who joined hands in the middle of the mountain when the first rays of light broke through. Electron microscopy has succeeded in forming a thin but actual join between the molecular and the cellular levels of biological organization. In so doing, it has united form with function and has established the foundations of a mathematically rigorous morphology (*52*).

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Trends in Polarography

J. Heyrovsky

For some 38 years I have carried on electrochemical research with the dropping-mercury electrode because of its exquisite properties as electrode material. Its physical conditions of dropping as well as the chemical changes that occur during the passage of the electric current are well defined, and the phenomena displayed at the dropping-mercury electrode proceed with strict reproducibility. Owing to the latter property the processes of the electrode can be exactly expressed mathematically. According to the registering apparatus, called a "polarograph," which automatically draws curves characteristic of the electrode processes, the electrochemical studies with the dropping-mercury electrode and the analytical method developed on the basis of these investigations have been called "polarography."

Apparatus

The capillary electrode is normally a tube 8 centimeters long and 5 to 6 millimeters wide with an inner bore of 0.05 to 0.1 millimeter (Fig. 1), from which the drops of mercury fall off every 3 to 6 seconds, according to the height of the mercury reservoir, which is about 40 centimeters above the tip of the capillary.

In order that the current passing through this electrode may be entirely governed by the composition of the solution surrounding it, the second electrode has to be indifferent, unpolarizable, and of a constant potential; most suitably, it is the layer of mercury at the bottom of the electrolytic vessel (Fig. 2).

To apply the external voltage to the cell we use a potentiometric arrangement, shown in Fig. 2. From a 2- or 4-volt lead accumulator, an increasing voltage E is branched off, and the corresponding current is determined by

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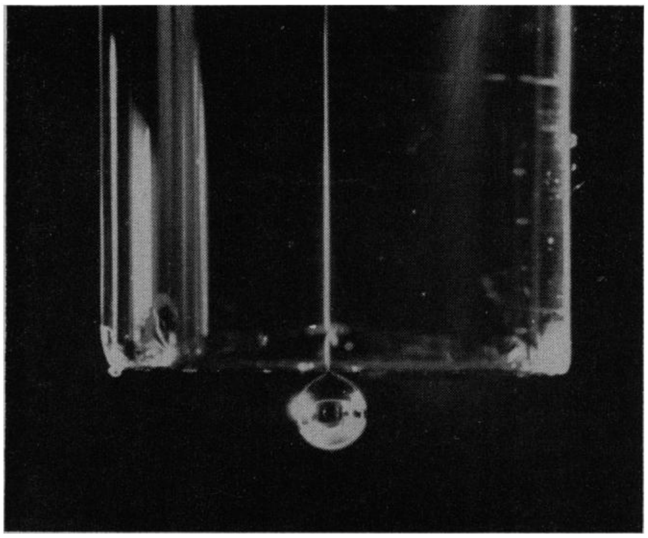
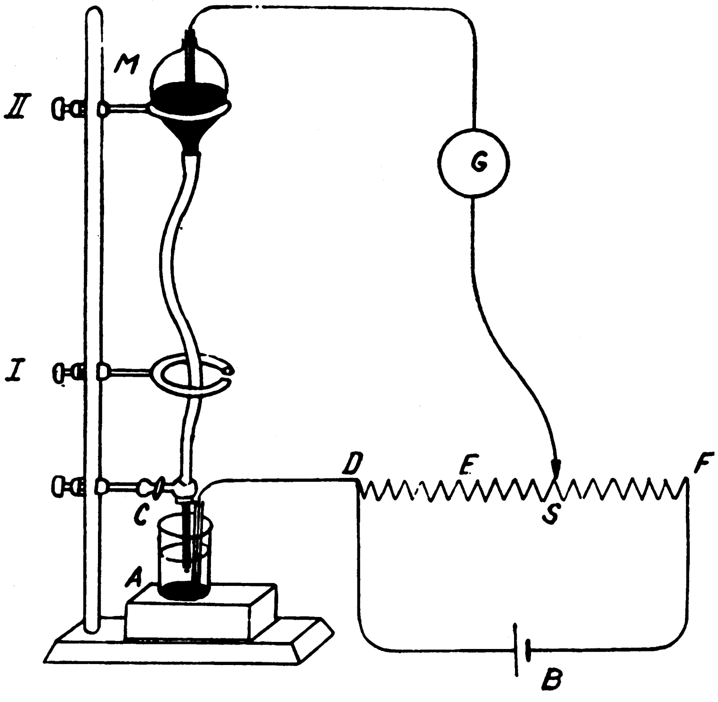
the deflection of the galvanometer. In such an arrangement the whole applied voltage *E* acts at the small polarizable electrode and determines its potential. The solution has to be conductive by an indifferent electrolyte (about 0.1 normal).

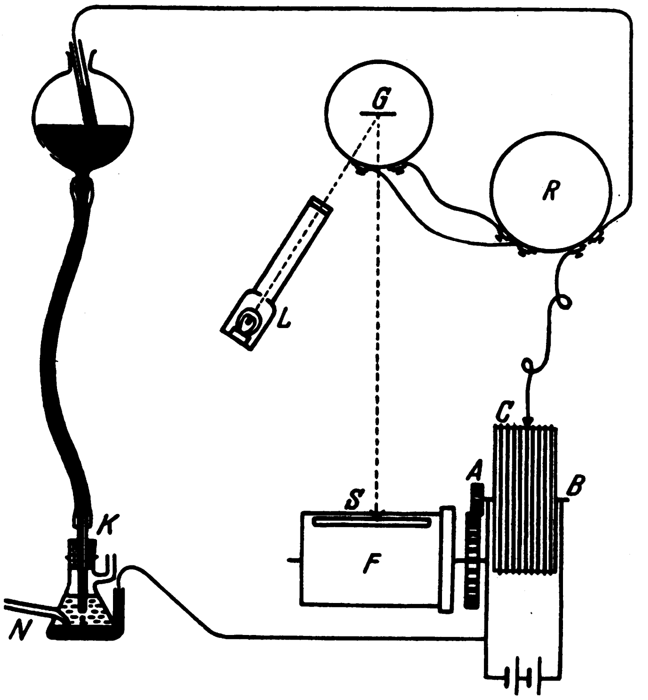
Until the year 1924 the galvanometer deflections were plotted by hand on the ordinate against the voltage applied by pushing the wheel of the Kohlrausch drum to different values. It took a couple of hours to obtain a full graph, point by point, from 0 to 2 volts. To accelerate the plotting of the curves, Shikata and I constructed in 1924 (*1*) an automatic device, the "polarograph" (Fig. 3), by rotating the Kohlrausch drum mechanically and by synchronously moving a photographic paper. This mechanism drew the current-voltage diagram—the "polarogram"—in less than 10 minutes, with all the advantages of automatic recording. The galvanometer has to be damped to register the mean current, instead of the instantaneous current, during each drop. It is not advisable to damp the motion of the galvanometer mirror so far that the oscillations disappear; the regularity of the oscillations provides a good check of the correct functioning of the apparatus (Fig. 4).

