STUDIES OF SELF-IONIZATION IN LIQUID HALOGEN AND INTERHALOGEN COMPOUNDS

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ABSTRACT

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This thesis is concerned with the measurement of the effect of pressure and temperature on the electrical conductivities of halogen and interhalogen compounds, and the theoretical interpretation of the results. The introductory pages summarize the relevant theoretical aspects of solvation, ion association and non-aqueous solvents and describe the aims of the research. The literature related to the proposed research is reviewed.

Measurements of conductivity (κ) were made over the pressure range 1 - 1000 bar, at temperatures up to 177°C. Isothermal plots of $\log\kappa$ against pressure were linear within experimental error. The isothermal pressure coefficient of conductivity is conveniently expressed as an 'activation volume' defined as $\Delta V_\kappa = -RT(\partial \ln \kappa / \partial P)_T$ Values obtained for the 'activation volume' are accounted for in terms of displacement to the right of the self-ionization equilibria:

$$2I_2 \rightleftharpoons I^+ + I_3^-$$

$$2IBr \rightleftharpoons I^+ + IBr_2^-$$

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

$$2BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$$

Ionization is accompanied by a reduction in the total volume of the system, arising from electrostriction of the solvent (the molecular liquid) around the ions. This volume change was estimated independently, using the Born model for solvation. However results were not in very good agreement with experiment. The possible reasons for this are discussed.

For iodine at all temperatures and iodine chloride at higher temperatures, the temperature coefficient of conductivity is negative at constant pressure but positive at constant density. The density change caused by thermal expansion is sufficient to displace the self-ionization equilbria to the left when the temperature is raised at constant pressure.

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CONTENTS

CHAPTER 1

1.1 INTRODUCTION

Many molten salts are thought to contain molecules in equilibrium with ions. Such compounds are distinguished from the fully ionized molten salts by a much lower conductivity which may have either a positive or a negative temperature dependence.

The temperature dependence of electrical conductivity for a wide range of metal halides has been studied by Grantham and Yosim[1]. As the temperature was raised from the melting point, they found that the conductivity usually increased but the rate of increase diminished with rising temperature. For some compounds the conductivity-temperature curve passed through a maximum whilst for mercuric iodide the conductivity decreased with rising temperature over the whole liquid range. Grantham and Yosim suggested that the melts consist of covalent molecules in equilibrium with ions, the conductivity being proportional to the product of the ion mobility and degree of dissociation. The ion mobility increased with increasing temperature while the degree of dissociation decreased with increasing temperature. Thus at lower temperatures an increase in conductivit is expected and observed. At higher temperatures, a conductivity maximum can occur. This decrease in the degree of dissociation was said to be due to the denisty change and Grantham and Yosim suggested that the conductivity would always increase with increasing temperature under conditions of constant density. Measurements involving pressure as an independent variable are required to confirm this.

Thus it was decided to study the effect of pressure on the self-ionization of halogen and interhalogen compounds with a view to determining the effect of volume on the equilibrium in these partially ionized liquids. The formation of ions in these media is accompanied by a large reduction in the volume of the system due to the solvation of the ions by the molecular form of the solvent. Because of this negative volume change, application of pressure favours the formation of ions and so increases the degree of

Previous work on fully ionized melts, such as the alkali metal nitrates[2] or halides[3], has shown that a pressure of 1000 bar reduces the conductivity by up to 10%. This decrease is attributed to a reduction in the mobilities of the ions, caused by the increase in density. The conductivities of non-aqueous solutions of fully dissociated electrolytes usually decrease with pressure for the same reason.[4-7] For aqueous solutions of strong electrolytes, increases in conductivity with pressure which are sometimes observed are attributed to changes in solvent structures or to the operation of a Grotthus mechanism e.g. for proton transfer[8]. For weak electrolyte solutions, the degree of ionization increases with pressure, because the solvation of the ions involves a net reduction in the volume of the system.[9, 10] The same consideration applies to the self-ionization of molecular liquids such as water.[11]

1.2 ELECTRICAL CONDUCTIVITY

Consider a system containing positive and negative ions. In an electric field E, an ion i will migrate with a constant velocity

$$V_i = U_i E \qquad (1.2.1)$$

where U_i is the electrical mobility of an ion i, V_i is positive for migration in the positive field direction. The migration of ions gives rise to a current density $I = \kappa E$, where κ is the conductivity and

$$\kappa = \sum_i |e_i c_i u_i| \qquad (1.2.2)$$

where $e = Z_i F$ is the charge on the i ion and all velocities are referred to the same standard.[12]

For a pure molten salt the equivalent conductivity

$$\Lambda = \frac{\kappa}{c_i|z_i|} \qquad (1.2.3)$$

where C_i is the concentration of i (i gm ions/cm^3) at that temperature and pressure. Similarly the molar conductivity may be defined as:

$$\Lambda = \frac{\kappa\,(\mathrm{M.Wt.})}{\rho} = \kappa V_m \qquad (1.2.4)$$

where ρ is the denisty at that temperature and pressure, V_m is the molar volume .

1.3 EMPIRICAL RELATIONS

One approach to the understanding of transport processes in liquids has been to develop simple empirical relations between the transport coefficients. One set of useful empirical relations are those between transport coefficients and temperature. These equations are quite closely obeyed for most ionic salts over a temperature range of about 100°C to 200°C. Thus molar conductivity, viscosity and diffusion can be expressed as

$$\Lambda, \frac{1}{\eta}, \frac{D}{T} = A_{\Lambda, \frac{1}{\eta}, \frac{D}{T}} \exp - \left[\frac{(E_p)_{\Lambda, \frac{1}{\eta}, \frac{D}{T}}}{RT} \right] \qquad (1.3.1)$$

From this purely empirical equation it is possible to define a number of parameters that are useful when comparing the effects of temperature and pressure on the transport properties.

We define[13]

$$(E_p)_\Lambda = -R \left(\frac{\partial \ln \Lambda}{\partial (1/T)} \right)_p \qquad (1.3.2)$$

$$(E_V)_\Lambda = -R \left(\frac{\partial \ln \Lambda}{\partial (1/T)} \right)_V \qquad (1.3.3)$$

$$(\Delta V)_{\Lambda} = -RT\left(\frac{\partial \ln \Lambda}{\partial P}\right)_T \tag{1.3.4}$$

Similarly an equivalent set of definitions may be derived for κ :

$$(E_p)_{\kappa} = -R\left(\frac{\partial \ln \kappa}{\partial (1/T)}\right)_P \tag{1.3.5}$$

$$(E_v)_{\kappa} = -R\left(\frac{\partial \ln \kappa}{\partial (1/T)}\right)_V = (E_v)_{\Lambda} \tag{1.3.6}$$

$$(\Delta V)_{\kappa} = -RT\left(\frac{\partial \ln \kappa}{\partial P}\right)_T \tag{1.3.7}$$

From the definition of molar conductivity, equations (1.3.2, 4, 5, and 7) may be related by

$$(E_p)_{\Lambda} = (E_p)_{\kappa} + \alpha RT^2 \tag{1.3.8}$$

$$(\Delta V)_{\Lambda} = (\Delta V)_{\kappa} + \beta RT \tag{1.3.9}$$

Now since Λ or logΛ is a single valued function of temperature and pressure for any given molten salt then^2:

$$d\ln\Lambda = \left(\frac{\partial \ln \Lambda}{\partial P}\right)_T dP + \left(\frac{\partial \ln \Lambda}{\partial T}\right)_P dT \tag{1.3.10}$$

and therefore:

$$\left(\frac{\partial \ln \Lambda}{\partial (1/T)}\right)_P = \left(\frac{\partial \ln \Lambda}{\partial (1/T)}\right)_V + T^2 \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial \ln \Lambda}{\partial P}\right)_T \qquad (1.3.11)$$

Thus from the definition of $(E_p)_\Lambda$, $(E_v)_\Lambda$ and ΔV_Λ equation (1.3.11) may be written as:

$$(E_p)_\Lambda = (E_v)_\Lambda + \Pi \, \Delta V_\Lambda \qquad (1.3.12)$$

where $\Pi = \alpha T/\beta$, α is the expansivity, and β the isothermal compressibility: both are assumed to be independent of pressure. Similarly:

$$(E_p)_K = (E_v)_K + \Pi \Delta V_K \qquad (1.3.13)$$

By analogy with the theories of activated processes in liquids, E_p has been called a constant pressure activation energy, E_v a constant volume activation energy, and ΔV an activation volume.

1.4 MEASUREMENT OF CONDUCTIVITY

In the simple Wheatstone bridge (fig. 1.4.1) used for d.c. resistance measurements, the galvanometer shows no deflection at balance; the potentials at A and B are therefore equal, whence $R_1/R_2 = R_3/R_4$. In the a.c. bridge (fig. 1.4.2) the battery is replaced by a sinusoidal alternating potential from an oscillator, and the galvanometer by a suitable detector. The condition for balance (i.e. no signals in the detector) is that the alternating potentials at A and B are of equal amplitude and exactly in phase, which leads to the relation $Z_1/Z_2 = Z_3/Z_4$ where the impedence Z is the a.c. analogue of resistance.

The design and construction of high precision conductance bridges was studied extensively by Grinnell Jones[14-20] and his colleagues and also by Shedlovsky[21] and the principles they laid down are the basis of today's designs.

Figure 1.4.1 Simple Wheatstone bridge circuit

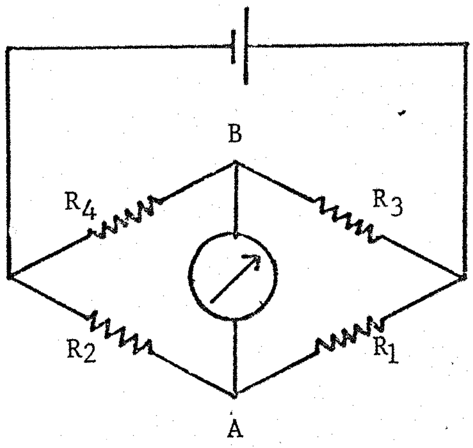


Figure 1.4.2 A.C. bridge circuit

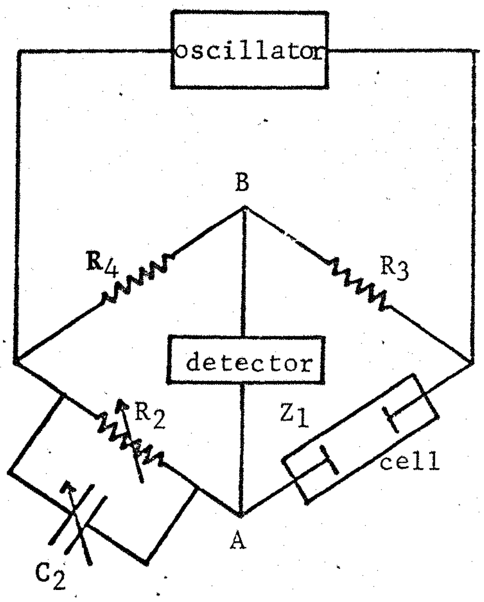
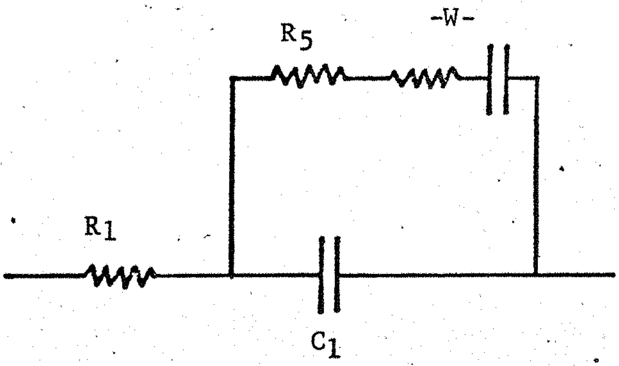


Figure 1.4.3 Network electrically equivalent to the cell



The object of conductance measurements is to determine the pure ohmic resistance R_1 of the solution or salt between the electrodes. If the cell impedance Z_1 consisted only of this resistance, then the measured resistance R_2 would equal the cell resistance R_1 at all frequencies and the capacitor C_2 in parallel with the measured resistance would be required only to compensate for capacity between the cell leads and for the small capacity in parallel with the cell due to the action of its electrodes as a capacitor with the solution as dielectric. In practice there are several sources of impedance which cause R_2 and C_2 to vary appreciably with frequency.

Polarization errors are usually minimised by the use of audio frequency alternating current for the measurements and by coating the electrodes with a heavy deposit of platinum black[22] when R_2 becomes practically independent of frequency. The use of a.c. complicates the electrical technique required for high accuracy measurements, owing to the need for compensation of capacitive and inductive effects in the circuit. However it is not always possible to platinize the electrodes since finely divided platinum may react with the solution or salt or may adsorb appreciable quantities of solute.

Thus it is necessary to eliminate electrode effects from cells without platinized electrodes by other means. The schematic representation of the network electrically equivalent to the conductance cell, as proposed by Ives[23], with the addition of the 'Warburg impedance' is shown in fig 1.4.3. In this figure, R_1, which is to be determined, is independent of frequency at audio frequencies. In series with R_1 is the capacity C_1 of the double layer of ions at the electrode surfaces which is also expected to be independent of frequency. The applied potential across the cell is usually only a few millivolts which is usually far too little to cause electrolysis at shiny platinum electrodes. However some electrolysis will normally occur and this electrolysis process is represented as a 'Faradaic leakage' in parallel with the double layer.

In general this consists of two parts; a pure resistance R_5, independent of frequency, and a Warburg impedence (-W-) at the electrodes. This impedence can be regarded as equivalent to a resistance and a capacitance in series, the impedence of both being the same at any one frequency but both varying inversely as $w^{\frac{1}{2}}$.

They can therefore be represented together by:

$$-W- = k(1 - i) / \sqrt{w}$$

where k is a constant of dimensions (resistance x time$^{-\frac{1}{2}}$). Solution of the balance conditions leads to the result that, if the impedance of the cell arm is denoted by Z, then:

$$1/R_2 = \text{real part of } Z^{-1}$$

from which R_2 may be determined in terms of R_1, R_5, C_1, k and w.

The following special cases can arise.

(1) R_5 infinite : the electrodes are ideally polarized and

$$R_2 = R_1 + (w^2 C_1^2 R_1^2)^{-1}$$

This condition is unlikely to arise in practice.

(2) If $W \ll R_5$

then
$$R_2 = R_1 + \frac{R_1 R_5 + R_5^2}{R_1 (1 + w^2 C_1^2 R_5^2) + R_5}$$

which since $R_1 \gg R_5$ approximates to

$$R_2 = R_1 + R_5 / (1 + w^2 C_1^2 R_5^2)$$

This is applicable to a conductance cell with grey platinized electrodes and also to one with shiny platinum electrodes in an aqueous solution. It is found in practice that R_1 is obtained by a linear extrapolation of R_2 against w^{-1}.

(3) If C_1 is very large, so that its impedence is small compared with that of the faradaic leakage, $R_2 = R_1$ at all frequencies. Heavily blacked platinum electrodes corresponds to this behaviour.

(4) Where $W \gg R_5$ but $W \ll R_1$ one obtains solutions approximating to

$$R_2 = R_1 + k / \sqrt{w}$$

This behaviour is found at silver electrodes in silvernitrate solutions and also at platinum electrodes in acid solutions. This does not generally apply for shiny platinum electrodes.

Thus, when using shiny platinum electrodes, it is necessary to measure at a number of frequencies and to extrapolate to infinite frequency.

Whilst a.c. measurements have the advantage in that polarization effects are eliminated, a great many new complications due to capacitive and inductive effects in the circuit are introduced.

1.5 THE BORN EQUATION

The introduction of a dissolved electrolyte to a solvent can produce several kinds of solute entities: ions-solvated or unsolvated, electrostatically associated groups of ions, covalently bound molecules and complex ions.

To understand the behaviour of ions in a solution, one must understand ion-solvent interactions. When ions are present in a solvent there will be ion-ion, as well as ion-solvent interactions in the solution. For the present the former will not be considered. The problem of deriving an expression of the free energy of ion-solvent interaction can be reduced to that of finding the work done when one transfers an ion from vacuum into a solvent. This work will include the energy of all the interactions between the ion and the surrounding solvent. However to work out exactly all the ion-solvent interactions, one must know the structure to the solvent, i.e. the dispositions of all the particles constituting the solvent and the forces between the ion and these particles. But the solvent may have a fairly complex structure. For example, there may be discrete solvent molecules, or they may be associated to a greater or lesser extent. Also, the ions themselves may have some effect on the solvent structure.

To overcome these problems, one can resort to modelistic thinking. A simple and approximate model for ion-solvent interactions was proposed by Born in 1920. In the Born model, an ion is viewed as a rigid sphere of radius r_i bearing a charge $z_i e_o$ where e_o is the electronic charge and the solvent is taken to be a structureless continuum. Thus the problem of ion-solvent interaction has now become that of finding the work done in transferring a charged sphere from vacuum into a continuum of dielectric constant ε_r. By considering a charged sphere equivalent to an ion, the Born model assumes that it is only the charge on the ion that is responsible for ion-solvent interactions. The interactions between the solvent and the ion are considered to be purely electrostatic in origin. The free energy ΔG_{I-S} of ion-solvent interactions is calculated using a thermodynamic cycle. The cycle is the following:

1. The ion (or charged sphere) is first considered in a vacuum and the work W_1 of stripping it of its charge $z_i e_o$ is computed.
2. This uncharged sphere is slipped into the solvent; this process will involve no work, i.e. $W_2 = 0$ because the only interactional work is assumed to arise from the charge on the ion.
3. Then, the charge on the sphere inside the solvent is restored to the full value $z_i e_o$ and the charging work W_3 is computed.
4. Finally, the ion is transferred from the solvent to vacuum. Since this transfer process is opposite to that involved in the definition of the free energy ΔG_{I-S} of ion-solvent interactions, the work W_4 associated with the last step of the cycle is equal to $-\Delta G_{I-S}$.

Thus $W_1 + W_2 + W_3 + W_4 = 0$

and $$\Delta G_{I-S} = \underset{\text{ion in vacuum.}}{\text{work of discharging}} + \underset{\text{ion in solvent}}{\text{work of charging}}$$

From basic electrostatics it follows that

$$\Delta G_{I-S} = -\frac{(Z_i e_o)^2}{8\pi\varepsilon_o r_i} + \frac{(Z_i e_o)^2}{8\pi\varepsilon_o\varepsilon_r r_i}$$

$$\Delta G_{I-S} = -\frac{(Z_i e_o)^2}{8\pi\varepsilon_o r_i}\left(1 - \frac{1}{\varepsilon_r}\right)$$

This is the free energy change resulting from the transfer of an ion from a vacuum to a solvent. If the term ΔG_{I-S} is negative, then ions exist more stably in the solvent than in vacuum. Since the dielectric constant of any medium is greater than unity, $1 > {}^1/\varepsilon_r$, and therefore ΔG_{I-S} is always negative. The Born equation predicts that the smaller the ion and the larger the dielectric constant ε_r, the greater will be the magnitude of the free-energy change in the negative direction. The Born model oversimplified the problem of ion-solvent interactions but does give answers of the same order of magnitude as experiment.

Since it is the heat of ion-solvent interactions, rather than the free energy, which is obtained directly from the experimentally measured heat changes which occur when solids containing ions are dissolved in a solvent, the enthalpy change (ΔH_{I-S}) associated with ion-solvent interactions can be obtained by differentiating ΔG_{I-S} with respect to temperature.

$$\Delta H_{I-S} = -\frac{(Z_i e_o)^2}{8\pi\varepsilon_o r_i}\left(1 - \frac{1}{\varepsilon_r} - \frac{T}{\varepsilon_r^{\,2}} \cdot \frac{\partial\varepsilon_r}{\partial T}\right)$$

The Born values for the heats of ion-solvent interactions calculated from the above equation are numerically too high, in some cases nearly 50% too high, when compared with 'experimental values'.

To obtain heats of interaction of individual ions with the solvent from the experimental measurements of heats of salt-solvent interactions, it was assumed that if one considered a salt in which the positive and negative ions are of equal radii; then the heat of the salt-solvent interactions can be split equally between the two species. The pair chosen for this purpose was KF because the radii of the K^+ and F^- ions are almost equal. The heats of hydration calculated in this way are referred to in later sections as 'KF-derived'.

However it was found that the experimental heats of interaction between ions and solvent did not vary inversely as the radius, as predicted by the Born equation. Of course, one can arbitarily adjust the values of the radii to differ from the crystallographic radii and then obtain better fit between theory and experiment. Latimer, Pitzer, and Slansky[24] found that by adding 0.85Å to the radii of the positive ions and 0.1Å to those of the negative ions, one can remove the discrepancy between the calculated and observed values. The constant 0.85Å was explained on the grounds that it was the radius of the oxygen atom in a water molecule i.e. (the negative end of the dipole).

Another approach at explaining the discrepancy between the Born theory and experiment centres around the value chosen for the dielectric constant ε_r. The Born theory uses the experimentally measured value for the bulk solvent e.g. 80 for water, but it is the effective value ε_{eff} near the ion which can be considered of greater significance to the charging process. If ε_{eff} near the ion is rather less than the bulk value, then by using ε_{eff} instead of ε_r in the Born equation the calculated ΔH_{I-S} will be lowered toward the experimental value.

One cannot however expect really good agreement between theory and experiment when the Born theory ignores the structure of the solvent. One must understand the structure of the solvent in the bulk far away from the ion and also near to the ion.

1.6 SOLVATION

Since water is the most important of the ionizing solvents, an understanding of its structure and properties is essential to the understanding of the behaviour of electrolyte solutions. Water is a bent molecule with a bond angle of 105°. The dipole moment of the isolated molecule acts along the bisector of the H - O - H angle with the negative end towards the oxygen nucleus. In the liquid state water exhibits properties characteristic of an associated liquid i.e. (high m.p., high b.p., high entropy of vapourisation, high dielectric constant). In liquid water, the water molecules are far from close packed. However, over short ranges and for short periods of time, liquid water retains the tetrahedrally co-ordinated structure of ice by 'hydrogen bonding'. From the study of the solubility of non-polar gases in non-polar solvents and in water, it has been shown that the water structure becomes more ordered through the influence of the dissolved molecules. It is said in the words of Frank and Evans[25] that 'the water builds a microscopic iceberg round the non-polar molecule'. At higher temperatures this effect is less marked due to thermal agitation. This iceberg effect is also found for non-polar solutes in water.

