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Fundamental Studies on Dissolution of Gold in Cyanide Solutions. II

On Equations of Reactions and Effects of Cyanide Strength and other Variables on Dissolution Rate*

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Even though numerous studies have been reported of the dissolution of gold in cyanide solutions, they leave several subjects to be further investigated, as they have not come to the same conclusion in some respects and remain ambiguous in others. For instance, although several investigators have discussed the equations representing the chemical reaction involved in the dissolution of gold, among which the Bodländer's one seems to be most reliable, the true equation has not yet been completely determined. The cyanide strength of solution, in which gold will dissolve with the maximum velocity, was proved to be a solution concentration of 0.25 per cent KCN in Maclaurin's work, while it appeared to be of 0.027 per cent in White's, so that there still remains a question to be solved. Reduction in the dissolution rate of gold is unexpectedly more greatly caused by the addition of lime than by that of potassium hydroxide, but a clear explanation of this fact has not yet been given. Furthermore the effect of salts fouling cyanide solution on the dissolution rate of gold is little known.

From both logical and practical standpoints, the author carried out a fundamental study, an outline of which will be described in the present and the following reports.

Kinetics of heterogeneous systems

According to the Nernst's theory, the rate of dissolution of a solid substance into the solution depends merely upon the diffusion rate of a solvent from the solution to the surface of solid; it is given by

$$\frac{dx}{dt} = \frac{D \cdot F}{V \cdot \delta} (a-x),$$  (1)

where \(D\) denotes the diffusion coefficient of the solvent, \(F\) the surface area of the solid, \(V\) the volume of the solution, \(\delta\) the thickness of the liquid layer adhering to the solid surface, \(a\) the concentration of solvent at the beginning of the process for the time \(t=0\), \(a-x\) the concentration after the time \(t\), and \(dx\) the corresponding amount of solid passing into solution in the time \(dt\).

This equation may however hold good merely in the case where the chemical reaction occurring on the solid surface proceeds with a practically infinite velocity (i.e., compared with the rate of diffusion). If the velocity of chemical reaction is slower than the rate of diffusion, it is the former that determines the rate of dissolution of the solid into the solution. Furthermore, there may be the case where the chemical reaction bears comparison with the diffusion in velocity.

Which of the above-mentioned cases is applicable to the dissolution of the solid in question may, from an experimental point of view, be determined by consideration on

* The 5th report of the Research Institute of Mineral Dressing and Metallurgy.
Some parts of this investigation were published in Japanese. (see J. Min. Inst. Japan 55 (1940), 7 and 60 (1944), 12.)
the following items:
1. When the rate of dissolution of the solid is conditioned only by the rate of diffusion, the coefficient of the velocity satisfies the logarithmic formula (i.e., equation 1) as is shown in a first order reaction.

\[
\frac{d \ln k}{dT} = \frac{d \ln D}{dT} = \frac{A}{RT^2}.
\]

At a temperature of 25°C, the quotient amounts to 1.25 per 10°C of the elevation of temperature (the energy of activation \(E_{\text{obs}} = 4.600 \text{ cal.}\)). It may however be larger than this value (i.e., commonly amounts to about 2) in the case where the chemical reaction velocity is slower.

3. The dissolution rate is remarkably affected by the stirring velocity; this relation is indicated by the following empirical formula:

\[
(Dissolution \ rate) = (Constant) \times (\text{Stirring velocity})^n,
\]

where the value of \(n\) amounts to 1 (by Wildermann) or 2/3 (by Brunner) or 4/5 (by von Name), while it is not much influenced when the chemical reaction is slower in velocity.

**Experimental procedure**

An apparatus was designed to bear a resemblance to the conditions in practice. This was accomplished by suspending a gold plate in cyanide solution by means of a glass hook, and by making small air bubbles pass through the solution near both sides of the gold plate (Fig. 1).

