where Z_+ is the cationic charge number, e the electronic charge, D the dielectric constant, d the sum of the fluoride and cation radii and $\Delta S'$ the entropy change in bringing together two species at one molar concentration, omitting their effect on the solvent. The latter value is estimated to be approximately -4 e.u.[17] When $-(\Delta F + T\Delta S')/Z_+$ is plotted *versus* d for the ions of Fig. 3, the $+2$ ions still lie somewhat below the $+3$, and the $+3$ below the $+4$. A decrease in the effective dielectric constant with increasing charge would account for such a trend.

For a given charge the variation of ΔF with radius is experimentally an higher inverse power of d than given by equation 5, if D is constant. Again such an effect can be explained by a variable dielectric constant which increases as d increases. Such a variation would be expected to arise from dielectric saturation in the intense electric fields near the cations.

Qualitatively the available data on fluoride complexing appear to be in agreement with the picture of an ionic type of complex. A quantitative treatment cannot be given at the present time.

One of us (M.S.T.) wishes to acknowledge the generous support of an American Association of University Women fellowship.

BERKELEY, CALIFORNIA

[17] This entropy change can be estimated roughly as minus R times the logarithm of the ratio of the number of positions available to the negative ions (or positive ions) before and after they are complexed. If the coördination number of the positive ion is assumed to be 6, there are $6N$ positions available to the negative ions when complexed, where N is Avogadro's number. Before complexing there are $55.6N$ positions. The resulting entropy change is -4 e.u. We are indebted to Professor H. S. Frank for this calculation.

[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORY, LOUISIANA STATE UNIVERSITY]

Influence of Foreign Electrolytes and Temperature in Electrochemical Kinetics. An Application of Polarography and Voltammetry at Constant Current

BY PAUL DELAHAY AND CALVIN C. MATTAX

RECEIVED MARCH 15, 1954

Conditions under which the effect of foreign electrolytes in electrochemical kinetics can be studied quantitatively are discussed. The influence of various salts of potassium and sodium (KF, KCl, KBr, KI, KNO_3, $K_4Fe(CN)_6$, $NaClO_4$, Na_2SO_4) on the rate of electron transfer in the reduction of iodate in alkaline solution on a mercury electrode is studied. The rate constant for electron transfer at the potential corresponding to the maximum of the electrocapillary curve (the difference of potential at the interface is *very approximately* equal to zero) is essentially proportional to the cation concentration. Comparison with data obtained on the effect of foreign salts on the rate of isotopic exchange is made, and Libby's interpretation is applied to the electrochemical reduction of iodate. It is shown that in general cations and anions may influence the rate of electron transfer depending on the electrode potential. The effect of foreign salt on the polarographic half-wave potential for irreversible electrode processes is discussed. The influence of temperature on the reduction of iodate, Ni(II), Cr(III) and oxygen on a mercury cathode is studied experimentally. Variations of the rate constant for electron transfer with temperature result from the dependence of the free energy of activation on temperature and from several other factors (variations of the transfer coefficient; variations of the potential (*vs.* N.H.E.) at which the difference of potential at the interface is equal to zero; complications resulting from consecutive reactions and from variations in the composition of the solution). Experimental rates were obtained by conventional polarography and voltammetry at constant current.

Part I. Influence of Foreign Salts

Introduction

The rate of electrochemical reactions is influenced by the presence of foreign electrolytes,[1-4] *i.e.*, electrolytes which are not involved in the stoichiometric equation of the electrode reaction. It is generally assumed that the nature of the anion is determinative, although the effect of cation has been reported.[3,5] The effect of foreign electrolytes has also been observed in polarography: in the case of reversible waves the shift in half-wave potential results from complexation and variations of activities[6]; however, these effects do not account for the shift in half-wave potential in the case of irreversible waves.[7] The present study will throw, it is hoped, some light on this subject and will show how the effect of foreign electrolytes in electrochemical kinetics can be measured and interpreted quantitatively.

Great care should be taken in the selection of a suitable electrode process in such a study, and the following conditions should preferably be fulfilled. (1) The substances involved in the electrode reaction should not form stable complexes with the electrolyte being studied. (2) The kinetic characteristics of the electrode process should not be affected by a change in the hydrogen ion activity, since the addition of foreign electrolyte obviously causes a change in the activity of this ion. (3) The electrode process should preferably be totally irreversible at the current densities being used; the influence of the backward reaction can then be neglected, and the interpretation of experimental data is simplified. Furthermore, the kinetics of the electrode reaction should essentially be controlled by a single rate-determining step. (4) Mercury electrodes should be preferred to solid electrodes because of better reproducibility of data.

