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REDUCTION OF CUPRIC OXIDE BY HYDROGEN.
II. CONVERSION OF HYDROGEN TO
WATER OVER FIXED BEDS

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Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section B

REDUCTION OF CUPRIC OXIDE BY HYDROGEN. II. CONVERSION OF
HYDROGEN TO WATER OVER FIXED BEDS

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DATE ISSUED

JAN 29 1960

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ABSTRACT

The conversion of H_2 to H_2O by reduction of CuO in fixed beds was quite rapid at $300^\circ C$. Residence times required for 99% conversion in a 1-in.-dia bed were 0.6 and 1.2 sec for 30% hydrogen-70% argon and 10% hydrogen-90% argon mixtures, respectively, at a total gas flow of 1 liter/min. The CuO used was 25-mil-dia wires with a surface area of $0.019 \text{ m}^2/\text{g}$. The residence time required for a given value of conversion decreased about 10% when the total flow rate was increased from 1 to 1.7 liters/min, which indicates that the reduction is mass-transfer controlled to a slight extent under the experimental conditions used.

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1.0 INTRODUCTION

The purpose of this investigation was to determine the conditions under which hydrogen can be quantitatively recovered from mixtures of gases by oxidation over fixed beds of CuO. The recovery of hydrogen from hydrogen-argon mixtures was studied initially, with the plan that the specific effects of chemically active diluent gases, such as O₂ and CO, would be determined later.

A convenient way to recover hydrogen is to convert it to water and condense the water vapor. The two most widely known methods of converting hydrogen to water are direct combination of H₂ and O₂ at low temperatures over a catalytic surface such as platinized asbestos and bed reduction of CuO at temperatures from 200 to 400°C. The bed reduction of copper oxide was chosen as the possibility with the best chance of success since catalytic surfaces for H₂ and O₂ recombination are easily poisoned by impurities in the gas. The effects of temperature and of particle size were confirmed by thermogravimetric studies.

Although the literature¹⁻⁸ contains a variety of data on the reduction of CuO, it is necessary to have information on several parameters in order to design a plant-scale facility. Parameters included in this study were mesh size of copper oxide, hydrogen concentration in the inlet gas stream, temperature, flow rate, and bed length.

The authors express sincere appreciation to R. A. Suehrstedt, R. H. Wick, and D. W. Jeffrey of the Massachusetts Institute of Technology Engineering Practice School who performed a large portion of the experimental work and who made many helpful suggestions. The authors also acknowledge the help of the groups headed by W. R. Laing, J. R. Sites, and R. L. Sherman of the Analytical Chemistry Division who made surface area determinations, gas analyses, and x-ray identifications, respectively.

2.0 DISCUSSION OF RESULTS

The conversion of H₂ to H₂O on a fixed bed of CuO increased with increasing bed length, temperature, hydrogen/argon ratio and decreasing mesh size of CuO. Bed residence time of the gas phase was found to be a useful comparative parameter. Thermodynamic data were taken from the literature to show theoretical conversion factors and the heat of reaction.

2.1 Temperature and Mesh Size

The percentage conversion of H₂ to H₂O increased with temperature in both fixed bed and thermogravimetric (Figs. 1 and 2) studies (see Sect. 3.0) and decreased with mesh size of the CuO (Fig. 3). Reduction was rapid at temperatures approaching 300°C. The thermogravimetric data

