

On the Formal Potential of the $\text{Co}^{3+}/\text{Co}^{2+}$ Couple at -5°C in 6.5 Molal HClO_4 Medium

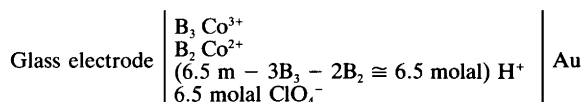
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Biedermann, G., Orecchio, S., Romano, V. and Zingales, R., 1986. On the Formal Potential of the $\text{Co}^{3+}/\text{Co}^{2+}$ Couple at -5°C in 6.5 Molal HClO_4 Medium. - Acta Chem. Scand. A40: 161-167.

In order to establish the formal potential, $E^{\circ'}$, of the $\text{Co}^{3+}/\text{Co}^{2+}$ couple, the e.m.f. of the cell:



was studied at -5°C as a function of the $\text{Co}^{3+}/\text{Co}^{2+}$ ratio in the range 0.1 to 4. The comprehensive set of redox potential data, covering the Cobalt(III) concentration interval 0.01 to 0.15 molal, may be explained with $E^{\circ'}$ ($I=6.5\text{molal}, -5^\circ\text{C}$) = $1841 \pm 2 \text{ mV}$.

A simple method is described to prepare pure and stable Cobalt(III)perchlorate solutions. No evidence has been found for the formation of dimeric Cobalt(III) species.

The standard potential at 25°C , $E^\circ(\text{Co}^{3+}/\text{Co}^{2+}, I=0)$, has been estimated on the basis of calorimetric data and the specific interaction theory to be $1.88 \pm 0.01 \text{ V}$.

The $\text{Co}^{3+}/\text{Co}^{2+}$ couple was first studied systematically in 1937 by Noyes and Deahl.¹ These investigators established that the cobalt redox pair, in nitric acid solutions, affords constant and reproducible potentials satisfying the criteria of reversibility. This requirement is especially easily fulfilled in the presence of the potential mediator Ag^+ , which forms some Ag^{2+} with Co^{3+} .

Noyes and Deahl¹ found the formal redox potential, $E^{\circ'}$, to be a function of the nitric acid concentration of the medium, which was made to increase from 1 to 4 M. This trend is difficult to explain as their cells contained a liquid junction e.m.f. of unknown magnitude. The estimates $E^{\circ'}$ (25°) = $1.84 \pm 0.01 \text{ V}$ and $E^{\circ'}$ (0°) = $1.81 \pm 0.01 \text{ V}$ cover all their data. These formal potentials are in reasonable agreement with the conclusions of the pioneers Jahn² and Lamb and Larson³,

who found 1.785 V and 1.817 V respectively by studying sulfate solutions.

The classic results of these researchers have recently been subjected to some criticism as discussed below.

The first line of objections is based on kinetic arguments. The mechanism of water and peroxide oxidation by cobalt (III) ions has been studied by several authors.^{1,4} It appears that the main part of the kinetic data may simply be explained by postulating the dimerization equilibrium: $2 \text{Co(III)} \rightleftharpoons [\text{Co(III)}]_2$.

This question was examined by Warnquist⁵ in 1970. He presented a few series of redox potential measurements in perchlorate media that clearly contradict the dimerization hypothesis.

In connection with a new kinetic investigation, Wells and Fox raised doubts concerning the validity of Warnquist's results.⁵ His use of silver ion as potential mediator was claimed to influence the

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mechanism of the establishment of the final redox potential value which is obtainable with gold electrodes. It is obvious, however, that, from the point of view of the thermodynamics, the route by which an equilibrium is attained is entirely immaterial.

The other type of criticism arises from the investigations of Rotinjan, Borisowa and Boldin⁶ who, since 1961, have repeatedly investigated the solubility and redox equilibria of freshly precipitated CoOOH. They found⁶ that their measurements in neutral and alkaline media may be best explained by assuming E° ($\text{Co}^{3+}/\text{Co}^{2+}$) to be as low as 1.4–1.5 V. Rotinjan and colleagues tried to corroborate⁶ this somewhat surprising conclusion by calorimetric and electrode kinetic arguments.

