TABLE III

COMPARISON OF POTENTIOMETRIC AND VAPOR PRESSURE RESULTS FOR HCl IN 50.00 WT. % DIOXANE–WATER, 25.00°

m	$\frac{\mathfrak{F}}{RT}\frac{dE^0}{dZ_1}$	$\int_0^m \frac{\partial \ln \gamma_\pm}{\partial Z_1} dm$	$\int_0^m m \, d \ln \gamma_\pm$
0.02467	$13.5_0 \pm 0.3$	0.0470	-0.0030_3
0.05060	$13.5_0 \pm .3$	0.1230	-0.0074_5

m	1000 ln α_1/α_2 Potentiom.	1000 ln α_1/α_2 Mass ratio	1000 ln α_1/α_2 Vapor comp.
0.02467	7.58 ± 0.3	$7.4_3 \pm 0.3$	$7.5_2 \pm 0.14$
0.05060	$14.1_1 \pm .3$	$14.3_6 \pm .3$	$15.5_6 \pm .5$

the mass ratio and of the vapor composition. The mean deviation of the two sets of values was less than 0.0004, and average values are listed in Table IV. The calculation requires prior knowledge of $\gamma_\pm$ as a function of m, but the results are very insensitive to the exact function chosen, as illustrated for two plausible functions in Table IV.

TABLE IV

DATA FOR NaOH in 50.00 WT. % DIOXANE–WATER AT 25.00°

	$\gamma_\pm$ from limiting law		$\gamma_\pm$ same as for NaCl		
m	ln α_1/α_2	β^*	ln α_1/α_2	β^*	$\sigma\beta^{*d}$
0.00000	....	$-29.63^{a,b}$	....	$-29.69^{a,c}$	..
.01189	-0.0098_5	-30.7_0	-0.0098_7	-30.7_6	0.9
.02415	$-.0184_0$	-29.7_6	$-.0184_6$	-29.8_4	.5
.03916	$-.0292_2$	-30.4_0	$-.0293_5$	-30.5_1	.3
.0523	$-.0381_5$	-30.7_0	$-.0383_5$	-30.8_2	.2
	Av.	-30.4	Av.	-30.5	

[a] Computed by weighted least squares *via* equation 5. [b] $b = -20.46$. [c] $b = -21.65$. [d] Standard deviation.

The calculation of β_{Na^+, OH^-} was based on the power series expansion, equation 20 of the preceding paper,[2] which was used in the form

$$\beta^* \equiv (1000 \ln \alpha_1/\alpha_2)/M_{12}m - 27.59m^{1/2} = \beta + bm + \ldots \quad (5)$$

At low molalities, β^* should vary linearly with m. For the data in Table IV, there is a slight but statistically insignificant drift in β^* with increasing m. The most probable value for β is -29.7, obtained by least-squares fitting of the data to equation 5. The most probable value for b, -21, is nearly equal to the corresponding quantity for NaCl.[2] On the other hand the data do not preclude the possibility that $b = 0$, in which case the limiting law is valid and $\beta = -30.4$. In any case, it is unlikely that the correct value of β_{Na^+, OH^-} differs from -29.7 by more than ± 1.0.

d ln K_W/dZ_1.—It follows from the definitions of the autoprotolysis constant K_W and of β that

$$d \ln K_w/dZ_1 = \beta_{H^+, OH^-} = \beta_{H^+, Cl^-} + \beta_{Na^-, OH^-} - \beta_{Na^+, Cl^-} \quad (9)$$

Upon substitution of numerical values for HCl, NaOH and NaCl,[2] d ln K_W/dZ_1 is predicted from vapor pressure data to be -19.8 ± 1. On the other hand, from potentiometric data for ln K_W (converted to the mole fraction scale),[7] the corresponding value is -22.3 ± 0.3. The discrepancy between the two values is significant and points to determinate error in at least one of the two sets of measurements. In view of experimental difficulties described by Harned and Fallon,[7] we believe that the determinate error may have occurred in the potentiometric measurements. The experimental difficulty was that the Ag–AgCl electrode did not function reversibly in the alkaline solutions which one has to employ in the measurement of K_W at the higher dioxane concentrations except in the presence of a large excess of sodium chloride.[7] Although Harned and Fallon took pains to minimize this error, the fact that the vapor pressure data are not subject to difficulties of this sort would tend to make them seem more reliable.

TALLAHASSEE, FLORIDA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE PENNSYLVANIA STATE UNIVERSITY]

Hydrodynamic Voltammetry at Solid Indicator Electrodes[1]

BY JOSEPH JORDAN, R. A. JAVICK AND W. E. RANZ[2]

RECEIVED NOVEMBER 20, 1957

A circulatory electrolysis cell assembly has been devised with controlled hydrodynamic characteristics, for the study at stationary solid indicator electrodes of current–voltage curves in flowing solutions. A new microconical platinum electrode is described and the relevant theoretical limiting current equation is derived. In a range of flow velocities between 25 and 500 cm./sec., oxygen, ferricyanide and aquo-ferric ion at the conical platinum microelectrode yielded sigmoid current–voltage waves with well-defined limiting currents. Implications are discussed to quantitative voltammetric analysis in flowing media. Oscilloscopic evidence is presented that the random fluctuations of the limiting currents, normally observed at the rotated platinum wire electrode, are due to turbulence. A constant limiting current, free of transient fluctuations, was obtained in a purely laminar gravitational flow using a "wall-less" electrolysis cell. The conical platinum microelectrode under suitable experimental conditions approximates the behavior of an electroanalytical flowmeter. Selected applications are considered as examples of an unorthodox approach to the measurement by electrochemical kinetics of rates of physical phenomena.

