

# CONTROLLED-POTENTIAL ELECTROLYSIS AND THE RATES OF HOMOGENEOUS REACTIONS

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## INTRODUCTION

Controlled-potential electrolysis was born in the work of Haber<sup>1,2</sup>, was nurtured by Fischer<sup>3</sup> and Sand<sup>4</sup> among others during the first part of this century, and entered a period of rapid growth when Hickling<sup>5</sup> devised the first automatic potentiostat in 1942. Other potentiostats were devised by Diehl<sup>6,7</sup>, Lingane<sup>8,9</sup>, and Penther and Pompeo<sup>10</sup> during the years that followed, and the flood gates opened in 1950. Very sophisticated instruments are now available commercially, and it has come to be recognized that controlled-potential electrolysis is of great value in elucidating the half-reactions that take place at dropping mercury electrodes and other voltammetric indicator electrodes. Two simple and straightforward kinds of applications are especially familiar and common. One consists of using controlled-potential electrolysis to prepare the product of the half-reaction on a comparatively large scale, then identifying that product by any convenient technique. The other consists of integrating the current with respect to time during an exhaustive controlled-potential electrolysis, calculating the value of  $n$  from the ratio of the quantity of electricity consumed to the number of moles of starting material taken, and deducing the nature of the half-reaction from the result.

These two applications will be briefly summarized in the pages that follow, but much more stress will be placed on other less well known and less widely used techniques that often furnish more direct information about half-reaction mechanisms and that, in particular, often provide data on the rates of homogeneous chemical reactions coupled with the electron-transfer processes. It is not possible to give a really comprehensive review in the space available here, and one is not attempted. What is intended is to outline these techniques, to summarize and compare their scopes and limitations, and to give a representative sample of the chemical systems to which they have been applied. It is hoped in this way to stimulate and facilitate their more frequent use in the future. Partly for the sake of convenience and conciseness, and partly because stirred mercury-pool working electrodes have been far more often used than any others, this review is restricted to their use and to correlations with polarographic data. Working electrodes made of platinum, graphite, or any other material serve equally well when

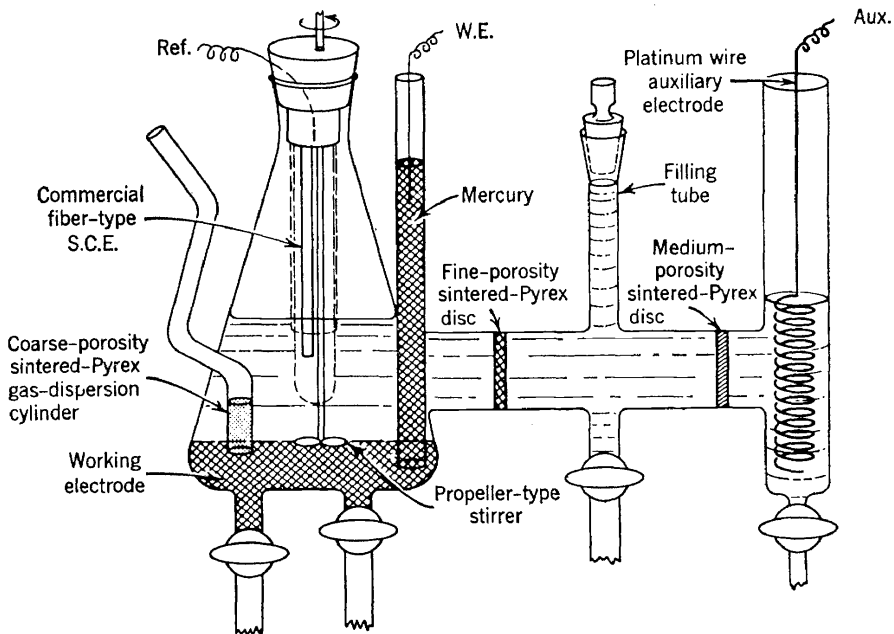
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the electrochemical circumstances permit their use. They provide information that can be correlated in exactly the same ways with voltammetric data obtained at similar indicator electrodes.

## FUNDAMENTAL CONSIDERATIONS

### THE SIMPLE O—R MECHANISM

It is convenient to begin with a brief description of the apparatus and experimental techniques employed in controlled-potential electrolysis. Cells having three electrodes are always used. A typical one<sup>11</sup> is shown in *Figure 1*. The electrolysis current flows between the mercury-pool working electrode and a platinum or graphite auxiliary electrode located in a separate compartment. The fritted glass discs and the stoppered central compartment, which is filled with the supporting electrolyte when the cell is in use, serve to prevent mixing of the solutions in the working-electrode and auxiliary-electrode compartments. Oxygen, chlorine, and other reducible substances are often formed at auxiliary anodes; if they were allowed to come into contact with working cathodes their reductions would increase measured current integrals and change the shapes of current-time curves. Other side reactions and even cyclic processes are sometimes possible. For similar reasons, dissolved air must be removed from the working-electrode compartment, just as in polarography, and a sintered-glass gas-dispersion cylinder is provided for this purpose. In extremely precise coulometric work one must worry about the trace of solution carried up onto the walls

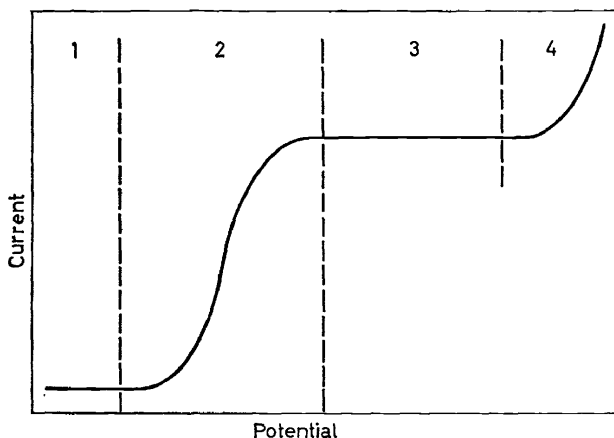


*Figure 1.* Double-diaphragm cell for controlled-potential electrolysis with a mercury-pool working electrode

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of the cell by entrainment in the gas stream<sup>12</sup>, but usually this is insignificant, and nitrogen or another inert gas is passed through the solution continuously during the electrolysis. The potentiostat monitors the difference between the potential of the working electrode and that of a reference electrode, compares it with a preset electrical potential, and continuously readjusts the voltage applied across the working and auxiliary electrodes so as to maintain this difference of potential constant and equal to the preset value. To prevent including any significant fraction of the  $iR$  drop through the cell in the potential presented to the potentiostat, the tip of the reference electrode must be placed as close to the surface of the pool as possible. Finally, to make the electrolysis proceed as quickly as possible, the solution is stirred by a propeller- or paddle-type stirrer whose blades are rapidly rotated in the pool-solution interface.

The current-potential curve for the substance of interest can be divided into four regions, as shown schematically in *Figure 2*. In region 1 the rate



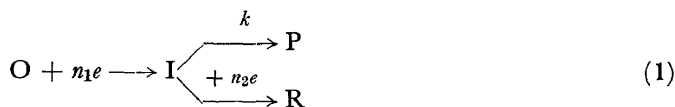
*Figure 2*. Idealized voltammogram

constant of the forward electron-transfer process is so small that the half-reaction does not occur at an appreciable rate, and the current is virtually equal to the residual current. In polarography the residual current is largely due to capacitative charging of the double layer around the growing mercury drop, but with a stirred pool electrode or any other electrode of constant average area double-layer charging occurs only at the very beginning of a controlled-potential electrolysis and consumes too small a quantity of electricity to be significant in anything except the coulometric determination of an exceedingly small amount of electroactive material<sup>13</sup>. Thereafter double-layer charging results only in noise attributable to fluctuations of electrode area produced by the violent stirring. The residual current in controlled-potential electrolysis may be due in part to electroactive impurities such as oxygen. If these are eliminated, as can be done by combining controlled-potential electrolytic purifications of the mercury and supporting electrolyte<sup>13, 14</sup> with extremely meticulous deaeration, it is due entirely to

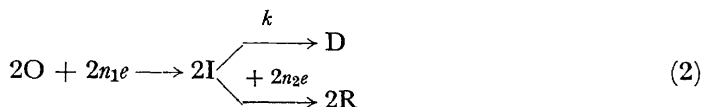
such processes as the reduction of hydrogen ion or water<sup>15</sup> or the oxidation of hydrazine, hydroxylamine, or some other reducing agent present in the supporting electrolyte. Totally irreversible half-reactions can be made to proceed in region 1, and values of  $an_a$  can be obtained from the dependence of the electrolytic rate constant on potential<sup>15, 16</sup>. This has little real advantage over the corresponding polarographic technique<sup>17</sup>, and exhaustive electrolyses in this region would be too slow to be worth considering.

In region 2 the electron-transfer process becomes faster. For a reversible half-reaction the ultimately attainable extent of reduction or oxidation is potential-dependent<sup>16, 18</sup>, and the formal potential of a reversible couple can be evaluated from data on the variation of the overall current integral  $Q_\infty$  [cf. eq. (17)] with potential<sup>19-21</sup>. Totally irreversible half-reactions, on the other hand, proceed to completion even in this region<sup>16</sup>.

Region 3, the mass-transfer-controlled region, is the one in which controlled-potential electrolyses are almost always performed. Two reasons are uniformly quoted for the choice. One is that the half-reaction of interest is driven to completion in this region while other half-reactions do not interfere; the other is that the electrolysis proceeds more rapidly in this region than it does in region 2. The first of these things is true in region 2 as well as in region 3 for the irreversible processes whose mechanisms we are usually attempting to decipher, and the second of them is not very persuasive in these days of automatic potentiostats, current integrators, and recorders. Branched-chain mechanisms like

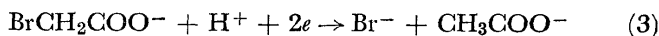


and



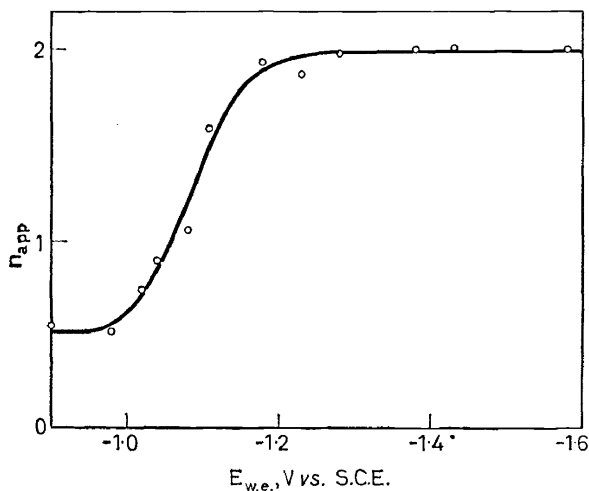
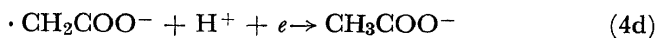
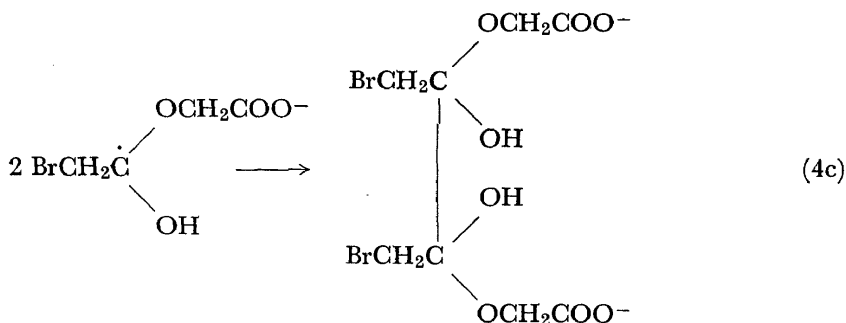
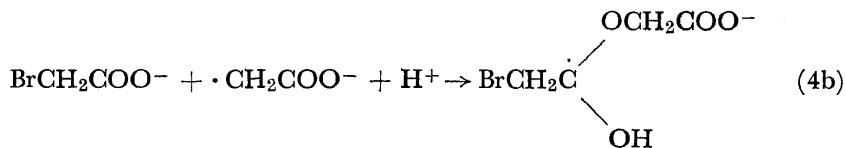
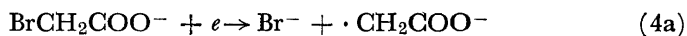
can be much more certainly and easily identified by electrolysis on the rising part of the wave than by electrolysis on the plateau. On the plateau the reduction of the intermediate I in either case is so fast that its concentration at the electrode surface is negligibly small, and consequently very little of it can undergo the chemical reaction. Only the reduction of O to R can be observed. On the rising part of the wave the situation may be very different. Unless the second electron-transfer step is much faster than the first, an appreciable fraction of the I will be carried away from the electrode surface into the bulk of the solution, where it is likely to be transformed into P or D before it can return to the electrode surface and undergo further reduction to R.

