In view of the uncertainty regarding the quantitative application of the Gronwall–La Mer–Sandved equation, it is useless to attempt to apply a more or less empirically extended activity coefficient equation in explanation of the curves in Figs. 4 and 6.   ·

Summary

The velocity of the persulfate–iodide ion reaction has been measured, in aqueous solution at 25°, between values of $\mu = 0.000625$ and $\mu = 0.025$, with an accuracy of about $\pm 1.5\%$.

The velocity was measured by adding small known amounts of thiosulfate to the reacting solution and noting the time of first appearance of iodine with the aid of a photo-cell circuit far more sensitive to traces of iodine than the visual starch test. The velocity constants, in solutions containing as few ions of valence higher than unity as possible, follow accurately the linear equation

$$\log k = -1.075 + 2\sqrt{\mu}$$

to at least as high a concentration as $\mu = 0.025$.

The small difference in the extrapolation of the plot of $\log k$ against $\sqrt{\mu}$ for univalent and bivalent ions may be qualitatively explained by the difference between the original Debye–Hückel limiting equation for the activity coefficient of an ion and the Gronwall–La Mer–Sandved extension for ions of higher valence than unity.

NEW YORK, N. Y.

THE SOLUBILITY OF GOLD IN MERCURY. III

BY ARTHUR A. SUNIER AND LAW G. WEINER

In earlier papers[1] the results of a study of the solubility of gold in mercury in the temperature interval 0 to 200° were presented. The present paper will deal with a similar study in the range 200 to 300°. The need of such a study will be apparent to all who critically examine the published data[2] in this range of temperature. Although the precision of measurement is not as great as that obtained in earlier papers, it is felt that the method and results are of sufficient interest to warrant publication at this time.

Materials

The mercury was carefully purified and tested as described in earlier papers. In one run (B) mercury was used which was obtained by evapora-

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[1] Sunier and Gramkee, THIS JOURNAL, **51**, 1703 (1929); Sunier and White, *ibid.*, **52**, 1842 (1930).

[2] Parravano, *Gazz. chim. ital.*, **48**, II, 123 (1918); Braley and Schneider, THIS JOURNAL, **43**, 740 (1921); Britton and McBain, *ibid.*, **48**, 593 (1926); Plaskin, *J. Russ. Phys.-Chem. Soc.*, **61**, 521 (1929).

tion from some earlier runs.   Gold in the form of foil, said to contain less than 0.01% impurity, was used in about half of the determinations; in the other half (F to J) gold residues from earlier runs were used. ' No difference in solubility could be traced to this procedure.

Apparatus

Two types of solubility tubes were used.   The first type will not be pictured as it differed only slightly from tubes used earlier.   The second type is pictured in Figs. 1 and 2 in the tube holders which will be described later.   Instead of having a vacuum in these tubes, they were filled with hydrogen at a pressure a little below that of the atmosphere.   At elevated temperatures a pressure greater than atmospheric was produced; consequently when the capillary A was broken, hydrogen issued from the capillary and the amalgam filtered through the fine capillary connecting the tubes R and H. It will be noted that the size of these tubes is somewhat smaller than those used earlier; this was necessary because of the increased solubility of gold at these higher temperatures.
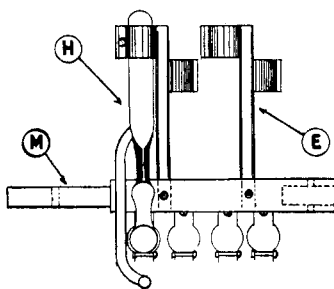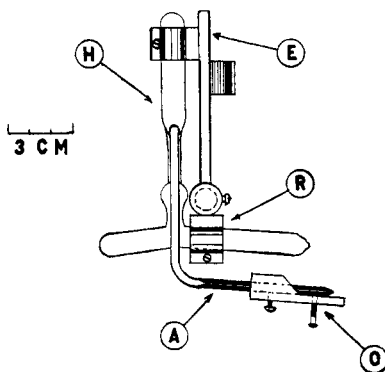

Fig. 1.   Fig. 2.