A time period of more than one and a half decades has now elapsed since the invention of voltammetry at the rotated platinum wire electrode (RPWE).[3] The behavior of the RPWE is intermediate between that of a "convection electrode" and a "diffusion electrode."[4,5] Mass transfer by diffusion and forced convection both are controlling factors of the limiting currents which depend on diffusion coefficients as well as on the prevailing hydrody-

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(1) Abstracted from a doctoral thesis by Richard A. Javick. Presented at the Eighth Pittsburgh Conference of Analytical Chemistry and Applied Spectroscopy, March, 1957.

(2) Department of Engineering Research of The Pennsylvania State University.

(3) H. A. Laitinen and I. M. Kolthoff, *J. Phys. Chem.*, **45**, 1079 (1941).

(4) J. Jordan, *Anal. Chem.*, **27**, 1708 (1955).

(5) I. M. Kolthoff and J. Jordan, THIS JOURNAL, **76**, 3843 (1954).

namic conditions. The literature reveals numerous attempts to correlate quantitatively at the RPWE limiting currents and hydrodynamic parameters.[6] As far as the dependence is concerned of limiting currents on rates of rotation of the RPWE, consistent results are conspicuous by their absence.[7] It appears impossible to interpret the available experimental data in terms of applicable theoretical hydrodynamic relationships. This situation may be accounted for as follows.

a. Because of effects such as "slipping" and frictional losses,[5] the rate of rotation of the RPWE does not represent a true measure of the rate of flow of the solution relative to the indicator electrode, which determines the convective mass transfer of the electroactive species and controls the limiting current. Consequently, the rate of rotation is *not* a significant parameter under the hydrodynamic conditions prevailing in the conventional electrolysis cells used in conjunction with the RPWE.[8]

b. Quite generally, the experimental situation at solid electrodes in stirred electrolysis cells is so complex, that the theoretical interpretation of the corresponding mass transfer process meets with insurmountable difficulties.[6]

It was anticipated that the impasse might be broken by constructing on the basis of judicious fundamental considerations, a suitable model "solid indicator electrode system" which meets the following requirements. 1. It should approximate geometric and hydrodynamic conditions for which a rigorous mass transfer equation is available. 2. The velocity of flow past the indicator electrode should be readily controlled, varied and measured. 3. In terms of indicator electrode area, cell resistance, temperature control, order of magnitude of limiting currents, concentration of supporting electrolytes and of electroactive species, it should be comparable to "typical polarographic experimental conditions" under which proportionality between limiting current and concentration is normally expected to prevail. A circulatory electrolysis cell assembly has been constructed accordingly and is described in this paper. In this cell, the solution flowed past a conical platinum microelectrode under conditions of negligible turbulence intensity ($<2\%$). Quantitative correlations between rate of flow and limiting currents are reported and discussed.

Unexplained random fluctuations of the limiting currents at the RPWE have been troublesome "ghosts" which have haunted polarographic investigators.[5] Results reported in this paper indicate that they are due to turbulent fluctuations in the flow. A limiting current free of fluctuations was recorded oscilloscopically when the solution was allowed to drain past the indicator electrode in a laminar gravitational flow (negligible turbulence), from a streamlined "flow tube." On the basis of results summarized in this paper, it appears that voltammetric limiting currents can be made use of for the measurement of rates of flow in liquids and of turbulence. A measurement of this type (of physical phenomena with the aid of electrochemical kinetics) is believed to be of considerable methodological interest. It represents the reversal of the customary approach in chemical kinetics, where reaction rates are normally determined by measurement of the rate of physical changes, such as volume, pressure, etc.

Experimental

Chemicals.—Reagent grade chemicals and conductivity water were used throughout.

Apparatus. Circulatory Electrolysis Cell Assembly.—The complete set-up is illustrated in Fig. 1. Its main components were a flow tube, an impeller pump and a thermostating compartment. The flow tube was made of Pyrex tubing, 10 cm. in diameter and 45 cm. in length, which was mounted vertically on suitable supports. Both ends of the tube were constricted to nozzles about 1 cm. in diameter. An additional piece of Pyrex tubing, 10 cm. in diameter and 15 cm. in length, was ring-sealed to the upper end of the flow tube and its top extremity was in turn constricted to a nozzle of 1 cm. in diameter. The ring-sealed portion of the flow tube, located between the two nozzles pointing upwards, was used as the "electrode compartment." Suitable holes were bored into its sides for accommodating the indicator electrode, the reference electrode and two pressure probe tubes. In conjunction with a suitable manometer the pressure tubes served to determine the rate of flow of the solution past the indicator electrode. In order to make the flow uniform a special "flow straightener" was designed. It consisted of a bundle of 170 vertical parallel channels, drilled into a Lucite block 2 cm. in height. The individual channels were separated from each other by solid walls 0.2 cm. in thickness. The straightener was positioned in the flow tube, 8.5 cm. above the bottom of the tube. The thermostating compartment consisted of a three-liter Pyrex beaker, with suitable outlets for the solution at the bottom and for nitrogen or oxygen at the top. It was closed with a Lucite cover with appropriate holes for a fritted glass gas dispersion cylinder, a cooling coil made of Pyrex, a magnetic setting mercury thermoregulator, a quartz immersion heater (supplied by Will Corporation) and an intake tube from the flow system. A Cenco electronic relay was used for coupling the heater and the thermoregulator. Tap water at about 20° was fed continuously through the cooling coil, while the heater was turned on intermittently by its automatic controls. With this arrangement, a temperature of 25.00 ± 0.05° was maintained readily in the circulating solution for any desired period of time. The solution was circulated as indicated by the arrows in Fig. 1 with the acid of a Jabsco impeller pump, Model 3010-01. The impeller blades were made of neoprene. The pump was operated by a Dunlap $^1/_4$ horsepower, split phase, 1750 r.p.m. electric motor to which it was coupled *via* a belt drive with appropriate pulley ratios. Connections between flow tube, thermostating com-

