

graphitization would produce in case it took place at 700° and did not in the determinations made at 650°. However, no indications of free graphite could be detected in the samples used, by microscopic methods or by solution in dilute acid.

A calorimetric determination of this quantity is now in progress in this Laboratory.

### Summary<sup>14</sup>

1. Equilibrium values for carbon monoxide and dioxide with alpha iron and iron carbide, Fe<sub>3</sub>C, at 650° and 700° and at a total pressure of one atmosphere have been determined.

2.  $\Delta F$  for the reaction  $3 \text{ Fe } (\alpha) + \text{ C (graphite) } = \text{ Fe}_3\text{C}$ , is found to be 3,138 cal. (positive) at 650°, and 2,281 cal. (positive) at 700°.

3. Use of these data gives values of  $\Delta H$  for this reaction of 19,163 cal. and 19,161 cal. at the temperatures 650° and 700°, respectively.

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[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, UNIVERSITY OF BRISTOL]

## AMALGAMS OF GOLD AND MERCURY

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In continuation of a systematic study of dental amalgams containing silver, tin and mercury,<sup>2</sup> preliminary experiments were carried out to determine the effect of gold, which is commonly added for its "benevolent influence."<sup>3</sup> It was found that the gold passes almost entirely into the solid phase, whether amalgams of pure tin or of pure silver or of both together are concerned.

The present work was therefore undertaken with a view to examining the nature of the binary system, gold-mercury, before proceeding further with the quaternary system. Published investigations of this system<sup>4</sup> show extraordinary discrepancies, and hence it was necessary to make new and careful determinations of the solubility of gold in mercury.

**Method.**—Parravano employed a fusion method, and Braley and Schneider used cooling curves in their research. In the present work a direct analysis of the liquid in contact with the solid phase has been made.

<sup>14</sup> The work embodied in this paper is taken from a thesis submitted in partial fulfillment of the requirements for the degree Doctor of Philosophy at the Iowa State College.

<sup>1</sup> Experimental work by G. T. B.

<sup>2</sup> Joyner, *J. Chem. Soc.*, **99**, 195 (1911). McBain, *Dental Cosmos*, June, 1912. Knight and Joyner, *J. Chem. Soc.*, **103**, 2247 (1913). Knight, *ibid.*, **105**, 639 (1914).

<sup>3</sup> McBain and Knight, *Rep. Sixth Internat. Congress Applied Chem.*, **1914**, Sect. IV, pp. 1-7; *Dental Cosmos*, **57**, 630 (1915).

<sup>4</sup> Parravano, *Gazz. chim. ital.*, [2] **48**, 123 (1918). Braley and Schneider, *THIS JOURNAL*, **43**, 740 (1921).

Two methods of analysis have been employed; the reduction of gold chloride by ferrous ammonium sulfate and, secondly, the evaporation of the mercury from the amalgam in a stream of coal gas at a temperature of  $350^{\circ}$  in a Pyrex tube heated by an electric current. Before being weighed, the gold residue was heated to redness in the blowpipe. In the subsequent tables of results the method of analysis will be indicated. All percentages are expressed as atoms per 100 total atoms.

**Materials.**—Our thanks are due to the Colston Research Society of the University of Bristol for a grant to defray the cost of the materials. Chemically pure gold wire was supplied by Messrs. Johnson and Matthey, London. The mercury was purified by agitation in contact with a solution of mercurous nitrate by a current of air, dried and distilled from a silica flask in a stream of air.

### Apparatus

Three designs of apparatus were used over different ranges of temperature.

**Apparatus I (Series I).**—The first apparatus is shown in Fig. 1.

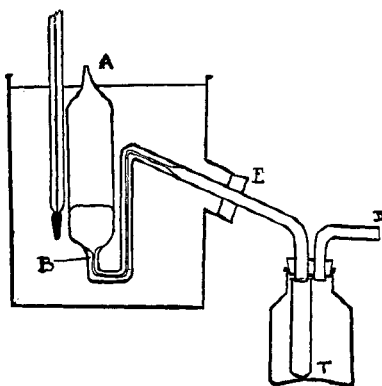


Fig. 1.

