TABLE IV

VARIATION OF HYDROXYARGENTOCYANIDE CONCENTRATION (x) WITH HYDROXIDE CONCENTRATION

Initial argentocyanide concentration, 0.004 M, bromide absent.

[NaOH], M	$x \times 10^5$, M	$S_{AgCN} \times 10^{16}$
0.1	23	3.0
.15	30	2.6
.2	36	2.3
.3	51	2.2
.4	67	2.1
.5	81	2.1
.6	108	2.3
.7	118	2.1
.8	145	2.3
.9	167	2.4
	Av.	2.3×10^{-16}

latter is known with considerably less accuracy than in the experiments in Tables I, II and III. Nevertheless, with less than 0.001 M of initial argentocyanide in 0.2 M sodium hydroxide, a plot of x against the square root of the argentocyanide concentration (at turbidity point) gives points which lie about the straight line shown as curve I in Fig. 3. Used in conjunction with equation 3, the slope of this line yields $1.4 \pm 1 \times 10^{-8}$ as the value of S_{AgOH}. Experiments in more dilute sodium hydroxide solution were used to obtain x at an argentocyanide concentration at turbidity point of 6×10^{-5} M. A plot of x against the square root of the sodium hydroxide concentration likewise appears to be linear, as shown by curve II, Fig. 3. The values of S_{AgOH} calculated from the slope of this curve is $1.6 \pm 1 \times 10^{-8}$. These values, obtained at 22 to 25°, are approximate only. They are of the same order as the generally-accepted value, *viz.*, 2×10^{-8} and therefore could provide additional quantitative support for the scheme of reaction.

In a future paper we intend to discuss the significance of the present results in an interpretation of the argentometric amperometric titration of cyanide.

Acknowledgments.—We thank the Graduate School of the University of Minnesota for a grant to carry out this work. J. T. Stock thanks the Education Officer, London County Council, for the award of a Robert Blair Fellowship.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Rotated Dropping Mercury Electrode as a New Electrode in Polarography

BY W. STRICKS AND I. M. KOLTHOFF

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The design, operation and characterisitics of a rotated dropping mercury electrode are described. The characteristics of current–voltage curves obtained at the new electrode differ from those observed at the conventional dropping mercury electrode. The effects of surface active substances, ionic strength and other factors on the limiting current are described and compared with those observed at the conventional dropping electrode. In a given supporting electrolyte limiting currents of various metal ions in the absence of surface active substances are proportional to the square root of their diffusion coefficients. The change of the limiting current with applied voltage is quite different from that observed at the conventional electrode. This is attributed to stirring effects. In the presence of suitable capillary active substances (gelatin), the c.v. curve has an appearance similar to that at the conventional dropping electrode. The limiting current of metal ions is proportional to concentration in the range 5×10^{-6} to 8×10^{-4} M. The half-wave potentials of metal ions both in the presence and absence of gelatin are independent of the concentration and slightly more negative than those observed at the conventional electrode. The analysis of the thallium wave is the same at the rotated as at the conventional electrode. The high sensitivity and the simple operation make the new electrode extremely useful for the analysis of electroactive substances at very low concentrations. For analytical purposes it is recommended to suppress stirring by addition of a suitable surface active substance. Even though the limiting current in the presence of such a substance is only about one half of that found in its absence, the new electrode is under these conditions of the order of ten times more sensitive than the conventional electrode.

Introduction

We developed a rotated dropping mercury electrode in which the mercury is dislodged in an upward direction into the solution from the tip of a rotated U-tube, the droptime being controlled by the dimensions of the electrode and by the speed of rotation. The new electrode which is denoted as R.D.M.E. combines the advantages of the conventional dropping mercury electrode D.M.E. with those of the rotated platinum electrode. The hydrogen overvoltage and precision of the new electrode are the same as those of the D.M.E., but the sensitivity of the R.D.M.E. can be made at least 10 times greater than that of the D.M.E. This increased sensitivity makes the R.D.M.E. more suitable for trace analysis. Electroactive species in solutions as dilute as 5×10^{-6} M can be detected and determined. In amperometric titrations it can be used at dilutions of the same order of magnitude as the rotated platinum electrode. The construction and manipulations of the new electrode are simple and it can therefore be used for routine work. In contrast to the conventional electrode the R.D.M.E. can be used without any modification for the analysis of systems with flowing liquids. For theoretical studies of electrode reactions the R.D.M.E. should be equally useful as the D.M.E. Moreover, the former provides valuable information on streaming effects at the interface mercury–solution and adsorption and desorption of capillary active substances.

The characteristics of the new electrode differ in many respects from those of the D.M.E. Thus the shape of the current–voltage curves is greatly affected by the concentration of supporting electrolyte and by the presence of capillary active substances. At low ionic strength and in the absence of surface active substances the limiting currents of easily reducible substances attain a maximum value at the potential of the electrocapillary zero and decrease both at more positive and more negative potentials. At sufficiently large ionic strength or in the presence of surface active substances the polarograms at the R.D.M.E. resemble those observed at the D.M.E. In the presence of a surface active substance the kind and concentration of supporting electrolyte have a similar effect on the limiting current and half-wave potential as at the D.M.E. Current–voltage curves with the new electrode do not exhibit maxima of the first kind (the "ordinary" maxima observed at the D.M.E.).

The present paper gives the design of the new electrode, some typical current–voltage curves and their interpretation at varying concentrations of supporting electrolyte in the presence and absence of capillary-active substances in aqueous solutions and a brief discussion of the applicability of the electrode for analytical purposes. More specific fundamental and analytical studies will be reported in subsequent publications.

Space does not permit to review the various modifications of the conventional dropping electrode and various stationary mercury electrodes with stirring or the rotated mercury electrode.

Experimental

Materials.—Conductivity water and commercial reagent grade chemicals were used in all experiments. Tank nitrogen, specified as 99.99% pure, was obtained from Linde Air Products Co.

Instrumentation.—Current–voltage curves were recorded with a Heyrovsky self-recording polarograph, with a Heyrovsky type Sargent Model XII-polarograph and with a Leeds and Northrup Electro-Chemograph Type E with damping switch in positions one or two. With zero damping the values of the average current recorded by the Leeds and Northrup instrument differed considerably from the current measured manually or with non-electronic polarographs. The deviations which were found to increase with increasing current could be eliminated by an increase in damping. With the damping switch in position one, currents up to 20 μa. were recorded correctly, while damping two was used for the measurement of higher currents. Under these conditions the current values obtained with the Leeds and Northrup Electro-Chemograph agreed with the manually obtained values within ±2%. Correct half-wave potentials at damping one or two were found as the average of the two $E_{1/2}$ values obtained from polarograms which were run with the same solution from positive to negative potentials and *vice versa*. The half-wave potentials obtained in this way were found to be in good agreement with the manual values. Current–voltage curves were also measured manually with the apparatus and circuit described by Lingane and Kolthoff.[1] Applied potentials are reported *vs.* the saturated calomel electrode (S.C.E.).

Construction and Characteristics of the Electrode

Construction.—Two types of electrodes (illustrated in Fig. 1) which are denoted as types A and B have been found suitable. Type A consists of three exchangeable parts, (1) the "top tube," about 25 to 35 cm. length of glass tubing of about 2 mm. inner and 7 mm. outer diameter; (2) the capillary, a piece of polarographic capillary tubing as supplied by E. H. Sargent & Co., Chicago (2–5 or 6–12 seconds), the length of which has to be adjusted according to the drop time required (3 to 10 seconds), and (3) an "end tube" as illustrated in Fig. 1. The length of the end tube is about 12 cm., its lumen 0.2 to 0.3 mm. and the diameter of the tip 0.4 to 1 mm. The distance *d* between tip and center of rotation was about 10 mm. with all electrodes used. The lower end of the tube is ground such that the tube is tapered off at the tip. The edge at the tip should be as thin as possible. In order to prevent electrolyte solution from creeping into the end tube during electrolysis, the end tube is treated with a liquid silicone preparation (G-E Dri Film SC 87, obtained from Central Scientific Co., Chicago) in the following way. A 10–20% solution of the silicone preparation in petroleum ether is sucked into the clean and dry end tube and left there for a few minutes whereupon air is passed through the tube to evaporate the petroleum ether. The end tube is now placed in a drying oven at 110° for 30 minutes, allowed to cool and rinsed with 0.01 M ammonia solution, distilled water, hot concentrated nitric acid and again with distilled water and dried at 110°.

