# The Corrosion of Silver by Potassium Cyanide Solutions and Oxygen

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During the last century numerous investigations have been made concerning the dissolution of silver in potassium cyanide solutions, chiefly with a view to the utilization of the reaction in industry. The fact that oxygen is a necessary factor in this reaction was for the first time pointed out by Elsner [1] (1846) and later on confirmed through experiments made by Bodländer [2] (1896), who investigated the corresponding reaction with gold. Elsner's experiments made it probable that the reaction was as follows:

$$4 \text{ Ag} + 8 \text{ KCN} + O_2 + 2 \text{ H}_2O = 4 \text{ KAg(CN)}_2 + 4 \text{ KOH} \tag{I}$$
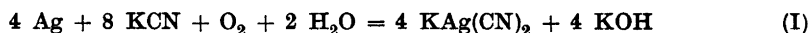
Bodländer admitted the correctness of this equation as an overall reaction, but found hydrogen peroxide as an intermediate:

$$2 \text{ Ag} + 4 \text{ KCN} + O_2 + 2 \text{ H}_2O = 2 \text{ KAg(CN)}_2 + \text{H}_2O_2 + 2 \text{ KOH} \tag{II}$$

The hydrogen peroxide reacts with silver and potassium cyanide:

$$2 \text{ Ag} + 4 \text{ KCN} + \text{H}_2O_2 = 2 \text{ KAg(CN)}_2 + 2 \text{ KOH} \tag{III}$$
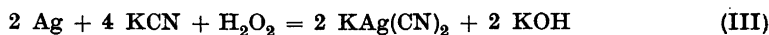
By adding equations (II) and (III) we obtain the overall reaction (I).

Raschig [3] (1928) has dealt with these problems in a paper giving a comprehensive review of former investigations. He explains the mechanism of the reaction by the assumption that silver gives off positive ions to the solution, itself obtaining a negative charge. Simultaneously oxygen is reduced to O_2^{--}. The silver ions combine with the cyanide ions, while the O_2^{--} ions combine with hydrogen ions from the water to form hydrogen peroxide.
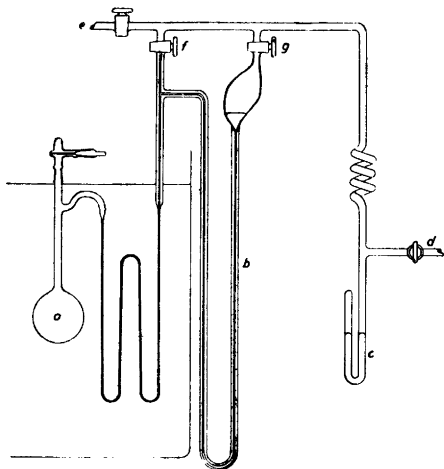
Fig. 1. Brønsted shaking apparatus. a)
reaction flask, b) manometer, c) manometer,
d) stopcock to gasometer containing oxygen,
e) stopcock to vacuum pump.

    With the object of investigating the kinetics, the rate of the reaction has
been followed by continuously measuring the oxygen absorption in a system
of silver, oxygen and potassium cyanide solution in which there is a deficit of
the latter.

TECHNIQUE

    The experiments were carried out in a Brønsted shaking apparatus (Fig. 1).
By means of a capillary tube the reaction flask (a) was connected to the mano-
meter (b) which in turn was connected to the closed manometer (c). At (d)
the apparatus was in communication with a gas holder containing oxygen and
at (e) with a vacuum pump. The flask (a) was closed by means of a cap with
an additional ground glass joint so that by turning this additional joint it was
possible to raise and lower a sheet of silver during the experiment. The volume
of the closed system, consisting of flask with cap and tubes up to the mano-
meter, was 71 ml.
    Into the flask was poured 11.5 ml of a solution the concentration of which
as regards potassium cyanide (kalium cyanatum Merck) varied, but the nor-
mality of which with regard to sodium hydroxide was always $N/10$. The cyanide
concentration was on beforehand determined by titration with silver nitrate
according to Liebig's method in the presence of ammonia and potassium
iodide.
    Above the solution a sheet of silver was fixed (pure silver containing 1 000
parts per 1 000 silver, the fineness being determined with an accuracy of 0.02
per cent by the Government Assay Office which has supplied the silver for the

