known water content saturated with potassium thiocyanate, and (2) the determination of the water content in *iso*-amyl-alcohol solutions which had been brought into equilibrium with pairs of hydrates of accurately known vapor pressure.

The results of the conductance—water-content determinations are given in Table I, and those of the vapor–pressure—water–content measurements are summarized in Table III. A vapor-pressure—composition diagram for the water–*iso*-amyl-alcohol mixtures is shown in Fig. 1, which is probably typical for liquids of limited but considerable miscibility.

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THE ACTION OF SODIUM SULFIDE ON FERRIC OXIDE.

BY J. C. WITT.

The color produced by the action of alkaline sulfides on compounds of iron and certain other metals has been noted by several investigators. De Koninck and Ledent[1] observed that when solutions of nickel, cobalt, or iron salts were treated with an excess of sodium sulfide, the mixture became dark, but remained clear and would pass unchanged through the finest filter papers. In the case of iron salts the color gradually changed to a bright green, resembling chrome sulfate or potassium manganate. The authors did not comment on the cause of the color. A number of years later, de Koninck[2] recommended the reaction as a test for iron. He stated that it was as delicate as the ferrocyanide reaction and could be used equally well with the ferrous or ferric ion. In very dilute solutions, the color changed from brown to green. In the presence of sodium chloride or sulfate, the formation of the green substance was retarded and then disappeared more quickly. The effect of the presence of zinc, aluminum, magnesium and cadmium was discussed. De Koninck was of the opinion that oxidation and reduction were not concerned in the change from brown to green but that the color was due to colloidal iron sulfide.

Konschegg and Malfatti[3] have studied the reaction between potassium sulfide and iron salts. They believe the color is not due to colloidal substances, but to the solution of some higher sulfide of iron in the alkali. They state that on dialysis the potassium is removed, leaving behind a black or brownish-black solution of iron sulfide. Szilard[4] has prepared what he terms heterogeneous colloidal hydrates, by treating the hydroxide of a metal with the salt of the same, or of a different metal. He has studied the hydroxides of uranium, thorium, zirconium. lead, yttrium,

[1] De Koninck and Ledent, *Z. angew. Chem.*, **1891**, p. 202.

[2] De Koninck, *Bull. soc. chim. Belg.*, **19**, 181; *J. Chem. Soc.*, **90**, 397 (1906).

[3] Konschegg and Malfatti, *Z. anal. Chem.*, **45**, 747 (1906).

[4] Szilard, *J. chim. phys.*, **5**, 636 (1907).

iron and copper. The resulting mixtures are highly colored and possess the properties of colloids. They do not show the characteristic reactions of the metals which they contain.

The reaction between sodium sulfide and ferric oxide seems to belong to the same class as the reactions mentioned above. A vivid green color is produced. The results obtained indicate a colloid rather than a solution of a higher sulfide of iron. If such a sulfide exists, it is unstable, for all attempts to isolate it have failed. It is difficult to understand why the iron would not pass through a dialyzing membrane, if it were present in true solution.

The present investigation suggested itself in connection with some work on the effect of sodium sulfide on portland cement.[1] With solutions of higher concentrations a green color was always produced and it soon became apparent that the depth of color was directly proportional to the concentration of the sulfide solution and also, in general, to the iron content of the cement. Further, the general effect of sulfide on the set and tensile strength of a given cement seemed related to the amount of iron present. With the object of obtaining data which might throw light on the rôle of the sulfide it was decided to study the product of the reaction between ferric oxide and sodium sulfide. Because of the small amount of iron in cement it was not practicable to use cement itself.

After several trials, the following method of preparation was developed. Five g. of finely powdered ferric oxide was placed in a porcelain evaporating dish, and mixed with 350 g. of crystalline sodium sulfide. The mixture immediately became greenish-black. On heating with a Bunsen burner the sulfide melted to a syrupy consistency. It was necessary to stir constantly to avoid spattering. As the water of crystallization evaporated the mass became very thick and viscid. On continued heating and stirring, the mass melted to a thin liquid and was poured while still hot into a beaker of water. Meanwhile small amounts of the mixture had been removed from time to time and a small quantity of dil. hydrochloric acid added. The sulfide mixture immediately dissolved. Ferric oxide remained undissolved in the cold. Invariably all the ferric oxide had disappeared by the time the mass melted. Also, at this stage, a few drops of the liquid added to a beaker of water produced temporarily a bright green coloration.