The previous requirements are fulfilled in the reduction of iodate on mercury in alkaline solution

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(1) P. Lukovtsev, S. Levina and A. Frumkin, *Acta Physicochim. U.R.S.S.*, **11**, 21 (1939).

(2) J. O'M. Bockris, *Chem. Revs.*, **43**, 525 (1948).

(3) J. Heyrovsky, *Discs. Faraday Soc.*, **1**, 212 (1947).

(4) R. Piontelli, *Int. Comm. Electrochem. Therm. Kin.*, Proc. 2nd meeting, Tamburini, Milan, 1950, pp. 185-196. A bibliographic survey is given.

(5) M. Tokuoka and J. Ruzicka, *Collection Czechoslov. Chem. Communs.*, **6**, 339 (1934).

(6) (a) J. J. Lingane, THIS JOURNAL **61**, 2099 (1939); (b) D. D. De Ford and D. L. Andersen, *ibid.*, **72**, 3918 (1950).

(7) P. J. Elving, *et al.*, *Anal. Chem.*, **23**, 1218 (1951).

(pH 12 to 14). The kinetics of this reaction can be studied conveniently by voltammetry at constant current or by polarography. The latter method was selected here since this study offered an opportunity to apply a treatment of irreversible waves recently developed by Koutecky.[8]

Experimental

Polarographic waves for iodate were obtained by standard polarographic procedures except that maximum currents during drop life instead of average currents were measured; the integration of current during drop life is not necessary, and the interpretation of data is simplified. A Sargent polarograph model XXI was used, and a fast recorder (Brown, 1 second full-scale deflection) was substituted for the recorder of the polarograph. The composition of the iodate solution was: 0.5 m*M* potassium iodate, 0.05 *M* sodium hydroxide, 0.002% gelatin and a varying amount of electrolyte. The solution was contained in both compartments of a H-cell, no agar–agar plug being placed between the two arms of the cell. The compartment of the cell in which the reference electrode is usually contained, was connected by a salt bridge (saturated potassium chloride) to a saturated calomel electrode. Diffusion of chloride in the arm of the cell with the dropping mercury electrode was thus avoided. The temperature of the solution was controlled at 30 ± 0.1°. Potentials of the dropping mercury electrode were corrected for the ohmic drop.

The rate constant for the reduction of iodate at a given potential was calculated by applying treatments of irreversible waves recently developed.[8–9] It was founded that the methods of calculation of Delahay[9a,b] and Koutecky[8] yield approximately the same results. The former is based on the application of equation of linear diffusion, while the expansion of the mercury drop is taken into account in the latter treatment.[10] The Koutecky treatment, which is fundamentally more rigorous than Delahay's approach, was applied here. Koutecky tabulated values of the parameter $k_{f,h}t_p^{1/2}/D^{1/2}$ ($k_{f,h}$ rate constant for electron transfer, t_p drop time, D diffusion coefficient of electrolyzed species) as a function of the ratio i/i_d of the maximum current i along the wave to the maximum diffusion current i_d. Since t_p is known, and D can be computed from i_d by means of the Ilkovič equation (with the numerical coefficient 708), values of $k_{f,h}$ can be calculated at various potentials along the iodate wave. Values of $k_{f,h}$ obtained in this fashion are *formal* rate constants, *i.e.*, $k_{f,h}$ is the product of the rate constant by the activity coefficient of iodate ion.

