially, then a minimum, and finally a renewed increase. The position of minimum conductivity depends on the strengths of the acid and base and on their modes of ionization.

Non-electrolytes.

The conductivities of solutions of non-electrolytes in sulphuric acid are lower than that of pure sulphuric acid. The conductivity also decreases with increasing concentration. For the non-electrolytes, the conductivity in such solutions is due to the hydroxonium and hydrogen sulphate ions from the auto-protolysis of the solvent sulphuric acid. The conductivity decreases because of the dilution of the acid by the non-conducting solute.

The conductivity measurements on titanium sulphate solutions were undertaken because they were expected to throw some light on the nature of the sulphate in solution and of its mode of ionization.

EXPERIMENTS AND RESULTS.

(a) Apparatus.

Conductivity Cell.

A "Pyrex" glass conductivity cell designed for small quantities of solution was used (Fig. 2). The capacity of the cell was about 10 ml. The electrodes were circular plates of heavy platinum sheet. Connection to each electrode was made by a globule of mercury, and for convenience the ends of the tubes carrying the connections were sealed with wax, so that the cell could be inverted during washing and changing of the solution. Two ground-glass stoppers protected the solution from atmospheric moisture.

For platinizing the electrodes, a solution of 2 g. of platinic chloride and 0.02 g. of lead acetate in 100 ml of water was prepared(22). The electrodes were platinized by immersing them in this solution and passing current from two accumulators: this was regulated by a rheostat so that a small stream of gas was evolved at the electrodes, and it was maintained for 15 minutes. The current was reversed every half minute. After the electrolysis, all traces of the platinizing solution (which is liable to be absorbed by the electrodes) were removed by replacing

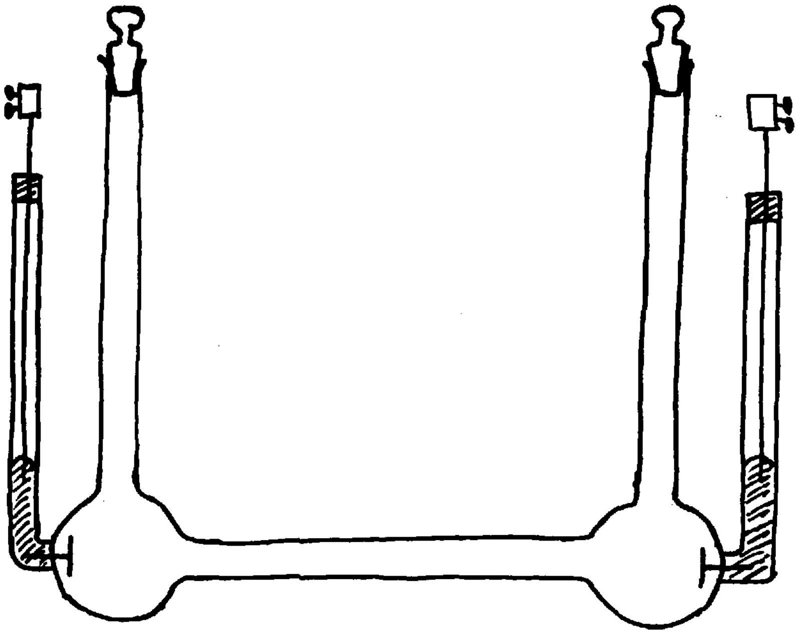

Figure 2. CONDUCTIVITY CELL.

the platinizing solution by dilute sulphuric acid solution and passing the current in each direction for about 2 minutes. The cell was then rinsed thoroughly with distilled water. The cell constant was determined by using 0.1N, potassium chloride solution as a conductivity standard.

Conductivity Apparatus.

A Mullard conductance meter Type E 7566 was used for the conductivity measurements. It had a self-contained Wheatstone bridge circuit with a 1,000-cycle oscillator and "magic-eye" bridge balance detector. Conductances ranging from 1 to 10^{-6} mho could be measured with an accuracy of about 1 - 2%.

(b) Materials (other than Titanium Sulphate Solution).

Sulphuric acid of minimum conductivity was used as a solvent. It was prepared by mixing weighed amounts of 20% oleum and of "Analar" sulphuric acid. The conductivity of the initial product was measured and the final adjustment was made by adding water or 20% oleum, drop by drop, as needed(9). In the present measurements the minimum conductivity was found to be 0.10323 $\text{ohm}^{-1}\text{cm}^{-1}$.

"Analar" potassium sulphate was dried at 120°C in an electric oven for 6 hours and stored in a desiccator over phosphorus pentoxide.

(c)Preparation of Solutions for Measurements.

The titanium sulphate solutions for the conductivity measurements were prepared by mixing a weighed quantity of the concentrated solution of titanium sulphate in sulphuric acid (described in Chapter 4.) with an appropriate weighed quantity of sulphuric acid of minimum conductivity.

For reference conductivities, solutions of potassium sulphate in sulphuric acid were prepared by dissolving weighed quantities of dried potassium sulphate in weighed quantities of sulphuric acid of minimum conductivity.

Metal sulphates (e.g. K_2SO_4) in sulphuric acid are quantitatively converted into hydrogen sulphates, and the composition of the potassium sulphate solutions were therefore expressed in terms of hydrogen sulphate(18). Potassium hydrogen sulphate was arbitrarily chosen as a reference strong electrolyte because the conductivities of its solution (which are easily prepared) can be measured accurately; also, among the many fully ionized metal sulphates, the potassium salt has "average" behaviour(19).

All the solutions were made up by weight. Their concentrations are expressed as moles of solute per kg. of solution, that is, in "molon" units (ω). This new unit was introduced by Gillespie and Solomons$^{(21)}$. Its advantages are that concentrations in molon units are independent both of the internal state of the system and of temperature. Mole fractions (moles of solute divided by total number of moles in the system) and molalities (moles of solute per kg. of solvent) can have more than one value in cases where the solute reacts with or is solvated by the solvent, or when the solvent is dissociated. Sulphuric acid is known to be appreciably self-dissociated, and the molality of the solute depends on whether or not the self-dissociation species are regarded as constituting part of the solvent. The stoichiometric molality is calculated on the assumption that the solute dissolves unchanged. Molarity (moles of solute per litre of solution) is independent of the internal state of the system but dependent on temperature. Concentrations expressed in molon units (ω) can be converted into molarity (c) by the simple equation, $c = \rho\omega$, where ρ is the density of the solution. For some sulphuric acid solutions the densities are not known, and the density of the pure solvent must be used as an approximation to the density of the solution.

(d) Measurements of Conductivities of Solutions.

The conductivity cell was filled with the solution and kept in a thermostat at 25° ± 0.05° for half an hour to ensure that the solution had reached the temperature of the thermostat. The conductivity was measured by standard methods by means of a Mullard conductance meter.

RESULTS.

Table V.

Potassium Sulphate.

Wt. of K_2SO_4 (g)	Wt. of solution (g)	w ($KHSO_4$)	Specific conductivity at 25°C 10^{-2} $ohm^{-1}cm^{-1}$
0.00920	16.45416	0.0064	1.0989
0.09596	16.72362	0.0664	1.4319
0.10488	17.48080	0.0688	1.4319
0.13290	17.09546	0.0892	1.6317
0.16680	18.16905	0.1054	1.1984
0.18239	16.2995	0.1284	2.1645
0.20482	16.49020	0.1425	2.1645
0.27526	17.52840	0.1802	2.5974
0.40764	16.81006	0.2783	3.663
0.59532	17.30496	0.3948	4.995
0.62636	17.48998	0.4110	5.0616

Table VI.

Titanium Sulphate.

Wt. of $Ti(SO_4)_2$	Wt. of solution (g)	w ($Ti(SO_4)_2$)	Specific conductivity at 25°C 10^{-2} $ohm^{-1} cm^{-1}$
0.01883	19.05956	0.0041	1.0989
0.07128	16.31402	0.0182	1.3320
0.09051	16.46180	0.0229	1.1988
0.14956	16.4655	0.0379	1.4650
0.23298	16.60610	0.0585	1.5984
0.32326	16.85138	0.0800	1.6650
0.38669	17.62572	0.0915	1.8432
0.50529	17.09336	0.1232	1.8315
0.66564	17.69922	0.1568	1.8981
0.67480	16.43634	0.1711	1.7716
1.14324	16.78191	0.2840	2.1978
1.43895	15.0000	0.3999	2.2644

Table VII.

Isopropyl Titanate.

