cated with fluorocarbon oil.[11] The lubricant served admirably to prevent seizure of the cap threads. The reactor was heated by a standard combustion furnace, with automatic control to ±5°. Samples were placed in weighed nickel boats. Gain in weight of the boat alone was negligible. Preheating and cooling were done in a nitrogen stream.

The cadmium metal and oxide were C.P. materials. The chloride was made by dehydration of the hydrate by fusion in platinum. The sulfide was prepared by the method given by Vanino,[12] using one-tenth the suggested amount of sulfuric acid.

Crystal Structure and Density.—Powder photographs were made with precipitated material which passed 200-mesh bolting cloth. A Philips 114.59-mm. camera was used, with the rotated sample mounted on a fine Pyrex fiber. Copper radiation was used with a nickel filter. The observed intensities were compared with a standard set of films prepared by the "sandwich" technique of Robertson,[13] assuming 75% absorption by each layer, as reported for Eastman Kodak Co. No-Screen film by Kaufman and Fankuchen.[14]

The calculated intensities were obtained from standard atomic scattering factors,[15] corrected for angle factor and multiplicity[16] and for absorption using the Claassen method.[17]

The back reflection photographs were also taken with filtered copper radiation, using a Philips 12-cm.-diameter precision focusing camera. The film was corrected for shrinkage using the fiduciary marks of the camera. Identical results were obtained with two samples, one from the cadmium sulfide reaction, and one from a precipitated cadmium fluoride.

The precipitated cadmium fluoride, which was also used for density and melting point measurements, was prepared by a modification of the method of Nuka,[18] in which a nearly boiling solution of 100 g. of cadmium nitrate tetrahydrate and 2 drops of 6 M nitric acid in a total volume of 125 ml. was treated with a filtered solution of 30 g. of ammonium fluoride in 75 ml. of water to which had been added enough hydrofluoric acid to make the resultant solution slightly acid. The precipitate was digested near boiling for about 15 min., before filtering and washing with warm water and ethanol. The material is microcrystalline and filters readily.

The density was determined at 25°, using the pycnometric method given by Bauer.[19] Benzene and benzene containing Aerosol OT[20] were used as immersion liquids. Their densities were determined by comparison with gas-free distilled water. Complete removal of air from the fine solid was extremely difficult.

Melting Point.—The melting point was determined in a graphite crucible, about 40 mm. long and 20 mm. in diameter. The crucible was supported by perforated nickel tubing inserted into a hole in the bottom. The tube and crucible were mounted in a vertical 25-mm.-diameter nickel tube wound with 22-gage nichrome wire over a 150-mm. section and well lagged with asbestos. The chromel–alumel thermocouple was introduced from the top of the furnace and nitrogen passed in through the perforated crucible support tube during the run.

Attempts to obtain satisfactory cooling curves were not successful because of the large volume decrease on fusion. As a result the melting point was determined by raising the furnace temperature to successive levels and ultimately determining the temperature at which the sample melted. The thermocouple was calibrated with silver by the same method in the same apparatus, taking the melting point of silver as 960.8°.[21]

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[11] du Pont FC-335, fluorocarbon oil, b.p. 210–240° (10 mm.).

[12] L. Vanino, "Handbuch der präparativen Chemie," Vol. I, Enke Verlag, Stuttgart, 1925, p. 565.

[13] J. M. Robertson, *J. Sci. Instruments*, **20**, 175 (1943).

[14] H. S. Kaufman and I. Fankuchen, *Anal. Chem.*, **21**, 24 (1949).

[15] "Int. Tabellen Bestimmung Kristallstrukturen," Borntraeger-Edwards, 1944, p. 571.

[16] C. W. Bunn, "Chemical Crystallography," Oxford University Press, London, 1945, p. 207.

[17] Reference (15), p. 583.

[18] P. Nuka, *Z. anorg. Chem.*, **180**, 235 (1929).

[19] N. Bauer in A. Weissberger, "Physical Methods of Organic Chemistry," Interscience Publishers, New York, N. Y., 1945, p. 99.

