Electrical Conduction and Diffusion Studies

of some

Hydrogen Bonded Crystals

Thesis submitted to
The University of Leicester by
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STATEMENT
I declare that the material contained in the thesis is the result of work carried out by me in the School of Chemistry at the Leicester Regional College of Technology, during my period of registration (3rd of July 1964-3rd of July 1967) as a Part-time student for the degree of Doctor of Philosophy in the Faculty of Science (Dept. of Chemistry) of the Leicester University.

The contents have not been presented and are not being concurrently presented for any other degree.

[Signature]

School of Chemistry,
Regional College of Technology,
LEICESTER.
From Untruth, lead me to truth,
From Darkness, lead me to LIGHT,
From Death, lead me into Immortality.

- Upanishads.
ACKNOWLEDGMENTS
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A method has been developed for studying proton conduction in solids (KHP, KH₄PO₄, NH₄H₂PO₄, KH₂AsO₄, and Oxali acid dihydrate), in which, hydrogen gas evolved on d.c. electrolysis of the solid, is collected and measured. These conductions have shown to be entirely protonic in nature.

The conductances of the solids mentioned above have also been measured as a function of the temperature by an A.C. method. The activation energies obtained experimentally have been interpreted in terms of the formation of proton defects in the crystal.

Comparisons have been made between activation energies obtained for polycrystalline samples, and single crystals. The effect of crystal orientation on the activation energy has also been investigated in the case of NH₄H₂PO₄ and KH₂PO₄. It is concluded that conductance data on single crystals are preferable to compressed pellets, provided the direction of measurement is specified.

The measurements on the H-bonded crystals have been repeated for the corresponding deuterated compounds and a comparison is made between them.

A tritium diffusion has been studied on a single crystal of NH₄H₂PO₄. It has been concluded that the "Einstein Relation" is obeyed; i.e., conduction and diffusion occur by the same mechanism.
CONTENTS
CHAPTER ONE

THE HYDROGEN BOND
1.1 INTRODUCTION

The term **Hydrogen Bond** was introduced in 1920 by Latimer and Rodebush\(^1\) to describe the association which can result when a proton, chemically bonded to an electronegative atom such as \(O, F, N\), interacts with another electronegative atom in the same or a different molecule. Since then a very large amount of experimental data has been accumulated regarding the occurrence and behaviour of the hydrogen bond in various systems, but no entirely satisfactory theory as to the nature of the interaction has been suggested which covers all the experimental facts. At first it was thought that an explanation could be found in terms of purely electrostatic interaction, but when in 1939 Robertson and Ubbelohde\(^2\) demonstrated that substitution of deuterium for hydrogen in oxalic acid dihydrate causes a large expansion of the short hydrogen bond, it was realised that a simple electrostatic model was incomplete.

No attempt will be made here to review all the work done on the hydrogen bond as several excellent reviews have already
been made\textsuperscript{3-6}. Instead, it is intended to select some of the problems involved in attempting to describe the nature of the hydrogen bond, and to consider some of the experimental methods which have contributed to the present state of knowledge.

1.2. DEFINITION AND KINDS OF HYDROGEN BONDS

Bearing in mind the widely differing types of hydrogen bond which exist, a formal definition covering all cases is difficult, but is best stated in the same general terms which have been used in (1.1). The hydrogen bond can then be defined as the interaction which exists when a hydrogen atom is situated on or near a line joining two other electronegative atoms, resulting in a closer approach between these atoms than their normal Van der Waals repulsion radii. Hydrogen bonding is then recognised as a specific interaction between an $-A-H$ bond of one molecule, described as the proton donor, and a $B$-atom of another molecule, described as the proton acceptor, forming a system $A-H-B$.

This definition removes any difficulty of deciding what is to be the maximum limit of hydrogen bond length, since for the $A-H-B$ system this will be the sum of the Van der Waals repulsion radii of $A$ and $B$. Any decrease in the $A-B$ distance
may then be attributed to hydrogen bonding. In the O-H...O system there is a continuous range of hydrogen bond length from the shortest known bond, 2.44\(\text{Å}^0\) in nickel dimethylglyoxime, upwards. In spite of this, hydrogen bonds are frequently classified into long and short, and it is obvious that no such distinction can justly be made. Nevertheless, there is evidence that in crystals, when the bond length falls below about 2.6\(\text{Å}^0\), quantum mechanical effects begin to make significant contributions in addition to the forces responsible for longer bonds.

1.3. THE NATURE OF THE HYDROGEN BOND

Latimer and Rodebush\(^1\) originally suggested that the hydrogen atom in a hydrogen bond may form a stable shell of four electrons thus becoming divalent. However, it is now known that this could only take place by use of 2s or 2p orbitals, and Prichard and Skinner\(^7\) have shown that the energy of these states is approximately 10 ev (240 kcals) above the 1s ground state. The stabilisation resulting from hydrogen bond formation is not sufficient to make the use of such high energy orbitals likely. Many workers consider that the hydrogen bond is essentially an electrostatic phenomenon, resulting from dipole-dipole interaction. In O...H---O
systems as in water and carboxylic acids for example, the dipole interaction will be as shown in figure-1.1

![Diagram of dipole interaction](image)

and

![Diagram of dipole interaction](image)

Purely electrostatic forces such as are involved in this model vary with \(1/r^2\) and therefore are significant over a considerable range of \(r\), they are also favoured by small sized atoms giving higher charge density and allowing closer approach.

\(F^- (1.34\text{Å})\) is the smallest anion, and is followed by \(O^- (1.40\text{Å})\) and \(N^- (1.71\text{Å})\). \(F-H...F\) systems are in general shorter and stronger than \(O-H...O\) systems which are in turn shorter and stronger than \(N-H...N\) systems. Calculation of dissociation energies of hydrogen bonds have been made assuming only dipole and Van der Waals forces to be involved. For example, in the case of acetic and formic acids, Davies has shown that 87% of the interaction energy may be accounted for. Agreement of the same order is found for interactions involving OH groups.
in Benzoic acid, O-Chlorophenol, and water, and as a result of these calculations Davies suggests that there is no practical need for the introduction of a special mechanism for the hydrogen bond, since at least 70% of the interaction energy may be attributed to electrostatic effects. The electrostatic model of the hydrogen bond has in general been accepted for the interaction in gaseous and liquid systems, e.g., formic acid vapour, liquid alcohols, etc., where thermal motion prevents any permanent association between individual molecules. In crystals, however, the fixed position and closer approach of molecules may allow other effects to become significant in addition to the electrostatic forces.

Coulson\(^9\) considers that some covalent contributions are present in certain hydrogen bond systems such as ice where the distance H\(\cdots\)O\(_2\) (in the system O\(_1\) —H\(\cdots\)O\(_2\)) is only 1.6 A\(^0\). Since the sum of the Van der Waals radii of H and O is 2.6 A\(^0\), the considerable shortening which is observed implies, according to Coulson, that some degree of covalent bonding is present.

In assessing the relative importance of electrostatic, covalent and other contributions to the hydrogen bond energy, it is customary to represent the complete wave function for the system in terms of the following structures:
Tsubomura has calculated the relative weights of these structures for an $O_1-O_2$ distance of 2.70 Å, obtaining the results 70, 8, 19, 1, and 1 percent respectively.

Pauling, Coulson and Danielson and others have made similar calculations, and the conclusion is that as the $O_1-O_2$ distance decreases the contribution from covalent type structures increases.

Further evidence that forces other than electrostatic interactions are involved in hydrogen bonding comes from a study of the effect of substituting deuterium for hydrogen in hydrogen bonded crystals. This isotope effect was first observed in oxalic acid dihydrate by Robertson and Ubbelohde. This crystal contains two types of hydrogen bond, one 2.5 Å and the other 2.8 Å in length. When D is substituted for H, it is found that a considerable expansion occurs in the direction of the shorter H-bond accompanied by a smaller contraction in the direction of the longer hydrogen bond. These changes in lattice
spacing have been attributed by Robertson and Ubbelohde to changes in the H-bond lengths, although Delaplane and Ibers have recently shown that both bonds expand. If electrostatic and/or van der Waals forces alone are responsible for H-bond formation then a contraction is to be expected on deuterium substitution, and in the case of some ionic crystals such as LiH, and HfH₄ such a contraction has been measured. Ubbelohde considers the isotope expansion to be a result of the close approach or overlap of potential energy functions for ionic and covalent descriptions of the H-bond. Such a system is represented in fig. 1.2a where overlap of the two functions is small, the description of the H-bond will be predominantly ionic. Where there is greater overlap as in fig. 1.2b each potential curve may affect the other with the result that the H-bond may best be described in terms of a modified potential function as in fig. 1.2c.

If the two minima lie at \( Uₐ \) and \( Uₗ \) above a reference zero then the difference in energy (or overlap) \( \Delta U \) will be

\[
\Delta U = Uₗ - Uₐ + 1/2 h (\sqrt{\gamma} - \sqrt{\gamma})
\]

where \( 1/2 h \sqrt{\gamma} \) and \( 1/2 h \sqrt{\gamma} \) are the zero point energies of the two forms.

The form with the lower potential energy will in general have
a. No overlap. No H-Bond or very weak interaction.

b. Overlap giving potential function with double minimum. H-Bond of intermediate strength.

c. Complete overlap giving single minimum. Very strong H-Bond.
the stronger force constant and therefore:

\[ \sqrt{2} = a \sqrt{1} \]

where \( a \gg 1 \)

\[ \Delta U = U_1 - U_2 + 1/2\hbar (\sqrt{1} - a\sqrt{1}) \]

\[ = U_1 - U_2 + 1/2\hbar \sqrt{1} (1 - a) \]

For a hydrogen bonded system:

\[ \Delta U_H = U_1 - U_2 + 1/2\hbar \sqrt{H} (1 - a) \]

and for a D-bonded system:

\[ \Delta U_D = U_1 - U_2 + 1/2\hbar \sqrt{D} (1 - a) \]

but

\[ \sqrt{H} = (2^{0.5}) \sqrt{D} \]

\[ \Delta U_H = U_1 - U_2 + (1/2) (2^{0.5}) \sqrt{D} (1 - a) \]

so:

\[ \Delta (U_H - U_D) = 1/2 \sqrt{D} (2^{0.5} - 1) (1 - a) \]

The quantity \( \Delta (U_H - U_D) \) represents the difference in overlap between the H and D systems. \( 1/2 \hbar \sqrt{D} (2^{0.5} - 1) \)

is a positive quantity and \( (1 - a) \) is a negative quantity, hence \( \Delta (U_H - U_D) \) is negative, showing that the overlap is closer for the H-system than for the D-system. Because of this, any quantum mechanical contribution to the bond is greater for H than for D, and thus the H-bonds will be shorter.
<table>
<thead>
<tr>
<th>Crystal</th>
<th>R (Å)</th>
<th>(measured values)</th>
<th>Ref.</th>
<th>(R_D-R_H) x10 Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxalic acid dihydrate</td>
<td>2.49</td>
<td>40.5</td>
<td>2</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>2.507</td>
<td>18.0</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.884</td>
<td>24.0</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.870</td>
<td>11.0</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>Acetylene dicarboxylic</td>
<td>2.56</td>
<td>34.0</td>
<td>61</td>
<td></td>
</tr>
<tr>
<td>dihydrate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Succinic acid</td>
<td>2.64</td>
<td>18.0 approx.</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Ice</td>
<td>2.76</td>
<td>1.5</td>
<td>62</td>
<td></td>
</tr>
<tr>
<td>β-H-Resorcinol</td>
<td>2.75</td>
<td>No measurable effect</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.70</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Urea</td>
<td>2.99</td>
<td>Small contraction</td>
<td>63</td>
<td></td>
</tr>
<tr>
<td>NH₄H₂PO₄</td>
<td>2.49</td>
<td>10.0</td>
<td>64</td>
<td></td>
</tr>
<tr>
<td>KH₃PO₄</td>
<td>2.52</td>
<td>9.7</td>
<td>63</td>
<td></td>
</tr>
<tr>
<td>KH₄AsO₄</td>
<td>2.54</td>
<td>8.7</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td>CuSO₄ 5H₂O</td>
<td>-</td>
<td>Small contraction</td>
<td>63</td>
<td></td>
</tr>
<tr>
<td>KHF₂</td>
<td>2.26</td>
<td>Small contraction</td>
<td>63</td>
<td></td>
</tr>
</tbody>
</table>
Table-1.1, gives data for those hydrogen bonded crystals in which the isotope effect has been studied. The conclusions which have been drawn from these studies are that only "short" hydrogen bonds (< 2.75Å), i.e. those in which the quantum mechanical contribution could be expected to be significant, show an expansion on deuterium substitution. Furthermore, the observed expansion depends on the type of H-bond arrangement in the crystal. For isolated acid dimers such as furoic acid the expansion is much less than for systems with a continuous chain or network of H-bonds such as in oxalic acid dihydrate.

Using the above facts, and also the results of thermal expansion studies, Ubbelohde and Gallagher have treated the hydrogen bond in crystals as a special case of acid-base equilibrium. They classify hydrogen bonds according to the type of equilibrium present for example:

1. \[ \text{A} \quad \text{H} \quad \text{...} \quad \text{A} \quad \text{H}_2 \quad \text{...} \quad \text{A} \] (e.g. carboxylic acids)
2. \[ \text{A} \quad \text{H} \quad \text{...} \quad \text{B} \quad \text{H} \quad \text{...} \quad \text{A} \] (e.g. acid hydrates, where \( B = \text{H}_2\text{O} \))
3. \[ \text{A} \quad \text{H} \quad \text{...} \quad \text{A} \quad \text{H}_2 \quad \text{...} \quad \text{A} \] (e.g. acid salts, \( \text{KH}_2\text{PO}_4 \) etc.)

In all these cases there must be two alternative basic sites for the proton, these sites normally having different proton affinities. Where the basicity is very different, there is
no appreciable overlap of the potential energy functions describing the two states, corresponding to the conditions in fig.1.2a. When the basicity of the states become comparable, then the crystal will contain a number of proton-transfer defect sites (cf. fig.1-2b,c ). When the proportion of such defect sites becomes sufficiently large (as in crystal containing net-works of H-bonds) it is considered that the co-operative effects will become significant leading to large values of the isotope expansion.

Other explanations of the isotope effect have been proposed; for example, Nordman and Lipscomb\(^\text{17}\) have considered the motion of the hydrogen and deuterium atoms in a one dimensional potential well between the two end atoms. The mean amplitude of vibration of H and D atoms averaged over a Boltzmann distribution have been calculated, and it has been shown that the mean amplitude is greater for D than for H.

Some aspects of the isotope effect are still not completely understood, in particular the variation of isotope expansion with temperature. There is, however, agreement that the explanation of the isotope effect requires the existence of some quantum mechanical mechanism for the hydrogen bond in crystals.
1.4. THE POSITION OF THE HYDROGEN ATOM IN HYDROGEN BOND:

In crystals, starting with an assumed model with 100% allegiance of the proton with one of the two groups, the various methods which have been developed to locate the proton are not sufficiently refined to permit an accurate assessment of the fraction of the defect sites arising from the proton transfer to the alternative position. Thermodynamically, unless the two potential energy minima are completely fused, above 0°K the protons will always be distributed statistically between the positions available to them in the crystal.

