CATIONS AND OXY-CATIONS OF IODINE

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BY

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SCOPE AND CONTENTS:

The behaviour of iodic acid, of mixtures of iodic acid and iodine, and of various other iodine compounds as solutes in sulphuric and fluorosulphuric acids has been studied, using mainly cryoscopic and conductimetric techniques. Evidence has been obtained for the existence of polymeric species containing iodine (V), of the oxy-cation IO^+, of the iodine cation, I^+, in small concentrations in equilibrium with its disproportionation products, and of the cations I_3^+, I_5^+ and I_2Cl^+. The reaction of iodosyl sulphate with disulphuric acid has been studied. Conductimetric studies have been made of solutions of water, potassium nitrate and potassium perchlorate in fluorosulphuric acid. The results of some spectrophotometric and nuclear magnetic resonance experiments are also reported.

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ADDENDUM

Since this work was completed, Arotsky et al* have published the results of conductimetric, cryoscopic and other studies of solutions of a number of iodine-containing compounds in sulphuric acid and oleum. Their conclusions differ in some respects from those reached in the present work. For example, $IOHSO_4$ is said to be a non-electrolyte in sulphuric acid solutions, whereas the present results indicate that it is about 50% ionized (Chapter III, Section 4). Iodic acid is said to give rise to the ion $H_2IO_3^+$ in sulphuric acid solutions. This conclusion is largely based on the result of a conductimetric titration of $H_2S_2O_7$ with HIO_3. However, Arotsky et al give, for comparison purposes, the result of a titration of $H_2S_2O_7$ with $KHSO_4$ in which the conductivity minimum is shown to occur at the mole ratio, $r_{min} = KHSO_4/H_2S_2O_7 = 0.2$, whereas it has been demonstrated, both theoretically and experimentally, by Flowers, Gillespie and Robinson (93), that in such a titration, $r_{min} = 0.56$. A detailed discussion of possible modes of ionization of HIO_3 in sulphuric acid solutions is given in Chapter III, Section 2 of this thesis.

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* J. Arotsky, H. C. Mishra and M. C. R. Symons, J. Chem. Soc. 2582 (1962).

CHAPTER I

INTRODUCTION

1. Compounds of "Positive" Iodine

Iodine is the most electropositive of the halogens, with the probable exception of astatine, about the chemistry of which relatively little is known. Thus of all the common halogens iodine is the most likely to form compounds in which it is present as a cation, or a cationic radical. A few classes of compounds are known in which iodine is definitely present in the form of cations, and in many other compounds the presence of cations or oxy-cations containing iodine has been suggested. The participation of iodine cations or oxy-cations as transient intermediates in many reactions of iodine compounds in aqueous solution has also been postulated. A review of compounds containing positive halogens has appeared (1), and the subject has also been discussed in some detail by Sidgwick (2).

Heptavalent iodine

Schmeisser and Brandle (3) have described the compounds IO_3ICl_2, and $IO_3\ I(NO_3)_2$, which might contain the ion IO_3^+, but whose structures have not been determined. Periodyl fluoride, IO_3F does not appear to react with Lewis acids, such as BF_3 and SbF_5, as it might be expected to do if the cation IO_3^+ were stable (4). Orthoperiodic acid is insoluble in nitromethane, but dissolves in a mixture of nitromethane and perchloric acid. This has been attributed to the formation of the ion $I(OH)_6^+$, rather than to IO_3^+ (5).

The same author reports (6) that in perchloric acid alone orthoperiodic acid decomposes, probably by dehydration. Mishra and Symons (7) claim that in aqueous acid, 100% sulphuric acid, and 65% fuming sulphuric acid, orthoperiodic acid gives respectively the ion $I(OH)_6^+$, a species containing pentavalent iodine, probably $H_2IO_3^+$, and the hitherto unkown iodine heptoxide I_2O_7. The ion IO_3^+ has been postulated as an intermediate in the reaction between periodate and iodide ions in aqueous solution (8) but the kinetic data do not permit the distinction between this ion and hydrated forms such as $I(OH)_6^+$.

Pentavalent iodine

The compounds $I_2O_5.2SO_3$, and $I_2O_4.3SO_3$, prepared by Muir (9) and recently re-examined by Lehmann and Hesselbarth (10) were formulated by the latter authors as iodyl disulphate, $(IO_2^+)_2 S_2O_7^{--}$ and the mixed iodyl-iodosyl trisulphate $(IO_2^+)(IO^+) S_3O_{10}^{--}$, although no structural evidence was cited. The compound having the empirical formula IOF_3, prepared by Aynsley, Nichols and Robinson (11) was considered by them to be $IO_2^+ IF_6^-$. However, in view of the general reluctance of iodyl fluoride, IO_2F, to form complexes with Lewis acids, Aynsley and Sampath (12) have suggested that the compound $IO_2F.AsF_5$ obtained by Schmeisser and Lang (4) and formulated by them as $IO_2^+ AsF_6^-$, is more likely to be $AsF_4^+ IO_2F_2^-$. The existence of the ion IO_2^+ in solutions of iodic acid in liquid hydrogen fluoride has been proposed, to explain the solubility of iodic acid in this solvent without apparent decomposition, although chloric and bromic acids are decomposed to chlorine dioxide and bromine respectively (13).

Schmeisser and Lang have suggested that iodine pentoxide is ionized in liquid HF to give IO_2^+ and IO_3^- (4). Myers and Kennedy have postulated the existence of IO_2^+ as an intermediate in the exchange of iodine between I_2 and IO_3^- in aqueous solution, and state that iodic acid forms "a double compound" with concentrated perchloric or sulphuric acids (14). Masson has reported the formation of a "white solid iodic-sulphuric complex" when iodine pentoxide is placed in fuming sulphuric acid (15). The occurrence of the iodyl cation as a reaction intermediate has also been proposed in the disproportionation of hypoiodite to iodide and iodate, in the reaction of iodide and iodate in acid solution, in the iodate-sulphite reaction and in the reaction of iodic acid with hydrogen peroxide (8). In all these cases, the hydrated form, $H_2IO_3^+$, is equally consistent with the kinetic data.

Trivalent iodine

Numerous salt-like compounds of trivalent iodine are known. The first of these to be reported was the acetate $I(O\,Ac)_3$, prepared by Schutzenberger (16) in 1861. Fichter and co-workers prepared $I(OCOCCl_3)_3$, $I(OCOCHCl_2)_3$, $I(OCOCH_2Cl)_3$, $I(CH_3SO_3)_3$, IPO_4, $I(ClO_4)_3.2H_2O$, and I_4O_9, which Bahl and Partington (45) formulated as $I(IO_3)_3$ (17, 18, 19). Oldham and Ubbelohde described the preparation of iodine (III) acyls of various long-chain fatty acids (20). Schmeisser and Brandle have recently prepared the nitrate $I(NO_3)_3$, unstable above 0^oC (3, 20). Roberts and Cady have prepared the fluorosulphate $I(SO_3F)_3$ by the reaction of iodine with peroxodisulphuryl fluoride, $S_2O_6F_2$ (21). Fichter and Stern found that on the electrolysis of a solution of

$I(OAc)_3$ in acetic anhydride, iodine was released at the cathode in accordance with Faraday's Laws (19). This does not of course prove the presence of I^{+++} ions in these solutions. The cation involved is more likely to be $I(OAc)_2^+$, in which iodine has a complete valency octet (2). All of these compounds are probably essentially covalent in the solid state, although as in the case of the acetate, they may be partly ionized in solution.

Aromatic iodoso-compounds, $ArIO$, react with acids to form compounds of the general type $ArIX_2$, where X can be F, Cl, or OAc. A chromate, $C_6H_5ICrO_4$, is also known. These compounds are often referred to as "salts", but they are probably covalent (2). The well-known diaryliodonium salts, $Ar_2I^+X^-$, are definitely ionic (22, 23).

A number of compounds of trivalent iodine are known which may be formulated as salts of the iodosyl cation IO^+. Chrétien (24) prepared a yellow sulphate, whose composition was the subject of some controversy (45, 25) but was shown by Masson and Argument to be $I_2O_3.SO_3$ or $(IO)_2SO_4$ (26). Dasent and Waddington have recently prepared the corresponding selenate, $(IO)_2SeO_4$ (27). The compound I_2O_4 has for a long time been regarded as iodosyl iodate, $IOIO_3$. A yellow compound prepared by the action of nitric acid on iodine, and originally considered to be the normal nitrate, $I(NO_3)_3$, has recently been shown to be $IONO_3$ (28). Dasent and Waddington (27) have argued against the presence of discrete IO^+ ions in the solid compounds on the following grounds.

1. Apart from the small solubility of the sulphate and selenate in their parent acids, none of the compounds is soluble without decomposition in any of a wide range of common solvents tested, including nitromethane, which dissolves salts of the nitrosyl cation, NO^+.

2. IO^+ has the same number of valence electrons as O_2 and might therefore be expected to have a triplet ground state, $^3\Sigma^-$, and to be paramagnetic. In fact $(IO)_2SO_4$, $(IO)_2 SeO_4$ and I_2O_4 are all diamagnetic.

3. The TeO molecule, which is completely isoelectronic with IO^+, has a stretching frequency of 796 cm^{-1}, so that IO^+ should have a stretching frequency of 800 cm^{-1} or higher. The only frequencies in the I.R. spectra of $(IO)_2SO_4$, $(IO)_2 SeO_4$ and I_2O_4 which can be attributed to the IO group occur in the range 550 - 660 cm^{-1}, expected for I-O single bond stretching frequencies. Dasent and Waddington have postulated the presence in the solids of polymerized I-O-I chains. The tetrahedral symmetry of the SO_4 and SeO_4 groups is essentially undisturbed, although this does not rule out some degree of covalent bonding between these groups and the I-O chains, while the vibrational frequencies of the iodate groups indicate that they are linked to the I-O chains by bonds comparable in covalent character with iodate-metal bonds in iodato-complexes (29). Wise and Hannan (94) have recently reported the I.R. spectrum of I_2O_4, but they do not seem to have examined the KBr region of the spectrum, and assign to the IO^+ ion a band at 1105 cm^{-1}, not found by Dasent and Waddington, which seems more likely to be due to a sulphate impurity.

Solutions of $(IO)_2 SO_4$ in sulphuric acid react with aromatic compounds to give either iodoso or iodonium compounds, indicating that IO^+ ions are probably present in the solutions (30, 31).

The IO^+ ion has been postulated as an intermediate in the iodate-iodide and iodate-sulphite reactions in aqueous solutions (8).

Univalent iodine

The species occurring in acidic aqueous solutions of hypoiodous acid, sometimes referred to as the iodine cation, is almost certainly the hydrated form, H_2OI^+, the hypoiodous acidium ion. Bell and Gelles have shown from thermodynamic considerations that the free iodine cation, I^+, would be so unstable in aqueous solution that it could exist only in immeasurably small concentrations (32). The "iodine cation" reported to be produced by the removal of iodide ions from solutions of iodine in absolute ethanol by precipitation with silver nitrate or by ion exchange techniques, (33) is almost certainly the ethanol analogue of the hypoiodous acidium ion, i.e. $C_2H_6O\ I^+$.

The iodine cation can be stabilized by co-ordination with suitable ligands. Carlsohn (34) first prepared a number of compounds of the general formula Ipy_2X and IpyX, where py represents a pyridine molecule, C_5H_5N. Compounds of the former type are regarded as being true ionic salts $Ipy_2^+\ X^-$. Carlsohn prepared the nitrate and perchlorate of the Ipy_2^+ ion, and Schmidt and Meinert (35) have recently obtained the fluoride, fluorosulphate, and hexafluoro-antimonate (VI). Compounds of the type IpyX are regarded as being covalent, and are mostly derived from organic acids, although a nitrate was prepared by Carlsohn, and Zingaro and Tolberg have prepared the

cyanide and fluoride (36). Substituted pyridines such as β-picoline, 2, 4-lutidine, 2, 6-lutidine and 2, 4, 6-collidine have also been used as ligands in similar compounds (34).

Symons and co-workers have shown that when iodine is dissolved in 65% fuming sulphuric acid, intensely blue solutions are formed, in which iodine exists in the +1 valence state, some of the sulphur trioxide being reduced to sulphur dioxide (35). Similar solutions are obtained from iodine monochloride, but without the production of sulphur dioxide (37). The solutions have an intense absorption band at 640 mμ and weaker bands at 500 and 410 mμ (36, 37, 39). The solutions are paramagnetic, and measurements by the conventional Gouy method lead to an effective magnetic moment of about 1.5 B.M. per iodine atom (37).

The proton N.M.R. peak of the solvent is broadened and shifted to higher field, indicating the presence of a paramagnetic species in the solutions. A value of μ_{eff} of 1.5 B.M. has been estimated from a study of the shift in the proton resonance as a function of concentration (38). Arotsky, Mishra and Symons have claimed, on the basis of electrical conductivity measurements on solutions of iodine, iodine monochloride and potassium iodide in 65% oleum, that complete ionization occurs, with the formation of the free iodine cation, I^+, according to:

$$I_2 + 3SO_3 + H_2S_2O_7 = 2I^+ + SO_2 + 2HS_2O_7^-$$

and

$$ICl + SO_3 + H_2S_2O_7 = I^+ + HS_2O_7^- + HSO_3Cl$$

The iodine cation would have two unpaired electrons, and should therefore be paramagnetic. The absorption spectrum was explained in terms of the effect on the energies of the 5p orbitals of I^+, of the ligand field due to four solvent molecules arranged in a square planar configuration about the I^+ ion (37). None of the evidence presented by Symons et al seems to be inconsistent with the formation of the species I_2^{++}, which would be isoelectronic in the valence shell with the O_2 molecule, and might therefore be expected to be paramagnetic. An alternative suggestion, by Moknach et al (39) that the blue colour is due to complexes of neutral iodine with polysulphuric acid molecules, similar to the starch-iodine complex, is clearly incorrect, since these authors make the wrong assumption that the iodine does not undergo oxidation in 65% oleum.

Evidence has been presented by various workers for the stabilization of hypoiodous acid in aqueous acid solutions, by the formation of a brown complex with iodine, I_3OH (40). This species may be regarded as the neutral base corresponding to the ion I_3^+. Masson (15) obtained brown solutions by the addition of iodine to solutions of $(IO)_2 SO_4$ in sulphuric acid. These solutions iodinated aromatic compounds, with the simultaneous precipitation of molecular iodine. From the stoichiometry of the reactions, Masson deduced the presence in the solutions of the ions I_3^+ and I_5^+. Similar solutions have been obtained by dissolving iodine in dilute oleums (36), and by the action of mercury sulphates on iodine in concentrated sulphuric acid (41).

2. Purpose of This Work

Sulphuric acid has proved to be a useful solvent for the stabilization of many cations which are too electrophilic to exist in more basic solvents. Examples are the oxy-cations NO_2^+, NO^+ (42) and AsO^+, (88) the triphenyl-carbonium ion, $(C_6H_5)_3C^+$ and the mesitoyl cation, $(CH_3)_3\ C_6H_2CO^+$ (43). The even stronger acid, fluorosulphuric acid, is also potentially useful in this respect.

It was the main purpose of this work to study the modes of ionization of suitable solutes in these two solvents, and thus to determine whether and under what conditions, ions such as IO_2^+, IO^+, I^+ and I_3^+ could exist in the solutions.

3. A Note on Concentration Units and Symbols

Concentrations in molal units (moles of solute per kg of solvent) are represented by the symbol m. Except where otherwise stated, molalities of solutions in sulphuric acid are corrected for any solvent used up in the reaction with the solute. Because of the complicated and sometimes uncertain nature of the reactions of many solutes with fluorosulphuric acid, molalities of solutions in this solvent are not so corrected.

The superscript "s" attached to any concentration symbol, refers to the stoichiometric concentration of a solute, e.g. $m^s(X)$ stands for the stoichiometric molality of X. Square brackets are also sometimes used to represent concentrations in molal units, and always refer to the actual concentration of a species, thus $[X]$ stands

for the actual molal concentration of X. All equilibrium constants are expressed in molal units of concentration.

The symbol w is used to represent concentrations in units of moles of solute per kg of solution. The name "molon" has recently been suggested for this unit (95). The molonity of a solution is related to the molarity M by the expression

$$M = \rho w$$

where ρ is the density of the solution. In the present work the densities of the solutions were not known, and to facilitate comparison with published conductivity data, the concentrations of solutions in sulphuric acid have been expressed as "pseudo" molarities, "M", given by

$$"M" = \rho_o w$$

where ρ_o is the density of the pure solvent.

CHAPTER II

EXPERIMENTAL

1. Preparation and Purification of Materials

Sulphuric acid

Sulphuric acid with a composition very close to 100% H_2SO_4 was prepared by mixing C.P. Reagent grade sulphuric acid (about 97% H_2SO_4) and Reagent grade fuming sulphuric acid (30% free SO_3) to give a product having the maximum freezing point of 10.37°C. This acid was adjusted to exactly the 100% composition in a conductivity cell before use. Small amounts of a very dilute oleum, or a dilute solution of water in sulphuric acid were added to bring the specific conductivity to its minimum value of 1.0432×10^{-2} ohm^{-1} cm^{-1}, and sufficient oleum was then added to bring the specific conductivity to that of the pure acid, 1.0439×10^{-2} ohm^{-1} cm^{-1}.

Fuming sulphuric acid

Oleums of known composition were obtained by distilling sulphur trioxide from Technical grade 65% oleum, or stabilized liquid sulphur trioxide ("Sulfan B"), into a weighed amount of sulphuric acid.

Fluorosulphuric acid

Technical grade fluorosulphuric acid was distilled twice at atmospheric pressure in the apparatus shown in Figure 1. The still was swept out with dry air for at least one hour before use

and warmed at intervals with the bunsen flame. Whenever possible the second distillation was made directly into the conductivity cell or other apparatus in which the acid was to be used. A low-boiling fraction was rejected each time, and the pure acid had a boiling point of 162-163°C.

Iodic acid

AnalaR iodic acid was recrystallized from 1 : 4 nitric acid. The crystals were filtered off and dried by suction on the filter for several hours. It was found that the iodic acid became dehydrated to some extent in the course of a few months, and it was necessary to recrystallize it again.

Iodine

AnalaR iodine was used without further purification.

Iodosyl sulphate

Iodosyl sulphate, $(IO)_2 SO_4$, was prepared by the method of Masson and Argument (26). 10.0 g of finely powdered iodine pentoxide and 5.1 g of iodine were stirred magnetically under 97% sulphuric acid for two or three days. The yellow product was filtered off on a sintered-glass filter in the dry-box, and washed three times with small portions of 97% sulphuric acid, and three times with anhydrous nitromethane. The product was freed from nitromethane by warming it gently under vacuum for a few hours. It was stored in a stoppered bottle in a desiccator over "Anhydrone". All subsequent handling of the compound was done in the dry-box.

Analysis: The compound reacts with water to produce iodine, iodic acid and sulphuric acid

$$5(IO)_2SO_4 + 8H_2O = 6HIO_3 + 2I_2 + 5H_2SO_4$$

A weighed portion was refluxed with water, and carbon tetrachloride added to extract the iodine liberated. The extract was treated with water, potassium iodide and a few drops of dilute acid, and the iodine titrated with standard $^N/_{10}$ sodium thiosulphate solution. The aqueous layer was acidified and potassium iodide added in excess. The iodine liberated was titrated with standard thiosulphate. From the ratio, R, of the second titre to the first, the oxidation number X of the iodine is given by

$$X = \frac{5R}{6 + R}$$

The results of a typical analysis were:

Oxidation number of iodine	2.99, 3.04	(Calculated 3.00)
% I	66.9 66.8	(Calculated 66.4)

Iodosyl iodate

Iodosyl iodate or "iodine dioxide", I_2O_4, was prepared by the method of Muir (9) as modified by Bahl and Partington (45). About 20 g of finely powdered iodic acid were heated with 70 g of concentrated sulphuric acid, until all had dissolved, and the vapours evolved showed traces of violet. This took about 40 minutes. The solution was allowed to cool, and kept in a desiccator over sulphuric acid for about a week. The supernatant liquid was poured off, and the yellow solid crust which had formed was broken up and drained

by suction on a sintered-glass filter. It was transferred to a porous plate and kept in a desiccator for one week, being taken out and ground to a powder from time to time. The resulting product was washed six times with cold water on a sintered glass filter until the washings were free from sulphate. It was washed with acetone until the washings were colourless, and then with dry ether, and dried overnight on a porous plate in the desiccator.

Analysis: The method of analysis was the same as that described above for iodosyl sulphate.

Results:

Oxidation number of iodine	3.99	4.01	(Calculated 4.00)
% I	78.3	78.5	(Calculated 79.9)

Iodine monochloride

Practical grade iodine monochloride was purified by freezing out about 80% of the material and rejecting the remaining liquid. This procedure was carried out four times in all (46).

Dipyridine iodine (I) nitrate

Dipyridine iodine (I) nitrate, $I(C_5H_5N)_2\ NO_3$ was prepared as described by Carlsohn (34). 5.1 g of silver nitrate were warmed with 6 ml of pyridine until it had all dissolved. The solution was cooled, and the solid product dissolved in 30 ml of chloroform. 7.8 g of iodine were added and the mixture stirred magnetically until the reaction was complete. The precipitated silver iodide was filtered off, and the filtrate poured slowly, with stirring, into 60 ml of ether. The precipitate of the product was filtered off, washed four times with 15 ml portions of ether containing a little

pyridine, and dried in a vacuum desiccator over sulphuric acid.

Dipyridine iodine (I) perchlorate

To a solution of 6 g iodine in 27 ml pyridine were added 5 g of mercurous perchlorate, and the mixture was stirred magnetically until the latter had dissolved. The solution was filtered, and the filtrate treated with 40 ml of benzene. Crystals of the product, $I(C_5H_5N)_2\ ClO_4$ separated, and were filtered off, washed with ether and dried in a vacuum desiccator over sulphuric acid.

Water

Distilled water was passed through an "Illcoway" Research Model ion-exchange column. Water of this purity was used for making up volumetric solutions, and in studies on water as a solute in fluorosulphuric acid.

Potassium nitrate

AnalaR potassium nitrate was dried at 120°C and stored in a desiccator over "Anhydrone".

Potassium persulphate

AnalaR potassium persulphate, $K_2S_2O_8$, was dried at 100°C and stored in a desiccator over "Anhydrone".

Potassium perchlorate

AnalaR potassium perchlorate was dried at 120°C and stored in a desiccator over "Anhydrone".

Potassium dioxodifluoro-iodate (V)

A saturated solution of potassium iodate in 50% aqueous hydrofluoric acid was allowed to evaporate slowly at room temperature in a

polyethylene beaker. In the course of a week, large rectangular crystals of KIO_2F_2 were formed. The supernatant liquid was poured off and the crystals washed once by decantation with 50% hydrofluoric acid. The crystals were dried by pressing them between pads of filter paper, and were then kept for 24 hours in a vacuum desiccator over sodium hydroxide pellets (47).

Analysis: A weighed portion was dissolved in distilled water and 5 ml of 2N sulphuric acid and excess potassium iodate added. The iodine liberated was titrated with standard sodium thiosulphate solution.

Results:

Oxidation equivalent: 39.41, 39.55, 39.50 g (Calculated 39.34 g)

$$KIO_2F_2 + 5KI + 3H_2SO_4 = 3I_2 + 2HF + 2H_2O + 3K_2SO_4$$

Dry air and nitrogen

Air and nitrogen were dried by passing them successively through tubes containing anhydrous calcium chloride and anhydrous magnesium perchlorate ("Anhydrone"). Glass wool plugs prevented dust of the drying agents from being carried along in the gas stream.

2. Electrical Conductivity Measurements

The conductivity bridge

The resistance of the conductivity cell containing a solution was measured by means of a Leeds and Northrup A.C. Bridge, (50) used in conjunction with a Hewlett-Packard Model 201 C oscillator, operated at 1000 c/s, and a General Radio Type 1231-B amplifier and null-detector, the output from which was fed into a pair of ear-phones. Balance of the bridge was indicated by minimum sound in the ear-phones. A 1000 c/s tuned circuit was incorporated into the amplifier circuit to cut out unwanted frequencies and give a sharper minimum.

The thermostat

Conductivity cells were immersed in an oil thermostat maintained at 25 $\pm$ 0.002°C, the temperature of which was checked periodically with a calibrated platinum resistance thermometer. For measurements at 0°C, cells were immersed in an ice-water bath.

Sulphuric acid conductivity cells

A diagram of a conductivity cell used for sulphuric acid solutions is given in Figure 2a. A convenient amount of solvent to use in such a cell was 200 g. Several cells were used, having cell constants between 20 and 45 cm^{-1}. The electrodes, C, were of heavy platinum foil and were held rigid by being sealed at the corners into the walls of the electrode compartments. Platinum wire contacts sealed through Pyrex were spot-welded to the electrodes and made contact with leads from the conductivity bridge via columns of mercury in the side-arms D. The electrodes were coated with platinum black by electrodeposition from an 0.3% solution of chloroplatinic acid in

0.025 N HCl, containing 0.025% lead acetate (48). A current of 20 ma was passed for about 20 minutes, with reversal every 50 seconds.

The cell design is essentially that of Gillespie, Oubridge and Solomons (49), differing only by the incorporation of the 500 ml flat-bottomed flask A at one end. Many of the solutes studied in the present work were of limited solubility or dissolved very slowly, and it was found convenient to hasten dissolution by the use of a Teflon or glass-coated magnetic stirrer introduced into A, which could be placed on a combined magnetic stirrer and hot-plate. When the hot-plate was used, the B24 cap on B was replaced by a drying-tube containing "Anhydrone", to allow for expansion of the air in the cell. Before a conductivity measurement, the contents of the cell were thoroughly mixed by tilting the cell so that the solution flowed back and forth between the end compartments A and B, a number of times.

Fluorosulphuric acid conductivity cells

Figure 2b is a diagram of a conductivity cell used for fluorosulphuric acid solutions. The construction and nature of the electrodes were the same as in the sulphuric acid cells described above. The flasks A were of 125 ml capacity, and the cell was conveniently used with about 70 g of the solvent. The cells were small enough to be weighed on a balance to 0.01 g. Because of the greater range of conductivities found in this solvent, the cells had three electrodes, forming effectively two conductivity cells in one. The constant of the cell formed by the electrode pair B and C was

about 2 cm^{-1} while that of the cell formed by C and D was between 20 and 30 cm^{-1}.

Calibration of conductivity cells

The specific conductivity, κ, of a solution is given by

$$\kappa = \frac{C}{R}$$

where R is the measured resistance of a conductivity cell containing the solution, and C is the cell-constant, characteristic of the particular cell used. The value of C is determined by measuring the resistance in the cell of a solution of known specific conductivity.

A convenient substance to use for cell calibration is minimum-conductivity sulphuric acid. Its specific conductivity at 25°C is 1.0432×10^{-2} ohm^{-1} cm^{-1} (49, 51) and is known to within 1 part in 5000. In experiments using sulphuric acid as solvent, the resistance at the minimum conductivity was of necessity determined at the beginning of each run in the course of adjusting the acid to the composition 100% H_2SO_4, so that the cells were in effect re-calibrated before each experiment. A typical cell showed random variations in the value of its cell constant as determined by this method, of no more than 1 part in 4000, in the course of thirteen experiments over a period of six months.

Minimum-conductivity sulphuric acid was also used to calibrate fluorosulphuric acid conductivity cells. The cell CD was calibrated directly in this way, while the cell constant of BC was determined later using a solution in fluorosulphuric acid having such a specific conductivity as to give an accurately measureable resistance in both

BC and CD.

Procedure for conductivity runs

The cells were cleaned before use with sulphuric acid-dichromate cleaning mixture, rinsed thoroughly with distilled water and dried at 120°C.

The solvent sulphuric acid was introduced into the cell by means of the weight-burette, Figure 3a, and adjusted to the composition 100% H_2SO_4 by the addition of weighed amounts of aqueous acid or oleum as described above.

Fluorosulphuric acid was distilled directly into a weighed cell, which was afterwards reweighed. Before the distillation, the cell was connected to the still and warmed gently with a bunsen flame for some time while dry air was passed through.

Solutes were added as described in a later section.

Before measurement of the conductivity of a solution the contents of the cell were thoroughly mixed, and the cell placed in the thermostat and allowed to come to temperature equilibrium. The resistance was measured, the solution agitated again, and the measurement repeated. This was continued until successive readings differed by less than 3 parts in 10,000.

3. Cryoscopy

The sulphuric acid cryoscope

The most accurate cryoscopic measurements in sulphuric acid have been made by an equilibrium method (62, 70). The experimentally much simpler Beckmann method used in the present work is however, quite adequate where the highest accuracy is not essential.

The cryoscope used is shown in Figure 4. It was designed so that it was possible to start with a small volume of a relatively concentrated solution in the lower portion, A, and dilute this up to four-fold by adding weighed amounts of 100% sulphuric acid. With most of the solutes studied, this was a more convenient way of changing the concentration than the addition of more solute. Temperatures were measured to within 0.001°C by means of a calibrated platinum resistance thermometer B, the ice-point of which was redetermined from time to time. The stirrer was a glass spiral, C, attached to a long shaft, into the upper end of which was sealed a soft-iron rod D, about 3 cm long. The upper end of the stirrer shaft ran in a closed guide-tube attached to the top of the cryoscope. The stirrer was raised by means of a powerful solenoid E, actuated every two seconds by an electronic relay. When the current was switched off, the stirrer fell under its own weight. The top of the cryoscope also carried a B14 outer joint for the thermometer and a shortened B19 inner joint, F, fitted with a cap, for the introduction of the solvent and solutes. All the ground glass joints were greased.

The cryoscope was surrounded by an air jacket when in use. The whole assembly, cryoscope, solenoid and air-jacket, was mounted on

a metal framework so that it could be moved about without interrupting the stirring.

Measurement of freezing points in sulphuric acid solutions

The cryoscope was cleaned with sulphuric-dichromate cleaning solution, rinsed with distilled water and dried at 120°C, before use.

100% sulphuric acid was prepared in a conductivity cell. One of the cell-caps was replaced by the siphon device shown in Figure 6 , and about 70 g of acid introduced into the weight burette (Figure 3a) by applying pressure at B. The burette was weighed, the acid delivered into the cryoscope and the burette reweighed. Immediately after use of the siphon, the caps A and B and the tubes C and D were replaced, to exclude moisture. The joints on C and D were greased. The freezing point of the solvent was checked before each run, and was usually found to be 10.368°C which was as high as could be obtained by adjustment of the acid to maximum freezing point in the cryoscope itself. It was never lower than 10.364°, showing that a negligible amount of water was picked up during the transfer operation.

A weighed amount of the solute was added and the lower part of the cryoscope warmed if necessary, to hasten dissolution. More dilute solutions were prepared by successive weighed additions of sulphuric acid from the conductivity cell.

To measure the freezing point of a solution the cryoscope and contents were cooled to within 2° of the freezing point by means of an ice-water bath. The air-jacket was then placed in position, and cooling continued more slowly until the temperature of the solution was between 2 and 3°C below the expected freezing point. The cryoscope, with the

jacket, was then transferred to a stirred water-bath, whose temperature had been adjusted to about 2^{o} below the expected freezing point. Freezing was induced by dropping into the cryoscope a small piece of platinum wire which had been cooled in liquid air. The lowest temperature reached was taken as the super-cooling temperature. As solid crystallized out, the temperature of the solution in the cryoscope rose, reaching a steady maximum value which was maintained for several minutes. This was taken as the observed freezing point, and was corrected for supercooling as described below.

The supercooling correction

As some of the solvent freezes out, the solution becomes more concentrated, so that the observed freezing point, T_1, is lower than the true freezing point, T, of the solution initially present in the cryoscope. The amount, $\delta T = T - T_1$, which must be added to the observed freezing point to give the true freezing point, is known as the supercooling correction. Gillespie, Hughes and Ingold (52) showed that δT is given by an expression of the form

$$\delta T = b \Theta s$$

where Θ is the freezing point depression, referred to the freezing point of the pure solvent, and s is the amount of supercooling. If the heat capacity of the apparatus is negligible, they showed that

$$b = C_p^l / \Delta H^f$$

where C_p^l is the molar heat capacity of the liquid solvent, and ΔH^f is the molar heat of fusion. If the heat capacity of the apparatus is not negligible, it can be shown that

$$b = (C_p^l + A/W) / \Delta H^f$$

where A is the heat capacity of the apparatus, and W is the number of moles of solvent. The effective heat capacity of the apparatus, i.e. the cryoscope and its surroundings, under the conditions of an experiment is very difficult to estimate. In the present work, the appropriate value of b was determined empirically by observing the apparent freezing points of the same solution with two different amounts of supercooling. Now if δT_1, θ_1 and s_1 refer to one experiment and δT_2, θ_2 and s_2 to the other, and θ is the true freezing point depression, we have

$$\delta T_1 = \theta - \theta_1 = b\,\theta_1\,s_1$$

$$\delta T_2 = \theta - \theta_2 = b\,\theta_2\,s_2$$

and $$b = (\theta_2 - \theta_1)/(\theta_1 s_1 - \theta_2 s_2)$$

In two different experiments, the value of b was found to be 0.017, compared with the value 0.0125 calculated by ignoring the heat capacity of the apparatus entirely.

The fluorosulphuric acid cryoscope

The cryoscope used for fluorosulphuric acid solutions is shown in Figure 5. It was based on a design by Glasgow, Streiff and Rossini (53). The annular space between the two walls of the vessel was connected via the ball and socket joint A and the stop-cock B to an efficient vacuum system. The walls of the annular space were silvered, except for narrow vertical strips on opposite sides of the cryoscope which were left clear so that the contents could be observed. The head

of the cryoscope was a B55 inner joint, carrying a guide-tube, C, for the stirrer, a B14 outer joint for the thermometer, a B19 inner joint, E, for the introduction of the solvent and solutes and a B19 inner joint, F, connected to a glass tube reaching down into the cryoscope, through which dry air could be passed (Figure 5).

The mechanically driven, reciprocating stirrer was made of nichrome alloy, and consisted of a "cage" of flat horizontal rings held together by four vertical rods. The stirrer shaft was connected at the upper end to a shaft from the motor by means of the bush G. The motor shaft ran through the Teflon collar, H.

Temperatures were measured to 0.001°C by means of a calibrated platinum resistance thermometer, D. This was mounted in a glass sleeve bearing a B14 inner joint. A short length of Teflon tubing ensured a tight fit between the thermometer and the sleeve, and paraffin wax was used to give a moisture-proof seal.

The cryoscope was mounted on a permanent metal framework, so that a large Dewar flask of liquid air could be placed in position around it.

Measurement of freezing points in fluorosulphuric acid solutions

Before use the cryoscope was cleaned in sulphuric- dichromate cleaning mixture, rinsed with distilled water and dried at 120° for several hours. Dry air was blown into the cryoscope while it was cooling to prevent condensation of moisture on the sides. The thermometer was rinsed with acetone and carefully wiped dry. After the cryoscope had been assembled, a slow stream of dry air was passed in through F and out via an "Anhydrone" guard-tube attached at E, for at least one

hour. At this stage, all the joints except E were greased with "Fluorolube" grease.

About 150 g of fluorosulphuric acid were distilled into the weight burette (Figure 7) which was then weighed. The joint C' on the weight burette was fitted onto the joint E on the cryoscope. Dry air was passed into the cryoscope for a further 20 minutes, leaving now via a guard tube connected to B'. The joint F was then capped, and a guard-tube attached to A'. The acid was allowed to run into the cryoscope through the Teflon stop-cock E'. The weight burette was removed and weighed, and the joint E greased and closed with a cap. To prevent the entry of moisture via the stirrer guide, C, a very slow stream of dry air was passed in continually through J all the time the stirrer was operating. At other times, J was closed with a cap, and the opening at H sealed with paraffin wax.

The procedure for measuring a freezing point was as follows. The stirrer was started, and a large Dewar flask containing liquid air placed in position around the cryoscope. With air at atmospheric pressure in the annular space the solution was allowed to cool to about $-70^{\circ}C$. The jacket was then partially evacuated to slow down the rate of cooling, and when the temperature was about $5^{\circ}C$ above the expected freezing point, the vacuum was adjusted to give a rate of cooling of about 0.5° per minute. The stop-cock B was then closed, isolating the evacuated jacket.

When the temperature was about 0.5° above the freezing point, the stop-watch was started, and readings of the thermometer resistance, with the bridge commutator at "normal", taken at 30 second intervals

for two minutes, and at 1 minute intervals thereafter. The solution was allowed to supercool by about 2°, and freezing was induced by the introduction of a short piece of platinum wire which had been cooled in liquid air. Recovery from supercooling was complete in about 5 minutes, and resistance readings were taken at 1 minute intervals during this time, and for a further 25 minutes. During the last 5 minutes, alternate resistance readings were taken with the commutator in the "normal" and "reverse" positions.

The shape of a cooling curve, or plot of thermometer resistance versus time, is shown diagramatically in Figure 8. Along AB the solute cools down to below its freezing point. At B, freezing commences, and along BC recovery from supercooling occurs as solid solvent separates under non-equilibrium conditions. Along CD, the solid and liquid phases are essentially in equilibrium, and the temperature decreases slowly as more solvent freezes, and the solution becomes more concentrated. The true freezing point of the solution is obtained by extrapolating the equilibrium portion of the curve, CD, back to cut AB at E, and correcting the extrapolated value for the difference between the normal and reverse readings.

The freezing point of the solvent was checked at the beginning of each run, and the freezing point depressions calculated from the value obtained. Values in the range -89.008 to $-89.018^{\circ}C$ were obtained.

4. Addition of Solutes

Solid solutes were added to a conductivity cell or cryoscope by means of a weight burette (Figure 3b) with a wide-bore stopcock, which could be suspended from the balance and was weighed before and after each addition.

Liquid solutes, and concentrated solutions were added from a weighed dropper (Figure 3c).

In the conductivity experiments on solutions of water in fluorosulphuric acid, the water was introduced beneath the surface of the solvent by means of a hypodermic syringe, which was weighed before and after each addition. The small amount of solvent on the outside of the needle was wiped off before the second weighing, using a hardened (Whatman 41H) filter-paper. The amount of solvent thus removed from the solution was negligible.

5. Spectroscopic Techniques

Raman spectra

A Hilger E612 Raman spectrometer was used in conjunction with a water-cooled mercury arc lamp. Samples were contained in Pyrex glass cells, surrounded by a jacket through which a saturated solution of sodium nitrite was circulated as an optical filter and as a coolant. The 4358 $\mathring{A}$ line of mercury was used as the exciting line. Spectra were recorded on Kodak IIaO spectroscopic plates with exposures of 2 to 4 minutes, and the positions of the lines were measured by means of a Leeds and Northrup No. 6700 A2 recording microphotometer. The iron arc spectrum was used for calibration. Raman shifts could be measured to $\pm$ 3 cm^{-1}.

Infra-red spectra

Samples for I.R. were prepared in the form of pressed KBr pellets. Spectra were recorded from 400 to 2000 cm^{-1} on a Perkin-Elmer Model 21 spectrometer.

Ultra-violet and visible spectra

Spectra were recorded at different times using Beckman Model B and Beckman DK spectrophotometers. Samples, and solvent references, were contained in matched 10 mm or 1 mm silica or "Corex" cells.

Nuclear magnetic resonance spectra

Proton spectra were run at 60 Mc/s and Fluorine^{19} spectra at 56.4 Mc/s on a Varian HR-60 N.M.R. spectrometer. Samples were

contained in 5 mm o.d. Pyrex tubes. When used, external references were contained in thin-walled capillaries mounted in the centre of the sample tube and held in position by a paraffin wax plug. Chemical shifts were measured by the "side band" technique.

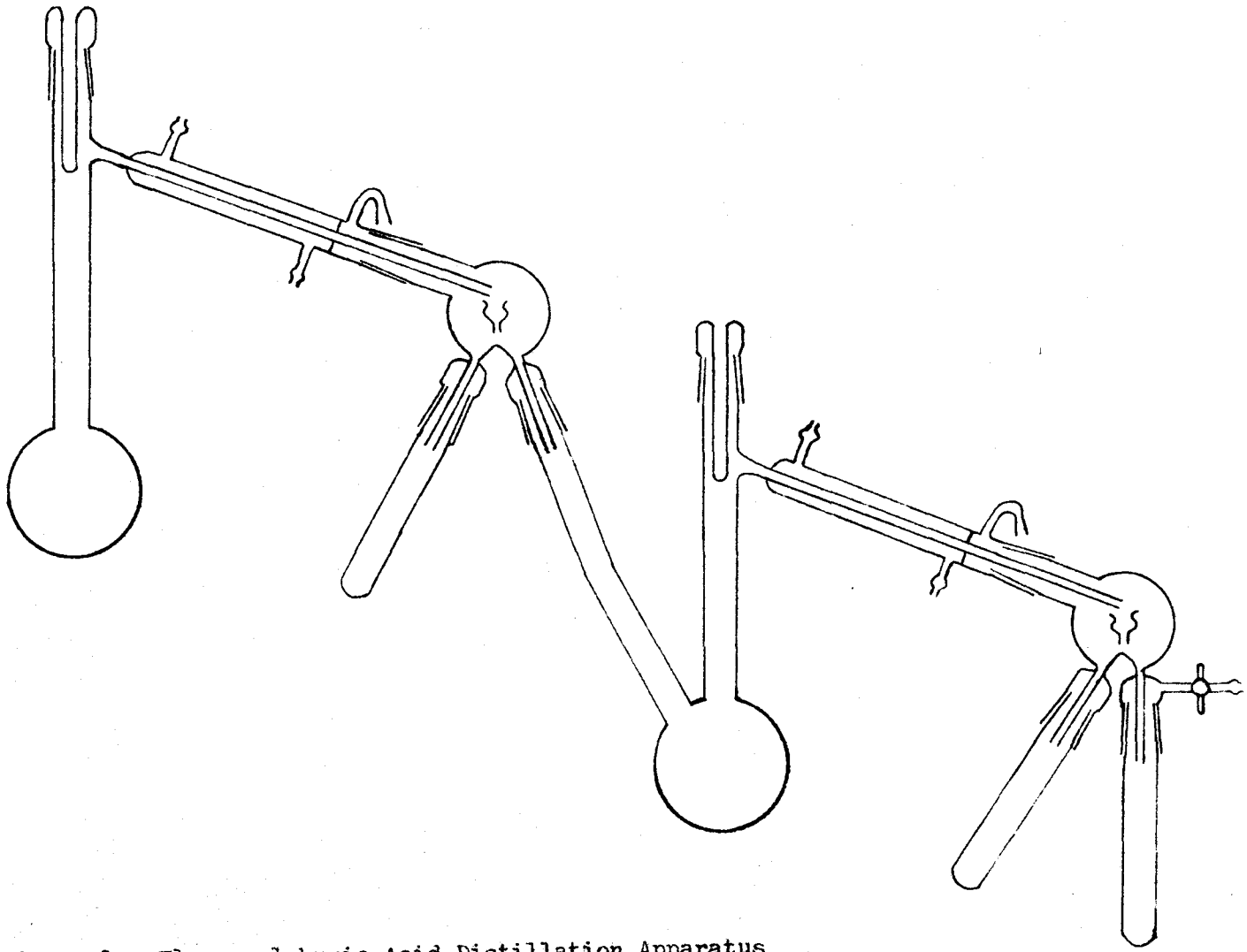


Figure 1. Fluorosulphuric Acid Distillation Apparatus

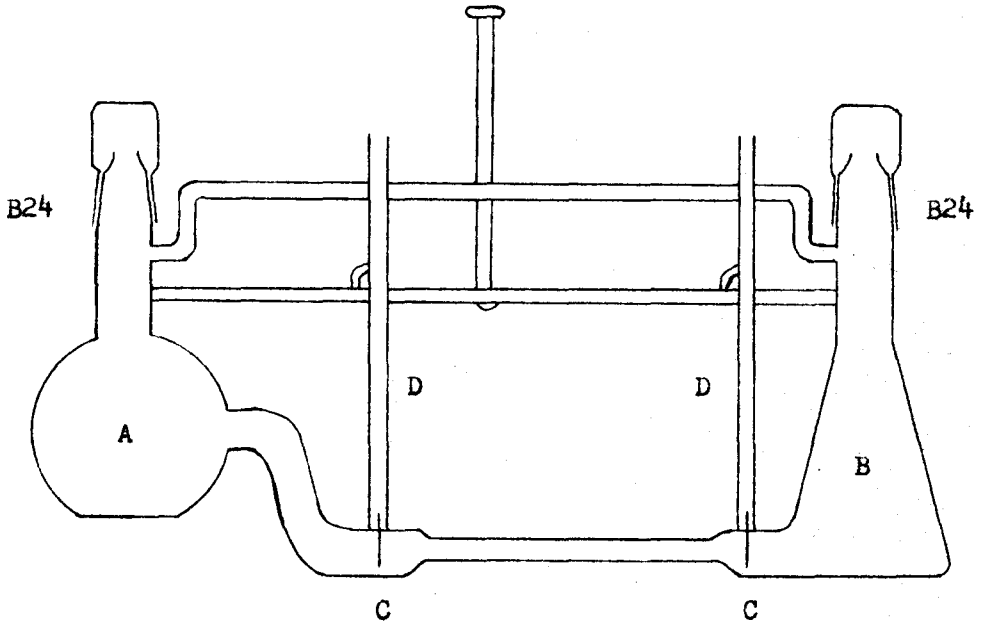


Figure 2 (a). Sulphuric Acid Conductivity Cell

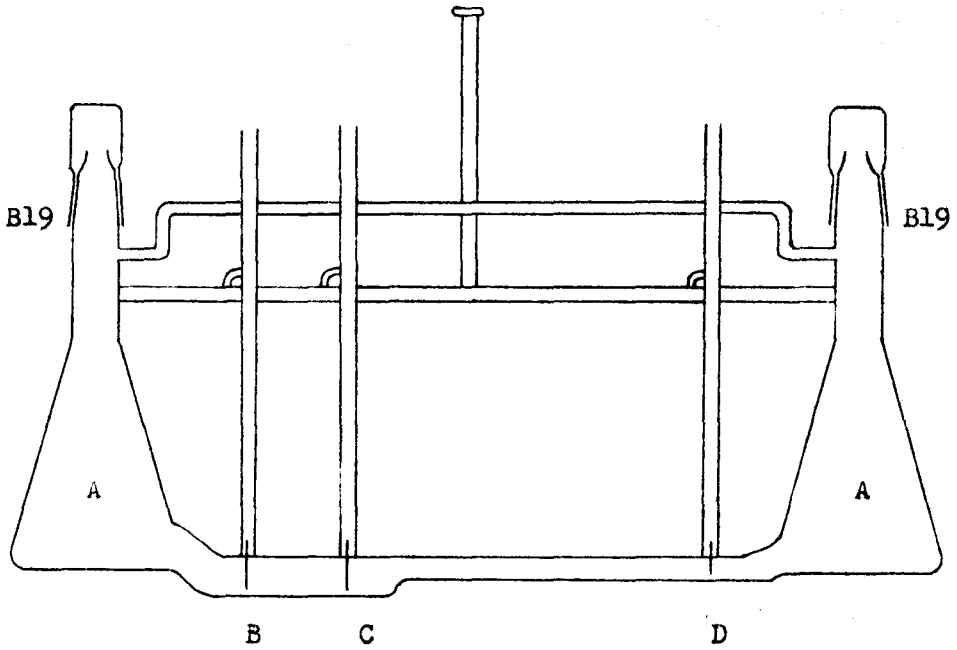


Figure 2 (b). Fluorosulphuric Acid Conductivity Cell

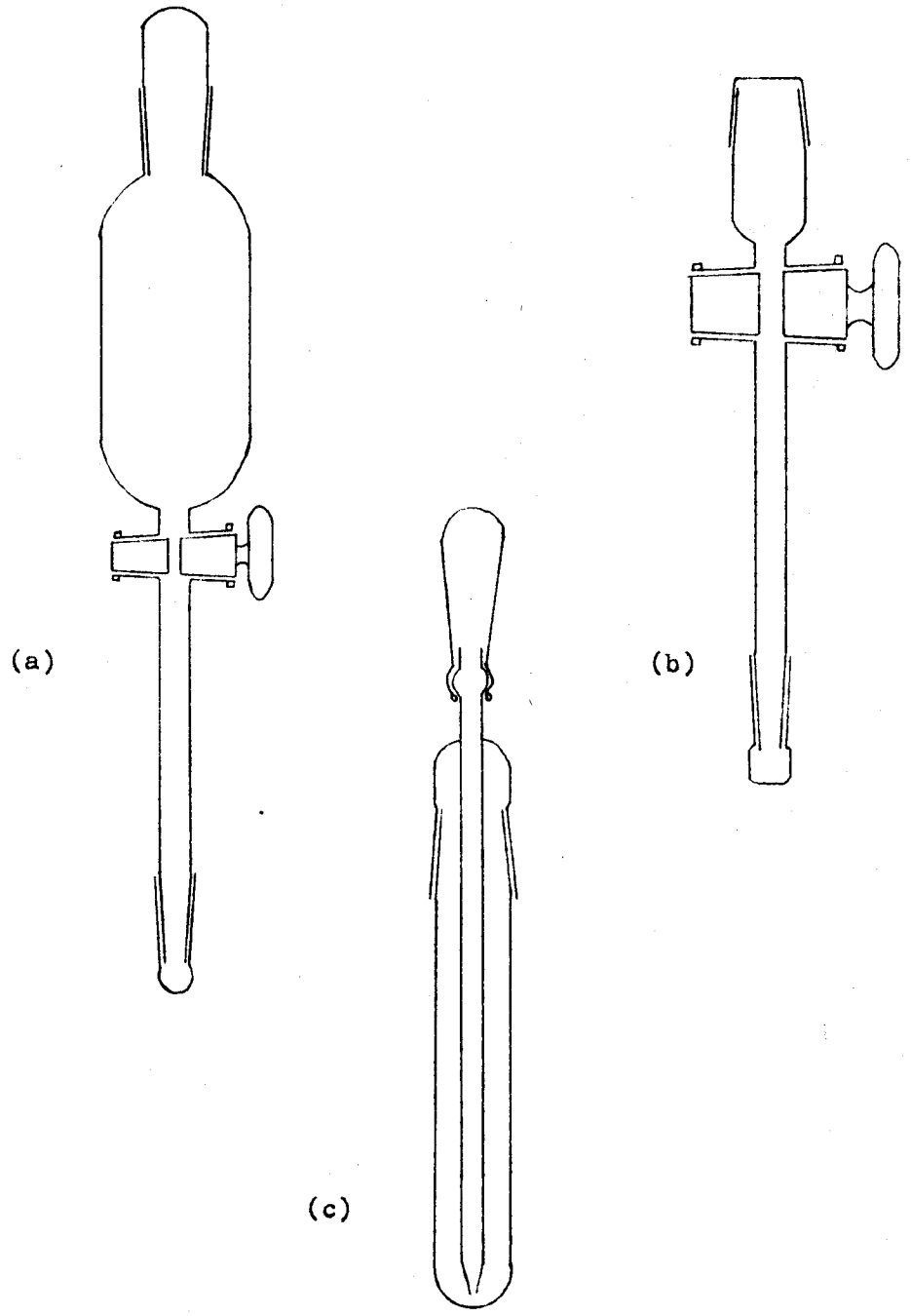


Figure 3

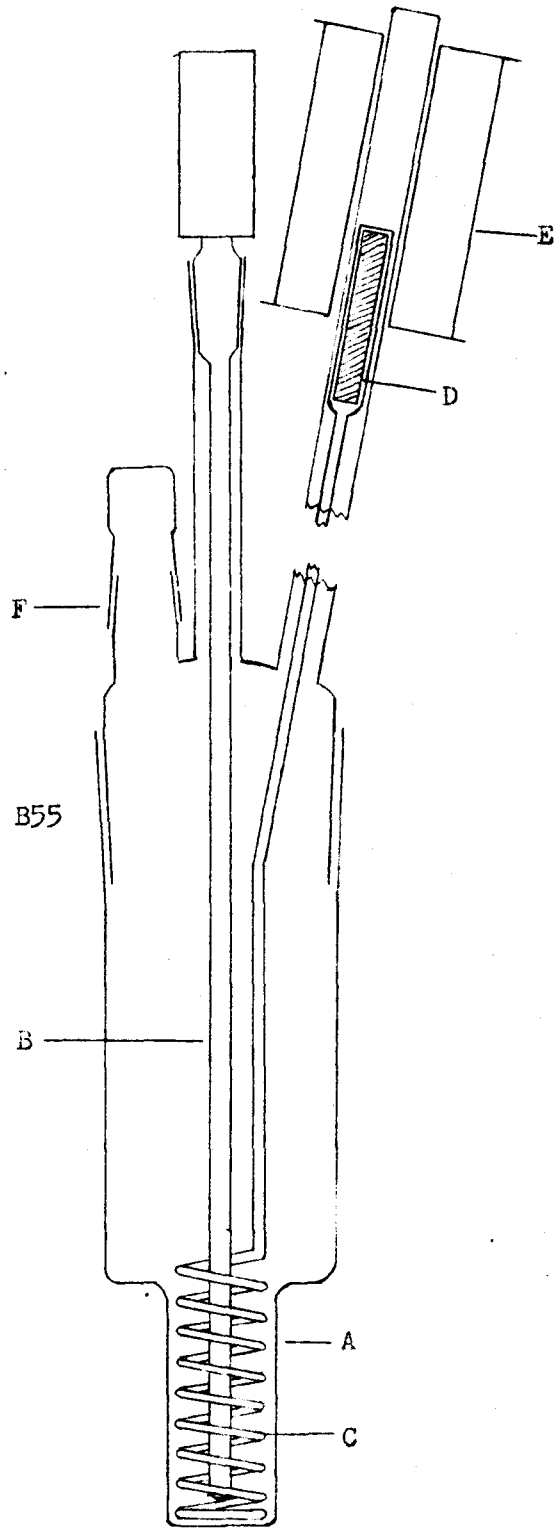


Figure 4. Sulphuric Acid Cryoscope

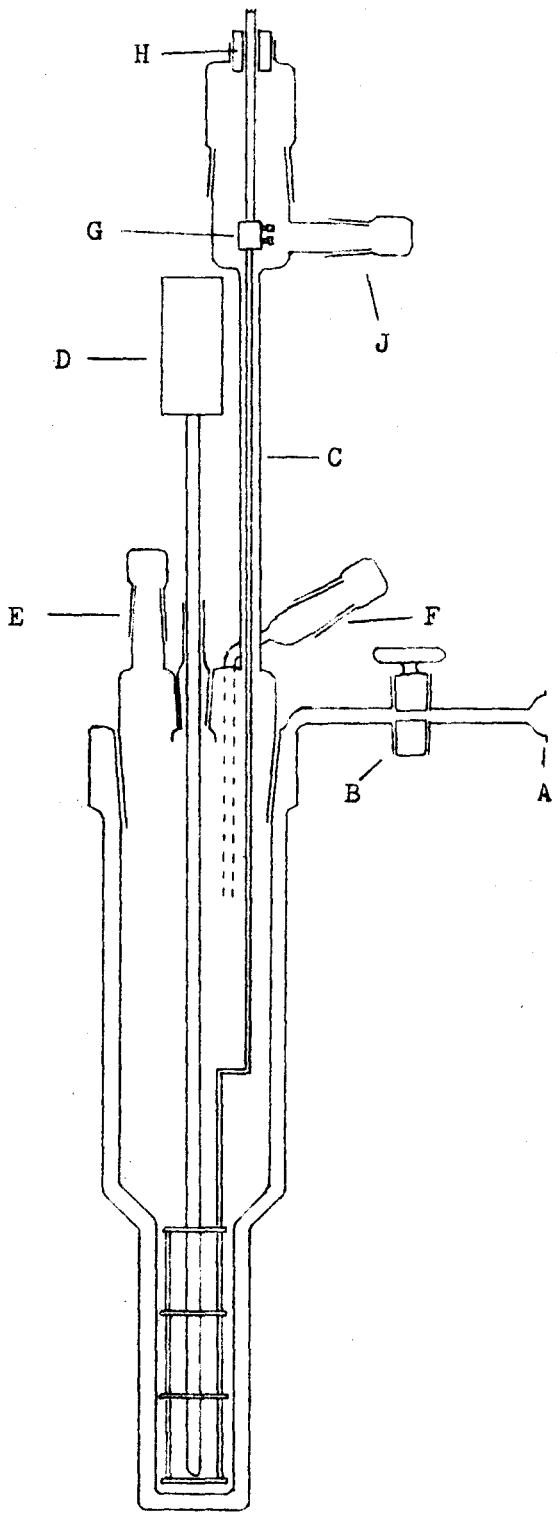


Figure 5. Fluorosulphuric Acid Cryoscope

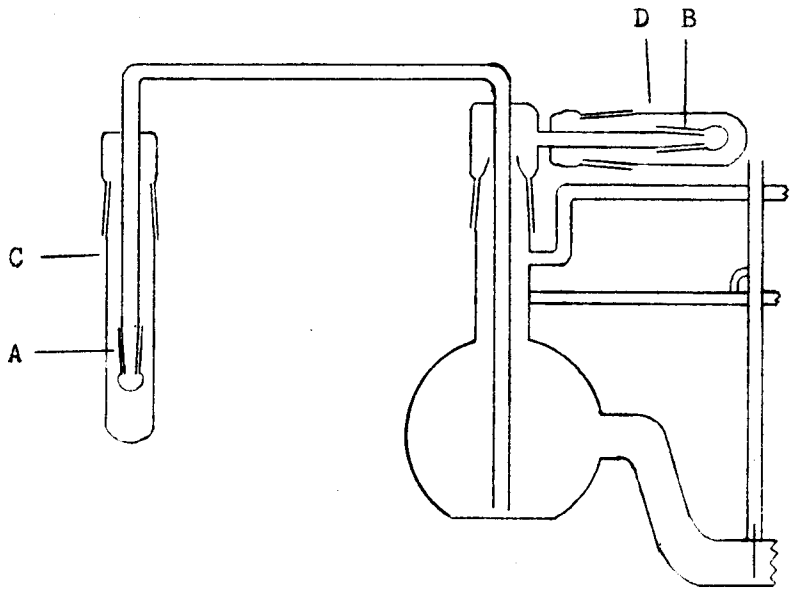


Figure 6. Sulphuric Acid Siphon

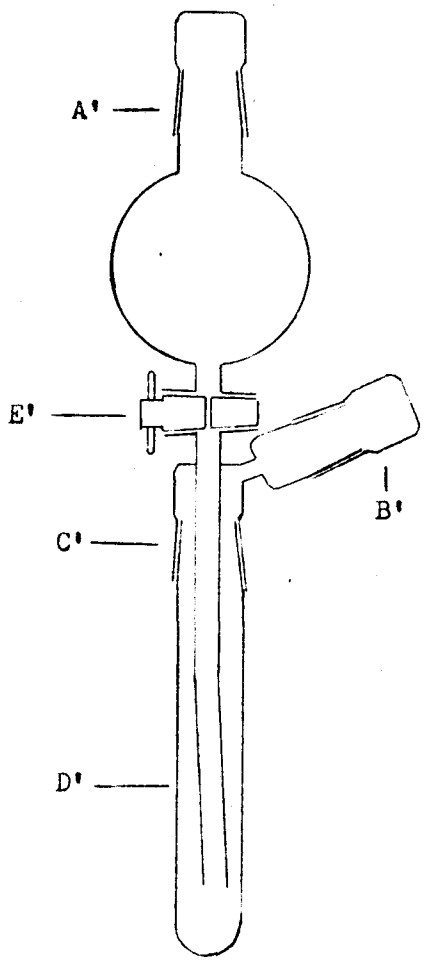


Figure 7. Fluorosulphuric Acid Weight Burette

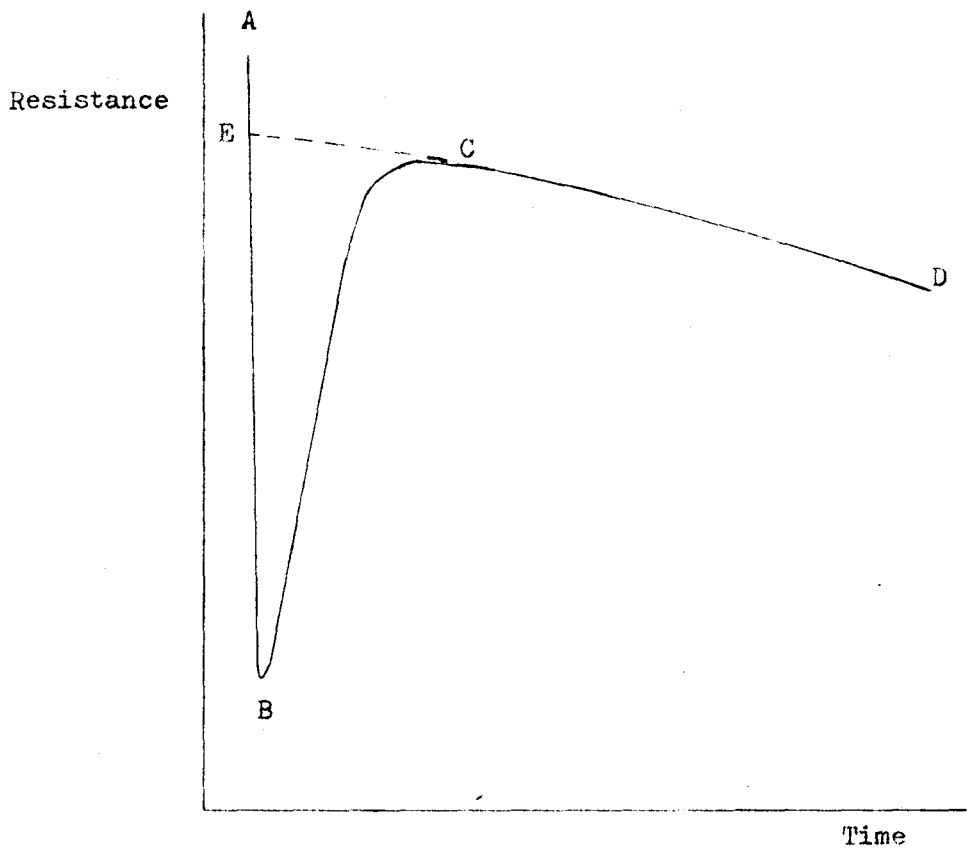


Figure 8. Diagram of Cooling Curve

CHAPTER III

SOLUTIONS IN SULPHURIC ACID

1. Sulphuric Acid as a Solvent

Introduction

The study of sulphuric acid as a solvent dates back to work by Hantzsch (54) in the period 1907 - 1911, and by Hammett (55, 56, 57) in the 1930's. Extensive studies have been made in recent years by Gillespie and co-workers, and several review articles dealing with this work have appeared (42, 43, 58). These studies have been useful in increasing our understanding of acid-base phenomena, and of electrolyte solutions in general, and have demonstrated the existence of many new ionic species.