This discrepancy in E° , compared with the classic results, can likely best be explained by these investigators⁶ neglect of several serious sources of errors. Sulphate complex formation and the hydrolysis of Co^{3+} as well as Co^{2+} were ignored. No attention was paid either to the decomposition of the Cobalt (III) ion or to the uncertainty inherent in the chemical potential of a colloidal precipitate as CoOOH. Their method⁶ of preparing Iron(II) perchlorate solutions, for instance, is known to give rise to chloride ion formation. This side reaction is probably the main reason for the deviation between the calorimetric data of Rotinjan *et al.*⁶ and those of Johnson and Sharpe.⁷

Hence we must regard the conclusion of these investigators⁶ with skepticism, until evidence is presented that these experimental imperfections have been eliminated.

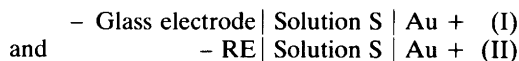
Method of investigation

We sought to ascertain the $\text{Co}^{3+}/\text{Co}^{2+}$ formal potential by adopting the approach which we developed for the study of the $\text{Ag}^{2+}/\text{Ag}^+$ couple⁸. In both cases the stabilization of the test solution represents the main problem. Because of this requirement, the measurements must be carried out at high acidities and at low temperatures. As a consequence, accurate e.m.f. data may be most readily obtained by employing a liquid junction-free cell technique.

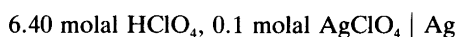
In short, we performed the work at -5°C and as ionic medium we chose 6.5 molal (5M at 25°C) HClO_4 . The reference state has accordingly been

so defined that the activity coefficients tend to unity as the composition of the test solution approaches 6.5 molal HClO_4 .

The formal potential was investigated by studying the e.m.f. of the cells:



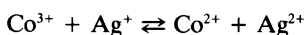
as a function of the $[\text{Co}^{3+}]/[\text{Co}^{2+}]$ ratio in a wide $[\text{Co}^{3+}]$ range. In the cell diagram, S stands for a test solution of the general composition: $\text{B}_3 \text{Co}^{3+}$, $\text{B}_2 \text{Co}^{2+}$, T Ag^+ , $(6.50 - 3\text{B}_3 - 2\text{B}_2 - \text{T} \cong 6.5 \text{ molal})\text{H}^+$, 6.50 molal ClO_4^- and RE stands for the reference half cell:



Silver ions were added, following Noyes and Deahl¹, as mediators to promote the attainment of a reversible redox potential, despite the inertness of the Co^{3+} ion. The ratio $[\text{Ag}^+]/([\text{Co}^{3+}] + [\text{Co}^{2+}])$ was made to vary between the limits 0.02 and 1; this variation was necessary in each case to obtain a reversible redox potential almost instantaneously upon the addition of a reagent solution.

In the absence of Ag^+ , gold electrodes, which were immersed into the same test solution, were often found to differ by as much as 100 mV. However, as a drop of an Ag^+ solution was added, the difference dropped immediately (as soon as the measurements could be made) to about 1 mV, and then it declined further to a few tenths of a mV.

We checked, by taking into account the equilibrium constant for



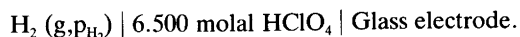
$K = 2.6 \cdot 10^{-3}$, that the establishment of this equilibrium in S did not appreciably affect the stoichiometric Co^{3+} and Co^{2+} concentrations; thus no correction was necessary.

A scrutiny of all our e.m.f. data (about 200) furnishes evidence that the value of the mediator Ag^+ concentration has no effect on the accuracy of the present measurements. No correlation could be found between the formal potential value calculated from eqns. (1) and (2) and the $[\text{Ag}^+]/([\text{Co}^{3+}] + [\text{Co}^{2+}])$ ratio.

