

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN, BROOKLYN, NEW YORK]

The Calculation of Electrochemical Kinetic Parameters from Polarographic Current-Potential Curves

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It is shown that Koutecký's calculations regarding irreversible polarographic waves lead to the prediction that a plot of $E_{d.e.}$ versus $\log i/(i_d - i)$, where i and i_d denote maximum currents during drop lives, should be linear within experimental error over nearly the entire rising portion of a totally irreversible wave involving a single rate-determining electron-transfer step. This contradicts a crucial prediction of another treatment, the previous experimental "confirmation" of which is shown to be fortuitous. Methods are proposed for evaluating the parameters αn_a and $k_{t,b}^0$ from polarographic data.

Introduction

Equations for the polarographic current-potential curve corresponding to a totally irreversible process whose rate is governed by a single electron transfer step have been obtained by several authors. The most rigorous solution is generally agreed to be that of Koutecký¹; a graphical procedure devised by Delahay and Strassner^{2,3} yields essentially identical values of the parameters αn_a and $k_{t,b}^0$. (These symbols, as well as most of the others used below, are defined by Delahay.⁴) Kern⁵ deduced from Koutecký's treatment that a plot of $E_{d.e.}$ versus $\log i/(i_d - i)$, employing average currents in the logarithmic term, should be linear and should have a slope of $-0.0591/\alpha n_a$ volt at 25°. This result has been accepted by others concerned with the subject.^{6,7}

On the other hand, a treatment due to Evans and Hush,⁸ Hush and Oldham,⁹ Kivalo, Oldham and Laitinen,¹⁰ and Randles¹¹ leads to the conclusion that such a plot should not be linear, but rather a curve whose asymptotes at the foot and top of the wave differ in slope by a factor of 2. The literature of this theory includes the assertion that "Experimental confirmation of this change of slope has been obtained... by Kivalo, Oldham and Laitinen."¹¹

Herein it is shown that this "confirmation" is wholly fortuitous. In addition, by straightforward numerical deductions from Koutecký's values, an equation is derived for the slope of a plot of $E_{d.e.}$ versus $\log i/(i_d - i)$ with maximum currents in the log term. This is somewhat more convenient in general and is better adapted to the particular case in which the drop time varies appreciably over the rising portion of the wave than the relationship based on average currents that was deduced by Kern.⁵ The derivation of this equation and some of its consequences are described below.

(1) J. Koutecký, *Collection Czechoslov. Chem. Commun.*, **18**, 597 (1953).

(2) P. Delahay, *J. Am. Chem. Soc.*, **73**, 4944 (1951).

(3) P. Delahay and J. E. Strassner, *ibid.*, **73**, 5219 (1951).

(4) P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, N. Y., 1954.

(5) D. M. H. Kern, *J. Am. Chem. Soc.*, **76**, 4234 (1954).

(6) P. Delahay, *Record of Chemical Progress*, **19**, 83 (1958).

(7) W. H. Reinmuth and L. B. Rogers, *J. Am. Chem. Soc.*, **82**, 802 (1960).

(8) M. S. Evans and N. S. Hush, *J. chim. phys.*, **49**, C159 (1952).

(9) N. S. Hush and K. B. Oldham, cited in ref. 10.

(10) P. Kivalo, K. B. Oldham and H. A. Laitinen, *J. Am. Chem. Soc.*, **75**, 4148 (1953).

(11) J. E. B. Randles, in "The Principles and Applications of Polarography and Other Electroanalytical Processes," by G. W. C. Milner, Longmans, Green and Co., London, 1957, pp. 48-64.