The reduction of bromoacetate in an ammoniacal ammonium bromide solution<sup>22</sup> provides an illustration. Electrolysis on the plateau of the wave gives no mechanistic information whatever. Coulometric measurements give  $n = 2$ ; bromide and acetate ions are formed by the overall half-reaction



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Electrolysis at any potential on the rising part of the wave would also give  $n = 2$  if eq. (3) told the whole truth. In reality, as is shown by *Figure 3*, the value of  $n_{app}$  [which will be defined by eq. (47)] decreases as the potential becomes less negative, and seems to approach a limiting value of  $\frac{1}{2}$  near the foot of the wave. This suggests a mechanism like



*Figure 3.* Plot of  $n_{app}$  against the potential of the mercury working electrode for reductions of bromoacetate ion in 1 *F* ammonia-1 *F* ammonium bromide

On the plateau of the wave the half-reactions (4a) and (4d) are both very fast, the lifetime of the radical anion is negligibly short, and reaction (4b) cannot occur to any measurable extent. On the rising part of the wave, convection carries a substantial fraction of the radical anion away from the electrode surface before it can be further reduced, and the existence of the alternative path represented by eqs. (4b) and (4c) then becomes immediately apparent. The exact nature of this path is not yet known with any certainty, and other reactions can certainly be envisioned to account for the data obtained. Another, and better characterized, case in which the starting material reacts with an intermediate will be discussed in a later section. For the moment it suffices to conclude that electrolysis on the rising part of the wave is peculiarly informative for such mechanisms and others that involve competing steps. There are three fundamental variables in controlled-potential electrolysis, as there are in other electroanalytical techniques: the composition of the solution, the rate of electron transfer, and the rate of mass transfer. If the second of these is sacrificed by performing electrolyses only on the plateau the scope and utility of the technique are greatly diminished.

Region 4 in *Figure 2* is generally avoided in controlled-potential electrolysis, for the intrusion of an extraneous half-reaction or the occurrence of a further reduction or oxidation can rarely be expected to be beneficial. Again, however, several reservations must be expressed. One is that, because the half-reaction responsible for the increase of current in this region will usually be totally irreversible, it will often proceed to a detectable extent in the time required for an exhaustive controlled-potential electrolysis even at a potential where it cannot be detected on a polarogram or stirred-pool voltammogram. Another is that, as will presently be discussed, part of the working electrode may be at a potential quite different from the one sensed and controlled by the potentiostat. For these two reasons it is less easy to avoid encroaching on region 4 than it may seem to be. Moreover, there are cases in which data obtained in region 4 are of great value in interpreting complex current-time curves obtained in region 3, and one of these will be described in connection with eq. (62).

It is convenient to consider the behaviour of the simple couple  $O + n_1e \rightarrow R$  when a solution of O is electrolyzed at a potential where the rate of the re-oxidation of R is negligible. If the couple is reversible this potential will lie on the plateau of the wave; for a totally irreversible couple it may lie either on the plateau or on the rising part of the wave. The current (in A) at any instant is given by

$$i = nFAk_0 C_0^\circ \quad (5)$$

where  $k_0$  is the heterogeneous rate constant for electron transfer at the potential in question and  $C_0^\circ$  is the time-dependent concentration of O at the surface of the electrode. The volume of the diffusion layer is so much smaller than that of the homogeneous bulk of the stirred solution that the steady-state approximation can be applied to the quantity of material contained in it. Fick's second law,

$$\frac{\partial C_O}{\partial t} = D_O \frac{\partial^2 C_O}{\partial x^2} \quad (0 \leq x \leq \delta) \quad (6)$$

valid between the electrode surface and some arbitrary point in the turbulent boundary layer  $\delta$  cm away from the surface of the electrode, thus becomes the ordinary differential equation

$$\frac{d^2 C_O}{dx^2} = 0 \quad (0 \leq x \leq \delta) \quad (7)$$

with the boundary conditions  $C_O = C_O^\circ$  at  $x = 0$  and  $C_O = C_O^b$  at  $x = \delta$ . The flux of O at the electrode surface is equal to the rate at which it is reduced:

$$D_O A \left( \frac{dC_O}{dx} \right)_{x=0} = A k_O C_O^\circ \quad (8)$$

while the rate at which O is transferred from the bulk of the solution into the diffusion layer is given by

$$-V \frac{dC_O^b}{dt} = D_O A \left( \frac{dC_O}{dx} \right)_{x=\delta} \quad (9)$$

Combining these equations, one obtains

$$C_O^\circ = \frac{\beta_O V}{A k_O + \beta_O V} C_O^b \quad (10)$$

and

$$C_O^b = C_O^{b,0} \exp \left( - \frac{\beta_O A k_O}{A k_O + \beta_O V} t \right) \quad (11)$$

in which  $C_O^{b,0}$  is the initial concentration of O in the bulk of the solution and  $\beta_O$  is a mass-transfer constant. Equations (5), (10), and (11) yield

$$i = \frac{\beta_O n F V A k_O C_O^{b,0}}{A k_O + \beta_O V} \exp \left( - \frac{\beta_O A k_O}{A k_O + \beta_O V} t \right) \quad (12)$$

A potential-dependent electrolytic rate constant  $\beta_O^*$  may be defined by writing

$$\beta_O^* = \frac{\beta_O A k_O}{A k_O + \beta_O V} \quad (13)$$

On the plateau of the wave, where  $k_O$  is very large, the value of  $\beta_O^*$  approaches that of  $\beta_O$ . In any event, whenever the rate of the re-oxidation of R can be neglected the dependence of current on time is expressed by the equation

$$i = \beta_O^* n F V C_O^{b,0} \exp(-\beta_O^* t) \quad (14)$$

This is Karp's derivation<sup>22</sup>; in this simple case the same result may be obtained much more easily by writing<sup>16, 23</sup>

$$-V \frac{dC_O^b}{dt} = V \beta_O^* C_O^b = \frac{i}{nF} \quad (15)$$

However, the analogous equation

$$i = \sum_j \beta_j^* n_j F V C_j^b \quad (16)$$

for a mechanism involving an electroactive intermediate conceals a tacit assumption that has not always been properly appreciated and that is sometimes false for a reason that will be described later.

Descriptions of the total quantity of electricity (in coulombs) consumed in an exhaustive electrolysis are obtained by integrating eq. (14) with respect to time:

$$Q_\infty = \int_0^\infty i dt = \frac{i^\circ}{\beta_O^*} = nF V C_{O^b}^{\circ} = nF N_O^\circ \quad (17)$$

where  $i^\circ$  is the initial current and  $N_O^\circ$  is the number of moles of O initially present. As is shown by eqs. (11) and (14), the bulk concentration of O and the current approach zero on prolonged electrolysis. The O will be quantitatively reduced to R if enough time is allowed. For 99.9 per cent completion one must have

$$\exp(-\beta_O t) = 0.001$$

or

$$t = 6.91/\beta_O^* \quad (18)$$

Typical values of  $\beta$  on the plateaus of the waves of various substances are about 0.003–0.005 sec<sup>-1</sup>, so that electrolyses there are 99.9 per cent complete in roughly half an hour. Values an order of magnitude higher can be obtained by ultrasonic agitation<sup>24</sup> or by extremely efficient mechanical stirring<sup>22</sup>. Smaller values can be obtained by increasing the volume of the solution or decreasing the efficiency of stirring, but these expedients are of only limited efficacy: electrolysis on the rising part of the wave, where  $\beta_O^*$  may be far smaller than  $\beta_O$ , is a far more powerful technique. This is important because a chemical step that escapes detection when  $\beta_O^*$  has one value may become very prominent when it has another.

In summary, there are four distinctive features of this simple case. One is that R is the only product obtained. The second is that the quantity  $Q_\infty/F N_O^\circ$  is equal to the integral value of  $n$ . The third is that the current decays exponentially with time, so that a plot of  $\ln i$  vs.  $t$  is linear and can be described by a single constant value of  $\beta_O^*$ . The fourth is that the three preceding things remain true in the face of variations of the stirring efficiency, the initial bulk concentration of O, or (as long as the rate of the re-oxidation of R remains negligible) the potential of the working electrode from one electrolysis to another. The first and third are true in this simple case even if the rate of re-oxidation is appreciable, although some O then remains



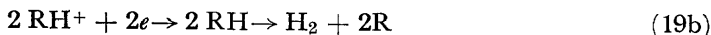
unreduced at the end of the electrolysis and the description of  $\beta_{\text{O}}^*$  becomes more complex<sup>16, 22</sup>, while the second becomes simply  $Q_{\infty}/F(\Delta N_{\text{O}}) = n$ , where  $\Delta N_{\text{O}}$  is the number of moles of O reduced. More complex mechanisms are recognized and identified, and the rate constants of their elementary steps are evaluated, by taking advantage of deviations from these four predictions.

Descriptions of controlled-potential electrolytic instrumentation and methodology are readily available elsewhere<sup>25-30</sup> and need not be given here. It is more important to stress some matters especially relevant to studies of the rates and mechanisms of homogeneous reactions.

The current that is measured at any instant during the course of a controlled-potential electrolysis includes the continuous faradaic current  $i_{f,c}$  (ref. 15), which reflects the slow reduction or oxidation of the solvent or of some major constituent of the supporting electrolyte. At mercury electrodes it usually arises from the reduction of hydrogen ion or water, and it increases exponentially as the potential of the working electrode becomes more negative. In acidic solutions it also depends on the concentration of acid present. It is large enough to be detected even in neutral or alkaline solutions at potentials as positive as  $-0.5$  V *vs.* S.C.E. It is therefore unusual for experimental plots of  $\ln i$  *vs.*  $t$  to be strictly linear over many decades even in the simple case just discussed. They are instead concave upward when the process of interest yields a current having the same sign as the continuous faradaic current, as is usually true for cathodic processes at mercury working electrodes. For anodic processes at mercury electrodes, such plots are usually concave downward. With other electrodes, such as platinum and graphite, concavity in either direction may be observed for both cathodic and anodic processes, depending on whether the anodic formation of oxygen or the cathodic formation of hydrogen predominates at the potential where the electrolysis is performed. The following discussion of the continuous faradaic current assumes that it is due to the reduction of hydrogen ion or water and that the process of interest is cathodic.

Correction for the continuous faradaic current is easily applied if neither O nor R affects the rate of evolution of hydrogen. Then this rate will be constant throughout the electrolysis, and one need only subtract the constant final current from the total current measured at any prior instant to obtain the current due to the reduction of O at that instant. Typical experimental and corrected plots are shown in *Figure 4*.

A word of caution is essential, however, because correction in this way is not always applicable. One situation in which it would not be is the one in which R is an amine or some other basic compound that can facilitate the reduction of protons by the familiar catalytic mechanism<sup>31</sup>



Another is the one in which O induces the reduction of hydrogen ion (or, in principle, of some other constituent of the supporting electrolyte, though no example of this has yet been definitely identified) by a mechanism like<sup>32</sup>



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auxiliary electrode; although the mercury electrode is an equipotential surface, the layer of solution in contact with it is not. In an asymmetrical cell there are two extreme alternatives. If the reference electrode is so placed that it senses the potential of the working cathode at the point where this is closest to the auxiliary electrode, every other point will be at a less negative potential with respect to the adjacent solution. At worst the point-to-point variations may be so large that part of the electrode is actually at a potential on the rising part of the wave even though the potentiostat is nominally maintaining the potential at a point on the plateau. At best the continuous faradaic current density will be smaller everywhere else than it is at the tip of the reference electrode. As the electrolysis proceeds and the current decreases, the variations of potential become smaller, and eventually are almost certain to become too small to detect: the potential difference between every point on the electrode surface and the adjacent solution becomes identical with that being maintained by the potentiostat. In the worst

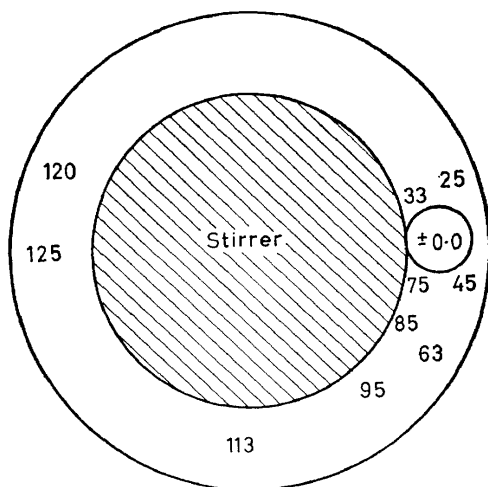


Figure 5. Variations of the potential of a mercury-pool electrode resulting from asymmetrical placement of the auxiliary electrode in a controlled-potential electrolytic cell.

case the result is an increase of the average value of the electrolytic rate constant  $\beta_0^*$ ; a plot of  $\ln i$  vs.  $t$  may be markedly concave downward. In the best case it causes the steady final current to exceed the average value of the continuous faradaic current during the electrolysis; correction in the above fashion will then be erroneous and will lead to a value of  $Q_\infty/F N_0^\circ$  that is smaller than  $n$ .

The other extreme is of course the one in which the reference electrode senses the potential at a point as far away from the auxiliary electrode as possible. Over most of the area of a pool cathode the potential will then be more negative than the nominal one. It may at worst be so much more negative as to encroach on a later wave, and a mixture of products will be

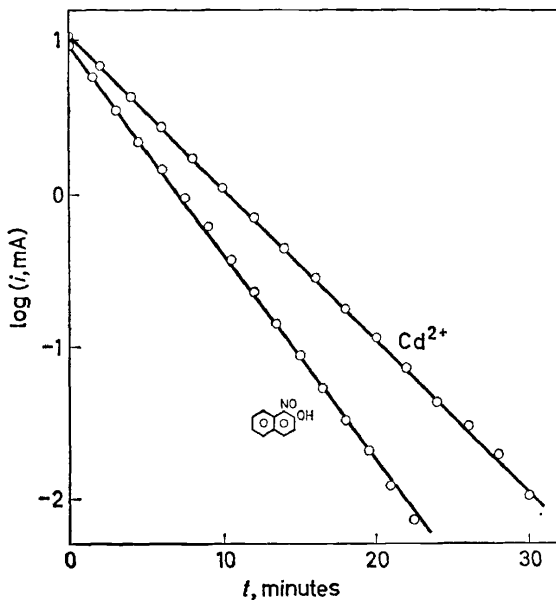
obtained if it does; at best the continuous faradaic current will be larger at the start of the electrolysis than it is at the end. In either event a plot of  $\ln i$  vs.  $t$  will be concave upward, and correcting the current integral in the manner described above will give a value of  $Q_{\infty}/F N_0^{\circ}$  that is larger than  $n$ . The placement of the reference electrode in the cell of *Figure 1* represents an attempt to compromise between these two extremes. Although the potential does vary across the surface of the pool whenever the current and the specific resistance of the solution are appreciable, its range of variation includes the desired value and the upward concavity of a plot of  $\ln i$  vs.  $t$  that tends to result from the more negative potential at one side of the pool is very nearly exactly counterbalanced by the opposing effect of the more positive potential at the other.