The e.m.f. of cell (I) may at -5°C be described by the following equation:

$$E_I = E^{\circ'} + 53.2 \cdot \log (m_{\text{Co}^{3+}} / (m_{\text{Co}^{2+}} \cdot m_{\text{H}^+})) - E_G^{\circ} \quad (1)$$

where E_G° represents the concentration independent term in the expression for the half-cell potential of the glass electrode. In each experiment, its exact value, which varies slowly with time, was determined prior to a series of redox potential measurements by comparison with the hydrogen electrode in the cell:

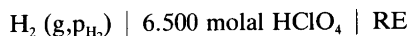


The details of this type of e.m.f. determination have been described in a previous article⁸.

The e.m.f. of cell (II) may at -5°C be described by the eqn.

$$E_{II} = E^{\circ'} + 53.2 \log (m_{\text{Co}^{3+}} / m_{\text{Co}^{2+}}) - E_{RE} \quad (2)$$

where E_{RE} represents the potential value of the RE half-cell. This E_{RE} value was determined, as was also E_G° , by comparison with the hydrogen electrode in the cell:



As the impedance of our glass electrode was at -5°C found to be as high as $10^{10} \Omega$, we felt it desirable to check its performance continuously, because a minute charge redistribution under these experimental conditions may give rise to a serious error.

Accordingly, in each series of measurements we also determined the e.m.f. of the cell:



$$E_{III} = E_{RE} - E_G^{\circ} - 52.21 \log m_{\text{H}^+} \quad (3)$$

Since the Ag^+/Ag electrode is as reliable at -5°C as at 25°C , and the hydrogen ion concentration changed but little, and consequently the liquid junction e.m.f. remained negligibly small, $E_{III} + 53.2 \log m_{\text{H}^+}$ should remain constant, when the redox potential in S is made to vary. This condition was found to be verified in each experiment and with each glass electrode to within $\pm 0.2 \text{ mV}$.

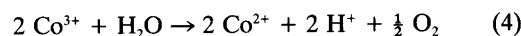
As usual, the e.m.f. measurements with cells (I) and (II) were carried out as a potentiometric titration. A cobalt (II) perchlorate reagent solution was added stepwise to the starting cobalt (III) perchlorate - rich solution, both having been adjusted with HClO_4 to the perchlorate mo-

lality level 6.50. This simple method was chosen because no reducing agent could be found which would react rapidly with Co^{3+} at -5°C . Fe^{2+} , VO^{2+} , Hg_2^{2+} and oxalic acid were tried.

When a small portion of a cobalt (II) perchlorate reagent solution was added, the redox potential in cells (I) and (II) was found to diminish, first rapidly, and in about ten minutes a value was attained, which then slowly declined further with a rate of $0.1\text{--}0.2 \text{ mV/h}$ for many hours or as long as we cared to measure.

In the first period of rapid change, the gold electrodes are brought to equilibrium with the new test solution, and the small temperature difference due to the addition is levelled off. The e.m.f. value at the end of the first period was used to calculate $E^{\circ'}$.

The decline in the second period is due to the decomposition of Co^{3+} by water:



The influence of this reaction on the $E^{\circ'}$ determination was negligible because a series of measurements, comprising about twenty points, could

