KINETICS AND MECHANISM OF GOLD AND SILVER DISSOLUTION IN CYANIDE SOLUTION

by

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ABSTRACT

The mechanism of cyanidation can be represented by the following reactions:

$$O_2 + 2\ H_2O + 2\ e^- \longrightarrow 2\ OH^- + H_2O_2$$

$$Au \longrightarrow Au^+ + e^-$$

$$Au^+ + CN^- \longrightarrow AuCN$$

$$AuCN + CN^- \longrightarrow Au(CN)_2^-$$

Overall reaction

$$2\ Au + 4\ CN^- + O_2 + 2\ H_2O \longrightarrow 2\ Au(CN)_2^- + 2\ OH^- + H_2O_2$$

Hydrogen peroxide formed may accumulate in the solution, may undergo partial catalytic decomposition on the surface of the metal (depending on its crystalline nature), or to a minor extent, may be reduced to hydroxyl ions. In these reactions, oxygen dissolved in water functions cathodically and the gold (or silver) as anode. The rate-determining step is mainly the rate at which the cyanide ions or the dissolved oxygen diffuse through the thin stagnant layer of the liquid at the surface of the metal. The rate of cyanidation follows the equation:

$$\text{Rate} = \frac{2\ A\ D_{CN^-}\ D_{O_2}[CN^-][O_2]}{\delta\{D_{CN^-}[CN^-] + 4\ D_{O_2}[O_2]\}}$$

where $[CN^-]$ and $[O_2]$ = the concentrations (in moles/ml) of cyanide and dissolved oxygen, respectively.

D_{CN^-} and D_{O_2} = the diffusion coefficients of cyanide and dissolved oxygen; 1.83×10^{-5} and 2.76×10^{-5} $cm^2.sec^{-1}$, respectively.

A = the surface area of the metal in contact with the aqueous phase, in cm^2

δ = the thickness of the boundary layer; varies between 2 and 9×10^{-3} cm, depending on the speed and method of agitation.

The rate is expressed in $g.equiv.sec^{-1}$.

Maximum rate of dissolution occurs when the molar ratio $\frac{[CN^-]}{[O_2]} = 6$. If $[CN^-] \ll 6\ [O_2]$, the rate of cyanidation will be independent of the oxygen concentration. If $[CN^-] \gg 6\ [O_2]$, the rate of cyanidation will be independent of the cyanide concentration.

With the exception of a few ions such as Na^+, K^+, Cl^-, NO_3^-, and SO_4^{2-}, which have no effect on the rate of dissolution, other ions either accelerate or retard the dissolution. Pb^{2+} seemingly plays a unique role: It may accelerate dissolution when present in small amounts or retard it when its concentration exceeds a certain limit.

Accelerating effect is attributed to metals that have a more negative potential under the conditions of dissolution, thus being replaced by gold. It is believed that these metals are deposited on the surface of gold thus altering its surface properties and leading to a decrease in the thickness of the boundary layer through which oxygen and cyanide ion diffuse. The retarding effect may be due to:

1. Consumption of oxygen from solution by the ions, e.g., Fe^{2+}, S^{2-}, HS^-.

2. Consumption of free cyanide from solution

   (a) Formation of complex cyanides, e.g., of the ions Fe^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Mn^{2+}.
   (b) Formation of thiocyanate.
   (c) Adsorption on gangue material, e.g., colloidal silica, alumina, or ferric hydroxide.

3. Formation of a film on the surface of the metal, which prevents the cyanide ion or oxygen from attacking it. This film may be due to:

(a) Sulfides--aurous sulfide is thought to be formed when sulfide ion is present in cyanide solution.
(b) Peroxides--CaO_2 was proved to be deposited on the surface when Ca^{2+} ion is present at pH > 10.8.
(c) Oxides--a gold oxide film is thought to be formed when strong oxidizing agents such as ozone are present, imparting a red color to the surface.
(d) Insoluble cyanides--Pb^{2+} at high concentration is thought to form an insoluble $Pb(CN)_2$ film.
(e) Other types--the presence of a very small amount of ethyl xanthate is thought to cause the formation of a metal xanthate film.

I N T R O D U C T I O N

According to Mellor (1923), the alchemists of the 18th century knew that gold is soluble in aqueous solution of potassium cyanide, and the early jewelers probably utilized this process in gilding. He also mentions that Scheele in 1783 and later Bagration in 1843 noted the solvent action of aqueous solutions of alkali cyanides on gold. Yet it was not until 1887 that the value of this observation was recognized, when MacArthur and the Forrests (1887) made use of cyanide in leaching gold from its ores. Since then, the process has spread to every gold and silver mining district in the world and has replaced the amalgamation process. According to Clennell (1915), in 1889 the world's consumption of cyanide did not exceed 50 tons, but in 1905 it was 10,000 tons. At present it is estimated at about 40,000 tons.

Recently, Soviet metallurgists showed interest in substituting for sodium cyanide an equally inexpensive but nontoxic reagent. Thus, Plaksin and Kozhukhova (1940, 1960), for example, reported that thiourea ($NH_2 \cdot CS \cdot NH_2$) in the presence of oxygen will extract gold from its ores better than cyanide will. More recently Kakovskii and Tyurin (1962) showed that ammonium polysulfide $(NH_4)_2S_x$ is also a good solvent for gold. None of these reagents, however, is used in commercial practice yet.

The present review deals mainly with the theoretical aspects of cyanidation; no attempt was made to cover papers describing operation of cyanide mills.

THE SOLUBILITY OF GOLD AND SILVER IN CYANIDE SOLUTIONS

Elsner (1846) was the first to recognize that atmospheric oxygen was essential for the dissolution of gold in cyanide solutions. Although he did not formulate the equation for the dissolution process, nevertheless the following equation was ascribed to him in Watt's Dictionary of Chemistry:

$$4\ Au + 8\ NaCN + O_2 + 2\ H_2O \longrightarrow 4\ NaAu(CN)_2 + 4\ NaOH$$

Dissolution of silver by cyanide ion can be represented by a similar equation. MacArthur and the Forrests (1887), the inventors of the cyanidation process, were unaware of the necessity of oxygen, however, and they thought that hydrogen was evolved according to the equation:

$$2\ Au + 4\ NaCN + 2\ H_2O \longrightarrow 2\ NaAu(CN)_2 + 2\ NaOH + H_2$$

This was later supported by Janin (1888, 1892). Maclaurin (1893) and Christy (1896) concluded from careful experiments that oxygen was essential for cyanidation, therefore deciding in favor of Elsner's equation.

Bodländer (1896) suggested that the dissolution should proceed through two steps according to the equations:

$$2\ Au + 4\ NaCN + O_2 + 2\ H_2O \longrightarrow 2\ NaAu(CN)_2 + 2\ NaOH + H_2O_2$$

$$H_2O_2 + 2\ Au + 4\ NaCN \longrightarrow 2\ NaAu(CN)_2 + 2\ NaOH$$

in which hydrogen peroxide is formed as an intermediate product. He supported his views by being able to detect H_2O_2 in the solutions. The overall equation for these steps is again Elsner's equation.

During this period a modification of the cyanidation process was discovered (Sulman, 1895), in which a mixture of potassium cyanide and bromo-cyanide, or even bromine water added to the cyanide solution, leads to the dissolution of gold without the necessity of the presence of oxygen. It was suggested that the reaction might go through the formation of cyanogen, which was thought to attack gold according to the following equations:

$$BrCN + KCN \longrightarrow KBr + (CN)_2$$

$$2\ Au + 2\ KCN + (CN)_2 \longrightarrow 2\ KAu(CN)_2$$

This led Christy (1896) to the belief that oxygen acts in a manner similar to bromine in liberating nascent cyanogen, which he believed might be the active agent for attacking gold. When he saturated a KCN solution with cyanogen gas, however, no satisfactory

results were obtained, although MacArthur and the Forrests (1887) in their original patent had mentioned that cyanogen gas can also be used for dissolving gold. Later, Skey (1897) and Park (1898) gave conclusive evidence that aqueous solutions of cyanogen do not exert the least solvent action on gold or silver.

MacArthur (1905) argued that if oxygen were necessary for the dissolution, then potassium cyanate, KCNO, which he believed to be formed by the oxidation of potassium cyanide, might be the effective agent responsible for the dissolution. This hypothesis was refuted by Green (1913), who showed that potassium cyanate had no action on gold.

Considerable advances in cyanidation practice were made during the next four decades following the invention of the process. During this period about twenty-five books on cyanidation were published (see Literature). Not much progress in the theoretical development was reported, however, until Barsky, Swainson and Hedley (1934) determined the free energies of the formation of complex auro- and argento-cyanide ions. From the data obtained, they calculated the free energy changes in the various reactions suggested. Their calculations were in favor of the Elsner and Bodländer equations, whereas Janin's equation was thermodynamically not feasible.

Boonstra (1943) was the first to recognize that the dissolution of gold in cyanide solutions is similar to a metal corrosion process in which oxygen dissolved in the solution is reduced to hydrogen peroxide and hydroxyl ion. On the basis of current density-potential measurements he pointed out that Bodländer's equation should be further divided into the following steps:

$$O_2 + 2\,H_2O + 2\,e^- \longrightarrow H_2O_2 + 2\,OH^-$$

$$H_2O_2 + 2\,e^- \longrightarrow 2\,OH^-$$

$$Au \longrightarrow Au^+ + e^-$$

$$Au^+ + CN^- \longrightarrow AuCN$$

$$AuCN + CN^- \longrightarrow Au(CN)_2^-$$

Thompson (1947) demonstrated the electrochemical action by successful experiments using KCN solutions, free from air, to which some gelatin was added. When the solution solidified, small spheres of gold were introduced in the jelly and their dissolution was studied by allowing a stream of oxygen to diffuse in one direction. In this way convection currents were eliminated. He observed that gold spheres were corroded on the side away from the source of oxygen (Fig. 1). This illustrated the formation of local cells in which the gold acted as anode.

