Chapter I

Introduction

INTRODUCTION

The study of the solid complexes takes increasing attention for their useful applications in many areas. They can be used to prepare metal oxides with different stoichiometric which can be used in catalytic and electronic fields. The thermal and electrical studies on solids are important to through light on the stability and the electronic structure.

An important aspect of the reactivity of solid state compounds is that reactions in the solid state proceed with a minimum molecular motion. This postulate assumes that there is a reaction cavity or defined area in which solid state reactions can occur, and this cavity is much more restrictive with respect to molecular motion than the corresponding reaction cavity in solution. This postulate explains a number of solid state reactions in which the structure of the product is related to the structure of the reactants in the crystal (1).

In an increasing number of areas of technology and hence industry, progress is recognized as being related to understanding the factors influencing the reactivity of solids and how they react and interact in specific environments. In general, the reactions which include solid reactions are very complex from the kinetic standpoint as they involve physical and chemical steps (2).

In recent years there has been a great interest for studing the electrical properties of complex compounds of transition metals in solid phase due to the observation of the variety of their electrical conductivities with the change in the valence of the transition metal ions and the types of their chemical and crystal structures. The electrical properties of these compounds are also sensitive to large number of variables among which impurities, pressure and thermal treatments which may have remarkable effects.

In the last four decades semiconductor equipment is being applied in various fields of science and engineering. During this time semiconducting properties were discovered in some chelated compounds. The ever-increasing interest in complexes with semiconducting properties is due to the fact that they may exhibit a combination of electrical, optical and physicochemical properties which are not encountered in inorganic materials (3). Also some applications of material made from inorganic semiconducting materials have some disadvantages that limit their applications.

Thermal analysis covers a series of techniques in which a property of material or a system is measured as function of temperature, where the system being subjected to a controlled temperature regime. In thermal analysis, the property is measured at the temperature imposed on the system. Typical measurements techniques, where the measurement is made at the programmed temperature, include: **differential thermal analysis** (DTA) and thermogravimetry (TG). The fact that the temperature is altered in thermal analysis means that special considerations must be given to thermodynamic and kinetic factors (4). Thermal analysis can be valuable in providing scaled down information on behavior which involves complicated temperature programming. In most thermal analysis studies, the starting material is a solid at the onset later, possibly during and because of the heat treatment, it may be possible that transition occurs either completely or partial to a liquid or a gas and it seems important to recognize this special position of solid phase.

One of the interesting applications of thermal analysis is the investigation of the behaviour and kinetics of solid state reactions. Kinetic measurements are perhaps most frequently undertaken to obtain information concerning the mechanism of a specified reaction. Such investigations may include characterization of reaction stoichiometry, particularly product compositions where mixtures are formed and the identification of intermediates. This information can be of value in contributing towards the theoretical development of the subject, generally by identifying the factors that control reactivity and understanding the significance of participating steps. Empirical measurements of reaction rates may also be of value in the development of industrial processes where the principal objective may be to establish the most effective and efficient condition that can be exploited in production so that costs, waste and pollution are minimized (5). In many cases, the kinetics of the thermal decomposition reactions were followed, depending on system investigated, by measurement the pressure of gas released in a closed volume as a function of time and by analysis of products by mass spectroscopy. However, more recently (DTA-TG) analytical techniques are more widely used, since they provide a rapid and convenient method for the quantitative investigation of decomposition reaction (6). The kinetic of solid state thermal decomposition reactions can be followed either by isothermal or non-isothermal (dynamic) methods. The time required for an adequate series of isothermal experiments is a considerable disadvantage, and when the amount of the reactants available is also limited, it becomes most desirable to obtain maximum information from a single kinetic experiment. Much attention has therefore been directed at the use of non-isothermal method to follow the kinetics of solid-state reactions (7).

The purpose of many kinetic studies is to obtain information concerning the reaction mechanism (8). Most solid state decomposition are governed by the movement of the reaction interface and hence the kinetics (9). The kinetics of the thermal decomposition of solid-state materials is highly complex and frequently controversial subject. The kinetics of the thermal decomposition of solids are affected by experimental factors (10), such as heating rate, particle size, sample mass and holder design. Two further important factors are the effect of enthalpy of reactions upon sample temperature and atmosphere. Moreover the use of different methods of kinetic analysis of both isothermal and non-isothermal thermogravimetric data obtained on one system to find activation energy and other kinetic parameters usually gives different results. Criteria for the excellence of kinetic fits reported in research publications aren't always specified and, in practice, identification of the preferred rate equation may be a personal decision between the research workers concerned based on undisclosed reasons (11).

The electrical conductivity in solids (12) is very important property to differentiate between various types of solids. The electrical conductivity of oxide materials encompasses a wide range of values, which characterize insulator, semiconductors and metallic materials. According to band theory if the valence bands, which contain electrons, are completely filled while the conduction bands are empty, the material is considered as insulators and shows a very poor conduction. If, on the other hand, the highest-lying occupied band contains large fractions of both occupied and empty states, the solid is a metal and shows a good conduction. Finally, if this highest occupied band contains only small concentration of occupied or empty states, the material is a semiconductor and shows an intermediate conductivity. There is, however, another difference in the electrical properties of these three materials. The most important of these is the effect of temperature on the electrical conductivity. As a general rule the electrical conductivity of metals decreases with increasing its temperature, while the conductivity of semiconductor and insulators shows a reverse temperature effect with the respect to the nature and behaviour of charge carries in these materials. In general the conductivity σ is given by:

$$\sigma = n\, e\, \mu$$

where n is the number of current carrying species, e is their charge and μ is their mobility.