Physical properties

The high boiling point and viscosity of sulphuric acid show that it is a highly associated liquid, presumably because of strong hydrogen-bonding between the molecules. It has been shown that the solid has a layer-type structure, in which each molecule is hydrogen-bonded to four others (59), and this structure probably persists to a considerable extent in the liquid. The existence of hydrogen bonds, of length 2.85 $\mathring{A}$, between sulphuric acid molecules has been inferred from X-ray diffraction data on 97% aqueous sulphuric acid (60, 61).

100% sulphuric acid has a high dielectric constant, and a high electrical conductivity.

Some of the physical constants of sulphuric acid are given in Table 1.

TABLE 1

Physical Constants of Sulphuric Acid

Property	Value	Temperature (°C)	Reference
Freezing point	10.371°		62
Boiling point	290 - 317°		63
Viscosity	24.54 centipoise	25	64
Density, d_4^{25}	1.8269	25	64
Dielectric constant	100	25	65, 66, 67
	120	10	65, 66, 67
Specific conductance	1.0439×10^{-2} ohm^{-1} cm^{-1}	25	49
Heat capacity	0.338 cal deg^{-1} g^{-1}	25	68
Heat of fusion	2560 cal mole^{-1}	10.37	69

TABLE 2

Equilibrium Constants for the Self-dissociation Reactions of Sulphuric Acid

	10°C	25°C
$K_{ap} = [H_3SO_4^+][HSO_4^-]$	1.7×10^{-4}	2.4×10^{-4}
$K_{id} = [H_3O^+][HS_2O_7^-]$	3.0×10^{-5}	4.2×10^{-5}
$K_{H_2S_2O_7} = [H_3SO_4^+][HS_2O_7^-]/[H_2S_2O_7]$	1.4×10^{-2}	1.4×10^{-2}
$K_{H_2O} = [H_3O^+][HSO_4^-]/[H_2O]$	1	1

Self-dissociation reactions

Sulphuric acid is an amphoteric solvent; that is, in addition to being a strong acid, it is also appreciably basic. This is shown by its extensive autoprotolysis:

$$2H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^- \quad [1]$$

Sulphuric acid is also self-dissociated in other ways. The primary self-dissociation may be considered to be:

$$2H_2SO_4 \rightleftharpoons H_2O + H_2S_2O_7 \quad [2]$$

Water is extensively ionized according to:

$$H_2O + H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^- \quad [3]$$

Disulphuric acid is partially ionized as an acid:

$$H_2S_2O_7 + H_2SO_4 \rightleftharpoons H_3SO_4^+ + HS_2O_7^- \quad [4]$$

Since $H_3SO_4^+$ and HSO_4^- are in equilibrium through the autoprotolysis reaction, the ions H_3O^+ and $HS_2O_7^-$ must also be in equilibrium:

$$2H_2SO_4 \rightleftharpoons H_3O^+ + HS_2O_7^- \quad [5]$$

This is known as the ionic self-dehydration reaction. Only four of the equilibria [1] to [5] are independent, and it is usual to discuss the self-dissociation of sulphuric acid in terms of equations [1], [3], [4] and [5]. Values of the equilibrium constants for these reactions, at 10° and 25°C, are given in Table 2. The values refer to concentrations in molal units.

The values of the self-dissociation constants at 10° were obtained from detailed studies of the freezing points of solutions of metal hydrogen sulphates, water and disulphuric acid (70, 71) each of which represses the self-dissociation equilibria in a different way. The values at 25° were

obtained from the values at 10°, and the electrical conductivities at 10° and 25°C of solutions of metal hydrogen sulphates, water and disulphuric acid (72).

The autoprotolysis ions, $H_3SO_4^+$ and HSO_4^- are, respectively, the strongest possible acid and base that can exist in sulphuric acid. A substance which behaves as a base in this solvent increases the concentration of the hydrogen sulphate ion:

$$B + H_2SO_4 = BH^+ + HSO_4^- \qquad [6]$$

An acid gives rise to the sulphuric acidium ion:

$$HA + H_2SO_4 = H_3SO_4^+ + A^- \qquad [7]$$

Using the values of the equilibrium constants given in Table 2, calculations of the concentrations of species present in solutions of a fully ionized base, a fully ionized acid, water, and disulphuric acid, at rounded molal concentrations of added solute, have been made. The values at 10°C are tabulated in reference (71) and those at 25°C in reference (73).

Cryoscopy

The cryoscopic method was used in Hantzsch's early work (54) and was later developed by Hammett et al (56, 57) and by Gillespie et al (52). Its easily accessible freezing point of 10.371°C and large cryoscopic constant, k = 6.12, make sulphuric acid a convenient solvent for cryoscopic measurements. From such measurements, ν, the number of moles of particles produced by one mole of a solute, may be obtained.

In the work of Hammett and Deyrup and in much of the work which followed, cryoscopic measurements were carried out in sulphuric acid to which sufficient water had been added to lower the freezing point to

about 10°C, in order largely to repress the solvent self-dissociation. However, the self-dissociation is not completely repressed by such concentration of water, and in addition the freezing point depressions of non-electrolytes and weak electrolytes have been found to be affected by the presence of water (74, 75, 76). This has been attributed to "salting-out" and "salting-in" effects of the oxonium hydrogen sulphate produced by the water (74). Now that the self-dissociation equilibria are well understood, and it is possible to allow for repression of self-dissociation, it is better to use 100% sulphuric acid as the cryoscopic solvent, as has been done in recent work (e.g. 75, 77).

The standard state chosen for sulphuric acid is the pure hypothetical undissociated solvent, whose freezing point has been shown to be 10.625°C (71). The freezing point depression, Θ, calculated from the freezing point T_* of the undissociated solvent, is given by

$$\Theta(1 + \beta\Theta) = k_* \phi \Sigma m_{ij} \qquad [8]$$

where k_* is the molal freezing point depression or cryoscopic constant, Σm_{ij} is the total concentration of all solute species in the solution, and ϕ is the molal osmotic coefficient. β is given by

$$\beta = \frac{1}{T_*} - \frac{\Delta Cp}{2\Delta H^f_*} \qquad [9]$$

where ΔCp is the difference in the heat capacities of the solid and liquid solvent, and ΔH^f_* is the heat of fusion of the undissociated solvent at the temperature T_*. The value of β has been computed to be 0.002 (78).

The cryoscopic constant k_* is defined by

$$k_* = \frac{R T_*^2}{M \Delta H^f_*} \qquad [10]$$

where M is the number of moles of solvent in 1 kg of solvent. k* has been shown to differ negligibly in value from k_o, defined by

$$k_o = \frac{RT_o^2}{M \Delta H_o^f} \qquad [11]$$

where the quantities with the subscript o refer to the pure solvent containing the equilibrium concentrations of self-dissociation products. The value of k_o has been shown to be 6.12 ± 0.02 (79). Henceforth the symbol k, without a subscript, will be used for the cryoscopic constant. The osmotic coefficient, ϕ, is defined by

$$\ln a_1 = \frac{-\phi \Sigma m_{ij}}{M} \qquad [12]$$

where a_1 is the activity of the solvent.

Now

$$\Sigma m_{ij} = \nu m^s + m_d \qquad [13]$$

where m^s is the stoichiometric concentration of the solute (corrected for the solvent used up in the reaction between solute and solvent), ν is the number of moles of particles (molecules or ions) produced by one mole of solute, and m_d is the total concentration of the products of the solvent self-dissociation. From [8] and [13] we have

$$\nu = \frac{\Theta(1 + 0.002\,\Theta)}{6.12\,\phi\, m^s} - \frac{m_d}{m^s} \qquad [14]$$

In general, ϕ is not known, and it is necessary to calculate an approximate value of ν denoted by ν', by setting ϕ equal to unity. Thus:

$$\nu' = \frac{\theta(1 + 0.002\,\theta)}{6.12\ m^s} - \frac{m_d}{m^s} \qquad [15]$$

For a solute which ionizes as a simple acid or base, or by simple dehydration to give H_3O^+ and HSO_4^- ions in equal amounts, the value of m_d may be obtained from the tables of concentrations of species in solutions of strong acids, strong bases and water (Tables 2, 3 and 6, of reference 71). Only the ionized fraction of a weak electrolyte is effective in repressing self-dissociation. The degree of ionization may initially be guessed, and a method of successive approximations employed, or it may be estimated from the electrical conductivity at 25°C.

For a "complex" base, which produces H_3O^+ and HSO_4^- in different amounts, a good approximation to m_d may be obtained by assuming that the autoprotolysis is essentially independent of the other equilibria, and that the concentration of autoprotolysis ions ($H_3SO_4^+$ and HSO_4^-) is determined by the amount of added HSO_4^-, while the concentrations of the other species (H_3O^+, $HS_2O_7^-$ and $H_2S_2O_7$, water being assumed to be fully ionized) are determined by the concentration of added H_3O^+. The concentration, m_α, of autoprotolysis ions for any stoichiometric concentration of HSO_4^- can then be determined from the table of concentrations of species for strong bases (Table 2 of reference 71).

$$m_\alpha = m(H_3SO_4^+) + m(HSO_4^-) - m^s(HSO_4^-)$$

The concentration, m_β, of the other self-dissociation species, for any stoichiometric concentration of H_3O^+, may be obtained from the table for water (Table 3 of reference 71).

$$m_\beta = m(H_3O^+) + m(HS_2O_7^-) + m(H_2S_2O_7) - m^s(H_3O^+)$$

The further approximation to ν thus obtained is denoted by ν'', where

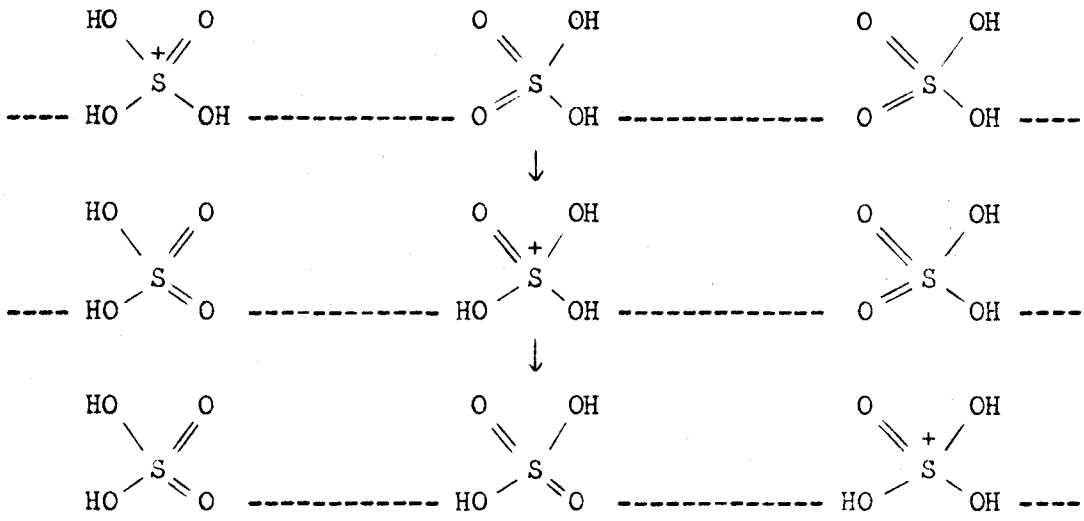
$$\nu'' = \frac{\theta(1 + 0.002\,\theta)}{6.12\,m^s} - \frac{m_\alpha + m_\beta}{m^s} \qquad [16]$$

The possible error in ν due to this approximation is much less than that which may be introduced by assuming that $\phi = 1$.

Electrical conductivities

Although a few measurements of the electrical conductivities of solutions in sulphuric acid were made by early workers, the first comprehensive studies were those of Gillespie and co-workers (80, 81).

The pure solvent has the high specific conductivity, $\kappa = 1.0439 \times 10^{-2}$ ohm^{-1} cm^{-1} at 25°C. The minimum conductivity, 1.0432×10^{-2} ohm^{-1} cm^{-1}, occurs at the composition 0.0019 mole H_2O kg^{-1} solution (49). The high conductivity is due primarily to the extensive autoprotolysis, and to the fact that both the ions thus formed, $H_3SO_4^+$ and HSO_4^-, have relatively high mobilities, much greater than those of any other ions in sulphuric acid. Cation transport numbers of a number of metal hydrogen sulphates in sulphuric acid have been measured (82) and show that the mobilities of the metal ions are extremely small, because of the high viscosity of the solvent. The hydrogen sulphate, and sulphuric acidium ions are unaffected by the high viscosity because they conduct almost entirely by a proton-transfer mechanism, illustrated very diagramatically below for the acidium ion.



Successive transfer of protons along hydrogen bonds results in the effective movement of $H_3SO_4^+$ ions through the solvent without the actual diffusion of individual ions.

Wyatt (83) has recently suggested an additional conductance mechanism which could operate in a highly self-dissociated solvent such as sulphuric acid. He proposes that in the presence of an electric field, there will be, in the autoprotolysis reaction, (Equation [1]) a slight preponderance of dissociations in which the transfer of a proton between the two solvent molecules involved takes place in the direction of the field. This will result in a net transport of charge in the field direction. The contribution of this effect to the total conductivity of a solution should be essentially independent of the solute concentration. It may account for up to 40% of the total conductivity of 100% sulphuric acid, so that the previously quoted values (e.g. 42) of the mobilities of the $H_3SO_4^+$ and HSO_4^- ions may need to be revised. The possible existence of this mechanism should not materially affect the conclusions reached in the present work.

The conductivities of solutions of acids and bases in sulphuric

acid are determined almost entirely by the concentrations of $H_3SO_4^+$ or HSO_4^- respectively. All simple bases ionizing according to Equation [6] to give one HSO_4^- ion, i.e. mono(hydrogen sulphates), have very similar molar conductances, and all bases which give rise to two HSO_4^- ions, i.e. di(hydrogen sulphates) have molar conductances approximately twice those of a mono(hydrogen sulphate) at the same HSO_4^- concentration (80). To a good approximation it may be assumed that solutions of two different bases having the same conductivity contain the same concentration of HSO_4^- ions, and solutions of two different acids having the same conductivity contain the same concentration of $H_3SO_4^+$. Thus electrical conductivity measurements provide a means of determining Υ, the number of moles of HSO_4^- or $H_3SO_4^-$ ions produced by one mole of a solute. The ratio of the concentration of a solution of a fully ionized mono(hydrogen sulphate) to the concentration of a base B having the same conductivity, gives the value of Υ for the base B. The strong bases $KHSO_4$ and H_2O are most commonly used for comparisons of this sort. At high concentrations it is immaterial which of the two is used, since their conductivity curves (plots of specific conductivity versus concentration), are almost identical. However the conductivity curve for water is initially much flatter than that for $KHSO_4$, owing to repression of the ionic self-dehydration of the solvent by H_3O^+, so that values of Υ obtained by comparison with H_2O differ appreciably at low concentrations from those obtained by comparison with $KHSO_4$. If little or no H_3O^+ is produced in the ionization of a solute, Υ-values should be obtained by comparison with $KHSO_4$, while if H_3O^+ is the cation produced in major amount, comparison should be made with H_2O.

Electrolyte behaviour in sulphuric acid

Bases

The alkali metal and some other metal hydrogen sulphates behave as fully ionized binary electrolytes (84) and are thus strong bases:

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

The corresponding normal sulphates are completely converted to the hydrogen sulphates:

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

Many organic compounds containing O, N, or P atoms behave as bases, forming their conjugate acids by the addition of a proton:

$$B + H_2SO_4 \rightleftharpoons BH^+ + HSO_4^-$$

Examples of strong bases of this type include ketones, carboxylic acids, esters, amines, amides and phosphines. A detailed review of the behaviour of organic compounds in sulphuric acid has been given by Gillespie and Leisten (43). Water, and phosphoric acid (42) are examples of inorganic substances which ionize as simple strong bases:

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

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

Many substances are only partly protonated in sulphuric acid solution. These include organic nitro-compounds, sulphonic acids and nitriles, and selenium dioxide (85) which is partially ionized according to

$$SeO_2 + H_2SO_4 = HSeO_2^+ + HSO_4^-$$

Many oxy and hydroxy-compounds behave as bases because they

are converted to sulphato-derivatives, with the elimination of water which ionizes as a base (42). These include substances with the general formulae XOH and X_2O.

$$XOH + 2H_2SO_4 = XSO_4H + H_3O^+ + HSO_4^-$$

$$X_2O + 3H_2SO_4 = 2XSO_4H + H_3O^+ + HSO_4^-$$

The sulphato-compound may be a non-electrolyte, or it may behave as a base either by protonation or ionization, or in a few cases it may behave as an acid.

Ethanol (84, 86) forms ethyl hydrogen sulphate which is practically a non-electrolyte

$$C_2H_5OH + 2H_2SO_4 = C_2H_5SO_4H + H_3O^+ + HSO_4^-$$

Nitric acid (87) provides an example of the formation of a fully ionized hydrogen sulphate.

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

Boric acid (77) is converted to the tri(hydrogen sulphate)

$$H_3BO_3 + 6H_2SO_4 = B(HSO_4)_3 + 3H_3O^+ + 3HSO_4^-$$

This behaves as an acid, and combines with a hydrogen sulphate ion

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

Thus the overall reaction is

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

Arsenic (III) oxide (88) provides an example of a sulphato-

compound which ionizes as a weak base

$$As_2O_3 + 3H_2SO_4 = 2AsOHSO_4 + H_3O^+ + HSO_4^-$$

$$AsO\,HSO_4 \rightleftharpoons AsO^+ + HSO_4^-$$

It is likely that both the base and the cation actually exist in the solvated forms, HO As $(HSO_4)_2$ and HO As HSO_4^+ respectively. At higher concentrations, polymeric species such as HO As (HSO_4) O As $(HSO_4)_2$ are also present.

When As_2O_3 is dissolved in a dilute oleum it is largely converted to $As(HSO_4)_3$.

$$As_2O_3 + 3H_2S_2O_7 = 2As(HSO_4)_3$$

It was suggested in a recent paper (89) that a solvated form of this compound, H As $(HSO_4)_4$, was present, and behaved as a weak acid,

$$H\,As(HSO_4)_4 + H_2SO_4 \rightleftharpoons H_3SO_4^+ + As(HSO_4)_4^-$$

but this now seems doubtful. At higher concentrations of As_2O_3, polymeric species, and in particular, the dimeric $\left[As(HSO_4)_2\right]_2 SO_4$ and $\left[As(HSO_4)_2\right]_2 O$ are formed in increasing amounts. At the mole ratio, $As_2O_3/H_2S_2O_7 = 0.33$, corresponding to the stoichiometric composition $As(HSO_4)_3$, all three species appear to be present, in equilibrium with some unreacted $H_2S_2O_7$. It is the latter which is responsible for most, if not all, of the acid behaviour of solutions of this composition. At the mole ratio 0.5, corresponding to the stoichiometric reaction

$$As_2O_3 + 2H_2S_2O_7 = \left[As(HSO_4)_2\right]_2 O$$

the species present are $\left[As(HSO_4)_2\right]_2 O$, HO As $(HSO_4)_2$ and $H_2S_2O_7$.

Acids

The majority of substances which behave as acids in aqueous solution, behave as bases of various types in sulphuric acid. Some examples have already been given.

The first acids of the sulphuric acid solvent system to be recognised were disulphuric acid, $H_2S_2O_7$ and the higher polysulphuric acids $H_2S_3O_{10}$ etc. which are present in oleums (90, 91). $H_2S_2O_7$ is ionized according to Equation [4], with $K_a = 1.4 \times 10^{-2}$ ($10^{\circ}C$). The higher polysulphuric acids are probably stronger than disulphuric acid.

Perchloric acid (86) probably behaves as an extremely weak acid in sulphuric acid, and fluorosulphuric acid is somewhat stronger (89).

When boric acid is dissolved in an equivalent amount of a dilute oleum, the moderately strong acid, ($K_a \approx 0.2$) $HB(HSO_4)_4$ is produced (77).

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

Other complex sulphato-acids have been obtained. Tetraphenyltin (42) gives a solution containing hexa(hydrogen sulphato) stannic acid

$$Ph_4Sn + 14\ H_2SO_4 = H_2Sn(HSO_4)_6 + 4PhSO_3H + 4H_3O^+ + 4HSO_4^-$$

Lead tetra acetate gives a solution containing hexa(hydrogen sulphato) plumbic acid (92)

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

Both of these are fairly weak dibasic acids.

Acid-base reactions

The neutralization reaction of an acid and a base in sulphuric acid takes place according to the equation

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

which is the reverse of the autoprotolysis reaction. Since the conductivity of the solutions is due mainly to the $H_3SO_4^+$ and HSO_4^- ions, such reactions can be followed conductimetrically. As a base is added to a solution of an acid, the concentration of $H_3SO_4^+$ decreases and that of HSO_4^- increases, causing the conductivity to decrease initially, pass through a minimum and increase again. The composition at the conductivity minimum depends on the strengths of the acid and base and on their modes of ionization. A detailed discussion has been given by Flowers, Gillespie and Robinson (93). They assume that the conductivity minimum will occur when the combined conductivity contribution of the autoprotolysis ions:

$$\mathcal{K} = 10^{-3} \rho \left\{ m(H_3SO_4^+) \lambda (H_3SO_4^+) + m(HSO_4^-) \lambda (HSO_4^-) \right\}$$

is a minimum. It can then be shown that the molal concentrations of these species at the minimum will be $m_{min}(H_3SO_4^+) = 0.0132$ and $m_{min}(HSO_4^-) = 0.0182$, at 25°C.

For the reaction of a simple acid HA, having

$$K_a = \frac{[H_3SO_4^+][A^-]}{[HA]}$$

with a simple base B, having

$$K_b = \frac{[BH^+][HSO_4^-]}{[B]}$$

the composition at the conductivity minimum at 25°C is given by

$$r_{min} = \left(\frac{m_b}{m^i_a}\right)_{min} = \left(1 + \frac{0.018}{K_b}\right) \left\{ \left(1 + \frac{0.013}{K_a}\right)^{-1} + \frac{0.0007}{a} \right\}$$

where $m^i_a = a$ is the initial molality of the acid, and m_b is the molality of added base.

For the reaction of a simple base B, with the acid $H_2S_2O_7$, it is first necessary to calculate the concentration of $HS_2O_7^-$ at the minimum:

$$\left[HS_2O_7^-\right]_{min} = \frac{a + (a^2 + 0.000327)^{1/2}}{3.89}$$

Then

$$\left[H_3O^+\right]_{min} = \frac{K_{id}}{\left[HS_2O_7^-\right]_{min}} = \frac{4.2 \times 10^{-5}}{\left[HS_2O_7^-\right]_{min}}$$

and, since the solution is electrically neutral:

$$\left[BH^+\right]_{min} = \left[HS_2O_7^-\right] + \left[HSO_4^-\right] - \left[H_3O^+\right] - \left[H_3SO_4^+\right]$$

The composition at the minimum conductivity is given by

$$r_{min} = \frac{\left[BH^+\right]_{min}}{a} \left(1 + \frac{0.018}{K_b}\right)$$

A similar treatment was derived for the reaction of a simple acid HA with the base H_2O.

It should be noted that this treatment assumes the salt, $BH^+\}\ A^-$ to be fully dissociated, and is inapplicable if this is not the case.

2. Solutions of Iodic Acid in Sulphuric Acid

Introduction

Lamb and Phillips (44) studied the solubility of iodic acid in solutions of sulphuric acid ranging in composition from 50% H_2SO_4 to 29% free SO_3. They obtained evidence for the existence of three different solid phases in equilibrium with the saturated solutions. The first, occurring in solutions below 77% H_2SO_4, they considered to be HIO_3, the second, occurring in the range 77 - 85% H_2SO_4 was thought to be the partly dehydrated form, HI_3O_8, while in acid above 85% H_2SO_4 the stable solid phase was considered to be I_2O_5. Masson (15) reported that iodine pentoxide reacted with fuming sulphuric acid to form a white complex of unknown composition, while Myers and Kennedy (14) stated that iodic acid forms a double compound with sulphuric acid. Mishra and Symons have claimed, on the basis of U.V. spectra and conductivity data, of which however no details were given, that iodic acid exists in solution in 100% sulphuric acid as the protonated species $H_2IO_3^+$ (7).

Cryoscopy and conductimetry

Iodic acid is only sparingly soluble in 100% sulphuric acid at room temperature, but by heating to about 60°C, solutions of concentrations up to about 0.045 molal could be obtained. These solutions deposited a white solid on long standing. The results of the cryoscopic experiments are shown in Table 3 and Figure 9, and conductivity data are presented in Table 4 and Figure 10. The results of a conductimetric "titration" in which a solution of disulphuric acid was added to a

solution of iodic acid are shown in Table 6 and Figure 11.

Discussion

A number of ionization schemes which may be considered are given below, together with the predicted values of ν and Υ.

$$HIO_3 + H_2SO_4 = H_2IO_3^+ + HSO_4^- \qquad [1]$$
$$\nu = 2,\ \Upsilon = 1,\ \nu-\Upsilon = 1$$

$$HIO_3 + 2H_2SO_4 = IO_2^+ + 2HSO_4^- + H_3O^+ \qquad [2]$$
$$\nu = 4,\ \Upsilon = 2,\ \nu-\Upsilon = 2$$

$$HIO_3 + 2H_2SO_4 = IO_2HSO_4 + H_3O^+ + HSO_4^- \qquad [3]$$
$$\nu = 3,\ \Upsilon = 1$$

In considering ionization according to Equation [1], Υ-values have been calculated by comparison with the conductivity curve for potassium hydrogen sulphate, and the values of ν have been corrected only for the repression of solvent autoprotolysis (Table 5B). Values of Υ appropriate to reactions such as [2] and [3] have been calculated by comparison with the conductivity curve for water, and the values of ν have been corrected for repression of the ionic self-dehydration reaction as well as that of the autoprotolysis reaction (Table 5A).

The almost constant Υ-value of 1.08 obtained by comparison with $KHSO_4$ is consistent with complete ionization according to Equation [1]. This value is rather larger than that predicted, but if, e.g. $CsHSO_4$ were used for the comparison, the value of Υ would be 1.02, differing negligibly from 1.00. The values of $\ddot{\nu}$, which range from 2.15 to 2.27, are substantially larger than the predicted 2.0, but not sufficiently so, in view of the large self-dissociation corrections, to rule out completely this scheme of reaction.

The values of ν and Υ given in Table 5A are not consistent either with complete ionization to give IO_2^+ according to Equation [2], or with reaction according to Equation [3] to give the monomeric IO_2HSO_4. They are consistent with ionization according to a scheme similar to [3], but involving polymeric forms of iodyl hydrogen sulphate, $(IO_2HSO_4)_n$, which may be partially ionized.

For the general reactions

$$n\ HIO_3 + 2n\ H_2SO_4 = (IO_2HSO_4)_n + n\ H_3O^+ + n\ HSO_4^- \qquad [4a]$$

and

$$(IO_2HSO_4)_n \rightleftharpoons (IO_2)_n\ (HSO_4)^+_{n-1} + HSO_4^- \qquad [4b]$$

we would have values of $\ddot{\nu}$ in the range $2 + \frac{1}{n}$ to $2 + \frac{2}{n}$, and values of Υ in the range 1 to $1 + \frac{1}{n}$, with $\ddot{\nu} - \Upsilon$ equal to $1 + \frac{1}{n}$ whatever the position of the equilibrium [4b]. For $n = 2$, we would have $\ddot{\nu} - \Upsilon = 1.5$, and for $n = 3$, $\ddot{\nu} - \Upsilon = 1.33$. Experimentally, $\nu - \Upsilon$ is greater than 1.5 at low concentrations, and becomes less than 1.5 at higher concentrations. This suggests an equilibrium involving possibly the monomeric, dimeric and trimeric forms of iodyl hydrogen

sulphate, along with small amounts of their ionized forms, although an equilibrium involving only the monomer and the trimer, or the monomer and some higher polymeric form would also fit the experimental results.

Several further reasons may be advanced for preferring some such scheme as this, to that of Equation [1].

When a solution of disulphuric acid is added to a solution of iodic acid in sulphuric acid, the conductivity at first decreases, passes through a minimum, and then increases as more disulphuric acid is added, as would be expected if iodic acid behaves as a base. If iodic acid were a fully ionized base, as required by Equation [1], the conductivity minimum would occur at the mole ratio $HIO_3/H_2S_2O_7$ = 0.60 with the concentrations used in this experiment (93). In fact (Figure 11) the minimum comes at $H_2S_2O_7/HIO_3$ = 1.32, i.e. $HIO_3/H_2S_2O_7$ = 0.76, in rather poor agreement with prediction. The mole ratio 0.76 gives a value for $K_b = \left[H_2IO_3^+\right]\left[HSO_4^-\right] / \left[HIO_3\right]$ of 0.07 mole kg^{-1}.

This value of K_b would lead to a value of γ, for an 0.05 m solution, of 0.63, compared with the constant value of 1.08 shown in Table 5B.

If some reaction similar to [4] occurs, then up to the mole ratio $H_2S_2O_7/HIO_3$ = 1.0 the reaction taking place is simply the removal of water by the disulphuric acid, forming sulphuric acid:

$$H_2O + H_2S_2O_7 = 2H_2SO_4$$

The subsequent reaction may be the titration of a weak base $(IO_2HSO_4)_n$, or the formation of more highly sulphated species, as

in the case of solutions of arsenic (III) oxide (88) and iodosyl sulphate, discussed in a later section of this chapter.

As mentioned above, a white solid was precipitated in the course of a few days from the more concentrated solutions of iodic acid in sulphuric acid. The separation of quite a large amount of this solid caused only a very small decrease in the conductivity of the solution. For example, in one experiment, the specific conductivities before and after separation of the solid were 1.433×10^{-2}, and 1.419×10^{-2} ohm^{-1} cm^{-1} respectively. If reaction [1] were occurring, the only solid that could conceivably separate out would be HIO_3, or a solvated form e.g. $HIO_3 . H_2SO_4$ ($H_2IO_3^+ . HSO_4^-$), and in this case a large decrease in conductivity would be expected. However if the solid were a higher polymeric form of the weakly ionized iodosyl hydrogen sulphate, the conductivity would not be expected to change very much, in agreement with observation.

Analysis of the white solid gave the results: Iodate (as I_2O_5) 78.8, 77.8, 78.6%; in approximate agreement with the formula $I_2O_5 . SO_3$ (calculated 80.7%).

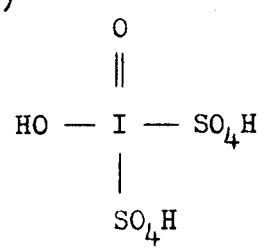
Iodic acid is very readily dehydrated, losing water in a dry atmosphere even at room temperature to give HI_3O_8. It is therefore most unlikely that it would retain the elements of water in the presence of a powerful dehydrating agent such as sulphuric acid.

Whatever the reaction, the limiting slope of the freezing-point curve at very low concentrations should not correspond to a value of ν greater than 1, because of repression of the solvent self-dissociation by H_3O^+ and HSO_4^- ions. If the freezing-point curve

(Figure 9) is extrapolated back to the freezing point of the pure acid, the initial slope corresponds to a value of ν greater than 1. The curve can be extrapolated back more smoothly to a slightly lower value of the freezing point, and then has a limiting slope corresponding to $\nu = 1$. This suggests that during the course of a cryoscopic run by the "dilution" method used, a small amount of water was picked up, leading to the low value for the f.p. of the "pure" solvent. The values of ν given in Table 5 for low concentrations may therefore be slightly too large. The initial value, $\nu = 1$ is equally consistent with ionization according to Equations [1], [2] or [3]. At very low concentrations iodyl hydrogen sulphate would probably be present mainly as the monomer, so that [2] or [3] would represent the reaction occurring.

Possible structures of the species formed

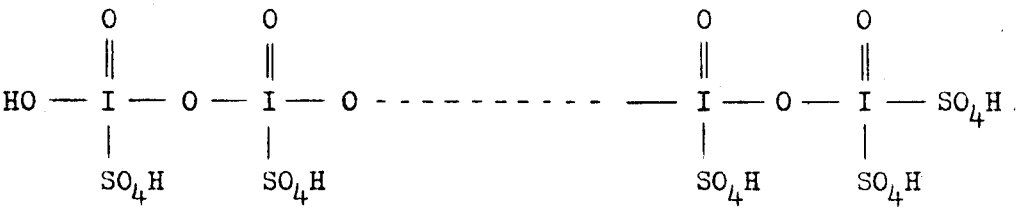
By analogy with the structures proposed by Gillespie and Robinson (88) for the species present in solutions of arsenic (III) oxide in sulphuric acid and oleums, we may consider the monomer of iodyl hydrogen sulphate to exist as the solvated form $IO_2HSO_4.H_2SO_4$ having the structure (I)



I

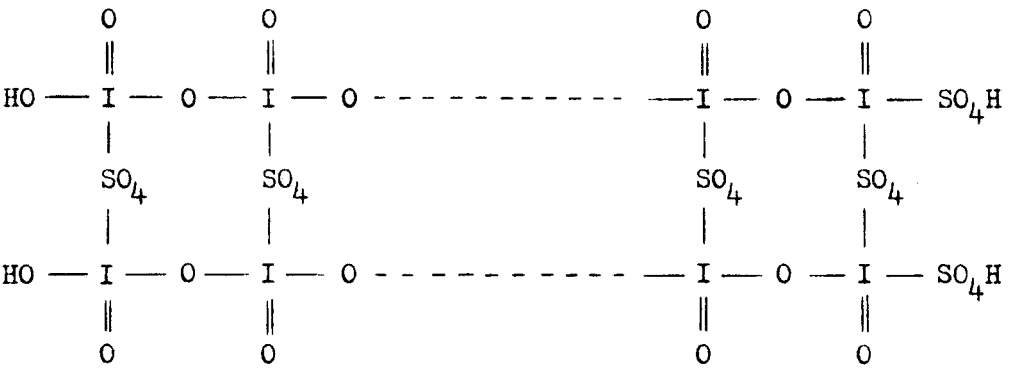
Polymeric forms could be built up by the elimination of solvent

molecules (II)



II

The repeating unit in such polymers is IO_2HSO_4 and the chain-ending groups are obtained from a solvent molecule. By cross-linking of two such chains, with the elimination of sulphuric acid, a polymer with the repeating unit $(IO_2)_2\ SO_4$ or $I_2O_5.SO_3$ can be built up (III).



III

This is possibly the structure of the white solid which separates out from the solutions. This, rather than I_2O_5, is presumably the solid phase found by Lamb and Phillips (44) to be in equilibrium with solutions of iodic acid in sulphuric acid stronger than 85%, and is also probably identical with the iodic-sulphuric complexes reported by Masson (15) and by Myers and Kennedy (14).

TABLE 3

Solutions of Iodic Acid in

Sulphuric Acid: Freezing Points

Experiment 42

Weight of HIO_3 0.5778 g
F.p. of solvent 10.367°C

Weight of H_2SO_4 (g)	m	F.p. (°C)
76.02	0.04357	9.928
89.90	0.03680	10.004
114.94	0.02873	10.093
167.87	0.01964	10.192
286.80	0.01148	10.272

Experiment 43

Weight of HIO_3 0.2058 g
F.p. of solvent 10.367°C

Weight of H_2SO_4 (g)	m	F.p. (°C)
73.93	0.01586	10.228
92.45	0.01269	10.261
130.20	0.00780	10.302
290.23	0.00403	10.336

Experiment*	m	F.p. (°C)
47	0.03673	9.988
50	0.03489	9.996
52	0.03154	10.055
53	0.04398	9.886

(Table 3 continued)

Experiment*	m	F.p. (°C)
56	0.03593	9.998
57	0.03292	10.023

* Fuller details of these experiments, in which iodine was subsequently added to the solutions, are given in Table 7.

TABLE 4

Solutions of Iodic Acid in

Sulphuric Acid: Conductivities at 25°C

Experiment 20

Weight of H_2SO_4 257.04 g

Weight of HIO_3 (g)	w	"M"	$10^2\kappa$ (ohm^{-1} cm^{-1})
0.1433	0.00317	0.00579	1.0481
0.3085	0.00681	0.01245	1.0593
0.4559	0.01006	0.01838	1.0755
0.5898	0.01301	0.02377	1.0947
0.8382	0.01847	0.03374	1.1400
1.0785	0.02375	0.04339	1.1945
1.3599	0.02991	0.05465	1.2681

Experiment 21

Weight of H_2SO_4 270.18 g

Weight of HIO_3 (g)	w	"M"	$10^2\kappa$ (ohm^{-1} cm^{-1})
0.3844	0.00808	0.01475	1.0648
0.7209	0.01513	0.02764	1.1100
1.0572	0.02216	0.04048	1.1754
1.3935	0.02917	0.05329	1.2550
1.5257	0.03192	0.05831	1.2922
1.7278	0.03612	0.06599	1.3483
2.0358	0.04251	0.07766	1.4332

Experiment*	w	"M"	$10^2\kappa$ (ohm^{-1} cm^{-1})
45	0.00976	0.01781	1.0719
49	0.01843	0.03356	1.1322

(Table 4 continued)

Experiment*	w	"M"	$10^2 K$ (ohm^{-1} cm^{-1})
51	0.00427	0.00780	1.0511
54	0.02655	0.04852	1.2115
55	0.01568	0.02864	1.1144
58	0.01175	0.02147	1.0868
59	0.03959	0.07234	1.3868
103	0.01030	0.01882	1.0759

* Fuller details of these experiments, in which iodine or $H_2S_2O_7$ was subsequently added to the solutions, are given in Tables 6 and 8.

TABLE 5

Solutions of Iodic Acid in

Sulphuric Acid: Values of ν and Υ

	A			B		
m	ν	Υ	$\nu - \Upsilon$	ν	Υ	$\nu - \Upsilon$
0.010	3.07	1.41	1.66	2.15	1.14	1.01
0.015	2.86	1.28	1.58	2.15	1.08	1.07
0.020	2.70	1.23	1.47	2.14	1.08	1.06
0.025	2.63	1.17	1.46	2.17	1.08	1.09
0.030	2.57	1.15	1.42	2.17	1.08	1.09
0.035	2.54	1.13	1.41	2.20	1.08	1.12
0.040	2.54	1.12	1.42	2.23	1.08	1.15
0.045	2.53	1.10	1.43	2.27	1.08	1.19

Notes A. Self-dissociation corrections to ν calculated assuming ionization according to:

$$HIO_3 + 2H_2SO_4 = IO_2HSO_4 + H_3O^+ + HSO_4^-$$

Υ obtained by comparison with conductivity curve for H_2O.

B. Self-dissociation corrections to ν calculated assuming ionization according to:

$$HIO_3 + H_2SO_4 \rightleftharpoons H_2IO_3^+ + HSO_4^-$$

Υ obtained by comparison with conductivity curve for $KHSO_4$.

TABLE 6

Conductimetric Titration of Iodic Acid with

Disulphuric Acid (25°C)

Experiment 59

Weight of H_2SO_4 268.98 g

Weight of HIO_3 1.8911 g

$H_2S_2O_7$ solution:

$\mathcal{K} = 3.005 \times 10^{-2}$ ohm^{-1} cm^{-1}

$w(H_2S_2O_7) = 0.673$ mole kg^{-1}

Weight of $H_2S_2O_7$ Solution Added (g)	Mole Ratio $H_2S_2O_7/HIO_3$	$10^2\mathcal{K}$ (ohm^{-1} cm^{-1})
0.0000	0.000	1.387
5.0294	0.316	1.258
9.8232	0.617	1.166
14.5462	0.913	1.111
21.4922	1.349	1.087
28.1720	1.769	1.102
32.4621	2.037	1.120
37.9078	2.375	1.143

At conductivity minimum $H_2S_2O_7/HIO_3 = 1.32$

$HIO_3/H_2S_2O_7 = 0.76$

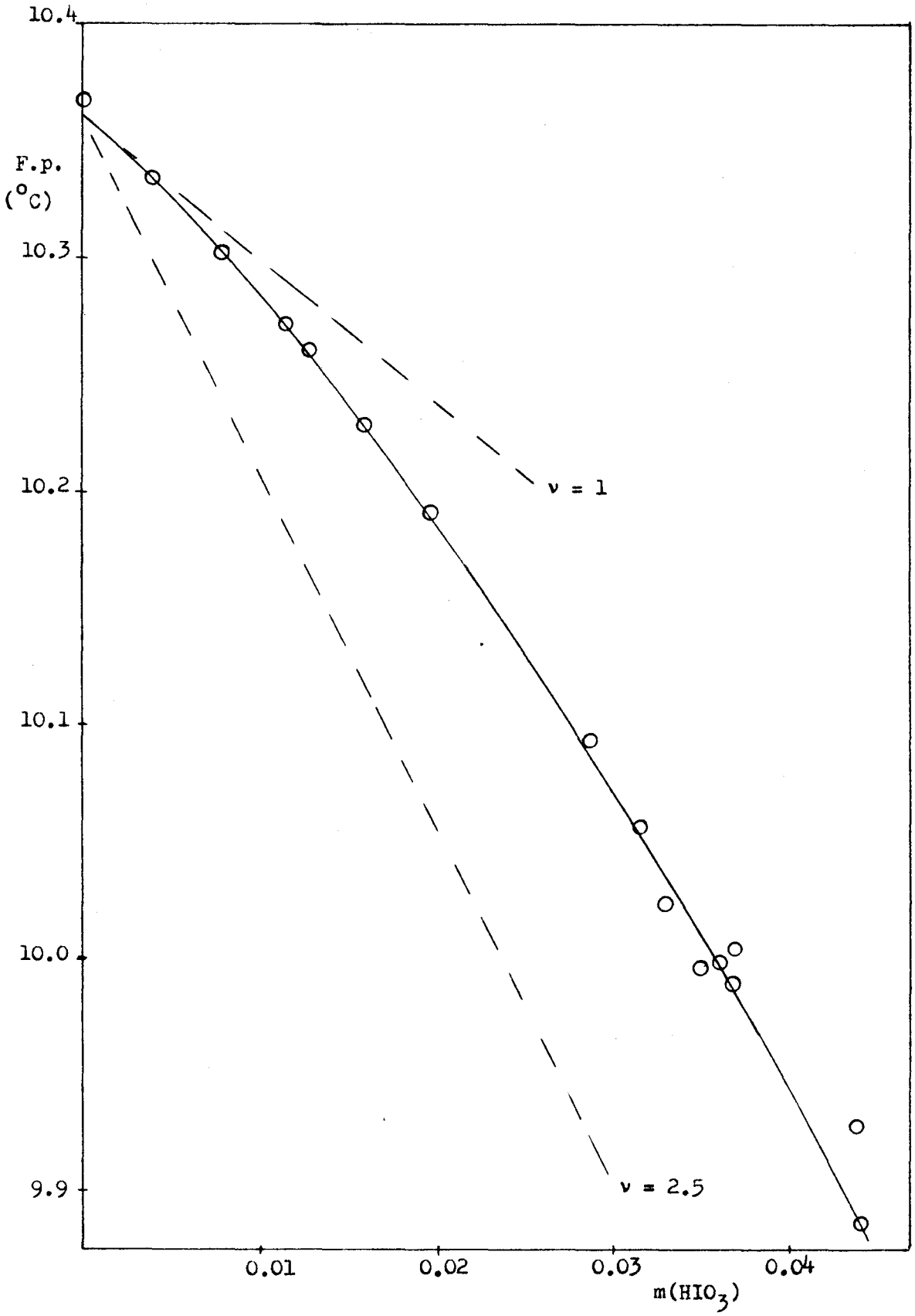


Figure 9. Solutions of HIO_3 in H_2SO_4: Freezing Points

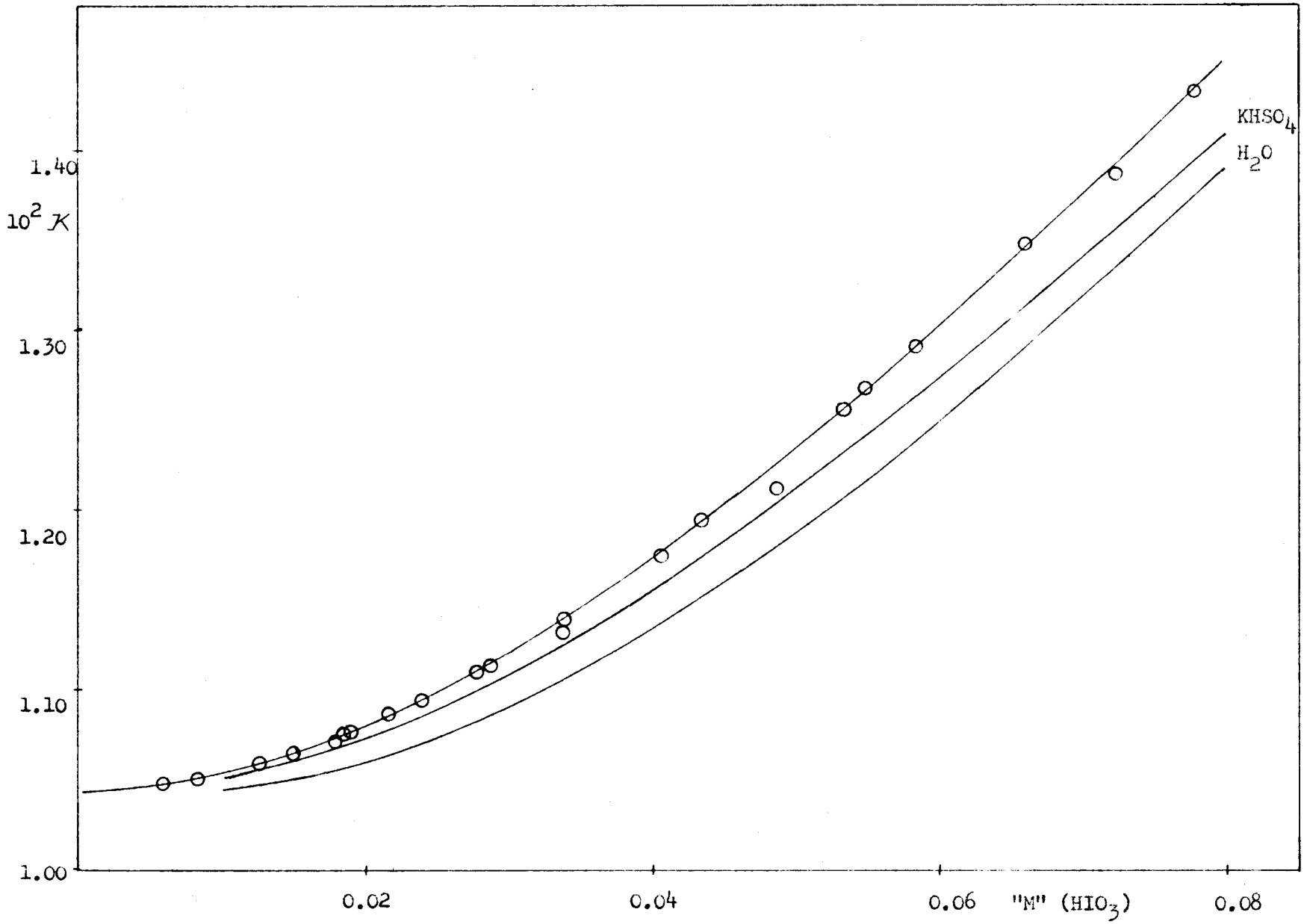


Figure 10. Solutions of HIO_3 in H_2SO_4: Conductivities at 25°C

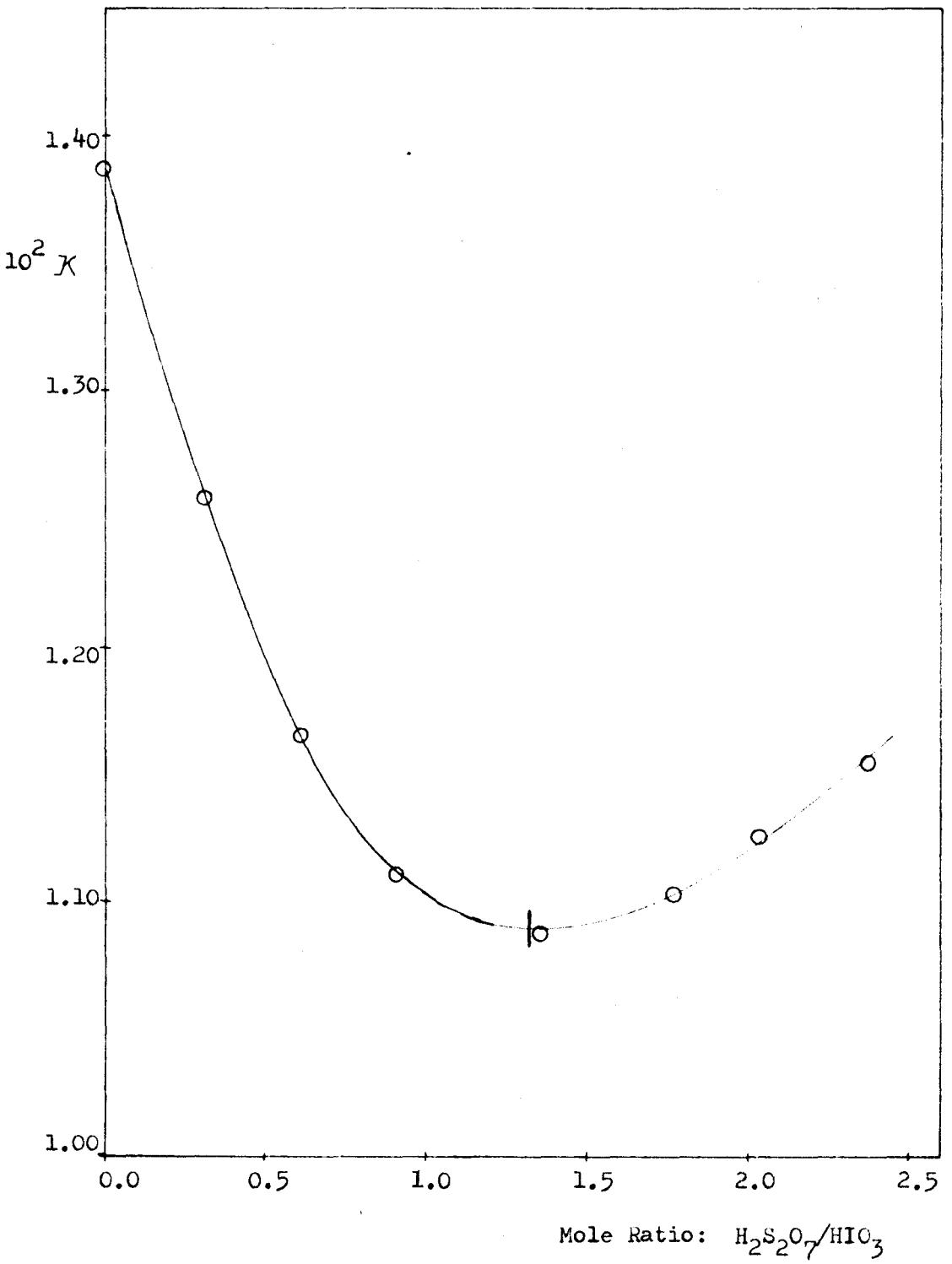


Figure 11. Conductimetric Titration of HIO_3 with $H_2S_2O_7$

3. Solutions of Iodic Acid and Iodine in Sulphuric Acid

Cryoscopy

Seven cryoscopic experiments were performed. In each, the starting solution contained iodine and iodic acid in a different mole ratio, and was subjected to successive dilutions with 100% sulphuric acid, to give a range of concentrations (Table 7). A curve of freezing point versus the stoichiometric concentration of iodic acid was plotted from the results of each experiment, and values of the freezing point at round molal concentrations of iodic acid were obtained by interpolation. The interpolated data were plotted on a set of graphs of freezing point versus the mole ratio I_2/HIO_3, each for a fixed stoichiometric molality of iodic acid. Examples of these curves are shown in Figure 12. From these curves were obtained values of the freezing points at the mole ratios of interest, namely I_2/HIO_3 = 0.33, 2.0 and 7.0, for each stoichiometric molality of iodine (Tables 9, 24, and 27)

Conductimetry

A series of experiments, in each of which successive additions of iodine were made to an initial solution of iodic acid, was carried out (Table 8). Curves were plotted of specific conductivity versus the mole ratio, I_2/HIO_3 (Figure 13 shows typical plots), and values of the conductivity at the mole ratios 0.33, 2.0 and 7.0 were obtained by interpolation (Tables 10, 25, and 28).

