CLX.—*The Conductivity of Copper Hydrosols.*

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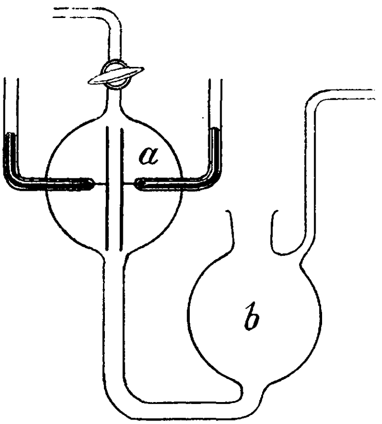
MEASUREMENT of the conductivities of metal hydrosols prepared by Bredig's method was undertaken with a view to examine the ionic equilibrium in such sols. It was found, however, that the concentration of stabilising electrolyte was so large as to preclude any evidence being obtained of the equilibrium between ions on the particle surface and those in solution.

Measurements were made in a cell of the form shown in Fig. 1, which was placed in a thermostat at 25°. A measured volume of water of conductivity averaging 0·8 gemmho was placed in the vessel *b*. The conductivity of this water could be kept constant for 7—14 days. At first a screw-adjusted spark gap was fitted in the opening of *b* through a vulcanite stopper, but later two stout metal wires carried by a two-holed rubber bung were found to be more suitable and were boiled with conductivity water on every occasion before use. The top of one of these wires was clamped. By altering the pressure of the clamp, the lower end was made to approach the lower end of the unclamped wire, both being below the surface of the water. By flicking the top of the unclamped wire, arcing could be started. The copper arc would not run continuously for more than a few seconds and had then to be restruck. The voltage used was 100, and the current passing when the arc had been struck about 5 amps. Electrolyte solutions were run into *b* from a burette, the electrodes being temporarily removed. The side tube of *b* was in communication with the air through soda–lime tubes, and the side tube of *a* was connected through a two-way tap with a water-pump or with the side tube of *b*. In this way the liquid in *b* could be drawn up into *a*, which contained platinum electrodes covered with grey platinum. Its conductivity having been determined, the liquid was allowed to flow back into *b*. This procedure was carried out every 5 minutes during arcing in order to keep the temperature down, and after the addition of electrolyte in order to ensure thorough mixing. Control experiments with conductivity water, but without arcing, showed no increase in conductivity of the water for 12—24 hours.

Fig. 1.

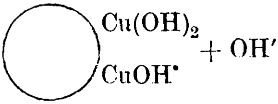


Since these experiments were completed, a paper has been published by Pennycuick (J., 1927, 2600) in which he gives the results of measurements of the conductivity of mixtures of platinum sols and various bases. He finds a slow shift in conductivity on titrating a sol with a base or on altering its temperature. With copper sols this slow alteration in conductivity was not so noticeable provided the cell was thoroughly cleaned out between each experiment. In addition, sols were prepared at 25° (although a greater amount of sputtered metal is produced at this temperature than at 0°) and only small concentrations of electrolytes were added. Copper sols give considerably smaller conductivities than either platinum or silver hydrosols. On continued arcing, the conductivity rises to a value which is constant for the particular sample of water used, thus :

	(1)	(2)
Water alone	$0·81 \times 10^{-6}$	$0·80 \times 10^{-6}$
Arcing 1 minute	1·48 ,,	1·51 ,,
,, 5 minutes	1·70 ,,	1·73 ,,
,, 10 ,,	1·50 ,,	1·54 ,,
,, 15 ,,	1·48 ,,	1·47 ,,
,, 30 ,,	1·48 ,,	1·46 ,,

After standing for 16 hours both these samples had a conductivity of $1{\cdot}51 \times 10^{-6}$. Beans and Eastlake (*J. Amer. Chem. Soc.*, 1915, **37**, 2667) have calculated that the conductivity of the metal particles and their stabilising ions is negligible compared with the above values. It appears probable that the conductivity of copper sols is due to cuprous or cupric hydroxide produced during arcing.

If cupric hydroxide is formed, the charged particle may be represented thus :



$$\bigcirc\begin{matrix}Cu(OH)_2\\ CuOH^{\bullet}\end{matrix} + OH'$$

Various electrolytes were added to copper sols which had been prepared by arcing for about 10 minutes in 75 c.c. of water. Col. 1

TABLE I.