The parts of the electrode are connected by means of Tygon tubing. In assembling the electrode it is most expedient to connect at first the top tube with the funnel of about 60 mm. length and 30 mm. diameter. A tightly fitting glass tube is used to hold the funnel rigidly in vertical position. The other end of the top tube is connected with the capillary tube which is kept in rigid position by means of a metal tube (Fig. 1). Before attaching the end tube to the capillary the electrode is placed into the holder of the stirrer and filled with mercury, making sure that the dropping from the capillary tube is regular. Now the end tube, provided with a piece of Tygon tubing, can be attached to the capillary, under which a tray or beaker should be placed to prevent mercury from spilling over the table. Care must be taken to provide an unbroken column of mercury between the lower end of the capillary and the upper end of the "end tube." This is best accomplished by allowing a space of 1 to 2 mm. between capillary and end tube and filling this space completely with mercury so that no air bubbles are present. The mercury cushion thus formed between the two tubes secures a regular and continuous flow of mercury through the electrode. A thin-walled tightly fitting metal tube is now slipped over the Tygon tubings, connecting the capillary with top and end tubes and the electrode is properly fixed in the center of rotation of the holder of the stirrer which, for this purpose, is provided with three screws at both the upper and lower end. Since the holder of the stirrer used was short (70 mm.) the top tube is held in position during rotation by means of a metal clamp at about half way the length of the top tube. At a given speed of rotation the rate of flow of mercury and the drop time are determined by the dimensions of the electrode, like height of mercury column, length and bore of capillary tube, diameter of tip and distance *d* between tip and center of rotation. The effects on the current–voltage curves of each of these variables can be studied separately by keeping others constant. This can be readily accomplished with type A electrode.

A simple modification is type B electrode (Fig. 1) which consists only of one piece of glass tubing, provided with a constriction to regulate the flow of mercury and with a tip at distance *d* of the same dimensions as in type A electrode. The proper adjustment of the dimensions of the constriction which substitutes the capillary of the type A electrode can be made by heating in the small flame of a blast pipe and pulling the lower part of the tube until the desired drop time is obtained. The length of the mercury column was kept in the same range as used in the type A electrode. Outer and inner diameter of the upper part of the tube and the funnel had the dimensions given for type A electrode. The tube below the constriction was 60 to 80 mm. long with an outer diameter of 3 to 4 mm. and a bore of 0.2 to 0.3 mm. The part of the tube to be immersed into the solution (about 30 mm. from lower end) is coated in the same way as described for type A electrode. The entire tube is carefully cleaned with dilute ammonia, water, hot concentrated nitric acid, rinsed with distilled water and dried at 110°. The tube is then inserted in the holder of the stirrer (Fig. 1), the funnel attached and kept in position in the same way as described for electrode A. The characteristics of the current–voltage curves obtained with type A and B electrodes are identical.

Another type electrode with an end piece designed in such a way as to allow the mercury to flow downwards instead of upwards into the solution was also used in some of our experiments. Since these experiments are not included in the present paper, this type electrode is not given in Fig. 1.

The funnel of the electrodes is filled with mercury to about three fourth of its height. Because of the relatively large dimensions of the funnel the height of the mercury column is kept practically constant during electrolysis.

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(1) J. J. Lingane and I. M. Kolthoff, This Journal, **61**, 825 (1939).

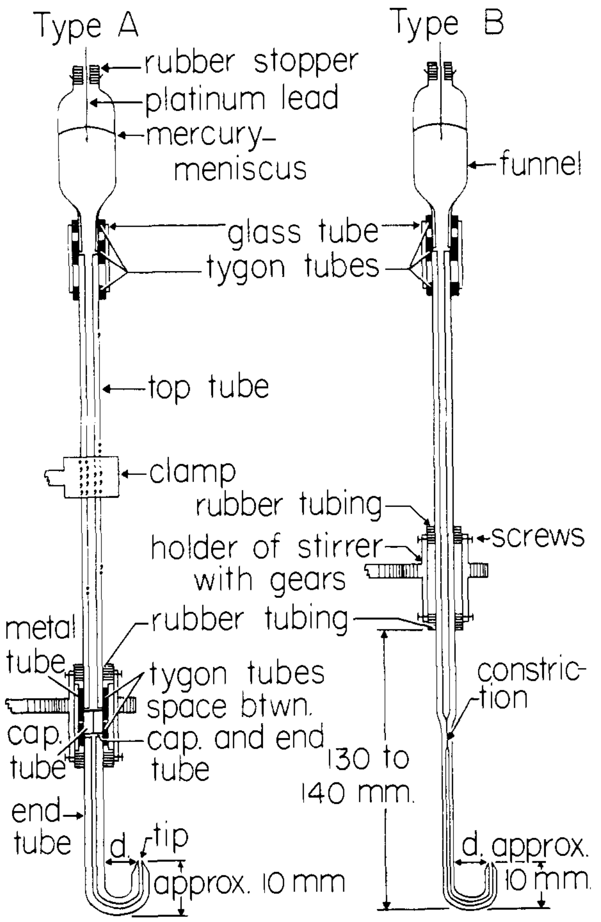

Fig. 1.—Rotated dropping mercury electrodes.

The funnel is provided with a rubber stopper with hole for a thin platinum wire lead.

The stirrer which holds the electrode is driven by means of a synchronous Bodine motor (Type KYC-23RB, provided with gears for speeds of 300, 210, 150 and 75 r.p.m. and Type KC-23, provided with gears for speeds of 900, 600 and 300 r.p.m.).

After each experiment the part of the electrode which had been in contact with the solution is thoroughly rinsed with distilled water and the adhering water removed by means of a piece of filter paper. If not in use, the electrode is kept filled with mercury by closing the funnel with a tightly fitting rubber stopper and by slipping a thick-walled piece of rubber tubing (about 30 mm. long) over the tip of the electrode and sealing the upper end of the rubber tube with a tightly fitting glass rod.

The electrolysis vessels used in combination with the new electrode were either a beaker of 250-ml. capacity or for smaller volumes of solution a cylindrical vessel of 10 cm. height and 6 cm. diameter. The electrolysis vessel is provided with a rubber stopper with holes for the electrode for inlet and outlet tubes for nitrogen, for a tube with sintered glass bottom which contains the salt bridge and with a hole which serves for introducing solutions into the cell by means of a pipet or buret. The volume of the solution to be electrolyzed was varied from 150 to 40 ml. and was found to have no effect on the current-voltage curves.

Characteristics of the Electrode.—The speed of rotation (r.p.m.), the rate of flow of mercury (m) and the drop time (t) determine the characteristics of the rotated dropping mercury electrode.

The speed of rotation was varied from 75 to 900 r.p.m. In general, speeds of 150 to 300 r.p.m. are most desirable. At these speeds the rate of flow of mercury of the rotated electrode was found to be practically the same as that of the unrotated electrode. For example with a given electrode in 0.1 M potassium chloride (open circuit) the rate of flow of the unrotated (m_0) and rotated electrode at 300 r.p.m. (m_{300}) was found to be 12.55 and 12.46 mg. sec.$^{-1}$, respectively. Some 16 electrodes with varying length of capillaries (type A) and varying constrictions (type B) and with tips ranging from 0.4 to 1 mm. in diameter have been used which had m values between 21 and 9 mg. sec.$^{-1}$. This range can be recommended for practical purposes. The value of m of the R.D.M.E. is considerably larger than that of the conventional D.M.E. which is of the order of 2.5 mg. sec.$^{-1}$.

The drop time (t_{300}) of electrodes rotated at a speed of 300 r.p.m. was varied from about 5 to 1.5 seconds as compared to drop times (t_0) of 10 to 2.5 seconds of the same electrodes in the unrotated state. Rotated electrodes with drop times markedly smaller than 1.5 seconds give relatively large residual currents while electrodes with t_{300}-values greater than 5 seconds have the disadvantage of yielding excessive current oscillations. The drop times were determined at speeds from zero to 900 r.p.m. at various potentials and also with an open circuit. The most convenient way to determine the drop time over the entire potential range is to electrolyze a mercury solution which is about 10^{-5} M in mercury and 0.1 M in supporting electrolyte (*e.g.*, KCl, $NaClO_4$) and to measure the time corresponding to a given number of galvanometer deflections (5 to 10) at any potential where the limiting current is observed. The time between the maximum and minimum deflection is equal to the drop time. With an open circuit, when no current flows through the cell, the drop time is determined by observing the ring shaped tracing of the rotated tip of the electrode. This apparent ring of mercury becomes brighter as the drop grows and suddenly disappears as the drop separates from the tip. Observing this separation allows counting the drops when the electrode is rotated at speeds not markedly greater than 300 r.p.m. Examples of the variation of drop time with the speed of rotation are illustrated in Fig. 2.

