

A Kinetic Study by Measurements of Steady-State Potentials of Platinum in Persulphate Solutions Containing Ammonium and Silver Salts

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The oxidation of ammonium ions by silver(II), which is presupposed to be a partial process of the silver(I) catalyzed self-decomposition of ammonium persulphate in acid solution, is investigated by measurements of the steady-state potential of a platinum electrode. From the dependence of the potential upon the concentrations of different ions taking part in the reactions, the kinetic laws of the oxidations of ammonium ions and water are determined. A mechanism of the oxidation of ammonium ions is proposed and is proved to be in accord with the laws obtained.

By measurements of the impedance of the electrode-solution interface it is shown that redox couples formed in the last-mentioned oxidation take part in the electron exchange between the electrode and the solution.

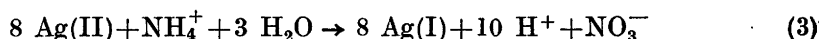
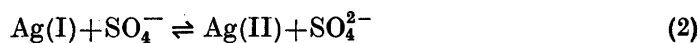
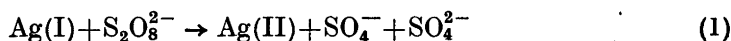
The principal features of the mechanism of the silver(I) catalyzed self-decomposition of ammonium persulphate in aqueous solution were clarified in a previous investigation (Fronæus and Östman¹), dealing with the silver(I) catalyzed reaction between cerium(III) and ammonium persulphate. A partial process of the mechanism proposed is the reaction between silver(II), formed as an intermediate, and the ammonium ions. Since this reaction is not rate-determining for the over-all reactions studied, the kinetic law for the partial process mentioned could not be obtained from the measurements performed. Actually, no experimental determination of this rate law has been reported but only assumptions (*cf.* Carman²), that have not been tested quantitatively.

The purpose of the present investigation is a further elucidation of this problem by determinations of the concentration ratio between silver(II) and silver(I) by emf measurements with a platinum electrode. Since the solutions to be studied contain several redox couples which are not exactly in equilibrium, the steady-state electrode potential is theoretically a so-called mixed potential (for previous literature about this conception, the reader is referred

to papers by Wagner and Traud³, and Kolthoff and Miller⁴), and this fact should be borne in mind when treating the emf values obtained. In order to determine whether several couples are actually involved in the adjustment of the electrode potential, measurements of the impedance of the electrode-solution interface have been chosen.

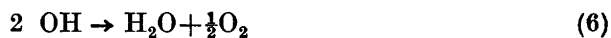
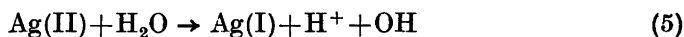
THEORETICAL

According to the mechanism for the silver(I) catalyzed decomposition of ammonium persulphate in acid solution, arrived at in the previous paper¹, we have the following set of homogeneous reactions as the predominating ones



where (1) is the rate-determining step and reaction (3) certainly involves several steps. The set of reactions has been extended somewhat, in that we take the backward process of (2) into consideration.

Furthermore, we have the oxidation of water, that should be of importance at low ammonium ion concentrations



Here (5) and (6) are not simple steps^{5,6}.

In preliminary measurements it was established that the presence of platinum surfaces has no effect on the rate of persulphate decomposition. Evidently the persulphate ions take no appreciable part in the electron exchange with the electrode, and the oxidizing agents formed as intermediates in the reactions above must be responsible for the high steady-state electrode potential obtained. Thus we regard the electrode reactions



and represent by



the further reactions that may be involved in the adjustment of the potential. The anodic current densities of (7), (8), and (9) are denoted i_1 , i_2 , and i_3 . Thus i_3 is the sum of anodic currents due to the oxygen-water couple and couples formed in the oxidation of the ammonium ion.

When a steady-state electrode potential has been attained the following relationship is valid

$$i_1 + i_2 + i_3 = 0 \quad (10)$$

Furthermore, denoting by r_1 , r_2 , r_3 and r_4 the rates of the reactions (1)–(4), and applying the steady-state approximation to Ag(II) and SO_4^- in the bulk of the solution by putting $d[\text{Ag(II)}]/dt = 0$ and $d[\text{SO}_4^-]/dt = 0$ ($t = \text{time}$), we get the equations

$$r_1 + r_2 \xrightarrow{\leftarrow} r_2 \xrightarrow{\leftarrow} r_3 - r_5 = 0 \quad (11)$$

