THE FUNDAMENTAL PRINCIPLES AND APPLICATIONS OF ELECTROLYSIS WITH THE DROPPING MERCURY ELECTRODE AND HEYROVSKÝ'S POLAROGRAPHIC METHOD OF CHEMICAL ANALYSIS[1]

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The polarographic method of chemical analysis, invented about sixteen years ago by Heyrovský (31), is based on the interpretation of current–voltage curves obtained by electrolyzing solutions of electroreducible or electroöxidizable substances, in a cell in which one electrode consists of mercury falling in small, slow drops from a glass tube with a very narrow capillary. From the current–voltage curves so obtained both the species and the concentration of the electroreducible or electroöxidizable substances in the solution can be determined, and under optimum conditions it is possible to detect and determine several substances simultaneously from a single c.v. (current–voltage) curve. The method is especially suitable for small concentrations (10^{-5} to 10^{-2} molar), and since the electrolysis can be carried out with a volume of solution as small as 0.1 cc. or even less, mere traces of substances can be determined. Since electrolysis is the most generally applicable method of carrying out oxidation–reduction reactions, it is evident that the number of substances subject to polarographic determination is potentially very great. The method can be used to detect and determine a large variety of organic substances, in addition to practically all the common electroreducible inorganic ions; hence it gives promise of becoming a universally applicable analytical technique in the various branches of chemistry and allied fields.

Although the polarographic method is a relatively new technique in electroanalytical chemistry, it has undergone a remarkably rapid development, due chiefly to the work of Heyrovský (38) and his school at the Charles University in Prague (Czechoslovakia) and of a few other investigators, notably Hohn (50) in Germany, Semerano (104) in Italy, and Shikata in Japan. Until recently the polarographic method was practically unknown in this country, and no complete review of the subject has heretofore been published. It is hoped that the present review of the fundamental principles of electrolysis with the dropping mercury electrode, which is based largely on our own experience, will help to stimulate the interest of chemists in this versatile technique.

I. THE PRINCIPLE OF THE POLAROGRAPHIC METHOD

A typical arrangement for obtaining current–voltage curves with the dropping mercury electrode is shown schematically in figure 1. In this diagram A is the electrolysis cell containing the solution to be analyzed, B is the dropping mercury electrode, and C is a stationary pool of mercury on the bottom of the cell which acts as the second electrode. The dropping electrode consists of a drawn-out capillary tube, whose internal diameter at the tip is about 0.03 mm., connected to a reservoir of mercury. Mercury drops issue from the capillary at the rate of about one drop every 2 to 4 sec. The drops are very small, having a maximum diameter at the breaking point of only about 0.5 mm. The cell is connected, in series with a calibrated galvanometer G, to the battery and rheostat, by means of which an E.M.F. from zero up to the maximum E.M.F. of the battery can be applied to the cell. The applied E.M.F. is measured with a potentiometer, or, if the rheostat is a slide wire of uniform resistance, it can be computed in the usual way from the E.M.F. of the battery and the position of the sliding contact on the wire. The current–voltage curves are obtained by gradually increasing the applied E.M.F. and noting the current indicated by the galvanometer. The current is ordinarily quite small, seldom exceeding 50 microamperes (5×10^{-5} amperes).

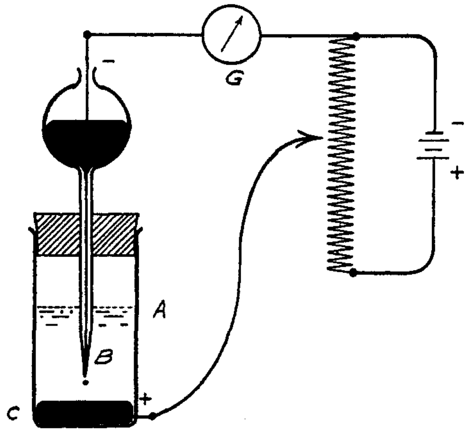

FIG. 1. Schematic representation of apparatus for obtaining current–voltage curves with the dropping electrode.

The dropping electrode is usually connected to the negative pole of the polarizing E.M.F., in which case cathodic current–voltage curves are obtained (electroreduction). In certain cases it is also possible to obtain anodic current–voltage curves (electroöxidation) by connecting the dropping electrode to the positive side of the polarizing E.M.F.

Since oxygen is readily reduced at the dropping electrode (124) and usually interferes with the current–voltage curves of other substances, it is generally necessary to remove dissolved air from the solution to be electrolyzed by bubbling an inert gas (nitrogen or hydrogen) through the cell before (but not during) the electrolysis.

The typical cathodic current–voltage curve shown in figure 2 was obtained by electrolyzing an air-free solution of 0.0013 *M* zinc sulfate in 0.1 *N* potassium chloride (65). In this polarogram the applied E.M.F. is plotted on the abscissa and the corresponding current on the ordinate. It will be noted that only an exceedingly small current, the "residual current," flowed through the cell until the decomposition potential was reached at an applied E.M.F. of about 1.0 volt. When the decomposition potential was exceeded continuous electrolysis began, involving the discharge of zinc ions at the dropping mercury cathode to form an extremely dilute zinc amalgam and the anodic dissolution of mercury, with the subsequent formation of calomel, at the large quiet anode. It will be noted that the current did not increase indefinitely with increasing applied E.M.F. after the decomposition potential was exceeded, but gradually approached a limiting value and finally became constant and independent of further increase in the applied E.M.F.

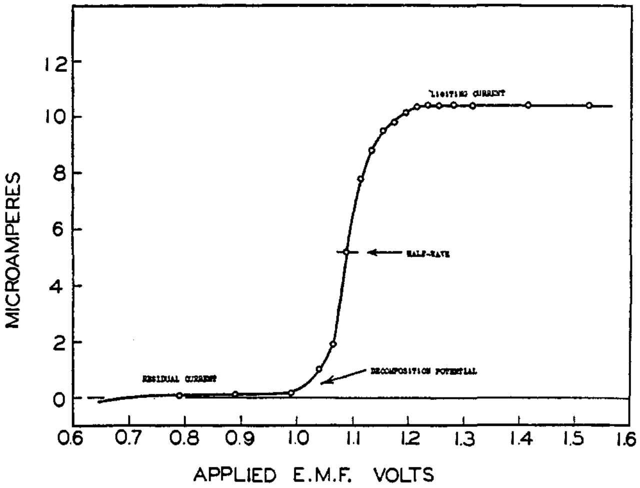

FIG. 2. Typical cathodic current–voltage curve obtained with the dropping mercury electrode.

Under optimum conditions, and with all other factors constant, the limiting current is directly proportional to the concentration of the electroreducible substance. This is the basis of quantitative polarography.

The limiting current is caused by a virtually complete state of concentration polarization at the dropping electrode. As a result of the discharge process, the concentration of the reducible material is depleted close to the surface of the dropping electrode, and this loss is compensated by diffusion of a fresh supply of reducible material from the body of the solution. The rate of diffusion depends directly on the difference in concentration between the depleted surface layer and the body of the solution. As the E.M.F. is increased above the decomposition potential, the current increases, the *average* concentration at the surface of the mercury drops decreases, and the rate of diffusion is correspondingly increased. As the applied E.M.F. is further increased, the concentration at the surface of the mercury drops becomes so small compared to the concentration in the bulk of the solution that the difference in concentration approaches a constant average value, equal simply to the concentration in the solution, and hence the rate of diffusion also becomes constant. From this point on the amount of material discharging, and thus the current, becomes constant and practically independent of further increase in the applied E.M.F. With an excess of some indifferent salt present in the solution, the limiting current is determined practically entirely by the rate of diffusion, and therefore is called a "diffusion current." Since the rate of diffusion attains a constant value, which is directly proportional to the concentration in the bulk of the solution, it is readily understandable why the diffusion current is directly proportional to the concentration in the body of the solution. A more complete quantitative interpretation of the diffusion current will be given in a later section.

With the dropping mercury electrode the current at each value of the applied E.M.F. is not constant but oscillates between a minimum and a maximum value as each mercury drop grows and falls. With a sensitive D'Arsonval galvanometer of relatively long period (ca. 15 sec.), the type usually employed to measure the current, the observed oscillations are not very large and the average current can be measured readily with a precision of better than 1 per cent.

It may be mentioned that the necessary conditions that must be fulfilled in order to obtain a limiting current are that at least one electrode of the cell be very small and that the concentration of the reducible substance be not too large. That is, conditions must be such as to favor the attainment of an extreme state of concentration polarization. Limiting currents are therefore not peculiar to the dropping mercury electrode, but may also be obtained with small solid electrodes, such as a platinum microelectrode, or with a small quiet mercury electrode. For example, in figure 3 is given a cathodic current–voltage curve obtained by electrolyzing an air-free solution of 1.75×10^{-3} *M* thallous chloride in 0.1 *N* potassium chloride, according to the technique already described, except that the dropping mercury electrode was replaced by a platinum microelectrode, consisting of a platinum wire 0.2 mm. in diameter sealed into the end of a glass tube in the usual way with 1 mm. left exposed (65). The first "wave" is due to the discharge of thallous ions and the second to the evolution of hydrogen. Mr. H. A. Laitenin in this laboratory has found that the diffusion current of thallous ions, and of various other ions, with a platinum microelectrode is directly proportional to the concentration of the ions.

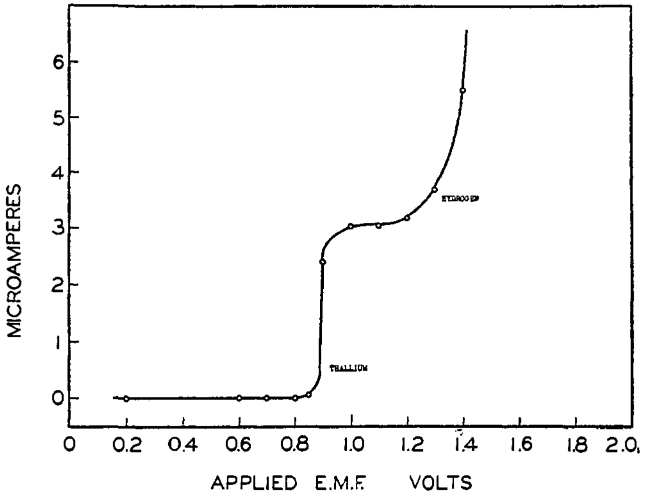

FIG. 3. Cathodic current–voltage curve obtained with a platinum microelectrode

Although a solid microelectrode is in certain respects simpler to use than the dropping mercury electrode, it has several disadvantages. With a solid microelectrode the current does not become steady immediately at each new setting of the applied E.M.F., and several minutes are required to obtain a steady reading. Solid microelectrodes are also sensitive to vibrations, which disturb the diffusion and cause irregular fluctuations in the current. Furthermore, the deposition of base metals at a platinum microelectrode is hindered by the evolution of hydrogen. The dropping mercury electrode has none of these disadvantages. The (average) current becomes steady immediately at each new setting of the applied E.M.F. and is independent of the time of electrolysis. Owing to the high overvoltage of hydrogen on mercury, even the alkali and alkaline-earth metals can be readily deposited, to give well-defined limiting currents (31, 89).

The favorable behavior of the dropping electrode is due to the fact that a fresh mercury surface is continuously being exposed by the growing drops; the phenemona at a given drop are exactly duplicated at its successor. Hence the current at any point on the current–voltage curve is solely a function of the potential of the dropping electrode, and is independent of the previous course of the electrolysis and of the length of time that the current has passed. A current–voltage curve obtained by increasing the E.M.F. in the usual way will generally be retraced exactly if the applied E.M.F. is gradually decreased to zero. These unique characteristics of the dropping electrode have made possible the development of the polarographic method.

The reason for using a relatively large, quiet pool of mercury as the second electrode of the cell is that such an electrode remains practically depolarized when the solution contains halide or other ions which form insoluble salts with mercury. It thus retains a practically constant potential independent of the applied E.M.F., and only the dropping electrode becomes polarized. For example, in solutions of chlorides the quiet electrode acquires a potential practically equal to the potential of a calomel electrode at the same chloride-ion activity.

The decomposition potential of a given solution is characteristic of the particular electroreducible substance present. Even more characteristic is the so-called "half-wave potential" (44), which, as its name implies, is the value of the applied E.M.F., or, better, the potential of the dropping electrode against an external reference electrode, at that point on a current–voltage curve where the current is equal to one-half of its limiting value (see figure 2). In contradistinction to the decomposition potential, which depends to some extent on the concentration of the reducible substance, the half-wave potential is, in general, entirely independent of the concentration of the reducible substance, provided that the composition of the solution with respect to foreign salts is kept constant (44). The half-wave potential of a given substance is also independent of the particular capillary used and of its drop time (44). The theory of the half-wave potential will be discussed in detail in a later section. It will suffice here to point out that qualitative polarographic analysis is based on the characterization of the half-wave potentials on the current–voltage curves of "unknown" solutions. By comparing the half-wave potential on an "unknown" current–voltage curve with the known values (38, 50, 44) for various substances, the substance responsible for the "polarographic wave" can be readily identified, and from the magnitude of the diffusion current its concentration can be determined.

When several electroreducible substances are present in the solution, each one will produce its own characteristic wave on the current–voltage curve, provided the half-wave potentials of the several substances are not too close together. The various half-wave potentials generally must differ from each other by at least 0.2 volt in order to obtain separate, well-defined waves. If the half-wave potentials of two substances are too close together, their waves will coalesce to give only a single wave on the current–voltage curve. In general, the half-wave potential of a given substance is not changed by the preceding discharge of another reducible substance. It may be noted, however, as one of the few exceptions to this general rule, that the half-wave potential of hydrogen discharge is decreased (shifted to more positive value) by adding to the solution certain substances which decrease the overvoltage of hydrogen on mercury, e.g., traces of platinum metals (111, 112) and certain proteins and organic compounds containing sulfur (6).

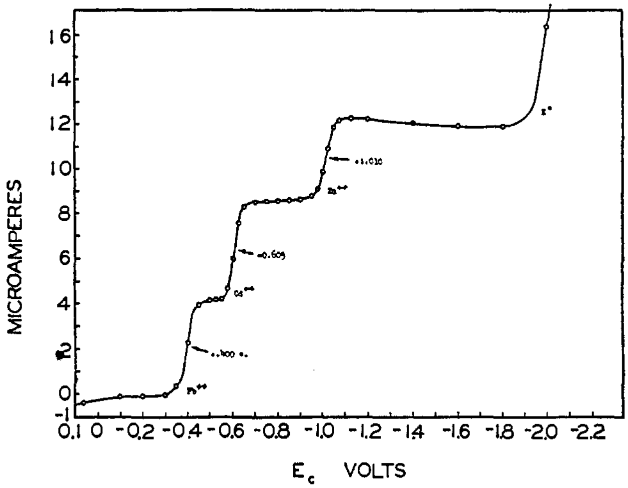

FIG. 4. Current–voltage curve of a solution containing several reducible ions

The concentration of each substance in a mixture can be determined from its own wave height; thus it is often possible to obtain a simultaneous qualitative and quantitative analysis for several constituents in an unknown solution from a single current–voltage curve. For example, the current–voltage curve in figure 4 was obtained by electrolyzing an air-free 0.1 *N* potassium chloride solution which contained lead nitrate, cadmium sulfate, and zinc sulfate, each at a concentration of about 5×10^{-4} molar (65). The individual heights of the three waves are in each case proportional to the concentrations of the respective ions.

The half-wave potentials of many simple (hydrated) metal ions are shifted to more negative values when complex-forming salts are added to the solution. This fact is often used to separate the polarographic waves of two metal ions which would otherwise coincide. For example, the half-wave potential of simple lead ions is only about 50 millivolts more positive than that of simple thallous ions, and hence the waves of these two ions practically coincide. However, by adding a large amount of potassium tartrate or potassium cyanide to the solution, the half-wave potential of lead is shifted by several tenths of a volt to a more negative value, while that of thallium remains practically unchanged; therefore in such a solution two well-separated waves are obtained, which allow the analytical separation of the two metals. It is possible in many cases to determine the instability (complex) constant of the complex formed from the magnitude of the shift in the half-wave potential (44).

The current–voltage curves do not always have the "ideal" shapes shown in the preceding figures, but are often distorted by so-called "maxima." That is, the discharge curve rises sharply, but, instead of gradually developing into a limiting current, the current increases abnormally and practically linearly with the applied E.M.F. until a certain potential is reached, and then decreases more or less rapidly towards a limiting value. A more or less sharp maximum or peak in the current-voltage curve thus results (see section VIII). The characteristics of such maxima and methods of eliminating them, which are necessary for purposes of quantitative polarographic analysis, will be discussed in detail in a later section.

II. THE POLAROGRAPH[2]

In 1925 Heyrovský and Shikata (46) invented an instrument called the polarograph, which automatically obtains, and photographically records, current–voltage curves. Since Heyrovský and Shikata (46, 38) and Hohn (50) have given excellent detailed descriptions of the construction and manipulation of the polarograph, only the principle of the instrument need be discussed here.

The principle of the polarograph is shown schematically in figure 5.

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[2] Various models of the Heyrovský polarograph may be purchased from the firm of Drs. V. and J. Nejedlý, Prague XIX, Vokovice, Husova tr. 76, Czechoslovakia. Polarographs are also manufactured by E. Leybolds Nachfolger A. G., Köln-Bayenthal, Bonner Str. 500, Berlin N. W. 7. The Leybold instrument has been described in detail by Hohn (50). The Leeds and Northrup Company of Philadelphia has constructed a few polarographs on special order, in which they incorporated the principles of their well-known "Micromax" potentiometer recorder. The details of this instrument may be obtained from Dr. V. M. Meloche of the University of Wisconsin or Dr. B. Clarke of the Bell Telephone Laboratories in New York City.

In this figure D is the electrolysis cell containing the solution to be analyzed. B is essentially a potentiometric bridge, consisting of a cylinder of insulating material wound with a rather low resistance wire (ca. 15 ohms) in exactly twenty turns, by means of which a variable E.M.F. is applied to the cell. Current for the bridge is obtained from the storage battery H, and the total potential drop across the bridge can be exactly adjusted to any desired value (usually 2 or 4 volts) by a regulating resistance and comparison against a Weston standard cell in the usual manner. Each turn of the bridge wire then corresponds to, let us say, 100 or 200 millivolts of applied E.M.F. The bridge is rotated by a small electric motor A. A roll of sensitive photographic paper is carried by the cylinder C, enclosed in a light-tight housing, and connected by a system of gears to the bridge so that the two revolve simultaneously. The gear ratio is accurately adjusted so that one complete revolution of the bridge (100 or 200 millivolts) corresponds to about 1 cm. on the photographic paper. G is a powerful galvanometer light, the beam of which is reflected onto the photographic paper by the mirror of the sensitive D'Arsonval galvanometer E. The galvanometer is connected into the circuit in parallel with an Ayrton shunt F, by means of which its sensitivity may be regulated. When current flows through the galvanometer, the light beam traces a thin line on the photographic paper parallel to the axis of the roll.

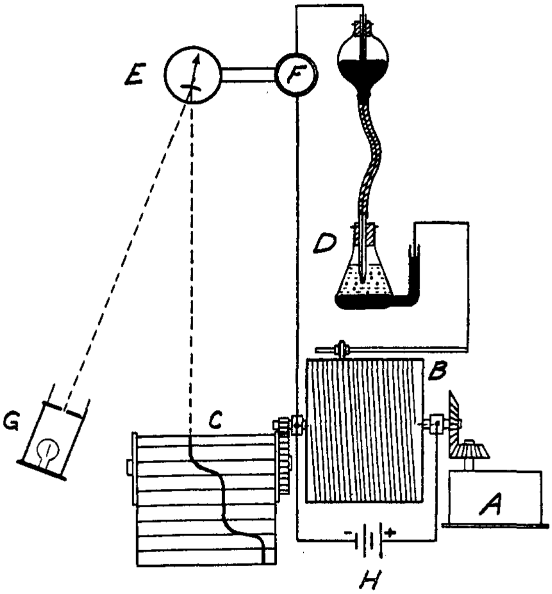

FIG. 5. Principle of the polarograph

With the cell in readiness and the dropping electrode in operation, the bridge is turned back until the moving contact (small grooved wheel) is at zero. The motor is then started, and the bridge and photographic roll revolve slowly at a uniform speed, which applies a uniformly increasing E.M.F. to the cell. As long as the applied E.M.F. is less than the decomposition potential, the current through the cell is very small (residual current), the beam of light from the galvanometer remains practically stationary, and the slow rotation of the drum traces a line along the circumference of the photographic roll. When the decomposition potential is reached, the increase in current through the cell circuit deflects the galvanometer, and the light beam traces a line approximately parallel to the axis of the roll; this is the discharge curve or polarographic wave. When the limiting current is reached and the light beam attains a constant displacement, the limiting current is traced as a circumferential line on the photographic roll.

The photographic roll is enclosed in a housing provided with a narrow collimating slit through which the light beam from the galvanometer enters. Each time the roll turns through a distance of 1 cm. (100 or 200 millivolts of applied E.M.F.) an auxiliary light, automatically flashed on, illuminates the entire length of the slit, and a thin line is printed on the paper. These lines mark the increments of applied E.M.F. The diffusion current is computed from the measured height of the polarographic wave and the known sensitivity of the galvanometer.

The polarograph has several advantages over manual measurement. In the first place, the curves can be obtained in a fraction of the time required to obtain them manually; a complete curve can be recorded in 10 min. or less. Several curves can be recorded on a single sheet of photographic paper, and a permanent record is thus obtained in a single operation. A continuous curve is obtained, instead of a series of points; hence very small waves, or slight peculiarities which might otherwise escape notice, are automatically detected.

Although a polarograph is very convenient, it is expensive and is not at all essential for obtaining current–voltage curves. For this reason we shall briefly describe a simple circuit which we have found very convenient for obtaining current–voltage curves manually, and with which most of the current–voltage curves that we studied were obtained (65, 66).

The principle of the circuit is shown in figure 6. The E.M.F. applied to the cell was regulated by means of a rheostat, consisting of two radio rheostats of the "potentiometer" type, connected in series. A four-dial precision resistance box (9999 ohms), indicated by R in figure 6, was connected in series with the cell; by measuring the potential drop across this resistance with a potentiometer the current through the cell could be readily determined by applying Ohm's law. This method of measuring the current is very precise and accurate, but was somewhat unhandy.

To facilitate the current measurement a galvanometer, with suitable shunts for regulating its sensitivity, was also connected in series with the cell and the standard resistance. The E.M.F. applied to the cell, the potentials of the dropping electrode and of the quiet electrode against a saturated calomel reference electrode (S.C.E. in figure 6), and the potential drop across the standard resistance were all measured with a potentiometer. In order to facilitate these readings, a circular six-position double-pole selector switch was used, as shown in figure 6. A Weston standard cell was also connected to one position of the selector switch for calibrating the potentiometer. Further details regarding the use of this simple circuit are described elsewhere (66).

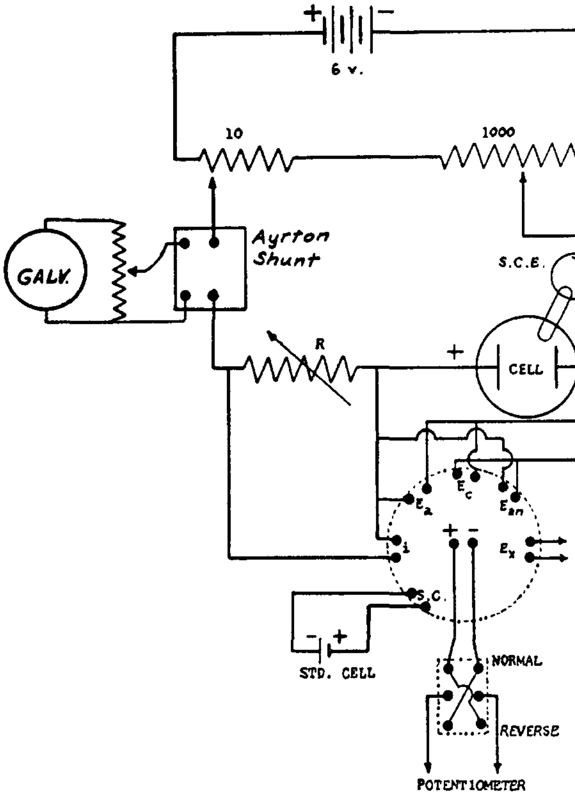

FIG. 6. Simple circuit for obtaining current–voltage curves manually

Although the manual method of measurement was not as convenient as the use of the almost automatic polarograph, it possessed the advantage of somewhat greater precision and accuracy, which was more important than convenience for our purpose of critically studying the polarographic method. The circuit in figure 6 has the additional advantage that the potentials of the dropping and quiet electrodes can be measured separately during the electrolysis. It should be mentioned that the magnitudes of the limiting and diffusion currents are entirely independent of the characteristics of the measuring circuit. On the other hand, the magnitude of the oscillations in the current during the formation of each mercury drop depends on the characteristics of the particular galvanometer used, and the heights of the maxima depend on the magnitude of the external resistance in the cell circuit (7), as will be discussed later.

Matheson and Nichols (78) have recently described a new type of polarograph, employing alternating current, and a cathode ray tube oscillograph. A similar instrument has also been described by Müller, Garman, Droz, and Petras (82). Schmidt (102) has recently described another modification of the Heyrovský polarograph.