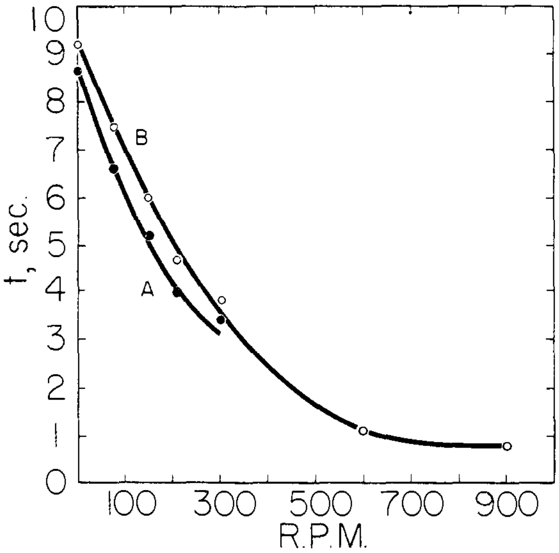

Fig. 2.—Drop time t, *vs.* speed of rotation r.p.m.: A, in 0.002 M KNO_3 with open circuit B, in 0.02 M KNO_3 10^{-5} N Hg_2SO_4 at −0.7 volt *vs.* S.C.E.

The drop time at various potentials of the rotated electrode at 300 r.p.m. in solutions of 0.1 M potassium chloride and 1.5×10^{-5} M mercuric chloride in the presence and absence of 0.005% gelatin is plotted in Fig. 3. It is seen that the curves in Fig. 3 generally are similar in shape to those obtained with the conventional dropping electrode. An irregularity between 1.2 and 1.4 volt is observed with some of the electrodes tested. Similar irregularities are sometimes found with the conventional electrode in solutions containing surface active substances. Drop time potential curves observed with the new electrode in the unrotated state also have the same shape as those at the conventional electrode. Sometimes slight variations of the drop time were observed after use of the electrode, particularly after applying potentials markedly more negative than −1.6 volt. In one instance the drop times t_0 and t_{300} with open circuit were 7.8 and 2.8 seconds before and 9.1 and 3.2 seconds after a complete polarogram (from 0.0 to 2.0 volt) had been taken. With the mercury flowing, the electrode recovered within about 15 minutes when the drop times attained their original values. Fortunately, variations in the drop time of the above order of magnitude have little effect on the limiting current at the R.D.M.E.

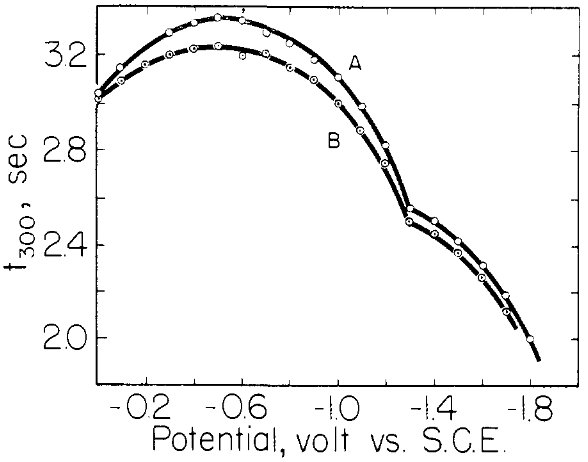

Fig. 3.—Drop time t_{300} *vs.* potential. Electrolyte: A, 1.5×10^{-5} M $HgCl_2$, 0.1 M KCl; B, 1.5×10^{-5} M $HgCl_2$, 0.1 M KCl, 0.005% gelatin.

As a first and rough approximation we assume that the drop of the R.D.M.E. has the form of a sphere, provided that the tip of the electrode is not markedly larger than 0.5 mm. in diameter. With this assumption the average radius of the drop $\bar{r}$ can be calculated in the same way as for the D.M.E.[2] from m and t

$$\bar{r} = 3/4 \left(\frac{3mt}{4\pi d}\right)^{1/3} \quad (1)$$

where m is the rate of flow of mercury, t the drop time of the rotated electrode and d the density of mercury (13.595 g. cm.$^{-3}$). The average radius of the drop for various electrodes, rotated at 210 r.p.m., varied from about 0.06 to 0.08 cm. and the average drop surface from about 0.045 to 0.08 cm.^{2}. A conventional dropping electrode of m = 2.02 mg. sec.$^{-1}$ and t = 3.83 sec. (open circuit) yields drops of average radius of 0.039 cm. and an average surface of 0.0187 cm.^{2}. The surface area of the drop of a R.D.M.E. with a tip not larger than 0.5 mm., rotated at 210 r.p.m., is thus about three to four times the area of the drop of the D.M.E. From the drop time of the rotated electrode and the speed of rotation (210 r.p.m.) it is estimated that for the various electrodes used the life of a drop extends over 5 to 18 revolutions. From the data for a given electrode at various speeds of rotation (Fig. 2) it is found that the number of revolutions during the life of a drop is 9.4, 15.0, 17.1, 17.5, 11.0, 11.5 at speeds of 75, 150, 210, 300, 600 and 900 r.p.m., respectively, thus indicating that the maximum number of revolutions survived by a drop occurs between speeds of 200 and 300 r.p.m. It is shown below that this is the speed range at which the highest sensitivity is obtained with all electrodes tested.

Residual Current.—Residual currents at the R.D.M.E. are somewhat larger than those at the D.M.E. As an example the residual current at the R.D.M.E. in 0.02 M sodium perchlorate is recorded in Fig. 4. At any speed of rotation at potentials more negative than −0.3 volt and in various electrolytes (KCl, KNO_3, $NaClO_4$, $HClO_4$, etc.) the residual current was found to be proportional to the applied e.m.f. with all electrodes tested. With a given electrode in 0.02 M potassium chloride the slope was found to be 0.50 μa. volt^{-1} at speeds ranging from 0 to 300 r.p.m. but increased to 0.80 and 0.88 at speeds of 600 and 900 r.p.m., respectively. The slope with a conventional dropping electrode in 0.1 M KCl is about 0.2 μa. volt^{-1} while that of Lee's[3] rotated mercury electrode in 0.02 M KCl is between 2 to 5 μa. volt^{-1}. At constant electrolyte concentration the residual current of the R.D.M.E. decreases in the presence of gelatin. For example in 0.02 M potassium nitrate the residual current at 300 r.p.m. and at −0.7 volt was found to be 0.26 and 0.16 μa. in the absence and presence of 0.01% gelatin. Increasing electrolyte concentration usually results in somewhat larger residual currents. Thus an electrode rotated at 300 r.p.m. at −0.7 volt gave residual currents of 0.26 and 0.35 μa. in 0.02 and 1 M sodium perchlorate, respectively. Under proper conditions the range of potentials available for study with the R.D.M.E. in aqueous media is not greatly different from that with the D.M.E. In aqueous tetraethylammonium bromide barium can be determined with the R.D.M.E.

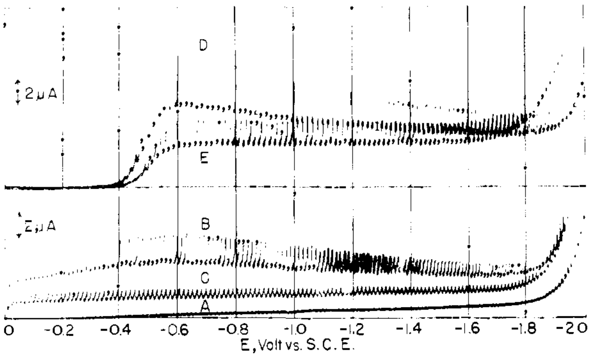

Fig. 4.—Current–voltage curves at the R.D.M.E. (210 r.p.m., m = 9.4 mg. sec.$^{-1}$, t_{210} = 4.5 sec. with open circuit), supporting electrolyte: 0.02 M $NaClO_4$: A, residual; B, 2.32×10^{-5} M Hg_2SO_4; C, 2.28×10^{-5} M Hg_2SO_4, 0.01% gelatin; D, 2.45×10^{-5} M Tl_2SO_4; E, 2.40×10^{-5} M Tl_2SO_4, 0.01% gelatin.