In metals, electrons are the main charge carriers and move throughout freely, they aren't localized or bound to atomic sites. There is therefore essentially no activation energy required for the conduction process. The number of mobile electrons is large and essentially constant, but their mobility gradually decreases with rising temperature due to electron-phonon collisions. Consequently, conductivity gradually drops with rising temperature. In semiconductors, the number of mobile electrons is usually small. This number may be increased in one of two ways, either by raising the temperature so as to promote more electrons from the valence band to the conduction band, or by doping with impurities that provide either electrons or holes. In the first of these, n and therefore, σ, rise exponentially with temperature (Intrinsic semiconductivity), the relatively small changes in μ with temperature are completely swamped by the much large changes in n. In the second of these, extra mobile carriers are generated by the addition of dopants at low temperature (Extrinsic conductivity). The concentration of these extra mobile carriers is much greater than the thermally generated intrinsic carrier concentration. Consequently concentration is independent on temperature and σ shows a slight decrease with temperature due to mobility effect mentioned above. In insulators, however, electrons are not free to move throughout the bulk of materials but are bound to atomic sites. They differ from semiconductors only in the magnitude of their conductivity, which are usually several orders of magnitude lower. Thus, the conductivity of insulators is also sensitive to both temperature and dopants.

Semiconductor with only a few electrons in the highest occupied doped level called n-type and those with only a few empties, or holes, are called p-type.

Inorganic solids that exhibit magnetic effects other than diamagnetism, which is a property of most substances, are characterized by having unpaired electrons on metal cations. Magnetic behaviour is thus restricted mainly to compounds of transition metals and lanthanides, many of them possess unpaired d and F electrons, respectively. Several magnetic effects are possible. The unpaired electrons may be oriented at random on the different atoms, in which case, the material is paramagnetic. They may be aligned so as to be parallel, in which case the material possess an overall magnetic moment and is called ferromagnetic. Alternatively, they may be aligned in antiparallel fashion, giving zero over all magnetic and antiferromagnetic behaviour. If the alignment of the spins is antiparallel but unequal numbers in the two orientations, net magnetic moment results and the behaviour is ferrimagnetic. Paramagnetic substances are attracted by a magnetic field, whereas, diamagnetic substances experience a slight repulsion. There is a strong and analogies between magnetic properties and corresponding electrical properties such as ferroelectricity. The susceptibility of the different kinds of magnetic materials are distinguished by their different temperature and magnetic field dependence as well as by their absolute magnitude. For all materials the effect of increasing temperature is to increase the thermal energy possessed by ions and electrons. There is, therefore, a natural tendency for increasing structural disorder with increasing temperature. For paramagnetic materials, the thermal energy of ions and electrons acts to partially cancel the ordering effect of the applied magnetic field. Indeed, as soon as the magnetic field is removed the orientation of the electron spins becomes disordered. Hence, for paramagnetic materials the magnetic susceptibility χ decreases with increasing temperature, in Curie/Curie-Weiss law fashion. For ferro- and antiferromagnetic materials, the effect of temperature is to introduce disorder into the otherwise perfectly ordered parallel/antiparallel arrangement of spins. For ferromagnetic materials, this leads to a rapid decrease in χ with increasing temperature. For antiferromagnetic materials, this leads to a decrease in the degree of antiparallel ordering, an increase in the number of disordered electron spins and hence an increase in χ.

I-1. THEORETICAL REVIEW AND METHODS OF CALCULATION:

I-1-a. Electrical Conductivity:

The electrical properties of solids can be classified into many groups depending on their electrical conductivity values (σ), as insulators; $\sigma < 10^{-12}$ $Ohm^{-1}. cm^{-1}$, semiconductors; $\sigma = 10^{-12} - 10^{2}$ $Ohm^{-1}. cm^{-1}$, metallic; $\sigma = 10^{-14} - 10^{6}$ Ohm^{-1} cm^{-1} and superconducting materials where the resistance of the sample is zero.

The semiconducting materials has been classified into two types:

1- *Intrinsic semiconductors*: in which the charge carriers originate from the pure materials by a thermal excitation process.

2- *Extirinsic semiconductors*: in which the charge carriers are present as a constant temperature-independent concentration (either at trace concentrations, doped into the crystal lattice, or in stoichiometric concentration at high concentration, in mixed valence compounds).

Two types of electrical conductivities are known DC and AC electrical conductivity.

I-1-a-i. DC-conductivity:

The resistance R of a sample of any material in ohmic region is defined by Ohm's law:

$$I = \frac{V}{R} \qquad (1)$$

where I is the current and V is the applied potential difference, and for a uniform current, the DC-conductivity σ_{DC} of the material is defined by the following equation:

$$\sigma_{DC} = \left(\frac{l}{s}\right)\left(\frac{1}{R_{DC}}\right) \qquad (2)$$

where l is the length of the sample and s is the cross-sectional area.