With ionic solutes, an intense electrical field due to the ionic charge is superimposed on the normal solute-solvent interaction. In very dilute solutions one can think of the effects produced by a single ion on successive layers of water molecules but this is not so in more concentrated solutions. In fact it is reasonable to talk of successive layers of water molecules round one particular ion only below about 0.1 molar. From data for the entropy of solution of a number of ions in water[25], the effect of the ionic charges is to reduce the entropy loss, that is, to promote increased disorder in the water when compared with the entropy loss caused by a neutral species i.e. KCl cf Ar.

One can summarize the description of the structure of water near an ion by referring to three regions. In the primary region next to the ion there is a layer of firmly oriented water molecules about the ion which move as and where the ion moves. Then there is a secondary region where the water structure is broken down due to the manner in which the first layer of water molecules is arranged. This arrangement is such that all these molecules could not participate in the normal tetrahedral water arrangement. Finally, at sufficient distance from the ion, the water structure is unaffected by the ion and displays the tetrahedrally bonded networks characteristic of bulk water.

The above description of the solvent surrounding an ion was used as the basis of a structural treatment of ion-solvent interations in the ion-dipole model. The charge distribution in the water molecule was, as a first approximation, taken as equivalent to an electric dipole. The total heat of solvation was viewed as consisting of three contributions. The first contribution was the interactions between the ion and the water molecules which are members of the primary solvent sheath, and the calculation involved the heat of ion-dipole interactions. The second contribution to the heat of solvation pertained to the interaction between a primary solvated ion and the surrounding solvent, which, as a first step, was reckoned to have the bulk structure of water. The calculation of this second part of the total heat of solvation followed the procedure of the Born model except that one was dealing with a primarily solvated ion rather than a bare ion. Since the solvent in the immediate neighbourhood of the primary solvated ion does not have the bulk structure, a correction to the second contribution was introduced to account for the structure breaking. The change in heat content due to the structure breaking around a primary solvated ion constituted the third contribution to the total heat of solvation of ions.

When the values of the heat of solvation calculated by ion-dipole theory were compared with the 'KF - derived' values, it was clear that this structural picture of solvation was in far better accord with the experimental result than the Born model was.

Clear-cut experimental evidence was produced to demonstrate that the difference in the absolute heats of solvation of ions of opposite charge but equal radii was neither zero nor independent of ionic radius. This difference should be zero according to the 'KF - derived' heats, and it should be radius independent according to the ion-dipole theory.

While the charge distribution in the water molecule may appear equivalent to an electrical dipole to an ion situated far away, the charge distribution is better represented as an electrical dipole plus quadrupole from the point of view of an ion in contact with the water molecule. Thus it was necessary to calculate the heat of ion-quadrupole interactions in the primary solvated ion.

The ion-quadrupole theory showed that ions of opposite charge but equal radii should have differing heats of solvation, as found experimentally. Interactions between the ions and dipoles induced in the water molecules were also taken into account. Heats of solvation calculated by the ion-quadrupole theory showed close agreement with experimental values (not 'KF - derived' values). It was possible to isolate experimental heats of solvation of ions relative to the hydrogen ion and to use these relative heats to yield an absolute heat of solvation of the hydrogen ion and, thus, the absolute heats of other ions.

This is the basic theory of the energetics of ion-solvent interactions. Viewing the water molecule as a dipole gives reasonable heats of solvation; viewing it as a quadrupole gives good results.

It is important to know how the microscopic dielectric constant varies with the distance from an ion. Ritson and Hasted[26] calculated the dielectric constant of water as a function of distance from a point electronic charge, using two different models, one based on Onsager's expression for the dielectric constant

$$\frac{(\varepsilon_r - n^2)\ (2\varepsilon_r + n^2)}{\varepsilon_r(n^2 + 2)^2} = \frac{N_o}{3\varepsilon_o} \cdot \frac{\mu_o^2}{3kT}$$

and the other on an empirical modification of Kirkwood's expression;

$$\frac{(\varepsilon_r - 1)\ (2\varepsilon_r + 1)}{9\varepsilon_r} = \frac{N_o}{3\varepsilon_o} + \frac{N_o}{3\varepsilon_o} \cdot \frac{\mu^2 g}{3kT}$$

Both models lead to very similar values for the local dielectric constant. There is a region of complete dielectric saturation up to about 2Å from the point charge, where the dielectric constant has the value of four or five arising from electron and atom polarization only. This is followed by a region of rapid rise ending at about 4Å from the point charge, and thereafter the dielectric constant is practically stationary at its ordinary bulk value. For monovalent ions the region of appreciable dielectric saturation is confined to the first layer of water molecules around the ion.

Schellman[27] has calculated the dielectric saturation effect near an ion in water, using a detailed molecular model of the region near the ion combined with a classical dielectric model at greater distances. He finds that the dielectric saturation effect should be very much smaller than the classical model alone would give e.g. at 5Å from a monovalent ion the dielectric constant is only 0.4 per cent less than its ordinary value, and even at 2Å it is only reduced by about 17 per cent. These conclusions give strong support to the practice of using the ordinary dielectric constant of water in calculating ionic interactions, even in comparatively concentrated solutions.

1.7 ION ASSOCIATION

When ions of opposite sign are close together, the energy of their mutual electrical attraction may be considerably greater than their thermal energy, so that they form a virtually new entity in the solution, of sufficient stability to persist through a number of collisions with solvent molecules. In the case of a symmetrical electrolyte, such ion-pairs will have no net charge, though they should have a dipole moment. They will therefore make no contribution to the electrical conductivity, while their thermodynamic effects will be those of removing a certain number of ions from the solution and replacing them by half the number of dipolar 'molecules'. With unsymmetrical electrolytes the position will be more complicated, since the simplest and most probable type of ion association, that involving only two particles, will result in the appearance of a new ionic species of a charge type not previously present; this will contribute to the conductivity; though less than would its constituent ions in the free state. In such cases further association to form neutral particles may also be reasonably expected.

Bjerrum[28] proposed that the average effects of ion pair formation may be calculated on the basis that alloppositely charged ions within a certain distance of one another are associated into ion-pairs. This critical distance, q , is given by

$$q = \frac{|z_1 z_2| e^2}{8\pi\varepsilon_o \varepsilon_r kT}$$

This is the distance at which the mutual potential energy of the two ions is equal to 2 kT. For a 1:1 electrolyte in water at 25°C $q = 3.57$Å; at distances closer to the central ion the population of oppositely charged ions on a sphere surrounding the central ion increases rapidly. The population also increases at greater distances but the rate of increase is less. There is no such effect with ions of like charge: there is small probability of finding them close to the central ion and the population shows no minimum. As regards the ions of opposite charge, if the distance of closest approach is 3.57 $|z_1 z_2|$ Å or more, it is assumed that there will be no ion pairs. If the ions can approach closer than this, Bjerrum would regard those within the sphere of radius 3.57 $|z_1 z_2|$ Å as 'undissociated' ion pairs. Bjerrum simplified the problem by subjecting the ions surrounding the central ion to the potential of this ion alone and neglecting the interionic forces of the surrounding ions.

Ion pair formation will be favoured by solvents of lower dielectric constant since the critical distance, q , is increased if the dielectric constant is lowered. Small ionic radii and large z_1 and z_2 will also favour ion-pair formation.

Despite a considerable agreement with experiment, there are features of the Bjerrum picture of ion-pair formation which are unsatisfactory. The first and most important defect of this theory is that it identifies, as ion pairs, ions which are not in physical contact, the only requirement being that ions approach closer than q . A second defect is the arbitrary nature of the choice of q as the distance beyond which ion pairs are formed.

Fuoss[29] pointed out that it was wrong to ignore the discrete molecular nature of the solvent. He suggests that two ions should be counted as a pair only if they are in contact (irrespective of the period of time) with no solvent molecule intervening. It should not be forgotten that in the region between the distance of closest approach and the Bjerrum critical distance there can be a large number of solvent molecules (of the order of several thousand). Of all the ions which penetrate into this shell and form ion-pairs, a few will get very close to the central ion. But in general the ion-pair will be held together by electrostatic forces operating through a large number of solvent molecules - large enough to justify considering that the solvent in this shell will have the properties, and the dielectric constant of the bulk solvent. It is very different for a 1:1 electrolyte in water where there is only room for about four water molecules in the shell in which ion-pair formation is expected. Here it is doubtful if one is justified in using the bulk dielectric constant in a region where the solvent molecules must be subject to dielectric saturation.

If the electrostatic forces are sufficiently strong, then it is possible that the ion-pair 'dipoles' may attract ions and triple ions may be formed. Triple ion formation has been suggested in solvents for which $\varepsilon < 15$. Further decrease of dielectric constant below a value of about 10 may make possible the formation of still larger clusters of four, five or more ions.

1.8 NON AQUEOUS SOLVENTS

Aqueous solutions of electrolytes have traditionally received far more attention than the corresponding non aqueous solutions; even though it has been realised for a long time that water cannot be regarded as the prototype of electrolyte solvents. Nevertheless, during recent years there has been an increasing interest in the behaviour of electrolytes in nonaqueous solvents with a view to investigating ion-ion and ion-solvent interactions under varied conditions. Electrostatic theories have been tested in media of varying dieletric constants and the theoretical implications of the present knowledge of non-aqueous electrolyte solutions have been considered in the current literature[30]. The study of the thermodynamics and transport properties of these solutions provides an opportunity for extending the range of properties from which the structure of electrolyte solutions may be inferred. The sharp distinction between protic and dipolar aprotic solvents that originated from their respective influences on the rates of reactions[31] has particularly emphasized the role played by hydrogen bonding on ion-solvent interactions. Other factors, such as dipole-dipole interactions and dispersion forces that contribute toward solvent structure, must be taken into account as well. Four types of strong solute-solvent interactions were suggested:[32] electrostatic, π-complex forming, hydrogen bonding, and structure promoting. Besides the ion-dipole interaction between solute and solvent H-bonding promotes anion solvation, and π-complex formation favours cation solvation. Thus small anions, which are the strongest hydrogen bond acceptors, show increased solvation due to hydrogen-bond interactions with protic solvents. The large anions show decreased solvation because of unfavourable structural interactions with a highly structured protic solvent like water. In dipolar aprotic solvents the determining factor is interaction due to mutual polarizability of solvent and anion. The larger the ion the larger is its polarizability and the halide ion energies, for instance, will then be in the reverse order to that in hydrogen bonding liquids.

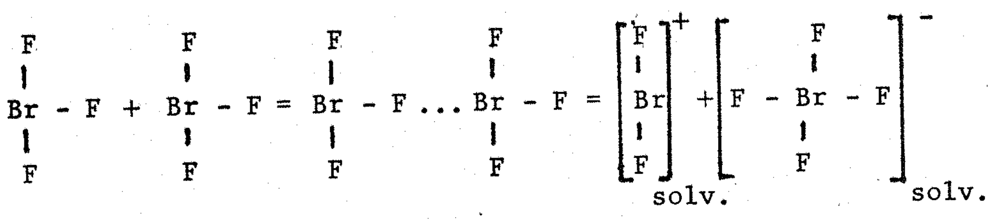
It is suggested that solvents containing atoms with unshared electron pairs such as nitrogen and oxygen, should make relatively good coordinating solvents for the cations, and it has indeed been confirmed that cations are strongly solvated in highly polar solvents with a negative charge localised on an oxygen atom[33]. Cations are sometimes poorly solvated and give rise to low solubilities in acetonitrile and nitromethane because the negative charge of the solvent dipole is not localised on a favourable electron donor atom[34] or is protected by bulky groups[32, 35]. Exceptions are usually explained in terms of very specific ion-solvent interactions, e.g., the solubilities of lithium halide in many solvents[36]. The only attempt to develop a quantitative relation between the solubility of simple salts and the dielectric constant of the solvent was carried out by Bjerrum[37]. However his formula gave poor results for the solubility calculation[38]. It seems apparent that the dielectric constant is not the main determinant of solubility, but rather ion solvation. The factors which influence electrolyte solubility also determine the degree of dissociation of dissolved salts. Dissociation is brought about by solvent molecules interposing themselves between anion and cation and thereby shielding their electric fields. Thus the higher the dielectric constant of a solvent the greater will tend to be its dissociating power. Ions, however, frequently modify solvent structure in their vicinity causing a change in effective dielectric constant. Therefore the solvent bulk dielectric constant is not an absolute indicator of its dissociating power. Specific ion-solvent interactions may play an equally important part in enabling solvent molecules to squeeze between the ions in an ion-pair and the extent of electrolyte dissociation may therefore give an indication of the degree of this specific solvation.

One view on how dissociation and self-ionization phenomena in non-aqueous solvents should be interpreted is that held by V. Gutman[39]. Ionizing solvents are inherently polar in character and when they dissolve chemical compounds ions are formed in solution. The ionizing properties of a solvent determine the extent of ionization. Unfortunately the terms ionizing properties and ionization have not been defined and it is this lack of definition that has been responsible for the lack of a classification of solvents for ionization phenomena in solution. The electrostatic theory explains ionization in solution so long as ions are introduced into the liquid medium, for example by dissolving an ionic crystal in a solvent. But it cannot account for the formation of ions from a substrate that does not contain ions, such as a covalent compound. Solvents may be classified as electron donors or electron acceptors. A donor solvent is characterised by its ability to donate electrons either by making an electron pair available to form a co-ordinate bond or by acting as a reducing agent. Different criteria for the donor properties must be used for these two distinct modes of making electrons available: donicity for the electron-pair donor (E.P.D.) in co-ordination reactions, and ionization potential for reducing agents have been considered.

There are borderline cases of solvent - solute interactions, where both of these quantities should be taken into account. In the same way, acceptor solvents can be divided into electron-pair acceptors (E.P.A.) and oxidising agents. The latter are characterised by electron affinity, but there is no characteristic property for Lewis acid strength.

Pure water and related solvents are subject to a certain amount of self-ionization - the solvent molecules may act either as E.P.D. or E.P.A. molecules. If one water molecule co-ordinates to the hydrogen atom of a similar molecule, the co-ordinate bond formed causes a change in electron density along the O - H bond of the second water molecule. This may lead to heterolytic fission of the O - H bond. The degree of self-ionization of a solvent is enhanced by increasing hydrogen bonding abilities of the solvent molecules - for example, liquid HF is more extensively self-ionized than water. Self-ionization is unlikely to be appreciable in a solvent in which the molecules are exhibiting almost wholly an E.P.D. or E.P.A. function.

Ionization does not depend on the co-ordinating and dielectic properties of the solvent molecules alone; it also depends on the properties of the bonds to be ionized. It will be favoured by a decrease in the energy of this bond and by an increase in its polarizability. Numerous solvents are thought to undergo self-ionization in the pure liquid states provided that solvent molecules act both as E.P.A.'s and E.P.D.'s. In liquid bromine trifluoride, fluoride bridges appear to be responsible for the association of solvent molecules and autoionization may occur:



$$\underset{\mathrm{F}}{\overset{\mathrm{F}}{\mathrm{Br}}}-\mathrm{F} + \underset{\mathrm{F}}{\overset{\mathrm{F}}{\mathrm{Br}}}-\mathrm{F} = \underset{\mathrm{F}}{\overset{\mathrm{F}}{\mathrm{Br}}}-\mathrm{F}\ldots\underset{\mathrm{F}}{\overset{\mathrm{F}}{\mathrm{Br}}}-\mathrm{F} = \left[\underset{\mathrm{F}}{\overset{\mathrm{F}}{\mathrm{Br}}}\right]^{+}_{\text{solv.}} + \left[\mathrm{F}-\underset{\mathrm{F}}{\overset{\mathrm{F}}{\mathrm{Br}}}-\mathrm{F}\right]^{-}_{\text{solv.}}$$

Similar autoionization equilibria appear to be present in liquid iodine, iodine bromide and iodine chloride.

The formation of ions from a non-ionic substrate in solution is essentially a chemical phenomenon and the dielectric constant of the solvent only affects the separation of the ions.

In E.P.D. solvents, ionization depends on the stabilization of the cation by co-ordination and, in some solvents, by solvation of the anions as well. In E.P.A. solvents the anion is stabilized by co-ordination and, again, solvation of the cation may occur, although to a lesser extent.

CHAPTER 2

2.1 PREVIOUS STUDIES IN FUSED SALTS

Negative temperature coefficients of electrical conductivity in molten HgI_2, $InCl_3$, and $InBr_3$ have been known for some time. This unusual behaviour was considered as peculiar to these three fused salts.[40] During the last few years maxima and subsequent negative temperature coefficients have been found in a number of molten salts. Riebling and Erickson[41] found that GaI_3 exhibited a broad conduction maximum. Grantham and Yosim[42] found maxima in the conductivity-temperature curves for the bismuth halide compounds, $BiCl_3$, $BiBr_3$, and BiI_3. They concluded that such apparently anomalous behaviour might not be unusual and proceeded to measure conductivities of halides to temperatures considerably higher than previously[1]. The electrical conductivities of molten CuCl, $HgCl_2$, $HgBr_2$, $CuCl_2$, InI_3, ZnI_2, $ZnCl_2$, TlCl, TlBr, TlI, and HgI_2 were measured to temperatures as high as 1200°C. Maxima in conductivity as the temperature was increased were found in the first six salts. In addition Grantham[43] measured the conductivities of $CdCl_2$, $CdBr_2$ and CdI_2, and a maximum was found for the chloride. Grantham and Yosim[1] concluded that for fused salts negative temperature coefficients of conductivity are not anomalies but probably common to all molten salts at high enough temperature and sufficiently reduced density. These maxima in fused salts were attributed to increasing covalency or ionic association as the density decreased. Since both temperature and density were simultaneously varied it was realised that constant volume conductivity measurements or isothermal measurements, in which only the density varied, were needed.

Johnson and Cubicciotti[44] reported the coexistence curve of $BiCl_3$ to the critical temperature. They found that the observed critical properties compared very well with those predicted for a normal molecular fluid and thus concluded that $BiCl_3$ is a molecular fluid near the critical temperature. They suggested that the molar electrical conductivity at the critical temperature should be near zero.

Grantham and Yosim[45] studied the electrical conductivity of the liquid and the saturated vapour of $BiCl_3$ and $HgCl_2$ to their critical temperatures, these compounds being chosen because of the widely different electrical conductivities near their melting points. $BiCl_3$ has a conductivity, the magnitude of which is associated with ionic fluids rather than molecular fluids whilst it has been well established that $HgCl_2$ is a molecular fluid which is slightly ionized. Calculation of the 'activation energy' for conduction at the melting point also suggests that near the melting point $BiCl_3$ may be an ionic fluid. The relatively low conductivity found by Grantham and Yosim near the critical temperature was consistent with Johnson and Cubicciotti's conclusion that $BiCl_3$ is essentially a molecular fluid in the vicinity of the critical temperature.

The effect of pressure on the electrical conductivity was first studied by Fray and Tomlinson[46]. They attempted to measure the pressure coefficient of conductivity for molten $NaNO_3$ and KNO_3 using an internally heated, externally cooled pressure vessel. They found that the nature of the pressurizing gas had little effect on the results, which suggests that there was negligible gas dissolution. Their cell was open to the pressurizing gas, but diffusion of dissolved gas into the capilliary part of the conductivity cell must have been slow. At high pressures their plots of log κ versus pressure tended to curve upwards, probably due to the effect of gas convection on the temperature gradients in their pressure vessel. In spite of this, their results at lower pressures are very similar to those of Barton, Cleaver and Hills[2]. They measured the effect of pressure on the electrical conductivity of molten alkali nitrates in an externally heated pressure vessel up to 1 kbar, and were able to demonstrate that no dissolved gas was present in their samples. It was shown in this work that log κ is linear in pressure up to 1 kbar. The activation volumes (ΔV_{κ} , ΔV_{Λ}) increase with increasing cation radius, $(E_p)_{\Lambda}$ remains fairly constant while $(E_V)_{\Lambda}$ decreases with increasing cation radius. The values of $-RT(\partial \ln \kappa / \partial P)_T$ obtained for $LiNO_3$, $NaNO_3$, KNO_3, $RbNO_3$ and $CsNO_3$ were respectively -0.8, 2.6, 5.7, 6.5 ml $mole^{-1}$ (all at 400°C) and 6.9 ml $mole^{-1}$ (at 450°C). In all cases a slight temperature dependence for ΔV_{κ} of about -0.005 ml $mole^{-1}$ $^{o}C^{-1}$ was observed.

The results for $LiNO_3$ and $NaNO_3$ have been verified by Schlichthärle, Tödheide, and Franck[47] who studied the electrical conductivity of these salts between 320°C and 475°C up to 12 kbar. Even at these high pressures log κ is a linear function of pressure. The value for the activation volume for $NaNO_3$ at 380°C was 2.5 ml $mole^{-1}$. A temperature dependence of the activation volume was found to be -0.002. ml $mole^{-1}$ $^{o}C^{-1}$. From PVT data, isochoric activation energies were calculated from measured isobaric activation energies. Their experiments were conducted in a piston-cylinder type apparatus.

Darnell, McCollum, and Yosim[48] measured the electrical conductivities of molten $BiCl_3$, $BiBr_3$ and BiI_3 at temperatures up to 886°C at a pressure of 5.4 kbars. At this elevated pressure the conductivity κ varies exponentially with $^{1}/_{T}$. This is in contrast to the behaviour of these molten salts at low pressures ($P < 0.1$ kbar) where Grantham and Yosim found a maximum in κ v T curves. They also measured the isothermal electrical conductivity of the bismuth halides at pressures from 3 to 14 kbars. At temperatures above the temperature of maximum conductivity at ordinary pressures, κ increases with increasing pressure. It was concluded that pressure inhibited the association of these salts at high temperature. This effect is predominant over the decreased conductivity expected from the lower ionic mobility in liquids at these elevated pressures. Their conductivity measurements were carried out in a piston cylinder apparatus.

