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On the Formal Potential of the Ag^{2+}/Ag^{+} Couple in 6.5 m $HClO_4$ Medium at −5 °C

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On the basis of potentiometric titrations with liquid-junction-free cells, consisting of a redox and a glass electrode, the formal potential Ag^{2+}/Ag^{+} in 6.5 m $HClO_4$ at −5 °C has been found to equal 1978 ± 2 mV. This represents a mean value deduced from data covering the $[Ag^{2+}][Ag^{+}]^{-1}$ range 0.005 to 0.1. Experimental conditions, needed to stabilize the Ag^{2+} ion for equilibrium analytical purposes, are described in some detail.

The fundamental properties of the colored silver species, prepared by anodic oxidation or ozonization, were firmly established by Noyes and his collaborators.[1] The oxidation products in acid solutions were identified by these authors as Ag(II), although evidence was presented that, in the solid phase, Ag(III) occurs as well. The formal potential of the Ag^{2+}/Ag^{+} couple in perchloric acid medium was determined in Noyes' laboratory to be as high as 2.00 V, while in a nitric acid medium, where complex formation occurs, it was found to be lower by 0.1 V.

The decomposition of Ag^{2+} was also studied by Noyes' research group.[1] They were able to conclude that the rate determining step is the oxidation of water to hydrogen peroxide. The sluggishness of this reaction is thus responsible for the existence of the Ag^{2+} ion, forming a redox couple with a standard potential which exceeds by far $E°(O_2/H_2O)$.

Silver(II) compounds, especially AgO, have recently received increasing interest as analytical reagents, and they are now commonly employed to solve many difficult problems, following the practical methods described by Lingane and Davis.[2]

No further quantitative study, however, appears to have been reported on any of the numerous redox, complex formation and solubility equilibria in which the silver(II) ion is known to participate. This stagnation is due, to course, to the great instability of Ag^{2+}. When conventionally purified reagents are used, one has to monitor the silver(II) concentration throughout the experiment. Further the high hydrogen ion concentration level, needed to suppress the Ag^{2+} hydrolysis and to avoid the precipitation of AgO or other basic salts, gives rise to high liquid-junction potentials in cells of traditional design.

The present work has been undertaken to find an approach which circumvents these principal experimental difficulties.

METHOD OF INVESTIGATION

Determination of the Ag^{2+}/Ag^{+} formal potential

In the present study we investigated the Ag^{2+}/Ag^{+} redox pair in the ionic medium 6.5 m $HClO_4$ at −5 °C. This proved to be the maximum temperature, where the decomposition of Ag^{2+} could be neglected in our experiments lasting for two-three hours. On the other hand, −5 °C represents the minimum at which a cell containing a glass electrode could be precisely measured with our equipment.

We have chosen perchloric acid as the medium partly to minimize the hydrolysis of Ag^{2+} and partly because it may conveniently be prepared in a state of high purity from perchloric acid dihydrate.[3] A high medium (salt concentration) level is of course unavoidable at low temperatures.

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Silver(II) ions have been generated at −5 °C prior to each series of emf measurements by anodic oxidation at a gold electrode using the cell

$$\mathrm{Ag}\ \Big|\ \begin{matrix}\mathrm{AgClO_4}\ 0.1\ \mathrm{m}\\ \mathrm{HClO_4}\ 6.5\ \mathrm{m}\end{matrix}\ \Big|\ \begin{matrix}\mathrm{HClO_4}\\ 6.5\ \mathrm{m}\end{matrix}\ \Big|\ \text{test solution } \mathrm{S_0}\ \Big|\ \mathrm{Au}$$

which was connected to a constant current supply.

Here S_0 denotes the starting solution:

$$\mathrm{Ag^+}\ m_1,\ \mathrm{H^+}\ (6.5\ \mathrm{m} - m_1),\ \mathrm{ClO_4^-}\ 6.5\ \mathrm{m}$$

while the silver(II) solution arising by oxidation will be represented by S. The symbol m stands for molality (mol $\mathrm{kg^{-1}}$).

