# THE SOLUBILITY OF GOLD.

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### ABSTRACT.

The solubilities of gold in various solutions as calculated from electrode potential and free energy data agree well with experimental results reported in the literature. In acid solutions gold dissolves as the ion $AuCl_4^-$. Formation of this ion requires that the solution contain excess $Cl^-$, and that it contain or be in contact with a fairly strong oxidizing agent. Naturally-occurring oxidizing agents whose effectiveness has been demonstrated both experimentally and theoretically are $MnO_2$, $O_2$, $Fe^{+++}$ and $Cu^{++}$. Neither $H^+$ nor $SO_4^{--}$ is sufficiently strong as an oxidizing agent to affect gold appreciably at ordinary temperatures. In naturally-occurring alkaline solutions gold is not significantly soluble unless sulfide is present. In sulfide solutions gold is carried as a complex ion, probably $AuS^-$; the fact that gold metal is soluble in $HS^-$ solutions at ordinary temperatures indicates that this ion is an exceptionally stable one. The effect of temperature on the solubility of gold cannot be predicted from available thermodynamic data, but experiments indicate that the solubility increases with rising temperature in both acid and alkaline solutions.

### INTRODUCTION.

DESPITE its chemical inertness, gold is sufficiently soluble to explain the known facts about its transportation in vein fluids and surface waters. Experimental work on the solubility of gold is voluminous, and the more recent papers provide fairly consistent data. The data have been ably summarized by Ogryzlo (1),[1] Smith (2) and Zvyagintsev and Paulsen (3). The purpose of the present paper is to show that the experimental results and geologic observations check reasonably well with predictions from thermodynamic data on gold solutions.

### THERMODYNAMIC DATA.

The pertinent data are the standard electrode potentials in Table I and the standard free energies of formation in Table II, both taken from Latimer (4). Either the electrode potentials or the free energies permit calculation of how far any given reaction will proceed. The electrode potentials provide the most direct means of calculation for oxidation-reduction processes; the free energies, although more cumbersome, are applicable to any reaction, whether it involves oxidation-reduction or not. The data of Tables I and II apply to solutions at a temperature of 25° C. and having concentrations of 1 mole/liter with respect to all soluble substances. Calculations for different concentrations are easy, but calculations for higher or lower temperatures cannot be made without further data.

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[1] Numbers in parentheses refer to Bibliography at end of paper.

TABLE I

STANDARD ELECTRODE POTENTIALS AT 25° C (IN VOLTS) (FROM LATIMER, 4)

In acid solutions:

| | | |
|---|---|---|
| (1) | $H_2 = 2H^+ + 2e^-$ | 0.000 |
| (2) | $H_2SO_3 + H_2O = SO_4^{--} + 4H^+ + 2e^-$ | $-0.20$ |
| (3) | $CuCl_2^- = Cu^{++} + 2Cl^- + e^-$ | $-0.5$ |
| (4) | $Fe^{++} = Fe^{+++} + e^-$ | $-0.771$ |
| (5) | $Au + 4Cl^- = AuCl_4^- + 3e^-$ | $-1.00$ |
| (6) | $2H_2O = O_2 + 4H^+ + 4e^-$ | $-1.229$ |
| (7) | $Mn^{++} + 2H_2O = MnO_2 + 4H^+ + 2e^-$ | $-1.28$ |
| (8) | $Cl^- = \frac{1}{2}Cl_2 + e^-$ | $-1.358$ |
| (9) | $Au = Au^{+++} + 3e^-$ | $-1.42$ |
| (10) | $Au = Au^+ + e^-$ | $-1.68$ |

In basic solutions:

| | | |
|---|---|---|
| (11) | $OH^- + Fe(OH)_2 = Fe(OH)_3 + e^-$ | $+0.56$ |
| (12) | $OH^- + Mn(OH)_2 = Mn(OH)_3 + e^-$ | $+0.40$ |
| (13) | $H_2O + 2OH^- + Cu_2O = 2Cu(OH)_2 + 2e^-$ | $+0.09$ |
| (14) | $4OH^- = O_2 + 2H_2O + 4e^-$ | $-0.401$ |
| (15) | $Au + 4OH^- = AuO_2^- + 2H_2O + 3e^-$ | ca. $-0.5$ |

The biggest gap in presently available physico-chemical data for gold, as for most other substances of interest in economic geology, is the lack of information at high temperatures. In the present paper we can only make calculations for 25° and then indicate probable directions of variation as the temperature changes.