Wt. of $Ti(OPr)_4$	Wt. of solution (g)	ω ($Ti(OPr)_4$)	Specific conductivity at 25°C 10^{-2} $ohm^{-1}cm^{-1}$
0.01859	16.49860	0.0032	1.2987
0.02425	16.87802	0.0041	1.7649
0.05133	17.26323	0.0085	1.8315
0.06416	18.28500	0.0100	1.9647
0.07661	17.5403	0.0125	2.1978
0.09665	16.97652	0.0163	2.3976
0.09707	16.96042	0.0164	2.5641
0.19694	17.63300	0.0319	3.1635
0.25187	17.69428	0.0407	3.9964
0.29650	17.89186	0.0474	3.9964
0.39349	17.41806	0.0646	4.7619
0.47111	18.48368	0.0728	5.6943
0.59141	17.64294	0.0958	5.8275

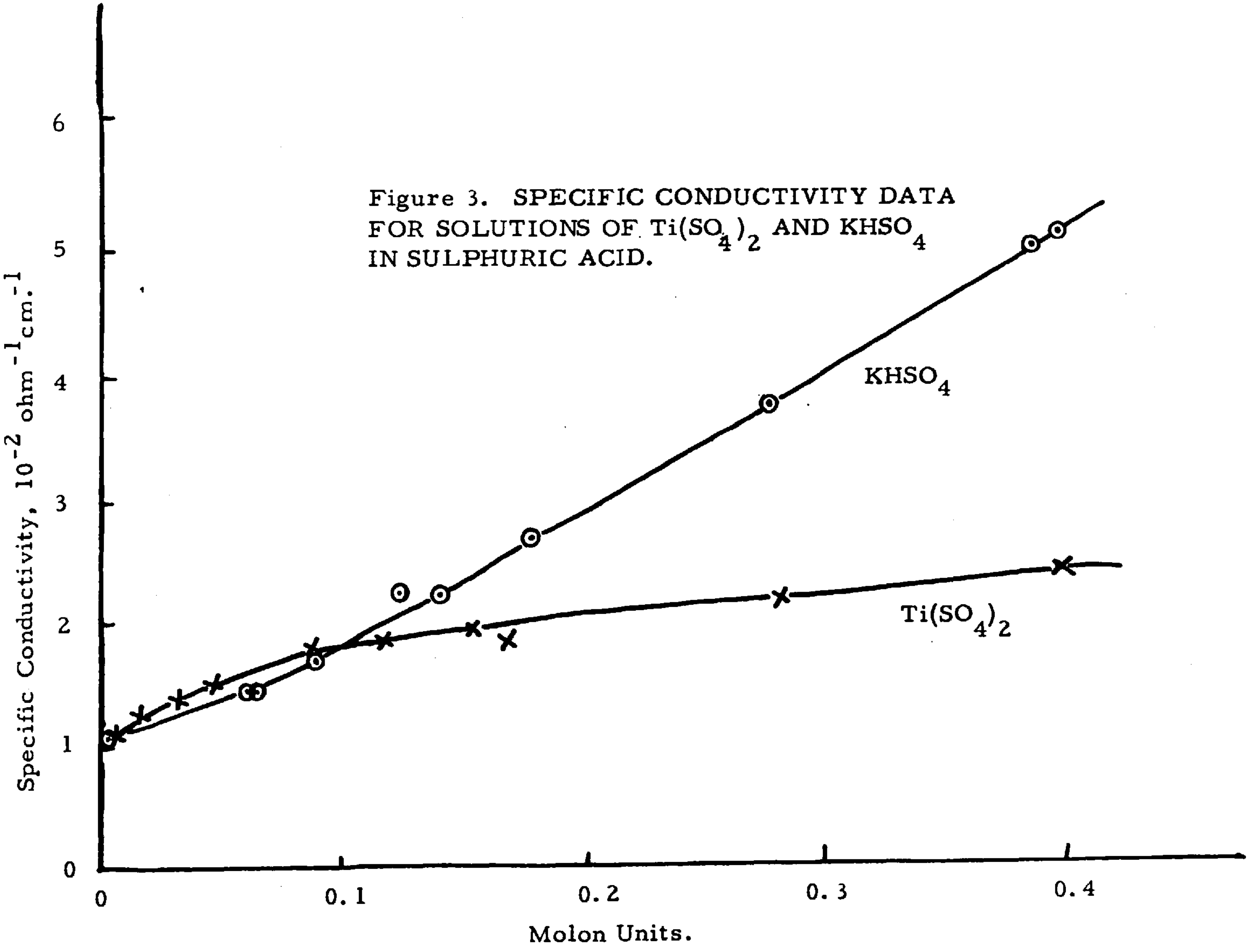

Figure 3. SPECIFIC CONDUCTIVITY DATA FOR SOLUTIONS OF $Ti(SO_4)_2$ AND $KHSO_4$ IN SULPHURIC ACID.

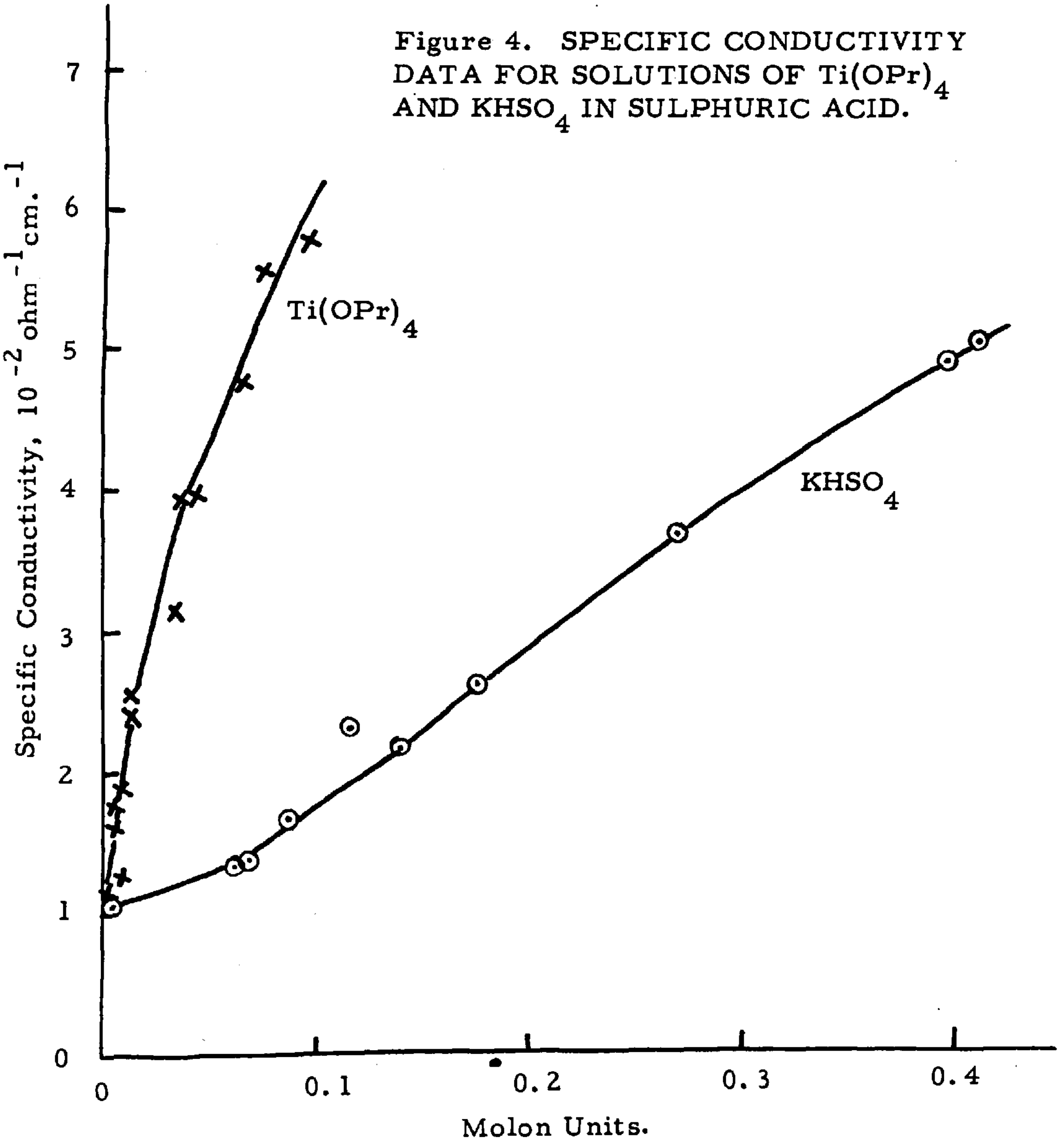

Figure 4. SPECIFIC CONDUCTIVITY DATA FOR SOLUTIONS OF Ti(OPr)$_4$ AND KHSO$_4$ IN SULPHURIC ACID.

For comparison the conductivities are required at rounded molar concentrations (c) or rounded molal concentrations (m) and the former are given in Table VIII. The molar concentrations (c) are obtained from the plot of k against ω by interpolation at the appropriate ω values calculated from the equation $\omega = c/\rho$; ρ , the density of the solution, is assumed to be equal to the density of pure sulphuric acid (1.8269 at 25°C)$^{(23)}$.

