COLLIGATIVE MEASUREMENTS IN ANHYDROUS HYDROGEN FLUORIDE

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SCOPE AND CONTENTS:

Techniques have been developed for making cryoscopic and vapour pressure measurements in anhydrous hydrogen fluoride. The cryoscopic constant for the solvent has been determined.

The techniques developed have been used to determine the mode and extent of the ionization of some acids and bases of the HF system. The formation and stability of polymeric ions in the solvent has been investigated and the formation of the previously unknown anion $As_2F_{11}^-$ has been shown. Cryoscopy has been used to detect a new polymeric 1:1 adduct of XeF_2 and SbF_5. Solutions of cyanides in HF have been investigated and the formation of a new polymeric cation $Hg_2CN_3^+$, formed when mercury cyanide dissolves in HF, has been suggested. The results of some experiments on solvolysis reactions are also reported.

ACKNOWLEDGEMENTS

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

PROPERTIES OF ANHYDROUS HYDROGEN FLUORIDE.

INTRODUCTION.

The early pioneer work on the solvent properties of HF by such workers as Moissan, Ruff, Bond, Klatt, Fredenhagen and Simons was carried out in platinum, gold, wax coated glass, copper or nickel apparatus. Progress was limited by the lack of inert materials and suitable techniques for handling high purity HF in a moisture free environment. The manufacture from 1945 of fluorine containing polymers resistant to attack by HF, encouraged a wide range of measurements to be made on the pure anhydrous material and interest in HF as an important solvent increased markedly.

The general properties of anhydrous hydrogen fluoride as a solvent in a wide variety of inorganic and organic reactions has been outlined in a number of useful reviews, by Simons(1,2), Mellor(3,4) and more recently by Hyman and Katz(5) and Kilpatrick and Jones(6). Many examples of the application of anhydrous hydrogen fluoride in organic, industrial and catalytic processes will be found in reviews by Simons(7), Burdon and Tatlow(8), Hudlicky (9) and Olah(10).

STRUCTURE AND PHYSICAL PROPERTIES.

A number of physical properties of anhydrous HF are summarized in Table I.1. They indicate that HF is highly associated in the gas, liquid and solid state. Tt is one of the most strongly hydrogen bonded solvents known, having a bond energy for the hydrogen bridge of about 7 k.cal. mole^{-1}. X-ray measurements on solid HF indicate a zig-zag chain with an H - F - H bond angle of 120.1° (11). Infrared measurements on the solid (12,13) support this structure. However, the exact nature of the associated vapour is still the subject of discussion in the literature. Much of this discussion is summarized in Simons,(1) Smith (14) and Franck et.al.(15,16). Simons (17) proposed a monomer - hexamer equilibrium for HF in the gas phase in order to explain the vapour density data. Later electron diffraction measurements in the gas phase (18) were interpreted in terms of short zig-zag chain polymers. However, further vapour density measurements were again interpreted in terms of a predominantly monomer $\rightleftharpoons$ hexamer equilibrium.(19) Dielectric polarization data.(20) indicated the cyclic nature of the hexamer. The gas phase infrared measurements of Smith (14) provided further evidence for the $(HF)_6$

TABLE 1.1

SOME PHYSICAL PROPERTIES OF HF.(5)

Freezing point	-83.55 °C (see text)
Boiling point	19.51 °C
Density	1.002 $g.ml^{-1}$ at 0 °C
Dielectric constant	84 (0 °C), 175 (-73 °C)
Viscosity	0.256 centipoise at 0 °C
Conductivity	10^{-6} $ohms^{-1}$ $cm.^{-1}$
L.H.of Fusion (23)	0.939 $k.cal.mole^{-1}$ (for M.W.20.0006)
L.H.of Vaporization	1.789 $k.cal.mole^{-1}$ (for M.W.20.0006)

TABLE 1.2

SOME PHYSICAL PROPERTIES OF HYDROGEN HALIDES AND WATER.*

	H_2O	HCl	HBr	HI
M.Pt. °C	0	-114.6	-88.5	-50.9
B.Pt. °C	100	-84.1	-67.0	-35.0
Liquid range °C	100	30.5	21.5	15.9
L.H. of Fusion ($k.cal.mole^{-1}$)	1.440	0.476	0.600	0.686
L.H.of Vaporization ($k.cal.mole^{-1}$)	9.720	3.860	4.210	4.724
D.Constant	84.2(0°C)	9.28(-95°C)	7.0(-85°C)	3.39(-50°C)

* From M.E.Peach and T.C.Waddington
p.85. reference (5)

polymer model since they were interpreted in terms of a monomer $\rightleftharpoons$ hexamer equilibrium with a secondary monomer$\rightleftharpoons$tetramer equilibrium. Clearly the exact degree of association in the gas phase is dependent on the temperature and pressure, the dimer and tetramer being more important at low pressure. The association gives rise to various anomalies in the volumetric and thermal properties of HF (21). Thus the specific heat and thermal conductivity are much greater than they would be in the absence of association. Jarry and Davis(19) studied the saturated vapour pressure and vapour density of HF over the temperature range 0 - 105°C. From this data they showed that the degree of association of the saturated vapour varied from about 4.7 to 2.4 over the temperature range studied.

The extent of polymerization and the nature of the polymers for HF in the liquid state is less clearly understood and the situation is probably far more complex. It cannot be assumed that the liquid is composed of the same species in the same proportions as the vapour. Dahmlos and Jung(22) calculated an association factor from the molar heat of fusion of HF of 3.7 . Jarry and Davis(19) found an association factor of 3.5 to 3.7 at the boiling point, for the saturated vapour in equilibrium with the liquid. That there is considerable association in the liquid is also clear from the relatively high heat of fusion, melting point, and long liquid range (c.f. HCl Table 1.2.). Infrared absorption bands (24,25) in liquid HF provide further evidence for polymerization by hydrogen bonding.

Studies on hydrogen halides in solid and liquid phases using slow neutron inelastic scattering techniques(26) were used to compare scattering data for HF_2^- and $H_2F_3^-$ ions and gave results emphasising the high degree of association of HF in the liquid phase.

The polymerization of the liquid is markedly affected by molecular interactions on addition of solute. Borodin and Sventitskii (27) have made a study of the concentration dependence of the ^{19}F chemical shift in such systems as HF - H_2O, HF - dioxane, HF - C_6H_6 and have discussed the change in the type and extent of polymerization of HF caused by solute interaction. They concluded that cyclic $(HF)_n$ polymers predominate at high HF concentration but zig-zag $(HF)_n$ polymers are more important at low concentration of HF.

The liquid range and dielectric constant for HF are similar to the values found for water, but the viscosity and surface tension are markedly lower than for water, since HF has a two-dimensional polymeric structure in contrast to the three-dimensional network found in water. From a practical point of view the favourable physical properties of low surface tension, viscosity and comparatively lower boiling point enable HF to be easily transferred in a vacuum line, easily filtered or evaporated and assist in the rapid attainment of homogeniety in solution experiments.

SOLVENT PROPERTIES.

Anhydrous HF is a powerful, non-oxidizing, highly mobile protonic solvent. As would be expected from its high dielectric constant HF is a good solvent for electrolytes which dissolve with extensive ionization. Its ability to form hydrogen bonds makes it an excellent solvent for many organic substances.

Simple ionic metal fluorides dissolve in HF as bases of the system (Chapter V):

$$MF + HF \rightarrow M^{+} + HF_2^{-}$$

Many organic substances are protonated in HF dissolving as bases and increasing the fluoride ion concentration. Water also behaves as a strong base (Chapter V).

Common strong acids of the water system do not in general exhibit acid properties in HF. Thus HCl has a solubility of only 0.17 M at 0°C (28), acetic acid acts as a base, and sulphuric acid slowly forms unionized fluorosulphuric acid (Chapter VIII). Several good fluoride ion acceptors, however, are capable of increasing the H_2F^+ concentration thus behaving as acids of the system, e.g. group V pentafluorides(29,30):

$$SbF_5 + 2HF \longrightarrow H_2F^+ + SbF_6^-$$

At higher concentrations SbF_5 and related molecules tend to associate in solution(29), further enhancing their acid strength (Chapter VI). A number of qualitative studies on these acids have been made(31,32,33).

The highly acidic nature of the solvent coupled with the high electronegativity of fluorine causes extensive solvolysis to the corresponding fluoride to occur for many solutes e.g. :

$$MCl + 2HF \longrightarrow M^+ + HF_2^- + HCl$$

A few substances e.g. WF_6, SF_6, SO_2, XeF_2 dissolve in HF to give solutions of low conductivity and it has to be concluded that they behave as non-electrolytes (Chapter III).

Determinations of the H_o Hammett acidity function for HF(25,45) indicate that the value for very pure anhydrous HF approaches - 11. Since the Hammett acidity function curve is extremely sensitive to traces of electrolyte impurity in the limiting region, the true value however may be only slightly lower than the value of -12 found for 100% sulphuric acid. Bases such as F^- markedly reduce the value of H_o while acids such as SbF_5 increase it greatly.

CONDUCTIVITY MEASUREMENTS.

(a) Self Ionization of Pure HF.

The specific conductivity of pure HF indicates that it undergoes self-ionization, which can be written as an autoprotolysis as follows:

$$3HF \rightleftharpoons H_2F^+ + HF_2^-$$

The autoprotolysis ions are written as H_2F^+ and HF_2^- as a convenience in the same way as the proton in water is normally written as H_3O^+. In fact both ions will be considerably solvated and exist as part of an associated hydrogen bonded network. The solvent ions show high equivalent conductivites. The mechanism of conduction is mainly by proton transfer along hydrogen bonded chains of solvent molecules as in other hydrogen bonded protonic solvents (e.g.H_2SO_4) rather than an ion migration mechanism. Since HF has such a low viscosity however, the ion diffusion mechanism makes a bigger contribution than in sulphuric acid(34,35). The ionic mobilities for H_2F^+ and HF_2^- at 0 ° and infinite dilution are 350 and 273 $ohms^{-1} cm^2 mole^{-1}$ respectively (29,36).

The conductivity of pure HF rises markedly in the presence of small concentrations of ionizing impurities, notably water. Conductivity techniques have in fact been used in order to determine the trace water content of purified anhydrous hydrogen fluoride (37).

Since anhydrous HF shows such an extremely high affinity for water it is still not certain what precise value should be given for the conductivity of 100% HF. The best values obtained are of the order of magnitude 1 x 10^{-6} ohms^{-1} cm^{-1} at 0° C.(38) The true value of the autoprotolysis constant $K = [H_2F^+][HF_2^-]$ is probably even lower than the value 10^{-12} found for such high purity acid (39).

(b) Dilute Solutions in HF.

A number of studies have been made on the ionization of solutes in dilute solution in HF using conductivity measurements. Fredenhagen and Cadenbach and Klatt(40,41,42) used this technique together with boiling point measurements to investigate the solution properties of a range of organic and inorganic compounds e.g. KF, H_2O, KNO_3, alcohol, acetone, acetic acid and a number of aromatic compounds. Kilpatrick and Luborsky(43,44) have made conductance measurements on methyl benzenes in HF and given equilibrium constants for:

$$Ar + 2HF \rightleftharpoons ArH^+ + HF_2^-$$

Kilpatrick and Lewis(36) made conductance measurements on solutions of NaF, KF, SbF_5, $NaSbF_6$ and evaluated ionic mobilities and transference numbers for the ions in solution. Hyman et.al.(30) and later Gillespie and Moss(29) have used conductivities to investigate further the SbF_5 - HF system. Kreshkov et.al.(46) have investigated the behaviour of a number of oxygen containing organo-silicon compounds by measuring their conductivities in HF. Frlec and Hyman(47) used conductivity to investigate the ionization and solubility of MoF_6 and related hexafluorides. Kilpatrick et.al.(48) similarly investigated the behaviour of nitronium fluoroborate in HF.

COLLIGATIVE MEASUREMENTS

An important contribution to our understanding of the behaviour of solutes in HF was made in the 1930's when Fredenhagen and later Klatt succeeded in making elevation of boiling point measurements in HF on a wide range of inorganic solutes, using gold and platinum apparatus. Fredenhagen(49) found the boiling point constant to be 1.9 $^{o}C\ mole^{-1}kg^{-1}$, about four times greater than that for water. Fredenhagen(50,51) investigated such important solutes as water, potassium fluoride, potassium perchlorate, potassium sulphate and a range of organic compounds - e.g. phenols, ketones and a number of organic acids. Klatt(42,52,53,54) also made boiling point elevation measurements, using acid stored in silver bottles having a specific conductivity of 10^{-3} to 10^{-4} $ohms^{-1}$ $cm.^{-1}$ at $-15^{o}C$.

He investigated the behaviour of a number of alcohols and phenols (42) e.g. methanol, acetone, m-nitrophenol, o-chlorophenol; and a number of organic acids e.g. formic acid, benzoic acid and acetic acid. He also investigated some cyanides and azides (55) which are further discussed in Chapter VII.

In many of the reactions investigated by Klatt and Fredenhagen slow solvolysis processes are involved and the interpretation of the results is inconclusive. However, these boiling point elevations were sensitive enough to detect the effect of substituents on the aromatic ring; e.g. $-NO_2$ or -Cl substituted in phenols lower the bascity of phenols, and a comparatively smaller boiling point elevation was observed. Nickolaev and Tananaev (56) in more recent boiling point elevation work determined activities for alkali metal and ammonium fluorides and several alkyl and aromatic amines. No experimental details or criteria for purity of HF are given but the boiling point elevations obtained on alkali metal fluorides and the non-electrolyte nitrobenzene give a value of the boiling point elevation constant of $1.9 \pm 0.05\ ^{\circ}\text{mole}^{-1}$ in agreement with that found by Klatt and Fredenhagen.

There have been some investigations on the behaviour of solutes in HF by means of vapour pressure measurements. Cady(57) made some measurements on the HF - KF system up to 0.46 mole fraction of HF saturated with KF. Kilpatrick and Luborsky(43) investigated the behaviour of BF_3 in anhydrous HF by means of conductivity and vapour pressure depressions. Rogers et.al.(58,59) made some vapour pressure measurements in their investigations of the IF_5-HF and BrF_5-HF systems. **McCaulay** and Lien(60) also measured lowering of vapour pressure in HF in connection with their study of the systems hydrocarbon-boron trifluoride-HF. Koerber and De Vries(61) studied the vapour pressure of the systems Hg_2F_2 - HF, CdF_2 - HF, PbF_2 - HF.

Cryoscopic measurements in the HF system have been largely restricted to high concentration phase diagram and thermo-chemical studies. Thus the phase diagrams of several fluoride - HF systems have been studied by a number of workers. Cady(57) studied the KF - HF system, Webb and Prideaux(62) investigated the RbF - HF system, Winsor and Cady(63) the CsF - HF system, Nikolaev and Malykov(64) the ClF_3 - HF system and Euler et.al.(65) the NaF - HF and NH_4F - HF systems. Westrum et.al.(66,67) have described some solution calorimetric measurements in anhydrous HF and have determined the enthalpies of solution of sodium and ammonium hydrogen fluoride in anhydrous HF. A number of workers(68,69,70,71) associated with the U.S.Atomic Energy Commission have described devices for studying the freezing point of the UF_6 - HF system. The freezing point diagram over the whole range of concentrations up to 100% UF_6 has been discussed in these papers. This work has now been extended to a study of the MoF_6 - HF system(72). Rogers et.al.(58) also made freezing point measurements over the whole range of concentrations up to 100% IF_5 and BrF_3 in their study of the IF_5 - HF and BrF_3 - HF systems.

The low freezing point and handling problems associated with anhydrous HF appears to have discouraged attempts to obtain dilute solution data by cryoscopic techniques. Cady made a few measurements in the KF - HF sytem in 1934. Nikolaev and Tananaev(56) in a paper on the activities of solution components in anhydrous HF calculate the value for the cryoscopic constant from the early values of ΔH_f as 1.3^{o} mole $^{-1}$.

PURPOSE OF THIS WORK.

There is now a considerable amount of qualitative data on the ionization of a wide range of solutes in the HF solvent system and an increasing amount of solubility data(47,73,74). There is however, a lack of quantitative data on the nature and extent of ionization of electrolytes in the system. Because of the uncertainties associated with the mobilities of the ions of the HF system the conductivity data often cannot be interpreted unambiguously. The interpretation of some of the early boiling point data is also uncertain due to solvolysis and impurity effects. It was the major objective of this work to extend the range of quantitative data available by developing suitable techniques for making systematic dilute solution studies of freezing point and vapour pressure depressions in pure anhydrous HF. The main effort has been to define normal non-electrolyte and electrolyte behaviour by making freezing point depression measurements on non-electrolytes and binary fluorides and hence to measure experimentally the cryoscopic constant for anhydrous HF. This development work has allowed subsequent quantitative evaluation of the ionization of a number of solutes whose behaviour in anhydrous HF is of particular interest.

CHAPTER II

EXPERIMENTAL TECHNIQUES

(a) General apparatus for handling HF.

Anhydrous HF readily reacts with glass and either reacts with or dissolves in most of the greases used in a conventional vacuum system. There are a number of metals e.g. copper, nickel and nickel alloys which do not readily react with anhydrous HF, because they form protective surface coatings of metal fluoride. However any oxide film reacts to produce water. High purity HF is generally handled in polychlorotrifluoroethylene (Kel-F) or polytetrafluoroethylene (Teflon) containers. Kel-F is harder, more readily machined or threaded and more transparent than Teflon. However, HF solutions of some solutes e.g. the $XeF_2.SbF_5$ adduct discussed in Chapter VI have been found to slowly attack Kel-F, presumably by removal of chlorine. The use of Swagelok unions made out of monel or Teflon removes the need to use greased joints.

A general view of the system,used for handling HF in completely dry conditions, which was constructed during the course of this investigation is shown in Fig.2.1 . The main manifold of the vacuum system was constructed out of $\frac{1}{2}''$ monel. Outlets were monel welded onto the main manifold. The line valves were Nupro 4BK monel bellows vales with Kel-F stem tips and gaskets; these gave excellent vacuum and corrosion resistance during some four years service. A diagram of the arrangement of outlets and cold traps is shown in Fig.2.2. Cold trap A was constructed from monel, which due to its relatively low thermal conductivity allowed liquid nitrogen to be retained in a surrounding cooling Dewar flask during overnight pumping. Waste HF which condensed in this monel cold trap was removed by pumping at outlet B through a 5 litre pyrex bottle which was half filled with soda-lime. The trap was warmed to about 70 ^{o}C and the HF pumped off by means of a water pump connected at B. The conditioned line was maintained in a completely dry state by keeping it at 80 - 100 ^{o}C using a heating tape wrapped around the main manifold. The protective fluoride layer was maintained by keeping the line filled with HF at these temperatures during periods of disuse. The second cold trap and the rest of the pumping system was constructed out of glass in the conventional way. During the transfer of HF in the vacuum system, control was maintained by means of a monel Bourdon

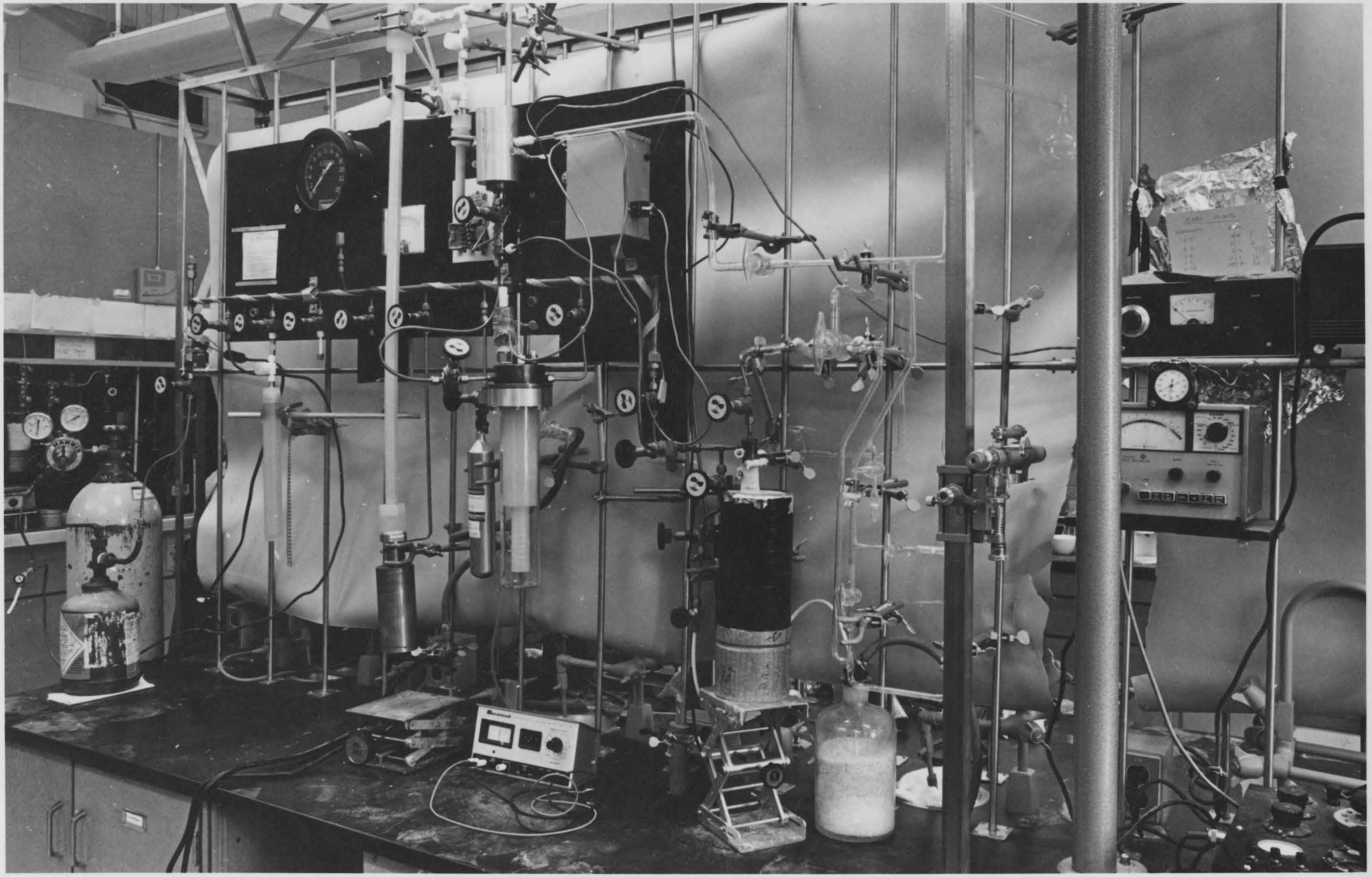


FIG. 2.1. THE APPARATUS

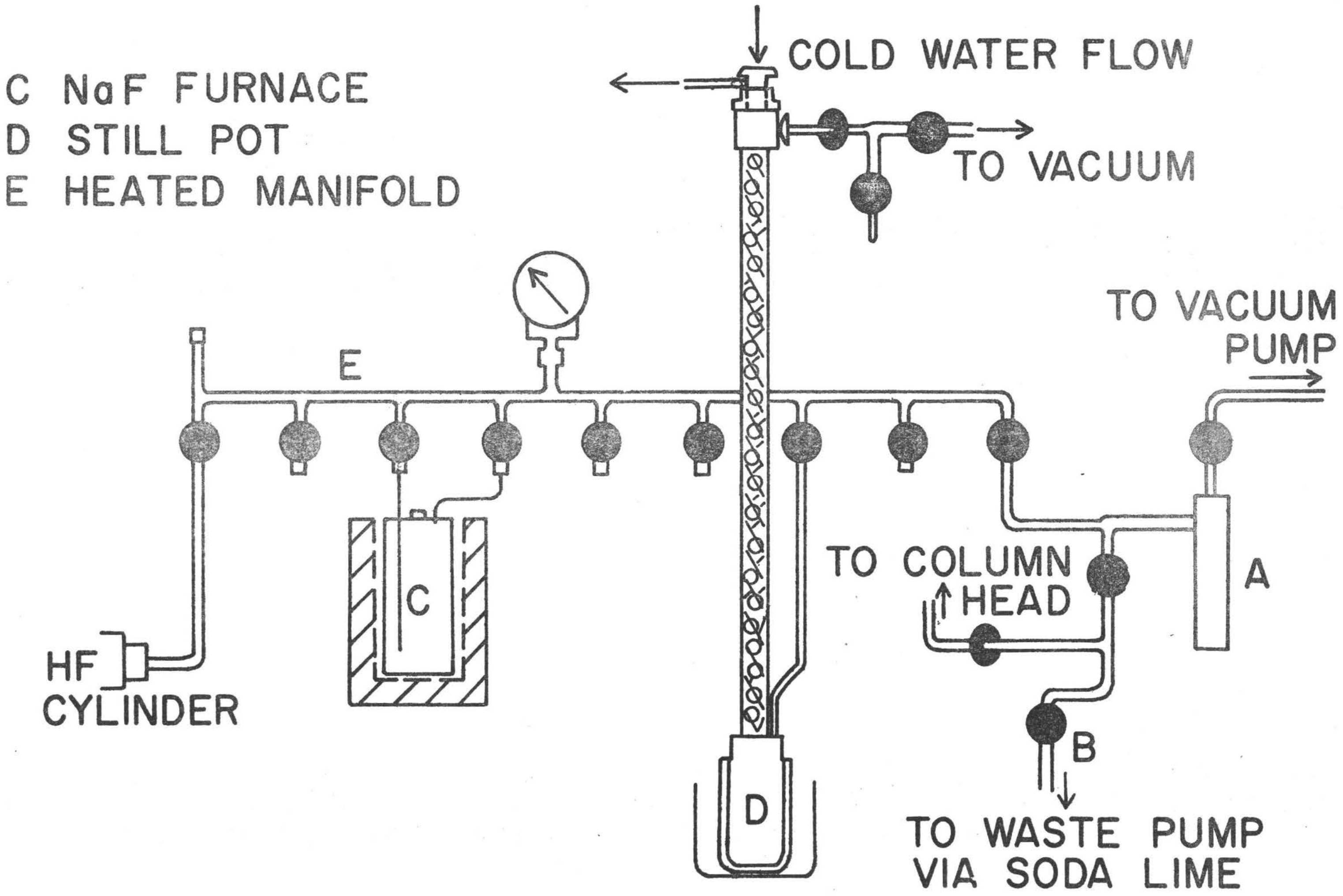
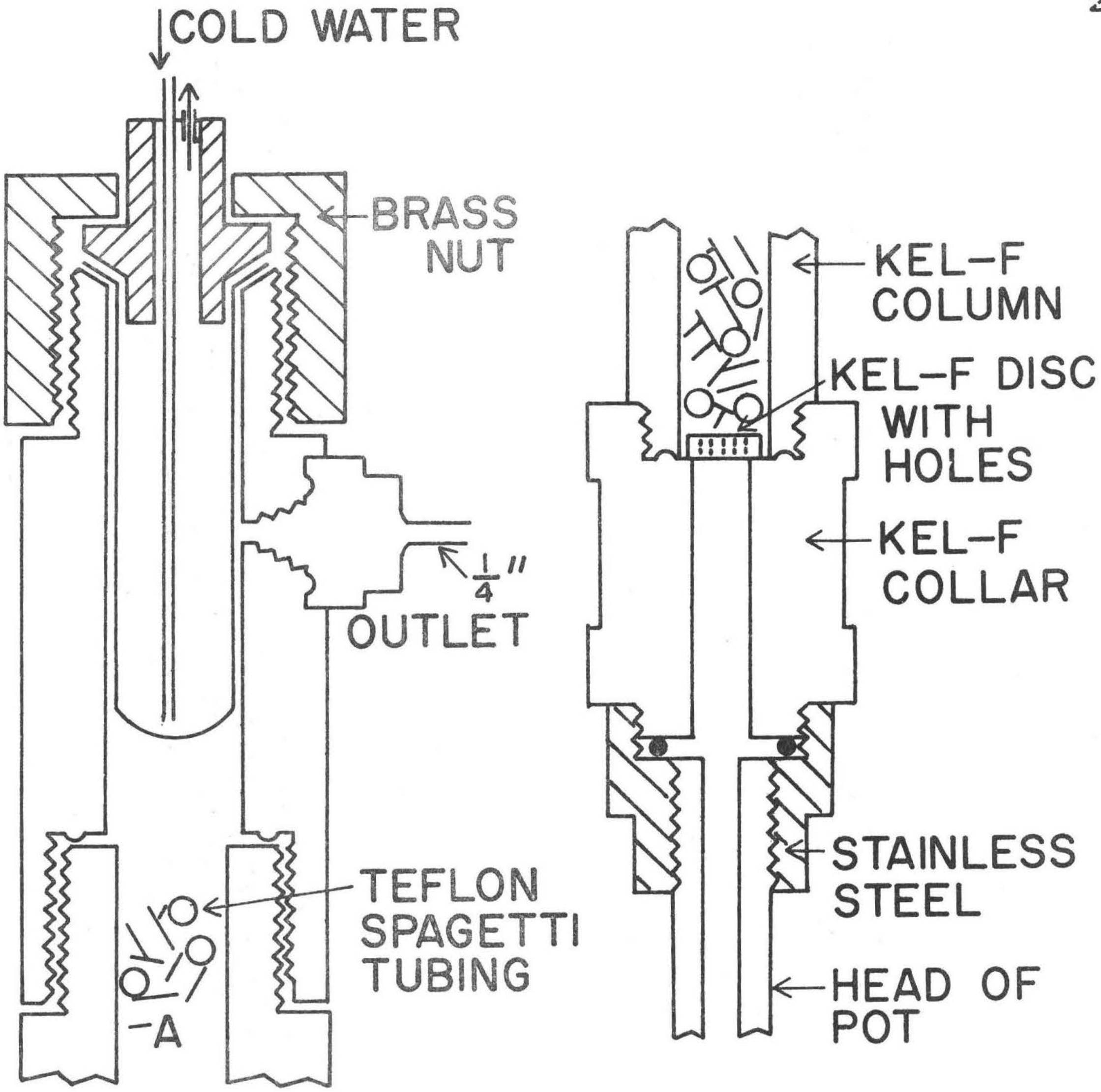


FIG. 2.2 HF VACUUM LINE

pressure gauge. The monel drying oven, traps and stillpot, were attached to the line using monel or Teflon Swagelok fittings. The distillation column, used to purify the HF as described in section (f) was a Kel-F tube $1\frac{1}{4}''$ diameter and $4'$ long packed with small lengths of Teflon tubing. The head of the column was provided with a silver plated copper cold finger. Some construction details of this distillation column are shown in Fig.2.3.