Solution S_0 itself was also prepared by electrolysis. A 6.5 m $HClO_4$ solution was placed in the anode compartment of the electrolysis cell, and silver metal, electrolytically precipitated on a platinum net, was then dissolved at room temperature by using current densities of 50 to 100 mA $\mathrm{cm^{-2}}$. The resulting solution was filtered through sintered glass to remove finely divided silver crystals (originating from the disintegration of the anode) as well as all the other floating material.

It is quite difficult to find the optimal conditions for the *generation of* Ag^{2+}. The yield with a gold anode is mainly determined by three variables: The current density, the temperature and the rate of stirring. A high current density and a low temperature enhance the overpotential for oxygen evolution. A vigorous agitation is needed to avoid local overheating and an excess of silver(II) ions in the vicinity of the anode.

As a best compromise, we electrolyzed with 5 mA $\mathrm{cm^{-2}}$ giving a yield of around 70% for an $[\mathrm{Ag^{2+}}][\mathrm{Ag^+}]^{-1}$ ratio not exceeding 0.075. The yield was determined by titration with a standard cerium(III) perchlorate solution.

Usually the $\mathrm{Ag^{2+}/Ag^+}$ ratio could not be raised beyond 0.10 corresponding to a redox potential value which is about 100 mV higher than the formal potential of the H_2O_2/H_2O couple in this medium. Above this threshold the silver(II) concentration remained constant or declined, whatever current was employed.

After having completed the electrolysis, a precooled glass electrode and several additional gold electrodes were immersed into solution S which was then connected to the precooled reference half-cell:

$$\mathrm{Ag|Solution\ S_0|=RE}$$

Two cells have been studied concurrently:

$$-\text{Glass electrode}|\mathrm{S}|\mathrm{Au}+ \qquad \text{(GE)}$$

and

$$-\mathrm{RE}|\mathrm{S}|\mathrm{Au}+ \qquad \text{(R)}$$

The emf of these cells may at −5 °C be put into the form (1) and (2), where $E^\circ(\mathrm{Ag^{2+}/Ag^+})$ denotes the formal (standard) potential sought, $m_{\mathrm{Ag^{2+}}}$, $m_{\mathrm{Ag^+}}$ and $m_{\mathrm{H^+}}$ stand for the molalities * of the $\mathrm{Ag^{2+}}$, $\mathrm{Ag^+}$ and $\mathrm{H^+}$ ions in the test solution S. The potential of the reference half-cell RE is symbolized by E_{RE}, while the concentration independent term in the equation for the half-cell potential of the glass elctrode is represented by E_g^0. Its actual value had to be measured in each experiment (see later).

$$E_{\mathrm{GE}} = E^0(\mathrm{Ag^{2+}/Ag^+}) + 53.21\ \log \frac{m_{\mathrm{Ag^{2+}}}}{m_{\mathrm{Ag^+}} + m_{\mathrm{H^+}}} - E_g^0 \qquad (1)$$

$$E_{\mathrm{R}} = E^0(\mathrm{Ag^{2+}/Ag^+}) + 53.21\ \log \frac{m_{\mathrm{Ag^{2+}}}}{m_{\mathrm{Ag^+}}} - E_{\mathrm{RE}} \qquad (2)$$

In accordance with the conventions generally adopted in equilibrium analysis, we have chosen 6.5 m $HClO_4$ (the background electrolyte) as the standard state. Thus the activity factors of the reacting species approach unity as the composition of the test solution tends to this solvent. Because in our experiment the sum $(m_{\mathrm{Ag^{2+}}} + m_{\mathrm{Ag^+}})$ never exceeded 5% of the perchlorate concentration level, the activity factors could be set to unity in eqns. (1) and (2). For the same reason the liquid-junction potential in cell (R) could be neglected.

To find a *criterion* how far we have succeeded to stabilize the Ag^{2+} ion (which was the main purpose of this work), we calculated on the basis of a comprehensive series of potentiometric measurements the value of the formal (standard) potential, $E^0(\mathrm{Ag^{2+}/Ag^+})$. Its random and systematic variation provides a direct answer to our question.

* In the Swedish chemical literature this concentration unit is often called weight molarity. This term appears to be more expressive and less likely to be confused with molarity which should properly be named as volume molarity.