III. FABRICATION OF THE CAPILLARIES AND THE DROPPING ELECTRODE

The capillaries are usually fabricated by drawing out the end of a 20-cm. length of Pyrex capillary tubing, of about 0.5 mm. internal diameter, until the internal diameter of the tip is about 0.03 to 0.04 mm. The end of the tube is thickened in the flame before drawing, so that the tip will not be too slender and fragile. The tip, which should have a uniform internal diameter, is cut off until the length of the narrowest part is about 2 cm. The exact dimensions must be decided by trial and error, until a capillary is obtained the drop time of which in 0.1 *N* potassium chloride can be readily adjusted to between 3 and 4 sec., by suitable adjustment of the pressure on the dropping mercury.

Maas (68) has made a very thorough study of the preparation of capillaries for the dropping electrode. He prepared the dropping electrode by cementing a 2- to 3-cm. length of commercial thermometer tubing (internal diameter about 0.03 mm.) into a wider glass tube, which was connected to the mercury reservoir. Siebert and Lange (109) also recommend this method; they used 6- to 8-cm. lengths of thermometer tubing of about 0.05 mm. internal diameter.

In order to obtain a strict linear relation between the diffusion current and the concentration of a given reducible substance, the drop time (time for the formation of each mercury drop) must not be too short. Maas (68) found that the drop time must be about 4 sec. or longer. We (65, 66) obtained a strict linear relation with capillaries the drop time of which in 0.1 *N* potassium chloride, with the dropping electrode disconnected from the polarizing E.M.F., was about 3 sec. If the drop time is too short, the diffusion current tends to be relatively too great at very small concentrations, i.e., less than about 10^{-4} *M*. On the other hand, if the drop time is too long, the current oscillations during the formation of each mercury drop are so great that it is difficult to measure accurately the average current. The optimum drop time is from 3 to 6 sec.

The capillary is usually connected to the mercury reservoir by a length of rubber pressure tubing, and the pressure on the dropping mercury can then be adjusted by simply raising or lowering the mercury reservoir. An ordinary leveling bulb is used as a mercury reservoir. This is a simple method, but it involves the danger of impurities from the rubber tube getting down into the very fine capillary tip and clogging it. In order to avoid all possible contamination from rubber connections, we sealed the capillary directly to the mercury reservoir, as shown in figure 7. The pressure applied to the dropping mercury was regulated by means of two mercury leveling bulbs, as shown in figure 8. The total pressure on the dropping mercury is equal to the height of the mercury column in the dropping electrode itself, plus or minus the pressure indicated by the open-end mercury manometer. The pressure required to operate the dropping electrode depends, of course, on the characteristics of the particular capillary used; it is usually between 20 and 60 cm. of mercury.

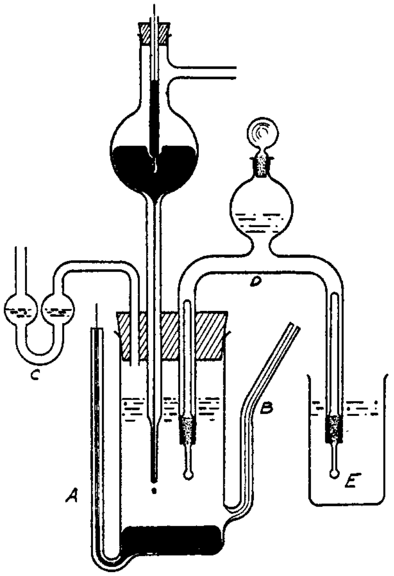

FIG. 7. Dropping electrode and electrolysis cell

When not in use the tip of the dropping electrode should be kept immersed in pure mercury, with the pressure reduced to prevent the mercury in the reservoir from draining out. Before the electrode is placed in a solution, the pressure is increased so that the mercury drops issue from the capillary and thus prevent the solution from entering the tip. After long use the capillary may become partially dirty on the inside and behave erratically. When this happens, the mercury is removed and aqua regia is sucked through the tip into the bulb, by partially evacuating the latter. The aqua regia is then removed by thorough rinsing with pure water, and the capillary is dried by drawing a current of dry *filtered* air through it. With these simple precautions it is possible to use a single capillary indefinitely. At the time of this writing we are using a capillary that has been in daily use for over a year, during which time it has been cleaned several times without noticeably changing its properties.

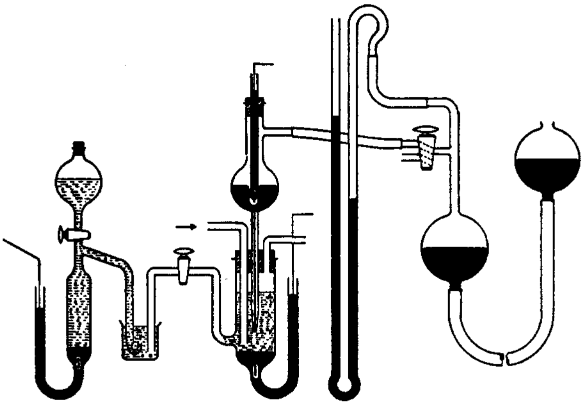

FIG. 8. Arrangement for regulating the pressure on the dropping mercury

IV. TYPES OF POLAROGRAPHIC CELLS

A few of the most common types of polarographic cells that have been described in the literature (mainly by Heyrovský) are shown in figure 9, which has been taken from the monograph of Hohn (50). These cells are very convenient for practical analytical work. Cells d and e are of the type most commonly used; electrical connection to the quiet electrode is made by means of a platinum wire sealed through the bottom of the cell as shown, and the side tubes are for the ingress and exit of nitrogen or hydrogen. Cells c and g are for the electrolysis of a very small volume of solution, and the arrangement shown under b is for the electrolysis of a single large drop. An ordinary small beaker may serve as a simple cell when the electrolysis can be carried out without removing air from the solution, as shown under a. Cell f is used for collecting and weighing the mercury drops. The vessel h is for freeing the mercury for the quiet electrode from air before introducing it into the cell; this is often desirable. The vessel, containing the proper amount of mercury, is connected into the gas line with one side tube connected to the gas inlet tube of the cell. After nitrogen or hydrogen has been passed through the system, the vessel is inverted so that the de-aired mercury flows into the cell.

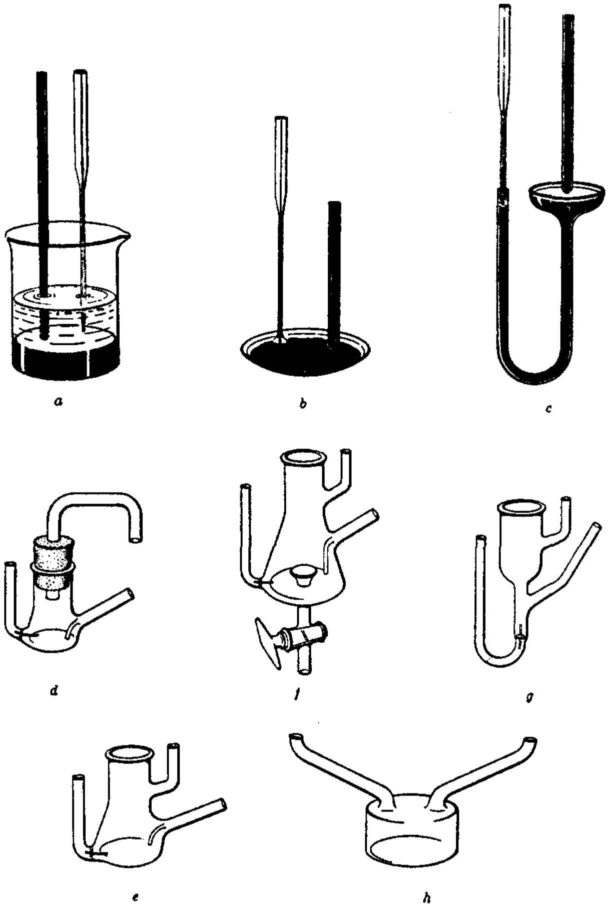

FIG. 9. Various types of polarographic cells

Majer (74) has recently described in detail various types of cells that are particularly suited for microchemical analysis, as well as other special apparatus for micropolarographic work.

In certain cases it may be necessary to work with the cell in a thermostat and to measure the potentials of the dropping electrode and of the quiet electrode against an external calomel reference electrode during the electrolysis. The cell shown in figure 7 (65, 66) is very suitable for these purposes. Mercury for the quiet electrode is poured into the cell until it rises part way into the capillary side tube A, and electrical connection is made by means of a platinum wire immersed in the mercury in this side tube. This method of making electrical connection eliminates troublesome platinum–Pyrex seals. The capillary side tube B is for the introduction of nitrogen or hydrogen, and C is a gas outlet trap, containing either pure water or a little of the cell solution. The salt bridge D, designed by Irving and Smith (58), is usually filled with the same solution as in the cell. The ground-glass plugs in the ends of this bridge effectively prevent mixing of the bridge and cell solutions. The external end of the bridge dips into an intermediate vessel E, filled with concentrated potassium chloride solution, into which the side arm of the calomel electrode also dips.

As already mentioned, oxygen is reduced at the dropping electrode; hence dissolved air must usually be removed from the solution to prevent the oxygen wave from masking the waves of other substances. The time required to remove dissolved air, by bubbling nitrogen or hydrogen through the solution, is usually about 15 to 30 min. The gas stream is stopped before the electrolysis, because its stirring effect causes irregular fluctuations in the current.

Instead of using a quiet mercury electrode as the second electrode of the cell, it is often more convenient to use an external calomel, or mercury–mercurous sulfate, electrode for this purpose, as recommended by Hohn (50) and Maassen (69). The external electrode is connected to the cell by a low-resistance salt bridge. This method is especially suitable for practical routine work, because it eliminates the use of the extra mercury for the quiet electrode.

V. THE POTENTIAL OF THE QUIET ELECTRODE AND ITS SIGNIFICANCE IN THE EVALUATION OF HALF-WAVE POTENTIALS

The half-wave potentials of a current–voltage curve are characteristic of the particular electroreducible, or electroöxidizable, substances present, provided the values are referred to an external reference electrode of constant known potential. However, when the current–voltage curves are obtained by use of the polarograph, the observed half-wave values are in terms of the total applied E.M.F. rather than of the potential of the dropping electrode itself; hence they depend on the potential of the quiet electrode as well as on that of the dropping electrode. Since the potential of the quiet electrode is a variable quantity, depending on the nature and concentration of the foreign salts present in the solution, the values of the half-wave applied E.M.F. are not characteristic of the reducible substances present. However, if the potential of the quiet electrode is known, the characteristic half-wave potentials of the dropping electrode can be deduced from the half-wave values of the total applied E.M.F.

If the potential of the dropping electrode is measured against an external reference electrode during the electrolysis (manual measurement), or if the external electrode is actually employed as the second electrode of the cell (measurement with the polarograph), the characteristic half-wave potentials will, of course, be obtained directly. This is the method that we prefer, but it is not common polarographic practice.

The usual practice is to measure the potential of the quiet electrode (usually the anode) against an external calomel reference electrode, either at the beginning or at the end of an experiment, and the potential of the dropping electrode is then computed from the simple relation,

$$E_a = E_{q.e.} - E_{d.e.} \tag{1}$$

In this equation E_a is the total E.M.F. applied to the cell, $E_{d.e.}$ is the potential of the dropping electrode, and $E_{q.e.}$ is the potential of the quiet electrode. The signs of $E_{d.e.}$ and $E_{q.e.}$ are taken to be negative when the electrode in question is negative to the calomel reference electrode, and positive when the electrode is positive to the calomel electrode. It is usually assumed that the potential of the quiet electrode remains constant during the electrolysis, and the half-wave potentials of the dropping electrode are then computed from the half-wave values of the applied E.M.F. by means of equation 1.

Majer (76) has shown that the quiet electrode remains depolarized during the electrolysis (retains a constant potential) if its area is greater than about 1 cm^2., and also if the solution contains halide ions or other ions that form insoluble salts with mercury. Our experience is in accord with that of Majer.

When the mercury for the quiet electrode is added to a dilute chloride solution, sufficient mercurous chloride is formed by interaction of the mercury with chloride ions, hydrogen ions, and dissolved oxygen to saturate the solution with calomel before the air is removed, and the quiet electrode thus acquires the potential of a calomel electrode corresponding to the particular chloride-ion activity. The same principle applies when the solution contains iodide, bromide, hydroxide, and various other ions that form insoluble compounds with mercury. Since the current passing through the polarographic cell is very small, usually less than 50 microamperes, the current density at the relatively large quiet electrode is exceedingly small. In a solution already saturated with a mercurous salt, the only effect of this small current at the quiet electrode will be to increase or decrease the amount of the solid mercurous salt, with no appreciable change in the potential-determining activity of the mercurous ion, and therefore the potential of the quiet electrode remains constant during the electrolysis.

VI. THE DIFFUSION CURRENT

It has already been mentioned that the phenomenon of a limiting current is caused by an extreme state of concentration polarization at the dropping electrode. When a limiting current is reached, the average concentration of the electroreducible substance at the surface of the mercury drops has been reduced to a very small minimum value, which is negligibly small compared to the concentration in the bulk of the solution. In other words, at potentials corresponding to the limiting current, the reducible substance is being reduced as fast as it reaches the surface of the dropping electrode. Under these conditions the current will evidently be determined by the rate of supply of the reducible substance from the body of the solution.

In the most general case reducible ions will be drawn to the depleted region very close to the surface of the dropping electrode by two forces: (*1*) a diffusive force, proportional to the concentration gradient between the surface of the mercury drops and the body of the solution, and (*2*) an electrical force, proportional to the electrical potential gradient around the mercury drops. In general, then, reducible ions are supplied to the surface of the dropping electrode partly by diffusion and partly by electrical migration, so that the limiting current can be regarded as the sum of a "diffusion current" and a "migration current" (53).

The current through an electrolyte solution is carried impartially by all the ions present. The fraction of the total current carried by any particular species of ion depends on its relative concentration in the solution, and, to a lesser degree, on its valence and intrinsic mobility; in other words, on its transference number in the particular solution in question. Therefore, if a large excess of an indifferent[3] salt is added to a solution of a reducible salt, the current through the solution will be carried practically entirely by the ions of the added salt. Under these conditions electrical migration of the reducible ions, and hence the migration component of the limiting current, will be practically completely eliminated,

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[3] An indifferent salt, in electroreductions, is one that is reduced at a more negative potential than the reducible substance in question, and one that does not form complexes, or react specifically in other ways, with the reducible substance. Because of their very negative reduction potentials, the salts of the alkalies and alkaline earths and ammonium salts are usually used as indifferent salts. Tetrasubstituted alkylammonium salts are commonly used in polarographic analysis for the alkali and alkaline-earth ions.

and the limiting current will be solely a diffusion current. From an analytical viewpoint the most important characteristic of the diffusion current is that, with all other factors constant, it is directly proportional to the concentration of the reducible ions.

The diffusion current, at a given concentration, is influenced by various factors, such as the geometrical properties of the particular capillary used, the pressure on the dropping mercury and the drop time, the diffusion coefficient of the reducible substance, and the temperature. In this section the influence of these factors will be discussed in some detail. The characteristics of the migration current will be considered later.

It may be well to emphasize that the current measured with the dropping electrode is an average value during the life of the mercury drops, that is, it is the average of the observed current oscillations as each mercury drop is formed. From the investigations of Ilkovič (54), who measured the actual change in current during the life of individual drops with an oscillographic arrangement, and from the theoretical discussion given below, it is known that the current often increases many fold during the life of each mercury drop. The actual variation depends on many factors, such as the concentration of both the reducible and foreign substances, the potential of the dropping electrode, and the resistance in the cell circuit (7, 54). However, the current oscillations occur with a period corresponding to the drop time, which is usually so much shorter than the period of the current-measuring galvanometer that the latter cannot follow the entire change in current, but simply oscillates with relatively small amplitude around the average value.

1. The Ilkovič equation for the diffusion current

Ilkovič (53) has derived an equation for the diffusion current in terms of the concentration of the reducible substance, its characteristic diffusion coefficient, the amount of mercury flowing from the capillary per second, and the drop time. The Ilkovič equation has recently been re-derived in a more exact way by MacGillavry and Rideal (72). Although space does not permit the detailed reproduction of these derivations, we shall outline the essential steps involved.

When an excess of some indifferent salt is present in the solution, the diffusion current will be determined by the amount of the reducible substance that diffuses up to the surface of the dropping electrode per second. The instantaneous value of the diffusion current, at any instant during the life of a mercury drop, is given by

$$i = nF(4\pi r^2 f) \qquad (2)$$

in which n is the number of electrons involved in the reduction of one molecule of the reducible substance (or the number of faradays of electricity required for the reduction of one mole), F is the faraday, r is the radius of the mercury drop at any time t^*, during its life, measured from the beginning of the drop formation, and f is the flux of the reducible substance (amount diffusing per square centimeter per second) *at the mercury-solution interface* (53). The method of derivation used by Ilkovič and by MacGillavry and Rideal consists in obtaining expressions for the flux, f, and the radius of the drop, r, from which an instantaneous value of the diffusion current can be computed. The average value of the diffusion current is then obtained by integrating over the life of the drop.

Because the expansion of the growing mercury drops causes a corresponding expansion of the surrounding solution, the diffusion of the reducible substance takes place in a medium that is moving with respect to the surface of the mercury drops. The diffusion layer around each mercury drop is a spherical shell, which expands and becomes thinner as the drop grows. The concentration of the reducible substance varies from a relatively very small value at the mercury–solution interface to its concentration in the body of the solution at the outside of the diffusion shell. On the basis of these considerations Ilkovič and MacGillavry and Rideal derived the following expression for the instantaneous current at any time, t^*, during the life of a drop.

$$i = 4\left(\frac{7\pi}{3}\right)^{1/2} nFD^{1/2}C\,\frac{r^2}{(t^*)^{1/2}} \tag{3}$$

In this equation C is the concentration of the reducible substance in the body of the solution, r is the radius of the mercury drop at the time t^*, and D is the diffusion coefficient of the reducible substance. The *average* current during the life of each drop, designated by i_d, is given by

$$i_d = (1/t)\int_0^t i\,dt = 24\pi^{1/2}nFD^{1/2}Cr^2_{\text{max.}}/(21)^{1/2}t^{1/2} \tag{4}$$

in which t is the drop time and $r_{\text{max.}}$ is the maximum radius of the drops.

If m is the weight of mercury flowing from the capillary per second, then the weight of an individual mercury drop is mt, and the volume of each drop, assumed to be spherical, will be given by

$$V = (4/3)\pi r^3_{\text{max.}} = mt/d \tag{5}$$

where d is the density of mercury (13.6 g. per cubic centimeter). Hence, in terms of m and t, the maximum radius of each drop is

$$r_{\text{max.}} = (3mt/4\pi d)^{1/3} \tag{6}$$

By substituting this expression for $r_{\text{max.}}$ into equation 4 and collecting all the numerical constants into a single term, we finally obtain

$$i_d = 0.627nFD^{1/2}Cm^{2/3}t^{1/6} \tag{7}$$

which is the equation for the diffusion current derived originally by Ilkovič. As will be shown later, diffusion currents calculated from the Ilkovič equation are, in most cases, in satisfactory agreement with the experimentally observed values.

We shall now consider the influence of the various factors, n, D, C, m, and t, on the diffusion current.

2. Influence of the geometrical characteristics of the capillary on the diffusion current

The quantities m and t in the Ilkovič equation obviously depend on the geometrical characteristics of the particular capillary used; they also depend on the pressure on the dropping mercury and, to a lesser degree, on the temperature. The observed effects can be interpreted satisfactorily by making use of the familiar hydrodynamical equation of Poiseuille,

$$W = \pi dPR^4t/8L\eta \tag{8}$$

In this equation W is the weight of a liquid of density d and viscosity coefficient η, that flows in t seconds from a capillary tube of radius R and length L under the pressure P. In the case of the dropping electrode, if t is taken as the drop time, then W will be the weight of a single drop, and the weight of mercury flowing from the capillary per second will be given by

$$m = W/t = \pi dPR^4/8L\eta \tag{9}$$

According to this equation m will be directly proportional to P, and t will be inversely proportional to P. In view of these relations the product $m^{2/3}t^{1/6}$ becomes

$$m^{2/3}t^{1/6} = (k'P)^{2/3}(k''/P)^{1/6} = kP^{1/2} \tag{10}$$

and the Ilkovič equation becomes

$$i_d = 0.627knFD^{1/2}\mathrm{C}\mathrm{P}^{1/2} \tag{11}$$

Therefore, if all other conditions are kept constant, the diffusion current should be directly proportional to the square root of the pressure on the dropping mercury. Ilkovič (53) and Maas (68), particularly the latter, have shown that this is actually the case.

For example, Ilkovič (53) found the following values of the diffusion current of 0.001 M mercuric chloride in 0.01 N sodium chloride, at various values of the pressure, P, on the dropping mercury.

i_d in mm.	28.0	30.5	33.0	35.5	37.5
P in cm.	39.1	46.3	53.2	62.4	70.1
$i_d/P^{1/2}$	4.48	4.49	4.46	4.49	4.48

The diffusion current is expressed in terms of millimeters of galvanometer deflection. As predicted by equation 11, the ratio $i_d/P^{1/2}$ was constant over a range of pressures that varied almost twofold.

From an analytical viewpoint an important conclusion to be drawn from the foregoing relations is that two different capillaries will give the same diffusion current in a given solution when the product $m^{2/3}t^{1/6}$ is the same for both. This conclusion has been verified with many different capillaries by Maas (68). For example, he obtained the data in table 1 with six different capillaries. These data were obtained by electrolyzing 0.005 *N* solutions of cadmium chloride in 0.1 *N* potassium chloride (air-free) at 25°C. It is seen that the linear relation between i_d and $m^{2/3}t^{1/6}$ is obeyed with an accuracy of about ±1.5 per cent.

TABLE 1

Linear relation between i_d and $m^{2/3}t^{1/6}$ (Maas)

CAPILLARY	t	$m^{2/3}t^{1/6}$	i_d	$i_d/m^{2/3}t^{1/6}$
	seconds	*mg.$^{2/3}$ sec.$^{-1/2}$*	*microamperes*	
1	6.43	0.784	6.92	8.83
2	9.28	0.814	7.26	8.92
3	5.90	0.854	7.88	9.23
4	4.89	1.108	10.05	9.07
5	4.10	1.288	11.73	9.11
6	3.17	1.508	13.82	9.16
Average				9.04 ± 0.12

It should be noted that the foregoing values of t and i_d were measured at a potential of the dropping electrode of -0.75 volt against a normal calomel electrode. As will be shown later, t, and hence the product $m^{2/3}t^{1/6}$, depend on the potential of the dropping electrode; therefore these quantities should be determined at the potential at which the diffusion current is measured.

It is interesting to compare the foregoing data of Maas with corresponding data obtained by Lingane (65) under the same conditions. Lingane electrolyzed a 0.005 *N* (0.0025 *M*) solution of cadmium sulfate in 0.1 *N* potassium chloride at 25°C., and found a diffusion current of 20.0 microamperes, with a capillary for which m was 2.626 mg. sec.$^{-1}$ and t was 2.88 sec. at $E_{d.e.} = -0.8$ volt against a saturated calomel electrode. Hence, in Lingane's experiment, the product $m^{2/3}t^{1/6}$ was equal to 2.28 mg.$^{2/3}$ sec.$^{-1/2}$, and the quotient $i_d/m^{2/3}t^{1/6}$ was $20/2.28 = 8.77$. This quotient agrees to within about 3 per cent with the foregoing average value found by Maas, even though the drop time was much shorter than, and the product $m^{2/3}t^{1/6}$ was about twice as great as, the average values of these quantities in Maas' experiments. This comparison of entirely independent data of different workers constitutes further confirmation of the linear relation between i_d and $m^{2/3}t^{1/6}$ predicted by the Ilkovič equation.

We may therefore state as a fairly accurate rule (within ca. ± 3 per cent) that *diffusion currents obtained under otherwise identical conditions with various different capillaries will bear the same ratios to each other as the products $m^{2/3}t^{1/6}$ of the various capillaries, provided the drop time is at least 3 sec. or greater.* The importance of this rule in quantitative polarography is at once evident, since it makes possible a simple correlation of diffusion currents obtained with different capillaries.

It is strongly recommended that future workers in the field of polarography include data for m, t, and the product $m^{2/3}t^{1/6}$ in their reports, so that the diffusion current data will be on a common basis for comparison. It has been more or less common practice to report diffusion current data in terms of millimeters of galvanometer deflection, and in many cases the sensitivity of the galvanometer has not been specified. It is hoped that future authors will convert such data to microamperes in their published reports, so that their results can be compared with those of other workers.

3. The product $m^{2/3}t^{1/6}$ as a function of the potential of the dropping electrode

It has been shown by various workers, Ilkovič (53), Maas (68), Kucera (63), and Lingane (65, 66), among others, that at a given pressure the amount of mercury flowing from a capillary per second, m, is practically constant and is independent of the potential of the dropping electrode. On the other hand, the weight of each mercury drop, W, and the drop time, t, are practically directly proportional to the interfacial tension at the mercury–solution interface (63). As is well known, the interfacial tension, σ, at a mercury–solution interface, and therefore t, vary with the potential of the dropping electrode; the parabolic curve obtained by plotting σ or t against the potential of the dropping electrode is the so-called electrocapillary curve of mercury. It is to be expected, therefore, that $m^{2/3}t^{1/6}$ will vary with the potential of the dropping electrode, approximately according to the sixth root of σ, and that i_d will vary correspondingly and not be strictly constant at various values of $E_{d.e.}$.