The transfer of high purity HF required the use of all Teflon or Kel-F valves. Most of these were Nupro Teflon diaphragm valves with $\frac{1}{4}''$ Swagelok couplings. These valves were found to have rather limited mechanical strength and had to be handled with great care in order to obtain a reasonable life on the Teflon threads. Alternative all Kel-F valves with greater mechanical strength were also used, constructed using a modification of the design developed at the Argonne National Laboratories(5,6,75).

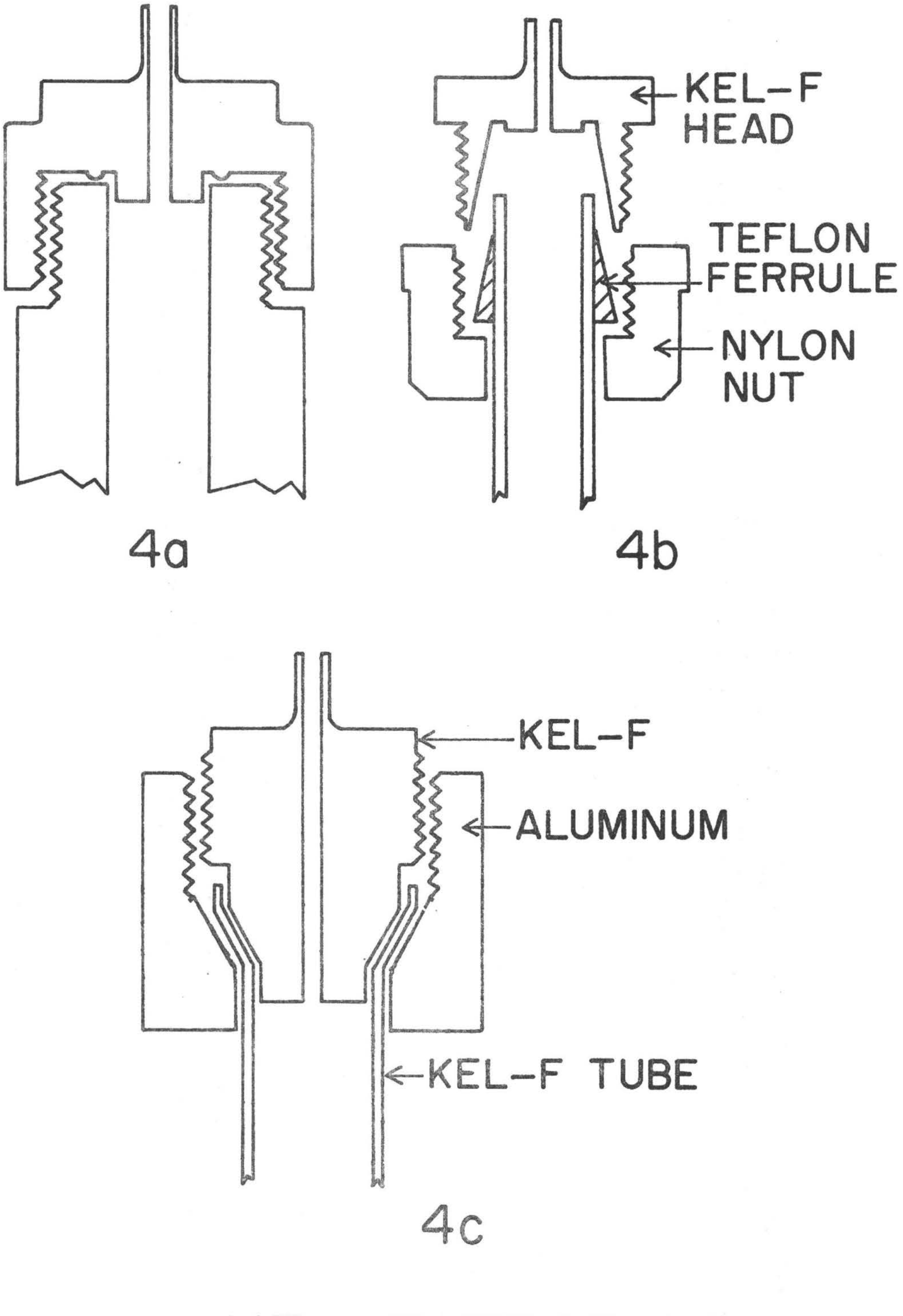
Various types of Kel-F vacuum traps were constructed for storing and transferring purified HF. Three different arrangements for obtaining a vacuum seal at the top of the trap are shown in Fig.2.4. Type 4a was only suitable for HF collection traps which did not require opening. The ferrule seal shown in Fig.4b was found to be more



a STILL HEAD
(ALL KEL F EXCEPT
COLD FINGER AND
BRASS LOCKING NUT)

b CONNECTION TO
MONEL POT

FIG. 2.3 HF DISTILLATION COLUMN DETAIL



4a 4b

4c

FIG. 2.4 KEL-F TRAP DETAIL

satisfactory than the flare type shown in Fig 4c , because it could be opened and vacuum sealed again without difficulty. The sealing ferrule was made from Teflon because of its better flexibility. The use of a nylon nut, rather than a metal one, on the Kel-F threads decreased the weight, so that the trap could be accurately weighed on a 200 g. capacity analytical balance, while providing reasonable mechanical strength. The ferrule seal traps could be easily undone in a dry box and generally gave a good vacuum seal even when only finger tight. All trap seals were leak tested on the sensitive pressure gauge described in section (c).

(b) Cryoscopy.

The development of a cryoscope for making freezing point depression measurements on dilute solutions in anhydrous HF went through a number of stages during the course of this work. All versions were similar in overall design to that shown in Fig 2.5 and described later in this section. Initially the thermometer well was constructed from monel welded to the cryoscope head. However it was found necessary to avoid contact between monel and some of the reactive solutions investigated and the use of noble metal plating was explored. Both gold and rhodium plating proved unsuitable for long term use particularly

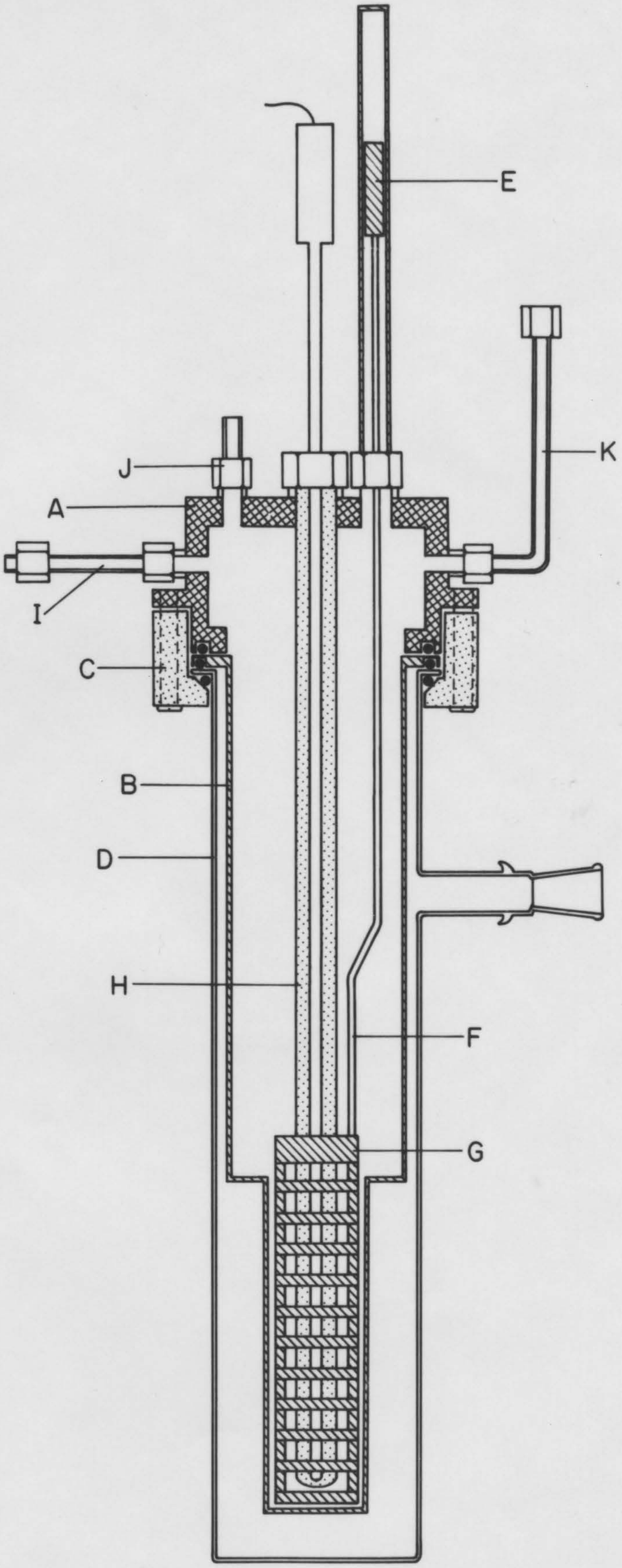


FIG. 2.5. THE CRYOSCOPE

when solutions of fluoride acceptors in HF were involved. Teflon coating of the head was also attempted. It turned out that permanent adhesion could not be obtained with either Teflon coatings or noble metal plating. After only a few runs peeling due to attack at a number of points showing surface imperfections was observed. The final version of the cryoscope employed a solid platinum well and relied on a protective metal fluoride coating on the monel head,which never in fact came into contact with the liquid. Some of the early work was carried out with a monel wire stirrer instead of the solid Teflon stirrer used in the final version. This cryoscope (Fig.2.5) was constructed with a monel head A and Kel-F pot B. An aluminum locking ring C carried screws to clamp the monel head, Kel-F pot and glass outer jacket together using Teflon and rubber O-rings. The glass jacket D could be evacuated independently. The whole apparatus and stirring device was a closed system that could maintain a vacuum of better than 1×10^{-3} m.m. The stirrer G was constructed from Teflon and was joined by a Kel-F covered monel connecting wire F to a Teflon covered soft iron core E. It was driven in a Teflon sleeve by means of a solenoid supplied by a variable frequency transistorised pulse generator. The cryoscope was attached to the vacuum line by Swagelok unions.

Drying and desorption of the Kel-F interior of the cryoscope was effected by prolonged flushing with dry nitrogen followed by overnight pumping on the heated vacuum line. A thermometer was inserted into the closed platinum well H which was 14" long and had a wall thickness of 0.015". In order to improve thermal contact the well contained a little pentane. Temperatures were measured to 0.001 °C. with a 25 ohm coiled filament platinum resistance thermometer, Mueller resistance Bridge and Null Voltmeter (Hewlett Packard 419A D.C.). The platinum resistance thermometers were checked at the ice point, and at the triple point of water using a Trans-Sonics Inc. Equiphase cell. In order to check that they were giving correct readings in the region of the freezing point of HF two platinum resistance thermometers were then compared at the CO_2 point.(76) The platinum resistance thermometer was used to calibrate a Hewlett-Packard quartz thermometer probe (Model 280 A.) The freezing point of the pure solvent was always recorded with a platinum resistance thermometer in order that it might be used as a criterion for purity. Some of the freezing point depressions were measured using the quartz thermometer which, although non-linear below -80 °C, could be set up to read small temperature differences to ± 0.001 °C.

Approximately 50 g. of the purified HF was fractionated into a weighed Kel-F trap and quantitatively distilled from the trap into the dry evacuated cryoscope through a Kel-F tube connected to I. Additions of powdered solids were made at J from weight droppers constructed from glass and Kel-F. Glass or Teflon syringes with 5" platinum needles were used for liquid additions. During the additions a positive pressure of dry nitrogen was maintained in the cryoscope by passing a controlled stream of extra dry nitrogen through a metal line into an inlet in the monel head. Gaseous solutes were condensed into the cryoscope by attaching pre-weighed bulbs containing the gas plus appropriate drying agents to I.

The cooling bath surrounding the glass outer jacket was liquid nitrogen. The cooling rate was controlled by adjusting the air pressure in the glass outer jacket.

(c) Vapour Pressure Measurements.

The pressure of corrosive fluoride systems cannot be measured using a conventional mercury manometer, glass spoon or spiral gauge or devices with heated filaments(77). An example of a diaphragm pressure gauge that has been adapted for corrosive fluoride work has been described by Sheft(78). The approach used in the present work was based on a strain gauge null instrument described by Brown and Pez(79) A diagram of the gauge is given in Fig.2.6 . It involves a beryllium-bronze alloy envelope mounted on a copper support. Very sensitive miniature semi-conductor strain gauges (type 2A-3A-120P from Ether Ltd., Stevenage, U.K.) were attached to the sides of the beryllium-bronze envelope with the strain gauge adhesive (Kodak 910). The envelope was then placed into an aluminum block via a tapered joint. The block was thick enough to serve as an effective thermal jacket. The outlet from the aluminum jacket was connected by means of a Swagelok coupling to the glass vacuum and manometer system Fig. 2.7 . The strain gauges formed two arms of a resistance bridge, and the three conductors from the gauges were sealed through outlets in the copper base and joined to the other elements of the bridge and the appropriate electronics as shown in Fig. 2.8.

For pressure measurements the interior and exterior spaces on each side of the beryllium-bronze envelope were evacuated and the bridge nulled so that the detector showed minimum voltage. When HF vapour entered the inside of the envelope and the gauge was then out of balance, the resistance of the strain gauges altered. Balance was restored by slowly leaking air through the sintered inlet A until the

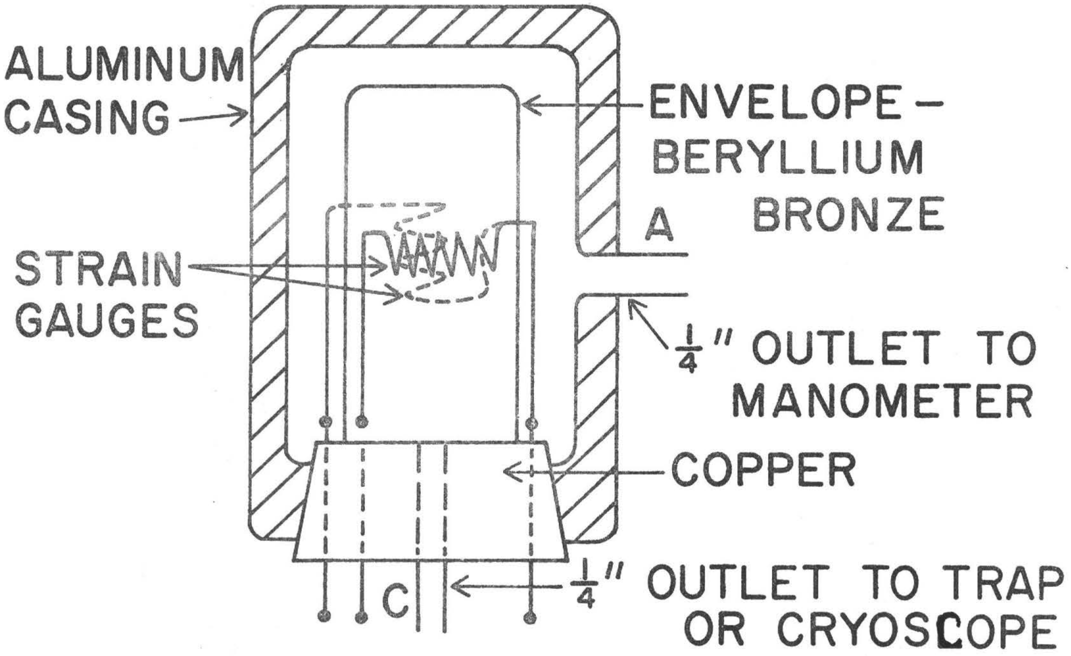


FIG. 2.6 PRESSURE GAUGE HEAD

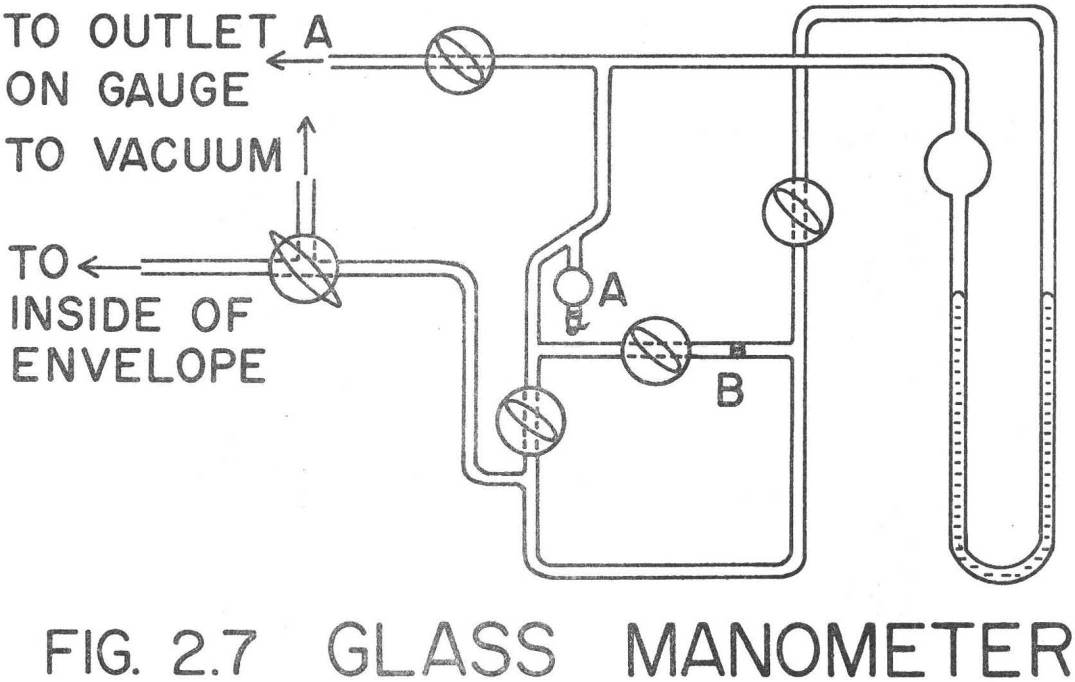


FIG. 2.7 GLASS MANOMETER SYSTEM FOR GAUGE

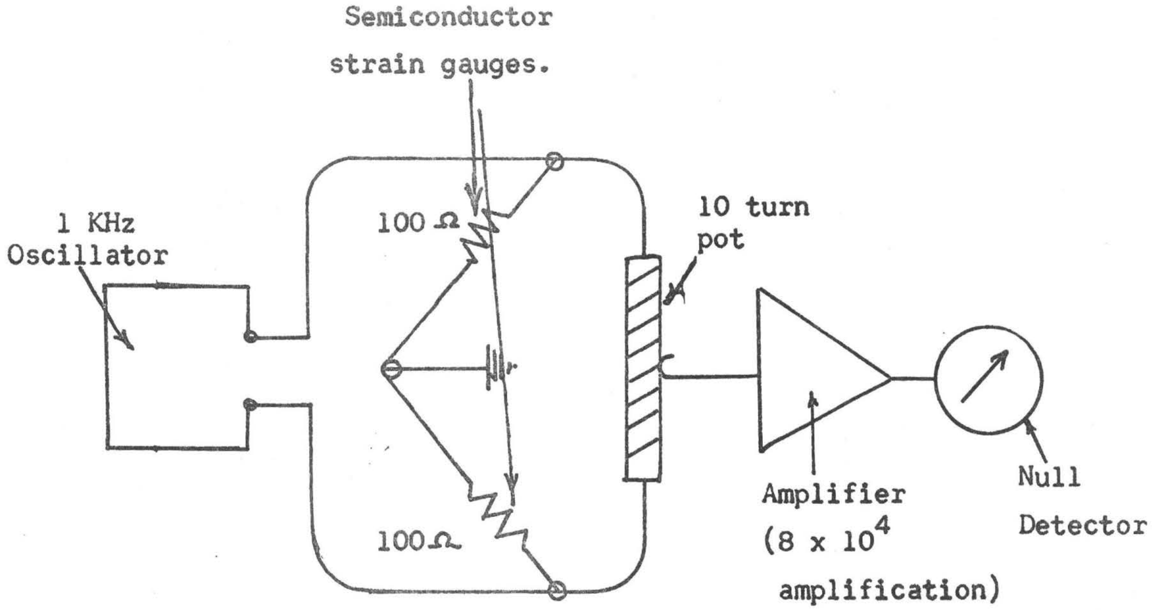


FIG.2.8 PRESSURE GAUGE BRIDGE CIRCUIT

pressure outside the envelope exactly balanced the pressure inside the envelope. If the null point was overshot the excess air pressure was reduced by pumping through sinter B. The balancing air pressure was then read from the mercury manometer using a cathetometer readable to 0.01 mm. In order to rule out the possibility of error due to hysteresis the zero was rechecked after each measurement by re-evacuating both sides of the envelope. The gauge showed no hysteresis effects over the pressure range 0 - 760 m.m. unless it had been subjected to sudden shock. The null point was stable over a 45 minute period and the accuracy of the null meter itself was more than adequate. The limiting factor on the accuracy was the reading of the mercury manometer with the cathetometer.

Solutions for vapour pressure measurements were made up in thin walled Kel-F traps attached at C. Solutions were frozen and pumped to check for residual air pressure and then allowed to equilibrate to a steady pressure at 0 ^{o}C by immersing the trap in a Dewar flask of distilled water ice. The steady pressure attained on standing and agitation was recorded and the zero rechecked. Because of the small loss of HF during equilibration the exact amount of solvent was determined by weighing the trap before and after the measurement.

(d) **Conductivities.**

Conductivity cells were constructed from Kel-F using traps similar to the Teflon ferrule type already described. Circular platinised platinum electrodes were held apart at a fixed distance using a perforated Kel-F cartridge as shown in Fig.2.9. The leads were shielded with heat shrinkable expanded Teflon spaghetti tubing and sealed through the top using small Teflon plugs and metal screws as shown in the diagram. Cell constants for the conductivity cells were determined with KCl solution in the usual way(80) and conductivities were measured on an Industrial Instruments Incorporated Bridge Model R.C.18. An ethyl acetate slush bath was used to obtain conductivites at -83.6 °C.

(e) Raman Spectroscopy.

Solutions for Raman spectroscopy were made up in small pre-conditioned Kel-F tubes Fig.2.10a. All samples fluoresced strongly unless high purity fractionated HF was used and the Kel-F tubes were properly conditioned. The clear Kel-F spaghetti tubing generally used for n.m.r. samples often contains significant amounts of plasticizer, and HF samples in contact with such Kel-F tubing invariably fluoresce even if the acid is very pure. The small Raman tubes which fitted the laser Raman sample holder were therefore constructed from less trans-

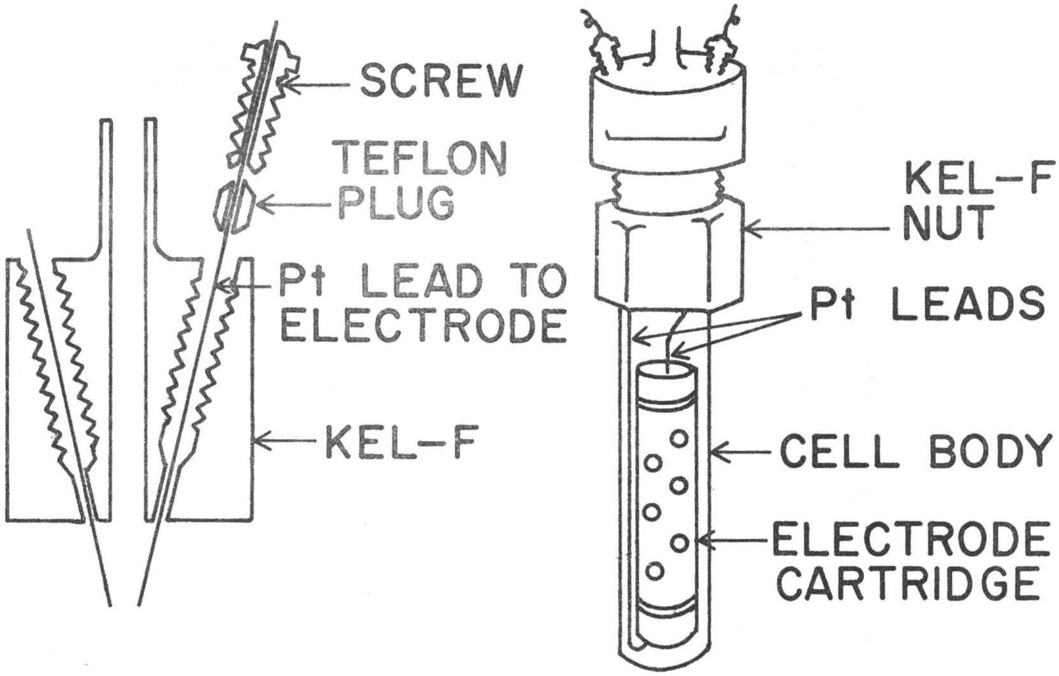
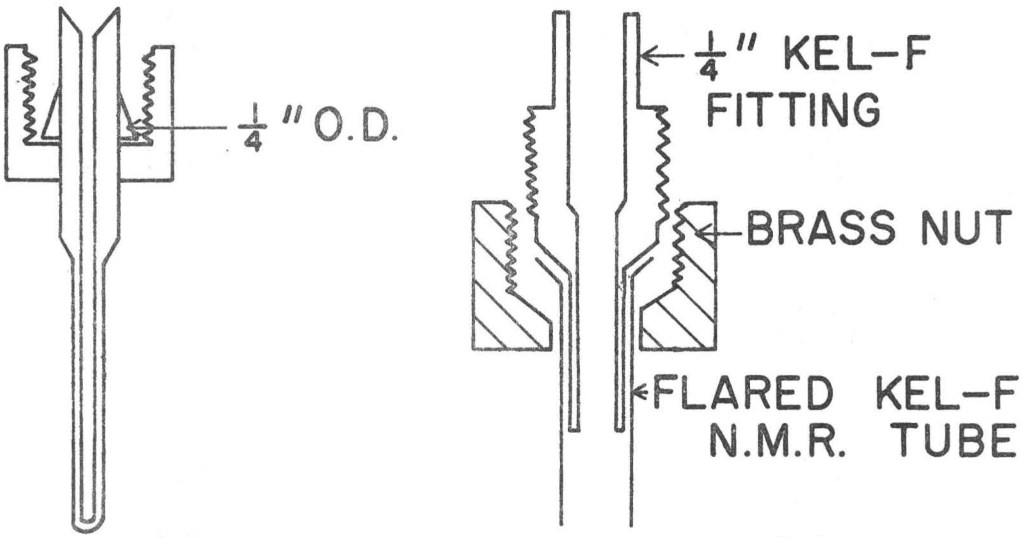


FIG. 2.9 CONDUCTIVITY CELL



10a

10b

FIG. 2.10
RAMAN & N.M.R. ADAPTERS

parent Kel-F tubing which was completely free from plasticizer. They were heat sealed at the bottom and fitted via a Teflon Swagelok to a Teflon valve. Each tube was treated with ClF in HF before use and then thoroughly conditioned in HF under pressure at 40 °C. The Raman spectra were recorded using a Spex Industries Model 1400 spectrometer employing a double monochromater and a phototube detector with an electrometer amplifier and recorder. The exciting radiation was the green 5145 Å line of a spectra Physics Model 140 argon-ion laser or the 6328 Å line of a Model 125 He/Ne laser. For low temperature spectra a longer Kel-F tube was mounted in a quartz tube with an evacuated jacket. Liquid nitrogen boiling from a Dewar flask was passed through the tube and the temperature recorded with a thermocouple.

(f) Nuclear Magnetic Resonance.

Nuclear magnetic resonance spectra were obtained using a Varian HR 60 high - resolution n.m.r. spectrometer. The samples were made up in 7" Kel-F spaghetti tubes heat molded at one end and flare fitted via a Kel-F connector to a valve at the other end (Fig.2.10). HF was distilled into the tube which was then sealed off by applying moderate heat and pressure.

(g) Preparation and Purification of Materials.

Hydrogen fluoride was obtained from Matheson Ltd., or the Harshaw Chemical Company, Cleveland. The manufacturer's analysis claimed minimum purity of 99.9%. Impurities may be H_2O, SO_2, H_2SO_4, HSO_3F, SiF_4 or H_2SiF_6. The HF was purified by slightly modified versions of the methods previously described (29,39). One approach was to form the bifluoride $NaHF_2$, which was heated to about 150 °C and pumped for prolonged periods to remove impurities. $NaHF_2$ was then heated to about 450 °C when it gave off dry hydrogen fluoride. Generally, however, it was found that fractional distillation was the best method of obtaining HF with a low conductivity. The HF was slowly refluxed in the Kel-F distillation column and was collected in a dry Kel-F trap at 0 °C. The purity of the HF was checked immediately prior to use by measuring its conductivity. These purification methods usually gave anhydrous hydrogen fluoride with a specific conductance of order of magnitude 10^{-5} ohms^{-1}cm.$^{-1}$ at 0 °C. Some of the early measurements on strong electrolytes were made with acids which had a specific conductance as high as 1×10^{-3} ohms^{-1}cm.$^{-1}$ In most cases the freezing point depressions obtained were in good agreement with later measurements using acid with specific conductivity

5×10^{-6} ohms^{-1}cm.$^{-1}$ Obviously water and other impurities have a greater effect on conductivities than on freezing point depressions. Sulphur dioxide, which is one of the major impurities apart from moisture, is not detected by the conductivity check. Manufacturer's specifications claimed a maximum SO_2 impurity of 0.01%. This would be removed however by pumping on the bifluoride at 150 °C, since alkali metal fluorosulphinites begin decomposing below 100 °C under vacuum(81).