The detection of the proton by X-ray diffraction is difficult because the scattering power of the proton is small. Some indication of its position can be obtained from a difference map in which an electron "density map" is drawn from observed and calculated data. In this way the peaks due to the heavier atoms are eliminated. The hydrogen bonds in nitric acid hydrates and salicylic acid have been investigated by this method. The former structure has been shown to be mainly \((\text{OH}_3)^+ \) \((\text{NO}_2^-)\) and the latter the covalent form \((\text{O-H} \ldots \text{O-C})\).

The advent of neutron diffraction techniques has been of considerable use in proton location, since the scattering power of the hydrogen for neutrons is much greater than for X-rays.
By this method, Peterson and Levy$^{20}$ have located the proton in KH$_3$F$_3$ crystals to within 0.1 Å of the centre of the F-H-F ions. In KH$_2$PO$_4$ at room temperature, Bacon and Pease$^{21}$ have found that the scattering density diagram shows an elliptical peak mid-way between the two oxygen atoms, indicating that there are two minima 0.35 Å apart.

The shapes of the magnetic resonance absorption spectra permit allocation of the protons to specific atoms in the crystals.$^{21-24}$ The crystals studied may be symbolised:

- (ClO$_4$)$^-$ ...............(OH$_3$)$^+$ Monohydrate and dihydrate
- (SO$_4$)$^-$ ..................(OH$_3$)$^+$ Monohydrate and dihydrate
- (NO$_3$)$^-$ ..................(OH$_3$)$^+$ Monohydrate and trihydrate
- C$_2$O$_4$H$_2$ .................(H$_2$O) Dihydrate

This method, however, gives neither the exact position of the proton nor the statistical estimate of the fraction of protons in the alternative position.

An indirect method of determining the position of the proton is by the determination of the residual entropy in the solid. Thus, Giaque and Stout$^{25}$ have found that the entropy of ice is 0.87 cal/deg/mole at 0°K, which is in very good agreement with Paulings value of 0.805 cal/deg/mole, which was calculated using a model with an unsymmetrical bond. The hydrogen bonds in
KHAPO₄, KH₂AsO₄, NH₄H₂PO₄, NH₄H₂AsO₄, and Na₂SO₄·10 H₂O have been shown to be unsymmetrical by this method.

In these unsymmetrical hydrogen bonds, the proton may switch over to the alternative site provided that it can surmount the potential energy barrier separating the two minima. Huggins has calculated the potential energy of various arrangements of the systems O—H....O in ice, and has found an energy barrier of about 2.2 kcal/mole, provided that:

1. the oxygen atoms remains 2.75 Å apart

and

2. the alternative charge on the oxygen atoms remains equal and unchanged by the movement of the proton.

With such a small energy barrier it is likely that the proton in an isolated intermolecular bond could readily move from one minimum to the other. In a crystal such as ice, however, the hydrogen bond can not be considered as an isolated case, since the movement of the proton will affect the changes on the oxygen atom and hence neighbouring bonds. In this case, the potential energy barrier in the crystal as whole may be as high as 10 kcal/mole.

The only established example of a hydrogen bond which is symmetrical with the proton situated at the mid point is the HF⁻ ion in KHF₂, which has been studied by Westrum and Pitzer. In the
crystals, the entropy is zero at $0^\circ K$, the dielectric constant is small, and no anomalous thermal effect appears between $0^\circ K$ and $300^\circ K$. The observed $F-F$ distance is $2.26^\circ A$, the shortest hydrogen bond known, and this is quite close to the value of $2.20^\circ A$ which Donohue has calculated for a symmetrical $F-H \cdots F$ bond. The bond energy of 27 kcal/mole is much higher than the longer hydrogen bonds (4 to 6 kcal/mole). The symmetrical position of the proton is also confirmed by the neutron diffraction and by the existence of three characteristic infra-red vibration frequencies corresponding to the three modes of vibration of the $F-H \cdots F$ system.

Assuming that the same relation holds for $O-H \cdots O$ bonds, Donohue has calculated that the $O-O$ distance for a symmetrical $O-H \cdots O$ bond should be $2.30^\circ A$. No $O-H \cdots O$ bond as short as this has yet been observed, the shortest is $2.44^\circ A$ in the nickel and palladium complexes of dimethylglyoxime. Rundle and Parasol have suggested that this bond is symmetrical but no confirmation of this has been carried out. Certain other $O-H \cdots O$ systems provide conditions in which the bond may be symmetrical, for example, the hydrogen maleate ion.
Dunitz, Levy and Hadzi\textsuperscript{35-37} have examined the infrared spectrum of maleic acid, anhydrous potassium hydrogen maleate, and some deuterated derivatives, and find them to be consistent with a symmetrical structure for the above ion, but neutron diffraction and entropy measurements are required before a firm conclusion can be drawn.

1.5. THE POTENTIAL FUNCTION FOR A HYDROGEN BONDED SYSTEM:

The experimental facts discussed in the previous section permit some generalisations to be made about the shape and the nature of the potential energy function describing a particular hydrogen bond system. The probable form of the potential curves in the complex $A \_ \_ H \_ \_ B$ for different strengths of the hydrogen bonds ($H \_ \_ B$) have been discussed by Magat\textsuperscript{38} and are shown in fig.1.2. In the case of a very weak hydrogen bond, the interaction which is primarily electrostatic in character
(fig-1.2a) leads to an increase in anharmonicity of the A—H bond. This is indicated by a decrease in the characteristic vibration frequency of the A—H group in the infra-red. When the hydrogen bond interaction becomes pronounced, corresponding to the case where a small potential energy barrier separates the two potential minima, the hydroxyl stretching frequency may be split due to tunnelling of the protons between the two minima. Blinc and Hadzi have studied the splitting of the OH bands due to tunnelling of protons and have obtained satisfactory agreement between observed and calculated frequencies in acid phosphates and related compounds.

When the potential energy barrier disappears as a result of still closer approach of the oxygen atoms, a potential energy trough with a marked anharmonicity may result as in fig-1.2c. This type of hydrogen bond was first envisaged by Ubbelohde from a study of thermal expansion of many hydrogen bonded crystals. When a crystal is heated the force with the greatest anharmonicity will in general show the greatest expansion, and it has been shown that several crystals which have a large isotope expansion of the hydrogen bond also show a large thermal expansion along the direction of the hydrogen bond.

Several attempts have been made to derive a potential energy function which will account for all these observations.
The most successful so far is that of Lippincott and Schroeder who have proposed a function based on a one-dimensional model of the hydrogen bond. In this, it is assumed that the hydrogen bond consists of a strong and a weak OH interaction, the strong bond being slightly stretched, and the weak bond highly stretched (fig-1.3). The potential energy of the system is assumed to consist of four parts:

1. $U_1$  
   the energy of the strong OH bond

2. $U_2$  
   the energy of the weak H....O bond

3. $U_3$  
   the Van der Waals repulsion energy of the oxygen atoms

and

4. $U_4$  
   the electrostatic attraction between the two oxygen atoms.

The potential energy is given by:

$$U = U_1 + U_2 + U_3 + U_4$$

![Diagram](image-url)
with, \[ U_1 = D \left[ 1 - \exp \left( -\frac{nr^2}{2R} \right) \right] \]

where,

\[
D = \text{dissociation energy of the strong OH interaction}
\]

\[
\Delta r = \text{the amount of stretching of the bond i.e. } r - r_0,
\]

\[
r_0 = \text{the equilibrium distance of OH}
\]

\[
n = \frac{K_0r_0}{D},
\]

and

with

\[
U_2 = -D \left\{ \exp \left[ -n^*(R - r - r)^2/2(R - r) \right] \right\}
\]

The asterisk is used to identify the properties of the weak, highly stretched OH interactions. \( R \) is the O...O distance and the other symbols have their usual significance.

and

\[
U_3 = A \exp \left( -bR \right)
\]

\[
U_4 = -B/R^m
\]

where \( A, B, b, \) and \( m \) are constants

Using this potential function, Lippincott and Schroeder have been able to obtain very good agreement between calculated and observed values of :
Fig 14 Plot of the interaction energy $E$ against the hydrogen bond length $A^\circ$
i. O—H distance as a function of O...O distance

ii. O—H frequency shift as a function of O...O distance,

and

iii. hydrogen bond energy as a function of O...O distance.

The calculated interaction in the O—H ... O system when plotted against H-bond length is found to have a minimum value around 2.70Å, this value therefore, being the preferred bond length. This is consistent with the fact that there are a large number of hydrogen bonded solids with H-bond length around this value45 (fig-1.4.).

One of the most interesting tests of the Lippincott model is the calculated curve of potential energy as a function of O—H ... O distance. Figure-1.5a, shows that the curve obtained for the short hydrogen bonds in oxalic acid dibydrate, and it is seen that no double minimum is obtained, but that the curve exhibits a large departure from parabolic form. This large anharmonicity has already been inferred from experimental data.

Lippincott has also calculated the potential energy curve for the motion of protons in ice (fig-1.5b). This shows the
FIG 15a THE POTENTIAL ENERGY CURVE FOR MOTION of HYDROGEN ATOM in OXALIC ACID DIHYDRATE

FIG 15b THE POTENTIAL ENERGY CURVE FOR MOTION of HYDROGEN ATOM in ICE
double minimum referred to earlier in the section. The hydrogen bond in ice resembles the long hydrogen bond in oxalic acid dihydrate, being of comparable length. It is, therefore, supposed that a similar type of curve would be obtained for these long bonds. The anharmonicity in the lower potential energy trough in this latter case is much less than for the short hydrogen bond, so that when the crystal is heated, the short bonds expand more readily than the long. This is in accordance with the experimental observation.

Pauling and others consider that the Lippincott function is empirical only, and Lippincott has stated that further calculations are being carried out to test the model further. On present information, however, it gives satisfactory qualitative and quantitative agreement with the ideas presented in this section on the nature of the hydrogen bond in crystals.
CHAPTER TWO

IONIC CONDUCTION AND DIFFUSION MECHANISMS IN SOLIDS
2.1. EQUILIBRIUM PROPERTIES OF DEFECT CRYSTALS

Much of the present day understanding of reactions and transport phenomena in crystals is derived from the classical work of Schottky, Wagner, Frenkel and others in the period about 1920-30. These workers were the first to realise the importance of lattice defects in the behaviour of solids, and put forward the fundamental ideas which are still the basis of current theories.

In ionic crystals, three kinds of lattice defect may be distinguished:

i. Interstitial defects, formed when an ion vacates its normal site and occupies a metastable position between the positions of minimum potential energy. This type of defect, consisting of the interstitial together with the vacancy is called a Frenkel Defect.

ii. Vacancy Defects, caused by unoccupied lattice sites. In this type, there are no interstitials, the ions simply being missing from the lattice. In order that the crystal remains electrically neutral, equivalent numbers of cation and anion vacancies must exist. This type of defect is known as a Schottky Defect.

iii. Substitutional Disorder in which lattice positions are occupied by foreign atoms.
In addition to these primary defects, electronic defects may occur, such as when there are excess electrons in the conduction band of the crystal. These and other electronic defects are of great importance in a study of the behaviour of semi-conductors, but do not affect conduction and diffusion processes in simple ionic crystals in the same way as do the types described above.

Any pure stoichiometric crystal in thermal equilibrium above 0°K must necessarily contain defects, since although energy is necessary for their formation, this leads to an increase in entropy, and therefore a lower Gibbs free energy of the crystal. The number of defects present may be derived by considering the formation process as the analogue of a chemical reaction. Thus for a Frenkel defect the process is

\[
\text{Ion on lattice point} + \text{UnoccupiedInterstitial position} \rightarrow \text{Ion in Interstitial position} + \text{Vacant lattice point}
\]

Application of the Law of Mass Action gives:

\[
\frac{n_i n_v}{(N - n_v)(N_i - n_i)} = K \ldots 2.1
\]
where,

\[ n_i = \text{number of ions in interstitial positions per unit volume at equilibrium} \]

\[ n_v = \text{number of vacancies per unit volume at equilibrium} \]

\[ N = \text{total number of ions (or total number of lattice sites)} \]

\[ N_i = \text{total possible number of interstitial sites} \]

For Frenkel disorder \( n_i \) must equal \( n_v \), and if the degree of disorder is small so that \( n_i \ll N N_i \) then

\[ n_i^2 = KN_i N \]

If \( E_i \) is the energy required to form the Frenkel defect then

\[ K = \exp \left( - \frac{E_i}{kT} \right) \]

whence,

\[ n_i = \sqrt{NN_i} \exp \left( - \frac{1}{2} \left( \frac{E_i}{kT} \right) \right) \]

A similar treatment for the formation of Schottky defects gives the equation
where, $E_v$ is the energy required to form both a cation and an anion vacancy, $n_v$ is the number of vacancies of each type, and $N$ is the number of ion pairs in the crystal.

Equations (2.2. and 2.3.) may be derived rigorously from statistical mechanisms, and more refined treatments take into account thermal expansion and polarisation effects which arise when defects are formed.

Although it is possible in principle for several types of defect to occur in a given crystal, the energy of formation of the various types will be different, with the result that the defect with the lowest energy of formation will predominate. Thus if the energy of formation of the defect may be calculated it becomes possible to predict which form of disorder will be most likely. The first calculations of this type were made by Jost who showed that the energy required to form a defect is considerably reduced when one takes account for the resulting polarisation of the surrounding medium. Jost showed that the energy of polarisation is given approximately by the equation:

$$n_v = N \exp \left[ -\frac{1}{2} \frac{E_v}{kT} \right]$$
\[ E_{\text{pol}} = -e^4/a \left( 1 - 1/\varepsilon \right) \] \[ \ldots 2.4 \]

where 
- \( e \) = electronic charge
- \( a \) = radius of the ion
- \( \varepsilon \) = dielectric constant of the ionic crystal

This negative energy will be greater for cations than for anions on account of the larger size of anions, and as a result the overall energy \( E_1 \) to form a Frenkel defect will be greater for the anion than the cation in a given crystal. This is in agreement with the observed fact that interstitial anions are extremely rare.

In a crystal where the anion and cation are of approximately the same size, Schottky has shown that, because of the high repulsive forces encountered by interstitial ions, Schottky defects are energetically preferred to Frenkel defects. When however, the difference in ionic size is appreciable, there is relatively more room for the small ion (usually the cation) in the interstitial position, so that the repulsive forces are not so great. This condition favours Frenkel defects, particularly in crystals with a high dielectric constant, since equation 2.4. shows that the stabilisation
is greater, the greater the value of $\mathcal{E}$.

Schottky disorder is therefore favoured in crystals such as alkali halides where the ionic sizes are not appreciably different and the dielectric constant is not particularly high. Frenkel disorder on the other hand requires considerable disparity of ionic size and high dielectric constant, conditions which are obtained in the silver halides.

2.2. IONIC CONDUCTIVITY IN CRYSTALS

When an E.M.F., is applied across an ionic solid, the current which flows may be carried in the solid by electrons, positive holes, cations or anions. The motion of electrons and positive holes is of importance in the field of semi-conductors, and the attention in this section is confined mainly to those solids which are pure ionic conductors, such as alkali halides.

The demonstration of ionic conductivity, and identification of the mobile ion is usually carried out by the method Tubandt. This method is an adaptation of the classical technique used for electrolyte solutions and is described with reference to figure-2.1.