Fig. 2. Absorption of oxygen in a system of silver, oxygen and a solution of potassium cyanide at 25° C. During the experiment are consumed $9.821 \cdot 10^{-4}$ Mol potassium cyanide, $4.829 \cdot 10^{-4}$ equiv. of silver, $1.220 \cdot 10^{-4}$ oxygen to B, $1.826 \cdot 10^{-4}$ Mol oxygen to A.
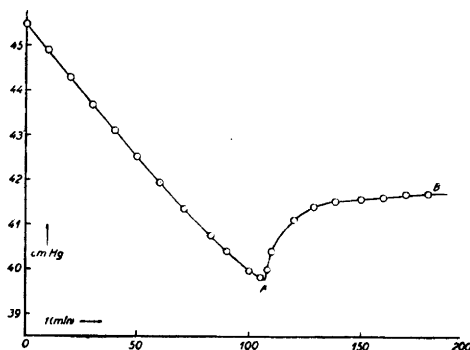
experiments). When no other statement is made, the sheet used was 40 mm long by about 7 mm wide and 0.6—0.8 mm thick. The apparatus was evacuated, the stopcocks f, g, and e being kept open. When the pumping had proceeded for one minute, stopcock f was closed, so that water vapour was removed from the rest of the system, and now the stopcocks g and e were closed. Oxygen was now passed from the gas holder into the flask. This oxygen was evacuated, fresh oxygen was admitted through stopcocks d and f, and the shaking apparatus was started. When the shaking had lasted for three minutes and the solution was saturated with oxygen, the oxygen pressure was read, this value being considered to correspond to the time zero; the silver sheet was lowered into the solution and readings were made at suitable intervals. When the oxygen pressure had become constant, the experiment was discontinued and the silver sheet was rinsed in water and weighed after having been left to dry on filter paper. The rate of the oxygen absorption was highly dependent on the speed at which the apparatus was shaken. The maximum rate of absorption was ascertained to occur at an average speed of 200 shakings per minute with an amplitude of 1.9 cm. By altering the speed to 220 or 180 shakings per minute it was possible to alter the slope of the curve in Fig. 2 considerably. The apparatus was therefore fitted with a speed regulator and the speed was kept constant at 200 shakings per minute.

In certain cases the experiment has, however, been discontinued before the oxygen pressure had become constant, in order to determine not only the weight of the silver sheet, but also the content of hydrogen peroxide by titration with potassium permanganate in a solution acidified with sulphuric acid.

Experiments have also been made to ascertain the conditions prevailing when silver was acted upon by a potassium cyanide solution to which hydrogen peroxide (Perhydrol Merck) had been added.
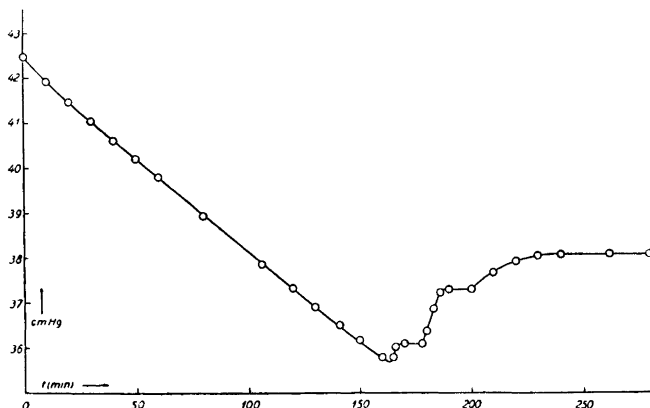
Fig. 3. Absorption of oxygen in a system of silver, oxygen and a solution of potassium cya-nide at 25° C. The silver plate is raised and lowered twice during the experiment. 10.736 · 10⁻⁴ Mol potassium cyanide, 5.256 · 10⁻⁴ equiv. of silver, 1.386 · 10⁻⁴ Mol oxygen are consumed.

EXPERIMENTAL RESULTS

1. Fig. 2 represents one of the approximately 50 experiments in which the experiment has been continued until the oxygen pressure above the solution had become constant. The trend of the curve was always as shown in the figure. During the first part of the experiment the absorption took place at an almost constant rate, followed by a sudden rise at the time corresponding to the point A in the figure, whereupon the pressure became constant. A determination of the amount of oxygen absorbed calculated on the basis of the difference between the initial and final pressure and the weight of the dissolved silver shows, when correlated to the amount of cyanide used, agreement with Elsner's overall reaction. (During the experiment there was usually a loss of cyanide amounting to 1—2 per cent, which may perhaps be due to hydrolysis of cyanide into formic acid, a small quantity of formic acid having been determined in the mixture $CN^- + H_2O_2$).