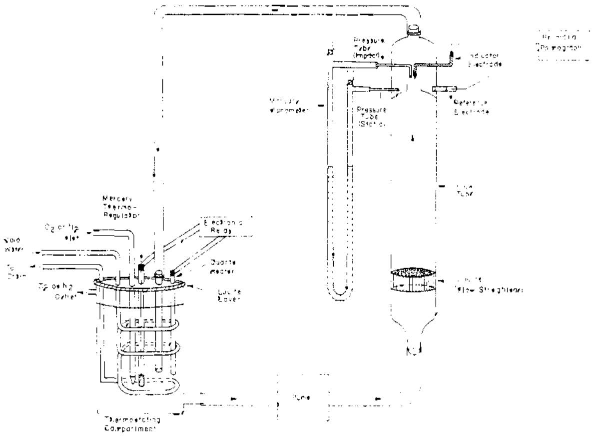

Fig. 1.—Circulatory electrolysis cell assembly.

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(6) For a review, see: P. Delahay, "New Instrumental Methods in Electro-Chemistry," Interscience Publishers, Inc., New York, N. Y., 1954, pp. 217–249.

(7) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. I, 2nd Ed., Interscience Publishers, Inc., New York, N. Y., p. 413.

(8) Trumpler and Zeller, *Helv. Chim. Acta*, **34**, 952 (1951).

partment and pump were made with flexible Tygon tubing. The total circulated volume of solution was 6 liters.

Gravity Flow Tube.—The solution was allowed to flow freely over the reference and indicator electrodes as illustrated in Fig. 2. The flow tube was made of Pyrex glass with calibrated distance markings. Flow velocities were computed with the aid of the equation

$$v = \sqrt{2g\Delta h} \qquad (1)$$

where v denotes the velocity of flow in cm./sec.; g the acceleration of gravity in cm./sec.^{2}, and Δh the relevant distance (expressed in cm.) from a calibration mark to the tip of the indicator electrode.

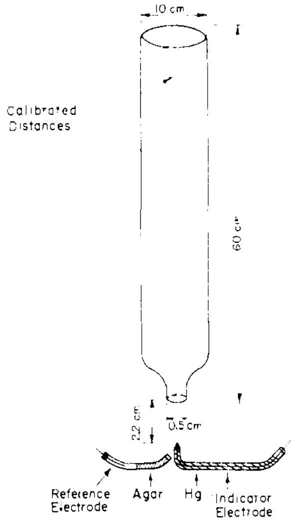

Fig. 2.—Gravity flow tube assembly.

Rotated Electrolysis Cell with Stationary Electrode.—For linear flow velocities up to 100 cm./sec. a rotated (but unstirred) polyethylene electrolysis cell was used, which has been described in an earlier paper.[4]

Conventional Rotated Platinum Wire Electrolysis Cell Assembly.—A cell previously described,[9] made from a 150-ml. Pyrex beaker, was used in conjunction with a synchronously rotated platinum wire microelectrode.

Stirred Electrolysis Cell with Stationary Platinum Wire Electrode.—A wire microelectrode was sealed at the bottom center of a 150-ml. Pyrex beaker. One hundred ml. of electrolyte was used into which was immersed directly the reference electrode-salt bridge assembly (*vide infra*). The solution was stirred with the aid of a propeller type glass stirrer with five concentric blades positioned 0.2 cm. above the tip of the indicator electrode. The blades were 1.0 cm. in length and 0.3 cm. in width. The stirrer was rotated synchronously at 600 r.p.m.

Indicator Electrodes.—On the basis of a preliminary critical review of the literature it was anticipated that a known theoretical heat transfer relationship may be applicable to predicting the mass transfer controlled limiting currents at a conical microelectrode. Accordingly, an electrode was constructed by sealing a piece of pure platinum wire, 0.05 cm. in diameter and 3 cm. in length, into Pyrex capillary tubing. Using a diamond grinding wheel and Carborundum abrasives the wire was subsequently ground to a "pencil point" shape. The conical platinum area of the electrode was of the order of 0.003 sq. cm. and had a surface roughness of less than 2×10^{-4} cm. The slant height of the platinum cone was 0.04 cm. The exact dimensions were determined accurately (±0.1%) with the aid of a microscope. Contact with the indicator electrode to copper lead wires was made with mercury. Conical microelectrodes of this type were used as stationary indicator electrodes in the Circulatory Electrolysis Cell Assembly, in the Rotated Polyethylene Cell and in the Gravity Flow Tube. The glass tubing to which the electrodes were fused was bent in convenient shapes for positioning in the various electrolysis cells as illustrated in Figs. 1 and 2, so that the point was directed into the flow. The electrodes used in the RPWE assembly on the one hand, and as stationary electrode in the Stirred Electrolysis Cell on the other, were made of pure annealed platinum wire, 0.4 cm. in length and 0.05 cm. in diameter.