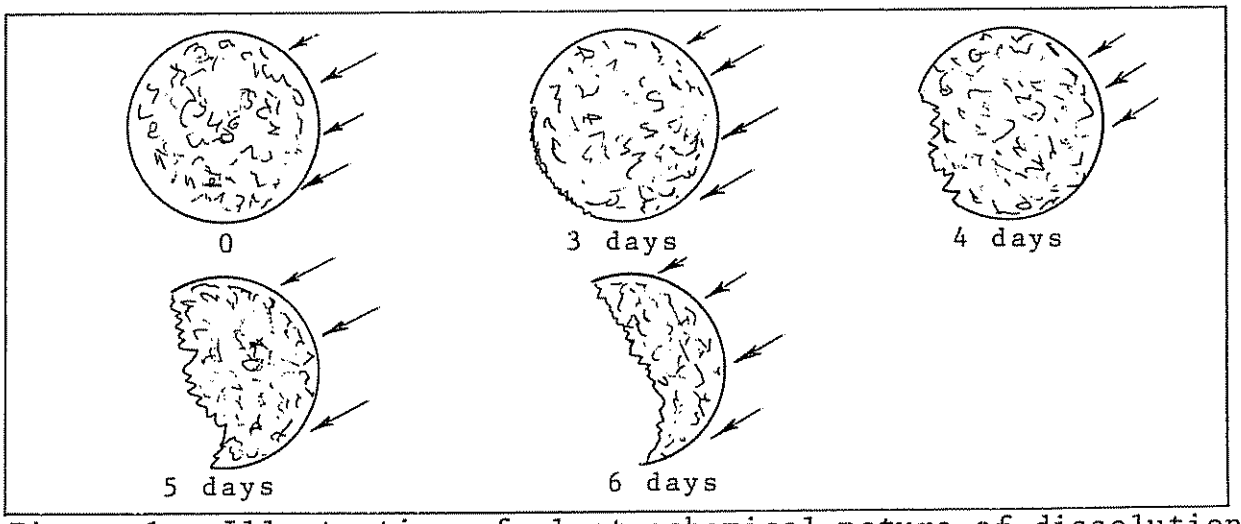


Figure 1.--Illustration of electrochemical nature of dissolution of gold particle (120 μ diam.) in KCN in presence of oxygen. Arrows indicate direction of flow of oxygen (Thompson, 1947).

It will be shown here that the dissolution process follows mainly the overall equation:

$$2\ Au + 4\ KCN + O_2 + 2\ H_2O \longrightarrow 2\ KAu(CN)_2 + 2\ KOH + H_2O_2$$

A similar equation can also be written for silver dissolution.

CYANIDE CONSUMPTION

During the dissolution of gold in cyanide solution, the ratio of cyanide consumption to the gold dissolved is two moles of the first to one equivalent of the latter (Table 1). This is in agreement with Elsner's and Bodländer's equation. Accordingly, the rate of gold dissolution is one-half the rate of cyanide consumption:

$$\text{Rate of dissolution} = \tfrac{1}{2}\frac{d(CN^-)}{dt}$$

Rate is expressed in equivalents per unit time, and (CN^-) is the number of molecules of KCN consumed in time t.

Table 1.--Consumption of cyanide caused by dissolution of gold (calculated from data by Kameda, 1949).

Time, hours	Amount of gold dissolved		Observed consumption of cyanide		Molar ratio KCN/Au
	mg	equivalent	mg	moles	
0.5	0.96	4.86×10^{-3}	0.62	9.52×10^{-3}	1.96
1.0	2.01	10.2	1.26	19.4	1.90
3.0	7.49	38.0	4.94	76.0	2.00
7.0	15.91	80.9	10.50	162.0	2.01
10.0	18.77	95.1	12.46	192.0	2.01
				Average	2.0

OXYGEN CONSUMPTION

Lund (1951) studied quantitatively the consumption of oxygen during the dissolution of silver in cyanide solutions in a closed system. The reaction was followed by measuring the drop in oxygen pressure with time; a typical plot of such behavior is shown in Figure 2. It is seen from this figure that during the first part of the experiment oxygen pressure decreases, then rises at point A in the figure, then it becomes constant. When the experiment was interrupted at point A, the solution was found to contain appreciable amounts of hydrogen peroxide, and when the silver sheet was again lowered into the solution, an evolution of gas on the sheet was clearly visible. When this evolution of gas stopped, the solution did not contain any H_2O_2. The sudden increase in pressure at A is obviously due to the catalytic decomposition of H_2O_2 on the silver sheet.

$$H_2O_2 \longrightarrow H_2O + \tfrac{1}{2}O_2$$

Further Lund (1951) found that during the first part of the experiment (part OA in Fig. 2), one mole O_2 is consumed for every 2.2 equivalents of silver dissolved (Table 2). In the latter part of the experiment when the pressure became constant (part AB in Fig. 2), the amount of silver dissolved was very small, ranging from 5 to 10 percent of the whole amount dissolved. Table 2 shows also that the rate of silver dissolution is twice the rate of oxygen consumption, or

$$\text{Rate of dissolution} = \frac{2\ d(O_2)}{dt}$$

where (O_2) is the number of moles of oxygen consumed in time t.

Table 2.--Consumption of oxygen during dissolution of silver. (Data by Lund, 1951.)

Time, minutes	Ag dissolved, equivalent	O_2 consumed, moles	$\frac{Ag}{O_2}$
10	2.96×10^{-5}	1.45×10^{-5}	2.05
20	7.76	3.07	2.50
30	9.36	4.17	2.25
40	12.42	5.40	2.30
120	36.06	16.00	2.25
		Average	2.2

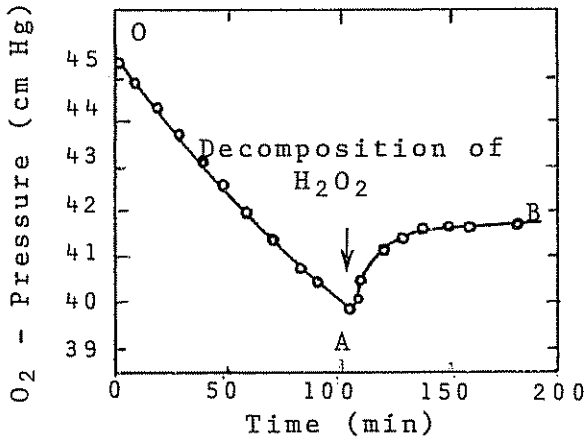


Figure 2.--Absorption of oxygen during dissolution of silver in cyanide solution (Lund, 1951).

THE ROLE OF HYDROGEN PEROXIDE

The formation of hydrogen peroxide during the dissolution of gold and silver in cyanide solutions has been confirmed by many investigators. For example, Kameda (1949) and Lund (1951) have measured the quantities of H_2O_2 liberated during the dissolution of gold and silver respectively. Some of these data are reproduced in Table 3. It is seen from Table 3 that 2.3 equivalents of metal are dissolved per mole of H_2O_2 liberated.

Table 3.--Formation of hydrogen peroxide during cyanidation.

	Metal dissolved		H_2O_2 formed		Metal equiv.	
	mg	equivalent	mg	moles	moles H_2O_2	Investigator
Gold	57.3	29.0×10^{-5}	5.11	15.0×10^{-5}	1.93	Kameda (1949), gravi-
	47.6	24.1	4.02	11.8	2.04	metrically
	13.4	6.8	0.36	1.03	(6.60)	
Silver		2.96×10^{-5}		1.43×10^{-5}	2.06	Lund (1951), volumet-
		7.76		3.09	2.50	rically
		9.36		4.00	2.24	
		12.42		5.51	2.26	
		36.06		14.76	2.44	
				Average	2.3	

Hydrogen peroxide formed may undergo catalytic decomposition according to:

$$H_2O_2 \longrightarrow H_2O + \tfrac{1}{2}\, O_2$$

This takes place either heterogeneously on the surface of the metal (Fig. 2), or homogeneously because of the presence of certain ions in solution, e.g., Cl^- (see for example Schumb and others, 1955). This explains why Kudryk and Kellogg (1954) were unable to detect H_2O_2 in their experiments, which involved solutions that contained KCl. The role of H_2O_2 in forming peroxides with metal ions in solution will be discussed later.

If Bodländer's mechanism were correct, then the gold or silver should be dissolved in cyanide solutions in the absence of oxygen but in the presence of hydrogen peroxide. Boonstra (1943) tested this reaction for gold and Lund (1951) tested it for silver. Both found that under these conditions the dissolution goes on very slowly (Table 4).

Table 4.--Dissolution of gold and silver in cyanide solutions.

	Weight dissolved, mg	Time required (min) cyanide + oxygen	cyanide + H_2O_2	Investigator
Gold	10	5 - 10	30 - 90	Boonstra (1943)
Silver	5	15	180	Lund (1951)

The addition of small amounts of H_2O_2 (3.5×10^{-4} moles/liter) has no effect on the rate of dissolution (Deitz and Halpern, 1953). Kameda (1949) reported that 0.6×10^{-2} to 0.9×10^{-2} moles/liter H_2O_2 accelerated the dissolution of gold, but more than 1.2×10^{-2} moles/liter H_2O_2 practically stopped it. He attributed the retarding effect to the oxidation of KCN. Lund (1951) confirmed the formation of potassium cyanate by the action of H_2O_2 on KCN according to:

$$KCN + H_2O_2 \longrightarrow KCNO + H_2O$$

He found further that potassium cyanate undergoes hydrolysis to potassium carbonate.

EFFECT OF THE PHYSICAL NATURE OF THE SURFACE

There is evidence that the physical nature of the surface of the metal leads to side reactions during dissolution. This may be one of the factors that produced contradictions in the literature.

Two experiments carried out by Lund (1951) demonstrated this effect clearly, but apparently it received little attention. A

silver sheet was etched in potassium cyanide solution in the presence of air and then rinsed with water, a white crystalline surface being obtained. When this sample dissolved in the cyanide solution, it was found that after a certain period of time the hydrogen peroxide that had accumulated in the solution decomposed rapidly at the surface of the sheet, liberating oxygen. When the sheet was etched in a different way, namely by immersing it in a mixture of KCN and H_2O_2 whereby it lost its crystalline appearance, no evolution of gas was observed. The rate of dissolution in the two experiments was the same.

Lund (1951) interpreted this observation by suggesting that in the first experiment the H_2O_2 formed during the dissolution decomposed catalytically on the edges of the silver crystals, whereas in the second, in which the surface did not show crystalline structure, the H_2O_2 did not decompose.

K I N E T I C S O F D I S S O L U T I O N

METHODS OF INVESTIGATION

The methods used to study the rate of dissolution of gold or silver in cyanide solution fall in one of the following groups:

1. Gold leaf test: Measuring the time required for a gold leaf to dissolve under certain prescribed conditions.

2. Plate or disc method: Measuring the weight of metal dissolved in unit time.

3. Current density-electrode potentials measurements: This method is based on the principle that on applying a certain potential to a gold electrode, the current density flowing will be proportional to the rate of gold dissolution.

The first method is simple and rapid and is often used for studying the factors affecting the rate of cyanidation. A single test is not sufficient to decide the effect of any factor, as results may not be reproducible. The average of at least four tests should be considered.