2. The trend of the curve obtained when the silver sheet was periodically liftet out of the solution beginning immediately when the rise in pressure had commenced, i. e. when the point A (Fig. 2) had been passed, will appear from Fig. 3. The rise in pressure stopped when the silver sheet was no longer in the solution, but began again as soon as the sheet was lowered into the solution. The presence of the silver sheet in the solution is thus necessary to produce the rise in pressure.

3. Other experiments were broken off at a time corresponding to point A in Fig. 2. By titration of the solution large quantities of hydrogen peroxide
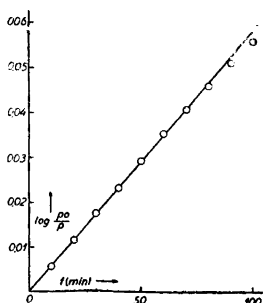
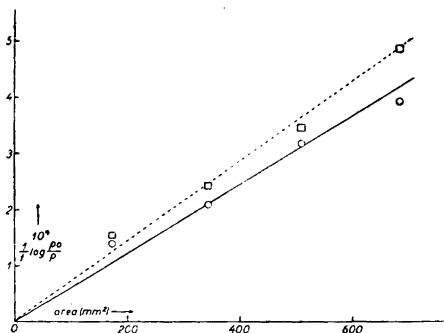Fig. 6. log p_0/p plotted against time. Results from experiment Fig. 2.

Fig. 7. The velocity constant plotted against the area of the silver plate (15° C and 25° C). The initial concentration of cyanide is 0.043 and of hydroxyl 0.1.

were found to be present. 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 had stopped, the solution did not contain any hydrogen peroxide. The sudden increase in pressure at A (Fig. 2) is obviously due to the catalytic decomposition of the hydrogen peroxide on the silver sheet.

4. The rate of absorption proved to be independent of the initial cyanide concentration within the range examined, where c_{CN}^- varied between 0.05 and 0.2, while it is dependent on the oxygen pressure, the reaction being approximately of the first order with regard to oxygen (see Fig. 6). Four experiments in which the initial oxygen pressure was 45, 29, 15, and 10 cm Hg, respectively, showed that the gradients of the tangent at $t = 0$ of the curve obtained by plotting log p_0/p against t were 0.000591, 0.000634, 0.000634, and 0.000644, respectively.

5. The rate at which the oxygen absorption took place was further dependent on the area of the surface of the silver sheet, this surface being assumed to be plane. In the course of four experiments this area was varied in the ratios of 1, 2, 3, and 4, the area of sheet 1 being 174 mm², that of 2 : 345 mm², that of 3 : 510 mm², and that of 4 : 686 mm². The initial concentrations of cyanide and hydroxyl ions were the same through all the experiments. It will be seen from Fig. 7 that the rate of oxygen absorption is proportional to the area of the surface.

A similar experimental series made at 15° C has been represented in the same figure. The ratio k_{25}/k_{15} is, as will appear from the figure, equal to 1.17. From the constants the activation energy of the reaction has been calculated to be 3.2 kg cal. according to the formula:
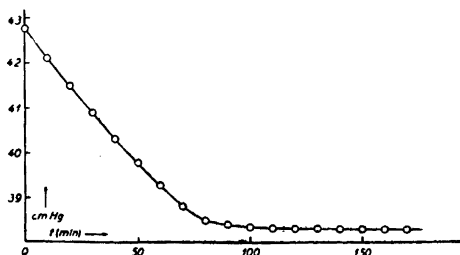
Fig. 4. Absorption of oxygen in a system of silver, oxygen and a solution of potassium cyanide at 25° C. During the experiment are consumed 6.152 · 10⁻⁴ Mol potassium cyanide, 3.041 · 10⁻⁴ equiv. of silver, 1.438 · 10⁻⁴ Mol oxygen. 1.324 · 10⁻⁴ Mol hydrogen peroxide is formed.
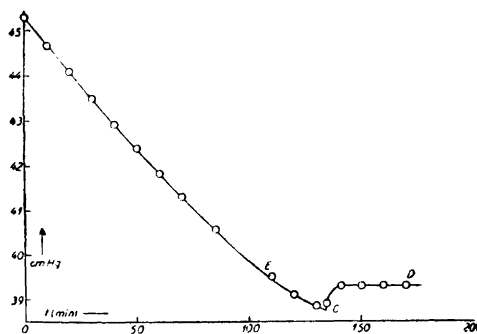
Fig. 5. Absorption of oxygen in a system of silver, oxygen and a solution of potassium cyanide at 25° C. During the experiment are consumed 9,821 · 10⁻⁴ Mol potassium cyanide, 4,848 · 10⁻⁴ equiv. of silver, 1,896 · 10⁻⁴ Mol oxygen to D, 2.056 · 10⁻⁴ Mol oxygen to C. 1.355 · 10⁻⁴ Mol hydrogen peroxide is formed.

