STUDIES OF CERTAIN PHYSICAL PROPERTIES OF THE HALOGEN FLUORIDES AND THEIR HYDROGEN FLUORIDE SOLUTIONS

By

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I INTRODUCTION

The tremendous post-war growth in the field of fluorine chemistry as a result of the increasing use and availability of fluorocarbons, halogen fluorides, and inorganic fluorides, both in industry and in the program of the Atomic Energy Commission, has created an increasing interest in the physical properties of the halogen fluorides and the various halogen fluoride systems.

A detailed study of the physical properties of the halogen fluorides was considered to be in order, and therefore the design and construction of equipment for the handling, purification and study of the halogen fluorides and their hydrogen fluoride solutions was undertaken. As will be described in detail in this work, studies were made of the magnetic susceptibilities of certain pure halogen fluorides. Conductance, cryoscopic and vapor pressure studies of the hydrogen fluoride solutions of these compounds were also made.

No previous work has been reported on the magnetic susceptibilities of these compounds. The electrical conductivities of the halogen fluorides have been measured using material of unknown purity but no data have been reported for the conductances of the hydrogen fluoride solutions of the halogen fluorides. There are some cryoscopic data on the pure compounds and on binary systems of bromine trifluoride and certain metallic salts, but none on the hydrogen fluoride solutions of the halogen fluorides. Vapor pressure data are available for the pure halogen fluorides, but not for their hydrogen fluoride solutions.

The extremely high reactivity of the halogen fluorides made the use of special handling methods and highly resistant materials necessary. In this work full use was made of the resistant properties of Monel[*], nickel, fluorinated polyethylene plastics, and quartz.

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[*] Trade mark of the International Nickel Company

II HISTORICAL SUMMARY

A. The Halogen Fluorides

Although our knowledge of the properties of the halogen fluorides has made significant strides since the end of World War II, these compounds have been known for some time. Kammerer[1] probably prepared iodine pentafluoride as early as 1862, but the preparation was placed on a practical basis by Moissan.[2] The major share of the early work on the halogen fluorides was done by Ruff and his co-workers who either discovered, or improved upon, the preparation of seven of the compounds, and studied many of their physical and chemical properties.[3-11]

There are seven known stable halogen fluorides, namely chlorine monofluoride, chlorine trifluoride, bromine monofluoride, bromine trifluoride, bromine pentafluoride, iodine pentafluoride, and iodine heptafluoride. Many of their physical properties are already known. There are several good reviews on the subject[12-14] and a chapter by Booth and Pinkston has been devoted to these compounds in Simons' Fluorine Chemistry.[15a]

This dissertation is primarily concerned with cryoscopic, conductance, and vapor pressure studies of the halogen fluorides and their hydrogen fluoride solutions, and magnetic susceptibilities of the purified halogen fluorides. Only work which is related to these topics will be discussed here.

The cryoscopic data which are available for the halogen fluorides are limited almost exclusively to the compounds themselves, and do not, in general, extend to their systems with other substances. Often, the only information available, other than data obtained in this laboratory, is the original data of Ruff and his co-workers.

Eutectic points at 3.1 and -0.4° C were observed by Haendler[17] for binary systems of bromine trifluoride with barium fluoride and sodium fluoride, respectively. The freezing points reported in the literature for the halogen fluorides are given in Table I.

The conductances of most of the halogen fluorides have been reported previously and the values obtained are shown in Table I. The conductances of bromine trifluoride and bromine pentafluoride have been reported to have negative temperature coefficients. This has been attributed, at least in the case of bromine trifluoride, to thermal instability of the ions.[18,19]

On the basis of the information available on the properties of iodine pentafluoride and bromine trifluoride as solvents,[20-22] the conductivities of these compounds have been attributed to the self-ionization equilibria

$$2BrF_3 = BrF_2^+ + BrF_4^-$$

and

$$2IF_5 = IF_4^+ + IF_6^-$$

The existence of compounds such as $KBrF_4$, KIF_6, $BrF_2[SbF_6]$, and $IF_4[SbF_6]$ lends support to this hypothesis.

Recently D. F. Smith[24] has shown that to a very small degree, a one-to-one complex, hydrogen fluoride-chlorine trifluoride ($HF \cdot ClF_3$), is formed in the vapor state. No evidence for complexes or intermediate

TABLE I

THE SPECIFIC CONDUCTANCES AND FREEZING POINTS OF THE HALOGEN FLUORIDES AND THEIR SOLUTIONS WITH OTHER COMPOUNDS AS REPORTED IN THE LITERATURE*

Compound	Freezing Point °C		Specific Conductance $ohms^{-1}cm^{-1}$	
ClF	-155.6	(6)	--	
ClF_3	-82.6	(10)	3×10^{-9} at ? °C	(13)
BrF_3	8.77	(16)	8.0×10^{-3} at 25°C	(18)
BrF_5	-61.3	(7)	8.5×10^{-7} at ? °C	(19)
IF_5	9.6	(9)	1.92×10^{-6} at 25°C	(12)
IF_7	6	(11)	--	
BrF_5 - HF (equimolar)	--		1×10^{-3} at ?°C	(19)
BrF_3 - KF	--		Increases markedly upon addition of KF	(18)
BrF_3 - SbF_5	--		Increases markedly upon addition of SbF_5	(18)
IF_5 - KF	--		Increases markedly upon addition of KF	(22)
IF_5 - KF	--		No noticeable change upon addition of KF	(12)
IF_5 - SbF_5	--		Increases markedly upon addition of SbF_5	(22)

* References are indicated in parentheses.

compounds was found in a study of the liquid-solid equilibria in the bromine-bromine trifluoride system;[25] liquid immiscibility and the absence of solid solution were observed.

The specific conductance of a single equimolar solution of bromine trifluoride-hydrogen fluoride was found by Hyman, Andrews and Katz[19] to be approximately 1×10^{-3} mho per centimeter. A negative conductance-temperature coefficient was observed with this solution.

There are no vapor pressure data available for halogen fluoride solutions of other compounds, and no magnetic susceptibility measurements have been reported on the halogen fluorides.

B. Hydrogen Fluoride

Hydrogen fluoride was first obtained by Marggraff in 1768[26] and first characterized in 1771 by Scheele.[27] It is prepared industrially by the reaction of sulfuric acid with fluorspar after which the reaction product is condensed and distilled. Highly purified hydrogen fluoride may be obtained from the decomposition of potassium bifluoride.

The physical properties of hydrogen fluoride have been studied rather extensively and there is an excellent review by Simons.[18b,18c]

Anhydrous liquid hydrogen fluoride resembles water and ammonia in its physical properties. Its boiling point is above that of hydrogen chloride just as the boiling points of water and ammonia are above those of hydrogen sulfide and phosphine, and its dielectric constant (83.6 at 0°C) is relatively high.[28] Simons[29] has reported that the liquid density is given as a function of temperature by the relation

$$d = 1.002 - .0022625t + .000003125t^2$$

where d is gm./ml. and t is the temperature in degrees Centigrade. The most recent vapor pressure data between 0° and 105°C are represented by either of the following relationships[30]

$$\log P = 8.38036 - \frac{1952.55}{353.52 + t}$$

or

$$\log P = 1.91173 - 918.24/t - 3.21542 \log t$$

where P is the vapor pressure in mm. of Hg and t is the temperature in degrees Centigrade.

The physical properties of hydrogen fluoride indicate that it is a most unusual liquid. Its high dielectric constant and ability to form very highly conducting solutions[18b] indicate that it is a polar liquid, yet its low viscosity (0.256 centipoise at 0°C) and low surface tension (10.1 dynes/cm. at 0°C)[30] indicate that the liquid is non-polar.

In the gaseous state hydrogen fluoride has been found to be a highly imperfect gas. Association occurs to a rather large extent and has been investigated by Simons[31] and others. There has been a considerable amount of dissagrement among the various workers as to which polymers are the most important. Some vapor density work seems to indicate that a six membered ring predominates, whereas dipole moment studies[32,33] and X-ray studies[34-36] seem to indicate a chain-like structure.

Recently Johnston[37] has measured the heat capacity, heat of fusion and heat of vaporization of hydrogen fluoride. No transitions such as are observed with the other hydrogen halides were found. The heat of fusion at the melting point (-83.37°C) was found to be 938.6 calories per mole. Johnston's melting point value is in slight disagreement with previously reported values of -83.07 and -83.0°C.[15b] Comparison of entropy values from heat capacity measurements and spectroscopic data showed a large discrepancy which was accounted for by assuming the gas to be a mixture of monomer, dimer, trimer, etc., as a consequence of hydrogen bonding. The recent spectroscopic work of D. F. Smith[24] seems to indicate, however, that at low temperatures only the hexamer is important in the vapor state, and that there is no evidence for polymers other than the tetramer and hexamer.

III PREPARATION AND HANDLING OF MATERIALS

The study of the halogen fluorides has increased greatly in the post-war period, partly as a result of the availability of materials which are highly resistant to the action of the halogen fluorides. The most important of these materials are fluorinated polyethylene plastics such as fluorothene and Teflon.*

In order to obtain the halogen fluorides in the pure form, it is necessary that they be separated in some manner from volatile and non-volatile impurities, and that they be stored in such a way that they do not become contaminated. The principal sources of contamination are usually corrosion products and decomposition products from the reaction with water vapor. In order to overcome the above difficulties a vacuum system, which has been described previously,[12] was constructed. This system, which is illustrated in Figure 1 and Plate 1, provided a means for fractional distillation of the impure halogen fluoride under its own pressure or in an inert atmosphere. It also provided a means of performing such operations as trap-to-trap distillations, vapor or liquid phase transfers, and preparation of hydrogen fluoride solutions of the halogen fluorides. The vacuum system was also provided with a tube containing cobaltic fluoride through which the hydrogen fluoride from the tank was passed in order to remove moisture.

In order to provide the maximum resistance to corrosion the vacuum line was constructed almost entirely of nickel and Monel except for the

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* E. I. duPont de Nemours and Co.

still head, storage containers and storage tubes which were constructed of fluorothene and Teflon. The valves were constructed of nickel, with phosphor-bronze bellows and fluorothene gaskets, except on the still take-off system where valve bodies constructed of fluorothene replaced those of nickel. In some places small valves containing brass bellows were used.

The general procedure for the purification of iodine pentafluoride and bromine pentafluoride is as follows: the commercially available halogen fluoride* was condensed or poured into a fluorothene container which could be sealed, and from which the material could be siphoned into the still pot. In this container the material was pretreated with chlorine trifluoride. This reacted with any iodine or bromine which might have been present to give iodine pentafluoride, or bromine pentafluoride, and chlorine. The mixture was then pulled through a nickel tube into the still pot where as much of the highly volatile components as possible was pumped off. The mixture remaining was then fractionally distilled, the constant boiling portion being collected directly in the large fluorothene storage container as shown in Figure 1 and Plate 1.

The procedures used for purifying and handling bromine trifluoride and chlorine trifluoride are described in later sections which deal with the experiments in which these compounds were used. The different types of experiments performed in this work required various methods of solution preparation. The specific procedures used will be described in the sections where they are applicable.

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* Harshaw Chemical Co.

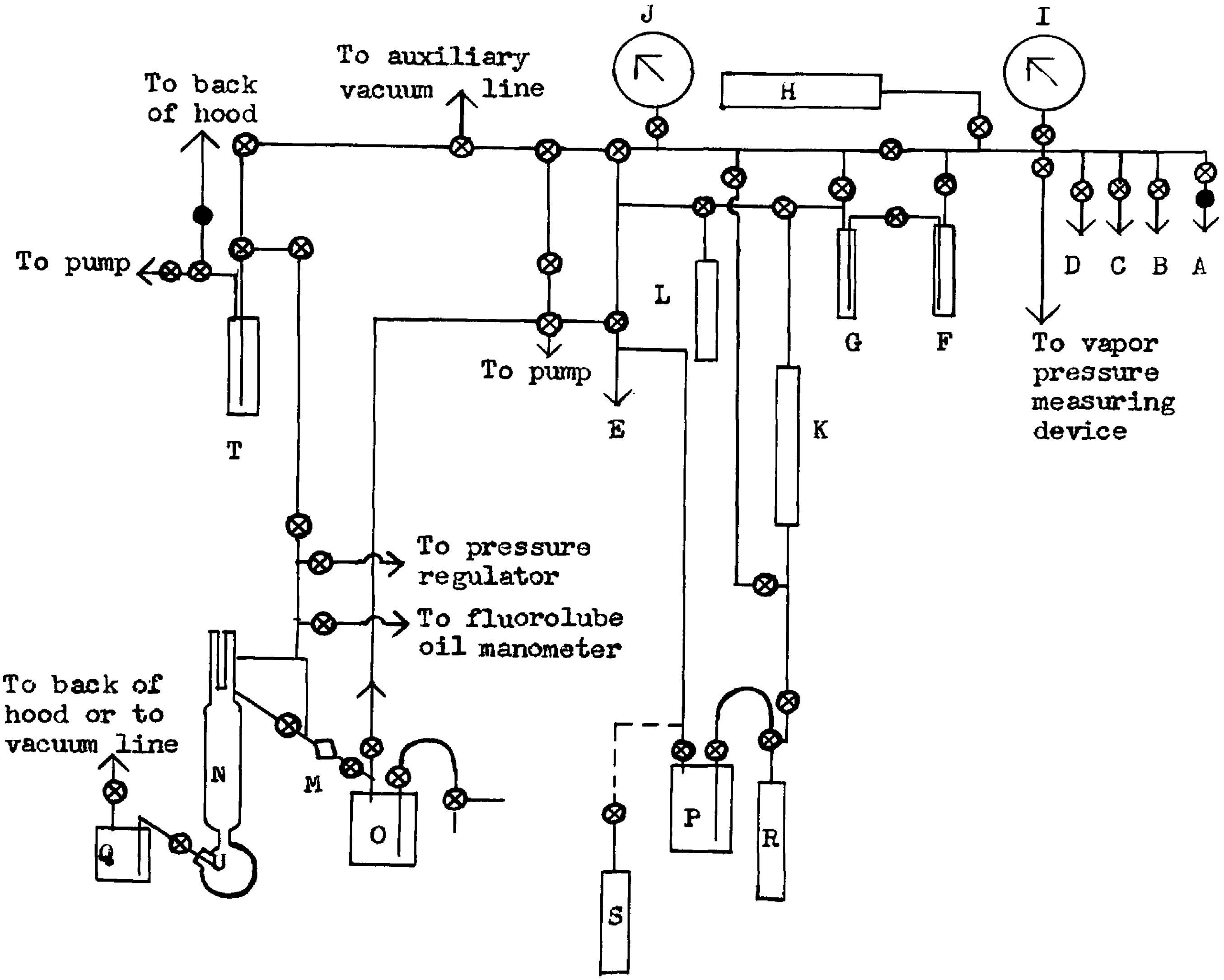


Figure 1. Schematic diagram of the still, gas-handling, and solution-handling system for halogen fluorides: A, to air drying system; B, C, and D, to tanks of hydrogen fluoride, chlorine trifluoride, and bromine pentafluoride; E, extra line outlet; F and G, aluminum traps for handling and storing materials; H, copper tank for storage of gases; I and J, Helicoid pressure gauges; K, cobalt trifluoride container; L, fluorothene storage tube; M, still head; N, still; O, and P, storage containers; Q, pretreating container; R and S, tubes or apparatus in which solutions are prepared; T, aluminum storage tube for materials to be discarded; U, still pot; ⊗ large valves with phosphor bronze bellows; • small valves with brass bellows.

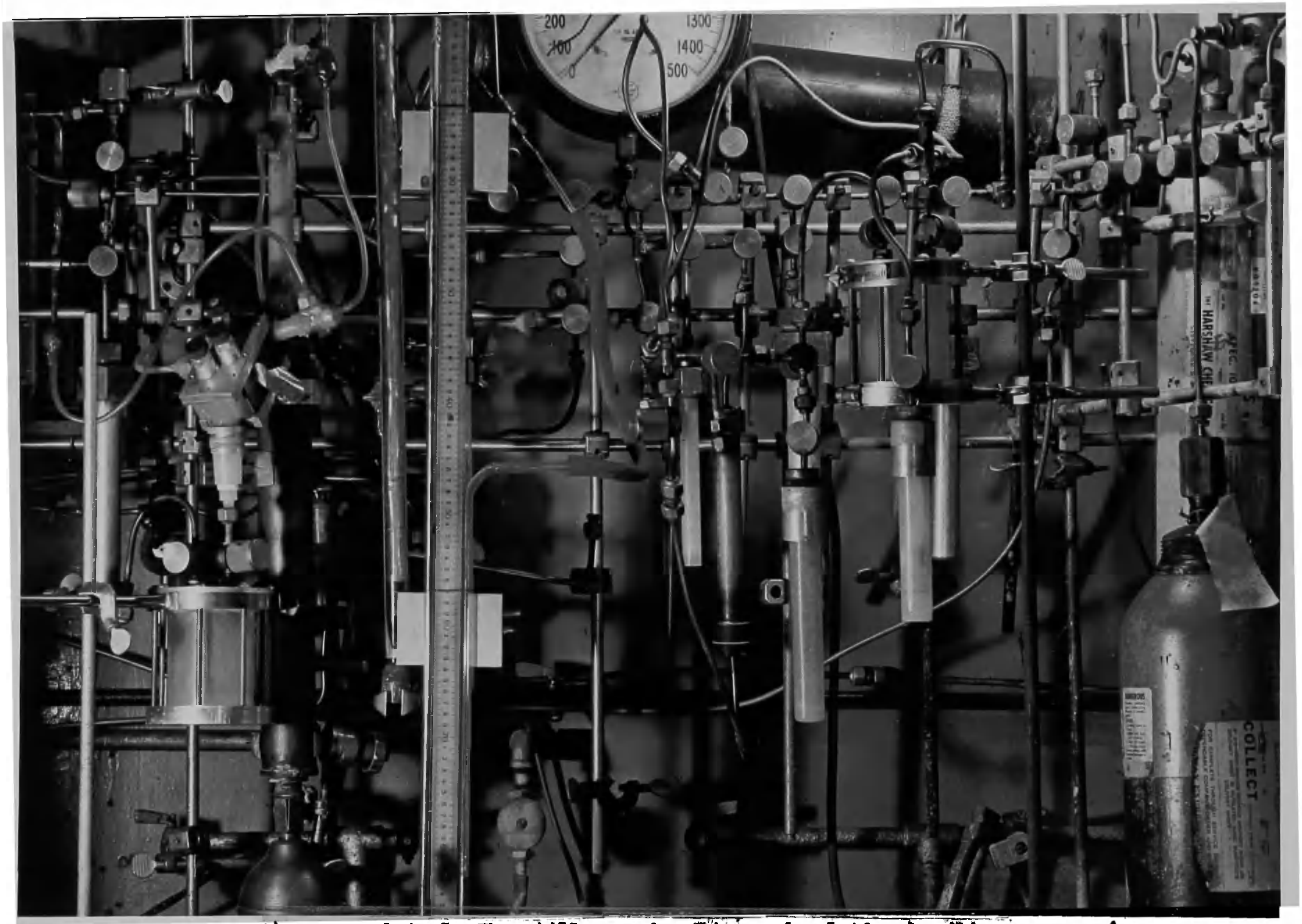


Plate 1. The still, gas-handling and solution handling system for the halogen fluorides

IV VAPOR PRESSURE STUDIES OF HALOGEN FLUORIDE-HYDROGEN FLUORIDE SOLUTIONS

A. Theoretical Aspects[38]

Whenever a substance is dissolved in a solvent the vapor pressure of the solvent is lowered. In 1888 F. M. Raoult was able to show that for a considerable number of solutes and solvents the equation

$$\frac{p^{\circ} - p}{p^{\circ}} = \frac{n_2}{n_2 + n_1} = x_2$$

was approximately followed. The pressures of the pure solvent and the solvent in solution are p° and p, respectively; n_1 and n_2 are the number of moles of solute and solvent in the solution, respectively; and x_2 is the mole fraction of the solute.

By subtracting unity from each side of the above equation, it is obvious that

$$\frac{p}{p^{\circ}} = 1 - x_2 = x_1$$

where x_1 is the mole fraction of the solvent.

The last mentioned equation is known as Raoult's law. It can be seen that in this idealized case the vapor pressure of a solvent in a solution is directly proportional to its mole fraction.

In the study of liquid mixtures an ideal solution is defined as one which obeys Raoult's law over the entire range of concentrations. For two volatile components, 1 and 2, if

$$p_1 = p_1^{\bullet} x_1$$

over the entire range of concentrations, then taking the logarithm of both sides and differentiating with respect to x_1

$$x_1 \frac{d\ln p_1}{dx_1} = 1$$

and, by use of the Duhem-Margules equation,

$$x_2 \frac{d\ln p_2}{dx_2} = 1$$

Integrating the latter equation and noting that $p_2 = p_2^{\bullet}$ when $x_2 = 1$,

$$p_2 = p_2^{\bullet} x_2$$

which is Raoult's law for the second component.

Thus if a mixture of two completely miscible liquids behaves ideally a plot of the partial pressure of either component should be a straight line passing through the origin, as shown in Figure 2-a. The total vapor pressure is the sum of the partial pressures, and in the ideal case would be the tie line connecting $p_1^{\bullet}$ and $p_2^{\bullet}$ in Figure 2-a.

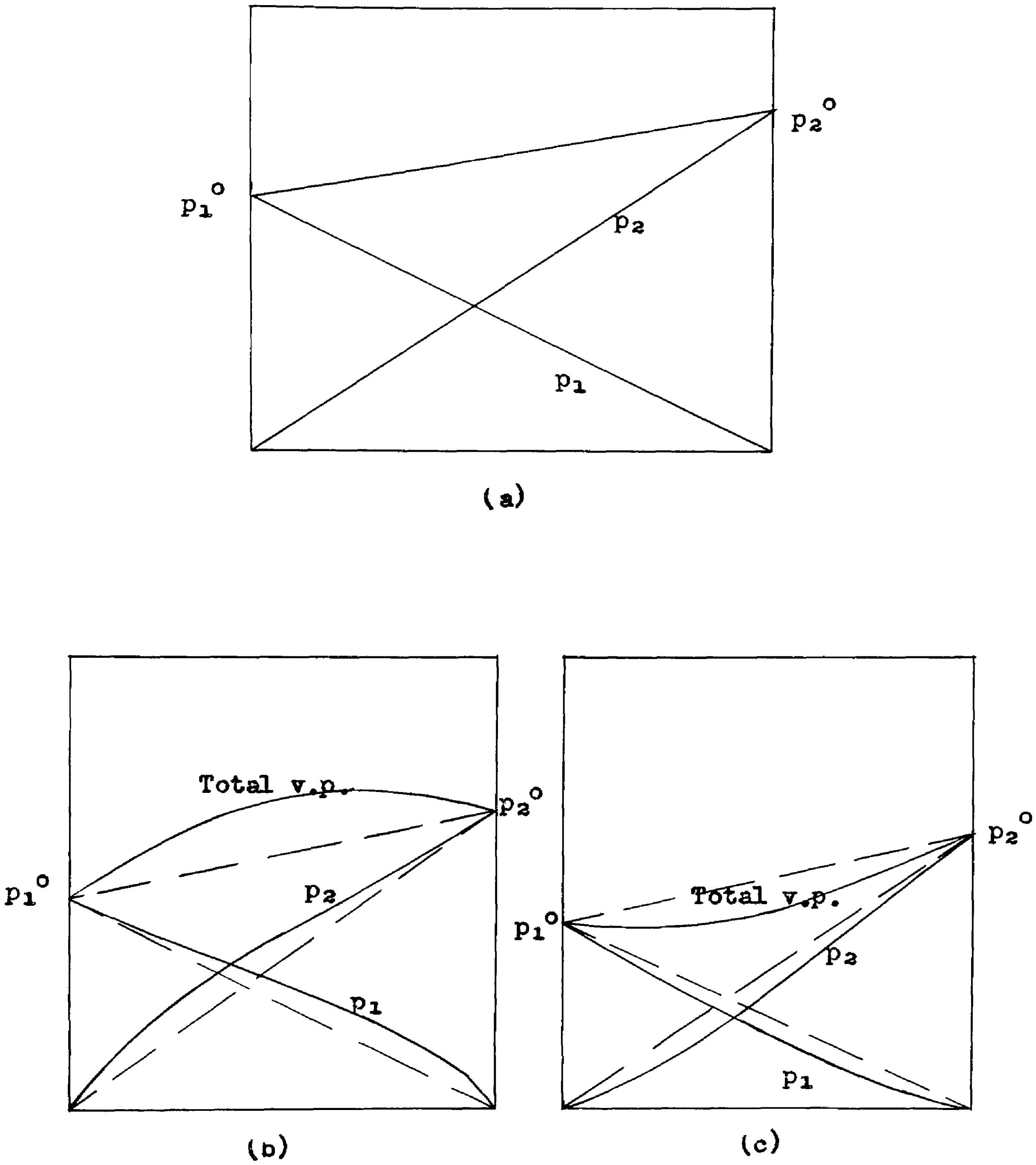
It should be noted that mixtures which behave ideally are generally found to be ones in which the components are similar both physically and chemically, since in the ideal solution there should be little difference between the environment of a given component in the pure liquid and in the mixture.

The principal reason that a solution may not show ideal behavior is that the intermolecular forces between the different molecules may be either larger or smaller than the intermolecular forces between the molecules of the pure substances, leading to negative or positive deviations from Raoult's law, respectively.

The type of vapor pressure-composition diagram obtained when the deviations from Raoult's law are positive is shown in Figure 2-b. It should be noted that the partial-pressure curves for the solvent approach ideality at infinite dilution, but the total-pressure curve does not.

The type of vapor pressure-composition diagram obtained when there are negative deviations from Raoult's law is illustrated in Figure 2-c.

In the illustrations shown, the curves for the total pressure show a maximum or a minimum. At the maximum or minimum points the vapor has the same composition as the liquid and the mixture is called an azeotrope. The azeotropic composition depends on the temperature. Actually the deviations are generally not so extreme as to cause a maximum or a minimum.



(a)

(b)

(c)

Figure 2. Typical vapor pressure-composition diagram.

B. Apparatus and Method

The Pressure Measuring Device

Design. The device for measurement of the vapor pressure above a mixture of halogen fluoride and hydrogen fluoride must of course be one which will not be affected by the high reactivity of these compounds. In this work the device which is illustrated in Figure 3 and Plate 2 was used. It consists essentially of the pressure-sensitive part of a Helicoid gauge* which is mounted in such a manner that its movement due to pressure within the Monel Bourdon Tube may be accurately determined by means of a micrometer screw. In actual practice there was a metal shaft about four inches long soldered to the tip of the tube. The micrometer screw made contact with a silver strip soldered to the end of the shaft. Added sensitivity was provided by having the tip of the micrometer screw and the shaft act as contacts which opened and closed the circuit of a magic eye tube when contact was made or broken. In this manner the point at which contact was made could be read to the nearest five-thousandths of a millimeter (0.005 mm.).

The gauge was provided with two valves, one of which provided a direct outlet to the vacuum line, and the other of which was attached directly to the tube containing the solution. The pressure sensitive part of the gauge was enclosed in an insulated box within which a constant temperature was maintained by means of a Cenco-deKhotinsky** regulator and an electric light bulb.

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* American Chain and Cable Co.
** The Central Scientific Co.

The Helicoid gauge which was used in this work was one which originally gave a full scale deflection of 1500 mm. of mercury, the total movement of the tip of the Bourdon tube being about 4 mm. over the full pressure range. This would give a theoretical sensitivity of about plus or minus one millimeter of mercury. In actual practice it was found that when calibrating the instrument the sensitivity was about plus or minus two mm. of mercury. When measuring the vapor pressures of solutions the reproducibility was generally observed to be plus or minus three to five mm. of mercury depending upon the difficulty encountered in bringing the solution into equilibrium with the vapor.

The solution was placed in a fluorothene tube machined with a female standard-taper top; the mating plug had a hole drilled through it and a nickel tube with a flare fitting threaded into the hole. The flare fitting was attached directly to the entrance valve of the gauge as illustrated in Figure 3. A small Teflon-covered magnetic stirrer was placed inside the tube.

Calibration. In order to calibrate the gauge, the entrance valve which ordinarily held the solution tube was attached directly to one arm of a differential mercury manometer. The other valve remained attached to the vacuum line. The pressure within the gauge was varied by changing the pressure within the vacuum line and was then read directly from the manometer. The micrometer screw was adjusted so that it just contacted the silver strip on the end of the shaft and the reading on the micrometer scale was recorded. A sample calibration curve is given in Figure 4.

Solution Preparation and Procedure

The halogen fluoride, the purification and storage of which is described above, was siphoned directly from the storage container (see Plate 3) into the previously weighed fluorothene tube. In the case of chlorine trifluoride a crude purification was obtained by distilling directly from the tank on the vacuum line into the tube and then distilling out of the tube until the vapor pressure became constant. Dry air was let into the tube, the valve over the tube was closed and the line cleaned by evacuating and heating. The tube was then removed from the storage container, closed with a plug, and weighed on a Torsion Balance.* The contents of the tube were frozen with a Dry Ice-carbon tetrachloride-chloroform bath placed around the tube. The assembly was then attached to the gauge and evacuated while still frozen. After evacuation the valve to the vacuum line was closed, and the contents were brought to the desired temperature by placing a Dewar flask containing water at that temperature around it. Agitation was accomplished by moving a magnet outside the tube. When the scale reading became constant the reading was taken.

The first hydrogen fluoride solution was prepared by freezing the contents of the tube again and condensing hydrogen fluoride into the tube from the tank on the vacuum line. The weighing and pressure-measuring procedures were identical to those indicated above. This procedure was repeated so that it was possible to obtain measurements of several samples of hydrogen fluoride solution from each sample of halogen fluoride prepared.

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* The Torsion Balance Co.

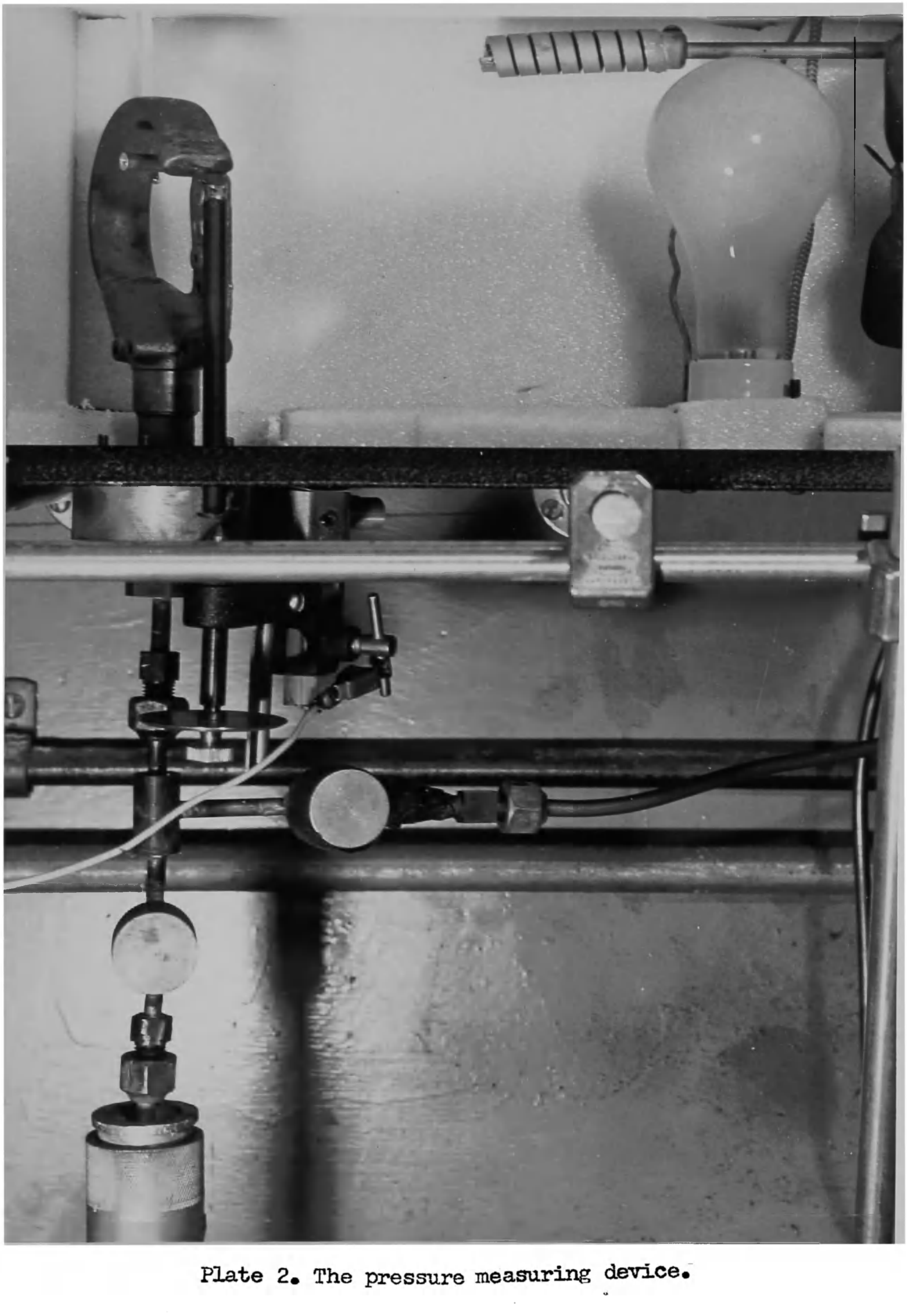

Plate 2. The pressure measuring device.

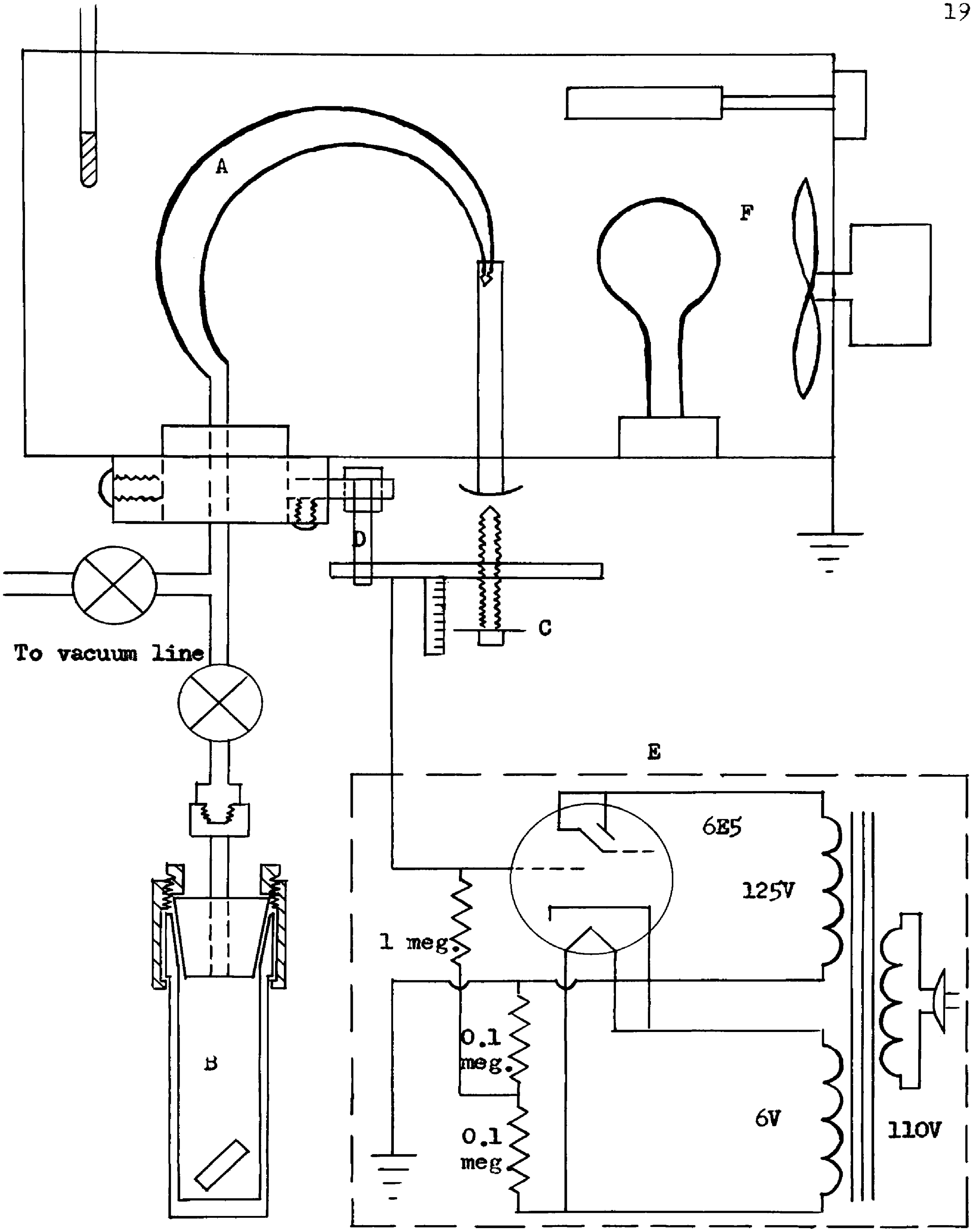

Figure 3. The pressure measuring device: A, Bourdon tube, B, solution tube and magnetic stirrer; C, micrometer; D, plastic rod; E, circuit diagram for the magic-eye tube; F, temperature control system.

