THE FLUOROSULPHURIC ACID
SOLVENT SYSTEM:
IODINE FLUOROSULPHATES

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SCOPE AND CONTENTS:

The cryoscopic constant for fluorosulphuric acid has been determined and the nature and concentration of the impurities in the solvent have been investigated.

The NMR and Gouy methods have been used to determine the magnetic susceptibility of solutions of iodine fluorosulphates. The NMR method has been shown to lead to spurious results.

Cryoscopy, conductivity and UV and visual spectrophotometry have been used to elucidate the state of iodine fluorosulphates in fluorosulphuric acid. Solutions of stoichiometry corresponding to fifth-, third-, half-, uni-, tri-, and hepta-valent iodine have been investigated. The highest valence state observed was that of iodine trifluorosulphate which has been shown to be an acid in fluorosulphuric acid. Measurements on fifth- and third-valent iodine solutions indicate that I_5^+ and I_3^+ are formed. Measurements on half- and univalent iodine solutions suggest that I_2^+ is formed. The observed magnetic moment of this species agrees well with that required by theory, 2.0 BM.

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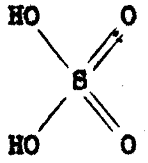
CHAPTER I

Introduction

The Fluorosulphuric Acid System

Fluorosulphuric acid was first prepared by Thorpe and Kirman in 1892(1) by means of the reaction of hydrogen fluoride and sulphur trioxide. Later several authors described preparative methods for this acid using fuming sulphuric acid and an ionic fluoride or fluorosulphate(2,3,4). Fluorosulphuric acid is a fuming liquid with a very wide liquid range (-89.00° to 162.5°C). It is a strongly associated liquid as indicated by its high boiling point compared to that of sulphuryl fluoride, SO_2F_2. Sulphuryl fluoride, which boils at -52°C, has a molecular weight of 102.06 compared to the molecular weight of fluorosulphuric acid, 100.07. It is one of the strongest protonic acids known. Barr(13) has shown that it acts as a weak acid in the sulphuric acid system and that sulphuric acid is a weak base in the fluorosulphuric acid system.

The structure of fluorosulphuric acid is proposed to be analogous to that of sulphuric acid with one hydroxyl group replaced by fluorine.



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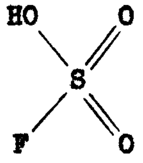

II

The Raman spectrum, described by Gillespie and Robinson(5) is satisfactorily assigned on the basis of this structure (II).

Fluorosulphuric acid reacts violently with water and has been shown to hydrolyse according to the reaction(6):

$$HSO_3F + H_2O \longrightarrow HF + H_2SO_4 \qquad \text{I-1}$$

This reaction has been studied by several authors(7,8,9) but has yet to be clearly understood. Woolf(8) has suggested that when the acid is added to an excess of water there is an initial rapid hydrolysis followed by a slow hydrolysis. The large heat of solution may cause the initial rapid hydrolysis. However, Senior(10) has shown by conductance measurements that water in excess fluorosulphuric acid does not cause complete hydrolysis but gives the stable equilibrium:

$$H_3O^+ + SO_3F^- \overset{K}{\rightleftharpoons} HF + H_2SO_4 \qquad \text{I-2}$$

with K = 0.22.

The properties of fluorosulphuric acid as a non-aqueous solvent were first considered by Woolf(11). He purified the acid by distilling it twice at atmospheric pressure, collecting the fraction boiling at 163.0 ± 0.5°C and redistilling this fraction under vacuum by trap to trap distillation. The specific conductance of the acid he obtained was 2.20×10^{-4} ohm^{-1}cm^{-1}. To account for this conductance, Woolf concluded that the predominant self-dissociation equilibrium was one of autoprotolysis:

$$2\,HSO_3F \rightleftharpoons H_2SO_3F^+ + SO_3F^- \qquad \text{I-3}$$

The abnormally high conductance of the fluorosulphate ion in water lead Woolf to suspect that conduction took place by a proton transfer mechanism.

Woolf suggested that the $S_2O_6F^-$ ion may be present in small concentration in the pure acid. Raman spectra of solutions of sulphur trioxide in fluorosulphuric acid(14) indicate that this anion is only formed in solutions containing excess fluorosulphate ion. Moreover, Barr(13) has shown that the addition of sulphur trioxide to a solution of potassium fluorosulphate causes a decrease in conductivity which can be accounted for by the replacement of fluorosulphate ion by the less mobile $S_2O_6F^-$ ion. Lehman and Kolditz(16) have prepared KS_2O_6F which they report as a weakly dissociated complex of sulphur trioxide and potassium fluorosulphate.

Electrolysis of the anhydrous acid gave a mole of hydrogen at the cathode for every two Faraday's of electricity and an oxidising solution at the anode. Woolf suggested that the anode reaction formed the peroxydifluorosulphate ion:

$$2\ SO_3F^- \longrightarrow S_2O_6F_2^- + e^- \qquad \text{I-4}$$

However, in the light of Dudley's work(12) on the electrolysis of fluorosulphuric acid solutions the likely anode reaction is one of complete oxidation to peroxydisulphuryldifluoride, $S_2O_6F_2$.

Woolf investigated several fluorides for acid-base character. Using conductimetric titration he found that antimony pentafluoride, auric fluoride, tantalum pentafluoride and platinum tetrafluoride were acids and arsenic trifluoride, antimony trifluoride, bromine trifluoride and iodine pentafluoride were bases.

Studies on the fluorosulphuric acid solvent system were extended by Barr(13). He obtained acid with a specific conductance of

1.085×10^{-4} ohm^{-1} $cm.^{-1}$, lower than that of Woolf, by simply distilling commercial acid twice at atmospheric pressure. Thompson(94) suggested that Woolf's method of final purification by trap to trap distillation under vacuum may concentrate hydrogen fluoride in the distillate and thus cause greater conductivity. Barr observed that the alkali metal fluorosulphates have similar conductances suggesting that the conductivity is mainly due to the common fluorosulphate ion. Determination of the transport numbers of the potassium and fluorosulphate ions gave 0.11 and 0.89 respectively. The abnormally large mobility of the fluorosulphate ion suggests that it does not conduct by a simple diffusion process.

Thompson adapted the non-equilibrium method of Rossini(17,18) for the determination of the freezing points of solutions in fluorosulphuric acid. Using cryoscopy, conductivity and ^{19}F nuclear magnetic resonance, he studied the behaviour of antimony pentafluoride and its reactions with sulphur trioxide in fluorosulphuric acid(15). From a precise knowledge of the dimerisation equilibrium of the $SbF_2(SO_3F)_4^-$ ion and the conductivity of the corresponding potassium salt and acid, he estimated the mobility of the fluorosulphuric acidium ion. For the autoprotolysis equilibrium constant Thompson obtained 3.6×10^{-8} $mole^2kg^{-2}$.

Several methods of preparation of fluorosulphates have been reported. Traube obtained alkali metal and ammonium fluorosulphates (a) by fusing mixtures of pyrosulphates and fluorides, (b) by reacting fluorides with sulphur trioxide and (c) by direct reaction of fluorosulphuric acid with the fluoride(19,20). Hayek, Puschmann and Czaloun have prepared chlorofluorosulphates from the metal chloride and fluorosulphuric acid(21). The reaction of sulphur trioxide with the fluoride has been used to prepare $TlSO_3F$, $AgSO_3F$(22), alkaline earth fluorosulphates, $Sb(SO_3F)_3$ and $2\ AsF_3 \cdot 3\ SO_3$(23). The latter compound has been shown to be a mixture of $AsF(SO_3F)_2$ and $AsF_2(SO_3F)$(24). $Al(SO_3F)_3$ has been prepared from aluminum chloride and fluorosulphuric acid(22). Fluorosulphates of silicon, titanium, arsenic and tin have been obtained by the reaction of silver fluorosulphate with the corresponding chloride in acetonitrile but the products contain coordinated solvent(22). Woolf(29) has prepared the nitrosyl fluorosulphate from nitrosyl chloride and fluorosulphuric acid in bromine trifluoride. The discovery of peroxydisulphuryldifluoride and fluorine fluorosulphate(26) provided new methods of preparation of fluorosulphates. NF_2SO_3F has been prepared from dinitrogen tetrafluoride and peroxydisulphuryldifluoride(27). Several transition metal oxyfluorosulphates have been prepared by reacting peroxydisulphuryldifluoride with the metal or metal chloride(27,28). Only the cis isomer of $SF_4(SO_3F)_2$ is obtained by the reaction of sulphur tetrafluoride and peroxydisulphuryldifluoride(30). Cady and co-workers have prepared the trifluorosulphates of bromine and iodine(31) and the anhydrous potassium salts, $KBr(SO_3F)_4$ and $KI(SO_3F)_4$(27). The nature of the mixed bromine fluoride fluorosulphates, $Br_2F_3(SO_3F)_3$ and $BrF(SO_3F)_2$(33) and iodine fluoride fluorosulphate, $IF_3(SO_3F)_2$(32) has yet to be completely understood. All of the halogen monofluorosulphates have been obtained. Fluorine fluorosulphate is prepared from fluorine and sulphur trioxide at temperatures in excess of 170°C(26), while the other monofluorosulphates are made by the reaction of the halogen with peroxydisulphuryldifluoride(31,33,35).

Iodine Cations and Oxy-cations

Of the common halogens iodine is the most electropositive and therefore the most likely to exhibit cationic properties. The experimental evidence suggests that the formally higher valence iodine cations such as IO_3^+ and IO_2^+ are of doubtful existence while there is justification for I^+, I_3^+, I_5^+ and IO^+.

Several seven-valent iodine compounds have been made,which may contain cationic iodine but no structural or conductimetric studies have been done. Schmeisser and Lang have claimed IO_3F is prepared by fluorinating periodic acid in hydrogen fluoride(36). Schmeisser and Brändle have prepared $IO_3[ICl_2]$ and $IO_3[I(NO_3)_2]$(37). On the basis of ultraviolet spectra, Symons(38) has suggested that ortho periodic acid is protonated in strongly acidic solutions giving $I(OH)_6^+$. However, the same author verifies the instability of periodic acid in 100% sulphuric acid. Ogier(39) claimed to have prepared I_2O_7 by ozonisation of iodine and more recently Symons has reported its preparation from periodic acid and 65% oleum(38).

The five-valent iodine oxy-cation, IO_2^+ has been postulated by several authors. Aynsley, Nichols and Robinson(40) suggested the formula $IO_2^+IF_6^-$ for the white crystalline oxyfluoride, IOF_3, which they prepared from I_2O_5 and IF_5. Schmeisser and Lang(36) prepared a 1:1 complex between iodyl fluoride, IO_2F and arsenic pentafluoride, which they formulated $IO_2^+AsF_6^-$. Aynsley and Sampath(41) were unable to prepare complexes of IO_2F with arsenic pentafluoride, sulphur trioxide or boron trifluoride. They suggested that Schmeisser's complex should be formulated $AsF_4^+IO_2F_2^-$ but did not apply this reasoning to IOF_3, which might similarly be formulated $IF_4^+IO_2F_2^-$. The pentavalent iodine cation IF_4^+ has been postulated to exist in the $IF_5 \cdot SbF_5$ complex(42) and to contribute to IF_5 conductivity(43). Aynsley and Sampath(41) were able to prepare the blue complex $IO_2F \cdot 0.8\ SbF_5$, which may exhibit ionic properties. By analogy with NO_2^+ Meyers and Kennedy(44) suggested IO_2^+ as an intermediate in the iodate-iodide exchange reaction. Muir(45) used the reaction of sulphur trioxide and the iodine oxides, I_2O_4 and I_2O_5, to prepare $I_2O_4 \cdot 3\ SO_3$ and $I_2O_5 \cdot 2\ SO_3$ which were recently verified and formulated as iodyl compounds, $(IO^+)(IO_2^+)S_3O_{10}^{=}$ and $(IO_2^+)_2S_2O_7^{=}$(46). No experimental evidence for this ionic formulation has been given. Senior(47) reported a white solid $I_2O_5 \cdot SO_3$, which precipitates from concentrated solutions of iodic acid in 100% sulphuric acid and which may be formulated as iodyl sulphate, $(IO_2^+)_2SO_4^{=}$. However, cryoscopic and conductimetric evidence suggest that the solid is polymeric. Symon's report(48) that iodic acid is simply protonated in 100% sulphuric acid to give $H_2IO_3^+$ is shown to be in error by Senior's work which demonstrates that the only pentavalent iodine cations in solution are of the type $(IO_2)_n(HSO_4)_{n-1}^+$. Similar studies in fluorosulphuric acid indicate a similar behaviour for iodic acid giving the cationic species $(IOF_2)_2SO_3F^+$(10). Recently the preparation of iodyl fluorosulphate, IO_2SO_3F has been reported(101).

The triply charged iodine cation, I^{+3}, is an unlikely tervalent iodine species since it would have the unstable outer electron configuration $5\,s^2\ 5\,p^2$. However, many compounds formally containing this cation are known. The acetate, $I(OOCCH_3)_3$, was first prepared by Schutzenberger(49) and since then improved methods have been developed and a wide range of analogous compounds with organic acid ligands have been prepared(51,52). During the electrolysis of a solution of iodine triacetate in acetic anhydride the iodine moves to the cathode, indicating the cationic nature of the iodine species(51). Several "I^{+3}" compounds with inorganic ligands are known. The iodine oxide, I_4O_9, which may be formulated as $I(IO_3)_3$, was first prepared by Ogier(39) from the reaction of ozone and iodine. More recent studies of this oxide have been made by Fichter and co-workers(53,54) and Bahl and Partington(55). Fichter and co-workers have prepared the phosphate, IPO_4(51) and a perchlorate, $I(ClO_4)_3 \cdot 2\ H_2O$(54). Recently Alcock and Waddington(63) have claimed to have made $I(ClO_4)_3$ by reacting iodine and silver perchlorate in ether. Several authors have reported the preparation of the nitrate. Schmeisser and Brändle(56) report that $I(NO_3)_3$ prepared from iodine trichloride and chlorine nitrate decomposes above 0°C. Kikindai(57) has shown that Millon's original preparation(58) from iodine and fuming nitric acid gives $IONO_3$ rather than $I(NO_3)_3$. Ushakov(59) claims that the trinitrate is obtained by the reaction of silver nitrate with iodine in methyl or ethyl alcohol. The trifluorosulphate has been prepared by Cady and Roberts(31).

Many compounds are known which may be formulated as derivatives of the iodosyl cation, IO^+. Iodine tetroxide may be formulated $IO^+IO_3^-$. Iodosyl nitrate, $IONO_3$, is mentioned above. The yellow solid which separates from 1:3 mixtures of iodine and iodic acid in fluorosulphuric acid has the formula $IOSO_3F$(10). Chrétien's yellow sulphate(61) has been shown by Masson and Argument(62) to be $(IO)_2SO_4$. An analogous selenate has been prepared(64). Both Fichter and Kappeler(54) and Lehmann and Hesselbarth(46) have obtained $I_2O_3 \cdot 3\ SO_3$, which may be written as $I_2(SO_4)_3$ or $(IO)_2S_3O_{10}$. The reaction of iodosyl sulphate with oleum gives a white solid which may be formulated $IOHS_2O_7$(62,66).

Dasent and Waddington(64) have used infra red studies to show that iodosyl sulphate, iodosyl selenate and iodine tetroxide contain networks of -IOI- chains. They argue that these compounds are polymeric and do not contain discrete IO^+ groups on the grounds that (a) no I-O stretching vibration comparable to that in TeO is observed, (b) the compounds are diamagnetic when it might be expected that IO^+ groups, being isoelectronic with the oxygen molecule in valence electrons, would be paramagnetic, and (c) apart from a slight solubility of the sulphate and selenate in their parent acids, the compounds are insoluble in the wide range of solvents tested, including nitromethane, which dissolves nitrosyl salts.

There is some evidence for tervalent iodine cations in solutions of $(IO)_2SO_4$, I_2O_4 and 1:3 iodine-iodic acid in 100% sulphuric acid. Conductimetric and cryoscopic studies by Gillespie and Senior(65) have shown that $IOHSO_4$ formed in these solutions is partially dissociated. The formation of iodoso derivatives of aromatic compounds in solutions of iodysyl sulphate in concentrated sulphuric acid(75,76) may be evidence for the existence of IO^+ ions.

Several compounds have been reported which may contain the singly charged iodine cation. The nitrate, INO_3, has been prepared in absolute alcohol by reacting silver nitrate and iodine(59,96). Cation exchange resins have been used to prepare I_2SO_4 in absolute alcohol(67). Ushakov(68) has shown that INO_3 undergoes extensive alcoholysis in absolute methanol. Schmeisser and Brändle(56) have reported that INO_3, which is prepared from $I(NO_3)_3$ and iodine, decomposes above 5°C. Birkenbach and Goubeau(69) attempted to prepare iodine perchlorate, $IClO_4$, from the reaction of silver perchlorate and iodine but they found that the product immediately reacted with the solvent used. However, Alcock and Waddington claim to have obtained iodine perchlorate from this reaction in absolute ethanol(63). Iodine fluorosulphate, ISO_3F, which recently has been prepared by Aubke and Cady(35) appears to be a covalent compound. The iodine cation with the outer electron configuration $5s^2\ 5p^4$ does not have a closed valency shell and Carlsohn has shown that the ion may be stabilised by coordinating ligands such as pyridine and β-picoline(70,86). Both Ipy_2X and IpyY series have been prepared with X as nitrate and perchlorate and Y as nitrate, benzoate and acetate. These compounds are discussed in a review of the positive character of the halogens by Kleinberg(25).

Bell and Gelles(71) have estimated the equilibrium constants for various hypothetical dissociation equilibria of iodine in water from thermodynamic considerations. According to their calculations, the most favourable univalent iodine cation is H_2OI^+, which would be 10^{-5} molar in a one molar iodine solution and their experimental determination of the dissociation involving this species agrees well with the theoretical value. However, reasonably high concentrations of the protonated hypoiodous acid are not possible due to disproportionation to iodate and iodide. Skrabal and Buchta(72) noted the basic character of hypoiodous acid in aqueous solution and suggested that the brown solutions formed when iodine is added to hypoiodous acid or when iodine is partially oxidised in water, contained the base I_3OH. Pavlov and Fiaklov(73) have shown by measuring the rate of exchange of iodine between hypoiodous acid and molecular iodine in aqueous solution that iodine is coordinated to the univalent iodine species in these solutions. The evidence for unipositive iodine species in concentrated sulphuric acid solutions is more compelling. Masson(74) observed that the brown solutions formed when iodine is added to iodosyl sulphate, $(IO)_2SO_4$, in concentrated sulphuric acid solutions reacted with chlorobenzene to form both iodo and iodoso derivatives. He postulated the presence of I_3^+ and I_5^+ to explain the stoichiometry of these reactions and demonstrated that solutions with stoichiometry corresponding to univalent positive iodine were largely disproportionated to I_3^+, I_5^+ and IO^+. Similar observations were reported by Birkenbach, Goubeau and Krall(77), who prepared their sulphuric acid solutions with iodine and mercurous or mercuric sulphate. Arotsky, Mishra and Symons(48) have given conductimetric evidence for I_3^+ formed from iodic acid and iodine in 100% sulphuric acid and have suggested that I_5^+ may be formed on the basis of change in visual and ultraviolet spectra when iodine is added to I_3^+ solutions. By cryoscopic and detailed conductimetric measurements, Senior has confirmed the existence of I_3^+ and I_5^+ in 100% sulphuric acid and demonstrated that solutions which correspond stoichiometrically to univalent positive iodine are largely disproportionated(10).

Symons and co-workers have made extensive investigations of the blue solutions formed when iodine or iodine chloride is dissolved in 65% oleum(48,78,79,80,81). They have concluded from conductimetric, magnetic and spectral studies that iodine in these solutions is quantitatively converted to I^+. They report an effective magnetic moment for I^+ of 1.4 BM by the Gouy method(80) and 1.5 BM by NMR studies(81). From ultra violet and visual spectral studies, univalent positive iodine is also claimed to be prepared in fluorosulphuric acid(80), iodine pentafluoride(82) and antimony pentafluoride(10). Fiaklov and Abarbachuk(83) have demonstrated the cationic nature of the iodine species formed when iodine is dissolved in antimony pentachloride. Structural studies on compounds such as $ICl_3 \cdot SbCl_5$ justify writing $(ICl_2^+)SbCl_6^-$(84). Arotsky and Symons(85) have recently reviewed the evidence for the halogen cations.

The present study was undertaken to investigate the nature of iodine cations, especially I^+, in fluorosulphuric acid. During the course of the work, the cryoscopic constant was redetermined and the nature of the "pure" solvent was investigated.

CHAPTER II

Experimental

1. Preparation and Purification of Materials

Fluorosulphuric Acid

Baker and Adamson fluorosulphuric acid was purified by double distillation in the still shown in Fig. 1. Dry air, entering at A and leaving by the magnesium perchlorate guard tubes B and C, was passed through the still for at least one hour before distillation and the receiver and lower stage of the still were flamed periodically during this time. Passage of dry air was continued during the distillation except when the final product was distilling, but exit C was closed during the second stage of distillation to prevent back distillation into the selector I. Only acid boiling between 162°C and 164°C was taken at both stages of the distillation, the lower boiling fractions being separated by selectors I and II. The selector is shown in detail in Fig. 2. The fluorosulphuric acid obtained by this procedure usually had a freezing point above -89.000°C and a conductivity between 1.26×10^{-4} ohm^{-1} cm^{-1} and 1.56×10^{-4} ohm^{-1} cm^{-1}.

Peroxydisulphuryldifluoride

Peroxydisulphuryldifluoride was prepared by the method of Dudley and Cady(26) in the reactor shown in Fig. 3. The reaction vessel F was a copper tube 7.5 cm. in diameter and 90 cm. long, filled with copper wire having a surface area of 150,000 cm.^{2} which had been coated with silver metal from a bath of silver cyanide complex. Heating was accomplished with nichrome wire wound around the vessel and connected to a variable voltage regulator. Sulphur trioxide was swept into the reactor at A by a stream of nitrogen metered by the rate meter at E and fluorine, diluted with nitrogen, was run into the reactor at B and metered at D. The fluorine flow rate was maintained slightly in excess of one half the sulphur trioxide flow rate or, in other words, slightly in excess of the stoichiometric requirement and the reaction vessel was maintained at between 120°C and 140°C. The product was collected in traps at C cooled with finely crushed dry ice. Final purification of the peroxide was accomplished by distillation at atmospheric pressure in a still protected from moisture by a magnesium perchlorate drying tube. The fraction boiling between 66.5 and 67.0°C was pure peroxydisulphuryldifluoride. The product was analysed by titration with standard thiosulphate of the iodine liberated by the addition of peroxydisulphuryldifluoride to aqueous potassium iodide solution. Three typical analyses were:

Oxidising equivalents of $S_2O_6F_2$, theoretical 2.00;
found 2.04, 2.00, 2.00.

Potassium Fluorosulphate

Potassium fluorosulphate was prepared as described by Barr(13) by adding fluorosulphuric acid to a concentrated solution of potassium hydroxide in water. The cooled solution was filtered and the crude potassium fluorosulphate recrystallised from water and washed with acetone and ether.

Disulphuryldifluoride

Disulphuryldifluoride was prepared as described by Gillespie and Rothenbury(87). Ozark Mahooning antimony pentafluoride purified by distillation was added to refluxing sulphur trioxide in excess of the molar ratio of one to five and the product was distilled from this mixture, treated with sulphuric acid to remove the sulphur trioxide and redistilled to give pure disulphuryldifluoride. B. Pt. 50 - 51°C.

Iodine

Shawinigan reagent grade iodine was used directly.

Sulphur Trioxide

Sulphur trioxide was distilled from Baker and Adamson 'Sulfan' in a still which was protected from moisture by a magnesium perchlorate drying tube.

Hydrogen Fluoride

Matheson's Hydrogen fluoride (anhydrous) was used directly.

2. Conductivity Measurements

Conductivity measurements at 25°C were made in the cell depicted in Fig. 4a, using the B and C electrodes which gave a cell constant of approximately 18 $cm.^{-1}$. Conductivities at dry ice temperatures were measured in the cell shown in Fig. 4b.

The electrodes were plated with platinum black by electrolysing a 0.3% solution of chloroplatinic acid in 0.05N hydrochloric acid containing 0.25% lead acetate. A current of 10 milliamps was passed for 10 minutes. The current direction was reversed every minute.

Cell constants were determined by making minimum conducting sulphuric acid in the cell. Minimum conducting sulphuric acid has a specific conductance of 1.0432×10^{-2} ohm^{-1} cm.^{-1} at 25°C. For the low temperature conductivity measurements, the cell constant was taken as unchanged at dry ice temperatures. Estimation of the change in cell constant with temperature change from 25°C to -78.5°C, using the coefficient of expansion of pyrex glass (92) showed the change to be less than 1%.

Conductivity runs at 25°C were carried out in an oil bath regulated with a toluene-mercury regulator to 25 ± 0.005°C. The temperature was measured with a platinum resistance thermometer to ± 0.001°C. Thermometer resistance readings were made on a Mueller resistance bridge (see Part 3).

For low temperature conductivity measurements, the cell was immersed in finely crushed dry ice in a Dewar. A small nichrome wire heater connected to a voltage regulator was set in the bottom of the Dewar to boil off carbon dioxide and thus maintain the equilibrium of solid carbon dioxide with an atmosphere of pure carbon dioxide gas (88). The cell was set 25 cm. above the heater and the platinum resistance thermometer was placed with its resistance coil equidistant between the electrodes and touching the glass tube joining them. The cell was completely covered with dry ice, a 2 cm. thick layer of glass wool was placed over this and a polystyrene cover, provided with holes for the thermometer well, heater leads and conductance bridge leads, closed the Dewar. The heater was operated until the temperature rose to a steady value. The expected steady temperature could be estimated from a knowledge of the atmospheric pressure by means of the expression:

$$t(^{\circ}C) = \frac{1349}{9.81137 - \log_{10}P} - 273.16 \qquad \text{II-1}$$

Heating was then discontinued and usually was not required again during a run even though the Dewar was opened several times to make additions to the cell. After each addition to the cell the dry ice at the top of the Dewar was broken up and additional dry ice added. Although the temperature over a run changed as the atmospheric pressure changed, the temperature for each conductivity measurement was regulated ± 0.01°C. The temperature was read to ± 0.001°C with a platinum resistance thermometer. All conductances were corrected to -78.52°C, the sublimation temperature of solid carbon dioxide at one atmosphere pressure, using the temperature coefficient of 0.122×10^{-4} ohm^{-1} $cm.^{-1}$/°C for a 0.01 m solution of potassium fluorosulphate. This factor was determined from the tangential slope at -78.5°C of a plot of the variation of the conductance of a 0.01 m potassium fluorosulphate solution with temperature (Fig. 5). The range of temperatures over which conductances were measured was -78.44 to -78.83°C and the maximum correction to the conductance was only 1.5%.

The solutions for conductivity measurements were prepared in the following manner. Fluorosulphuric acid was distilled directly into the cell, weighing the cell before and after addition of acid. Addition of solid solutes was made with the weight dropper shown in Fig. 6a. Liquid solutes and solutions in fluorosulphuric acid were added by means of the dropper shown in Fig. 6b. After each addition the cell was shaken well and readings were taken followed by further shaking until a steady conductance value was attained. In the low temperature measurements, it was found more convenient to shake the Dewar and its contents rather than take the cell out. The conductance of solutions was measured with a Wayne-Kerr Universal bridge operating at 1000 cps.

3. Cryoscopy

The theory for the cooling curve method for determination of freezing points is given by Mair, Glasgow and Rossini(17) and a detailed account of its application to fluorosulphuric acid cryoscopy is given in R. C. Thompson's thesis(15).

The cryoscope which is shown in Fig. 7a was a double walled vessel. The space between the walls, A, could be evacuated to any desired pressure and the walls in this space were coated with silver, except for a narrow vertical strip through which the solution could be observed. The glass or monel stirrer, C, was operated through a teflon seal at E by a six volt electric windshield-wiper motor. The platinum resistance thermometer, B, was sealed at D to a glass sleeve fitted with a male B14 joint, which fitted into the top of the cryoscope at I. A Leeds Northrup platinum resistance thermometer (No. 1331405) was used in conjunction with a Mueller resistance bridge (Leeds Northrup No. 1338840) for temperature measurement. The thermometer calibration was checked by measuring the resistance at the triple point of water in a Trans-Sonics Inc. 'Equiphase cell'.

The procedure for cryoscopy was as follows. The cryoscope was dried by passing dry air in at F for two hours. Fluorosulphuric acid was distilled into the weight dropper shown in Fig. 7b, which was then attached to the cryoscope at F and dry air was passed through for another half hour leaving now by J (Fig. 7b). A moisture guard tube was attached to the weight dropper at K and the acid was run into the cryoscope to a level just above the small diameter part of the cryoscope. The amount of acid introduced was determined by the difference in weight of the dropper. F and G were now closed and throughout the remainder of the experiment dry air was passed in at H, leaving through E. Additions of solute were made through F using the droppers shown in Figs. 6a and 6b. For very hygroscopic solutions, a second container with a B19 joint and cap was employed and rather than reintroducing the dropper (Fig. 6b), made wet by atmospheric moisture into the solute solution, the dropper was put into the second container and the solute container was capped. The dropper and second container were washed and dried after each addition.

For the determination of the freezing point, a Dewar of liquid air was placed around the lower part of the cryoscope, which was suspended at the neck L in a stand. The temperature was allowed to fall to -70°C before the interannular space, A, was evacuated to give the desired cooling rate. Cooling rates of between 0.2 and 0.5°C per minute yielded the best results. The acid was allowed to supercool 2°C before initiating freezing by introducing a small platinum strip cooled in liquid air. Readings were made every minute, from the maximum temperature reached, for ten minutes, then alternately reverse and normal current direction readings were made on the resistance thermometer every two minutes for a further twelve minutes. A typical cooling curve with the extrapolation to the freezing point is shown in Fig. 8. Taylor and Rossini(18) describe a geometrical method for this extrapolation, but the cooling curve was extrapolated visually in this work and the freezing point is estimated to be accurate to ± 0.005°C(15).

4. Nuclear Magnetic Resonance Spectroscopy

Fluorine NMR spectra were taken on a Varian Associates high resolution spectrometer operated at 56.4 Mc. The spectra were calibrated by a side band technique using a Muirhead-Wigan, D-890-A, decade oscillator. Some spectra were integrated on a Varian Associates NMR Integrator, model V-3521.

Low temperature spectra were obtained by boiling off liquid air through a Varian Associates variable temperature probe accessory, model V-4340. Temperatures were measured by a copper-constantan thermocouple with a Leeds Northrup temperature potentiometer. Fluorine spectra were run in sealed glass tubes of 5 mm. diameter.

Proton NMR spectra were taken on the above spectrometer operated at 60 Mc. and on a Varian Associates A-60 spectrometer. Precision NMR tubes were used for the spectra taken on the A-60. In all spectra presented in this thesis the field strength increases from left to right and NMR shifts are given in cycles per second.

5. Magnetic Susceptibility Measurements

Magnetic susceptibility measurements on iodine solutions in fluorosulphuric acid were made by the Gouy method and both the NMR shift method of Dickinson(89) and the NMR signal broadening method(90) were investigated.

The expression for the weight susceptibility determined by the Gouy method is(91):

$$\chi_g = \frac{\alpha + \beta(F - \delta)}{w} \times 10^{-6} \qquad \text{II-2}$$

where α is the correction for the susceptibility of the air displaced when the sample is introduced (0.029 x sample volume in cc.), β is a constant characteristic of the Gouy tube and magnet used, F is the force (weight increase) observed when the sample is placed in the magnetic field, δ is the correction applied for the susceptibility of the empty Gouy tube, and w is the weight of the sample. For this work, a 7,000 gauss magnet with a 1.4 cm. pole gap was used in conjunction with a Mettler Gramatic balance. A Gouy tube, 1.2 cm. in diameter, with a ground glass cap to protect the solutions from moisture was suspended in the pole gap. A polythene bag provided with close-fitting holes for the pole pieces and fitted to a glass tube extended from the balance protected the Gouy tube from air drafts. The magnet was mounted on tracks and could be moved away from the sample by turning a screw. An average of at least three different readings was taken for each weighing and the variation between readings was never more than ± 0.2 mg.

The Gouy tube was standardised with a solution of nickel chloride in water$^{(91)}$, which was analysed gravimetrically with dimethylglyoxime. The weight susceptibility of such a solution is given by:

$$\chi_{NiCl_2} = \left[\frac{10{,}030}{T} C - 0.720(1 - C)\right] \times 10^{-6} \qquad \text{II-3}$$

where C is the nickel chloride concentration in gm. per gm. of solution. For this work, C = 0.05249 gm./gm. solution, α = 0.142, δ = 10.90 mg. and standardisation gave β = 0.204.

The susceptibilities of the iodine solutions were corrected for solvent and iodine fluorosulphate diamagnetism.

Both fluorine and proton NMR were tried for the determination of solution susceptibilities. For calibration of shift, an external reference was used. The reference was contained in a narrow capillary which was held in a concentric position in the NMR tube by a glass bead attached to the bottom of the capillary. Susceptibilities of Fe(III) solutions determined by Gouy method were used to calibrate signal broadenings.