Darnell and McCollum[49] also measured the electrical conductivity of molten $HgCl_2$ and HgI_2 to 805°C and 620°C respectively at a pressure of 5.4 kbar. The electrical conductivity of the $HgCl_2$ was also measured from 557°C to 634°C at a pressure of 20.5 kbar. At these elevated pressures the maximum in the κ v temperature curve for $HgCl_2$ found at ordinary pressures is removed and κ varies exponentially with $^1/_T$. In the case of HgI_2, pressurization to 5.4 kbar changes the sign of the temperature coefficient of conductivity from its negative value at ordinary pressures to a positive value. As with $HgCl_2$, κ varies exponentially with $^1/_T$. The conductivities of molten $HgCl_2$ and HgI_2 were also measured from 3 to 20 kbar at constant temperature. As before a piston-cylinder high pressure apparatus using an internal furance was used.

Cleaver and Smedley[50] measured the conductivities of molten $HgCl_2$, $HgBr_2$ and HgI_2 up to 1 kbar at temperatures between 260°C and 370°C. At 300°C, the activation volume, ΔV_κ , for $HgCl_2$, $HgBr_2$, and HgI_2 was -50 ml mole^{-1}, -65 ml mole^{-1} and -102 ml mole^{-1} respectively. The Born equation was used to estimate the volume changes associated with the ionization $2HgX_2 \rightleftharpoons HgX^+ + HgX_3^-$ (X = halogen), with results in reasonable accord with the experimental values. The isochoric temperature coefficients of conductivity were calculated and found to be positive in accordance with the suggestion of Grantham and Yosim that the conductivity at constant density increases with temperature. They also performed d.c. electrolysis experiments which showed that the increase in conductivity with pressure was not caused by the onset of electronic conductivity. An externally heated, argon gas pressurized vessel was used for the conductivity measurements.

Cleaver, Spencer and Smedley[3] also measured the conductivities of the chlorides, bromides and iodides of the five alkali metals, and the bromide and chloride of silver up to 860°C and a pressure of 1 kbar. The volumes ΔV_Λ were calculated to be independent of temperature for each salt. ΔV_Λ was zero for the lithuim halides, and increased as the ions were changed in the sequences $Li^+ \rightarrow Cs^+$ or $Cl^- \rightarrow I^-$. The equivalent conductivity decreases with pressure to an extent which depends on the sizes of the ions present. The pressure coefficient is very small if one ion is much smaller that the other, but relatively large if the ions are of comparable size. The ΔV_{Λ} values were used to find the temperature dependence of conductivity at constant density from that at constant pressure. Conductivity increases less steeply with temperature at constant volume than at constant pressure; the difference between the two coefficients being small for lithium salts but relatively large for potassium, rubidium and cesium salts.

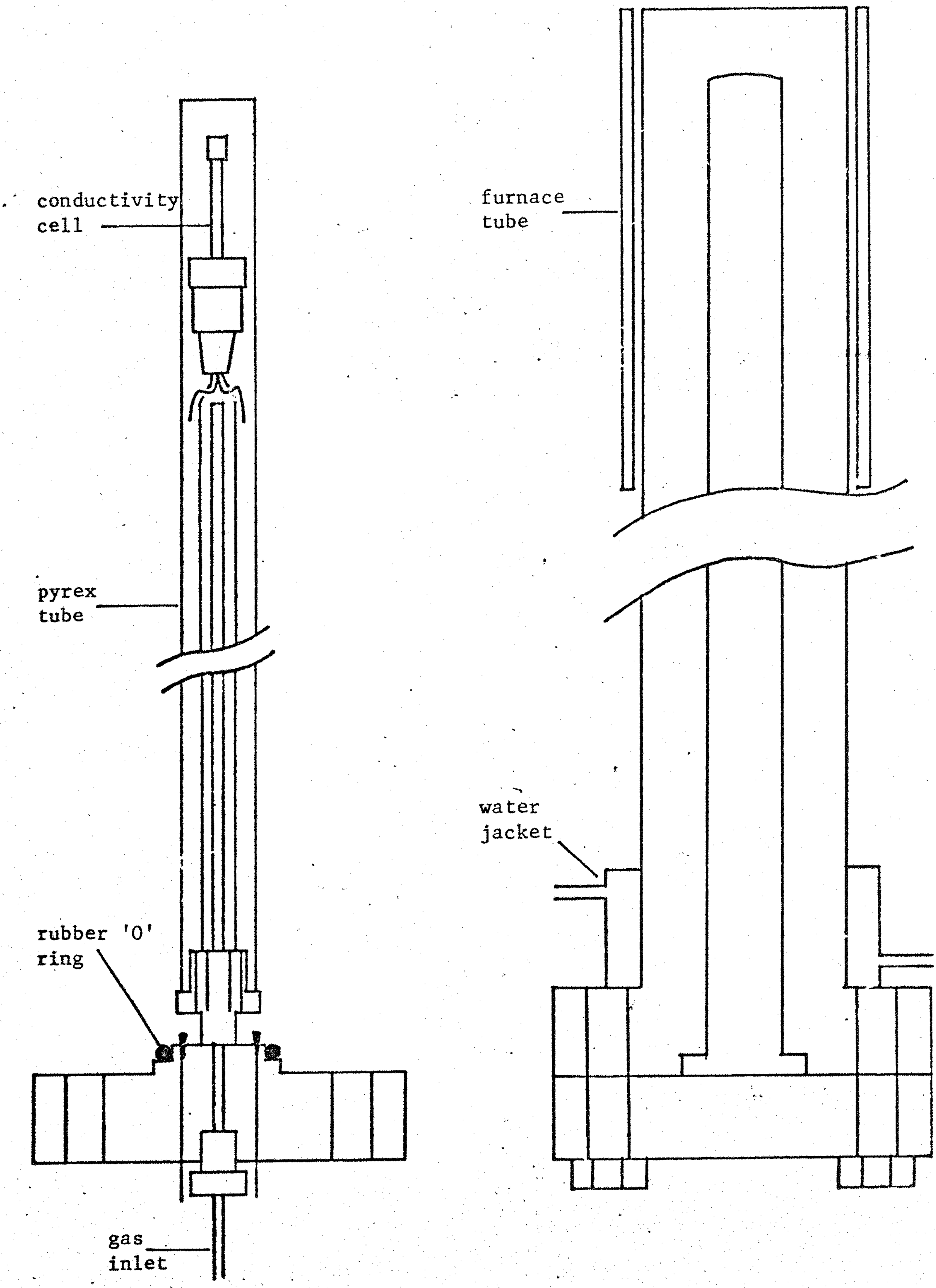
Bannard and Treiber[51] have measured the temperature dependence of the conductivity of HgI_2 to over 800°C at pressures up to 3.75 kbar using an internally heated gas pressurized pressure vessel. The temperature derivative of conductivity was found to change sign above pressures of 2.5 kbar, i.e to assume a positive value. This result lends support to the suggestion that all liquids would go through a conductivity maximum with temperature at the appropriate density. They also suggest that complete ionization of the salt could be brought about at a pressure of 5 - 6 kbar, which is the pressure estimated for complete ionization by Cleaver and Smedley.

CHAPTER 3

3.1 HIGH PRESSURE APPARATUS

The pressure vessel (fig. 3.1.1) was made from Nimonic 105 (H. Wiggin and Co., Hereford, England). It was of 2.5 cm i.d., 7.5 cm o.d., and 75 cm long and was mounted vertically. The upper end was heated by an external furnace. The furnace windingswere in three sections, the centre one being shunted by a rheostat. The top winding was disconnected and the rheostat adjusted to give an isothermal zone over the length of the cell, approximately 8 cm. The temperature gradient was reduced to 0.25°C or less. The temperature profile in this range did not change when the pressure was raised from atmospheric to 1000 bar. At the lower end, the vessel was cooled by a water jacket, below which was a flange closure and rubber O-ring seal. The lower flange carried a port for admission of argon, and six electrical terminals insulated by conical Nylon sleeves. Two of these terminals were of mild steel and were used to make connections to the conduction cell; the remaining four were of chromel and alumel, two of each, and were connected internally and externally to wires of these metals. The internal wires were insulated with glass-fibre sleeving. If two thermocouples were used, one junction was placed at the top of the cell and the other at the bottom. If only one were used then the junction was placed as near as possible to the electrodes. The temperature was constant to within ± 0.25°C for all measurements in a given pressure cycle. A pressure of 1 kbar changes the e.m.f. of a chromel-alumel couple by an amount corresponding to about 0.1°C, which is too small to warrant application of a correction[52]. Pressures were measured to ± 5 bar with a Bourdon gauge (Budenberg Gauge Co., Ltd.). Argon (99.9%) was taken directly from cylinders and compressed to the working pressure by a diaphragm compressor (Pressure Products Ltd., model 3033).

Figure 3.1.1 Pressure vessel with cell in position



3.2 MATERIALS

Iodine (B.D.H. 99.5%) was refluxed for several hours in water to remove inorganic impurities, extracted with benzene and recrystallised from benzene and sublimed once under vacuum at 50°C. Published values[53-56] for the conductivity of pure liquid iodine range from 0.6 to 6.0 x 10^{-5} ohm^{-1} cm^{-1} at 140°C. The most recent value obtained was that by Bearcroft and Nachtrieb[56] (1.21 x 10^{-5} $ohm^{-1} cm^{-1}$ at 140°C). Values obtained for the conductivity in this work (1.01 x 10^{-5} ohm^{-1} cm^{-1} at 144°C) agree fairly well with those of other workers and thus confirm the purity of our sample.

To obtain a pure sample of iodine bromide proved to be a major problem. Iodine bromide (B.D.H.) was placed in an all glass apparatus which consisted of three tubes joined together, such that the compound could be sublimed from one tube to another under vacuum. Sublimation was carried out twice and fractional recrystallisation was also performed twice from the melt. The third tube of the apparatus was a conductivity cell so that a check could be made on the purity of the sample. The lowest value obtained for the conductivity of this sample at 45°C was 3 x 10^{-3} $ohm^{-1} cm^{-1}$ which is about 10 times greater than accepted values. Traces of a colourless liquid, probably water, were found in the apparatus and it was then decided to make iodine bromide from the elements. It was prepared in a manner similar to that of Gutman[57]. Br_2(40 gms) was dried overnight with $CaCl_2$ and KBr to remove moisture and chlorine. This method is mentioned in Gmelin[58]. Iodine(42 gms) was placed in an evacuated glass apparatus similar to the one described above and the tube containing the iodine was cooled in CO_2/acetone while the Br_2 was allowed to distill into the tube. The apparatus was then placed in a water bath at 45°C for approximately 20 hours. Most of the contents of this tube were then sublimed into another tube leaving behind a small amount of unreacted iodine. There was a large amount of excess bromine present which was pumped off while the tube was cooled in ice. The product was again sublimed. It was at this point that the receiving tube cracked. It had been cooled in liquid nitrogen during the sublimation and was warming to room temperature. This had happened previously when attempting to purify the B.D.H. sample. It was realised that at this temperature IBr was sticking to the side of the glass tube and was sometimes breaking the tube as it warmed to room temperature. After this CO_2/acetone was used for cooling purposes and no more tubes cracked. The product was placed in another tube with some $CaCl_2$ and this was sublimed twice through a tube containing a glass wool plug to stop $CaCl_2$ from coming over. This product was fractionally recrystallised twice and the measured conductivity was 12×10^{-3} ohm^{-1} cm^{-1} Another sublimation lowered the conductivity to 8×10^{-3} $ohm^{-1}cm^{-1}$ which was still much too high. Since the value was higher than that of the B.D.H. sample it was decided to take a fresh B.D.H. sample and start again. The bottle was opened in a glove box and IBr placed in the usual glass apparatus. After three fractional recrystallisations, a value of 2.3×10^{-3} ohm^{-1} cm^{-1} was obtained for the conductivity. Some $CaCl_2$ was added to the sample which was then sublimed through a tube with a glass wool plug. When subliming iodine bromide, one obtains a bromine rich compound whilst an iodine rich compound is left behind. The excess bromine tends to dissolve the iodine bromide. By cooling the iodine bromide in ice it is possible to pump away the excess bromine. At 45°C a value of 3.77×10^{-4} $ohm^{-1}cm^{-1}$ was obtained for the conductivity of IBr. This is lower than the value of Fialkov and Goldman[59] (6.4×10^{-4} ohm^{-1} cm^{-1} at 45°C) but in good agreement with the values of Gutman[57] ($3.96 - 4.20 \times 10^{-4}$ ohm^{-1} cm^{-1} at 55°C) and Bruner and Bekier[60] (3.078×10^{-4} ohm^{-1} cm^{-1} at 40°C).

Iodine chloride (B.D.H.) proved much easier to purify than iodine bromide. The purification was carried out in a similar manner, i.e. sublimiation under vacuum with $CaCl_2$ present. It was found that iodine chloride would not sublime when using a CO_2/acetone trap.

However liquid nitrogen which is below the melting point of chlorine solved this problem. After two sublimations a conductivity of 6.7 x 10^{-3} $ohm^{-1}cm^{-1}$ at 35°C was obtained. Then after subliming away any liquid present and some of the solid, the conductivity of the remainder was measured. This procedure was performed a second time and the value obtained for the conductivity was 4.79 x 10^{-3} $ohm^{-1}cm^{-1}$ at 35°C which is in reasonable agreement with the values of Cornog and Karges[61] (4.58 x 10^{-3} ohm^{-1} cm^{-1} at 35°C), Fialkov and Shor[62] (4.52 x 10^{-3} ohm^{-1} cm^{-1} at 35°C) and Emeleus and Greenwood[63] (4.61 x 10^{-3} ohm^{-1} cm^{-1} at 45°C)

Purification of bromine trifluoride was carried out in an all quartz apparatus which consisted of three U-tubes which could be isolated from one another and the atmosphere by means of quartz taps. Underneath the centre U-tube there was another tap which was to have been used to drain off the purified liquid. The apparatus was evacuated and about 15 ml of BrF_3 was run into the end trap from the cylinder. Most of this was then distilled from the first trap to the second trap and then to the third trap. Also by pumping on the liquid the more volatile impurities, bromine, hydrogen fluoride, bromine monofluoride, and bromine pentafluoride were removed and the change in colour of the liquid from dark red to light yellow, due to the removal of the least volatile impurity, bromine, afforded a convenient visual indication of progress in the purification procedure. The apparatus was not well designed since much time was spent in removing the air which came in when the apparatus was filled from the cylinder. A better apparatus would have consisted of three bulbs, each with two arms, joined in a similar manner to the U-tubes. This arrangement would have enabled the air present to have been removed easily. The taps were lubricated by KelF grease which reacted with liquid BrF_3 but which seemed unaffected by the vapour. There was thus some contamination at the first tap when the liquid was run in from the cylinder. 'Rotaflow' teflon taps would probably have been better than the grease lubricated taps used even though BrF_3 slowly attacks pyrex glass.

Different groups of workers[64-66] agree on the value of the conductivity at 25°C which is 8.0×10^{-3} ohm^{-1} cm^{-1} and our value (7.79×10^{-3} ohm^{-1} cm^{-1} at 28°C) is in reasonable agreement with this. Quarterman, Hyman, and Katz[65] showed that slight bromine impurity lowered the conductivity of BrF_3. This is possibly the reason for our low value.

3.3. CONDUCTANCE MEASUREMENTS

Conductances were measured with a Wayne-Kerr transformer ratio arm bridge (type B221), using an external oscillator (Advance, type J1) and tuned amplifier null detector (General Radio, type 1232A).

Ideally, we would like to use a closed cell for our measurements for several reasons.

1. To stop the sample from picking up moisture from the atmosphere when being transferred to the pressure vessel, or, when in the pressure vessel from the argon. Cornog and Karges[61] reported that the conductivity of iodine chloride rose by a factor of three when exposed to the atmosphere for 100 minutes.
2. To stop diffusion of dissolved argon gas from the exposed surface of the melt into the region between the electrodes.
3. To protect the walls of the pressure vessel from attack by corrosive vapours.[67]
4. To protect copper conductivity leads inside the pressure vessel from attack.

The first cell tried with iodine was a teflon piston cell with tungsten electrodes (fig. 3.3.1). This cell proved unsuccessful in that it leaked from around the piston and also from around the electrodes. There was also a suspicion that under pressure the cell was deforming and thus that the cell constant was changing.

It was thus decided to revert back to an open glass cell with a glass float (fig. 3.3.2). The insert floated on the molten sample, Conductivity cells used with iodine

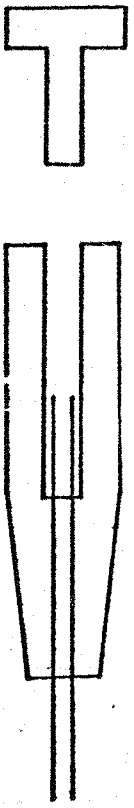


Figure 3.3.1

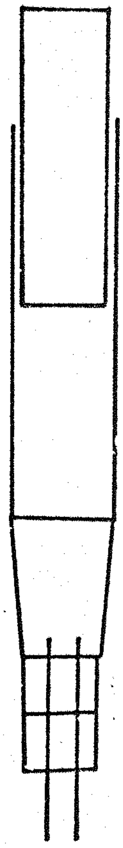


Figure 3.3.2

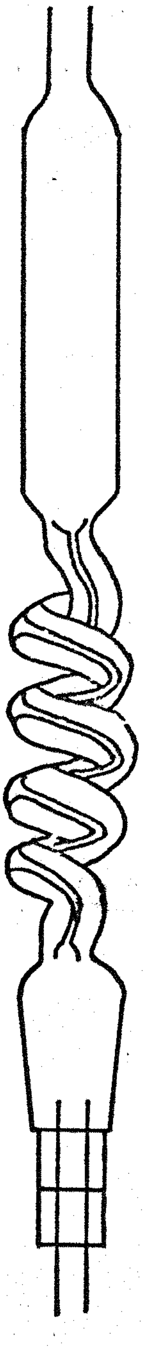


Figure 3.3.3

reducing the exposed surface area. This lowered the rate of evaporation, and also restricted the rate of diffusion of dissolved gas into the region between the electrodes. This cell was used to obtain the results for iodine. In an effort to reduce still further the rate of evaporation and the rate of diffusion of argon, a similar cell with a capilliary opening was tried (fig. 3.3.3). No results were obtained with this cell.

The tungsten electrodes were cleaned with sodium nitrite and the cells were boiled in conc. nitric acid, distilled water, and then oven dried before use. The cell was held in a B14 Quickfit socket on a long glass tube such that it was positioned in the isothermal zone of the pressure vessel. The glass tube was supported on a central stainless steel rod. An inverted glass tube was placed over the cell, with the open end extending downwards into the cold part of the vessel (fig. 3.1.1). This tube partially protected the walls of the pressure vessel from attack by corrosive vapours which condensed on the lower part of the inside wall of this tube.

The cell was filled under vacuum and set up as described above and then the whole unit was pushed up into the pressure vessel which was at the required working temperature. The vessel was sealed, and a suitable time was allowed for the cell and the vessel to reach equilibrium (approx.1 hour). The pressure was raised in stages to 1000 bar, and then reduced, again in stages, to near atmospheric pressure, readings being taken at each pressure. About 20 - 30 minutes was allowed between each reading to allow for temperature equilibration.

Whilst the pyrex cell proved adequate for iodine, it was of no use for the more reactive interhalogens. When attempting to measure the conductivity of IBr in a cell with tungsten electrodes during the purification procedure, it was noted that the reading on the Wayne-Kerr bridge rose quite rapidly with time and that a large capacitance factor appeared indicating an electrode reaction. Replacing the cell with another which had platinum-blacked platinum electrodes temporarily solved this problem. A steady conductivity value was obtained and the capacitance factor disappeared.

For reasons listed earlier a closed cell is required for measurements on the conductivity of the interhalogens. A teflon bag cell was designed by Dr. R.J. Powell (fig. 3.3.4). This consisted of a thin walled (0.007 in.) tube 2in. in length and of diameter 0.285 in. At the lower end was a flange $^{11}/_{16}$ in. in diameter and ⅛ in. thick. The top part of the cell was ½ in. in diameter and ¾ in. in length. For part of this length inside there was a screw thread (⅜ B.S.F.). Beyond this point there was a slight inward taper. A threaded stopper also tapered slightly beyond the threads such that the seal was made on this tapered flat part. There was also a smaller screw thread inside the stopper for half of its length. A soda glass electrode holder, with electrodes of platinum, could be inserted into the teflon tube if the teflon was warmed. The upper and lower surfaces of the soda glass flange were ground flat. The cell was placed between the two pieces of stainless steel (see diagram) which were such that the one piece could be screwed into the other. There was a teflon washer between the surface of the lower piece of metal and the lower surface of the soda glass. This part of the cell was tightened as much as possible but there was always the danger of overtightening and shattering the soda glass. In practice it was found that the cell leaked slightly from around this bottom seal.

Initially the cell was mounted as before in a B24 socket on a glass tube but on heating the socket usually cracked due to the expansion of the steel. Thereafter a glass tube was pushed up inside the stainless steel over the insulated conductivity leads which were brought out through two holes lower down the tube (fig. 3.3.5).