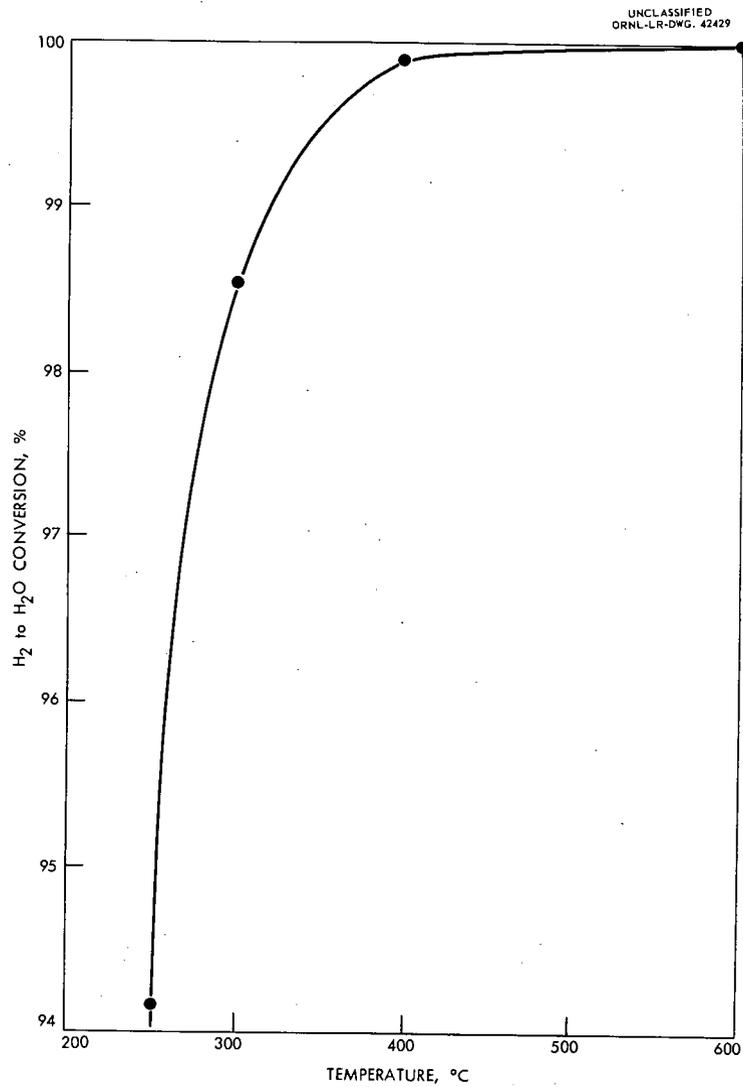


Fig. 1. Effect of temperature on oxidation of hydrogen by a fixed bed of CuO. Bed dimensions: 1 in. dia, 6 in. long. 25-mil-dia CuO wire, 0.019 m²/g. Reduction gas: 66% H₂ - 33% argon, 150 cc/min.

