

oxidation potential of the indicator from the iron and cerium potentials and obtained the results given in Part B of Table II. For the formal potential of the ferrous-ferric couple in 1 *M* sulfuric acid, the value 0.68 v. was taken.⁴ The accepted value of 1.44 v. for the cerous-ceric couple also refers to 1 *M* sulfuric acid. In addition, we have calculated the indicator potential directly from the potential of the quinhydrone couple, which is known to be 0.696 v. in 1 *M* sulfuric acid.⁵ It is seen that all these give a very good agreement. The use of a mercury-mercurous sulfate reference electrode in 1 *M* sulfuric acid gave potentials 20 millivolts greater than with quinhydrone. Since the formal potential of the mercurous sulfate electrode is 0.674 v. in 1 *M* sulfuric acid,⁴ this constitutes an additional check. As final values, we suggest 1.06 v. for the formal oxidation potential of the indicator and 1.12 v. for the color change.

The end-point errors calculated from the new indicator potential are negligible in sulfuric acid solutions and quite small for hydrochloric acid (about 0.1% in the latter case). The potential of the indicator itself should not be greatly affected by the medium because the iron-phenanthroline complex is quite a stable one. Therefore, the

(4) Given in the very useful table of formal potentials compiled by C. S. Garner in E. H. Swifts' book, "A System of Chemical Analysis," Prentice-Hall, Inc., New York, N. Y., 1939, pp. 540-543; see also G. F. Smith and C. A. Getz, *Ind. Eng. Chem., Anal. Ed.*, **10**, 191 (1938).

(5) F. Hovorka and W. C. Dearing, *THIS JOURNAL*, **57**, 446 (1935).

use of the same potential in sulfuric and hydrochloric acids is justifiable.

The potential of the ferrous α, α' -dipyridyl complex, determined in the same manner and reported to be identical with that of the phenanthroline complex^{1b} is similarly revised to 1.06 v. The potential of the nitrophenanthroline-ferrous complex, determined by a different method, was found to be approximately 1.25 v.⁶ Since the observations of Smith and Getz⁷ agree with this value, there seems to be no necessity for revising it.

Steigman, Birnbaum and Edmonds⁸ found the potential of the ruthenium α, α' -dipyridyl complex to be 0.58 v. greater than that of the ferrous-ferric couple in *M* nitric acid. The formal potential of the latter is 0.74 v. The resulting indicator potential, 1.32 v. does not differ seriously from the value 1.33 v. calculated by them.

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Summary

The oxidation potential of ferrous-phenanthroline and of ferrous α, α' -dipyridyl in *M* sulfuric or hydrochloric acid is 1.06 v. instead of the reported value of 1.14 v.

(6) L. P. Hammett, G. H. Walden and S. M. Edmonds, *ibid.*, **56**, 1092 (1934).

(7) G. F. Smith and C. A. Getz, *Ind. Eng. Chem., Anal. Ed.*, **10**, 304 (1938).

(8) J. Steigman, N. Birnbaum and S. M. Edmonds, *ibid.*, **14**, 30 (1942).

MINNEAPOLIS, MINNESOTA RECEIVED OCTOBER 26, 1942

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Oxidation Potential of the Chromocyanide-Chromicyanide Couple and the Polarography of the Chromium Cyanide Complexes¹

BY DAVID N. HUME² AND I. M. KOLTHOFF

Although it is well known that the chromocyanide ion is a powerful reducing agent, liberating hydrogen from aqueous solutions in the presence of platinum, no determination of the oxidation potential of the chromocyanide-chromicyanide couple has ever been reported. In the present investigation, the potential has been measured in 1 *M* potassium cyanide, both polarographically and by classical methods.

(1) Abstracted from a thesis submitted by David N. Hume to the Graduate Faculty of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Du Pont Fellow in Chemistry, 1942-1943

Experimental

In the polarographic measurements, the conventional apparatus and technique were used.³ Many of the experiments were made with an automatic Heyrovský polarograph, Type VIII. Others were made with the manual apparatus of Lingane and Kolthoff.⁴ The temperature was kept constant at 25.00 \pm 0.04° by means of a water thermostat. The polarographic cells had provision for the use of both a mercury pool and an external reference electrode. A saturated calomel electrode was used as a working and reference anode and all potentials are given

(3) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941.