Description and Discussion of Results

Plots of log $k_{f,h}$ against potential are shown in Fig. 1 for the reduction of iodate for a varying concentration of sodium sulfate. Note that the addition of sulfate causes a marked shift of the line log $k_{f,h}$ *vs.* E toward less cathodic potentials, and that the slope of this line remains unchanged. The linear dependence between log $k_{f,h}$ and E is to be expected from the equation

$$k_{f,h} = k^0_{f,h} \exp\left(-\frac{\alpha n_a F E}{RT}\right) \qquad (1)$$

where $k_{f,h}$ is the rate constant for the electrode reaction, $k^0_{f,h}$ the value of $k_{f,h}$ at the potential $E = 0$ (*vs.* N.H.E.), α the transfer coefficient, n_a the number of electrons in the rate-determining step ($n_a = 1$ very often), and the other symbols are conventional. Equation 1 is applicable to electrode processes whose kinetics is controlled by a single rate-determining step. When this is not the case, the logarithm of the apparent rate constant $k_{f,h}$ deduced from polarographic data is not a linear function of potential.[11]

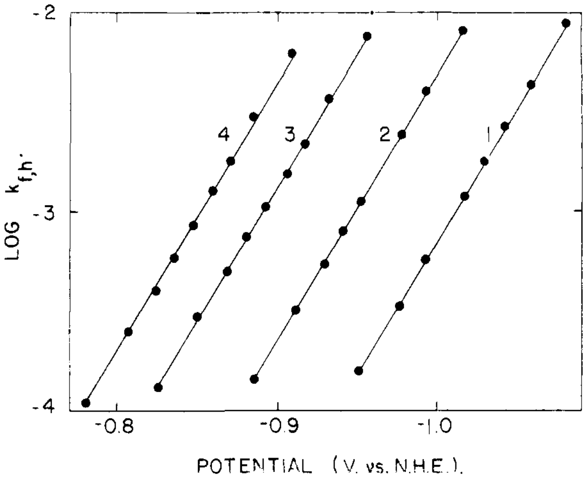

Fig. 1.—Plot of log $k_{f,h}$ against potential for the reduction of iodate in presence of sodium sulfate: 1, no sodium sulfate; 2, 0.1 *M* sodium sulfate; 3, 0.75 *M*; 4, 1.5 *M*.

By applying (1) to the data of Fig. 1 and similar data obtained with various electrolytes we calculated the values of $k^0_{f,h}$ plotted in Fig. 2. The value of αn_a was 0.77 ± 0.02 in all cases. The ionic strength was used to characterize the ionic contents of the solution, but it should be emphasized that this procedure is somewhat arbitrary

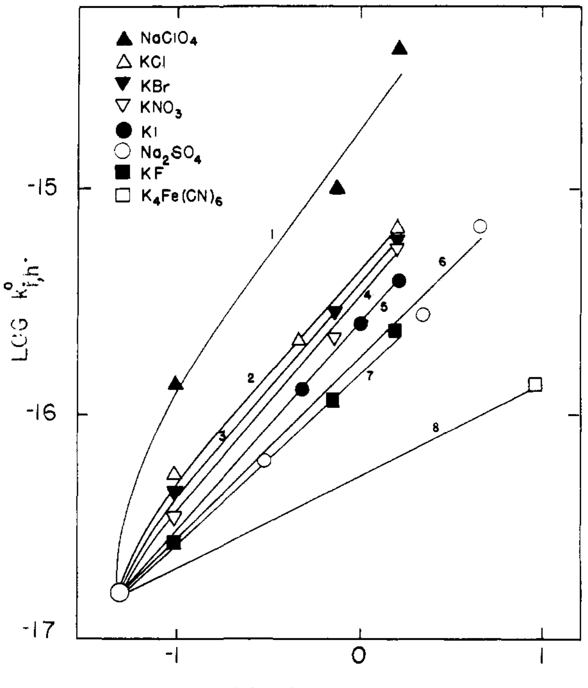

Fig. 2.—Plot of log $k^0_{f,h}$ against logarithm of ionic strength for the reduction of iodate.

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[8] J. Koutecky, *Chem. Listy*, **47**, 323 (1953); *Collection Czechoslov. Chem. Communs.*, **18**, 597 (1953).

[9] (a) P. Delahay, THIS JOURNAL, **73**, 4944 (1951); (b) P. Delahay and J. E. Strassner, *ibid.*, **73**, 5219 (1951); (c) M. G. Evans and N. S. Hush, *J. chim. phys.*, **49**, C159 (1952); (d) P. Delahay, THIS JOURNAL, **75**, 1430 (1953).

[10] For details see P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, N. Y., 1954, Chap. IV.

[11] T. Berzins and P. Delahay, THIS JOURNAL, **75**, 5716 (1953).

since the concentration of salt might be utilized just as well.