$$E \ (1/298—1/288) = R \ \ln \ k_{25}/k_{15}$$

where R is the gas constant, k_{25} and k_{15} the velocity constants for the monomolecular reaction at 25° C and at 15° C, respectively, while 298 and 288 are the absolute temperatures.

6. In all the above mentioned experiments the silver sheet had previously been etched in a potassium cyanide solution in the presence of air and then rinsed in water to give the sheet a white, crystalline appearance.

By altering the preliminary treatment of the silver sheet, the surface of the latter was altered, and the experiments with such sheets produced oxygen-absorption curves of an altered appearance as regards the last part of the curve. When thus the silver sheet preparatory to the experiment was kept immersed in a mixture of potassium cyanide and hydrogen peroxide with a large excess of hydrogen peroxide, it lost its crystalline appearance and became perfectly bright, while at the same time an evolution of oxygen took place on the sheet. When such a sheet, after rinsing and drying, was lowered into the potassium cyanide solution, the oxygen absorption curve would exhibit a trend as the one represented in Fig. 4, the curve being readily reproducible. When in the experiment the initial concentration of cyanide ions was greater, a slight break would occur in the curve (Fig. 5). After having maintained a constant oxygen pressure for some time, the experiment was discontinued,

the silver sheet was weighed, and the hydrogen peroxide content in the solution was determined. It will be seen from the explanations beneath the illustrations that the quantities of silver and cyanide were equivalent. The quantity of oxygen absorbed corresponded in the experiment illustrated in Fig. 4 to 93.5 per cent of the quantity consumed according to equation (II). It will be seen from the curves that during the first part of the experiment the oxygen absorption occurred at the same rate as in the other experiments, while it may be seen from the final horizontal part of the curve that hydrogen peroxide was not, or practically not, decomposed catalytically on the plate.

7. To ascertain whether the primary reaction proceeds according to the equation:

$$2 \text{ Ag} + O_2 = 2 \text{ Ag}^+ + {}^-O-O^- \qquad (IV)$$
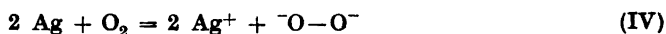
the quantity of oxygen absorbed, the silver dissolved and the content of hydrogen peroxide in the solution were determined simultaneously during five experiments which were discontinued after periods of 10, 20, 30, 40, and 120 minutes, respectively.

Table 1. *Simultaneous determinations of silver dissolved, oxygen absorbed, and hydrogen peroxide formed, at 25° C.*

(1)	(2)	(3)	(4)	(5)	(6)
Min.	Equiv. Ag dissolved $\times \frac{1}{2} \times 10^5$	Mol. O_2 absorbed $\times 10^5$	Mol. "H_2O_2" formed $\times 10^5$	(2)−(4)	$\dfrac{(2) + (4)}{2}$ − (3)
10	1.48	1.45	1.43	0.05	0.00
20	3.38	3.07	3.09	0.29	0.16
30	4.68	4.17	4.00	0.68	0.17
40	6.21	5.40	5.51	0.70	0.46
120	18.03	16.00	14.76	3.27	0.40