If the current is thought of as the flow of charged particles, the criterion for the applicability of Ohm's law is that the average velocity, V of such particles is proportional to the field strength, E. In this way we define the mobility μ (which has a value in the range of 10^{-14} to 10^{-4} $cm^2.V^{-1}.s^{-1}$ at 293K for dielectrics) by equation:

$$<V> = \mu E \qquad (3)$$

The electrical conductivity of organic compounds is attributed to the drift of charge carriers: electrons and holes. Hence, the conductivity may be described by:

$$\sigma = \sigma_e + \sigma_h = qn\,(\mu_e + \mu_h) = qn\mu \qquad (4)$$

where q is the charge per particles (the value of charge on an electron being 1.62 x 10^{-19} coulomb), n is the particle density, i.e. concentration of electrons and holes, σ_e and σ_h are their respective conductivity and μ_e and μ_h are their respective mobilities.

More generally, if different types of charge operate in the same material:

$$\sigma = \Sigma_i\, \sigma_i = \Sigma_i\, (n_i\, q_i\, \mu_i) \qquad (5)$$

and the transport number for each type is defined as the fraction of total current carried, i.e.

$$t_i = \frac{n_i\, q_i \mu_i}{\Sigma_i\, (n_i\, q_i\, \mu_i)} \qquad (6)$$

Semiconductors and insulators are characterized by values of conductivity in the range of a temperature dependence of the form:

$$\sigma = \sigma_o \exp\left(\frac{-E_a}{kT}\right) \qquad (7)$$

Over a wide temperature range, the temperature dependence may be more complicated, implying perhaps that different mechanisms prevail at different temperature, even so the plot of log σ against T^{-1} is used to display forbidden regions are called energy gaps or band gaps, Fig.(I-1). The highest occupied band is called the valence band (VB) and the lowest occupied band is called the conduction band (CB) and they are separated by the band gap.

The number of charge carriers per unit volume present in conduction band n can be calculated (13) using equation:

$$n = 2\,(2\pi m^{*}kT/h^{2})^{3/2}\,\exp(-E_a/kT) \qquad (12)$$

where m* is the effective mass of charge carriers (assumed to be equal to the rest mass of electron), h is the Plank's constant and E_a is the activation energy. This equation is approximated as:

$$n = 2\mathrm{x}2.36\mathrm{x}10^{21}\mathrm{x}T^{3/2}\,\exp(-E_a/kT) \qquad (13)$$

I-1-a-ii. AC-conductivity:

Many investigators have reported that the conductivity of some organic and organometallic semiconductors under AC fields may be higher by several orders of magnitude than that under DC fields. This phenomenon may be associated with the polarization of the molecules.

The available experimental results about the frequency dependence of AC conductivity have revealed a considerable similarity of behaviour for a very wide range of materials ordered and disordered, conducting by electrons, holes ions, polarons, etc., involving various types of chemical bonds and various electronic energy level structures (14). Empirical relation can express the frequency dependence of AC conductivity.

