

Mass Transport

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One of the fundamental laws of electrochemistry is Faraday's Law, which relates the charge passed in an electrochemical experiment (Q) to the number of moles of analyte electrolyzed (N):

$$Q = nFN$$

The differential form of this Law is:

$$\frac{dQ}{dt} = i = nF \frac{dN}{dt}$$

that is, the current is directly proportional to the rate of electrolysis. The rate at which electrons are transferred between the electrode surface and molecules in the interfacial region is influenced by the relative values of the applied potential and the standard redox potential; however, once the molecules in the interfacial region have been electrolyzed, molecules need to be transported from the bulk solution in order to maintain electrolysis. Hence, the current also depends critically on the rate of mass transport between the interfacial region and the bulk solution (indeed, in the majority of electroanalytical experiments, it is the mass transport that is rate-determining, not the electron transfer).

Broadly speaking, there are two types of mass transport behavior. In the first, the concentration-distance profiles at a given potential

Concentration-distance profiles (generated using DigiSim[®] simulation software) are used to illustrate the effect of mass transport on the current response for controlled-potential experiments. Linear diffusion, radial diffusion, and convection-diffusion under semi-infinite conditions are considered, together with two limiting cases for finite diffusion.

change continually with time. In the second, a steady-state is attained; that is, after an initial change, the concentration-distance profiles at a given potential are independent of time. Steady-state behavior requires that the rate of charge transfer at the electrode surface and the rate of mass transport to the electrode surface are identical. This requirement can be met only under certain conditions, which will be discussed below.

Three types of mass transport are available in an electrochemical experiment:

- a) Diffusion - molecular motion down a concentration gradient
- b) Convection - molecular motion imposed by bulk motion of the medium (e.g., vibrations or stirring)
- c) Migration - molecular motion down an electric gradient

Migration is generally eliminated by the addition of a fully dissociated electrolyte, which acts as the ionic charge carrier. Convection can also be eliminated to a certain extent by using an unstirred solution, although it is difficult to completely eliminate natural convection (e.g., due to vibrations and density gradients). In addition, diffusion-only conditions can only be maintained for a short time (10 - 20 seconds) which places limitations on the experiment (particularly the scan rate). Diffusion is common to

all voltammetry experiments due to the concentration gradients set up between the interfacial region and the bulk solution; however, the current response for diffusion-only experiments depends on the flux at the electrode surface, which in turn depends on the electrode size and geometry.

There is a group of electrochemical experiments (called hydrodynamic techniques) in which forced convection of the solution is used. The mass transport in these experiments is a combination of convection and diffusion. There are a number of ways in which this can be achieved, but only one (the rotating disk electrode) will be used as a representative example.