6. Visual and UV Absorption Spectra

Absorption spectra were taken on a Bausch and Lomb Spectronic 505. One centimeter path length cuvettes with inserts to vary the path length down to 0.05 mm. facilitated study of iodine solutions at concentrations comparable to those used in conductance measurements. Spectra were taken at temperatures down to -90°C in a quartz Dewar provided with quartz windows. The Dewar was closed at the top with a rubber bung. Low temperatures were attained inside the Dewar by passing cold air into it from a liquid air boiler. Temperatures were measured with a copper-constantan thermocouple and a Leeds Northrup temperature potentiometer.

Fluorosulphuric acid in a cell of 1 cm. path length was used as the blank for all spectra.

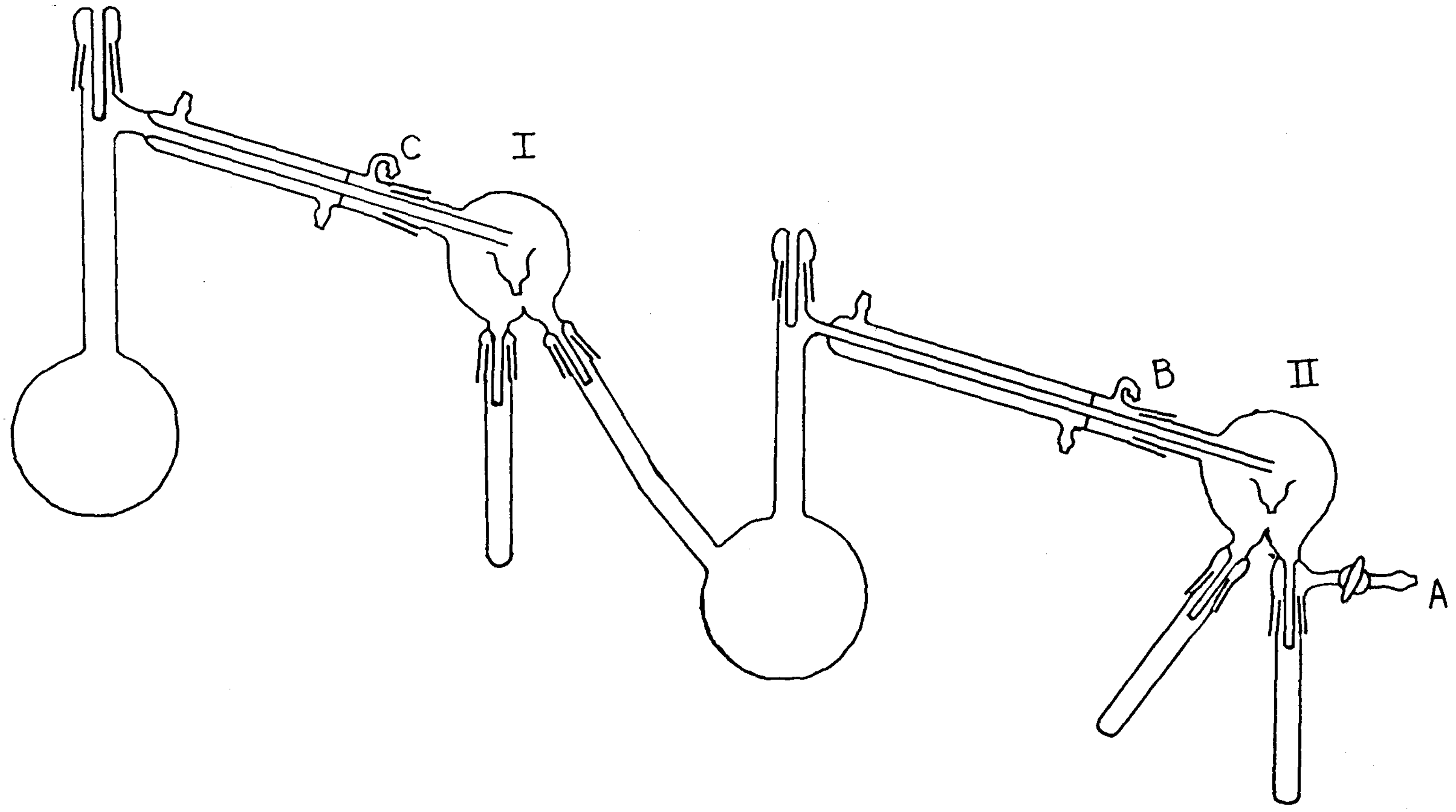

Figure 1 The Fluorosulphuric Acid Distillation Apparatus

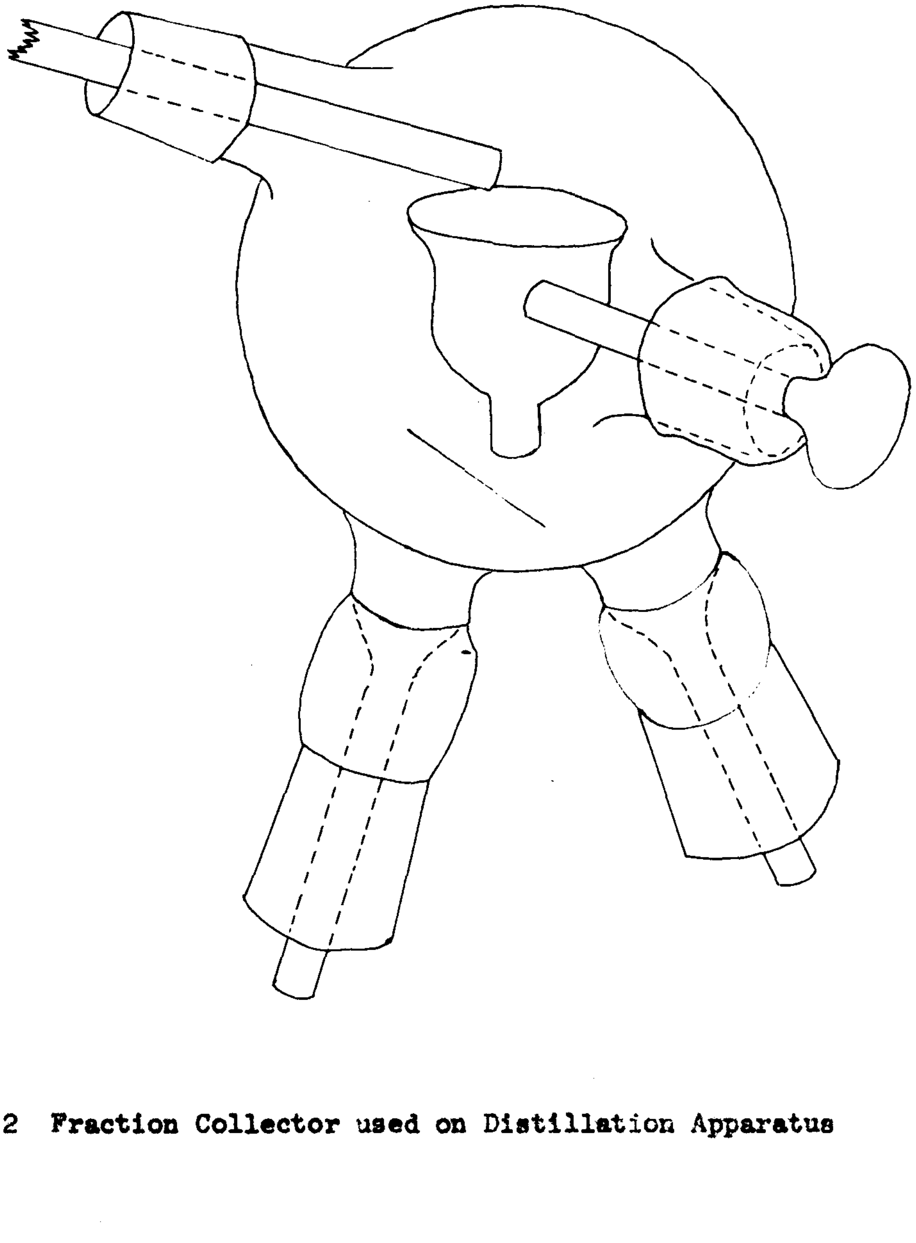

Figure 2 Fraction Collector used on Distillation Apparatus

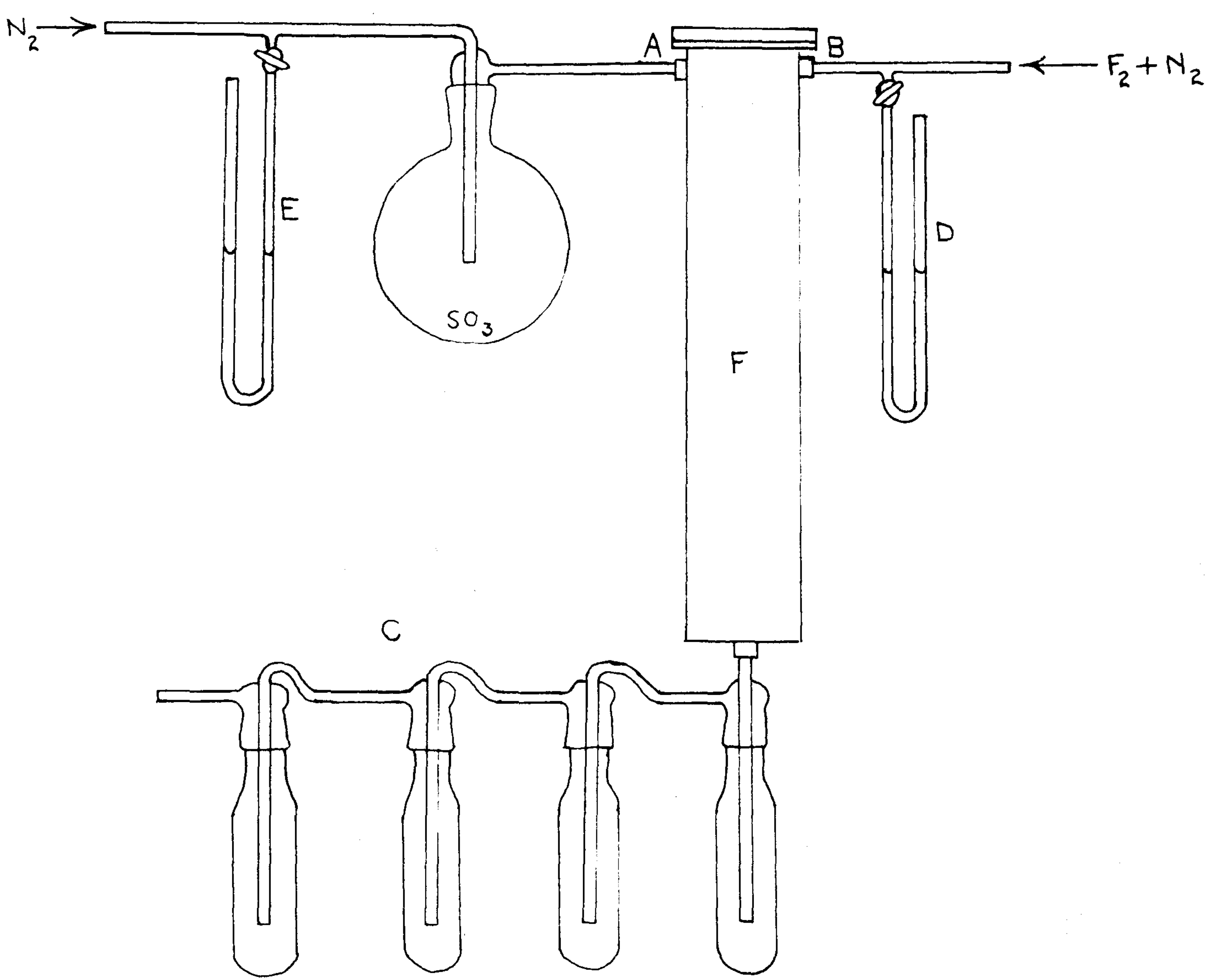

Figure 3 Apparatus for Preparation of Peroxydisulphuryldifluoride

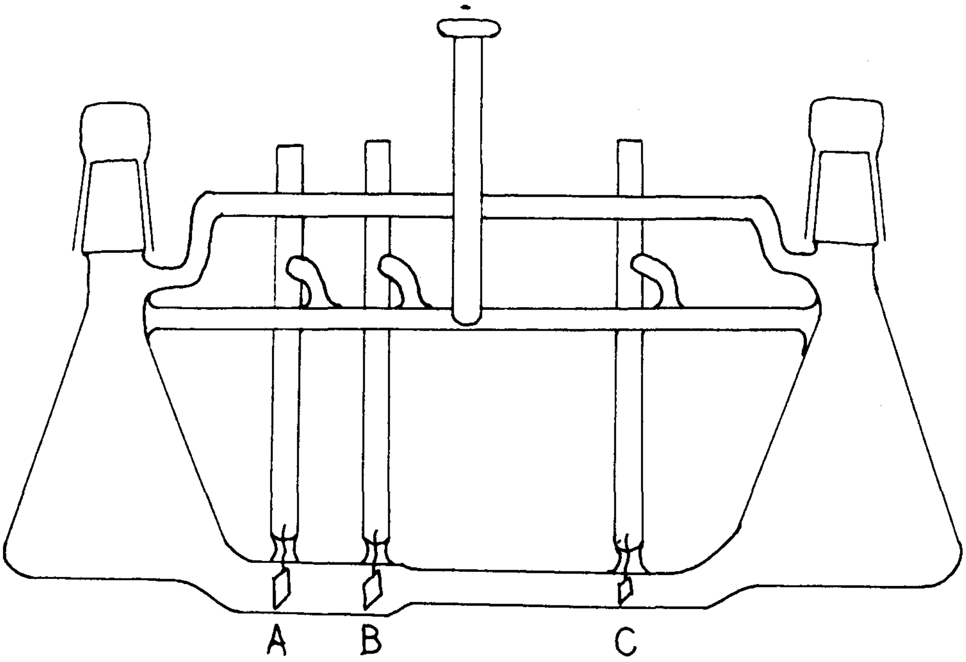

Figure 4A Conductivity Cell

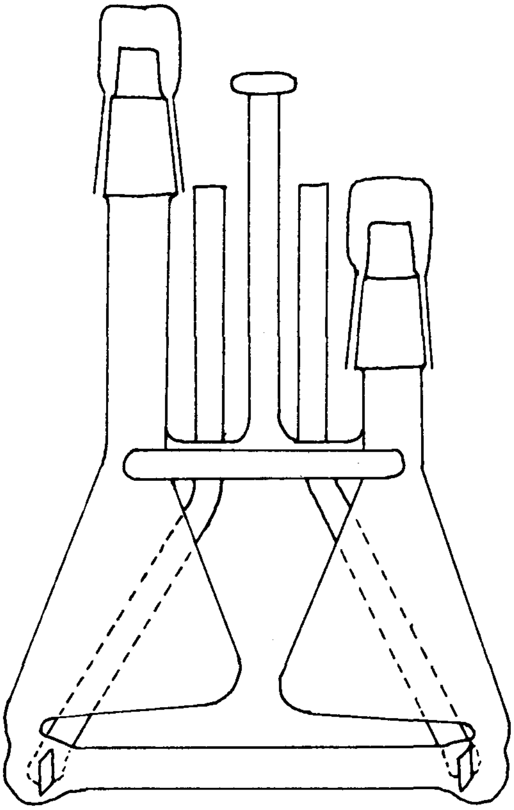

Figure 4B Low Temperature Conductivity Cell

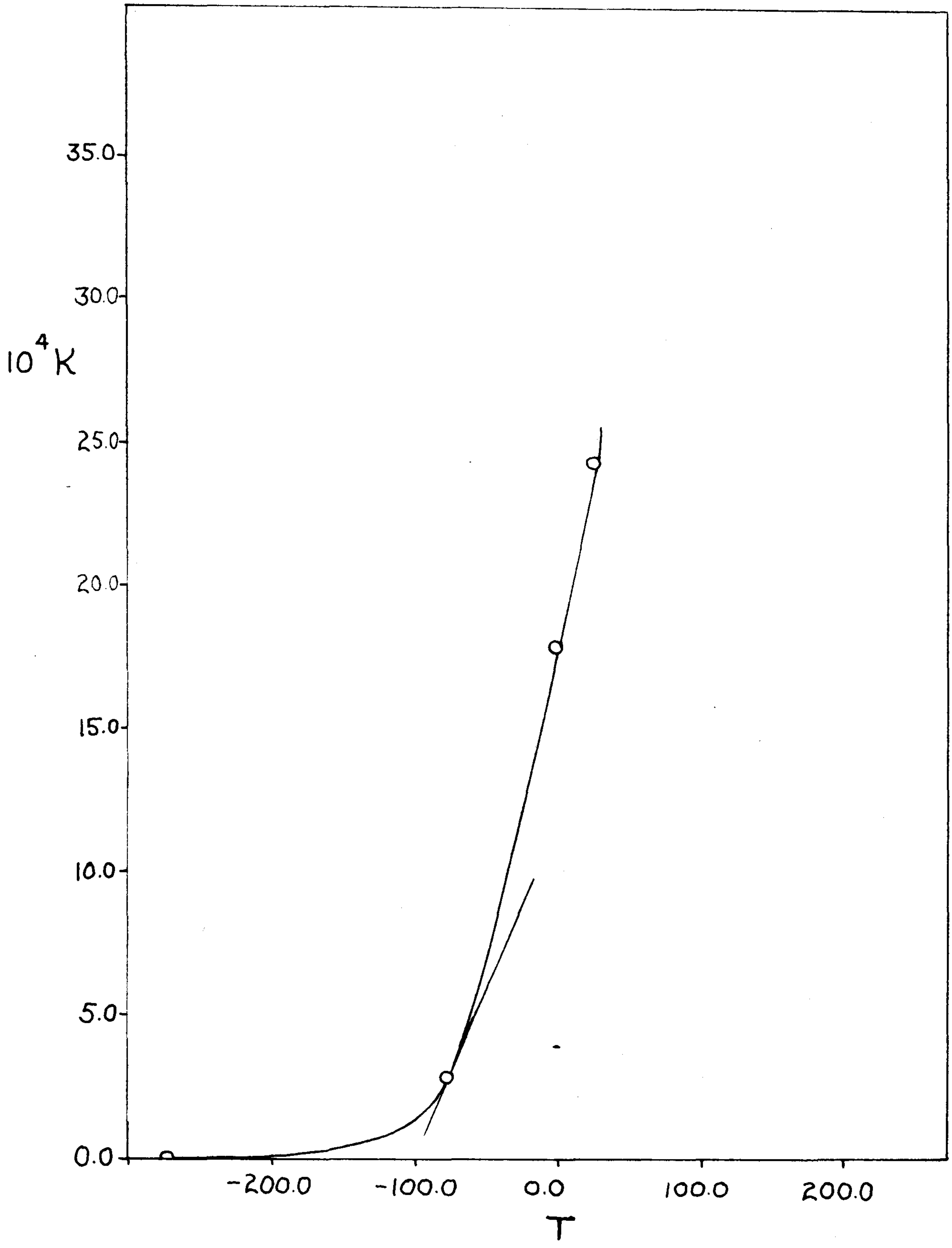

Figure 5 Variation of Potassium Fluorosulphate Conductivity with Temperature

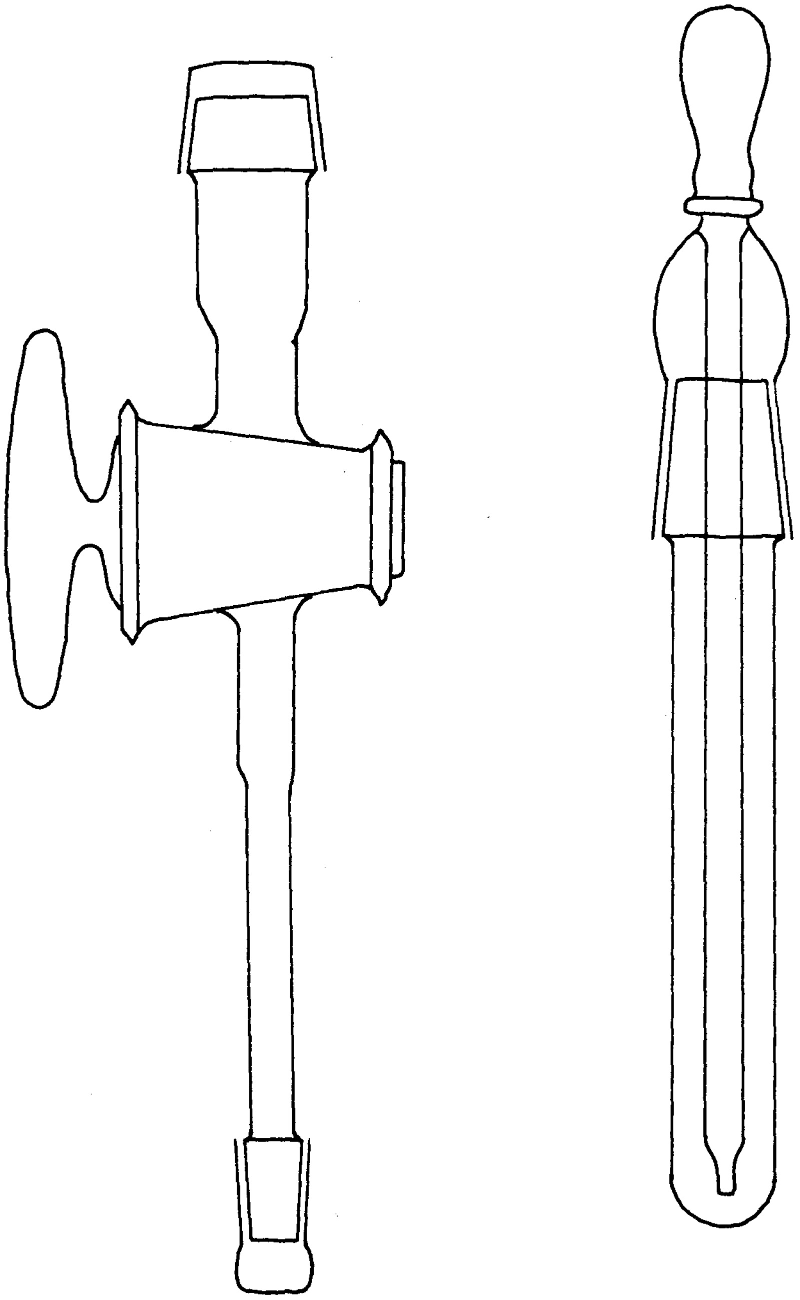

Figure 6A

Figure 6B

Droppers for Solute Additions

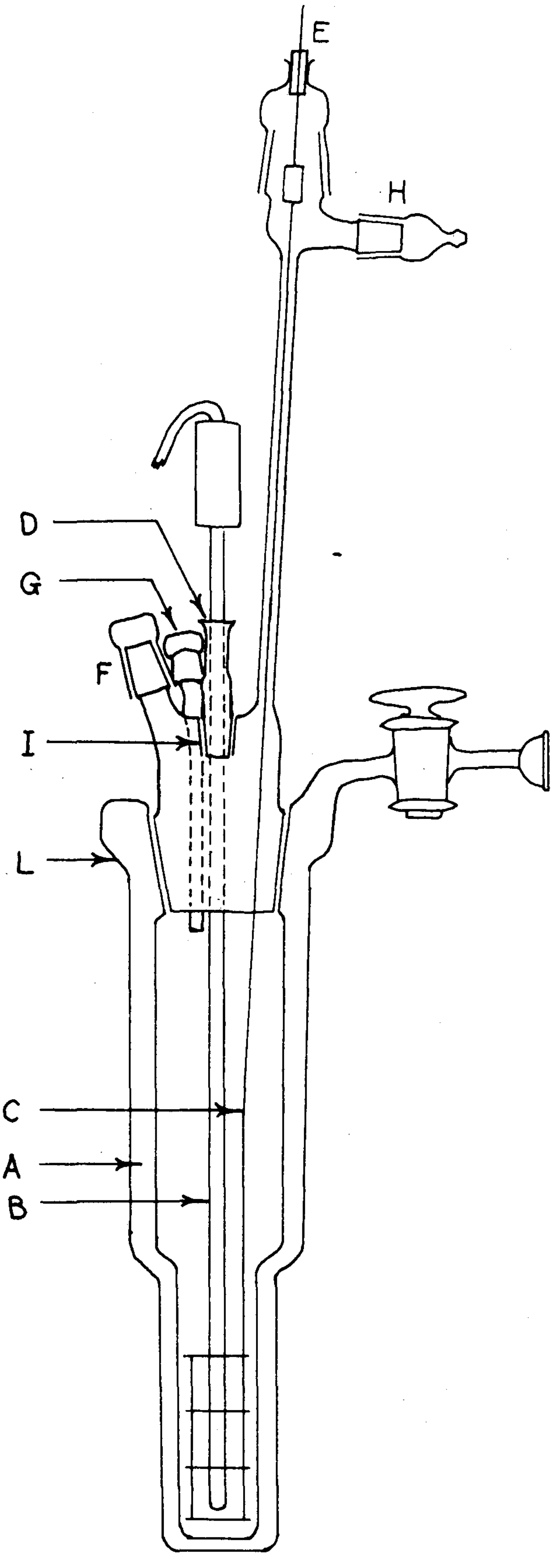

Figure 7A The Cryoscope

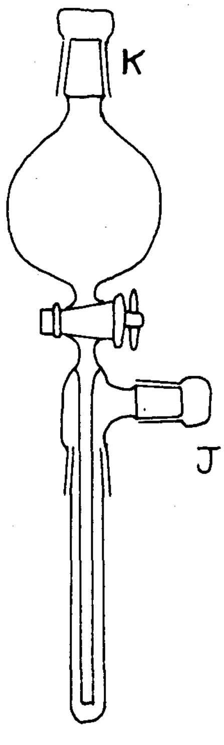

Figure 7B Weight Dropper used for Additions of HSO_3F to the Cryoscope

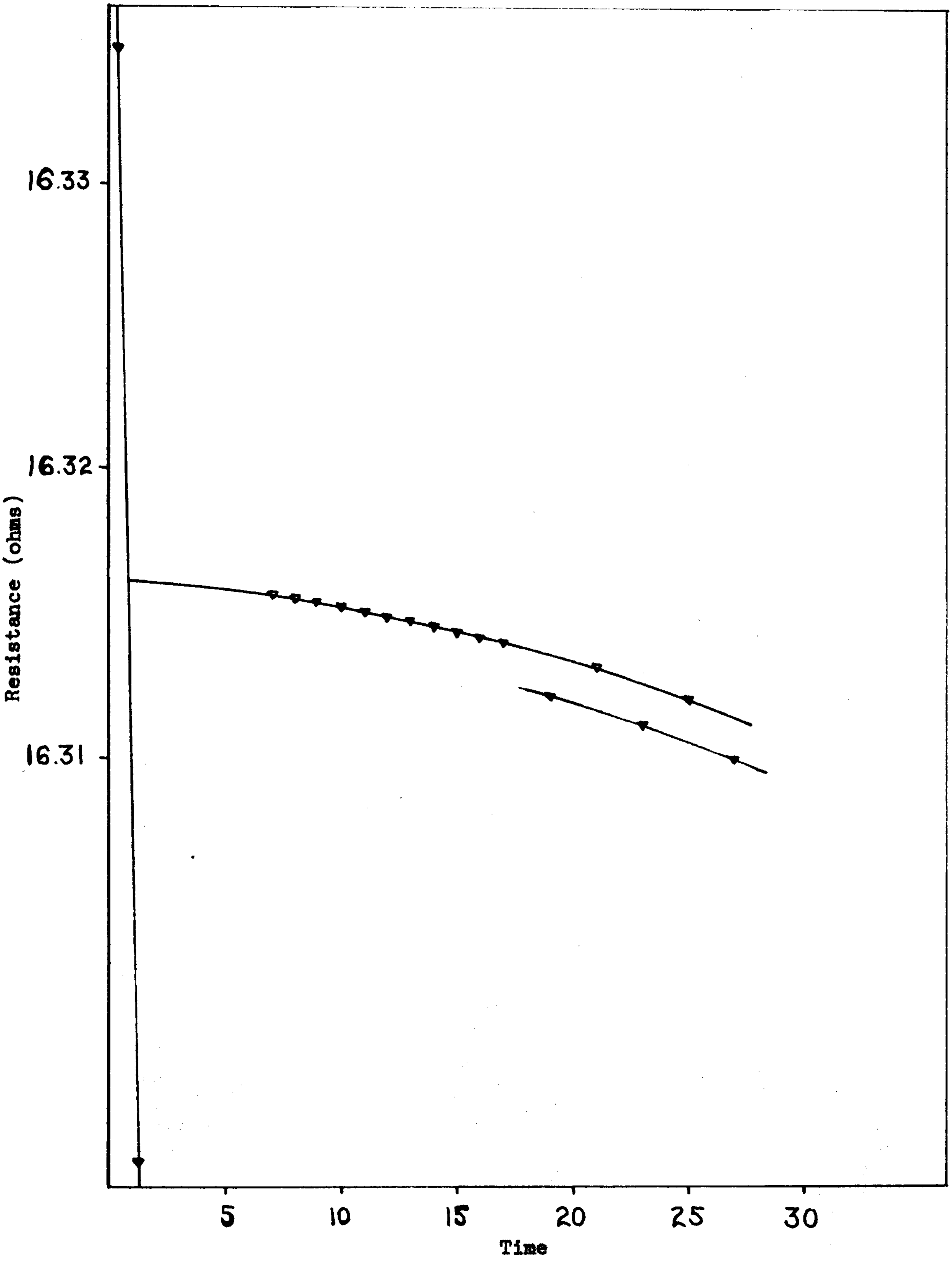

Figure 8 Cooling Curve

CHAPTER III

The Cryoscopic Constant and Solutions of Some Bases

For dilute solutions, the freezing point depression caused by the presence of the solute is governed by the expression(60):

$$\Delta T = \left[\frac{RT_o^2 M}{1000\Delta H_f}\right] m$$

$$= k_f m$$

where: ΔT is the freezing point depression

R is the gas constant

T_o is the freezing point of the pure solvent

ΔH_f is the latent heat of fusion per mole of the solvent

M is the molecular weight of the solvent

m is the molality of the solute

k_f is the cryoscopic constant.

This expression applies only when the solute is unchanged in the solvent. A more general expression is:

$$\Delta T = k_f \nu m \qquad \text{III-1}$$

where ν is the number of particles produced per molecule of solute. When the latent heat of fusion is unknown, the cryoscopic constant may be determined from the freezing point depression caused by solutes whose behaviour in the solvent is known.

Thompson(15) estimated the cryoscopic constant of fluorosulphuric acid from the cryoscopy of trinitrobenzene, potassium fluorosulphate and barium fluorosulphate. Trinitrobenzene is a very weak base in fluorosulphuric acid(94). Allowing for the small amount of protonation on the basis of Barr's conductance measurements(94), Thompson arrived at a value for k_f of 3.35 ± 0.05. The cryoscopy of potassium fluorosulphate, a 1:1 electrolyte, and barium fluorosulphate, a 1:2 electrolyte, gave the same value. The cryoscopy plot for potassium fluorosulphate showed positive deviation from ideality and thus a limiting slope was used to determine the cryoscopic constant. However, as will be shown later, the initial curvature at low concentrations in plots of freezing point depression against molality for many solutes is not caused by non-ideality as first suggested but results from reactions of the solute with trace impurities in the solvent.

Table I and Fig. 9 give the results of the cryoscopy of two non-electrolytes, peroxydisulphuryldifluoride and disulphuryldifluoride. The results of conductivity measurements on solutions of the former are given in Chapter V and it seems safe to assume that disulphuryldifluoride acts as a non-electrolyte. This plot exhibits no curvature in the concentration range studied and gives a value for the cryoscopic constant of 3.93 ± 0.05. Sulphur trioxide acts as a non-electrolyte in fluorosulphuric acid also(13) and, if the initial curvature of Thompson's sulphur trioxide cryoscopy plot, reproduced from his thesis in Fig. 10, is ignored, the cryoscopic constant determined from this slope is 3.93 ± 0.05. Similarly, the sulphur trioxide cryoscopy from this work, Expt. 8 in Table I and Fig. 12, gives $k_f = 3.98 \pm 0.05$. The alkali metal fluorosulphates produce two particles per molecule in fluorosulphuric acid and, if the straight line part of Thompson's plots, Fig. 10, between 0.01 and 0.09 molal is taken as ideal, this also gives a value for the cryoscopic constant of 3.93 ± 0.05. Similarly, potassium fluoride which gives three particles according to:

$$KF + HSO_3F \longrightarrow HF + K^+ + SO_3F^- \qquad \text{III-2}$$

gives the value 3.93 ± 0.05 from an ideal section of Thompson's cryoscopy plot between 0.015 and 0.09 molal in Fig. 10. No satisfactory explanation can be given for the low slope of Thompson's barium fluorosulphate plot(15). Incomplete dissociation, which would give a decreasing slope with increasing solute concentration, has been suggested by Thompson to account for the absence of the positive deviations from ideality usually observed with ionic fluorosulphates, but even for an incompletely dissociated 2:1 electrolyte,the slope at low concentrations is expected to be that of three particles,which is not the case in Fig. 10.