In our experiments the ratio $m_{Ag2+}m_{Ag+}^{-1}$ was successively diminished by adding portionwise a dilute (0.05 to 0.06 m) cerium(III) perchlorate reagent solution, also containing 6.5 m $HClO_4$. This reducing agent was chosen because even at −5 °C the reaction (3) was found to go instantaneously to completion. A few minutes ensuing the introduction of this reagent the different gold redox electrodes were found to agree within 0.2 to 0.3 mV, and then the E_R value declined slowly with a rate of about 1 mV/h as before the addition.

$$Ce^{3+} + Ag^{2+} \rightarrow Ce^{4+} + Ag^{+} \quad (3)$$

The emf measurements were carried out as potentiometric titrations which also served to determine the starting value of the Ag^{2+} concentration in solution S.

The *equivalence point* of the cerium(III) titration was evaluated by a Gran − type[4] extrapolation. Because the densities of the reagent and the silver test solutions differed but little (both may approximately be regarded as 6.5 m $HClO_4$) the Gran function[4] could be calculated in molality terms, the two units (m and M) being proportional to each other.

The equivalence points derived by the E_{GE} and E_R data never differed more than a few tenths of one percent. A Gran function[4] was also constructed from the emf measurements beyond the equivalence point where the Ce^{4+}/Ce^{3+} couple determines the redox potential. Somewhat lower silver(II) contents were now obtained, differing, however, at most only by one percent from the results deduced from the Ag^{2+} side of the titration.

Once the equivalence point was ascertained, the differences $(E^0(Ag^{2+}/Ag^{+}) - E_g^0)$ and $(E^0(Ag^{2+}/Ag^{+}) - E_{RE})$ could be calculated for each point of a series.

To evaluate the *formal (standard) potential* itself, we measured also prior to and following each potentiometric titration the emfs of the cells

$$Pt, H_2(p_{H_2})|HClO_4\ 6.5\ m|glass\ electrode + \quad (GH)$$

$$E_{GH} = E_g^0 + 26.61 \log p_{H_2} \quad (4)$$

and

$$Pt, H_2(p_{H_2})|HClO_4\ 6.5\ m|RE + \quad (RH)$$

$$E_{RH} = E_{RE} + 26.61 \log p_{H_2} - 26.61 \log m_{H+}^2 \quad (5)$$

With the help of the vapor pressure[5] and enthalpy of dilution[6] data reported in perchloric acid solutions, we estimated that the water vapor pressure in these cells at −5 °C does not exceed 2 Torr. Thus p_{H_2} could be set equal to the actual barometric pressure.

The results of all our calculations are illustrated in Fig. 1. This shows $E^0(Ag^{2+}/Ag^{+})$ as a function of log m_{Ag2+}/m_{Ag+} for the six silver concentration levels studied, ranging from 0.087 to 0.315 m.

Fig. 1 illustrates that with the emf data of the

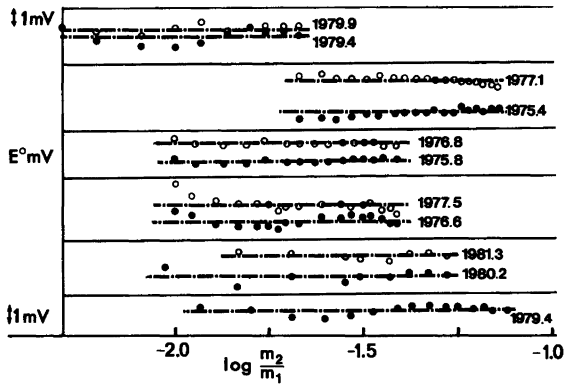

Fig. 1. The standard (formal) potential, $E^0(Ag^{2+}/Ag^{+})$, as a function of log m_{Ag2+}/m_{Ag+} at different total silver concentration, $(m_{Ag2+} + m_{Ag+})$, levels. The circles represent the E^0 values from the E_{GE} and the dots from the E_R data. The total silver concentration diminishes from the uppermost to the lowest sector in succession: 0.315, 0.283, 0.227, 0.170, 0.111 and 0.087 m. The horizontal lines symbolize the labelled average $E^0(Ag^{2+}/Ag^{+})$ values.

present precision, no systematic deviation in $E^0(Ag^{2+}/Ag^+)$ can be detected as the main variable $\log [Ag^{2+}]/[Ag^+]$, which is proportional to the redox buffer capacity, sweeps from its minimum -2.2 to its maximum -1.