Solutes.

Rigorous precautions were taken to avoid traces of moisture contaminating the solutes used in this work. Dry weight droppers and syringes were removed from desiccators in a dry box or glove bag. The dry box had a vacuum port through which was circulated extra dry nitrogen, for some fifteen minutes before entry. The dry box atmosphere was circulated through a number of liquid nitrogen traps. Hygroscopic solutes were weighed out in a large dry box (S.Blickman Inc.) which contained a Mettler H6 balance. Liquid solutes such as trifluoracetic acid and fluorosulphuric acid were handled in gas tight syringes, and the end of the platinum needle was sealed with heat shrinkable Kel-F spaghetti tubing before removal from the dry box.

Fluorosulphuric Acid.

Fluorosulphuric acid obtained from Baker and Adamson was purified by double distillation using the method described by Barr, Gillespie and Thompson(82). Only fractions boiling between 162 ° and 164 °C were taken at both stages of the distillation. This method yielded acid of freezing point -89.00 °C.

Disulphuryldifluoride.

Disulphuryldifluoride ($S_2O_5F_2$), was prepared as described by Gillespie and Rothenbury(83). The product was redistilled to give pure disulphuryldifluoride of boiling point 50 - 51 °C.

Sulphur Dioxide.

Sulphur dioxide was obtained from a commercial cylinder (Matheson anhydrous grade) and dried over P_2O_5.

Tungsten and Sulphur Hexafluoride.

WF_6 and SF_6 were condensed from Ozark Mahoning and Matheson (anhydrous grade) cylinders and the purity checked by gas phase infrared.

Xenon Difluoride.

Xenon difluoride was prepared in this laboratory by Dr. T.A. O'Donnell by mixing approximately equimolar amounts of xenon and fluorine in a glass bulb and exposing to U.V. radiation.

Alkali Metal and Ammonium Fluoride.

Purified grade alkali metal and ammonium fluorides were dried by heating at approximately 120 °C whilst pumping on a metal vacuum line for ~ 2 days. A sample of LiF was supplied by Dr. C.R.Masson of the National Research Council that had been purified by passing anhydrous HF through the melt.

Nitro-Aromatic Compounds.

Eastman Company reagent grade p-nitrotoluene was recrystallized twice from methanol and dried in a vacuum desiccator over P_2O_5. Melting point 51.2 ° to 51.7 °C. Reagent grade 2,4-dinitrotoluene was re-crystallized twice from methanol and dried in a vacuum desiccator over P_2O_5. Melting point 69.8° to 70.2 °C.

Acetonitrile and Trifluoroacetic Acid.

Reagent grade acetonitrile and trifluoracetic acid obtained from Eastman Company was dried over molecular seives.

Antimony Pentafluoride.

Antimony pentafluoride was obtained from Ozark Mahoning Company and distilled twice in glass apparatus in an atmosphere of dry air. Boiling point 142 ° to 143 °C.

Arsenic Pentafluoride.

AsF_5 was obtained from Research Inorganic Chemical Company, California, who claimed 99% purity. Traces of PF_5 were removed by twice distilling from a Kel-F trap cooled in a dry ice-acetone slush bath, taking the middle fraction each time.

Phosphorus Pentafluoride.

PF_5 was condensed from Matheson cylinders into glass bulbs and used directly. The purity of AsF_5 and PF_5 was checked by gas phase infrared using a stainless steel cell with AgCl windows.

Niobium Pentafluoride.

Technical grade Ozark Mahoning NbF_5 was purified by vacuum sublimation in glass apparatus. Melting point 80 °C.

Tetraethylammonium hexafluoroantimonate.

Et_4NSbF_6 was prepared by the method described by Bacon et.al.(84) using Et_4NOH and SbF_5 solutions in excess 48% hydrofluoric acid. The product was purified by precipitation from dichloromethane solution using carbon tetrachloride.

Tetraethylammonium hexafluorarsenate.

Et_4NAsF_6 was prepared by condensing anhydrous HF onto Et_4NCl and pumping off the HCl. AsF_5 was then condensed into the solution until precipitation was complete. HF was decanted off and the product purified by re-crystallization from acetone-ether mixture and dried in a vacuum desiccator over P_2O_5.

Cyanides and Potassium Sulphate.

AgCN, $Hg(CN)_2$, NaCN and K_2SO_4 were Analar grade obtained from British Drug Houses. They were dried at $\sim$ 100 °C whilst being pumped on a vacuum line for $\sim$ 12 hours before use.

Potassium Iodate and Periodate.

Analar grade KIO_3 and KIO_4, obtained from British Drug Houses, were dried and used directly.

Sulphuric Acid.

100% sulphuric acid was prepared as described by Gillespie et.al.(85).

CHAPTER III

THE DETERMINATION OF FREEZING POINTS AND THE CRYOSCOPIC CONSTANT

(a) The determination of the freezing point.

The freezing point of dilute solutions in HF is the temperature at which HF crystals are in thermodynamic equilibrium with liquid phase having the original composition i.e. the temperature at which an infinitesimal amount of crystalline HF is in equilibrium with solution. The value of the freezing point was estimated from the time - temperature cooling curve following the fundamental principles discussed by White(86) and Mair, Glasgow and Rossini(87). When an appreciable degree of supercooling is encountered the temperature maximum attained after supercooling (i.e. T in Fig.3.1.) may be significantly lower than the true equilibrium freezing point T'. The idealised cooling curve in Fig.3.1. shows how the extrapolation of the equilibrium portion of the cooling curve DC intersects the line AB at the true freezing point T'. For cooling curves of the type shown in Fig,3.1 where a significant amount of supercooling is observed Taylor and Rossini(88) describe a geometrical method for making the extrapolation

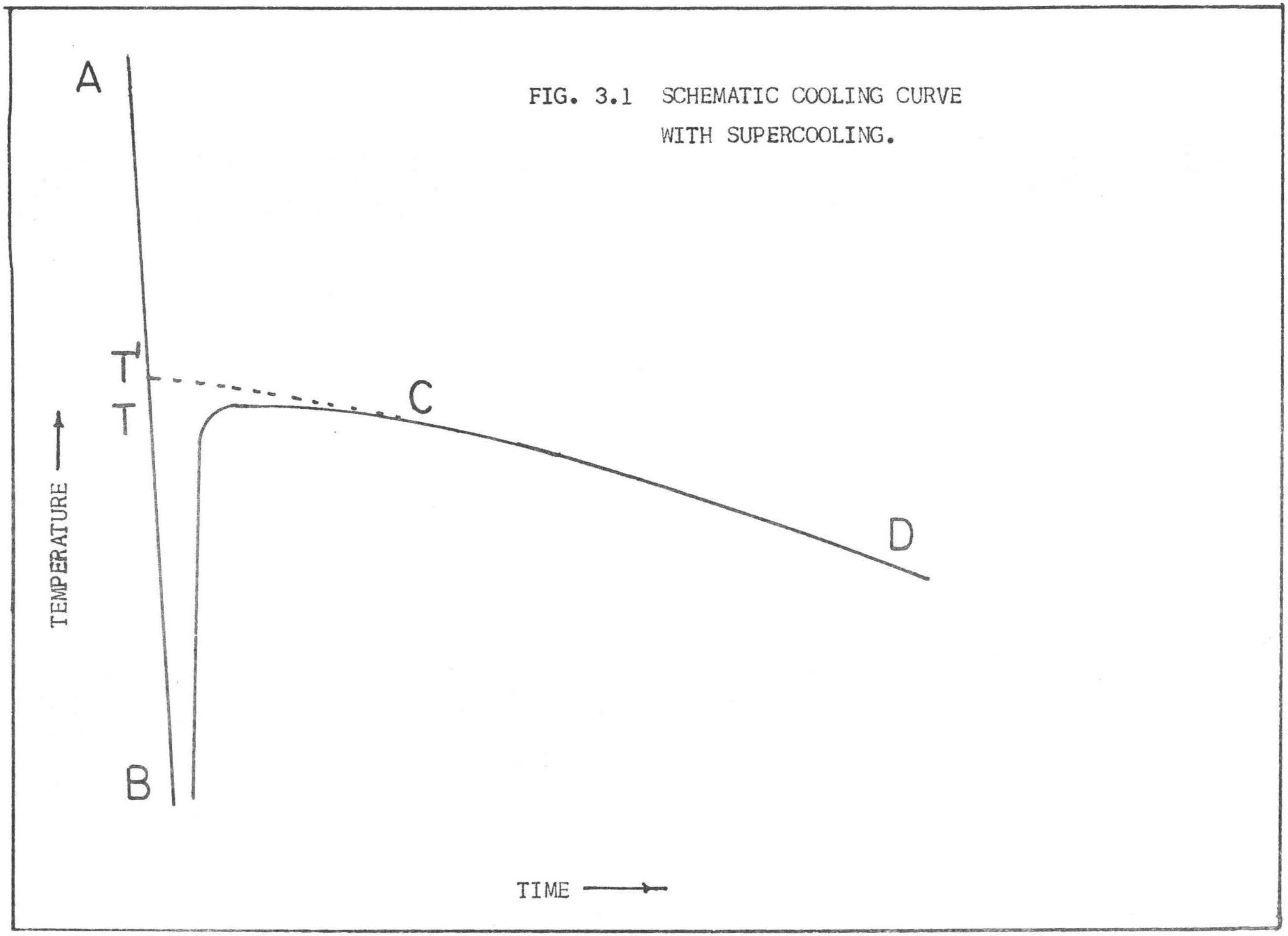


FIG. 3.1 SCHEMATIC COOLING CURVE WITH SUPERCOOLING.

to the true freezing point T'. However, HF was found to be an excellent cryoscopic solvent in that supercooling did not occur to any appreciable extent and visual extrapolation of the cooling curve gave freezing points reproducible to ± 0.005 °C. Fig.3.2 shows typical cooling curves for HF with cooling rates of 0.4 °C/min. to 0.9°C/min. Measurements with cooling baths of different temperatures, from a toluene slush bath at -95 °C to a liquid nitrogen bath at -196 °C showed that the extent of supercooling in HF is only about 0.05 °C to 0.06 °C, and no seeding is necessary to obtain separation of the solid phase. The behaviour of HF in this respect contrasts markedly with that found for many solvents. For example fluorosulphuric acid, although it has a freezing point in the same region as HF, supercools considerably unless seeding is employed(89). In fact the steady maximum temperature maintained for some three minutes from the time when solid HF began to separate out was found to correspond, for the dilute solutions used in this work, to the true freezing point, within the experimental limits and the extrapolation correction did not make a significant difference to the freezing point depression. The possible experimental error in the freezing point depression was estimated to be 0.005 °. In cases where a run was extended over a

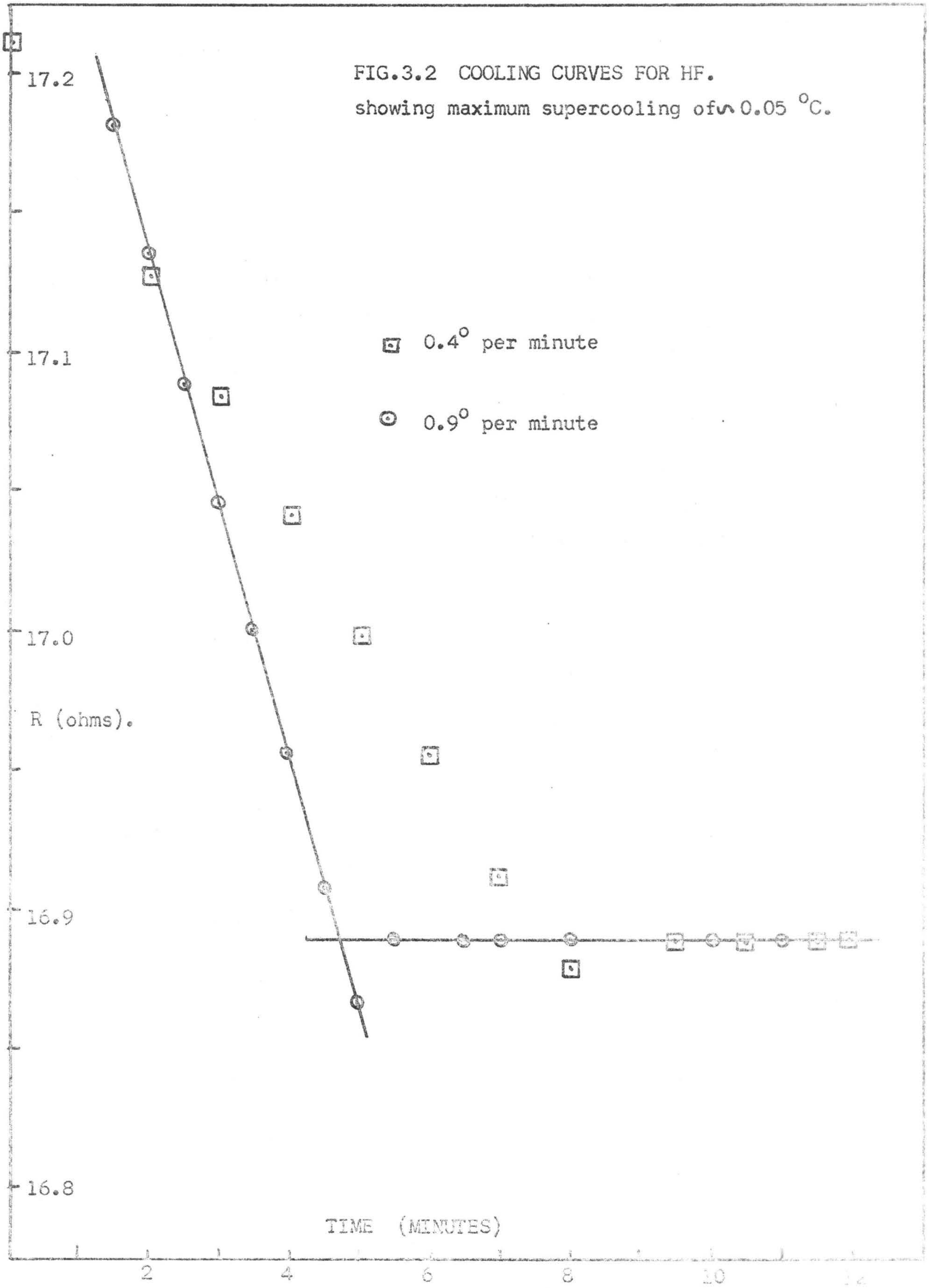


FIG.3.2 COOLING CURVES FOR HF.
showing maximum supercooling of ∼ 0.05 °C.

long period (i.e. 24 hours) small changes in the freezing point can occur due to slow absorbance of traces of water or other impurities from the Kel-F. The error in the freezing point depression in these cases is approximately ± 0.01 °C.

It was necessary to distill the purified HF into the cryoscope under its own vapour pressure. The initial freezing point measured under these conditions corresponds strictly to the triple point for HF. If a freezing temperature was taken with dry nitrogen above the HF, additional uncertainties arose because of the difficulty in controlling the pressure above the solution under cooling conditions and because of the slight solubility of nitrogen in liquid HF, which gave freezing point depressions of the order of 0.01 °. It was found that the most reliable and reproducible depressions in the freezing temperature were obtained by making measurements under the vapour pressure of the solvent or solution.

The literature values for the freezing point of HF(22,23,57,58,70) vary over a range from -83.76 °C to -83.01 °C. The commonly quoted freezing point for HF is that given by Hu, White and Johnstone(23) as 189.79 ± 0.02 °K (i.e. -83.36 °C). This is an estimated 'true melting point' for pure HF, allowing for about 0.2% impurity which these authors considered was not removed by distillation. The measured values found by Hu et.al. varied with the fraction of solid melted, from -83.58 °C when one-eighth had melted to -83.50 °C when one third had melted. Rogers et.al.(58) have reported a value for the freezing point of HF as high as -82.9 °C, using acid straight from a commercial cylinder and measuring the temperature with a calibrated thermocouple. Rutledge, Jarry and Davis(19,70) however, using the middle fraction from a commercial cylinder purified further by distilling the HF onto sodium fluoride and then onto cobalt trifluoride, obtained values for the melting point varying from -83.76 °C to -83.6 °C. The value -83.6 °C was used as a calibration point for their measurements of UF_6 - HF eutectic temperature.

In the course of this work it was found that the normal reproducible freezing temperature obtained for HF samples freshly fractionated from the Kel-F column having conductivity$\sim 10^{-5}$ ohms^{-1}cm^{-1} and condensed into degassed Kel-F traps was -83.57 °C. This value will be lower than the true freezing point as conventionally defined because it was not measured under 1 atmosphere pressure but under the vapour pressure of the liquid, i.e. it is a triple point temperature. Applying the usual thermodynamic equation(90) for the melting process we have:

$$\frac{dT}{dP} = \frac{T(v_1 - v_s)}{\Delta H_f}$$

where v_1 and v_s are the specific volumes of liquid and solid respectively and ΔH_f is the latent heat of fusion per g. For HF at 189.8 ^{o}K, ΔH_f is 46.93 cal per g$^{(23)}$ i.e. 46.93 x 4.184 x 10^7 ergs per g. Taking ρs at the melting point$^{(1)}$ as 1.638 and using $\rho_L = 1.0020 - 0.0022625t + 0.000003125t^2$ to calculate the density of the liquid at t ^{o}C we have:

$$v_1 = \frac{1}{\rho_L} = 0.8246 \quad \text{and} \quad v_s = \frac{1}{\rho_s} = 0.6105$$

Hence

$$\frac{dT}{dP} = \frac{189.8 \times 0.2141}{46.93 \times 4.184 \times 10^7} \quad {}^{o}K \ \text{dyne}^{-1} \ \text{cm}^{2}$$

$$= \frac{189.8 \times 0.2141 \times 1.013 \times 10^6}{46.93 \times 4.184 \times 10^7} \quad {}^{o}K \ \text{atmosphere}^{-1}$$

$$= 0.021 \ {}^{o}K \ \text{atmosphere}^{-1}$$

Thus the temperature at which crystallization commences in the present work, i.e. under the vapour pressure of HF, will be about 0.02 ^{o} lower than the true freezing point. However, the corrected value of the freezing point at one atmosphere pressure of -83.55 ^{o}C is still not as high as some of the others quoted above, which were obtained on unfractionated HF for which no criteria of purity was given. In view of this a careful check into the reliability of the system was made.

The calibrated platinum resistance thermometers, checked as described in Chapter II at the ice point and triple point of water and compared in solid CO_2, were used in the HF cryoscope to determine the freezing point of purified toluene. This is given in the National Bureau of Standards paper of Mair et.al.(87) as -94.983 °C. The freezing point of the toluene was in fact more difficult to determine accurately than the freezing point of HF since considerable supercooling occurred and the system became waxy causing the stirrer to stick soon after recovery from supercooling. A typical cooling curve is shown in Fig.3.3. Nevertheless the freezing point was found to be within 0.02 ° of the value given by Mair et.al. When pure HF was in the cryoscope the low viscosity and absence of supercooling enabled efficient stirring to be maintained until a considerable fraction of the solvent had crystallized out, the temperature remaining constant for several minutes. The freezing temperature of the HF was found to be independent of the rate of cooling within the limits used (0.4 ° to 0.9 °C per minute) and independent of the rate of stirring

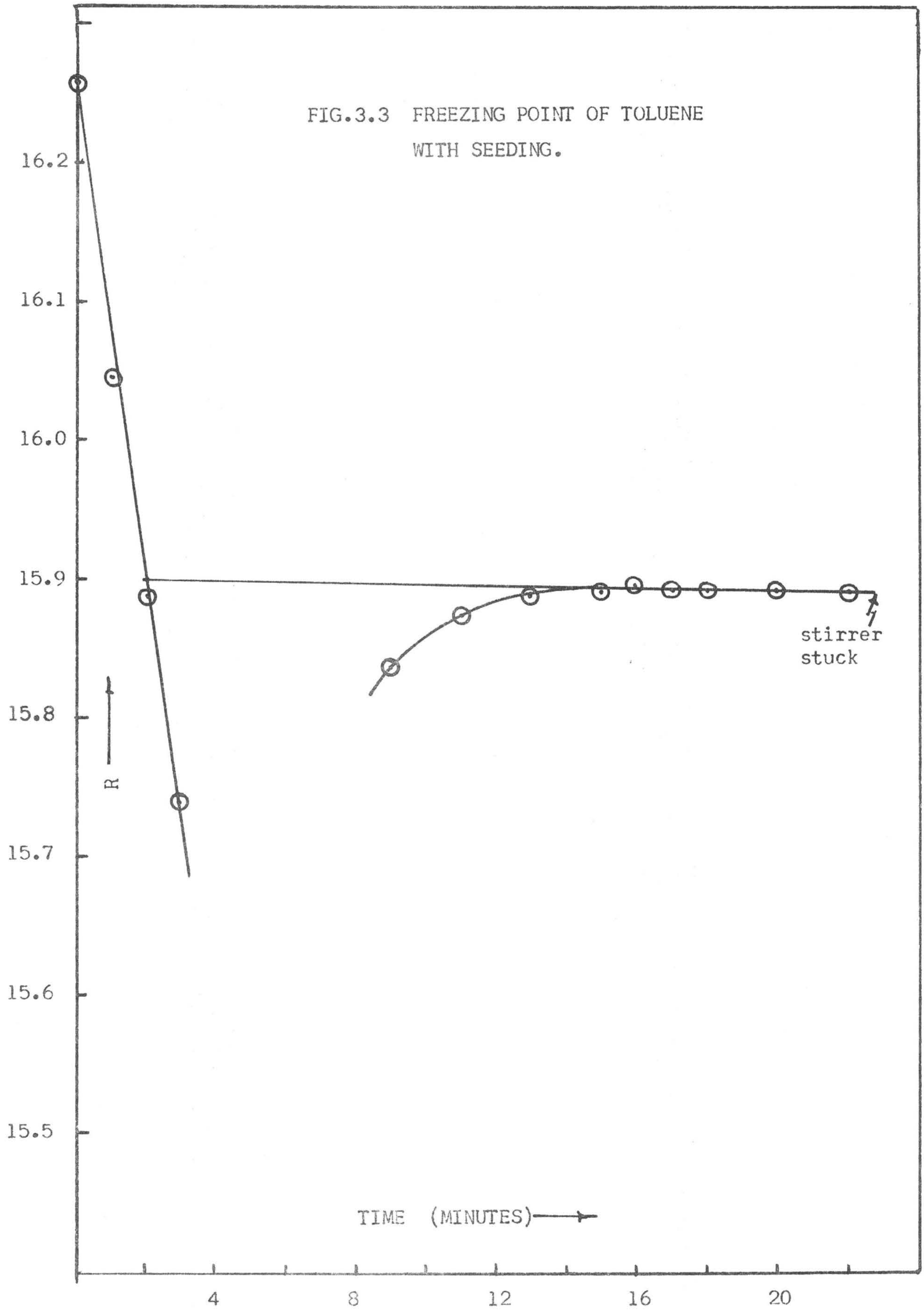


FIG.3.3 FREEZING POINT OF TOLUENE WITH SEEDING.

within the limits used (i.e. 75 - 150 strokes per minute). However the freezing temperature of HF could be as much as 0.05 ° lower than the highest values found in this work unless there was prolonged pumping, heating and exposure of the cryoscope to HF vapour before distillation of the fractionated HF into the cryoscope. It was of course essential to always make certain that the cryoscope maintained a good vacuum over a 24 hour period. Unless these rigorous precautions were taken a drift downwards of 0.05 ° in 24 hours was often observed in the freezing temperature of HF or its solutions. The highest value of the freezing temperature of pure HF obtained in this work, measured under its own vapour pressure, was -83.565 ± 0.005 °C. A large number of samples used had a freezing temperature of -83.570 ± 0.005, which was the value normally obtained. We are unable to explain the small difference between this reproducible value and the higher values reported by some of the workers cited above. However, it should be recognised that the value given in this work was obtained routinely with highly purified HF of conductivity $\backsim 10^{-5}$ ohms^{-1} cm^{-1}, in a system which gave the correct freezing point for toluene and is therefore probably reliable.

(b) The cryoscopic constant.

The heat of fusion ΔH_f was reported by Hu et.al.(23) to be 46.93 ± 0.04 cal g^{-1} at their estimated true melting point of 189.79 °K.

This value can be used in the usual equation(91) for solid-liquid equilibrium in order to obtain a value of the cryoscopic constant. The relationship, which assumes thermodynamic ideality for dilute solutions with ΔH_f constant over the range of the freezing point depression is :

$$\Delta T = \frac{RT_o^2 . M}{1000 \ \Delta H_f} . m$$

$$= k_f m$$

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

Substituting the above value of ΔH_f in :

$$k_f = \frac{RT_o^2 M}{1000 \ \Delta H_f}$$

gives an expected value of k_f of 1.52 deg.mole^{-1}kg.$^{-1}$ which is higher than that previously suggested (56). A general expression for cases where the solute undergoes association or dissociation in the solvent is:

$$\Delta T = k_f \nu m$$

where ν is the number of moles of dissolved particles (molecules or ions) produced per mole of solute.

In order to make an experimental determination of the cryoscopic constant for HF a search was conducted for solutes which might dissolve in HF as non-electrolytes, i.e. having a ν value of 1. Polynitro aromatic compounds have been found to be non-electrolytes in H_2SO_4 and Gillespie et.al.(89,92) used polynitro aromatic compounds and disulphuryl difluorides as non-electrolytes in the fluorosulphuric acid solvent system. Unfortunately many of these substances which might be expected to dissolve in HF without appreciable ionization were found to be too insoluble to give freezing-point depressions which could be measured with sufficient accuracy. Stable octahedral hexafluorides might be expected to dissolve readily in HF without ionization(93). Tungsten hexafluoride(74), for example, has a reported solubility of 3.14 moles per 1000g HF at room temperature. However, it was found that these solutes, which do not in fact ionize appreciably or interact in any other way with the solvent have large temperature coefficients of solubility so that the maximum solubility at

-83 °C was very low. The solubilities found at -83 °C, for some of the non-electrolytes investigated are shown in Table 3.1.

Fluorosulphuric acid, sulphur dioxide and xenon difluoride all dissolve in HF without appreciably increasing the conductivity and are all sufficiently soluble at the freezing point to obtain accurate freezing point depressions. The experimental points for these non-electrolytes fell close to a common straight line with some very slight curvature at concentrations higher than 0.2 molal. The freezing point depressions obtained for dilute solutions of these solutes are given in Table 3.2 and Fig. 3.4. Some freezing point depressions for the less soluble compounds SF_6 and $S_2O_5F_2$ are also included in Fig. 3.4 and Table 3.2. Completeness of solubility of volatile solutes was checked by measuring the pressure in the cryoscope at the freezing point. The slope of the cryoscopic plot for all the non-electrolytes investigated gave a value of $1.55 \pm 0.05^{\circ}$ mole^{-1} kg.$^{-1}$ for the cryoscopic constant of HF in good agreement with the calculated value of 1.52 $^{\circ}$K mole^{-1}kg.$^{-1}$ discussed earlier.

Further confirmation of the cryoscopic constant was found from the freezing point depressions obtained for dilute solutions of strong bases of the system for which ν is 2. These are discussed

TABLE 3.1

SOLUBILITY OF SOME NON-ELECTROLYTES AT -83 °C.

Compound	Maximum Concentration at F.Pt.
SF_6	0.08 molal
$S_2O_5F_2$	0.20 molal
Trinitrobenzene	0.05 molal
WF_6	0.03 molal

TABLE 3.2

FREEZING POINT DEPRESSIONS OF SOME NON-ELECTROLYTES.

