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REDUCTION OF CUPRIC OXIDE BY HYDROGEN.

I. FUNDAMENTAL KINETICS

W. D. Bond  
W. E. Clark

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Chemical Development Section B

REDUCTION OF CUPRIC OXIDE BY HYDROGEN. I  
FUNDAMENTAL KINETICS

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W. E. Clark

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# ABSTRACT

Basic studies of the kinetics of the reduction of copper oxide were made to establish the effect of the solid phase on the overall reaction kinetics. The reaction  $\text{CuO(s)} + \text{H}_2\text{(g)} \longrightarrow \text{Cu(s)} + \text{H}_2\text{O(g)}$  consisted of an induction stage, an acceleration or autocatalytic stage terminating at about 35% reduction of the oxide, and a decreasing-rate stage. The reduction rates for each stage were dependent on the nature of the initial oxide, the degree of subdivision of the oxide, and the temperature, but were independent of the mass of the oxide phase. Addition of the reaction product copper had no measurable effect on the reaction. Water vapor in concentrations of 25 mg per liter of hydrogen prevented reduction at 112°C. The inhibiting effect decreased rapidly as the temperature was increased and disappeared entirely at 190°C. Once reduction had started, water vapor had practically no effect.

The acceleration and decay stages were very closely approximated by a semiempirical equation based on the initial reaction occurring on certain active nuclei followed by a rapid growth of these nuclei by a branching-chain mechanism. The reduction rate reached a maximum and subsequently decreased as considerable interference occurred among the branching nuclei. Arrhenius plots gave an activation energy of  $13.5 \pm 1.2$  kcal for the reduction.

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## 1.0 INTRODUCTION

Reduction of copper oxide by hydrogen is a convenient way of converting elemental hydrogen to the oxide for removal from gas streams. The purpose of this investigation was to make a fundamental study of the kinetics of the hydrogen-copper oxide reaction, which is necessary for the design of a commercial scale process. A study of the rate of conversion of hydrogen to water by a fixed bed of CuO is reported separately.<sup>1</sup>

Many studies<sup>2-8</sup> of the reduction of copper oxide by hydrogen have been reported in the literature. All agree that the reduction consists of three stages—induction, autocatalytic or acceleratory, and decay—and that the reaction occurs on certain active nuclei. Several workers<sup>2-6</sup> have reported that water vapor markedly affects the beginning of the reduction, although little effect is observed once the reaction has begun. Others<sup>8</sup> report that water vapor has no effect on the onset of the reaction. Some<sup>2-5</sup> have reported that the autocatalysis of the reaction is primarily a result of the solid product, copper, whereas others<sup>7-8</sup> report that copper gives no measurable effect and that the autocatalysis is the result chiefly of the crystal structure of the initial oxide.

The reduction has been shown to involve adsorbed hydrogen.<sup>6-8</sup> The rate of reduction is only slightly affected by hydrogen in the 200-700 mm range.

Mathematical expressions for the reduction rate at various times differ widely.<sup>4-6</sup>

The authors express appreciation to L. M. Ferris for the loan of the automatic recording thermogravimetric balance and to the groups of W. R. Laing, R. L. Sherman, and G. R. Wilson of the Analytical Chemistry Division for their analytical work.

## 2.0 DISCUSSION OF RESULTS

The variables included in this study were the method of preparing the copper oxide and its initial surface area, temperature, mesh size, water vapor, and the reaction products.

### 2.1 Typical Reduction-Time Curves

Curves of fraction reduced vs time are always sigmoid (Fig. 1). The reduction consists of three distinct stages: induction, autocatalysis, and decreasing rate. The same curve was obtained with 1 or 2 g of oxide, which shows that the reduction curve is independent of the mass of the oxide. Self-heating effects would result if too large a sample was used. The reduction curves were reproducible to  $\pm 3\%$ . The reduction rate always reached a maximum at about 35% reduction regardless of the nature of the oxide (Fig. 2).

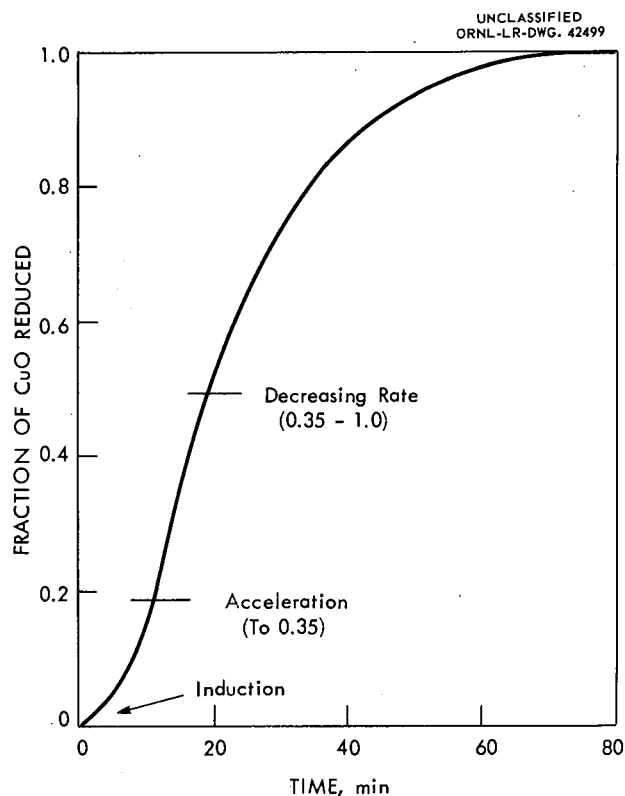


Fig. 1. Typical curve for reduction of CuO by H<sub>2</sub>. CuO prepared by calcination of Cu(NO<sub>3</sub>)<sub>2</sub> · 3 H<sub>2</sub>O; particle size < 44 μ; H<sub>2</sub> flow rate 2.0 liters/min; temperature 148°C.

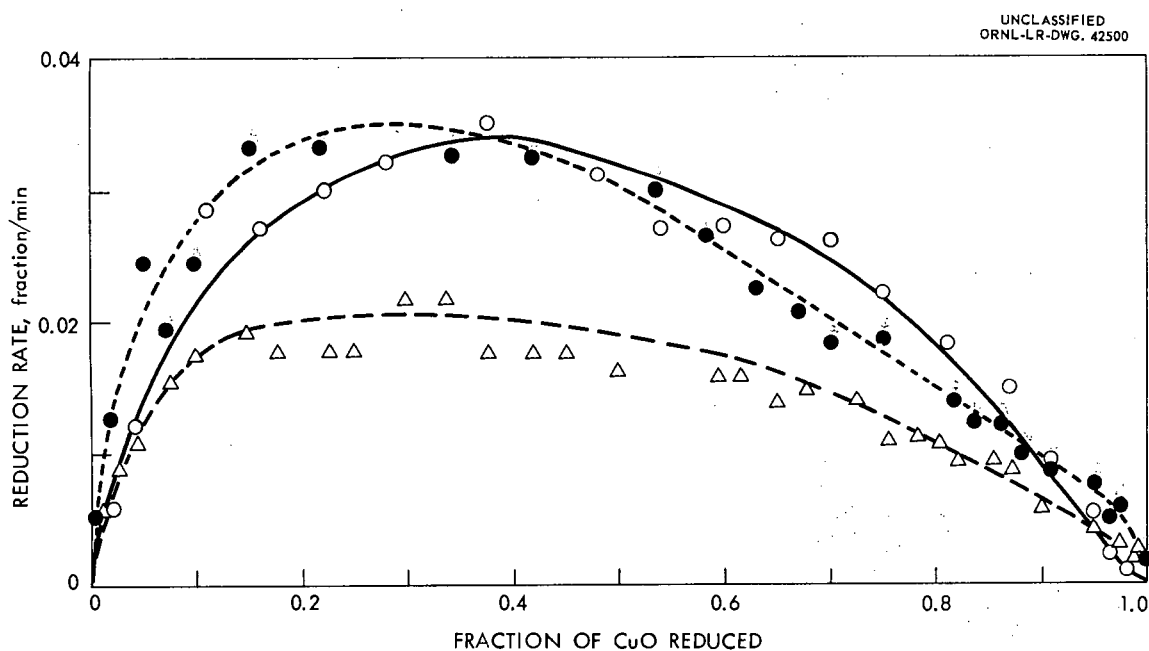


Fig. 2. Dependence of reduction rate on fraction of CuO (< 44 μ particle size) reduced by H<sub>2</sub>, 2.0 liters/min. ●, temperature = 190°C, CuO from calcining of Cu(OH)<sub>2</sub>, initial surface area 0.43 m<sup>2</sup>/g; ○, temperature = 148°C, CuO from calcining of Cu(NO<sub>3</sub>)<sub>2</sub> · 3 H<sub>2</sub>O, initial surface area 0.49 m<sup>2</sup>/g; Δ, 148°C, commercial grade CuO.