The extent to which m, t, and the product $m^{2/3}t^{1/6}$ vary with the potential of the dropping electrode, in air-free 0.1 N potassium chloride solution, is illustrated by the data in table 2 (65, 66; see also reference 53).

The collection of a specified number of mercury drops, required for the determination of m, was accomplished without admitting air to the cell and without removing the cell from the thermostat, by means of the simple arrangement shown in figure 10. The detailed manipulations are described elsewhere (66).

It will be noted from the data in table 2, that m was practically constant and independent of the potential of the dropping electrode. The drop time, t, on the other hand, first increased, then passed through a maximum, and finally decreased quite rapidly, with increasing negative potential. The drop weight behaved similarly. A plot of either the drop weight, or t, against $E_{d.e.}$ gives the electrocapillary curve in this solution.

TABLE 2

The product $m^{2/3}t^{1/6}$ as a function of the potential of the dropping electrode in 0.1 N potassium chloride

P = 21.8 ± 0.2 cm.; temperature = 25°C.; air was removed from the solution with purified nitrogen

$E_{d.e.}$	i	m	t	$m^{2/3}t^{1/6}$
volts vs. S.C.E.	*microamperes*	*mg. sec.$^{-1}$*	*seconds*	*mg.$^{2/3}$ sec.$^{-1/2}$*
0.0	−0.18	2.651	2.75	2.27
−0.5	+0.10	2.621	3.08	2.29
−0.8	0.21	2.626	2.88	2.28
−1.1	0.29	2.625	2.66	2.24
−1.5	0.38	2.672	2.18	2.18
−1.9	0.70	2.681	1.56	2.08

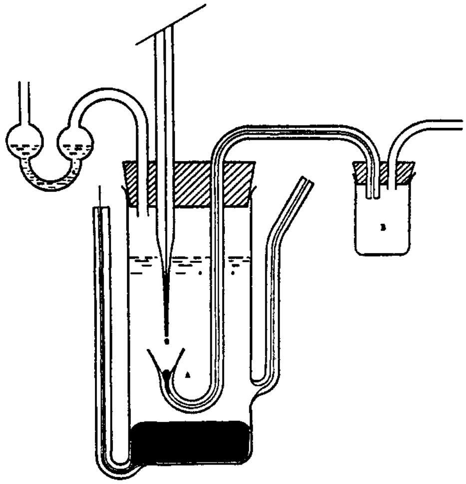

Fig. 10. Arrangement used to collect mercury drops for the determination of the amount of mercury flowing from the capillary per second.

The change in the product $m^{2/3}t^{1/6}$ with increasing negative potential followed the same general course as the electrocapillary curve, but the variation in $m^{2/3}t^{1/6}$ was, of course, much less, because it depends on only the sixth root of t. At potentials from zero up to about -1.0 volt, the product $m^{2/3}t^{1/6}$ was constant to within about ±1 per cent, but at potentials more negative than -1.0 volt it decreased rapidly.

It was also found (65, 66) that the product $m^{2/3}t^{1/6}$ was the same in 0.001 N as in 1 N chloride solutions, and also the same as in 0.1 N potassium chloride at the same potential when cadmium or thallous ions were discharging. Furthermore, the presence of oxygen and its simultaneous discharge with thallous ions had no appreciable effect on the product $m^{2/3}t^{1/6}$.

In addition to being independent of the potential of the dropping electrode, m is also practically independent of the medium in which the mercury drops form, that is, independent of the interfacial tension at the surface of the mercury drops, provided the pressure and the temperature are kept constant. This is demonstrated by the following data, which we obtained when the mercury drops were forming in various media. The same capillary was used as in table 2, and the pressure was kept constant at 21.8 cm.

MEDIUM	t	m
	seconds	*mg. sec.*$^{-1}$
Water	3.20	2.69
0.5 N KCl	3.00	2.65
0.1 N KI	2.39	2.64
Air	20.1	2.64

According to the Ilkovič equation i_d is directly proportional to $t^{1/6}$, and therefore it is to be expected that i_d will not be strictly constant at various potentials, but should decrease appreciably at potentials more negative than about -1.0 volt. This effect has actually been demonstrated by Ilkovič (53). For example, in the electrolysis of 0.001 M mercuric chloride in 0.01 N sodium chloride, he obtained the data given in table 3. It is evident that the decrease in i_d with increasing negative potential must be taken into account when comparing the diffusion currents of the same concentration of two different substances, if the half-wave potentials of the two substances are far apart.

4. The relation between the diffusion current and the concentration of the reducible substance

With all other conditions constant, it is evident from equation 7 that the diffusion current should be directly proportional to the concentration of the reducible substance. This is, of course, the most important characteristic of the diffusion current from an analytical viewpoint. The linear relation between i_d and C has been verified by many workers, in the reduction of both organic substances and inorganic ions (38, 50, 65, 66, 68).

We (65, 66) tested the relation between i_d and C in the discharge of thallous, lead, cadmium, zinc, iodate, and ferricyanide ions from 0.1 N potassium chloride solutions containing a trace of methyl red to eliminate the maxima. In the case of the four metal ions the linear relation was obeyed within about ±1.5 per cent over a concentration range from 10^{-4} to 10^{-2} molar, after proper correction was made for the residual current found with the 0.1 N potassium chloride solution alone (table 2). In the case of iodate ions the linear relation was obeyed from 10^{-4} to 10^{-3} molar, and in the case of ferricyanide ions from 10^{-4} to 3×10^{-3} molar (65, 66).

TABLE 3

Variation of i_d with the potential

$E_{d.e.}$	t (TEN DROPS)	i_d	$i_d/t^{1/6}$
volts	*seconds*	*mm.*	
−0.65	20.3	31.2	18.89
−0.85	19.7	31.0	18.88
−1.05	18.55	30.8	18.93
−1.25	17.5	30.4	18.87
−1.45	15.7	30.0	18.96
−1.65	13.65	29.5	19.06

In order to obtain strict proportionality between i_d and C, the drop time should be at least 3 sec. or longer (66, 68). The linear relation seems to hold for all cases in which the electroreduction is reversible. When the electroreduction is irreversible, as it is in the case of nitrate ions, iodate ions, and many organic compounds, the linear proportionality may hold only under certain specified conditions, and only over a limited range of concentrations.

Certain investigators, notably Hamamoto (20) and Maas (68), found that the diffusion currents at very small concentrations (less than about 10^{-4} molar) were greater than would correspond to strict proportionality with the concentration. When the concentration of the reducible ions is very small, the diffusion current is usually not strictly constant but often increases with increasing negative potential. Several empirical methods for evaluating the diffusion current under such unfavorable conditions have been discussed by Hohn (50), Maas (68), and Borcherdt, Meloche, and Adkins (5). It should be realized that the apparent diffusion current is the sum of the true diffusion current and a "residual current." In the absence of electroreducible substances (e.g., in the electrolysis of a pure solution of potassium chloride), the residual current is due to the so-called "charging current," or "condenser current," which is discussed in a later section. The residual current increases with increasing negative potential, and therefore, even though the true diffusion current may remain constant, the apparent diffusion current tends to increase with increasing negative potential. The best method for evaluating the true diffusion current is to determine the residual current in the medium in which the electrolysis is to be carried out without any of the reducible substance present, and to subtract the "blank" so obtained from the apparent diffusion current (65, 66). It is possible that the proportionately larger values of i_d at small concentrations, found by Hamamoto and Maas, were due to the fact that they did not adequately correct for the residual current.

Even when maxima are satisfactorily eliminated and proper correction is made for the residual current, there are cases where the corrected diffusion current is poorly defined and changes with the potential. These unfavorable cases are most frequently encountered in irreversible reductions (reduction of uranyl ion and of several organic compounds), and they require much more study before satisfactory analytical procedures can be developed.

5. Direct test of the Ilkovič equation

In order to obtain data for a direct test of the Ilkovič equation, Lingane and Kolthoff (66) measured the diffusion currents of thallous, lead, cadmium, zinc, iodate, and ferricyanide ions over a concentration range from 10^{-4} to 10^{-2} molar in 0.1 N potassium chloride containing a trace of methyl red to eliminate the maxima. The (corrected) diffusion currents were in all cases directly proportional to the concentration of the reducible ions. In table 4 are given the experimentally determined diffusion current constants of the foregoing ions (obtained with the same capillary under identical conditions), compared with the corresponding values computed from the Ilkovič equation.

In order to calculate the diffusion current constants of the various ions from the Ilkovič equation, it was necessary to know their diffusion coefficients in 0.1 N potassium chloride. Since such data are not available in the literature, we (66) computed the various diffusion coefficients by means of the relation,

$$D_i = \frac{RT\lambda_i^0}{zF^2} \tag{12}$$

In this equation, which was first derived by Nernst (84), D_i is the characteristic diffusion coefficient (per mole) of an ion when it is free to diffuse independently of other ions, λ_i^0 is the equivalent ionic conductance of the ion at infinite dilution, z is its valence without regard to sign, and R, T, and F are the gas constant per mole, the absolute temperature, and the faraday, respectively. The fundamental principles underlying this equation have been discussed in detail by Lingane (65).

It is a well-known principle that the ions of a diffusing salt can diffuse more or less independently if a large excess of some other salt is present at equal concentrations on both sides of the diffusion layer (1, 59). Since polarographic diffusion currents are measured with a relatively small concentration of the reducible ions in a solution containing a large excess of an indifferent salt, the reducible ions are more or less free to diffuse independently of the other ions in the solution, and equation 12 can therefore be used to compute their diffusion coefficients.

TABLE 4

Comparison of the experimentally determined and the calculated diffusion current constants of several reducible ions

In 0.1 N potassium chloride at 25°C.

ION	$m^{2/3}t^{1/6}$*	K		DIFFERENCE
		Observed	Calculated	
	mg.$^{2/3}$ sec.$^{-1/2}$	*microamperes per millimole per liter*		*per cent*
Tl^+	2.28	6.13	6.17	−0.7
Pb^{++}	2.28	8.78	8.67	+1.3
Cd^{++}	2.28	8.00	7.40	+8.1
Zn^{++}	2.24	7.65	7.27	+5.0
IO_3^-	2.18	26.3	26.2	+0.4
$Fe(CN)_6^{---}$	2.28	3.78	4.12	−8.3

* The data for $m^{2/3}t^{1/6}$ are given for the potentials at which the diffusion currents were measured.

It should be noted that equation 12 is based on the assumption that the diffusing ions behave as ideal solutes, and therefore it is strictly valid only at infinite dilution. In any actual solution the diffusing ions will be subject to interionic forces, which cause them to deviate more or less from ideal behavior. It might be thought that the effect of interionic forces could be corrected for in equation 12 by simply employing the value of the equivalent ionic conductance of the ion in question at the particular ionic strength of the solution (71, 72). However, this results in an overcorrection, because, as McBain and Liu (79) have pointed out, the effect of interionic forces is much smaller in the process of diffusion than it is in the more complicated process of electrolytic conduction. It is an experimental fact that the diffusion coefficient of a salt decreases relatively much less than its equivalent conductance with increasing ionic strength (79). Since there is no better alternative at present, we assumed, in interpreting our experimental results, that the various reducible ions behaved as ideal solutes, and that their diffusion coefficients in 0.1*N* potassium chloride were the same as at infinite dilution.

For convenient reference the diffusion coefficients of various ions at infinite dilution are given in table 5. When the numerical values of *R*

TABLE 5

Calculated diffusion coefficients at infinite dilution of various ions at 25°C.

ION	λ^0	D	ION	λ^0	D
	ohm^{-1} *cm.*^{2} *equiv.*$^{-1}$	*cm.*^{2} *sec.*$^{-1}$ $\times 10^5$		*ohm*$^{-1}$ *cm.*^{2} *equiv.*$^{-1}$	*cm.*^{2} *sec.*$^{-1}$ $\times 10^5$
H^+	350	9.34	Ni^{++}	52	0.69
Na^+	50.5	1.35	OH^-	196	5.23
K^+	74	1.98	Cl^-	76	2.03
Li^+	39	1.04	NO_3^-	72	1.92
Tl^+	75	2.00	CH_3COO^-	41	1.09
Cs^+	79	2.11	IO_3^-	41	1.09
Pb^{++}	73	0.98	BrO_3^-	54	1.44
Cd^{++}	54	0.72	SO_4^{--}	81	1.08
Zn^{++}	54	0.72	$Fe(CN)_6^{---}$	100	0.89
Cu^{++}	54	0.72			

(8.317 volt-coulombs), *F* (96,500 coulombs), and *T* (298°K.) are substituted into equation 12, we obtain,

$$D_i = 2.67 \times 10^{-7}\lambda_i^0/z \text{ cm.}^2 \text{ sec.}^{-1} \qquad (13)$$

The diffusion coefficients in table 5 were calculated by means of this equation, using data for the equivalent ionic conductances at infinite dilution taken from the compilation given by MacDougall (70).

The constant 0.627 in equation 7 refers to the current expressed in amperes, the concentration in moles per cubic centimeter, and the product $m^{2/3}t^{1/6}$ in the units gm.$^{2/3}$sec.$^{-1/2}$ When the current is expressed in microamperes, the concentration in millimoles per liter, and the product $m^{2/3}t^{1/6}$ in the units mg.$^{2/3}$sec.$^{-1/2}$, and the numerical value of *F* is inserted into equation 7, we obtain

$$i_d = 605nD^{1/2}Cm^{2/3}t^{1/6} \qquad (14)$$

The diffusion current constant, corresponding to $C = 1$, should therefore be given by

$$K = 605nD^{1/2}m^{2/3}t^{1/6} \qquad (15)$$

This equation, with values of D from table 5 and values of the product $m^{2/3}t^{1/6}$ from table 2, was used to compute the calculated values of K in table 4. For example, from table 5 the diffusion coefficient of lead ions is 0.98×10^{-5} cm.^{2} sec.$^{-1}$, from table 2 the product $m^{2/3}t^{1/6}$ at $E_{d.e.} = -0.7$ volt (at which potential the diffusion current of lead was measured) was 2.28 mg.$^{2/3}$ sec.$^{-1/2}$, and $n = 2$ in the discharge of lead ions. Therefore, the calculated diffusion current constant of lead ions is

$$K = 605 \times 2 \times (0.98 \times 10^{-5})^{1/2} \times 2.28 = 8.67 \text{ microamperes per millimole per liter}$$

which may be compared with the experimentally determined value, 8.78, given in table 4.

It may be mentioned that the only other direct tests of the Ilkovič equation to be found in the polarographic literature are in his original paper (53). Ilkovič tested his equation in only two cases: in the discharge of 0.001 M cadmium ions from 0.1 N sulfuric acid and in the discharge of 0.001 N hydrogen ions from 0.1 N potassium chloride. He found that the observed diffusion current of cadmium ions was 9 per cent *smaller* than the value he calculated. However, in calculating the diffusion coefficient of the cadmium ions he overlooked the valence in equation 12 and obtained the incorrect value 1.20×10^{-5} cm.^{2} sec.$^{-1}$ Hence his calculated value of the diffusion current of cadmium ions was too large.

In view of the complexity of the diffusion processes at the dropping electrode, the agreement between the observed and calculated values of K in table 4 is really remarkably good. It is evident that the Ilkovič equation, and the postulates on which it is based, must be essentially correct. It furnishes a sound theoretical basis for quantitative polarography, and Ilkovič deserves much credit for its derivation.

6. The "condenser current" and its influence in the measurement of very small diffusion currents

It has already been mentioned that a small current, known as the residual current, is observed before the discharge of a reducible substance begins. Even in the electrolysis of very pure air-free solutions of difficultly reducible salts, such as potassium chloride, an appreciable residual current is found long before the discharge of the ions of the indifferent salt, e.g., potassium ions, finally begins (table 2). The residual current increases in approximately direct proportion to the applied E.M.F., and, as has been pointed out in the preceding section, it must be subtracted from the total observed diffusion current of a given substance in order to obtain the true diffusion current. This correction often amounts to several tenths of a microampere, and it becomes greater the more negative the potential at which the substance in question is reduced (table 2).

It is obvious, therefore, that the accuracy with which small diffusion currents can be measured is greatly dependent on the accuracy of the correction for the residual current. It is also evident that the minimum detectable concentration of a reducible substance will depend on the accuracy with which the residual current can be measured. For example, if the uncertainty in the measurement of the residual current is ± 0.05 microampere, and if the diffusion current constant of a given substance is 10 microamperes per millimole per liter, then the minimum concentration of this substance that could possibly be detected would be of the order of 10^{-5} M, and would probably have to be somewhat greater in order to detect the substance with certainty. An exact knowledge of the residual current is therefore of great importance when small concentrations of reducible substances are being determined.

In a pure solution of an indifferent salt, that is, in the complete absence of reducible or depolarizing substances, the residual current is due to a so-called "charging current," or "condenser current." It is well known that when a metal, or in fact almost any solid, is placed in an electrolyte solution, an electrical double layer of positively and negatively charged ions establishes itself at the solid–solution interface. This double layer is analogous to an ordinary condenser. The orientation of the charges during its formation causes a small current to flow across the interface, similar to the instantaneous current that flows across an ordinary condenser when it is being charged or discharged. Since the surface of the dropping electrode increases continuously as the mercury drops form, the double layer is being formed continuously on each new element of the freshly forming surface; hence a small continuous charging current results. This is the "condenser current" (54).

As is well known, the change in the strength and the sign of the double layer at a mercury–solution interface is responsible for the parabolic shape of the electrocapillary curve of mercury (15). At potentials more positive than correspond to the maximum in the electrocapillary curve the mercury side of the double layer is apparently positively charged, while at potentials more negative than the electrocapillary maximum it is negatively charged. At the maximum itself there is presumably no double layer at the mercury–solution interface. It follows, therefore, that the direction in which the condenser current flows, i.e., from the mercury to the solution, or *vice versa*, should depend on the sign of the charge on the mercury surface and that it should change direction at the electrocapillary maximum. Since there is no double layer at the electrocapillary maximum, the condenser current should be zero at this point. These predictions are verified by the residual current curves shown in figure 11. These curves were obtained by Maas (68) by electrolyzing a 0.1 N solution of pure sodium chloride from which the air had been displaced by purified hydrogen. The curves were recorded with a polarograph, using the full sensitivity of the galvanometer.

Curve 1 in this polarogram is practically a "pure" condenser current, and it is seen that it is approximately directly proportional to the potential of the dropping electrode up to about -1.6 volts, where the discharge of sodium ions begins. The electrocapillary maximum in 0.1 *N* chloride solution is at about -0.56 volt, so the condenser current should have been zero at this potential. Actually it is seen that the current was zero at a somewhat more positive potential, at about -0.35 volt. Up to -0.35 volt the current was negative, that is, positive electricity flowed from the dropping electrode to the solution, whereas above -0.35 volt positive electricity flowed from the solution to the electrode. It will be noted that the current oscillations during the formation of the individual mercury drops decreased with increasing negative potential and finally practically disappeared between -0.45 and -0.55 volt. As the potential was increased above -0.55 volt, the oscillations reappeared and their magnitude increased with increasing negative potential. The current oscillations are an approximate measure of the magnitude of the charging current during the formation of the individual mercury drops. In agreement with the theory of the electrocapillary curve, the minimum in the oscillations occurred at the potential corresponding to the maximum in the electrocapillary curve, where the double layer disappears (68, 124).

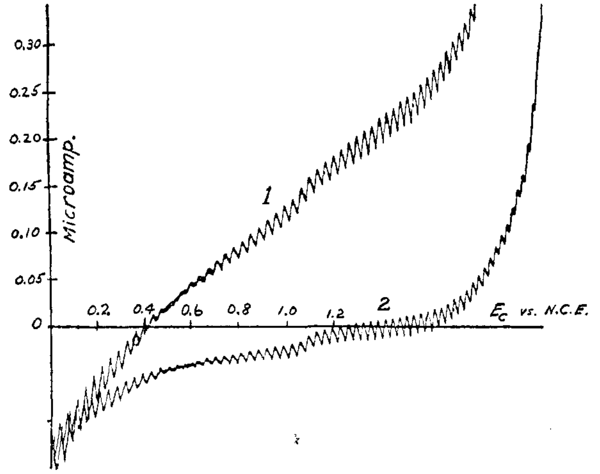

FIG. 11. Condenser current curves in pure 0.1 *N* sodium chloride according to Maas (obtained with polarograph).

It should be mentioned that Ilkovič (55) measured the potential–time curves of individual mercury drops falling into a very pure, air-free solution of 0.1 N potassium chloride. At potentials more positive than the electrocapillary maximum he found that the potential of an individual drop becomes more positive during its growth. At the potential of the electrocapillary maximum the potential remained practically constant during the life of a drop, while at more negative potentials it became more negative during the life of each drop. These results confirm the idea that the double layer changes sign at the electrocapillary maximum and that no double layer exists at the maximum itself.

It will be noted from curve 1 in figure 11 that the residual current was slightly greater than zero (0.03 microampere) at the maximum in the electrocapillary curve (-0.56 volt). This was probably due to the reduction of a trace of oxygen remaining in the solution, because it is practically impossible to remove the very last traces of oxygen from a solution by simply bubbling hydrogen or nitrogen through it (68). In most cases a residual current will include a small "faradayic" current due to the reduction of traces of reducible impurities in the solution. That is,

$$i_r = i_c + i_f \tag{16}$$

where i_r is the total residual current, i_c is the condenser current, and i_f is the faradayic current.

If the double layer behaves as a condenser, the *average* charging current during the life of a drop should be given by

$$i_c = kq\psi \tag{17}$$

where k is the capacity of the double layer, q is the *average* rate at which fresh mercury surface is being exposed to the solution (cm.^{2} per second) during the life of a drop, and ψ is the average potential difference between the mercury and the solution (55, 68). Since i_c is zero at the potential corresponding to the electrocapillary maximum, and since k remains fairly constant for small changes in the potential, equation 17 can be written as

$$i_c = kq(\psi_{\text{max.}} - \psi) = kq(E_{\text{max.}} - E) \tag{18}$$

where $\psi_{\text{max.}}$ is the absolute potential difference between the mercury and the solution at the electrocapillary maximum, and i_c is the condenser current at some other potential ψ. Since the potential of the quiet electrode remains constant during the electrolysis, and since the potential of the solution is a constant, $(\psi_{\text{max.}} - \psi)$ can be replaced by $(E_{\text{max.}} - E)$, where E is the potential of the dropping electrode with respect to an external reference electrode. Since q and k can be measured, this equation allows us to calculate i_c at various potentials of the dropping electrode.

Ilkovič (55) calculated the capacity of the double layer in specially purified 0.1 *N* potassium chloride from his measurements of the potential-time curves of individual mercury drops. On the negative branch of the electrocapillary curve (−1.3 volts) he found a value for *k* of 22.3 microfarads per square centimeter, while on the positive side of the electrocapillary maximum (−0.18 volt) he found a value for *k* of 42.2 microfarads per square centimeter. These results are in agreement with the measurements of Philpot (92), who found values for *k* of 21.8 and 48.8 microfarads per square centimeter on the negative and the positive side of the electrocapillary maximum, respectively. In this connection important investigations by Proskurnin and Frumkin (96) of the capacity of the double layer in solutions of sodium sulfate, potassium chloride, sodium hydroxide, and sulfuric acid should be mentioned.

It is interesting to compare the value of i_c computed by means of equation 18 with the data for the residual current in 0.1 *N* potassium chloride given in table 2. It can be derived that the area exposed per second by the growing mercury drops is given by

$$q = (4\pi)^{1/3}(3/d)^{2/3}m^{2/3}t^{-1/3} = 0.0085m^{2/3}t^{-1/3} \text{ cm.}^2 \text{ per second} \qquad (19)$$

where d is the density of mercury, t is the drop time, and m is expressed in milligrams per second. From the data in table 2 we find that m was 2.67 mg. per second, and t was 2.18 sec. at −1.5 volts, and hence q was 0.0126 cm.^{2} per second. Since $E_{\text{max.}}$ is equal to −0.56 volt with respect to the normal calomel electrode, and k is equal to 22 microfarads per square centimeter, we calculate for i_c at −1.5 volts,

$$i_c = 22 \times 0.0126 \times (-0.56 + 1.5) = 0.28 \text{ microampere} \qquad (20)$$

This agrees fairly well with the experimentally observed value of 0.38 microampere in table 2. It should be mentioned that the change in ψ during the life of a drop has been neglected in deriving equation 18, because it cannot be calculated theoretically; hence the calculated value of i_c is probably somewhat too small. It is evident, however, that about three-fourths of the residual current in table 2 is a condenser current.