Limiting Current.—Examples of current-voltage curves obtained with a typical R.D.M.E. are illustrated in Fig. 4. At speeds from 0 to 300 r.p.m. the current oscillations were perfectly regular throughout the entire potential range. At speeds from 300 to 900 r.p.m. the oscillations were found to be irregular. With the use of conventional polarographs the amplitude of the oscillations relative to the current decreases with increasing speed of rotation, the drop time being an inverse function of the number of r.p.m. As was anticipated, polarograms recorded from positive to negative potentials and *vice versa* were found to be identical.

At a given speed of rotation the limiting current depends on the dimensions of the electrode. The sensitivity of the electrode decreases markedly with tips smaller than 0.4 mm. in diameter. These electrodes also have the smallest drop time (unrotated t_0 = 2.4 sec.). The distance d was about 10 mm. for all electrodes used. The height of the mercury column was varied from 32 to 50 cm. Columns markedly smaller than 40 cm. gave rise to irregularities in the polarograms at potentials more negative than −1.2 volt. These irregularities were caused by insufficient mercury supply to the electrode tip during rotation.

The shape of the current-voltage curves at the R.D.M.E. is markedly affected by the concentration of the supporting electrolyte and by the presence of surface active substances.

Effect of Concentration of Supporting Electrolyte.—At low electrolyte concentrations (0.01 to 0.1 M) in the absence of surface active substances the limiting current exhibits a maximum value at the potential of the electrocapillary zero and decreases markedly both at more positive and more negative potentials (Fig. 4, curve B). This change of limiting current with potential which has been observed with all electrodes tested becomes more pronounced as the speed of rotation is increased from 75 to 300 r.p.m. and diminishes again at speeds greater than 300 r.p.m. The proportionality between limiting current and concentration of electroactive substance has been tested in solutions at a given concentration of supporting electrolyte with various ions and electrodes at various poten-

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[2] I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1952, p. 79.

[3] T. S. Lee, This Journal, **74**, 5001 (1952).

TABLE I

LIMITING CURRENTS (μa.) OF MERCUROUS AND THALLOUS IONS IN 0.02 M KNO_2

(300 r.p.m., $t_0 = 9.22$, $t_{300} = 3.87$ sec., open circuit). Currents corrected for residual.

Metal concn., M^a	Mercury at −0.3 v.		Mercury at −0.7 v.		Mercury at −1.0 v.		Thallium at −0.7 volt: In absence of gelatin		Thallium at −0.7 volt: In presence of 0.01% gelatin	
	i	i/c^b	i	i/c	i	i/c	i	i/c	i	i/c
4×10^{-6}	0.79	19.7	0.78	19.4	0.67	16.7	...	..	...	..
10^{-5}	1.96	19.6	1.97	19.7	1.65	16.5	1.48	14.8	...	..
2×10^{-5}	...	..	...	..	...	..	2.98	14.9	...	..
3×10^{-5}	6.03	20.1	5.69	19.0	4.82	16.1	...	..	...	..
5×10^{-5}	9.94	19.9	9.65	19.3	8.09	16.2	7.33	14.7	4.12	8.2
10^{-4}	19.50	19.5	19.08	19.1	15.97	16.0	14.46	14.5	8.12	8.1
2×10^{-4}	40.50	20.2	39.60	19.6	32.60	16.3	29.17	14.6	16.2	8.1
3×10^{-4}	60.90	20.3	58.30	19.4	45.90	15.3	...	..	...	..
4×10^{-4}	80.90	20.2	78.10	19.5	59.40	14.9	56.70	14.2	32.2	8.1
6×10^{-4}	...	..	...	..	...	..	...	..	48.3	8.1
8×10^{-4}	...	..	...	..	...	..	...	..	64.0	8.0

[a] M refers to molarity of Hg_2^{++} and Tl^+ ion. [b] i/c is current of 10^{-4} M solution.

tials (−0.3 to −1.4 volt). Some of the data for mercurous and thallous ion in 0.02 M potassium nitrate, obtained with an electrode rotated at 300 r.p.m., are listed in Table I. The values of the limiting current were obtained by measuring the average of the galvanometer deflections which was assumed to correspond to the average current. At potentials in the vicinity of the electrocapillary zero potential (−0.3 and −0.7 volt) the average deviation from linearity between current and concentration was about ±1% throughout the entire concentration range tested. At more negative potentials (−1.0 volt) the deviation from linearity increased at concentrations greater than 2×10^{-4} M.

As the concentration of the supporting electrolyte was increased, the region of the maximum limiting current widened over a larger potential range and at a certain electrolyte concentration (0.5 to 1.0 M) the limiting current region attained the shape of a straight line (see Fig. 5). The current at the electrocapillary zero hardly changed with the electrolyte concentration. The observations illustrated in Fig. 5 were made with electrodes of various characteristics in solutions of various metal ions such as thallium, cadmium, lead, copper and zinc, and of various supporting electrolytes, potassium chloride, sodium perchlorate and sodium nitrate. In some experiments in chloride solutions of concentrations as large as 1 M in KCl and relatively large metal concentrations (3×10^{-4} M and larger in metal) the current increased at both the negative and positive side of the electrocapillary zero and the polarogram then exhibited a minimum at this potential.

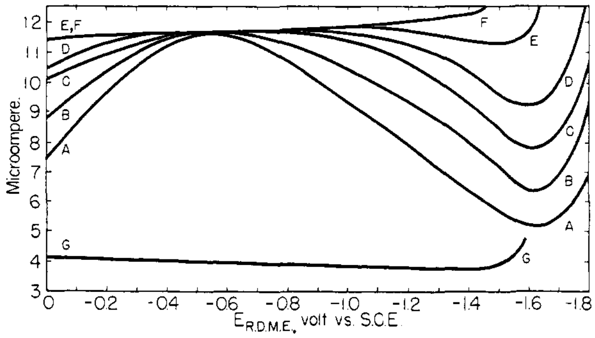

Fig. 5.—Current–voltage curves of 5×10^{-5} M Hg_2SO_4 in sodium nitrate solutions of various concentrations in $NaNO_3$ (210 r.p.m., $t_{210} = 5.3$ sec., $m_0 = 9.37$ mg. sec.$^{-1}$, open circuit): A, 0.01; B, 0.05; C, 0.10; D, 0.25; E, 0.50; F, 1.00 M $NaNO_3$; G, 1.00 M $NaNO_3$, 0.01% gelatin. Current corrected for residual.

Presence of Gelatin.—Upon the addition to the solution of small amounts of surface active substances which, like gelatin, are adsorbed at the interface mercury-solution throughout the entire potential range the limiting current at the R.D.M.E. is markedly decreased, the decrease being most extensive at the electrocapillary zero potential. The variation of the limiting current at −0.7 volt of a 2.5×10^{-5} M thallous sulfate solution (0.02 M in KNO_3) with increasing gelatin concentration is illustrated in Fig. 6. When the concentration of gelatin was of the order of 0.008%, further addition had practically no effect on the limiting current and the appearance of the entire wave was now similar to those at the conventional D.M.E. (see Figs. 4C, 4E, 5G). Limiting currents of thallium at various concentrations in the presence of 0.01% gelatin are given in Table I. At this gelatin concentration the limiting current of thallium was found to be proportional to the thallium concentration from 5×10^{-6} to 8×10^{-4} M. The effect of gelatin on the thallium wave was found to be independent of the kind and concentration of supporting electrolyte in a range from 0.02 to 1 M. As was to be expected, gelatin has practically no effect on the limiting current at the unrotated electrode.

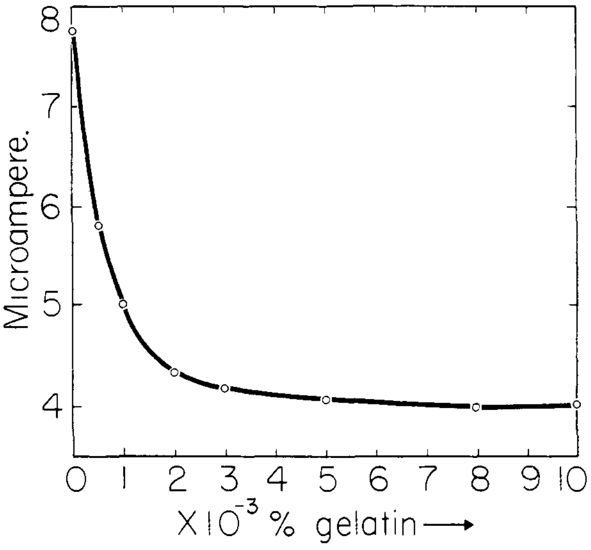

Fig. 6.—Limiting current of thallium (2.5×10^{-5} M Tl_2SO_4, 0.02 M KNO_3, 300 r.p.m.) *vs.* gelatin concentration. Current measured at −0.7 volt and corrected for residual.

