[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ROCHESTER]

THE SOLUBILITY OF GOLD IN MERCURY. II

BY ARTHUR A. SUNIER AND CHESTER M. WHITE

RECEIVED JANUARY 17, 1930 PUBLISHED MAY 8, 1930

Although several investigators[1] have worked on the system gold–mercury, the majority of the results have been confined to temperatures above 100°, and strangely enough the few values between 0 and 80° disagree remarkably with each other—differences of several hundred per cent. being common in this temperature range. Quite recently a rather precise piece of work was published by Sunier and Gramkee on the solubility of gold in mercury from 80 to 200°, using the tube of Sunier and Hess[2] slightly modified. It was thought advisable, therefore, to continue these measurements with the apparatus just mentioned. This paper will present results on the solubility of gold in mercury from 7 to 80°. In spite of the low apparent solubility (0.1 to 0.5%) in this temperature range, the precision of measurement is considered to be excellent, the average deviation from the mean for all the determinations being about 5 parts per thousand, which corresponds on the average to about 0.001 atomic %.

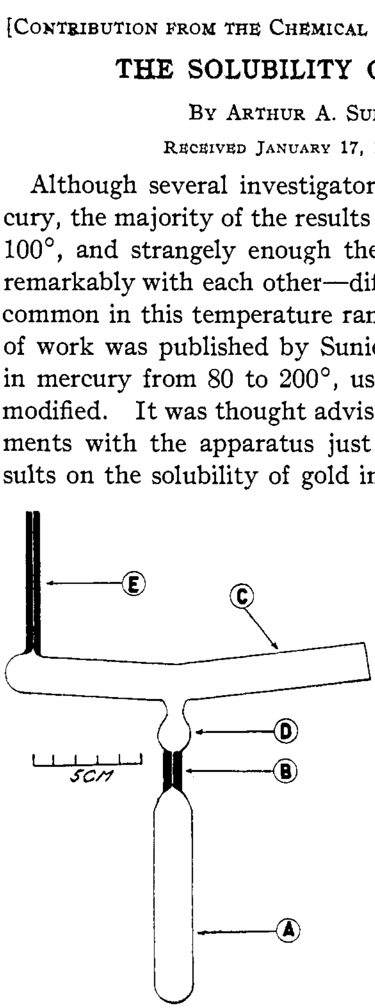


Fig. 1.—Solubility tube.

Materials.—Mercury was covered with a considerable amount of dilute nitric acid and air was aspirated through the mercury for a week; it was then distilled several times in an all-glass apparatus under diminished pressure, according to the method of Hulett and Minchin.[3] Samples of this mercury yielded no weighable residues when slowly evaporated at 270° in a current of air. The gold was used in the form of foil which had been rolled from a bar of gold said to contain less than 0.05% impurity.

Apparatus.—The solubility tube, Fig. 1, a modification of the one used by Sunier and Gramkee, was made of pyrex glass and consisted of a sample tube, A, capillary filter, B, a tube for preparing amalgams, C, the cup, D, and the capillary, E, both of which were used in filtering the amalgams. The dimensions of the tube were increased at lower temperatures to accommodate larger volumes of mercury.

The shaking and sampling apparatus differed considerably from that used in the

---

[1] Parravano, *Gazz. chim. ital.*, **48**, II, 123 (1918); Braley and Schneider, THIS JOURNAL, **43**, 740 (1921); Britton and McBain, *ibid.*, **48**, 593 (1926); Sunier and Gramkee, *ibid.*, **51**, 1703 (1929); Kasanzeff, *Ber.*, **11**, 1255 (1878), determined the solubility of gold in mercury at 0, 20 and 100°.

[2] Sunier and Hess, THIS JOURNAL, **50**, 662 (1928).

[3] Hulett and Minchin, *Phys. Rev.*, **21**, 288 (1905).

first research, and since it proved so satisfactory it will now be briefly described. The apparatus was designed with a view to making it possible to handle the low and high sides independently or simultaneously at will.[4] Figures 2 and 3 give front and side views, respectively, of the apparatus; these views correspond to the sampling and rotating positions, respectively. The apparatus is built in two units which are nearly identical; each unit is capable of carrying four solubility tubes; only one tube, however, is shown in Fig. 2 in order not to complicate the figure.