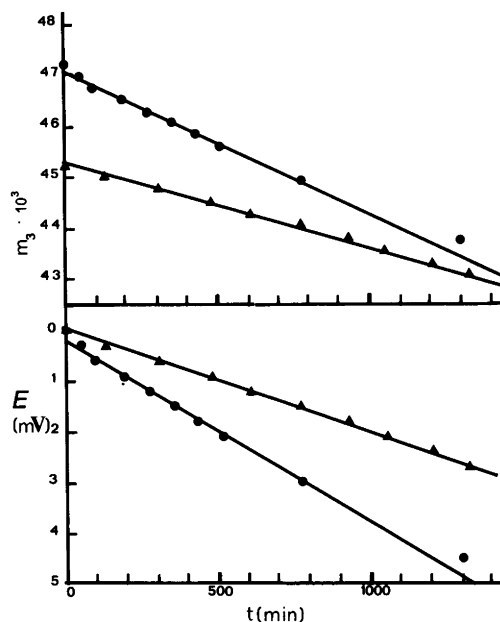


Fig. 1. Lower part: Decay ($E_t - E_0$) of the E_t value versus time. Upper part: The corresponding decrease of Co(III) molality. Dots refers to $[\text{Ag}]_T = 0.051 \text{ molal}$, triangles to $[\text{Ag}]_T = 0.020 \text{ molal}$.

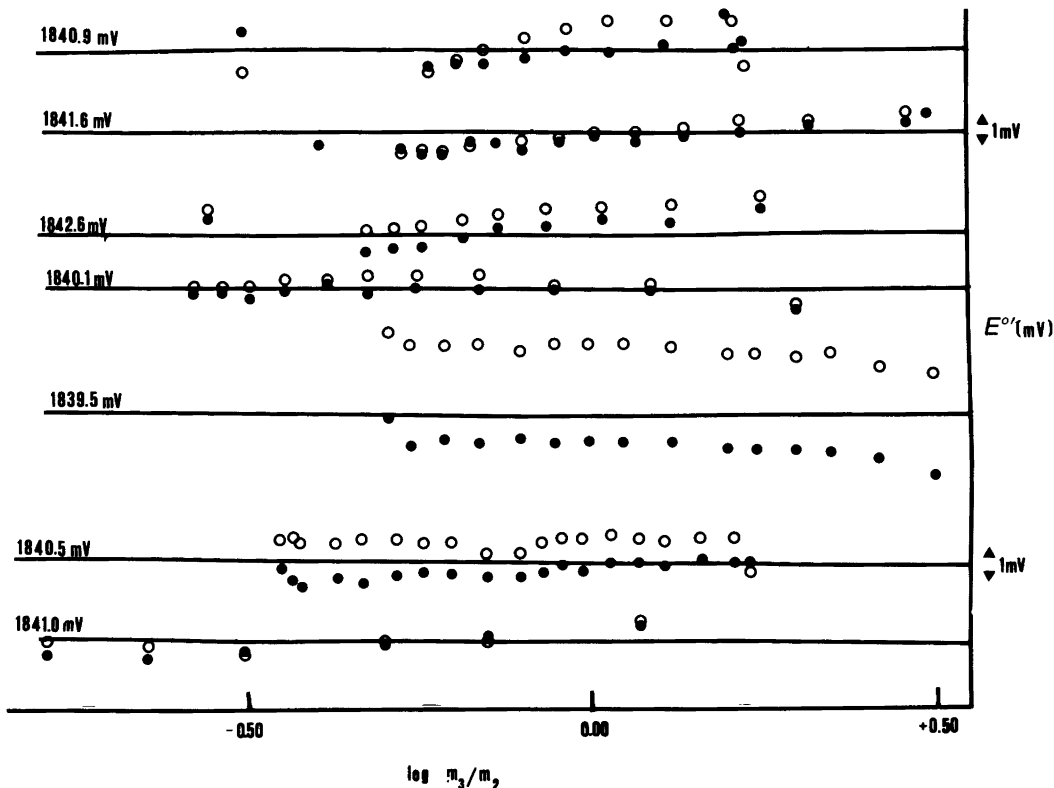


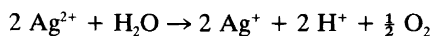
Fig. 2. The formal potential $E^{\circ}(\text{Co}^{3+}/\text{Co}^{2+})$ as a function of $\log m_3/m_2$ at different total cobalt concentration levels. The circles represent the E° values from E_j , and the dots from the E_i data. The total cobalt concentration is ranging between 0.2 and 0.05 molal. The horizontal lines symbolize the labelled average $E^{\circ}(\text{Co}^{3+}/\text{Co}^{2+})$ for each titration.

be finished in 3 to 4 h. In this time the redox potential diminished because of reaction (4) by about 0.5 mV, corresponding to a 2% decrease in the $[\text{Co}^{3+}]$. Often the two or three gold electrodes immersed into the same solution differed by as much as 0.2 mV, but in some cases the difference rose to 1 mV.