In the second method, if the cyanide concentration is kept constant during the test, then the dissolution follows a zero order reaction, as the surface area does not change during the course of the reaction (Fig. 3).

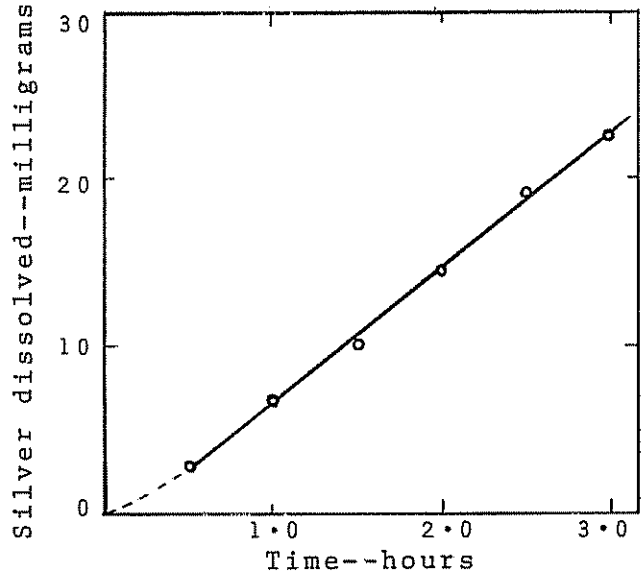


Figure 3.--Dissolution of silver plate in NaCN (0.0096 mole/liter) at 24°C and 3.4 atm O_2 (Deitz and Halpern, 1953).

In the third method the rate of dissolution (equivalent $cm^{-2}sec^{-1}$) is related to the current density by the relation:

$$\text{Rate} = \frac{I}{n\ F}$$

where I = current density, amp cm^{-2}

F = Faraday constant = 96,500 coulomb per equivalent

n = 1 = equivalents of charge per mole of metal dissolved.

Good agreement was obtained between this method and the second method (Kudryk and Kellogg, 1954). Results from this method are not always applicable to cyanidation practice, however, because of the external emf applied.

RELATIVE RATES OF DISSOLUTION OF GOLD AND SILVER

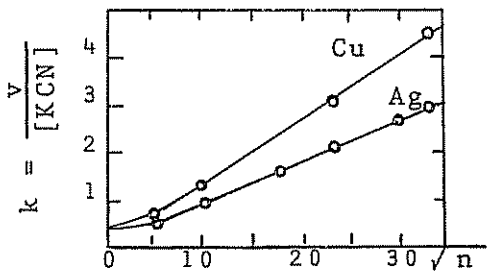
Under exactly the same conditions, silver dissolves at about half the rate at which gold dissolves (rate expressed in grams/unit time), provided that the solutions are kept uniform by mild agitation only. If the rates of dissolution are expressed in gram atoms/unit time, however, then gold dissolves at the same rate as silver, as the atomic weight of gold is nearly twice that of silver. Kakovskii and Kholmanskikh (1960) found further that copper also dissolves at the same rate as gold and silver, as will be clarified later in discussion of the mechanism of dissolution. The rate of dissolution of gold from a gold-silver alloy, however, is not proportional to the gold content of the alloy (Plaksin and Shibaev, 1936; Plaksin and Shabarin, 1940).

EFFECT OF SURFACE AREA

As in any heterogeneous reaction, the rate of gold and silver dissolution is directly proportional to the surface area. Kameda (1949) found a linear relation between the size of a gold particle (10 to 100μ) and the time required for its dissolution. Lund (1951) found a linear relation between the dissolution rate constant and the surface area of the silver, which was in the form of a plate.

EFFECT OF SPEED OF AGITATION

Many investigators studying the dissolution of gold and silver in cyanide solution reported that the rate increased with the speed of agitation. Quantitative data were presented by Kakovskii and Kholmanskikh (1960), which revealed interesting facts. The rate of dissolution of silver and copper increases linearly with the square root of the speed at which a disc of these two metals is revolved in the solution (Fig. 4). For gold, however, the rate increases only up to a certain speed of agitation (150 rpm), after which it drops and becomes nearly constant (Fig. 5). These authors suggested that the dissolution of gold may follow two mechanisms, depending on the speed of agitation of the sample. Cathro (1963) confirmed that the rate of dissolution of gold decreases at higher speeds of agitation.



n = rpm of metallic disc

Figure 4.--Dependence of rates of dissolution of silver and copper on speed of stirring, oxygen pressure = 1 atm (Kakovskii and Kholmanskikh, 1960).

EFFECT OF CYANIDE CONCENTRATION

Sodium, potassium, ammonium, calcium, strontium, and barium cyanides have the same dissolving power per mole of cyanide radical, for either gold or silver (Julian and Smart, 1921). Mainly sodium and calcium cyanide are used in practice.

The rate of gold dissolution increases linearly with increasing cyanide concentration until a maximum is reached, beyond which a further increase in cyanide does not dissolve gold, but

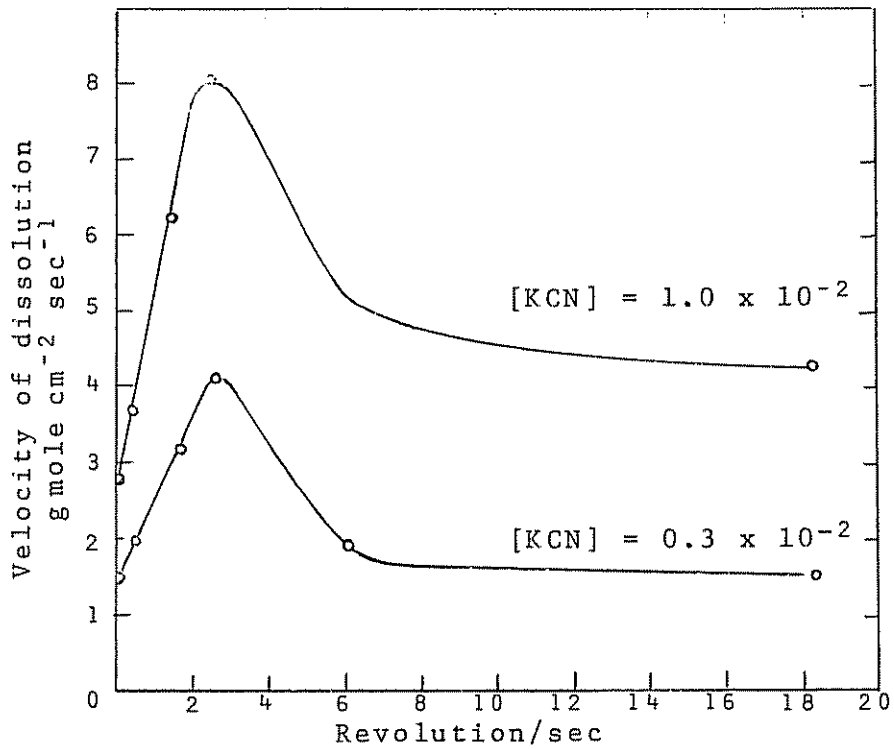


Figure 5.--Decrease in rate of gold dissolution at high speeds of agitation and at two different cyanide concentrations, g mole/liter. Temp. 25°C, p_{O_2} = 1 atm, [KOH] = 10^{-3} g mole/liter (plotted from data by Kakovskii and Kholmanskikh, 1960).

on the contrary it has a slight retarding effect (Fig. 6). Below this maximum the rate can therefore be expressed by:

$$\text{Rate of dissolution} = k_1[CN^-]$$

where k_1 is a constant and $[CN^-]$ is the concentration of the free cyanide.

The value of this maximum concentration (at atmospheric pressure and room temperature) was reported differently by various investigators (Table 5).

Table 5.--Maximum cyanide concentration for gold dissolution at atmospheric pressure and room temperature.

	% KCN	
Maclaurin (1893)	5.00	
Maclaurin (1895)	0.25	
White (1919)	0.027	
Barsky and others (1934)	0.07	(0.05% NaCN)
Beyer (1936)	0.10	
Kameda (1949)	0.03	
Kudryk and Kellogg (1954)	0.0175	
Kakovskii and Kholmanskih (1960)	0.0085	

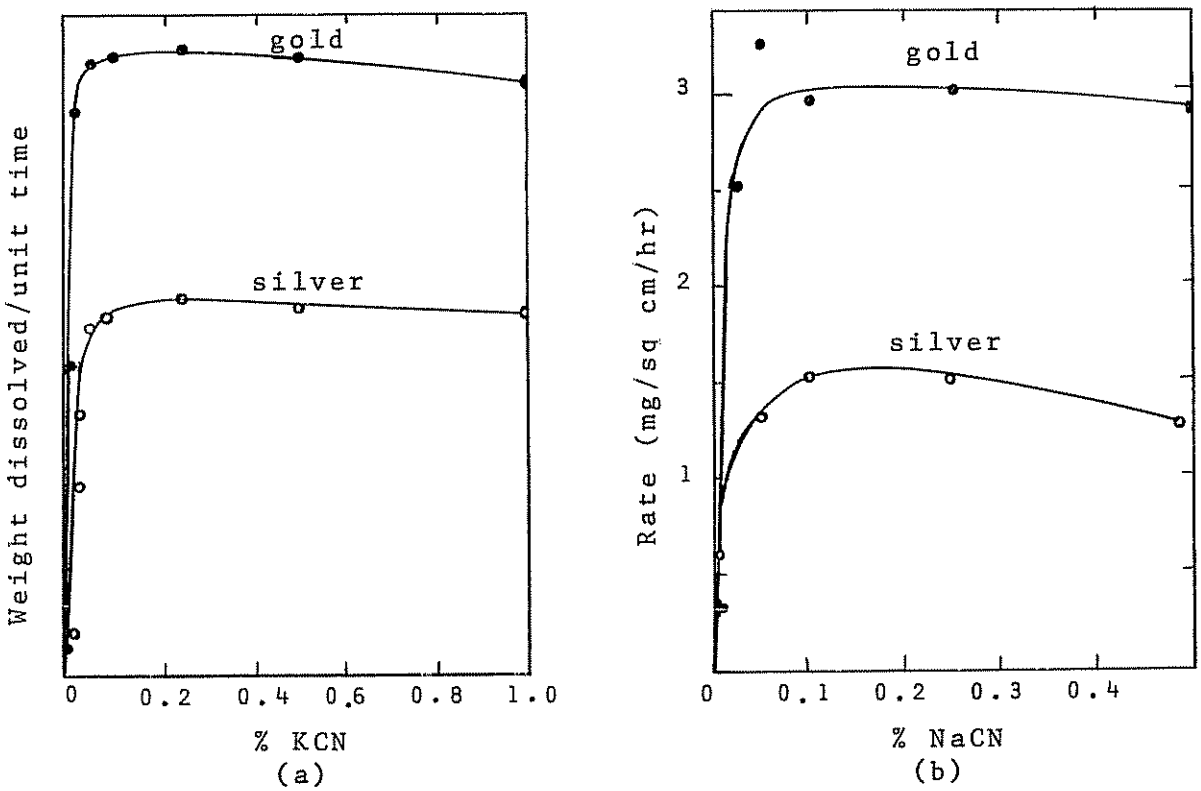


Figure 6.--Effect of cyanide concentration on the rate of dissolution of gold and silver; (a) Maclaurin (1893), (b) Barsky and others (1934).