Before undertaking numerical calculations, we can make a few qualitative predictions at once from Table I. The table is arranged in the usual manner, with the reduced form of each electrode reaction on the left and the oxidized form on the right, and with the oxidized form increasing in oxidizing power downward. This means that the oxidized form of any couple will react readily with the reduced form of any couple above it in the series, but will not react (or will react only to a slight extent) with the reduced form of a couple below it. It is immediately apparent, then, that gold cannot be soluble in ordinary acids, because all of the gold ions (AuCl₄⁻,

TABLE II

STANDARD FREE ENERGIES OF FORMATION AT 25° C
(IN CALORIES/MOLE) (FROM LATIMER, 4)

| | | | |
|---|---|---|---|
| $Cl^-$ | $-31,330$ | $H^+$ | 0 |
| $CuCl_2^-$ | $-58,300$ | $H_2O(1)$ | $-56,690$ |
| $Cu^{++}$ | $+15,910$ | $OH^-$ | $-37,585$ |
| $AuCl_4^-$ | $-56,200$ | $H_2S(aq)$ | $-6,520$ |
| $Fe^{++}$ | $-20,310$ | $HS^-$ | $+2,950$ |
| $Fe^{+++}$ | $-2,530$ | $S^{--}$ | $+23,420$ |
| $Mn^{++}$ | $-48,600$ | $SO_4^{--}$ | $-176,100$ |
| $MnO_2$ | $-102,900$ | $H_2SO_3(aq)$ | $-128,535$ |

$Au^{+++}$ and $Au^+$) are well below the $H_2$—$H^+$ couple. In other words, the gold ions should be reduced by molecular hydrogen to gold metal, but the metal would not be dissolved by hydrogen ion. Also the table shows at once that neither of the simple gold ions, $Au^+$ or $Au^{+++}$, can exist in solution in geologic environments, since these ions are stronger oxidizing agents than free chlorine. On the other hand, reactions 5 and 7 suggest that gold may be oxidized by $MnO_2$ in acid solution, provided that $Cl^-$ is present to form $AuCl_4^-$. Free oxygen should also be capable of oxidizing gold in acid solution (reactions 5 and 6). Solutions of ferric ion, $Fe^{+++}$, and cupric ion, $Cu^{++}$, are weaker oxidizing agents than $AuCl_4^-$; nevertheless the potentials of reactions 3 and 4 are close enough to the potential of reaction 5 so that with high concentrations these ions might be capable of bringing minute amounts of gold into solution. These predictions and others will now be examined quantitatively.

### METHOD OF CALCULATION.

To say that gold is not soluble in acid means more precisely that the solubility in acid is extremely small. Just how small it is can be calculated from an equation obtained by combining electrode reactions 1 and 5:

$$Au + 3H^+ + 4Cl^- = AuCl_4^- + 3/2H_2 \qquad (16)$$
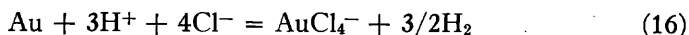
Subtraction of the electrode potentials gives for the electromotive force of this reaction

$$E = -1.00 - 0.00 = -1.00 \text{ volts}$$

From this figure the free energy change for the reaction is derived by the relation

$$\Delta F° = -nfE$$

where $\Delta F°$ means the free energy change at 25° C when the concentrations of $H^+$, $Cl^-$ and $AuCl_4^-$ are 1 mole/liter (1M) and the pressure of $H_2$ is 1 atmosphere; $n$ is the number of electrons transferred, as shown by the equation (in this case $n = 3$, since each Au atom loses 3 electrons and each of 3 hydrogen ions picks up 1 electron); and $f$ is the Faraday constant, 23,066 cal/volt/equivalent. Substituting,

$$\Delta F° = -3 \times 23,066 \times (-1.00) = +69,200 \text{ cal}$$

This same result can also be obtained by adding free energies of formation from Table II for all the substances in equation 16. By definition, the free energy of formation of an element (in its standard state) is zero, and the free energy of formation of $H^+$ in 1M solution is also defined as zero. From Table II, the free energy of $AuCl_4^-$ is $-56,200$ cal, and that of $Cl^-$ is $-31,330$. Hence

$$\Delta F° = \text{free energy of products} - \text{free energy of reactants}$$
$$= -56,200 + 3/2 \times 0 - 0 - 3 \times 0 - 4 \times (-31,330)$$
$$= -56,200 + 125,320 = +69,120 \text{ cal}$$

The slight discrepancy between 69,200 calculated from electrode potentials and 69,120 calculated directly from free energies is of no consequence for present purposes. So many variables are uncontrolled in the geologic environments to which these calculations will be applied that we can hope for no more than order-of-magnitude figures.