Nevertheless, at the end of each series, the test solution was left to stand for 2–3 h. Then a sample was analyzed for the actual $[\text{Co}^{3+}]$ and E° was evaluated with the new analysis results. This value agreed with E° data of the main series to within one mV.

These arguments are illustrated in Fig. 1, which shows the decline of the redox potential and of the $[\text{Co}^{3+}]$ in two typical experiments. The difference in the rate is due to the variation of the Ag^+ mediator concentration. The higher the

$[\text{Ag}^+]$ was chosen, the more rapid was the decline. Hence reaction (4) occurs mainly *via* the mediator:



By this means the equilibrium $\text{Co}^{3+} + \text{Ag}^+ \rightleftharpoons \text{Co}^{2+} + \text{Ag}^{2+}$ is disturbed, leading to a decrease of the Co^{3+} concentration. This view is in agreement with the generally experienced redox inertness of the Co^{3+} ions.

In the preliminary phase of this work, we also studied the reactions $\text{Ag}^{2+} + \text{Co}^{2+} \rightleftharpoons \text{Ag}^+ + \text{Co}^{3+}$ and $\text{Co}^{3+} + \text{Ce}^{3+} \rightleftharpoons \text{Co}^{2+} + \text{Ce}^{4+}$ by potentiometric titrations. However, at -5°C these redox equilibria were found to be established very slowly, especially in the vicinity of the equivalence point. As a consequence, only a small part

of the Gran diagram⁹ could be used for the analysis and for the evaluation of $E^{\circ}(\text{Co}^{3+}/\text{Co}^{2+})$. Both sets of redox potential data – obtained with closely agreeing Pt and Au electrodes – may be explained by assuming $E^{\circ} = 1832 \pm 5$ mV. This imprecise estimate almost coincides with our final value.

Results and discussion

The final series of redox potential measurements with cells (I) and (II), comprising more than 200 points, are represented graphically in Fig. 2, which shows E° as a function of $\log m_3/m_2$ as deduced from the measurements with cells (I) and (II); here m_3 stands for Co^{3+} molality and m_2 for Co^{2+} molality.

As can be seen, in several cases the $[\text{Co}^{3+}]/[\text{Co}^{2+}]$ ratio varied by a factor of 10. The E_I and E_{II} data cover the $[\text{Co}^{3+}]$ range 0.015 to 0.170 molal and the $[\text{Co}^{3+}]/[\text{Co}^{2+}]$ interval 0.1 to 4.

In each experiment, the magnitude of the formal redox potential E° is recognized to exhibit a random variation with $\log m_3/m_2$ and the maximum deviation from the arithmetic mean does

not exceed 1 mV, which may be regarded as resulting from the uncertainty of the E_I and E_{II} measurements. Moreover, the indicated means of the individual series also vary randomly, and the maximum deviation from the grand average is only somewhat greater than the corresponding deviations in the individual series from their individual means. In the absence of any evidence for a systematic trend, we would suggest the mean of the individual series which are labelled in Fig. 2 as the most probable value for the formal potential

$$E^{\circ} (6.5 \text{ molal HClO}_4, -5^{\circ}\text{C}) = 1841 \pm 2 \text{ mV} \quad (5)$$

This estimate of uncertainty represents the maximum error covering all our results.

In view of the controversy concerning the dimerization of cobalt (III) ions, which has been going on for many years, a plot of E° versus $\log [\text{Co}^{3+}]$ is shown in Fig. 3. Obviously, with data of the present precision, no dimers can be detected. If dimers were formed in appreciable amounts, a plot of this kind should exhibit a monotonously decreasing function.