Derivation of the Equation.—Koutecký¹ gave values for the function $F(\chi)$, where χ and the subsidiary variable λ that is used here for the sake of convenience are defined by the equation

$$\lambda = \sqrt{\frac{7}{12}} \chi = k_{t,b} \frac{t^{1/2}}{D_0^{1/2}} \quad (1)$$

Assuming that diffusion to the electrode surface is linear (this is one of the assumptions that leads to the Ilkovič equation for the diffusion current), the value of $F(\chi)$ is equal to the ratio i/i_∞ for a polarographic wave on which the current, i , is determined by the rate of a single electron-transfer step. The quantity i_∞ is the current that would flow at the same potential if the rate of the over-all process were strictly diffusion-controlled. Both i and i_∞ are defined as maximum currents during a drop life. Equation 1 is written here for the totally irreversible case, in which the rate of the backward reaction is negligibly small over the entire rising portion of the wave. When this is true, i_∞ will already be equal to the diffusion current, i_d , when the potential first becomes sufficiently negative to cause i to deviate significantly from zero.

Neglecting changes in the structure of the electrical double layer⁶

$$k_{t,b} = k_{t,b}^0 \exp(-\alpha n_a F_y E/RT) \quad (2)$$

which, when combined with eq. 1, yields

$$E = \frac{0.434RT}{\alpha n_a F_y} \log \frac{k_{t,b}^0 t^{1/2}}{D_0^{1/2}} - \frac{0.434 RT}{\alpha n_a F_y} \log \lambda \quad (3)$$

On the basis of the values given by Koutecký it may be shown that $\log \lambda$ is a linear function of $\log i/(i_d - i)$ over nearly the entire rising portion of the wave. The values are shown in Fig. 1, in which the straight line represents the least-squares "best" equation

$$\log \lambda = -0.1300 + 0.9163 \log i/(i_d - i) \quad (4)$$

which is valid from $0.1 \leq i/i_d \leq 0.94$ with a mean error of only ± 0.0043 in $\log i/(i_d - i)$. This is well within the experimental error involved in the most careful measurements from recorded polarograms. The behavior of the curve beyond these extremes cannot be reconciled with the prediction of Randles, *et al.*

On combining eq. 3 and 4, therefore, it follows from Koutecký's results that an irreversible wave of the type described above must obey the equation (at 25°)

$$E_{d.e.} = \frac{0.05915}{\alpha n_a} \log \frac{1.349 k_{t,b}^0 t^{1/2}}{D_0^{1/2}} - \frac{0.0542}{\alpha n_a} \log \frac{i}{i_d - i} \quad (5)$$

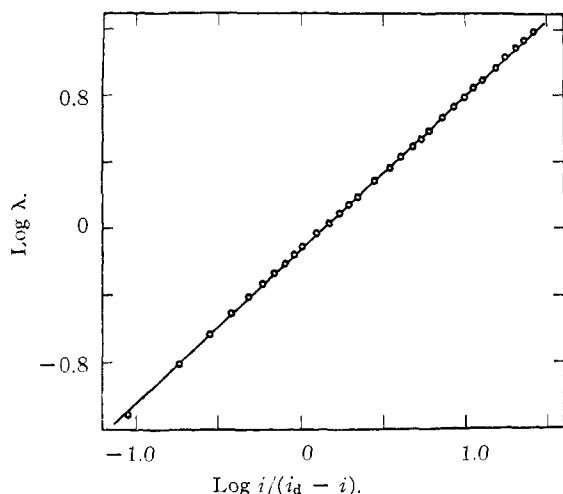


Fig. 1.—Plot of $\log \lambda$ versus $\log i/(i_d - i)$. Circles represent the values given by Koutecký; the straight line represents eq. 4.