Nevertheless, it is so desirable to be able to feel quite confident that any curvature of a plot of  $\ln i$  vs.  $t$  reflects deviations from the simple mass-transfer-controlled case that more stringent measures are in order. Two are available. One is to employ a cell in which the electric field is uniform. Booman and Holbrook<sup>33</sup> placed a circular auxiliary electrode in a toroidal compartment located above the annular working electrode of *Figure 5*. Karp<sup>22</sup> used a cell in which the stirrer shaft passed upward through the pool from a bearing beneath it, so that a large horizontal piece of platinum gauze or a flat spiral of heavy platinum wire having nearly the same diameter as the pool could be used as the auxiliary electrode. In either cell a sintered-glass diaphragm is used to separate the solution being electrolyzed from the supporting electrolyte in the auxiliary-electrode compartment.

Another course takes advantage of the fact that the variations of potential are proportional to both the current and the specific resistance of the solution. It consists of employing solutions that contain such low concentrations of electroactive material that the current does not exceed perhaps 50 mA at the start of the electrolysis, and such high concentrations of supporting electrolytes that the specific resistance is no larger than about 10 ohm-cm. In the cell of *Figure 1* the former value corresponds to an initial concentration of about  $1/n$  mM for an electrolysis performed on the plateau of a wave with ordinary stirring; the latter is approximately the value for a 1 *F* aqueous solution of potassium chloride. Under these conditions the variation of potential across the pool is very unlikely to exceed something like 40 mV. If the reference electrode is placed at a point whose distance from the auxiliary electrode is near the mean of the least and greatest distances, the variation can hardly have any perceptible effect except in an electrolysis conducted on the steeply rising portion of a wave. In such a case or if a more concentrated solution must be electrolyzed, as is sometimes desirable to reveal a dimerization or some other pseudo-second-order reaction of an intermediate, the specific conductance of the solution should be increased in proportion to the initial current. An attempt to obtain a large yield of product by electrolyzing a solution containing a great deal of electroactive material but not much supporting electrolyte in a non-uniform cell is little more than an open invitation to confusion if the mechanism is not known to be completely straightforward.

Finally, to conclude this description of the behaviour of the simple O—R mechanism, we must examine the current-time curve more closely.

Although an exponentially decreasing current is one of the uniquely distinctive features of this mechanism, the criterion loses much of its utility if the experimenter does nothing more than plot  $\ln i$  vs.  $t$  and examine the linearity of this plot. Two factors combine to render small but significant deviations from linearity invisible. One is the nature of the plot; the other is the noise that arises from fluctuations in the rate of mass transfer and from random momentary excursions of the charging current away from zero, both of which result from instantaneous variations of electrode area caused by the violent stirring. These have the effects shown in *Figure 6*. Both of these



*Figure 6.* Plots of  $\log i$  against time for the reductions of cadmium(II) and 1-nitroso-2-naphthol in acetate buffers at potentials on the plateaus of their respective waves

plots appear to be linear, but in fact one of them is and the other is not. A far superior way of applying what is really the same criterion is based on the parameter  $Q_R$  defined by the equation<sup>35</sup>

$$Q_R = \int_t^{\infty} i \, dt = Q_{\infty} - \int_0^t i \, dt = Q_{\infty} - Q_t \quad (21)$$

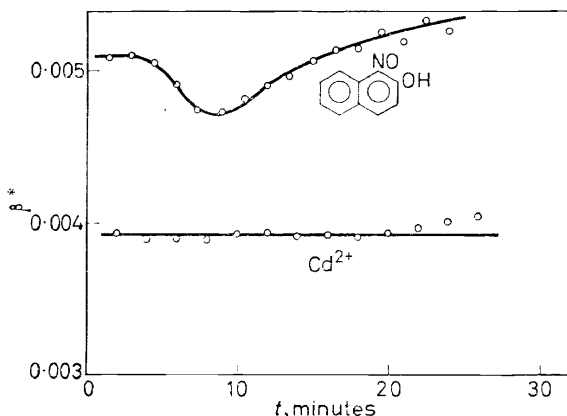
Equation (14) for the simple O—R mechanism may be written

$$i = i^{\circ} \exp(-\beta_O^* t) \quad (22)$$

Consequently 
$$\frac{Q_R}{Q_{\infty}} = \exp(-\beta_O^* t) \quad (23a)$$

or 
$$\beta_O^* = -\frac{1}{t} \ln \frac{Q_R}{Q_{\infty}} \quad (23b)$$

Although eq. (23a) has the same functional form as eq. (22), the current integral can be measured far more precisely than the current itself, and in addition it is virtually completely immune to instantaneous fluctuations of stirring efficiency. Hence a plot of the right-hand side of eq. (23b) against time is a horizontal straight line for the simple O—R mechanism, provided only that the average stirring efficiency remains constant throughout the electrolysis. The requirement is easily satisfied, and constancy of  $\beta_O^*$  within about 0.5 per cent is obtained without difficulty. *Figure 7* shows such



*Figure 7.* Plots of  $\beta^*$ , computed from eq. (23b), against time for the data of *Figure 6*

plots for the data of *Figure 6*. Whereas the value of  $\beta_O^*$  is strictly constant in the reduction of cadmium(II), excepting for a small drift very near the end of the electrolysis that might result either from a tiny error in  $Q_\infty$  or from a tiny continuous faradaic current, pronounced variations are apparent in the curve for 1-nitroso-2-naphthol. These of course reflect the mechanistic complications involved in the reduction of the latter; it may be said in passing that the shape of this curve is uniquely diagnostic of an ECE mechanism involving a fairly fast intervening chemical step.

Plots of  $\log Q_R$  vs.  $t$  are useful in kinetic analysis as well as in the study of reaction mechanisms. With the aid of a logarithmic strip-chart recording potentiometer, such plots are easily obtained with either of the two most widely used kinds of current integrators. In one of these<sup>11</sup>, a servomotor rotates the shaft of a d.c. tachometer generator at such a rate that the output of the generator is always numerically equal to an  $iR$  drop of opposing polarity obtained by passing the electrolysis current through a standard resistor. The gear train intervening between the shafts of the motor and generator is connected to a mechanical revolution counter. The number of revolutions made by the counter shaft during any interval is proportional to the quantity of electricity accumulated during that interval. We have attached a 40-turn helical potentiometer provided with a precision dial and a slip clutch to the gear train of such an integrator. After a preliminary electrolysis is performed to obtain the value of  $Q_\infty$ , a suitable small d.c.

voltage is applied across the terminals of the helical potentiometer and the slider is set to a point from which it will just be returned to zero at the end of the electrolysis. The output of the potentiometer is then proportional to  $Q_R$  and is recorded on a logarithmic recorder as the electrolysis proceeds. Reversing the polarity of the voltage applied across the potentiometer and setting the slider initially at one end of its traverse, one may obtain an automatic record of the variation of  $Q_t$ . As  $\ln Q_t$  has no special significance, a linear recorder is more convenient than a logarithmic one for this purpose. If the signal proportional to  $Q_t$  is connected to the X-input terminals of an X-Y recorder whose Y-input terminals are connected across a standard resistor in series with the working electrode, one obtains plots of  $i$  vs.  $Q_t$  like those described by Hanamura<sup>36</sup> and Rechnitz<sup>28</sup>.

Operational-amplifier integrators<sup>33, 37</sup> amplify the signal obtained by passing the electrolysis current through a standard input resistor, and provide a current output that is proportional to this signal and that is used to charge a low-leakage precision capacitor. The voltage across this capacitor at any instant is proportional to the value of  $Q_t$ . A cathode follower may be used to connect the capacitor to the input terminals of a T-Y recorder, thus providing plots of  $Q_t$  vs.  $t$ . To obtain plots of  $Q_R$  (or, with a logarithmic recorder,  $\log Q_R$ ) vs.  $t$ , one need only reverse the leads from the cathode follower to the recorder input and interpose a steady d.c. voltage that opposes the output of the cathode follower and that is initially adjusted to be numerically equal to the expected final value of that output. It would be a simple matter to add analogue computation circuitry to either of these arrangements to provide plots of  $\beta^*$  vs.  $t$  directly, but corrections for continuous faradaic currents would then be even more difficult to apply than they are to plots of  $\log Q_R$  vs.  $t$ , and we have therefore not undertaken this addition.

Kinetic analyses of mixtures of electroactive substances are easily performed with such instruments and will be described in a subsequent section.

## PRODUCT IDENTIFICATION

It has long been recognized that much valuable information about the course of a controlled-potential electrolytic process can be obtained by identifying, and preferably also determining, the product or products obtained. The identification can sometimes be made by simple chemical tests. Absorption spectroscopy, both infrared and visible-ultraviolet, is widely used. Gas chromatography and other chromatographic techniques, nuclear magnetic resonance and electron-spin resonance spectroscopy, mass spectrometry, and measurements of the volume of evolved gas have also been employed as dictated by the nature of the product.

There have been many researches in which controlled-potential electrolysis has been used to prepare solutions containing a lower oxidation state of an element, and in which these solutions have then been studied by polarography, absorption spectroscopy, or some other technique<sup>21, 38-42</sup>. Those who have done such work have generally focussed their attentions on the properties of the products rather than on the mechanisms of the reductions by which they are obtained, and have therefore usually been content to show by coulometric measurements that these reductions are

quantitative in a gross stoichiometric sense. The oxidation of chromium(II) in chloride media has been studied in more detail. Jones and Anson<sup>43</sup> electrolyzed perchloric acid solutions containing comparable concentrations of chromium(II) and chloride, and determined the consumption of chloride by potentiometric titrations of the resulting solutions with silver(I). They found that one mole of chloride could be consumed in the oxidation of each mole of chromium(II), so that the product must have been the chloropenta-aquochromium(III) ion, and concluded that the oxidation occurs preferentially by electron transfer through a chloride ion adsorbed onto the surface of the electrode and acting as a bridge between the electrode and a chromium(II) ion. In concentrated solutions of hydrochloric acid, polarograms and visible-absorption spectra<sup>44</sup> indicate that the dichlorotetraaquochromium(III) ion is the principal product.

In the reduction or oxidation of an organic compound, however, any one value of  $n$  may often correspond to any of a number of possible products. Those concerned with organic substances have therefore generally recognized the necessity of supplementing their coulometric measurements with more direct and unambiguous information about the identities of the products obtained. The coulometric  $n$ -value may be ambiguous in either of two somewhat different ways. It is often possible to write two quite different half-reactions for which  $n$  is the same. For example, the fact that  $n = 1$  for the anodic wave of mercaptobenzothiazole (= RSH) might mean that the half-reaction is



or that it is



but it is the mercury(I) salt that is actually obtained<sup>45</sup>. Another source of ambiguity arises from the fact that the coulometric measurement is often powerless to reveal the occurrence of a chemical reaction that follows the last electron-transfer step. For example, an  $n$ -value of 2 for the reduction of cyclohexyl nitrate<sup>46</sup> might correspond to the half-reaction



but in an initially unbuffered solution, whose pH increases as the electrolysis proceeds, the nitrate ester hydrolyzes to give cyclohexanol and nitrate ion, and this hydrolysis has no effect on either the coulometric result or the current-time curve. Similarly, knowing that  $n = 4$  in a reduction of nitrobenzene provides no clue to whether phenylhydroxylamine or *p*-aminophenol has been produced. It will be shown below that it is sometimes possible to obtain rate data for chemical processes like these by electro-metric measurements alone, and there are other techniques that can be invoked when the electro-metric ones fail. Nevertheless, product identification is, and will certainly continue to be, an important part of the complete elucidation of the mechanism of a half-reaction occurring in a controlled-potential electrolysis.

This is so widely recognized that the point will not be detailed here. Even a somewhat incomplete list of references<sup>1, 2, 45-121</sup> suffices to show that



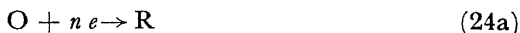
product identification has played a notable part in the development of our present understanding of the overall courses of many half-reactions. In this connection, special mention must be made of Adams' review<sup>122</sup> of the use of electron-spin resonance spectroscopy in identifying and characterizing free-radical products of controlled-potential electrolyses, especially in aprotic solvents.

In the future it will become more and more customary to monitor the concentrations of intermediates during controlled-potential electrolyses. Scheffel<sup>123</sup> made periodic measurements of the absorbance of a solution during electrolysis with a dropping mercury electrode, and several authors since Lingane and Small<sup>39</sup> have done the same thing during controlled-potential electrolyses with large pool electrodes. It is about equally common to obtain polarograms at various stages of a controlled-potential electrolysis. However, it is not possible to write a continuous equation for the time dependence of the concentration of any species when the electrolysis is interrupted to make such measurements, and continuous monitoring is therefore much to be preferred. It was apparently Cover<sup>124</sup> who first circulated the solution from the working-electrode compartment of a controlled-potential electrolysis cell into a spectrophotometric cell and back again. An intermediate whose half-life is at least equal to the time of residence in the circulating loop should be easy to detect and study in this way or by any of a number of equivalent techniques. Cover recorded the absorbance at a single fixed wavelength, but an oscilloscopic spectrophotometer could equally well be used to obtain complete spectra. A suitable indicator electrode, either in the working-electrode compartment or in an external cell through which the solution is circulated, can be used to provide a record of the limiting current of some intermediate or product, and Valenta and Koryta<sup>125</sup> obtained an oscilloscopic presentation of the current-potential curve as an electrolysis proceeded. A related possibility is to follow the decay of an intermediate when an only partly completed electrolysis is interrupted, as has been done in studying the reductions of *m*- and *p*-nitrophenol<sup>126</sup>. Another interesting recent development is the spectroscopic detection of very unstable intermediates in the diffusion layers at solid electrodes, using multiple internal reflectance techniques<sup>127-129</sup>. The natures and behaviours of the intermediates have often had to be inferred from the structures of the products finally obtained; direct observation of the intermediates themselves will often permit inference to be replaced by certainty.