Table VIII.

Interpolated Specific Conductivities at 25°C, (10^{-2} ohm^{-1}cm^{-1}).

c (mole l^{-1})	$KHSO_4$	Solute:	
		$Ti(SO_4)_2$	$Ti(OPr)_4$
0.02	1.095	1.140	2.022
0.04	1.143	1.230	2.750
0.06	1.202	1.325	3.350
0.08	1.278	1.410	3.884
0.10	1.348	1.486	4.362
0.12	1.430	1.563	4.820
0.14	1.500	1.630	5.230
0.16	1.579	1.700	5.631
0.18	1.684	1.760	
0.20	1.810	1.810	
0.30	2.220	1.900	
0.40	3.030	2.010	
0.50	3.640	2.110	
0.60	4.220	2.200	
0.70	4.828	2.300	

(e) Determination of the General Behaviour of Titanium Sulphate in Sulphuric Acid.

To determine whether the overall reaction of titanium sulphate in sulphuric acid is basic or acidic, about 19g. of a solution of titanium sulphate obtained from titanium tetrachloride (see Chapter 4), having a concentration of about 0·18 molon, was taken, and potassium sulphate (a base) was added a small quantity at a time. The conductivity was measured in each case; the results are given below (Table IX).

Results.

Wt. of solution = 18·81g.

Concentration of titanium sulphate = ·1792 molon.

Conductivity of the solution = $1{\cdot}908 \times 10^{-2}$ ohm^{-1} cm^{-1} at 25°C.

Table IX

Wt. of K_2SO_4, g.	Specific Conductivity at 25°C., 10^{-2} ohm^{-1} cm.$^{-1}$
0	1·9080
0·01242	2·0061
0·01171	2·0982
0·01381	2·1865
0·01410	2·2272
0·01362	2·2899

The conductivity of the titanium sulphate in sulphuric acid solutions steadily increases on addition of potassium sulphate; in the overall reaction with sulphuric acid titanium sulphate must therefore be regarded as a base.

Discussion of the Results.

Comparison of the conductivities of solutions of titanium sulphate and isopropyl titanate in sulphuric acid with those of potassium sulphate shows that γ, the number of HSO_4^- ions formed by one molecule of titanium sulphate, is one in dilute solutions; γ decreases with increasing concentration. This shows that titanium sulphate behaves as a weak base in sulphuric acid solution.

For isopropyl titanate γ is two in dilute solutions; the value increases with increasing concentration. It must be concluded that isopropyl titanate also has a basic overall reaction in sulphuric acid. The increase of γ suggests that the products formed from the isopropyl residues react further with sulphuric acid giving more HSO_4^- ions, a type of reaction already broadly indicated from earlier studies of aliphatic alchols (see Chapter I).

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Chapter 7.

Cryoscopic Measurements on Solutions of Titanium Sulphate in Sulphuric Acid.

Chapter 7. Cryoscopic Measurements on Solutions in Sulphuric Acid.

GENERAL.

As far back as 1890, there were investigations of the effect of different solutes on the freezing point of sulphuric acid(1,2,3,4). The first solutes studied were water and sulphur trioxide and in these earlier investigations, the measurements were made on compositions selected at random and so widely spaced that to derive precise conclusions was impossible. Hantzsch(5,6) was the first to make systematic measurements of the depression by solutes of the freezing point of sulphuric acid. Hantzsch showed that the purity of sulphuric acid could not be adequately controlled by chemical analysis; cryoscopic measurements were the most sensitive test for purity because pure sulphuric acid has the maximum freezing point.

Almost in the same period, Oddo et al(7,8,9) made similar measurements in much the same way as Hantzsch had done. Their results were somewhat different, largely on account of the inaccurate experimental methods which constituted the best techniques available at that time. Some of Hantzsch's qualitative conclusions required modification; for example, alcohols were found by Oddo and Scandola to be esterified with sulphuric acid and did not behave as simple bases, as Hantzsch had concluded. They recommended the use as solvent, not of pure sulphuric acid, but of sulphuric acid containing a small amount of water.

Improvements in the experimental technique were made by Hammett and Deyrup(10) and by Treffers and Hammett(11), and then later by Gillespie et al(12). In principle, the Beckmann method was used in order to measure the freezing points, but the earlier apparatus was greatly improved.

Treffers and Hammett designed an all-glass apparatus with magnetic stirring for the freezing-point determination. The cell was designed to avoid rubber closures and prevent absorption of moisture from the air. Later Gillespie et al(12) designed a freezing-point cell similar to that used by Treffers and Hammett; it will be described in detail later.

(a) The Solutes, Water and Sulphur Trioxide.

In a study of the solvent sulphuric acid and of solutes in that solvent, it is of fundamental importance to know the behaviour of water and sulphur trioxide as solutes in sulphuric acid. The reasons are that (i) many substances when dissolved in sulphuric acid give water as a reaction product; and (ii) it is the first step in investigation of the self-ionisation of sulphuric acid. Many relevant papers have been published, e.g. by Hantzsch(6), Oddo and Scandola(7), Robles and Moles(13), Hammett and Deyrup(10), Gillespie(14), Gable et al(15), Kunzler and Giauque(16), Gillespie et al(17) and Bass et al(18,29). All these workers found that water and sulphur trioxide both depress the freezing point of sulphuric acid; pure sulphuric acid has the maximum freezing point. The somewhat varying freezing-point values for pure sulphuric acid are listed in Table I.

Table I.

	Freezing point of 100% sulphuric acid
Hantzsch (1908)	10.46°C
Oddo and Scandola (1908)	10.43
Robles and Moles (1936)	10.52
Gillespie (1950)	10.36
Gable, Be~~r~~tz and Maron (1950)	10.37
Kunzler and Giauque (1952)	10.371
Gillespie and Oubridge (1956)	10.365 (Beckmann method)
Bass and Gillespie (1960)	10.371 (equilibrium method)

(b) Self-dissociation of Sulphuric Acid.

The freezing-point curve for the water-sulphur trioxide system consists of two almost linear portions with a rounded maximum in between. At concentrations not too near the rounded maximum, water behaves like a base, ionizing extensively but not completely according to the equation

$$H_2O + H_2SO_4 = H_3O^+ + HSO_4^-,$$

Along the nearly linear branch of the sulphur trioxide curve sulphur trioxide is converted almost completely into disulphuric acid, which is ionized as a weak acid according to the equation

$$H_2S_2O_7 + H_2SO_4 = H_3SO_4^+ + HS_2O_7^-.$$

The rounding of the freezing-point maximum is due to the self-ionization of sulphuric acid. The primary self-dissociation reaction of sulphuric acid is into water and disulphuric acid

$$2H_2SO_4 = H_2O + H_2S_2O_7.$$

Both the products formed ionise in sulphuric acid, water extensively and disulphuric acid partially, according to the equations:

$$H_2O + H_2SO_4 = H_3O^+ + HSO_4^-$$

$$H_2S_2O_7 + H_2SO_4 = H_3SO_4^+ + HS_2O_7^-.$$

The ions $H_3SO_4^+$ and HSO_4^- are in equilibrium as a result of the proton-transfer reaction (autoprotolysis) of the solvent:

$$2H_2SO_4 = H_3SO_4^+ + HSO_4^-.$$

It follows that the ions H_3O^+ and $HS_2O_7^-$ must also be in equilibrium,

$$2H_2SO_4 = H_3O^+ + HS_2O_7^-;$$

this reaction is called the ionic self-dehydration reaction of sulphuric acid.

The hydrogen sulphate ~~in~~ ion HSO_4^- is formed in both modes of self-ionization of sulphuric acid; the hydroxonium ion H_3O^+ is formed in the first mode; therefore the addition of water, which produces both these ions, will repress both self-ionization reactions.

Moreover, since the sulphuric acidium ion $H_3SO_4^+$ is formed in both modes of self-ionization, and the hydrogen disulphate ion $HS_2O_7^-$ is formed in the first mode, sulphur trioxide will again repress both self-ionization reactions. Therefore the rounding of the freezing-point maximum is observed on both sides(14,18).

(c) Sulphuric Acid as a suitable Cryoscopic Solvent.

Sulphuric acid has a high freezing-point and a relatively large molal freezing-point depression or cryoscopic constant. There are two ways of obtaining the cryoscopic constant of a solvent; either (i) it can be calculated from the calorimetrically determined latent heat of fusion of the solvent; or (ii) it can be derived from the depression of freezing point caused by a solute which is believed not to ionise or react in any way with the solvent. In the case of sulphuric acid both methods have been used to evaluate the value of k_f(12). Many workers have determined the cryoscopic constant of sulphuric acid by the method (ii) using various solutes, and the results are listed in Table 2.

