50. *The Solubility of Cupric Oxide in Salt Solutions.*

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Berzelius (" Traité de Chimie," 1846, 2nd French Edtn., II, 528) observed that cupric oxide does not dissolve in aqueous ammonia unless some salt, *e.g.*, ammonium carbonate, is present. A similar phenomenon has been observed when certain aqueous salt solutions are employed instead of ammonia. Copper oxide, in aqueous sodium citrate or oxalate (the anions of both these salts possess high co-ordinating tendencies), contained in a flask open to the atmosphere, dissolved relatively rapidly, whereas when a stoppered flask was used only a small amount of oxide dissolved even after considerable time. Further experiments showed that the presence of carbon dioxide was necessary for the solution of the oxide to occur to any appreciable extent. The following table shows the results obtained for the rate of solution of cupric oxide, under arbitrarily fixed conditions, in the following solutions : (A) 0·2*N*-sodium citrate, (B) 0·2*N*-sodium citrate + 0·02*N*-sodium hydroxide, (C) 0·2*N*-sodium citrate + 0·02*N*-sodium hydrogen carbonate, (D) 0·54*N*-ammonium hydroxide, (E) 0·54*N*-ammonium hydroxide + 0·02*N*-ammonium carbonate, (F) 0·54*N*-ammonium hydroxide + 0·02*N*-sodium hydroxide, and (G) 0·2*N*-sodium oxalate, all in atmospheres free from carbon dioxide, and in the following solutions, in atmospheres of carbon dioxide : (H) 0·2*N*-sodium citrate and (I) 0·2*N*-sodium oxalate.

Copper dissolved (mg.).

Time (days).	Solution A.	B.	C.	D.	E.	F.	G.	H.	I.
2	5	1	25	1	20	1	trace	97	16
5	8	2	42	3	19	1	trace	153	60
10	9	2	68	3	21	1	trace	195	82
20	11	3	112	3	22	1	0·1	238	95

Precipitated cupric oxide (B.D.H.), " A.R." sodium citrate, oxalate, and hydroxide and ammonium carbonate, and specially prepared carbonate-free ammonium hydroxide were employed. 1 G. of copper oxide was weighed into each of six 100-c.c. Pyrex conical flasks, into each of which were then delivered 50 c.c. of the particular solution. The flasks were immediately placed in a large desiccator containing the requisite atmosphere. The vapour pressure of water (and of ammonia in the relevant experiments) in the desiccator was adjusted to prevent evaporation from the flasks. From time to time a flask was removed, the residual copper oxide filtered off and washed with 2% sodium acetate solution, and the dissolved copper in the filtrate determined by means of salicylaldoxime. The rate of solution of the copper oxide at room temperature in the various solutions was thus determined.

It is apparent from these results that an important factor controlling the rate and extent of the solution of copper oxide in the various salt solutions is the hydroxyl-ion concentration. Consider first the ammonia solutions. Ammonium hydroxide is a weak base and contains a relatively small concentration of hydroxyl ions. It dissolves copper oxide by virtue of the tendency which ammonia molecules possess to co-ordinate with copper and form complex ions of the type $[Cu(NH_3)_4]^{\bullet\bullet}$. Such solution probably occurs initially according to the equation $CuO + 4NH_3,H_2O = [Cu(NH_3)_4](OH)_2 + 3H_2O$. Conductivity measurements indicate that complex compounds of this type are highly dissociated in aqueous solution and therefore solution of copper oxide in aqueous ammonia will bring about a rapid increase in hydroxyl-ion concentration.

It can be seen from the following equation for the solution of copper oxide in aqueous sodium oxalate, $CuO + Na_2C_2O_4 + 3H_2O = Na_2[Cu(C_2O_4)_2(H_2O)_2] + 2NaOH$, that reactions of this type must also be accompanied by an increase in the alkalinity of the solution.

This view is supported by the above experiments, which show that a small added amount of alkali hydroxide very markedly reduces the rate and extent of the solution of the copper oxide. The action of carbon dioxide therefore probably depends upon its power of neutralising the alkalinity produced in the above reactions, with the formation of hydrogen carbonate and a consequent reduction in hydroxyl-ion concentration. The inhibiting action of the hydroxyl ions is probably due to one of two causes.

(*a*) If the reaction between the copper oxide and the co-ordinating ion or molecule is an ionic one, the rate will depend upon the copper-ion concentration which will diminish as hydroxyl-ion concentration increases.

(*b*) If the reaction is between solid copper oxide and the co-ordinating molecule or anion, then it is possible that the inhibiting effect of the hydroxyl ions is due to the formation of a surface film of hydroxyl groups on the copper oxide, which will prevent the access of the co-ordinating molecules or anions to the copper atoms in the oxide lattice. The large inhibiting effect of relatively small concentrations of hydroxyl ions supports this explanation.

It is known that zinc oxide dissolves far more readily in aqueous ammonia containing ammonium carbonate than it does in aqueous ammonia alone. This is probably due to similar causes. It is also probable that the above offers an explanation of the part played by carbon dioxide in accelerating certain types of metallic corrosion (cf. Riley, *Proc. Roy. Soc.*, **1934**, *A*, **143**, 399).

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