Hence, if t is constant and independent of potential, a plot of $E_{d.e.}$ versus $\log i/(i_d - i)$ for such a wave should be linear and should have a slope equal to $-0.0542/\alpha n_a$ volt over the aforementioned range of validity of eq. 4. One may then write

$$E_{d.e.} = E_{1/2} - \frac{0.0542}{\alpha n_a} \log \frac{i}{i_d - i} \quad (6)$$

$$E_{1/2} = \frac{0.05915}{\alpha n_a} \log (1.349 k_{t,h}^0 t^{1/2}/D_0^{1/2}) \quad (7)$$

$$E_{3/4} - E_{1/4} = -0.0517/\alpha n_a \quad (8)$$

Delahay wrote an equation⁴ essentially identical with eq. 7. The difference between eq. 6 and Kern's equation⁵ employing average currents obviously reflects the manner in which the ratio of the average to the maximum current varies over the rising portion of the wave. Equation 8 indicates that the value of $E_{3/4} - E_{1/4}$ is not only a useful descriptive parameter, but also embodies a real physical significance, in dealing with totally irreversible waves.

More recently Koutecký and Čížek¹² have considered the effect of the correction for spherical diffusion. This consists of the second term on the right-hand side of the equation

$$i/i_d = F(\chi) - \xi_0 H_c(\chi) \quad (9)$$

where

$$\xi_0 = 50.4 D_0^{1/2} t^{1/2} / m^{1/2} \quad (10)$$

Values of the function $H_c(\chi)$ are tabulated by Koutecký and Čížek. The constant 50.4 is almost exactly equal to 1.5 times Koutecký's value of 34 for A in the equation¹³ $I = I^0(1 + AD_0^{1/2} t^{1/2} / m^{1/2})$. On the other hand, Strehlow and von Stackelberg¹⁴ proposed $A = 17$ and produced a large body of data in its support.¹⁵ Lingane and Loveridge¹⁶ proposed $A = 39$ and obtained 32.6 ± 0.9 experimentally.¹⁷

(12) J. Koutecký and J. Čížek, *Collection Czechoslov. Chem. Commun.*, **21**, 836 (1956).

(13) J. Koutecký, *Českoslov. čas. fys.*, **2**, 117 (1952).

(14) H. Strehlow and M. v. Stackelberg, *Z. Elektrochem.*, **54**, 51 (1950).

(15) H. Strehlow, O. Mädrich and M. v. Stackelberg, *ibid.*, **55**, 244 (1951).

(16) J. J. Lingane and B. A. Loveridge, *J. Am. Chem. Soc.*, **72**, 438 (1950).

(17) B. A. Loveridge, Ph.D. Thesis, Harvard University, 1947.

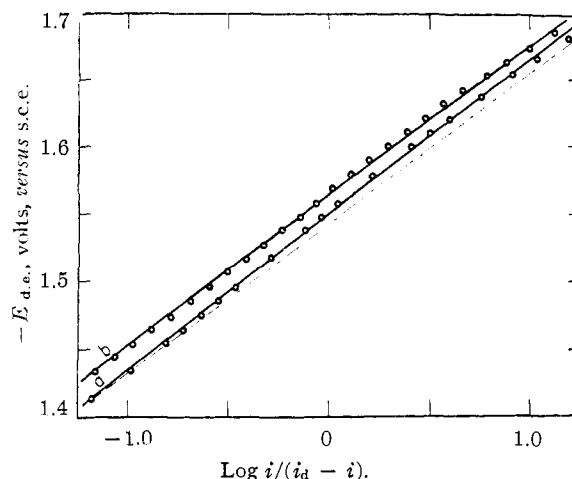


Fig. 2.—Log plots, uncorrected for variations of drop time with potential, for the wave of 1.0 mM hydrogen ion in 0.10 F potassium chloride. Curve a: $t = 4.7$ sec. at -1.50 v., slope = -118 mv.; curve b: $t = 2.6$ sec. at -1.50 v., slope = -107 mv. The dashed line is parallel to curve b.