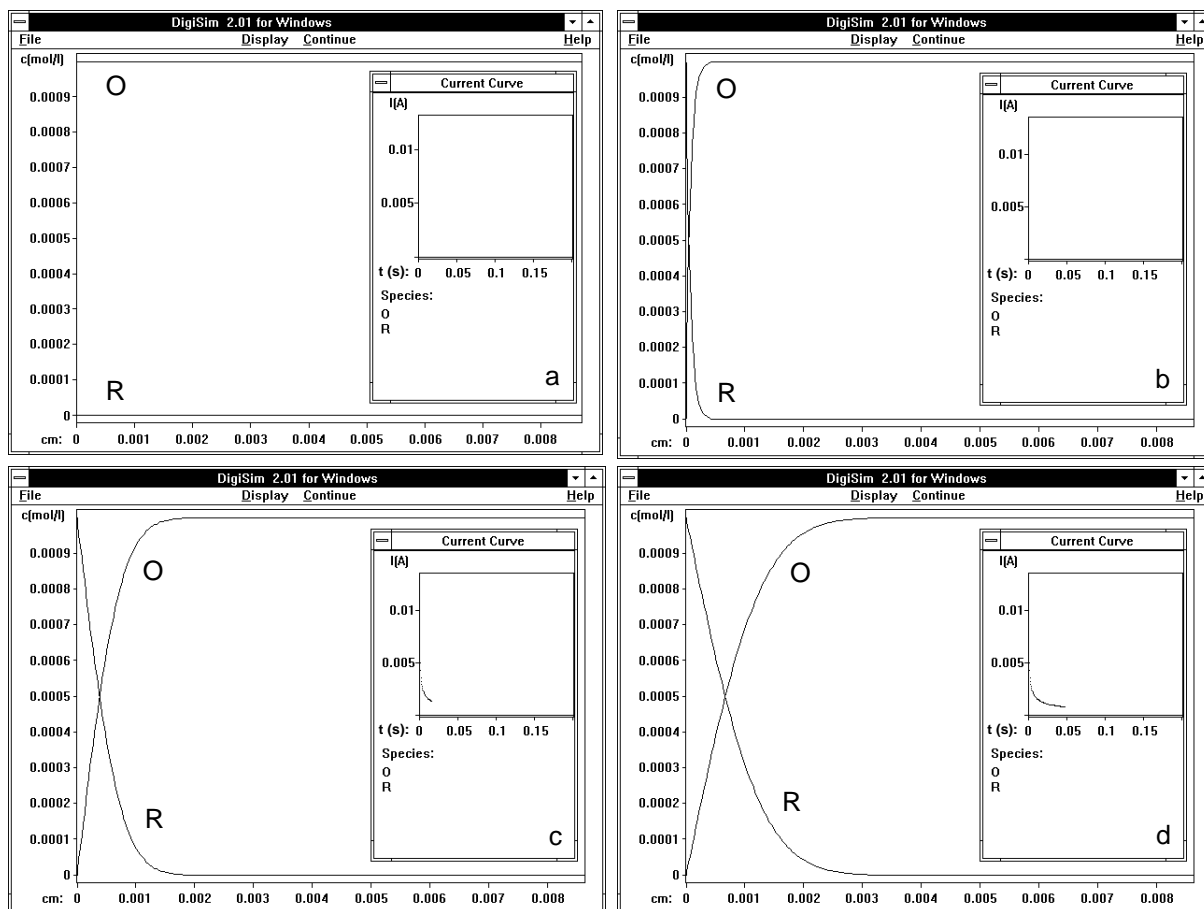
The aim of this article is to review how the current response is affected by the type of mass transport used in a given experiment. The concentration-distance profiles shown here are generated using CV—The Movie™ in DigiSim[®]. In all cases, the simple one-electron transfer redox reaction ($O + e = R$) is used, and the electron transfer kinetics are fast relative to the time scale of the experiment; that is, the current is always mass-transport-controlled.

Linear Diffusion at a Planar Electrode

The simplest model for linear diffusion at a planar electrode as-

F1

Concentration profiles for linear diffusion following a potential step. $t = 0$ (a), 2 (b), 10 (c) and 50 ms (d).



sumes that the electrode is perfectly flat and has infinite dimensions. In this model diffusion is perpendicular to the electrode surface (i.e., the lines of flux are parallel), and the edges are not significant when compared to the surface area. The results derived from this model can be used for 'real' electrodes, provided these are not too small (i.e., dimensions in millimeters).

The effect of linear diffusion can be shown using chronoamperometry. The initial potential is positive of the formal redox potential for the electron transfer reaction, and the potential is stepped to a value at which the electron transfer reaction occurs instantaneously (i.e., the magnitude of a faradaic current is limited only by the rate of diffusion) and it is held at this potential. When the potential step is applied, the concentration of O at the electrode surface changes from that of the bulk solution (1 mM) to zero, whereas that of R changes

from 0 to 1 mM (**F1a** and **b**). This sets up a concentration gradient between the electrode surface and the bulk solution for both O and R. Hence, there is diffusion of O towards the electrode surface and of R away from the electrode surface. The region next to the electrode surface where the concentrations of O and R differ from those in the bulk solution is known as the *diffusion layer*. The diffusion of O and R increases the thickness of the diffusion layer (**F1c** and **d**); hence, the magnitude of the diffusion layer is time-dependent, which means that the diffusion-controlled current i is also time-dependent and is given by the Cottrell equation:

$$i = - \frac{nFAD^{1/2}C}{\pi^{1/2}t^{1/2}}$$

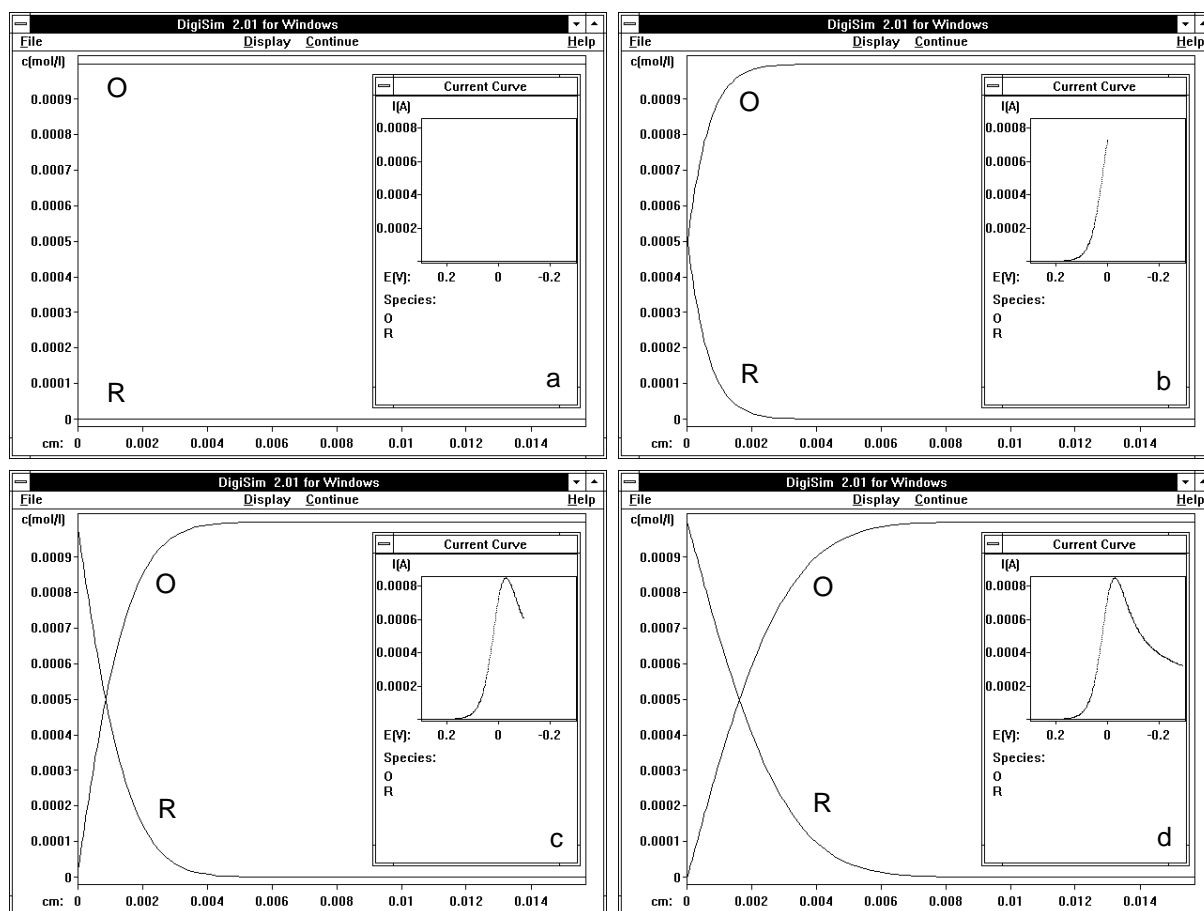
- where D = diffusion coefficient
- C = concentration of O in the bulk solution
- A = electrode area

The concentration profiles for a linear potential sweep voltammetry experiment are shown in **F2**. The values of the scan rate and the standard heterogeneous electron transfer rate constant k_s (1 V s^{-1} and 1 cm s^{-1}) are such that the current is only limited by the rate of diffusion. These are similar to those for chronoamperometry. As the redox potential is approached, there is a net conversion of O to R at the electrode surface, and concentration gradients are set up between the electrode surface and the bulk solution. The thickness of the diffusion layer increases with time, and both peaks show the $t^{-1/2}$ dependence that is characteristic of diffusion-limited currents.

It is important to note that diffusion-only conditions cannot be maintained indefinitely, since natural convection due to, for example, vibrations, will start to have an effect after about 10 - 20 seconds. This places a lower limit on the

F2

Concentration profiles for linear diffusion during a linear potential sweep.



scan rate that can be used for a given potential range. Linear sweep voltammograms (including cyclic voltammograms) recorded at lower scan rates cannot strictly be analyzed using the models developed for linear sweep voltammetry under diffusion-only conditions.

Convection-Diffusion at a Planar Rotating Electrode

The rotation of the working electrode in rotating disk experiments brings analyte molecules from the bulk solution towards the electrode, resulting in mass transport that is faster than diffusion-only experiments. This faster mass transport allows steady-state conditions to be set up, provided the scan rate (which determines the rate of electrolysis) is slow enough ($0.02 - 0.05 \text{ V s}^{-1}$) and the rotation rate is fast enough (at least 10 rad s^{-1}).