A comparison of the polarograms in Fig. 4 shows that the same concentration of gelatin suppressed the mercury wave to a considerably larger extent than the thallium wave. Generally the suppressive effect of gelatin was found to be larger for heavy metal ions which can be bound by gelatin. In contrast to thallium, which is not bound by gelatin, the limiting current of heavy metal ions in the presence of a constant gelatin concentration is therefore not proportional to the metal concentration, the i/c values of these metals becoming larger with increasing metal concentration. For

TABLE II

LIMITING CURRENTS i(μa.) AT R.D.M.E. (300 R.P.M.) AND DIFFUSION COEFFICIENTS D OF VARIOUS IONS AT A CONCENTRATION OF 10^{-4} M

(t_{300} = 2.80 sec.) (t_0 = 8.00 sec., m_{300} = 12.46 mg. sec.$^{-1}$)

		μ = 0.1, i measured at −0.7 v.			μ = 1.0, i measured at −1.4 v.		
Ion	$D \times 10^5$,[a] cm.^{2} sec.$^{-1}$	Supporting electrolyte	i/n[b]	$(i/n)/D^{1/2} \times 10^{-3}$	Supporting electrolyte	i/n	$(i/n)/D^{1/2} \times 10^{-3}$
Cu(II)	0.72	0.1 M HClO$_4$	9.08	3.38	M KCl	9.75	3.63
Hg_2^{++}	.92	.1 M KCl	10.50	3.46	0.0005 M HNO$_3$ M NaNO$_3$	10.15	3.35
Hg_2^{++}	.92	.1 M KCl, .005% gelatin	3.04	1.00			
Pb^{++}	.98	.1 M HClO$_4$	10.00	3.20			
Zn^{++}	.72	......	...	..	M NaClO$_4$	9.15	3.41
Cd^{++}	.72	......	...	..	M NaClO$_4$	9.60	3.55
Tl^+	2.00	.1 M HClO$_4$	15.10	3.37	M KCl	15.00	3.35
Tl^+	2.00	.1 M HClO$_4$ .0075% gelatin	6.80	1.52	M NaClO$_4$	15.20	3.39
Cysteine	0.704	.05 M Borax .1 M KCl	− 3.94[c]	−1.49	....	...	..
Cysteine	.704	.05 M Borax, .1 M KCl .0075% gelatin	− 3.66[c]	−1.38	....	...	..
Cystine	.53	.1 M HClO$_4$	7.64	3.32	....	...	..
Cystine	.53	.1 M HClO$_4$ .005% gelatin	2.80	1.22	....	...	..
Tl^{+}[d]	2.00	.1 M KCl	11.60	2.59	....	...	..
Tl^{+}[d]	2.00	.1 M KCl .01% gelatin	4.90	1.10	....	...	..
CNS^{-}[d]	1.78	.1 M NaClO$_4$	− 4.60	−1.10	....	...	..
CNS^{-}[d]	1.78	.1 M NaClO$_4$ .01% gelatin	− 4.87	−1.15	.....	...	..
C_6H_5HgCl[d]	1.11[e]	Phosphate pH 7 0.04 M KCl	3.54 8.40	1.06 2.50	....	...	..
C_6H_5HgCl[d]	1.11[e]	Phosphate pH 7 0.04 M KCl .01% gelatin	3.53 3.56	1.06 1.07	....	...	..

[a] All D-values were taken from reference 2 if not stated otherwise. [b] n is number of faradays required per mole of electrode reaction. [c] i was measured at −0.35 v.; in 0.1 M HClO$_4$ i was −3.97 μa. at +0.1 v. [d] The electrode used for these experiments was rotated at 210 r.p.m. and its characteristics were: t_{210} = 1.55 sec., t_0 = 2.45 sec., m_{210} = 21.20 mg. sec.$^{-1}$. The limiting current (i) of CNS$^-$ was measured at +0.45 v. [e] D was calculated from data in reference 4, the two figures in columns 4 and 5 refer to the first and second wave of C$_6$H$_5$HgCl. The height of the second wave was measured at −1.3 v., taking the prolonged plateau of the first wave as base line.

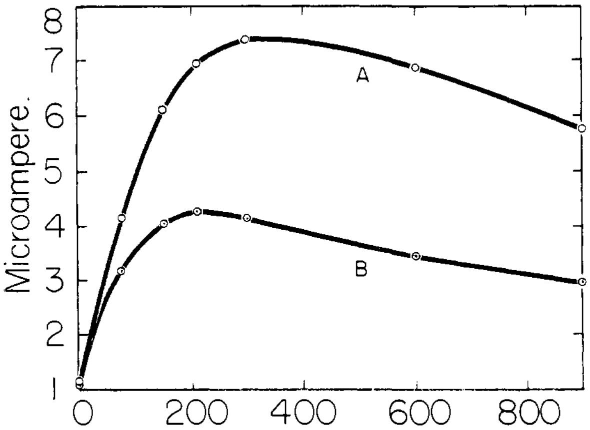

Fig. 7.—Limiting current at R.D.M.E. in 2.5 × 10^{-5} M Tl$_2$SO$_4$, 0.02 M KCl $vs.$ speed of rotation (r.p.m.): A, in absence; B, in presence of 0.01% gelatin. Current measured at −0.7 volt and corrected for residual.

instance the i/c values of cupric copper in 0.02 M potassium nitrate 0.005% in gelatin were 3.4 and 8.2, at copper concentrations of 10^{-5} M and 7 × 10^{-5} M, respectively. The i/c remained constant at 8.2 upon further increase of the copper concentration up to 8 × 10^{-4} M.

Effect of Speed of Rotation.—Limiting currents of various electroactive cations and anions in the presence and absence of gelatin were measured at speeds of rotation from 75 to 900 r.p.m. The variation of the limiting current of thallium with speed of rotation is illustrated in Fig. 7. With all electrodes tested the limiting current at a given potential was found to attain a maximum value at speeds of 200 to 300 r.p.m., a further increase in speed resulting in a decrease of current. This behavior was found with various reducible substances at various concentrations of several supporting electrolytes in the presence and absence of gelatin.

Effect of Temperature.—The effect of temperature on the limiting current of 2.25 × 10^{-5} M thallous sulfate in 0.1 M potassium chloride in the absence of gelatin was studied over a range from 2 to 51° at speeds from 0 to 210 r.p.m. The residual current and the shape of the current voltage curves were found to be unaffected by the temperature. The temperature coefficient of the limiting current was independent of the speed of rotation and equal to that found with the unrotated electrode. It was found to be of the order of 1.5% per degree between 2 and 25° and of 0.8% per degree between 25 and 51°. This is of the same order of magnitude as that of the diffusion current at the D.M.E.

The drop time of the R.D.M.E. did not change with temperature. The same temperature coefficients were obtained with two electrodes of different characteristics.

Limiting Currents of Various Ions.—Polarograms were run of solutions of various metal ions and of organic compounds under comparable conditions at which the i/c values were found to be constant. As an illustration Table II gives the limiting currents of 10^{-4} M solutions of several ions at ionic strengths 0.1 and 1 and the infinite dilution values of the diffusion coefficients, usually employed in polarographic work.[2] The constancy of the ratio $(i/n)/D^{1/2}$ in Table II as well as the log plot of the current *vs.* the diffusion coefficient in Fig. 8A, which is a straight line of slope 0.5, indicate that the limiting current at the R.D.M.E. in the absence of surface active agents is a linear function of the root of the diffusion coefficient. This relation which has been verified with various supporting electrolytes at various ionic strength and with electrodes of different characteristics is thus the same for both the rotated and the conventional dropping mercury electrodes. Since gelatin suppresses the limiting current at the R.D.M.E. of different metal ions to a different extent the i-$\sqrt{D}$ relation can not hold for metal solutions containing gelatin. Thus the ratios $(i/n)/D^{1/2}$ calculated for 10^{-4} M solutions of thallium and copper (even at concentrations larger than 7×10^{-5} M) in 0.02 M KNO_3, 0.01% gelatin were found to be 1.81×10^3 and 1.51×10^3, respectively. An extensive study of the effect of various surface active substances is under way. Preliminary work with starch as a suppressor indicates that the proportionality with $D^{1/2}$ holds for thallium, cadmium and lead.