## 2.2 Effect of Method of Preparing the CuO and Its Surface Area

The oxide produced from calcining of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  at  $400^\circ\text{C}$  was reduced more rapidly than that obtained from calcining of  $\text{Cu}(\text{OH})_2$  at  $400^\circ\text{C}$  or from oxidized copper wires crushed to the same mesh size (Fig. 3). For example, at  $190^\circ\text{C}$  the oxide from calcining of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  was reduced completely in 16 min, whereas the oxides from calcining of  $\text{Cu}(\text{OH})_2$  and from oxidizing of copper wires required 98 and 35 min, respectively, for complete reduction.

The reactivity of the oxide is clearly an effect of the nature of the oxide, probably one of crystallite structure within the individual particles, since a wide difference in reactivity is observed between different oxides of the same mesh size classification and approximately the same initial nitrogen-adsorption surface area. This difference also shows that reaction occurs on certain active nuclei; otherwise the initial rates would be approximately the same. The total surface area is not necessarily related to the number of active nuclei for the adsorption or reaction of specific gases. The nitrogen-adsorption surface area of the copper product is much higher than for initial copper oxide (Table 1). The measured surface areas are accurate to  $\pm 15\%$  so that within experimental error the product surface areas do not differ greatly. These results indicate that reaction between CuO and hydrogen creates pores and cracks such that large surface areas are produced.

These results are not directly comparable to those of previous workers. Pavlyuchenko and Rubinchik<sup>8</sup> are the only other investigators who have made a study of the reduction of oxides from different preparations. Unfortunately, they did not report mesh sizes and surface areas of their starting materials and a complete qualitative comparison of data is not possible. They did observe that for material prepared by any one method the reactivity was of the same order as its visually estimated state of subdivision. They believe that the reactivity to hydrogen is due principally to the dimensions of the original CuO crystals.

The final calcination temperature used in different preparations also probably has an important effect on the reactivity of the oxides, since heat treatment may either increase or decrease the number of active centers by cracking or by sintering effects.

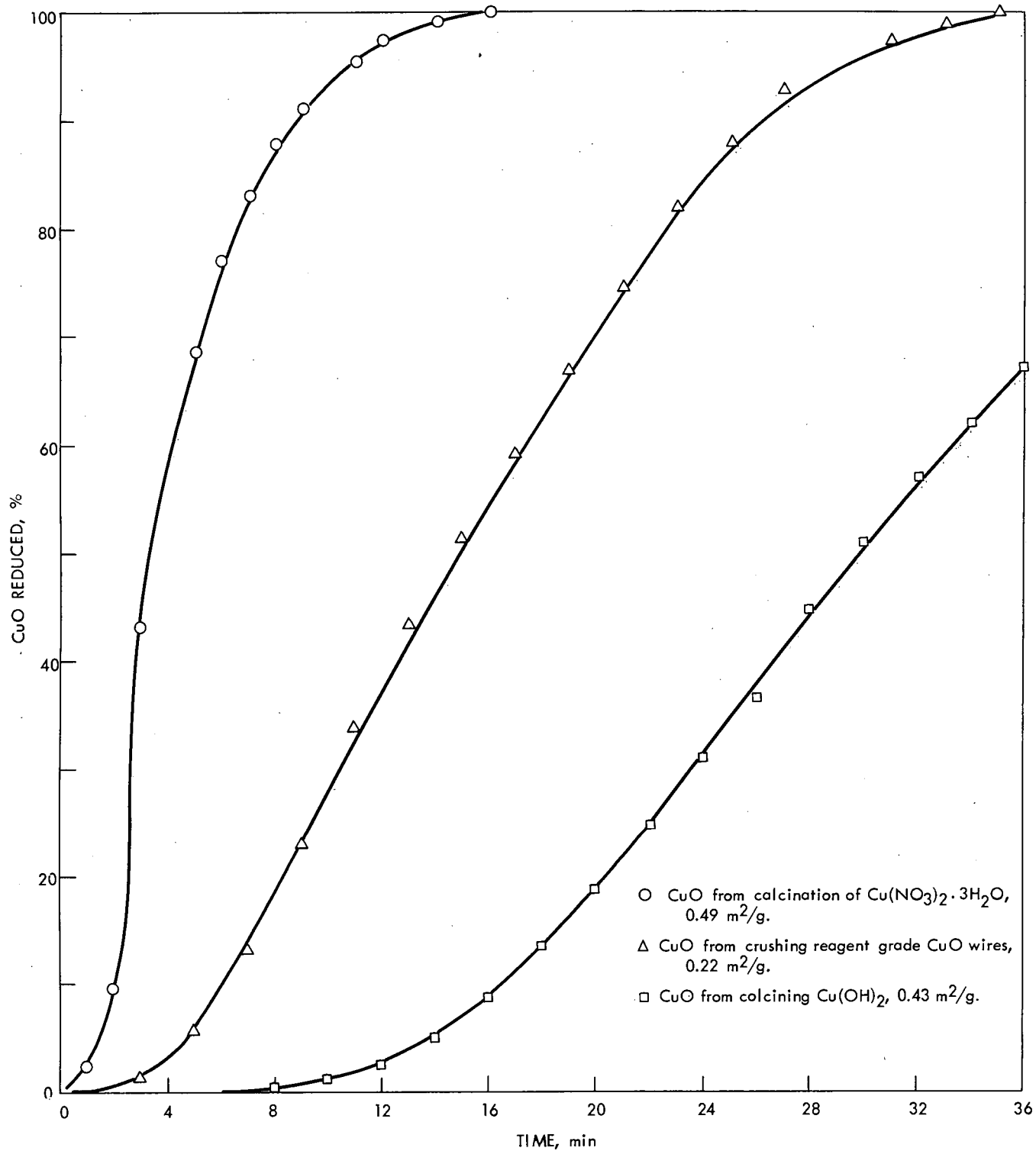


Fig. 3. Effect of nature of oxide on rate of reduction of CuO by hydrogen. Particle size  $< 44 \mu$ ; hydrogen flow rate 2.0 liters/min; temperature  $190^\circ\text{C}$ .

Table 1. Surface Area of Initial Oxides and Reduction Products

Temp. of Reduction, °C	CuO Preparation	Size of CuO, $\mu$	Surface Area, $m^2/g$	
			CuO	Cu Product
190	Calcining of $Cu(NO_3)_2 \cdot 3H_2O$	< 44	0.49	1.1
	Calcining of $Cu(OH)_2$ at 400°C	< 44	0.43	1.3
148	Crushing of reagent-grade CuO wires and calcining at 600°C	< 44	0.22	0.98
	Calcination of $Cu(NO_3)_2 \cdot 3H_2O$ at 400°C	< 44	0.49	1.3
	Crushing of reagent-grade CuO wires; contained some $Cu_2O$	149-297	0.019	0.82

### 2.3 Effect of Temperature

Increasing the temperature of the reduction markedly increased the rate of reduction of all oxides regardless of the method of preparation (Fig. 4). The total reduction time decreased by factors of 6 to 10, depending on the oxide, as the temperature was raised from 148 to 216°C (Table 2). The fact that increasing the temperature caused the induction period to disappear completely is also significant. The results are in general agreement with those of other investigations.<sup>2-8</sup>

Table 2. Total Reduction Times for Different Oxide Preparations

H<sub>2</sub> flow rate: 2.0 liters/min  
Particle size: < 44  $\mu$

Reduction Temp., °C	Total Reduction Time, min		
	CuO from Calcining of $Cu(NO_3)_2 \cdot 3H_2O$	CuO from Crushing of Reagent-grade Wires	CuO from Calcination of $Cu(OH)_2$
112	241	328 <sup>a</sup>	-
148	76	97	102 <sup>b</sup>
190	16	35	98
216	7	17	-

<sup>a</sup> 79.7% reduced.

<sup>b</sup> 48% reduced.

