trite, hydrogen peroxide, saturated chlorine water and potassium permanganate are, respectively, used to liberate the iodine.

3. A rapid and reliable method is proposed which is capable of detecting one mg. iodine as iodide in the presence of 500 mg. of cyanide.

[Contribution from the Chemical Laboratory of the University of Wisconsin.]

A STUDY OF THE CHEMISTRY OF GOLD AT HIGH TEMPERATURES AND PRESSURES.[1]

By Harold H. Morris.

Received April 2, 1918.

This contribution to the chemistry of gold is the result of one of a series of investigations undertaken in the chemical laboratory of the University of Wisconsin on the deposition and alteration of various minerals due to the effects of heat and of aqueous vapor pressure. A particular study was made of the compounds of gold because of the relation of such a study to the theories concerning the deposition of gold in nature.[2]

The apparatus used here is described in detail, since it is expected that only slight modifications will be necessary in carrying on further work in this field. It consisted of an electrically heated steel bomb, and a platinum platinum-rhodium thermocouple used in connection with a potentiometer for temperature measurements.

The steel bomb was of the general type of the Morey bomb,[3] the several parts of which are shown in cross section in Fig. 1, which is drawn to scale. The material used in the construction was electric chrome-vanadium steel. The three principal parts of the bomb are A, B and E. The body

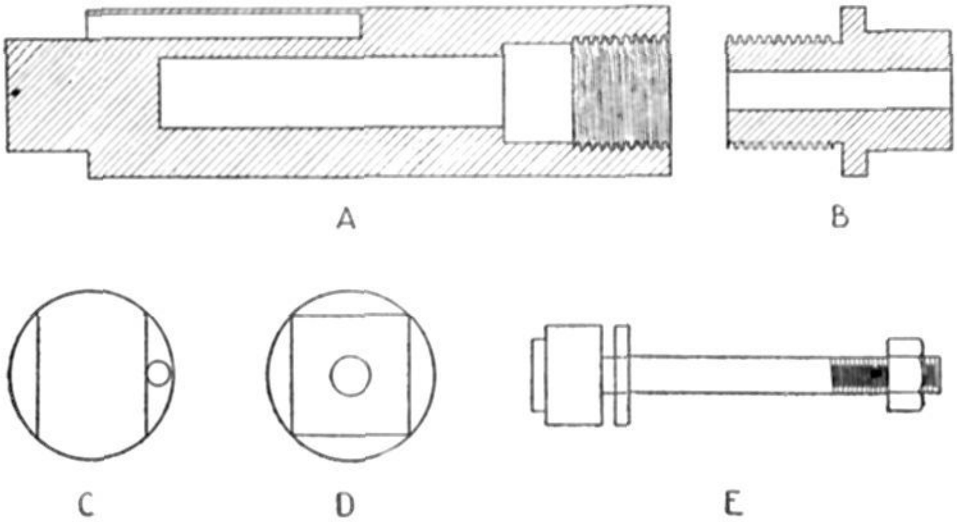

Fig. 1.

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[1] A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Lenher and Morris, *Econ. Geol.*, [3] 13, 161.

[3] Morey, This Journal, 26, 215 (1914).

of the bomb A consisted of a cylinder 3 inches in diameter and 12 inches long. The two sides of the bottom were squared off for 1.5 inches so that it might be set in a steel plate having a corresponding opening. This plate was fastened to the floor and acted as a vise. The bottom of the bomb is shown in C. A hole $^7/_{16}$ inch in diameter and 5 inches deep in the wall of the bomb A and C, provided a place for the thermocouple which was encased in a quartz tube.

The chamber in the center of the bomb where the reactions were carried on was $6^3/_8$ inches deep, and $1^1/_4$ inches in diameter. Closure was effected by the parts shown in B and E. The end of the plunger fitted tightly into the top of the central chamber shown in A, while a copper gasket $^1/_8$ inch thick rested on the seating immediately above. The stem of the plunger, $^5/_8$ inch in diameter, moved easily through the opening in the plug B, $^3/_4$ inch in diameter, and was held in place by a nut at its outer end. The cylindrical portion in A corresponding to the end of the plunger was made with a 5° taper so that a slight loosening of the plunger allowed it to move freely. The plug B was provided with an Acme thread of 8 turns to the inch. The top of the plug was cut down to a square $2^1/_8$ inches on a side, a top view of which is shown in D. The object of constructing the cap of 2 pieces was to avoid turning the copper gasket on the seating either during the opening or closing of the bomb. Such tendency toward turning as resulted when the plug was tightened was obviated by inserting an iron washer between the top of the plunger and the bottom of the plug. When the bomb was opened the small nut at the end of the plunger was first loosened, then as the plug was turned out it exerted a straight pull on the plunger, which brought the copper gasket out with it. A 36-inch spanner wrench was used for removing the plug.

