CHAPTER I

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Processes involving the chemical transformation of solids plays an increasingly important role in modern technology as sophisticated and costly solids can be produced by reactions of others ,precursory solids. To obtain the desired purity, strucure and texture of the the material, a very careful control of the reaction is necessary.

I-1.Spinels and their properties:

A large class of compounds having a wide range of chemical and physical properties is known to crystallize in the spinel structure which may simultaneously accommodate metal ions among the octahedral and tetrahedral sites in the lattice.The spinels contain divalent"A" and trivalent"B" cations and divalent"X" anions. For the spinel with the composition AB_2X_4 the two extreme distributions of cations among the two sites "A" and "B" are possible, the normal $A[B_2]X_4$ and the inverse $B[A\ B]X_4$ distribution$^{(1-3)}$, where the ions in the octahedral sites are in the square brackets. In the inverse spinels one-half of the "B" cations are in the tetrahedral sites and the other half of the "B" cations plus the "A" cations occupy the octahedral sites. Datta et.el.(4) and Hafner et. al.(5) showed that there are many intermediate spinels which are in between the normal and the inverse arrangements.

Oxide and sulphide spinels represent a large class of inorganic materials which possess many important properties not found in the more limited binary oxides and sulphides.The usual routes to these compounds generlly involve reaction at high temperature for long periods of times. These conditions are required to overcome the slow reaction kinetics that occur when two solids are brought together.

Many compounds with spinel structure have been reported in literature. Almost all of them are oxidic spinels (AB_2O_4). However, a few non-oxidic spinels are also known. A large number of cations have been found to occur in the spinel structure(1,6-8).

The distribution of cations between octahedral and tetrahedral sites in the spinels has been extensively studied,as for example,magnesium ferrite(9,10),it was reported that the equilibrium distribution varies from the inverse spinel at low temperature to random spinel at high temperature.

Another important spinel type compound is cobalt chromite.Makkonen(11)reported that the two oxides Co_3O_4 and $CoCr_2O_4$ are miscible in all proportion as the lattice parameter varies linearly as a function of chromium content. On the other hand , Hand and Laitinen(12) observed that $Co(CrCo)O_4$ are stable in air and inert atmosphere at 1000°C and decomposed at 1450°C. For qualitative purpose, Makkonen(11)reported a normal structure for $Co_{3-x}Cr_xO_4$ spinel.

I-2.Kinetics of Formation of Spinels in the Solid State:

Although solid state reactions wre recognized during many reactions , as evidenced by the work of some workers a very little was done toward understanding their mechanisms.Some of the earliest quantitative work on the kinetic of solid -phase reactions was done by Tammann(13,14) and Jander(15). Wagner(16) has given a quantitative thermodynamic theory of solid-state reactions based on a model in which the reactants meet at a flat interface where the reaction products are formed. The problem is treated essentially as a one-dimensional problem.Jander(15)has discussed the case of diffusion-limited reactions between spherical particles and a reactant which may be another solid - phase, a liquid or a gas. A similar approach was followed by Ginstling and Brounshtein(17). Carter(18,19) has given a solution for the case in which the molar volume of the product is different from that of the reactants which was found to describe the growth of $ZnAl_2O_4$ formed by the reaction of Al_2O_3 powder with ZnO vapour and which is also applicable to solid-solid reactions.However, a limited number of studies has been carried out on the kinetics and mechanisms of formation of Spinels in the solid-state.

I-3. Methods Used for Kinetic Analysis of Solid-State Reaction Data:

There is considerable diversity of mechanisms by which solids react and there are a variety of factors which may control, determine, influence or modify the rate limiting processes. The rate of a solid- state decomposition reaction is usually assumed to be directly proportional to the area of the active interface. Thus, a comparison of the fractional reaction (α) - time curves, measured for a particular reaction with theoretical expresions, derived for appropriate nucleation and growth models, can be used as evidence for the identification of the geometry of interface advance. This method has been widely used and has yeilded important mechanistic informations(20). Here, we shall briefly discuss some important methods of kinetic analysis which we shall use for analyzing kinetic data obtained for spinel formation reactions.