When the liquid was poured into distilled water a portion of it—largely the excess sulfide—mixed with the water. The remainder formed a black, amorphous, somewhat gelatinous precipitate. No iron remained in the liquid. When most of the sulfide liquor had been removed by filtration under suction, a small amount of the precipitate produced the characteristic green color if placed immediately in water. When more sulfide was

Witt, *Phil. J. Sci.*, Sec. A., 11, 273 (1916).

added to this highly colored solution, a precipitate was again obtained. Alternate solution and precipitation could be produced a number of times. However, when the precipitate was exposed to the air for a few minutes it did not produce the green color on addition of water only, but by adding a small amount of sulfide and boiling.

After the behavior of the substance in respect to sulfide had been learned, a larger quantity was prepared. The precipitate was quickly filtered out in a Büchner funnel and the excess liquid removed by suction. The solid material was then placed in a flask, boiling water was added, and the mixture stirred. The flask was covered, the liquid was allowed to cool, and afterward portions of the clear green liquid were withdrawn by pipets for examination. Unless otherwise stated, all the tests hereafter described were made with this liquid, or with the precipitate before adding water. For convenience we shall call the precipitate formed by pouring the sulfide into water—the precipitate; the solution left after filtration—the filtrate, and the green liquid produced by placing the precipitate in water—the sol.

The following methods were employed to determine the nature of the reaction products: (1) extraction of the precipitate with alcohol; (2) indirect analysis of the sol and the filtrate; (3) dialysis of the sol; (4) oxidation and reducton.

Extraction with Alcohol.—Since it was impossible to wash the precipitate with water—because of the formation of the green liquid—extraction with alcohol suggested itself. A portion of the precipitate was placed in a Soxhlet apparatus and extracted for 24 hours, or until fresh portions of the solvent contained no more solids. The residue was then dried as much as possible in a current of hydrogen (to avoid oxidation). It was impossible to purify the solid completely, but several determinations were made to obtain some idea of its composition. There were found to be present sulfur and iron, with small amounts of sodium, and sulfur as sulfate. The test indicated that the pure precipitate contained no sodium in chemical composition and consisted only of iron or of iron and sulfur.

Indirect Analysis.—It was not possible to free the solid entirely from the filtrate nor to dry it without decomposition. Therefore indirect analysis[1] was resorted to for calculating the relative amounts of iron and of sulfur present. A new portion of the precipitate was prepared and separated from the filtrate. Some of the green sol was prepared from this by the addition of water. Aliquot portions of the sol and of the filtrate were then analyzed, with the following results (g. per liter).

Sol: Iron, 0.0672; sodium, 0.7486; total sulfur, 0.4443.

Filtrate: Iron, none; sodium, 74.4100; total sulfur, 43.7438.

[1] Cf. Neidle and Witt, THIS JOURNAL, **37**, 2365 (1915).

The ratio of the sulfur to the sodium in the filtrate (S/Na) is 0.5879. Since there is no sodium in chemical combination with the iron, all the sodium in the liquid is due to adsorption (by the precipitate).

If we assume the sulfide ion and the sodium ion are adsorbed in approximately the same proportion as they are present in the filtrate, we have $0.5879 \times 0.7486 = 0.4401$ g., the total sulfur due to adsorption. This leaves only 0.0042 g. to be combined with 0.0672 g. of iron, or approximately 1 atom of sulfur to 12 atoms of iron. Although these figures cannot be considered exact because the relative amounts of the two ions adsorbed are not accurately known, the two attempts to analyze the precipitate indicated that it contains neither sodium nor sulfur in chemical combination. A number of considerations indicate that the precipitate is colloidal and that the green liquid is a sol, among which may be mentioned the following.

Evidently the color is not due to a substance in suspension. No separation of solid and liquid could be effected either by filtering or by centrifuging.

