CHAPTER I

ELECTRON PARAMAGNETIC RESONANCE AND D.C. ELECTRICAL CONDUCTIVITY OF TRANSITION METAL IONS DOPED OXIDE GLASSES: AN INTRODUCTION.

1.1 INTRODUCTION:

Electron paramagnetic resonance (EPR) spectrum was first of all obtained in 1945 by Zavoisky\textsuperscript{1,2} in USSR and in 1946 by Cummerow and Halliday\textsuperscript{3} in U.S.A. Electron paramagnetic resonance is the phenomenon of resonant absorption of microwave radiation among the Zeeman components of the electronic ground state of a paramagnetic species. In 1947 Bagguley and Griffiths\textsuperscript{4} performed an experiment in the x-band of microwave frequencies, a frequency region which remained the one most commonly used during the following four decades. This leads to an important method for obtaining information about the magnetism of the electronic ground state of the paramagnetic system. Electron paramagnetism occurs whenever a system possesses a resultant non-zero total angular momentum in its electronic system. Therefore, study of electron paramagnetism of a system gives the properties of angular momentum, both of spin and orbit, in the electronic ground state which in turn gives valuable information about the interaction of paramagnetic ion with the surroundings. Such studies are most commonly performed with transition metal ions and rare earth ions because
their inner electron shells are partially filled. Other paramagnetic systems that can be used are:

(i) Atoms, molecules and free radicals having an odd number of electrons, like atomic hydrogen, NO, NO$_2$, O$_2$, diphenyl picryl hydrazyl (DPPH).

(ii) Colour centres which involve trapped electrons or holes.

(iii) Conduction electrons in semiconductors and metals.

(iv) Paramagnetic species obtained from diamagnetic substance by disrupting its normal bonds either by exposing it to high energy radiation or by subjecting it to mechanical stress.

1.2. ELECTRON PARAMAGNETIC RESONANCE:

The simple EPR theory is as follows. Consider unpaired electrons in an isolated metal ion or atom having electronic spin and orbital angular momentum $\vec{S}$ and $\vec{L}$, respectively. The total electronic angular momentum is $\vec{J} = \vec{L} + \vec{S}$. The circulation of mass is represented by angular momentum and the circulation of charge is represented by magnetic dipole moment. Therefore, on an atomic scale the circulation of electrons relate the magnetic dipole moment, $\vec{M}$ with $\vec{J}$. Assuming Russel-Saunders coupling so that $\vec{L}$, $\vec{S}$ and $\vec{J}$ are all
good quantum numbers, we may write the following relation for a free atom or ion

$$\mathbf{\alpha} = - g \beta \mathbf{J}$$

where $g$ is the Lande $g$-factor given by

$$g = 1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}$$

and $\beta$ is the Bohr magneton and its value is $|e| h / 4\pi mc$ with $e(m)$ is the charge (rest mass) of the electron, $h$ is the Planck's constant and $c$ is the velocity of light in vacuum. The ground state of the isolated ion is degenerate. If this paramagnetic ion is placed in a strong static magnetic field $H$, the Hamiltonian for the interaction is written as

$$\mathbf{H} = - \mathbf{\alpha} \cdot \mathbf{H} = g \beta J_z H = g \beta J_z H$$

(1.1)

where the $z$ axis chosen to be the direction of the applied static field. The solutions for the energy are then

$$E = g \beta HM$$

(1.2)

where magnetic quantum number $M$ is equal to $-J$, $-J + 1$, $-J$, $J-1$ or $J$. Thus the degeneracy of the ground state is lifted and it is split into a set of $2J+1$ evenly spaced levels each of which corresponds to one value of $M$ and their spacing is directly proportional to $H$. 
The coupling most commonly used to produce the magnetic resonance is an alternating magnetic field applied perpendicular to the static field. If we write the alternating field of angular frequency $\omega$ in terms of amplitude $H_0^O$, we get a perturbing term in the Hamiltonian of

$$J_{\text{pert}} = g \beta J_x H_0^O \cos \omega t$$  \hspace{1cm} (1.3)

The operator $J_x$ has nonvanishing matrix elements, $\langle M' | J_x | M \rangle$, for $M' = M \pm 1$. Consequently the allowed transitions are between levels adjacent in energy, giving

$$\hbar \omega = \hbar \nu = g \beta H$$  \hspace{1cm} (1.4)

Fig. 1.1 shows the energy levels of an ion with $J = \frac{1}{2}$ in a magnetic field. Application of microwave radiation of energy $\hbar \nu$ may cause resonance transitions at a field given by $\hbar \nu / g \beta$.

When the paramagnetic ions are incorporated in a solid, there are interactions between a paramagnetic ion and neighbouring ions. These interactions are mainly of two types: (a) interaction between paramagnetic ions, and (b) interaction between paramagnetic ion and diamagnetic neighboring ions. The former type of interaction can be reduced effectively to a small value by diluting the paramagnetic ions in the diamagnetic...
FIG. 1.1 THE ENERGY LEVEL OF AN ION WITH $J = 1/2$ IN A MAGNETIC FIELD. APPLICATION OF MICROWAVE RADIATION OF ENERGY $h\nu$ CAUSES RESONANCE AT A FIELD GIVEN BY $h\nu/g_\beta$. 
The large electric fields created by the diamagnetic neighbors partially or fully "quench" the orbital motion of the electrons. In such a situation the spectroscopic splitting factor need not be isotropic because part of the magnetic moment arising from the orbital motion of the electrons is modified by the electric field. The total $g$-value (spin plus orbit) may then be anisotropic by an amount that depends on the magnitude of the orbital contribution to the magnetic moment and on the asymmetry in the crystal field.

Once the resonance condition, $h\nu = g\beta H$ is achieved there are other factors which control the continuous absorption of energy by the magnetic system. The population in the Zeeman components obeys Boltzmann distribution* and at any temperature the lower state is

*Electrons obey Fermi-Dirac statistics, and the use of Boltzmann statistics here should not be thoughtlessly accepted. We suppose that the electrons on a Cu$^{2+}$ ion, for example, definitely obey the Pauli exclusion principle insofar as they compete with each other for quantum states within the ion. Once the paramagnetic properties of the ions are so determined, however, our assumption of independent, non-interacting Cu$^{2+}$ ions implies a spatial separation and, in effect, a spatial distinguishability of particles. This spatial distinguishability means that Boltzmann statistics is appropriate.
more populated than the upper one. When the absorption of microwave power occurs, there is tendency to equalise the populations and unless there is some other mechanism which maintains the population difference constantly, paramagnetic resonance absorption ceases to be significant. These mechanisms are called relaxation processes in which lattice plays a significant role. It acts like a huge reservoir to which the magnetic system transfers energy with a characteristic time $T_1$, called the spin-lattice relaxation time. This is a characteristic of a given magnetic ion in a lattice and normally it increases with decrease of temperature of the reservoir. For systems where the spins are strongly coupled to vibrational modes (short $T_1$), the lifetime of a given magnetic state is short, resulting in an uncertainty in the energy which manifests itself as a broad absorption line in the EPR spectrum. Other factors that can contribute to the width of EPR absorption lines from solid samples are:

(i) Anisotropy of $g$ factors and hyperfine interactions or spin-spin interactions.

(ii) Interaction with magnetic dipoles of neighbouring electronic and nuclear spins.

(iii) Exchange interactions with the neighboring unpaired electrons.
The factor (i) is important only for glass sample or powder sample. The effect of (ii) factor can be reduced by studying the ion in systems where magnetic ions are far apart. The exchange narrowing is a common occurrence for solid free radicals, which often have very sharp EPR lines. Since the exchange interaction is strongly dependent on the distance between magnetic ions, it is not present when studying magnetically dilute systems.