Table 2.

Values of k_f for Sulphuric Acid.

	k_f	Solutes	Refs.
Hantzsch	7	Trichloroacetic acid 2:4-Dinitromesitylene 1:3:5-Trinitrobenzene 2:4:6-Trinitrotoluene Picric acid Phthalic anhydride Oxalic acid Methyl sulphate.	6
Oddo and Scandola	6.81	Phosphorus oxychloride Sulphuryl chloride.	7
Hammett and Deyrup	6.00 6.26 6.11	Trichloroacetic acid 1:3:5-Trinitrobenzene Picric acid.	10
Robles and Moles	6.55	Trichloroacetic acid Picric acid Nitrobenzene 2:4:6-Trinitrotoluene.	13
Gillespie, Hughes and Ingold	5.98	Sulphuryl chloride Chlorosulphonic acid.	12

Differences occur in the value of k_f because almost all the solutes listed above react in varying degrees with the solvent.

Table 3 shows values of k_f calculated from the molar heat of fusion determined by different workers.

Table 3.

Authors	Heat of fusion of sulphuric acid	Derived value of k_f	Refs.
Pickering	2355 cal.g-mole^{-1}	6.65	1
Brönsted	2550 " "	6.15	19
Rubin and Giauque	2560	6.12	20

The most accurate of these values is believed to be the last, 6.12, which was recalculated by Gillespie(21) from a recent and accurate value of the heat of fusion determined by Rubin and Giauque(20). This value is used in the present work for calculation of ν.

(d) Calculation of ν.

ν is defined as the number of moles of dissolved particles (molecules or ions) produced by one mole of any solute.

From the freezing-point depressions produced by a solute in sulphuric-acid solution, ν can be calculated from the expression(22)

$$\nu = \theta(1 + 0.002\ \theta)/k_f.g.m. - md/m,$$

where θ is the freezing point depression;

k_f is the cryoscopic constant of sulphuric acid(21) = 6.12;

g is the osmotic coefficient of the solvent(17);

m is the molality of the solute;

md is the total concentration of the self-dissociation species(18).

Generally g is not known and is assumed to be equal to one(17); the equation then becomes

$$\nu = \theta(1 + 0.002\ \theta)/6.12\ m - md/m.$$

When sulphuric acid containing a small amount of water to repress the autoprotolysis was used and it was not desired to measure the exact degree of ionization of all the compounds studied, but rather to establish a general mode of ionization, the results were expressed in terms of the van't Hoff i-factor, which is

$$i = \frac{\Delta\theta}{\Delta m\ k_f}$$

where $\Delta\theta$ is the change in the freezing point depression caused by a small change Δm in the molality of the solute and k_f is the cryoscopic constant of sulphuric acid = 6.12. The values of i approximate sufficiently closely to the more precise ν values(23).

(e) Correction of Results for Supercooling.

A correction for supercooling of the solution is added to each observed freezing point value. This correction is related to the molar heat capacity and heat of fusion of the solvent(12,17), and for sulphuric acid it is given by the expression $\delta T = 0.0125 s\theta$, where s is the amount of supercooling (the observed freezing point of the solution minus the supercooling temperature), and θ is the observed freezing-point depression (the freezing point of pure sulphuric acid, i.e. 10.365°C, minus the observed freezing-point of the solution).

EXPERIMENTS AND RESULTS.

(a) Apparatus.

The freezing-point cell(12) (see Fig. 1) was made of "Pyrex" glass. It had a ground-in head carrying two standard ground joints, one accommodating the thermometer and the other a stopper, and two sealed-in, vertical tubes closed at the top to act as guides for the electromagnetic stirrer. The stirrer consisted of a glass spiral joined at the top to two vertical glass rods, to the upper end of each of which a closed glass tube containing a soft-iron rod was sealed. Two solenoids were supported on each of the guide tubes and an intermittent direct current was passed through them. The period of the intermittent current supply was controlled by a mercury switch, rocked by a cam driven by an electric motor. The freezing point cell was supported in an air-jacket provided with an upward-sloping side arm; the air-jacket was placed in a water-bath. All the ground joints, except the one with the stopper through which the solutions were introduced, were greased with "Apiezon M" grease to prevent ingress of water vapour during the measurements.

A "Stantel" thermistor, type F23, having a resistance of about 2000 ohms at ordinary temperature,

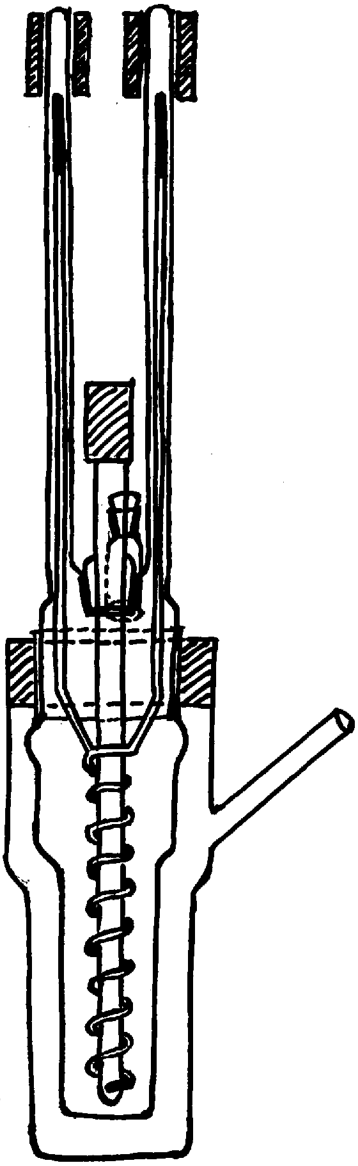

Figure 1. FREEZING-POINT CELL.

was used to measure the temperatures of the solutions. The remainder of the apparatus comprised a vernier potentiometer (type 4363, H. Tinsley and Co. Ltd), a self-contained reflecting galvanometer unit, a decade box of low-inductive standard resistors (H. Tinsley and Co. Ltd.), a standard cadmium cell and two accumulators. These were connected in the way shown in Fig. 2 to measure the resistance of the thermistor. The thermistor was calibrated by comparison with a mercury thermometer with high sensitivity (large bulb, narrow capillary, and short range). The ice point was determined by immersing the thermistor and thermometer in a "Thermos" flask containing pure melting ice, well stirred, and measuring the thermistor resistance. The temperature was then raised by about 0.5° at a time and the resistance values were measured. The calibration was repeated six times at each point; the mean resistance values are given in Table 4 and plotted against temperature in Fig. 3.

(b) Procedure.

To measure the freezing-point, a weighed quantity of sulphuric acid was introduced into the cell and allowed to remain over-night to absorb any moisture present. The temperature of the water-bath was adjusted so that the temperature of the sulphuric acid

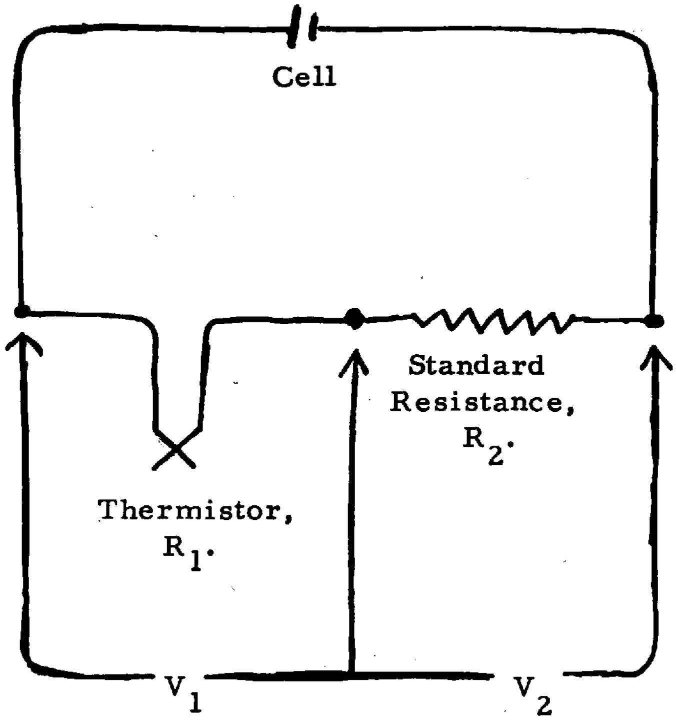

Figure 2. CIRCUIT DIAGRAM FOR MEASUREMENT OF THERMISTOR RESISTANCE.

$$R_1/R_2 = V_1/V_2 = \frac{\text{Potentiometer reading 1}}{\text{Potentiometer reading 2}}$$