The tubes were shaken in an air-bath, shown diagrammatically in its final form in Fig. 3, of about one cubic foot capacity.   One five-hundred watt heater made of nichrome ribbon was placed in each corner (H) of the bath as indicated.   Suitable combinations of heaters could be made, to enable a more even distribution of heat, and one heater was placed in circuit with a suitable rheostat to give the fine adjustments of heat required.   A four bladed fan (F) rotated for the most part at 600 r. p. m. was placed at one end of the bath.   Through the other end of the bath was placed the brass shafting, having a diameter of 16 mm., holding the eight solubility tubes.   This shaft was made in three parts, A, B, C.   The first part was the longest and was held in place by suitable self-aligning bearings (not shown) and was connected with a double eccentric mechanism (which need not be described in detail) in such a way that the shaft oscillated back and forth through an angle of about ninety degrees about eleven times per minute. Parts B and C were of about equal length and were so constructed that they could be removed from or fastened to part A with little difficulty.   Figures 1 and 2 give front and side views of part B, to scale.   Four pairs of clamps were provided on each of these sections.   In Figs. 1 and 2 only one solubility tube is shown in place so as not to complicate the figures.

The thermometer was placed in a small metal cup (N) containing about 50 g. of bismuth solder.   As some of the thermometer emerged from the bath, a glass chimney

was provided in later runs. This chimney could be electrically heated to very nearly the temperature of the bath, thus eliminating large stem corrections. Temperature measurements were made with a nitrogen-filled mercury thermometer standardized against a similar thermometer recently standardized by the Physical Laboratory of the Taylor Instrument Company. It is believed that most of the recorded temperatures are accurate to ±0.2°. In the runs up to 275° a Beckmann thermometer was inserted in another metal cup (not shown) in the opposite end of the bath; this thermometer rarely showed changes of 0.1° when the apparatus was working smoothly.
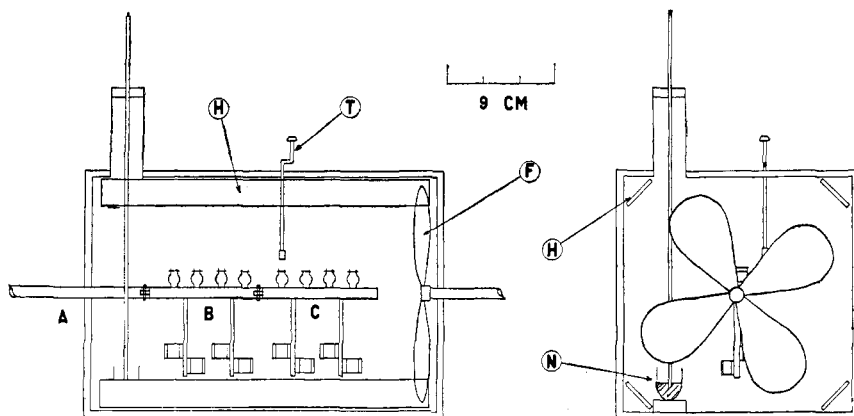

Fig. 3.

The air-bath was very heavily lagged with transite and magnesia board. It was provided with a mica window, kept covered except when it was desired to inspect the tubes. The top of the bath was provided with removable sections to allow inserting the brackets with care and also breaking the capillaries.

Experimental Procedure

The tubes of the first type were filled in the same way as described in earlier papers. Tubes of the second type were supplied with mercury and for the most part about 100% excess gold, using Britton and McBain's data as a guide. These elements were placed in part R of the tube (Fig. 2) and the tube R was sealed as indicated. The capillary was connected to a Hy-vac pump and the tube was thoroughly evacuated, then it was filled with hydrogen and re-evacuated, this flushing process being repeated three or four times. Then, when the pressure of hydrogen was a little less than that of the atmosphere, the capillary was sealed off as indicated. A slight indentation was made on the capillary A, to keep the breaker block in position; the capillary was also file marked a little below the point where the screw O touches the capillary. The tube was next placed in the clamps and the breaker block fastened on in the proper place by means of the screw (not lettered), and also by means of some small asbestos blocks (not shown).

