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Figure 1

Figure 1: Figure 1

Abstract

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ON THE INFLUENCE OF SURFACE-ACTIVE SUBSTANCES ON THE RATE OF DISSOLUTION OF GOLD IN CYANIDE SOLUTIONS

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In studying the kinetics of the dissolution of gold in aqueous alkaline solutions of acetone cyanohydrin, it was found that gold dissolves in them much more rapidly than in aqueous potassium cyanide solutions. As is known, cyanohydrins decompose in alkaline media with the formation of cyanide ions and ketones. It was therefore suggested that the observed increase in the rate of dissolution of gold may be explained by the presence of surface-active substances in the solution (in this case, the simplest ketone–acetone). In view of the importance of the noted phenomenon for the metallurgy of noble metals, a study was carried out of the influence of surface-active substances on the rate of the process of cyanidation of gold. The choice of gold as the dissolving metal is determined by the fact that, according to our investigations (1), the process of its dissolution in cyanide solutions, with increasing intensity of stirring, passes from the diffusion region into the kinetic region (2), and the influence of additions can accelerate the process only in the presence of kinetic complications.

Fig. 1. Dependence of the values of the rate constants of the Au dissolution reaction on the dosage of surface-active substances.
1—acetone, 2—*n*-butyl alcohol, 3—diisopropyl ether, 4—*n*-octyl alcohol.

The apparatus and method of carrying out the experiments were conventional (see (2, 3)). Conditions of the first series of experiments: oxygen pressure above the solution 1 atm, temperature 298°K, alkali concentration 4.0—$2.5 \cdot 10^{-2}$ mol/l, potassium cyanide 2.6—$3.0 \cdot 10^{-3}$ mol/l, disk rotation rate 8.6 rev/sec. The following surface-active additives were tested: acetone, *n*-butyl and *n*-octyl alcohols, diisopropyl alcohol, diisopropyl ether (Fig. 1).

With an increase in the concentration of acetone in the cyanide solution, the rate constant of the reaction increases sharply, reaching a maximum at a con-

centration equal to $4.5 \cdot 10^{-3}$ mol/l, and then again decreases approximately to the initial value, thereafter remaining almost independent of the concentration of acetone (Fig. 1, 1). Approximately the same in character, but somewhat weaker quantitatively, is the effect exerted by butyl alcohol (Fig. 1, 2): the maximum rate is attained when its concentration is equal–

of $1.1 \cdot 10^{-2}$ mol/l, but an excess of alcohol causes a smoother and slower decrease in the rate of dissolution of Au. It should be noted that the favorable action of the alcohol is especially clearly noticeable at higher alkalinity of the pulp. Diisopropyl ether (Fig. 1, 3) acts analogously to the preceding reagents. Curve 4 reflects the influence of additions of octyl alcohol–the latter greatly retards the process of gold dissolution. Consequently, with increasing surface activity of the reagent, its concentration at which the maximum dissolution rate is observed decreases, but the passivating influence of an excess of reagent also increases; and for the most surface-active reagents (octyl alcohol), even at small additions only their negative action is observed.

For acetone, butyl alcohol, and diisopropyl ether, the absolute value of the maximum reaction-rate constant ranges within $1.49—1.56 \cdot 10^{-6}$ $\mathrm{l \cdot cm^{-2} \cdot sec^{-1}}$ and does not depend on the magnitude of the surface activity of the reagents used. The maximum value of the rate constant is 3.6 times higher than in the dissolution of Au in cyanide solutions without additions of surface-active substances ($0.43 \cdot 10^{-6}$ $\mathrm{l \cdot cm^{-2} \cdot sec^{-1}}$), which is in good agreement with the data of our earlier investigations–$0.5—0.6 \cdot 10^{-6}$ at 298 K (see ([2])).

To explain the reasons for the increase in the rate of gold dissolution upon addition of organic surface-active substances, two hypothetical mechanisms may be proposed: a physical (adsorption) mechanism and a chemical (reduction) mechanism.