HSO_3F		XeF_2		SO_2	
T_o = -83.590		T_o = -83.570		T_o = -83.575	
m	ΔT °C	m	ΔT °C	m	ΔT °C
0.1125	0.160	0.0148	0.020	0.1060	0.170
0.1691	0.275	0.0299	0.045	0.2187	0.330
0.2218	0.345	0.0567	0.090	0.2645	0.405
0.2713	0.420	0.0622	0.095	0.3256	0.505
0.3595	0.550	0.0779	0.140	0.3880	0.590
0.4082	0.630	0.1016	0.167		

SF_6		$S_2O_5F_2$	
T_o = -83.570		T_o = -83.580	
m	ΔT°C	m	ΔT°C
0.0423	0.065	0.0875	0.135
0.0725	0.115	0.1375	0.215
		0.1746	0.280

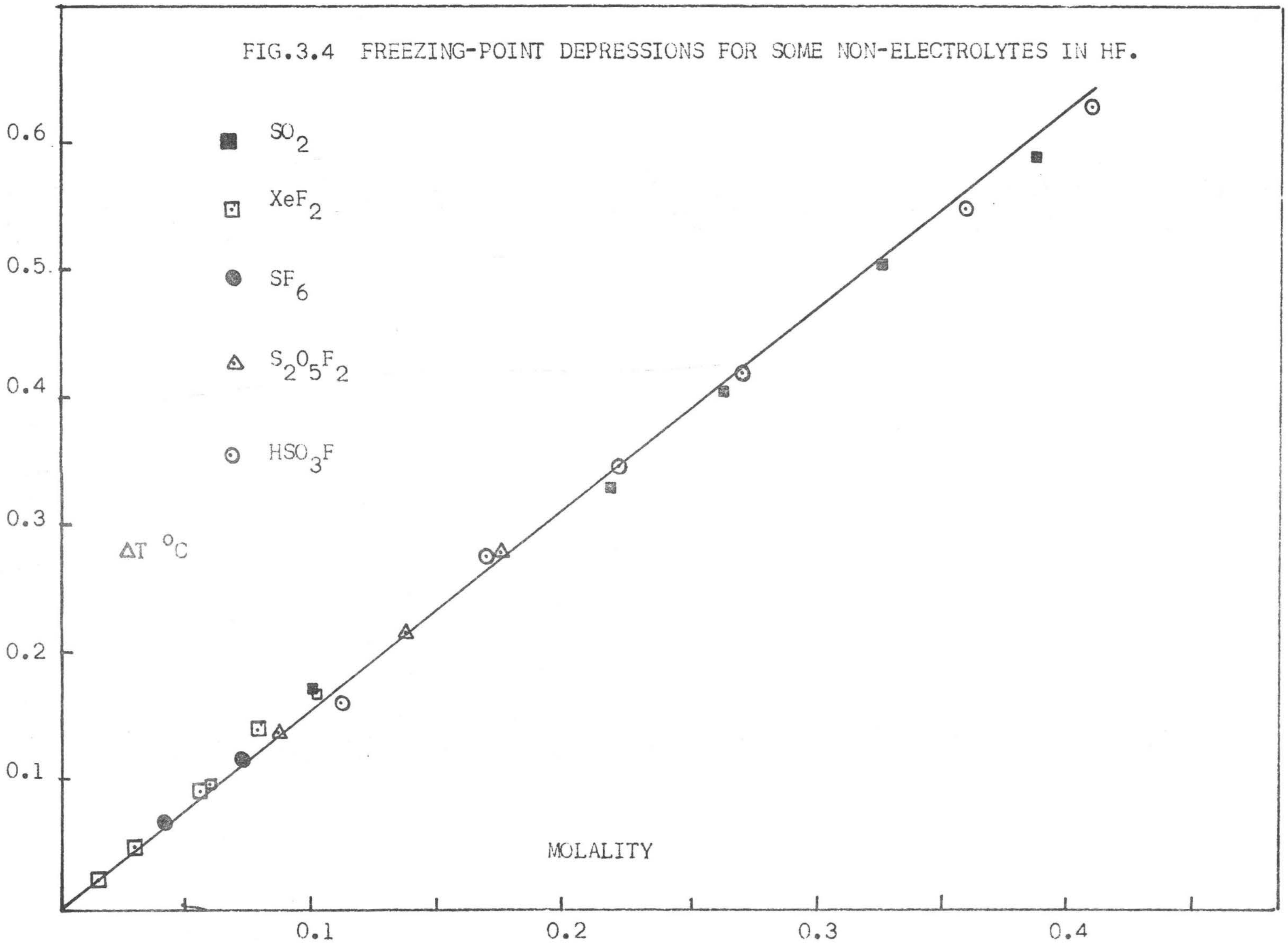


FIG.3.4 FREEZING-POINT DEPRESSIONS FOR SOME NON-ELECTROLYTES IN HF.

in detail in the next chapter but it should be noted here that the cryoscopic plots for simple alkali metal and ammonium fluorides at concentrations below 0.15 molal fall on a common line whose limiting slope is, within experimental limits, twice that shown in Fig.3.4 for non-electrolytes. The mean experimental value of the cryoscopic constant from all the results was found to be 1.55 ± 0.05 ^{o}C mole $^{-1}$ kg.

CHAPTER IV

VAPOUR PRESSURE MEASUREMENTS

During the course of this work it became apparent that the cryoscopic technique could not be used to fully investigate the mode of ionization of all the solutes of interest, because many solutes had a low solubility at the freezing point and some of the systems involved temperature dependent equilibria. Thus the range of colligative measurements was expanded to include the measurement of vapour pressure of dilute solutions in HF as described in Chapter II.

In order to first establish reliable functioning of the gauge for measuring the vapour pressure of solutions in HF, a series of measurements on the variation of the vapour pressure of pure HF with temperature were made. The vapour pressures obtained over the temperature range were less accurate than the value for 0°C because of difficulty in controlling the temperature and measuring it accurately while temperature equilibration was established. Nevertheless the vapour pressure data obtained as a function of temperature were in good agreement with that obtained by other workers(15,19) as shown in Fig. 4.1.

Calorimetric measurements by Hu et.al.(23) show anomalies in the latent heat of vaporization for HF, the value increasing with increase in temperature from 0 ° to 20 °C. Such anomalous temperature dependence for the vapour pressure and latent heat is found in other liquids which are associated in both the liquid and vapour state, for example formic acid and acetic acid(94). Armitage et.al.(21) have treated such behaviour quantitatively in a theoretical explanation based on the equilibrium $6HF \rightleftharpoons (HF)_6$ and assuming ideal gas behaviour.

The main concern in the present work was to establish the criteria for normal electrolyte behaviour in anhydrous HF for substances of known ν value in order to be able to investigate the mode of ionization of other solutes at 0 °C. Table 4.1 and Fig.4.2 summarize some vapour pressure depression data for potassium fluoride at 0 °C. Although single vapour pressure measurements were reproducible to better than 0.05 mm the error in vapour pressure depression measurements could be as high as ± 1 mm, because of small hysteresis and temperature effects. In view of this vapour pressure depressions were only used for relatively high concentrations (i.e. $>$ 0.2 molal) and less emphasis was placed on vapour pressure depression measurements than on the freezing

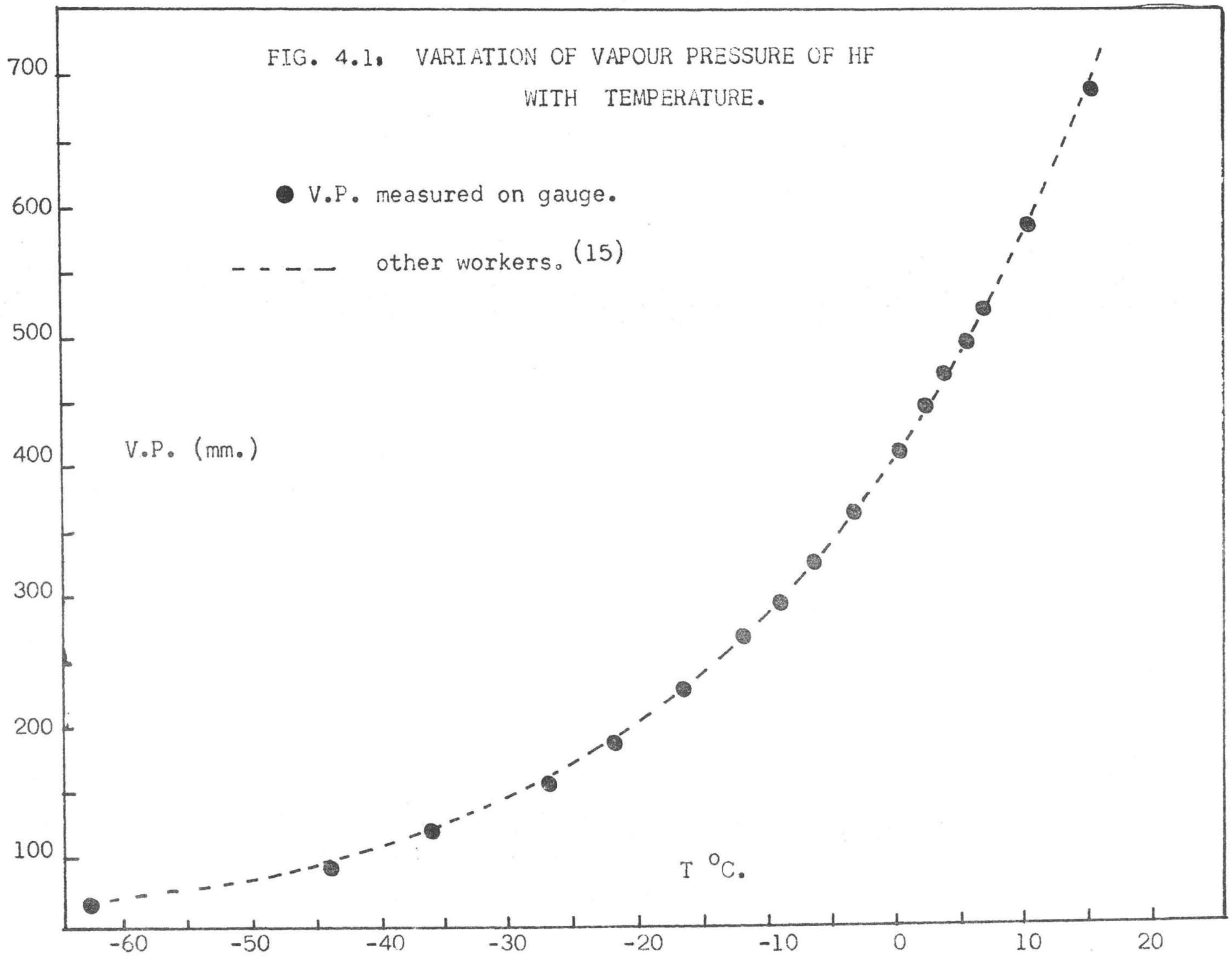


FIG. 4.1. VARIATION OF VAPOUR PRESSURE OF HF WITH TEMPERATURE.

TABLE 4.1

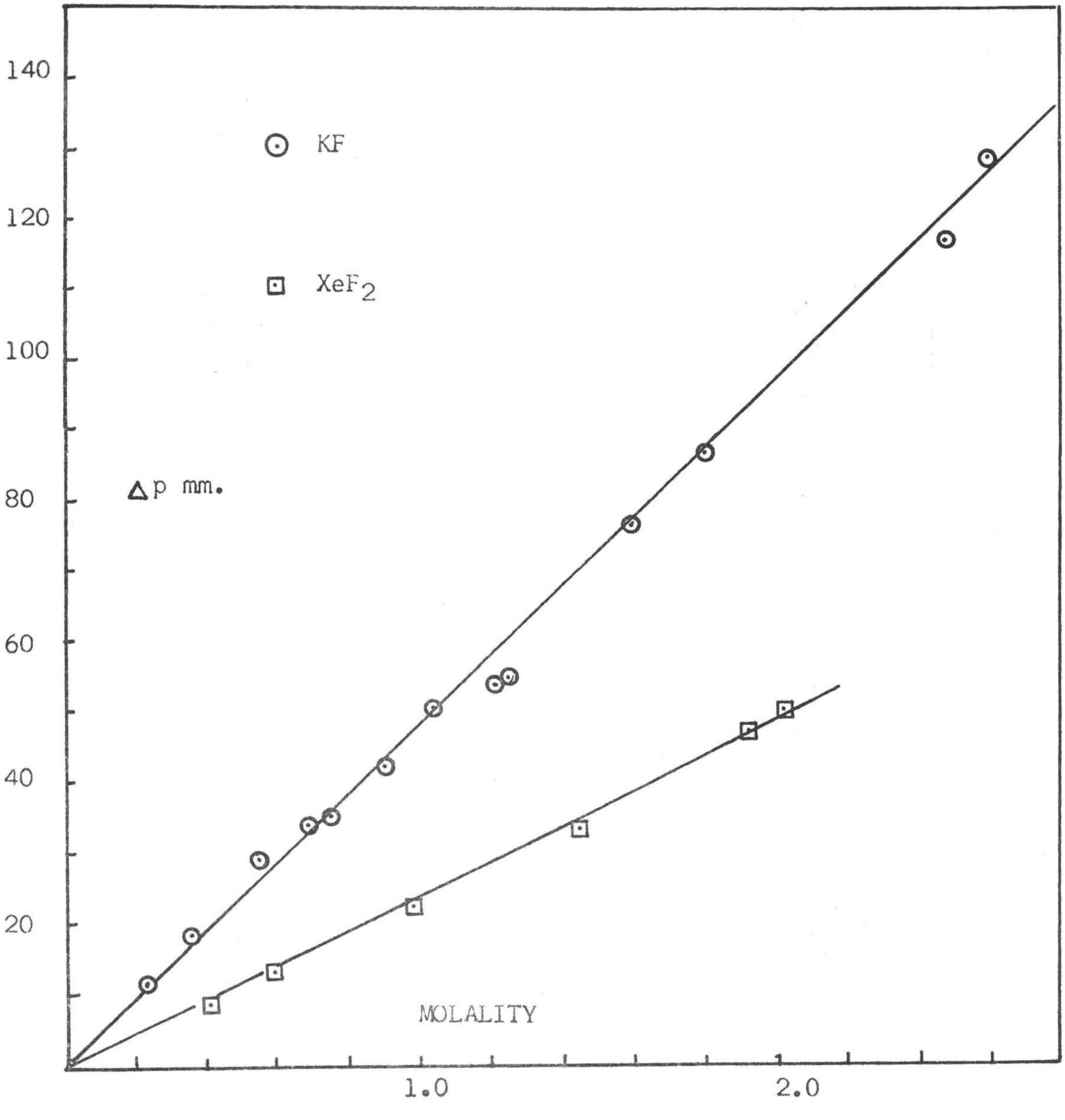
VAPOUR PRESSURE DEPRESSION MEASUREMENTS AT 0 °C.

V.P. of HF at 0 °C = 363.8 mm

KF		XeF$_2$	
Molality	ΔP mm ± 1 mm	Molality	ΔP mm ± 1 mm
0.221	10.8	0.391	8.4
0.340	* 18.0	0.575	12.6
0.541	* 29.0	0.957	21.4
0.693	* 34.0	1.412	32.6
0.753	34.9	1.905	46.6
0.914	42.1	1.978	48.2
1.060	* 51.0		
1.231	53.1		
1.270	55.0		
1.599	76.1		
1.793	80.7		
2.471	116.1		
2.604	128.5		

* These results obtained in a cryoscope of large volume and measured only to the nearest mm , others obtained using trap technique.

FIG.4.2 VAPOUR PRESSURE DEPRESSIONS AT 0 °C.



point depression measurements. The slope of the vapour pressure plot for potassium fluoride is 49 mm. mole^{-1}, and assuming a ν value of 2 this corresponds to a molal vapour pressure depression of 24.5 $\pm$ 1 mm. Deviations from ideality up to concentrations of 2.5 molal. are not apparent.

In order to confirm the validity of this experimental estimate of the molal vapour pressure depression, further measurements were made on the non-electrolyte XeF_2. The data for vapour pressure depressions obtained for dilute solutions of XeF_2 in HF is summarized in Table 4.1. The slope of the plot in Fig.4.2 for XeF_2 is 23 mm.mole^{-1} just under half that found for the KF plot. Thus the vapour pressure depression for 1 mole of undissociated solute was estimated to be 24 $\pm$ 1 mm. This value is considerably greater than expected from a Raoult's law calculation. If Raoult's law is applicable the relative lowering of vapour pressure $\frac{p^o - p}{p^o}$ should be equal to $\frac{1}{51}$ for a molal solution of non-electrolyte (taking the M.W. of HF as 20). Thus the predicted molal freezing point depression ΔP is :

$$363.8 \cdot \frac{1}{51} = 7.13$$

Hence the experimentally measured molal vapour pressure depression corresponds to a molecular weight for HF of 67 , or an association factor of 3.4. The association factor for HF from vapour density measurements on the saturated vapour in equilibrium with the liquid was measured as a function of temperature by Jarry and Davis(19). Although the average was reported as approximately 3.5, the value at 0 °C was found to be about 4.7. Since it is likely that the extent of molecular association in HF is altered by the presence of a solute, the degree of association predicted for HF from these vapour pressure measurements is in reasonable agreement with that estimated for the pure liquid by other methods. The use of the vapour pressure depression data for KF and XeF_2 for determining the extent of ionization of unknown solutes is unaffected by these complications since direct comparisons at a given molality are used to estimate ν values. Although more fundamental data is required on the vapour pressure depression technique it is clearly possible to use it for the HF system in order to obtain reliable ν values. It has been used in the present work to find ν values at 0 °C for $Hg(CN)_2$, K_2SO_4 and KIO_3 which are discussed in Chapters VII and VIII.

CHAPTER V

SOLUTIONS OF BASES

(a) Ionic Fluorides

In order to determine the extent and mode of ionization of solutes whose behaviour in HF is unknown, it was necessary to investigate the cryoscopic behaviour of dilute solutions of a number of simple binary electrolytes. Conductivity measurements on dilute solutions of alkali metal and ammonium fluorides indicate that they dissolve in HF with complete ionization(95). Freezing-point depression measurements made on dilute solutions of lithium, sodium, potassium and ammonium fluoride are summarized in Table 5.1 and Fig.5.1. The cryoscopic plots for all these fluorides fall close to a common line below about 0.1 molal. Table 5.2 giving freezing-point depressions for higher concentrations of KF and the line representing ideal behaviour in Fig. 5.1 indicate how deviations from ideality become increasingly significant as the concentration of solute increases. It should however be noted that these more concentrated solutions give less accurate freezing point depressions than the dilute solutions

TABLE 5.1

FREEZING POINT DEPRESSIONS FOR DILUTE SOLUTIONS OF ALKALI METAL AND AMMONIUM FLUORIDES.

KF

T_o = -83.580

T_o = -83.570

m	ΔT^oC
0.0177	0.060
0.0328	0.100
0.0707	0.220
0.0722	0.225
0.1095	0.330
0.1231	0.370
0.1347	0.400
0.1521	0.440
0.1874	0.530
0.2216	0.615
0.2624	0.715

NaF

T_o = -83.575

m	ΔT^oC
0.0323	0.095
0.0770	0.238
0.0832	0.265
0.1227	0.363
0.1456	0.455
0.1788	0.545
0.2114	0.625
0.2614	0.765
0.2951	0.850
0.3279	0.915

LiF

T_o = -83.570

m	ΔT^oC
0.0834	0.264
0.1609	0.466
0.2214	0.630
0.3290	0.908
0.4414	1.210

NH_4F

T_o = -83.58

m	ΔT^oC
0.0554	0.170
0.1248	0.370
0.2124	0.590
0.3041	0.805
0.3606	0.990

TABLE 5.2

FREEZING-POINT DEPRESSIONS FOR KF SOLUTIONS AT HIGHER CONCENTRATIONS

$T_{o_I} = -83.58$ $T_{o_{II}} = -83.59$

Run	m	ΔT °C ± 0.05 °	ΔT °mole^{-1}
I	1.269	3.12	2.45
I	1.298	3.15	2.42
II	1.735	4.23	2.43
II	1.790	4.36	2.43
II	1.827	4.43	2.42

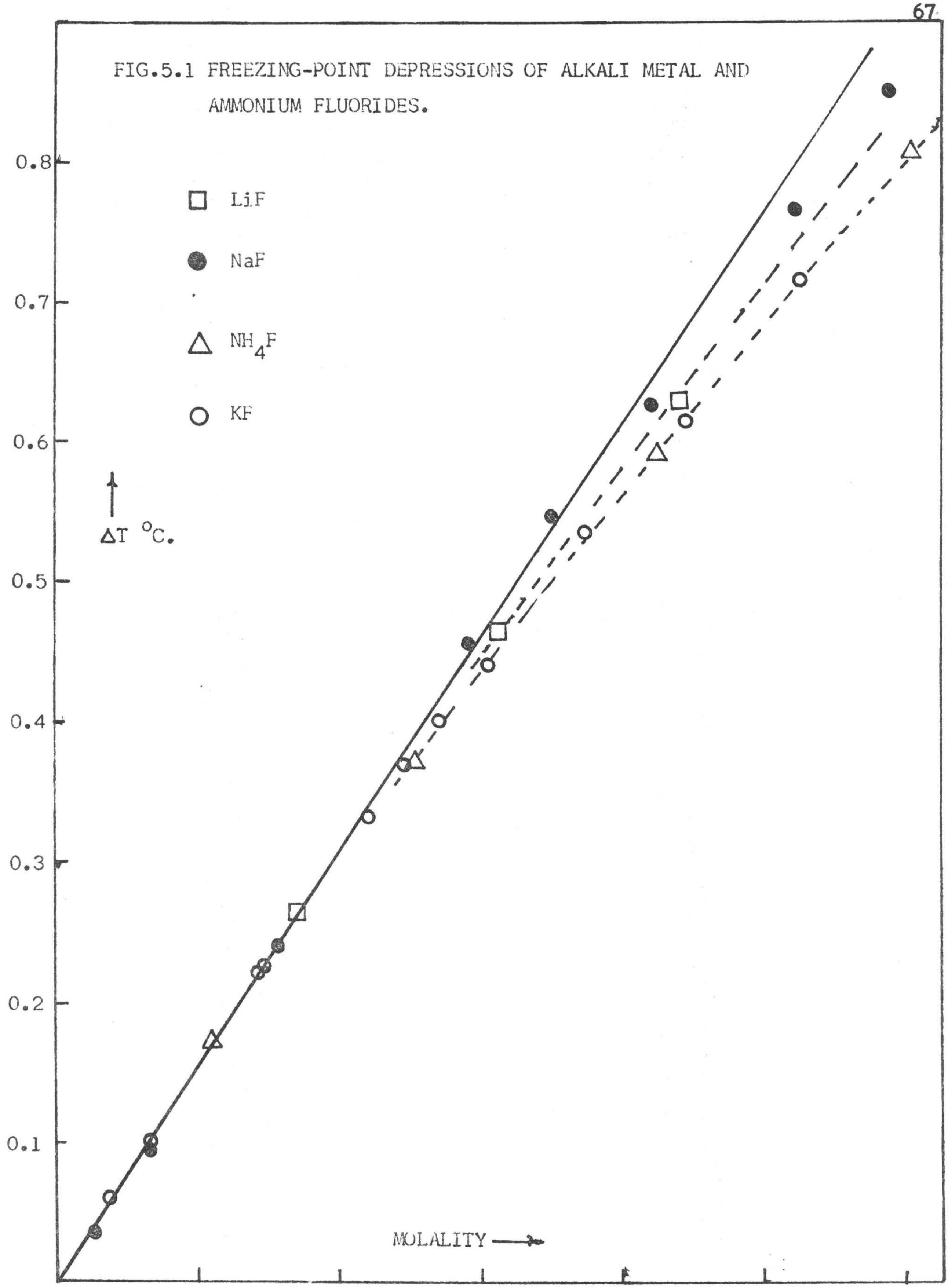


FIG.5.1 FREEZING-POINT DEPRESSIONS OF ALKALI METAL AND AMMONIUM FLUORIDES.

because the greater rate of change of composition as solvent crystallizes out increases the difficulty in obtaining a true freezing point by extrapolating the cooling curve.

Fig.5.1 shows that with increasing concentration there are distinct differences between the curves for different binary fluorides, indicating varying deviations from ideality. The differences in behaviour of the various fluorides are greater than the experimental error and may be reasonably attributed to differences in the extent of solvation of the cations, and to the influence of interionic effects. Similar differences have been observed in other strong acid solvents and agree reasonably well with expectations based on the $\frac{\text{charge}}{\text{radius}}$ ratio for the cations since increase in this ratio produces greater solvation. In sulphuric acid(96) lithium was found to be anomalous in that it was solvated less than sodium. Conductivity measurements in fluorosulphuric acid indicated an increase in the extent of solvation of the cations in the series $NH_4^+ < K^+ < Na^+ < Li^+$(97). Phase studies of the HF alkali metal fluoride system by Opalovskii and Fedotova(98,99) have also shown that the tendency to be solvated depends on the ionic radii of the cation but that sodium and lithium do not fit in a regular trend with potassium and ammonium. The freezing-point depressions obtained in the present work for dilute solutions of alkali metal fluorides and ammonium fluoride in HF follow the trend $Na^+ > K^+ \gtrsim NH_4^+$, with LiF coming between NaF and KF and presumably indicate that the extent of solvation decreases along this series. Any interionic attractions have an opposite effect to that produced by ion solvation. In solvents such as H_2SO_4 or HSO_3F the dielectric constant is high and the solvated ions are large because of the large size of the solvent molecules, hence interionic forces in such solvents are extremely small. However, the deviations observed for solutions in HF are in the opposite direction to those observed in H_2SO_4 and HSO_3F(100, 89). This appears to indicate that interionic attractions are more important in HF than in H_2SO_4 or HSO_3F even though the dielectric constant is so high (~ 175 at $-73\ ^{\circ}C$). Presumably the effect of interionic forces is due to the small size of the solvated ions in HF, which in this respect is similar to water.

The limiting slope of the cryoscopic plot for dilute solutions of all these strong bases is in excellent agreement with that expected for ν equals 2, corresponding to a cryoscopic constant of $1.55 \pm 0.05\ ^{\circ}C\ mole^{-1}kg$. Thus the data for all these simple alkali metal and ammonium fluorides provide good confirmation of the value of the cryoscopic constant.

(b) Incompletely Ionized Bases.

Cryoscopic data obtained at -83 °C can be used to calculate the degree of dissociation and the equilibrium constant for incomplete protonation of weak bases. The accuracy with which this can be done is limited by the accuracy with which ν can be determined. The calculation of ν can be done approximately using the expression:

$$\Delta T = \nu k_f m$$

where k_f is the cryoscopic constant, and m is the total stoichometric molality of solute. This equation, however, ignores any non ideal behaviour of the solution and neglects any small amount of solvent used in the ionization. It is clear from the results discussed above for the alkali metal fluorides that the deviations from ideality become significant as the concentration increases, and that in all cases where the concentration exceeds 0.1 molal these deviations must be allowed for when accurate values of ν are being evaluated. Some allowance can be made for these deviations from ideal behaviour for extensively ionized bases by comparing the freezing-point depression produced by a given base with that produced by some appropriate fully ionized base e.g. potassium or ammonium fluoride. For very weak bases where the major portion of the solute is unionized the best ν values are obtained by comparison with non-electrolytes. When the proper comparison is made with an electrolyte having a cation of comparable size ν values can be calculated with an accuracy of better than 5% and in the case of a simple dissociation process the degree of dissociation can then be calculated from the relationship:

$$\alpha = \nu - 1.$$

Thus the degree of ionization, α, for a given base can be determined with sufficient accuracy to determine the order of magnitude of the dissociation constant, K_b, from the relation:

$$K_b = \frac{[BH^+][HF_2^-]}{[B]} = \frac{\alpha^2 m}{1-\alpha} \quad \text{............ 5.1}$$

where B represents a weak base ionizing according to the equation:

$$B + 2HF \rightleftharpoons BH^+ + HF_2^-$$

Water.

Several workers have given values for the degree of ionization of water as a base in anhydrous HF. The conductivity and boiling point data obtained by Fredenhagen and Klatt suggested that water is incompletely protonated in HF:

$$H_2O + HF \rightleftharpoons H_3O^+ + F^-$$

Conductivities at -15 °C were used by Fredenhagen to estimate a value of 0.15 for the ionization constant of the above protonation. Klatt's estimate of 0.18 at approximately 20 °C was in reasonable agreement with this. Later work by Clifford(102), who made an estimate of the base strength of water by measuring the solubility of CaF_2 in the anhydrous HF - water system, indicated a higher value of 0.55 for this equilibrium constant. N.M.R. studies on the proton shift of the H_2O - HF system(28) have indicated a value for the equilibrium constant of water as a base in liquid HF of 0.22. Recent conductivity measurements at 0 °C(95) show that at very low concentrations of water in HF the conductivity approaches very close to that for KF. An accurate value of the equilibrium constant is difficult to determine from the conductivity data because of uncertainty about the exact values of ion mobilities. Comparisons of the conductivities of HF solutions of water with those of potassium fluoride, based on the assumption that H_3O^+ has the same mobility as K^+, indicate a value of 0.3 at 0°C.

In order to make an accurate evaluation of the degree of ionization of water in HF at low temperature, freezing-point depression measurements were made on dilute solutions in anhydrous HF. The freezing-point depressions obtained are given in Table 5.3 and Fig.5.2. Fig.5.2 shows how the freezing-point depressions obtained approach those given by the same concentration of alkali metal or ammonium fluoride at low concentration. If the freezing-point depressions obtained for water are compared with those obtained for the same concentration of potassium or ammonium fluoride it becomes clear that the degree of dissociation of water is higher than has been previously suggested. The ν values approach 2 at low concentration and the K_b is of the order 4. In fact the small difference between the freezing-point depression produced by a given concentration of water and that produced by the same concentration of ammonium fluoride may be largely due to a small difference in the degree of solvation of the two cations. Thus it must be concluded that at this very low temperature water is essentially fully protonated in anhydrous HF. On other grounds it has been concluded that the degree of polymerization of HF is markedly affected by changes in temperature and the presence of small quantities of water. It is therefore not surprising that the transfer of a proton from HF polymers to the solvated water molecule changes with decreasing temperature.

TABLE 5.3

FREEZING-POINT DEPRESSIONS

FOR DILUTE SOLUTIONS OF WATER.

