

Therefore, plots of $i\tau_k^{1/2}$ versus i exhibit a limiting value which is independent of current density and the value of K may be calculated from this limit.

Chronopotentiometry may be used in the characterization of metal complexes and in this respect it is a better method than polarography since the measurable value of $K(k_f + k_b)^{1/2}$ may be as large as $500 \text{ s}^{-1/2}$ (cf. $5 \text{ s}^{-1/2}$ for polarography). It should be pointed out, however, that many complex dissociation reactions follow a multi-step reaction path and therefore the rate constants measured may only have formal significance. Nevertheless, chronopotentiometry will indicate whether the complex is electroreduced *directly* or whether there is a preceding kinetic step.

Conclusion. A brief account has been given of some of the principles and applications of chronopotentiometry. More detailed consideration of its basic theory and of its developments makes rewarding reading but cannot be included here. The chronopotentiometric method is in the happy position of being already well established, but still full of further promise.

Linear sweep methods

Introduction. Another set of conditions which can conveniently be imposed on the micro-electrode is that of steadily rising voltage. The scan of voltage might be $\pm 2 \text{ V}$ from its rest potential which would encompass most electrode reactions. For each reacting component there will be an electrode potential at which electroreduction or oxidation takes place and the observed current will depend on the number and concentration of species present. The method was first developed by Randles²⁰ in 1948 following earlier experimental studies by Matheson and Nichols.²¹ Davis and Seaborn²² extended the method instrumentally and the theoretical basis was established by Sevcik,²³ Berzins and Delahay,²⁴ and by Delahay.²⁵ The signal generator can take a variety of forms depending on the sweep rate. This will also determine the form of display, which may be by pen-recorder but which almost always is made on a cathode-ray oscilloscope. Because of this the method is often known as 'cathode-ray polarography'.

Theory. The principal features of the method can be derived from consideration of a single charge-transfer reaction, i.e., as before, an electroreduction,



The applied potential, E , can be represented by

$$E = E_i - vt \quad (4.15)$$

where E_i is the initial potential and v is the rate of potential change in volts s^{-1} . By combining eqn. (4.15) with the Nernst equation and Fick's law of diffusion, an expression can be derived which relates the flux of reductant to the potential at the electrode surface. This expression is a complex differential equation and it can be solved by the *summation of an integral in small successive increments*. As the applied voltage approaches that of the reversible potential for this reaction, a small current flows, the magnitude of which grows rapidly but which then becomes limited at a potential beyond $E_{1/2}$ by the consequent depletion of reactant. As before, the diffusion profiles spread out into the solution, the rate of diffusive transport falls and with it the observed current. The current is thus seen to pass through a well defined maximum (see Fig. 4.1c), the value of which is described by the equation

$$i_p = \frac{0.447 F^{3/2} A n^{3/2} D^{1/2} c v^{1/2}}{R^{1/2} T^{1/2}} \quad (4.16)$$

The numerical constant of eqn. (4.16) may vary slightly from one derivation to another because, as emphasized above, the solution is obtained by summation of finite increments of an integral. It is also dependent on whether the product of the electrode is an insoluble film or is soluble in the metal or solution. Although the derivation of eqn. (4.16) is beyond the scope of this book, it is easy to experimentally verify that the peak height is indeed a linear function of $v^{1/2}$, c , and the electrode area.

For reversible processes the peak potential E_p , is close to the reversible half-wave potential and is given by eqn. (4.17):

$$E_p = E_{1/2} - 1.1 \frac{RT}{nF} \quad (4.17)$$

E_p is independent of sweep rate and concentration for a reversible process. For an *irreversible* process, E_p is progressively displaced towards higher overpotentials the more irreversible the electrode process, i.e., the displacement is a function of: k_{fh} , the forward rate constant; and, α , the transfer coefficient. E_p is also a function of the sweep rate. The relationship for the peak current of an irreversible process is the same as that for a reversible process except that the numerical constant is slightly different (approximately 0.497) and more important, $n^{3/2}$ is replaced by $n(\alpha n_a)^{1/2}$, where n_a is the number of electrons involved in the activated step. The proportionality between the peak current and the square root

of the transfer coefficient, α , is a disadvantage to the analytical applications of this method to irreversible processes because α is modified by the presence of traces of adsorbed material on the electrode surface. The accidental contamination of a test solution with such material may result in significant error. It is of interest to note that the chronopotentiometric method of analysis is unaffected by a variation in α ; the expression relating $\tau^{1/2}$ to c does not involve α and is the same for both reversible and irreversible processes.