Two slabs of the salt $M\ X$ are sandwiched between two
electrodes of metal M. When a potential is applied in the direction indicated the two following extreme possibilities exist:

i - Only the cations move:

In this case the cathode will grow at the expense of the anode, and the weight of the two slabs will remain unchanged.

ii - Only the anions move:

The $X^-$ ions then react at the M interface to form new layers of salt. Hence, the anode decreases in weight, and slab-1 increases at the expense of slab-2.

If both ions contribute to the current then the result will be intermediate between these two cases and the transport number of the two ions may be determined by weighing.

![Fig. 2.1](image-url)
A collection of transport numbers in solid salts is given in table-2.1.

**TABLE-2.1.**

TRANSMISSION NUMBERS OF SOME COMPOUNDS

<table>
<thead>
<tr>
<th>Compound</th>
<th>T(°C)</th>
<th>t⁺</th>
<th>t⁻</th>
<th>tₑ</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaF</td>
<td>550</td>
<td>1.00</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td>400</td>
<td>1.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>0.95</td>
<td>0.05</td>
<td>0.00</td>
</tr>
<tr>
<td>NaBr</td>
<td>600</td>
<td>0.96</td>
<td>0.04</td>
<td>0.00</td>
</tr>
<tr>
<td>KCl</td>
<td>600</td>
<td>0.88</td>
<td>0.12</td>
<td>0.00</td>
</tr>
<tr>
<td>AgCl</td>
<td>200</td>
<td>1.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>AgBr</td>
<td>200</td>
<td>1.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Ag₂S</td>
<td>180</td>
<td>0.01</td>
<td>0.00</td>
<td>0.99</td>
</tr>
<tr>
<td>PbI₂</td>
<td>270</td>
<td>0.45</td>
<td>0.55</td>
<td>0.00</td>
</tr>
<tr>
<td>CuCl₂</td>
<td>300</td>
<td>0.98</td>
<td>0.00</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>110</td>
<td>0.03</td>
<td>0.00</td>
<td>0.97</td>
</tr>
<tr>
<td>Cu₆O</td>
<td>1000</td>
<td>0.00</td>
<td>0.00</td>
<td>1.00</td>
</tr>
</tbody>
</table>

It is seen that halides are mainly pure ionic conductors, while sulphides and oxides are mainly electronic conductors. In the ionic conductors the current is carried predominantly by the cation, and it is only at high temperatures that contributions from the anions become significant.

The mechanism of the ionic conduction is explained in terms of the motion of the lattice defects. If the crystal lattice were perfect, i.e. with no defects, movement of the ions and hence the conductance would be negligible, since a high activation energy would be required to disrupt the perfect ionic arrangement.

However, a lattice vacancy provides a site to which an adjoining ion may hop and repetition of this process is equivalent to the motion of the ion in one direction, or to the motion of the vacancy in the opposite direction.

The movement of a defect to an adjacent position can only occur provided the ion involved has sufficient energy to surmount the potential barrier separating the two equilibrium positions. The movement of the interstitials or vacancies in an applied electric field may be treated as follows.
Let the height of the potential energy barrier be $U$. For an isotropic crystal, the activation energy required will be the same along any set of axes at right angles. If $\nu$ is the frequency with which an interstitial ion can vibrate, then the probability $q$ per unit time that a jump to an adjacent site can occur is

$$q = \nu \exp \left( - \frac{U}{kT} \right) \quad \ldots \quad 2.5$$

In the presence of an applied electric field, the potential energy barrier is lowered in the field direction by an amount $(1/2) e a E$.

where

- $e$ = the effective charge on the ion
- $a$ = the distance between adjacent sites
- $E$ = the applied E.M.F.

In the direction against the field, the potential energy barrier is raised by the same amount, and at right angles to the field, the barrier height remains unchanged as shown in fig-2.2.
Fig-2.2a  In the absence of a field, or at right angles to field

Fig-2.2b  In the direction of applied field.
The probability of the interstitial ion hopping in the field direction is now

\[ q_\rightarrow = \sqrt{V} \exp \left\{ - \left[ \frac{(U - 1/2 e a E)}{kT} \right] \right\} \text{sec}^{-1} \]

and against the field

\[ q_\leftarrow = \sqrt{V} \exp \left\{ - \left[ \frac{(U + 1/2 e a E)}{kT} \right] \right\} \text{sec}^{-1} \]

So migration of the defect in the field direction is now favoured. The overall rate of drift \( U \) in the field direction is:

\[ U = \sqrt{V} a \exp \left\{ - \left[ \frac{(U - 1/2 e a E)}{kT} \right] \right\} - \sqrt{V} a \exp \left\{ - \left[ \frac{(U + 1/2 e a E)}{kT} \right] \right\} \]

i.e., the difference in probability times distance travelled in each jump.

or

\[ U = \sqrt{V} a \exp \left\{ - \frac{U}{kT} \right\} \exp \left\{ - e a E / 2kT \right\} - \exp \left\{ e a E / 2kT \right\} \text{cm/sec} \]

\[ = \sqrt{V} a \exp \left\{ - \frac{U}{kT} \right\} 2 \operatorname{Sinh} \left( \frac{e a E}{2kT} \right) \text{cm/sec} \]

At low field strengths such as are commonly used in practice, \( e a E \ll kT \) so \( \operatorname{Sinh} \left( \frac{e a E}{2kT} \right) \) may be replaced by \( \left(\frac{e a E}{2kT}\right) \)
Hence,

\[ U = \gamma a \exp \left( - \frac{U}{kT} \right) \cdot e \frac{e}{2kT} \]

\[ = \gamma a^2 e \frac{e}{kT} \exp \left( - \frac{U}{kT} \right) \text{ cm/sec} \]

The mobility of the defect V is defined as the rate of movement under unit potential gradient.

Thus,

\[ V = \gamma a^2 \frac{e}{kT} \exp \left( - \frac{U}{kT} \right) \text{ cm/sec} \]

The conductivity \( \sigma_i \) is defined as

\[ \sigma_i = n e V \]

where,

\[ n_i \text{ is the number of interstitials per cm}^3 \]

Thus,

\[ \sigma_i = n_i \gamma a^2 \frac{e^2}{kT} \exp \left( - \frac{U}{kT} \right) \]

The number of interstitial ions/cm\(^3\) has already been shown to be

\[ n_i = \sqrt[3]{N} N_i \exp \left( - \frac{1}{2} E_i / kT \right) \]

So substituting for \( n_i \) gives

\[ \sigma_i = \sqrt[3]{N} N_i \gamma a^2 e^{2/kT} \exp \left( - \frac{1}{2} E_i / kT \right) \exp(-U/kT) \ldots 2.6 \]

This equation is of the form

\[ \sigma_i = \sigma_o \exp \left( - \frac{E}{kT} \right) \ldots \ldots 2.7 \]

where,

\[ E = \left( U + \frac{1}{2} E_i \right) \]
The form of this equation shows that a plot of \( \ln \sigma \) against \( 1/T \) should be linear, with slope \(- (U + 1/2E_1)/k\)

\[ \text{[or} - (U + 1/2E_v)/k \text{depending on the type of defect present.]} \]

Experimentally it is usually found that a plot of \( \log \sigma \) against \( 1/T \) for ionic crystals is linear over a limited temperature range only. Over an extended temperature range however, the graph invariably shows a break, dividing it into two distinct portions as shown in fig-2,3. Such a graph may be represented by the equation

\[ \sigma' = a \exp \left( -E_1/kT \right) + b \exp \left( -E_2/kT \right) \]

where, \( a < b \), and \( E_1 < E_2 \).

The conduction in the high temperature region is reproducible and independent of previous thermal treatment, whereas in the low temperature region, the results are much less reproducible and are very sensitive to previous sample treatment and the degree of purity. The results at high temperature confirm that conduction takes place by a simple activation process, and the composite activation energy \((U + 1/2E)\) may be determined from the slope of the line.

Several explanations have been put forward to account for the low temperature region. Smekal has suggested that the low activation energy is due to migration of ions along internal cracks or grain boundaries the arrangement of which will be
Fig 2.3 The temperature dependence of the ionic conductivity of some alkali halide (KCl).
irreproducible and very dependent on thermal treatment.
Although this suggestion was superceded by others, it has never
been ruled out, and still remains a valid explanation in the
light of more recent studies on dislocations in crystals.

The currently accepted view of the low temperature region
is that the lower activation energy is due to the presence
of divalent impurities in the crystal. Great advances have
been made since about 1948 in the production of ultra pure
solids for semi-conductor work and this has led to increased
awareness of the presence and effects of significant amounts
of impurities in solids used for the earlier conductance work.

If divalent cations exist as an impurity in, for example,
NaCl, then to preserve electrical neutrality a Na⁺ ion
must be omitted for every divalent impurity cation present.
These impurity controlled defects will be present at all
temperatures in the same concentration, but their effect on
conduction will be much more marked at lower temperature
where the number of thermally controlled defects is small.
Under these conditions the conduction may be expected to follow
the equation
\[ \sigma = \sigma_0 \exp \left( - \frac{U}{kT} \right) \]

The observed activation energy being that for migration of defects already present due to the impurities.

At higher temperatures the number of thermal defects becomes relatively more important, and the conductivity follows the expression

\[ \sigma' = \sigma_0 \exp \left( \frac{U + \frac{1}{2} E_v}{kT} \right) \]

This interpretation gives a method for measuring separately the energy of defect migration $U$, and the energy of formation $E_v$, since these two quantities may be obtained from the slopes of the higher and lower temperature regions of the experimental plot.

This explanation of the break in the conduction curve may be substantiated experimentally by showing that the conductivity of an ionic crystal may be varied in the low temperature region by deliberately incorporating altervalent ions in the lattice. A convincing demonstration of this has been carried out by Etzel and Maurer who measured the conductance of NaCl crystals containing known amounts of Cd$^{++}$. Their results are shown in Fig 2.4, which shows that the conductance of NaCl increases progressively with increase in Cd$^{++}$ content, but the slope of the
Figure 2.4 Temperature dependence of the ionic conductivity of NaCl containing foreign ions.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Mol ratio Cd/Na $10^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>686</td>
</tr>
<tr>
<td>B</td>
<td>19</td>
</tr>
<tr>
<td>C</td>
<td>1</td>
</tr>
<tr>
<td>D</td>
<td>0</td>
</tr>
</tbody>
</table>

Conductivity in ohm cm.
plot remains constant, indicating that the effect is determined entirely by the preexponential factor, and that a single activation energy is involved. Kelting and Witt have carried out a similar study of KCl doped with various amounts of Sr and their results are shown in Fig-2. Again the slopes in the low temperature region are similar, and all the plots merge into a single line at higher temperatures.

Another mechanism involving the interaction of lattice defects to form associated complexes has also been considered to affect the low temperature region of the conduction. This will be referred to in the next section.

2.3 SELF DIFFUSION IN IONIC CRYSTALS

In the absence of an applied electric field it is still possible for ions to move through the crystal by the process of self-diffusion, and this process is also assumed to occur by migration of interstitial or vacancy defects. The expression for the diffusion rate may be derived using the same model as in the previous section.

Consider two parallel planes AB and CD in a crystal separated by a distance "a" equal to the distance between adjacent interstitial (or lattice) positions fig-2.6.
The ionic conductivity of KCl crystals containing various amounts of SrCl₂. In units of $10^{-5}$ the numbers refer to the following mole fractions: $M_1 = 0.7$, $M_2 = 6.1$, $M_3 = 35$, $M_4 = 1.9$, $M_5 = 12$, $M_6 = 1.0$, $M_7 = 0$. 

Fig. 2.5
Let there be $n_1$ interstitial ions/unit area in plane AB and a concentration gradient $dn_1/dx$ in the direction $X$.

Thus in the plane CD there will be $[n_1 + a(dn_1/dx)]$ interstitial ions per unit area.

The number of interstitials in the unit of volume EFGH is $n_1a$ and in the volume GHKL is $[(n_1 + a dn_1/dx) a]$, a difference in concentration of $a^2 dn_1/dx \text{ cm}^{-3}$. If $q$ is the probability that an interstitial ion may hop, then the total number crossing the volume ABCD will be:

$$q.a^2 \cdot dn_1/dx, \text{ cm}^{-3} \text{ sec}^{-1}$$

The rate of diffusion is assumed to follow Fick's law which may be formulated as
\[
dn_1/dt = D \cdot dn_1/\ dx^2
\]

where,

\(D\) is the diffusion coefficient.

The rate at which interstitial ions cross the plane \(GH\) is therefore,

\[
dn_1/dt = q \ a^2 \ d^2n_1/dx^2
\]

so that the diffusion coefficient for interstitial ions \(D_1\)

\[
D_1 = q \ a^2
\]

as in the previous section

\[
q = \sqrt[\gamma] \ exp \ ( - U / kT )
\]

so

\[
D_1 = \gamma \ a^2 \ exp \ ( - U / kT ) \ cm^2\sec^{-1} \ldots 2.8
\]

At a given temperature, the total diffusion in the solid will be proportional to the fraction of ions which are in interstitial positions, i.e.,

\[
D = (n_i/N)D_1
\]

Combining this with equation 2.8., and substituting for \(n_i\) from equation 2.2. gives
which is of simple form

$$D = D_0 \exp \left( \frac{E}{kT} \right)$$

where,

$$E = \left( U + \frac{1}{2} E_c \right)$$

Again, as in the previous section, a similar expression may derived for diffusion of vacancies, and modifications may be introduced to take account of the thermal expansion and other effects.

Equation 2.10 is of the same form as that derived for the ionic conductivity, and many experimental studies have confirmed the linear relationship between log $D$ and $1/T$. This type of plot frequently shows a break similar to that found in conductivity results, and the diffusion measurements are also interpreted in terms of the two activation energies $U$ and $E_i$ (or $E_v$).

The experimental study of self diffusion in ionic crystals requires the use of a radioactive tracer technique. A thin layer of labelled material is usually applied to the surface of a
single crystal by vacuum evaporation, and the tracer ions
allowed to diffuse into the crystal for a known time
at constant temperature. The concentration of tracer at various
distances into the crystal is then determined so that a solution
to the diffusion equation may be obtained. The technique commonly
used is to remove slices of the solid of known thickness and to
count the activity either of the removed material or of the
remaining crystal. Microtome techniques are mostly used
for sectioning ionic crystals; precision grinding in special
lathes and other devices is also used, but this is more
suitable for metals and alloys.

If \( n^* \) is the concentration of radioactive ions/cm\(^3\) at a
distance \( x \) into crystal. Then Ficks law may be written as

\[
\frac{dn^*}{dt} = D \frac{d^2 n^*}{dx^2}
\]

The solution to this equation is of the form

\[
n^*(x,t) = \frac{n_0}{A} \exp \left( -\frac{x^2}{4Dt} \right)
\]  

where, \( t \) is the annealing time, \( n^* \) is
the initial activity at the surface,
and \( A \) is a constant.
If the diffusion process obeys Fick's law then a plot of \( \ln n^*_{(xt)} \) against \( x^2 \) should be a straight line with a slope \( 1/4Dt \), so that if \( t \) is known, \( D \) may be calculated.