The heating furnace was constructed of a piece of 3-inch iron pipe 20 inches long, attached firmly to a circular piece of sheet iron 10 inches in diameter, the edges of which were turned up at right angles so that it could be bolted to the sheet iron jacket which surrounded the whole. The pipe was covered with alundum cement, dried, and wound with No. 18 nichrome wire, the terminals being carried out at either the top or the bottom of the furnace. A 10-inch cylinder of sheet iron 20 inches long was placed around the pipe and bolted to the sheet iron plate at the bottom. This jacket was filled with finely powdered magnesium oxide and asbestos, and a cover bolted into place. Two short pieces of $^3/_8$-inch pipe provided with caps fastened to the sides of the jacket slightly above the center, rested in supports as indicated in the diagram, and permitted the furnace to be rotated to any angle. The lower end of the 3-inch pipe was covered by a cap screwed to the bottom of the furnace. A small hole was cut through this cap to allow introduction of the thermocouple.

Above the cap was placed a plug of asbestos about 3 inches deep so that the bomb, when in place, would be in about the center of the furnace, and so be more evenly heated.

The heating of the furnace was controlled by means of a rheostat. The wiring of the switchboard used in connection with the furnace is shown in Fig. 2. The light A indicated whether or not current was on the line. The fuse plugs C and D were provided with 15-ampere fuses. The resistance wire in the rheostat was No. 18 nichrome wire in one-foot sections. The light B .was connected so that it would burn when the switch E was opened, provided the heating coil in the furnace was intact, and it also served as an additional heat control. The current delivered at the board' was from a 110-volt alternating circuit. The junction of the thermocouple was encased in a quartz tube and inserted through the lower end of the furnace into the opening provided for it in the steel bomb. The outer ends of the couple were connected by means of copper wire to the potentiometer, the junction of the wires being maintained at 0°.

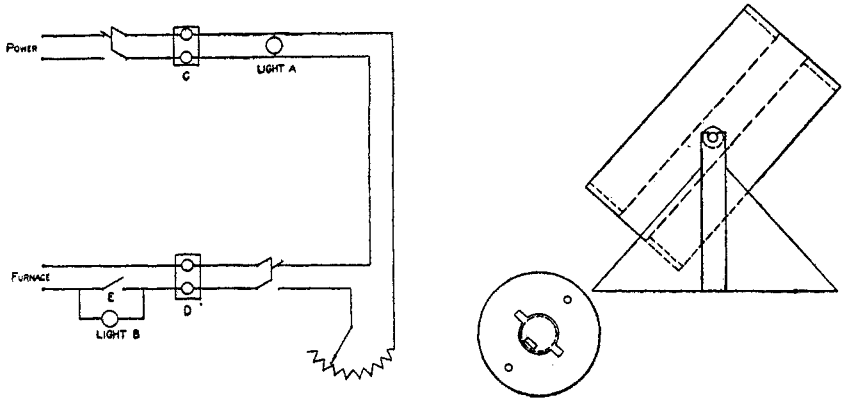

Fig. 2.

Standardization of Apparatus.

Two standardized thermocouples were recalibrated using boiling naphthalene and boiling sulfur. The curves accompanying the instruments were found to be correct.

One couple was placed in position in the bottom of the bomb, and the other was placed inside the bomb. Simultaneous readings were taken throughout the range of temperatures to be used. It was found that the difference in temperature between the couple in the bottom of the bomb and the one inside the bomb did not exceed 5°, which was about the limit of accuracy of the temperature reading as a whole.

Method of Experimentation.