The cryoscopic behaviour of small concentrations of hydrogen fluoride, potassium fluoride, sulphur trioxide and solutes which give fluorosulphate ion suggests that the solvent, prepared by distillation as it was throughout this work, contains trace amounts of impurities which react with the solute initially to prevent the solute from making its normal contribution to freezing point depressions. When hydrogen fluoride is added to the solvent there is initially an elevation, then a depression of the freezing point, suggesting the presence of excess free sulphur trioxide, which reacts with hydrogen fluoride to form fluorosulphuric acid.

$$HF + SO_3 \longrightarrow HSO_3F \qquad \text{III-3}$$

The maximum freezing point of the acid will correspond to the state where equal concentrations of hydrogen fluoride and sulphur trioxide are present in the solvent. Hereafter the reaction of solute with solvent impurities will be referred to as a cryoscopic titration. The cryoscopic titration of excess free sulphur trioxide in the pure solvent with hydrogen fluoride is shown in Fig. 11 and the experimental results are given in Table I. There is considerable scatter of experimental points due, probably, to the volatility of hydrogen fluoride and reaction with the glass cryoscope, but from the end point of the titration, the concentration of sulphur trioxide is estimated to be 0.004 ± 0.001 m. In Experiment 7, care was taken to prevent the loss of hydrogen fluoride by keeping the cryoscope and weight dropper below -40°C. The slope for this experiment, although greater than for the other experiments, is still lower than that for a non-electrolyte but it is not possible to conclude whether this is due to dimerisation or loss of hydrogen fluoride.

When excess hydrogen fluoride is added to fluorosulphuric acid and back titrated with sulphur trioxide the freezing point rises to a maximum and decreases again as shown in Fig. 12. The experimental results are given in Table I. The molality of free excess sulphur trioxide in the solvent can be computed by subtraction of the molality of the excess free hydrogen fluoride, determined from the end point of the cryoscopic titration with sulphur trioxide, from the total amount of hydrogen fluoride added at the start. This gives a sulphur trioxide molality of 0.0059 m.

As shown in Fig. 10, all the cryoscopic plots for alkali metal fluorosulphates exhibit a low initial slope, which is probably due to the reaction of the fluorosulphate ion with the excess sulphur trioxide in the solvent.

$$SO_3F^- + SO_3 \longrightarrow S_2O_6F^- \qquad \text{III-4}$$

Gillespie and Robinson$^{(14)}$ have reported Raman evidence for the presence of $S_2O_6F^-$ ions in fluorosulphuric acid solutions of sulphur trioxide and potassium fluorosulphate. Thus, initially, cryoscopy will indicate the presence of only one particle, the alkali metal cation. The cryoscopic end point, when the excess sulphur trioxide is titrated, is the concentration at the intersection of the initial slope of one and the slope of two observed when the solute is making a full contribution to freezing point lowering. The molality of excess sulphur trioxide found in this way is 0.0072 m. The smooth curvature at the end point suggests that III-4 is an equilibrium.

Cryoscopically water acts in the same way as the alkali metal fluorosulphates. The results are given in Table III and plotted in Fig. 13. The water was added as a solution in fluorosulphuric acid to prevent any splattering that may occur when water is added directly into the cryoscope$^{(15)}$. The results are consistent with the equilibrium proposed by Senior$^{(10)}$ from conductance measurements.

$$H_3O^+ + SO_3F^- \rightleftharpoons HF + H_2SO_4 \qquad \text{III-5}$$

The hydrolysis is not observed cryoscopically since both sides of III-5 have the same number of particles. Both fluorosulphate and hydrogen fluoride can react with the excess sulphur trioxide in the solvent to account for the initial low slope of the cryoscopy plot and estimation of the sulphur trioxide molality by the procedure outlined for the fluorosulphates gives 0.0072 m.

Thompson's potassium fluoride cryoscopy plot, Fig. 10, also has a small initial slope indicating the reaction with excess sulphur trioxide. In this experiment three particles is the full contribution of the solute according to III-2. It is not possible to ascertain the initial slope of the cryoscopy plot for potassium fluoride since the first experimental point is at 0.0077 m KF. However, assuming that the reaction of hydrogen fluoride with sulphur trioxide via III-3 is the dominant reaction initially, the hydrogen fluoride produced according to III-2 will react with excess sulphur trioxide to form solvent. The removal of hydrogen fluoride will reduce the initial contribution to the freezing point depression to that of two particles and the removal of the excess sulphur trioxide will, in effect, cancel the contribution of one of those particles, thereby reducing the initial slope of the potassium fluoride cryoscopy plot to that of one particle. The cryoscopic end point derived from the intersection of a slope of one and the slope of three observed above 0.015 m KF gives a sulphur trioxide molality of 0.0054 m.

Thus far, only sulphur trioxide has been considered as an impurity and it is seen that there is a variation in free excess sulphur trioxide concentration in the distilled solvent. Water is probably also present as an impurity, as shown below, and would act to reduce the sulphur trioxide concentration. If sulphur trioxide were the only impurity in the solvent, there would be a correlation between the freezing point of the original solvent and the same amount of sulphur trioxide found by cryoscopic titration. However, the correlation is poor,as shown in Table II. The acid used in the potassium fluoride experiment has the highest freezing point but does not have the lowest sulphur trioxide molality. Any attempt to correlate the freezing points of the original acid to the sulphur trioxide concentrations as determined by cryoscopic titration suggests that there are variable concentrations of impurities. The presence of water in the solvent is indicated by comparing Thompson's sulphur trioxide cryoscopy, Fig. 10, with Experiment 8 in Table I and Fig. 12. The pure acid in Experiment 8 has a higher freezing point (-89.005°C) than that used by Thompson (-89.015°C), suggesting a lower water concentration in the former experiment. This is born out in the cryoscopy plots. The concentration of sulphur trioxide required after the cryoscopic end point and before a slope corresponding to one particle is attained is less in Experiment 8, Fig. 12, than in Thompson's experiment, Fig. 10. Presumably the sulphur trioxide reacts with water or its reaction products before contributing fully to depression of the freezing point. In addition, no curvature at low concentrations is noted in Thompson's barium fluorosulphate experiment, Fig. 10, where the low freezing point of the pure acid suggests a high concentration of water and consequent absence of free sulphur trioxide.

If the decomposition reaction III-3 were an equilibrium, the end point of the hydrogen fluoride titration with sulphur trioxide would be curved due to repression of the equilibrium. From the experimental results, Experiment 8 in Table I and Fig. 12, it is not possible to state whether there is any curvature but, if it is assumed that there is, it is possible to put an upper limit on the concentration of the decomposition products at the end point. The dotted line in Fig. 12 represents the maximum curvature allowed by the experiment. The temperature at the intersection of the extrapolations of the straight parts of the hydrogen fluoride and sulphur trioxide cryoscopy plots in Fig. 12 represents the freezing point of an hypothetical acid containing no decomposition products which can react with the solute. The difference between this temperature and that of the lowest point of the dotted curve is the freezing point depression caused by the presence of the decomposition products at the end point. This freezing depression, 0.008°C, represents a total molality of 0.002 m which gives $k_d(=m_{SO_3} \times m_{HF}) = 10^{-6}$.

In summary, it may be stated that the fluorosulphuric acid obtained by distillation at atmospheric pressure contains small amounts of excess sulphur trioxide in the order of 0.0055 ± 0.0020 m and there is some evidence for the presence of water. From the shape of the cryoscopic titration plots of hydrogen fluoride with sulphur trioxide it is not possible to state whether III-3 is an equilibrium.

In Table III and Fig. 14 are given the results of the cryoscopy of some bases. Lithium fluorosulphate is seen to behave like potassium fluorosulphate. The two organic sulphonyl fluorides dissolve with difficulty in fluorosulphuric acid and judging from the gradual darkening of the solutions, are slowly decomposed by the solvent if left for any time at room temperature. Dissolution was improved by using stirring of large amplitude. The normal amplitude was used during the freezing point determination since any stirring which broke the surface of the solvent in the cryoscope prevented supercooling. It was assumed that no decomposition occurred if the cryoscope temperature was kept below -10°C. These sulphonyl fluorides are even weaker bases than trinitrobenzene(94) and may be non-electrolytes. Tetramethylurea produces 2.56 particles per molecule and is thus partially diprotonated in fluorosulphuric acid. Hantzsch has reported that tetraethylurea is partially diprotonated in 100% sulphuric acid(93).

TABLE I

Solutions of Some Non-electrolytes: Freezing Point Depressions

Solute	Expt.	T_o	$w_{solvent}$	w_{solute}	m	ΔT
$S_2O_5F_2$	1	-89.007	125.025		.0028	.017
			126.951		.0082	.034
			129.580		.0153	.061
			131.664		.0208	.076
			134.095		.0269	.109
			136.274		.0322	.126
$S_2O_6F_2$	2	-88.994	148.770	1.640	.0556	.216
	3	-88.996	150.929	0.281	.00879	.032
			153.757	0.643	.0193	.074
			159.437	1.348	.0385	.152
			163.585	1.860	.0518	.203
HF	4	-89.000	124.921		.0048	+ .012
			127.704		.0121	.013
			129.886		.0177	.030
			131.670		.0221	.044
			133.496		.0265	.058
			136.324		.0330	.080
			139.027		.0390	.100
	5	-88.996	127.378		.0072	+ .005
			128.939		.0116	.018
			131.468		.0185	.040
			134.319		.0260	.064

TABLE I (Continued)

Solute	Expt.	T_o	$w_{solvent}$	w_{solute}	m	ΔT
HF	6	-89.007	124.276		.0243	.040
			124.929		.0301	.061
			126.332		.0425	.092
	7	-88.996	127.600		.0035	+.011
			129.269		.0074	.004
			130.821		.0109	.014
			133.063		.0158	.035
			135.662		.0213	.054
			139.061		.0283	.079
			144.356		.0384	.116
HF	8	-89.005	135.831	0.000	.0000	.000
SO_3			135.895	0.064	.0248	.050
			136.162		.0058	.029
			136.853		.0209	.000
			138.143		.0485	.103
			139.756		.0824	.242
			140.755		.1029	.330
			142.296		.1341	.459

TABLE II

Correlation of Pure Acid Freezing Points and Excess Sulphur Trioxide Molality

Solute	Expt.	T_o	SO_3m Excess
HF	4	-89.000	.0040
HF	5	-88.996	.0045
HF	7	-88.996	.0033
$HF-SO_3$*	8	-89.005	.0059
H_2O	9	-88.994	.0072
KSO_3F	141†	-89.005	.0072
KSO_3F	62†	-88.999	.0072
KF	Table XXXVI†	-88.987	.0054

* - back titration

† - Thompson's thesis

TABLE III

Solutions of Some Electrolytes: Freezing Point Depressions

Solute	Expt.	T_o	$w_{solvent}$	w_{solute}	m	ΔT
H_2O	9	-88.994	138.763		.0032	.010
			140.325		.0075	.038
			141.789		.0114	.066
			143.307		.0153	.095
			145.080		.0198	.129
			147.470		.0257	.177
$LiSO_3F$	10	-88.983	144.540	1.105	.0721	.547
				1.990	.130	1.021
				3.640	.238	1.927
Ortho-meta dimethyl benzene sulphonyl fluoride	11	-89.005	132.995	0.480	.0192	.073
				0.915	.0366	.133
				1.370	.0548	.197
				1.810	.0724	.261
				2.275	.0910	.325
Methyl sulfonyl fluoride	12	-88.988	147.830	0.360	.0248	.100
				0.760	.0523	.211
				1.130	.0780	.312
				1.510	.1041	.413
Tetramethyl urea	13	-89.028	125.265	0.0840	.00578	.056
				0.1438	.00989	.095
				0.2326	.0160	.156
				0.3378	.0232	.229
				0.4275	.0294	.294

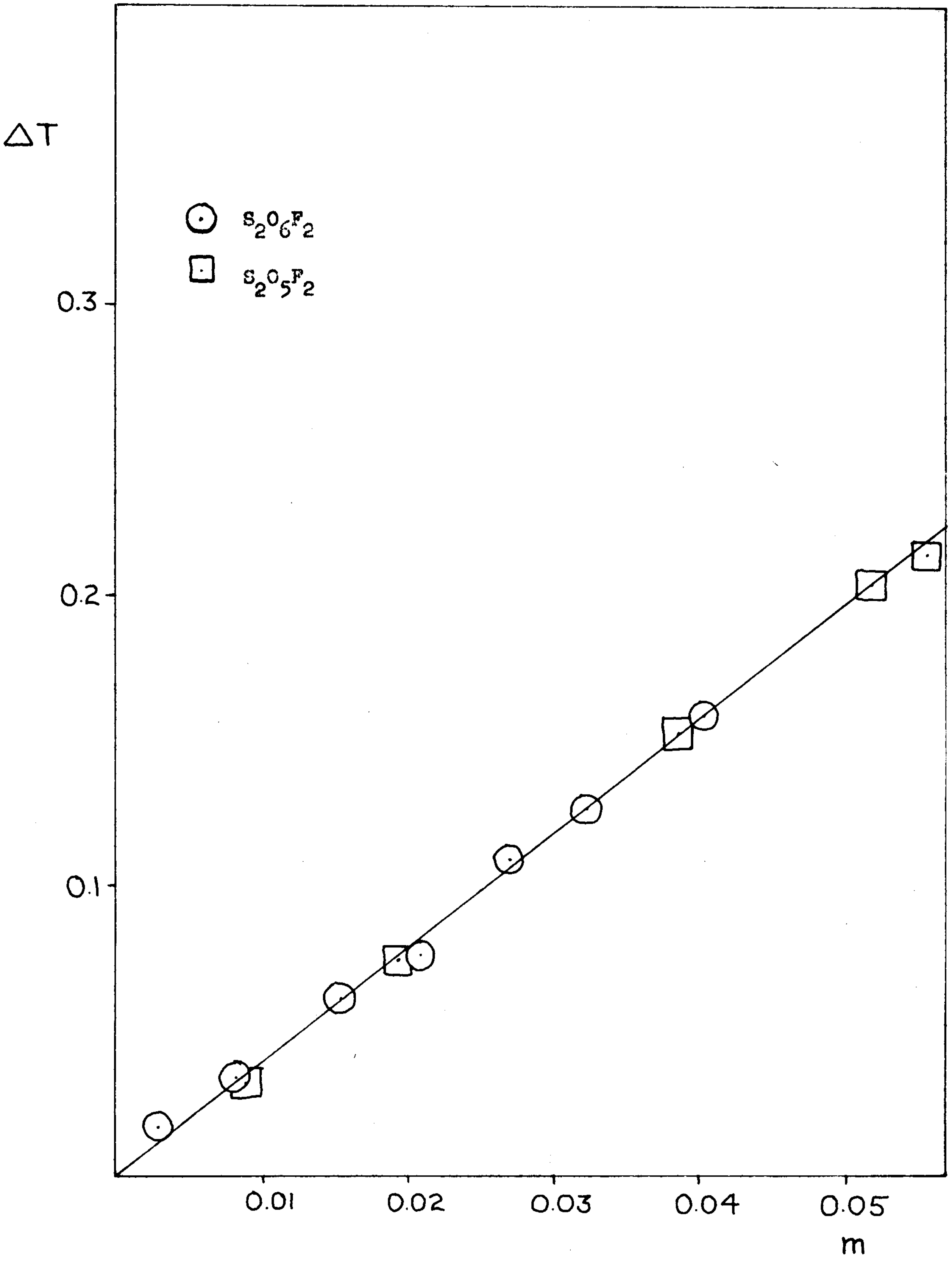

Figure 9 Solutions of $S_2O_6F_2$ and $S_2O_5F_2$: Freezing Point Depressions

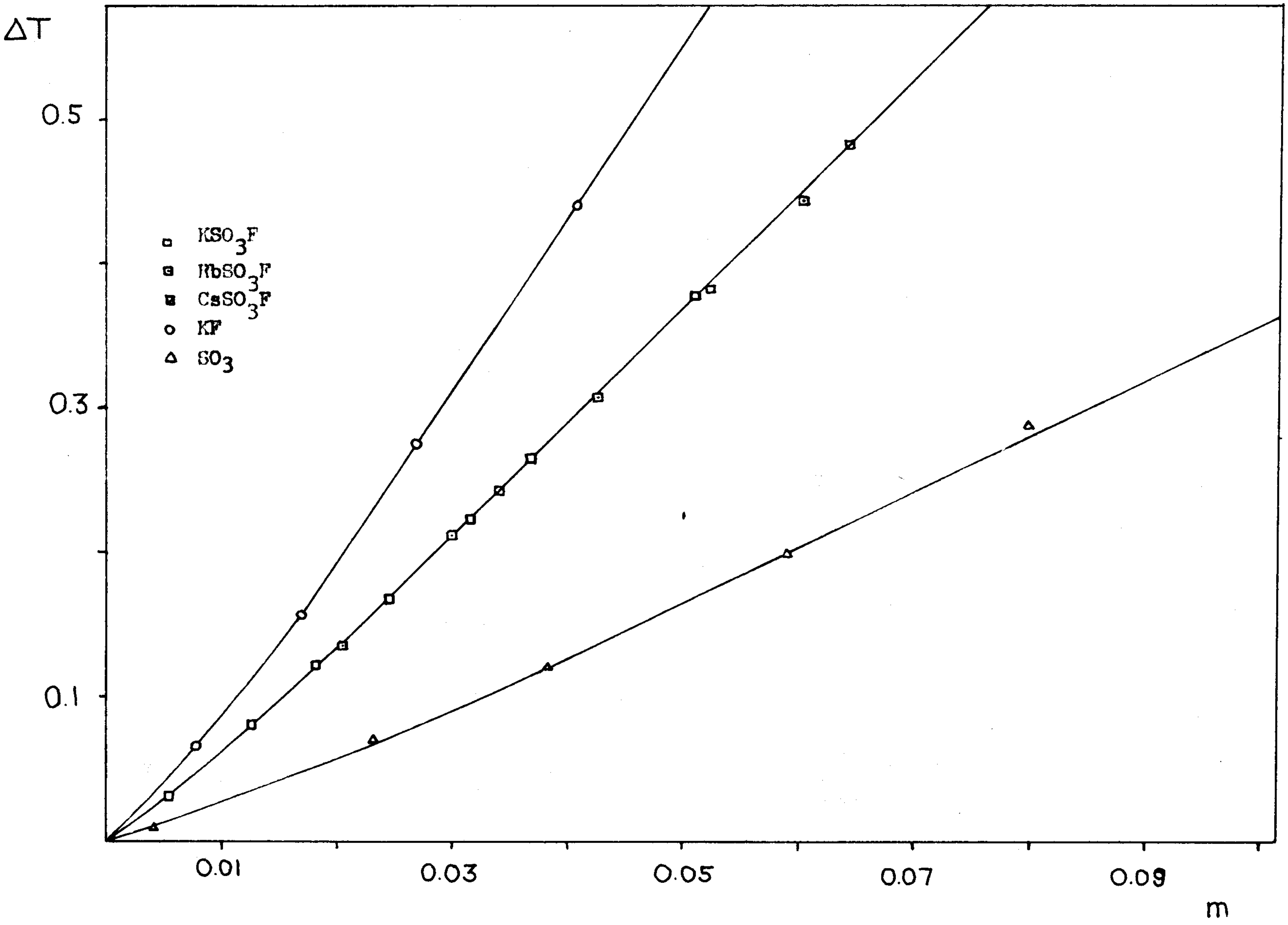

Figure 10 Solutions of Alkali Metal Fluorosulphates, KF and SO_3 : Freezing Point Depressions

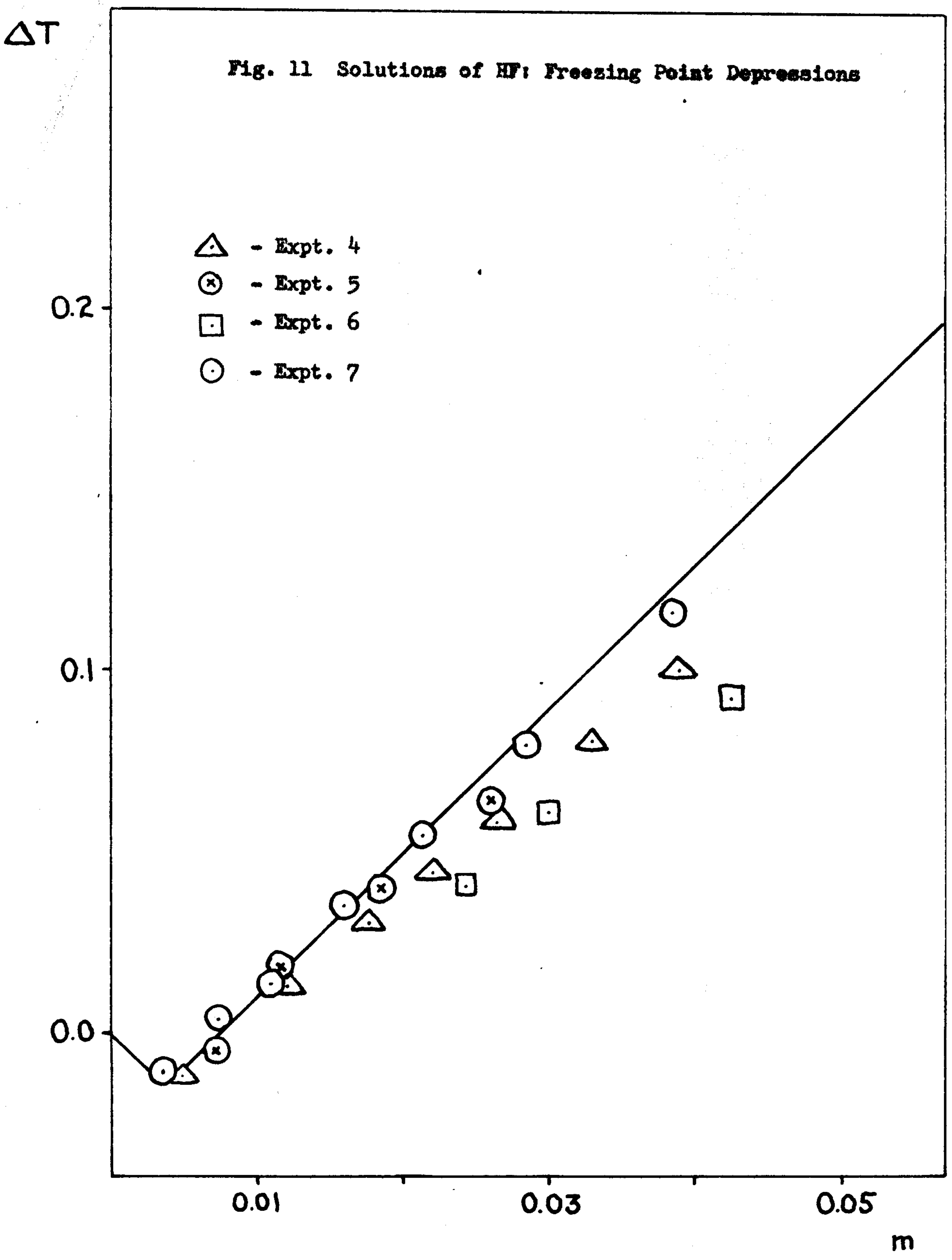

Fig. 11 Solutions of HF: Freezing Point Depressions

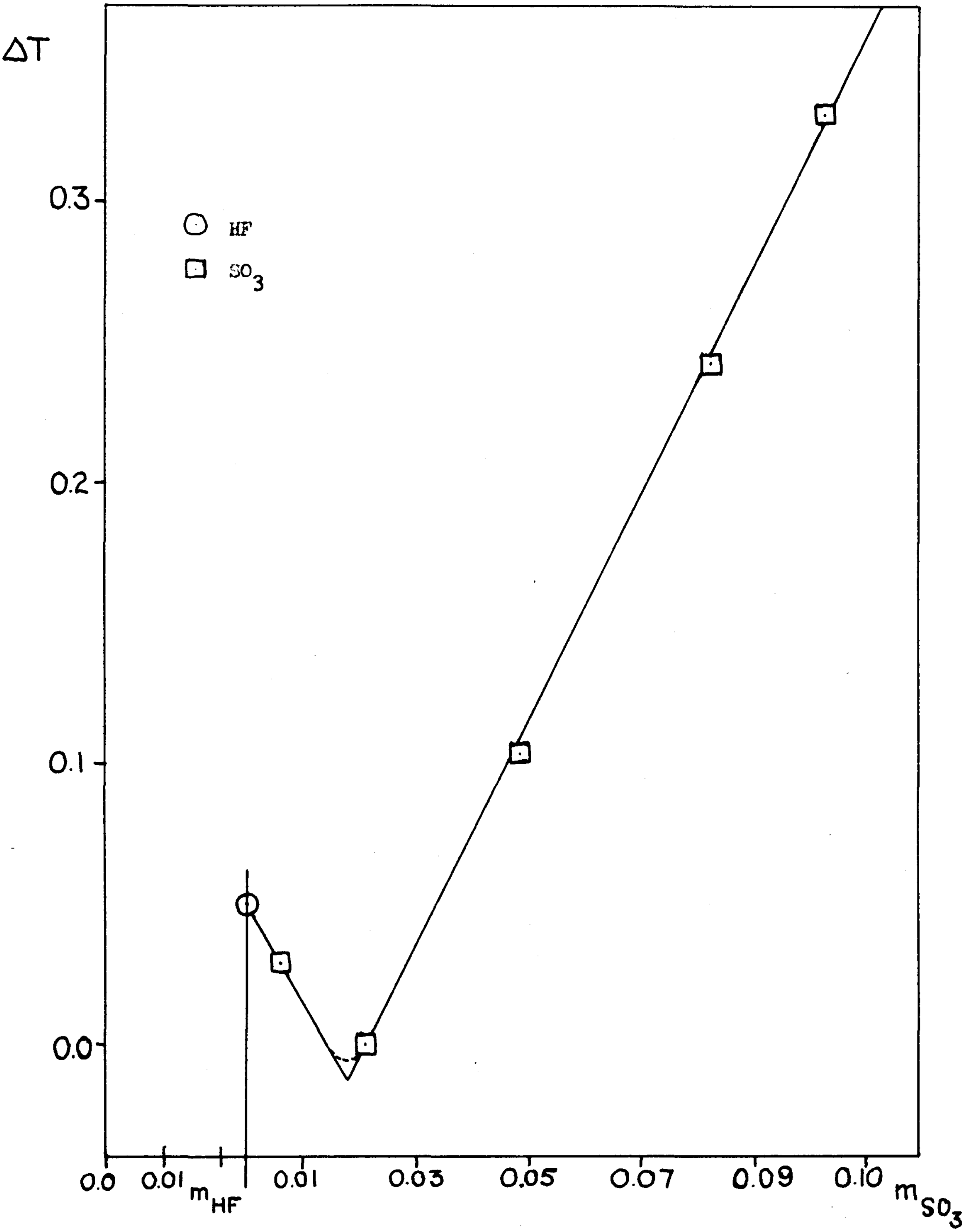

Figure 12 Cryoscopic Titration of HF with SO_3

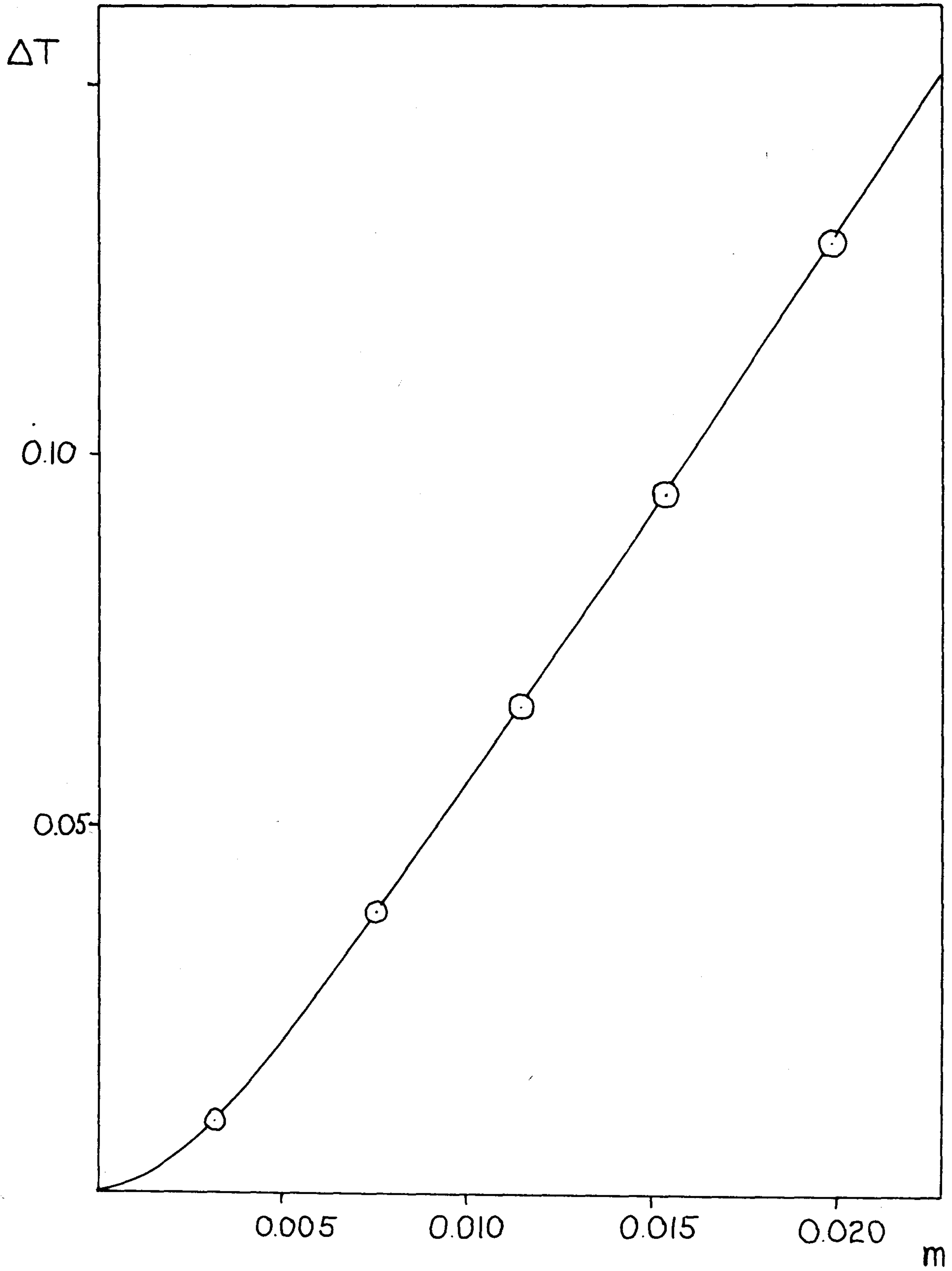

Figure 13 Solutions of H_2O : Freezing Point Depressions

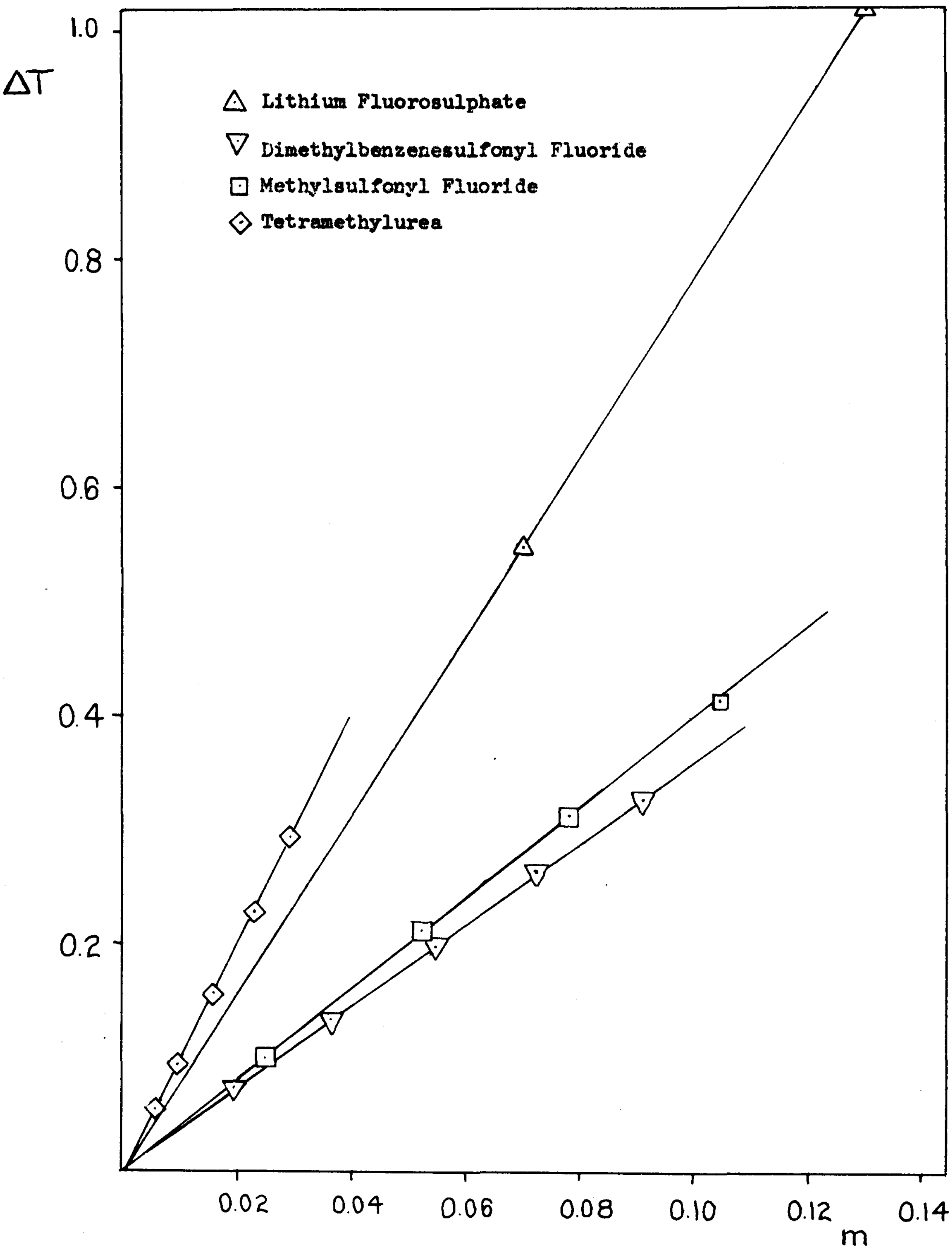

Figure 14 Solutions of Miscellaneous Solutes : Freezing Point Depressions

CHAPTER IV

Magnetic Susceptibilities of Iodine Fluorosulphates in Fluorosulphuric Acid

The magnetic moment of the 'iodine cation' formed when iodine is dissolved in 65% oleum has been determined by Symons and co-workers(78,80) using the Gouy method. Their values range from 1.4BM ($\chi_M = 821 \times 10^{-6}$ cgs) to 2.5BM ($\chi_M = 2520 \times 10^{-6}$ cgs) but they give 1.4BM as their most reliable value(80). Greenwood and co-workers have reported a similar value, 2.0BM, for the 'iodine cation' formed from iodine in iodine pentafluoride when traces of water are present. In quoting these magnetic moments, the authors have assumed that all of the iodine is present as the iodine cation, I^+, which would have a spin only magnetic moment of 2.83BM. The low magnetic moments have been explained in terms of the Kotani theory or by invoking low-lying singlet states(85) for the solvated cation. Earlier, Symons(79) suggested that the 'iodine cation' underwent disproportionation in 65% oleum and, the decrease in μ_{eff} with increasing concentration of iodine reported by this author(78) makes this explanation attractive, but in recent publications(80,85), this hypothesis has been discarded in favour of complete formation of I^+.