The capacity of the double layer can also be computed approximately from the slope of the condenser current curve. From equation 18 we see that the capacity is given by

$$k = (\mathrm{d}i_c/\mathrm{d}E)/q \qquad (21)$$

that is, k is equal to the slope of the condenser current curve divided by the average area exposed per second. Even if the residual current includes a small faradayic current, it may be assumed that the latter will be practically constant over a small range of potentials, and the slope of the residual current curve will be practically equal to $\mathrm{d}i_c/\mathrm{d}E$. For example, the slope of curve 1 in figure 11 is approximately 0.20 microampere per volt, and q in this experiment of Maas was 0.0086 cm.^{2} per second (68). The value of k calculated from these data is $0.20/0.0086 = 23$ microfarads per square centimeter, which is in reasonably good agreement with the value 22 found by Ilkovič and Philpot by different methods. Since the condenser current curve in figure 11 is approximately a straight line at potentials more negative than the electrocapillary maximum, it is evident that the capacity of the double layer is approximately constant between about -0.4 volt and -1.4 volts. It will be noted that the slope of the curve (and hence the capacity of the double layer) is larger on the positive side of the electrocapillary maximum, in agreement with the results of Ilkovič, Philpot, and Proskurnin and Frumkin.

The capacity of the double layer (and hence the magnitude of the condenser current) depends on the nature of the ions in the solution. Capillary-active ions which are strongly adsorbed at the mercury–solution interface increase the capacity of the double layer on one or the other branch of the electrocapillary curve. For example, the capacity of the double layer is about twice as great in a solution containing iodide ions as it is in a chloride solution (on the positive side of the electrocapillary curve) (15). This corresponds to a decrease in the thickness, or a compression, of the double layer acting as a condenser. The effect of capillary-active non-electrolytes (octyl alcohol) has been investigated by Proskurnin and Frumkin (96).

In order to eliminate as far as possible the uncertainty in the measurement of very small diffusion currents, due to the residual current, Ilkovič and Semerano (57) recommend that the condenser current be "compensated" by sending a current of equal magnitude through the current-measuring galvanometer in a direction opposite to that of the condenser current. Recent models of the polarograph are equipped with a device for automatically compensating, or balancing out, the residual current, at all values of the applied E.M.F. (50, 68). Curve 2 in figure 11 was obtained by Maas (68) by compensating the residual current in this way.

7. *The influence of temperature on the diffusion current*

Ilkovič (56) has recently shown that the effect of temperature on the diffusion current can be readily interpreted as due chiefly to the change in the diffusion coefficient of the reducible substance with temperature. We have seen that the diffusion coefficient of an ion is directly proportional to both the absolute temperature and the equivalent conductance of the ion at infinite dilution. The equivalent conductances of most ions increase by about 2 to 2.5 per cent per degree. At $T = 298°$K. an increase of one degree will increase the value of T by about 0.3 per cent. Furthermore, m increases by about 0.5 per cent per degree, owing to the decrease in the viscosity of mercury with increasing temperature (63, 56). Hence, from the cumulative effect of these three factors, it is to be expected that the diffusion current will increase by about 1.6 per cent per degree increase in temperature (56). This prediction is in reasonably good agreement with the experimental results of Nejedlý (83), Kemula (61), and Majer (73), who found that the temperature coefficient of the diffusion current was about 2 per cent per degree for most metal ions.

From the analytical viewpoint it is evident that the temperature should be controlled to at least ±0.5°C., or better, in order to keep errors due to the temperature effect within ±1 per cent.

8. Influence of the solvent on the diffusion current constant

The influence of a change in the nature of the solvent on the diffusion current constant of a given reducible substance can be predicted from the Ilkovič equation. According to equation 15 the diffusion current constant, K, depends on the quantities D, m, and t. We have shown that m for a given capillary at a given pressure on the dropping mercury and a constant temperature is practically independent of the medium in which the drops form. The drop time, being proportional to the interfacial tension, will vary with the nature of the medium, but, since K depends on only the sixth root of t, considerable variations in the latter will have only a relatively small effect on K. Therefore, with the same capillary at a given temperature and pressure, it is evident that any change in K in going from water to some non-aqueous solvent will be due chiefly to a change in the diffusion coefficient of the reducible substance. In general, the diffusion coefficients of most reducible substances are smaller in non-aqueous solvents than in water. It is to be expected, therefore, that the diffusion current constants of most substances will be smaller in non-aqueous solvents than in water.

Perrachio and Meloche (89) have recently studied the diffusion currents of the various alkali ions in alcohol–water, dioxane–water, ethylene glycol–water, and glycerol–water mixtures. They found that the diffusion currents were smaller in these solvents than in pure water. The diffusion currents in the glycerol–water mixtures were the smallest of all; this is to be expected because of the relatively great viscosity and correspondingly small diffusion coefficients in these mixtures. Quantitative interpretation of their results is not possible because the requisite diffusion coefficient data are not available. Qualitatively, however, their data are in accord with the foregoing predictions.

VII. THE MIGRATION CURRENT AND ITS INFLUENCE ON THE LIMITING CURRENT

1. Relation between limiting currents in the absence of added salt and diffusion currents in the presence of an excess of indifferent salt

In the preceding section we considered the characteristics of the diffusion current, which is the special name applied to the limiting current when an excess of some indifferent salt is present in the solution. If there is no other salt present, the current will be carried entirely by the ions of the reducible salt, and therefore the reducible ions will be subject to electrical migration as well as to diffusion. Under these conditions the limiting current will evidently depend on the amount of reducible ions supplied by electrical migration as well as by diffusion. In this section we shall consider the effect of this electrical migration on the limiting current, and also the relation between limiting currents without added salt and diffusion currents in an excess of indifferent salt.

TABLE 6

Influence of various concentrations of potassium chloride, potassium nitrate, and hydrochloric acid on the limiting current of lead chloride

50 cc. of 0.00095 *M* lead chloride plus 0.2 cc. of 0.1 per cent sodium methyl red, with various concentrations of added electrolytes. Temperature = 25°C.; P = 21.8 cm.; $m^{2/3}t^{1/6}$ = 2.28 mg.$^{2/3}$ sec.$^{-1/2}$

ADDED SALT	i_l		
	KCl	KNO_3	HCl
equivalents per liter	*microamperes*	*microamperes*	*microamperes*
0	17.6	17.6	17.6
0.0001	16.3	16.2	15.7
0.0002	14.9	15.0	14.6
0.0005	13.3	13.4	12.7
0.001	11.8	12.0	11.2
0.005	9.8	9.8	9.5
0.1	8.35*	8.45*	†
1.0	8.00*	8.45*	†

* Corrected for the residual current.

† Maxima present, and diffusion currents not well defined.

In the reduction of cations it has been found that the limiting current without added salt is roughly twice as great as the diffusion current obtained with an excess of indifferent salt in the solution. As indifferent salt is added to the pure solution of a salt of a reducible cation, the limiting current decreases very rapidly with the first small additions and then more slowly as the concentration of indifferent salt is increased, until it finally becomes practically constant and independent of further additions of the indifferent salt when the concentration of the latter has been made about fifty times larger than that of the reducible salt. Several examples of this behavior have been given by Šlendyk (110) and Lingane (65). A typical example is given in table 6 (65).

It has been found that anion limiting currents without any added salt are *increased* by the addition of indifferent salt. For example, we (65) found a limiting current of 2.40 microamperes for a pure solution of 1.5×10^{-4} *M* potassium iodate (reduction of iodate), which increased to 3.70 microamperes when the solution was made 0.1 *N* in potassium chloride (see table 7).

In order to account for these observed effects, Heyrovský (36) and Ilkovič (53) proposed the idea that the limiting current, without added salt or with only a relatively small amount of added salt, was the sum of a diffusion current, i_d, and a migration current, i_m. In the reduction of cations the limiting current should be increased by the electrical migration, because cations will be impelled towards the negatively charged electrode. Hence Heyrovský and Ilkovič write

$$i_l = i_d + i_m \quad \text{(cation reduction)} \tag{22}$$

where i_l is the total limiting current. In the electroreduction of anions the limiting current should be decreased by the electrical migration, because anions will be repelled from the negatively charged electrode, so that in this case we have

$$i_l = i_d - i_m \quad \text{(anion reduction)} \tag{23}$$

This formal division of the limiting current into two parts is based on the concept, already explained, that in the absence of added salt the reducible ions are subject to both a diffusive force and an electrical force. These forces are assumed to act independently of each other; each is assumed to contribute its share to the total flux of reducible ions and hence to the total limiting current. This concept of the independent action of a diffusive force and an electrical force is not new; it was used by Nernst (84), Haskell (23), Planck (94), and various other investigators, and it is incorporated in the modern theory of electrolytic diffusion and the diffusion potential (87, 30, 22).

A second postulate made by Heyrovský is that the migration current is given by the product of the *total* limiting current and the transference number T_i of the reducible ions, that is,

$$i_m = T_i i_l \tag{24}$$

When no other salt is present, the transference number in this equation will be designated thus, T_i^0, to indicate that it is the transference number of the reducible ion in the pure solution of the reducible salt. When extraneous salt is added to the solution, the transference number will be decreased from T_i^0 to some value T_i, which will depend on the *relative* concentrations and the mobilities of the various ions. As extraneous salt is added to the solution, T_i decreases very rapidly.

Heyrovský and Ilkovič assume that the diffusion current, i_d, is the same in the pure solution of the reducible salt as in the presence of an excess of added salt. On the basis of this assumption we find, by combining equations 22 and 23 with equation 24,

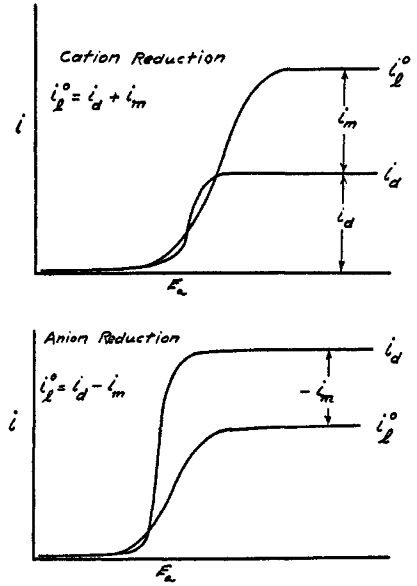

FIG. 12. Relation between limiting currents without added salt and diffusion currents with an excess of added salt (schematic).

$$i_l^0/i_d = 1/(1 - T_+^0) \quad \text{(cation reduction)} \tag{25}$$

$$i_l^0/i_d = 1/(1 + T_-^0) \quad \text{(anion reduction)} \tag{26}$$

In these equations i_l^0 is the initial limiting current without any foreign salt in the solution. Since the transference numbers of most reducible ions are in the neighborhood of 0.5, it is evident that the limiting current in most cation reductions should be decreased to about one-half of its initial value by adding an excess of foreign salt to the solution, whereas the initial limiting current in most anion reductions should be increased to about one and one-half times its initial value. These relations are shown schematically in figure 12 for the case in which $T_i^0 = 0.5$.

In deriving the foregoing relations Heyrovský assumed that the diffusion component of the limiting current was constant and independent of the presence of foreign salt. However, MacGillavry (71) and Lingane (65) have shown that this is only an approximation to the facts, because the diffusion component of the limiting current changes appreciably when foreign salt is added to the solution. According to the Ilkovič equation (see preceding section), with all other factors constant,

$$i_d = kD^{1/2} \tag{27}$$

When an excess of foreign salt is present in the solution, the diffusion coefficient in this equation will be the characteristic diffusion coefficient of the reducible ion (equation 12). However, when no foreign salt is present, the reducible ions are not free to diffuse according to their characteristic diffusion coefficient, but must diffuse at a rate proportional to the diffusion coefficient of the reducible salt itself. It is readily derived (23, 30, 65, 87, 94, 116), that the diffusion coefficient of an ideal salt is given by

$$D_{\mathrm{salt}} = \frac{RT}{F^2}\left(\frac{\lambda_+^0\lambda_-^0}{\lambda_+^0 + \lambda_-^0}\right)\left(\frac{1}{z_+} + \frac{1}{z_-}\right) = \frac{D_+D_-(z_+ + z_-)_-}{z_+D_+ + z_-D_-} \tag{28}$$

where λ_+^0 and λ_-^0 are the equivalent conductances of the positive and negative ions of the salt at infinite dilution, z_+ and z_- are the valences, and D_+ and D_- are the characteristic diffusion coefficients of the ions. This equation, like equation 12, has been derived on the assumption that the ions behave as ideal solutes, and it therefore will be strictly correct only at infinite dilution. However, no appreciable error should result in applying it to pure solutions of reducible salts, when the ionic strength is small. In general, D_{ion} and D_{salt} will not be equal (except in the special case when $\lambda_+^0 = \lambda_-^0$ and $z_+ = z_-$), and hence it is evident from equation 27 that the diffusion component of the limiting current in the pure solution of a reducible salt will in general be different from the diffusion current in an excess of added salt.

When an excess of foreign salt is present, the diffusion coefficient in equation 27 will be D_{ion}, given by equation 12, whereas in a pure solution of a reducible salt the diffusion coefficient will be D_{salt}, given by equation 28. It is evident, therefore, that

$$i_d^0 = kD_{\mathrm{salt}}^{1/2} \tag{29}$$

$$i_d = kD_{\mathrm{ion}}^{1/2} \tag{30}$$

where i_d^0 is the diffusion component of the limiting current without added salt, and i_d is the diffusion current with an excess of foreign salt present. From equation 7 we see that k in the foregoing equations is given by

$$k = 0.627nFCm^{2/3}t^{1/6} \tag{31}$$

The first four terms in this expression are obviously the same with or without indifferent salt present in the solution, and we have shown in the preceding section that the product $m^{2/3}t^{1/6}$ is practically independent of the composition of the solution. It is evident, therefore, that k will be the same with and without foreign salt present, and that the change in i_d as foreign salt is added to the solution is almost entirely due to the change in the effective diffusion coefficient.

By combining equations 29 and 30 with equations 22, 23, and 24, we obtain

$$i_l^0/i_d = (D_{\text{salt}}/D_{\text{ion}})^{1/2}[1/(1 - T_+^0)] \quad \text{(cation reduction)} \tag{32}$$

$$i_l^0/i_d = (D_{\text{salt}}/D_{\text{ion}})^{1/2}[1/(1 + T_-^0)] \quad \text{(anion reduction)} \tag{33}$$

These expressions should be more accurate than the simpler equations 25 and 26 derived by Heyrovský.

MacGillavry (71) has also derived an equation for the ratio i_l^0/i_d in cation reductions. In the notation of this paper his equation is

$$\frac{i_l^0}{i_d} = \left(1 + \frac{z_+}{z_-}\right)^{1/2}\left(1 + \frac{z_+\delta_+^0}{z_-\delta_-^0}\right)^{1/2}\left(\frac{\delta_+^0}{\delta_+}\right)^{1/2}\left(\frac{t^0}{t}\right)^{1/6} \tag{34}$$

where δ_+^0 and δ_-^0 are the absolute mobilities at infinite dilution of the cation and anion of the reducible salt, δ_+ is the absolute mobility of the reducible cation in the presence of an excess of added salt, and t^0 and t are the drop times, at constant pressure, without and with added salt. Since

$$\delta_i^0 = \lambda_i^0 / zF^2$$

and

$$D_{\text{ion}} = RT\lambda_i^0 / zF^2$$

it can be shown that the *first two* terms in MacGillavry's equation are identical with equation 32. The third term is a correction for the decrease in the absolute mobility of the reducible cation (salt effect) when foreign salt is added to the solution, and the last term is a correction for the change in drop time when foreign salt is added. We have already shown that the change in t as indifferent salt is added is small, unless the added salt is strongly capillary-active, and therefore the ratio t^0/t will generally be close to unity. Since only the sixth root of this ratio is involved, the last term will be so close to unity in most cases that it can be safely neglected.

Formally then, the essential difference between MacGillavry's equation and equation 32 is the correction, $(\delta_+^0/\delta_+)^{1/2}$, for the decrease in the absolute mobility of the reducible cation as indifferent salt is added to the solution. However, this difference is more apparent than real, because if the true (measured) values of D_{ion} and D_{salt} are used in equations 32 and 33, these equations become theoretically just as exact as equation 34. Unfortunately, we have no exact knowledge of the decrease in the absolute mobility of an individual ion with increasing ionic strength. Qualitatively, there is good reason for believing that the mobility of an ion decreases much less rapidly than its equivalent conductance with increasing ionic strength. The equivalent conductance of an ion is a true measure of its mobility only at infinite dilution but not at any finite concentration (79, 87). Furthermore, there are practically no reliable diffusion coefficient data in the literature for the salts and ions with which we are concerned, at various ionic strengths. For these reasons we shall assume, in the following interpretation of experimental data, that the various salts and ions behave as ideal solutes.

In order to test the foregoing relations, we (65) determined the initial limiting currents, with no added salt, and the diffusion currents, in 0.1 N or 0.9 N potassium chloride, of various thallous salts, lead chloride, cadmium sulfate, and potassium iodate. The various thallous salts were chosen so that the transference number of the thallous ion would differ as much as possible in the various cases. A trace of methyl red (one drop of a 0.1 per cent solution of sodium methyl red per 50 cc.) was added to the solutions to eliminate the maxima otherwise present. Special experiments showed that this very small amount of methyl red had no appreciable influence on either the limiting or the diffusion currents. The results obtained are given in table 7.

The transference numbers of the reducible ions in the pure solutions of the reducible salts, given in the fourth column, were calculated in the usual way from the equivalent conductances of the ions of the reducible salt. The fifth column of the table contains the observed ratios of the initial limiting currents to the final diffusion currents, i_l^0/i_d. The values of this ratio computed according to the simple Heyrovský relation (equation 25 or 26) are tabulated in the sixth column, while the last column contains the values of i_l^0/i_d computed according to equation 32 or equation 33.

It will be noted that the values of i_l^0/i_d calculated according to equation 32 or equation 33 are, in most cases, in better agreement with the observed values of this ratio than the values calculated according to the simpler equations of Heyrovský (equation 25 or equation 26). Cadmium sulfate and potassium iodate are the only exceptions; in these cases, equation 25 or equation 26 gave better results.

It will be noted that the observed values of the ratio are, in most cases, less than the calculated values. This is perhaps due to unavoidable traces of salt impurities in the pure solutions of the reducible salts, which would decrease i_l^0 appreciably, e.g., traces of alkaline impurities from the glass of the cell, or traces of dissolved mercury from the quiet electrode. In view of the difficulty of completely eliminating such salt impurities, the agreement between the observed and calculated ratios is as good as can be reasonably expected.

TABLE 7

Comparison of initial limiting currents and diffusion currents of various reducible ions

REDUCIBLE SALT	i_l^0	i_d	T_i^0 (CALCULATED)	RATIO i_l^0/i_d		
				Observed	Calculated by equation 25	Calculated by equation 32
	microamperes	*microamperes*				
0.001 M TlCl	11.6	6.10*	0.500	1.90	2.00	2.00
	11.6	5.95†	0.500	1.95	2.00	2.00
0.0013 M TlOH	13.9	8.15*	0.277	1.71	1.39	1.66
0.0026 M TlOH	26.7	15.85*	0.277	1.69	1.39	1.66
0.0026 M $TlC_2H_3O_2$	34.2	15.85*	0.646	2.16	2.83	2.37
0.0005 M $TlIO_3$	6.55 (Tl^+)	3.30*	0.646 (Tl^+)	1.99	2.83	2.37
0.00095 M $PbCl_2$	17.6	8.35*	0.483	2.11	1.93	2.39
	17.6	8.00†	0.483	2.20	1.93	2.39
0.001 M $CdSO_4$	12.7	8.00*	0.400	1.59	1.67	1.83
0.00015 M KIO_3	2.40 (IO_3^-)	3.70*	0.356 (IO_3^-)	0.65	0.74‡	0.84§

* In 0.1 N potassium chloride corrected for the residual current.

† In 0.9 N potassium chloride corrected for the residual current.

‡ Calculated by equation 26.

§ Calculated by equation 33.

It is interesting to note that a correction for the decrease in the absolute mobilities of the reducible cations when foreign salt is added, as recommended by MacGillavry (equation 34) (71), would increase the calculated ratios of i_l^0/i_d. Hence such a correction would actually increase the differences between the observed and calculated values of this ratio. The foregoing experimental data indicate that such a correction is not justified, and that other unknown factors (specific salt effects, etc.) are operative to a certain degree. The decrease in the diffusion current of lead ions between 0.1 N and 1 N potassium chloride (table 6) is an example of such a specific salt effect (probably $PbCl_3^-$ or $PbCl_4^{--}$ formation).

It should be mentioned that the limiting currents of uncharged (especially organic) substances should be practically entirely diffusion currents, because uncharged substances are not subject to electrical migration. The limiting currents of uncharged substances should therefore be constant and independent of the presence of foreign salts (53). Experimentally, however, this is difficult to demonstrate, because the reduction of most uncharged (organic) substances involves the action of hydrogen ions, and, if no foreign acid is present, the necessary hydrogen ions must be furnished by the dissociation of water molecules. The reduction of uncharged substances is thus a much more complicated problem than the reduction of ions (80). It has been found, for example, that the limiting current of oxygen in potassium chloride solutions is practically constant and independent of the concentration of the salt up to about 0.1 N (50, 124), but that in very concentrated salt solutions the limiting current of oxygen is greatly decreased (50).

2. Increase, or "exaltation," of the migration current by the preceding discharge of an uncharged substance

We have seen that the migration current is equal to the product of the total limiting current and the transference number of the reducible ions (equation 24). If some uncharged substance, which is reduced at a more positive potential than the reducible ion in question, is added to a pure solution of a reducible salt, the resulting total limiting current will be the sum of that due to the reduction of the uncharged substance and that of the reducible ions. That is,

$$i_{\text{total}} = i_u + i_l \qquad (35)$$

where i_u is the limiting current of the uncharged substance and i_l is that of the reducible ions. Under these conditions the migration current of the reducible ions will be increased or "exalted" (42), and if we assume that the transference number of the reducible ions is not influenced by the preceding discharge of the uncharged substance, the exalted migration current should be given by

$$i_m = (i_u + i_l)T_i^0 \qquad (36)$$

The effect of this exaltation of the migration current will be to increase the limiting current in cation reductions and to decrease it in anion reductions. This effect has been demonstrated by Heyrovský and Bureš (42), who found that the initial limiting currents of potassium and sodium ions in very dilute, pure solutions of the alkali chlorides were increased by the preceding discharge of oxygen. This effect of oxygen is shown by the curves in figure 13, which we (65) have obtained. Curve 1 in this figure was obtained by electrolyzing a pure 9.4×10^{-4} N solution of potassium chloride, from which the air had been completely removed with nitrogen. Curve 2 was obtained after saturating the solution with pure oxygen. It is seen that the limiting current of the potassium ions was increased more than twofold by the preceding discharge of oxygen.

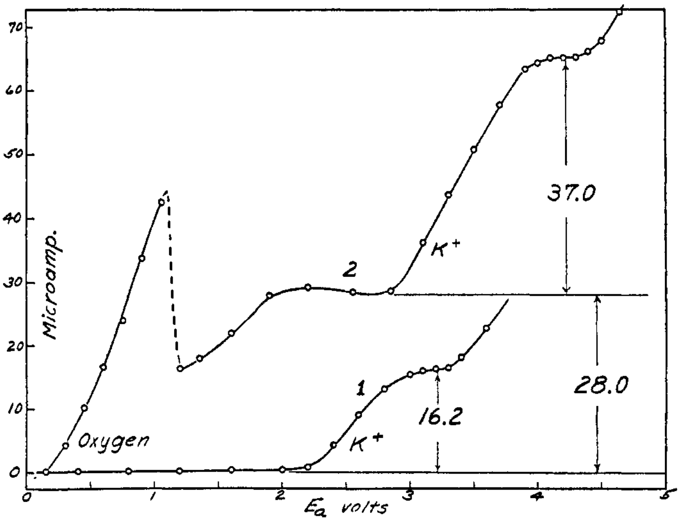

FIG. 13. Exaltation of the limiting current of potassium ions by the preceding discharge of oxygen.

If we represent the initial limiting current, in the absence of foreign salts and without a reducible non-electrolyte present, by i_l^0 and the migration current under the same conditions by i_m^0, then

$$i_m^0 = i_l^0 T_i^0 \tag{37}$$

Hence the exaltation of the migration current by the preceding discharge of the uncharged substance should be given by

$$i_m - i_m^0 = (i_u + i_l - i_l^0)T_i^0 \tag{38}$$

We also have the relations

$$i_l^0 = i_d \pm i_l^0 T_i^0 \tag{39}$$

$$i_l = i_d \pm (i_u + i_l)T_i^0 \tag{40}$$

where the plus sign refers to cation reductions and the minus sign to anion reductions. If we assume that i_d is unaffected by the preceding discharge of the uncharged substance, we find that the exaltation of the limiting current in cation reductions should be equal to the exaltation of the migration current and should be given (42) by

$$i_l - i_l^0 = i_m - i_m^0 = i_u T_+^0/(1 - T_+^0) = i_u \lambda_+^0/\lambda_-^0 \tag{41}$$

On the other hand, in anion reductions the limiting current should be decreased by the same amount that the migration current is increased. It is interesting to note that in the special case where T_i^0 is exactly 0.5, the exaltation should be simply equal to the limiting current of the uncharged substance, that is,

$$\Delta i_m = i_u$$

when $T_+^0 = 0.5$.

