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Kinetics of Reduction of Copper Oxide

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Abstract: Reduction include induction, autocatalysis and decay. During reduction of sintered copper it was observed that it was a zero order reaction and it was not autocatalytic. Copper oxide was reduced at wide variety range of temperatures. Studies showed that with the increase in temperature the rate of reduction will also increases in all the cases. When the thin film of copper oxide was reduced using optical techniques, it was observed that thin film was reduced to copper at low temperature without altering uniformity of thin film.

Keywords: Autocatalysis, Thermal decomposition, diffusion, Activation energy, Rate constant, decay

I. INTRODUCTION

Numerous studies on the reduction of the copper oxides in the bulk state by hydrogen have been reported in the literature, Most of the investigators agree' that reduction of copper consists of three stages a) Induction b) Autocatalytic and acceleratory c) decay and the reaction occur on certain active nuclei. However, several areas of disagreement also have been observed. It has been [1-3] reported that the autocatalysis of the reaction is primarily a result of the solid product copper. In contrast to this, others have reported [4-6] that copper has no measurable effect and that the autocatalysis is the result chiefly of the crystal structure of the initial oxide. Clark and bond [7] and bond have studied the kinetics of reduction of CuO to establish the effect of the solid phase on the overall kinetics.

The reaction $\text{CuO(s)} + \text{H}_2(\text{g}) \rightarrow \text{Cu(s)} + \text{H}_2\text{O(g)}$ consisted of an induction stage, an autocatalytic stage and a decreasing-rate stage, the reduction rates for each stage depended on the nature of the starting oxide, addition of cu had no effect on reaction. While studying the reduction of sintered copper oxide, Spasov and Manchova [8] reported the induction period in the kinetics run probably connected with the rate of formation of nuclei of the new metal phase which in turn was depended on the temperature. The reduction process was of zero order and it was not autocatalytic.

Kurchatov and Lambiev [9] studied the low temperature reduction of copper oxide with hydrogen. The influence of temperature, briquetting was studied on the process of CuO and Cu₂O reduction. With increase of temperature the reduction rate increases in all cases. The redaction rate of CuO was higher than that of Cu₂O at all temperatures. The reduction curves of CuO and Cu₂O agreed perfectly between zero and 80 percent reduction at all the investigated temperatures with Prout and Tompkins equation, modified by Bond and Clark, $\log [(a-x)/(1-x)] = kt + c$ where

a = constant = 0.6, k = rate constant and x = ± degree of reduction

Wieder and Czanderna [10] have showed no evidence for presence of Cu₂O while studying the reduction of CuO thin film on glass substrate by hydrogen to Cu at 162°C.

Czanderna [11] has studied the reduction of CuO_{0.67} thin film (500⁰Å) in hydrogen using the gravimetric and optical techniques. The composition CuO_{0.67} can be reduced to copper in hydrogen at low temperature (25⁰) without appreciably altering the film uniformity. The data obtained were used to conclude that the reduction process is a nucleation and growth phenomenon.

In what follows, we have studied the kinetics of reduction of CuO and CuO_{0.67} (in the thin film state) by hydrogen in the temperature range 150°-252⁰C to elucidate the mechanism of reduction.

II. EXPERIMENTAL

Copper films were evaporated uniformly on to a glass substrate and oxidized to copper oxide in oxygen (76 torr) At lower temperature (160°C -200°C), CuO_{0.67} was formed while at above 300°C, CuO was formed. The mass change was measured with a microbalance during evaporation, oxidation and during subsequent reduction The films were reduced In 76 torr of hydrogen at temperatures ranging from 160°C to 252°C in the case of CuO and at 160°C and 200°C in the case of CuO_{0.67}

III. RESULTS

Curves of fraction reduced vs time were plotted as shown in fig.1 for the reduction of CuO_{0.67} and in fig. 2 for the reduction of CuO. The sigmoidal shape was obtained in each reduction cycle. The shape of this curve is typical for a nucleation, growth and depletion mechanism. The same carves were obtained with different file thicknesses which show that the reduction curve is

independent of the mass of the oxide. The reduction rate reached a maximum at approximately 50 % reduction regardless of the nature of the oxide.