Meites and Meites¹⁸ gave $A = 31.5 \pm 4.6$ as the mean of the experimental data then available. Many systems are also known for which $A = 0$ within experimental error.^{17,19}

Typically, $t^{1/2}/m^{1/2}$ is of the order of 1 mg.^{-1/2} sec.^{1/2} in polarographic work, while $D_0^{1/2}$ is not often widely different from 2.5×10^{-3} cm. sec.^{-1/2}. Taking A as 34 then gives $\xi_0 = 0.12$. Values of the constants γ_1 and γ_2 in the equation

$$E_{d.e.} = \frac{0.05915}{\alpha n_a} \log \frac{\gamma_1 k_{t,h}^0 t^{1/2}}{D_0^{1/2}} - \frac{\gamma_2}{\alpha n_a} \log \frac{i}{i_d - i} \quad (11)$$

have been computed for several values of ξ_0 by the procedure outlined above and are given in Table I. The entire variation of γ_1 from $\xi_0 = 0$ (which corresponds to eq. 5) to $\xi_0 = 0.2$, which is so high that it would rarely be encountered in practice, corresponds to only 0.01 volt in $E_{1/2}$ for $\alpha n_a = 0.5$; the accompanying variation of γ_2 corresponds to only 1.5% in the slope of the log plot. From this it may be concluded that the correction for spherical diffusion will not often be worth applying; when it is, linear interpolation between the values in Table I will surely suffice.

TABLE I

VALUES OF THE PARAMETERS γ_1 AND γ_2

See eq. 11 and the accompanying text. The fourth column of this table gives the mean deviation of the values of $\log i/(i_d - i)$ from the "best" equation of the form of eq. 4. The calculations were restricted to the range $0.1 \leq i/i_d \leq 0.94$ for the sake of uniformity.

| ξ_0 | γ_1 | γ_2 | Mean deviation |
|---------|------------|------------|----------------|
| 0 | 1.349 | 0.05420 | 0.0043 |
| 0.1 | 1.232 | .05479 | .0065 |
| 0.2 | 1.124 | .05499 | .0069 |

Experimental

Polarograms were obtained with a locally constructed and carefully calibrated recording polarograph for which the nominal recorder pen speed was 1 second full-scale. No damping was used. Previous experience with this instrument had indicated that in undamped operation it recorded maxi-

(18) L. Meites and T. Meites, *J. Am. Chem. Soc.*, **73**, 395 (1951).

(19) L. Meites, *ibid.*, **73**, 1581 (1951).

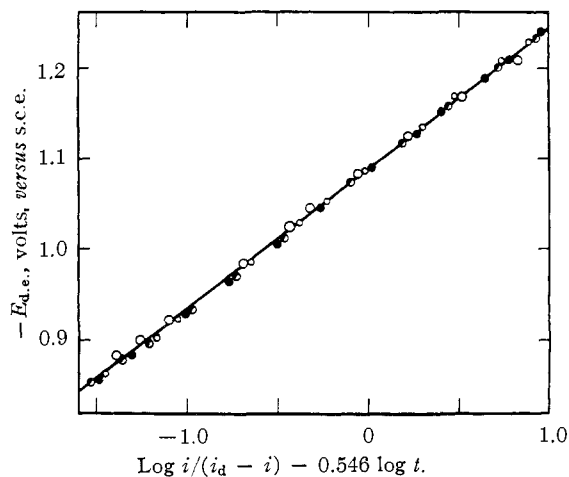


Fig. 3.—Log plots, corrected for variations of drop time with potential, for the wave of 1.0 mM chromate ion in 0.10 *F* sodium hydroxide. The drop time at -0.80 v. was 7.5 (large open circles), 5.5 (small open circles), 4.1 (half-solid circles) or 3.4 sec. (solid circles). The data yield the values $\alpha n_a = 0.35$, $k_{i,h}^0 = 1.2 \times 10^{-9}$ cm./sec.

imum currents that were in good agreement with those obtained under similar conditions by Grenier²⁰ using oscillographic techniques. The initial and span voltages were measured at the time of each experiment with a Rubicon precision potentiometer. The rate of polarization was usually 0.8 mv./sec. Corrections for iR drop in both the polarograph and the cell were applied in the usual fashion.