$$\sigma_{AC}\,(\omega)\ \alpha\ \omega^{m} \qquad (14)$$

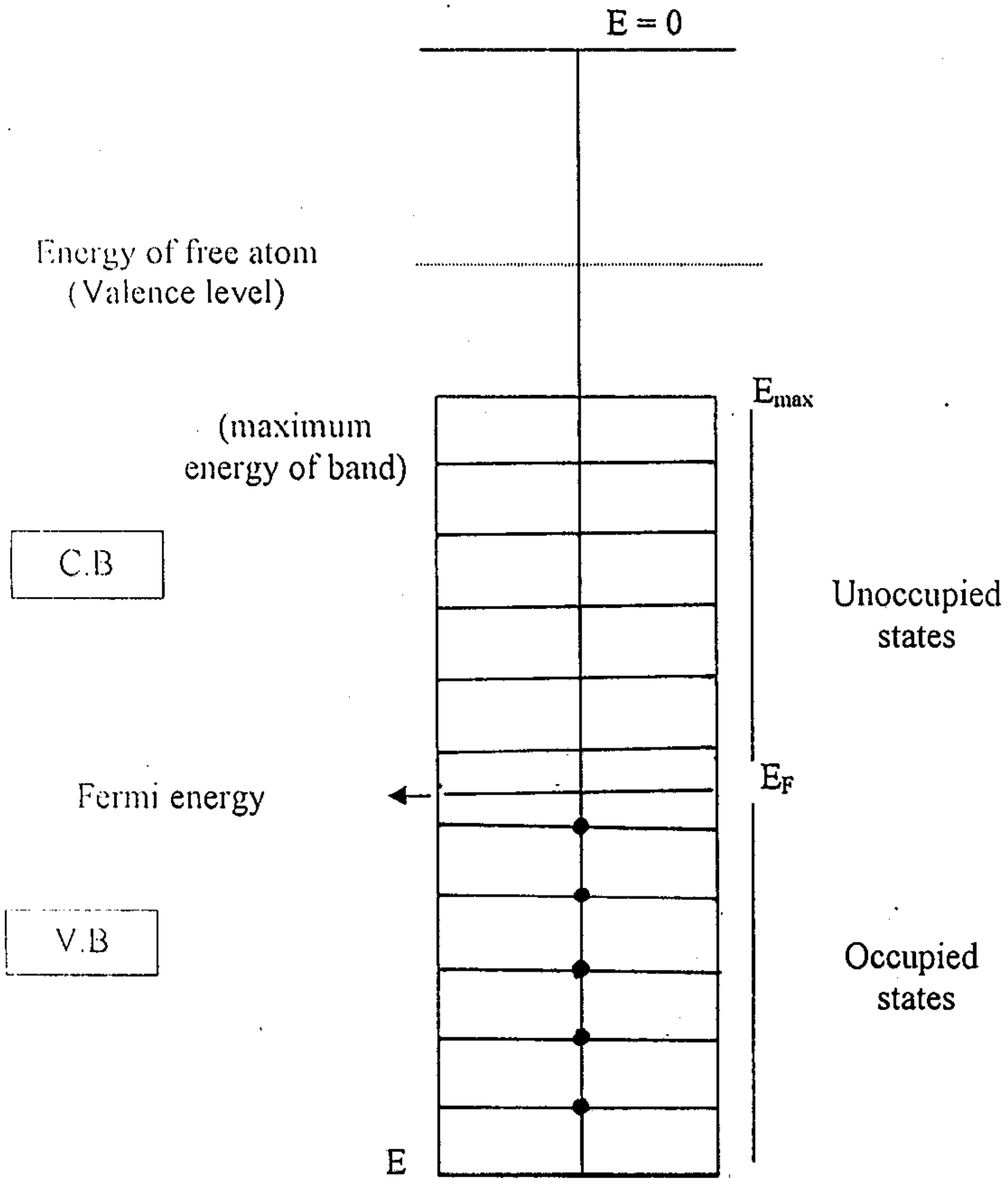

Fig.(1-1): Energy-level scheme of a partly filled band.

E_F is Fermi energy, which is the energy of the electrons with the highest velocity of translation. The highest occupied band is called valence band (V.B) and the lowest unoccupied band, the conduction band (C.B).

where m is not a constant for all substances, but is a function of temperature, approching unity at low temperatures and decreasing to 0.5 or less at high temperatures. So in this relation

$$\sigma_{AC}(w) = [\sigma_{(w)} - \sigma_{DC}]\ \alpha\ \frac{\omega^2}{\omega^2 + t/\tau^2} \qquad (15)$$

$\sigma_{(\omega)}$ and σ_{DC} are respectively, the total and DC conductivities, and τ is the relaxation time. This type of frequency is closely related to the frequency dependence of the real part of the permittivity.

$$\left(\frac{\varepsilon(\omega)}{\varepsilon_o} - \frac{\varepsilon(\infty)}{\varepsilon_o}\right)\ \alpha\ \frac{1}{\omega^2 + 1/\tau^2} \qquad (16)$$

where $\varepsilon(\infty)$ is the value of $\varepsilon(\omega)$ at frequencies $\omega >> 1/\tau$. So we found that:

a- σ_{AC} has weaker temperature dependence than σ_{DC}. Generally n decreases with increasing temperature. The ω^2 dependence is not very sensitive to temperature.

b- There is no correlation between $\sigma_{AC}(\omega)$ and σ_{DC}.

c- $\sigma_{AC}(\omega)$ either follows a power law of Eq. (14) with $n < 1$ or follows a ω^2 dependence of Eq. (15). In some cases is possible that there are two types of frequency dependence are superimposed.

I-1-a-iii. Dilectric properties of solids:

Polarization of the medium is alignment of the molecular moment and it produces by the applied electronic field. Study of dielectric properties of materials is interesting and has a practical value (15). The investigation of the dielectric properties of loss and permittivity has become well established and frequently used method of probing molecular motions in the solid state.

behind the oscillation of the field. This lag will be accompanied by a decrease in the polarization and in the reaction against the applied field. Above this frequency, the molecules will be no longer able to relax. The relationship between the alternating field E and the polarization P of the sample [Eq. (19)] lead to the complex dielectric constant ε* (ω) which is frequency dependent [Eq. (27)]. According to Debye(17) the frequency of the complex dielectric constant ε* for independent dipoles with the same relaxation time, τ is given by:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + J\omega\tau} \tag{28}$$

where

$$\tau = \frac{1}{\omega} = \frac{1}{2\pi f} \tag{29}$$

since

$$\varepsilon^* = \varepsilon`(\omega) - J\varepsilon``(\omega) \tag{30}$$

where ε` is the real part and called dielectric constant and ε`` is the imaginary part and called dielectric loss parameter. Equation (28) can be rewritten to give:

$$\varepsilon` = \varepsilon_\infty + \frac{(\varepsilon_s - \varepsilon_\infty)}{1 + \omega^2\tau^2} \tag{31}$$

and

$$\varepsilon`` = \frac{(\varepsilon_s - \varepsilon_\infty)\,\omega\tau}{1 + \omega^2\tau^2} \tag{32}$$

according to equation (32) the position of the peak maximum of dielectric loss ε`` (ω) versus the frequency is lying at $\omega\tau = 1$. Equations (31) and (32) are the Debye equations, which are reasonably applicable to most dispersions at electrical frequencies. The most important parameter of them is the loss factor tan δ.

$$\tan\delta = \frac{\varepsilon``}{\varepsilon`} \tag{33}$$

$$\tan\delta = \frac{(\varepsilon_s - \varepsilon_\infty)\,\omega\tau}{\varepsilon_s - \varepsilon_\infty\,\omega^2\,\tau^2} \qquad (34)$$

The value of tan δ (loss tangent) as well as the other parameters of dielectrics for given specimens of material are not strictly constant and depend on various external factors such as temperature and the applied voltage. The theoretical dependence of loss tangent on the frequency of voltage applied to a dielectric is represented in Fig.(I-2).