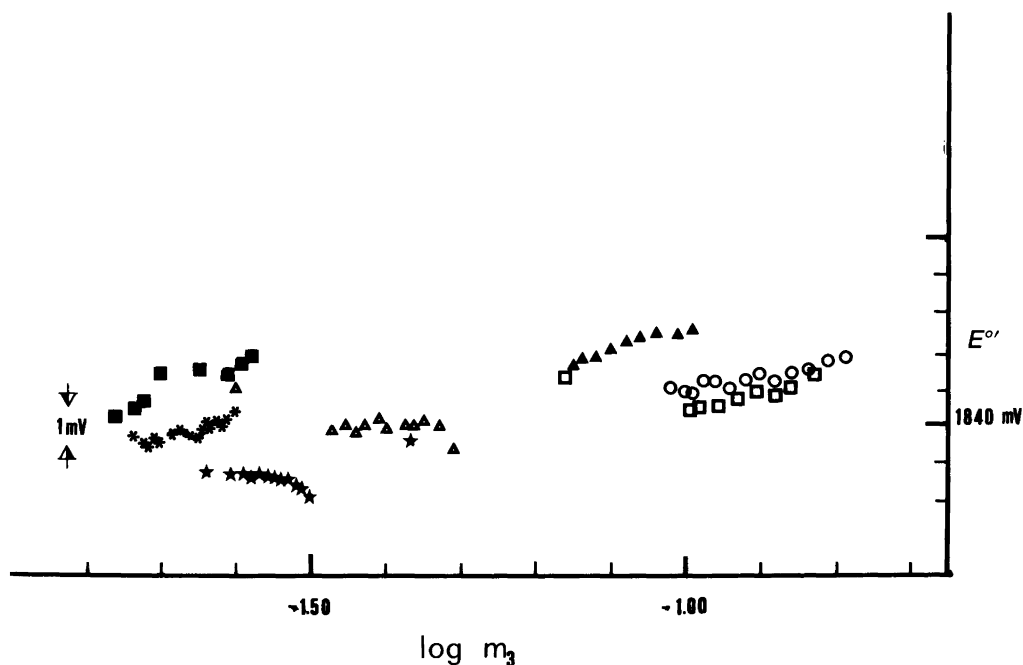


Fig. 3. Plot of the formal potential E° against $\log m_3$ (m_3 — Co^{3+} molality). The different symbols refer to seven different experiments.

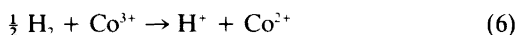
Hence our measurements are in complete agreement with Warnquist's conclusions,⁵ who has also been unable to find dimers.

It is difficult to compare our results – eqn. (5) – with those of the previous investigators. Noyes and Deahl studied at 0°C the redox potentials in 3 and 4 M nitric acid.¹ Warnquist⁵ published some redox potential data in NaClO₄ medium at 3°C; however the large liquid junction potential in his cell makes the conclusion uncertain.

Estimate of the standard potential at 25°C

Obviously it would be of great practical interest to get an idea of the Co³⁺/Co²⁺ standard potential at the ionic strength I = 0 at 25°C so as to put it in a proper relation to the great number of other data obtained under similar conditions.

To this end, we first estimated the enthalpy change of the cell reaction



to be –8.56 kJ/mol and obtained, by using the Gibbs – Helmholtz equation, E° (I=6.5 m HClO₄, 25°C) = 1873 mV. The reaction enthalpy estimate is based on Johnson and Sharpe's measurements in 4M HClO₄ medium⁷ and Fontana's data¹⁰ in 0.5 M HClO₄ medium. As the enthalpies of dilution of strong electrolytes are rather small, no serious error is likely to arise by this neglect of the ionic strength dependence.

This conclusion is supported by comparison of our enthalpy value with the reaction enthalpies for (6) in 3 and 4M HNO₃, which are derivable from Noyes and Deahl's e.m.f. data¹ to be –7.9 kJ/mol.