At the beginning of the experiment the quantity of silver dissolved was equivalent to the quantity of hydrogen peroxide formed, which indicates that the course of the reaction was as described by equation (IV). As the experiment proceeded, the difference between dissolved silver and hydrogen peroxide content gradually increased (Table 1, column 5). It is obvious that the hydrogen peroxide formed took part in the process of dissolution of the silver. It will be seen from equations (II) and (III) that half of the dissolved silver in equivalents (Table 1, column 2) + the quantity of hydrogen peroxide formed,

in moles (column 4) should be equal to twice the quantity of oxygen consumed, in moles (column 3). The results found (column 6) do not agree completely with this, but this is possibly due to errors in the hydrogen peroxide titration, which was difficult to carry out on account of the small amounts of standard solution used, or more probably to the formation of small quantities of formic acid which also consumes permanganate, for which reason the H_2O_2 content is given in inverted commas in the table.

8. The question now arises whether free cyanide ions are present at the time when the decomposition of the hydrogen peroxide commences. To obtain an answer to this question, a number of experiments were made which were broken off at the time corresponding to point A (Fig. 2). The silver sheet was weighed, replaced in the apparatus, which was evacuated. The silver sheet was again lowered into the liquid, and the decomposition process was allowed to proceed to completion. The silver sheet showed a further loss in weight equal to 5 to 10 per cent of the total loss, a fact which indicates that cyanide ions must be present in the solution at the moment when the decomposition commences. A comparison between the experiment illustrated in Fig. 2, in which decomposition took place, and that of Fig. 5, in which practically no decomposition occurred, also shows that in cases where there is no decomposition, the primary absorption of oxygen is greater which in turn means that silver was dissolved during the time corresponding to the last sloping part of the curve, i. e. from E to C. The quantity of silver dissolved after the discontinuation of the experiment at constant oxygen pressure was the same in the two cases in which the initial concentration of cyanide ions was the same.

9. For further elucidation of the process of dissolution of the silver sheets, additional experiments have been made, not in the Brønsted apparatus, but in a test tube into which oxygen at constant pressure was passed. The silver sheet was suspended from a scale of an analytical balance and immersed in the solution in the test tube. The sheet was frequently weighed during the process of solution, the test tube with the reagent solution being for this purpose replaced by a test tube with water. The curve representing the relationship between loss in weight and time is given in Fig. 8. At the beginning the order of the reaction is zero, corresponding to the fact that the oxygen pressure is kept constant. At the time A an evolution of oxygen was observed to begin in the solution. As shown above, the solution at this time still contained small quantities of free cyanide ions which could dissolve silver. The explanation of the increased rate of absorption will be discussed later.

10. We have already in connection with the process of dissolution: oxygen, potassium cyanide and silver, seen that the hydrogen peroxide formed must take part in the dissolution of the silver. This assumption was confirmed by
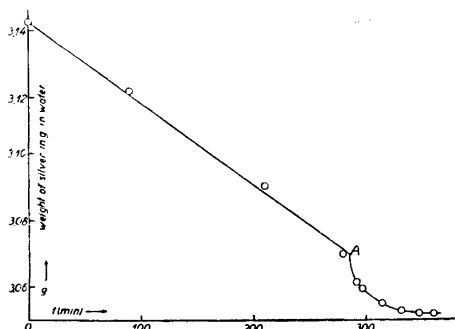
Fig. 8. *Loss in weight of the silver plate plotted against time in a system of silver, oxygen and a solution of potassium cyanide at an oxygen pressure of 1 atm. at 25 ° C.*

direct experiments with hydrogen peroxide, potassium cyanide and silver. The experiments were made in test tubes. Potassium cyanide solution free from oxygen, and hydrogen peroxide solution were poured into a test tube, and the mixture was aerated by means of nitrogen which was freed from oxygen by passing through a furnace in which reduced copper was held at 300° C. The test tube was placed in a thermostat below the analytical balance from which the silver sheet was suspended, immersed in the liquid, and the silver sheet was weighed periodically. In the course of a few hours a small quantity of silver was dissolved, e. g., in a cyanide concentration of 0.05 and a hydrogen peroxide concentration of 0.02 a quantity of 5 mg silver was dissolved in the course of three hours, while no catalytic decomposition of the hydrogen peroxide was observed on the sheet. It proved difficult to reproduce these experiments, but small amounts of silver were dissolved in all cases.