A large round piece of brass rod, R, was drilled to slip over the axle, G, and was fitted with suitable clamps to hold the tubes firmly in position. A cotter pin through G served to hold R in position. The axle G was supported by the square brass rod H, which in turn, was securely clamped to rigid supports (not shown in Figs. 2 and 3). A smaller rod M was fixed to R in a manner indicated, and was connected by the long rod J to the eccentric; thus a motion could be given the tubes as indicated by the full and dotted lines in Fig. 3. The rods JJ could easily be detached from the eccentric and were used in rotating the tubes through 180° at the time of filtering.

The two units differ only in the rods H and I. Rod H was never removed from the bath and was always used to support the four tubes that corresponded to the high side. When the other unit (constituting the low side) was to be inserted in the bath, the peg N on the rod I was put in the hole indicated on the rod H; then the movable rod Q was pushed to the left until the two rods I and H were securely fastened together. It should be apparent then that each set of tubes could be inserted in the bath, rotated and sampled independently of the other set.

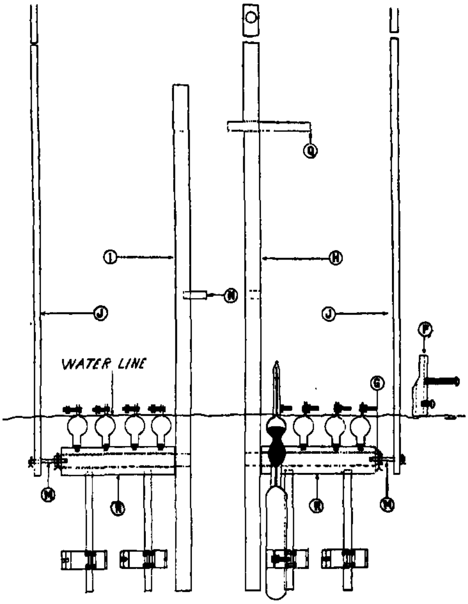


Fig. 2.—Shaking and sampling apparatus.

The tubes were immersed in a thermostat, which was very heavily lagged and contained 334 liters of water.[5] The top of the thermostat was partly covered in all the runs except in those at 70 and 80° where it was completely enclosed to prevent excessive evaporation of the water. Two or three centimeters of the sampling tubes projected above the water level in all the runs except in series I, where the entire tube was submerged. A revolving shaft, loaded with forty oil sample bottles, produced the necessary agitation within the bath. The bath could be heated by steam and by six 500-watt heaters; it could be cooled to temperatures below that of the room by running cold water through a special cooling coil, or by adding finely mashed ice directly to the water; this latter procedure was resorted to in run F (7°). In some of the runs a thermoregulator

---

[4] Mr. Law G. Weiner, working in the laboratory, first applied this idea (but his apparatus was necessarily quite different) in determining the solubility of gold in mercury at high temperatures.

[5] It is hoped to publish in another place further details concerning this type of thermostat, which has proved very satisfactory during the eight years of its use.

was used; in others hand regulation was resorted to. In either case variations of temperature as large as 0.1° occurred very rarely and only for a very short time. A Beckmann thermometer inserted in the bath was read at frequent intervals and indicated that the average temperature variation was about ±0.02°.

The temperatures were read from two mercury thermometers (graduated in tenths of a degree) which were compared with thermometers recently standardized by the Bureau of Standards. Temperatures are recorded to the nearest 0.02°, which was readable with ease.

Experimental Procedure

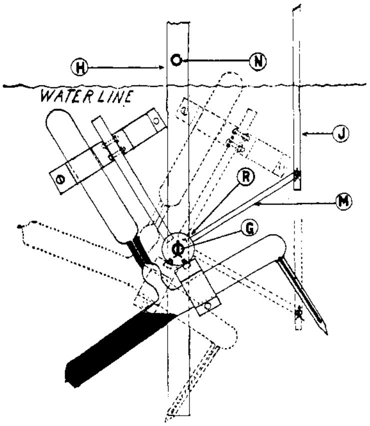


Fig. 3.—Shaking apparatus (side view).