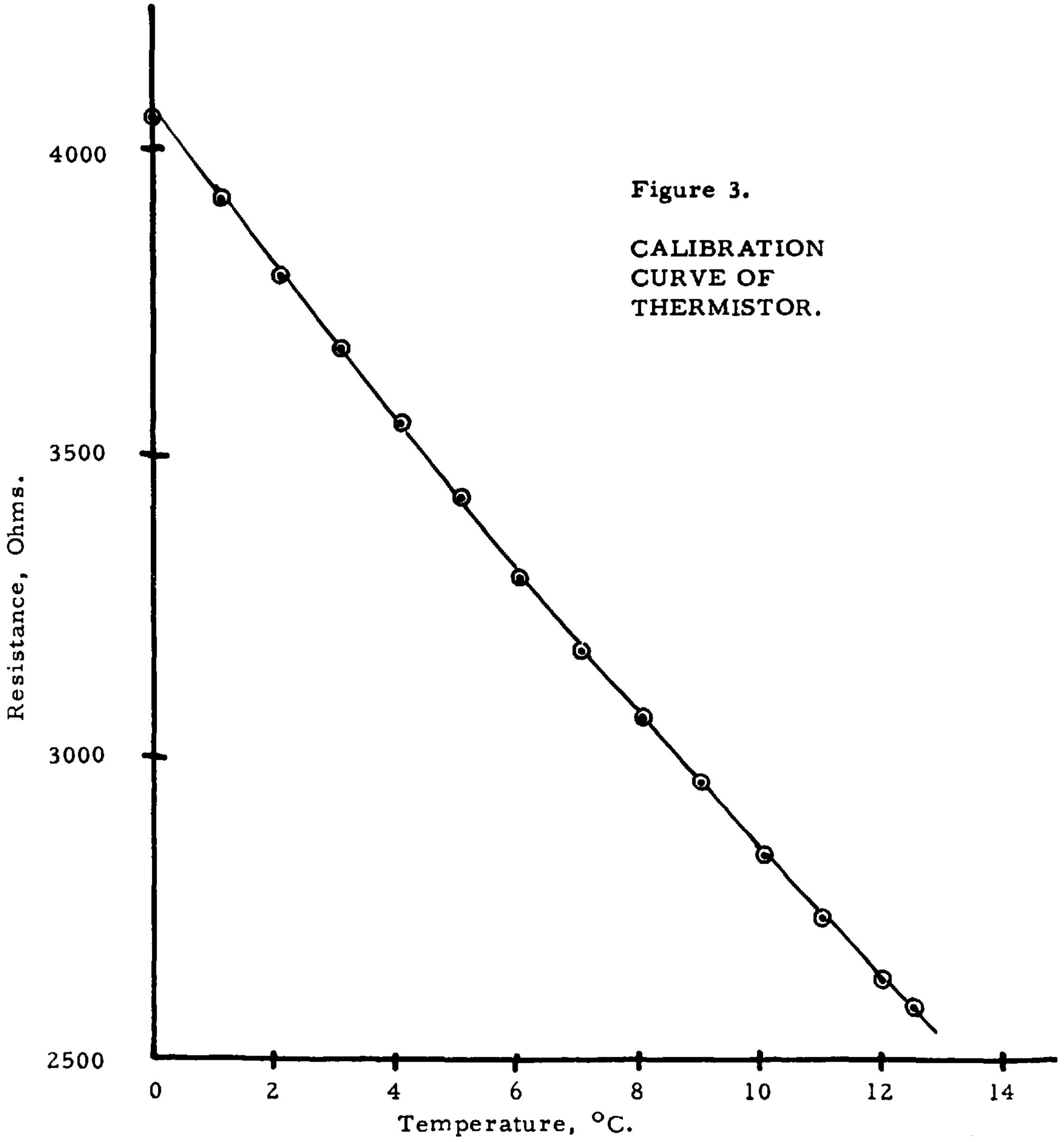

Figure 3.

CALIBRATION
CURVE OF
THERMISTOR.

Table 4.

Calibration of the "Stantel" Thermistor.

Temperature °C	Thermistor Resistance ohms	Temperature °C	Thermistor Resistance ohms
0	4055	6.5	3225
0.5	3984	7.0	3170
1.0	3918	7.5	3116
1.5	3856	8.0	3060
2.0	3799	8.5	3006
2.5	3738	9.0	2592
3.0	3672	9.5	2893
3.5	3618	10.0	2837
4.0	3554	10.5	2780
4.5	3490	11.0	2731
5.0	3426	11.5	2681
5.5	3350	12.0	2632
6.0	3290	12.5	2589

was reduced to about 2°C. below the expected freezing point. To start the crystallisation, a small piece of solid carbon dioxide was inserted down the side arm of the air-jacket, so that it touched the outside of the cell. The temperature of the sulphuric acid dropped and then rose as it started to freeze. The temperature just before crystallisation was taken as the supercooling temperature. The steady maximum temperature reached after crystallisation was the freezing point of the sulphuric acid.

Small weighed quantities of solutions of titanium sulphate in sulphuric acid were then introduced into the freezing point cell, the contents stirred, and the freezing point determined as above.

(c) Test of Freezing-point Apparatus.

The concentrations of five samples of sulphuric acid of suitable selected compositions were determined by the conventional barium sulphate method, and the freezing point of each sample was determined by the procedure described above.

The observed freezing points (Table 5) were plotted against composition (see Fig. 4), and for comparison the standard data of Gillespie(24) (Table 6) were also inserted. The present results are seen to be in satisfactory agreement with those of Gillespie.

Table 5.

Measured Freezing Points of Sulphuric Acid Solutions.

Concentration of sulphuric acid, %	Freezing point, °C
99.68	8.96
99.7^4	9.31
99.77	$9.{}^{4}2$
99.8^4	9.51
99.85	9.70

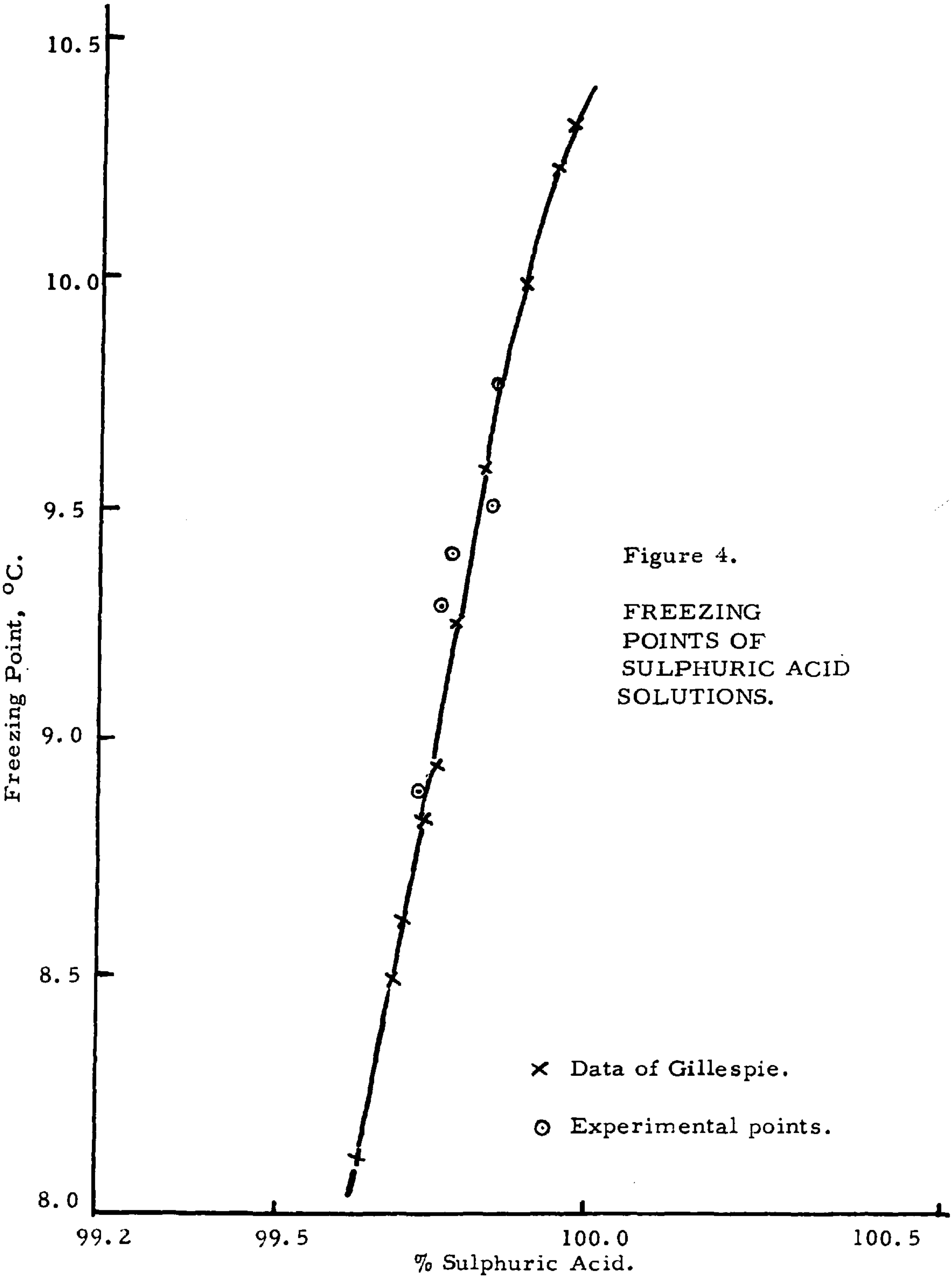

Figure 4.