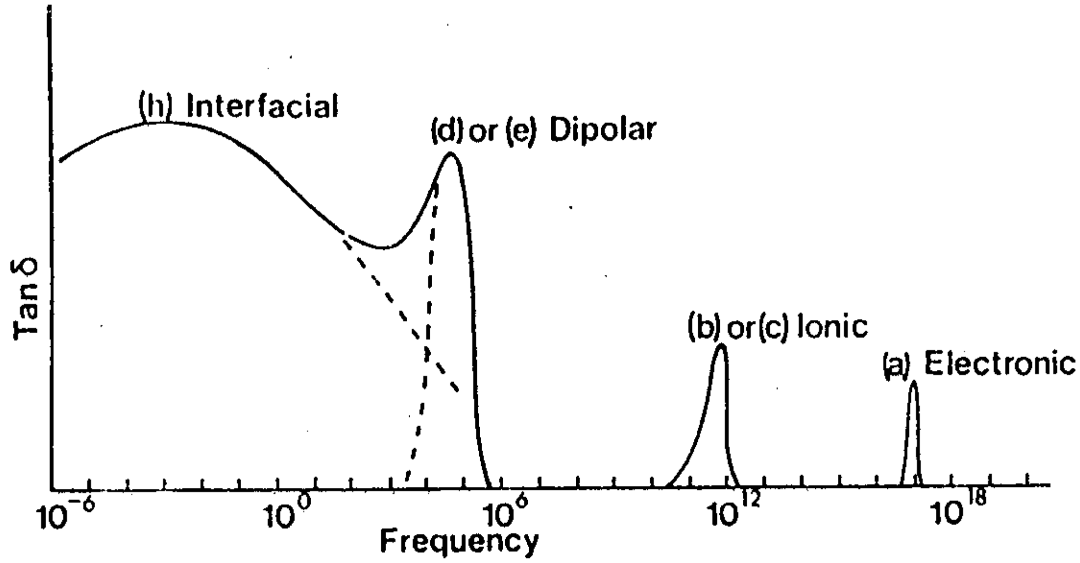

Fig.(I-2): Theoretical dependence of loss tangent on the frequency and voltage applied to a dielectric.

The absorption current in dielectric materials can be attributed to several causes:

1- In polar dielectric due to the orientation of dipole molecules.

2- In nonpolar dielectric due to the inhomogenity in the electrical properties of a dielectric.

The formation of space charges in a dielectric under the action of an external electric field and also due to initiate the processes of redistribution of charges with time in the volume of dielectric. The condition of the maximum of dielectric losses in a polar dielectric at a given temperature is :

$$\omega_{max}\,\tau = 1 \qquad (35)$$

where τ is the time of the relaxation of dipoles as in needed to observe the greatest loss of energy to overcome the resistance of the medium by dipoles.

The types of dielectric can be classified into simple dielectrics, paraelectrics and ferroelectric that subdivided into ferrielectric and antiferroelectric. To distinguish between the macroscopic properties of simple dielectrics and paraelectrics we must define the former which is exhibiting only the ionic and electronic polarization. This is characterized by a permittivity less than 40 that are little dependent on the structure. On contrast, paraelectrics contain a strong permanent electric dipole in each unit cell that is associated with permittivity greater than 20- up to 1000 or more. Those low-permittivity substances having small concentrations of permanent dipoles are referred to as "polar". They are intermediate between simple dielectrics and paraelectrics.

Ferroelectrics exhibit polarization that is not a linear function of applied field. Ferrielectric and antiferroelectric states exist when permanent electric dipoles in opposition respectively incompletely and completely balance out. The term "electret" is used for substances that have very stable moments. That is once polarized, they stay polarized for many years (18).

I-1-b. Magnetic Susceptibility:

Substances may be classified according to their response to an inhomogeneous magnetic field. Diamagnetic substance will tend to move towards the weakest region of the inhomogeneous magnetic field, while, paramagnetic substance will tend to move to the strongest region of the magnetic field.

Magnetic properties arise from the spin and orbital motion of the electrons. When a substance is placed in a magnetic field, there will be field-induced motion of the electrons in this material in such a direction as to generate a magnetic moment, which is opposed to the applied field. As a result the material will be repelled by the stronger part of a nonuniform magnetic field and is said to be diamagnetic. It is usually the principal effect for materials in which all electron spins are paired.

Substances, which contain one or more unpaird electron, have a permanent magnetic moment, which exists in the absence of a magnetic field and arises from the net spin and orbital angular momenta of the unpaired electrons. Such substances are said to be paramagnetic (19). When a paramagnetic substance is placed in an external magnetic field, the permanent atomic or molecular magnetic moments align themselves in the same direction as the field and consequently are attracted to it.