Hence we suggest as the most probable estimate for the formal (standard) potential the mean of the means of the individual series which are labelled in Fig. 1:

$$E^0(Ag^{2+}/Ag^+) = 1978 \pm 2 \text{ mV} \quad (6)$$

This uncertainty limit is seen to cover the glass electrode as well as the silver reference half-cell data.

Our result (6) is entirely consistent with the final conclusion of the Noyes' group. These investigators[1] estimated with a quite different technique that $E^0(Ag^{2+}/Ag^+)$, in the ionic medium 4 M (5 m) $HClO_4$, is 2000 mV at 25 °C and 1982 mV at 0.2 °C.

We calculated from these data, by assuming the standard enthalpy change for $Ag^{2+} + \frac{1}{2}H_2 \rightarrow Ag^+ + H^+$ to remain constant in the temperature range -5 to 25 °C, that $E^0(-5\,°C, 5\text{ m } HClO_4)$ is 1978 ± 3 mV. This excellent agreement is of course accidental but the compatibility with the classical data inspires some confidence to our simple approach.

We have also calculated in the same manner the *formal* (apparent standard) *potential of the* Ce^{4+}/Ce^{3+} *couple* from the E_{GE} and E_R measurements beyond the equivalence point, and obtained the estimate $E^0(Ce^{4+}/Ce^{3+}) = 1751 \pm 2$ mV.

This value is not far from the results deduced for this couple at 25 °C by our predecessors. Conley[7] has suggested the value of 1743.1 mV for $E^0(Ce^{4+}/Ce^{3+}, 1\text{ M } HClO_4)$, while Sherill[8] and his collaborators concluded that $E^0(Ce^{4+}/Ce^{3+}, 2.4\text{ M } HClO_4)$ is 1731 mV.

Sherill's research group[8] has also found evidence that the Ce^{4+} ion represents an acid of such a high strength that its protolysis cannot be safely neglected even at our acidity and temperature level. Baes and Mesmer[9] presented recently a survey of this question and corroborated Sherills main conclusions.[8] Thus until new light is cast on this problem our estimate should be regarded as a conditional constant only.

This difficulty does not arise with Ag^{2+}. Spectrophotometric[10,11] and kinetic[1] evidence has been offered that its protolysis may be regarded as negligible for a perchloric acid concentration exceeding 3 M.

Comparison of the glass with hydrogen and silver half-cells

On the basis of the agreement which was found in the preceding section between the E^0 values originating from the E_{GE} and E_R data, we may infer that it is a close approximation to express the half-cell potential of the glass electrode by the equation:

$$E_g = E_g^0 + 53.21 \log m_{H^+}\gamma_{H^+}$$

where E_g^0 is an isothermal constant and γ_{H^+} stands for the activity factor of hydrogen ion.

Because of the great value the glass electrode represents in this type of work, we decided to study its behavior *directly* under our rather special experimental conditions.

Two main types of error may arise.

At a temperature as low as -5 °C the glass electrode resistance rises to 10^{10} Ω (*cf.* the Experimental section). As a consequence, insufficient isolation may cause leakage currents which falsify the emf determination.

Moreover, as the acidity is made to exceed about 1 M, the glass electrode exhibits growing deviations from the hydrogen half-cell. This discrepancy, the "acid error", may attain as much as 6 mV in a 3 M HCl solution.[12]

The results now to be described illustrate that these principal sources of error are negligible with electrodes prepared from modern glass types and when an electrometer, functioning as an impedance converter only, is employed for the emf measurements.