The values reported by Maclaurin should be rejected, because pure KCN was not available at that time, and according to his method of preparation, KCN would have contained excess KOH. The value of this maximum will be discussed later.

The decrease in the rate at high cyanide concentration was a point of discussion from the very beginning of the cyanidation process. Maclaurin (1893) attributed it to the decrease in solubility of oxygen at high cyanide concentrations. According to Barsky and others (1934), however, the solubility of oxygen is practically independent of cyanide concentration below 2 percent (Table 6).

Table 6.--Solubility of O_2 in cyanide solutions (Barsky and others, 1934).

NaCN percent	O_2 mg/liter	NaCN percent	O_2 mg/liter
0.0	8.20	0.10	7.96
0.01	8.25	0.25	8.29
0.02	7.90	0.50	8.33
0.05	8.02	2.00	8.36

Later, Maclaurin (1895) suggested that the decrease in the rate at high cyanide concentrations was due to the increase in viscosity of the solution, and resultant slower movement of the ions. He measured the viscosity of different cyanide concentrations up to 50 percent and found that the viscosity increases with increasing concentration. From his data, however, one can hardly find a change in the viscosity of the solution up to 10 percent KCN. Therefore his conclusions cannot be valid at the concentration under consideration. Kameda (1949) examined the effect of increasing viscosity of a 0.03 percent KCN solution by adding various amounts of sugar. He reported that the viscosity of the solution had an inappreciable influence on the rate of dissolution. According to Harned and Owen (1958), the viscosity of aqueous solutions of potassium cyanide at concentrations up to 10^{-2} g mole/liter is only 0.1 percent greater than the viscosity of pure water.

Nobody attributed the decrease in the rate at high cyanide concentrations to the obvious cause, namely, the increase of pH of the solution. Cyanide ion undergoes hydrolysis according to:

$$CN^- + HOH \rightleftharpoons HCN + OH^-$$

As will be seen later, the rate of dissolution decreases with increasing pH of the solution. The pH value of cyanide solutions of different concentrations is shown in Table 7.

Table 7.--pH of KCN solutions.

KCN %	Calculated pH = 11.699 + ½ log [KCN]	Observed (Beyers, 1936)
0.01	10.16	10.02
0.02	10.31	10.28
0.05	10.40	10.45
0.10	10.51	10.61
0.15	10.66	10.68
0.20	10.81	10.76

EFFECT OF OXYGEN PRESSURE

As already mentioned, oxygen is essential for the dissolution of gold by cyanide solutions. Atmospheric air is the oxidizing agent universally used in cyanide gold mills. In this application the equilibrium concentration of O_2 is 8.2 mg/liter for dilute cyanide solutions, which would be approached only under ideal conditions of aeration and agitation, and only if the gangue minerals do not consume oxygen.

At high cyanide concentration (above about 0.1 percent NaCN), the rate of dissolution is directly proportional to the oxygen partial pressure (Fig. 7). Under these conditions the rate of dissolution

follows the equation:

$$\text{Rate of dissolution} = k_2 \, [O_2]$$

where k_2 is a constant and $[O_2]$ is the concentration of dissolved oxygen.

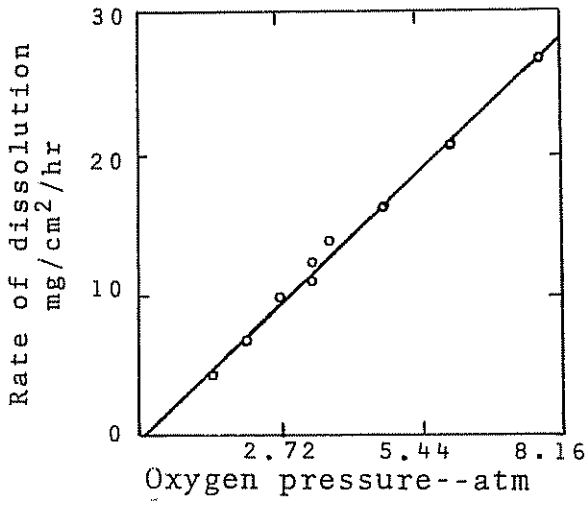


Figure 7.--Effect of oxygen partial pressure on rate of dissolution of silver in 0.055 mole/liter NaCN at 24° C (Deitz and Halpern, 1953).

The rate does not increase indefinitely with increasing oxygen pressure, however; there is a certain pressure beyond which further increase does not affect the rate (Fig. 8).

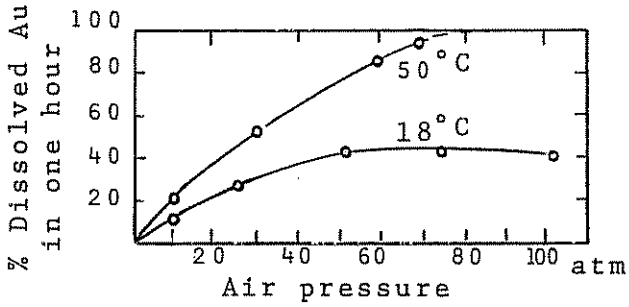


Figure 8.--Effect of very high pressure on rate of dissolution of gold in 1 percent KCN solutions (Tronev and Bondin, 1937).

At low cyanide concentration (below about 0.1 percent) and high oxygen pressure, the rate of dissolution depends only on the cyanide concentration (Fig. 9).

An examination of data presented in the literature reveals that there is a certain ratio of cyanide ion concentration to oxygen concentration in solution, at which the rate of dissolution reaches a maximum. This ratio is between 4.62 and 7.65 (Table 8).

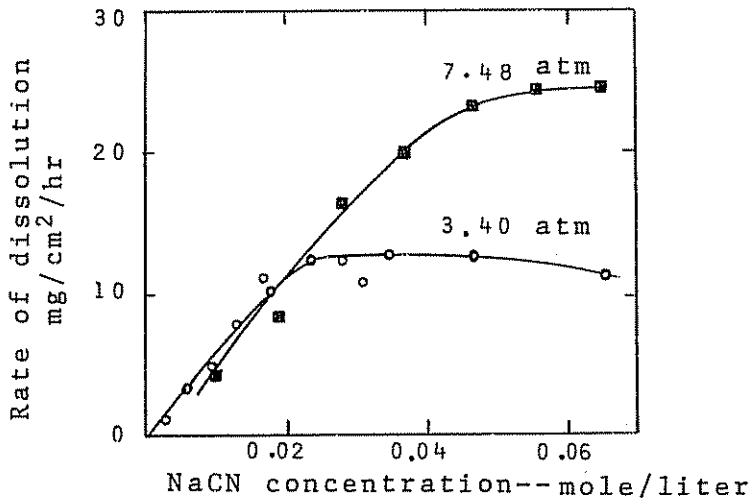


Figure 9.--Rate of dissolution of silver at different O_2 pressures and different NaCN concentrations at 24°C (Deitz and Halpern, 1953).

Table 8.--Limiting rate of dissolution of gold, silver, and copper at different cyanide and oxygen concentrations.

Metal	Temp. °C	P_{O_2} atm	$[O_2]$ in solution mole/liter	$[CN^-]$ mole/liter	$\frac{[CN^-]}{[O_2]}$ lim. rate	Investigator
Gold	25	1.00	1.28×10^{-3}	6.0×10^{-3}	4.69	Kakovskii and
	25	0.21	0.27	1.3	4.85	Kholmanskikh
	35	1.00	1.10	5.1	4.62	(1960)
	25	1.00	1.28	8.8	6.8*	
	25	0.21	0.27	1.7	6.3*	
Silver	24	7.48	9.55×10^{-3}	56.0×10^{-3}	5.85	Deitz and
	24	3.40	4.35	25.0	5.75	Halpern (1953)
	35	2.70	2.96	22.0	7.40	Kakovskii and
	25	1.00	1.28	9.4	7.35	Kholmanskikh
	35	1.00	1.10	8.1	7.35	(1959)
	25	0.21	0.27	2.0	7.40	
Copper	25	1.00	1.28×10^{-3}	9.8×10^{-3}	7.65	Kakovskii and
	35	1.00	1.10	8.3	7.65	Kholmanskikh
						(1960)

*At high speeds of agitation, greater than 150 rpm.

It is interesting to examine the effect of oxygen partial pressure on the maximum rate of dissolution at high speeds of agitation. As shown in Table 9, the rate is no longer proportional to p_{O_2} but to the square root of the oxygen partial pressure, which

again supports the suggestion that a different mechanism should be operating.

Table 9.--Dependence of maximum rate of gold dissolution on oxygen partial pressure at low and at high speeds of agitation (from data by Kakovskii and Kholmanskikh, 1960).

	rpm	Temp. °C	P_{O_2} atm	v_{max}	$\frac{v_{max}}{P_{O_2}}$	$\frac{v_{max}}{P_{O_2}^{1/2}}$
Low speed of agitation	30	25	1.00	3.8×10^{-9}	3.8×10^{-9}	-----
	30	25	0.21	0.9	4.3	-----
	100	25	1.00	6.2	6.2	-----
	100	25	0.21	1.13	6.12	-----
	100	35	1.00	6.4	6.4	-----
	100	35	0.21	1.7	7.7	-----
High speed of agitation	365	25	1.00	5.3	-----	5.3×10^{-9}
	365	25	0.21	2.4	-----	5.2
	1100	25	1.00	4.45	-----	4.45
	1100	25	0.21	2.09	-----	4.54

EFFECT OF TEMPERATURE

Increasing the temperature is expected to increase the rate of the dissolution reactions, but to decrease the oxygen content of the solution. Therefore there should be an optimum temperature for the maximum rate of dissolution of gold and silver. Julian and Smart (1921) found that at 85°C the rate was maximum (Fig. 10), whereas Meyer (1931) found the maximum rate to be at 80°C. Above 110°C decomposition of cyanide is appreciable.