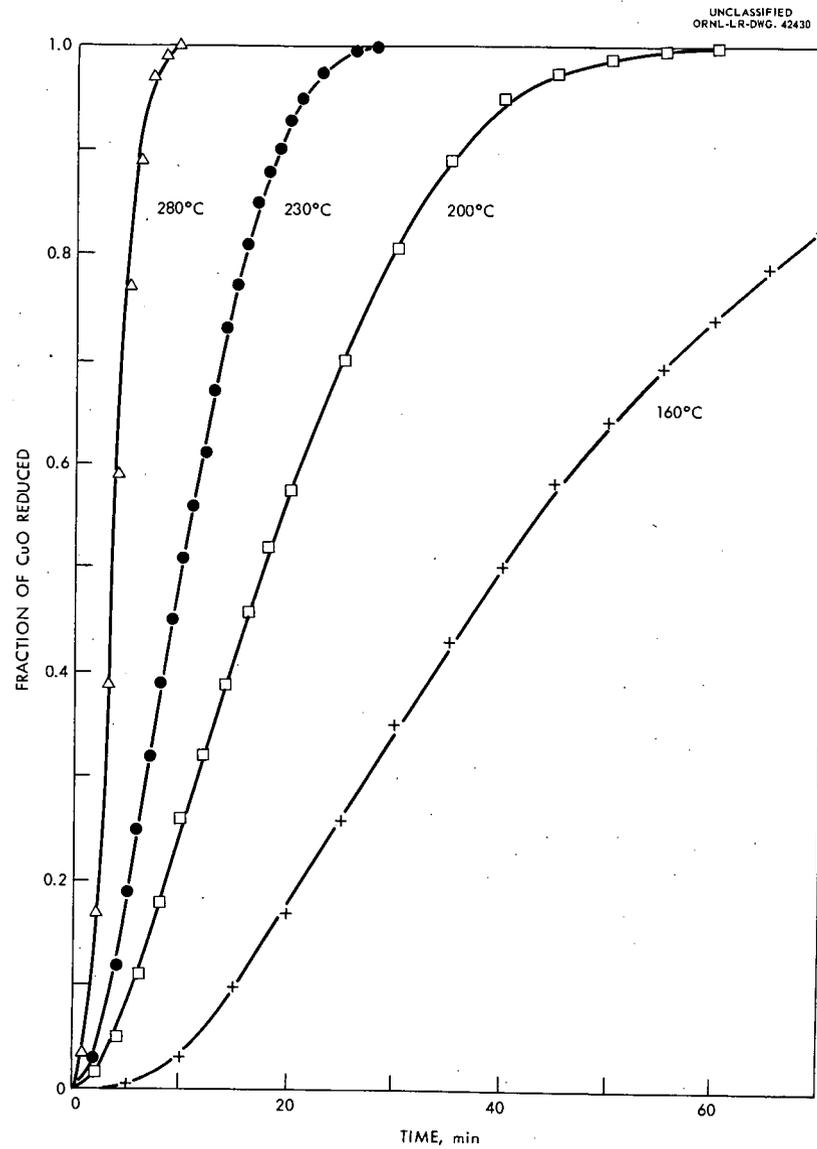


Fig. 2. Effect of temperature on the CuO-H₂ reaction. Thermogravimetric study. H₂, 2000 cc/min; 1.00 g of wire-form CuO (25 mil dia), 0.019 m²/g.

are plotted as weight fraction of CuO reduced vs time since the total reduction time was independent of the mass of the oxide. Little appeared to be gained by crushing the commercial wire-form oxide, since at 280°C the reduction rate of the uncrushed oxide was adequate. Theoretical conversion was not achieved in a CuO bed 6 in. long and 1 in. dia at any of the temperatures investigated (Figs. 1 and 4).

2.2 Bed Length

The percentage conversion of H₂ increased as the bed length was increased from 0.25 to 1.25 in. (Fig. 5). Varying the hydrogen concentration from 1 to 30% did not change the characteristics of the reduction shown by the curves in Fig. 5 for 30%. Complete data are tabulated in the appendix (Sects. 5.1 and 5.2).

In general, the reduction curves show an induction period, then an increase in reduction rate to a maximum, and finally a slow decline. These curves are of the general type that would be predicted from previous kinetic studies.¹⁻⁸ The reduction behavior can be explained by reaction at active centers on the copper oxide followed by rapid growth of the active nuclei as a result of the initial reaction. Thus, active centers are first multiplied at the bed inlet where hydrogen initially meets the copper oxide. Because of the rapid growth of nuclei, active centers are soon being created at a rate such that a sufficient number are available to remove most of the hydrogen at the bed inlet before it progresses very far down the bed. Under such conditions the rate of conversion is nearly constant. Finally, as the active zone approaches the end of the bed, the number of active centers begins to decrease rapidly and the conversion rate drops abruptly. The length of curve corresponding to a near-constant reduction rate should increase with increasing bed length according to this theory, and this was observed experimentally. Also, visual observation showed most of the reaction taking place at the bed entrance and a sharp band between the copper and the copper oxide. There were a few scattered specks of copper in the CuO about 1 mm from the CuO-Cu boundary.

In an actual process the induction period could be eliminated by pre-treating the bed with hydrogen. Hydrogen would be passed through the bed at reduction temperature until water was produced abundantly and then the hydrogen would be shut off. The bed would be flushed free of H₂ and H₂O by an inert gas and stored under inert gas for future use. Several copper oxide beds were treated in this way and stored overnight under argon. The following day the beds were immediately reactive to hydrogen, showing no evidence of an induction period.

