values with increasing content of sulfuric acid so that the change in composition of solution is better illustrated by the results for sulfuric acid. In the figure, the results have been plotted. Ordinates represent percentage of water in the residue, and abscissas, the percentage of sulfuric acid in solution. This brings out clearly the range of conditions under which each hydrate forms, this being represented by the length of the horizontals. The conditions for the trihydrate are very narrow while the pentahydrate forms under the widest range, being stable in contact with solutions containing as much as 49% of sulfuric acid.

Solutions which are in equilibrium with two solid hydrates should have the same vapor pressure as that of the hydrates themselves.[1] The vapor pressure of the solutions in Nos. 7–9 of the table, for instance, should be equal to that of a mixture of the solid pentahydrate and trihydrate. Whether this way of determining the vapor pressures of hydrates will offer any advantage in accuracy or convenience has not yet been tested. Where the solubility of the salt is slight, as it is in the solution in equilibrium with anhydrous salt and monohydrate (Nos. 18–19), the vapor pressure of the solution is nearly that of the sulfuric acid solution alone.

I plan to extend this method to a number of sulfates which form more than one stable hydrate.

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ELECTRIC SYNTHESIS OF COLLOIDS.

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The present work was undertaken with a view to elucidate the process of formation of sols by the electric method first utilized by Bredig[2] for the preparation of sols in water, and subsequently modified by Svedberg[3] for obtaining sols in non-aqueous media and of various substances besides metals. Bredig's own method is now a general one and has been extended by others to media other than water.

Much difference of opinion exists as to the process of formation of the sol by these methods. Wo. Ostwald, and others,[4] hold that the process is of an electro-chemical nature and the substance goes into the liquid in the atomic form, under electric forces and afterwards becomes aggregated. Benedicks[5] and others lay stress on the thermal side of the process and are of the opinion that the metal partly volatilizes and partly

[1] Foote and Scholes, THIS JOURNAL, 33, 1309 (1911).

[2] *Z. angew. Chem.*, 1898, 951.

[3] *Ber.*, 39, 1703 (1906).

[4] Cf. Ostwald's *Grundriss der Kolloid Chemie.*

[5] *Z. Chem. Ind. Kolloide*, 11, 263 (1912).

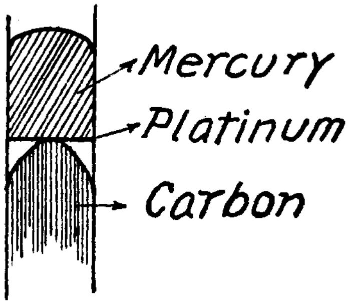
melts. Kutscheroff[1] has made experiments to prove his view of the process. He has studied the formation of sols using pairs of different metals as the two electrodes in Svedberg's method and has measured the amounts of the metals that pass into solution. He concludes that the metals go into the liquid as changed atoms, as shown by the fact that the ratio of the quantities of each passing into colloidal solution is the same as that of their equivalent weights. He, however, separates the coarse particles formed by the process by decantation and considers their formation to be due to a different process, possibly thermal, but adduces no reason for such assumption. His results show wide divergence from those of Svedberg. This divergence is due, possibly, to the uncertainty of the measurements, as we have to deal with small quantities of substances, and to Kutscheroff's arbitrary separation of the coarser particles.

Further, in cases of metals of variable valency, in calculating the ratio of the equivalent weights, in some cases he takes the metal to act with both valencies, sometimes with only one, thus acting quite arbitrarily, as pointed out by Benedicks. These considerations show that his data have not much significance.

Benedicks holds the view that the process of colloid formation is mainly of a thermal character and that the metal melts under the conditions into fine drops which remain suspended.

It seems possible that, under the intense heat of the powerful arcs produced in all these methods, the metal volatilizes and the surrounding liquid effects a sudden and rapid cooling and hence the vapor condenses to fine solid particles, resulting in a colloidal solution. Hence it was thought that if by any means the vapor of a substance which was solid at the ordinary temperature was produced in a liquid in which the substance was insoluble, a colloidal solution might be obtained.

To investigate the thermal effect it was decided to heat, under water, a substance which is insoluble in water. This was realized in the following way: The substance was finely powdered. A thin platinum wire was joined with two binding screws at the end of two stout copper wires clamped to two stands. These were in circuit with the adjustable resistance, two storage cells, an ammeter and a key. The platinum wire was thin enough to fuse with a current of 4 amps. in air. It was raised to a dull red heat by adjusting the resistance with a suitable current. The platinum wire was dipped in the pow-



Figure

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[1] *Z. Chem. Ind. Kolloide*, 11, 165 (1912).

dered substance, which melted and stuck to the wire. In this way, with a little care, a thin, uniform coating of the substance was obtained on the wire.

