TABLE I

THERMODYNAMIC FUNCTIONS AT 298°K.

	ΔH_f°, kcal./mole	ΔF_f°, kcal./mole	S°, e.u.		ΔH_f°, kcal./mole	ΔF_f°, kcal./mole	S°, e.u.
H^+	0	0	0	SCN^-	-11.8		
H_2O	-71.6			Pb^{++}	21.0	13	11
F^-		-80.8		Pb_9^{----}	64		
Cl^-	-65.7	-44.1	-30.3	Tl^+		5.7	
ClO_3^-	-47.7	-17.7	15	Zn^{++}		-25	
Br^-	-59.0	-39.9	-30.3	Hg^{++}	45.2	31	35
I^-	-45.3	-29	-25	Ag^+	26	17.5	23
IO_3^-		-42.4		Mn^{++}		-26	
Se_2^-	-19.0			BH_4^-	-15.7		
Te_2^-	-27.8			Ca^{++}	-100.0	-100	-21
Te_4^-	-29.7			Li^{++}	-49	-54	8
NO_3^-	-77.6	-42.8	- 5	Na^+	-38.1	-43.6	15.1
NH_3	-16.1	-2.7	24.7	K^+	-40.5	-47.0	21.4
NH_4^+	-16.1	- 2.7	24.7	Rb^+	-39	-47.5	29
NH_2^-	10.1	34	-10	Cs^+	-40.5	-48	29
NH_2OH	-24.6			$^1/_2e_2^-$ (am)	40.5	44.4	2
Guanidinium ion	-20.0			e^- (am)	43.5		

both the positive and negative ions fall upon a line if the absolute entropy of H^+ in ammonia is taken as -25 e.u. This plot is shown in Fig. 1. Since the slope of the line (as drawn) is unity, the coefficient of the Z/r_e^2 term in the Powell–Latimer equation must be approximately the same for both ammonia and water. At least for monatomic ions, it would appear that absolute entropies in water are simply 23 units higher than in ammonia.

Values for NO_3^- and ClO_3^- are included in Fig. 1, but since the Powell–Latimer equation applies only to the monatomic ions, it is not surprising that they fall off the curve. The experimental data for

dipositive ions in ammonia are so incomplete that it is not possible to ascertain the dependence of the entropies on the charge on the ion with any accuracy and the tentative values for Ca^{++}, Pb^{++} and Hg^{++} have not been plotted in Fig. 1.

A recalculation has been made of many of the thermodynamic functions for ions in ammonia.[7] A number of these new values differ from those previously tabulated by Jolly,[2] and a new summary is therefore given in Table I.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Verification of a Theory of Irreversible Polarographic Waves

BY PEKKA KIVALO, K. B. OLDHAM AND H. A. LAITINEN

Two independent schools have recently derived equations of totally irreversible waves; the equations are identical. The equation predicts that at the foot of the wave, the current obeys relationships that are typical of kinetic control; at the head of the wave, however, diffusion controlled relationships apply. Several expressions have been derived from the basic equation. Experimental verification of these expressions furnishes a convincing proof of the validity of the theory of irreversible waves.

During recent years, two independent approaches have been made to the problem of the interpretation of completely irreversible polarographic waves. The treatment employed by Delahay and Strassner[1–3] differs only in minor respects from that due to Evans, Hush and Oldham.[4–6] The basic equation of the polarographic wave, as derived by Delahay,[1,2] is identical in all but mathematical terminology from that obtained by Hush and Oldham.[6] The symbolism and method of the latter workers has been retained in the present paper because it

is more amenable to mathematical treatment than the graphical procedure of Delahay.

The purpose of the theoretical section of the present paper is to present some of the implications of the theory and, in particular, to derive relationships that may be readily tested experimentally. The experimental section is devoted to the verification of these relationships. Such verifications of the theory as have hitherto been reported,[2,6] have been of a somewhat scanty nature.