2.3. THE RELATIONSHIP BETWEEN IONIC CONDUCTION AND DIFFUSION

Equation 2.6 for the conduction due to motion of a defect is

\[
\sigma = (N N_i^0)^0 \sqrt{a e^2 / kT} \exp \left\{ \frac{U + 0.5 E}{kT} \right\}
\]

and equation 2.9 for the diffusion of the defect is

\[
D = (N_i / N)^{0.5} \sqrt{a e^2} \exp \left\{ \frac{U + 0.5 E}{kT} \right\}
\]

Provided that the same type of defect (interstitial or vacancy) is responsible for both conduction and diffusion then the following simple relationship is obtained between \( \sigma^3 \) and \( D \)

\[
\frac{\sigma^3}{D} = \frac{N e^2}{kT} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad 2.12
\]

This is known as the Einstein Relation, and its verification provides additional information about the defect properties of
the solid.

When only one kind of defect is responsible for the transport in the crystal, and in the absence of other complicating factors, the Einstein Relation has been verified for many solids. As a typical example of a diffusion study the results of Mapother, Crooks, and Maurer on NaCl may be cited; in this work, the conduction and the diffusion were measured independently over a range of temperature on the same single crystal samples. The self-diffusion coefficient of the sodium ions was determined by using $^{23}$Na; fig. 2.7., shows a plot of the observed diffusion coefficient, together with values calculated from the observed conductivity. The close agreement between the different measurements confirms that in NaCl, diffusion and conduction process are due to the migration of one type of defect only.

The Einstein relation is not always obeyed, because one or several complicating factors may be operative in the transport process. Even in some apparently simple diffusion mechanisms it is sometimes necessary to modify the relation to

$$\frac{\sigma}{D} = f \left[ \frac{N \Theta}{kT} \right]$$

where $f$ is a correlation factor which is less than unity.
Fig 2.7- Temperature dependence of self-diffusion coefficient of sodium in sodium chloride. Directly measured.

- Calculated from measured conductivity
This is due to the fact that an ion, having arrived at a previously vacant site B by hopping from a neighbouring site A, now has a greater probability of returning to A than to any other neighbouring site. A will certainly be vacant, but whether or not the other sites are vacant is purely a matter of chance. "Forward and backward" jumps such as this do not contribute to diffusion, but will of course contribute to the conductivity.

In crystals containing Schottky defects, the cation and anion vacancies have a mutual attraction, and will tend to form a double vacancy or vacancy pair, with adjacent ions missing from the lattice. This vacancy pair is a neutral entity, and under an applied E.M.F., will not contribute to conductivity. Its random motion through the crystal does contribute to diffusion, and so the existence of vacancy pairs also leads to a breakdown in the Einstein relation. This deviation will be in the sense that D calculated from conductivity will be less than D obtained directly from experiment. Fig.2.7. shows that in the lower temperature region of NaCl the calculated D is in fact less than observed D, in agreement with the above. At higher temperatures the deviation from the Einstein relation disappears because the vacancy pairs tend to dissociate into single vacancies.
This chapter has presented briefly some of the ideas which are used in dealing with the defect properties of ionic crystals. No attempt has been made to include effects arising from mobile electrons and electronic defects, which can if present, add a further complication to the interpretation of experimental data. Most of the experimental work has been carried out on alkali halides, silver halides and some oxides and sulphides of metals such as copper, iron, silver, etc. Although the mechanism of ion movement in these crystals is fairly well understood it is difficult to make broad generalisation about other materials, and past experience has shown that the behaviour of each solid or group of related structures must be interpreted in terms of its own experimental data.
CHAPTER THREE

PLAN AND OBJECT OF THE RESEARCH WORK
The work on ionic conduction in solids referred to in the previous chapter, has shown that in solids such as the alkali halides, electrical conduction is due mainly to motion of cations. Virtually no work has been reported on ionic conduction in hydrogen bonded solids such as $\text{KH}_2\text{PO}_4$, $\text{KHF}_2$ etc. In salts containing two types of cation, one which is a proton, e.g. $\text{KH}_2\text{PO}_4$, it is to be expected that conduction will be due to motion of the proton rather than the $\text{K}^+$. This is also expected to be so far a crystal such as an organic acid where the larger anions are the main structural units of the lattice. In a salt such as $\text{KHF}_2$, conduction due to $\text{K}^+$ or $\text{H}^+$ depends on whether the $\text{HF}_2^-$ ion behaves as a complex anion or whether the proton can be separated easily from it.

In a hydrogen bonded crystal, motion of a proton through the lattice will be conditioned by the force field of the H-bonds present. One may therefore expect that conduction data in such crystals will yield information about the role of the H-bonds in the solid, but little work has been done in this field. Pollock and Ubbelohde have reported some measurements of conduction in a number of organic acids, but their measurements
did not identify the charge carriers, and so the possibility of electronic conduction has not been excluded. Furthermore, this work did not include measurements on deuterated acids, and from the introductory work described in Chap. I it is evident that some significant differences between H and D bonds might be found.

The object of this present work is therefore to measure the electrical conduction of a number of hydrogen bonded solids covering a range of H-bond types with comparative measurements on the deuterated compounds. These measurements may then be treated by the same procedures as for other ionic conductors [see sec. 2(2)] and in principle it should then be possible to obtain activation energies which are related to the H-bond system of the crystal.

In attempting to treat conduction data in this way, it is necessary to demonstrate that the protons do in fact move through the crystal. This requires D.C. Electrolysis measurements on the solids to show that hydrogen may be evolved at the cathode, and also to correlate the amount of gas produced with the quantity of electricity passed through the crystal.
Most of the experimental work on solid ionic conductors has been carried out using D.C. This inevitably leads to polarisation effects with the result that steady currents through the solid cannot easily be obtained\(^5\). In this research, it has been decided to use 1600 C.P.S. A.C. to avoid polarisation.

Complimentary information about the motion of a proton through a crystal may be obtained from a study of the diffusion of tritium. The principles and techniques involved in this have been described in Sec.2.(3). It is a further object of this work to try and measure diffusion rates in H-bonded crystals to find out if results can be obtained which agree with electrical conduction work. It is recognised that a significant isotope effect is to be expected in tritium diffusion i.e. the rate of diffusion of \(^3\)H may be different from \(^1\)H, but the information which may be obtained about this cannot be fully judged until measurements have been made.
CHAPTER FOUR

EXPERIMENTAL METHODS
4.1. PURIFICATION OF MATERIALS

All substances (KHF₄, KI₆PO₄, NH₄H₂PO₄, and oxalic acid dihydrate) were purified by crystallising three times from deionised water. A.R. substances were used for this purpose. Where possible single crystals were grown from the third batch of the crystallisation.

KH₆AsO₄ was prepared by neutralising ignited K₂CO₃ (A.R.) with an equivalent amount of As₂O₃ in hot distilled water. Owing to silicate impurities in the As₂O₃, the solution had to be filtered and the amount of As₂O₃ corresponding to the weight of insoluble residue was then added in the second crystallisation. The KH₆AsO₄ was recrystallised three times from deionised water. Finally greenish white crystals of KH₆AsO₄ were obtained, filtered, dried and kept in a desiccator.

4.2. PREPARATION OF DEUTERATED SUBSTANCES

KH₆PO₄, NH₄H₂PO₄, and oxalic acid dihydrate were deuterated as follows:

A known amount of the substance was taken in a dry flask and known amount of 99.97% D₂O, sufficient in volume to dissolve

* KHF₄ was crystallised in a polythene vessel because it dissociates to KF and HF, and reacts with glass.
the substance at room temperature, was added. The flask containing the substance in heavy water was slightly warmed to ensure complete dissolution and this diluted heavy water was distilled off (A) under vacuum. This process was repeated and finally the substance was redissolved in 99.97% heavy water and single crystals were grown by slow evaporation in a dry box. The deuterium content of the substance thus obtained was calculated from the volume of the heavy water used and the amount of the substance taken, and was found to be 99.97% D.

In order to use the minimum quantity of pure heavy water the diluted D₂O (A) obtained from preliminary crystallisations was used several times for different substances, until its deuterium content fell to about 60% D.

Pollock has confirmed experimentally that when furoic acid is deuterated in the manner stated above, the theoretical calculation of enrichment agrees with the experimental value.

A similar method was used for deuterating KH₄AsO₄ except that before adding heavy water the substance was heated to 200°C under vacuum to dehydrate the substance; the reaction then follows the scheme:

\[
\text{KH}_4\text{AsO}_4 \xrightarrow{\text{HEAT}} \text{KAsO}_3 + \text{H}_2\text{O} \\
\text{KD}_2\text{AsO}_4 \\
\]

31
KHF$_2$ was not deuterated by the distillation technique because during distillation of heavy water from KDF$_2$ under vacuum it is possible to lose DF, leaving KF instead of KDF$_2$. KDF$_2$ was thus prepared in a dry box by three slow crystallisation in a polythene bottle, using each time 99.97% D$_2$O.

4.3. PREPARATION OF KAg$^{110}$ (CN)$_2$ FOR USE IN A SILVER COULOMETER

AgNO$_3$ (6.4509gms A.R.) was dissolved in deionised water (10.0ml) and Ag$^{10}$ NO$_3$ (50-micro-curies) was added to it. KCN (2.4481 gms A.R.) was then added to this solution to precipitate Ag$^{110}$ CN. The solution was filtered and the precipitate washed several times with water to remove any traces of Ag$^{10}$ NO$_3$. Pinkish coloured substance was thus obtained, which was dried and kept in a desiccator.

1% KAg$^{10}$ (CN)$_2$ solution was made by dissolving Ag$^{110}$ CN (3.8774 gms) and KCN (1.4680 gms) in 300.0mls of deionised water.
4.4 PREPARATION OF SAMPLES FOR CONDUCTANCE MEASUREMENTS

Single crystals are always preferable to polycrystalline samples in conductance measurements and diffusion work, but in some cases (e.g. KHF$_2$ and oxalic acid dihydrate) it was found difficult to grow large single crystals. In most of the d.c., electrolysis work therefore, compressed discs of polycrystalline materials were used. These discs were made with a press and die of the type conventionally used for preparing KBr discs for spectroscopic work. The powdered material was added to the die in a dry box followed by pumping under vacuum for several hours, and the disc prepared by pressing at 25 tons/sq. inch. Only a brief pumping period was used for oxalic acid dihydrate to avoid surface dehydration.

4.5 ELECTROLYSIS OF SOLIDS

The detection and measurement of proton conduction in solids involves d.c. electrolysis of the crystal, to determine whether or not hydrogen is evolved at the cathode, and to measure the amount of gas evolved in relation to the quantity of electricity passed through the crystal.
The same technique has been applied to all the solids studied and is discussed below:

Various designs of electrolysis cell were tried before the type shown in fig-4.1, was finally adopted. The cell was made from a B-34 cone/socket, the cone having a ground face X against which the pellet or crystal of the substance was cemented with a small amount of Araldite Epoxy Resin around its circumference.

Electrical contact with the two faces of the pellet was made by mercury in the tube-A and in the body of the socket-B; in these experiments A was made the anode and B the cathode. Any evolution of hydrogen from the pellet into B causes a displacement of the mercury in the capillary tube C, the position of the mercury is followed with a travelling microscope. The gas collects in the small bulb E, and is always under constant pressure. The whole assembly was immersed in a thermostat controlled to 0.01°C. The side arm F joined to the socket isolates the platinum contact of the cathode compartment from the thermostat liquid. After electrolysis, any gas which has collected may be removed for analysis by rotating the whole cell through 180° and pumping out through tap Y.

After having attached the pellet to the cone-X with Araldite, the cell was left in dry air for one day to form a hard araldite surface. The cell was then assembled and evacuated...
hard for one day to remove any moisture adsorbed on the surface of the sample (with oxalic acid dihydrate a very brief evacuation was performed). The cell was then filled with dry mercury up to the mark shown in figure-4.1., and left in the thermostat to reach temperature equilibrium. A silver coulometer (using radioactive silver-110) was joined in series with the electrolysis cell, and a voltage of about 100 volts applied to the system from a stabilised d.c., power supply (this applied voltage was different for different substance used). Before starting the electrolysis the position of the mercury meniscus was checked as a function of time to ensure a steady state. During electrolysis, the movement of the mercury and the current flowing through the pellet were recorded as a function of time.

4.6. MEASUREMENT OF THE QUANTITY OF ELECTRICITY PASSED THROUGH A CRYSTAL

When a potential of 100 volts d.c., was applied to the specimen in the electrolysis cell, a current of the order of the one micro-amp flowed through the solid. This current was not constant with time and eventually decayed to zero. Typical time/current plots are shown in fig-4.2. A conventional silver coulometer was used initially to measure the quantity of electricity passed through the sample, but it was found that the change in
weight produced in the silver cathode was too small to measure with accuracy.

For this reason a coulometer using a radioactive tracer technique was developed. This coulometer used as electrolyte, a solution of silver argentocyanide, labelled with silver-110. Silver was chosen as a cation because silver-110 has a long half life and decays by a reasonably strong β-emission, which is helpful in the counting technique. Furthermore Sharan has reported that silver-110 can be deposited on the electrode as much as 99.98%, using even carrier free silver nitrate solution labelled with silver-110. Silver argentocyanide solution was used because it gives a thin strongly adherent film of silver on the electrode, which can be counted easily. The coulometer was constructed and calibrated as shown in fig-4.3. The body of the coulometer was machined from a nylon block, with a close fitting platinum anode inserted at A. The cathode was a 16 mm diam copper disc, the size chosen to fit in the counting planchet under a Geiger Müller counter (MX-123). The lead and one side of the disc were coated with insulating paint, so that deposition occurred on one side only. The coulometer was calibrated by passing known quantities of electricity through it, and counting the resulting activity.
Fig. 4.3 A Silver Coulometer For Measuring Small Currents
produced in the cathode.

The current flowing through the coulometer during calibration was determined by measuring the potential across a standard resistance in series with the coulometer. The potential was measured with a Pye 7601 potentiometer and the time for which the current flowed was measured directly to $10^{-8}$ sec., with a Labgear decatron counter which was started and stopped by the same switch which controlled the current. Small currents about 0.5 milli-amp were used to minimise heating effects in the coulometer, and the constancy of the current was observed by measuring the potential across R at regular intervals.

After each calibration-experiment the copper cathode was washed in deionised water to remove any traces of silver-argentocyanide (labelled with silver-110), disconnected from the lead and mounted with wax on a counting tray with the active side upwards. The activity of the copper plate was measured with an end-window G.M. counter (MX123 type for which the working conditions had been found by normal methods). The total quantity of electricity passed through the coulometer calculated from the current and the time, was converted into an equivalent volume of hydrogen which would have been evolved at N.T.P., using Faraday's Laws of electrolysis. A graph was
Figure 4.4: Activity of $\text{A}_{2}\text{O}$ deposited on Cu disc ~ Volume of Hydrogen evolved.

Volume of H$_2$ at N.T.P (ml x 10$^{-2}$)

C.P.M. x 10$^2$
plotted of "theoretical" volume of hydrogen evolved against activity produced on the cathode disc. This graph (fig-4.4) was then subsequently used to correlate the actual quantity of gas evolved during electrolysis of a hydrogen bonded crystal with the quantity of electricity passed.