A certain volume of mercury (depending on the temperature of the run) was charged in the tube D (Fig. 1) with about 100% excess of gold, using Britton and McBain's data as a guide, with the solubility tube in a horizontal position. A rubber tube and pinch clamp on the capillary E prevented the mercury from running out. After sealing off at D, the mixture was transferred to the opposite end of the tube and the capillary E was attached to a Cenco Hyvac pump. When the tube was thoroughly evacuated and outgassed, the capillary was sealed off and file marked.

To determine the solubility at a certain temperature saturation was (with two exceptions, Runs E and F) attained from both the high and the low sides. A total of eight tubes was made up and four were placed in each rack. One set was introduced and rotated for two and one-half to three hours when the bath was about 5° above the solubility temperature. This constituted the high side of the run. The temperature was then allowed to drop to the desired point when the remaining four tubes were inserted; all eight tubes were then shaken for three to four hours (in one case six hours) at constant temperature. By running the high and low side determinations together, considerable time was saved.

When it was time to sample, the connecting bars JJ were slipped from the eccentric and used as handles to rotate the tubes through 180°. Water was allowed to run out until the entire length of capillary E projected above the water level. A piece of brass rod (P), drilled to fit the capillary, was provided with two screws, one of which (lower) held the breaker fast while the second produced the necessary pressure above the file mark, which would break the capillary.[6] After filtration, the tubes were taken from the bath. The sampling tubes were cut off and their contents transferred to weighed crucibles. Some of the empty used tubes were cleaned thoroughly and repaired and were thus used for more than one determination.

To analyze the amalgams, the evaporation method was used which Sunier and Gramkee have shown to yield results 0.2% high if proper precautions are taken. Since it was known that hydrogen would not be available at all times during the course of this research, air was used in place of hydrogen. Carefully performed experiments seem to indicate that the results are identical in both cases. It should be noted that occasionally a small amount of a red powder was visible on the sides of some of the capsules when

---

[6] This improved breaker was designed and used by Mr. Law G. Weiner in another research.

held below 300°. On heating to about 550° this powder always disappeared, thus indicating that some mercuric oxide was formed at the lower temperatures. These observations appear to be in accord with the free energy changes for mercuric oxide given by Lewis and Randall,[7] who made use of data determined by Taylor and Hulett.[8] The capsules were placed on iron supports in a large pyrex tube, which was electrically heated. Air was passed through the tube, which was heated to 270° until no mercury was visible. Since the danger of bumping was lessened with these dilute amalgams, a higher evaporation temperature was employed. After heating the gold residues for ten to twelve hours at 450 to 550°, they were weighed and then reheated for three more hours when they were again weighed. If their weights differed by more than two-tenths of a milligram, the residues were further heated until this degree of constancy was obtained.

To test the entire experimental arrangement, six tubes were made up with weighed amounts of gold and mercury,[9] and were carried through the entire procedure. The results are given in Table I. The average differences in the values in columns four and five are seen to be a little less than 2 parts per thousand, which would appear to be very good, considering the small amount of gold weighed; furthermore, the averages of these two columns differ by less than one part per thousand.

TABLE I

ANALYSIS OF AMALGAMS OF KNOWN CONCENTRATION

No.	Gold taken, g.	Mercury taken, g.	Atomic % taken	Atomic % found	Diff., p. p. t.
1G	0.1957	67.357	0.2959	0.2958	0.4
2G	.1945	68.426	.2898	.2901	1.0
3G	.1740	67.517	.2628	.2631	1.0
4G	.1881	67.910	.2824	.2829	1.7
5G	.1961	68.433	.2921	.2906	5.0
6G	.1998	68.096	.2990	.2985	1.7
		Average	.2870	.2868	1.8

Experimental Results

In Table II will be found complete data for two temperatures, while Table III contains a summary of all the data obtained. In Table IV will be found the solubility at rounded temperatures, taken from the log N *vs.* $1/T$ plot.

TABLE II

SOLUBILITY OF GOLD IN MERCURY. COMPLETE DATA FOR TWO TEMPERATURES

No.	Temp., °C.	Approx. wt. of Au at start	Wt. of gold, g.	Wt. of amalgams, g.	Atomic % sol.
1E	High side	0.4	0.1176	92.240	0.1296
2E	at	.4	.1402	117.456	.1280
3E	20.00	.4	.0942	72.741	.1299
4E	Low side	.4	.1478	115.573	.1307

---

[7] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Company, **1923**, pp. 483, 484.