Implications of the Equation of the Irreversible Wave.—The basic equation derived by Hush and Oldham[6] to express the instantaneous current, i_t (in microamperes), passed by a dropping mercury electrode in consequence of the totally irreversible reduction

(1) P. Delahay, THIS JOURNAL, 73, 4944 (1951).
(2) P. Delahay and J. E. Strassner, ibid., 73, 5219 (1951).
(3) P. Delahay, ONR report No. 7, Project NR-051-258 (1952).
(4) M. G. Evans and N. S. Hush, J. chim. phys., 49, C159 (1952).
(5) N. S. Hush and K. B. Oldham, Nature, in press.
(6) N. S. Hush and K. B. Oldham, Trans. Faraday Soc., in press.

$$Ox + ne^- \xrightarrow{k} Rd \qquad (1)$$
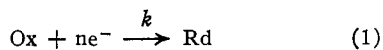
occurring at its surface, is

$$i_t = \sqrt{\frac{7}{3}} \left(\frac{36\pi}{d^2}\right)^{1/3} NFCD^{1/2}m^{2/3}t^{1/6} \sqrt{Z} \exp. Z \operatorname{erfc} \sqrt{Z} \qquad (2)$$

where d is the density of mercury (13534 mg. cm.$^{-3}$ at 25°); N is the total number of electrons transferred per molecule of Ox; F is the faraday (96500 coulombs mole^{-1}); C is the bulk concentration of Ox (millimoles liter^{-1}); D is the diffusion coefficient of Ox (cm.^{2} sec.$^{-1}$); m is the rate of flow of mercury (mg. sec.$^{-1}$), and t is the drop age (sec.). The complement of the error function is denoted by "erfc"; it is defined by

$$\operatorname{erfc} y = 1 - \frac{2}{\sqrt{\pi}} \int_0^y \exp(-y^2)dy \qquad (3)$$

The dimensionless parameter Z is given by

$$\left(\frac{DZ}{t}\right)^{1/2} = k = k_0 \exp \frac{-n\alpha FE}{RT} \qquad (4)$$

where n is the number of electrons involved in the rate determining step of reaction (1) (a whole number, less than or equal to N); α is the corresponding transfer coefficient; E is the potential applied to the electrode (corrected for ohmic drop, in volts *versus* any reference electrode and measured in accordance with the European convention, as is usual polarographic practice); R is the gas constant (8.314 volt coulomb mole^{-1} °C.$^{-1}$); T is the absolute temperature; k is the unimolecular velocity constant of reaction (1) (in the heterogenous units, cm. sec.$^{-1}$) at potential E, and k_0 is the value acquired by this rate constant at the zero of the potential scale upon which E is measured.

It is convenient at this juncture to define certain other symbols that will be employed later. The symbol i_d will be used to denote the instantaneous value of the diffusion-limited current. The function γ will be defined as the ratio of i (at a given value of E and t) to i_d (at the same value of t). The symbol $\bar{i}$ will be used to denote the mean current over the drop life. The subscript "m" will be applied to denote the conditions pertaining at the instant before the drop becomes disconnected. The function β will be defined as the ratio $\bar{i}/i_m$. The symbol h will be employed to denote the effective mercury head (the reservoir height, in cm., less a small back-pressure correction[7]). The term P will be used as an abbreviation for the first five terms on the right-hand side of equation (2).

It is instructive to consider the two limiting forms acquired by equation (2). As the potential becomes very negative, k assumes large values and consequently Z approaches infinity. Under these conditions it is legitimate to employ power expansions of $\exp Z$ and $\operatorname{erfc}\sqrt{Z}$, which give the limiting form of (2) to be

$$(i_t)_{\gamma \geq 0.9} = \frac{PD^{1/2}m^{2/3}t^{1/6}}{\sqrt{\pi}} \left(1 - \frac{1}{2Z}\right) \qquad (5)$$

(7) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. I, Second Edition, Interscience Publishers, Inc., New York, N. Y., 1952, pp. 78–86.