FREEZING POINTS OF SULPHURIC ACID SOLUTIONS.

Table 6.

Freezing Points of Sulphuric Acid Solutions (Gillespie[24]).

Wt. of solution g	Wt. of H_2SO_4 g	H_2SO_4 %	Freezing point, °C
125.61	125.58	99.98	10.282
125.64	125.58	99.95	10.181
125.71	125.58	99.90	9.875
125.79	125.58	99.83	9.579
125.86	125.58	99.78	9.264
125.92	125.58	99.73	8.948
125.98	125.58	99.68	8.656
127.38	127.04	99.73	8.840
127.45	127.04	99.67	8.513
127.52	127.04	99.62	8.180

(d) Materials.

(e) Preparation of 100% Sulphuric Acid.

100% sulphuric acid was prepared by mixing "Analar" sulphuric acid and 20% oleum in approximately correct proportions; the freezing point was then adjusted to the maximum by addition, drop by drop, of "Analar" sulphuric acid or oleum (25,26,17).

(f) Preparation of Solutions for Freezing Point Determinations.

The solutions were prepared by adding weighed quantities of a concentrated solution of titanium sulphate in sulphuric acid (described in Chapter 4) to sulphuric acid in the freezing-point apparatus. All solutions were made up by weight and their concentrations were expressed in molon units (w)(27), i.e. moles of solute per kilogram of solution. For the calculation of i-factor the concentrations are required in molalities (m), i.e. moles of solute per kilogram of solvent. The two quantities $\underline{w}$ and $\underline{m}$ are related by the equation(28)

$$w = \frac{m}{(1 + \frac{mW}{1000})},$$

where W is the molecular weight of the solute. The sulphuric acid used had the freezing point 9.87°C, and its H_2SO_4 content was not less than 99.85%. All the freezing points given are corrected for supercooling.

RESULTS.

The results of the freezing points determinations are given in Tables 7 and 8.

Table 7.

Freezing Points of $Ti(SO_4)_2$ Solutions in Sulphuric Acid.

Wt. of $Ti(SO_4)_2$ (g.)	Wt. of solution (g.)	w ($Ti(SO_4)_2$)	m ($Ti(SO_4)_2$)	Freezing point °C
0.27227	28.40580	0.03995	0.03957	8.82
0.25060	40.07840	0.05415	0.05345	8.72
0.39221	29.65612	0.05513	0.05441	8.24
0.59710	40.87586	0.06089	0.06001	8.13
0.52060	33.26650	0.06523	0.06422	7.55
0.51666	30.95342	0.06958	0.06843	7.42
0.72124	42.16996	0.07129	0.07009	7.38
0.68866	38.60742	0.07435	0.07305	7.12
0.52060	29.03490	0.07474	0.07342	6.96
0.60522	31.87658	0.07914	0.07767	6.85
0.89489	46.39960	0.08039	0.07887	7.04
1.02816	49.64568	0.08633	0.08458	6.74
0.68866	32.74642	0.08766	0.08586	6.84
0.85555	40.34710	0.08839	0.08655	7.08
1.19805	52.7837	0.09285	0.09083	6.62
1.06963	42.58108	0.10471	0.10214	6.54
1.20626	44.00536	0.11426	0.11121	6.26

Table 8.

Freezing Points of $Ti(OPr)_4$ Solutions in Sulphuric Acid.

Wt. of $Ti(OPr)_4$ (g.)	Wt. of solution (g.)	w ($Ti(OPr)_4$)	m ($Ti(OPr)_4$)	Freezing point °C
0.22069	43.64940	0.01445	0.01438	8.22
0.22070	41. 9586	0.01520	0.01512	8.64
0.30176	44.2287	0.01950	0.01937	7.64
0.30176	41.40460	0.02083	0.02069	7.11
0.34006	44.28304	0.02195	0.02178	6.78
0.63316	45.83894	0.03948	0.03894	3.88
0.73643	46.38716	0.04537	0.04466	3.62
1.13300	56.48478	0.05733	0.05620	2.26
0.99618	47.76606	0.05960	0.05839	1.96
1.13300	48.49236	0.06678	0.06525	1.36

Graphs of freezing points against molalities in titanium sulphate and isopropyl titanate solutions in sulphuric acid are shown in Figs. 5 and 6. To eliminate random errors, the freezing points corresponding to the molalities were taken from the graphs and i-values were calculated from the expression

$$i = \frac{\Delta\theta}{6.12\,\Delta m},$$

where $\Delta\theta$ is the depression in freezing point caused by a small difference in molality, Δm, of the solute (see Tables 9 and 10).

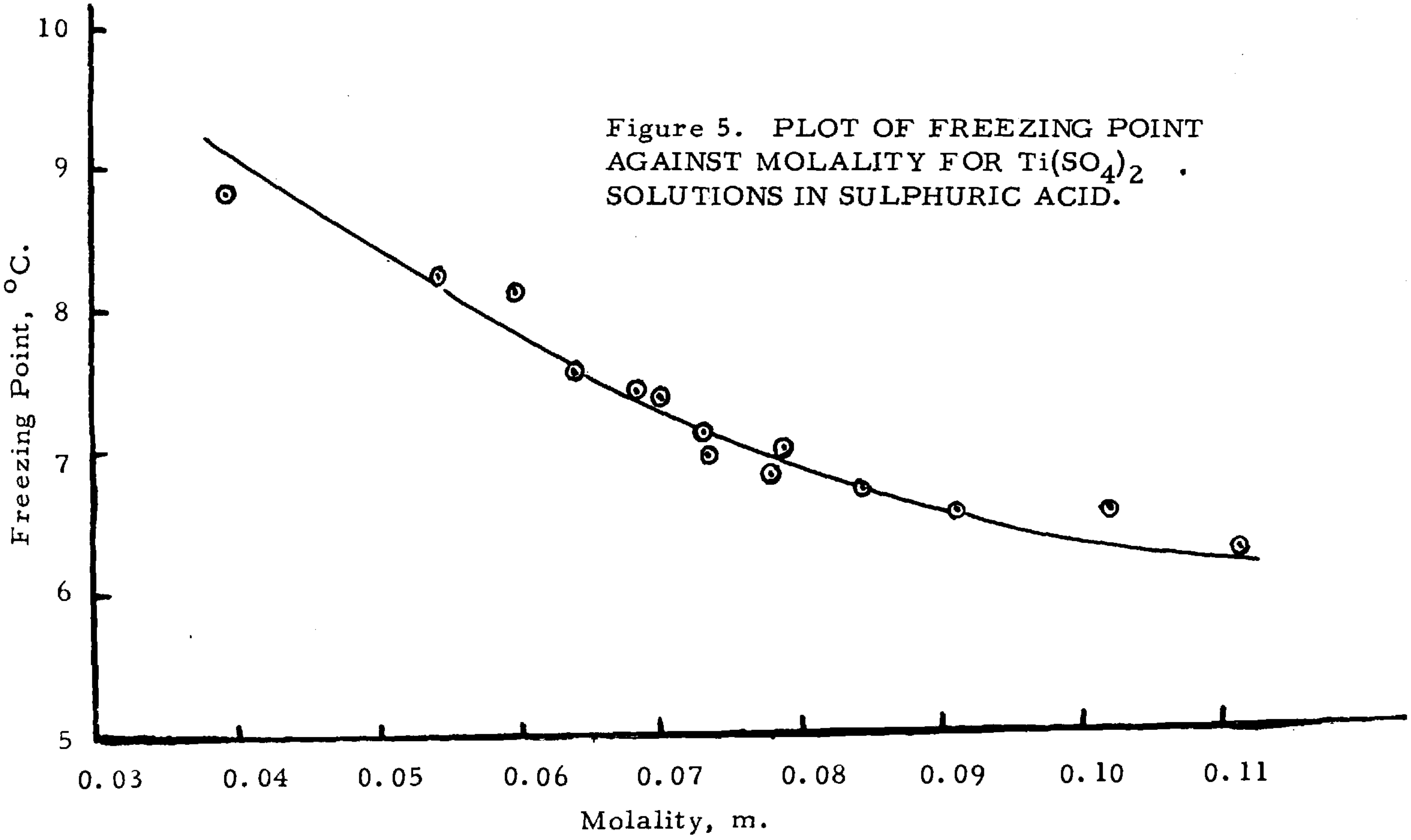

Figure 5. PLOT OF FREEZING POINT AGAINST MOLALITY FOR $Ti(SO_4)_2$. SOLUTIONS IN SULPHURIC ACID.