![Fig. 1. Dissolving flask.](image)

The cyanide solution container consisting of a glass conical flask was immersed in a thermostat to maintain the temperature constant (commonly at 25°C). The complete arrangement of apparatus is shown in Fig. 2. The air supply was first passed through a scrubbing tower (2) containing sulfuric acid to remove moisture and then a flowmeter by means of which the air supply was maintained constant (usually 3.45 l. per hour). From the flowmeter the air passed through a scrubbing tower (5) containing potassium hydroxide to remove CO₂ gas and then those (6, 7, 8) containing potassium cyanide of nearly the same strength as that in the dissolution flask to be saturated with HCN gas. Pure gold plates, 0.05 cm. or 0.066 cm. thick, in the form of rectangular plate of 2.015 cm. long and 1.001 cm. wide, or 2.032 cm. long and 1.082 cm. wide respectively, were used after annealed at a temperature of 600°C for 3 hours. In individual tests 500 c.c. of the solution of potassium cyanide, due to its superiority over the sodium cyanide in purity, was used. In making a test, the solution was placed in the flask, the gold plate was immersed, the air was turned on and adjusted so that the flowmeter scale read a constant division. A time reading was taken immediately. At the end of each 30 mins. or one hour the supply was cut off and the gold was removed from the apparatus, washed with water, alcohol, and ether, then weighed on the assay balance. The rate of dissolution was expressed as the number of mg. of gold dissolved per 1/2 or 1 hour from the total surface or 1 sq. cm. of the surface. This was calculated in each case from the loss in weight.

Besides the procedure outlined above the author employed others, which will be described as occasion demands.
Equations representing chemical reactions involved in dissolution of gold

The following equations have been obtained by several investigators:

Elsner's equation:

\[ 4\text{Au} + 8\text{KCN} + \text{O}_2 + 2\text{H}_2\text{O} = 4\text{KAu}(...) + 4\text{KOH}, \quad K = 10^{96.0} \]

Bodlaender's:

\[ 2\text{Au} + 4\text{KCN} + \text{O}_2 + 2\text{H}_2\text{O} = 2\text{KAu}(...) + 2\text{KOH} + \text{H}_2\text{O}_2, \quad K = 10^{96.0} \]

\[ 2\text{Au} + 4\text{KCN} + \text{H}_2\text{O}_2 = 2\text{KAu}(...) + 2\text{KOH}, \quad K = 10^{38.8} \]

(Over-all equation is thus the same as Elsner's.)

Janin's:

\[ 2\text{Au} + 4\text{KCN} + 2\text{H}_2\text{O} = 2\text{KAu}(...) + 2\text{KOH} + \text{H}_2, \quad K = 10^{-9.0} \]

Bettel's:

\[ 2\text{Au} + 6\text{KCN} + 2\text{H}_2\text{O} + \text{O}_2 = \text{KAu}(...) + \text{KAu}(...) + 4\text{KOH}, \]

\[ 2\text{Au} + 2\text{KCN} + \text{KAu}(...) = 3\text{KAu}(...) \]

It may hereby be observed that the reactions for metallic silver are analogous.

Besides, it has been suggested by Christy, and Julian and Smart, that the dissolution of gold and other metals in cyanide solution depends primarily upon the electromotive force exerted. Julian attached great weight to the formation of local voltaic circuits.

Whether the reactions proposed are possible was examined by the titration of KCN amount required for dissolution of gold and by the detection of hydrogen peroxide expressed as the intermediate compound by Bodlaender.

The consumption of potassium cyanide caused by dissolution of gold is given in Table 1.