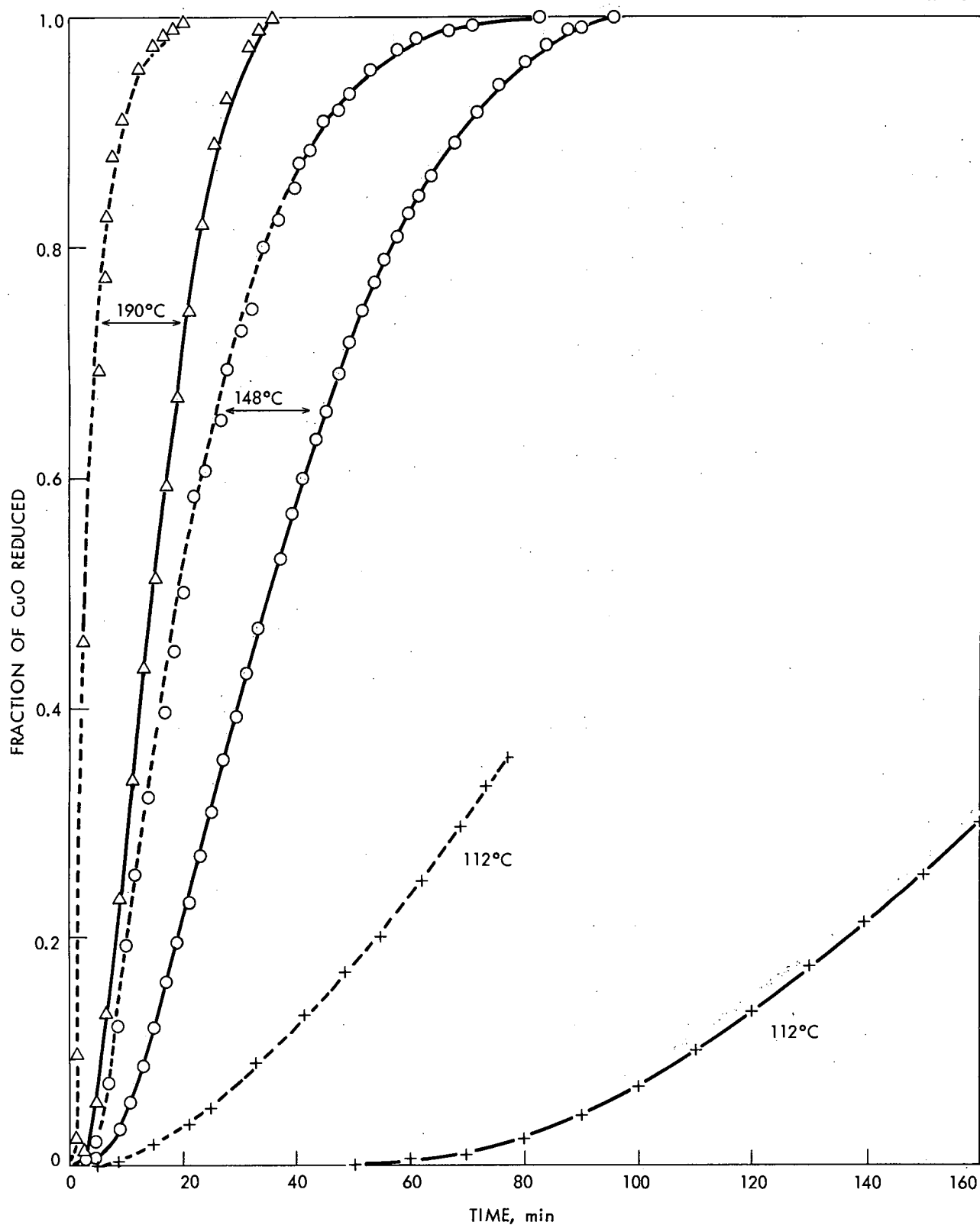


Fig. 4. Effect of temperature and method of preparation of CuO on rate of reduction; particle size  $< 44 \mu$ , hydrogen flow rate 2.0 liters/min. Solid lines, CuO produced by crushing reagent-grade CuO wire; dashed line, CuO produced by calcination of  $\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$ .

#### 2.4 Effect of Mesh Size

The effect of mesh size was investigated only very briefly. A single massive piece of CuO weighing 1.6 g, obtained by calcining  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , was reduced at  $200^\circ\text{C}$  and the results were compared with those from the same material crushed to  $<44\mu$  (Fig. 5). The total reduction time was only about twice as great for the single massive piece. There was little difference in the rate until 90% reduction was reached, beyond which point the reaction slowed rapidly for the massive CuO. This is probably a result of the CuO becoming completely covered with metallic copper, after which diffusion of hydrogen to the reaction site controlled the rate. The results indicate that the initial reaction probably occurs at active nuclei and is followed by rapid growth of the nuclei. In this case initial particle size would be less important than in a reaction controlled by total surface.

These results are consistent with previous investigations with similar starting material.<sup>2-8</sup> Pavlyuchenko and Rubinchik<sup>8</sup> were able to show that crushing eliminates abnormally long induction periods.

#### 2.5 Effect of Water Vapor

Saturation of the hydrogen with water vapor at  $27^\circ\text{C}$  completely prevented initial reaction from taking place at  $112^\circ\text{C}$ , but this retardation effect disappeared at  $190^\circ\text{C}$  (Table 3). Once reaction had begun, however, water vapor in this concentration had no great effect on the reduction rate (Fig. 6). These results indicate that water vapor is adsorbed at active sites in preference to hydrogen at lower temperatures. At  $112^\circ\text{C}$  the adsorbed water vapor completely masks the active sites from hydrogen. The decrease in the inhibiting effect of water vapor with increasing temperature shows that hydrogen is more strongly adsorbed than water vapor at higher temperature.

The results are consistent with those of many previous workers,<sup>2-6</sup> but are in disagreement with the conclusions reached by Pavlyuchenko and Rubinchik,<sup>8</sup> who state that water vapor has practically no effect on the reduction. Their conclusions were based on experiments performed at  $183^\circ\text{C}$ , which was too high a temperature for the retardation effect of their oxide to be observed. Since adsorption phenomena are involved, the temperature at which the retardation effect ceases to exist will be a function of the number of active sites in the initial oxide used and of the partial pressure of the water vapor.

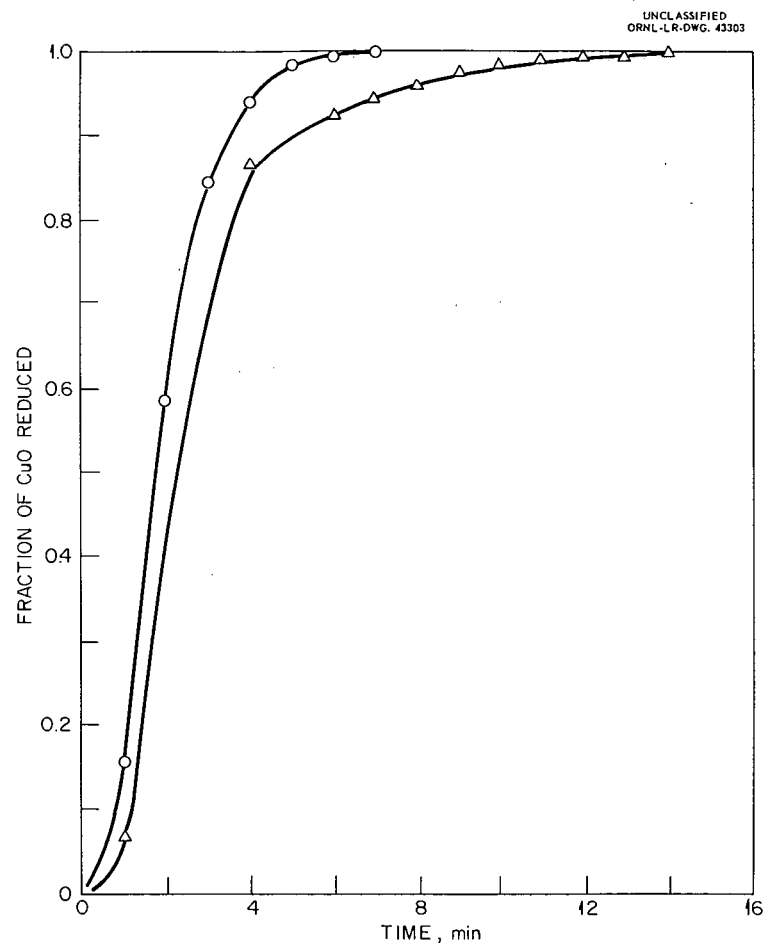


Fig. 5. Effect of particle size on reduction of CuO by hydrogen. CuO prepared by calcination of  $\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$ ; hydrogen flow rate 2.0 liters/min; temperature  $216^\circ\text{C}$ . O 1.000 g of CuO ( $<44 \mu$  particle size); Δ 1.668 g single massive piece of CuO.