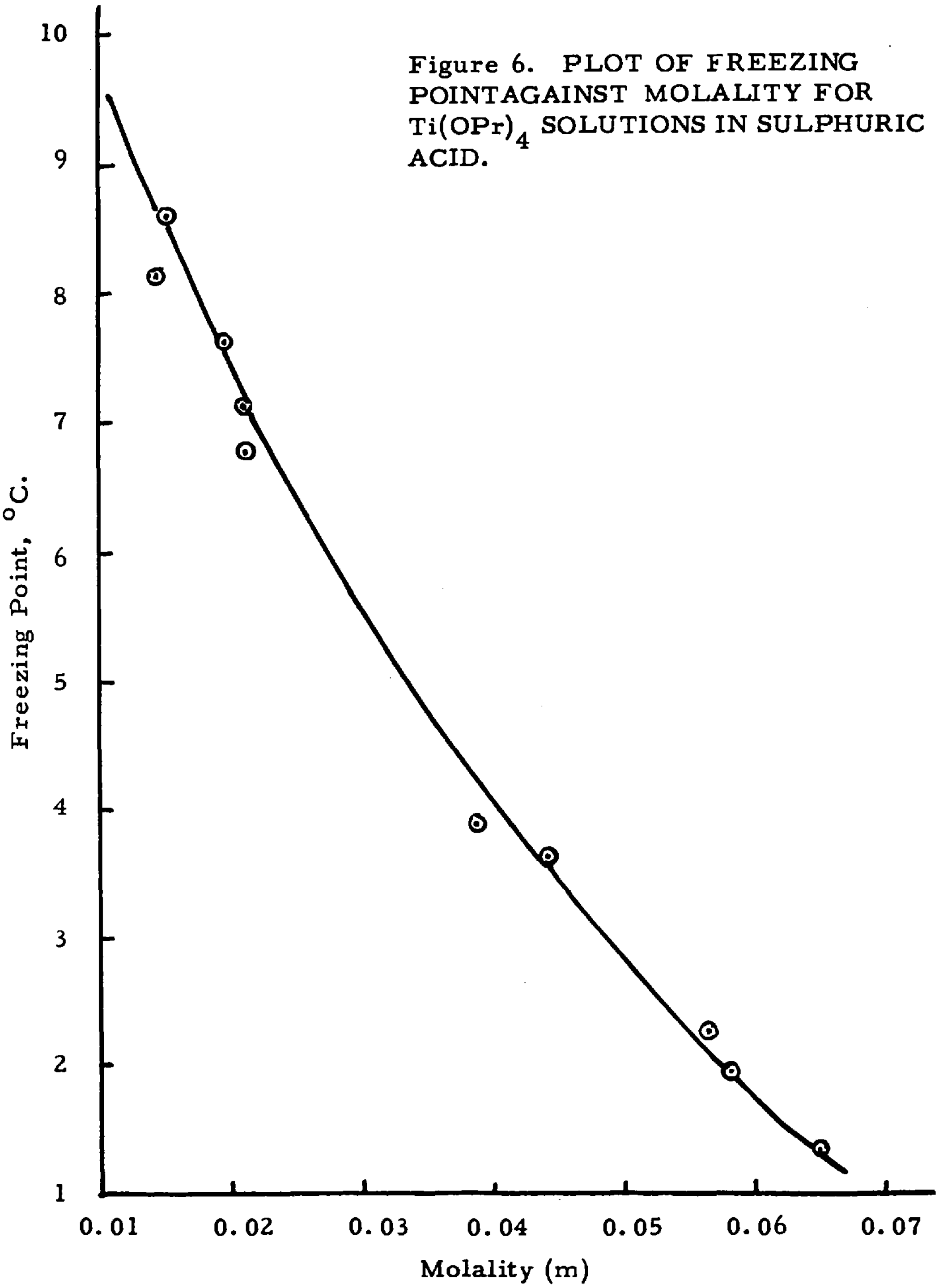

Figure 6. PLOT OF FREEZING POINTAGAINST MOLALITY FOR $Ti(OPr)_4$ SOLUTIONS IN SULPHURIC ACID.

Table 9.

Values of i for $Ti(SO_4)_2$ in Sulphuric Acid.

m	f.p. °C	Δm	$\Delta \theta$	i
0.05	8.55			
0.055	8.22	0.005	0.33	10.8
0.06	7.84	0.005	0.38	12.4
0.065	7.55	0.005	0.29	9.5
0.07	7.31	0.005	0.24	7.8
0.075	7.10	0.005	0.21	6.9
0.08	6.94	0.005	0.16	5.2
0.085	6.80	0.005	0.14	4.6
0.09	6.68	0.005	0.12	3.9
0.095	6.60	0.005	0.08	2.6
0.10	6.52	0.005	0.08	2.6
0.105	6.42	0.005	0.10	3.3
0.11	6.30	0.005	0.12	3.9

Table 10.

Values of i for $Ti(OPr)_4$ in Sulphuric Acid.

m	f.p. °C	Δm	$\Delta\theta$	i
0.015	8.45			
0.02	7.25	0.005	1.20	39.2
0.025	6.29	0.005	0.96	31.3
0.03	5.39	0.005	0.90	29.4
0.035	4.65	0.005	0.74	24.2
0.04	3.98	0.005	0.67	21.9
0.045	3.36	0.005	0.62	20.2
0.05	2.80	0.005	0.56	18.3
0.055	2.29	0.005	0.51	16.7
0.06	1.83	0.005	0.56	18.3

Discussion of the Results.

The values of i, which is equivalent to ν (the number of moles of ions or molecules produced by one mole of $Ti(SO_4)_2$ when dissolved in sulphuric acid) decreases with increasing concentration (Table 9). The i values for isopropyl titanate also decrease with increasing concentration (Table 10). Both titanium compounds apparently show incomplete ionization in sulphuric acid solutions.

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Chapter 8.

General Discussion.

CHAPTER 8 GENERAL DISCUSSION

The solubility values obtained by dissolving titanyl sulphate in sulphuric acid show a wide spread in the sulphur trioxide region. This is probably due to the slow attainment of equilibrium between the solid and the solution, also observed by Sagawa (1,2) He treated hydrated titanium oxide with sulphuric acid (with varying proportions of sulphur trioxide or water), and the solutions were placed in a thermostat at 100°C, and shaken for 3 to 4 weeks. The solubility of titanium dioxide was found to be very small, the highest value obtained being about 0.6%. The same experiment was repeated at 150°C, but even at that temperature the attainment of equilibrium was still slow. In the present experiments, the maximum time of shaking of the solutions was only 24 hours at room temperature and the maximum solubility of titanium dioxide was found to be 0.7%. The slow attainment of equilibrium may be contributed to by the slow adjustment of the complex equilibrium likely to arise in the solution itself. This may involve at least some of the large number of compounds intermediate between the oxides and hydroxides of the aqueous system and the sulphates and hydrogen sulphates of the sulphuric acid system (see Figure 1).

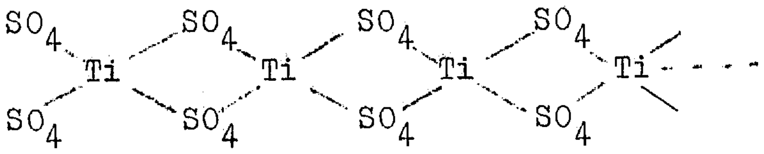
Figure 1

$$
\begin{array}{l|lll}
 & \multicolumn{3}{l}{\xrightarrow{\quad H_2O \quad}} \\
 & \mathrm{TiO_2} & \mathrm{TiO(OH)_2} & \mathrm{Ti(OH)_4} \\
\mathrm{SO_3} & \mathrm{TiO(SO_4)} & \mathrm{TiO(OH)(HSO_4)} & \mathrm{Ti(OH)_3(HSO_4)} \\
 & \mathrm{Ti(SO_4)_2} & \mathrm{TiO(HSO_4)_2} & \mathrm{Ti(OH)_2(HSO_4)_2} \\
 & & \mathrm{TiSO_4(HSO_4)_2} & \mathrm{Ti(OH)(HSO_4)_3} \\
\downarrow & & & \mathrm{Ti(HSO_4)_4}
\end{array}
$$

The formulae given in Figure 1 are empirical and they do not necessarily represent the actual molecular constitutions of the compounds which may be much more complex.

