magnesium chloride precipitates are far more gelatinous in character than are those with calcium chloride and show apparently more absorptive properties.

The writer wishes to express his appreciation to Dr. Victor Lenher whose many valuable suggestions during the progress of this work made its early completion possible.

Summary

A method has been presented for determining the solubilities of various chlorides in selenium oxychloride.

The solubilities of 22 chlorides at 25° have been established and the solid phases investigated, showing that while a number of the chlorides do not unite with selenium oxychloride, others form characteristic double compounds.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF SWARTHMORE COLLEGE]

THE ACTION OF SOLUTIONS OF ALKALI HYDROXIDES ON COPPER OXIDE AND ON COPPER, AND THE EXISTENCE OF SALTS OF CUPRIC ACID

BY H. J. M. CREIGHTON

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The majority of text-books on inorganic chemistry ignore the solution of copper hydroxide in concentrated solutions of alkali hydroxides.

Löw[1] found that copper hydroxide dissolves in a solution of sodium hydroxide and that the resulting blue solution might be diluted with 4–5 volumes of water and boiled without decomposition, but that precipitation of copper oxide took place on boiling when the blue solution was diluted with 10 volumes of water. These blue solutions were decolorized by merely shaking with copper oxide, and a bright blue powder, which decomposed into sodium oxide and cupric oxide, settled when the solution was allowed to stand for several days. According to Donath,[2] a blue solution is formed on treating copper oxide with a concentrated solution of potassium hydroxide. The color of this solution is intensified by the addition of alkali tartrate and destroyed by the addition of potassium cyanide.

While the formation of these blue solutions suggests the possible existence of salts of a cupric acid, analogous to the compounds formed by the interaction of alkali hydroxides and lead or tin hydroxides, Fischer[3] points out that the blue color is due to a colloidal suspension of copper hydroxide, because the greater part of the hydroxide settles out and, also, because on filtering the solution the cupric oxide gel remains in the filter. Ley[4] prepared a solution of colloidal copper hydroxide by hydrolyzing copper succinimide and dialyzing the product of hydrolysis, but the color of the colloidal solution was brown. The addition of electrolytes, such as chlorides and nitrates, to this solution precipitated

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[1] Löw, *Z. anal. Chem.*, **9**, 463 (1870).

[2] Donath, *ibid.*, **40**, 137 (1901).

[3] Fischer, *Z. anorg. Chem.*, **40**, 39 (1904).

[4] Ley, *Ber.*, **38**, 2199 (1905).

gelatinous copper hydroxide. Like the majority of metallic hydroxides, Ley's colloidal copper hydroxide was positively charged and migrated to the cathode. By adding alkali hydroxide to suspensions of copper protalbate or lysalbate, Paal and Leuze[5] prepared a deep bluish-violet liquid hydrosol of copper hydroxide which, during dialysis, became a dirty-blue to violet by reflected and brownish-violet by transmitted light, perhaps owing to dehydration of the colloid.

While several investigators claim to have prepared solutions of salts of cupric acid, there has been some doubt as to their existence. In an investigation of the action of chlorine on copper hydroxide suspended in solutions of potassium hydroxide, Mawrow[6] failed to obtain evidence of the formation of the red solution previously described by Krüger[7] and which was supposed to contain a salt of cupric acid. On the other hand, Brauner and Kuzma[8] found that during the oxidation of a solution containing both copper and tellurium with ammonium persulfate an intense ruby-red coloration was produced, which they attributed to the formation of a derivative of cupric acid.

A number of years ago the observation that a 5 *N* solution of potassium hydroxide in which a copper rod had been immersed for several months had turned blue led the writer to study these solutions. The results obtained seem to indicate that the blue color is due to the formation of salts of cupric acid, such as K_2CuO_2, and not to the presence of colloidal hydroxide.

While, in the absence of air, solutions of 5 *N* potassium or sodium hydroxide have been kept in contact with bright copper wire for 7 years without becoming even faintly blue, in the presence of air a blue color is noticeable in a few days. The intensity of the color gradually increases. At the end of several months the content of copper, in one instance, amounted to 0.0724 g. in 100 cc. of the alkali solution. On the other hand, copper oxide interacts with alkali hydroxide solutions in the absence of air to form blue solutions. The blue alkali hydroxide solutions are also formed by passing an electric current of high density between copper electrodes immersed in concentrated potassium or sodium hydroxide solutions at a temperature of from 80 to 90.[9] The blue solutions are most conveniently and quickly prepared by this method, or by digesting copper oxide with concentrated solutions of alkali hydroxide at 80 to 90° for several hours. By the latter method a concentration of from 0.0350 to 0.0450 g. of copper in 100 cc. in 5 *N* potassium or sodium hydroxide has been obtained in 8 to 10 hours; by the former a much higher concentration of copper can be attained in a very much shorter time. Solutions

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[5] Paal and Leuze, *Ber.*, **39**, 1545 (1906).