The concentration profiles for a simple rotating disk experiments

under mass-transport controlled conditions are shown in **F3**. These are different from those shown in **F2** (for which the same potential wave form was used) in that the thickness of the diffusion layer is independent of time. This is a consequence of steady-state conditions (e.g., if the rotation rate was too slow to allow steady-state conditions, the thickness of the diffusion layer would slowly increase with time). Since the thickness of the diffusion layer does not change with time, the mass-transport limited current is a plateau.

One advantage of convection-diffusion is that the mass transport is stable, unlike diffusion-only experiments. In addition, the mass transport is mathematically well-defined and can be controlled by varying the rotation rate. By increasing the rate of rotation, the rate of convection increases to the outer boundary of the diffusion

layer, and the thickness of this layer is decreased.

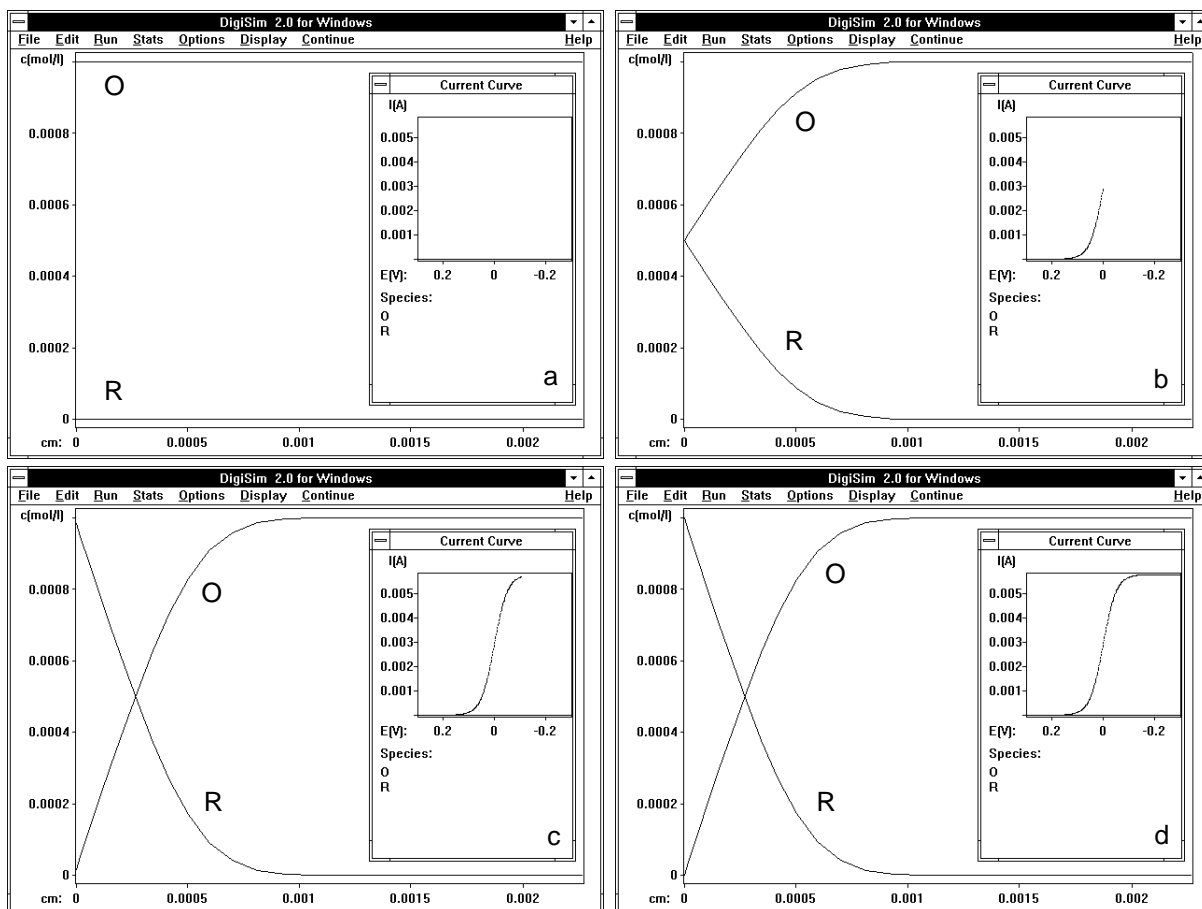
Radial Diffusion at Disk/Hemispherical Microelectrodes

Steady-state conditions can only be set up if there is a constant supply of the electroactive species from the bulk solution to the electrode. In the above example, this was achieved using convection (rotation of the working electrode). It can also be achieved using radial diffusion.

