Soviet-era science, translated into English

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1960

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Abstract

Full Text

PHYSICAL CHEMISTRY

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THE CATALYTIC ACTION OF COPPER IONS IN THE DISSOLUTION OF METALS WITH OXYGEN DEPOLARIZATION

(Presented by Academician P. A. Rebinder, 11 X 1959)

Many cases have been described in the literature ($^{1,\ 2,\ 3-7}$) of an increase in the rate of redox processes in the presence of ions possessing variable valence. Many authors are inclined to see the cause of this in the catalytic nature of the action of such ions, but their influence on the rate of dissolution of metals has been studied less fully.

In the dissolution of noble metals, the decisive stage of the process is their depolarization (^{8}), i.e., the removal of electrons from the surface of the metals, since the complex-formation process itself proceeds sufficiently rapidly and without kinetic complications (for example, $\mathrm{AgCl} + 2\mathrm{CN}' = \mathrm{Ag(CN)}_2' + \mathrm{Cl}'$). The action of an oxygen oxidant, which accepts electrons in several stages, is usually accompanied by appreciable kinetic complications (^{1}), but copper ions, changing their valence by accepting or donating one electron, and also promoting the formation of free radicals (^{2,5}), can greatly facilitate the depolarization process. This phenomenon may have practical significance for accelerating the dissolution of metals from ores and industrial products. In order to study in more detail the catalytic action of copper ions, the process of dissolution of silver in ammonia solutions was investigated.

The thermodynamic probability of the reaction was calculated:

$$2\mathrm{Ag} + {}^1/{}_2\mathrm{O}_2\ (\mathrm{g}) + \mathrm{H}_2\mathrm{O} + 4\mathrm{NH}_3\ (\mathrm{soln.}) = 2\mathrm{Ag(NH}_3)_2^+ + 2\mathrm{OH}', \qquad (1)$$

$$\Delta G^0 = 2(-4.13) + 2(-37.60) - (-56.70) - 4(-6.36) = -1.32\ \mathrm{kcal.}$$

The decrease in free energy under standard conditions is comparatively small, but for real conditions (the concentrations of the silver complex and hydroxyl ion are 10^{-3}, ammonia is 2.5 mol/l) the situation will be more favorable:

$$\Delta G = \Delta G^0 + RT \ln \frac{[\mathrm{Ag(NH}_3)_2^+][\mathrm{OH}']^2}{[\mathrm{NH}_3]^4 P_0^{1/2}} = -1.32 + 1.3643 \lg \frac{(10^{-3})^2 (10^{-3})^2}{(2.5)^4\, 1^{1/2}} =$$

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Fig. 1. Kinetic curves of the dissolution of silver in ammonia solution with various additives: 1 –NH_3 3.36 g-mol/l; 2 –the same + $(NH_4)_2SO_4$ 0.11 g-mol/l; 3 –the same, Cu^{++} 0.11 g-ion/l; 4 –the same + $(NH_4)_2SO_4$ 0.11 g-mol/l, Cu^{++} 0.01 g-ion/l

Figure 1: Fig. 1. Kinetic curves of the dissolution of silver in ammonia solution with various additives: 1 –NH_3 3.36 g-mol/l; 2 –the same + $(NH_4)_2SO_4$ 0.11 g-mol/l; 3 –the same, Cu^{++} 0.11 g-ion/l; 4 –the same + $(NH_4)_2SO_4$ 0.11 g-mol/l, Cu^{++} 0.01 g-ion/l

$$= -1.32 + 1.3643 \lg 2.5 \cdot 10^{-14} = -1.32 - 18.54 = -19.86 \text{ kcal.}$$

According to this calculation, silver should dissolve readily in ammonia solutions in the presence of oxygen; however, the possibility is not excluded that kinetic complications may reduce the rate of this process.

To clarify this question, experiments were carried out on the dissolution of silver in pure ammonia solution and with various additives. The experiments were conducted in an autoclave with a magnetic stirrer ([9]), using the rotating-disk method ([10]). The ammonia concentration was the same in all experiments and was 3.3 mol/l, the temperature 67°, the total pressure 2 atm (oxygen partial pressure about 1.5 atm), the surface area of the silver disk 2 cm^2, and the number of revolutions was 2800 per minute. The influence of the following additives on the

dissolution rate: ammonium sulfate, 0.11 g-mol/l (experiments 2 and 4), copper ions*–0.01 g-ion/l (experiments 3 and 4); experiment 1–with ammonia alone.