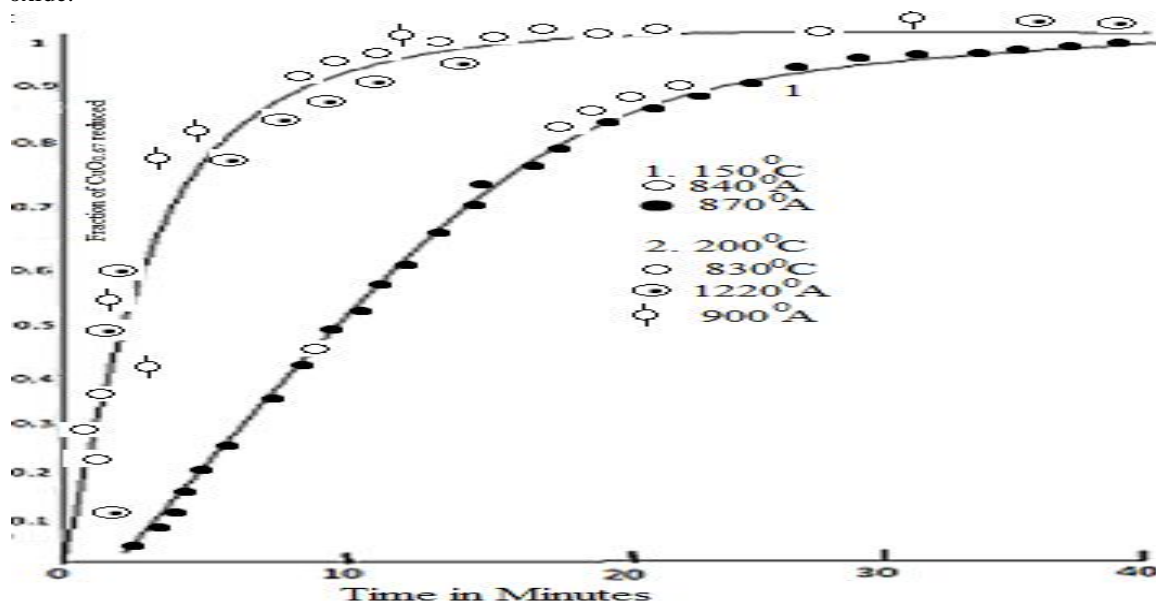


Fig 1 Rate of reduction of $\text{CuO}_{0.67}$ by hydrogen at 76mm of Hg

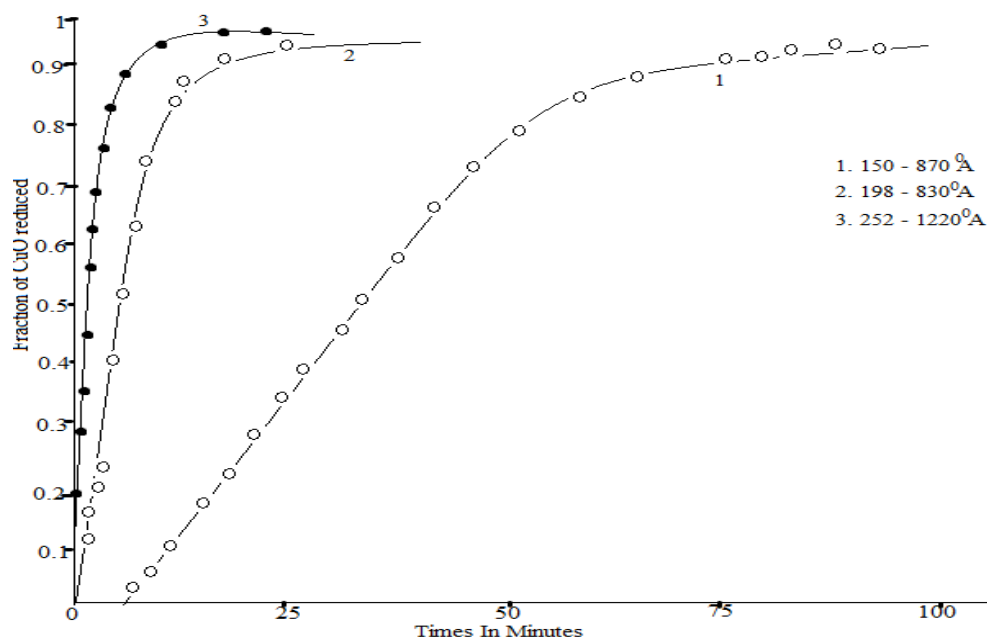


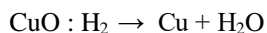
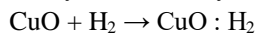
Fig 2 Rate of reduction of CuO by hydrogen at 76mm of Hg

Increasing the temperature of the reduction markedly increased the rate of reduction of these oxides. It has been reported that the $\text{CuO}_{0.67}$ was reduced more rapidly than that of CuO , For example at 200°C the $\text{CuO}_{0.67}$ was reduced completely in 25 minutes whereas CuO required 85 minutes. The initial reduction rates for these two oxides were markedly different (fig.1 & 2)

The reactivity of the oxide is clearly an effect of the nature of the oxide and probably depends on the crystallite structure within the individual particles since a wide difference in reactivity is observed between these two oxides of nearly the same film thickness. This difference also shows that reaction occurs on certain active nuclei, otherwise the initial rates would be approximately the same. To explain the autocatalytic nature of the thermal decomposition of solid, several theories and mathematical expressions have been developed[12].

These theories and equations also are applicable to reactions between a gas and a solid when the rate is controlled by chemical reaction and not by adsorption or diffusion of the reactant gas to the solid surface.

The reduction of CuO by hydrogen is considered to be governed by either chemical reaction or diffusion of water away from the reaction site. Also since Pavlyuchenke and Rubinchik have shown that the reaction involves adsorbed hydrogen the reduction may be visualized as taking place in essentially the same way as thermal decomposition reaction