As will be shown in Chapter V, peroxydisulphuryldifluoride reacts with iodine in fluorosulphuric acid to form fluorosulphates of iodine with the iodine in different positive valence states corresponding to the stoichiometry of the reactants. The magnetic susceptibilities of the iodine in the 2:1 and 1:1 $I_2/S_2O_6F_2$ solutions decreases with increasing iodine molality as shown in Table IV and Fig. 15. This suggests that the iodine in these solutions is not present simply as an iodine cation but takes part in some equilibrium. The type of equilibrium involved will be discussed in conjunction with the conductance measurements on this solution in Chapter V.

The Gouy method was used to measure the magnetic susceptibility of solutions with stoichiometry corresponding to I_3SO_3F and I_5SO_3F. The results are given in Table IV. The small paramagnetic susceptibility exhibited by the iodine in these solutions cannot be assigned unequivocally to I_3^+ and I_5^+ which, conductimetric and cryoscopic evidence suggest, may be present in these solutions. On the basis of valence bond structures for these cations no paramagnetism is expected, although the presence of low-lying excited states could cause 'temperature independent paramagnetism'$^{(91)}$. However, the small paramagnetism could be accounted for in other ways. The presence of I_2^+, I^+ or its dimer, I_2^{++}, could give rise to the paramagnetism. These species could arise from disproportionation reactions:

$$2\,I_3^+ \rightleftharpoons I^+ + I_5^+ \qquad \text{IV-1}$$

$$3\,I_3^+ \rightleftharpoons 2\,I_2^+ + I_5^+ \qquad \text{IV-2}$$

$$3\,I_5^+ \rightleftharpoons I^+ + 2\,I_7^+ \qquad \text{IV-3}$$

or from oxidation of I_3^+ or I_5^+ by sulphur trioxide which is present in small concentrations in the solvent. The susceptibility of the

0.0953m I_2 solution in Experiment 17 was measured a second time after an interval of six days and no increase in paramagnetism was noted, which indicates that the solvent itself does not oxidise the iodine in solutions of 3:1 $I_2/S_2O_6F_2$ stoichiometry. There is evidence from conductance measurements given in Chapter V that the iodine in 5:1 $I_2/S_2O_6F_2$ solutions is oxidised by the solvent itself. If the paramagnetism of these solutions resulted from oxidation by a small concentration of free excess sulphur trioxide,it would be expected that as the iodine concentration increased, the paramagnetism would be gradually overcome by the increasing concentration of diamagnetic iodine species. The decrease in χ_{MI} with increasing iodine molality in Experiment 17 suggests that sulphur trioxide oxidation does occur. 'Temperature independent paramagnetism' and disproportionation could still account for part of the iodine paramagnetism but neither of these effects would vary with iodine concentration.

An attempt was made to apply NMR techniques for the measurement of magnetic susceptibilities (81,90,95) to these solutions. Dickinson (89) has shown that a molecule contained in an hypothetical sphere of macroscopic dimensions but small compared to the sample size, lying in a medium of volume susceptibility χ_v,experiences a field given by:

$$H = H_o\,[1 + (4\pi/3 - \alpha)\chi_v] \qquad \text{IV-4}$$

where H_o is the field external to the sample and α is a constant characteristic of the sample shape. For a cylindrical sample of infinite length, $\alpha = 2\pi$ and IV-4 becomes:

$$H = H_o(1 + 2\pi/3\chi_v) \qquad \text{IV-5}$$

If H_o is the hypothetical field strength at which nuclear magnetic resonance occurs in the absence of medium susceptibility effects, then the field strength, H', at which resonance will occur in the presence of the medium, is given by:

$$H' = H_o(1 + 2\pi/3\chi_v) \qquad \text{IV-6}$$

If the molecule is now placed in a medium of volume susceptibility χ_v', the field strength at which resonance will occur is given by:

$$H'' = H_o(1 + 2\pi/3\chi_v') \qquad \text{IV-7}$$

The shift, $\Delta\delta$, observed in going from the one medium to the other is then given by:

$$\Delta\delta = \frac{H'' - H'}{H_o} = 2\pi/3(\chi_v' - \chi_v) = 2\pi/3\Delta\chi_v \qquad \text{IV-8}$$

Thus when the molecule in a diamagnetic medium of susceptibility χ_v is transferred to a paramagnetic medium of susceptibility χ_v' the resonance is shifted to high field. The expression, IV-8, can be used for the determination of the magnetic susceptibility of paramagnetic ions in solution. For solutions of low concentration, the volume susceptibility of the solvent in solution can be assumed to be the same as that of the pure solvent and IV-8 simplifies to give:

$$\frac{\Delta\delta}{M} = \frac{2\pi}{3000}\chi_M \qquad \text{IV-9}$$

where χ_M is the molar susceptibility of the paramagnetic species in solution and M is the molarity. The expression IV-9 is only applicable, according to Dickinson's assumptions(89), where there is no interaction between the species undergoing resonance and the magnetic species apart from a bulk susceptibility interaction. Intermolecular effects are accounted for in IV-9 by introducing an interaction factor, q.

$$\frac{\Delta\delta}{M} = (2\pi/3 - cq)\,\frac{\chi_M}{1000} \qquad \text{IV-10}$$

Thus positive interaction can cause the shift, Δδ, to be reduced below that expected for the paramagnetic species of susceptibility χ_M and can even cause the direction of shift to be reversed if the interaction is strong enough.

From χ_M the effective magnetic moment, μ_{eff}, of the paramagnetic species in solution may be obtained from$^{(91)}$:

$$\mu_{eff} = \sqrt{\frac{3kT\chi_M}{N}} \qquad \text{IV-11}$$

where N is Avogadro's number, T is the temperature in degrees absolute and k is the Boltzmann constant.

Connor and Symons$^{(81)}$, using an expression like IV-9, have determined the magnetic susceptibility of iodine dissolved in 65% oleum. Assuming all of the iodine is present as I^+, they give a value of 1.5BM for the effective magnetic moment in good agreement with the value obtained by them$^{(80)}$ using the Gouy method. Senior has confirmed their NMR work$^{(10)}$.

The results of NMR shift measurements on 1:1 and 3:1 $I_2/S_2O_6F_2$ solutions are given in Table VI and are plotted in Fig. 16. The results at low iodine concentrations are plotted in greater detail in Fig. 17. In the same figures are plotted the expected variations in shift with molarity which have been calculated from the susceptibilities determined by the Gouy method (Table IV). The expected shifts were calculated using IV-8 and are given in Table V. The densities which were used to convert the weight susceptibilities to volume susceptibilities and the molalities to molarities were determined from the weight of the solutions used for each Gouy susceptibility measurement and the volume, 4.60 cc., occupied by the solution in the Gouy tube. They are probably accurate to ± 2%. None of the molecules used to detect the paramagnetic susceptibility of these solutions shows the expected dependence of shift, $\Delta\delta$, on iodine molarity which suggests some interaction with the paramagnetic species. As the charge associated with the resonating nuclei goes from positive (H^+), through neutral (trinitrobenzene and $S_3O_8F_2$) to negative (SO_3F^-), the interaction, q, increases and in the last case the shift is to low rather than high field. In the last case the fluorine resonance of fluorosulphuric acid was used and the fluorosulphate ion resulting from autoprotolysis and that associated with the positive iodine species, which will exchange rapidly with the solvent, probably causes the large positive interaction and resultant down-field shift. Dickinson(89) has made similar observations with aqueous solutions of transition metal cations and this behaviour is to be expected for positively charged paramagnetic species. The fluorosulphuric acid proton undergoes a negative interaction with the paramagnetic species. Dickinson has reported negative interactions for cupric, chromic and nickel chlorides with the water proton. Both trinitrobenzene and $S_3O_8F_2$, which are neutral in solution and not expected to interact with the paramagnetic species, exhibit positive interaction.

As pointed out by Senior(10), the use of nuclei in the solvent molecule, especially in an highly associated solvent, for the determination of paramagnetic susceptibility, does not give simply the effect of bulk susceptibility. First there will be an interaction, since any charged paramagnetic species will be solvated and second, any ionic species will affect the structure of the solvent and cause a shift(90). Birchall(97) has shown that the addition of ionic fluorosulphates to fluorosulphuric acid shifts the proton resonance to low field. This is described as the result of two effects; (a) a large shift to low field resulting from a greater degree of hydrogen bonding due to the fluorosulphate ion, and (b) a small shift to high field caused by the breaking up of hydrogen bonding by the cation. A proton taking part in a hydrogen bond is less shielded than that associated with a single acid molecule. Since the shifts reported by Birchall (e.g., -0.822 ppm for a 0.697 m $CsSO_3F$ solution) are not small compared to the shifts reported in this work (Experiment 20, Table VI), the use of nuclei in associated solvents such as 65% oleum or fluorosulphuric acid for the determination of magnetic susceptibilities probably will not lead to correct results. It is surprising that the magnetic susceptibility of iodine dissolved in 65% oleum as determined by the NMR method(81,10) agrees with that found by the Gouy method(80). The NMR shift may, in this instance, be a combination of a negative interaction as observed for fluorosulphuric acid in this work and a positive interaction resulting from the association of the 'iodine cation' and the hydrogen containing $HS_2O_7^-$ ion which would exchange with the solvent. No hydrogen containing anions are present in fluorosulphuric acid.

The 3:1 $I_2/S_2O_6F_2$ solution exhibits an unusual dependence of shift on concentration in its proton resonance, Fig. 16. The initial negative shift is considerably greater than that reported by Birchall$^{(97)}$ for the alkali metal fluorosulphates. The decreasing negative shift with increasing concentration above 0.3m may result partly from the breaking up of hydrogen bonding in the solvent.

The variation of shift for solvent fluorine and proton resonances with change in temperature in the 1:1 $I_2/S_2O_6F_2$ solution is given in Table VII. The decrease in the low field shift of the fluorine resonance with decreasing temperature is probably the result of a number of effects; change in solvent structure, change in solvation and change in the solute equilibria which is discussed in Chapter V. The shift of the proton resonance is probably the result of similar effects, but the shift goes through a maximum at -13°C and begins decreasing very rapidly below -60°C. These observations can be qualitatively related to the effect of temperature change on the solute equilibria and the intensity of the 640 mμ absorption in the visual spectra, Chapter V.

The fluctuating magnetic fields produced by paramagnetic ions in solution provide a mechanism for spin-lattice relaxation of the resonating nucleus. The expression which relates the effective magnetic moment, μ_{eff}, of the paramagnetic species to the spin-lattice relaxation time is:

$$\frac{1}{T_1} = \frac{A\gamma^2 \eta N_p \mu_{eff}^2}{kT} \qquad \text{IV-12}$$

where γ is the magnetogyric ratio for the resonating nucleus, η is the viscosity of the solvent, N_p is the number of paramagnetic ions per cubic centimeter, k is the Boltzmann constant, T is the temperature in degrees absolute and A is a constant. A has been assigned several different values by different authors(90,98,99). The spin-lattice relaxation time, T_1, which determines the signal width in liquids of low viscosity is related to signal width by:

$$\Delta = \frac{1}{2\pi T_1} \qquad \text{IV-13}$$

where Δ is the width at half height.

Rather than using IV-12, the relation between μ_{eff} and T_1 is usually established by assuming a μ_{eff} for one paramagnetic ion and determining other magnetic moments on the basis of this standard. This method gives reasonable values of μ_{eff} for ions other than those in which there is orbital contribution to the magnetic moment(90).

Connor and Symons(81) have used signal broadening to measure the magnetic moment of the 'iodine cation' in 65% oleum. The signal widths obtained by them are much smaller than those predicted by the expression IV-12 with A = 16/15 but by comparison with the signal widths obtained by Morgan(100) for $Cr(en)_3^{+3}$ in a water-glycerol mixture of the same viscosity as 65% oleum they obtain a magnetic moment for I^+ of 1.1BM comparable to their result from the Gouy method.

The line widths of the fluorine and proton signals of fluorosulphuric acid and the fluorine signal of $S_3O_8F_2$ in 1:1 $I_2/S_2O_6F_2$

solutions are given in Table VIII and plotted in Fig. 18. If it is assumed that the broadening of the signal is due to the presence of the paramagnetic species alone, the order of line width at the same iodine molality for the different nuclei may be explained in terms of IV-12 by the change in the effective viscosity. The fluorine of fluorosulphuric acid, through exchange with fluorosulphate ion will spend more time near a positively charged paramagnetic species than will the proton of the acid. Thus the viscosity associated with the former will be effectively increased and the signal will be broader than for the proton.

The signal broadening for fluorine in $S_3O_8F_2$ and the proton in the solvent do not show a linear dependence on iodine concentration. This suggests that the paramagnetic species in these solutions is not formed quantitatively, but takes part in some equilibrium process.

An attempt was made to standardise the proton NMR line widths in fluorosulphuric acid with solutions of some known paramagnetic species. It was found that ferric chloride dissolved in fluorosulphuric acid with the addition of potassium fluorosulphate. A small amount of solid deposited if the solution was allowed to stand, but this was readily filtered off. Table IX gives the results of Gouy susceptibility measurements and the NMR line widths for these solutions and these are plotted against each other in Fig. 19. From this plot the χ_g for the 1:1 $I_2/S_2O_6F_2$ solutions in Experiment 28 are determined from the line widths and these are compared with χ_g determined by the Gouy method in Table VIII. It can be seen that the agreement is not good. This is not unexpected when it is considered that the paramagnetic species formed by ferric chloride in fluorosulphuric acid may differ in charge and solvation properties from the iodine species.

The NMR methods for the determination of magnetic susceptibilities in fluorosulphuric acid do not appear to give the correct results. Part of the failure of the shift method and scatter of experimental points may be attributed to the shape of the sample. Dickinson(89) has shown that in order for the sample to approximate to one of infinite length required for IV-5, the ratio of sample length to sample diameter must be greater than 10 to 1 with the resonance being observed at the middle of the sample. This requirement is not met exactly in this work due to the construction of the probe in the spectrometer which has the resonance sensing coil placed only 1 cm. from the bottom of the sample. This allows a length to diameter ratio of less than 5 to 1 for one half of the NMR tube and would cause shifts to be smaller than expected.

Table IV

Magnetic Susceptibility Measurements (Gouy Method)

Expt.	Solution	m_{I_2}	v_g	F(avg.)	χ_g x 10^6	χ_M† x 10^6
14	HSO_3F	0.000	7.968	-23.52	-0.311	----
15	1:1 $I_2/S_2O_6F_2$	0.235	8.133	-18.21	-0.166	357.2
16	1:1 $I_2/S_2O_6F_2$	0.0108	7.7986	-23.07	-0.300	507.6
		0.0253	7.9942	-22.55	-0.280	646.7
		0.0508	8.0874	-21.68	-0.254	590.6
		0.0879	8.0113	-20.54	-0.232	483.5
		0.170	7.8687	-18.38	-0.176	444.5
		0.328	8.1687	-15.55	-0.099	387.2
		0.879	8.8029	-10.79	+0.019	279.4
		4.67	10.7283	-10.79	+0.015	125.4
17	3:1 $I_2/S_2O_6F_2$	0.0953*	8.1411	-23.34	-0.294	103.2
		0.0953	8.1411	-23.00	-0.286	146.2
		0.179	8.1093	-22.07	-0.264	148.2
		0.373	8.2658	-20.99	-0.232	128.8
		0.801	9.7953	-18.68	-0.148	138.1
		1.83	9.6776	-18.62	-0.148	80.5
		3.58	10.4294	-22.27	-0.207	41.1
18	5:1 $I_2/S_2O_6F_2$	0.620	8.7745	-24.90	-0.309	98.0
21	2:1 $I_2/S_2O_6F_2$	0.0479	7.9737	-21.36	-0.250	659.8
		0.0913	8.1456	-19.98	-0.210	581.0
		0.162	8.3542	-17.68	-0.148	542.2

† - defined as cgs. units per 127 gm. iodine

* - remeasured after 6 days

Table V

Expected NMR Shifts Determined from Gouy Magnetic Susceptibility Measurements

Expt.	Solution	m_{I_2}	M_{I_2}	e	χ_v x 10^6	$\Delta\chi_v$ x 10^6	$\Delta\delta$ (ppm.)
14	HSO_3F	0.00	0.00	1.73	-0.539	0.000	0.00
15	1:1 $I_2/S_2O_6F_2$	0.235	0.377	1.77	-0.294	+0.245	0.513
16	1:1 $I_2/S_2O_6F_2$	0.0108	0.0182	1.70	-0.510	+0.029	0.061
		0.0253	0.0436	1.74	-0.487	+0.052	0.109
		0.0508	0.0873	1.76	-0.446	+0.093	0.195
		0.0879	0.147	1.74	-0.405	+0.134	0.281
		0.170	0.272	1.72	-0.303	+0.236	0.495
		0.328	0.508	1.78	-0.176	+0.363	0.760
		0.879	1.21	1.92	+0.037	+0.576	1.23
		4.67	3.59	2.33	+0.035	+0.574	1.22
17	3:1 $I_2/S_2O_6F_2$	0.0953	0.164	1.77	-0.508	+0.031	0.065
		0.179	0.298	1.76	-0.446	+0.093	0.195
		0.373	0.600	1.80	-0.418	+0.121	0.254
		0.801	1.37	2.13	-0.316	+0.223	0.467
		1.83	2.42	2.10	-0.311	+0.228	0.478
		3.58	3.80	2.27	-0.470	+0.069	0.144

Table VI

Magnetic Susceptibility Measurements (NMR Shift Method)

Experiment 19, 3:1 $I_2/S_2O_6F_2$ Resonance shifted: ^1H in HSO_3F

Reference: ^1H in HSO_3F. Temperature: 28°C.

m_{I_2}	M_{I_2}	Δδ (ppm)
0.625	1.09	-0.817
0.490	0.875	-1.482
0.236	0.393	-2.635
0.116	0.198	-2.500

Experiment 20, 1:1 $I_2/S_2O_6F_2$ Resonance shifted: ^1H in HSO_3F

Reference: ^1H in HSO_3F. Temperature: 28°C.

m_{I_2}	M_{I_2}	Δδ (ppm)
4.67	3.59	+1.585
0.754	1.04	+1.970
0.108	0.180	+0.542
0.042	0.072	+0.359
0.0053	0.0090	+0.125

Experiment 22, 1:1 $I_2/S_2O_6F_2$ Resonance shifted: ^1H in trinitrobenzene

dissolved in HSO_3F. Reference: ^1H in H_2O. Temperature: 28°C.

m_{I_2}	M_{I_2}	$\delta_{obs.}$ (ppm)	Δδ (ppm)
0.00	0.00	-4.617	0.000
0.514	0.750	--	--
0.114	0.188	--	--
0.046	0.0750	-4.496	+0.121
0.023	0.0375	-4.567	+0.050
0.011	0.0188	-4.600	+0.017

Table VI (Continued)

Experiment 23, 1:1 $I_2/S_2O_6F_2$ Resonance shifted: ^{19}F in $S_3O_8F_2$

Reference: ^{19}F in $S_3O_8F_2$. **Temperature:** 28°C.

m_{I_2}	M_{I_2}	$\delta_{obs.}$ (ppm)	$\Delta\delta$ (ppm)
0.000	0.000	-0.083	0.000
0.514	0.750	+0.351	+0.434
0.143	0.234	+0.127	+0.210
0.029	0.0469	0.000	--
0.014	0.0234	0.000	--

Experiment 24, 1:1 $I_2/S_2O_6F_2$ Resonance shifted: ^{19}F in HSO_3F

Reference: ^{19}F in HSO_3F. Temperature: 27.3°C.

m_{I_2}	M_{I_2}	$\Delta\delta$ (ppm)
0.235	0.377	-0.636
0.118	0.195	-0.372
0.078	0.131	-0.257
0.059	0.098	-0.204
0.047	0.077	-0.167

Table VII

Variation of Magnetic Susceptibility with Temperature (NMR Method)

Experiment 25, 1:1 $I_2/S_2O_6F_2$ **Resonance shifted: ^{19}F in HSO_3F**

Reference: ^{19}F in HSO_3F.

m_{I_2}	M_{I_2}	Δδ (ppm)	T(°C)
0.235	0.377	-0.636	27.3°C
0.235	0.377	-0.569	0.0
0.235	0.377	-0.530	-24.0
0.235	0.377	-0.471	-47.6
0.235	0.377	-0.465	-74.0

Experiment 26, 1:1 $I_2/S_2O_6F_2$ **Resonance shifted: ^{1}H in HSO_3F**

Reference: ^{1}H in HSO_3F.

m_{I_2}	M_{I_2}	Δδ (ppm)	T(°C)
0.1862	0.303	+0.595	28.0
0.1862	0.303	+0.608	1.5
0.1862	0.303	+0.620	-13.0
0.1862	0.303	+0.612	-28.0
0.1862	0.303	+0.608	-43.5
0.1862	0.303	+0.605	-60.0
0.1862	0.303	+0.518	-75.0
0.1862	0.303	+0.376	-87.0

Table VIII

Line Widths of NMR Spectra in 1:1 $I_2/S_2O_6F_2$ Solutions

Experiment 23 Resonance broadened: ^{19}F in $S_3O_8F_2$

m_{I_2}	M_{I_2}	Δ (cps)
0.000	0.000	3.5
0.514	0.750	13.2
0.143	0.234	7.6
0.029	0.0469	4.2
0.014	0.0234	3.5

Experiment 24 Resonance broadened: ^{19}F in HSO_3F

m_{I_2}	M_{I_2}	Δ (cps)
0.235	0.377	14.6
0.118	0.195	17.8
0.078	0.131	7.7
0.059	0.098	7.0
0.047	0.077	5.4

Experiment 25 Resonance broadened: ^1H in HSO_3F

m_{I_2}	M_{I_2}	Δ (cps)	T(°C)
0.235	0.377	14.6	27.3
		14.8	0.0
		19.2	-24.0
		23.8	-47.6
		34.7	-74.0

Table VIII (Continued)

Experiment 26 Resonance broadened: ^{1}H in HSO_3F

m_{I_2}	M_{I_2}	Δ (cps)
0.1862	0.303	5.6

Experiment 28 Resonance broadened: ^{1}H in HSO_3F

m_{I_2}	M_{I_2}	Δ (cps)	$\chi_g \times 10^6$ (of Fe^{+3})	$\chi_g \times 10^6$ (Gouy Method)
4.67	3.59	27.5	+0.085	+0.015
0.879	1.21	10.5	-0.140	+0.019
0.328	0.508	7.5	-0.185	-0.099
0.170	0.272	5.3	-0.220	-0.176
0.0879	0.147	1.5	~ -0.280	-0.232
0.0508	0.0873	2.0	~ -0.280	-0.254
0.0253	0.0463	1.5	~ -0.280	-0.280

Table IX

NMR Line Widths and Magnetic Susceptibilities (Gouy Method) of Fe III Solutions

Experiment 27

w gm.	F (avg.) (mgm.)	$\chi_g \times 10^6$	Δ (cps)
8.0637	+21.05	+0.825	180
8.0220	-11.56	-0.001	20.5
7.8556	-23.22	-0.302	2.0
7.979	-24.03	-0.311	0.5

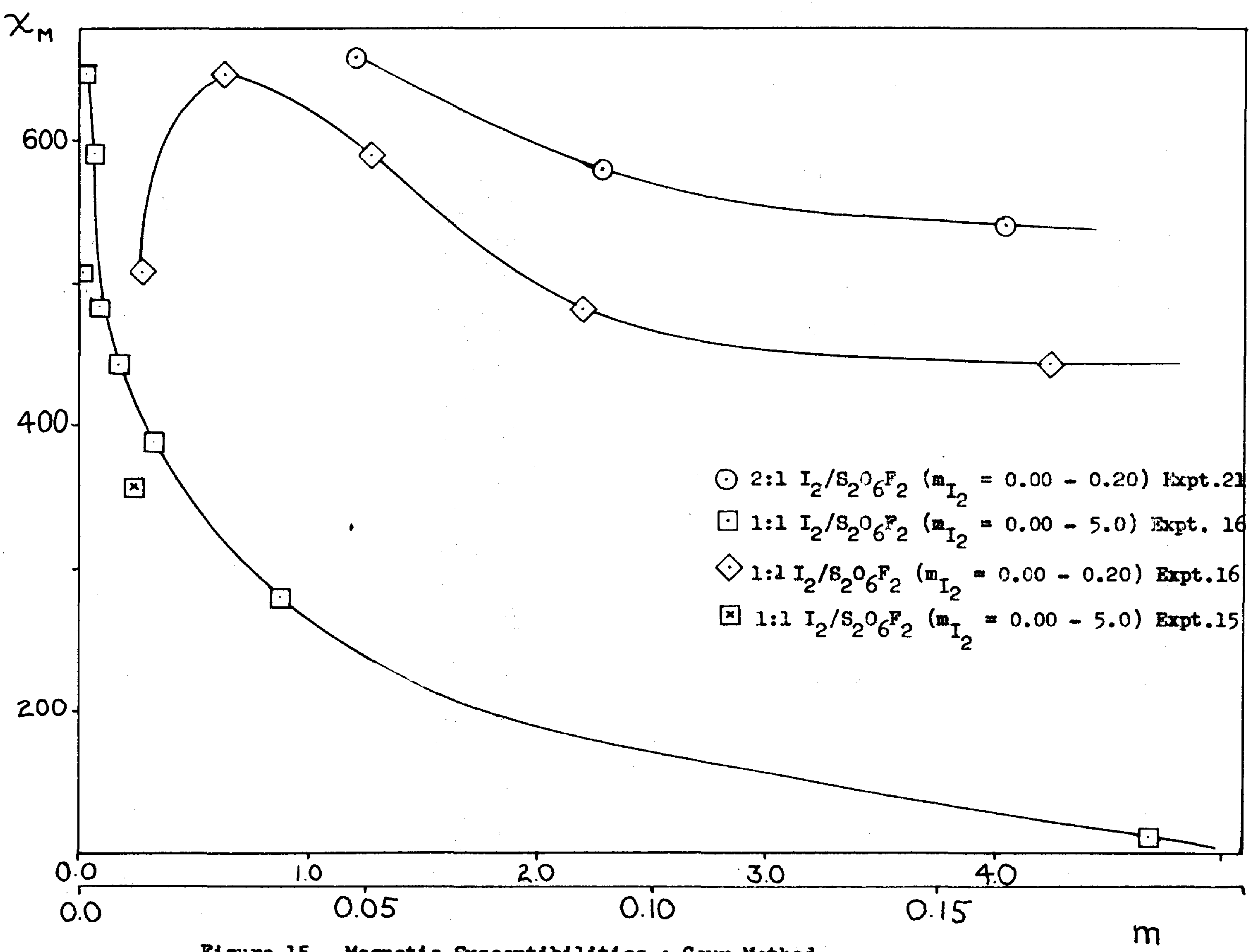

Figure 15 Magnetic Susceptibilities : Gouy Method

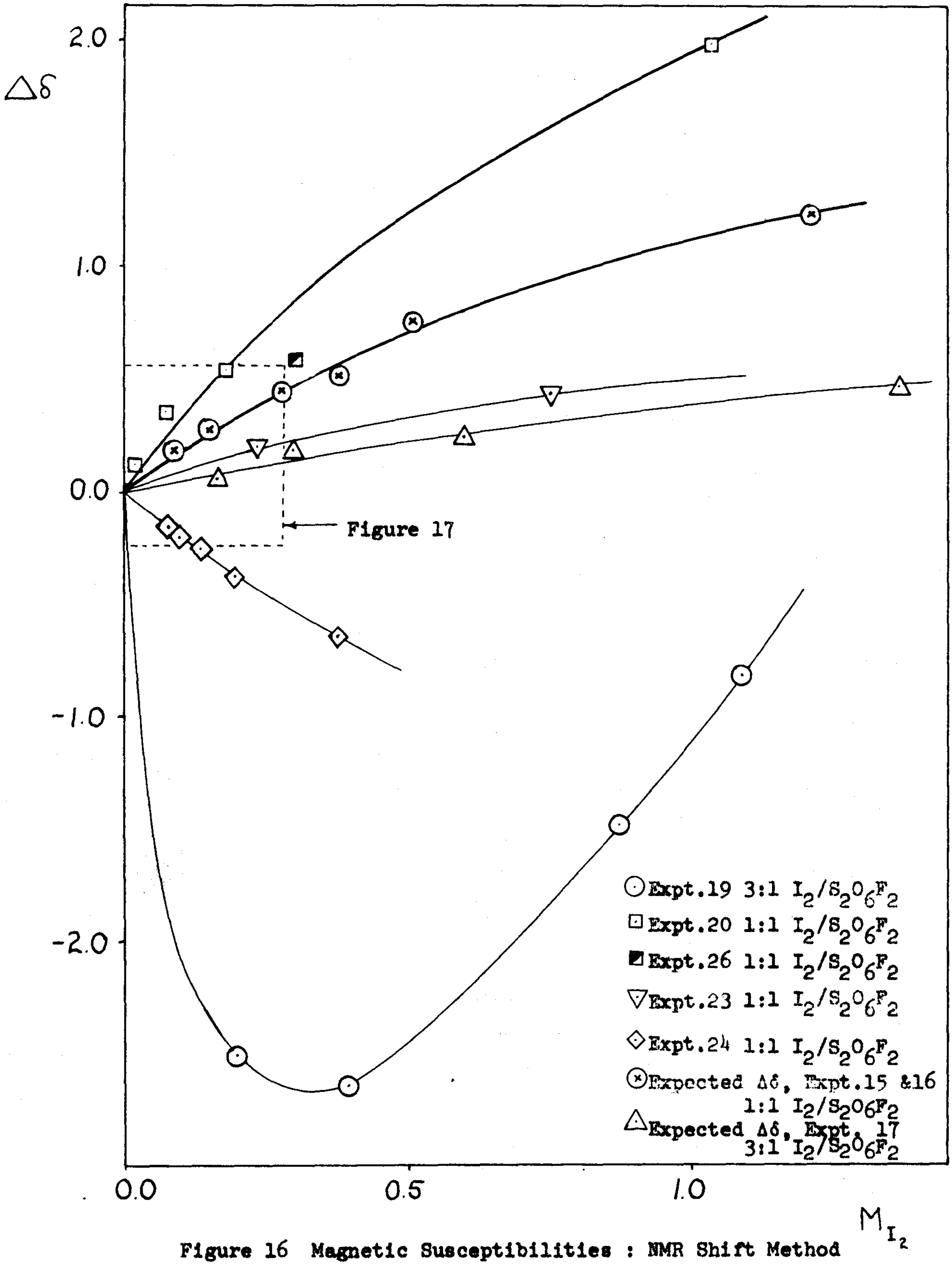

Figure 16 Magnetic Susceptibilities : NMR Shift Method

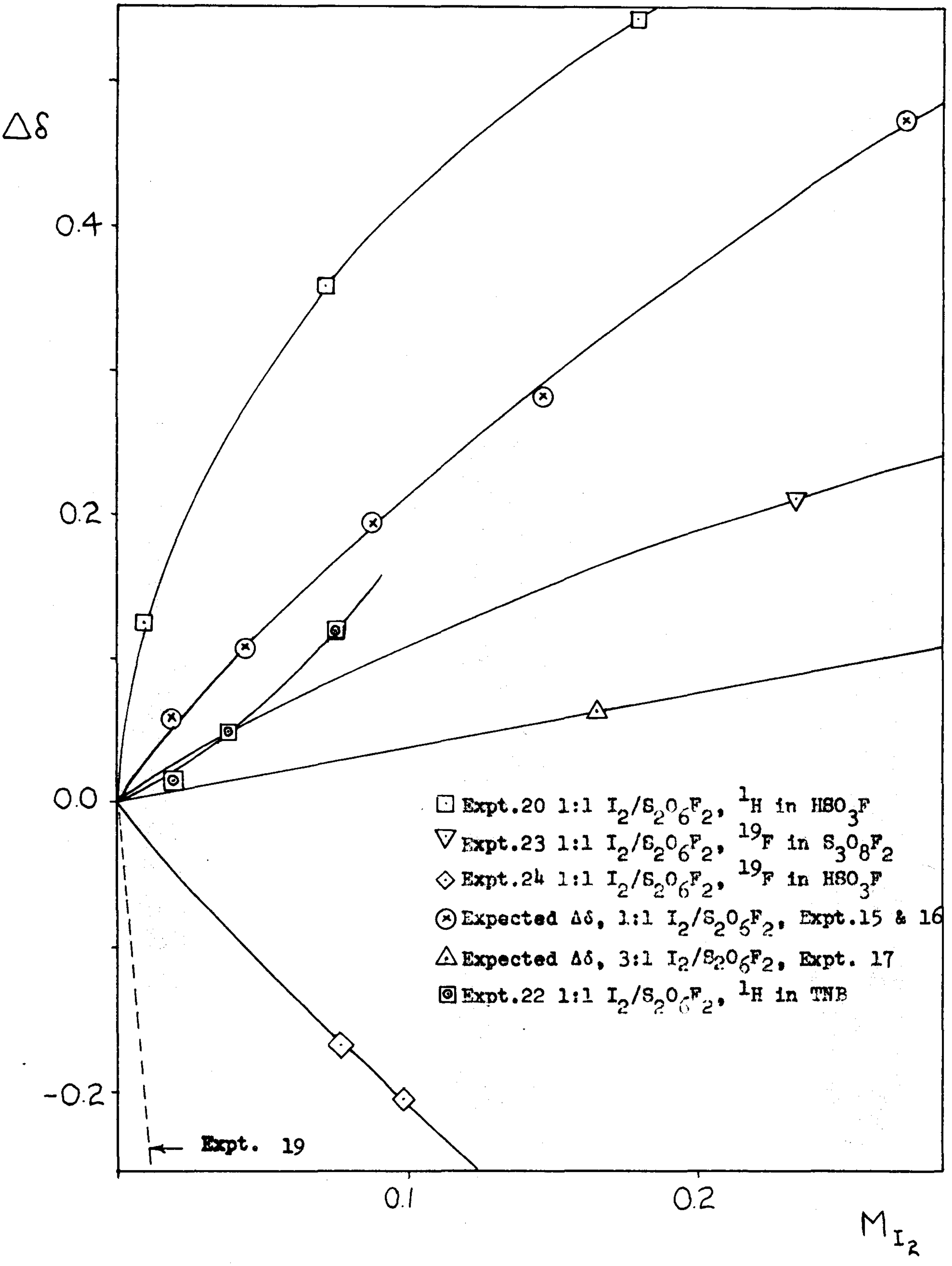

Figure 17 Magnetic Susceptibilities : NMR Shift Method
(Detail of Figure 16)