The effect of increasing temperature on the rate of dissolution of gold and silver was studied by some investigators who also were able to calculate the activation energy of the process. Table 10 gives a summary of the data available, and Figure 11 shows a typical Arrhenius' plot for silver.

It is seen from Table 10 that the activation energy of the dissolution of gold, silver, and copper ranges from 2 to 5 Kcal/mole, which is typical for processes controlled by diffusion. It is very important to note, however, that the value of 14.1 Kcal/mole found for gold dissolution under similar conditions but at a high speed of agitation (1,100 rpm), is typical of a process controlled by chemical reactions. This is again convincing evidence that there must be two mechanisms for gold dissolution, depending on the speed of stirring. At low speeds the rate is diffusion controlled, but at high speeds the rate is chemically controlled.

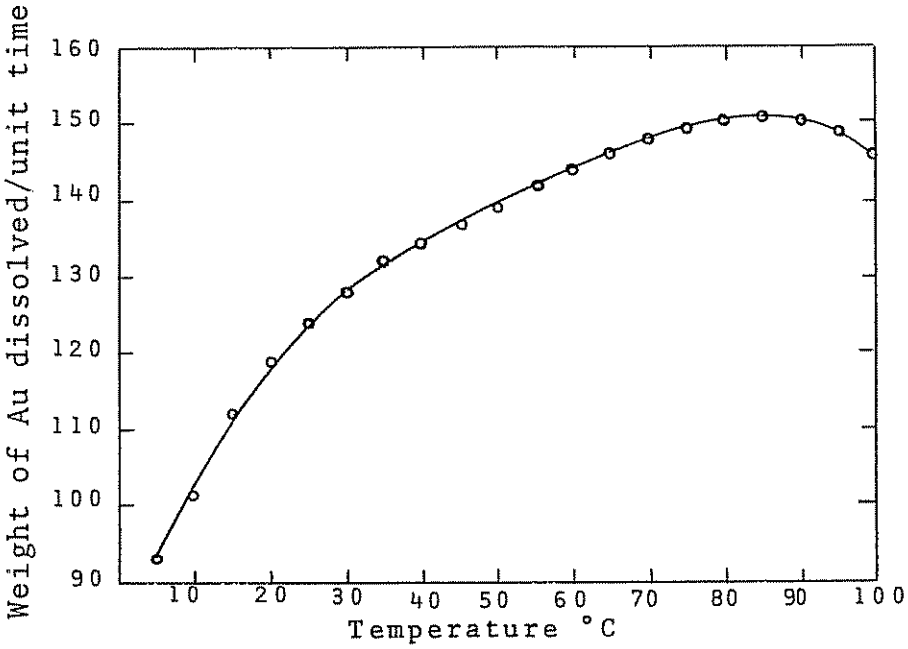


Figure 10.--Effect of temperature on rate of dissolution of gold in 0.25 percent KCN (Julian and Smart, 1921).

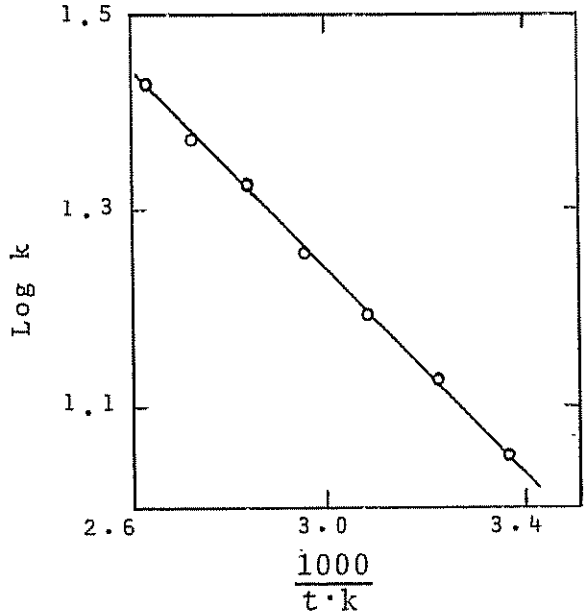


Figure 11.--Effect of temperature on rate of silver dissolution in 0.037 mole/liter NaCN solution, oxygen pressure 3.4 atm (Deitz and Halpern, 1953).

Table 10.--Activation energy for the dissolution reaction of gold, silver, and copper in cyanide solutions.

	Temp. range, °C	P_{O_2} atm	Cyanide conc. KCN%	Cyanide conc. NaCN%	[KOH] g mole/liter	rpm	Activation energy Kcal/mole	Investigator
Gold	15 - 40	0.21	0.03	----	----	----	5.245	Kameda (1949)
	27 - 72	0.21	0.01 - 0.5	----	10^{-3}	100 - 500	3.5 - 4.0	Kudryk and Kellogg (1954)
	25 - 45	1.00	0.0195	----	10^{-3}	100	3.487	Kakovskii and Kholmanskikh (1960)
	15 - 35	1.00	0.0195	----	10^{-3}	1100	14.1	Kakovskii and Kholmanskikh (1960)
	30 - 60	1.00	----	----	----	200 - 1600	6.2	Cathro (1963)
Silver	15 - 25	0.21	0.043	----	10^{-1}	----	3.200	Lund (1951)
	24 - 110	3.40	----	0.18	----	895	2.400	Deitz and Halpern (1953)
	15 - 50	1.00	0.05	----	10^{-3}	1100	3.477	Kakovskii and Kholmanskikh (1959)
Copper	25 - 45	1.00	0.0355	----	10^{-3}	1100	3.162	Kakovskii and Kholmanskikh (1960)

EFFECT OF HYDROGEN ION CONCENTRATION

Water saturated with HCN gas and oxygen attacks gold with the formation of AuCN, which is insoluble, and hydrogen peroxide (Cambi, 1958):

$$2\ Au + 2\ HCN + O_2 \longrightarrow 2\ AuCN + H_2O_2$$

It is essential that the cyanide solution should be kept alkaline for the following reasons:

(1) To prevent the hydrolysis of the cyanide ion:

$$CN^- + H_2O \rightleftharpoons HCN + OH^-$$

(2) To prevent cyanide decomposition by atmospheric CO_2:

$$CN^- + H_2CO_3 \rightleftharpoons HCN + HCO_3^-$$

In both reactions HCN is liberated and it has no dissolving action on gold. Excess alkalinity, however, also decreases the rate of dissolution (Fig. 12). At higher alkalinity, the decrease in rate is more abrupt. The alkalinity of cyanide solutions should therefore be carefully controlled to achieve high dissolution rates of gold and silver. In cyanidation practice, the pH of mill solutions usually ranges from 11 to 12.

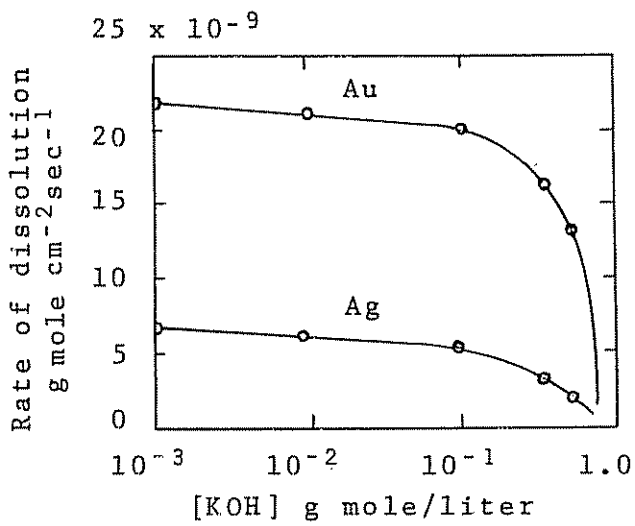


Figure 12.--Effect of pH on rate of dissolution of gold and silver in KCN (after Kakovskii and Kholmanskikh, 1959, 1960).

EFFECT OF FOREIGN IONS

Most gold occurs as native metal, nearly all alloyed with various amounts of silver. Certain minerals are characteristically associated with gold, and the most important are pyrite, galena, zinc blend, arsenopyrite, stibnite, pyrrhotite, and chalcopyrite. Various selenium minerals and magnetite may also be present. In Witwatersrand, South Africa, uraninite, and to a lesser extent, thucholite are associated with the gold ore; uranium is recovered as a by-product of gold milling. Carbonaceous matter is associated with some gold ores. The most common gangue minerals are quartz, feldspar, micas, garnet, and calcite.

Although the gangue minerals are insoluble in cyanide solution, some metallic minerals are soluble to some extent (Table 11). Carbonaceous matter in gold ore is a source of trouble, because it adsorbs gold cyanide complex.

With the exception of a few ions such as Na^+, K^+, Cl^-, NO_3^-, and SO_4^-, which have no effect on the rate of dissolution of gold and silver in cyanide solution, ions may have an accelerating or a retarding effect. Lead (II) ions may have either an accelerating or a retarding effect, depending on their concentration in solution. The study of the effect of these foreign ions on cyanidation is complicated because the dissolution process is composed of two simultaneous reactions:

(a) The oxidation reaction involving the formation of the auro- or the argento-cyanide ion, e.g.:

$$Ag + 2\ CN^- \longrightarrow Ag(CN)_2^- + e^-$$

(b) The reduction of oxygen according to:

$$O_2 + 2\ H_2O + 2\ e^- \longrightarrow H_2O_2 + 2\ OH^-$$

Which of these reactions is affected by the foreign ion is usually difficult to say, and many contradictory statements are found in the literature. Data available were mainly obtained by studying the effect of foreign ion in the gold leaf test.

An approach to this problem is to study the effect of the foreign ion on the cathodic and the anodic reactions separately. This can be simply achieved by studying the change in potential-current density characteristics of the gold (or silver) electrode in two separate experiments:

1. Gold electrode + $Au(CN)_2^-$ + CN^- + foreign ion, oxygen being excluded from the system.

2. Gold electrode + O_2 + H_2O + foreign ion, in the absence of cyanide ion.

Table 11.--Solubility of minerals and metals in cyanide solutions.