(4) J. J. Lingane and I. M. Kolthoff, *THIS JOURNAL*, **61**, 825 (1939)

with respect to it as zero. Corrections were made for residual current and for iR drop, the resistance of the cell being determined experimentally. The same capillary was used in all the measurements. It had a drop time of 3.18 sec. and a value of 1.98 for $m^{2/3}t^{1/3}$ at the potential of the saturated calomel electrode.

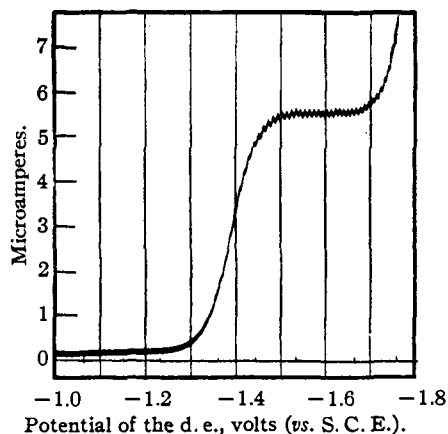


Fig. 1.—Polarogram of 1.54 millimolar potassium chromicyanide in 1.00 *M* potassium cyanide and 0.01% gelatin.

The Preparation of Potassium Chromicyanide and Potassium Chromocyanide.—Potassium chromicyanide, $K_2Cr(CN)_6$, was prepared by the method of Christensen.⁵ A good crop of clear yellow crystals was obtained. The product was further purified by recrystallization from water. Aqueous solutions of this product became opalescent, and developed a faint odor of hydrogen cyanide after standing for several days. Solutions made up with an excess of potassium cyanide were stable, no turbidity appearing even after several weeks.

Because of its great instability, no attempt was made to isolate potassium chromocyanide in the pure state. Solutions of the compound were first obtained by the addition of excess potassium cyanide to electrolytically prepared, neutral chromous chloride. This procedure invariably resulted in the formation of a small amount of reddish-brown precipitate; further investigation showed the method described below to be preferable.

It was found that a smooth reduction took place when 0.01 *M* or 0.1 *M* solutions of potassium chromicyanide in 1.0 *M* potassium cyanide were electrolyzed with a mercury cathode. The anode and cathode compartments were separated by a sintered glass disk, and the cathode solution was protected from air by an atmosphere of hydrogen. A platinum anode was used and sodium hydroxide or sulfate employed as the anolyte. With an applied voltage of 4.5 v. and a current density of 0.2 amp./sq. dm. at the cathode, the reduction was quite rapid. A deep orange-red color first appeared, which became lighter as the reduction progressed. When about 50% reduction had taken place, hydrogen began to evolve at the mercury surface, and the progress of the reduction became much slower. Under the conditions used, the reduction was seldom greater than 75%, even after four or five hours. Reduction of a chromicyanide solution without the addition of potassium

cyanide resulted in the formation of a large amount of dark brown precipitate. The chromocyanide ion evidently is unstable in the absence of free cyanide, and decomposes to chromous cyanide or hydroxide.

The Reduction of Chromicyanide Ion at the Dropping Electrode.—It was found that solutions 0.001 *M* in potassium chromicyanide and 0.1 *M* in potassium chloride or sodium hydroxide gave a poorly-defined reduction wave. In 1.0 *M* cyanide medium, with a trace of gelatin present as a maximum suppressor, a well-defined and reproducible wave was obtained (Fig. 1). The data of Table I show the half-wave potential to be independent of concentration.