Particular care was taken to avoid possible contamination by traces of surface-active materials. The cell was of the double-diaphragm type: it consisted of a working-electrode compartment containing the solution being studied and provided with a sintered-glass gas-dispersion cylinder for deaeration by pure nitrogen, together with a silver-silver chloride reference electrode of the type described by Meites and Moros.²¹ The bridge compartment of this electrode was always thoroughly cleaned and refilled with fresh saturated potassium chloride just before each polarogram was recorded. This arrangement served to prevent contamination by agar, which might have occurred in the cell used by Kivalo, Oldham and Laitinen.¹⁰

Polarograms were obtained for a number of systems known to give totally irreversible waves. These included nickel(II) in potassium nitrate and in potassium chloride media, hydrogen ion and hydrogen peroxide in dilute potassium chloride, chromate ion in dilute sodium hydroxide and arsenic(III) in dilute hydrochloric acid.

Results and Discussion

In agreement with eq. 6, but in contravention of the theory of Randles, *et al.*, the data obtained in this work confirmed what has been known to polarographers for decades: except in unusual circumstances, a plot of $E_{d.e.}$ versus $\log i/(i_d - i)$ is linear over nearly the entire rising portion of the wave. It was also found that the slope of such a plot depends to some extent on the drop time employed, which has not been previously demonstrated. This is shown by Fig. 2. It reflects the variation of t with $E_{d.e.}$. It can be shown empirically that, over any range of potentials up to about 0.5 volt in width, this variation can be described by an equation of the form

$$\log t = k_1 + k_2 E_{d.e.} \quad (12)$$

with an error that does not exceed a few hundredths of a unit in $\log t$. Together with eq. 5, this results in a linear variation of $E_{d.e.}$ with $\log i/(i_d - i)$.

(20) J. W. Grenier, Ph.D. Thesis, Yale University, 1955.

(21) L. Meites and S. A. Moros, *Anal. Chem.*, **31**, 23 (1959).

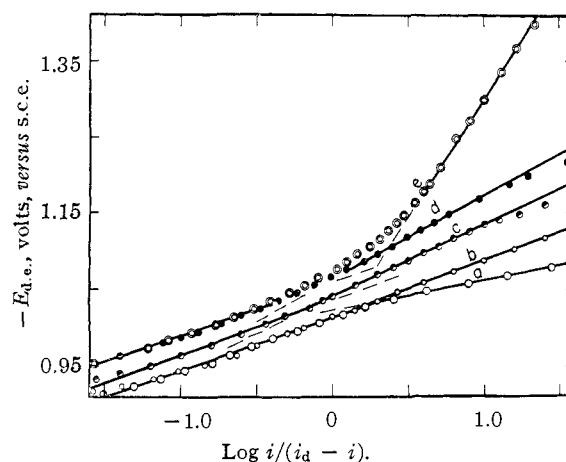


Fig. 4.—Log plots for the wave of 1.0 mM nickel ion in 0.10 *F* potassium chloride. The concentration of Triton X-100 was (a) 0.0002, (b) 0.001, (c) 0.002, (d) 0.0022 or (e) 0.0025%. With 0.0002% Triton X-100 t was 3.3 sec. at -1.0 v.

However, the value of k_2 for any one capillary depends on the height of the mercury reservoir (and also on the composition of the supporting electrolyte, the range of potentials in question, etc.), and therefore the slope of the log plot varies slightly with mercury pressure. The effect is most pronounced for waves occurring at relatively negative potentials where the electrocapillary curve is steepest.