The general method of performing the experiments was as follows: The inside of the bomb was thoroughly cleaned with a brush and distilled water. The solutions or materials to be used were placed in a quartz tube, which was covered with a quartz crucible, and lowered into the bomb by means of a platinum wire. Sufficient water was added to fill the compartment about one-half full outside of the test tube, which was always an excess. Before the cover of the bomb was screwed into place the thread was covered with graphite; this aided in making the bomb tight, and yet facilitated the removal of the top as it did not become rusted in. The experiments usually required about 24 hours for completion. After heating for the desired length of time the current was shut off and the bomb allowed to cool slowly in the furnace.

Preparation of Materials.

The water used in all experiments was first distilled from sodium hydroxide and potassium permanganate, and then from sulfuric acid and permanganate in order to free it from all organic reducing materials.

Gold hydroxide was prepared in the following manner: Pure gold hydroxide was dissolved in water, filtered through an asbestos felt, and the gold precipitated by passing in sulfur dioxide. The gold was collected, washed thoroughly, and melted into a small button. This was dissolved in aqua regia and the nitric acid removed by repeated evaporation in the presence of hydrochloric acid. The resulting gold chloride was dissolved in water, and after standing a few hours the solution was filtered through an asbestos felt and the gold re-precipitated with sulfur dioxide. The process of separating the gold, washing, melting, etc., was repeated, and when the clear solution of gold chloride was again obtained it was warmed and an excess of pure magnesium oxide added. The resulting precipitate of a mixture of gold hydroxide and magnesia was washed by decantation until the washings gave no further test for chlorides with silver nitrate. The magnesia was then extracted by treatment with warm dil. nitric acid. Lastly, a treatment with warm conc. nitric acid, followed by washing till the wash water contained no magnesium, gave pure gold hydroxide. This material, when dried on a steam bath to a dark brown powder, was readily and completely soluble in cold hydrochloric acid.

Experiments with Gold Hydroxide.

In some preliminary experiments performed in this laboratory by Mr. W. G. Crawford[1] on the decomposition of gold oxide by heat under the pressure of aqueous vapor, it was found that the oxide decomposed completely at 315°. Below that temperature a lighter yellow material formed in part, but on treatment of this whole residue with boiling conc. hydro-

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[1] Unpublished notes.

chloric acid it was noticed that the red-brown oxide dissolved at once, while the lighter material dissolved more slowly, but completely.

Boiling conc. hydrochloric acid was used as the reagent to determine whether the oxide had been completely decomposed, working on the supposition that the undecomposed oxide would dissolve, leaving insoluble such metal as had been formed. In this latter work it soon appeared that this was not a sharp separation, since small amounts of gold were easily dissolved in the presence of an excess of the oxide, which at once became auric chloride on treatment with hydrochloric acid, and it was only when decomposition had gone on to a very marked extent that the gold remained insoluble.

It was found that the solvent action of auric chloride and hydrochloric acid on metallic gold takes place with the formation of aurous chloride, and further that the aurous chloride may be titrated with potassium permanganate using preventative solution.

In a series of experiments in which a few milligrams of gold hydroxide were heated with water in a quartz tube a slight reduction to metal was obtained at 274–279°. Incomplete reduction was obtained by heating 14 hours to 300–310° and by heating 10 hours at 315–321°; 13.5 hours at 318–322° gave complete reduction to metal.

One preparation of gold hydroxide gave partial decomposition as low as 135° and complete reduction at 260° by 5 hours' heating. In some cases this material gave yellow solutions containing gold. This marked lowering of the decomposition point of gold hydroxide was evidently due to the presence of small amounts of inorganic salts, since the addition of a trace of magnesium chloride to the gold hydroxide and water, with subsequent heating to 264°, gave a distinctly yellow solution containing gold, while beautifully crystallized gold appeared in the bottom of the tube. Slightly larger amounts of magnesium chloride gave gold in solution but with the difference that no free metal was obtained. This solution, after standing in the air for a short time, precipitated a mirror of gold on the sides and bottom of the beaker.

In view of the fact that crystalline gold was obtained when small quantities of magnesium chloride were used, and no free metal appeared when the concentration was increased, it appeared that magnesium chloride might be a solvent for gold at high temperatures, depositing the gold in the crystalline form as the solution became saturated on cooling. It was found, however, that magnesium chloride solution at 260–270° exerted no solvent action on gold leaf.

Sodium chloride in small amounts heated with gold oxide to 260–268° gave gold in solution and a precipitate of metal. In this case the metal was spongy, quite different from the well-formed crystals obtained when magnesium chloride was used.