Let us first consider the arguments in favor of the adsorption mechanism. Alcohols, ketones, and simple ethers possess pronounced surface activity, and during dissolution of Au in cyanide solutions a clearly expressed passivation of its surface by oxygen is observed ([2],[4],[5]), with the dissolution rate being the lower, the more strongly the Au surface is passivated. Therefore it may be assumed that, when surface-active substances are introduced into the solution, the latter, being adsorbed on the Au surface, will displace oxygen. A similar depassivation mechanism was proposed by A. N. Frumkin (([6]), $p.274$). The activating action of organic reagents is possible only at a definite ratio of the concentrations of these reagents and oxygen, which can be clearly illustrated by the maxima on the curves in Fig. 1. The optimal ratio of the concentrations of the depassivator and the passivator (oxygen) is: for acetone 3.5, for butyl alcohol 8.6, and for diisopropyl ether 18. Thus, acetone is the most active. If these ratios are higher than the optimum ones, apparently excessive adsorption of organic reagents on the metal surface already takes place, and its passivation is then caused not by oxygen but by adsorbed organic molecules. Thus, by changing the concentration of reagents in the solution, one can change the degree of passivation of the metal surface and its character (predominant adsorption of oxygen or of the

Figure 2. Effect of the intensity of stirring of the solution on the action of surface-active substances. 1 —at 18.1 rev/s, 2 —8.6 rev/s

Figure 2: Figure 2. Effect of the intensity of stirring of the solution on the action of surface-active substances. 1 —at 18.1 rev/s, 2 —8.6 rev/s

Figure 3. Effect of temperature on the depassivating action of butyl alcohol. 1 —288°, 2 —298°, 3 —313° K

Figure 3: Figure 3. Effect of temperature on the depassivating action of butyl alcohol. 1 —288°, 2 —298°, 3 —313° K

depassivator).

Let us now consider the second possible depassivation mechanism—when molecules of adsorbable alcohol or acetone enter into oxidation-reduction interaction with the passivated surface of gold, reduce it, and themselves are oxidized in the process. In our opinion, this mechanism is less probable. To clarify this question, experiments were carried out on the dissolution of Ag in cyanide solutions (diffusion regime) in the presence of acetone; in these experiments the same values of the limiting cyanide concentrations were found as in experiments without acetone additions. The limiting cyanide concentrations are determined ([3]) by the concentration of oxygen in the solution, i.e., of the oxidizing agent. Since the addition of acetone to the solution did not change the value of the limiting cyanide concentration, it may be concluded that the oxygen concentration in the solution also did not change, i.e., the latter is not consumed in the oxidation of acetone, and the stoichiometric coefficients of the pro-

of the reaction taking place ((7), p. 170). This is also true for dissolution in cyanide solutions in the presence of acetone. In addition, experiments with additions of diisopropyl ether showed that it has a noticeable depassivating effect, although it is a considerably weaker reducing agent than acetone. Still more convincing is the comparison of the depassivating action of butyl and octyl alcohols (Fig. 1), whose reducing properties do not depend on the length of their hydrocarbon chain.

Fig. 2. Effect of the intensity of stirring of the solution on the action of surface-active substances. **1** —at 18.1 rev/s, **2** —8.6 rev/s

Fig. 3. Effect of temperature on the depassivating action of butyl alcohol. **1** —288°, **2** —298°, **3** —313° K

According to our experiments, octyl alcohol does not possess depassivating properties and, even in small additions, passivates the metal; this can be explained only by the greater adsorption and surface activity of octyl alcohol in comparison with butyl alcohol (8).

It is of interest to clarify certain details of the depassivating action of surface-

active substances: whether they completely eliminate the passivating action of oxygen and whether they return the process of gold dissolution in cyanide solutions to the diffusion region, from which it had been removed by oxygen as a result of intensive stirring of the solution. For this it was necessary to check the dependence of the dissolution rate on the intensity of stirring, since the processes of dissolution of Au in cyanide solutions in the diffusion and kinetic regions can be most clearly distinguished by the effect of stirring intensity on the dissolution rate (2). For this purpose, additional experiments with butyl alcohol were carried out at other disk rotation rates (Fig. 2).