Similarly, the limiting form of (2) for the most positive potentials is

$$(i_t)_{\gamma \leq 0.1} = PD^{1/2}m^{2/3}t^{1/6} \sqrt{Z} = Pm^{2/3}t^{2/3}k \qquad (6)$$

Equations (5) and (6) are approximations of (2) valid to better than 5% in the ranges of γ indicated. Equation (5) is of the same form as the Ilkovic Equation, to which it reduces when Z becomes infinite. On the other hand, (6) is an equation typical of kinetically controlled currents. It is apparent that i is proportional to electrode area and independent of D.

The maximum limiting current will be given by

$$(i_d)_m = \frac{PD^{1/2}m^{2/3}t_m^{1/6}}{\sqrt{\pi}} \qquad (7)$$

and since it has been shown[7] that m is directly proportional to h and t_m is inversely proportional to h, it follows that the maximum current at the head of an irreversible polarographic wave is directly proportional to the square root of the effective reservoir height. However, since m and t occur to the same power in (6), i_m will be independent of h at the foot of the wave.

The Shape of Irreversible Waves.—By using an undamped high-speed recorder it is possible to determine the variation of i_m as a function of a gradually increasing negative potential. The shape of the wave is most aptly described in terms of the variation of the ratio γ_m with increasing negative potential.

From equations (2) and (7), it is readily shown that

$$\gamma_m = \sqrt{\pi} \sqrt{Z_m} \exp Z_m \operatorname{erfc} \sqrt{Z_m} \qquad (8)$$

Since Z_m and E are related by equation (4) thus

$$\ln Z_m = \ln \frac{k_0^2 t_m}{D} - \frac{2n\alpha FE}{RT} \qquad (9)$$

equation (8) defines the shape of irreversible polarographic waves.

Equation (8) shows that γ_m is a function of Z_m only. Therefore at any constant value of γ_m (*e.g.*, 0.5, corresponding to the half-wave potential, $E_{1/2}$), Z_m must be constant. Under these conditions, equation (9) predicts that $-E_{1/2}$ will vary linearly with log t_m and that

$$\frac{\Delta \log t_m}{\Delta - E_{1/2}} = \frac{2n\alpha F \log e}{RT} = 33.8n\alpha \text{ volt}^{-1} \qquad (10)$$

at 25°.

If values are ascribed to the constants k_0 and $n\alpha$, equations (8) and (9) enable the wave shape to be calculated uniquely since t_m and D are readily determined. A comparison of experimental and theoretical wave shapes is reported in the experimental section of this paper.

The physical significance of Z_m is clear. Z_m takes values between 0 and infinity as γ_m varies from zero to unity. At low values of Z_m, the limiting form of (8) shows that the current is kinetically controlled, whereas diffusion control becomes increasingly operative as Z_m approaches infinity. The changeover can be said to occur at the point of inflection at which $Z_m = 1/4$. The inflection point occurs at $\gamma_m = 0.545$ and not at $E_{1/2}$ as in the case with reversible waves.

A convenient method of representing polarographic waves is by the "log plot," *i.e.*, a plot of the function $\log [(i_d)_m - i_m/i_m]$ *versus* $-E$. If t_m is assumed to be constant over the range of a polarographic wave, from equations (8) and (9)

$$\frac{d}{dE} \log \frac{(i_d)_m - i_m}{i_m} = \frac{n\alpha F \log e}{RT}\left[\frac{1}{1 - \gamma_m} - \frac{2Z_m}{\gamma_m}\right] \quad (11)$$