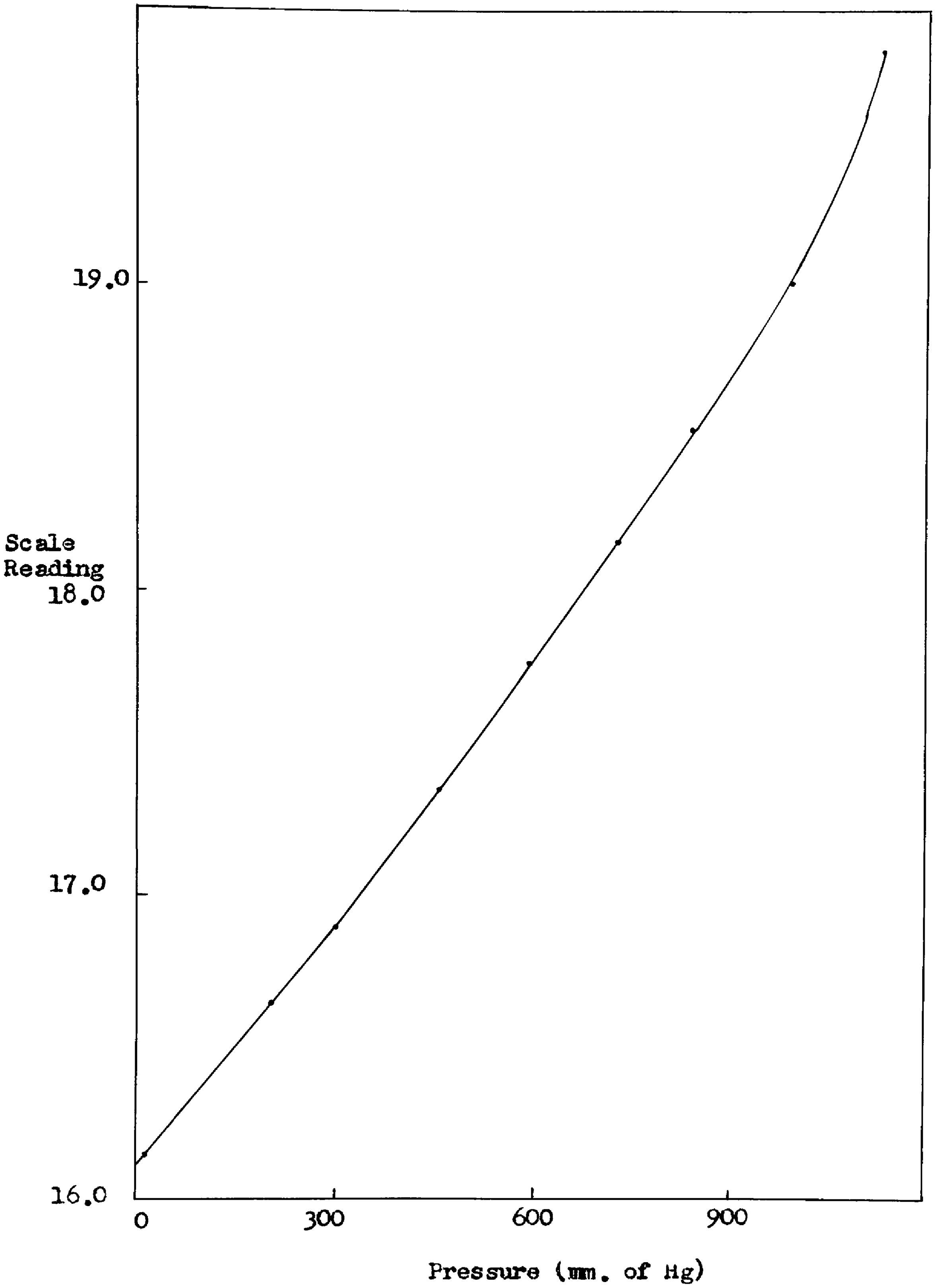

Figure 4. Sample calibration curve for the pressure measuring device.

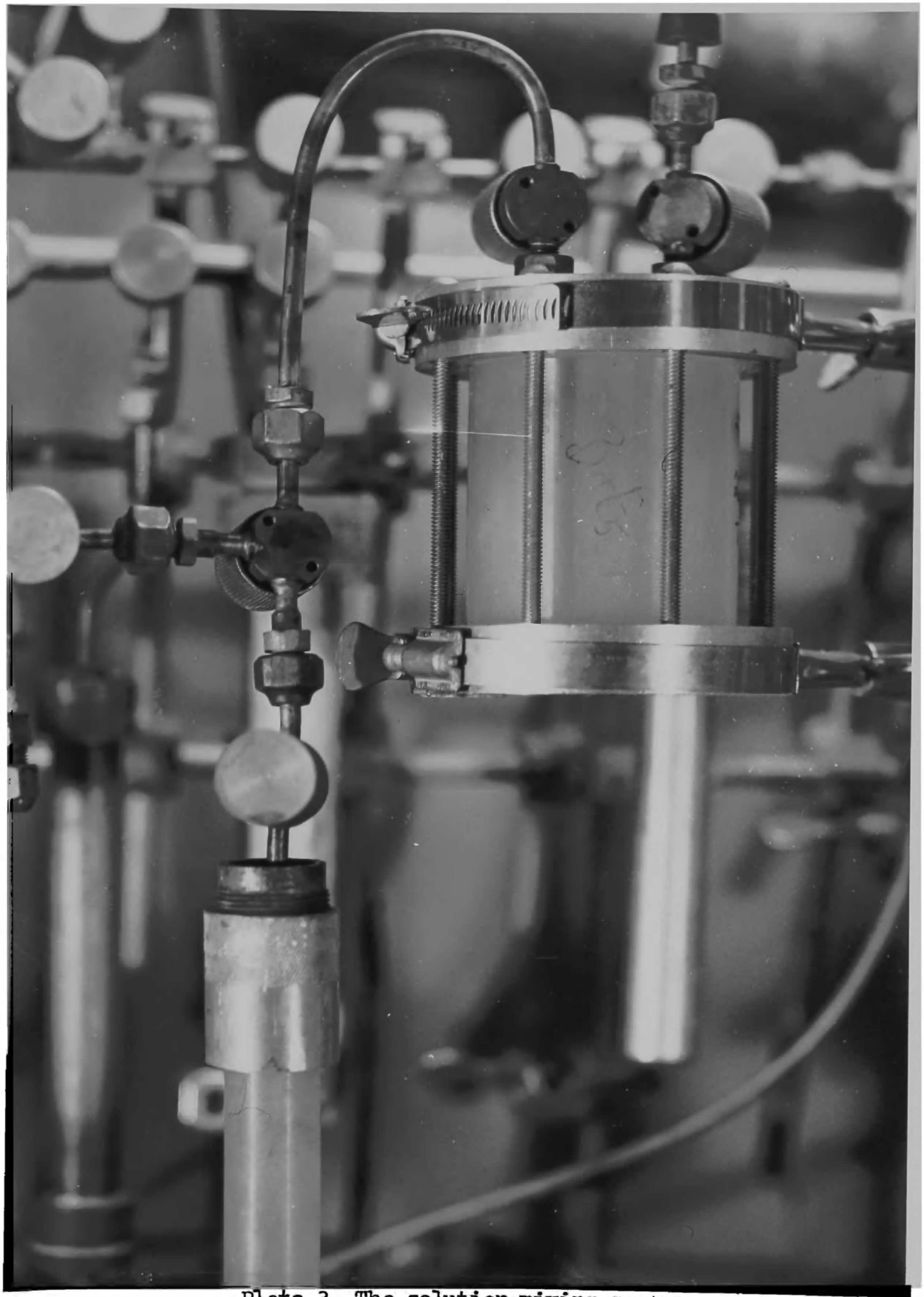

Plate 3. The solution mixing system.

C. Data and Calculations

Each run indicated in the following tables was started with a single sample of halogen fluoride.

The observed vapor pressures for solutions of bromine pentafluoride and hydrogen fluoride are given in Table II and Figure 5. The observed vapor pressures for solutions of iodine pentafluoride and hydrogen fluoride are given in Table III and Figure 6, and the observed vapor pressures for solutions of chlorine trifluoride and hydrogen fluoride are given in Table IV and Figure 7.

The bromine pentafluoride runs at 25°C show large errors because the temperature was close to room temperature and it was not possible to control the temperature of the top of the tube and tapered plug.

The error indicated for each vapor pressure value is based upon the accuracy with which that particular reading could be reproduced after changing the pressure slightly.

D. Discussion of the Results

The vapor pressures of the halogen fluoride-hydrogen fluoride solutions illustrated in Figures 5, 6, and 7 all show a marked positive deviation from Raoult's law. If it is possible to consider the bromine pentafluoride solutions as a typical case, it also appears that there is a very marked increase in this deviation with increasing temperature.

It is actually quite difficult to draw definite conclusions from the shape of the vapor pressure curves because very little is known about

TABLE II

THE VAPOR PRESSURES OF BROMINE PENTAFLUORIDE-HYDROGEN FLUORIDE SOLUTIONS AT 0, 15, and 25°C

Temperature °C	Mole Percent HF	Pressure mm.
	Run I*	
25.0	0.00	337 ± 5
25.0	2.40	649 ± 10
25.0	3.55	696 ± 5
25.0	15.0	988 ± 5
25.0	37.9	1000 ± 5
25.0	46.2	990 ± 5
	Run II*	
25.0	17.4	846 ± 5
25.0	42.8	927 ± 10
25.0	62.0	980 ± 10
	Run III*	
25.0	100.0	920 ± 10
25.0	87.8	1077 ± 10
25.0	59.3	1145 ± 30
	Run IV	
0.0	0.0	142 ± 3
0.0	51.2	300 ± 3
0.0	69.0	350 ± 3
0.0	82.1	368 ± 3
0.0	91.5	380 ± 3
	Run V	
15.0	0.0	258 ± 3
0.0	0.0	136 ± 3
15.0	63.3	612 ± 6
0.0	63.3	334 ± 6
	Run VI	
0.0	26.8	240 ± 5
15.0	26.8	505 ± 10
15.0	47.5	585 ± 5
0.0	78.6	365 ± 10
15.0	78.6	640 ± 5

*The pressures found for hydrogen fluoride from the tank are 398 ± 3 mm at 0°C and 664 ± 5 mm at 15°C.

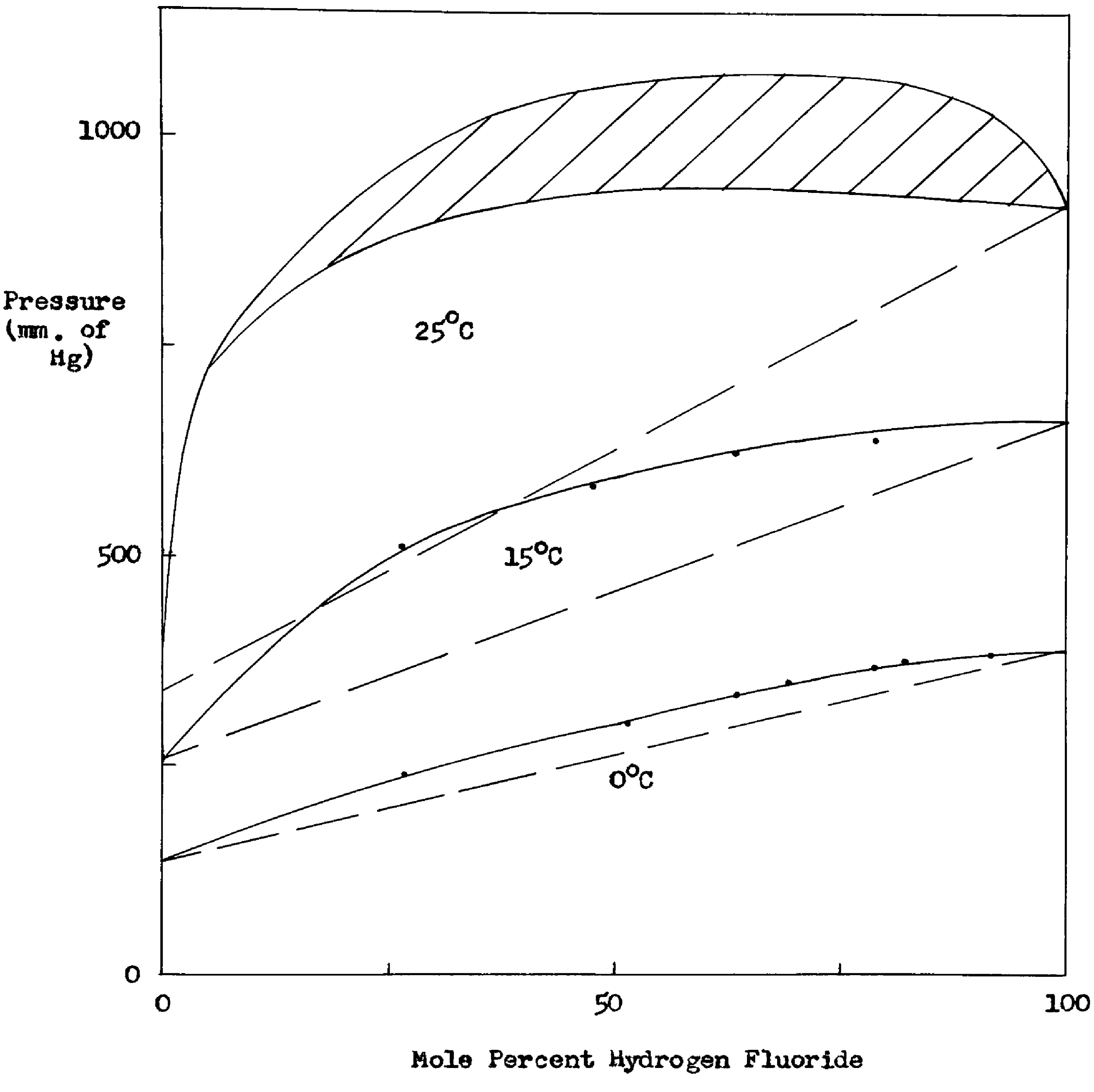

Figure 5. Vapor pressure-composition diagrams for bromine pentafluoride-hydrogen fluoride solutions at 0°, 15° and 25°C. Erratic results obtained at 25°C made it necessary to show only the most probable area for the curve.

TABLE III

THE VAPOR PRESSURES OF IODINE PENTAFLUORIDE-HYDROGEN FLUORIDE SOLUTIONS AT 15°C

Mole Percent HF	Pressure mm.
Run I	
0.0	3 ± 3
24.5	246 ± 5
36.2	217 ± 3
70.5	537 ± 3
82.6	597 ± 3
Run II	
13.4	155 ± 3
59.1	447 ± 3

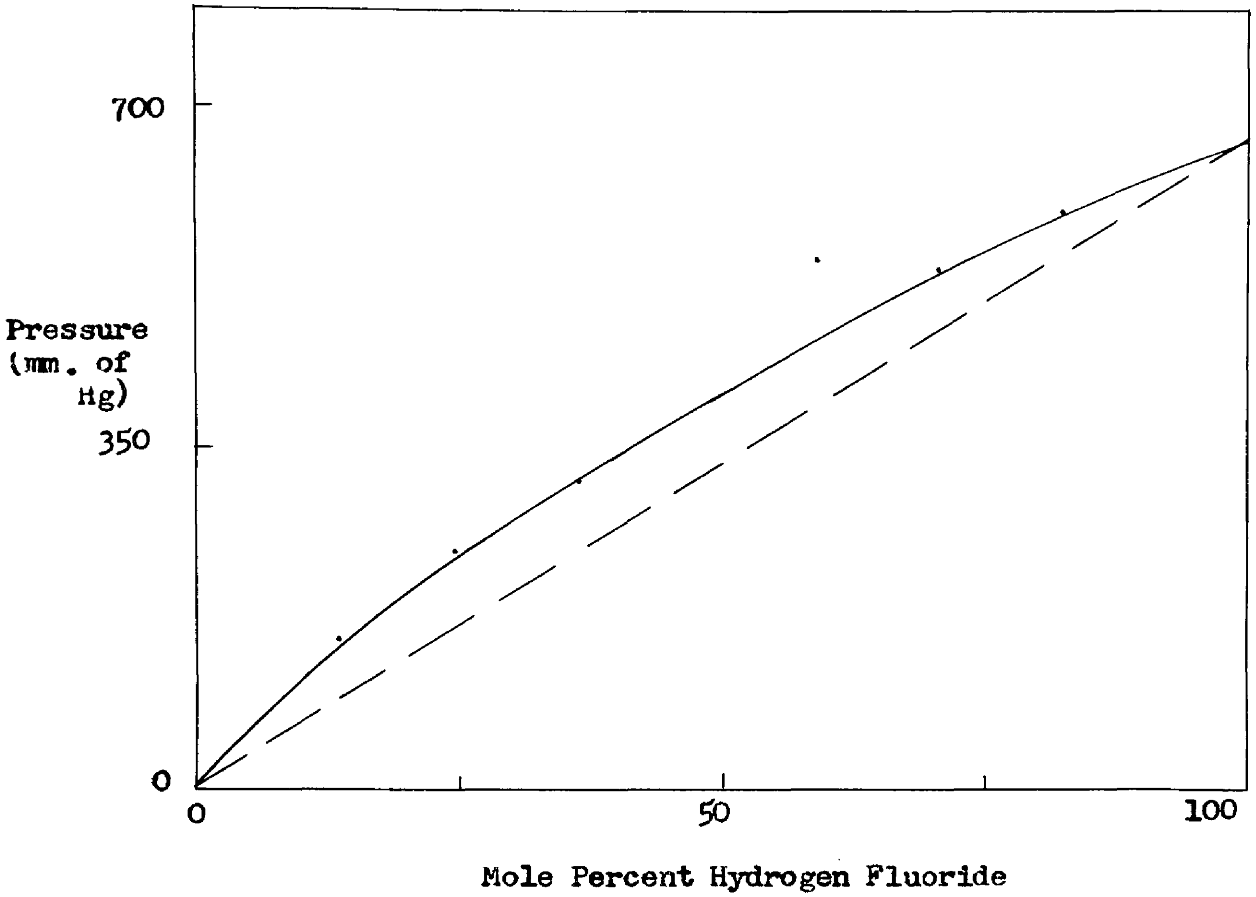

Figure 6. Vapor pressure-composition diagram for iodine pentafluoride-hydrogen fluoride solutions at 15°C.

TABLE IV

THE VAPOR PRESSURES OF CHLORINE TRIFLUORIDE-HYDROGEN FLUORIDE SOLUTIONS AT ZERO DEGREES

Mole Percent HF	Pressure mm.
0.0	448 ± 3
10.5	562 ± 5
33.2	592 ± 5
69.0	645 ± 5
86.0	527 ± 5

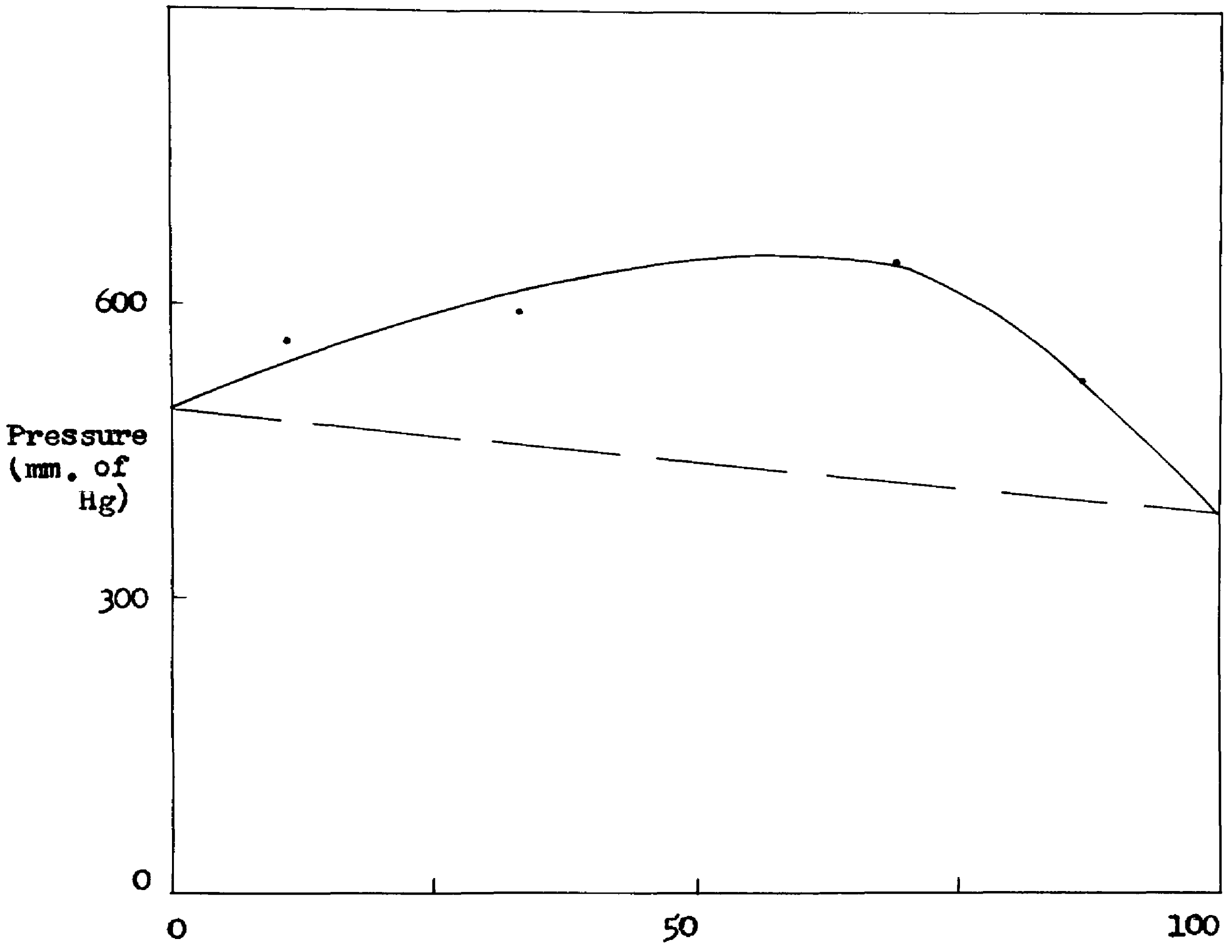

Figure 7. Vapor pressure-composition diagram for chlorine trifluoride-hydrogen fluoride solutions at 0°C.

the liquid state of the halogen fluorides themselves, and because our knowledge of the liquid state of hydrogen fluoride is qualitative at best.

The dielectric constants of the halogen fluorides are apparently appreciably lower than that of hydrogen fluoride. Thompson[12,50] has found the dielectric constant of liquid iodine pentafluoride to follow the relation

$$\epsilon = 46.22 - 0.388t \quad ,$$

that of BrF_5 to follow the relation

$$\epsilon = 9.02 - 0.0117t \quad ,$$

and that of chlorine trifluoride to follow the relation

$$\epsilon = 4.754 - 0.0187t$$

He also found that the dielectric constant of chlorine trifluoride increases markedly when hydrogen fluoride is added. The dielectric constant of hydrogen fluoride has been found by Fredenhagen[28] to vary from 174.8 at -73°C to 83.6 at 0°C. There is some doubt as to the accuracy of these results, however.

The above data lead to the conclusion that the halogen fluorides, although undoubtedly somewhat associated, are less associated than hydrogen fluoride in the liquid state. It is therefore not surprising that the solutions show an appreciable positive deviation from Raoult's law. Chlorine trifluoride-hydrogen fluoride mixtures would in fact be expected to show the greatest deviation, and this seems to be the case when Figures 5, 6 and 7 are compared. The great difference between the dielectric constants of liquid hydrogen fluoride and of the halogen fluorides does not, however, explain the fact that there is less deviation at lower temperatures. This decreasing deviation would seem to indicate that there are actually two effects superimposed.

Recently D. F. Smith[24] has shown by means of spectroscopic studies of mixtures of chlorine trifluoride and hydrogen fluoride in the vapor state that the complex

$$\underset{F}{\overset{F}{F\text{-}Cl}} \; . \; . \; . \; F\text{-}H$$

is formed to a very small degree. The equilibrium constant is

$$K = \frac{[\text{Complex}]}{[ClF_3]\,[HF]} \approx 10^{-4} \text{ per mm.}$$

and the heat of formation is -3.92 kcal. per mole.

Although Smith was not able to find any evidence for it, it is also possible that hydrogen bonding might occur at lower temperatures and in the liquid. If this were the case, the deviations noted would be the result of the interaction of two effects: the negative deviation caused by complex formation or hydrogen bonding, and the positive deviation caused by the very different intermolecular atmospheres of the halogen fluorides and hydrogen fluoride, the former becoming increasingly important at lower temperatures.

Another possible cause of the phenomena noted could be that the association of hydrogen fluoride is broken down to some extent by the presence of halogen fluorides. This would increase the vapor pressure of the hydrogen fluoride above the solution. It is also quite possible that such an effect could decrease with decreasing temperature as is noted in Figure 5. Actually both of the processes mentioned above are probably present in the solutions to some degree.

V CRYOSCOPIC STUDIES OF THE HALOGEN FLUORIDES AND THEIR HYDROGEN FLUORIDE SOLUTIONS

A. Theoretical Aspects[38,39]

Cryoscopic Studies of Pure Materials

The principal variables which influence the state of a pure material are temperature and pressure. When a pure crystalline solid is heated under its own vapor pressure a temperature is reached at which the solid suddenly liquifies. At this point the liquid, solid, and vapor are in equilibrium. As is obvious, there is one more phase present at this particular point, which is known as the triple point, and therefore the system becomes invariant.

In actual practice it is generally found that the temperature at which the transition occurs is only slightly dependent upon the pressure. For most purposes the temperature at which the transition occurs is determined at atmospheric pressure. This temperature is known as the freezing point of the substance.

Since it is rarely if ever possible to obtain a substance which is absolutely pure the freezing point which is measured should, if possible, be corrected in some manner for the effect of dissolved impurities. The effect of a solute upon the freezing point of a pure substance is given in the following equation

$$\Delta T_f = \frac{R T_0^2 N_s}{L_f}$$

where $\triangle T_f$ is the freezing point lowering, R is the molar gas constant, T_o is the freezing point of the pure solvent and N_s is the mole fraction of solute.

This can be simplified to

$$\triangle T_f = \frac{R\,T_o\,m}{L_f \times (1000/M_1)}$$

or

$$\triangle T_f = K_f m$$

where K_f is defined by the equation

$$K_f = \frac{R\,T_o^2}{L_f \times 1000/M_1}$$

M_1 is the molecular weight of the solvent, and m is the molality.

A typical cooling curve for a compound containing a small amount of dissolved impurity is given in Figure 8. As the temperature of the sample is reduced the plot of temperature versus time resembles curve AB. At B the sample has supercooled and just begun to crystallize. The process of crystallization releases heat so that the temperature suddenly rises to C. Continued cooling causes the crystallization of more solid, the temperature following along the curve CE. This occurs because the solid is essentially pure solvent thus causing the solute to concentrate in the liquid phase and lower its freezing point. At E the entire sample is frozen. An extrapolation of curve CDE to A gives the time and temperature at which fusion would have occurred without supercooling. At time $T_{1/2}$ the sample will be half frozen and the concentration of impurity will be x/2, if the rate of cooling is constant. At this point the solute

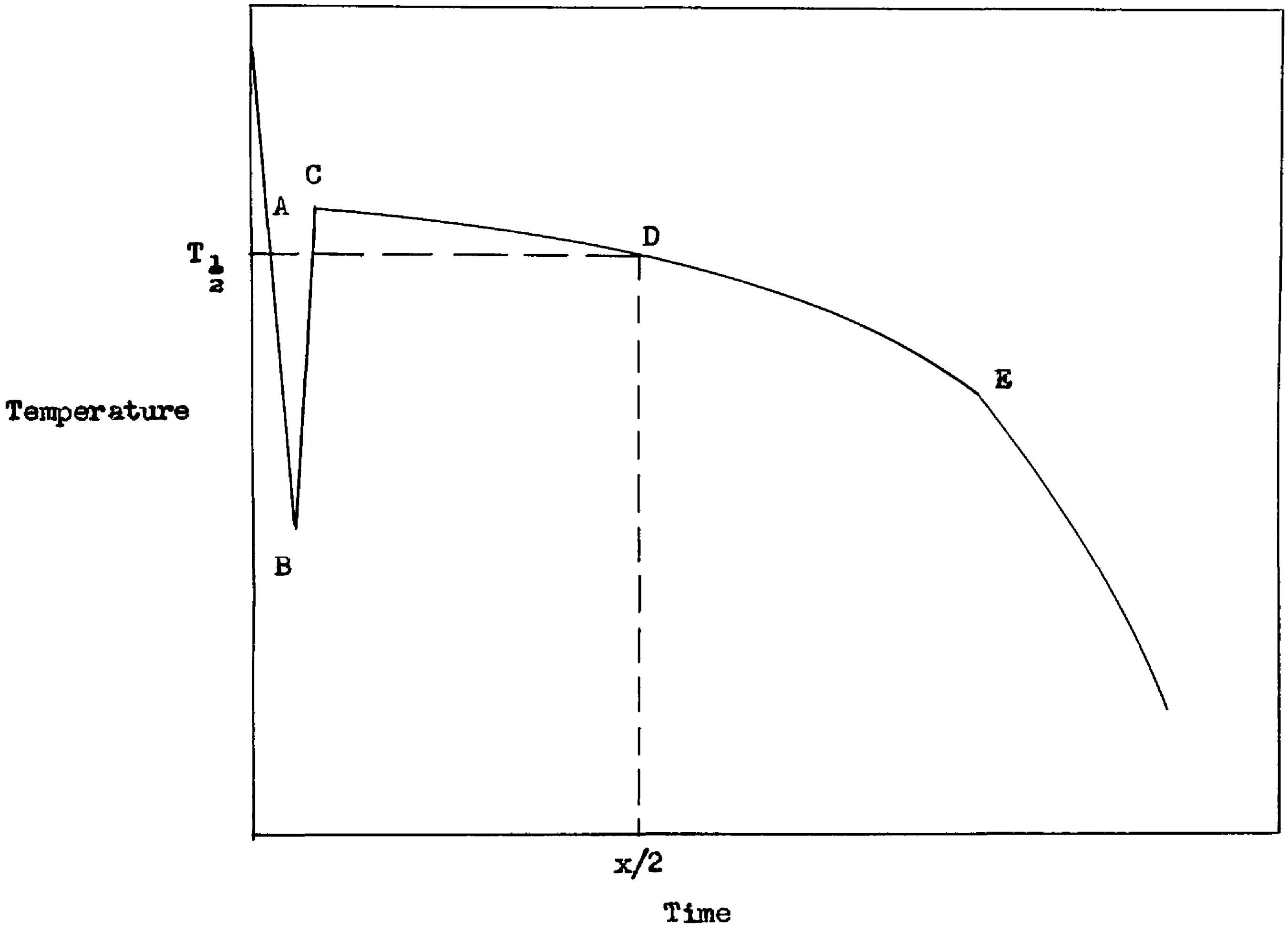

Figure 8. Typical cooling curve for a solvent containing a small amount of solute.

concentration will be double that at point A. It can be seen from the relation

$$\Delta T_f = K_f m$$

that the freezing point depression at D would be double that at A, so that

$$T_0 - T_f = 1/2(T_0 - T_{1/2}).$$

The true freezing point T_0 may therefore be determined from the cooling curve of a sample containing a small amount of impurity by the above method which was developed by White and modified by Witschonke.[40]

Two-Component Liquid-Solid Phase Equilibria

The same general considerations mentioned in the previous section will hold in a discussion of the phase equilibria of two-component systems. It is obvious from the preceding discussion that the presence of a substance other than the solvent will introduce a third variable, namely, concentration. As discussed in the previous section the freezing point of the system will be taken as the point at which the liquid-solid transition occurs under a pressure of one atmosphere.

The simplest type of two-component liquid-solid system is one in which the components do not react to form another compound. Such a system is illustrated in Figure 9. The freezing points of the various mixtures of two such components would fall along the curve CDE. The freezing point curves of A in B, and B in A, intersect at D. When a mixture of any composition between A and x', or x' and B, is cooled, the solid phase which separates first is pure A or pure B, respectively.

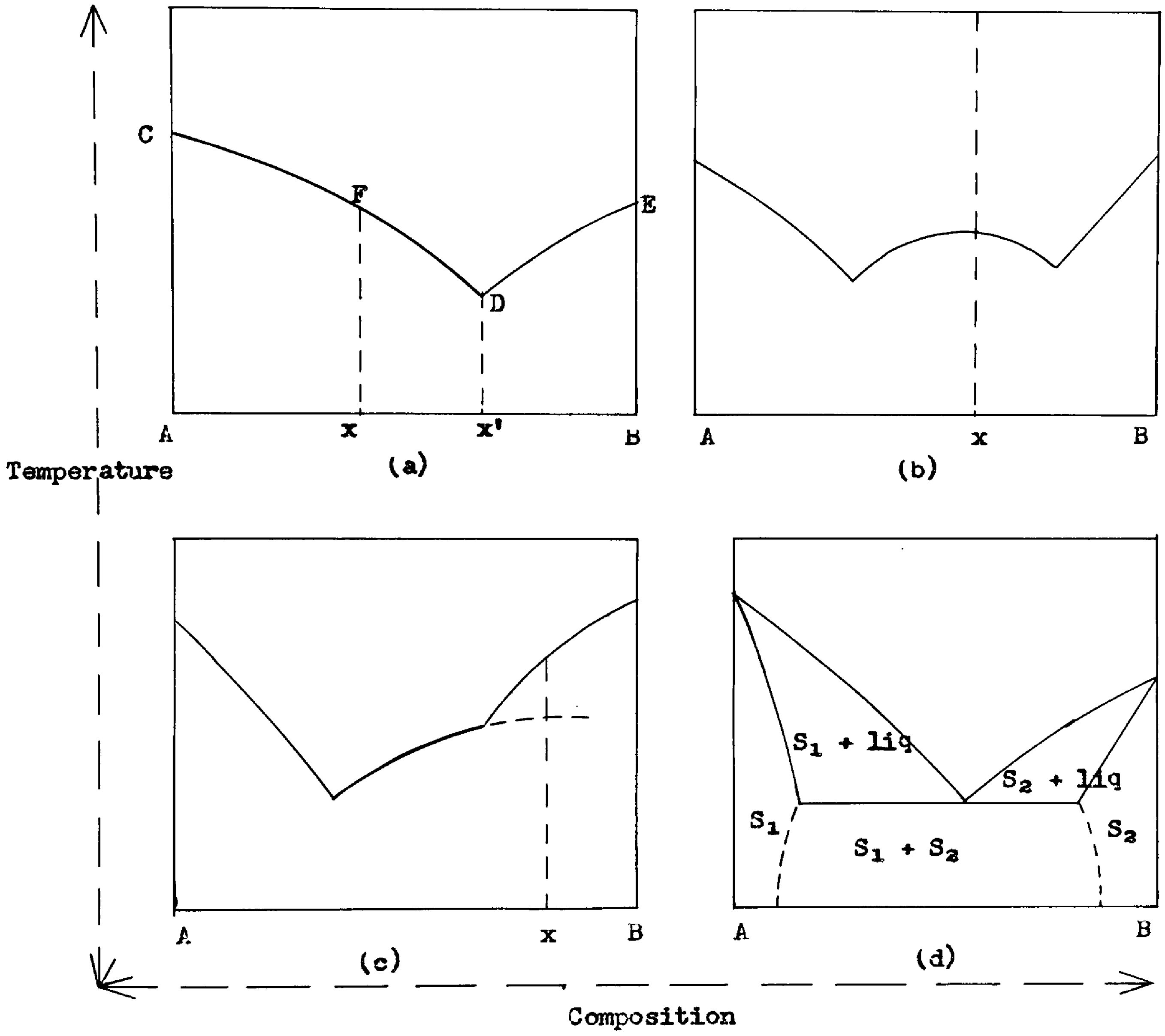

Figure 9. Some typical phase diagrams for two component systems.

At x', however, both solids crystallize out of the solution at the same time. Thus an additional solid phase has been introduced and the system becomes invariant.

A typical cooling curve, such as would be obtained when a solution of composition x is cooled, is illustrated in Figure 10. The explanation of this curve is identical with that given for Figure 9 except that a eutectic halt occurs just prior to total solidification. This halt was not shown in Figure 8 since it would be very difficult to observe with only a very small amount of solute.

When compound formation occurs the situation can become considerably more complicated. The simplest case is that in which a stable compound is formed. If the diagram shown in Figure 9b is divided into two parts at x, the resulting two sections are each identical with Figure 9a.

A considerably more complicated situation arises when the compound formed is unstable as illustrated in Figure 9c. In this case the freezing point and composition of the compound formed can only be obtained by extrapolation,as illustrated. A cooling curve for such a system, of composition x, differs from that shown in Figure 10 only in that the first transition may be quite indefinite.

The systems described above are all ones in which the components are completely miscible in the liquid state, and in which the only solids which appear at points other than the eutectic point are pure components or compounds. Other systems which might be included in this general group would be combinations of the occurrences mentioned above.