B is a very fine constriction preventing solid entering the capillary tube. Heating was by a glycerol bath, which entirely surrounded the capillary, thereby eliminating the risk of solidification. Cooling in the wide tube involved no error, any solid formed being carried into the tube T by the liquid drops. Stirring of the contents was effected by aspirating a stream of air through A and removal of amalgam by suction at D. Approximately 6 cc. of liquid was present in the apparatus, which was employed between room temperature and  $150^{\circ}$ .

**Apparatus II (Series II).**—Owing to the difficulty in obtaining a suitable liquid, and in closing E at high temperatures, the next apparatus—see Fig. 2—was designed.

It was constructed of Pyrex glass, and was entirely enclosed in an electrically heated air oven. The thermometer bulb was completely immersed in the liquid, and the stem was a sliding fit in the neck of the apparatus; in this way reflux condensation of the mercury was avoided. Amalgam was forced over by hydrogen through a tightly packed glass-wool filter into a small glass bucket, which was then immediately withdrawn. Before removing the sample for analysis the filter was rinsed with the amalgam, and the first few drops were discarded. The apparatus was primarily designed for use at  $150^{\circ}$  to  $350^{\circ}$ , but results were also obtained in the range  $60^{\circ}$  to  $150^{\circ}$ , yielding a satisfactory confirmation of the first series. In these experiments, as in those of the first series, samples were taken for analysis approaching equilibrium from both higher and lower temperatures. Stirring was effected by shaking with the hand, as the apparatus was light and compact.

**Apparatus III (Series III).**—This apparatus was designed for use with amalgams above the boiling point of mercury.

As is shown in the diagram (Fig. 3), it is but a small modification of the last one, enabling the amalgams to be maintained under a pressure of hydrogen in excess of the vapor pressure of mercury at the high temperatures employed. Amalgam was collected in the tube T, which was attached to the rest of the apparatus by a sealing-wax joint. A sample was removed for analysis by reducing the pressure in T by means of the 3-way tap B. The temperature of the furnace was then at once lowered to approximately 350°, the pressure released and the tube T removed. Obviously it was not possible to take duplicate samples for analysis as was the case in Series I and II. Stirring was performed by similar manipulation of the tap A. Pressure was applied from a cylinder of hydrogen through an "Endurance" regulating gage; pressures up to four atmospheres and temperatures from 300° upwards were employed. The apparatus was constructed of Pyrex glass, and the spirals and taps were of soft glass, the ground joints being made air-tight by sealing wax. The spirals were introduced to take up strains, rubber joints having proved useless.

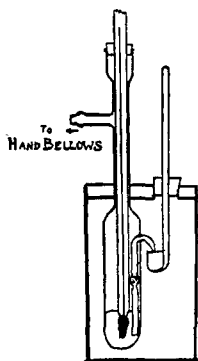


Fig. 2.

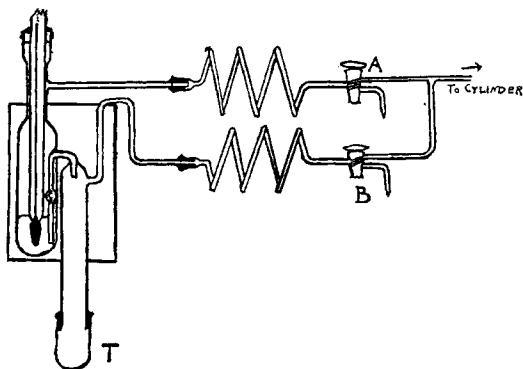


Fig. 3.

**Temperature.**—In Series I and II ordinary mercury thermometers reading in degrees to 250° and 350°, respectively, were employed. A nitrogen-filled mercury thermometer was used in Series III. All three thermometers were compared with another nitrogen-filled thermometer that had just been calibrated by the National Physical Laboratory under standard conditions of exposed stem.

TABLE I  
EXPERIMENTAL RESULTS

In Series I and II the ferrous ammonium sulfate method of gold analysis was employed throughout.