TABLE I
THE INFLUENCE OF THE CONCENTRATION OF CHROMICYANIDE ION ON THE DIFFUSION CURRENT AND HALF-WAVE POTENTIAL OF ITS REDUCTION IN 1 *M* KCN AND 0.01% GELATIN

(<i>M</i> × 10 ³)	<i>i</i> _d (μa.)	<i>i</i> _d / <i>C</i>	$\pi^{1/2}$ / (vs. S. C. E.)	$\frac{n}{\text{sq. cm./sec.}} \times 10^8$
0.198	0.64	3.27	-1.380	0.8
0.582	1.90	3.27	-1.385	.82
1.54	5.22	3.39	-1.383	.89
3.40	11.63	3.42	-1.384	.90
			Average	-1.383

The diffusion current, however, is not strictly proportional to the concentration, if the latter is greater than about millimolar. This may be due to incomplete suppression of the "water wave," for it was noted that in the absence of gelatin, the diffusion current, although fairly well-defined, was about a third greater than in the presence of 0.005–0.01% of gelatin. At concentrations greater than about 5 millimolar, the diffusion current was no longer independent of the potential, but increased slowly with increasingly negative potentials.

By substitution into the Ilkovič equation

$$i_d = 605 n D^{1/2} C m^{2/3} t^{1/3}$$

the values in the first two columns of Table I, and the value of 2.16 $\text{mg.}^{2/3} \text{sec.}^{-1/3}$ for $m^{2/3}t^{1/3}$ at -1.6 v., the diffusion coefficient values for chromicyanide ion given in the last column were obtained. The theoretical value for ferricyanide ion is 0.89×10^{-8} , and the experimentally determined value is 0.75×10^{-8} from the data of Kolthoff and Lingane.⁶

From the data of the current-voltage curve of a solution 1.54 millimolar in potassium chromicyanide, 1.0 *M* in potassium cyanide and 0.01% in gelatin, values of $\log [(i_d - i)/i]$ were plotted against the potential of the dropping electrode (Fig. 2). A good straight line was obtained with a slope of 60 millivolts per unit log term; this indicates that the reaction is reversible and involves a one-electron change. A one-electron change is also indicated by the height of the wave. The results have no analytical importance as chromi-

(5) O. T. Christensen, *J. prakt. Chem.*, [2] **31**, 163 (1885).

cyanide is not readily formed by the addition of cyanide to chromic salts.

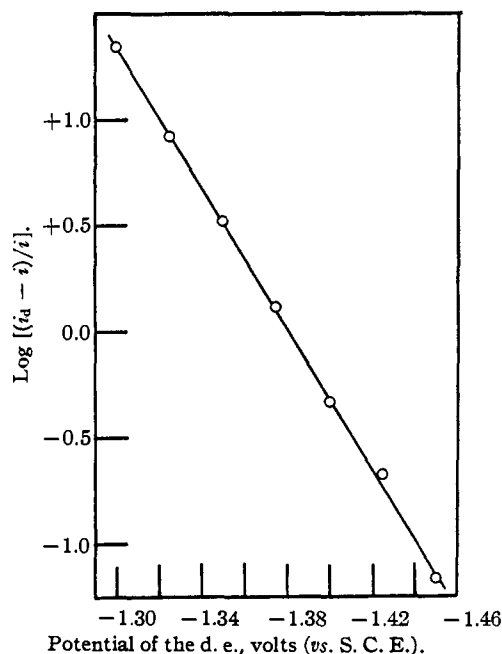
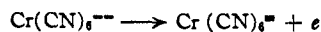


Fig. 2.—Analysis of the wave of chromicyanide ion in 1.00 *M* potassium cyanide and 0.01% gelatin.

The Anodic Oxidation of Chromocyanide Ion at the Dropping Electrode.—Current-voltage curves were obtained from a number of chromocyanide solutions prepared as described above. In each case, there was some chromicyanide present so that its wave appeared on every polarogram. Chromocyanide ion was found to be oxidized at the dropping electrode at potentials more positive than -1.385 v., giving a typical anodic wave (Fig. 3). The anodic and cathodic waves combined to give but one wave, indicating again that the reaction



is reversible at the dropping electrode. The presence of a trace of gelatin or thymol was found to be necessary for a well-defined diffusion current.