In every run but one, equilibrium was attained from both the high and low sides. Eight tubes were made up, four being placed in bracket B and four in bracket C. When bracket B was fastened to the shaft A (by means of a screw) the oscillating mechanism was set in motion and the temperature of the bath was raised to five or ten degrees above the solubility temperature and held there for three or four hours. Then the temperature was lowered to about one degree above the solubility temperature, when a section of the top of the bath was removed and bracket C was quickly inserted and fastened to

the end of bracket B.   The temperature was then quickly brought to the desired point and held there manually for another three-hour period.

When it was time to sample, the shaking mechanism was stopped and the shaft ABC was rotated 180 degrees; the tubes thus were brought to the sampling position (in Fig. 2 the tubes are shown in the shaking position).   A very narrow (1 × 7 cm.) section of the top was next removed and the special breaking tool (T Fig. 3) placed over the head of the breaking screw O, Fig. 2.   A slight turn of the tool sufficed to break the capillary in the proper place, thus allowing the amalgam to filter properly.   The capillaries of the eight tubes were broken one by one, this operation taking about five minutes. After filtration the bath was allowed to cool somewhat, then the tubes were removed from the bath.   The sampling tubes H were cut off when cool; their contents were then carefully transferred to weighed crucibles.

The amalgams were analyzed by the method described in the first paper of this series.   For the purpose of developing technique and checking the method of analysis, the various preliminary experiments described in the first paper were repeated; the results were essentially the same as those presented earlier and need not be repeated. It may be said that when the weight of the gold residue approximated 1 g., the last traces of mercury were removed with difficulty; in fact on the average the analysis yielded results about 0.5% high.

Experimental Results

In Table I will be found data for the second run made at 239.2°.   In Table II will be found a summary of the results obtained in all of the runs. It will be noted that some of the numbers in column two are placed in

TABLE I
SOLUBILITY OF GOLD IN MERCURY.   COMPLETE DATA FOR ONE TEMPERATURE

No.	Temp., °C.	Gold at start, g.	Amalgam, g.	Gold, g.	Atomic % sol.
B1	High side	4.0	23.040	1.139	5.02
B2	.	4.0	22.849	1.176	5.23
B3	239.2	4.0	24.809	1.210	4.96
B4		4.0	24.876	1.249	5.10
B5	Low side	4.0	16.658	0.839	5.12
B6		4.0	22.580	1.151	5.18
B7	239.2	4.0	32.486	1.594	4.99
B8		4.0	14.222	0.695	4.97
				Average	5.07

TABLE II
SOLUBILITY OF GOLD IN MERCURY.   SUMMARY OF EXPERIMENTAL DATA

Series no.	No. of detns.	Temp., °C.	Atomic % soly.	Av. dev. (from the mean) p. p. h.
C	5(3)	200.0	2.99	1.8
A	5(2)	219.6	3.67	2.9
B	8	239.2	5.07	1.7
G	8	260.2	6.50	2.4
D	7	269.6	7.81	3.6
F	7(1)	279.6	9.07	3.0
E	7	292.6	12.58	4.5
J	5(2)	299.5	13.95	1.5

parentheses; these indicate those tubes omitted from the computation of the average because the results were more than four times the deviation from the mean. The letters in column 1 indicate the order in which the runs were made. It will be noted that determinations H and I are missing. Eight tubes were made up for each of these determinations and the run conducted in the usual way, but at the end of the experiment it was evident that all of the gold had gone into solution, since no residue remained. This absence of excess gold was the first indication that the data of Britton and McBain were in error at the higher temperatures. Determination J was then made, four of the tubes containing a little less than 14 atomic % of gold, which is 50% more than the value of the solubility at 300 recorded by Britton and McBain; the other four tubes contained 100% excess of gold. These eight tubes were run for six hours, attaining equilibrium only from the low side. At the conclusion of the run the tubes containing the lesser quantity of gold had no residue, but the analyses showed that these tubes were apparently only slightly below the saturation point, hence the results are averaged in with those containing the larger amounts of gold.