"Charging" and Kinetic Currents

Next, the forms of the current-voltage curves were classified according to the various processes occurring at the dropping electrode. The most fundamental of these is the "charging" current which accompanies every drop formation, conveying to the drop the charge corresponding to the externally applied potential. Since this charge depends on the capacity of the dropping electrode and does not involve any electrolytic changes, the current is also termed "capacity current" or "nonfaradic current" (Fig. 5). It is very small, of the order of 10^{-7} ampere per







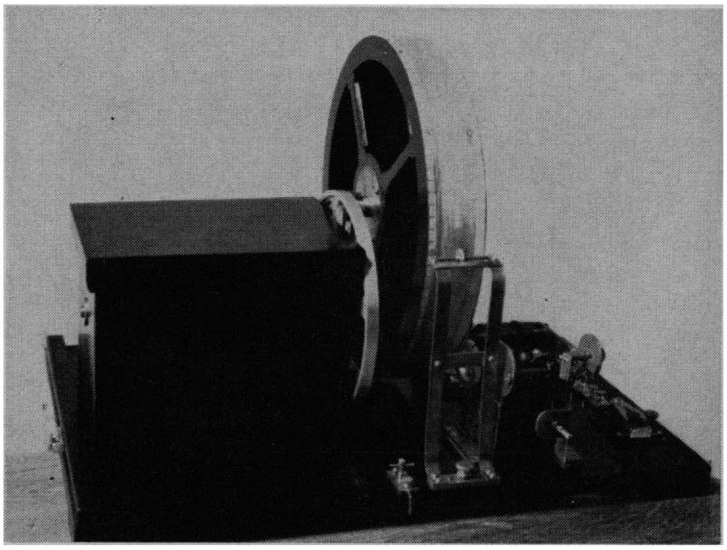
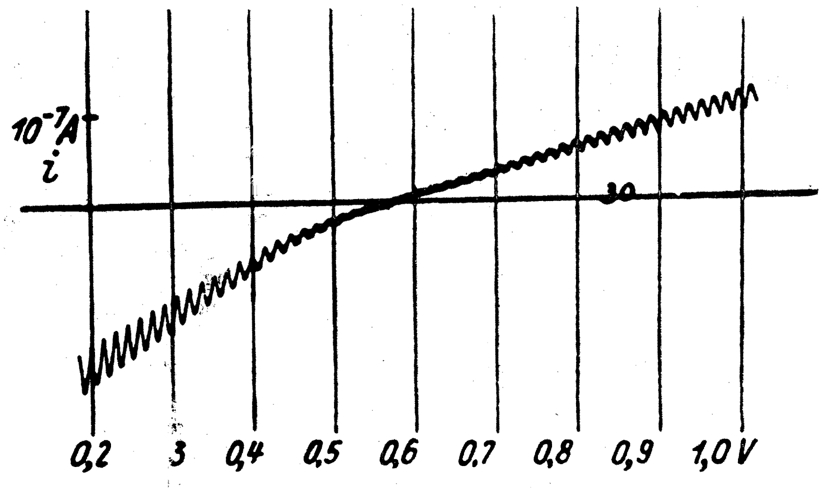


Fig. 1 (top left). Mouth of the dropping-mercury electrode. Fig. 2. (top right). The simplest polarographic arrangement. Fig. 3 (bottom left). Scheme of the polarograph. Fig. 4 (bottom right). The first polarograph.



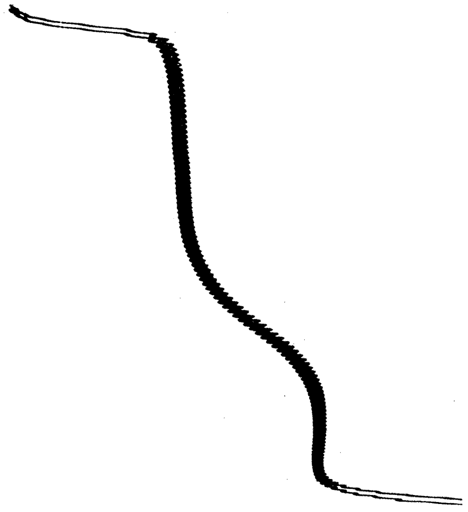
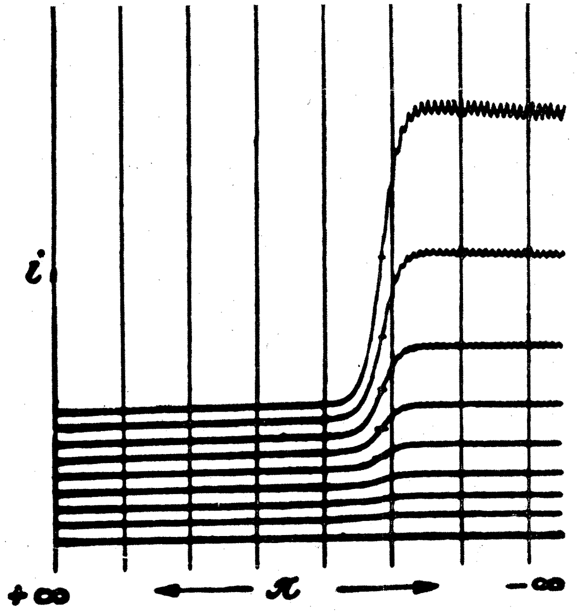


Fig. 5 (left). Capacity current in 0.1*M* KCl freed from air. Fig. 6 (right). Diffusion current of oxygen reduction in 0.1*M* KOH. The curve is repeated to show the reproducibility.



