$$\frac{(F^0)}{(T)_{\text{AlCl}}} = \frac{1}{3}\left[\frac{(\Delta F^0)}{(T)} + \frac{(F^0)}{(T)_{\text{AlCl}_3}} + 2\,\frac{(F^0)}{(T)_{\text{Al}}}\right] = -67.09 \qquad (4)$$

Then with the function $-(F^0 - E_0^0)/(T)_{\text{AlCl}} = 59.45$[2] we have

$$E_0^0/T = -7.64 \text{ or } E_0^0 = -10.7 \text{ kcal.} \qquad (5)$$

E_0^0 represents the energy necessary to form aluminum monochloride with all materials in their standard states at 0° K. by the reaction

$$\text{Al(s)} + {}^1/_2\text{Cl}_2\text{(v)} \longrightarrow \text{AlCl(v)} \qquad (6)$$

Our value is to be compared with the recent determination by Gross[8,9] of −11.6 kcal. for the $\Delta H°$ of the reaction at 25°, which to this accuracy equals E_0^0.

Since all the thermodynamic values other than this E_0^0 had already been known, the entire equilibrium picture for this reaction can be constructed. Values for the logarithm of the equilibrium constant as a function of temperature are given in Fig. 3. The temperature necessary for a given fraction of aluminum chloride reacting with aluminum to form aluminum monochloride is shown as a function of total pressure in Fig. 4.

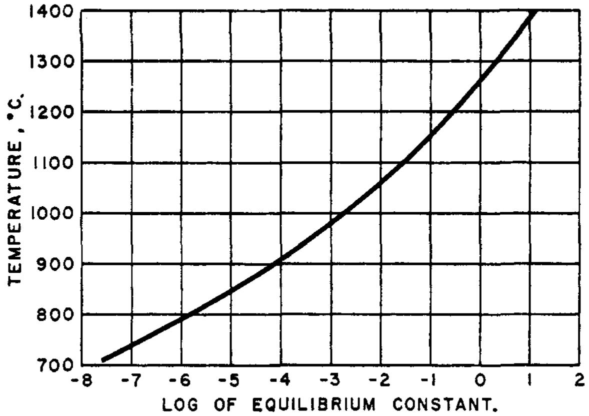

Fig. 3.—Effect of temperature on equilibrium constant for the reaction $\text{AlCl}_3 + 2\text{Al} \rightarrow 3\text{AlCl}$.

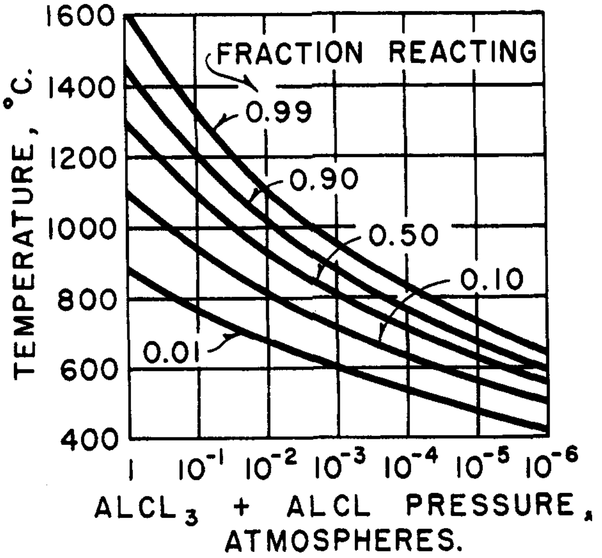

Fig. 4.—Temperature necessary for a given fraction of aluminum chloride reacting with aluminum to form aluminum monochloride as a function of pressure.

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[8] P. Gross, C. S. Campbell, P. J. C. Kent and D. L. Levi, *Discussions Faraday Soc.*, **4**, 206 (1948).

[9] P. Gross, "The Refining of Non-Ferrous Metals, Institution of Mining and Metallurgy," London, 1950, p. 461.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS AND FROM THE CHEMISTRY LABORATORY OF NORTHWESTERN UNIVERSITY]

Studies on the Oxidation of Potassium Ruthenocyanide[1,2]

BY DONALD D. DEFORD AND ARTHUR W. DAVIDSON

Titrimetric, spectrophotometric and polarographic data indicate that the ruthenocyanide ion is oxidized to ruthenicyanide ion upon treatment with strong oxidizing agents. The chemical behavior of the ruthenicyanide ion in solution is described. The standard potential of the ruthenocyanide–ruthenicyanide couple is estimated to be −0.86 ± 0.05 volt. Attempted preparation of crystalline potassium ruthenicyanide has been unsuccessful.