$T_o = -83.58$

m	ΔT °C
0.1134	0.335
0.1398	0.402
0.2098	0.575
0.2616	0.701
0.3261	0.865
0.3928	1.020

ν range 1.95 to 1.90

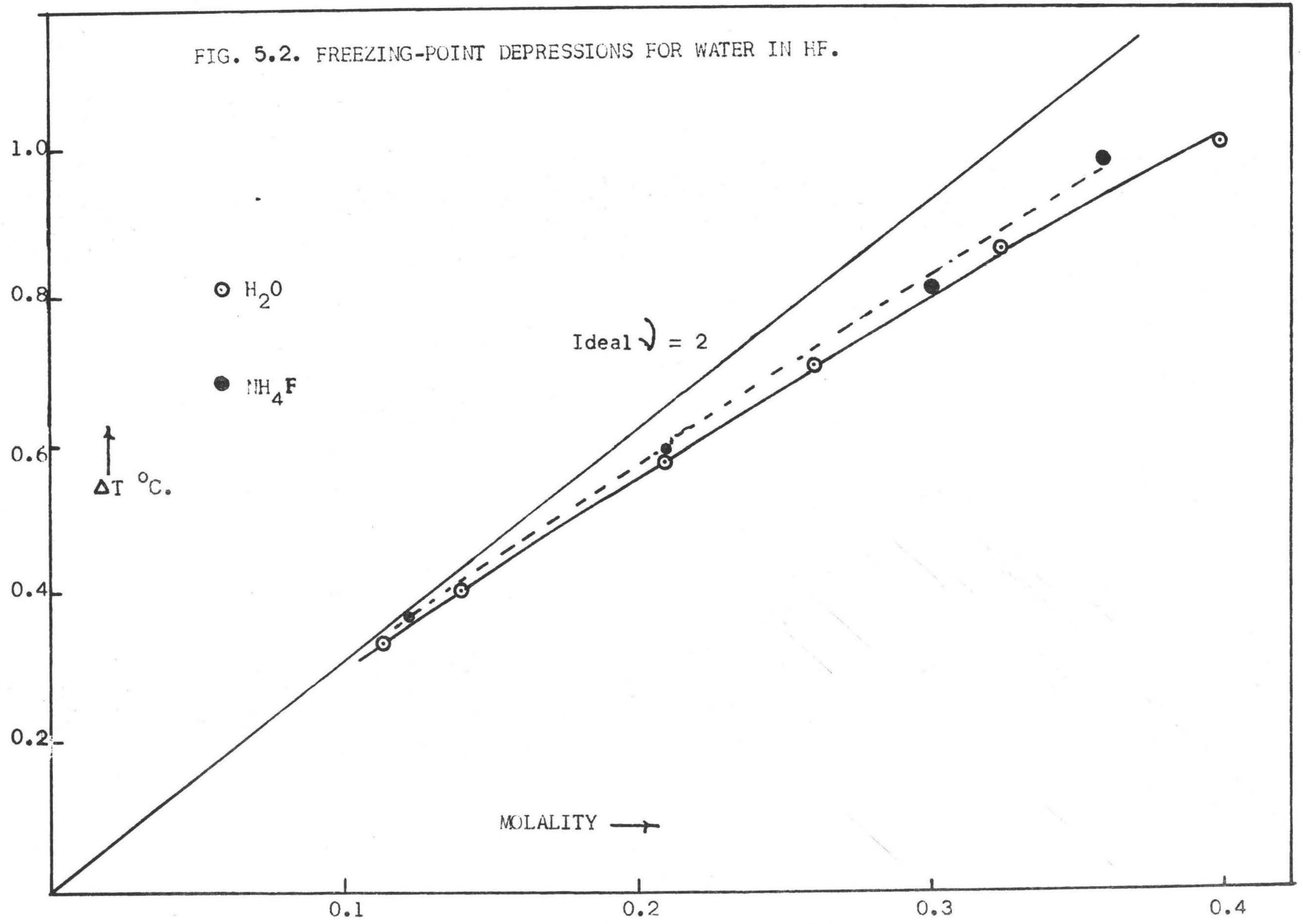


FIG. 5.2. FREEZING-POINT DEPRESSIONS FOR WATER IN HF.

Nitro Compounds.

In order to make some quantitative comparisons of the acid strength of anhydrous HF with that of other strongly acidic solvents (e.g. H_2SO_4 and HSO_3F), freezing point depression measurements were attempted on dilute solutions of some very weak bases. Gillespie et.al.(89) investigated the degree of ionization of 2,4 - dinitrotoluene in fluorosulphuric acid by the cryoscopic technique. The comparison with the fluorosulphuric acid data is particularly useful since the freezing point of fluorosulphuric acid (-89 °C) is very close to that of HF. This is important because Thompson found that the degree of ionization of some weak bases in strongly acidic solvents like fluorosulphuric acid increases with decrease in temperature, an observation which supports the conclusions reached in the case of water discussed above. The freezing point data for 2,4 - dinitrotoluene in anhydrous HF is shown in Table 5.4 and Fig 5.3. The freezing point curve has a slope very slightly greater than that expected for an ideal non-electrolyte indicating a very small degree of ionization. Since nearly all the solute is undissociated comparison with the non-electrolyte line gives more reliable ν values. The low ν values become very close to those of a non-electrolyte as the concentration

TABLE 5.4

FREEZING POINT DEPRESSIONS FOR WEAK BASES.

2.4-Dinitrotoluene

$T_o = -83.575$

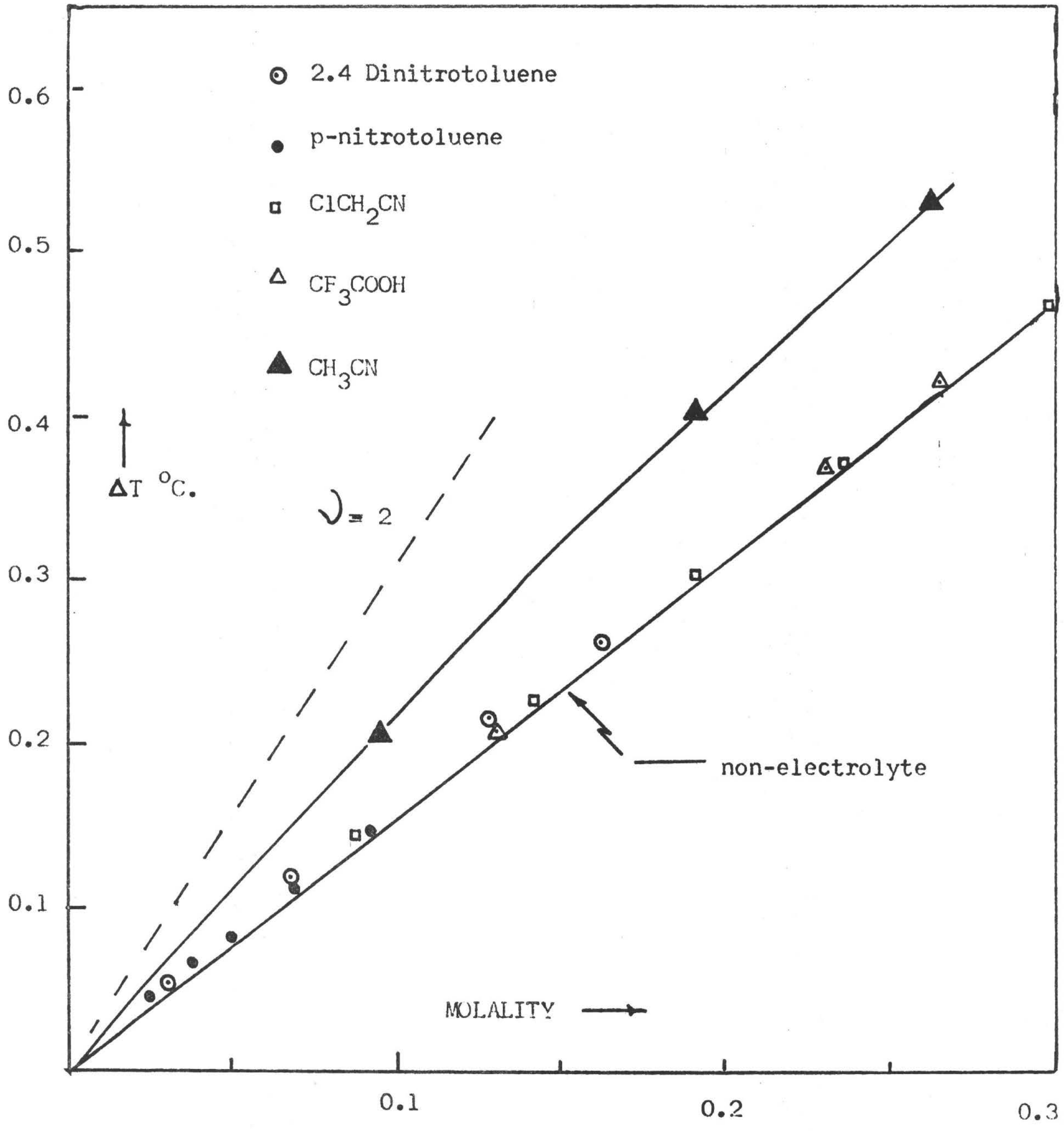
m	ΔT °C	ν
0.0297	0.052	1.18
0.0678	0.118	1.12
0.1272	0.215	1.09
0.1629	0.260	1.03

p-Nitrotoluene

$T_o = -83.595$

m	ΔT °C	ν
0.0254	0.043	1.10
0.0375	0.064	1.10
0.0491	0.080	1.05
0.0680	0.110	1.04
0.0930	0.145	1.01

FIG.5.3 FREEZING-POINT DEPRESSIONS OF SOME WEAK BASES IN HF.



approaches 0.1 molal. The ionization constant is too small to be accurately evaluated from the cryoscopic data, but is of the same order ($\sim 10^{-4}$) as found in 100% sulphuric acid$^{(103)}$.

In fluorosulphuric acid 2,4-dinitrotoluene has ν values of 1.49 to 1.30 for the concentration range 0.02 to 0.01 molal with K_b about 1.4×10^{-2}. In sulphuric acid 2,4-dinitrotoluene appears to be an extremely weak base. Since H_o values indicate that 100% H_2SO_4 is a somewhat stronger acid than anhydrous HF it is surprising that the 2,4-dinitrotoluene ionizes to the extent it does at low concentration. This may be another example of the acid strength of HF increasing at low temperature. It is clear from this data that the acid strength of HF is significantly less than fluorosulphuric acid but at the low temperature of these measurements can approach that of 100% sulphuric acid when in very pure state.

p-Nitrotoluene.

p-Nitrotoluene was found by Gillespie et.al.$^{(103)}$ to be a weak base in 100% sulphuric acid. The ionization constant was found by both conductivity and cryoscopy to be about 0.1. p-Nitrotoluene has a low solubility in HF at the freezing point but will form a pale yellow solution. Cryoscopic data in Table 5.4 and Fig.5.3 show that it behaves almost as a non-electrolyte, exhibiting only very small deviations from the freezing point curve expected for a non-electrolyte. The ν values of less than 1.1 at low concentration correspond to a very low basic dissociation constant. This result fits into the general pattern showing that HF is a less acidic medium than 100% H_2SO_4 or HSO_3F. There is however not the difference between the two weak bases in HF that we might have expected. The acid strength of HF is clearly very sensitive to very small traces of water. The freezing point of the acid used for the measurements on p-nitrotoluene was 0.02 °C lower than the best value and it is probable that "buffering" by the fluoride ion in HF containing even minute traces of water has a significant effect in the attempted evaluation of these very low basic dissociation constants. Other examples of the serious effect of minute amounts of water on the solubility of substances that dissolve in HF via protonation were found during the course of this work. For example silver cyanide does not dissolve to any appreciable extent in HF of conductivity 10^{-3}ohm^{-1} cm^{-1} taken straight from a commercial cylinder but has a solubility of $\sim$0.5M at -83 °C in carefully purified HF of conductivity 10^{-5} ohm^{-1}cm^{-1}.

Acetonitrile.

Acetonitrile has been shown to be 50% protonated in 100% sulphuric acid before solvolysis to the amide (104). An ionization

TABLE 5.5

FREEZING POINT DEPRESSIONS OF WEAK BASES.

CH_3CN

T_o = -83.580

m	ΔT °C	ν	$10^2 K_b$
0.095	0.205	1.39	4.5
0.193	0.401	1.34	3.6
0.262	0.530	1.31	3.6
0.388	0.748	1.24	3.5
0.474	0.890	1.22	3.6

$ClCH_2CN$

T_o = -83.575

m	ΔT °C	ν
0.0886	0.145	1.06
0.1413	0.225	1.02
0.1902	0.302	1.02
0.2370	0.370	1.01
0.2977	0.465	1.01

CF_3COOH

T_{o_I} = -83.580 $T_{o_{II}}$ = -83.59

Experiment	m	ΔT °C
I	0.1316	0.205
I	0.2320	0.365
II	0.2305	0.365
II	0.2649	0.420

constant for acetonitrile in sulphuric acid was found by conductimetric measurements to be 0.16(101). The cryoscopic data for acetonitrile in anhydrous HF are shown in Table 5.5 and Fig.5.3. The ν values varied over the range 1.4 to 1.22 and the ionization constant was calculated from equation 5.1 to be 3.6×10^{-2}. Because of the higher ν values associated with this weak base the ionization constant could be evaluated with a reasonable degree of precision, and provides further quantitative confirmation of the fact that HF is generally a less acidic solvent than H_2SO_4 and HSO_3F. Freezing-point depressions were also made on solution of CH_2ClCN in order to make quite certain that the freezing point data could really distinguish between the different degrees of dissociation of these weak bases of the system. Fig.5.3 shows the marked decrease in freezing-point depression caused by the less basic chloro-substituted solute, the graph being only slightly above that given by a non-electrolyte. The data tabulated in Table 5.5 indicates ν values very slightly greater than unity.

Freezing-point depressions on trifluoroacetic acid show a similar situation. Although acetic acid is a reasonably strong base in the HF system Table 5.5 and Fig.5.3 shows that trifluoracetic acid behaves essentially as a non-electrolyte in anhydrous HF.

CHAPTER VI

SOLUTIONS OF FLUORIDE ACCEPTOR ACIDS

INTRODUCTION.

It is well known that good fluoride acceptors e.g. SbF_5 are capable of accepting fluoride ion from HF producing an increase in the H_2F^+ concentration and acting as acids of the HF system. Clifford et.al.(32,74) made some generalizations on the strengths of these fluoro acids by investigating the solvolysis of salts and the ability of HF solutions of Lewis acids to dissolve sparingly soluble metal fluorides. They claimed from the observed solvolysis of the salts that BF_3 was a weak acid, but that PF_5 and SbF_5 were strong acids of the HF system. This work did not distinguish quantitatively between the relative strengths of PF_5, AsF_5 or SbF_5. The use of BF_3, PF_5 and various metal fluorides (e.g. Ti, Nb and Ta fluorides) to increase the acid strength of HF has been investigated by McCaulay and Lien(33) who measured acid strength by attempting to extract the weak bases m- and p-xylene from a solution in n-heptane by means of HF and metal fluorides. Kilpatrick and Luborsky(43) have measured the conductivity and vapour pressure of BF_3 in HF and evaluated the equilibrium constant for the dissociation of BF_3 in HF.

The strong tendency of SbF_5 and AsF_5 to accept a further fluoride to establish a co-ordination number of 6 is also seen in the formation of adducts with xenon fluorides, which from crystal structure studies are believed to be partly ionic. Many of these fluorides and adducts show a tendency to form fluorine bridged polymeric ions (29,114). However, little is known about the formation and stability of either the polymeric anions or the xenon-containing species in dilute solution. Colligative measurements are particularly useful for the quantitative evaluation of the extent of ionization of these acids and adducts and for the detection of polymerization in solution. Such measurements have been made on the SbF_5 - SbF_6^- - HF and the corresponding arsenic (V) systems, and on PF_5 in anhydrous HF solution. SbF_5 has been cryoscopically titrated with XeF_2 and the formation of a new 1 : 1 adduct of XeF_2 and SbF_5, involving fluorine bridged polymeric ions has been detected.

Solutions of SbF_5

SbF_5 is miscible with liquid HF in all proportions. The first quantitative study of solutions of SbF_5 in HF was made by Kilpatrick and

Lewis(36) who studied the electrical conductivities of the solutions and concluded that SbF_5 is a strong acid. Subsequently Hyman et.al.(30) studied conductivities of the SbF_5 - HF system over the whole range of composition and reported that the infrared and Raman spectra of SbF_5 solutions in HF indicated the presence of the SbF_6^- ion. On the basis of the conductivity data these workers postulated an equilibrium involving an undissociated ion pair:

$$SbF_5 + 2HF \overset{K_1}{\rightleftharpoons} H_2F^+SbF_6^- \overset{K_2}{\rightleftharpoons} H_2F^+ + SbF_6^-$$

giving values of the equilibrium constants for a 20 mole % SbF_5 solution at 0 °C as $K_1 = 4.4 \times 10^{-4}$, $K_2 = 1.7 \times 10^{2}$ and $K = K_1K_2 = 7.3 \times 10^{-2}$. These values indicate that SbF_5 is a moderately weak acid at these higher concentrations. Gillespie and Moss(29) measured the conductivity in HF at low concentrations and studied the ^{19}F and ^{1}H n.m.r. spectra of the system over a wide concentration range. They interpreted the results in terms of the reactions:

$$2HF + SbF_5 \rightleftharpoons H_2F^+ + SbF_6^-$$

and

$$SbF_6^- + nSbF_5 \rightleftharpoons \left[Sb_n\, F_{5n+1}\right]^-$$

Freezing point measurements on dilute solutions of SbF_5 in HF obtained during this work are summarized in Table 6.1 and Fig.6.1.

The additions of the highly viscous SbF_5 were made by filling Kel-F spaghetti tubing to a predetermined length with SbF_5 in the dry box and then forcing the pentafluoride onto frozen HF by passing dry nitrogen through the Kel-F tube. The freezing-point depressions are slightly lower than those given by potassium or ammonium fluoride, with ν values decreasing slightly with increasing concentration. The use of alkali metal fluorides (which give M^+ and HF_2^-) as comparison electrolytes in the determination of ν values for acids (which give H_2F^+ and MF_6^-) may lead to additional uncertainty in the value of ν. A better comparison may be to use $KSbF_6$ but it is not soluble enough at the freezing point. The ν value of 1.9 for SbF_5 at low concentration, obtained by comparison with potassium or ammonium fluoride, indicates that SbF_5 is almost fully ionized in dilute solution in anhydrous HF, behaving as a strong acid of the system by ionizing as shown in the equation:

$$SbF_5 + 2HF \rightleftharpoons SbF_6^- + H_2F^+ \qquad \text{...........} \; 6.1$$

The fact that the apparent ν is slightly less than 2 in dilute solution may be due to the fact that ionization is incomplete or that even at low concentration some of the polymeric species $Sb_2F_{11}^-$ is produced. However it should be noted that comparison with Et_4NSbF_6 indicates even higher ν values corresponding to complete ionization.

TABLE 6.1

FREEZING-POINT DEPRESSIONS FOR SOLUTIONS OF SbF_5 AND Et_4NSbF_6 IN HF.

SbF_5			Et_4NSbF_6	
m	ΔT °C	$\sim\nu$	m	ΔT °C
0.043	0.13	2	0.0277	0.09
0.061	0.18	2	0.0517	0.15
0.091	0.27	2	0.1039	0.28
0.195	0.52	1.90	0.1421	0.38
0.243	0.64	1.90	0.1602	0.43
0.301	0.77	1.88		
0.360	0.93	1.88		
0.414	1.04	1.85		

TABLE 6.2

SbF_5-SbF_6^-

$T_o = -83.575$ °C

Molality of solute added to HF	Mole ratio SbF_6^-: SbF_5	Freezing Point. (°C)
SbF_5 0.091	-	-83.838
SbF_6^- added		
0.025	0.274	-83.871
0.045	0.483	-83.861
0.059	0.648	-83.868
0.116	1.270	* -83.936
0.128	1.410	-83.947

* solution appeared cloudy.

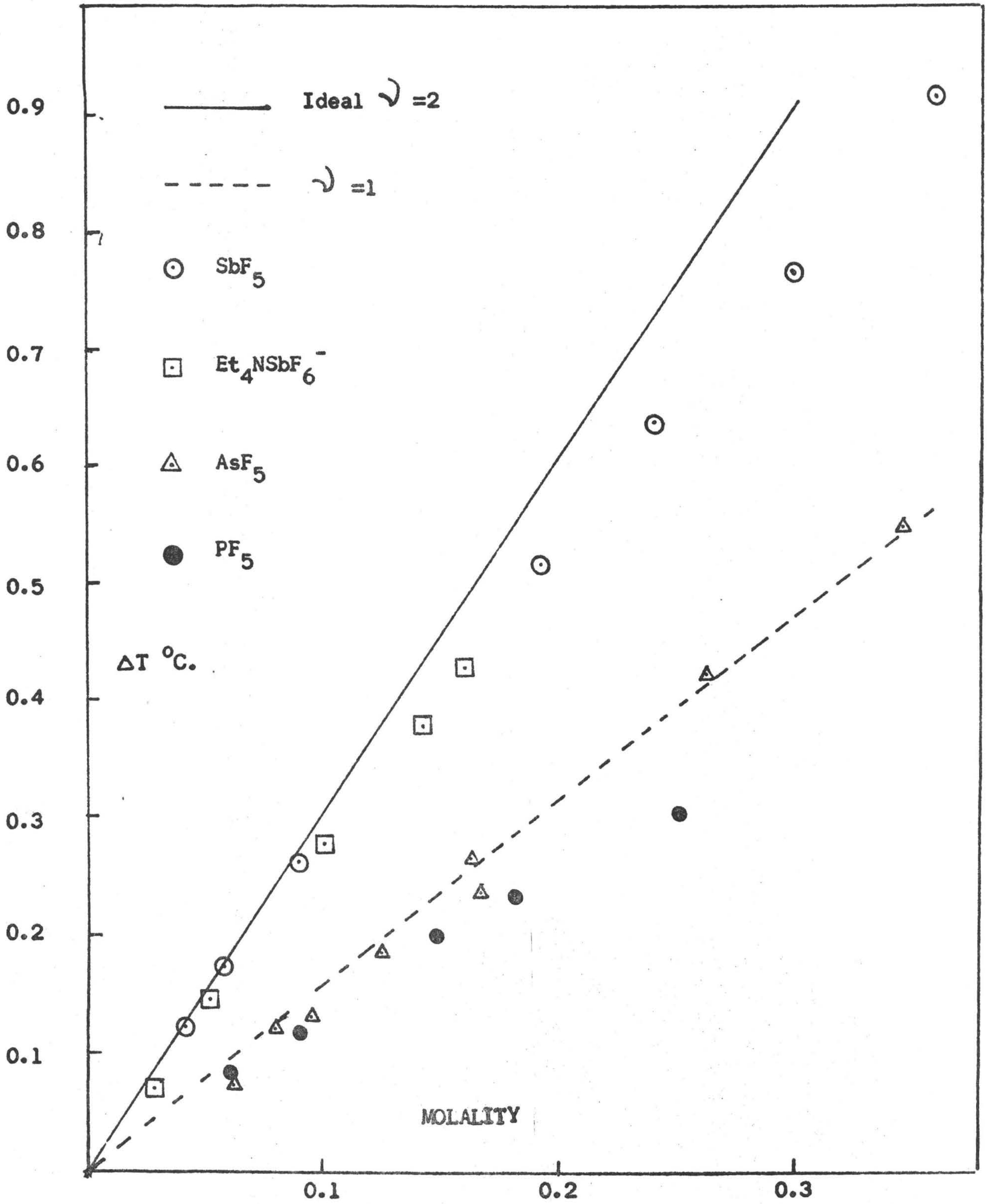


FIG.6.1. FREEZING-POINT DEPRESSIONS FOR GROUP V PENTAFLUORIDES.

In order to further investigate the formation of the polymeric species in these dilute solutions, freezing point measurements were made on SbF_5 - SbF_6^- solutions in HF. The solubility of $KSbF_6$ was found to be less than ~ 0.02 molal at -83 °C; but Et_4NSbF_6 was appreciably soluble, the solubility limit not being reached when additions were stopped at a concentration of ~ 0.2 molal. Freezing-point depressions for Et_4NSbF_6 are shown in Table 6.1 and Fig.6.1. The results of these measurements indicate that ionization into Et_4N^+ and SbF_6^- is essentially complete, but accurate ν values cannot be determined since the degree of interionic attraction and the extent of solvation may be lower for this large cation than for K^+ and NH_4^+ and comparisons may not be strictly valid. Hence we have:

$$Et_4NSbF_6 \longrightarrow Et_4N^+ + SbF_6^- \quad \ldots\ldots\ldots\ldots\ 6.2$$

After investigating the behaviour of SbF_5 and SbF_6^- separately in dilute solution, serial additions of Et_4NSbF_6 were made to an approximately 0.1 molal solution of SbF_5 in HF. It can be seen from equations 6.1 and 6.2 that the number of particles in solution remains constant if on adding SbF_6^- to SbF_5 the following process takes place completely:

$$SbF_5 + SbF_6^- \longrightarrow Sb_2F_{11}^- \quad \ldots\ldots\ldots\ldots\ 6.3$$

Hence we would expect the freezing point to remain constant if the polymeric ion $Sb_2F_{11}^-$ is produced quantitatively in the solution. On the other hand if Et_4NSbF_6 goes into solution without interaction a freezing-point depression corresponding to the introduction of two additional particles should be observed. The data in Table 6.2 and Fig.6.2 shows that additions of Et_4NSbF_6 to an 0.091 molal solution of SbF_5 produce a small freezing-point depression but that after the first addition the freezing point remains almost constant until after the 1 : 1 mole ratio has been reached. If $Et_4NSb_2F_{11}^-$ precipitated out of solution or higher polymers such as $Sb_3F_{16}^-$ were formed, a freezing-point elevation would be observed. Thus we conclude from the constancy of the freezing point, after a very small depression, that there is substantial but probably not complete formation of $Sb_2F_{11}^-$. Hence the equilibrium given by equation 6.3 moves in favour of $Sb_2F_{11}^-$ formation on addition of SbF_6^- to SbF_5, but apparently no significant amount of $Sb_3F_{16}^-$ is formed. The break occurring at the 1 : 1 ratio is consistent with the formation of $Sb_2F_{11}^-$, followed by the ionization of Et_4NSbF_6 without interaction. The freezing-point depression at the highest concentration of SbF_6^- investigated is lower than would be expected for excess Et_4NSbF_6 going into solution. However the

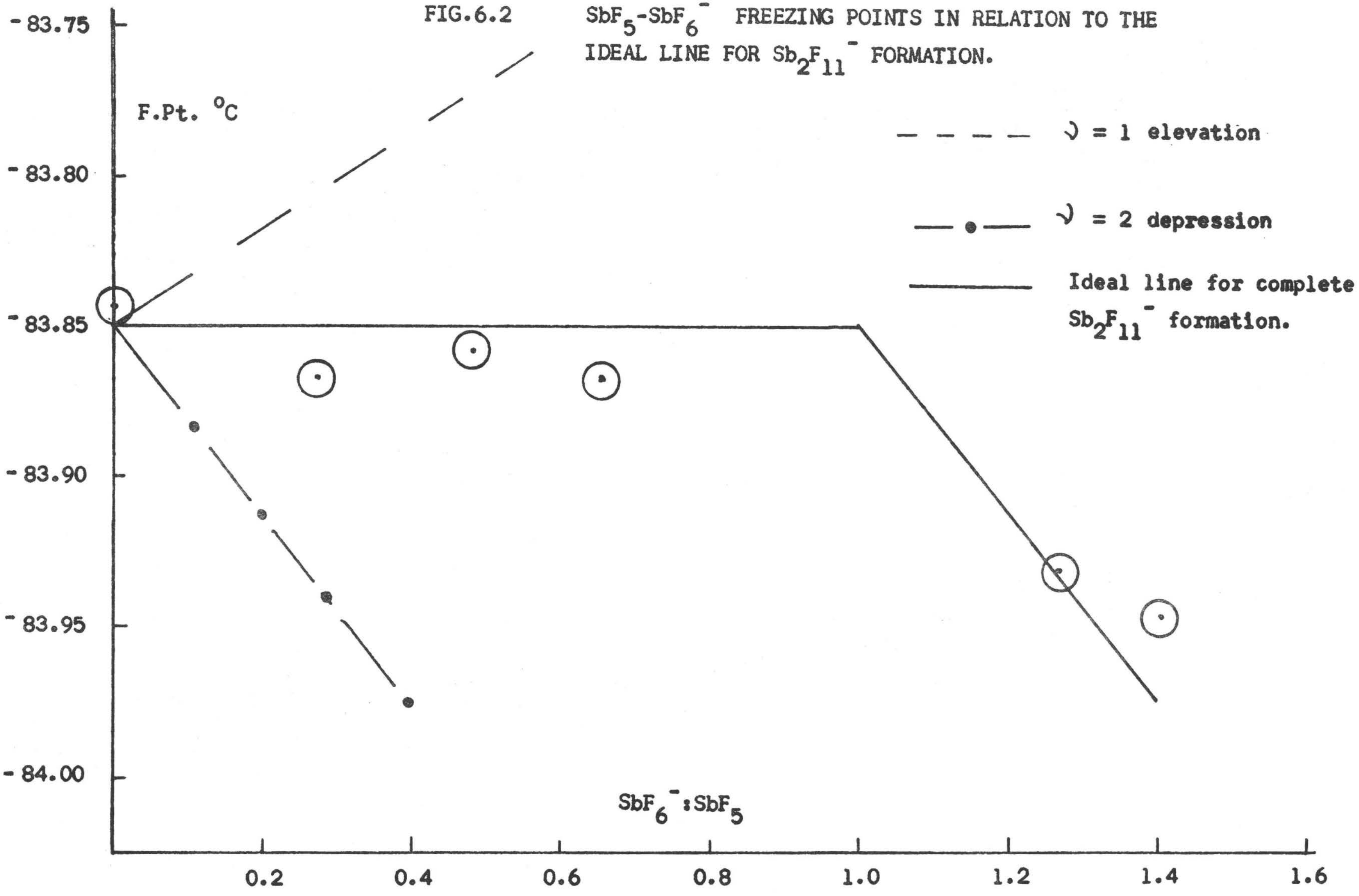


FIG.6.2 SbF_5-SbF_6^- FREEZING POINTS IN RELATION TO THE IDEAL LINE FOR $Sb_2F_{11}^-$ FORMATION.

solution was by this time slightly cloudy when cooled to -83 °C, indicating that the $Et_4NSb_2F_{11}$ had a low solubility at the freezing point. At higher SbF_5 concentrations (i.e. ∽ 0.2 molal), there was a considerable amount of precipitation at the freezing point, on adding Et_4NSbF_6, but the product was soluble on warming to room temperature. However, it has been shown by Bacon, Gillespie and Dean(84) that much higher concentrations of the 1 : 1 mixture can be obtained in the solvent SO_2 and give a ^{19}F n.m.r. spectrum at -80 °C characteristic of the $Sb_2F_{11}^-$ ion(29).