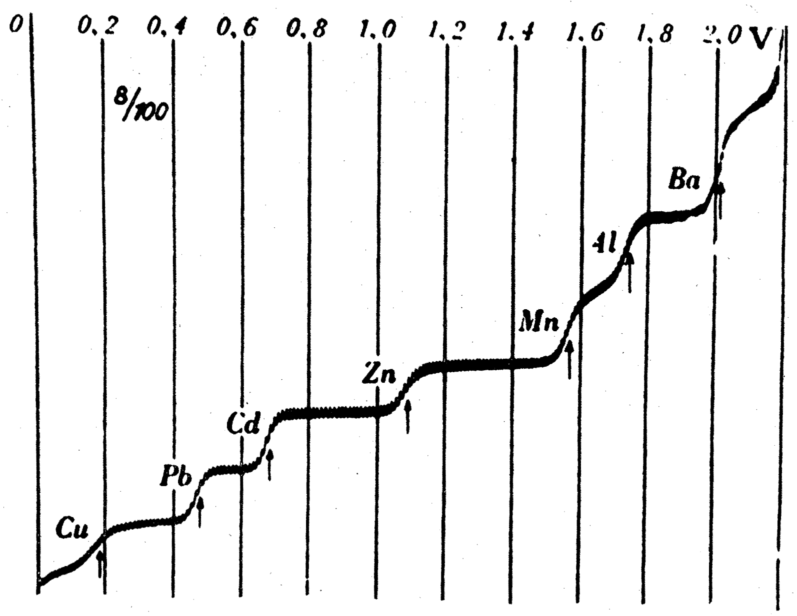


Fig. 7 (left). Constancy of the half-wave potential in solution of various concentrations of $CdCl_2$. Fig. 8 (right). Polarographic spectrum showing seven cations in the solution.

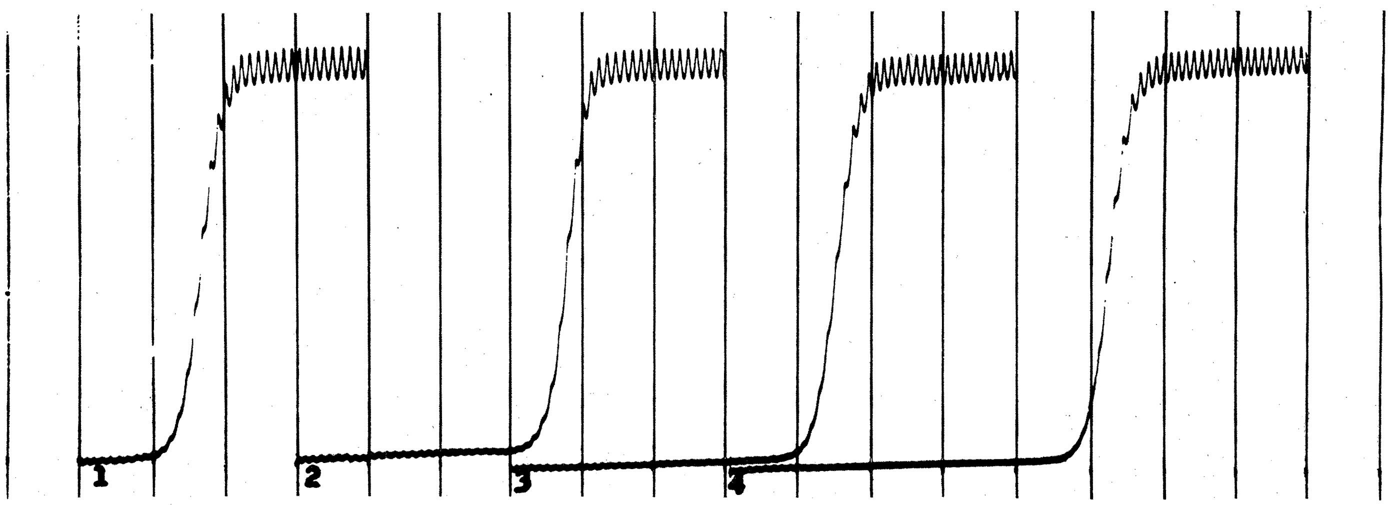


Fig. 9. Shift of the reduction wave of Pb^{++} ions due to the increasing concentration of NaOH. The curves start from the potential of —0.28 v from the saturated calomel electrode. Abscissa, 100 mv. Concentration of lead ions, $5.10^{-4}M$. Concentration of the electrolyte: (1) 1*M* KNO_3; (2) $1.2 \times 10^{-4}M$ NaOH, 1*M* KNO_3; (3) 0.1*M* NaOH, 0.9*M* KNO_3, 1*M* NaOH.

volt, and ordinarily is regarded as negligible. However, the charging current plays an important role in oscillographic polarography, where it is considerably greater. At a certain potential an electrolytic process starts—reduction or oxidation—which is shown by the passage of the current due to electrolysis. In the simplest case, molecules or ions of the reducible or oxidizable substances interchange electrons with the electrode and thereby are removed from the electrode surface. Then new molecules of the electroactive substance—the depolarizer—diffuse from the interior of the solution to the surface of the electrode. Ilkovič (*2*) has calculated the current governed by diffusion to the surface of the expanding drop, deducing (in 1933) the formula of the "diffusion current":

$$i_d = 0.627\, nF \cdot D^{1/2} \cdot m^{2/3} \cdot t^{1/6} \cdot C$$

where n is the number of electrons involved in the reaction; F, the charge of Faraday; D, the diffusion constant; m, the rate of flow of mercury through the capillary; t, the drop time; and C, the concentration. This is the most exact electrochemical law announced since Faraday's laws in 1833. When corrected for spherical diffusion according to the method of Koutecky (*3*), the agreement with experimental results is completed. Figure 6 gives the reproducibility of a polarogram, showing the diffusion current due to atmospheric oxygen in an alkaline solution.

From this law the equations for the current-voltage curves due to the reductions and oxidations of depolarizers were deduced, and from these equations the rule of constancy of the half-wave potentials $E_{1/2}$ follows (*4*). These values introduced new electrochemical constants (Figs. 7, 8), which have thermodynamic significance in that they give affinities of electrode reactions. Also, constants of complexes can be derived from such equations (*5*) (Fig. 9).