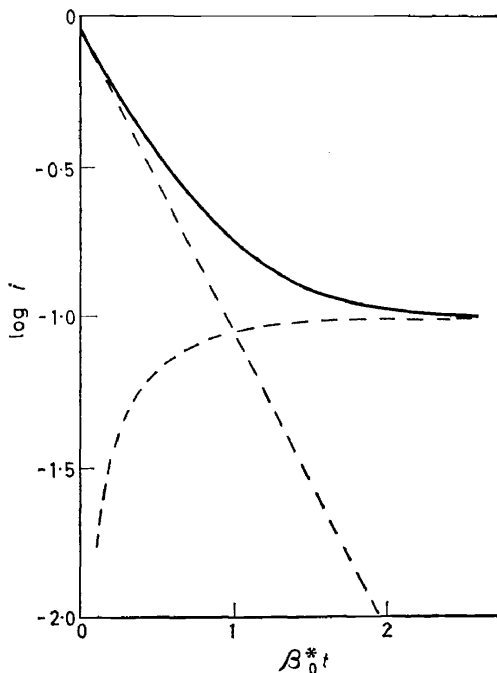
The identification and determination of electrolysis products have received rather short shrift here because, though they do provide information about the nature of the reaction mechanism, they alone have rarely been used to obtain quantitative information about the rates of the steps involved. One can of course sometimes tell that one sequence of reactions is much more rapid than another that must start from the same intermediate, and it is easy to imagine mechanisms for which rate data could be obtained by studying the effects of the initial concentration and the mass-transfer coefficients on the relative yields of two or more products. The first of these is too qualitative to require discussion; the second may be regarded as a potentially valuable complement to the techniques to which the remainder of this paper is devoted.

LOUIS MEITES  
**CATALYTIC PROCESSES**

One common and frequently investigated reaction scheme is that in which the product of a half-reaction reacts chemically with hydrogen ion, water, or some other electrolytically inactive major constituent of the supporting electrolyte to regenerate the starting material or some other electroactive substance. In its simplest form this scheme may be represented by the equations



If the second of these reactions is sufficiently slow to permit neglecting the extent to which it proceeds in the diffusion layer, and if the initial concentration of Z is so large that it remains virtually constant for a long time, a plot of  $\ln i$  vs.  $t$  will have the shape shown in *Figure 8*. Its initial portion is nearly linear, but it is concave upward and as time goes on the current approaches a constant value  $i_\infty$  that exceeds the continuous faradaic current  $i_{f,c}$  obtained with the supporting electrolyte alone under exactly the same conditions.



*Figure 8.* The effect of the catalytic step represented by eq. (24b) on a plot of  $\log i$  against time. The straight dashed line is the plot that would be obtained if the catalytic step did not take place; the curved one shows how the catalytic current increases toward its steady-state value as the electrolysis proceeds and the bulk concentration of R increases. The solid line represents the total current that will be obtained. Even in this rather favourable case, where  $kC_Z$  is so large that  $C_R^{b,ss}/C_O^{b,0}$  slightly exceeds 0.1, very precise measurements of the currents during the initial part of the electrolysis would be needed to reveal the time dependence of  $i_c$  and permit this situation to be distinguished from that of *Figure 4*.

This difference provides an easy way of distinguishing this behaviour from the superficially similar one shown in *Figure 4*. The catalytic current  $i_c^{ss}$  at the steady state is defined by the equation

$$i_c^{ss} = i_\infty - i_{f,c} \quad (25)$$

In the final steady state one has

$$\frac{dC_O^{b,ss}}{dt} = 0 = - \frac{i_c^{ss}}{n F V} + k C_R^{b,ss} C_Z \quad (26)$$

subject to the provisions mentioned above. The bulk concentration of R at the steady state,  $C_R^{b,ss}$ , can be computed by taking advantage of the facts that

$$i_c^{ss} = \beta_O^* n F V C_O^{b,ss} \quad (27a)$$

and 
$$C_O^{b,ss} + C_R^{b,ss} = C_O^{b,0} \quad (27b)$$

Values of  $\beta_O^*$  have generally been obtained from either the intercept or the initial slope of a plot of  $\ln i$  vs.  $t$ , but a better procedure is to plot the value of  $\beta_O^*$  defined by the equation

$$\beta_O^* = - \frac{1}{t} \ln \left( 1 - \frac{Q_t}{n F N_O^0} \right) \quad (28)$$

against time and extrapolate to  $t = 0$ ; the intercept is equal to  $\beta_O$ . After the steady-state concentrations of O and R have been calculated from eqs. (27), the pseudo-first-order rate constant  $kC_Z$  is easily calculated from eq. (26). The rate equation for the catalytic step can be deduced by varying the concentration of Z and the initial concentration of O, and the value of  $k$  is finally obtained in a perfectly straightforward fashion.

This technique has been applied to a number of chemical systems since it was first described by Meites and Moros<sup>15</sup>. Badoz-Lambling<sup>130</sup> employed it in a qualitative interpretation of data previously obtained<sup>131</sup> in oxidations of bromide ion at platinum electrodes in acidic aqueous solutions containing chloride. Rechnitz and Laitinen<sup>132</sup> employed it in studying the mechanism of the oxidation of molybdenum(v) by perchlorate ion in acidic solutions. Moros and Meites<sup>133</sup> employed it in studying the reaction between manganese(I) and hydrogen cyanide in sodium cyanide solutions, with the results shown in *Figure 9*. The catalytic reaction proves to be half-order with respect to manganese(I). This was confirmed by spectrophotometric and amperometric data on the rates of decay of the concentrations of manganese(I) over a wide range of experimental conditions, and was attributed to the operation of an equilibrium between a monomeric species of manganese(I) that reacts with hydrogen cyanide and a dimeric one that does not. Rechnitz and McClure<sup>134</sup> applied a similar treatment to data obtained in reductions of iridium(IV) in perchloric acid media, but Page and Zinser<sup>135</sup> were unable to confirm their results and suggested another explanation of the steady-state currents reported.

As has been pointed out repeatedly<sup>15, 136, 137</sup>, one major advantage of this technique is that the current is a direct and simple measure of the rate

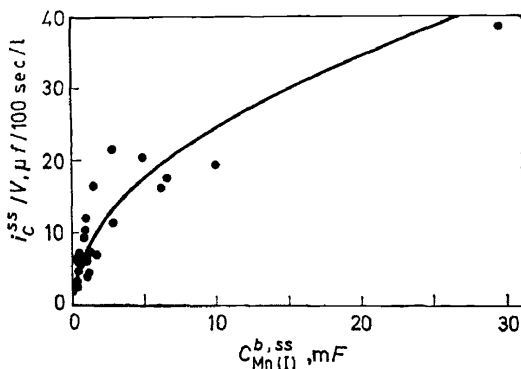


Figure 9. Dependence of the steady-state catalytic current on the steady-state concentration of manganese(II) in 1 *F* sodium cyanide solutions. The solid line represents the equation  $i_c^{ss} = k (C_{Mn(II)}^{b,ss})^{\frac{1}{2}}$

of the catalytic process. It is not applicable in the above form to fast catalytic reactions, for these proceed so extensively in the diffusion layer that eq. (26) becomes invalid. It may appropriately be regarded as a convenient way of dealing with catalytic processes too slow to be detected or precisely studied by the more familiar polarographic technique.

This is almost the only use of controlled-potential electrolysis for which amperometric measurements are superior to coulometric ones. It is easy to evaluate the steady-state current from a current-time curve obtained with a T-Y recording potentiometer connected across a standard resistor in series with the working electrode. An equivalent technique is to obtain the steady-state current from the equation

$$i_{\infty} = \left( \frac{\Delta Q}{\Delta t} \right)_{t \gg 1/\beta_0^*} \quad (29)$$

with the aid of a direct-reading current integrator. In principle this is advantageous because it swamps out the variations of current that arise from fluctuations of stirring efficiency<sup>138</sup>, but in this situation the advantage is very slight.

Theoretically it is also possible to evaluate  $kC_Z$  from coulometric data alone. The rate of the catalytic process increases as the electrolysis proceeds and R accumulates in the bulk of the solution; at the end of the electrolysis it is larger than its average value during the electrolysis. This is shown by the dashed curve in Figure 8. A plot of  $Q_t$  vs.  $t$  has the shape shown in Figure 10. Extrapolating the linear final portion back to  $t = 0$  yields an intercept  $Q_{t=0}$  from which an apparent value of  $n$  can be computed:

$$n_{app,t=0} = \frac{Q_{t=0}}{F N_0^c} \quad (30)$$

This would be equal to the true value of  $n$  if the steady final current were constant throughout the electrolysis. That is the behaviour of the continuous faradaic current, for which a similar extrapolation yields a theoretically exact correction. But when a catalytic step is involved the correction is

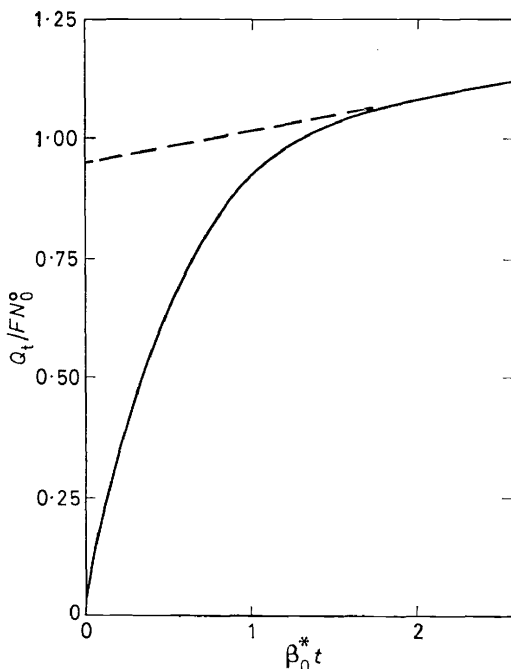


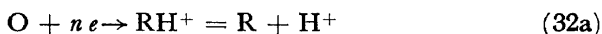
Figure 10. Plot of  $Q_t/FN_0$  against  $\beta_0^*t$  for the catalytic mechanism represented by eqs. (24). The dashed straight line shows the extrapolation that would be performed to evaluate the right-hand side of eq. (30). The numbers on the ordinate axis pertain to  $n = 1$

larger than it should be, and therefore  $n_{\text{app}, t=0}$  is smaller than  $n$ . This is another way of distinguishing this situation from that of Figure 4 despite the apparent similarity between the plots of  $\ln i$  vs.  $t$ . The relation between  $n_{\text{app}, t=0}$  and  $n$  in a catalytic process is

$$\frac{n_{\text{app}, t=0}}{n} = \frac{\beta_0^*}{\beta_0^* + k C_Z} \quad (31)$$

if the catalytic step is correctly described by eq. (24b). Geske and Bard<sup>139</sup> felt that the catalytic process would be difficult to detect unless  $kC_Z \geq 0.1 \beta_0$ , but as it is easily possible to obtain values of  $Q_t$  precise to  $\pm 0.1$  per cent their estimate seems far too pessimistic. At the same time, however, it is clear that much precision is lost in evaluating  $kC_Z$  by means of eq. (31). In the writer's opinion coulometric data are more useful for identifying this mechanism than for evaluating the rate constant of its chemical step. This is especially true if the catalytic step is not first-order with respect to R. Then the steady-state catalytic current is not proportional to the concentration of R, and the value of  $n_{\text{app}, t=0}/n$  is not independent of the initial concentration of O. The order of the reaction with respect to either R or Z is easier to deduce from the amperometric data than from the coulometric one.

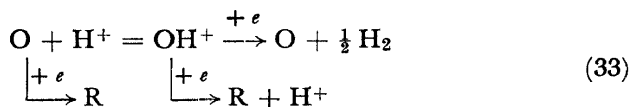
One distinctive feature of the above mechanism is that it yields a steady-state catalytic current that is independent of potential<sup>15, 133</sup>. The catalytic current produced by the mechanism<sup>15</sup>



is governed by the rate and equilibrium constants for the protonation of R and by the electrochemical kinetic parameters for the reduction of  $RH^+$ , and increases exponentially as the potential of the working electrode becomes more negative. The one example uncovered to date arises in acidic solutions of vanadium(II) ( $= R$ ) obtained from the reduction of vanadium(III) or vanadium(IV), and the observed behaviour is more complex than the one described here in that the catalytic current depends not only on the composition of the supporting electrolyte, the concentration of vanadium(II) at the steady state, and the potential, but also on the time even though all of the vanadium remains in the divalent state. Israel and Meites<sup>21</sup> attributed this to a very slow equilibrium among different species of vanadium(II); in addition, it appears that  $RH^+$  actually consists of a hydronium ion serving as a bridge between the electrode and a bisulphatovanadium(II) complex ion, for the catalytic current depends on the concentrations of both hydronium and bisulphate ions.