It is seen from Fig. 2 that the rate constant $k^0_{f,h}$ *increases* very markedly with ionic strength even at low ionic strengths. Such variations cannot be accounted for by the Debye–Hückel theory or modified forms of this theory. An interpretation based on variations in the liquid–liquid junction potential must also be rejected because of the order of magnitude of the change in $k^0_{f,h}$. Thus, a tenfold increase in $k^0_{f,h}$ would correspond to a variation of 0.078 volt in the junction potential (see equation 1, $\alpha n_a = 0.77$); this appears impossible. Another possible explanation would be that the iodate wave is shifted because of variations in the hydrogen ion activity. This interpretation also must be ruled out because it is observed that $E_{1/2}$ is essentially independent of *p*H under the present experimental conditions.[12] It must therefore be concluded that the presence of ions, which are not involved directly in the electrode reaction, influences the rate of the activation step in the reduction of iodate.

The values of $k^0_{f,h}$ plotted in Fig. 2 are calculated at $E = 0$ in the normal hydrogen electrode scale. Actually one should consider values of $k_{f,h}$ at the potential E (*vs.* N.H.E.) at which the difference of potential at the interface is equal to zero. Any change of this potential, which might result from a variation in the composition of solution, would then be automatically taken into account. Unfortunately this value of E is not known with precision, although it is probably not very different from the potential at the maximum of the electrocapillary curve (E.C.M.). However the orientation of molecules of water results in a difference of potential.[13] The shift in potential resulting from dipole orientation probably does not exceed a few hundredths of a volt[14] although this datum is quite uncertain. Because of this uncertainty it is useful to calculate $k^0_{f,h}$ on the basis of an arbitrary but highly reproducible zero of the scale of potentials, *i.e.*, in the normal hydrogen electrode scale. However, results must be corrected to lend themselves to further interpretation. The corrected results are shown in Fig. 3 where values of log $k_{f,h}$ at the E.C.M. potential are plotted against the logarithm of the cation concentration. This choice of ordinate will become apparent from the following discussion. Values of the E.C.M. potential (expressed *vs.* S.C.E.) used in this correction are listed in Table I. The E.C.M. potential for the electrolyzed solution (iodate, sodium hydroxide, gelatin; see "Experimental") was −0.500 v. *vs.* S.C.E. These potentials were determined by the mercury drop method.[15]

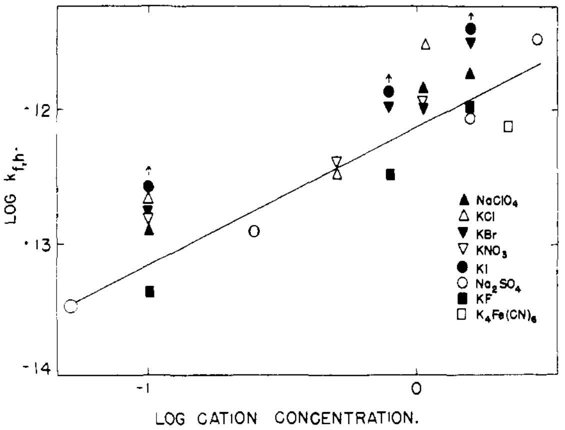

Fig. 3.—Plot of log $k_{f,h}$ against logarithm of cation concentration for the reduction of iodate. Values of $k_{f,h}$ calculated at the potential corresponding to the maximum of the electrocapillary curve. Points for potassium iodide are shifted downward by three units. Open circle in the left lower corner represents data obtained without the addition of foreign electrolyte, *i.e.*, with potassium iodate, gelatin and sodium hydroxide (see data in text).

TABLE I

POTENTIAL AT THE ELECTROCAPILLARY MAXIMUM (v. *vs.* S.C.E.)