The filling and stoppering of this cell under vacuum presented problems. The glass apparatus shown in fig. 3.3.6 was used for this purpose. The cell was held in the B14 socket and the idea was to melt the IBr and pour it in. This proved difficult since the IBr solidified in the top

Figure 3.3.4 Teflon cell

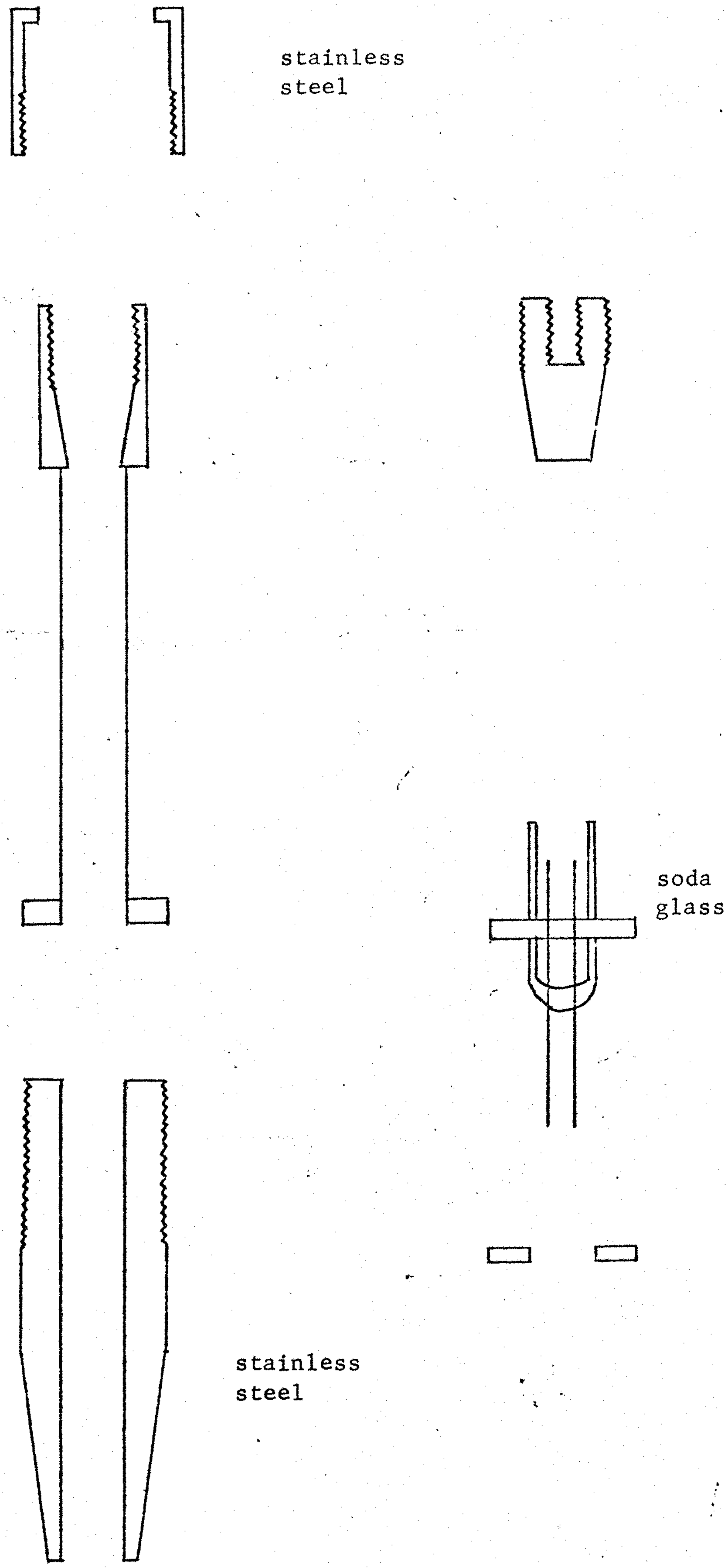


Figure 3.3.5 Cell holder

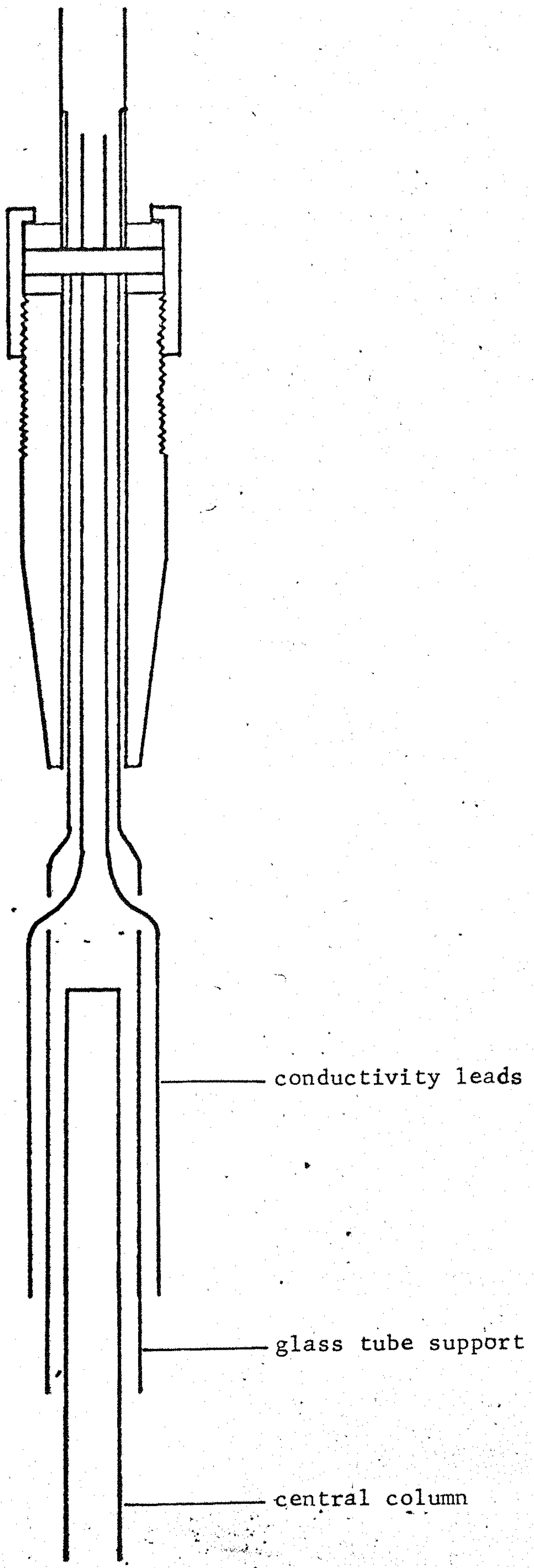
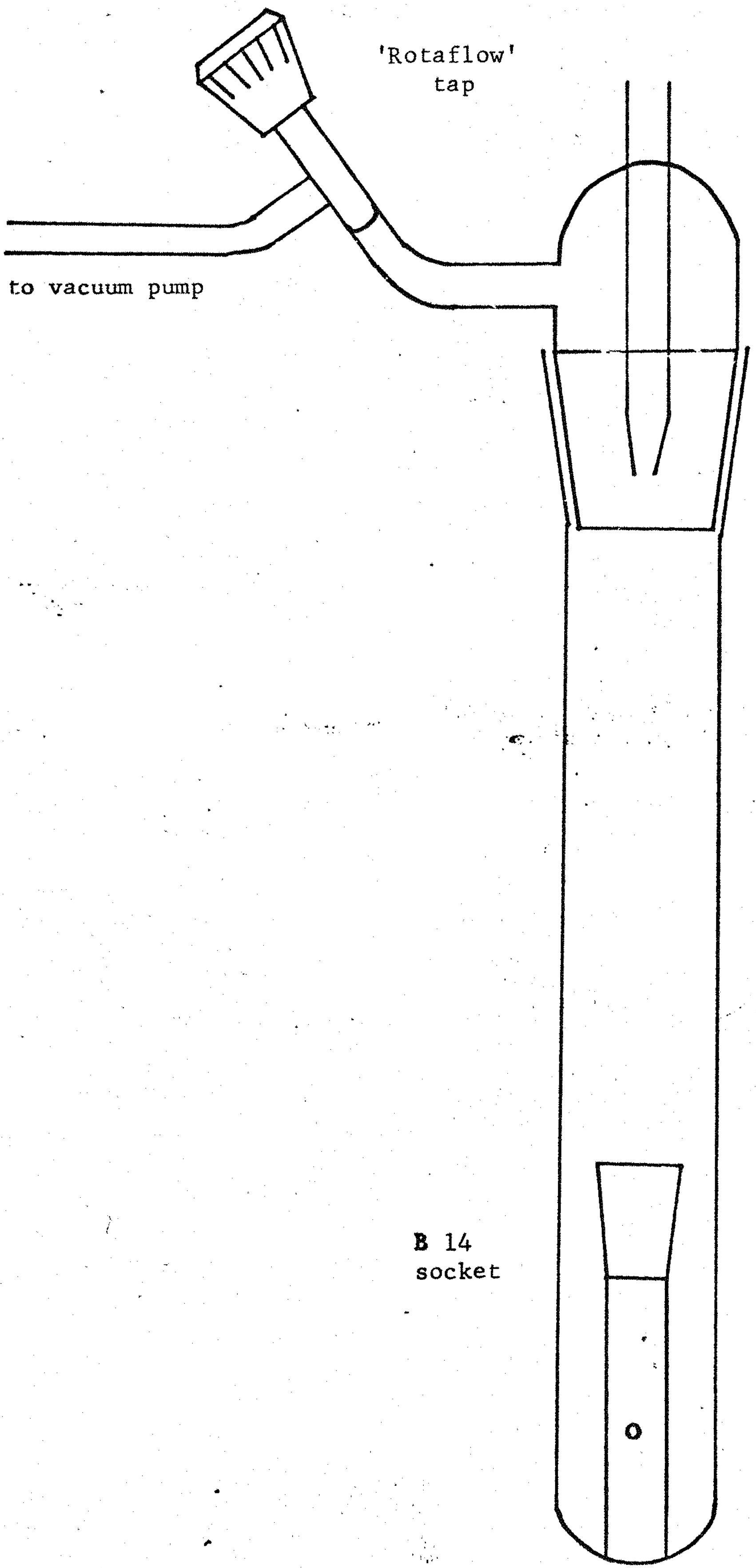


Figure 3.3.6. Apparatus used to fill teflon cell



half of the cell or in the nozzle feeding the cell but not before quite a large amount overflowed into the glass vessel. It also proved difficult to melt the IBr once it had solidified. The glass apparatus was opened in a glove box and the top part replaced with a similar piece except that in place of a tube and feeding nozzle there was a "blue cap" through which was inserted a metal rod onto the end of which was screwed the stopper. Then the apparatus was evacuated and the stopper screwed in. This method was messy and not very satisfactory.

A pressure cycle was attempted with this cell at 70°C but the results were not reproducible; over a period of time the conductivity rose at a fixed pressure and temperature. On removing the cell it was discovered that the electrodes had been stripped of platinum black, so thereafter shiny platinum electrodes were employed with no further trouble. Shiny platinum electrodes were also used with ICl and BrF_3. A new method for filling the cell was also devised. The teflon tap shown in fig. 3.3.7 screwed into the top of the cell. A glass tube with a screw thread on one end was a push fit into the top of this teflon tap when warmed. The cell was now evacuated, and the IBr melted and poured into the cell via the glass tube. If the IBr solidified it could be melted with a hot air blower; thus it was possible to completely fill the cell. When the cell was full, the tap could be closed and excess IBr in the tube could be melted back into the stock supply of IBr. Then by warming the teflon-glass joint the cell could be removed. This method of filling proved to be easy and efficient in that it did away with an enclosing vessel and also prevented spillage of IBr. This cell was used to obtain the results for IBr. These teflon cells were loaded into a cold pressure vessel to prevent the possibility of bursting due to trapped air and were likewise removed from a cold vessel.

In an effort to stop the minor leakage which took place around the base of the cell, shiny platinum electrodes were sealed through a circular alumina disc with a lead zirconate/lead titanate/pyrex 'glass'.[68]

Figure 3.3.7 Teflon tap

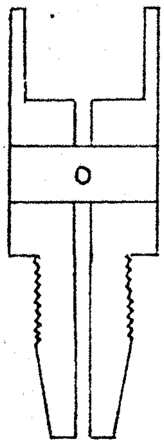
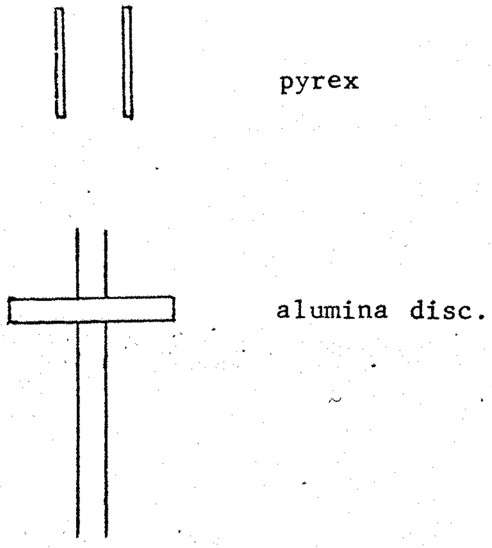


Figure 3.3.8 New electrode arrangement

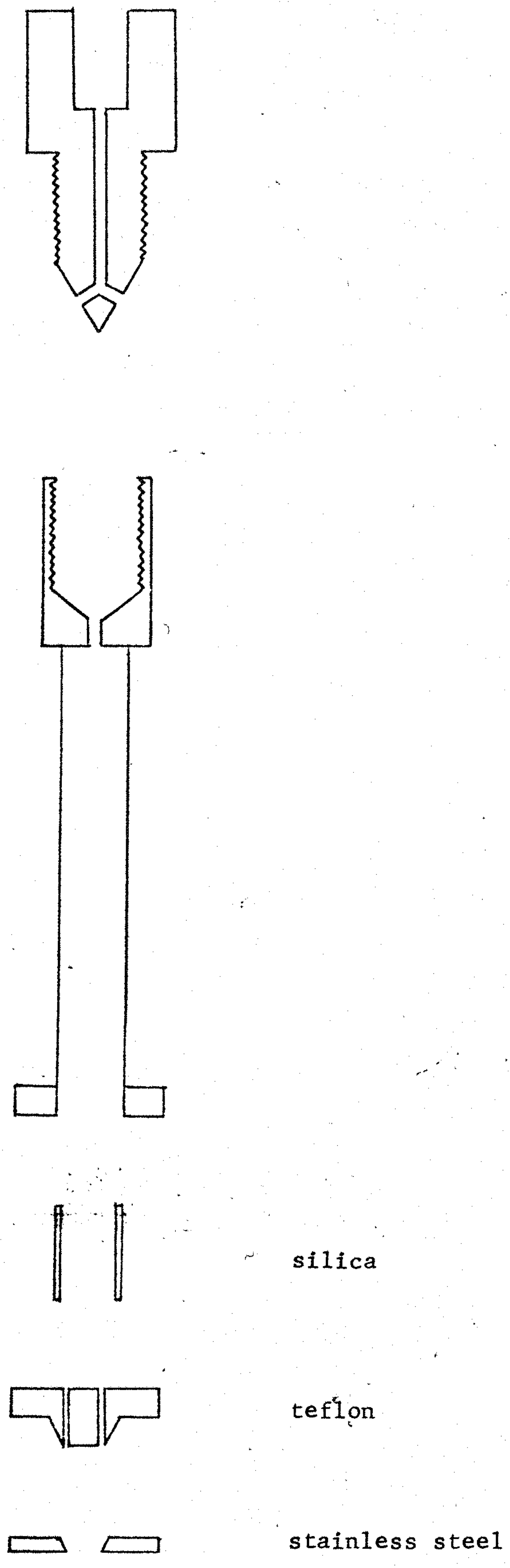


This meant that the metal parts of the cell were able to be tightened rather more than was possible with the soda glass electrode holder. A glass tube about ½in. long was used to prevent the electrodes from being squashed (fig. 3.3.8). This arrangement was used for the work on iodine chloride. It was noticed that the surface of the 'glass' became pitted after prolonged exposure to iodine chloride. Even so this appeared to have no noticeable effect on the conductivity measurements. An unsuccessful attempt was made to seal tungsten electrodes through an alumina disc for use with iodine.

For the measurements on BrF_3, poly-chlorotrifluoroethylene cells with shiny platinum electrodes were used. It seemed likely that BrF_3 would probably react with the 'glass' so the electrodes were pushed through a teflon disc. A stainless steel backing plate then compressed the cone on the teflon disc to effect the seal around the electrodes. The top of the cell was also redesigned such that the seal was made on an edge rather than on a flat surface as before. This new arrangement is shown in fig. 3.3.9. Of course, to fill the cell the plug had to be unscrewed slightly and then it was necessary to wrap teflon tape and to put Kel F grease around the top of the cell so that it would hold a vacuum. The original intention was to run the BrF_3 out of the purification apparatus into the cell through a tap but in view of the effect of BrF_3 on grease this was not possible. Instead the BrF_3 was distilled into the cell. When the cell was full the stopper was screwed in and the excess BrF_3 in the threads and the stopper could be pumped away. As a precaution a teflon O-ring was used to seal the pressure vessel in place of a rubber one, since rubber burns spontaneously when in contact with BrF_3.

It will be seen in the results (fig. 4.1.8) that the conductivity of BrF_3 at 42°C is higher than at 28°C at atmospheric pressure. According to other workers BrF_3 has a negative temperature coefficient and thus the reverse should be true. It was intended to do a pressure run at a higher temperature (approx 55°C) but the cell behaved in an erratic manner with

Figure 3.3.9 Poly-chlorotrifluoroethylene cell



an ever increasing conductivity. On removing the cell from the vessel, the BrF_3 had changed in colour from pale yellow to orange. It would seem that this colour change was due to decomposition of bromine trifluoride and this may account for the higher value of κ at 42°C. However the pressure coefficient obtained at 42°C should be valid since it is the relative change in κ that is important.

All cell constants were determined using 0.01 Demal KCl at 25°C. A frequency dependence was found for the cells with shiny platinum electrodes when determining the cell constant. Measurements were made at differing frequencies from 2,000 Hz to 50,000 Hz and a plot of conductivity against $(\text{frequency})^{-\frac{1}{2}}$ levelled out at about 20 kHz. Thus the 50 kHz value was used to determine the cell constants.

No frequency dependence was found for the conductivity of iodine, iodine bromide, or iodine chloride. However a large frequency dependence was found with bromine trifluoride as can be seen in the results. As above, a plot of conductivity against $(\text{frequency})^{-\frac{1}{2}}$ showed that the 50 kHz value could be used.

CHAPTER 4

4.1. RESULTS

The experimental results are presented in figs. 4.1.1 - 4.1.8 as plots of log κ against pressure for I_2, IBr, ICl and BrF_3 and in fig. 4.1.9 as a plot of κ against temperature for ICl. Individual values of κ, log κ and pressure for each isotherm are listed in appendix A. Also listed are the individual values of κ and temperature for each isobar. Measurements were made over the frequency range 2 to 50 kHz. Between these limits, the conductivity of I_2, IBr and ICl varied by less than 0.1% and the usual extrapolation to infinite frequency was considered to be unnecessary. A frequency dependence was observed for BrF_3; values of κ at various frequencies are listed in Appendix A. The value of the conductivity of BrF_3 at 50 kHz has been used in the plot of log κ against pressure, since plots of conductivity against $(\text{frequency})^{-\frac{1}{2}}$ levelled out at approximately 20 kHz. For all the salts studied log κ is a linear function of pressure, with no suggestion of curvature or hysteresis. This indicates that argon did not penetrate into the conductance path during the experiments and that ΔV_{κ} is not pressure dependent over the range studied.

The results can be expressed in terms of an 'activation volume' ΔV_{κ}, defined by the equation $\Delta V_{\kappa} = -RT(\partial \ln \kappa / \partial P)_T$. This is a convenient manner in which to express the results. ΔV_{κ} has been calculated to 95% confidence limits from a least squares computer program. The values are listed in Table 4.1. For all four compounds studied ΔV_{κ} was always negative and increased numerically with increasing temperature.

The activation energies at constant (atmospheric) pressure $(E_p)_{\kappa}$ given by equation 1.3.5 at various temperatures are shown in Table 4.2. For iodine and iodine bromide $(E_p)_{\kappa}$ was calculated from log κ values obtained by extrapolating the log κ versus pressure graphs to zero pressure. The conductivity data of Greenwood and Emeleus[63] was used to calculate $(E_p)_{\kappa}$

Table 4.1 Activation Volumes $\Delta V_{\ddagger}$ at Various Temperatures

Iodine

$T/^{\circ}C$	$\Delta V_{\ddagger}$ cm^3/mol
144	-24.04
150	-25.55
167	-28.17
177	-31.14

Iodine Bromide

70	-4.37
79	-5.44
89	-5.93

Iodine Chloride

47	-5.57
51	-7.24
54	-9.05
54	-8.65
61	-8.60
65	-10.57
68	-11.02
81	-15.79
96	-20.43

Bromine Trifluoride

28	-8.06
42	-10.28

Table 4.2 Isobaric and Isochoric Activation Energies

$T/^{\circ}C$	$(E_p)_K$ K joule/mol	$(E_v)_K$ K joule/mol
	Iodine	
144	-3.71	10.42
150	-3.71	10.99
167	-3.71	11.41
177	-3.71	12.26
	Iodine Bromide	
70	-3.79 (approx)	
79	-3.79 (approx)	
89	-3.79 (approx)	
	Iodine Chloride	
40	0	1.990
47	-1.328	1.925
65	-5.188	0.921
81	-7.304	1.695
96	-7.304	4.079
	Bromine Trifluoride	
28	-0.924	
42	-1.552	

for iodine chloride and the data of Hyman, Surles, Quarterman and Popov[66] was used to calculate $(E_p)_\kappa$ for bromine trifluoride.

The activation energies at constant volume $(E_V)_\kappa$ have been calculated by equation 1.3.13 for I_2 and ICl at various temperatures and are shown in Table 4.2. Values for the thermal pressure coefficient (γv), where $\gamma v = \alpha / \beta$, for I_2 and ICl have been obtained in this laboratory by P.N. Spencer (not yet published) and these were used in the calculation of $(E_V)_\kappa$.

The conductivity of IBr and ICl was measured at atmospheric pressure whilst that of I_2 and BrF_3 was obtained by extrapolating the log κ versus pressure graphs to zero pressure (these values of κ are given in Section 3.2) This was done to check the purity of the samples.

The temperature dependence for the conductivity of iodine was calculated to be -5.17×10^{-8} $\mathrm{ohm^{-1}\ cm^{-1}\ {}^{o}C^{-1}}$ which compares with -4.25×10^{-8} $\mathrm{ohm^{-1}\ cm^{-1}\ {}^{o}C^{-1}}$ found by Bearcroft and Nachtrieb[56].

