

Isotopic Exchange of Copper between Cupric Nitrate and the Metal.

By J. F. DUNCAN and B. W. OAKLEY.

[Reprint Order No. 5771.]

The isotopic exchange of copper between cupric nitrate and powdered metal has been studied. Although rapid apparent exchange reactions are observed it is shown that they are critically dependent on the nature of the surface, and are in particular enhanced in oxidising environments. By carefully preparing a fresh unoxidised copper surface by electrolysis it is shown that the true exchange reaction between the clean metal surface and the solution is not complete even after 14 hours.

ISOTOPIC exchange reactions between metals and aqueous solutions of their salts have been studied by a number of previous workers (Haissinsky, *J. Chim. phys.*, 1948, **45**, 224; 1949, **46**, 298; Haissinsky and Cottin, *ibid.*, p. 476; Baerg and Winkler, *Canad. J. Chem.*, 1953, **31**, 319, 521; Rollin, *J. Amer. Chem. Soc.*, 1940, **62**, 86). In almost all cases they report a rapid initial reaction for a few minutes, followed by a slow loss of activity from solution during many hours or days. Baerg and Winkler (*loc. cit.*) suggested that the kinetics of the silver ion-metal exchange reaction indicate the occurrence of several different exchange reactions on the surface of the same specimen of metal, which was interpreted as due to the presence of crystal faces of different orientation. We obtain similar results to theirs with the analogous copper system, but our results show that the exchange reaction between metallic copper and cupric nitrate is very slow. In this case the apparent rapid exchange reaction is due to secondary surface reactions, probably with an oxide film.

EXPERIMENTAL AND RESULTS

50 ml. of a solution of cupric nitrate, of appropriate concentration and pH (adjusted by addition of a little ammonia solution), were stirred vigorously, the speed of the stirrer being recorded. Radioactive ^{64}Cu (half-life 12.88 hr.) as nitrate, obtained by pile irradiation of cupric nitrate, was added to give an activity of about 8000 counts/min./ml. About 0.5 g. of electrolytic copper powder (~200 mesh) was next added. At varying intervals afterwards, 0.5 ml. of solution was removed through a sintered-glass filter attached to the bottom of the pipette. This was placed in a small beaker and presented in a reproducible position to the window of a Geiger-Müller counter, and the activity determined with the usual corrections for circuit paralysis time, background, decay, etc.

Results.—In most cases, any loss of activity from solution occurred within 10 min., the solution remaining unchanged thereafter. To elucidate the nature of the reaction occurring, the effect of the following variables was studied.

(a) *Stirring rate.* The total percentage drop in activity obtained when the solution activity had become constant was dependent on the rate at which the cupric nitrate was agitated (see Fig. 1). At high stirring rates considerable scatter of the results was obtained owing to the presence of variable amounts of air bubbles.

(b) *Environment.* The percentage uptake of activity was redetermined when using (i) oxygen and (ii) nitrogen from cylinders at constant stirring rate, with a gas flow as great as could be allowed without causing loss of liquid. Table 1 shows that oxygen causes con-

TABLE 1. *Observed percentage change in activity under different conditions.*

(Solution stirred at 450 rev./min.; pH = 2.)

Condition of experiment	Wt. of Cu, g.	Loss (%) of activity from solution
(1) Normal stirring in air	0.494	2.3
(2) Air blown through solution	0.495	3.2
(3) Oxygen blown through solution	0.493	6.5
(4) Nitrogen blown through solution	(a) 0.483, (b) 0.494	(a) 1.1, (b) 0.1

siderable enhancement of the initial reaction. This suggests that the initial reaction is associated with the surface oxidation of the copper.

(c) *pH Dependence.* To satisfy ourselves that these effects were not associated with other changes in environment, the reaction was followed at constant stirring rate in solutions of different pH and different cupric-ion concentrations. The magnitude of the initial loss of activity from solution was found to be constant for $0.8 < \text{pH} < 3.6$, falling to zero at $\text{pH} \sim 0$ (see Fig. 2). This is in accordance with the suggestion that the activity loss is due to the presence of a surface-oxidised copper, since at high acidity, surface oxidation would be small.

FIG. 1. Variation of percentage drop in activity with stirring rate.

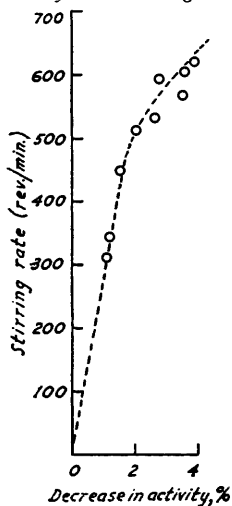


FIG. 2. Effect of pH. (0.496 ± 0.001 g. copper. Stirring rate 540 revs./min. N-copper nitrate.)

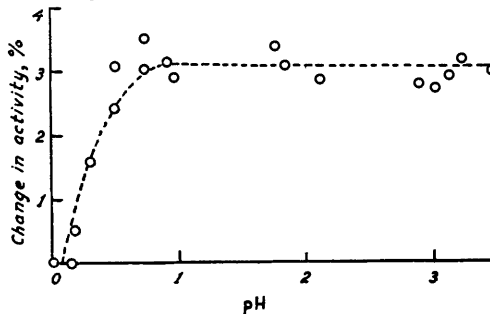


FIG. 4. Effect of immersion of copper in 20-vol. hydrogen peroxide, prior to reaction with active cupric nitrate.