[6] Mawrow, *Z. anorg. Chem.*, **23**, 233 (1900).

[7] Krüger, *ibid.*, **2**, 658 (1892).

[8] Brauner and Kuzma, *Ber.*, **40**, 3362 (1907).

[9] Grube and Feucht have recently found that a blue solution is obtained when a hot, concentrated solution of potassium hydroxide is electrolyzed between cobalt electrodes. By means of electromotive-force measurements they have shown that the blue color of the solution is due to the presence of CoO_2^{--} ions and not to colloidal cobalt hydroxide. *Z. Elektrochem.*, **28**, 568 (1922).

containing 100 mg. of copper in 100 cc. are quite transparent and intensely blue, the color being very like that of solutions containing the $\mathrm{Cu(NH_3)_4}^{++}$ ion.

Blue solutions, containing as much as 0.0650 g. of copper in 100 cc., have been prepared by dissolving freshly precipitated copper hydroxide in 5 *N* potassium hydroxide solution. These solutions behaved in all respects like those prepared by digesting copper oxide in potassium hydroxide or by the electrical method. Their stability is decreased by the presence of suspended copper hydroxide, and when much of this is present the solutions decompose on boiling.

The blue color imparted to melted potassium hydroxide on the addition of a small quantity of copper oxide may, possibly, be due to the same substance which gives the blue color to the solutions prepared by the methods just described.

When an electric current of 0.5 ampere is passed between a platinum cathode and a copper anode of 10 sq. cm. area immersed in 5 *N* potassium hydroxide solution at 80°, a deep blue color is immediately produced on the anode. After 2 or 3 seconds this color fades, the salmon pink of the anode changes to black and oxygen is evolved. When the current is increased to 8 amperes the evolution of oxygen is increased, the black copper oxide gradually disappears from the anode and, in a few minutes, the electrolyte in the neighborhood of this electrode becomes a distinct blue. As soon as the blue color is distributed throughout the solution copper begins to deposit on the cathode in a powdery form. Solution of copper at the anode and its precipitation at the cathode then take place simultaneously, and after a short time the rates of these two processes become equal and a limiting concentration of copper in the electrolyte is reached. During electrolysis the anode remains a bright pink, notwithstanding the large volume of oxygen evolved at this electrode. It is suggested that the production of the blue color in the solution is probably due to the formation of the anion of cupric acid.

$$\begin{array}{l}
\mathrm{Cu} + 2\oplus = \mathrm{Cu}^{++} \qquad (1)\\
\mathrm{Cu}^{++} + 4\mathrm{OH}^- \rightleftharpoons \mathrm{CuO_2}^{--} + 2\mathrm{H_2O} \qquad (2)\\
\quad +\\
\quad 2\ominus = \downarrow \mathrm{Cu}\ \text{(at the cathode)}
\end{array}$$

If this view is correct, then the formation of blue solutions by digesting copper oxide with alkali hydroxides may be represented by the equation

$$\mathrm{CuO} + 2\mathrm{OH}^- \longrightarrow \mathrm{CuO_2}^{--} + \mathrm{H_2O} \qquad (3)$$

Discharge of cupric ions at the cathode can be prevented and solutions containing a higher concentration of copper obtained by carrying out the electrolysis in a diaphragm cell. In this way solutions have been obtained which contain 0.0968 g. of copper in 100 cc. in 5 *N* potassium hydroxide. If electrolysis is continued after this concentration has been reached, copper continues to dissolve from the anode but copper oxide precipitates, indicating that the limiting solubility of potassium cuprate in 5 *N* potassium hydroxide has been reached. The solubility of alkali cuprate increases with the concentration of the alkali hydroxide employed. Thus, on electrolyzing solutions of 5 and 10 *N* sodium hydroxide between copper electrodes in a diaphragm cell, the maximum copper concentration attained was 0.0720 g. and 0.2400 g. in 100 cc., respectively.

