pH of precipitation	Ni, %	Co, %	K, %	Cl, %	Composition (OH/Ni)
8.2	41.5	32.2	0.9	0.00	0.23
8.2	40.5	32.8	.1	.00	.18
9.8	46.5	26.6	.03	.00	.44
11.5	58.1	12.7	.01	.00	.78

The compositions, expressed as the OH/Ni equivalent ratio above, may be directly compared with the "as precipitated" compositions given in Fig. 3. With the possible exception of the material precipitated at pH 9.8, the agreement is probably within the over-all errors involved. Near pH 10, the composition of these materials appears to be more unstable, and it is conceivable that the washing and drying could alter the composition to the extent observed.

X-Ray Diffraction by Basic Nickel Carbonates.—Debye–Scherrer patterns were obtained with both the washed and dried precipitates just described and with other representative precipitates wet with their mother liquor. Those prepared at pH's less than 10 produced only diffuse halos; faint lines due to nickel hydroxide were evident using samples precipitated at higher pH's.

Discussion of Results.—Attempts were made to relate in some logical way, the observed equivalent ratio of OH^{-1} to CO_3^{-2} absorbed by the precipitate to the concentration ratio of these groups as ions in the solution. Such efforts showed that the hydroxide content of the precipitates was always unaccountably too high. The rapid change in composition in the pH vicinity of pK_2 suggests an effect arising from the redistribution of carbonate species with pH. However, such influence, if correct, must be obscured by at least equally important unknown factors.

[Contribution from the School of Chemistry, University of Minnesota]

Convection Controlled Limiting Currents (Convection Currents). I. The Platinum Wire Convection Electrode

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Under specified conditions of stirring a platinum convection electrode yields convection controlled limiting currents. These convection currents are defined by the equation $i_{\text{conv}} = nFA\tau C$ where nF denotes the number of coulombs per mole involved in the electrode process, A the area of the indicator electrode and C the concentration of the electroactive species. τ is the "convection coefficient" which depends on the efficiency of stirring and on the hydrodynamic characteristics of the electrolysis cell. While limiting currents at the dropping electrode and at conventional wire electrodes are diffusion controlled, the limiting currents at the convection electrode are independent of the diffusion coefficient of the electroactive species. The convection current of iodide increases 2.1% per 1° increase in temperature. Within wide limits it is independent of the viscosity of the medium. Upon a relative increase of 29% of the viscosity of a dilute iodide solution by addition of glycerol the convection current decreased only 1%. The convection electrode has the further advantage over diffusion electrodes that the relation between convection current and concentration need to be established by one reaction only as it holds for all other reactions.

Current–voltage curves of electroreducible or oxidizable substances at stationary, vibrating and rotating platinum wire electrodes[1] yield "waves" with a "limiting current region" at potentials where the rate of the electrode process is large as compared to the rate of supply of the electroactive species to the surface of the indicator electrode.[2,3] The ordinary type of limiting currents is diffusion controlled.[1,4,5] In a preliminary communication[6] we reported that, under specified conditions, convection controlled limiting currents can be obtained at the rotated platinum wire electrode. These "convection currents" do not depend on the diffusion coefficient of the electroactive species. When convection currents prevail, the thickness of the "boundary layer"[7] at the electrode becomes very small and attains a limiting value (v.i.).

Experiments presented in this paper indicate that limiting boundary layers are not attained with the customary rotated platinum electrode, but that with an auxiliary stirrer convection currents are observed within a wide range of stirring rates.

Experimental

Materials.—C.P. chemicals and conductivity water were used throughout.

Apparatus.—Current–voltage (c.v.) curves were recorded with a Sargent Model XXI polarograph at a chart speed of 2.53 cm./minute and a rate of change of applied potential, $\Delta V/\Delta t$, of 2.47 mv./sec. In manual current–voltage determinations potentials were measured with a Leeds and Northrup Type K2 potentiometer and currents with a General Electric Mirror and Scale Galvanometer (maximum sensitivity, 10^{-8} a. per scale division; period, 3.7 sec.), equipped with a suitable Ayrton shunt. Unless otherwise stated, all limiting current values reported have been corrected for residual currents.

Electrodes and Electrolysis Cell.—A Hume–Harris saturated calomel reference electrode (SCE) and salt bridge[8] were used in all experiments. Potentials reported in this paper are referred to this SCE.

Rotated platinum indicator electrodes were made of annealed platinum wire, approximately 0.3 mm. in diameter and 4 mm. in length. They were sealed into a glass tube into which an auxiliary stirrer could be concentrically mounted by means of a ground glass joint. The stirrer was made of glass in the form of a rectangular propeller with 4

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(1) For a review see: I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., pp. 402–419.