11. Experiments have further been made in the Brønsted apparatus with hydrogen peroxide, potassium cyanide and a sheet of silver, in which the rise in pressure due to the oxygen evolution was measured and the silver sheet was weighed after the conclusion of the experiment. It also proved difficult to reproduce these experiments, due to difficulties in obtaining identical silver sheets. The course of the experiment was dependent on the concentrations of hydrogen peroxide and potassium cyanide and on the nature of the surface of the silver. A curve belonging to either of three different classes of curves was, however, always obtained. First, an almost horizontal curve in the cases in which there was a great excess of potassium cyanide as compared to the hydrogen peroxide concentration, refer equation (III). The second case is illustrated in curve I, Fig. 9. Here there is a great excess of hydrogen peroxide as compared to potassium cyanide. In this case hydrogen peroxide is immediately decomposed while silver is at the same time dissolved. Finally the course of the experiment when the hydrogen peroxide surplus is smaller is

illustrated by curve II. In this case the decomposition of hydrogen peroxide will only set in when a fairly long time has elapsed. The quantity of silver dissolved was smaller than the quantity equivalent to the amount of cyanide added. This seems to indicate an interaction between cyanide and hydrogen peroxide.

12. A number of experiments on this problem on the whole confirmed Masson's [4] experiments. According to Masson the following reactions take pl ace:

$$KCN + H_2O_2 = KCNO + H_2O \tag{1}$$

$$KCN + 2 H_2O = HCOOK + NH_3 \tag{2}$$
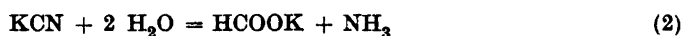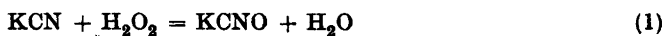
four fifth of the cyanide being consumed according to equation (1), one fifth according to equation (2).

When 0.2 molar solutions of potassium cyanide and hydrogen peroxide were mixed, they reacted on each other. In the course of four hours practically all cyanide had been consumed to form potassium cyanate which was partly hydrolysed into carbonate; about 10 per cent of the cyanide was converted into formic acid, the quantity of which was determined by addition of mercuric chloride to the solution to which on beforehand acetic acid and sodium chloride had been added; the mercurous chloride formed was determined by iodometry. It was also ascertained whether the solution contained any nitrous oxide (by combustion analysis in a Christiansen [5] gas-analysis apparatus) or any nitrite or nitrate (according to Blom [6]), but the results were negative.

DISCUSSION

It has been shown in the preceding that the velocity of the reaction in the system $Ag + KCN + O_2$ is:

    1. of the 1st order with respect to the oxygen pressure,

    2. independent of the cyanide ion concentration,

    3. proportional to the area of the surface of silver, the latter being considered to be a plane,

    4. dependent on the speed at which the shaking is effected (the trend of the curve in fig. 8 may be explained with a view to this fact, as the decomposition of the hydrogen peroxide on the surface of the silver results in a more vigorous agitation of the liquid around the silver, which in turn results in a greater speed of dissolution).

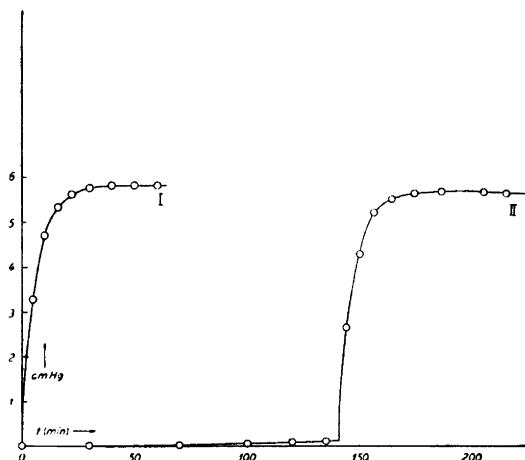   5. Finally the temperature coefficient of the reaction is small.

Fig. 9. Oxygen pressure in a system of silver, hydrogen peroxide and a solution of potassium cyanide at 25° C. During the experiment are consumed I. $1.700 \cdot 10^{-4}$ Mol potassium cyanide, $0.834 \cdot 10^{-4}$ equiv. of silver, $4.163 \cdot 10^{-4}$ Mol hydrogen peroxide, $1.861 \cdot 10^{-4}$ Mol oxygen evolved. II. $4.242 \cdot 10^{-4}$ Mol potassium cyanide, $2.086 \cdot 10^{-4}$ equiv. of silver, $4.830 \cdot 10^{-4}$ Mol hydrogen peroxide, $1.839 \cdot 10^{-4}$ Mol oxygen evolved.