The term inside the square brackets in (11) is variable with potential; however, it rapidly approaches unity as Z_m becomes small and acquires the value 2 as Z_m tends to infinity. Hence it is to be expected that the log plot for an irreversible reduction will be of an hyperbolic form, such that the gradient of the log plot in the region corresponding to the head of the wave will be twice that of the lower section. Such a doubling of log plot slope has been previously reported[5,6] for results based upon average currents. According to equation (11)

$$\left(\frac{d}{dE} \log \frac{(i_d)_m - i_m}{i_m}\right)_{\gamma_m \to 1} = \frac{2n\alpha F \log e}{RT} = 33.8\ n\alpha\ \text{volt}^{-1} \quad (12)$$

and

$$\left(\frac{d}{dE} \log \frac{(i_d)_m - i_m}{i_m}\right)_{\gamma_m \to 0} = \frac{n\alpha F \log e}{RT} = 16.9\ n\alpha\ \text{volt}^{-1} \quad (13)$$

at 25°.

The *β*-Function.—From the definition of *β*, a few transformations yield

$$\beta = \frac{\int_0^{Z_m} Z^{2/3} \exp Z\ \text{erfc}\ \sqrt{Z}\, dZ}{Z_m^{5/3} \exp Z_m\ \text{erfc}\ \sqrt{Z_m}} \quad (14)$$

which shows that *β* is a function of Z_m only. The form of this function, and its derivation, are discussed elsewhere.[6] The function *β* attains the value 3/5 when Z_m is small (base of wave) and the Ilkovic value 6/7 at the head of the wave and on the diffusion plateau.

Experimental

In the experiments two recording polarographs were used: for the current–voltage curves the Sargent Model XXI was employed with 0.75 v. span and damping setting 0; for the *β*-curves a Leeds and Northrup Type E Electro-chemograph was used with constant potential, applying damping 0 and 2. Because the damping is capacitative only in the latter instrument, no additional ohmic drop is caused provided the potential is kept constant. The potentials were checked with a Rubicon potentiometer. The current–time curves were recorded manually using a Du Mont Type 304 H cathode-ray oscillograph, a Sargent Model III manual polarograph and a stop watch. At its highest sensitivity setting the oscillograph had a Y-axis deflection of 32.4 inches per volt. The ohmic drop across a 9420 ohm resistor was fed in the Y-input of the oscillograph and the X-axis sweep was synchronized with the drop using a 32 µf external condenser.

An H-cell having a 20-mm. fine sintered glass plug separating the two compartments was used. The solution for analysis was placed in both compartments so that the liquid level was about 1 cm. higher in the cathode compartment than in the anode compartment. The reference electrode was a saturated calomel electrode (S.C.E.) connected to the anode compartment by means of a salt bridge containing saturated potassium chloride solution and ending with an agar plug. The a.c. resistance of this cell was 580 ohms (minimal value at instant of drop fall) using 0.2 *N* potassium nitrate solution and 60.0 cm. mercury head. The ohmic drop corrections were the products of this value and the maximum current. The experiments were performed at 25 ± 0.1°. Oxygen was removed from the solu-

tions with oxygen-free nitrogen. The dropping electrode (A) used had an *m*-value of 1.935 mg./sec. and *t* = 4.50 sec. (open circuit and mercury head 60.0 cm. in 0.2 *N* KNO₃). For the $E_{1/2}$ *vs.* log t_m experiment another dropping electrode (B) was used with *t* = 2.09 sec. (open circuit and mercury head 64.0 cm.) and an *m*-value of 3.195 mg./sec. In the experiments with varying mercury head a correction was made for the back-pressure which was calculated to be 1.5 cm.[7] The supporting electrolyte throughout the experiments consisted of 0.2 *N* potassium nitrate and 0.005% gelatin.