Reference Electrodes.—In all experiments silver-silver chloride reference electrodes, saturated in potassium chloride, were used. For experimental convenience, a unified half cell-agar salt bridge assembly, described by Lingane[10] was adapted with minor modifications. For instance, one such modification consisted in bending the electrode as illustrated in Fig. 2.

Electrical Instrumentation.—A Leeds and Northrup Electrochemograph, Type E, was used for recording current–voltage curves and limiting currents. The instrument was operated at a chart speed of 0.0847 cm./sec. and a rate of change of applied potential, $\Delta V/\Delta t$, of 3.33 mv./sec.

For high speed studies of the fluctuations on the limiting current region, a precision resistor was connected in series with the electrolysis cell. A low level preamplifier (Tektronix, Type 122) was coupled in parallel and the output signal fed to the vertical plates of a suitable cathode ray oscilloscope (Tektronix, Type 315-D). Oscilloscopic records were photographed with the aid of a conventional 35 mm. camera or with a Polaroid Land Camera.

Manometric Determination of Rates of Flow.—In the circulatory electrolysis cell assembly the linear flow velocity of the solution past the indicator electrode was varied between 20 and 500 cm./sec. The velocity was determined by measuring the difference in pressure existing between a static pressure tube and an impact tube.[11] The two tubes were positioned as illustrated in Fig. 1 and made of stainless steel hypodermic needles one of which was bent at an angle of 90°. From the manometer reading, the linear velocity of the solution was computed by use of the equation

$$v = \sqrt{2g\Delta H(\rho_{\text{man}} - \rho_{\text{soln}})/\rho_{\text{soln}}} \qquad (2)$$

where ΔH is the manometer reading expressed in cm., while ρ_{man} and ρ_{soln} denote the density (in g./cm.^{3}) of the manometer fluid and of the solution, respectively. In a range of velocities between 50 and 500 cm./sec., the flow rates evaluated from eq. 2 are considered accurate to ±1% or better. At slower velocities the accuracy was appreciably poorer: for instance at 25 cm./sec., the corresponding error was ±5%.

In all experiments with the conical indicator electrode, the latter was positioned in such a manner that the direction of flow was similar to that illustrated in Fig. 1 and 2, *i.e.*, the solution streamed first toward the apex of the cone and then along the slant height to its base. The reference electrode was positioned with a view to avoiding any disturbance in the lines of flow of the solution around the indicator electrode. The cell resistances were of the order of 300-500 ohm.

All potentials reported in this paper have been corrected for *iR* drops and are referred to the saturated silver–silver chloride electrode (SSCE), the potential of which is +0.197 v. *versus* the normal hydrogen electrode.[10] All experiments were carried out at 25.00°. All currents reported have been corrected for residual currents.

Results

For the sake of convenience, most experiments were carried out in a 0.1 *M* solution of potassium chloride, saturated with air. The dissolved oxygen (2.36×10^{-4} *M* at the prevailing atmospheric pressure) served as the electroactive species. For comparison, a limited number of determinations were made with ferric ion in 0.1 *M* perchloric acid and with potassium ferricyanide in 1 *M* potassium chloride. Under the experimental conditions, all these electroactive species yielded "one step" reduction waves, which were "irreversible" in shape, *i.e.*, their ascending parts were controlled by the rate of electron transfer as well as by mass

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(9) I. M. Kolthoff and J. Jordan, THIS JOURNAL, **74**, 382 (1952).

(10) J. J. Lingane, "Electroanalytical Chemistry," Interscience Publishers, New York, N. Y., 1953, pp. 263–264.

(11) P. W. Mullen, "Modern Gas Analysis," Interscience Publishers, Inc., New York, N. Y., 1955, p. 48.

transfer.[4] The half-wave potentials varied accordingly with the velocity of flow of the solutions. The range of potentials where limiting currents prevailed depended also on the flow rate. Two typical current–voltage curves of oxygen, obtained at a slow and fast velocity, are illustrated in Fig 3. In each instance, the limiting current was measured at the "optimum potential," *i.e.*, in the middle of the limiting current region. The residual currents did not depend on the rate of flow. By suitable experiments, covering a range of concentrations of the electroactive species between 10^{-5} and 10^{-3} M, it was quite generally ascertained that the limiting currents in this study were always "true limiting currents,"[4] *i.e.*, they were controlled exclusively by mass transfer and were proportional to the bulk concentration of the electroactive species, everything else being equal. In a given electrolysis cell assembly and at the same indicator electrode, the ratio at a constant flow velocity between limiting current i_1, on the one hand, and concentration C, on the other, was constant for a given electroactive species; the standard deviation of a single i_1/C value, determined with the Electrochemograph, varied between 1 and 2%.

Characteristics of Limiting Currents under Conditions of Ideal "Gravity" Flow.—In the gravity flow tube limiting currents recorded oscilloscopically or with the Electrochemograph yielded virtually ideal straight lines without any fluctuations. In a typical experiment, an oscilloscopic trace was obtained of the cathodic limiting current of 10^{-3} M ferricyanide in 1 M potassium chloride. The current was recorded at constant potential as a function of time over a period of 1/12 of one second. At the beginning of this time period the velocity of flow of the solution past the indicator electrode was 190.9 cm./sec., as compared to 190.7 cm./sec. at the end. Within the experimental error of the oscilloscopic limiting current determination (± 0.3%), this was equivalent to a measurement at a constant velocity of 190.8 cm./sec. The sensitivity of the experimental set-up was such that a fluctuation of the order of 0.5 μa. (0.3% of the average limiting current of 170μa.) would have been readily detected provided it occurred at frequencies not exceeding 10^3 c.p.s. The instantaneous response to rapid transient flow rate variations of the "gravity tube assembly" was highlighted by inserting, in the jet of solution emerging from the flow tube, a six-bladed stirrer rotating at 600 r.p.m. The stirrer was positioned above the indicator and reference electrodes and interrupted the steady flow 60 times each second. A corresponding fluctuation in the limiting current was obtained instantaneously on the scope. The frequency of the "oscilloscopic" disturbance was 60 c.p.s.