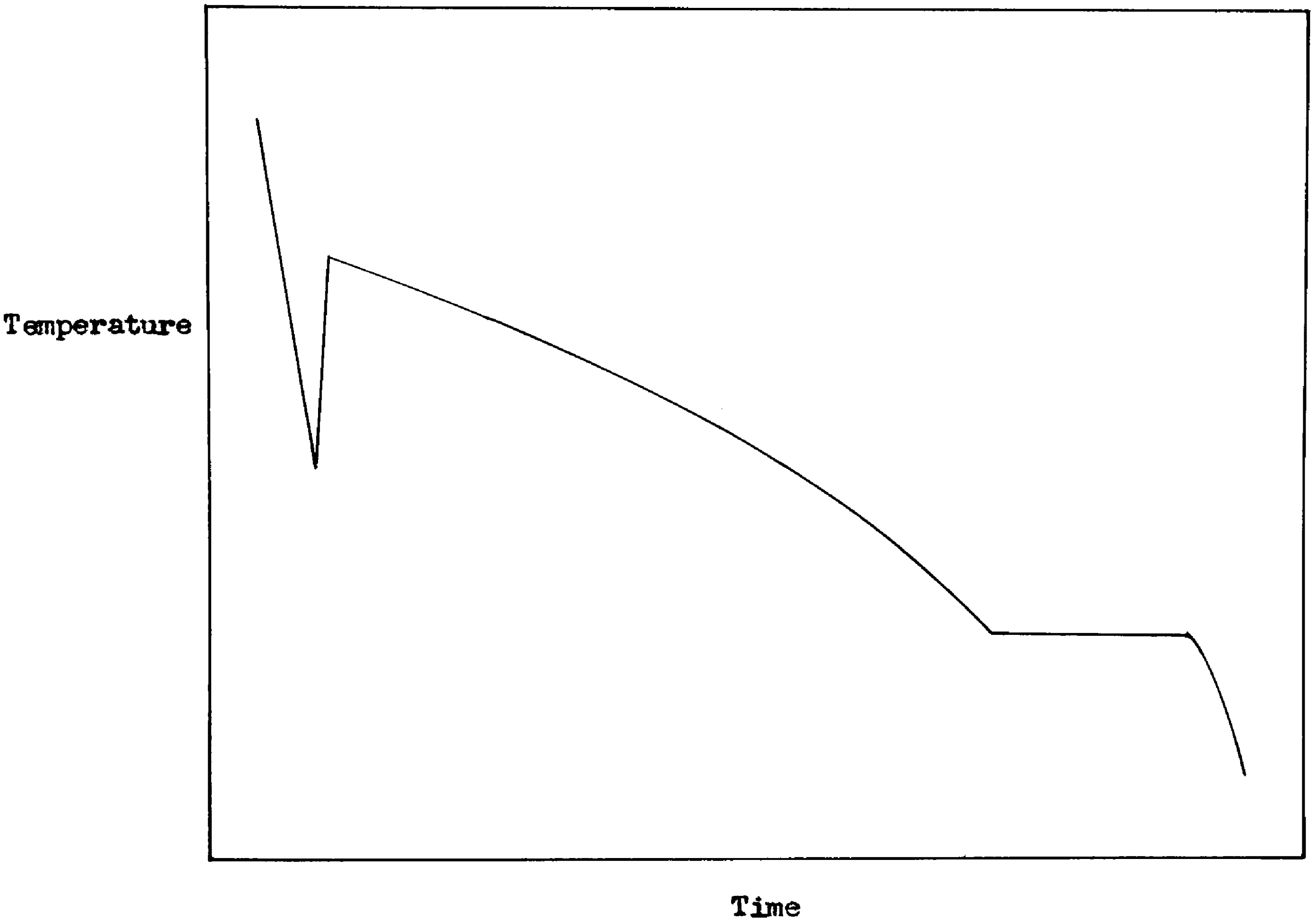

Figure 10. Typical cooling curve for a sample of a two component system with no compound formation.

Other types of liquid-solid phase equilibria which can occur are ones in which the components form mixed crystals, an unbroken series of solid solutions, or solid solutions with partial miscibility. A detailed discussion of these other situations will be omitted here except for the case of solid solution formation with partial miscibility in the solid phase. In this case, as illustrated in Figure 9d, solid A can dissolve a given amount of solid B, and solid B can dissolve a given amount of solid A. If the limits of solubility are exceeded two solid phases are formed and it is thus possible to have one liquid phase and two solid phases, which can be solid solutions or pure compounds, existing at the same time. When this occurs the system becomes invariant and a transition, or a eutectic point, is possible. Figure 9d shows such a system with a eutectic point.

B. Apparatus and Method

The Freezing Point Cell

The cell, which is illustrated in Figure 11 and in Plate 4, was used for the determination of the freezing points of the hydrogen fluoride solutions, and of the pure halogen fluorides. It was constructed entirely of fluorothene and Teflon, the thermocouple being the only metallic part of the cell. The cell consists of a fluorothene tube with a machined female standard-taper top into which is inserted a Teflon plug. The thermocouple leads are wound around a tube attached to the plug; grooves for the wire were machined along the tube. The plunger itself which operates through a hole in the tube and plug, consists of a fluorothene cylinder machined on the outside to resemble a helical gear.

For most of these measurements vigorous and satisfactory stirring was obtained by using a reciprocal stirring action with a stroke of about one and one-half inches. In the determination of the freezing point of pure iodine pentafluoride, however, circular stirring was used for some of the measurements.

The cell as described above was not air-tight. To prevent air and vapors from being pumped into and out of the tube by the action of the reciprocal stirrer the cell was fitted with a hood which was fabricated from thin sheet fluorothene. The hood was tightly sealed around the tube and the plunger arm, and the seal at the plunger arm was lubricated with Fluorolube oil* to permit free action through the hood. When the plunger was in operation the sides of the hood expanded and contracted but did not allow vapor to enter or leave the enclosed system.

In actual operation the cell was enclosed in a glass air-jacket. The freezing point assembly plus the air jacket was inserted into a one-liter Dewar flask filled with appropriate coolant. A clear Dewar flask wrapped with transparent Scotch tape was used to observe whether or not there was any immiscibility in the liquid phase. Sometimes an intermediate bath of trichlorofluoromethane was used instead of the air jacket. Whether an intermediate bath was used, and whether Dry Ice-acetone or liquid nitrogen were used as coolants, depended upon the rate of cooling

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* "Fluorolube S" was obtained from the Hooker Electrochemical Co., Buffalo, N. Y.

desired. The rate of cooling was also controlled to some extent by the use of air jackets of various sizes.

This cell, when used with reciprocal stirring, was quite satisfactory for most purposes. When the freezing points of the pure liquids were determined, however, it was found that these liquids froze on the sides of the tube and jammed the stirrer. Since it is important to know when the liquid is completely frozen in order to determine the degree of impurity, this is a serious objection to the use of the reciprocal stirrer. The use of vigorous circular stirring for measurements of the freezing point of pure iodine pentafluoride proved to be somewhat more satisfactory, and some satisfactory runs were obtained with reciprocal stirring followed by manual shaking after the plunger had jammed.

With pure bromine pentafluoride the reciprocal stirrer was inadequate since the stirrer froze in when only about 20 percent of the material was frozen. A rough determination of the purity of bromine pentafluoride was obtained using a different type of cell illustrated in Figure 12. This cell was completely sealed and stirring was accomplished by very vigorous shaking of the entire cell by means of a single-cylinder reciprocal-action air motor. This apparatus, when used as described, did not permit the use of an air jacket between the cell and the cooling medium and thus presented a serious safety hazard. This method, however, could probably be modified to permit the use of an air jacket and under such conditions might also prove useful for cryoscopic studies of solutions with high vapor pressures such as chlorine trifluoride-hydrogen fluoride mixtures.

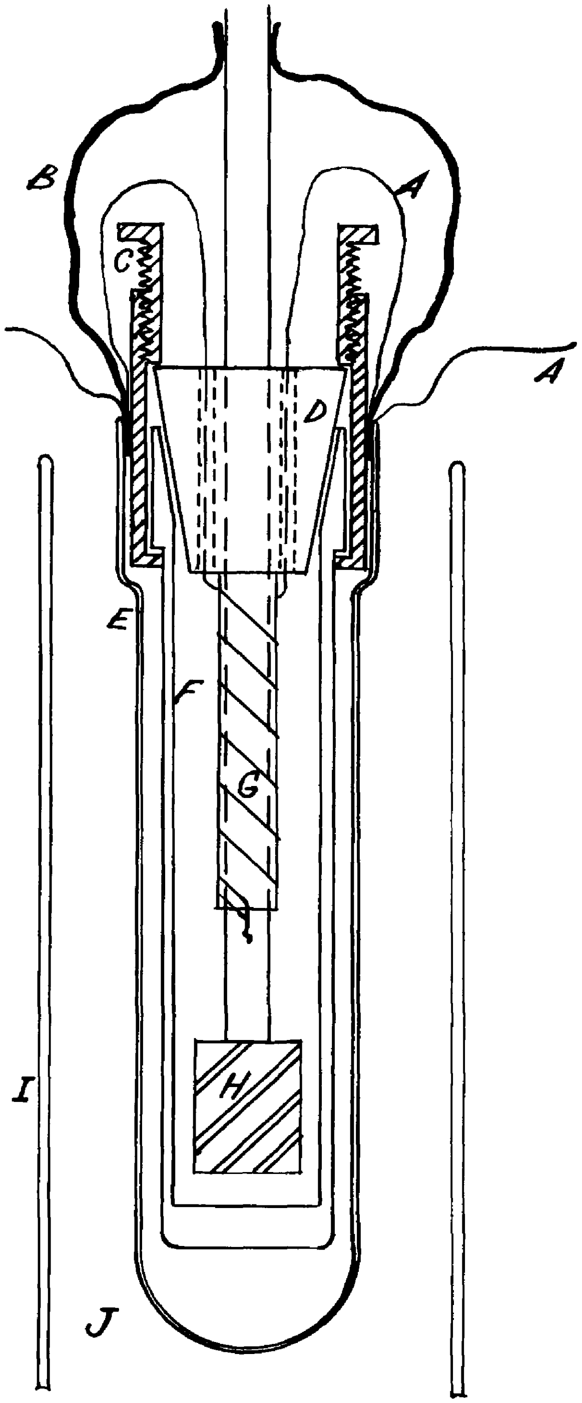

Figure 11. The freezing point cell: A, thermocouple leads; B, hood; C, aluminum collar; D, fluorothene plug; E, air-jacket; F, fluorothene tube; G, thermocouple tube; H, fluorothene plunger; I, Dewar flask; J. coolant.

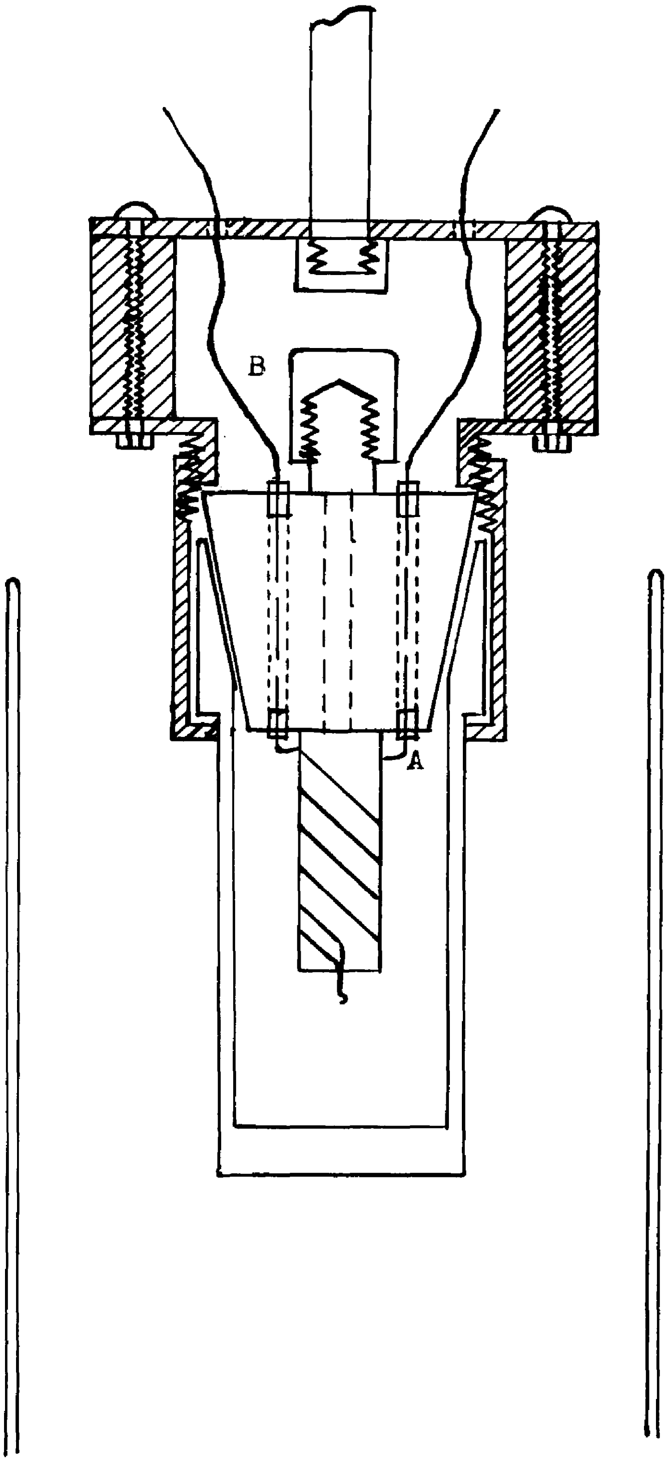

Figure 12. The freezing point cell used with pure bromine pentafluoride: A, tapered Teflon plugs; B, brass cap.

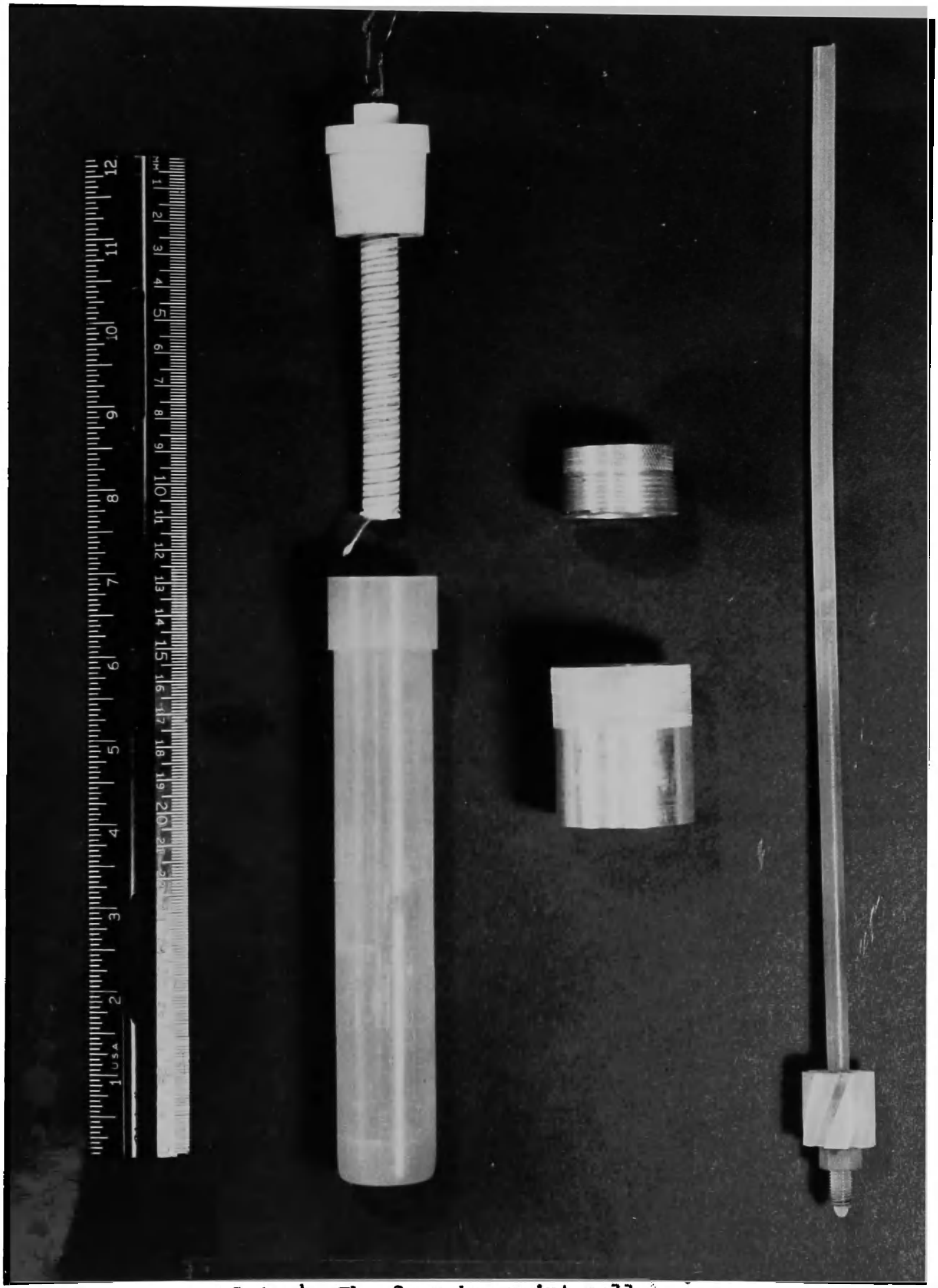

Plate 4. The freezing point cell.

An attempt was made to discover whether there were any solid state transitions in iodine pentafluoride in the region between its freezing point (+9.4°C) and -20°C. For this purpose a simple apparatus consisting of a fluorothene tube with a standard taper top, plus a thermocouple sealed through a fluorothene plug, was used. A slow rate of cooling was achieved by use of a large air jacket and a coolant mixture of ice and water to which alcohol was added at a steady rate.

Temperature Measurement

Thermocouple calibration and construction. The thermocouples used were prepared from a single spool each of number 24 copper wire and number 24 constantan wire obtained from the Leeds and Northrup company. The junctions were silver soldered.

The thermocouples were calibrated at three temperatures within the range of freezing point measurements made and were exposed to iodine pentafluoride before calibration. Calibration points at -63.5°C and at -38.85°C were obtained by using the reciprocal-action freezing point cell (Figure 11) with purified chloroform and with mercury, respectively.

For the mercury calibration point the plunger was removed and a small glass tube inserted. Air was bubbled through this tube to provide agitation. The thermocouple itself was coated with a thin layer of fluorothene to prevent amalgamation. A third calibration point was obtained at -78.39°C by using an equilibrium mixture of crushed Dry Ice and carbon dioxide vapor. To obtain the latter point a platinum resistance thermometer* which had been calibrated by the Bureau of Standards was used.

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* Leeds and Northrup serial #1016073.

The thermocouple which was to be calibrated was placed around the resistance thermometer while attached to the plug of the freezing point cell and the entire assembly was placed in a one-liter Dewar flask containing crushed Dry Ice (see Figure 14). The Dewar was covered with a cork and the mixture allowed to come to equilibrium. The resistance of the platinum resistance thermometer was measured by means of a Mueller Bridge[*] which was also calibrated by the Bureau of Standards. The Bureau of Standards certificate indicated that the resistance differences could be read to ± 0.02% on the Mueller Bridge. The correct temperature was obtained from the Bureau of Standards equation

$$R_t = R_0 \, [1 - \alpha t - \alpha v(1 - t/100)t/100].$$

R_t is the resistance at t degrees Centigrade and the values for the constants α and v are 0.00392604 and 1.4919, respectively. R_0 has previously been found to be 25.5031 ohms.[12]

The calibration data are given in the following table.

TABLE V

CALIBRATION DATA FOR THE COPPER-CONSTANTAN THERMOCOUPLE

Compound	Δ E (microvolts)	T'°C[*]	T"°C	ΔT'°C
$CHCl_3$	1422	-63.7 ± .02	-63.5	+0.2
Hg	2254	-38.80 ± .02	-38.85	-0.05
CO_2	2726	-78.78 ± .02	-78.39	+0.39

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[*] Leeds and Northrup, type G-1, serial #1011419.

ΔE is the difference between the potential of the cold junction at 0°C and that of the thermocouple to be calibrated, T'° is the temperature obtained from the standard thermocouple tables,[40] and T'' is the temperature of the freezing points of chloroform and mercury,[41] or the temperature of the crushed Dry Ice mixture, read from the resistance thermometer. The experimental errors shown are the errors in reading the cooling curves. It should be noted that the above procedure actually calibrated the entire system for the determination of ΔE. The calibration curve is plotted in Figure 13.

The method for obtaining ΔE for all the cryoscopic work is given below.

The ice-point reference. The measurement of temperature by means of a thermocouple requires a steady and accurately known reference temperature since the potential measured (ΔE) depends upon the temperature of the two junctions. The ice point is the most convenient reference point for this type of work.

The ice point was obtained by the use of a modification of a device described by White.[43] The glass tube illustrated in Figure 15 was filled with crushed ice prepared from water which was distilled and then deionized. This ice was then washed by passing pure chilled water through the side tubes and then was left partially filled with water and ice. The thermocouple was placed into the ice mixture through the center tube and the entire assembly was placed in a Dewar flask containing crushed ice. This device holds the temperature steady at $0.0000 \pm .0001$°C for

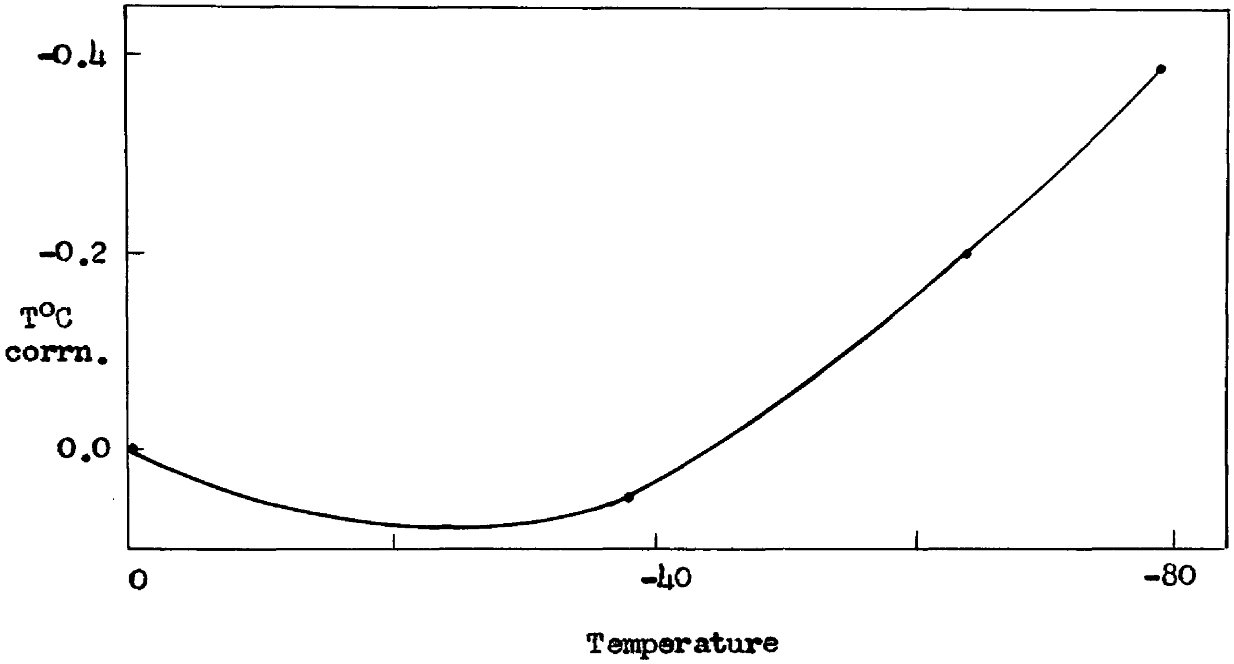

Figure 13. Thermocouple calibration curve for corrections to be applied to temperatures obtained from standard thermocouple tables.

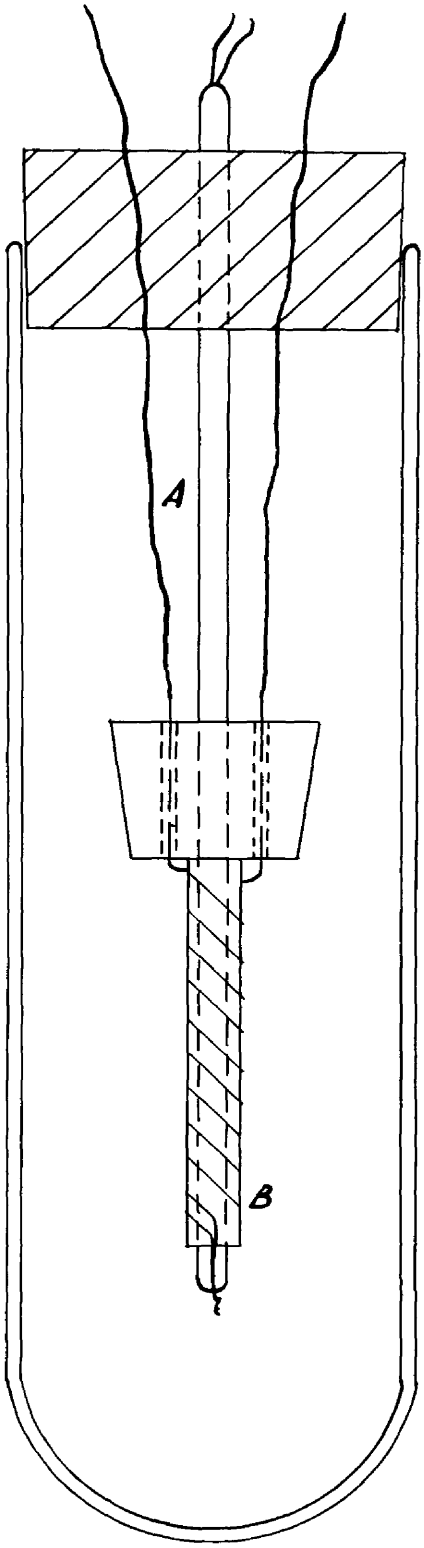

Figure 14. Diagram of the apparatus for obtaining the calibration point at -78.39°C: A, the platinum resistance thermometer; B, the tapered fluorothene plug and thermocouple from the freezing point cell.

up to 24 hours according to White. This accuracy is, of course, far greater than that required for these measurements.

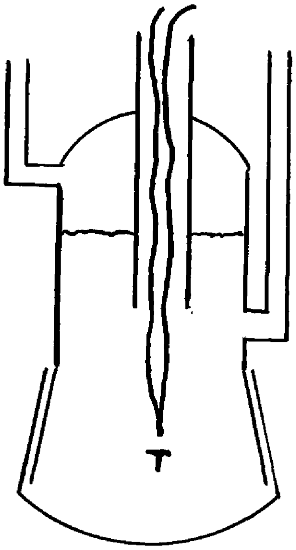

Figure 15. The ice-point tube: T is a thermocouple.

The determination of Δ E. The difference in potential (Δ E) between the thermocouple in the freezing point cell and the reference thermocouple was determined by use of a Brown Recording Potentiometer and a Leeds and Northrup type K-2 Potentiometer. A simple device was used to provide a steady bucking potential which could be varied at will (see Figure 16). With this device it was possible to obtain an output potential of such a magnitude that the recording potentiometer, when used in conjunction with a Leeds and Northrup D. C. amplifier, had a sensitivity of one-quarter to one-half degree per inch. The zero line on the recording potentiometer is thus equal to the bucking potential and Δ E is obtained directly by adding the bucking potential to the potential recorded. The bucking

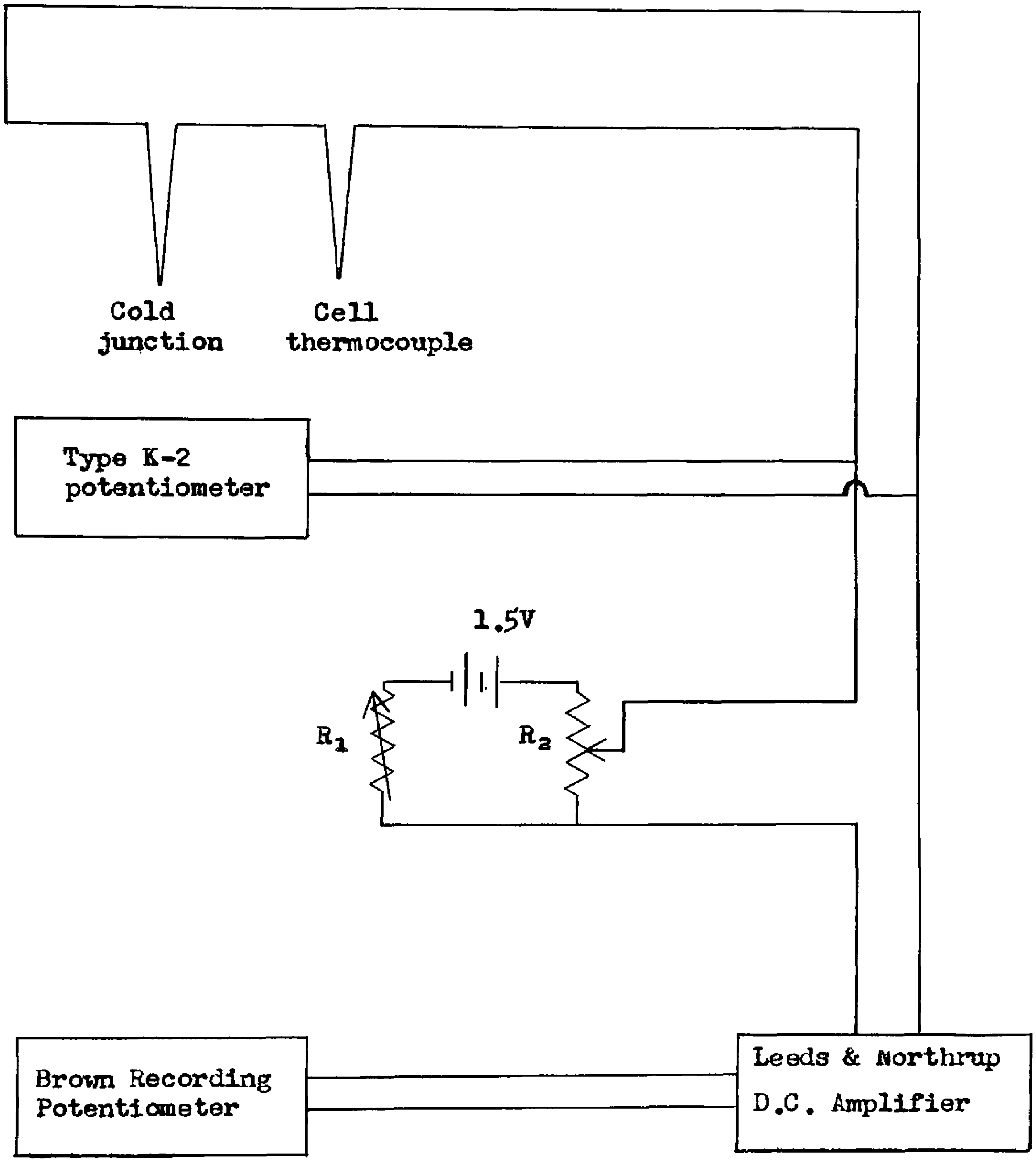

Figure 16. The apparatus for the determination of temperature using a thermocouple: R_1, standard decade resistance box; R_2, student potentiometer; a known bucking voltage is taken from R_2.

voltage was determined directly with the type K-2 potentiometer. The bucking voltage was found to have a maximum variation of plus or minus one microvolt during a period of twelve hours.

The type K-2 potentiometer was also connected directly across the thermocouple leads so that readings could be taken while the recorder was operating. Immediately after the reading on the K-2 potentiometer was read it was thrown out of balance and the contact closed for an instant. This put a mark on the chart of the recording potentiometer and thus the readings of the two potentiometers were simultaneously recorded on the same graph. The type K-2 potentiometer thus served as a calibrating device for the recording potentiometer.

The above set up for the recording of thermocouple values when making phase studies is very convenient as it permits one to record cooling curves directly with a recording potentiometer over any given temperature range.

Handling Procedures and Preparation of Solutions

Preparation of the solutions. The halogen fluoride, the purification and storage of which has been described above, was siphoned directly from the storage container (Plate 3) into a previously weighed fluorothene tube fitted with a plug and a valve. The valve over the tube was then closed and the line cleaned by evacuation and heating. The tube and valve assembly was then removed and weighed on a Torsion Balance. The assembly was then placed on the metal vacuum line and the liquid was frozen by use of a Dry Ice-acetone mixture. The valve was then opened and hydrogen fluoride was condensed directly into the tube from a tank connected to the line. The weighing procedure was repeated as described above.

After the solution was prepared it was chilled to just above the freezing point, the plug and valve were removed, and the stirring assembly was inserted into the tube. The amount of impurity introduced by this brief exposure to the atmosphere is considered to be negligible.

Hydrogen fluoride. The freezing point of the hydrogen fluoride obtained directly from the cylinder was determined to be -82.9 ± 0.1°C by the procedure indicated above. This agrees reasonably well with previously recorded values of -83.37°C,[37] and -83.07°C.[15b] The hydrogen fluoride from the cylinder was thus assumed to be suitable for these measurements.

It was not possible to determine the approximate amount of impurity present in the hydrogen fluoride because the stirrer jammed before an appreciable fraction of the material froze out, and poor cooling curves were obtained.

Hydrogen fluoride-potassium fluoride solutions. The cooling curves for several hydrogen fluoride-potassium fluoride solutions were run at high hydrogen fluoride concentrations to help complete the data of Cady.[44] For this purpose a weighed amount of potassium bifluoride* was placed in the fluorothene tube and a weighed amount of hydrogen fluoride was added as described above.

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* Merck & Co.

C. Data and Calculations

On the following pages the data for the cryoscopic studies are presented in tabular and graphical form.

The freezing points for each individual solution were determined from the recorded cooling curves (some illustrations of which are given in Figures 17, 18 and 21). The error indicated for each freezing point is estimated from the particular cooling curve involved; however, none of the values are better than ± 0.02°C as this is the approximate limit of the accuracy of the thermocouple calibration. Very large errors for certain points indicate, in general, that the slope of the freezing point curve was very steep.

Other information regarding the following tables is presented either as a footnote to the table in question, or in the text immediately preceding the table.

TABLE VI

CRYOSCOPIC DATA FOR IODINE PENTAFLUORIDE-HYDROGEN FLUORINE SOLUTIONS*

Weight HF (gm.)	Weight IF_5(gm.)	Mole Percent HF	Freezing Point°C	Eutectic Point°C
0.26	140.8	1.99	8.11 ± 0.02	---
0.26	137.7	2.06	8.00 ± 0.03	---
0.52	231.3	4.51	6.70 ± 0.02	---
1.40	203.1	7.10	4.46 ± 0.06	---
1.00	127.6	8.00	4.46 ± 0.06	---
3.37	153.0	19.6	-0.24 ± 0.06	---
6.90	138.8	35.6	-6.00 ± 0.06	---
9.75	118.9	47.7	-10.36 ± 0.02	-83.4**
11.08	118.8	50.87	-10.06 ± 0.06	---
12.87	115.9	55.19	-12.20 ± 0.02	---
16.55	108.5	62.87	-15.10 ± 0.06	-80 to -85**
22.15	104.2	70.19	-17.5 ± 0.3	---
23.70	85.2	75.5	-20.5 ± 0.3	---
26.10	93.7	75.7	-20.4 ± 0.1	---
26.26	64.5	81.2	-23.15 ± 0.06	-83.55
32.10	59.5	85.69	-25.9 ± 0.3	---
31.55	54.8	86.47	-26.7 ± 0.3	-83.58
28.85	34.88	90.19	-31.2 ± 0.3	-83.49
40.8	34.43	92.9	-53.1 ± 0.5	-83.49
41.17	21.18	95.59	-44.8 ± 1.0	-83.49
42.28	17.00	96.52	-52.0 ± 0.3	---
42.35	6.90	98.5	-72.9 ± 0.4	-83.43
46.55	3.00	99.5	-83.49 ± 0.06	-83.49

*The eutectic point is at 99.5 mole percent hydrogen fluoride and -83.49°C.

The experimental error given for the freezing point is taken as the maximum error in reading each individual cooling curve. This error increases with increasing hydrogen fluoride concentration because of the increasing slope of the cooling curve. In all cases the error listed here is the same as, or greater than, the error in the thermocouple calibration.

