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

THE SOLUBILITY OF GOLD IN MERCURY

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Although three rather extensive researches on the system gold-mercury have been published[1] within the last ten years, the disagreement in the various results is most remarkable, particularly at lower temperatures. Quite recently rather precise results on the system silver-mercury, using a new type of solubility tube, have been published by Sunier and Hess;[2] it has therefore been thought advisable to redetermine the solubility of gold in mercury using the apparatus just referred to. This paper will present the results obtained on this system between the temperatures 80 and 200°.

Materials.—Mercury which had been run through a five foot Meyer column containing mercurous nitrate and distilled in an all-glass apparatus at reduced pressure according to the method of Hulett and Minchin[3] was used in the first three determinations. The mercury collected in the evaporation of amalgams was used for the remaining determinations. Thousand-fine gold foil obtained from the Philadelphia Mint was used in preparing the amalgams of known concentration and in the first few determinations. The gold residues were used to make up the samples for the later determinations.

Apparatus.—The solubility tube, Fig. 1, a modification of the one used by Sunier and Hess, was made of pyrex glass and consisted of the sample tube, A, a capillary filter finely constricted at B, a glass wool filter, C, the upper tube, D, in which the amalgams were prepared and the capillary, E, which is used in the sampling of amalgams. This capillary had a diameter of one-half millimeter.[4]

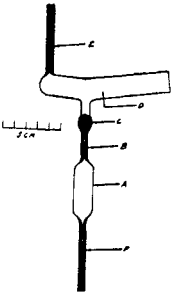


Fig. 1.—Solubility tube.

The solubility tubes were fastened to a rack made of square brass rod and built in a figure H; a side view of the rack is shown in Fig. 2. The tubes in this position are ready for sampling; when turned 180 degrees about the point P the tubes are in the shaking position. The rack (holding four tubes) pivots about the point P and is held in either position by the lock L. The amalgams were shaken by pivoting the vertical rod R in the center and imparting a pendulum-like motion to the tubes on the lower end of the rod of such an amplitude as to completely transfer the amalgams from

[1] Parravano, *Gazz. chim. ital.*, (II), **48**, 123 (1918); Braley and Schneider, THIS JOURNAL, **43**, 740 (1921); Britton and McBain, *ibid.*, **48**, 593 (1926); 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**, 388 (1905).

[4] There was, of course, the *possibility* that the mercury in the capillary did not become saturated with gold (since diffusion processes alone must be relied upon to accomplish this); then, on breaking the capillary for sampling, this mercury would drop into the main body of the amalgam, causing a dilution effect. Because of this possibility the bore of the capillary was made so small that no appreciable error would be caused if no gold at all was to be found in the small portion of mercury. The excellent agreement of the determinations from both the low and high sides gave added proof that no error arose from this cause.

one end of the tubes to the other. The motion imparted to the rod was obtained by a motor-driven eccentric.

The thermostat, a ten-gallon copper tank heavily lagged, containing heavy cylinder oil, was heated by four 500-watt immersion heaters and agitated by four double paddle stirrers (1000 r.p.m.). Thermal balance was obtained at each temperature by two grid heaters of variable resistance placed on opposite sides of the bath. The mercury thermoregulator operating a 40-watt elongated bulb kept the temperature constant to less than 0.05° over a three-hour period.

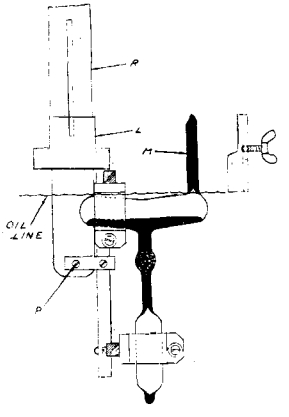


Fig. 2.—Sampling devices.

All temperatures were read from two mercury thermometers graduated in degrees, one standardized by the Physical Laboratory of Taylor Instrument Companies and the other recently standardized by the Bureau of Standards.