**Table 1. Consumption of cyanide caused by dissolution of gold.**

<table>
<thead>
<tr>
<th>Time (hr.)</th>
<th>Amount of gold dissolved (mg)</th>
<th>Consumption of KCN theoretically calculated by Elsner's eq. (mg)</th>
<th>Consumption of KCN observed (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.96</td>
<td>0.63</td>
<td>0.65</td>
</tr>
<tr>
<td>1.0</td>
<td>2.01</td>
<td>1.33</td>
<td>1.28</td>
</tr>
<tr>
<td>3.0</td>
<td>7.49</td>
<td>4.93</td>
<td>4.94</td>
</tr>
<tr>
<td>7.0</td>
<td>15.91</td>
<td>10.50</td>
<td>10.51</td>
</tr>
<tr>
<td>10.0</td>
<td>18.77</td>
<td>12.39</td>
<td>12.48</td>
</tr>
</tbody>
</table>

**Table 2. Leaf gold.**

<table>
<thead>
<tr>
<th>Composition (%)</th>
<th>Weight per leaf (mg)</th>
<th>Size (cm, by cm)</th>
<th>Thickness (by calculation) (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>Ag</td>
<td>Cu</td>
<td></td>
</tr>
<tr>
<td>94.59</td>
<td>4.74</td>
<td>0.66</td>
<td>about 13</td>
</tr>
</tbody>
</table>

According to these results, two parts in atomic weight of KCN are proved to be sufficient for the solution of one part of gold.

The determination of the amount of hydrogen peroxide formed during the process of dissolution of gold was made by modifying the method adopted by Bodlaender. Spongy gold or leaf gold (Table 2) was used so that its dissolution may be quickened as much as possible and result in instantaneous formation of the greatest possible amount of H₂O₂. Calcium hydroxide was used to catch hydrogen peroxide formed according to the following equation:

\[ \text{Ca(OH)}_2 + \text{H}_2\text{O}_2 = \text{CaO}_2 + 2\text{H}_2\text{O}. \]

Calcium peroxide thus precipitated was filtered off and dissolved with HCl or H₂SO₄, being converted to hydrogen peroxide, which was titrated with permanganate solution. A qualitative analysis using spongy gold was first made by means of the five methods described in Treadwell's...
Analytical Chemistry, and it was proved that hydrogen peroxide was actually formed. In a quantitative analysis, pure leaf silver, 0.0000205 cm. thick (by calculation), in the form of square plate of 11.2 cm. long, approximately 27 mg. in weight was also used besides leaf gold (Table 2). Typical data are given in Table 3.

Table 3. Typical results of quantitative analysis of hydrogen peroxide formed.

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample</th>
<th>Solution used</th>
<th>Time of dissolution (min.)</th>
<th>Amount of H₂O₂ proved (mg.)</th>
<th>Amount of H₂O₂ calculated by Elsner's eq. (mg.)</th>
<th>Percentage of H₂O₂ proved (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>Spongy gold</td>
<td>13.40</td>
<td>1.0% 10</td>
<td>0.2</td>
<td>39</td>
<td>0.356</td>
</tr>
<tr>
<td>14*</td>
<td>Leaf gold</td>
<td>47.6</td>
<td>0.8% 20</td>
<td>1.7</td>
<td>17</td>
<td>4.020</td>
</tr>
<tr>
<td>15*</td>
<td></td>
<td>57.3</td>
<td>20</td>
<td></td>
<td>25</td>
<td>5.113</td>
</tr>
<tr>
<td>4</td>
<td>Leaf silver</td>
<td>53.8</td>
<td>5</td>
<td>0.5</td>
<td>13</td>
<td>5.061</td>
</tr>
<tr>
<td>17*</td>
<td></td>
<td>54.7</td>
<td>5</td>
<td>1.7</td>
<td>17</td>
<td>4.954</td>
</tr>
</tbody>
</table>

* The solution was cooled with ice as soon as the sample finished to dissolve into it.

The maxima of hydrogen peroxide formed were proved to be regarding gold 100 per cent of the theoretical amount of hydrogen peroxide that should be formed by Bodlaender’s equation, and regarding silver 59.7 per cent, the former being larger than 66.7 per cent obtained by Bodlaender.

Barsky, Swaison and Hedley have compared the free energies of Elsner’s equation, Bodlaender’s and Janin’s, with the respective equilibrium constants and found that both Elsner’s equation and Bodlaender’s are possible.