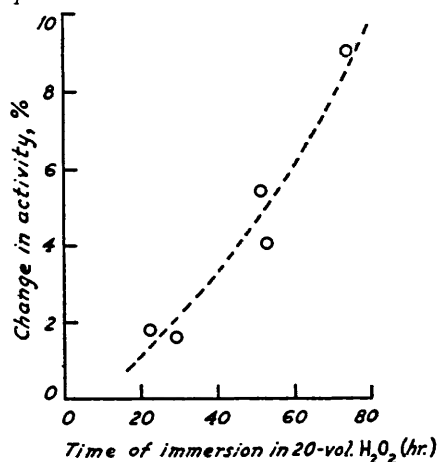
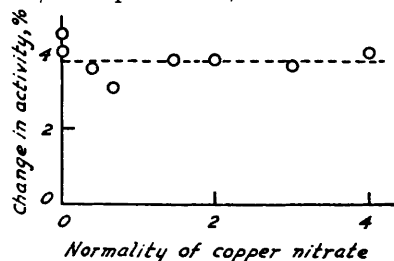


FIG. 3. Effect of copper nitrate concentration. (0.499 ± 0.001 g. copper. Stirring rate 540 revs./min. pH = 2.00.)



(d) *Concentration.* At a pH of 2 and with a stirring rate of 540 rev./min., the concentration was varied over the range 0.001—4N-cupric nitrate (see Fig. 3). The percentage activity drop was independent of concentration. Hence the magnitude of the apparent exchange reaction is proportional to the concentration. This would not be expected if the reaction were a simple surface exchange but it would occur if the reaction took place in either a chemically formed or an adsorbed surface layer the amount of which was proportional to the cupric-ion concentration.

(e) *State of copper surface.* If the copper powder (inactive) is added to inactive cupric nitrate, and after 15 min. or more the solution is seeded with active copper nitrate, no loss in activity from the solution occurs, except when the solution is thoroughly saturated with oxygen by bubbling (see Table 2). A similar result is obtained with copper powder which has been previously etched in acid.

TABLE 2. *Pretreatment of copper.*(pH = 2; 540 rev./min.; N-cupric nitrate; 0.497 ± 0.002 g. of copper.)

Pre-treatment	Change in activity, %
(1) None	2.3
(2) Cu left for 1 hr. in N-Cu(NO ₃) ₂	0.0
(3) As (2), oxygen blown into reacting solution	2.4
(4) Etched for $\frac{1}{2}$ min. in 8N-HNO ₃ ; dried on filter-paper before use in exchange reaction	0.2

By setting the copper aside for varying periods in solutions of 20-vol. hydrogen peroxide, it was found that the activity loss from solution in a subsequent exchange experiment was dependent on the length of time the copper had been in the peroxide solution; in many cases it was very large (see Fig. 4).

Since it is now clear that the rapid uptake of activity obtained in most cases is due to a secondary surface reaction, it follows that a careful preparation of the surface of the copper is necessary if we are to be sure that we are measuring the true exchange reaction between copper metal and cupric ions. For this purpose an electrolytic method of preparation is probably most satisfactory.

A flat piece of copper wire gauze (~150 mesh) was made one electrode in a conventional electrolytic apparatus for the analysis of copper in solution. The other electrode was a cylindrical piece of platinum gauze inside which the copper gauze rotated. The solution (N/100-copper nitrate) was electrolysed for 2 hr. Electrolysis was stopped, but stirring was continued, and the copper activity was then introduced into the system. Aliquot portions of the solution were removed at different times and the activity was measured. The results are quoted in Table 3.

TABLE 3. *Observed initial drop in activity after electrolysis.*

State of copper gauze before experiment	Change in activity initially, %	State of copper gauze before experiment	Change in activity initially, %
Cathode	(a) 0.0, (b) 0.1	Anode	(a) 4.35, (b) 4.25

There was a significant change in activity obtained when the copper gauze had been used as the anode. Anode electrolysis would probably lead to some surface oxidation and presumably this accounts for the observed change. No change in activity was initially detectable after the copper had been used as cathode, although there was a slow loss extending over many hours. This was, however, only about $\frac{1}{2}$ % per hr., but was continuous for at least 14 hr. It was calculated that, if complete exchange with a monolayer on the surface took place, a change of about $\frac{1}{2}$ % in the activity would occur if the superficial area of the wire could be taken as equal to its real area. As the real surface is probably an order of magnitude greater than the apparent surface, it is clear that any exchange reaction which is occurring is very slow. We conclude therefore that, unless copper is unique in this respect, the rate of isotopic exchange between a clean metal surface and an aqueous solution of its ions is much slower than is commonly believed.

We thank the Director of the Atomic Energy Research Establishment, where this work was done, for permission to publish this paper, and Dr. E. Glueckauf for helpful discussion.

ATOMIC ENERGY RESEARCH ESTABLISHMENT, HARWELL, NEAR DIDCOT, BERKS.
 [Present address (J. F. D.): UNIVERSITY, MELBOURNE,
 AUSTRALIA.]

[Received, September 30th, 1954.]