In solid-state reactions, the rate of change of the fractional of material reacted (α) with respect to time "t" is often expressed according to the ordinary kinetic equation:

$$\left(\frac{d\alpha}{dt}\right) = k \; f(\alpha)$$

where f (α) depends upon the characterstic reaction mechanism and "k" is the rate constant.

Under isothermal conditions, the rate constant "k" is independent of reaction time and we have:

$$g(\alpha) = k\,t = \int_0^{\alpha} \frac{d(\alpha)}{f(\alpha)}$$

A plot of g(α) versus time(t) should thus give a straight line if the correct form of g(α) is used. Table(1) lists some of the more important kinetic equations given in literature$^{(20-26)}$.

The function f(α), (and hence g(α)) depends on the mechanism controlling the reaction and on the size and shape of the reacting particles. In diffusion-controlled reactions, D_1, is for one-dimensional diffusion process governed by a parabolic law, with constant diffusion cofficient; 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, and D_4 is the

Table 1. Kinetic equations examined in this work

Reaction model	$g(\alpha)$	$f(\alpha)$	$g(\alpha)$ symbol
One-dimensional diffusion	α^2	$(1/2\alpha)$	D_1
Two-dimensional diffusion	$\alpha + (1-\alpha)\ln(1-\alpha)$	$(-1/\ln(1-\alpha))$	D_2
Jander equation, three-dimensional diffusion	$(1-(1-\alpha)^{1/3})^2$	$(3(1-\alpha)^{2/3}/2(1-(1-\alpha)^{1/3}))$	D_3
Ginstling-Brounshtein equation, three-dimensional diffusion	$(1-2/3\,\alpha)-(1-\alpha)^{2/3}$	$(3/2((1-\alpha)^{-1/3}-1))$	D_4
Two-dimensional phase boundary reaction	$(1-(1-\alpha)^{1/2})$	$(2(1-\alpha)^{1/2})$	R_2
Three-dimensional phase boundary reaction	$(1-(1-\alpha)^{1/3})$	$(3(1-\alpha)^{2/3})$	R_3
First-order kinetics	$(-\ln(1-\alpha))$	$(1-\alpha)$	F_1
Random nucleation: Avrami equation	$(-\ln(1-\alpha))^{1/2}$	$2(1-\alpha)(-\ln(1-\alpha)^{1/2})$	A_2
Random nucleation: Eroféev equation	$(-\ln(1-\alpha))^{1/3}$	$3(1-\alpha)(-\ln(1-\alpha)^{2/3})$	A_3

function for a diffusion - controlled reaction starting on the exterior of a spherical particle. If the reaction is controlled by a movement at an interface at constant velocity and nucleation occurs virtually instantaneously, then for such phase-boundary controlled reaction ,equations relating α and t are obtained for simple geometrical systems.The function R_1 for a one-dimensional phase-boundary reaction; R_2 for a circular disc reacting from the edge inward and the function R_3 is obtained for a sphere reacting from the surface inward.Some solid -state reactions appear to follow first-order kinetics(F_1 function).In this case , the rate - determining step is nucleation process and there is equal probability of nucleation process at each active site. In the phase-boundary reactions,it is assumed that the nucleation step occurs virtually instantaneously, so that the surface of each particle is covered with a layer of product. Nucleation of the reactant, however, may be a random process,not followed by rapid surface growth. As nuclei grow larger, they must eventually impinge on one another,so that growth ceases where they touch. This process has been considered by Avrami and by Erofeev, who have given the functions A_2 and A_3, respectively.

