



FUNDAMENTALS OF ELECTROCHEMISTRY

Second Edition

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It can be seen that the ohmic potential drop ϕ_{ohm} differs from the overall potential drop ϕ_{σ} in the electrolyte as given by Eq. (4.25). The difference between these two values corresponds exactly to the diffusional potential drop ϕ_d for the given concentration ratio that was given in Eq. (4.19).

Thus, the potential difference in electrolytes during current flow is determined by two components: an ohmic component ϕ_{ohm} proportional to current density and a diffusional component ϕ_d , which depends on the concentration gradients. The latter arises only when the D_j values of the individual ions differ appreciably; when they are all identical, ϕ_d is zero. The existence of the second component is a typical feature of electrochemical systems with ionic concentration gradients. This component can exist even at zero current when concentration gradients are maintained artificially. When a current flows in the electrolyte, this component may produce an apparent departure from Ohm's law.

As the diffusional field strength \mathbf{E}_d depends on the coordinate x in the diffusion layer, the diffusion flux density (in contrast to the total flux density) is no longer constant and the concentration gradients dc_j/dx will also change with the coordinate x .

4.3.3 The General Case

Generally, an electrolyte may contain several ionic reactant species but no obvious excess of a foreign electrolyte. Then, as already mentioned, a calculation of the migration currents [or coefficients α in equations of the type (4.22)] is very complex and requires computer use.

Often, we need only a qualitative estimate; that is, we want to know whether the limiting current is raised or lowered by migration relative to the purely diffusion-limited current, or whether α_j is larger or smaller than unity. It is evident that α_j will be larger than unity when migration and diffusion are in the same direction. This is found in four cases: for cations that are reactants in a cathodic reaction (as in the example above) or products in an anodic reaction, and for anions that are reactants in an anodic reaction or products in a cathodic reaction. In the other four cases (for cations that are reactants in an anodic or products in a cathodic reaction, and for anions that are reactants in a cathodic or products in an anodic reaction), we have $\alpha_j < 1$, a typical example being the cathodic deposition of metals from complex anions.

4.4 CONVECTIVE TRANSPORT

Convective transport is the transport of substances with a moving medium (e.g., the transport of a solute in a liquid flow). The convective flux is given by

$$J_{kv,j} = v c_j, \quad (4.31)$$

where v is the linear velocity of the medium and c_j is the concentration of the substance. In electrolyte solutions, the convective flux is always electroneutral because of the medium's electroneutrality.

In electrochemical cells we often find convective transport of reaction components toward (or away from) the electrode surface. In this case the balance equation describing the supply and escape of the components should be written in the general form (1.38). However, this equation needs further explanation. At any current density during current flow, the migration and diffusion fluxes (or field strength and concentration gradients) will spontaneously settle at values such that condition (4.14) is satisfied. The convective flux, on the other hand, depends on the arbitrary values selected for the flow velocity v and for the component concentrations (i.e., is determined by factors independent of the values selected for the current density). Hence, in the balance equation (1.38), it is not the total convective flux that should appear, only the part that corresponds to the true consumption of reactants from the flux or true product release into the flux. This fraction is defined as the difference between the fluxes away from and to the electrode:

$$\Delta J_{kv,j} = nFv(c_j - c'_j), \quad (4.32)$$

where c'_j is the concentration of substance j in the flow leaving the electrode.

For the present argument and in what follows, we assume that the migrational transport is absent (that we have uncharged reaction components or an excess of foreign electrolyte).

Let us estimate the ratios of diffusion and maximum convective fluxes, $J_{d,j}/J_{kv,j} = D_j \times \text{grad } c_j / c_j v$. The order of magnitude of the concentration gradient is c_j / δ . Therefore,

$$\frac{J_{d,j}}{J_{kv,j}} \approx \frac{D_j}{\delta v}. \quad (4.33)$$

In aqueous solutions $D_j \approx 10^{-5} \text{ cm}^2/\text{s}$; a typical value of δ is 10^{-2} cm . It follows that the convective and diffusional transport are comparable even at the negligible linear velocity of 10^{-3} cm/s of the liquid flow. At larger velocities, convection will be predominant.

4.4.1 Flow-by Electrodes

Flow of the liquid past the electrode is found in electrochemical cells where a liquid electrolyte is agitated with a stirrer or by pumping. The character of liquid flow near a solid wall depends on the flow velocity v , on the characteristic length L of the solid, and on the kinematic viscosity ν_{kin} (which is the ratio of the usual rheological viscosity η and the liquid's density ρ). A convenient criterion is the dimensionless parameter $\text{Re} \equiv vL/\nu_{\text{kin}}$, called the *Reynolds number*. The flow is laminar when this number is smaller than some critical value (which is about 10^3 for rough surfaces and about 10^5 for smooth surfaces); in this case the liquid moves in the form of layers parallel to the surface. At high Reynolds numbers (high flow velocities) the motion becomes turbulent and eddies develop at random in the flow. We shall only be concerned with laminar flow of the liquid.

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