2.3 Residence Time

The percentage conversion of hydrogen increased with residence time of the gas stream in the void volume of the CuO bed at 300°C (Fig. 6). The points on the curve are accurate to ±10%, and were calculated from

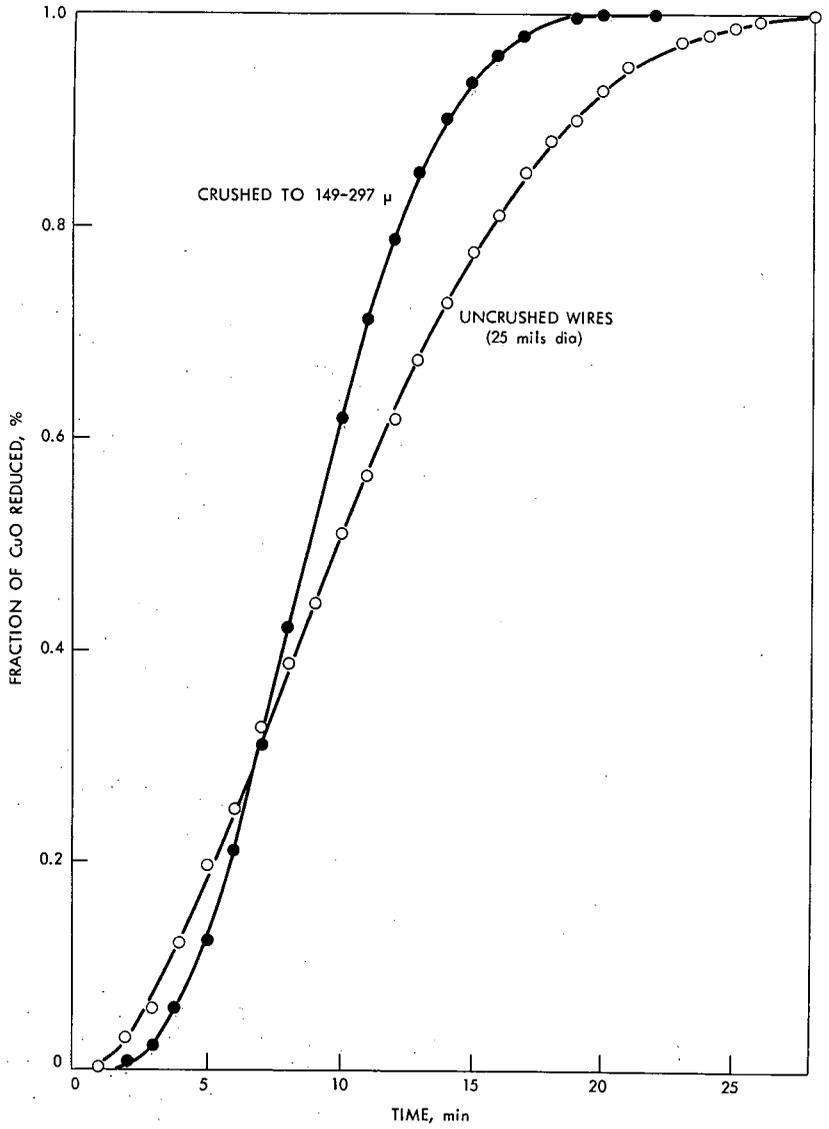


Fig. 3. Effect of particle size on the CuO-H_2 reaction. Thermogravimetric study. Temperature 200°C ; H_2 , 2000 cc/min; 1.00 g of CuO .

