[Contribution from the Department of Chemistry, Temple University]

THE REDUCTION OF MIXED OXIDES. COPPER AND ZINC OXIDES

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To explain in part the fact that the first metallic age in history was the bronze age, H. G. Wells[1] states, "Bronze is not only harder than copper, but the mixture of tin and copper is more fusible and easier to reduce." It would be interesting to determine the source of his information on this latter point. Various patents have been issued for catalysts made from the reduction of an intimate mixture of different oxides. Taylor[2] gives an instance of a copper-zinc catalyst[3] made by the reduction of a copper oxide-zinc oxide mixture, in which it is indicated that some zinc is reduced at a lower temperature than is usual for the pure substance.

This investigation was taken up to determine whether the zinc was actually reduced at a low temperature and, if possible, to determine the extent of the reduction.

Two substances were used. One, which will be designated as No. 1, was pure cuprous oxide. It was made by fusing the oxide, cooling the melt and breaking it into small granules. These were sifted to uniform size and those about the size of small grains of wheat were taken. The other, which will be designated as No. 2, was a mixture of zinc and cuprous oxides made in the same way.

Analysis of the Oxides

The sample taken was dissolved in nitric acid. When solution was complete, sulfuric acid was added and the nitric acid driven off. The copper was then determined as metallic copper deposited on a rotating platinum cathode. When the copper was removed, the solution was evaporated to small bulk and neutralized with ammonium hydroxide. A small amount of ferric hydroxide precipitated in the case of No. 2. This was filtered from the solution and determined as ferric oxide. The zinc was then determined as zinc ammonium phosphate.

Table I

Analysis of Oxide No. 1

Wt. of sample, g.	Wt. of copper, g.		Copper, %
0.5165	0.4575		88.58
0.5028	0.4457		88.64
		Av.	88.61[a]

[a] 88.82% of copper in pure cuprous oxide.

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[1] Wells, "The Outline of History," Chap. 11, paragraph 5.

[2] Taylor, *J. Phys. Chem.*, **30**, 154 (1926).

[3] French pat. 580,905.

TABLE II

ANALYSIS OF OXIDE MIXTURE NO. 2

Wt. of sample, g.	Wt. of copper, g.	Copper, %
0.5021	0.4074	81.14
0.5003	0.4073	81.41
	Av.	81.28

$ZnNH_4PO_4$, g.	Zn, %	Fe_2O_3, g.	Fe, %
0.0807	6.17	....	..
....	..	0.0018	0.25

Reduction of the Oxides

The reduction tube was made of glass tubing of medium thickness with a bulb in the center for the oxide. A plug of glass wool kept the catalyst in position and prevented it from falling into the tube below the bulb and thus obstructing the flow of gases. A thermometer was imbedded in the oxide so that the temperature recorded was that of the mass itself.

The heater consisted of a piece of Pyrex tubing of large internal diameter, wrapped with a thin layer of asbestos paper, followed by a coil of Nichrome wire which was then covered with thick sheets of asbestos paper. This was connected in series with a variable resistance by means of which the temperature in the tube could be regulated at will. When the reduction tube was in place, the bulb containing the oxide was about 15 cm. from each end of the heater. It was held in position by two asbestos plugs which also closed the heater and enabled the temperature to be regulated more closely. The temperature varied from 290 to 305°. It was necessary to hold the temperature at 290° during the early stages of the reduction, for the heat evolved as the reduction proceeded caused an increase in the temperature of the oxide.

The hydrogen was ordinary cylinder hydrogen which was passed over heated copper turnings in a quartz tube, then dried by passing through a calcium chloride tower. It was then led into the reduction tube. The effluent gases passed through a U-shaped calcium chloride tube which was protected from the air by a smaller tube filled with calcium chloride. From this smaller tube the gases passed to the air. The calcium chloride tubes were filled with hydrogen before weighing, and the whole apparatus was filled with hydrogen before starting the heater. The time for complete reduction was six hours.

TABLE III

REDUCTION OF NO. 1

Wt. of sample, g.	H_2O, g.	O_2, %
5.0027	0.6514	11.52

From the analysis of this oxide given in Table I, the percentage of oxygen by difference was 11.39.