(2) G. E. Kimball, *J. Chem. Phys.*, **8**, 199 (1940).

(3) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 577.

(4) H. A. Laitinen and I. M. Kolthoff, *J. Phys. Chem.*, **45**, 1061, 1079 (1941).

(5) I. M. Kolthoff and J. Jordan, This Journal, **74**, 4801 (1952).

(6) I. M. Kolthoff and J. Jordan, *ibid.*, **75**, 4869 (1953).

(7) S. Goldstein, Editor, "Modern Developments in Fluid Dynamics," The Clarendon Press, Oxford, England, 1938, Vol. I, p. 50 ff.; Vol. II, pp. 656, 676 ff.

(8) D. N. Hume and W. E. Harris, *Ind. Eng. Chem., Anal. Ed.*, **15**, 465 (1943).

blades of 10 × 5 × 2 mm. each. The circular ground glass joint axis had a mean diameter of about 10 mm.; thus the total amplitude of the stirring was 2 × 10 + 10 = 30 mm. in cross section. The auxiliary stirrer was located 25 mm. above the electrode. The auxiliary stirrer and/or the electrode were rotated at 300, 600 or 900 r.p.m. by a synchronous motor and precision gears. In a few experiments at 1100 r.p.m. a non-synchronous motor was used and its speed checked with a revolution counter. Unless otherwise stated, the rotated platinum wire electrode was used in a downward "vertical" position, concentric with the axis of rotation; in a few experiments the wire was bent in a "horizontal" position at right angles to the axis of rotation.

Experiments were also carried out in stirred solutions with a stationary platinum wire electrode sealed into a suitably bent glass tube, the electrode pointing vertically upwards. Stirring was provided by a propeller (with six asymmetrically bent blades located 10 mm. above the electrode) which was rotated at 900 r.p.m.

A 250-ml. Pyrex beaker (height 8.5 cm., diameter 7 cm.) served as electrolysis cell which was closed with a rubber stopper with appropriate holes for inserting the indicator electrodes, stirrers, salt bridge and in- and outlet tubes for nitrogen. The resistance of the cell was about 300 ohm in 0.1 *M* perchloric acid.

Procedure.—The indicator electrode was stored in 10 *M* nitric acid. Before use, it was washed with distilled water and cleaned of anodic and cathodic surface contaminations by short-circuiting for 10 minutes against the SCE in an air-saturated 0.1 *M* perchloric acid solution. Care was taken to eliminate irregularities due to anodic film formation or hydrogen sorption.[9]

All experiments were carried out in a water thermostat kept constant within ±0.02°. If desired, oxygen was removed by bubbling high purity Linde nitrogen through the solution with the aid of a Corning fritted glass gas dispersion tube.

Results and Discussion

Characteristics of Convection Currents.—The system

$$I_2 + 2e \rightleftarrows 2I^- \qquad (1)$$

was selected for investigation of the influence of auxiliary stirring because the corresponding electro-oxidation and reduction waves are reversible at the rotated platinum wire electrode.[10] Automatically recorded limiting currents obtained with auxiliary stirring exhibited appreciable fluctuations, the mean value differing about 3% from the extreme values. These fluctuations were not observed when the c.v. curves were measured manually. The limiting current obtained manually was found equal to the mean of the automatically recorded current within an experimental error of 1%.

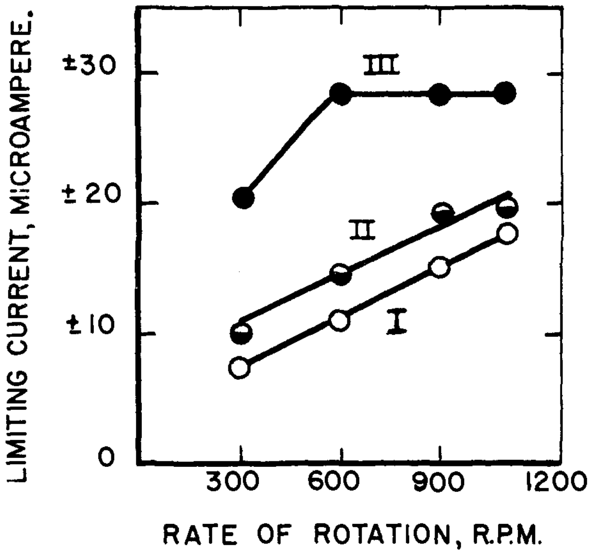

Fig. 1.—Plot of limiting currents (corrected for residual currents) at 25° *vs.* rate of rotation of auxiliary stirrer and/or vertical electrode: I, 10^{-4} *M* iodine in 0.1 *M* KI plus 0.1 *M* $HClO_4$; limiting current at 0.0 v. without auxiliary stirring; II, 2 × 10^{-4} *M* KI in 0.1 *M* $HClO_4$; limiting current at +0.75 v. without auxiliary stirring; III, limiting currents with auxiliary stirring. Same solutions as I and II.