1.3 TOTAL HAMILTONIAN OF INTERACTIONS:

The energy of an atom or radical containing unpaired electrons and nuclei with non-zero spins may be expressed in terms of the Hamiltonian operator\(^6,7\).

\[
\mathcal{H} = \mathcal{H}_{\text{el}} + \mathcal{H}_{\text{CP}} + \mathcal{H}_{\text{LS}} + \mathcal{H}_{\text{SS}} + \mathcal{H}_{\text{Ze}} + \mathcal{H}_{\text{HF}} + \mathcal{H}_{\text{Zn}} + \mathcal{H}_{\text{II}} + \mathcal{H}_{\text{Q}} \quad (1.5)
\]

The first three terms constitute the atomic Hamiltonian and the last six form the spin Hamiltonian. \(\mathcal{H}_{\text{el}}\), the electronic Hamiltonian operator is the sum of the kinetic energy of electrons, \(p_i^2/2m\), the potential energy of the electrons relative to the nuclei, \(-Z_n e^2/r_{ni}\), and mutually repulsive energies, \(e^2/r_{ij}\):

\[
\mathcal{H}_{\text{el}} = \sum_i \frac{p_i^2}{2m} - \sum_{i,n} \frac{Z_n e^2}{r_{ni}} + \sum_{i,j} \frac{e^2}{r_{ij}} \quad (1.6)
\]

where the subscript \(n\) is for nuclei and \(i\) and \(j\) are for electrons. The electronic energy is usually of the order
of $10^4$ to $10^5\text{cm}^{-1}$, and so it is in the optical region of the spectrum, many orders of magnitude larger than the Zeeman energies.

$\mathcal{H}_{\text{CF}}$, the crystal field term shifts and splits the electronic energy. This crystal field arises from the charges of the ions in ionic compounds and from the chemical bonds in covalent compounds. Essentially it is a stark effect arising from the electrostatic potential of the form

$$v = \sum_{i,j} \frac{Q_i}{r_{ij}}$$

(1.7)

where $Q_j$ is the ionic charge and index $i$ is for electrons. Eq (1.7) is in the point charge approximation, and ordinarily only nearest-neighbor ligands are taken into account.

The spin-orbit interaction for an atom is written as:

$$\mathcal{H} = \lambda \overrightarrow{L} \cdot \overrightarrow{S}$$

(1.8)

where $\lambda$ is the spin-orbit coupling constant, and $\overrightarrow{L}$ is the orbital angular momentum and $\overrightarrow{S}$ is the spin angular momentum. It is of the order of $10^2\text{cm}^{-1}$ for first transition series and $10^3\text{cm}^{-1}$ for the rare earths. This is much smaller than the typical crystal field splitting.
for the first transition series and exceeds crystal field splittings for the rare earths.

\[ J_{SS} \] represents the mutual interaction between the magnetic dipoles. It is of the form

\[ J_{SS} = D \left[ S_z^2 - \frac{1}{3} S (S+1) \right] + E \left( S_x^2 - S_y^2 \right) \]  (1.9)

This energy (0 to 10 cm\(^{-1}\)) is usually of the same order of magnitude as the electronic Zeeman energy, and the spectrum becomes angular dependent. For axial symmetry \( E = 0 \).

The electronic Zeeman term

\[ J_{Ze} = \beta \vec{H} \cdot (\vec{L} + 2\vec{S}) \]

\[ = \beta \vec{S} \cdot \vec{H} \]  (1.10)

has a magnitude of about 0.3 cm\(^{-1}\) at x band (10\(^{10}\) Hz) and is sometimes anisotropic. The nuclear Zeeman term

\[ J_{Zn} = - \sum_i e_n i \beta_n \vec{H} \cdot \vec{l} \]  (1.11)

is about 1/1840 times the electronic Zeeman term and is usually isotropic. \( J_{Ze} \) and \( J_{Zn} \) are the main interactions in electron paramagnetic resonance and nuclear magnetic resonance, respectively.

The hyperfine interaction is of the form

\[ J_{HF} = \vec{S} \cdot \sum_i \vec{A}_i \cdot \vec{l}_i \]  (1.12)
and the nuclear spin-spin interaction is of the form

$$\mathcal{H}_{II} = \sum \mathbf{I}_i \cdot \mathbf{J}_{ij} \cdot \mathbf{I}_j$$  \hspace{1cm} (1.13)

The hyperfine coupling constants $A_i$ are usually anisotropic while most nuclear magnetic resonance studies deal with isotropic spin-spin coupling constants. $\mathcal{H}_{HF}$ is of the order of $10^{-1} - 10^{-3}$ cm$^{-1}$.

These Hamiltonian terms given by Eqs (1.12) and (1.13) are responsible for the structure that is observed in magnetic resonance spectra.

The main quadrupolar energy term, $\mathcal{H}_Q$ is

$$\mathcal{H}_Q = \frac{e^2 Q}{4I(2I-1)} \left( \frac{\partial^2 V}{\partial z^2} \right) \left[ 3I_z^2 - I(I+1) + \eta (I_x^2 - I_y^2) \right]$$  \hspace{1cm} (1.14)

where $Q$ is the quadrupole moment, $\frac{\partial^2 V}{\partial z^2}$ is the field gradient and $\eta$ is the asymmetry parameter:

$$\eta = \left( \frac{\partial^2 V}{\partial x^2} \frac{\partial^2 V}{\partial y^2} \right) / \left( \frac{\partial^2 V}{\partial z^2} \right)$$  \hspace{1cm} (1.15)

For axial symmetry $\eta = 0$ and its value is of the order of $10^{-3}$ cm$^{-1}$.

The first three terms in Eq. (1.5) are much greater in energy than the main Zeeman terms and therefore they should be treated separately in the calculation. First the secular equation with $\mathcal{H}_{el}$, $\mathcal{H}_{CF}$ and $\mathcal{H}_{LS}$ is solved and then the effect of these terms
on the spin Hamiltonian is calculated. If $\mathcal{H}_{LS}$ is much less than the crystal field splitting, $\Delta E_{CF}$, the wavefunction of the ground crystal field state will contain admixture of the next higher state of the order of $\lambda / \Delta E_{CF}$. In general this is the situation for the elements of first transition series.

The effect of this admixture of higher crystal field states into ground state is that the $g$-factor of a transition metal ion deviates from its free electron value by an amount which is proportional to spin-orbit coupling constant and inversely proportional to the crystal field splittings.

1.4 SCOPE OF EPR:

Over the past four decades, EPR has been successfully used for a variety of problems of atomic or molecular system in which unpaired electrons occur. EPR technique has been applied to many fields.

1. EPR is singularly useful when information is desired about the valence state, location of impurity in the matrix, symmetry and orientation of paramagnetic centers.

2. EPR together with optical and thermal studies gives clear understanding of the nature of colour centers in solids.
3. EPR technique is useful in getting regarding the phase transitions:

4. EPR is used to study the way in which ions like VC\(^{2+}\), N\(_2\)C\(^{2+}\), enter the host to get the information about the conjugation of such ions with the surrounding ligands.

5. EPR is used to study the nuclear spin and nuclear quadrupole moments of free radicals.

6. EPR technique is useful in detecting free radicals\(^9\)\(^-\)\(^11\) in chemical systems, revealing possible important mechanism. Analysis of the hyperfine structure allows to determine the unpaired electron distribution in different parts of the radicals.

7. EPR technique is used in obtaining information on radicals stabilized in biomolecules such as nucleic acids and proteins\(^9\)\(^,13\).

