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).

in 1863 and 1866.[1] They devoted themselves mainly to the qualitative work. Henry,[2] in 1855, studied the solubility of gold in mercury and showed that mercury dissolved at least 0.14% of gold. Kasantseff[3] pressed amalgams through a chamois skin and found that the gold retained some mercury. He also isolated crystals of amalgams at various temperatures by passing the amalgam through capillary tubes. From this he determined the solubilities of gold in mercury at various temperatures.

Souza,[4] in 1875, made amalgams of gold, which he heated to constant weight and found that the gold retained about 10% of mercury. From this he assumed that a compound of gold and mercury with the formula Au_9Hg was formed.

In 1876 Merz,[5] heating gold in the presence of mercury vapor, found that gold took up 10% of mercury vapor, and assumed that compounds Au_9Hg and Au_8Hg existed.

In 1881 Merz[6] and Weith, on heating gold amalgams, found that the mercury distilled from the amalgam at a red heat, but that the gold retained 0.1% of mercury until a temperature slightly below its melting point was reached.

Wilm,[7] in 1893, dissolved gold in sodium amalgam, and on boiling the product in nitric acid, found that from 9.5 to 11.5% by weight of mercury remained with the gold. He concluded that amalgams up to 10% of mercury were in a state of solid solution. Henry[8] obtained similar results, but Kasantseff and Knaffl[8] later opposed the work of these men.

Various authors report native amalgams of gold which correspond to the formulas Au_2Hg_3 and Au_2Hg_2. Louis tried to prepare compounds according to these formulas but was not very successful.

In 1908 G. McP. Smith,[9] in studying diffusion phenomena, stated that "although intermediate crystals have not been obtained, compounds of mercury and gold do appear to be formed."

Parravano[10] in 1918 made a fusion diagram of amalgams containing from 0 to 35% gold. He found that a horizontal line was obtained at 100°, and states that this line corresponds to a reaction between a solid separating at a higher temperature and the liquid to form a new solid, stable at a lower temperature. In 1919 Parravano studied the conduc-

[1] Rose, "Metallurgy of Gold," 6th Ed., 1915.

[2] Henry, *Phil. Mag.*, [4] 9, 458 (1855).

[3] Kasantseff, *Ber.*, 11, Ref., 1255 (1878).

[4] Souza, *ibid.*, 8, 1616 (1875).

[5] Merz and Weith, *ibid.*, 9, 1050 (1876).

[6] Merz and Weith, *ibid.*, 14, 1440 (1881).

[7] Wilm, *Z. anorg. Chem.*, 4, 325 (1893).

[8] *Loc. cit.*

[9] G. McP. Smith, *Ann. Phys.*, 25, IV, 252 (1908).

[10] Parravano, *Gazz. chim. ital.*, 48, II, 123–39 (1918); 49, I, 1–6 (1919).

tivity of the gold end of the diagram, finding that the conductivity decreases as the percentage of mercury increases. He, however, determined the conductivity in amalgams containing only 10% of mercury or less.

Materials.

The gold used in this experiment was prepared by dissolving gold in aqua regia, removing the excess of nitric acid by repeated evaporation and precipitation with pure ferrous sulfate.

The mercury was prepared by redistillation of c. p. mercury.

Apparatus.