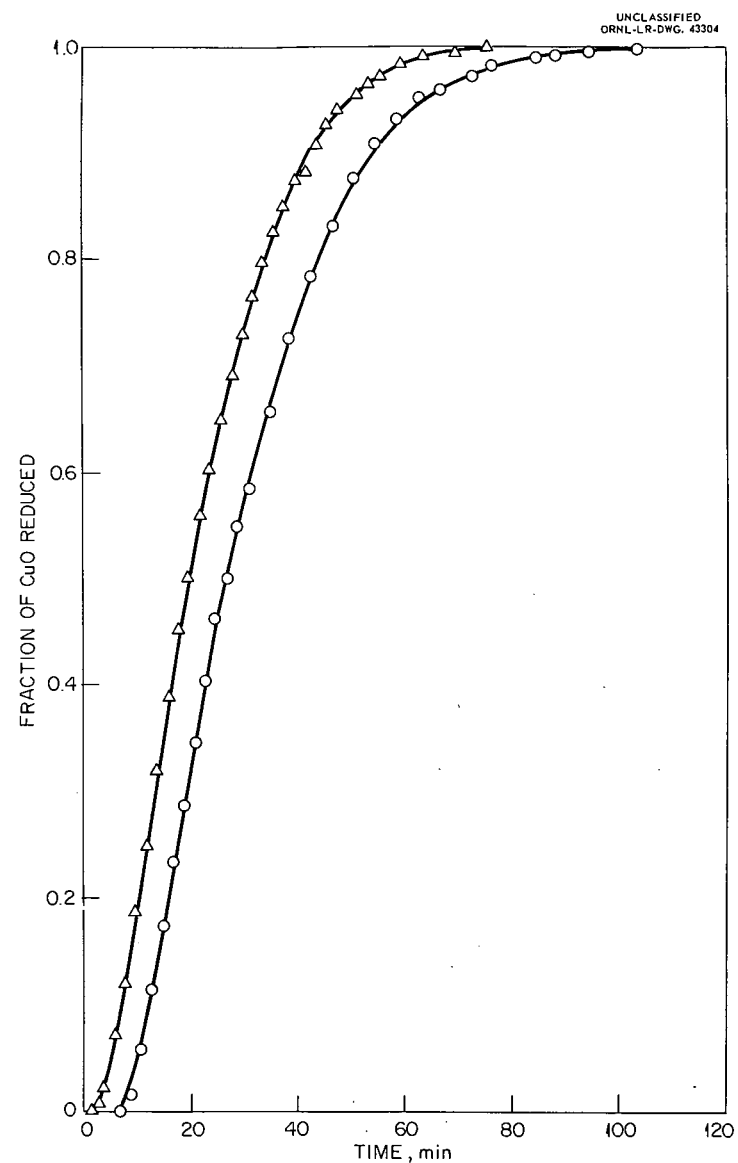


Fig. 6. Effect of water vapor on reduction of CuO by hydrogen. CuO prepared by calcination of  $\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$ ; hydrogen flow rate 2.0 liters/min; temperature  $148^\circ\text{C}$ . Δ no water in inlet  $\text{H}_2$ ; O 25 mg  $\text{H}_2\text{O}$  per liter in inlet  $\text{H}_2$ .

Table 3. Effect of Water Vapor on Induction Time

CuO prepared by calcination of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  ( $< 44 \mu$ )  
 $\text{H}_2$  flow rate: 2.0 liters/min;  $\text{H}_2$  saturated with  
 $\text{H}_2\text{O}$  at  $27^\circ\text{C}$  (25 mg/liter)

Temp., $^\circ\text{C}$	Induction Time, min	
	With $\text{H}_2\text{O}$	Without $\text{H}_2\text{O}$
112	No reaction in 90 min	7
148	7	2
190	0	0

## 2.6 Effect of Metallic Copper

The addition of copper powder, obtained from a previous experiment under exactly the same conditions, to the oxide prior to reduction had no measurable effect, within experimental error, on the reduction rate (Fig. 7). Results were the same at 112 and  $190^\circ\text{C}$ . Copper metal per se is therefore not responsible for the autocatalysis of the reactions.

These results are in agreement with the data of some previous workers<sup>7,8</sup> but are contrary to the observations of Pease and Taylor,<sup>2</sup> who reported a marked increase in the initial reduction rate as a result of added copper granules. This difference is not understood unless the nature of the oxide was different in the control and in the variable experiment. Under no circumstances could the reaction be catalyzed by adding copper powder to a carefully controlled oxide starting material. Care was always taken to use oxide from the same oxide preparations.

The copper product may have an indirect effect in the autocatalysis but this is not simply because the reaction product is copper. During the actual reduction process, where copper is produced in situ, mechanical strain with subsequent cracking of the CuO particles would no doubt occur. Such cracks would lead to an increase in surface area and in the number of active centers at which reaction may take place. In this case, however, it is the effects on the CuO as a result of the formation of copper in situ that are responsible for the autocatalysis rather than the fact that the material is copper.

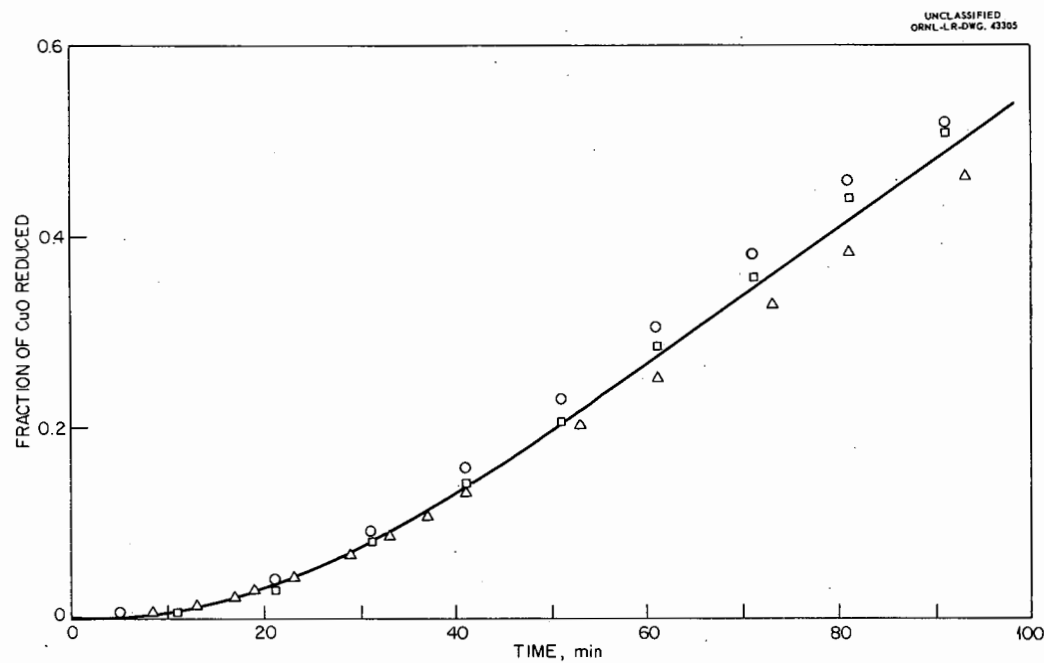


Fig. 7. Effect of adding metallic copper prior to reduction. CuO prepared by calcination of  $\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$ ; particle size  $< 44 \mu$ ;  $\text{H}_2$  flow rate 2.0 liters/min; temperature  $112^\circ\text{C}$ . O 1 g CuO + 0.802 g Cu;  $\Delta$ ,  $\square$  1 g CuO.