### INDUCED PROCESSES

The commonest (but not the only) induced process is that represented by the mechanism<sup>15</sup>



in which the protonated form of an electroactive substance can accept electrons to yield hydrogen gas and the deprotonated form as an alternative to the normal path. In this situation a plot of  $\ln i$  vs.  $t$  should be strictly linear [and therefore capable of being described by a single constant value of  $\beta^*$  obtained from eq. (23b)] after correction for the continuous faradaic and catalytic currents if these are large enough to be significant, but the similarly corrected current integral exceeds the value described by eq. (17). Unless the rate of the induced process is limited by the rate of protonation or the rate of formation of a protonated bridge, the excess quantity of electricity may be expected to be potential-dependent. This has been found to be true in all of the cases studied thus far. Usually the excess quantity of electricity has amounted to only a few per cent of the total, which is so little that the process would escape detection in polarographic experiments.

Constancy of  $\beta^*$  is absolutely essential to the diagnosis of an induced process. If the  $iR$  drop across the pool is appreciable and if the reference electrode is so located that part of the pool is at a potential more negative than that being maintained by the potentiostat, some hydrogen ion or water may be reduced at that part in the ordinary electrochemical way. The total quantity of electricity will again exceed the expected value and R will again be the only product obtained. In this case the rate of hydrogen evolution will decrease as the current due to the main process decreases, but the relation between these will be approximately exponential rather

than linear. A plot of  $\ln i$  vs.  $t$  will be concave upward, but as long as the excess consumption of electricity is small the concavity is likely to be too small to detect; a much more sensitive observation is that  $\beta^*$  will appear to decrease toward a constant value as the electrolysis proceeds. In addition, because the  $iR$  drop across the pool at any instant is approximately proportional to the initial concentration of O, region 4 of *Figure 2* will be invaded farther and farther as that concentration is increased, and the value of  $Q_\infty$  will increase more rapidly than the concentration does; for a pseudo-first-order induced process, on the other hand,  $Q_\infty$  is strictly proportional to the initial concentration of O.

The reduction of hydrogen ion is induced in this way by the reductions of manganese(II) in cyanide solutions<sup>20, 133</sup>, of dimethylglyoxime<sup>32</sup>, and of vanadium(III) in acidic sulphate solutions<sup>21</sup>, and it also appears that the reduction of vanadium(V) in perchloric acid solutions induces the reduction of perchlorate ion<sup>21</sup>. The induced reduction of hydrogen ion also appears to be fairly common in reductions of aquo-metal ions, where  $\text{OH}^+$  is an aquo-complex in which a molecule of water serves as a bridge between the electrode and the metal ion. The addition of an electron to this bridge may result in the reduction of the metal ion, or it may yield hydrogen gas and the hydroxo-complex. The excess consumption of electricity is often very small, but controlled-potential coulometric analyses are generally better based on reductions of complexes with chloride, ammonia, and other ligands that are either aprotic or much more weakly acidic than water.

In other circumstances a superficially similar process may cause too little electricity to be consumed. For example, the anodic oxidation of lanthanum hexaboride appears to yield a soluble intermediate that can be further oxidized [to lanthanum(III) and boric acid] either electrolytically or by chemical reaction with hydrogen ion: the coulometric  $n$ -value is smaller than it should be, and mass spectrometry shows that some hydrogen gas is formed<sup>140</sup>. This is more properly regarded as an example of the mechanism represented by eq. (69), for the dependence of the excess quantity of electricity on potential and on the mass-transfer coefficients will differ from that in a true induced process.

### RELATED MECHANISMS

The catalytic and induced processes described above involve the formation of electroactive species by the reactions of R and O, respectively, with a substance Z, usually hydrogen ion or water, that is ordinarily inert. This section presents descriptions of mechanisms that involve other kinds of reactions of R and O.

*Subsequent Reactions.* The mechanism in which the product R of the



primary half-reaction rearranges, decomposes, or reacts with some electro-lytically inert constituent of the solution Z to give the inert product P, was briefly discussed by Geske and Bard<sup>139</sup>. If the electrolysis is performed at a

potential where the rate of re-oxidation of R is negligible, the occurrence of reaction (34b) has no effect on either the current-time curve or the current integral. Information about the rate of this reaction can be obtained in any of three ways. One is to follow the concentration of R or P spectrophotometrically or by some other convenient technique. If reaction (34b) did not occur at all, the concentration of R in the bulk of the solution at any instant would be given by

$$C_R^b = C_O^{b,0} [1 - \exp(-\beta_O^* t)] \quad (35)$$

whereas, if the subsequent reaction is first-order with respect to R and sufficiently slow to permit most of the R to escape from the diffusion layer before it reacts, it will be given by

$$C_R^b = \frac{\beta_O^* C_O^{b,0}}{k C_Z - \beta_O^*} [\exp(-\beta_O^* t) - \exp(-k C_Z t)] \quad (36)$$

A value of  $\beta_O^*$  will be available from eq. (23b), and  $k C_Z$  is easily evaluated. A second general approach is provided by reversal coulometry<sup>141</sup>: after some measured fraction of the O has been reduced, the potential is changed to a value at which R is re-oxidized. The quantity of electricity consumed in the re-oxidation would be equal to that consumed in the prior reduction if the inactivation step did not occur. The quantity actually consumed will be smaller, and the difference increases as  $k C_Z$  increases. Bard and Tatwawadi employed this technique to evaluate the rate of hydrolysis of *p*-benzoquinoneimine obtained in the oxidation of *p*-aminophenol. A third technique is available when the O—R couple is reversible. Electrolysis at a potential on the rising portion of the wave of O would then give currents (eq. 37) conforming to the equation<sup>16</sup>

$$i = \beta_O^* n F V C_O^{b,0} \exp[-(\beta_O^* + \beta_R^*)t] \quad (37)$$

if O alone were present initially, if R and O were contained in the same phase throughout, and if the inactivation reaction did not occur. The overall current integral would be given by

$$Q_\infty = \frac{\beta_O^*}{\beta_R^*} n F V C_O^{b,0} = n F V C_O^{b,0} \exp[n F (E_{O,R}' - E)/R T] \quad (38)$$

However, the inactivation reaction will eventually result in complete conversion to P if the equilibrium constant of reaction (34b) and the concentration of Z are sufficiently large. Consequently  $Q_\infty$  will be given by eq. (17) rather than by eq. (38), and the current will exceed that described by eq. (37). Unless  $k C_Z$  is very large a plot of  $\ln i$  vs.  $t$  will be concave upward, and analysis of it should provide a value of  $k C_Z$  in fairly straightforward fashion.

The closely related mechanism





involving two competing inactivation steps, was also discussed by Geske and Bard<sup>139</sup>. It differs from the preceding case in that the pseudo-first-order rate constant for inactivation is equal to  $(k_1C_{Z_1} + k_2C_{Z_2})$  rather than simply to  $kC_Z$ . Product identification would be invaluable in diagnosing this mechanism. Once the diagnosis has been made, values of the pseudo-first-order rate constant might be obtained by any of the techniques applicable to the mechanism of eqs. (34). Values of  $k_1$  and  $k_2$  could then be obtained in either of two ways. One would be to determine the ratio of the concentrations of  $P_1$  and  $P_2$  present at the end of the electrolysis or at any instant while it is in progress. This ratio will be equal to  $k_1C_{Z_1}/k_2C_{Z_2}$  and will be independent of both  $\beta_O^*$  and time if both inactivation reactions are first-order with respect to R. Another would be to vary  $C_{Z_1}$  and  $C_{Z_2}$  independently in replicate electrolyses and to correlate their variations with those of the pseudo-first-order rate constant.

*Prior Reactions.* The mechanism represented in eq. (40) is familiar as the



one responsible for the kinetic current in polarography. Its behaviour in controlled-potential electrolysis was first discussed by Bard and Solon<sup>142</sup>; Gelb and Meites<sup>35</sup> described procedures for evaluating  $k_f$  and  $k_b$  and also discussed variant mechanisms in which both Y and O are electroactive, as might be the case with a mixture of complexes. The overall current integral is unrevealing because it corresponds to the quantitative reductions of both Y and O as long as the rate of re-oxidation of R is negligible, but plots of  $\ln i$  vs.  $t$  have the shapes shown in *Figure 11*<sup>142</sup>. The lowermost curve represents the limiting case in which  $k_f$  is much smaller than either  $\beta_O^*$  or  $k_b$ , so that O is present at only a very small concentration and is consumed as rapidly as it is produced from Y. In this case one has very nearly

$$i = \beta_O^* n F V C_O^b = \beta_O^* n F V \left( \frac{K}{K+1} \right) C \approx \beta_O^* n F V K C \quad (41)$$

where  $K = k_f/k_b$  and  $C$  is the sum of the concentrations of Y and O. The current is small because the bulk concentration of O is small, and is almost constant because the concentration of Y decreases only very slowly. The solid line represents the other extreme, where  $K$  is so large that the concentration of Y is always too small to be perceptible. Intermediate cases give curves that are concave upward and that can be dissected into two linear segments in the fashion illustrated by *Figure 4*; from the slopes of these segments and the value of the initial current it is possible to compute both  $k_f$  and  $k_b$ <sup>35</sup>.

Bard and Solon<sup>142</sup> also described the behaviour of three special cases of the preceding mechanism. One of them, expressed by eq. (42), is that



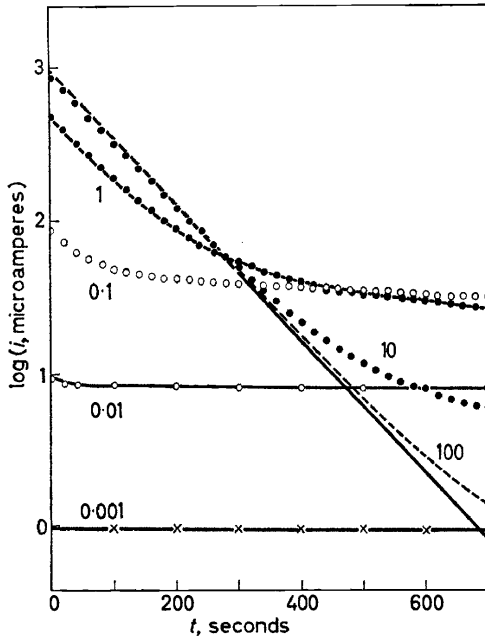


Figure 11. Plots of  $\log i$  against time for the mechanism represented by eq. (40) with  $C = 10^{-4}$   $M$ ,  $\beta_0^* = 0.01 \text{ sec}^{-1}$ , and  $k_f = 10^{-4} \text{ sec}^{-1}$ . The number beside each curve gives the corresponding value of  $K$ .

in which  $O$  undergoes an irreversible pseudo-first-order inactivation by reacting with some constituent of the supporting electrolyte. This is equivalent to the mechanism of eq. (40) with  $k_f = 0$ , but what is contemplated here is starting with  $O$  rather than with the equilibrium mixture of  $Y$  and  $O$ , which would be uninteresting if  $k_f$  were zero because it would contain no  $O$  and would yield no current. A plot of  $\ln i$  vs.  $t$  is linear but  $Q_\infty$  is smaller than  $nFN_0^\circ$  and is given by

$$Q_\infty = \frac{\beta_0^*}{\beta_0^* + k_b} n F N_0^\circ \exp(-k_b t_1) \quad (43)$$

where  $t_1$  is the time that elapses between the addition of  $O$  to the supporting electrolyte and the start of the electrolysis. Allied to this is the mechanism



in which the concentration of  $Z$  is comparable to the initial concentration of  $O$  and therefore varies appreciably during the course of the electrolysis, and so does the mechanism



## CONTROLLED-POTENTIAL ELECTROLYSIS

in which O is inactivated by a pseudo-second-order reaction. These were considered as models for data obtained in oxidizing and reducing  $\alpha,\alpha$ -diphenylpicrylhydrazyl in acetonitrile containing tetra-*n*-butylammonium bromide as the supporting electrolyte<sup>143</sup>. The mechanism represented by eqs. (44) might be encountered in work with non-aqueous solvents containing a little water (= Z) that could cause the hydrolysis of the substance being studied. Usually it would be advantageous to convert this case into the mathematically simpler one represented by eq. (42) by deliberately adding a large excess of Z to the supporting electrolyte. The mechanism described by eqs. (45) is probably very rare.

*Reactions of the Product with the Starting Material.* Each of the above mechanisms involves a reaction of either O or R with an electrolytically inert substance. Another family of mechanisms involves reactions of O with R. Geske and Bard<sup>139</sup> discussed the simplest member of this family



in which the product P is electrolytically inert at the potential employed. A solution in closed form could not be obtained, but the results of numerical computations were used to construct a plot of  $Q_{\infty}/FN_0^{\circ}$  against  $k/\beta_0^*$ , from which a value of the latter could be obtained after the former had been evaluated coulometrically. It is convenient to speak of the apparent value of  $n$ , which is defined by an equation similar to eq. (30):

$$n_{app} = Q_{\infty}/F N_0^{\circ} \quad (47)$$

As  $k/\beta_0^*$  approaches zero,  $n_{app}$  approaches  $n$ ; as  $k/\beta_0^*$  increases without limit,  $n_{app}$  approaches  $n/2$ . In either of these extreme cases a plot of  $\ln i$  vs.  $t$  is strictly linear. The first of them is uninteresting because it is merely a reduction of O to R. The second might be diagnosed by product identification; in addition, the value of  $n_{app}$  will often be half-integral and half-reactions that appear to be reversible in cyclic voltammetry, oscillopolarography, and other fast techniques will fail to obey eq. (38).