Linear and radial diffusion are shown in **F4**. For linear diffusion, the current decreases with time. Since longer times are required for molecules to diffuse to the electrode surface, a steady state cannot be achieved. In contrast, for radial diffusion, as the diffusion layer moves further out into the bulk solution, the area of the diffusion layer boundary increases and more

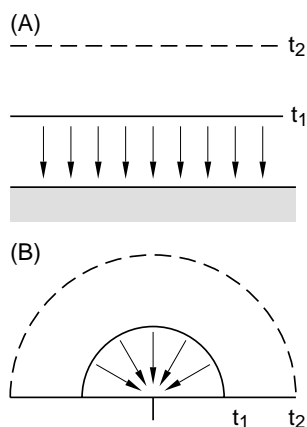
F3

Concentration profiles for convection-diffusion during a linear potential scan.



F4

Lines of flux for linear diffusion (a) and radial diffusion (b).



of the solution contributes to the flux at the electrode. This increase in area compensates for the increase in the time required to resupply the electrode surface by diffusion.

The simulation of mass-transport at disk microelectrodes is a two-dimensional problem and as yet cannot be performed by DigiSim. However, the behavior of disk microelectrodes can be approximately modeled using a hemi-

spherical geometry, which is a geometry option in DigiSim.

Both linear and radial diffusion can occur at hemispherical electrodes. The relative contribution of each type of diffusion depends on the time scale of the experiment and the size of the electrode. The voltammograms for hemispherical electrodes under various experimental conditions are shown in **F5**. In **F5a**, the electrode radius is 1 mm, and the scan rate is 0.02 V s^{-1} ; the shape of the voltammogram is characteristic of linear diffusion. However, if the radius is decreased to $1 \mu\text{m}$, then a sigmoidal voltammogram is obtained at the same scan rate (**F5b**), which is indicative of steady-state behavior (this is also shown in **F6** by the concentration-distance profiles). If the scan rate is now increased to $10,000 \text{ V s}^{-1}$, a linear diffusion-controlled voltammogram is once more obtained (**F5c**).

The relative contributions of linear and radial diffusion are deter-

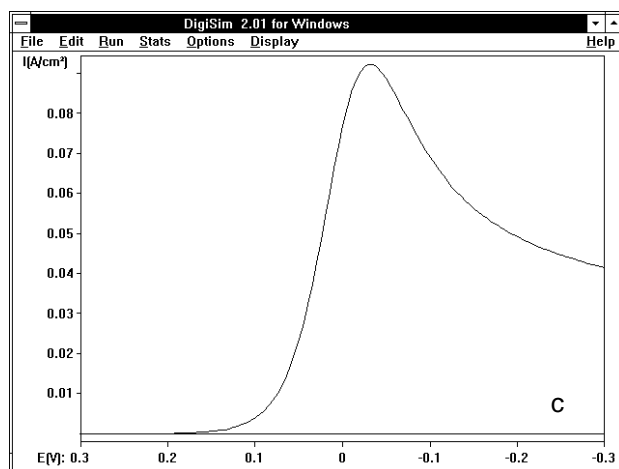
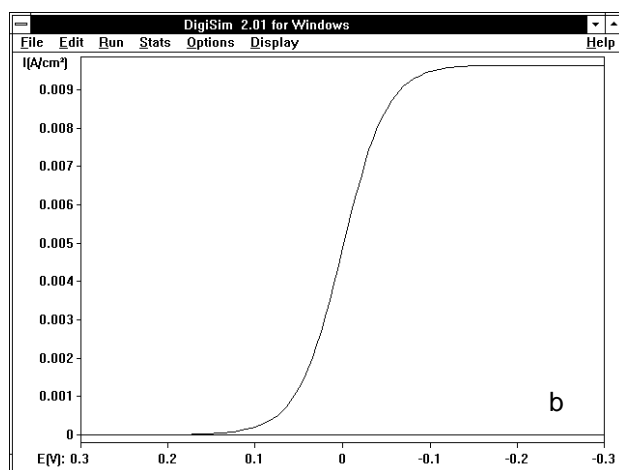
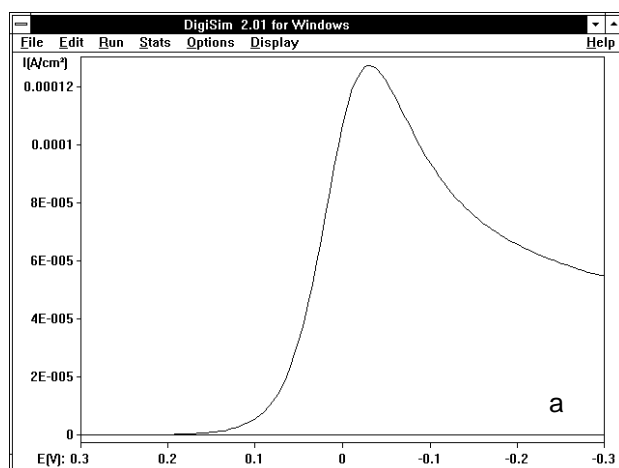
mined by the relative magnitudes of the electrode radius and the parameter d , which is given by the equation:

$$d = (2Dt)^{\frac{1}{2}}$$

where D is the diffusion coefficient and t is the time of the experiment. Essentially, d is the distance moved by a molecule during the experiment; it has also been described as the diffusion layer thickness. If $d \gg r$, then radial diffusion predominates, whereas if $r \gg d$, linear diffusion is dominant. Hence, radial diffusion occurs for long experiments (e.g., slow scan rates) and small electrodes (micron-sized electrodes). It should be noted that there is a gradual transition between radial and linear diffusion. For example, if d and r are approximately equal, then there are significant contributions from both linear and radial diffusion. Voltammograms

F5

Comparison of current responses at a hemispherical electrode a) Scan rate = 0.02 V s^{-1} , electrode radius = 1 mm. b) Scan rate = 0.02 V s^{-1} , electrode radius = $1 \mu\text{m}$. c) Scan rate = $10,000 \text{ V s}^{-1}$, electrode radius = $1 \mu\text{m}$.



recorded under such conditions are more difficult to interpret, and it is standard practice to adjust the electrode size and/or the scan rate so that only one type of diffusion is significant.

Finite Diffusion

The experiments discussed above were all performed under

semi-infinite diffusion conditions; that is, the diffusion layer thickness (d) is very small relative to the thickness of the diffusion medium (δ). In contrast, for finite diffusion, $d > \delta$, and the current response is significantly different.

In the limiting case that $d \gg \delta$, mass transport within the diffusion medium can be ignored. This gives rise to a well-defined current re-

sponse, the shape of which depends on the mass transport across the outer boundary. In DigiSim, two limiting cases are considered: no communication across this boundary (blocked boundary; for example, a thin-layer cell), and perfect communication (open boundary; for example, diffusion from solution across a film on the electrode surface).

A blocked boundary simulation is shown in **F6a**, which consists of a symmetrical peak. The absence of diffusional effects is further illustrated by CV-The Movie (**F6b**), which shows that the concentrations at a given potential are uniform throughout the diffusion medium.

An open boundary simulation is shown in **F7a**, and the current response is sigmoidal. This steady-state behavior is a consequence of maintaining the concentrations at the outer boundary of their initial values. The concentration profiles (**F7b**) are similar to those shown above for the diffusion layers of other steady-state systems.

The above examples were based on the condition that $d \gg \delta$. If d is decreased (by decreasing D or t) or if δ is increased, then mass transport within the diffusion medium can no longer be ignored. The behavior is intermediate between that shown in **F6** and **F7** and the semi-infinite behavior described above.