From equation 41 we see that the exaltation of the limiting current should be independent of the concentration of the reducible ions and should depend only on the magnitude of the limiting current of the uncharged substance. Hence it should be possible to increase cation limiting currents many fold by simply increasing the concentration of the uncharged substance and to suppress entirely anion limiting currents. It should be realized, however, that equation 41 will no longer apply with extremely small concentrations of the reducible salt, because under these conditions the electrical potential gradient at the surface of the mercury drops will be so great that the ordinary laws of ionic transfer and conduction will no longer apply.

In curve 2 of figure 13 the limiting current of oxygen, i_u, is 28.0 microamperes. Since the transference number of the potassium ion in potassium chloride is 0.493, we calculate from equation 41 that the exaltation of the potassium ion limiting current by the preceding discharge of oxygen should be $28.0 \times 0.493/0.507 = 27.2$ microamperes. The observed exaltation is $37.0 - 16.2 = 20.8$ microamperes.

Similar experiments were carried out with 9.4×10^{-4} N sodium chloride. In the absence of oxygen the limiting current of sodium ions was 12.5 microamperes. When the solution was saturated with pure oxygen, the limiting current of sodium ions was 26.5 microamperes, while that of the oxygen was 30.0 microamperes. Hence the observed exaltation was $26.5 - 12.5 = 14.0$ microamperes. Since the transference number of the sodium ion in sodium chloride is 0.400, the calculated exaltation is $30.0 \times 0.400/0.600 = 20.0$ microamperes.

Although the discrepancy between the calculated and observed exaltation in the foregoing cases is in the neighborhood of 25 per cent, the agreement is sufficiently good to show that Heyrovský's theory of the exaltation is at least approximately correct. The discrepancies can be accounted for by the fact that hydroxide ions are a product of the reduction of oxygen, and, when the latter is discharging simultaneously with the alkali ions, the solution close to the surface of the mercury drops is actually equivalent to a mixture of the alkali chloride and hydroxide. Hence the transference numbers of the alkali ions, in the solution close to the surface of the electrode, are considerably less than in the pure solutions of the alkali chlorides, and the exaltation is correspondingly decreased. For example, in the case of potassium chloride the calculated diffusion current in the absence of oxygen is $(1 - 0.493)16.2 = 8.2$ microamperes, and it was the same when oxygen was discharging. Therefore the observed migration current when oxygen was discharging was $37.0 - 8.2 = 28.8$ microamperes. The effective transference number of the potassium ion during the simultaneous discharge of oxygen, calculated from this value of the migration current, is $28.8/65.0 = 0.443$, instead of the value 0.493 in pure potassium chloride. This corresponds to a ratio of hydroxide to chloride ions of about 1/5 close to the surface of the mercury drops, which is a logical value. Heyrovský and Bureš apparently did not recognize the necessity of correcting for the decrease in the effective transference numbers of the alkali ions due to the accumulation of hydroxide ions at the surface of the mercury drops, probably because they saturated their solutions with air instead of pure oxygen, in which case the correction will be much less.

Heyrovský and Bureš state that they also obtained the exaltation effect with barium and manganous ions and by using other reducible nonelectrolytes in place of oxygen, e.g., quinone. The reduction of uncharged substances practically always involves hydrogen ions, which in neutral solutions must be furnished by the dissociation of water molecules at the surface of the mercury drops, with the subsequent accumulation of hydroxide ions. Hence with practically all uncharged substances the formation of hydroxide ions at the electrode surface must be taken into account.

From equation 41 we see that the exaltation of the sodium and potassium ion limiting currents should be directly proportional to the equivalent conductances of the two alkali ions, when the anion in both cases is the same. The exaltation of the potassium ion limiting current will therefore be considerably greater than that of the sodium ion, at a given value of i_u. In a mixture of potassium and sodium chlorides the observed exaltation will be intermediate between the characteristic exaltations of the two alkali ions. Heyrovský and Bureš recommend this behavior for determining the ratio of the two alkali chlorides in a mixture.

3. *Exaltation of the migration current by the preceding discharge of a reducible ion*

The apparent limiting current of a reducible cation can be increased or exalted by the preceding discharge of a reducible ion, as well as by the preceding discharge of a reducible non-electrolyte. This effect is shown in figure 14. Curve 1 in this figure was obtained by electrolyzing a 9.4×10^{-4} N potassium chloride solution that had been freed from air with pure nitrogen. Curve 2 was obtained after addition of sufficient thallous chloride solution to make the concentration of the latter 8.3×10^{-4} (the concentration of the potassium chloride being reduced to 8.6×10^{-4} N).

Without thallous chloride present the potassium ion limiting current was 15.8 microamperes, and it was increased to 20.1 microamperes by the preceding discharge of the thallous ions. Without thallous chloride present, the calculated diffusion current of potassium ions was $15.8(1 - 0.493) = 8.0$ microamperes. Since thallous, potassium, and chloride ions all have practically the same equivalent conductances, the effective diffusion coefficient of the potassium ions will be the same with or without thallous chloride present, but the diffusion current of potassium ions was decreased to $8.0 \times 8.6/9.4 = 7.3$ microamperes by the increase in volume when the thallous chloride solution was added. Hence the migration current when thallous chloride was present was $20.1 - 7.3 = 12.8$ microamperes.

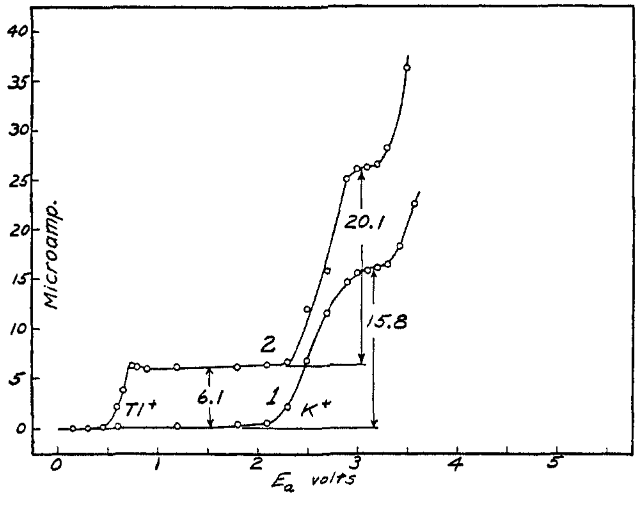

FIG. 14. Exaltation of the limiting current of potassium ions by the preceding discharge of thallous ions.

It should be realized that when the potential corresponding to the limiting current of potassium ions was reached, in the presence of thallous chloride, the thallous ion migration current was also increased, as well as that of the potassium ions, by the increased current. Hence only a part of the apparent increase in the potassium ion limiting current was actually due to the exaltation of the potassium ion limiting current, and the remainder was due to the exaltation of the migration current of the thallous ions during their simultaneous discharge with potassium ions! In the solution containing almost equal concentrations of thallous chloride and potassium chloride, since the equivalent conductances of all the ions are very nearly the same, the transference numbers of the thallous and potassium ions were practically the same and were equal to 0.25, while that of the chloride ion was 0.5. Since the total limiting current was 26.2 microamperes, the migration currents of the thallous and the potassium ions should each have been equal to $0.25 \times 26.2 = 6.55$ microamperes, and the total migration current should have been equal to 13.1 microamperes. This calculated migration current agrees very well with the observed value of 12.8 microamperes. In this special case, where the concentrations of the thallous and potassium chlorides were equal, the current at the potential corresponding to the discharge of potassium ions was actually almost the same with or without thallous chloride present, and the apparent exaltation of the potassium ion limiting current can be regarded as due entirely to the exaltation of the migration current of the thallous ions themselves.

Although the foregoing exaltation phenomena have little practical value, they have important theoretical significance, because they furnish further confirmation of Heyrovský's theory of the migration current.

VIII. MAXIMA ON CURRENT–VOLTAGE CURVES

1. The Heyrovský–Ilkovič theory of maxima

One of the characteristic features of the current–voltage curves with the dropping mercury electrode is the more or less pronounced maxima, which are often present unless special measures are taken to prevent their occurrence. Maxima may also occur with quiet mercury electrodes (16, 26, 28), but these are not reproducible, in contradistinction to those obtained with the dropping mercury electrode, which are perfectly reproducible (48). The shapes of maxima vary from very acute peaks, with a rapid and almost discontinuous decrease of the current after the maximum, to rounded humps with a gradual decrease in current following the maximum (figure 15).

The shapes of current–voltage curves showing maxima are generally independent of the direction in which the applied E.M.F. is changed; if, after the maximum has been passed by increasing the E.M.F. in the usual way, the E.M.F. is then decreased gradually, the curve will in most cases retrace itself exactly over the maximum (figure 16). In certain cases, when the maxima are very acute, the potential at which the peak of the maximum is reached may be somewhat different with decreasing E.M.F. from that with increasing E.M.F. For example, Heyrovský and Vas-

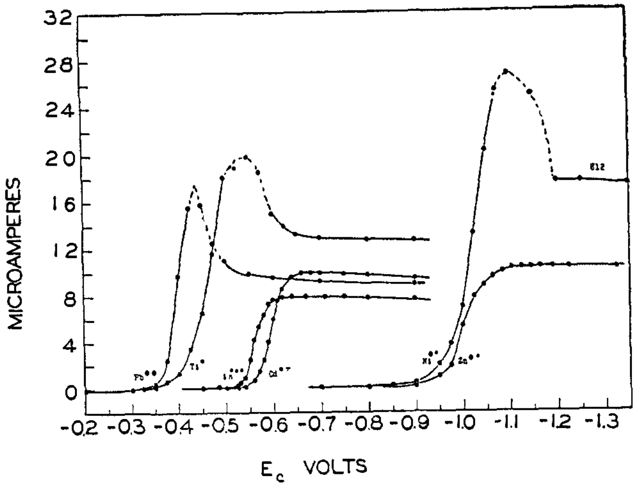

FIG. 15. Typical current-voltage curves of various metal ions in 0.1 N potassium chloride, showing various types of maxima.

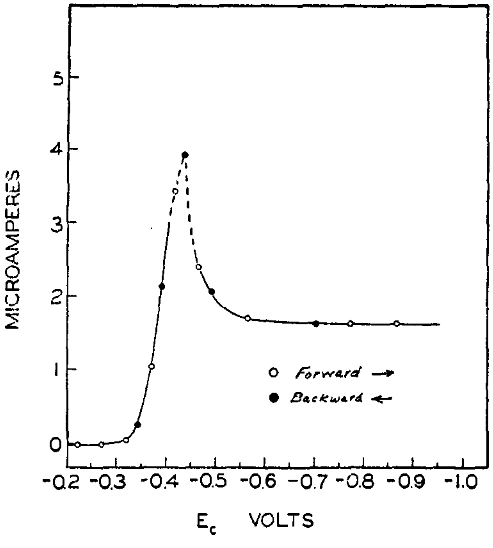

FIG. 16. Independence of the shape of the lead maximum of the direction in which the E.M.F. is applied. 2.75 × 10^{-4} M lead nitrate in 0.1 N potassium chloride.

cautzanu (48) found that the peak of the oxygen maximum was about 50 millivolts more negative with increasing applied E.M.F. than with decreasing applied E.M.F., but the height of the maximum was practically the same in the two cases. We have verified this behavior.

Just as on other parts of a current–voltage curve, the current at the maximum appears to be independent of the time of electrolysis. If the applied E.M.F. is kept constant at a value at or near the peak of a maximum, the current remains constant indefinitely.

The maximum due to a given electroreducible substance may be either acute or rounded, depending on the composition of the solution. For example, Varasova (122) found that the acute maximum of oxygen (figure 13) was very small in extremely dilute potassium chloride solutions, but that it became more and more pronounced with increasing potassium chloride concentration and attained its greatest value in about 0.001 *N* potassium chloride. (Mr. C. S. Miller in this laboratory found the most pronounced maximum at a somewhat greater concentration of potassium chloride.) With increasing salt concentration the maximum decreased and became more rounded. Quite generally, a maximum will be most pronounced at a certain intermediate concentration of foreign salt; in distilled water and in concentrated salt solutions the oxygen maximum disappears (47).

An interesting feature when the maximum is very acute is that the current–voltage curve often is a straight line, and not the usual S-shaped curve, before the peak of the maximum is reached. In such a case the slope of the straight line is proportional to the reciprocal of the resistance of the cell in accordance with Ohm's law (52). This indicates that the potential of the dropping electrode remains constant from the beginning of the discharge and that no concentration polarization occurs until the maximum is reached. Immediately after the maximum is passed and the current decreases suddenly, the dropping electrode becomes almost completely polarized. In weakly acid mercurous nitrate solutions this sudden increase in polarization may amount to as much as 1 volt (43). Conclusive proof that the electrode remains depolarized during the discharge of mercurous ions until the peak of the maximum is reached and that polarization sets in at the peak was obtained by Heyrovský from measurements of the interfacial tension at the mercury–solution interface during the electrolysis (35). He found that the interfacial tension, in a slightly acid mercurous nitrate solution, remained practically constant until the peak of the maximum was reached, instead of changing according to the electrocapillary curve. As soon as the maximum was passed, the interfacial tension changed abruptly and followed the electrocapillary curve.

It is still problematical whether the slope of the straight part of the current–voltage curve preceding an acute maximum corresponds exactly to the reciprocal of the cell resistance. Ilkovič (54) assumes that the resistance of the surface film surrounding the electrode is different from that in the bulk of the solution, and that it varies with the distance from the electrode. In this connection reference is made to the important investigations of Hoekstra (49), who studied the current–voltage curves obtained with scraped electrodes. He found a constant apparent resistance at various values of the current, which was several times greater than that calculated from the dimensions of the cell and the specific conductance of the solutions (see also reference 12).

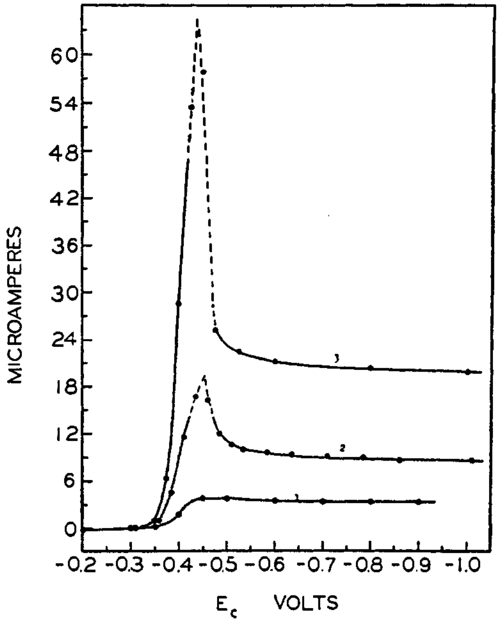

Fig. 17. Relative heights of maxima obtained with various concentrations of lead ions in 0.1 *N* potassium chloride. Curve 1, 3.3×10^{-4} *M* lead nitrate; curve 2, 1×10^{-3} *M* lead nitrate; curve 3, 2.3×10^{-3} *M* lead nitrate.

The height of the maximum of a given electroreducible substance is greatly dependent on its concentration. Reducible metal ions in dilute alkali chloride solutions usually do not yield maxima when the concentration of the metal ion is very small, but maxima appear and become more and more pronounced as the concentration of the metal ion is increased (figure 17). As a rule, there is no linear relation between the height of a maximum and the concentration of the reducible substance. For example, in the electrolysis of nickel chloride solutions, without any foreign salt present, Emelianova and Heyrovský (11) found that the ratio

$i_{\text{max.}}/i_l$ was equal to 1:1 in a 0.0005 *N* solution, to 2.7:1 in a 0.0025 *N* solution, to 6:1 in a 0.0062 *N* solution, and to 6.5:1 in a 0.01 *N* solution.

The magnitudes of the maxima depend on the drop time, becoming smaller the slower the drop time (35).

The exact interpretation of the maxima is one of the most difficult problems in polarography. Heyrovský (35) attributes the maxima to an adsorption of the electroreducible substance on the growing mercury drops, whereby the concentration of the reducible substance is increased above its value in the body of the solution and normal concentration polarization is prevented. This adsorption is supposed, by Heyrovský, to be caused by the unhomogeneous electric field around the charged drops, which he assumes is identical with the electrokinetic potential at the mercury–solution interface. Since pronounced maxima are found only with the dropping electrode, and since the adsorptive force must be established sooner than the electrokinetic potential can be built up, Ilkovič (54) assumes that the unhomogeneous field responsible for the adsorption is caused by the charging current (not the total current) rather than by the electrokinetic potential. The drop in potential around a mercury drop caused by the charging current, i_c, is i_cW, where W is the resistance in the surface film surrounding the drop. From fairly involved calculations Ilkovič concludes that the electric field created by the charging current is much greater than that due to the electrokinetic potential gradient. If the electric field due to the charging current were homogeneous, i.e., if $\mathrm{d}(i_cW)/\mathrm{d}x$ were constant and independent of the distance x from the surface of the electrode, it would cause only a motion of ions, and particles subject to dielectric polarization would simply become polarized and oriented, but would undergo no movement. However, the field created by the charging current is not homogeneous, because W varies greatly with x; hence the unhomogeneous field causes a motion of dipolar molecules as well as ions. Ilkovič assumes that the attraction of dipolar molecules to the surface of the mercury drop by the unhomogeneous electric field takes place to an appreciable extent only when the concentration of the reducible substance has been reduced to a small value by the discharge process.

To clarify Ilkovič's view the following citation is given (54). "Let us now, from this viewpoint, explain the case of a maximum due to the depolarizing action of a solution which contains only one electrolyte, e.g., that due to the deposition of nickel from the solutions of its chloride. At voltages at which the rate of the deposition of nickel ions is smaller than the rate of their adsorption, the current is an 'adsórption' one and can increase with increasing voltage. However, as soon as the voltage is reached at which at the *very beginning* of the formation of the drop the rate of deposition of the ions exceeds the rate of their adsorption, the exhaustion of the surface layer starts. At this instant a large electric force acts at the cathode, which cannot be depolarized, there being no reducible matter present in the exhausted surface film. However, the water molecules of the surface film are polarizable owing to their dipole character. They must be, therefore, polarized in the strong field, their oriented polarized layer thus constituting the increase of the 'back E.M.F.' observed at the fall of the maximum. Under such conditions now the electric field in the solution is considerably shortened so that no more ions can be attracted to the surface by adsorptive force. The current due to the deposition of nickel ions is now furnished only by the penetration of these cations through the polarized layer of water molecules and thus becomes a 'diffusion current.' The suppressive action of adsorbable particles on the maximum is similar to that of water molecules, *viz.*, in that they increase the polarization owing to their dipole moment and thus counterbalance the unhomogeneous electric field due to the charge of the small mercury electrode."

The Heyrovský–Ilkovič interpretation of the maxima involves certain difficulties. We have seen in a previous section that both the charging current and the charge of the double layer (electrokinetic potential) change sign at the maximum in the electrocapillary curve. It is evident, therefore, that the *direction* of the electric field responsible for the adsorption must also change at the electrocapillary maximum, regardless of whether this field is due to the electrokinetic potential (Heyrovský) or to the charging current (Ilkovič). Hence reducible ions of a given sign should be adsorbed, by electrical attraction, only on one side or the other of the electrocapillary maximum, but not on both sides. On the negative side of the electrocapillary maximum the field is in the right direction to cause adsorption of positive ions, but on the positive side of the electrocapillary maximum the field is in the opposite direction, and hence positive ions should be repelled, not attracted and adsorbed. Actually it is found, in contradiction of the Heyrovský–Ilkovič theory, that the discharge of positive ions gives rise to maxima on *both* sides of the electrocapillary maximum, e.g., lead and nickel ions are discharged on opposite sides of the electrocapillary curve, but the current–voltage curves of both of these ions show prominent maxima (figure 15).

There is also a possibility that the maxima may be connected in some way with an electrostatic stirring effect at the surface of the mercury drops. Frumkin and Bruns (16), working with a quiet mercury cathode, showed experimentally that with relatively large current densities the surface of the mercury is in active motion. This is due to differences in the potential and the surface tension at various spots on the mercury surface. Consequently, local currents flow between such spots and cause a stirring effect in the solution close to the surface of the electrode, as shown by Bruns, Frumkin, Jofa, Vanjukova, and Zolotarewskaja (10), and by Stackelberg, Antweiler, and Kieselbach (113). Antweiler (4) has obtained experimental evidence that such a stirring effect actually exists with the dropping mercury electrode in cases where maxima occur. There is probably some connection between the charging current and this stirring effect. When the mercury is uncharged (isoelectric point), it is claimed that no maximum, and apparently no stirring effect, occurs.

At present it is not possible to give an exhaustive treatment of all the factors responsible for the occurrence of maxima. From a practical viewpoint, and also in connection with the further development of the theory, various observations made by Heyrovský and his school regarding the suppression and elimination of maxima are of great interest, and will now be discussed.

2. Suppression and elimination of maxima

Heyrovský (35) distinguishes between "positive" and "negative" maxima, according to whether a given maximum occurs on the positive or the negative side of the maximum in the electrocapillary curve. In the absence of capillary-active substances the maximum in the electrocapillary curve is at about −0.6 volt against the normal calomel electrode. In figure 15 the lead maximum is a positive maximum, while that of nickel is a negative maximum.

Maxima can be suppressed, and in most cases eliminated, by adding to the solution traces of certain capillary-active electrolytes and non-electrolytes, and various capillary-inactive ions and charged colloids. In this connection it should be realized that the capillary activity of a given substance, and hence its ability to suppress maxima, depends on the sign of the charge on the mercury (35).

Considering first the effect of capillary-inactive ions, there seems to be a close relation between the sign of the charge of the mercury on the one hand, and the signs and valences of the ions on the other. Thus, in the suppression of positive maxima, trivalent anions are usually much more effective than divalent, and the latter more so than univalent anions, while the valence of the cation is practically without effect. The converse is true for negative maxima, in which case the valence of the cation plays the predominant rôle. Heyrovský (35) states, "The dilutions in which cations of different valency cause the same degree of suppression of a negative maximum are in the same ratio as their power of precipitating (flocculating) a negative lyophobic colloid, say arsenic trisulfide. Indeed, the Hardy–Schulze rule has been found to hold strictly for the suppression of maxima; thus the dilutions at which ions of potassium, calcium, and lanthanum, respectively, produce suppression to the same extent were found to be in the ratio 1:160:10000." However, it is doubtful whether the Schulze–Hardy rule holds strictly in the suppression of maxima. For example, Emelianova and Heyrovský (11) found the negative maximum of nickel just suppressed in 0.11 N potassium chloride, in 2.2×10^{-3} N magnesium chloride, in 1.1×10^{-3} N calcium chloride, in 3×10^{-5} N barium chloride, in 2×10^{-5} N aluminum chloride, and in 1×10^{-6} N lanthanum chloride. It is not clear why barium ions in this respect behave as trivalent cations, quite differently from calcium and magnesium ions.

Mr. C. S. Miller in this laboratory found the difference in the suppressive effect of barium ions on the one hand, and of calcium and magnesium ions on the other, much smaller. He also studied the effect on the maxima of additions of a deficiency of sodium hydroxide to the nickel chloride solution. The alkali causes the partial separation of basic nickel salt, presumably as a positively charged colloid. One would expect, therefore, that the negative nickel maximum would be suppressed completely in the presence of this colloid. Actually it was found that the ratio of the maximum current to the limiting current remained almost unchanged in the presence of various amounts of the positive colloid. Another exception to the rule given by Heyrovský was found by Mr. Miller in the case of the positive oxygen maximum. In 0.001 N potassium chloride a very pronounced, acute maximum occurs, the maximum current being much greater than the limiting current (figure 13). Addition of potassium ferrocyanide to this solution, in concentrations ranging between 10^{-5} and 6×10^{-5} molar, hardly affected the maximum, and at a concentration of 0.001 M ferrocyanide the maximum was even slightly more pronounced instead of suppressed. Also at other concentrations of potassium chloride no pronounced effect of ferrocyanide ions was found. It is evident, therefore, that care must be exercised in generalizing Heyrovský's rule.

From Herasymenko's study (26) of the effect of salts on the maximum in the reduction of uranyl ions (first wave), cations of various valency (K^+, Na^+, Mg^{++}, Al^{+++}) were found to have the same effect, and there was also hardly any difference between the effect of chloride and sulfate ions. Since the uranyl ions (first wave) are reduced on the positive side of the electrocapillary maximum, one would expect that sulfate ions would be much more effective in suppressing the maximum than chloride ions.

The following peculiar phenomenon is also hard to explain on the basis of Heyrovský's rule. Heyrovský and Dillinger (43) found that in a mixture of nickel and manganous chloride two pronounced negative maxima occurred. The nickel maximum was suppressed by addition of barium ions, but that of manganese was much less affected. On the basis of Heyrovský's rule both maxima should have been equally suppressed.

From a practical point of view the effect of *capillary-active* ions on maxima is of much greater importance than that of capillary-inactive ions. Heyrovský (38, 35) states that negative dyes and negative colloids (he used a negative colloidal solution of a barium soap) suppress the positive thallium maximum very easily, whereas positive dyes and positively charged colloids cause a suppression of negative maxima. For example, the positive maximum of thallium is easily suppressed by acid fuchsin (anion), but that of nickel is hardly affected. On the other hand, basic fuchsin (cation) suppresses the negative nickel maximum completely.