Experimental Procedure

The fine capillary, E (Fig. 1), was sealed off and file marked. About 4 cc. of mercury and a 300% excess of gold (using Britton and McBain's data as a guide) were put into the tube, D, which was then sealed off. Capillary F was attached to a Cenco pump, the air evacuated to about 5 mm. and sealed off near the lower end of Tube A.

For a determination of the solubility at a certain temperature, eight tubes were made up and saturation was attained from the low and then from the high temperature side, four tubes being used in each. In the first case the bath was raised to the desired temperature as quickly as possible (requiring at least an hour), the materials were shaken for three hours after thermal balance was obtained and then sampled.

For the corresponding high-side determination the bath was held for three hours at least 5° (sometimes 10 to 15°) above the desired temperature and then allowed to drop back to the determination temperature. This was succeeded by the usual three-hour shaking at constant temperature and sampling. The good agreement is sufficient evidence that equilibrium was attained.

When the tubes were ready to be sampled, the shaker was stopped, the lock L raised and the tubes inverted (with the aid of a brass rod not shown) to the position shown in Fig. 2. The fine capillary was broken at the file mark, M, by means of the apparatus, shown separately in Fig. 2, which is a square brass rod drilled to fit the capillary and fitted with a thumb screw. The capillary is broken by tightening the thumb screw. Both the tipping and breaking devices have greatly facilitated the sampling procedure and have been proved to be very reliable. After filtration the tubes were removed from the bath, wiped clean and cooled. The sample tubes were cut off and the amalgam samples transferred to weighed crucibles.

The evaporation method of analysis for gold was employed, the amalgams being heated in porcelain crucibles placed on iron supports in a large pyrex tube heated by gas. A stream of dry hydrogen was passed through the tube, which was held at about 200° (higher temperatures increase the danger of loss of samples through bumping) until no mercury could be detected with the eye; then the temperature was raised to 500–550° and held there for twelve to sixteen hours in the final runs. The apparatus used is apparently similar to that of Britton and McBain in their Series

III, the percentage of gold running from about 7 to 55% in this series; at lower temperatures and percentages of gold, they used the ferrous ammonium sulfate method of analysis; in neither case is any mention made of the precision of analysis, no blank determinations being recorded. This being the case, considerable preliminary work was done before adopting the evaporation method of analysis; a few of the results obtained will now be presented.

This method of analysis was checked as follows: weighed samples of gold foil heated at 500° for four hours in the stream of hydrogen showed no change in weight; samples of mercury slowly evaporated at 200° and then heated to 500° yielded no weighable residue; lastly, four mixtures of gold and mercury were prepared and the mercury was slowly evaporated at 200°; then the samples were heated to 300° for four hours. Additional heating periods are indicated in Table I. The pieces of gold foil weighed 0.4082, 0.3673, 0.4199, 0.3517 g., respectively; the mercury weighed about 50 g. in each case. The results of this experiment are given in Table I.

TABLE I

EVAPORATION OF MERCURY FROM GOLD-MERCURY MIXTURES

Temp., °C.	Heating period, hours	Percentage of mercury still present in gold			
300	4	6.77	7.14	14.5	6.74
300	4	3.27	3.48	8.38	2.84
400	4	0.76	0.70	2.26	0.43
450	4	0.17	0.23	1.14	0.17

This procedure yielded results 0.2% high, hence in later work (Table II and following) higher temperatures were used with much better results. Merz and Weith[5] found that gold retained about 0.33% of mercury after heating gold amalgams at the temperature of sulfur vapor (445°) for sixty hours.

To test the whole experimental arrangement, four tubes were made up containing weighed amounts of gold and mercury and carried through the entire procedure. Table II shows the excellent results obtained, especially for such a low percentage of gold.