Concn., mole/l.	0.1	0.5	0.75	1.0	1.5
KF	−0.46	.....	−0.46	.....	−0.48
KCl	− .52	−0.525	.....	−0.55	− .56
KBr	− .52	.....	− .525	.....	− .54
KI	− .77	.....	− .78	.....	− .78
KNO_3	− .485	.....	.....	−0.525	....
$K_4Fe(CN)_6$	.....	−0.50	.....	.....	....
$NaClO_4$	− .475	.....	− .50	.....	− .53
Na_2SO_4	− .42	.....	− .425	.....	− .44

It is seen from Fig. 3 that, with the exception of iodide, the nature of the anion is of secondary importance in determining the variations of the rate constant at the E.C.M. potential. This observation can be explained as follows. Iodate ion under the experimental conditions prevailing in this study is reduced at rather negative potentials—around −1 volt *versus* the normal hydrogen electrode. Anions are repelled from the electrode at such negative potentials, as is indicated by the identical shape the electrocapillary curve exhibits for these various ions.[13] Hence, values of $k_{f,h}$ are approximately the same whether a univalent ion such as fluoride or a highly charged ion such as ferrocyanide is present. The case of iodide is an exception because this ion is strongly adsorbed on mercury even at potentials as negative as those at which iodate ion is reduced.[13] Another conclusion which can be drawn from Fig. 3 is that *the rate constant* $k_{f,h}$ *at the E.C.M. potential is approximately proportional to the concentration of cation in the range of concentrations we explored.* There is some scattering of data, but this is to be expected on account of experimental errors and the uncertainty about the potential at which the potential difference at the interface is equal to zero. Furthermore, it is not at all certain that a linear relationship should be obtained. At any rate the results of Fig. 3 and the above interpretation indi-

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(12) I. M. Kolthoff and E. E. Orlemann, THIS JOURNAL, **64**, 1970 (1942).

(13) D. C. Grahame, *Chem. Revs.*, **41**, 441 (1947).

(14) G. Kortüm and J. O'M. Bockris, "Textbook of Electrochemistry," Elsevier Press, Houston, Texas, 1951, Vol. II, p. 360. See also the discussion by J. T. G. Overbeek, "Electrochemical Kinetics," National Bureau of Standards Circular 524, 1953, pp. 213–225. However, see H. Strehlov, *Z. Elektrochem.*, **56**, 119 (1952).

(15) "Electrical Phenomena at Interfaces," J. A. V. Butler, Editor, Methuen, London, 1951, p. 32.

cate indirectly that cations are not adsorbed on the mercury electrode to any appreciable extent, because if this were not so, the number of cations at the interface would not be a linear function of the bulk concentration of cation. Actually there is some evidence that cations of alkali metals are virtually not adsorbed since the electrocapillary curve at potentials markedly more negative than the E.C.M. potential remains unchanged when the nature of the cation is changed.[13]

The foregoing observations seem to be related to similar observations on the effect of salts on the rate of isotopic exchange. Cases in which the rate of isotopic exchange is proportional to the concentration of anion have been reported; for example in the exchange between Ce(III) and Ce(IV) in presence of fluoride ion.[16] Libby[17] has advanced a very interesting explanation for this effect of foreign electrolytes. By transposing his explanation to the reduction of iodate ion, one concludes that the effect of cation results from the formation of a transitory collision complex between iodate ion and the cation; the cation is probably part of the bridge between the iodate ion and the electrode in the electron transfer process. The number of such complexes formed per unit of time is proportional to the concentration of cation, and consequently the rate of electron transfer is proportional to the cation concentration.

In conclusion, either anions or cations or both types of ions may modify the rate of electron transfer in electrode process. *Thus, at potentials markedly more negative than the E.C.M. potential the cation is of primary importance, while the anion is important at less cathodic potentials.* It is to be expected that the influence of the cation on the rate of electron transfer increases when the charge of the ion increases. This is indeed the case. It was observed by Tokuoka and Ruzicka[5] that the tangent potential (45°) for the reduction of nitrate is shifted toward less cathodic potentials by approximately 0.4 volt in presence of divalent ions (Mg^{++}, Ca^{++}, Sr^{++}) and by 0.9 volt for trivalent ion (La(III), Ce(III)). A quantitative study of the effect of the valence of the ion is now being made.