A small second anodic wave was sometimes observed appearing at -1.05 v. The height of this wave, as compared to the first one, was quite variable, sometimes being nearly as great as that of the reversible wave, and sometimes being vanishingly small. When curves were taken at intervals on a chromicyanide solution being electrolytically reduced, it was noted that the second wave was most prominent during the first stages of the reduction, while the solution was strongly

colored. Prolonged electrolysis to the point of evolution of hydrogen and lightening of the red color caused the disappearance of the second wave. The total anodic and cathodic current of the reversible couple diminished during this process, as if some of the chromium were irreversibly removed to an inactive state. After the disappearance of the second wave, the total anodic and cathodic current remained unchanged with further electrolysis. Apparently, the chromocyanide ion is appreciably unstable with respect to some other forms even in 1 *M* potassium cyanide. Since the second anodic wave in no way affected the reversible wave, an extensive investigation of the properties of the former was not made at this time.

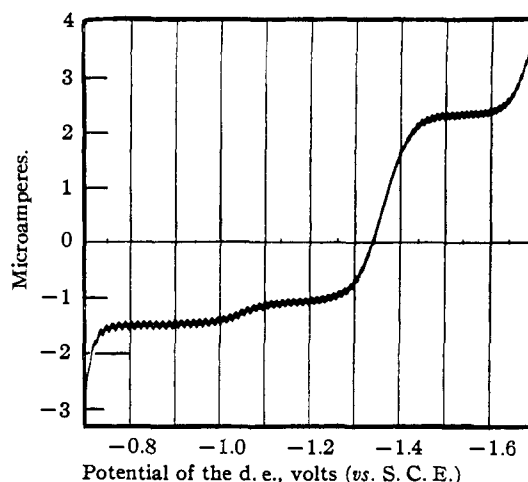


Fig. 3.—Polarogram of a mixture of chromocyanide and chromicyanide ions in 1.00 *M* potassium cyanide and 0.01% gelatin; total chromium concentration 2 millimolar.

The same reversible composite anodic-cathodic wave was obtained regardless of whether the solution was prepared by electrolytic reduction of chromocyanide, by reduction with sodium amalgam, or by addition of alkali cyanide to a chromous chloride solution. Since previous magnetic susceptibility measurements have shown that the chromium ions in a solution prepared in the latter manner have only two unpaired electrons,⁶ there can be little doubt that it is the chromocyanide which is present.

The chromocyanide solutions were found to decompose at an appreciable rate. In the course of extended measurements, the anodic current was found to decrease and the cathodic current to increase by the same amount. Thus, the diffusion coefficients of the two ions appear to be very

(6) D. N. Hume and H. W. Stone, *THIS JOURNAL*, **63**, 1200 (1941).

nearly the same. The half-wave potential of the composite wave was found to be -1.385 v., in striking agreement with that of the cathodic wave. In such a system, in which the electrode reactions are reversible, and the diffusion coefficients of the two ions are the same, the half-wave potential of the composite wave is identical with the formal oxidation potential of the couple.⁷

Classical Determination of the Oxidation Potential of the Chromocyanide-Chromicyanide Couple.—Simultaneously with the dropping-electrode measurements, observations were made of the potential of a quiet mercury electrode in the same solution. This mercury pool behaved as an inert, noble metal electrode. The potential was established instantaneously, and never deviated by more than 3 to 5 millivolts from the potential of a dropping electrode to which no potential was being applied. From the potential of the quiet electrode and the relative concentrations of divalent and trivalent chromium determined from the heights of the anodic and cathodic waves (here using the polarograph simply as an analytical tool), the potential at which equal concentrations would be present was calculated by use of the Nernst expression. The results shown in Table II indicate a satisfactory agreement with the polarographic half-wave potential.

TABLE II
POTENTIAL OF THE CHROMOCYANIDE-CHROMICYANIDE
COUPLE IN 1 M KCN AT A QUIET MERCURY ELECTRODE.
TOTAL CHROMIUM CONCENTRATION 0.001 M

Observed potential, ^a v.	Cr(III):Cr(II)	0.059 log (Ox./Red.) (millivolts)	Calculated potential (Ox./Red.) = 1
-1.389	24:26	2.1	-1.387
-1.387	10.3:11.0	1.7	-1.385
-1.386	30.0:32.5	2.1	-1.384
-1.395	8.0:10.0	5.7	-1.389
-1.355	23:5.0	39	-1.394
-1.320	26:1.5	73	-1.393
		Average	-1.389 ^c

^a Against the S. C. E. ^b From the relative heights of the polarographic waves. ^c Or -1.143 on the hydrogen scale.