Since mercury distills from a gold amalgam when heated (above the boiling point of mercury), and is almost completely expelled at red heat, a special bomb was made so that the amalgam could be heated under pressure and thus prevent the mercury from distilling. A pressure gage was attached to the bomb and means provided whereby a thermocouple could be introduced.
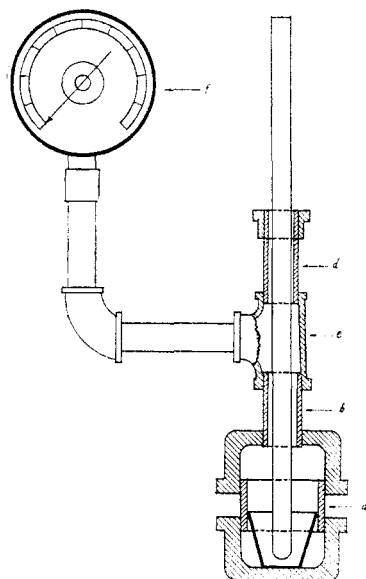
The bomb was made of a piece of 37 mm. pipe, a. A cap was placed at each end. The upper cap had a 6 mm. hole in which a short nipple b. was screwed. A "tee," e, was screwed onto this nipple and another nipple, d, and a packing nut or cap was screwed into the top of the "tee." A quartz tube was placed down through the inside of the "tee" and reached almost to the bottom of the bomb. The quartz tube was fastened in by means of asbestos packing, and the joint made air-tight. The side arm of the "tee", led to a pressure Gage f.

The crucible containing the amalgam was placed in a. The quartz tube led down into the amalgam and acted as a holder for the thermocouple. The bomb was heated in a pot furnace.

The thermocouple was made of constantin and iron and was standardized against the melting point of tin and antimony, and the boiling points of sulfur and distilled water. For the temperature below 0° it was standardized against an accurate thermometer to —20°, and the freezing point of mercury. All readings were taken on a sensitive Siemens and Halske millivoltmeter.

Fig. 1.

Experimental.

A. Amalgams.—The amalgams were made by adding the mercury to the gold and gently warming whereby the mercury distributed itself through the gold. The amalgam was then placed in the crucible in the bomb; the bomb screwed together and the whole heated until the amalgam was liquefied. The heat was then shut off and the furnace and bomb allowed to cool and the rate of cooling observed.

B. Cooling Curves.—The inverse-rate curve was used in order that any small heat effects would be easily noticed. In this method the ord-

inate represents the temperature and the abscissa represents the time necessary for the temperature to fall through a definite small interval (1° in this case).

C. **Analysis of Amalgams.**—Each amalgam was analyzed after the cooling curve was taken, the method of analysis being as follows. The amalgam was broken up in a mortar, and the mercury dissolved out from a weighed sample by means of nitric acid; the gold was then filtered off, dried, ignited to low redness and weighed, the difference in weight being mercury.

The method first used was to weigh the amalgam and dissolve it in aqua regia. The solution was then evaporated to dryness, taken up with water and again evaporated in order to remove the excess of nitric acid. The residue dissolved in water, and the gold was reduced to the metallic state by means of ferrous sulfate, filtered off, washed, dried and weighed. The two methods were compared and it was found that if the amalgam was broken up so that no large lumps remained the mercury could be removed from the gold by means of nitric acid. When 9.8335 g. gold was added to 29.9194 g. of mercury the aqua regia method gave 9.8325 g. of gold, and the nitric acid 9.8330 g.

D. **Freezing Mixture.**—Carbon-dioxide snow and ether were used to determine the freezing point of the amalgams containing from 80 to 100% mercury. Of these amalgams both the freezing points and the melting points were determined. The amalgam was slowly cooled and the temperature of freezing was noted. After the amalgam had solidified it was

TABLE I.

Composition of amalgam.		Temp. of heat effects, ° C.		
% Hg.	% Au.	I.	II.	III.
8	92	680	580	. . .
14	86	520	418	. . .
15	85	520	390	. . .
20	80	450	390	. . .
25	75	390	. . .	. . .
28	72	420	390	. . .
30	70	450	390	100
35	65	490	100	. . .
40	60	455	100	. . .
45	55	415	100	. . .
50	50	350	100	. . .
55	45	250	100	. . .
57	43	250	100	. . .
60	40	260	100	. . .
65	35	280	100	. . .
70	30	297	100	. . .
75	25	290	100	. . .
80	20	100	—41	. . .
82	18	85	—41	. . .
85	15	—41	. . .	. . .
90	10	—38	—41	. . .
95	5	—38	—40	. . .
100	. .	—38.85	. . .	. . .

further cooled and then allowed to warm up slowly until melted and the melting point was determined.   Check determinations were made on all points and three in the case of any doubtful ones.