Solutions of AsF_5

Hyman, Lane and O'Donnell(45) have reported that AsF_5 forms conducting solutions in HF and have obtained a Raman spectrum for a 5.5 mole % solution of AsF_5 in HF. They interpreted the data in terms of the ionization:

$$AsF_5 + 2HF \rightleftharpoons H_2F^+ + AsF_6^-$$

The Raman spectra indicates free AsF_5 in solution at 5.5 mole%, but does not clearly distinguish between AsF_6^- and $As_2F_{11}^-$.

In the present work a cryoscopic study of AsF_5 in HF was made. The AsF_5 was condensed from a weighed Kel-F trap onto frozen HF. Vapour pressure measurements obtained by connecting the pressure gauge directly to the cryoscope indicated complete solubility of the added AsF_5, since no appreciable pressure of AsF_5 was observed above the solution at -80 °C. The freezing point data obtained for AsF_5 is shown in Table 6.3 and Fig. 6.1. The cryoscopic plot is coincident with that given by the non-electrolytes of the system indicating a ν value of 1. It might therefore at first sight be concluded that AsF_5 behaves simply as a non-electrolyte. However in view of the reported conductivity of solutions of AsF_5 in HF(45,105) an alternative explanation must be considered. The formation of a previously unreported $As_2F_{11}^-$ would be consistent with both the conductivity and cryoscopic data since the equation:

$$2AsF_5 + 2HF \longrightarrow As_2F_{11}^- + H_2F^+ \quad \ldots\ldots\ldots\ldots \quad 6.4$$

corresponds to a ν value of 1 and would give a conducting solution. In order to substantiate this postulation further conductivity measurements were made, in collaboration with R. Hulme, on dilute solutions of AsF_5 in HF. The results are shown in Table 6.4 and Fig 6.3 together with those for SbF_5. It is clear that although the solutions are strongly conducting, the conductivity at -83.6 °C is about half that shown by an equimolar solution of SbF_5, at the same temperature. The vapour pressure of the solution in the conductivity cell was found to be 367 mm. for an 0.243 molal solution at 0 °C. Pure HF has a vapour

TABLE 6.3

FREEZING-POINT DEPRESSIONS OF SOLUTIONS OF AsF_5

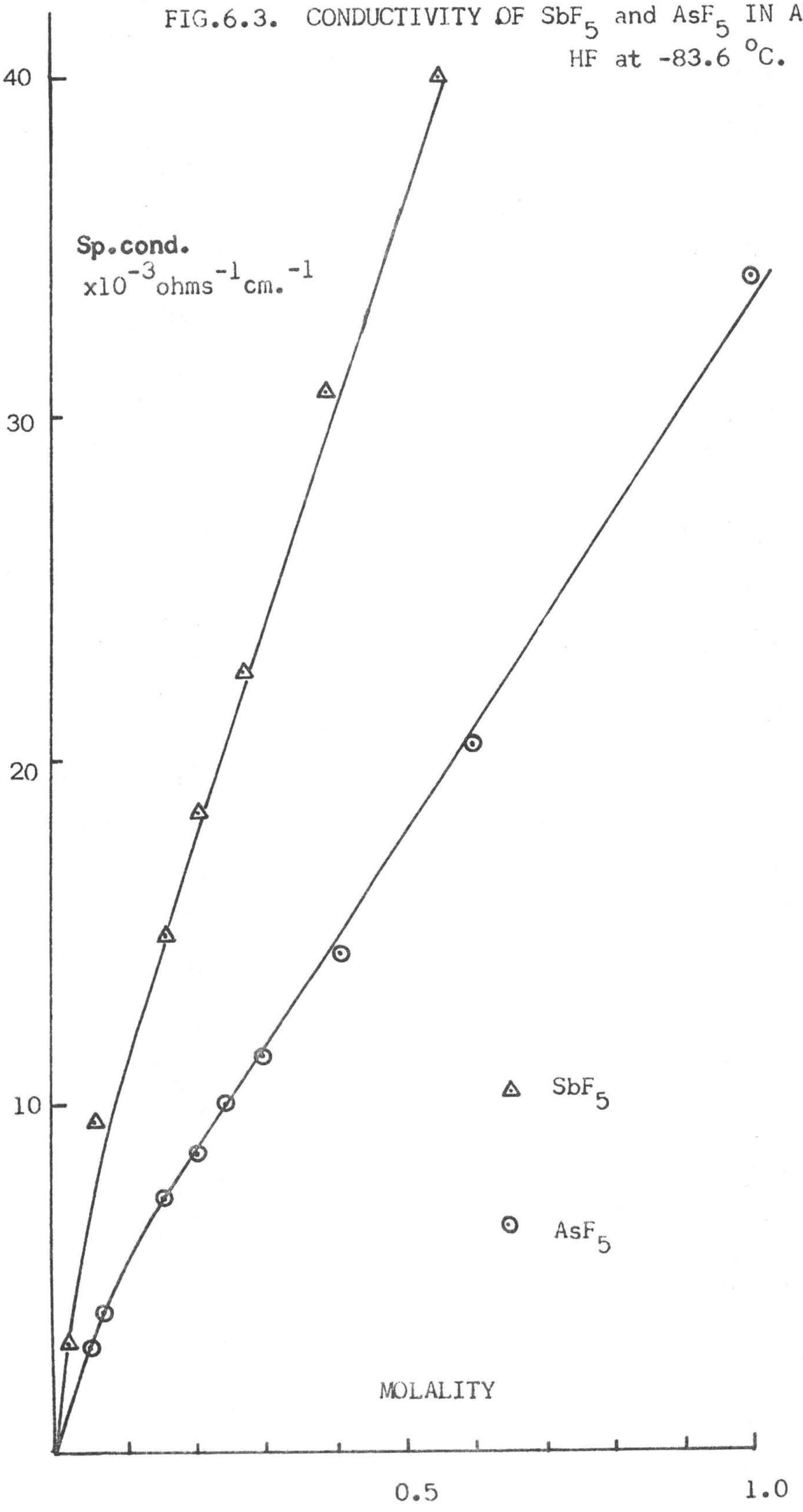
Experiment	m	ΔT °C	$\underset{\sim}{\nu}$
II	0.063	0.077	0.78
III	0.080	0.125	1.00
II	0.095	0.137	0.93
II	0.126	0.192	0.97
I	0.163	0.270	1.06
II	0.166	0.237	0.92
I	0.262	0.425	1.04
I	0.345	0.550	1.02
I	0.523	0.840	1.03

TABLE 6.4

CONDUCTIVITY OF AsF_5 AND SbF_5 IN ANHYDROUS HF AT -83.6°C

AsF_5		SbF_5	
Molality	Specific Conductivity ($\times 10^{-4} ohm^{-1} cm.^{-1}$)	Molality	Specific Conductivity ($\times 10^{-4} ohm^{-1} cm^{-1}$)
0.0222	15.7	0.016	8.02
0.0444	30.1	0.052	50.5
0.0666	39.9	0.121	121
0.0888	49.1	0.155	150
0.111	58.3	0.205	186
0.133	66.9	0.271	228
0.155	74.4	0.388	314
0.178	80.8	0.598	432
0.200	87.5	0.911	539
0.222	93.9		
0.244	101		
0.294	116		
0.348	131		
0.402	145		
0.597	207		
1.049	344		

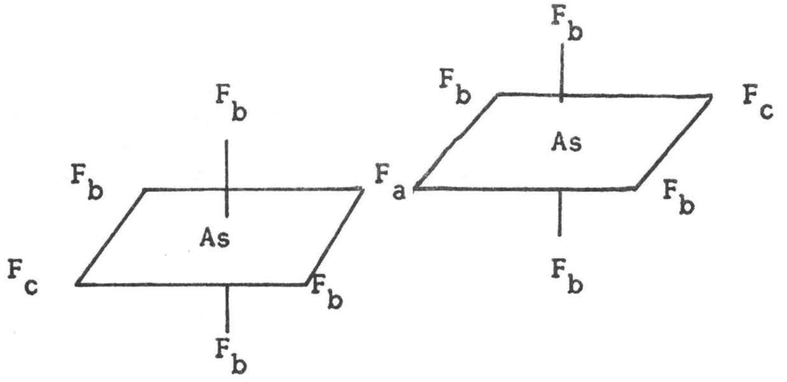
FIG.6.3. CONDUCTIVITY OF SbF_5 and AsF_5 IN ANHYDROUS HF at -83.6 °C.



pressure of 364 mm. at 0 °C and the maximum depression expected, even if AsF_5 completely ionized is approximately 13 mm. The maximum possible vapour pressure of AsF_5 above the solution is thus 16 mm., which is equivalent to less than 0.4% of the amount added. The most reasonable explanation of the ν value of 1 that is consistent with these conductivity results is that shown by equation 6.4 involving the formation of the polymeric anion $As_2F_{11}^-$ even in dilute solution.

About the time that these observations were made an n.m.r. study by Brownstein(106) suggested that $As_2F_{11}^-$ is an intermediate in the fluorine exchange that occurs in the system AsF_5 - Bu_4NAsF_6. The species $As_2F_{11}^-$ had been previously postulated to account for differences observed in the infrared spectra of NOF_3xAsF_5 and $NOF_2^+AsF_6^-$ (107), but no definite evidence for the existence of $As_2F_{11}^-$ was available. However Dean et.al.(108) of this laboratory recently obtained solid products from the interaction of equimolar amounts of AsF_5 with Et_4NAsF_6 or Bu_4NAsF_6 in SO_2 or anhydrous HF, by removing the solvent at -78 °C. These salts had low vapour pressures at 0 °C of approximately 0.5 mm. for the Et_4N^+ adduct and 2.1 mm. for the Bu_4N^+ adduct and the vapour was shown by the infrared spectrum to be AsF_5. The ^{19}F n.m.r. spectrum of the Bu_4N^+ adduct was obtained by Dean et.al.

in sulphuryl chlorofluoride at $-140\ ^{o}C$. The complex spectrum in the fluorine-on-arsenic region showed a single line attributed to AsF_6^- at +61.6 p.p.m. from external $CFCl_3$ and three resonances at +21.1, +48.4 and +85.0 p.p.m. from external $CFCl_3$, with intensities 1 : 8 : 2 assigned to the $As_2F_{11}^-$ anion:



The fine structure in the spectrum compared well with that observed for the $Sb_2F_{11}^-$ ion.

The interesting difference between the behaviour of SbF_5 and AsF_5 in dilute HF solution indicates that the AsF_6^- ion is at least as strong a Lewis base as SbF_6^-. In the system SbF_5 - HF this work has shown that the process:

$$SbF_5 + 2HF \rightleftharpoons SbF_6^- + H_2F^+ \qquad \ldots\ldots\ldots\ldots 6.1$$

has a large equilibrium constant. Nevertheless conductivity and freezing point data indicates that a significant amount of $Sb_2F_{11}^-$ may be present. At higher concentration, approaching 20 mole %, the concentration of $Sb_2F_{11}^-$ is large enough to be seen in the n.m.r. spectrum. Hence it would appear that the equilibrium 6.3 given by:

$$SbF_5 + SbF_6^- \rightleftharpoons Sb_2F_{11}^- \quad \ldots\ldots\ldots\ldots 6.3$$

has a relatively small equilibrium constant and the concentration of the polymeric ion $Sb_2F_{11}^-$ is low in dilute solution, since little free SbF_5 is available.

The AsF_5 results can be explained if it is assumed that AsF_5 is a weaker acceptor in HF than SbF_5, and the equilibrium constant for the process:

$$AsF_5 + 2HF \rightleftharpoons AsF_6^- + H_2F^+ \ldots\ldots\ldots\ldots\ldots 6.5$$

is small, but that AsF_6^- is a better donor than SbF_6^- and hence the equilibrium constant for :

$$AsF_5 + AsF_6^- \rightleftharpoons As_2F_{11}^- \quad \ldots\ldots\ldots\ldots\ldots\ldots 6.6$$

is large. In this case then, in dilute solution, the equilibrium 6.6 is almost completely over to the right hand side. This scheme is in fact reasonable providing AsF_6^- is at least as good a donor as SbF_6^- or the acid "As_2F_{10}" stronger than "Sb_2F_{10}". In a competition experiment involving equimolar amounts of AsF_6^-, SbF_6^- and SbF_5 in sulphuryl chlorofluoride, Dean(109) found from low temperature n.m.r. that a mixture of ions was formed including significant amounts of $Sb_2F_{11}^-$ and the mixed species $AsSbF_{11}^-$. This result indicates that AsF_6^- has a base strength equal to or greater than SbF_6^- with respect to SbF_5.

The formation of this new polymeric anion $As_2F_{11}^-$ was further investigated by carrying out a cryoscopic titration of AsF_6^- with AsF_5. In this case the Et_4NAsF_6 has such a low solubility at the freezing point that unstable freezing points and evidence of super-saturation were observed at concentration $\sim$ 0.1 molal. However, the addition of AsF_5 to a 0.093 molal solution of Et_4NAsF_6 caused an immediate elevation of the freezing point, indicating either the formation of polymers higher than $As_2F_{11}^-$ (e.g. $As_3F_{16}^-$) or precipitation from solution of $Et_4NAs_2F_{11}$, the latter being much more likely. Continued addition of AsF_5 caused further elevation in the freezing point as shown in Table 6.5, and the formation of a precipitate was observed. Elevations continued up to approximately the 1:1 mole ratio where there was a levelling off followed by depressions in the freezing point as AsF_5 was added. These depressions continued until additions were stopped beyond the 3:1 mole ratio and correspond to those expected for AsF_5 going into HF solution, i.e. to a ν value of 1, as

TABLE 6.5

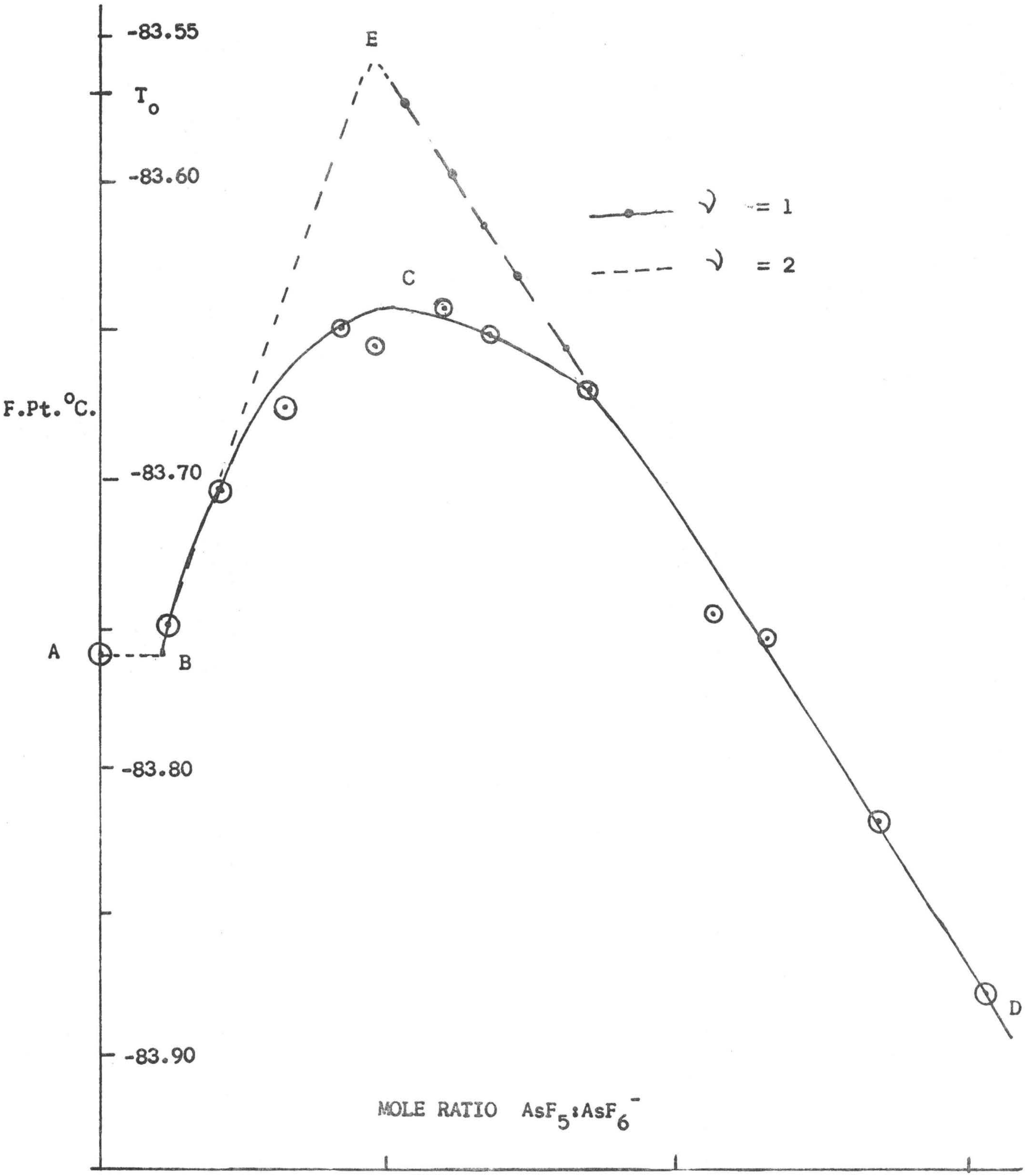
CRYOSCOPIC TITRATION OF AsF_6^- WITH AsF_5

Weight of HF = 49.89g. T_o = -83.57.

Et_4NAsF_6 = 0.0932 molal F.Pt.of solution = -83.76°C.

Weight of AsF_5 added	Molality AsF_5	Mole ratio $AsF_5:AsF_6^-$	Freezing Point °C.
0.1710	0.0202	0.216	-83.750
0.1604	0.0390	0.423	-83.705
0.1947	0.0620	0.665	-83.675
0.1132	0.0754	0.805	-83.645
0.1121	0.0886	0.950	-83.655
0.1192	0.1027	1.101	-83.640
0.2018	0.1265	1.356	-83.654
0.2903	0.1607	1.724	-83.670
0.3044	0.1966	2.108	-83.755
0.1730	0.2170	2.327	-83.755
0.2978	0.2522	2.704	-83.825
0.2968	0.2872	3.080	-83.885
0.2616	0.3180	3.410	-83.930

FIG.6.4 CRYOSCOPIC TITRATION OF Et_4NAsF_6 WITH AsF_5



shown in Fig.6.4. The break at 1:1, shown in Fig.6.4 indicates the formation of the slightly soluble $Et_4NAs_2F_{11}$, according to the reaction

$$AsF_5 + AsF_6^- \longrightarrow As_2F_{11}^-$$

The maximum of the curve, C in Fig.6.4 corresponding to the 1:1 mole ratio, shows the slight solubility of $Et_4NAs_2F_{11}$. The total depression at this point is ~ 0.07 °C, which gives a solubility for $Et_4NAs_2F_{11}$ of ~ 0.023 molal at the freezing point of HF. The region AB where the freezing point is constant corresponds to the formation of $Et_4NAs_2F_{11}$ in solution. The solubility of $Et_4NAs_2F_{11}$ given by point B is ~ 0.025 molal in agreement with that given above. The point of intersection of BE and DE at 1:1 mole ratio is close to the freezing point of HF and the slopes of BE and DE are consistent with changes in ν of 2 and 1 respectively.

Solutions of PF_5

In this system there was a considerable equilibrium pressure of PF_5 above the solution at the freezing point (see Table 6.6.) and because of this ν values could not be obtained with the usual accuracy. The concentration of the solution was estimated by measuring the pressure of PF_5 in the cryoscope at the freezing point and calculating

TABLE 6.6

FREEZING-POINT DEPRESSIONS ON SOLUTIONS OF PF_5

Weight of HF = 62.68 g. $T_o = -83.58$

Total Weight Added	ΔT °C	Pressure at F.Pt.(mm.)	Estimated amount in Solution(g.)	$\sim m$	$\sim \nu$
0.5487	0.085	14	0.4817	0.061	0.90
0.8290	0.120	23	0.7186	0.091	0.85
1.4000	0.201	50	1.1600	0.147	0.88
1.762	0.234	58	1.484	0.188	0.80
2.302	0.305	69	1.966	0.249	0.79

the amount remaining out of solution, using the known volume of free space in the cryoscope and assuming ideal gas behaviour. A serious error in this calculation is introduced by the fact that the temperature of the PF_5 in the vapour state was not known accurately and was not likely to be uniform. Calculations based on an assumed value of -60 °C for the average temperature of the vapour give ν values less than 1 as shown in Table 6.6 and Fig.6.1. The data is however useful enough to show that PF_5 is a much weaker acid than SbF_5 and AsF_5. Solutions of PF_5 in HF are essentially non-conducting. The conductivity of a 0.5 molal solution at -83.6 °C was found to be 5×10^{-4} $\text{ohms}^{-1}\text{cm.}^{-1}$ in acid of conductivity 10^{-4} $\text{ohms}^{-1}\text{cm.}^{-1}$. Thus there is no evidence that the low ν value can be ascribed to the formation of polymeric ions analogous to those found for SbF_5 and AsF_5.

The order of acid strength for the group V pentafluorides investigated follows the trend $SbF_5 > AsF_5 > PF_5$, with acceptor strength decreasing along this series. This agrees with the conclusions of Gillespie et.al.(110) in the fluorosulphuric acid solvent system where conductivity measurements show the acid strength increases in the order : $PF_5 \sim NbF_5 > AsF_5 > SbF_5$. The conclusion that SbF_5 is a stronger Lewis acid than either AsF_5 or PF_5 is substantiated by the observation that its complexes with organic bases, such as amines, are more stable than those of AsF_5 and PF_5(111). Since electronegativity decreases along the series this increase in Lewis acid strength is perhaps best correlated with a decreased shielding by ligands, as the size of the central atom increases.

Cryoscopy on solutions of NbF_5 in HF was also attempted. However, the solubility of NbF_5 at -83 °C was found to be less than 0.05 molal. This in itself is some evidence for the fact that NbF_5 is not a good fluoride acceptor in HF.

SbF_5 - XeF_2

(a) XeF_2 as a fluoride ion donor.

Several workers have demonstrated that xenon difluoride acts as a fluoride ion donor to MF_5 (where M = As, Sb or Ta) by forming a number of adducts between XeF_2 and MF_5. Thus Edwards, Holloway and Peacock(112) reported a yellow 1 : 2 adduct $XeF_2.SbF_5$ m.pt. 63 °C and a straw coloured compound $XeF_2.2TaF_5$ m.pt. 81 °C. Peacock made $XeF_2.2SbF_5$ by dissolving XeF_2 in SbF_5 to form a pale yellow-green solution from which the stable adduct crystallized. These workers suggested a possible formulation of the adduct as a fluorine bridged compound, $F_5SbFXeFSbF_5$ with a high degree of ionic character. Maslov et.al.(113) investigated the phase diagram of the XeF_2-SbF_5 system by differential thermal analysis and reported four congruent melting compounds:

		melting point. °C.
Mustard	$XeF_2.SbF_5$	161
Mustard-yellow	$XeF_2.1.5SbF_5$	86.5
Yellow	$XeF_2.2SbF_5$	63
Green	$XeF_2.6SbF_5$	34

Binenboym, Selig and Shamir(105) have reported a complex of composition $XeF_2.AsF_5$ prepared by heating AsF_5 and XeF_2 at 150 °C or by exposing a mixture of xenon, fluorine and AsF_5 to sunlight. They found this white solid to be soluble in anhydrous HF to give a pale yellow non-conducting solution with a solubility of ∼ 0.4M at 0 °C. Sladky, Bullinger and Bartlett(114) reported further adducts of the type $2XeF_2.MF_5$, $XeF_2.MF_5$ and $XeF_2.2MF_5$ (where M = Pt, Ir, Os, Ru,and Rh) prepared from BrF_5 solutions. On the basis of Raman and infrared spectroscopy they formulated these adducts as the salts $Xe_2F_3{}^+MF_6{}^-$, $XeF^+ MF_6{}^-$, and $XeF^+ M_2F_{11}{}^-$ and determined the crystal structure of the $Xe_2F_3{}^+ AsF_6{}^-$ compound. Holloway and Knowles(115) reported the preparation of the pale yellow or pale green adducts $XeF_2.TaF_5$, $XeF_2.2TaF_5$, $XeF_2.NbF_5$, $XeF_2.2NbF_5$, $XeF_2.RuF_5$, $XeF_2.2RuF_5$ by direct combination of components.

The crystal structure determination of $Xe_2F_3^+AsF_6^-$ together with the vibrational spectra were interpreted in terms of the ionic formulation: F - Xe - F - XeF^+, with the cation containing a bridging fluorine between two xenon atoms (114). Recently a crystal structure determination by McRae,Peacock and Russell(116) on $XeF_2.2SbF_5$ was shown to be consistent with $XeF^+Sb_2F_{11}^-$, a notation which the authors stressed they used as a formalism only, since they regarded the compound as an essentially covalent molecule with a Xe-F distance of 2.23 Å between xenon and the fluorine and antimony: $F-Xe\underset{2.23}{\cdots\cdots}F-Sb-F$ The Xe-F-Sb angle of 147 ° is very similar to that in the $Sb_2F_{11}^-$ unit.

A study on the formation and stability of these xenon fluorine cations in solution was attempted by cryoscopically titrating XeF_2 in HF solution with SbF_5, in the expectation that XeF_2 would act as a base and the nature and properties of the Xe-F cation thus formed in solution could be investigated.

(b) Cryoscopic titration of XeF_2 with SbF_5

It is clear that if step-wise additions of SbF_5 are made to dilute solutions of XeF_2 in HF, the various possible modes of interaction can be distinguished by cryoscopy. It was shown in Chapter III that XeF_2 dissolves in HF essentially as a non-electrolyte and earlier in the present Chapter it was shown that SbF_5 is essentially fully ionized into SbF_6^- and H_2F^+. If SbF_5 is added to XeF_2 in HF the following possibilities can be distinguished:

(a) If no interaction occurs SbF_5 will go into solution and give a freezing-point depression corresponding to $\nu = 2$.

(b) If a 1 : 1 adduct of the type $XeF_2.SbF_5$ is formed without ionization the freezing point will remain constant until the mole ratio 1 : 1 is reached, since there will be no change in the number of particles. After 1 : 1 mole ratio the freezing-point depression should correspond to an increase in ν of 2.

(c) The formation of the ions XeF^+ and SbF_6^- would result in the SbF_5 giving a depression corresponding to $\nu = 1$ until the 1 : 1 mole ratio is reached, the break followed by an increased depression corresponding to $\nu = 2$.

(d) The formation of $Xe_2F_3^+$ according to either of the equations

1) $2XeF_2 + SbF_5 \rightarrow Xe_2F_3^+ + SbF_6^-$

2) $2XeF_2 + 2SbF_5 \rightarrow Xe_2F_3^+ + Sb_2F_{11}^-$

would result in no initial change in the freezing point but equation 1) would give a break at 1:2 and equation 2) at 1:1 SbF_5:XeF_2.

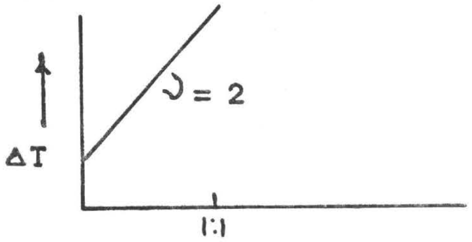
(e) The process $XeF_2 + 2SbF_5 \longrightarrow XeF^+ + Sb_2F_{11}^-$ would give rise to initial depressions corresponding to $\nu = 1$ followed by a break at mole ratio SbF_5:XeF_2 = 2:1.

(f) The formation of an insoluble product would cause an elevation in the freezing point, with a break indicative of the ratio of SbF_5:XeF_2 in the adduct. These possibilities are summarized in Fig.6.5.

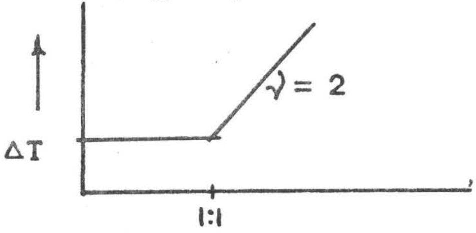
The results of the cryoscopic titration are given in Table 6.7 and Fig.6.6. They show an elevation in the freezing point when SbF_5 is added to XeF_2, in HF. After the 1:1 mole ratio the SbF_5 goes into solution with a ν value of 2, indicating that it ionizes without interaction, as shown by the ideal curves on Fig.6.6. Thus we conclude that a 1:1 adduct is formed, and since the freezing point becomes close to that of the pure acid at 1:1, the product is almost insoluble in HF at -83 °C. This very low solubility at the freezing point rules out the possibility of assessing the degree of ionization of the adduct by cryoscopy.