Application to Polarography

It is customary in polarography to characterize electrode processes by their half-wave potential. Such a procedure, which is justified in the case of reversible processes, does not lend itself to a rational interpretation of irreversible processes.[9,11] One deduces from Koutecky's work that $k_{f,h} \cdot t_p^{1/2}/D^{1/2} = 0.76$ at the half-wave potential, or in view of equation 1, that $E_{1/2}$ is

$$E_{1/2} = \frac{RT}{\alpha n_a F} \ln \frac{k^0_{f,h} t_p^{1/2}}{0.76 D^{1/2}} \qquad (2)$$

Variations in the concentration of foreign electrolyte affects the factors $k^0_{f,h}$ and D in equation 2. In addition the transfer coefficient α might also be influenced, and the drop time t_p might vary (variation in interfacial tension). Finally the potential (*vs.* N.H.E.) at which the potential difference at the interface is equal to zero varies in many cases with the salt contents. *As a result, the variations of $E_{1/2}$ with salt concentration are so complex that not much progress can be expected from the sole consideratin of half-wave potentials in the case of irreversible electrode processes.*

Part II. Influence of Temperature

Studies on the influence of temperature in electrochemical kinetics have dealt almost entirely with hydrogen and oxygen evolution,[18] although a few other electrode processes have also been studied.[19] Two quantities, the transfer coefficient α and the heat of activation, are generally reported. Some problems pertaining to the determination of the heat of activation have been discussed by Agar.[20] The present study deals with the determination of the above two quantities and their use in the elucidation of the mechanism of electrode reactions.

Experimental

Rate constants were obtained by voltammetry at constant current, and the experimental method previously described was applied.[21] The calomel electrode, with respect to which the potential of the working electrode was measured, was at the same temperature as the solution being electrolyzed. A proper correction was made to refer the potential of the working electrode to the N.H.E.[22] The concentration of oxygen, in the study of the reduction of this substance, was determined by the Winkler method. The working electrode was a mercury pool.

Description and Discussion of Results

Potential–time curves for totally irreversible processes obey the equation[23]

$$E = \frac{RT}{\alpha n_a F} \ln \frac{nFk^0_{f,h}C^0}{i_0} + \frac{RT}{\alpha n_a F} \ln \left[1 - \left(\frac{t}{\tau}\right)^{1/2}\right] \qquad (3)$$

where C^0 is the bulk concentration of reducible species in mole cm.$^{-3}$, i_0 the current density, t the time at which E is calculated, and τ the transition time. It follows from (3) that a plot of log $[1 - (t/\tau)^{1/2}]$ against E yields a straight line whose reciprocal slope is $2.3RT/\alpha n_a F$. Hence, αn_a can be obtained from such a plot, and $k^0_{f,h}$ can be calculated from the value of E at time $t = 0$ (equation 3). Examples of logarithmic plots are given in Fig. 4 for the reduction of oxygen. Note the shift toward less cathodic potentials as the temperature is raised. Values of αn_a and log $k^0_{f,h}$ deduced from the data of Fig. 4 and similar data for three other processes are plotted in Figs. 5 and 6.

It is seen from Fig. 5 that the product αn_a varies slowly with temperature for processes 1, 3 and 4 while there is a pronounced variation of αn_a for process 2. Possible explanations for the variations of αn_a are as follows:

(1) All the processes studied here, except the reduction of chromium(III), involve the transfer of several electrons. The processes were analyzed on the assumption that the kinetics of the over-all reaction involves only one rate-determining step. This assumption may not be entirely valid in some cases, as for example in the reduction of Ni(II). In this process it is probable that the electrochemical reaction actually involves two steps

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[16] H. C. Hornig and W. F. Libby, *J. Phys. Chem.*, **56**, 869 (1952).

[17] W. F. Libby, *ibid.*, **56**, 863 (1952).

[18] J. O'M. Bockris in "Electrochemical Constants," National Bureau of Standards Circular No. 524, 1953, pp. 243–262.

[19] See for example J. E. B. Randles and K. W. Somerton, *Trans. Faraday Soc.*, **48**, 937, 951 (1952).

[20] J. N. Agar, *Discs. Faraday Soc.*, **1**, 81 (1947).

[21] P. Delahay and C. C. Mattax, THIS JOURNAL, **76**, 874 (1954).

[22] S. Glasstone, "An Introduction to Electrochemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1942, p. 232. There is some uncertainty about the temperature correction, but this is unimportant here.

[23] P. Delahay and T. Berzins, THIS JOURNAL, **75**, 2486 (1953).