TABLE 7

Solutions of Iodic Acid and Iodine in

Sulphuric Acid: Freezing Points

Experiment 52

Weight of HIO_3 0.4436 g
Weight of I_2 0.2048 g
Mole ratio I_2/HIO_3 0.320
F.p. of solvent 10.366°C

Weight of H_2SO_4 (g)	$m^S(HIO_3)$*	F.p. (°C)
80.44	0.03134	9.645
95.52	0.02640	9.766
126.44	0.01994	9.928
178.43	0.01413	10.069
282.09	0.00894	10.194

Experiment 53

Weight of HIO_3 0.4935 g
Weight of I_2 0.4069 g
Mole ratio I_2/HIO_3 0.572
F.p. of solvent 10.364°C

Weight of H_2SO_4 (g)	$m^S(HIO_3)$*	F.p. (°C)
64.33	0.04360	9.164
82.49	0.03400	9.438
118.87	0.02359	9.741
178.52	0.01571	9.966
288.49	0.00972	10.138

* Uncorrected for solvent used in reaction.

(Table 7 continued)

Experiment 56

Weight of HIO_3	0.4391 g
Weight of I_2	1.1562 g
Mole ratio I_2/HIO_3	1.825
F.p. of solvent	10.365°C

Weight of H_2SO_4 (g)	$m^s(HIO_3)$*	F.p. (°C)
69.95	0.03567	8.966
84.98	0.02936	9.233
115.82	0.02154	9.559
175.08	0.01426	9.855
280.03	0.00891	10.071

Experiment 57

Weight of HIO_3	0.4288 g
Weight of I_2	1.3971 g
Mole ratio I_2/HIO_3	2.258
F.p. of solvent	10.368°C

Weight of H_2SO_4 (g)	$m^s(HIO_3)$*	F.p. (°C)
74.51	0.03271	8.944
93.42	0.02608	9.243
124.50	0.01958	9.538

* Uncorrected for solvent used in reaction.

(Table 7 continued)

Experiment 47

Weight of HIO_3	0.4864 g
Weight of I_2	4.3205 g
Mole ratio I_2/HIO_3	6.156
F.p. of solvent	10.364°C

Weight of H_2SO_4 (g)	$m^s(HIO_3)^*$	F.p. (°C)
75.81	0.03646	7.475
93.96	0.02942	8.054
119.99	0.02304	8.584
168.62	0.01640	9.136
289.11	0.00956	9.598

Experiment 50

Weight of HIO_3	0.4407 g
Weight of I_2	4.4258 g
Mole ratio I_2/HIO_3	6.960
F.p. of solvent	10.364°C

Weight of H_2SO_4 (g)	$m^s(HIO_3)^*$	F.p. (°C)
71.36	0.03510	7.398
86.50	0.02895	7.921
117.17	0.02138	8.594
177.62	0.01410	9.242
283.01	0.00885	9.643

* Uncorrected for solvent used in reaction.

(Table 7 continued)

Experiment 48

The initial solution for this experiment was 75.27 g of the final solution from Experiment 45 (Table 8).

Mole ratio I_2/HIO_3 = 8.037

Weight of H_2SO_4 (g)	$m^s(HIO_3)^*$	F.p. (^oC)
73.68	0.00976	9.615
90.86	0.00791	9.777
120.77	0.00595	9.948
170.97	0.00421	10.099
276.22	0.00261	10.223

* Uncorrected for solvent used in reaction.

Interpolated Freezing Points at

Round Stoichiometric Molalities of Iodic Acid

(F.p.s in ^oC)

Mole ratio I_2/HIO_3

$m^s(HIO_3)^{**}$	0.320	0.572	1.825	2.258	6.156	6.860	8.037
0.010	10.170	10.130	10.030	9.975	9.665	9.605	9.605
0.015	10.050	9.985	9.830	9.755	9.255	9.175	
0.020	9.930	9.845	9.630	9.530	8.855	8.750	
0.025	9.805	9.705	9.430	9.305	8.455	8.325	
0.030	9.685	9.565	9.225	9.080	8.050	7.900	
0.035	9.560	9.425	9.020	8.860	7.660	7.470	

** Corrected for solvent used in reaction.

TABLE 8

Solutions of Iodic Acid and Iodine in

Sulphuric Acid: Conductivities at 25°C

Experiment 51

Weight of H_2SO_4 252.36 g
Weight of HIO_3 0.1896 g
$w(HIO_3)_{initial}$ 0.00427 mole kg^{-1}

Weight of I_2 (g)	I_2/HIO_3	$10^2\kappa$ (ohm^{-1} cm^{-1})
0.0000	0.000	1.0511
0.0833	0.305	1.0677
0.1570	0.574	1.0722
0.5807	2.123	1.1055
0.9893	3.616	1.1509
2.0518	7.500	1.2635
2.2988	8.403	1.2654

Experiment 45

Weight of H_2SO_4 246.47 g
Weight of HIO_3 0.4233 g
$w(HIO_3)_{initial}$ 0.00976 mole kg^{-1}

Weight of I_2 (g)	I_2/HIO_3	$10^2\kappa$ (ohm^{-1} cm^{-1})
0.0000	0.000	1.0719
0.1900	0.308	1.1335
0.3642	0.596	1.1553
1.1554	1.892	1.2692
1.7807	2.916	1.3785
2.7742	4.542	1.5728
3.9418	6.454	1.8091

(Table 8 continued)

Weight of I_2 (g)	I_{2/HIO_3}	$10^2\kappa$ (ohm^{-1} cm^{-1})
4.5878	7.512	1.8505
4.9088	8.037	1.8524

Experiment 58

Weight of H_2SO_4 244.77 g
Weight of HIO_3 0.5070 g
$w(HIO_3)_{initial}$ 0.01175 mole kg^{-1}

Weight of I_2 (g)	I_{2/HIO_3}	$10^2\kappa$ (ohm^{-1} cm^{-1})
0.0000	0.000	1.0868
0.0657	0.090	1.1088
0.1808	0.247	1.1539
0.2702	0.369	1.1818
0.7425	1.015	1.2505
1.5095	2.063	1.3871
3.0464	4.164	1.6950
4.5249	6.186	2.0039
5.1064	6.980	2.0999

Experiment 55

Weight of H_2SO_4 256.71 g
Weight of HIO_3 0.7099 g
$w(HIO_3)_{initial}$ 0.01568 mole kg^{-1}

Weight of I_2 (g)	I_{2/HIO_3}	$10^2\kappa$ (ohm^{-1} cm^{-1})
0.0000	0.000	1.1144
0.0992	0.096	1.1515

(Table 8 continued)

Weight of I_2 (g)	I_{2/HIO_3}	$10^2 K$ (ohm^{-1} cm^{-1})
0.2698	0.260	1.2202
0.4033	0.388	1.2567
1.3139	1.265	1.4046
2.2733	2.188	1.5817
3.9516	3.804	1.9173
5.8450	5.627	2.295
6.8530	6.597	2.477

Experiment 49

Weight of H_2SO_4 236.32 g
Weight of HIO_3 0.7663 g
$w(HIO_3)_{initial}$ 0.01843 mole kg^{-1}

Weight of I_2	I_{2/HIO_3}	$10^2 K$ (ohm^{-1} cm^{-1})
0.000	0.000	1.1322
0.3168	0.283	1.2725
0.5620	0.502	1.3257
2.0355	1.817	1.6117
3.4013	3.037	1.9039
5.5639	4.967	2.3716
7.6418	6.822	2.767

Experiment 54

Weight of H_2SO_4 250.16 g
Weight of HIO_3 1.1744 g
$w(HIO_3)_{initial}$ 0.02668 mole kg^{-1}

Weight of I_2	I_{2/HIO_3}	$10^2 K$ (ohm^{-1} cm^{-1})
0.0000	0.000	1.2115

(Table 8 continued)

Weight of I_2	I_{2/HIO_3}	$10^2\mathcal{K}$ (ohm^{-1} cm^{-1})
0.2068	0.122	1.3071
0.4671	0.276	1.4212
0.5985	0.353	1.4650
1.4543	0.858	1.6224
2.4791	1.463	1.8233
3.5598	2.101	2.0393
4.1124	2.427	2.158

Experiment 62

Weight of H_2SO_4	228.72 g
Weight of HIO_3	1.3602 g
$w(HIO_3)_{initial}$	0.03380 mole kg^{-1}

Weight of I_2	I_{2/HIO_3}	$10^2\mathcal{K}$ (ohm^{-1} cm^{-1})
0.0000	0.000	1.3024
0.3515	0.179	1.4853
0.6333	0.323	1.6141
2.1222	1.082	1.9306
3.8338	1.953	2.2986
6.8301	3.480	2.9169
10.0608	5.126	3.5157
12.7944	6.519	3.954
13.9529	7.109	4.080

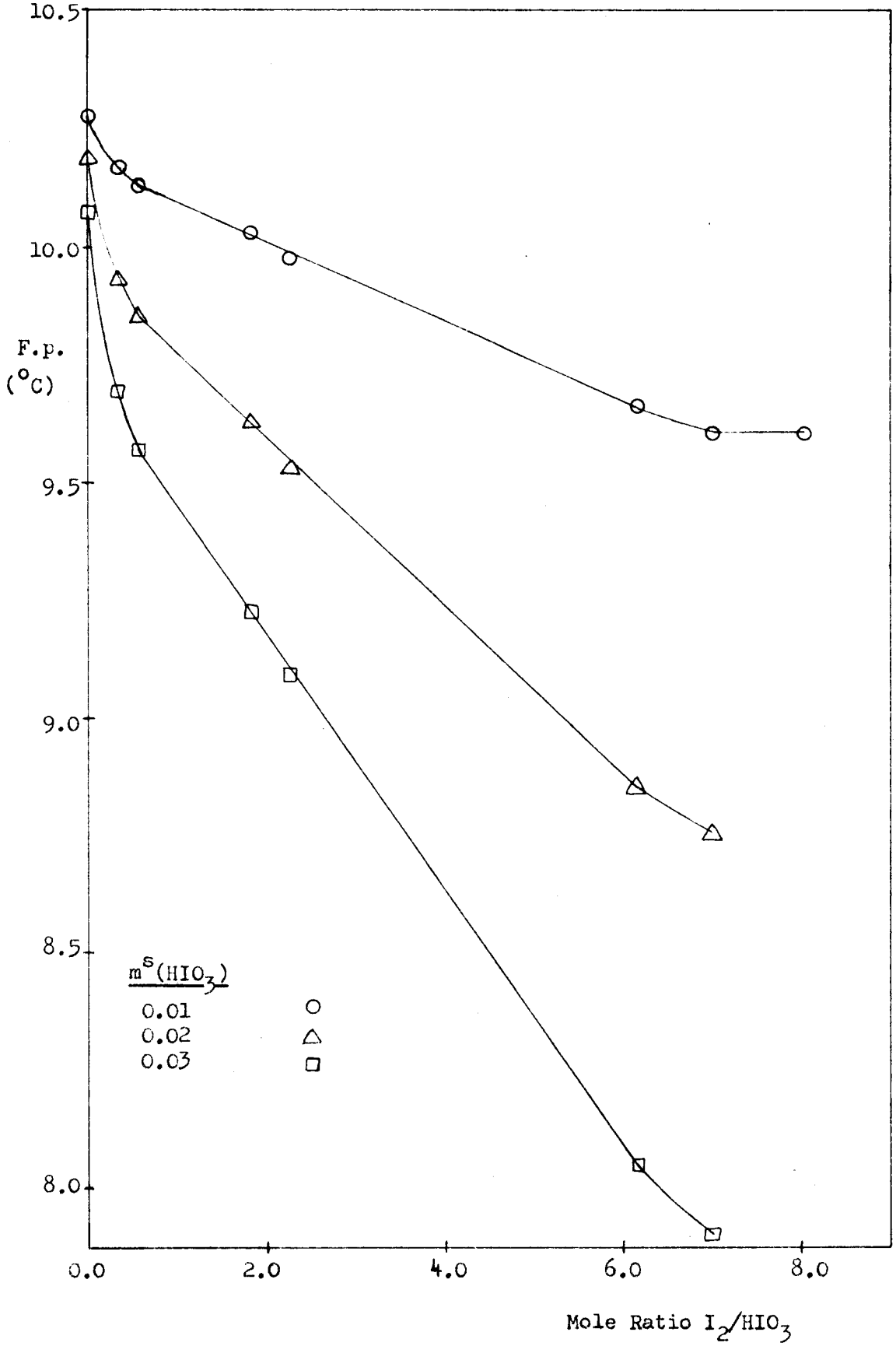


Figure 12. Curves of F.p. versus Mole Ratio I_2/HIO_3 (interpolated)

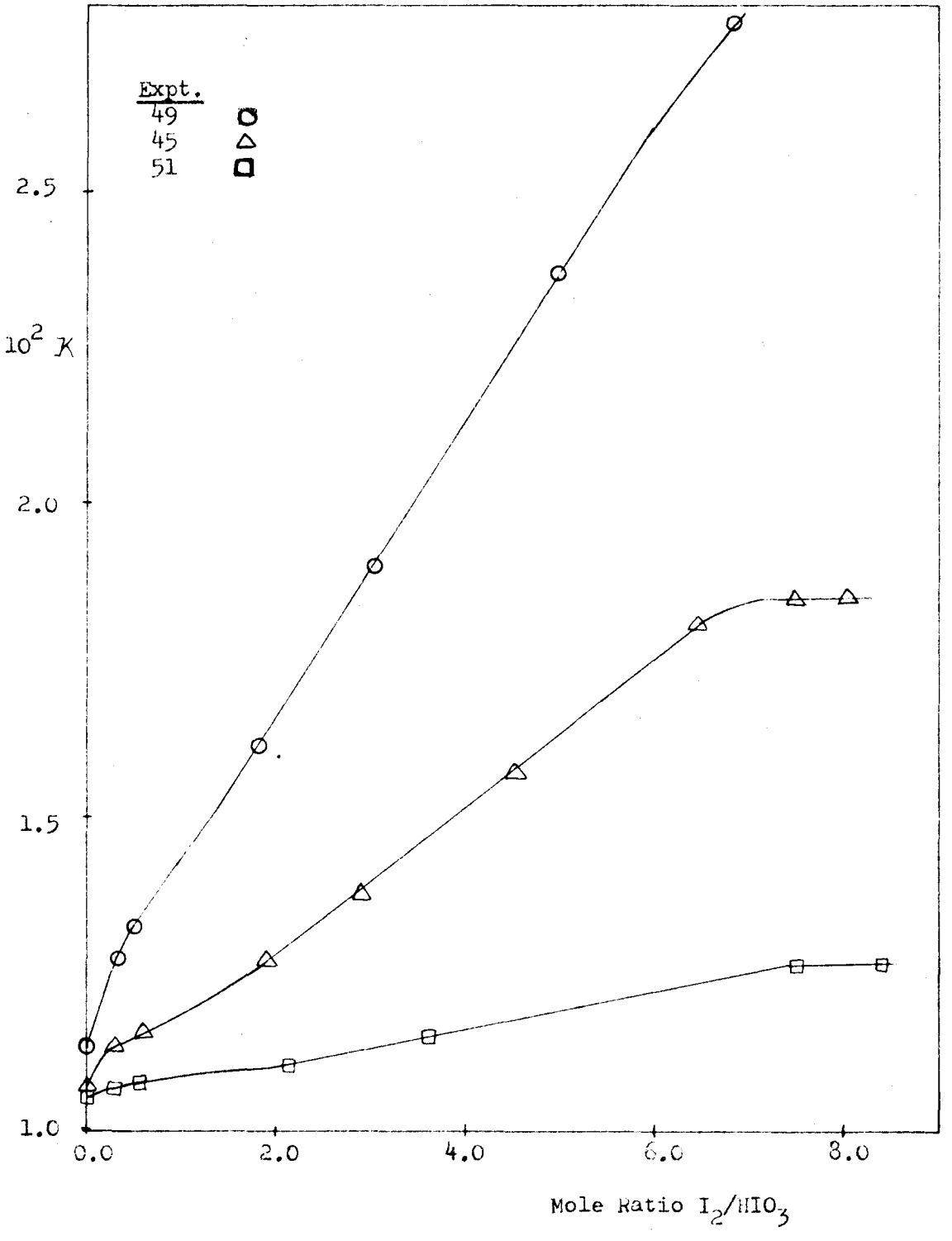


Figure 13. Solutions of HIO_3 and I_2 in H_2SO_4: Conductivities at 25°C

4. Solutions of Iodosyl Sulphate and of "HIO_3 + 0.33 I_2" in Sulphuric Acid

Introduction

Chrétien (24) obtained a yellow compound of trivalent iodine, to which he assigned the composition $I_2O_3 \cdot SO_3 \cdot 1/2\,H_2O$, by heating iodic acid in the presence of concentrated sulphuric acid. The composition of this compound was the subject of some controversy (25, 45), mainly concerned with the number of molecules of water of hydration. Masson and Argument (26) showed that the compound could be obtained in quantitative yield as a bright yellow crystalline precipitate by stirring together under concentrated sulphuric acid exactly equivalent amounts of iodine pentoxide and iodine, according to the equation:

$$3\,I_2O_5 + 2\,I_2 = 5I_2O_3$$

They determined the composition of the product in two ways, in each of which the compound was analysed while wet with its saturated solution in sulphuric acid. In the first method, barium sulphate dissolved in the sulphuric acid was used as an "indicator" to show the amount of the latter in the wet solid. In the second method the ternary phase system I_2O_3 - SO_3 - H_2O was studied over the range of solvent composition from $H_2SO_4 \cdot H_2O$ to H_2SO_4, by the Schreinemakers "wet residues" method. By both methods, the composition of the compound was shown conclusively to be $I_2O_3 \cdot SO_3$, without any water of hydration.

The compound was found not to be stable in media more aqueous than $H_2SO_4 \cdot H_2O$. Its solubility in 96% sulphuric acid was reported as 0.024 moles per litre at room temperature.

Masson and Race (30) showed that solutions of $I_2O_3 \cdot SO_3$ in

sulphuric acid reacted with aromatic compounds, C_6H_5X, where X = H, CH_3, Cl, Br, I, to form the sulphates of the corresponding diaryliodonium ions, $(XC_6H_4)_2I^+$, while Masson and Hanby (31) showed that with nitrobenzene and benzene sulphonic acid, the corresponding m-iodoso compounds, ArIO, were produced. Masson and co-workers considered $I_2O_3 . SO_3$ to be iodosyl sulphate $(IO)_2SO_4$. In solution in sulphuric acid they regarded it as a source of trace amounts of I^{+++} cations, which they considered to be the active species in the aromatic substitutions:

$$IO^+ + 2H^+ \rightleftharpoons I^{+++} + H_2O$$

$$ArH + I^{+++} = ArI^{++} + H^+$$

$$ArI^{++} + ArH = Ar_2I^+ + H^+$$

However the reactions could be formulated just as satisfactorily, regarding IO^+ as the active species in the second step of the above scheme.

Cryoscopy and conductimetry

Interpolated freezing-point and conductivity data for solutions containing iodic acid and iodine at the mole ratio I_2/HIO_3 = 0.33 are given in Table 9 and Figure 14, and Table 10 and Figure 15, respectively.

The results of cryoscopic experiments on solutions of iodosyl sulphate are given in Table 12 and Figure 16 and those of conductimetric experiments in Table 13 and Figure 17. The most concentrated solutions studied were obtained by warming the mixture, and were supersaturated at room temperature, depositing yellow crystals in the course of a few days.

Discussion

A number of possible ionization schemes are given below, together with the predicted values of ν and Υ. In the case of iodosyl sulphate, the ν and Υ values refer to this compound as solute, while for solutions of iodic acid and iodine, the values refer to iodic acid as solute.

$$(IO)_2SO_4 + H_2SO_4 = 2IOHSO_4 \qquad [1a]$$
$$\nu = 4\text{–}2,\ \Upsilon = 2\text{–}0,\ \nu\text{–}\Upsilon = 2$$

$$3HIO_3 + I_2 + 9H_2SO_4 = 5IOHSO_4 + 4H_3O^+ + 4HSO_4^- \qquad [1b]$$
$$\nu = 6\text{–}4.33,\ \Upsilon = 3\text{–}1.33,\ \nu\text{–}\Upsilon = 3$$

$$(IO)_2SO_4 + 7H_2SO_4 = 2I(HSO_4)_3 + 2H_3O^+ + 2HSO_4^- \qquad [2a]$$
$$\nu = 6,\ \Upsilon = 2,\ \nu\text{–}\Upsilon = 4$$

$$3HIO_3 + I_2 + 24H_2SO_4 = 5I(HSO_4)_3 + 9H_3O^+ + 9HSO_4^- \qquad [2b]$$
$$\nu = 7.67,\ \Upsilon = 3,\ \nu\text{–}\Upsilon = 4.67$$

$$(IO)_2SO_4 + 7H_2SO_4 = 2H_3O^+ + 2I(HSO_4)_4^- \qquad [3a]$$
$$\nu = 4,\ \Upsilon = 0,\ \nu\text{–}\Upsilon = 4$$

$$3HIO_3 + I_2 + 24H_2SO_4 = 9H_3O^+ + 5I(HSO_4)_4^- + 4HSO_4^- \qquad [3b]$$
$$\nu = 6,\ \Upsilon = 1.33,\ \nu\text{–}\Upsilon = 4.67$$

The ranges of ν and Υ quoted for [1a] and [1b] take into account the possibility of partial ionization of iodosyl hydrogen sulphate:

$$IOHSO_4 \rightleftharpoons IO^+ + HSO_4^- \qquad [4]$$

Whatever the extent of ionization of this compound, the differences, ν–Υ, would always have the constant values given.

Similarly, for the reactions represented by [2] and [3], the values of ν-Υ will have the constant values shown, whatever the position of the possible equilibrium:

$$I(HSO_4)_3 + HSO_4^- \rightleftharpoons I(HSO_4)_4^- \qquad [5]$$

The values of Υ for iodosyl sulphate were obtained by comparison with potassium hydrogen sulphate, and the values of ν were corrected for the repression of solvent autoprotolysis only (Table 14). Values of Υ for the solute "$HIO_3 + 0.33\ I_2$" were obtained by comparison with the conductivity curve for nitric acid (80), which is ionized in a manner analogous to that represented by combination of Equations [1b] and [4]:

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

The differences between values of Υ for "$HIO_3 + 0.33\ I_2$" calculated by comparison with water, potassium hydrogen sulphate, and nitric acid are quite small, except at very low concentrations. Values of ν were corrected for repression of autoprotolysis of the solvent using the experimental Υ-values to estimate $m^S(HSO_4^-)$, and for repression of ionic self-dehydration assuming that $m^S(H_3O^+) = 1.33\ m^S(HIO_3)$, as required by Equation [1b] (Table 11).

The values of ν and Υ for both solutes are in best agreement with reaction according to Equations [1a] and [1b], with about 50% ionization of iodosyl hydrogen sulphate according to Equation [4]. The values of ν for $(IO)_2SO_4$ lie in the range 3.63 to 2.76, while Υ varies from 1.44 to 0.75. ν-Υ is initially 2.19, becoming virtually constant at 2.01 at higher concentrations, in good agreement with the predicted value. Values of the equilibrium constant, K_b, for reaction [4] were calculated from the

conductivity data for solutions of $(IO)_2SO_4$, and are given by

$$K_b = \frac{[IO^+][HSO_4^-]}{[IOHSO_4]} = \frac{\gamma[HSO_4^-]}{2-\gamma}$$

where $[HSO_4^-]$ is the actual molal concentration of HSO_4^-, including that due to unrepressed self-ionization of the solvent.(Table 15 (b))

For the solute "HIO_3 + 0.33 I_2", ν lies in the range 5.48 to 4.89, with γ between 2.12 and 1.82. The values of $\nu-\gamma$ are close to 3, as predicted for Equation [1b]. Values of K_b, given in this case by

$$K_b = \frac{(\gamma - 1.33)[HSO_4^-]}{(3-\gamma)}$$

are shown in Table 15 (a).

The two sets of values of K_b are each reasonably constant, but those obtained from the data on $(IO)_2SO_4$ are larger than those obtained from the "HIO_3 + 0.33 I_2" results. The stoichiometric concentrations of $IOHSO_4$ in the latter case are lower than those in the former, so that the two sets of values are not strictly comparable. However, since both sets of values tend to decrease with increasing concentration, it might have been expected that the values in the latter case would actually be the larger. A possible reason for the discrepancy may be the occurrence in solutions of $(IO)_2SO_4$ of some reaction according to Equation [2a], with an increase in the concentration of HSO_4^-. This reaction leads to the production of H_3O^+, and so the corresponding reaction for the solute "HIO_3 + 0.33 I_2", for which H_3O^+ ions are already produced in reaction [1b], should be of less importance.

The limiting slopes at low concentrations of the freezing-point

curves (Figures 12 and 16) for the solutes "HIO_3 + 0.33 I_2 and $(IO)_2SO_4$, correspond approximately to $\nu = 1.67$ and 2 respectively, as required by Equations [1].

TABLE 9

Solutions of Iodic Acid and Iodine in Sulphuric Acid: Interpolated Freezing Points at the Mole Ratio I_2/HIO_3 = 0.333

$m^s(HIO_3)$	F.p. (°C)
0.010	10.170
0.015	10.050
0.020	9.925
0.025	9.800
0.030	9.670
0.035	9.555

TABLE 10

Solutions of Iodic Acid and Iodine in Sulphuric Acid: Interpolated Conductivities at the Mole Ratio I_2/HIO_3 = 0.333

Experiment	"m^s" (HIO_3)	$10^2\mathcal{K}$ (ohm^{-1} cm^{-1})
51	0.00780	1.069
45	0.01781	1.138
58	0.02147	1.176
55	0.02864	1.250
49	0.03356	1.298
60	0.04117	1.386
54	0.04852	1.465
62	0.06176	1.622
122	0.1043	2.055

TABLE 11

Solutions of Iodic Acid and Iodine in Sulphuric Acid: Values of ν and Υ at the Mole Ratio I_2/HIO_3 = 0.333

$m^s(HIO_3)$	ν	Υ	$\nu - \Upsilon$
0.01	5.48	2.12	3.36
0.02	4.97	1.94	3.03
0.03	4.89	1.82	3.07
0.04	4.71	1.73	2.98

TABLE 12

Solutions of Iodosyl Sulphate in

Sulphuric Acid: Freezing Points

Experiment 64

The initial solution for this experiment was 69.79 g of the final solution from Experiment 63 (Table 13).

Weight of H_2SO_4 (g)	m	F.p. (^{o}C)
67.91	0.07059	9.267
85.31	0.05612	9.482
115.25	0.04149	9.695
176.94	0.02699	9.922
281.62	0.01695	10.085

Experiment 124

Weight of $(IO)_2SO_4$ 1.0638 g
F.p. of solvent 10.368^{o}C

Weight of H_2SO_4 (g)	m	F.p. (^{o}C)
72.53	0.03855	9.786
88.59	0.03154	9.884
120.15	0.02324	10.004
191.18	0.01459	10.142

Experiment*	m	F.p. (^{o}C)
72	0.03776	9.806
125	0.05612	9.535

* Fuller details of these experiments, in which $H_2S_2O_7$ was subsequently added are given in Table 16.

TABLE 13

Solutions of Iodosyl Sulphate in

Sulphuric Acid: Conductivities at 25°C

Experiment 22

Weight of H_2SO_4 291.64 g

Weight of $(IO)_2SO_4$ (g)	w	"M"	$10^2\kappa$ ($ohm^{-1}cm^{-1}$)
0.1626	0.00146	0.00267	1.0484
0.3540	0.00318	0.00580	1.0552
0.8613	0.00771	0.01409	1.0796
1.4266	0.01275	0.02329	1.1130
2.1730	0.01937	0.03538	1.1626
2.6700	0.02376	0.04340	1.1974
3.4239	0.03039	0.05552	1.2505
4.3339	0.03834	0.07005	1.3138

Experiment 63

Weight of H_2SO_4 236.79 g

Weight of $(IO)_2SO_4$ (g)	w	"M"	$10^2\kappa$ ($ohm^{-1}cm^{-1}$)
0.1829	0.00202	0.00370	1.0509
0.6868	0.00760	0.01388	1.0788
1.1371	0.01257	0.02297	1.1124
1.7850	0.01973	0.03606	1.1639
2.4066	0.02661	0.04862	1.2165
3.3250	0.03677	0.06718	1.2933
4.3846	0.04848	0.08859	1.3785
6.3400	0.07010	0.12809	1.5254

(Table 13 continued)

Experiment*	w	"M"	$10^2 \mathcal{K}$ (ohm^{-1} cm^{-1})
78	0.03279	0.05991	1.2544
123	0.02491	0.04550	1.1950

* Fuller details of these experiments, in which $H_2S_2O_7$ was subsequently added are given in Table 17 (b).

TABLE 14

Solutions of Iodosyl Sulphate in

Sulphuric Acid: Values of ν and γ

m	ν	γ	$\nu - \gamma$
0.02	3.22	1.14	2.08
0.03	3.06	1.00	2.06
0.04	2.94	0.91	2.03
0.05	2.86	0.85	2.01
0.06	2.80	0.79	2.01
0.07	2.76	0.75	2.01

TABLE 15 (a)

Values of K_b for $IOHSO_4$, from the

Conductivities of Solutions of HIO_3 + 0.33 I_2

$m^s(HIO_3)$	γ	$[HSO_4^-]$	$K_b = \frac{(\gamma - 1.33)[HSO_4^-]}{(3 - \gamma)}$
			(mole kg^{-1})
0.01	2.12	0.0308	0.028
0.02	1.94	0.0451	0.026
0.03	1.82	0.0596	0.025
0.04	1.73	0.0698	0.022

TABLE 15 (b)

Values of K_b for $IOHSO_4$, from the

Conductivities of Solutions of Iodosyl Sulphate

$m\{(IO)_2SO_4\}$	γ	$[HSO_4^-]$	$K_b = \frac{\gamma[HSO_4^-]}{2 - \gamma}$
			(mole kg^{-1})
0.02	1.14	0.0329	0.044
0.03	1.00	0.0385	0.039
0.04	0.91	0.0440	0.037
0.05	0.85	0.0493	0.036
0.06	0.79	0.0537	0.035
0.07	0.75	0.0585	0.035

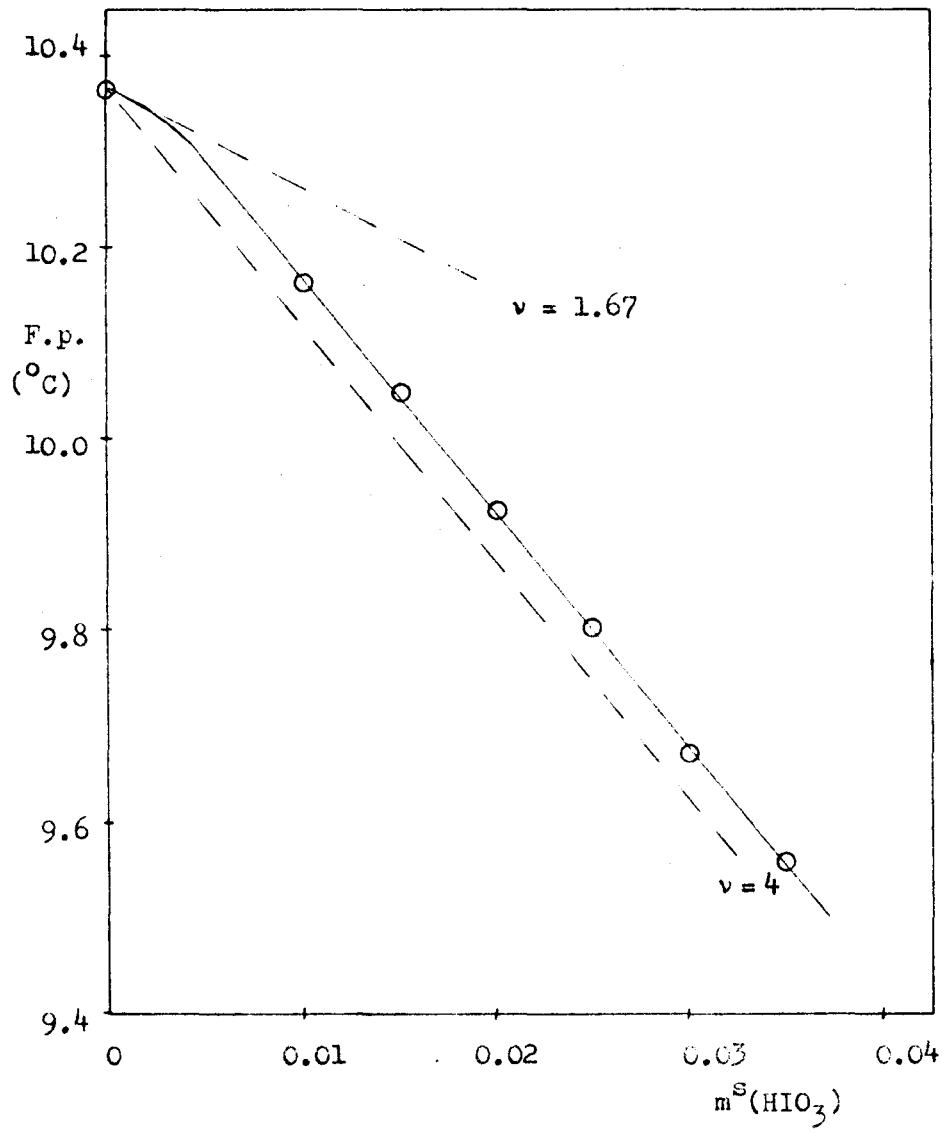


Figure 14. Solutions of HIO_3 + 0.33 I_2 in H_2SO_4
Interpolated Freezing Points

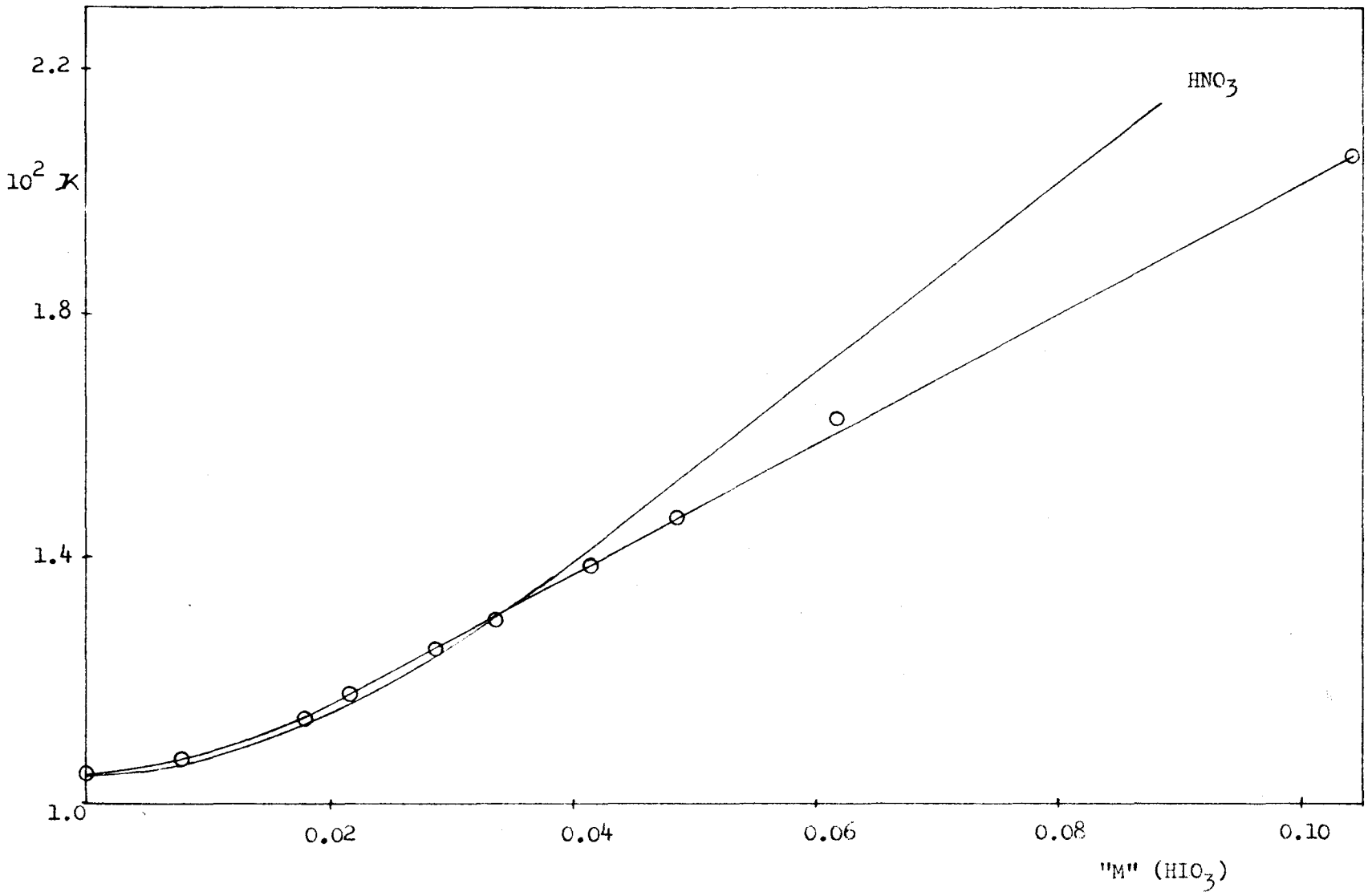


Figure 15. Solutions of HIO_3 + 0.33 I_2 in H_2SO_4: Interpolated Conductivities (25°C)

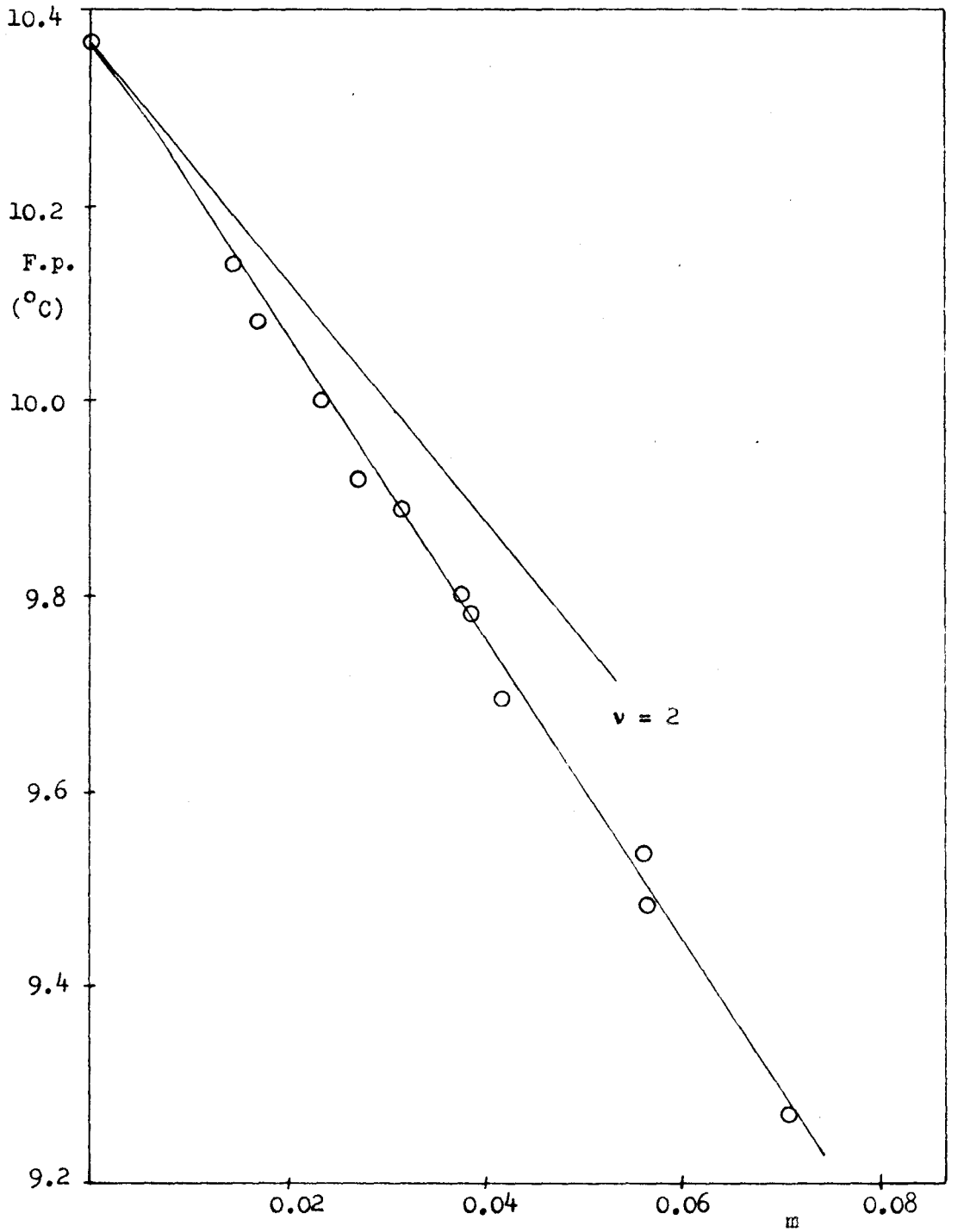


Figure 16. Solutions of $(IO)_2SO_4$ in H_2SO_4: Freezing Points

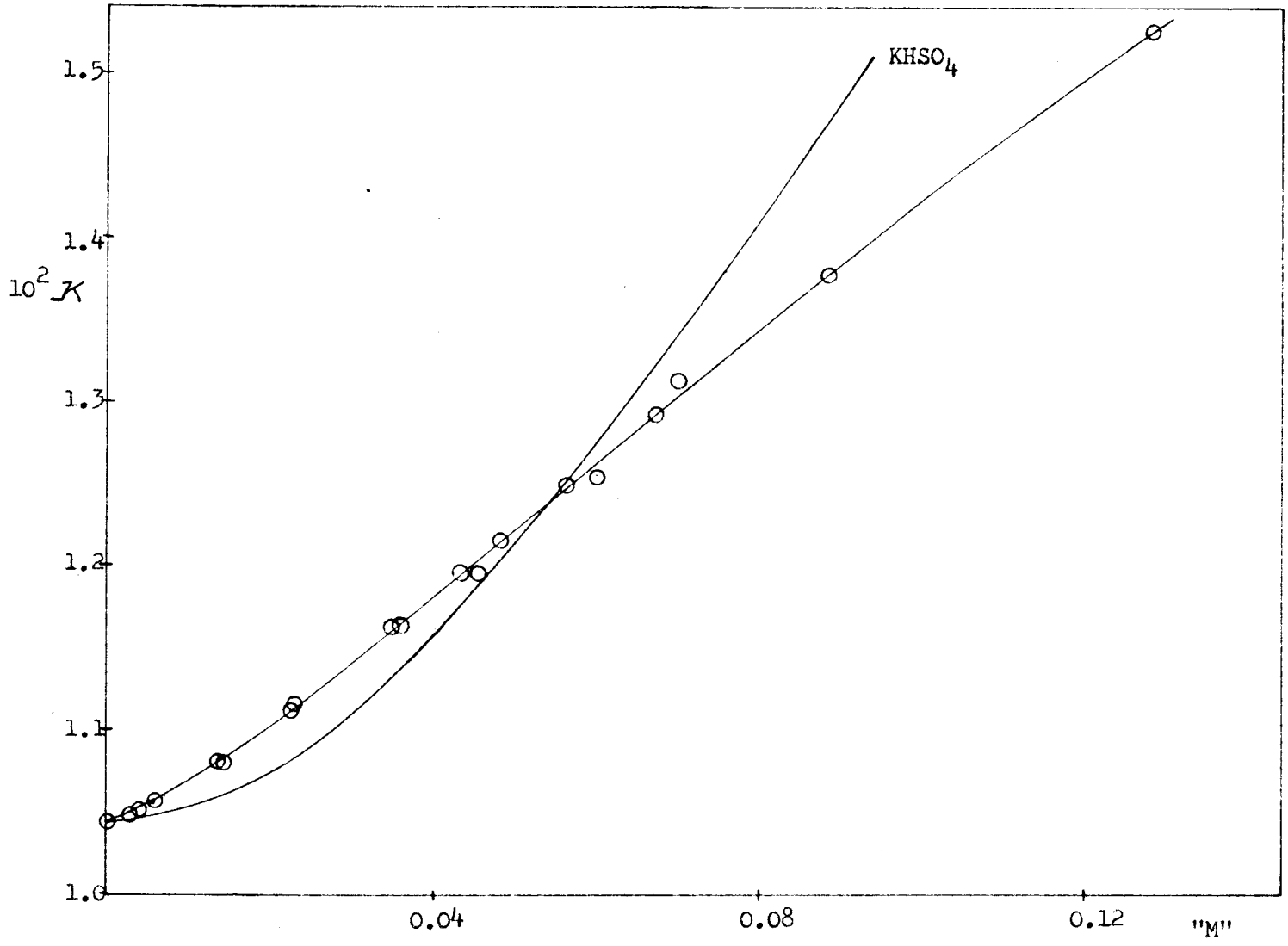


Figure 17. Solutions of $(IO)_2SO_4$ in H_2SO_4: Conductivities at 25 C

5. The Reaction Between Iodosyl Sulphate and Disulphuric Acid

Introduction

Masson and Argument (26) found that when sufficient sulphur trioxide was added to a saturated solution of iodosyl sulphate in sulphuric acid to bring the composition of the solvent above 100% H_2SO_4, the solid phase in equilibrium with the solution was no longer the yellow $(IO)_2SO_4$, but a white crystalline, extremely moisture-sensitive substance, which they showed to have the composition $I_2O_3.4SO_3.xH_2O$ where x could not be determined with certainty. The most probable formula was considered to be $I_2O_3.4SO_3.H_2O$, which can be rewritten as $I_2(SO_4)_3.H_2SO_4$, a solvated form of the normal sulphate of trivalent iodine, $I_2(SO_4)_3$, prepared by Fichter and Kappeler (18), or as the acid $HI(SO_4)_2$. When aqueous sulphuric acid was added, to bring the composition of the medium below 100% H_2SO_4, the white compound decomposed, releasing iodine and iodine pentoxide, which then recombined to give iodosyl sulphate. The saturated solution in equilibrium with the white solid is yellow, and Symons (36) has shown that there is no change in the U.V. spectrum as the composition of the medium is changed from aqueous sulphuric acid to oleum. Thus although the solid phase in equilibrium changes, there is no corresponding sudden change in the nature of the species present in solution.

In the present work, the reactions occurring on the addition of a solution of disulphuric acid to a solution of iodosyl sulphate in 100% sulphuric acid were studied cryoscopically, and conductimetrically.

Cryoscopy

The results of two experiments, in which a solution of $H_2S_2O_7$ was added to a solution of $(IO)_2SO_4$ in 100% sulphuric acid, and the freezing point measured after each addition, are given in Table 16 and Figure 18. The freezing point rose initially as $H_2S_2O_7$ was added, passed through a maximum close to the mole ratio $H_2S_2O_7/(IO)_2SO_4 = 1.4$ and then fell again.

Conductimetry

As $H_2S_2O_7$ was added to a solution of $(IO)_2SO_4$ in 100% sulphuric acid, the conductivity at first decreased, passed through a minimum, and then increased (Table 17b, Figure 19). The final addition of oleum was carefully made, so as to bring the composition of the solute as close as possible to the stoichiometry $(IO)_2SO_4 + 2H_2S_2O_7$. Small weighed amounts of potassium sulphate were added to the resulting solution, whereupon the conductivity at first decreased, passed through a rather shallow minimum, and then rose sharply (Table 17b, Figure 19).

Similar results were obtained when disulphuric acid was added to a solution of $HIO_3 + 0.33\ I_2$ (Table 17a, Figure 19). A solution of this composition may be regarded as containing the solute "$I_2O_3 + 0.6\ H_2O$". Conductivities have been plotted against the mole ratio $H_2S_2O_7/"I_2O_3"$. At the mole ratio $H_2S_2O_7/"I_2O_3" = 1.6$, the composition of the solution is the same as that of a solution of $I_2O_3.SO_3$ or $(IO)_2SO_4$. Thus we have $H_2S_2O_7/(IO)_2SO_4 = H_2S_2O_7/"I_2O_3" - 1.6$.

Discussion

Two main types of reaction may be considered. The reaction

may be a simple neutralization of the base IO HSO_4 by the acid $H_2S_2O_7$. In this case HSO_4^- ions would be replaced in the solution by $HS_2O_7^-$, in a reaction which may be written:

$$\left.\begin{array}{c} \text{IO } HSO_4 \\ \downarrow\uparrow \\ IO^+ + HSO_4^- \end{array}\right\} + H_2S_2O_7 = H_2SO_4 + \left\{\begin{array}{c} \text{IO } HS_2O_7 \\ \downarrow\uparrow \\ IO^+ + HS_2O_7^- \end{array}\right. \qquad [1]$$

The position of the conductivity minimum could be determined by the method of Flowers, Gillespie and Robinson (93) only if the compound IO HS_2O_7 were fully ionized. Since the ion $HS_2O_7^-$ is a weaker nucleophile than HSO_4^-, the compound IO HS_2O_7 might be expected to be more fully dissociated than IO HSO_4 and would certainly not be less so. Thus there would probably be an increase, and certainly no decrease in the number of solute particles, and the freezing point would either be depressed on the addition of $H_2S_2O_7$, or remain unchanged. The observed initial rise in the freezing point is thus inconsistent with this reaction. The observed freezing point at the mole ratio $H_2S_2O_7/(IO)_2SO_4$ = 2.0, corresponding to completion of reaction [1], is also much too high to be consistent with the formation of IO HS_2O_7, ionized to any appreciable extent.

Alternatively, one or more of a series of sulphato or hydrogensulphato-iodine (III) compounds might be produced. A number of possible species is shown below in order of increasing sulphation:

IO HSO_4 ; $(HSO_4)_2$ I O I $(HSO_4)_2$; $I(HSO_4)_3$.

The neutral form of each species is shown, and it must be remembered that in principle each one may be capable of behaving as a base, with

the loss of a hydrogen sulphate ion, and formation of the corresponding cation, or as an acid, with the uptake of a hydrogen sulphate ion from the solvent, accompanied by the formation of the sulphuric acidium ion.

We shall consider first the mole ratio $H_2S_2O_7/(IO)_2SO_4 = 2.0$, for which the simplest overall reaction would be

$$(IO)_2SO_4 + H_2SO_4 + H_2S_2O_7 = 2\,I(HSO_4)_3 \; . \qquad [2]$$

Figure 19 shows that a solution of this composition can be titrated to a conductivity minimum with the base $KHSO_4$ (added as K_2SO_4), and must thus contain an acid of the sulphuric acid solvent system. We may suppose that the species written above as $I(HSO_4)_3$ is actually the acid $HI(HSO_4)_4$, which is partly ionized.

$$HI(HSO_4)_4 + H_2SO_4 \rightleftharpoons H_3SO_4^+ + I(HSO_4)_4^- \; . \qquad [3]$$

The dissociation constant for this acid, K_a, is given by

$$K_a = \frac{\left[H_3SO_4^+\right]\left[I(HSO_4)_4^-\right]}{\left[HI(HSO_4)_4\right]}$$

A value for K_a may be obtained by comparing the conductivities of solutions of $HI(HSO_4)_4$ (Table 18, Figure 20) with those of $H_2S_2O_7$ solutions (89). As discussed previously, the concentration of the sulphuric acidium ion, $H_3SO_4^+$, must be the same in solutions of any acids having the same conductivity. Concentrations of $H_3SO_4^+$ at round values of the stoichiometric concentration of $H_2S_2O_7$ have been calculated from its known dissociation constant (Table 4 of reference 73).

Thus by comparison of the conductivity curves of the two acids, the concentration of $H_3SO_4^+$ in any given solution of $HI(HSO_4)_4$ may be determined. The concentration of the anion $I(HSO_4)_4^-$ will not be exactly the same as the concentration of $H_3SO_4^+$, because of the self-dissociation of the solvent, but concentrations of the anion A^- of any acid HA, corresponding to given concentrations of $H_3SO_4^+$, have also been calculated previously (Table 2 of reference 73). The concentration of the unionized acid is given by

$$\left[HI(HSO_4)_4\right] = m^s\left\{HI(HSO_4)_4\right\} - \left[I(HSO_4)_4^-\right] .$$

Values of K_a obtained in this way are reasonably constant, the mean value being 0.009 mole kg^{-1} (Table 19).

The positions of the conductivity minima in the titrations of $HI(HSO_4)_4$ with $KHSO_4$ may also be used to estimate a value for K_a. By the method of Flowers, Gillespie and Robinson (93) the mole ratio $r_{min} = \left\{KHSO_4/HI(HSO_4)_4\right\}_{min}$ at the conductivity minimum is given by

$$r_{min} = \left(1 + \frac{0.013}{a}\right)^{-1} + \frac{0.0007}{a}$$

where a is the initial molal concentration of the acid. Values of K_a obtained by this method are very much smaller than the value obtained from the conductivities, (Table 20). If we use the value $K_a = 0.009$, obtained from conductivity measurements, to calculate the value of r_{min} in Experiment 123, we obtain $r_{min} = 0.40$, compared with the experimental value of 0.175.

Alternatively, it may be assumed that $I(HSO_4)_3$ has no acidic properties, but that the acid behaviour is due to an equilibrium concentration of $H_2S_2O_7$, arising from a reaction such as :

$$2\ I(HSO_4)_3 \rightleftharpoons I_2O(HSO_4)_4 + H_2S_2O_7 \quad . \qquad [4]$$

The concentration of $H_2S_2O_7$ is taken to be that necessary to give rise to the observed conductivity. Then using the method of Flowers et al for the special case where the acid being titrated is $H_2S_2O_7$, we calculate $r_{min} = 0.37$, which is very nearly the same as the value obtained by assuming that the acid is $HI(HSO_4)_4$.

Thus the conductivity results, and the position of the minimum in the $KHSO_4$ titration, lead to quite different estimates of the acidity of solutions at the mole ratio $H_2S_2O_7/(IO)_2SO_4 = 2.0$.

A possible explanation for the discrepancy might be that the addition of $KHSO_4$ somehow destroys the acid more rapidly than in a simple acid-base titration. It is however very difficult to imagine any reasonable mechanism by which this could occur.

It is probable therefore that the $KHSO_4$ titration gives a reasonably accurate estimate of the amount of acid present in solutions at the mole ratio $H_2S_2O_7/(IO)_2SO_4 = 2.0$, and that a large part of the conductivity in these solutions is due to ions other than those produced by self-dissociation of the solvent. This possibility will be discussed in more detail after consideration of the cryoscopic results.

In Figure 18, points A and A' represent the observed initial freezing points, in Experiments 72 and 125 respectively, of the

solutions containing partly ionized $IOHSO_4$. At the mole ratio $H_2S_2O_7/(IO)_2SO_4$ = 2.0, points B and B' show the predicted freezing points for the production of two moles of solute particles from each mole of stoichiometric $(IO)_2SO_4$, i.e. for $\nu = 2$, with no repression of solvent self-dissociation. Points B and B' agree rather closely with the observed freezing points at this mole ratio. This would be in agreement with reaction according to Equation [2] to produce two moles of the non-electrolyte $I(HSO_4)_3$ or the weak acid $HI(HSO_4)_4$. However, as shown above, such a simple picture does not agree with the conductivity results.