4.2 ERRORS

The errors involved in measuring κ arise from five sources:

1. the error in determining the cell constant
2. the error in measuring the resistance of the cell
3. the error in extrapolating these resistances to infinite frequency
4. the error in measuring resistance caused by temperature fluctuations, as κ is temperature dependent.
5. the error in measuring the pressure, as κ is pressure dependent

As far as 1. was concerned, we were not particularly interested in measuring absolute conductances, but relative changes due to pressure, so this source of systematic error is not thought to be important. However for the reason mentioned above, it was useful to know the cell constant. The cell constants were estimated to be accurate to 0.04%

The combined error in measuring resistance and extrapolating to infinite frequency was estimated to be 0.2%.

A temperature fluctuation of 0.5°C (the maximum which is likely to have occurred) would cause the conductance to change by up to 0.1% depending on the value of $(E_p)_\kappa$. Another source of error arises from measuring the pressure. The pressure gauge could be read accurately to 5 atmospheres and the change in conductivity over this range is up to 0.05% . This gauge was tested on a dead weight tester and the results obtained are shown in appendix B. Thus the total error in the conductivity is not more than 0.4%.

Figure 4.1.1 Electrical Conductivity Isotherms for I_2

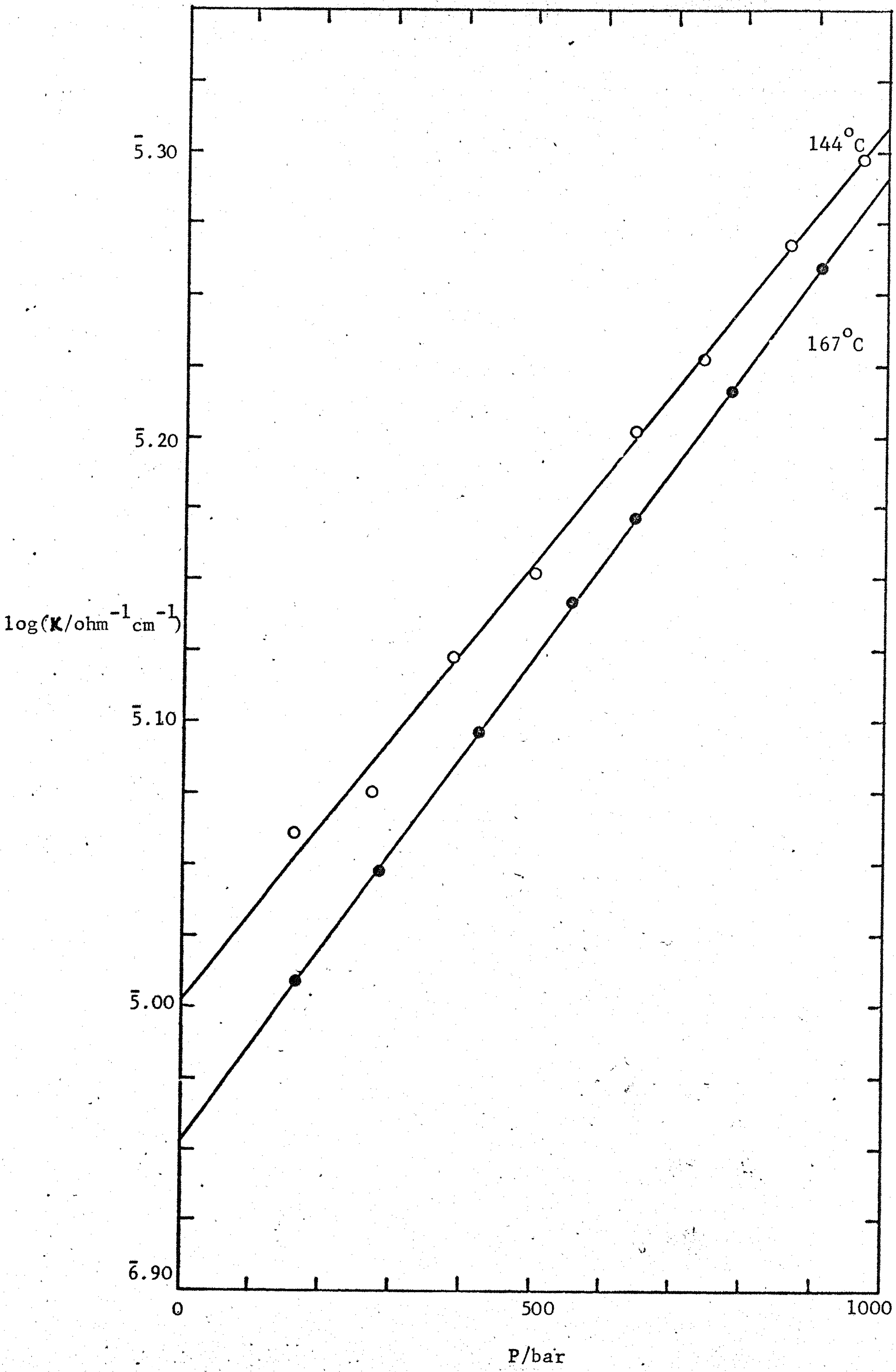


Figure 4.1.2 Electrical Conductivity Isotherms for I_2

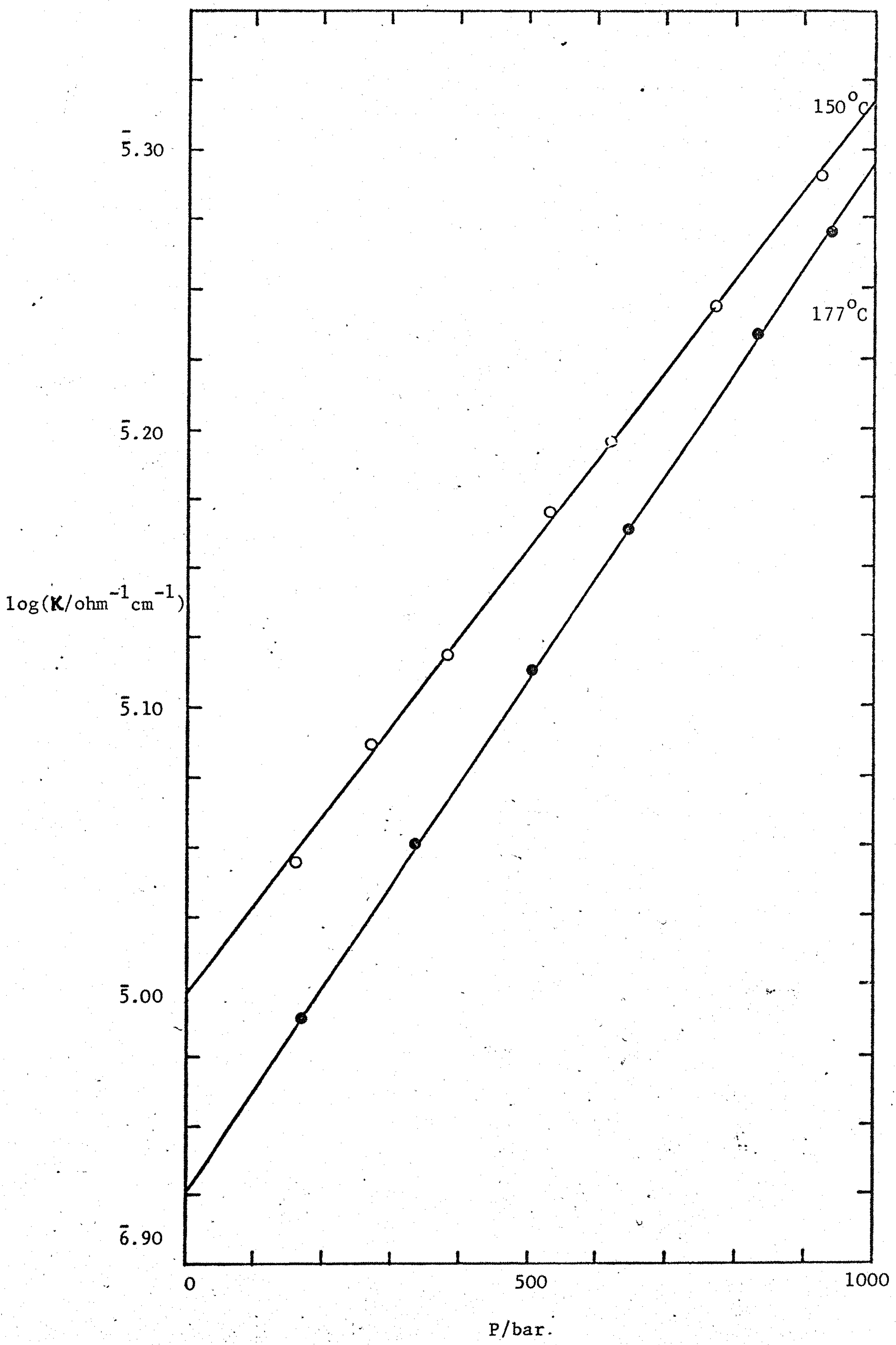


Figure 4.1.3 Electrical Conductivity Isotherms for IBr

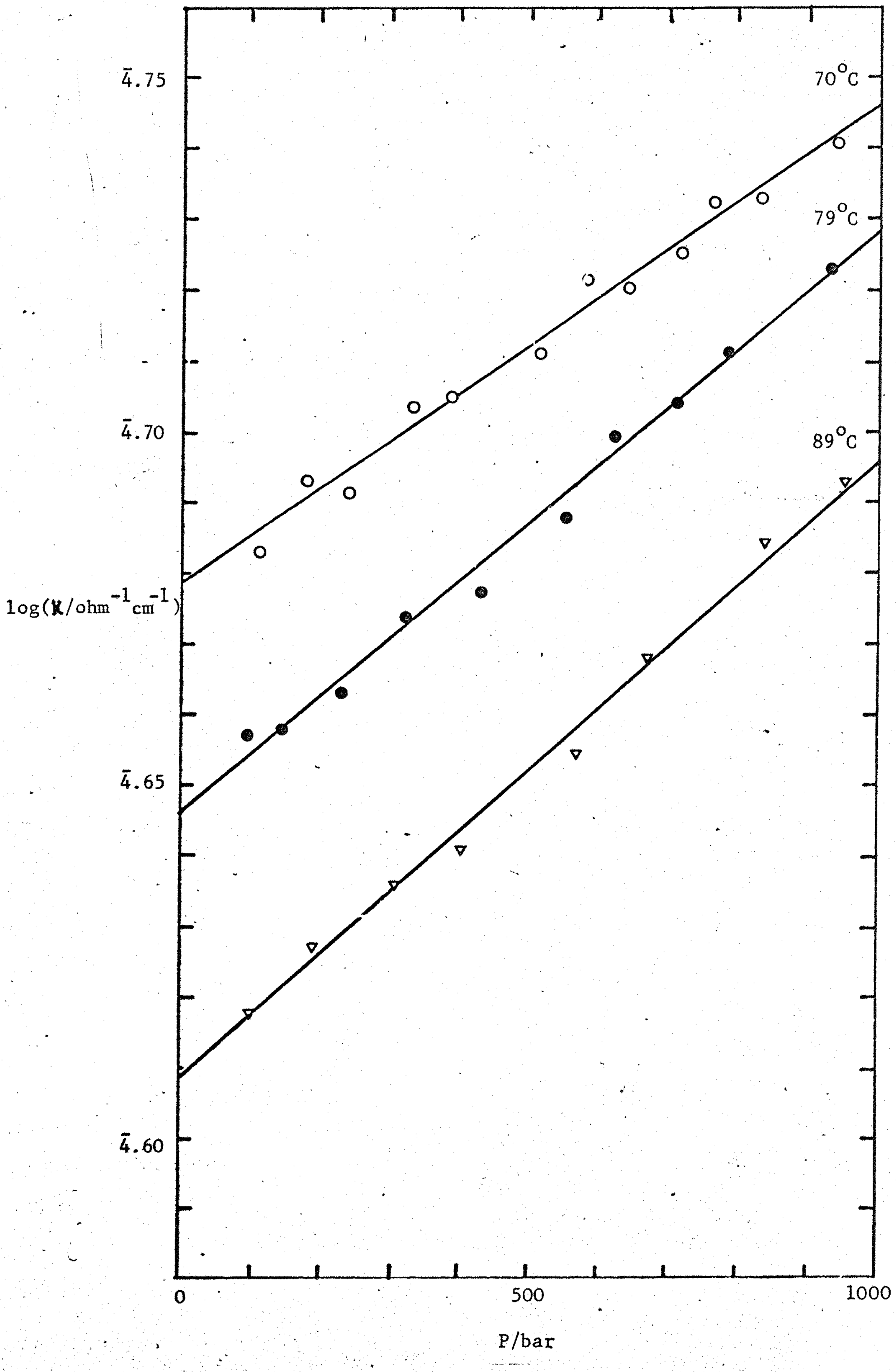


Figure 4.1.4 Electrical Conductivity Isotherms for ICl

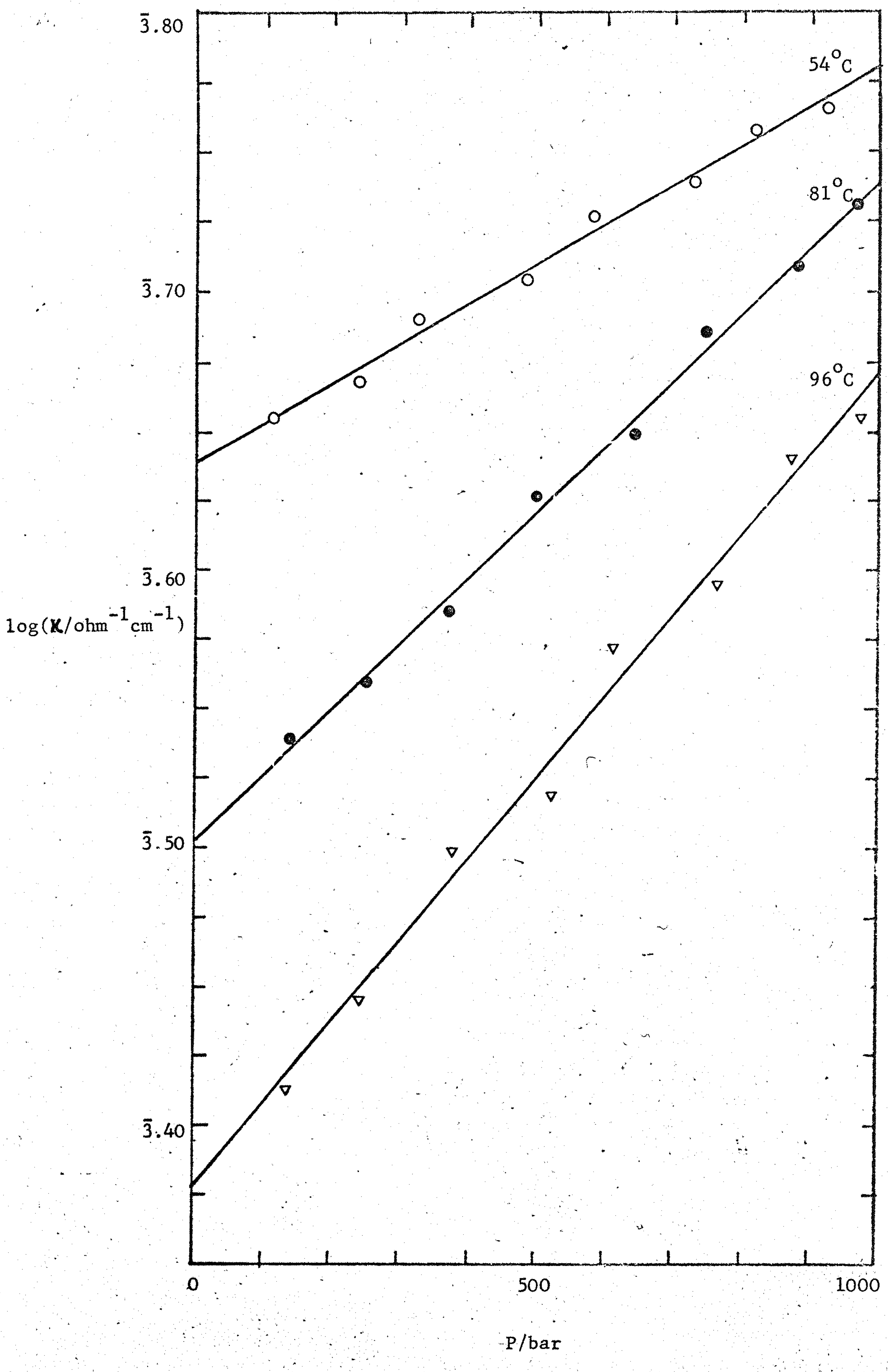


Figure 4.1.5 Electrical Conductivity Isotherms for ICl

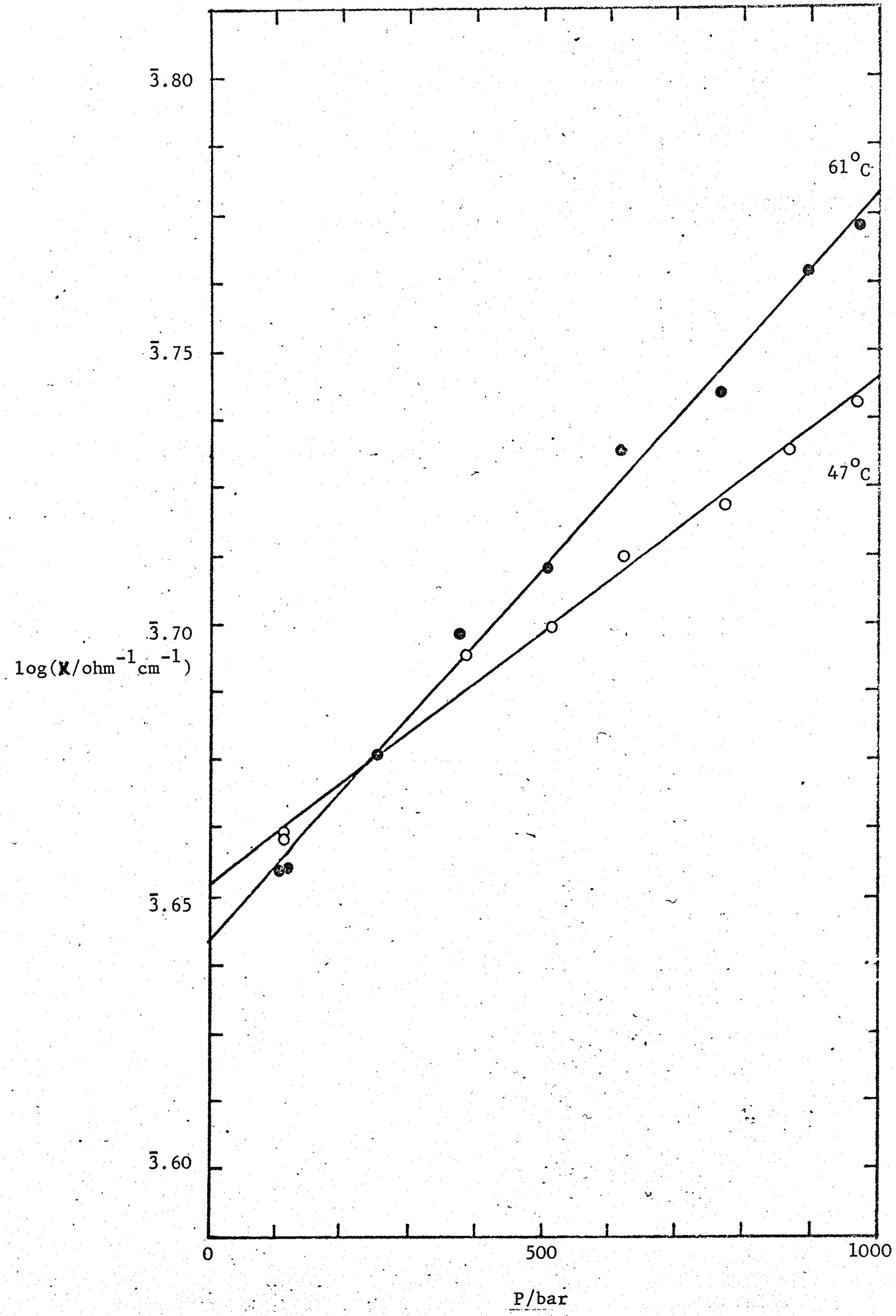


Figure 4.1.6 Electrical Conductivity Isotherms for ICl

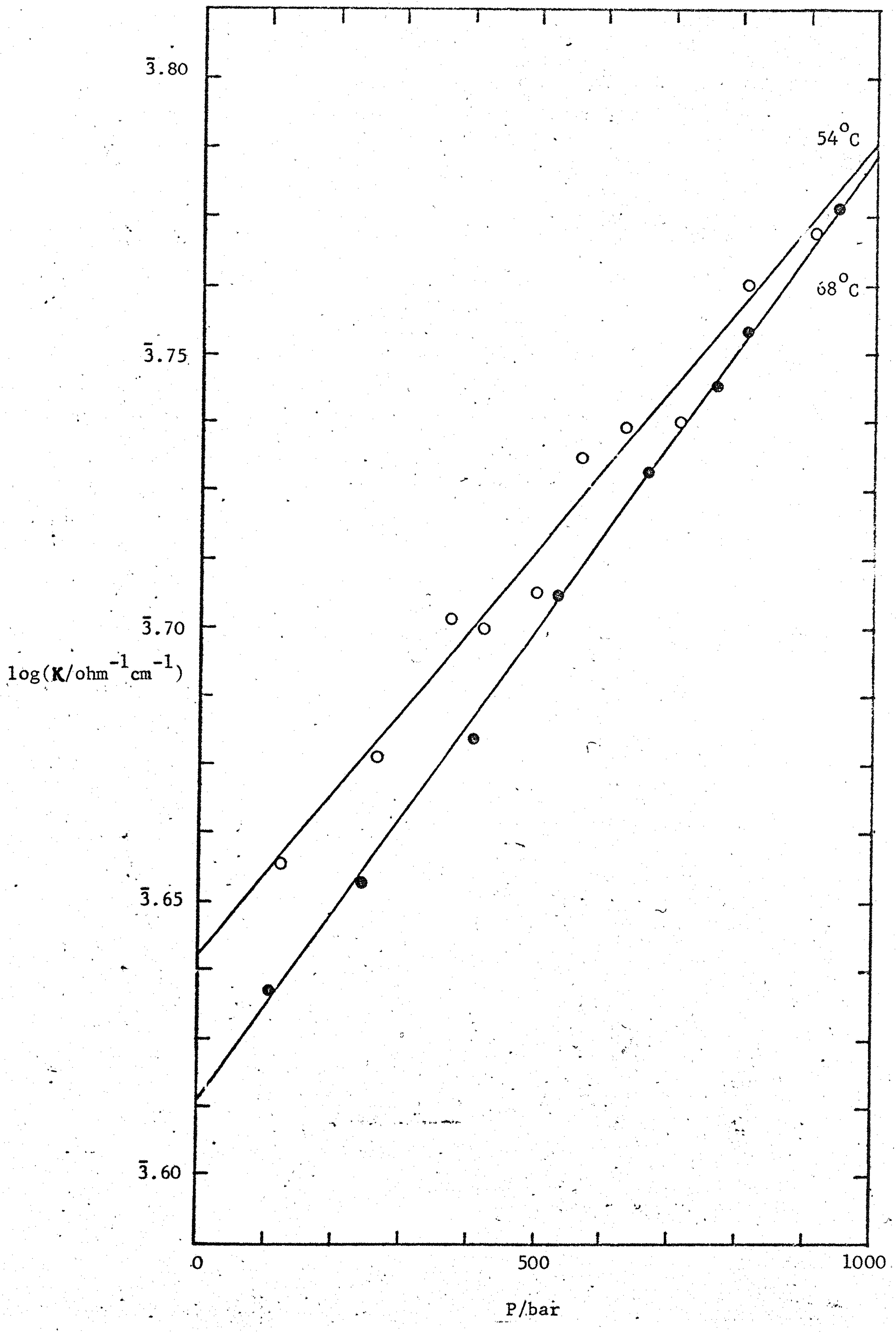


Figure 4.1.7 Electrical Conductivity Isotherms for ICl

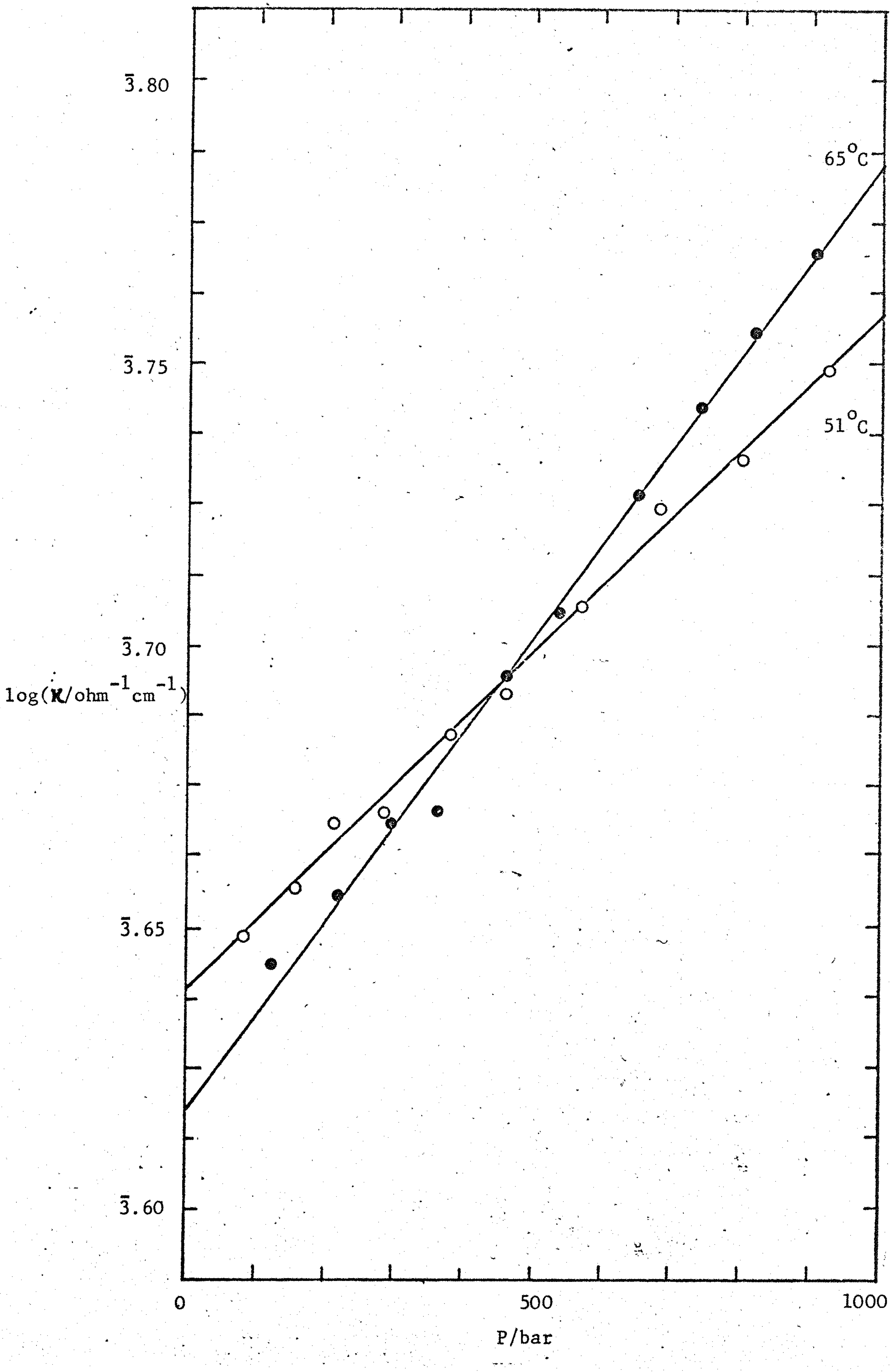


Figure 4.1.8 Electrical Conductivity Isotherms for BrF_3

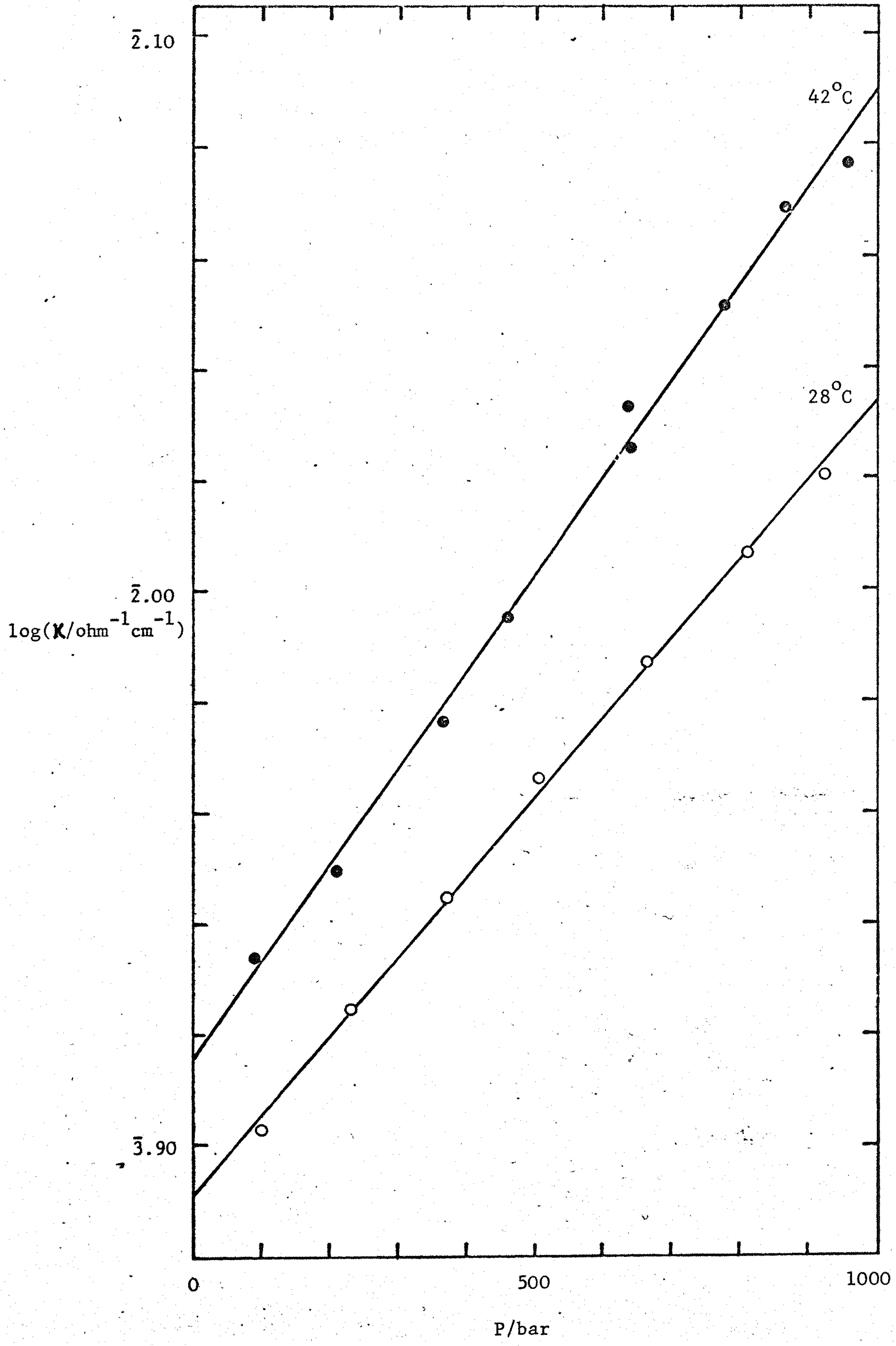
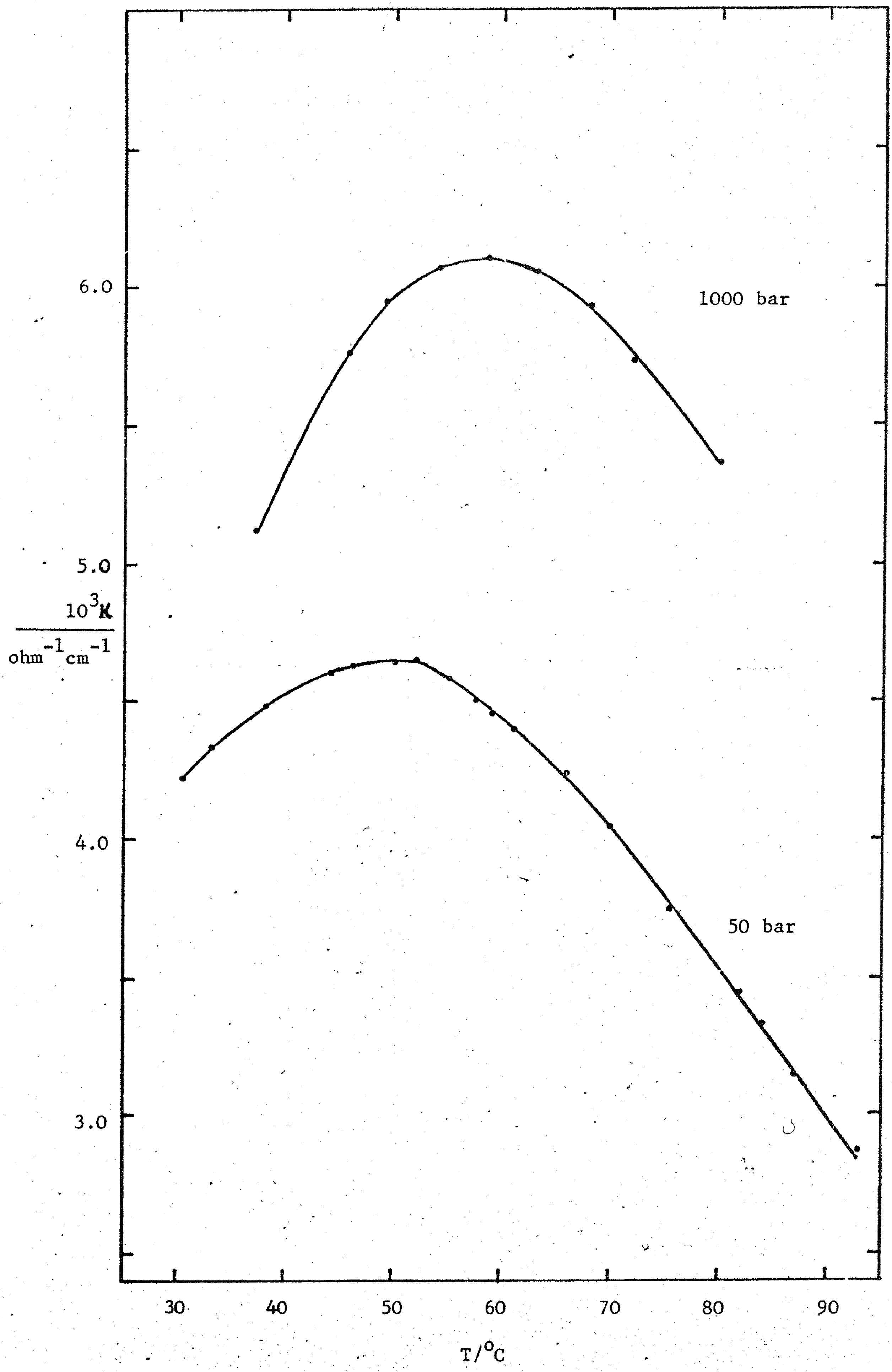


Figure 4.1.9 Electrical Conductivity Isobars for ICl



CHAPTER 5

5.1 TEMPERATURE DEPENDENCE OF CONDUCTIVITY AT CONSTANT DENSITY

To prove the postulate of Grantham and Yosim[1] that under conditions of constant density the conductivity would always increase with increasing temperature it is necessary to show that $(E_v)_\kappa$ is positive. $(E_p)_\kappa$ for ICl[69] and IBr[69] in equilibrium with their vapours is positive just above the melting point but becomes negative as the temperature is raised, whilst $(E_p)_\kappa$ for I_2[56] and BrF_3[69] is always negative. Thus if $(E_p)_\kappa$ is negative or very small ΔV_κ must be negative, since $(E_v)_\kappa = (E_p)_\kappa - (\alpha T/\beta)\, \Delta V_\kappa$.

Table 4.1 shows that ΔV_κ for I_2 is indeed a large negative volume, increasing numerically with increasing temperature, whilst ΔV_κ for IBr, ICl and BrF_3 is a somewhat smaller negative volume which also increases numerically with increasing temperature. The energy term $-(\alpha T/\beta)\, \Delta V_\kappa$ is therefore positive and is sufficiently large to make $(E_v)_\kappa$ positive for I_2 and ICl over the temperature range covered in this work. Table 4.2 shows values of $(E_p)_\kappa$ and $(E_v)_\kappa$ at various temperatures. These results confirm the suggestion made by Grantham and Yosim that the decrease in conductivity with increasing temperature is due essentially to the density change. If the density is held constant, κ increases with temperature in the 'normal' way. We may infer that the observation of a negative value for $(E_p)_\kappa$ for a partly ionized liquid makes it likely that ΔV_κ will be large and negative; for only if this is so can $(E_v)_\kappa$ be positive.

5.2 EFFECT OF PRESSURE ON DEGREE OF IONIZATION

The conductivity of I_2, ICl, IBr and BrF_3 has been attributed [56, 57, 63, 64] to slight self-ionization with the formation of complex ions.

$$2I_2 \rightleftharpoons I^+ + I_3^- \qquad (5.2.1)$$

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

$$2IBr \rightleftharpoons I^+ + IBr_2^-$$

$$2BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$$

The degree of ionization increases with pressure, because the solvation of the ions involves a net reduction in the volume of the system. We now consider whether our results can be accounted for in terms of the displacement of the above equilibria to the right with pressure. Cleaver and Smedley[50] accounted for their results on the effect of pressure on the degree of ionization of the mercuric halides in this way with reasonable success. The effect of pressure on ion mobilities is ignored for the present.Let c denote the concentration, a the activity and $f_\pm$ the mean ion activity coefficient of the ions I^+ and I_3^-. For equilibrium (5.2.1)

$$K = \frac{a_{I^+} \cdot a_{I_3^-}}{a^2_{I_2}}$$

Since the ionic concentrations are relatively small, we ignore changes in the activity of the molecular species and write

$$K' = a_{I^+} \cdot a_{I_3^-} = c^2 f_\pm^2$$

Using standard thermodynamics, the change in standard partial molar volume when ionization (5.2.1) takes place is given by

$$\overline{\Delta V^o} = -RT(\partial \ln K'/\partial P)_T = -2RT(\partial \ln c/\partial P)_T - 2RT(\partial \ln f_\pm/\partial P)_T \qquad (5.2.2)$$

Assuming, as a first approximation, that the ion mobilities are independent of pressure at constant temperature,