8. EPR technique is also used in dating materials\(^14\). Ikeya and Miki\(^15\)\(^,16\) have developed a new dating method with EPR which has been applied to dating of food or materials of various age.

9. EPR technique has been used to photosensitive charge transfer luminescence and photoconductivity.
EPR technique is also a powerful tool for determining the co-ordination environment of transition metal ions, rare earth ions or color centres in glasses.

PRESENT INVESTIGATIONS:

Electron paramagnetic resonance of 3d transition metal ions has been quite well understood and therefore, these ions serve as excellent candidates to probe the crystal fields. In the present work ulticomponent borate, phosphate and sulphate glasses oped with transition metal ions (VO$^{2+}$ and/or Cu$^{2+}$) re prepared and detailed investigations about the chemical state of VO$^{2+}$ and Cu$^{2+}$ are presented.

Chapter 2 describes the theory developed by s to analyse EPR spectra characterized by $\mathbf{H} = \beta \mathbf{g} \cdot \mathbf{S}$.

In chapter 3 fabrication of furnace is escribed which we have used to prepare glasses. In his chapter EPR studies of VO$^{2+}$ in the (i) Li$_2$O.MgO.B$_2$O$_3$
(ii) Li$_2$O.CaO.B$_2$O$_3$ (iii) Li$_2$O.ZnO.B$_2$O$_3$ (iv) Li$_2$O.SrO.B$_2$O$_3$
(v) Li$_2$O.CdO.B$_2$O$_3$ and (vi) Li$_2$O.BaO.B$_2$O$_3$ glasses are escribed.

Chapter 4 deals with EPR and optical spectra studys of VO$^{2+}$ and Cu$^{2+}$ in singly and mixed proportions.
in (i) $\text{Li}_2\text{O}.\text{B}_2\text{O}_3$ (ii) $\text{ZnO}.\text{B}_2\text{O}_3$ and (iii) glasses.

Chapter 5 contains the EPR and c studies of (i) $x(\text{CuO}.V_2\text{O}_5).\{(1-x)(\text{Na}_2\text{C.P}_2$

$\times(\text{CuO}.2V_2\text{O}_5).\{(1-x)(\text{Na}_2\text{O}.\text{P}_2\text{O}_5)$ with $0 \leq x$.

(ii) $x \text{CuSO}_4.\frac{1}{2}(1-x)(\text{K}_2\text{SO}_4.\text{ZnSO}_4)$ with containing 2 mol% of Vanadium Sulphate.

Theoretical optical basicity of has also been calculated and given.

In chapter 6 the variation of d. conductivity with temperature of the fo] is given:

(i) $2\text{Li}_2\text{O}.3\text{B}_2\text{O}_3\times[x\text{CuO}(0.09-x)V_2\text{O}_5]$ where is the base glass and $x \leq 0.09$.

(ii) $x \text{CuSO}_4.\frac{1}{2}(1-x)(\text{K}_2\text{SO}_4.\text{ZnSO}_4)$ containing Vanadium Sulphate with $0.0 \leq x \leq 0.4$.

1.6 GLASSES:

The structure of a solid formed its liquid state depends on many factors factor is its rate of cooling. If the li at sufficiently slow rate, the transform into solid is discontinuous as evidence change in volume at a particular temper:
reezing (melting) temperature, $T_m$, the solid thus obtained has its atoms or molecules stacked in a regular manner with the periodicity extending over large distances as compared to the atomic dimensions and is said to exist in 'crystalline' state. X-ray diffraction patterns show sharp rings. However, if the liquid is cooled fast enough the transformation to solid state is continuous and the volume-temperature curve which is a straight line undergoes a change in slope at a particular temperature, $T_g$, usually referred to as 'glass transition' temperature, Fig 1.2. The substance possesses liquid-like properties above this temperature and has a value of viscosity about $10^{15}$ poise ($=10^{14} \text{NS/m}^2$) at $T_g$. Below $T_g$, the rearrangement of atoms and molecules become slow and the structure sets frozen and it behaves like a solid. This resultant solid shows, instead of sharp rings, a few broad diffused haloes and thus possesses short-range order only, i.e. periodicity is maintained only upto a few angstroms and not to large distances. Such a solid is called glass. The American Society for Testing Materials (ASTM) has defined glass as "Glass is an inorganic product of fusion which has been cooled to rigid condition without crystallization". The definition is restrictive by the use of word 'inorganic', since any organic substances form glasses. The definition
Figure 1.2. Volume - temperature relationship for glass-forming system.
given by Jones is "A glass is a material formed by cooling from the normal liquid state, which has shown no discontinuous change at any temperature, but has become more or less rigid through a progressive increase in its viscosity", however it includes the organic substances as well. But glasses can also be prepared without cooling from the liquid state, e.g., glass coatings are deposited from the vapour and sometimes with chemical reactions. Consequently, the broader definition: "Glass is an amorphous solid", is preferred. A material is 'amorphous' when it has no long range order, i.e. there is no regularity in the arrangement of its atomic or molecular constituents on a scale larger than a few times the size of the molecular constituents. A 'solid' is a rigid material and does not flow when subjected to moderate forces.

Glasses are categorised in many groups such as inorganic oxide, chalcogenide, halide glasses etc., Metals and their alloys have also been obtained in amorphous state by 'splat cooling technique' employing very high cooling rate, the glasses thus obtained are known as 'metallic glasses'. The present work is, however, confined to borate, phosphate and sulphate glasses, which come under inorganic oxide glasses, ASTM definition is therefore adequate.
1.6.2 INORGANIC OXIDE GLASSES:

In principle any substance, if cooled from the liquid state fast enough to prevent crystallization, can be made into a glass. However only a limited number of oxides, such as P2O5, B2O3, SiO2 etc., have been made into glassy state at normal cooling rate, because of their high viscosity at the melting point\(^21\). These substances are known as glass formers.

X-ray diffraction pattern of glasses shows diffused pattern which is different from that of crystals. It means that glasses do not form periodic three dimensional network like crystals and exhibit complete absence of long range order but possesses only the short range order. This order extends up to \(10 \text{ to } 20 \text{ Å}^{22,23}\). These considerations led Zachariasen to formulate the following four rules for glass formation:

(i) An oxygen atom is linked to, not more than two glass-forming atoms.

(ii) The co-ordination number of glass-forming atom is small (three or four).

(iii) The oxygen polyhedra share corners with each other, not edges or faces, and at least three corners in each oxygen polyhedron.

(iv) Polyhedra are shared to form continuously random three dimensional network (CRN). Doremus\(^24\), after
reviewing various x-ray diffraction studies, has given the conclusion in support of CRN model.

The oxides such as $B_2O_3$, $P_2O_5$, $SiO_2$ etc. which form glasses satisfy the above rules. These oxides are, therefore, called 'glass-formers' or 'network formers'. Addition of alkali or alkaline-earth oxides such as Li$_2$O, K$_2$O, CaO or MgO etc. modifies the glass network by making it open. These oxides are, therefore, known as 'glass-modifiers or 'network-modifiers'. The action of the modifiers is to break up the continuous network by introducing 'dangling' or 'non-bridging' oxygens. The non-bridging oxygen carries a single negative charge and is compensated by a positive alkali ion nearby. The metal ion goes into interstices and distribute themselves randomly in glass network. Distribution of metal ions in these glasses is uncertain. Some studies have given the possibility of non-uniform distribution of metal ions and of their 'clustering' in the network.

The present studies deal with borate, phosphate and sulphate glasses, therefore introduction of these glasses is given below.