Limiting Current Fluctuations in Stirred and Flowing Electrolytes.—In contradistinction to the situation in the gravity flow tube, current–voltage curves at the RPWE in conventional electrolysis cells yielded invariably fluctuations on the limiting current regions. Similar fluctuations were obtained at a stationary platinum wire electrode in stirred solutions as well as in the rotated electrolysis cell and in the circulatory assembly. In a given electrolysis cell assembly and at given rates of electrode rotation, stirring and/or flow, the characteristics of the fluctuations were the same, irrespective of the electroactive species (oxygen, ferric ion or ferricyanide ion). Quite generally, whenever fluctuations prevailed, their magnitude, in terms of the average limiting current, depended on the hydrodynamic design of the experimental assembly and on the velocity of flow of the solution. Some pertinent numerical data are summarized in Table I.

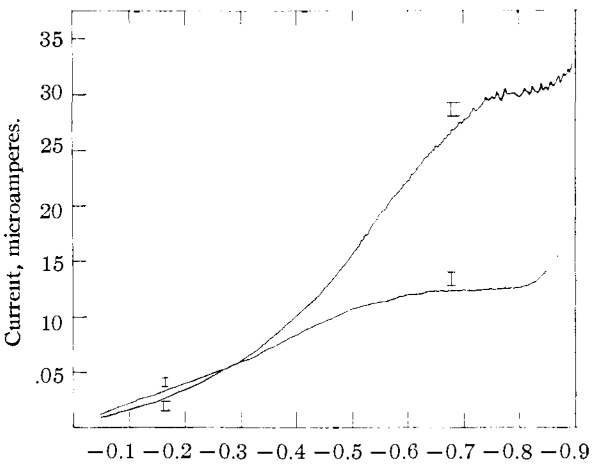

Fig. 3.—Typical current–voltage curves of 2.36 × 10^{-4} M oxygen in flowing solutions. Linear flow velocities in the circulatory electrolysis cell assembly: I, 74.7 cm./sec.; II, 496 cm./sec.

TABLE I

CHARACTERISTICS OF FLUCTUATIONS ON LIMITING CURRENTS[a]

(1) Type of electrolysis cell	(2) Order of flow velocity past indicator electrode (cm./sec.)	(3) Relative magnitude of fluctuations, of limiting current[b]	(4) Order of frequency of fluctuations (c.p.s.)
Gravity flow tube[c] ("wall-less cell")	200	0.0	. . .
Circulatory assembly[c]	100	±0.5	0.5–1
	500	±1.5	1–3
Rotated polyethylene cell with stationary electrode[c]	2–100	±4 to ±5	1–5
Stirred electrolysis cell with stationary platinum wire electrode	60	±8	1–5
Conventional rotated platinum wire electrode cell assembly, 600 r.p.m.	Not known	±1 to ±3[d]	1–5

[a] Electroactive species (10^{-4}–10^{-3} M): oxygen in 0.1 M KCl, ferric ion in 0.1 M perchloric acid, ferricyanide in 1 M potassium chloride. [b] The average limiting current was integrated over all fluctuations and was within experimental error equal to the arithmetic mean of the maxima and minima on the fluctuations. [c] Microconical platinum indicator electrode. [d] Magnitude of fluctuations varied with distance of indicator electrode from bottom of cell and with angle at which electrode was bent relative to axis of rotation.

Variation of Limiting Currents as Function of Flow Velocity.—Quantitative relationships between limiting currents of oxygen and rates of flow were studied at the conical platinum electrode in the circulatory electrolysis cell assembly where the periodic fluctuations did not exceed ± 1.5% of the average current. The relevant current values recorded with the Electrochemograph were treated as though they did not vary with time within an experimental error of ±2%. A logarithmic plot of oxygen limiting currents *versus* rate of flow yielded a distribution of points which could be fitted equally well by several straight lines with slopes ranging from 0.46 to 0.50. The limiting current of oxygen was measured at a potential between −0.75 and −0.80 v.; the corresponding flow velocities varied from 25 to 500 cm./sec.

The study of the limiting currents of ferric ion in 0.1 *M* perchloric acid was restricted to velocities of flow between 10 and 100 cm./sec., because at higher velocities of flow the corresponding current–voltage wave became extremely drawn out in shape and did not yield a well-defined limiting current. In a set of experiments, carried out in the rotated polyethylene electrolysis cell, a logarithmic plot of the limiting current of 10^{-3} *M* ferric iron *versus* rate of flow yielded points which approximated a straight line with a slope of 0.45 ± 0.05. The limiting current of iron was measured in a range of potentials between ±0.25 and +0.35 v.