TABLE II

ANALYSIS OF AMALGAMS OF KNOWN CONCENTRATIONS

Residues heated for twelve hours at 480°

	I	II	III	IV
Gold foil, g.	0.1221	0.1371	0.1344	0.1219
Atomic % of gold taken	.1821	.2089	.2018	.1830
Atomic % of gold found	.1824	.2099	.2026	.1829

Experimental Results

In Table III will be found complete data for two temperatures, while Table IV summarizes all of the data obtained thus far. Table V gives the

[5] Merz and Weith, *Ber.*, **14**, 1438 (1881).

solubility of gold in mercury at rounded temperatures and compares these values with those obtained from an empirical equation presented later.

TABLE III

SOLUBILITY OF GOLD IN MERCURY

Complete data for two temperatures

No.	Temp., °C.	Gold at start, g.	Amalgam, g.	Gold, g.	Mercury, g.	Atomic % sol.
1		1.2	53.682	0.3660	53.316	0.694
2	Low side 101.2	1.2	55.241	.3726	54.868	.686
3		1.2	50.465	.3445	50.120	.694
4		1.2	48.152	.3313	47.821	.700
1		1.2	55.406	.3834	55.022	.704
2	High side 101.2	1.2	55.141	.3775	54.763	.696
3		1.2	55.258	.3808	54.877	.701
4		1.2	57.369	.3956	56.974	.701
					Av.	.697
1		2.4	29.944	.6951	28.248	2.442
2	Low side 182.3	2.4	30.355	.7289	29.626	2.442
3		2.4	33.271	.7942	32.477	2.427
1		2.4	35.230	.8404	34.389	2.426
2	High side 182.3	2.4	33.840	.8080	33.032	2.428
3		2.4	30.904	.7400	30.164	2.435
4		2.4	34.347	.8241	33.523	2.440
					Av.	2.434

TABLE IV

SOLUBILITY OF GOLD IN MERCURY (SUMMARY OF EXPERIMENTAL DATA)

No. of detns.	8	8	8	4	8	7	7
Temp., °C.	80.8	101.2	121.7	142.1	159.2	182.3	201.1
At. % sol.	0.467	0.697	1.021	1.482	1.847	2.434	2.875[a]
Av. dev., p.p.t.	12.8	6.4	12.1	1.3	3.4	2.5	24.7

[a] This value is a result of seven determinations made by Mr. O. Fitzsimmons, working in this Laboratory, using the tube developed by Sunier and Hess and evaporating amalgams in a vacuum of 0.003 mm. and flaming the residues. A run at 100.1° using this method of analysis gave results in substantial agreement with those presented here. Both methods of analysis are thus quite satisfactory.

TABLE V

SOLUBILITY OF GOLD IN MERCURY AT ROUNDED TEMPERATURES (FROM LOG N *vs.* $1/T$ PLOT)

Temp., °C.	80.0	100.0	120.0	140.0	160.0	180.0	200.0
100 N (from curve)	0.459	0.684	0.996	1.385	1.871	2.380	2.849
100 N (calcd.)	0.457	0.688	0.994	1.380	1.864	[a]	[a]
Error, p.p.t.	4	6	2	4	4	[a]	[a]

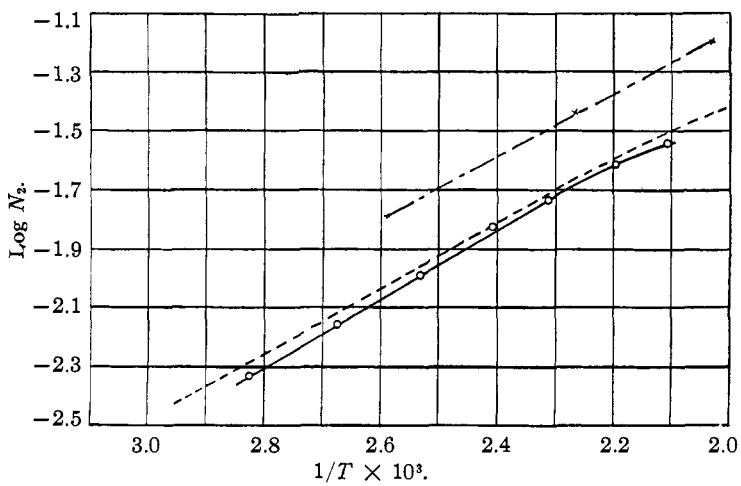
[a] Equation not valid above 160°.