TABLE IV

REDUCTION OF No. 2

Wt. of sample, g.	H_2O, g.		O_2, %
5.0026	0.6695		11.90
5.0013	0.6727		11.96
		Av.	11.93

From the analysis of this oxide mixture given in Table II we calculate the following: 81.28% of copper corresponds to 91.51% of cuprous oxide, to 10.23% of oxygen; 6.17% of zinc corresponds to 7.68% of zinc oxide, to 1.51% of oxygen; 0.25% of iron corresponds to 0.36% of ferric oxide, to 0.11% of oxygen; total, 11.84% of oxygen.

Discussion of the Results

From the above data it is certain that at 300° the zinc oxide in such a mixture is completely reduced. We have in this case a zinc catalyst on a support made of a copper catalyst, and the zinc catalyst has been reduced at a temperature much below that which could have been used if the zinc were the sole metallic oxide present. If this result is perfectly general, that is, if the presence of another oxide lowers the temperature of reduction, it offers an important method for the preparation of very active catalysts. Another case which can be offered in support of this view is that of copper and nickel oxides, which has been studied by Armstrong and Hilditch.[4] Further work on this point is contemplated, using the oxides of metals more difficult to reduce than zinc.

It is hazardous to make a general explanation for any phenomenon from a single example, but several explanations suggest themselves. Cuprous oxide occurs in nature as cuprite, which belongs to the isometric system, and zinc oxide occurs as zincite, which is in the hexagonal system. When the melt containing both is cooled, the presence of one would prevent the units in the lattice structure of the other from arranging themselves in the normal way. This would cause the forces between the units in the lattice structure to be altered and the mixture would be expected to show a difference in its reaction toward hydrogen when compared with either substance in the pure state.

Taylor, in a private communication, suggests that if the substance is a mixed lattice of the two oxides, under these circumstances the oxide ion cannot be regarded as belonging to any particular metal ion. The oxide ion, therefore, shares the properties of the two individual oxides and is intermediate between the two. It is hoped that further work, using different proportions of the same oxides and mixtures of different oxides, will bring forth an explanation of this point.

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[4] Armstrong and Hilditch, *Proc. Roy. Soc.*, (London) **102A**, 27 (1922).

The writer wishes to thank Dr. H. S. Taylor for initiating and sustaining this work with his helpful suggestions.

Summary

It has been shown that in a mixture of zinc and copper oxides the zinc oxide is completely reduced with hydrogen at 300°.

An explanation of the reduction at this relatively low temperature has been offered.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE ACTIVITY COEFFICIENT OF HYDROGEN CHLORIDE IN AQUEOUS SOLUTIONS WITH BARIUM AND LANTHANUM CHLORIDES AT 25°[1]

BY MERLE RANDALL AND GERALD F. BRECKENRIDGE

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In this paper are given the results of three series of measurements of the electromotive force of the hydrogen-calomel cell, with hydrochloric acid and with mixtures of hydrogen and barium chlorides and hydrogen and lanthanum chlorides, respectively. The concentration of both chlorides in each series was varied over wide limits.

Other investigators have measured similar cells, using hydrochloric acid at fixed concentrations, 0.001, 0.01, or 0.1 *M*, but the results of the measurements do not permit an adequate test of the principle of the ionic strength, in solutions of constant ionic strength, when the proportion of the acid is varied.[2] Loomis, Essex and Meacham[3] used mixtures of hydrogen chloride and potassium chloride at a total constant molality of chloride ion of 0.1 *M*, but their results are inconclusive. Since the presentation of this work Güntelberg[4] has published measurements with the hydrogen-silver chloride cell and mixtures of hydrogen chloride with potassium, sodium, cesium and lithium chlorides at 0.1 *M* total chloride ion concentration.

Harned and Åkerlöf[5] have also published measurements of the hydrogen-calomel cell with mixtures of lithium, sodium and potassium chlorides at constant molalities of 0.1, 1 and 3 *M*.

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[1] Presented at the Symposium on Strong Electrolytes, Los Angeles Meeting of the American Chemical Society, August 4, 1925.

[2] For a discussion of the methods of calculating activity coefficients in mixtures, and discussion of the older work, see (a) Lewis and Randall, THIS JOURNAL, **43,** 1112 (1921); (b) "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923,** Chap. XXVIII. Also (c) Harned and Brumbaugh, THIS JOURNAL, **44,** 2729 (1922). (d) Harned, *ibid.*, **48,** 326 (1926).

[3] Loomis, Essex and Meacham, *ibid.*, **39,** 1133 (1917).

[4] Güntelberg, *Z. physik. Chem.*, **123,** 199 (1926).

[5] Harned and Åkerlöf, *Physik. Z.*, **27,** 411 (1927).