[20] American Cyanamid Company.

[21] *Chem. Eng. News*, **27**, 702 (1949).

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

A Theory of Irreversible Polarographic Waves[1,2]

BY PAUL DELAHAY AND JACOB E. STRASSNER

An equation for irreversible polarographic waves is derived by assuming that the current at any point of the wave is controlled by the rate of the electrode process and by the rate of diffusion of the substance reacting at the electrode. The dependence of the rate constant for the electrode process on the potential of the dropping mercury electrode is interpreted on the basis of the theory of absolute rates. The free energy of activation and the transfer coefficient for a given electrode reaction are computed from the corresponding current–voltage curve. The theory is applied to the reduction of iodate ion, and some experimental factors that might possibly affect the rate of electrode processes are examined. Relatively large variations of the rate of the electrode process are caused by the addition of gelatin. The number of electrons involved in the rate determining step of the reduction of iodate ion is calculated for solutions of various pH.

Although several treatments of irreversible waves have been reported[3–6] in the recent years, there is still a need for a satisfactory theory of these waves, as pointed out by Laitinen.[7] In the present paper, we report a new theory of irreversible waves which was developed by assuming that the current at any point of an irreversible wave is controlled by the rate of the electrode process and by the rate of diffusion of the substance reacting at the electrode.

General Equation for Irreversible Waves

We consider the case of an irreversible cathodic wave corresponding to an electrode process of the first order. Moreover, we assume that the influence of the reverse anodic process is negligible. This assumption is valid, provided that the cathodic overvoltage is at least a few tenths of a volt. No serious limitation is introduced by this condition, since many irreversible waves actually involve overvoltages of at least half a volt. Under these

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[1] Paper presented before the Division of Physical and Inorganic Chemistry of the XIIth International Congress of Pure and Applied Chemistry held in New York in September, 1951.

[2] Abstracted from a thesis to be submitted by J. E. Strassner in partial fulfillment of the requirements for the degree of Master of Science.

[3] H. Eyring, L. Marker and T. C. Kwoh, *J. Phys. Colloid Chem.*, **53**, 1453 (1949).

[4] N. Tanaka and R. Tamamushi, *Bull. Chem. Soc. Japan*, **22**, 187 (1949).

[5] R. Tamamushi and N. Tanaka, *ibid.*, **22**, 227 (1949); **23**, 110 (1950).

[6] P. Van Rysselberghe, THIS JOURNAL, **68**, 2047 (1947).

[7] H. A. Laitinen, in "Annual Review of Physical Chemistry," G. K. Rollefson, and R. E. Powell, Editors, Annual Reviews, Inc., Stanford, California, 1950, Vol. I, p. 307.

conditions, the number dN of moles of substance reduced in time dt is proportional to the concentration C of reducible substance at the surface of the mercury drop. Thus, one has per unit area

$$dN = KC\,dt \qquad (1)$$

where K is the rate constant of the electrode process.

Equation (1) is identical with the first equation of a previous paper,[8] in which an equation was derived for "kinetic" polarographic currents. The following equation for the instantaneous current was derived in this paper

$$i = 1255\ nm^{2/3}t^{2/3}C_0K[1 - \phi(Kt^{1/2}D^{-1/2})]\exp(K^2tD^{-1}) \qquad (2)$$

where m is the rate of flow of mercury in mg. sec.$^{-1}$, t is the time in sec., C_0 is the concentration of reducible substance in millimoles per liter, K is the rate constant in cm. sec.$^{-1}$, D is the diffusion coefficient of the reducible substance in cm^2. sec.$^{-1}$, and $\phi(Kt^{1/2}D^{-1/2})$ represents the error integral $\frac{2}{\sqrt{\pi}}\int_0^{Kt^{1/2}D^{-1/2}} e^{-z^2}\,dz$. The current i is expressed in microamperes in formula (2).