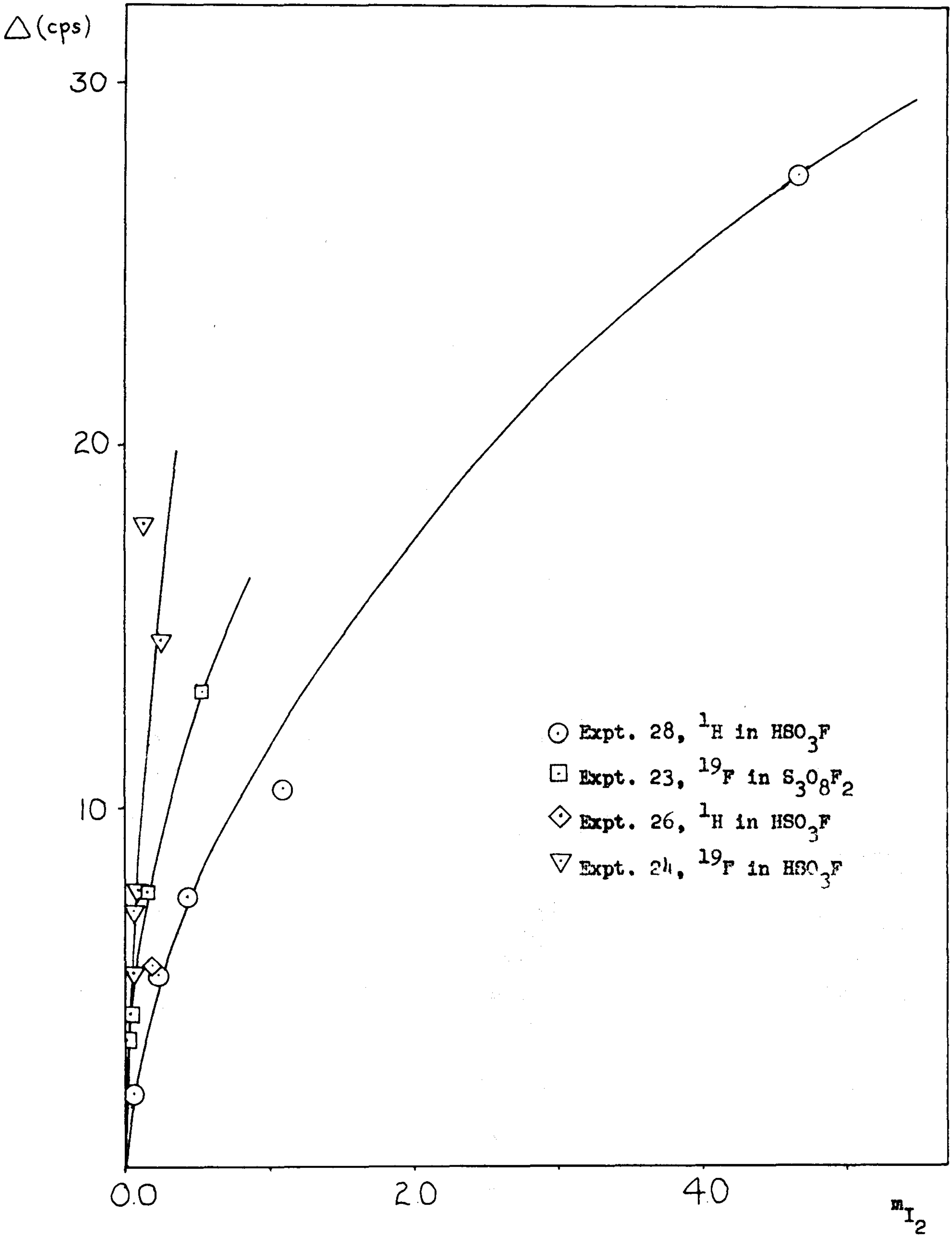

Figure 18 NMR Line Widths : 1:1 $I_2/S_2O_6F_2$ Solutions

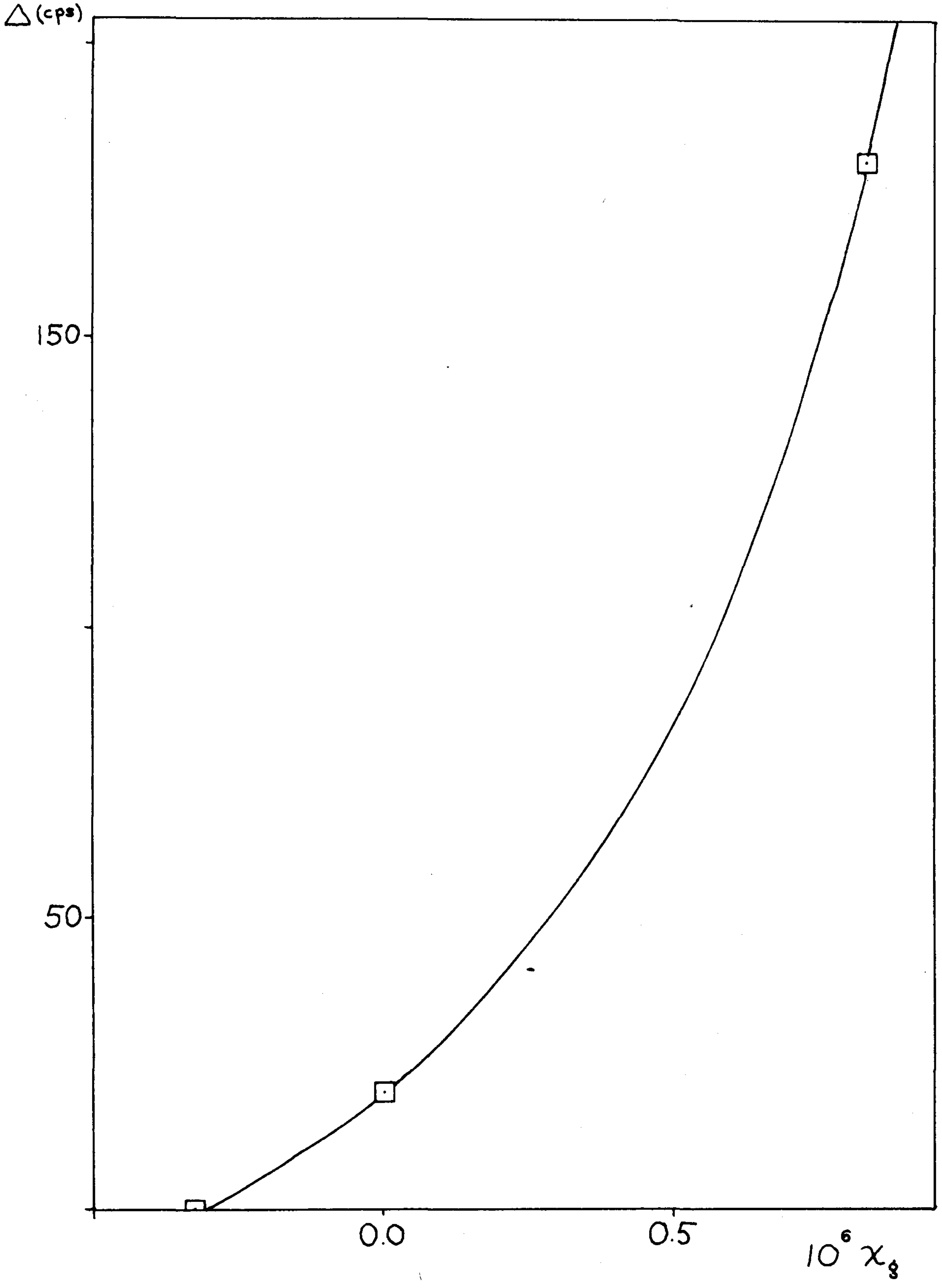

Figure 19 NMR Line Widths : Fe(III) Solutions (Expt. 27)

CHAPTER V

Visual and UV Spectra, Cryoscopy and Conductivity

From the freezing point depression and a knowledge of the cryoscopic constant, k_f, the expression III-1 can be used to determine the number of particles formed per molecule of solute, ν. In this chapter, ν will denote the number of particles formed per molecule of iodine, I_2, added to the solution.

The number of fluorosulphate ions formed in solution per molecule of solute, γ, is also given in terms of molecular iodine, I_2. The γ values in this work were determined by a direct comparison of the conductivity due to the solute with that of potassium fluorosulphate at the same concentration. The potassium fluorosulphate conductivities at 25°C were taken from reference 94 and those at -78.52°C are given in Table X and Fig. 20. It is assumed that the conductivity of the cations formed in the iodine fluorosulphate solutions is the same as that of the potassium cation. This assumption is reasonable as the potassium cation contributes only 11% to the total conductivity of the potassium fluorosulphate(94).

Peroxydisulphuryldifluoride

The results of cryoscopic measurements on peroxydisulphuryldifluoride are given in Table I and Fig. 9. The conductivity measurements at 25°C are presented in Table XI and Fig. 21. The very small conductivity observed was at the limit of the accuracy of the method and cannot be definitely attributed to peroxydisulphuryldifluoride. The same order of conductance increase ($\sim 10^{-5}$ ohm^{-1} cm^{-1}) was obtained when a conductivity run was carried out in which an empty dropper was used. In this run the cell was opened, the empty dropper was inserted and withdrawn, the cell was closed and shaken and then the conductance was read. The change in conductivity observed with peroxydisulphuryldifluoride is probably due to atmospheric moisture and we may conclude, therefore, that $S_2O_6F_2$ is a non-electrolyte.

1:7 $I_2/S_2O_6F_2$

The work of Roberts and Cady$^{(34)}$ suggests that no higher fluorosulphates than iodine trifluorosulphate are formed from iodine in excess peroxydisulphuryldifluoride. The present work indicates that this is also true in fluorosulphuric acid. The results of the cryoscopy of a solution of 1:7 $I_2/S_2O_6F_2$ are given in Table XII and Fig. 22. The plot gives a ν of 6.32 in reasonable agreement with the reaction:

$$I_2 + 7\ S_2O_6F_2 \longrightarrow 2\ I(SO_3F)_3 + 4\ S_2O_6F_2 \qquad \text{V-1}$$

$$\nu = 6.0$$

The fluorine NMR spectrum of the 0.1082 m iodine solution, which was used to make additions to the cryoscope in experiment 35, consisted of two peaks separated by 89 cps in the fluorine-on-sulphur region of the spectrum. The large peak at lowest field can be assigned to the solvent on the basis of the mole ratio of the solvent to solutes. The small peak to high field of the solvent peak was shown to be that of peroxydisulphuryldifluoride by the addition of a further amount of the peroxide to the solution. The results discussed in the section on 1:3 $I_2/S_2O_6F_2$ solutions indicate that iodine trifluorosulphate undergoes exchange with the solvent which accounts for the absence of a peak due to iodine trifluorosulphate from the NMR spectrum of the 1:7 $I_2/S_2O_6F_2$ solution. The iodine trifluorosulphate probably contributes to the solvent peak as a result of rapid exchange. Integration of the spectrum gave a solvent-to-peroxide peak area ratio of 11.8. The stoichiometry of the dropper solution, assuming reaction according to V-1, requires a solvent to peroxide fluorine ratio of 11.6 and, if the large peak to lowest field is due to both the solvent and iodine trifluorosulphate, the required ratio is 12.4. The NMR spectrum at -90°C also consisted of the two peaks observed at 25°C, indicating that the exchange between iodine trifluorosulphate and the solvent is not stopped at temperatures down to the freezing point of the solvent.

The fluorine NMR spectrum of a solution of iodine dissolved in an excess of peroxydisulphuryldifluoride consists of two peaks; a peroxide peak and an iodine trifluorosulphate peak. In a solution with the $I_2/S_2O_6F_2$ mole ratio of 1:43 the iodine trifluorosulphate absorption lies 372 cps to low field of that of the peroxide.

1:3 $I_2/S_2O_6F_2$

The results of cryoscopic measurements on solutions of 1:3 $I_2/S_2O_6F_2$ stoichiometry are given in Table XII and Fig. 22. The results of the conductivity measurements at 25°C and -78.52°C are given in Tables XI and XIII respectively. The conductivity run at 25°C is plotted in Fig. 21 and that at -78.52°C in Fig. 23. The ν value, 1.93, and the very small γ values (<0.1) at both temperatures suggest the same reaction as in the 1:7 $I_2/S_2O_6F_2$ solution:

$$I_2 + 3\ S_2O_6F_2 \longrightarrow 2\ I(SO_3F)_3 \qquad \text{V-2}$$

$$\nu = 2.0,\ \gamma = 0.0$$

The small conductivity probably arises from an ionisation of iodine trifluorosulphate. In order to determine whether iodine trifluorosulphate acts as a base or an acid, two experiments were carried out in which potassium fluorosulphate was added to a solution of the trifluorosulphate (Table XIV and Figs. 24 and 25).

When the mole ratio of potassium fluorosulphate to iodine trifluorosulphate exceeds 1 to 5, the conductivity of the solution falls below that of potassium fluorosulphate alone at equal potassium fluorosulphate molalities, indicating the removal of fluorosulphate ion by the iodine trifluorosulphate. Thus iodine trifluorosulphate acts as a very weak acid.

$$I(SO_3F)_3 + 2\ HSO_3F \xrightleftharpoons{K_{V-3}} H_2SO_3F^+ + I(SO_3F)_4^- \qquad V\text{-}3$$

Cady and Lustig have reported the preparation of the potassium salt, $KI(SO_3F)_4$(27). The conductivity does not pass through a minimum when potassium fluorosulphate is added to iodine trifluorosulphate (Fig. 25), as expected for the conductimetric titration of an acid with a base. This is probably due to the presence in the solvent of traces of water which acts as a base(10).

Since the fluorosulphuric acidium ion is responsible for ~95% of the conductivity of the solutions of acids(15), it is possible to estimate the molality of $H_2SO_3F^+$ from a comparison of the conductivity of iodine trifluorosulphate (Fig. 21) with that calculated for $H_2SO_3F^+$(15) and determine K_{V-3}. The concentration of $H_2SO_3F^+$ in the 1:3 $I_2/S_2O_6F_2$ solutions is comparable to that of the impurities in the solvent and for this reason it is not possible to determine K_{V-3} exactly, but an estimate from the information in Fig. 21 gives $\sim 10^{-5}$. The ionisation of iodine trifluorosulphate provides a mechanism for exchange of fluorosulphate with the solvent and accounts for the absence of an NMR signal due to this compound in fluorosulphuric acid solutions.

Fig. 26 shows the visual and UV spectrum of a 0.124 m solution of iodine trifluorosulphate in fluorosulphuric acid containing a trace of water. Spectra taken at 28°C and -85°C are given. A 0.03 cm. path length was used and thus the spectrum is equivalent to that of a 0.00372 m solution of iodine trifluorosulphate in a cell of 1 cm. path length. It is virtually impossible to keep water out of these solutions and its presence is easily detected since the products of the reaction with water have a much higher extinction coefficient than that of iodine trifluorosulphate. The addition of water causes those peaks which are characteristic of the spectrum of 1:1 $I_2/S_2O_6F_2$ solution at 25°C, 488 mμ and 640 mμ, to appear in the iodine trifluorosulphate spectrum. From a comparison of the height of the 640 mμ peak in the room temperature spectrum in Fig. 26 and in the spectrum of the 1:1 solution in Fig. 34, it is estimated that the iodine molality which causes the 1:1 spectrum in Fig. 26 is 0.004 m or 1/15th of the total iodine in the solution. The peak at 360 mμ may be due to $IOSO_3F$ which is discussed below. The presence of excess peroxydisulphuryldifluoride in the solutions removes the 1:1 absorption and the resultant spectrum of a 0.00014 m solution in a cell of 1 cm. path length is shown in Fig. 26. There is no absorption above 300 mμ.

The reaction between iodine trifluorosulphate and water at low temperatures was studied by cryoscopy (Table XV, Fig. 27) and conductivity at -78.52°C (Table XVI, Fig. 28). There is an initial decrease in the number of particles with the addition of water at the rate of -0.19 particles per molecule of water added, then the water begins to contribute two particles per molecule in the normal manner (Chapter III, Fig. 13). The intersection of a slope corresponding to $\nu = 2.0$, the normal slope for water, drawn through the last point on the plot and the initial slope of -0.19 corresponds to a water molality of 0.052 m which is close to the iodine trifluorosulphate molality, 0.056 m, and suggests that the low temperature reaction occurs between one iodine trifluorosulphate molecule and one water molecule. The low temperature conductivity measurements lead to the same conclusion. The intersection of the small initial slope corresponding to $\gamma = 0.075$ with the slope of water in fluorosulphuric acid given by the last three points in the plot corresponds to a water molality of 0.027 m. The iodine trifluorosulphate molality in this experiment is 0.020 m. These results suggest the reaction:

$$I(SO_3F)_3 + H_2O \longrightarrow IOSO_3F + 2\ HSO_3F \qquad \text{V-4}$$

The initial removal of particles may be accounted for by the polymerisation of iodosyl fluorosulphate and the small initial conductivity may be the result of ionisation of the iodosyl fluorosulphate.

When the solution of iodine trifluorosulphate and water from the conductivity experiment (experiment 45) was warmed to 25°C, it turned from a pale green to a dark green-blue irreversibly and upon standing deposited a yellow solid not unlike the behaviour of Senior's 3:1 HIO_3/I_2 solution in fluorosulphuric acid(10). This green-blue colour, which is characteristic of the iodine oxidation state of one, suggests that disproportionation occurs.

3:1 $I_2/S_2O_6F_2$

The cryoscopy of the 3:1 $I_2/S_2O_6F_2$ solution (Table XII, Fig. 29) gives $\nu = 1.26$ particles and the conductivity experiments at 25°C (Table XI, Fig. 30) and -78.52°C (Table XIII, Fig. 31) give $\gamma_{25°C} = 0.69$ and

$\gamma_{-78.52°C} = 0.65$ respectively. These results are consistent with the reaction:

$$3\ I_2 + S_2O_6F_2 \longrightarrow 2\ I_3^+ + 2\ SO_3F^- \qquad \text{V-5}$$

$$\nu = 1.33,\ \gamma = 0.67$$

It should be noted that in any reaction in which fluorosulphate ion is formed, ν must be determined from the slope of the freezing-point-concentration plot after the initial small slope caused by the presence of free excess sulphur trioxide in the solvent (Chapter III). The preparation of the third-valent iodine cation, I_3^+, in 98% and 100% sulphuric acid has been reported by several authors(10,48,74,77) and Senior(10) has given cryoscopic and conductimetric evidence for it in 7:1 I_2/HIO_3 mixtures in fluorosulphuric acid. The spectrum of a 0.0112 m I_3SO_3F solution at 28°C using a 0.01 cm. path length which is given in Fig. 32 is essentially the same as that given by Aubke and Cady(35). A similar spectrum is given by Symons for I_3^+ in 100% sulphuric acid(48). The spectrum of the above I_3SO_3F solution in fluorosulphuric acid at -85°C is also given in Fig. 32. These spectra indicate that I_3^+ probably does not disproportionate since the characteristic absorptions of the 1:1 (Fig. 34), 2:1 (Fig. 37) and 5:1 (Fig. 33) $I_2/S_2O_6F_2$ solution spectra are not observed. The 354 mμ absorption (-85°C) and 640 mμ absorption observed in the 1:1 $I_2/S_2O_6F_2$ solution spectra, Fig. 34, and the 344 mμ peak of the 5:1 $I_2/S_2O_6F_2$ solution spectra, Fig. 33, are missing. The absorptions 305 mμ and 470 mμ are probably characteristic maxima for I_3^+ at 28°C.

5:1 $I_2/S_2O_6F_2$

Symons(48) has shown that when iodine is added to solutions of 100% sulphuric acid containing I_3^+ there is no increase in the conductivity. This is accounted for by the reaction:

$$I_3^+ + I_2 \longrightarrow I_5^+ \qquad \text{V-6}$$

The conductivity of fluorosulphuric acid solutions of I_3SO_3F to which iodine has been added slowly increases with time indicating oxidation of the iodine or I_5^+ by the solvent. The results of a cryoscopy experiment (Table XII, Fig. 29) in which the temperature of the solution probably never rose above -20°C and thus oxidation was considerably reduced give $\nu = 0.86$ which suggests the reaction:

$$5\ I_2 + S_2O_6F_2 \longrightarrow 2\ I_5^+ + 2\ SO_3F^- \qquad \text{V-7}$$

$$\nu = 0.80$$

It is not possible to state whether the experimental ν value, slightly larger than that required by V-7, indicates oxidation of the I_5^+ by the solvent or dissociation of I_5^+ to I_3^+ and iodine.

The spectrum of the 5:1 $I_2/S_2O_6F_2$ solution at 28°C and -85°C is given in Fig. 33. The iodine molality was 0.0093 m and the path length was 0.03 cm. The peaks at 344 mμ and 240 mμ which are more intense at -85°C, are probably due to I_5^+. Symons has suggested that I_5^+ in 100% sulphuric acid absorbs at 330 mμ and 450 mμ(48). The absorption at 466 mμ which shifts to 452 mμ at -85°C is present in both the I_3^+ and I_5^+ spectra. The peaks at 466 mμ and 272 mμ in Fig. 33 may be due to I_3^+. The underlying absorption may cause the 305 mμ peak of I_3^+ (Fig. 32) to appear at shorter wave lengths than usual. In the spectrum taken at 28°C, the short wave length peak of I_3^+ may be lying under the broad absorption at 344 mμ. Alternatively, only a small concentration of I_3^+ may be present in the solution at 28°C and the absorption at 466 mμ may be common to both I_5^+ and I_3^+.

1:1 and 2:1 $I_2/S_2O_6F_2$

The spectra of the 1:1 and 2:1 $I_2/S_2O_6F_2$ mixtures contain the three peaks at 640 mμ, 488 mμ and 409 mμ (Figs. 34, 35, 36, 37) although the 488 mμ peak is obscured by the I_3^+ absorption at 470 mμ in the 1:1 $I_2/S_2O_6F_2$ solutions containing traces of water and in 2:1 $I_2/S_2O_6F_2$ solutions. The presence of these three peaks indicates that these solutions contain the same iodine species and the evidence to be presented in the following sections suggests that the peaks are due to I_2^+. The variation of the conductivity with iodine molality for both of these solutions (Figs. 30, 31) indicates that an equilibrium is involved which removes fluorosulphate ion as iodine molality is increased.

(1) 1:1 $I_2/S_2O_6F_2$

The 1:1 $I_2/S_2O_6F_2$ solution has been studied in this work by cryoscopy (Table XII, Fig. 22), conductivity at 25°C (Table XI, Fig. 30) and -78.52°C (Table XIII, Fig. 31), magnetic susceptibilities (Chapter IV, Table IV, Fig. 15) and visual and UV spectra at several temperatures and iodine concentrations (Figs. 34, 35 and 36). The properties of the solution at room temperature differ from those at ~-80°C and it is convenient to divide the discussion into two parts.

(a) Results at 25°C

The spectrum of the 1:1 $I_2/S_2O_6F_2$ solution at room temperature, Fig. 34, is very similar to that of iodine and iodine chloride in 65%

oleum(80), iodine and iodine chloride in iodine pentafluoride containing a little water(82) and 1:2 I_2/HIO_3 and 1:1 $I_2/K_2S_2O_8$ in fluorosulphuric acid(10). The spectrum is the same in all these solvents and is unaffected by the different solvation properties of the various solvents or the character of the associated anion. The addition of water to the solution gives rise to the I_3^+ peaks in the spectrum as shown in Fig. 35 at the expense of the characteristic 'iodine cation' peaks at 640 mμ, 488 mμ, and 409 mμ. The I_3^+ absorptions in Fig. 35 are not at exactly the same frequency as those in Fig. 32 because in the former case the peaks are shifted slightly by other absorptions lying under them. An 'iodine cation' peak at 488 mμ causes the I_3^+ peak at 470 mμ to be shifted to longer wave lengths and the strong shoulder which covers the 200 - 300 mμ region shifts the 307 mμ absorption of I_3^+ to shorter wave lengths. I_3^+ probably arises from a reaction of water with the 'iodine cation' such as:

$$\text{"}4\ I^{+}\text{"} + H_2O \longrightarrow I_3^{+} + IO^{+} + 2\ H^{+} \qquad \text{V-8}$$

Change in iodine concentration appears to have little effect on the spectrum of the 'iodine cation'. The spectrum in Fig. 34 is taken with a 0.0186 m iodine solution using a 0.01 cm. path length which gives effectively the spectrum of a 0.000186 m iodine solution with a 1 cm. path length. Fig. 35 shows the spectrum of a 0.00019 m iodine solution taken with a 1 cm. path length. Therefore the intensities of the two spectra are comparable. It can be seen that a 100-fold increase in concentration gives a fall in the intensity of the 640 mμ peak from 0.67 to 0.55 optical density. This result is discussed in more detail at the end of this section. The 488 mμ and 409 mμ peaks behave similarly, which suggests that the 640 mμ, 488 mμ and 409 mμ absorptions arise from the same species. Several possible equilibria may be examined for an explanation of the spectra, magnetic susceptibilities and conductivities. To facilitate the calculation of equilibrium constants interpolated γ values, taken from Fig. 30 and listed in Table XVII, were used.

Symons and co-workers$^{(80)}$ have claimed that all of the iodine in 65% oleum is present as I^+. The analogous reaction in the iodine and peroxydisulphuryldifluoride system would be:

$$I_2 + S_2O_6F_2 \longrightarrow 2\ I^+ + 2\ SO_3F^- \qquad \text{V-9}$$

However, experimentally γ is less than 1.0, which eliminates V-9, which requires $\gamma = 2.0$. The equilibrium:

$$2\ ISO_3F \quad \overset{K_{V-10}}{\rightleftharpoons} \quad 2\ I^+ + 2\ SO_3F^- \qquad \text{V-10}$$

$$2\ m_{I_2}(1-\alpha) \qquad 2\ m_{I_2}\alpha \qquad 2\ m_{I_2}\alpha$$

does not give a constant K_{V-10} when the experimental γ values are substituted into the expression for the equilibrium constant:

$$K_{V-10} = \frac{[I^+][SO_3F^-]}{[ISO_3F]} = \frac{m_{I_2}\ \gamma^2}{2(1-\frac{\gamma}{2})} \qquad \text{V-11}$$

for which $\alpha = \frac{\gamma}{2}$. The calculated K_{V-10} are given in Table XVIII. According to V-11 and Fig. 15, χ_{MI^+} at $m_{I_2} = 0.03$ m, where $\gamma = 0.646$, would be 1990×10^{-6} cgs units which corresponds to $\mu_{eff} = 2.19$ BM. The expected spin only moment for I^+ which would have two unpaired electrons is 2.83 BM.

Another possible equilibrium might be:

$$I_2(SO_3F)_2 \quad \overset{K_{V-12}}{\rightleftharpoons} \quad I_2^{++} + 2\ SO_3F^- \qquad \text{V-12}$$

$$m_{I_2}(1-\alpha) \qquad m_{I_2}\alpha \qquad m_{I_2}\alpha$$

for which $\alpha = \frac{\gamma}{2}$ and K_{V-12} is given by:

$$K_{V-12} = \frac{m_{I_2}^2 \ \gamma^3}{2 - \gamma} \qquad \text{V-13}$$

The experimental γ values do not give a constant K_{V-12} as shown in Table XVIII. It is expected that I_2^{++}, which is isoelectronic in its outer shell with O_2, would have a magnetic moment of 2.83 BM, the spin only value for two unpaired electrons$^{(50)}$. The equilibrium V-12 gives at m_{I_2} = 0.03 m for which $\gamma = 0.646$, $\chi_{M_{I_2^{++}}} = 3980 \times 10^{-6}$ which corresponds to $\mu_{eff} = 3.10$ BM. This value is greater than the expected 2.83 BM.

The equilibrium:

$$I_2(SO_3F)_2 \rightleftharpoons I_2SO_3F^+ + SO_3F^- \qquad \text{V-14}$$

does not seem likely since $I_2SO_3F^+$ would probably be diamagnetic or weakly paramagnetic by analogy with I_3^+ (Table IV, Chapter IV).

Any equilibria of the sort:

$$2\ I^+ + 2\ SO_3F^- \rightleftharpoons \frac{1}{2} I_3^+ + \frac{1}{2} SO_3F^- + \frac{1}{2} I(SO_3F)_3 \qquad \text{V-15}$$

$$2\ I^+ + 2\ SO_3F^- \rightleftharpoons \frac{4}{14} I_5^+ + \frac{4}{14} SO_3F^- + \frac{8}{14} I(SO_3F)_3 \qquad \text{V-16}$$

and the related equilibria with the dimer I_2^{++} in place of I^+ may be eliminated as possibilities since the concentration of the I_3^+ or I_5^+ required by the experimental γ values would be readily detected in the spectrum. The γ value of 0.698 at m_{I_2} = 0.0186 m iodine would require approximately 90% disproportionation of I^+ to I_3^+ and $I(SO_3F)_3$ which would give rise to an I_3^+ molality of 0.0082 m according to V-15. This concentration of I_3^+ would be detected in Fig. 34 when it is considered that the molality of I_3SO_3F in Fig. 32 is 0.0112 m. Disproportionation to I_5^+ and $I(SO_3F)_3$ does not seem probable for the additional reason that, if the iodine in the 1:1 $I_2/S_2O_6F_2$ solutions disproportionates to these species, the iodine in the 3:1 $I_2/S_2O_6F_2$ solutions would be expected to do so and as shown above there is no evidence for disproportionation of I_3SO_3F.