1.6.3 BORATE GLASSES:

The theory of borate glass structure due to J. Krogh-Moe is by now widely, if not universally accepted.
Taking into account the extensive studies of borate glasses by Infra-red and Raman spectroscopies made by Krogh-Moe and Konijnendijk and Stevels, H. Kawazoe, H. Hosono and T. Kanazawa made Fig.1.3, a model of alkali borate glasses. This Fig. shows a schematic change of the borate groups appearing in the alkali borate glasses as a function of alkali oxide content. Boric oxide glasses consist of boroxol group and BO$_3$ triangles. It is well known that addition of 1 mol of R$_2$O (alkali oxide) to boric oxide forms 2 mol of BO$_4$ tetrahedra. At $x \approx 17$, where $x$ is R$_2$O mol%, BO$_3$ triangles attached to two BO$_4$ tetrahedra start forming. Diborate groups tend to dominate as $x$ increases from 20 to 30 or two BO$_4$ groups are adjoining as shown in Fig.1.4. For $x \geq 30$ diborate, triborate and boroxol ions with non-bridging oxygen appear. Many other authors postulated that non-bridging oxygens start to appear at $x \approx 17$. It should be remembered that conversion of some dominant borate groups to other should be continuous and the boundaries between two adjacent regions in Fig.1.3 should be viewed as smearing.

1.6.4 PHOSPHATE GLASSES:

Phosphate glass is not studied extensively due to the difficulties of obtaining P$_2$O$_5$ glass, since P$_2$O$_5$ glass being hygroscopic, rapidly reacts with atmospheric
Fig. 1.3. Schematic representation of changes of borate groups in alkali borate glasses.
Fig. 1a. Atomic arrangements of boron groups and borato ions.
moisture. The basic structure of pure P₂O₅ glass consists of a continuous random network (CRN) of quasi-tetrahedral PO₄ units in which only three of the oxygen atoms of each unit bridge to neighboring PO₄ units, while the fourth non-bridging oxygen is double-bonded to the central phosphorus atom to satisfy the valency of phosphorus. It is found that the double-bonded P=O length is shorter than that of the single bonded P-O. When metal ions of high polarizing power like Li⁺ or Be⁺⁺ are added, the terminal oxygens associated with the P=O bonds are now converted to bridging oxygens as a result of the occupancy of network-forming positions by the added metal ions. The overall network is thus strengthened progressively with further addition of these ions. Less polarizing ions such as Na⁺, Ba⁺⁺ or Pb⁺⁺ initially have the same effect, but beyond a certain concentration at which all the P = O bonds are "opened", nonbridging oxygens begin to form and additional metal ions are now taking modifying cation positions.

One molecule of alkali oxide opens four P = O units in the P₂O₅ structure and hence at 20 mol% Li₂O or Na₂O, no P = O units remain in the phosphate structure. For alkaline-earth oxides the corresponding concentration is at 33 mol%.
Fig. 1.5. Showing the four sulphate ions (enclosed by bigger circles) surrounding the central potassium (not directly visible) ion as per the model.

Fig. 1.6. Showing the different stages of zinc ion attaining octahedral co-ordination with oxygen ions. The octahedral configuration is shown in part.
1.6.5 SULPHATE GLASSES:

Sulphate glasses are ionic glasses. Unlike other glasses such as borate and phosphate, glasses of purely ionic materials are generally obtained from binary, ternary and more complicated systems rather than from simple compounds\textsuperscript{34-37}. The intrinsic nature of glass formation in purely ionic materials does not seem to originate from the possibility of polymeric structures of anions\textsuperscript{34}. It has been tried to explain the formation of glass in such ionic system on the basis of (i) distortion of anions\textsuperscript{38,39} (ii) differential field strengths of cations\textsuperscript{40} and (iii) the low liquidus temperature\textsuperscript{41,42}. P.S.L. Narasimham and K.J. Rao\textsuperscript{43} studied phase equilibria, glass forming regions, molar volumes and refractive indices, glass transition and crystallization behaviour, microhardness and the elastic constants of $\text{K}_2\text{SO}_4\cdot2\text{ZnSO}_4$ glass to understand the nature of these ionic glasses. They\textsuperscript{43} proposed random close packing model for the sulphate glasses. The proposed model is:

(i) The sulphate ions are randomly close packed.

(ii) Potassium ions maintain an environment of four sulphate ions which are so oriented that the central potassium ions have an oxygen co-ordination of 12 as shown in Fig 1.5. (This is the highest
co-ordination possible for K⁺ ion since
$$r_{K^+} : r_{O^{2-}} : 1.33 : 1.32^{44}.$$ 

(iii) Zinc ions are octahedrally co-ordinated (Fig 1.6) to six sulphate ions and in the region of zinc ions the tetrahedral sulphate units are packed in such a way that more oxygen-oxygen contacts from different sulphate ions become possible.

1.7 VANADYL ION:

Vanadium (atomic number, Z=23) belongs to the first series transition metal group (iron group with incomplete 3d shell, 29 ≥ Z ≥ 21) and has the electronic configuration \([\text{Ar}]^{18} 3d^3 4s^2\). The common valence states of Vanadium are V²⁺, V³⁺, V⁴⁺ and V⁵⁺. V⁵⁺ state is diamagnetic. V³⁺ state although paramagnetic, is usually not observed by EPR probably due to internal electric field effects. V²⁺ is oxidatively unstable. V⁴⁺ with electronic structure \([\text{Ar}]^{18} 3d^1\) exists almost exclusively as VO²⁺ ion (Vanadyl Ion). The chemistry of VO²⁺ ion has been reviewed by Selbin⁴⁵,⁴⁶. VO²⁺ contains a single unpaired d electron attached to the V⁴⁺ ion and would be similar to the other d¹ configuration ions. In solids or in solutions, usually vanadium occurs co-ordinated with other groups particularly with oxygen, having total co-ordination number five or six.
However, one very short V-O bond, in general, preserves the identity of the VO$^{2+}$ ion. In most of the cases, complexes containing the VO$^{2+}$ ions have characteristic purple or blue colour. The spectrum of the blue solutions of VO(H$_2$O)$_5^{++}$ has been measured many times. There is one band system in the visible with a maximum at 13,000 cm$^{-1}$ and a shoulder at 16,000 cm$^{-1}$. In the near ultraviolet a second band system with a shoulder at 41,700 cm$^{-1}$ appears. The first band system was interpreted by Jørgensen and Furlani, both using the simple crystal field model. Jørgensen treated the molecule as a strongly distorted octahedron and Furlani considered only $C_3v$ point group symmetry. These models are unable to account for all the observed bands. The energy level scheme for the hydrated vanadyl ion situated in the octahedral and tetragonal crystalline fields is shown in Fig. 1.7.

The parameters $D_s$ and $D_t$ show the degree of tetragonality present in the field. It is obvious from Fig 1.7 that the ground state may be $e$ or $b_2$ orbital depending on the relative values of $D_s$ and $D_t$. Magnetic data on vanadyl complexes indicate that an orbitally non-degenerate $b_2$ is the ground state. Thus one d electron in VO$^{2+}$ is placed in $b_2$ orbital.
Fig. 1.7. Energy level scheme of VO$^{2+}$ in crystal of octahedral and tetragonal symmetry.
Palma-Vittorelli et al.\textsuperscript{51} pointed out and allhausen and Gray\textsuperscript{52} showed that a pure crystalline field, which only considers $\sigma$-bonding to be present, is not adequate, but for an accurate description of the electronic structure of the vanadyl ion and its complexes one must include $\pi$ bonding between vanadium and oxygen. Ballhausen and Gray\textsuperscript{52} gave the molecular orbital theory of $\text{VO}^{2+}$ in the complex $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$ bonded with five other oxygens belonging to water molecules (ligands) as shown in Fig. 1.8. Similar structure for the co-ordination of oxygen atoms to the vanadium ion in oxide glasses was taken by other workers\textsuperscript{53-56}. For these surroundings, $\text{V}^{4+}$ is assumed to have a $C_{4v}$ point symmetry group. This assumption is consistent\textsuperscript{55} with the EPR and optical data. The transformation scheme for the metal and ligand orbitals in such a symmetry is given Table 1.1.