FIG.6.5 CHANGES IN ν FOR THE INTERACTION OF XeF_2 AND SbF_5

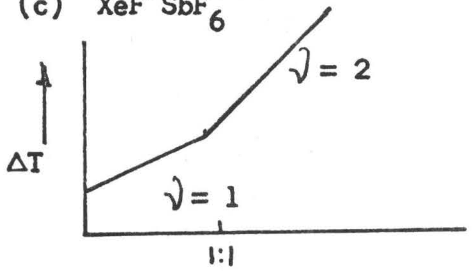
(a) Non interaction



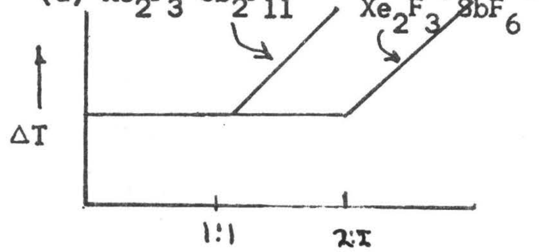
(b) $XeF_2 \cdot SbF_5$



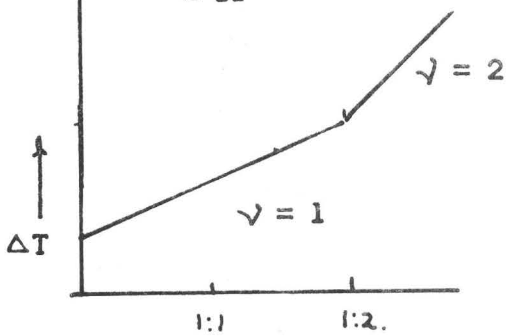
(c) $XeF^+SbF_6^-$



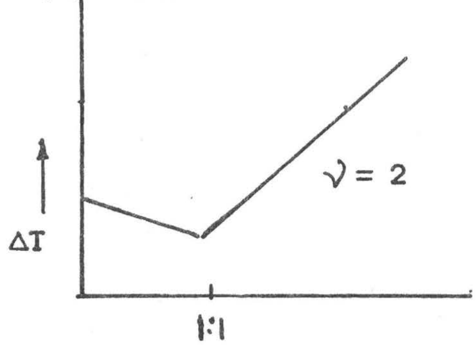
(d) $Xe_2F_3^+Sb_2F_{11}^-$



(e) $XeF^+Sb_2F_{11}^-$



(f) Insoluble 1:1 adduct



Freezing point vs. mole ratio SbF_5:XeF_2
depression

TABLE 6.7

CRYOSCOPIC TITRATION OF XeF_2 WITH SbF_5

T_o = -83.570

Molality of XeF_2 added = 0.1016 Freezing Point = -83.737

Molality of SbF_5 added	Mole ratio SbF_5:XeF_2	Freezing Point °C.
0.021	0.20	-83.676
0.062	0.61	-83.605
0.120	1.18	-83.615
0.149	1.46	-83.702
0.204	2.00	-83.845
0.251	2.47	-83.985
0.304	2.99	-84.149

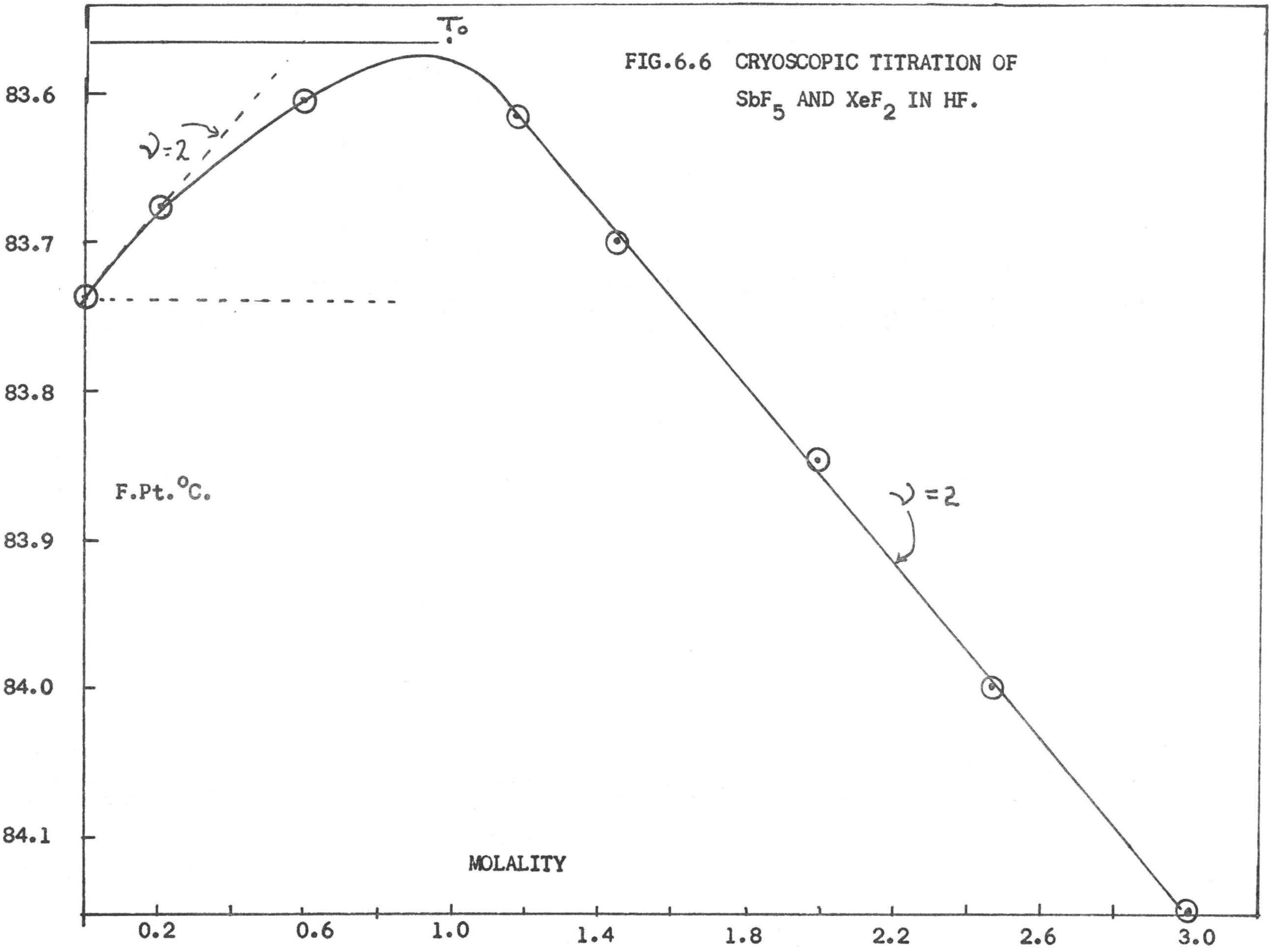


FIG.6.6 CRYOSCOPIC TITRATION OF SbF_5 AND XeF_2 IN HF.

Previously reported adducts between SbF_5 and XeF_2 have not included a 1:1 adduct, apart from the $XeF_2 \cdot SbF_5$ indicated in the phase diagram study of the XeF_2-SbF_5 system(113). In an attempt to characterize the 1:1 adduct formed in the cryoscopic titration, a small quantity of the precipitate was recovered after removing the HF and dismantling the cryoscope. This sample gave a poorly resolved Raman spectrum, but the strongest bands were found in the Xe-F stretch region at 600 cm.$^{-1}$ with a band in the XeF bending region at $\sim$ 150 cm.$^{-1}$. Since the $Xe_2F_3^+$ ion is characterized by strong Raman bands in these regions(114) it seemed likely that the 1:1 adduct was $Xe_2F_3^+Sb_2F_{11}^-$.

In order to confirm this formulation for the new adduct a pure sample was prepared outside the cryoscope by dissolving XeF_2 in HF in a Kel-F trap and adding the amount of SbF_5 required to make the mole ratio exactly 1:1. A very pale yellow precipitate was immediately observed which went white on cooling in HF. The product was re-crystallized from anhydrous HF using two Kel-F traps connected by flexible Teflon tubing. The compound thus isolated, melted at $\sim$ 128° C with some signs of decomposition. It turned green on heating or exposure to moisture and attaked Kel-F when left standing in a trap for several days. The product gave a similar Raman spectrum to that shown by the sample isolated in the cryoscopic experiment(Table 6.8.) but with much better resolution. In particular the same strong bands at 145 cm.$^{-1}$ and $\sim$600 cm.$^{-1}$ were observed in the spectrum confirming the conclusion that the 1:1 adduct may be formulated as $Xe_2F_3^+Sb_2F_{11}^-$ rather than $XeF^+SbF_6^-$.

An X-ray powder photograph of the compound was taken in order to compare the d-spacing with that of the other previously reported XeF_2-SbF_5 adduct. The d-spacings for this compound were calculated from the cell dimensions given by Peacock(116). The d-spacings (Table 6.9.) for the adduct formed in this work did not appear on the table generated for Peacock's compound, indicating that it was a different compound.

The low solubility of the adduct prevented an evaluation of its ionization in HF by cryoscopy. An 0.064 molal solution (calculated assuming a molecular weight for the adduct of 772) gave a vapour pressure depression at 0 °C of approximately 4 mm. Even considering that this measurement could be in error by 25%, it gives some preliminary indication that the adduct is extensively ionized in HF, since by comparison with XeF_2 this depression corresponds to a ν of approximately 2.4.

TABLE 6.9

X-RAY POWDER DATA ON 1:1 ADDUCT BETWEEN XeF_2 and SbF_5

d(Å)	Intensity	d(Å)	Intensity
4.93	s	2.797	vvw
5.22		2.885	
4.44	ms	2.254	vw
4.23	ms	2.058	w
3.87	ms	1.973	vvw
4.04		2.014	
3.71	w		
3.562	ms	1.791	w
3.079	vvw	1.669	w
2.885	vvw	1.344	vw
2.979		1.361	

TABLE 6.8

THE RAMAN SPECTRUM OF 1:1 ADDUCT OF XeF_2 AND SbF_5(cm.$^{-1}$)

145	s	617	s
270	m	647	m
290	m	671	ms
469	s	690	w
593	m		

CHAPTER VII

SOLUTIONS OF CYANIDES.

INTRODUCTION.

In 1939 Klatt(55) used conductivity and boiling point measurements to investigate solutions of some cyanides and azides in anhydrous HF. He found the solutions appreciably conducting, was able to recover the solute unchanged on evaporation, and reported ν values varying with concentration over the range 1.6 at 0.7 molal to 1.2 at 1 molal. These ν values were based on a boiling point elevation constant of 1.9 and assumed ideal solutions. More accurate ν values can be obtained by comparison with a reference electrolyte, such as KF thereby making some allowance for deviation from ideality. If ν values are recalculated from Klatt's data making appropriate comparison with KF, a reasonably constant value of 1.4 is obtained. Klatt's original observation has been interpreted(6) in terms of a simple protonation:

$$Hg(CN)_2 + 2HF \rightleftharpoons Hg(CN)_2H^+ + HF_2^- \quad \ldots\ldots\ 7.1$$

However, there is clearly some inconsistency since if such protonation went to completion ν would equal 2, but if mercury cyanide behaved as a weak base in solution, would not be constant over a wide concentration range. In view of these inconsistencies a further detailed investigation of mercury cyanide in HF solution was carried out, using the previously untried approaches of cryoscopy and vapour pressure, in an attempt to discover the nature of the species present and the extent of protonation involved. During the course of this new study it was necessary to establish the behaviour of HCN in solution, and in turn therefore colligative data on sodium cyanide solutions were obtained. Dove and Hallett(117) studied solutions of silver cyanide in anhydrous HF by conductriometric and spectroscopic methods. We carried out cryoscopic measurements on the solutions and these provide further evidence for the species suggested by these workers. In order to unambiguously understand the nature of the species in solution in the case of mercury cyanide, it was necessary to compare conductivity and n.m.r. data with that obtained by colligative techniques. The required conductivity data was obtained in collaboration with Dr. R. Hulme using the techniques previously described(29).

Cryoscopy on mercury cyanide solutions.

The first measurement of the freezing point depressions for dilute solutions of mercury cyanide were made by dropping solid mercury cyanide onto frozen HF, allowing the system to warm just sufficiently for the solute to dissolve and for the solution to become uniform, and then re-freezing. Thus the solution warmed only a few degrees above the freezing point before being re-cooled. Further mercury cyanide additions were always made to the frozen solution and the above procedure repeated. The freezing point depressions obtained in this way are shown in Table 7.1 and Fig.7.1. They follow a straight line very close to that expected for a non-electrolyte. The data is self consistent and indicates that the ν value for fresh solutions of mercury cyanide, which have not been allowed to warm above -70 °C, is equal to 1. However on occasions when the system was allowed to warm up to approximately -50 °C for about 30 minutes before the freezing point of the solution was measured, it was found that the freezing point depressions were greater than in the set of measurements described above. Clearly some reaction, which is very slow at -83 °C, becomes readily measurable at higher temperature. In view of this a detailed investigation on the change of ν with time was conducted and it became apparent that the behaviour of mercury cyanide in HF solution was much more complicated than the data obtained from cold fresh solutions indicated. A typical history of an $Hg(CN)_2$

solution is summarized in Table 7.2.

It was found that if a dilute solution of mercury cyanide in HF was left stirring at room temperature for several days, successive ν values drifted upwards to a limiting value of 2, at which point a heavy white precipitate was observed in the cryoscope. Further investigation revealed that once the fresh solution of mercury cyanide was allowed to warm up appreciably above -70 °C, the freezing point became steady at a constant reproducible value, before very slow change to the limiting ν value of 2. This freezing point was stable over a 12 hour period if mercury cyanide was kept stirring at 0 °C between successive freezing point checks. This value of the freezing point did not change even if the solution was re-cooled and stirred at -83 °C for some two hours before measuring the freezing point.

Once it had been established that there was indeed a real and stable ν value for solutions that had warmed up appreciably above the freezing point, a second set of cryoscopic data was obtained by allowing the solution to warm up to 0 °C and stirring for about half an hour after each addition of solute. Each point was repeated twice before a further addition was made to ensure that the solution had reached equilibrium. Although this procedure was laborious it yielded a second set of self consistent data shown in Table 7.3 and Fig 7.1. Over the concentration range up to 0.4 molal this data gave a constant ν value of ≈ 1.45 which is in reasonable agreement with that calculated from Klatt's boiling point data. This satisfactory agreement incidentally indicates that no appreciable amount of volatile material (e.g. HCN) was lost from the solution in the boiling point measurements. Such a loss of volatile material is a possible disadvantage of the boiling point method that is much more likely to be avoided in the cryoscopic method.

Since in the case of this solute some equilibrium process appeared to be involved, an additional check on the value of ν at temperatures above the freezing point was made by carrying out vapour pressure depression measurements at 0 °C. The vapour pressure depressions obtained over a wide range of concentrations are shown in Table 7.4 and Fig.7.2. Comparison of the vapour pressure depressions produced by mercury cyanide at 0 °C with those obtained for KF and XeF_2(Chapter IV) gives a ν value of 1.4, which is reasonably constant over the concentration range. Since this value of ν is for solutions considerably more concentrated than those used in the cryoscopic work, the agreement between the ν values is remarkably good and shows that ν is not appreciably dependent on the temperature and concentration.

TABLE 7.1

FREEZING-POINT DEPRESSIONS ON 'COLD' MERCURY CYANIDE SOLUTIONS

(Solute dissolved below -70 °C.)

T_o = -83.585 °C.

m	ΔT °C
0.0504	0.087
0.1167	0.172
0.1848	0.301
0.2669	0.429
0.2906	0.490
0.3886	0.585

ν value = 1.03.

TABLE 7.3

FREEZING-POINT DEPRESSIONS ON '0 °C' MERCURY CYANIDE SOLUTIONS

(Solute dissolved at 0 °C)

T_o = -83.570 °C

m	ΔT°C	ν
0.0377	0.085	1.45
0.0872	0.198	1.48
0.1613	0.326	1.43
0.2512	0.535	1.48
0.3082	0.626	1.44
0.3305	0.676	1.46

TABLE 7.2

THE VARIATION OF THE FREEZING POINT DEPRESSION OF A SINGLE $Hg(CN)_2$ SOLUTION WITH TIME

Concentration of solution = 0.3305

Approx. age of solution. (Discounting time frozen)	Time maintained at given temperature before f.pt. was taken.	ΔT °C	ν
Fresh	-70 ° fresh solution	0.478	1.01
Warming to 0°C allowed			
1 hour	+ 2° for 45 mins.	0.678	1.43
2 hours	0° for 70 mins.	0.678	1.43
3 hours	0° for 40 mins.	0.678	1.43
3½ hours	-80° for 30 mins.	0.675	1.43
16 hours	0° for 12 hours	0.677	1.43
Solution allowed to warm > 0°C			
30 hours	+20° for 12 hours	0.741	1.58
42 hours	+20° for 12 hours	0.824	1.74
4 days	+20° for 2 days	0.910	1.92
1 week	+20° for 3 days	0.930	1.97

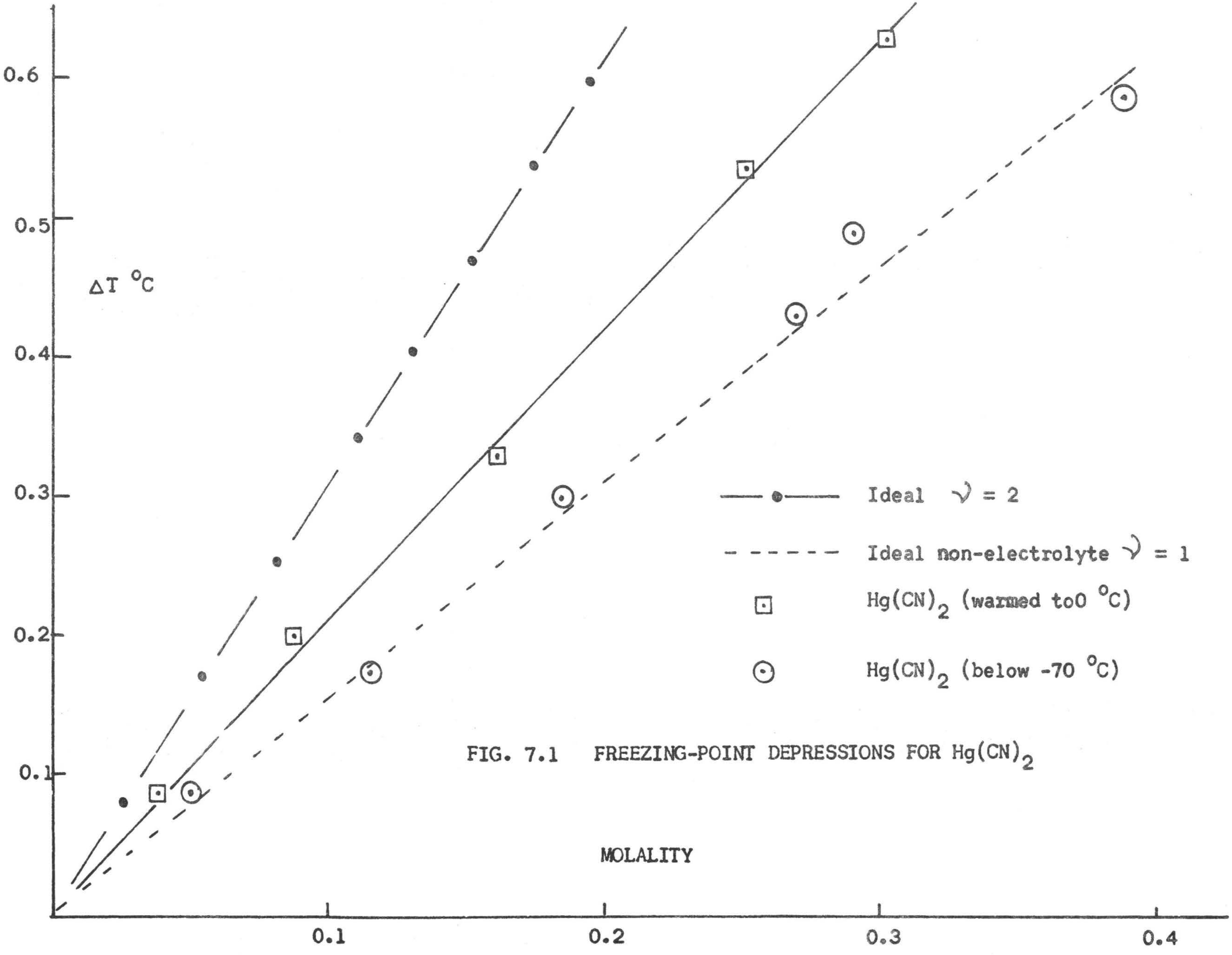


FIG. 7.1 FREEZING-POINT DEPRESSIONS FOR $Hg(CN)_2$

TABLE 7.4

VAPOUR PRESSURE DEPRESSION FOR MERCURY CYANIDE AT 0 °C.

m	ΔP mm. $\pm$ 1mm.
1.16	41.8
1.35	48.3
1.76	56.5
1.97	64.5
2.26	75.4
2.92	88.7
3.29	110.0
3.51	127.0

TABLE 7.5

CONDUCTIVITY FOR MERCURY CYANIDE ($ohm^{-1}cm^{-1} \times 10^{-4}$)

m	Conductivity at 0 °C	Conductivity at -83.6°C
0.021	46.2	-
0.049	74.2	-
0.088	116.0	-
0.141	173.0	38.5
0.200	227.0	51.0
0.300	312.0	65.9
0.390	371.0	81.2
0.544	473.0	101.0
0.951	697.0	151.0

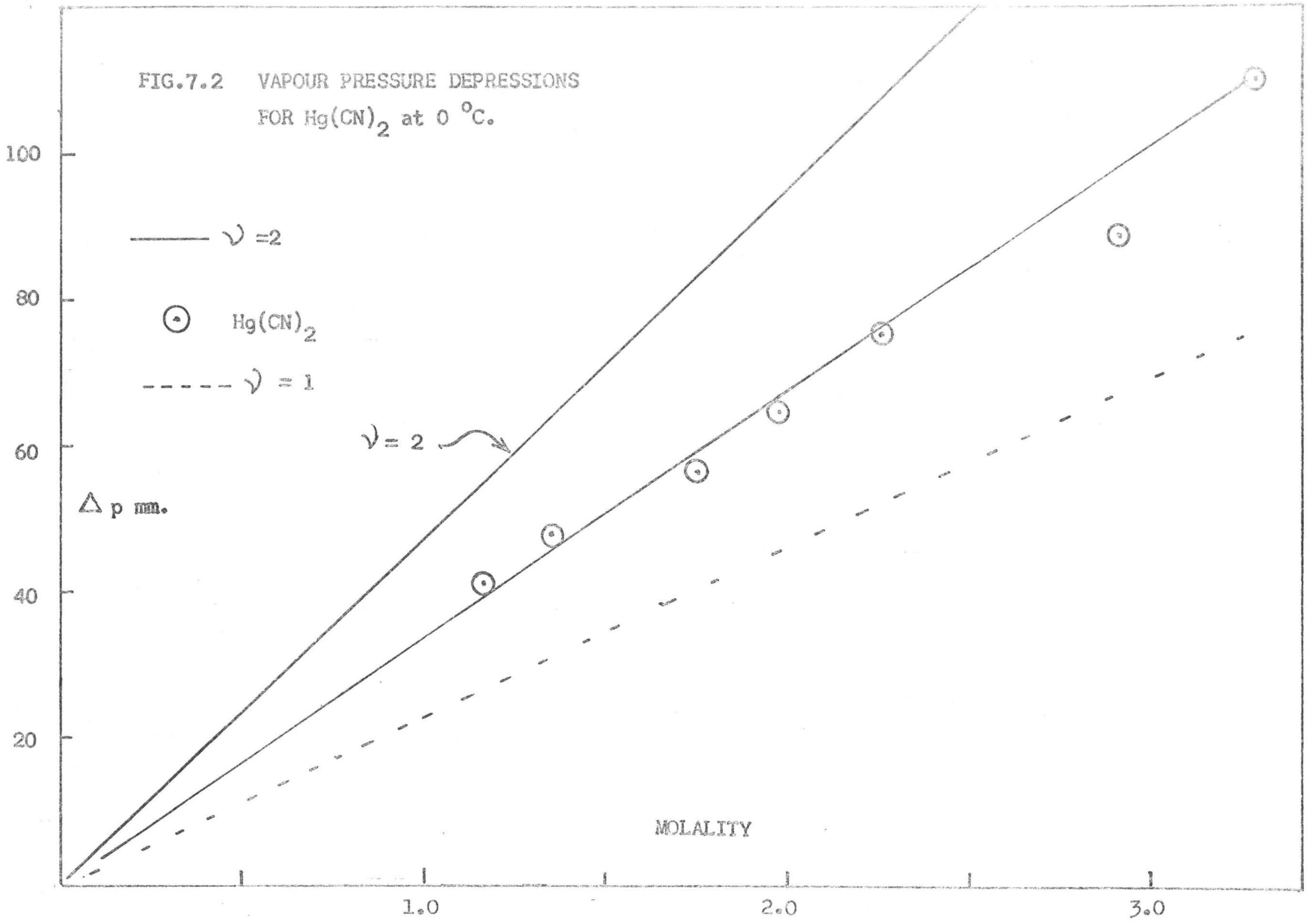


FIG.7.2 VAPOUR PRESSURE DEPRESSIONS FOR $Hg(CN)_2$ at 0 °C.

The ν value of unity indicated by the first data (Table 7.1 and Fig.7.1) indicates that mercury cyanide initially dissolves either as unionized molecules, or that polymeric ions are produced according to an equation such as:

$$2Hg(CN)_2 + 2HF \longrightarrow [Hg(CN)_2]_2 H^+ + HF_2^- \quad \ldots\ldots\ 7.2$$

It was difficult to make up cold fresh solutions of $Hg(CN)_2$ in small cells to measure the conductivity of a uniform solution without allowing it to warm above -80 °C. The conductivities that were measured however, were less than 0.1 of an equimolar KF solution at -80 °C. Thus the formation of the protonated polymer as in equation 7.2 is unlikely, since this would give a conductivity 0.5 of that of an equimolar KF solution. The low ionic concentration shown by conductivity measurements suggests that in sufficiently cold solution mercury cyanide dissolves initially as unprotonated monomeric molecules. Values of ν of 1.45 for solutions which had been warmed to 0 °C indicated that the solute is behaving as a weak base, but the data are not consistent with the equilibrium:

$$Hg(CN)_2 + 2HF \rightleftharpoons Hg(CN)_2H^+ + HF_2^-$$

because constant values for the equilibrium constant for such a process are not obtained. Data on acetonitrile discussed in Chapter V makes it clear that we would not expect this constant ν value for the simple protonation process.

These solutions corresponding to a ν of 1.45 were found to conduct at all temperatures between 0 and -83.6 °C (Table 7.5and Fig.7.3) but to a lesser extent than KF. Comparison of the conductivity of $Hg(CN)_2$ with KF over the temperature range 0 to -83 °C confirms the conclusions reached by comparing the cryoscopic and vapour pressure data, i.e. that the nature of the solution does not change over this temperature range. Such comparisons can be used to determine the number of HF_2^- ions produced per mole of solute, which will be called γ. However the interpretation of conductivity data to determine such γ values is more difficult in HF than in solvents such as H_2SO_4 and HSO_3F where cations other than those from the self dissociation of the solvent have a comparatively low mobility (35 ,118). The determination of γ, in this case the number of HF_2^- ions produced per mole of $Hg(CN)_2$, depends on making conductivity measurements on an appropriate standard electrolyte which has a cation of approximately the same mobility as the cation derived from mercury cyanide. On size considerations it is reasonable to assume that the mobility of the

TABLE 7.6

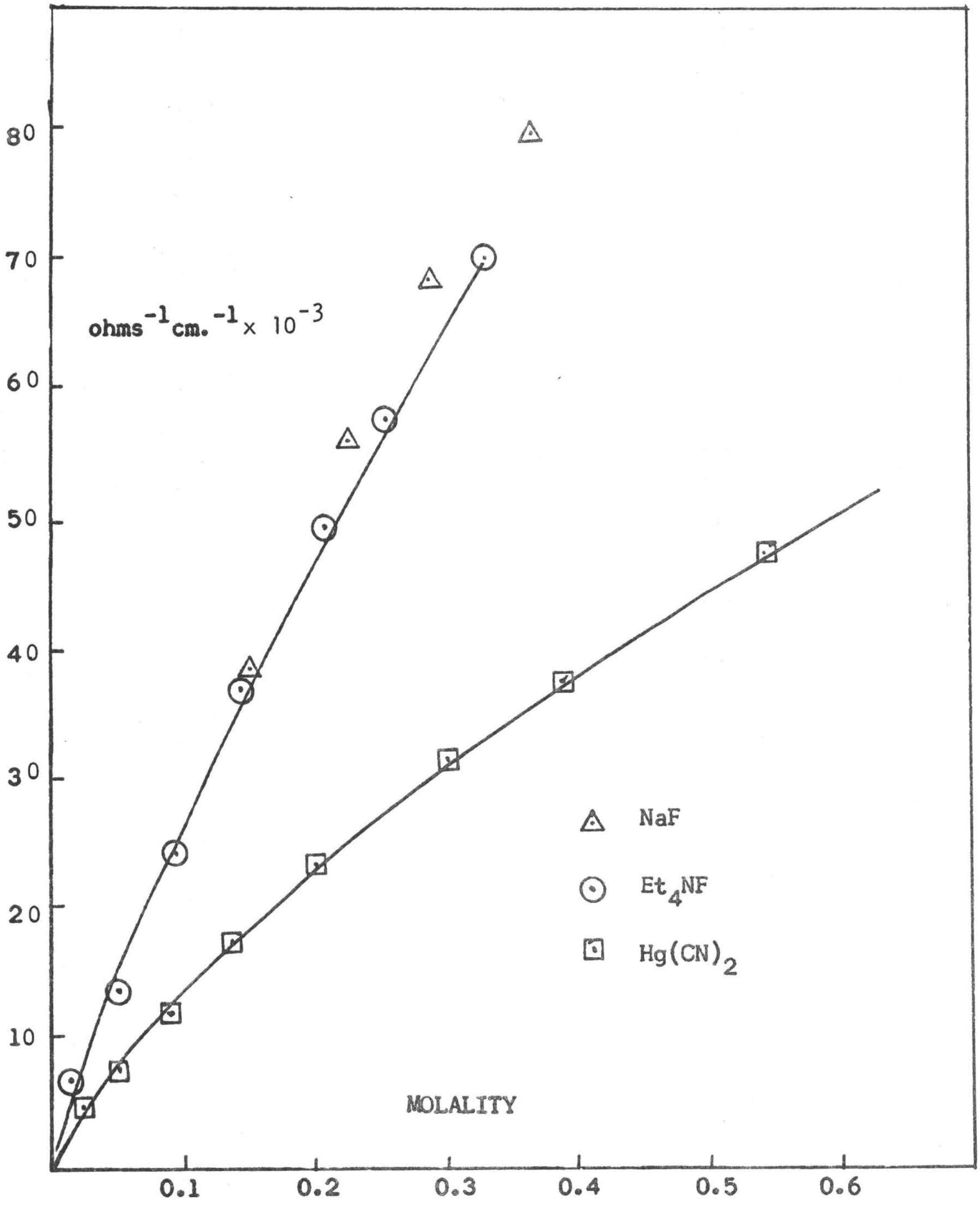
CONDUCTIVITIES OF FLUORIDES IN HF($ohm^{-1}cm^{-1} \times 10^{-4}$)

NaF			Et_4NF	
m	Conductivity 0 °C	Conductivity -83.6 °C	m	Conductivity 0 °C
0.150	375	87.5	0.017	64.4
0.226	555	125	0.050	138
0.285	678	155	0.096	244
0.364	796	186	0.144	363
0.443	900	203	0.213	492
0.534	1080	258	0.254	575
0.722	1296	322	0.329	700

REPRESENTATIVE γ VALUES FOR $Hg(CN)_2$

m	γ
0.05	0.47
0.10	0.45
0.20	0.43
0.30	0.41
0.40	0.39
0.50	0.37
0.54	0.37

FIG.7.3 CONDUCTIVITY OF $Hg(CN)_2$ AT 0 °C



tetraethylammonium cation Et_4N^+ is comparable with that derived from mercury cyanide and hence Et_4NF can be used as a suitable electrolyte with which to compare the mercury cyanide conductivity data. The conductivity data for Et_4NF is shown in Table 7.6, together with the ratio of the conductivities of Et_4NF and $Hg(CN)_2$ giving the γ values over the concentration range studied. This data supports the conclusion reached from cryoscopy and vapour pressure measurements that $Hg(CN)_2$ exhibits weak base behaviour but the process is not a simple protonation.