In 1943 Wiesner (*6*) discovered currents of another sort, controlled by the rate of the chemical reaction yielding

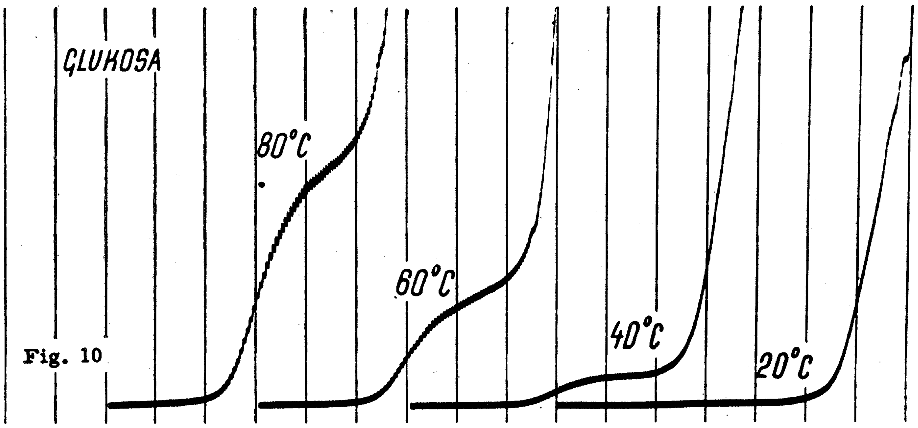


Fig. 10

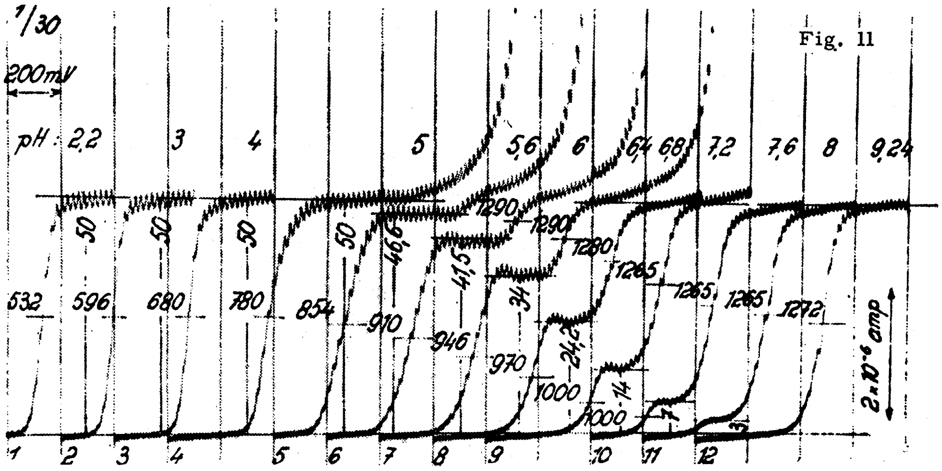


Fig. 11

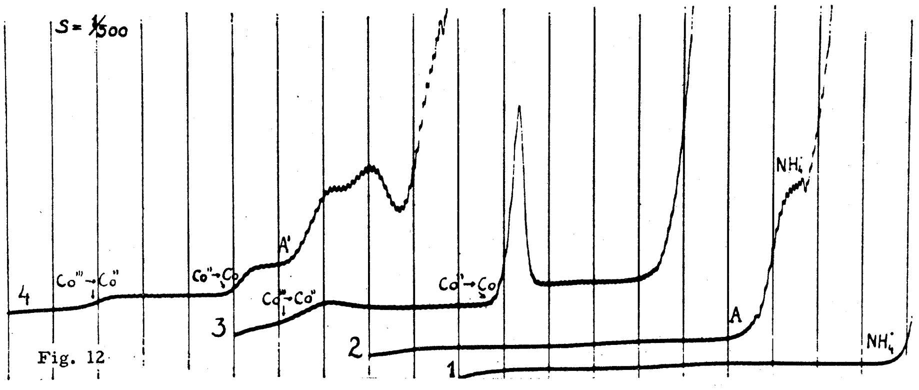


Fig. 12

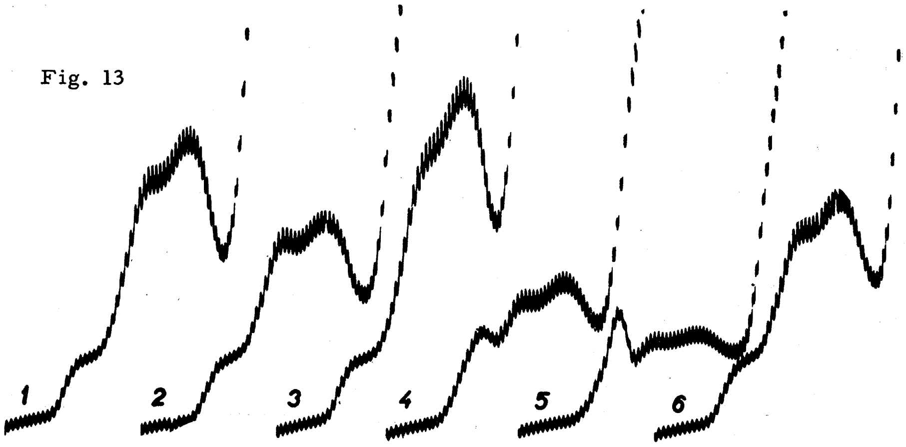


Fig. 13

Fig. 10. Kinetic currents of glucose at various temperatures. Fig. 11. Polarographic reduction waves of phenylglyoxylic acid in buffer solutions of various *p*H. Fig. 12. The effect of proteins in ammoniacal solutions without and with cobalt. Fig. 13. Brdička's test with blood sera of various pathological states: (i) feverish state; (ii) hepatic tumor, suspected; (iii) stomach cancer, suspected; (iv) normal serum; (v) hepatic cirrhosis; (vi) arteriosclerosis.

the depolarizer at the electrode. For example, formaldehyde or glucose give at ordinary temperature much smaller waves than would be expected from the Ilkovič formula (Fig. 10). Evidently a slower process than diffusion furnishes the depolarizer. In the case of formaldehyde, the molecules of methylene glycol $H_2C(OH)_2$ (*7*) have to be dehydrated to form the actual depolarizer, which is H_2CO. The current is governed by the rate of the dehydration, which of course depends on the *p*H. Such currents are termed "kinetic"; they make it possible to measure the rates of fast chemical reactions. Wiesner and Los (*8*) obtained from the currents due to glucose the kinetic constants of mutarotation and calculated the amount of the free aldehyde in 0.655*M* glucose at 25°C as 0.0030 percent. From the height of the two waves which appear in the reduction of a reducible acid, we are able to calculate the very high rates of the recombination of the ions with kinetic constants of the order of 10^7 to 10^{11} (Fig. 11).