A high negative electromotive force like the −1.00 volt of the present example, and a high positive $\Delta F$ like the 69,200 cal of this example, both indicate that the reaction is displaced far to the left at equilibrium—in other words, that the amount of gold which will go into $AuCl_4^-$ is inappreciable. To get a figure for the amount, we need a value for the equilibrium constant of equation 16, which can be calculated from the relation

$$\Delta F^\circ = - RT \ln K$$

in which $R$ is the gas-law constant, 1.987 cal/mole; $T$ is absolute temperature; and $K$ is the equilibrium constant. For present purposes $T$ will be uniformly 298°, so that the formula can be rearranged and simplified as follows:

$$
\begin{aligned}
\log K &= \ln K/2.303 \\
&= - \Delta F^\circ/2.303RT \\
&= - \Delta F^\circ/2.303 \times 1.987 \times 298 \\
&= - \Delta F^\circ/1365
\end{aligned}
$$

The factor 2.303 is introduced to change natural logarithms to decimal logarithms. In the present example,

$$\log K = - 69,200/1365 = \text{ca.} - 51$$
$$K = \frac{(AuCl_4^-)(H_2)^{3/2}}{(H^+)^3(Cl^-)^4} = 10^{-51}$$

Strictly $\log K$ turns out to be −50.7, but the approximate value, −51, is more than sufficiently accurate for this calculation. If now we suppose that the acid concentration is 1M ($H^+ = 1$, $Cl^- = 1$), and if we suppose further than no $H_2$ is present except what is produced in the reaction (making the number of moles of $H_2$ always 3/2 the number of $AuCl_4^-$), we may substitute in the equation for $K$:

$$K = \frac{(AuCl_4^-)(3/2 \times AuCl_4^-)^{3/2}}{(1)^3(1)^4} = 10^{-51}$$

$(AuCl_4^-)^{5/2} = 0.55 \times 10^{-51}$; approximately $AuCl_4^- = 10^{-20}$ mole/liter. Hence the amount of Au in solution is $10^{-20}$ gram-atom or approximately $2 \times 10^{-18}$ gram/liter (atomic weight of Au = 197, approximately $2 \times 10^2$). In other words, the solubility of gold in 1M HCl is so small that the concentration of dissolved gold would be equivalent to about 1 gram in a volume of water equal to that in the Gulf of Mexico. Raising the concentration of acid to 10M would increase the solubility 1,000 times, but the

amount of gold in solution would still be negligibly small ($2 \times 10^{-15}$ gram/liter).

For a second example, consider the effect on gold of $MnO_2$ in contact with an acid chloride solution. The equation is a combination of electrode reactions 5 and 7:

$$2Au + 12H^+ + 3MnO_2 + 8Cl^- = 3Mn^{++} + 2AuCl_4^- + 6H_2O \quad (17)$$
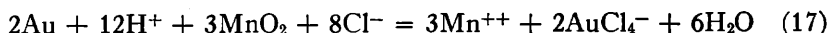
Using the same procedure as before, we obtain $E = +0.28$ volt, $\Delta F^\circ = -38,000$ cal, and $K = $ ca. $10^{28}$. The positive electromotive force, negative free energy change, and large equilibrium constant all mean that equation 17 is displaced far to the right; in other words, that gold is readily soluble in a mixture of $MnO_2$ and 1M HCl. The large coefficients of $H^+$ and $Cl^-$ in equation 17, however, mean that the solubility is very sensitive to changes in the concentrations of these ions. In order to calculate the effect of concentration, we set up the expression for the equilibrium constant,

$$K = (Mn^{++})^3(AuCl_4^-)^2/(H^+)^{12}(Cl^-)^8 = \text{ca. } 10^{28}$$

We assume that no $Mn^{++}$ is present except what is produced in the reaction; in other words, 3/2 moles of $Mn^{++}$ will be present for every mole of $AuCl_4^-$. (If more $Mn^{++}$ is present, the solubility will be decreased.) Then

$$(AuCl_4^-)^5 = 8/27 \times 10^{28} \times (H^+)^{12}(Cl^-)^8$$

From this equation the concentrations in Table III are calculated. The figures are only approximate, since we are concerned here only with orders of magnitude.

<div align="center">

TABLE III.

SOLUBILITIES OF GOLD IN HCl + $MnO_2$ AT 25° C.

</div>

| Concentration of | | Solubility of Au | |
|---|---|---|---|
| $H^+$ (mole/l) | $Cl^-$ (mole/l) | mole/l | gram/l |
| $10^{-4}$ | 1 | $10^{-4}$ | 0.02 |
| $10^{-5}$ | 1 | $10^{-6.5}$ | $10^{-4}$ |
| $10^{-6}$ | 1 | $10^{-9}$ | $2 \times 10^{-7}$ |
| 1 | $10^{-4}$ | 0.1 | 20 |
| 1 | $10^{-6}$ | $10^{-4}$ | 0.02 |
| 1 | $10^{-8}$ | $10^{-7}$ | $2 \times 10^{-5}$ |
| $10^{-2}$ | $10^{-2}$ | $10^{-2}$ | 2 |
| $10^{-3}$ | $10^{-3}$ | $10^{-5}$ | $2 \times 10^{-4}$ |
| $10^{-4}$ | $10^{-4}$ | $10^{-10}$ | $2 \times 10^{-8}$ |