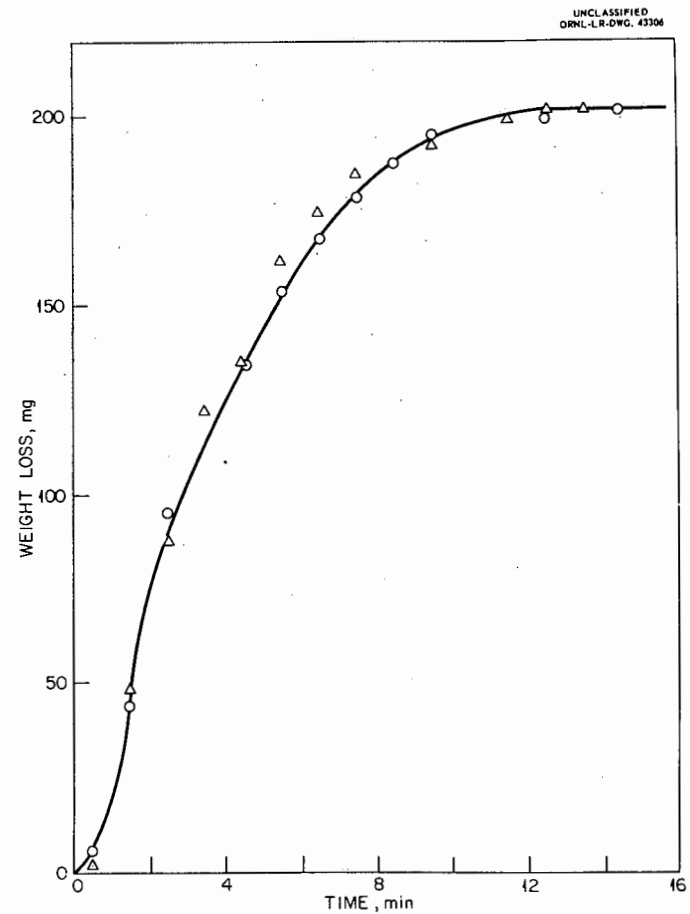
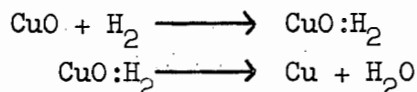


Fig. 8. Effect of hydrogen flow rate. CuO, 1 g, prepared by calcination of  $\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$ ; particle size  $< 44 \mu$ ; temperature  $190^\circ\text{C}$ .  $\Delta$  4.0 liters/min; O 2.0 liters/min.

## 2.7 Kinetic Equation

Theory and Derivation. Several theories and mathematical expressions have been developed for explaining the autocatalytic nature of the thermal decomposition of solids.<sup>9-11</sup> These theories and equations are also applicable to reactions between a gas and a solid when the rate is controlled by chemical reaction and not by adsorption, mass transfer, or diffusion of the gas to the solid surface. Since the reaction rate was found to be independent of the flow rate used in this study (Fig. 8), and to be only slightly affected by hydrogen pressure in the range 200-700 mm Hg in a previous study,<sup>8</sup> the rate of reduction of CuO by hydrogen is considered to be governed by the chemical reaction and not by the above phenomena. Also, since Pavlyuchenko and Rubinchik<sup>8</sup> have shown that the reaction involves adsorbed hydrogen, the reduction may be visualized as taking place in essentially the same way as a thermal decomposition reaction:



where the colon denotes the adsorption boundary layer.

If the adsorption step is much faster than the decomposition step, the overall behavior of the reaction is like that of a thermal decomposition reaction.

The autocatalytic nature of solid reactions has been explained by various workers<sup>9</sup> on the general hypothesis that such reactions proceed by formation of nuclei at certain localized spots in the reactant, followed by relatively rapid growth of these nuclei. If the free energy of activation of the Cu-CuO interface reaction is less than that for the formation of new nuclei, the growth of existing nuclei predominates over the formation of new ones. Thus the product phase assumes the form of compact individual nuclei distributed in the matrix of the reactant phase. These nuclei can grow in one of several geometric configurations, depending on the nature of the material, and the different configurations require different mathematical expressions.

Prout and Tompkins<sup>10</sup> have derived\* in an elegant manner an equation of general applicability for autocatalytic decomposition reactions which proceed by the growth of chains. When the maximum rate is observed at 50% decomposition their equation is

$$\frac{dx}{dt} = kx(1-x) \quad (1)$$

---

\* See Appendix for details of this derivation.

where  $dx/dt$  = rate of reaction

$x$  = fraction decomposed

$1 - x$  = fraction remaining

$k$  = specific rate constant

Integration and rearrangement of the equation leads to

$$\log \frac{x}{1-x} = k_1 t + c \quad (2)$$

where  $C = kt_{\max}$  and  $t_{\max}$  = time at which the rate is a maximum.

In general, two constants are required, one for the period of increasing rate and one for the period of decreasing rate. This is a result of the asymmetry of the  $x$ - $t$  curves. The asymmetry is said to result from collapse of the original crystal structure at the maximum rate of reduction. In several cases the collapse of crystal structure has been observed with a microscope.<sup>10</sup>

Since the maximum rate occurred at about 35% reduction in this study, it was necessary to add an empirical correction term to eq. 1 in order to make the equation valid from 0-100% reduction:

$$\frac{dx}{dt} = k(a + x)(1 - x) \quad (3)$$

where  $a = 0.3$  for the maximum rate at  $x = 0.35$ . Integration of eq. 3 gives

$$\log \frac{(0.3 + x)}{(1 - x)} = k_0 t \quad (4)$$

where  $k_0 = 1.89 k_1$ .

Prout and Tompkins explain adherence to eq. 2 by the formation of certain active nuclei which grow by a branched chain mechanism as a result of the reaction process. A constant number of nuclei is assumed to be originally present in the crystal. The majority of such nuclei are present on the surface, but some can be within the mass. In each case the nuclei are situated at lattice imperfections or grain boundaries. Since it has been shown that the lattice constant of a two-dimensional surface is about 5% less than that of the corresponding three-dimensional system,<sup>12</sup> lateral strains are consequently set up which are relieved by formation of Smekel cracks.<sup>10</sup> At the mouth of such cracks nucleus formation will be favored, from which the reaction can spread into the crystal along the cracks and product gases can find free passageway from the crystal. As the reaction proceeds, the inner surfaces of the crevices will be progressively covered with an array of product molecules of different dimensions. The new surface array will set up lateral strains leading ultimately to further cracking that is perpendicular to the inner surface, thus producing

further penetration into the crystal. This cracking phenomenon is repeated over and over, producing a series of branchings. The crevices produced by the branchings allow free passage of product gases out of the crystal. The branchings produce inhomogeneous deformation which may ultimately lead to mechanical disruption of the crystal. The reaction rate reaches a 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 decrease as interference among the growing chains steadily increases.

Supporting Data. Plots of the data according to eq. 3 show that this equation closely approximates the reduction process (Fig. 9). The equation is obeyed from 3 to 90% reduction. Only one constant is used to describe the whole reduction rather than one for acceleration and one for decay.<sup>10</sup> A slightly better fit of the data would be obtained if two constants were used, but in this case little would be added to the interpretation of the overall reduction process. One constant sufficiently approximates the data with only a slight amount of sinusoidal curvature about the straight line drawn through the experimental points. Computed values of the reaction constants for all data are given in Table 4.

Table 4. Values of  $k_0$  for Different Oxides

Oxide Preparation	$k_0, \text{min}^{-1}$			
	112°C	148°C	190°C	216°C
Calcination of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	0.00909	0.0389	0.212	0.48
Crushing of commercial-grade CuO wires	0.00498	0.026	0.0655	0.154
Calcination of $\text{Cu}(\text{OH})_2$	--	--	0.0415	--

Deviations from eq. 3 would be expected at the very beginning and at the end of the reaction since any small error in measurement of the fractions reduced will introduce large errors in the value of  $(0.3 + x)/(1 - x)$ . However, they will not be so great as the variations shown toward the end of the reduction. The equation is not obeyed beyond 90% reduction. It is likely that the remaining CuO is enclosed completely in the copper particles with little chance of growth of existing nuclei and that the reaction rate is controlled by either diffusion or surface area.

Although an empirical correction term is necessary for the Prout-Tompkins equation to describe a large part of the reduction process, it seems reasonable that the reduction occurs in a way closely approximating the mechanism envisioned above.