All of the solubilities are expressed in atomic per cent. of gold. A table giving the solubility at rounded temperatures will, it is hoped, be presented in another paper.

Discussion of Results

In Fig. 4 the results are plotted as atomic per cent. of gold *versus* temperature. A log N vs. $1/T$ plot was constructed but there was a marked departure from a straight line, pointing most certainly to the fact that pure gold is not the solid phase but rather some compound of gold and mercury whose formula is not known at present.

The researches of both Parravano and Plaskin were carried out employing cooling curves. Britton and McBain analyzed the liquid phase in equilibrium with the solid phase, but no blank runs were recorded so it is difficult to estimate the probable accuracy of their results. It is hardly possible that the maximum reported by them is due to analytical errors; it would seem rather to be due to an error in sampling, but even this is not wholly satisfactory since below 225° their results are essentially in agreement with the present results. This marked discrepancy in the results at 300° led to the execution of some supplementary experiments which will be discussed under "Supplementary Experiments."

It may be well to discuss briefly, at this point, several possible sources of error in the present experiments. On the analytical side it is believed that 1% would be a very liberal estimate of the maximum error, and this error was occasioned by the large residues of gold obtained in several of the experiments—residues of 2 to 4 g. being obtained in runs D and E. In later runs a definite effort was made to keep the residues below one gram.

Occasionally it would be found that in several tubes of a given run the gold strips were not transferred from one end of the tube R to the other end, hence the attainment of equilibrium was hindered to some extent. Then, further, spattering tended to result especially with the larger weights of gold. If the tiny droplets of mercury or amalgam produced on the walls of the tube were not gotten into the main body of the amalgam in subsequent oscillations of the tube, a slight dilution effect (in the low side tubes) would be produced at the time of sampling when these droplets
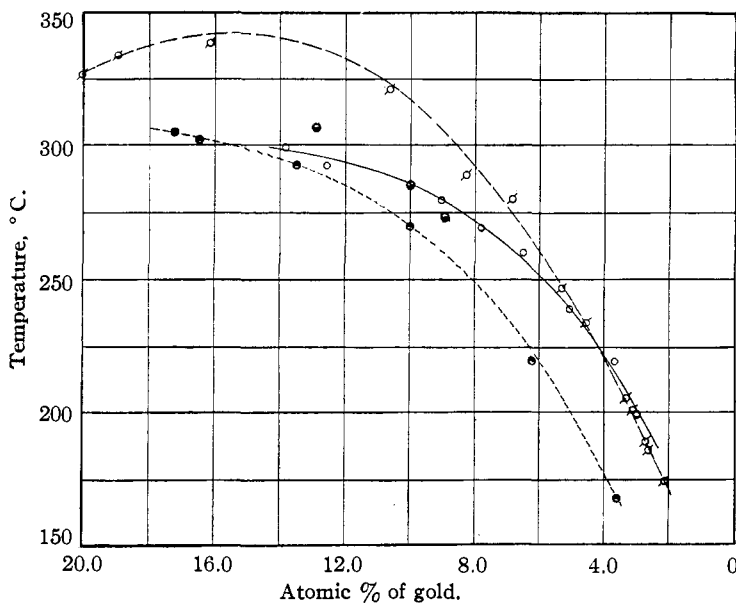

Fig. 4.—Solubility of gold in mercury: - -◐- -, Parravano; —∅—, Britton and McBain; ◒, Plaskin; —O—, Authors.

coalesced with the main portion of the amalgam. This is believed to be one of the greatest sources of error in the present experiments where such small amounts of amalgam are involved. It may be that this source of error can be eliminated by making the tube R straight and of smaller bore, and making a little larger the bulb and tube connecting the tubes H and R.

In the two earlier papers mention was made of a slight error which may have arisen from the capillary used in admitting air when filtering the amalgams. Such an error was eliminated in the present experiments by the new design of the solubility tube.

Temperature constancy and uniformity in an air-bath is rather difficult to obtain and this is believed to be largely responsible for the rather poorer precision of measurement in the present experiments.