There are more complex forms of magnetic behaviour than the diamagnetic and paramagnetic effects. Cooperative interionic interactions may lead to long-range ordering resulting in ferromagnetism, antiferromagnetism or ferrimagnetism. In ferromagnetic materials, the electron spins are aligned parallel due to cooperative interactions between spins on neighbouring ions in the crystal structure. In general not all spins are parallel in a given material unless: (i) very high magnetic fields and (ii) low temperatures. In antiferromagnetic materials, the electron spins are aligned antiparallel and have a canceling effect.

The experimental determination of magnetic properties involves measurement of the magnetic susceptibility. The volume magnetic susceptibility; χ, is defined by(19):

$$\chi = \text{I`} / \text{H} \qquad (36)$$

where "I`" is the intensity of magnetization induced by the field strength "H", per unit volume of substance. The quantity "I`" is a measure of the extent to which magnetic dipoles tends to orient themselves parallel to the direction of the field. The quantity χ is a dimensionless quantity, which is positive for paramagnetic substances and negative for diamagnetic substances. Often the susceptibility is defined as the weight susceptibility χ_g where:

$$\chi_g = \chi / \text{density} \qquad (37)$$

$$\chi_g = \frac{2ml g}{M`(H_0^2 - H_1^2)} \qquad (38)$$

where m = net pull on the sample = pull on the sample – (- push on empty tube) [where the empty glass tube is diamagnetic and repelled with magnetic field], l is the length of the sample inside tube in cm, g is the acceleration due the gravity (980 cm/sec^2), M` is the mass of sample in gram, H_o is the magnetic field in Gauss between poles and H_1 is the magnetic field in Gauss up the sample. The unit of χ_g is e.m.u/gm. The molar magnetic susceptibility; χ_M is given by equation:

$$\chi_M = \chi_g.\mathit{molecular\text{-}\ weight} = \frac{2ml g}{M(H_0^2 - H_1^2)} \times \mathit{molecular\text{-}\ weight} \qquad (39)$$

and it has units of e.m.u./mole. For normal paramagnetic and dimagnetic substances χ_M is constant independent of field strength.

When substance has an unusually large χ_M, it is referred to as a ferrimagnetic material. Ferromagnetism results when magnetic dipoles in a substance can interact with one another causing extensive alignment of the moments with the field; very large values of I' result. For these materials the susceptibility is field-strength dependent.

The susceptibility of different kinds of magnetic material are distinguished by their different temperature dependence. Many paramagnetic substances obey the simple Curie law, especially at high temperature. This states that the magnetic susceptibility is inversely proportional to temperature:

$$\chi_M = C/T \qquad (40)$$

where C is the Curie constant. Often, however, the Curie-Weiss law provides a better fit to the experimental data: (20)

$$\chi_M = C/(T+\theta) \qquad (41)$$

where θ is an empirical constant called the Weiss constant. The deviation from the Curie law is due to interionic or intermolecular interactions. As a result of these interactions the orientations of the magnetic dipoles are influenced by the orientations of the neighbors. The Curie constant can be obtained by plotting χ_M^{-1} versus T, where straight line with slope equal to C is obtained.

The deviation from the Curie-Weiss law can also be observed by plotting $\chi_M T$ versus T.

For all materials, the effect of increasing temperature is to increase the thermal energy possessed by ions and electrons. There is therefore, a natural tendency for increasing structural disorder with increasing temperature. For paramagnetic materials, the thermal energy of ions and electrons acts to partially cancel the ordering effect of the applied magnetic field. Thus, χ_M decreases with increasing temperature in Curie/Curie-Weiss law fashion (20).

For ferro and antiferromagnetic materials, the effect of temperature is to introduce disorder into the otherwise perfectly ordered parallel/antiparallel arrangement of spins. For ferromagnetic materials, this leads to a rapid decrease in χ with increasing temperature. For antiferromagnetic materials, this leads to decrease in the degree of antiparallel ordering, an increase in the number of disorder electron spins and hence an increase in χ (20).

The magnetic properties of materials are often expressed in terms of the magnetic moment; μ` , since this is a parameter that may be related directly to the number of unpaired electrons present. The relationship between χ_M and μ is:

$$\chi_M = \frac{N\beta^2\mu^2}{3KT} \qquad (42)$$

where N is Avagadro's number, β is the Bohr magneton and k is Boltzmann's constant. Substituting for N, β and k givses:

$$\mu_{eff} = 2.83\sqrt{\chi_M T} = 2.83\sqrt{C} \qquad (43)$$

this equation holds for substances that obey the Curie law: $\chi_M = C/T$. While for the substances obey the Curie-Weiss law, μ` should be calculated from the susceptibility by equation:

$$\mu_{eff} = 2.38\sqrt{\chi_M(T+\theta)} = 2.83\sqrt{C} \qquad (44)$$

I-1-c. Kinetic Analysis of Non-Isothermal TG Data:

With dynamic technique, the temperature of the system is usually set to increase at a constant rate; β, and the function g(α) is given by Doyle's equation$^{(21)}$:

$$g(\alpha) = (A/B)\int_0^T \exp(-E/RT)dT = \frac{AE}{R\beta}P(x) \tag{45}$$

where g(α) depends on the mechanism controlling the reaction and on the size and shape of the reacting particle. The function P(x) has been defined as:

$$P(x) = \frac{e^{-X}}{x}\int_x^{\infty}\frac{e^{-u}du}{u} \tag{46}$$

where u=E/Rt and x is the corresponding value of u at which a fraction α of the material has decomposed.