where the colon denotes the adsorption boundary layer, if the adsorption step is much faster than the decomposition step, the overall behaviour of the reaction is like that of a thermal decomposition reaction.

Prout and Tompkins have derived an equation of applicability for autocatalytic decomposition reaction. This is based on the initial reaction occurring on certain active nuclei followed by a rapid growth of these nuclei by a branching-chain mechanism as a result of the reaction process.

The reaction rate reaches a to maximum when the rate of growth of branches is equal to their rate of termination by interference with each other and the rate will subsequently decreases as interference among the growing chains steadily increases.

When the maximum rate is observed at 50 % decomposition then Prout and Tompkins equation is

$$\frac{dX}{dt} = K \times (1 - X) \quad \text{(equation-1)}$$

Where $\frac{dX}{dt}$ = rate of reaction

X = Fraction decomposed

1 - X = Fraction remains (not decomposed)

K = Specific rate constant On integrating and rearranging the equation became

$$\text{Log} (1 - X) = -Kt + C \quad \text{(equation-2)}$$

Where

$$C = -K t_{\text{max}}$$

t_{max} = time at which the rate is maximum

IV. CONCLUSIONS

Plots of the data according to equation-2 show that this equation closely approximates the reduction process (figures 3 & 4), In the case of CuO_{0.67} equation- 2 is generally obeyed from zero to 90 % reduction at 200°C and from 2 to 85 % reduction at 150°C (fig. 3), while in the case of CuO, the range is from 0.75 to 90 % reduction (fig.4). The equation is not obeyed beyond 90 % reduction. It is likely that the remaining oxides (CuO and CuO_{0.67} are enclosed completely in the copper particles with little chance of growth of existing nuclei and that the reaction is controlled by diffusion.