At the mole ratio $H_2S_2O_7/(IO)_2SO_4$ = 1.0, points C and C' represent the theoretical freezing points for $\nu = 1$, and D and D' those for $\nu = 2$, with no repression of solvent self-dissociation in either case. The value $\nu = 1$ would be consistent with formation of the dimeric species $I_2O(HSO_4)_4$:

$$(IO)_2SO_4 + H_2SO_4 + H_2S_2O_7 = I_2O(HSO_4)_4 \qquad [5]$$

Although the observed freezing points at the 1.0 mole ratio lie far below C and C', the initial slopes of the freezing point curves are not much less than those of the lines AC and A'C', so that the formation of this species may be important when the amount of added $H_2S_2O_7$ is small. The value $\nu = 2$ would be consistent with formation of the fully ionized salt $IO^+ I(HSO_4)_4^-$

$$(IO)_2SO_4 + H_2SO_4 + H_2S_2O_7 = IO^+ + I(HSO_4)_4^- \qquad [6]$$

Points D and D' are in much better agreement with experiment, although they actually lie below the observed curves in each case. It may be supposed that reaction according to Equation [6] predominates,

but that some of the unionized species $I_2O(HSO_4)_4$ is also produced.

At $H_2S_2O_7/(IO)_2SO_4$ mole ratios greater than 2.0, the observed freezing point curves have smaller slopes than the theoretical curves BE, B'E' for $H_2S_2O_7$, indicating that some $H_2S_2O_7$ is probably used up in a reaction even beyond this mole ratio.

At the conductivity minimum, in both the "titrations" of $(IO)_2SO_4$ with $H_2S_2O_7$, and the "back-titrations" with $KHSO_4$, the conductivity of the solutions is considerably greater than that of 100% sulphuric acid. It has been shown (93) that at the conductivity minimum in an acid-base titration the concentrations of $H_3SO_4^+$ and HSO_4^- are almost the same as in 100% sulphuric acid, namely 0.013 and 0.018 molal, respectively. Thus the excess conductivity over that of the solvent must be due to ions produced from the solute. The conductivity minimum in the titration of $(IO)_2SO_4$ with $H_2S_2O_7$ comes quite close to the mole ratio 1.0, and the conductivity at this ratio differs very little from that at the minimum. Thus at this ratio also, most of the difference between the actual conductivity and that of the solvent, must be due to solute ions. It has been suggested (58) on the basis of transport number measurements (82) that the ions K^+ and H_3O^+ have ionic mobilities of about 5 in sulphuric acid solutions. These ions are small and highly solvated, so that formally larger, but less solvated ions, such as IO^+ and $I(HSO_4)_4^-$ may not unreasonably be considered to have mobilities of up to about 10, although very little information is available on this matter.

If we arbitrarily assign ionic mobilities of 10 ohm^{-1} cm^2 g. $equiv^{-1}$ to these ions, the conductivity at the 1.0 ratio can be explained in terms

of almost complete ionization to IO^+ and $I(HSO_4)_4^-$, according to Equation 6, which is in reasonably good agreement with the freezing-point results.

For example, in Experiment 78, the specific conductivity, $\mathcal{K}$, at the 1.0 ratio is 1.148×10^{-2} ohm^{-1} cm^{-1}. The excess over the solvent conductivity of 1.044×10^{-2} ohm^{-1} cm^{-1} is 0.104×10^{-2} ohm^{-1} cm^{-1}. The contribution to $\mathcal{K}$ from a molal concentration m, of ions having a mobility λ, in a solution of density ρ, is given by

$$\mathcal{K} = \frac{\rho m \lambda}{1000} \qquad [7]$$

Putting $\mathcal{K} = 0.104 \times 10^{-2}$, $\lambda = 10$ and $\rho = 1.83$ gives $m = 0.057$. Since the stoichiometric concentration of $(IO)_2SO_4$ is 0.030 molal, the maximum possible value of m for iodine-containing ions would be 0.060.

It was suggested earlier that at the 2.0 mole ratio also, a large part of the observed conductivity might be due to iodine-containing ions. Since it is probable that at least some free $H_2S_2O_7$ is present in the solution at this ratio, it may be assumed for simplicity that this is the only acid present. Its concentration may be calculated from the observed value of r_{min} in the $KHSO_4$ titration. Then the difference between the observed conductivity of the solution at the 2.0 ratio, and that of an oleum of this concentration, is the conductivity contribution of the iodine-containing ions. Again assuming the value 10 for the mobilities of such ions, it can be shown that, just as at the 1.0 ratio, almost all the iodine must be present in the form of ions.

One possibility is that the iodine-containing ions result from an equilibrium of the type:

$$2I(HSO_4)_3 \rightleftharpoons IO^+ + I(HSO_4)_4^- + H_2S_2O_7 \qquad [8]$$

However the concentration of $H_2S_2O_7$ determined from r_{min} would be accompanied, in an equilibrium of this sort, by concentrations of IO^+ and $I(HSO_4)_4^-$ too small to account for the observed conductivity, unless their mobilities had improbably high values of the order of 20.

It is proposed that at the 2.0 ratio, about half the iodine is present as IO^+ ions, and most of the remainder as the anions $I(HSO_4)_4^-$ and $I(HSO_4)_3(HS_2O_7)^-$, in equilibrium with free $H_2S_2O_7$:

$$I(HSO_4)_3(HS_2O_7)^- + H_2SO_4 \rightleftharpoons I(HSO_4)_4^- + H_2S_2O_7 \qquad [9]$$

To make this explanation consistent with the observed freezing points at the mole ratio 2.0, it is necessary to suppose that a small fraction of the iodine is present in polymeric forms, such as $I_2O(HSO_4)_4$, or $I_2SO_4(HSO_4)_4$, which could be formed in the reaction:

$$2I(HSO_4)_3 \rightleftharpoons (HSO_4)_2 \; I \; SO_4 \; I(HSO_4)_2 + H_2SO_4 \qquad [10]$$

Consider again the example of Experiment 78. We have $r_{min} = 0.14$, from which we can calculate the concentration of $H_2S_2O_7$ to be 0.0115 molal. For a solution of $H_2S_2O_7$ of this concentration, $\mathcal{K} = 1.070 \times 10^{-2}$, while experimentally, at the 2.0 mole ratio, $\mathcal{K} = 1.167 \times 10^{-2}$ ohm^{-1} cm^{-1}. The difference, which is the conductivity contribution of the iodine-containing ions, is 0.097×10^{-2} ohm^{-1} cm^{-1}. Substituting this value for $\mathcal{K}$ in Equation 7 we obtain m = 0.053. Since the stoichiometric molality of $(IO)_2SO_4$ is 0.030 in this experiment, the maximum possible value would be m = 0.060. Thus, if the value $\lambda = 10$ is correct, 88% of the iodine present is in the form of ions.

In Experiment 72, the stoichiometric molality of $(IO)_2SO_4$ is 0.034, so that at the mole ratio 2.0, we expect the concentration of $H_2S_2O_7$ to be about 0.013 molal. The freezing point of a solution of $H_2S_2O_7$ of this concentration is 10.340°C. The observed freezing point is 9.950°, so that the additional depression due to iodine-containing species is 0.390°C. This corresponds to $\nu = 1.87$ for $(IO)_2SO_4$. If it is assumed that all of the iodine which is not in the form of monomeric ions is present as unionized dimers, this means that 87% of the iodine is in the form of ions.

This explanation is thus consistent with both the cryoscopic and conductimetric results.

Because of the apparent complexity of the system, and the various arbitrary assumptions that must be made in the interpretation of the experimental results, it is not possible to treat the system in a more quantitative manner than that outlined here.

Since the anions $I(HSO_4)_4^-$ and $I(HSO_4)_3\ HS_2O_7^-$ do not appear to undergo solvolysis to any great extent, it follows that the neutral species $HI(HSO_4)_4$ and $HI(HSO_4)_3\ HS_2O_7$ must be rather strong acids of the sulphuric acid solvent system. Unfortunately it appears that these acids cannot be obtained in solutions which do not contain a large excess of $H_2S_2O_7$.

It is not necessary to suppose that at the mole ratio $H_2S_2O_7/(IO)_2SO_4 = 1.0$, the only iodine-containing ions are IO^+ and $I(HSO_4)_4^-$. The reaction

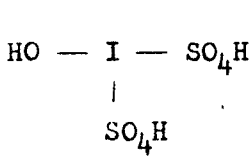
$$I(HSO_4)_4^- + H_2S_2O_7 \rightleftharpoons I(HSO_4)_3\ HS_2O_7^- + H_2SO_4$$

presumably begins to compete with the reaction to produce $I(HSO_4)_4^-$ as soon as any significant concentration of the latter is present in the solution.

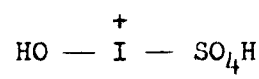
Thus at the mole ratio 1.0 there will still be some partly dissociated $IOHSO_4$ remaining in the solution, and the concentration of HSO_4^- will be greater than in 100% sulphuric acid. This is in qualitative agreement with the observation that the conductivity minimum comes at a mole ratio greater than 1.0.

Possible structures of the species formed

The behaviour of iodosyl sulphate in solutions in sulphuric acid and oleum is similar in many respects to that of arsenic (III) oxide. By analogy with the structures proposed by Gillespie and Robinson (88) for the arsenic-containing species, it is suggested that iodosyl hydrogen sulphate and the iodosyl cation are actually present in the solutions as the solvated forms (I) and (II) respectively



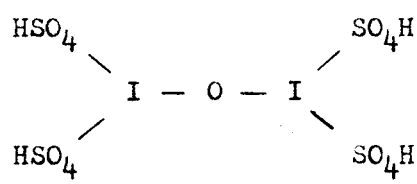
I



II

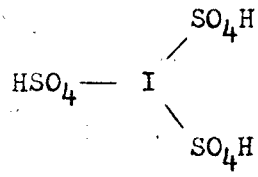
This is in agreement with the apparent reluctance of trivalent iodine to form double bonds with oxygen, shown by the existence of the iodosyl cation in a polymeric form in its solid salts (27).

The dimer $I_2O(HSO_4)_4$ (III) can then be formed by the elimination of water between a pair of the monomer units (I).

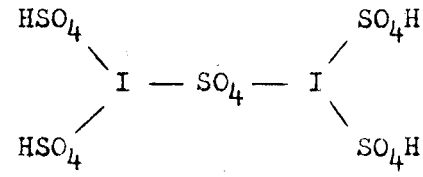


III

Similarly the proposed dimer $I_2SO_4(HSO_4)_4$ (V) could be formed by elimination of a sulphuric acid molecule between two molecules of the trihydrogen sulphate (IV)

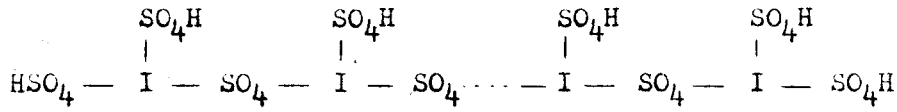


IV



V

Further polymerization of V would give a polymer with the repeating unit $HI(SO_4)_2$ (VI) corresponding to the white compound described by Masson and Argument (26).



VI

TABLE 16

Cryoscopic Titrations of

Iodosyl Sulphate with Disulphuric Acid

Experiment 72

Weight of H_2SO_4 83.86 g

Weight of $(IO)_2SO_4$ 1.2046 g

$H_2S_2O_7$ solution:

$\mathcal{K} = 2.873 \times 10^{-2}$ ohm^{-1} cm^{-1}

$w(H_2S_2O_7) = 0.581$ mole kg^{-1}

Weight of $H_2S_2O_7$ solution added (g)	Mole Ratio $H_2S_2O_7/(IO)_2SO_4$	F.p. (°C)
0.0000	0.000	9.806
3.1308	0.576	9.912
4.8572	0.895	9.944
7.3978	1.362	9.968
10.5953	1.949	9.953
13.6431	2.512	9.897
16.7406	3.086	9.821
20.9182	3.846	9.709
25.5049	4.694	9.591

Interpolated freezing points at integral mole ratios

$H_2S_2O_7/(IO)_2SO_4$	m^s $(IO)_2SO_4$	F.p. (°C)
0.0	0.0378	9.806
1.0	0.0357	9.951
2.0	0.0341	9.950

(Table 16 continued)

Experiment 125

Weight of H_2SO_4 75.23 g
Weight of $(IO)_2SO_4$ 1.6037 g

$H_2S_2O_7$ solution:

$w(H_2S_2O_7) = 3.085$ mole kg^{-1}

Weight of $H_2S_2O_7$ solution added (g)	Mole Ratio $H_2S_2O_7/(IO)_2SO_4$	F.p. (°C)
0.0000	0.000	9.535
0.3595	0.261	9.620
1.0764	0.791	9.724
1.5252	1.120	9.754
2.0514	1.507	9.757
2.7628	2.030	9.709
3.6550	2.685	9.575
4.1876	3.076	9.459

Interpolated freezing points at integral mole ratios

$H_2S_2O_7/(IO)_2SO_4$	m^s $(IO)_2SO_4$	F.p. (°C)
0.0	0.0561	9.535
1.0	0.0558	9.746
2.0	0.0553	9.712

TABLE 17 (a)

Conductimetric Titrations of the Mixed Solutes

HIO_3 + 0.333 I_2 with Disulphuric Acid

Experiment 60

Weight of H_2SO_4	221.61 g
Weight of HIO_3	0.8832 g
Weight of I_2	0.4258 g
Mole ratio I_2/HIO_3	0.334

$H_2S_2O_7$ solution:

$$\mathcal{K} = 3.005 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$w(H_2S_2O_7) = 0.673 \text{ mole kg}^{-1}$$

Weight of $H_2S_2O_7$ solution added (g)	Mole Ratio $H_2S_2O_7/"I_2O_3"$	$10^2 \mathcal{K}$ (ohm^{-1} cm^{-1})
0.0000	0.000	1.386
4.9803	0.801	1.249
9.9458	1.600	1.155
14.3648	2.310	1.112
16.9449	2.724	1.103
19.6152	3.156	1.103
22.5056	3.622	1.112
27.7808	4.470	1.143
33.4493	5.382	1.187

At conductivity minimum:

$$H_2S_2O_7/"I_2O_3" = 2.92$$

$$\mathcal{K} = 1.101 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$$

(Table 17 (a) continued)

Experiment 122

Weight of H_2SO_4	207.70 g
Weight of HIO_3	2.1183 g
Weight of I_2	1.0197 g
Mole ratio I_2/HIO_3	0.334

$H_2S_2O_7$ solution:

$w(H_2S_2O_7)$ = 3.622 mole kg^{-1}

Weight of $H_2S_2O_7$ solution added (g)	Mole Ratio $H_2S_2O_7/"I_2O_3"$	$10^2 \mathcal{K}$ (ohm^{-1} cm^{-1})
0.0000	0.000	2.055
0.1434	0.052	2.022
0.3787	0.137	1.971
0.5516	0.199	1.932
0.8207	0.296	1.878
1.1343	0.410	1.817
2.4531	0.886	1.580
3.2750	1.182	1.463
4.6556	1.682	1.308
6.0762	2.195	1.219
6.7323	2.431	1.201
7.8896	2.850	1.196
8.4932	3.067	1.206
9.5415	3.446	1.240
11.0624	3.995	1.311

At conductivity minimum:

$H_2S_2O_7/"I_2O_3"$ = 2.67

$\mathcal{K}$ = 1.192×10^{-2} ohm^{-1} cm^{-1}

TABLE 17 (b)

Conductimetric Titrations of Iodosyl Sulphate with Disulphuric Acid, and of "$HI(HSO_4)_4$" with Potassium Sulphate (25°C)

Experiment 78

Weight of H_2SO_4 185.19 g
Weight of $(IO)_2SO_4$ 2.3465 g

$H_2S_2O_7$ solution:

$\mathcal{K} = 2.873 \times 10^{-2}$ ohm^{-1} cm^{-1}
$w(H_2S_2O_7) = 0.581$ mole kg^{-1}

Weight of $H_2S_2O_7$ solution (g)	Mole Ratio $H_2S_2O_7/(IO)_2SO_4$	$10^2 \mathcal{K}$ (ohm^{-1} cm^{-1})
0.0000	0.000	1.254
0.9153	0.087	1.238
2.0560	0.195	1.220
2.8010	0.265	1.209
3.4318	0.325	1.201
4.1427	0.392	1.192
5.1290	0.485	1.182
5.9486	0.563	1.174
7.3182	0.693	1.164
8.8924	0.842	1.155
10.8196	1.024	1.147
12.7365	1.206	1.144
15.1029	1.429	1.146
16.5846	1.570	1.150
18.5265	1.754	1.156
20.9814	1.984	1.167

(Table 17 (b), Experiment 78 continued)

At conductivity minimum:

$$H_2S_2O_7/(IO)_2SO_4 = 1.22$$

$$\mathcal{K} = 1.144 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$$

Weight of K_2SO_4 (g)	Mole Ratio $K_2SO_4/(IO)_2SO_4$	$10^2\mathcal{K}$ (ohm^{-1} cm^{-1})
0.0655	0.0611	1.160
0.1802	0.1682	1.158
0.2243	0.2094	1.160
0.3026	0.2825	1.167
0.5089	0.4751	1.206

At conductivity minimum:

$$K_2SO_4/(IO)_2SO_4 = KHSO_4/\text{"}HI(HSO_4)_4\text{"} = 0.14$$

$$\mathcal{K} = 1.157 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$$

(Table 17 (b) continued)

Experiment 123

Weight of H_2SO_4 194.19 g
Weight of $(IO)_2SO_4$ 1.8647 g

$H_2S_2O_7$ solution:

$w(H_2S_2O_7) = 2.974$ mole kg^{-1}

Weight of $H_2S_2O_7$ solution (g)	Mole Ratio $H_2S_2O_7/(IO)_2SO_4$	$10^2 \mathcal{K}$ (ohm^{-1} cm^{-1})
0.0000	0.000	1.195
0.1696	0.103	1.182
0.5429	0.331	1.159
1.0061	0.613	1.139
1.2654	0.771	1.131$_5$
1.4751	0.898	1.127
1.7458	1.063	1.125
1.9780	1.205	1.125
2.2749	1.385	1.127
2.7507	1.675	1.137
3.2775	1.996	1.153

At conductivity minimum:

$H_2S_2O_7/(IO)_2SO_4 = 1.12$

$\mathcal{K} = 1.124 \times 10^{-2}$ ohm^{-1} cm^{-1}

Weight of K_2SO_4 (g)	Mole Ratio $K_2SO_4/(IO)_2SO_4$	$10^2 \mathcal{K}$ (ohm^{-1} cm^{-1})
0.0344	0.0404	1.148
0.0789	0.0927	1.143
0.1421	0.1670	1.141

(Table 17 (b) continued)

Weight of K_2SO_4 (g)	Mole Ratio $K_2SO_4/(IO)_2SO_4$	$10^2 \mathcal{K}$ (ohm^{-1} cm^{-1})
0.1975	0.2321	1.142
0.2747	0.3228	1.148
0.3394	0.3988	1.157

At conductivity minimum:

$$K_2SO_4/(IO)_2SO_4 = KHSO_4/"HI(HSO_4)_4" = 0.175$$

$$\mathcal{K} = 1.140 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$$

TABLE 18

Solutions of $(IO)_2SO_4 + 2H_2S_2O_7$ in Sulphuric Acid: Conductivities at 25°C

Experiment	$m^s\{HI(HSO_4)_4\}$	$10^2\kappa$ (ohm^{-1} cm^{-1})
60	0.0348	1.109
123	0.0498	1.153
78	0.0597	1.167
122	0.0953	1.258

TABLE 19

Values of K_a for "$HI(HSO_4)_4$", from the Conductivities of Solutions of $(IO)_2SO_4 + 2H_2S_2O_7$

$m^s\{HI(HSO_4)_4\}$	$[H_3SO_4^+]$	$[I(HSO_4)_4^-]$	K_a (mole kg^{-1})
0.04	0.0196	0.0132	0.0097
0.06	0.0220	0.0175	0.0091
0.08	0.0243	0.0210	0.0086

TABLE 20

Values of K_a for "$HI(HSO_4)_4$" from

Conductimetric Titrations with K_2SO_4

Experiment	$m^s\{HI(HSO_4)_4\}$	r_{min}	K_a(mole kg^{-1})
78	0.0597	0.14	0.0019
123	0.0498	0.175	0.0025

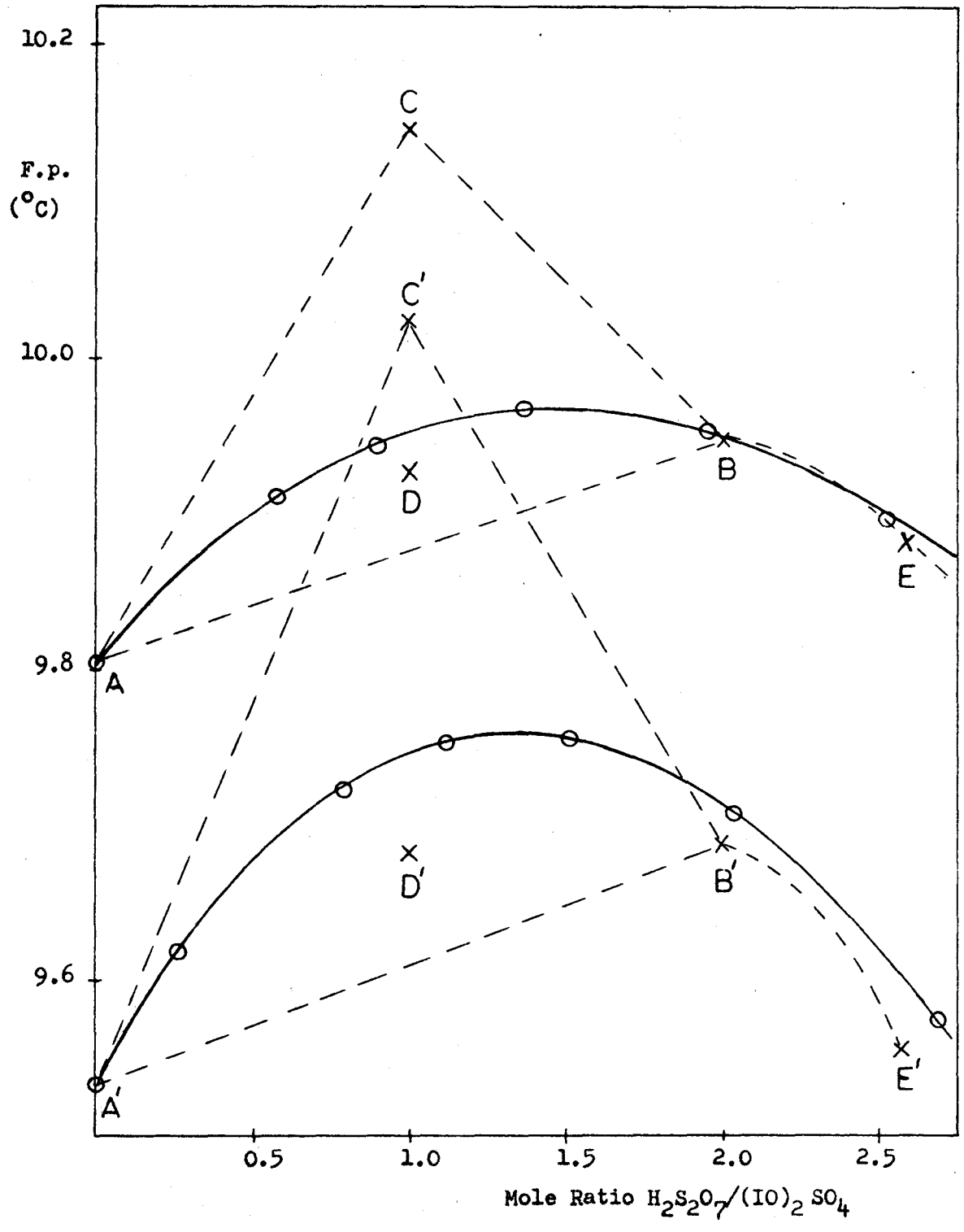


Figure 18. Cryoscopic Titrations of $(IO)_2SO_4$ with $H_2S_2O_7$

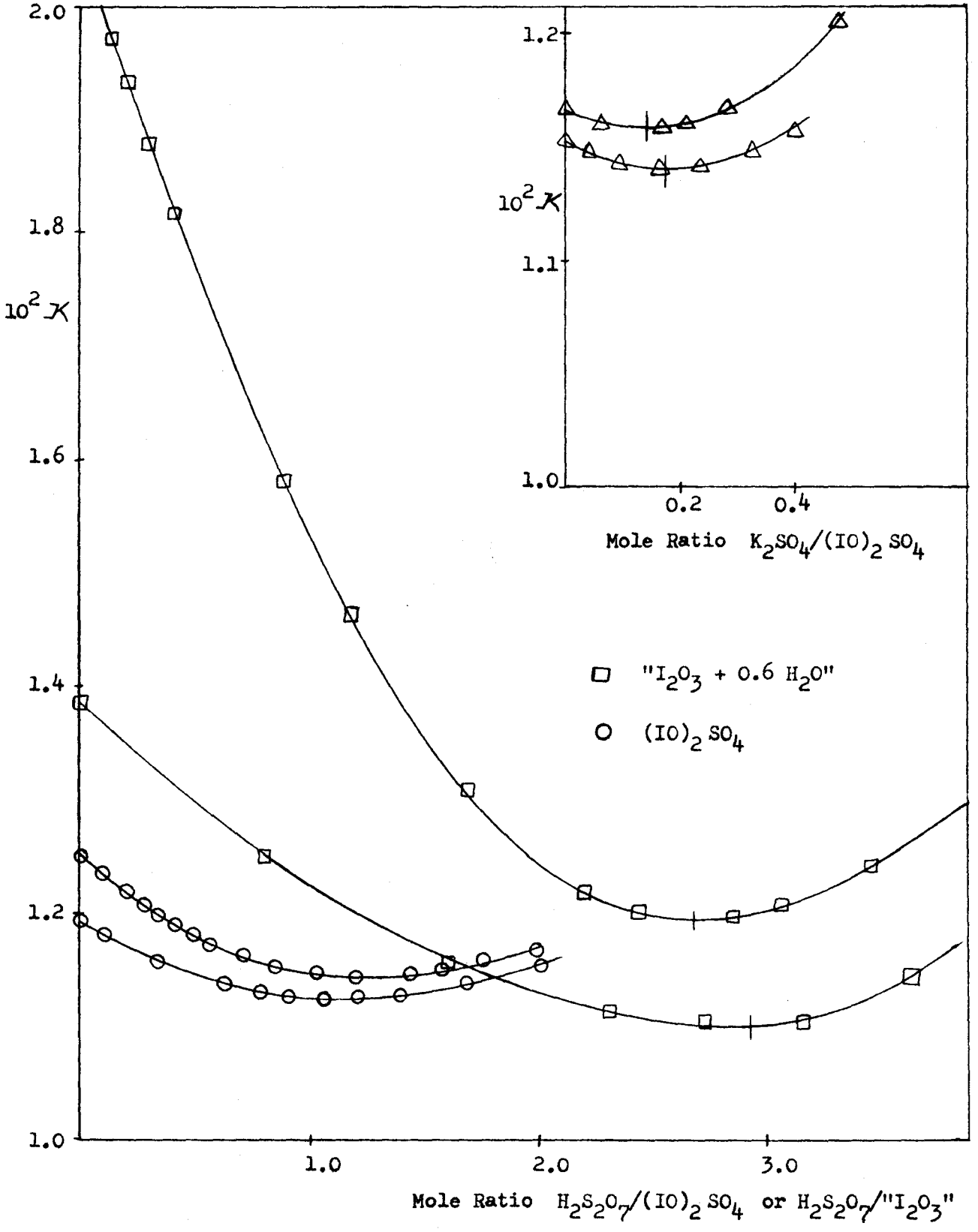


Figure 19. Conductimetric Titrations of $(IO)_2SO_4$ and of $"I_2O_3 + 0.6\ H_2O"$ with $H_2S_2O_7$. Inset: Titrations of $I(HSO_4)_4$ with $KHSO_4$

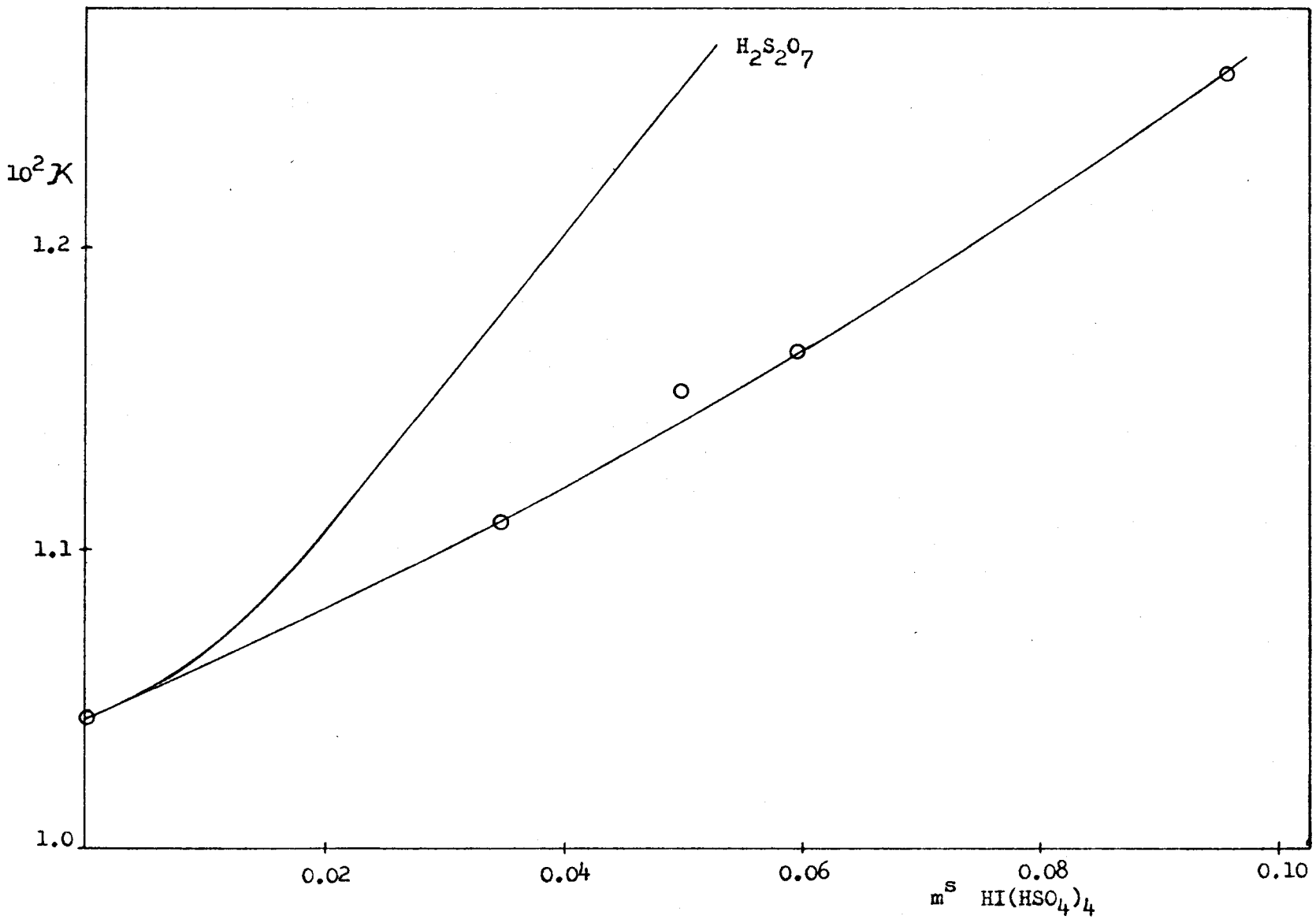


Figure 20. Solutions of $HI(HSO_4)_4$ in H_2SO_4: Conductivities at 25°

6. Solutions of Iodine Dioxide in Sulphuric Acid

Introduction

Iodine dioxide, $(IO_2)_n$ was first prepared by Millon (96) by the reaction of hot concentrated sulphuric acid on iodic acid, and decomposition of the intermediate product with cold water. Detailed instructions for the preparation by this method were given later by Muir (9) and Bahl and Partington (45).

Iodine dioxide is a pale yellow, non-hygroscopic solid which decomposes to iodine and iodine pentoxide when heated above 130°C. It in insoluble in most solvents, but reacts slowly with cold water, and some organic solvents,with the release of iodine. According to Muir, 100 ml of 99% sulphuric acid dissolve 1.54 g of the compound, and it is somewhat more soluble in sulphuric acid monohydrate, $H_2SO_4.H_2O$,in which there is partial decomposition to iodine and iodic acid.

The formula for iodine dioxide has usually been written as I_2O_4 and for a long time it has been considered to be iodosyl iodate, $IO^+ IO_3^-$, although there has been no direct evidence for this. Very recently Dasent and Waddington (27) have shown that its IR spectrum can be interpreted in terms of this formulation, although it must be assumed that the iodosyl cation exists in the form of polymeric chains, with I-O single bonds, rather than as discrete IO^+ cations.

Cryoscopy and conductimetry

A single conductivity run was carried out, in which the final concentration (ca. 0.03 m) was limited by the amount of material available, rather than by the solubility (Table 22,Figure 22).

A weighed portion of the final solution from the conductivity run was transferred to the cryoscope and used as the starting solution in a cryoscopic experiment, by the usual "dilution" method (Table 21, Figure 21).

Discussion

Values of ν, Υ and $\nu-\Upsilon$ are given in Table 23. Υ-values were estimated by comparison with the conductivity curve for water.

In view of its formulation as iodosyl iodate, and the results, discussed in preceding sections of this chapter, for solutions of iodic acid and iodosyl sulphate, the most probable ionization scheme may be written

$$2I_2O_4 + 6H_2SO_4 = (IO_2HSO_4)_2 + 2IOHSO_4 + 2H_3O^+ + 2HSO_4^- \qquad [1]$$

$$\nu = 4.5\text{-}3.5,\ \Upsilon = 2\text{-}1,\ \nu-\Upsilon = 2.5$$

The ranges of ν and Υ quoted take into account the partial ionization of $IOHSO_4$, and are based on the assumption that iodyl hydrogen sulphate is present as the unionized dimer. Experimentally ν lies between 4.8 and 4.0, Υ between 2.05 and 1.58, and $\nu-\Upsilon$ between 2.78 and 2.45, in quite good agreement with the predicted values. The rather high values at low concentrations may be due to the presence of an appreciable amount of monomeric iodyl hydrogen sulphate, and to partial ionization of this species.

The experimental results are not consistent with other possible ionization schemes, such as:

$$I_2O_4 + H_2SO_4 \rightleftharpoons HI_2O_4^+ + HSO_4^- \qquad [2]$$

$$\nu = 2,\ \Upsilon = 1,\ \nu-\Upsilon = 1$$

$$I_2O_4 + 2H_2SO_4 \qquad 2HIO_2^+ + 2HSO_4^- \qquad [3]$$

$$\nu = 4,\ \Upsilon = 2,\ \nu-\Upsilon = 2$$

$$I_2O_4 + 2H_2SO_4 = I_2O_3^+ + H_3O^+ + 2HSO_4^- \qquad [4]$$

$$\nu = 4,\ \Upsilon = 2,\ \nu-\Upsilon = 2$$

If I_2O_4 contained quadrivalent iodine, or existed as discrete molecules, some such scheme as [2], [3] or [4] might possibly be followed. Thus the present results lend some additional support to the formulation of I_2O_4 as iodosyl iodate.

TABLE 21

Solutions of Iodine Dioxide in

Sulphuric Acid: Freezing Points

Experiment 66

The initial solution in this experiment was 65.89 g of the final solution from Experiment 65 (Table 22).

Weight of I_2O_4 0.6323 g

Weight of H_2SO_4 (g)	m	F.p. ($^{\circ}C$)
65.26	0.03092	9.801
80.11	0.02514	9.908
114.37	0.01758	10.053
180.47	0.01111	10.174
285.62	0.00701	10.247

TABLE 22

Solutions of Iodine Dioxide in

Sulphuric Acid: Conductivities at $25^{\circ}C$

Experiment 65

Weight of H_2SO_4 187.23 g

Weight of I_2O_4 (g)	w	"M"	$10^2 \kappa$ (ohm^{-1} cm^{-1})
0.0813	0.00137	0.00251	1.047
0.2993	0.00506	0.00924	1.070
0.6517	0.01101	0.02011	1.132
0.9981	0.01686	0.03081	1.215
1.4033	0.02371	0.04331	1.324
1.8138	0.03064	0.05598	1.443

TABLE 23

Solutions of Iodine Dioxide in

Sulphuric Acid: Values of ν and Υ

m	ν	Υ	$\nu - \Upsilon$
0.010	4.83	2.05	2.78
0.015	4.52	1.82	2.70
0.020	4.30	1.70	2.60
0.025	4.15	1.63	2.52
0.030	4.03	1.58	2.45

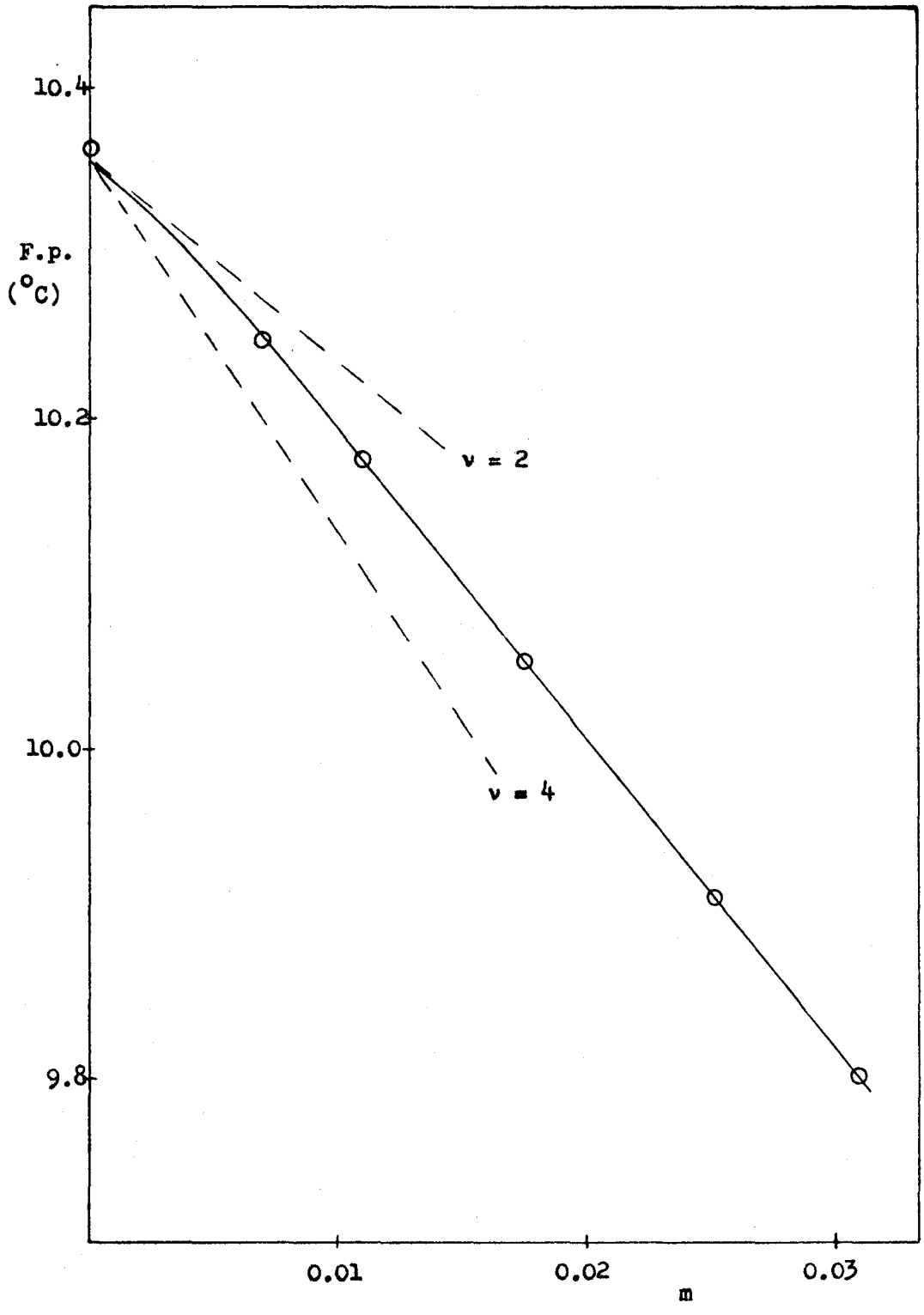


Figure 21. Solutions of I_2O_4 in H_2SO_4: Freezing Points

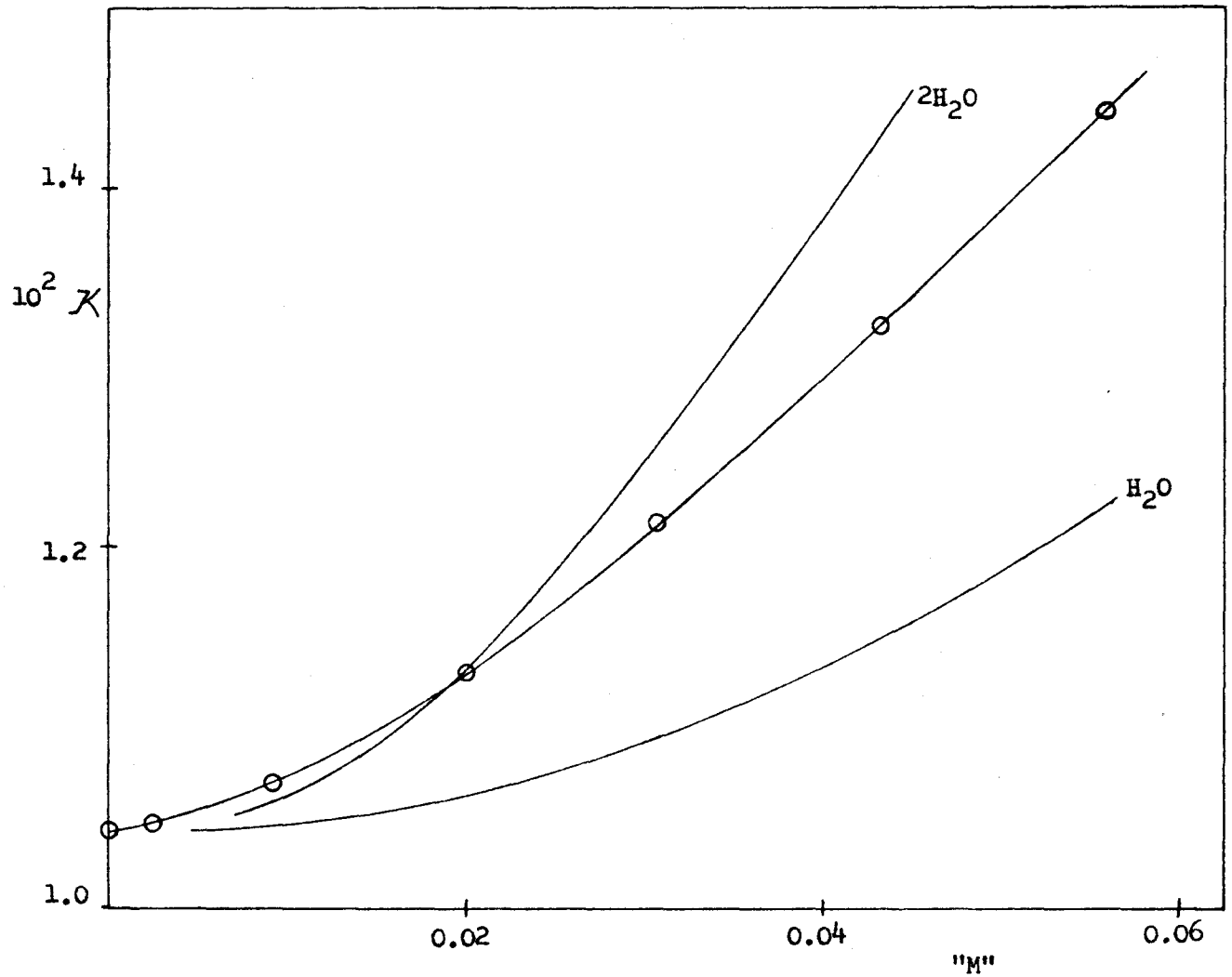


Figure 22. Solutions of I_2O_4: Conductivities at 25°C

7. Solutions of Iodic Acid and Iodine in Sulphuric Acid: Mole Ratios, I_2/HIO_3, greater than 0.33

Introduction

Birkenbach, Goubeau and Krall (41) obtained brown solutions by stirring iodine with a suspension of mercurous or mercuric sulphate in concentrated sulphuric acid. The solutions contained only traces of mercury salts, the mercury sulphates being converted to a white insoluble mercuric iodide-sulphate complex of uncertain composition. Similar solutions were obtained by the oxidation of iodine in sulphuric acid with iodate, periodate, permanganate or manganese dioxide. The solutions reacted violently with benzene, forming p-di-iodobenzene and molecular iodine. It was concluded that the solutions contained a complex between the iodine cation, I^+, and molecular iodine. The maximum amount of iodine which would go into solution corresponded to a complex $I^+.3/2\ I_2$.

Masson (15) showed that iodine dissolved in solutions of iodosyl sulphate in concentrated sulphuric acid, ($H_2SO_4.H_2O$ to H_2SO_4), forming brown solutions. The solutions reacted smoothly with chlorobenzene, to give a mixture of chlorotri-iodobenzenes and a precipitate of elementary iodine. The rapidity of this reaction, and the fact that the brown solute was stable only in strongly acid media, led to the conclusion that the iodine was present in a cationic form. From the stoichiometry of the reactions with chlorobenzene, of solutions containing different ratios of iodine to iodosyl sulphate, Masson deduced the existence in the solutions of the ions I^+, I_3^+ and I_5^+.

Solutions of the stoichiometry corresponding to the formation of I^+:

$$IO^+ + I_2 + 2H^+ = 3I^+ + H_2O$$

reacted with chlorobenzene giving traces of iodonium compounds, in addition to the iodo-compounds. Such solutions slowly deposited iodosyl sulphate on keeping. It was concluded that the equilibrium concentration of I^+ was probably small, and that the solutions contained mainly an equilibrium mixture of IO^+, I_3^+ and I_5^+.

The reactions of I_3^+ and I_5^+ with aromatic compounds were represented:

$$I_3^+ + ArH = H^+ + ArI + I_2$$

$$I_5^+ + ArH = H^+ + ArI + 2I_2$$

Masson attempted to demonstrate the cationic nature of the iodine-containing species by transport measurements using the moving boundary method, but the results were inconclusive.

An alternative possibility, that the brown solute was formed by the reaction of I^{+++} with iodine to form triply charged complex ions:

$$I^{+++} + nI_2 = I_1^{+++}{}_{+2n}$$

was rejected because it failed to explain the aromatic iodinations satisfactorily.

Symons (36) obtained brown solutions, supposed to contain I_3^+, by dissolving iodine in dilute oleums. These solutions have

absorption bands at 290 and 460 mμ. Arotsky, Mishra and Symons (37) claim to have obtained blue solutions, with the intense absorption band at 640 mμ thought to be characteristic of I^+, by oxidizing iodine with an equivalent amount of iodic acid in dilute oleums and in 100% sulphuric acid.

The mole ratio $I_2/HIO_3 = 2.0$

Interpolated freezing points are given in Table 24 and Figure 23 (curve A), and interpolated conductivities in Table 25 and Figure 24 (curve A). The Υ-values quoted (Table 26) are the means of pairs of values obtained by comparison with the conductivities of solutions of water and of potassium hydrogen sulphate. In correcting the values of ν (Table 26) for repression of solvent self-dissociation, $m^s(HSO_4^-)$ was estimated from the experimental Υ-values, and it was assumed that $m^s(H_3O^+) = 1.75\ m^s(HIO_3)$, as predicted by Equation [3] below. The following reaction schemes may be considered:

$$HIO_3 + 2I_2 + 8H_2SO_4 = 5I^+ + 3H_3O^+ + 8HSO_4^- \qquad [1]$$
$$\nu = 16,\ \Upsilon = 8,\ \nu-\Upsilon = 8$$

$$HIO_3 + 2I_2 + 8H_2SO_4 = 5IHSO_4 + 3H_3O^+ + 3HSO_4^- \qquad [2]$$
$$\nu = 11,\ \Upsilon = 3,\ \nu-\Upsilon = 8$$

$$4HIO_3 + 8I_2 + 17H_2SO_4 = 5I_3^+ + 7H_3O^+ + 5IOHSO_4 \qquad [3]$$
$$\nu = 8.5\text{-}7.25,\ \Upsilon = 4.25\text{-}3$$
$$\nu-\Upsilon = 4.25$$

If the compound $IHSO_4$ shown in Equation [2] were partly ionized:

$$IHSO_4 \rightleftharpoons I^+ + HSO_4^-$$

then depending on its degree of dissociation, ν and Υ could vary between the limits appropriate to the extreme cases represented by Equations [1] and [2], but $\nu-\Upsilon$ would always be equal to 8.0.

Experimentally ν lies between 8.5 and 7.7, Υ between 3.5 and 3.3, and $\nu-\Upsilon$ between 5.0 and 4.4, in poor agreement with Equations [1] and [2].

Equation [3] represents complete disproportionation of I^+ to IO^+ and I_3^+. Iodosyl hydrogen sulphate will of course be only partly dissociated, and depending on its extent of dissociation ν and Υ may lie within the ranges shown. The experimental values of ν and Υ fall within these ranges, while the values of $\nu-\Upsilon$ are in fairly good agreement with the predicted value of 4.25. Thus Equation [3] probably represents the predominant mode of ionization in these solutions. However the observed values of $\nu-\Upsilon$ are in fact somewhat larger than 4.25, indicating that reaction according to [1] or [2] probably occurs to some extent.

The disproportionation of I^+ can be written:

$$4I^+ + H_2O + 2HSO_4^- \rightleftharpoons IO^+ + I_3^+ + 2H_2SO_4$$

Since the forward reaction involves a decrease in the number of solute particles from 7 to 2, it is obvious that the equilibrium will be shifted in favour of an increasing amount of disproportionation as the concentration increases. In fact $\nu-\Upsilon$ approaches 4.25 more closely at the higher concentrations, in qualitative agreement with this prediction.

These results are in agreement with the conclusion of Masson (15) that the cation I^+ is largely disproportionated in sulphuric acid solutions. In the much more dilute solutions studied spectrophotometrically by Arotsky, Mishra and Symons (37), a greater proportion of I^+ could exist in equilibrium. As will be shown in a later chapter, solutions of this stoichiometry have strong absorption bands both at 640 mμ, due to I^+, and at 460 mμ, due to I_3^+.

The mole ratio $I_2/HIO_3 = 7.0$

Interpolated freezing points are shown in Table 27 and Figure 23 (curve B) and interpolated conductivities in Table 28 and Figure 24 (curve B). Values of Υ were obtained by comparison with the conductivities of solutions of potassium hydrogen sulphate. Corrections to ν for the repression of solvent self-dissociation were calculated assuming $m^s(HSO_4^-) = 8\ m^s(HIO_3)$, and $m^s(H_3O^+) = 3\ m^s(HIO_3)$ as required by Equation [4], (Table 29).

The reaction to give I_3^+ would take place according to:

$$HIO_3 + 7I_2 + 8H_2SO_4 = 5I_3^+ + 3H_3O^+ + 8HSO_4^- \qquad [4]$$

$$\nu = 16,\ \Upsilon = 8,\ \nu - \Upsilon = 8$$

Experimentally, $\Upsilon = 8.1$ and $\nu = 15$, in good agreement with the predicted values. The slightly low value of ν may be partly accounted for by incomplete ionization of the water produced (97). Both ν and Υ would also be decreased if the reaction

$$I_3^+ + I_2 = I_5^+$$

became important before formation of I_3^+ was complete.

The Υ-values are slightly larger than expected, particularly

if the formation of I_5^+ is important. This may be partly accounted for by the large size and small extent of solvation of the ion I_3^+, resulting both in a higher ionic mobility for I_3^+ than for the more solvated K^+, and in less interference with proton-transfer conduction by HSO_4^-, (73) and partly by the neglect of the differences in density between the solutions and the pure solvent involved in the use of "pseudo" molar concentration units.

The alternative hypothesis, considered and rejected by Masson, (15) that triply charged complex ions are formed, may be represented by the equation:

$$3HIO_3 + 21I_2 + 24H_2SO_4 = 5I_5^{+++} + 9H_3O^+ + 24HSO_4^- \quad [5]$$
$$\nu = 12.7, \ \Upsilon = 8$$

This ionization scheme is not consistent with the freezing-point results, since the observed values of ν are considerably higher than that predicted by Equation [5].

Mole ratios, I_2/HIO_3, greater than 7.0

In experiments in which iodine was added in excess of the mole ratio $I_2/HIO_3 = 7.0$, it was observed that although iodine continued to dissolve, the curves of both conductivity and freezing point versus the mole ratio, began to level off just below the mole ratio 7.0, and that above this ratio there was very little further increase in either the conductivity or the freezing-point depression (Figures 12 and 13).

The added iodine must thus take part in a reaction in which there is no increase in the number of solute particles, and no increase in the concentration of hydrogen sulphate ions. This reaction can only be

$$I_3^+ + I_2 = I_5^+$$

as suggested by Masson (15). Formation of I_5^+ by this reaction appears to become important before the mole ratio 7.0 is reached. This accounts for the levelling off of the freezing-point and conductivity curves below this ratio, and, in part at least, for the low value of ν at the mole ratio 7.0.