$$r_1 - r_2 + r_2 - r_4 = 0 \quad (12)$$

If r_1 is not equal to r_4 the redox potential e_1 of the silver couple will be different from the redox potential e_2 of the $\text{SO}_4^- - \text{SO}_4^{2-}$ couple. However, since the reaction (1) is the rate-determining step we can presume that r_1 and r_4 ($< 2 r_1$) are very small in comparison with r_2 and r_3 , so that $r_2 \approx r_3$ and hence $e_1 \approx e_2$. If we further presume that the absolute value of the difference between $e_1 \approx e_2$ and the steady-state potential e_0 of the electrode is sufficiently small to permit us to put the concentrations of the last-mentioned two couples close to the interface approximately equal to the concentrations in the bulk of the solution, we have the following relationship (*cf.* Fronæus ⁷) for i_1 and i_2 at the steady-state potential.

$$i_n = i_{0,n} \left(\exp \left\{ \frac{\alpha_n (e_0 - e_1) F}{RT} \right\} - \exp \left\{ - \frac{(1 - \alpha_n) (e_0 - e_1) F}{RT} \right\} \right) \quad (13)$$

($n = 1$ and 2)

Here $i_{0,n}$ is the exchange current density and $0 < \alpha_n < 1$. But for small absolute values of $(e_0 - e_1)$ this expression can be replaced by

$$i_n = \frac{i_{0,n} (e_0 - e_1) F}{RT} \quad (14)$$

Now $RTF^{-1}i_{0,n}^{-1}$ is equal to the electron transfer resistance ⁷ $R_{t,n}$ of the electrode reactions (7) and (8), and using eqn. (10) we get

$$e_1 - e_0 = \frac{i_3}{R_{t,1}^{-1} + R_{t,2}^{-1}} \quad (15)$$

In the emf measurements below we will presuppose that the difference $e_1 - e_0$ is negligible and from variations in e_0 calculate the corresponding variations in the concentration ratio between silver(II) and silver(I). It should be emphasized that a very small value of i_3 does not imply that the transfer resistance $R_{t,3}$ of (9) is very high (*cf.* Fronæus ⁷).

Adding eqns. (11) and (12) we obtain $r_3 + r_4 + r_5 = 2 r_1$. According to the results of the previous investigation ¹ we have $r_1 = \text{constant} \cdot [\text{Ag(I)}][\text{S}_2\text{O}_8^{2-}]$. If the complex formation between Ag^+ and the anions present is neglected $[\text{Ag(I)}]$ can be replaced by $[\text{Ag}^+]$. Then we try to use the expression $[\text{Ag}^{2+}]^j \cdot \varphi$ for $r_3 + r_4 + r_5$, where φ may be a function of the concentrations of different species except silver(II) and persulphate, and get the relationship

$$\frac{[\text{Ag}^{2+}]}{[\text{Ag}^+]} = \text{constant} \frac{[\text{S}_2\text{O}_8^{2-}]^{\frac{1}{j}}}{[\text{Ag}^+]^{\frac{j-1}{j}} \varphi^{\frac{1}{j}}} \quad (16)$$

Thus by determining the dependence of $[Ag^{2+}][Ag^+]^{-1}$ upon the different concentrations it should be possible to obtain the value of j and the expression for φ .

MEASUREMENTS AND CALCULATIONS

Chemicals used. Sodium persulphate solutions were prepared by mixing equivalent amounts of solutions containing potassium persulphate and sodium perchlorate, cooling down to about 5°C and filtering off the potassium perchlorate precipitated. The concentration of the sodium persulphate solution was determined as described previously (Fronæus and Östman⁸).

Other chemicals used were prepared as before¹ or were commercial preparations of analytical grade.

Emf measurements. The cells measured were of the following type



The solution of the right half-cell was obtained by mixing different solutions containing ammonium or sodium persulphate, ammonium, silver, and sodium perchlorates, perchloric acid, and ammonium or sodium sulphate. The sodium perchlorate was supplied in order to keep the ionic strength equal to 1 M. The measurements were carried out at a temperature of 25.0°C.

At first when the platinum electrodes were used no steady potentials were obtained. However, when the electrodes had been kept in decomposing persulphate solutions for some days, fairly steady potentials were attained when the electrodes were immersed in new solutions. Probably this fact must be ascribed to the formation of an oxide of platinum on the surface of the electrodes (*cf.* Bowden⁹, Ershler¹⁰). In order to get reliable results every cell solution was freshly prepared many times, and different platinum electrodes were used. Then it was found that within 1 or 2 mV, the same emf mean values were obtained with different electrodes.