Current Due to Catalytic Processes; Phenomenon of Maxima

In comparison with the kinetic currents, the polarographic currents due to catalytic processes in the evolution of hydrogen, especially those due to —SH groups, are very much higher. For example, cystine and proteins in NH_3 buffers containing cobalt ions give a "catalytic" wave as cystine without the catalyst 500 to 700 times higher. Of these reactions the most noteworthy is the serological reaction of Brdička (*9*) (Fig. 12), to which many publications relate. This is characterized by the "protein double wave" (Fig. 13), which has been found to depend on the pathological state of the patient. All inflammations cause an increase of the protein wave. In the nonfeverish state it is cancer which is invariably manifested by an elevated protein wave. After the removal of the cancerous center, the reaction becomes normal; metastases

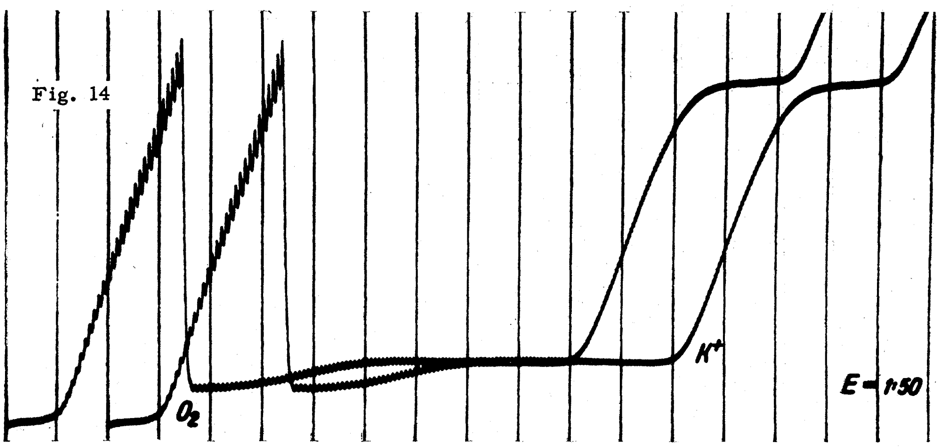


Fig. 14

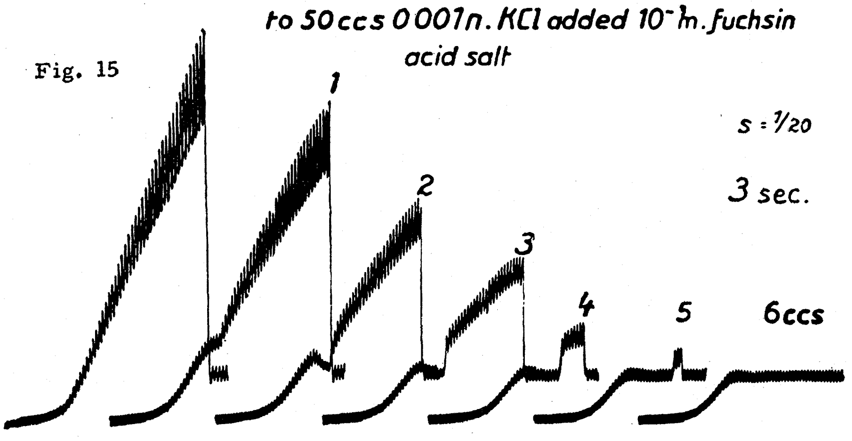


Fig. 15

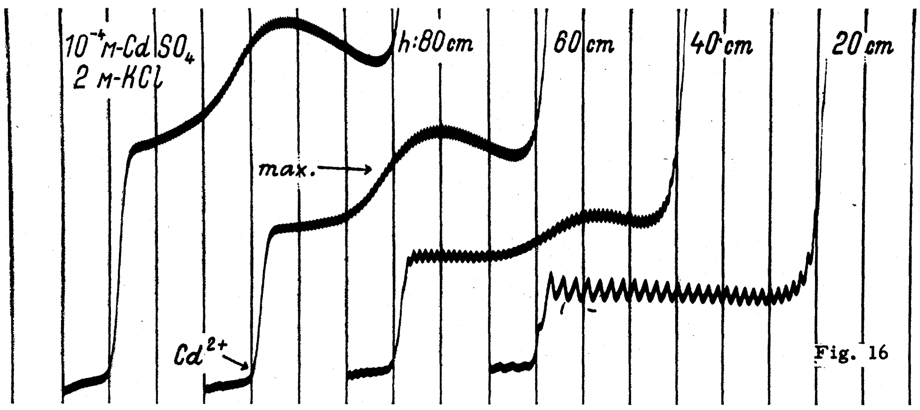


Fig. 16

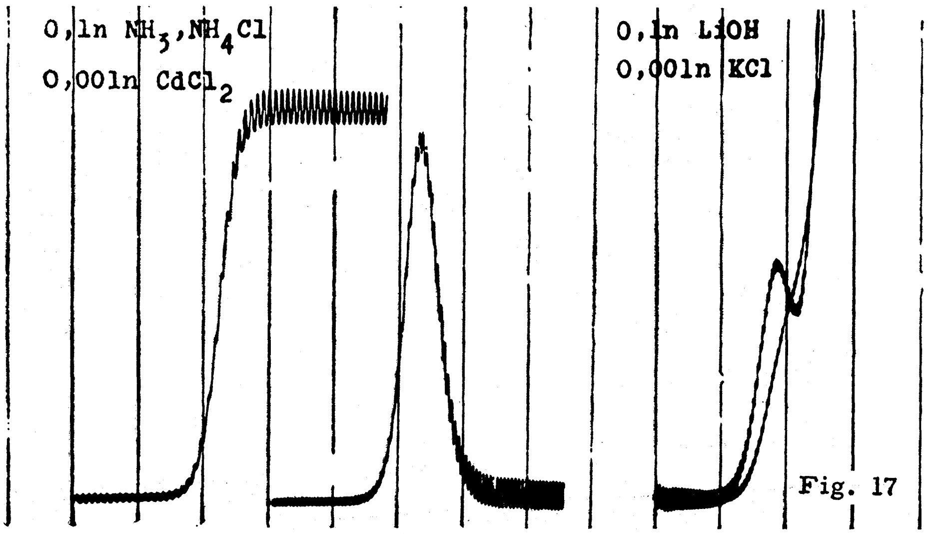


Fig. 17

Fig. 14. Maximum of the first order on the wave of oxygen in 0.001*M* KCl. Fig. 15. Suppression of the maximum by a solution of fuchsin acid salt. Fig. 16. Maximum of the second order due to $CdSO_4$ in 2*M* KCl, showing influence of increasing the rate of flow of mercury. Fig. 17. Primitive and derivative polarographic curves: (left) $CdCl_2$ in ammonia buffer solution; (right) 0.001*M* KCl in 0.1*M* LiOH.

elevate it. It has been ascertained that the proteins responsible for the cancer reaction are mucoproteins belonging to the γ_2-globulins. Electrophoresis shows that the mucoproteins are akin to the serum component MP-2. On the other hand, liver diseases lower the protein wave, so that in liver troubles the polarographic test is specific.