TABLE 24

Solutions of Iodic Acid and Iodine in Sulphuric Acid: Interpolated Freezing Points at the Mole Ratio I_2/HIO_3 = 2.0

$m^s(HIO_3)$	F.p. (°C)
0.010	10.010
0.015	9.800
0.020	9.590
0.025	9.380
0.030	9.170
0.035	8.965

TABLE 25

Solutions of Iodic Acid and Iodine in Sulphuric Acid: Interpolated Conductivities at the Mole Ratio I_2/HIO_3 = 2.0 (25°C)

Experiment	"M^s" (HIO_3)	$10^2\kappa$ (ohm^{-1} cm^{-1})
51	0.00778	1.102
45	0.01772	1.279
58	0.02134	1.376
55	0.02841	1.540
49	0.03325	1.656
54	0.04810	2.080
62	0.06073	2.321
103	0.01872	1.302

TABLE 26

Solutions of Iodic Acid and Iodine in Sulphuric Acid: Values of ν and Υ at the Mole Ratio I_2/HIO_3 = 2.0

$m^s(HIO_3)$	ν	Υ	$\nu - \Upsilon$
0.010	8.5	3.52	5.0
0.015	8.3	3.51	4.8
0.020	8.1	3.43	4.7
0.025	7.9	3.39	4.5
0.030	7.8	3.35	4.4
0.035	7.7	3.33	4.4

TABLE 27

Solutions of Iodic Acid and Iodine in Sulphuric Acid: Interpolated Freezing Points at the Mole Ratio I_2/HIO_3 = 7.0

$m^s(HIO_3)$	F.p. (°C)
0.010	9.605
0.015	9.175
0.020	8.750
0.025	8.325
0.030	7.895
0.035	7.465

TABLE 28

Solutions of Iodic Acid and Iodine in Sulphuric Acid: Interpolated Conductivities at the Mole Ratio I_2/HIO_3 = 7.0

Experiment	"m^s" (HIO_3)	$10^2 \kappa$ (ohm^{-1} cm^{-1})
51	0.00774	1.264
45	0.01750	1.852
58	0.02103	2.100
55	0.02786	2.508
49	0.03250	2.788
62	0.05826	4.083

TABLE 29

Solutions of Iodic Acid and Iodine in Sulphuric Acid: Values of ν and Υ at the Mole Ratio I_2/HIO_3 = 7.0

$m^s(HIO_3)$	ν	Υ	$\nu - \Upsilon$
0.010	16.0	7.60	8.4
0.015	15.5	8.10	7.4
0.020	15.2	8.13	7.1
0.025	15.0	8.15	6.9
0.030	14.9	8.16	6.7
0.035	14.8	8.10	6.7

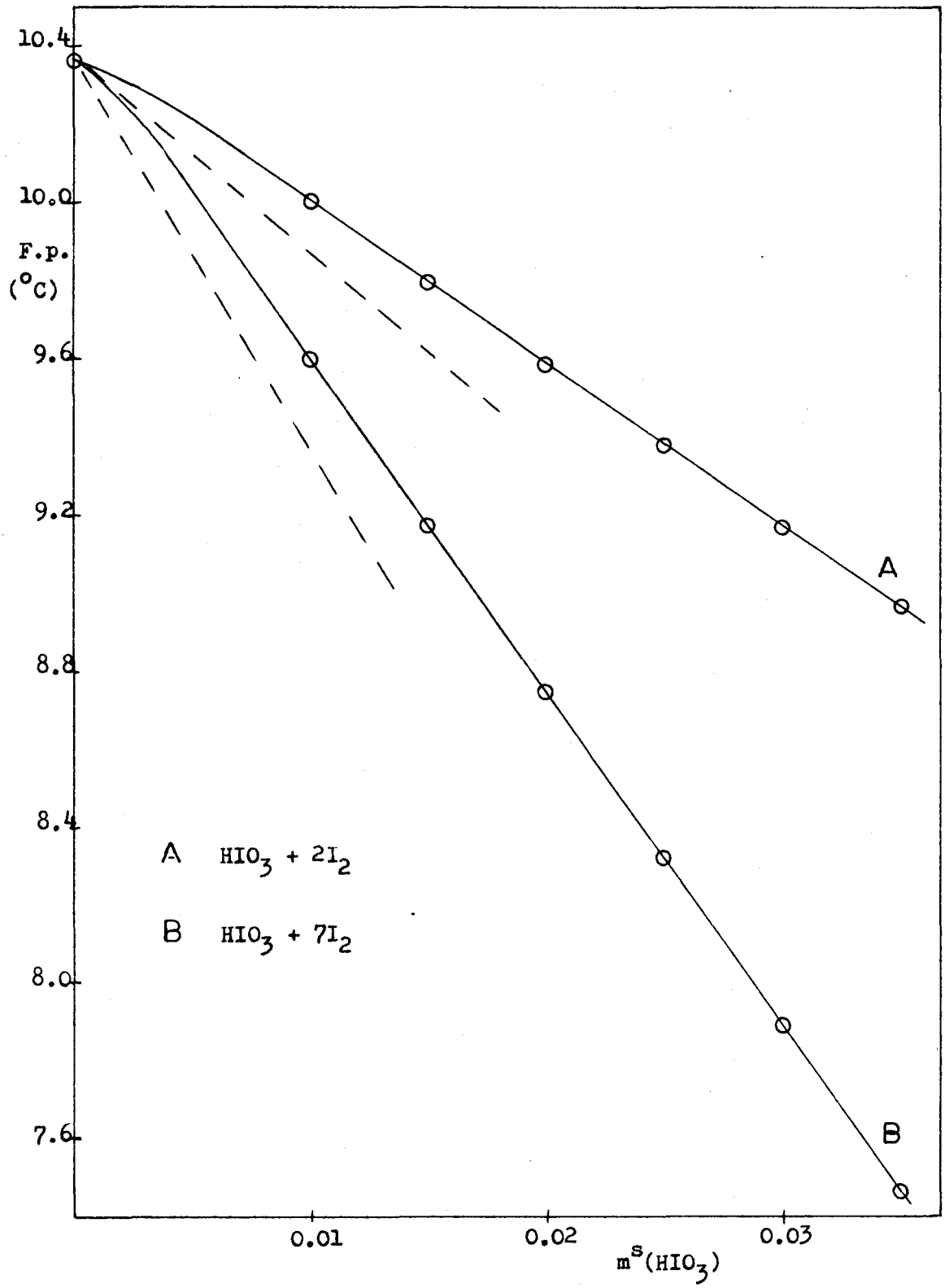


Figure 23. Solutions of "$HIO_3 + 2I_2$" and "$HIO_3 + 7I_2$" in H_2SO_4: Interpolated Freezing Points

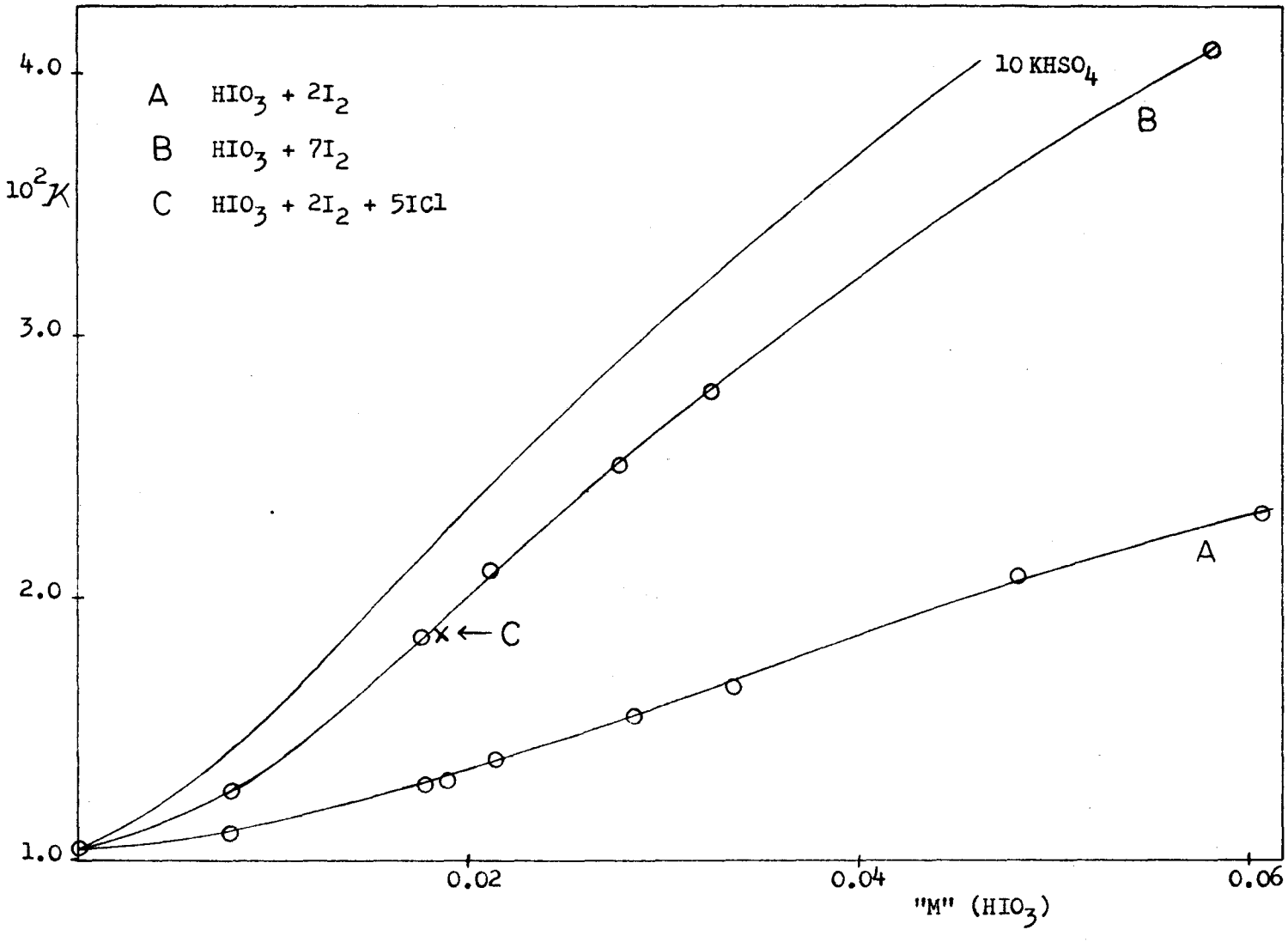


Figure 24. Solutions of "$HIO_3 + 2I_2$" and "$HIO_3 + 7I_2$" in H_2SO_4: Interpolated Conductivities

8. Solutions of Iodine Monochloride in Sulphuric Acid, and the Reaction of Iodine Monochloride with Solutions containing Iodic Acid and Iodine in the Mole Ratio $I_2/HIO_3 = 2.0$

Solutions of iodine monochloride

The specific conductivities of two solutions of iodine monochloride in sulphuric acid are recorded in Table 30(a). The solutions had an appreciable vapour pressure of iodine monochloride, so that the concentrations reported may be a little too high.

The very small increase in conductivity produced by iodine monochloride shows that it is an extremely weak electrolyte in sulphuric acid. It is not possible to reach any conclusion concerning the nature of the ionization involved. Iodine monochloride may simply be partially protonated:

$$ICl + H_2SO_4 \rightleftharpoons HICl^+ + HSO_4^-$$

It may react to form HCl and I^+:

$$ICl + H_2SO_4 \rightleftharpoons I^+ + HCl + HSO_4^-$$

In the latter case the iodine cation would almost certainly react with excess iodine monochloride to form the ion I_2Cl^+, whose existence is discussed below. The observed conductivity is so small that it could even be due to traces of impurities in the iodine monochloride.

The reaction of iodine monochloride with "$HIO_3 + 2I_2$"

The results of a conductivity run, in which successive additions of iodine monochloride were made to a solution containing iodic acid and iodine in the mole ratio $I_2/HIO_3 = 2.0$, are shown in Table 30(b) and in Figure 25 which is a plot of specific conductivity versus the mole ratio

ICl/HIO_3.

The iodine monochloride dissolved readily in the iodic acid-iodine solution, and produced an increase in the conductivity much greater than that produced by iodine monochloride alone. At mole ratios less than $ICl/HIO_3 = 5.0$, the solutions did not smell of iodine monochloride. At the mole ratio $ICl/HIO_3 = 5.0$, corresponding to the solute composition $HIO_3 + 2I_2 + 5ICl$, the conductivity was only a little lower than that of a solution of "$HIO_3 + 7I_2$" at the same stoichiometric concentration of iodic acid (Point C in Figure 24). The value of Υ, for HIO_3 as solute, was 7.64. This is in reasonably good agreement with the value $\Upsilon = 8.0$ predicted for the reaction:

$$HIO_3 + 2I_2 + 5ICl + 8H_2SO_4 = 5I_2Cl^+ + 3H_3O^+ + 8HSO_4^-$$

analogous to that occurring in solutions of "$HIO_3 + 7I_2$". The result is equally consistent with the existence of an equilibrium:

$$2I_2Cl^+ \rightleftharpoons I_3^+ + ICl_2^+$$

which would not alter the conductivity appreciably.

The electrical conductivity of pure iodine monochloride has been attributed (113) to the self-dissociation:

$$2ICl \rightleftharpoons I^+ + ICl_2^-$$

The ion I^+ is almost certainly a solvated species, and may well be I_2Cl^+ or $I^+.ICl$, so that the self-dissociation reaction could be written:

$$3ICl \rightleftharpoons I_2Cl^+ + ICl_2^-$$

TABLE 30(a)

Solutions of Iodine Monochloride in

Sulphuric Acid: Conductivities at 25°C

Experiment 69

Weight of ICl (g)	"M"	$10^2 K$ (ohm^{-1} cm^{-1})
0.9062	0.0515	1.053
1.3593	0.0773	1.065

TABLE 30 (b)

Addition of Iodine Monochloride to a Solution of

"$HIO_3 + 2I_2$" in Sulphuric Acid: Conductivities at 25°C

Experiment 103

Weight of H_2SO_4 249.87 g

Weight of HIO_3 (g)	Weight of I_2 (g)	Weight of ICl (g)	Mole Ratio ICl/HIO_3	$10^2 K$ (ohm^{-1} cm^{-1})
0.4537	0.0000	0.0000		1.076
0.4537	1.3101	0.0000	0.000	1.302
0.4537	1.3101	0.3673	0.877	1.388
0.4537	1.3101	1.1303	2.699	1.601
0.4537	1.3101	1.7091	4.081	1.771
0.4537	1.3101	2.1415	5.113	1.883

At the mole ratio ICl/HIO_3 = 5.0 :

"M^S" (HIO_3) = 0.01856

$K = 1.872 \times 10^{-2}$ ohm^{-1} cm^{-1}

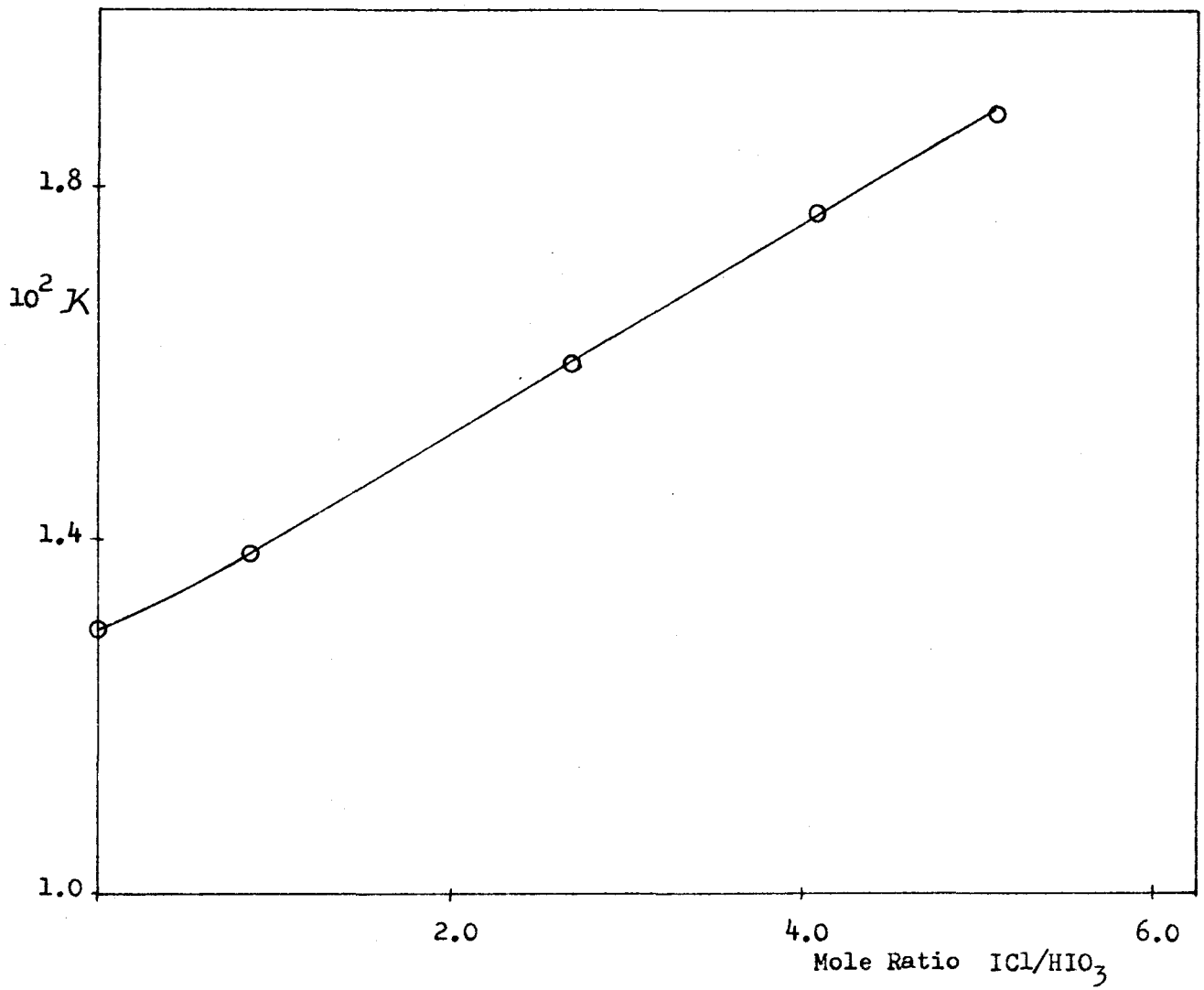


Figure 25. Solutions of "HIO_3 + $2I_2$" + ICl in H_2SO_4: Conductivities at 25°C

9. Solutions of Dipyridineiodine (I) Salts in Sulphuric Acid

Introduction

It was hoped that when the compounds Ipy_2NO_3 and Ipy_2ClO_4 were dissolved in sulphuric acid they would decompose in such a way as to release the free iodine cation, and that disproportionation of the latter would be slow enough to permit its presence to be detected.

Dipyridineiodine (I) nitrate

The results of a conductivity run are shown in Table 31 and Figure 26. The solutions were pale yellow, showing that an iodosyl compound is formed, presumably through oxidation of I^+ by the nitronium ion, NO_2^+, with reduction of the latter to NO^+:

$$Ipy_2NO_3 + 5H_2SO_4 = \underset{\gamma = 5-4}{2pyH^+ + NO^+ + H_3O^+ + IOHSO_4 + 4HSO_4^-}$$

Taking K_b for $IOHSO_4$ as 0.025 mole kg^{-1}, it can be shown that γ should decrease from approximately 4.5 at 0.01 "M" to 4.2 at 0.04 "M". In fact γ is almost constant, with values close to 4.4, in this concentration range, in fair agreement with prediction (Table 32).

If I^+ were produced quantitatively, the reaction would be

$$Ipy_2NO_3 + 5H_2SO_4 = \underset{\gamma = 5}{2pyH^+ + NO_2^+ + H_3O^+ + I^+ + 5HSO_4^-}$$

in less satisfactory agreement with experiment.

Dipyridineiodine (I) perchlorate

The results of a conductivity run are shown in Table 33 and Figure 26. The solutions were deep green, showing that in these solutions I^+ is disproportionated to about the same extent as in solutions of

comparable concentrations, since these are also green. For complete disproportionation to I_3^+ and trivalent iodine, which, since no water is produced, would be in the form of $I(HSO_4)_3$ rather than $IOHSO_4$, we have the equation:

$$4Ipy_2ClO_4 + 12H_2SO_4 = 8pyH^+ + 4HClO_4 + I_3^+ + I(HSO_4)_3 + 9HSO_4^-$$

For the reaction as written, $\gamma = 2.25$, but since either $I(HSO_4)_3$, or $H_2S_2O_7$ in equilibrium with it, would behave as an acid, removing some of the HSO_4^-, the value of γ would be reduced to a value between 2.25 and 2.0. The experimental γ value is 2.1, which is within the predicted range.

For the formation of I^+, we have:

$$Ipy_2ClO_4 + 3H_2SO_4 = 2pyH^+ + HClO_4 + I^+ + 3HSO_4^-$$
$$\gamma = 3$$

This is in poor agreement with the experimental results, showing that extensive disproportionation of I^+ occurs.

In the course of several weeks the solution became completely colourless, and smelled strongly of chlorine, showing that the perchloric acid had been reduced. The species oxidized may have been either "I^+" or pyridine. If "I^+" was not oxidized, it must have reacted in some other way, possibly with the pyridine to form an iodo-compound, accounting for the disappearance of the green colour. No attempt was made to investigate this reaction further.

TABLE 31

Solutions of Dipyridineiodine (I) Nitrate in Sulphuric Acid: Conductivities at 25°C

Experiment 70

Weight of H_2SO_4 218.11 g

Weight of Solute (g)	"M"	$10^2\kappa$ (ohm^{-1} cm^{-1})
0.1424	0.00343	1.060
0.5398	0.01300	1.239
1.2677	0.03043	1.805
1.8125	0.04341	2.245

TABLE 32

Solutions of Dipyridineiodine (I) Nitrate in Sulphuric Acid: Values of γ

"M"	γ
0.01	4.4
0.02	4.3
0.03	4.4
0.04	4.4

TABLE 33

Solutions of Dipyridineiodine (I) Perchlorate in Sulphuric Acid: Conductivities at 25°C

Experiment 80

Weight of H_2SO_4 186.88 g

Weight of Solute (g)	"M"	$10^2\kappa$ (ohm^{-1} cm^{-1})
0.1132	0.00288	1.047
0.3411	0.00866	1.070
0.6833	0.01731	1.136
1.0975	0.02774	1.254
1.5207	0.03835	1.403

TABLE 34

Solutions of Dipyridineiodine (I) Perchlorate in Sulphuric Acid: Values of Y

"M"	Y
0.01	2.10
0.02	2.10
0.03	2.05
0.04	2.10

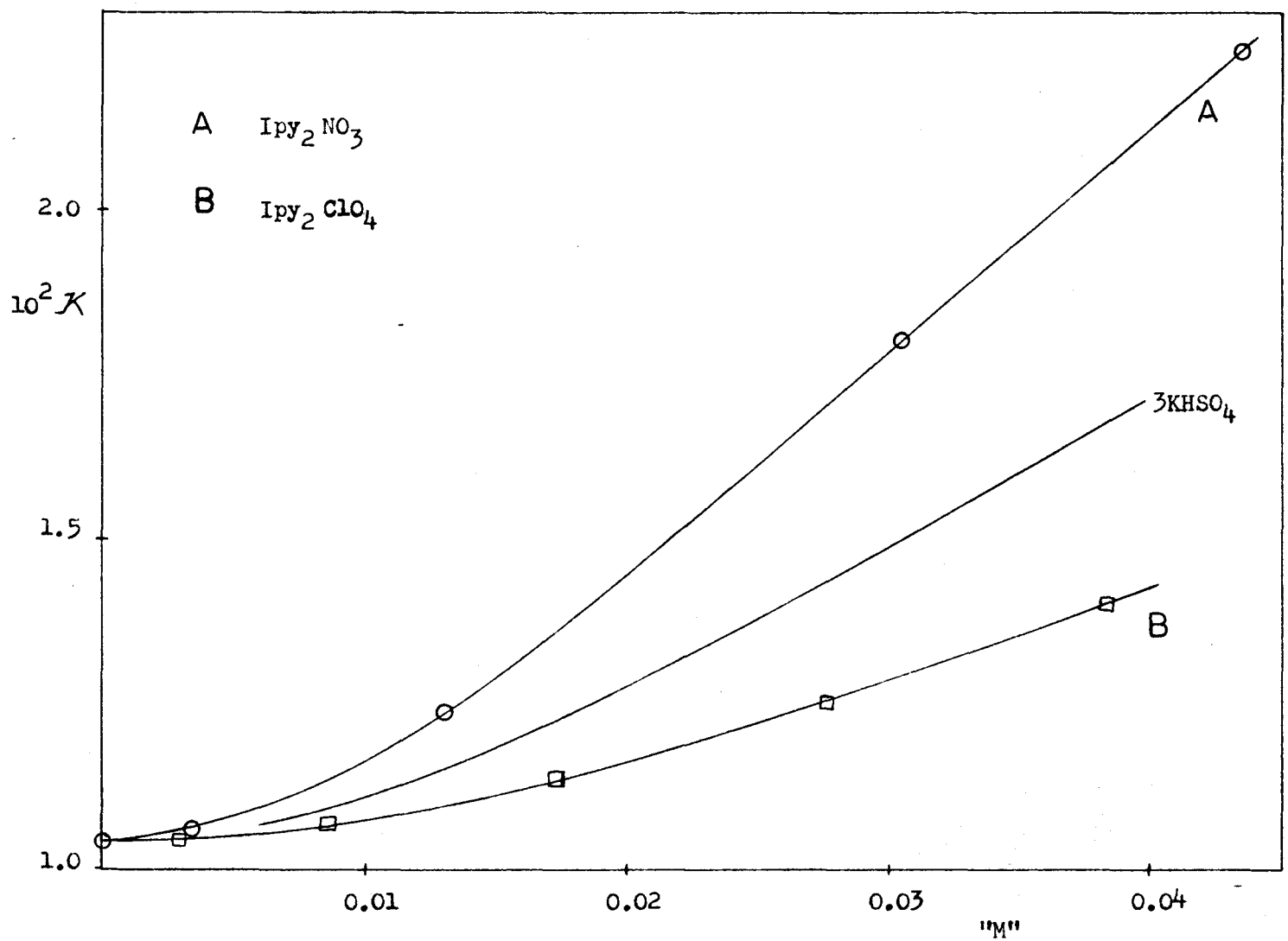


Figure 26. Solutions of Dipyridineiodine (I) Salts in H_2SO_4: Conductivities at 25°C

CHAPTER IV

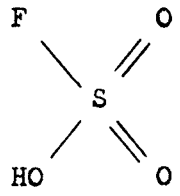
SOLUTIONS IN FLUOROSULPHURIC ACID

1. Fluorosulphuric Acid as a Solvent

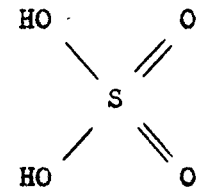
Introduction

Fluorosulphuric acid, HSO_3F, is a stronger acid than sulphuric acid. This is shown by the fact that it behaves as a weak acid of the sulphuric acid solvent system (89), while sulphuric acid behaves as a weak base in fluorosulphuric acid (98). Measurements of the Hammett acidity function H_o confirm this conclusion (98).

The fundamental vibrational frequencies determined from the Raman spectrum have been satisfactorily explained on the basis of the tetrahedral structure (I) analogous to that of sulphuric acid (II).



I



II

The high boiling point of fluorosulphuric acid indicates extensive association, presumably by intermolecular hydrogen-bonding. The shift of the Raman line assigned to the OH wagging vibration of HSO_3F, in solutions of HSO_3F in AsF_3, suggests the breaking down in these solutions of the hydrogen-bonded structure existing in the pure acid

(99). Since there is only one proton per molecule, the opportunity for forming extended hydrogen-bonded structures will be less than in sulphuric acid and this is reflected in the much lower viscosity, freezing point and boiling point of fluorosulphuric acid as compared with those of sulphuric acid. Some physical properties of fluorosulphuric acid are given in Table 35.

The first studies of fluorosulphuric acid as a solvent were made by Woolf (101) who studied the conductivities of solutions of various fluorides. More fundamental and accurate studies of the fluorosulphuric acid solvent system have been made by Barr (98) and by Thompson and Gillespie (100), the latter work being done concurrently with that described in this thesis.

Self-dissociation reactions

The conductivity of the pure solvent is probably due mainly to the products of the autoprotolysis reaction:

$$2HSO_3F \rightleftharpoons H_2SO_3F^+ + SO_3F^- \qquad [1]$$

Autoprotolysis is much less extensive than in sulphuric acid, and Barr (98) has estimated the value of K_{ap} to be 1×10^{-7} mole^2 kg^{-2}.

Acids of the fluorosulphuric acid solvent system may be defined as substances which ionize in fluorosulphuric acid to give the fluorosulphuric acidium ion, $H_2SO_3F^+$, and bases as substances which ionize to give the fluorosulphate ion, SO_3F^-.

Evidence has been obtained in the course of the present work for the presence of free sulphur trioxide in "pure" fluorosulphuric acid. Detailed studies by Thompson, (100) of the freezing points of solutions of water, sulphur trioxide, and potassium fluoride, indicate

TABLE 35

Some Physical Constants of

Fluorosulphuric Acid

Property	Value	Temperature	Reference
Freezing point	$-89.00^{\circ}C$		100
Boiling point	$163^{\circ}C$		98
Density d_4^{25}	1.7264	$25^{\circ}C$	98
Viscosity	1.56 centipoise	$25^{\circ}C$	98
Specific conductivity	1.085×10^{-4} ohm^{-1} cm^{-1}	$25^{\circ}C$	98
Cryoscopic constant	3.35 ± 0.05		100

that the sulphur trioxide is present not as an impurity, but as a product of the self-dissociation reaction:

$$HSO_3F \rightleftharpoons HF + SO_3 \qquad [2]$$

There is no evidence for the existence of a third self- dissociation reaction discussed by Woolf, (101) namely:

$$HSO_3F \rightleftharpoons HSO_3^+ + F^- \qquad [3]$$

Electrical conductivities

Barr (98) measured the conductivities of solutions of a number of fully ionized bases in fluorosulphuric acid. These included alkali metal fluorosulphates, benzoic acid and acetic acid. He found that they all had very similar molecular conductivities, indicating that in each case most of the current was carried by the common ion, SO_3F^-. This was confirmed in the case of potassium fluorosulphate by the direct determination of the transport number of K^+, which was found to be 0.11 ± 0.02.

Thompson (100) measured the conductivity of solutions of barium sulphate, which is also a fully ionized base, producing two fluorosulphate ions, and found that its molecular conductivity, at the same concentration of fluorosulphate ions, was about twice that of an alkali metal fluorosulphate. He also found the transport number of Ba^{++} to be 0.075 ± 0.020.

The $H_2SO_3F^+$ and SO_3F^- ions are considered to conduct by a proton-transfer mechanism similar to that discussed earlier for the autoprotolysis ions of sulphuric acid. This accounts for their abnormally high mobilities.

Thus by comparing the conductivities of solutions of any base B with those of a fully ionized base, in the same way as described for sulphuric acid solutions (Chapter III), values of Υ, in this case the number of moles of fluorosulphate ions produced by one mole of B, may be determined. Barr (98) determined the degrees of ionization of a number of weak bases, mostly organic nitro-compounds, by this method, and hence calculated their K_b- values. Solutions of the fully ionized base, potassium fluorosulphate, have been used for comparison purposes in the estimation of all Υ-values reported in this chapter.

Cryoscopy

Thompson (100) developed a technique for measuring freezing points of solutions in fluorosulphuric acid, and determined the freezing-point depressions produced by the non-electrolyte, trinitrobenzene, the 1 : 1 electrolytes, benzoic acid and some alkali metal fluorosulphates, and the 1 : 2 electrolyte, barium fluorosulphate. Plots of the freezing-point depression, θ, versus the molal concentration were initially linear, but showed positive deviations from linearity due to non-ideality at rather low concentrations. The freezing-point depression curves of the 1 : 1 electrolytes all had the same initial slope, which was twice the initial slope of the curve for trinitrobenzene, while the initial slope of the curve for barium fluorosulphate was three times that for trinitrobenzene. The cryoscopic constant was determined from the initial slopes of the freezing-point depression curves to be 3.35 ± 0.05. The heat of fusion of fluorosulphuric acid has not been measured, so that the cryoscopic constant cannot be calculated thermodynamically.

Because of the non-ideality of the solutions at the higher concentrations, only the initial slope is of much value in the determination of ν, the number of moles of solute particles produced by one mole of a solute. Thus we can only get information concerning the mode of ionization of a solute at low concentrations.

Examples of the freezing-point depression curves obtained by Thompson for various solutes are shown in Figure 27.

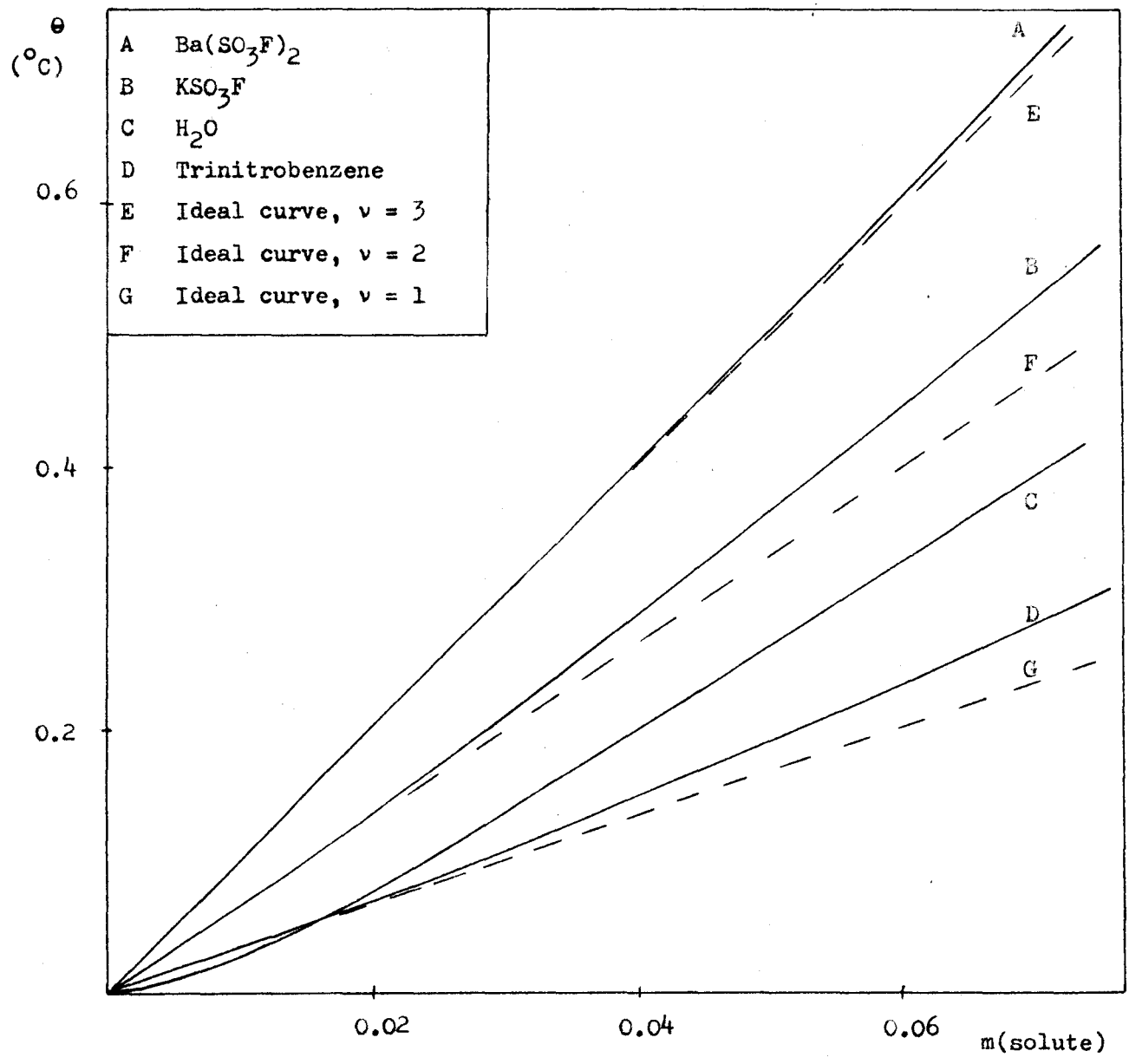


Figure 27. Freezing-point Depression Curves for Some Typical Solutes in HSO_3F. (From the work of Thompson)

2. Solutions of Water in Fluorosulphuric Acid

Introduction

Many of the solutes studied in the present work were expected to produce water in their reactions with fluorosulphuric acid. It was therefore necessary to study the behaviour of water itself as a solute, and in particular to find out whether it gave stable solutions with reproducible conductivities, before attempting to study more complicated solutes.

The equilibrium:

$$HF + H_2SO_4 \rightleftharpoons HSO_3F + H_2O$$

was studied by Traube and Reubke (109) and by Lange (110). These workers used much higher concentrations of water than were used in the present studies, and reported that the Law of Mass Action was not obeyed.

Thompson (100) has measured the freezing points of solutions of water in fluorosulphuric acid. As will be shown, the behaviour of water in fluorosulphuric acid can best be represented by the equilibrium

$$H_3O^+ + SO_3F^- \rightleftharpoons H_2SO_4 + HF$$

Whatever the position of this equilibrium, one mole of water should give rise to two moles of solute particles, so that the freezing-point depression curve should have the same initial slope as that of a 1 : 1 electrolyte. However, it was found that the initial slope was much less than this, although at higher concentrations the curve ran roughly parallel to those of 1 : 1 electrolytes (Figure 27). This was interpreted in terms of the reaction of a small amount of water with

sulphur trioxide resulting from the self-dissociation of the solvent:

$$HSO_3F \rightleftharpoons HF + SO_3$$

Similar behaviour has been observed in the present work in the case of solutes which are considered to produce water in their reactions with fluorosulphuric acid.

Gillespie and Robinson (99) showed that the Raman spectra of solutions of water in fluorosulphuric acid contained several lines characteristic of the fluorosulphate ion, and a line at 910 cm^{-1} characteristic of sulphuric acid. This is consistent with the mode of ionization proposed in the present work.

Conductimetry

Three conductivity runs were made at 25°C. In one of these experiments the conductivities were also measured at 0°C (Table 36, Figures 28 and 29). For comparison, the conductivities of solutions of potassium fluorosulphate at 0°C and 25°C were also measured (Table 37). The conductivities at 25°C were in excellent agreement with the values obtained by Barr (98).

The solutions of water in fluorosulphuric acid appeared to be quite stable, and their conductivities changed very little with time. In the most dilute solutions some drifting of the conductivity was observed, but this was very slight, a change of 1% in the conductivity over a period of four hours being the largest observed. No signs of attack by the solutions on the glass apparatus were apparent.

Discussion

Values of Υ at 25°C are given in Table 38. They are very nearly constant over most of the concentration range studied. Since fluorosulphuric acid is partly hydrolysed in aqueous solution (102), the most likely reaction in the present case is partial or complete hydrolysis of the solvent to hydrogen fluoride and sulphuric acid. Any water which did not react with the solvent in this way would presumably be fully protonated, so we may write the equilibrium:

$$H_3O^+ + SO_3F^- \rightleftharpoons HF + H_2SO_4 \qquad [1]$$

Sulphuric acid has been shown to behave as a very weak base ($K_b = 1 \times 10^{-4}$) in fluorosulphuric acid (98)

$$H_2SO_4 + HSO_3F \rightleftharpoons H_3SO_4^+ + SO_3F^- \qquad [2]$$

while conductivity measurements on solutions of potassium fluoride (100) indicate that hydrogen fluoride is also a rather weak base:

$$HF + HSO_3F \rightleftharpoons H_2F^+ + SO_3F^- \qquad [3]$$

We can probably neglect the ionization of HF and H_2SO_4 without much error. The equilibrium constant for reaction [1] is then given by:

$$K = \frac{[HF][H_2SO_4]}{[H_3O^+][SO_3F^-]} = \frac{(1 - \Upsilon)^2}{\Upsilon^2}$$

Thus Υ should be independent of concentration, in agreement with experiment. The values of K at 25°C (Table 38) vary from 0.31 to 0.16 over the concentration range 0.06 m to 0.18 m, which, considering the great sensitivity of K to very small changes in Υ, is quite satisfactory constancy.

On the other hand, the experimental results do not fit the equilibrium:

$$H_2O + HSO_3F \rightleftharpoons H_3O^+ + SO_3F^- \qquad 4$$

for which the equilibrium constant would be:

$$K' = \frac{[H_3O^+][SO_3F^-]}{[H_2O]} = \frac{\gamma^2 \, m^s(H_2O)}{1 - \gamma}$$

(see Table 38).

The addition of sulphuric acid would be expected to shift equilibrium [1] to the left, and so to increase the conductivity. In two experiments in which 100% H_2SO_4 was added to a solution of water in HSO_3F this was found to be the case, the increase in conductivity being far greater than could possibly have resulted from the simple ionization of H_2SO_4 as a base (Table 36). Now we have

$$[H_3O^+] = \gamma \, m^s(H_2O)$$

$$[SO_3F^-] = \gamma \, m^s(H_2O)$$

$$[HF] = (1 - \gamma) \, m^s(H_2O)$$

$$[H_2SO_4] = (1 - \gamma) \, m^s(H_2O) + m^s(H_2SO_4)$$

so that

$$K = \frac{(1 - \gamma)\left\{(1 - \gamma) \, m^s(H_2O) + m^s(H_2SO_4)\right\}}{\gamma^2 \, m^s(H_2O)}$$

where the γ-values still refer to the solute H_2O. The values of K lie within the same range as those calculated from the conductivity

of water alone (Table 39).

The specific conductivities of solutions of KSO_3F were decreased by a factor of 1.32 on going from 25°C to 0°C (Table 37), while those of solutions of water were decreased only by a factor of about 1.17 (Experiment 113, Table 36). The change in the mobility of the fluorosulphate ion with temperature must be the same in both cases, and any difference in the effect of temperature on the mobilities of the ions K^+ and H_3O^+ would be too small to account for the observed difference in behaviour. The most probable explanation is that as the temperature is lowered, the equilibrium [1] is shifted to the left, that is, in favour of a greater concentration of the ions H_3O^+ and SO_3F^-. Values of Y and K at 0°C are given in Table 40.

F^{19} NMR spectra of solutions of water and potassium fluoride

The F^{19} NMR spectra of solutions of water and of potassium fluoride in fluorosulphuric acid were examined at room temperature and at temperatures down to - 83°C (Figure 30). The spectra observed in the two cases were very similar. At 20°C a single rather broad peak was observed, at about 12,500 c/s to high field of the solvent resonance. As the temperature was lowered this peak broadened still further, until at - 50° it had merged with the base-line. At - 83°C the spectrum consisted of two fairly sharp peaks, the larger at about + 12,500 c/s from the solvent peak, the smaller at + 11,600 c/s.

The larger of the two peaks in the spectrum of the potassium fluoride solutions is almost certainly due to HF, while the smaller peak is probably due to a small amount of silicon tetrafluoride produced by attack of HF on the glass. The chemical shift between the

two peaks is 900 c/s, or 16 ppm, while the chemical shift between the F^{19} resonances in the pure liquids, HF and SiF_4, is reported to be 26 ppm. (103). The difference could easily be accounted for by medium effects on going from the pure liquids to fluorosulphuric acid solution. The two peaks in the spectrum of solutions of water at - 83°C must therefore also be due to HF and SiF_4, showing that HF is present in these solutions, in agreement with Equation [1]. The solutions examined were much more concentrated than those studied in the conductimetric experiments, which is probably why some attack on the glass occurred. The collapse of the two peaks, and their re-appearance as a single broad peak as the temperature is raised shows that fluorine exchange occurs between HF and SiF_4 in these solutions.

Evidence for the presence of free sulphur trioxide in fluorosulphuric acid

The three conductimetric experiments on water at 25°C gave parallel conductivity curves, slightly displaced horizontally with respect to each other. All the curves have an initial portion of much smaller slope than the rest of the curve. This suggests that the water added initially does not contribute to the conductivity, but takes part in some other reaction. It is postulated that it reacts with a small concentration of free sulphur trioxide present in the solvent, to form sulphuric acid. The conductimetric experiments do not give any evidence to show whether this is present as an impurity, or in an equilibrium:

$$HSO_3F \rightleftharpoons HF + SO_3 \qquad [5]$$

However, some qualitative observations on the reaction of iodine with fluorosulphuric acid shed some light on this point. Iodine is slightly soluble in fluorosulphuric acid, giving reddish solutions similar in appearance to those in benzene or toluene. These solutions rapidly become brown, owing to oxidation of the iodine to I_3^+ and I_5^+. The addition of potassium fluoride, but not that of potassium fluorosulphate, slows down this oxidation considerably, but a rather large amount of KF must be added before the rate becomes negligibly small. This suggests that the oxidizing agent is free SO_3, removed by combination with the HF produced in the reaction of KF with the solvent:

$$KF + HSO_3F = K^+ + SO_3F^- + HF$$

The fact that a considerable amount of KF has to be added to stop the oxidation altogether suggests the existence of an equilibrium such as [5].

The cryoscopic results obtained by Thompson (100) for solutions of water, sulphur trioxide and potassium fluoride are also more consistent with the existence of the equilibrium [5] rather than with the presence of SO_3 as an impurity.

The slightly different conductivity curves obtained in different experiments with water suggest that the concentration of SO_3 in the "pure" solvent varies slightly from one sample to another. Some fractionation of SO_3 and HF probably occurs in the distillation of the solvent. The lower boiling fraction, which is rejected, may contain an excess of the more volatile HF, while the portion collected contains an excess of SO_3. The amount of fractionation would not neces-

sarily be constant from one experiment to another, which would explain the slightly different conductivity curves obtained for water in different experiments.

We may attempt, in estimating Y-values, to allow for the water used up in reaction with SO_3, by subtracting from the concentration of water in any solution, the concentration (about 0.009 m) at which the flat portion of the conductivity curve ends. When this is done, the values of Y obtained are much more constant, and K = 0.12 at 25°C (Table 41). However, in calculating theoretical Y-values for solutes which react to produce water, the value K = 0.2 (Table 38) has been used, since this makes some allowance for the reaction of H_2O with SO_3 which must occur in these cases also. In practice, the values of Y are not much different whichever of the two values of K is used.

Calculation of theoretical Y-values for solutes which produce water

Consider a solute S, which ionizes

$$S \xrightarrow{HSO_3F} aX^+ + b\,H_3O^+ + (a+b)\,SO_3F^-$$

where aX^+ represents the total number of moles of all cations other than H_3O^+ produced by one mole of S. The ions H_3O^+ and SO_3F^- will be in equilibrium with H_2SO_4 and HF, according to Equation [1]. Suppose that out of b moles of H_3O^+, x moles react to produce H_2SO_4 and HF. Then we may write

$$K = \frac{[H_2SO_4]\,[HF]}{[H_3O^+]\,[SO_3F^-]} = \frac{x^2}{(b-x)(a+b-x)}$$

This is a quadratic equation in x, with one real, positive root. Having solved this equation, we have:

$$Y = a + b - x$$

In calculating the values of Y expected for various reactions, in the remainder of this work, the value of K has been taken to be 0.2. Whenever, in the discussion of ionization schemes in fluorosulphuric acid, the ions H_3O^+ and SO_3F^- are written as products of the same reaction, the existence of the equilibrium [1] is always implied.

TABLE 36

Solutions of Water, and of Water and Sulphuric Acid in Fluorosulphuric Acid: Conductivities

Experiment 100 — 25°C

Weight of HSO_3F 77.01 g

Weight of H_2O (g)	$m^s(H_2O)$	$10^4\kappa$ (ohm^{-1} cm^{-1})
0.0000	0.0000	1.17
0.0711	0.0512	74.81
0.1135	0.0818	124.4
0.1615	0.1164	176.9
0.2562	0.1846	274.2
Weight of H_2SO_4 (g)	$m^s(H_2SO_4)$	
0.1232	0.0163	282.5
0.3575	0.0473	294.0
0.6131	0.0812	302.8
1.1911	0.1577	313.3

Experiment 101 — 25°C

Weight of HSO_3F 75.96 g

Weight of H_2O (g)	$m^s(H_2O)$	$10^4\kappa$ (ohm^{-1} cm^{-1})
0.0000	0.0000	1.26
0.0122	0.0089	5.83
0.0478	0.0349	54.55
0.0629	0.0460	73.84
0.1022	0.0747	121.1
0.1395	0.1019	164.1
0.2143	0.1565	241.4

(Table 36 continued)

Weight of H_2SO_4 (g)	$m^s(H_2SO_4)$	$10^4\kappa$ (ohm^{-1} cm^{-1})
0.1612	0.0216	249.9
0.4179	0.0561	259.0
0.7468	0.1002	266.0
1.5168	0.2035	273.5
2.3004	0.3087	275.5

Experiment 113 — 25° and 0°C

Weight of HSO_3F 113.77 g

Weight of H_2O (g)	$m^s(H_2O)$	$10^4\kappa$ (ohm^{-1} cm^{-1})		$\frac{\kappa(25)}{\kappa(0)}$
		25°C	0°C	
0.0000	0.0000	1.38	0.78	1.77
0.1098	0.0536	84.16	73.41	1.146
0.2780	0.1356	207.8	178.9	1.162
0.3560	0.1737	260.2	222.8	1.168
0.4216	0.2057	303.3	258.5	1.173

TABLE 37

Solutions of Potassium Fluorosulphate in Fluorosulphuric Acid: Conductivities

Experiment 112 — 25° and 0°C

Weight of acid 107.45 g

Weight of KSO_3F (g)	m	$10^4\mathcal{K}$ (ohm^{-1} cm^{-1})		$\frac{\mathcal{K}(25)}{\mathcal{K}(0)}$
		25°C	0°C	
0.0000	0.0000	2.00	1.20	1.66
0.0678	0.0046	12.43	9.19	1.353
0.3364	0.0227	56.51	42.75	1.322
0.5081	0.0342	83.29	63.09	1.320
1.1042	0.0744	170.3	128.8	1.322
2.2617	0.1523	316.8	239.7	1.322

TABLE 38

Solutions of Water in

Fluorosulphuric Acid: Values of γ, K and K' at 25°C

$m^s(H_2O)$	γ	$K = \frac{(1-\gamma)^2}{\gamma^2}$	$K' = \frac{\gamma^2 m^s}{1-\gamma}$
0.06	0.64	0.31	0.07
0.08	0.68	0.23	0.11
0.10	0.69	0.21	0.15
0.12	0.69	0.21	0.18
0.14	0.70	0.20	0.22
0.16	0.70	0.18	0.26
0.18	0.71	0.16	0.32
	Mean	0.21	

TABLE 39

Solutions of Water and Sulphuric Acid in

Fluorosulphuric Acid: Values of γ and K at 25°C

Experiment 100

$m^s(H_2O) = 0.1846$

$m^s(H_2SO_4)$	γ	K
0.00	0.70	0.18
0.04	0.76	0.20
0.08	0.79	0.22
0.12	0.81	0.24
0.16	0.82	0.27
	Mean	0.22

(Table 39 continued)

Experiment 101

$m^s(H_2O) = 0.1565$

$m^s(H_2SO_4)$	γ		K
0.00	0.71		0.17
0.04	0.75		0.22
0.08	0.79		0.25
0.12	0.81		0.29
		Mean	0.23

TABLE 40

Solutions of Water in Fluoro-

sulphuric Acid: Values of γ and K at 0^oC

$m^s(H_2O)$	γ		$K = \frac{(1-\gamma)^2}{\gamma^2}$
0.05	0.74		0.123
0.10	0.78		0.080
0.15	0.80		0.063
0.20	0.81		0.055
		Mean	0.081

TABLE 41

Solutions of Water in

Fluorosulphuric Acid: Values of Υ and K at 25°C,

"Corrected" for Reaction with Sulphur Trioxide

$m^S(H_2O)$	Υ	$K = \frac{(1-\Upsilon)^2}{\Upsilon^2}$
0.06	0.74	0.13
0.08	0.76	0.10
0.10	0.75	0.12
0.12	0.74	0.12
0.14	0.74	0.12
0.16	0.74	0.12
0.18	0.75	0.11
	Mean	0.12

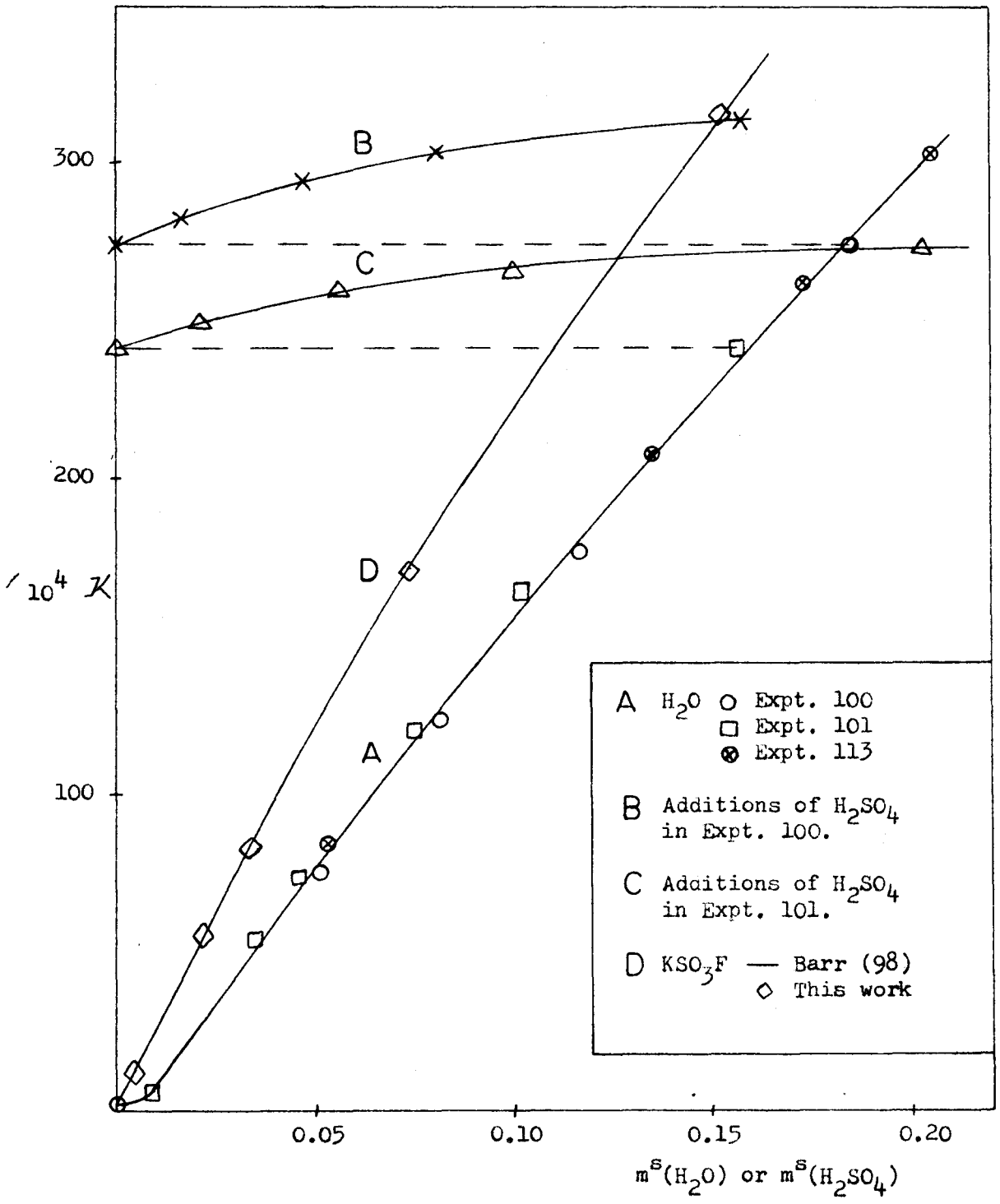


Figure 28. Solutions of H_2O and of H_2O and H_2SO_4 in HSO_3F: Conductivities at 25°C

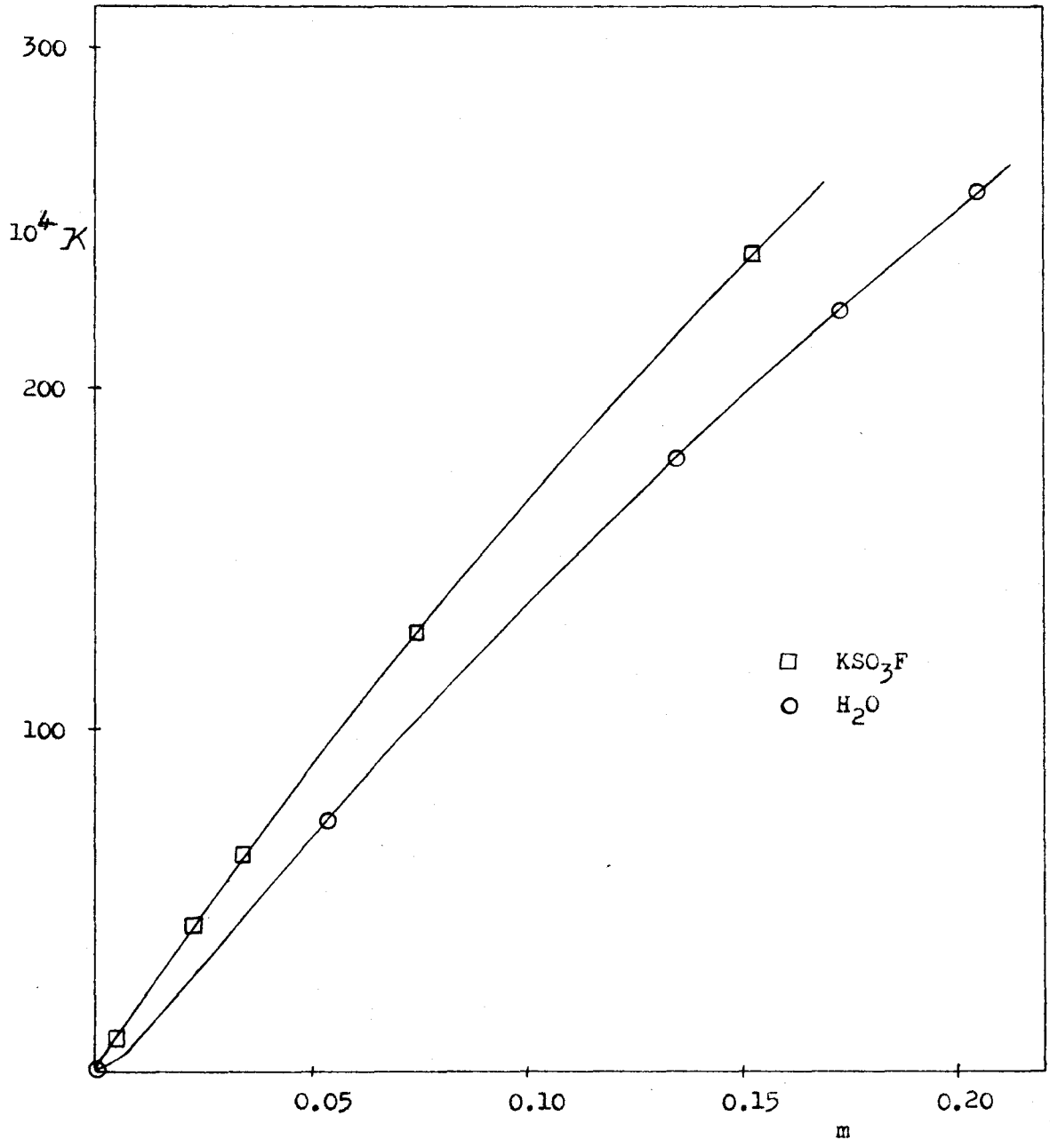


Figure 29. Solutions of H_2O and of KSO_3F in HSO_3F: Conductivities at 0°C

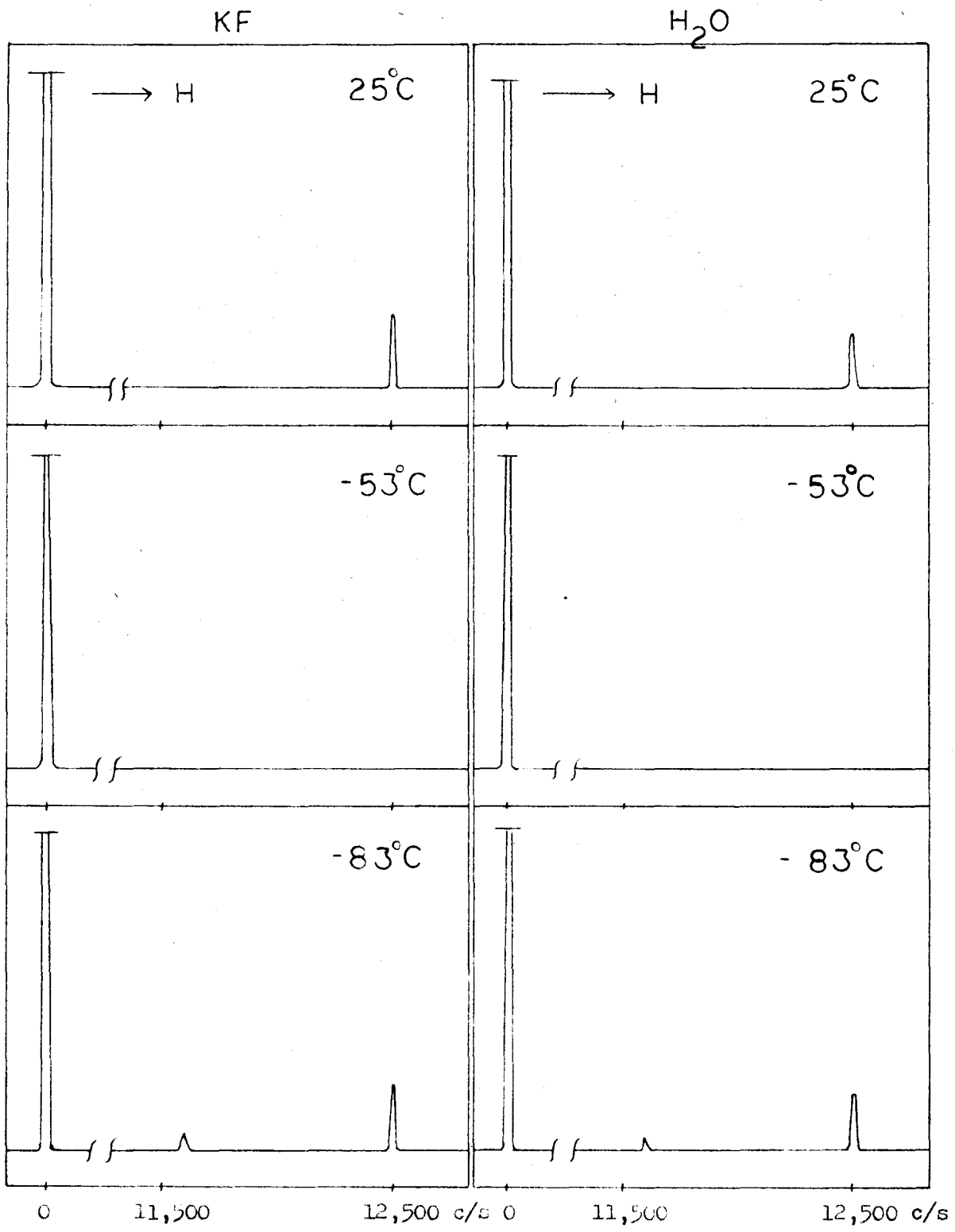


Figure 30. Solutions of KF and of H_2O in HSO_3F: F^{19} NMR Spectra (at 56.4 Mc/s)

3. Solutions of Potassium Nitrate in Fluorosulphuric Acid

Potassium nitrate ionizes in sulphuric acid to give the nitronium ion, NO_2^+ (87).

$$KNO_3 + 3H_2SO_4 = K^+ + NO_2^+ + H_3O^+ + 3HSO_4^-$$

The Raman spectrum of a solution of KNO_3 in fluorosulphuric acid has been examined, and contains, in addition to lines which can be assigned either to fluorosulphuric acid or to the fluorosulphate ion, a well-defined line at 1400 cm^{-1} (104) characteristic of the nitronium ion (Table 42 (a)). Thus potassium nitrate ionizes in fluorosulphuric acid in the same way as it does in sulphuric acid:

$$KNO_3 + 3HSO_3F = K^+ + NO_2^+ + H_3O^+ + 3SO_3F^-$$

$$\Upsilon = 2.50$$

The results of a conductivity run on potassium nitrate in fluorosulphuric acid are given in Table 42 (b) and Figure 31. The experimental Υ-values are in good agreement with the value 2.50 predicted allowing for the reaction of H_3O^+ and SO_3F^-. Thus the method of calculating Υ-values discussed in the preceeding section works well in this simple case, and may be used with some confidence in considering the behaviour of more complicated solutes.