A range of sweep times can be employed. The lower level, $\approx 0.1 \text{ V s}^{-1}$ is set by the onset of convective mixing at long polarization times. An upper limit of, say, 100 V s^{-1} is set by the increasing magnitude of the capacity current. Interference from this contribution to the total current and from residual (impurity) currents can be minimized by electronic subtractive procedures and these are described below, but eventually it becomes difficult to resolve the diffusion current at high frequencies (i.e., high sweep rates). In this method, the extreme voltage at the end of each scan is immediately returned to zero. Alternatively, the scanning procedure can simply be reversed, whereupon the applied voltage is reduced to zero in a reverse linear sweep of the same magnitude (but different sign) as the rising portion. The resultant voltammogram is shown in Fig. 4.1d; the peak height is given as before by eqn. (4.16). For reversible processes the two peak voltages are separated by $2.3RT/nF$ volts but with increasing irreversibility the peak separation becomes progressively greater.

The method is normally applied as a single sweep or as a cyclic sweep to a solid micro-electrode. If the voltage scanning is successively repeated, the electrode system may be slow to recover from the continuous depletion and from other effects of the electrode reaction. This is not a serious problem with the dropping mercury electrode (see below). The more serious limitation of the method is the need to compensate for the ohmic drop.

Instrumentation and procedure. Linear sweep methods are not so simple in their primary instrumentation as, for example, is chronopotentiometry. A very slow linear sweep may be generated by a motor-driven potentiometer, but generally an electronic system is used which may, in its crudest form, be a constant current source feeding a standard capacity; or, funds permitting, a sophisticated function generator. The basic circuit diagram is shown in Fig. 4.8. The values of peak current and peak voltage can be read off an illuminated screen of the oscilloscope or photographed.

The cell is basically that illustrated in Fig. 4.7. However, the separation

of the electrodes of this cell must be small when it is used for linear sweep voltammetry because the effects of ohmic drop must be minimized. Correction for ohmic drop and capacity current can be made by compensation methods or by an approximation based on a number of assumptions. iR compensation requires *active* compensation by a feedback circuit and, for a *known* cell resistance, the progressively changing iR component can be fed back to the voltage source. The capacity current, however, must be eliminated by a difference method employing a matched twin electrode system; one electrode in contact with the system of interest and the other in an identical system of supporting electrolyte, but *without* the electroactive species under investigation.

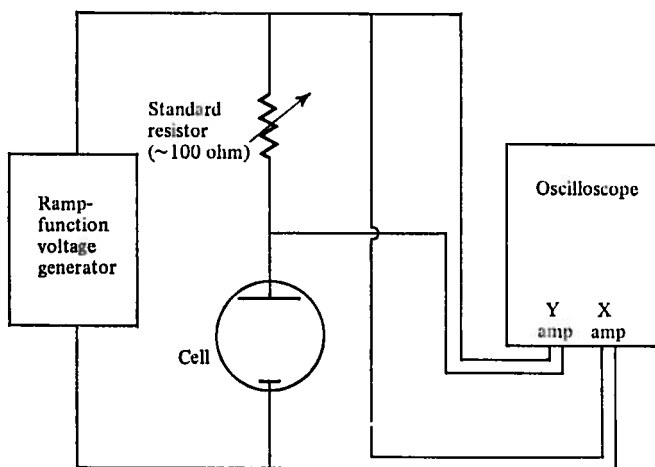


Fig. 4.8.

If neither of these methods can be used, correction for iR drop and the capacity current can be accomplished by calculation or by the rather less effective constructional methods. Delahay²⁶ reasoned that the 'true' electrode potential was related to the applied potential by

$$E = E_t - vt + r(i_f + i_c) \quad (4.18)$$

where r is the cell resistance, i_f the faradaic current, and i_c the capacity current. The third term on the right-hand side of eqn. (4.18) alters the effective rate of change of potential. If the new rate of change of voltage, v , is approximated to a linear function, then it is possible to calculate a correction for the peak current i_p . Delahay²⁶ has tabulated some corrections to i_p as a function of the ohmic drop.

The preparation, manipulation, and deoxygenation of the cell solution are exactly the same as described in the chronopotentiometry section and will not be repeated here.

Applications of linear sweep voltammetry. The principal advantages of the single sweep method lie in its rapidity of response. Commercial instruments employing this principle enable a single determination of concentration to be made in less than a second. Thus many samples can be evaluated or, for kinetic purposes, changes in concentration can be readily monitored. The extent of the sweep can be controlled such, that a sequence of electrode reactions can be truncated and this may be important in preventing deterioration of a solid micro-electrode.

The use of reverse scanning and triangular cyclic voltammetry offers further advantages in that the reoxidation of the electrode products may also be studied. It is particularly interesting to observe the constancy and separation of the peak voltages which are instant criteria of electrode reversibility. But the most noticeable consequence of irreversibility is the absence of the reverse wave and, for a totally irreversible reaction, the return current is almost wholly cathodic (see Fig. 4.10c).

The sensitivity of the method is similar to that of chronopotentiometry and concentrations of 10^{-2} – 10^{-5} M can be determined with a precision of 1–5 per cent. By using all the compensation devices, it is claimed that the sensitivity can be increased to 10^{-7} M.