Another type of polarographic current-voltage curves, closely connected with Kučera's anomalous maximum on the electrocapillary curve, are sharp maxima of current, which at a certain voltage fall to the limiting diffusion current (*10*) (Fig. 14). An inspection of the dropping electrode through the microscope reveals vehement streaming of the electrolyte along the lines of force to the electrode. Such maxima are very easily suppressed by slight traces of adsorbable matter, like fatty acids, dyestuffs (Fig. 15), gelatin, and other colloids, and in this way indicate very sensitively the degree of purity of solutions. The practical applications of the phenomenon of maxima are manifold. They are termed maxima of the first order when formed in dilute electrolytes (Fig. 16). In concentrated solutions there appear rounded maxima of the second order, due to the adhesion of the solution to the moving mercury surface; they are also suppressed by colloids like gelatin (Fig. 17).

I have referred only to the polarography of aqueous solutions. However, similar types of curves and electrode reactions may be followed in many nonaqueous conducting solutions—for example, in acetonitrile, dioxane, alcohols, glacial acetic acid, sulfuric acid, liquid ammonia, and fused salts. In all of them Ilkovič's law has been found to hold good at all temperatures.

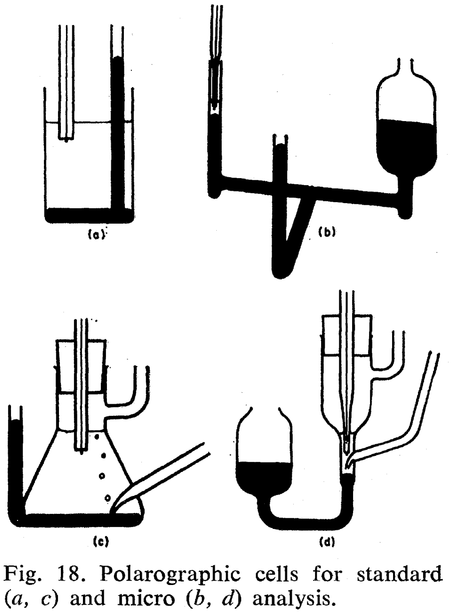


Fig. 18. Polarographic cells for standard (*a, c*) and micro (*b, d*) analysis.

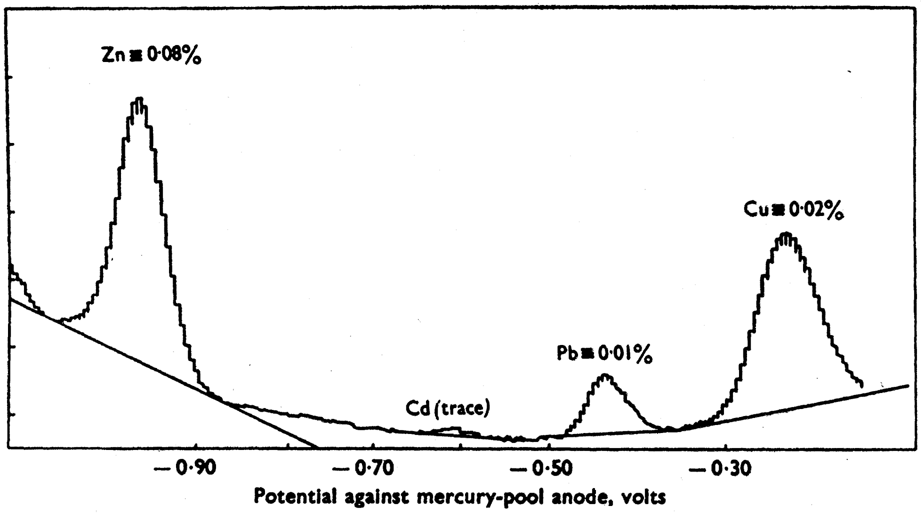


Fig. 19. Square-wave polarogram of an analysis of aluminum alloy: 200 mg of sample in 100 ml of 1*M* KCl.

The current-voltage curves are reproducible enough to yield with sufficient exactness even their derivative curve $(di/dE) - E$ (Fig. 18) (*11*). Since at the half-wave potential the ordinary curve has an inflection, the derivative curve shows there a maximum whose height is proportional to the concentration of the depolarizer. The potential of the maximum indicates the quality. There are several methods of obtaining the derivative curve automatically.

Sensitivity of the Method

The sensitivity of the polarographic method is high, showing depolarizers in a $5 \times 10^{-6}M$ concentration even in 0.1 cubic centimeter and, in a special vessel, even in 0.005 cubic millimeter, in which 5×10^{-11} gram of a depolarizer may be ascertained (Fig. 19). The most sensitive test is that of ruthenium, which is shown in a $5 \times 10^{-10}M$ concentration (*12*). With the Barker's "square wave polarograph" (*13*), where the charging current is practically eliminated and the electrolytic one is strongly amplified, curves of a derivative character are obtained which show 10^{-8} mole per liter (Fig. 20).

Most sensitive of all is polarography combined with measurement of radioactivity (Fig. 21) (*14*). The method consists in measuring the activity of the β and γ radiation of mercury drops on which the radioactive metal has been deposited. Isotopes, of course, cannot be distinguished, but, for example, from a mixture of radioactive zirconium-95 and niobium-95, the daughter substance, zirconium-95, can be separated, because it is deposited at the electrode, whereas niobium remains in solution. This radioactive technique promises wide applications through enabling one not only to carry out quick, accurate analyses and separations of radionuclides but also to learn the basic electrochemistry of very dilute solutions and electrode reactions. The sensitivity is that of radioactive methods.

All the afore-mentioned polarographic methods are used for analytical determinations, qualitative and quantitative, in microdoses as well as macrodoses of inorganic or organic depolarizers. If the substance to be determined is not a depolarizer it may be chemically converted into a depolarizer and so determined. For example, benzene is no depolarizer, its traces in air are noxious, and microdetermination is de-