Discussion of Results.—The measurement of the half-wave potentials is reliable to about ± 3 millivolts. Taking -1.385 v. as a good mean among the half-wave potentials of the chromic and composite waves, and the classically determined potential, and taking 0.246 v. as the potential of the saturated calomel electrode against the standard hydrogen electrode, the value

(7) Reference 2, p. 167; J. J. Lingane, *Chem. Rev.*, **30**, 1 (1941).

of -1.139 v. is obtained for the formal oxidation potential of the chromocyanide-chromicyanide couple in 1.00 M potassium cyanide (according to the sign convention of Lewis and Randall, this would be written $E = 1.139$ v.). There is considerable experimental uncertainty in the last figure, and liquid junction potentials have been disregarded, but the result is certainly reliable to within 10 millivolts, and we propose the rounded-off value of -1.14 v.

Because it depends upon the ratio of the activities of a trivalent and a quadrivalent ion, the potential of the couple should vary considerably with ionic strength, becoming markedly more negative with decreasing electrolyte concentration. Since chromocyanide is unstable in the absence of excess cyanide, direct measurement of the standard potential (zero ionic strength) is not possible. One may estimate its order of magnitude, however, by comparison with the ferrocyanide-ferricyanide couple. Kolthoff and Tomsicek⁸ found the standard potential to be 0.3560 v., and the formal potential to be 0.458 v. in 0.5 M potassium chloride or bromide, and 0.456 v. in 0.5 M potassium nitrate. From this and other data, it was concluded that the salt effect was relatively independent of the anions. From the data of Linhart,⁹ the value of 0.496 is found for the formal potential in 1 M potassium chloride. Thus there is a difference of 140 mv. between the standard potential and the formal potential in a univalent potassium salt of unit ionic strength. Since the chromocyanide-chromicyanide couple is exactly analogous in charge type, this would make the standard potential -1.28 v., the most strongly negative reversible ionic potential yet reported.

The potential of the chromous-chromic couple in acid medium is reported as being approximately -0.4 v. on the hydrogen scale.¹⁰ Considering the chromocyanide-chromicyanide electrode as a chromous-chromic ion electrode, and substituting the appropriate potentials in the Nernst expression, one obtains the result that the chromicyanide ion is more stable than the chromocyanide ion by a factor of about 10^{12} in 1 M potassium cyanide.

Summary

The reduction of chromicyanide and oxidation of chromocyanide ions at the dropping mercury

(8) I. M. Kolthoff and W. J. Tomsicek, *J. Phys. Chem.*, **38**, 943 (1935).

(9) G. A. Linhart, *THIS JOURNAL*, **39**, 615 (1917).

(10) G. Grube and P. Schlecht, *Z. Elektrochem.*, **32**, 178 (1926).

electrode were studied and found to be reversible in 1 *M* potassium cyanide. The oxidation potential of the chromocyanide–chromicyanide couple was determined both polarographically and by

classical means, and found to be -1.14 v. in 1 *M* potassium cyanide. The standard potential was estimated to be -1.28 v.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Osmotic Pressure and Viscosity Measurements with Cellulose Acetate Fractions¹

BY A. BARTOVICS AND H. MARK

Flory,² Huggins³ and Powell, Clark and Eyring⁴ have recently very considerably extended our theoretical knowledge of dilute high polymer solutions, and developed equations for the dependence of osmotic pressure and specific viscosity of such solutions upon concentration of the solute. Fuoss and Mead^{5a} and Flory^{5b} have carried out osmotic pressure and viscosity measurements with fractionated polyvinyl chloride and polyisobutylene samples. It is the purpose of this paper to contribute some similar results obtained with cellulose acetate fractions.