Formula (2) is the general equation for polarographic currents controlled by the rate of a first order electrode process and by the diffusion of the substance reacting at the electrode. It was shown before[8] that the current is practically controlled by the rate of reaction when $KD^{-1/2}$ is smaller than 0.05 sec.$^{-1/2}$. The current is almost completely controlled by diffusion when $KD^{-1/2}$ is larger than 5 sec.$^{-1/2}$. Finally, the current is controlled simultaneously by rate of reaction and by diffusion when $KD^{-1/2}$ is comprised between 0.05 and 5 sec.$^{-1/2}$.

In the case of an irreversible electrode process the rate constant is a function of the potential of the dropping mercury electrode. The initial segment of the wave corresponds to very low currents which are mainly controlled by the rate of the electrode reaction. As the potential of the dropping mercury electrode becomes more negative, in the case of a cathodic wave, the rate constant and the current increase. Under these conditions, the current is controlled by rate of reaction and by diffusion. In the upper plateau of the wave, the product $KD^{-1/2}$ is larger than 5 sec.$^{-1/2}$, and the current is practically controlled by diffusion. When $KD^{-1/2}$ is larger than 5 sec.$^{-1/2}$, equation (2) gives results which are almost identical to those obtained from the Ilkovic equation.[9] Thus, the Ilkovic equation is applicable to the limiting current of an irreversible wave. From the foregoing discussion it appears that the shape of an irreversible wave is determined by the dependence of the rate constant K on the potential of the mercury drop. If K increases rather slowly with the potential, a flat wave is observed. If K increases rapidly with the potential, a steep wave is obtained.

Variation of the Rate of the Electrode Process with Potential

The equation for an irreversible wave is obtained by introducing, in formula (2), the value of K calculated in terms of the potential of the dropping mercury electrode. The following formula will be applied

$$K = \frac{kT}{h}\,\delta \exp \frac{-\Delta F^* + \alpha n_a F\eta}{RT} \qquad (3)$$

where k is the Boltzmann constant; h the Planck constant; T the absolute temperature; δ the average distance, in solution, between two molecules or ions of the substance reacting at the electrode, in cm.; ΔF^* the free energy of activation of the electrode process; n_a the number of electrons involved in the rate determining reaction; F the faraday; η the overvoltage for the electrode process; R the gas constant; and α the transfer coefficient.

Equation (3) differs by the factor δ from the equation for K which is reported in the literature.[10] The difference results from the fact that the rate constant K of equation (1) is expressed in cm. sec.$^{-1}$, whereas the rate constant defined in the literature in connection with formula (3) is in sec.$^{-1}$. The advantage of using a special rate constant in the study of heterogeneous processes was mentioned previously.[8]

The overvoltage η in formula (3) is equal to the algebraic difference between the experimental potential for a given point of the wave and the reversible potential corresponding to the same value of the current. The reversible potential is calculated by application of the suitable equation developed in the theory of reversible waves.[11] The reversible half-wave potential used in these calculations is computed from thermodynamic data.[11] The overvoltage in formula (3) is always considered as a positive quantity.

It has often been suggested that the rate constant K is given by a formula similar to equation (3) in which the overvoltage is replaced by the potential of the electrode with respect to the normal hydrogen electrode. However, such a formula cannot be applied in the case of a cathodic wave occurring in the positive range of potentials (with respect to the normal hydrogen electrode) since the calculated rate constant of the electrode process would decrease with the potential of the mercury drop, whereas the rate constant actually increases. Such a contradiction is avoided when formula (3) is applied.

Calculation of Free Energy of Activation and Transfer Coefficient

According to formula (3), a plot of the logarithm of the rate constant K against the overvoltage η yields a straight line whose slope is proportional to the product αn_a of the transfer coefficient α by the number of electrons n_a involved in the rate determining reaction. Moreover, the value of log K at zero overvoltage is a linear function of the free energy of activation ΔF^* for the electrode process. Thus αn_a and ΔF^* can be calculated from a log K–η plot. The quantity δ which is needed in the calculation of ΔF^* is taken as being equal

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[8] P. Delahay, THIS JOURNAL, **73**, 4944 (1951).

[9] Equation (2) is identical with the Ilkovic equation when K is infinite. See reference 8.