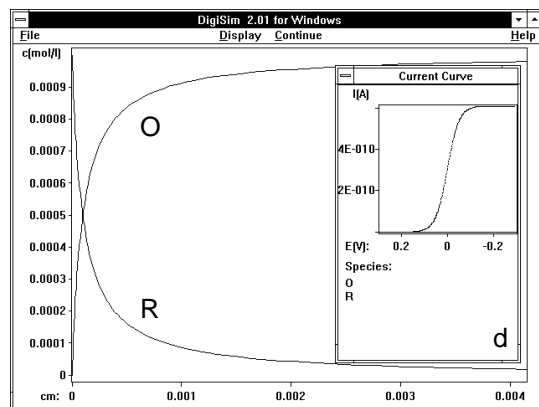
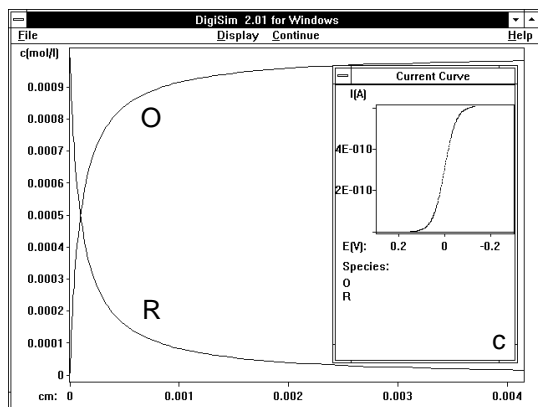
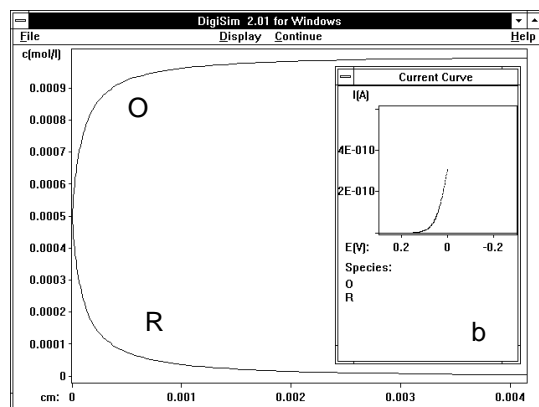
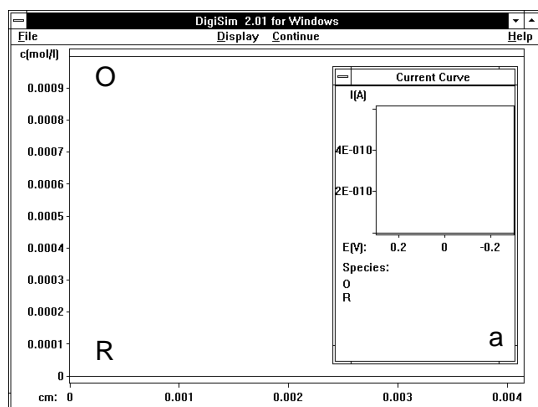
Although mass transfer can be very complicated, electrochemical experiments are typically designed so that there is one dominant mode of mass transport. This simplifies the mathematical treatment of mass transport, which in turn facilitates the quantitative description of the current response.

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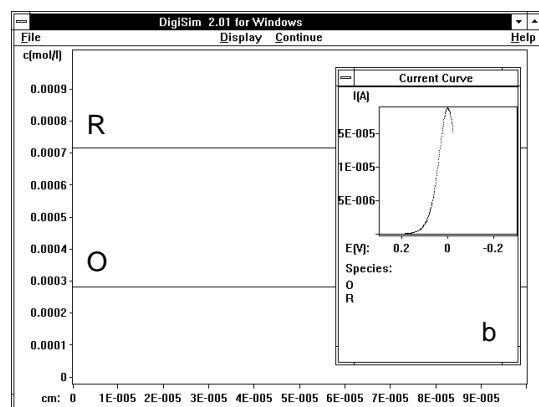
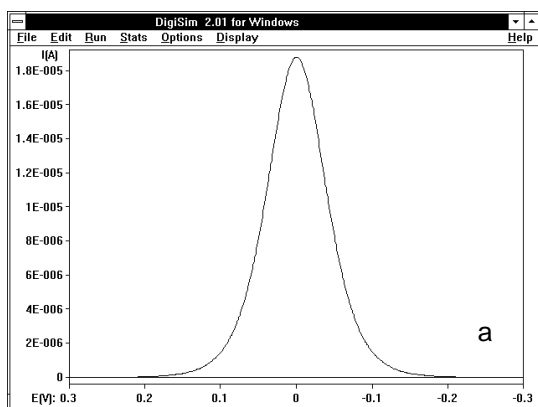
F6

Concentration profiles for radial diffusion at a hemispherical electrode ($r = 1 \mu\text{m}$).



F7

Linear sweep voltammogram (a) and concentration profile (b) for finite diffusion at a blocked boundary.



F8

Linear sweep voltammogram (a) and concentration profile (b) for finite diffusion at an open boundary.