Discussion

From an electrochemical point of view, the situation in the vicinity of the electrodes in the gravity flow tube experiments represents a virtually ideal "wall-less electrolysis cell." By hydrodynamic criteria, the free jet emerging from the streamlined nozzle and surrounded on its outer interphase by air is expected to yield a laminar flow, with a constant velocity, *v*, past any point of the conical microelectrode surface. In contradistinction to this, it can reasonably be expected that the velocity of flow of the solution around a wire electrode, in a conventional non-streamlined stirred electrolysis cell such as a Pyrex beaker,[9] will exhibit turbulent fluctuations around a mean velocity which is defined by the equation

$$\bar{v} = \frac{1}{t_2 - t_1} \int_{t_1}^{t_2} v_t \mathrm{d}t \qquad (3)$$

where $\bar{v}$ denotes the mean flow velocity in the time interval between t_1 and t_2, v_t is the instantaneous velocity of flow, and $(t_2 - t_1) >> (\bar{v} - v_t)$. It is believed that the experimental evidence presented in this paper indicates conclusively that the fluctuations on the limiting current regions observed in stirred electrolysis cells and at the RPWE are due to turbulent fluctuations of the velocity of flow at the indicator electrode surface. The degree of turbulence is expected to be smaller in the circulatory electrolysis cell assembly than in conventional electrolysis cells. *Ceteris paribus*, turbulence is expected to be relatively greater at high rates of flow than at low flow velocity. As can be seen in Table I, the fluctuations on the limiting currents, obtained in various electrolysis cells and at various rates of flow, varied in all instances as turbulent fluctuations would be expected to vary under the experimental conditions.

The classical method for deriving a limiting current equation under steady-state conditions of concomitant control by diffusion and forced convection relied on the assumption that a convection-free diffusion layer with a linear concentration gradient exists at the electrode interface. The thickness of this "Nernst Diffusion Layer" (NDL) was postulated to vary with the rate of flow of the solution and to be independent of diffusion coefficients (*i.e.*, independent of the specific nature of the diffusing substances). Recent investigations and theoretical appraisals have indicated that the NDL treatment is phenomenologically not warranted and yields only approximate results.[6,12,13] More rigorous derivations were based on hydrodynamic theory and involve the solution of simultaneous differential equations accounting for mass transfer by diffusion as well as by convection without implying the existence of a discrete NDL. Using this approach, limiting current equations for conditions of simultaneous control by convection and diffusion have been derived for certain types of idealized solid indicator electrodes (*e.g.*, an infinite plane).[6,14] Under the conditions prevailing in voltammetry (where electrical migration effects are eliminated by the use of a supporting electrolyte), the hydrodynamic derivations for mass transfer to an indicator electrode are analogous to those of heat transfer to a solid probe. With the aid of dimensional analysis, theoretical relationships derived for heat transfer can be adapted to mass transfer.[4,15,16] Formally, both heat and mass transfer relationships can be expressed in terms of certain "dimensionless numbers." These are listed in Table II as functions of the significant mass and heat transfer parameters. Generally, both heat and mass transfer can be described by equations of the form

$$N_{\mathrm{Nu}} = \varphi(N_{\mathrm{Re}}, N_{\mathrm{Pr}}) \qquad (4a)$$

$$N_{\mathrm{Sh}} = \varphi(N_{\mathrm{Re}}, N_{\mathrm{Sc}}) \qquad (4b)$$

In comparable geometric and hydrodynamic situations, a heat transfer relationship of the type of eq. 4a can be adapted to mass transfer (eq. 4b) by substituting the expressions in column 4 of Table II for those in column 2 of the table. For laminar flow under geometric conditions similar to those prevailing at the conical platinum microelectrode, the solution of the relevant partial differential equations yields the expression for heat transfer

$$N_{\mathrm{Nu}} = \frac{4}{3\sqrt{3}} N_{\mathrm{Re}}{}^{1/2} N_{\mathrm{Pr}}{}^{1/3} \qquad (5)$$

where the numerical factor on the right side is a "friction drag coefficient."[17] The analogous mass transfer relationship is

$$N_{\mathrm{Sh}} = \frac{4}{3\sqrt{3}} N_{\mathrm{Re}}{}^{1/2} N_{\mathrm{Sc}}{}^{1/} \qquad (6)$$

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(12) N. Ibl, *Chimia*, **9**, 135 (1955).

(13) Y. Okinaka and I. M. Kolthoff, THIS JOURNAL, **79**, 3326 (1957).

(14) B. Levich, *Disc. Faraday Soc.*, **1**, 37 (1947); *Acta Physicochim. U.S.S.R.*, **19**, 177, 133 (1944).

(15) W. E. Ranz, "Electrolytic Methods for Measuring Water Velocities," Pennsylvania State University, 1957.

(16) B. L. Bircumshaw and A. C. Riddiford, *Quart. Rev.*, **6**, 157 (1952).

(17) H. A. Johnson and M. W. Rubesin, *Trans. A.S.M.E.*, **71**, 447 (1949).