4.7 IDENTIFICATION OF GAS PRODUCED DURING ELECTROLYSIS OF SOLIDS

The gas evolved on the electrolysis of hydrogen bonded crystals was shown qualitatively to be hydrogen, by injecting into a freshly prepared palladium chloride solution (1.1%). A black precipitate of palladium was observed, but this method was not useful for quantitative estimation. In subsequent experiments gas chromatography was used employing a Katharometer detector. A column (7 metre long, 7 mm diameter) was filled with Linde 5A°, molecular sieve. Before filling the column, the molecular sieve (calcium aluminium silicate) was activated by heating to 300°C for three hours under an atmosphere of argon and was then cooled. The gas to be analysed was diluted with argon carrier gas and admitted to the column using a special technique as shown in fig-4.5. The temperature of the column was kept at 30°C with a flow rate of argon of 80ml/hr.
The injection of gas was carried out as follows. In fig-4.5
A, is a sampler which fits on to the electrolysis cell at the
tap Y (fig 4.1) and to which all the gas evolved in the electrolysis
is transferred by pumping out under vacuum. The carrier gas comes
via D from one arm of the detector and then passes via B
to the column. When the system has reached equilibrium, the taps
are turned so that the carrier gas sweeps the contents of the tube
A into the column.

It was observed that if air was injected through C, two
peaks were obtained on the pen recorder which were later shown
to be due to oxygen and nitrogen. When pure hydrogen
was injected a peak before oxygen and nitrogen was observed.
These peaks come after about three minutes from injection (fig-4.6).
The gas evolved on electrolysis gave exactly the same retention
time as a sample of pure hydrogen.

To find the amount of hydrogen produced during the electrolysis
the column was calibrated by injecting various known volumes of
pure hydrogen, and drawing a calibration graph of recorder peak
height against amount of the hydrogen injected at N.T.P.
The amount of hydrogen injected was determined by filling
the gas sampler A with pure hydrogen at different pressure.
The volume of the sampler was determined by weighing the mercury
which filled it completely. The graph between the peak height
Fig 4.6 Gas Chromatogram Of Air
Fig. 4.7 Peak height against volume of hydrogen.

Volume of hydrogen at N.T.P. in 10 ml.
and the corresponding volume of hydrogen at N.T.P., gave a straight line shown in fig-4.7 from which the volume of the hydrogen evolved in the electrolysis was obtained.

4.8 A.C. CONDUCTANCE OF SOLIDS

The a.c. conductance of the crystals and the pellets was measured by using the cell shown in figure-4.8. The specimen was sandwiched between two flat platinum electrodes A, to each of which was a long platinum lead B. These platinum wires were enclosed in capillary tubes and the entire assembly was held under slight pressure with two P.T.F.E., discs-C. A copper constantan thermocouple D was also enclosed in a glass tube with the junction just touching the platinum disc. The whole cell was then assembled in a glass vessel which can be evacuated through tap-E. The exits from the vessel were sealed with Araldite Epoxy resine. The cell was then inserted in a cylindrical furnace in which the temperature was controlled by a variable transformer. The cell was first evacuated hard to remove any moisture on the surface of the sample and dry air was then admitted and tap-E closed.

The a.c., conductance was measured with a Wayne-Kerr B-221 Transformer Ratio Arm Bridge, which directly gives the conductance
of the sample. The specific conductance was worked out from the dimensions of each sample, which could be measured accurately with a micrometer, the diameter being fixed to 16 mm. The conductance measurements were taken for several heating and cooling cycles for each sample. The activation energy was obtained from the slope of the straight line obtained by plotting the logarithm of specific conductance against $1/T^\circ K$. The best slope was determined by the method of least squares, using a digital computer.

4.8 PREPARATION OF TRITIUM LABELLED AMMONIUM DIHYDROGEN PHOSPHATE

A saturated solution of labelled ammonium dihydrogen phosphate ($\text{NH}_4 \, \text{H}_2 \text{PO}_4$) was prepared by dissolving 1.08 gm purified ammonium dihydrogen phosphate in a small amount of water containing 5.5 milli-curies of tritium. The dissolution was assisted by gentle warming and the solution was then cooled and kept in contact with the crystallised salt.

* For crystals log of conductance was plotted against $1/T^\circ K$
4.9 TECHNIQUE USED IN DIFFUSION EXPERIMENTS

The techniques described here were carried out on single crystals of ammonium dihydrogen phosphate. This choice was determined by the readiness with which good single crystals of this material may be obtained.

For the sectioning of the sample in diffusion experiments a Base Sledge Microtome (Measuring and Scientific Equipment Ltd., London) was taken as being the most suitable for this type of work. This instrument has a very rigid base and specimen transport mechanism, but the sample holding device supplied is designed mainly for biological specimens and was quite unsuitable for holding single crystals. The microtome was adapted for single crystal work by making the sample holder illustrated in fig 4.9.

The funnel A was machined from brass, and was mounted on three levelling screws B on the base plate C. This base plate was attached to the microtome instead of the usual sample holder, and the funnel and base plate assembly could then be moved in a vertical direction using the microtome ratchet mechanism, which allowed vertical movement in steps of one-micron.

The crystal specimen D was cemented to a removable anvil E which was a close fit on the spindle F. A locating screw ensured that the anvil and crystal were always replaced in the
FIG 4.9  Schematic Diagram for Sectioning

Single Crystal
same orientation.

With this microtome, the knife remains stationary, and the sample is sectioned by moving it past the knife blade G. The material which was removed in each slice (usually 5-micron thick) fell into the funnel and was transferred to the counting bottle mounted at H. To facilitate quantitative removal of the sectioned material, the inside surface of the cone was highly polished, and any fragments which adhered to the knife blade were removed with a camel hair brush. The complete microtome was mounted inside a perspex glove box which was swept out with dry nitrogen.

A crystal of ammonium dihydrogen phosphate was cemented to the anvil with Eastman Kodak 910 adhesive and the upper face of the crystal made approximately parallel to the plane of the knife by levelling the funnel assembly with the screws B. Levelling was completed by taking a few slices off the crystal with the knife. The anvil and crystal were then removed from the microtome and a thin layer of tritium labelled ammonium dihydrogen phosphate applied to the upper face of the crystal by applying a film of the labelled solution and evaporating the liquid rapidly under a high vacuum. The more usual technique of vacuum deposition was not applicable here because of decomposition of the salt on heating.
The labelled crystal and the attached anvil were then annealed in an oven at known temperature (to \(\pm 0.01^\circ C\)) for a known time. The anvil and specimen were then replaced on the microtome. The construction of the sample holder was such that the crystal was necessarily in the same position as before removal, but as a check on its position, an optical level method was used, as shown in fig-4.10.

![Fig.4.10. Schematic diagram for the optical levelling device.](image-url)
A small optically flat mirror M was placed on the crystal surface C after the initial levelling, and the position of the reflected light spot marked on a sheet of graph paper on the wall as shown. When the sample was replaced on the microtome after levelling, the position of the light spot was checked, and it was found that this was always reproducible to ± 1" of its original position. This corresponds to a reproducibility of ± 15-micron in the specimen position.

Sections 10-micron thick were then removed from the crystal down to a total "depth" of 500-micron. The material removed in each section was carefully collected in a separate sample bottle. To each bottle was then added 5.0ml liquid gel scintillator (Nuclear Enterprises NE210), the bottle closed with a screw cap, and heated gently on a water bath with continuous shaking until a colourless gel was formed, with the solid particles held in suspension. The activity of the samples was then determined by counting in an I.D.L. 2021 tritium counter.

This counting technique was adopted because ammonium dihydrogen phosphate is insoluble in the liquids commonly used in scintillation counting, eg toluene, xylene, and other liquids in which it is soluble, give large quenching effects in the liquid scintillator.
The I.D.L., tritium counter has two photomultiplier tubes arranged such that the counting sample is put between them. These two tubes are in coincidence to each other, which allows cancellation of all noise pulse which are usually produced, due to the high voltage applied to the photomultiplier tubes. This system gives a counting efficiency for tritium as high as 42%. To minimise the counting error, at least 10,000 counts were recorded and then converted to counts per minute. The recorded activity was corrected for back-ground, the latter being obtained by counting a blank sample of gel scintillator under the same conditions as all other samples.
CHAPTER - FIVE

Conduction in KH$_2$F$_5$ and KDF$_3$
5.1 D. C. MEASUREMENTS

When a d.c. voltage was applied to a pellet of potassium hydrogen difluoride in the electrolysis cell described in chapter-4, evolution of gas occurred at the cathode, causing a displacement of mercury in the capillary tube-C. A current of the order of 50-microamp flowed through the pellet with an applied voltage of 100 volts. This current diminished with time, and eventually fell to zero. This effect has been observed in other solids, e.g. cesium halides, and is generally attributed to polarisation.

The gas evolved from the crystal was shown to be hydrogen by gas chromatography and the amount of hydrogen produced agreed with that required by Faraday's Law to within 10%.

The quantity of electricity passed was calculated as described in chapter-4.6.

If potassium ions in KHF₂ migrate as well as, or instead of protons, then a dilute K/Hg amalgam will be produced in the cathode compartment. An alternate source of the observed hydrogen could then be from the reaction:

\[ \text{KHF}_2 + \text{K/Hg} \rightarrow 2\text{KF} + 0.5 \text{H}_2 \]
The pressure at which the hydrogen is evolved is very nearly one atmosphere, and it may be assumed that the activity coefficient of potassium in a dilute amalgam is unity. The change in the free energy accompanying the above reaction may be calculated from the Reaction Isotherm:

\[ \Delta G = \Delta G^\circ - R T \ln \frac{a^{\text{K}^+} a^{\text{F}^-}}{a^{\text{KHF}^-} a^{\text{H}^+}} \]

Since \( \text{KHF}^-, \text{KF} \) and \( \text{H}_2 \) are in their standard states, this becomes:

\[ \Delta G = \Delta G^\circ + R T \ln \frac{1}{(C)} \]

where \((C)\) is the concentration of potassium in the amalgam.

The standard free energies of \( \text{KHF}^- \) and \( \text{KF} \) are \(-204.73\) kcal / mole and \(-127.42\) kcal / mole, respectively, from which it follows that \( \Delta G \) for the reaction is negative down to negligible concentration of potassium in the amalgam. This means that any trace of potassium liberated at the cathode due to migration of potassium ion can lead to the production of hydrogen by the above reaction.
A cell was therefore set up containing a dilute potassium amalgam in the cathode compartment; as soon as this cell was assembled, hydrogen evolution began without application of any voltage. Subsequent application of a voltage merely increased the rate of evolution of gas, and evolution continued when the voltage was switched off.

In all other cells containing only pure mercury in the cathode, no movement of the mercury meniscus was observed until the voltage was applied, and the movement stopped immediately the voltage was switched off. After electrolysis in these latter cells, the mercury in the cathode was analysed for potassium by reaction with benzophenone in dry tetra-hydrofuran. The benzophenone-potassium complex contains an unpaired electron, and can be detected by E.S.R. down to about $10^{-7}$ molar. No potassium was detected in the mercury, so it has been concluded from the above results that, at the temperature of these measurements ($35^\circ$C) conduction in solid KHF$_2$ is due to migration of protons only.

An attempt was made to obtain an activation energy for the proton migration by measuring the rate of evolution of hydrogen at four different temperatures, but this did not yield satisfactory results. This was attributed to the varying current/
time characteristics of the different samples used.

5.2 A.C. MEASUREMENTS

A.C. conductance measurements were made on pellets of KHF₆ and KDF₆ over the temperature range of 25-230°C. At the lower temperatures the results were not very reproducible on repeated heating and cooling, but above about 100°C the reproducibility became satisfactory. The results of a typical set of measurements on KHF₆ and KDF₆ are summarised in fig-5.1 and 5.2 respectively, these data in each case covering several heating and cooling cycles of the same sample.

The plots of log of $\sigma'$ against 1/T are linear up to the transition point from $\alpha$-phase to $\lambda$-phase (196°C) at which a sharp discontinuity occurs. From the linear portions of the graphs the following activation energies have been obtained using the method of Least Squares.

<table>
<thead>
<tr>
<th></th>
<th>$E$ ((\alpha)-phase) Klaus/mole</th>
<th>$E$ ((\lambda)-phase) Klaus/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>KHF₆</td>
<td>21.7 ± 0.4</td>
<td>19.8 ± 0.2</td>
</tr>
<tr>
<td>KDF₆</td>
<td>23.5 ± 0.3</td>
<td>20.9 ± 0.4</td>
</tr>
</tbody>
</table>
All the samples studied showed the same behaviour, the scatter in the values of the activation energies being shown in Table 5.1.

### TABLE 5.1

Results of A.C. conduction measurements

<table>
<thead>
<tr>
<th>Compound</th>
<th>E(( \omega ) -phase)</th>
<th>Ln( \gamma )</th>
<th>E(( \phi ) -phase)</th>
<th>Ln( \gamma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>KHF(_m) sample No.1</td>
<td>20.7( \pm)0.2</td>
<td>7.8</td>
<td>18.6( \pm)0.1</td>
<td>9.0</td>
</tr>
<tr>
<td>2</td>
<td>22.6( \pm)0.8</td>
<td>10.6</td>
<td>21.5( \pm)0.1</td>
<td>12.5</td>
</tr>
<tr>
<td>3</td>
<td>21.7( \pm)0.2</td>
<td>9.8</td>
<td>19.2( \pm)0.3</td>
<td>9.6</td>
</tr>
<tr>
<td>4</td>
<td>21.7( \pm)0.4</td>
<td>9.4</td>
<td>19.8( \pm)0.2</td>
<td>7.0</td>
</tr>
<tr>
<td><strong>Mean Value</strong></td>
<td>21.7( \pm)0.4</td>
<td>9.4</td>
<td>19.7( \pm)0.2</td>
<td>9.5</td>
</tr>
<tr>
<td>KDF(_m) sample No.1</td>
<td>24.4( \pm)0.2</td>
<td>10.8</td>
<td>25.6( \pm)0.1</td>
<td>15.7</td>
</tr>
<tr>
<td>2</td>
<td>22.7( \pm)0.5</td>
<td>10.1</td>
<td>17.1( \pm)0.3</td>
<td>8.1</td>
</tr>
<tr>
<td>3</td>
<td>23.5( \pm)0.3</td>
<td>10.5</td>
<td>19.9( \pm)0.4</td>
<td>9.3</td>
</tr>
<tr>
<td>4</td>
<td>23.5( \pm)0.3</td>
<td>10.8</td>
<td>20.9( \pm)0.4</td>
<td>11.0</td>
</tr>
<tr>
<td><strong>Mean Value</strong></td>
<td>23.5( \pm)0.3</td>
<td>10.5</td>
<td>20.7( \pm)0.2</td>
<td>11.0</td>
</tr>
</tbody>
</table>
FIG 5 I  A C Conduct of KHF₂ Pellet.
FIG 52  A.C. CONDUCT. of KDF₂
PELLET.
5.3 DISCUSSION OF EXPERIMENTAL RESULTS

KHF₃ was chosen for the initial work because it is known that there is only one type of hydrogen bond in the crystal and also that this is a symmetrical bond. This means that there can only be one form of "proton defect" present. If the proton is in its bonded position then there is only one site available; if it is not in its normal bonded position then it is considered permissible to treat the resultant defect as of the Schottky or Frenkel type. A Schottky defect would require equal numbers of H⁺ and F⁻ ions to be vacant from the lattice, and in the absence of experimental evidence to the contrary it will be assumed that this type of disorder is less likely than interstitial protons or Frenkel type defects. The variation of conductance with temperature can then be expected to give information about the energy of formation and/or migration of these defects.

Davis and Westrum⁷¹ have measured the electrical conductance of KHF₃ over the range 193-245°C, and have observed a sharp break in the conductance curve at 196°C—the transition temperature from α to β-phase. They have also reported a linear relationship between \( \log \sigma \) and \( 1/T \) in the β-phase region (although
their published results do not in fact show this) with an activation energy of 20.9 kcal/mole; a value which is in good agreement with the results obtained from this present work.