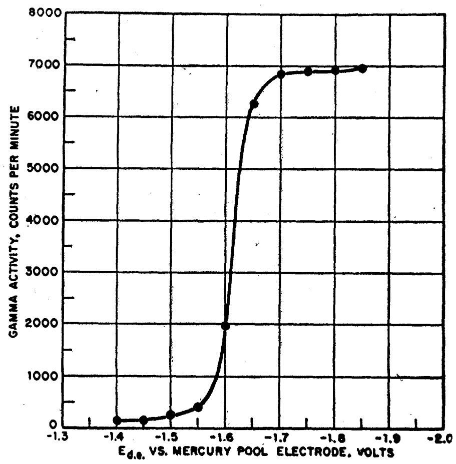
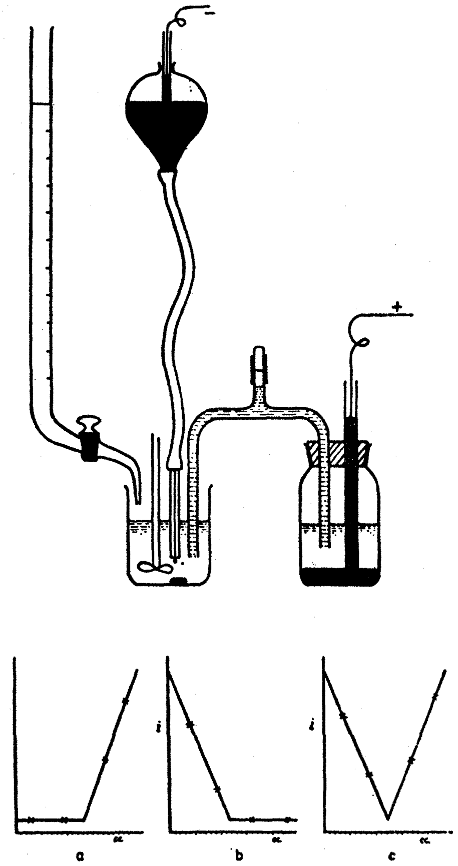
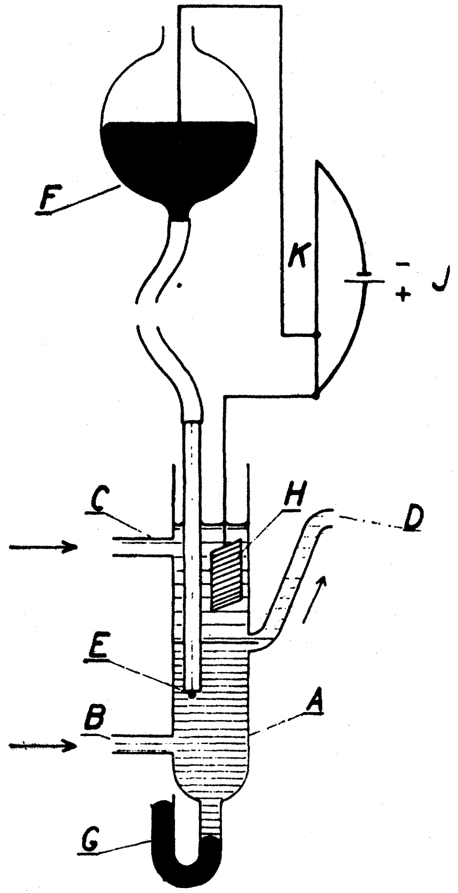


Fig. 20. Plotting of radioactivity of mercury drops against the applied potential.





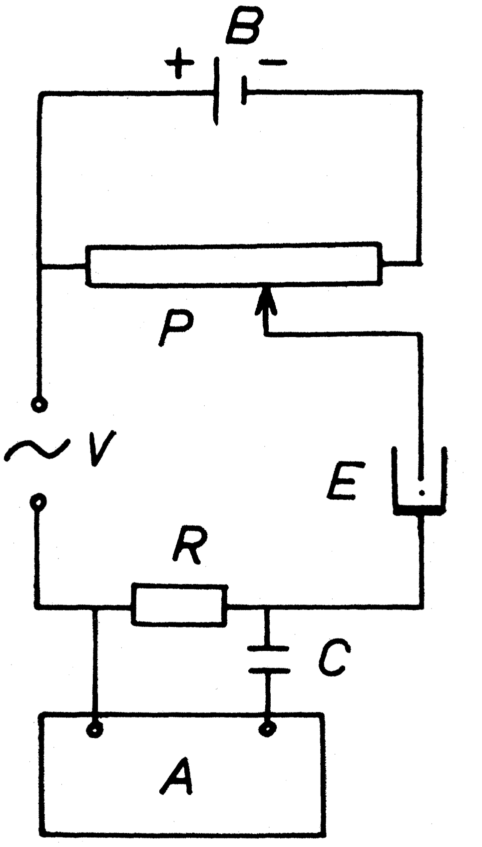


Fig. 21 (left). Limiting current titrations, arrangement and diagrams. (*a*) Lead salt in burette, sulfuric acid in beaker; (*b*) sulfuric acid in burette, lead salt in beaker; (c) lead salt in beaker. Fig. 22 (middle). Scheme of a continuous polarographic analyzer. (*E*) Indicating electrode; (*H*) redox electrode of constant potential; (*B*) inlet of solution to be analyzed; (*C*) inlet of redox mixture. Fig. 23 (right). Circuit of Breyer's alternating-current polarography. (*B*) Lead accumulator; (*P*) potentiometer; (*V*) alternating voltage; (*R*) ohmic resistance; (*C*) condenser; (*A*) voltmeter for alternating voltage.

sired. The smallest traces of benzene are easily converted by nitration into nitrobenzene and, after alkalization, exactly determined in respiration, in blood, or in urine.

Related Methods

A new trend in volumetric analysis was introduced in 1926 by polarographic titrations (*15*), later called "polarometric" by Majer (*16*) and "amperometric" by Kolthoff (*17*), which use the limiting current to indicate the end point. The indicating electrode may be, instead of the dropping electrode, a rotating or vibrating electrode of solid metal. The accuracy of the polarographic titration here reaches 0.3 percent. For the titration graph, two readings of the current before and two after the equivalent point suffice. The method does not require a "polarograph"; a potentiometer and a galvanometer of less sensitivity suffice (Fig. 22).

On the basis of experience with the "polarograph," special continuous polarographic analyzers have been constructed which follow for many weeks without interruption the content of solutions flowing through the cell (Fig. 23). These analyzers are used for the automatic control and regulation of technical processes in industry, for recording the presence in the atmosphere of noxious gases such as SO_2, HCN, and CO, and for other purposes.

Breyer and his co-workers (*19*) introduced in 1944 the "tensammetric" method, which uses the dropping-mercury arrangement by applying a slowly increasing voltage with superposed alternating voltage (Fig. 24) of some 10 to 30 millivolts and 50 hertz frequency. The alternating current which passes through the polarographic cell is measured, and the current-voltage curve is recorded. The method resembles the method from which it is derived inasmuch as it gives peaks at the half-wave potentials of reversible depolarizers, but it is very sensitive to adsorbable substances which change the surface tension of the mercury electrode (Fig. 25)—hence the name *tensammetry.* The changes in capacity due to adsorption produce, on the current-voltage curves, peaks often 100 times higher than the normal height of the wave of the organic compound. The chief advantage of Breyer's tensammetric method is that it can determine with high sensitivity many organic substances which are polarographically inactive, provided they are surface-active.