$$-2RT(\partial \ln c/\partial P)_T \approx -2RT(\partial \ln \kappa/\partial P)_T = 2\,\Delta V_\kappa \qquad (5.2.3)$$

Comparing equations (5.2.2) and (5.2.3)

$$2\,\Delta V_\kappa = \overline{\Delta V^o} + 2RT(\partial \ln f_\pm/\partial P)_T. \qquad (5.2.4)$$

We would like to estimate the volume terms on the right side of equation (5.2.4), and compare them with $2\Delta V_K$ determined experimentally. $\overline{\Delta V^o}$ may be considered in two parts

$$\overline{\Delta V^o} = \overline{\Delta V_1^o} + \overline{\Delta V_2^o}$$

$\overline{\Delta V_1^o}$ is the volume of the ions I^+ and I_3^- minus the volume of two I_2 molecules, and has been calculated from the appropriate bond lengths and van der Waals radii. As Table 5.1 shows, $\overline{\Delta V_1^o}$ is a relatively small volume in comparison with $\overline{\Delta V_2^o}$. $\overline{\Delta V_2^o}$ is the volume change in the solvent when ionization occurs, the solvent in this case being molecular I_2. $\overline{\Delta V_2^o}$ is negative, and represents the electrostriction of the solvent when solvation sheaths are formed around the ions. The standard partial molar free energy of solvation of a spherical ion of charge Ze and radius r, in a solvent of permittivity ε is given by the Born equation.

$$\overline{\Delta G^o} = -\frac{Ne^2Z^2}{2r}\left(1-\frac{1}{\varepsilon}\right)$$

Differentiating with respect to pressure, we obtain for the standard partial molar volume change on solvation[70]:

$$\overline{\Delta V_2^o} = \left(\frac{\partial \overline{\Delta G^o}}{\partial P}\right)_T = \sum_{\text{ions}}\left(\frac{Ne^2Z^2}{2r^2}\left(1-\frac{1}{\varepsilon}\right)\left(\frac{\partial r}{\partial P}\right)_T - \frac{Ne^2Z^2}{2r\varepsilon^2}\left(\frac{\partial \varepsilon}{\partial P}\right)_T\right) \tag{5.2.5}$$

The terms in the square brackets can be evaluated if ε, r and their pressure derivatives are known. Unfortunately not all of these quantities are available for iodine and the interhalogens and so this calculation is not possible. Since iodine is a non-polar molecule, use can be made of the Clausius-Mosotti function $V_m(\varepsilon - 1)/(\varepsilon + 2)$. $(\partial\varepsilon/\partial P)_T$ can be found by assuming that the Clausius-Mosotti function is invariant with pressure. The resulting expression for $(\partial\varepsilon/\partial P)_T$ is

$$(\partial\varepsilon/\partial P)_T = ((\varepsilon - 1)(\varepsilon + 2)\beta_T)/3 \tag{5.2.6}$$

where β_T is the isothermal compressibility. Cleaver and Smedley checked

Table 5.1 Volume Terms

Species	Molecular Volume (10^{-30} m^3)
I_2	75.34
* I^+	41.63
I_3^-	113.10
* IBr	66 24
* IBr_2^-	90.84
ICl	59.07
ICl_2^-	77.12
BrF_3	45.53
* BrF_2^+	43.32
BrF_4^-	55.59

* estimated volumes

	ΔV_1	ΔV_2	ΔV_o
$2I_2 \rightleftharpoons I^+ + I_3^-$	4.05	-92.0	-88.0
$2IBr \rightleftharpoons I^+ + IBr_2^-$	-0.01	-94.8	-94.8
$2ICl \rightleftharpoons I^+ + ICl_2^-$	0.61	-97.2	-96.6
$2BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$	7.85	-101.4	-93.6

the validity of the approximation and concluded that the accuracy was sufficient having regard to the other approximations inherent in the Born model for solvation. They showed that the contribution to $\overline{\Delta V^{o}}$ from the term containing $(\partial r/\partial P)_T$ is relatively small. They also evaluated the last term in equation (5.2.4), $RT\ (\partial \ln f\pm/\partial P)_T$, by use of the Debye-Hückel expression for the mean ion activity coefficient in a uni-univalent electrolyte solution[71]. The expression for $f\pm$ is:

$$\ln f\pm \quad = \quad - \frac{(4.15 \times 10^{6})\ c^{\frac{1}{2}}}{(\varepsilon\ T)^{3/2}} \qquad (c \text{ in mol/dm}^{3})$$

Differentiating with respect to P,

$$RT\ \left(\frac{\partial \ln f\pm}{\partial P}\right)_T = \frac{(4.15 \times 10^{6})\ c^{\frac{1}{2}}}{2(\varepsilon\ T)^{3/2}} \left(-RT\ \left(\frac{\partial \ln c}{\partial P}\right)_T + \frac{3RT}{\varepsilon}\ \left(\frac{\partial \varepsilon}{\partial P}\right)_T\right)$$

Again assuming that $-RT(\partial \ln c/\partial P)_T \approx \Delta V_K$,

$$RT\ \left(\frac{\partial \ln f\pm}{\partial P}\right)_T \approx \frac{(2.08 \times 10^{6})\ c^{\frac{1}{2}}}{(\varepsilon\ T)^{3/2}} \left(\Delta V_K + \frac{3RT}{\varepsilon}\ \left(\frac{\partial \varepsilon}{\partial P}\right)_T\right) \qquad (5.2.7)$$

Cleaver and Smedley found that this term was insignificant for mercuric chloride and mercuric bromide but was certainly not insignificant for the more highly conducting mercuric iodide. They showed that the biggest contribution to $\overline{\Delta V^{o}}$ arises from the term $(Ne^2Z^2/2r\varepsilon^2)\ (\partial\varepsilon\ /\ \partial\ P)$ of equation (5.2.5). Substituting the expression for $(\partial\varepsilon/\partial P)$ from equation (5.2.6)

$$\overline{\Delta V_2^{o}} \approx - \sum_i (Ne^2Z_i^2\ \beta_T/6r_i)\ (\varepsilon - 1)\ (\varepsilon + 2)/\varepsilon^2 \qquad (5.2.8)$$

The factor $(\varepsilon - 1)\ (\varepsilon + 2)/\varepsilon^2$ is very close to unity for values of ε greater than 5. Fortunately ε for iodine is 11.1 at 118°C and 13.0 at 168°C [72]. If equations (5.2.4) and (5.2.5) are now combined and the terms involving $(\partial r/\partial P)_T$ and $\ln f\pm$ are omitted, the resulting expression for ΔV_K is

$$\Delta V_K \approx - \sum_i \frac{(Ne^2Z^2)\,\beta_T}{12r_i} \qquad (5.2.9)$$

This indicates that the largest pressure coefficients for conductivity in slightly ionized liquids are likely to arise when the ions produced are small and the liquid has high compressibility.