Calcium chloride and gold hydroxide were heated together to 281°, 292°, 322° and 353°. In each case yellow gold-bearing solutions were obtained, together with a light yellow residue. Only at the temperature of 353° with 15% calcium chloride was there a slight reduction to metal.

The yellow residue was washed free from soluble chlorides, and on treatment with nitric acid it took on the dark reddish brown color characteristic of gold hydroxide. The nitric acid was decanted and found to be free from calcium and chlorine. The residue on solution in hydrochloric acid showed no calcium. The calcium chloride had no other effect on the hydroxide than to prevent its reduction to metal and to change its color to a light yellow.

It is interesting to note that under these conditions sodium and magnesium chlorides readily cause the reduction of the gold to metal, while in the work of Diemer[1] on the reduction of auric chloride to aurous chloride by sulfur dioxide in the presence of alkali chlorides, it was shown that sodium chloride and magnesium chloride were most effective in preventing complete reduction, while calcium chloride was the least effective.

In each of these experiments the yellow solutions obtained were reduced to metallic gold on standing in the air, the gold forming a mirror on the walls of the container.

Experiments with Calcite and Gold Chloride.

The gold chloride used in these experiments was made by dissolving gold hydroxide, prepared as previously described, in hydrochloric acid, the very slight excess of acid in the clear solution being neutralized with calcite. When effervescence had ceased the quartz tube containing crystals of calcite and the gold chloride solution was placed in the bomb and heated.

A series of experiments at various temperatures yielded the following facts: The first step in the reaction of gold chloride and calcite is the formation of gold hydroxide, but at higher temperatures the hydroxide is decomposed giving free gold.

At 279° much of the gold present was converted to hydroxide which adhered to the surface of the calcite. Very little metal was formed at this temperature. Undecomposed hydroxide was found up to 312°, but the amount of free metal continually increased with rise of temperature. At 310° it was found possible to grow crystals of gold on the surface of the calcite. These crystals were in forms belonging to the isometric system. At 320° the surface of the calcite became almost entirely covered with a plating of gold with the characteristic bright yellow color, but no crystals were visible in the coating even when highly magnified.

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[1] Diemer, THIS JOURNAL, **35**, 552 (1913).

At 327° the gold plating began to show well-formed crystals of gold adhering to it. Temperatures of 330–337° gave complete reduction of the gold in solution to metal. The gold appeared entirely in the crystalline form except that portion which formed the plating on the surface of the calcite. Nearly all of the crystals adhered to this metallic coating.

The best plating and crystal formation on the surface of the calcite was produced by raising the temperature to 330° for a time, then lowering it to 320–325°. The higher temperature gave a reduction to metal, while the lower temperature maintained for some hours promoted crystal growth.

A solution of gold chloride distinctly acid with hydrochloric acid was heated with calcite to 324°. Gold was precipitated but the calcite was not plated. At the end of the heating the solution was still strongly acid so that when pressure was released in the bomb, effervescence immediately recommenced.

Fig. 3 shows a crystal of calcite from Cumberland, England, which was heated for 3 hours to 300°, and during a few minutes to 358°, in the presence of strong gold chloride solution. Slight plating resulted. It was returned to the bomb with fresh gold chloride solution and heated for a day, reaching a maximum temperature of 343° without materially improving the plating. On heating for 2 days longer, reaching a maximum temperature of 347°, the plating shown in Fig. 3 resulted.

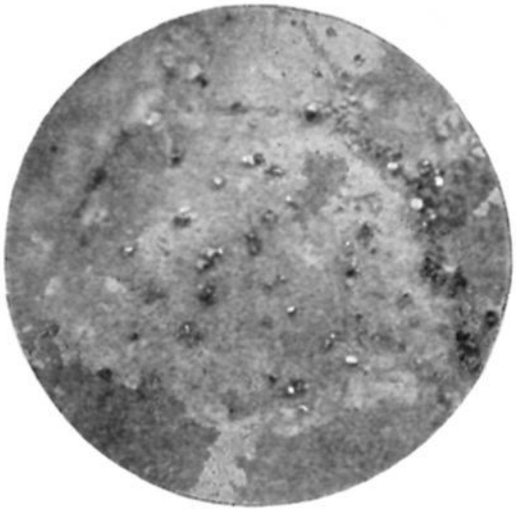
Fig. 3.