Davis and Westrum have commented on the irreproducibility of their results in the $\alpha$-phase region, which they attribute to supercooling of the $\beta$-phase. This effect has also been observed in this work, and it has been found that results in the $\alpha$-phase region are reproducible (as shown in fig-5.1 and 5.2) as long as the sample is not converted to $\beta$-phase and then cooled.

In the tetragonal unit cell of KH$_2$F, the F-H-F$^-$ ions are arranged alternately parallel to each of the two (101) plane diagonals, whereas in the $\beta$-modifications the alignment may be parallel to any one of the four body diagonals. Extra space is required for this arrangement as is confirmed by the large expansion observed at the transition point. This has been followed experimentally by a simple dilatometer experiment, the result of which is shown in fig-5.3. When a sample is cooled from $\beta$ to $\alpha$-phase, the flaws produced on contraction will not be reproducible and these will contribute to a higher conductance as is found.
FIG. 5.3 Volume Change of KHF$_2$ with Temp.
The agreement between the activation energies for \( \alpha \) and \( \beta \) phases shows that the conductance mechanism is the same in each case, and that this mechanism is therefore independent of the overall packing of the structural units in the crystal. In a system of isolated H-bonded units such as in KHR\(_{1/2}\), motion of a proton through the lattice must start by formation of a Frenkel type defect followed by migration of the interstitial proton through the lattice. Each of these processes will have its own activation energy, and as described in chapter 2, the equation for the conductance may be represented by

\[
C' = C_0^2 \exp \left( - \frac{U + 0.5 E_i}{kT} \right)
\]

where \( U \) is the activation energy required for the defect migration and \( E_i \) is the activation energy required for the defect formation. It is expected that the energy for the migration of an interstitial proton will be small for an open lattice such as is being considered here and so the observed activation energy is attributed to the formation of defects. The energy of forming the defects is therefore twice the observed activation energy from the conductance plot i.e.,
The formation of a Frenkel defect in KHF$_2$ involves the breaking of the F-H-F bond system, and Ketelaar\textsuperscript{33} has calculated this to be about 30-50 kcal/mole, the calculation is inexact because of uncertainties in the lattice energy of KHF$_2$. It is to be expected that the experimental value for the defect formation will be of similar magnitude to the F-H-F bond energy and the results obtained confirm this. If a precise value of the F-H-F bond energy were available one would expect the energy of proton defect formation in KHF$_2$ to be smaller than the thermodynamic value; this is because the presence of neighbouring fluoride ions in the lattice will facilitate the removal of the proton.

The small but significant difference which has been observed in the activation energies for KHF$_2$ and KDF$_2$ indicates that the binding of the F-D-F system is stronger than the F-H-F. This is in agreement with Ubbelohde\textsuperscript{5} report that deuterium substitution causes a small contraction of the H-bond

<table>
<thead>
<tr>
<th></th>
<th>$E_1$ (α-phase) kcal/mole</th>
<th>$E_1$ (β-phase) kcal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>KHF$_2$</td>
<td>43.4 ± 0.4</td>
<td>39.6 ± 0.2</td>
</tr>
<tr>
<td>KDF$_2$</td>
<td>47.0 ± 0.3</td>
<td>41.4 ± 0.2</td>
</tr>
</tbody>
</table>
in KHF₂, the contraction also implying a stronger association in the deuterium compound.
CHAPTER - SIX

Conduction of Acid Phosphate and Arsenates
6.1. **INTRODUCTION**

In this chapter, the experimental results for \( \text{NH}_4\text{H}_2\text{PO}_4 \), \( \text{KH}_2\text{PO}_4 \) and \( \text{KH}_2\text{AsO}_4 \) are discussed. These substances are grouped together because of the similarities in crystal structure, and because they all contain an unsymmetrical \( O--H\ldots O \) bond. The hydrogen bond lengths are similar (\( \sim 2.5\text{\(\AA\)} \)), and all three compounds exhibit similar behaviour on deuterium substitution. \( \text{NH}_4\text{H}_2\text{PO}_4 \) also contains a \( N--H\ldots O \) bond, but this is not considered to play a dominant role in the crystal.

6.2. **D.C. MEASUREMENTS**

When a D.C. voltage was applied to pellets or crystals of these substances in the electrolysis cell, evolution of hydrogen gas was observed in the cathode compartment. Using the Silver-110 coulometer, it was found that the amount of hydrogen evolved agreed with the quantity required by Faraday's Law to within 10%, indicating that conduction is predominantly protonic in these solids. No analysis was carried out for potassium or ammonium compounds in the mercury of the cathode, since the results of the gas analyses agreed with those of Murphy and Schmidt who have also concluded that conduction in \( \text{KH}_2\text{PO}_4 \) and \( \text{NH}_4\text{H}_2\text{PO}_4 \) is essentially protonic.
### TABLE 6.1

A.C. Conduction Results of pellets

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Activation Energy (kcal/mole)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(U+1/2E)$_H$</td>
<td>(U+1/2E)$_D$</td>
<td></td>
</tr>
<tr>
<td>NH$_4$H$_2$PO$_4$</td>
<td>12.0 ± 0.3</td>
<td>17.3 ± 0.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10.9 ± 0.1</td>
<td>16.2 ± 0.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12.5 ± 0.5</td>
<td>13.6 ± 0.6</td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>11.8 ± 0.3</td>
<td>15.4 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>KH$_2$PO$_4$</td>
<td>11.8 ± 0.7</td>
<td>11.4 ± 0.01</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.3 ± 0.3</td>
<td>9.3 ± 0.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.9 ± 0.2</td>
<td>10.1 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>8.7 ± 0.3</td>
<td>10.6 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>KH$_2$AsO$_4$</td>
<td>7.1 ± 0.1</td>
<td>7.9 ± 0.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.3 ± 0.5</td>
<td>7.8 ± 0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.1 ± 0.1</td>
<td>8.6 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>7.2 ± 0.2</td>
<td>8.1 ± 0.2</td>
<td></td>
</tr>
</tbody>
</table>

* (U+1/2E)$_H$ = Observed activation energy for H-compound.

** (U+1/2E)$_D$ = Observed activation energy for D-compound.
6.3 A.C. MEASUREMENTS

A.C. conduction was measured for pellets of ammonium dihydrogen phosphate, potassium dihydrogen phosphate, potassium dihydrogen arsenate and their respective deuterated derivatives. Measurements were also made on single crystals of \( \text{NH}_4\text{H}_2\text{PO}_4 \), \( \text{ND}_4\text{D}_2\text{PO}_4 \), and \( \text{KH}_4\text{PO}_4 \). These measurements were made over the approximate temperature range 20-200°C; as in the case of KHF₂, the results at low temperatures were somewhat variable, but became reproducible above about 50 or 60°C; provided that the samples were first annealed. The results of typical sets of measurements for different samples of compound are summarised in table 6.1.

Plots of the experimental results for the individual compounds are shown in Figs. 6.1-6.4. The linear relationship obtained indicates that one conduction mechanism is operative over the temperature range studied. The conduction is then given by the equation:

\[
\sigma = \sigma_0 \exp \left( - \frac{U + \frac{1}{2} E}{kT} \right)
\]

The values of the activation energies recorded in table 6.1 are average values for all crystallographic directions. Since \( \text{KH}_2\text{PO}_4 \) and \( \text{NH}_4\text{H}_2\text{PO}_4 \) readily form good single crystals, it was convenient to study the effect of crystal orientation on activation
FIG. 6.1 A.C. Conduct. of
NH₄H₂PO₄ Pellet

\[ \text{\( \log \text{sp. conduct} \)} \]

\[ \text{\( \frac{1}{T} \times 10^{3} \text{ oK}^{-1} \)} \]

\( \text{NH}_4\text{H}_2\text{PO}_4 \)

\( \text{ND}_4\text{D}_2\text{PO}_4 \)
FIG 6.2 A.C. CONDUCT.
of
NH₄H₂PO₄ SINGLE CRYSTAL.

\( T \times 10^3 \, ^{\circ}K^{-1} \)

\[ (U + 1.5E)_H = 15.4 \, \text{keV/mole} \]
\[ (U + 1.5E)_D = 11.8 \, \text{keV/mole} \]

\( \bigcirc \) NH₄H₂PO₄

\( \square \) ND₄D₂PO₄
FIG 6.3  A.C. Conductance of KDP O₄₅ Pellet
energy. Good single crystals of these substances were selected, and screened copper electrodes attached to various faces with silver cement (Johnsone-Mathey type FS 49R/H). Table 6.2 gives the activation energies observed for the various indicated electrode configurations.

<table>
<thead>
<tr>
<th>Direction</th>
<th>( \text{NH}_4\text{H}_2\text{PO}_4 )</th>
<th>( \text{KH}_2\text{PO}_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>y</td>
<td>15.4 ± 0.2</td>
<td>10.6 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>21.4 ± 0.5</td>
<td>14.3 ± 0.9</td>
</tr>
<tr>
<td></td>
<td>23.6 ± 0.5</td>
<td>5.8 ± 1.6</td>
</tr>
<tr>
<td></td>
<td>15.8 ± 0.6</td>
<td>8.5 ± 1.2</td>
</tr>
<tr>
<td></td>
<td>19.8 ± 0.4</td>
<td>14.4 ± 1.4</td>
</tr>
<tr>
<td></td>
<td>24.4 ± 0.5</td>
<td>14.5 ± 1.5</td>
</tr>
<tr>
<td></td>
<td>23.7 ± 0.4</td>
<td>8.8 ± 1.3</td>
</tr>
<tr>
<td>Mean</td>
<td>20.6 ± 0.4</td>
<td>11.7 ± 1.2</td>
</tr>
</tbody>
</table>
FIG 63  A,C, Conduct of K$_2$HPO$_4$

$10^4$ LOG of SP CONDUCT

- $\bullet$ $\text{KHPO}_4$ Pellet
- $\square$ Single crystal

(only Log of conduct plotted against $1/T$)
FIG 64  A C CONDUCTION of
KH₂₂₃₂AsO₄ PELLET

\[ \text{Log of Conductivity} \]

\[ \frac{1}{T} \times 10^3 \text{ °K} \]

- \( \text{O} \) \( \text{K} \) \( \text{H}_2\text{AsO}_4 \)
- \( \text{X} \) \( \text{K}_2\text{D}_2\text{AsO}_4 \)
Specific conductance were not recorded in these measurements because of the uncertainties in sample dimensions and in electrode contact area, but the activation energies should be independent of these factors. The remaining measurements on these materials is the comparison of activation energy for a H and D compound. Fig.6.2. gives the data for NH₄H₂PO₄ and ND₄D₂PO₄, the direction of measurement being along the c-axis in each case.

6.4. DISCUSSION OF RESULTS

The KH₂PO₄ structure (and the isomorphic NH₄H₂PO₄ and KH₂AsO₄) consists essentially of PO₄ tetrahedra joined by four hydrogen bonds to neighbouring tetrahedra in such a way that each phosphate or arsenate group has two protons associated with it. This results in an open hydrogen bonded network. The motion of protons in this type of structure is much more complex than in KH₆, since the hydrogen bonds are unsymmetrical, and there already exist two alternative and equivalent sites for the proton within the O---H...O bond. Above the Curie temperature (123°K for KH₂PO₄) there is a statistical distribution between these two sites and because of the tunnel effect, protons will always be able to move from one potential minimum to another irrespective of the presence of an applied E.M.F.
The hydrogen bonds in KH₂PO₄, NH₄H₂PO₄ and KH₂AsO₄ lie approximately in a plane at right angles to the c-axis of the tetragonal unit cell, and it is considered instructive firstly to consider proton motion along the c-direction, i.e., in which the protons are moving out of the plane of the H-bonds. As in the case of KHF₆, such a process is equivalent to breaking the H-bonds, and the observed activation energy may be interpreted in terms of the energy of the hydrogen bond.

An assumption made in all this work is that it should be relatively easy for a "free" or interstitial proton to move throughout an open lattice, i.e., that the activation energy for mobility of a defect (U) should be small. (Experimental evidence is presented later to support this). If this is so, then the observed activation energy (U + \( \frac{1}{2} E \)) can be regarded as referring to defect formation; with U << E and thus the energies of formation of a defect (E) in NH₄H₂PO₄ and KH₂PO₄ in a direction normal to the plane containing the H-bonds are 30.8 kcal/mole and 21.2 kcal/mole respectively. In KH₂PO₄ the energy of each H-bond is of the order of 5 kcal/mole (exact data are not available) so it seems justifiable to conclude that in KH₂PO₄ the conduction mechanism is a complex one involving the simultaneous breaking of four H-bonds. Since there are four H-bonds associated with each phosphate group, this conduction process must involve re-arrangement of all the protons around each phosphate ion.
A similar conclusion may be drawn for NH₄H₂PO₄, but in this compound there are also N--H...O bonds. Although these are of much less importance from an overall structural aspect they represent an additional restriction on proton motion, and this may account for the higher activation energy observed for NH₄H₂PO₄.

Murphy⁷ has reported d.c., conductance measurements on pure and doped NH₄H₂PO₄, and has obtained a value of activation energy of 18.4 kcal/mole for conduction in the pure salt. It is not clear from Murphy's paper to which crystallographic direction this value refers but the value is comparable with the figure of 15.8 kcal/mole obtained along the c-axis in the present work. From the results on ammonium dihydrogen phosphate doped with small amounts of sulphate ion and barium ion Murphy obtains an activation energy of 10.5 kcal/mole which he attributes to the energy for defect migration, and his conclusion therefore is that the conduction process involves the breaking of two hydrogen bonds.

There are two objections to this conclusion:

1. The conduction process must involve the two steps of defect formation followed by migration. It is the first of these steps which should be related to the H-bond energy rather than the second.
2. The value of 10.5 kcal/mole seems a very high value for the migration of the small proton in an open crystal lattice such as the acid phosphate.
If Murphy's value of 18.4 kcal/mole was due to formation of defects by breakage of H-bonds then his results could agree with our own conclusions. The higher value which he observes may be attributed at least in part to his d.c. methods; which usually give higher activation energies because of polarisation.

A comparison of results obtained in this work for K$_3$PO$_4$ may be made with a recent paper by O'Keeffe and Perrino$^{77}$ which describes d.c. conductances on pure and doped samples of this material. These workers have observed a break in the log $\sigma$ against 1/T plot, and from the slopes of the two portions they have obtained activation energies corresponding to $(U + \frac{1}{2}E) = 18.0$ kcal/mole in the region above 180$^\circ$C and $U$ to be 12.7 kcal/mole below 180$^\circ$C. These results refer to conduction along the c-axis, and the lower temperature value 12.7 kcal/mole is the value which is to be compared with the figure 10.3 kcal/mole given in table-6.2. It is possible that the break in the conduction curve observed by O'Keeffe could be due to thermal treatment. They do not indicate whether their results cover several heating and cooling cycles but Harris and Vella$^{78}$ have obtained different curves for heating and cooling runs. In the present work a break in the conduction plot was observed but this disappeared after annealing the crystal at high temperatures, and then repeated heating and cooling gave the same line.
O'Keeffe and Perrino (like Murphy) attribute their low temperature activation energy to defect migration, and one can then obtain from their results the value of 10.8 kcal/mole as the energy of defect formation. On Murphy's interpretation this would indicate that two H-bonds are broken in the conduction process, whereas the view favoured from the present results is that four H-bonds are involved.