In Fig. 1 are plotted the results of a systematic study of the effect of auxiliary stirring on the limiting current at 25° of iodine and iodide at a platinum wire electrode rotated at varying speeds between 300 and 100 r.p.m. The limiting currents with auxiliary stirring were the same for iodine and iodide and were larger than in the absence of auxiliary stirring. The convection current of both species increased from 20.4 μa. at 300 r.p.m. to 28.2 at 600 r.p.m. but did not change further at 900 and 1100 r.p.m.

The convection currents at 900 r.p.m. were proportional to concentration in the range investigated between 2.5 × 10^{-6} *M* and 2.5 × 10^{-4} *M* for iodine and between 5 × 10^{-6} *M* and 5 × 10^{-4} *M* for iodide.

Convection currents of iodine and iodide were also attained at a stationary electrode using a very efficient stirrer and a rate of 900 r.p.m.

The position of the indicator electrode affects the convection current. At 900 r.p.m. the "horizontal" electrode yielded a value of 150 × 10^3 μa./equiv. per liter as compared to 141 × 10^3 μa./equiv. per liter with the "vertical" electrode. Bubbling of nitrogen through the solution during electrolysis decreased this value of the vertical electrode to 122 × 10^3 μa./equiv. per liter. With the vertical electrode the volume of the solution in the electrolysis cell could be varied between 120 and 180 ml. without affecting the convection current. This current decreased when the indicator electrode was moved more than 5 mm. from the central longitudinal axis of our electrolysis cell.

Sensitivity of Convection Electrode.—Convection currents are determined by the rate of convective supply of the electroactive species to the electrode surface. We have postulated that convection currents, expressed in microamperes, are given by the equation

$$i_{\text{conv.}} = nFA\tau C \qquad (2)$$

where nF is the number of coulombs per mole involved in the electrode process, A the area of the indicator electrode expressed in sq. cm., τ the volume of solution—expressed in microliters per second per unit electrode area (= 10^{-3} cm. × sec.$^{-1}$)—which reaches the electrode surface, and C the bulk concentration of the electroactive species in moles per liter. τ is called the "convection (or transport) coefficient" and is determined at a given temperature solely by the hydrodynamic conditions prevailing in the electrolysis cell. Quite generally, gains in transfer by convection as a result of increased rates of stirring are counteracted by losses due to friction at the walls of the

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(9) I. M. Kolthoff and N. Tanaka, *Anal. Chem.*, in press.

(10) I. M. Kolthoff and J. Jordan, THIS JOURNAL, **75**, 1571 (1953); *Anal. Chem.*, **25**, 1883 (1953).

electrolysis cell and by "slipping" of the solution at its areas of contact with the stirrer.[7] From Fig. 1 it appears that up to 600 r.p.m. a net gain of convection efficiency prevails with increasing rates of stirring, the gains and losses compensating each other at faster rates of stirring under our experimental conditions. Equinormal solutions of any electroactive species will yield equal convection currents at a given temperature, if the rate of electrolysis is not a controlling factor. Under these conditions they provide a simple means for the determination of the number of electrons, n, involved in the electrode reaction.

It is convenient to characterize convection electrodes by their "sensitivity," S, expressed in μa./equiv./liter

$$S = i_{\text{conv.}}/nC \qquad (3)$$

With both iodine and iodide we found a sensitivity of 141×10^3 μa./equiv. per liter. With thallium (I) in 0.1 M alkali hydroxide[11] a sensitivity for the reduction wave of 140×10^3 and for the anodic wave of 141.5×10^3 was observed. The independence of convection currents of the diffusion coefficient is strikingly illustrated by the thallic complex of ethylenediaminetetraacetic acid. A 10^{-4} M solution of this complex at 25° yielded a limiting current of only 2 μa. at the rotated electrode (900 r.p.m.), but with auxiliary stirring a convection current of 28 μa. ($S = 140 \times 10^3$).

Effects of Viscosity and Temperature.—At a given temperature the viscosity of the medium appears to have little effect on convection currents. A solution 2×10^{-4} M in potassium iodide and 0.1 M in perchloric acid in a glycerol–water mixture, containing 10% w./w. glycerol, yielded at 25° and 900 r.p.m. a convection current of -27.9 μa., as compared to -28.2 μa. in the absence of glycerol. The difference is only 1%, while the difference in viscosity is 29%.