To examine this question in detail, we measured with a Cary electrometer of type 401 the emf of the cell:

$$-\text{Pt, } H_2(p)|H^+\ h,\ Na^+ \text{ or } Li^+\ (5M-h),\ ClO_4^-\ 5\ M|\text{glass electrode}+ \quad (G)$$

as a function of h both at 25 °C and at -5 °C. The hydrogen ion concentration of the test solution was varied in several ways.

In the majority of cases we introduced successively small portions of purified and dried $NaHCO_3$ or Na_2CO_3 crystals. This method was especially convenient at -5 °C, since the complication associated with the cooling of the

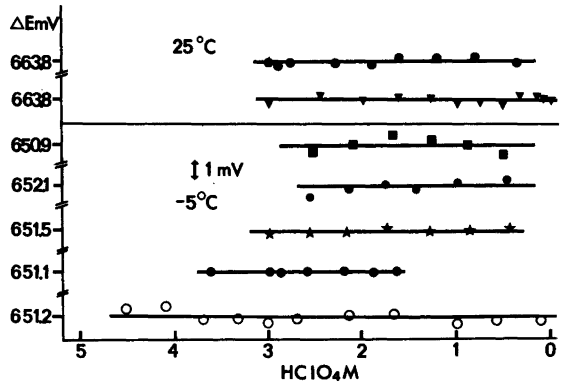

Fig. 2. Comparison of glass and hydrogen half-cells. The emf of cell (G) as a function of hydrogen ion concentration in several perchlorate media. Upper part: 25 °C, lower part: −5 °C. The different symbols denote individual series of measurements. The horizontal lines represent the average E_G values. Symbols from top to the low edge: (1), ●, alkalification with $NaHCO_3$; (2), ▼, with 3 M NaOH; (3), ■, with Na_2CO_3; (4), ●, with Na_2CO_3; (5), ★, with Na_2CO_3; (6), ●, dilution with 3.5 m $LiClO_4$ and (7), ○, alkalification with 5 M NaOH.

reagent solutions could be eliminated. A few experiments were also made by adding 5 M NaOH and also by diluting the 3 M $HClO_4$ solution with 3 M $LiClO_4$.

With the help of the vapor pressure [5] and of the enthalpy of dilution [6] data reported for these concentrated perchloric acid and alkali perchlorate solutions at 25 °C, we may estimate that the vapor pressure change, occurring upon neutralization, gives rise at both temperatures to a correction term lower than 0.1 mV in the potential of the hydrogen half-cell. This correction could therefore be neglected.

The result of our E_G *measurements are graphically represented in Fig. 2.* This diagram shows the emf of cell (G) to remain uninfluenced to within the experimental uncertainty as the hydrogen ion concentration is diminished from 5 M to less than 10^{-3} M. The spread of the $E_G(h)$ data around the mean is seen to be as low as ±0.2 mV at 25 °C, while it rises to ±0.5 mV at the lower temperature.

Hence we may conclude that in perchlorate media the acid error is unappreciable. As a consequence, the deviations found by Buchböck,[13] MacInnes and Belcher,[14] Dole [12] and others cannot be explained by a change occurring upon acidification in the chemical potential of one of the species participating in the electrode reaction, but rather by a special property of the glass type used by these investigators. This conclusion is in accordance with the classical study of Hubbard *et al.*[15]

The sluggish response of our hydrogen electrodes at −5 °C requiring an equilibration period of at least an hour, rendered these E_G measurements quite difficult.

A more convenient check on the glass electrode behavior, however, could be obtained by studying instead the emf of the cell:

glass electrode|Ag^+ *B*, H^+ (6.5 m − *B*),
ClO_4^- 6.5 m|Ag+ (B)

which has always been found to reattain equilibrium within 15 min.

The emf of cell (B) may at −5 °C be put into the form:

$$E_B = E_B^0 + 53.21 \log m_{Ag^+}/m_{H^+}$$

where $E_B^0 = E_{Ag}^0 - E_g^0$ represents an isothermal constant, provided the glass electrode may be regarded to be equivalent with the hydrogen half-cell.

In each series of experiments the sum $E_B + 53.21 \log m_{H^+}/m_{Ag^+}$ has proved to remain unaffected to

Table 1. A series of E_B measurements at -5 °C. Determination of E_B^0.