Mineral			% Dissolved in 24 hours	Reference
Gold minerals	Calaverite	$AuTe_2$	Readily soluble	Johnston (1933)
Silver minerals	Argentite	Ag_2S	Readily soluble	Leaver, Woolf, and Karchmer (1931)
	Cerargyrite	$AgCl$		
	Proustite	Ag_3AsS_3	Sparingly soluble	
	Pyrargyrite	Ag_3SbS_3		
Copper minerals	Azurite	$2\ CuCO_3 \cdot Cu(OH)_2$	94.5	Leaver and Woolf (1931)
	Malachite	$CuCO_3 \cdot Cu(OH)_2$	90.2	
	Chalcocite	Cu_2S	90.2	
	Cuprite	Cu_2O	85.5	
	Bornite	$FeS \cdot 2\ Cu_2S \cdot CuS$	70.0	
	Enargite	$3\ CuS \cdot As_2S_5$	65.8	
	Tetrahedrite	$4\ Cu_2S \cdot Sb_2S_3$	21.9	
	Chrysocolla	$CuSiO_3$	11.8	
	Chalcopyrite	$CuFeS_2$	5.6	
Zinc minerals	Smithsonite	$ZnCO_3$	40.2	Leaver and Woolf (1931)
	Zincite	ZnO	35.2	
	Hydrozincite	$3\ ZnCO_3 \cdot 2\ H_2O$	35.1	
	Franklinite	$(Fe,Mn,Zn)O \cdot (Fe,Mn)_2O_3$	20.2	
	Sphalerite	ZnS	18.4	
	Gelamine	$H_2Zn_2SiO_4$	13.4	
	Willemite	Zn_2SiO_4	13.1	
Iron minerals	Pyrrhotite	FeS	Readily soluble	Hedley and Tabachnick (1958)
	Pyrite	FeS_2	Sparingly soluble	
	Hematite	Fe_2O_3		
	Magnetite	Fe_3O_4	Practically insoluble	
	Siderite	$FeCO_3$		
Arsenic minerals	Orpiment	As_2S_3	73.0	
	Realgar	As_2S_2	9.4	
	Arsenopyrite	$FeAsS$	0.9	
Antimony minerals	Stibnite	Sb_2S_3	21.1	
Lead minerals	Galena	PbS	Soluble at high alkalinity	Lemmon (1940)

In the first experiment, the effect of the foreign ion on the reduction of oxygen on the gold surface can be studied, and in the second experiment, the effect of the same ion on the anodic reaction of gold dissolution in cyanide. The assembly described by Kudryk and Kellogg (1954) serves this purpose most conveniently. The results of such tests should be interpreted with care, however, as the application of external emf to cause dissolution does not correspond to actual cyanidation practice. Thus, for example, under these conditions oxygen is reduced to OH^- and not to H_2O_2.

Another approach to the study of the effect of foreign ions on the dissolution was reported by Ivanovskii (1957, 1958), Plaksin and Ivanovskii (1958), and Benard (1965). These authors used radioactive indicators of the ions being studied and in this way they were able to study the mechanism by which these ions affect the dissolution process.

Accelerating Effect

Haden (1938) reported that small amounts of lead and mercuric salts accelerate the dissolution. This was confirmed later by Kameda (1949) and by Fink and Putnam (1950) (Fig. 13). Fink and Putnam found further that bismuth and thallium salts also accelerate the dissolution. From calculations of electrode potentials in cyanide solutions, they concluded that gold metal can actually displace the ions of only these four metals. The same authors suggested that the rapid dissolution of gold in the presence of these ions might be due to alteration in the surface character of gold by alloying with the displaced metals. This view was also suggested by Kameda (1949) to explain the accelerating effect of lead salt.

Because dissolution is a diffusion-controlled process, it is quite possible that a change in the surface character of the metal may lead to a decrease in the thickness of the boundary layer through which the reactants diffuse to reach the metallic surface. It should be noted that adsorption depends on the surface character of the solid.

The addition of lead salts to cyanide solutions is a common mill practice aimed at counteracting the harmful effect of sulfides. Addition of excessive lead salts may cause a retardation in the rate of dissolution of the gold, as will be described later.

Retarding Effect

The presence of metallic cations such as

$$Fe^{2+},\ Cu^{2+},\ Zn^{2+},\ Ni^{2+},\ Mn^{2+},\ Ca^{2+},\ \text{and}\ Ba^{2+}$$

(the latter two only at high alkalinity) has a retarding effect (Beyers, 1936; Plaksin and Sulova, 1936; Plaksin and Suvorovskii, 1938; and Kameda, 1949). Pb^{2+} plays a unique role in cyanidation,

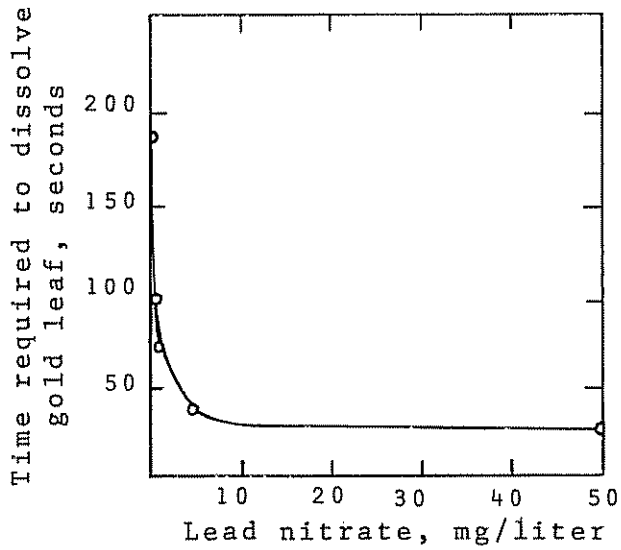


Figure 13.--Effect of lead ion on dissolution of gold in buffered 0.1 percent NaCN solution (Fink and Putnam, 1950).

and there has been much confusion regarding its effect on the rate of dissolution of gold. Besides the accelerating action already described, some reports describe a retarding effect (Beck and Gartell, 1935; Beyers, 1936; Thompson, 1947). Kameda (1949, 1950) studied this problem rather extensively. It can be concluded from his data that when Pb^{2+} is present in very small amounts as compared to the CN^- ion, an accelerating effect is observed, whereas when the $[Pb^{2+}]/[CN^-]$ ratio exceeds a certain value there is a retarding effect.

It is also well known that the sulfide ion has a retarding effect on the rate (Julian and Smart, 1921; Kameda, 1949; and Fink and Putnam, 1950). Similarly, certain flotation agents such as xanthate ion, which is sometimes used to concentrate the sulfides with which gold is associated, decrease the rate of dissolution.

The retarding effect may be due to one or more of the following reasons:

1. Consumption of oxygen from solution:

Because oxygen is necessary for gold dissolution, any side reactions in which the cyanide solution is deprived of its oxygen content will lead to a decrease in the rate. Pyrrhotite accompanying gold in some ores decomposes in alkaline medium forming ferrous hydroxide and sulfide ion:

$$FeS + 2\ OH^- \longrightarrow Fe(OH)_2 + S^{2-}$$

In presence of oxygen, ferrous hydroxide is easily oxidized to ferric hydroxide:

$$2\ Fe(OH)_2 + \tfrac{1}{2}\ O_2 + H_2O \longrightarrow 2\ Fe(OH)_3$$

while sulfide ion is partly oxidized to thiosulfate and polysulfide:

$$2\ S^{2-} + 2\ O_2 + H_2O \longrightarrow S_2O_3^{2-} + 2\ OH^-$$

$$S^{2-} + H_2O \longrightarrow HS^- + OH^-$$

$$2\ HS^- + \tfrac{1}{2}\ O_2 \longrightarrow S_2^{2-}\ H_2O$$

thus contributing to the depletion of oxygen from solution.

2. Consumption of free cyanide from solution:

   (a) Formation of complex cyanides: Some copper, zinc, and iron minerals that may be associated with gold ore dissolve in cyanide solution and therefore deplete the solution of its cyanide content, e.g.:

   $$ZnS + 4\ CN^- \longrightarrow [Zn(CN)_4]^{2-} + S^{2-}$$

   (b) Formation of thiocyanate: Sulfide ion liberated, when the ore contains sulfide minerals, reacts with cyanide and oxygen to form thiocyanate ion, which has no action on gold:

   $$S^{2-} + CN^- + \tfrac{1}{2}\ O_2 \longrightarrow CNS^- + 2\ OH^-$$

   (c) Adsorption on gangue material: Auriferous ores and concentrates may contain quartz, aluminosilicates, or other silicates which, if finely divided in an aqueous alkaline medium, form colloidal silica and alumina; if iron sulfides are present in the ore, ferric hydroxide is also formed. According to Zablotskaya (1955), these gangue materials have a strong adsorptive capacity for potassium cyanide.

3. Film formation on the surface of the metal:

   (a) Sulfides: The retarding effect of the sulfide ion in the cyanide solution is well-known (Fig. 14; see also Plaksin and Ivanovoskii, 1940; and Gritzuk, 1942). It can be seen that as little as 0.5 ppm of the sulfide ion retards the dissolution. This cannot be accounted for by the depletion of the solution of its cyanide or oxygen contents, as the leaching solution usually contains excess oxygen and excess cyanide. It is believed that an insoluble aurous sulfide film is formed on the gold, which protects it from dissolution.

   Kudryk and Kellogg (1954) studied qualitatively the effect of sulfide ion on the electrode potential

of gold in KCN solution in the absence of oxygen and, in a separate experiment, its effect on the electrode potential of gold in the absence of KCN but in the presence of oxygen. They found that in the first case little change was observed, whereas in the second, the potential was greatly affected. They concluded that the trace sulfide poisons the gold surface toward the cathodic reduction of oxygen but does not affect the anodic reaction.

(b) Peroxides: Calcium ion has no effect on gold dissolution (Barsky and others, 1934). At pH >11.5, however, the rate of dissolution is greatly reduced. At the same pH, solutions kept alkaline by $Ca(OH)_2$ show a remarkable decrease in the rate of gold and silver dissolution when compared with others kept alkaline with KOH (Fig. 15). Kameda (1949) was the first to suggest that the decrease may be due to the formation of calcium peroxide on the metal surface, which prevents the reaction with cyanide. Calcium peroxide was thought to be formed by the reaction of lime with H_2O_2 accumulating in solution according to:

$$Ca(OH)_2 + H_2O_2 \longrightarrow CaO_2 + 2\ H_2O$$

He was able by chemical analysis to identify the precipitate formed as calcium peroxide. Later, Deitz and Halpern (1953) confirmed this suggestion by means of x-ray diffraction analysis. They also found that $Ba(OH)_2$ behaves similarly.

Lime is one of the reagents commonly used in cyanide mills to adjust the pH of the pulp and to help settling. Its use must therefore be carefully considered.