The mechanism of the reaction may be illustrated as follows:

$$O_2 \text{gas} \rightleftharpoons O_2 \text{diss.} \qquad\qquad \pm 1$$

$$O_2 \text{diss.} + Ag_{\text{solid}} \rightarrow X| \qquad\qquad 2$$
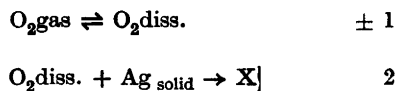
where the reaction $\pm$ 1 represents the solution of oxygen in water and reaction 2 the fact that the dissolved oxygen diffuses to the silver sheet and reacts with the latter.

On the condition that the concentration of dissolved oxygen is stationary the following expression is obtained for the determination of the velocity of the reaction of the flow s:

$$c_{o_2} \text{gas}/s = 1/k_1 + k_{-1}/k_1 k_2 q, \qquad\qquad \text{(Christiansen[7])}$$

where q is the area of the surface of the silver. As $k = aq$ (a is a constant), it is only the second term which will have to be taken into account.

$k_1/k_{-1} = K_1 = c_d/c_g$, i. e. Ostwald's coefficient of absorption (c_d is the concentration of oxygen in the solution, c_g the concentration over the solution). Hence $s = K_1 k_2 \ qcg$.

This expression is in agreement with the one which according to the experiments apply for the flow found:

$$s = kqcg,$$ *i. e.* it is reaction 2 which determines the velocity.

If the velocity is determined by a flow of oxygen molecules through a diffusion layer δ at the silver sheet, the expression for the flow is according to Nernst [8] $s = Dq/\delta \times c_d$, where D is the coefficient of diffusion. The concentration of oxygen molecules on the silver has been taken to equal zero. This equation is also in agreement with the equation of the reaction examined (Fig. 6).

The ratio of $Dq/\delta \times K_1$ at 15° C and at 25° C is equal to 1.11, as D is proportional to T/η according to Stoke-Einstein's law, η is the viscosity and T the absolute temperature. The ratio between the velocities found is 1.17, which means that the velocity is obviously determined by a diffusion.

During the reaction there is thus a flow of oxygen molecules towards the silver, the latter is subjected to autoxidation and dissolved through the action of the cyanide ions present. In the course of the reaction cyanide ions obviously prevent a catalytic decomposition on the surface of the silver of the hydrogen peroxide formed. In certain cases the decomposition is prevented completely (Fig. 4), in others (Fig. 2) the decomposition commences when a certain low cyanide ion concentration has been reached, dependent on the properties of the silver surface. An explanation of this phenomenon may perhaps be found in the fact that by treatment with a mixture of cyanide ions and hydrogen peroxide the surface area is reduced considerably and all crystalline edges eliminated, so that the sheet is more readily kept covered by cyanide ions, which are adsorbed by the sheet in some way or other.

SUMMARY

Solution of silver in a potassium cyanide solution to which oxygen is being added proceeds according to the equation:

$$2\ Ag + O_2 = 2\ Ag^+ + O_2^{--}$$
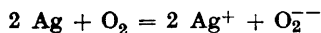
The hydrogen peroxide formed is decomposed on the silver due to a catalytic effect when the cyanide ion concentration is small. The cyanide ion concentration at which this decomposition begins depends on the preliminary treatment

to which the silver sheet has been subjected. The hydrogen peroxide formed takes part in the process of dissolution according to the equation:

$$2 \text{ Ag} + \text{H}_2\text{O}_2 + 4 \text{ CN}^- = 2 \text{ Ag(CN)}_2^- + 2 \text{ OH}^-$$
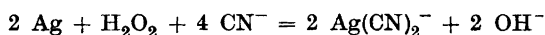
The process of dissolution is of the 1st order with regard to the oxygen pressure and has an activation energy of 3.2 kg cals from 15°C to 25°C. The "activation energy" of the quantity $T/\eta \times K$, where η is the viscosity, is 1.8 kg cals. This seems to indicate that the velocity of the reaction is determined by a diffusion of oxygen molecules towards the silver.

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