If we select $10^{-6}$ gram/liter (1 part per billion) as an arbitrary dividing line between significant and non-significant concentrations of gold, Table III indicates that the metal is appreciably soluble in the presence of $MnO_2$ in HCl more dilute than 0.001M, or in still smaller concentrations of either $H^+$ or $Cl^-$ provided the other is present in large amount. Concentrations of $H^+$ of 0.001M and higher are not uncommon in geologic environments, especially in the oxidized zones of ore deposits; so high a concentration of $Cl^-$ is less common, but concentrations up to 0.025M are reported in a few

mine waters (see analyses in Emmons (5), pp. 87–89, and Clarke (6), pp. 646–647).

It should be noted that the driving force of the $MnO_2$ reaction is not, as is commonly stated, the formation of $Cl_2$ or of "nascent" chlorine. As Table III shows, gold is dissolved in appreciable amounts by concentrations of HCl far too small to produce chlorine by reaction with $MnO_2$. The reaction goes because of the great stability of $AuCl_4^-$; the function of the $MnO_2$ is to oxidize the gold, and the function of the $Cl^-$ is to tie up the oxidized gold in this ion. The solution must be acid because $MnO_2$ is an effective oxidizing agent only in the presence of $H^+$.

The method of calculation illustrated by these two examples will be used for other reactions in the following sections.

### SOLUBILITY OF GOLD IN ACID SOLUTIONS.

For gold to dissolve in an acid solution requires two things: the presence of chloride ion (to form $AuCl_4^-$) and the presence of an oxidizing agent considerably stronger than $H^+$ alone. These requirements eliminate HCl and other common acids, by themselves, as solvents for gold. The inability of acids to affect the metal (except at high temperatures) has been demonstrated experimentally for inorganic acids by Ogryzlo (1) and others, and for organic acids by Fetzer (7).

The reaction with $MnO_2$ and HCl discussed in the last section is the one which Emmons long ago (8, pp. 405–408) suggested for the transportation of gold in supergene waters, and which he demonstrated both by experiment and by field observation.

Besides $MnO_2$, a few other naturally-occurring oxidizing agents are capable of oxidizing gold in acid chloride solutions. One is atmospheric oxygen, for which a reaction may be written by combining electrode reactions 5 and 6:

$$2Au + 6H^+ + 3/2O_2 + 8Cl^- = 2AuCl_4^- + 3H_2O \qquad (18)$$
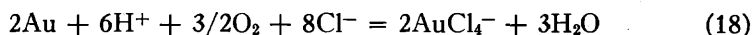
Calculation gives $E = +0.23$ volt, $\Delta F° = -32,000$ cal, $K =$ ca. $10^{23}$. Like the $MnO_2$ reaction, this one is sensitive to changes in $H^+$ and $Cl^-$. Table IV shows the solubility of gold at representative values of these ions. on the assumption that $O_2$ has a constant partial pressure of 0.2 atmosphere,

### TABLE IV.

#### SOLUBILITY OF GOLD IN HCl + $O_2$ AT 25° C.

| Concentration of | | Solubility of Au | |
|---|---|---|---|
| $H^+$ (mole/1) | $Cl^-$ (mole/1) | mole/1 | gram/1 |
| 1 | 1 | high | high |
| $10^{-4}$ | 1 | 0.1 | 20 |
| $10^{-6}$ | 1 | $10^{-7}$ | 0.00002 |
| $10^{-7}$ | 1 | $10^{-10}$ | $2 \times 10^{-8}$ |
| 1 | $10^{-4}$ | $10^{-5}$ | 0.002 |
| 1 | $10^{-5}$ | $10^{-9}$ | $2 \times 10^{-7}$ |
| $10^{-2}$ | $10^{-2}$ | $10^{-3}$ | 0.2 |
| $10^{-3}$ | $10^{-3}$ | $10^{-10}$ | $2 \times 10^{-8}$ |
| $10^{-2}$ | $10^{-3}$ | $10^{-7}$ | $2 \times 10^{-5}$ |

The table indicates that gold should dissolve appreciably in well-aerated surface waters of only slight acidity, provided that the concentration of $Cl^-$ is high. If $Cl^-$ is low (say, below 0.001M or 35 p.p.m.), the acidity required is above that to be expected in natural waters. Under any circumstances the reaction will be very slow, as are most processes involving molecular oxygen.