I-4. Electrical Conduction in Solids:

The electrical conductivity in solids is very important property to differentiate between various types of solids. The electrical conductivity of oxides and sulphides materials encompasses a wide range of values which characterize insulators, semiconductors and metallic materials . In general, metals are good conductors and insulators very poor conductors, while semiconductors show intermediate condutivities. 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 conductivities of semiconductors and insulators show a reverse temperature effect with respect to the nature and behaviour of charge carriers in these materials many differences must be considered. In metals electrons are the main charge carriers and move throughout freely, they are not localized or bound to atomic sites. There is therefore essentially no activation energy required for the conduction process. In insulators, however, electrons are not free to move throughout the bulk of the materials but are bound to atomic sites. In semiconductors, however the number of freely moving electrons is far less than the number present in metals but generally somewhat greater than the number present in insulators(27).

In predominating ionic compounds(28) charge trasport occurs by the simultaneous motion of ionic and electronic charge carriers. Generally,only one type of carriers dominates charge transport , and so contributions from minority carriers are often neglected. Such compounds tend to be categorized either as semiconductors or as solid electrolytes, depending on whether electronic or ionic charge carriers predominate.

The electrical conductivity of a solids is simply the sum of the partial conductivities associated with each type of charge carriers and is given by;

$$\sigma = \sum_j \sigma_j \qquad (1)$$

Each partial conductivity σ_j , which represent transport of either ionic or electronic carriers is given by:

$$\sigma_j = C_j Z_j Q_j U_j \qquad (2)$$

in which C_j is the carrier density,

$Z_j Q_j$ is the effective charge, and

U_j is the mobility of the $j^{\underline{th}}$ species.

The fraction of total conductivity contributed by each carriers,

$$t_j = \sigma_j / \sigma \qquad (3)$$

where t_j is the transference number. By definition, the sum of the individual transference numbers must be unity.

When dealing with mixed ionic and electronic conductors one is generally concerned with the relative magnitude of the ionic transference number t_i ,which includes cation and anion contributions, and the electronic transference number which represent the sum of the electron and hole transference numbers $t_n + t_p$. Although mixed conduction plays an important role in many processes, there are only few mixed-oxides and sulphides about which enough knowledge on mixed transport exists.

The electrical conductivity-temperature dependance ,generally ,is given by:

$$\sigma = \frac{C}{T}\exp(-E_a/RT) \qquad (4)$$

over a wide temperature range , the temperature dependence may be more complicated , implying perhaps that a different mechanism prevail at a different temperature; even so the plots of $\ln\sigma$ against $1/T$ is the most convenient general method of displaying experimental data, and the $-R(d\ln\sigma/dT)$ may be considered as the activation energy analogous to the Arrhenius activation energy of a chemical reaction.

The activation energy required for the migration of charge carriers in the case of semiconductors and insulators is much greater than metals with essentially zero activation energy . This difference in the activation energies is responsible for the observed differences in the temperature dependence of the electrical conductivities of the three types of materials. Electrical properties of a semiconductors depending on the mobility and the concentration of charge carriers are sensitive to its preparation methods.

Oxide-spinels with general formula AB_2O_4 can be devided into four groups(6) according to their conductivity:

a- Aluminates, possessing a low electric conductivity (resistivity, $R_{(900^oC)} = 10^5 - 10^6$ ohm-cm)

b-Chromites, with medium electric conductivity($R_{(900^oC)} = 10^3 - 10^4$ ohm-cm.)

c-Ferrites, with fairly high electrical conductivity($R_{(900^oC)} = 10 - 10^2$ ohm-cm.)

d-magntite, with an extremely high electrical conductivity, approach metallic($R_{(300^oC)} = 10$ ohm-cm.)

The conductivity in aluminates is controlled by the divalent cation, and the conductivity of the chromites and ferrites is controlled by the trivalent cation(except Ferrous oxide compounds).

Sulphide-spinels of type AB_2S_4 have been reported in the litrature(29-45). All sulphide -spinels , chromites(29-37), cobaltites (38,39), and titanates(40-45) are metallic conductors with high electrical conductivity($R=10^{-2}-10$ ohm-cm). The electrical conductivity in $CuCr_2S_4$ was investigated by Lotgering et.al.(29).The conduction was attributed to the double exchange between Cr^{+3} and Cr^{+4} ions.