TABLE 42(a)

Potassium Nitrate in Fluorosulphuric Acid: Raman Spectrum (Frequencies in cm^{-1})

KNO_3 in HSO_3F	HSO_3F (99)	SO_3F^- (99)	H_2SO_4 (99)	NO_2^+ (104)
400	391 405	408	392	
428 ?			422	
555	555 560	562	563	
592		608		
811		808		
839	850			
893 907 ?			910	
			976	
1090		1083		
1183	1178		1137 1195	
1230 1244	1230	1235		
			1368	
1408				1400
1434	1445			

TABLE 42(b)

Solutions of Potassium Nitrate in

Fluorosulphuric Acid: Conductivities at 25°C

Experiment 79

Weight of HSO_3F 80.22 g

Weight of KNO_3 (g)	m	$10^4 \kappa$ (ohm^{-1} cm^{-1})
0.0000	0.00000	1.74
0.1702	0.02098	123.5
0.3032	0.03738	211.4
0.4337	0.05348	289.5

Solutions of Potassium Nitrate in

Fluorosulphuric Acid: Values of Y

m	Y
0.02	2.48
0.03	2.53
0.04	2.56
0.05	2.58

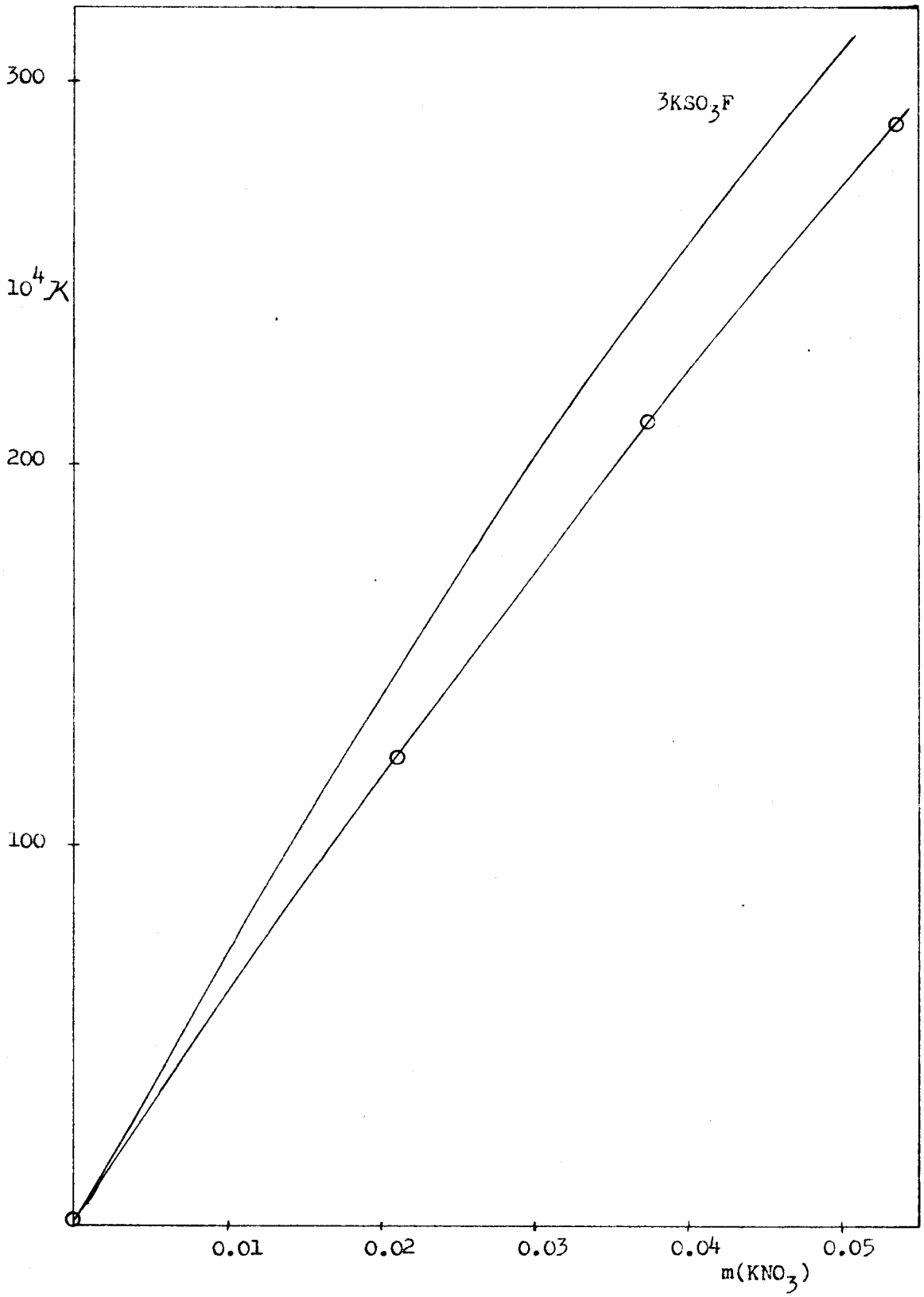


Figure 31. Solutions of KNO_3 in HSO_3F: Conductivities at 25°C

4. Solutions of Iodic Acid in Fluorosulphuric Acid

Cryoscopy

The results of two cryoscopic runs are shown in Table 43 and Figure 32. The initial slope of the freezing-point depression curve corresponds to the value $\nu = 3$.

Conductimetry

Conductimetric results are shown in Table 44 and Figure 33. The solvent used in one run (Experiment 90) had a rather high conductivity, and the values of $\mathcal{K}$ plotted in Figure 33 were obtained by subtracting a small constant correction from the experimental specific conductivities to allow for this. The results then agree very well with those of the other experiments. The conductivities of solutions of iodic acid were small compared with those of solutions of potassium fluorosulphate and water. Values of Υ are given in Table 45.

Raman spectrum

The Raman spectrum of a saturated solution of iodic acid in fluorosulphuric acid was examined. It contained, in addition to lines due to the solvent, two rather weak lines attributable to the fluorosulphate ion, two attributable to sulphuric acid, and one line, at 649 cm^{-1}, which is presumably due to an iodine - containing species (Table 46).

F^{19} NMR spectra

The F^{19} NMR spectra of solutions of iodic acid in fluorosulphuric acid were recorded at room temperature and at - 80°C.

(Figure 34). The spectra contained a small peak B, in addition to the peak A due to the solvent. At room temperature peak B was at about 780 c/s to high field of A, and was about 20 c/s wide. As the solution was cooled, B shifted to higher field relative to A, and became sharper. At - 80°C. the chemical shift of B relative to A was + 915 c/s, and the line width was about 10 c/s. From the oscilloscope trace, it appeared that the shift and narrowing of B were virtually complete at - 55°C. Thus the fluorine atoms responsible for peak B are exchanging slowly with the fluorine of the solvent at room temperature, and the exchange is effectively stopped at - 55°C.

Integrated spectra showed that peak B corresponded to 1.7 ± 0.2 fluorine atoms per molecule of iodic acid, by comparison with the fluorine in the solvent, or in one experiment, with fluorine in trisulphuryl fluoride, $S_3O_8F_2$, added in a known concentration. No significant changes in this value were observed on cooling the solutions from room temperature to - 80°C, or on the addition of potassium fluorosulphate.

It is not possible to decide definitely whether peak B is due to fluorine atoms linked to sulphur or to iodine, since either could give peaks in this region of the spectrum.

A white solid slowly separated out from the rather concentrated solutions of iodic acid used in these experiments, but this was not isolated.

Discussion

We may at once rule out a number of possible ionization schemes.

Simple protonation:

$$HIO_3 + HSO_3F \rightleftharpoons H_2IO_3^+ + SO_3F^- \qquad [1]$$

$$\nu = 2 \quad \Upsilon = 1$$

would give too small a value for ν, and would not account for the appearance of the peak B in the NMR spectrum.

The freezing-point curve does not have the initial portion of small slope, characteristic of the freezing-point curves of water, and of solutes which react to produce water (Figures 27 and 32). The observed Υ-values are also too small to be consistent with reactions such as [2], [3], and [4] in which water is produced.

$$HIO_3 + 2HSO_3F = IO_2SO_3F + H_3O^+ + SO_3F^- \qquad [2]$$

$$\Upsilon = 0.7$$

$$HIO_3 + 5HSO_3F = IO(SO_3F)_3 + 2H_3O^+ + 2SO_3F^- \qquad [3]$$

$$\Upsilon = 1.4$$

$$HIO_3 + 8HSO_3F = I(SO_3F)_5 + 3H_3O^+ + 3SO_3F^- \qquad [4]$$

$$\Upsilon = 2.1$$

A further possibility is the replacement of the hydroxyl group or of one or both oxygen atoms in the iodic acid molecule by fluoride or fluorosulphate groups. A number of reactions of this type is known. Boric acid (105) reacts with fluorosulphuric acid to form boron trifluoride:

$$B(OH)_3 + 3HSO_3F = BF_3 + 3H_2SO_4$$

Arsenic (III) oxide (106) reacts to form $2AsF_3.3SO_3$ which is believed to be a complex of $AsF(SO_3F)_2$ and $AsF_2(SO_3F)$. (107, 100).

$$As_2O_3 + 6HSO_3F = 2AsF_3.3SO_3 + 3H_2SO_4$$

Some possible reactions of this type are given below:

$$HIO_3 + HSO_3F = IO_2F + H_2SO_4 \qquad [5]$$
$$\nu = 2 \quad \gamma = 0$$

$$HIO_3 + 2HSO_3F = HIO_2F_2 + H_2SO_4 + SO_3 \qquad [6]$$
$$\nu = 3 \quad \gamma = 0$$

$$HIO_3 + 3HSO_3F = IOF_2(SO_3F) + 2H_2SO_4 \qquad [7]$$
$$\nu = 3 \quad \gamma = 0$$

$$HIO_3 + 5HSO_3F = IF_3(SO_3F)_2 + 3H_2SO_4 \qquad [8]$$
$$\nu = 4 \quad \gamma = 0$$

As written, all of these reactions have $\gamma = 0$. However, the iodine - containing species could be partially protonated, or, in the case of reactions [7] and [8], partially dissociated to give fluorosulphate ions, accounting for the observed conductivity. Reaction [8] requires too large a value of ν, and may certainly be rejected. Reaction [5], with only one covalently-bound fluorine per iodine atom,is not in agreement with the NMR results. Reactions [6] and [7] come closest to agreement with the NMR results, giving 2 covalent fluorine atoms on iodine, compared with 1.7 found experimentally. As will be shown in a later section, dioxodifluoroiodate (V) acid behaves as a moderately strong base in fluorosulphuric acid (K_b = 0.01 mole kg^{-1}), so that the initial slope of the freezing point curve would give $\nu > 3$, if reaction occurred according to Equation [6]. Ionization of the species $IOF_2(SO_3F)$, produced according to Equation [7],

$$IOF_2(SO_3F) \rightleftharpoons IOF_2^+ + SO_3F^- \qquad [9]$$

would also give too large a value of ν. The shape of the conductivity curve (Figure 33) does not fit an equilibrium of the type shown in Equation [9], for which the equilibrium constant, K_1, would be given by

$$K_1 = \frac{[IOF_2^+][SO_3F^-]}{[IOF_2SO_3F]} = \frac{\gamma^2 m^s(HIO_3)}{1 - \gamma}$$

The value of K_1 is not constant, but increases steadily with increasing concentration (Table 45). For an equilibrium involving instead a dimeric species:

$$(IOF_2SO_3F)_2 \rightleftharpoons (IOF_2)_2 SO_3F^+ + SO_3F^- \qquad [10]$$

the equilibrium constant would be

$$K_2 = \frac{[(IOF_2)_2SO_3F^+][SO_3F^-]}{[(IOF_2SO_3F)_2]} = \frac{\gamma^2 m^s(HIO_3)}{0.5 - \gamma}$$

The value of K_2 remains fairly constant over a considerable range of concentration (Table 45). The slow separation from concentrated solutions of a white precipitate which is almost certainly polymeric is consistent with the presence of polymeric species in solution.

Complete ionization according to Equation [10] would give a γ-value of 0.5. The limiting slope of the conductivity curve at low concentrations corresponds approximately to $\gamma = 0.6$. This may be due to the presence at low concentrations of some of the monomer, ionized according to [9]. Similarly, the increase in K_2 at higher concentrations may be due to the formation of polymers, which are stronger bases than the dimer.

The value $\nu = 3$ derived from the limiting slope of the freezing-point curve is also in agreement with complete ionization according to Equation [10] at low concentration, i.e. with the over-

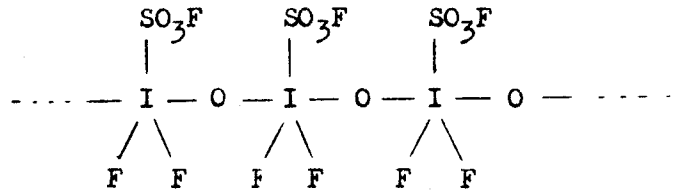
all reaction:

$$2HIO_3 + 6HSO_3F = (IOF_2)_2 SO_3F^+ + SO_3F^- + 4H_2SO_4 \qquad [11]$$

$$\nu = 3,\ \Upsilon = 0.5$$

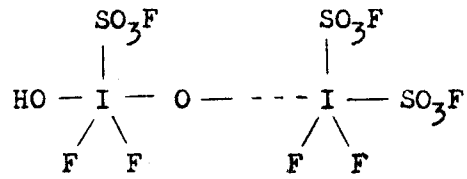
For an 0.1 molal solution, the most concentrated solution studied cryoscopically, the observed Υ-value of 0.3 still corresponds to $\nu = 2.8$, not greatly different from 3.

An infinite polymer of IOF_2SO_3F would probably have the oxygen-bridged structure (I)



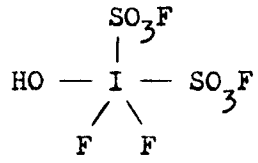
I

Finite polymeric chains would require chain-terminating groups, which would probably be derived from a solvent molecule (II).

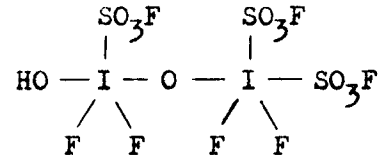


II

The monomer and dimer would then be solvated forms of IOF_2SO_3F and $(IOF_2SO_3F)_2$, having the structures (III) and (IV) respectively.



III



IV

Structure IV has two fluorine atoms per iodine atom, in approximate agreement with the NMR results. The fluorine atoms on the two iodine atoms are not equivalent. However they are in very similar environments, and it is possible that their chemical shifts are so similar that separate peaks due to the two kinds of fluorine cannot be resolved. Spin-spin coupling between the two kinds of fluorine would broaden the peaks, making it still harder to resolve them, if they were close together. If polymeric species of different sizes were continually being formed and broken down, in a series of rather mobile equilibria, this would tend to average the environment of a given fluorine nucleus and we would expect to observe only a single peak. The fact that peak B remains rather broad, even after the slow exchange of fluorine with the solvent has effectively been stopped is consistent with some such explanation as the above.

The fluorine resonance may also be broadened by coupling with iodine, which has a quadrupole moment (spin quantum number, $I = 5/2$)(108).

The Raman spectrum does not give much definite information, but it is not inconsistent with the reaction scheme postulated.

To explain the difference between the value of 1.7 fluorine atoms per iodine atom given by NMR, and the value of 2 required by reaction [11], we may suppose that some reaction, e.g. [5], giving a

species having an F/I ratio less than 2, also occurs to a small extent.

TABLE 43

Solutions of Iodic Acid in

Fluorosulphuric Acid: Freezing Points

Experiment 104

Weight of HSO_3F 151.66 g

Weight of HIO_3 (g)	$m(HIO_3)$	Freezing Point (°C)	θ
0.0000	0.00000	- 89.017	0.000
0.4991	0.01871	- 89.226	0.209
1.1879	0.04452	- 89.565	0.548
1.8067	0.06773	- 89.812	0.795
2.7202	0.1020	- 90.278	1.261

Experiment 105

Weight of HSO_3F 143.95 g

Weight of HIO_3 (g)	$m(HIO_3)$	Freezing Point (°C)	θ
0.0000	0.00000	- 89.014	0.000
0.2908	0.01148	- 89.130	0.116
0.6563	0.02592	- 89.303	0.289
1.0484	0.04140	- 89.485	0.471
1.4951	0.05904	- 89.700	0.686
2.0425	0.08067	- 89.964	0.950

TABLE 44

Solutions of Iodic Acid in

Fluorosulphuric Acid: Conductivities at 25°C

Experiment 90

Weight of HSO_3F 90.86 g

Weight of HIO_3 (g)	$m(HIO_3)$	$10^4 \kappa$ (ohm^{-1} cm^{-1})	$10^4 \kappa^*$ (corrected) (ohm^{-1} cm^{-1})
0.0000	0.00000	4.23	1.10
0.1601	0.01002	16.53	13.40
0.4599	0.02878	32.01	28.88
0.8834	0.05529	49.43	46.30
1.3204	0.08260	65.48	62.35
2.1089	0.1319	92.32	89.19
3.2409	0.2027	127.9	124.8

* κ corrected = $\kappa - 3.13 \times 10^{-4}$. 3.13×10^{-4} ohm^{-1} cm^{-1} is the difference between κ for the solvent used in this experiment and that for the solvent in Experiment 92.

Experiment 92

Weight of HSO_3F 77.57 g

Weight of HIO_3 (g)	$m(HIO_3)$	$10^4 \kappa$ (ohm^{-1} cm^{-1})
0.0000	0.00000	1.10
0.1255	0.00920	13.17
0.4847	0.03553	33.13
0.9941	0.07286	55.56
1.7303	0.1268	84.71

(Table 44 continued)

Weight of HIO_3 (g)	$m(HIO_3)$	$10^4\kappa$ (ohm^{-1} cm^{-1})
2.3377	0.1714	107.3
3.1483	0.2307	135.9

Experiment**	$m(HIO_3)$	$10^4\kappa$ (ohm^{-1} cm^{-1})
93	0.00417	7.78
94	0.00710	11.34
95	0.00180	4.47
96	0.00262	5.69
98	0.01913	21.40

**The results of these experiments, in which iodine was subsequently added, are reported in detail in Tables 48, 55, 62, and 65.

TABLE 45

Solutions of Iodic Acid in

Fluorosulphuric Acid: Values of γ, K_1 and K_2

$m(HIO_3)$	γ	$K_1 = \frac{m\gamma^2}{1-\gamma}$	$K_2 = \frac{m\gamma^2}{0.5-\gamma}$
0.02	0.43_5	0.0067	0.058
0.04	0.36	0.0082	0.038
0.06	0.32	0.0092	0.035
0.08	0.30	0.0103	0.036
0.10	0.29	0.0116	0.039
0.14	0.27	0.0139	0.044

(Table 45 continued)

$m(HIO_3)$	γ	$K_1 = \frac{m\gamma^2}{1-\gamma}$	$K_2 = \frac{m\gamma^2}{0.5-\gamma}$
0.18	0.26	0.0166	0.051
0.22	0.25_5	0.0192	0.058

TABLE 46

Solutions of Iodic Acid in

Fluorosulphuric Acid: Raman Spectrum (Frequencies in cm^{-1})

HIO_3 in HSO_3F	HSO_3F (99)	SO_3F^- (99)	H_2SO_4 (99)
397	391		392
	405	409	
			422
553	555		
	560	562	563
616		608	
649			
		786	
843	850		
902			910
954	960		976
1092		1083	
1114			1137
			1195
1209	1178	1235	
	1230		
1359			1368

(Table 46 continued)

HIO_3 in HSO_3F	HSO_3F (99)	SO_3F^- (99)	H_2SO_4 (99)
1434	1445		
1578?			

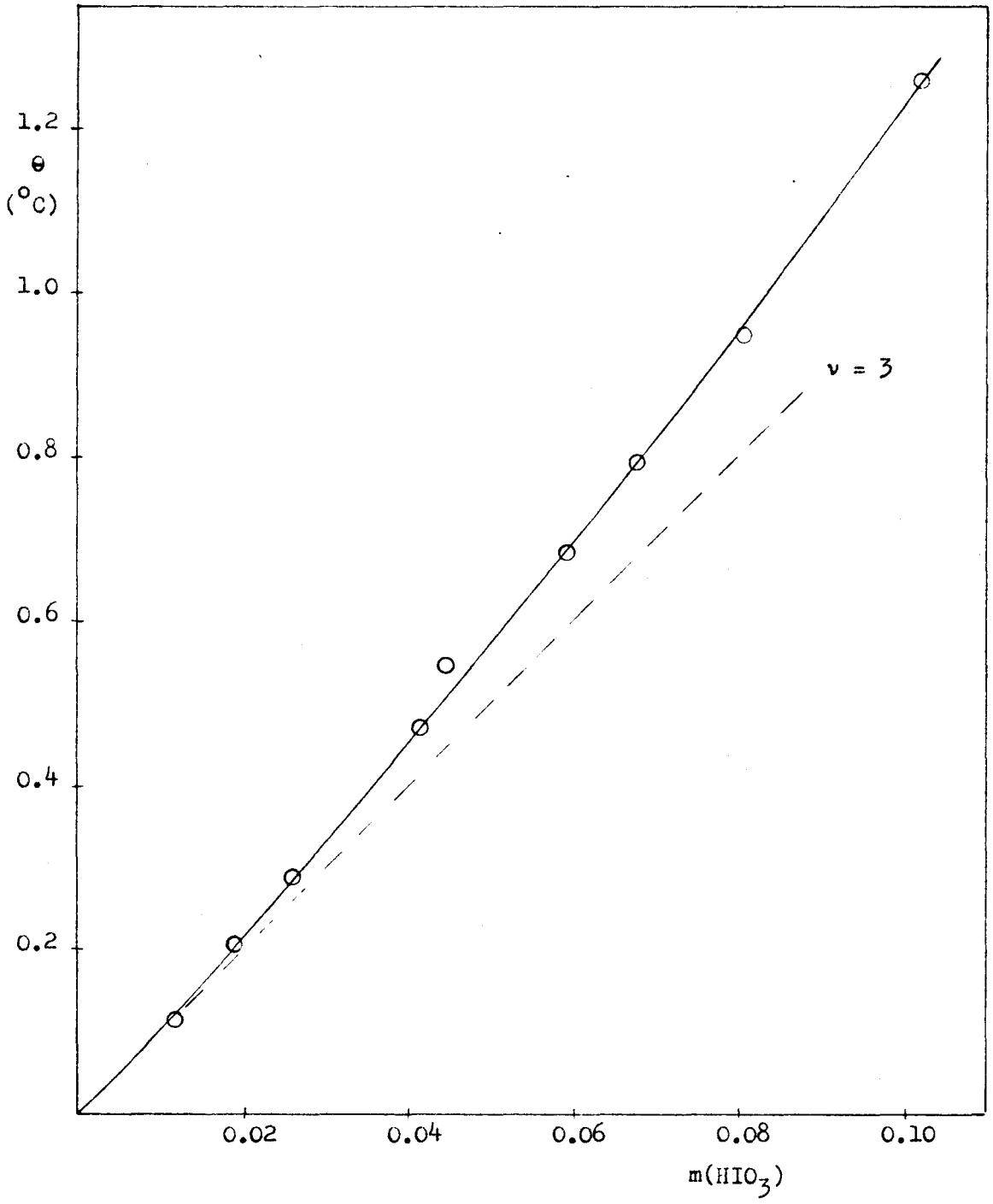


Figure 32. Solutions of HIO_3 in HSO_3F: Freezing-point Depressions

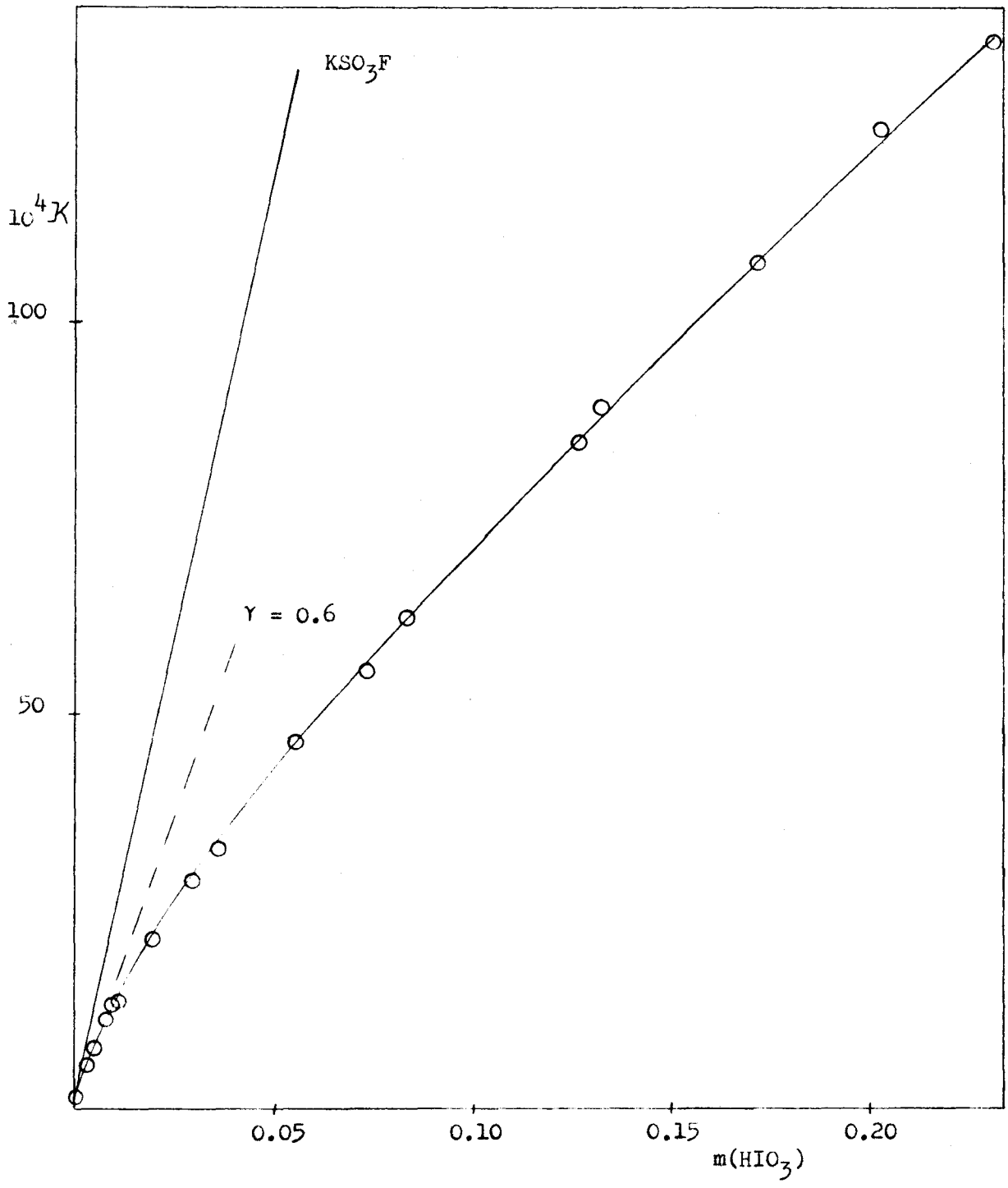


Figure 33. Solutions of HIO_3 in HSO_3F: Conductivities at 25°C

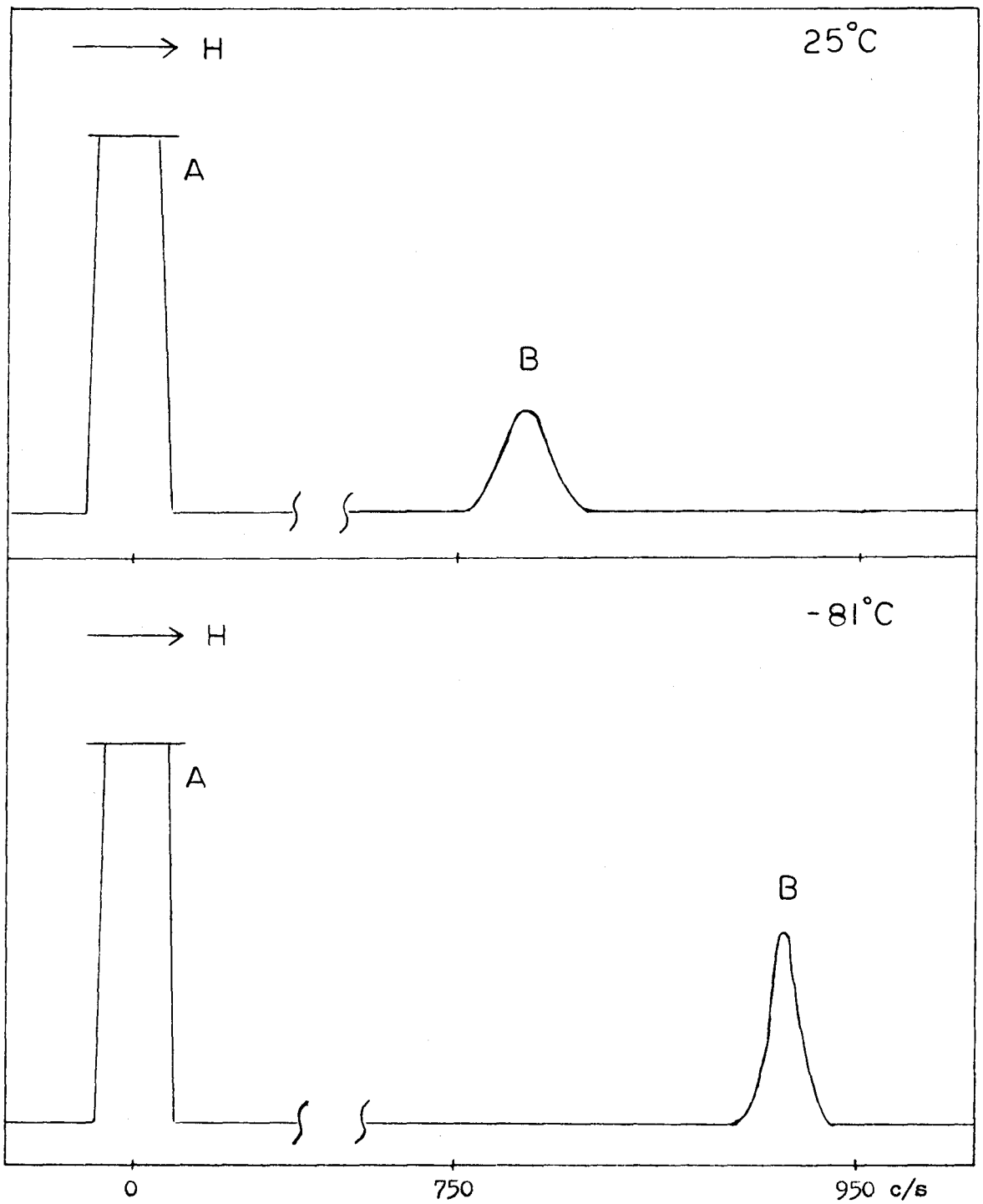


Figure 34. Solutions of HIO_3 in HSO_3F: F^{19} NMR Spectra (at 56.4 Mc/s)

5. Solutions of Iodosyl Sulphate and of "HIO_3 + 0.33 I_2" in Fluorosulphuric Acid

Cryoscopy

Only the mixed solute HIO_3 + 0.33 I_2 was studied cryoscopically. The solutes, in exactly the mole ratio I_2/HIO_3 = 0.33, were added in the form of a concentrated solution in fluorosulphuric acid. This solution was deep blue-green in colour, and slowly deposited a yellow solid on standing (Table 47 Figure 35).

Conductimetry

Two conductimetric runs were done on solutions of iodosyl sulphate (Table 51 Figure 36). The compound appeared to be insoluble in fluorosulphuric acid in the cold, but dissolved on gentle heating to give a blue-green solution. The addition of a small amount of potassium fluorosulphate to the solution at the end of a run caused a further increase in the conductivity, showing that the solute was behaving as a base. A 5 ml portion of a solution of iodosyl sulphate in fluorosulphuric acid was hydrolysed by adding it drop-wise to 30 ml of ice-cold water, and analysed as described in Chapter II, to determine the oxidation state of the iodine. Within experimental error, this was found to be 3, so that a change in the net oxidation state of the iodine was not responsible for the production of the blue colour.

Successive additions of iodine were made to a solution of iodic acid in the conductivity cell giving I_2/HIO_3 ratios close to 0.33. Several further additions of iodic acid, each followed by additions of iodine, were made. From each set of results, a value of

the specific conductivity at the mole ratio 0.33 was obtained by interpolation (Tables 48 and 49, Figure 36).

Fluorine^{19} NMR spectrum

The F^{19} NMR spectrum of a solution of HIO_3 + 0.33 I_2 in fluorosulphuric acid was recorded at room temperature, at - 46.5°C and at - 83°C. At room temperature only a single peak, due to the solvent was present in the spectrum. At - 83°C a second peak was present, at about 1000 c/s to high-field of the solvent peak. This peak was about 50 c/s wide. As the temperature was raised, this peak moved closer to the solvent peak and became still broader. At - 46.5°C the chemical shift, relative to the solvent peak, was + 945 c/s and the width of the peak was 140 c/s. Above this temperature, the peak became indistinguishable from the base-line (Figure 37).

Isolation and analysis of the solid separating from concentrated solutions of HIO_3 + 0.33 I_2

The yellow solid was filtered off on a sintered-glass filter in the dry-box, washed twice with fluorosulphuric acid, and freed from the solvent by heating to 50°C under vacuum for eight hours.

The yellow solid turned brown very rapidly on exposure to moist air. A small portion was treated with water and the iodine liberated was filtered off. A portion of the filtrate gave a precipitate with nitron reagent, showing the presence of fluorosulphate ion. A second portion gave a precipitate with barium chloride only after some time, showing that sulphate ion is formed slowly, by the hydrolysis of fluoro-sulphate.

Portions of the compound were analysed for iodine by the method described for the analysis of iodosyl sulphate, in Chapter II. The results agreed with the formula $IOSO_3F$.

Results:

Oxidation number of iodine	2.99, 2.94
% I	51.84 52.83
(Calc. for $IOSO_3F$: 3.00, 52.44)	

Infra-red spectrum of iodosyl fluorosulphate

Dasent and Waddington (27) have examined the IR spectra of several iodosyl compounds, and it was therefore hoped that confirmation of the formula $IOSO_3F$ could be obtained by examination of the IR spectrum of the yellow compound. The compound reacted with Nujol, turning brown with the release of iodine. It was therefore necessary to prepare samples in the form of KBr discs.

The spectrum obtained was very complicated. It contained all the peaks expected for an ionic fluorosulphate, in addition to several others. The relative intensities of the absorption peaks varied from one sample to another, and it seems likely that some of them were due to decomposition products arising from unavoidable exposure to moisture during the preparation of the KBr discs. Small amounts of water would cause disproportionation to elementary iodine and a compound of pentavalent iodine, possibly iodic acid, with the release of fluorosulphuric acid.

Unfortunately the fluorosulphate ion has two strong peaks (at 565 and 583 cm^{-1}) in the same region as the characteristic absorption (27) of the polymeric IO^+ cation (553 - 600 cm^{-1}) so that it was not

possible to confirm the presence of the latter from the spectrum.

Table 53 shows that all the observed peaks except those at 635 and 875 cm^{-1} may be tentatively accounted for in terms of an ionic fluorosulphate contaminated with fluorosulphuric acid. There are no peaks which can definitely be assigned to iodic acid. The peak at 635 cm^{-1} is probably not due to iodic acid, since the strong band of iodic acid at 760 cm^{-1} is not found. The peak at 635 cm^{-1} could possibly be due to IO^+, although it is at a somewhat higher frequency than has previously been reported for this polymeric ion (27).

Discussion

The solutions have the blue colour said to be characteristic of the iodine cation, I^+. The net oxidation number of the iodine is 3, so that trivalent iodine must be extensively disproportionated in these solutions. That this disproportionation cannot be complete, is shown by the separation of the iodosyl salt from concentrated solutions.

The freezing-point depression curve for HIO_3 + 0.33 I_2 has an initial portion of small slope, indicating that water is one of the products of the reaction. Making allowance for this, the freezing-point curve indicates an initial ν-value of about 4.35, (Figure 35).

The conductivities are rather low, the Υ-values for the solute HIO_3 + 0.33 I_2 being smaller than those for water (Table 50). The Υ-values for $(IO)_2SO_4$ are also rather low (Table 52).

Reaction to produce the partly ionized base, $IOSO_3F$ would occur in the case of the solutes HIO_3 + 0.33 I_2, and $(IO)_2SO_4$ respectively,

according to

$$3HIO_3 + I_2 + HSO_3F = 5IOSO_3F + 4H_3O^+ + 4SO_3F^- \quad [1a]$$

$$\nu = 6\text{-}4.3, \ \Upsilon = 2.4\text{-}0.9$$

$$(IO)_2SO_4 + 2HSO_3F = 2IOSO_3F + H_2SO_4 \quad [1b]$$

$$\Upsilon = 2\text{-}0$$

The observed value of Υ for $HIO_3 + 0.33\ I_2$ is too small to be consistent with the formation of even the completely undissociated compound, $IOSO_3F$.

Disproportionation to univalent and pentavalent iodine, i.e. to the iodine cation and the species believed to be produced in solutions of iodic acid, would give the overall reactions:

$$12HIO_3 + 4I_2 + 46HSO_3F = 10I^+ + 5(IOF_2SO_3F)_2 + 6H_3O^+ + 20H_2SO_4 + 16SO_3F^- \quad [2a]$$

$$\nu = 4.75, \ \Upsilon = 1.1$$

$$2(IO)_2SO_4 + 8HSO_3F = 2I^+ + (IOF_2SO_3F)_2 + 4H_2SO_4 + 2SO_3 + 2SO_3F^- \quad [2b]$$

$$\Upsilon \leqslant 1$$

The observed values of ν and Υ are too small to be consistent with these reactions, unless a large part of the univalent iodine is present as unionized ISO_3F. There is some evidence for the formation of this compound in the reaction of peroxodisulphuryl fluoride with excess iodine (21). If it were formed quantitatively we would have $\nu = 4$ and $\Upsilon = 0.35$ for [2a] and $\Upsilon = 0$ for [2b]. In reaction [2b], SO_3 is written as a reaction product.

It is possible that this could react with $(IOF_2SO_3F)_2$ to give, e.g., $IOF(SO_3F)_2$. If such a reaction did not occur, the SO_3 would lower the conductivity, possibly by replacing the very mobile SO_3F^- ions by $S_2O_6F^-$ (98) and we would predict a smaller value of γ than 1.0.

Disproportionation to give the ion I_3^+ would lead to the overall reactions:

$$21HIO_3 + 7I_2 + 68HSO_3F = 5I_3^+ + 10(IOF_2SO_3F)_2 + 3H_3O^+ + 40H_2SO_4 + 8SO_3F^- \quad [3a]$$

$$\nu = 3.1, \ \gamma = 0.3$$

$$7(IO)_2SO_4 + 26HSO_3F = 2I_3^+ + 4(IOF_2SO_3F)_2 + 13H_2SO_4 + 10SO_3 + 2SO_3F^- \quad [3b]$$

$$\gamma \leqslant 0.3$$

In reaction [3b] there is again some uncertainty as to whether free SO_3 would be present, or whether this would react with $(IOF_2SO_3F)_2$. If free SO_3 were present, γ would be less than 0.3.

To account for the low values of ν and γ observed, it is necessary to postulate extensive disproportionation according to reactions [3a] and [3b], or according to [2a] and [2b] with the formation of ISO_3F. The colour of the solutions, and the formation of $IOSO_3F$, show that reactions [2] and [1] must be important. Thus the solutions probably contain iodine in four different valence states. It is not possible from the data available to derive any more quantitative information on this very complicated system. It is tentatively proposed that the new peak appearing in the NMR spectrum at low temperatures is due to the species $(IOF_2SO_3F)_2$ or to some similar species containing pentavalent iodine. The reason for

its appearance only at low temperatures, is probably that the various disproportionation equilibria provide a more rapid mechanism for exchange of fluorine with the solvent than is available in solutions of iodic acid alone, (Figure 37).

TABLE 47

Solutions of Iodic Acid and Iodine in Fluorosulphuric acid: Freezing Points at the Ratio I_2/HIO_3 = 0.333

Experiment 108

Weight of HSO_3F 131.20 g

Composition of concentrated solution

Weight of HSO_3F	33.5461 g
Weight of HIO_3	3.8302 g
Weight of I_2	1.8408 g
I_2/HIO_3	0.333

Weight of solution added (g)	$m^s(HIO_3)$	Freezing Point (°C)	θ (°C)
0.0000	0.00000	- 89.018	0.000
3.4803	0.01440	- 89.193	0.175
6.8019	0.02757	- 89.387	0.369
10.6815	0.04227	- 89.603	0.585
14.0913	0.05464	- 89.780	0.762
17.3311	0.06590	- 89.953	0.935
20.4861	0.07650	- 90.124	1.106

(Table 47 continued)

Experiment 110

Weight of HSO_3F 135.13 g

Composition of concentrated solution

Weight of HSO_3F	36.4018 g
Weight of HIO_3	3.0917 g
Weight of I_2	1.4898 g
I_2/HIO_3	0.334

Weight of solution added (g)	$m^s(HIO_3)$	Freezing Point (°C)	θ (°C)
0.0000	0.00000	- 89.017	0.000
5.1041	0.01571	- 89.206	0.189
10.1987	0.03035	- 89.423	0.406
15.4380	0.04451	- 89.640	0.623
20.7276	0.05794	- 89.838	0.821
26.3318	0.07126	- 90.039	1.022

TABLE 48

Solutions of Iodic Acid and Iodine in Fluorosulphuric Acid: Conductivities at I_2/HIO_3 Ratios Close to 0.333, at 25°C

Experiment 92

Weight of HSO_3F 77.57 g

Weight of HIO_3 (g)	Weight of I_2 (g)	$m^s(HIO_3)$	I_2/HIO_3	$10^4\kappa$ ($ohm^{-1}\ cm^{-1}$)
0.0000	0.0000	0.0000		1.10
3.1483	0.0000	0.2307	0.000	135.9
3.1483	1.2206	0.2307	0.269	210.6
3.1483	1.5136	0.2307	0.333	230.0
3.1483	1.8460	0.2307	0.406	251.5

Experiment 93

Weight of HSO_3F 99.45 g

Weight of HIO_3 (g)	Weight of I_2 (g)	$m^s(HIO_3)$	I_2/HIO_3	$10^4\kappa$ ($ohm^{-1}\ cm^{-1}$)
0.0000	0.0000	0.00000		1.33
0.0730	0.0000	0.00417	0.000	7.78
0.0730	0.0300	0.00417	0.285	6.16
0.0730	0.0494	0.00417	0.469	7.90
0.0730	0.0784	0.00417	0.745	10.90
0.2943	0.0784	0.01677	0.186	22.57
0.2943	0.1355	0.01677	0.320	27.00
0.2943	0.2180	0.01677	0.515	35.26
0.6307	0.2180	0.03606	0.198	47.47

(Table 48 continued)

Weight of HIO_3 (g)	Weight of I_2 (g)	$m^s(HIO_3)$	I_2/HIO_3	$10^4\kappa$ (ohm^{-1} cm^{-1})
0.6307	0.3344	0.03606	0.367	56.99
0.6307	0.4636	0.03606	0.509	68.11
1.2616	0.4636	0.07216	0.255	85.58
1.2616	0.6062	0.07216	0.333	96.15
1.2616	0.7370	0.07216	0.405	106.2
1.7818	0.7370	0.1019	0.287	118.4
1.7818	0.8798	0.1019	0.342	128.3
1.7818	1.0750	0.1019	0.418	142.3

TABLE 49

Solutions of Iodic Acid and Iodine in Fluorosulphuric Acid: Interpolated Conductivities at the Ratio I_2/HIO_3 = 0.333

Experiment	$m^s(HIO_3)$	$10^4\kappa$ (ohm^{-1} cm^{-1})
92	0.2307	230.0
93	0.00417	6.7
	0.01677	27.5
	0.03606	54.8
	0.07216	96.2
	0.1019	126.5
98	0.01913	27.1

TABLE 50

Solutions of Iodic Acid and Iodine in Fluorosulphuric Acid: Values of Υ at the Ratio $I_2/HIO_3 = 0.333$

$m^s(HIO_3)$	Υ
0.04	0.60
0.08	0.54
0.12	0.51
0.16	0.48
0.20	0.47

TABLE 51

Solutions of Iodosyl Sulphate in

Fluorosulphuric Acid: Conductivities at 25°C

Experiment 73

Weight of HSO_3F 93.24 g

Weight of $(IO)_2SO_4$ (g)	m	$10^4\kappa$ (ohm^{-1} cm^{-1})
0.0000	0.00000	1.38
0.1551	0.00436	6.43
0.6743	0.01894	19.40
1.3179	0.03702	31.20
2.4923	0.07000	49.91

Experiment 75

Weight of HSO_3F 89.54 g

Weight of $(IO)_2SO_4$ (g)	m	$10^4\kappa$ (ohm^{-1} cm^{-1})
0.0000	0.00000	1.25
0.5762	0.01685	16.67
1.2264	0.03586	29.53
1.7944	0.05248	39.54
2.6102	0.07290	52.72
A small amount of KSO_3F was added:		53.62

TABLE 52

Solutions of Iodosyl Sulphate in Fluorosulphuric Acid: Values of Υ

m	Υ
0.02	0.37
0.04	0.32
0.06	0.30
0.08	0.28

TABLE 53

The Infra-red Spectrum of Iodosyl Fluorosulphate

(Frequencies in cm^{-1})

$IOSO_3F$	SO_3F^- (111)	HSO_3F (99)	HIO_3 (112)	I - O - I in iodosyl compounds (27)
562 m	565* m	555***	568 w	553 - 600
		560***		
580 s	583* s			
635 m			635 m	
732 s	710 - 767 s		717 m	
			760 s	
800 w	785**s		805 s	
845 m		840		
875 m				
950 w	970 - 975 w	960		
1025, 1050, 1070 s	1057 - 1095 s			
1165 s		1145	1165 m	
1205, 1228 s	1235 - 1277 s	1220		
1295 s	1287 - 1304 s			

* KSO_3F

** $AgSO_3F$ and $NaSO_3F$ only

*** From Raman spectrum (99)

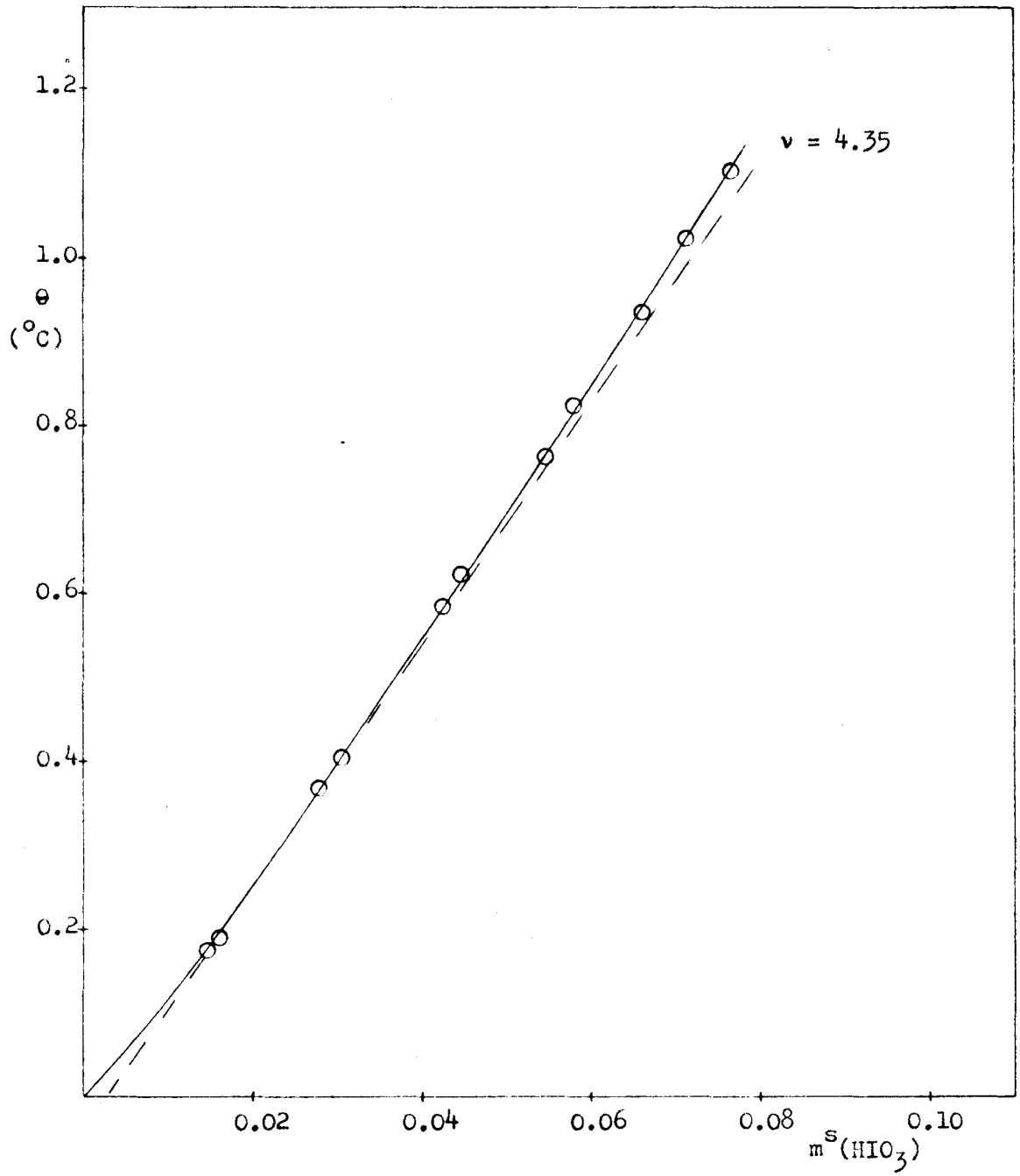


Figure 35. Solutions of "HIO_3 + 0.33 I_2" in HSO_3F: Freezing-point Depressions

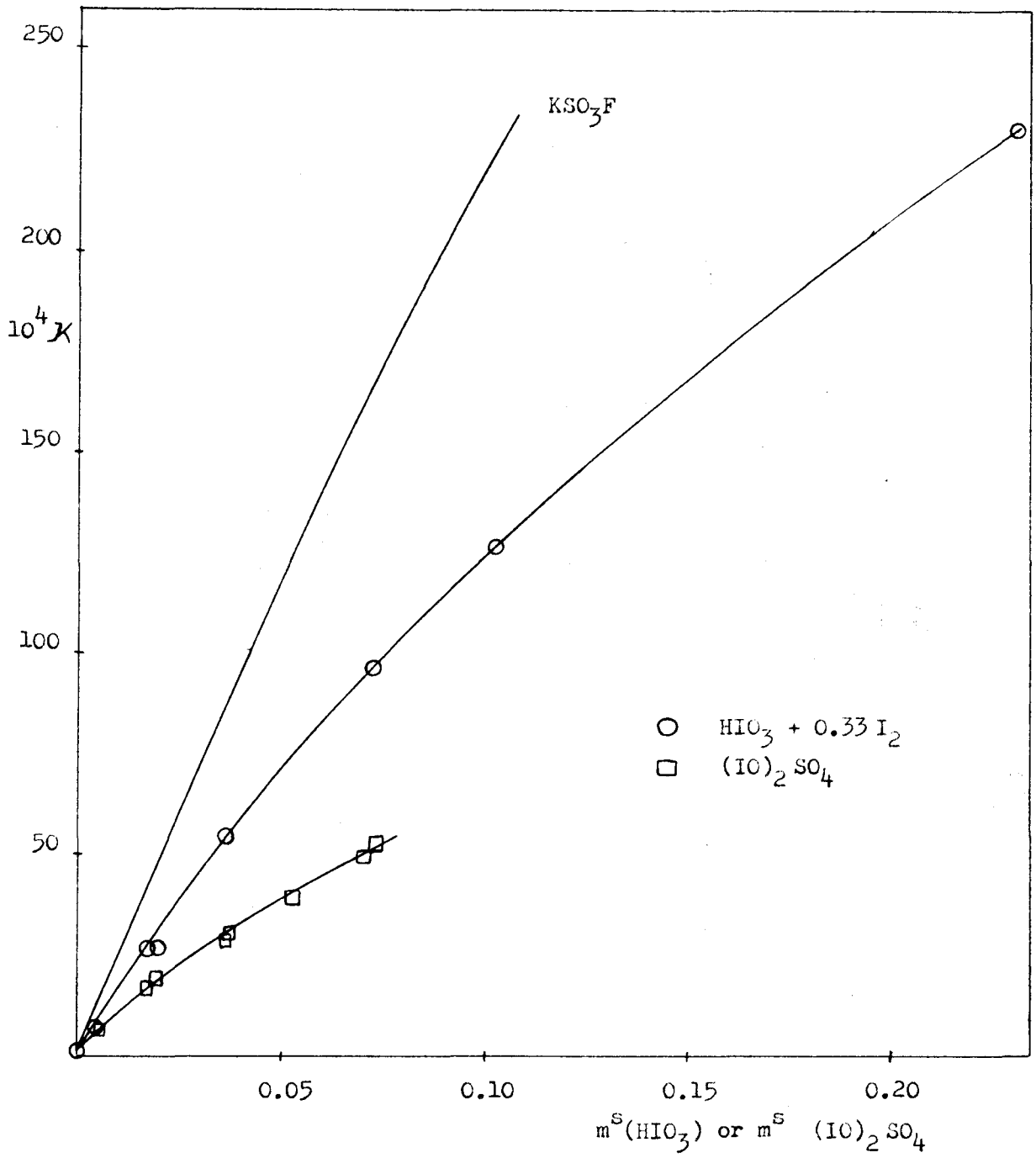


Figure 36. Solutions of "$HIO_3 + 0.33\ I_2$" and of $(IO)_2\ SO_4$ in HSO_3F: Conductivities at 25°C

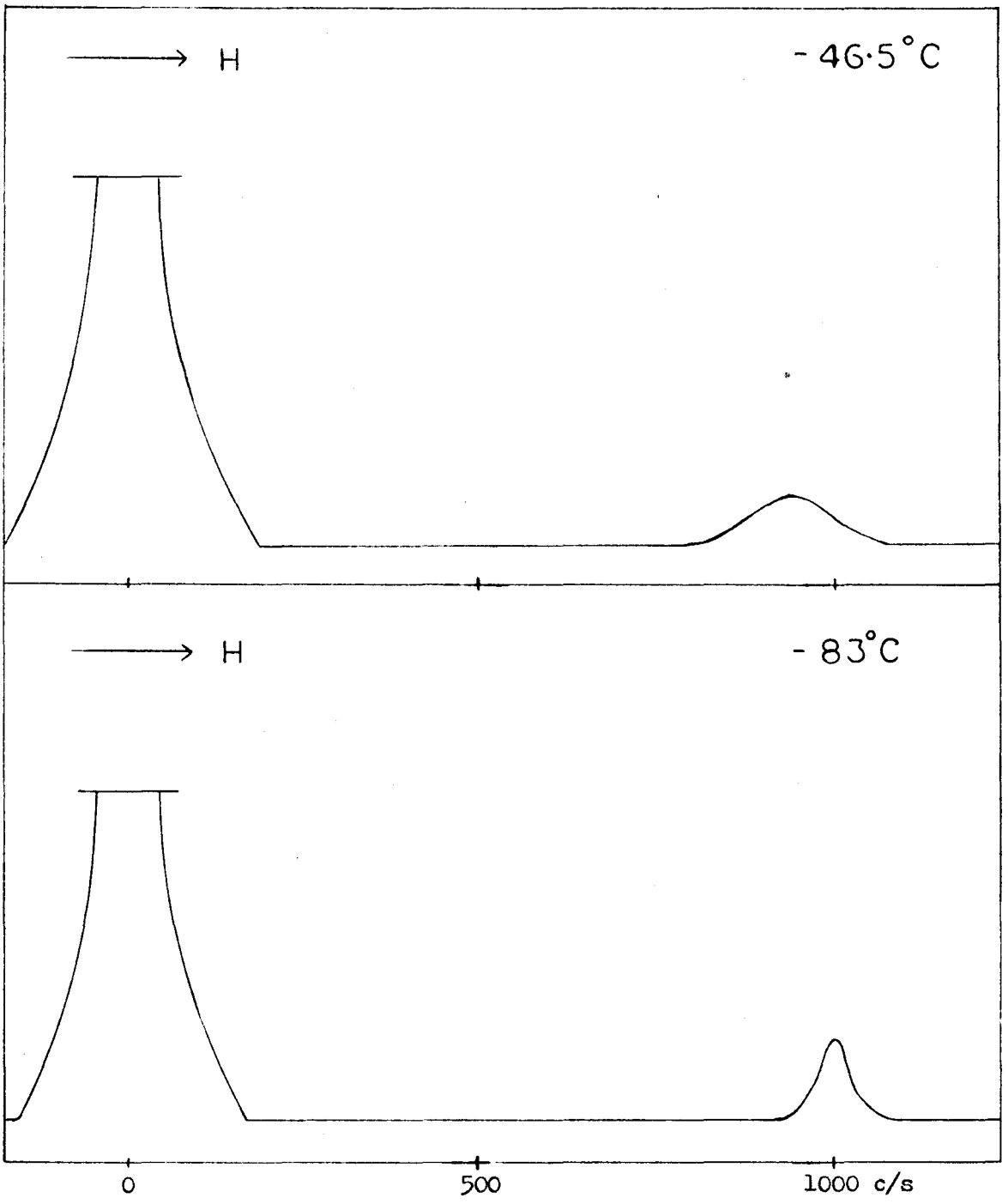


Figure 37. F^{19} NMR Spectra of a Solution of "HIO_3 + 0.33 I_2" in HSO_3F (56.4 Mc/s)

6. Solutions of "$HIO_3 + 2I_2$" and of "$K_2S_2O_8 + I_2$" in Fluorosulphuric Acid

Introduction

Arotsky, Mishra and Symons (37) have reported the formation of blue solutions, with the strong absorption band at 640 mμ, considered to be characteristic of the iodine cation, by the oxidation of iodine with potassium peroxodisulphate, $K_2S_2O_8$, in fluorosulphuric acid.