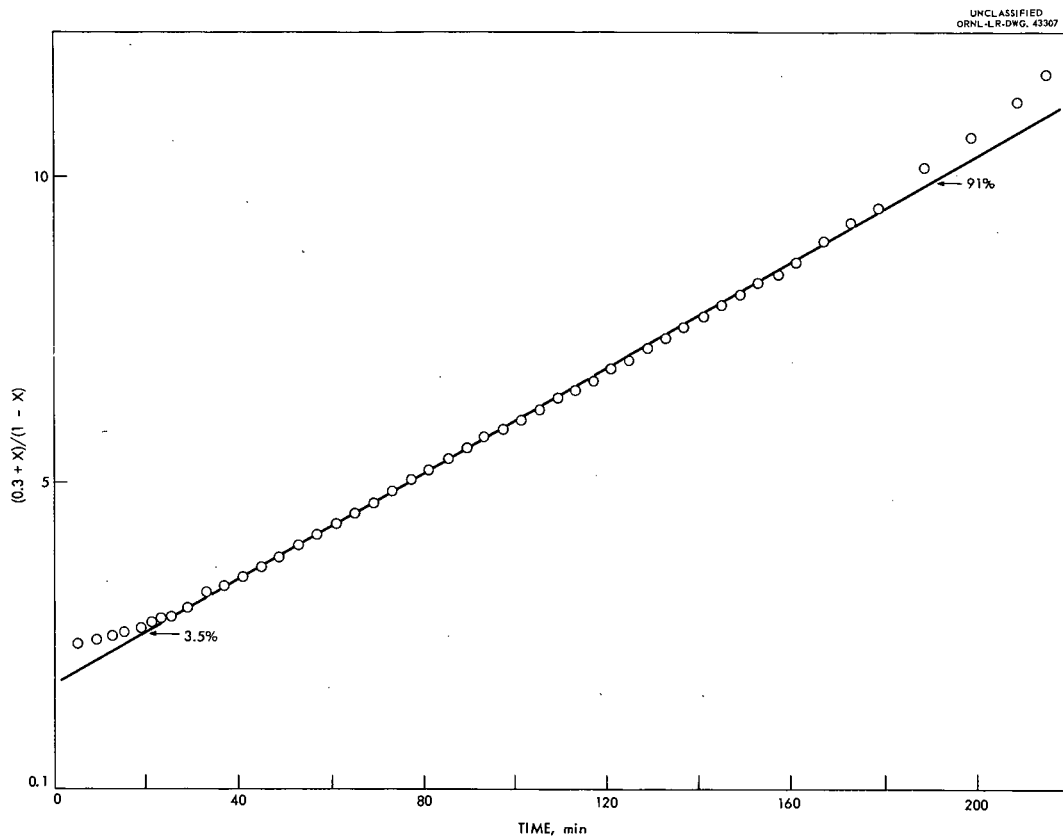


Fig. 9a. Test of kinetic equation. CuO prepared by calcining  $\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$ . Size  $< 44 \mu$ , temperature  $112^\circ\text{C}$ .

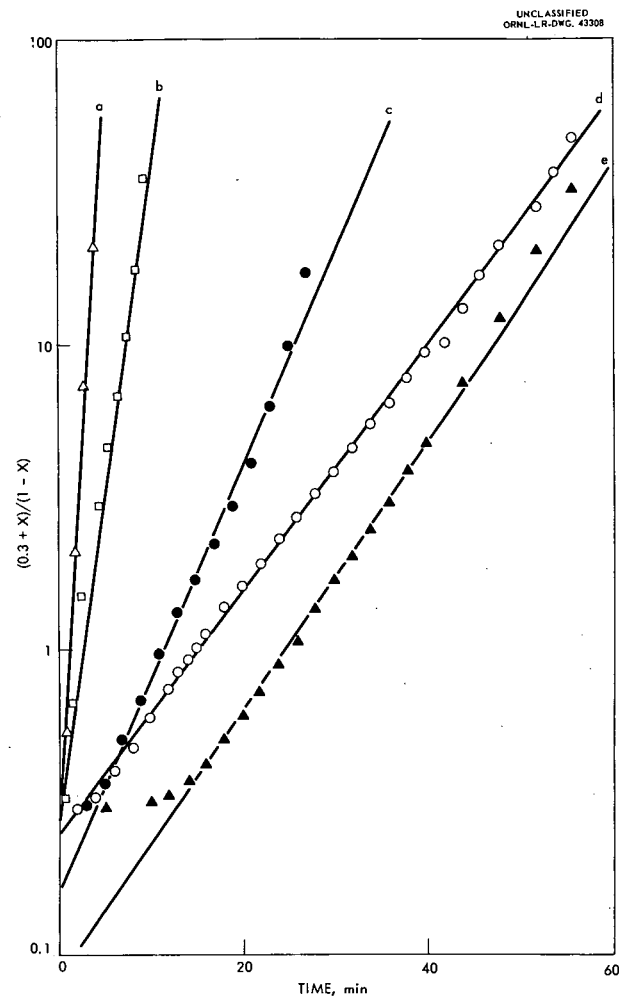


Fig. 9b. Test of kinetic equation. a, b, d: CuO prepared by calcining  $\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$ ,  $< 44 \mu$  size; respective reduction temperatures,  $216$ ,  $190$ , and  $148^\circ\text{C}$ . c: commercial grade CuO,  $< 44 \mu$  size; reduction temperature  $190^\circ\text{C}$ ; e: CuO prepared by calcining  $\text{Cu}(\text{OH})_2$ ;  $< 44 \mu$  size; reduction temperature  $190^\circ\text{C}$ .

Activation Energy. Arrhenius plots show an activation energy of 14.7 kcal for the oxide from calcination of copper nitrate and 12.3 kcal for the oxide from oxidized copper wires after crushing (Fig. 10). Activation energy for the reduction of CuO from calcining of  $\text{Cu}(\text{OH})_2$  was not determined since only one temperature was used. Within the accuracy of the plots ( $\pm 20\%$ ), the activation energy is considered to be the same for the two oxides used.

### 3.0 EXPERIMENTAL DETAILS

The experimental method consisted in measuring the weight loss of copper oxide as a function of time in an atmosphere of excess hydrogen by means of a semiautomatic recording thermobalance.

#### 3.1 Chemicals

Three types of CuO were used: a wire form of reagent-grade CuO from Mallinckrodt, CuO prepared by calcination of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , and CuO prepared by calcination of  $\text{Cu}(\text{OH})_2$  which was obtained by precipitation of a copper nitrate solution with ammonium hydroxide. All chemicals used in the preparations were reagent grade. Chemical analysis, x-ray diffraction analysis, and surface areas as determined by nitrogen adsorption are given in Table 5 for each oxide.

The preparation of CuO from  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  consisted in weighing 150 g of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  into a 250-ml evaporating dish, carefully heating on a hot plate until most of the water of hydration had been removed, and then heating in a muffle furnace at  $400^\circ\text{C}$  for 22 hr. The product was lightly crushed and screened. About 75% of the material was found to be  $< 44 \mu$ .

The preparation of CuO from  $\text{Cu}(\text{OH})_2$  consisted in preparing the hydroxide, calcining in a muffle furnace at  $400^\circ\text{C}$  for 20 hr, and crushing and screening the product. The  $\text{Cu}(\text{OH})_2$  was prepared by careful neutralization of 1 liter of 1 M  $\text{Cu}(\text{NO}_3)_2$  with 2 M  $\text{NH}_4\text{OH}$ , decanting the supernatant liquid, washing the precipitate by decantation with three 500-ml portions of deionized water, and transferring the precipitate to a suction filter and air drying under suction for 24 hr.

The wire-form CuO was crushed to 149-297 and to  $< 44 \mu$ . In each case the material was dried for 20 hr at  $600^\circ\text{C}$  under a stream of dry oxygen flowing at a rate of 1.6 liters/hr before use. The hydrogen, obtained as electrolytic hydrogen from the Southern Oxygen Company, was passed through a platinum-asbestos catalytic recombiner and then through a charcoal trap cooled by liquid nitrogen to remove any traces of oxygen and water. The catalytic recombiner was a commercial model (Baker and Co., Newark, N. J.) with a capacity of 5 ft<sup>3</sup>/hr at 50 psi.