A great field that has opened since 1938 is "oscillographic polarography" (*20*), which substitutes the cathode-ray oscillograph for the galvanometer and voltmeter (Fig. 26). This brings the velocity of recording a polarographic curve to 1/50 second, and the accuracy of analytical determinations is about the same as in classical polarography.

Significance

We often hear it said that polarography did not bring anything new into chemistry except an improvement in analytical methods. That is decidedly not so, since in the study of reductions

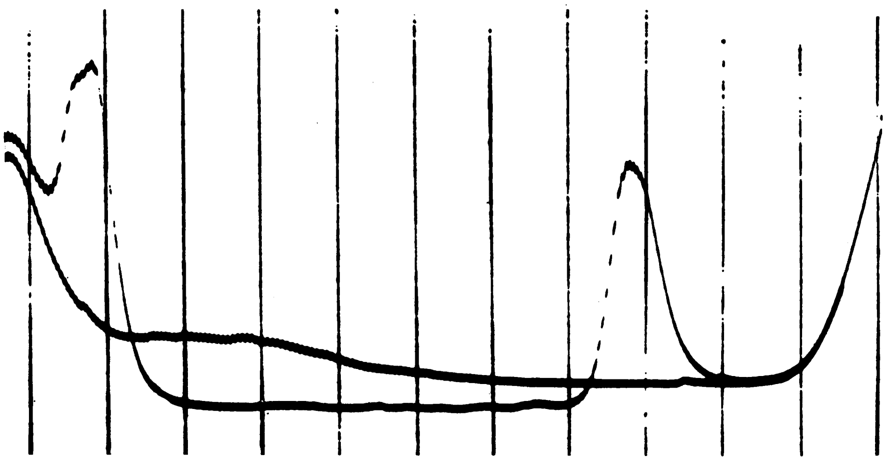


Fig. 24. Tensammetric maxima due to adsorption and desorption of cyclohexanol in acetate buffer solution. (Upper curve) pure solution.

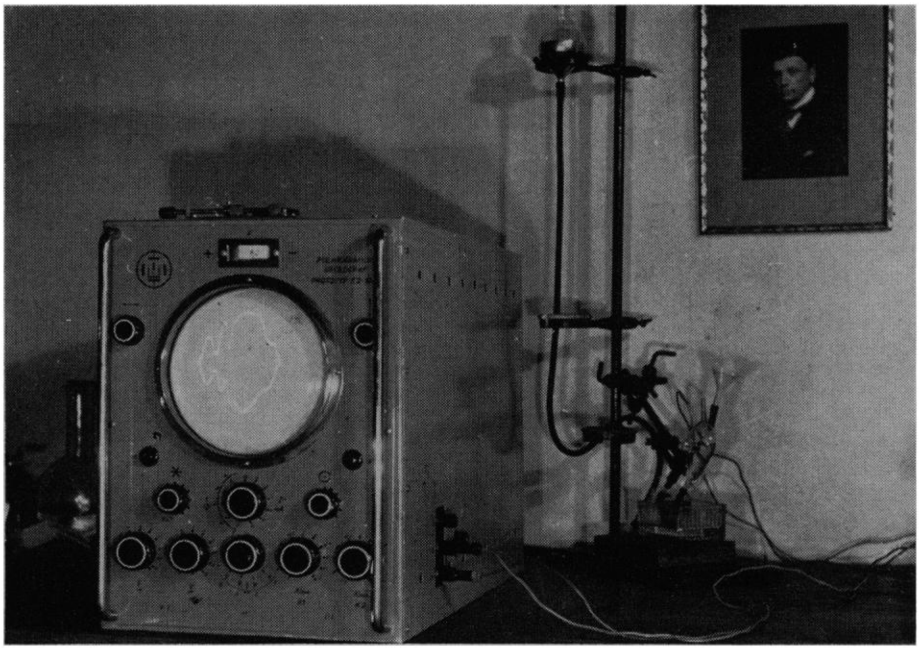


Fig. 25. Oscilloscope for polarographic analysis.

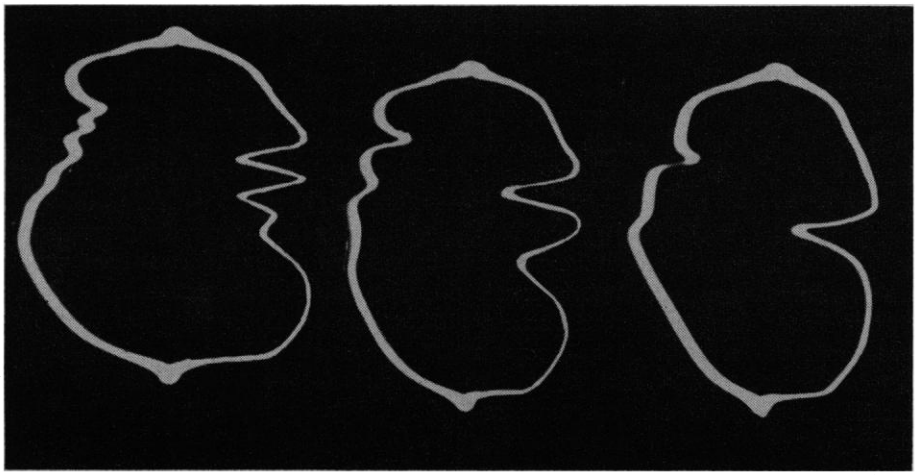


Fig. 26. Oscillographic diagram $dE/dt = f\ (E)$ of *o*- and *m*-nitrophenol, apart and in mixture.

or oxidations many otherwise inaccessible physicochemical constants are determinable. Polarography helps in the investigation of the chemical structure of organic, and lately even of inorganic, compounds. Striking are the results arrived at by polarographic studies of complexes of cobalt, nickel, iron, and chromium—complexes whose current-voltage curves disclose strange valencies. Vlček proved, for example, that cobalt in dipyridyl complexes is reduced from Co^{III} to Co^{II}, and from Co^{II} to Co^{I} (*21*), and as a result of these studies succeeded in preparing monovalent Co $(dipyridyl)_2{}^{I}$ complex. He also proved from polarographic curves the complex compounds of zero-valent nickel and cobalt, and in the carbonyls, negatively divalent iron and cobalt. The Cr^{III} tripyridyl complex may be successively reduced to Cr^{II}, Cr^{I}, and Cr^{0} in three equal steps. So far it is the only known instance in electrochemistry in which a trivalent cation can acquire, three times, one electron after another.

Although the analytical application of polarography is highly advanced at present, the field of its utilization in basic chemical problems is just beginning to open.

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