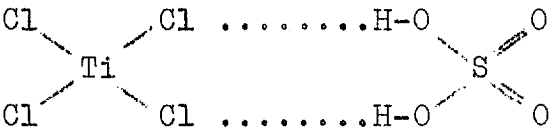
In the aqueous region, the solubility values are much less than those in the sulphur trioxide region under the same experimental conditions; the solubility decreases with increasing sulphuric acid concentration, and is minimum at100% sulphuric acid. The very sparing solubility of titanium sulphate in sulphuric acid may be due to it being polymeric, like plumbic sulphate in sulphuric acid(3). The structure of titanium sulphate in sulphuric acid has not been determined, but it is reasonable to expect it to be similar to that of plumbic sulphate as in Figure II.

Figure II



Tellurium dioxide also resembles titanium dioxide in being insoluble in 100% sulphuric acid; on treatment with sulphuric acid it forms a sulphate which polymerises and becomes insoluble(9). Moreover sulphuric acid itself is a highly associated liquid with strong hydrogen bonds between the molecules(4, 5). The study of pure sulphuric acid crystals at -160°C, shows that it has a layer-type structure in which each sulphuric acid molecule is hydrogen-bonded to four others(6). The high viscosity and boiling point of sulphuric acid are also evidence of strong association in the liquid, and unless a solute is strongly solvated, either because it is ionic or because it forms strong hydrogen bonds with sulphuric acid, it is unlikely to be able to disrupt sufficiently the structure of the sulphuric acid to enable it to dissolve.

The final product from the reaction of titanium tetrachloride and sulphuric acid is a highly solvated complex of the approximate composition $TiO_2,10SO_3,24H_2O$; the yellow intermediate compound formed is $TiCl_4$, H_2SO_4. Both these compounds are practically amorphous to X-rays, an unfortunate fact because their structures cannot be deduced by X-ray crystallographic techniques. The exact formulation of solid compounds is often possible only when their crystal structures are known, and this is true especially for hydrates. But the simplest structure for $TiCl_4,H_2SO_4$ must be:



The tetrahedral molecule $TiCl_4$ and the tetrahedral SO_4 group are joined together by two hydrogen bonds. These hydrogen bonds are relatively very weak, because on dropwise addition of more 100% sulphuric acid to $TiCl_4,H_2SO_4$ hydrogen chloride gas is evolved in a very vigorous reaction.

The final product of the reaction of titanium tetrachloride and sulphuric acid ($TiO_2,10SO_3,24H_2O$), contains a relatively large proportion of molecules of water. In crystalline compounds water can be present as (i) co-ordinated water; (ii) anion water; (iii) lattice water, or (iv) zeolitic water$^{(7,8)}$. Co-ordinated water functions as a neutral ligand and partly or wholly fills all the co-ordination positions associated with the metal atoms ; it is similar in function to the ammonia in metal ammines. In this case the maximum number of water molecules present is often six per cation, e.g. $\{Cr(H_2O)_6\}Cl_3$ etc.

An odd number of water molecules present in a crystalline compound often suggests that one of the water molecules is present as anion water, i.e. water closely associated with the anion. For example, in $CuSO_4,5H_2O$ four water molecules exist as co-ordinated water and the fifth is held to the sulphate ion by two hydrogen bonds; it is at the same time loosely held by other hydrogen bonds to two of the co-ordinated water molecules. Other hydrated sulphates such as $NiSO_4,7H_2O$, $ZnSO_4,7H_2O$ etc. also contain one molecule of anion water.

Lattice water does not directly associate with any particular anion or cation, but fills cavities in the crystal structure. This may happen if neither cation nor anion has a strong tendency to attract water molecules, or if water molecules are present in excess of those with which the ions can associate. The extra water in heavily hydrated sulphates such as $Na_2SO_4,12H_2O$; $MgSO_4,12H_2O$; $Co_2(SO_4)_3,18H_2O$; $Al_2(SO_4)_3,18H_2O$, etc. is lattice water.

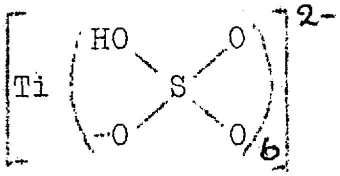
Zeolitic water molecules occupy more or less random positions in the crystal lattice and they are lost continuously upon dehydration. Such water occurs, for example, in natural and synthetic zeolites, silicate minerals of the clay type, and some hydrated sulphates such as $Cr_2(SO_4)_3,15H_2O$.

Although the structure is not known, it appears likely that the large excess of water molecules in $TiO_2,10SO_3,24H_2O$ are present as lattice water.

The study of the solutions of titanium sulphate in sulphuric acid by ultraviolet spectrophotometry shows that the solutions contain a complex which strongly absorbs light of wave length 2550A, in which H_2SO_4 molecules and HSO_4^- ions are combined in nearly equal proportions; but of course this particular complex is not necessarily the only complex in the solution. A very straightforward deduction of the formula of this complex species is that it is an anion complex $\left[Ti(HSO_4)_6\right]^{2-}$ formed by the following equation:-

$$Ti(SO_4)_2 + 2H_2SO_4 + 2HSO_4^- \rightleftharpoons \left[Ti(HSO_4)_6\right]^{2-}$$

Formation of such a complex is expected by analogy with other similar complexes (3,9), such as $\left[Pb(HSO_4)_6\right]^{2-}$ and $\left[Sn(HSO_4)_6\right]^{2-}$. It is also fully consistent with the general behaviour of titanium in six-covalent complexes. Like other complex ions of titanium, (10,11,12) such as TiF_6^{2-}, $TiCl_6^{2-}$ etc., the $\left[Ti(HSO_4)_6\right]^{2-}$ ion is expected to be a regular octahedron with HSO_4^- groups covalently attached to the titanium atom through oxygen, i.e.



Conductivity data suggest that in dilute solutions one HSO_4^- group is present in solution per atom of titanium; as the concentration increases, the number of HSO_4^- groups becomes less than one. The complex ion $\left[Ti(HSO_4)_6\right]^{2-}$ would evidently function as a base in the sulphuric acid system, and the presence of about one HSO_4^- ion per complex in dilute solution suggests that the complex is relatively unstable and appreciably dissociated.

Freezing point measurements indicate that approximately three molecules or ions are present in solution for each atom of titanium (or molecule of $Ti(SO_4)_2$). This can be accounted for in a generally satisfactory manner if it is assumed that in the above equation for formation of $[Ti(HSO_4)_6]^{2-}$ the equilibrium does not proceed very far to the right under the experimental conditions. In any case the freezing point data are necessarily very sensitive to traces of moisture during the measurements, and the apparently high i values at low titanium concentration are believed to be due to inevitable slight contamination of the solutions with moisture. The values in the neighbourhood of three found at the higher concentrations are to be regarded as the most reliable, and they may still be high. Even though the Beckmann method for the freezing point measurements is simple and convenient for most systems, for a highly hygroscopic solvent like sulphuric acid, it is preferable to use the equilibrium method.

In the equilibrium method, a quantity of the solid solvent and solution are stirred together in a Dewar flask until a steady equilibrium temperature is obtained; then a sample of the solution is withdrawn and analysed.(13,14) The flask containing the solution and a conductivity cell for the determination of solute concentration are permanently connected to the cryoscope (Dewar flask fitted with a double lid, thermometer, stirrer etc.) Leakage of atmospheric moisture is prevented by maintaining an inert atmosphere (dry nitrogen) between the two lids. Small quantities of solution are added to the cryoscope by applying a slight pressure of dry nitrogen. Samples of solutions for analysis are withdrawn by suction into the conductivity cell through a tube fitted with a sintered glass disc to exclude solids. The possible source of error for the equilibrium method is that the true equilibrium between the solid phase and the solution may not be established. There may be a slow freezing out or melting of the solid phase, and thus the liquid in contact with the crystal will not have the same composition as that of the bulk liquid, so that the measured freezing point will be slightly different from the true equilibrium temperature. However Bass and Gillespie (14) have found that good agreement was obtained between different experiments and once "equilibrium" had been established, the temperature did not vary more than one thousandth of a degree in several hours.

In the Beckmann method the proper equilibrium between the solid phase and the liquid is difficult to maintain. Under the usual conditions of the method the external bath temperature is lower than that of the solution in the cryoscope and the solid may be continually freezing out. If crystallisation is not sufficiently rapid, the liquid will be at a slightly lower temperature than the true freezing point of the solution. In a supercooled solution, crystallisation is very rapid and it is possible that a non-equilibrium solid may be formed containing solvent. All these factors could lead to observed temperatures lower than the true freezing points of the solutions, and hence high i values.

Results obtained from the solutions of isopropyl titanate in sulphuric acid are necessarily complicated by the presence of organic substances in the solution; they are confirmatory but less significant. The variations of γ and i values with concentration show that the organic groups undergo further reactions in excess sulphuric acid.(15)

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