The bonding scheme in $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$ is as follows\textsuperscript{52}, Fig. 1.9. A very strong $\sigma$ bond is formed between the $2p_z + 2s$ hybrid of the oxygen ($\sigma_5$) and the $3d_z^2 + 4s$ hybrid of the vanadium ion, $2p_x$ and $2p_y$ orbitals ($\Pi_5$) on the oxygen make strong $\pi$ bonds with the $3d_{xz}$, $3d_{yz}$ orbitals on the metal ion. The $3d_z^2 - 4s$ hybrid, together with the orbitals $3d_{x^2-y^2}$
Figure 1.8. Bonding Scheme for VO$^{2+}$
Table 1.1. Orbital Transformation Scheme in $C_{4v}$ Symmetry

<table>
<thead>
<tr>
<th>Representation</th>
<th>Vanadium Orbitals</th>
<th>Ligand Orbitals</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_1$</td>
<td>$3d_z^2 + 4s$</td>
<td>$\sigma_5$</td>
</tr>
<tr>
<td></td>
<td>$4s-3d_z^2$</td>
<td>$\frac{1}{2}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)$</td>
</tr>
<tr>
<td></td>
<td>$4p_z$</td>
<td>$\sigma_6$</td>
</tr>
<tr>
<td>$e$</td>
<td>$3d_{xz}, 3d_{yz}$</td>
<td>$\pi_y(2p_x, 2p_y)$</td>
</tr>
<tr>
<td></td>
<td>$4p_x, 4p_y$</td>
<td>$\frac{1}{\sqrt{2}}(\sigma_1-\sigma_3, \sigma_2-\sigma_4)$</td>
</tr>
<tr>
<td>$b_1$</td>
<td>$3d_{x^2-y^2}$</td>
<td>$\frac{1}{2}(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4)$</td>
</tr>
<tr>
<td>$b_2$</td>
<td>$3d_{xy}$</td>
<td>non bonding</td>
</tr>
</tbody>
</table>
Figure 1.9. Structure of the VO(H₂O)²⁺ molecule ion.
and $4p_x$, $4p_y$ and $4p_z$, are then just capable of five σ-bonds directed in a tetragonal pyramid with the $V^{4+}$ ion located at its base. $3d_{xy}$ vanadium orbital is a non-bonding orbital.

The ordering of the molecular orbitals proposed by Ballhausen and Gray and the position of the unpaired electron are given in Fig. 1.8; the unpaired electron is seen to be lying in the nonbonding $b_2$ vanadium orbital ($3d_{xy}$ or $^2B_{2g}$ state). The band system in $V^{4+}$ is due\(^5\) to transitions $b_2 \rightarrow e^*_\pi$ and $b_2 \rightarrow b^*_1$ which is supported by intensity calculations and band polarization measurements. The first-ultraviolet band is due to the transition\(^5\) $e^*_\pi \rightarrow b_2$.

The splitting factor $g$, the value of which is close to $g_e$, is anisotropic because of the proximity of the $e^*_\pi$ and $b^*_1$ levels to the $b_2$ level; its values are given by

$$g_n = g_e \left[ 1 - \frac{4A\alpha^2}{\Delta E(b_2 \rightarrow b_1^*)} \right] \quad (1.16)$$

$$g_\perp = g_e \left[ 1 - \frac{\lambda \gamma^2}{\Delta E(b_2 \rightarrow e^*_\pi)} \right] \quad (1.17)$$

where $g_e = 2.0023$, $\lambda$ is the spin-orbit coupling constant, $(1-\alpha^2)$ and $(1-\gamma^2)$ indicate the covalency rates. $(1-\alpha^2)$ gives an indication of the influence of the σ-bonding
between the vanadium atom and the equatorial ligands, while \( (1-\gamma^2) \) indicates the influence of \( \pi \) bondings with the vanadyl oxygen. \( \Delta E \) denotes the energy separation.

The \( g \)-values and hyperfine structure constants of \( V^{4+} \) ions in various systems are given\(^{33,53} \) in Table 1.2. It is noted that with increasing tetragonal distortion the value of \( g_\perp \) increases and exceeds that of \( g_\parallel \). In fact, in almost all cases of vanadyl complexes \( g_\parallel < g_\perp \). Covalent bonding reduces the hyperfine splitting\(^5^8 \) due to the nuclei of the paramagnetic centre itself, because this splitting depends on \( \langle \frac{1}{r^3} \rangle \). However, it increases the super-hyperfine splitting due to the nuclei of the ligands surrounding the ion in question.

1.8 CUPRIC (\( Cu^{2+} \)) ION:

Copper (atomic number, \( Z = 29 \)) belongs to the first series transition metal group and has the electronic structure \([Ar]^{18} 3d^{10} 4s^1\). We are interested only in divalent copper, which has the electronic configuration \([Ar]^{18} 3d^9\). Cupric ion configuration can be regarded as a single positive hole in the filled d-shell and the spectral behavior of the complex should be as found in \( VO^{2+} \), only with the level order inverted. In an octahedral field the five fold orbital level of
Table 1.2. g-values and hyperfine structure constants of $V^{4+}$ in various systems.

<table>
<thead>
<tr>
<th>Systems</th>
<th>$\epsilon_\parallel$</th>
<th>$\epsilon_\perp$</th>
<th>$A_{\parallel} \times 10^4$ cm$^{-1}$</th>
<th>$A_{\perp} \times 10^4$ cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V^{4+}$ in TiO$_2$</td>
<td>1.956</td>
<td>1.914</td>
<td>142</td>
<td>31</td>
</tr>
<tr>
<td>$V^{4+}$ in GeO$_2$</td>
<td>1.963</td>
<td>1.921</td>
<td>134</td>
<td>37</td>
</tr>
<tr>
<td>$V_0^{2+}$ in glass</td>
<td>1.936</td>
<td>1.976</td>
<td>172</td>
<td>60</td>
</tr>
<tr>
<td>$V_0(H_2O)_5^{2+}$</td>
<td>1.933</td>
<td>1.980</td>
<td>182</td>
<td>71</td>
</tr>
<tr>
<td>$V_0^{2+}$ in Phthalocyanin</td>
<td>1.966</td>
<td>1.989</td>
<td>158</td>
<td>56</td>
</tr>
</tbody>
</table>
Cu$^{2+}$ ion splits into an upper triplet ($^2T_{2g}$) and a low-lying doublet ($^2E_g$). A tetragonal or rhombic field splits the $E_g$ doublet, leaving two Kramers doublets, and paramagnetic resonance is observed for the lower of these. The magnetic properties of the lowest orbital singlet are modified slightly by an admixture of the excited states through spin-orbit interaction. This type of admixture results in an anisotropic g-value for the EPR spectrum. Splitting of the free ion ground state of Cu$^{2+}$ under the action of crystalline fields is shown in Fig 1.10.