[8] Taylor and Hulett, *J. Phys. Chem.*, **17**, 565 (1913).

[9] In making up the knowns, a small amount of mercury was probably vaporized during the outgassing procedure; this constituted a source of error which was not present in the regular procedure.

Table II (*Concluded*)

No.	Temp., °C.	Approx. wt. of Au at start	Wt. of gold, g.	Wt. of amalgams, g.	Atomic % sol.
5E	(see text)	0.4	0.1391	111.089	0.1279
6E	at	.4	.1467	117.360	.1276
7E	20.00	.4	.1304	103.300	.1292
				Average	.1290
1I	High side	1.0	0.3080	67.269	0.4680
2I	at	1.0	.3047	66.955	.4652
3I	80.40	1.0	.3084	67.525	.4669
5I		1.0	.3175	70.010	.4636
6I	Low side	1.0	.3213	70.783	.4626
7I	at	1.0	.3144	69.793	.4605
8I	80.40	1.0	.3063	67.141	.4663
				Average	.4647

Table III

Solubility of Gold in Mercury (Summary of Experimental Data)

Series no.	No. of detns.	Temp., °C.	Atomic % sol.	Av. dev. (from the mean), p.p.t.
F	5	6.96	0.1006	8.2
E	7	20.00	.1290	7.7
D	6	29.68	.1638	4.7
C	6	39.98	.2045	5.4
B	4	49.50	.2461	4.1
A	6	60.32	.3152	5.2
H	7	70.36	.3753[a]	3.1
I	7	80.40	.4647[a]	4.3

[a] Several years ago Mr. C. B. Hess, working in this Laboratory, made some determinations of the solubility of gold in mercury; his results, which were distinctly preliminary in character, are tabulated here

No. of detns.	Temp., °C.	Av. atomic % sol.
3	69.2	0.375
3	83.8	.498

The method of analysis was nearly identical with that used by Fitzsimmons; whose method was described in the first paper of this series. The temperatures were read from uncalibrated thermometers, hence it did not seem proper to include these results in Table II. It should be pointed out that the agreement in the two series of determinations is all that could be desired.

Table IV

Solubility of Gold in Mercury at Rounded Temperatures (from Log N *vs.* $1/T$ Plot)

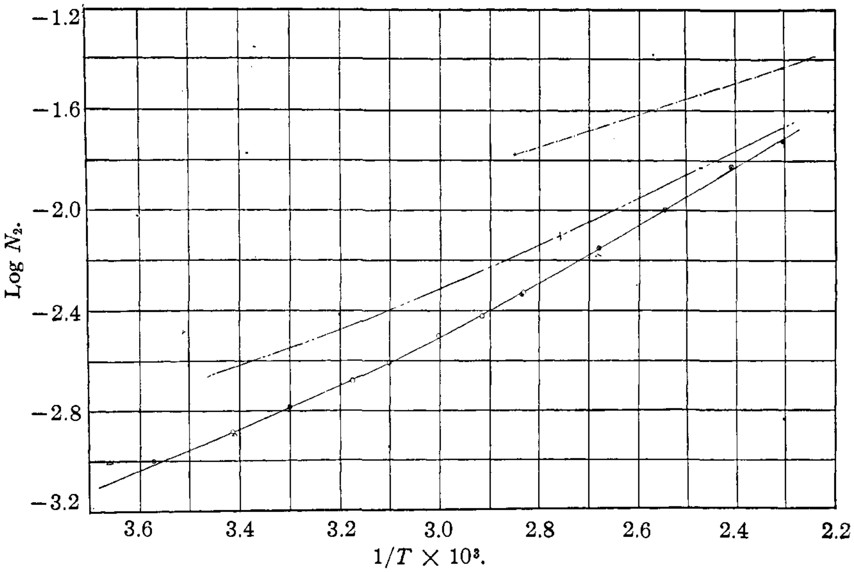
Temp., °C.	0	10	20	30	40
Atomic % sol.	(0.0813)[a]	0.1038	0.1306	0.1629	0.2014
Temp., °C.	50	60	70	80	
Atomic % sol.	0.2489	0.3076	0.3767	0.4614	

[a] Extrapolated value.