Potassium ruthenocyanide, $\text{K}_4\text{Ru(CN)}_6$, was first prepared by Claus[3] almost one hundred years ago. The properties of this compound, and of other ruthenocyanides and their derivatives, have been studied by a number of investigators[4] since that time. From the position of ruthenium in the periodic table, one would expect to find a close similarity between potassium ruthenocyanide and potassium ferrocyanide. The work of previous investigators has verified this expectation. In spite of the fact that these similarities have been known for many years, no previous investigation has been undertaken to determine whether ruthenocyanide ion can be oxidized to ruthenicyanide, $\text{Ru(CN)}_6^{\equiv}$, under conditions similar to those under which ferrocyanide is oxidized to ferricyanide. The present

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[1] Most of the work reported in this article is abstracted from the doctoral thesis of Donald D. DeFord, University of Kansas, 1948. The remainder was done by D. D. D. at Northwestern University. The work was supported by a grant from the Research Corporation.

[2] Presented at the Symposium on the Less Familiar Elements at the Detroit Meeting of the American Chemical Society, April, 1950.

[3] C. Claus, "Beitrage zur Chemie der Platinmetalle," Dorpat, 1854, p. 97.

[4] (a) G. A. Barbieri, *Atti accad. nazl. Lincei*, [6] **9**, 1015 (1929); (b) A. K. Bhattacharya, *J. Indian Chem. Soc.*, **13**, 284 (1936); (c) D. M. Bose, *Indian J. Physics*, **9**, 277 (1934–1935); (d) H. Dufet, *Compt. rend.*, **120**, 377 (1895); (e) J. L. Howe, THIS JOURNAL, **18**, 981 (1896); (f) J. L. Howe and E. D. Campbell, *ibid.*, **20**, 29 (1898); (g) F. Krauss and G. Schrader, *Z. anorg. Chem.*, **165**, 59 (1927); (h) F. Krauss and G. Schrader, *ibid.*, **173**, 63 (1928); (i) W. Manchot and J. Dusing, *ibid.*, **212**, 109 (1933); (j) W. Manchot and J. Dusing, *Ber.*, **63**, 1226 (1930); (k) R. Samuel and A. R. R. Despande, *Z. Physik*, **80**, 395 (1933); (m) R. Samuel and M. J. Khan, *ibid.*, **84**, 87 (1933).

investigation was undertaken to ascertain the nature of the products formed upon oxidation of ruthenocyanide under various conditions and to prepare, if possible, potassium ruthenicyanide, $K_3Ru(CN)_6$, by such oxidation.

The only previous study of the effect of oxidizing agents upon solutions of potassium ruthenocyanide is that of Krauss and Schrader,[4h] who found that colorless solutions of the ruthenocyanide changed through yellow to red-brown in color when chlorine was passed through the solution. Treatment of the red-brown solutions with sulfuric acid yielded a dark green precipitate of composition corresponding to the formula $Ru(CN)_3 \cdot 5H_2O$. This product is analogous to the Berlin green which is formed when potassium ferrocyanide is subjected to similar treatment. No attempt was made to identify the intermediate products formed during the oxidation.

Experimental

Preparation of Potassium Ruthenocyanide.—Potassium ruthenocyanide was prepared by a modification of the method previously described by Howe[4e] and by Krauss and Schrader.[4g] Approximately 4 g. of ruthenium metal residues was fused in a silver crucible either with 16 g. of a mixture of equal parts of sodium hydroxide and sodium peroxide or, more effectively, with a mixture of 10 g. of sodium hydroxide and 6 g. of potassium nitrate. The fused melts were dissolved in water, and the solution was treated with a small volume of ethanol to reduce the ruthenate to hydrous ruthenium dioxide, which was coagulated by boiling the solution and then separated by centrifugation. The crude dioxide was dissolved in hot concentrated hydrochloric acid, and the solution was treated with concentrated sulfuric acid and evaporated to fumes of sulfuric acid in order to remove chloride. The cooled solution was transferred to the distilling flask of an all-glass distillation apparatus similar to that described by Thiers, Graydon and Beamish.[5] The ruthenium was distilled from this solution with the aid of a water slurry of sodium bismuthate, added in successive small portions, as an oxidizing agent. The ruthenium tetroxide was absorbed in a 4 *M* solution of potassium hydroxide, cooled in an ice-bath. After the distillation had been completed, the contents of the receiver were allowed to stand for a few minutes at room temperature and were then heated to boiling and treated with a slight excess of a concentrated solution of potassium cyanide. Boiling was continued until evaporation had proceeded to the point of incipient crystallization of potassium ruthenocyanide. The solution was then allowed to stand for several hours at room temperature. The precipitated potassium ruthenocyanide trihydrate was removed by filtration and was washed, first with 50% and then with 95% ethanol. The anhydrous salt, which was employed in the preparation of all solutions, was obtained from the trihydrate by drying the latter at 115° for 12 hours.