Contrary to the result observed by Löw[1] with solutions prepared by dissolving copper oxide in alkali hydroxide, blue solutions prepared by digesting copper oxide in 5 *N* potassium or sodium hydroxide have been kept in contact with the oxide for years without the color fading to an appreciable extent. The blue solutions do not decompose on boiling, and unlike those prepared by Fischer[3] they do not precipitate copper oxide on standing. A blue solution in 5 *N* potassium hydroxide placed in a bottle ($^2/_3$ filled) 8 years ago has retained its color and copper oxide has not separated. The blue solutions may be greatly diluted without copper oxide separating for a long time. If the initial concentration of the blue component in the alkali solution is such that on the addition of water its concentration then exceeds its solubility in the alkali of reduced concentration, precipitation of copper oxide would be expected to take place. This may account for the precipitation observed by Löw. Potassium cyanide destroys the blue color and hydrogen sulfide precipitates copper sulfide, doubtless owing to the removal of cupric ions of Equilibrium 2.

In agreement with Fischer's observation,[3] the blue color is removed from the copper solutions on filtering—provided the volume of solution passed through the filter is not too great—and a colorless filtrate containing no copper is obtained. When, however, several portions of the blue solution are passed through the same filter paper, the filtrate soon runs through blue. The filter paper turns greenish and usually this color gradually changes to brown, although in some instances the color of the paper was still green at the end of several months. Microscopic examination of the green filter papers showed that the pores were not filled with the green substance, but that the majority of the long fibers were colored green or blue, their structure remaining unchanged. In view of the fact that after a quantity of the solution has run through the filter the filtrate becomes blue, it is suggested that the initial removal of copper from the solution may be due to chemical combination between the blue component and the cellulose of the paper, rather than to precipitation of a copper oxide gel. This suggestion is supported by the fact that apparently chemical combination does take place between the blue component and guncotton or cottonwool, in each case cuprous oxide being subsequently precipitated.

Blue solutions which have been allowed to stand for a time, so as to allow any suspended matter contained in the hydroxide to settle, do not show the Tyndall effect. Unlike solutions of colloids, they diffuse readily. A blue solution formed in 5 *N* potassium hydroxide by the electrical method diffused in 2 days from one vertical arm of an H-shaped vessel uniformly through potassium hydroxide of the same concentration contained in the other arm of the vessel. On the other hand, numerous unsuccessful attempts have been made to dialyze the blue solutions, concd. alkali hydroxide being used as the liquid outside of the dialysis cell. The failure of these attempts may be due to chemical interaction between the blue component of the solution and the material of the dialysis cell (as in the case of filter paper), rather than to precipitation of a gel. With this exception, the blue solutions do not behave like colloidal solutions. Moreover, their color is quite different from that of the solutions of colloidal hydroxide prepared by Ley.[4]

If the color of the blue solutions is due to the presence of an alkali cuprate, then an increase in the copper concentration should occur at the anode during electrolysis, owing to the migration of CuO_2^{--} ions to the positive electrode. Since these ions when discharged probably would react with the hydroxyl ions present in the solution, an evolution of oxygen, resulting from the reaction,

$$CuO_2 + 2OH^- \longrightarrow CuO_2^{--} + H_2O + O \qquad (4)$$

should be expected at the anode when an electric current is passed through a blue solution. Further, a discharge of the cupric ions present in Equilibrium 2 should take place at the cathode. In order to test these conclusions the electrolysis of a number of blue solutions in 5 *N* potassium hydroxide was studied. To preclude the possibility that evolution of oxygen at the anode resulted merely from the discharge of hydroxyl ions, the voltage employed in several of the experiments was kept well below the decomposition voltage of the 5 *N* potassium hydroxide used in preparing the blue solutions. This was found to be 1.44 volts, while with a blue solution containing 0.0505 g. of copper in 100 cc. the decomposition voltage was about 1 volt.

A large volume of blue solution (containing 0.0505 g. of copper in 100 cc. of 5 *N* potassium hydroxide) was electrolyzed for 120 hours between platinum electrodes in a special H-shaped vessel, constructed so that the gases evolved at the electrodes could be collected and measured. A voltage of 1.20 was employed. The total quantity of electricity passed through the solution was 199.6 coulombs. As soon as the current was started, a fine, steady stream of bubbles arose from the anode which continued throughout the duration of the experiment. This gas proved to be oxygen. Soon after the start of the experiment a film of pink copper appeared on the cathode, and not until the blue color had faded considerably in the neighborhood of this electrode was there evidence of the liberation of hydrogen. The solution around the cathode became colorless before the end of the period of electrolysis. The weight of copper that deposited on the cathode amounted to 0.0468 g., and a dark, adherent substance containing 0.0031 g. of copper separated on the anode. A small quantity of a dark colored powder which contained copper was deposited at the bottom of the cell immediately below the anode. Above this electrode 0.0137 g. (9.56 cc. at 0° and 760 mm.) of oxygen was collected. The deposit on the anode can be attributed to decomposition of discharged CuO_2^{--} ions,

$$CuO_2 \longrightarrow CuO + O \qquad (5)$$

and that on the bottom of the cell either to supersaturation of the solution with potassium cuprate at the surface of the anode and its subsequent decomposition, or to some of the copper oxide falling from the electrode. On the assumption of a discharge of CuO_2^{--} ions at the anode, the weight of oxygen evolved should have been 0.0165 g., whereas it was about 17% less than this. Results similar to the foregoing were obtained in a repetition of this experiment.