**The eutectic was reached in these cases by manual shaking after the plunger had jammed.

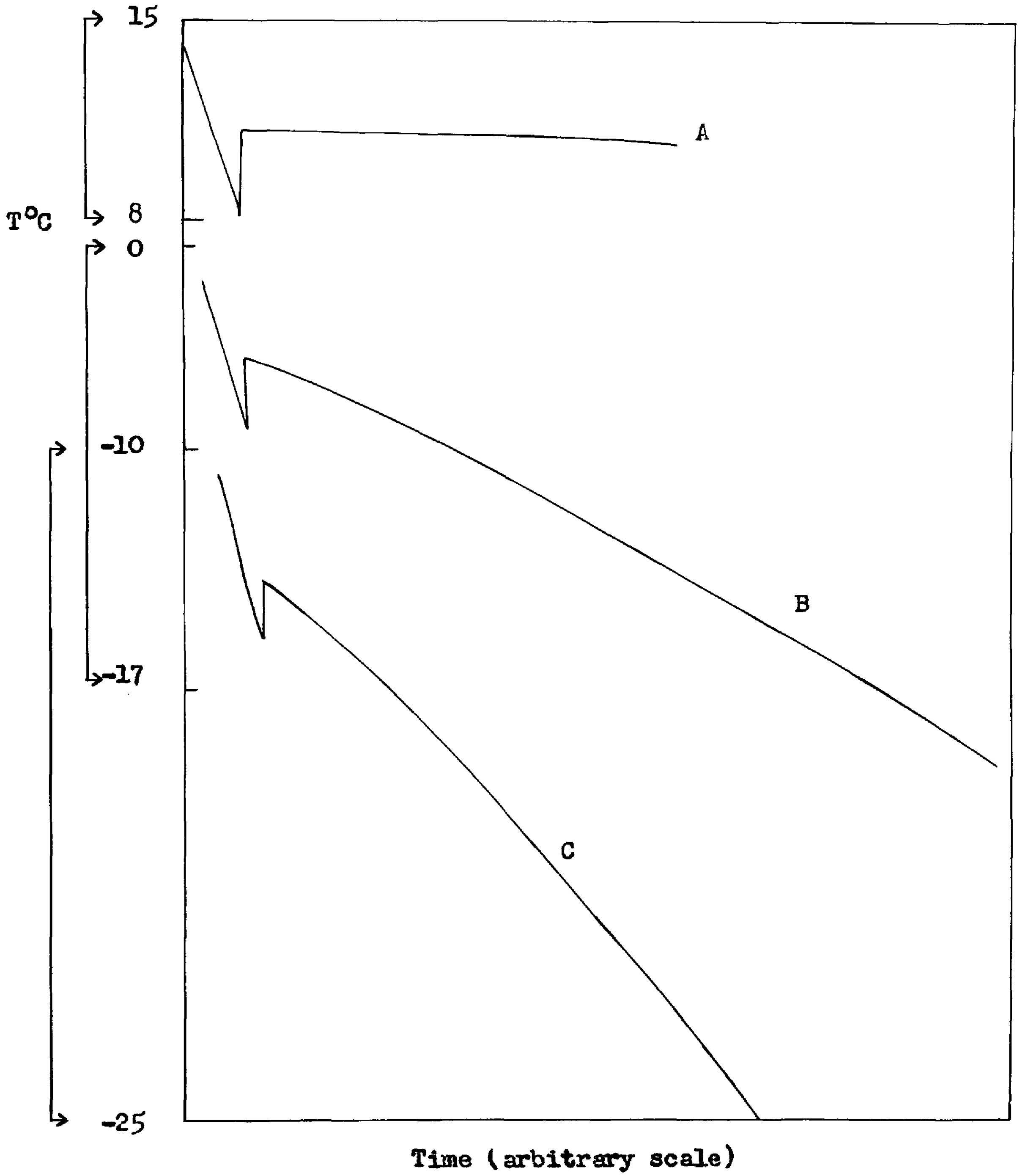


Figure 17. Some representative cooling curves for iodine pentafluoride-hydrogen fluoride solutions: A, iodine pentafluoride from storage container; B and C, 19.6 and 55.2 mole percent hydrogen fluoride, respectively. The curves are incomplete because stirrer jammed before freezing was complete.

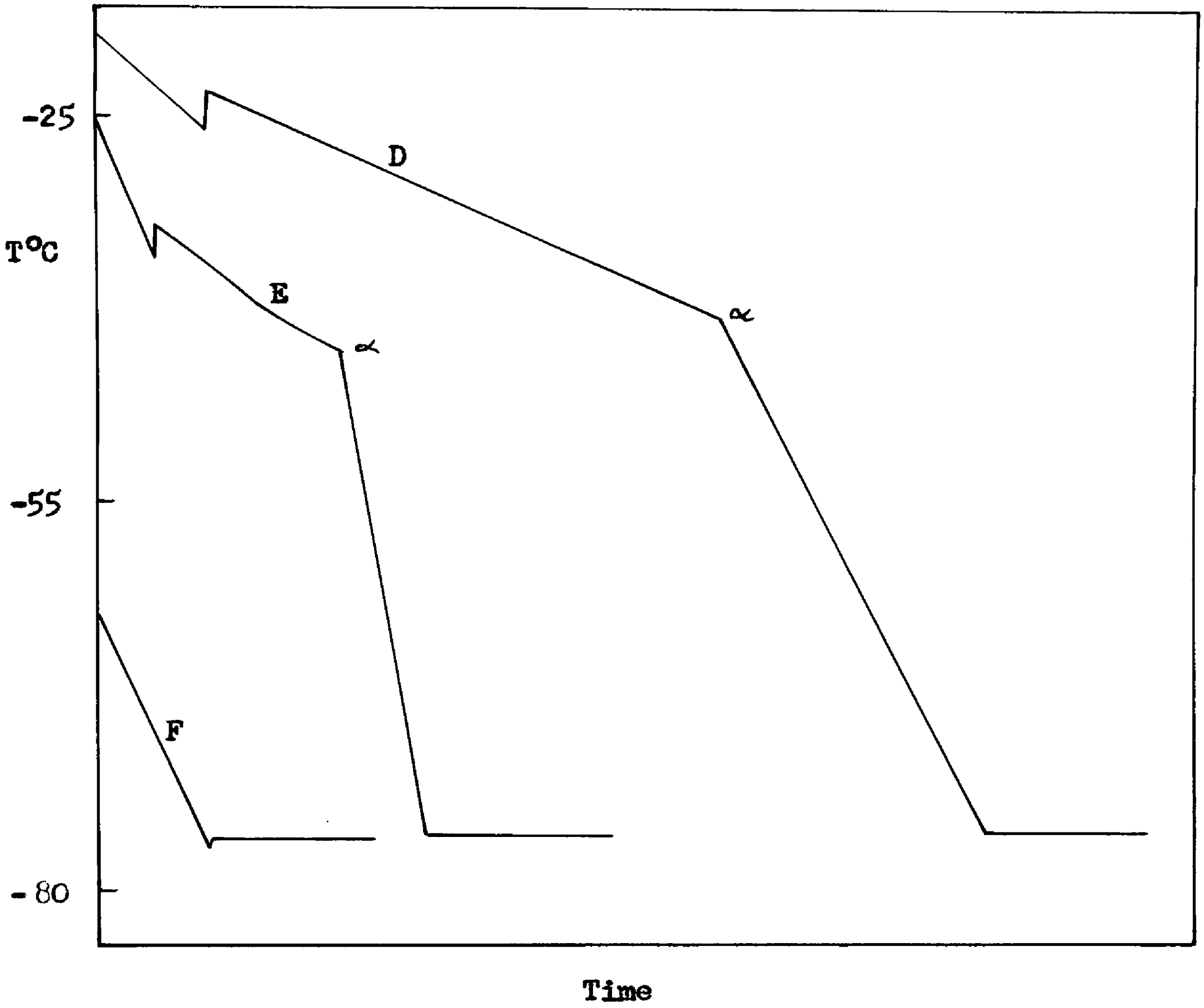
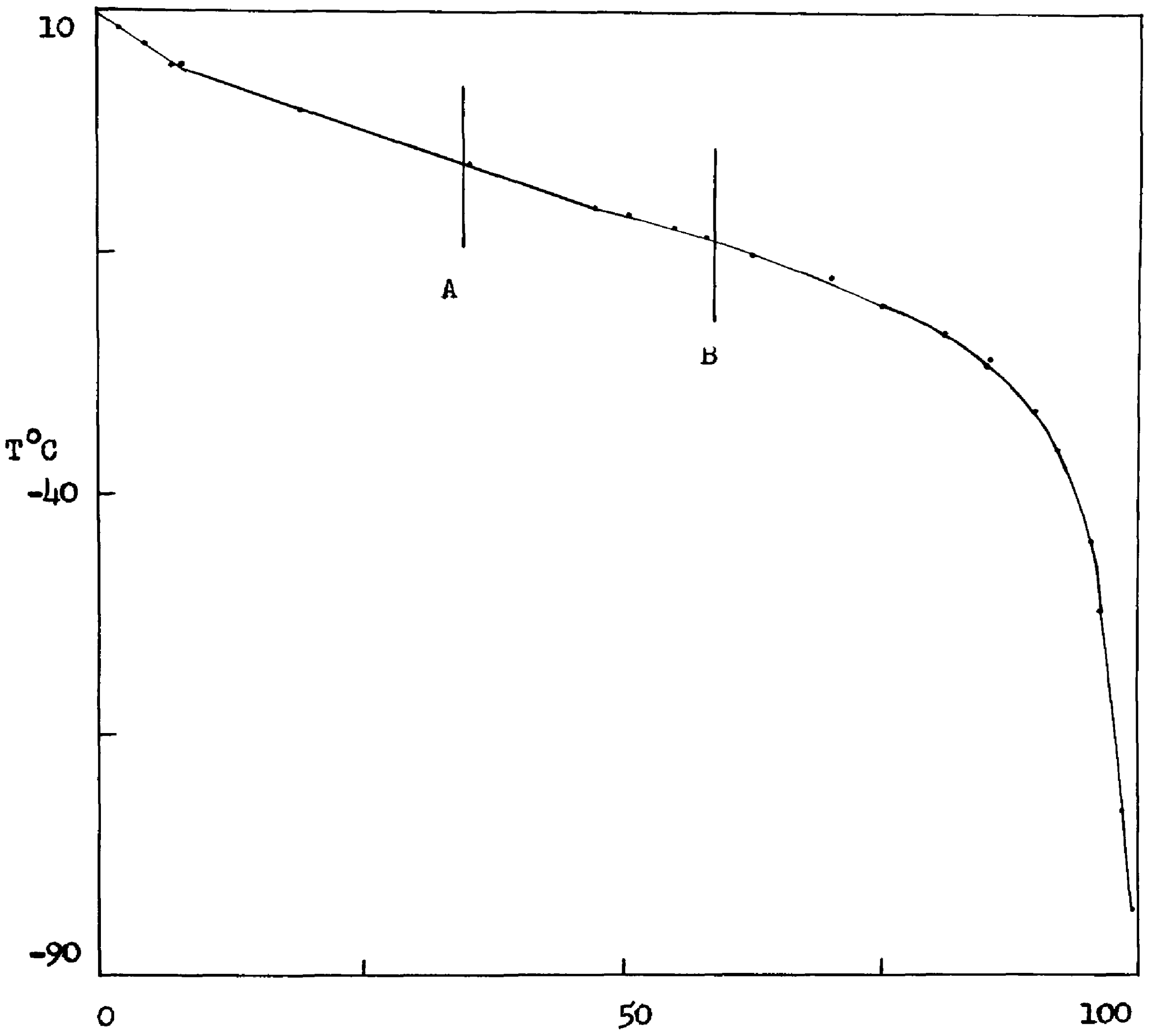


Figure 18. Some representative cooling curves for iodine pentafluoride-hydrogen fluoride solutions: D, E and F contain 81.2, 90.2, and 99.5 mole percent hydrogen fluoride respectively. At the point indicated by ∝ the cooling bath was changed from Dry Ice-acetone to liquid nitrogen.



Mole Percent Hydrogen Fluoride

Figure 19. Phase diagram of the system iodine pentafluoride-hydrogen fluoride. Detail of portion AB is given in Figure 20.

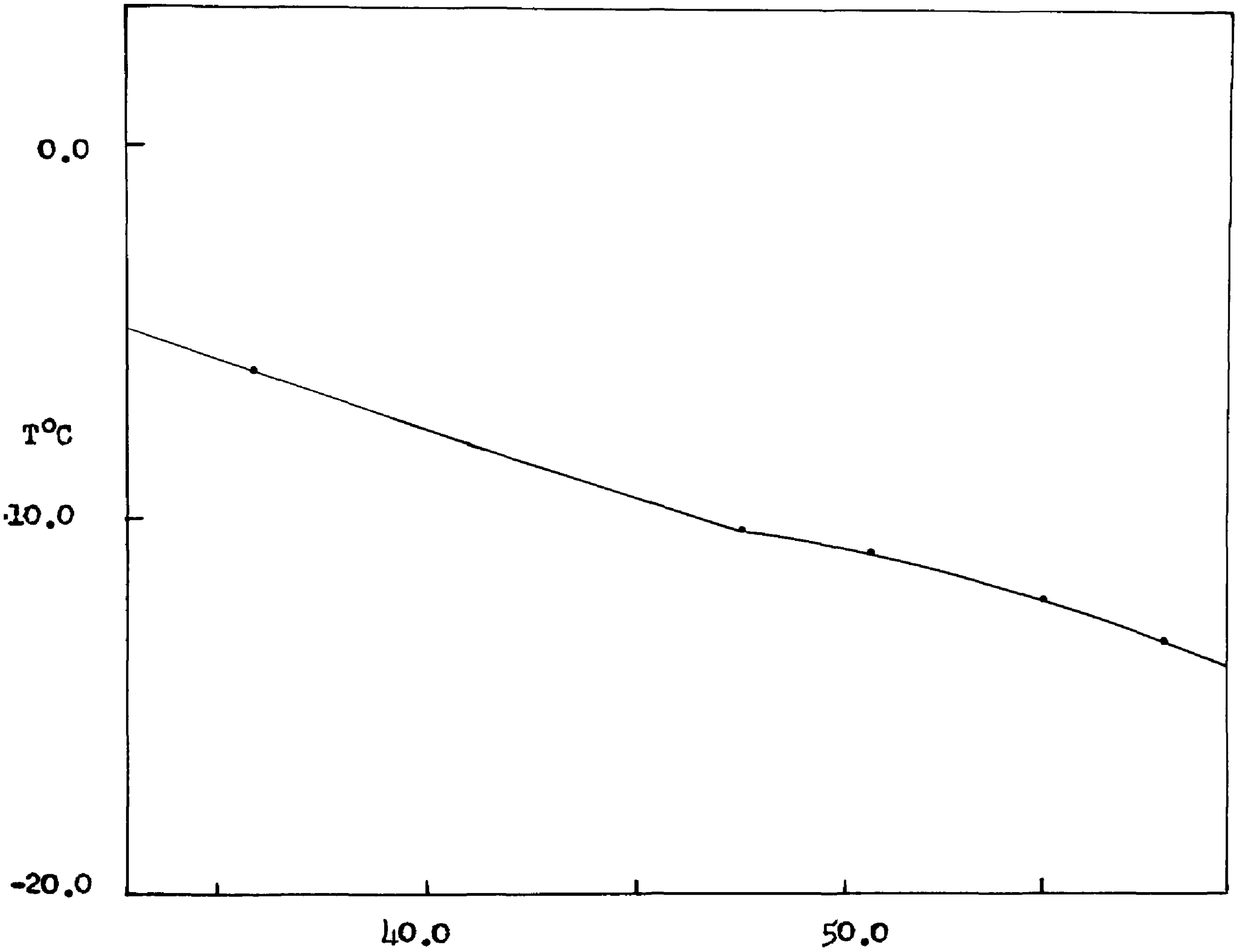


Figure 20. Detail of the phase diagram of the system iodine pentafluoride-hydrogen fluoride showing a possible peritectic point.

TABLE VII

CRYOSCOPIC DATA FOR BROMINE PENTAFLUORIDE-HYDROGEN FLUORIDE SOLUTIONS

Weight HF(gm.)	Weight IF$_5$(gm.)	Mole Percent HF	Freezing Point °C	Eutectic Point °C
0.28	106.5	2.25	-62.20 ± 0.02	---
0.82	116.6	5.79	-62.69 ± 0.07	---
1.82	107.1	12.9	-63.50 ± 0.02	---
2.54	102.0	17.9	-63.75 ± 0.02	---
3.30	110.6	20.7	-64.08 ± 0.03	---
3.81	95.8	25.8	-64.43 ± 0.02	---
6.05	92.5	36.3	-64.96 ± 0.03	---
9.90	88.9	49.3	-65.62 ± 0.02	---
12.89	76.6	59.5	-66.1 ± 0.1	---
17.29	74.6	67.0	-66.70 ± 0.02	---
27.57	53.1	81.9	-68.40 ± 0.02	---
36.02	37.6	89.3	-72.7 ± 0.4	---
39.45	27.9	92.5	-78.2 ± 0.4	-85.61
43.10	22.0	94.5	-84.5 ± 0.4	-85.61
44.67	13.4	96.7	-84.98 ± 0.03	---
44.20	5.45	98.6	-83.94 ± 0.03	---

The eutectic point is at 95.2 mole percent hydrogen fluoride and -85.61°C.

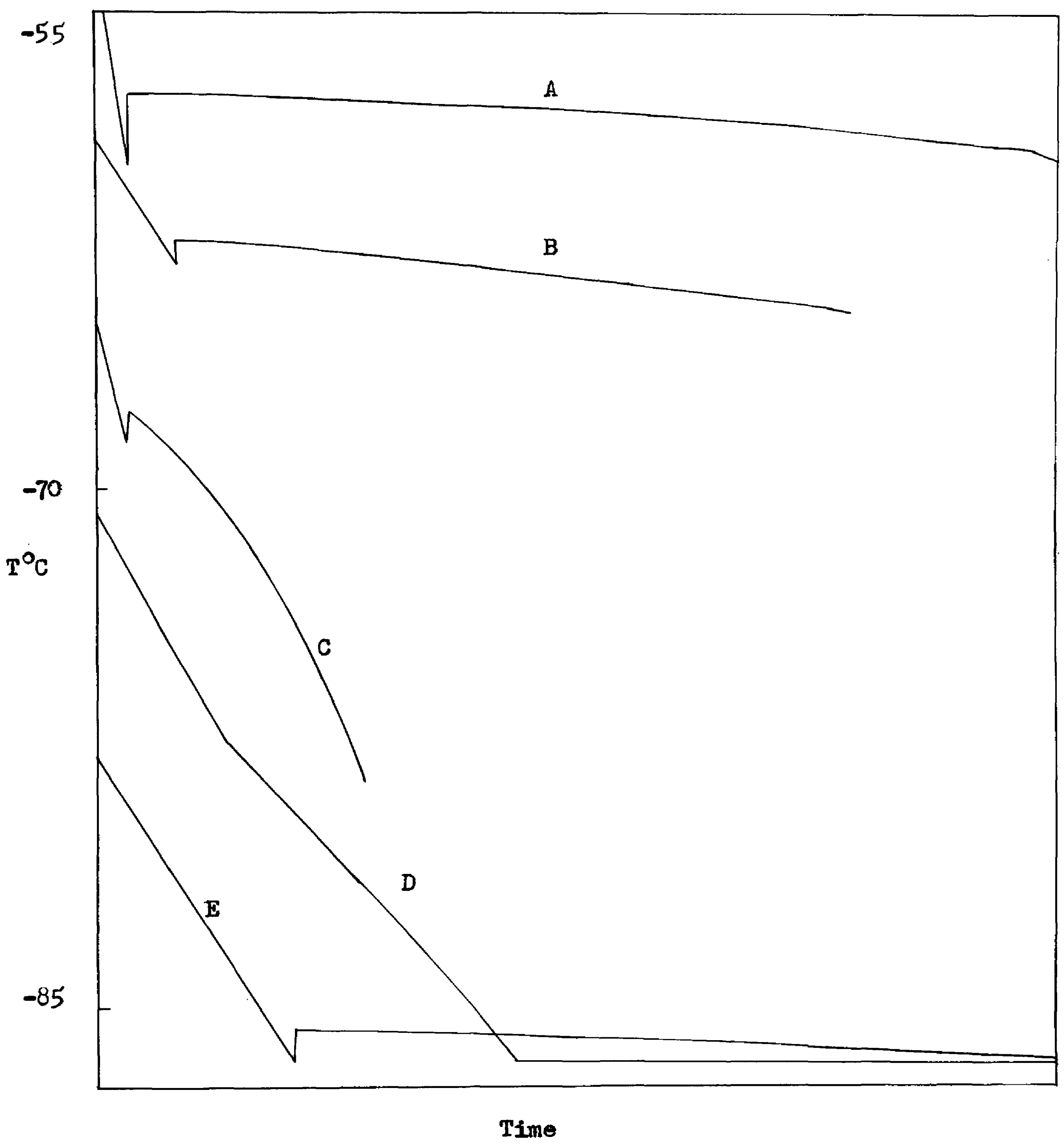


Figure 21. Some typical cooling curves of bromine pentafluoride-hydrogen fluoride solutions: A, bromine pentafluoride from storage container; B, C, D and E contain 25.8, 81.9, 92.5 and 96.7 mole percent hydrogen fluoride, respectively. The time scale and coolant used for A and B are different than those for C, D and E.

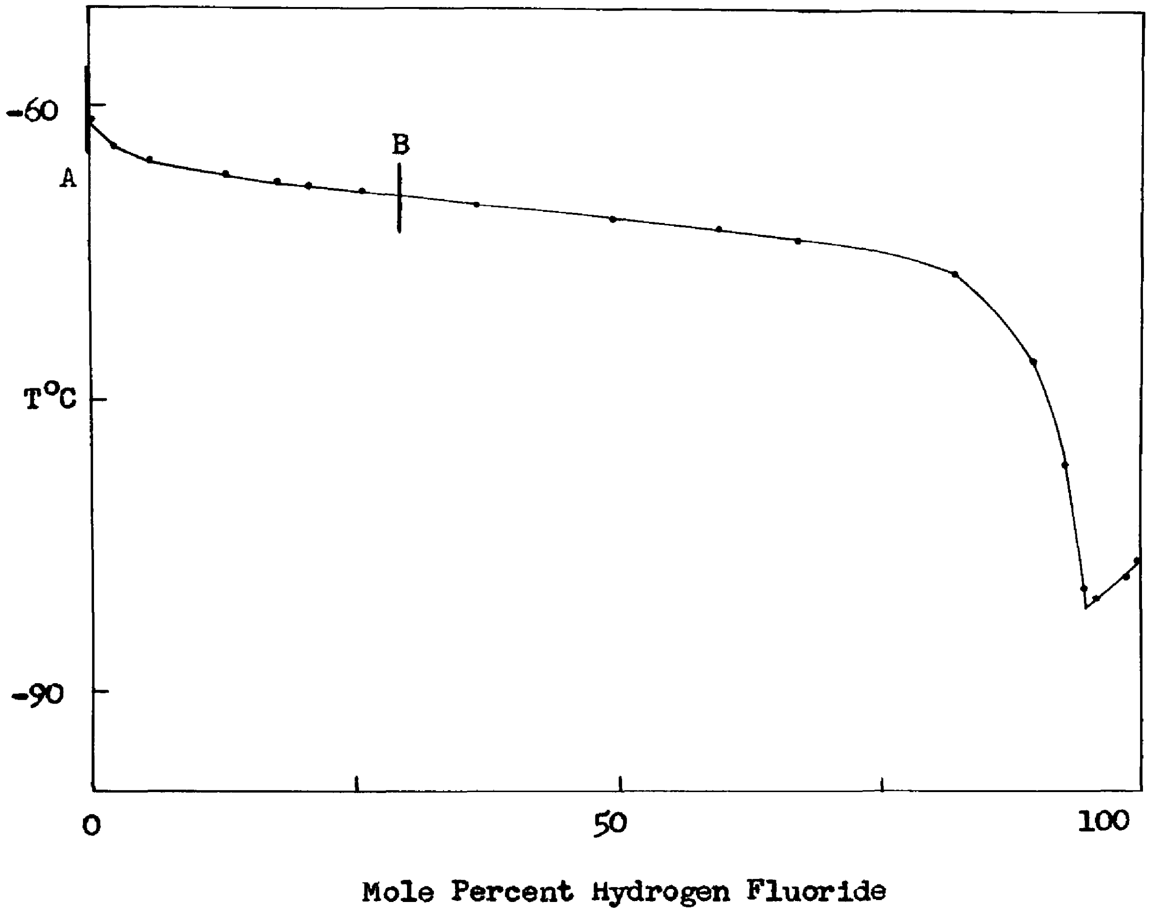
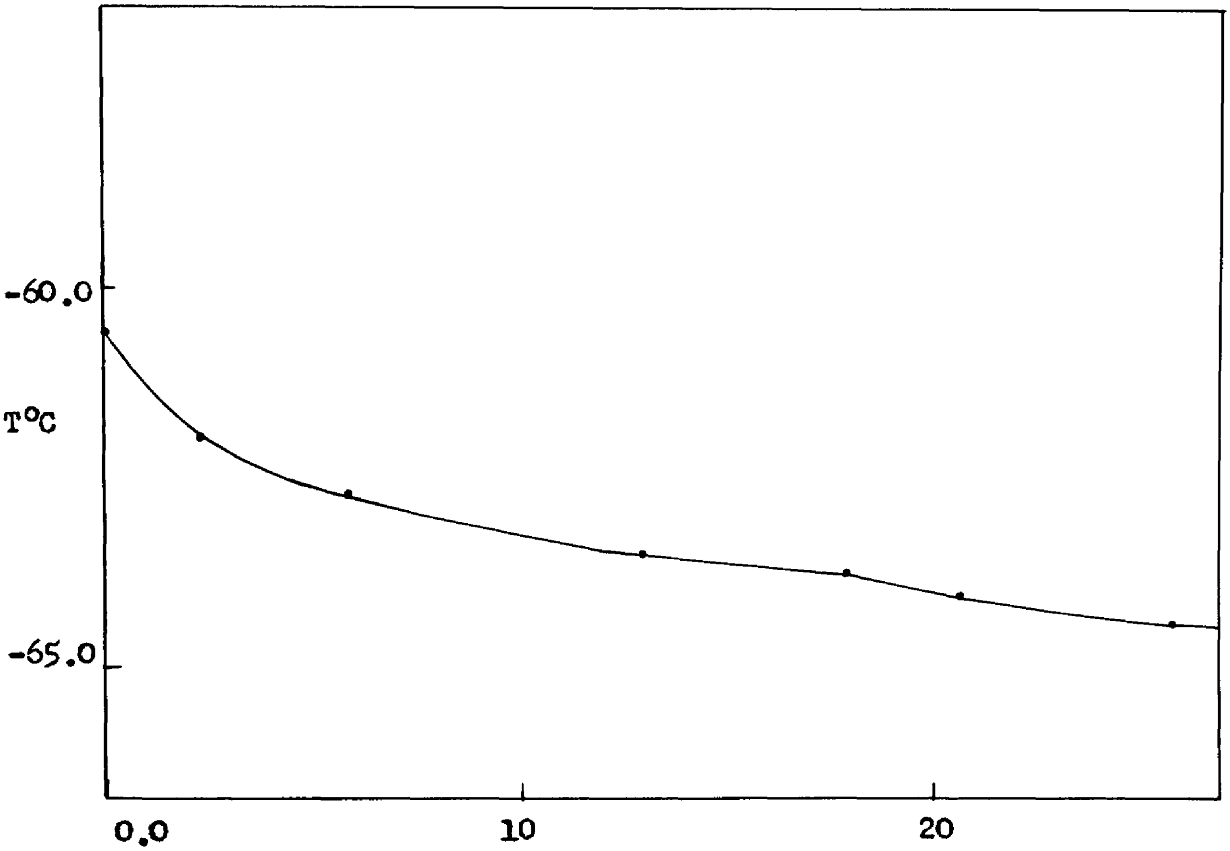


Figure 22. Phase diagram of the system bromine pentafluoride-hydrogen fluoride. Detail of the portion AB is shown in Figure 23.



Mole Percent Hydrogen Fluoride

Figure 23. Detail of the phase diagram of the system iodine pentafluoride-hydrogen fluoride showing a possible transition in the solid phase.

The freezing points of iodine pentafluoride and bromine pentafluoride were calculated by the method of Witschonke[40] and are tabulated in Table VIII. Also tabulated is the measured freezing point of hydrogen fluoride taken directly from the cylinder. The Witschonke method was not used for hydrogen fluoride because the stirrer jammed before an appreciable percentage of the hydrogen fluoride had frozen.

TABLE VIII

THE FREEZING POINTS OF IODINE PENTAFLUORIDE, BROMINE PENTAFLUORIDE, AND HYDROGEN FLUORIDE

Compound	This Work		Previously Reported	
	F.P.°C	m_i	F.P.°C	Reference
Iodine pentafluoride	9.427 ± 0.02	0.0086	9.6 9.425	(9) (12)
Bromine pentafluoride	-60.63 ± 0.026	0.026	-61.3	(7)
Hydrogen fluoride	-82.9 ± 0.1	---	-83.09 -83.37	(15b) (37)

m_i is the molal concentration of impurity calculated by the method of Witschonke.

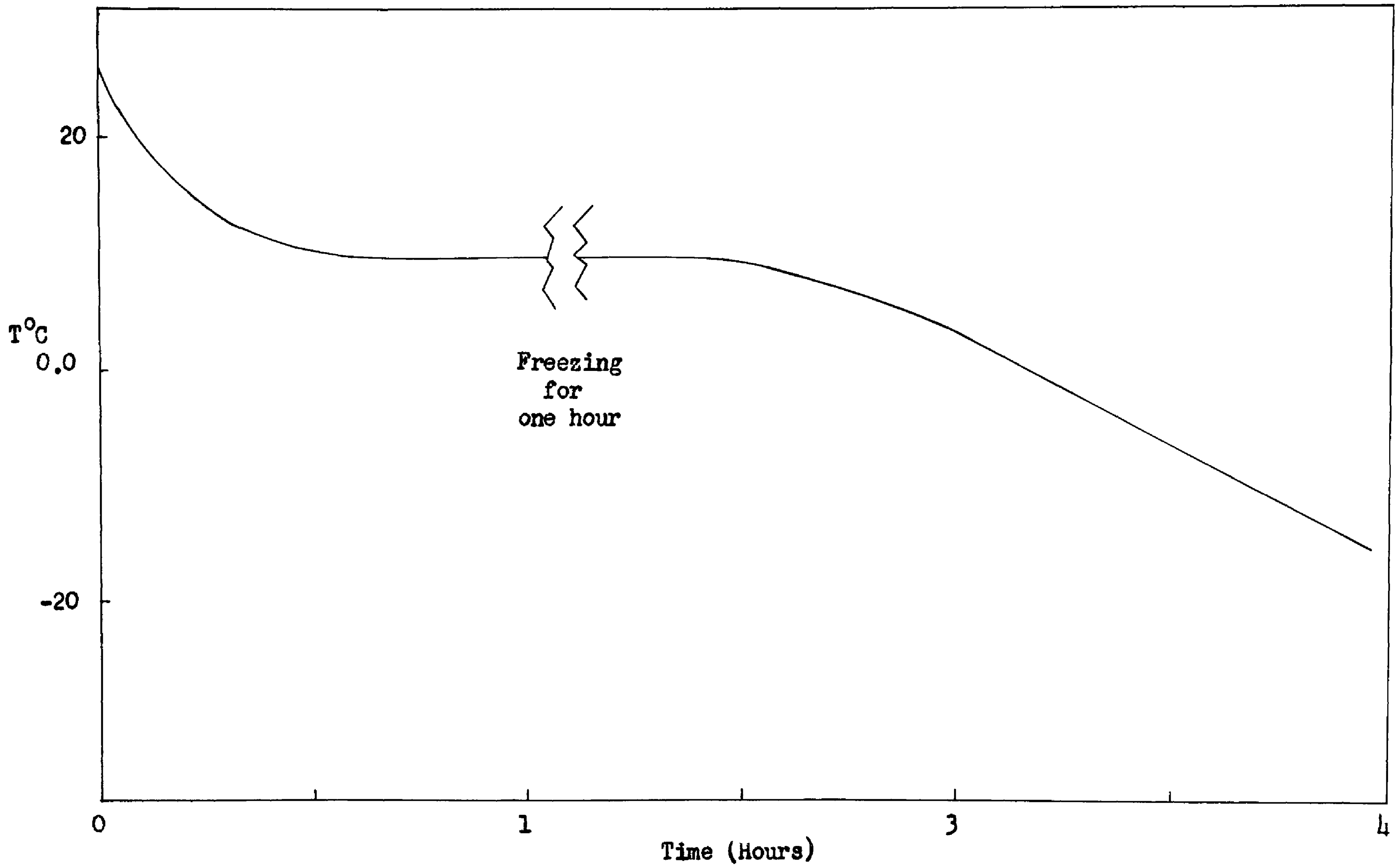


Figure 24. Cooling curve for pure iodine pentafluoride.

TABLE IX

CRYOSCOPIC DATA FOR SEVERAL HYDROGEN FLUORIDE-POTASSIUM FLUORIDE SOLUTIONS

Weight HF(gm.)	Weight KHF_2(gm.)	Mole Percent HF	F. P. °C
55.75	1.2990	99.39	-83.80 ± 0.03
45.37	0.5905	99.65	-83.34 ± 0.03
42.57	0.3004	99.81	-83.22 ± 0.04

CRYOSCOPIC DATA REPORTED BY CADY FOR HYDROGEN FLUORIDE-POTASSIUM FLUORIDE SOLUTIONS*

Mole Percent HF	F.P.°C	F.P.°C**
100.00	-83.7	-83.0
98.75	-85.2	-84.5
97.32	-86.9	-86.2

*The freezing points reported by Cady were obtained using an uncalibrated thermocouple. The values which he reported (F.P.°C) have therefore been corrected for thermocouple error (F.P.°C**) by taking his reported value for the freezing point of hydrogen fluoride as a calibration point. If Johnston's data for the freezing points of hydrogen fluoride are used no agreement is obtained.

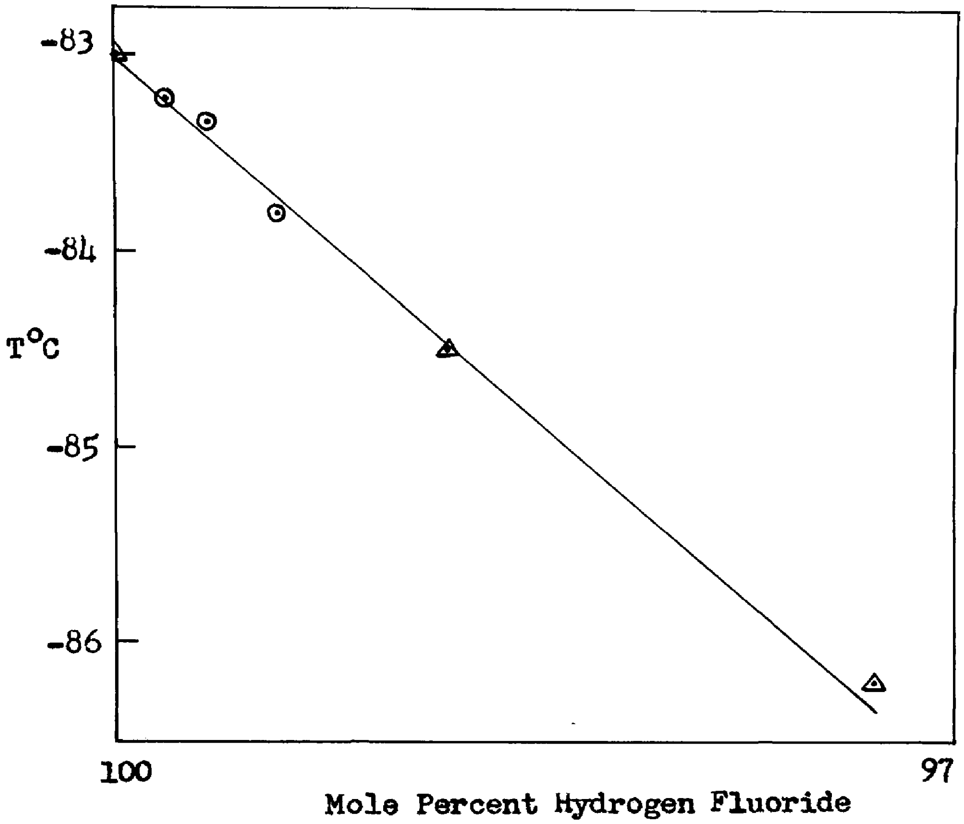


Figure 25. Detail of the phase diagram of the system hydrogen fluoride-potassium fluoride: ⊙ determined in this work; △ determined by Cady.

Cryoscopic constants were determined from large scale plots of the phase diagrams and by use of the relation,[38]

$$K_f = \frac{\Delta T_f M_2 w_1}{1000 w_2}$$

where K_f is the cryoscopic constant, ΔT_f the freezing point depression, M_2 the molecular weight of the solute, w_2 the weight of solute and w_1 the weight of solvent. ΔT_f was determined from the slope of the freezing point curve at infinite dilution.

Heats of fusion were determined by use of the relation[38]

$$\ln N_1 = \frac{-L_f \ \Delta T_f}{R T_o^2}$$

where L_f is the molar heat of fusion, N_1 the mole fraction of solvent and T_o is the freezing point of the pure material in degrees Kelvin.

Values of these constants were determined for iodine pentafluoride, bromine pentafluoride, and hydrogen fluoride and are tabulated in Table X. When this method is used for obtaining heats of fusion it must be assumed that solid solutions are not formed.

TABLE X

CRYOSCOPIC CONSTANTS AND HEATS OF FUSION OF BROMINE PENTAFLUORIDE, IODINE PENTAFLUORIDE AND HYDROGEN FLUORIDE

Compound	K_f Degrees Per Mole	L_f Kcal. Per Mole	System Studied
IF_5	12.2	2.69	HF in IF_5
BrF_5	14.0*	1.0*	HF in BrF_5
HF	1.53	1.0	BrF_5 in HF
HF	1.16	1.32	KF in HF

*This value is very doubtful because the shape of the freezing point curve made ΔT difficult to obtain.

D. Discussion of the Results

The Pure Materials

The freezing points of bromine pentafluoride and iodine pentafluoride as determined in this work are appreciably lower than those reported by Ruff. The freezing point for iodine pentafluoride is, however, in excellent agreement with previous work done in this laboratory,[12] although a slightly different method was used. It is not at all surprising that the freezing points obtained here differ from those presented by Ruff, since the earlier studies were hampered by a lack of adequate materials for the purification and handling of the halogen fluorides. The data are listed in Table ~~IX~~ VIII along with the molal impurity in each sample as calculated by the method of Witschonke.[40] The freezing points obtained by other workers are also listed.