A portion of the initial product was further purified by recrystallization from water. Since titration of the recrystallized product indicated no detectable improvement in purity, the initial product was employed in most of the subsequent studies.

A second group of crystals was recovered from the initial preparation by the addition of ethanol to the mother liquor. This product was dissolved in water, reprecipitated by the addition of ethanol, removed by filtration and washed with 95% ethanol. This product was used only in the preliminary experiments of this study.

Titration Experiments.—Solutions of potassium ruthenocyanide of known concentration were prepared by dissolving weighed amounts of the dry salt in water and diluting to known volume. The ceric ammonium sulfate employed in the titrations was standardized against reagent grade potassium ferrocyanide, using the *o*-phenanthroline ferrous complex as the indicator. Potential measurements were made with a Beckman Model G *p*H meter, bright platinum serving as the indicator electrode and a saturated calomel electrode as the reference electrode.

Spectrophotometric and Polarographic Measurements.—All spectrophotometric measurements were made with a Beckman model DU spectrophotometer, using 1-cm. fused silica absorption cells. A hydrogen discharge lamp served as the light source.

A Sargent Model XXI visible recording polarograph was used to obtain all polarograms, including those obtained manually as well as those recorded automatically. Potential settings were made by means of the voltmeters with which the instrument is equipped. These voltmeters were previously calibrated by means of a potentiometer. Potential settings are considered to be reliable to better than ±0.02 volt. A large saturated calomel electrode, making contact with the test solution through a saturated potassium chloride salt bridge and a sintered glass disc, was used as the cathode. Unless otherwise stated, all potentials reported were corrected for *iR* drop in the cell, in the current measuring resistor, and in the voltage divider network of the polarograph. The platinum microelectrode consisted of a short length of 0.5-mm. diameter platinum wire sealed into the side of 6-mm. diameter glass tubing. The exposed portion of the wire was approximately 5 mm. in length. This electrode was rotated at 500 r.p.m. by means of a small synchronous motor operating through a gear train. The same electrode, without rotation, was also used as a stationary microelectrode. All measurements were carried out at 27.0 ± 0.5°. Since all studies were made at potentials considerably more positive than the half-wave potential for the reduction of oxygen, dissolved air was not removed from the solutions. The resistances of the solutions, including the resistance of the reference cathode, were measured by means of a Wheatstone bridge, with a 1000-cycle per second power source.

Results and Discussion

Action of Oxidizing Agents on Ruthenocyanides.—It was found that mildly acidified colorless solutions of potassium ruthenocyanide became brilliant yellow when treated with strong oxidizing agents such as hydrogen peroxide, sodium bismuthate or ceric sulfate. Ozone or chlorine produced a similar yellow color with neutral solutions of potassium ruthenocyanide. In order to simplify the subsequent discussion it has been assumed that the yellow color of these solutions was due to the presence of ruthenicyanide ion. Data which will be presented in the following sections tend to support the validity of this assumption.

The ruthenicyanide solutions obtained by oxidation, if very dilute (*ca.* 10^{-3} *M*), were reasonably stable at room temperature for several hours. The solutions became increasingly unstable as the concentration of ruthenicyanide or of acids was increased. As decomposition proceeded the solutions changed from yellow to yellow-green, then to dark green, and finally deposited a green precipitate. The final product is apparently the green ruthenium(III) cyanide, $Ru(CN)_3 \cdot 5H_2O$, previously reported by Krauss and Schrader.[4h]

Many attempts were made to prepare solutions of potassium ruthenicyanide of sufficiently high concentration that the solid product could be crystallized from the solution. Although these attempts included oxidation with a wide variety of oxidizing agents under a wide variety of conditions, in no case was a successful separation achieved. The product was invariably heavily contaminated with the green decomposition product. Attempts at the electrolytic preparation of the crystalline salt, including electrolysis at controlled potential, likewise were unsuccessful. The difficulty at-

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(5) R. Thiers, W. Graydon and F. E. Beamish, *Anal. Chem.*, **20**, 831 (1948).

tending the satisfactory crystallization of potassium ferricyanide from solutions in which it has been prepared by the oxidation of potassium ferrocyanide is well known. It is not surprising, therefore, that even greater difficulties have been encountered in attempts to crystallize the much more unstable potassium ruthenicyanide.