[10] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp. 584–587.

[11] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1949, pp. 141–195.

to the average distance in solution between two ions or molecules of the substance reacting at the electrode. Actually, δ is the proportionality factor used in the conversion of a volume concentration to a surface concentration.[8] Therefore, the quantity δ is no longer equal to the average distance between two ions or molecules in solution if the substance reacting at the dropping mercury electrode is adsorbed at the surface of the mercury drop. This effect of adsorption is not taken into account in the present paper. Moreover, the concentration of reacting substance at the surface of the mercury drop varies with the current, and consequently the distance δ is not independent from the current. This effect is also neglected.

The values of the rate constant K needed in the preparation of a log K–η plot are obtained as follows: the current i for a given point of the wave is calculated in per cent. of the limiting current i_∞, and the rate constant K is determined, on the basis of this ratio i/i_∞, by a graphic procedure previously reported.[8] The value of the diffusion coefficient of the reacting substance, which is needed in the determination of K, is calculated by application of the Ilkovic equation to the limiting current.

Case of a Cathodic Process Involving Hydrogen Ion.—The foregoing treatment is applicable to electrode reactions of the first order. Quite often, irreversible electrode reactions involve hydrogen ion, and the above treatment is apparently not applicable to these cases. Actually, these irreversible waves can be analyzed by the present theory provided that the supporting electrolyte is buffered. It may then be assumed that the concentration of hydrogen ion at the surface of the mercury drop remains constant in the course of the electrode reaction. This assumption implies that the rate of combination and/or dissociation of the components of the buffer system is infinite. Since this is not the case,[8,12] relatively small deviations from the theory may result.

Experimental Verification for the Reduction of Iodate Ion

Since a thorough study of the polarographic reduction of iodate ion was made by Orleman and Kolthoff,[13] this experimental part should be considered only as an example of application of the theory just discussed.

Experimental.—Waves were recorded with a Sargent polarograph model XXI. An H-cell[14] with a saturated calomel electrode was used throughout the work. Unless otherwise specified, the rate of flow of mercury was 2.03 mg. per second for a head of mercury of 588 mm. This value of m, which was measured at −1.4 volts (S.C.E.) for a 0.5 M sodium hydroxide solution, was used in all the calculations. Differences of potential were measured with a Leeds and Northrup student potentiometer. Potentials were corrected for the ohmic drop in the polarographic circuit. Values of the pH below 10 were determined with a Beckman pH-meter model G. A saturated solution of monopotassium tartrate was used as standard.[15] Values of the pH above 10 were calculated. All data correspond to a temperature of 30 ± 0.03°. The universal buffer of Britton and Robinson[16] was used in the preparation of all the solutions except those exhibiting a pH of 0.94 and 13.7. The concentration of each constituent of the buffer mixture was twice that recommended in the literature.[16] The solution of pH 13.7 was prepared with sodium hydroxide, the solution of pH 0.94 with perchloric acid. The standard solution of potassium iodate was prepared from the C.P. product dried several hours at 105°.

Waves similar to those reported by Orleman and Kolthoff[13] were obtained. These waves were analyzed by the method discussed in the previous section. The diffusion coefficient of iodate ion was calculated by application of the Ilkovic equation to the limiting current of each wave.

Influence of the Concentration of Gelatin.—log K–η plots are given in Fig. 1 for 10^{-3} M potassium iodate solutions in sodium hydroxide at pH 13.7, and for various concentrations of gelatin. The wave obtained with a gelatin-free solution could not be analyzed because of the presence of a maximum. Figure 1 shows that the log K–η curve is shifted toward more negative potentials as the concentration of gelatin increases. The free energy of activation ΔF^* and the product αn_a, determined from the data of Fig. 1, are given in Table I. The drop time and the potential, at which the drop time and the diffusion current were measured, are also listed in Table I.