Some very strong gold chloride solution was prepared by saturating conc. hydrochloric acid with gold hydroxide. This gave a solution which was acid to litmus but which did not effervesce with calcite. On heating a piece of calcite with this solution for 2 days to a maximum temperature of 334° all the gold was removed from the solution and the calcite was found to be thickly covered with a bright yellow pulverulent coating containing a few bright crystals of metal. A second experiment, using the same materials and heating for one day to 336°, gave exactly similar results.

In these experiments the strength of gold chloride solution used produced a rather high concentration of calcium chloride. This salt appeared to exert a stabilizing action on the gold hydroxide, and the plating out of metallic gold was prevented. This same behavior is possible when a strongly acid gold chloride solution is heated with calcite, forming calcium chloride during the neutralization, and explains many unsuccessful attempts to obtain well plated calcite in solutions of more than moderate concentrations of gold chloride.

Magnesite and gold chloride solution at 322° gave crystals of gold on the surface of the magnesite, but in this case the crystals were fern shaped, appearing under the microscope as elongated crystals twinning to form strands and filaments. Magnesite and gold chloride heated to 332° gave good gold plating on the magnesite, but again the crystals adhering to this coating took the form of long threads, instead of the perfect cubes and octahedra such as were obtained on calcite.

Under the varying conditions of the many experiments performed on gold solutions, crystals of gold of various habits were produced. In some cases the crystals appeared as thin plates in the shape of perfect triangles, hexagons, or polygons; again long threads, in some cases over an inch in length, were produced. These always appeared under the microscope as composed of many crystals grown end to end. Cubes, tetrahedra, and many combinations of the forms of the isometric system were very common. In general, it may be said that whenever the gold was deposited from solutions by heat and pressure it was crystalline, showing more or less perfect forms.

Gold Chloride and Alkali Chlorides.

A series of experiments was next undertaken to determine the temperature at which gold chloride would decompose when heated under the pressure of aqueous vapor, and also the effect of the presence of alkali chlorides on this decomposition point.

Several preparations of gold chloride which were slightly acid to litmus were heated to the critical temperature of water, 365–372°, without decomposition. At the end of the experiments no free metal was found, and no change in the appearance of the solution was noted. Slightly higher heating (379°) gave complete reduction, the metal appearing in the crystalline form.

The crystals in this case were especially fine and of a great variety of form. Some practically perfect octahedra were produced, as well as chains of crystals. In other experiments where the gold chloride was heated to 400°, 435° and 445° complete reduction was obtained in each case. The experiment at 445° gave fern-shaped crystals as much as one-half inch long.

The work of Cailletet and Coloradeau[1] gives the critical temperature of water as 365°. In the present work it was found that gold chloride was stable up to a temperature of 372°, but was decomposed at 379°. There appeared to be some relation between the critical temperature of water and the decomposition of gold chloride, which was substantiated

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[1] Cailletet and Coloradeau, *Compt. rend.*, 106, 1489 (1888).

by the work of Holborn, Henning, and Baumann,[1] who give the critical temperature of water as 374°.

After having determined the stability of gold chloride, the effect of the addition of small amounts of alkali chlorides was next investigated. In the first of these experiments one small crystal of calcium chloride was added to 10 cc. of gold chloride solution, and the mixture heated to 352°. A few small crystals of gold resulted. The same solution was again heated, this time to 387°, but no further reduction took place. Gold chloride solution containing 10% calcium chloride was heated to 404° for nearly a day without the slightest reduction to metal being obtained. Gold chloride containing 8% calcium chloride was heated for an equally long time to 454°, and in this experiment a few small crystals were obtained.

From these experiments it is evident that if sufficient calcium chloride is added a solution is obtained which may be heated nearly a hundred degrees above the critical temperature of water before decomposition starts.

Gold chloride solution containing 8% magnesium chloride gave no reduction to gold at 383°, while the same solution heated to 454° showed incipient reduction to metal.

A gold chloride solution containing 8% sodium chloride heated to 460° showed no reduction to metallic gold in the solution. At the very top of the tube an inch and a half above the solution some strands of metallic gold had formed which extended directly across the tube, a distance of nearly an inch. Under the microscope these strands appeared to consist of many small crystals attached end to end. On allowing this solution to stand in the air, gold crystallized out on the sides of the tube. It is characteristic of all of these solutions that after heating they precipitated a mirror of gold on the walls of the containing vessel if allowed to stand in the air, but in this case the gold appeared as well-formed crystals.