Precipitation Reactions of Ruthenocyanide and Ruthenicyanide Ions.—Both ruthenocyanide and ruthenicyanide ions yield characteristic precipitates with most of the heavy metal ions. A summary of these precipitation reactions is shown in Table I. The ruthenicyanide solutions used were prepared immediately before each test by adding an excess of ceric sulfate to a solution of potassium ruthenocyanide which had been made approximately 0.1 *M* in sulfuric acid. Solutions of ruthenicyanide ion prepared by the use of other oxidizing agents and by electrolytic oxidation gave the same precipitation reactions provided the oxidation was essentially complete.

TABLE I

Cation	Color of precipitate	
	$Ru(CN)_6^{-4}$	$Ru(CN)_6^{-3}$
Ag^+	White[c]	Red-brown
Bi^{+3}	White[a]	No. ppt.
Cd^{+2}	White[a]	Yellow-brown
Co^{+2}	Blue[b]	Rust brown
Cr^{+3}	Pale blue-green	Red-brown
Cu^{+2}	Green[a,d]	Brown
Fe^{+2}	Pale blue[e]	Violet[g]
Fe^{+3}	Violet[a]	No ppt.[f]
Hg^{+2}	White[a]	Gray
Hg_2^{+2}	White	. . .
Mn^{+2}	White[a]	Brown
Ni^{+2}	Pale blue-green[a]	Brown
Pb^{+2}	White	. . .
Sb^{+3}	White	White[g]
Sn^{+2}	White	White[g]
Sn^{+4}	White[a]	No ppt.
Zn^{+2}	White[a]	Yellow

[a] Ref. 4e. [b] Ref. 4e reports a pale red ppt. [c] Ref. 4g. [d] Ref. 4g reports a light brown ppt. [e] The color is probably due to the presence of a trace of ferric ion. [f] Solution becomes red-brown in color. [g] The precipitates formed in these cases very likely contain ruthenocyanide, since the cation involved is capable of reducing ruthenicyanide.

The precipitation reactions previously reported for ruthenocyanide ion have been confirmed except in the case of cobalt, which was found to give a blue rather than a pale red precipitate. The precipitation reactions of ruthenicyanide ion are, in general, quite similar to those of ferricyanide ion[6] except in the case of bismuth, which gives a brown precipitate with ferricyanide but no precipitate with ruthenicyanide, and in the case of chromic ion, which gives no precipitate with ferricyanide but a red-brown precipitate with ruthenicyanide. Both ferricyanide and ruthenicyanide yield red-brown solutions, but no precipitate, with ferric ion.

Acidified solutions of potassium ruthenicyanide which have been treated with an amount of stannous chloride just sufficient to discharge the yellow color give the characteristic precipitation reactions of ruthenocyanide with cobaltous or ferric ions.[7] This behavior is good evidence that hexacyanoruthenate(III) ion, rather than one of its decomposition products such as, for example, aquopentacyanoruthenate(III) ion, is the principal oxidation product of ruthenocyanide, and is the ion responsible for the characteristic precipitates listed in column 3 of Table I.

Oxidimetric Titration of Potassium Ruthenocyanide.—A typical curve for the potentiometric titration of potassium ruthenocyanide with ceric ammonium sulfate is shown in Fig. 1. In the example shown, a 5.00-ml. sample of 0.0485 *M* potassium ruthenocyanide solution was treated with 5.0 ml. of 1.0 *M* sulfuric acid, and after dilution to 100 ml. was titrated with 0.0996 *M* ceric ammonium sulfate solution which was 0.5 *M* in sulfuric acid. The potentials for the first portion of the curve were rapidly established and quite steady. In the region immediately preceding the theoretical equivalence point and in the entire region beyond this point, the potential of the indicating electrode first slowly increased for several seconds after the addition of each increment of oxidant, then passed through a maximum, and decreased continuously thereafter. Since no steady potential was ever attained in this region, the potentials shown in the figure are the maximum values obtained after the addition of each increment of reagent. These potentials are, of course, of no value for the location of the end-point in the titration. The observed behavior indicates that the ruthenicyanide which is formed during the titration is extremely unstable in the presence of excess oxidizing agent.

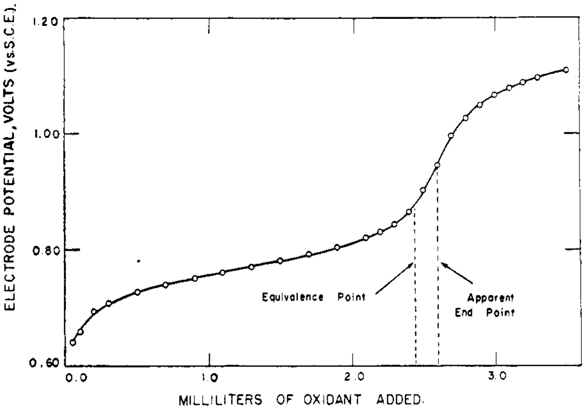

Fig. 1.—Potentiometric titration of potassium ruthenocyanide with ceric ammonium sulfate.