For the emf E in mV we have

$$E = E_0 + 59.16 \log \frac{[Ag^{2+}]}{[Ag^+]} \quad (17)$$

where E_0 should be approximately constant. Taking the value 2 000 mV for the standard potential e_1^0 of the silver couple (*cf.* Noyes *et al.*¹¹) and 560 mV for the potential of the quinhydrone electrode we get $E_0 \approx 1\,400$ mV. Then we find from the E -values in Tables 1 and 2 that $[Ag^{2+}] < 3 \times 10^{-4}[Ag^+]$. Thus, unless the complex formation between Ag^{2+} and the anions of the solutions is very strong, and this is not probable, the concentration of silver(II) is so low that we can put the concentration of silver(I) approximately equal to the total silver concentration. The values of $[H^+]$ and $[SO_4^{2-}]$ in the tables were calculated from the concentrations of perchloric acid and sulphate, the secondary dissociation constant $K_s = 8.5 \times 10^{-2}$ M being used for sulphuric acid (Fronæus¹²).

The emf values obtained in the presence of ammonium ions in the cell solutions are collected in Table 1. In order to determine an empirical expression for the right member of (16) we write

$$\frac{[Ag^{2+}]}{[Ag^+]} = \text{constant} [Ag^+]^a [NH_4^+]^b [H^+]^c [SO_4^{2-}]^d [S_2O_8^{2-}]^e \quad (18)$$

Table 1. *Emf and electrode impedance measurements on persulphate solutions containing ammonium and silver salts.*

[Ag ⁺] mM	[NH ₄ ⁺] mM	[H ⁺] mM	[SO ₄ ²⁻] mM	[S ₂ O ₈ ²⁻] mM	<i>E</i> mV	<i>R</i> _i ⁻¹ ohm ⁻¹ cm ⁻²
3.00	200	380	30	100	1 192	0.40
3.00	500	380	30	100	1 183	0.37
3.00	400	380	0	100	1 188	0.43
3.00	450	145	30	100	1 156	0.40
3.00	500	115	65	100	1 147	0.35
1.50	100	380	30	20	1 134	0.28
3.00	100	380	30	20	1 160	0.32
6.00	100	380	30	20	1 177	0.40
12.00	100	380	30	20	1 192	0.47
6.00	200	380	30	100	1 207	0.67
6.00	500	380	30	100	1 199	0.67

The derivative $\partial E/\partial \log [\text{Ag}^+]$ is found to be approximately constant and gives $a = 0.8$, except for the lowest silver(I) concentration, where a higher value is obtained which must be excluded. By combining the other E -values all the exponents in (18) can be determined, and we get $b = -0.4$, $c = 1.1$, $d \approx 0$, and $e = 1.0$. An equating of the right-hand members of (16) and (18) gives $j = e^{-1} = 1.0$ and an expression for φ . Then we have

$$r_3 + r_4 + r_5 = \text{constant} \frac{[\text{Ag}^{2+}][\text{NH}_4^+]^{0.4}}{[\text{Ag}^+]^{0.8}[\text{H}^+]^{1.1}} \quad (19)$$

In order to obtain an empirical expression for $r_4 + r_5$ emf measurements were also performed in the absence of ammonium ions. The E -values are given in Table 2. Eqn. (18) is applied, and it is found that also in this case $\partial E/\partial \log [\text{Ag}^+]$ is constant except for $[\text{Ag}^+] = 1.50$ mM. The following exponents are arrived at: $a = 0.8$, $c = 1.0$, $d \approx 0$, and $e = 0.8$. Thus $j = 1.2$ and for $r_4 + r_5$ we get

$$r_4 + r_5 = \text{constant} \frac{[\text{Ag}^{2+}]^{1.2}}{[\text{Ag}^+]^{1.2}[\text{H}^+]^{1.2}} \quad (20)$$

Table 2. *Emf and electrode impedance measurements on sodium persulphate solutions containing silver salts.*

[Ag ⁺] mM	[H ⁺] mM	[SO ₄ ²⁻] mM	[S ₂ O ₈ ²⁻] mM	<i>E</i> mV	<i>R</i> _i ⁻¹ ohm ⁻¹ cm ⁻²
3.00	380	30	100	1 215	0.18
3.00	380	0	100	1 223	0.20
3.00	145	30	100	1 190	0.20
3.00	115	65	100	1 185	0.18
1.50	380	30	20	1 162	0.13
3.00	380	30	20	1 182	0.14
6.00	380	30	20	1 197	0.16
12.00	380	30	20	1 213	0.23
6.00	380	30	100	1 230	0.23

It should be emphasized that the real dependence of $r_3+r_4+r_5$ and r_4+r_5 upon $[\text{SO}_4^{2-}]$ cannot be ascertained from the measurements without information about the complex formation.