Photomicrographs were made of the compounds, and eutectics were found in order that the structures of the amalgams at these points might be observed.   It was found that polished specimens could be photographed without etching.

Data and Results.

Table I gives the results obtained by the cooling of the various amalgams, the composition of the amalgam being given in atomic per cent. Under the heading "Temperature of Heat Effects," "I" indicates the first effect noticed as the amalgam cooled, which is the heating effect, "II" indicates the second effect, while "III" is the third effect.   Only one amalgam (30% Hg, 70% Au) showed three points on the cooling curve. Fig. 2 shows the phase-rule diagram obtained from the data of Table I.

Discussion of Results.

From Fig. 2, the phase diagram obtained from the heat effects as given in Table I, it is seen that the mercury dissolves in the gold to form a solid solution, the limit of this solubility being 15 atomic per cent. of mercury or 15.18% by weight.   This is in accordance with the results obtained
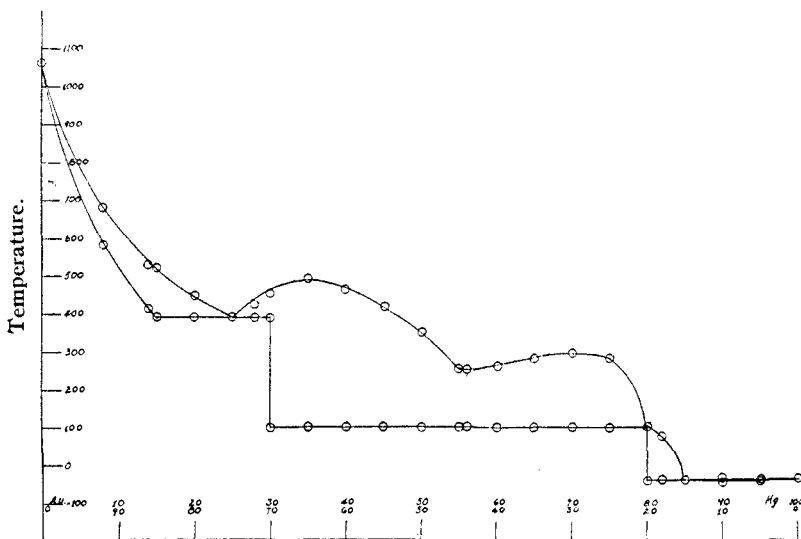

Fig. 2.—Composition in atomic per cent.

by Wilson[1] and Parravano,[1] who both stated that a solid solution was formed.   However, they worked only with the amalgams up to 10% of mercury, and so did not give the limit of solubility.

[1] *Loc. cit.*

A compound between mercury and gold is formed as a concentration of 35 atomic per cent. of mercury and 65 atomic per cent. of gold. This compound, which freezes at $490°$, and corresponds to the formula Au_2Hg, froms a eutectic with the above solid solution which freezes at $390°$. The composition of the eutectic is given as 25 atomic per cent. of mercury and 75 atomic per cent. of gold.

At the composition of 70 atomic per cent. of mercury and 30 atomic per cent. of gold a second compound is formed which has the formula Au_5Hg_5. This compound, however, does not form a true eutectic with the compound Au_2Hg.

A third compound is formed at a composition of 20 atomic per cent. of gold and 80 atomic per cent. of mercury. This compound has the formula $AuHg_4$. It forms a concealed maximum at $100°$. This concealed maximum is a break in the curve which is due to the decomposition of the compound $AuHg_4$ at its melting point into Au_2Hg_5 and Hg, the decomposition being shown by the following reaction:

$$2AuHg_4 \rightleftharpoons Au_2Hg + 3Hg$$
$$\text{solid} \qquad \text{solid} \quad \text{liquid}$$
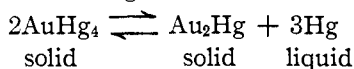
The reaction from left to right is effected by the addition of heat, while abstraction of heat, or cooling, would cause the reaction to go to the left.