From the data of Table II and from Fig. 8 it is seen that the anodic currents of cysteine and of thiocyanate are markedly smaller than the values which would be expected from their diffusion coefficients if the i-$\sqrt{D}$ relation would hold for these compounds. However, this relation is obeyed (Table II, Figs. 8B and 8C) with regard to the thallium wave in the presence of 0.01% gelatin, the anodic waves of cysteine and thiocyanate being practically unaffected by gelatin.

Also some cathodic limiting currents, not obeying the i-$\sqrt{D}$ relation, have been observed at the R.D.M.E. An example is phenylmercury chloride (C_6H_5HgCl) which is reduced at the conventional D.M.E. in two single electron steps of equal height.[4] At the R.D.M.E. this compound gives two reduction steps of different height, the first well-defined step being markedly lower than the second step which is ill-defined. Both limiting currents are proportional to the concentration. Upon addition of increasing amounts of gelatin the first wave remained unchanged while the second wave became well-defined and its height was reduced until both waves had the same height at a gelatin concentration of 0.008%, when further addition of gelatin had no more effect on the height of the wave. In one instance a 6×10^{-5} M solution of phenylmercury chloride in a phosphate buffer pH 7 ($\mu = 0.1$) gave two waves of limiting currents of 2.12 μa. (at −0.7 volt) and 5.04 μa. (at −1.3 volt), respectively. In the presence of 0.008% gelatin the limiting currents of the two waves were 2.12 and 2.14 μa., respectively. From Table II and Fig. 8C it is seen that the limiting current of the first wave obeys the i-$\sqrt{D}$ relation with regard to thallium in the presence of gelatin, while in the absence of gelatin this relation is maintained with regard to thallium and the second wave of phenylmercury chloride.

The present experiments allow the conclusion that electrode processes at the R.D.M.E., involving the dissolution of mercury or the formation of surface active reaction products (like $(C_6H_5)_2Hg$ in the reduction of C_6H_5HgCl[4]) yield limiting currents which are not suppressed by gelatin.

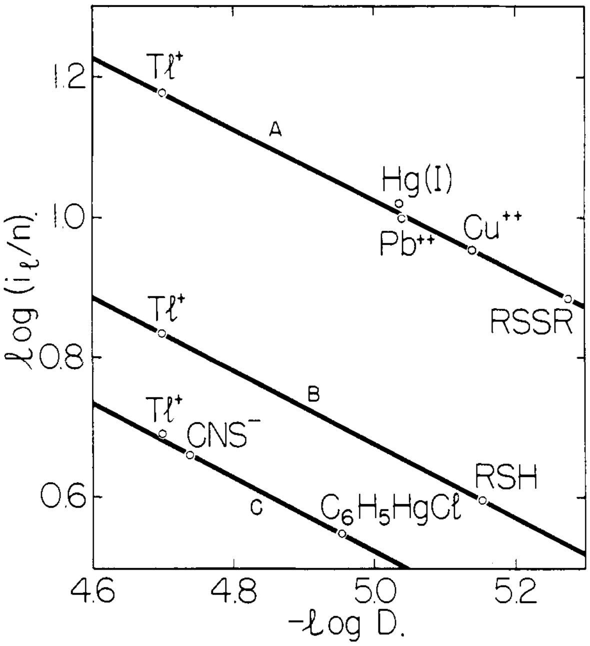

Fig. 8.—Log (i_l/n) (i_l measured at −0.7 volt) *vs.* log D of: A, 10^{-4} M Tl^+, Hg_2^{++}, Pb^{++}, Cu^{++} and cystine (RSSR) in 0.1 M perchloric acid and of B, 10^{-4} M Tl^+ in 0.1 M $HClO_4$, 0.01% gelatin and 10^{-4} M cysteine (RSH) in 0.05 M borax, 0.1 M KCl (i_l of cysteine measured at −0.35 volt) (300 r.p.m., t_{300} = 3.1 sec., m_{300} = 12.46 mg. sec.$^{-1}$). C, 10^{-4} M Tl^+ in 0.1 M KCl, 0.01% gelatin, 10^{-4} M KCNS in 0.1 M $NaClO_4$ and 10^{-4} M C_6H_5HgCl (first wave) in phosphate buffer pH 7, μ = 0.1 (210 r.p.m., t_{210} = 1.55 sec., m_{210} = 21.20 mg. sec.$^{-1}$). i_l of KCNS measured at +0.45 volt.

Half-wave Potentials.—Half-wave potentials of several metal ions measured at the R.D.M.E. were found to be independent of the metal concentration (5×10^{-6} to 8×10^{-4} M). $E_{1/2}$ values of thallium in the presence and absence of 0.01% gelatin are listed in Table III. The values were reproducible to ±5 mv. It is seen that the half-wave potential of thallium at the R.D.M.E. is 25 to 30 mv. more negative than the value observed at the unrotated electrode and the D.M.E. Both in the presence and absence of gelatin the $E_{1/2}$ values are practically independent of the speed of rotation between 75 and 900 r.p.m. At the lower r.p.m. (between 75 and 210 r.p.m.) $E_{1/2}$ is about 7 mv. more negative in the presence than in the absence of gelatin.

TABLE III

HALF-WAVE POTENTIALS AND PROPORTIONALITY CONSTANTS k_s AND k_a OF THALLIUM AT R.D.M.E. AT VARIOUS SPEEDS OF ROTATION

All solutions were 5×10^{-5} M in Tl^+ and 0.02 M in potassium chloride. k_s and k_a refer to millimolar solutions.

	In absence of gelatin			In presence of 0.01% gelatin		
R.p.m.	$E_{1/2}$, v. *vs.* S.C.E.	ks	ka	$E_{1/2}$, v. *vs.* S.C.E.	ks	ka
0	−0.452[a]	21.5	15.1	−0.452	22.2	15.5
75	− .477	82.6	21.9	− .484	63.0	(12.7)
150	− .478	122.2	31.2	− .486	80.8	15.1
210	− .481	138.8	31.5	− .485	85.6	16.6
300	− .480	146.6	34.6	− .484	82.4	16.6
600	− .480	135.2	32.0	− .482	69.5	15.1
900	− .482	114.6	25.0	− .480	59.4	(14.0)

[a] $E_{1/2}$ at D.M.E. is −0.451 volt in 0.02 M KNO_3.[2]

A plot of log $i/(i_l - i)$ *vs.* potential (i_l is limiting current) for the thallium wave in the presence of gelatin is illustrated in Fig. 9. The plot is a straight line of slope $\Delta E/\Delta \log i/(i_l - i)$, 0.061, indicating that the thallium wave at the R.D.M.E. analyzes

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(4) R. Benesch and R. E. Benesch, THIS JOURNAL, **73**, 3391 (1951); R. E. Benesch and R. Benesch, *J. Phys. Chem.*, **56**, 648 (1952).

in the same way as it does at the D.M.E. Similar plots were obtained for thallium solutions of ionic strength of 0.1 (i_l measured at -0.7 volt) in the absence of gelatin and with electrodes of various characteristics. The analysis of the thallium waves at the unrotated electrode in the absence and presence of gelatin was also identical with those at the conventional D.M.E.

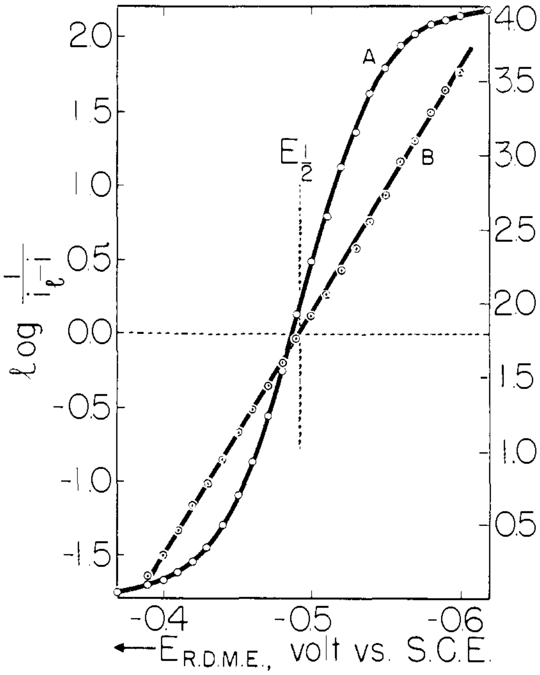

Fig. 9.—A, c–v curve and B, plot log $i/(i - i_1)$ *vs.* E of 5.54×10^{-5} M Tl^+ in 0.1 M $HClO_4$, 7.5×10^{-3}% gelatin (300 r.p.m., $t_{300} = 3.1$ sec., $m_{300} = 12.464$ mg. sec.$^{-1}$).