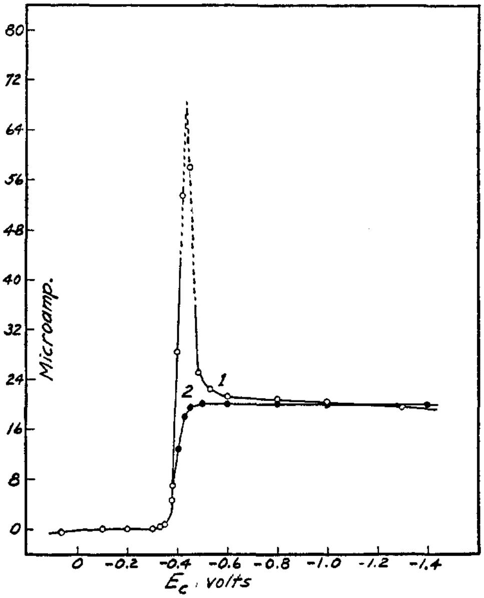

FIG. 18. Suppression of the positive lead maximum by anionic methyl red in neutral solution. Curve 1, 50 cc. of 2.3×10^{-3} M lead nitrate in 0.1 N potassium chloride; curve 2, 0.1 cc. of 0.1 per cent sodium methyl red added.

In practical analytical work the occurrence of maxima is a nuisance, but fortunately they can usually be eliminated by the addition of suitable capillary-active ions. Lingane (65) found, for example, that the positive maxima of thallium and lead in neutral solutions are completely suppressed by traces of the sodium salt of the ordinary indicator methyl red (figure 18). However, in accordance with Heyrovský's rule, the positive lead maximum is not suppressed by the cation form of methyl red in acid medium (figure 19). On the other hand, the negative maximum of nickel in neutral medium was found to be unaffected by the anion form of methyl red, but in acid medium the maximum was completely eliminated by the cation form of the dye; this is also in accord with Heyrovský's rule.

Methyl red is itself reduced at the dropping electrode, but the concentrations of the dye used to suppress maxima are so small (less than 0.001 per cent) that they hardly affect the diffusion current of the substance to be determined.

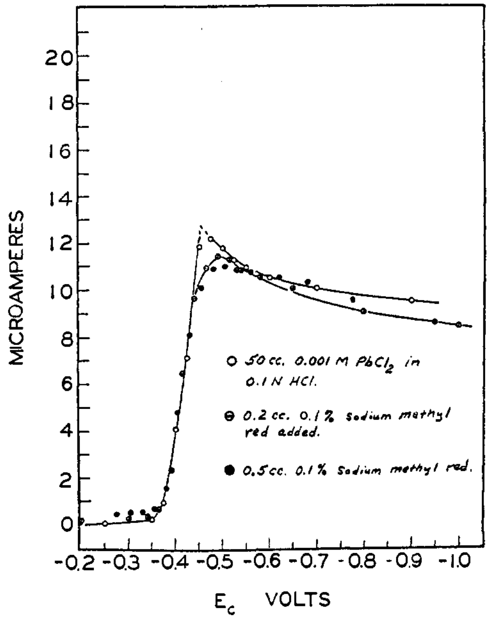

FIG. 19. Failure of cationic methyl red to suppress the lead maximum in acid solution.

The analytical significance of the elimination of maxima is demonstrated in figure 20 by the current-voltage curve of a mixture of lead and cadmium ions without and with methyl red present. In the absence of the dye no definite measure of the diffusion current of the lead ions can be obtained, but a well-defined diffusion current for lead results when the maximum is eliminated by the addition of methyl red (65).

One should not infer from the foregoing examples that strongly capillary-active anions invariably suppress only positive maxima, and capillary-active cations suppress only negative maxima. We have already cited several exceptions to this rule from the work of Heyrovský and Dillinger. The degree of polarizability of the ions, their specific ability to be adsorbed on mercury at various potentials, and their effect of shifting the electrocapillary zero also have to be taken into account. That positive dyes can be as effective as negative dyes in suppressing the positive oxygen maximum is evident from the work of Rayman (98). Furthermore, Hamamoto (20) has demonstrated that positively charged alkaloid ions have a great suppressive effect on the positive oxygen maximum.

Capillary-active non-electrolytes can also be very effective in suppressing and eliminating maxima in certain cases. In general, it is not to be expected that a given capillary-active non-electrolyte will be able to suppress maxima over the entire voltage range, because the adsorbability of such substances usually reaches a maximal value at a certain characteristic potential. It is to be expected that sulfur-containing organic substances should be effective in eliminating maxima, since such substances are usually capillary-active. Heyrovský (35) mentions the great effect of traces of α-naphthol in suppressing maxima, and Maas (68) found that naphthalene was effective. Oxygen, which in its own electroreduction gives a very pronounced maximum, suppresses the maxima of various metal ions, e.g., nickel ions.

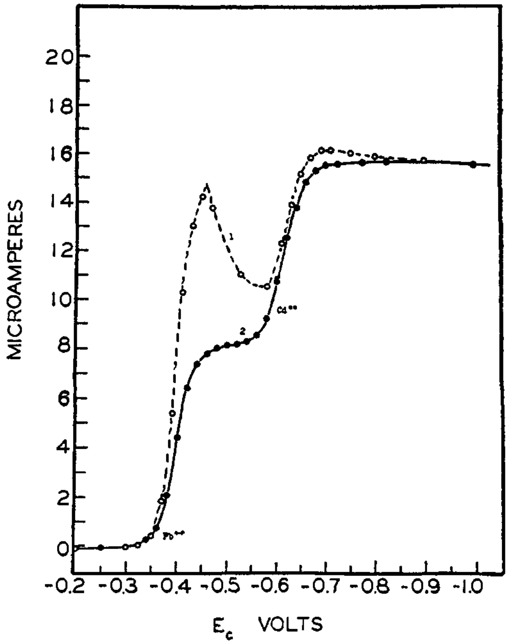

FIG. 20. Current-voltage curves of a neutral 0.1 N solution of potassium chloride containing 0.001 M lead and cadmium ions. Curve 1, no methyl red present; curve 2, 0.1 cc. of 0.1 per cent sodium methyl red added per 50 cc.

We (65) found that gelatin, even in very low concentrations, was able to suppress the maxima of various metal ions over a wide range of potentials. The use of gelatin to suppress maxima has also been recommended by Hohn (50). The suppressive effect of gelatin on the lead maximum is shown in figure 21. It will be noted that a concentration of gelatin of 0.02 per cent was ample to suppress the lead maximum completely. When the concentration of the gelatin is greater than about 0.01 per cent it decreases the diffusion currents, probably because it decreases the diffusion coefficient of the reducible ions. We have also found that gelatin completely eliminates the maximum of thallium in both acid and alkaline medium, and that it eliminates the maximum of nickel in both neutral and ammoniacal medium. From the cases so far studied it appears that gelatin is effective in suppressing many maxima. In practical work, however, its suppressive effect on the diffusion current, when it is present at concentrations greater than about 0.01 per cent, must be taken into account. Furthermore, it is our experience that the addition of gelatin may actually be harmful, instead of beneficial, in

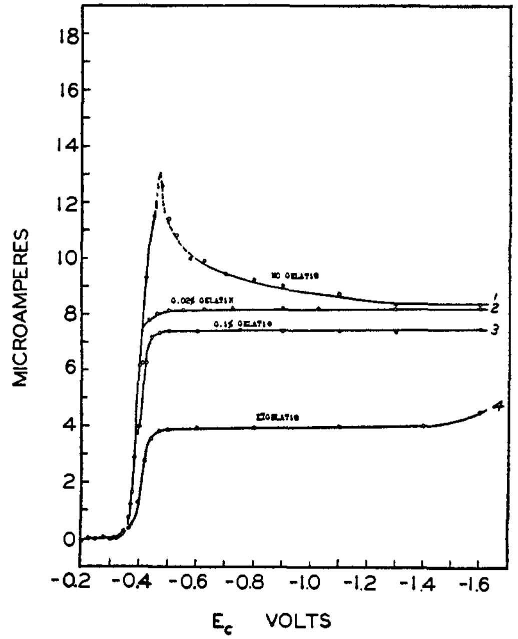

FIG. 21. Suppression of the lead maximum by gelatin in neutral potassium chloride solution, 0.001 *M* lead chloride in 0.1 *N* potassium chloride. Curve 1, no gelatin present; curve 2, 0.02 per cent gelatin; curve 3, 0.1 per cent gelatin; curve 4, 1 per cent gelatin.

certain cases, particularly when the electroreduction is irreversible. A more extensive study of the influence of gelatin is necessary before it can be generally applied in practical analytical work.

3. Phenomena at the electrocapillary zero

Heyrovský claims that no maximum occurs when the electroreduction of a substance takes place at the potential corresponding to the electrocapillary zero (maximum in the electrocapillary curve), where the mercury is apparently uncharged and the interfacial tension has its maximal value (35). This statement may be correct so far as the electroreduction of capillary-inactive ions and molecules is concerned, but, to say the least, it is doubtful that it is true in the electroreduction of capillary-active substances (128). For example, no maximum occurs in the discharge of the capillary-inactive cadmium ions from chloride solutions, because the discharge potential of cadmium ions under these conditions is very close to the electrocapillary zero (-0.6 volt in chloride solutions) (figure 15). Cadmium iodide, on the other hand, gives a very pronounced maximum, even though the half-wave potential of cadmium in very dilute iodide solutions is practically the same as in chloride solutions. The occurrence of the (positive) maximum is explained (35) by the fact that the iodide ions are strongly capillary-active, and they shift the electrocapillary zero to a more negative potential so that it no longer coincides with the discharge potential of the cadmium ions. Other capillary-active anions, such as S^{--}, CN^-, CNS^-, etc., shift the electrocapillary zero in a similar way, while capillary-active cations shift it to a more positive potential (15).

Care must be exercised in the interpretation of the effect of these capillary-active ions on maxima. Capillary-active anions are adsorbed on positively charged and uncharged mercury (increasing adsorption with increasing positive charge), and they therefore attract an almost equivalent amount of cations to the surface in a triple layer (123). For this reason the total effect of capillary-active ions may be very complicated. For example, Lingane (65) found that the positive maximum due to lead ions in 0.1 N potassium chloride was almost completely suppressed when the solution was made 0.001 N with respect to iodide ions. On the other hand, in the absence of potassium chloride the lead maximum was considerably accentuated in 0.001 N and 0.005 N potassium iodide, and was not completely eliminated even in 1 N potassium iodide (in the latter case the lead was present chiefly as PbI_4^{--} anions). It is probable that a similar effect of iodide ions will be found in the case of cadmium and other metal ions.

Heyrovský and Vascautzanu (48) have demonstrated the effect of thiocyanate ions in shifting the electrocapillary zero and the resultant effect on the slight negative maximum of cadmium nitrate. They found that the slight negative maximum in a 0.005 *M* cadmium nitrate solution was eliminated by the addition of sufficient potassium thiocyanate to make its concentration 0.001 *N*. With further additions of thiocyanate ions the electrocapillary zero was shifted to more negative potentials, and the cadmium maximum reappeared on the positive side of the electrocapillary zero.

Similar phenomena were observed (48) in the electroreduction of (undissociated) maleic acid. The current–voltage curve of 0.02 *M* maleic acid in 1 *N* hydrochloric acid shows a pronounced maximum (note the occurrence of a maximum at this high electrolyte concentration), which, according to Heyrovský and Vascautzanu, is a negative maximum. When the maleic acid solution was made about 0.002 *N* with respect to potassium iodide the maximum disappeared, but it reappeared again as a positive maximum when the electrocapillary zero was shifted to still more negative potentials by further addition of iodide.

Instead of changing the location of the electrocapillary zero, use can be made of complex formation to shift the discharge potentials of metal ions which are normally reduced on the positive side of the electrocapillary zero to more negative values, until they coincide with the electrocapillary zero, and the maxima then disappear. By adding a large excess of the complex-forming salt, the discharge potentials can, in certain cases, be shifted to such negative values that the maxima are changed from positive to negative maxima (48).

4. Influence of external resistance in the cell circuit on the maxima

Brdička (7) has recently shown that the acute maximum accompanying the discharge of mercurous ions from a slightly acid mercurous nitrate solution was greatly suppressed and almost completely eliminated by a high resistance in series with the cell. As the external resistance was increased from 26 to 5000 ohms the maximum decreased markedly, but the peak of the maximum was at the same value of the total applied E.M.F , that is, at the same value of the *total* potential drop across both the external resistance and the cell. The current–voltage curves during the deposition of mercury (depolarized electrode) were straight lines up to the peak of the maximum, the slope being determined by the total resistance according to Ohm's law. The maximum occurred at the same total applied E.M.F., independent (within a certain range) of the external resistance, which means that the potential of the dropping electrode itself at the peak of the maximum was shifted to more positive values with increasing external resistance, or that the value of E_c at the maximum became smaller with increasing external resistance. At first glance this effect of external resistance is difficult to understand, since with the same value of E_c we would expect the same current, independent of the external resistance. This actually is the case with the quiet mercury electrode, since in this case the external resistance cannot have an effect upon the height and location of the maximum.

In order to interpret the peculiar effect obtained with the dropping electrode, we must realize that the measured values of the current and of E_{cell} are average values; the actual values of i and E_{cell} vary during the growth of the drop. In the one extreme case in which the external resistance is zero, the applied E.M.F. is equal to E_{cell}. Under these conditions the latter is constant during the growth of the drop, and, as will be shown below, the current during the formation of a drop when the electrode is *depolarized* will increase with the area of the drop. In the other extreme case, in which the internal resistance is negligibly small with regard to the external resistance, E_{cell} will increase during the growth of the drop when the electrode is depolarized, but the current will remain practically constant after the very early stage of the formation of the drop. Hence the fluctuation of the galvanometer when dealing with a depolarized dropping electrode should decrease with increasing external resistance and finally should disappear.

Let us now compare the change of the current during the formation of a drop (depolarized electrode) in the two extreme cases when the average E_{cell} is the same, but when the external resistance in one case is equal to zero and in the other case is infinitely great. Naturally, with the same average E_{cell} the average current measured will be nearly the same. In the absence of an external resistance the current should increase during the formation of the drop, but, on the other hand, with a large external resistance in the circuit the current remains practically constant after the very early stages of the formation of the drop. As the average current is the same in both cases, the *current density* during the early stages of the formation of the drop in the presence of a large external resistance is much greater than in the absence of external resistance. It has been stated earlier in this section that an acute maximum is characterized by a sudden polarization due to an exhaustion of depolarizer in the immediate vicinity of the growing drop. The drop then remains polarized, and the current drops from the maximum to the value of the diffusion current. Since the current density during the early stages of the formation of the drop is, with the same average E_{cell}, much greater with a large external resistance in the circuit than in the absence of an external resistance, the critical exhaustion of the depolarizer (maximum) will be obtained at a smaller average E_{cell} when the external resistance is great than when there is no external resistance in the circuit. From this it follows that the height of the maximum must also decrease with increasing external resistance. Brdička (7) calculated the change of the current with time as a function of the external resistance. His derivations are given below in a condensed form.

When the dropping electrode is depolarized and the external resistance is equal to zero, the current is determined by Ohm's law:

$$i = \frac{E_a}{W_i} \tag{42}$$

in which W_i is the internal resistance and E_a is equal to the total applied E.M.F. The internal resistance changes with the size of the mercury drop. According to Ilkovič (54)

$$W_i = \frac{\rho}{4\pi r} \tag{43}$$

in which ρ denotes the specific resistance of the electrolyte and r the radius of the mercury drop considered to be spherical. Earlier in this paper it has been shown that r is a simple function of the time t,

$$r = at^{1/3} \tag{44}$$

in which a is a function of the characteristics of the capillary used (equation 6). From equations 42, 43, and 44 it follows that

$$i = \frac{E_a 4\pi a t^{1/3}}{\rho} \tag{45}$$

The average current, i', according to Ilkovič (52) is

$$i' = \frac{4\pi E_a a}{t_{\text{max.}}} \int_0^{t_{\text{max.}}} t^{1/3}\,\mathrm{d}t = \frac{E_a}{W'} = \frac{E_a}{4/3 W_{\text{min.}}} \tag{46}$$

in which W' is the mean resistance which is equal to 4/3 $W_{\text{min.}}$, where $W_{\text{min.}}$ is the minimum resistance at the moment when the drop falls. When the drop is depolarized and the external resistance in the circuit is equal to W_e, the current at any time t is given by

$$i = \frac{E_a}{W_i + W_e} = E_a \frac{4\pi a t^{1/3}}{\rho + 4\pi a t^{1/3} W_e} \tag{47}$$

and the mean current, i', by

$$\begin{aligned} i' &= \frac{E_a 4\pi a}{t_{\text{max.}}} \int_0^{t_{\text{max.}}} \frac{t^{1/3}\,\mathrm{d}t}{\rho + 4\pi a t^{1/3} W_e} \\ &= \frac{E_a}{W_e}\left\{1 - \frac{3}{2}\frac{W_{\text{min.}}}{W_e} + 3\left(\frac{W_{\text{min.}}}{W_e}\right)^2 - 3\left(\frac{W_{\text{min.}}}{W_e}\right)^3 \ln\left(1 + \frac{W_e}{W_{\text{min.}}}\right)\right\} \end{aligned} \tag{48}$$

The mean resistance, W', is given by the expression,

$$W' = \frac{W_e}{1 - \frac{3}{2}\frac{W_{\text{min.}}}{W_e} + 3\left(\frac{W_{\text{min.}}}{W_e}\right)^2 - 3\left(\frac{W_{\text{min.}}}{W_e}\right)^3 \ln\left(1 + \frac{W_e}{W_{\text{min.}}}\right)} \quad (49)$$

Brdička writes this expression in a simplified form:

$$W' = W_e + \alpha W_{\text{min}}. \quad (50)$$

in which α depends upon the ratio $W_{\text{min}}./W_e$ as shown in the following table:

$W_{\text{min.}}/W_e$	1/1000	1/100	1/10	1	10	100
α	1.499	1.493	1.457	1.378	1.336	1.334

In the electrolysis of a slightly acid mercurous nitrate solution, the minimum resistance of which was 1008 ohms, Brdička found that equation 50 was valid within 2 per cent when the external resistance was varied from 26 to 8026 ohms.

From equation 45 it is evident that with the depolarized electrode the current should increase with $t^{1/3}$ during the formation of a drop when the external resistance is zero. On the other hand, it is seen from equation 47 that the current should not change during the formation of the drop when the external resistance becomes so great that ρ is negligibly small compared to $4\pi a t^{1/3} W_e$. If this extreme condition is fulfilled, we can write, instead of equation 47

$$i = \frac{E_a}{W_e}$$

Brdička (7) determined current–time curves during the formation of a drop in the neighborhood of the maximum in slightly acid mercurous nitrate solutions with the aid of a galvanometer of extremely short period with various external resistances in the circuit. In the absence of an external resistance the current increased continuously and rapidly during the formation of each drop, apparently in direct proportion to the increase of the area. With increasing external resistance the rate of increase of the current during the growth of the drop became increasingly less. Indeed, with a large external resistance the current became almost constant after the early stages of drop formation. The current–time curves obtained by Ilkovič (1936) in the electrolysis of oxygen in 0.002 N potassium chloride solutions in the immediate neighborhood of the maximum are also of interest in this connection and can be interpreted in a similar way.

IX. EQUATIONS OF POLAROGRAPHIC WAVES AND THE SIGNIFICANCE OF THE HALF-WAVE POTENTIAL

The steeply rising part of a current-voltage curve between the decomposition potential and the potential at which a constant limiting or diffusion current is reached is known as a "polarographic wave." In this section we shall consider the relations that exist between the potential of the dropping electrode and the corresponding current at each point on a polarographic wave, that is, the equations of polarographic waves.

In the usual type of electrolysis experiment, employing large electrodes, relatively large concentrations of reducible or oxidizable substances, and thorough stirring, the concentration polarization is reduced to a minimum and the current increases almost without limit after the decomposition potential is exceeded. Under these conditions the current-voltage curve is practically a straight line, which follows Ohm's law, with a slope equal to the reciprocal of the resistance of the cell. On the other hand, in electrolyses with the dropping mercury electrode, and platinum microelectrodes in unstirred solutions, conditions are such that concentration polarization is favored as much as possible, rather than eliminated. Hence the normal polarographic waves (no maximum present) obtained with the dropping electrode are not straight lines but definitely S-shaped curves. The current at each point on a normal polarographic wave is an exponential function of the potential of the dropping electrode.

1. Electrodeposition of simple metal ions

If the electrodeposition of metal ions at the dropping mercury cathode takes place reversibly according to the equation

$$M^{n+} + ne + Hg \rightleftarrows M(Hg)$$

then the potential at each point on the polarographic wave should be given by

$$E = E_a^0 - (RT/nF) \ln (a_a/a_0) \qquad (51)$$

In this equation a_a is the activity of the deposited metal atoms in the amalgam formed on the surface of the mercury drops, a_0 is the activity of the reducible metal ions in the layer of solution at the *surface of the drops*, and E_a^0 is the standard or normal potential of the metal amalgam, that is, the E.M.F. of the cell

$$M(Hg)(a = 1) \mid M^{n+}(a = 1) \parallel \text{reference electrode}$$

If we introduce the usual relation between concentration and activity, equation 51 becomes

$$E = E_a^0 - (RT/nF) \ln (f_a/f_s) - (RT/nF) \ln (C_a/C_0) \qquad (52)$$

in which f_a is the activity coefficient of the metal atoms in the amalgam and f_s is the activity coefficient of the reducible metal ions in the solution.

When an excess of foreign salt is present in the solution, the reducible ions reach the surface of the dropping electrode entirely by diffusion, and the current is governed by the rate of diffusion. In turn, the latter will depend directly on the difference in concentration between the depleted surface layer and the body of the solution, so Heyrovský and Ilkovič (44) write

$$i = K(C - C_0)$$

or

$$C_0 = C - (i/K) \tag{53}$$

in which i and C_0 are the current and the corresponding concentration in the depleted surface layer at each point on the wave, and C is the concentration in the body of the solution. When a constant diffusion current is reached, C_0 will be reduced to a constant minimum value, and since this minimum value is negligibly small compared to C, we have

$$i_d = KC \quad \text{or} \quad C = i_d/K \tag{54}$$

The validity of this equation, in which K is the diffusion current constant, has already been demonstrated.

Heyrovský and Ilkovič (44) assume that the average concentration of the amalgam at any point on the wave is directly proportional to the current, that is, $C_a = ki$. According to these authors (44) k is inversely proportional to the square root of the diffusion coefficient of the metal atoms in mercury.

When the foregoing relations are introduced into equation 52, we obtain

$$E = E_a^0 - (RT/nF) \ln (f_a kK/f_s) - (RT/nF) \ln (i/(i_d - i)) \tag{55}$$

where E and i are corresponding values at any point on the polarographic wave.

Now the half-wave potential, designated by $E_{1/2}$, is defined as the potential of the dropping electrode at the point on the polarographic wave where $i = i_d/2$. It is evident that when $i = i_d/2$ the last log term in equation 55 is zero, and hence we find that

$$E_{1/2} = E_a^0 - (RT/nF) \ln (f_a kK/f_s) \tag{56}$$

and

$$E = E_{1/2} - (RT/nF) \ln (i/(i_d - i)) \tag{57}$$

This is the equation of the polarographic wave in the electrodeposition of simple metal ions, first derived by Heyrovský and Ilkovič (44).

If equation 57 is valid, it is evident that a plot of E against ln $(i/(i_d - i))$ should give a straight line with a slope equal to RT/nF, and the potential where the log term is equal to zero should be the half-wave potential. This prediction and the general validity of equation 57 in the deposition of various metal ions have been verified experimentally by Tomeš (119) and Lingane (65). For example, the current-voltage curve of 0.001 M thallous chloride in 0.9 N potassium chloride, together with the straight line obtained by plotting E against log $(i/(i_d - i))$, is given in figure 22. The slope of the straight line is 0.061 volt, in good agreement with the theoretical value 0.059 volt for the electrodeposition of a univalent metal ion, and the potential corresponding to a value of zero for the log term is the half-wave potential of the current-voltage curve. Tomeš (119) and Lingane (65) have also verified equation 57 in the electrodeposition of lead, cadmium, and indium ions from 0.1 N and 1 N potassium chloride. Some typical results (65) are shown in figures 23 and 24. In all these cases the log plot is a good straight line, with a slope in close agreement with the theory, which should be 0.030 volt for cadmium and lead ions and 0.020 volt for trivalent indium ions.

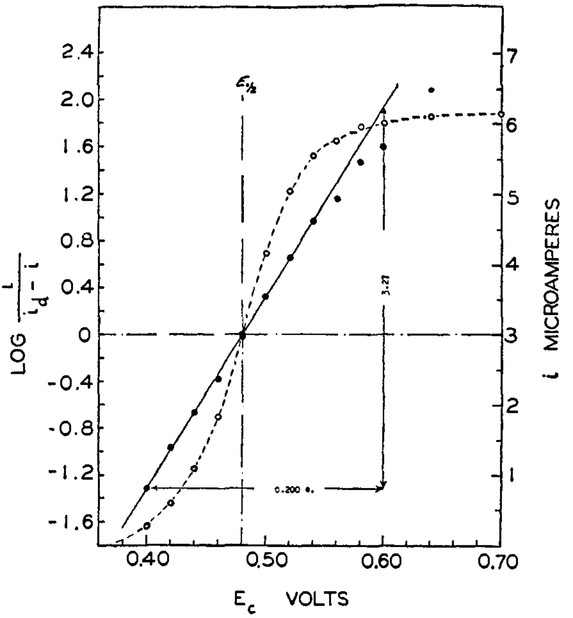

Fig. 22. Test of equation 57 in the discharge of 0.001 M thallous chloride from 0.9 N potassium chloride.