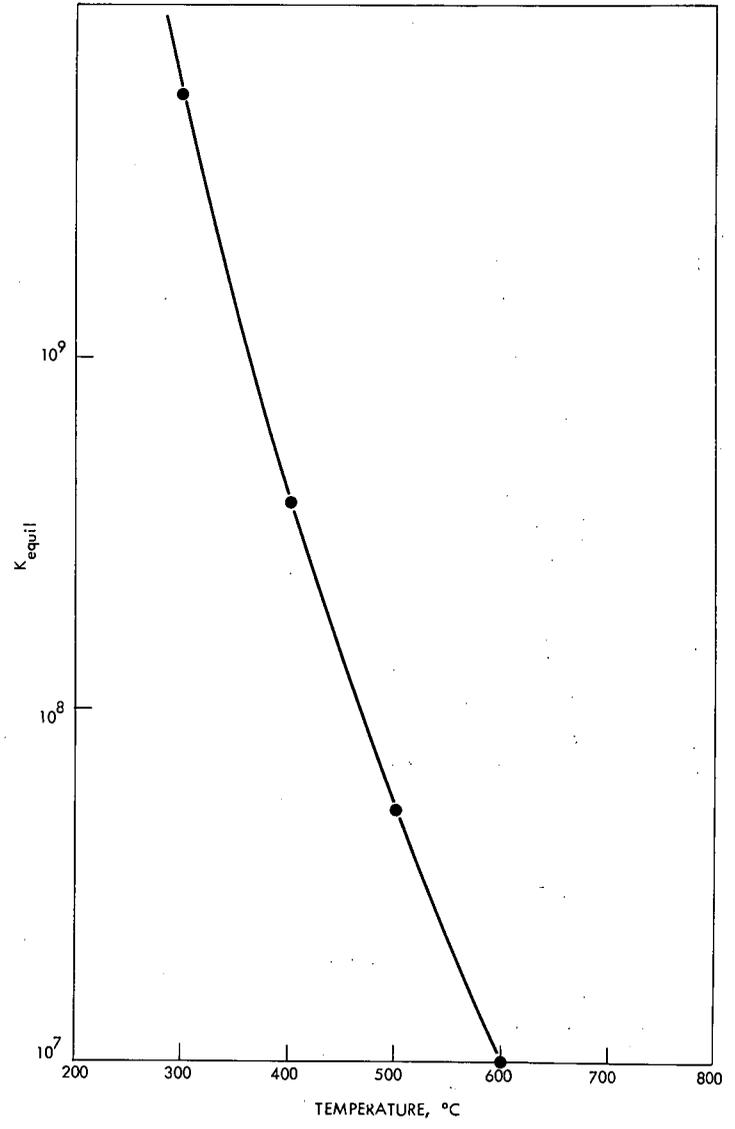


Fig. 4. Thermodynamic equilibrium constants for the reaction $\text{CuO} + \text{H}_2 \rightleftharpoons \text{Cu} + \text{H}_2\text{O}$. Data from Dushman's tabulation.¹⁰ $K = P_{\text{H}_2\text{O}}/P_{\text{H}_2}$; ΔH at $25^\circ\text{C} = 22.94$ kcal.