It is difficult to determine whether the concentration of copper in the solution around the anode increases during electrolysis. During the long period of electrolysis which is necessary on account of the low concentration of copper in the blue solutions, the colored component is apt to be carried by ordinary diffusion to the cathode where cupric ions are discharging. Furthermore, there is a continuous stirring of the anolyte by the oxygen evolved at the positive electrode. For these reasons the ordinary H-shaped transference apparatus cannot be used. The change in the copper concentration at the anode has been studied, however, by electrolyzing a blue solution, containing 0.0363 g. of copper in 100 cc. of 5 N potassium hydroxide, between platinum electrodes in a long tube with 7 bends. It was found that at the end of 48 hours the solution in the cathode limb of the apparatus had become colorless and that there was no further deposition of copper on the cathode. At the end of 100 hours the deposit on the anode and that on the bottom of the arm of the vessel immediately beneath this electrode were found to contain 0.0039 and 0.031 g. of copper, respectively. A volume of 50 cc. of the solution immediately surrounding the anode was found to contain 0.0179 g. of copper. Since 50 cc. of the solution contained 0.0182 g. of copper originally, the final weight of copper in this volume indicates that the concentration of copper increased in the anodic section during electrolysis. In another experiment the weight of copper in 50 cc. of 5 N potassium hydroxide solution increased from 0.0484 to 0.0571 g. (including the weight of copper contained in the deposits on the anode and the bottom of the cell) during electrolysis.

The results of the foregoing experiments not only support the conclusion that the blue color of the solutions described is due to alkali salts of cupric acid, but they also indicate that the color cannot be due to the presence of colloidal copper hydroxide. If the latter were true, the blue color should not have faded around the cathode during electrolysis; rather it should have increased in intensity near this electrode, since colloidal metallic hydroxides in general, and colloidal copper hydroxide in particular,[4] are positively charged and migrate to the cathode under the influence of an electric current.

Summary

1. Blue solutions containing copper have been prepared by the following methods: (a) by dissolving copper hydroxide in concentrated alkali hydroxide; (b) by digesting copper oxide in concentrated alkali hydroxide at 80° to 90°; (c) by electrolyzing concentrated alkali hydroxide between copper electrodes with a high current density at 80° to 90°. The blue solutions obtained by these methods are identical in their behavior. The blue substance which is formed when copper oxide is added to melted potassium hydroxide may be the same as the blue component of these solutions.

2. The blue solutions do not exhibit the characteristic properties of colloidal solutions, particularly those of the solutions of colloidal hydroxide prepared by Ley.

3. Evidence is put forward which indicates that the blue color of the solutions is due to the presence of an alkali salt of cupric acid. The formation of the salt by Method b can be represented by the equation, $CuO + 2OH^- \longrightarrow CuO_2^{--} + H_2O$; by Method c by the equations, $Cu + 2 \oplus \longrightarrow Cu^{++}$, and $Cu^{++} + 4OH^- \rightleftharpoons CuO_2^{--} + 2H_2O$.

4. The solubility of alkali cuprates in alkali hydroxides, though quite low, increases rapidly with the concentration of the hydroxide. The potassium salt is apparently more soluble than the sodium salt.

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[Contribution from the Soils Laboratory, Agricultural Experiment Station, University of Missouri]

THE RELATION OF HYDROGEN-ION CONCENTRATION TO THE FLOCCULATION OF A COLLOIDAL CLAY

By Richard Bradfield[1]

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In a recent study in this Laboratory of the minimum amounts of various electrolytes required to flocculate a colloidal clay solution it was found that when dipotassium phosphate was mixed with the colloidal clay in quantities just below that required to cause flocculation and the electrolyte requirement of this phosphated solution then determined, the presence of this salt required the addition of much larger quantities of the other electrolytes than did the untreated colloid.

Two possible explanations were suggested. (1) The protective action might be due to the absorption of the negative phosphate and hydroxyl ions by the negative clay particle, thus increasing its negative charge and consequently the amount of positive ions required to bring it to the isoelectric point. It is a well-established fact that the phosphate ion is held

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[1] The author wishes to express his indebtedness to Professor M. F. Miller for critically reading the manuscript and to his assistant, Franklin Davis, for the determinations of the electrolyte requirement.