The liquid contains iron, yet gives no test for either the ferric nor the ferrous ion. This indicates either a sol, or that the iron is present as a complex ion.

At about 30° the liquid, though brilliant green, contained only 0.0672 g. of iron per liter. The color was still apparent in dilutions of 1 : 1000. One of the well-known characteristics of metallic sols is the intense color produced by very small quantities of a metal. This equivalent of iron present as any ordinary ferrous salt would produce a practically colorless solution.

Several electrolytes other than sodium sulfide were capable of producing a precipitate containing iron, that could not be explained ionically.

Dialysis.—One hundred cc. of the sol was placed in a collodion bag for dialysis. At the end of 36 hours the color changed to brown, but the outside liquid remained clear. After a few days more, a precipitate resembling hydrous ferric oxide appeared inside the bag, leaving the liquid clear and colorless. The dialysis was allowed to continue for several weeks after substances ceased to come through. The contents of the bag and the concentrated diffusate were analyzed. The sulfur and all but a trace of the sodium had passed through. All but a trace of the sulfide had been oxidized to sulfate.

The general behavior of the liquid during dialysis indicated that oxidation was taking place. Apparently the sulfide ion was being removed by both dialysis and oxidation, and when the concentration was very low, the iron became oxidized from contact with the air and precipitated as hydrous ferric oxide. To eliminate any changes due to oxidation, a second dialysis was performed in an atmosphere of carbon dioxide. The

apparatus employed was suggested by the one recommended by Neidle.[1] A parchment paper bag of about 300 cc. capacity was immersed in a large beaker containing several hundred cc. of the green liquid. Distilled water, recently boiled, was run into the bag and maintained automatically at a constant level. The beaker rested on a small electric hot-plate. The current was regulated by a rheostat so that the contents of the beaker were kept just below the boiling point. The whole apparatus was enclosed in a bell jar, connected with a Kipp generator furnishing carbon dioxide. Before heating the liquid, the air in the apparatus was washed out by a current of carbon dioxide. The exit of the gas was then closed but the generator left connected, so that in case any leak developed, the gas would be forced out but no air could enter. Provision was made by which some of the liquid could be removed for examination without disturbing the experiment or admitting any air.

The changes in the liquid were considerably different from those observed during the dialysis in presence of air. There was no change in color for 48 hours, but at the end of that time a dark—almost black—precipitate commenced to appear. The liquid was clear and colorless. At the end of a week, some of this liquid was removed. It was found to contain no substance in solution. Portions of the black precipitate were removed and tested. No sulfur was present. A solution in hydrochloric acid resulted in the ferrous ion. Due to the very small amount of iron contained in the original green liquid, the total mass of the precipitate was too small for making a complete analysis. The results of the dialysis support the belief that the green liquid is a sol, and that the dispersed phase contains no sodium nor sulfur in combination, though its exact composition has not been determined.

The sol may be preserved for 2 or 3 months if sealed in a tube, but in contact with the air is not stable. The color fades and after several weeks a brown precipitate forms, apparently the same as that formed during the dialysis in presence of air. The total iron is found in the precipitate. All the sulfide becomes oxidized to sulfate.

Interesting results may be obtained by drawing air through the green sol. The green changes to brown and analysis shows that the green just disappears when all but a trace of the sulfide has been oxidized to sulfate. When the color change is complete, another sol is formed in which the iron is all in the ferric condition—resembling colloidal hydrous ferric oxide. No test for either ferrous or ferric iron can be obtained. If this brown sol is sealed in a tube, its appearance remains unchanged for months. However, the iron may be precipitated by boiling for a few minutes or by drawing air through the sol for several days.

[1]   Neidle, THIS JOURNAL, 38, 1270 (1916).

Oxidation of Sulfide by Ferric Oxide.—When ferric oxide is warmed with sodium sulfide solution for a few minutes in contact with air, the oxidation of sulfide to sulfate is only slight, and might be accounted for by the presence of atmospheric oxygen. However, since after the operation the iron is in the ferrous condition, it seemed likely that oxygen from the ferric oxide combines with the sodium sulfide. This reaction was traced by comparing the amount of sulfide oxidized in absence of air with the amount of ferric oxide reduced by the sulfide. As has been stated, the film cannot be completely removed from the unchanged ferric oxide by washing alone. Therefore, it was necessary to find some solvent for the film that would not attack the ferric oxide. 50 % acetic acid was found to fulfill these requirements. It dissolved the film readily but when left in contact with ferric oxide on the steam-bath overnight, only a trace of iron was in solution.