Equation (5.2.9) was used to calculate ΔV_K for I_2, IBr, ICl, and BrF_3. The Born equation refers to spherical ions of radius r. For each ion, the value of r used was that of a sphere having the same volume. The atomic radii used were[73] (in 10^{-10} m): F, 1.35; Cl, 1.80; Br, 1.95; I, 2.15. The bond lengths of I_2, IBr, ICl, and BrF_3 were taken as 2.66, 2.50 (estimated), 2.32, and 1.81 and 1.72[73]. The I - I bond length[73] in I_3^- was taken as 2.90. The I - Br bond length[73] in IBr_2^- was taken as 2.50. The I - Cl bond length[73] in ICl_2^- was taken as 2.36. The Br - F bond length[73] in BrF_4^- was taken as 1.88. This value was also used for the Br - F bond length in BrF_2^+ as no data was available. The compressibility of I_2[74] was taken as 50×10^{-6} bar^{-1} which is its approximate value at 140°C. The same value was also used for the compressibility of IBr since this value is approximately that of bromine[75] at room temperature. The compressibility of ICl[74] at 50°C is approximately 50×10^{-6} bar^{-1}. No compressibility data are available for BrF_3. The iodine value was used. For all four compounds, ΔV_K calculated by equation (5.2.9) is approximately -45 ml/mol (see Table 5.1) i.e. somewhat larger than the experimental values. In Table 5.1 ΔV_K calculated by equation 5.2.9 has been multiplied by two and listed as ΔV_2 (see equation 5.2.8).

ΔV_1 and ΔV_2 have also been calculated (Table 5.2) assuming different self-ionizations, in an effort to determine the effect of ion size on these quantities. Larger ions gave rise to numerically smaller values of ΔV_2. However this is partially offset by the smaller values of ΔV_1. Nevertheless ion size does make some difference to the value of ΔV^o.

Table 5.2. Volume Terms

Species	Molecular Volume (10^{-30} m^3)
ICl	59.07
* I^+	41.63
Cl^-	24.84
ICl_2^-	77.12
* I_2Cl^+	94.01
I_2	75.34
I^-	45.83
I_3^-	113.10

* estimated volumes

	ΔV_1	ΔV_2	ΔV_o
$ICl \rightleftharpoons I^+ + Cl^-$	7.40	-115.6	-108.2
$2ICl \rightleftharpoons I^+ + ICl_2^-$	0.61	-97.2	-96.6
$3ICl \rightleftharpoons I_2Cl^+ + ICl_2^-$	-6.06	-84.4	-90.5
$I_2 \rightleftharpoons I^+ + I^-$	12.12	-105.4	-93.3
$2I_2 \rightleftharpoons I^+ + I_3^-$	4.05	- 92.0	-88.0
$3I_2 \rightleftharpoons I_3^+ + I_3^-$	0.18	- 76.8	-76.6

Ion pair formation has been considered a possible reason for the experimental values of ΔV_K being less than the calculated values. It was supposed that the solvation of ion pairs would lead to a smaller reduction in the volume of the system than would the solvation of individual ions. The concentration of ions necessary for ion-pair formation has been calculated from Bjerrum's equation for the critical distance, q, for ion-pair formation where $q = |Z_1Z_2| e^2/8\pi\varepsilon_o\varepsilon_r kT$. For all four compounds ε_r has been taken as 12. This is the approximate value of ε_r for iodine at 140°C. We have assumed that the ions are arranged in a lattice and are distance q apart. The concentrations c_B, equal to $1/2q^3N$, are shown below.

BrF_3	c_B	$= 6.71 \times 10^{-5}$ moles/cm^3
ICl	c_B	$= 9.23 \times 10^{-5}$ moles/cm^3
IBr	c_B	$= 1.09 \times 10^{-4}$ moles/cm^3
I_2	c_B	$= 1.75 \times 10^{-4}$ moles/cm^3

It was thus necessary to calculate c, the actual concentration of ions, and to compare this with C_B to see if ion-pairs were formed. The results of this calculation (see below) show that ion-pair formation should not occur in I_2 or IBr but does occur in ICl and may occur in BrF_3.

Values of c are also necessary to calculate the term $RT(\partial \ln f\pm/\partial P)_T$. Bearcroft and Nachtrieb[56] have done experiments in which they measured the conductivity of solutions of potassium iodide in iodine, iodine chloride in iodine, and iodine bromide in iodine. From the potassium iodide experiments they calculated a value for K_2 where $K_2 = K(I_2) = (I^+)(I^-)$ and K is the dissociation constant for the formal equilibrium $I_2 \rightleftharpoons I^+ + I^-$. I^- is used in this equilibrium for the sake of simplicity. They have assumed that the iodide ion exists as I_3^- or larger anionic aggregates, I_{2n-1}^-, that have high mobility. Their high mobility is then said to be due to a Grotthus - like charge - transport mechanism, in which iodide ions are transferred from the polyiodide species to iodine molecules. With this value of K_2 they then calculated values of K_1 for the dissociation constant of the equilibrium $IX \rightleftharpoons I^+ + X^-$ (X = Br or Cl) where $K_1 = (I^+)(X^-)/(IX)$. This equilibrium refers to IX in a solution of iodine. It is reasonable to expect that K_1 has a similar value in pure IX. From these values of K_2 and K_1 we could calculate c. However, Bearcroft and Nachtrieb assumed that potassium iodide ion-pairs were in equilibrium with dissociated potassium ions and iodide ions. We have recalculated K_2 from their data assuming that there are no potassium iodide ion-pairs present.

The ionic dissociation of iodine is considered to be

$$I_2 \rightleftharpoons I^+ + I^-$$

and K is designated as the dissociation constant. Then for pure iodine

$$\kappa_{I_2} = \kappa^+ + \kappa^- = (I^+)\Lambda_{I^+} + (I^-)\Lambda_{I^-}$$

where the Λ's are the ionic equivalent conductances in units of $\mathrm{ohm}^{-1}\mathrm{cm}^{+2}\mathrm{equiv}^{-1}$ (approximated by their limiting values, Λ_o) and the bracketed quantities refer to quantities in equivalents per cm^3. Since in pure iodine, $(I^+) = (I^-)$ it follows that

$$\kappa_{I_2} = (I^-)(\Lambda_{oI^+} + \Lambda_{oI^-}) = (I^-)\Lambda_{oI_2}$$

It is assumed that all cation equivalent conductances are essentially equal (i.e. $\Lambda_{oK^+} = \Lambda_{oI^+}$). The conductance due to potassium iodide is equal to the sum of the conductances of K^+ and I^-.

$$\kappa_{KI} = \kappa_{K^+} + \kappa_{I^-} = (K^+)_{KI}\Lambda_{oK^+} + (I^-)_{KI}\Lambda_{oI^-} = (I^-)_{KI}\Lambda_{oKI}$$

The subscripts refer to the concentration of ions produced from iodine or potassium iodide. Moreover, on the assumption that $\Lambda_{oK^+} = \Lambda_{oI^+}$, $\Lambda_{oKI} = \Lambda_{oI_2}$. The total conductance of a solution of potassium iodide in iodine is then

$$\kappa = \kappa_{I_2} + \kappa_{KI} = \Lambda_{oI_2}((I^-)_{I_2} + (I^-)_{KI}) = \Lambda_{oI_2}(I^-)_T \quad (T = \text{Total})$$

From the law of mass action

$$(I^+)\ (I^-)_T = K(I_2) = K_2$$

Material balance requires that

$$(I^-)_T = (I^-)_{I_2} + (I^-)_{KI}$$

$$(K^+) = (I^-)_{KI} = c_{KI}$$

$$(I^+) = (I^-)_{I_2}$$

This leads to

$$K_2 = (I^-)_{I_2}\ ((I^-)_{I_2} + (I^-)_{KI})$$

To simplify, let $x = (I^-)_{I_2} + (I^-)_{KI} = (I^-)_T$, and $y = (I^-)_{KI}$

Then $$\kappa = x\,\Lambda_{oI_2}$$

and $$K_2 = x(x - y).$$

Combining these two equations gives

$$K_2 = (\kappa^2/\Lambda^2_{oI_2}) - (\kappa y/\Lambda_{oI_2})$$

Rearranging this equation gives

$$\kappa^2 = \kappa y \Lambda_{oI_2} + K_2 \Lambda^2_{oI_2}$$

For pure iodine, $y = o$, and $K_2 = x^2 = \kappa_o^2/\Lambda^2_{oI_2}$. Since $\kappa_o = 1.21 \times 10^{-5}$ $ohm^{-1} cm^{-1}$, $K_2 = 1.464 \times 10^{-10}/\Lambda^2_{oI_2}$.

We have plotted a graph of κ^2 against κy for a solution of KI in I_2 using the data of Bearcroft and Nachtrieb. Λ_o was obtained from the slope and used to calculate K_2. c was then found as $(K_2)^{\frac{1}{2}}$. Using the values show

y/mole cm^{-3}	κ/ohm^{-1}cm^{-1}
o	1.21×10^{-5}
4.286×10^{-6}	11.99×10^{-5}
9.778×10^{-6}	22.23×10^{-5}
2.896×10^{-5}	66.27×10^{-5}

gives Λ_{oI_2} = 22.9 ohm^{-1} cm^{+2} equiv^{-1} and K_2 = 2.79 x 10^{-13} equiv^2/cm^6. Since $K_2 = c^2$, c is found to be 5.28 x 10^{-7}equiv/cm^3. If the assumption that $\Lambda_{K^+} = \Lambda_{I^+}$ is correct, then different metal iodide solutes should give the same values for Λ_{oI_2}, and hence for K_2 and c. Using Bearcroft and Nachtrieb's data for TlI in I_2 gives Λ_{oI_2} = 30, K_2 = 1.57 x 10^{-13} and c = 3.96 x 10^{-7}equiv/cm^3 which is reasonable agreement.

In a similar manner we have calculated c for IBr, ICl and BrF_3. For a solution of KBr in IBr [57]

y/mole cm^{-3}	κ/ohm^{-1}cm^{-1}
o	0.461 x 10^{-3}
2.23 x 10^{-5}	2.44 x 10^{-3}
5.62 x 10^{-5}	4.12 x 10^{-3}
9.48 x 10^{-5}	5.61 x 10^{-3}

Λ_{oIBr} = 64.5 ohm^{-1}cm^{2}equiv^{-1}, K_2 = 3.84 x 10^{-11} and c = 6.2 x 10^{-6}moles/cm

For a solution of KCl in ICl [61]

y/mole cm^{-3}	κ/ohm^{-1}cm^{-1}
o	4.583 x 10^{-3}
3.138 x 10^{-5}	4.797 x 10^{-3}
6.582 x 10^{-5}	5.230 x 10^{-3}
19.75 x 10^{-5}	6.491 x 10^{-3}
39.5 x 10^{-5}	8.494 x 10^{-3}

Λ_{oICl} = 15.1 ohm^{-1}cm^{2}equiv^{-1}, K_2 = 9.21 x 10^{-8} and c = 3.03 x 10^{-4} moles/cm^3

For a solution of NH_4Cl in ICl [61]

y/mole cm^{-3}	κ/ohm^{-1} cm^{-1}
o	4.588 x 10^{-3}
26.33 x 10^{-5}	6.642 x 10^{-3}
52.66 x 10^{-5}	8.558 x 10^{-3}

Λ_{oICl} = 11.3 ohm^{-1}cm^{2}equiv^{-1}, K_2 = 1.65 x 10^{-7} and c = 4.06 x 10^{-4} moles/cm^3.

For ICl, c has been taken as 3.5 x 10^{-4} moles/cm^3.

For a solution of $KBrF_4$ in BrF_3 [76].

y/mole cm^{-3}	κ/ohm^{-1} cm^{-1}
o	8.00×10^{-3}
4.52×10^{-5}	10.34×10^{-3}
8.78×10^{-5}	13.45×10^{-3}
16.49×10^{-5}	19.80×10^{-3}

$\Lambda_{o_{BrF_3}}$ = 100.3 ohm^{-1}cm^{2}equiv^{-1}, $K_2 = 6.36 \times 10^{-9}$ and $c = 7.97 \times 10^{-5}$moles/c

With these values of c, it is now possible to evaluate the term $RT(\partial \ln f_{\pm}/\partial P)_T$. We have taken the values 12 and 50×10^{-6} bar^{-1} for ε_r and β_T respectively for all four compounds and the results are listed in Table 5.3. Thus it is now possible to compare $2\Delta V_{\kappa}$ (where ΔV_{κ} is the experimentally determined quantity) with $\Delta V^{o} + 2RT(\partial \ln f_{\pm}/\partial P)_T$ and this is done in Table 5.3. As can be seen, agreement is not too good. It was stated earlier that there may be ion-pairs present in BrF_3. Also the calculations for this compound may be out somewhat due to the values chosen for ε_r and β_T. It would appear that ion-pairs are present in ICl so agreement is not likely since this is not considered in the treatment by Cleaver and Smedley. In IBr and I_2 ion-pairs do not appear to be present, yet agreement between calculation and experiment is not good.

We have calculated the Debye length $1/\kappa_D$ from the Debye-Hückel theory, where κ_D is defined by

$$\kappa_D^2 = \frac{4\pi e^2 \sum_i n_i z_i^2}{\varepsilon kT}$$

and d, where $d = 2/\kappa_D$, which is the calculated distance apart of the ions such that their solvent shells just touch. From a knowledge of c, it is possible to calculate d' which is the actual distance apart of the ions since $d' = (1/2Nc)^{1/3}$. If $d' \overset{<}{\ngtr} d$ then it is assumed that the solvation sheaths are overlapping. Results of these calculations appear below:

Table 5.3 Volume Terms

	BrF_3	ICl	IBr	I_2
Temperature/^{o}C	27	50	80	140
c/moles cm^{-3}	7.97×10^{-5}	3.5×10^{-4}	6.2×10^{-6}	5.28×10^{-7}
$RT(\partial \ln f_{\pm}/\partial P)_T/cm^3$	+21.7	+52.0	+7.9	-0.07
$\Delta V^{o}+2RT(\partial \ln f_{\pm}/\partial P)_T/cm^3$	-50	+7	-79	-88
$2\Delta V_{K}$ /cm^3	-16	-14	-11	-45

	d/cm	d'/cm
BrF_3	8.46×10^{-8}	2.18×10^{-7}
ICl	4.18×10^{-8}	1.33×10^{-7}
IBr	3.29×10^{-7}	5.12×10^{-7}
I_2	1.22×10^{-6}	1.16×10^{-6}

Comparing d and d' shows that in BrF_3, ICl and IBr the solvent is NOT likely to be shared by the ions present. This may or may not be the case in I_2 where d and d' are very close. Thus the volume change on ionization would be lower than that expected. It is worth noting that Cleaver and co-workers (not yet published) have found that molten salts with high values of κ have low ΔV_κ values (eg $\kappa = 0.3\ \mathrm{ohm}^{-1}\mathrm{cm}^{-1}$ for CdI_2 and $\Delta V_\kappa = -3\ \mathrm{cm}^3/\mathrm{mol}$). This has been explained by the disappearance of the molecular form of the solvent in such highly conducting salts.

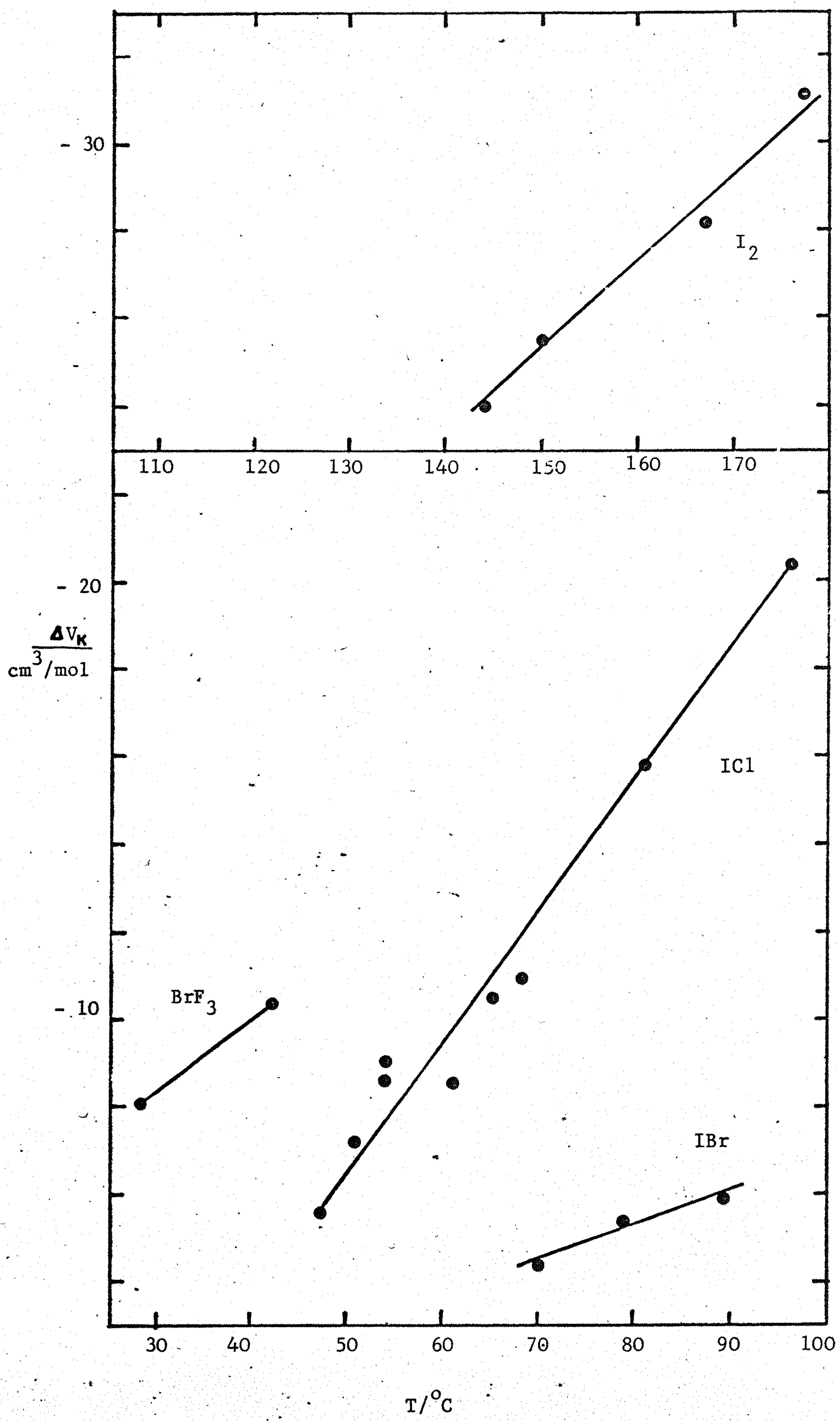
5.3 TEMPERATURE DEPENDENCE OF ΔV_κ

Fig. 5.3.1 illustrates that ΔV_κ for I_2, IBr, ICl and BrF_3 varies linearly with temperature, becoming numerically greater as the temperature rises. This may be interpreted in terms of the approximate equation (5.2.9) in which ΔV_κ and β_T are the only temperature dependent quantities. Taking logarithms and differentiating,

$$\partial \ln(-\Delta V_\kappa)/\partial T = \partial \ln \beta_T/\partial T$$

i.e. the relative increase in $(-\Delta V_\kappa)$ with temperature should be equal to the relative increase in isothermal compressibility if the theory leading up to equation (5.2.9) is correct. Values for $\partial \ln(-\Delta V_\kappa)/\partial T$ have been taken from this work for iodine and compared with $\partial \ln \beta_T/\partial T$ calculated from known β_T values. In this case, $\partial \ln(-\Delta V_\kappa)/\partial T$ and $\partial \ln \beta_T/\partial T$ were respectively $3.2 \times 10^{-3}\mathrm{K}^{-1}$ (approx.) and $2.6 \times 10^{-3}\mathrm{K}^{-1}$ (approx). This agreement provides further support for the model and for

Figure 5.3.1 Temperature Dependence of ΔV_K



the approximate equation (5.2.9). It was not considered worthwhile to do this comparison for ICl due to the considerable experimental uncertainty in the values of β_T.

5.4 FURTHER WORK

Measurements of ε_r, r, and their pressure derivatives are required for the evaluation of equation 5.2.5. Also the value of c for iodine and the interhalogens is required to calculate the term $RT(\partial \ln f\pm/\partial P)_T$. More accurate data is also required for the compressibility and thermal pressure coefficient. In our calculations to find c, we have assumed that no ion pairs are present. There is a need for more accurate measurements in the low concentration range to see if the solute does exist to some extent as ion-pairs.