E_B mV	$-\log \frac{m_{Ag^+}}{m_{H^+}}$	E_B^0 mV
26.8	1.299	95.9
25.4	1.326	96.0
24.0	1.351	95.9
22.7	1.375	95.9
21.6	1.397	95.9
20.5	1.417	95.9
18.5	1.457	96.0
16.2	1.491	95.5
15.6	1.507	95.8
14.9	1.523	95.9
14.0	1.537	95.8
13.4	1.553	96.0
12.8	1.565	96.1
12.1	1.578	96.1
11.4	1.591	96.1
10.2	1.614	96.1
9.2	1.637	96.3

within a few tenths of a mV, when the ratio m_{H^+}/m_{Ag^+} was made to vary within wide limits. This conclusion is illustrated in Table 1 by a short series of measurements.

Conclusions

The results of this preparatory work appear to show, that under the present experimental conditions, the standard methods of equilibrium analysis may be applied to study the Ag^{2+} ion. The hydrolysis of this ion and of two other strong oxidizing agents, Co^{3+} and Ce^{4+}, is now being investigated in these laboratories. The conclusions concerning their protolysis will form the subject of forthcoming communications.

EXPERIMENTAL DETAILS

Materials

The *solvent* 6.5 m $HClO_4$ has been prepared from perchloric acid dihydrate crystals as described earlier.[3] The resulting solutions were analyzed by titration against a purified $KHCO_3$ preparation.

Cerium(III) perchlorate reagent solutions have been made by fuming with azeotropic perchloric acid a solution of cerium chloride heptahydrate crystals which were first purified by recrystallization from water.

The chloride-free stock solution was analyzed for cerium(III) by oxidizing in an aliquot Ce^{3+} to Ce^{4+} by ammonium peroxodisulfate following the procedure suggested by Gleu.[16]

As the hydrolysis of Ce^{3+} is negligible[17] for pH < 5, the proton excess in the cerium perchlorate stock could be directly determined by titration with an NaOH solution using methyl red as indicator.

Silver(I) perchlorate solutions were prepared *in situ* by electrolysis, their silver content was determined by titration with a standard ammonium thiocyanate solution using Volhard's method.

A short comment on the *analysis of Ag(II) solutions* is perhaps appropriate here.

Iodometry proved to be inconvenient because a great iodide excess must be introduced to keep the silver iodide in solution, and thereby strictly anaerobic conditions must be kept to avoid air oxidation during the titration.

Thallium(I) perchlorate reacts slowly and its solubility in 6.5 m $HClO_4$ is very low.

With iron(II) as reductometric reagent, we obtained large errors because at room temperature a variable and uncontrollable part of the Ag^+ ions is rapidly reduced to metallic silver.

Cerium(III) seems to be the most suitable reducing agent, it was always found to provide precise and accurate data to within 1%.

Gold electrodes, which in accordance with Lingane's and Davies' results[2] have proved to be superior to platinum, were made by cathodically precipitating from a potassium tetracyanoaurate-(III) solution a thin layer of gold onto a platinum foil. In each experiment, several gold electrodes were immersed into the test solution; they never deviated more than 0.5 mV from each other.

Platinized platinum and silver electrodes were prepared by electrolysis according to the prescriptions of Harned[18] and Brown,[19] respectively.

On the rate of decomposition of the Ag^{2+} ion. We measured at -5 °C the decline of the emf of the cells (GE) and (R), E_{GE} and E_R, with test solutions in which the perchloric acid concentration was kept at

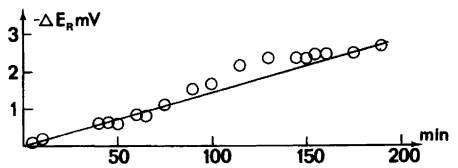

Fig. 3. The emf of cell (R), E_R, as a function of time with a solution of initial composition: Ag^{2+}: 0.011, Ag^+: 0.137, H^+: 6.4 and ClO_4^-: 6.5 m. Temperature -5 °C. The line represents the equation: $E_R(t) - E_R(\text{zero}) = \triangle E_R(\text{mV}) = -0.014\ t(\text{min})$.

the 6.4 m and the silver(I) perchlorate concentration at the 0.137 m level, while the initial silver(II) concentration, $[Ag^{2+}]_0$, was made to vary from 0.0025 to 0.011 m. As these $[Ag^{2+}]_0$ values were chosen to lie so far below the concentration of perchloric acid and silver perchlorate, the hydrogen and silver(I) concentration increase, concomitant with the Ag^{2+} decomposition, could be entirely neglected.