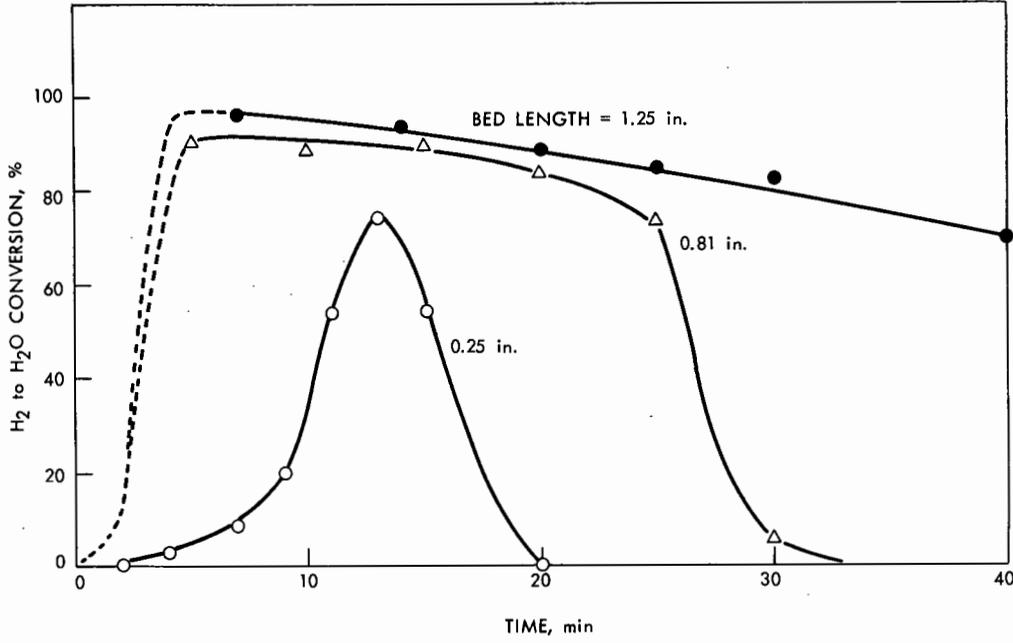


Fig. 5. Effect of bed length on conversion of hydrogen to water. Reduction gas: 30% H₂ - 70% argon, 1200 cc/min. Temperature 300°C; bed dia 1 in.; 34 g of Cu per inch; 25-mil-dia CuO wires, 0.019 m²/g.

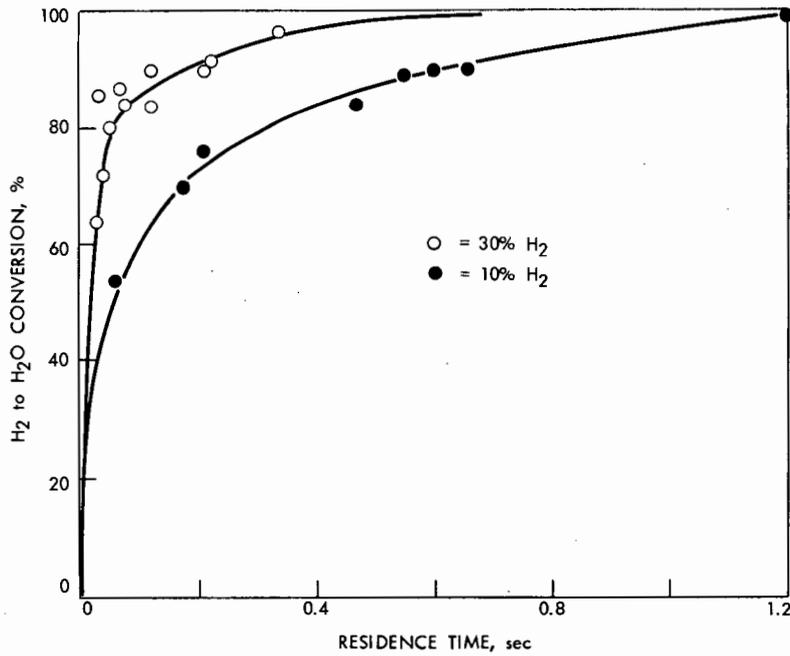


Fig. 6. Effect of residence time in the conversion of hydrogen to water in a fixed bed of CuO. Temperature 300°C. Bed dia, 1 in. 25-mil-dia CuO wire, 0.019 m²/g.

the peak values and constant conversion sections of the previously determined percentage conversion vs time curves. The details of the calculations are shown in the appendix (Sect. 5.2). Relatively short residence times were required for 99% conversion, about 1.2 and 0.6 sec for 10 and 30% H₂ concentrations, respectively. For long residence times the curves approach 100% conversion asymptotically. Thus the residence time required for 99% conversion is about twice that for 90% conversion.

One experimental determination was made with 1% H₂ in order to observe the order-of-magnitude effect of a fairly low inlet H₂ concentration. With 0.4 sec residence time and a temperature of 300°C, conversion was not very different from that with 10% H₂:

Inlet H ₂ Concentration, %	H ₂ Conversion, %
1	76
10	84
30	97

This indicates that extremely long residence times will not be required for the conversion of moderately dilute H₂ streams.