Although the purely electrostatic model proved quite successful in some early work$^{59,60}$, it has been shown by several investigators$^{61,62}$ that covalency effects are quite significant in many copper complexes. If the observed $g_\parallel$ and $g_\perp$ values are about 2.35 and 2.05, respectively, then the cupric ion is co-ordinated by six ligands which form an octahedron elongated along one axis. If the ligand octahedron is compressed along one axis, the relation $g_\perp > g_\parallel = 2.0$ holds$^{64}$. By the tetrahedrally co-ordinated cupric ion in ZnO crystals, the observed values were $g_\parallel = 0.74$ and $g_\perp = 1.531$. For configuration satisfying condition $g_\parallel \approx 2.35$ and $g_\perp \approx 2.05$, the molecular orbital theory was developed by Maki and McGarvey$^{66}$ and modified by Kivelson and Neiman$^{67}$. 
Fig. 1.10. Splitting of the free ion ground state of Cu$^{2+}$ under the action of crystalline fields.

Fig. 1.11. Effect of tetragonal distortion on the octahedral symmetry of a d$^9$-system.
Antibonding hole orbitals given below are constructed from 3d orbitals of cupric ion and the 2s and 2p orbitals of the four-ligand oxygen ions which are at the corners of a square plane and nearer to the ion than those two on the perpendicular axis.

They are constructed and labelled in a $D_{4h}$ symmetry with the assumption that the components of the lower symmetry are small.

The four ligands are placed on the $+x$ and $+y$ axes. They are labelled by superscripts starting with one on the $+x$ axis and proceeding counter clockwise.

\[ B_{1g} = \alpha' d_{x^2-y^2} - \frac{1}{2} \beta' \left[ - \sigma_x^{(1)} + \sigma_y^{(2)} + \frac{1}{2} \sigma_x^{(3)} - \sigma_y^{(4)} \right] \] (1.18)

\[ B_{2g} = \beta' d_{xy} - \frac{1}{2} \beta' \left[ p_y^{(1)} + p_x^{(2)} - p_y^{(3)} - p_x^{(4)} \right] \] (1.19)

\[ A_{1g} = \alpha' d_{z^2} - \frac{1}{2} \beta' \left[ \sigma_x^{(1)} + \sigma_y^{(2)} - \frac{1}{2} \sigma_x^{(3)} - \sigma_y^{(4)} \right] \] (1.20)

\[ E_g = \begin{cases} 
\beta' d_{xz} - \frac{1}{\sqrt{2}} \beta' & \left[ p_z^{(1)} - p_z^{(3)} \right] \\
\beta' d_{yz} - \frac{1}{\sqrt{2}} \beta' & \left[ p_z^{(2)} - p_z^{(4)} \right] 
\end{cases} \] (1.21)

Here $\sigma_k^{(1)}$ are sp hybridized $\sigma$ orbitals of the ligands.

Interactions with the axial oxygens are neglected since they are expected to be small. In any case, they should effect only the $A_{1g}$ orbital and this orbital does not
effect the EPR parameters. Normalization of the ground state $B_{4g}$ orbital yields

$$\alpha^2 + \beta^2 - 2 \alpha \beta S = 1$$  \hspace{1cm} (1.22)

where $S$ is the overlap integral. The overlap of other orbitals are neglected because they are small. For purely ionic bond $\alpha^2 = 1$, $\alpha' = 0$ and for covalent bond $\alpha^2 = \alpha'^2 = \frac{1 + S}{2}$. The normalized covalency of $Cu^2+ \sigma$ bonding of $\sigma$ or $\pi$ symmetry is expressed as follows:

$$\int_\sigma = \frac{200 (1 - S) (1 - \alpha^2)}{1 - 2S} \% \hspace{1cm} (1.23)$$

$$\int_\pi = 200 (1 - \beta^2) \% \hspace{1cm} (1.24)$$

Using the above molecular orbital scheme, the EPR parameters are related to $\alpha^2$, $\beta^2$ and $\beta_{s}^2$ in the following form:

$$\varepsilon_{II} = \varepsilon_{e} - \frac{8 \lambda_{o}}{\Delta E_{xy}} \left[ \alpha^2 \beta_{s}^2 - f(\beta_{s}) \right]$$  \hspace{1cm} (1.25)

$$\varepsilon_{\perp} = \varepsilon_{e} - \frac{2 \lambda_{o}}{\Delta E_{xz}} \left[ \alpha^2 \beta^2 - g(\beta) \right]$$  \hspace{1cm} (1.26)

$$A_{II} = p \left[ - \frac{2}{7} (\frac{4}{7} + K_{o}) + \varepsilon_{II} - \varepsilon_{e} - \frac{8 \lambda_{o}}{\Delta E_{xy}} f(\beta_{s}) \right.$$  
$$\left. + \frac{3}{7} (\varepsilon_{\perp} - \varepsilon_{e}) - \frac{\varepsilon_{o}}{7 \Delta E_{xz}} g(\beta) \right]$$  \hspace{1cm} (1.27)
\[ A_\perp = P \left[ \alpha^2 \left( \frac{2}{7} - K_0 \right) + \frac{11}{14} (g_\perp - g_e) - \frac{11}{7} \frac{\lambda_0}{\Delta E_{xz}} \right] \]

where

\[ f(\beta) = \alpha' \beta^2 + \frac{11}{2} \alpha' \beta (1 - \beta_1^2)^{1/2} T(n) \]

\[ g(\beta) = \alpha' \beta^2 + \frac{11}{\sqrt{2}} \alpha' \beta (1 - \beta_1^2)^{1/2} T(n) \]

In these equations the notations of the constants and their numerical values are those used by earlier workers \(^{66-69}\), \(\lambda_0\), the spin-orbit coupling constant \(^{71}\) for the free Cu\(^{2+}\) ion, is \(-828\) cm\(^{-1}\). \(P(=2\gamma\beta_0 \langle \vec{r}^3 \rangle)\) is \(0.036\) cm\(^{-1}\) \(^{59}\), \(S\) in Eq. (1.21) is \(0.076\) \(^{67}\), \(T(n)=0.220\) \(^{63}\), \(K_0\) stand for Fermi-contact interaction and its value is \(0.33\) \(^{72}\); \(f(\beta)\) and \(g(\beta)\) are assumed to be nearly constant and quite small ( \(=0.051\) ). \(\Delta E_{xy}\) and \(\Delta E_{xz}\) are the energies required for the transitions \(d_{x^2-y^2} \rightarrow d_{xy}\) and \(d_{x^2-y^2} \rightarrow d_{xz,yz}\) respectively. The coefficients \(\alpha', \beta_1^2\) and \(\beta^2\) characterize, respectively, the in-plane \(\sigma\) bonding, in-plane \(\pi\) bonding and out of plane \(\pi\) bonding of the Cu\(^{2+}\) ion; their values lie between 0.5 and 1.0, the limits for pure covalent and pure ionic bonding. In most of the cases a single ligand field band is observed in the optical spectra of Cu\(^{2+}\) ions which makes difficult the straightforward determination of bonding parameters. However, three \(d-d\) transitions \((d_{x^2-y^2} \rightarrow d_{z^2}, d_{xy}, d_{yz,zx})\) are expected \(^{73}\) from the ligand field model of Cu\(^{2+}\). Jørgensen \(^{74}\) interpreted the
spectra of \( \text{Cu}^{2+} \) complexes in terms of an energy diagram essentially as shown in Fig.1.11. The limit of this type of tetragonality is evidently a square planar complex. Some authors\(^7\) have interpreted the single observed absorption band as the envelope of all three \( d-d \) transitions. However, these workers found that in some cases a unique decomposition into three components was not possible. Holmes and McClure\(^7\) found that for \( \text{CuSO}_4 \cdot 5\text{H}_2\text{O} \), resolution of the observed band into two components was definite but the fitting of the third component band at shortest wavelength, was questionable. Various other authors\(^6,67,77\) have placed the \( d_{x^2-y^2} \rightarrow d_{z^2}, d_{xy} \) transitions under the observed band and the remaining \( d_{x^2-y^2} \rightarrow d_{xz}, d_{yz} \) transition is considered to be hidden under the intense charge transfer absorption in the near-ultraviolet region. The latter decomposition seems to be a more reasonable choice for square planar cupric complexes. Bjerrum et al.\(^7\) analysed absorption spectra of \( \text{Cu}^{2+} \) ion using this decomposition and assumed an approximation that of the two components under the observed band, the one at shorter wavelength has same maximum position as does the envelope itself (This obtains because the higher lying component is much stronger than the component at somewhat longer wavelength). So the observed band is interpreted as \( d_{x^2-y^2} \rightarrow d_{xy} \).
Acid base concept had been a subject of considerable controversy and several definitions of acids and basis are available. At first Arrehenius\textsuperscript{79} defined an acid as a compound that dissociates in solution to give hydrogen ions, and a base as a compound yielding hydroxyl ions in solution. Arrehenius's acid-base theory relied exclusively on the phenomena observed in aqueous solution and is of limited applicability in non-aqueous systems.