Next, we employed the specific interaction theory¹¹ to calculate the medium effect in 6.5 m HClO₄. The interaction coefficient for H⁺–ClO₄[–] was taken from Robinson and Stokes' tables,¹² for Co²⁺–ClO₄[–] from the isopiestic measurements of Libus and Sadowska.¹³ The interaction coefficient $\epsilon(\text{Co}^{3+}\text{--ClO}_4^-)$ was assumed to equal $\epsilon(\text{Fe}^{3+}\text{--ClO}_4^-)$ which was previously estimated to be 0.56 molal^{–1}.¹⁴

In this way we obtained: E° (I=0, 25°C) = 1887 mV.

An attempt was also made to carry out a similar estimate from Noyes and Deahl's precision data.¹

First we calculated the liquid junction e.m.f.

arising from the junctions 3M HNO₃/2M HClO₄ and 4M HNO₃/2M HClO₄. The method described in a previous article from this laboratory¹⁵ was used. A Henderson type distribution was assumed, the conductances were assumed to be additive, and the activity factors in the transition zone were calculated with the specific interaction theory.

The conductances and transport numbers in nitric acid solutions published by Haase *et al.*¹⁶ were employed for these calculations. For perchloric acid solutions, the data previously obtained in this laboratory¹⁷, were used.

To estimate the medium effect in 3 and 4M HNO₃, the interaction coefficients of Co²⁺–NO₃[–] and of H⁺–NO₃[–] were calculated from Robinson and Stokes' tables.¹² The value for $\epsilon(\text{Co}^{3+}\text{--NO}_3^-)$ was taken equal to $\epsilon(\text{Cr}^{3+}\text{--NO}_3^-)$, also derivable from Robinson and Stokes' tables.¹²

We deduced, by these lengthy calculations, from the 3M HNO₃ data E° = 1869 mV and from the 4M HNO₃ measurements E° = 1864 mV. This difference probably provides an idea of the magnitude of the uncertainty to which this type of approximate calculations gives rise. To this we have to add the uncertainty of Noyes and Deahl's e.m.f. measurements which were carried out with conventionally prepared reagents.¹

We would like to propose the mean value derived from the two sets of data as E° (I=0, 25°C) = 1.88 ± 0.01 V.

The fair agreement between the two investigations, separated by almost 50 years, leaves little doubt that the classic approach may be regarded as correct, and that the criticism raised against it lacks experimental foundation.

Experimental

Materials and analysis. Perchloric acid and silver perchlorate solutions were prepared, purified and analyzed following the usual practice in our laboratories.⁸

Cobalt (II) perchlorate solutions were made from cobalt(II) perchlorate hexahydrate crystals. This starting material was obtained by dissolving a sample of cobalt carbonate in an excess of hot azeotropic perchloric acid. On cooling, finely divided Co(ClO₄)₂(H₂O)₆ crystals precipitated. They were finally purified by double recrystallization from water.

The cobalt(II) content of the stock solutions

was obtained by titration with a standardized EDTA reagent solution. Murexid was applied as indicator. Its perchloric acid concentration could be determined simply by titration with a standardized NaOH solution, using methyl red indicator, because the hydrolysis of Co^{2+} is negligible at $\text{pH} < 4$.

Cobalt(III) perchlorate solutions containing 6.5 molal HClO_4 were prepared from $\text{Co}(\text{ClO}_4)_2(\text{H}_2\text{O})_6$ crystals and concentrated HClO_4 (prepared from crystals of $\text{HClO}_4(\text{H}_2\text{O})_2$) by anodic oxidation with gold electrodes. The temperature was maintained at -5°C , and the current density at around 25 mA/cm^2 . This value represents a compromise: the Joule heating then is still negligible but the overpotential for oxygen evolution is considerable. Vigorous stirring prevented the development of a local excess of Co^{3+} in the vicinity of the anode.