Another possible oxidizing agent is ferric ion, $Fe^{+++}$:

$$Au + 3Fe^{+++} + 4Cl^- = AuCl_4^- + 3Fe^{++} \qquad (19)$$

for which $E = -0.23$ volt, $\Delta F° = +16,000$ cal, $K = $ ca. $10^{-12}$. Ferric ion, of course, is a much weaker oxidizing agent than either $O_2$ or $MnO_2$, a fact which is reflected in the positive free energy change and the small $K$. Nevertheless, with sufficiently high concentrations of $Fe^{+++}$ and $Cl^-$, gold is appreciably soluble, as Table V shows. The theoretical figures in Table V check fairly well with experiments described in the literature. McCaughey (9) reports that gold dissolved slowly at 38–43° C in a solution containing

TABLE V.

SOLUBILITY OF GOLD IN $Fe^{+++}$ + $Cl^-$ AT 25° C.

| Concentration of | | Solubility of Au | |
|---|---|---|---|
| $Fe^{+++}$ (mole/1) | $Cl^-$ (mole/1) | mole/1 | gram/1 |
| 1 | 1 | $5 \times 10^{-4}$ | 0.1 |
| 0.1 | 0.1 | $10^{-5}$ | 0.002 |
| 0.01 | 0.01 | $10^{-7}$ | $2 \times 10^{-5}$ |
| 0.001 | 0.001 | $5 \times 10^{-9}$ | $10^{-6}$ |
| 1 | $10^{-5}$ | $5 \times 10^{-9}$ | $10^{-6}$ |
| $10^{-6}$ | 1 | $10^{-8}$ | $2 \times 10^{-6}$ |

about 0.1M $Fe^{+++}$ and about 2.4M $Cl^-$, reaching 0.023 gram/liter after 185 hours, but equilibrium had not yet been attained. With these concentrations the theoretical solubility at 25° is about 0.035 gram/liter, which agrees with the experimental figure as closely as can be expected. Brokaw (10), working with solutions of 0.1M $Cl^-$ and 0.03M $Fe^{+++}$, reports no detectable solution of gold at 18–25° C. The theoretical solubility under these conditions would be about 0.0006 gram/liter, or about 0.00003 gram in the 50 cc samples which Brokaw used. Since Brokaw was using a balance sensitive to 0.00001 gram, he should have been barely able to detect a solubility of this magnitude. The fact that he did not may mean that equilibrium had not been reached even after the 34 days of his experiment, or that his $FeCl_3$ contained a trace of $FeCl_2$, or that the thermodynamic data are somewhat inaccurate. In any event it seems clear that $FeCl_3$ must be fairly concentrated to affect gold significantly.

The effect of $Fe^{++}$ in decreasing the solubility of gold, which would be predicted from equation 19, is borne out by McCaughey's observation that less gold was dissolved in solutions to which $FeSO_4$ had been added. Statements in the older literature that gold can be dissolved by ferric sulfate or by ferric sulfate plus sulfuric acid have been repeatedly proved wrong by experiment (1), and are likewise refuted by the above thermodynamic

data. Compounds of ferric ion can affect gold only when $Cl^-$ is present to form $AuCl_4^-$.

Another conceivable oxidizing agent is cupric ion, $Cu^{++}$:

$$Au + 3Cu^{++} + 10Cl^- = AuCl_4^- + 3CuCl_2^- \qquad (20)$$

for which $E = -0.50$ volt, $\Delta F° = 34{,}500$ cal, $K = $ ca. $10^{-25}$. From these data a solubility of about 0.0001 gram/liter may be calculated for concentrations of $Cu^{++}$ and $Cl^-$ both 1M at 25° C. McCaughey (9) reports a minimum solubility of 0.0018 gram/liter for concentrations of 2.4M $Cl^-$ and 0.13M $Cu^{++}$ at 38–45° C, conditions for which the theoretical figure would be 0.0002 gram/liter at 25° C. The agreement between theory and experiment is poor, but both indicate clearly that $Cu^{++}$ has less effect on gold than $Fe^{+++}$, and that gold can dissolve in copper solutions under natural conditions only if concentrations of both $Cu^{++}$ and $Cl^-$ are abnormally high.

An oxidizing agent weaker than $Cu^{++}$ cannot affect gold appreciably at ordinary temperatures. This may be illustrated by considering another possible naturally-occurring oxidizing agent, sulfuric acid. This substance can act as an oxidizing agent in two ways: (1) by the addition of an electron to $H^+$, forming $H_2$; (2) by the addition of two or more electrons to the sulfur of $SO_4^{--}$, forming $H_2SO_3$, S, or $H_2S$. The inadequacy of $H^+$ as an oxidizing agent for gold has been demonstrated above; the inadequacy of $SO_4^{--}$ may be shown by combining reactions 2 and 5 from Table I:

$$2Au + 8Cl^- + 12H^+ + 3SO_4^{--} = 2AuCl_4^- + 3H_2SO_3 + 3H_2O \quad (21)$$
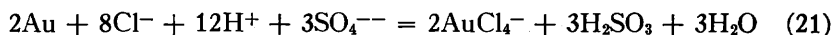
In this equation $SO_4^{--}$ is given the benefit of everything that will help it act as an oxidizing agent—an acid solution, and an adequate supply of $Cl^-$ to unite with the oxidized gold. Calculation gives $E = -0.8$ volt, $\Delta F° = $ ca. $+110{,}000$ cal, and $K = 10^{-81}$. If $Cl^-$, $H^+$ and $SO_4^{--}$ all have concentrations of 1M, and if no $H_2SO_3$ is present except that produced in the reaction, the solubility of gold is about $10^{-16}$ mole/liter or $2 \times 10^{-14}$ gram/liter. Hence even at concentrations greater than could be expected in natural solutions the solubility is negligibly small.

In summary, oxidation-reduction potentials indicate that gold should be soluble at normal temperatures in acid waters containing $Cl^-$ and any one of several moderately strong oxidizing agents ($MnO_2$, $O_2$, $Fe^{+++}$, $Cu^{++}$). The solubilities indicated, however, are appreciable only under conditions which would be fairly uncommon in nature. This conclusion agrees with experimental results and with the observation that gold is sometimes transported in supergene waters, but only locally and in small amounts.

### SOLUBILITY OF GOLD IN ALKALINE SOLUTIONS.

In alkaline solution $AuCl_4^-$ becomes unstable, changing to $AuO_2^-$ if sulfide is not present:

$$AuCl_4^- + 4OH^- = AuO_2^- + 2H_2O + 4Cl^-$$

The free energy change for this reaction, calculated from the figures in Table II, is $-$ 34,000 cal, the high negative value indicating the much greater stability of $AuO_2^-$. In any solution not containing sulfide ion and having a pH over 8, $AuO_2^-$ should be the dominant ion.

Gold should be dissolved by strongly basic solutions, with atmospheric oxygen acting as the oxidizing agent, according to the reaction (from electrode reactions 14 and 15, Table I):

$$2Au + 3/2O_2 + 2OH^- = 2AuO_2^- + H_2O \qquad (22)$$

For this reaction $E =$ ca. $-$ 0.1 volt, $\Delta F^\circ =$ ca. $+$ 14,000 cal/mole, and $K =$ ca. $10^{-10}$. In 1M $OH^-$, if the partial pressure of $O_2$ is 0.2 atmosphere, the solubility of gold should be about 0.001 gram/liter; in 0.0001M $OH^-$ (about the upper limit of alkalinity in naturally-occurring solutions) the solubility is only $10^{-6}$ gram/liter. In nature at ordinary temperatures, therefore, gold should not be appreciably affected by atmospheric oxygen in the presence of alkaline solutions. Nor can any form of iron, copper or manganese affect the metal in alkaline solution, since $Fe(OH)_3$, $Cu(OH)_2$ and $Mn(OH)_3$ are relatively feeble oxidizing agents; comparison of electrode potentials for reactions 11, 12, 13 and 15 in Table I shows this relationship clearly.

For alkaline solutions containing sulfide ion, chemical data are scanty and the problem is more complicated. The artificially prepared gold sulfide, AuS, is known to be soluble in excess $S^{--}$ and $S_x^{--}$ (Mellor (11), pp. 610–614), proving the existence of some kind of complex sulfide ion. Smith (2) and Latimer and Hildebrand (12) consider $AuS^-$ as the most probable ion, although some $AuS_2^-$ may form also. Experimentally, one of the most perplexing facts about the chemistry of gold is its ability to dissolve in solutions of $HS^-$ of moderate concentration even at room temperature, whereas it dissolves in $S^{--}$ (i.e., more alkaline solutions) only in concentrated solutions at high temperature. This characteristic of gold has been demonstrated by Ogryzlo (1), by Zvyagintsev and Paulsen (3), and by Lindner and Gruner (13). None of these authors have suggested a mechanism for the reaction.

The difficulty is that in order to dissolve gold it must be oxidized, and a solution of NaHS or KHS seems to contain no oxidizing agent of anywhere near sufficient strength. (In most of the experimental work atmospheric oxygen was rigorously excluded.) The strongest oxidizing substance present is $HS^-$, which would have to react according to the equation

$$Au + HS^- = AuS^- + \tfrac{1}{2}H_2 \qquad (23)$$
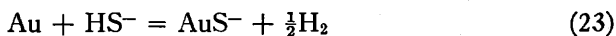
This seems patently absurd; a metal immune to attack by strong acids should be completely indifferent to a very weak acid like $HS^-$. The only possibility is that $AuS^-$ may be exceptionally stable, sufficiently so to pull the reaction to the right in spite of the weakness of $HS^-$. If we make this assumption, it is possible to get a measure of the stability of $AuS^-$ from the solubilities found by Ogryzlo and by Zvyagintsev and Paulsen. The data

are not entirely consistent, but suggest a solubility of about 0.0001 mole/liter of AuS⁻ in 2M HS⁻ at room temperature. This gives an equilibrium constant for equation 23 of about $10^{-6}$, which leads to $\Delta F° = $ ca. $+ 8,000$ cal. Using $+3,000$ cal as the free energy of formation of HS⁻, we find for the free energy of formation of AuS⁻, $\Delta F° = $ ca. $+11,000$ cal.