For a quantitative treatment, the extension of the Arrehenius concept by Bronsted and Lowery\textsuperscript{80,81} offers a decided advantage. According to this theory an acid is defined as species that is capable of donating one or more protons to another substance (base) that can accept the proton. This definition can be represented by the equation.

\[
A^{n+} \rightleftharpoons B^{(n-1)+} + H^+ \quad (1.29)
\]

The chief limitation of this theory is its dependence upon the proton transfer concept. For obvious reasons the proton transfer acid-base theory offers practically no application in glass.
Acid base concept was further advanced by Lewis who defined an acid as any species that is capable of accepting a pair of electrons to form a covalent bond by sharing with electron donor; and a base as any species that can donate a pair of electrons to form a covalent bond with the acid. Thus ability of any species to donate electrons to form covalent bond is called Lewis basicity. This theory considers acid-base functions and related processes independently of the solvent.

Because $O^{2-}$ ions are not stable as free gaseous particles so they require stabilization by an environment of cations. The process of surrounding an anion by cations lowers its energy by tightening electron cloud. This in turn decreases the basicity of the oxide ion i.e. reduction in the donor properties of oxide. So oxyanion such as sulphate or phosphate are much less basic than free $O^{2-}$ ion. This reduction in donor properties depends upon the polarizability of the cation and is more for highly polarizing cation. The lowering of donor properties i.e. the reduction in Lewis strength of oxide has been expressed in terms of the optical basicity. Optical basicity is the ratio of $h'/h_0^{2-}$ where $h_0^{2-}$ and $h'$ are the Jørgensen $h$-functions for oxide in its 'unpolarized' and polarized forms respectively.
In view of the importance of basicity generally, it is desirable to understand the role of the polarizing cations by relating their properties in some definite manner to optical basicity. Duffy and Ingram reported that the optical basicity is related quantitatively to the following:

1. The tendency of the cations A, B, ... to reduce the donor properties of oxide; this is expressed by empirical "basicity moderating" parameters, $\gamma_A$, $\gamma_B$, ... so that increasing $\gamma$ corresponds to increased lowering of the oxide $h$-functions.

2. The oxidation number $Z_A$, $Z_B$, ... of the cations; this might be expected since in, say, NaPO$_3$ glass each sodium ion 'neutralises' one sixth of the negative charge whereas each phosphorous neutralises five sixth.

3. The ratio of the cations with respect to the total number of oxides $r_A$, $r_B$, ... in NaPO$_3$ glass, for example, $r_{Na}=\frac{1}{2}$.

The relationship between (1)-(iii) and optical basicity is arrived at by expressing the lowering of the $h$-function of the oxide as:

$$(h_{0^2-} - h') = \frac{Z_A}{|Z_0|} h_{0^2-} (1 - \frac{1}{\gamma_A}) + \frac{Z_B}{|Z_0|} h_{0^2-} (1 - \frac{1}{\gamma_B}) + ...$$

($z_0$ is the oxidation number of oxide and $|Z_0| = 2$. Dividing $\Sigma_i(1)$ throughout by $h_{0^2-}$, substituting for $h'/h_{0^2-}$ and
rearranging we get

\[ \Lambda = \frac{Z_A r_A}{2} \frac{1}{Y_A} + \frac{Z_B r_B}{2} \frac{1}{Y_B} + \cdots \]  

(1.31)

because \( 1 = \frac{Z_A r_A}{2} + \frac{Z_B r_B}{2} + \cdots \)

Thus value of \( Y \) can be obtained by using experimentally determined values of optical basicity (\( \Lambda \)) values. \( \Lambda \) is obtained using probe ions such as Pb\(^{2+} \) or Bi\(^{3+} \) which depends upon medium. Whenever a medium contains different types of oxide (differing in h-functions), there is the possibility of the probe ion co-ordinating preferentially with one type of oxide rather than co-ordinating in a manner that will represent the basicity of the bulk medium. So we choose water as a medium in which all oxides are identical. The optical basicity \( \Lambda_{\text{Pb(II)}} \) of water was used in Eq. (1.31) and the corresponding value of \( Y_H \) was found equal to 2.5. This value of \( Y_H \) and \( Y_{Ca} = 1.00 \) fit the relationship:

\[ Y = 1.36 (x - 0.26) \]  

(1.32)

where \( x \) is the Pauling Electronegativity\(^87 \) of hydrogen or calcium (1.0). Eq. 1.32 can be used generally to calculate \( Y \) for other elements. Using these values of \( Y \), theoretical optical basicity (\( \Lambda_{\text{th}} \)) can be calculated
for any medium by Eq. (1.31). The theoretical optical
basicity, $\Lambda$th serves in the first approximation as a
measure of the ability of oxygen to donate a negative
charge in the glasses. In other words the optical
basicity reflects the Lewis basicity of oxide glasses.
Thus $\Lambda$th can be used to classify the covalent/ionic
characteristics of the glasses, since an increasing $\Lambda$th
indicates decreasing covalency.

1.10 ELECTRICAL CONDUCTIVITY:

When a d.c. electric field is applied to the
glass, the alkali ions with positive charge $e$ will move
towards negative electrode. This gives rise to a d.c.
conduction. The d.c. conductivity $\sigma$ has Arrenhius
like temperature dependence written as $^88$

$$\sigma = \sigma_0 \exp \left(- \frac{W}{kT}\right) \quad (1.33)$$

where the pre-exponential factor $\sigma_0$ and an effective
activation energy of conduction, $W$, are temperature
independent, $k$ is the Boltzmann constant, and $T$ is
the absolute temperature.

Various attempts have been made to derive Eq. (1.33)
theoretically. The type of model used by Frenkel for
ionic transport in crystalline solids is generally
adopted for glasses $^89$. The current carriers, e.g., an
alkali ion is considered to be in a potential well
undergoing thermal vibrations. In the absence of an applied electric field it will execute random jumps according to its probability of surmounting the energy barrier. In the presence of a field, however, it will move from well to well preferentially in the direction of the applied field. Stevels\textsuperscript{90}, for example, derived the following relation:

\[ \sigma = \frac{\nu_c b \lambda e^2 n}{6kT} \exp \left( \frac{-U}{kT} \right) \]  \hspace{1cm} (1.34)

where $\nu_c$ is the thermal vibration frequency, $b$ is the number of adjacent wells an ion can jump into, $\lambda$ is the average distance between two neighboring wells or adjacent sites, $k$ is the Boltzmann constant, $n$ is the number of mobile ions per cm$^3$, and $U$ is the energy barrier. Mazurin\textsuperscript{91} derived a slightly different equation:

\[ \sigma = \frac{\nu_c \lambda e^2 n}{3kT} \exp \left\{ \frac{-\left( \frac{U_D}{2} + U_A \right)}{kT} \right\} \]  \hspace{1cm} (1.35)

$U_D$ is the energy required to dissociate an ion from its potential well and $U_A$ is the energy required for migration. Thus if an 'effective activation energy' $W$ is used to represent $\frac{U_D}{2} + U_A$,:

\[ \sigma = \frac{\nu_c \lambda e^2 n}{3kT} \exp \left( -\frac{W}{kT} \right) \]  \hspace{1cm} (1.36)
If the variation of $W$ with temperature is slight, then a plot of $\log \sigma$ against $1/T$ should give a straight line, from the slope of which the activation energy for conduction is obtained.