TABLE II

RELATION BETWEEN COMPARABLE MASS AND HEAT TRANSFER PARAMETERS[15,16]

(1) Heat transfer[a,b] Designation of dimensionless no.	(2) Definition of dimensionless no.	(3) Mass transfer[a,c] Designation of dimensionless no.	(4) Definition of dimensionless no.
Nusselt no.	$N_{\mathrm{Nu}} \equiv \frac{q^0 L}{k(T - T^0)}$	Nusselt no. or Sherwood no.	$N_{\mathrm{Sh}} \equiv \frac{f^0 L}{D(C - C^0)}$
Prandtl no.	$N_{\mathrm{Pr}} \equiv \frac{\nu s \rho}{k}$	Schmidt no.	$N_{\mathrm{Sc}} \equiv \frac{\nu}{D}$
Reynolds no.	$N_{\mathrm{Re}} \equiv \frac{vl}{\nu}$	Reynolds no.	$N_{\mathrm{Re}} \equiv \frac{vl}{\nu}$

[a] Definition of symbols used: v, flow velocity of solution, cm./sec.; ν, kinematic viscosity cm.^{2}/sec.; L(cm.), characteristic dimension (along which solution flows) of electrode or heat transfer probe; q, heat transfer rate per unit area, cal./cm.^{2} sec.; f^0, flux, mass transfer rate per unit area, mole/cm.^{2} sec.; k, thermal conductivity of solution, cal./cm. sec. degree; D, diffusion coefficient of electroactive species, cm.^{2}/sec.; T, temperature, degree; C, concentration of electroactive species, moles/cm.^{3}; ρ, density of solution, g./cm.^{3}; s, specific heat of solution, cal./g. degree; the superscript zero denotes the surface of the heat transfer probe or of the indicator electrode. [b] To a solid probe immersed in a liquid. [c] To an indicator electrode.

Whenever 100% current efficiency prevails, the mass transfer flux, f^0, at the electrode surface is correlated with the limiting current

$$i_l = nFAf^0 = nFAN_{\mathrm{Sh}}D(C - C^0)/L \qquad (7)$$

where i_l is expressed in amperes, nF denotes the number of coulombs per mole involved in the electrode reaction and A the effective area of the indicator electrode expressed in cm.^{2}. The situation on limiting current regions is characterized by extreme concentration polarization,[4] *i.e.*

$$C^0 \ll C;\ C - C^0 \approx C \qquad (8)$$

Using the appropriate expressions for the Sherwood, Schmidt and Reynolds numbers from column 4 of Table II, eq. 6, 7 and 8 yield the limiting current equation for the microconical platinum indicator electrode

$$i_l = \frac{4}{3\sqrt{3}}\, nFACv^{1/2}D^{2/3}L^{-1/2}\nu^{-1/6} \qquad (9)$$

where L denotes the slant height of the cone. A critical inspection of eq. 9 reveals that, except for the numerical "drag coefficient," it is identical with numerous theoretical and semi-theoretical expressions derived in the literature for solid indicator electrodes of various geometries under conditions of laminar flow.[6,14,18,19] As far as the relationship is concerned between the limiting current on the one hand and nF, C, $v^{1/2}$, $D^{2/3}$, $\nu^{-1/6}$ on the other, eq. 9 is also similar to the determining terms in the limiting current equation at the rotating dropping mercury electrode recently derived by Okinaka and Kolthoff.[13]

Experimental Verification of the Theoretical Limiting Current Equation 9

a. Proportionality between Limiting Current and Bulk Concentration of the Electroactive Species.—As in all other known instances which involve a steady-state situation and forced convection, the limiting currents in this investigation were found to be proportional to concentration within 1 or 2%. Therefore, the microconical platinum electrode is suited for direct quantitative analysis, *provided all other experimental variables in eq. 9 are kept constant.* The latter limitation seems to have been frequently overlooked in attempts to use solid voltammetric indicator electrodes for analytical purposes in flowing media as, *e.g.*, the determination of oxygen in blood *in vivo*.[20] Excellent accuracy has been reported over short time intervals, followed by a "long range irreproducibility." From eq. 9, it is evident that on the basis of an uncorrected direct linear calibration with known concentrations of a given electroactive species, solid indicator electrodes can only be used for quantitative analytical purposes as long as the velocity of flow is kept constant. The rate of blood circulation is a function of blood pressure which, of course, may vary appreciably.

b. Relationship between Limiting Current and Velocity of Flow.—Equation 9 holds only for laminar flow. Under conditions of extreme turbulence,[14,21] the limiting current is expected to be proportional to v rather than to $v^{1/2}$. For the limiting current of oxygen in a range of flow velocities between 1 and 25 cm./sec., Trumpler and Zeller[8] have reported at brass and copper amalgam indicator electrodes the empirical relationship: $i_l = \text{const. } v^{0.434}$. In the experiments described in this paper, it was generally found that limiting currents were proportional to $v^{0.45 \pm 0.05}$. This compares with a value of 0.50 for the theoretical velocity exponent in eq. 9.

Analytical Significance of Hydrodynamic Voltammetry.—For a medium of constant viscosity and at a given indicator electrode eq. 9 can be written in the form

$$i_l = \text{const. } Cv^{0.5} \qquad (10)$$

This implies that electroöxidizable or electroreducible substances *can* be determined by comparing limiting currents measured at different rates of flow: However, the corresponding flow velocities must be accessible to measurement by independent methods and corrected for in accordance with eq. 10. Applications are anticipated to quantitative analysis in circulating body fluids, in rivers and streams, as well as in continuous reaction processes. If the concentration of the electroactive species is constant (not necessarily known, merely constant), eq. 10 can be simplified to

$$i_l = \text{const. }' v^{0.5} \qquad (11)$$

It is evident from eq. 11 that a limiting current may serve as an "electroanalytical flowmeter" (EAFM). Typically, the functioning of the EAFM is visualized as depending on the comparison of a limiting current determined *in situ* at an unknown flow velocity (*e.g.*, the limiting current of oxygen in arterial blood *in vivo*, or in a river), with the corresponding limiting current obtained in a circulatory electrolysis cell assembly at a known velocity.