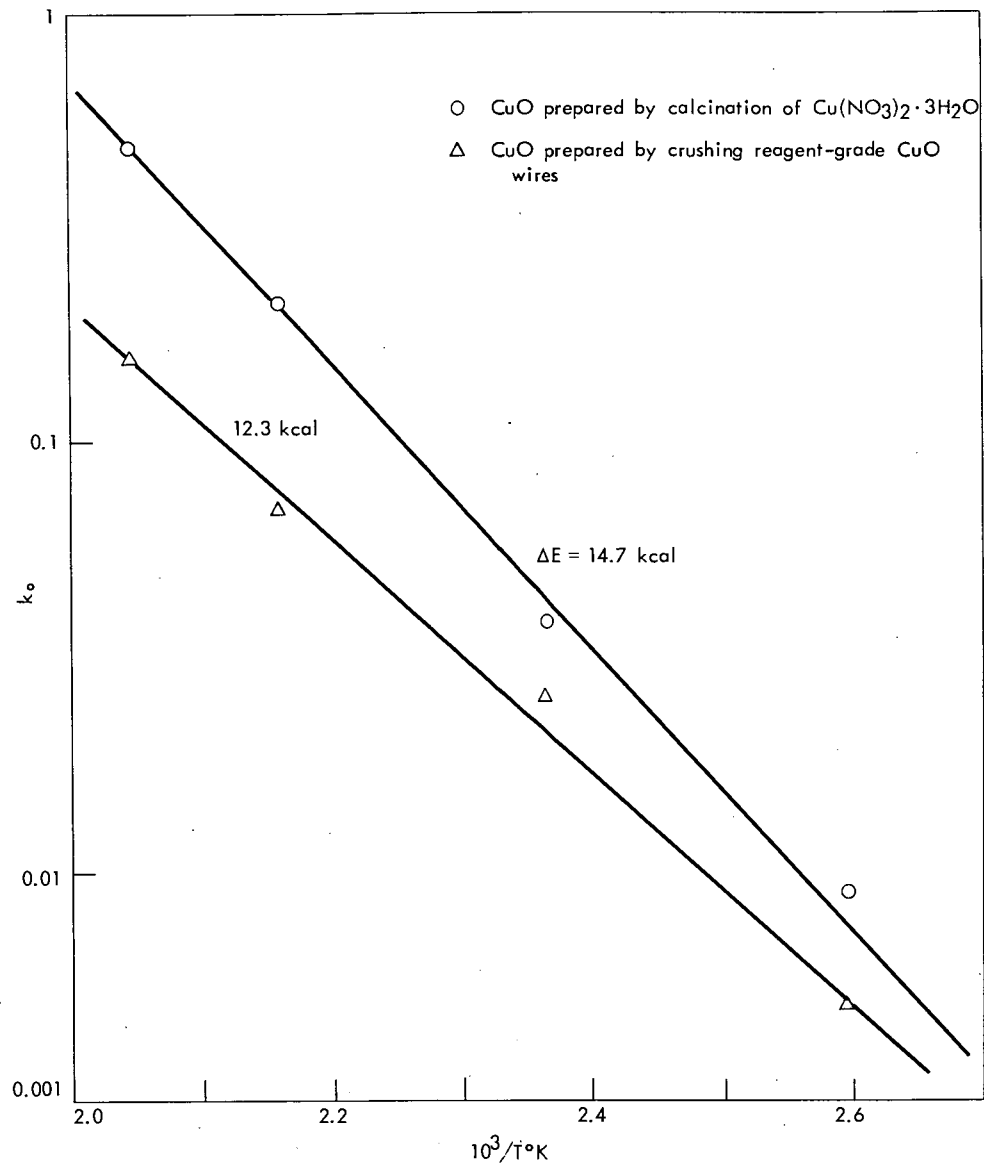


Fig. 10. Arrhenius plot rate constants.

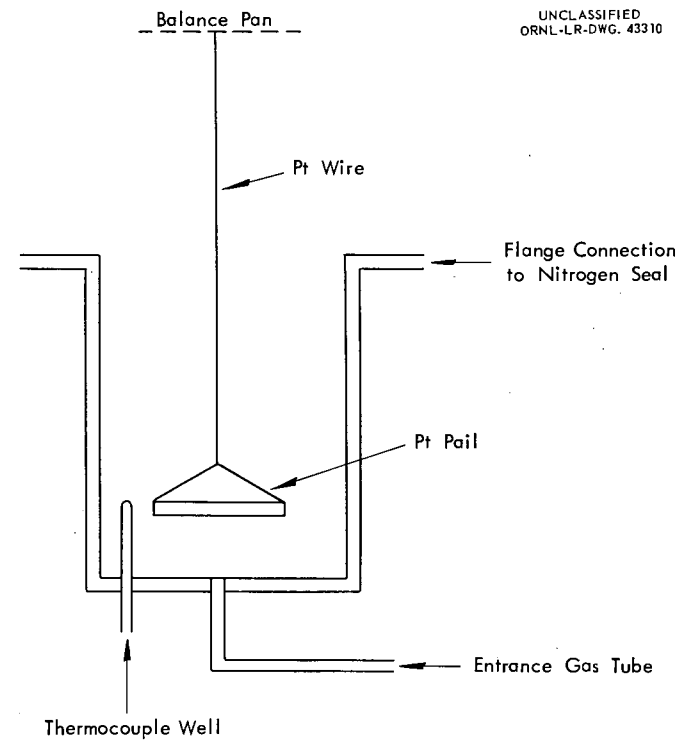


Fig. 11. Reduction chamber.

Table 5. Purity and Surface Areas of Copper Oxides Used

Oxide	Weight Loss by H <sub>2</sub> Reduction, % <sup>a</sup>	Surface Area, m <sup>2</sup> /g	Chemical <sup>b</sup> Analysis, % Cu	X-ray Diffraction Analysis <sup>c</sup>
Mallinckrodt reagent- grade CuO wires				
Uncrushed	16.5-16.8	0.050	83.70	Cu, Cu <sub>2</sub> O, and CuO present
Crushed to 149-297 μ	18.3-18.6	0.019	81.59	Cu <sub>2</sub> O and CuO present
Crushed to <44 μ	20.0-20.3	0.22	-	CuO present
Calcination of Cu(NO <sub>3</sub> ) <sub>3</sub> ·3H <sub>2</sub> O (<44 μ)	20.0-20.3	0.49	79.32	CuO present
Cu(OH) <sub>2</sub> (<44 μ)	20.0-20.3	0.43	-	CuO present

<sup>a</sup>Theoretical weight loss for pure CuO is 20.11%.

<sup>b</sup>Pure CuO is 79.89% copper.

<sup>c</sup>No other lines present.

### 3.2 Apparatus

The apparatus used has been described previously.<sup>13</sup> Basically, it consisted of a reduction chamber and a semiautomatic recording thermogravimetric balance. The reduction chamber was a cylindrical nickel vessel, 2 in. i.d., equipped with a helium seal through which the sample was suspended from the balance (Fig. 11). The reduction vessel was heated by a platinum-wound resistance furnace with temperature control by a platinum-rhodium thermocouple and a Pyrovane controller and recorder. The recorder was calibrated with a glass thermometer for different temperature settings. The Pyrovane controlled the temperature to  $\pm 20^\circ\text{C}$  and required 7-10 min to complete the temperature cycle. The sample was contained in a platinum pail 1 in. dia and 1/8 in. deep. The hydrogen was preheated by spiraling the entrance nickel tubing into 12 turns around the reaction vessel. The gas flow was measured by calibrated rotameters.

### 3.3 Operational Procedure

One-gram samples of CuO were weighed in the tared platinum pail on a conventional analytical balance. The pail was then hung on the Nichrome wire and lowered into the reduction chamber, and the recording balance set

for automatic control. Dry helium was admitted at 2.0 liters/min. The inert atmosphere was necessary when the temperature chamber was above room temperature to prevent formation of reducible nickel oxides. The furnace was then turned on, and, when the desired temperature had been obtained, an additional 1-2 hr was allowed for any weight loss due to adsorbed water. No decrease in weight was observed for any of the samples as the temperature was raised from ambient to the reduction temperature.

Hydrogen was then admitted to the reduction chamber, the helium was immediately shut off, and the final regulation was made to a flow rate of 2.0 liters/min. This whole operation required about 0.5 min. The volume of the reduction chamber and the associated gas lines was about 500 ml so that the helium gas was displaced in less than 1 min. The displacement time was also measured by the recording balance since an object weighs less in hydrogen than in helium. After reaction had stopped, helium was admitted to the reduction chamber, the hydrogen was shut off, and the sample was allowed to cool to room temperature under an atmosphere of flowing helium. The sample was then removed from the chamber and weighed in air on a different analytical balance as a check on the recording balance. The difference between the initial weight of the pail and sample and the weight observed after reduction in air should equal the weight loss recorded by the thermobalance.