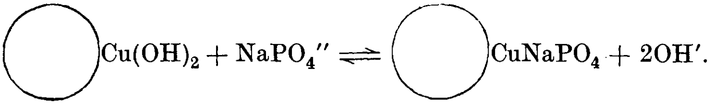
Electrolyte.	1.	2.	3.	4.	5.
NaCl	0	1·6	1·6	—	
	1·25	4·1	4·3	— 0·2	
	2·5	6·5	6·9	— 0·4	
	3·75	9·1	9·3	— 0·2	
	5·0	11·7	11·8	— 0·1	
	7·5	16·5	16·5	±	
	12·5	24·6	24·9	— 0·3	
NaOH	(1) 0	1·5	1·5	—	
	5·0	2·7	3·7	— 1·0	— 0·5
	10·0	5·2	6·4	— 1·2	— 0·6
	15·0	8·1	9·5	— 1·4	— 0·6
	25·0	14·7	16·4	— 1·7	— 0·6
	(2) 5·0	29·2	31·2	— 2·0	— 0·6
	10·0	58·4	60·5	— 2·1	— 0·6
Na_3PO_4	0	1·5	1·5	—	
	0·75	2·5	1·8	+ 0·7	
	1·5	3·6	2·2	+ 1·4	
	2·5	4·4	2·5	+ 1·9	
	5·0	5·3	3·3	+ 2·0	
	7·5	6·4	4·4	+ 2·0	
	12·5	7·3	5·5	+ 1·8	
	17·5	8·3	6·6	+ 1·7	
	22·5	9·2	7·5	+ 1·7	
HNO_3	(1) 0	1·5	1·5	—	
	5·0	2·4	3·8	— 1·4	— 1·1
	10·0	3·2	5·6	— 2·4	— 2·4
	15·0	4·0	7·4	— 3·4	— 3·8
	25·0	5·1	11·3	— 6·2	— 6·5
	(2) 5·0	26·6	85·6	— 59·0	— 58·4
	10·0	52·9	168·9	— 116·0	— 116·2
$AlCl_3$	0	1·6	1·6	—	
	1·25	2·3	2·4	— 0·1	
	2·5	2·9	3·0	— 0·1	
	5·0	4·1	4·4	— 0·3	
	7·5	5·3	5·7	— 0·4	
	25·0	12·1	13·1	— 1·0	

in the table gives the number of c.c. of electrolyte added to 75 c.c. of copper sol; col. 2 the conductivity observed ($\times 10^6$); col. 3 the increase in conductivity observed when the same volume of electrolyte is added to 75 c.c. of conductivity water, plus the conductivity due to the concentration of copper sol in the mixture given in col. 1; col. 4 gives the difference (col. 2—col. 3); and col. 5 gives the value of this difference calculated on the assumptions stated below.

When sodium chloride solution is added to a copper sol, the observed conductivity of the mixture does not differ appreciably from the sum of the calculated conductivities of its components : adsorption of the chloride, if any, is small. With sodium and other hydroxides the conductivity of the mixture is definitely less than that of its components. If this diminution were due to repression of the ionisation of copper hydroxide by sodium hydroxide, the difference calculated on the assumption that the increase in conductivity of the sols over that of the water used is due to cupric and hydroxyl ions only is that given in col. 5. The greater difference observed is probably due to the specific adsorption of sodium hydroxide.

The increase in conductivity when sodium phosphate is added to the sol is more difficult to explain. A similar increase in conductivity is observed when aluminium chloride is added to a negatively charged sol such as platinum. It may possibly be due to the substitution of hydroxyl ions for slower-moving ions by a reaction at the particle surface such as

$$Na_3PO_4 \rightleftharpoons NaPO_4'' + 2Na^{\cdot}$$



$$\bigcirc Cu(OH)_2 + NaPO_4'' \rightleftharpoons \bigcirc CuNaPO_4 + 2OH'.$$

When a very dilute acid solution is added to a copper sol, hydrogen and hydroxyl ions are used up and the sol appears to become saturated again with copper hydroxide from the particle surface. Col. 5 gives $C_{\mathrm{HNO_3}}(\mu_{\mathrm{H}^{\cdot}} - \mu_{\mathrm{Cu}^{\cdot\cdot}})$, the difference calculated on this assumption, the repression of ionisation of copper hydroxide by increasing concentration of cupric ions being neglected. The agreement is fairly good and is further evidence for the presence of copper hydroxide in the sol.

Finally, the addition of aluminium chloride shows that this salt probably reacts like an acid with the sol owing to hydrogen ions produced by hydrolysis.

It is to be inferred from these experiments that the particle surface in copper hydrosols prepared by Bredig's method is largely covered by copper hydroxide, which saturates the water in which the particles are dispersed.

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