Additional aspects of the method

1. *Series and stepwise reactions.* Where two electroreducible species are reduced at sufficiently differing potentials, two separate peak currents are observed. Gokhshtein and Gokhshtein²⁷ have derived a cumbersome

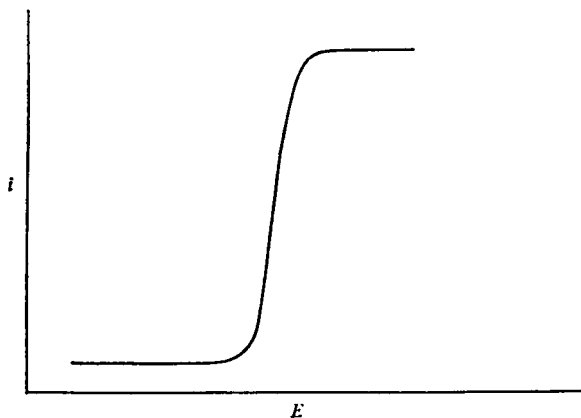


Fig. 4.9.

expression relating the two peaks to the concentration of the two electroactive species. These workers suggest that a relationship of such complexity would be unacceptable in routine analysis but if the peak separation, ΔE , is greater than a certain value (0.177 volts for a reversible reaction, and slightly greater for an irreversible reaction), then adjacent peaks can be analysed separately. From the Gokhshtein equations, it is

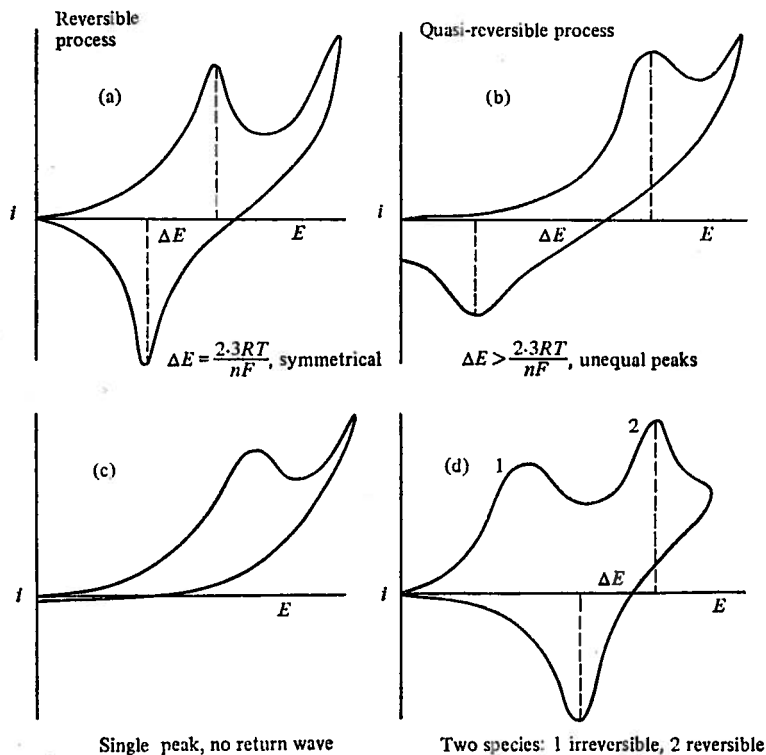


Fig. 4.10.

also confirmed that the second peak current is a function of $v^{1/2}$ and $D^{1/2}$ as in the case of a single species. It is immaterial whether the two peaks originate from the reduction of two separate electroactive species, or originate from the stepwise reduction of two of one species, the analysis is the same.

2. *Electrode process preceded by a controlling homogeneous reaction.* Linear sweep voltammograms of an electroreduction controlled by a preceding chemical reaction have a characteristic shape, Fig. 4.9. The

depolarizer is formed at a constant rate at the electrode surface and provided the diffusion of the inactive component is more rapid than its transformation to the active form, it cannot be depleted from the electrode surface; the 'peak' current is thus independent of potential. The peak has the shape of a conventional polarographic current-voltage curve and its height is independent of the sweep rate. RDI

3. *Reverse sweep voltammetry*. As mentioned earlier (page 86), cyclic or reverse sweep voltammetry has a number of applications in the measurement of the reversibility of a system. The relationship expressing the reversible and irreversible peak current and peak potential for the anodic sweep is exactly the same as for the cathodic, except that the sign of the potential displacement is reversed.

Figure 4.10 shows the cyclic voltammograms of a variety of reversible and irreversible systems, illustrating the separation of the cathodic and anodic peaks as a function of the reversibility of the system. 90

Conclusion. This brief description of linear sweep voltammetry deals with its essential aspects; it is a complementary method to chronopotentiometry. It involves somewhat more complex equipment but the results are often of more general significance because the voltage is controlled throughout. It has been made the basis of rapid routine analysis, and cyclic voltammetry is a most useful precursor study to other, more detailed investigations.

There are other voltammetric methods (a.c. polarography, R.F. polarography, etc.) all of which make use of different initial waveforms. However, the general principles and procedures are the same and their details can be found in several standard texts.²⁸⁻³¹

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