The dissolution-rate curves are given in Fig. 1. The linear character of these curves makes it possible to calculate the specific rates (v) of dissolution of silver in solutions of different composition. In a solution containing only ammonia (experiment 1), $v = 4.3 \cdot 10^{-9}$ g-mol $\cdot$ cm^{-2} $\cdot$ sec^{-1}; in a solution containing ammonia and ammonium sulfate (experiment 2), $1.7 \cdot 10^{-8}$; in a solution containing ammonia and the copper-ammonia complex (experiment 3), $5.4 \cdot 10^{-8}$, and in the presence in the solution of NH_3, the copper complex, and $(NH_4)_2SO_4$ (experiment 4), $7.2 \cdot 10^{-8}$ g-at $\cdot$ cm^{-2} $\cdot$ sec^{-1}.

To study the dependence of the rate of dissolution of silver on the ammonia concentration, experiments were carried out under the following conditions: temperature 70°, oxygen pressure 3 atm, copper-ion concentration 0.01 g-ion/l, ammonia concentration from 0.09 to 3.3 g-mol/l. The results of the experiments are presented in Fig. 2. From the data obtained it follows that the dissolution rate increases proportionally to the first power of the ammonia concentration in the solution.

Fig. 1. Kinetic curves of the dissolution of silver in ammonia solution with various additives:

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Fig. 2. Dependence of the rate of dissolution of silver on the ammonia concentration

Figure 2: Fig. 2. Dependence of the rate of dissolution of silver on the ammonia concentration

1 –NH_3 3.36 g-mol/l; **2** –the same + $(NH_4)_2SO_4$ 0.11 g-mol/l; **3** –the same, Cu^{++} 0.11 g-ion/l; **4** –the same + $(NH_4)_2SO_4$ 0.11 g-mol/l, Cu^{++} 0.01 g-ion/l

Fig. 2. Dependence of the rate of dissolution of silver on the ammonia concentration

To determine the effect of the concentration of the copper–ammonia complex, a third series of experiments was carried out: temperature 70°, oxygen pressure 3 atm, ammonia concentration 2.3 g-mol/l, copper concentration variable. The results of this series of experiments are presented in Fig. 3.

Discussion of the results

As was assumed, the reaction under study is complicated by the slowly proceeding process of depolarization—the rate of dissolution of silver in pure ammonia solutions is very small. The addition of ammonium sulfate noticeably increases the dissolution rate, but its effect is considerably weaker than that of the copper-ammonia complex. The addition of ammonium sulfate to a solution containing copper ions and ammonia increases the rate of dissolution of silver by approximately the same amount ($7.2 \cdot 10^{-8} - 5.4 \cdot 10^{-8} = 1.8 \cdot 10^{-8}$) as in the absence of copper ($1.7 \cdot 10^{-8} - 0.4 \cdot 10^{-8} = 1.3 \cdot 10^{-8}$). The action of ammonium sulfate apparently is not catalytic (it may be considered as a buffer with respect to strong alkalis, the hydroxyl ion, which retards the reduction of oxygen), whereas the copper ammine complex can readily accept one electron and facilitate the depolarization of the dissolving noble metal. In ammoniacal solutions copper changes its valence more readily than in sulfate solutions (1), and the reaction product—the ion $Cu(NH_3)_2^+$—is stable and can accumulate in solution in appreciable quantity, whereas the ion Cu^+ disproportionates ($2Cu^+ = Cu^{++} + Cu;\ K_0 = 7 \cdot 10^5$). For the reaction *

$$Cu(NH_3)_4^{++} + e = Cu(NH_3)_2^+ + 2NH_{3\,(\mathrm{p-p})} \tag{2}$$

$$\Delta G^0 = -15.52 + 2(-6.36) - (-29.11) = +0.87\ \text{kcal}; \quad K_0 = 0.23; \quad E_0 = +0.038\ \text{V}.$$

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* Copper was added to the solution in the form of hydroxide (II), so as not to introduce the sulfate ion, which also somewhat accelerates the dissolution of silver in ammonia solutions.