Experimental evidence to be presented in the section on solutions of 2:1 $I_2/S_2O_6F_2$ stoichiometry suggests that the iodine cation which causes the absorption spectrum with maxima at 640 mμ, 488 mμ and 409 mμ is I_2^+. The primary reaction in the 1:1 $I_2/S_2O_6F_2$ mixture would then be:

$$I_2 + S_2O_6F_2 \longrightarrow \frac{4}{5} I_2^+ + \frac{4}{5} SO_3F^- + \frac{2}{5} I(SO_3F)_3 \qquad \text{V-17}$$

$$\gamma = 0.80$$

The limiting γ value at low iodine molalities is 0.77 (Fig. 30) in good agreement with V-17. Since iodine trifluorosulphate behaves as a weak acid, the products of V-17 would take part in the equilibrium:

$$SO_3F^- + I(SO_3F)_3 \rightleftharpoons I(SO_3F)_4^- \qquad \text{V-18}$$

This equilibrium would account for the negative deviation of the conductivity from linearity but it does not account for the decrease in molar magnetic susceptibility of the iodine with increasing iodine molality (Fig. 15) and the relative decrease in the intensity of the I_2^+ absorption at 640 mμ with increasing iodine molality (Figs. 34, 35 and 36). Dimerisation of I_2^+ to form a diamagnetic species I_4^{++} would account for these observations.

Three possible equilibria which may fit the experimental results are:

$$\frac{4}{5} I_2^+ + \frac{4}{5} SO_3F^- + \frac{2}{5} I(SO_3F)_3 \rightleftharpoons \frac{1}{2} I_3^+ + \frac{1}{2} SO_3F^- + \frac{1}{2} I(SO_3F)_3 \qquad V\text{-}19$$

$$\frac{4}{5} I_2^+ + \frac{4}{5} SO_3F^- + \frac{2}{5} I(SO_3F)_3 \rightleftharpoons \frac{4}{5} I_2SO_3F + \frac{2}{5} I(SO_3F)_3 \qquad V\text{-}20$$

$$\frac{4}{5} I_2^+ + \frac{4}{5} SO_3F^- + \frac{2}{5} I(SO_3F)_3 \rightleftharpoons (ISO_3F)_2 \qquad V\text{-}21$$

These equilibria would be accompanied by V-18 also. Disproportionation of I_2^+ to iodine trifluorosulphate and I_3^+, as in V-19, occurs in the 2:1 $I_2/S_2O_6F_2$ system discussed below but does not take place in the 1:1 $I_2/S_2O_6F_2$ mixtures. This is apparent from the spectra (Figs. 34, 35 and 36), where although the relative intensity of the I_2^+ peak at 640 mμ is decreasing with increasing molality, no I_3^+ peaks (Fig. 32) appear. Apparently the presence in the 1:1 $I_2/S_2O_6F_2$ solution of a larger concentration of iodine trifluorosulphate than in the 2:1 $I_2/S_2O_6F_2$ solution prevents reduction of I_2^+ to I_3^+ in the former. Association to form a stable free radical, I_2SO_3F, as in V-20, would seem unlikely. Dimerisation of I_2SO_3F would be required to account for the decrease in magnetic susceptibility with increase in iodine molality.

Iodine monofluorosulphate has been prepared by Aubke and Cady(35). Dimerisation or polymerisation of this fluorosulphate is required to provide a driving force in V-21 since an equilibrium involving ISO_3F would have an equal number of particles on both sides of the equilibrium. The equilibria V-18 to V-21 are all accompanied by at least one other equilibrium and the conductivity results alone are insufficient to check the validity of these equilibria absolutely.

The relative decrease in the intensity of the 640 mμ peak with increasing iodine molality is accompanied by a relative increase in the absorption below 300 mμ, suggesting that the product formed from I_2^+ at higher iodine molalities, I_4^{++} or $(ISO_3F)_2$, must absorb in this region of the spectrum. It is a reasonable assumption that all of the iodine in the 0.00019 m solution used for the spectra in Fig. 35 is present as iodine trifluorosulphate and I_2^+ and thus it is possible to determine the molal extinction coefficient for the 640 mμ peak, $\varepsilon_{I_2^+(640)}$. This gives the value 4310 and from this the molality of I_2^+ in the 0.0186 m and 0.093 m solutions used for the spectra at 28°C in Figs. 34 and 36 are calculated to be 0.013 m and 0.036 m respectively. From the χ_M taken from Fig. 15 at the concentrations of the spectra solutions ($\chi_M = 508 \times 10^{-6}$ cgs units assumed for 0.00019 in solution) and the molality for the I_2^+, the molar magnetic susceptibility for I_2^+ can be calculated and the effective magnetic moment, μ_{eff}, determined. This gives in order of increasing m_{I_2}; $\mu_{eff} = 1.76$ BM, 2.09 BM and 2.28 BM. The expected effective magnetic moment of I_2^+ which would have a $^2\pi_{3/2}$ ground state is 2.0 BM.

(b) Low Temperature Results

The results of the cryoscopy of the 1:1 $I_2/S_2O_6F_2$ solution, Table XII and Fig. 22, give $\nu = 1.20$. The conductivity measurements at -78.52°C are given in Table XIII and Fig. 30. The spectrum of this solution, Fig. 33, changes as the temperature is lowered and several new peaks appear. The characteristic peaks of I_3^+ at 350 mμ and 470 mμ appear shifted slightly from the positions in Fig. 32 because of the underlying shoulder below 300 mμ and the 'iodine cation' peak at 488 mμ. A strong peak appears at 354 mμ. The absorption at 640 mμ increases to a maximum at -20.0°C then decreases until, at -92.0°C, its intensity is approximately one-third of that at 25°C. The shift, $\Delta\delta$, of the proton resonance of the solvent in this solution exhibits a related behaviour with a maximum shift observed at -13°C (Table VII). The similar behaviour of these two observations suggests that the 640 mμ peak is probably that of the paramagnetic species in solution. The changes in the spectrum with temperature occur largely over the temperature range -75°C to -90°C and for this reason the γ values determined at -78.52°C are not strictly comparable to the ν values for this solution. Table XIX gives the interpolated γ values for the 1:1 $I_2/S_2O_6F_2$ solution at -78.52°C. This system is probably governed by two equilibrium constants; one involving the disproportionation of I_2^+ to I_3^+ and $I(SO_3F)_3$ which will be discussed in the next section and another involving the species which gives rise to the peak at 354 mμ. For this reason, the γ values are insufficient to absolutely test any proposed equilibria. The equilibria V-18 and V-19 would account for the experimental results. The right side of V-19 has $\nu = 1.5$ and the formation of $I(SO_3F)_4^-$ by V-18 would give a lower ν value. Further association to form $I_3I(SO_3F)_4$ may occur. $I_3I(SO_3F)_4$ has the stoichiometry required for iodine monofluorosulphate(35) and is analogous to the salt $KI(SO_3F)_4$(27). The absorption maximum at 354 mμ may be due to the $I(SO_3F)_4^-$ ion.

(2) 2:1 $I_2/S_2O_6F_2$

When iodine is added to the 1:1 $I_2/S_2O_6F_2$ solution the optical density of the 640 mμ absorption in the spectrum (Fig. 34, $m_{I_2} = 0.0186$) increases until at 2:1 $I_2/S_2O_6F_2$ (Fig. 37, $m_{I_2} = 0.0372$) the optical density (1.11) is twice that of the 1:1 $I_2/S_2O_6F_2$ solution (0.55). This observation is not consistent with the assignment of the 640 mμ absorption to either I^+ or I_2^{++} since in the 2:1 solution these species would be accompanied by species of lower valence according to:

$$2\ I_2 + S_2O_6F_2 \longrightarrow I^+\ (\tfrac{1}{2}\ I_2^{++}) + I_3^+ + 2\ SO_3F^- \qquad \text{V-23}$$

$$4\ I_2 + 2\ S_2O_6F_2 \longrightarrow 3\ I^+(\tfrac{3}{2}\ I_2^{++}) + I_5^+ + 4\ SO_3F^- \qquad \text{V-24}$$

The spectrum of the 2:1 $I_2/S_2O_6F_2$ solution, Fig. 37, has absorptions characteristic of I_3^+ (300 mμ and 475 mμ, underlying the 488 mμ absorption of the 1:1 $I_2/S_2O_6F_2$ solution) but their intensity relative to the 640 mμ peak is too low to agree with V-23. Characteristic peaks due to 5:1 $I_2/S_2O_6F_2$ solutions are absent from the spectrum also. In addition, if I^+ or I_2^{++} is the species causing the 640 mμ absorption, a decrease in the optical density at this frequency would be expected as iodine was added to the 1:1 $I_2/S_2O_6F_2$ solution.

The behaviour of the 640 mμ peak is consistent with the formation of a half-valent iodine species. In dilute solution where disproportionation and association reactions are not important, the addition of iodine to the 1:1 $I_2/S_2O_6F_2$ solution up to 2:1 stoichiometry may be accounted for by:

$$\tfrac{4}{5}\ I_2^+ + \tfrac{4}{5}\ SO_3F^- + \tfrac{2}{5}\ I(SO_3F)_3 + I_2 \longrightarrow 2\ I_2^+ + 2\ SO_3F^- \qquad \text{V-25}$$

The greater magnetic susceptibility of the iodine in the 2:1 $I_2/S_2O_6F_2$ solutions compared to the 1:1 $I_2/S_2O_6F_2$ solutions, Table IV and Fig. 15, is also explained by V-25.

The results of a conductivity experiment on the 2:1 $I_2/S_2O_6F_2$ solution are given in Table XI and Fig. 30. Interpolated γ values are given in Table XX. The conductivity at low iodine molalities approaches that of potassium fluorosulphate in agreement with the reaction:

$$2\ I_2 + S_2O_6F_2 \longrightarrow 2\ I_2^+ + 2\ SO_3F^- \qquad \text{V-26}$$

and the negative curvature of the plot suggests that some association or disproportionation reaction is occurring which removes fluorosulphate ions.

The spectrum of the 2:1 $I_2/S_2O_6F_2$ solution was taken at two different iodine molalities; 0.0372 m with a 0.01 cm. path length, Fig. 37, and 0.164 m with a 0.005 cm. path length, Fig. 36. A comparison of these spectra indicates an increase in the concentration of I_3^+ relative to the I_2^+ concentration at higher iodine molality. This suggests that the following reaction is occurring:

$$\begin{array}{ccccccccc} I_2^+ & + & SO_3F^- & \xrightleftharpoons{K_{V-27}} & \frac{1}{8}\,I(SO_3F)_3 & + & \frac{5}{8}\,I_3^+ & + & \frac{5}{8}\,SO_3F^- \\ m_{I_2}(1-\alpha) & & m_{I_2}(1-\alpha) & & m_{I_2}\frac{\alpha}{8} & & m_{I_2}\frac{5\alpha}{8} & & m_{I_2}\frac{5\alpha}{8} \end{array} \qquad \text{V-27}$$

Since the concentration of iodine trifluorosulphate in these solutions is small and K_{V-3} is small the effect of the equilibrium V-3 can be ignored and, substituting $\alpha = \frac{8}{3}(1-\gamma)$:

$$K_{V-27} = \frac{3\left[\frac{1-\gamma}{3}\right]^{1/8}\left[\frac{5(1-\gamma)}{3}\right]^{5/8}}{m_{I_2}^{5/8}\,[8\gamma-5]\,\gamma^{3/8}} \qquad \text{V-28}$$

Equilibrium constants K_{V-27} calculated from interpolated γ values are given in Table XXI. K_{V-27} is reasonably well behaved, suggesting that

V-27 is the predominant reaction which removes fluorosulphate ion as the iodine molality is increased.

If the description of the 1:1 $I_2/S_2O_6F_2$ solution as consisting of the iodine species I_2^+ and $I(SO_3F)_3$ (V-17) in dilute solution is correct, it should be possible to calculate the concentration of I_2^+ in a 2:1 $I_2/S_2O_6F_2$ solution from the optical density of the 640 mμ peak and the extinction coefficient calculated for I_2^+ from the spectrum of the 1:1 $I_2/S_2O_6F_2$ solution given in Fig. 35 ($\epsilon_{I_2^+(640)} = 4310$). From the optical density of the 640 mμ peak in Fig. 37, the molality of I_2^+ in the 0.0372 m iodine solution is 0.0258 m. Calculation of the I_2^+ molality by:

$$[I_2^+] = \frac{m_{I_2}}{3}(8\gamma - 5) \qquad \text{V-29}$$

for the equilibrium V-27 at the same iodine molality gives 0.0284 m. The I_2^+ molality calculated from the spectrum is in fair agreement with that calculated from V-29 which substantiates the argument that the 2:1 and 1:1 $I_2/S_2O_6F_2$ solutions contain I_2^+. From the spectrum given in Fig. 36 for a 0.164 m iodine solution the I_2^+ molality is 0.116 m and, according to V-29, the I_2^+ molality is 0.114 m. The agreement between the I_2^+ molality as calculated by the two methods at two different iodine molalities lends weight to the explanation of the results by the disproportionation of I_2^+ according to V-27.

The extinction coefficient of I_3^+ at 28°C for the peak at 305 mμ may be calculated from the spectrum for a 0.0168 m iodine solution in Fig. 32. This gives $\epsilon_{I_3^+(305)} = 8820$ in terms of moles of I_3^+. Using this value and the optical density of the peak at 302 mμ in Fig. 37, the I_3^+ molality in this 2:1 $I_2/S_2O_6F_2$ solution ($m_{I_2} = 0.0372$) is 0.0036 m.

The molality in this solution may be calculated for the equilibrium V-27 from the expression:

$$[I_3^+] = \frac{5}{3} m_{I_2} (1 - \gamma) \qquad \text{V-30}$$

This gives $[I_3^+] = 0.0056$ m. Similarly the spectrum in Fig. 36 gives $[I_3^+] = 0.043$ m and V-30 gives $[I_3^+] = 0.038$ m for a total iodine molality of 0.164 m. The agreement is only fair, suggesting that V-27 may not describe the equilibrium in the 2:1 $I_2/S_2O_6F_2$ solutions exactly.

At $m_{I_2} = 0.05$, the molality of I_2^+ would be 0.038 m by V-29 and, if all of the paramagnetism is caused by this cation, χ_M for I_2^+ becomes 1725×10^{-6} cgs units. This molar susceptibility corresponds to an effective magnetic moment of 2.08 BM. This value agrees favourably with the effective magnetic moment expected for the $^2\pi_{3/2}$ state of I_2^+, 2.0 BM(50).

The variation of K_{V-27} calculated from γ values for different iodine molalities and the discrepancies between I_2^+ and I_3^+ molalities calculated from V-29 and V-30 and those calculated from spectra indicate that V-27 does not exactly describe the state of the iodine in these solutions. The iodine may also take part in equilibria like those suggested for the 1:1 $I_2/S_2O_6F_2$ solutions (V-18 to V-21).

The results of the studies on the 1:1 and 2:1 $I_2/S_2O_6F_2$ solutions indicate that the predominant paramagnetic species which gives rise to the 640 mμ absorption is probably I_2^+. The I_2^+ ion would have a $^2\pi_{3/2}$ ground state and since the splitting between this state and the diamagnetic $^2\pi_{1/2}$ state would probably be greater than kT(50), we would expect the magnetic moment of the $^2\pi_{3/2}$ state alone, 2.0 BM. The effective magnetic moment determined for the 1:1 and 2:1 $I_2/S_2O_6F_2$ systems is in agreement with this value. Electron spin resonance studies may confirm the existence of I_2^+.

The equilibria governing the behaviour of the iodine fluorosulphates in the 1:1 $I_2/S_2O_6F_2$ solutions is not clear. With a precise knowledge of $\epsilon_{I_2^+(640)}$, it may be possible to determine the I_2^+ molality over a range of iodine molalities at 25°C and -78.52°C and with the conductivity results, determine the nature of the equilibria governing this system. Low temperature magnetic susceptibility measurements would confirm the presence of I_2^+, which is indicated by the low temperature spectra.

Table X

Potassium Fluorosulphate Conductivities at -78.52°C

Experiment 29 **Weight Acid = 73.090 gm.**

$^{w}\mathrm{KSO_3F}$	$^{m}\mathrm{KSO_3F}$	$K \times 10^6$
0.0000	0.000	4.505
0.0144	0.0014	41.33
0.0365	0.0036	100.88
0.1223	0.0120	335.06
0.1764	0.0174	491.24
0.2126	0.0209	589.03
0.2728	0.0269	741.36
0.3189	0.0314	853.42

Experiment 30 **Weight Acid = 92.150**

$^{w}\mathrm{KSO_3F}$	$^{m}\mathrm{KSO_3F}$	$K \times 10^6$
0.0000	0.000	2.021
0.2715	0.0212	586.77
0.2802	0.0219	604.04
0.2924	0.0228	629.30
0.3091	0.0241	664.49
0.3423	0.0267	735.81
0.6283	0.0491	1283.43

Table XI

Conductivity at 25°C : Peroxydisulphuryldifluoride and Iodine Fluorosulphates

Peroxydisulphuryldifluoride

Experiment 31

Weight Acid = 111.500

Composition of Concentrated Solution:

Weight HSO_3F = 19.9457

Weight $S_2O_6F_2$ = 1.9102

Weight of Solution Added	$m_{S_2O_6F_2}$	K x 10
0.000	0.0000	1.378
2.2104	0.0086	1.529
4.2620	0.0163	1.645
6.4985	0.0244	1.772
8.6062	0.0318	1.953
10.4686	0.0384	2.216

Table XI (Continued)

1:3 $I_2/S_2O_6F_2$

Experiment 32

Weight Acid = 125.560

Composition of Concentrated Solution:

Weight HSO_3F = 19.0531

Weight $S_2O_6F_2$ = 1.9437

Weight I_2 = 0.8308

Weight of Solution Added	m_{I_2}	$K \times 10^4$
0.000	0.0000	1.404
1.5445	0.0018	1.714
3.4771	0.0041	2.120
4.9249	0.0057	2.342
6.4209	0.0073	2.617
8.2674	0.0093	2.878
10.9077	0.0121	3.189
16.2653	0.0174	3.765
20.9145	0.0218	4.213

1:1 $I_2/S_2O_6F_2$

Experiment 33

Weight Acid = 110.480

Composition of Concentrated Solution:

Weight HSO_3F = 22.9855

Weight $S_2O_6F_2$ = 1.7169

Weight I_2 = 2.2013

Weight of Solution Added	m_{I_2}	$K \times 10^4$
0.000	0.0000	1.438
1.1102	0.0032	7.266
1.9356	0.0056	11.76
3.3953	0.0097	19.06
4.5065	0.0127	24.10
5.9150	0.0165	30.03
8.2880	0.0227	39.15
10.8826	0.0293	48.19
13.3811	0.0354	55.99
16.0612	0.0417	63.62

Table XI (Continued)

2:1 $I_2/S_2O_6F_2$

Experiment 46

Weight Acid = 46.270

Composition of Concentrated Solution:

Weight HSO_3F = 20.0859

Weight $S_2O_6F_2$ = 3.1257

Weight I_2 = 8.0199

Weight of Solution Added	m_{I_2}	K x 10^4
0.0000	0.000	17.34
1.0295	0.0222	65.36
2.1352	0.0453	112.51
3.0842	0.0647	149.01
4.1265	0.0853	185.53
4.8621	0.0995	209.34
5.8101	0.1175	237.62
7.1164	0.1415	273.81
8.2876	0.1624	303.02

3:1 $I_2/S_2O_6F_2$

Experiment 34

Weight Acid = 113.680

Composition of Concentrated Solution:

Weight HSO_3F = 22.3049

Weight $S_2O_6F_2$ = 1.4273

Weight I_2 = 5.4895

Weight of Solution Added	m_{I_2}	K x 10^4
0.0000	0.0000	1.262
1.3192	0.0085	15.27
3.0502	0.0195	33.01
4.6024	0.0291	47.82
5.0780	0.0320	52.37
6.7342	0.0419	67.76
7.9326	0.0490	78.50
8.9289	0.0548	87.24
9.9489	0.0607	95.94

Table XII

Cryoscopy: Iodine Fluorosulphates

1:7 $I_2/S_2O_6F_2$

Experiment 35

Weight Acid = 138.350

T_o = -88.998°C

Composition of Concentrated Solution:

Weight HSO_3F = 14.340

Weight $S_2O_6F_2$ = 2.145

Weight I_2 = 0.3936

Weight of Solution Added	m_{I_2}	ΔT(°C)
3.180	0.0021	0.051
6.810	0.0044	0.106
10.760	0.0067	0.166
14.360	0.0088	0.218

1:3 $I_2/S_2O_6F_2$

Experiment 36

Weight Acid = 125.505

T_o = -89.000°C

Composition of Concentrated Solution:

Weight HSO_3F = 20.860

Weight $S_2O_6F_2$ = 2.745

Weight I_2 = 1.1706

Weight of Solution Added	m_{I_2}	ΔT(°C)
5.845	0.0083	0.063
9.185	0.0128	0.097
12.915	0.0176	0.135
17.740	0.0234	0.182
21.755	0.0282	0.213

1:1 $I_2/S_2O_6F_2$

Experiment 37

Weight Acid = 124.000

T_o = -88.997°C

Composition of Concentrated Solution:

Weight HSO_3F = 23.725

Weight $S_2O_6F_2$ = 2.147

Weight I_2 = 2.7483

Weight of Solution Added	m_{I_2}	ΔT(°C)
2.9573	0.0088	0.043
4.4084	0.0131	0.061
6.5348	0.0191	0.089
8.9631	0.0258	0.125
11.6230	0.0323	0.155
14.1652	0.0395	0.186

3:1 $I_2/S_2O_6F_2$

Experiment 38

Weight Acid = 122.945

T_o = -89.003°C

Composition of Concentrated Solution:

Weight HSO_3F = 14.380

Weight $S_2O_6F_2$ = 0.768

Weight I_2 = 2.945

Weight of Solution Added	m_{I_2}	ΔT(°C)
1.2595	0.0065	0.026
3.4177	0.0175	0.080
6.2901	0.0316	0.145
8.3548	0.0432	0.197
10.5295	0.0516	0.242
12.3911	0.0598	0.281

Table XII (Continued)

5:1 $I_2/S_2O_6F_2$

Experiment 39

Weight Acid = 126.565

T_o = -88.998°C

Composition of Concentrated Solution:

Weight HSO_3F = 13.135

Weight $S_2O_6F_2$ = 0.531

Weight I_2 = 3.266

Weight of Solution Added	m_{I_2}	ΔT(°C)
1.2744	0.0076	0.028
3.1847	0.0189	0.060
4.8848	0.0285	0.084
6.9776	0.0404	0.139
8.7342	0.0505	0.167
11.0103	0.0624	0.206

Table XIII

Conductivity at -78.52°C: Iodine Fluorosulphates

1:3 $I_2/S_2O_6F_2$

Experiment 40

Weight Acid = 82.330

Composition of Concentrated Solution:

Weight HSO_3F = 19.9718

Weight $S_2O_6F_2$ = 0.7457

Weight I_2 = 0.3160

Weight of Solution Added	m_{I_2}	K x 10^6
0.0000	0.0000	2.656
3.3748	0.0023	5.099
4.8114	0.0033	6.035
5.9411	0.0040	6.652
7.5677	0.0050	7.110
9.3942	0.0061	7.672
11.3061	0.0072	8.496
14.2633	0.0088	8.841

1:1 $I_2/S_2O_6F_2$

Experiment 41

Weight Acid = 91.970

Composition of Concentrated Solution:

Weight HSO_3F = 19.8725

Weight $S_2O_6F_2$ = 0.9336

Weight I_2 = 1.1863

Weight of Solution Added	m_{I_2}	K x 10^6
0.0000	0.0000	2.172
1.5269	0.0035	52.33
3.2670	0.0073	103.26
5.4596	0.0120	159.71
6.9084	0.0149	193.69
8.2534	0.0175	223.59
10.1326	0.0213	260.27
12.1002	0.0250	296.62

3:1 $I_2/S_2O_6F_2$

Experiment 42

Weight Acid = 75.365

Composition of Concentrated Solution:

Weight HSO_3F = 21.0131

Weight $S_2O_6F_2$ = 0.7772

Weight I_2 = 2.9699

Weight of Solution Added	m_{I_2}	K x 10^6
0.0000	0.0000	2.96
2.0681	0.0127	236.57
3.1962	0.0193	355.46
4.3699	0.0261	474.15
5.6136	0.0331	596.37
6.7654	0.0394	706.27
7.9393	0.0456	811.43

Table XIV

Conductivity at 25°C: Potassium Fluorosulphate Additions to

1:3 $I_2/S_2O_6F_2$ Solutions

Experiment 43

Weight Acid = 101.820

m_{I_2}	w_{KSO_3F}	m_{KSO_3F}	$K \times 10^4$
0.0000	0.0000	0.0000	1.127
0.0067	0.0000	0.0000	2.156
0.0067	0.0035	0.0002	2.464
0.0067	0.0142	0.0009	3.529
0.0067	0.0177	0.0011	3.943
0.0067	0.0209	0.0013	4.342
0.0067	0.0305	0.0020	5.578
0.0067	0.0479	0.0031	7.870

Experiment 47

Weight Acid = 49.011

m_{I_2}	w_{KSO_3F}	m_{KSO_3F}	$K \times 10^4$
0.0000	0.0000	0.0000	2.065
0.0587	0.0000	0.0000	2.961
0.0587	0.0323	0.0047	12.384
0.0587	0.0440	0.0065	16.12
0.0587	0.0640	0.0094	22.75
0.0587	0.0840	0.0123	29.67
0.0587	0.1321	0.0194	45.50
0.0587	0.1473	0.0217	51.08

Table XV

Cryoscopy: Water Additions to a 1:3 I_2/S_2O_6F Solution

Experiment 44

Weight Acid = 125. 505

T_o = -89.000°C

m_{I_2}	w_{H_2O}	m_{H_2O}	ΔT(°C)
0.0282	0.0000	0.0000	0.213
0.0282	0.0464	0.0179	0.199
0.0282	0.0941	0.0364	0.190
0.0282	0.1407	0.0543	0.248
0.0282	0.1866	0.0720	0.335

Table XVI

Conductivity at -78.52°C: Water Additions to a 1:3 $I_2/S_2O_6F_2$ Solution

Experiment 45

Weight Acid = 82.770

m_{I_2}	w_{H_2O}	m_{H_2O}	$K \times 10^6$
0.000	0.0000	0.0000	3.921
0.010	0.0000	0.0000	9.091
0.010	0.0199	0.0113	43.06
0.010	0.0412	0.0235	81.01
0.010	0.0630	0.0359	238.29
0.010	0.0838	0.0477	485.44
0.010	0.1032	0.0588	705.55

Table XVII

Interpolated γ and χ_M at 25°C for 1:1 $I_2/S_2O_6F_2$ Solutions

m_{I_2}	γ	$\chi_M^* \times 10^6$
0.01	0.759	508
0.02	0.692	634
0.03	0.646	642
0.04	0.613	622
0.05	0.592	593

* magnetic susceptibility per 127 gm. iodine.

Table XVIII

Equilibrium Constants at 25°C for 1:1 $I_2/S_2O_6F_2$ Solutions

m_{I_2}	K_{V-10}	K_{V-12}
0.01	4.7×10^{-3}	3.5×10^{-5}
0.03	9.3×10^{-3}	17.9×10^{-5}
0.05	12.4×10^{-3}	36.9×10^{-5}

Table XIX

Interpolated γ at -78.52°C for 1:1 $I_2/S_2O_6F_2$ Solutions

m_{I_2}	γ
0.005	0.52
0.010	0.48
0.015	0.46
0.020	0.44
0.025	0.43

Table XX

Interpolated γ and χ_M at 25°C for 2:1 $I_2/S_2O_6F_2$ Solutions

m_{I_2}	γ	$\chi_M \times 10^6$
0.02	0.92	----
0.04	0.91	----
0.06	0.90	636
0.08	0.90	598
0.10	0.89	569
0.12	0.88	553
0.14	0.87	546
0.16	0.87	543
0.18	0.86	541

Table XXI

Equilibrium Constants at 25°C for 2:1 $I_2/S_2O_6F_2$ Solutions

m_{I_2}	γ	K_{V-27}
0.02	0.92	2.72
0.06	0.90	1.76
0.10	0.89	1.43
0.14	0.87	1.48
0.18	0.86	1.34