Of the fifty-six determinations, eight have been omitted, because the deviation of each was greater than four times the average deviation from the mean for that temperature. All solubilities are given in atomic per cent. (atoms of gold per 100 total atoms). Atomic weights as follows were used in the calculations: Au = 197.2, Hg = 200.61.

Discussion of Results

From the log *N* *vs.* $1/T$ plot (Fig. 4) it is seen that the present results are considerably lower than most of the previously published values. The present work appears to be in excellent agreement with the data presented by Sunier and Gramkee, the respective values reported at 80° being 0.4614% and 0.459%. The determination of Kasanzeff at 100° is in good agreement with the work of Sunier and Gramkee. Kasanzeff's three determinations were made about fifty years ago by an apparently crude method (the whole article of this author is really only an abstract, three paragraphs long). Britton and McBain's values are high at lower temperatures, but approach the authors' values as the temperature is raised.[10]



△, Kasanzeff; — - —, Parravano; — - - —, Britton and McBain; -⊗-, Sunier and Gramkee; -⊙-, Authors.

Fig. 4.—Solubility of gold in mercury.

Qualitative proof of the solubility at 25° was obtained from some preliminary experiments. Weighed quantities of gold and mercury, which corresponded to an average value of Britton and McBain's data at 18°,

---

[10] From unpublished work of Mr. Law G. Weiner, working in this Laboratory, it appears that these investigators are low at about 230°. Incidentally, he does not find the maximum which they report.

were sealed in pyrex test-tubes and rotated for four hours at constant temperature (25°). At the end of this period, the gold foil was plainly visible, thus indicating that Britton and McBain's data are high at these lower temperatures. Braley and Schneider's results, which differ so radically from the present work, could not be conveniently plotted. It would seem that some serious error had been made in obtaining their data, which indicate a solubility of 15 atomic per cent. at 20°. Parravano has only two determinations in the temperature range plotted in Fig. 4; the results obtained in these determinations would appear to be much too high. It is well known that fusion curve methods often give high results if proper precautions are not taken.

The present results, however, are higher than the values which one gets from the equation of Sunier and Gramkee, $\log_{10} N = (-1167.4/T) + 0.996$, which was valid from 80 to 160°; consequently, when both sets of data are plotted, the resulting curve is not a straight line, nor was it possible to obtain a simple equation for this curve. Of the three possibilities, (1) solid phase may not be the one indicated, (2) an actual transition may take place at the temperature where the break occurs, (3) the latent heat of fusion of the solid phase is a function of the temperature, the last one seems to offer the best explanation; it should be mentioned, however, that the nature and composition of the solid phase in equilibrium with the solution has not been determined by any of the above-mentioned, investigators,[11] each (with one exception) suggesting a different compound. It would seem that evidence has been obtained in another research, unpublished but mentioned earlier, which tends to prove that the maximum in the solubility curve reported by Britton and McBain is quite likely in error, and thus the formula of the compound suggested by these workers is in error. Very recently Pabst[12] has published the results of an x-ray investigation of this system. Solid solutions appear to be present in the concentration range 0 to 15% mercury. Work in the range considered in this paper has apparently not been completed, but the author makes the general statement that there are several other phases of undetermined structure in the mercury-rich end of the diagram. It is to be hoped that these investigations may be continued and that other methods may be used in attempting to check the results that may be obtained.

At this point it might be well to mention the few sources of error in the apparatus and method. In the first paper attention was called to the error that might arise if the bore of capillary E was too large. In runs

---

[11] Since this was written it has been possible to look into the recent publication of I. N. Plaskin [*J. Russ. Phys.-Chem. Soc.*, **61**, 521 (1929)] who declares that the compound $AuHg_2$ is stable under the conditions existing in the experiments recorded in the present paper. It is hoped to discuss Plaskin's work more fully in the near future.

[12] Pabst, *Z. physik. Chem.*, **3B**, 443 (1929).