In a previous work⁸ we arrived at the conclusion that r_4 is proportional to $[\text{SO}_4^-]$. Then, if we have a redox equilibrium between the couple $\text{SO}_4^- - \text{SO}_4^{2-}$ and the silver couple, r_4 should be proportional to $[\text{Ag}^{2+}][\text{Ag}^+]^{-1}[\text{SO}_4^{2-}]$. For r_5 Noyes *et al.*¹³ have found complicated expressions, but at low concentrations of silver(II) r_5 seems to be proportional to $[\text{Ag}^{2+}]^2[\text{Ag}^+]^{-1}$ and decreases for increasing values of $[\text{H}^+]$. Since the two last-mentioned rate laws are of different form, our empirical laws (19) and (20) can be applicable only within limited ranges of concentration.

Electrode impedance measurements. For a description of the apparatus used and the theory on which the calculations are based the reader is referred to a recent work⁷. The impedance of the electrode-solution interface can be represented by an equivalent circuit, consisting of a resistance R_p and a capacity C_p connected in parallel. From the measurements R_p was calculated at different values of the frequency ν of the polarizing alternating current. Then the conductance R_p^{-1} was plotted against $\nu^{-\frac{1}{2}}$ and extrapolated to $\nu = \infty$. For the intercept R_i^{-1} on the R_p^{-1} -axis we have

$$\frac{1}{R_i} = \frac{1}{R_{i,1}} + \frac{1}{R_{i,2}} + \frac{1}{R_{i,3}} \quad (21)$$

Also in these measurements it was found that in the beginning no steady values were obtained. R_i decreased continuously when the small polarizable platinum electrode was immersed in a decomposing persulphate solution, but after a few days the electrode gave reproducible impedances with fresh solutions. It is evident that the exchange current densities increased when a surface oxide was formed on the electrode.

If the over-all electrode reactions (7) and (8) are identical with the corresponding electron transfer steps, then $i_{0,1}$ should be proportional to $[\text{Ag}^{2+}]^{\alpha_1}[\text{Ag}^+]^{1-\alpha_1}$ and $i_{0,2}$ proportional to $[\text{SO}_4^-]^{\alpha_2}[\text{SO}_4^{2-}]^{1-\alpha_2}$ (*cf.* Frønaes and Östman¹⁴). Furthermore, if we have a redox equilibrium between these two couples and assume that the transfer coefficients α_1 and α_2 are approximately equal to 0.5, we should have the relationship

$$\frac{1}{R_{i,1}} + \frac{1}{R_{i,2}} = 10^{0.5E/59} (K_1[\text{Ag}^+] + K_2[\text{SO}_4^{2-}]) \quad (22)$$

where K_1 and K_2 are constants.

The final values of R_i^{-1} obtained from the measurements are given in the last columns of Tables 1 and 2. It is seen that the differences between the values belonging to one and the same table are rather small, but in Table 2 the variation is on the whole in qualitative agreement with the variation in $R_{i,1}^{-1}$ that can be expected according to eqn. (22). On the other hand, the term $R_{i,2}^{-1}$ seems to be of minor importance.

From (22) it is obvious that for small values of E and $[\text{Ag}^+]$ the quantity $R_{i,1}^{-1}$ will be small, and thus the difference $e_1 - e_0$ in eqn. (15) may be appreciable.

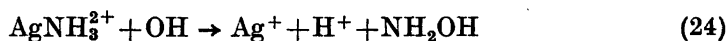
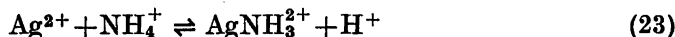
Possibly this is the reason of the surprisingly small E -value in Table 1 for $[\text{Ag}^+] = 1.50 \text{ mM}$.

Comparing the values of R_i^{-1} in Table 1 with those in Table 2 we find that, if ammonium ions are supplied but the concentrations of the other ions given in the tables are kept constant, the values of R_i^{-1} increase considerably, though the values of E decrease. The only explanation of this fact is that the couples formed in the different stages in the oxidation of ammonium ions take part in the electron exchange between electrode and solution, and thus the term $R_{i,3}^{-1}$ in (21) increases.