In each experiment we monitored for two to three hours the $E_{GE} = E_{GE}$ (time) and $E_R = E_R$ (time) values that were found to diminish during this period by two to four mV, corresponding to a reduction of $[Ag^{2+}]$ by 8 to 16%.

A typical series with $[Ag^{2+}]_0 = 0.011$ m is illustrated in Fig. 3. The rate of redox potential diminishment has proved in each case to increase somewhat as the instantaneous Ag^{2+} concentration slowly declined. Often this acceleration exceeded just barely the experimental uncertainty of 0.1 to 0.2 mV h^{-1} in $\frac{dE_R}{dt}$.

The rate of initial decrease for the three most carefully organized experiments gave the following data:

$[Ag^{2+}]_0$m	0.011,	0.007,	0.0025
$\left(\frac{dE_R}{dt}\right)_0$ mV/h	-0.80 ± 0.1,	-1.5 ± 0.2,	-2.6 ± 0.3

Thus the rate of redox potential decline is increased sharply by dilution. Moreover, the product $[Ag^{2+}]_0 \left(\frac{dE_R}{dt}\right)_0 = k$ appears to remain uninfluenced by the silver(II) concentration value started with. One obtains with these data the k values (mV h^{-1} m): -0.009, -0.0105 and -0.007. This result may be interpreted so that the most probable k value is -0.009 (mV h^{-1} m) with an uncertainty of ±0.002 units.

We have to recall now that the silver(I) concentration was kept virtually constant in these experiments. Consequently dE_R/dt may be set equal to 23.10 $[Ag^{2+}]^{-1}$ d $[Ag^{2+}]/dt$, thus $k = 23.10$ $d[Ag^{2+}]/dt$.

We would like to suggest on the basis of these measurements that the decomposition of Ag^{2+} is kinetically of the zero order. The reduction of this ion appears to be a heterogeneous reaction occurring mainly on the surface sites of the material the solution comes into contact with.

This conclusion is in accordance with the experience that we gathered in this project. Unless the test solution is made carefully dust-free by filtration and kept protected, the life-time of a strong oxidizing agent, as Ag^{2+}, Ce^{4+} or Mn^{3+}, will be very short, even when the hydrogen ion concentration is high and the temperature is low.

Equipment

All the emf measurements were carried out in a large (50 litres) *glycerine-ethanol (volume ratio 5:1) bath* kept at -5.0 ± 0.1 °C. The temperature was measured with a calibrated Beckmann thermometer. The vigorously agitated bath has been thermostated by a cooling and a heating element which were activated by a relay.

The emfs of our cells were determined by a Cary 401 *electrometer* of the Varian Company. It was periodically checked with a standard cell connected in series with resistors ranging from 10^8 to 10^{12} Ω. The output of the electrometer was read by a digital voltmeter of the Dynamco Company.

The (direct current) *resistance* of the cells containing a glass electrode was determined by measuring with a Keithley electrometer of type 640, the potential drop cells (GE) and (GH) generated in a resistor (of 100 to 1000 megohms) as well as the emfs themselves.

At -5 °C we obtained as much as (9.8 ± 1) 10^9 Ω, while the cell resistance dropped to (2.3 ± 0.1) 10^8 Ω at 25 °C. This value is quite close to the 200 M Ω specified for type 39000 glass electrode by the manufacturer, the Beckman Company.

In each experiment several resistors were employed which furnished consistent results, indicating the absence of serious systematic errors. Moreover, the measurement cycle was in each case renewed several times, but no hysteresis was detected. Thus the minute currents drawn from cells (GE) and (GH) do not cause any appreciable polarization.

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