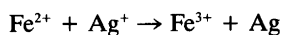
A current yield of about 85% is attainable under these experimental conditions. At this threshold, the redox potential of the solution exceeds the half-cell potential of the $\text{H}_2\text{O}_2\text{-H}_2\text{O}$ couple by about 0.1 V. A similar observation concerning the maximum yield was made with Ag^{2+} solutions⁸. In both cases the stability of the oxidized form is clearly due to the slowness of peroxide formation from water.

The difficulties reported in reference 18 could be avoided by using purified reagents.

The concentration of the cobalt(III) ions produced by anodic oxidation was determined by withdrawing a sample, using a precooled pipette, and discharging it into an excess of cold iron(II) sulphate solution. Immediate reduction to Co^{2+} has always been found to occur.

The amount of the sample was first determined from the weight increase of the flask, and then the excess of iron(II) ion was determined by titration with a standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution. Ferroin served as indicator.

Under the conditions prevailing during the analysis (low $[\text{Ag}^+]$ and subzero temperature), no complication was encountered as the reaction



was inhibited. The same method was used to monitor the Co^{3+} concentration in the course of the e.m.f. measurements.

Equipment. Gold, platinized platinum and silver electrodes were prepared in the conventional way by cathodic reduction.⁸

Glass electrodes of type Ingold LOT 271-77 were used. They were found, by the method described previously,⁸ to be equivalent with the hydrogen electrode, under the present experimental conditions.

The e.m.f. measurements were carried out by using the equipment built for the study of the $\text{Ag}^{2+}\text{-Ag}^+$ couple.⁸

References

1. Noyes, A. A. and Deahl, T. J. *J. Am. Chem. Soc.* 59 (1937) 1337.
2. Jahn, S. Z. *Anorg. Chem.* 60 (1908) 292.
3. Lamb, A. B. and Larson, A. T. *J. Am. Chem. Soc.* 42 (1920) 2024.
4. Wells, C. F. and Fox, D. *J. Inorg. Nucl. Chem.* 38 (1976) 107. This publication contains a complete list of references concerning the kinetics of Co(III) oxidation of H_2O and H_2O_2 . Cf. also Rosseinsky, D. R. and Jaregui, G. A. *J. Chem. Soc. (Faraday Transaction 1)* 75 (1979) 473.
5. Warnquist, B. *Inorg. Chem.* 9 (1970) 682.
6. Rotinjan, A. L., Borisowa, L. M. and Boldin, R. W. *Electrochimica Acta* 19 (1974) 43. This article provides references to previous work.
7. Johnson, D. A. and Sharpe, A. G. *J. Chem. Soc. (London)* (1964) 3490.
8. Biedermann, G., Maggio, F., Romano, V. and Zingales, R. *Acta Chem. Scand.* A35 (1981) 287.
9. Gran, G. *Acta Chem. Scand.* 4 (1950) 559; *Analyst* 77 (1952) 661.
10. Fontana, B. J. AEC-TID 5290, 1958; *Stability Constants Vol. 1* (1964) p. 37.
11. Brönsted, J. N. *J. Am. Chem. Soc.* 44 (1922) 877; *ibid.* 45 (1923) 2898.
12. Robinson, R. A. and Stokes, R. H. *Electrolyte Solutions*. 2nd Ed. (revised) Butterworth, London, 1970.
13. Libus, Z. and Sadowska, T. *J. Phys. Chem.* 73 (1969) 3229.
14. Biedermann, G. *Ionic Media in Dahlem Workshop on the Nature of Seawater* Berlin, 1975.
15. Biedermann, G. and Douheret, G. *Chem. Scripta* 16 (1980) 144.
16. Haase, R., Sauermann, P. F. and Ducker, K. M. Z. *Phys. Chem. N.F.* 43 (1964) 218.
17. Biedermann, G. and Douheret, G. *Chem. Scripta* 16 (1980) 138.
18. Bawn, C. E. H. and White, A. G. *J. Chem. Soc. (London)* (1951) 331.

Received August 13, 1985.