In this case the conditions of passivation and depassivation change substantially with an increase in the intensity of stirring of the solution, the consequence of which is a shift of the maximum of the curve to the right along the abscissa axis and a decrease in the maximum rate constant of the reaction; this is apparently due to the stronger passivating action of oxygen at elevated stirring intensity. At a disk rotation rate of 18.1 rev/s, the maximum rate constant of the reaction is $1.05 \cdot 10^{-6}$ $\mathrm{l} \cdot \mathrm{cm}^{-2} \cdot \mathrm{s}^{-1}$, and the corresponding concentration of butyl alcohol is $2.0 \cdot 10^{-2}$ mol/l, whereas at 8.6 rev/s these values are, respectively, $1.56 \cdot 10^{-6}$ and $1.1 \cdot 10^{-2}$. Consequently, organic additives do not completely remove the passivating action of oxygen and do not return the process to the diffusion region: with more intensive stirring, the depassivating action of organic reagents is manifested more weakly.

To further refine the mechanism of the depassivating action of organic reagents, the influence of temperature was studied. The experiments were

were carried out with additions of *n*-butyl alcohol, at 18.1 rev/sec and temperatures of 288, 298, and 318°K (Fig. 3).

From these data Arrhenius plots were constructed for the following concentrations of butyl alcohol: $C = 0$—in the absence of a depassivator, $C = 1 \cdot 10^{-2}$ mol/liter—in the region close to the maximum values of the reaction-rate constants, and $C = 6 \cdot 10^{-2}$ mol/liter, when, as a result of additions of alcohol, the rate constants become minimal but approximately constant. Accordingly, for these concentrations the following equations were calculated: $\lg k = 5.017 - 3390/T$; $\lg k = 3.385 - 2840/T$; $\lg k = 7.203 - 4100/T$, and the experimental activation energies are 15.5, 13.0, and 18.8 kcal/mol, which agree well with those obtained earlier (12). With an increase in the concentration of the depassivator, the activation energy first decreases to 13.0 kcal/mol, and then rises sharply—to 18.8 kcal/mol. However, the depassivator does not change the character of the process: even under optimal conditions it proceeds in the kinetic region, and the decrease in activation energy, compared with dissolution without organic additives, amounts to only 2.5 kcal/mol. It is interesting to note that the positive effect of the depassivator is more pronounced at low temperatures: at 288°K the reaction-rate constant increases by a factor of 1.8, whereas at 318° it increases only by a factor of 1.25. In addition, the increase in dissolution rate also depends on the intensity of stirring (see Fig. 2): at 8.6 rev/sec the increase in rate is 3.6-fold, while at 18.1 rev/sec it is 2.4-fold.

Consequently, increasing the intensity of stirring and the temperature weakens the action of depassivating additives.

The phenomena found can be explained on the basis of the following assumptions: both oxygen molecules and molecules of the organic reagent can be adsorbed on the surface of the dissolving metal. Oxygen is adsorbed rapidly but reacts slowly with the metal and, being in excess, passivates it by changing the character of the bonds with the metal (9), while organic additives, being adsorbed, displace part of the oxygen, but in excess they strongly block the surface of the metal and hinder its depolarization by oxygen. The adsorption character of the action of organic reagents is confirmed by the comparatively small magnitude of the change in activation energies and by the dependence of the change in dissolution rate on temperature and stirring intensity, since the rate of attainment of adsorption equilibrium depends on these variables. To ensure the maximum dissolution rate, an optimal ratio of oxygen and organic depassivator in the solution is necessary.

In conclusion, it should be noted, first, that what has been set forth in the article may be of interest for other cases of dissolution of metals with oxygen depolarization in the kinetic regime and, second, that such a complex process could be studied only by applying the rotating-disk method with an equally accessible surface.

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Note: Figure translations are in progress. See original paper for figures.