Supplementary Experiments

Britton and McBain performed two supplementary experiments concerning which the following is said: "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 reformation of the solid phase by complete inversion of the tube and furnace. Tube I contained a mixture of 30% 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°. 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°."

Unfortunately no mention is made of further runs in the concentration range 8 to 18%. To supply this needed information several runs were made by the present authors with the special object of determining whether or not a maximum in the solubility curve was to be found at about 14.3%, this being the value given by Britton and McBain.

The tubes used in the present supplementary experiments were similar to those used in runs A to J; the capillary connecting the tubes H and R (Fig. 2) had a larger bore and the capillary A was affixed to the bottom of the sampling tube H. Weighed quantities of gold and mercury, as indicated in Table III, were introduced into the tubes, which were then evacuated to 0.3 mm. The tubes were now placed in the brackets, rocked back

TABLE III

RESULTS OF SUPPLEMENTARY RUNS

Tube no.	Gold, g.	Mercury, g.	Atomic % gold	Temperature, °C. Disappearance of gold	Reapp. of gold	From curve
K1	4.906	40.80	10.90	290.9	288	
K2	4.905	40.80	10.90	289.6	288	
K3	4.896	40.80	10.88	291.4	288	
		Average	10.89	290.6		290
L1	6.695	40.80	14.30	300.6	294	
L2	6.608	40.80	14.15	298.0	294	
L3	6.704	40.80	14.35	300.6	294	
		Average	14.27	299.7		299

and forth and observations of the disappearance and reappearance of the solid phase on complete inversion of the tubes were made through the mica window. Considerable care was exercised in determining the solubility temperature. In another research involving non-metallic solutions it has been shown[3] that a rate of heating of 0.1° per minute gave a result accurate

[3] Sunier, J. Phys. Chem., 34, 2582 (1930).

to about one-half of one degree.   It is difficult to estimate what the corresponding error would be in metallic systems such as the one under consideration, but from preliminary observations in this Laboratory it would appear that the error would be no greater than that just mentioned.   The solubility temperature was determined at a number of different rates of heating, 1, 0.25, 0.1° per minute.   In Table III the results are for a rate of 0.1° per minute.

From an inspection of Table III it is apparent that these supplementary runs corroborate the data presented in Table II, and thus no maximum in the curve is found for a temperature of 300°.   Considerable confidence is placed in these runs using the synthetic method; indeed it appears such a promising method that it is being used in another research in this system in the temperature range 300 to 400°.

Summary

About fifty determinations of the solubility of gold in mercury have been made, in the temperature interval 200 to 300°, with a modified solubility tube and an air-bath.   No maximum in the solubility curve is found, the results being confirmed by six supplementary runs using the synthetic method.

ROCHESTER, NEW YORK

THE COMPRESSIBILITY ISOTHERMS OF HELIUM AT TEMPERATURES FROM −70 TO 200° AND AT PRESSURES TO 1000 ATMOSPHERES

BY R. WIEBE, V. L. GADDY AND CONRAD HEINS, JR.

This is the eighth report of a series from this Laboratory concerning the physical properties at high pressures of gases and their mixtures that are of interest in the commercial synthesis of ammonia.[1]   It was thought desirable to include helium in this program since its properties would assist in the solution of several problems of importance.   The knowledge of the compressibility of a gas which is chemically inactive and only slightly adsorbed by most catalysts will aid greatly in the determination of the adsorption of various gases on catalysts at high pressures.   It will also be of value in the theoretical study of gases under high pressures.

The gas was obtained from the Amarillo Helium Plant of the U. S.

[1] (a) Bartlett, THIS JOURNAL, 49, 65 (1927); (b) 49, 687 (1927); (c) 49, 1955 (1927); (d) Bartlett, Cupples and Tremearne, ibid., 50, 1275 (1928); (e) Bartlett, Hetherington, Kvalnes and Tremearne, ibid., 52, 1363 (1930); (f) 52, 1374 (1930); (g) Kvalnes and Gaddy, ibid., 53, 394 (1931).