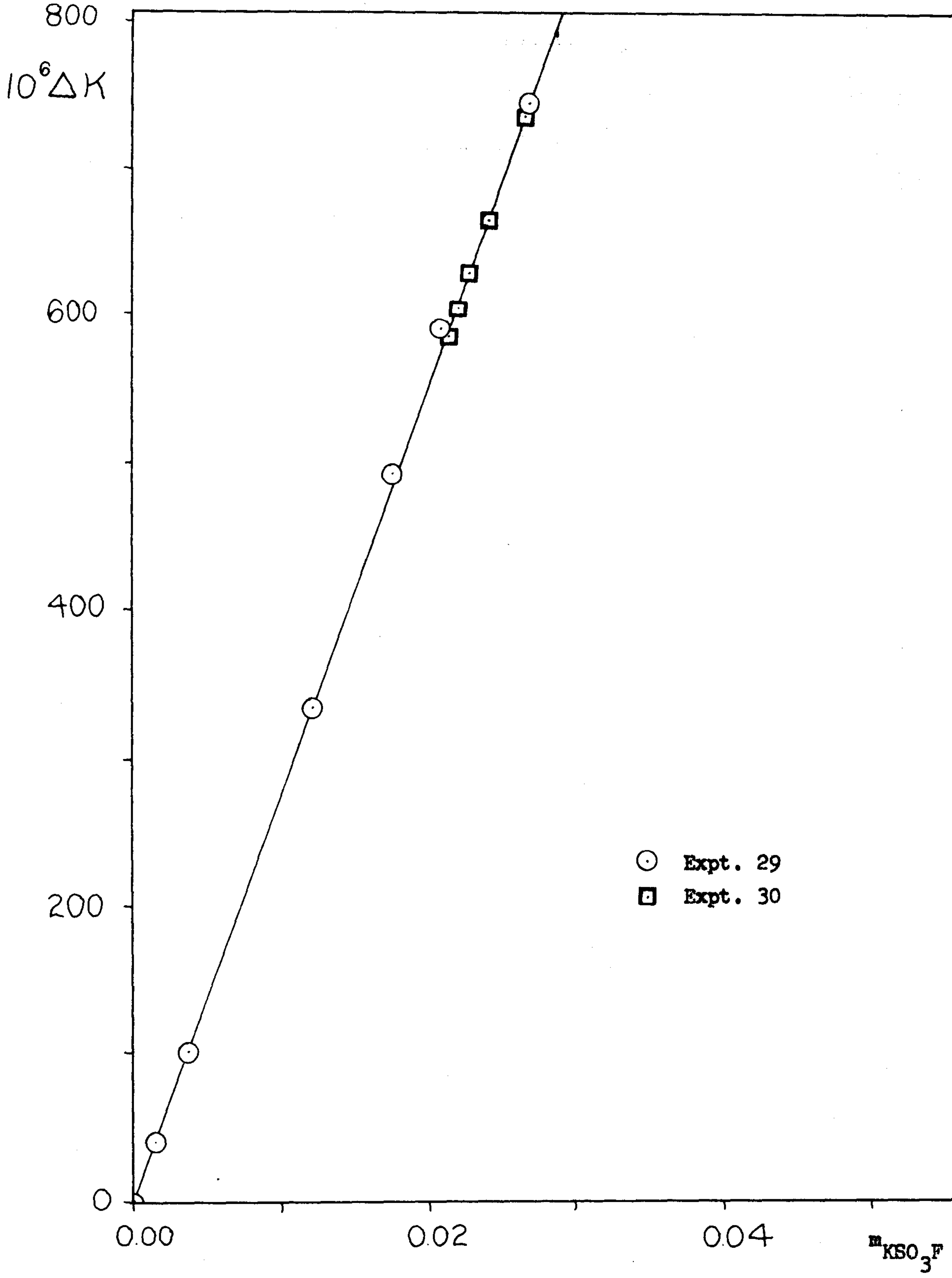

Figure 20 Conductivity at -78.52°C: Potassium Fluorosulphate

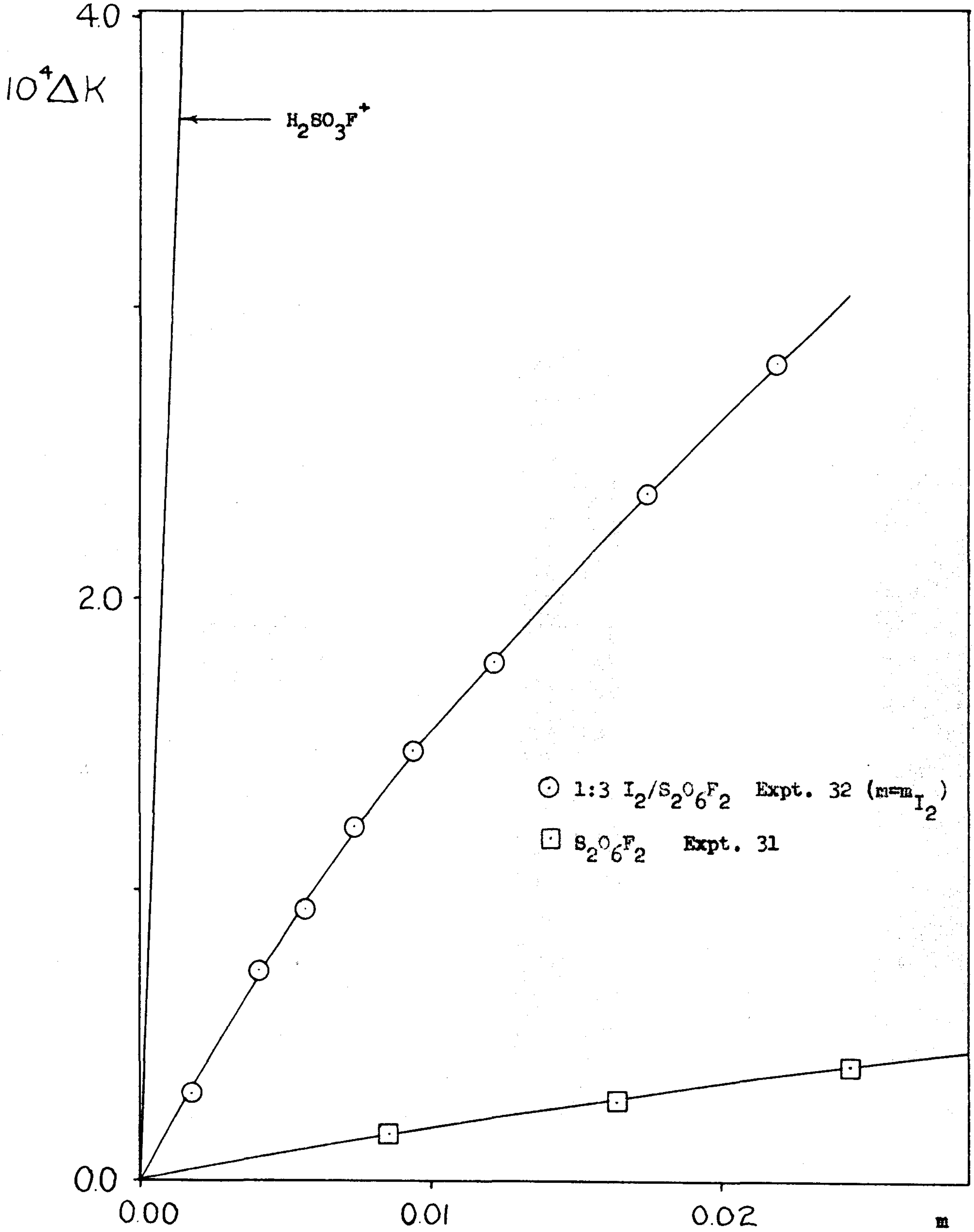

Figure 21 Conductivity at 25°C: $S_2O_6F_2$ and 1:3 $I_2/S_2O_6F_2$

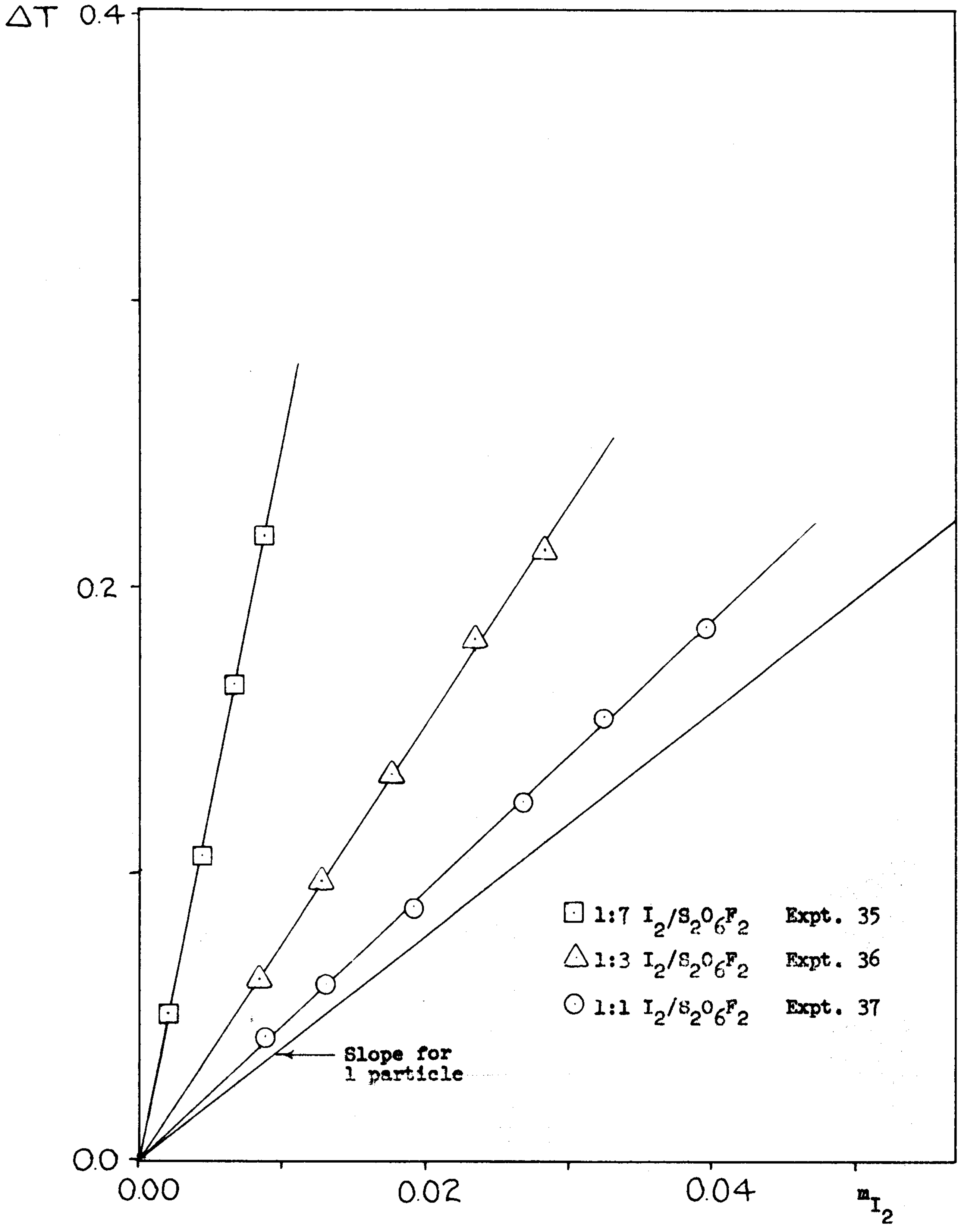

Figure 22 Cryoscopy: 1:7, 1:3 and 1:1 $I_2/S_2O_6F_2$

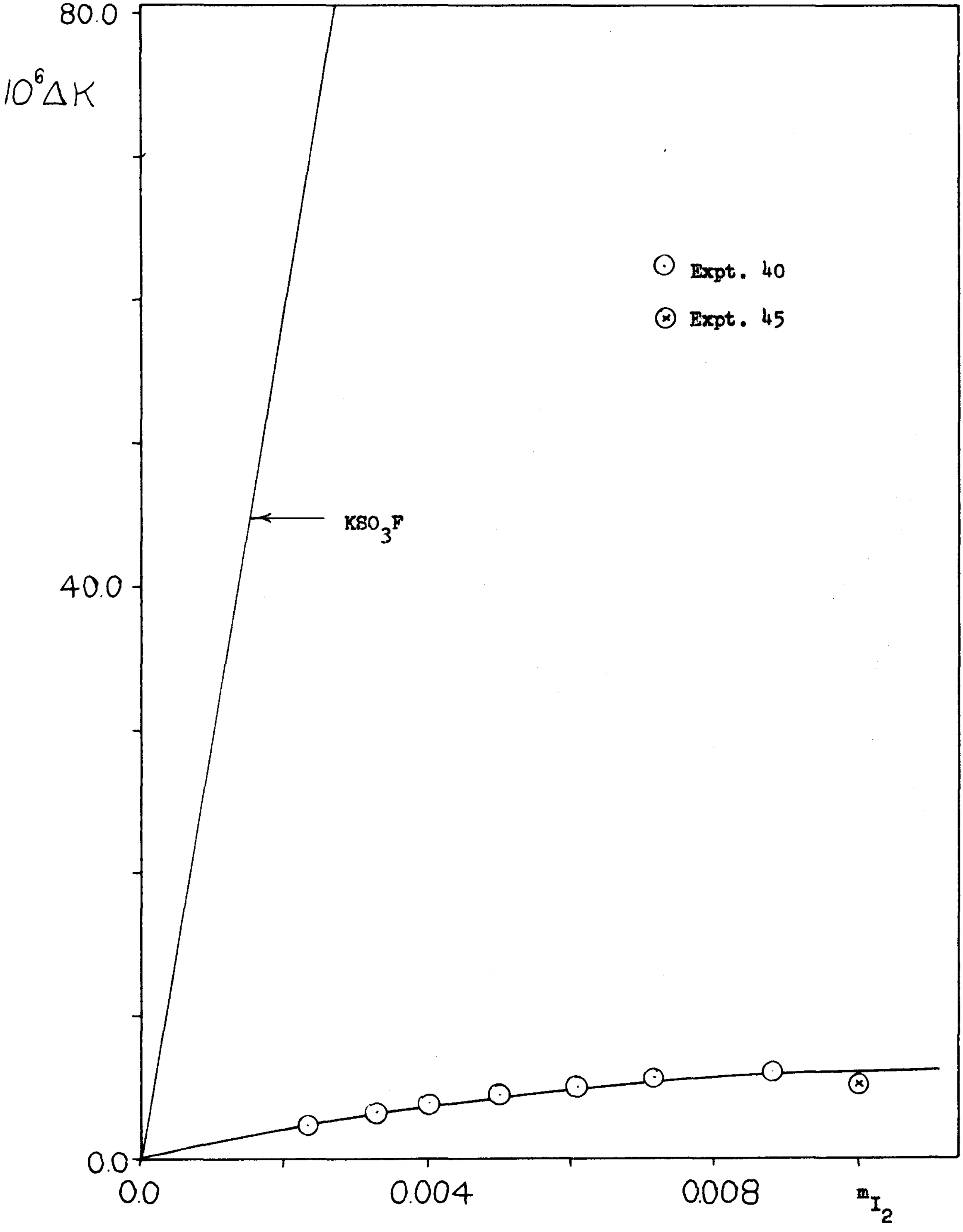

Figure 23 Conductivity at -78.52°C: 1:3 $I_2/S_2O_6F_2$

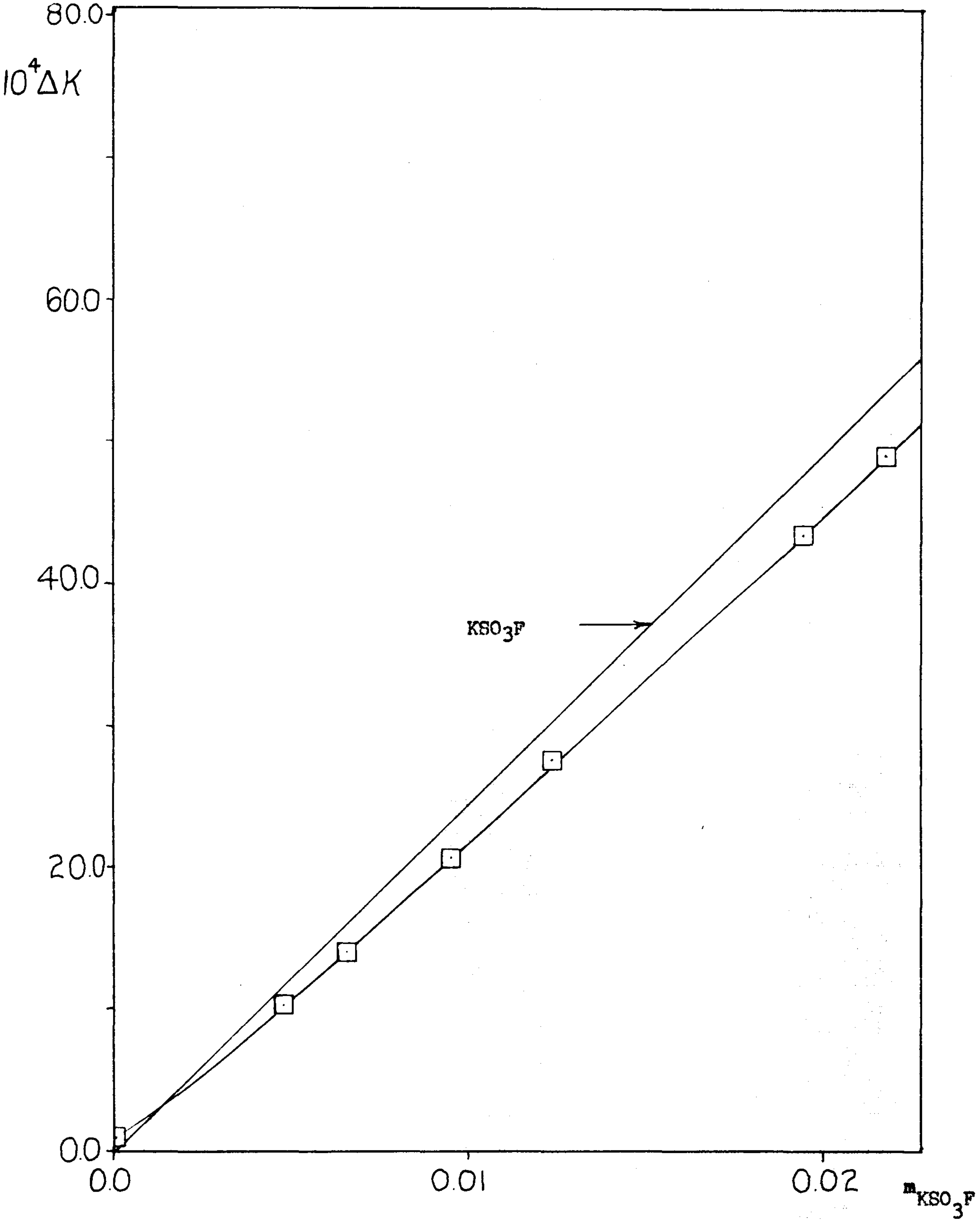

Figure 24 Conductivity at 25°C: Additions of KSO_3F to $I(SO_3F)_3$ (Expt. 47)

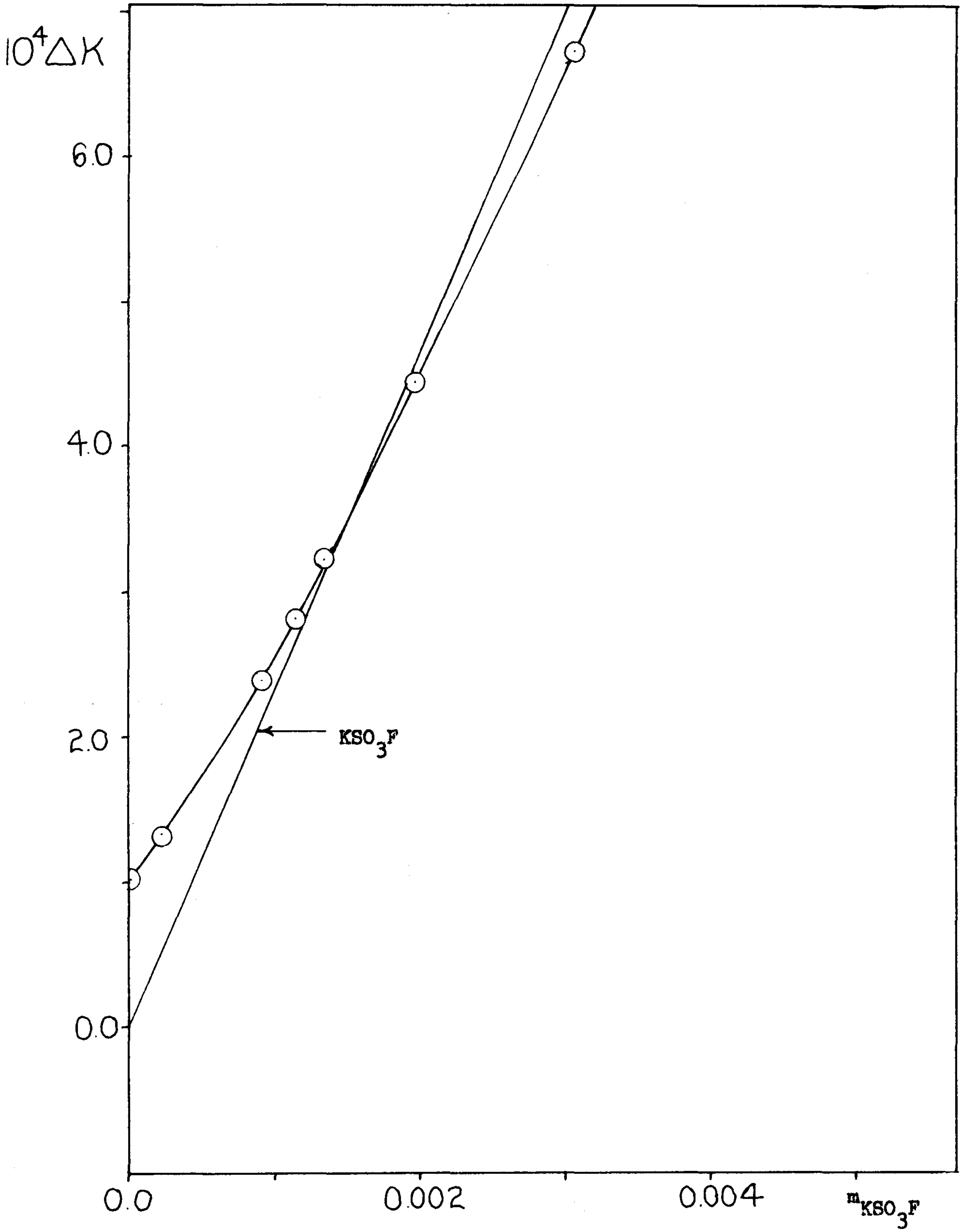

Figure 25 Conductivity at 25°C: Additions of KSO_3F to $I(SO_3F)_3$
(Expt. 43)

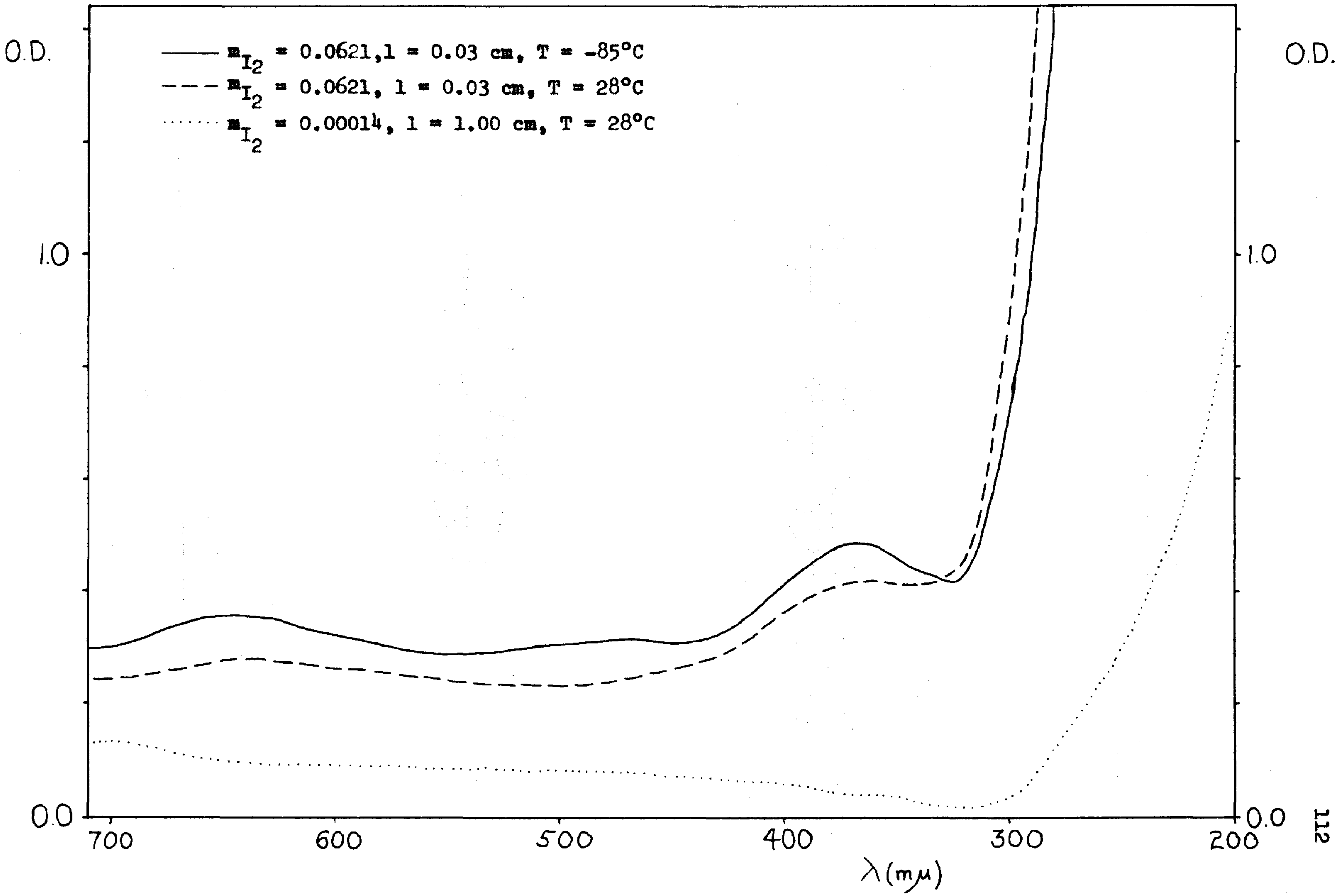

Figure 26 1:3 $I_2/S_2O_6F_2$ Spectra

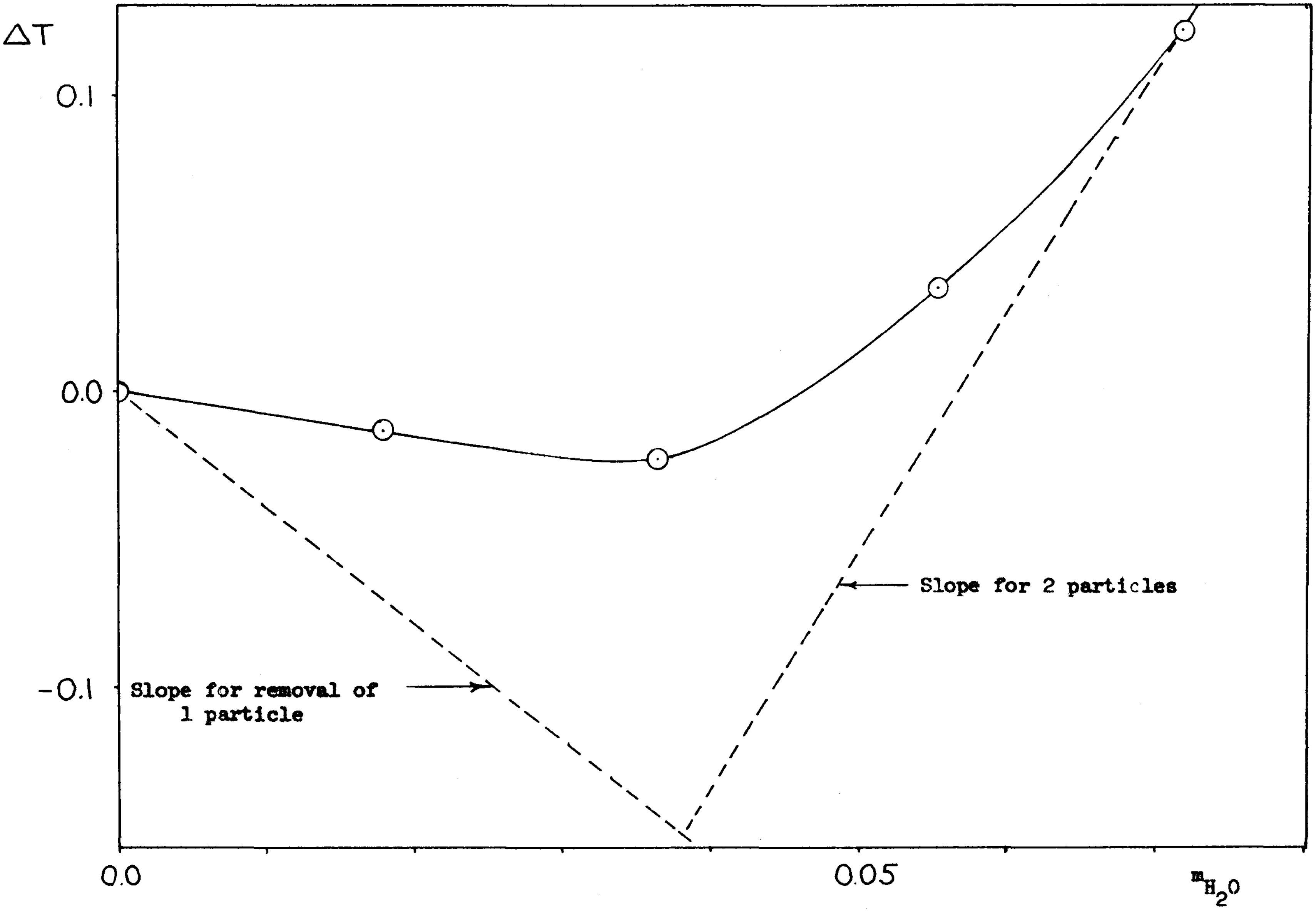

Figure 27 Cryoscopy: H_2O Additions to $I(SO_3F)_3$ (Expt. 44)

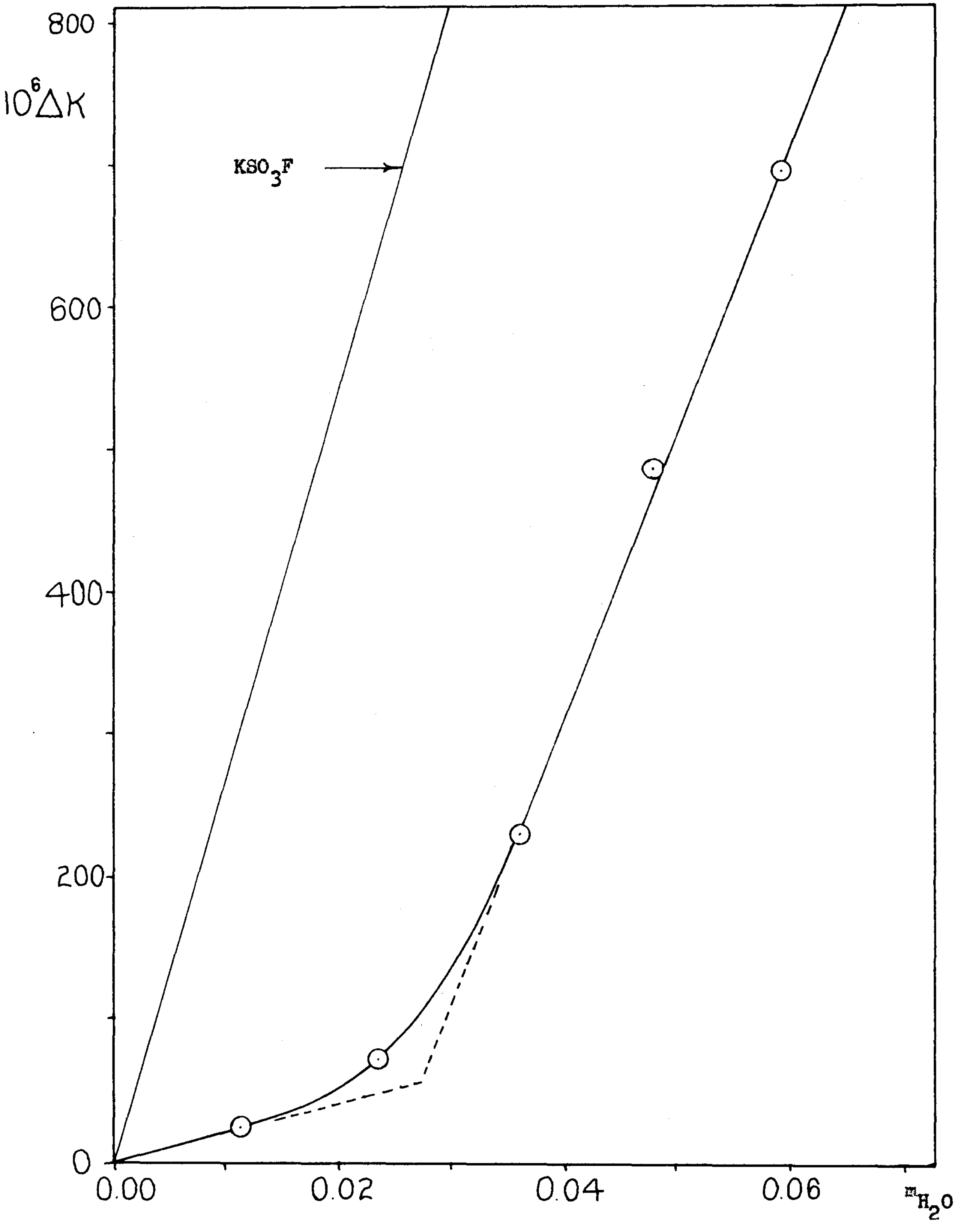

Figure 28 Conductivity at -78.52°C: H_2O Additions to $I(SO_3F)_3$
(Expt. 45)