With this figure we can compare the stabilities of $AuO_2^-$ and AuS⁻ by calculating the free energy changes in the reactions

$$2HS^- + AuO_2^- = AuS^- + S + 2OH^-$$

$$2H_2O + 2S^{--} + AuO_2^- = AuS^- + S + 4OH^-$$
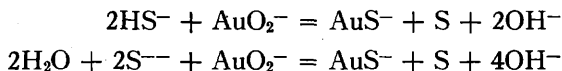
for which $\Delta F° = $ ca. $-54,000$ and $-71,000$ cal, respectively. The high negative values mean that AuS⁻ is very much more stable than $AuO_2^-$, so that an alkaline solution containing even a trace of sulfide must have its dissolved gold in the form of AuS⁻.

The extent of solubility of gold as AuS⁻ at ordinary temperatures can be estimated from the approximate value of $K$, $10^{-6}$, derived for equation 23. If no hydrogen is present from any other source, the solubility is $1.3 \times 10^{-4} \times (HS^-)^{2/3}$, which means that it is appreciable (ca. $3 \times 10^{-6}$ gram/liter) even at HS⁻ concentrations as low as $10^{-6}$ M.

As Smith (2) has pointed out, the fact that gold itself will not dissolve in solutions of $S^{--}$ does not mean that gold cannot be carried in such solutions. The solubility of gold sulfide in excess sulfide suggests that transportation in this manner is possible, but no quantitative data are available.

In summary, gold can be carried in alkaline solutions as $AuO_2^-$ if sulfide is absent or as a complex sulfide ion if sulfide is present. The most probable complex sulfide is AuS⁻, which appears to form from metallic gold in solutions of HS⁻ but not in solutions of $S^{--}$. A possible interpretation of the solubility of gold in HS⁻ is that the ion AuS⁻ is extraordinarily stable, so stable that the hydrogen of HS⁻ is reduced to $H_2$. If this interpretation is correct, significant amounts of gold should be held in solution even by dilute, approximately neutral solutions of HS⁻. Naturally-occurring alkaline solutions do not affect metallic gold appreciably in the absence of HS⁻.

### SOLUBILITY OF GOLD IN SEA WATER.

In sea water, which is a slightly alkaline solution without appreciable sulfide ion, the solubility of gold is very small. A rough value can be calculated from equation 22 and a similar equation involving $AuCl_4^-$:

$$2Au + 3/2O_2 + 2OH^- = 2AuO_2^- + H_2O \qquad (22)$$

$$2Au + 3/2O_2 + 8Cl^- + 3H_2O = 2AuCl_4^- + 6OH^- \qquad (24)$$
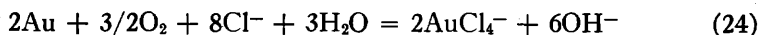
For equation 22 we have obtained an equilibrium constant equal to ca. $10^{-10}$; for equation 24 the constant (calculated from electrode reactions 5 and 14) is $10^{-60}$. In sea water of normal salinity the concentration of Cl⁻ is about 0.55M, and for water in contact with air we may take the partial pressure of $O_2$ as 0.2 atmos. The pH of sea water ranges from about 7.5

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TABLE VI.

CALCULATED SOLUBILITIES OF GOLD IN SEA WATER AT 25° C. IN CONTACT WITH AIR
(IN MOLE/LITER).

| pH | $OH^-$ | $AuCl_4^-$ | $AuO_2^-$ | Total Au |
|----|--------|------------|-----------|----------|
| 7   | $10^{-7}$   | $3 \times 10^{-11}$ | $3 \times 10^{-13}$ | $3 \times 10^{-11}$ |
| 7.5 | $10^{-6.5}$ | $10^{-12}$          | $10^{-12}$          | $2 \times 10^{-12}$ |
| 8   | $10^{-6}$   | $3 \times 10^{-14}$ | $3 \times 10^{-12}$ | $3 \times 10^{-12}$ |
| 8.5 | $10^{-5.5}$ | $10^{-15}$          | $10^{-11}$          | $10^{-11}$          |

to 8.4, so that the $OH^-$ range is between $10^{-5.6}$ and $10^{-6.5}$ mole/liter. Calculations covering this range give the figures shown in Table VI.