Discussion

The variation in the shape of c–v curves at varying concentrations of supporting electrolyte (Fig. 5) and the effect of gelatin upon the limiting current at the R.D.M.E. can be accounted for by a streaming effect in the mercury and in the solution.

This streaming effect also occurs at the conventional D.M.E. and has been described by Frumkin, Levich, Krjukova, Kabanow[5] and by von Stackelberg.[6] An English review of part of the Russian work was given by Smith.[7]

While the diffusion current at the D.M.E. is governed by transport of the electroactive species through radial motion, polarographic maxima have been ascribed to tangential motions at the surface of the drop. Extensive studies by Frumkin and his co-workers[5] and by v. Stackelberg[6] led to the assumption that tangential motions at the interface of the mercury drop can be the result of two different causes and accordingly two kinds of maxima, those of the "first" and of the "second" kind are distinguished. Maxima of the first kind occur over a relatively narrow potential range at the positive or negative side of the electrocapillary zero potential but not at this potential itself. They can be suppressed by surface active substances and by an increase in ionic strength. Maxima of the second kind at the D.M.E. are observed only at a large ionic strength (μ = 2 to 3). They are most pronounced at the potential of the electrocapillary zero and usually extend over the entire potential range. They are also suppressed by surface active substances.

The theory of the maxima of the first kind implies inhomogeneous polarization of the drop, caused by a "screening effect" of the wall of the capillary. The design of the new electrode probably excludes such a "screening effect" and in fact no maxima of the first kind have been observed at the new electrode up to limiting currents of 80 μa., immaterial whether it was in the rotated or unrotated state.

Antweiler[6] has demonstrated that there is a vortex motion within a drop of mercury which flows out of a capillary. This vortex motion is transmitted to the solution which moves tangentially to the drop surface, giving rise to enhanced convective currents. Frumkin, *et al.*, showed experimentally and theoretically that this tangential streaming at the mercury–solution interface varies with the potential of the mercury and with the ionic strength of the solution. Diagrams illustrating the relation between potential and velocity of motion at various ionic strengths are reproduced in Fig. 10. The rate of the motion is largest at the potential of the electrocapillary zero at which point the rate is independent of the ionic strength. At other poten-

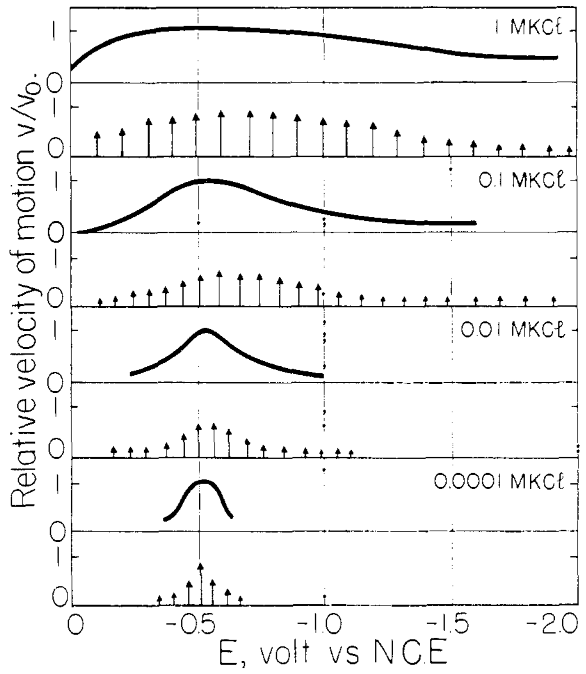

Fig. 10.—Relative velocity of motion of potassium chloride around mercury drop. Arrows indicate experimental values and curves are constructed from calculated values, both obtained by Frumkin, *et al.*[6,8] v_0 is velocity at potential of electrocapillary zero, v velocity at any other potential.

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[5] A. Frumkin and B. Levich, *J. phys. Chem. U.S.S.R.*, **19**, 573 (1945); **21**, 689, 953, 1183, 1335 (1947); T. A. Krjukova and B. N. Kabanow, *ibid.*, **15**, 475 (1941); **20**, 1179 (1946); **21**, 365 (1947); *J. Gen. Chem. U.S.S.R.*, **15**, 294 (1945); *Acta physicochim. U.S.S.R.*, **22**, 381 (1947); *Sawodskaja Lab.*, **14**, 511, 639 (1948).

[6] M. von Stackelberg, *Fortschr. chem. Forsch.*, **2**, 229 (1951).

[7] G. S. Smith, *Chem. and Ind.*, 619 (1949).

tials the rate of streaming is a function of the electrolyte concentration. The potential range at which streaming occurs widens with increasing ionic strength. The similarity in shape between the curves in Fig. 10 and c–v curves at the R.D.M.E. at various ionic strength in Fig. 5 is striking. Maxima of the second kind at the D.M.E. can be suppressed by gelatin, this substance also causing the large suppression of the limiting current at the R.D.M.E. All these observations indicate that the large limiting currents at the R.D.M.E. in the absence of surface active substances are to be attributed to stirring effects which are responsible for maxima of the second kind. Apparently the streaming effect is enhanced by rotation and is observed at the R.D.M.E. under conditions at which maxima of the second kind are not observed at the D.M.E.

For a complete mobile interface Levich[8] derived the following equation for currents involving maxima of the second kind at the D.M.E.

$$i = \sqrt{8\frac{\pi}{2}}\left(\frac{Dv}{r}\right)^{1/2}(c - c_0)r^2$$

where v is velocity of solution at the interface, r radius of drop, c and c_0 concentration of electroactive species in the bulk and at the interface, respectively. It is of interest to note that with our electrode we also found the relation $i = fD^{1/2}$.

The analysis of the thallium wave (see Fig. 9) allows the conclusion that the reduction of thallium at the R.D.M.E. is reversible and that the wave equation has a form similar to that derived for the D.M.E.

$$E_{\text{R.D.M.E.}} = E_{1/2} - \frac{0.059}{n}\log\frac{i}{i_1 - i} \qquad (1)$$

where i_1 is the limiting current. $E_{1/2}$ is then given by

$$E_{1/2} = E_a{}^{\circ} - 0.059 \log a_{\text{Hg}} - 0.059 \log f_a/f_s - 0.059 \log k_s/k_a \qquad (2)$$

or

$$E_{1/2} = E' - 0.059 \log k_s/k_a \qquad (3)$$

where k_s and k_a are proportionality constants, relating current and concentration of ion in solution and metal in mercury, respectively, and $E' = E_a{}^{\circ} - 0.059 \log a_{\text{Hg}} - 0.059 \log f_a/f_s$.

Applying the Ilkovic equation to the data at the unrotated electrode, the values for the constant $i_d/CnD^{1/2}m^{2/3}t^{1/6}$ were found to range from 590 to 640 which compares favorably with the value 607 derived from the D.M.E. This justifies the assumption that the ratio k_s/k_a for the unrotated electrode is equal to $D_s{}^{1/2}/D_a{}^{1/2}$ where D_s and D_a are the diffusion coefficients of the metal ion in the solution and of the metal in the mercury, respectively. From the values of $D_s = 2 \times 10^{-5}$ cm.^{2} sec.$^{-1}$,[2] $D_a = 0.99 \times 10^{-5}$ cm.^{2} sec.$^{-1}$ [9] and $E_{1/2}$ of thallium at the unrotated electrode (Table III) the constant E' in equation 3 was calculated to be -0.4430. Values of k_a for the rotated electrode were now calculated by substituting the experimental values of k_s and $E_{1/2}$ into equation 3. From Table III it is seen that in the absence of gelatin k_a increases with the speed of rotation up to the speed (300 r.p.m.) at which the maximum limiting current is attained, whereupon a decrease of k_a ensues as the speed is still further increased. In the presence of gelatin the k_a values are practically the same for the unrotated and rotated electrode. Similar observations were also made with other ions. Thus, from the $E_{1/2}$ values of lead ion in the presence of 0.05% starch as suppressor at the rotated (210 r.p.m., -0.395 volt) and unrotated electrode (-0.378 volt), from the values $D_s = 0.98 \times 10^{-5}$ cm.^{2} sec.$^{-1}$ and $D_a = 1.16 \times 10^{-5}$ cm.^{2} sec.$^{-1}$ and from the experimental values of k_s (24.0 unrotated, 100.0 rotated in presence of 0.05% starch) the k_a values in the presence of starch were found to be 26 and 28 for the unrotated and rotated electrode, respectively.