In order to avoid the difficulty caused by the decomposition of ruthenicyanide in the relatively slow potentiometric titration, rapid titrations with *o*-phenanthroline ferrous ion as indicator were tried. In duplicate titrations under the same conditions as those outlined in the preceding paragraph, the end-point was found to occur at 2.45 ml. Considering the unstable character of the ruthenicyanide ion, this result agrees quite satisfactorily with the theoretical requirement of 2.435 ml. for the oxidation of ruthenocyanide to ruthenicyanide,

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(6) Gmelin, "Handbuch der anorganischen Chemie," eighth ed., System No. 59 Part B, Verlag Chemie G.m.b.H., Berlin, 1932, pp. 643-652.

(7) The precipitate resulting from the reaction between either stannous or stannic ion and ruthenocyanide ion forms very slowly in acid solution.

and is strong evidence that this is the reaction which occurs during the titration.

Spectrophotometric Studies.—The absorption spectra of the hexacyanide complexes of dipositive iron, ruthenium and osmium are shown in Fig. 2. The spectrum of potassium ferrocyanide is that reported by Yamasaki.[8] The spectrum of potassium osmocyanide, and that of potassium ruthenocyanide given by the dashed curve, are those reported by Samuel and Despande.[4k] The spectrum of potassium ruthenocyanide as determined in the present investigation is indicated by the lower solid curve. A freshly prepared 0.1118 M solution was used for the measurements at wave lengths between 275 and 300 mμ, and a 0.001118 M solution for the shorter wave lengths. All measurements were made at room temperature (*ca.* 24°). Since the method and apparatus used in the present investigation were considerably more refined than those available to Samuel and Despande, it is probable that the spectrum reported here is more reliable than that reported previously.

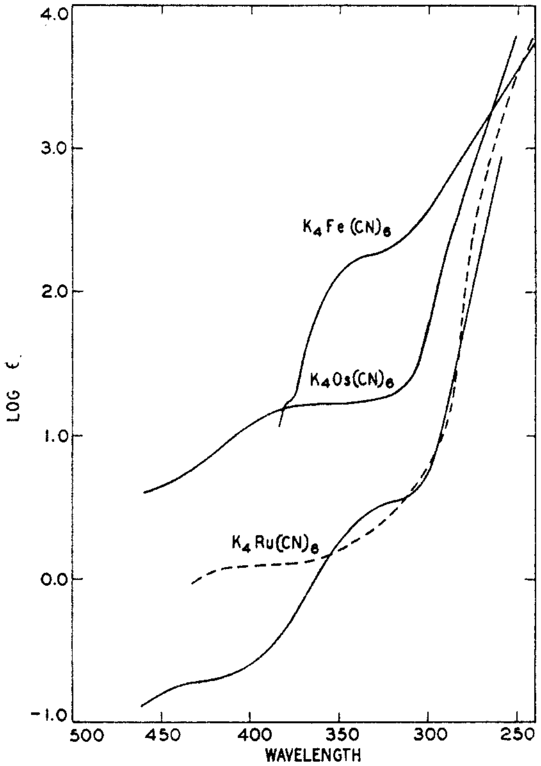

Fig. 2.—Absorption spectra of potassium ferrocyanide, potassium osmocyanide and potassium ruthenocyanide.

It was noted that the molar extinction coefficient of potassium ruthenocyanide increases slightly as the concentration of the solution is decreased, and very markedly, roughly 2% per degree, with increasing temperature. These phenomena have not been investigated in detail, but they indicate the probable existence of an association or dissociation equilibrium in the solution. Apparently no similar studies have been made on solutions of ferrocyanides.

The striking similarity between the absorption spectra of the cyanide complexes of these elements in their dipositive oxidation states suggested that ruthenicyanide ion might possess an absorption spectrum very similar to that of ferricyanide. The absorption spectra of several of the yellow solutions prepared by treating potassium ruthenocyanide with various oxidizing agents were therefore determined and compared with the previously reported[9] spectrum of potassium ferricyanide. A typical absorption curve for such a solution, together with Samuel's curve for potassium ferricyanide, is shown in Fig. 3. This solution was prepared by treating 3.0 ml. of 0.0112 M potassium ruthenocyanide with 0.05 ml. of 3% hydrogen peroxide and 0.10 ml. of 0.2 M HCl. The solution was warmed momentarily on the water-bath to hasten the oxidation and was then quickly cooled and diluted to 25 ml. The final solution was brilliant yellow in color and neutral to litmus. The absorption spectrum was determined as rapidly as possible after preparation of the solution. This solution shows absorption peaks at 300, 328, 355 and 455 mμ. Solutions prepared by the action of other oxidizing agents possessed similar absorption spectra, all with the same four characteristic absorption peaks at the wave lengths stated above. The pronounced similarity between these absorption spectra and that of potassium ferricyanide affords still further evidence for the existence of the ruthenicyanide ion in the solutions being studied.