The weight loss-vs-time curves obtained by the described technique were reproducible to  $\pm 5$  mg (Fig. 12).

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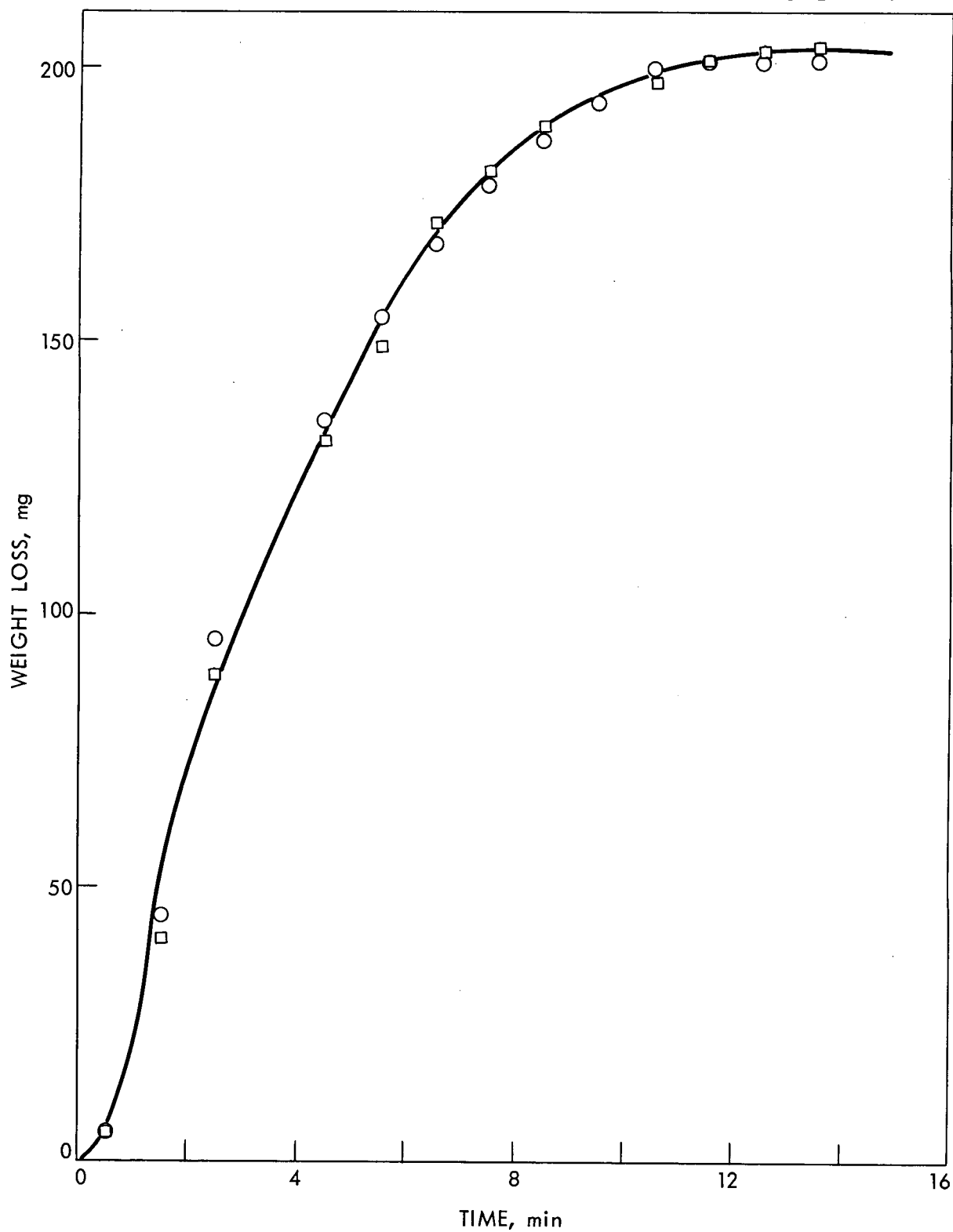


Fig. 12. Reproducibility of weight loss curves.  $\text{CuO}$ , 1.00 g, particle size  $< 44 \mu$ , prepared by calcination of  $\text{Cu}(\text{NO}_3) \cdot 3\text{H}_2\text{O}$ ; hydrogen flow rate, 2.0 liters/min; temperature,  $190^\circ\text{C}$ .

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## 5.0 APPENDIX

### 5.1 Derivation of Prout-Tompkins Equation

The growth of nuclei is imagined to take place according to the equation

$$\frac{dn}{dt} = k_1 N_0 + (k_3 - k_4) N \quad (1)$$

where  $dn/dt$  = rate of formation of nuclei

$k_1$  = nucleation rate constant

$N_0$  = initial number of potential nuclei-forming sites

$k_3$  = rate constant for branching of nuclei

$k_4$  = rate constant for termination of branching nuclei

$N$  = total number of active nuclei at time  $t$

If the nucleation rate constant is very large, the potential nucleus-forming sites are soon exhausted and eq. 1 is replaced by

$$\frac{dn}{dt} = (k_3 - k_4) N \quad (2)$$

Equation 2 is valid after the time necessary to exhaust the  $N_0$  sites. Alternatively, if  $k_1$  is small and the formation of new nuclei still persists, the second term soon becomes larger than the first and eq. 2 is a good approximation of the rate of nucleus formation.

The rate of decomposition,  $dx/dt$ , of the solid to its products may reasonably be supposed to be proportional to the number of active nuclei present:

$$\frac{dx}{dt} = k' N \quad (3)$$

Equations 2 and 3 cannot be integrated directly as they stand to yield  $x$  as some function of  $t$  unless the functional dependence of  $k_3$  and  $k_4$  on  $x$  is known. In the absence of any general theory which gives  $k_3$  and  $k_4$  as a function of  $x$ , further assumptions are necessary. Prout and Tompkins were able to show that, for decomposition in which the maximum decomposition rate occurs at  $x = 0.5$ , the approximate boundary conditions are

$$k_4 = k_3 \frac{x}{x_1} \quad (4)$$

where  $x_1$  = fraction decomposed at point of inflection.

Equation 4 results from eq. 2, since at  $t = 0$  and  $x = 0$ ,  $k_4$  must be zero since interference will be nil, while at  $t = T_1$ ,  $x = x_1$ ,  $dx/dt$  passes through a maximum and  $k_3 = k_4$ . If it is assumed that  $k_3$  is independent of  $x$ , eqs. 1 and 2 may be integrated. From eqs. 2 and 4,

$$\frac{dn}{dt} = k_3 \left(1 - \frac{x}{x_1}\right) N \quad (5)$$

From eqs. 3 and 5,

$$\frac{dn}{dx} = k \left(1 - \frac{x}{x_1}\right) \quad (6)$$

where  $k = k_3/k'$ . On integration eq. 6 yields

$$N = k \left(x - \frac{x^2}{x_1}\right) \quad (7)$$

which changes to

$$\frac{dx}{dt} = k_3 x \left(1 - \frac{x}{x_1}\right) \quad (8)$$

when decomposition occurs at  $x = 0.5$ . Integration of eq. 8 yields

$$\log \frac{x}{1-x} = k_3 t + C \quad (9)$$

For the present work the maximum occurred at  $x = 0.35$ . Substitution in eq. 7 gives

$$N = kx \left(\frac{0.7 - x}{0.7}\right) \quad (10)$$

which would mean that at 70% reacted no active nuclei would be present. Thus there must be an integration constant associated with eq. 7 for the present case. With the constant of integration, I equals 0.3 k, eq. 7 becomes

$$N = k \left(\frac{0.3 + 0.7 x - x^2}{0.7}\right) \quad (11)$$

Rearrangement gives

$$N = k \frac{(0.3 + x)(1 - x)}{0.7} \quad (12)$$

Substituting for N in eq. 3 gives

$$\frac{dx}{dt} = k_3 \frac{(0.3 + x)(1 - x)}{0.7} \quad (13)$$

Integration of this equation gives

$$\log \frac{(0.3 + x)}{(1 - x)} = k_0 t + C' \quad (14)$$

$$\text{where } k_0 = \frac{1.3}{0.7} k_3$$

$$C' = \frac{1.3}{0.7} C$$

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