Temperature, °C.	Percentage of gold		Mean
	Sample 1	Sample 2	
18 <sup>a</sup>	0.212	...	0.212
18	.287	...	.287
47 <sup>a</sup>	.373	0.398	.388
52.5	.313	.273	.293
77 <sup>a</sup>	.494	.582	.538

TABLE I (Concluded)

Temperature, °C.	Percentage of gold		Mean
	Sample 1	Sample 2	
80.5	.635	.611	.623
92 <sup>a</sup>	.727	.715	.721
99.5 <sup>a</sup>	.739	.885	.812
103.5	.946	.866	.906
108 <sup>a</sup>	.987	.916	.952
128	1.460	1.489	1.474
132 <sup>a</sup>	1.462	...	1.462
145 <sup>a</sup>	1.681	1.658	1.667

## SERIES II

Temp., °C.	% Gold	Temp., °C.	% Gold	Temp., °C.	% Gold
64	0.379	143	1.591	201.5 <sup>a</sup>	3.137
65.4	.378	147.5	1.628	206 <sup>a</sup>	3.302
93.0	.597	149	1.630	207 <sup>a</sup>	3.265
	.602	153 <sup>a</sup>	1.785	206.5	3.345
98	.676	155 <sup>a</sup>	1.815	207.5	3.732
	.687	158	1.920	234 <sup>a</sup>	4.559
105	.736	159	1.929	234.5 <sup>a</sup>	4.601
106.5	.753	163	2.028	241	5.225
114.5	.948	163.5	2.052	247	5.300
115.5	.944	172	2.212	258.5	6.585
121	1.216	173	2.212	259 <sup>a</sup>	6.036
	1.237	174 <sup>a</sup>	2.260	259.5	6.725
122.5	1.101	174.5 <sup>a</sup>	2.158	260 <sup>a</sup>	6.753
133.5	1.421	186.2	2.616	287.5 <sup>a</sup>	(7.601)
136	1.409	189.5	2.746	288	8.542
142.5	1.576	192.5 <sup>a</sup>	2.615	291	8.716
				292.5 <sup>a</sup>	(7.709)

## SERIES III

Temp., °C.	% Gold	Temp., °C.	% Gold	Temp., °C.	% Gold
280	6.89	334	18.92	370	39.48
289	8.30	339	16.14	378	42.99
321	10.67	343.5	27.16	386	42.96
327 <sup>b</sup>	20.49	354	32.96	398	52.00
327 <sup>b</sup>	23.27	361	33.32	410.5	55.33
331	18.32	366	34.48		

<sup>a</sup> These points were obtained from the side of low temperature and lower concentration, whereas the others were obtained from the side of higher temperature and concentration; the two sets of results coincide.

<sup>b</sup> The apparent discrepancy in the two values is due to the two points being one on either side of the eutectic—see the graph. This also accounts for the order observed in the temperatures and concentrations following these two points.

These values are arranged in the order of temperatures, not in the order in which they were obtained. Initial mixtures of gold and mercury of widely differing compositions were employed, and the samples in this series were removed after the mixture had been heated for some time at about 450°, and then cooled to the desired temperature. In the majority of cases a considerable excess of gold was present, but in the region 8–20% of gold the initial concentrations had necessarily to be chosen on either side of the maximum on the curve.

The evaporation method of analysis for gold was employed.

A satisfactory indication of the correctness of the above data has been obtained in the following manner. Two tubes having a narrow constriction in the middle, like an hour-glass, and containing known mixtures of gold and mercury were sealed, and then heated in a small electric furnace provided with windows, and observations were made on the disappearance and re-formation of solid phase by complete inversion of the tube and furnace. Tube I contained a mixture of 30% of gold and 70% of mercury; some solid was still present at 348° but none at 355°; the temperature of complete liquefaction determined from the curve was 352°.