The coated wire was then placed in a beaker containing "conductivity" water just covering the binding screws at a temperature of about 2°.

A current of 15 amperes was then sent through the wire. This could be done without fusing the wire, as the surrounding cold water carries the heat very rapidly by convection. Very soon the liquid becomes colored and a sol is formed. Thus with sulfur a milky white coloration, which becomes deeper as the current continues, is obtained in five minutes. Sols of selenium and arsenic have also been obtained in this method. Arsenic shows a very fine cone when a beam of sunlight is passed through it (Tyndall phenomenon), but its yield is very small.

Certain organic substances, such as α-naphthol, benzophenone, dibenzyl, anthracene, etc., were treated in the above way and a sol-like formation was observed in most cases. But most of these substances are slightly soluble at a high temperature, so that on cooling an opalescence due to the separation of fine particles is visible. Hence no definite conclusion can be drawn from these observations.

The temperature to which the wire is raised in this way is, after all, not so high, so it was decided to utilize the intense heat of the carbon arc.

An arc between two carbon electrodes was struck under water with 220 volts and a current of 2 amperes. The electrodes were placed vertically one above the other. The lower one was coated with the substance in the following way: The substance was melted in a crucible and the carbon rod with a flat head was dipped into it and hence a thick coating was obtained. The centre of the coating was scooped out with a knife, forming a small hole exposing the carbon. The upper carbon electrode was rubbed to a point and was held just above the coated one so that the pointed end of the former was just above the hole exposing the carbon in the latter. On striking an arc, bubbles of water vapor rise with a hissing sound. These bubbles also carry with them vapors of the substance as shown by the fact that fine particles like little puffs of smoke with characteristic color come out and condense on the side of the beaker (or the vessel containing water and in which the arc is immersed) as small drops, if the depth of water above the arc be not too great. The outer layer of the bubbles condenses and in some cases forms a skin; when the bubble rises just above the surface, it breaks—the gas included within it goes away as a little puff of smoke.

In this way it is possible to obtain dispersions of S, Se, P, dibenzyl and β-naphthol.

When the arc is struck, the carbon electrodes become enormously heated. The distance between the two electrodes can be easily regulated so that it is possible to strike an arc with one just above and very near the coating, which becomes very much heated and the processes described previously take place. By a little practice the arc can be struck in the desired way.

Non-conducting substances were chosen to exclude any possibility of their taking part in the arc. Most organic substances are decomposed, however, at the high temperature of the arc, so very few of them may be used. It seems that both sulfur and selenium decompose water at the high temperature; these colloidal solutions show slight acid taste.

Sulfur, selenium, and phosphorus give good results. The deposit of phosphorus on carbon was obtained with white phosphorus melted under hot water. The low melting point of phosphorus presents some difficulties; the deposit melts and falls off to the bottom of the vessel when the arc is struck; but by repeated treatment of the same sample, fair yields are obtained. Another inconvenience is that the whole of the substance vaporized cannot be condensed completely under water, as part of it passes off as a vapor and another part condenses as a thin skin on the side of the beaker. With a small current density the yield is better. Since the liquid becomes hot during the experiment, it is better to cool the water with a freezing mixture.

In all cases "conductivity" water was used. With previously cooled water and with a current of 0.6 ampere good results are obtained in the case of selenium. The selenium sol improves on standing; this may be attributed to the oxidation of H_2Se by the atmospheric oxygen. If a little dilute nitric acid is added the effect is instantaneous. The sol is of brown color and is fairly stable.

Generally, when the sol is just prepared and is not disturbed, the upper part of the vessel contains the concentrated sol with the deep brown color.

All of these sols show the Tyndall phenomenon, a homogeneous cone of light being visible in all cases and they are fairly stable. The cone breaks up and finally disappears on the addition of electrolytes (*e. g.*, $ZnSO_4$, $BaCl_2$, etc.).

Also some observations were carried out with cadmium, mercury and copper.

Cadmium.—A deposit of the metal was made as usual on one of the carbon electrodes with a small hole exposing the carbon.

If the arc strikes directly on the metal, a green color is visible, but if it strikes on the carbon no color is noticeable. Little puffs of smoke containing particles of cadmium come out as in the case of sulfur. The hot cadmium reacts with water and some hydroxide is formed from the metal.