The flow rate had a minor effect on H₂ conversion. Increasing the total flow rate of the 10% H₂ gas stream to 1670 cc/min increased the conversion 15% above that at 1000 cc/min. This increase, which is slightly greater than the experimental error (+ 10%), indicates that the reduction is to a slight degree mass-transfer controlled under these conditions.

3.0 EXPERIMENTAL

3.1 Fixed Bed Studies

The experimental apparatus is shown schematically in Fig. 7. Hydrogen and argon were metered through calibrated rotameters and mixed in a Y tube. When the flow rate reached steady state, the flow was diverted through a vertically supported silica reaction tube containing a packed bed of CuO of known weight and length. The reaction tube was 18 in. long and 15/16 in. i.d. Heating was by a split-tube electric furnace mounted vertically around the reaction tube. After leaving the reaction tube, the gases were passed through a drying bulb containing indicating Drierite before entering the exit sample bottles. Inlet and exit gas samples were taken in 100- or 300-cc sample bottles by appropriate stopcock arrangements. Sampling times varied from 2 to 45 min depending on the bed length and inlet hydrogen concentrations.

The inlet gas was preheated in the upper part of the reduction tube with electrical heating tape. Wads of glass wool were placed at three equally spaced points along the preheated zone to induce turbulence and thus assure complete mixing and uniform temperature. The inlet gas temperature was measured by a glass-encased thermocouple placed in the glass