In Coats-Redfern method $^{(22)}$, the function g(α) is approximated to the form:

$$g(\alpha) = \frac{ART^2}{\beta E}\left[1 - \frac{2RT}{E}\right]e^{-E/RT} \tag{47}$$

where α is the fraction of sample decomposed at time t and β is the heating rate.

The equation has been written in the form:

$$-\ln\left[g(\alpha)/T^2\right] = -\ln\frac{AR}{\beta E}\left(1 - \frac{2RT}{E}\right) + \frac{E}{RT} \tag{48}$$

The quantity ln[AR/βE(1-2RT/E)] appears to be reasonably constant for most values of E and in the temperature range over which most reaction occur. The correct form of g(α) must be used in equation (48) in order to allow the calculation of activation energy. A plot of $-\ln[g(\alpha)/T^2]$ versus $1/T$ should result in a straight line of slope (E/R) from which the activation energy (E) can be calculated.

Another approximate integral method which is recently used to obtain kinetic parameters from dynamic TG curves is that proposed by Ozawa(23). A master curve has been derived from the TG data obtained at different heating rates (β) using Doyle's equation (24) and assuming that $[(AE/R\beta)P(E/RT)]$ is a constant for a given fraction of material decomposed. The function P(E/RT) was approximated by the equation:

$$\log P(E/RT) = -2.315 - 0.4567(E/RT) \qquad (49)$$

so that,

$$-\log \beta = 0.4567(E/RT) + \text{constant} \qquad (50)$$

hence the activation energy may be obtained from the TG data obtained at different heating rates, by the plot of $\log \beta$ versus $1/T$ for different α-values. The frequency factor; A was calculated from equation:

$$\log A = \log g(\alpha) - \log\left[\frac{E}{\beta R} P(E/RT)\right] \qquad (51)$$

The calculation of E is independent of the reaction model used to describe the reaction, whereas the frequency factor depends on the determined form of $g(\alpha)$.

In the composite methods of analysis of dynamic data (25), the results obtained not only at different heating rates but also with different values of α, are superimposed on one master curve. In the application of composite method (I), use has been made of the modified Coats-Readfern equation (24):

$$\frac{g(\alpha)}{T^2} = \frac{AR}{\beta E} e^{-(E/RT)} \qquad (52)$$

the equation was rewritten in the form:

$$\ln[\beta\ g(\alpha)/T2] = \ln(AR/E) - (E/RT) \qquad (53)$$

Therefore, the dependence of ln[β(g(α)/T2)], calculated for different α-values at their respective β values, on 1/T must give rise to a single master straight line for the correct form of g(α), and hence a single activation energy and frequency factor can readily be calculated. The second approach for composite analysis of data depends on Doyle's equation:

$$g(\alpha) = AE/R\beta\ P(E/RT) \qquad (54)$$

again, using the approximation given above for the function P(E/RT), this equation may be rewritten as:

$$\log g(\alpha)\ \beta = [\log AE/R - 2.315] - 0.4567\ E/RT \qquad (55)$$

hence, the plot of the left side of this equation, for different values of α at their respective β values versus 1/T must give rise to a single master straight line, from the slope and intercept of which single values for both E and logA may be calculated. The composite approach involves a complete analysis of all non-isothermal curves into a single curve.

The kinetic analysis of non-isothermal data was performed with reference to the different models of heterogeneous solid-state reactions, based on the composite method of analysis, then the model which will give best fit to the experimental data will be used to calculate kinetic parameters, assuming different methods previously discussed.

Table (I-1) lists some of the more important kinetic equations given in the literature (24-30) which we have examined to find the most appropriate kinetic expression and reaction model which describes the reaction under various conditions. In the diffusion controlled reaction, the reaction rate is governed by diffusion, e.g. of a gaseous product through a continuos product layer; D_1 is for one dimensional diffusion process governed by a parabolic law, with constant diffusion coefficient; D_2 is a two dimensional diffusion-controlled process into a cylinder, D_3 is Jander's equation for a diffusion controlled reaction in a sphere, D_4 is the Ginstling-Braunshtein equation for a diffusion controlled reaction starting on the exterior of a spherical particle and D_5 the Zhuravlev-Lasokhim-Tempel'man diffusion equation. If the reaction is controlled by movement of an interface at constant velocity and nucleation occurs virtually instantaneously, then for such phase boundary controlled reaction.

equation relating α and t are the R_2 function (contracting area) for a circular disc reacting from the edge inward, and the contracting sphere or R_3 model for a sphere reacting from the surface inward. If the solid - state reaction is controlled by nucleation followed by growth, then in this case we may have Mampel unimolecular law, in which the rate-determining step is the nucleation process described by F_1 function or first order kinetics. Function F_2 and F_3 are given, for second and third order kinetic respectively. In phase boundary reactions, it is assumed that the nucleation step occurs instantaneously, so that the surface of each particles covered with a layer of product nucleation of the reactants, however may be a random process, not followed by rapid surface growth. As nuclei grow larger they may eventually impinge on one another, so that growth ceases where they touch. Avrami and Erofeev, who have given the functions A_2, A_3 and A_4, have considered this process. For branching nuclei, Prout-Tompkins gave the function B_1. The E_1 function is for the exponential low.