I-5.Catalytic Activity of Solid-Spinels type compounds:

Catalytic reaction may be carried out in a liquid in which the spinels(solid catalyst)being in a powdered form. The activity of the oxo-and sulpho-spinels depends on the area of the powder form and the specific activity of the surface of the spinels. The reactivity of the spinel semiconductors are very closely connected to the electronic processes occuring inside and on the surface of semiconductors,and are in the final estimate due to them.

The catalytic reaction occurs by:

1)chemisorption of the reactants on the suface,

2) interaction of the adsorbed compexes, and

3)desorption of the products.

The rate determining step of the catalytic reactions is the formation of the chemisorbed complex, which may be held to the surface by ionic or covalent bonds.The formation of the chemisorbed complex occurs by an electron transfer at the surface leading to adsorbed ions. This transfer is dependent on the relative electro-negativity of the surface and of the molecular fragments. Schwab et.al.(46) ivestigated hydrogen peroxide catalysis by ferrites,and concluded that the Fe^{2+} ions on the spinel sublattices could act as active centers for the decomposition reaction .The most favorable position for Fe^{2+} ions in the case of the inverse ferrites was found to be the octahedral sites,clearly the effective number of Fe^{2+} ions was increased due to the possibility of electron hopping with adjacent Fe^{3+}ions. Fahim et.al.(47) studied the decomposition of hydrogen peroxide over chromite spinels(e.g.$NiCr_2O_4$)and showed that Cr^{5+}/Cr^{6+}could act as active centers as well to Cr^{2+}/Cr^{3+} redox centers.(48). Mucka et.al.(49-55)studied the decomposition of H_2O_2over the two oxide mixtures($NiO-U_3O_8$,$NiO-Mn_2O_3$,$NiO-CeO_2$,$NiO-V_2O_5$ and $NiO-MoO_3$) and cocluded that the Ni^{2+}/Ni^{3+} act as active centers for the decomposition reaction in additive to the other metal ions centers.

I-6. The Present Study:

The study of the solid-state reaction has received considerable attention recently , but due to the complexity of the solid-state reaction there is no general explanation has yet been obtained . However , the chemical transformations of solids plays an increasingly essential role in the modern technology , as important and costly solids can be produced by reactions of other solids. A very careful control of the reaction is necessary,to obtain the desired purity,structure and texture of the materials(56).

The most important chemical operations in petroleum industries are now based on catalytic solid - solid reactions. Solid spinels were found to be very useful in many industrial uses. As example, ferrites(57-59) are used as controller or circuit element in electronic industry and used in permanent magnets due to its large coercive force, chromites brick is used as cladding in ovens which are used for the production of steel.

The present study comprises the following investigations:-

1) Pure and mixed oxides of the types $CuO-Fe_2O_3$ and $CuO-Cr_2O_3$ and pure and mixed **sulphides** of the type $CuS-Cr_2S_3$ were prepared from A.R. salts solutions by precipitation and co-precipitation methods. Samples wre calcined at different temperature for different durations.
2) The kinetics and mechanism of spinel formation reaction in the systems $CuO-Fe_2O_3$, $CuO-Cr_2O_3$ and $CuS-Cr_2S_3$ were carreid out.
3) The parent materials calcined samples and spinels were studied and characterized by chemical analysis, X-ray diffraction pattern, differential thermal analysis-thermogravimetry, infrared spectral and electron microscopy.
4) Electrical conductivity measurements were determined for samples and spinels calcined at different temperatures and for various durations.

5) Reactivities of the materials under investigation were determined towards H_2O_2 decomposition, and the results were discussed in terms of theories on heterogeneous catalysis.

This study thus afford the opportunity for an interesting comparison between the behaviour of solids obtained under different conditions and using some modern physico-chemical techniques.