From these facts, it may be concluded that Bodlaender’s equations express the true reactions that take place when gold and silver are dissolved in dilute cyanide solutions and that when Bodlaender’s second reaction proceeds with comparatively greater velocity, Elsner’s equation which gives the same final products as the sum of Bodlaender’s is also possible.

Effect of certain fundamental variables

1. The order of reaction and the thickness of the adhering layer δ. In the author’s experiment, the rate of dissolution of gold tended to decrease at the beginning and increase rapidly after 6~8 hours, being twice as that at the beginning. Determination of the order of reaction was therefore made in two cases where the passivity of gold surface did not happen at the beginning. In the case where the gold plate was dissolved under air agitation in 0.01 per cent solution of KCN, the reaction was found to be of the second order concerning potassium cyanide. This seems to show that the rate of dissolution of gold depends mainly upon the velocity of chemical reaction. On the other hand, in the case of dissolving the gold plate under oxygen agitation in 0.03 per cent solution of KCN, the reaction was found to be of the first order concerning potassium cyanide. Accordingly it seems that the dissolution rate δ conditioned only by the diffusion rate of KCN. In this case, as the dissolution rate of gold was measured to be 1.75 mg. per sq. cm. per 1/2 hour at the beginning, the thickness of δ being calculated by the following equation:

\[
\frac{dx}{dt} = \frac{D_{KCN}}{\delta} \cdot \frac{F}{V} \cdot a_{KCN}. \quad (5)
\]

Thus δ=0.009 cm.
This value is larger than that estimated by Brunner, viz. 0.03~0.05 mm., and smaller than that of Plank and Urmanczy, viz. 0.07 cm.

2. The effect of temperature on the
dissolution of gold. This was examined under air agitation in 0.03 per cent solution of KCN, within a temperature range of 15~40°C. (Fig. 3).

![Effect of temperature and stirring velocity on rate of dissolution.](image)

**Fig. 3. Effect of temperature and stirring velocity on rate of dissolution.**

The ratios of dissolution rates are as follows:

\[ (15°C.):(25°C.)=1:1.32, \]
\[ (20°C.):(30°C.)=1:1.36, \]
\[ (25°C.):(35°C.)=1:1.37, \]
\[ (30°C.):(40°C.)=1:1.29. \]

These values are appreciably larger than 1.25, and smaller than 2 (see p. 86).

Equation 2 indicates that \( \log k \) is directly proportional to \( 1/T \) and this was found to agree fairly well with observation: the experimental points line up almost exactly along a straight line. A, viz. the energy of activation, can be calculated from the inclination of the straight line and was found to be 5,245 cal.

3. The effect of stirring velocity. In the author's experiment the stirring velocity was indicated by the amount of air passed through the dissolution flask per 1/2 hour. This amount does not however show strictly the true stirring velocity, because this affects the amount of oxygen dissolved, which is required for dissolution of gold. Therefore equation 3 does not hold strictly good in these experiments. The values of \( s \) are obtained from Fig. 3 as follows:

Under nitrogen agitation:

\[ 0.28 \approx (3/10) \text{ (at } 25°C.) \]

Under air agitation:

\[ 0.52 \approx (1/2) \text{ (at } 15°C, 25°C, 30°C.) \]
\[ 0.34 \approx (1/3) \text{ (at } 40°C. \)

These are smaller than those of Brunner, etc. In other words, the dissolution rate is affected to a rather slight degree by the stirring velocity. From this, it appears that the dissolution rate depends rather upon the reaction velocity.

4. The effect of varying oxygen concentration in solution. The dissolution rates were compared in the cases where the gas passed through the dissolution flask was nitrogen, air, and oxygen respectively. In the case of nitrogen, a dissolution flask specially designed was used to expel oxygen from cyanide solution as much as possible but it appeared that the removal of oxygen was not complete. The experimental results are presented in Fig. 4.