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As another methodologically interesting application, eq. 11 can be made use of for the stochastic characterization of relative velocities. For instance, the rate of motion (relative to the ambient ocean) of ships on the high seas might be determined by comparing the limiting current of oxygen obtained in a sample of sea water in a "calibration assembly" aboard, with the limiting current measured using the same indicator electrode immersed alongside the ship in the ocean.

Acknowledgment.—This investigation was supported in part by Research Grants H-2342 and H-2342(C) from the National Heart Institute, National Institutes of Health, Public Health Service.

UNIVERSITY PARK, PA.

[CONTRIBUTION FROM THE JOHN CURTIN SCHOOL OF MEDICAL RESEARCH, THE AUSTRALIAN NATIONAL UNIVERSITY]

The Ion $Fe(CNS)_2^+$. Its Association Constant and Absorption Spectrum

BY D. D. PERRIN

RECEIVED DECEMBER 26, 1957

Association constants of the complexes $FeCNS^{++}$ and $Fe(CNS)_2^+$ have been calculated from absorbance and oxidation–reduction potential measurements. Values at 18° by the two methods are $K_1 = 145$ and 133; $K_2 = 14$ and 10, respectively, at ionic strengths of 0.56 and 0.65. Estimates at $\mu = 0$ are $K_1^0 = 1090$, $K_2^0 = 40$. The absorption spectrum of $Fe(CNS)_2^+$ shows a maximum near 4850 Å., with a molar absorbance index of 9800. $Fe(CNS)_2^+$ is the major light absorbing species for thiocyanate concentrations greater than 0.04 *M*.

Dilute aqueous solutions of ferric and thiocyanate ions contain the complex[1-4] $FeCNS^{++}$, for which consistent values of the association constant[3-6] and the molar absorbance index[4-6] have been derived from spectrophotometric measurements. Although qualitative evidence from a range of experimental methods indicates that at higher thiocyanate concentrations complexes of higher thiocyanate content are present,[1,4,5,7] few quantitative studies have been reported. Estimates of the association constants of the complexes, $Fe(CNS)_x^{(3-x)+}$, ($x = 1$ to 6), have been made using solvent distribution[8] and spectrophotometry,[5] but the results obtained were not in good agreement. A later estimate[6] of the association constant of $Fe(CNS)_2^+$, from kinetic studies, did not support earlier values.

The present investigation was undertaken in an endeavor to measure the association constant of the ion $Fe(CNS)_2^+$ and to obtain its absorption spectrum. In this way it was hoped to assess the significance of this species in the ferric thiocyanate system. Competitive complex formation was minimized by using perchlorate solutions since Rabinowitch and Stockmayer[9] found no evidence of complex formation by ferric ion with perchlorate concentrations of up to 3 *M*. Subsequent data[10] suggest that under the present experimental conditions about 2% of the ferric ion not present in thiocyanate complexes would exist as ferric perchlorate ion pairs. This would not significantly affect the results obtained.

Experimental Methods

Reagents.—All reagents were of A.R. grade and were used without further purification. Stock solutions of ferric perchlorate were prepared from ferric ammonium sulfate by precipitation of ferric hydroxide with ammonia; the precipitate was washed repeatedly with distilled water at the centrifuge and then redissolved in excess perchloric acid. Ferrous perchlorate was freshly prepared by double decomposition from ferrous sulfate and barium perchlorate solutions. Concentrations of freshly prepared sodium thiocyanate solutions were checked by argentometric titration.

Spectrophotometry.—All absorbance measurements were made at 18 ± 0.3°, using a Beckman model DU quartz photoelectric spectrophotometer. Silica inserts and a range of optical cells provided light paths from 0.14 to 100 mm.

Known concentrations of ferric perchlorate, perchloric acid, sodium perchlorate and sodium thiocyanate were mixed in that order and diluted to the desired volume. Absorbance measurements were commenced within two minutes of mixing, and a series of readings was taken at each wave length to allow correction for any observed fading. Fading was slight but significant only at higher thiocyanate concentrations. All readings were taken within 30 minutes of mixing.

Variation of Absorbance with Thiocyanate Concentration.—If, as appears to be generally accepted, thiocyanate ion forms a series of colored complexes with ferric ion, the variation of the absorbance of the system with increasing thiocyanate concentration should enable their association constants and absorption spectra to be calculated.

In a constant environment, from the law of mass action

$$Fe(CNS)_x^{(3-x)+}] = K_x[Fe(CNS)_{x-1}^{(4-x)+}]\theta = K_1K_2 \ldots K_x[Fe^{+++}]\theta^x \quad (1)$$

$$[Fe^{+++}]_0 = \sum_{x=0}^{x=n} [Fe(CNS)_x^{(3-x)+}] = [Fe^{+++}](1 + K_1\theta + K_1K_2\theta^2 + \ldots + K_1K_2 \ldots K_x\theta^n) \quad (2)$$

$$A_1\ \text{cm.} = \sum_{x=0}^{x=n} \epsilon_x[Fe(CNS)_x^{(3-x)+}] = [Fe^{+++}](\epsilon_1K_1\theta + \epsilon_2K_1K_2\theta^2 + \ldots + \epsilon_nK_1K_2 \ldots K_n\theta^n) \quad (3)$$

where K_x is the association constant for the complex, $Fe(CNS)_x^{(3-x)+}$, θ is $[CNS^-]$, A is the absorbance, ϵ is the molar absorbance index, and $[Fe^{+++}]_0$ is the total ferric ion concentration. At the concentrations used in the present

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