I-2. Literature Survey and Aim of The Work:

Recently analysis of the electrical properties of the chelated compounds has received great altention. (31-33) The presence of more than one transition metal complex in the chelated compound may give us more information on the electrical properties and the mechanism of the charge transfer in these compounds.

Thermal analysis and kinetic studies of the thermal decomposition of chelated compounds have drawn the interest of several investigators (34 -36), because the thermal decomposition of such materials results in products such as oxides or metals, which may possess pores, lattice imperfections and other characteristics, necessary for its formation as reactive solids and some of them considered as economic and catalyst precursors.

A considerable amount of work has been concentrated on the electrical conductivity of chelated compounds, especially those containing π electrons of unsaturated organic compounds which are able to move over the entire organic molecules causing a considerable conductivity (37).

Pyridine carboxylic acids are considered as a very important class of organic compounds. Studies on complexes of pyridine monocarboxylic acids with the first row transition elements were studied by many authors (38,39).

The electrical properties of 2-amino- 3-hydroxypyridine and 2-amino pyridine complexing with Mn(II), Fe(II), Co(II), Ni(II), Nd(II), Gd(III) and Yb(III) (40-44) in different molar ratio, were investigated. It was reported that the conductivity increases due to complexation and the charge transport occurs by the hopping mechanism. The electrical conduction of the coordination complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with the poly (Schiff base) liqand CPSB, derived from 4. 4'-diamino diphenyl methane and 5, 5'- methylene bis-salicy laldehyde was investigated. It was found that these complexes behave as n-type semiconductor.

The thermal behaviour of chelated compounds of Zn(II) with picolinic, nicotinic and isonicotinic acids has been studied using thermogravimetric and differential thermal analysis techniques. (45) The decomposition was found to proceed by the dehydration of water followed by loss of the organic liqand to give ZnO.

The thermal decomposition of Cu(II) nicotinate and isonicotinate was studied (39) to investigate the effect of liqand moiety on the thermal stability of the compounds. The final product was found to be metallic copper. The decomposition was found to be starting by homolytic RC(O)O-Cu bond scission, which is equivalent to electron transfer from $RC(O)O^-$ to Cu(II).

Pyridine carboxylate complexes of Co(II) and Ni(II) were prepared and their stereochmistry were characterized (46) by means of X-ray and magnetic measurements. They showed similar structure such as Ag(II) carboxylate complexes.

Mixed ligand complexes of Ni(II) with p-aminosalicylic acid as primary liqand and pyridine, β-picoline, 8-hydroxyquinoline and nicotinic acid as secondary liqand were synthesized. The structure of compounds we characterized using reflectance spectra, magnetic susceptibility and IR-studies (47).

Eight complexes of the general fomula L_nCuX were synthesized (L=nicotinic acid or Et-nicotinate, X=Cl, Br, I and n=1 or 2) (48). It was found that both nicotinic and its ester act as mondentate liqands with the ring N- as coordination center, N...H-O. Hydrogen bond in the free nicotinic acid changes to dimeric hydrogen bond upon complex formation. All complexes were found to be diamagnetic and their chemical individuality was proved by means of their X-ray powder patterns.

The complexes of Cu(II), Ni(II), Co(II) and Zn(II) with o-, m- and p-pyridine carboxylic and aminobenzoic acids were synthesized and their structures were established by means of spectra and magnetic measurements (49)

The preparation and structural characterization of air stable, high-spin trans [Cr(nic-N)$_2$ (H$_2$O)$_4$]; and trans [Zn (nico-N)$_2$ (H$_2$O)$_4$] were reported. (50) The Cr-complex possess the space group P_1 with Z=1, a=7.0101, b=7.223, c=8.851 Å, α = 68.08°, β=68.76°, γ=63.07°; which Zn-complex has configuration similar to that of Cr complex with the nicotinate arranged in trans fashion.

The crystal structure of nicotinic acid has been determined with X-ray method (51) . The compound exhibit monoclinic structure with space group P_2, lc, a=7.186, b=11.688, c=7.231 Å, β=113.55°, Z=4.

The crystal structure of isonicotinic acid was also investigated by X-ray. It was found to be crystallized (52) in triclinic structure with space group PT; a=7.231, b=7.469, c=6.392 Å; α=114.88, β=106.19, γ=103.66. Molecules related by translation along the b axis are linked in infinite chains by means of O-H...N hydrogen bonds with an O...N distance of 2.582 Å. These chains are joined by weak C-H...O hydrogen bonds to from a sheet parallel to the (100) plane.

The pyridine carboxylic acids have two different donor sites: the oxygen atoms of the carboxylic acid group and the nitrogen atom in the carboxylic acid.

From the literature survey, till now there are no studies concerning the electrical properties of nicotinic and isonicotnic acids as well as their complexes. Therefore, this work was designed to prepare simple and mixed metal complexes of Zn(II), Cu(II), Co(II) and Ni(II) with nicotinic as well as isonicotinic acid.

The main goals concentrated upon studying the electrical conductivity, dielectric constant, dielectric loss, magnetic susceptibility and the kinetic of thermal decomposition of the complexes in their solid state. The study involves characterization of the complexes by infrared spectra, thermal analysis (DTA and TG) beside the elemental analysis measurements.