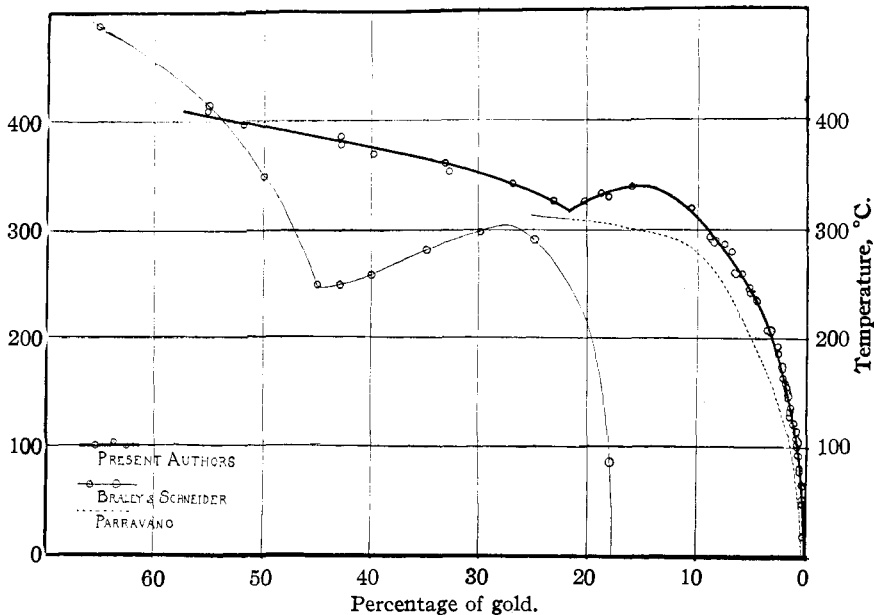


Fig. 4.—Solubility-temperature diagram.

Tube II contained 50% of gold and 50% of mercury; some solid was still present at 398° but none at 406°; the temperature of complete liquefaction was 392°.

**Discussion of Results.**—The three series of points—79 in number, involving more than 100 separate determinations—have been plotted in Fig. 4, in which the results of the previous workers have been indicated for the purposes of comparison. Four points only show serious deviations from the smooth curve. Where the results from different series overlap, good agreement is recorded.

Our results show that the solubility of gold rises slowly with increasing temperature as far as about 300°, where the rise becomes much more rapid, passing through a maximum temperature of 342° at 14.6% of gold. The

curve then descends to a minimum of  $320^{\circ}$  in the region of 22% of gold, from which point the gold solubility increases extremely rapidly with temperature as far as this investigation has been carried.

The rather flat maximum appears to indicate the formation of a compound,  $\text{AuHg}_6$ , containing 14.3% of gold. The minimum corresponds to the formation of a eutectic between the compound and another solid phase as yet undetermined.

Comparing these results with those obtained in the two previous studies of gold amalgams, it must be observed that notable discrepancies exist. The curve obtained by plotting the values published by Parravano is of somewhat the same general form that was obtained by us as far as the maximum, but differs appreciably in the actual values, and also in not indicating the formation of a compound within the range examined. It should be pointed out, however, that Parravano obtained only a comparatively few points, which do not define at all well the direction of the curve in the region where we have found evidence of a maximum.

The discrepancy between the gold solubilities found by Braley and Schneider and in this research is extreme, the values being of a totally different order. For example, the previous workers stated that a compound,  $\text{AuHg}_4$ , forms a eutectic with a solution of gold in mercury which freezes at  $-41^{\circ}$ , the composition of this eutectic being 85% of mercury and 15% of gold, whereas our curve indicates a temperature of  $+341^{\circ}$  for the liquid phase of that composition in equilibrium with solid phase. The work of Braley and Schneider appears to be gravely in error, and no reliance can be placed upon the compounds deduced therefrom. To test their statement that up to 15% of gold dissolves in mercury at room temperature to form a liquid it is necessary only to prepare any mixture of mercury and gold up to that amount, and feel the solid present. Our work does not extend to systems containing between 60 and 100% of gold, where the cooling curves may have given more trustworthy information.

### Summary

A portion of the binary system gold-mercury has been carefully examined by numerous analyses of the liquid phase in contact with the solid phase at temperatures up to  $410^{\circ}$ , employing initial concentrations of gold varying from 0 to 60 atom-per cent.

A graph is given which shows the change in the solubility of gold in mercury with temperature. The flat maximum would indicate the existence of a compound,  $\text{AuHg}_6$ .

No confirmation of the previous work of Braley and Schneider could be obtained. The solubility of gold in mercury at room temperature is only 0.2%, whereas they published a value greater by seventy-five fold.