In order to explain the γ values increasing to ~ 0.5 at low concentration and the constant ν value of 1.45 for these solutions the following process involving the formation of the polymeric cation $Hg_2CN_3^+$ is suggested:

$$2Hg(CN)_2 + 2HF \rightleftharpoons Hg_2CN_3^+ + HCN + HF_2^- \quad \ldots\ldots\ldots \; 7.3$$

At completion this scheme gives a ν value of 1.5 and a γ value of 0.5. In order to obtain support for the suggestion given in equation 7.3 , a cryoscopic study of sodium cyanide was carried out to establish whether HCN was completely soluble as unprotonated molecules in HF, or if the lone pair on the nitrogen makes HCN basic enough to be protonated in HF.

Cryoscopy on sodium cyanide solutions.

Sodium cyanide dissolves readily in HF. Cryoscopy on the solutions can be used to distinguish between the following two possible modes of ionization:

$$NaCN + 2HF \longrightarrow Na^{+} + HCN + HF_2^{-} \quad \ldots\ldots\ldots 7.4$$

$$NaCN + 4HF \longrightarrow Na^{+} + HCNH^{+} + 2HF_2^{-} \quad \ldots\ldots 7.5$$

Values of ν of 3 and 4 would be expected for the reactions given in equations 7.4 and 7.5 respectively. The cryoscopic data for sodium cyanide is summarized in Table 7.7 and Fig 7. 4. A mean ν value of 2.94 is found for the sodium cyanide solution, by making comparisons with the sodium fluoride data. Hence we conclude that HCN is soluble in HF as a non-electrolyte as shown in equation 7.4. This conclusion is confirmed by the fact that solutions of HCN in HF are non-conducting(117). The ^{19}F n.m.r. spectrum of HCN in HF shows no peaks apart from that due to solvent even when cooled to -90 °C. Dove and Hallett(117) found only a single line in the proton n.m.r. in addition to that of the solvent. The chemical shift of this line with respect to external T.M.S. varies slightly with concentration and temperature and the line has been assigned to HCN(117). Dr.R. Hulme of this laboratory, used quantitative n.m.r. to estimate the

TABLE 7.7

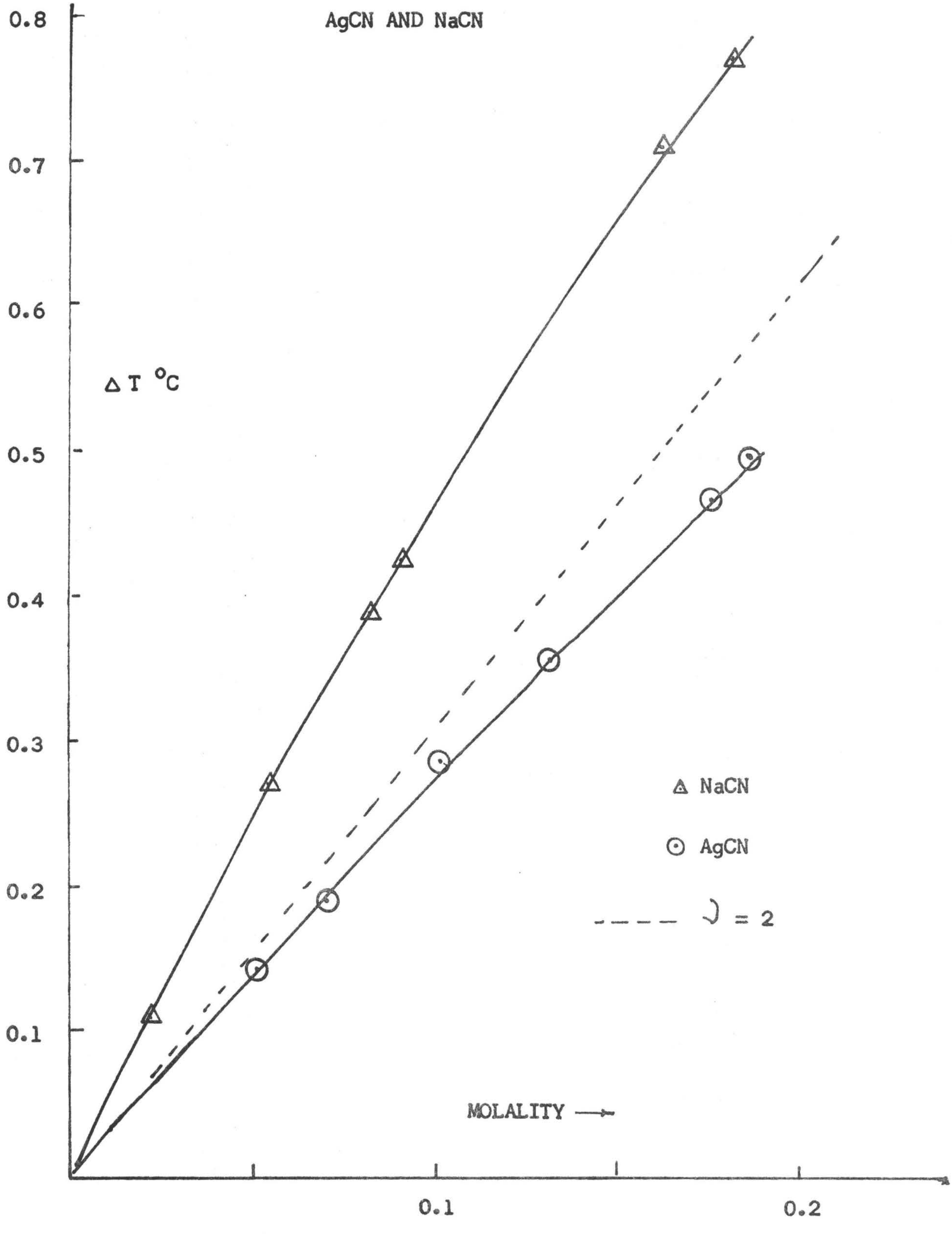
FREEZING-POINT DEPRESSIONS FOR SODIUM CYANIDE SOLUTIONS

$T_o = -83.588$

m	ΔT °C
0.0219	0.110
0.0563	0.270
0.0837	0.390
0.0925	0.425
0.1634	0.710
0.1717	0.770
0.2680	1.140

ν value = 2.95

FIG. 7.4 FREEZING-POINT DEPRESSIONS ON SOLUTIONS OF AgCN AND NaCN



amount of HCN produced when $Hg(CN)_2$ is dissolved in HF, by making comparison solutions containing small known amounts of Me_4NBF_4 and integrating the peaks. The results indicate approximately 0.5 molecules of HCN are produced per molecule of $Hg(CN)_2$. Since we have shown that HCN dissolves unprotonated, this result provides further support for equation 7.3.

Raman Spectra.

Raman spectra were obtained for solutions of mercury cyanide in water and in anhydrous HF. The spectrum in water showed only three strong bands at 416 cm^{-1}, 1652 cm^{-1} and 2206 cm^{-1}, which have been assigned to Hg-C, H_2O and -CN respectively. When mercury cyanide was dissolved in anhydrous HF, fresh solutions gave rise to a much more complicated Raman spectrum in which at least twelve bands could be distinguished as shown in Table 7. 8. The appearance of two strong bands and additional weaker ones in the region ~ 400 - 700 cm^{-1} characteristic of Hg-CN, is consistent with the formationof the polymeric cation. However unambiguous assignments of the bands in the -CN stretch region was not possible due to the presence of HCN. The spectrum of HCN in HF could not be obtained because the solution either boiled when placed in the laser beam or fluoresced at low temperature.

TABLE 7.8

RAMAN SPECTRA OF $Hg(CN)_2$ IN HF

(cm.$^{-1}$)		(cm^{-1})	
204	w	1053	w
266	w	1211	m
348	w	1299	m
391	mw	2104	mw
453	s	2169	mw
648	w	3207	Broad
672	s		

Infrared Spectra.

Poorly resolved infrared spectra in the - C N region were obtained by R.Hulme of this laboratory from solutions of mercury cyanide in HF. Three bands at 2130 cm.$^{-1}$, 2245 cm.$^{-1}$ and 2260 cm.$^{-1}$ were observed. Dove and Hallett(117) have shown that a solution of HCN in HF absorbs at 2138 cm.$^{-1}$. The other two bands at 2245 and 2266 cm.$^{-1}$ are at a higher frequency than that shown by $HgCN_2$, which absorbs at 2190 cm.$^{-1}$. Since the cyanide stretching frequencies for metal cyanide complexes generally increase as the co-ordination number of the metal atom decreases(119) the two higher frequencies observed for solutions in HF are consistent with a species in which the Hg:CN ratio is more than 1:2, as in the polymeric cation proposed.

All this evidence is consistent with the equilibrium postulated in equation 7.3 going to completion at low concentration of mercury cyanide. It should be recalled that cryoscopic data showed that mercury cyanide initially goes into solution as molecules before any formation of a polymeric cation and loss of HCN, therefore the following is suggested as the course of the overall reaction leading to the formation of $Hg_2(CN)_3^+$:

$$Hg(CN)_2 + 2HF \rightleftharpoons Hg(CN)_2H^+ + HF_2^-$$

$$Hg(CN)_2H^+ \longrightarrow HgCN^+ + HCN$$

$$HgCN^+ + Hg(CN)_2 \longrightarrow Hg_2CN_3^+$$

It is not surprising that we do not find any Hg-F complexes or free Hg^{2+} in solution in view of the low solubility found for HgF_2 in HF. The species $HgCN^+$ suggested above as arising during the course of the reaction has been suggested in aqueous systems by several workers. For example Asperger and Pavlovik(120) suggested $HgCN^+$ as an intermediate in the reaction between mercuric and ferrocyanide ions in a study of the catalytic action of Hg^{II} ions in the reaction between potassium ferrocyanide and nitrobenzene. In a similar study Emschwiller(121) has suggested $HgCN^+$ as an intermediate in the catalytic process, and Peschanski(122) in an isotopic exchange study on Hg^I and Hg^{II} in water gave an equilibrium constant of 9 for the process:

$$Hg^{2+} + Hg(CN)_2 \rightleftharpoons 2Hg(CN)^+$$

In the HF system R. Hulme of this laboratory has precipitated adducts of the composition $HgCN.BF_4$ by adding BF_3 to solutions of mercury cyanide in HF and has also shown that the conductivity of mercury cyanide in HF decreases when HCN is introduced. Both these observations are consistent with the equilibrium proposed for the formation of the polymeric cation involving $HgCN^+$. The reduction in the conductivity of solutions of mercury cyanide in HF on adding HCN presumably means that there is a species in solution with such a strong affinity to cyanide that it adds on CN^-, converting F^- to HF.

The polymeric cation proposed when mercury cyanide dissolves in HF presumably has the linear structure $\mathrm{N{\equiv}C{-}Hg{-}C{\equiv}\overset{+}{N}{-}Hg{-}C{\equiv}N}$ The final decomposition of the solutions after several days was not investigated in detail. Since HgF_2 is almost completely insoluble, the value of 2 for ν, found after decomposition of the warm solution, presumably represents the overall process:

$$\mathrm{Hg(CN)_2 + 2HF \longrightarrow HgF_2\downarrow + 2HCN}$$

Silver Cyanide.

Klatt(55) attempted to make boiling point elevation measurements on silver cyanide but reported that it did not have sufficient solubility to allow reliable ebullioscopic measurements. We found that the solubility of silver cyanide is in fact dependent on the purity of the HF. For acid of conductivity 10^{-3} $\mathrm{ohms^{-1}\ cm^{-1}}$ taken straight from a commercial cylinder, the solubility at the freezing point was less than 0.1 molal. However, using carefully fractionated HF, having a conductivity of 10^{-5}ohms^{-1}cm^{-1}, the solubility limit at the freezing point was not reached although measurements were made up to 0.2 molal. Presumably the solvent of higher conductivity is less acidic because of the presence of the strong base H_2O, as discussed in Chapter IV; hence this result suggests that AgCN dissolves by protonation.

During the course of our investigation Dove and Hallett(117) reported on the n.m.r. and infrared behaviour of silver cyanide in HF, and gave a solubility of at least 3.2 molar solution at 20 °C. These workers reported that they obtained stable solutions which had conductivities very similar to an equimolar solution of KF at 0 °C. Proton n.m.r. of silver cyanide solutions in HF showed 1 protonated CN group per AgCN. The infrared spectrum of AgCN in HF showed absorption at 2147 cm.$^{-1}$ with a shoulder at 2138 cm.$^{-1}$. The relative intensity of these bands was shown by Dove and Hallett to alter with the HCN:Ag^+ ratio in the solution. The band at 2147 cm.$^{-1}$ is strongest at a ratio of 2:1, with the shoulder at 2138 cm.$^{-1}$ increasing at ratios of HCN:Ag^+ exceeding 2:1. This shoulder was assigned to free HCN when HCN:$Ag^+ >$ 2:1. On the basis of this evidence Dove and Hallett proposed that AgCN dissolved in HF in the following way:

$$\begin{gathered}\mathrm{AgCN} + 2\mathrm{HF} \rightleftharpoons \mathrm{HCNAg}^+ + \mathrm{HF}_2^- \\ 2\ \mathrm{HCNAg}^+ \rightleftharpoons (\mathrm{HCN})_2\mathrm{Ag}^+ + \mathrm{Ag}^+\end{gathered} \qquad \ldots\ldots\ldots 7.6$$

assigning the band 2147 to $(\mathrm{HCN})_2\mathrm{Ag}^+$ and assuming that the shoulder at 2138 $\mathrm{cm.}^{-1}$ was due to HCNAg^+ when ratio HCN : Ag $<$ 2:1 but due to uncomplexed HCN when the ratio HCN : $\mathrm{Ag}^+ >$ 2:1. They calculated that the solution of AgCN contained 40.5% of the silver as the ion $(\mathrm{HCN})_2\mathrm{Ag}^+$.

The proposal by Dove and Hallett for silver cyanide corresponds to a ν value of 2 wherever the equilibrium lies. Thus cryoscopic measurements cannot be used to determine the position of equilibrium of the reaction. The freezing point data for silver cyanide in HF is shown in Table 7.8 and Fig.7.4. The ν value of 1.8 for silver cyanide clearly rules out the possibility that silver cyanide goes into solution in a way analagous to that found for NaCN, i.e.

$$\mathrm{AgCN} + 2\mathrm{HF} \longrightarrow \mathrm{HCN} + \mathrm{Ag}^+ + \mathrm{HF}_2^-$$

The cryoscopic data could be interpreted in terms of incomplete protonation of AgCN. However it is in general agreement with the conclusions reached by Dove and Hallett, although the observation that ν is less than 2 suggests the possibility that the dissociation of AgF is incomplete.

TABLE 7.9

FREEZING-POINT DEPRESSIONS ON SILVER CYANIDE SOLUTIONS

$T_o = -83.570\ ^{\circ}C$

m	$\Delta T\ ^{\circ}C$
0.0525	0.140
0.0715	0.189
0.1046	0.288
0.1324	0.355
0.1766	0.465
0.1882	0.493

ν value = 1.8

TABLE 7.10

FREEZING-POINT DEPRESSIONS ON SILVER FLUORIDE SOLUTIONS

$T_o = -83.58\ ^{\circ}C$

m	$\Delta T\ ^{\circ}C$	ν	K_b
0.0531	0.145	1.77	0.14
0.1024	0.261	1.69	0.16
0.1317	0.321	1.64	0.15
0.1403	0.334	1.64	0.16

The formation of some complex species such as AgF_2^- would account for the incomplete dissociation. However, work by McCaulay and Lien(123) on the reaction of arenes with AgF in anhydrous HF indicate that AgF dissolves in HF as a base, decreasing the acidity of the HF and inhibiting acid catalyzed reactions. Thus AgF is unlikely to act as a fluoride acceptor and form AgF_2^-. The early conductivity data of Klatt on AgF in HF indicated that solutions of AgF had almost as great a conductivity as KF. This has been interpreted as strong base behaviour according to the equation:

$$AgF + HF \longrightarrow Ag^+ + HF_2^-$$

In order to determine the extent of the association between Ag^+ and F^-, cryoscopic measurements on AgF were undertaken. AgF is a difficult compound to obtain in a high state of purity. Thermal decomposition of $AgBF_4$ at 200 °C has been shown to be a reliable method (124) and gave a pale yellow-orange sample of AgF. The freezing point data given by this AgF is shown in Table 7.10. The data confirms the indications of the AgCN experiment that AgF is not fully ionized as a base in HF. The basic dissociation constant was found to be ~ 0.15. The value is slightly higher than that given by Clifford et.al.(125) from E.M.F. measurements in the system, Ag(s) AgF,TIF(HF) TIF_3(s)(Pt); which was 0.087 at 0 °C, but considering the temperature difference the agreement is reasonable. The ν value predicted for the process 7.6, i.e. AgCN dissolving in HF, by the ν of 1.7 for AgF is $\sim$ 1.85 in reasonable agreement with that found experimentally.

CHAPTER VIII

SOLVOLYSIS REACTIONS

The major emphasis of this work has been on the application of colligative measurements to those solutes which involve either acidic or basic ionization or give rise to polymeric ions in solution. There are however, a number of solutes that undergo solvolysis whose behaviour in HF is incompletely understood, the overall reactions frequently being time or temperature dependent. This chapter reports on some preliminary investigations on solutes of this type and indicates the way in which the techniques developed in this project may be used in more detailed and comprehensive studies of such solutions.

The cryoscopic and vapour pressure measurements are particularly useful in combination in cases where the reaction involves a slow solvolysis, since a comparison of ν values at -83 °C and at 0 °C is then possible.

Solutions of Sulphates.

Solutions of K_2SO_4 in HF were investigated by Fredenhagen in the 1930's (40,51). His boiling point data indicated that K_2SO_4

dissolved in HF with a ν of 6, and he interpreted his results in terms of four ions per "molecule" of K_2SO_4. The ionization scheme suggested on the basis of these results was:

$$K_2SO_4 + 4HF \longrightarrow 2K^+ + HSO_3F + H_3O^+ + 3F^- \quad ......8.1$$

although obviously this is not in agreement with the experimental observations. In a recent review article Kilpatrick and Jones(6) have drawn attention to discrepancies in the early conductivity and boiling point data on K_2SO_4 and concluded that "further investigation of this system is needed".

Table 8.1 shows that the freezing point of K_2SO_4 is essentially constant when the solution has been maintained at room temperature for a period of a week, with a ν value of 5. The freezing point depressions obtained for different concentrations of K_2SO_4 are also given in Table 8.1 and give a ν value of 5 over the concentration range studied, i.e. up to 0.15 molal. In this concentration range errors due to deviations from ideality are probably small. The cryoscopic data for K_2SO_4 is consistent with the reaction:

$$K_2SO_4 + 2HF \longrightarrow 2K^+ + H_2SO_4 + 2HF_2^- \qquad (\nu = 5)$$

In view of the higher ν values reported by Fredenhagen from

TABLE 8.1

FREEZING-POINT DEPRESSIONS OF POTASSIUM SULPHATE

EXPERIMENT I

Concentration = 0.1604 molal $T_o = -83.59$ °C

History of Solution	ΔT °C
16 hours at room temperature	1.25
27 hours at room temperature	1.29
5 hours at -50 °C	1.25
1 week at room temperature	1.28

EXPERIMENT II

m	ΔT °C
0.063	0.51
0.083	0.65
0.083 (by re-dilution)	0.64
0.116	0.88
0.153	1.18

$\nu = 5$ at -83 °C.

the boiling point data the possibility of further solvolysis of H_2SO_4 was investigated. Vapour pressure depression measurements obtained at 0 °C, are shown in Table 8.2 and Fig.8.2. The solutions were allowed to stand for 2 - 3 hours before the vapour pressure depressions were measured. The vapour pressure depressions plotted in Fig.8.2 have a slope three times that given by KF, indicating a ν value of 6 in agreement with that reported on the basis of boiling point measurements. This increase in ν at the higher temperature of these measurements may be due to solvolysis of H_2SO_4 according to :

$$H_2SO_4 + 3HF \longrightarrow H_3O^+ + HSO_3F + HF_2^- \quad \ldots\ldots\ldots\ldots 8.2$$

This possibility was investigated by making freezing point measurements on H_2SO_4 in HF, and by obtaining a ^{19}F n.m.r. spectrum from solutions of K_2SO_4 in HF.

The first n.m.r. spectrum was obtained from a solution which had been maintained at temperatures below -60 °C. The spectrum was repeated after the solution had warmed up to room temperature. Finally the spectrum was run a third time after the same solution had been cooled to -50 °C. For the spectrum at -70 °C a small peak at approximately 233 p.p.m. from the solvent line was observed. This small peak

TABLE 8.2

VAPOUR PRESSURE DEPRESSIONS FOR K_2SO_4 SOLUTIONS AT 0 °C.

V.P. of HF = 364 mm.

m	ΔP.(mm.)
0.081	11
0.151	20
0.256	40
0.365	52
0.469	68

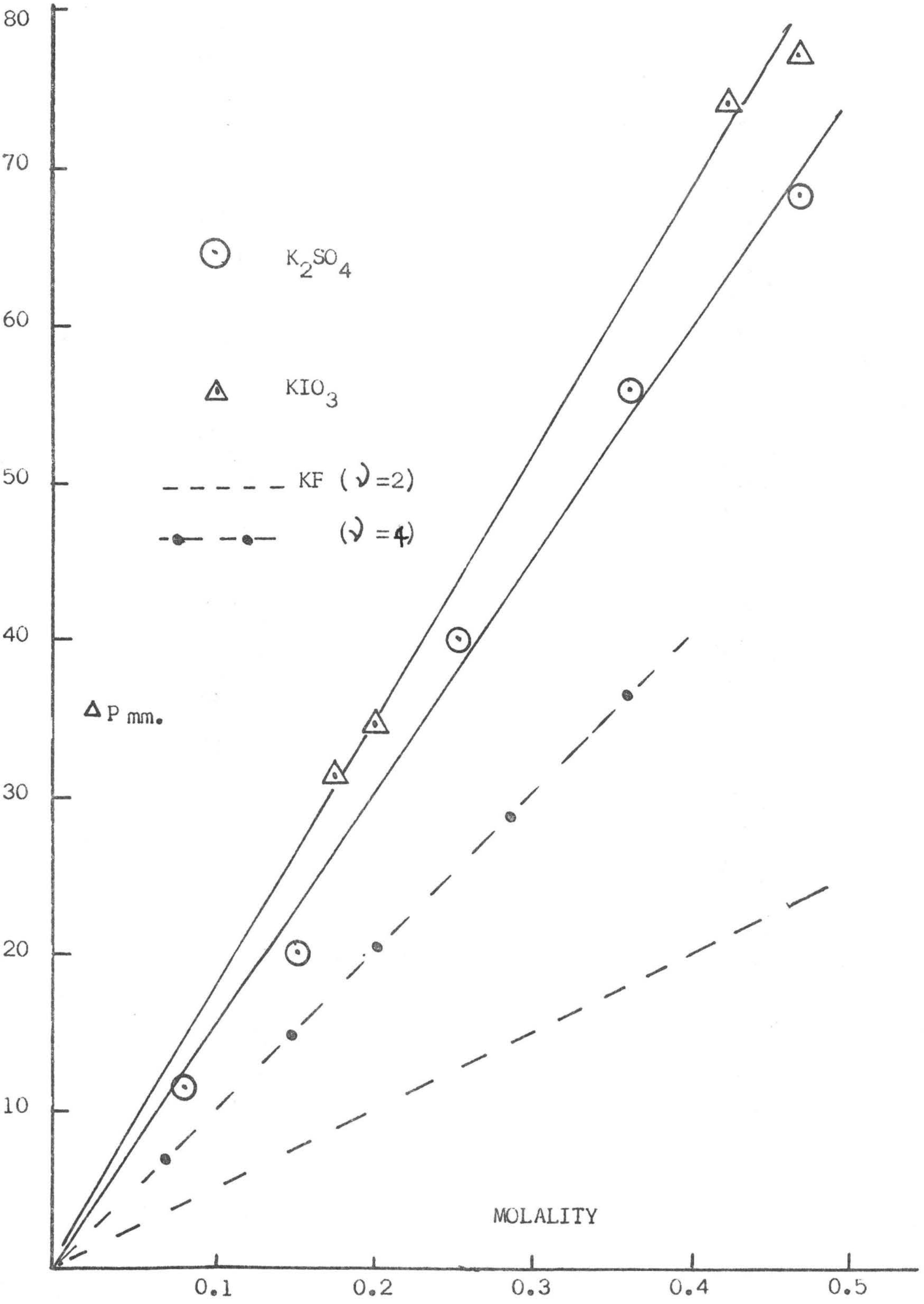
ν = 6 at 0 °C.

TABLE 8.3

FREEZING-POINT DEPRESSIONS FOR SOLUTIONS OF 100% H_2SO_4

Max. warm up.	m	ΔT °C	ν
-40 °	0.0524	0.086	1.05
-20 °	0.0921	0.152	1.06
+20 °	0.1931	0.340	1.13
+20 °	0.1931 (after 8 hours)	0.345	1.15

FIG. 8.2 VAPOUR PRESSURE DEPRESSIONS FOR KIO_3 AND K_2SO_4



increased markedly in size when the spectrum was run at room temperature In the third spectrum at -50 °C the line decreased again but not to the original small signal size. The single line with chemical shift -42 p.p.m. with reference to external $CFCl_3$, was assigned to HSO_3F on the basis of comparison with a standard solution of HSO_3F in HF. This experiment confirmed that a temperature dependent endothermic equilibrium process producing fluorosulphuric acid was involved and is consistent with equation 8. 2.

Some freezing point data for solutions of 100% sulphuric acid in HF is shown in Table 8.3. The data indicates that in fresh solutions H_2SO_4 is essentially unionized in HF at low temperature. The amount of solvolysis detected at the freezing point was small since ν increased to only 1.15 over a period of 8 hours. It has been shown previously (Chapter V) that any HSO_3F produced would be expected to remain unionized in solution. Thus all the evidence to date is consistent with the initial formation of H_2SO_4 at the freezing point which at higher temperature undergoes solvolysis to form HSO_3F.

Solutions of Iodates.

Solutions of iodates are of particular interest since they may give rise to new oxy- and fluoro- anions containing iodine. For example plausible solvolysis reactions for KIO_3 are:

(1) $KIO_3 + 4HF \rightarrow K^+ + IO_2F_2^- + H_3O^+ + HF_2^-$ ($\nu = 4$)

(2) $KIO_3 + 7HF \rightarrow K^+ + IOF_4^- + 2H_3O^+ + 2HF_2^-$ ($\nu = 6$)

(3) $KIO_3 + 10HF \rightarrow K^+ + IF_6^- + 3H_3O^+ + 3HF_2^-$ ($\nu = 8$)

All these possibilities should be distinguishable by colligative techniques. Conductivity measurements made in this laboratory by Winfield(126) on solutions of iodates showed that the solutions were strongly conducting and that there is some increase in conductance with time. Fresh solutions gave γ values of ~ 2, increasing somewhat with time. Some colligative data on solutions of potassium iodate have been obtained in this investigation. Freezing point and vapour pressure depressions are shown in Table 8.4. All these measurements were made 2 - 3 hours after the preparation of the solutions. Both the vapour pressure at 0 °C and the freezing point appear to give a constant ν of ~ 7. This suggests that during this time solvolysis had proceeded at least to the stage represented by equation (2) and probably to some extent according to equation (3).

These preliminary results are consistent with the suggestion that extensive solvolysis of iodates occurs as indicated above. The

TABLE 8.4

FREEZING-POINT AND VAPOUR PRESSURE DEPRESSIONS FOR SOLUTIONS OF POTASSIUM IODATE.

Freezing-Point Depressions. $T_o = -83.59\ ^oC$

m	$\Delta T\ ^oC$	ν
0.109	1.16	6.9
0.153	1.61	6.9
0.207	2.14	6.8
0.299	3.12	6.8

Vapour Pressure Depressions at 0 ^oC.

m	ΔP (mm.)
0.175	31.5
0.201	35
0.413	74
0.477	77

ν value from vapour pressure = 7.1

application of the techniques developed during the course of this work should, when used in conjunction with conductance and spectroscopic measurements, enable a detailed elucidation of the nature of these interesting solvolysis reactions.

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