SUMMARY AND CONCLUSIONS

A summary of important results and conclusions of various parts of the present dissertation is given below.

In the first part of the present study, the kinetics of formation of some oxide and sulphide spinels were investigated. Stoichiometric mixtures of $CuO-Fe_2O_3$, $CuO-Cr_2O_3$ and $CuS-Cr_2S_3$ were prepared by the co-precipitation method from solutions of A.R. salts and calcination at different temperatures. The actual amount of each metal in each mixture was determined by chemical analysis and the various prepared samples were characterized and studied by differential thermal analysis-thermogravimetry(DTA-TG), infrared spectral analysis(IRA), X-ray diffraction (XRD) and electron microscopy(EM) techniques.

The kinetics of the solid-solid spinel formation reactions were followed in the temperature range 500-800°C for $CuO-Fe_2O_3$ and $CuO-Cr_2O_3$ systems and 200-300°C for $CuS-Cr_2S_3$ system using a titrimetric technique. Kinetic analysis of the reactions were discussed in view of solid state reaction models based on diffusion of reactants through continueous product layer, phase boundary reactions, first-order reactions and random nucleation models. Kinetic analysis of data by linear regression analysis according to various theoretical models showed that the spinel formation reactions are best described by the three-dimensional diffusion controlled,Jander's equation(D_3),two-dimensional diffusion process(D_2) and Ginstling-Brounshtein three-dimensional controlled equation(D_4)which gave the highest correlation coefficient than the other models.

Kinetic analysis was carried out in the range of weight fraction (α) values in the range $0.06 < \alpha < 0.47$; $0.18 < \alpha < 0.70$ and $0.16 < \alpha < 0.41$ for $CuFe_2O_4$,$CuCr_2O_4$ and $CuCr_2S_4$,respectively.It was found that the $CuFe_2O_4$,$CuCr_2O_4$ and $CuCr_2S_4$ formation are increased with the temperature of calcination.The activation energies of spinel formation were calculated according to the two-dimensional diffusion controlled(D_2),three-dimensional diffusion Jander's equation (D_3)and the three-dimensional diffusion-controlled Ginstling -Brounshtein equation(D_4).The activation energies of the spinel formation are 59.4 ± 1.5 , 97.6 ± 3.5 and 24.6 ± 1.6 $kJ.mol^{-1}$ for $CuFe_2O_4$, $CuCr_2O_4$ and $CuCr_2S_4$ spimel,respictively. The variation in activation energy of the spinel formation reaction was explained on thebases of the energy required for the metal ion to diffuse through the crystal lattice. The radius of Cr(III) is larger than Fe(III) and this increases the activation of $CuCr_2O_4$ than $CuFe_2O_4$ .On the other hand, the relatively much lower activation energy for the formation of $CuCr_2S_4$ spinel is understood in view of the fact that metal sulphides have lower melting point and hence higher mobility and lower energy for diffusion of the metal ions in the lattice.

In the second part, the electrical conductivity of $CuO-Fe_2O_3$,$CuO-Cr_2O_3$ and $CuS-Cr_2S_3$ systems were investigated. The electrical properties of solids are sensitive to a large number of variables of which chemical composition,irradiation and thermal treatments have important effects.The electrical conductivity was followed for all samples calcined for 5 hrs. in the temperature range 500-800°C for $CuO-Fe_2O_3$ and $CuO-Cr_2O_3$ and in the range 200-300°C for $CuS-Cr_2S_3$ system. The electrical conductivity (σ) was carried out in the temperature range from room temperature up to 350°C. Results showed that Fe_2O_3 and $CuFe_2O_4$are n-type semiconductors, CuO , Cr_2O_3 , $CuCr_2O_4$ are P-type semiconductors while CuS , Cr_2S_3 and $CuCr_2S_4$ have metallic conduction. The dependence of ln σ against (1/T) gave rise to a single straight line relationship for all samples except $CuFe_2O_4$ which shows a break (T_b) at about 200°C. The break in copper ferrite is due to the conversion of the conduction character from P-type to n-type. The activation energies for the electrical conductivity were calculated according to linear regression analysis and lie in the range of 29.3 - 33.2 and 62.3 - 80.0 $kJ.mol^{-1}$ for $CuO-Fe_2O_3$ mixture below and above, T_b,respectively; 19.8 - 26.0 $kJ.mol^{-1}$ for $CuO-Cr_2O_3$ and 4.2 - 5.7 $kJ.mol^{-1}$ for $CuS-Cr_2S_3$ mixture.

In the third part , the H_2O_2 decomposition in aqueous solution over the oxide and sulphide systems were carried out . The reactivity of H_2O_2 decomposition in aqueous solution serves as a convenient test for investigation of the properties of various catalytic systems.The first-order reaction rate constant were measured in the range 30 - 50°C for samples calcined in the temperature range 500 - 800°C for the oxide samples , and in the range 200 - 300°C for the sulphide samples.

It was found that ,the hydrogen peroxide decomposition rate constant decreases with increasing the calcination temperature for the oxide samples,while it increases with increasing calcination temperature for sulphide samples. For $CuO-Fe_2O_3$ system it was found that the reactivity of CuO is higher than that of both Fe_2O_3 and $CuO-Fe_2O_3$ mixture. This is due to CuO is P-type semiconductor whereas $Fe_2O_3$is n-type, For $CuO-Cr_2O_3$ system the reactivity of CuO is more than that for Cr_2O_3 and $CuO-Cr_2O_3$ mixture for samples calcined below 700°C,while for samples calcined above 700°C the reactivity of Cr_2O_3 is the higher. This is due to the presence of CuO as P-type with active Cu^{+} / Cu^{2+} centers at low temperature while at temperature above 700°C $Cr_2O_3$is P-type with Cr^{2+}/ Cr^{3+} and Cr^{5+} / Cr^{6+} active centers.For $CuS-Cr_2S_3$ system the reactivity of CuS is more higher than that of Cr_2S_3 and $CuS-Cr_2S_3$ mixture for samples calcined at 200°C, and above 200°C the reactivity of Cr_2S_3 is more higher than that of both CuS and CuS-Cr_2S_3.Th results were discussed in view of an electronic and a chain reaction mechanism involving the hydroxyl and the perhydroxyl radicals as chain carriers.Such a mechanism could explain the kinetics of the decomposition reaction using different catalysts and under various conditions.