Of the 48 final determinations only five have been omitted. Of these one was rejected because the deviation was greater than four times the average deviation from the mean for that temperature; the other four

constituted the high side at 140° and were rejected because the gold spattered during evaporation; considering the remarkable agreement of the determination from the low side (1.3 p.p.t.) the high-side determination was not repeated. All solubilities are given in atomic per cent. (atoms of gold per 100 total atoms).

Discussion of Results

In Fig. 3 the results are plotted as log N *vs.* $1/T$. It is seen that the values obtained by Parravano and Britton and McBain are greater than those obtained by the authors. The dashed line represents the best line obtained from a plot of Britton and McBain's data, which are on the



×——–, Parravano; – – – –, Britton and McBain; —○—, Authors.

Fig. 3.—Solubility of gold in mercury.

average 5–10% higher than those presented here. Their analytical procedure, discussed earlier, may account for the high results. The data of Parravano are on the average about 75% high, as compared with those presented here. A fusion method was used by Parravano, so it is difficult to judge where error may have crept in, unless it be due to supercooling which is so likely to give trouble in such cases. Braley and Schneider's results are so very different (and are not plotted in Fig. 3) from the others just mentioned and those presented here, that it seems probable that some serious error was made during the conduct of the research. Kasanzeff's results, obtained so long ago, are indeed remarkable for their probable accuracy; his results are in substantial agreement with those presented in this paper. Kasanzeff pressed his amalgams through chamois skin and also filtered them through a fine capillary; analytical details are rather scanty—indeed the whole article is really an abstract only three paragraphs long.

A large plot was carefully constructed and used in determining the equation of the straight line, which can be used for temperatures up to 160° only. The equation found is $\log_{10} N = -1167.4(1/T) + 0.966$. The solubility values in Table V were obtained from the large plot and by means of this equation.

It will be noted that when $\log N$ is plotted against $1/T$, the resulting line is not straight at higher temperature. This, it appears, may be true for one or more of three reasons (even though ideal solutions may be in question): (1) the latent heat of fusion of the solid phase is a function of the temperature; (2) the solid phase may not be the one indicated; (3) an actual transition in the solid phase may take place at the temperature where the break occurs. These possibilities will not be discussed at present. If gold amalgams are not ideal solutions the significance of the slope of the $\log N$ *vs.* $1/T$ curve is rather complicated. Studies along these lines are also under way, not only for amalgams, but other systems. It may be mentioned that some years ago Hildebrand,[6] after a rather thorough research on the vapor pressures of gold and some other amalgams, concluded that the rather large positive deviations from Raoult's law which were encountered might be explained on the assumption of compound formation; more recently,[7] however, the same investigator has said that the gradual accumulation of evidence tends to cast doubt upon this explanation and confirm the theory that internal pressure differences may be largely responsible for such deviations.

Summary

1. A method of preparing and analyzing gold amalgams has been described which yields results 2 parts per thousand high.

2. The solubility tube described earlier has been found suitable (with only slight modification) for the investigation of the system gold-mercury. Fifty-six determinations have been made in the range of temperature 80 to 200°; the present results are considerably lower and the precision of measurement is considerably higher than those previously reported by most other workers.

3. The empirical equation $\log_{10} N = -1167.4(1/T) + 0.966$ expresses the experimental results to 160°, but not above this temperature.

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[6] Hildebrand, THIS JOURNAL, **35**, 501 (1913).

[7] Hildebrand, "Solubility," Chemical Catalog Company, New York, 1924, p. 84 and Chap. XVI.