The results given in table-6.1 and 6.2 show that the average activation energy over all directions in a single crystal is greater than for pellets of the same substance. This is in agreement with other similar observations on alkali halides and indicates that grain boundaries and other macroscopic flaws result in easier migration of the conducting species.

It is also seen from table-6.1 that the activation energy decreases in the order $\text{NH}_4\text{H}_8\text{PO}_4 - \text{KH}_2\text{PO}_4 - \text{KH}_2\text{AsO}_4$. This is consistent with the facts that protons are more strongly held in $\text{NH}_4\text{H}_8\text{PO}_4$ than in the potassium salts due to the presence of $\text{N}--\text{H}...\text{O}$ bonds, and that protons are more firmly held in phosphates than in arsenates.

A comparison of the activation energies obtained for $\text{H}$ and $\text{D}$ substituted compounds gives conflicting results. Measurements on single crystals of $\text{NH}_4\text{H}_8\text{PO}_4$ and $\text{ND}_4\text{D}_2\text{PO}_4$ show that in the same crystallographic direction, the value is
higher for H than for the D crystal (fig-6.2). However table 6.1 shows that for pellets, consistently higher values are obtained for the D substituted compounds than the H compounds.

The results on single crystals agree with the observed expansion of the hydrogen bond on D substitution. This expansion is assumed to reflect a weaker interaction in the D compounds, and this should then require a smaller activation energy for breakage in the conduction process. The isotope effect in hydrogen bonded crystals is however markedly dependent on crystallographic direction, and in the compounds being discussed here the observed expansion along the direction of the H-bond is accompanied by a contraction normal to the H-bond direction. (This contraction is particularly pronounced in NH$_4$HPO$_4$.) In any direction in the crystal for which deuterium substitution results in contraction, it is reasonable to assume that the contraction will result in a stiffening of the lattice vibrations, and that this may result in a higher activation energy for any ionic motion along this direction. In a polycrystalline sample, these defects may outweigh the lower activation energy, with the result that an overall increase in activation energy for D compounds may be justified. Only one other comparison between activation energies for a H and D crystal can be made. Schmidt has obtained the value of 13.4 kcal/mole for conduction along the c-axis of KD$_2$PO$_4$. 
while Harris\textsuperscript{76} has reported the figure of 13.9 kcal/mole
for the same direction in KH\textsubscript{2}PO\textsubscript{4}. This similarity in these
results and also the data obtained from the present research
indicate that it is not possible to draw useful conclusion
from the comparison of H- and D-substituted compounds of the
acid phosphate type.
CHAPTER - SEVEN

Conduction of Oxalic Acid Dihydrate
7.1. INTRODUCTION

Oxalic acid dihydrate is the most complex of the hydrogen bonded crystals which have been examined in this work. Like the acid phosphates it contains a continuous spiral network of H-bonds but the H-bonds forming this spiral are of two different lengths, 2.51 Å and 2.88 Å. Also, in addition to these, there is a third crystallographically independent H-bond 2.87 Å in length, which lies approximately at right angles to the direction of the other two.

7.2. D.C. MEASUREMENTS

D.C. electrolysis was carried out as described previously the temperature being 35°C and with an applied voltage of 60 v. When the applied voltage was switched off, it was found that a back e.m.f., remained which slowly decayed to zero. This was attributed to the formation of an electrochemical cell by the products of electrolysis, hydrogen and (presumably) oxygen. The gas evolved in the cathode was shown to be hydrogen, but any products liberated at the anode were not identified. The Silver-110 coulometer indicated that hydrogen evolved in electrolysis corresponded to only 10% of the volume required by Faraday's Law. Part of this discrepancy may be attributed to recombination of the electrolysis products with the pellet, but it does not seem plausible to infer any electronic conductivity in oxalic acid dihydrate on the basis of these measurements.
FIG 7.1 Variation in sp conduct with temp of \((\text{COOH})_2\text{H}_2\text{O}\)
FIG 7.2. Variation in Specific Conductance with Temp. of Oxalic Acid Dihydrate.
7.3. A.C. MEASUREMENTS

The results of A.C. measurements on pellets of (COOH)$_2$ 2H$_2$O and (COOD)$_2$ 2D$_2$O are shown in figs. 7.1-7.4. Measurements were restricted to an upper temperature of about 80°C to avoid dehydration, but were continued down to about -70°C. Activation energies for the upper and lower temperature regions are given in table 7.1.

**TABLE 7.1.**

Activation Energies in H- and D- oxalic acid dihydrate pellet.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Activation Energies (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Higher temperature (U + $\frac{1}{2}$ E)</td>
</tr>
<tr>
<td>(COOH)$_2$ 2H$_2$O</td>
<td>11.0 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>10.7 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>12.0 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>10.6 ± 0.7</td>
</tr>
<tr>
<td>Mean</td>
<td>11.1 ± 0.3</td>
</tr>
<tr>
<td>(COOD)$_2$ 2D$_2$O</td>
<td>14.0 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>10.3 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>14.1 ± 0.2</td>
</tr>
<tr>
<td>Mean</td>
<td>12.8 ± 0.3</td>
</tr>
</tbody>
</table>
Fig. 7.3. Variation in Specific Conductivity with temp. of Deutrated Oxalic Acid Dihydrate pellet.
FIG 7.4 Variation in Specific Conductance with Temp. of Deuterated Oxalic Acid Dihydrate
No measurements were made on single crystals because of the difficulty of obtaining good crystals of a sufficiently large size.

7.4. DISCUSSION OF RESULTS

Oxalic acid dihydrate has been the subject of numerous studies in an attempt to determine the nature of the H-bonds in crystal. The expansion of the crystal on deuterium substitution is the largest of any substance so far examined and this has been attributed to pronounced quantum mechanical effects as described in chapter-1. The work of Lippincott on the shape of the potential energy function for the short H-bond agrees with the observed thermal expansion of the crystal indicating a broad anharmonic potential well for the short bond.\textsuperscript{1,45}

On this basis it might be expected that a marked difference in the activation energy for the H- and D- acids would be observed in the conduction results, but the figures in the table-7.1, show only a small difference. The values found for oxalic acid pellets are in the same sense as for the acid phosphates i.e., the D-compound shows a higher activation energy than the H-compound. It is concluded that any differences in
activation energy for H- and D- oxalic acid are small, and do not relate to the large isotope expansion in this crystal. Furthermore, because of the presence of three different H-bonds in the crystal it is not possible to derive any useful information about the mechanism of proton conduction.

The conduction plots show a marked departure from linearity at low temperatures, an effect which is quite reproducible. The low activation energies in this region agree with the assumption made previously that motion of a "free" proton through an open molecular lattice should be relatively easy.
CHAPTER - EIGHT

Tritium Diffusion in NH₄H₂PO₄
FIG. 8.1 Distribution of tritium in
$NH_2H_3PO_4$, single crystal
Temp. 93.0 °C

$\log(CPM)$ vs. $(\text{Thickness}) x 10^5 \text{ cm}^2$
Fig. 8.2. Distribution of tritium in ammonium dihydrogen phosphate single crystal.

Log (C.P.M.)

Temp. 110.0 °C

(Thickness) × 10^6 cm^-2
Fig. 8.3. Distribution of tritium in Ammonium dihydrogen phosphate single crystal.

Temp. 65.0°C
Fig. 8.1. Distribution of tritium in ammonium dihydrogen phosphate single crystal.

Temp. 61.0 °C

(Thickness)² x 10⁶ cm²
8.1. INTRODUCTION

The experimental results described in previous chapters have been interpreted on the basis that conduction in the compounds concerned is due to motion of protons only, and that this process involves the breaking of one or more hydrogen bonds. An independent approach to this process may be obtained from a study of the diffusion of tritium in the crystals, which as described in chapter 2 can show whether or not conduction and diffusion occur by the same mechanism.

As far as known at present, no previous study of tritium diffusion in a H-bonded crystal has been made, and this chapter describes results obtained with ammonium dihydrogen phosphate. These results are regarded as exploratory in nature, with the following general aims:

1. to establish the basic experimental technique for studying diffusion, and to derive some conclusions on the suitability of alternative methods.

2. to find out if the Einstein equation (2.12) is obeyed, approximately or otherwise, and to indicate the direction which any further work on this technique should follow.
8.2. EXPERIMENTAL RESULTS

The diffusion of tritium in single crystal of ammonium dihydrogen phosphate was carried out as described in chapter-4, the direction of measurements being parallel to the c-axis, i.e., in the same direction as the conduction measurements. Results were obtained at four temperatures, and the diffusion profiles obtained by the micro-tome sectioning method are shown in Figs. (8.1-8.4). The diffusion coefficients obtained from the slopes of these lines are given in table-8.1, the line of the best fit being obtained by the method of Least Squares.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Slope</th>
<th>Diffusion Coefficient (cm²/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>64.0</td>
<td>- 3.45 x 10⁻³</td>
<td>6.06 x 10⁻¹¹</td>
</tr>
<tr>
<td>65.0</td>
<td>- 1.95 x 10⁻⁴</td>
<td>1.80 x 10⁻¹⁰</td>
</tr>
<tr>
<td>93.0</td>
<td>- 1.22 x 10⁻³</td>
<td>8.79 x 10⁻¹⁰</td>
</tr>
<tr>
<td>110.0</td>
<td>- 2.79 x 10⁻⁵</td>
<td>3.93 x 10⁻¹⁰</td>
</tr>
</tbody>
</table>
The activation energy for the diffusion process was then obtained from the Least Squares plot of \( \log(D) \) against \( 1/T \left( \text{°K}^{-1} \right) \). Figure 8.5 gives the following diffusion equation:

\[
D = 3.04 \times 10^{-4} \exp \left( \frac{-10.0 \times 10^3}{kT} \right)
\]

An alternative way of comparing the conductance and diffusion results is to use the above equation to calculate \( D \) at various values of \( T \left( \text{°K} \right) \), and then to use these values of \( D_{\text{calc}} \) to evaluate the conductance \( \sigma' \), assuming that the Einstein equation is obeyed. This has been done in Fig.8.6, which shows a plot of \( \log \sigma'_{\text{calc}} \) against \( 1/T \) together with the experimentally determined plot.

### 8.3. DISCUSSION OF RESULTS

It is evident from figures-8.1-8.4, that there is considerable scatter in the results for the activity/thickness relationship. At first it was assumed that this was due to uneven diffusion into the crystal via surface flaws. Rogers and Hughes have drawn attention to the importance of this effect, and have shown by autoradiography that even distribution of the
FIG. 8.5. Variation in Diffusion Coefficient with Temp
Fig 8.6 Temp Dependence of Conductivity of Proton in NH$_4$H$_2$PO$_4$ Single Crystal

$\log_{10}$ of Conductance vs. $1/T \times 10^3$ K$^{-1}$

- O Directly Measured
- □ Calculated from Diffusion Coefficient
active isotope over the crystal surface is not always achieved; but that deposition occurs in patches at surface flaws which permit "channelling" of the active species into the crystal. It has since been found however, that when cutting hard specimens such as ammonium dihydrogen phosphate the specimen holder and even the micro-tome knife deform by several microns, with the result that the thickness of the sample removed is not as reproducible as previously assumed.

The diffusion via cracks and flaws must always be present to some extent, but if this were the predominant cause of the scatter in these results then one would expect the values of \( D \) to be large i.e., rapid diffusion. The experimental values obtained are in fact typical slow diffusion figures, cf

\[
D = 8.27 \times 10^{-9} - 4.49 \times 10^{-11} \text{ cm}^2/\text{sec} \text{ for cyclohexane at } 243-203 ^\circ \text{K, and } D = 5.81 \times 10^{-9} \text{ cm}^2/\text{sec} \text{ for sodium-22 in sodium at } 25^\circ \text{C temperature.}
\]

A rapid diffusion is obtained for the first 20-50 \( \mu \) into crystal as shown from the first few points on the diffusion profiles. This is likely to be due to the solution method of applying radio-isotope to the crystal surface, since even with the rapid evaporation of the solution, equilibration of a surface layer of finite thickness will occur.
It is evident from the results that further modifications to the basic microtome design are required if hard specimens are to be sectioned with accuracy. (This has in fact been put in hand in preparation for other investigations).

If the Einstein Relation were obeyed in ammonium dihydrogen phosphate, then, leaving aside other factors which are discussed later, the calculated conductivity line in fig-8.6, should have the same slope as the experimental line. If the diffusion and conductivity were measured on the same samples, then the actual values of calculated and observed conduction should also agree, but in this work different samples were used, and no correction was made for differences in sample dimensions.

The similarity in slope obtained in fig-8.6, indicates that the Einstein Relation is at least approximately obeyed even allowing for experimental error. However, some difference between the observed and calculated slopes is to be expected due to the Isotope Effect in the diffusion process. In previous studies of diffusion in ionic crystals, the ratio of the masses of the labelled and "host" species is always close to unity, but in the present case this is no longer so.
As indicated in chapter-2, the activation energy from the diffusion experiments may be interpreted in the same way as that obtained from conduction. Therefore the results of this diffusion work may be considered to represent the effect of tritium substitution on the breaking of the hydrogen bonds in the crystal. If deuterium substitution results in a weaker H-bond, with consequent lowering of the activation energy for conduction as indicated in chapter-6, then tritium substitution in the crystal should have a similar and greater effect. This view is in agreement with the observed results, the relevant activation energies being:

\[
\begin{array}{ccc}
\text{NH}_4\text{H}_2\text{PO}_4 & 15.4 \text{ kcals/mole} & \text{Conduction} \\
\text{ND}_4\text{D}_2\text{PO}_4 & 11.8 \text{ kcals/mole} & \text{Conduction} \\
\text{NH}_4\text{H}_2\text{PO}_4 & 10.0 \text{ kcals/mole} & \text{Diffusion}^* \\
\end{array}
\]

It is concluded from these results that the Einstein Relation is obeyed for ammonium dihydrogen phosphate and that diffusion in this crystal occurs by the same mechanism as electrical conduction. Further general conclusions are given in the following chapter.

* Labelled with tritium.
CHAPTER - NINE

Conclusion
The objects of this work have been outlined in chapter-3. It is now possible to summarise the work which has been done and to draw some general conclusions in addition to the specific conclusions which have been given in the chapters dealing with individual compounds.

A method has been developed for studying proton conduction in solids, in which hydrogen gas evolved on electrolysis of the solid is collected and measured. A coulometer utilising Silver-110 has been used to enable small quantities of electricity to be measured and correlated with the amount of hydrogen evolved on electrolysis. Conduction in $\text{KH}_3\text{PO}_4$, $\text{NH}_4\text{H}_2\text{PO}_4$, $\text{KH}_3\text{AsO}_4$ has shown to be entirely protonic by this method. This means that in these substances it is easier for the proton to move in the lattice than the other cation, even though this may mean, (in the case of $\text{KHF}_2$) the breaking up of a stable anion. Proton conduction has also been verified in Oxalic acid dihydrate although in this substance a discrepancy was found between the measured and calculated volume of hydrogen evolved.