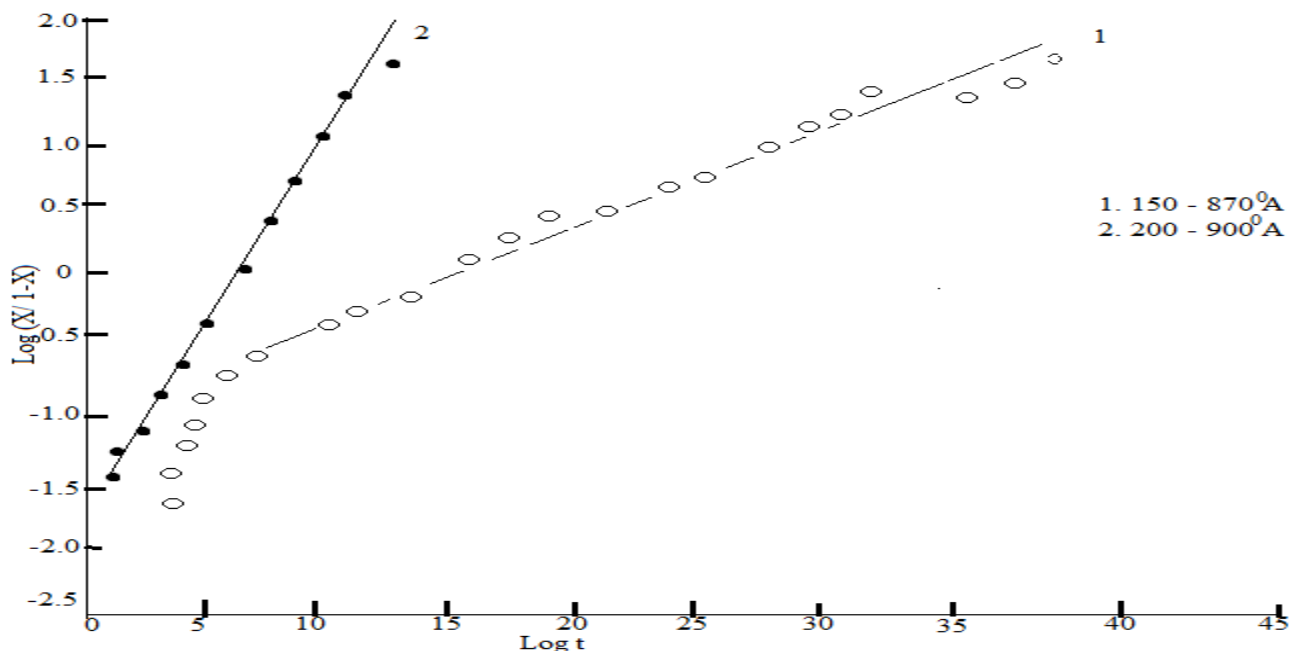


Fig. 3 Rate of reduction of CuO_{0.67} by hydrogen according to equation 2

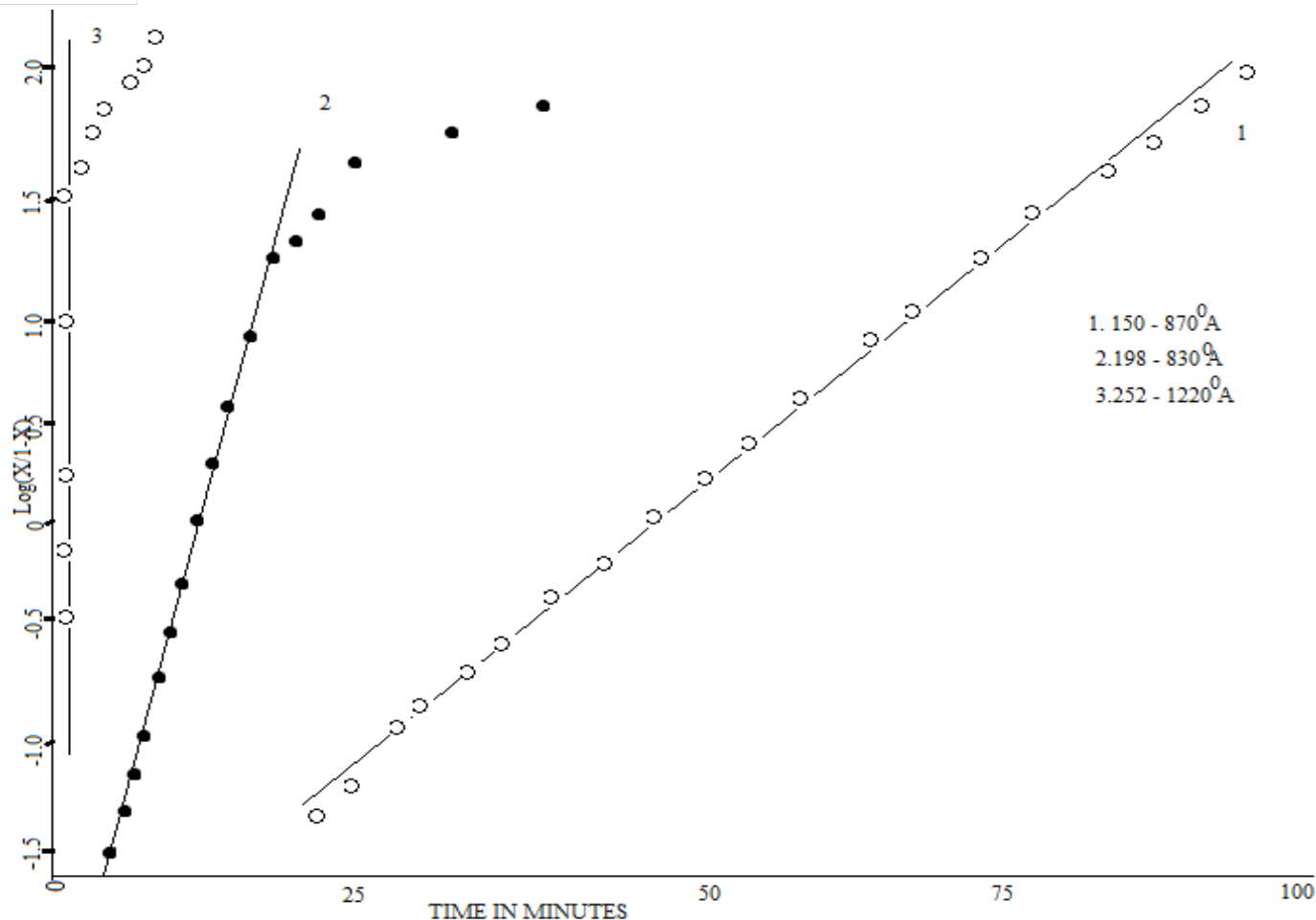


Fig. 4 Rate of reduction of CuO by hydrogen according to equation 2

Table 1 and table 2 show the reaction rate constants determined from the slopes of the plots of figures 3 and 5 for CuO_{0.67} and CuO reduction respectively.

S.No	Temperature °C	K ₁ (Mole fraction reduced per minute)	Δ E _a (Activation energy)
1	150 °C	9.5X 10 ⁻²	10.2 ± 0.7 Kcal/mol
2	200 °C	3.8X 10 ⁻¹	10.2 ± 0.7 Kcal/mol

Table 1

Table shows the details of reaction rate constant of CuO_{0.67} reduction procedure.