Because of this effect, it is preferable to use eq. 5 in the form

$$E_{d.e.} = E' - \frac{0.0542}{\alpha n_a} \left[\log \frac{i}{i_d - i} - 0.546 \log t \right] \quad (13)$$

where

$$E' = \frac{0.05915}{\alpha n_a} \log \frac{1.349 k_{i,h}^0}{D_0^{1/2}} \quad (14)$$

The value of αn_a is best obtained from the slope of a plot of $E_{d.e.}$ versus $[\log i/(i_d - i) - 0.546 \log t]$; according to eq. 13, this slope is equal to $-0.0542/\alpha n_a$ volt. The intercept of the same plot, which is equal to E' , can then be used to calculate $k_{i,h}^0$ by means of eq. 14 with the aid of an estimate of D_0 obtained in the customary way.

Figure 3 shows such plots for the reduction of chromate ion from 0.1 *F* sodium hydroxide. Here, as in all of the other cases investigated, all of the data obtained at different mercury pressures conform to a single straight line. Over the stated range of validity of eq. 4, the mean difference between our experimental points and the best straight line through them was slightly less than 2 mv.

The data shown in Fig. 4 were obtained in an effort to confirm the evidence presented by Kivalo, Oldham and Laitinen¹⁰ in support of the prediction that the log plot for a totally irreversible wave involving a single rate-determining electron-transfer step consists of two straight lines. Curve a in this figure has almost exactly the same shape as the log plot given by these authors. Its upper portion indicates that the current is increasing more rapidly than eq. 5 predicts: this appears to be due to a not quite completely suppressed maximum. A definite maximum was indeed obtained in this system in the absence of a maximum suppressor, and the concentration of Triton X-100 used in

obtaining curve a (0.0002%) is far below what experience has shown to be needed for the complete suppression of maxima. The remaining curves in Fig. 4 demonstrate that the apparent agreement between the theoretical predictions and experimental results of Kivalo, Oldham and Laitinen¹⁰ is attributable to their accidentally having chosen a concentration of maximum suppressor that happened to produce a log plot conforming to their predictions. Attempts to duplicate their results under exactly the same conditions that they employed (0.5 mM nickel(II) in 0.20 *F* potassium nitrate containing 0.005% gelatin, *t* = 3.5 sec.) gave instead a strictly linear log plot like curve b in Fig. 4.

Acknowledgment.—It is a pleasure to acknowledge the helpful advice of Professor Joseph Jordan.

Summary.—From the results of computations by Koutecký as applied to the form of a totally irreversible polarographic wave involving a single rate-determining electron-transfer step, it is shown that a plot of $E_{d.a.}$ versus $\log i/(i_d - i)$, where *i* and i_d represent maximum currents during the drop lives, is linear over nearly the entire rising portion of the wave provided that *t* is constant. It is suggested that αn_a and $k_{t,0}$ can best be evaluated from the slope and intercept, respectively, of a plot of $E_{d.a.}$ versus $[\log i/(i_d - i) - 0.546 \log t]$, which prevents errors that might otherwise result from variations of *t* with $E_{d.a.}$. Both this deduction and the results of experimental measurements are in disagreement with another description of the form of the current-potential curve for such a process, and what has been taken to be experimental confirmation of that description is shown to be merely fortuitous.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, GEORGETOWN UNIVERSITY, WASHINGTON, D. C.]

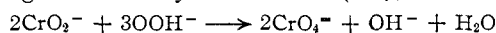
The Kinetics of the Oxidation of Cr(III) to Cr(VI) by Hydrogen Peroxide¹

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The rate of the oxidation of Cr(III) to Cr(VI) by aqueous alkaline hydrogen peroxide is first order in total Cr(III) concentration and in total hydrogen peroxide concentration. The base dependence is interpreted in terms of a Hammett-type acidity function: the rate is half order in effective hydrogen ion activity. The rate of the reaction is slowed by prior aging of Cr(III) in the basic medium and by the presence of CO₂. Mechanistic implications of these results are noted.