The Phase Diagrams

The phase diagram of the iodine pentafluoride-hydrogen fluoride system (Figure 19) looks very much like that of a simple two-component system with a eutectic point at 99.5 percent hydrogen fluoride, except that at 5.0 and at 48.8 mole percent hydrogen fluoride there are slight discontinuties. The discontinuity which occurs at 48.8 mole percent hydrogen fluoride, although it is very slight, seems to be a peritectic point. This point is shown in the detail of the phase diagram shown in Figure 20. The very small change in slope at concentrations just above the peritectic point makes it very difficult to extrapolate the curve in order to determine the composition of the compound which may be formed.

The fact that there is an indication of compound formation below fifty mole percent hydrogen fluoride is surprising and an effort was made to determine whether there was any solid-phase transition in iodine pentafluoride at the apparent peritectic and at the discontinuity at five mole percent. The method used, which is described above, was quite crude, and the lack of evidence for a solid-state transition by that method does not prove that solid-state transitions do not occur. The curve obtained for the slow cooling of iodine pentafluoride is shown in Figure 24.

The phase diagram of the bromine pentafluoride-hydrogen fluoride system also appears at first glance to be a simple two-component system without compound formation. The eutectic point in this case occurs at 95.2 mole percent hydrogen fluoride. There is apparently a very slight discontinuity at eighteen mole percent hydrogen fluoride, however, as can be seen in the detail of the phase diagram in Figure 23. It should be noted that this discontinuity looks similar to that which occurs at five mole percent hydrogen fluoride on the iodine pentafluoride-hydrogen fluoride phase diagram.

The two discontinuities mentioned above are probably due to a solid state phase change. Many substances are capable of existing in various crystalline forms which are so related to one another that at a given temperature the relative stability of each pair of allotropic forms undergoes a change. Each crystalline variety has its own solubility and thus there is a break in the solubility curve at the transition temperature.

This is a rather common occurrence, two examples of which are water solutions of ammonium nitrate[45] and thallous picrate.[46]

It is quite possible that a transition of this type would not have been detected by the simple device used in this work. The phase change which occurs when all the material is in the solid state may take a very long time to come to equilibrium. If this was the case the curve obtained in this work would have been smooth, as indeed it was. The phase diagram, however, might show the change observed because of the change in solubility of the new crystalline form.

The unusual concave shape of the bromine pentafluoride-hydrogen fluoride phase diagram at low hydrogen fluoride concentrations has been known to occur in other systems. The system iron-ferrous sulfide is an example[47] in which the phase diagram is that of a simple two component system except for the shape at low iron concentrations. The system iron-ferrous sulfide does not form solid solutions.

A concave freezing curve may sometimes be explained on the basis of solid solution formation. The cooling curves obtained in the regions of the transitions indicated, however, that the mixture contained liquid down to temperatures near those of the eutectic point. This qualitative observation was made by manual shaking of the apparatus after the stirrer had jammed due to freezing. An observation of this type would not eliminate the possibility of solid solution formation with a very steep solidus-liquidus curve.

Heats of Fusion

The heats of fusion obtained from the cryoscopic data are presented in Table X. In general if they are compared with heats of fusion calculated from heats of vaporization and heats of sublimation the agreement is very poor. The heats of fusion oftained here for iodine pentafluoride and bromine pentafluoride are 2.69 and 1.0 kilocalories per mole, respectively, while those calculated from Ruff's data on the vapor pressure of the solid combined with heats of vaporization obtained in this laboratory[49,50] are 3.80 and 1.76 kilocalories per mole, respectively. A possible explanation of these results is that the assumption that solid solutions are not formed is incorrect. Actually it is possible that solutions with a very steep liquidus-solidus curve are formed. This would invalidate any heat of fusion calculations based upon the phase diagrams presented.

VI DENSITIES AND AVERAGE MOLAR VOLUMES OF HALOGEN FLUORIDE-HYDROGEN FLUORIDE SOLUTIONS

A. Theoretical Aspects

A partial molal quantity is defined as the partial derivative of an extensive quantity with respect to the number of moles of a particular substituent, when taken at constant temperature, pressure, and composition. Thus the partial molal volume of substituent 1 in a two-component solution is

$$\bar{V}_1 = \left(\frac{\partial V}{\partial n_1}\right)_{P,\,T,\,n_2} \qquad (1)$$

where V is the volume of the solution, P and T are the pressure and temperature, respectively, and n_1 and n_2 are the number of moles of each constituent.

There are a number of general relations between partial molal quantities which apply to these quantities for any extensive property. In general

$$\bar{G}_1 = \frac{\partial G}{\partial n_1}, \quad \bar{G}_2 = \frac{\partial G}{\partial n_2}, \ \ldots \qquad (2)$$

where G is the extensive property and the same restrictions and definitions given above hold.

Since in each of the above equations the concentration of the remaining constituents remains constant, for a change in G at constant temperature and pressure

$$dG = \frac{\partial G}{\partial n_1}\, dn_1 + \frac{\partial G}{\partial n_2}\, dn_2 + \ldots \qquad (3)$$

or $$dG = \overline{G}_1 dn_1 + \overline{G}_2 dn_2 + \;.\;. \qquad (4)$$

If the relative proportions of the constituents remain unchanged, then integration from $n_1 = n_2 = 0$ and $G = 0$ to $n_1 = n_1$, $n_2 = n_2$, and $G = G$ yields

$$G = \overline{G}_1 n_1 + \overline{G}_2 n_2 + \;.\;.\;. \qquad (5)$$

For any infinitesimal change in composition

$$dG = n_1 \partial \overline{G}_1 + \overline{G}_1 \partial n_1 + n_2 \partial \overline{G}_2 + \overline{G}_2 \partial n_2 + \;.\;.\;. \qquad (6)$$

and subtracting (5) from (6)

$$n_1 \partial \overline{G}_1 + n_2 \partial \overline{G}_2 + \;.\;.\;. = 0 \qquad (7)$$

and dividing by ∂n_1

$$n_1 \frac{\partial \overline{G}_1}{n_1} + n_2 \frac{\partial \overline{G}_2}{\partial n_1} + \;.\;.\;. = 0 \qquad (8)$$

When dealing with one mole of solution we may define the average value of the extensive property per mole as

$$gi = \frac{G}{n_1 + n_2} + \;. \qquad (9)$$

and since $n_1 + n_2 + \;.\;.\;. = 1$, and $N_1 + N_2 + \;.\;.\;. \equiv 1$, (10)

from Equation 5

$$gi = \overline{G}_1 n_1 + \overline{G}_2 \overline{n}_2 + \;.\;.\;.\;. \qquad (11)$$

Dividing Equation 7 by $n_1 + n_2 + \;.\;.$ we obtain

$$N_1 \partial \overline{G}_1 + N_2 \partial \overline{G}_2 + \;.\;.\;. = 0 \qquad (12)$$

and dividing the above by ∂N_1

$$N_1 \frac{\partial G_1}{\partial N_1} + N_2 \frac{\partial G_2}{\partial N_2} + . . . = 0 \qquad (13)$$

With a two-component solution it is possible to plot the average value of the extensive property per mole, g_i, versus mole fraction. The tangent to the curve obtained at any point will intersect the ordinates of each pure component at points which are the partial molal volumes of the substituents in question at the composition of the point at which the tangent touches the curve.

B. Apparatus and Method

To calculate the apparent molal volumes and equivalent conductances of the halogen fluoride-hydrogen fluoride solutions at 25°C, it was necessary to determine the densities of the solutions at 25°C. The pycnometer illustrated in Figure 26 was constructed for this purpose.

Since it was extremely difficult to fill the pycnometer to a given mark while it was on the vacuum line, it was calibrated separately for each solution, according to the following procedure. The pycnometer was weighed and placed on the vacuum line. Solutions were prepared and weights of each component were determined in the same manner as will be described for the conductance cell, except that each solution was prepared from a new sample of halogen fluoride. It was necessary to have the upper level of the solution come up into the narrow neck of the pycnometer. The pycnometer was then placed in a water bath at 25°C and when equilibrium was reached the height of the solution in the neck was marked. The pycnometer was then cleaned and re-weighed. Benzene at 25°C was added to the mark and it was weighed again. Knowing the density of the benzene, the volume of solution which the pycnometer had contained could be determined.

A somewhat smaller pycnometer was used for the iodine pentafluoride solutions, but the procedure followed was the same.

C. Data and Calculations

Since the data required for the calculation of the densities of the solutions also was sufficient to calculate the average molal volume of the solution by the use of

$$v_i = \frac{\text{Volume of Solution Measured}}{\text{Total number of moles}}$$

where v_i is the average molal volume, this quantity has been calculated for each solution and is given in the table on page 77. The ideal molal volume of the solution was also calculated from

$$v_i' = N_1 \bar{V}_1 + N_2 \bar{V}_2$$

where v_i' is the ideal molal volume of the solution, N_1 and N_2 are the mole fractions of constituents 1 and 2, and $\bar{V}_1$ and $\bar{V}_2$ are the molal volumes of the pure constituents.

In order to give a better picture of the change in volume due to non-ideality, the percent change in v_i was obtained from

$$\Delta v_i' \text{ (percent)} = \frac{100\ (v_i' - v_i)}{v_i'}$$

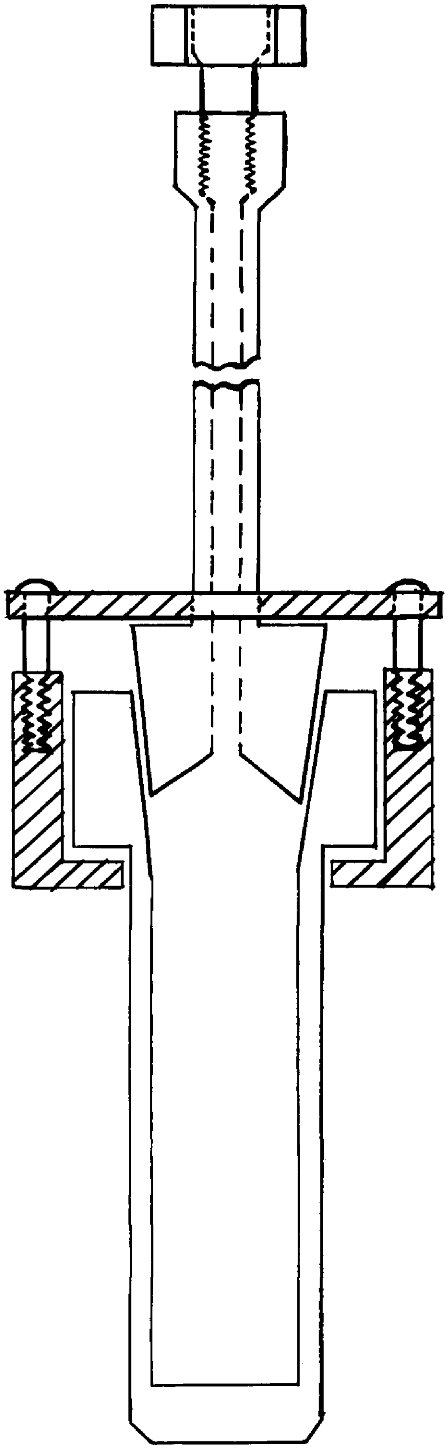


Figure 26. The pycnometer; all parts are of fluorothene except the clamping device.

TABLE XI

DENSITIES AND AVERAGE MOLAL VOLUMES FOR HALOGEN FLUORIDE-HYDROGEN FLUORIDE SOLUTIONS AT 25°C*

Weight (grams) XF_n	Weight (grams) HF	Weight Percent HF	Mole Percent HF	Volume Observed cc.	d gm./cc.	v_i' (ideal) cc.	v_i (measured) cc.	$\Delta v_i'$ Percent
				Iodine Pentafluoride				
2.674	0.3188	10.7	56.0	1.135	2.64	40.9	39.8	-2.7
1.433	1.100	43.5	89.5	1.475	1.72	25.7	24.0	-6.6
1.527	1.829	54.5	92.6	2.320	1.51	24.3	23.5	-3.3
				Bromine Pentafluoride				
2.99	10.45	77.8	97.4	11.9	1.13	22.2	22.2	0.0
13.98	5.08	26.6	76.1	10.7	1.79	32.8	32.1	-2.1
19.07	3.67	16.2	62.9	11.4	1.97	39.4	38.9	-1.3
22.02	2.49	10.2	49.8	11.4	2.15	46.0	45.4	-1.3
27.87	0.00	0.0	0.0	11.3	2.47	70.8	70.8	--
				Chlorine Trifluoride				
20.44	0.00	0.00	0.00	11.3	1.82	50.8	50.8	--
15.54	3.79	19.6	53.0	12.1	1.60	35.0	33.8	-3.4

* Check runs with Benzene indicated that the densities are accurate to one percent.

d^{25}_{HF} = 0.946 gm./cc.[15a], V_i = 20.9 cc.

$d^{25}_{IF_5}$ = 3.19 gm./cc.[15a], V_i = 66.5

$d^{25}_{benzene}$ = 0.874 gm./cc.

XF_n symbolizes a general halogen fluoride.

Since the densities are estimated to be accurate to about one percent, it is obvious that if the values of $\Delta v_i'$ are low they will only be indicative of the order of magnitude of the effect.

D. Discussion of the Results

The primary reason for the determination of the densities of the hydrogen fluoride solutions of some of the halogen fluorides was to obtain data for the calculation of the equivalent conductivities which are discussed in the next section. The values obtained, which are given in Table XI and plotted on Figure 27, were sufficient for that purpose.

The values obtained for percent $\Delta v_i'$ are small, negative, and of the order of magnitude of five percent or less. This indicates that for these solutions there is always a small decrease in the average molal volumes of the solutions, and thus there is always a small decrease in the partial molal volumes of the constituents upon mixing. This might indicate that the pure substituents have a more open structure in the liquid state. The hydrogen bonded structure of hydrogen fluoride, for example, may be broken up in the solution. Also, some type of association may occur in the mixture. Both of these effects might occur.

There is only one previous report on partial molal volumes in a halogen fluoride system. Stein and Vogel[48] have studied the system bromine trifluoride-bromine pentafluoride and have reported a decrease of less than one percent in the partial molal volume.

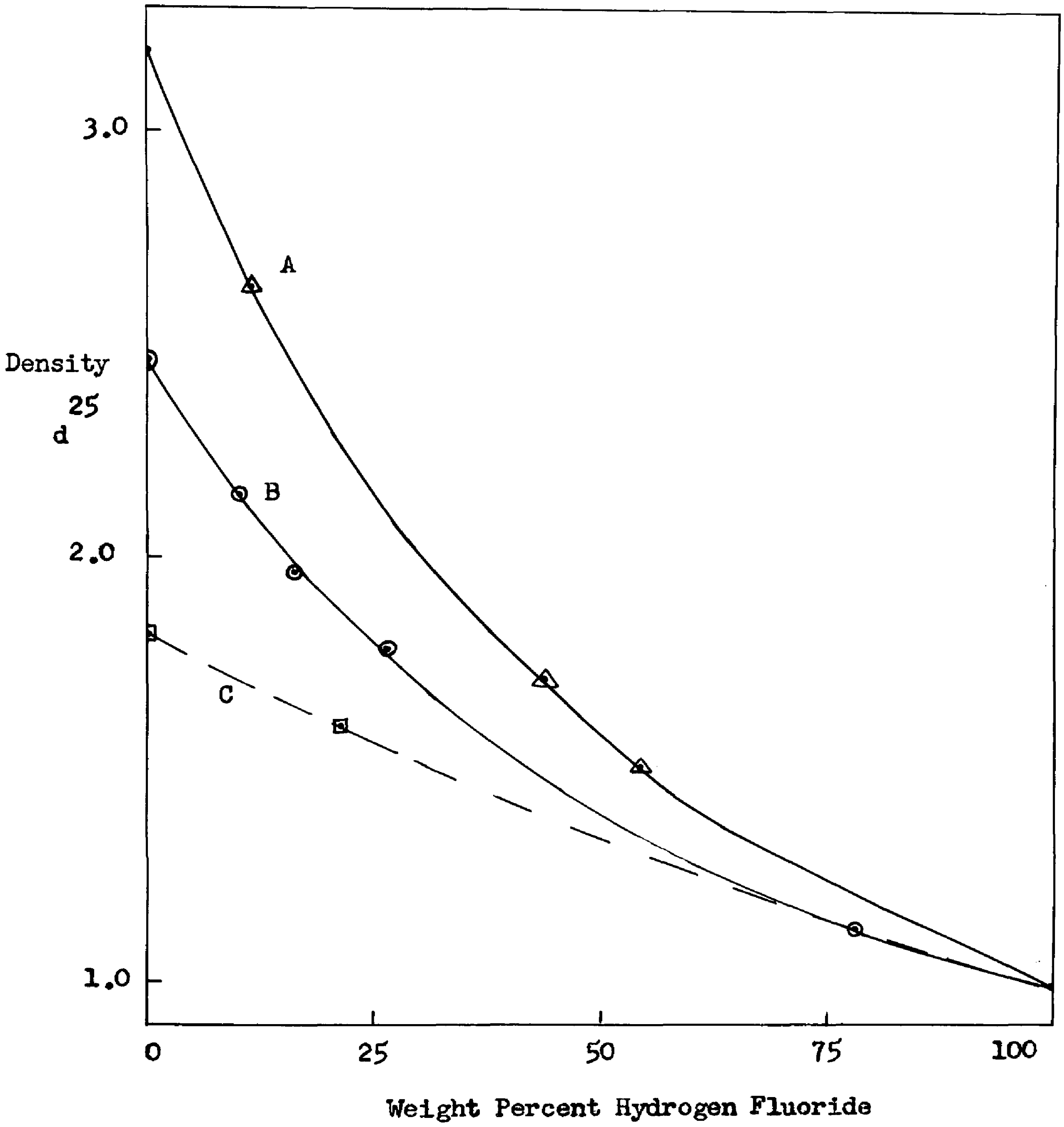


Figure 27. Densities of hydrogen fluoride solutions of some halogen fluorides: A, iodine pentafluoride; B, bromine pentafluoride; C, chlorine trifluoride.

VII CONDUCTANCE STUDIES OF THE HALOGEN FLUORIDES AND THEIR HYDROGEN FLUORIDE SOLUTIONS

A. Theoretical Aspects[61]

Measurement

When an electrical potential difference is applied to a liquid containing ions, the ions will be subjected to an accelerating force which will give rise to an electric current. Generally it is found, however, that when direct current measurements are made the resistance of the liquid does not strictly obey Ohm's law because of electrode processes which may tend to increase the apparent resistance of the liquid.

This effect is largely offset by the use of an alternating electric field. Thus the measurement becomes an impedance rather than a resistance measurement. The current which results from the use of an alternating field stems from two sources. The first, and the one which is of major importance here, is the migration of ions in the field. The second is reorientation of the charge distribution. At frequencies in the audio range the current component which is due to reorientation is not conductive since no net long range migration can occur and the redistribution can take place in a very short time.

When conductance measurements are made in the range of audio frequencies it has been found[62] that part of the measured impedance is not due to the solution itself, but as in the direct current measurements, is due to electrode processes. This effect may have both a resistive and a reactive component.

Generally these effects can be eliminated by the use of platinized-platinum electrodes, the very large surface area of which reduces the electrode reactances to a negligible magnitude. In this work, however, the nature of the solutions whose conductance was being measured made it necessary to use unplatinized platinum electrodes since a finely divided surface would have been chemically attacked.

In order to overcome the above difficulties use has been made of the fact that the resistive and reactive components of the electrode processes have been found to vary approximately linearly with the inverse square root of the frequency.[12] Thus if the sum of the resistive components of the solution and of the electrode processes are plotted against the inverse square root of the frequency and extrapolated to infinite frequency, the resistive component of the solution alone is obtained.

Specific and Equivalent Conductances

The specific conductance of a conductor is defined as the reciprocal of the resistance of a cube with sides one square centimeter in area, and has units of reciprocal ohms per cm.

Since it is obviously very difficult and impractical to design a cell of exactly these dimensions, a given conductance cell is calibrated by the use of a solution of known conductance.

The resistance of any conductor of constant cross sectional area varies directly with its length (d) and inversely with its area (a). That is

$$R = \rho \frac{d}{a}$$

where R is the total resistance and ρ is the specific resistivity. In this work we shall designate the specific conductance by L and thus

$$L = \frac{1}{\rho} \quad \text{ohms}^{-1}\text{cm}^{-1}$$

By Ohm's law

$$R = \frac{E}{I} = \frac{d}{La} = \frac{K}{L}$$

where I is the current, E is the applied potential and K is a constant known as the cell constant and has units of reciprocal centimeters. K can be determined for any cell if R is measured when the cell contains a solution of known specific conductance.

For a given electrolyte the quantity of electricity which a solution can carry depends upon the number of current carrying particles contained in a given volume and thus upon the concentration of the current carrying species. In order to determine the current carrying ability of all the ions produced by a solute a quantity called the equivalent conductance is defined. It is a measure of the current carrying power of all the ions resulting from the dissociation of one gram-equivalent of the solute. In actual practice this quantity is obtained from the specific conductance by multiplying the specific conductance by the volume of solution occupied by one gram equivalent of the solute. The equivalent conductance Λ is therefore obtained from

$$\Lambda = L\,V = \frac{1000\ L}{\text{Equivalent concentration}}$$

The equivalent conductance of strong electrolytes generally approaches a limiting value at infinite dilution. This is presumably a measure of the conducting power of one gram-equivalent of the electrolyte when it is completely dissociated. Very often the molar conductance M is used. For uni-equivalent substances M and Λ are identical.

The equivalent conductances of weak electrolytes depend upon the degree of ionization, and thus as the concentration becomes very low the increasing ionization causes a sharp increase in conductance so that an extrapolation to infinite dilution is practically impossible in actual practice.

In general, for water solutions, the equivalent conductance increases with increasing temperature owing to decreasing viscosity of the medium. With weak electrolytes, however, this is not always true. The conductance of weak electrolytes depends principally upon the degree of ionization of the electrolyte and since weak electrolytes probably have a definite heat of ionization in solution this can cause a decrease in ionization with increasing temperature. In practice the equivalent conductances of weak electrolytes are often observed to increase to a maximum and then decrease as the temperature is increased.

Non-aqueous Solutions

The above discussion applies principally to solutions in water. Actually other solvents cover a wide range of similarity or dissimilarity to water depending upon their ionizing power and thus upon their dielectric constant. Although solvents of high dielectric constant very often show conductance behavior similar to that of water solutions, a case in point being hydrogen fluoride solutions,[15b,83] with solvents of low dielectric constant it is very often found that there is a minimum in the equivalent conductance at some concentration. In aqueous solutions the equivalent conductance rises steadily as dilution is increased. The conductance minimum appears to move to higher concentrations as the dielectric constant of the medium increases.

The equivalent conductances of strong electrolytes at infinite dilution in solvents such as alcohols, nitriles or nitro- derivatives can be obtained by methods similar to that for water. For media of low dielectric constant such a procedure is not possible.

B. Apparatus and Method

The Conductance Bridge

The conductance bridge used in this work has been described in detail elsewhere.[12] The bridge consisted principally of an audio-frequency generator, a selective detector, and the bridge circuit; the latter included a ratio box, standard resistors and standard capacitors. Balance was detected on an oscilloscope by means of Lissajous figures, and a reference signal was used to give the horizontal deflection. The oscilloscope was used in such a manner that both the magnitude and the relative phase of the bridge output could be observed. Thus it was possible to observe both Rs and Cs, the resistance and capacitance settings at balance, on the standard decades. A simplified circuit diagram of the bridge is shown in Figure 28.

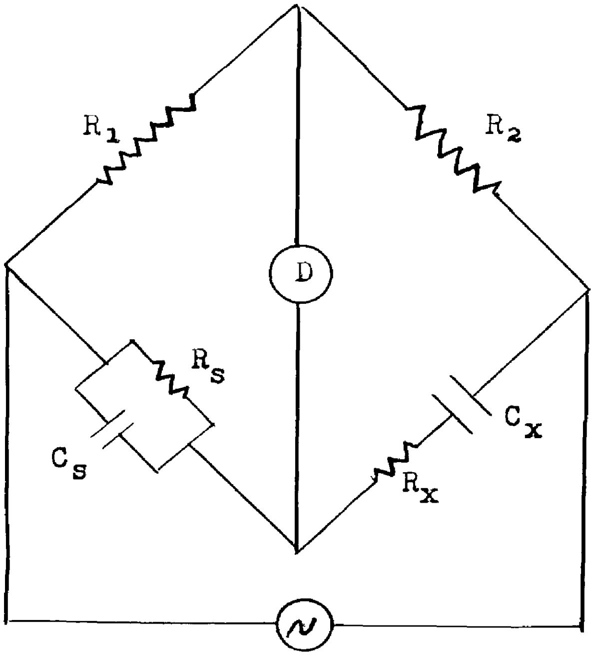


Figure 28. Simplified bridge circuit: R_1 and R_2 are 1:1 ratio resistors ($R_1=R_2$); R_s is a standard decade resistance box, C_s is a standard decade capacitance box; R_x and C_x are the resistive and capacitive components of the unknown impedance; D is the detector; ∿ is the signal generator.

The bridge is at balance when C_x and R_x are equivalent to the parallel combination of R_s and C_s. It has been shown[12] that

$$R_x = \frac{R_s}{1 + \omega^2 C_s^2 R_s^2} .$$

Thus it is seen that it is necessary to know the frequency in order to calculate R_x. The signal generator produced five fixed frequencies. These were 4000, 2000, 1000, 600, and 400 cycles per second, respectively. In order to obtain a plot of R_x versus $1/\sqrt{f}$, measurements of R_x were made at each of the above frequencies for a given conductance measurement.

The Conductance Cells

Cell design. The two cells illustrated in Figures 29 and 30 were used in this work. They were both constructed entirely of fluorothene except for the platinum plates, platinum leads, and copper-constantan thermocouples. Cell I was used for pure iodine pentafluoride and for iodine pentafluoride-hydrogen fluoride mixtures. Cell II was used for pure chlorine trifluoride, pure bromine pentafluoride, and for their hydrogen fluoride solutions.

The only major difference between the two cells was that in Cell I fluorothene wax was used extensively for sealing purposes. The use of wax was avoided in Cell II because its high solubility in bromine pentafluoride and in chlorine trifluoride gave trouble. Cell II was also designed to have a much lower cell constant than cell I because of the very low conductivities of bromine pentafluoride and chlorine trifluoride.

It was necessary to change the wax in Cell I after each use with hydrogen fluoride. Such a procedure was not necessary with Cell II.

As can be seen in the illustrations, the cells are of the dipping electrode type and were constructed so that the entire electrode assembly is a part of the tapered plug which fits into the tube. In both cells the platinum leads were shielded so that the level of the liquid did not effect the cell constant. Both cells were fitted with valves so they could be attached directly to the vacuum line and the solutions prepared directly in them.

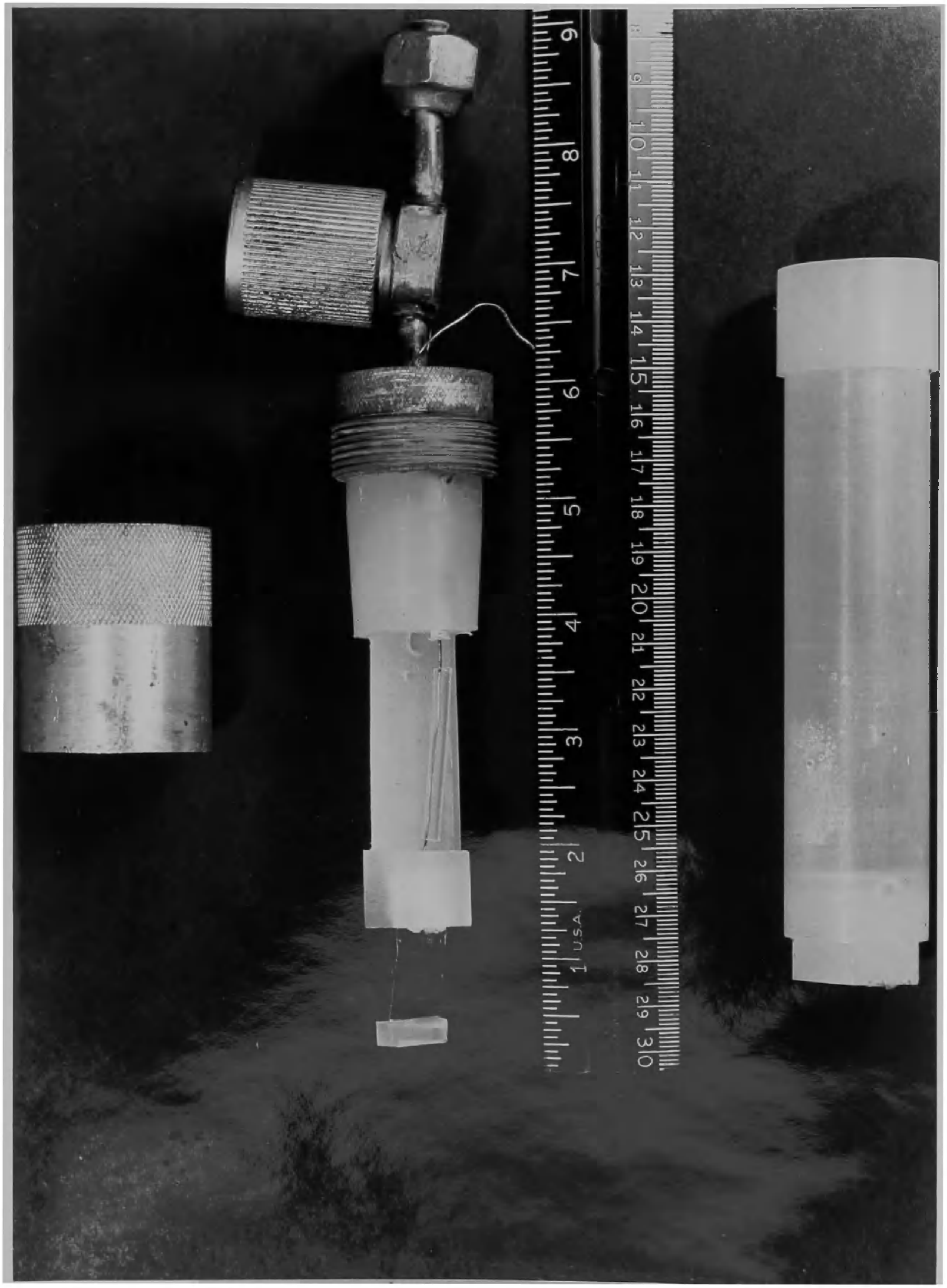


Plate 5. Conductance cell II.

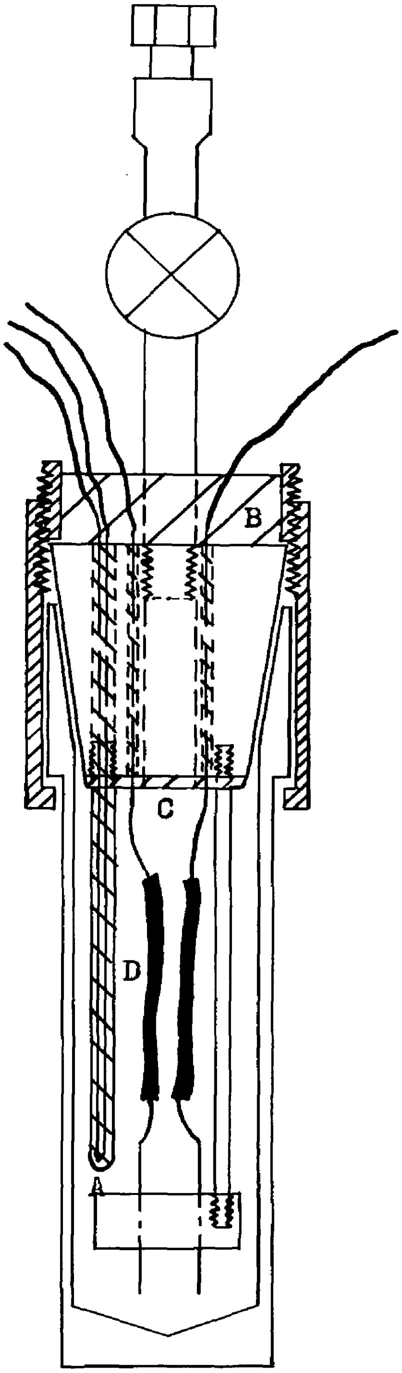
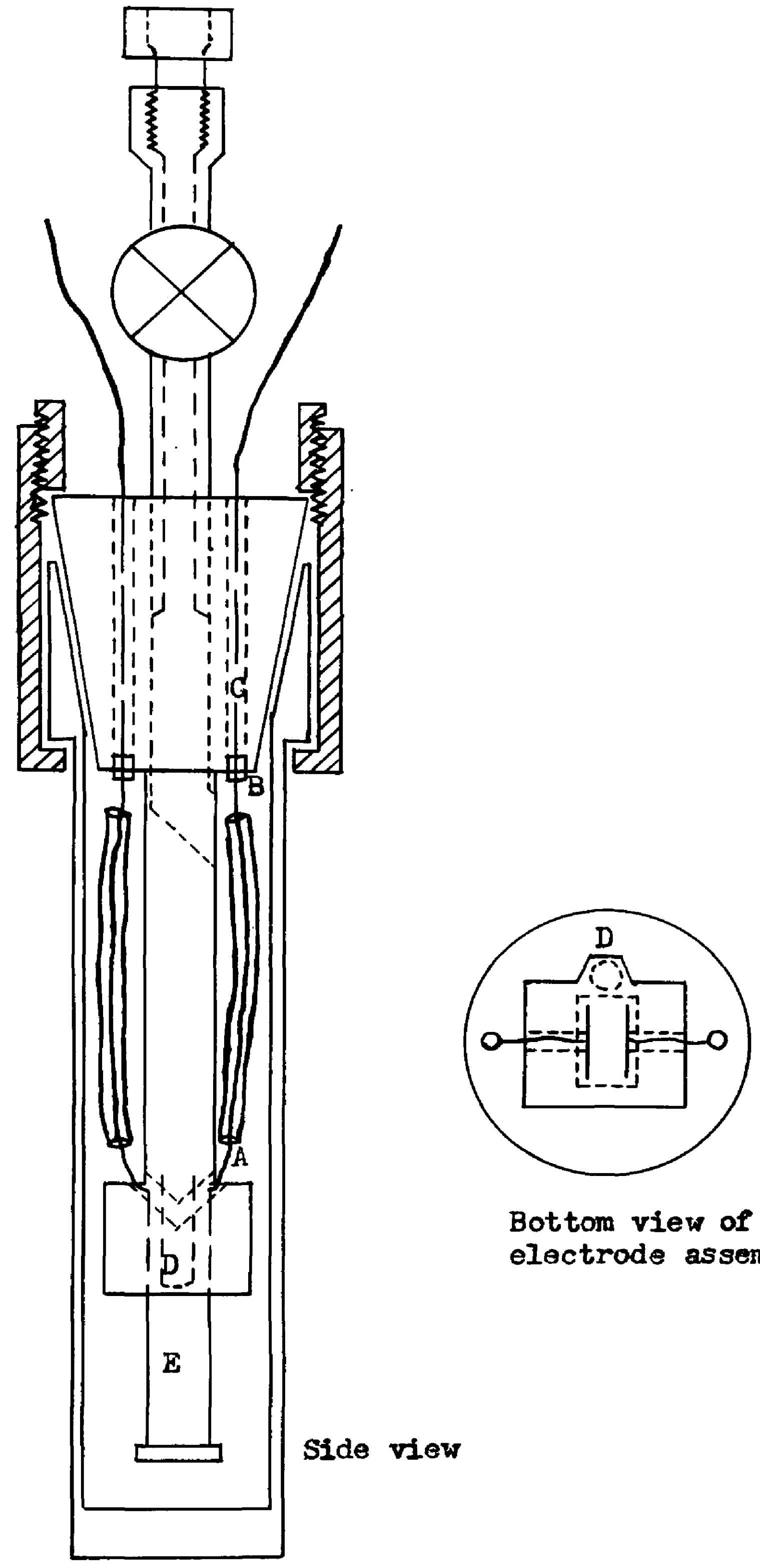


Figure 29. Conductance cell 1; A, fluorothene thermocouple well; B and C, fluorothene wax seals; D, fluorothene insulation.



Bottom view of electrode assembly

Side view

Figure 30. Conductance cell II; A, fluorothene tubes; B, Teflon packing plug; C, fluorothene wax packing; D, thermocouple well (shown only in lower part of side view); E, platinum plates.

Cell calibration. Both cells were calibrated periodically to determine whether any change had occurred in the cell constants due to handling. The data and procedures for some of these calibrations are given here.

Cell I was initially calibrated over the range of temperature from about 0 to 30°C using a very dilute potassium chloride solution. The potassium chloride solution contained 0.3663 gm potassium chloride per 1000 cc. of water. The data obtained are given in Table XII.

Since the concentration of the standard solution was lower than those for which conductance data is given in standard conductance tables, the data of Brenner[64] and Shedlovsky[65] were used to calculate the specific conductance of the potassium chloride solution over the temperature range indicated. Brenner tabulated the coefficients below versus temperature and potassium chloride concentration. Using his data the following coefficients $\frac{d\Lambda}{\Lambda dt}$ are obtained for 0.3663 gm potassium chloride per liter of water. The units of Λ are $cm^2\ equiv^{-1}ohm^{-1}$.

Tempeature °C	0	5	10	15	20	25
$\frac{d\Lambda}{\Lambda\ dt}$	.0298	.0272	.0249	.0229	.0212	.0197

Shedlovsky determined the equivalent conductances of potassium chloride solutions at 18 and 25°C. The equivalent conductance of the above potassium chloride solution is 121.0 $ohm^{-1}\ cm^{-1}$ at 18°C, and 143.6 $ohm^{-1}\ cm^{-1}$ at 25°C. The equivalent conductances of the above potassium chloride solution at various temperatures were determined from these data by a method of successive approximation.