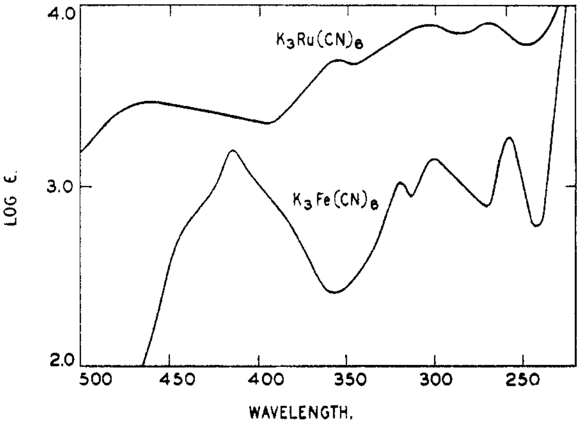

Fig. 3.—Absorption spectra of potassium ferricyanide and potassium ruthenicyanide. The ordinate scale for the potassium ruthenicyanide curve is purely arbitrary.

Since the concentration of potassium ruthenicyanide in the solutions employed in the spectrophotometric studies was in all cases unknown, it has been impossible to calculate the molecular extinction coefficients. Furthermore, since the solutions were too unstable to be studied after complete oxidation, all of the solutions contained some unoxidized ruthenocyanide The lack of sharpness in the absorption peaks shown in Fig. 3 is probably due to the relatively heavy background absorption of unoxidized potassium ruthenocyanide in the solution. However, no difficulty is encountered in identifying ruthenicyanide in the presence of ruthenocyanide by spectrophotometric methods, since the latter ion exhibits no absorption peaks but rather only a

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(8) K. Yamasaki, *Bull. Chem. Soc. Japan*, **15**, 461 (1940).

(9) R. Samuel, *Z. Physik*, **70**, 43 (1931).

continuously increasing absorption as the wave length is decreased.

Polarographic Studies with the Stationary Platinum Microelectrode.—Considerable difficulty was experienced in obtaining well-defined and reproducible polarograms of the oxidation of potassium ruthenocyanide in potassium chloride as a supporting electrolyte. In most of the experiments a trace of greenish precipitate formed on the microelectrode during the electrolysis. The formation of this decomposition product probably accounts for the erratic behavior observed. In several studies, however, quite satisfactory polarograms were obtained. An example of one of these polarograms, which was obtained manually by the electrolysis of 0.000593 *M* potassium ruthenocyanide in 0.2 *M* potassium chloride as a supporting electrolyte, is shown in Fig. 4. No evidence for the formation of decomposition products was noted during this particular electrolysis. The polarographic wave is well defined and symmetrical about the half-wave point. The analysis plot of the wave, which is also shown in Fig. 4, is a straight line with a reciprocal slope of 0.059 volt per unit change in the log term, in perfect agreement with the theoretical curve for a reversible one-electron oxidation. The half-wave potential is 0.72 volt *versus* the saturated calomel electrode. The relationship between diffusion current and concentration was not investigated.

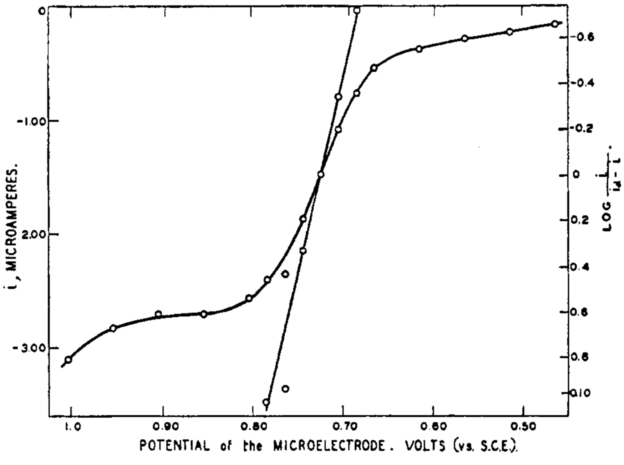

Fig. 4.—Polarogram and analysis plot of the polarographic wave for the oxidation of 0.000593 *M* $K_4Ru(CN)_6$ in 0.2 *M* KCl at the stationary platinum electrode.