It may be in the case of IBr and ICl that dissociation into the elements is important. At 100°C the degree of dissociation of IBr is 13.4% [77]. There is then the possibility that iodine acts as a Cl^- or Br^- acceptor in competition with the interhalogen.

$$2ICl \rightleftharpoons I_2 + Cl_2$$

$$ICl + I_2 \rightleftharpoons I^+ + I_2Cl^-$$

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

Dissociation into the elements is not expected to be very pressure dependent and whichever ionization takes place should make little difference to our calculations. However the conductivity as a function of iodine concentration could be measured.

The assumption has been made that the mobility of the ions does not vary with pressure. It may well decrease and the measured ΔV_K values would be lower than expected. Alternatively if a Grotthus-type mechanism operates, the mobility may increase with pressure as in the case of H^+ in H_2O, for which $-RT(\partial \ln \Lambda_0^{H^+}/\partial P)$ is negative. Measurements of the pressure dependence of the conductivity of a solution of KI in iodine could be used to see if this is so. If a Grotthus-type mechanism is involved in the transport of charge,

$$(\Lambda)_{\mathrm{KI\ in\ I_2}} \approx \Lambda_{\mathrm{I^-}}$$

Then

$$-RT\left(\frac{\partial \ln \Lambda}{\partial P}\right) \approx -RT\left(\frac{\partial \ln \Lambda_{\mathrm{I^-}}}{\partial P}\right)$$

$$(\Delta V_{\Lambda})_{\mathrm{expt}} \approx -RT\left(\frac{\partial \ln v_{\mathrm{I^-}}}{\partial P}\right)$$

since $\Lambda_{\mathrm{I^-}} = Fv_{\mathrm{I^-}}$ where $v_{\mathrm{I^-}}$ is the electrical mobility of the $\mathrm{I^-}$ ion.

E.m.f. measurements of a_+ and a_- would permit a more rigourous examination of the theory of Cleaver and Smedley. All that is needed is a cell in one half of which the iodide activity is known (a solution of KI in I_2) and an electrode reversible to iodide ions (Ag, AgI). A knowledge of the pressure dependence of the activity would permit direct calculation of $\overline{\Delta V^o}$ from the equation $\overline{\Delta V^o} = -RT(\partial \ln K'/\partial P)_T$ where $K' = a_{\mathrm{I^+}}\, a_{\mathrm{I^-}}$.

APPENDIX A

Experimental results of electrical conductivity (κ) versus pressure (P).

Iodine

Temperature	P/bar	$10^6\kappa/\text{ohm}^{-1}\text{cm}^{-1}$	$\log_{10}(\kappa/\text{ohm}^{-1}\text{cm}^{-1})$
144°C	270	11.89	$\bar{5}.0751$
	500	14.19	$\bar{5}.1520$
	735	16.88	$\bar{5}.2274$
	965	19.87	$\bar{5}.2982$
	860	18.51	$\bar{5}.2675$
	645	15.95	$\bar{5}.2028$
	385	13.28	$\bar{5}.1232$
	160	11.51	$\bar{5}.0610$
150°C	160	11.07	$\bar{5}.0442$
	380	13.16	$\bar{5}.1192$
	615	15.69	$\bar{5}.1957$
	770	17.53	$\bar{5}.2438$
	925	19.52	$\bar{5}.2904$
	530	14.80	$\bar{5}.1703$
	270	12.18	$\bar{5}.0858$
167°C	280	11.15	$\bar{5}.0471$
	550	13.86	$\bar{5}.1419$
	905	18.16	$\bar{5}.2591$
	775	16.45	$\bar{5}.2163$
	645	14.86	$\bar{5}.1719$
	420	12.47	$\bar{5}.0959$
	165	10.21	$\bar{5}.0089$

1 bar = 101, 325 Nm^{-2}

Temperature	P/bar	$10^6\kappa$/ohm^{-1}cm^{-1}	$\log_{10}(\kappa$/ohm^{-1}cm$^{-1})$
177°C	170	9.753	$\bar{6}.9892$
	505	12.98	$\bar{5}.1134$
	940	18.62	$\bar{5}.2701$
	830	17.15	$\bar{5}.2342$
	645	14.58	$\bar{5}.1637$
	335	11.23	$\bar{5}.0503$
Iodine Bromide			
		$10^4\kappa$/ohm^{-1}cm^{-1}	
70°C	110	4.816	$\bar{4}.6827$
	235	4.912	$\bar{4}.6913$
	510	5.142	$\bar{4}.7111$
	715	5.313	$\bar{4}.7253$
	940	5.505	$\bar{4}.7408$
	830	5.409	$\bar{4}.7331$
	640	5.252	$\bar{4}.7203$
	385	5.073	$\bar{4}.7053$
	175	4.936	$\bar{4}.6934$
	330	5.053	$\bar{4}.7035$
	580	5.265	$\bar{4}.7214$
	755	5.399	$\bar{4}.7323$
79°C	145	4.549	$\bar{4}.6579$
	320	4.717	$\bar{4}.6737$
	620	5.005	$\bar{4}.6994$
	785	5.145	$\bar{4}.7114$
	930	5.283	$\bar{4}.7228$
	710	5.060	$\bar{4}.7041$
	550	4.871	$\bar{4}.6876$
	430	4.751	$\bar{4}.6768$

Temperature	P/bar	$10^4\kappa$ /ohm^{-1}cm^{-1}	$\log_{10}(\kappa$ /ohm^{-1}cm$^{-1})$
	230	4.600	$\bar{4}.6628$
	95	4.539	$\bar{4}.6569$
89°C	100	4.148	$\bar{4}.6178$
	400	4.374	$\bar{4}.6409$
	670	4.655	$\bar{4}.6679$
	955	4.926	$\bar{4}.6925$
	835	4.830	$\bar{4}.6840$
	565	4.511	$\bar{4}.6543$
	305	4.323	$\bar{4}.6358$
	190	4.237	$\bar{4}.6271$
Iodine Chloride			
		$10^3\kappa$ /ohm^{-1}cm^{-1}	
51°C	380	4.836	$\bar{3}.6844$
	680	5.299	$\bar{3}.7242$
	925	5.604	$\bar{3}.7485$
	800	5.404	$\bar{3}.7327$
	570	5.088	$\bar{3}.7066$
	460	4.912	$\bar{3}.6913$
	280	4.681	$\bar{3}.6704$
	155	4.533	$\bar{3}.6563$
	80	4.454	$\bar{3}.6488$
	210	4.661	$\bar{3}.6684$
65°C	365	4.679	$\bar{3}.6701$
	535	5.077	$\bar{3}.7056$
	815	5.691	$\bar{3}.7552$
	905	5.878	$\bar{3}.7692$
	740	5.523	$\bar{3}.7421$
	650	5.323	$\bar{3}.7261$

Temperature	P/bar	$10^3\kappa/\mathrm{ohm}^{-1}\mathrm{cm}^{-1}$	$\log_{10}(\kappa/\mathrm{ohm}^{-1}\mathrm{cm}^{-1})$
	460	4.949	$\bar{3}.6945$
	295	4.656	$\bar{3}.6680$
	220	4.527	$\bar{3}.6558$
	125	4.406	$\bar{3}.6440$
54°C	710	5.466	$\bar{3}.7377$
	495	5.090	$\bar{3}.7067$
	265	4.747	$\bar{3}.6764$
	125	4.540	$\bar{3}.6570$
	370	5.036	$\bar{3}.7021$
	565	5.393	$\bar{3}.7317$
	810	5.785	$\bar{3}.7623$
	910	5.909	$\bar{3}.7715$
	630	5.453	$\bar{3}.7367$
	420	5.022	$\bar{3}.7009$
68°C	665	5.349	$\bar{3}.7283$
	810	5.675	$\bar{3}.7540$
	765	5.551	$\bar{3}.7444$
	945	5.969	$\bar{3}.7759$
	530	5.084	$\bar{3}.7062$
	405	4.788	$\bar{3}.6801$
	240	4.506	$\bar{3}.6538$
	105	4.310	$\bar{3}.6345$
54°C	110	4.513	$\bar{3}.6544$
	325	4.899	$\bar{3}.6901$
	580	5.318	$\bar{3}.7257$
	815	5.723	3.7576

Temperature	P/bar	$10^3\kappa/\mathrm{ohm}^{-1}\mathrm{cm}^{-1}$	$\log_{10}(\kappa/\mathrm{ohm}^{-1}\mathrm{cm}^{-1})$
	925	5.816	$\bar{3}.7647$
	730	5.482	$\bar{3}.7389$
	485	5.043	$\bar{3}.7027$
	235	4.644	$\bar{3}.6669$
81°C	250	3.616	$\bar{3}.5582$
	495	4.226	$\bar{3}.6260$
	745	4.840	$\bar{3}.6848$
	965	5.368	$\bar{3}.7298$
	875	5.113	$\bar{3}.7087$
	645	4.460	$\bar{3}.6493$
	370	3.837	$\bar{3}.5840$
	135	3.457	$\bar{3}.5388$
96°C	135	2.588	3.4130
	375	3.153	3.4987
	610	3.729	3.5716
	870	4.371	3.6406
	970	4.516	3.6548
	765	3.925	3.5939
	525	3.299	3.5183
	245	2.787	3.4451
47°C	110	4.568	$\bar{3}.6597$
	380	4.944	$\bar{3}.6941$
	615	5.154	$\bar{3}.7122$
	865	5.389	$\bar{3}.7315$
	965	5.501	$\bar{3}.7405$

Temperature	P/bar	$10^3\kappa$ /ohm^{-1}cm^{-1}	$\log_{10}(\kappa$ /ohm^{-1}cm$^{-1})$
	770	5.267	$\bar{3}.7215$
	510	5.003	$\bar{3}.6992$
	250	4.739	$\bar{3}.6757$
	110	4.583	$\bar{3}.6611$
61°C	115	4.519	$\bar{3}.6551$
	370	4.993	$\bar{3}.6984$
	610	5.394	$\bar{3}.7319$
	890	5.814	$\bar{3}.7645$
	970	5.921	$\bar{3}.7724$
	765	5.521	$\bar{3}.7420$
	505	5.125	$\bar{3}.7097$
	250	4.739	$\bar{3}.6757$
	105	4.514	$\bar{3}.6546$
Bromine Trifluoride			
		$10^3\kappa$ /ohm^{-1}cm^{-1}	
28°C	505	9.252	$\bar{3}.9662$
	230	8.410	$\bar{3}.9248$
	100	8.003	$\bar{3}.9033$
	370	8.807	$\bar{3}.9448$
	665	9.701	$\bar{3}.9868$
	810	10.15	$\bar{2}.0065$
	925	10.49	$\bar{2}.0208$
42°C	775	11.27	$\bar{2}.0518$
	955	11.92	$\bar{2}.0764$
	865	11.72	$\bar{2}.0688$
	635	10.79	$\bar{2}.0332$

Temperature	P/bar	$10^3\kappa$ /ohm^{-1}cm^{-1}	$\log_{10}(\kappa$ /ohm^{-1}cm$^{-1})$
	365	9.479	$\bar{3}.9768$
	210	8.907	$\bar{3}.9497$
	90	8.599	$\bar{3}.9345$
	460	9.895	$\bar{3}.9954$
	640	10.61	$\bar{2}.0257$

Frequency dependence of the conductivity of bromine trifluoride.

Temperature	P/bar	$10^3\kappa$ /ohm^{-1}cm^{-1}	Frequency/kHz
28°C	505	5.662	2
		7.970	5
		8.902	10
		9.252	20
		9.252	50
	230	5.373	2
		7.369	5
		8.131	10
		8.410	20
		8.410	50
	100	5.231	2
		7.067	5
		7.752	10
		8.003	20
		8.003	50

Temperature	P/bar	$10^3\kappa$ /ohm^{-1}cm^{-1}	Frequency/kHz
	370	5.525	2
		7.658	5
		8.505	10
		8.807	20
		8.807	50
	665	5.832	2
		8.315	5
		9.309	10
		9.701	20
		9.701	50
	810	5.988	2
		8.609	5
		9.692	10
		10.15	20
		10.15	50
	925	6.097	2
		8.840	5
		9.990	10
		10.49	20
		10.49	50
42°C	775	7.885	2
		10.16	5
		11.08	10
		11.23	15
		11.27	20
		11.27	50

Temperature	P/bar	$10^3\kappa$ /$\mathrm{ohm}^{-1}\mathrm{cm}^{-1}$	Frequency/kHz
	955	8.150	2
		10.81	5
		11.66	10
		11.85	15
		11.92	20
		11.92	50
	865	7.899	2
		10.59	5
		11.46	10
		11.65	15
		11.72	20
		11.72	50
	635	7.734	2
		9.928	5
		10.62	10
		10.77	15
		10.79	20
		10.79	50
	365	7.350	2
		8.921	5
		9.361	10
		9.432	15
		9.479	20
		9.479	50

Temperature	P/bar	$10^3\kappa$ /ohm^{-1}cm^{-1}	Frequency/kHz
	210	7.194	2
		8.495	5
		8.821	10
		8.888	15
		8.907	20
		8.907	50
	90	7.109	2
		8.306	5
		8.571	10
		8.599	15
		8.599	20
		8.599	50
	460	9.332	5
		9.796	10
		9.895	15
		9.895	20
		9.895	50
	640	7.705	2
		9.829	5
		10.43	10
		10.55	15
		10.61	20
		10.61	50

Experimental results of electrical conductivity (κ) versus temperature for iodine chloride

P/bar	Temperature/ ^{o}C	$10^3\kappa$ /ohm^{-1}cm^{-1}
50	52	4.651
	59	4.456
	61	4.397
	66	4.236
	70	4.045
	75.5	3.752
	82	3.454
	84	3.332
	87	3.151
	93	2.873
	38	4.480
	33	4.329
	30.5	4.221
	38	4.480
	44	4.607
	46	4.632
	50	4.641
	57.5	4.505
	55	4.583
1000	45.5	5.760
	49	5.946
	54	6.073
	58.5	6.107
	63	6.058
	68	5.936
	72	5.735
	80	5.374
	37	5.120

APPENDIX B

A deadweight tester was used to check the accuracy of the Bourdon gauge used in this work.

The results appear below:

Pressure in p.s.i.	Equivalent pressure in atm*.	Gauge reading in atm.
2,000	136.1	135
4,000	272.1	270
6,000	408.2	405
8,000	544.2	545
10,000	680.3	675
12,000	816.3	820
14,000	952.4	955
15,000	1020.4	1025
14,000	952.4	955
12,000	816.3	820
10,000	680.3	680
8,000	544.2	545
6,000	408.2	410
4,000	272.1	270
2,000	136.1	135

*1atm = 1.013 bar = 101, 325 Nm^{-2}

REFERENCES

1. L. Grantham and S.J. Yosim, J. Chem. Phys., (1966), 45, 1192
2. A.F.M. Barton, B. Cleaver and G.J. Hills, Trans. Faraday Soc., (1968) 64, 208
3. B. Cleaver, P.N. SPENCER and S.I. Smedley, J.C.S. Faraday Transactions 1, (1972) vol. 68, 1720
4. S.B. Brummer and G.J. Hills, Trans.Faraday Soc., (1961) 57, 1823
5. B. Howard, Thesis (London 1964)
6. S.B. Brummer, J. Chem. Phys., (1965), 42, 1636
7. F. Barriera and G.J. Hills, Trans. Faraday Soc., (1968) 64, 1359
8. G.J. Hills and P.J. Ovenden, Adv. Electrochem.Electrochem. Eng. (Interscience, New York, 1966) 4, 185
9. S.D. Hamann and W. Strauss, Trans. Faraday Soc., (1955) 51, 1684
10. D.A. Lown, H.R. Thirsk and Lord Wynne-Jones, Trans. Faraday Soc. (1968) 64, 2073
11. S.D. Hamann, J. Phys. Chem., (1963), 67, 2233
12. M. Blander, Molten Salt Chemistry (Interscience, New York, London, Sydney, 1964)
13. S.B. Brummer and G.J. Hills, Trans. Faraday Soc., (1961), 57, 1823
14. G.Jones and G.M. Bollinger, J.A.C.S., 51, (1929) 2407
15. G. Jones and G.M. Bollinger, ibid., 53, (1931),411
16. G. Jones and G.M. Bollinger, ibid., 53, (1931), 1207
17. G. Jones and B.C. Bradshaw, ibid., 55, (1933), 1780
18. G. Jones and S.M. Christian, ibid., 57, (1935), 272
19. G. Jones and D.M. Bollinger, ibid., 57, (1935), 280
20. G. Jones and M.J. Prendergast, ibid., 59, (1937), 731
21. T. Shedlovsky, ibid., 52, (1930), 1793
22. F. Kohlrausch, Wied. Ann., 60, (1897), 315
23. F.S. Feates, D.J.G. Ives, and J.H. Pryor, J. electrochem. Soc., 103 (1956), 580
24. W.M. Latimer, K.S. Pitzer and C.M. Slansky, J. Chem. Phys., 7, 108, (1939)
25. H.S. Frank and M.W. Evans, J. Chem. Phys., 13, (1945), 507.
26. D.M. Ritson and J.B. Hasted, J. Chem. Phys., 16, (1948), 11.
27. J.A. Schellman, J. Chem. Phys., 26, (1957), 1225

28. N. Bjerrum, K. danske vidensk. Selsk., 7 (1926) No. 9; 'Selected Papers', p.108, Einar Munksgaard, Copenhagen (1949)

29. R.M. Fuoss, J.A.C.S., 80, (1958) 5059

30. J. Padova, J. Phys. Chem., 72, 692, (1968)

31. A.J Parker, J. Chem. Soc., (London), 1328 (1961)

32. A.J. Parker, Quart. Rev. (London), 16, 163, (1962)

33. H.E. Zaugg, B.W. Harrom and S. Borgwardt, J.A.C.S., 82, 2895,(1960)

34. E. Price, in 'The Chemistry of Nonaqueous Solvents', vol. 1, 1966 Chapter 2.

35. J. Miller and A.J. Parker. J.A.C.S., 83, 117 (1961)

36. M.M. Markowitz, W.N. Hawley, D.A. Boryta, and R.F. Harris, J. Chem.Eng. Data, 6, 325, (1961)

37. N.Bjerrum, in 'Chemistry at the Centenary (1931) Meeting, Brit. Assn. Advan. Sci., p.34.

38. H.N. Parton, in 'Electrochemistry', Pergamon Press, London, 1964, p.455.

39. V. Gutman, Chemistry in Britain, (1971), 7, 102

40. I.K. Delimarskii and B.F. Markov, 'Electrochemistry in Fused Salts', 12, 15, (Sigma Press, Washington D.C. 1961)

41. E.F. Riebling and C.E. Erickson, J. Phys. Chem., 67, 307, (1963)

42. L.F. Grantham and S.J. Yosim, J. Phys. Chem., 67, 2506, (1963)

43. L.F. Grantham, J. Chem. Phys., 44, 1509, (1966)

44. J.W. Johnson and D. Cubicciotti, J. Phys. Chem., 68, 2235, (1964)

45. L.F. Grantham and S.J. Yosim, J. Phys. Chem., 72, 762, (1968)

46. D. Fray, Thesis, London 1965.

47. A. Schlichthärle, K. Tödheide and E.U. Franck, J. Chem. Phys. Report 19th Ann. Meeting Soc. Chim. Phys., (Montpellier) 1968, p.70.

48. A.J. Darnell, W.A. McCollum, and S.J. Yosim, J. Phys. Chem., 73, 4116, (1969)

49. A.J. Darnell and W.A. McCollum, J. Chem. Phys., 55, 116, (1971)

50. B. Cleaver and S.I. Smedley, Trans. Faraday Soc., 67, 1115, (1971)

51. J.E. Bannard and G. Treiber, High Temperatures - High Pressures (1973), vol. 5. pp 177 - 182.

52. F. Birch, Rev. Sci. Instr., (1939) 10, 137

53. G.N. Lewis and P. Wheeler, Z Physik. Chem., 56, 179 (1906)

54. M. Rabinowitsch, Z. Physik. Chem., 119, 83, (1926)

55. W.A. Plotnikov, J.A. Fialkov, and W.P. Tschalij, ibid., A172, 307, (1935)

56. D.J. Bearcroft and N.H. Nachtrieb, J. Phys. Chem., (1967) 71, 316, 4400

57. V. Gutman, (Tech. Hochschule Vienna) Monatsh 82, 156 - 69, (1951)

58. Gmelin,'Handbook of Inorganic Chemistry'

59 Y.A. Fialkov and N.I. Goldman, J. Gen. Chem. Russia,(1941), 11, 910

60. L. Bruner and E. Bekier, Z. Electrochem., 18, 369, (1912)

61. J. Cornog and R.A. Karges, J.A.C.S., 54, 1882, (1932)

62. Y.A. Fialkov and O.I. Shor, J. Gen. Chem. Russia, (1948) 18, 14

63. H.J. Emeleus and N.N. Greenwood, J. Chem, Soc., (1950) 987

64. A.A. Banks, H.J. Emeleus, and A.A. Woolf, J.C.S. (1949) 2861

65. L.A. Quarterman, H.H. Hyman and J.J. Katz, J.P.C. (1957), 61, 912

66. H.H. Hyman, T. Surles, L.A. Quarterman, A. Popov, J. Phys. Chem., (1970), 74, 2038

67. P. Elliot, Corrosion Science, (1972), vol. 12, pp 291 - 293

68. I.B.M. Technical Report, TR22 - 437 by R.A. Delaney and R.K. Spielberger I.B.M. Components Division, East Fishkill, U.S.A.

69. Quarterly Reviews 1950, 'Interhalogen Compounds and Polyhalides' by A.G. Sharpe.

70. S.D. Hamann,'Physico-Chemical Effects of Pressure', (Butterworths, London, 1957)

71. R.A. Robinson and R.H. Stokes, 'Electrolyte Solutions' (Butterworths, London 1959)

72. J. Jander and C. Lafrenz, 'Ionizing Solvents' (Wiley, 1970)

73. L. Pauling, 'The Nature of the Chemical Bond' (2nd edition 1950)

74. P.N. Spencer (not yet published)

75. G.W.C. Kaye and T.H. Laby, 'Physical and Chemical Constants'

76. A.A. Woolf and H.J. Emeleus, J.C.S. (1949) 2865

77. N.N. Greenwood, Review of Pure and Applied Chem., 1, 84, (1951).