The compound $AuHg_4$ has been reported in work previously done.[1] It forms a eutectic with the solution of gold in mercury which freezes at $—41°$. The composition of this eutectic is 85 atomic per cent. of mercury and 15 atomic per cent. of gold.

A horizontal line is obtained at $100°$ between the compositions 80% mercury and 20% gold, and 30% mercury and 70% gold. At 80% mercury and 20% gold it corresponds to the freezing point of the compound $AuHg_4$. At this point the temperature in the cooling curve remained constant for 180 seconds, which indicates that a large amount of heat was evolved. The amount of heat evolved as the percentage of gold was increased gradually decreased and at the composition of 30% mercury and 70% gold the temperature under the same conditions of cooling remained constant for only 5 seconds. This horizontal line indicates that a transformation takes place in the solid state. Since the time of change gradually decreases as the percentage of gold increases it would indicate that the compound $AuHg_4$ is present and that it gradually decreases toward the gold end of the diagram.

Summary.

Cooling curves for the amalgams of gold were made and a phase diagram constructed.

It has been found that (in the gold–mercury system) there are two eutectics, and three compounds, namely, Au_2Hg, Au_2Hg_5 and $AuHg_4$.

[1] Parravano, *loc. cit.*

The compound $AuHg_4$ decomposes into Au_2Hg_5 and Hg at its melting point.

Photomicrographs were made of the eutectics and compounds both as cooled in air and quenched just below the freezing point. Because of difficulty of reproduction these are not published.

The authors wish to express their gratitude to Dr. G. McP. Smith for the original conception of the problem and also the method of attack.

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[CONTRIBUTION FROM THE WALKER LABORATORY, RENSSELAER POLYTECHNIC INSTITUTE.]

NITROSO R-SALT, A NEW REAGENT FOR THE DETECTION OF COBALT.

BY H. S. VAN KLOOSTER.

As is well known, Tschugaeff's reagent dimethylglyoxime affords an extremely sensitive means of detecting nickel even in the presence of large quantities of cobalt. Experiments show that one part of nickel in 400,-000 parts of water still gives a red coloration, and it is possible to detect nickel in the presence of 5,000 times its weight of cobalt.

It is interesting to note that an oxime of the naphthalene series affords an easy and sensitive means for the detection of cobalt in the presence of an excess of nickel and that it can also be applied when other metals are present in the solution.

Although a number of related compounds have been described in the literature, this oxime itself has not been described.

Hoffmann[1] mentions the preparation of the nitroso compound of Schaeffer's salt (sodium 2,6-β-naphtholsulfonate) which yields with ferrous salts green, and with cobalt salts brownish-red dyes. The iron dye is known as naphthol green B and its formula is given as $(C_{10}H_5NO_5SNa)_2Fe$.[2] Knecht[3] finds that cobalt salts form brown coloring matters while nickel salts produce yellow colors.

By treating R-salt (sodium 2,3,6-β-naphtholdisulfonate) with nitrous acid a similar nitroso derivative is formed to which the following structure must be ascribed.
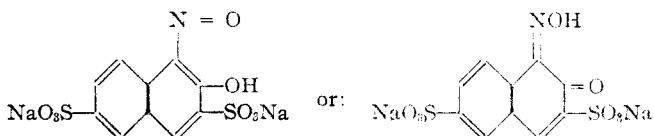
Calc., Na: 12.20.   Found: 11.96, 11.63.

[1] Hoffmann, *Ber.*, **18**, 46 (1885).

[2] Green, "Organic coloring matters," London, 1908, p. 170.

[3] Benedict-Knecht, "The Chemistry of Coal Tar Colors," London, 1886, p. 153.