Cryoscopy

Only the mixed solute, $HIO_3 + 2I_2$, was studied cryoscopically. The solutes, in the exact stoichiometric ratio, were added in the form of a concentrated solution in fluorosulphuric acid (Table 54. Figure 38).

Conductimetry

A solution of iodic acid was prepared in the conductivity cell. Several additions of iodine were made, giving I_2/HIO_3 ratios close to 2.0. Further additions of iodic acid were made, each followed by several additions of iodine (Table 55). From each set of results an interpolated value of the specific conductivity at exactly the ratio 2.0 was obtained (Table 56. Figure 39). A similar procedure was followed for solutions of iodine and potassium peroxodisulphate. In this case the initial solution was one of iodine in fluorosulphuric acid (Table 58). Some oxidation of the iodine by free SO_3 in the solvent occurred, which may have led to errors at the lower concentrations. Interpolated values of specific conductivity at the ratio $I_2/K_2S_2O_8 = 1.00$ were obtained

(Table 59, Figure 40)

Discussion

The freezing-point depression curve for $HIO_3 + 2I_2$ has an initial portion of small slope, indicating that water is produced in the reaction of this solute with fluorosulphuric acid. Allowing for this, the initial ν-value can be estimated to be approximately 8.1. The value of Υ for $HIO_3 + 2I_2$ ranges from 2.6 to 2.4 (Table 57) while the Υ-value for $K_2S_2O_8 + I_2$, calculated with respect to I_2 as solute, has a constant value of 2.6 (Table 60). The experimental ν and Υ-values are much too low to be consistent with quantitative formation of the iodine cation:

$$HIO_3 + 2I_2 + 8HSO_3F = 5I^+ + 3H_3O^+ + 8SO_3F^- \qquad [1a]$$
$$\nu = 16, \ \Upsilon = 6.56$$

$$K_2S_2O_8 + I_2 + 4HSO_3F = 2K^+ + 2I^+ + 4SO_3F^- + 2H_2SO_4 \qquad [1b]$$
$$\Upsilon = 4$$

The observed value of ν is also too small to be consistent with the formation of undissociated ISO_3F:

$$HIO_3 + 2I_2 + 8HSO_3F = 5ISO_3F + 3H_3O^+ + 3SO_3F^- \qquad [2a]$$
$$\nu = 11, \ \Upsilon = 2.1$$

$$K_2S_2O_8 + I_2 + 4HSO_3F = 2K^+ + 2ISO_3F + 2SO_3F^- + 2H_2SO_4 \qquad [2b]$$
$$\Upsilon = 2$$

The constancy of Υ for $K_2S_2O_8 + I_2$ with concentration is also inconsistent with the reversible dissociation:

$$ISO_3F \rightleftharpoons I^+ + SO_3F^-$$

Rather extensive disporportionation of univalent iodine must therefore occur in these solutions. The lower oxidation state involved can only be that represented by the ion I_3^+, while the higher oxidation state could be trivalent or pentavalent iodine.

For disproportionation involving the trivalent state, we have

$$4HIO_3 + 8I_2 + 12HSO_3F = 5IOSO_3F + 5I_3^+ + 7H_3O^+ + 12SO_3F^- \quad [3a]$$
$$\nu = 7.25, \ \Upsilon = 2.3$$

$$2K_2S_2O_8 + 2I_2 + 6HSO_3F = IOSO_3F + I_3^+ + 4K^+ + 5SO_3F^- + 3H_2SO_4 + SO_3 \quad [3b]$$
$$\Upsilon \leqslant 2.5$$

For disproportionation involving the pentavalent state the equations would be:

$$14HIO_3 + 28I_2 + 62HSO_3F = 20I_3^+ + 5(IOF_2SO_3F)_2 + 12H_3O^+ + 20H_2SO_4 + 32SO_3F^- \quad [4a]$$
$$\nu = 6.35, \ \Upsilon = 1.9$$

$$7K_2S_2O_8 + 7I_2 + 24HSO_3F = (IOF_2SO_3F)_2 + 4I_3^+ + 14K^+ + 18SO_3F^- + 12H_2SO_4 + 6SO_3 \quad [4b]$$
$$\Upsilon \leqslant 2.6$$

In Equations [3b] and [4b], SO_3 is written as a reaction product. If this did not react in some other way, it would lower the conductivity, and hence the value of Υ predicted for these reactions, by replacing SO_3F^- ions by $S_2O_6F^-$ (98).

Extensive, but not complete disproportionation according to Equations [3a] or [3b] would fit the experimental results fairly well.

However in view of the extensive disproportion of trivalent iodine in fluorosulphuric acid solutions, discussed in the preceeding section, the reactions represented by Equations [4a] and [4b] must also play some part. The system is obviously very complicated and it does not seem possible to give a more quantitative description on the basis of the present results.

The disproportionation equilibria involve a considerable decrease in the number of particles on going from left to right, e.g.

$$14I^+ + 10SO_3F^- + 2H_2SO_4 \rightleftharpoons 4I_3^+ + (IOF_2SO_3F)_2 + 6SO_3$$

where the left hand side involves 26 molecules or ions, and the right hand side only 11. The position of these equilibria should thus be very concentration dependent, the extent of disproportionation increasing with increasing concentration. Thus it is quite probable that at the very low concentrations ($m^s(HIO_3) \approx 0.0001$) studied spectrophotometrically, almost all the iodine is present as I^+, in agreement with the findings of Symons and co-workers, which are confirmed by the present work (see Chapter V). The deviations of the freezing-point depression curve at higher concentrations, due to non-ideality, from the ideal slope corresponding to $\nu = 8.1$, are much smaller than are usually observed for strong electrolytes, suggesting that ν may actually be decreasing with increasing concentration (compare Figures 27 and 38). This would be consistent with an increasing amount of disproportionation at higher concentrations.

TABLE 54

Solutions of Iodic Acid and Iodine in Fluorosulphuric Acid: Freezing Points at the Mole Ratio I_2/HIO_3 = 2.0

Experiment 107

Weight of HSO_3F 130.02 g

Composition of concentrated solution

Weight of HSO_3F	34.1961 g
Weight of HIO_3	1.7873 g
Weight of I_2	5.1610 g
I_2/HIO_3	2.001

Weight of solution added (g)	$m^B(HIO_3)$	F.p. (°C)	θ (°C)
0.0000	0.00000	- 89.008	0.000
3.2493	0.00605	- 89.124	0.116
6.4462	0.01176	- 89.285	0.277
9.5236	0.01706	- 89.437	0.429
12.7474	0.02240	- 89.595	0.587
17.2069	0.02946	- 89.807	0.799
22.6994	0.03765	- 90.028	1.020

TABLE 55

Solutions of Iodic Acid and Iodine in Fluorosulphuric Acid: Conductivities at I_2/HIO_3 Ratios Close to 2.0 (25°C)

Experiment 96

Weight of HSO_3F 89.50 g

Weight of HIO_3 (g)	Weight of I_2 (g)	$m^s(HIO_3)$	I_2/HIO_3	$10^4 K$ (ohm^{-1} cm^{-1})
0.0000	0.0000	0.00000		1.34
0.0413	0.0000	0.00262	0.000	5.69
0.0413	0.0869	0.00262	1.458	12.50
0.0413	0.1169	0.00262	1.961	16.75
0.0413	0.1711	0.00262	2.870	24.81
0.0783	0.1711	0.00497	1.514	25.92
0.0783	0.2264	0.00497	2.004	33.58
0.0783	0.3068	0.00497	2.715	45.66
0.1250	0.3068	0.00794	1.701	44.95
0.1250	0.3431	0.00794	1.946	50.36
0.1250	0.3878	0.00794	2.150	56.81
0.1668	0.3878	0.01060	1.611	56.84
0.1668	0.4792	0.01060	1.991	69.48
0.1668	0.5458	0.01060	2.267	79.55
0.2705	0.5458	0.01719	1.398	77.44
0.2705	0.7825	0.01719	2.005	107.7
0.2705	0.9266	0.01719	2.374	126.8
0.4793	0.9266	0.03045	1.340	122.0
0.4793	1.3365	0.03045	1.933	168.6
0.4793	1.4585	0.03045	2.109	183.2
0.8029	1.4585	0.05101	1.259	176.4
0.8029	2.3281	0.05101	2.009	260.8
0.8029	2.4893	0.05101	2.149	276.2

(Table 55 continued)

Experiment 94

Weight of HSO_3F 80.23 g

Weight of HIO_3 (g)	Weight of I_2 (g)	$m^s(HIO_3)$	I_2/HIO_3	$10^4 K$ (ohm^{-1} cm^{-1})
0.0000	0.0000	0.00000		1.77
0.1001	0.0000	0.00710	0.000	11.34
0.1001	0.1994	0.00710	1.380	33.13
0.1001	0.3183	0.00710	2.203	50.47
0.1001	0.4733	0.00710	3.277	75.29

TABLE 56

Solutions of Iodic Acid and Iodine in Fluorosulphuric Acid: Interpolated Conductivities at the Mole Ratio $I_2/HIO_3 = 2.0$ (25°C)

Experiment	$m^s(HIO_3)$	$10^4 K$ (ohm^{-1} cm^{-1})
94	0.00710	46.2
96	0.00262	17.0
96	0.00497	33.5
96	0.00794	52.0
96	0.01060	70.0
96	0.01719	107.5
96	0.03045	174.3
96	0.05101	259.5
98	0.01913	109.0

TABLE 57

Solutions of Iodic Acid and Iodine in Fluorosulphuric Acid: Values of Y at the Mole Ratio I_2/HIO_3 = 2.0

$m^s(HIO_3)$	Y
0.01	2.59
0.02	2.59
0.03	2.53
0.04	2.45
0.05	2.40

TABLE 58

Solutions of Potassium Peroxodisulphate and Iodine in Fluorosulphuric Acid: Conductivities at 25°C

Experiment 84

Weight of HSO_3F 73.49 g

Composition of $K_2S_2O_8$ solution

Weight of HSO_3F 20.6360 g

Weight of $K_2S_2O_8$ 0.7509 g

Weight of I_2 (g)	Weight of $K_2S_2O_8$ solution (g)	$K_2S_2O_8/I_2$	$10^4 \kappa$ (ohm^{-1} cm^{-1})
0.0000	0.0000		1.58
0.1266	0.0000	0.000	12.64
0.1266	1.5705	0.409	25.99
0.1266	3.7633	0.980	39.58
0.1266	5.8652	1.527	51.11
0.4618	5.8652	0.419	85.98
0.4618	9.5029	0.678	117.2
0.4618	13.4734	0.962	131.0
0.4618	14.8316	1.059	135.5
0.6371	14.8316	0.767	159.5
0.6371	16.7775	0.868	164.3
0.6371	20.5529	1.063	174.0
1.2010	20.5529	0.564	211.3
1.7997	20.5529	0.376	218.0
2.0622	20.5529	0.328	224.2

(Table 58 continued)

Experiment 85

Weight of HSO_3F 87.60 g

Weight of I_2 (g)	Weight of $K_2S_2O_8$ (g)	$m^s(I_2)$	$K_2S_2O_8/I_2$	$10^4\mathcal{K}$ (ohm^{-1} cm^{-1})
0.0000	0.0000	0.00000		1.20
0.0563	0.0000	0.00253	0.000	5.45
0.0563	0.0140	0.00253	0.234	10.22
0.0563	0.0688	0.00253	1.147	18.70
0.0563	0.1150	0.00253	1.918	19.18
0.1792	0.1150	0.00806	0.602	41.35
0.1792	0.2119	0.00806	1.110	55.02
0.1792	0.2829	0.00806	1.472	65.39
0.3704	0.2829	0.01666	0.717	88.80
0.3704	0.3818	0.01666	0.968	101.9
0.3704	0.4202	0.01666	1.065	107.1
0.7395	0.4202	0.03326	0.534	156.4
0.7395	0.6936	0.03326	0.881	185.8
0.7395	0.8137	0.03326	1.033	198.9

TABLE 59

Solutions of Potassium Peroxodisulphate and Iodine in Fluorosulphuric Acid: Interpolated Conductivities at the Mole Ratio $K_2S_2O_8/I_2$ = 1.000

Experiment	$m^s(I_2)$	$10^4\mathcal{K}$ (ohm^{-1} cm^{-1})
84	0.00646	40.0
84	0.02090	133.3
84	0,02723	170.9

(Table 59 continued)

Experiment	$m^s(I_2)$	$10^4\kappa$ (ohm^{-1} cm^{-1})
85	0.00253	17.4
85	0.00806	52.1
85	0.01666	103.4
85	0.03326	196.2

TABLE 60

Solutions of Potassium Peroxodisulphate and Iodine in Fluorosulphuric Acid: Values of Y at the Ratio $K_2S_2O_8/I_2$ = 1.000

$m^s(I_2)$	Y
0.01	2.63
0.02	2.63
0.03	2.63

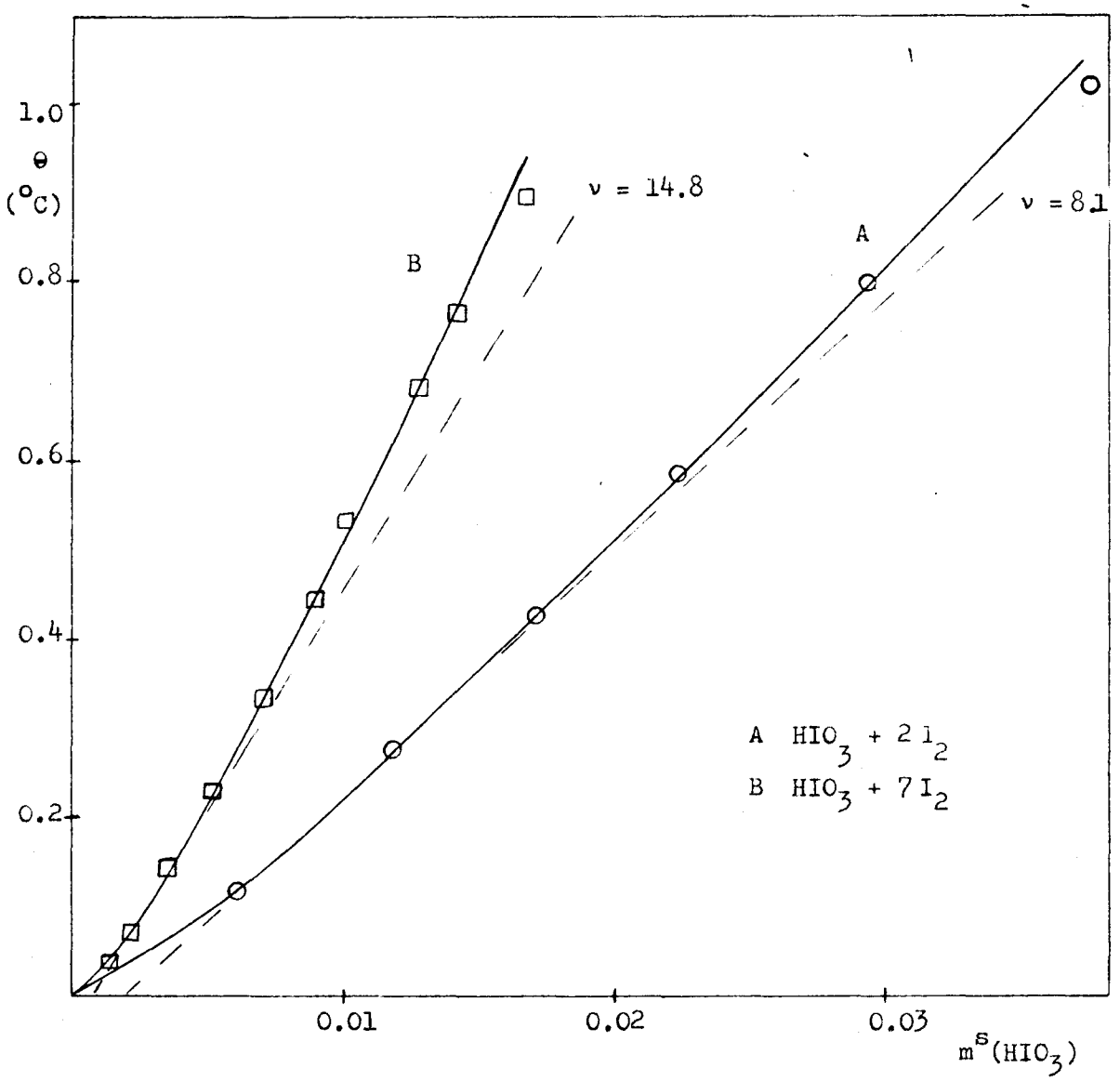


Figure 38. Solutions of "$HIO_3 + 2\,I_2$" and "$HIO_3 + 7\,I_2$" in Fluorosulphuric Acid: Freezing-point Depressions

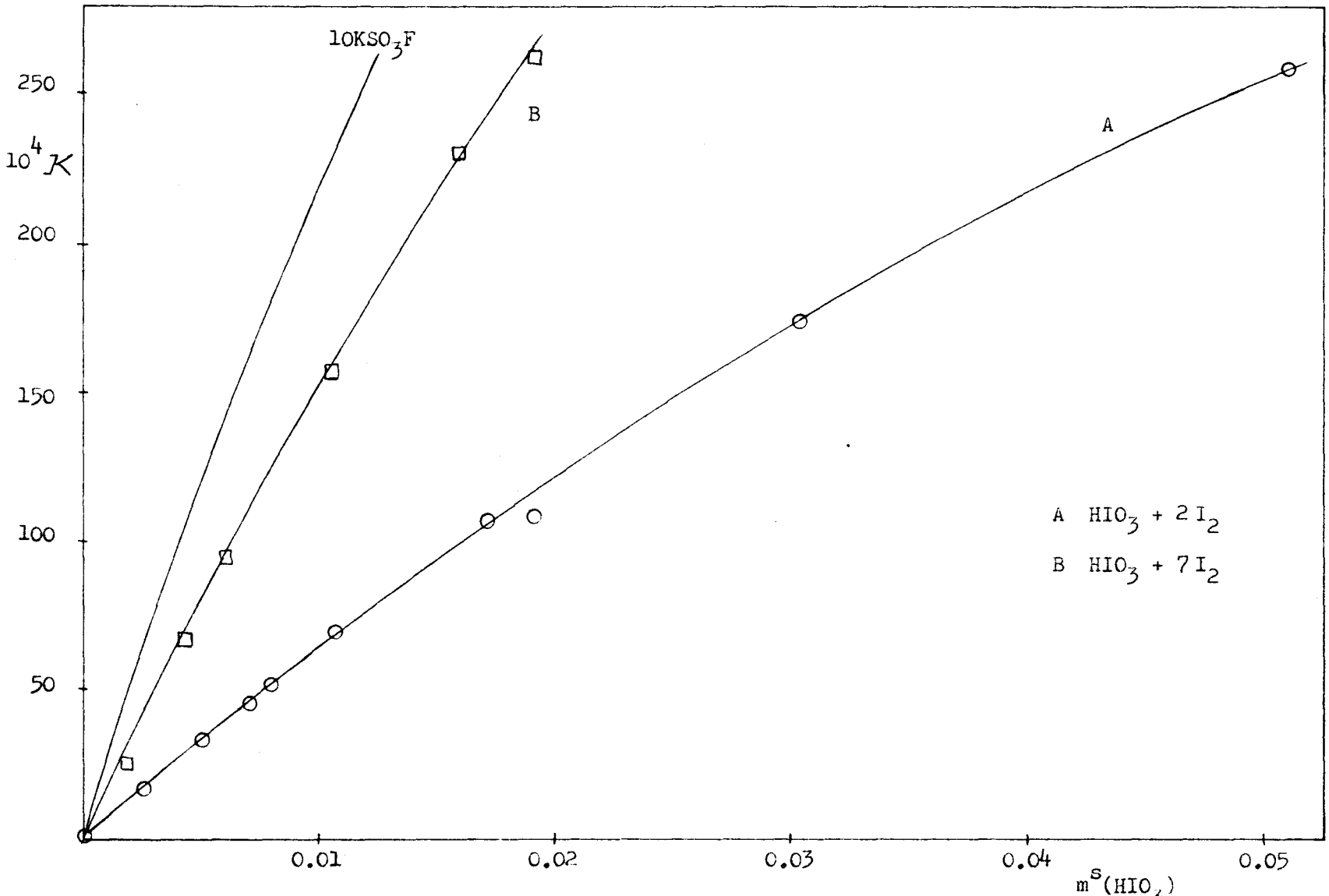


Figure 39. Solutions of "$HIO_3 + 2\,I_2$" and "$HIO_3 + 7\,I_2$" in HSO_3F: Conductivities at 25°C

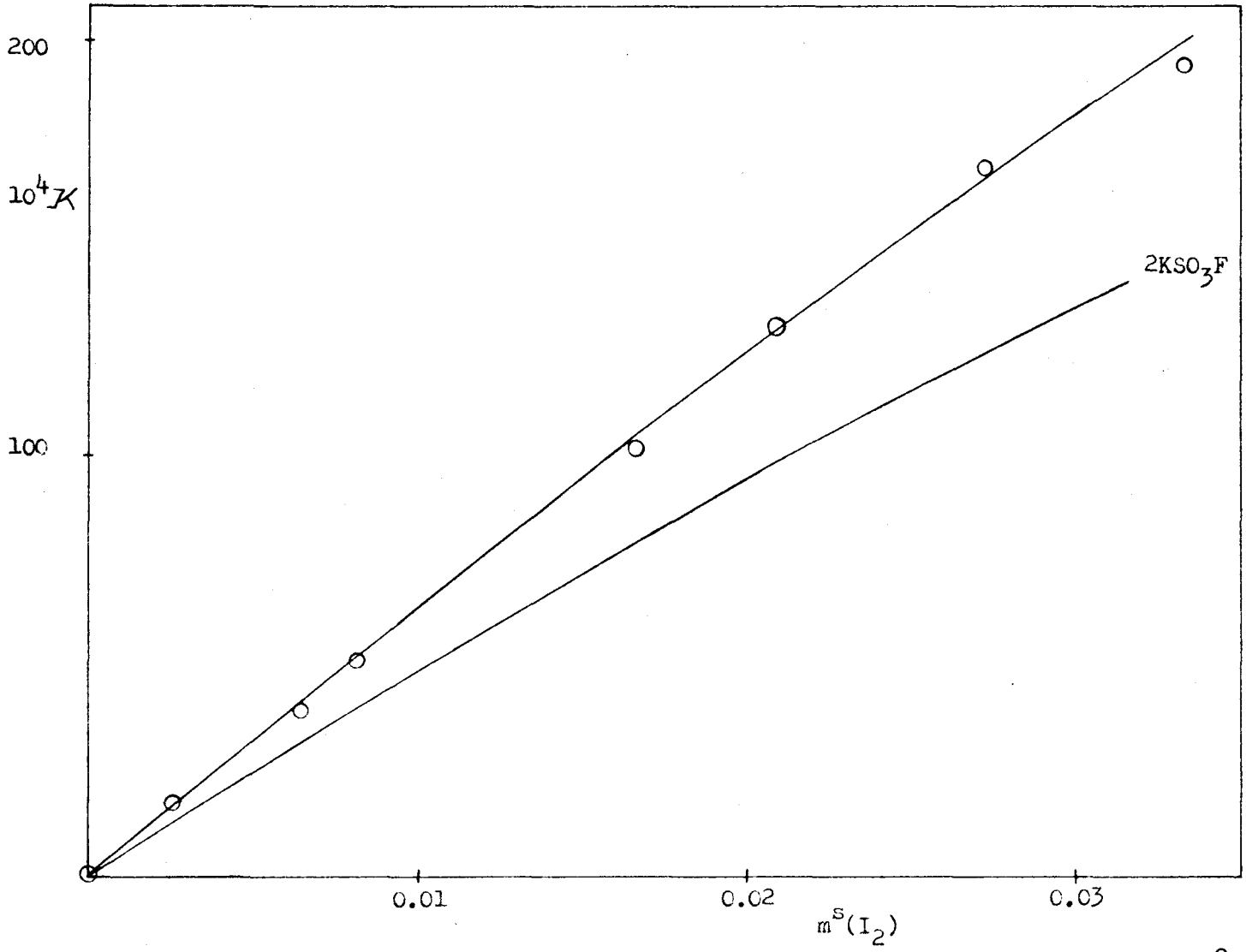


Figure 40. Solutions of "$K_2S_2O_8 + I_2$" in HSO_3F: Interpolated Conductivities at 25°C

7. Solutions of "$HIO_3 + 7I_2$" in Fluorosulphuric Acid

Cryoscopy

The solutes were added as a concentrated solution in fluorosulphuric acid, containing HIO_3 and I_2 in exactly the mole ratio $I_2/HIO_3 = 7.0$ (Table 61, Figure 38)

Conductimetry

A solution of iodic acid was prepared in the conductivity cell. Several additions of iodine were made, giving I_2/HIO_3 mole ratios in the region of 7.0. Further additions of iodic acid were made, each followed by several additions of iodine. From each set of results an interpolated value of the specific conductivity at exactly the 7.0 ratio was obtained (Tables 62, 63, Figure 39)

Discussion

For the reaction analogous to that occurring in sulphuric acid:

$$HIO_3 + 7I_2 + 8HSO_3F = 5I_3^+ + 3H_3O^+ + 8SO_3F^-$$

the predicted value of Υ is 6.56. This is in good agreement with the observed values (Table 64). The freezing-point depression curve shows the same sort of behaviour as that for water. The initial slope is much smaller than that of the remainder of the curve, tending to confirm that water is being produced in the reaction. The best estimate that can be obtained of the slope of that part of the curve above the anomalous portion, but before non-ideality becomes serious, gives a value for ν of 14.8, in reasonably good agreement with the predicted value of 16 (Figure 38).

TABLE 61

Solutions of Iodic Acid and Iodine in Fluorosulphuric Acid: Freezing Points at the Mole Ratio I_2/HIO_3 = 7.0

Experiment 106

Weight of HSO_3F (initial) 144.26 g

Composition of concentrated solution:

Weight of HSO_3F	33.8642 g
Weight of HIO_3	0.5619 g
Weight of I_2	5.6742 g
Mole Ratio, I_2/HIO_3	6.997

Weight of solution added (g)	$m^s(HIO_3)$	F.p. (°C)	θ (°C)
0.0000	0.000000	- 89.008	0.000
2.3190	0.001263	- 89.047	0.039
6.7147	0.003567	- 89.151	0.143
13.6885	0.006998	- 89.343	0.335
20.5135	0.01015	- 89.540	0.532
29.9959	0.01409	- 89.771	0.763

(Table 61 continued)

Experiment 109

Weight of HSO_3F (initial) 132.69 g

Composition of concentrated solution

Weight of HSO_3F	33.1830 g
Weight of HIO_3	0.7245 g
Weight of I_2	7.3206 g
Mole ratio, I_2/HIO_3	7.003

Weight of solution added (g)	$m^s(HIO_3)$	F.p. (°C)	θ (°C)
0.0000	0.000000	- 89.015	0.000
2.7842	0.002062	- 89.085	0.070
7.1249	0.005142	- 89.245	0.230
12.8104	0.008950	- 89.461	0.446
18.8457	0.01274	- 89.696	0.681
25.6215	0.01669	- 89.910	0.895

TABLE 62

Solutions of Iodic Acid and Iodine in Fluorosulphuric Acid: Conductivities at I_2/HIO_3 Mole Ratios Close to 7.0 (25°C)

Experiment 95

Weight of HSO_3F 95.91 g

Weight of HIO_3 (g)	Weight of I_2 (g)	$m^B(HIO_3)$	Mole Ratio I_2/HIO_3	$10^4 \kappa$ (ohm^{-1} cm^{-1})
0.0000	0.0000	0.000000		1.45
0.0303	0.0000	0.001796	0.000	4.47
0.0303	0.2518	0.001796	5.759	25.15
0.0303	0.2816	0.001796	6.440	25.02
0.0303	0.3010	0.001796	6.884	25.07
0.0303	0.3236	0.001796	7.401	25.19
0.0744	0.3236	0.004410	3.014	41.08
0.0744	0.6310	0.004410	5.878	67.33
0.0744	0.7188	0.004410	6.696	67.71
0.0744	0.7525	0.004410	7.010	67.77
0.1024	0.7525	0.006069	5.093	87.86
0.1024	0.8822	0.006069	5.971	92.11
0.1024	1.0459	0.006069	7.079	94.69
0.1764	1.0459	0.01046	4.110	125.1
0.1764	1.5074	0.01046	5.923	150.1
0.1764	1.8053	0.01046	7.093	158.2
0.2691	1.8053	0.01595	4.649	187.5
0.2691	2.3847	0.01595	6.141	220.6
0.2691	2.7481	0.01595	7.076	231.7

TABLE 63

Solutions of Iodic Acid and Iodine in Fluorosulphuric Acid: Interpolated Conductivities at the Mole Ratio $I_2/HIO_3 = 7.0$ (25°C)

Experiment	$m^s(HIO_3)$	$10^4\kappa$ (ohm^{-1} cm^{-1})
95	0.001796	25.1
	0.004410	67.8
	0.006069	94.6
	0.01046	157.7
	0.01595	231.0
98	0.01913	262.3

TABLE 64

Solutions of Iodic Acid and Iodine in Fluorosulphuric Acid: Values of Y at the Mole Ratio $I_2/HIO_3 = 7.0$

$m^s(HIO_3)$	Y
0.004	6.5
0.008	6.4
0.012	6.50
0.016	6.56
0.020	6.55

8. **Solutions of Iodic Acid and Iodine in Fluorosulphuric Acid: A Note on the Shape of Curves of Specific Conductivity Versus the Mole Ratio I_2/HIO_3**

In the conductivity run, Experiment 98, (Table 65) successive additions of iodine were made to an initial solution of iodic acid in fluorosulphuric acid, to cover the whose range of I_2/HIO_3 ratios up to 8.0. Figure 41 shows the results of this experiment, plotted as a curve of specific conductivity, K, versus the mole ratio I_2/HIO_3, along with similar curves constructed from interpolated data from other experiments, for round values of $m^s(HIO_3)$.

The curves are initially fairly flat, rising more steeply beyond the mole ratio 0.333, passing quite smoothly through the region of the mole ratio 2.0, and beginning to level off between the ratios 4.0 and 5.0. In the curve for Experiment 98, a sharp break occurs in the curve at exactly the ratio 7.0, and above this ratio the conductivity remains almost constant, actually decreasing very slightly with the addition of more iodine.

The constancy of the conductivity beyond the ratio 7.0 shows that the extra iodine takes part in a reaction which does not increase the concentration of SO_3F^- ions. This reaction must be:

$$I_3^+ + I_2 = I_5^+$$

as was shown to occur in sulphuric acid (Chapter III).

The sharpness of the break at the 7.0 ratio shows that very little of this reaction occurs below the 7.0 ratio. The rounding off of the curves below this ratio is therefore not due to the formation

of I_5^+ before the formation of I_3^+ is complete, but to the fact that significant concentrations of the iodine cation, I^+, are present at lower I_2/HIO_3 ratios. The lower dotted line A (Figure 41) shows approximately the shape of the conductivity curve expected for $m^S(HIO_3) = 0.005$ if no I^+ were formed, while the upper line, B, shows the behaviour predicted if I^+ were present in the stoichiometric amount at the ratio 2.0. The experimental curve approximates closely to B at the higher ratios showing that

$$I^+ + I_2 = I_3^+$$

is the main reaction occurring at these ratios.

TABLE 65

Solutions of Iodic Acid and Iodine in Fluorosulphuric Acid: Conductivities at 25°C

Experiment 98

Weight of HSO_3F 116.09 g

Weight of HIO_3 (g)	Weight of I_2 (g)	$m^s(HIO_3)$	I_2/HIO_3	$10^4\kappa$ (ohm^{-1} cm^{-1})
0.0000	0.0000	0.00000		1.11
0.3906	0.0000	0.01913	0.000	21.40
0.3906	0.1176	0.01913	0.209	22.06
0.3906	0.1876	0.01913	0.333	27.12
0.3906	0.2819	0.01913	0.501	34.55
0.3906	0.5653	0.01913	1.004	58.41
0.3906	1.1227	0.01913	1.995	108.6
0.3906	1.6205	0.01913	2.879	156.2
0.3906	2.1689	0.01913	3.853	198.3
0.3906	2.9207	0.01913	5.189	231.1
0.3906	3.2531	0.01913	5.780	245.2
0.3906	3.9405	0.01913	7.001	262.3
0.3906	4.1506	0.01913	7.373	261.8
0.3906	4.5170	0.01913	8.025	260.4

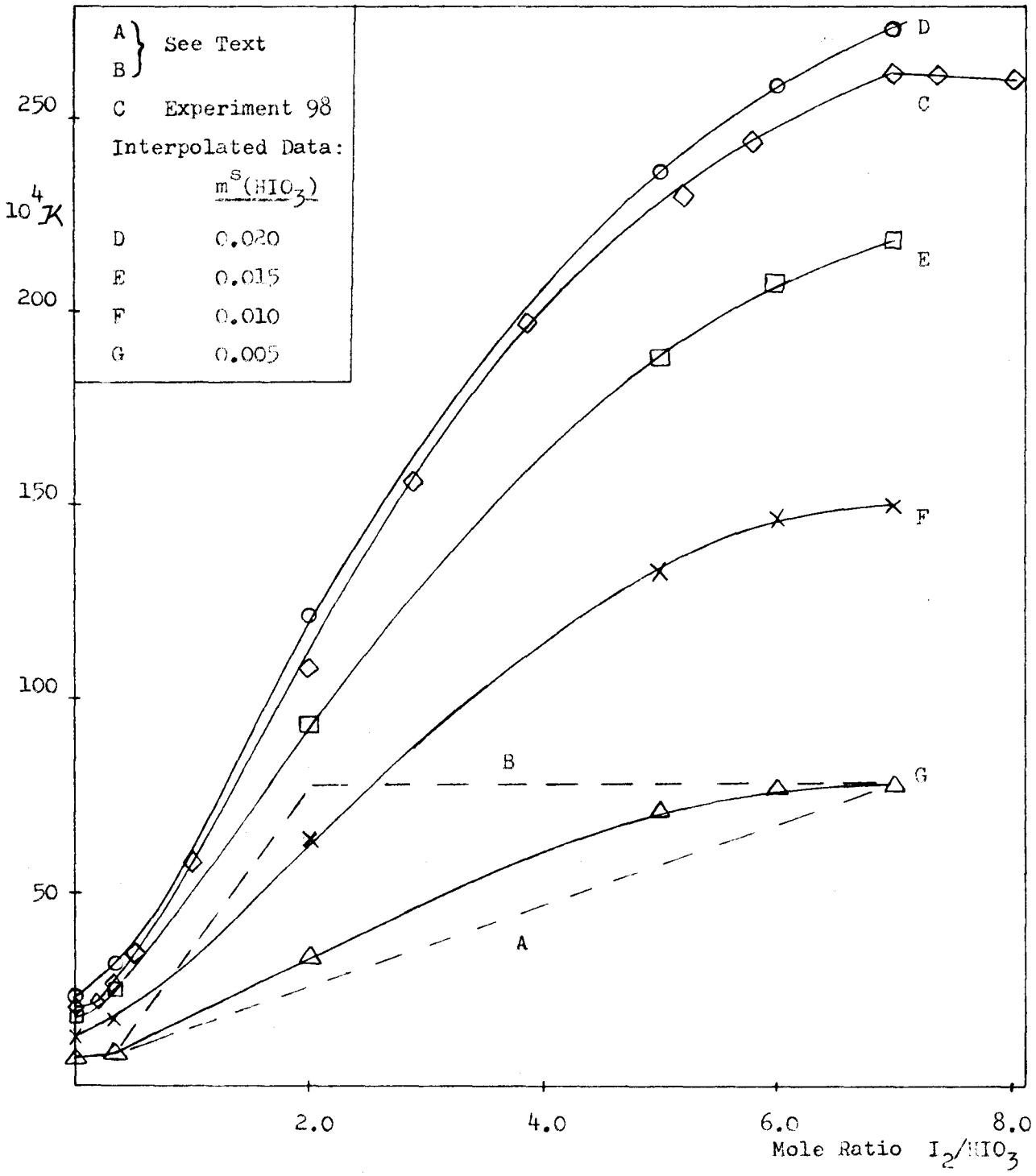


Figure 41. Solutions of HIO_3 and I_2 in HSO_3F: Conductivities at 25°C

9. Solutions of Iodine Monochloride in Fluorosulphuric Acid

Arotsky, Mishra and Symons (37) claim to have obtained blue solutions, containing the iodine cation, I^+, by dissolving iodine monochloride in fluorosulphuric acid. In the present study, this claim has been tested by a study of the conductivities of solutions of iodine monochloride in fluorosulphuric acid.

Conductimetry

The results of a conductivity run are shown in Table 66 and Figure 42. At the end of the experiment the effect on the conductivity of adding a solution of sulphur trioxide in fluorosulphuric acid, to the solution in the cell, was studied (Figure 43).

Discussion

Blue solutions of iodine monochloride in fluorosulphuric acid were not obtained. The most dilute solution studied was a dirty green colour. More concentrated solutions were brown. Values of Υ, which are quite low, and decrease with increasing concentration, are given in Table 67. These values of Υ are clearly too small to be consistent with complete reaction according to

$$ICl + HSO_3F \rightleftharpoons I^+ + SO_3F^- + HCl \qquad [1]$$

For an equilibrium reaction according to Equation [1], the equilibrium constant would be given by

$$K_1 = \frac{[I^+][SO_3F^-][HCl]}{[ICl]} = \frac{\Upsilon^3 m^2}{1-\Upsilon}$$

where $m = m^{S}(ICl)$. The values of K_1 calculated from this expression (Table 67, Column 3) show a considerable variation with concentration.

Since the probable existence of the ion I_2Cl^+ in sulphuric acid has been demonstrated (Chapter III, Section 8), we may consider an equilibrium:

$$2ICl + HSO_3F \rightleftharpoons I_2Cl^+ + SO_3F^- + HCl \qquad [2]$$

for which the equilibrium constant would be

$$K_2 = \frac{[I_2Cl^+][SO_3F^-][HCl]}{[ICl]^2} = \frac{\gamma^3 m}{(1-2\gamma)^2}$$

The values of K_2 (Table 67, Column 4) decrease slightly with increasing concentration, but are much more constant than the values of K_1.

A third reaction which may be considered is partial protonation of ICl:

$$ICl + HSO_3F \rightleftharpoons HICl^+ + SO_3F^- \qquad [3]$$

having an equilibrium constant:

$$K_3 = \frac{[HICl^+][SO_3F^-]}{[ICl]} = \frac{\gamma^2 m}{1-\gamma}$$

K_3 (Table 67, Column 5) is somewhat less constant than K_2.

Thus a reversible reaction according to Equation [2] best fits the conductivity data. The high values of K_2 at low concentrations, and the green colour of very dilute solutions, may be accounted for by

supposing that some I^+ is also formed according to Equation [1], this reaction being of greatest importance at low concentrations.

The addition of sulphur trioxide caused a marked increase in the conductivity, up to an SO_3/ICl mole ratio of about 0.8, after which further additions of SO_3 caused the conductivity to decrease (Figure 43). At an SO_3/ICl ratio close to 3.0, the solution was a dirty olive-green colour.

This may be accounted for by supposing that sulphur trioxide takes part in a reversible reaction with the hydrogen chloride produced in reactions [1] and [2], to form chlorosulphuric acid:

$$HCl + SO_3 \rightleftharpoons HSO_3Cl \qquad [4]$$

The removal of HCl by this reaction would displace the equilibria [1] and [2] to the right, increasing the concentration of fluorosulphate ions, and thereby increasing the conductivity. The addition of sulphur trioxide to a solution of potassium fluorosulphate in fluorosulphuric acid decreases the conductivity and it has been suggested that this is due to the replacement of the highly mobile SO_3F^- ions by the less mobile $S_2O_6F^-$ ions (98).

$$SO_3F^- + SO_3 \rightleftharpoons S_2O_6F^- \qquad [5]$$

In the present case, when the rate of removal of fluorosulphate ions by reaction [5] exceeds their rate of formation by the displacement of the equilibria [1] and [2], the conductivity will begin to decrease as more SO_3 is added, in agreement with the experimental results.

An indication that the production of the green (or blue) colour

in very dilute solutions of iodine monochloride in fluorosulphuric acid may be related to the presence of free sulphur trioxide, comes from the observation that when a trace of iodine monochloride was added to a solution of potassium fluoride in fluorosulphuric acid, the solution formed was brown. When potassium fluoride was added to a green solution of iodine monochloride in fluorosulphuric acid, the solution became brown. Thus when sulphur trioxide is removed in the equilibrium:

$$HF + SO_3 \rightleftharpoons HSO_3F$$

the corresponding displacements of equilibria [4] and [1] also remove the iodine cation from the solution.

TABLE 66

Solutions of Iodine Monochloride and of Iodine Monochloride and Sulphur Trioxide in Fluorosulphuric Acid: Conductivities at 25°C

Experiment 99

Weight of HSO_3F 88.66 g

Composition of SO_3 solution

Weight of HSO_3F 11.2493 g
Weight of SO_3 8.5348 g

Weight of ICl (g)	Weight of SO_3 solution added (g)	$m^s(ICl)$	SO_3/ICl	$10^4\kappa$ ($ohm^{-1}\,cm^{-1}$)
0.0000	0.0000	0.00000		1.19
0.0552	0.0000	0.00383	0.000	2.92
0.1833	0.0000	0.01273	0.000	11.37
0.4522	0.0000	0.03141	0.000	23.29
0.8090	0.0000	0.05618	0.000	31.58
1.6388	0.0000	0.1138	0.000	52.88
1.6388	0.2265	0.1137	0.121	61.33
1.6388	1.7403	0.1126	0.929	104.2
1.6388	2.1844	0.1122	1.166	102.9
1.6388	3.1643	0.1116	1.688	99.80
1.6388	4.9627	0.1103	2.647	93.55

TABLE 67

Solutions of Iodine Monochloride in Fluorosulphuric Acid: Values of γ, K_1, K_2 and K_3

m	γ	$K_1 = \frac{\gamma^3 m^2}{1-\gamma}$	$K_2 = \frac{\gamma^3 m}{(1-2\gamma)^2}$	$K_3 = \frac{\gamma^2 m}{1-\gamma}$
		(mole^2 kg^{-2})	(mole kg^{-1})	(mole kg^{-1})
0.02	0.30	0.000015	0.0034	0.0026
0.04	0.26	0.000036	0.0028	0.0035
0.06	0.23	0.000059	0.0027	0.0043
0.08	0.21	0.000079	0.0023	0.0046
0.10	0.20	0.000095	0.0021	0.0048

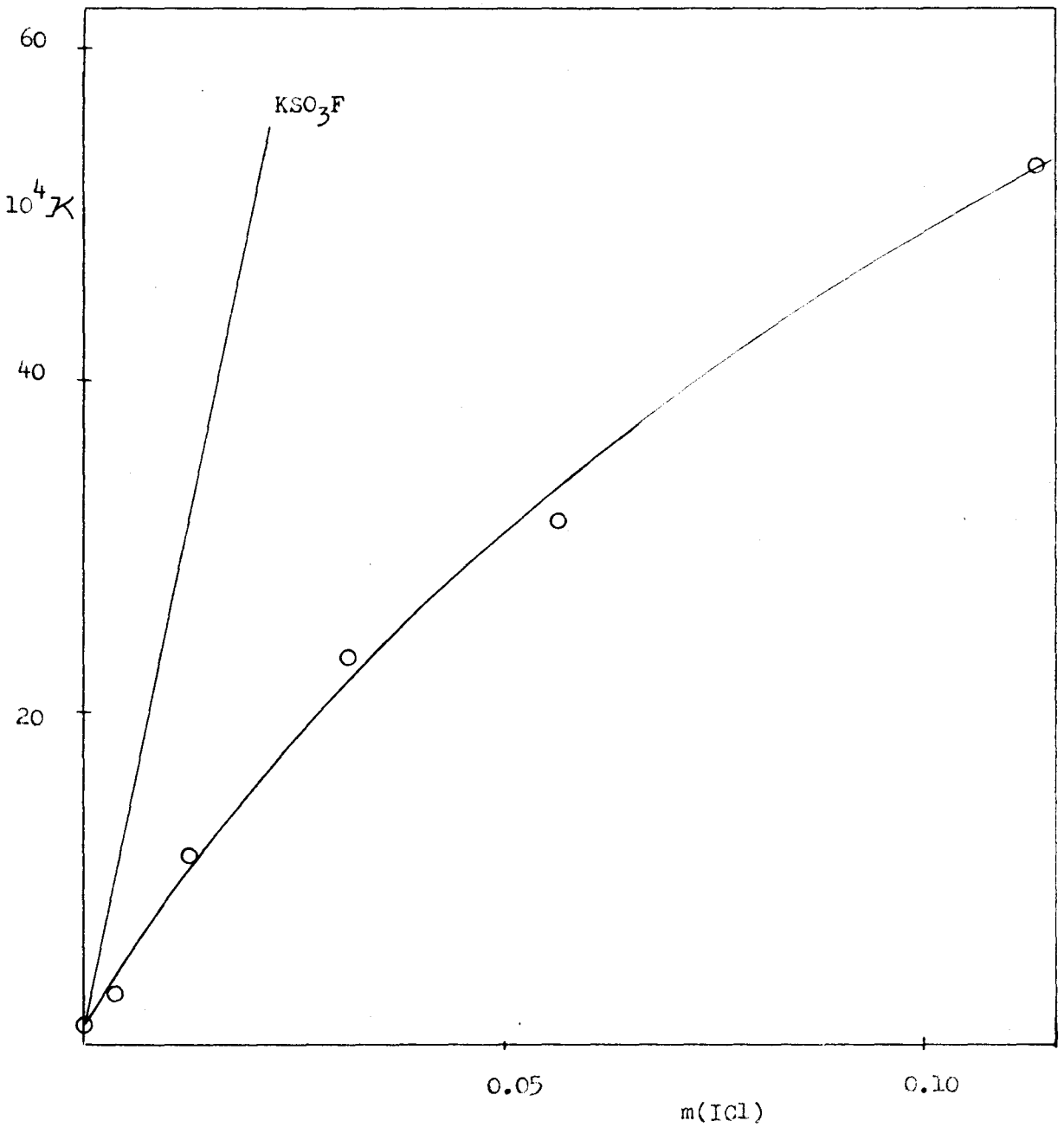


Figure 42. Solutions of ICl in HSO_3F: Conductivities at 25°C

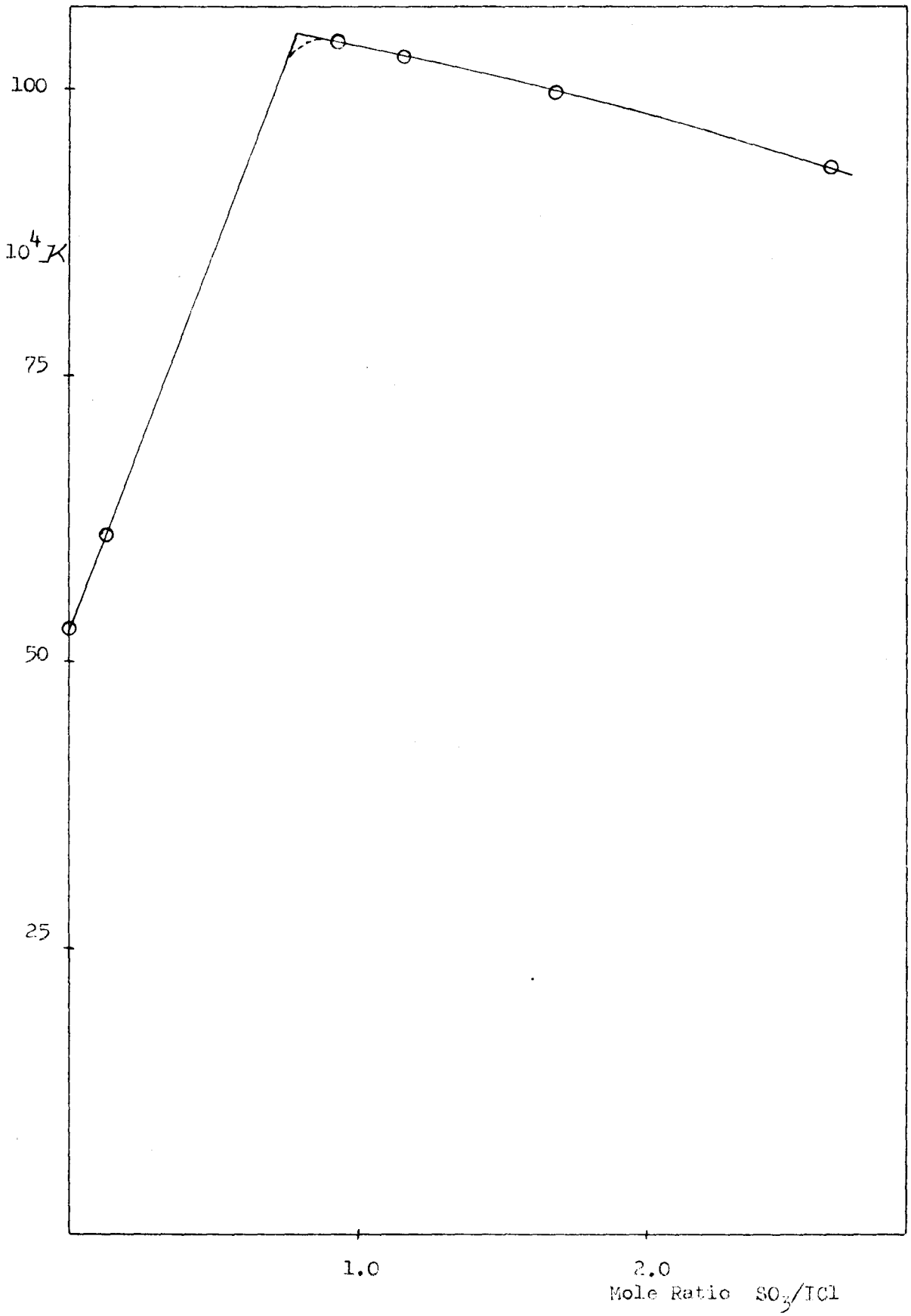


Figure 43. Solutions of ICl and SO_3 in HSO_3F: Conductivities at 25°C

10. Solutions of Dipyridineiodine (I) Salts in Fluorosulphuric Acid

The results of conductivity runs on dipyridineiodine (I) nitrate and perchlorate are shown in Tables 68 and 69 and Figure 44. The solutions of the nitrate were bright green, while those of the perchlorate were yellow.