Results and Discussion

In order to test experimentally the equations derived from the theory of irreversible waves, the hexaaquonickel(II) ion was chosen to be used in a nitrate supporting electrolyte where the reduction proceeds irreversibly.[8]

The Current–Time Relationship.—The oscillographic technique has been widely used for the investigation of the current–time relationship. No ohmic drop correction is necessary provided the current has the true limiting value. The situation is, however, different if the rising portion of curve is studied. Depending upon the measuring resistance and the gradient of the current–voltage curve at a particular potential, the current–time curve for a drop-life is more or less distorted. In order to obtain the correct i_m-t curve at a constant potential the following graphical method was used. A family of i_m-t curves recorded at constant applied potentials at 5–10 millivolt intervals were plotted on the same graph, the ordinate being the applied potential and the abscissa time. The current (corrected for residual) is also plotted as ordinate such that increasing current is in the direction of decreasing negative potentials and such that the origin of each curve is at the corresponding applied potential. The scale unit of current, 1 microampere, is equal to 10 millivolts to take into account ohmic drop caused by a total of 10,000 ohms resistance in the circuit. The correct i_m-t curve was obtained by sliding on a constant potential line from curve to curve and recording the corresponding current and time. Figure 1 shows experimental points obtained in this way at the beginning of the reduction wave of a 4 millimolar nickel solution. The experimental points follow closely the theoretical $t^{2/3}$ behavior as is predicted by equation (6).

The Dependence of the Current on the Mercury Head.—The theory predicts that at the beginning of the wave, the current should be independent of the mercury head whereas the limiting current is proportional to $\sqrt{h}$. The experiment was conducted using a 4 millimolar nickel solution. The mercury head was varied between 35.0 and 79.0 cm. at a set of potentials. In Fig. 2 the results are shown. The current corresponding to lowest mercury head was taken as reference and the relative increase was plotted against the square root of relative increase of the mercury head. As can be seen, the current at the bottom of the wave (γ_m small) is almost independent of the mercury head, whereas at the limiting current it is practically directly proportional to $\sqrt{h}$.

The Dependence of $E_{1/2}$ upon Droptime.—The testing of equation (10) was performed using
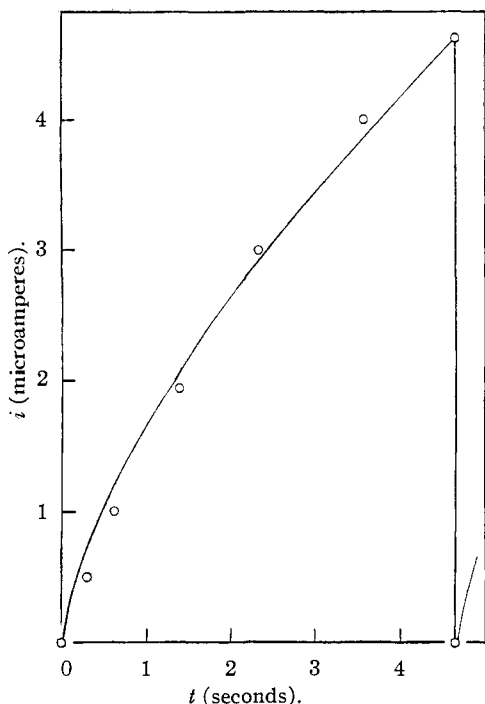
(8) Ref. (7), p. 186.

Fig. 1.—The growth of current during the life of a drop, determined oscillographically. Lower portion of irreversible wave (γ_m = 0.1). Circles are experimental and the line is for i proportional to $t^{2/3}$.