Because the electric conduction is due to ionic motion, there is an interaction between the ionic diffusion coefficient $D$ and the d.c. electric conductivity $\sigma$, given by:

$$\sigma = C \frac{e^2 D}{kT} \tag{1.37}$$

where $C$ is the alkali ionic charge concentration. In fact the experimental observations indicate a slight deviation from the prediction of this Nernst-Einstein equation and often the coefficient $f$ is introduced to modify the expression as

$$\sigma = C \frac{e^2 D}{f kT} \tag{1.38}$$

The magnitude of $f$ is normally found to range from 0.2 to about 0.7. The origin of this discrepancy is the subject of controversy.

The dependence of resistivity on temperature has been investigated by a number of workers and their results generally fall into the following two groups:

1. Resistivity $\rho$ is given by:

$$\log \rho = X + YT + ZT^2 + \ldots \tag{1.39}$$
where $X, Y, Z$ etc. are constants. These results are quoted especially by those who have made measurements in or near the molten state of glass.

2. Resistivity is given by

$$\log \rho = A + \frac{B}{T}$$

(1.40)

where $A$ and $B$ are constants. Rasch and Hindrichsen\textsuperscript{92} gave this relation for the first time, therefore, it is often referred to by their names. Comparing this relation with Eq.(1.33) and (1.36) we get:

$$A = \log \frac{3kT}{ne^2\nu c A^2}$$

(1.41)

$$B = \frac{W}{k}$$

(1.42)

It is noted from Eq.(1.34) that the pre-exponential term $\sigma_0$ varies with the logarithm of the absolute temperature $T$ and therefore a plot of $\log \sigma$ vs $\frac{1}{T}$ should not give a straight line. However the temperature dependence of $\sigma$ is mainly due to exponential term in Eq.(1.33) and therefore over a limited range of temperature plot $\log \sigma$ vs $\frac{1}{T}$ may be taken as a straight line and the activation energy can be calculated from the slope of the line with reasonable accuracy.

Effect of variation in composition on the electrical conductivity of glasses was studied by many workers. It
is found that the alkalies greatly increase conductivity, Na$_2$O more so than K$_2$O. Al$_2$O$_3$ slightly increases the conductivity. ZnO, MgO, PbO, Fe$_2$O$_3$, BaO or CaO decreases conductivity although all except CaO have but little effect. Studies of glasses containing both Na$_2$O and K$_2$O show that the conductivity of the glass decreases to that of the glass containing either of the two alkali oxides.

In borate glasses the mixed alkali effect decreases with increasing temperature and disappears above 623K from Na-K borate glass. This effect persisted up to 1223K in Li-K borate glasses. Lengyel et al. measured the electrical conductivity of M$_2$O$_4$B$_2$O$_3$ glasses (M=Li, Na, K, Li+Na, Na+K or Li+K). They found that the electrical conductivity of borate glasses containing only one kind of alkali decreases with increasing size of the alkali. For mixtures, the conductivity has a minimum at about the ratio 1:1 and this minimum is more pronounced in Li$_2$O·K$_2$O·B$_2$O$_3$ glass.

Narasimham et al. measured the d.c. conductivity in K$_2$SO$_4$-ZnSO$_4$ glasses over a sufficiently wide range of temperature. According to them, ln$\sigma$ vs $\frac{1}{T}$ curve is nonlinear and can be divided into three distinguishable
linear regions; the first two being just above and below the glass transition temperature and the third well below the glass transition temperature. D.C. conductivity of these glasses is discussed on the basis of random close packing of sulphate ions. In these glasses $K^+$ and $Zn^{2+}$ ions are present in distinct environments of their own. It is the essentially fully ionic nature (as contrasted rigid covalent networks) of these glasses which seems to allow for fairly distinct environments and hence distinct barriers to migration. However, above the glass transition temperature the rigid anion framework of the glass is broken down, the very high ionic potential (charge to radius ratio) allows the $Zn^{2+}$ ions to form charged clusters which change the value of the conduction parameters.

OXIDE GLASSES CONTAINING TRANSITION METAL IONS

Oxide glasses containing transition metal ions were first reported by Denton et al. to have semiconducting properties. Since then a great deal of work has been carried out mostly on vanadate glasses. Mackenzie reviewed the necessary conditions for oxide glasses to act as a semiconductor. He showed that although all inorganic glasses are ionic conductors, electronic conduction may become dominant in a certain temperature range. Electronic conductivity is due to the
transfer of electrons between adjacent Vanadium ions of different valency. The conductivity of the glass depends upon the concentration of transition metal oxide and the ratio of higher and lower valency states of the transition metal ions which is determined by the proportion of other oxides in the glass composition and by the melting conditions, i.e. by melting temperature, the surrounding atmosphere and the rate of cooling.

A detailed theoretical approach to the activation energy of semiconducting oxide glasses has been treated by Mott. The electrical conductivity is given by

\[ \sigma = \frac{\gamma_{\text{ph}} e^2 C (1-C)}{k T R} \exp(-2 \omega R) \exp(-\frac{E}{kT}) \]  

(1.43)

where \( \gamma_{\text{ph}} \) is the phonon frequency,

\( \omega \) is the rate of the wavefunction decay,

\( C \) is the ratio of the ion concentration in the low valency state to the total concentration of transition metal ions,

\( R \) is the average hopping distance,

and \( E \) is the activation energy.

Further \( E = E_H + \frac{1}{2} E_D \)

where \( E_H \) is the polaron hopping energy and \( E_D \) is the disorder energy arising from the energy difference of
neighbors between two hopping sites. It was predicted by Mott that $E$ tends to zero as $T$ approaches zero, thus giving a decreasing slope of the $\ln \sigma$ vs $\frac{1}{T}$ plot.

Provided $R$ remains constant, equation (1.41) predicts a maximum of $\sigma$ at $C = \frac{1}{2}$. Experimental data frequently give a maximum at a quite different value of $C$ and various explanations have been given. However, the term $C(1-C)$ gives such a flat maximum that $\log \sigma$ would appear constant over the range 0.2 to 0.8 within the limits ±0.1 which are a reasonable estimate of the variability of such measurements on different glasses. Linsley et al. suggested that a maximum occurring at $C = 0.2$ is due to a large fraction of the oxidized TM ions being excluded from the conduction process and $\sigma$ should depend on $C$ as $\sigma C(0.4-C)$ in this case but even this dependence on $C$ gives broader maximum than actually observed experimentally. Further more the observed maxima of conductivity are usually associated with minima of the activation energy.

When an oxide glass mixed with two TM elements is prepared then it is usually found that its resistivity and activation energy are lower than those for the same concentration of all one TM element. This is explained on the basis of electron hopping between TM ions of the same and different chemical elements. Some workers have also reported that the resistivity
increases when two TM elements are added to the composition of other oxide glass. Acc to the bridge bonds in case of two TM elements, the bridge bonds in glass contain two TM elements and they inhibit the hopping of electrons, leading to a decrease in the conductivity.
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