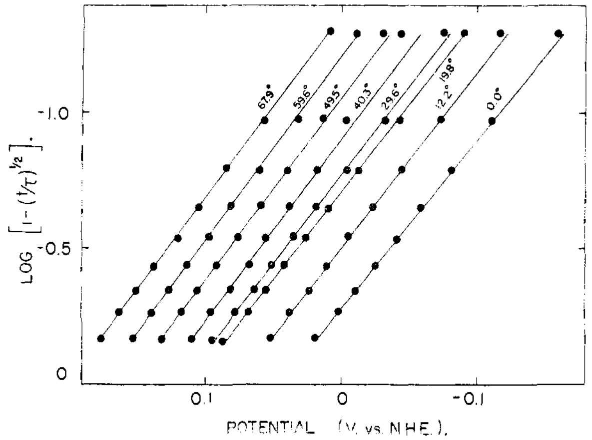

Fig. 4.—Plot of log $[1-(t/\tau)^{1/2}]$ *versus* potential for the irreversible reduction of oxygen at different temperatures in acetate buffer of pH 4.6.

which can be characterized at a given potential by two rate constants k_1 and k_2. At low temperatures one may assume that k_1 is much smaller than k_2; the kinetics of the electrode process is then entirely controlled by the first step. As the temperature is increased, k_1 increases more rapidly than k_2, and the kinetics of both steps must be considered. As a result, there is an abnormal variation of the transfer coefficient with temperature and of log $k^0_{f,h}$ with $1/T$ (Fig. 6, curve 2).

(2) It is probable that in some cases the variation of the product αn_a is due to a variation in the transfer coefficient α. There is no fundamental reason for assuming that the transfer coefficient is temperature independent.

(3) Finally, the formation of complex ions and the subsequent variation in the composition of the solution might influence the value of αn_α for substances such as chromium(III).

It is apparent from the foregoing observations that the effect of temperature on electrode processes is complex. In addition to variations of rate constant arising from the dependence of the free energy of activation on temperature, there are several complications: (1) variations of the transfer coefficient; (2) variations of the potential at which the difference of potential at the interface is equal to zero; (3) occurrence of stepwise processes; (4) changes in the composition of the solution. As a result, *heats of activation for electrode processes may embody the simultaneous variations of several factors.*

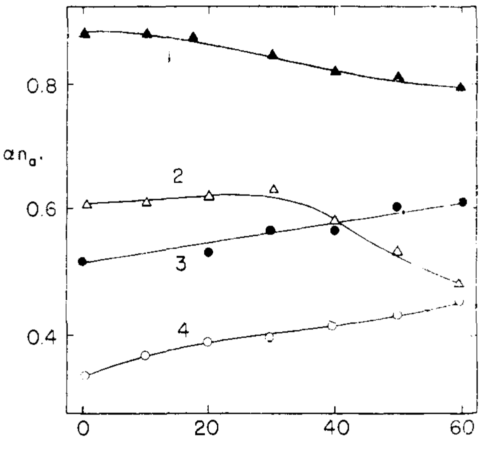

Fig. 5.—Variations of αn_a with temperature: 1, 1 mM iodate in 1 M sodium hydroxide; 2, 4 mM nickel(II) in 1 M potassium chloride; 3, 7 mM chromium(III) in 0.5 M potassium nitrate; 4, oxygen saturated in acetate buffer, pH 4.6.

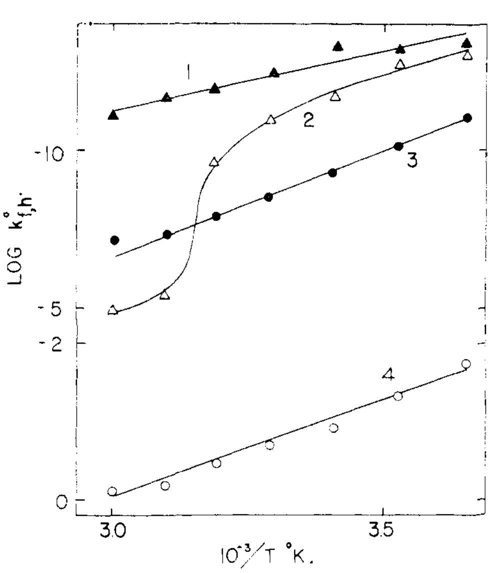

Fig. 6.—Variations of log $k^0_{f,h}$ with reciprocal of absolute temperature; same notations as in Fig. 5.

Acknowledgment.—The authors gladly acknowledge their indebtedness to the Office of Naval Research under whose sponsorship this study was made.

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