The limiting anodic current at a rotated dropping thallium amalgam electrode in 0.05 M potassium nitrate was found to increase with rate of rotation (from 75 to 300 r.p.m.) in the absence of gelatin but to remain unaffected by the speed of rotation and to be equal to the limiting current at the unrotated electrode in the presence of 0.01% gelatin. Again, at the amalgam electrode k_a is found unaffected by rotation in the presence of gelatin while in the absence of the suppressor k_a increases with speed of rotation. In the absence of gelatin streaming effects within the mercury and in the aqueous solution close to the interface are enhanced by rotation and k_a as well as k_s increase until an optimum speed (300 r.p.m.) is attained. In the presence of gelatin the electrode interface is made immobile, streaming effects are eliminated and the transfer of metal into the mercury is unaffected by rotation. The transport of electroactive species from the solution to the interface increases with rate of rotation both in the presence and absence of gelatin. In the presence of gelatin when k_a is the same at the unrotated and rotated electrode the difference in half wave potentials of thallium measured at both electrodes should be equal to 0.0591 log $(k_s)_r/(k_s)_0$ (r denotes rotated). Using data in Table III at 210 r.p.m., the calculated difference is 0.035 volt in good agreement with the experimentally observed difference of 0.033 volt. With a divalent metal like lead the calculated difference is 0.0175 volt, while in the presence of starch as suppressor a value of 0.017 volt was found.

The half-wave potential should not be affected by rotation when the oxidized and reduced forms in an electrode reaction are both soluble in the aqueous phase. Thus, for instance, the half-wave potential of the anodic cysteine wave, which corresponds to the dissolution of mercury to form mercurous cysteinate, is the same at both the R.D.M.E. and the D.M.E. Solutions of 2×10^{-5} to 10^{-4} M cysteine in 0.05 M borax, pH 9.2, gave a half-wave potential of -0.510 volt ± 3 mv. at the R.D.M.E. (300 r.p.m.) as compared to -0.520 volt[10] at the D.M.E.

The high limiting currents at the R.D.M.E. in the presence of surface active substances, as compared with those at the D.M.E. are accounted for by both its larger area and by a higher rate of transportation. Comparison of the average area and "effective thickness of diffusion layer" ($\delta = nF\bar{A}\cdot$

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[8] B. Levich, *Disc. Faraday Soc.*, **1**, 37 (1947).

[9] N. H. Furman and W. C. Cooper, THIS JOURNAL, **72**, 5667 (1950).

[10] W. Stricks and I. M. Kolthoff, *ibid.*, **74**, 4646 (1952).

DC/i, where $\bar{A}$ is average area of electrode, D diffusion coefficient of metal ion, n its valence, C concentration and i limiting current)[11] of a typical D.M.E. with those of a typical R.D.M.E., shows that $\bar{A}$ and δ are of the order of 0.02 cm.^{2} and 0.058 mm. for the D.M.E. and 0.05 cm.^{2} and 0.016 mm. for the R.D.M.E. (210 r.p.m.). Thus the average area of a drop at a R.D.M.E. is about three times as large as that at the D.M.E. while the "thickness of the diffusion layer" is about 1/3.6 of that at the D.M.E. These two factors give the R.D.M.E. in the presence of a suppressor a sensitivity of the order of ten times as large as that of a D.M.E. In the unrotated state $\bar{A}_0$ and δ_0 of the above electrode were found to be 0.06 cm.^{2} and 0.05 mm., respectively, indicating that the higher limiting currents at the unrotated electrode are almost entirely due to the larger surface of its drops.

From the analytical viewpoint limiting currents generally should be measured in the presence of a suitable surface active agent which suppresses the stirring completely. For analytical purposes it would be very risky not to suppress the stirring, because traces of surface active agents often are found in solutions. Moreover, the electro-active compound or its reaction product at the electrode may be surface active and thus cause complications in the interpretation of the limiting currents.

If used as an indicator electrode in amperometric titrations, addition of maximum suppressors is not required, the limiting current being proportional to the concentration of electroactive species at a given potential.

Acknowledgment.—This investigation was supported by a research grant (C-721 (C6)) from the National Cancer Institute, U. S. Public Health Service.

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[11] J. A. V. Butler, "Electrical Phenomena at Interfaces," The Macmillan Co., New York, N. Y., 1951, Chap. VIII.

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Mercury Exchange between Mercuric Chloride and *p*-Chloromercuribenzoic Acid

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It has been possible to produce ^{203}Hg-labeled *p*-chloromercuribenzoic acid using an exchange reaction between mercuric chloride and *p*-chloromercuribenzoic acid. The velocity constant k_2 for the mercury exchange reaction was found to be of second order and had a value of 1.09 ± 0.03. The activation energy was found to be 12.0 ± 0.6 kcal./mole.

It has been possible to produce ^{203}Hg-labeled *p*-chloromercuribenzoic acid using an exchange reaction between mercuric chloride and *p*-chloromercuribenzoic acid. This reaction was accomplished by mixing solutions of radioactive mercuric chloride and inactive *p*-chloromercuribenzoic acid in a thermostat and separating the components after a suitable period for analysis. By establishing the quantity of mercuric chloride and *p*-chloromercuribenzoic acid present and measuring the radioactivity of both fractions, the specific activity could be determined. The velocity constant k_2 for the mercury exchange reaction

$$^{203}HgCl_2 + ClHgC_6H_4CO_2H \rightleftarrows HgCl_2 + Cl^{203}HgC_6H_4CO_2H$$

was calculated from

$$k_2 = -\frac{2.303}{(a+b)t}\log\left(1 - \frac{b_i^x}{b_{i\infty}^x}\right)$$

where

k_2 = velocity constant in l. mole^{-1} sec.$^{-1}$
a = concn. of $HgCl_2$ in mole/l. at $t = 0$
b = concn. of $ClHgC_6H_4CO_2H$ in mole/l. at $t = 0$
t = reaction time in sec.
$b_i^x/b_{i\infty}^x$ = ratio of spec. activity of $ClHgC_6H_4CO_2H$ at t and t_∞

The reaction was of second order as k_2 was found to be independent of the concentrations of *p*-chloromercuribenzoic acid and mercuric chloride. Concentration variation of $HgCl_2$ ($0.85 \times 10^{-3} - 3.94 \times 10^{-3}$ mole/l.) and *p*-$ClHgC_6H_4CO_2H$ ($0.32 \times 10^{-3} - 2.78 \times 10^{-3}$ mole/l.) gave at 5.0° a constant k_2 of 1.09 ± 0.03. The exchange experiments were carried out at four different temperatures and the second-order velocity constants calculated. The results are summarized in Table I.

TABLE I

MERCURY EXCHANGE BETWEEN MERCURIC CHLORIDE AND *p*-CHLOROMERCURIBENZOIC ACID

Temp., °C.	k_2, l. mole^{-1} sec.$^{-1}$
5.0	1.09 ± 0.03
17.0	2.70 ± 0.04
25.0	5.4 ± 0.2
49.5	26.0 ± 1.6

The activation energy was calculated from an Arrhenius plot of these velocity constants and found to be 12.0 ± 0.6 kcal./mole.

Experimental

Materials.—The *p*-chloromercuribenzoic acid was obtained from Bios Laboratories, Inc., New York, N. Y. As Hg tracer was used a mixture of ^{197}Hg and ^{203}Hg, obtained by irradiating 2 g. of HgO for a week in a neutron beam with a flux of 5×10^{11} n/cm.^{2} sec. in the Joint Establishment Experimental Pile at Kjeller, Norway. The γ-decay curve showed two components with half-lives of 49.0 days and 66.5 hr., corresponding to the values reported for ^{197}Hg and ^{203}Hg.[1]

Counting Equipment.—All measurements were performed with a hollow anode γ-counter (Philips Nr. 18.508), inside of which glass tubes containing the test solutions could be introduced.

Analytical Procedure.—Mercuric chloride was assessed by a colorimetric method, described by Sandell[2] using dithizone.

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[1] J. M. Cork, D. W. Martin, J. M. Leblanc and C. E. Branyan, *Phys. Rev.*, **85**, 386 (1952).

[2] E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, Inc., New York, N. Y., 1944, p. 321.