two capillaries with different m-values and a 0.5 millimolar nickel solution. Table I shows the results of these experiments. The agreement with the theory is fairly good as can be judged from the reasonable constancy of $n\alpha$. It might be pointed out that the relationship between $E_{1/2}$ and drop-time is independent of the m-value.
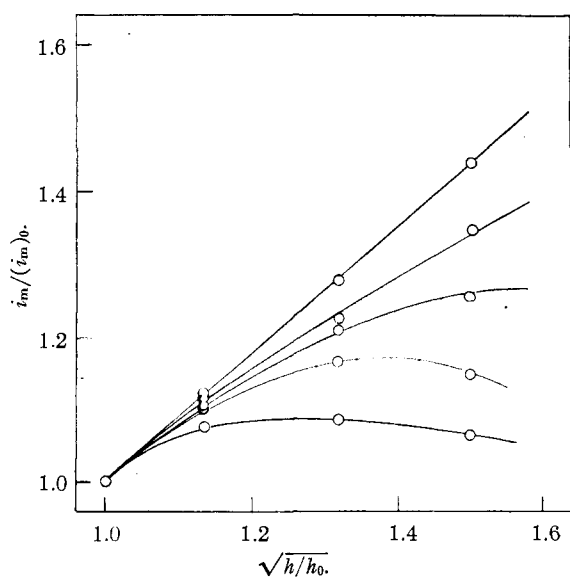
TABLE I

El.	H, cm.	t_m, sec.	$-E_{1/2}$ cor. v. vs. S.C.E.	$\dfrac{\Delta \log t_m}{33.83\Delta - E_{1/2}}$ $= n\alpha$
A	35	7.66	0.9589	..
A	45	5.95	.9691	0.31
A	60	4.47	.9798	.33
A	79	3.47	.9905	.32
B	48	2.75	1.006	.28
B	64	2.09	1.016	.29

Av. . .31

preferably zero. The experiments described above were obtained with an increasing polarization of 0.93 millivolt/sec. and checked using constant potentials. In one series of experiments the rate of increase of polarization was 3.3 millivolts/sec., but this resulted in a distortion of the i–E curve, especially at large drop times.

The Current–Voltage Curve.—One of the most convincing proofs of the theory is that the theoretical current–voltage curve has the same shape as the experimental one. In Fig. 3, the curve represents an experimental polarogram of a 0.5 millimolar nickel solution with the same slow rate of polarization as before. The points are obtained according to the theory from equations (8) and (9). The half-wave potential was used to "fit" the theoretical points to the curve. Additionally the following data were used: t_m = 3.47 sec.; D = 0.69 × 10⁻⁵ cm.² sec.⁻¹; $n\alpha$ = 0.40 and, as calculated from $E_{1/2}$, k_0 = 1.24 × 10⁻¹⁰ cm. sec.⁻¹.

In Fig. 3 the plot of log $(i_d)_m - i_m/i_m$ against the potential is also shown. As can be seen the slope of the log plot approximately doubles as expected from equations (12) and (13). The $n\alpha$ values obtained here were 0.32 and 0.37, respectively.
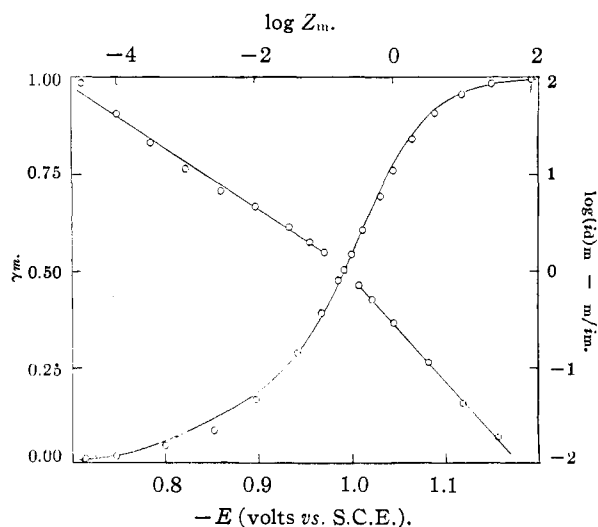

Fig. 2.—Effect of variation of reservoir height on the maximum current at various points in the reduction wave of Ni⁺⁺. Circles are experimental. The upper curve is for γ_m = 1.00, the others for γ_m = 0.78, 0.54, 0.20 and 0.10.