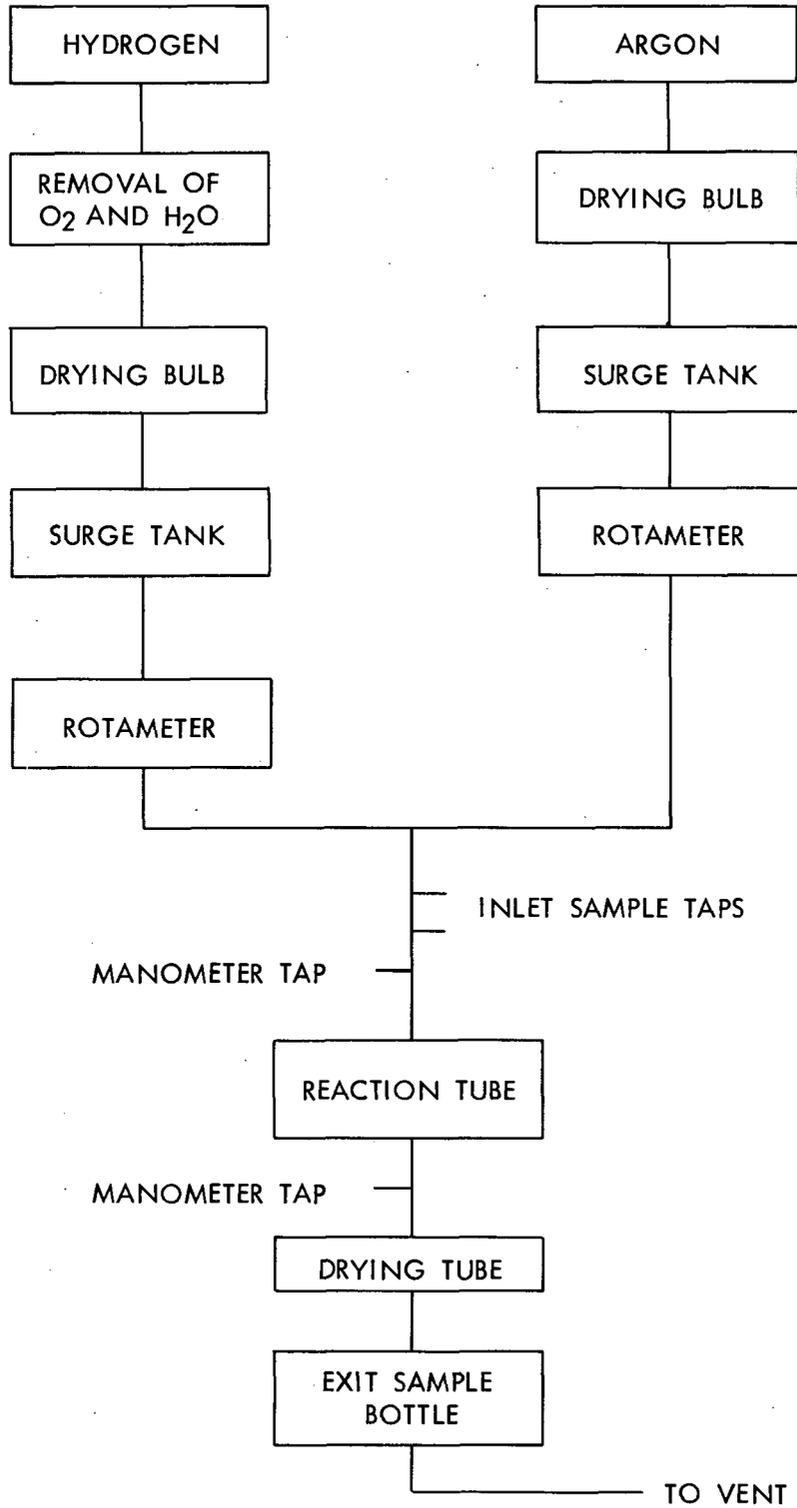


Fig. 7. Block diagram of apparatus.

wool packing above the bed. The temperature of the furnace was controlled by an auxiliary thermocouple placed against the outside of the reaction tube at the bed-gas interface.

In order to achieve a cylindrical bed of CuO with well-defined edges, approximately 1 in. of sand was placed on a glass wool support in the tube. The copper oxide was placed on the sand. Pressure taps were located at points immediately before and after the bed, and the pressures at these points were measured by open-end manometers. The manometer fluid was Meriam Red Oil, sp. gr. 0.827. The pressure drop across the bed was approximately 5 cm of the oil and was independent of the bed length.

The copper oxide was obtained from Mallinckrodt as the reagent grade wire form and was used as obtained. The wires were about 20 mils dia and their length varied from about 1 to 10 mm. Chemical analysis showed 83.8% Cu. The only impurities found by qualitative x-ray diffraction analysis were metallic copper and Cu₂O. The nitrogen adsorption surface area of the material was 0.019 m²/g.

Electrolytic hydrogen was used and was purified of O₂ and H₂O by being passed through a Deoxo unit and a Drierite bulb before entering the reaction tube. The argon received only the drying treatment.

3.2 Thermogravimetric Studies

The experimental technique and apparatus have been discussed elsewhere.⁸⁻⁹ One-gram samples of CuO and a hydrogen flow rate of 2000 cc/min were used.

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5.0 APPENDIX

5.1 Experimental Parameters

Run No.	Bed Length, in.	Gas Flow Rate, cc/min	H ₂ Concentration, %	Wt of H ₂ O Formed, g
1	3.3	1000	10	4.6656
2	0.75	1000	10	4.3183
3	0.375	1200	30	2.326
4	0.91	1200	30	4.8761
5	0.25	1200	30	1.2162
6	0.25	1000	10	0.9107
7	1.25	1200	30	7.6523
8	1.75	1000	10	4.6318
9	1.5	1670	10	7.2086
10	1.2	1000	1	1.1936

All experiments were carried out at 300°C.

5.3 Sample Calculations of Residence Time

For Run 2:

Pure CuO = 5.94 g/cc

Wt of CuO in bed = 25.4 g

Volume of CuO = $25.4/5.94 = 4.28$ cc

Bulk volume of bed = $(1.90)(3.14)(1.19)^2 = 8.48$ cc

Void volume = 4.20 cc

Residence time = $4.20/1000 = 0.00420$ min = 0.252 sec (based on total unreactive bed)

To get the residence time at any time the percentage conversion—time curves are graphically integrated to find the total quantity of H₂ reacted. The percentage of the bed that is reacted can be computed from the hydrogen consumed. The residence time is given by the product of the fraction of the bed unreacted and the residence time for the initial unreacted bed.

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