TABLE XII

CALIBRATION OF CELL I USING A SOLUTION CONTAINING 0.3663 GRAMS OF POTASSIUM CHLORIDE PER LITER OF WATER

		Frequency					
Temperature		4000	2000	1000	600	400	R(ohms)*
29.5	C_s	0.008	0.030	0.087	0.30	0.40	208
	R_s	216	219	225	230	247	
	γ**	0.002	0.007	0.013	0.07	0.66	
	R_x	216	218	222	216	233	
23.4	C_s	0.007	0.027	0.090	0.18	0.35	229
	R_s	241	243	254	259	275	
	γ	0.002	0.007	0.018	0.03	0.06	
	R_x	240	241	249	251	260	
20.3	C_s	0.007	0.021	0.078	0.16	0.30	247
	R_s	256	258	268	273	286	
	γ	0.002	0.005	0.015	0.03	0.05	
	R_x	255	257	264	266	273	
18.1	C_s	0.006	0.017	0.054	0.10	0.20	260
	R_s	270	272	280	284	293	
	γ	0.002	0.004	0.007	0.01	0.02	
	R_x	269	271	278	281	287	
17.3	C_s	0.007	0.018	0.067	0.14	0.25	264
	R_s	272	274	284	286	300	
	γ	0.002	0.004	0.012	0.02	0.04	
	R_x	271	272	280	279	290	
15.4	C_s	0.005	0.015	0.053	0.100	0.20	279
	R_s	287	291	300	303	314	
	γ	0.001	0.003	0.009	0.01	0.03	
	R_x	287	290	297	299	306	
12.8	C_s	0.005	0.014	0.051	0.10	0.20	296
	R_s	306	309	318	323	335	
	γ	0.002	0.003	0.009	0.01	0.03	
	R_x	306	308	315	319	326	

Continued next page

TABLE XII - continued

Temperature		Frequency					R(ohms)*
		4000	2000	1000	600	400	
9.7	C_s	0.005	0.013	0.047	0.01	0.18	314
	R_s	322	324	333	336	348	
	γ	0.002	0.003	0.009	0.015	0.029	
	R_x	322	323	330	331	338	
0.0	C_s	0.003	0.008	0.030	0.06	0.12	405
	R_s	415	418	428	433	445	
	γ	0.001	0.002	0.006	0.01	0.02	
	R_x	415	417	425	429	437	

* R is obtained by extrapolating a plot of R_x versus $1/\sqrt{f}$ to infinite frequency.

** $\gamma = \omega^2 R_s^2 C_s^2$

C_s is in microfarads.

R_s is in ohms.

A sample calculation of the equivalent conductance at 14°C is given here. The mean value of $d\Lambda / \Lambda\, dt$ between 14° and 18°C is estimated to be 0.0233 cm^{-1} from a plot of Brenner's data.

First approximation: $d\Lambda = 0.0233 \times 4 \times 124.0 \ cm^2 equiv^{-1} ohm^{-1}$

$= 11.6 \ cm^2 equiv^{-1} ohm^{-1}$

$\Lambda = 124.0 - 11.6 = 113.0$

Second approximation: $d\Lambda = 0.0233 \times 4 \times 113 = 10.5$

$\Lambda = 124.0 - 10.5 = 113.5$

This was repeated at 10°, 5° and 0° C using in each case the value of Λ obtained at the preceding temperature as a first approximation. The specific conductance (L) was then calculated from the equation

$$L = \frac{M\Lambda}{1000} \quad . \quad ohm^{-1}cm^{-1}$$

The values of L versus T for the solution of 0.3663 gm potassium chloride per liter of water are plotted in Figure 31.

Using the conductances calculated in this manner the cell constants (K) were calculated from

$$K = L_{KCl} \cdot R \quad cm^{-1}$$

where the values of R are obtained from plots of R_x versus the inverse square root of the frequency. Figure 32 is a plot of the cell constant versus temperature. Since we are mainly interested in the cell constant at 25°C the slight errors caused by the above approximations at lower temperatures are not considered to be important.

A second cell constant run was made at 24.9°C after several iodine pentafluoride solutions had been measured. For this determination a solution of 0.7459 gm. potassium chloride per liter of water was used.

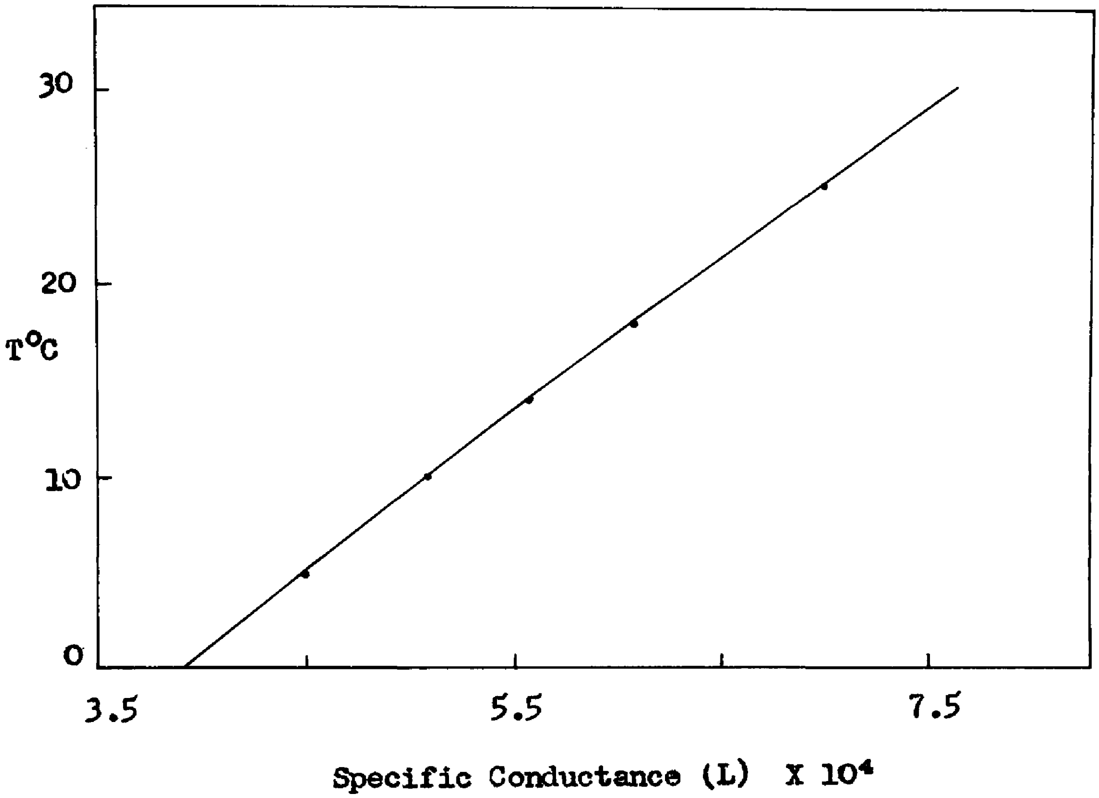


Figure 31. Specific conductance versus temperature for a solution containing 0.3663 grams of potassium chloride per liter of water.

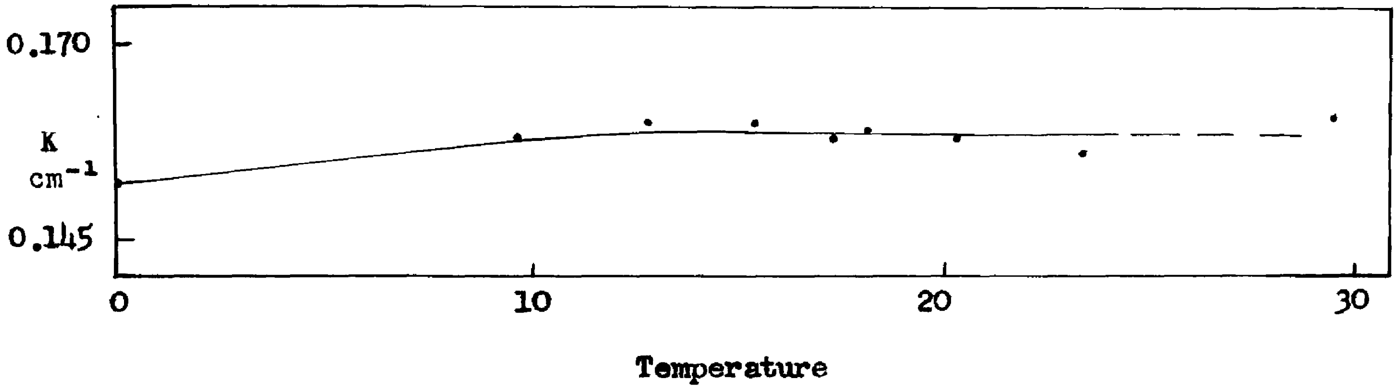


Figure 32. The cell constant of cell I at various temperatures.

The specific conductance of this solution has been found to be 0.001410 cm^{-1} ohm^{-1}.[42] The pertinent data are given in Table XIII. The cell constant of 0.159 cm^{-1} is in close agreement with that obtained above.

TABLE XIII

CALIBRATION DATA FOR CELL I USING A SOLUTION CONTAINING 0.7459 GRAMS POTASSIUM CHLORIDE PER LITER OF WATER AT 24.9°C

	Frequency					R	K
	4000	2000	1000	600	400	ohm	cm^{-1}
C_s	0.021	0.043	0.143	0.27	0.53	114	0.159
R_s	120	122	127	125	134		
γ	0.004	0.004	0.013	0.02	0.03		
R_x	119	121	125	123	130		

Cell II was first calibrated over a range of temperature from 6 to 21°C using the solution containing 0.7459 gm. potassium chloride per liter of water. The pertinent data are given in Table XIV. Figure 33 is a plot of specific conductance versus temperature for a potassium chloride solution of this concentration.[42] Figure 34 shows a plot of the cell constant (K) versus temperature for this cell.

After this cell was used for the conductance runs with the halogen fluorides and their hydrogen fluoride solutions it was necessary to replace the bottom fluorothene support. This caused a slight change in the cell constant. The cell was then recalibrated at 25°C and at approximately -78°C. Since the cell constant at -78°C was desired for the cell

TABLE XIV

CALIBRATION DATA FOR CELL II

Temperature		Frequency					R	K
		4000	2000	1000	600	400	ohms	cm^{-1}
25.0	C_s	0.154	0.360	0.99	--	2.74	44.0	0.0622
	R_s	47.3	50.4	59.0	--	82.0		
	γ	0.034	0.052	0.135	--	0.32		
	R_x	45.7	47.6	52.0	--	62.2		
22.4	C_s	0.153	0.363	0.96	1.75	2.75	46.5	0.0623
	R_s	44.8	50.0	60.0	66.0	86.0		
	γ	0.035	0.052	0.131	0.19	0.34		
	R_x	47.2	47.0	53.0	55.5	64.0		
16.2	C_s	0.135	0.300	0.640	1.49	2.42	52.0	0.0614
	R_s	54.1	55.5	65.5	72.0	91.0		
	γ	0.034	0.044	0.119	0.16	0.31		
	R_x	52.3	53.2	55.0	61.7	69.6		
6.1	C_s	0.100	0.220	0.650	1.14	1.88	63.4	0.0506
	R_s	66.6	69.0	80.4	85.4	104.4		
	γ	0.028	0.036	0.108	0.134	0.244		
	R_x	64.8	66.6	72.6	76.6	83.9		

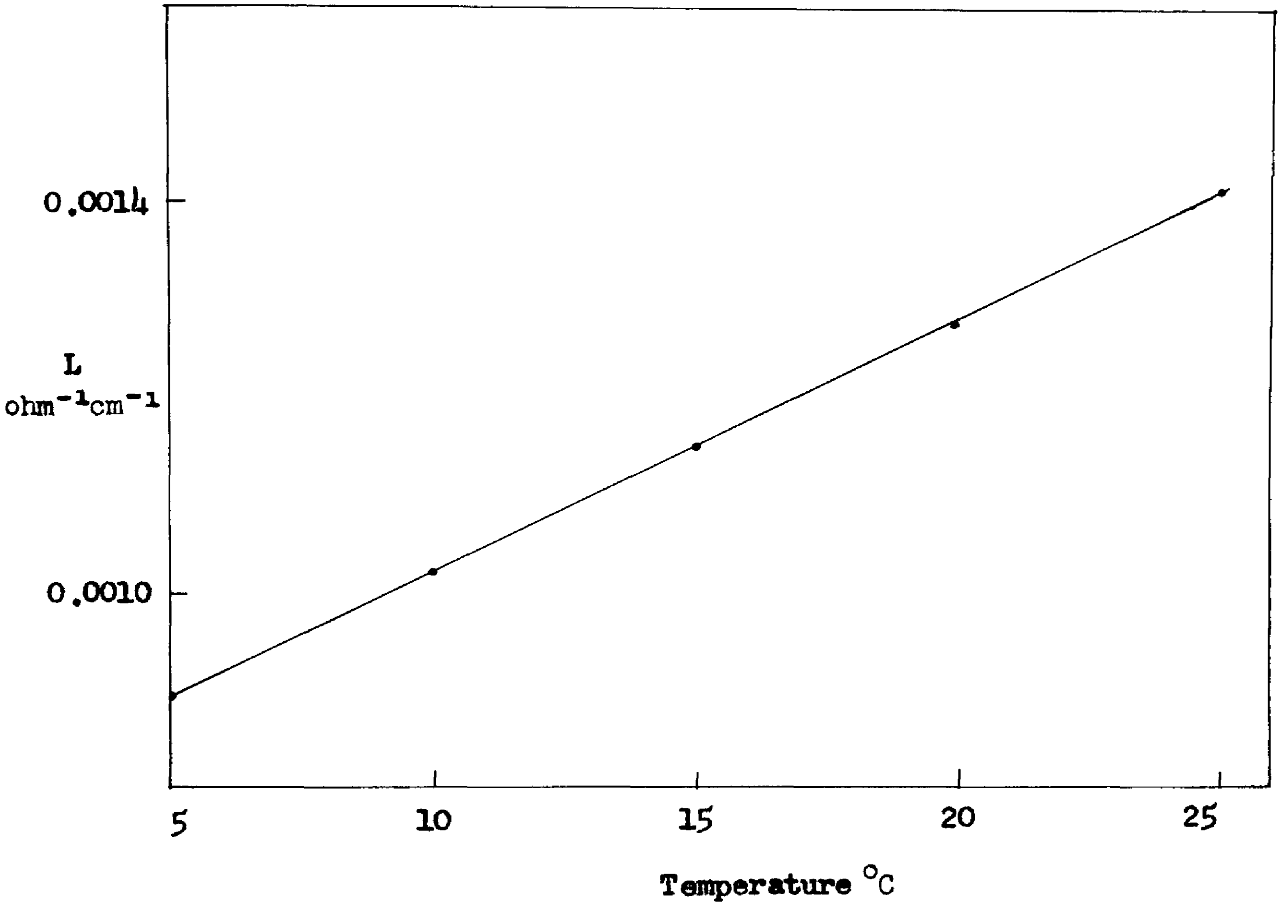


Figure 33. Specific conductance versus temperature for 0.001N potassium chloride. Data from the Handbook of Chemistry and Physics.

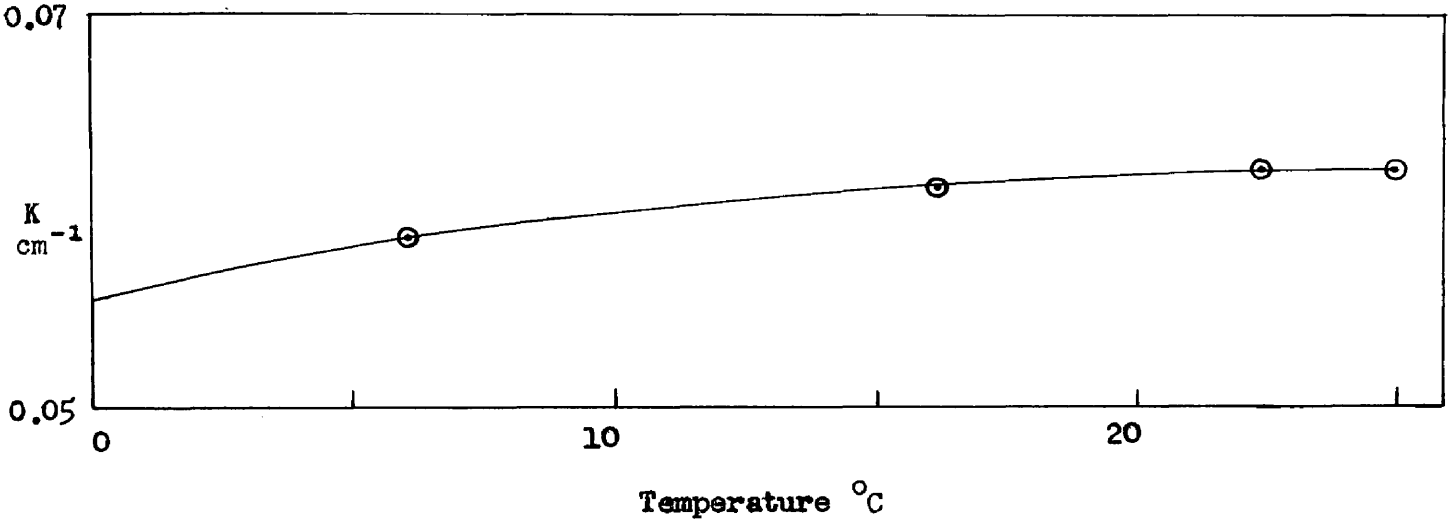


Figure 34. Cell constant of cell II at different temperatures.

before the support was changed, it was assumed that the percent change at 25°C was the same as the percent change at -78°C. The data for the recalibration at 25°C are given in Table XV.

The procedure for the calibration of cell II at -78°C was as follows: solutions of two grams of potassium hydroxide per liter of ethanol, two milliliters of concentrated hydrochloric acid per liter of ethanol, and two milliliters of concentrated hydrochloric acid per liter of acetone, were prepared. The conductances of these solutions at -78°C were determined approximately by using the glass cell illustrated in Figure 35. The measurements were made while this cell was immersed in a Dry Ice-acetone mixture. The cell constant of the glass cell has previously been shown to be 0.888 at 25°C.[11] The total distance between the plates of this cell is 36mm. at 25°C and changes by less than one mm. on cooling to -78°C. It is therefore reasonable to assume that the cell constant of the glass cell changed less than two percent on cooling. Measurements were then made on the same solutions in cell II at -78°C. The data for these runs are tabulated in Table XVI.

It can be seen from the data of Table XVI that when the cell constant at 25°C is 0.054 cm^{-1}, the average value for the cell constant at -78°C is 0.060 ± 0.005. Assuming that the change due to replacement of the support was the same at each temperature, the cell constant was 0.071 ± 0.006 cm^{-1} at -78°C when it was 0.0622 cm^{-1} at 25°C.

TABLE XV

RECALIBRATION OF CELL II AT 25°C

	Frequency				R	K
	4000	2000	1000	600	ohm	cm^{-1}
C_s	0.033	0.083	0.360	0.666	38.6	0.0541
R_s	39.0	39.2	40.0	40.0		
γ	0.001	0.002	0.008	0.010		
R_x	39.0	39.1	39.7	39.6		

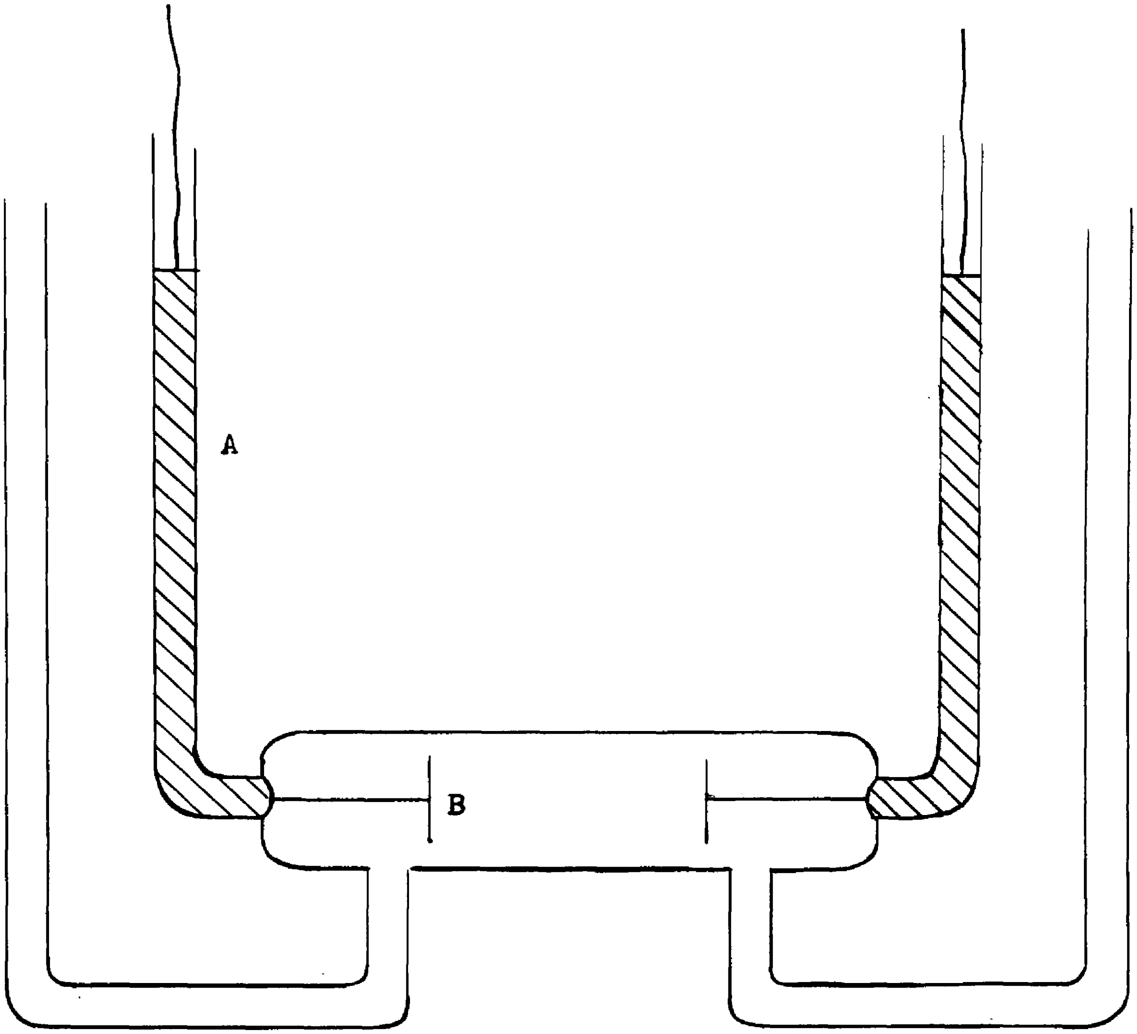


Figure 35. The glass conductance cell; A, mercury contact; B, platinum electrodes.

TABLE XVI

CALIBRATION OF CELL II AT -70°C

Cell	Frequency					R	K
	4000	2000	1000 ohms	600	400	ohm	cm^{-1}
	A. Two grams of potassium hydroxide per liter of ethanol						
Glass	30,800	31,200	31,700	32,000	32,200	29,500	
Cell II	1,840	1,850	1,850	1,850	1,850	1,850	0.055
	B. Two milliliters of concentrated hydrochloric acid per liter of ethanol.						
Glass	32,200	32,900	33,400	33,600	33,700	30,500	
Cell II	2,250	2,250	2,260	2,260	2,260	2,240	0.065
	C. Two milliliters of concentrated hydrochloric acid per liter of ethanol.						
Glass	21,600	22,200	22,200	22,200	22,200	20,000 to 22,600	
Cell II	1,510	1,510	1,510	1,510	1,510	1,510	0.066 to 0.060

$$K_{mean} = 0.060 \pm 0.005 \text{ cm}^{-1}$$

C_s was found to be negligible therefore only R_x is given above.

Sample Preparation and Handling Procedures

For the conductance work it was found necessary to carefully distil the halogen fluoride directly into the weighed conductance cell. If the compound was siphoned through the metal line, or if the distillation was so rapid as to form a spray, impurities were introduced into the cell and high conductance values were obtained.

The iodine pentafluoride was siphoned from the storage container into an auxiliary tube and then distilled from the tube into the cell. Bromine pentafluoride was distilled directly from the storage container into the cell. The setup is illustrated in Figure 36.

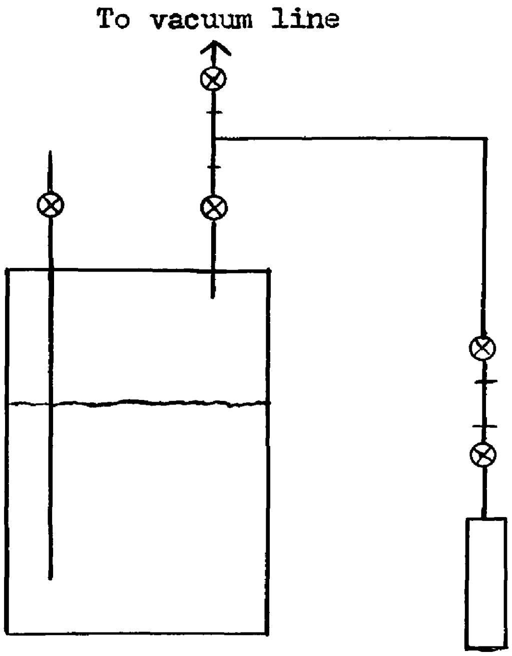


Figure 36. The Mixing System for Bromine Pentafluoride Solutions

Chlorine trifluoride was distilled directly from a half empty tank since it was not possible to fractionally distil it with the equipment used for iodine pentafluoride and bromine pentafluoride. The chlorine trifluoride was assumed to be fairly pure since its conductance was very close to conductances previously reported.

Following the addition of the halogen fluoride the cell was removed from the line, reweighed, and returned to the line. The leads from the conductance bridge were connected, a bath at the desired temperature was placed around the tube, and the thermocouple was inserted into the thermocouple well. The temperature-versus-time curve was recorded by a Brown recording potentiometer. When the slope became zero the temperature of the interhalogen was assumed to be the same as that of the bath. The resistance of the cell was then measured at various frequencies by use of the conductance bridge.

The hydrogen fluoride solutions were prepared by condensing hydrogen fluoride directly into the halogen fluoride samples prepared as above. The weighing and conductance measuring procedure was repeated as above. In this manner it was possible to prepare several hydrogen fluoride solutions from each sample of halogen fluoride.

For most of these runs the hydrogen fluoride was passed slowly over cobaltic fluoride to remove moisture. Measurements of the hydrogen fluoride conductance, however, indicated that it was rather impure from a conductance standpoint. The main difficulty appeared to be that impurities desorbed from the sides of the plastic tube into the hydrogen fluoride. This difficulty was not encountered with the halogen fluorides.

Because of the above difficulty very few measurements were made at extremely high hydrogen fluoride concentrations.

The temperature bath was manually controlled. Temperature was read on a calibrated mercury thermometer whose scale was subdivided to tenths of a degree. For those measurements done at 0° and -78°C an ice-water or Dry Ice-acetone bath was used. Generally the temperature was alternately raised and lowered to determine whether the effect being measured was reversible.

C. Data and Calculations

In the following pages the conductance data for certain halogen fluorides and their hydrogen fluoride solutions is presented in tabular and graphical form. Information pertaining to the calculation of certain of the quantities presented in the tables is given here.

The specific conductance of hydrogen fluoride, recorded as L_{HF}, was obtained by subtracting the conductance of the starting solvent from the specific conductance of the solution (L). L is obtained from the equation

$$L = K \cdot \frac{1}{R}$$

where K is the cell constant discussed in the previous section, and R, the total resistance of the cell, is obtained by plotting R_x versus the inverse square root of the frequency and extrapolating to infinite frequency. Actually in many cases R_x was found to be very small and R_x at four thousand cycles per second was taken as R. The specific circumstances under which this was done are discussed below in the tables concerned. The plots used to obtain R from R_x are discussed in the section on theory (above). In most cases C_s was negligible and therefore only R_x was given.

Molar conductances of hydrogen fluoride in the solutions were calculated by use of the equation

$$M = \frac{1000\ L_{HF}}{C}$$

where M is the molar conductance and C is the molarity defined by

$$C = \frac{\text{number of equivalents of HF}}{\text{total weight/density}}$$

The units of M are $\text{ohms}^{-1}\text{cm}^{2}\text{moles}^{-1}$ and will not be repeated in the tables following.

The densities of some halogen fluoride-hydrogen fluoride solutions were determined in this work and the data are given in Table XI and Figure 27.

In some cases the conductances of the solutions at temperatures other than 25°C were determined in order to discover whether there was any unusual temperature-conductance relationship. In the case of iodine pentafluoride-hydrogen fluoride solutions the variation in the temperature-conductance relationship at various concentrations was quite slight and in order to make the effect obvious it was necessary to plot the percent change in conductance at 20°C versus concentration of hydrogen fluoride.

The percent change in conductance at 20°C was determined for each solution whose conductance had been measured at various temperatures, by determining the slope of plots of specific conductance versus temperature for those solutions at 20°C and then using the equation

$$\text{percent change at } 20^{\circ}\text{C} = \frac{\text{slope X 100}}{\text{conductance at } 20^{\circ}\text{C}}$$

Although some solution conductances were determined in run A using the contaminated iodine pentafluoride and in run D using the contaminated bromine pentafluoride, these have been omitted here because the contamination rendered them meaningless.

The probable error for each run is presented with the data in question. Other pertinent information regarding each specific table is given below each table.

For the conductance runs already presented the hydrogen fluoride from the cylinder was slowly passed over cobaltic fluoride to remove any moisture which may have been present. It was found, however, that the conductance of the hydrogen fluoride was rather high, 2-5 x 10^{-4} at 25°C compared to 1.5 x 10^{-6} at 15° previously reported,[15b] and that it drifted rather rapidly. Apparently impurities desorbing from the walls of the fluorothene tube caused this effect.

In order to get some idea of the shape of the equivalent conductance curve for the iodine pentafluoride-hydrogen fluoride solutions a few determinations were made starting with hydrogen fluoride which had been dried over cobaltic fluoride and stored in a new fluorothene tube. The conductance was changing with time during the run and the results are probably not accurate to better than twenty percent. R_x measurements were made at four thousand cycles only, and the values of the specific conductance of hydrogen fluoride (L_{HF}) were obtained by subtracting the conductance of the hydrogen fluoride alone from the measured conductance of the solution.

The results are tabulated in Table XXI.

TABLE XVII

THE SPECIFIC CONDUCTANCE OF IODINE PENTAFLUORIDE AT VARIOUS TEMPERATURES*

T°C	Frequency					R	L
	4000	2000	1000 ohms	600	400	ohms	X 10^6 ohm^{-1}
			Run A**				
30.1	5993	5994	5998	6000	6000	5992	2.67
25.2	6491	6498	6500	6501	6504	6488	2.47
25.0	6562	6563	6563	6563	6567	6559	2.44
20.3	7147	7149	7151	7151	7157	7140	2.27
15.1	7897	7899	7901	7904	7905	7893	2.01
11.4	8532	8530	8529	8529	8531	8529	1.86
			Run B***				
25.8	30320	30350	30360	30365	30370	30330	0.538
23.6	32250	32250	32280	32300	32310	32230	0.516
17.9	35200	35270	35310	35320	35320	35200	0.460
13.0	38750	38775	38800	38820	38830	38700	0.419
			Run C****				
25.0	28020	28080	28140	28150	28160	27800	0.572
21.9	29290	29380	29420	29440	29450	29200	0.544
16.9	31820	31880	31910	31930	31935	31800	0.498
15.4	32730	32790	32820	32830	32840	32700	0.487

* C_s was negligible for all these runs. The values given are for R_x (in ohms) at the various frequencies.

** The iodine pentafluoride in this run was distilled into the cell very rapidly and apparently carried over some impurities.

*** The cell constant for this run was 0.163 cm^{-1}, the slight change being due to a change in height of the insulation around the platinum leads of cell I.

**** In this run the average error for R is 100 ohms, and the average error for L is 0.002 X 10^{-6}. This error is due to erratic plots of R_x versus $1/\sqrt{f}$.

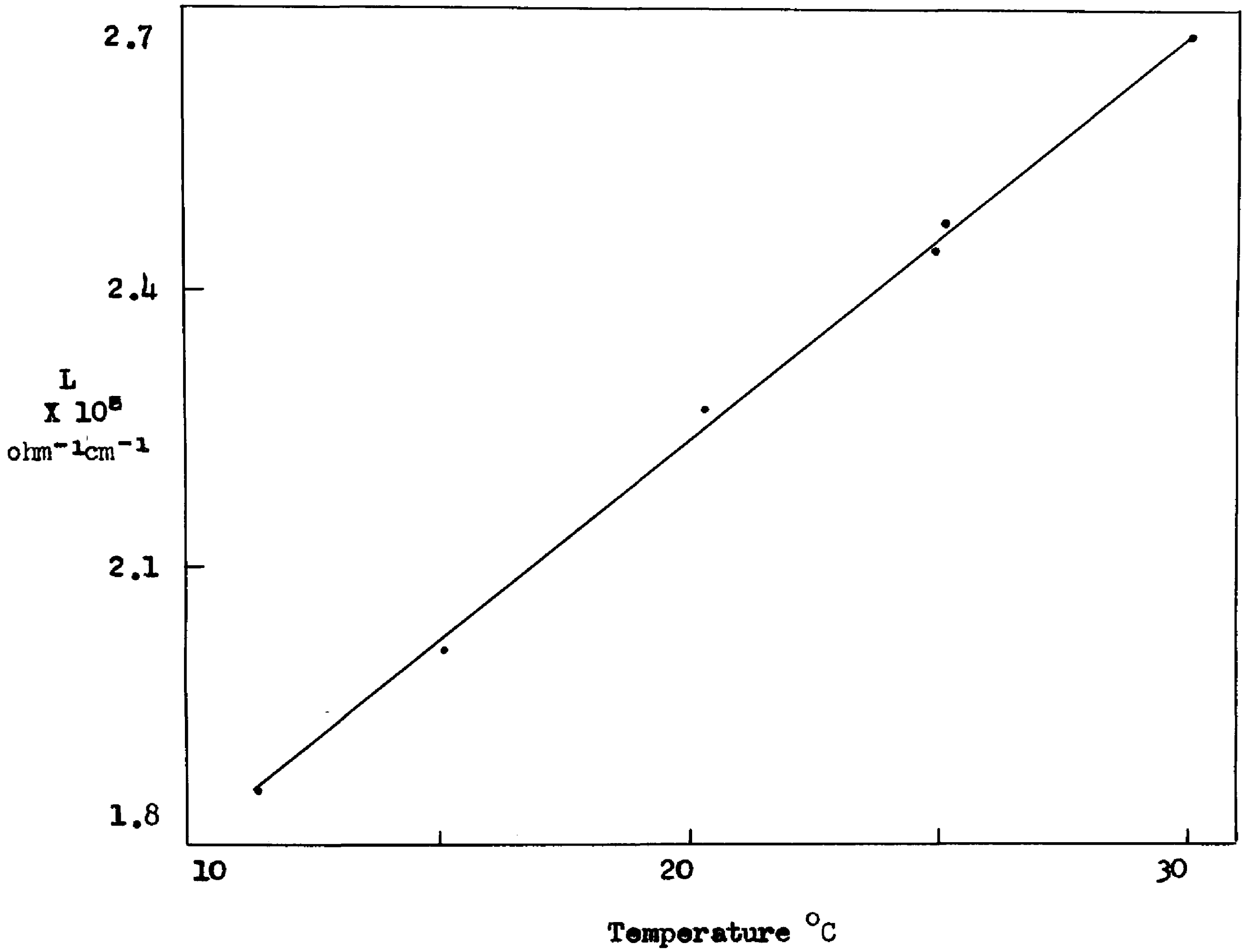


Figure 37. Specific conductance as a function of temperature for iodine pentafluoride (run A).