The reactions to give the free I^+ ion are, in the two cases

$$Ipy_2\,NO_3 + 5HSO_3F = 2pyH^+ + NO_2^+ + H_3O^+ + I^+ + 5SO_3F^- \quad [1]$$

$$\Upsilon = 4.4$$

$$Ipy_2\,ClO_4 + 3HSO_3F = 2pyH^+ + I^+ + HClO_4 + 3SO_3F^- \quad [2]$$

$$\Upsilon = 3$$

In fact the perchlorate has a value of Υ only slightly greater than 2, while the nitrate has an almost constant Υ-value of 3.45.

These Υ values can be accounted for almost entirely in terms of fluorosulphate ions corresponding to the cations other than I^+. Evidently I^+ cannot be formed to any appreciable extent. Although it is possible that the iodine is present as un-ionized ISO_3F, it is equally likely that it is oxidized to a higher valence state by NO_2^+ or $HClO_4$. The different colours of the solutions suggest that the state of the iodine is not the same in the two cases, but unfortunately it is not possible to reach any certain conclusions about this from the present results.

TABLE 68

Solutions of Dipyridineiodine (I) Nitrate in Fluorosulphuric Acid: Conductivities at 25°C

Experiment 77

Weight of HSO_3F 91.68 g

Weight of Ipy_2NO_3	m	$10^4\kappa$ (ohm^{-1} cm^{-1})
0.0000	0.00000	1.33
0.2110	0.00663	55.55
0.4863	0.01538	122.6
0.8701	0.02734	209.3

TABLE 69

Solutions of Dipyridineiodine (I) Perchlorate in Fluorosulphuric Acid: Conductivities at 25°C

Experiment 81

Weight of HSO_3F 76.81 g

Weight of Ipy_2ClO_4	m	$10^4\kappa$ (ohm^{-1} cm^{-1})
0.0000	0.00000	1.15
0.0619	0.00210	11.69
0.1613	0.00546	29.13
0.2867	0.00971	50.43
0.4430	0.01499	75.83

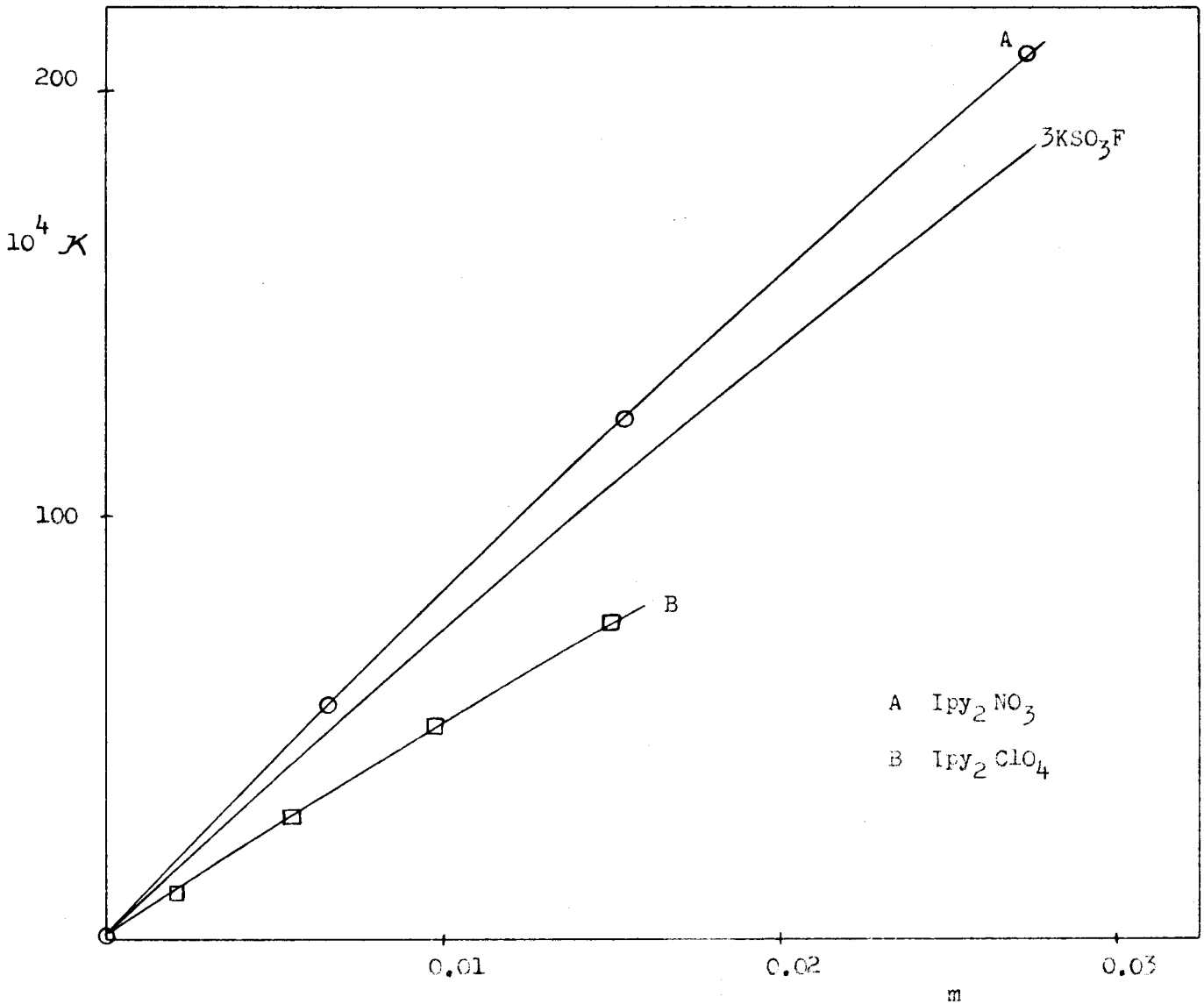


Figure 44. Solutions of Dipyridineiodine (I) Salts in HSO_3F: Conductivities at 25°C

11. Solutions of Potassium Dioxodifluoroiodate (V) in Fluorosulphuric Acid

The results of a conductivity run are shown in Table 70 and Figure 45.

One possible reaction is the solvolysis of the salt, to give the free acid HIO_2F_2 in solution:

$$KIO_2F_2 + HSO_3F = K^+ + SO_3F^- + HIO_2F_2 \qquad [1]$$

The compound HIO_2F_2 might behave as a simple base, being completely or partially protonated:

$$HIO_2F_2 + HSO_3F \rightleftharpoons H_2IO_2F_2^+ + SO_3F^- \qquad [2]$$

The value of K_b for this reaction is given by

$$K_b = \frac{[H_2IO_2F_2^+][SO_3F^-]}{[HIO_2F_2]} = \frac{\gamma(\gamma-1)m}{2-\gamma}$$

Values of γ and K_b are shown in Table 71. The values of γ are slightly greater than 1, decreasing with increasing concentration. K_b is reasonably constant over the concentration range covered.

An alternative reaction is the formation of the species $(IOF_2SO_3F)_2$, considered to be present in solutions of iodic acid in fluorosulphuric acid:

$$KIO_2F_2 + 3HSO_3F = K^+ + H_3O^+ + 1/2(IOF_2SO_3F)_2 + 2SO_3F^- \qquad [3]$$
$$\gamma = 1.6$$

The observed values of γ are too small to be consistent with this reaction.

TABLE 70

Solutions of Potassium Dioxodifluoroiodate (V) in Fluorosulphuric Acid: Conductivities at 25°C

Experiment 119

Weight of HSO_3F 60.25 g

Weight of KIO_2F_2 (g)	m	$10^4\kappa$ (ohm^{-1} cm^{-1})
0.0000	0.00000	1.34
0.1506	0.01059	35.98
0.5712	0.04016	111.8
1.0843	0.07625	191.0
1.3725	0.09651	230.7
1.7381	0.1222	276.3

TABLE 71

Solutions of Potassium Dioxodifluoroiodate (V) in Fluorosulphuric Acid: Values of Υ and K_b

m	Υ	$K_b = \frac{\Upsilon(\Upsilon - 1)\,m}{2 - \Upsilon}$
0.02	1.24	0.008
0.04	1.17	0.010
0.06	1.13	0.011
0.08	1.11	0.011
0.10	1.08	0.009

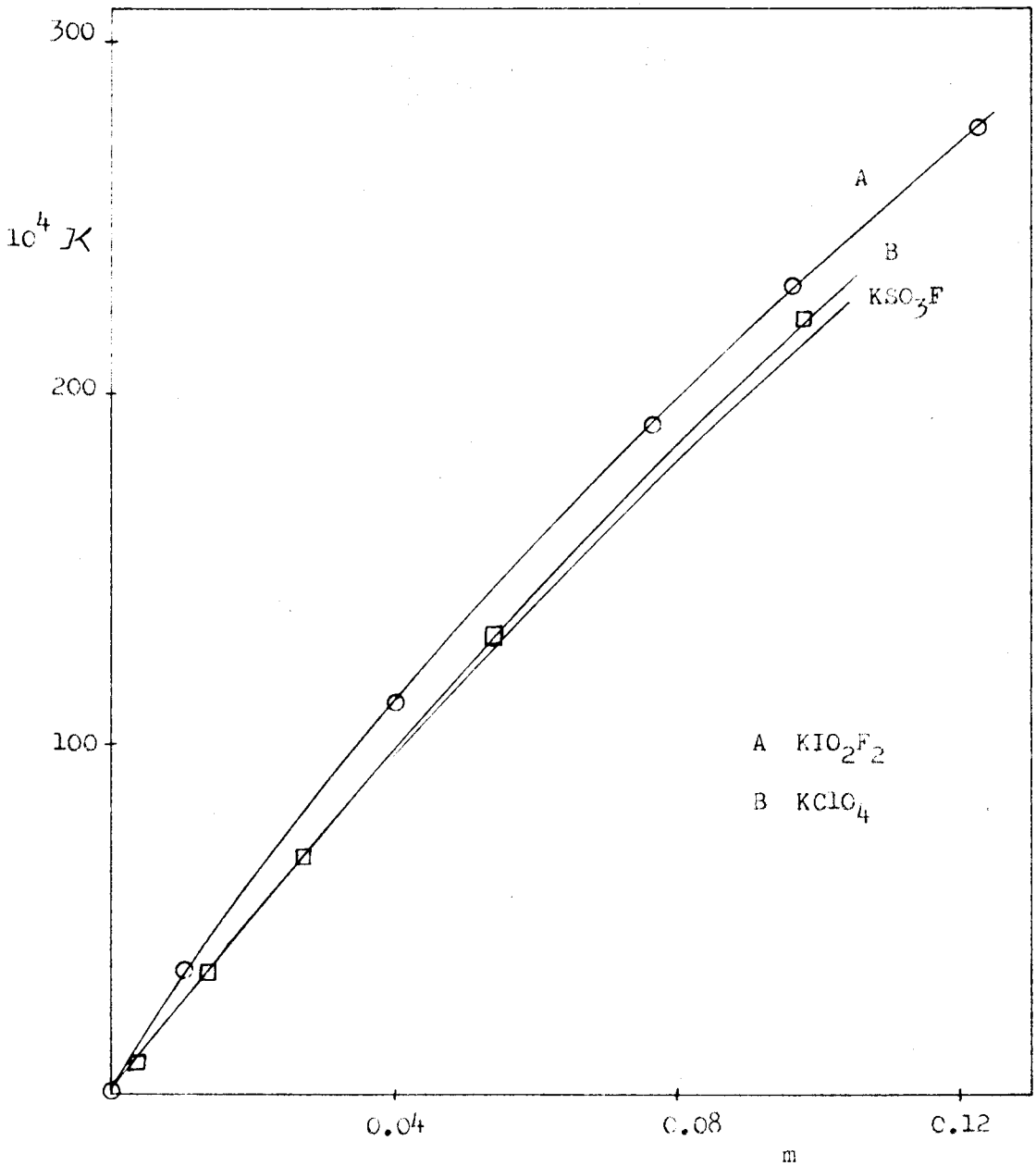


Figure 45. Solutions of KIO_2F_2 and of $KClO_4$ in HSO_3F: Conductivities at 25°C

12. Solutions of Potassium Perchlorate in Fluorosulphuric Acid

The results of a conductimetric experiment on potassium perchlorate are shown in Table 72 and Figure 45. The conductivities are very slightly greater than those of solutions of potassium fluorosulphate of the same concentration. The results indicate that potassium perchlorate undergoes complete solvolysis

$$KClO_4 + HSO_3F = K^+ + SO_3F^- + HClO_4$$

and that in addition perchloric acid probably behaves as a very weak base in fluorosulphuric acid

$$HClO_4 + HSO_3F \rightleftharpoons H_2ClO_4^+ + SO_3F^-$$

If it behaved as an acid, the conductivity would be slightly less, instead of slightly greater, than that of potassium fluorosulphate. The difference between the conductivities of solutions of potassium fluorosulphate and potassium perchlorate is however so small that it could quite possible be accounted for by a small difference in the viscosities due to the presence of perchloric acid in the latter solutions.

TABLE 72

Solutions of Potassium Perchlorate in

Fluorosulphuric Acid: Conductivities at 25°C

Experiment 83

Weight of HSO_3F 91.41 g

Weight of $KClO_4$ (g)	m	$10^4 \kappa$ (ohm^{-1} cm^{-1})
0.0000	0.00000	1.19
0.0426	0.00336	9.60
0.1729	0.01365	35.66
0.3402	0.02686	68.05
0.6858	0.05414	131.0
1.2426	0.09812	221.5

CHAPTER V

ULTRA-VIOLET AND VISIBLE ABSORPTION SPECTRA

1. Introduction

Arotsky, Mishra and Symons (37) have studied the absorption spectra of solutions of iodine and iodine monochloride in 65% oleum. They found a strong absorption band at 640 mμ, and weaker bands at 500 and 410 mμ. In solutions of iodine, but not of iodine monochloride, they found a band at 280 mμ which was attributed to sulphur dioxide. Under a variety of conditions, the ratios of the optical densities at 640, 500 and 410 mμ always remained the same, so these three bands were assigned to a single species, considered to be the iodine cation, I^+, formed in the reactions:

$$I_2 + 3SO_3 + H_2S_2O_7 = 2I^+ + SO_2 + 2HS_2O_7 \qquad [1]$$

$$ICl + SO_3 + H_2S_2O_7 = I^+ + HSO_3Cl + HS_2O_7^- \qquad [2]$$

The spectrum was explained by supposing the iodine cation, which has the configuration $5s^2\ 5p^4$, to be surrounded by four solvent molecules. These molecules will tend to avoid the filled p orbital (p_z, say), and will therefore lie in the plane of the half-filled p_x and p_y orbitals. The energy of the configuration having a filled p_z orbital will thus be lowered relative to that of the configuration in which the filled orbital is p_x or p_y. These levels are described as $^3\Sigma^-$ and $^3\Pi_i$ respectively. The $^3\Pi$ level will be split into $^3\Pi_2$,

$^3\Pi_1$ and $^3\Pi_0$ levels, of which $^3\Pi_2$ will be the closest to the ground state. The observed absorption bands are due to the three $^3\Pi_i \rightarrow {}^3\Sigma^-$ transitions, the lowest energy transition being the most intense.

Symons (36) has also studied the absorption spectra of the brown solutions of iodine in dilute oleums, which have absorption bands at 460 and 290 mμ, attributed to I_3^+. Solutions of iodosyl sulphate in sulphuric acid and oleum have no well-defined absorption bands. Absorption begins at about 450 mμ, levels out to a plateau in the region of 330 mμ and rises steeply beyond 300 mμ (36).

2. <u>Absorption spectra of solutions of iodine and of iodine monochloride in 65% oleum</u>

The spectra of solutions of iodine and iodine monochloride in 65% oleum were studied using 1 cm and 1 mm cells. Absorption maxima were found at 640, 500 and 410 mμ, in agreement with the findings of Arotsky et al (37). A typical spectrum is shown in Figure 46(a). Plots of (optical density/sample thickness) versus the stoichiometric concentration of I^+, for the absorption maximum at 640 mμ, gave the same straight line, within experimental error, for both solutes, (Figure 47), i.e. the Beer-Lambert Law is obeyed over the range of concentrations studied. This is consistent with the quantitative formation of I^+ in both cases, according to Equations [1] and [2]. From the slope of the curve, the extinction coefficient, ϵ_{640}, for I^+ at 640 mμ, was found to be 12.1×10^2, in poor agreement with the value $\epsilon_{640} = 18.5 \times 10^2$ reported by Arotsky et al (37). From a diagram of the absorption spectrum of an 0.0005 M solution of iodine in 50% oleum, given by Moknach et al, (39) the value $\epsilon_{640} \approx 13 \times 10^2$ may be estimated, in better agreement

with the present result than with that of Arotsky et al.

3. Absorption spectra of solutions of iodic acid and iodine in sulphuric acid

Solutions containing iodic acid and iodine in different mole ratios were prepared by mixing together appropriate amounts of a solution of iodic acid and of a solution containing iodic acid and iodine in the mole ratio $I_2/HIO_3 = 7$, and diluting the mixtures with 100% sulphuric acid.

Solutions containing the solutes in the mole ratio $I_2/HIO_3 = 7.0$, have the absorption maximum at 460 mμ, attributed to I_3^+ (36). There is also strong absorption at lower wavelengths, which is presumably the beginning of the band at 290 mμ found by Symons (36), (Figure 46 (b)).

Solutions containing the solutes in the mole ratio $I_2/HIO_3 = 2.0$, corresponding to the stoichiometric formation of I^+, have the strong absorption band at 640 mμ characteristic of I^+, and also a strong band at about 460 mμ, overlapping with the 500 and 410 mμ bands of I^+, showing that a considerable concentration of I_3^+ is present, owing to disproportionation of I^+ (Figure 46 (b)).

Insufficient data were obtained to permit a quantitative treatment, but the results indicate that only about one-third of the stoichiometric amount of iodine is present as I^+, the rest having undergone disproportionation. This is a considerably higher proportion of I^+ than seems to be present in the much more concentrated solutions ($M^s(HIO_3) \approx 0.01$) studied cryoscopically and conductimetrically. Since the disproportionation reaction:

$$4I^+ + H_3O^+ + 3HSO_4^- \rightleftharpoons I_3^+ + IO^+ + 3H_2SO_4$$

involves a decrease in the number of solute particles from 8 to 2, the position of the equilibrium would be expected to be very concentration-dependent, the extent of disproportionation increasing with increasing concentration, so that this result is not surprising.

Solutions having mole ratios, I_2/HIO_3, between 2.0 and 7.0, absorbed strongly at 640 mμ as well as at 460 mμ when first made up, but in the course of a few days their colour changed from green to brown, and the peak at 460 mμ grew, while that at 640 mμ decreased in intensity (Figure 46 (c)). Thus the reaction of I_3^+ with iodic acid, to form I^+, must be much more rapid than the subsequent disproportionation of the latter to give IO^+ and I_3^+.

4. Absorption spectra of solutions in fluorosulphuric acid

The absorption spectra of solutions of iodic acid and iodine at the mole ratios I_2/HIO_3 = 0.33, 2.0 and 7.0, and of a solution of equimolar amounts of iodine and potassium peroxodisulphate, in fluorosulphuric acid, were examined. The positions of the absorption maxima, and the optical densities at 640 mμ (for solutions in a 1 cm cell) are shown in Table 73.

The spectra of iodic acid-iodine solutions with I_2/HIO_3 = 0.33 and 2.0, and of the I_2-$K_2S_2O_8$ solution, were similar to those of solutions of iodine or iodine monochloride in 65% oleum, except that the position of one of the absorption maxima shifted from 500 to 485 mμ.

Assuming $\epsilon_{640} = 12.1 \times 10^2$ for I^+, as found for oleum solutions, the results indicate that in solutions with I_2/HIO_3 = 0.33, about two-fifths of the stoichiometric amount of trivalent iodine is disproportionated to give I^+, and species containing pentavalent iodine.

In solutions with I_2/HIO_3 = 2.0, the observed optical density corresponded to about 90% of the stoichiometric concentration of I^+, while for the iodine-peroxodisulphate solution the optical density corresponded to about 95% of the stoichiometric concentration of I^+. Since, as has already been shown,(Chapter IV) the position of the equilibrium in the disproportionation of I^+ should be very concentration-dependent, these results are not inconsistent with the extensive disproportionation of I^+ indicated by the results of cryoscopic and conductimetric studies on very much more concentrated solutions.

A solution with I_2/HIO_3 = 7.0 had strong absorption bands at both 640 and 465 mμ. This indicates that in addition to the I_3^+ expected at this mole ratio, a considerable amount of I^+ was also present. It is suggested that during the preparation of the solution some oxidation of iodine by the free SO_3 in the solvent occurred, as well as oxidation by iodic acid. Thus the net oxidation state of the iodine in the solution would be higher than that corresponding to I_3^+.

5. Absorption spectrum of a solution of iodine in antimony pentafluoride

A solution of iodine in antimony pentafluoride had the characteristic blue colour of solutions of I^+ in other solvents, and showed the same characteristic absorption maxima, indicating the presence of I^+ in this solution also.

6. Discussion

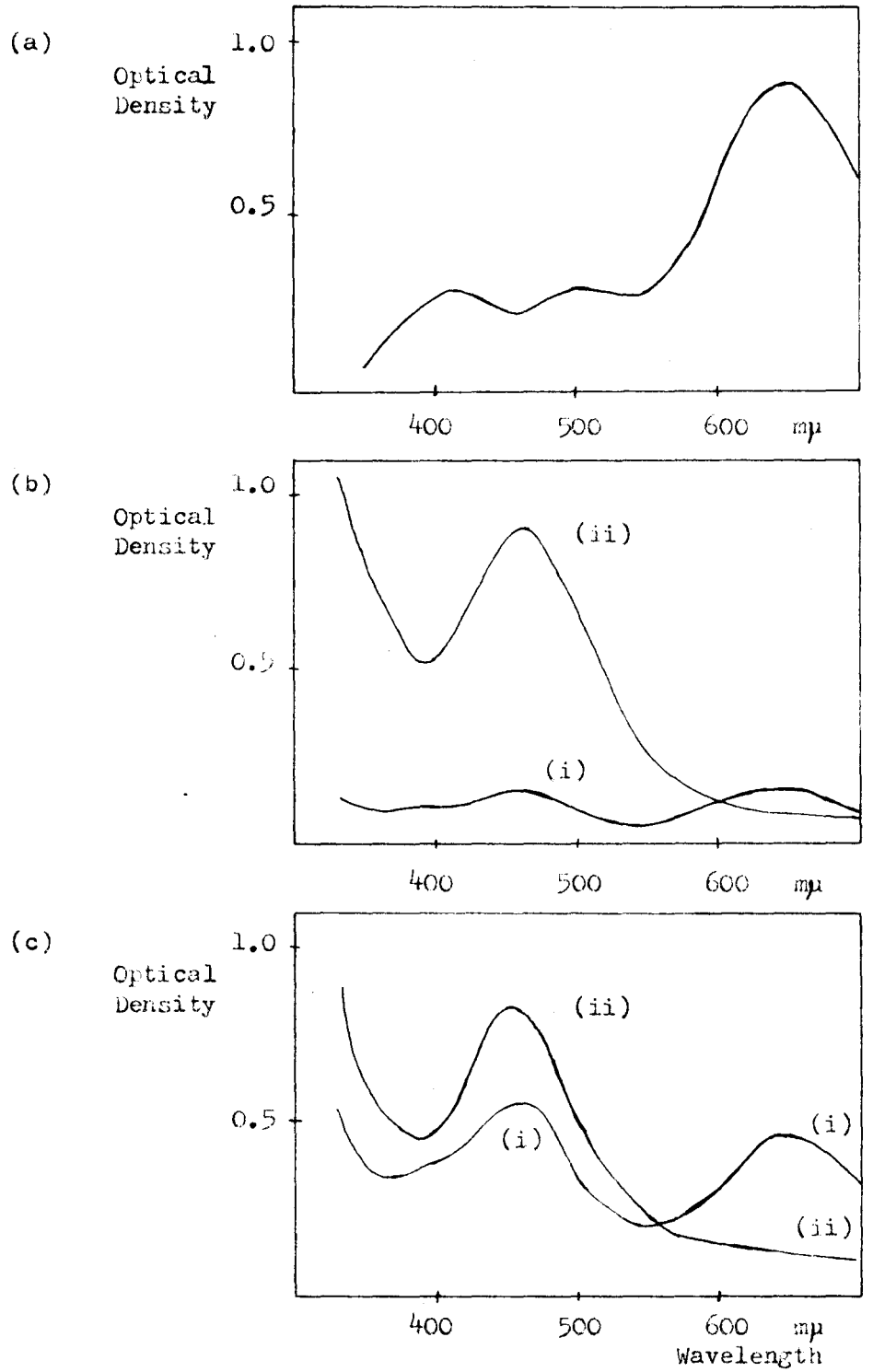
The almost identical spectra of the blue solutions in 65% oleum, fluorosulphuric acid, and antimony pentafluoride, show that the same species is present in each solvent, and that it can therefore contain only iodine. While it is almost certainly solvated, it cannot be

covalently bonded to any specific solvent molecule. The production of this species in SbF_5 shows that it cannot be the ion ISO_3^+, which was discussed and rejected on other grounds by Arotsky, Mishra and Symons (37). All the evidence is consistent with this species being the iodine cation, I^+.

TABLE 73

Absorption Spectra of Solutions in Fluorosulphuric Acid

Solute	Concentration	Positions of Maxima (wavelengths in mμ)	Optical Density at 640 mμ (solutions in 1 cm cell)
$HIO_3 + 0.33I_2$	$M^S(HIO_3) = 7.66 \times 10^{-4}$	410, 485, 640	0.32
$HIO_3 + 2I_2$	$M^S(HIO_3) = 0.93 \times 10^{-4}$	405, 485, 640	0.50
$HIO_3 + 7I_2$	$M^S(HIO_3) = 0.65 \times 10^{-4}$	465, 640	0.48
$K_2S_2O_8 + I_2$	$M^S(I_2) = 1.91 \times 10^{-4}$	400, 485, 640	0.44



(a) I_2 in 65% Oleum

(b) (i) $HIO_3 + 2\,I_2$ in H_2SO_4 (ii) $HIO_3 + 7\,I_2$ in H_2SO_4

(c) $HIO_3 + 3.5\,I_2$ in H_2SO_4. (i) After 10 minutes (ii) After 4 days

Figure 46. Absorption Spectra of Solutions in H_2SO_4 and 65% Oleum

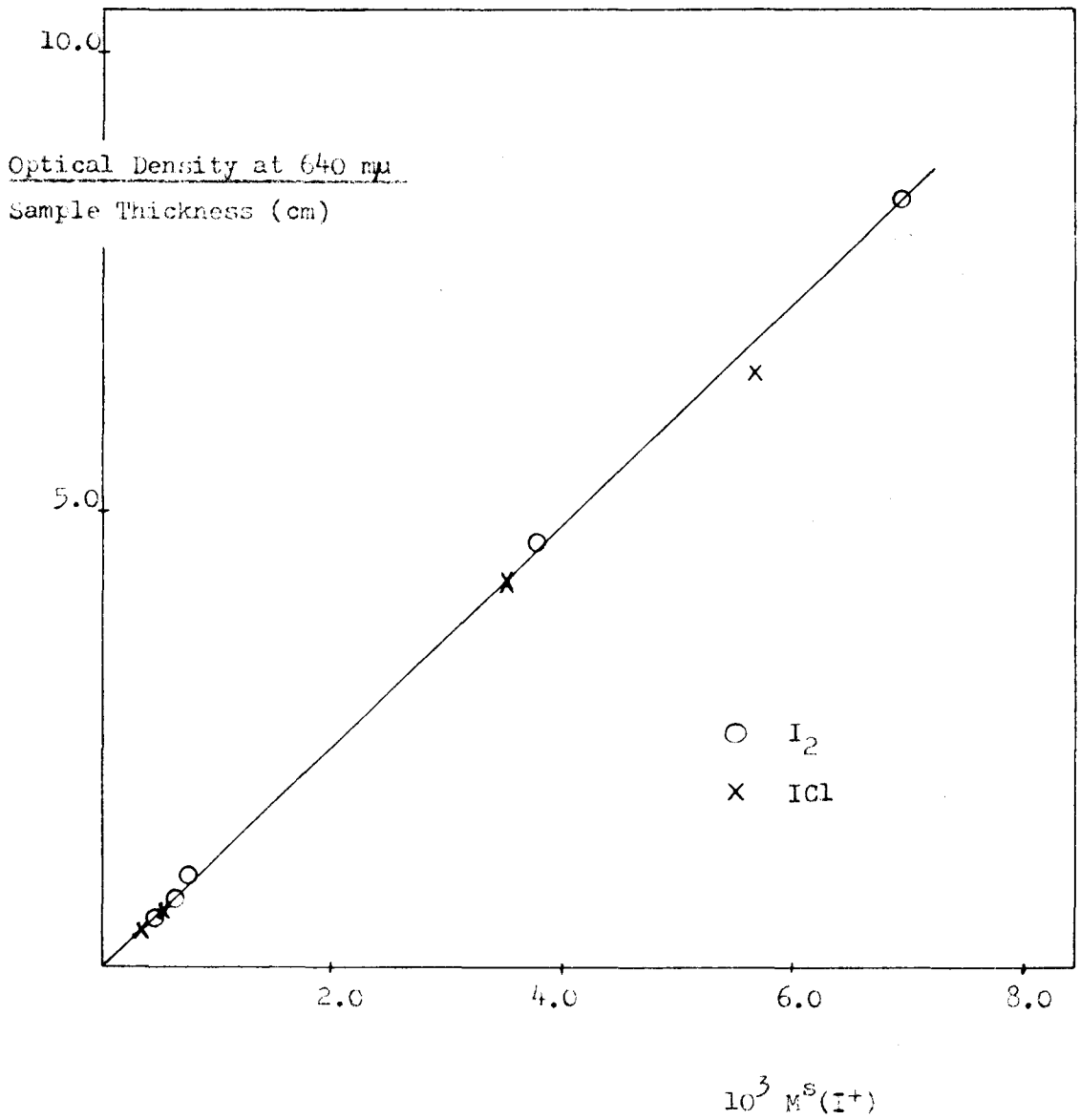


Figure 47. Beer-Lambert Law Plot for Solutions of I_2 and ICl in 65% Oleum

CHAPTER VI

NUCLEAR MAGNETIC RESONANCE SPECTRA OF

SOLUTIONS CONTAINING THE IODINE CATION

1. Introduction

The magnetic field, H, acting on a molecule situated in a spherical cavity in a medium of volume magnetic susceptibility χ_v is given by:

$$H = H_o\left[1 + \left(\frac{4\pi}{3} - \alpha\right)\chi_v\right] \qquad [1]$$

where H_o is the external applied field, and α is a numerical factor depending upon the shape of the specimen. For a cylinder whose length is large compared with its radius, $\alpha = 2\pi$, and we have:

$$H = H_o\left(1 - \frac{2\pi}{3}\chi_v\right) \qquad [2]$$

Thus a molecule situated in a diamagnetic medium, for which χ_v is negative, "sees" a magnetic field larger than the applied field, while a molecule in a paramagnetic medium "sees" a field smaller than the applied field. In a nuclear magnetic resonance experiment, a given nucleus in a molecule will therefore resonate at a higher applied field when it is in a solution containing paramagnetic ions, than it would in a similar solution in the absence of the paramagnetic ions.

The relation (119) between the shift, δ, (in ppm) of the nuclear resonance, and the molar concentration c of paramagnetic ions is

$$\frac{d\delta}{dc} = \frac{2\pi}{3}\chi_M \qquad [3]$$

where χ_M is the molar susceptibility of the solute, which is related to the effective magnetic moment, μ_{eff}, of a solute molecule or ion by

$$\chi_M = \frac{N\mu^2_{eff}}{3kT} \qquad [4]$$

where N is the Avogadro number.

When there is covalent interaction, e.g. complex formation, between the molecule containing the resonating nucleus, and the paramagnetic ion, resulting in a finite density of unpaired electrons at the resonating nucleus, Equation [3] is not valid, and it is necessary to introduce a quantity q, the "interaction factor" (119) and Equation [3] becomes:

$$\frac{d\delta}{dc} = \left(\frac{2\pi}{3} - q\right)\chi_M \qquad [5]$$

There is still a linear relationship between shift and concentration (119, 120) but the slope is different, and if q is sufficiently large, the shift may even be to low field.

Equations [3] and [4] have been used as the basis for a method of measuring the magnetic moments of transition metal ions in aqueous solution (121).

The interaction of nuclear magnetic moments with the magnetic fields due to unpaired electrons in paramagnetic substances provides a mechanism for spin-lattice relaxation. It has been observed in many instances that the presence of paramagnetic ions in a solution

substantially reduces the spin-lattice relaxation time, T_1, for nuclei in the solution. The contribution to $1/T_1$ due to the presence of paramagnetic ions is given by an expression of the form:

$$\frac{1}{T_1} = \frac{A N_{ion} \mu^2_{eff} \gamma^2 \eta}{kT} \qquad [6]$$

where N_{ion} is the number of paramagnetic ions per cc, γ is the magnetogyric ratio for the relaxing nucleus, η is the viscosity of the solution, and A is a numerical factor. The width at half-height, Δ, in c/s, of a nuclear magnetic resonance line is given by

$$\Delta = \frac{1}{\pi T_2} \qquad [7]$$

where T_2 is the spin-spin relaxation time. In general, for solutions, $T_1 = T_2$, so that the effect of paramagnetic ions is to broaden the NMR lines for resonating nuclei in a solution. Different theoretical values of the factor A in Equation [6] have been calculated by different workers. Bloembergen, Purcell, and Pound (122) give $12\pi^2/5$, Pople, Schneider and Bernstein (123) give $4\pi^2$, while Abragam (124) gives $16\pi^2/15$ for the value of this constant. In practice one ion of known magnetic moment, e.g. Cu^{++} (123) is taken as a standard, and an empirical value of A obtained. A relation of this sort with such a value of A holds for ions which are in S-states, or in which the orbital angular momentum of the electrons is effectively quenched, but ions with strong spin-orbit coupling, for which electron-spin relaxation is rapid, are relatively ineffective in relaxing nuclear spins, and the broadening of NMR lines by such ions is much smaller than predicted. Published

data from several sources has been summarized by Pople, Schneider and Bernstein (123).

Connor and Symons (38) measured the shifts and broadening of the proton resonance in solutions of iodine in 65% oleum. They observed a shift of the proton resonance to high field, varying approximately linearly with concentration. From the shifts they obtained the value μ_{eff} = 1.5 BM for the iodine cation, assuming all the iodine to be present as this species, in fair agreement with the value μ_{eff} = 1.44 BM obtained by Arotsky, Mishra and Symons (37) by the Gouy method. For an ion with two unpaired electrons, the "spin-only" value of μ_{eff} is 2.83 BM. Many second and third row transition elements also have values of μ_{eff} smaller than the "spin-only" value.

The line-broadening observed by Connor and Symons (38) also varied approximately linearly with concentration, but was less than predicted for an ion with μ_{eff} = 1.5 by about a factor of 60. This is not surprising, since I^+ has a ^3P ground state, and would be expected to have very strong spin-orbit coupling.

It was claimed by Arotsky, Mishra and Symons (37) on the basis of conductimetric studies of solutions of iodine monochloride in 65% oleum, that I^+ is produced quantitatively in these solutions, according to:

$$ICl + SO_3 + H_2S_2O_7 = I^+ + HSO_3Cl + HS_2O_7^-$$

Measurements of the magnetic susceptibilities of solutions of ICl in 65% oleum by the Gouy method led to the value μ_{eff} = 1.54 BM

for the iodine cation (37).

2. Proton magnetic resonance spectra of solutions of iodine and iodine monochloride in 65% oleum

The shifts and line widths of the proton resonance in solutions of iodine and iodine monochloride in 65% oleum were measured. A capillary containing the pure oleum was used as a reference (Tables 74, 75, Figures 48, 49).

The results for solutions of iodine are in reasonably good agreement with those of Connor and Symons (38), as shown by Figures 48 and 49. The solutions were made up by weight, and a constant value of 2.00 (125) has been assumed for the density of the solutions in converting concentrations into molar units.

The slope of the curve of shift versus concentration is slightly greater than was found by Connor and Symons (Figure 48) and leads to the value μ_{eff} = 1.6 BM, compared with their value of 1.5 BM.

The line widths observed for solutions of iodine were slightly smaller than those reported by Connor and Symons, but the slope of the curve of line width versus concentration (Figure 49) is almost the same for most of its length as that obtained by them.

There is a marked difference between the results obtained for solutions of iodine monochloride, and those reported above for solutions of iodine. The curve of shift versus concentration has a much smaller initial slope than that for solutions of iodine, and the slope decreases with increasing concentration, becoming negative above "M^S"(ICl) $\approx$ 1.0 (Figure 48). The proton resonance signal is not broadened as much as

in solutions of iodine, and the slope of the curve of line width versus concentration decreases with increasing concentration, although it does not become negative in the concentration range studied (Figure 49). This indicates that if the species responsible for the shift and broadening of the proton resonance line is the iodine cation, it is not produced quantitatively in solutions of iodine monochloride, and suggests the existence of an equilibrium:

$$ICl + SO_3 + H_2S_2O_7 \rightleftharpoons I^+ + HClSO_3 + HS_2O_7^-$$

which does not lie far over to the right at higher concentrations. If unreacted ICl can combine with I^+:

$$I^+ + ICl \rightleftharpoons I_2Cl^+$$

as it appears to do in sulphuric and fluorosulphuric acid solutions, this would explain the decrease in shift with increasing concentration observed in the more concentrated solutions.

There is no discrepancy between these results, and the conclusion drawn from the absorption spectra (Chapter V) that I^+ is produced quantitatively or almost quantitatively in very dilute solutions of ICl in 65% oleum. However, the results are hard to reconcile with the value $\mu_{eff} = 1.54$ obtained by Arotsky, Mishra and Symons (37) from measurements by the Gouy method of the magnetic susceptibility of solutions of ICl in 65% oleum, at concentrations up to 1.0 M, and with the conductimetric results reported by these authors, which they interpreted as indicating the quantitative formation of I^+ in solutions of ICl in 65% oleum.

The linearity of the curve of shift versus concentration for

solutions of iodine in 65% oleum is consistent with the quantitative formation of I^+ in these solutions. However, the value of μ_{eff} obtained from the slope of this curve is probably not very reliable for the following reasons:

1. It has been shown that in solutions of metal hydrogen sulphates and other bases in sulphuric acid (126, 127) and of metal fluorosulphates in fluorosulphuric acid (127) the proton resonance of the solvent is shifted to low field by amounts which are not negligible by comparison with the shifts to high field observed in the present work. For example, in a 1.0 M solution of potassium hydrogen sulphate in sulphuric acid, the proton resonance is shifted by - 0.1 ppm relative to its position in the pure solvent, while in a 1.0 M solution of potassium fluorosulphate in fluorosulphuric acid the shift in the proton resonance is - 0.65 ppm. Similar studies have not been made on oleum solutions, but shifts of the same order of magnitude would probably occur in these solutions also. Thus the observed shifts to high field are probably the resultants of a large shift to high field caused by the bulk paramagnetism, and a smaller shift to low field, which would be produced by any base. The value of μ_{eff} obtained from the slope of the curve of shift versus concentration is therefore only a lower limit, the actual value probably being greater by several per cent.

2. The assumption, involved in the use of Equation [3] to estimate μ_{eff}, that there is insufficient covalent interaction between the solvent and an iodine cation to give a finite density

of unpaired electrons at the resonating proton is also not justifiable a priori, since I^+ must certainly be strongly solvated.

3. Proton magnetic resonance spectra of solutions of iodic acid and iodine in fluorosulphuric acid

Proton-resonance shifts in solutions of iodic acid and iodine in fluorosulphuric acid have been measured in only a few instances (Table 76).

In a solution containing the solutes in the mole ratio I_2/HIO_3 = 7.0, corresponding to the formation of I_3^+, the proton resonance underwent quite a large shift to low field, as in solutions of other non-paramagnetic bases in this solvent (127). In solutions containing the solutes in the mole ratios I_2/HIO_3 = 0.33 and 2.0 the proton resonance was shifted to high field. It appears that in this case too, the observed shift was the resultant of a "normal" shift to low field, and a larger shift to high field due to the presence of a paramagnetic species, presumably I^+, in the solutions.

Broadening of the resonance lines was also observed in solutions containing I^+, although this was not so pronounced as in oleum solutions because of the much lower viscosity of fluorosulphuric acid. The resonance line was also noticeably broadened in the solution containing I_3^+, although no obvious explanation for this can be given.

TABLE 74

Solutions of Iodine in 67%

Oleum: Proton Magnetic Resonance Spectra

$w^s(I)$	"M^s" (I)	δ(ppm)	Δ (c/s)
0.066	0.132	0.26	7.1
0.211	0.422	0.84	21
0.248	0.496	1.00	24
0.458	0.916	1.82	42

TABLE 75

Solutions of Iodine Monochloride in

67% Oleum: Proton Magnetic Resonance Spectra

$w^s(ICl)$	"M^s" (ICl)	δ (ppm)	Δ (c/s)
0.165	0.330	0.15	7.6
0.352	0.704	0.26	15.2
0.461	0.922	0.30	18.9
0.774	1.548	0.23	23.1

TABLE 76

Solutions of Iodic Acid and Iodine in

Fluorosulphuric Acid: Proton Magnetic Resonance Spectra

Solute	$w^s(I^+ \text{ or } I_3^+)$*	δ(ppm)	Δ (c/s)
$HIO_3 + 0.33I_2$	0.0812	0.11	3.0

(Table 76 continued)

Solute	$w^s(I^+ \text{ or } I_3^+)$*	δ(ppm)	Δ(c/s)
$HIO_3 + 0.33I_2$	0.1830	0.21	4.5
$HIO_3 + 0.33I_2$	0.2372	0.23	5.6
$HIO_3 + 2I_2$	1.5505	0.58	13.7
$HIO_3 + 7I_2$	0.8491	- 0.97	6.5

* For $HIO_3 + 0.33I_2$, $w^s(I^+) = 0.5\ w^s(IO^+) = 5/6\ w^s(HIO_3)$

For $HIO_3 + 2I_2$, $w^s(I^+) = 5\ w^s(HIO_3)$

For $HIO_3 + 7I_2$, $w^s(I_3^+) = 5\ w^s(HIO_3)$

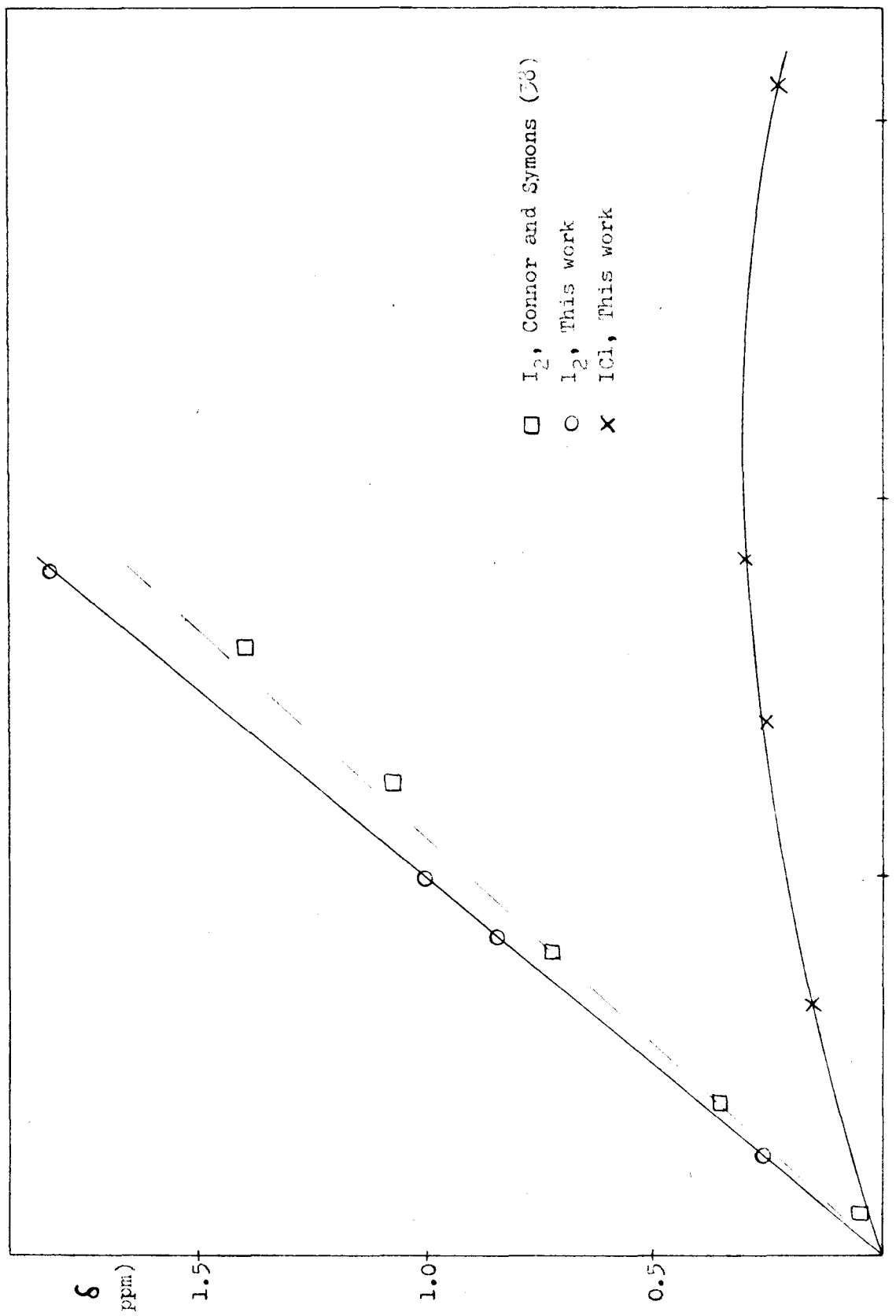


Figure 48. Shifts of Proton Resonance in Solutions of I_2 and ICl in 67% Oleum

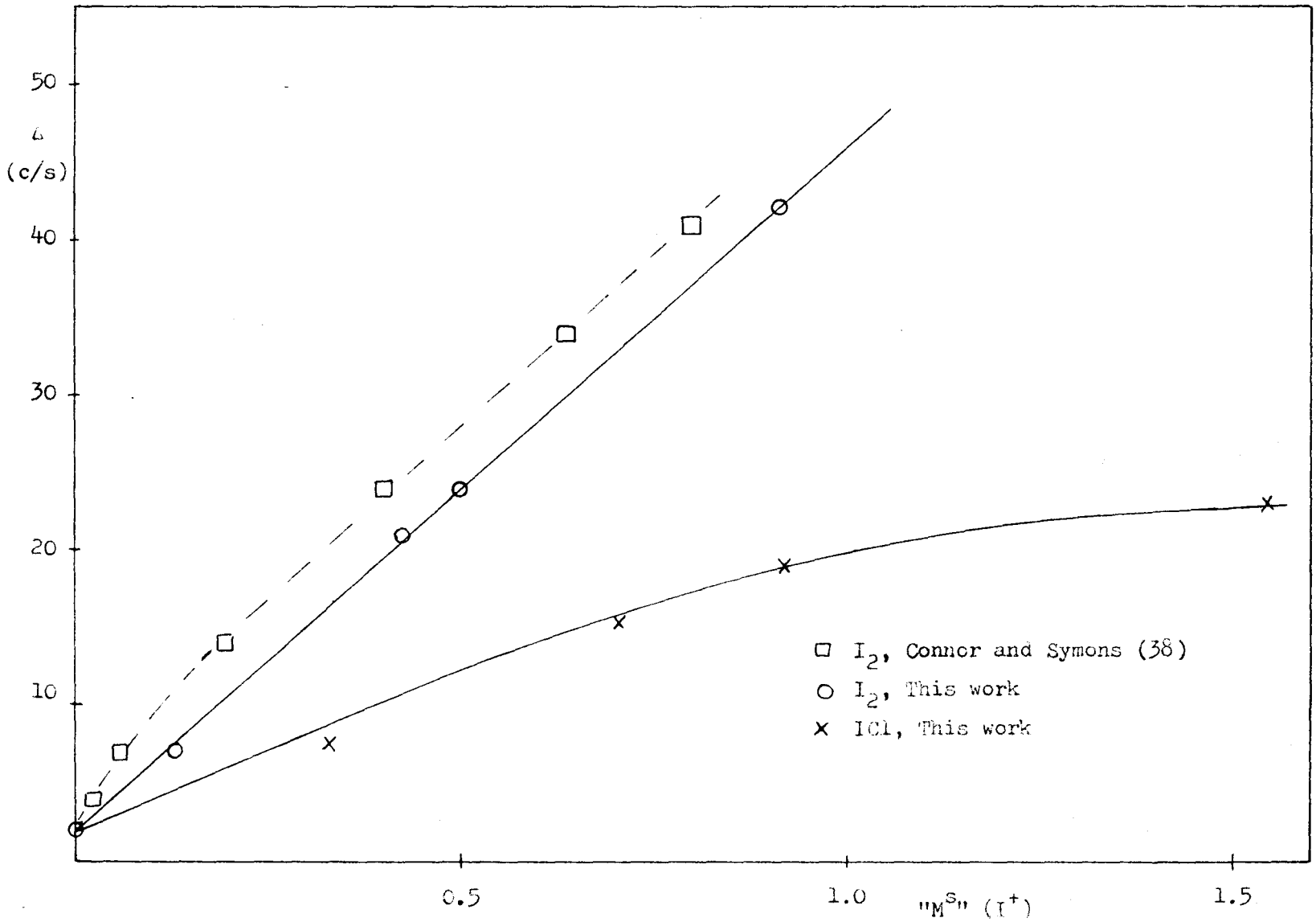
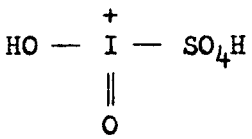


Figure 49. Line Widths of Proton Resonance Signal in Solutions of I_2 and ICl in 67% Oleum

CHAPTER VII

SUMMARY AND GENERAL DISCUSSION

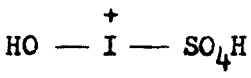
No evidence has been obtained for the existence of the iodyl cation, IO_2^+, in appreciable concentrations. The chemistry of pentavalent iodine in sulphuric and fluorosulphuric acid solutions appears to be dominated by the tendency to achieve a high coordination number through the formation of readily polymerized hydroxy-, sulphato-, fluoro- or fluorosulphato-compounds. If the iodyl cation does exist in solutions of iodic acid in sulphuric acid to any extent, it is almost certainly in a solvated form, such as (I):



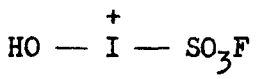
I

Evidence has been presented for the existence of the iodosyl cation, IO^+ and the covalent species, $IOHSO_4$, in sulphuric acid solutions. In fluorosulphuric acid solutions this valence state is largely disproportionated, but small concentrations of IO^+ and the corresponding covalent $IOSO_3F$ probably exist. Trivalent iodine appears to prefer a coordination number greater than unity, as shown by the polymeric nature of the iodosyl cation in its solid sompounds, and it is therefore probable that in sulphuric and fluorosulphuric acid solutions the iodosyl cation

is present in solvated forms such as (II) and (III).



II



III

The existence of this ion in the solvated forms may help to explain why it is stable in sulphuric acid, but extensively disproportionated in fluorosulphuric acid. It would be hard to understand why the simple IO^+ ion should differ in stability in the two solvents, but there is no reason why the two different species (II) and (III) should necessarily be equally stable. The iodine cation, one of the disproportionation products of IO^+, seems to be more stable in fluorosulphuric acid than in sulphuric acid, and this may also partly account for the extensive disproportionation of IO^+ in fluorosulphuric acid solutions.

It has been shown that in moderately concentrated solutions, the iodine cation, I^+, is extensively disproportionated in both sulphuric and fluorosulphuric acids, although it does appear to exist in small concentrations in these solvents. This ion is unusual in that it is the only ion reported to exist as a stable entity which has only six electrons in the valence shell. It has the configuration $5s^2\ 5p^4$ with unpaired electrons in two of the p orbitals. The presence of two unpaired electrons accounts for the paramagnetism of solutions containing this ion, and has been claimed to account for the observed absorption spectrum.

Such an ion would be expected to be very unstable, and it is not surprising that it readily undergoes reaction with nucleophilic reagents, resulting either in disproportionation or in the formation of stable ions

such as Ipy_2^+. Its instability in sulphuric acid may be due as much to the presence of water resulting from the self-dissociation of the solvent, and, in the case of the solutions studied in the present work, from the reaction of iodic acid and iodine with sulphuric acid, as to the insufficiently weak basicity of the solvent. Similarly the extensive disproportionation of the iodine cation in the moderately concentrated solutions in fluorosulphuric acid studied cryoscopically and conductimetrically, may have been due to the presence of water, or the relatively easily dehydrated sulphuric acid, in these solutions. The apparent stability of I^+ in strong oleums, in which the concentration of free water is exceedingly small, is consistent with this picture.

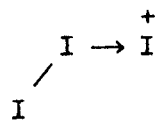
Unfortunately, no evidence has been obtained for the formation of I^+, either by Symons and co-workers (35, 36, 37, 38) or in the present work, that is not equally consistent with the formation of I_2^{++}, provided that the absorption spectrum could be adequately explained in terms of the latter ion. In order to obtain definite information it would be desirable to make cryoscopic measurements on solutions containing only the iodine cation and the characteristic anion of the solvent. Cryoscopic studies of solutions of iodine in 65% oleum might be feasible. No cryoscopic work on 65% oleum has been reported, but some studies of freezing points of solutions in disulphuric acid have recently been described (114). The free iodine cation might be obtained in fluorosulphuric acid solutions by the oxidation of iodine with peroxodisulphuryl fluoride, $S_2O_6F_2$. The only products of such a reaction would be the iodine cation and the fluorosulphate ion:

$$I_2 + S_2O_6F_2 = 2I^+ + 2SO_3F^-$$

In the absence of water and sulphuric acid the iodine cation might not undergo disproportionation in such solutions.

New physical evidence has been obtained for the existence of the ions I_3^+ and I_5^+, whose existence in sulphuric acid solutions had previously been suggested on chemical grounds. The ion I_2Cl^+ has not been previously reported, but if the ion I_3^+ is regarded as a complex between the iodine cation and an iodine molecule, it is not surprising that the iodine cation can react similarly with a molecule of iodine monochloride. It would be interesting to know whether the ion I_2Br^+ could be formed in a similar way.

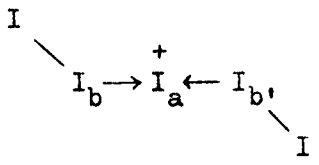
The ions I_3^+ and I_5^+ may be regarded as being formed by co-ordination of the iodine cation, I^+, with one and two iodine molecules respectively. Once the covalent bond is formed, the two outer iodine atoms in I_3^+ will be indistinguishable, and the positive charge will reside mainly on the central atom. The central atom will have two bonding and two non-bonding pairs of electrons in its valence shell, in an approximately tetrahedral arrangement, (115) so that the ion will have the non-linear structure (IV) (cf. $TeBr_2$, $\angle$ Br Te Br = 98 $\pm$ 3°, reference 116)



IV

The central atom I_a in I_5^+ will have two bonding and three non-

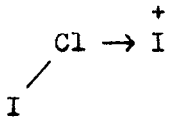
bonding pairs of valence electrons. These electron pairs will be disposed in a trigonal-bipyramidal arrangement about I_a, with the non-bonding pairs in the equatorial positions and the bonding pairs in the two axial positions (115) with $\angle I_b I_a I_{b'} \approx 180^\circ$ (cf. the linear ions I_3^- (117) and ICl_2^- (118) in which the central atom has the same electron configuration). The electron configuration of the atoms I_b and $I_{b'}$ will be similar to that of the central atom in I_3^+, so that the ion will have the structure (V).



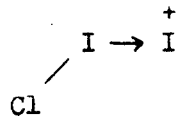
V

The positive charge will reside mainly on I_b and $I_{b'}$.

It is not possible to predict with confidence whether the ion I_2Cl^+ will have the symmetrical structure (VI) or the unsymmetrical structure (VII).



VI



VII

In either case, the central atom would have four pairs of valence electrons, arranged approximately tetrahedrally, leading to the non-linear structures shown.

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