Polarographic Studies with the Rotated Platinum Microelectrode.—A typical polarogram obtained on electrolyzing a solution of 0.000593 *M* potassium ruthenocyanide in 0.2 *M* potassium chloride is shown in Curve 1 of Fig. 5. In this case, and in all other similar cases studied, the wave is not well-defined and no diffusion current region is observed. This behavior is very similar to that exhibited by ferrocyanide ion on oxidation at the rotated microelectrode,[10] and suggests that the electrode reaction is slow in comparison with the rate of diffusion. Curve 2 in Fig. 5 was obtained after electrolysis of the solution for several minutes at an applied potential of 1.5 volts. The polarogram shown was obtained immediately after this electrolysis. In this case a well-defined diffusion current region was obtained. After the solution had stood for several minutes the diffusion range became less well-defined and eventually disappeared completely. This behavior also is analogous to that exhibited by ferrocyanide,[10] and suggests that the electrode reaction may involve an intermediate substance formed during the evolution of oxygen at the microelectrode.

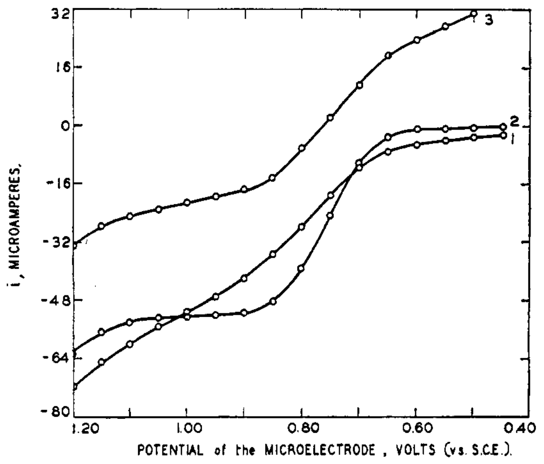

Fig. 5.—Polarograms for the oxidation of 0.000593 *M* $K_4Ru(CN)_6$ in 0.2 *M* KCl at the rotated platinum electrode: (1) no prior electrolysis, (2) after electrolysis at +1.5 volts for several minutes, (3) after electrolysis with large platinum anode at +1.1 volts for two hours. Potentials shown were not corrected for *iR* drop in the circuit components.

Curve 3 in Fig. 5 was obtained after the solution used in the previous two runs had been subjected to electrolysis for two hours at an applied potential of 1.1 volts. A large platinum gauze anode was used in conjunction with the saturated calomel cathode for this electrolysis. At the end of the electrolysis the solution was brilliant yellow in color, indicating the presence of an appreciable quantity of ruthenicyanide ion. The polarogram shown was obtained immediately after the conclusion of this electrolysis. The wave obtained in this case is no longer symmetrical about the half-wave point, but the half-wave potential, after correction for *iR* drop in the circuit components, is 0.72 volt, in perfect agreement with the corrected half-wave potential obtained from Curve 2. The agreement in half-wave potentials for the oxidation wave and the composite wave indicates that the electrode reaction is reversible. The unsymmetrical character of the wave may possibly arise from the presence of decomposition products which are oxidized or reduced at potentials in the vicinity of the half-wave potential of the ruthenocyanide–ruthenicyanide couple.

In Fig. 6 the current–voltage curve, together with the analysis plot of this curve, is shown for the electrolysis of 0.000593 *M* potassium ruthenocyanide in 0.2 *M* potassium chloride under the same conditions as were used for Curve 2, Fig. 5. As in that case, the wave is perfectly symmetrical about

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(10) H. A. Laitinen and I. M. Kolthoff, *J. Phys. Chem.*, **45**, 1079 (1941).

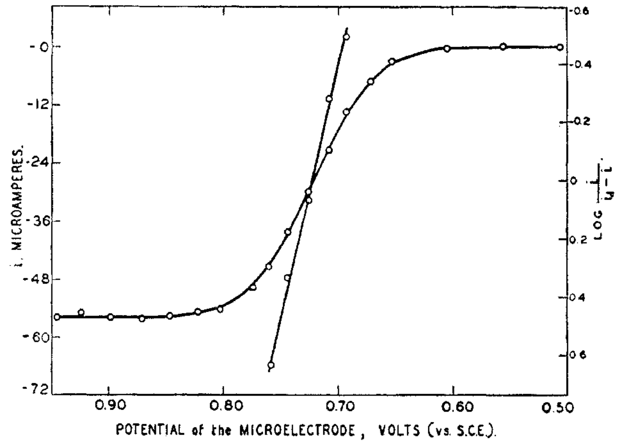

Fig. 6.—Polarogram and analysis plot of the polarographic wave for the oxidation of 0.000593 M $K_4Ru(CN)_6$ in 0.2 M KCl at the rotated platinum electrode. Solution subjected to prior electrolysis at +1.5 volts for 3 min. Potentials shown were corrected for iR drop in the circuit components and currents were corrected for the residual current.