The foregoing derivations are based on the assumption that the rate of

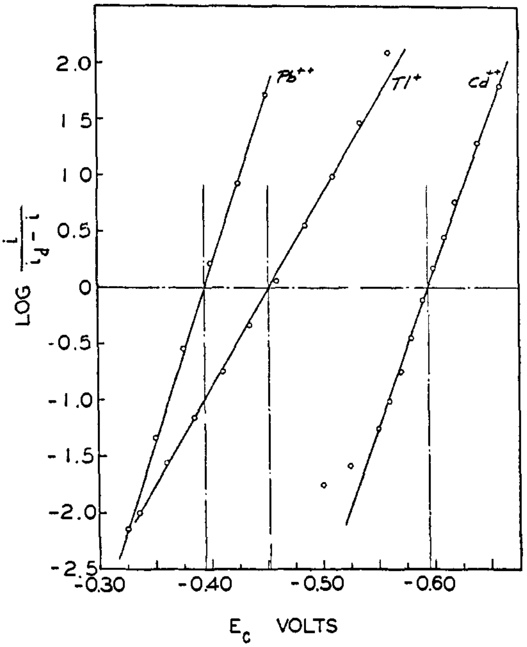

FIG. 23. Test of equation 57 in the discharge of lead, thallous, and cadmium ions from 0.1 N potassium chloride.

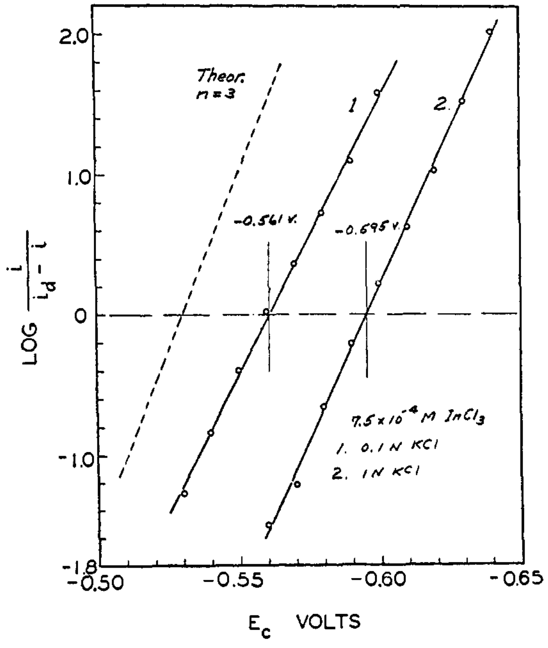

FIG. 24. Test of equation 57 in the discharge of indium ions from 0.1 and 1 N potassium chloride.

diffusion is the current-determining factor. If this condition is not fulfilled, the slope of the current–voltage curve will be less than corresponds to equation 57. In such a case the plot of E against ln $(i/(i_d - i))$ may still be a straight line, but the slope may not correspond to the true value of n. For example, we (65) found that the log plot of the current–voltage curve of nickel in ammoniacal medium was a straight line, but that its slope was less than corresponds to the known n value of 2. When gelatin was added to the solution, the slope deviated still more from the theoretical value. This abnormal behavior may be caused by a certain degree of irreversibility ("chemical polarization") in the deposition of nickel ions under these conditions. We (65) found that the slope of the log plot of the current–voltage curve of lead in neutral medium is also markedly changed (apparent value of n less than 2) when gelatin is present in the solution.

By differentiating equation 57 we obtain

$$\mathrm{d}E/\mathrm{d}i = -(RT/nF)[(1/i) + (1/(i_d - i)] \qquad (58)$$

$$\mathrm{d}^2E/\mathrm{d}i^2 = (RT/nF)[(1/i^2) - (1/(i_d - i)^2)] \qquad (59)$$

Since the slope of the polarographic wave is $\mathrm{d}i/\mathrm{d}E$, we see from equation 58 that the slope or steepness of the wave depends on both the valence, n, and the concentration of the reducible ions. Hence at a given value of E the slope of the wave should be greater, the greater the concentration of the reducible ions, and at a given concentration the steepness of the wave should be greater, the greater the valence of the reducible ions. In other words, at a given concentration the wave of a divalent ion should rise more steeply than that of a univalent ion. These characteristics of the waves are actually found experimentally.

By setting the second differential (equation 59) equal to zero, we find that the curve of equation 57, and hence the polarographic wave, should have a point of inflection when i is equal to $i_d/2$. The half-wave potential thus corresponds to the true inflection point of the wave, and is therefore a significant constant for each reducible metal ion (44).

We see from equation 56 that $E_{1/2}$ should depend on the values of E^0_a, K, k, f_a, and f_s. At a given concentration of foreign salts, E^0_a, K, and f_s will be constant and independent of the concentration of the reducible ions. Since the amalgams formed on the surface of the mercury drops are usually very dilute, we may safely assume that they behave as ideal solutions, and hence it is to be expected that k and f_a will also be almost constant in the range of amalgam concentrations involved in polarographic electrolyses. It is to be expected, therefore, that with a given composition of the solution with respect to foreign salts, the values of $E_{1/2}$ should be practically constant and independent of the concentration of the reducible ions (38, 44). This has actually been found to be true by many investigators, and it is demonstrated by the data in table 8 that we have obtained (65). The constancy of $E_{1/2}$ at various concentrations of the reducible ions is obviously one of the most important characteristics of polarographic waves from the standpoint of qualitative polarographic analysis.

Since f_s will decrease with increasing ionic strength, it is evident from equation 56 that the half-wave potentials of metal ions should be shifted to somewhat more negative values as the concentration of foreign salt is increased. However, since only the logarithm of f_s is involved, a considerable change in the activity coefficient should have only a relatively small effect on the half-wave potential.

TABLE 8

Constancy of the half-wave potentials of several metal ions at various concentrations in 0.1 N potassium chloride

Half-wave potentials at 25°C. in volts, referred to the saturated calomel electrode

C	HALF-WAVE POTENTIALS			
	Tl^+	Pb^{++}	Cd^{++}	Zn^{++}
millimoles per liter	*volts*	*volts*	*volts*	*volts*
0.05	(−0.45)			
0.1	−0.462	−0.396		
0.2			−0.594	−0.990
0.5	0.457	0.396	0.593	0.989
1.0	0.460	0.392	0.594	
2.0	0.456	0.397	0.601	0.999
5.0	0.459	0.394	0.598	0.992
10.0		0.398	0.605	−1.003
Average.....	−0.459 ± 3	−0.396 ± 3	−0.599 ± 5	−0.995 ± 6

It should also be mentioned that the half-wave potential of a given metal ion is usually not influenced by the preceding discharge of other metal ions or uncharged substances. The half-wave potentials of metal ions in mixtures are, in general, the same as in their single solutions. In fact, the same is true for most reducible substances, both inorganic and organic. The half-wave potential is also independent of the particular capillary used and of the rate of dropping (44).

According to Heyrovský and Ilkovič (44), the product kK in equation 56 is equal to $(D_s/D_a)^{1/2}$, where D_a is the diffusion coefficient of the metal atoms in the amalgam formed on the surface of the mercury drops and D_s is the diffusion coefficient of the reducible metal ions in the solution. Heyrovský and Ilkovič assume that the quantity $(D_s/D_a)^{1/2}$ is practically equal to unity. On the basis of this assumption, and since the quotient f_a/f_s will also be of the order of unity, it follows that $E_{1/2}$ for a given metal ion should be at least approximately equal to E_a^0. Furthermore, if we employ the usual convention that the activity of a solid metal is unity, then E_a^0 will be identical with the ordinary standard or normal potential of the metal, E_M^0. Hence the half-wave potentials of the various metal ions should be about the same as the ordinary standard potentials. This is demonstrated by the following comparison of the values of $E_{1/2}$ and E_M^0 of various metals, referred to the saturated calomel electrode. The $E_{1/2}$ values of copper, sodium, and potassium ions have been taken from the compilation given by Heyrovský (38).

	Cu^{++}	Pb^{++}	Tl^+	Cd^{++}	Zn^{++}	Na^+	K^+
$E_{1/2}$ vs. S.C.E..........	+0.12	−0.396	−0.459	−0.599	−0.995	−2.12	−2.14
E_M^0 vs. S.C.E............	+0.10	−0.372	−0.582	−0.647	−1.008	−2.96	−3.17

It will be noted that the $E_{1/2}$ values are in most cases fairly close to the ordinary reversible standard potentials, except for the alkali metal ions whose half-wave potentials are of the order of 1 volt more positive than the corresponding standard potentials.

The experimentally determined half-wave potentials of a large number of inorganic ions are shown in figure 25. This chart was compiled by V. Majer (44), and it is appropriately called a "polarographic spectrum" in analogy to the ordinary optical spectrum of the elements.

In certain cases the reduction of metal ions at the dropping electrode may proceed simply to a lower valence state, rather than to the metallic state. This is the case, for example, in the reduction of ferric, chromic, and cobaltic ions, which are respectively reduced to ferrous, chromous, and cobaltous ions. In such a case the reduction may be represented by

$$M^{n+} + me \rightleftarrows M^{(n-m)+}$$

If this reduction takes place reversibly, the potential of the dropping electrode at any point on the wave should be given by

$$E = E^0 - (RT/mF) \ln (f_{\text{red.}}/f_{\text{ox.}}) - (RT/mF) \ln (C^0_{\text{red.}}/C^0_{\text{ox.}}) \qquad (60)$$

where $C^0_{\text{red.}}$ and $C^0_{\text{ox.}}$ are, respectively, the concentrations of the reduced and oxidized forms at the surface of the dropping electrode, and $f_{\text{red.}}$ and $f_{\text{ox.}}$ are the corresponding activity coefficients. It is evident that in this case E^0 is the ordinary standard oxidation–reduction potential of the system. In such a reduction the dropping electrode simply functions as an indifferent electrode. If the solution originally contains none of the reduced form of the metal ions, it may be readily shown that the equation of the

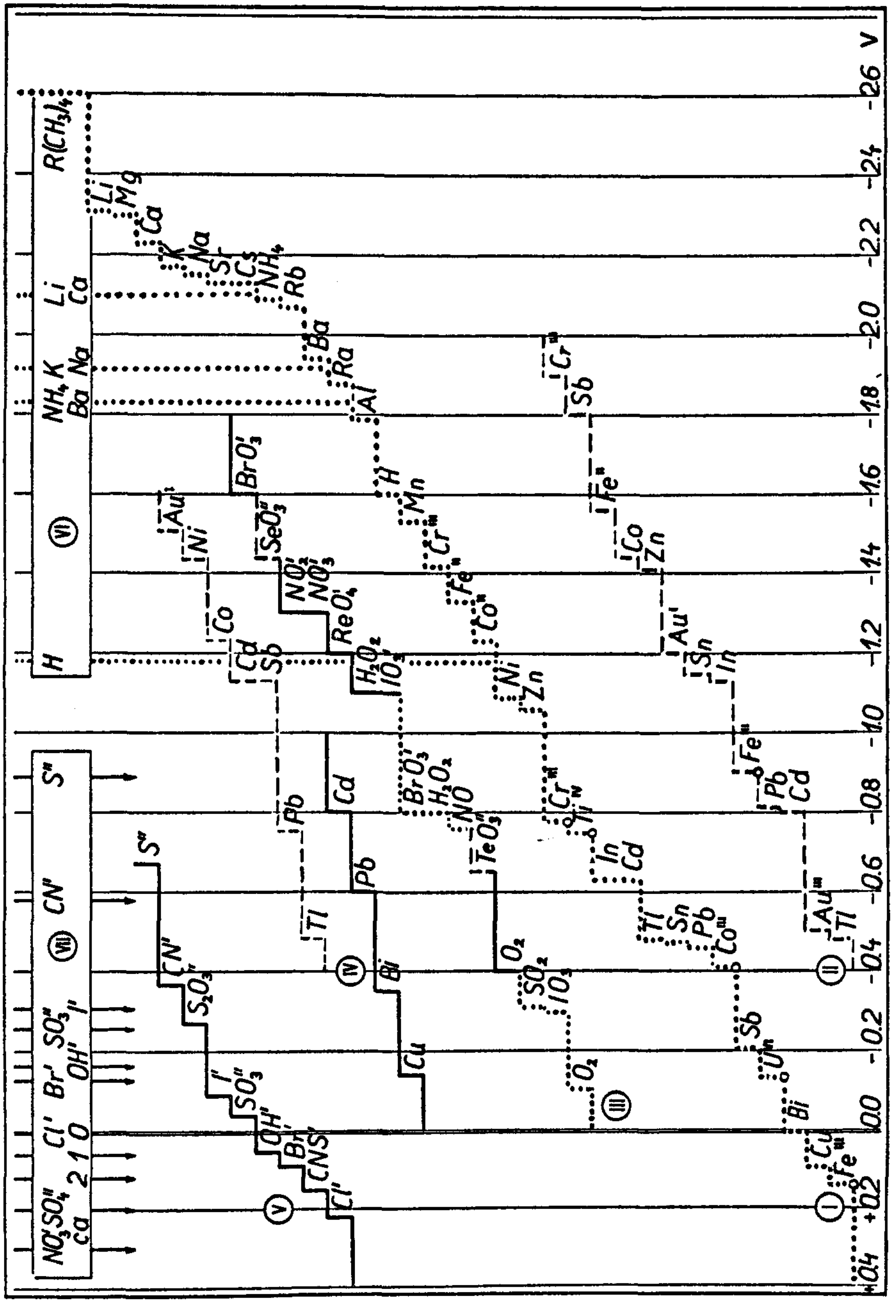
+0.4
+0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
-1.6
-1.8
-2.0
-2.2
-2.4
-2.6 V
I
II
III
IV
V
VI
VII
NO_3' SO_4'' ca
2 1 0
Cl' Br' OH'
SO_3'' I'
CN'
S''
H
NH_4 K Ba Na
Li Ca
$R(CH_3)_4$
Cl'
CNS'
Br'
OH'
SO_3''
I'
S_2O_3''
CN'
S''
Cu
Bi
Pb
Cd
BrO_3'
SeO_3''
NO_2'
NO_3'
ReO_4'
H_2O_2
IO_3'
Au
Ni
Co
Cd
Sb
Pb
Tl
O₂
SO_2
IO_3'
TeO_3''
NO
H_2O_2
BrO_3'
Li
Mg
Ca
K
Na
Sr
Cs
NH_4
Rb
Ba
Ra
Al
H
Mn
Cr'''
Fe''
Co''
Ni
Zn
Cr'''
Tl^{IV}
In
Cd
Tl
Sn
Pb
Co'''
Sb
U^{IV}
Bi
Cu
Fe'''
Cr''
Sb
Fe''
Co
Zn
Au'
Sn
In
Fe''
Pb
Cd
Au'''
Tl

FIG. 25

polarographic wave should be identical in form with equation 57. Hence, just as in the electrodeposition of metal ions, the half-wave potential in the electroreduction of simple metal ions should correspond to the true inflection point of the wave and should be independent of the concentration of the reducible ions (44). In agreement with this prediction, the current-voltage curves obtained by Prajzler (95) show that the half-wave potential in the reduction of chromic to chromous ions is independent of the concentration of chromic ions.

2. Electrodeposition of complex metal ions

Although the deposition of metal ions from complex salts is much used in practical polarographic work (38, 50, 93, 106), the detailed kinetics of such reductions have not yet been thoroughly studied. Experimentally, it is found that the half-wave potentials of metal ions are shifted to more negative values by complex formation (figure 25). The half-wave potentials of complex metal ions are also generally independent of the concentration of the metal ion complex, provided an excess of the complex-forming substance is present (44).

Heyrovský and Ilkovič (44) assume that the reduction of complex metal ions takes place in two steps according to the scheme

$$MX_b^{(bm-n)} \rightleftarrows M^{n+} + bX^{m-} \tag{61}$$

$$M^{n+} + ne + Hg \rightleftarrows M(Hg) \tag{62}$$

They further assume that the dissociation of the complex proceeds rapidly enough to maintain equilibrium between the complex ions, the free metal ions, and the complex-forming anions at the surface of the dropping

FIG. 25. "Polarographic spectrum" according to V. Majer. Values of the half-wave potentials of inorganic ions in various media. I. Reduction and deposition potentials of cations in neutral or acidic solution. II. Reduction and deposition potentials of ions in alkaline solution. III. Reduction potentials of anions and molecules in neutral (solid line) or in acidic (dotted line) solution and in ammonia buffer (dashed line). NO_3^- and NO_2^- in 0.1 N lanthanum chloride. IV. Reduction potentials of complexes. Solid line, in 10 per cent sodium potassium tartrate; dashed line, in 1 N potassium cyanide. V. Depolarizing potentials of anions (anodic polarization). VI. Deposition potentials of cations of the commonly used indifferent electrolytes present in excess (1000 ×) in the solution. VII. Potentials of the large mercury reference electrode in solutions containing the usual anions in ca. 1 N concentration. (The numbers 0, 1, and 2 refer to chloride concentrations of 1, 0.1, and 0.01 N.) All values are the potentials at the half diffusion current except those which are marked by a little circle signifying the contact point of a 45° tangent at a 2-cm. wave. The values of the potentials refer to the 1 N calomel electrode as zero and to room temperature.

electrode. If this assumption is correct, the concentration of free metal ions at the electrode surface should be given (44) by

$$(\mathrm{M}^{n+}) = K_c(\mathrm{MX}_b^{(bm\,-\,n)-})/(\mathrm{X}^{m-})^b \tag{63}$$

where K_c is the equilibrium constant (complex constant) of equation 61. On the basis of these assumptions Heyrovský and Ilkovič predict that the negative shift in the half-wave potential should be equal to $(RT/nF)\ \ln K_c$, when the concentration of the complex-forming anions, X^{m-}, is unity. It should be realized that this can be true only if the diffusion coefficient of the complex metal ions is the same as that of the simple (hydrated) metal ions. If the diffusion coefficients of the simple and complex metal ions are not equal, the negative shift in the half-wave potential will also depend on the logarithm of the ratio of the two diffusion coefficients, in addition to the logarithm of the complex constant. As yet these postulates have not been thoroughly tested experimentally.

The kinetics of the reduction of complex metal ions is undoubtedly much more complicated than the scheme represented by equations 61 and 62. In certain cases the rate of dissociation of the complex may be slower than the discharge of the liberated metal ions, and equilibrium will then not be maintained during the discharge. For example, Pines (93) has obtained evidence that the rate of dissociation of the various complex zinc cyanides is relatively slow, and that equilibrium is not maintained at the surface of the dropping electrode. Brochet and Petit (9) and Foerster (13), from studies of the alternating current electrolysis of complex metal cyanides, have obtained data which lead to the same conclusion. Furthermore, Herman (29) has obtained evidence that the dissociation of gold cyanide and gold hydroxide complexes and the rate of conversion of one complex into the other are relatively slow processes. If these interpretations are correct, it is evident that the actual concentration of free metal ions at the surface of the dropping electrode will be smaller than we would calculate from equation 54, and the rate of dissociation of the complex, rather than its rate of diffusion, should be the current-determining factor.

It is also conceivable that the reduction of very stable complex metal ions may take place by the direct capture of electrons from the electrode without preliminary dissociation. In such a case the rate of the direct interaction of the complex metal ions with electrons, and not the rate of dissociation of the complex, should be the current-determining factor on the polarographic wave. If the positively charged central ion in the complex is well shielded the capture of electrons may be hindered, and the potential of the dropping electrode will then not correspond to equilibrium conditions.

Tomeš (119) has studied the kinetics of the reduction of the weak electrolyte mercuric cyanide, a case quite similar to the reduction of complex metal ions. In this case the reduction apparently takes place reversibly. Tomeš found that the current–voltage curve was not symmetrical with respect to the half-wave point, and that consequently the half-wave potential was shifted to more negative values with increasing concentration of the mercuric cyanide (no excess cyanide present). He also found that the half-wave potential was greatly dependent on the pH of the solution, owing to the hydrolysis of the liberated cyanide ions at the surface of the mercury drops. Tomeš showed that these results correspond with the theory on the basis that the reduction takes place reversibly.

The discharge of hydrogen. The discharge of hydrogen ions at the dropping electrode has been the subject of numerous investigations, which are discussed by Professor Heyrovský in an accompanying paper in this Journal. Therefore we shall mention only a few of the more important results obtained. On the basis of theoretical consideration Heyrovský (32) predicted that the discharge potential (not $E_{1/2}$) of hydrogen ions should be shifted to more positive values with increasing hydrogen-ion concentration, according to

$$(2RT/F)\ \Delta \ln C_{\mathrm{H^+}}$$

These predictions were experimentally verified by Herasymenko (25). Herasymenko and Šlendyk (27) have also shown that the overvoltage of hydrogen is shifted to more negative values with increasing concentration of neutral salts in the solution. They showed that the negative shift in the overvoltage was greater, the greater the valence of the cations of the neutral salt, but that in all cases the discharge potential approached a limiting constant value with increasing concentration of the neutral salt.

Tomeš (119) has recently made a careful study of the discharge of hydrogen from strong and weak acids. In the discharge of hydrogen from hydrochloric acid in the presence of excess lithium chloride or calcium chloride, he found that $E_{1/2}$ was not constant, but was shifted by 0.028 volt to more positive values for a tenfold increase in the concentration of hydrochloric acid. In the discharge of hydrogen ions from acetic acid in the presence of excess lithium chloride, Tomeš found that $E_{1/2}$ was shifted by 0.087 volt to more negative values per tenfold increase in the acetic acid concentration. He also found, in the discharge of hydrogen from buffer mixtures of acetic acid and lithium acetate in excess lithium chloride, that $E_{1/2}$ was shifted to more negative values with increasing concentration of the lithium acetate at a constant concentration of acetic acid, but that with a constant concentration of lithium acetate $E_{1/2}$ was shifted by 0.027

volt to more positive values per tenfold increase in the acetic acid concentration.

Heyrovský and Müller (45), and especially Novák (86), have studied the discharge of hydrogen and deuterium at the dropping electrode from mixtures of light and heavy water. Novák found that the half-wave potential of hydrogen from hydrochloric acid was 0.087 volt more negative in heavy water (99.6 per cent) than in ordinary water. The hydrogen overvoltage in light and heavy water and the separation coefficient of hydrogen and deuterium at the dropping mercury electrode have been exhaustively discussed by Heyrovský (39).

3. Reduction of organic compounds

According to Heyrovský and Ilkovič (44), the reversible reduction of organic compounds at the dropping electrode may be represented by the equation

$$\mathrm{R} + n\mathrm{H}^+ + ne \rightleftarrows \mathrm{RH}_n \tag{64}$$

In the majority of cases n is equal to 2. If this reduction takes place reversibly the potential of the dropping electrode should be given by

$$E = E^0 - (RT/nF) \ln (C^0_{\mathrm{RH}_n}/C^0_{\mathrm{R}}) + (RT/F) \ln C^0_{\mathrm{H}^+} \tag{65}$$

If the solution originally contains none of the reduced form RH_n, we may assume that $C^0_{\mathrm{RH}_n} = ki$. Furthermore, C^0_{R} at the surface of the dropping electrode should be related to the concentration of R in the body of the solution, C_{R}, by an expression analogous to equation 53, that is,

$$C^0_{\mathrm{R}} = C_{\mathrm{R}} - i/K = (i_d - i)/K \tag{66}$$

where, as before, K is the diffusion current constant. Hence equation 65 becomes

$$E = E^0 - (RT/nF) \ln (i/(i_d - i)) - (RT/nF) \ln kK + (RT/F) \ln C^0_{\mathrm{H}^+} \tag{67}$$

It is evident then that, if the reduction takes place reversibly, the current–voltage curve should be symmetrical about the half-wave point. Hence at a constant value of the hydrogen-ion concentration the half-wave potential should be constant and independent of the concentration of the reducible organic substance (44). This is found to be true in many cases (115).

Furthermore, E^0 is the ordinary reversible oxidation–reduction potential of the system. From equation 67 we see that the half-wave potential when $i = i_d/2$ should be given by

$$E_{1/2} = E^0 - (RT/nF) \ln kK + (RT/F) \ln C^0_{\mathrm{H}^+} \tag{68}$$

According to Heyrovský and Ilkovič the product kK in this equation is equal to $(D_{ox.}/D_{red.})^{1/2}$, where $D_{ox.}$ and $D_{red.}$ are, respectively, the diffusion coefficients of the oxidized and reduced forms of the reducible substance. Since $(D_{ox.}/D_{red.})^{1/2}$ will usually have a value close to unity, the half-wave potential in reversible reductions should be practically coincident with the reversible oxidation–reduction potential of the system at a given pH. Müller and Baumberger (81) and Tachi (115) have demonstrated that this is true in the reduction of quinone, in the oxidation of hydroquinone, and in the reversible oxidation and reduction of various other organic substances at the dropping electrode.