![Effect of varying oxygen concentration in solution on rate of dissolution.](image)

**Fig. 4. Effect of varying oxygen concentration in solution on rate of dissolution.**

In the case where the stirring velocity is 3.45 l. per hour the quotient of dissolution rate with oxygen to that with air becomes 6.94/2.80 = 2.5.

In view of oxygen content, Elsnner's equation becomes

\[ 2Au+H_2O+1/2 O_2 \rightarrow 2Au^+ + 2OH^- \text{. (6)} \]

It therefore seems probable that the dissolution rate would be proportional to the square root of oxygen content. Since the ratio of oxygen concentration in oxygen to that in air is \( Co_2/C_{air} = 5.0, \) the square root of it becomes 2.24. The experimental datum nearly coincides with this value. E. Yamazaki has proved the fact analogous to the above results on the dissolution of silver and concluded that Bodländer's equations are not possible, because the rate of
dissolution in this case should be proportional to oxygen concentration according to the following equation:

\[ 2\text{Au} + 2\text{H}_2\text{O} + \text{O}_2 \rightarrow 2\text{Au}^+ + 2\text{OH}^- + \text{H}_2\text{O}_2. \]

The author assumes that the passivity of gold at the beginning of the process is due to the fact that Bodlaender's second reaction hardly takes place. If the dissolution rate in the initial stage is thereby employed in place of above-mentioned one with air, the quotient becomes \(6.94/1.50 = 4.7\). This indicates that the dissolution rate is nearly proportional to oxygen concentration.

5. **The effect of viscosity of solution.**

This was examined with varying additional amount of sugar in 0.03 per cent solution of KCN. The viscosity of solution was found to exert an inappreciable influence on the rate of dissolution.

6. **The effect of additional amount of hydrogen peroxide.** It is well known that the addition of hydrogen peroxide causes very rapid dissolution of gold due to its oxidizing power. In the author's experiment, it was found to exercise its maximum influence at 0.02~0.03 per cent of hydrogen peroxide in 0.03 per cent solution of KCN. In the concentration of over 0.04 per cent of \(\text{H}_2\text{O}_2\), potassium cyanide seems to be decomposed by it and to be converted to cyanate, resulting in practical cessation of dissolution of gold after certain time.

From several experimental results above-mentioned, the author comes to the conclusion that the dissolution of gold may correspond to the case where the velocity of chemical reaction bears comparison with that of diffusion.

**Effect of cyanide strength of solution on dissolution rate of gold**

J. S. Maclaurin\(^{(5)}\) found that the rate of dissolution of pure gold, or pure silver, in potassium cyanide solution passes through a maximum when proceeding from dilute to concentrated solutions. The maximum is reached when the solution contains 0.25 per cent of KCN. E. Beyers\(^{(6)}\) and T. Matsukawa\(^{(7)}\) also obtained the experimental results analogous to the foregoing statement, while, H. A. White\(^{(8)}\) found that the maximum solution rate is at about 0.027 per cent KCN, when the solution is saturated with oxygen. Barsky, Swaison and Hedley\(^{(1)}\) found that the maximum rate of dissolution of gold was obtained with 0.05 per cent solution of NaCN.

The author determined the dissolution rates of gold and silver every 1/2 hr. for 12~20 hrs. in various cyanide strengths of solutions. In Figs. 5 and 6 the rates of

![Fig. 5. Effect of cyanide strength of solution on dissolution rate of gold.](image)

![Fig. 6. Effect of cyanide strength of solution on dissolution rate of silver.](image)
White suggests that, since both cyanide and oxygen molecules must appear at the gold surface in the ratio called for by Elsner's equation, the rate of dissolution should be governed by the rates of diffusion of these two species of molecules. The experimental results mentioned in the preceding section led the author to the confidence in White's suggestion. A consideration was therefore made of the cyanide strength with which the maximum rate of dissolution is obtained, as follows:

As both cyanide and oxygen molecules must appear at the gold surface in the ratio required by Elsner's equation in order to make the conditions of dissolving gold most favorable, the concentrations of both species of molecules must be as follows:

\[ C_{\text{KCN}} : C_{\text{O}_2} = 130.21 : 8.00. \]  

(7)

And these may be conditioned by individual rates of diffusion.