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Fig. 3. Dependence of the rate of dissolution of silver on the concentration of copper

Figure 3: Fig. 3. Dependence of the rate of dissolution of silver on the concentration of copper

The standard free energy of this process is close to zero, but if the concentration of the ammine complex of monovalent copper in solution is small (owing to oxidation by oxygen), then the divalent copper complex will readily accept electrons, be reduced, and then transfer the electrons obtained to oxygen (this process is especially facilitated by the one-electron character of both reactions). The thermodynamic probability of the latter reaction may be illustrated by the following calculation:

Fig. 3. Dependence of the rate of dissolution of silver on the concentration of copper

$$2\mathrm{Cu(NH_3)_2^+} + \tfrac{1}{2}\mathrm{O_{2(g)}} + \mathrm{H_2O} + 4\mathrm{NH_{3(p-p)}} =$$

$$= 2\mathrm{Cu(NH_3)_4^{++}} + 2\mathrm{OH'}, \tag{3}$$

$$\Delta G^0 = 2(-29.11) + 2(-37.60) - 2(-15.52) - (-56.70) = -20.24\ \text{kcal}.$$

The calculation presented and the experiments performed confirm that the ammine complex of monovalent copper is readily, and without kinetic complications (which are often observed in reactions between dissolved substances), oxidized by oxygen entering the solution from the gas phase. The absence of kinetic complications in the transfer of electrons from the metal to oxygen by copper ammine complexes is confirmed by the following simple experiment: if metallic copper is added to a solution containing the ammine complex of divalent copper and the flask is closed with a stopper, rapid decolorization occurs (reduction of copper to the monovalent state); when the flask is opened, the solution again turns blue (oxidation by atmospheric oxygen).

As a result of the intense course of reaction (3), the concentration of the ammine complex of monovalent copper in solution is greatly decreased, and the ammine complex of divalent copper can readily exhibit the properties of a depolarizer —accept electrons from the surface of silver and transfer them to oxygen, i.e., act as a catalyst for the process of dissolution of silver in ammoniacal solutions, accelerating this process. The calculation of the reduction potential of copper in ammoniacal solution (reaction 2) that we have given, and the value of the standard potential of silver in ammoniacal solution (+0.372 V), make it possible to conclude that, for successful transfer of electrons from the surface of silver to the ions $Cu(NH_3)_4^{++}$, a low concentration in the solution of the ammine complexes of silver and monovalent copper is necessary. In the presence of oxygen the concentration of the ion $Cu(NH_3)_2^{+}$ is very small and the poten-

[*] The free energies of formation of the substances participating in the reactions were calculated by us using the most recent data, since the values given in handbooks are often incorrect ([12]). Thus, for example, the value $\Delta G^0 = -40.8$ kcal for $Cu(NH_3)_4^{++}$, given in Latimer' s handbook ([13]), is erroneous.

the potential of reaction (2) will satisfy the requirements imposed on catalyst potentials—to lie between the potentials of the reacting substances: silver and oxygen ([6]).

The somewhat simplified representation given by us of the catalytic action of copper ions in an ammoniacal solution is in good agreement with the increase in the rate of dissolution of silver caused by them.

The data given in Fig. 2 indicate that the dissolution of silver in ammoniacal solutions is a first-order reaction with respect to ammonia, whose rate constant $\left(k = \frac{Q}{sct}\right)$, in the presence of the catalyst—copper ions—reaches a value of $2.1\text{-}2.4 \cdot 10^{-8}\ \mathrm{l}^{-1} \cdot \mathrm{cm}^{-2} \cdot \mathrm{sec}^{-1}$. This is approximately 2-3 orders of magnitude lower than the values of the rate constants of heterogeneous reactions of metal dissolution controlled by the rate of diffusion.

Of particular interest are the experiments whose results are given in Fig. 3. For certain experimental conditions (solution composition, temperature, oxygen pressure) there is a certain "limiting" concentration of the copper-ammonia complex, above which the rate of dissolution of silver remains practically constant. This limiting concentration is associated with the rate of diffusion of the reacting components to the surface of the silver and is characteristic of multicomponent heterogeneous reactions (for example, reactions of dissolution of noble metals in cyanide solutions in the presence of oxygen). The existence of a limiting concentration of the copper-ammonia complex is convincing evidence that it participates in the reaction of dissolution of silver in ammoniacal solutions, transferring electrons from the metal to oxygen, increasing the rate of the process, reducing the harmful effect of kinetic complications, i.e., acting as a catalyst.

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Received
10 IX 1959

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