DISCUSSION OF THE REACTION MECHANISM

If the concentrations of silver(I) and persulphate are kept constant then we have $r_3 + r_4 + r_5 = \text{constant}$. From Tables 1 and 2 it is evident that by the supply of ammonium ions the E -values decrease 20—38 mV. This means that $[\text{Ag}^{2+}]$ is from 2 to 5 times smaller in the presence of the ammonium ions, and from the empirical law (20) it is seen that approximately the same decrease must be valid for $r_4 + r_5$. Accordingly, for the ammonium ion concentrations used we have $r_4 + r_5 < r_3 < 4(r_4 + r_5)$.

However, it was found experimentally that the rate of the oxygen evolution was slight in the presence of ammonium ions and not at all as great as could be expected from these calculations. In order to explain this fact it must be presumed that the OH radicals, which are probably formed intermediately in the reactions (4) and (5), are made use of to a certain extent in one (or several) of the steps of the over-all reaction (3). For this reason the following mechanism is proposed for the first steps (*cf.* Fronæus and Östman¹).



(23) is presupposed to be a rapid complex equilibrium and (24) a slow step. Then r_3 should be proportional to $[\text{AgNH}_3^{2+}][\text{OH}]$, and substituting for $[\text{AgNH}_3^{2+}]$ the mass law expression we get

$$r_3 = \text{constant} \frac{[\text{Ag}^{2+}][\text{NH}_4^+][\text{OH}]}{[\text{H}^+]} \quad (25)$$

Then, since $r_3/8$ is the rate at which ammonium ions are consumed in reaction (3), the steady-state approximation applied to OH in the solution gives

$$r_4 + r_5 - \frac{r_3}{8} - r_6 = 0 \quad (26)$$

The mechanism proposed evidently requires that $r_3 \leq 8(r_4 + r_5)$, and this condition is satisfied according to the calculations above. Now we substitute the empirical expression (20) for $r_4 + r_5$ with the exponents rounded off to 1.0.

Furthermore, the rate r_6 of reaction (6) should be proportional to $[\text{OH}]^2$, and then we have

$$k_1 \frac{[\text{Ag}^{2+}]}{[\text{Ag}^+][\text{H}^+]} = k_2 \frac{[\text{Ag}^{2+}][\text{NH}_4^+][\text{OH}]}{[\text{H}^+]} + k_3[\text{OH}]^2 \quad (27)$$

where k_1 , k_2 , and k_3 are constants. From (27) it is seen that if the first term in the right member predominates then $[\text{OH}]$ is proportional to $[\text{Ag}^+]^{-1}[\text{NH}_4^+]^{-1}$. On the other hand, if the second term predominates then $[\text{OH}]$ is proportional to $[\text{Ag}^{2+}]^{0.5}[\text{Ag}^+]^{-0.5}[\text{H}^+]^{-0.5}$. Thus, within limited ranges of concentration it should be possible to represent $[\text{OH}]$ by an expression of the form

$$[\text{OH}] = \text{constant} [\text{Ag}^{2+}]^{\varepsilon_1} [\text{Ag}^+]^{\varepsilon_2} [\text{NH}_4^+]^{\varepsilon_3} [\text{H}^+]^{\varepsilon_4} \quad (28)$$

with the following conditions fulfilled

$$\begin{aligned} 0 < \varepsilon_1 < 0.5 \\ -1 < \varepsilon_2 < -0.5 \\ -1 < \varepsilon_3 < 0 \\ -0.5 < \varepsilon_4 < 0 \end{aligned}$$

For ε -values close to the middles of the intervals we then obtain

$$r_3 = \text{constant} \frac{[\text{Ag}^{2+}]^{1.2}[\text{NH}_4^+]^{0.5}}{[\text{Ag}^+]^{0.7}[\text{H}^+]^{1.2}} \quad (29)$$

Combining this expression with (20) and taking into account that $r_3 > r_4 + r_5$, we can predict that if the resulting expression for $r_3 + r_4 + r_5$ is represented approximately by a law similar to (29) the exponents of $[\text{Ag}^{2+}]$ and $[\text{H}^+]$ will be unchanged, the exponent of $[\text{Ag}^+]$ will be slightly higher and that of $[\text{NH}_4^+]$ slightly lower than in (29). This conclusion is verified by the experimentally determined law (19), and it is evident that the mechanism proposed can explain the measurement results in a very satisfactory way.

The author is grateful to Miss K. Anderson for valuable assistance in the experimental work.

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Received September 15, 1956.