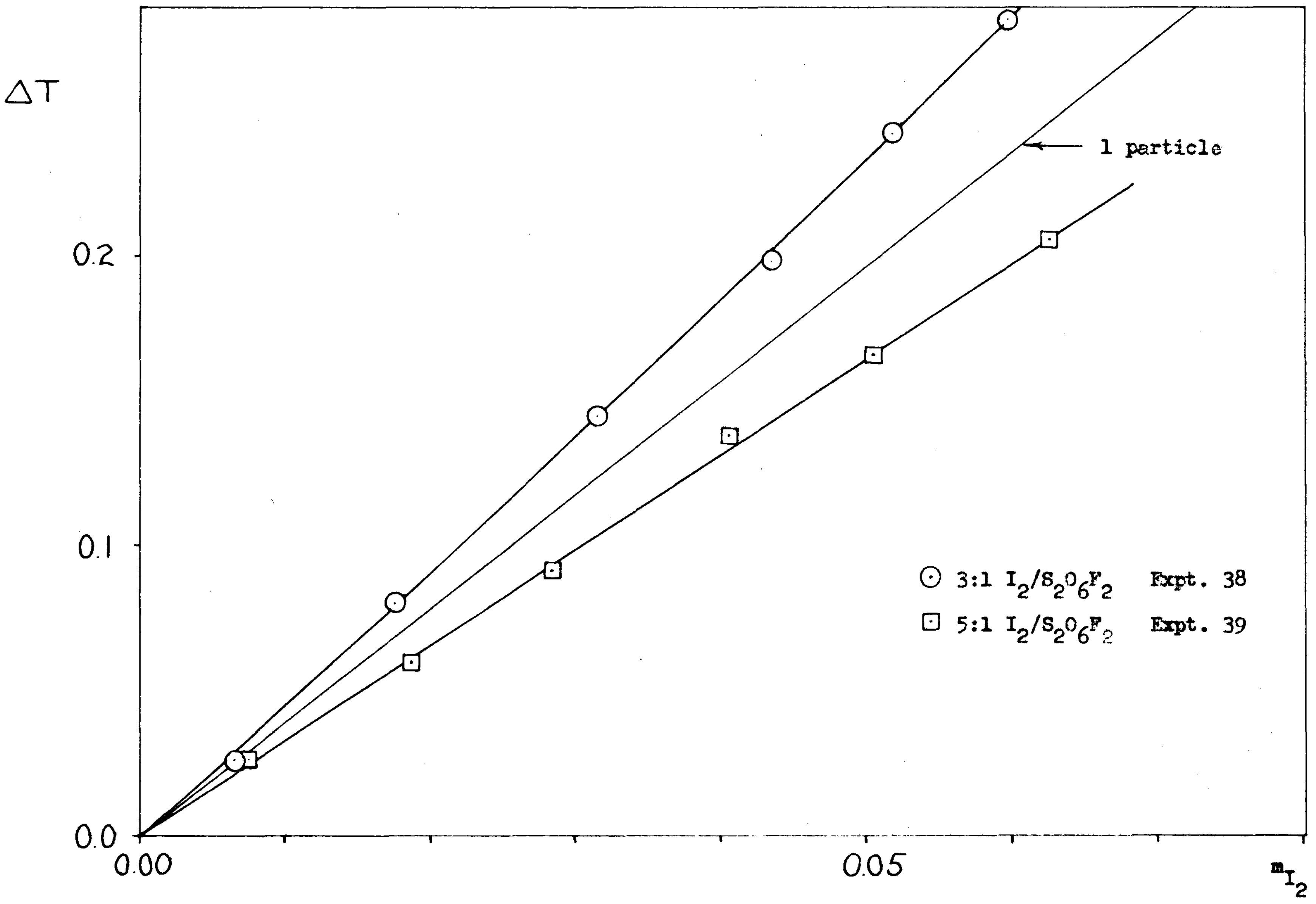

Figure 29 **Cryoscopy: 3:1 and 5:1 $I_2/S_2O_6F_2$**

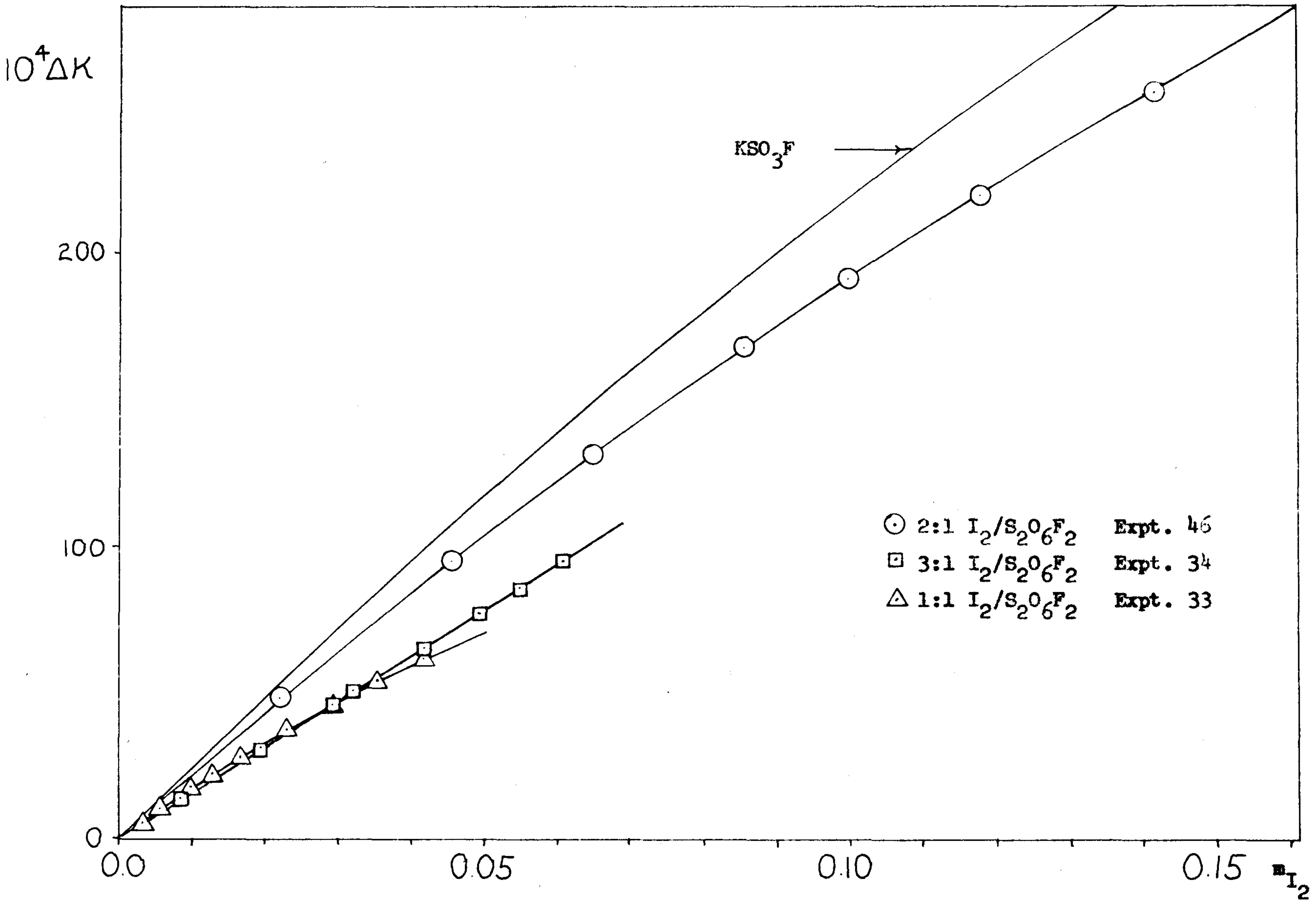

Figure 30 Conductivity at 25°C: 1:1, 2:1 and 3:1 $I_2/S_2O_6F_2$

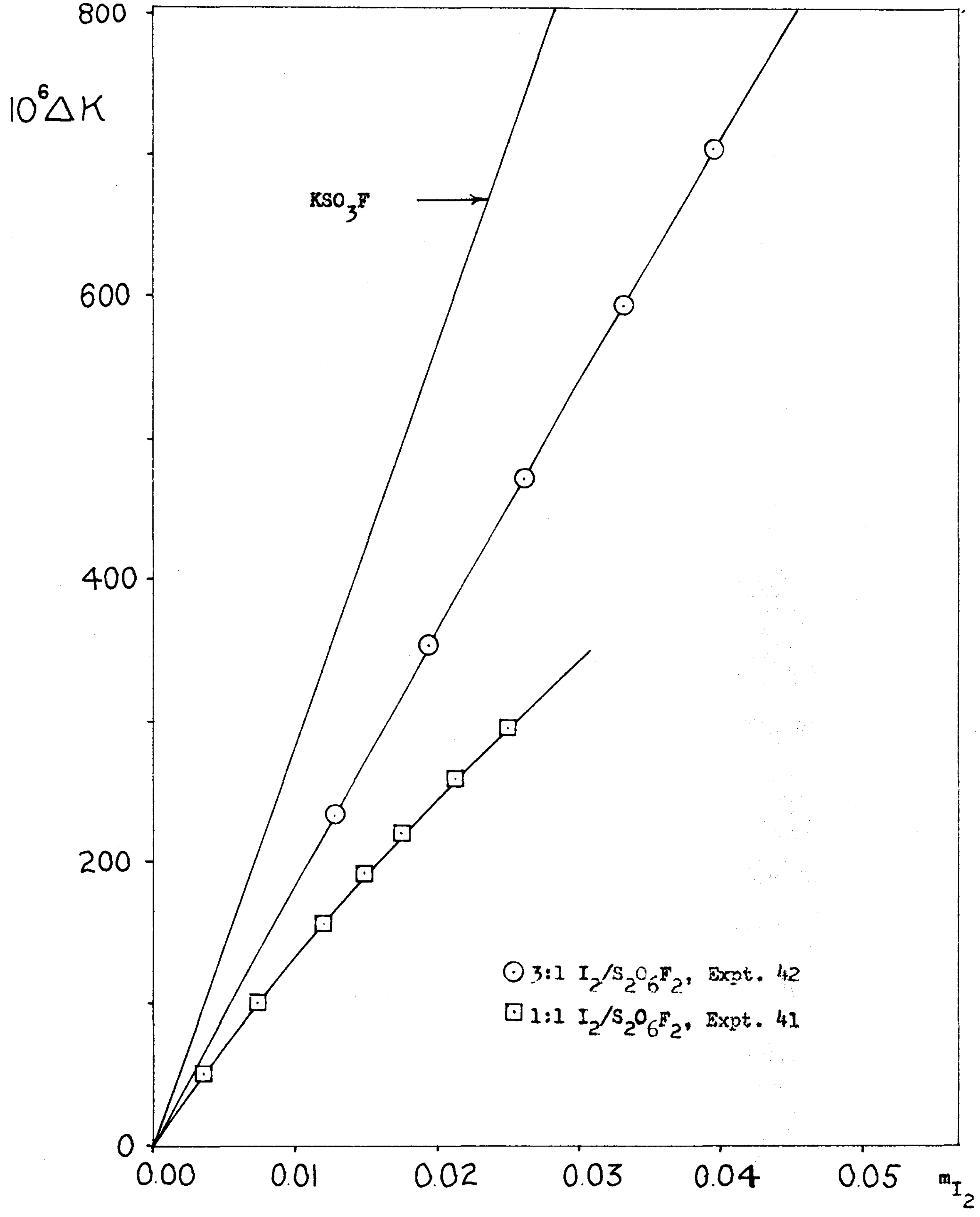

Figure 31 Conductivity at -78.52°C : 1:1 and 3:1 $I_2/S_2O_6F_2$

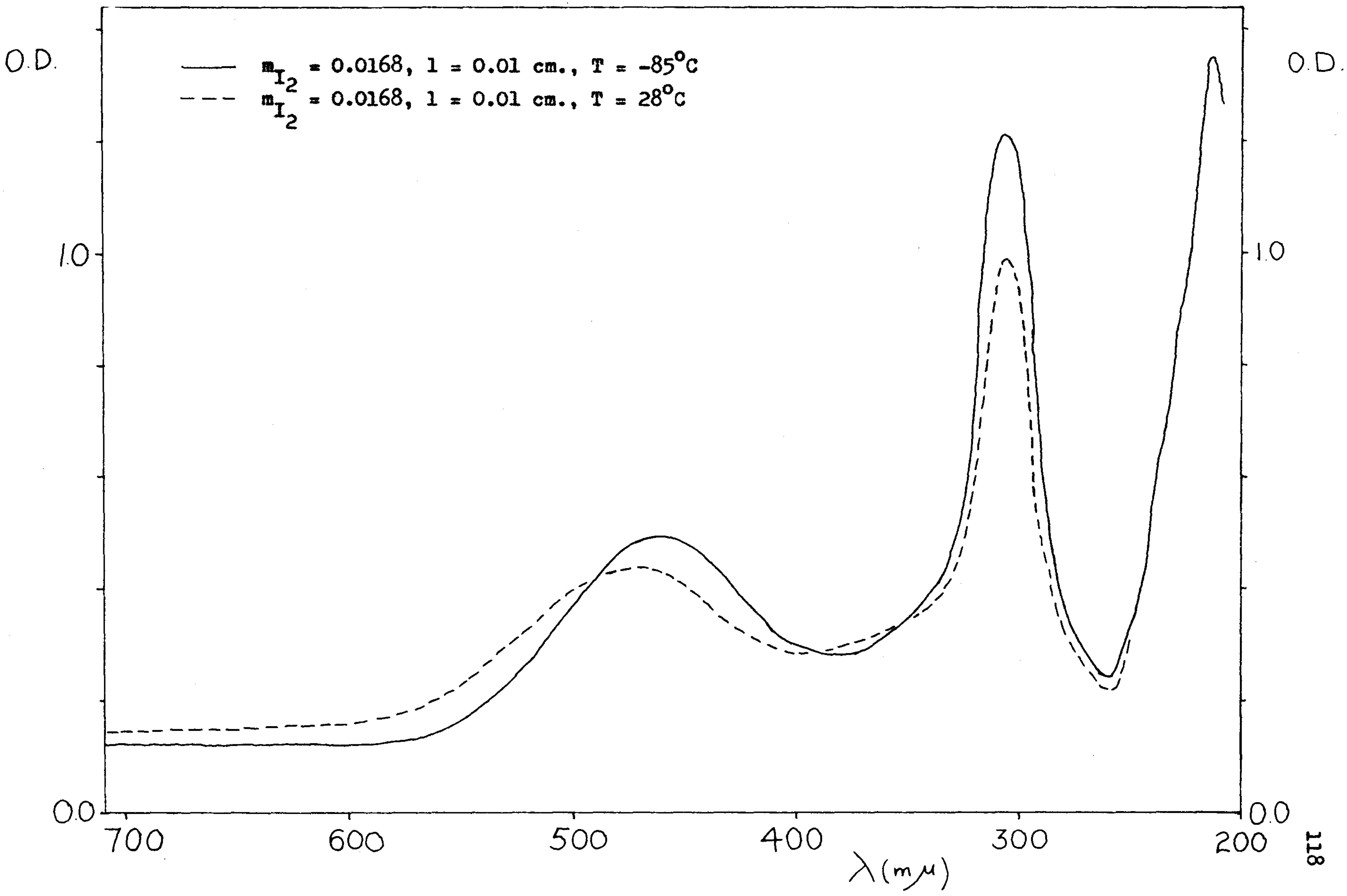

Figure 32 3:1 $I_2/S_2O_6F_2$ Spectra

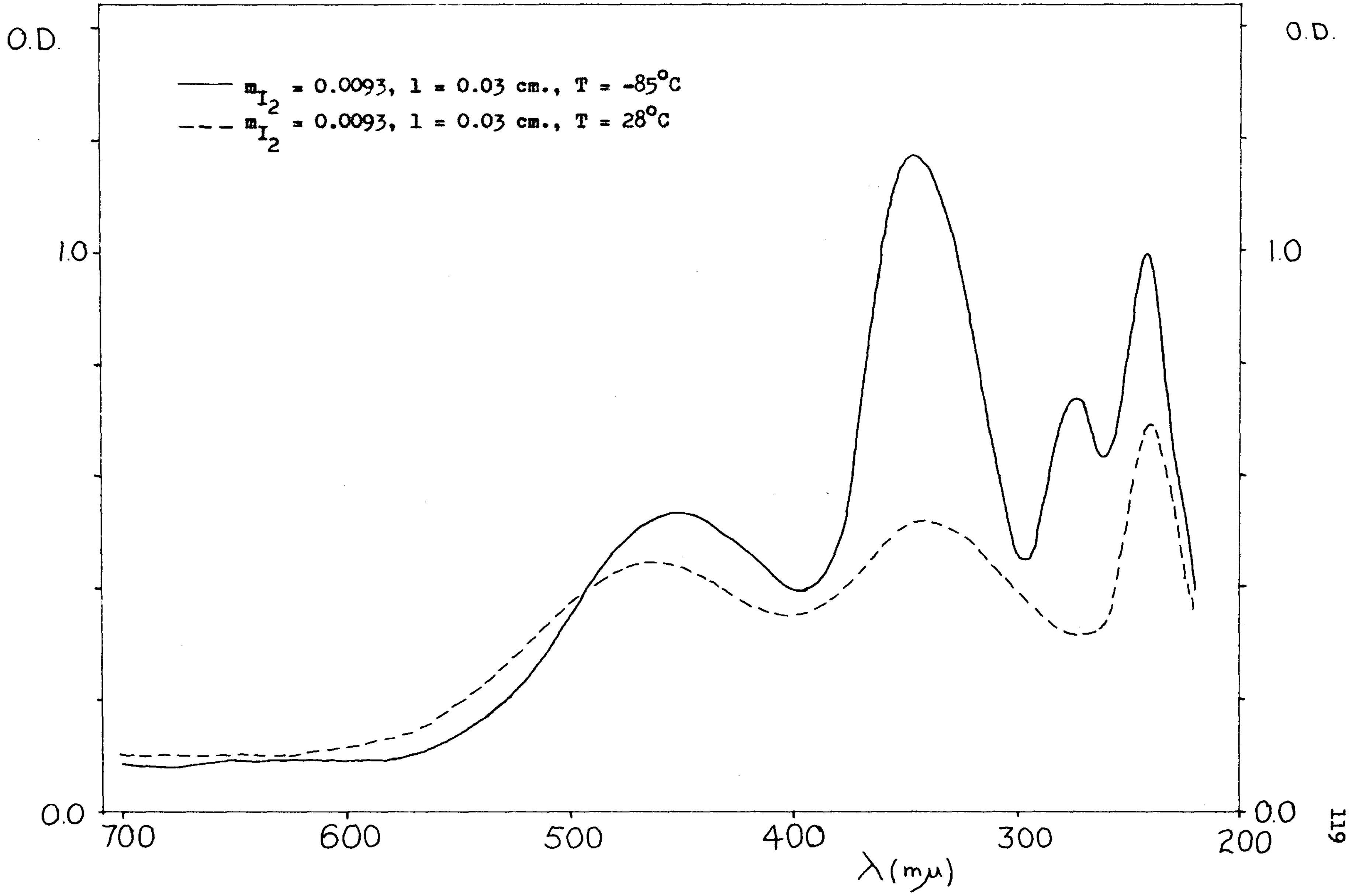

Figure 33 5:1 $I_2/S_2O_6F_2$ Spectra

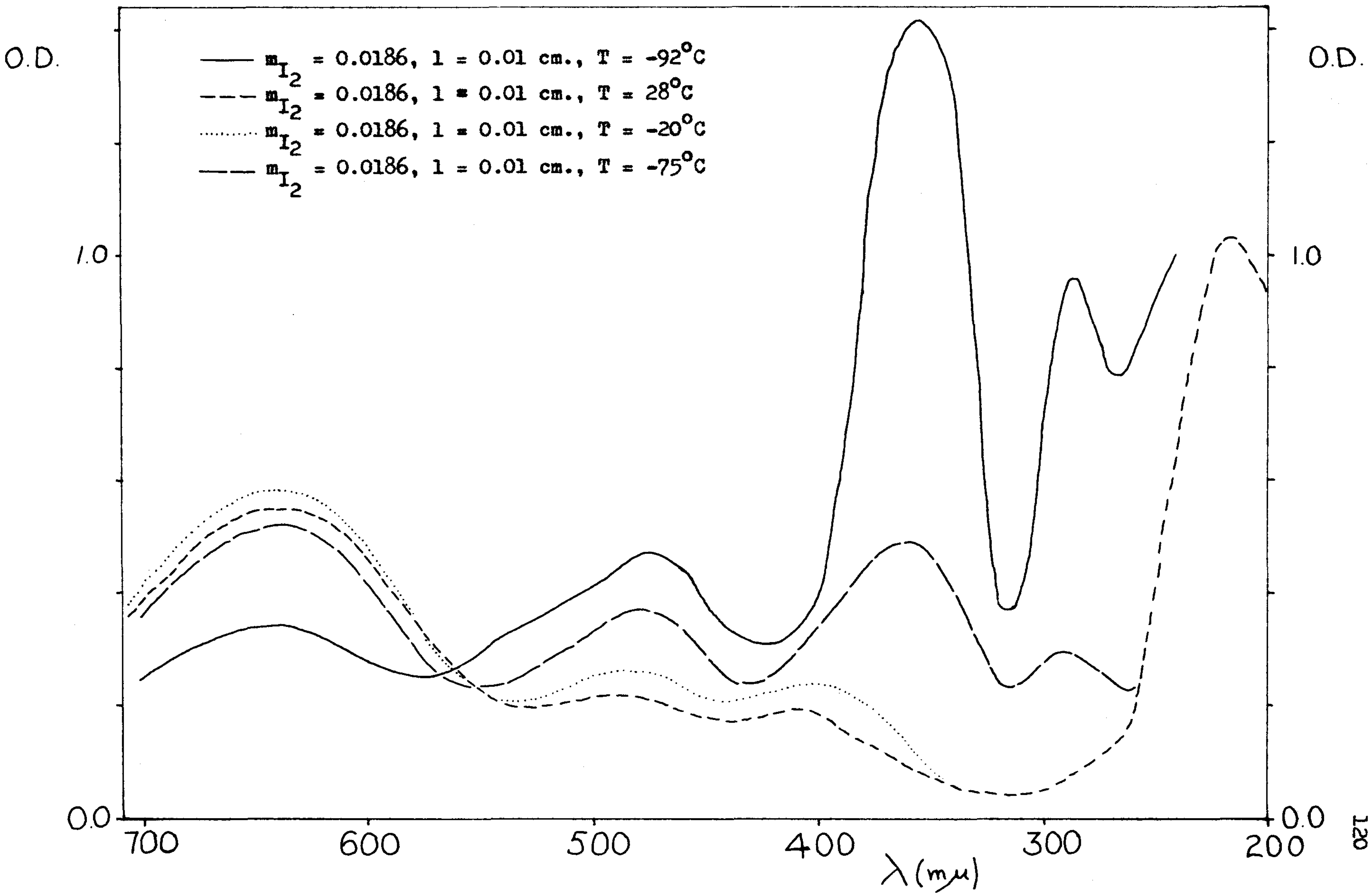

Figure 34 1:1 $I_2/S_2O_6F_2$ Spectra: Variable Temperature

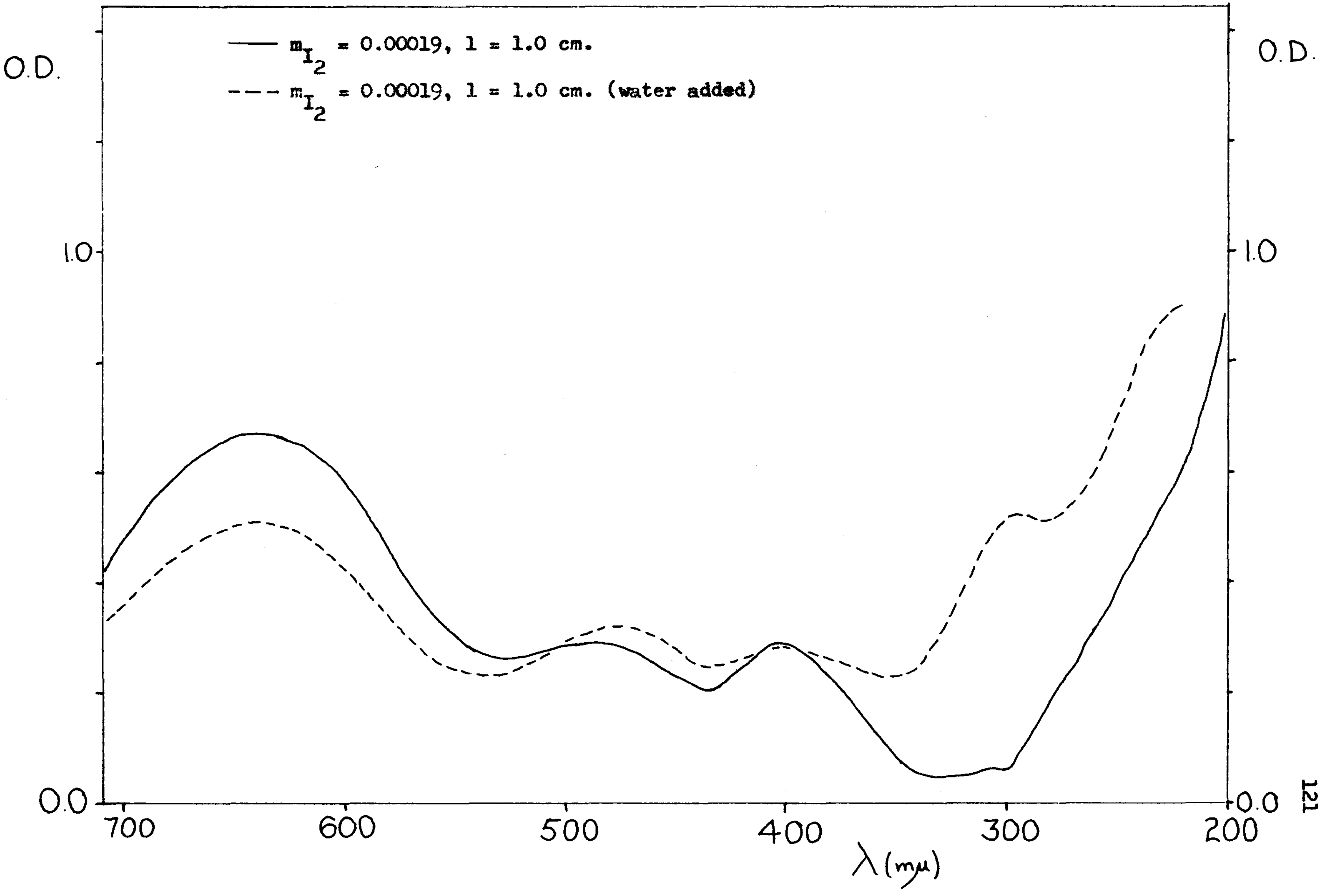

Figure 35 1:1 $I_2/S_2O_6F_2$ Spectra: Effect of Water (T = 28°C)

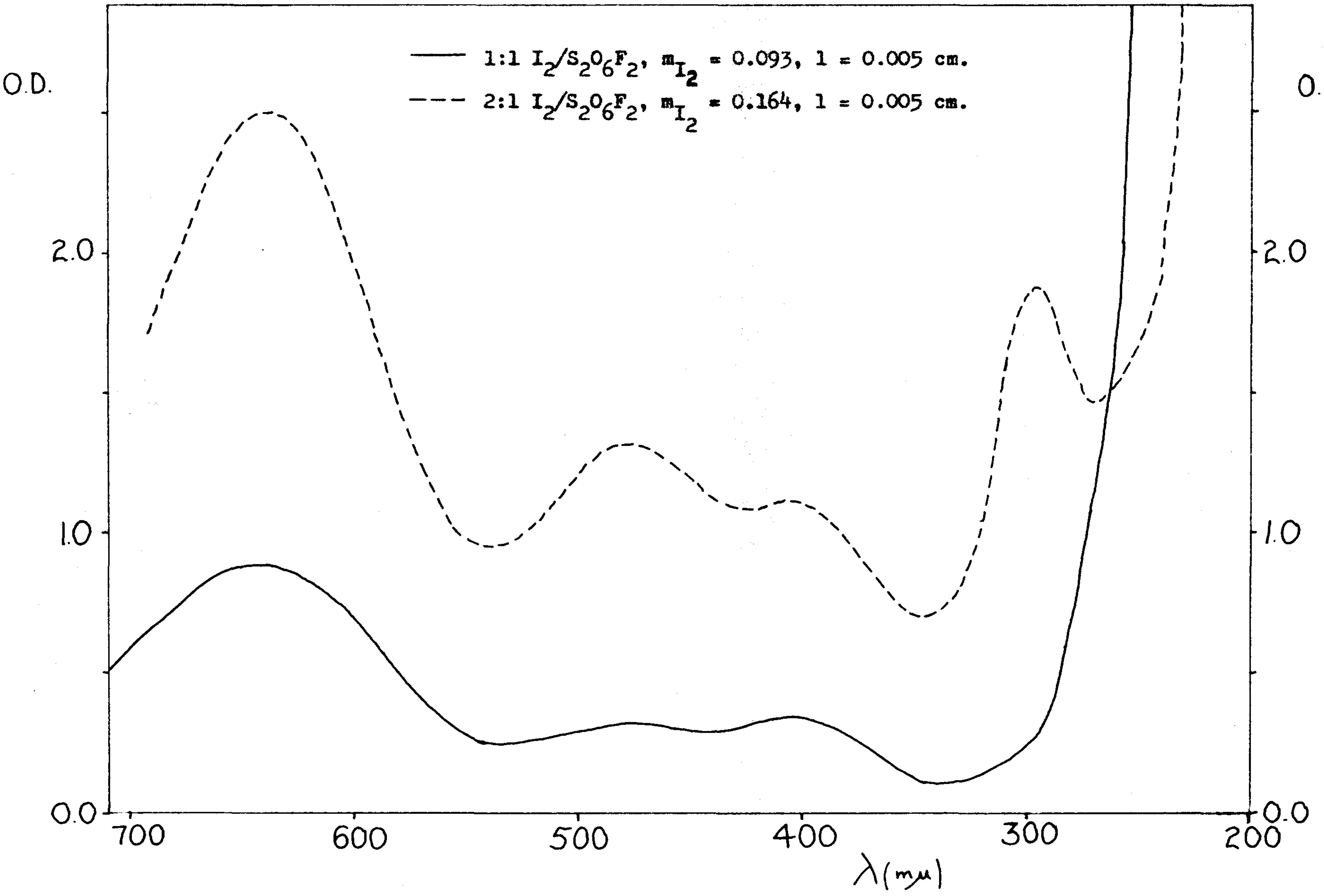

Figure 36 1:1 and 2:1 $I_2/S_2O_6F_2$ Spectra at High Concentrations (T = 28°C)

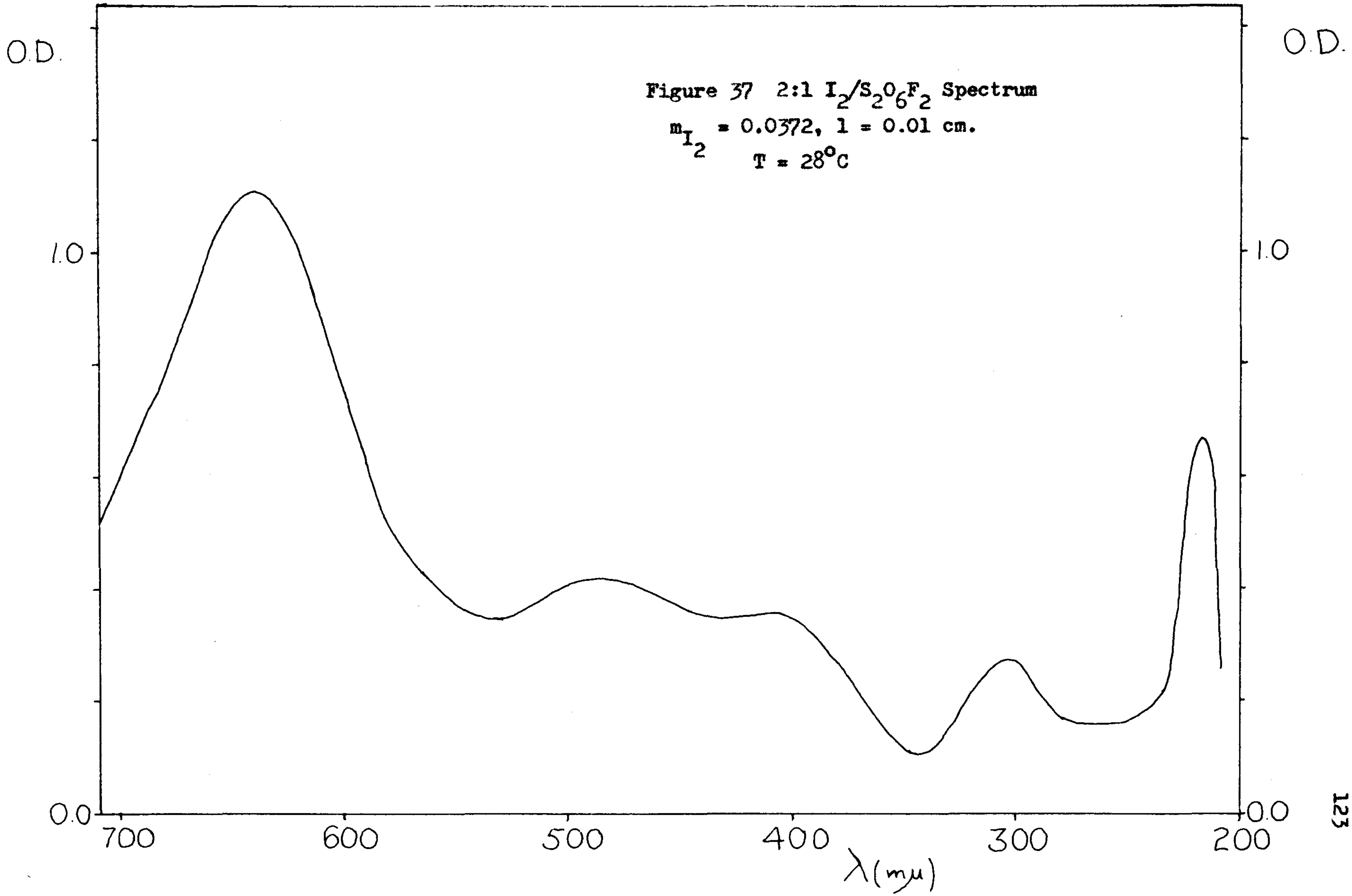

Figure 37 2:1 $I_2/S_2O_6F_2$ Spectrum
m_{I_2} = 0.0372, l = 0.01 cm.
T = 28°C

APPENDIX

List of Symbols

K - equilibrium constant in molal units

BM - Bohr Magneton

χ_g - weight magnetic susceptibility, cgs units

χ_{NiCl_2} - weight susceptibility of $NiCl_2$ solution, cgs units

k_f - cryoscopic constant

m - molality of the solute

m_X - molality of the solute X

ν - number of moles of particles produced in solution by one mole of solute

T_o - initial freezing point of fluorosulphuric acid (°C)

χ_M - magnetic susceptibility per mole of iodine species

χ_{MX} - magnetic susceptibility per mole of iodine species X

χ_v - volume magnetic susceptibility, cgs units

H_o - the field external to the sample

μ_{eff} - effective magnetic moment (BM)

$\Delta\delta$ - shift caused by change of medium (ppm)

T_1 - spin-lattice relaxation time

Δ - NMR signal width at half height (cps)

w_g - weight of sample in Gouy tube

M_{I_2} - iodine molarity

$[X]$ - molality of the solute X

γ - number of moles of fluorosulphate ions formed per mole of solute

$\epsilon_{I_2^+(640)}$ - molal extinction coefficient of I_2^+ at 640 mμ

$\epsilon_{I_3^+(305)}$ - molal extinction coefficient of I_3^+ at 305 mμ

l - path length for spectra

κ - specific conductance (ohm^{-1}cm^{-1})

$\Delta\kappa$ - specific conductance corrected for solvent conductivity (ohm^{-1}cm^{-1})

O.D. - optical density

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