Between 25 and 36° an average temperature coefficient of 2.1% per degree was found for the anodic iodide convection current. This effect is accounted for by the characteristics of a quasi-rigid limiting boundary layer of the order of 10^{-5} cm.[7, 12–14]

Analysis of Current–Voltage Waves of Iodide at the Convection Electrode.—The equation of a reversible anodic wave corresponding to the $I^- \rightarrow I_2$ oxidation (reaction 1) is

$$E_{\text{c.e.}} = E^0 + \frac{RT}{nF}\ln(f_{I_2} \times [I_2]_0/f^2{}_{I^-} \times [I^-]^2{}_0) = \text{const.} + 0.030 \log i/(i_{\text{conv}} - i)^2 \qquad (4)$$

where $E_{\text{c.e.}}$ denotes the potential of the convection electrode (c.e.), f activity coefficients and the subscript zero concentration at the electrode surface. The plot of $E_{\text{c.e.}}$ *vs.* $\log i/(i_{\text{conv}} - i)^2$ for the c.v. wave of 2×10^{-4} M iodide in perchloric acid gave a straight line with a slope of 0.028 v. which is in satisfactory agreement with a value of 0.030 v. for reversible electroöxidation. The half-wave potential is dependent on the magnitude of the convection current

$$(E_{1/2})_{\text{c.e.}} = \text{const.} + 0,030 \log \frac{2}{i_{\text{conv}}} \qquad (5)$$

The half-wave potential at 900 r.p.m. of a 2×10^{-4} M iodide solution was $+0.49_0$ v., and that of a 2×10^{-5} M solution was $+0.52_3$ v., a difference of 0.03_3 v. as compared to a calculated value (eq. 5) of 0.030 v.

Comparison of Platinum Wire Diffusion and Convection Electrodes.—The expression

$$i_d = nFACD/l \qquad (6)$$

has been reported to hold for "steady state diffusion currents" at the stationary platinum wire electrode in unstirred solutions.[4] In eq. 6 i_d denotes the diffusion current, D the diffusion coefficient of the electroactive species and l the "effective thickness of the diffusion layer." Using as a stationary indicator electrode the same platinum wire which served as a convection electrode we obtained in unstirred solutions at 25° i_d/C values of 2.82×10^3 μa./mole per liter for iodine and -2.56×10^3 for iodide; this ratio of 1.10 is in satisfactory agreement with eq. 6 which predicts a ratio equal to $2D_{I_2}/D_{I^-}$ or 1.08. From the area of our electrode (0.075 sq. cm.), the experimental data and eq. 6 we calculate a value of 0.06 cm. for the thickness of the diffusion layer at the stationary electrode. This compares with a "boundary layer" at the convection electrode of the order of 10^{-5} cm. At rotated wire electrodes without auxiliary stirring the diffusion layer is considerably smaller than 0.06 cm. However, no exact relation at rotated wire electrodes can be given between the diffusion current on the one hand and the thickness of the diffusion layer, the diffusion coefficient, or the rate of stirring on the other. Empirically it has been found at 25° and 600 r.p.m. (no auxiliary stirring) that limiting currents change with $D^{1/2}$ in some instances[5] and with $D^{2/3}$ in others.[15] In our present experiments without auxiliary stirring we find that i_{I_2}/i_{I^-} is equal to $[D_{I_2}/D_{I^-}]^{0.5}$ at 600 r.p.m., but to $[D_{I_2}/D_{I^-}]^{0.2}$ at 1100 r.p.m. Apparently the rotated wire electrode without auxiliary stirring is intermediate in this respect between a convection and a diffusion electrode. Recent theoretical developments support this view. Levich[16] and Tobias, *et al.*,[17] have shown conclusively that the assumption of a stagnant diffusion layer at the rotated electrode is incorrect and that diffusion and convection through a "diffusion-boundary-layer"[16] both contribute appreciably to the current which depends on diffusion coefficients as well as on the prevailing hydrodynamic conditions.

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

[12] H. Eyring, J. W. Fredricksen and D. McLachlan, Jr., *Proc. Nat. Acad. Sci. U. S.*, **34**, 245 (1934).

[13] H. Eyring and P. Gibbs, *Science*, **112**, 104 (1951).

[14] A. Fage and H. C. H. Townend, *Proc. Roy. Soc. (London)*, **A135**, 668 (1932).

[15] I. M. Kolthoff, J. Jordan and A. Heyndrickx, *Anal. Chem.*, **25**, 884 (1953).

[16] B. Levich, *Disc. Faraday Soc.*, **1**, 37 (1947); *Acta Physicochim. U.R.S.S.*, **19**, 117 (1944).

[17] C. W. Tobias, M. Eisenberg and C. R. Wilke, *J. Electrochem. Soc.*, **99**, 360 (1952).