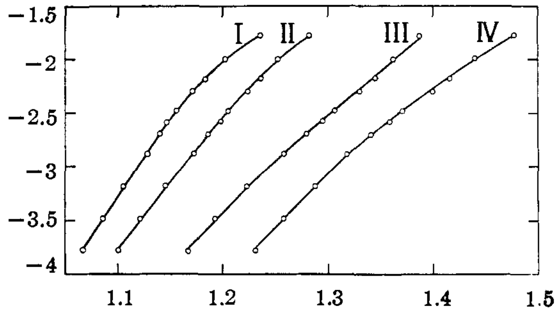

Fig. 1.—Logarithm of rate constant K against overvoltage for the reduction of 10^{-3} M potassium iodate in 0.5 M sodium hydroxide. Concentration of gelatin in per cent.: I, 0.001; II, 0.005; III, 0.01; IV, 1.0.

TABLE I

ΔF^* AND αn_a FOR THE REDUCTION OF IODATE ION

Concn. of gelatin, %	[illegible] sec.	E at i_∞ volts, S.C.E.	ΔF,* kcal.	αn_a
0.001	2.76	−1.373	36.6	0.89
.005	2.81	−1.368	34.0	.76
.01	2.69	−1.448	31.0	.61
1.0	2.63	−1.588	31.7	.60

Influence of the Head of Mercury.—Waves resulting from the reduction of 10^{-3} M potassium iodate in 0.5 M sodium hydroxide (containing 0.01% of gelatin) were determined with four different heads of mercury comprised between 475 and 809 mm. From the analysis of these waves we obtained: $\Delta F^* = 31 \pm 1$ kcal., and $\alpha n_a = 0.60 \pm 0.03$.

Influence of the Concentration of Iodate Ion.—Waves resulting from the reduction of iodate ion at various concentrations in 0.5 M sodium hydroxide (containing 0.01% gelatin) were recorded. The analysis of waves obtained with 2×10^{-5}, 10^{-4}, 10^{-3} and 5×10^{-3} M potassium iodate solutions gave practically the same free energy of activation and the same transfer coefficient. We obtained $\Delta F^* = 33 \pm 2$ kcal., and $\alpha n_a = 0.62 \pm 0.04$.

Influence of the pH of the Supporting Electrolyte.—Waves obtained with 10^{-3} M potassium iodate in buffered supporting electrolytes (containing 0.01% gelatin) were analyzed. The corresponding values of ΔF^* and αn_a are given in Table II. The drop time and the potential at which the drop time and the diffusion current were measured are also listed in Table II. The values of ΔF^* and αn_a corre-

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(12) J. Koutecky and R. B. Brdicka, *Collection Czechoslov. Chem. Commun.*, **12**, 337 (1947).

(13) E. F. Orleman and I. M. Kolthoff, THIS JOURNAL, **64**, 1044, 1970 (1942).

(14) J. J. Lingane and H. A. Laitinen, *Ind. Eng. Chem., Anal. Ed.*, **11**, 504 (1939).

(15) J. J. Lingane, *Anal. Chem.*, **19**, 810 (1947).

(16) H. T. S. Britton, "Hydrogen Ions," Vol. I, D. Van Nostrand Company, Inc., New York, N. Y., 1943, p. 313.

sponding to *p*H 0.94 are uncertain because of a possible distortion of the iodate wave by the current resulting from the anodic oxidation of mercury.

TABLE II

ΔF^* AND αn_a FOR THE REDUCTION OF 10^{-3} *M* POTASSIUM IODATE IN PRESENCE OF 0.01% GELATIN

*p*H	*t*, sec.	*E* at i_∞ volts, S.C.E.	ΔF,* kcal.	αn_a
0.94	3.61	−0.248	34.6	1.13
1.91	3.59	−0.418	25.3	0.59
4.06	3.57	−0.702	25.4	.53
6.03	3.24	−1.124	21.4	.28
7.82	2.99	−1.316	23.5	.31
9.69	2.75	−1.384	33.1	.61
11.6	2.78	−1.387	32.7	.63
13.7	2.62	−1.525	31.0	.61