Rate data will be elusive near these extremes, but it should often be possible to attain an intermediate situation in which  $n_{app}$  does vary with the experimental parameters and in which product identification will show that both R and P have been obtained in roughly comparable amounts. This can be done either by changing the composition of the supporting electrolyte so as to vary the pseudo-second-order rate constant  $k$  or by changing the stirring efficiency and the potential of the working electrode so as to vary  $\beta_0^*$ . The mechanism appears to be fairly common: examples of it are found in the oxidation of tetraphenylborate ion<sup>78</sup>, in the reduction of niobium(v)<sup>144</sup>; and in the reduction of bromoacetate ion<sup>22</sup>. As was mentioned above, the last of these must involve the slightly more complex variant



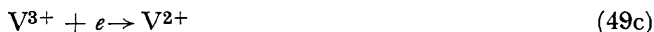
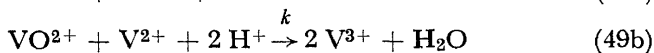
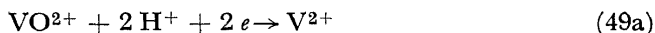
As in any other situation where an intermediate can be consumed either by further reduction or by a homogeneous reaction, electrolysis on the plateau of the wave is peculiarly disadvantageous here, for the concentrations of both O and I are then negligibly small at the surface of the electrode and reaction (48b) cannot occur to a significant extent. On decreasing the values of  $\beta^*$  by performing the electrolysis on the rising part of the wave, the rate of reaction (48b) becomes appreciable and its occurrence becomes easy to detect. Whereas  $n_{\text{app}}$  varies only from  $n$  to  $n/2$  for the mechanism of eqs. (46) as  $k/\beta_{\text{O}}^*$  varies from zero to extremely large values, it varies from  $(n_1 + n_2)$  to  $n_1/2$  for the mechanism of eqs. (48).

Geske and Bard<sup>139</sup> further discussed the effect of a competing pseudo-first-order inactivation of R by reaction with an electrolytically inert substance Z, present in large excess, to yield a different product P':



The effect of this reaction is to increase  $n_{\text{app}}$  above the value it would have if reactions (46a) and (46b) took place alone; the magnitude of the increase depends on the ratio  $k'/k$ .

Israel and Meites<sup>21</sup> studied an example of a mechanism in which O and R react to give an electroactive product. Shorn of complications arising from proton reduction and the variety of species present in each oxidation state, this could be represented by the equations



Because the half-wave potential of vanadium(III) is more positive than that of vanadium(IV) under the conditions employed, it is possible to perform the electrolysis at a potential where  $\beta^*$  is larger for vanadium(III) than for vanadium(IV). As a result the current passes through a maximum. At the instant when it does, the pseudo-second-order rate constant of eq. (49b) is described by

$$k = \frac{\beta_3^* i}{2 V (\beta_3^* - \beta_4^*) C_2 C_4} \quad (50)$$

where the subscripts denote the oxidation states. The concentrations of vanadium(II) and (IV) can be obtained from the current and the value of  $Q_i$  at the maximum,  $\beta_3^*$  can be obtained from the slope of either the rising or the falling segment of a plot of  $\ln i$  vs.  $t$ , and  $\beta_4^*$  can be computed from the initial current. In this way Israel and Meites obtained values of  $k$  in good agreement with those previously reported by others who had used more familiar techniques.

## PARALLEL REACTIONS AND KINETIC ANALYSIS

Because they will be needed in the following section, it is appropriate to digress here to give the equations describing the behaviour of a mixture of chemically unrelated electroactive substances.

CONTROLLED-POTENTIAL ELECTROLYSIS

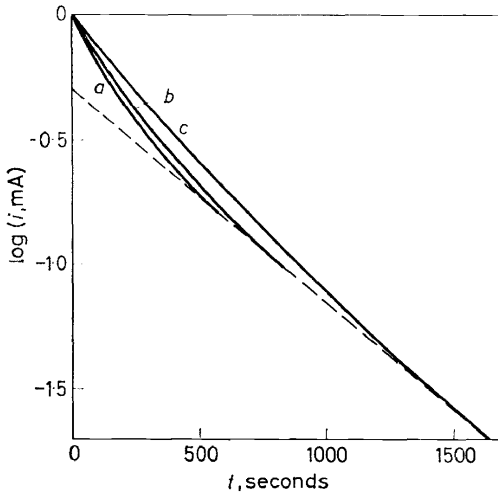
If there are no chemical interactions among the species involved, the simultaneous reduction of two substances  $O_1$  and  $O_2$



will yield a current-time curve obeying the equation

$$i = \beta_1^* n_1 F V C_1^{b,0} \exp(-\beta_1^* t) + \beta_2^* n_2 F V C_2^{b,0} \exp(-\beta_2^* t) \quad (52)$$

where  $C_1^{b,0}$  and  $C_2^{b,0}$  are the initial bulk concentrations of  $O_1$  and  $O_2$  and where the potential-dependent rate constants  $\beta_1^*$  and  $\beta_2^*$  are described by equations like eq. (13). A plot of  $\ln i$  vs.  $t$  has the shape shown in *Figure 12*.



*Figure 12.* Plots of  $\log i$  against time for a mixture of two reducible substances, computed from eq. (52) by assuming  $i_1^0 (= \beta_1^* n_1 F V C_1^{b,0}) = i_2^0 (= \beta_2^* n_2 F V C_2^{b,0}) = 0.5$  mA,  $\beta_2^* = 0.002$  sec<sup>-1</sup>, and  $\beta_1^* =$  (a) 0.008, (b) 0.006, or (c) 0.004 sec<sup>-1</sup>

It may be dissected into two strictly linear portions by extrapolating the second linear segment back to  $t = 0$ , subtracting the extrapolated current  $i_2$  (we make the tacit but trivial assumption that  $\beta_2^* < \beta_1^*$ ) from the total current  $i$  at each of a number of instants during the interval covered by the extrapolation, and plotting  $\ln(i - i_2)$  [ $= \ln i_1$ ] against time. The intercept  $i_2^0$  and slope  $\beta_2^*$  of the extrapolated line give the quantity of electricity consumed by the more slowly reducible constituent:

$$Q_2 = i_2^0 / \beta_2^* \quad (53)$$

That consumed by the more rapidly reducible one can be computed either from the intercept and slope of the difference plot or, more precisely, from the equation

$$Q_1 = Q_\infty - Q_2 \quad (54)$$

These equations are easily generalized to mixtures of three or more reducible substances.

This is the basis of the use of controlled-potential electrolysis in kinetic analysis. The value of the ratio  $\beta_1^*/\beta_2^*$  is of primary importance: as it approaches 1 the plot of  $\ln i$  vs.  $t$  becomes more and more nearly linear, and the dissection becomes more difficult and less reliable. Large values of the ratio are about equally undesirable if both  $O_1$  and  $O_2$  have to be determined, for the small currents due to  $O_2$  are then difficult to separate from the continuous faradaic current. The optimum situation is that in which the ratio lies between about 3 and 10. The value of the ratio  $Q_1/Q_2$  is also important, for reasons too familiar in kinetic analysis to require lengthy discussion here.

There are two reasons why plots of  $\ln Q_R$  vs.  $t$  are superior to plots of  $\ln i$  vs.  $t$  for this purpose. The first and more important is that, as was mentioned above, the former are smoother and therefore yield very much more precise results because they are virtually unaffected by momentary fluctuations of the electrode area and the stirring efficiency. MacNevin and Baker<sup>145</sup> obtained rather poor results in controlled-potential coulometric analyses based on the use of eq. (53) even in the much more favourable situation in which only a single electroactive substance was present. The other is that the extrapolation of a plot of  $\ln Q_R$  vs.  $t$  gives  $\ln Q_2$  and thus avoids the necessity of numerical calculation.

Electrolysis at a potential where both  $O_1$  and  $O_2$  yield their limiting currents is not often attractive, although it has been successfully employed in the writer's laboratory to analyze mixtures of hydrogen and zinc ions, because the ratio of the two mass-transfer coefficients will not often be sufficiently different from 1. In the common case where both  $O_1$  and  $O_2$  yield totally irreversible waves, it will usually be easy to find a potential that is on the plateau of one wave but on the rising part of the other, or even on the rising parts of both if either the half-wave potentials or the values of  $an_a$  are appreciably different. Polarographic data will be of but restricted utility in the search for such a potential, for two reasons. One is that the polarographic half-wave potential is not the one of interest here. This is illustrated by the fact that the half-wave potential of hydrogen peroxide is over half a volt more negative at an efficiently stirred mercury pool electrode than it is at a dropping electrode in the same solution. The difference between the two is explicitly given by<sup>22, 146</sup>

$$E_{\frac{1}{2}, \text{pool}} - E_{\frac{1}{2}, \text{dme}} = - \frac{0.05916}{a n_a} \log \frac{1.349 \beta_0 V t^{\frac{1}{2}}}{D_0^{\frac{1}{2}} A} \quad (55)$$

at 25°, where  $t$  is the drop time at the polarographic half-wave potential. This was confirmed experimentally by Karp<sup>22</sup>. The other is that the double-layer effect may cause the value of  $an_a$  at the stirred pool to be quite different from that at the dropping electrode because different ranges of potential are involved. Directly useful data may be secured either by stirred-pool voltammetry under the same mass-transfer conditions that will be used in the electrolysis or by electrolyzing solutions of  $O_1$  and  $O_2$  separately at various potentials, applying eq. (23b) to the data obtained, and comparing

the values of  $\beta_1^*$  and  $\beta_2^*$ . Incidentally it may be mentioned that if the electrolysis is performed at a potential where  $O_1$  yields its limiting current it does not matter whether the reduction of  $O_1$  is irreversible or not. Great care must be taken to minimize variations of potential across the surface of the pool whenever an electrolysis for this purpose, or for any other in which rate data are important, is undertaken on the rising portion of a wave.

In the writer's laboratory these ideas have been applied to the analyses of a number of binary and ternary mixtures of electroactive substances. Figure 13 is a transcription of a plot of  $\ln Q_R$  vs.  $t$ , obtained with the electro-mechanical instrument described above, for the electrolysis of a solution

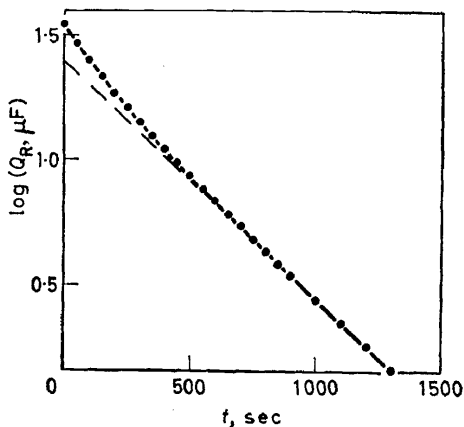


Figure 13. The points are transcribed from a plot of  $\log Q_R$  obtained automatically in the electrolysis, at  $-1.37$  V vs. S.C.E., of a solution containing  $5.00$   $\mu$ moles of zinc(II) and  $12.48$   $\mu$ moles of cobalt(II). The supporting electrolyte contained  $2$   $F$  ammonia,  $1$   $F$  ammonium citrate, and  $4$   $F$  ammonium chloride. The measured value of  $Q_\infty$  was  $34.90$   $\mu$ F, and the extrapolation shown by the dashed line gave  $Q_{C_0} = 24.85$   $\mu$ F. These values correspond to  $12.48$   $\mu$ moles of cobalt(II) and, by difference,  $5.02$   $\mu$ moles of zinc(II).

containing zinc(II) ( $= O_1$ ) and cobalt(II) ( $= O_2$ ) at a potential that was near the plateau of the zinc wave but near the foot of the cobalt wave. Table 1 shows the results obtained in analyzing a number of similar mixtures in this way. Since the relative error of  $Q_2$ , about  $\pm 0.5$  per cent, considerably exceeds that of  $Q_\infty$ , which is only about  $\pm 0.1$  per cent, the values of  $Q_1$  become less and less precise as  $Q_2/Q_1$  increases. The best results are therefore secured when  $Q_2/Q_1$  is less than about 3. The lower limit to  $Q_2/Q_1$  will be largely governed by the error in correcting for the continuous faradaic current, which was very small in these experiments.

Similar dissections were employed by Ficker and Meites<sup>138</sup> to interpret the plots of  $\ln i$  vs.  $t$  obtained during the controlled-potential anodic stripping of zinc from amalgams containing cobalt. There are, however, reaction mechanisms for which the overall current integral obtained by summing the values of  $i_j/\beta_j^*$  does not agree with the one measured directly by using a current integrator, and these are considered below.

Table 1. Results of kinetic analyses

A solution containing 2  $F$   $\text{NH}_3$ , 1  $F$   $(\text{NH}_4)_3\text{Cit}$ , 4  $F$   $\text{NH}_4\text{Cl}$ , and known amounts of  $\text{Zn(II)}$  and  $\text{Co(II)}$  was electrolyzed at  $-1.50$  V *vs.* S.C.E. to evaluate  $Q_{\text{Co}}$ . Another identical solution was then electrolyzed at a potential between  $-1.35$  V and  $-1.41$  V while  $\log Q_{\text{R}}$  was automatically plotted against  $t$ . Extrapolation of this plot gave  $\log Q_{\text{Co}}$ , and  $Q_{\text{Zn}}$  was obtained by difference.