Therefore, according to equation 1

\[ \frac{D_{\text{KCN}} \cdot F}{V \cdot \delta} (a_{\text{KCN}} - x) : \frac{D_{\text{O}_2} \cdot F}{V \cdot \delta} (a_{\text{O}_2} - x) = 130.21 : 8.00. \]

In the initial stage, \( x = 0 \).

Thus \( D_{\text{KCN}} \cdot a_{\text{KCN}} : D_{\text{O}_2} \cdot a_{\text{O}_2} = 130.21 : 8.00. \)

(8)

As the cyanide solution may be considered to be saturated with oxygen,

\[ a_{\text{O}_2} = 0.00620 \text{ g/l, at } 25^\circ \text{C}. \]

According to G. Tammann and V. Jessen, the diffusion constant of oxygen are \( D_{\text{O}_2} = 3.06 \text{ sq. cm. per day.} \)

And the diffusion constant of cyanide can be calculated by virtue of the following equation:

\[ D_{\text{KCN}} = 0.04485 \frac{l_{K^+} \cdot I_{CN^-}}{l_{K^+} + I_{CN^-} ((1 + 0.0034(t-18))} \]

(sq. cm. per day),

where \( l \) denotes the ionic conductance; \( l_{K^+} = 73.50 \) and \( l_{CN^-} = 78.0 \) (from Landolt's Table).

Accordingly, \( D_{\text{KCN}} = 1.737 \text{ sq. cm. per day.} \)

Likewise, \( D_{\text{NaCN}} = 1.401 \text{ sq. cm. per day.} \)

Combining these values with equation 8, we get

\[ a_{\text{KCN}} = 0.0235\%. \]

(9)

As the cyanide molecules which react with the gold are assumed to be CN\(^-\) ions, the extents of hydrolytic dissociation and electrolytic dissociation should furthermore be considered. These were calculated theoretically by the author to be about 5.9% and 98.8% respectively in the concentration of KCN above-mentioned. When corrections were applied to equation 9, the apparent concentration of potassium cyanide in (main) solution becomes \( a'_{\text{KCN}} = 0.0252\% \).

Likewise \( a'_{\text{NaCN}} = 0.0236\% \).

This value appears to coincide nearly with the experimental results. In the cyanide solutions of below above-mentioned concentration, the rate of supply of cyanide may be insufficient for that required by Elsner's equation in a manner that cyanide and oxygen and this causes reduction in the dissolution rate. On the other hand, in the solution of over above-mentioned concentration the rate of supply of cyanide may be too great and cyanide molecules in excess may be useless for the dissolution of gold, because the rate of supply of oxygen is constant.

A. W. Fahrenwald and J. Newton found that the dissolution rate of gold is directly proportional to the pressure of oxygen, provided that cyanide strength of solution is increased in the same ratio as the oxygen pressure. From this observation they also support White's suggestion.

The consideration above-mentioned also applies to the dissolution of silver.

Summary

1. The author believes that Bodlaender's equations express the true reactions occurring in the dissolution of gold and silver in cyanide solution, as he could find, modifying Bodlaender's method, nearly 100 per cent of the theoretical amount of hydrogen peroxide. He also confirms the truth of Elsner's equation which gives the same final products as the sum of Bodlaender's equations.

2. The order of reaction was estimated and the effect of temperature, of rate of agitation, of viscosity of solution and of varied atmosphere were examined, and he concludes that the dissolution of gold may correspond to the case where the velocity of chemical reaction bears comparison with that of diffusion.

3. The maximum rates of dissolution of gold and silver were obtained experimental-
ly with 0.03 per cent solution of KCN and it was calculated to be 0.025 per cent on the assumption that both cyanide and oxygen molecules must appear at the gold surface in the ratio required by Elsner's equation to make the conditions of dissolving gold most favorable.

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