Experimental

A. Material.—Fifteen fractions of cellulose acetate were studied; their preparation and characterization was described in a previous paper.⁶ They were the final result of a threefold fractionated precipitation of an Eastman Kodak Co. Cellulose Acetate having 38.6% acetyl, 0.06% ash content and a melting point of 250°. All fractions used in this investigation had inside the limits of error almost the same melting point, acetyl and ash content; they differed only by their osmotic pressure and specific viscosity.

B. Viscosity Measurements.—The determinations were made in acetone with an ordinary Ostwald viscometer, which had a capillary tube about 10 cm. long and with a 0.4 mm. bore. Exactly 5 ml. of the liquid was introduced into the large bulb of the viscometer by means of a pipet. The apparatus was then suspended in a constant temperature bath (30 or 40 \pm 0.1°). After the viscometer and contents had acquired the temperature of the bath, suction was applied at the capillary arm of the viscometer until the level of the liquid rose above the upper graduation mark. The liquid was then allowed to

flow back through the capillary, and the time required for the surface of the liquid to pass from the upper to the lower mark was noted by means of a stop watch.

Within the concentration range used in these experiments, the densities of solvent and solution differed by less than 0.2% and can be neglected. The specific viscosity, η_{sp} , of a solution is therefore calculated directly from the time observations as follows

$$\eta_{sp} = \frac{t_s - t_0}{t_0} = \frac{t_s}{t_0} - 1 = \eta_r - 1$$

where t_s and t_0 are the times of flow of the solution and solvent, respectively, and η_r is the relative viscosity of the solution.

C. Osmotic Measurements.—Two methods were used. The static, as described by Herzog and Spurlin⁷ and Meyer,⁸ and the dynamic, which was introduced by van Campen⁹ and Obogi and Broda¹⁰ and recently very substantially improved by Fuoss and Mead.^{5a} These authors describe the procedure in their paper so clearly and in such detail that it seems to be sufficient to refer to their article. The results of both methods agreed with exception of the lowest molecular weight fractions, where it was difficult to arrive at a satisfactory equilibrium with the static method. This seems to be due to the diffusion of the solute through the membrane. For these fractions the dynamic values were used. All osmotic measurements were carried out in acetone at 25°.

TABLE I
VALUES FOR M_2 AND $[\eta]$ FOR SEVERAL CELLULOSE ACETATE FRACTIONS

Fraction	$k' = 0.70; \mu = 0.43$						
	2	4	8	9	11	13	15
$M_2 \times 10^8$	126	92	63	52	45	31	25
$[\eta]^*$	31.0	25.0	19.0	16.5	15.5	12.0	10.5

* The concentration c_v is expressed in volume fractions.

Results and Discussion

Figure 1 shows the specific viscosities of five selected fractions (2, 4, 8, 9 and 13) divided by the volume fraction of the solute plotted against this volume fraction. It can be seen that the three

(7) R. O. Herzog and H. M. Spurlin, *Z. physik. Chem., Bodenstein Festband*, 239 (1931).

(8) K. H. Meyer, "Natural and Synthetic High Polymers," Interscience Publ. Co., New York, N. Y., 1942, p. 12.

(9) P. van Campen, *Rec. trav. chim.*, 50, 915 (1931).

(10) R. Obogi and E. Broda, *Kolloid-Z.*, 69, 172 (1934).

(1) This paper is part of A. Bartovics' Doctor's thesis, Polytechnic Institute of Brooklyn, January, 1943. Its main content was presented at the A. C. S. meeting in Buffalo, New York, in September, 1942.

(2) P. J. Flory, *J. Chem. Phys.*, 10, 51 (1942).

(3) M. L. Huggins, *J. Phys. Chem.*, 42, 911 (1938); 43, 439 (1939); *THIS JOURNAL*, 64, 1712, 2716 (1942).

(4) R. E. Powell, C. R. Clark and H. Eyring, *J. Chem. Phys.*, 9, 268 (1941).

(5) (a) R. M. Fuoss and D. J. Mead, *J. Phys. Chem.*, 47, 59 (1943);

(b) P. J. Flory, *THIS JOURNAL*, 65, 372 (1943).

(6) A. M. Sookne, H. A. Rutherford, H. Mark and Milton Harris, *J. Research Natl. Bur. Standards*, 29, 123 (1942).