Three 500-cc. volumetric flasks were connected with a hydrogen generator and placed on a steam-bath. The first contained 20 cc. of 10% sodium sulfide solution; the second, an equal quantity of the same solution, plus 5 g. ferric oxide; and the third, 5 g. ferric oxide. All the air was displaced from the flasks and they were kept on the steam-bath overnight. Fifty cc. of 50% acetic acid was added to each flask, and the mixture allowed to remain for 24 hours longer on the steam-bath. The flasks were then disconnected, cooled, and made up to volume. A portion of the contents of each was filtered and 50-cc. portions were removed for analysis. The solution in the first was analyzed for sulfate; that in the second for sulfate and iron, that in the third for iron only.

The difference in sulfate content between the first and second flasks must have been due to the reaction with ferric oxide, since the air was excluded. The iron in solution in the second flask was due to the action of the sulfide, since in the third flask no iron went into solution with the same amount of acetic acid.

The values given below were calculated from the results of the analyses (50-cc. portions):

	G.
Sulfate (SO_4) formed by reaction with ferric oxide	0.0216
Equivalent to oxygen	0.0144
Ferric oxide (Fe_2O_3) reduced by action of sodium sulfide	0.0425
Equivalent to oxygen, assuming Fe_2O_3 is reduced to Fe	0.0128
Equivalent to oxygen, assuming Fe_2O_3 is reduced to FeO	0.0043

The necessary amount of oxygen for oxidizing the sodium sulfide can be obtained from the ferric oxide, assuming a molecule gives up all its oxygen as can be seen from the above results.

This relation is expressed by the equation,

$$4Fe_2O_3 + xNa_2S \longrightarrow 8Fe + 3Na_2SO_4 + (x - 3)Na_2S.$$
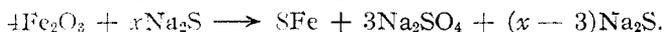
Summary.

When ferric oxide is treated with an excess of sodium sulfide a black amorphous substance is formed. On removing most of the remaining sodium sulfide and adding water, a brilliant green solution is produced. The results obtained on studying the solution indicate that the color is due to a colloid and not to a true solution of some iron compound. The exact composition of the dispersed phase has not been determined but apparently it contains neither sulfur nor sodium in chemical combination.

The colloid is reversible. It is precipitated by a relatively large amount of sodium sulfide, and is regenerated when the precipitating agent is removed. This process may be repeated several times.

Sodium sulfide acts also as a protecting agent. The sol can exist only in the presence of a small amount of the sulfide. When the last trace is removed either by dialysis or by oxidation, the colloid is precipitated.

By drawing air through the sol until the sulfide is oxidized to sulfate, a new sol is prepared. This is brown in color and apparently consists of colloidal hydrous ferric oxide. The iron compound is eventually precipitated, though it may remain colloidal for a time.

The green sol contains less than 0.07 g. of iron per liter and cannot be dialyzed in the presence of air. It is therefore exceedingly difficult to determine the exact composition of the dispersed phase.

CHICAGO, ILLINOIS.

STRUCTURE OF GOLD AMALGAMS AS DETERMINED BY METALLOGRAPHIC METHODS.[1]

BY S. A. BRALEY AND R. F. SCHNEIDER.

Introduction.

In connection with some diffusion experiments by G. McP. Smith,[2] it was found that the recorded data on gold amalgams were conflicting and uncorrelated. Most of the work covered only a small part of the equilibrium diagram, while no attempt appears to have been made to apply cooling curves in the study. The present work was attempted to obtain cooling curves of the amalgams and to construct a complete equilibrium diagram of the gold-mercury system.

Historical.

The amalgams of gold were studied by Sonnenschein and Rammelsberg

[2] G. McP. Smith, Z. anorg. Chem., 88, 616 (1914).