Taken		Found	
$\mu\text{moles Co}$	$\mu\text{moles Zn}$	$\mu\text{moles Co}$	$\mu\text{moles Zn}$
1.25	5.00	1.24 <sub>5</sub>	5.00
		1.26 <sub>0</sub>	5.01
4.99	5.00	5.02	4.97
		4.97	5.03
12.48	5.00	12.4 <sub>3</sub>	5.0 <sub>2</sub>
		12.5 <sub>4</sub>	4.9 <sub>2</sub>
24.97	5.00	24.8 <sub>5</sub>	5.0 <sub>8</sub>
		25.1	4.9 <sub>2</sub>
		25.1	4.9 <sub>4</sub>
49.90	5.00	50.1	4.8
		50.2	4.7
		49.7	5.1
		49.6	5.2
49.90	50.02	50.3	49.7
		49.6	50.2
		49.8	50.1

### CONSECUTIVE REDUCTIONS

The mechanism represented by equations (56a) and (56b) was first



discussed by Gelb and Meites<sup>35</sup>, who invoked eq. (16) to obtain

$$i = \beta_{\text{O}}^* n_1 F V C_{\text{O}}^{b, \text{O}} \exp(-\beta_{\text{O}}^* t) + \frac{\beta_{\text{O}}^* \beta_{\text{I}}^* n_2 F V C_{\text{O}}^{b, \text{O}}}{\beta_{\text{I}}^* - \beta_{\text{O}}^*} [\exp(-\beta_{\text{O}}^* t) - \exp(-\beta_{\text{I}}^* t)] \quad (57)$$

This describes a plot of  $\ln i$  *vs.*  $t$  that is strictly linear whenever  $\beta_{\text{O}}^*$  and  $\beta_{\text{I}}^*$  are exactly equal but that must be concave upward if they are not. If they do differ, there will be a drift of the values of  $\beta^*$  computed from eq. (23b), and if they differ sufficiently it will be possible to dissect a plot of  $\ln i$  *vs.*  $t$  into two linear segments having slopes equal to  $\beta_{\text{O}}^*$  and  $\beta_{\text{I}}^*$ .

However, these conclusions must be taken with a rather large grain of salt, for they are based on assumptions that are not revealed by eqs. (56) as they stand. The problem is most conveniently discussed by supposing that the electrolysis is performed at a potential where both O and I yield their limiting currents, so that the potential-dependent electrolytic rate



## CONTROLLED-POTENTIAL ELECTROLYSIS

constants  $\beta_O^*$  and  $\beta_I^*$  are equal to the mass-transfer coefficients  $\beta_O$  and  $\beta_I$ , respectively. It is further simplified by supposing that  $\beta_O$  and  $\beta_I$  are identical; both may then be represented by a single parameter  $\beta$ . In these circumstances the derivation of eq. (57) would take the following path:

$$i = \beta n_1 F V C_O^b + \beta n_2 F V C_I^b \quad (58a)$$

$$C_O^b = C_O^{b,0} \exp(-\beta t) \quad (58b)$$

$$\frac{dC_I^b}{dt} = \beta C_O^b - \beta C_I^b \quad (58c)$$

$$C_I^b = \beta C_O^{b,0} t \exp(-\beta t) \quad (58d)$$

It is eq. (58d) that claims our present attention. It describes a bulk concentration of I that is equal to zero both at the start and at the end of the electrolysis, but that reaches a finite maximum value, given by eq. (59)

$$C_I^{b,\max} = C_O^{b,0}/e \quad (59)$$

at the instant when  $t = 1/\beta$ . As was pointed out by Mason<sup>147</sup>, this prediction traduces the physical reality of the situation assumed. On the plateau of its wave I would be reduced immediately upon being formed from O at the surface of the electrode, and no appreciable amount of it could be swept into the bulk of the solution. Regardless of the ratio of the mass-transfer coefficients  $\beta_O$  and  $\beta_I$ , any O reaching the electrode surface undergoes the  $(n_1 + n_2)$ -electron reduction to yield R directly; the concentration of I never becomes significant anywhere in the solution; a plot of  $\ln i$  vs.  $t$  must be strictly linear; and eq. (58a) is fallacious.

The fallacy arises from eq. (16), which is based on the tacit assumption that the concentration of each electroactive species is always higher in the bulk of the solution than it is at the surface of the electrode. In reality all these equations are founded on the supposition that ions or molecules of I formed by the reduction of O will be carried away from the surface of the electrode by convection before they can be further reduced, so that their reduction does not occur until they return to the surface of the electrode at some later instant. There are two circumstances in which this can be so. One arises when the heterogeneous electron-transfer rate constant for the reduction of I is small, as it is when the potential of the working electrode lies on the rising portion of the wave of I. The other arises when I must undergo some homogeneous chemical transformation before further reduction can occur. This is a special case of the "ECE" mechanism to be discussed below: it corresponds to the situation in which the transformation of I into the reducible species [J in eqs. (65b) and (65c)] is slow enough to permit the virtually quantitative escape of I into the bulk of the solution but is nonetheless so fast that its occurrence is not otherwise detectable. It is unjustifiable to employ eq. (57) in any circumstances but these.

The case in which I is directly reduced without any intervening chemical transformation was treated independently by Mason<sup>147</sup> and Karp<sup>22</sup>. Assuming that the electrolysis is performed at a potential where O yields

its limiting current, Karp obtained the following description of the current-time curve for the mechanism of eqs. (56):

$$i = FVC_0^{b,0} \left\{ \beta_0 n_1 + \frac{\beta_0 n_2 A k_I}{A k_I + V \beta_I} \exp(-\beta_0 t) + \frac{\beta_0 \beta_I^2 n_2 A k_I V}{(A k_I + V \beta_I) [(\beta_I - \beta_0) A k_I - \beta_0 \beta_I V]} \left[ \exp(-\beta_0 t) - \exp\left(-\frac{\beta_I A k_I}{A k_I + V \beta_I} t\right) \right] \right\} \quad (60a)$$

It is convenient to rewrite this in a form suitable for comparison with eq. (57) by letting

$$\beta_I^* = \frac{\beta_I A k_I}{A k_I + V \beta_I} \quad (60b)$$

[compare eq. (13)]; the result is

$$i = \beta_0 FVC_0^{b,0} \left[ n_1 + \frac{\beta_I^*}{\beta_I} n_2 \right] \exp(-\beta_0 t) + \frac{\beta_0 (\beta_I^*)^2 n_2 F V^2 C_0^{b,0}}{A k_I (\beta_I^* - \beta_0)} [\exp(-\beta_0 t) - \exp(-\beta_I^* t)] \quad (60c)$$

where  $k_I$  is the heterogeneous rate constant for the reduction of I. At a potential where both I and O yield their limiting currents,  $k_I \gg \beta_I V/A$  and  $\beta_I^* = \beta_I$ , and eqs. (60a) and (60c) become

$$i = FVC_0^{b,0} \left\{ \beta_0 (n_1 + n_2) \exp(-\beta_0 t) + \frac{\beta_0 \beta_I^2 n_2 V}{A k_I (\beta_I - \beta_0)} [\exp(-\beta_0 t) - \exp(-\beta_I t)] \right\} \quad (61)$$

Because the second term within the braces is negligibly small regardless of the relative values of  $\beta_0$  and  $\beta_I$ , this predicts that a plot of  $\ln i$  vs.  $t$  will be strictly linear, as is in fact true.

This problem has been discussed at some length because it arises in every mechanism that involves the further reduction of an electroactive intermediate formed at the electrode surface. Applying eq. (16) to any such mechanism will yield a result that should be regarded with suspicion. Its predictions will be correct within the precision of measurement now attainable if the rate at which the intermediate escapes from the electrode surface substantially exceeds the rate at which it is further reduced, but they may be qualitatively as well as quantitatively wrong if this is not so.

As was stated above, plots of  $\ln i$  vs.  $t$  obtained on the rising portion of the wave of I (but on the plateau of the wave of O) can be dissected into two linear segments by the procedure described in the preceding section. In contrast to what is true in simultaneous reductions, however, the ratio of the current integrals corresponding to these two segments, which is given by

$$\frac{Q_1}{Q_2} = 1 + \frac{2(\beta_0 - \beta_I) A k_I}{\beta_0 \beta_I V} \quad (62)$$

if  $n_1 = n_2$ , is equal to the ratio of the quantities of electricity actually consumed in the two steps only in the special case where  $k_I \ll \beta_I V/A$ . This corresponds to points very near the foot of the wave of I. As the potential becomes more and more negative, more and more of the I is reduced before it can escape into the bulk of the solution, and  $Q_1$  increases while  $Q_2$  decreases. The effect of potential on the value of  $k_I$  deduced from eq. (62) could be used to evaluate  $an_a$  for the reduction of I in a range of potentials that is inaccessible to polarographic measurements in view of eq. (55), and this might prove useful in studying double-layer effects on the rates of electron-transfer processes.

This mechanism is involved in the reduction of niobium(v) in concentrated hydrochloric acid<sup>144</sup>. There are two waves on the polarogram, but electrolysis at any potential yields niobium(III), together with some niobium(II) arising from a complication that may be ignored for the present purpose. A plot of  $\ln i$  vs.  $t$  for an electrolysis on the plateau of the first wave can be dissected to yield two linear segments whose slopes  $\beta_1^*$  and  $\beta_2^*$  are widely different. The value of  $\beta_1^*$  is independent of potential if the stirring efficiency is unchanged, but that of  $\beta_2^*$  increases as the potential becomes more negative and does so in a manner consistent with eq. (60b) and the expected dependence of  $k_I$  on potential. On the plateau of the second wave a plot of  $\ln i$  vs.  $t$  consists of a single straight line. This shows that the segmented plot obtained on the plateau of the first wave arises from a mass-transfer-controlled initial step followed by a slow further reduction (rather than, say, a disproportionation that yields an electroactive product) of the product of that step, and provides an example of the occasional necessity of invading region 4 of Figure 2.

The closely related branched mechanism

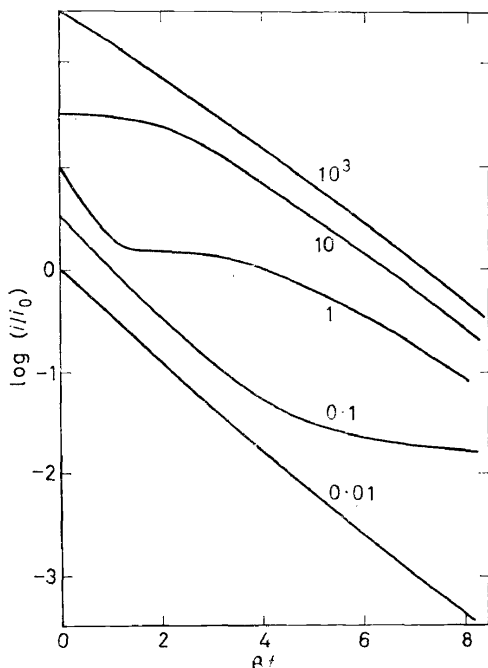


in which the irreversible pseudo-first-order transformation of I into an electrolytically inert species P competes with its further reduction, was considered by Karp<sup>22</sup>. If the heterogeneous rate constant for the reduction of I is large,  $n_{app}$  will be equal to  $(n_1 + n_2)$  and a plot of  $\ln i$  vs.  $t$  will be linear. Otherwise  $n_{app}$  will lie between  $n_1$  and  $(n_1 + n_2)$  and a plot of  $\ln i$  vs.  $t$  may be concave either upward (if  $k$  is so small that most of the I eventually returns to the electrode surface and is further reduced) or downward (if  $k$  is large enough to preclude the reduction of any I that escapes from the diffusion layer).

The ECE mechanism



first achieved popularity when it was shown to be involved in the reduction of *p*-nitrosophenol and the oxidation of *p*-aminophenol. Its behaviour in controlled-potential electrolysis was considered briefly by Bard and Mayell<sup>148</sup> and in more detail by Gelb and Meites<sup>35</sup>, who made the simplifying assumption that  $k$  is small enough to permit I to escape from the diffusion layer before any significant fraction of it can be transformed into J, and by Karp<sup>22</sup>, who did not. Coulometry and product identification show that  $n_{\text{app}} = (n_1 + n_2)$  and that R is the only product obtained on exhaustive electrolysis. In a number of cases where  $k$  is fairly small, these observations have served to show that the overall value of  $n$  exceeds the one deduced from polarographic measurements and thus to permit the gross identification of the mechanism, but they do not provide a rigorous proof that an ECE mechanism is involved and yield no information about the rate of the intervening chemical step. Both may be obtained from plots of  $\ln i$  vs.  $t$ . *Figure 14* shows the plots computed by Karp and Rodgers from equations that take the extent of reaction (64b) in the diffusion layer into account. Those for very small and very large values of  $k$  are not very revealing, for many other mechanisms yield plots having shapes similar to those of both, but the one for  $k = \beta$  appears to be uniquely diagnostic for the ECE mechanism. The conditions described in the caption of *Figure 14* imply that the electrolysis is performed at a potential where both O and J yield their limiting currents.



*Figure 14.* Plots of  $\log(i/i_0)$  for the ECE mechanism represented by eqs. (64). It is assumed that  $\beta^* = \beta_0^* = \beta_1^* = 10^{-3}$  sec<sup>-1</sup> and that  $D_O = D_I = D_J = 10^{-6}$  V/A cm<sup>2</sup>/sec. The number beside each curve gives the corresponding value of  $k/\beta$ . The ordinate scale pertains to the lowermost curve, for which  $k/\beta = 0.01$ ; each successive curve above this is shifted upward 0.5 unit along the ordinate axis.

## CONTROLLED-POTENTIAL ELECTROLYSIS

If  $k$  is about an order of magnitude larger than  $\beta_0$  and  $B_J$  the current remains nearly constant for some time after the electrolysis is begun, then starts to decay rapidly; if  $k$  is still larger the initial plateau shrinks and the plot becomes more and more nearly linear. Hence, as is true for other mechanisms as well, controlled-potential electrolysis is best suited to the identification and study of processes that are too slow to be handled conveniently by chronopotentiometry, potential-step chronoamperometry, and other faster techniques. Here its upper limit, if  $\beta_0 = \beta_J = 0.02 \text{ sec}^{-1}$ , which is a realistic estimate of the mass-transfer coefficient that can be obtained with very efficient stirring of the electrode-solution interface, is probably about  $k = 1 \text{ sec}^{-1}$ .