Such calculations are not to be taken too seriously, since in solutions as concentrated as sea water the activities of ions are markedly different from their concentrations; the values in Table VI may well be in error by one or two orders of magnitude. Nevertheless, these calculated figures bear a striking resemblance to Haber's (14) experimentally determined value, $2 \times 10^{-11}$ mole/liter. A possible interpretation is that sea water obtains its gold largely by dissolving the native metal with the aid of oxygen, and that the amount in solution is limited by the equilibria in equations 22 and 24.

### EFFECT OF TEMPERATURE AND PRESSURE.

The effects of temperature and pressure on the solubility of gold are not predictable because thermodynamic data are lacking. Experimentally McCaughey (9) showed that the solubility in solutions containing $Fe^{+++}$ and $Cu^{++}$ is increased by a rise in temperature, although some of the apparent increase may be due to higher reaction rates rather than to shifts of equilibrium. Ogryzlo's work (1) with solutions in bombs at 200°–300° C indicates that oxidation by free oxygen goes farther at high temperatures, but again the apparent increase may reflect chiefly a speeding up of the reaction. Ogryzlo shows further that even the reaction with HCl alone, with no oxidizing agent present stronger than $H^+$, becomes appreciable at high temperatures and pressures. In alkaline sulfide solutions the experiments of Ogryzlo and of Zvyagintsev and Paulsen (3) demonstrate a marked increase in solubility at high temperatures—showing that gold differs in this respect from mercury, whose complex sulfide ion becomes less stable as the temperature rises. Any gold solution, therefore, appears able to hold more gold at high temperatures than at low temperatures, so that simple cooling provides an adequate mechanism for the deposition of the metal from vein solutions.

The effect of pressure, as distinct from temperature, has not been investigated experimentally. The effect is probably negligible on the reactions which do not involve a gas (e.g., equations 19 and 20), but may be large if a gas is produced or consumed. Reactions requiring both $H^+$ and $Cl^-$ (equations 17 and 18) would necessarily be aided by increased pressure at high temperatures, since the pressure determines how much HCl will

remain in solution. The direct solution of gold by HCl alone at high temperatures (1) must likewise depend on pressure. In neutral or slightly alkaline solutions the solubility of gold as $AuS^-$ should depend on pressure insofar as pressure determines the solubility of $H_2S$ and hence the concentration of $HS^-$. From such general considerations it appears that in most solutions gold is more soluble at high pressures than at low pressures, and accordingly can be precipitated by release of pressure.

### COLLOIDAL SOLUTIONS.

Frondel (15) has shown that gold sols, especially when protected by colloidal silica, are stable at high temperatures. If gold originally present in true solution at high temperatures is reduced to the metal as the temperature falls, it may well appear first as a colloid rather than as a precipitate, and in this form may be transported in quantities larger than would be expected in true solution. The common association of gold with sulfides is explained by Zvyagintsev and Paulsen (16) as a surface effect of the sulfides on gold sols, since their experiments show that gold coagulates more readily on sulfides than on quartz, calcite, or barite.

### SUMMARY.

1. Solubilities of gold calculated from thermodynamic data agree reasonably well with experimental results.

2. In acid solutions gold may be transported as the ion $AuCl_4^-$, provided that reducing agents are absent. The metal is dissolved by an acid solution provided that the solution contains $Cl^-$ and that a fairly strong oxidizing agent is present. At high temperatures and pressures the hydrogen ion of the acid is a sufficiently strong oxidizing agent; at low temperatures a substance like $MnO_2$, $O_2$, $Fe^{+++}$, or $Cu^{++}$ must be present in addition. The requirement that an oxidizing agent be present, or at least that a reducing agent be absent, probably means that gold would not be transported in acid vein solutions at low temperatures, since such solutions would contain reducing agents like $H_2S$ and $Fe^{++}$. On the other hand, solution and transportation of gold in acid solution is probably the mechanism of supergene movement of gold.

3. The solubility of gold in naturally-occurring alkaline solutions which do not contain sulfide is negligible.

4. Gold may be transported in alkaline sulfide solutions, even in dilute solutions near the neutral point. The gold is probably present as the very stable ion $AuS^-$.

5. Gold may be precipitated from solution by any one of a number of mechanisms, but there is no need to call on one more complicated than a fall in temperature or pressure or both.

6. If a solution of gold at high temperature and pressure is cooled, part of the metal may be forced out of solution but may appear as a sol rather than as a precipitate. In this form it may remain in suspension down to low temperatures.

7. Because gold may be transported in solutions of various compositions, the presence of gold in a vein deposit gives little information as to the character of the vein fluids.

8. In sea water gold is probably present as both $AuO_2^-$ and $AuCl_4^-$. A limit to the amount dissolved may be set by the formation of these ions from metallic gold with the aid of dissolved oxygen.

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