Discussion of Experimental Results

Diagrams log K–η.—From the diagram of Fig. 1 and from similar log K–η plots determined in this investigation, one concludes that the logarithm of the rate constant K is approximately a linear function of the overvoltage. This observation confirms the conclusions of the theory of absolute rate which are embodied in formula (3). It should be added that the linear relationship between log K and η is only a first approximation. Figure 1 shows that the segment of the line log K–η corresponding to the upper half of the iodate wave is not linear. This curvature is probably caused by a variation of the transfer coefficient with the potential of the dropping mercury electrode. Moreover, a slight degree of curvature in the line log K–η is to be expected since the drop time varies slightly with potential,[18] whereas values of t used in the calculation of K were assumed to be independent of potential. In the present calculations the values of ΔF^* and αn_a were always computed from the slope of the initial segment of the log K–η curve.

It was also observed that the diagram log K–η for a given electrode reaction does not depend on the characteristics m and t of the dropping mercury electrode which is used in the recording of the wave. This is to be expected since the log K–η relationship is determined by the nature of the electrode process.

Free Energy of Activation and Transfer Coefficient.—The free energy of activation and the transfer coefficient do not vary with the concentration of iodate. On the other hand, the addition of gelatin modifies the quantities ΔF^* and αn_a. Table I shows that the effect of gelatin is especially pronounced for concentration of gelatin below 0.01%. For concentrations of gelatin larger than 0.01% there is practically no change in the values of ΔF^* and αn_a. This seems to indicate that the variations of ΔF^* and αn_a are caused by adsorption of gelatin at the surface of the mercury drop. In addition to the influence of gelatin, it is likely that the rate of the electrode process depends on the ionic strength of the supporting electrode.[13] This effect is under study in this Laboratory at the present.

Mechanism of the Reduction of Iodate Ion.—From Table II one concludes that the product αn_a of the transfer coefficient by the number of electrons involved in the rate-determining step is either approximately 0.3, or 0.6, or 1.2. This variation of αn_a can be accounted for either by a variation of α with *p*H or by a change of n_a with *p*H. Only the second hypothesis will be retained here since it may be assumed that the transfer coefficient for a given electrode reaction does not vary appreciably when the composition of the supporting electrolyte is changed. Furthermore we shall assume that the number of electrons n_a is equal to one when αn_a is equal to 0.3. On the basis of these hypotheses, one concludes that the rate determining step in the reduction of iodate ion involves one electron between *p*H 6 and 8. Above *p*H 8 and between *p*H 6 and 2, the rate-determining step involves two electrons. Below *p*H 1, four electrons are involved in the rate-determining step. The latter value of n_a is possibly erroneous because the log K–η plot used in the analysis of the iodate wave at *p*H 0.94 (Table II) may have been affected by a distortion of the iodate wave (see above). The *p*H limits are only approximate, and furthermore it is likely that two mechanisms are involved in the *p*H range corresponding to the transition from one mechanism to another. This is probably the case for the solutions at *p*H 0.94 and 4.06.

On the basis of the foregoing analysis one reaches the following conclusions. The transfer coefficient for the polarographic reduction of iodate ion, in presence of 0.01% gelatin, is approximately 0.3. In the absence of gelatin, α is larger than 0.45 (see Table I). The free energy of activation for the mechanism involving the transfer of two electrons is about 32 kcal. in basic solution and about 25 kcal. in acid solution. When one electron is transferred in the activation step, the free energy of activation is about 22 kcal. In very acid solution ($p\text{H} < 1$), the four electron transfer involves a free energy of activation of the order of 35 kcal.: All these values of ΔF^* are given for solutions containing 0.01% of gelatin. The shape of the iodate wave is mainly determined by the number of electrons involved in the activation step. When n_a is equal to one, a flat wave is obtained; when n_a is equal to two a rather steep wave is observed.

Conclusion

In the present theory, the equation for the current at any point of an irreversible wave is derived without postulating any relationship between the potential of the dropping mercury electrode and the rate constant of the electrode process. Consequently, the present analysis of irreversible waves is more general than previous treatments[3–5] in which a relationship between rate constant and potential was introduced in the initial step of the derivation.

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(18) Ref. 11, pp. 71–74.