The conductances of the solids mentioned above have also been measured as a function of the temperature by an A.C., method. Satisfactory plots of log of conductance against reciprocal temperature have been obtained showing that conductance
in the crystals is governed by a simple activation process.
The simple theory of defects in solids has been applied to the results and the activation energies obtained experimentally have been interpreted in terms of the formation of proton defects in the crystal. For KHF₄ which contains discrete F--H...F units, the activation energy may be interpreted as the breaking of one hydrogen bond, but in crystals containing "co-operative" networks of bonds such as KH₂PO₄ etc., the results indicate that several H-bonds are broken simultaneously in the conduction process.
This approach to the interpretation of the results is limited to crystals containing only one type of H-bond.
In oxalic acid dihydrate containing three types of H-bond, it is not possible to decide how many bonds are involved.

Comparisons have been made between activation energies obtained for polycrystalline samples and single crystals (where possible). The effect of crystal orientation on the activation energy has also been investigated in the case of NH₄H₂PO₄ and KH₂PO₄; and the result has been shown to be markedly dependent on crystal direction. It is concluded from this that conductance data on single crystals are preferable to compressed pellets, but only if the direction of the measurements is specified.
The measurements on the H-bonded crystals have been repeated for the corresponding deuterated compounds. In the case of KHF₆ and the acid phosphates, the results are in agreement with expectations based on X-rays studies of the isotope effect, i.e., that a solid which shows an expansion of the lattice on D-substitution (acid phosphates) gives a lower activation energy for conduction in the D-compound than in the H-compound. Conversely if the lattice contracts on D-substitution (KHF₆) then the D-compound has the higher activation energy. Oxalic acid dihydrate is anomalous in this respect - there is little difference between the values for the H- and D-acid in spite of a large isotope expansion.

Again it is concluded that any further comparisons between H- and D-compounds should be carried out on a single crystals, and only measurements which are in the same crystal direction compared with each other.

The diffusion of tritium in crystals of NH₄H₂PO₄ has been studied by the well established microtome sectioning technique. This technique requires precise engineering in the construction of auxiliary apparatus and scatter in experimental results have been traced to faults in the construction of the apparatus.

Nevertheless the diffusion of tritium in a H-bonded crystal has been shown to be feasible proposition by this method,
and some preliminary results have been obtained which show that this is a promising field for further study. It has been concluded from the results on \( \text{NH}_4 \cdot \text{H}_2\text{PO}_4 \), that the Einstein Relation is obeyed and that therefore conduction and diffusion occur by the same mechanism, even though the activation energy obtained from the diffusion work differs from that obtained from conduction. It is probable that further study of tritium diffusion in H-bonded crystals will yield useful information about the role and nature of the H-bond in the crystals. However it is not likely that such detailed diffusion mechanisms can be obtained as has been possible in ionic crystals such as alkali halides because of the isotope effect on the diffusion process.\(^8\)\(^9\)\(^4\)
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APPENDIX
An example of typical experimental results are given in this appendix. Information given in the previous text was obtained from such sets of results.
D.C. CONDUCTANCE OF POTASSIUM HYDROGEN DIFLUORIDE

Temp. 40.0 C
Vots. 100.0

No movement of mercury meniscus was observed for 98 hours and current was switched on thereafter.

<table>
<thead>
<tr>
<th>Time (hr)</th>
<th>Current (micro-amp)</th>
<th>Hg-displacement (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>50.0</td>
<td>0.000</td>
</tr>
<tr>
<td>0.50</td>
<td>28.5</td>
<td>0.482</td>
</tr>
<tr>
<td>1.00</td>
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<td>0.942</td>
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<tr>
<td>2.00</td>
<td>13.0</td>
<td>1.142</td>
</tr>
<tr>
<td>4.00</td>
<td>7.4</td>
<td>1.734</td>
</tr>
<tr>
<td>7.00</td>
<td>5.0</td>
<td>2.244</td>
</tr>
<tr>
<td>20.75</td>
<td>2.4</td>
<td>3.272</td>
</tr>
<tr>
<td>24.10</td>
<td>2.0</td>
<td>3.442</td>
</tr>
<tr>
<td>50.20</td>
<td>1.5</td>
<td>4.362</td>
</tr>
<tr>
<td>78.30</td>
<td>1.0</td>
<td>5.152</td>
</tr>
<tr>
<td>80.75</td>
<td>1.0</td>
<td>5.688</td>
</tr>
</tbody>
</table>

Volume of gas evolved in the cathode compartment at N.T.P.

\[
\text{Volume of gas} = \text{Volume of mercury displaced at N.T.P.} = 11.09 \times 10^{-8} \text{ ml of Hydrogen at N.T.P.}
\]

Activity of Silver-110 deposited on Cu-electrode

\[
\text{Activity} = 898.0 \text{ cpm} = 11.80 \times 10^{-8} \text{ ml at N.T.P. (from graph 4.4)}
\]
A.C. CONDUCTANCE OF KHF₂ / KDF₂

Cell constants

<table>
<thead>
<tr>
<th></th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>KHF₂ pellet</td>
<td>13.920 x 10⁻² cm⁻¹</td>
</tr>
<tr>
<td>KDF₂ pellet</td>
<td>15.418 x 10⁻² cm⁻¹</td>
</tr>
</tbody>
</table>

<table>
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<th>KHF₂</th>
<th>Temp. 10⁺log(sp.conduct)</th>
<th>KDF₂</th>
<th>Temp. 9⁺log(sp.conduct)</th>
</tr>
</thead>
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<td>(°C)</td>
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<td>(°C)</td>
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<td>134.4</td>
<td>2.104</td>
<td>83.0</td>
<td>0.086</td>
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<td>135.0</td>
<td>2.152</td>
<td>124.0</td>
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<td>135.5</td>
<td>2.417</td>
<td>125.0</td>
<td>0.336</td>
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<td>139.5</td>
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<td>0.974</td>
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<td>192.0</td>
<td>3.468</td>
<td>152.0</td>
<td>0.966</td>
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<td>200.0</td>
<td>5.305</td>
<td>154.0</td>
<td>1.161</td>
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<td>160.0</td>
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<td>5.517</td>
<td>188.6</td>
<td>2.169</td>
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<td>212.6</td>
<td>5.519</td>
<td>192.1</td>
<td>2.228</td>
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<tr>
<td>217.1</td>
<td>5.619</td>
<td>196.0</td>
<td>3.719</td>
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<td>219.9</td>
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<td>4.502</td>
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<td>219.9</td>
<td>5.662</td>
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<td>4.553</td>
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<td>5.647</td>
<td>207.1</td>
<td>4.575</td>
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<td>224.1</td>
<td>5.682</td>
<td>211.5</td>
<td>4.576</td>
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<td>5.759</td>
<td>213.0</td>
<td>4.614</td>
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<tr>
<td>234.3</td>
<td>5.973</td>
<td>220.9</td>
<td>4.951</td>
</tr>
</tbody>
</table>
D.C. ELECTROLYSIS OF NH₄H₂PO₄ PELLET

Temp 57.51 °C
Volts 60.0

No displacement of mercury meniscus was noticed in 90 hours
and thereafter the potential was applied.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Current (micro-amp)</th>
<th>Hg-displacement (cm)</th>
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<tbody>
<tr>
<td>0.0</td>
<td>70.25</td>
<td>0.0</td>
</tr>
<tr>
<td>5.0</td>
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<td>15.0</td>
<td>7.50</td>
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<td>30.0</td>
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<td>0.186</td>
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<td>4.50</td>
<td>0.210</td>
</tr>
<tr>
<td>75.0</td>
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<tr>
<td>95.0</td>
<td>2.00</td>
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<tr>
<td>105.0</td>
<td>2.00</td>
<td>0.332</td>
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<td>0.740</td>
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</table>

Activity of silver-110 deposited on Cu-electrode = 1072 cpm
Equivalent amount of hydrogen at N.T.P. (from fig.4.4) = 12.25 x 10⁻² ml

Equivalent amount of hydrogen evolved (taking the volume of Hg-meniscus displacement) = 11.45 x 10⁻² ml
A.C. CONDUCTION OF NH₄H₂PO₄ SINGLE CRYSTAL

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>8+log(conduct)</th>
<th>Temp (°C)</th>
<th>9+log(conduct)</th>
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<td>0.875</td>
<td>41.0</td>
<td>0.698</td>
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<td>48.3</td>
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<td>54.5</td>
<td>0.845</td>
</tr>
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<td>56.3</td>
<td>1.204</td>
<td>60.0</td>
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<td>1.493</td>
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<td>75.0</td>
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<td>86.4</td>
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<tr>
<td>125.5</td>
<td>3.025</td>
<td>121.2</td>
<td>2.413</td>
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</table>
A. C. CONDUCTION OF $\text{NH}_4\text{H}_2\text{PO}_4/\text{ND}_4\text{D}_2\text{PO}_4$

Cell constants:

<p>| | | |</p>
<table>
<thead>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{NH}_4\text{H}_2\text{PO}_4$</td>
<td>pellet</td>
<td>$14.57 \times 10^{-2}$ cm$^{-1}$</td>
</tr>
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<td>$\text{ND}_4\text{D}_2\text{PO}_4$</td>
<td>pellet</td>
<td>$29.99 \times 10^{-2}$ cm$^{-1}$</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>$\text{NH}_4\text{H}_2\text{PO}_4$</th>
<th></th>
<th>$\text{ND}_4\text{D}_2\text{PO}_4$</th>
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<tr>
<td>Temp</td>
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<td>Temp</td>
<td>$8+\log(\text{Sp. Cond.})$</td>
</tr>
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<td>(°C)</td>
<td></td>
</tr>
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<td>0.577</td>
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D.C ELECTROLYSIS OF KH₂PO₄

Temp.  
26.6 °C

Volts.  
200.0

No movement of mercury meniscus was observed in 86 hours and potential was applied across the pellet thereafter.

<table>
<thead>
<tr>
<th>Time (hr)</th>
<th>Current (micro-amp)</th>
<th>Hg-meniscus movement(cm)</th>
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<tr>
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<td>0.58</td>
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Silver coulometer calculation was done in the same ways as KHF₂ and results agreed within 10%.

Volume of gas produced during electrolysis at N.T.P.

= Volume of mercury displaced at N.T.P.  
= 0.05626 ml at N.T.P.

Activity of silver-110 deposited on the Cu-electrode

= 581.01 cpm.  
= 0.0601 ml of hydrogen at N.T.P.  

( from fig 4.4 )
A.C. CONDUCTION OF KH₄PO₄ SINGLE CRYSTAL

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### A.C. Conduction Results of Potassium Dihydrogen Phosphate

#### Cell Constants

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<th>$\text{KDP}_2\text{PO}_4$</th>
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<td>0.18054 cm$^{-1}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.11590 cm$^{-1}$</td>
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#### Table of Temperature and Conductivity

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<th>Temp (°C)</th>
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<th>Temp (°C)</th>
<th>9+log(Sp. Cond)</th>
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A. C. CONDUCTANCE OF \( \text{KH}_2\text{AsO}_4 / \text{KD}_2\text{AsO}_4 \)

**Cell constants**

<p>| | | |</p>
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<th></th>
<th></th>
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<td>( \text{KH}_2\text{AsO}_4 )</td>
<td>pellet</td>
<td>( 14.1235 \times 10^{-2} ) cm(^{-1} )</td>
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<tr>
<td>( \text{KD}_2\text{AsO}_4 )</td>
<td>pellet</td>
<td>( 15.567 \times 10^{-2} ) cm(^{-1} )</td>
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<table>
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<th>( \text{KH}_2\text{AsO}_4 )</th>
<th>( +\log(\text{sp. conduct}) )</th>
<th>( \text{KD}_2\text{AsO}_4 )</th>
<th>( +\log(\text{sp. conduct}) )</th>
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<td>Temp (°C)</td>
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TRITIUM DIFFUSION EXPERIMENT

Temp  93.0°C

Time  65.0 hours

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<th>c.p.m.</th>
<th>log (cpm)</th>
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<tr>
<td>Temp (°C)</td>
<td>D(cm²/sec)</td>
<td>Ln (D) (theoretical)</td>
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<tr>
<td>-----------</td>
<td>------------</td>
<td>----------------------</td>
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<tr>
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<tr>
<td>110.0</td>
<td>3.931 x 10⁻¹⁰</td>
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</table>

D₀ (i.e., Y-intercept) = 3.035 x 10⁻⁴ cm/sec
Slope = -4.9809 x 10³ deg⁻¹
Activation energy for diffusion = 9.45 kcal/mole
Standard error of slope = 0.089
VERIFICATION OF EINSTEIN RELATIONSHIP

<table>
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<tr>
<th>$I/T \ (°K)$</th>
<th>$\text{Ln} \ (\sigma')$</th>
<th>Slope</th>
<th>$I/T \ (°K)$</th>
<th>$\text{Ln} \ (\sigma')$</th>
<th>slope</th>
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<td>$x 10^3$</td>
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<td>$x 10^3$</td>
<td>$x 10^3$</td>
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<tr>
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<td>-7.780$x 10^3$</td>
<td>2.500</td>
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<tr>
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<td></td>
<td>2.550</td>
<td>-9.892</td>
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</tr>
<tr>
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<td>2.600</td>
<td>-10.123</td>
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<tr>
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<td>3.100</td>
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$\text{Ln} \ (\sigma')$ is the experimental values for $\log_e(\text{conductance})$ of ammonium dihydrogen phosphate single crystal

$\text{Ln} \ (\sigma')$ is the theoretical values for $\log_e(\text{conductance})$ calculated from diffusion data (i.e., $N_e D/kT$)
D.C. ELECTROLYSIS OF OXALIC ACID DIHYDRATE

Temp 41.2°C
Volts 60.0

No displacement of mercury was observed in 67 hours and the potential was applied thereafter.

<table>
<thead>
<tr>
<th>Time (hr)</th>
<th>Current (Micro-amp)</th>
<th>Hg-meniscus movement(cm)</th>
</tr>
</thead>
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<td>0.0</td>
<td>380.0</td>
<td>0.0000</td>
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<tr>
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</tr>
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<td>25.5</td>
<td>0.0500</td>
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<tr>
<td>30.20</td>
<td>22.0</td>
<td>0.0600</td>
</tr>
<tr>
<td>32.0</td>
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</tr>
<tr>
<td>47.10</td>
<td>19.0</td>
<td>0.0950</td>
</tr>
</tbody>
</table>

Volume of gas evolved in the cathode compartment at N.T.P.

= Volume of mercury displaced at N.T.P.

= $8.26 \times 10^{-2}$ ml at N.T.P.

Activity of silver-110 deposited on the Cu-electrode

= 5503.5 cpm

= $5.1 \times 10^{-2}$ ml at N.T.P. (from fig.4.4)
A.C. CONDUCTANCE OF OXALIC ACID DIHYDRATE

Cell constants

<table>
<thead>
<tr>
<th></th>
<th>Pellet</th>
<th>cm$^{-1}$</th>
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<tbody>
<tr>
<td>Oxalic acid dihydrate</td>
<td>1.353 x 10$^{-1}$</td>
<td>cm$^{-1}$</td>
</tr>
<tr>
<td>Deuterated dihydrate</td>
<td>1.109 x 10$^{-1}$</td>
<td>cm$^{-1}$</td>
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</tbody>
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<table>
<thead>
<tr>
<th>oxalic acid dihydrate</th>
<th>Deuterated oxalic acid</th>
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<tbody>
<tr>
<td>Temp (°C)</td>
<td>10+log(st.conduct)</td>
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<tr>
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