the half-wave point; the analysis plot is a straight line with a reciprocal slope of 0.059 volt, indicating that the electrode reaction is reversible in character. The half-wave potential is 0.72 volt.

The current–voltage curves for the oxidation of potassium ruthenocyanide in 1.0 M potassium chloride as a supporting electrolyte were very similar to those obtained in the 0.2 M potassium chloride solutions except that the half-wave potential was 0.76 volt.

Satisfactory current–voltage curves could not be obtained in 0.05 M hydrochloric acid as a supporting electrolyte because of the rapid decomposition of the solution, which resulted in the deposition of a blue precipitate on the sintered glass disc separating the saturated calomel reference electrode from the solution. No oxidation waves were observed in the 0.05 M sodium hydroxide as a supporting electrolyte, since oxygen evolution began before the half-wave potential for the oxidation of ruthenocyanide was reached.

The reproducibility of the magnitude of the diffusion current for the oxidation of potassium ruthenocyanide in 0.2 M potassium chloride as a supporting electrolyte was of the order of ±2%. The magnitude of the diffusion current appears to vary somewhat as the length of the prior electrolysis and the elapsed time before the recording of the polarogram is varied by a few minutes. Within the limits of experimental error, the diffusion current was found to be proportional to the concentration of potassium ruthenocyanide in the concentration range between 0.0006 and 0.0012 M. Solutions outside this concentration range were not studied.

The Standard Potential of the Ruthenocyanide–Ruthenicyanide Couple.—Although the data presented in this paper do not permit a precise calculation of the standard potential of the ruthenocyanide–ruthenicyanide couple, it is of interest to estimate the order of magnitude of this potential. If one makes the reasonable assumption that the diffusion coefficients of the two ions are approximately equal, then the half-wave potential for the oxidation of the ruthenocyanide ion is approximately equal in magnitude but opposite in sign to the formal potential[11] of the ruthenocyanide–ruthenicyanide couple in the particular solution being studied. If one assigns a value of −0.25 volt to the potential of the saturated calomel electrode, then the formal potential of the ruthenocyanide–ruthenicyanide couple may be calculated to be −0.97 volt in 0.2 M potassium chloride and −1.01 volts in 1.0 M potassium chloride. The corresponding formal potentials of the ferrocyanide–ferricyanide couple are −0.44[12] and −0.48[13] volt. These two formal potentials are 0.08 and 0.12 volt, respectively, more negative than the standard potential, which is −0.36 volt.[12] If one assumes that the formal potentials of the ruthenium couples are more negative than the standard potential by an equal amount, then it follows from the polarographic data that the standard potential of the ruthenium couple is −0.89 volt.

In the potentiometric titration experiments it was found that the measured potential of the indicating electrode at the half-way point in the titration (50% oxidation of the ruthenocyanide) was 0.80 volt for titrations carried out in 0.1 M sulfuric acid and 0.90 volt for titrations carried out in 1.0 M sulfuric acid. The formal potentials of the ruthenocyanide–ruthenicyanide couple in these solutions are then −1.05 and −1.15 volts, respectively. The corresponding formal potentials of the ferrocyanide–ferricyanide couple[14] are −0.57 and −0.69 volt. By the application of the same reasoning as was employed in the case of the polarographic data, values of −0.84 and −0.82 volt, respectively, may be calculated from the potentiometric titradata for the standard potential of the ruthenocyanide–ruthenicyanide couple.

Consideration of the results of the preceding calculations yields −0.86 ±0.05 volt as the most probable value of the standard potential of the ruthenocyanide–ruthenicyanide couple.

EVANSTON, ILL. RECEIVED JULY 20, 1950

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(11) The thermodynamic convention, as outlined by W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938, is employed in reporting formal and standard potentials.

(12) I. M. Kolthoff and W. J. Tomsicek, *J. Phys. Chem.*, **39**, 945 (1935). The value employed here was obtained by interpolation.

(13) D. Davidson, THIS JOURNAL, **50**, 2622 (1928).

(14) H. H. Willard and G. D. Manalo, *Anal. Chem.*, **19**, 462 (1947).