It is of importance that the increase of polarization during the drop-life be as small as possible or

Fig. 3.—The smooth curve is an experimental plot of γ_m versus $-E$; the circles are calculated from equations (20) and (21). The two linear plots are portions of the log plot of the same wave; circles are experimental and the "best straight lines" were used in the calculation of log plot gradients.

Strassner and Delahay[9] have recently reported $n\alpha$ values for the reduction of hexaaquonickel in

(9) J. E. Strassner and P. Delahay, iTH JOURNAL, 74, 6232 (1952).

various concentrations of gelatin. They report a value of 0.45 for 0.005% gelatin, which is in fair agreement with the value obtained here considering that the temperature (35°) and supporting electrolyte concentration ($1N$) were different in their experiments.

Generally speaking it must be realized that $n\alpha$ is not necessarily constant along the wave, as pointed out by Strassner and Delahay.[9] It is also very sensitive to stirring effects[10] (see Fig. 3, bottom of the wave, where the slightly too high current is probably caused by stirring at the surface of the mercury electrode).
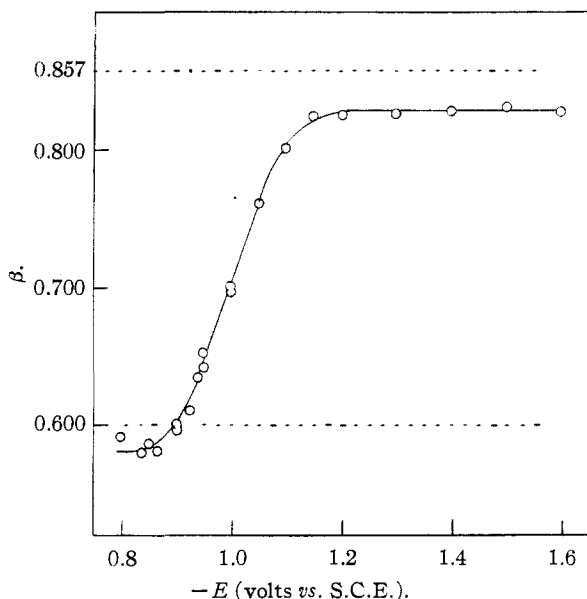
As to the actual electrode process, it is conceiv-

Fig. 4.—Plot of the variation of β with potential. Circles are experimental points. The dashed lines represent the theoretical limits of β.

(10) E. F. Orlemann, Ph.D. Thesis, University of Minnesota, 1941, observed stirring at the foot of the iodate reduction wave even in the absence of a visible maximum.

able that $n = 1$, in other words, that the addition of the first electron is rate determining, although no proof can be presented.

The β-Curve.—In this experiment a 4 millimolar nickel solution was electrolyzed. According to the theory, the ratio $i/i_m = \beta$ should be about 0.857 at the limiting current and then it should decrease along the rising portion of the wave in the direction of more positive potential to a limiting value of 0.60. Figure 4 shows the results of the experiment, which agree approximately with the theory. The same curve was also obtained with one millimolar concentration of nickel.

It should be pointed out that in the rising portion of the wave a small ohmic drop decreases somewhat both i and i_m, but the correction almost cancels out for the ratio i/i_m; hence it is here neglected.

It will be seen that the upper limit of β is only 0.83 and not the Ilkovic value 0.86. A similar discrepancy that has been observed previously[11] can be explained in terms of the modified Ilkovic equation.[12]

Conclusion

It has been shown that the reduction of hexaaquonickel(II) ion is in good agreement with the theory of totally irreversible polarographic waves. Some experiments (which are being continued), have been performed on the irreversible reduction wave of hydrogen ion; the results show the same features as do those for nickel ion, hence it can be assumed that the theory has general validity.

The change of the dependence of the current on the mercury head, with change of potential over the rising portion of the wave, serves as a simple and rapid test of an irreversible polarographic process.

(11) Ref. (7), p. 75.
(12) Ref. (7), p. 44.