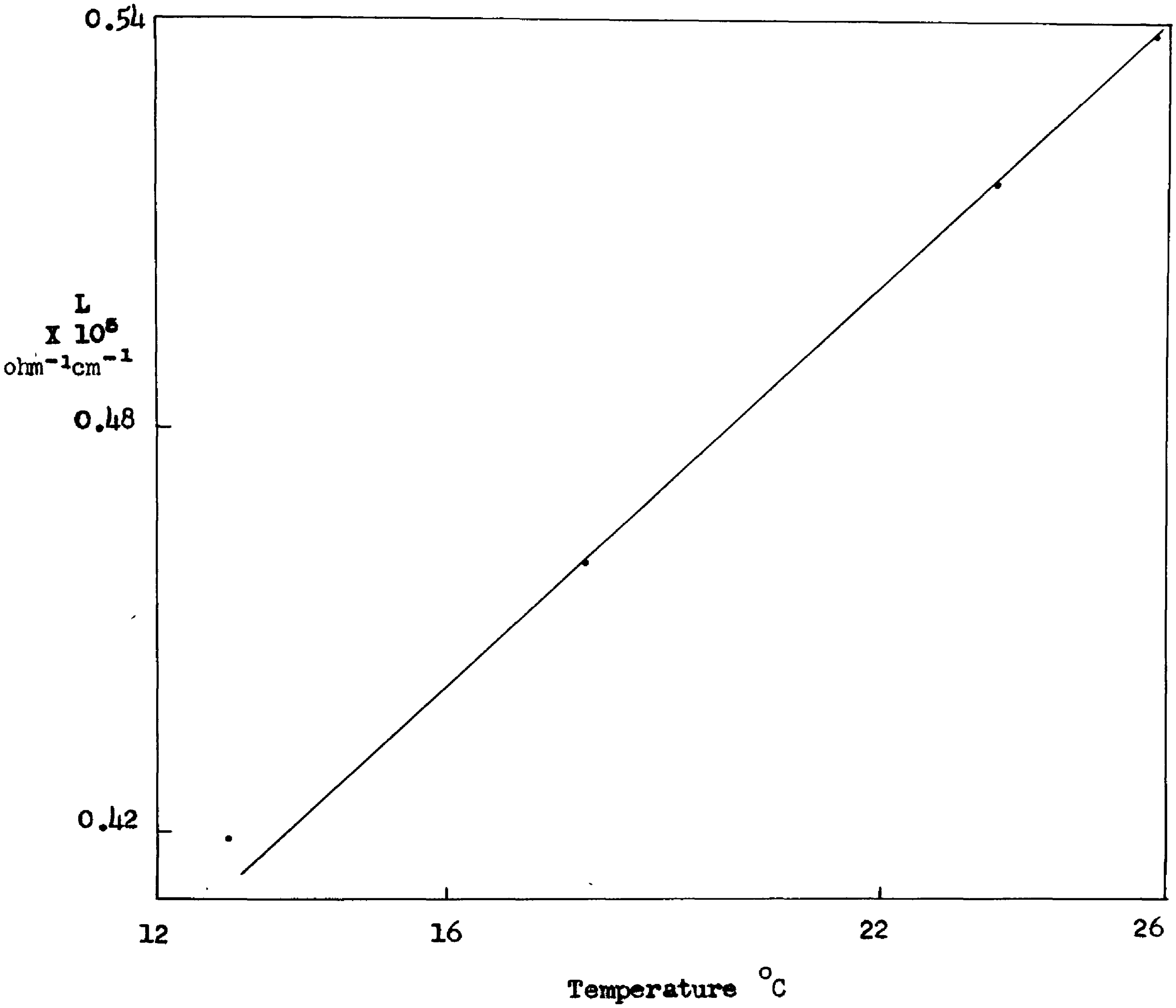


Figure 38. Specific conductance as a function of temperature for iodine pentafluoride (run B).

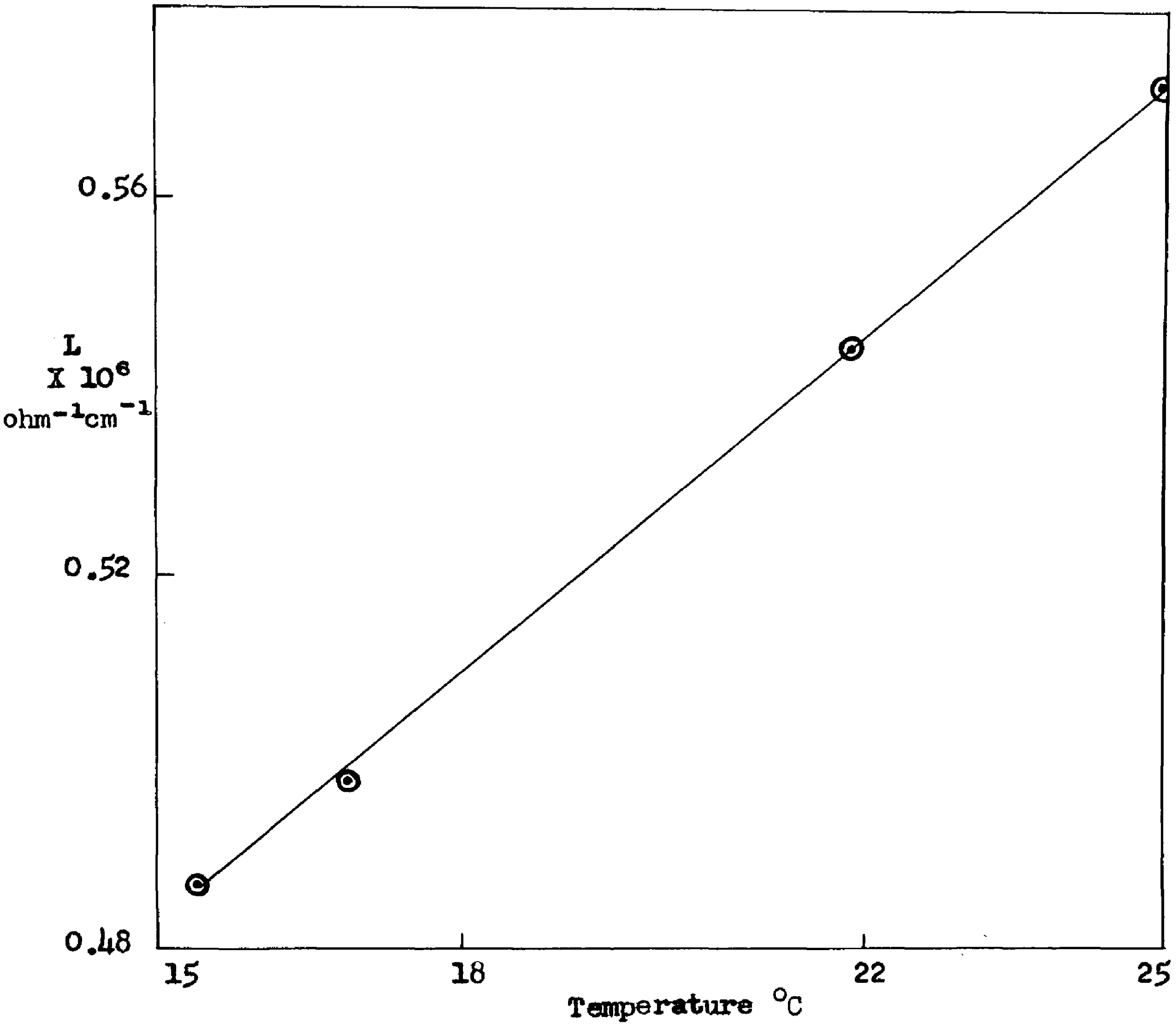


Figure 39. Specific conductance as a function of temperature for iodine pentafluoride (run C).

TABLE XVIII

THE SPECIFIC CONDUCTANCES OF BROMINE PENTAFLUORIDE AND CHLORINE TRIFLUORIDE AT VARIOUS TEMPERATURES

	Frequency					R	L
T°C	4000	2000	1000	600	400	X 10^{-3}ohms	X 10^{7}cm^{-1} ohms^{-1}
			kilohms				
				Run D*			
25.0	122	122	122	122	122	122	5.08
19.1	134	135	135	135	136	133	4.73
12.2	137	138	139	139	139	136	4.45
5.8	141	143	144	144	144	139	4.21
				Run E**			
25.0	736	772	790	800	800	680	0.91
				Run F***			
25.0	626	627	629	630	630	625	0.991
0.0	629	--	--	--	--	629	0.884
60	900	--	--	--	--	900	0.78
			Chlorine Trifluoride[3]			R	L
			R_x X 10^{-6} ohms			X 10^{-6}ohms	X 10^{9} ohm^{-1} cm^{-1}
25.0	12.8	--	--	--	--	12.8	4.86
-78	10.8	--	--	--	--	10.8	6.5

* The bromine trifluoride for this run was rapidly distilled, and probably contained some impurity from the metal vacuum line. There is an error of plus or minus one thousand ohms in R due to erratic curves for R_x versus $1/\sqrt{f}$. The corresponding error in L is about plus or minus one percent.

** For runs B and C the bromine pentafluoride was very carefully distilled. The error here is about plus or minus five percent due mainly to the use of auxiliary resistors of doubtful accuracy. The value at -60°C is approximate since the cell constant for -78°C is used. Where frequency variation is omitted it is negligible compared to other errors.

*** The error at -78°C is approximately plus or minus ten percent due to cell constant error.

TABLE XIX

CONDUCTANCES OF IODINE PENTAFLUORIDE-HYDROGEN FLUORIDE SOLUTIONS

RUN B'*

			Frequency								
T°C	Grams HF	C at 25°C	4000	2000	1000 ohms	600	400	R ohms	L $\text{ohms}^{-1}\text{cm}^{-1}$	L_{HF} $\text{ohms}^{-1}\text{cm}^{-1}$	M at 25°C
25.0	0.07	0.16	18910	18920	18930	18950	18960	18880	0.865	0.335	0.02
22.7	0.07	--	19770	19800	19810	19820	19830	19750	0.825	0.317	---
19.0	0.07	--	21140	21160	21170	21190	21240	21090	0.773	0.300	---
16.6	0.07	--	22150	22160	22170	22190	22200	22130	0.738	0.289	---
25.0	0.28	0.625**	15310	15320	15330	15330	15340	15290	1.068	0.538	0.0086

* This run was started by adding hydrogen fluoride to the sample used in pure iodine pentafluoride run B. There are 70.59 grams of iodine pentafluoride in each solution. The error in the weight of hydrogen fluoride is plus or minus 0.02 gram and is probably the major source of error in these measurements.

** Measurements at higher concentration were not obtained because of leakage of hydrogen fluoride from the cell.

TABLE XX

CONDUCTANCES OF IODINE PENTAFLUORIDE-HYDROGEN FLUORIDE SOLUTIONS

RUN C'*

	Grams		Frequency					R	L	L_{HF}	M
T°C	HF	at 25°C	4000	2000	1000 ohms	600	400	ohms	$ohms^{-1}cm^{-1}$	$ohms^{-1}cm^{-1}$	at 25°C
25.0	0.028	0.061	24110	24130	24130	24130	24130	24100	0.662	0.090	0.015
25.0	0.038	0.083	22030	22060	22060	22070	22080	22000	0.724	0.152	0.018
25.0	0.69	1.47	14113	14140	14150	14150	14150	14120	1.127	0.555	0.0038
16.2	1.84	3.75	10100	10105	10110	10110	10110	10100	1.578	1.085	0.0033
20.8	1.84	3.75	9345	9350	9354	9354	9355	9340	1.706	1.172	0.0033
25.2	1.84	3.75	8768	8769	8769	8772	8773	8760	1.818	1.244	0.0033
25.0	3.74	7.28	4967	4968	4970	4971	4974	4960	3.210	2.638	0.0036
25.0	6.42	11.3	1441	1442	1445	1448	1452	1437	11.04	10.47	0.0092
19.9	6.42	11.3	1445	1445	1447	1449	1454	1442	11.01	10.48	0.0092
14.5	6.42	11.3	1445	1445	1447	1449	1454	1442	11.03	10.55	0.0092
24.8	15.1	20.6	264	265	267	269	273	263	60.6	60.0	0.029
19.5	15.1	20.6	266	267	269	269	275	265	60.1	59.6	0.029
14.5	15.1	20.6	268	268	270	271	277	267	57.5	57.0	0.029
25.5	22.9	23.7	139	139	142	142	147	139	115	115	0.049
19.3	22.9	23.7	141	142	144	144	150	141	113	113	0.049
14.9	22.9	23.7	144	144	147	147	153	143	111	111	0.049

* This run was started by adding hydrogen fluoride to the iodine pentafluoride in run C. There was a total of 72.78 grams of iodine pentafluoride in each solution.

The hydrogen fluoride used in the first two solutions was weighed out in a small fluorothene tube and then condensed into the cell. The error in hydrogen fluoride concentration in these solutions is about 25%. This leads to a very large uncertainty in the calculated specific and equivalent conductances of hydrogen fluoride in these solutions. The values obtained for these solutions are assumed to be good only to an order of magnitude.

In cases where measurements have been made at temperatures other than 25°C, the equivalent conductances at 25°C have been calculated using specific conductances at 25°C, which have been obtained from plots of specific conductance versus temperature.

Although the above measurements could be repeated and are probably consistent within themselves to about one percent, the over-all error in conductance may be as high as five percent.

TABLE XXI

CONDUCTANCES OF IODINE PENTAFLUORINE-HYDROGEN FLUORIDE SOLUTIONS WITH VERY HIGH HYDROGEN FLUORIDE CONCENTRATIONS*

Grams IF_5	C HF	R ohms (at 4000 cycles)	L ohms^{-1}cm^{-1} X 10^{-4}	L_{HF} ohms^{-1}cm^{-1} X 10^{-4}	M at 25°C
0.0	---	545	2.9	---	---
1.4	48	280	5.7	2.8	0.063
3.5	45	225	7.1	4.2	0.092
6.2	44	205	7.8	4.9	0.11

* Starting with 15.05 grams of hydrogen fluoride, and measured at 25°C. See previous page for other information concerning this table.

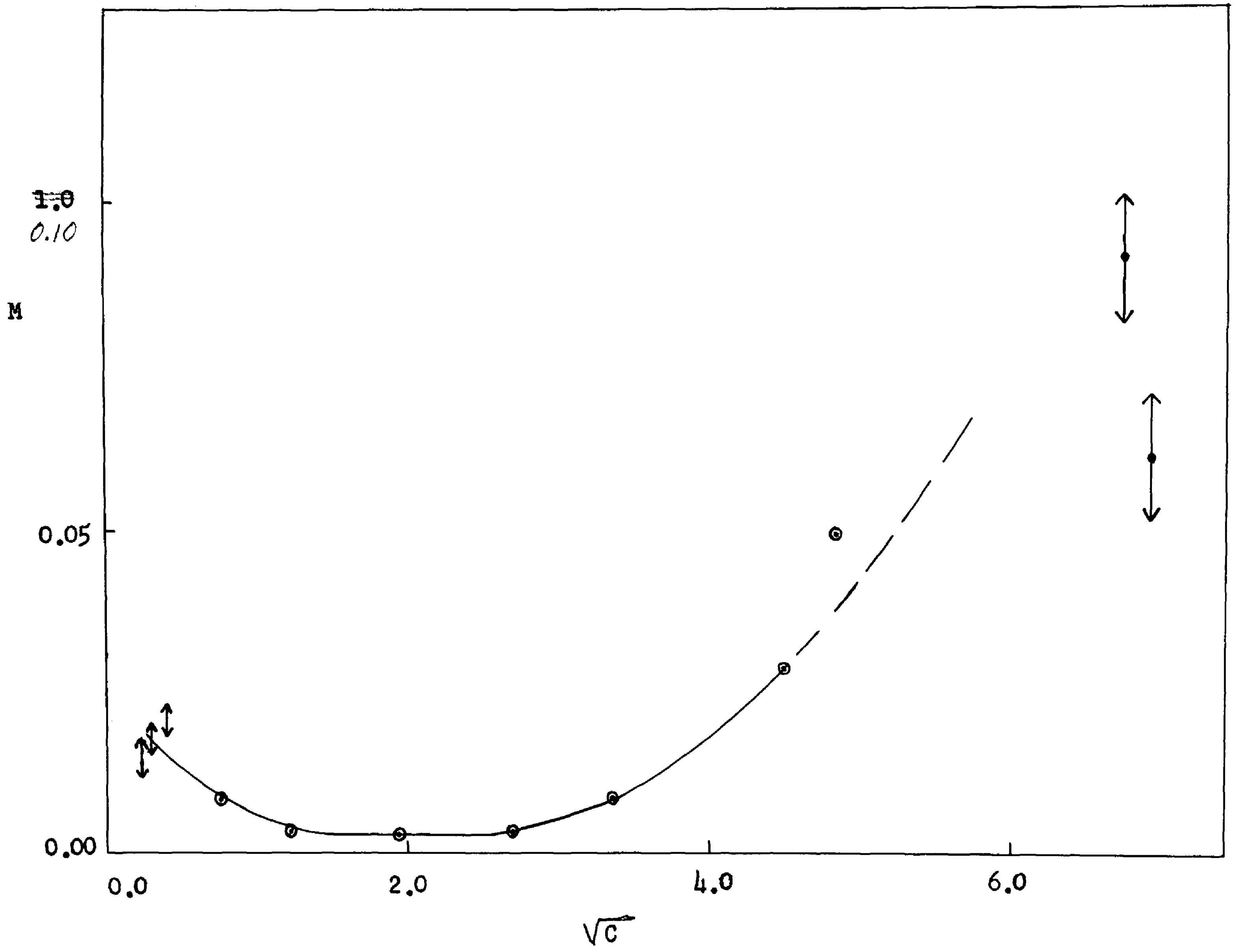


Figure 40. Molar conductance versus the square root of the molarity of hydrogen fluoride for iodine pentafluoride-hydrogen fluoride solutions at 25°C.

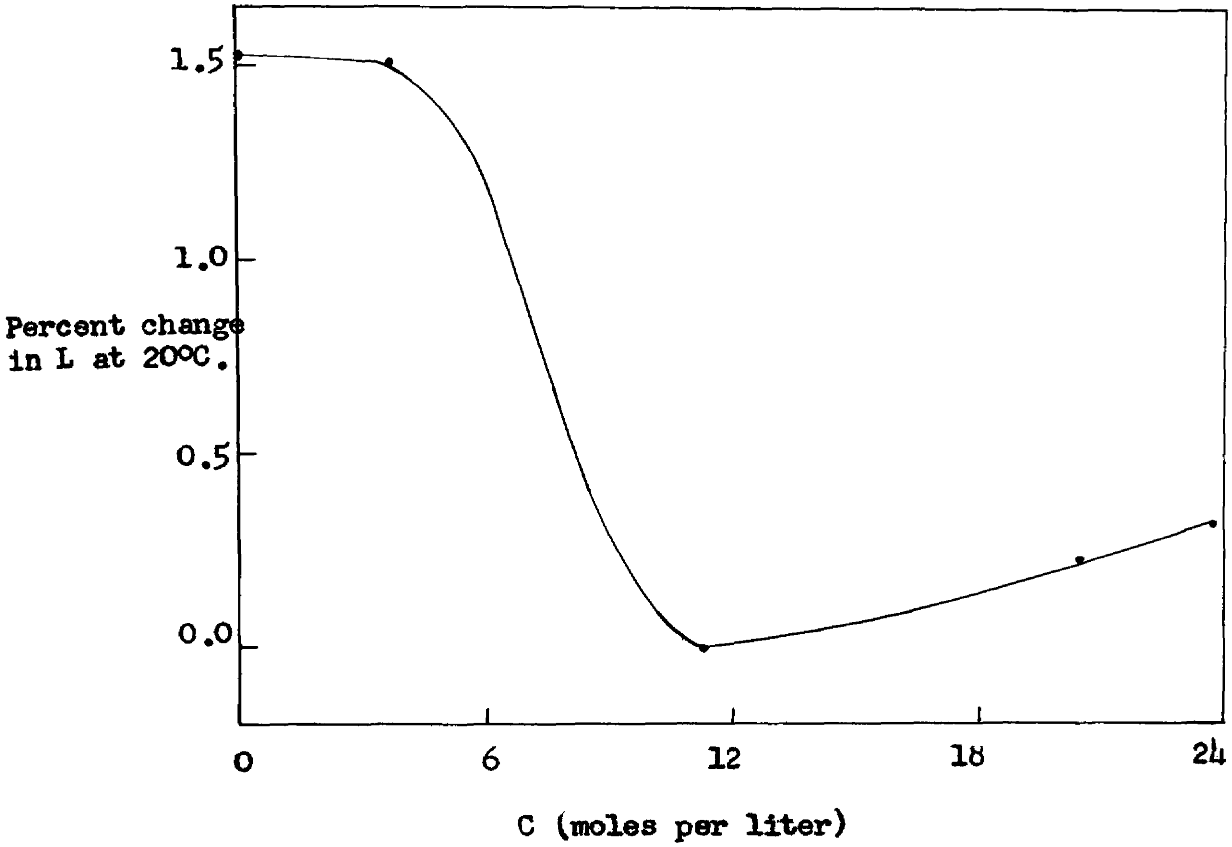


Figure 41. Percent change in specific conductance of iodine pentafluoride-hydrogen fluoride solutions versus molar concentrations of hydrogen fluoride (data from run C').

TABLE XXII

CONDUCTANCES OF BROMINE PENTAFLUORIDE-HYDROGEN FLUORIDE SOLUTIONS

RUN E'*

T°C	Grams HF	C_{HF} at 25°C	R ohms at 4000 Cycles	L ohms^{-1}cm^{-1} X 10^7	L_{HF} ohms^{-1}cm^{-1} X 10^7	M X 10^4 at 25°C
25.0	0.19	0.32	187,000	3.34	2.43	7.6
0.0	0.19	---	162,000	3.43	---	---
-60	0.19	---	252,000	2.8	---	---
25.0	0.40	0.64	78,300	8.05	7.14	11.2
0.0	0.40	---	76,000	7.30	---	---
-60	0.40	---	130,000	5.46	---	---
25.0	1.05	1.64	26,050	23.8	23.8	14.5
15.5	1.05	---	26,100	23.5	---	---
0.0	1.05	---	27,500	20.2	---	---
25.0	2.25	3.38	8,900	70.0	70.0	20.7

* This run was started by adding hydrogen fluoride to the bromine pentafluoride used in run E. There was a total of 77.00 grams of bromine pentafluoride in each solution.

The cell was leaking hydrogen fluoride during this run and therefore all values of conductance at higher concentrations are probably low. There is no way of estimating the error due to loss of hydrogen fluoride.

There is a considerable error in the values at about -60°C because the readings were actually taken as the last resistance measurement before the solution began to freeze. The error is therefore due to making the measurement at a temperature other than that at which the cell was calibrated (the calibration at -78°C was used), and also to the fact that the readings had to be made rapidly.

Readings were taken at four thousand cycles only since the variation with frequency was found to be very slight.

TABLE XXIII

CONDUCTANCES OF BROMINE PENTAFLUORINE-HYDROGEN FLUORIDE SOLUTIONS

RUN F'*

T°C	Grams HF	C_{HF} at 25°C	R ohms at 4000 cycles	L ohms^{-1}cm^{-1} X 10^7	L_{HF} ohms^{-1}cm^{-1} X 10^7	M at 25°C X 10^4
25.0	0.27	0.43	103,500	5.99	5.00	11.8
0.0	0.27	--	102,700	5.41	--	--
-60	0.27	--	122,000	5.8	--	--
25.0	0.38	0.60	60,600	10.2	9.2	15.4
0.0	0.38	--	59,300	9.54	--	--
25.0	0.53	0.83	34,400	18.0	17.0	20.5
0.0	0.53	--	30,000	18.8	--	--
-60	0.53	--	8,000	88	--	--
25.0	0.93	1.47	13,700	45	44	30
0.0	0.93	--	12,700	44	--	--
-60	0.93	--	4,000	175	--	--
25.0	2.13	3.20	3,000	190	190	60
0.0	2.13	--	2,700	206	--	--
-60-70	2.13	--	1,400	500	--	--
25.0	4.23	5.94	840	739	738	125
0.0	4.23	--	875	635	--	--
-60-70	4.23	--	1,000	710	--	--
25.0	6.86	8.84	496	1250	1250	154
0.0	6.86	--	525	1080	--	--
-60-70	6.86	--	900	780	--	--

* This run was started by adding hydrogen fluoride to the bromine pentafluoride in run F. There was a total of 77.59 grams of bromine pentafluoride in each solution.

There is a potentially large error in the values for the conductances at very low temperatures since the cell was calibrated only at -78°C.

The over-all errors in the conductances are probably about five percent for the solutions at lower concentrations because of some uncertainty in the values for the auxiliary resistances used with the conductance bridge. Precision resistors in the proper range were not available.

Resistances were measured at four thousand cycles only since the change with frequency was small.

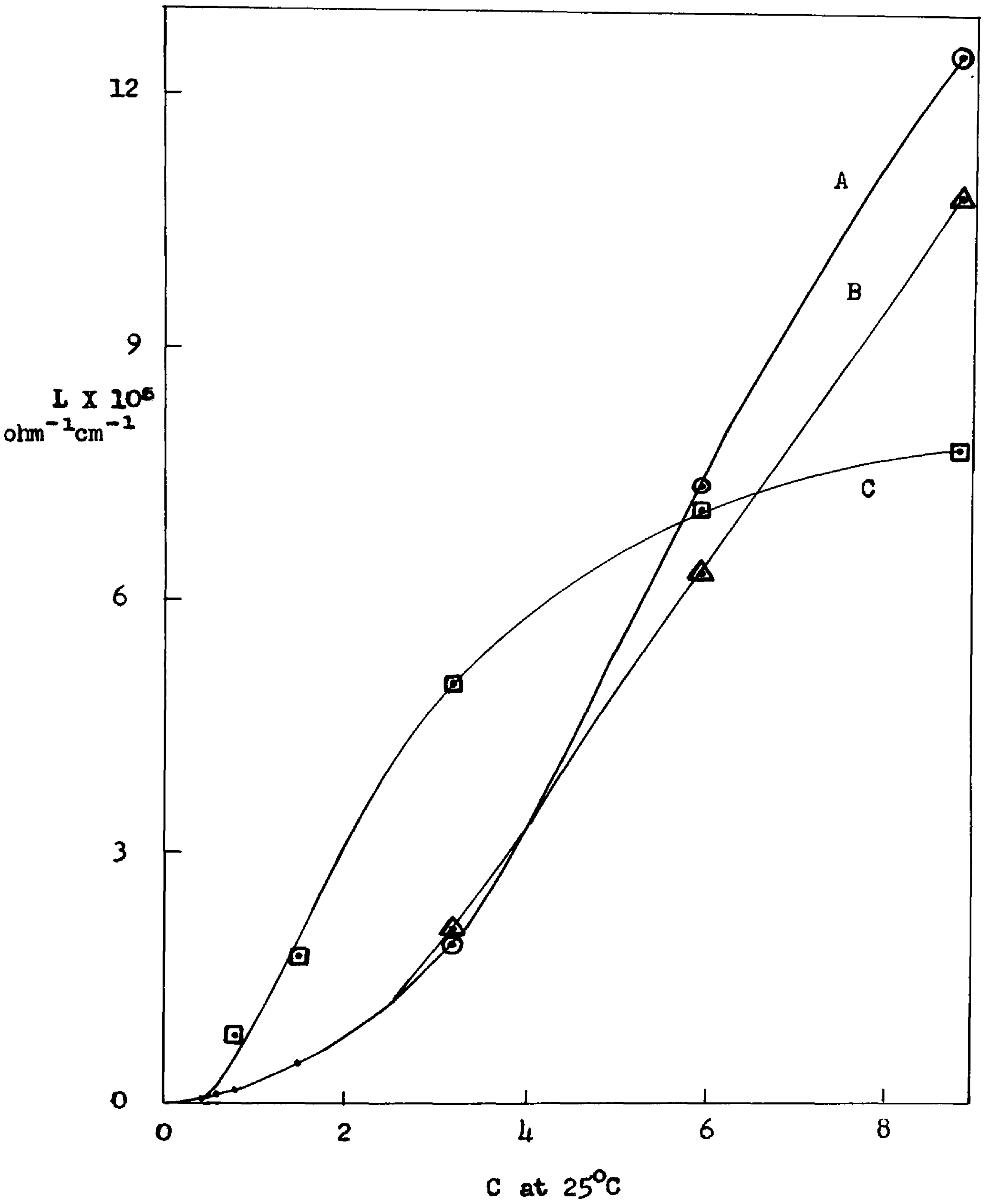


Figure 42. Specific conductance-concentration relationship of bromine pentafluoride-hydrogen fluoride solutions based upon run F' only: A, 25°C; B, 0°C; C, -60 to -70°C.

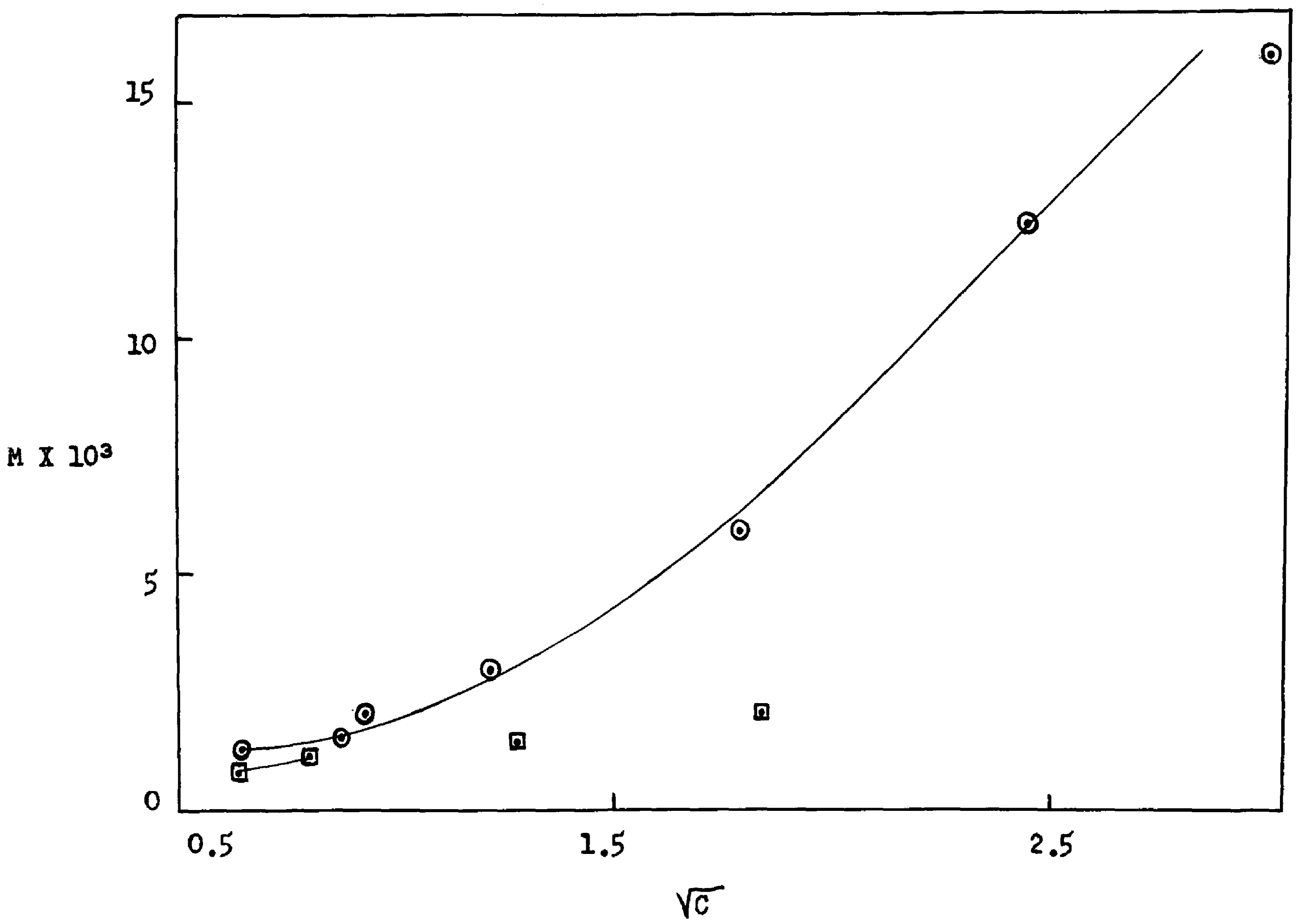


Figure 43. Molar conductance versus the square root of the molarity of hydrogen fluoride for bromine pentafluoride-hydrogen fluoride solutions at 25°C: ⊙ run F'; ⊡ run E'. The points in run E' were drifting due to loss of hydrogen fluoride.

TABLE XXIV

CONDUCTANCES OF CHLORINE TRIFLUORIDE-HYDROGEN FLUORIDE SOLUTIONS*

T^oC	Grams HF	C_{HF} at 25^oC	R ohms at 4000 cycles $X\ 10^{-3}$	L $ohms^{-1}cm^{-1}$ $X\ 10^{8}$	L_{HF} $ohms^{-1}cm^{-1}$ $X\ 10^{8}$	M at 25^oC $X\ 10^{8}$
25.0	0.62	1.0	2,100	2.96	2.47	2.47
-78	0.62	--	1,530	4.5	--	--
25.0	0.84	1.35	960	5.49	6.00	4.45
-78	0.84	--	740	9.5	--	--
25.0	1.62	2.57	142	43.7	43.2	16.8
-78	1.62	--	85	82.5	--	--
25.0	3.05	4.67	18	350	350	75
-78	3.05	--	15	460	--	--

* This run was started by adding hydrogen fluoride to the chlorine trifluoride used for the pure chlorine trifluoride run. There was a total of 56.05 grams of chlorine trifluoride in each addition.

The over-all errors in conductances are probably about five percent due to uncertainty in the resistance values for the auxiliary resistances used on the conductance bridge. Precision resistors in the proper range were not available.

For the low temperature measurements there is an uncertainty of ten percent due to uncertainty in the value for the cell constant.

Resistances were measured at four thousand cycles only for the same reasons mentioned previously.

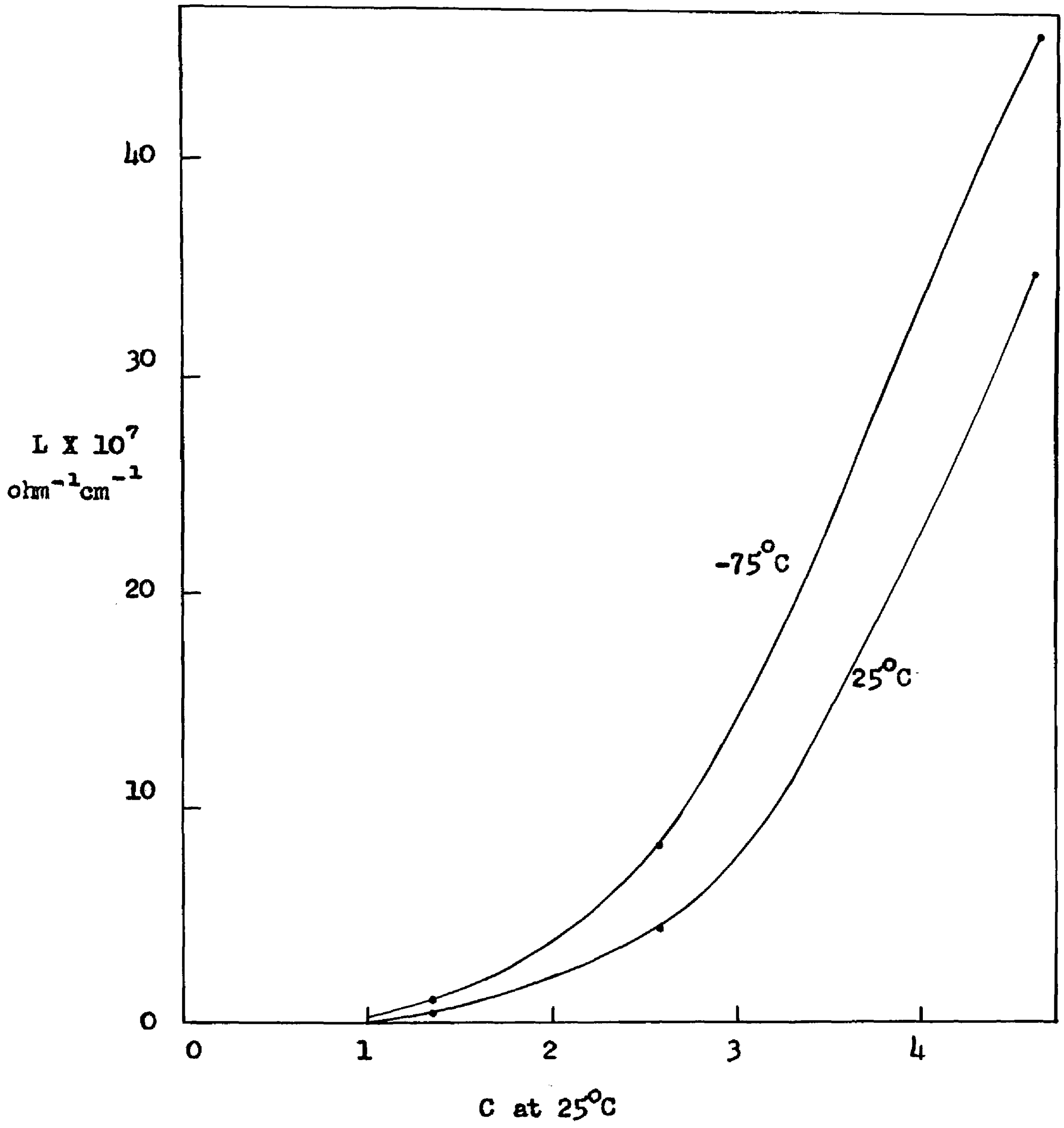


Figure 44. Specific conductance-concentration relationships for chlorine trifluoride-hydrogen fluoride solutions at two different temperatures.