Acid dependencies of the rates of oxidation-reduction reactions of oxyions in acid solution have been interpreted in terms of protonated intermediates.³ This investigation was undertaken in order to obtain information on oxidation mechanisms in highly basic media. The system chosen is the oxidation of Cr(III) to Cr(VI) by alkaline hydrogen peroxide. This reaction often is used in analysis for Cr.⁴ The stoichiometry of the reaction, assuming minimum hydration of Cr(III), is



Experimental

Distilled water used in these studies was passed through a mixed-bed ion exchange resin to remove traces of metal ions. Cr(H₂O)₆(ClO₄)₃ was prepared by the method of Phipps and Plane.⁵ Stock solutions were kept at pH 2.5 to control colation (polymerization).⁶ Solutions of NaOH and KOH were prepared by dissolving NaOH and KOH pellets in water. Some of these solutions then were saturated with Na₂CO₃ or K₂CO₃. Carbonate-free NaOH solutions were prepared by precipitating carbonate as barium carbonate followed by filtration in a carbon dioxide free atmosphere. Excess barium was removed as the chromate after digestion at 90–95° for 1 hr. The chromate concentration in the resulting solution was determined spectrophotometrically at 374 mμ. Carbonate-free base was stored in polyethylene bottles fitted with air-tight serum caps from

which solution was removed by means of a hypodermic syringe. Carbon dioxide-free air was forced into the bottles to maintain a slight positive pressure.

Stock solutions of H₂O₂ were prepared by dilution of 30% hydrogen peroxide which contained no stabilizers. These solutions were kept under refrigeration and standardized daily with Ce(IV).⁷ Reaction mixtures prepared by dilution of these H₂O₂ stock solutions gave an H₂O₂ analysis within 1% of that calculated from the concentration of the stock solutions.

Rate measurements were made spectrophotometrically at 594 mμ. At this wave length CrO₄²⁻ does not absorb. Spectrophotometric measurements were made using Beckman model DK and DU spectrophotometers. A Varian model 11 recorder and Beckman ERA 5800 were used in conjunction with the DU for rate measurements. The sample compartment of the DU was thermostated to ±0.1° by circulation of thermostated water. Quartz spectrophotometer cells of 1, 5 and 10 cm. length were used. Alkaline samples of Cr(III) exhibited absorption peaks at 594 and 425 mμ. Beer's law was obeyed at both wave lengths. The measured extinction coefficient at 594 mμ was 27.1, which compares favorably to that which Symons⁸ observed in KOH glasses containing Cr(III) (26.9 ± 0.2). The peak at 425 mμ was more sensitive to changes due to aging of Cr(III) than was the peak at 594 mμ. After aging for four days, further peaks appeared between 360 and 400 mμ (Fig. 1). These peaks appeared to be related to the peaks in the reflectance spectrum of basic chromium rhododithionate observed by Schaffer.⁹ Schaffer interpreted these peaks as being due to the Cr–O–Cr grouping. The red color of peroxy-chromium compounds was not observed in the concentration ranges used in this study¹⁰ but does appear when more concentrated H₂O₂ is employed.

The reaction medium was prepared in the form of two solutions; A, an aged solution 0.080 *M* in chromium(III) and 0.050 *M* in sodium hydroxide and, B, an alkaline hydrogen peroxide solution of varying composition.

A was aged at 25°, usually for 1 hr., before initiating the reaction by mixing of solutions A and B. Heating effects

(1) Taken from a portion of a thesis to be submitted by Michael Baloga to the Graduate School of Georgetown University in partial fulfillment of the requirements for the Ph.D. Degree. Presented in part at the May 1961 meeting of the Chemical Society of Washington.

(2) Research grants from the National Science Foundation and the Smith, Kline and French Foundation are gratefully acknowledged.

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(6) (a) H. T. Hall and H. Eyring, *ibid.*, **72**, 782 (1950); (b) N. Bjerrum, *Z. physik. Chem.*, **59**, 336 (1907); **73**, 724 (1910); **110**, 656 (1924); (c) C. Altman and E. L. King, *J. Am. Chem. Soc.*, **83**, 2825 (1961).

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