S.No	Temperature °C	K ₁ (Mole fraction reduced per minute)	Δ E _a (Activation energy)
1	150 °C	4.2X 10 ⁻²	14.2 Kcal/mol
2	198 °C	2.1X 10 ⁻¹	14.2 Kcal/mol
3	252 °C	1.2	14.2 Kcal/mol

Table 2

Table shows the details of reaction rate constant of CuO reduction procedure.

using the values of table-1 , the activation energy of 10.2 ± 0.7 Kcal/mol for the reduction of CuO_{0.67} was calculate with the help of Arrhenius equation, using the values of table-2, Arrhenius plot gave an apparent activation energy of 14.2 Kcal/mol for CuO (fig.5)

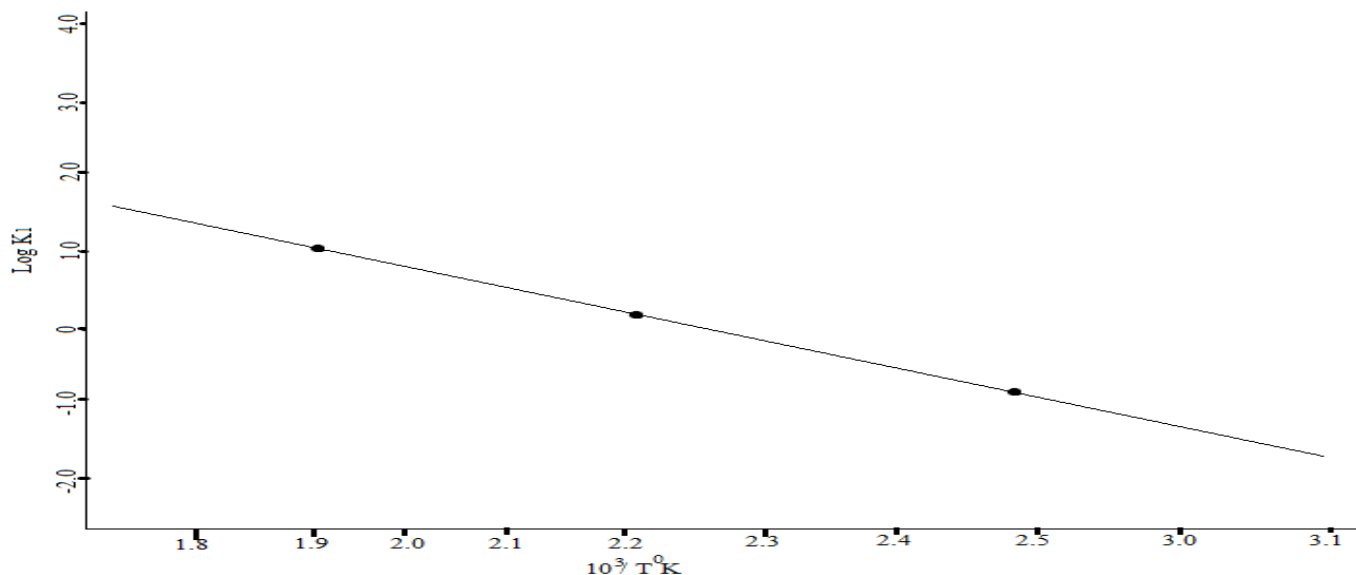


Fig- 5 Temperature dependence of rate constants for reduction of CuO by hydrogen

Thus the two oxides required different activation energy. The reaction rate of the reduction of $\text{CuO}_{0.67}$ are higher than that of the CuO (table-1 and table-2), This may be attributed to the different densities of the oxides. It has been reported that the rate of reduction decreases with increasing density of copper oxide. $\text{CuO}_{0.67}$ has been shown to possess a lower density than CuO and consequently a faster rate of reduction of $\text{CuO}_{0.67}$ is expected. The present results proves the above conclusion.

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