Taking the Nernst diffusion-layer thickness at face value, the lifetime  $t$  of I in the diffusion layer is approximately

$$t = D_I \left( \frac{A}{\beta_I V} \right)^2 \quad (65)$$

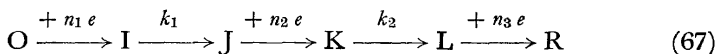
The fraction of it that can be transformed into J in the diffusion layer during this interval is therefore given by

$$1 - \exp(-kt) = 1 - \exp\left(-\frac{k D_I A^2}{(\beta_I)^2 V^2}\right) \quad (66)$$

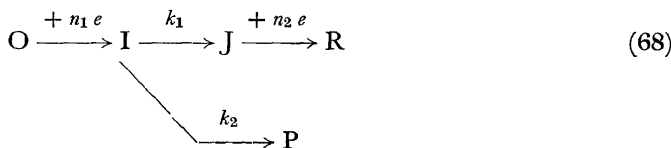
With typical values of  $D$ ,  $A$ ,  $\beta$ , and  $V$ , about 97 or 98 per cent of the I will escape into the bulk of the solution, as all of it is assumed to do in the simplified treatment, even if  $k/\beta_I$  is as large as 100. In that event it will scarcely be possible to detect the chemical step at all. This means that the extent of a chemical reaction in the diffusion layer cannot be worth taking into account if the reaction is slow enough to have an observable effect. Despite the danger inherent in applying eq. (16) to a mechanism in which the product of one reduction is itself electroactive, there is every indication that it can be used with confidence whenever a chemical step intervenes between successive electrolytic ones.

Several examples of the ECE mechanism have been identified by applying these equations and ideas<sup>21, 144, 149</sup>. No doubt many others remain to be studied. For example, there is every reason to believe that it should be easy to obtain the rate constants for the decompositions of amino- and hydroxy-substituted hydrazobenzenes<sup>64, 150</sup> in this way.

The related schemes



and



in which the intermediates I and K and the product P are electrolytically inert, were discussed by Gelb and Meites<sup>35</sup> and by Bard and Mayell<sup>148</sup>,

respectively. The former may yield very complex plots of  $\ln i$  vs.  $t$ , but coulometric measurements will give  $n_{\text{app}} = (n_1 + n_2 + n_3)$  unless one of the homogeneous steps is so slow that the electrolysis is discontinued before it has gone to completion. The latter yields current-time curves very like those for the uncomplicated ECE mechanism, but if  $k_2/k_1$  is appreciable  $n_{\text{app}}$  will be smaller than  $(n_1 + n_2)$ ; it will be independent of  $C_{\text{O}}^{b,0}$ , although it may depend on pH, temperature, and other experimental conditions if the pseudo-first-order rate constants  $k_1$  and  $k_2$  have different algebraic forms or temperature dependences. No example of either case is yet known.

### PSEUDO-SECOND ORDER REACTIONS OF INTERMEDIATES

The mechanism represented by equations(69) in which the dimer D is



electrolytically inert at the potential employed, was discussed by Bard and Mayell<sup>148</sup> and the writer<sup>151</sup>, both of whom used eq. (16) and assumed  $\beta_{\text{O}}^* = \beta_{\text{I}}^* (= \beta)$ . As a solution in closed form is not available, fairly lengthy numerical computations are needed to evaluate the bulk concentration of I at various times and to integrate this or its square with respect to time to obtain the value of  $Q_{\infty}$ , the relative yield of D or R, or some equivalent measure of the relative extents of reactions (69b) and (69c). Bard and Mayell presented their results in the form of plots of  $n_{\text{app}}$  vs.  $\log C_{\text{O}}^{b,0}$  for several values of  $\beta/k$ ; the writer deduced an empirical equation that could be used to compute the value of  $kC_{\text{O}}^{b,0}$  from experimental values of  $n_{\text{app}}$  and  $\beta$ , and discussed the problem of evaluating the latter from a plot of  $\ln i$  vs.  $t$ .

Exhaustive electrolysis yields a mixture of D and R, whose identification naturally serves to demonstrate the occurrence of the second-order step. If a value of  $\beta$  is available, the ratio of their final concentrations could be combined with the results of the above calculations to obtain the value of  $kC_{\text{O}}^{b,0}$ . Plots of  $\ln i$  vs.  $t$  are rather insensitive to variations of  $k$ , and the mechanism is probably best, and certainly most conveniently, studied with the aid of coulometric data, for the value of  $n_{\text{app}}$  decreases from  $(n_1 + n_2)$  when  $k = 0$  toward  $n_1$  as  $k$  increases without limit. An even more obvious peculiarity is that  $n_{\text{app}}$  decreases similarly on increasing the initial concentration of O. Such variations of  $n_{\text{app}}$  with  $C_{\text{O}}^{b,0}$  have been observed with many chemical systems, including not only the familiar reductions of aryl ketones but also the reductions of picric acid<sup>152, 153</sup> and benzylidimethylanilinium ion<sup>98, 148</sup> and the oxidations of hydrazine<sup>154-157</sup> and hydroxylamine<sup>158</sup>, although all of these involve steps in addition to those represented by eqs. (69).

As it does when it is made for other mechanisms, the assumption  $\beta_{\text{O}}^* = \beta_{\text{I}}^*$  implies that the electrolysis is performed at a potential where both O and I yield their limiting currents and that the mass-transfer coefficients of O and I are equal. As we have seen, the first of these implications means that the concentration of I at the surface of the electrode must be vanishingly

small at every instant throughout the electrolysis, so that no significant amount of I can escape into the bulk of the solution and the dimerization cannot occur to any detectable extent. Attempts to describe the situation exactly at a stirred-pool electrode are bound to be unrewarding because mass-transfer coefficients vary across the surface of such an electrode. For pseudo-first-order reactions it is permissible to take an average value as has implicitly been done in all of the cases thus far described, but for a pseudo-second-order reaction such an average would be misleading except at a rotating disc or other electrode where the thickness of the Nernst diffusion layer might justifiably be taken as constant.

These things do not mean that the calculations are devoid of real significance; what it does mean is that they represent a situation slightly different from the one explicitly described by eqs. (69). There must be an intervening reaction:



which is fast enough to have no visible effect on a plot of  $\ln i$  vs.  $t$  but slow enough to cause nearly all of the I to be carried away from the surface of the electrode into the bulk of the solution before it can be converted into J and further reduced. Plots of  $\ln i$  vs.  $t$  for the mechanism of eqs. (69) are nearly horizontal near  $t = 0$ <sup>151</sup>, as are those for the ECE mechanism corresponding to  $k_2 = 0$  when  $k_1/\beta$  is about 10 (ref. 22). It would probably be impossible to deduce the occurrence of reaction (70b) from current-time data if  $k_1/\beta$  were larger than about 4. On the other hand, the argument of eqs. (65) and (66) suggests that the transformation of I into J in the diffusion layer will not become extensive enough to be important unless  $k_1/\beta$  exceeds about 400, or an even larger value if  $D_1A^2/\beta_1V^2$  is smaller than usual. In this range of values of  $k_1/\beta$  the descriptions of eqs. (69) can be expected to agree closely with experimental data.

The mechanism represented by equations (71) which differs from that



of eqs. (70) only in that it involves the dimerization of I rather than J, was discussed by Bard and Mayell<sup>148</sup>. Each of these schemes involves the dimerization of an intermediate in the ECE mechanism, and their behaviours depend on the relative magnitudes of  $k_1$ ,  $k_2$ , and the electrolytic rate constants  $\beta_O^*$  and  $\beta_J^*$ . If  $\beta_O^* = \beta_J^*$ , plots of  $\ln i$  vs.  $t$  will be very similar to those for the

ECE mechanism unless  $k_2$  is so large that the dimerization is sufficiently extensive to preclude much further reduction of the electroactive intermediate, while plots of  $n_{app}$  vs.  $\log C_{O}^{b,0}$  will resemble those computed for the mechanism of eqs. (69) unless both  $k_1$  and the heterogeneous rate constant for the reduction of J are so large that the further reduction is fast enough to preclude much dimerization.

Much of the foregoing discussion can be summarized by asserting that the reaction mechanisms of interest in controlled-potential electrolysis can be divided into two broad classes: consecutive mechanisms that yield a single ultimate product and an integral  $n$ -value independent of the experimental conditions, and branched mechanisms that yield a mixture of products and a non-integral and variable value of  $n_{app}$ . Current-time curves and their dependence on the experimental parameters are needed to elucidate consecutive mechanisms, into which very little insight can be obtained by coulometric measurements or by identifying the products of exhaustive electrolyses. With most branched mechanisms, on the other hand, the current-time curves are unrevealing but detailed information about the rates of the chemical steps can be obtained by combining coulometric data with values of the mass-transfer coefficients. The mechanisms of eqs. (70) and (71) reward both amperometric and coulometric investigation because they combine consecutive and branched paths.

### CONSTANT-CURRENT-CONTROLLED-POTENTIAL ELECTROLYSIS

Constant-current-controlled-potential electrolysis is a technique specially devised for the study of branched mechanisms. Experimentally it consists of adding a concentrated solution of the starting material at a rate that is continuously and automatically controlled so as to maintain a constant current during a controlled-potential electrolysis. Karp<sup>22</sup> employed a commercially available motor-driven syringe like that used for automatic titrations by Lingane<sup>159</sup>. Its motor may be actuated by any of a number of control devices; Karp used a commercial relay controller. A transmitting potentiometer, across whose terminals a small d.c. voltage is applied, is attached to the gear train to provide an output voltage proportional to the total volume of reagent added at any instant. This voltage may be presented to the X-input terminals of an X-Y recording potentiometer while either a standard resistor in series with the working electrode or the output of a d.c. tachometer generator driven by the gear train of the burette is presented to the Y-input terminals, or a T-Y recorder may of course be used instead. At the steady state both the current  $i$  and the rate  $\rho$  at which O is added become constant and a horizontal line is obtained on the chart. A mechanical counter attached to the gear train of the burette provides a convenient visual indication of the volume delivered at any instant and permits measurements of  $\rho$  at the steady state if it is the current that is recorded in following the approach to the steady state.

If the half-reaction is simply  $O + ne \rightarrow R$ , the values of  $i$  (in A) and  $\rho$  (in moles per litre of the solution being electrolyzed per second) are



easily related by writing

$$\frac{dC_O^{b,ss}}{dt} = -\frac{i}{nFV} + \rho = 0 \quad (72)$$

so that

$$\frac{i}{FV\rho} = n \quad (73)$$

For the ECE mechanism of eqs. (64), it is more convenient to write

$$\frac{dC_O^{b,ss}}{dt} = -\beta_O^* C_O^{b,ss} + \rho = 0 \quad (74a)$$

$$\frac{dC_I^{b,ss}}{dt} = \beta_O^* C_O^{b,ss} - kC_I^{b,ss} = 0 \quad (74b)$$

$$\frac{dC_J^{b,ss}}{dt} = kC_I^{b,ss} - \beta_J^* C_J^{b,ss} = 0 \quad (74c)$$

and

$$i = \beta_O^* n_1 FVC_O^{b,ss} + \beta_J^* n_2 FVC_J^{b,ss} \quad (74d)$$

from which evidently

$$\frac{i}{FV\rho} = n_1 + n_2 \quad (75)$$

This result can of course be generalized to any sequence of consecutive chemical or electrochemical steps, and it remains true even in the limiting situation represented by eqs. (56), whereas eq. (57) fails even though it seems to be founded on similar assumptions.

For a branched mechanism, however, the value of  $i/FV\rho$  cannot be exactly integral, although it may be very nearly so if one of the competing steps is very much faster than the other. Karp obtained an exact expression for the mechanism of eqs. (63) much simpler than the one that describes the variation of current with time in an ordinary controlled-potential electrolysis, as well as exact descriptions of the steady-state bulk concentrations of the intermediates in a number of the above mechanisms. For instance, if the mechanism is described by eqs. (56) and if the electrolysis is performed at a potential where O yields its limiting current the steady-state bulk concentration of I is simply.

$$C_I^{b,ss} = \rho/Ak_1 \quad (76)$$

Determining the effect of potential on this concentration by amperometry, spectrophotometry, or any other convenient technique thus provides another way of evaluating  $an_a$  for reaction (56b) under unusual conditions, and one that is likely to be both simpler and more precise than the one based on eq. (62).

An obvious variation of the technique, in which the speed of the motor is controlled by analogue-computation circuitry that causes the current to vary in a predetermined fashion<sup>160</sup>, is now under investigation in the writer's laboratory.

## CONCLUSION

This paper has stressed the use of controlled-potential amperometric and coulometric data in elucidating the mechanisms of complex electrode reactions and in evaluating the rate constants of individual homogeneous chemical steps. There is room for much further development and application of these techniques, but it is quite clear that these will be well worth the trouble they will cost.

There has been far too much emphasis on the caution that must be exercised in employing controlled-potential electrolytic data to explain polarographic processes. It is true that the mass-transfer rates are entirely different, and that processes invisible in polarography may become very prominent in controlled-potential electrolysis as a result. This is not a disadvantage but an advantage. It greatly increases one's ability to perceive all of the truth: a supposed mechanism that does not account for the results obtained by both techniques can certainly not be complete and may possibly be quite wrong.

The reader must not be misled by the number of mechanisms that have been cited here with the remark that examples of them have not yet been found. Each of these has been envisioned as a possible model for a particular chemical system but has been found not to fit the data obtained. This demonstrates not a limitation of the technique but the fineness of the discriminations that it permits. It can, and it is to be hoped that it will, render valuable service to many more electrochemists than have employed it so far.

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