(c) Oxides: Andrejew (1913) reported that ozone when added to cyanide solution decreased the rate of dissolution of gold. He concluded that a layer of gold oxide, which caused a visual change of the gold to brick red, produced the retarding effect. Plaksin and Sinel'nikova (1939) reported, however, that potassium cyanide is oxidized by ozone according to:

$$3\ KCN + O_3 \longrightarrow 3\ KCNO$$

(d) Insoluble cyanides: The retarding effect of Pb^{2+} was attributed by Thompson (1947) to an insoluble film of $Pb(CN)_2$ deposited on the gold surface. Kameda (1949) detected the presence of lead on the surface of gold when the cyanide solution contained Pb^{2+} ions, but he did not identify its nature.

(e) The rate of dissolution decreases with the addition of as little as 0.4 ppm of potassium ethyl xanthate (Kameda, 1949; McCreedy and others, 1961). This is in agreement with the fact that when flotation is used to concentrate the sulfides with which gold is associated, prior to cyanidation, difficulties are frequently faced. Kameda also reported that the gold surface turned reddish, which led him to suggest that a gold xanthate film was probably formed. Barbin (1961) confirmed this suggestion by using potassium xanthate marked with S^{35}.

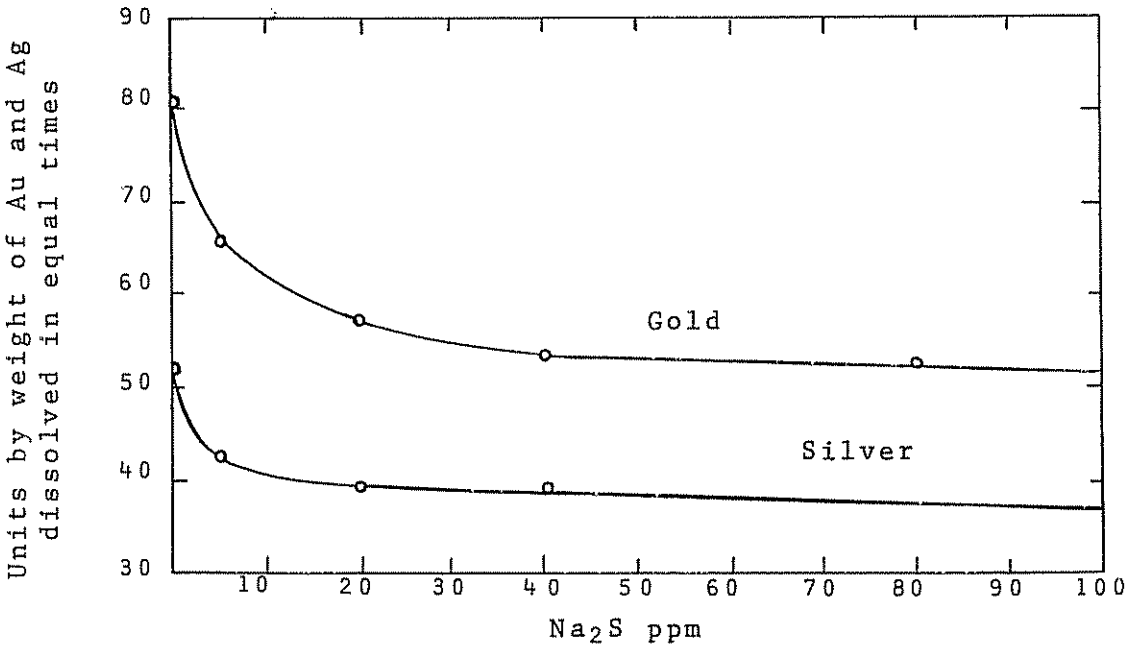


Figure 14.--Effect of Na_2S in a 0.25 percent KCN solution on rate of gold and silver dissolution (Julian and Smart, 1921).

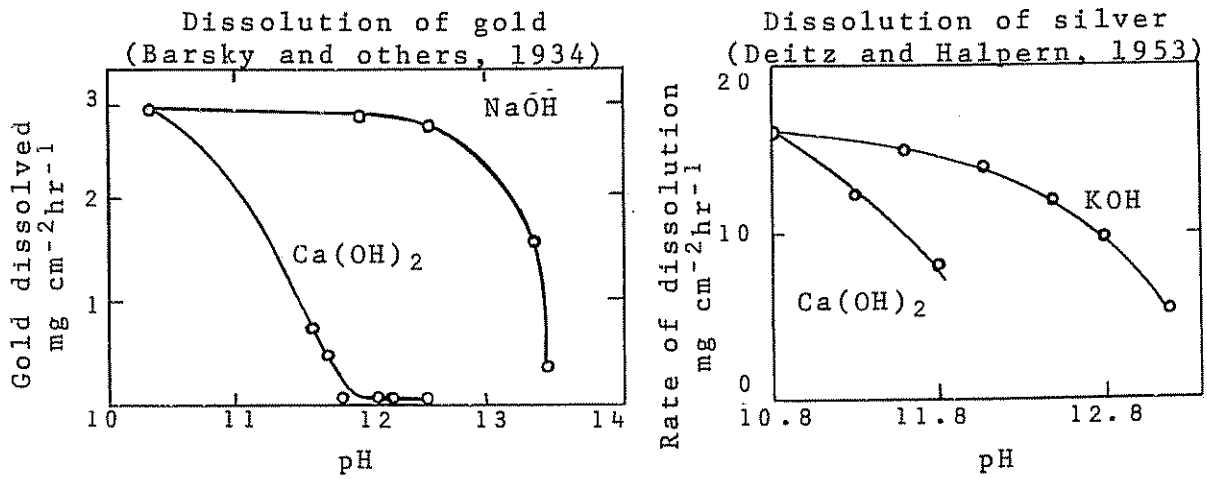


Figure 15.--Retarding effect due to calcium ions at high alkalinity.

MECHANISM OF CYANIDATION

On the basis of the studies already reviewed, one can conclude that the dissolution process is a heterogeneous reaction, which is controlled by the diffusion of both of the reacting species (dissolved oxygen and the cyanide ion) through the Nernst boundary layer. This conclusion is based on three experimental facts that characterize such processes, namely:

1. The rate of dissolution depends on the surface of the metal in contact with the liquid phase.

2. The rate of dissolution depends on the speed of stirring.

3. The rate is only slightly affected by the increase of temperature, the process requiring an activation energy of only 2 to 5 Kcal/mole.

The results also lead to the conclusion that the proper equation for the dissolution reaction should be:

$$2\ Au + 4\ KCN + O_2 + 2\ H_2O \longrightarrow 2\ KAu(CN)_2 + 2\ KOH + H_2O_2$$

A similar equation can also be written for the dissolution of silver. This conclusion is based on the following facts:

1. For every equivalent of metal dissolved, two moles of cyanide were consumed (Table 1).

2. For every two equivalents of metal dissolved, one mole O_2 was consumed (Table 2).

3. Hydrogen peroxide is formed during the dissolution of gold or silver, and for every two equivalents of metal dissolved, one mole H_2O_2 was produced (Table 3).

4. Experiments carried out by Boonstra and by Lund showed that the dissolution of gold and silver respectively in $KCN + H_2O_2$ in the absence of oxygen was a slow process. Thus the reaction:

   $$H_2O_2 + 2\ Au + KCN \longrightarrow 2\ KAu(CN)_2 + 2\ KOH$$

   i.e., the reduction step

   $$H_2O_2 + 2\ e^- \longrightarrow 2\ OH^-$$

   takes place to a minor extent only.

The dissolution reaction is a corrosion process in which oxygen takes up electrons at one part of the metallic surface (the cathodic zone), while the metal gives them up at another

(the anodic zone), as shown in Figure 16 (Habashi, 1965, 1966). Two simultaneous reactions are taking place: the oxidation reaction involving the formation of the auro- or argento-cyanide complexes, e.g.:

$$Au \longrightarrow Au^+ + e^-$$

$$Au^+ + 2\ CN^- \longrightarrow Au(CN)_2^-$$

and the second involving oxygen reduction on the metallic surface:

$$O_2 + 2\ H_2O + 2\ e^- \longrightarrow H_2O_2 + 2\ OH^-$$

According to Fick's law:

$$\frac{d(O_2)}{dt} \doteq \frac{D_{O_2}}{\delta} A_1\{[O_2] - [O_2]_i\}$$

$$\frac{d(CN^-)}{dt} = \frac{D_{CN^-}}{\delta} A_2\ \{[CN^-] - [CN^-]_i\}$$

where respectively

$\frac{d(CN^-)}{dt}$ and $\frac{d(O_2)}{dt}$ = the rates of diffusion of CN^- ion and O_2, in moles/sec.

D_{CN^-} and D_{O_2} = the diffusion coefficients of cyanide and dissolved oxygen, $cm^2\ sec^{-1}$.

$[CN^-]$ and $[O_2]$ = the concentration of CN^- and O_2 in the bulk of the solution in moles/ml.

$[CN^-]_i$ and $[O_2]_i$ = the concentration of CN^- and O_2 at the interface in moles/ml.

A_1 and A_2 = the surface area at which the cathodic and anodic reactions take place, in cm^2.

δ = the thickness of the boundary layer, in cm.

If we assume that the chemical reactions at the metal interface are very rapid as compared with the rates at which the cyanide ion and O_2 diffuse through stagnant layer, then these will be consumed as soon as they reach the surface of the metal, i.e.,

$$[O_2]_i = 0 \text{ and } [CN^-]_i = 0$$

Therefore,

$$\frac{d(O_2)}{dt} = \frac{D_{O_2}}{\delta} A_1 \; [O_2]$$

$$\frac{d(CN^-)}{dt} = \frac{D_{CN^-}}{\delta} A_2 \; [CN^-]$$

Inasmuch as the rate of metal dissolution is twice the rate of oxygen consumption and one-half the rate of cyanide consumption, therefore

$$\text{rate of dissolution} = 2 \frac{d(O_2)}{dt} = 2 \frac{D_{O_2}}{\delta} A_1 \; [O_2]$$

$$= \tfrac{1}{2} \frac{d(CN^-)}{dt} = \tfrac{1}{2} \frac{D_{CN^-}}{\delta} A_2 \; [CN^-]$$

It follows that at the steady state

$$2 \frac{D_{O_2}}{\delta} A_1 \; [O_2] = \tfrac{1}{2} \frac{D_{CN^-}}{\delta} A_2 \; [CN^-]$$

or

$$\frac{A_1}{A_2} = \tfrac{1}{4} \cdot \frac{D_{CN^-}}{D_{O_2}} \cdot \frac{[CN^-]}{[O_2]}$$

If A is the total surface area of the metal plate* in contact with the solution, then

$$A = A_1 + A_2$$

Therefore,

$$\text{Rate} = \frac{2 \; A \; D_{CN^-} \; D_{O_2} [CN^-][O_2]}{\delta \{ D_{CN^-} [CN^-] + 4 \; D_{O_2} [O_2] \}}$$

From this equation it follows that at low cyanide concentration, the first term in the denominator may be neglected in comparison with the second, so that the equation simplifies to:

$$\text{Rate} = \tfrac{1}{2} \frac{A \; D_{CN^-}}{\delta} [CN^-]$$

$$= k_1 \; [CN^-]$$

This coincides with the experimental fact (Fig. 9) that at low cyanide concentration the rate of dissolution depends only on the cyanide concentration.