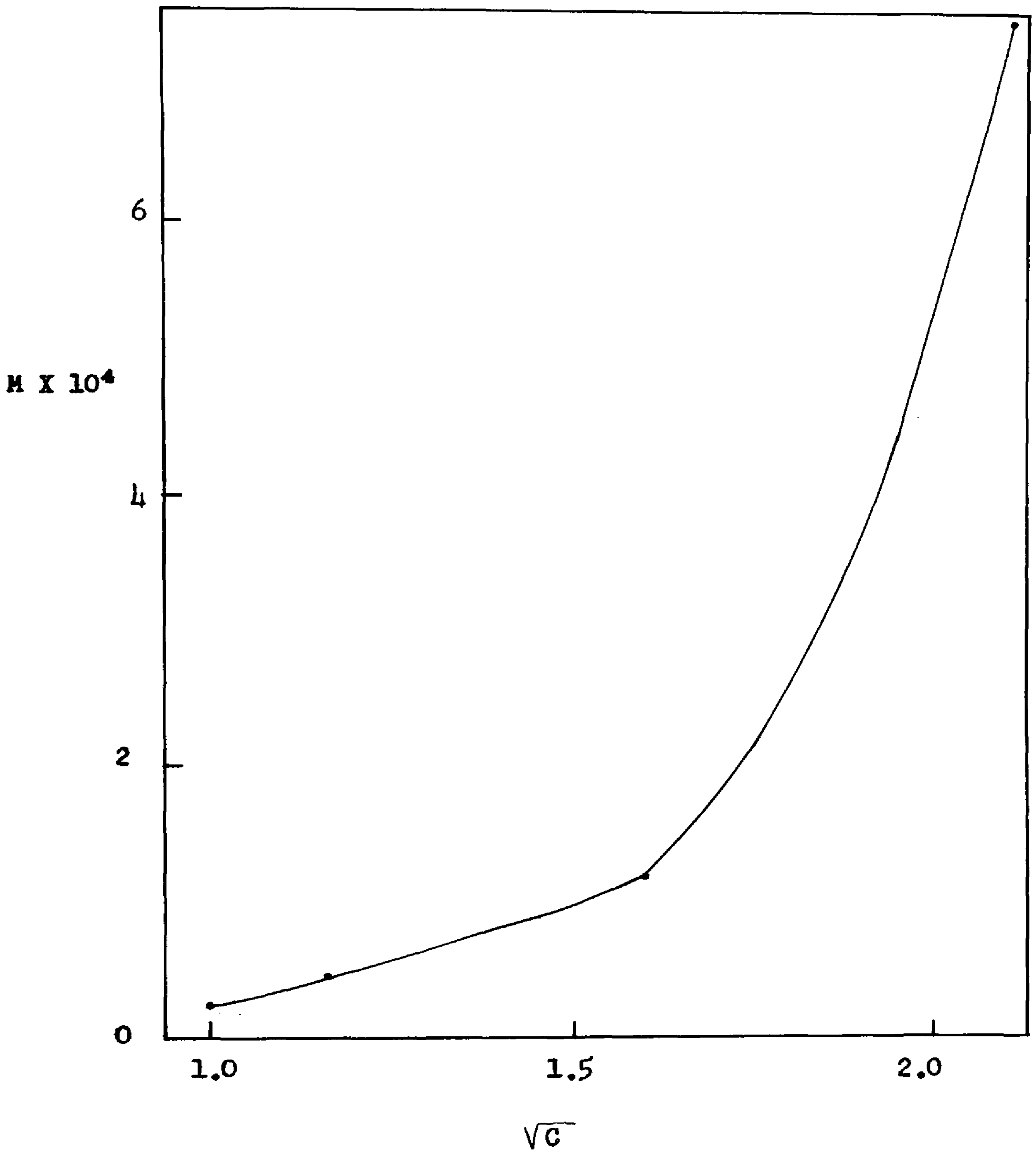


Figure 45. Molar conductance versus the square root of hydrogen fluoride molarity for solutions of hydrogen fluoride in chlorine trifluoride at 25°C.

D. Discussion of the Results

Conductances of the Halogen Fluorides

The specific conductances which have been determined for the halogen fluorides in this work are in general in good agreement with, or somewhat lower than, conductances reported previously. In the following table the results obtained in this research are compared with the best previously reported result.

TABLE XXV

SPECIFIC CONDUCTANCES OF THE HALOGEN FLUORIDES

Compound	L Best Value Obtained Here in $ohms^{-1}cm^{-1}$ at 25°C	L Best Previously Reported Value $ohms^{-1}cm^{-1}$	Reference
IF_5	5.3×10^{-6}	1.92×10^{-5} at 25°C	12
BrF_5	9.1×10^{-8}	8.5×10^{-7} at ? °C	19
ClF_3	4.9×10^{-9}	3×10^{-9} at ? °C	13

Emeléus, Woolf, and Sharpe,[20-22] suggested that the conductivity of iodine pentafluoride is due to self-ionization according to the equilibrium reaction

$$2IF_5 = IF_4^+ + IF_6^-$$

This assumption is based upon reactions such as

$$SbF_5 + IF_5 = (IF_4^+)(SbF_6^-)$$

and

$$KF + IF_5 = K^+IF_6^-$$

each of which causes an increase in conductance. If, however, potassium fluoride is added to the antimony pentafluoride-iodine pentafluoride solution a neutralization reaction of the type

$$KIF_6 + IF_4SbF_6 = KSbF_6 + 2IF_5$$

results.

If it is possible to draw an analogy between iodine pentafluoride and bromine pentafluoride it would seem that the conductivity of bromine pentafluoride would be due to the equilibrium

$$2BrF_5 = BrF_4^+ + BrF_6^-$$

The conductance of bromine pentafluoride has been found in this work to vary only slightly with temperature. Previously it had been reported to have a negative temperature coefficient, however the purity of the material used previously seems to have been somewhat less than that obtained in this work and it is therefore somewhat doubtful whether the results can be compared. A small or negative temperature coefficient might be assumed to be due to thermal instability of the ions in question.

The conductance of chlorine trifluoride is so extremely low that it is somewhat doubtful whether what conductance it does demonstrate is dependent upon a self ionization, such as that proposed for bromine trifluoride,

$$2BrF_3 = BrF_2^+ + BrF_4^-$$

or the presence of impurities. It is interesting to note, however, that chlorine trifluoride appears to have a negative temperature coefficient, of conductance, as does bromine trifluoride.

Conductances of Halogen Fluoride-Hydrogen Fluoride Solutions

The conductances of the hydrogen fluoride solutions of the halogen fluorides present a rather more complicated problem than that of the pure halogen fluorides. It can be seen from Figures 40, 43 and 45 that, although the curves for bromine pentafluoride and chlorine trifluoride are rather incomplete, there is probably a minimum in the molar conductance-concentration curve for each of the series of solutions measured. This is in full agreement with other work done with solutions of substances in non-aqueous solvents. The position of the minimum in this type of curve can sometimes be estimated by use of the expression[35]

$$\frac{D^3}{C_{min}} = k$$

where C_{min} is the concentration at which the minimum occurs, D is the dielectric constant of the medium, and k is a constant which applied to a given electrolyte in different solvents. Unfortunately the dielectric constants of the mixtures are not known and the position of the minimum is not known in some cases. The molar conductances at the minimum can be roughly approximated from the figures mentioned. The values are roughly as follows.

IF_5-HF	3×10^{-3}
BrF_5-HF	7×10^{-4}
ClF_3-HF	8×10^{-5}

The reason for the occurrence of a minimum is obscure at best, but might be due to some type of ion association.

The equivalent conductance of hydrogen fluoride in these solutions over the whole range of concentrations measured seems to be extremely low and thus it appears that hydrogen fluoride acts as a very weak electrolyte.

A negative temperature coefficient, or a tendency toward it, seems to be quite general as can be seen in Figures 41, 42 and 44. The most probable explanation is that the negative temperature coefficient is associated with thermal instability of the ions.

It is difficult to say just what the current carrying species are in these solutions on the basis of this work. On analogy with the potassium fluoride-iodine pentafluoride system it might be assumed that an equilibrium such as

$$HF + IF_5 = H^+ + IF_6^-$$

exists, while an analogy with the antimony pentafluoride-iodine pentafluoride system might indicate that an equilibrium such as

$$HF + IF_5 = HF_2^- + IF_4^+$$

is most important.

This work does not provide any way of differentiating between the two mechanisms. A similar situation exists for the bromine pentafluoride-hydrogen fluoride and chlorine trifluoride-hydrogen fluoride systems.

VIII MAGNETIC SUSCEPTIBILITIES OF THE HALOGEN FLUORIDES

A. Theoretical Aspects

Every substance possesses magnetic properties to some degree. These properties manifest themselves in one of three ways; diamagnetism, paramagnetism, or ferromagnetism. The general behavior of substances possessing these different types of magnetism may be described as follows: if two magnetic poles designed as m_1 and m_2 are separated by a distance r, then the force between the poles is

$$F = \frac{m_1 \, m_2}{\mu r^2}$$

where the quantity μ is assumed to be equal to unity in a vacuum. The quantity represented by μ is the magnetic permeability of the medium. It is a measure of the tendency of the magnetic lines of force to pass through the medium rather than through a surrounding vacuum. For paramagnetic substances μ is slightly greater than unity, for ferromagnetic substances it is much greater than unity (of the order of 10^3) and for diamagnetic substances it is very slightly less than unity.

If the strength of the magnetic field is $\underline{H}$, the product $\mu\underline{H}$ can be shown[86] to be

$$\mu H = 4\pi \underline{I} + \underline{H}$$

and therefore

$$\mu = \frac{4\pi \underline{I}}{\underline{H}} + 1$$

where $\underline{I}$ is the intensity of the magnetism induced by the field in the medium. Vector quantities are denoted by an underline. The relationship between $\underline{H}$ and $\underline{I}$ is defined by

$$\underline{I} = K\underline{H}$$

where K is the volume susceptibility.

It has been found that in general the diamagnetic susceptibility of a substance is independent of temperature or field strength, whereas the paramagnetic susceptibility of a substance has an inverse temperature relationship. Ferromagnetic susceptibilities vary with both temperature and field strength.

The classical theory of diamagnetism is due to Langevin,[67] who showed that when a magnetic field is applied to a system of electrons moving about a nucleus there is a precession of the electron orbits. The angular velocity of the precession is equal to $-e\underline{H}/2mc$ where e and m are the charge and mass of the electron and c is the velocity of light.

It can also be shown that the classical magnetic moment of an electron in its orbit is

$$M_\mu = \frac{\overline{e\,\omega\,r_I^2}}{2c}$$

where $\bar{\omega}$ is the average angular velocity of the electron and $\overline{r_I^2}$ is the mean square radius of the orbit projected perpendicular to the field. The change in the orbital magnetic moment in the field $\underline{H}$ due to the superimposed precession is given by

$$M = \frac{\overline{er_1^2\,(\,\omega - e\underline{H}/mc)}}{2c} - \frac{er_1^2}{2c}$$

$$= -\frac{e^2\overline{r_1^2}\,\underline{H}}{4mc}$$

For a system of n orbits oriented at random to the field, that is, for a spherically symmetrical atom

$$\bar{r}_1^2 = 2\bar{r}^2/3$$

where $\bar{r}^2$ is the mean square radius of the orbit. Thus for a spherically symmetrical atom

$$M_\mu = -\frac{e^2H}{6mc^2}\sum_n \bar{r}^2$$

and

$$\chi_M = \frac{N \; \Delta M_\mu}{H}$$

$$= -N \frac{e^2}{6mc^2}\sum_n \bar{r}^2$$

where χ_M is the molar susceptibility and N is Avogadro's number.

This clearly shows that the magnetic susceptibility of a diamagnetic substance should be independent of temperature and field strength, that it is negative, and that it would be expected to be present in all atoms or molecules regardless of whether or not there is a permanent magnetic moment which overshadows it.

The equation obtained above can also be shown to hold from a quantum-mechanical viewpoint except that the value of $\bar{r}^2$ is different. Van Vleck,[58] and Pauling,[59] have calculated $\bar{r}^2$ and obtained

$$\bar{r}^2 = a_0^2 \frac{n^4}{(Z-s)} \left\{1 + \frac{3}{2}\left[1 - \frac{\ell(\ell+1) - \frac{1}{3}}{n^2}\right]\right\}$$

where n and ℓ are the total and azimuthal quantum numbers a_0 is the radius of the 1s orbit for hydrogen, and (Z -s) is the effective nuclear charge. There is also a positive term in the quantum mechanical expression which cannot be evaluated and which is generally assumed to be negligible.

The exact calculation of (Z-s) is difficult but various approximate methods have been used to estimate it. W. R. Angus[60] has determined (Z-s) and thus χ_M for a large number of atoms or ions. A comparison of the results obtained here with those obtained by Angus's method of approximation will be presented in section VIII-D.

B. Apparatus and Method

The Gouy Magnetic Balance

The magnetic susceptibilities of the halogen fluorides were determined by the Gouy method.[61,63] The Gouy magnetic balance used in this work is illustrated in Figure 46 and has been described in detail elsewhere.[64] The Gouy method consists essentially of suspending a cylindrical sample of the material to be measured between the poles of an electromagnet in such a manner that one end of the sample is in a region of uniform high field intensity and the other end is in a region of low or negligible field intensity; the change in weight of the sample when a magnetic field is applied is measured.

The pole pieces of the magnet illustrated are adjustable along their common axis. There are 1440 turns of copper wire around each pole, the total resistance for both coils in series being about five ohms. Any current from one to twenty amperes may be applied to the coils. When high currents are used it is necessary to cool the coils by circulation of oil through the windings. The source of power was a D. C. generator operating at 110 volts. The current from the generator was varied by means of series resistors and could be controlled to one-tenth of an ampere.

The change in weight of the sample is measured by suspending it into the field from one arm of a semi-micro balance. Weight changes as small as two-hundredths of a milligram can be detected when this arrangement is used.

The field strength of the magnet with various values of applied current was determined by measuring the change in weight of samples of a standard nickel chloride solution (29.20% $NiCl_2$ by weight). The field strength was calculated from the following relation:

$$\frac{1}{2} (K_1 - K_2) H^2A = g \Delta w$$

where

K_1 = volume susceptibility of the liquid

K_2 = volume susceptibility of air

A = area of the tube, parallel to the pole faces, from septum to reference mark; found to be 1.88 cm^2.

g = gravitational constant

Δw = apparent change in weight of the sample when placed in the field.

H = field strength

The results obtained are tabulated in Table XXVII, and shown graphically in Figure 48.

The calibration of the field strength by this method is only approximate since it assumes that the susceptibility tube contains a uniform sample, and that the septum is perfectly flat. This method actually gives a quantitative calibration of a particular magnetic susceptibility tube so that the exact magnetic susceptibility of any other material placed in it may be determined.

The Susceptibility Tube

The susceptibility tube which was used in this work is illustrated in Figure 53. It was constructed entirely of Vycor* to resist the corrosive action of the halogen fluorides. The tube is a double or compensated tube with the halves separated by a septum. This reduced the change of weight of the tube itself in the field to nearly zero. Correction values for the empty tube are given in Table XXVI.

The tube was recalibrated after each run to correct for the corrosive action of the compounds used. The calibration data mentioned above are for the initial calibration. Subsequent calibration data were essentially the same.

For each calibration the tube was filled to a specific reference mark about four inches above the septum. When the susceptibility of the halogen fluorides was determined, however, the tube was filled above the mark since it is very difficult to transfer an exact quantity of halogen fluoride. This did not materially effect the results because the field strength at that point was negligible and the densities of the substances were known.

Sample Preparation and Procedures

It was found that the halogen fluorides could not be distilled directly from the metal vacuum line into the magnetic susceptibility tube

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* Corning Glass Co.

without introducing minute quantities of paramagnetic material. For this reason the small Vycor apparatus illustrated in Figure 47 was constructed. The halogen fluorides were distilled or siphoned directly from the storage containers into the apparatus illustrated and distilled from there into the susceptibility tube.

In the case of bromine trifluoride a sample was distilled directly from the tank into an aluminum tube on the vacuum line and then redistilled from the aluminum tube to the Vycor apparatus. The sample was then redistilled into the susceptibility tube. The bromine trifluoride thus obtained was probably contaminated with bromine monofluoride since the sample had a brownish color. A small amount of contamination with a diamagnetic substance, however, would not materially affect the result of the measurement. The elimination of paramagnetic or ferromagnetic metallic salts was accomplished by this procedure. The constancy observed for the susceptibilities of a given substance at different field strengths showed that ferromagnetic materials were absent.

Susceptibility measurements were made on each substance at 5, 8, 11, 15 and 20 amperes, corresponding to a range in field strength from 4000 to 12,000 Oersteds.

After each sample had been measured the residual magnetism of the pole pieces was removed by slowly reducing the current and repeatedly reversing its direction by means of a reversing switch.

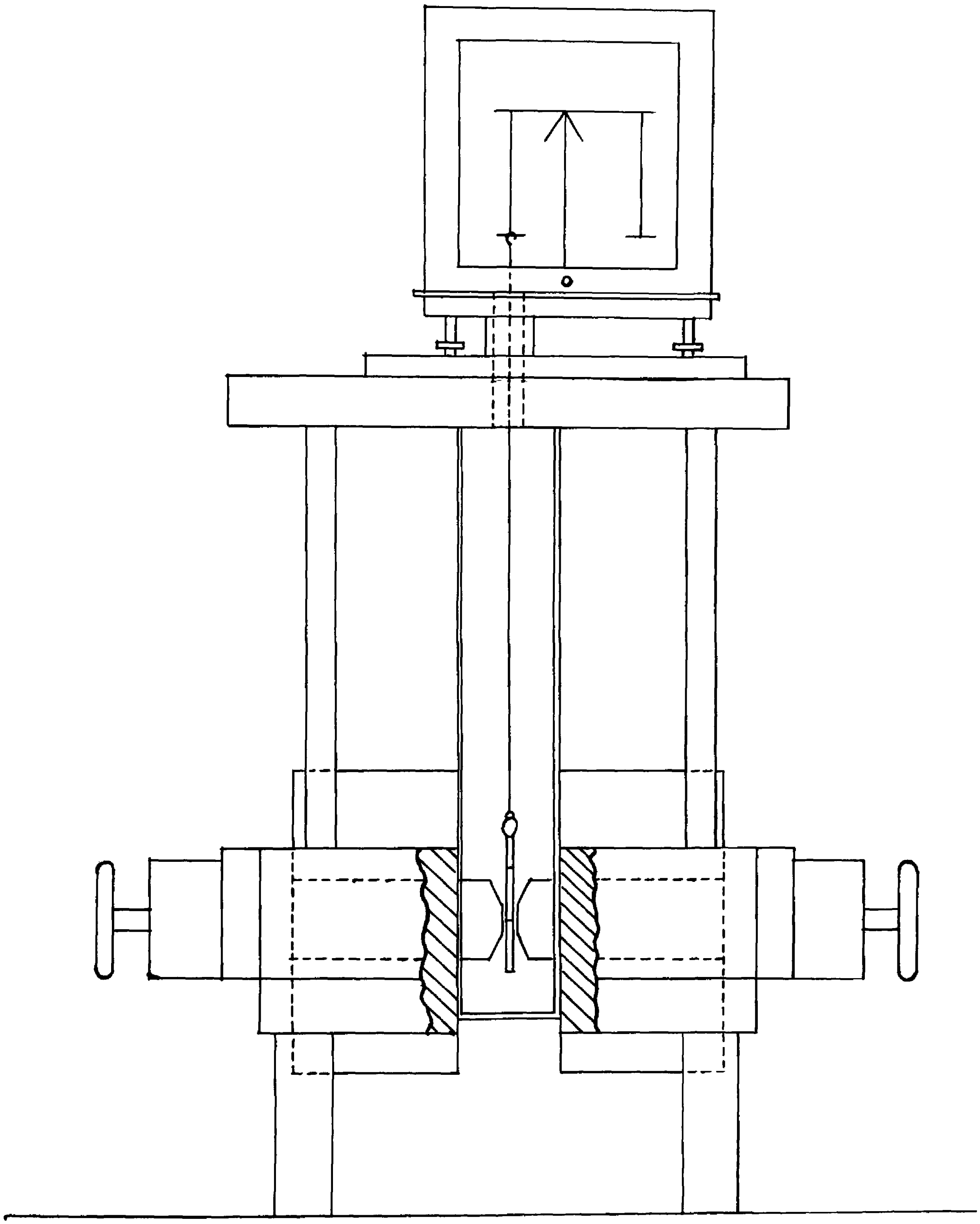

Figure 46. The Gouy magnetic balance.

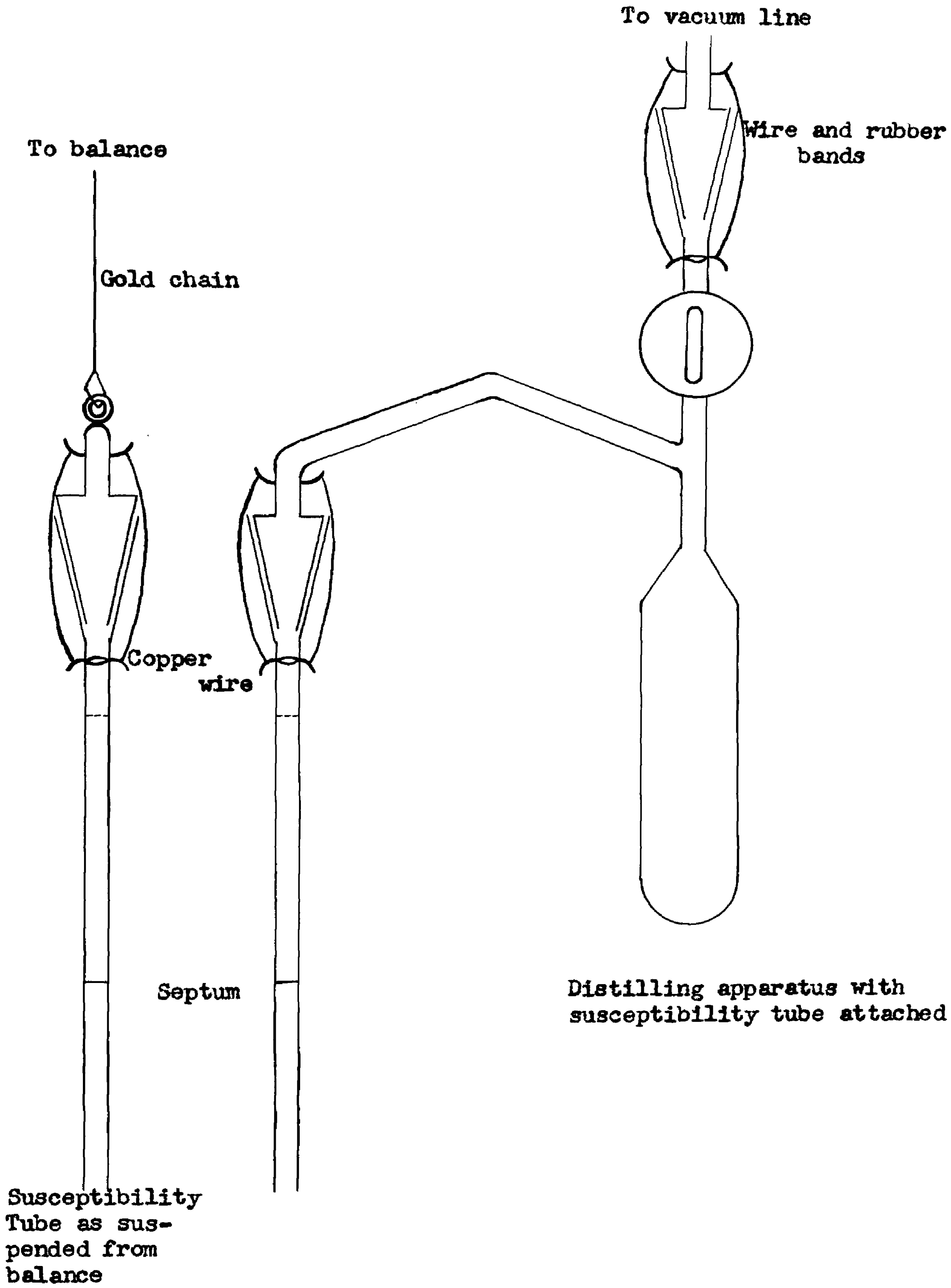

Figure 47. Diagram of the Vycor susceptibility tube and distilling apparatus.

TABLE XXVI

APPARENT WEIGHT CHANGES FOR THE EMPTY SUSCEPTIBILITY TUBE
— CALIBRATION I —

Current Amp.	Weight (gm)	△ Weight (gm)
0	15.26255	
5	15.26247	-0.00008
8	15.26235	0.00020
11	15.26217	0.00030
15	15.26205	0.00050
20	15.26184	0.00070

TABLE XXVII

FIRST CALIBRATION OF THE SUSCEPTIBILITY TUBE WITH NICKEL CHLORIDE

Current Amp.	Weight (gm.)	△Weight Corr.	Hcalc Oersteds	H* Oersteds
0	17.83925			
5	17.86585	0.0267	4770	4780
8	17.90310	0.0641	7325	7360
11	17.93580	0.0964	9080	9060
15	17.96825	0.1295	10500	10470
20	17.9973	0.1587	11600	--

* Unpublished work of Robert E. Vander Vennen

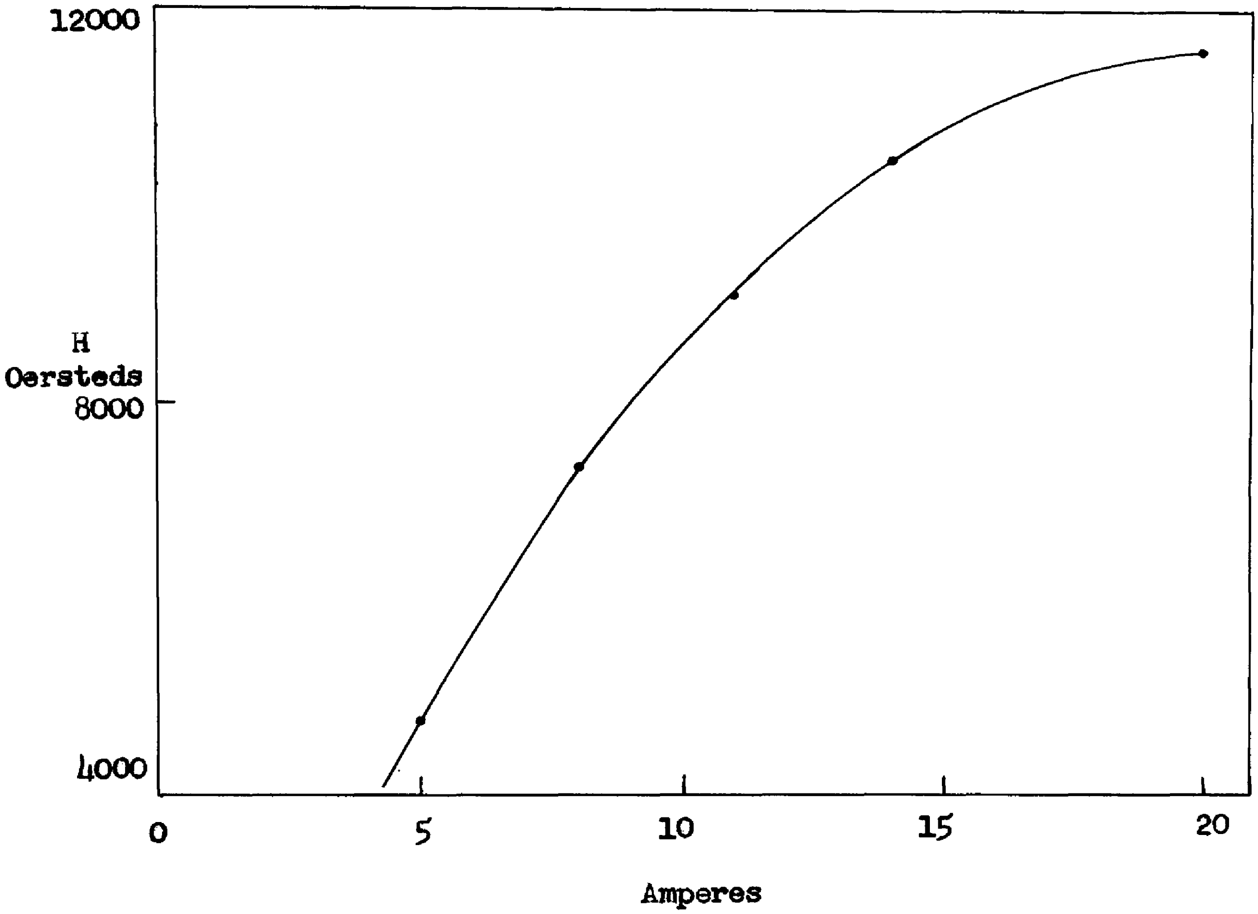

Figure 48. Calibration curve for the Gouy balance.

C. Data and Calculations

In the following pages the magnetic susceptibility data for certain halogen fluorides will be presented in tabular form. Information pertaining to the calculation of certain of the tabulated quantities will be presented first. The magnetic susceptibility of a substance may be determined without a knowledge of H by a relative method. The apparent changes in weight of both a substance of known, and of unknown susceptibility are measured using the same values of current and the same susceptibility tube.

From the relation given on page

$$H^2 = \frac{2g \quad \Delta w}{K_1 - K_2}$$

Thus for two substances, one of known magnetic susceptibility, and one of unknown magnetic susceptibility, whose apparent weight change has been measured at the same field strength

$$\frac{2g \quad \Delta w_1}{K_1 - K_2} = \frac{2g \quad \Delta w_X}{K_X - K_2}$$

$$K_X = \frac{\Delta w_X}{\Delta w_1} \quad (K_1 - K_2) + K_2$$

where K_1, K_2, g, and Δw_1 have been defined previously, K_X is the volume susceptibility of the unknown, and Δw_X is the apparent change in weight of the unknown when placed in the magnetic field.

The specific susceptibility of the unknown (χ_w) is defined as the volume susceptibility divided by the density. The final equation used in these calculations is therefore

$$\chi_w = \frac{\dfrac{\Delta w_x}{\Delta w_1}(K_1 - K_2) + K_2}{d}$$

where χ_w is the gram susceptibility. Molar susceptibilities (χ_M) are calculated by multiplying the specific susceptibility by the molecular weight of the substance.

All Δw values given are corrected for the apparent change in weight of the susceptibility tube when placed in the magnetic field.

In the following tabulation of results the first calibration has been omitted since it has already been presented in the previous section.

TABLE XXVIII

THE MAGNETIC SUSCEPTIBILITY OF IODINE PENTAFLUORIDE AT 25°C

Current Amperes	Weight Grams	Δw (corrected) Grams	$\chi_w \times 10^6$
0.0	21.35420		
5.0	21.35220	-0.00192	-0.266
8.0	21.34945	0.00455	0.262
11.0	21.34695	0.00695	0.265
15.0	21.34455	0.00915	0.261
20.0	21.34245	0.01105	0.257

Average $\chi_w = -0.262 \times 10^{-6}$

Average deviation = 0.003×10^{-6}

$\chi_M = -58.1 \times 10^{-6}$

The density at 25°C was taken to be 3.19 gm. per cc.[18b]

TABLE XXIX

THE MAGNETIC SUSCEPTIBILITY OF BROMINE PENTAFLUORIDE AT 25°C*

Current Amperes	Weight Grams	Δw (corrected) Grams	$\chi_w \times 10^6$
0.0	21.50600		
5.0	21.50450	-0.00142	-0.256
8.0	21.50240	0.00344	0.257
11.0	21.50050	0.00526	0.259
15.0	21.49870	0.00699	0.258
20.0	21.49705	0.00861	0.260

Average $\chi_w = -0.258 \times 10^{-6}$

Average deviation = 0.001×10^{-6}

$\chi_M = -45.1 \times 10^{6}$

* The calibration data on the following page was used for this run. The density at 25°C was taken as 2.47 gm. per cc.[16b]

TABLE XXX

APPARENT WEIGHT CHANGES FOR THE EMPTY SUSCEPTIBILITY TUBE FOR THE SECOND CALIBRATION

Current Amperes	Weight Grams	Δw Grams
0.0	16.48971	
5.0	16.48963	-0.00008
8.0	16.48955	0.00016
11.0	16.48947	0.00024
15.0	16.48940	0.00031
20.0	16.48937	0.00034

TABLE XXXI

SECOND CALIBRATION OF THE SUSCEPTIBILITY TUBE WITH NICKEL CHLORIDE

Current Amperes	Weight Grams	Δw (corrected) Grams	Hcalc. Oersteds	H' Oersteds
0.0	19.04710			
5.0	19.07335	0.0263	4745	4780
8.0	19.11030	0.0634	7380	7360
11.0	19.1431	0.0960	9060	9060
15.0	19.1749	0.1281	10480	10470
20.0	19.2035	0.1567	11610	---

TABLE XXXII

THE MAGNETIC SUSCEPTIBILITY OF CHLORINE TRIFLUORIDE AT 30°C

Current Amperes	Weight Grams	Δw (corrected) Grams	$\chi_w \times 10^6$
0.0	21.04250		
5.0	21.04130	-0.00112	-0.272
8.0	21.03947	0.00287	0.289
11.0	21.03795	0.00431	0.284
15.0	21.03645	0.00574	0.286
20.0	21.03515	0.00701	0.287

Average χ_w = -0.286 X 10^{-6} (5 ampere run omitted).

Average deviation = 0.002 X 10^{-6}

χ_M = -26.4 X 10^{-6}

The density at 30°C is taken as 1.80 gm per cc.[16b]

TABLE XXXIII

APPARENT WEIGHT CHANGES FOR THE EMPTY SUSCEPTIBILITY TUBE FOR THIRD CALIBRATION

Current Amperes	Weight Grams	Δw Grams
0.0	16.42760	
5.0	16.42750	-0.00010
8.0	16.42740	0.00020
11.0	16.42730	0.00030
15.0	16.42720	0.00040
20.0	16.42710	0.00050

TABLE XXXIV

THIRD CALIBRATION OF THE SUSCEPTIBILITY TUBE WITH NICKEL CHLORIDE

Current Amperes	Weight Grams	Δw (corrected) Grams	Hcalc. Oersteds	H' Oersteds
0.0	19.01725			
5.0	19.0441	-0.0268	4770	4780
8.0	19.0810	0.0637	7360	7360
11.0	19.1137	0.0965	9080	9060
15.0	19.1465	0.1293	10500	10470
20.0	19.1753	0.1581	11600	

TABLE XXXV

THE MAGNETIC SUSCEPTIBILITY OF BROMINE TRIFLUORIDE AT 28°C

Current Amperes	Weight Grams	Δw (corrected) Grams	$\chi_w \times 10^6$
0.0	21.29060		
5.0	21.28880	-0.00170	-0.267
8.0	21.28660	0.00380	0.250
11.0	21.28465	0.00565	0.246
15.0	21.28270	0.00730	0.236
20.0	21.28100	0.00910	0.240

Average $\chi_w = -0.248 \times 10^{-6}$

Average deviation $= 0.010 \times 10^{-6}$

$\chi_M = -33.9 \times 10^{-6}$

The density at 28°C is taken as 2.79 grams per cc.[15b]

D. Discussion of the Results

The prediction of magnetic susceptibilities has met with varying degrees of success depending upon the method which has been used. Pascal[61] devised an empirical table of atomic magnetic susceptibilities from experimental data for organic compounds. His tables have proven to be quite successful in predicting the susceptibilities of most organic compounds but not those of inorganic compounds. The most successful treatment of this problem from a theoretical point of view is due to Angus[60] who calculated a set of ionic susceptibilities.

In this work we are interested in Angus's ionic susceptibilities for Cl^{+3}, Br^{+3}, Br^{+5}, I^{+5} and F^{-1}. His values for $-\chi_M \times 10^6$ are 8.39, 17.67, 11.84, 22.17, and 7.25, respectively. The table on the following page shows a comparison between the experimental and calculated magnetic susceptibilities for the compounds whose susceptibilities were determined here and for a few other liquid fluorides.

There is an appreciable difference between the calculated and experimental values. This is not surprising when one considers that the calculations are based upon the assumption that the actual ions mentioned do exist. Since the compounds listed are undoubtedly covalent in character, this assumption would cause some error. Angus has shown that his values will generally predict the magnetic susceptibility of ionic compounds very accurately. It is also possible that the positive term of the quantum mechanical equation is not negligible in these cases and contributes to the differences between the calculated and experimental values.

TABLE XXXVI

MAGNETIC SUSCEPTIBILITIES FOR SOME LIQUID FLUORIDES

Compound	$\chi_M \times 10^6$	
	Observed	Calculated
SF_6	-44*	-45
SeF_6	-51*	-51
TeF_6	-66*	-61
MoF_6	-26*	-55
WF_6	-40*	-66
ClF_3	-26	-30
BrF_3	-34	-39
BrF_5	-45	-55
IF_5	-58	-66

* Reference[62]

IX SUMMARY

Procedure, equipment, and techniques for handling the halogen fluorides and their hydrogen fluoride solutions, and for measuring their vapor pressures, freezing points, apparent molal volumes, conductivities and magnetic susceptibilities, have been developed and are described in detail.

New values were obtained for the conductivities and freezing points of certain relatively pure halogen fluorides. The purities were estimated from the cooling curves obtained.

The vapor pressure curves for the hydrogen fluoride solutions of iodine pentafluoride, bromine pentafluoride and chlorine trifluoride were determined and the temperature variation of the positive deviation from Raoult's law is interpreted in terms of various processes which might occur in the liquid phase.

Phase diagrams for the systems iodine pentafluoride-hydrogen fluoride and bromine pentafluoride-hydrogen fluoride were obtained. Eutectic points were observed in the region of high hydrogen fluoride concentration in both cases. Discontinuities in the freezing point curves are discussed in terms of possible solid-state transitions and unstable compound formation.

The apparent molal volumes of some of the solutions were measured and found to be slightly smaller than would be expected if the solutions were ideal. A more open structure in the pure liquids than in the solutions is postulated to explain these observations.

Conductance measurements of the hydrogen fluoride solutions of several halogen fluorides were made at various temperatures. The data obtained indicated that hydrogen fluoride acts as an extremely weak electrolyte in solution with the halogen fluorides and that the conducting species are thermally unstable.

The magnetic susceptibilities of several of the pure halogen fluorides were measured and compared to values predicted by Angus. The observed values are, in general, lower than calculated, the deviations becoming larger the heavier the molecules. This was to be expected since the calculations are based upon an ionic model.

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