The reduction of many organic substances at the dropping electrode does not take place reversibly; in fact, irreversible reductions are more common than reversible reductions. For example, the reduction of nitro compounds, of most unsaturated compounds, and of aldehydes and ketones is an irreversible process at the dropping electrode. According to Heyrovský and Ilkovič (44) and Tachi (115), even in such cases the half-wave potential is a characteristic constant, at a given pH, of the particular substance and is independent of its concentration. This has been demonstrated by Vopička (125) in the irreversible reduction of fumaric and maleic acids. In the irreversible reduction of these substances the negative shift in $E_{1/2}$ with increasing pH is usually different from what we would expect from equation 68. For example, Vopička found that the shift in the half-wave potential of maleic acid with increasing pH was twice as great, and that of fumaric acid three times as great, as would be expected from equation 68. This difference makes possible the differentiation of these two stereoisomers in alkaline medium.

The effect of the structure of organic compounds, particularly aldehydes and ketones, on their reduction potentials at the dropping electrode has been studied by Shikata and Tachi (108), Winkel and Proske (126), Adkins and Cox (3), and Tachi (115). The reduction potentials of the various isomeric dinitrophenols and dinitrobenzenes have been studied by Shikata and Hozaki (107). Tables of the reduction potentials of a variety of organic substances have also been given by Heyrovský (38) and Hohn (50). The reduction of organic compounds at the dropping electrode is discussed in detail by Dr. O. H. Müller in an accompanying paper in this Journal.

X. ANODIC CURRENT–VOLTAGE CURVES WITH THE DROPPING ELECTRODE

So far we have discussed the current–voltage curves obtained with the dropping electrode functioning as cathode, that is, electroreductions. It is also possible to obtain current–voltage curves, and limiting currents, with the dropping electrode functioning as the anode of the cell.

Revenda (99) has shown that limiting currents are obtained with the dropping mercury anode in dilute solutions of halide, cyanide, sulfide, thiocyanate, hydroxide, and other ions which form insoluble or complex compounds with mercury. In such cases the primary electrode reaction is the anodic dissolution of mercury,

$$2\mathrm{Hg} \rightleftarrows \mathrm{Hg}_2^{++} + 2e \tag{69}$$

In solutions containing no ions which form insoluble or complex mercury salts, this reaction sets in at the dropping anode at about +0.3 volt (99), and with increasing positive potential the corresponding current increases rapidly and apparently without limit. If the anodic dissolution of mercury takes place reversibly, the potential of the dropping anode should be given approximately by

$$E = 0.518 + (RT/2F) \ln C^0_{\mathrm{Hg}_2^{++}} \tag{70}$$

where 0.518 volt is the standard potential of the mercury electrode against the normal calomel electrode, and $C^0_{\mathrm{Hg}_2^{++}}$ is the concentration of mercurous ions formed at the surface of the mercury drops. If the solution contains ions which form insoluble or complex mercury salts, the dropping anode will be depolarized and the current will increase rapidly when the potential is made sufficiently positive so that the concentration of mercurous ions at the surface exceeds the solubility product, or the complex constant, of the particular insoluble or complex mercury salt. For example, if the solution contains chloride ions, the dropping anode will be depolarized when the concentration of mercurous ions at the electrode surface exceeds the value $S/(C^0_{\mathrm{Cl}^-})^2$, where S is the solubility product of mercurous chloride (6×10^{-19}) and $C^0_{\mathrm{Cl}^-}$ is the concentration of chloride ions at the electrode surface. Hence from equation 70 we calculate that in a 0.001 N chloride solution the dropping electrode should become depolarized and the current should increase at a potential of about +0.16 volt. This is in good agreement with the experimental value of +0.17 volt found by Revenda.

When the dropping electrode is depolarized by chloride ions, the observed current is a measure of the rate of precipitation of mercurous chloride at the electrode surface. This rate, in turn, depends on the rate of diffusion of chloride ions up to the electrode from the body of the solution. As the potential is made more and more positive, the rate of diffusion of chloride ions approaches a constant value, and hence a limiting current results. The same principles apply in the case of other ions which form insoluble or complex salts with mercury. Revenda found that these anodic limiting currents were proportional to the concentration of the depolarizing ion, and that when several depolarizing ions were present in the solution each one produced its own characteristic wave on the current–voltage curve.

The potential at which a given ion at a given concentration depolarizes the dropping anode is, of course, more negative the more insoluble, or the more complex, the resulting mercurous salt is. The depolarization potentials of various ions, determined by Revenda, are indicated in figure 25.

It is also possible for the dropping electrode to function simply as an indifferent anode in certain (chiefly organic) oxidation reactions. For example, Müller and Baumberger (81) have shown that hydroquinone can be oxidized to quinone to give a limiting current at the dropping anode. The range of potentials over which the dropping electrode can function as an indifferent anode is limited, of course, by the potential at which the dropping electrode becomes depolarized by depolarizing ions that may be present in the solution. For example, in a pure solution of potassium nitrate the dropping electrode can function as an indifferent anode up to a potential of about +0.3 volt, in solutions containing chloride ions up to a potential of about +0.2 volt, but in solutions containing sulfide ions only at potentials more negative than about −0.7 volt. In this respect the dropping mercury anode is quite limited in its application and less suitable than a platinum microanode. It should be possible to use a platinum microanode up to the potential at which oxygen evolution begins, that is, up to about +1.0 volt.

XI. ANALYTICAL APPLICATIONS OF THE POLAROGRAPHIC METHOD AND POLAROMETRIC TITRATIONS

1. General applications

It is impossible in the space available to give a detailed discussion of the many applications of the polarographic method in the various branches of chemistry and allied fields. We shall, therefore, confine the present brief review to a mere outline of practical polarographic analysis and to a few examples which demonstrate the versatility of the method. For more extensive discussions of practical details the reader is referred to the monographs of Heyrovský (38), Semerano (104), and particularly that of Hohn (50), and the papers of Hohn (51), Kemula (60), Thanheiser and Maassen (117), Maassen (69), and Winkel and Proske (127). The applications of the method in microanalysis have been discussed by Heyrovský (34), Hamamoto (21), and Heller, Kuhla, and Machek (24). Details of special apparatus for micropolarographic analysis, with which a volume of solution as small as 0.005 cc. may be analyzed, have been discussed by Majer (74). Applications of polarographic analysis in physiological chemistry and medicine have been made by Tropp (120), Seuberling (105), Rosenthal (100), Mandai (77), Petráček (91), and Brdička (6).

We have seen that, under optimum conditions, the half-wave potential is a characteristic constant for each electroreducible substance (qualitative analysis), while the diffusion current is proportional to its concentration (quantitative analysis). In general, the optimum conditions for practical polarographic analysis are as follows: (*a*) The migration current of reducible ions should be eliminated by having an excess of an indifferent salt present in the solution. (*b*) Maxima should be eliminated. (*c*) The diffusion current should be well defined, and preferably directly proportional to the concentration of the reducible substance (after proper correction for the residual current). (*d*) The concentration of foreign or indifferent electrolytes should be large enough so that a small variation in their concentration will not appreciably affect the diffusion current. (*e*) Adsorption of electroreducible ions (particularly heavy-metal ions) by the glass wall of the cell must be prevented. Such adsorption may be particularly marked when dealing with very small concentrations of heavy-metal ions (e.g., micropolarographic determination of lead ions), but it can usually be prevented by acidifying the solution. (*f*) Since diffusion current constants vary with the temperature, the latter should be controlled to at least ±0.5°C.

In general the most suitable medium (i.e., nature and concentration of foreign electrolytes) for the polarographic determination of a given substance must be determined by trial. In order to eliminate maxima and obtain well-defined diffusion currents and to insure a practically constant composition of the solution with respect to foreign electrolytes, Hohn (50, 51) recommends the use of so-called "Grundlösungen" or "regulating solutions." These are composed of suitable salts, or salt mixtures, with the addition, when necessary, of substances which will suppress maxima. Some of the regulating solutions contain complex-forming salts, buffer mixtures, or reagents which will precipitate, or otherwise remove, interfering ions from the solution to be analyzed. The solution to be analyzed is added to about five or ten times its volume of the proper regulating solution. The most favorable composition of the regulating solution for each substance, or group of substances, to be determined must be established by preliminary experiments. Hohn (50) has given a list of regulating solutions that he found to be most suitable for the determination of various metal ions. The reader is referred to his monograph and also to the papers of Maassen (69) and Thanheiser and Maassen (117) for details of their use.

The residual current of each regulating solution should be determined in a "blank" experiment, and the value obtained subtracted from the observed diffusion currents in this particular regulating solution to obtain the true diffusion currents.

When the (corrected) diffusion current of a given substance is directly proportional to its concentration, the diffusion current constant of the substance in the particular regulating solution used may be determined in preliminary experiments with known amounts of the substance. The concentration of this substance in the solution analyzed is thus obtained simply by dividing the (corrected) diffusion current of the substance by the diffusion current constant. When the diffusion current is not directly proportional to the concentration, an empirical calibration curve may be used.

The concentration of the particular substance responsible for a given wave on an "unknown" polarogram can also be determined in the following manner (50, 51). The polarogram of the "unknown" solution is first obtained in the usual way. A known amount of the substance in question is then added to the solution, and a second polarogram is obtained. From the increase (corrected for the residual current) of the diffusion current caused by the known addition, the original concentration of the substance can be easily computed by simple proportion. The particular advantage of this method is that the "calibration" (i.e., the diffusion current constant) is obtained under identically the same conditions with which the original polarogram was obtained, and accidental differences in composition are minimized. Obviously, this "internal standard" method can be used only when the diffusion current is directly proportional to the concentration.

When dealing with mixtures of electroreducible substances, it is often possible to detect and determine several of the constituents from a single current–voltage curve (figure 4). There is no difficulty in detecting and determining a trace of one substance in the presence of a large excess of another electroreducible substance when the former is reduced at a more positive potential than the latter. On the other hand, when a large excess of a more easily reducible substance is present in the solution of the substance to be determined, the *direct* determination of the microconstituent becomes very difficult and often almost impossible. For example, it is easy to detect directly and to determine a trace of lead or cadmium in zinc or zinc salts, since the former ions are reduced at a more positive potential than zinc ions (figure 25), but it is impossible to determine directly a trace of zinc or cadmium in lead salts without previous separation. In cases like the latter, Ilkovič and Semerano (57) recommend that the diffusion current of the interfering major constituent be "compensated" by sending a current of equal magnitude through the current-measuring galvanometer in an opposite direction from an outside source. In this way the wave of the microconstituent can be obtained on the polarogram, but the current oscillations in this case are usually so large that the diffusion current cannot be determined accurately.

In order to determine a microconstituent in the presence of a large excess of a more easily reducible substance, it is usually necessary to resort to preliminary chemical or physical methods of separation. For instance, a trace of zinc in lead salts can be determined by first precipitating the lead with sulfate and then determining the zinc in the filtrate. It is often not necessary to filter off the precipitate of the interfering major constituent. Furthermore, the precipitation of the major constituent need not be quantitatively complete; it is usually necessary only to reduce its concentration to a value of about the same order of magnitude as that of the microconstituent to be determined. When such precipitation methods are used to remove interfering ions the possibility of coprecipitation of the microconstituent must always be kept in mind.

When the half-wave potentials of two electroreducible metal ions are close together, their waves tend to overlap. Many such combinations may occur, as shown by the "polarographic spectrum" in figure 25. In such cases it is often possible to separate the two waves by adding a reagent, or by employing a regulating solution which contains a reagent, that forms a stable complex with one of the constituents but forms no complex, or a much less stable one, with the other. For example, the polarogram of a solution of potassium chloride containing lead and thallous ions shows only a single wave, but in the presence of potassium cyanide, tartrate, or an excess of hydroxide ions, the half-wave potential of lead is shifted to a more negative value while that of thallium remains virtually unchanged (figure 25). The result is the appearance of two separate waves, from which the concentrations of the lead and thallium can be found. If the single wave due to two substances cannot be resolved by complex formation, classical chemical methods of separation must be employed. It will be obvious that in the case of overlapping waves the previous chemical separation must be quantitatively complete.

Overlapping waves of organic substances can sometimes be resolved, or separated, by suitable adjustment of the pH of the solution. For example, in acid medium the waves due to a mixture of fumaric and maleic acids nearly overlap, but in alkaline medium two separate waves are obtained.

It should also be mentioned that the diffusion current of a given substance may, in certain cases, be influenced by the preceding discharge of another substance. For example, Lingane (65) found that the diffusion current of iodate was greatly decreased by the preceding discharge of thallous or cadmium ions. This peculiar effect has not yet been explained and is being further investigated.

Regarding the precision and accuracy of polarographic analysis the following brief statement may be made. Diffusion currents are easily reproducible within 1 per cent. When the proper correction for the residual current is applied, the concentration of a reducible substance can be determined within about ±2 per cent when its concentration is greater than 10^{-4} M and within about ±10 per cent when the concentration is between 10^{-4} and 10^{-5} M. On the basis of our experience we do not recommend the polarographic method for concentrations smaller than about 10^{-5} M.

A unique advantage of the polarographic method is that the composition of the solution remains virtually unchanged, because the quantity of electricity passed through it is so very small. Hence after the electrolysis the sample can be used for other purposes, if desired.

One of the most useful applications of the polarographic method is the detection and determination of reducible metal ions in various substances. Typical examples of such applications are the determination of traces of lead in citric acid and the determination of traces of copper, lead, and cadmium in commercial zinc and zinc salts (38). Hohn (50, 51) has developed procedures for the rapid determination of copper, zinc, iron, lead, and nickel in brass and similar alloys. Thanheiser and Maassen (117) and Maassen (69) have applied the polarographic method to the determination of copper, nickel, and cobalt in steel. A rapid method for the polarographic determination of aluminum, zinc, manganese, and lead in commercially important magnesium alloys has been developed by Gull (18). Knoke (62) employed the polarographic method for the determination of zinc oxide in lithopone. The possibility of polarographically differentiating various rare-earth metals in mixtures has been studied by Noddack and Bruckl (85). Leach and Terry (64) have employed the polarographic method for the determination of scandium in aluminum salts. A simple method for the rapid determination of sodium and potassium, after preliminary separation by the perchlorate method, has been developed by Abresch (2). The polarographic determination of the alkali metals has also been studied by Majer (73), Heyrovský and Bureš (42), Lohnis, Meloche, and Juday (67), and Perrachio and Meloche (89). The polarographic microdetermination of manganese in biological material has been studied by Hamamoto (21). The use of "dithizone" for group separations of metal ions prior to their polarographic determination in mineral waters has been studied by Heller, Kuhla, and Machek (24). Preliminary "dithizone" separations have also been used by Stout and his collaborators (114) for the polarographic determination of small amounts of iron, manganese, copper, bismuth, lead, cadmium, zinc, nickel, and cobalt in plant ash. These few examples illustrate the usefulness of the polarographic method for the determination of metal ions in a variety of different materials.

Various oxygen-containing anions are reducible at the dropping electrode and may be polarographically determined. As examples, we may mention nitrate and nitrite (118), molybdate (121), bromate and iodate (101), and selenite and tellurite ions (103). It should be mentioned, however, that these reductions are irreversible, and that the shapes of the current-voltage curves are greatly influenced by the composition of the electrolysis medium, especially by traces of polyvalent cations such as lanthanum ions (118). Hence in practical work the composition of the medium must be carefully controlled (by a regulating solution).

It has already been mentioned that oxygen is reducible at the dropping electrode. Vítek (124) has made use of this fact for the determination of oxygen in various technical gases. Petering and Daniels (90) have recently employed the polarographic determination of oxygen for studying the photosynthesis and respiration of green algae (*Chlorella pyrenoidosa*) and the respiration rate of yeast, blood cells, and animal tissue. According to these authors the polarographic method is superior to the classical manometric and Winkler methods for investigations of this kind, especially when the oxygen uptake is very small.

The suppression of the prominent oxygen maximum by various capillary-active substances, such as dyes (98), lyophilic colloids (122), fatty acids (97), and alkaloids (20), may be used for determining traces of such substances. For example, Gosman and Heyrovský (17) determined certain capillary-active impurities in petroleum and its distillates by their suppressive effect on the oxygen maximum. Heyrovský, Smoleř, and Šťastný (38) employed the same principle for differentiating between natural and synthetic vinegar.

It has been mentioned that substances which decrease the overvoltage of hydrogen on mercury catalyze the evolution of hydrogen and cause the appearance of a catalytic wave at potentials more positive than the "normal" discharge potential of hydrogen. For example, the discharge of hydrogen from strong acids is catalyzed by traces of noble-metal ions, such as platinum, ruthenium, and palladium (112, 111). This phenomenon may be utilized for the detection and determination of very minute amounts of these noble-metal ions. The distinguishing characteristic of such catalytic waves is that they are ten to twenty times larger than the waves due to simple reduction of the same concentration of the catalyst ion. Perrhenate ions in acetate buffers containing hydrogen sulfide also catalyze the discharge of hydrogen and cause the appearance of a catalytic wave. Heyrovský (37) utilized this fact for detecting traces of rhenium in manganous salts. The discharge of hydrogen is also catalyzed by various quinoline derivatives, such as quinine, quinidine, cinchonine, and cinchonidine (88).

Various proteins and organic compounds containing a sulfhydryl group (e.g., cystine, cysteine) catalyze the evolution of hydrogen from the ammonium ion in ammonia–ammonium chloride buffers containing a small concentration of cobalt or nickel ions (6, 40). The presence of cobalt or nickel ions is essential for the production of a catalytic wave. Proteins give the catalytic wave with either cobaltous or cobaltic ions, but with sulfhydryl compounds a catalytic wave is obtained only with cobaltous and not with cobaltic ions (differentiation between proteins and catalytic sulfhydryl compounds). Brdička (6, 8) has utilized the catalytic effects due to the sulfhydryl groups in denatured blood serum for the clinical diagnosis of cancer. According to his results the catalytic effect is smaller with carcinomatic than with non-carcinomatic serum. Rosenthal (100) has described several other practical applications of these catalytic effects in biological chemistry.

The polarographic method gives promise of becoming a valuable tool in organic chemistry. A large variety of organic substances, including various aldehydes and ketones, nitro compounds, azo and diazo compounds, quinones, and simple unsaturates, are reduced and give well-defined waves with the dropping electrode. Applications of the polarographic method in organic chemistry are discussed in detail by Dr. O. H. Müller in an accompanying paper in this Journal.

From the foregoing brief review it will be evident that the polarographic method is rapidly attaining an important place in quantitative and qualitative analysis. However, much fundamental and systematic research still remains to be done before the method can be used reliably and accurately for general analytical purposes. More systematic investigations of the effect of the nature of the solvent on diffusion currents, the elimination of maxima, and irreversible oxidations and reductions are particularly needed. In order to avoid possible disappointments, we wish to warn practical analytical chemists that the method is still in the developmental stage. When dealing with complex and unfamiliar mixtures, it is imperative to test the reliability of the method with synthetic mixtures of composition closely comparable to that of the unknown.

2. *Polarometric titrations*

A new method of electrometric titration employing the dropping electrode has recently been introduced by Heyrovský (33) and Heyrovský and Berezický (41). The method is based on the decrease of the diffusion current of a reducible substance when it is removed from solution by titration with a suitable reagent or on the sudden increase in current at the equivalence point when the reagent is titrated with a solution of a reducible substance. The general principles of the method have recently been discussed by Majer (75), who coined the name "polarometric titration" for it and studied the direct and reverse titration of lead with sulfate.

The application of polarization phenomena to titrations is not new.

The "dead-stop end point" method of Foulk and Bawden (14) and the method of Guzmán and Rancaño (19) are based on the sudden polarization or depolarization of an indicator electrode at the equivalence point and a corresponding abrupt change in current. However, these methods are based on "chemical polarization," whereas polarometric titrations with the dropping electrode are based on concentration polarization. Hardly any work has been done as yet to introduce polarometric titrations into general volumetric practice. At the present time, systematic studies of the method are being conducted in this laboratory, and from the results obtained so far we predict that in the future polarometric titrations will become as important and useful in volumetric analysis as potentiometric titration methods.

Since we are planning to publish more extensive papers on the subject in the near future and space in this paper is limited, we shall confine the present discussion to the basic principles of polarometric titrations, and a few examples which indicate its possibilities. Suppose that we titrate a dilute solution of lead ions with oxalate in a polarographic cell, with the applied E.M.F. maintained constant at a value such that the diffusion current of lead is obtained, and measure the diffusion current after each addition of the standard oxalate solution. The titration curve will be as shown schematically in figure 26a. The diffusion current decreases continuously during the titration as the lead ions are removed by precipitation as lead oxalate. When the equivalence point is reached, and the precipitation of lead is fairly complete, the current becomes constant and independent of further addition of oxalate. When the solubility of the precipitate is negligibly small the break at the equivalence point will be sharp, and the final constant current will be very small and practically equal to the condenser current. If the solubility of the precipitate at the equivalence point is not negligible, the titration curve will be more or less curved in the region of the equivalence point. In such a case (e.g., titration of Pb^{++} with SO_4^{--}) the end point is found from the intersection of the extrapolated straight portions of the curve after correction for the dilution effect, much in the same way as the end points of conductometric titrations are determined. If the solution being titrated contains another reducible substance which is reduced at the particular value of the applied E.M.F. but which is not precipitated or otherwise removed by the reagent employed, the final constant current will be almost equal to the diffusion current of this substance. For example, this would be the case if a solution of lead were titrated with oxalate without removing air from the solution.

Suppose that the ion to be determined is not electroreducible at the particular value of the applied E.M.F. used, but the reagent ion is. This is the case, for example, when barium is titrated with chromate in neutral solution with the applied E.M.F. at 1.5 volts or less. The curve of this titration is shown schematically in figure 26b.

The sharpest break at the equivalence point, and the most accurate results, are to be expected when the ion being titrated and the reagent ion are both reducible at the particular applied E.M.F. In such a case the titration curve will be V-shaped. For example, in the titration of lead ions with chromate the titration curve is as shown schematically in figure 27a, because both lead and chromate ions are reducible at the dropping electrode.

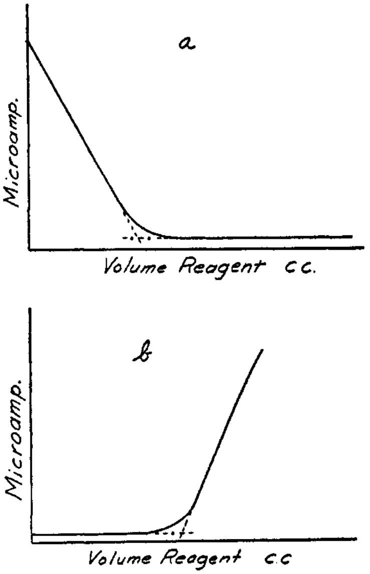

FIG. 26

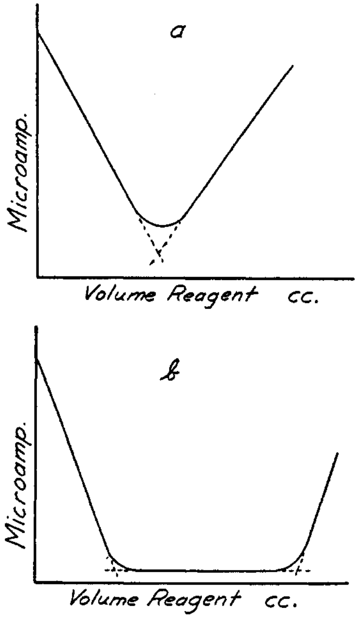

FIG. 27

FIG. 26. Schematic representation of polarometric titration curves
FIG. 27. Schematic representation of polarometric titration curves

The foregoing titrations have actually been performed in this laboratory with excellent results. The polarometric titration method promises to be particularly valuable in cases for which reversible indicator electrodes are not available for titration by the classical potentiometric method. Polarometric titrations are also especially suitable for very small concentrations. For example, a 10^{-4} molar lead solution can easily be titrated with chromate.

It is also to be expected that use can be made of fractional precipitation for determining two substances by a single titration. For example, if the solubilities of lead chromate and barium chromate are sufficiently different, and if barium ions do not coprecipitate with lead chromate, it should be possible to titrate a solution containing lead and barium ions with chromate. If the foregoing conditions are fulfilled, the titration curve should be as shown schematically in figure 27b. The first break corresponds to the complete precipitation of lead and the second to that of barium.

Many other types of polarometric titrations are possible. We have titrated chloride ions with silver by employing the dropping electrode as anode (see section X). In this case the current is originally negative, decreases to zero at the equivalence point, and then becomes positive when an excess of silver ions has been added. The titration curve is practically a straight line, and the equivalence point is indicated by zero current. Under suitable conditions various oxidation–reduction and complex-formation reactions can also be made the basis of polarometric titration methods. In future publications limitations of the polarometric titration method will be discussed.

XII. SUMMARY

1. The fundamental principles of polarography developed by Heyrovský and his school have been discussed in detail. Applications of the method to problems in physical, organic, and analytical chemistry, and in allied fields have been pointed out.

2. From the analytical viewpoint much systematic work remains to be done before the polarographic method can be generally applied. It is anticipated that polarometric titrations will become an important method in volumetric analysis

3. The "apparent diffusion current" is the sum of the true diffusion current and the condenser current.

4. The factors determining the occurrence of maxima are involved and not completely understood.

5. Quite generally an electroreducible substance is characterized by its constant "half-wave potential." When the electroreduction on the dropping mercury electrode is reversible, a mathematical analysis of the polarographic wave yields the number of electrons involved in the electroreduction.

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