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*The simple case of a flat plate was considered, although spheres, pellets, or other geometry can also be considered, after correcting for the change in area during dissolution.

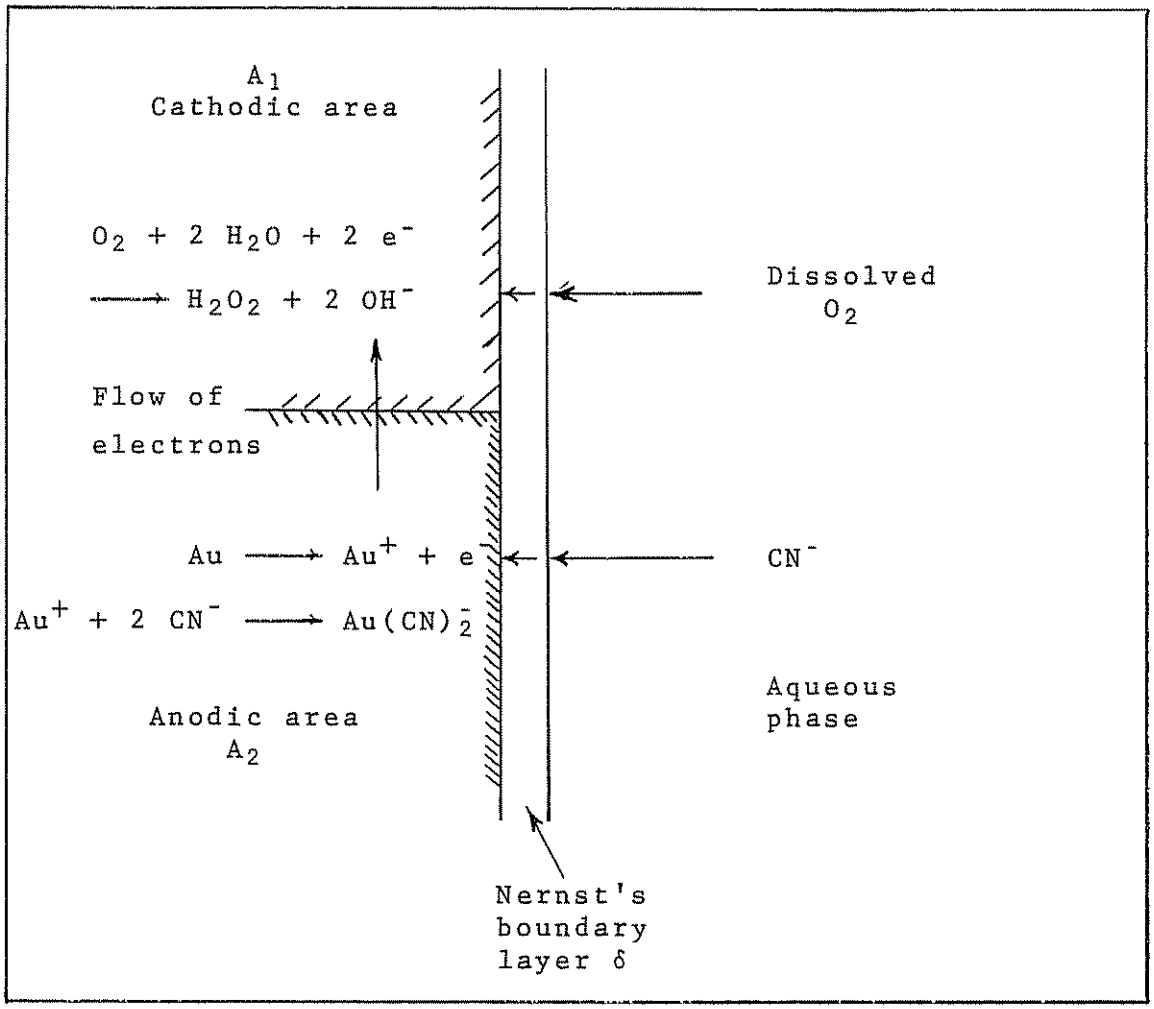

Figure 16.--Schematic representation of dissolution of gold in cyanide solution (Habashi, 1966).

In the same manner, it follows also from the same equation that at high cyanide concentration, the second term in the denominator may be neglected in comparison with the first, and the equation simplifies to:

$$\text{Rate} = 2 \frac{A\ D_{O_2}}{\delta} [O_2]$$

$$= k_2\ [O_2]$$

This coincides also with the experimental fact (Fig. 9) that at high cyanide concentration, the rate of dissolution depends only on the oxygen concentration.

It can also be deduced from the same equation that when

$$D_{CN^-}\ [CN^-] = 4\ D_{O_2} [O_2]$$

then

$$\text{Rate} = \frac{\sqrt{D_{O_2}\ D_{CN^-}}}{2\ \delta} A\ [O_2]^{\frac{1}{2}}\ [CN^-]^{\frac{1}{2}}$$

This means that at these concentrations of cyanide and oxygen, the rate of dissolution changes its dependence from one to the other, which corresponds to the breaks shown in Figure 9.

It is therefore evident that the condition governing the dependence of rate of dissolution on either cyanide or oxygen concentration is given by:

$$D_{CN^-} [CN^-] = 4 D_{O_2} [O_2]$$

This equation can be transformed into the form:

$$\frac{[CN^-]}{[O_2]} = 4 \frac{D_{O_2}}{D_{CN^-}}$$

As shown in Table 12, the average ratio $D_{O_2}/D_{CN^-} = 1.5$, therefore

$$\frac{[CN^-]}{[O_2]} = 6$$

Table 12.--Estimated values of diffusion coefficients.

Temp., °C	KCN %	D_{KCN} sq. cm/sec	D_{O_2} sq. cm/sec	$\frac{D_{O_2}}{D_{KCN}}$	Investigator
18	----	1.72×10^{-5}	2.54×10^{-5}	1.48	White (1934)
25	0.03	2.01	3.54	1.76	Kameda (1949)
27	0.0175	1.75	2.20	1.26	Kudryk and Kellogg (1954)
Average		1.83×10^{-5}	2.76×10^{-5}	1.5	

Actually the experimental values given in Table 8 range from 4.6 to 7.4, which should be regarded as good agreement. Further, at room temperature and at atmospheric pressure, 8.2 mg O_2 is dissolved in 1 liter of water. This corresponds to 0.27×10^{-3} moles/liter. Therefore, maximum rate of dissolution should occur at KCN concentration equals $6 \times 0.27 \times 10^{-3}$ moles/liter or 0.01 percent solution. This is again very near to the last two experimental values given in Table 5.

The value of δ can be calculated directly from the equation after substituting the values of diffusion coefficients from Table 12:

$$\delta = \frac{10.1 \times 10^{-5} [CN^-][O_2]}{v \{1.83[CN^-] + 11.04[O_2]\}} \text{ cm}$$

where v is the rate expressed in gram equivalent cm^{-2} sec^{-1} and the concentrations in brackets are expressed in gram moles/ml.

Table 13 gives values of δ calculated from experimental data of various investigators. It can be seen from Table 13 that δ ranges between 2×10^{-3} and 9×10^{-3} cm, which is a typical thickness for a boundary layer in a diffusion-controlled process.

There is more than one reason to believe that the dissolution of gold at speeds of agitation exceeding 150 rpm behaves according to a different mechanism. The following can be mentioned:

1. Rate decreases, then becomes constant.
2. Rate is proportional to $P_{O_2}^{\frac{1}{2}}$ (and not P_{O_2}).
3. Activation energy 14.1 Kcal, which is typical of chemically controlled reactions.
4. The limiting concentration of KCN is increased.

Data are insufficient to permit discussion in detail.

From the technical point of view the above results can be stated in the following way: Neither the concentration of dissolved oxygen alone (i.e., degree of aeration of the solution) nor the concentration of free cyanide alone are important in actual practice; it is the ratio of the two concentrations. Therefore, if much effort is spent to achieve ideal aeration while the solution is deficient in free cyanide, then this effort is wasted and the rate of cyanidation will not achieve its maximum. And vice versa: If excess cyanide is added while the oxygen content of the solution is below the theoretical value, then this excess cyanide is wasted. It is therefore recommended to analyze for and control both free cyanide and dissolved oxygen contents of the solutions so that their molar ratio equals 6. The pH of the solution should also be kept within a very narrow range, as excessive alkalinity (pH >13) is detrimental.

Table 13.--Thickness of boundary layer calculated according to equation.

Metal	Rate of dissolution: mg / $cm^2 hr$	Rate of dissolution: equiv. / $cm^2 sec$	$[CN^-]$ %	$[CN^-]$ mole/ml	p_{O_2} atm	$[O_2]$ mole/ml	Speed of stirring, rpm	δ cm	Method of stirring	Ref.*
Gold	3.0	4.22×10^{-9}	0.25 NaCN	51.0×10^{-6}	0.21	0.27×10^{-6}	air bubbling	3.4×10^{-3}	stationary plate	1
	2 x 1.75	4.94	0.03 KCN	4.6	0.21	0.27	air bubbling	2.2	stationary plate	2
	1.0	1.40	0.10 KCN	15.4	0.21	0.27	100	9.7	rotating cylinder	3
	-----	8.00	-----	8.0	1.00	1.28	150	4.5	rotating disc	4
Silver	1.5	3.87	0.25 NaCN	51.0	0.21	0.27	air bubbling	3.7	stationary plate	1
	5.0	12.80	-----	10.0	3.40	4.35	895	5.1	stationary disc, solution agitated by mechanical stirrer	5
	-----	26.00	-----	15.0	1.00	1.28	1,100	1.8	rotating disc	6

*1. Barsky and others, 1934.
2. Kameda, 1949.
3. Kudryk and Kellogg, 1954.
4. Kakovskii and Kholmanskikh, 1960.
5. Deitz and Halpern, 1953.
6. Kakovskii and Kholmanskikh, 1959.

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