The solutions obtained in these experiments were separated from the metallic gold and reheated. Heating to a temperature of 504° gave no further reduction to metal.

Following the investigation of the stability toward heat of the double chlorides of gold with those of sodium, calcium and magnesium, a series of experiments was undertaken which had for its object a study of the deportment of these double chlorides with calcite and magnesite. In detail these experiments were as follows:

Gold chloride containing 8% sodium chloride when heated with calcite to 347° caused the calcite to become fairly well covered with small crystals of gold. Solutions of the same strength heated to 399° gave only a few flakes of gold in the tube. These flakes were in the form of thin plates, some triangular, others hexagonal or polygonal.

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[1] Holborn, Henning, Baumann, *Ann. phys.*, 31, 945 (1910).

Since sodium chloride solution under pressure is a solvent for gold,[1] it is not surprising that no great amount of metal separates under the above conditions.

Fig. 4.

A gold chloride solution containing 8% sodium chloride and a piece of magnesite was not changed by heating to 336°, the solution at the end appearing exactly as it had at first. This same solution with magnesite heated to 490° gave only a very few crystals of gold on the magnesite.

Calcite when heated to 444° with gold chloride solution containing 8% of magnesium chloride gave nearly complete reduction to metal. The calcite was not plated with the gold. The metal appeared as exceptionally beautiful fern-shaped crystals. Two of these crystals are shown in Figs. 4 and 5.

A series of experiments was next performed in which calcite was heated with a saturated solution of silver chloride in saturated sodium chloride solution, to which was added gold chloride saturated with sodium chloride. In these experiments gold crystals were obtained on the calcite at temperatures as low as 322°. The gold was free from silver, the latter apparently remaining entirely as chloride. Heating to a temperature of 465° failed to give any metallic silver or a silver-gold alloy.

Calcium bicarbonate solution when heated with gold chloride had no effect on the rate of decomposition of the chloride. The solution showed practically no reduction below, and complete reduction above the critical temperature of water.

Magnesium bicarbonate, on the other hand, heated with gold chloride to 348°, gave a complete precipitation of the gold from solution. The gold appeared for the most part as crystals of the metal, but there was also present a small amount of hydroxide.

Fig. 5.

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[1] Lenher, *Econ. Geol.*, **4**, 562 (1909).

Summary.

A steel bomb for work at high temperatures and pressures is described. The details of construction of an electric furnace for heating the bomb are given.

Gold is soluble in auric chloride which is acid with hydrochloric acid at the boiling temperature. Aurous chloride is formed, which may be titrated with potassium permanganate.

Pure gold hydroxide when heated with water in a closed bomb is decomposed, yielding metallic gold, at 322°.

Small quantities of inorganic salts lower this point of decomposition as much as 70°. Magnesium chloride and sodium chloride act in this way, while calcium chloride has a slight tendency to prevent decomposition.

Calcite when heated with gold chloride under pressure becomes plated with gold above 310°. Excellent gold crystals may be obtained as part of the gold plating. The reaction goes on in two steps, the first step being the formation of auric hydroxide, while the second is the reduction of the hydroxide to metal.

Magnesite heated with gold chloride under the same conditions may be gold plated. The crystals formed in this case show a different crystal habit from those obtained on calcite.

Gold chloride may be heated under the pressure of aqueous vapor as high as the critical temperature of water before metallic gold is caused to separate.

Gold chloride solution to which has been added small amounts of sodium chloride, magnesium chloride, or calcium chloride, is much more stable toward heat than gold chloride solution alone, only incipient reduction being obtained at 450–460°.

The stability of these double chloride solutions is also exhibited toward calcite and magnesite, which only became slightly plated with metallic gold when heated to 500°.

Calcium bicarbonate has no effect on the stability of gold chloride toward heat.

Magnesium bicarbonate acts like the normal carbonate when heated with gold chloride, causing the formation of gold hydroxide and metal at 322°.

This investigation was undertaken at the suggestion of Professor Victor Lenher, and I take this opportunity of expressing my deep appreciation of his advice and encouragement which have been so helpful both in the laboratory and in the classroom.

MADISON. WISCONSIN.