This sol being unstable, soon coagulates; the precipitate is found to consist of a mixture of cadmium and its hydroxide. Copper also behaves similarly, the sol is unstable and the precipitate is a mixture of metallic copper and copper oxide.

It may here be incidentally remarked that if the lower carbon electrode, on which the deposits of the above substances were made, be fitted with a platinum cup as shown in the figure and mercury placed in it, then on lighting an arc between the mercury and the carbon electrodes, a copious formation of the sol of mercury is observed. This sol has a grayish color and is not brown as observed by Lottermoser.[1]

The sol is quite stable. On the addition of hydrochloric acid, there is a precipitate, which does not dissolve in excess of concentrated hydrochloric acid, even on long standing and vigorous shaking. The filtrate also does not give any test of mercury salts. Evidently, colloidal solution of mercury is obtained in a state of great purity. The sol is charged negatively, as shown by its migration in an electric field.

This method is very rapid and gives very good yield with mercury, and is also very convenient.

The works of Traube-Mengarini and Scala[2] and Masamichi Kimara[3] show that heat alone may lead to the formation of sols. While trying to prepare a sol of α-naphthol or of mercuric iodide by the first method, it was observed that both substances have appreciable solubilities at the boiling temperature of water. Now if such a solution be rapidly cooled by immersing a test tube containing the liquid in a freezing mixture of ice and common salt, a suspension of small crystals resembling a sol is formed. The sol is not so fine as those obtained by chemical methods, but it resembles ordinary sols in its behavior towards electrolytes. Thus the thermal effect may be conceived to be due to the solubility of the substance at the high temperature of the experiment.

The conditions of these experiments being such that a rapid fall from a high to a low temperature takes place, we may have a release of supersaturation in the form of fine particles, resulting in a sol.

Though such an explanation may be applied to special cases, it cannot explain all cases in general, since it depends on the specific nature of the substance and the medium.

The process of sol formation by the electric method is that as already stated, under the intense heat of the arc discharge, the electrodes volatilize and subsequently, being condensed, form sols.

Many metals react very rapidly at this high temperature with water and although the substances are very rapidly cooled, yet there is time for their action on water to take place. This is shown by the fact that

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[1] *J. prakt. Chem.*, [ii] **57**, 484 (1898).

[2] *Mem. R. Accad. Lincei,* [v] **8**, 576 (1911).

[3] *Mem. Coll. Sci. Eng. Kyōtō,* **5**, 211 (1913).

the unstable sol of copper or cadmium consists of a mixture of the metal and the hydroxide.

It has been found out that the sol, when shaken with benzene, is divided into two parts, the hydroxide goes to the benzene layer while the metal remains in the aqueous layer. Copper sol prepared by Bredig's method was observed to be a mixture of the metal and the hydroxide. Blake[1] has observed that silver sol by Bredig's method reacts alkaline. In this case the particles consist mainly of the free metal but the little silver oxide (Ag_2O) present is sufficient to produce a red coloration with phenolphthalein, since silver hydroxide ($AgOH$) is a strong base.

The stability of metal sols prepared by these methods in water can be easily understood if we view it in the light of the above remarks. We know that sols of Au, Pt, Ag, etc., are only stable in water when prepared by electric methods, whereas those of more electropositive metals are unstable. In the case of Au, Pt, Hg and Ag, there is very little or no chemical action between the metals and water, so that the sol obtained consists entirely of metallic particles as shown by analysis.

In the cases of Cu, Cd, etc., we have a mixture of metal and its hydroxide due to chemical action with water.

Now the colloidal metallic hydroxides show electric migration to the cathode and hence are positively charged, the opposite is the case with the metallic particles. As a consequence, a colloidal solution of the one precipitates that of the other. This seems to be the explanation of the varying stability of different metallic sols in water prepared by these methods.

It is seen that a silver sol prepared by Bredig's method is fairly stable, though it has been found to be alkaline to indicators. The very small amount of Ag_2O formed remains completely in the state of ordinary solution and not as a sol, since no trace of alkali or Ag_2O is obtained in the coagulum produced by neutral electrolytes. It is well known that alkalies in very small concentrations stabilize a metallic colloidal solution and hence the small amount of alkali due to the solution of silver hydroxide makes the silver sol more stable. Consequently, the foregoing explanation can be consistently applied in the study of the stability of metallic colloidal solutions in general prepared by electric methods in water.

In conclusion, it may be stated that the high temperature of the arcing electrodes may explain the formation of sols simply as a thermal process.

My best thanks are due to Professors Rây and Bhaduri.

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[1] *Am. J. Sci.*, [iv] **16**, 431 (1903).