A to F, the only available capillary had such a diameter that a 2-cm. length contained about 0.6 g. of mercury; but since the tubes were made up twelve hours or more before being used (and the gold was always in contact with the mercury during this interval) the mercury may well have become saturated with gold at room temperature, which was 25° or a little higher. It should be quite evident that in the runs at 20 and 30° the concentration of gold in the mercury in the capillary was nearly the same as in the main body of the amalgam; the same was nearly true of the runs at 7 and 40°. In the runs at 50 and 60° the concentration of gold in the mercury in the capillary was about half (see Tables III or IV) that in the main body of the amalgam; thus the results at 50 and 60° may, at the *most*, be low by $(0.6/2/80)100 = 0.4\%$. The capillary available for the runs at 70 and 80° had a bore sufficiently fine so that no appreciable error arose from this cause.

In a few of the runs the folded strips of gold foil caught occasionally on the sides of the tubes and were not transferred with the amalgam every time; therefore, an excess of gold was not always in contact with the amalgams for the entire shaking period. Since the authors feel that a better technique was developed in the later runs, the first determination was not weighed as heavily as the succeeding ones. (The series numbers in Table III indicate the order in which the runs were made—A first, B next, etc.)

Run F (7°) gave high results probably because the sampling tube was not long enough to contain the large volume of amalgam; consequently, some of it remained in the filter cup with the excess gold, after the tubes were taken from the bath. Possibly some of this more concentrated amalgam might have fallen into the filtered portion while the sampling tube was being broken. Three determinations were omitted from the average in this determination because their deviation was more than four times the average.

Throughout the temperature range 7 to 80°, the temperature coefficient of solubility was such that one-tenth degree corresponded to about 2 parts per thousand change in the solubility; since the temperature of the bath was held to ±0.02°, it would appear that no appreciable error arose from this cause.

In conclusion then it is felt that since the method of analysis of very dilute amalgams (described above) has proved so reliable and since the precision of measurement in the various determinations is so good, the values presented in Table IV appear to be considerably more accurate than those published heretofore.

Bearing of Data on the Metallurgy of Gold.—The amalgamation process for the mining of gold consists essentially of treating the crushed ore with mercury, which amalgamates with the gold and leaves impurities on the surface of the mercury. Later the solid amalgam which settles out, is distilled to remove the mercury from the metal.

The explanations which have been put forth to account for the extraction of gold by mercury are rather indefinite and somewhat confusing. Mellor[13] states, "The gold is miscible with mercury in all proportions. . . ." Evans[14] says, "Gold is soluble in mercury. . . .," and farther on he writes, "It should be pointed out that the actual catching of the gold grains by amalgamated plates is a process of surface adhesion; the dissolution of the adhering gold in the mercury to form an amalgam occurs slowly after the grains have been caught." From these quotations, it is seen that solubility is believed to play an important part in the formation of the amalgam. From the present results, however, the solubility appears to be 0.1306 atomic per cent. at 20°. A simple calculation shows that 100 pounds of mercury would only dissolve 2 ounces of gold (the amount found in a ton of some ores) which is far too small an amount to form a 10% amalgam which Schnabel[15] mentions as being fluid.

At present, therefore, the best mechanism seems to be that of surface adhesion followed by only very slight solubility effects. The gold particles, after being coated with mercury, settle to the bottom under gravity. The nature of this solid phase has not been determined as yet, as mentioned earlier.

Summary

1. Amalgams as dilute as 0.3% have been prepared and analyzed, by a method described, with a precision approaching one part per thousand.
2. An improved type of apparatus is described for shaking the solubility tubes and sampling the amalgams.
3. Fifty-six determinations of the solubility of gold in mercury have been made with the tube described earlier (with slight modifications). The results are lower and the precision of measurement is much higher than those previously reported.
4. The bearing of the present data on the well-known amalgamation process for mining gold is briefly discussed.

ROCHESTER, NEW YORK

---

[13] Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Company, **1923**, Vol. III, p. 497.

[14] Evans, "Metals and Metallic Compounds," Longmans, Green and Co., **1923**, Vol. IV, pp. 113, 116.

[15] Schnabel, "Handbook of Metallurgy," Macmillan Co., New York, **1905**, p. 924.