

CHEMICAL KINETICS

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ELECTRODE KINETICS:
PRINCIPLES AND METHODOLOGY



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Chapter 2

Mass Transport to Electrodes

KEITH B. OLDHAM and CYNTHIA G. ZOSKI

1. Introduction

The investigation of electrode kinetics has one paramount advantage over other kinetic studies: the rate of the electron transfer reaction



can be measured directly rather than needing to be inferred from concentration changes. This advantage is a consequence of Faraday's law, which asserts the proportionality of the electron-transfer rate

$$\text{Reaction rate} = \frac{i}{nAF} \quad (2)$$

to the faradaic current i divided by the electrode area A . In eqn. (2), n is the number of electrons and F is Faraday's constant.

On the other hand, electrode kinetic studies are at a disadvantage compared with investigations of homogeneous kinetics because concentrations are not uniform and surface concentrations can rarely be measured directly (optical methods can sometimes provide direct measurement of the product concentration [1]). This means that the converse situation to that in classical homogeneous kinetics exists in electrode kinetics: concentration information needs to be inferred from reaction rates.

To calculate concentrations at the electrode surface requires a knowledge of

- (a) the stoichiometry of the electrode reaction;
- (b) the bulk concentrations of the species involved;
- (c) the rate of the reaction [or equivalently, because of relationship (2), the faradaic current] since the onset of the experiment;
- (d) the laws governing mass transport for the particular electrode geometry; and
- (e) the prevailing experimental conditions.

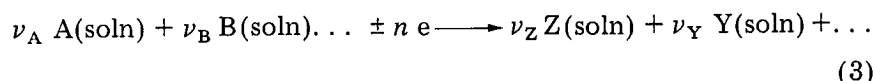
This chapter is concerned with how one uses items (a)–(e) to calculate concentrations at the electrode surface. In the electrochemical literature, expressions for surface concentrations are seldom regarded as the end result of a transport prediction. Instead, one usually assumes that the surface concentrations of the species involved in the electrode reaction

References pp. 141–143

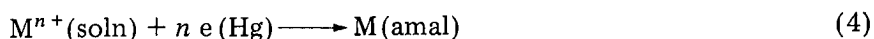
obey either a thermodynamic relation (nernstian conditions) or a particular kinetic expression (volmerian conditions), so that the result of the analysis of mass transport can be presented as a relationship between the experimentally observable variables: current, cell potential, and time. In this chapter, we shall primarily report relationships involving concentrations, since these are the kinetically significant variables.

1.1 SPECIES INVOLVED IN TRANSPORT

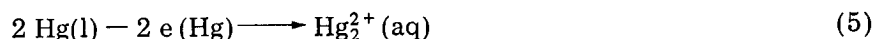
Throughout this chapter, we shall specifically *exclude* electrode reactions that consume or generate *insoluble* species. Thus, the most general electrode reaction is



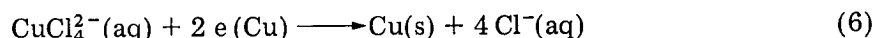
where the ν s are stoichiometric coefficients, A, B, . . . are reactant species and Z, Y, . . . are product species. Usually, all the species are dissolved in the electrolyte solution, but an important exception occurs in the reduction of certain metal ions at a mercury electrode to produce an amalgam



Cases in which one of the reactants or products is the material of the electrode itself, as in



or



are not excluded.

There is, of course, always an ample supply of the electrolytic solvent (often water) and of the electrode material (often a metal) at the interface, but all other species must be transported to and from the electrode surface as illustrated in Fig. 1.

Usually, there is no significant impediment to the transport of electrons, through this may not be true of some semiconductor electrodes [2-7]. When there is more than one reactant, it is usually possible to adjust bulk concentrations (or adopt other experimental strategies such as buffering) so that all reactants except one are in such excess that their transport poses no difficulty. This is an analog of the "isolation technique" familiar to kineticists. The same is true of product species: it is generally possible to arrange experimental conditions so that, at most, only one product species is subject to a transport restriction.

Hence, we shall customarily ignore all but one reactant species and all but one product species. Moreover, we shall assume that the stoichiometric coefficients of these species are both unity. This is not an essential

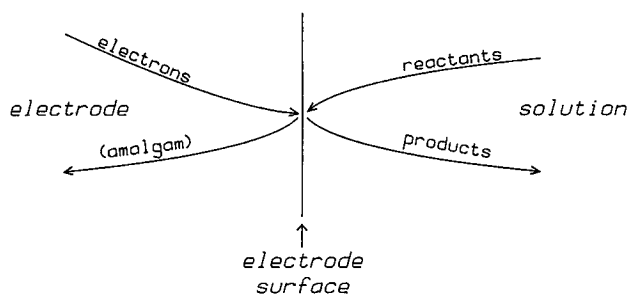


Fig. 1. Transport to and from the electrode surface.

assumption, but it does serve to simplify our arguments and covers the majority of practical examples. Thus, for a reduction experiment, the electrode reaction may be abbreviated to



where O (for oxidized species) is the single reactant species we need consider and R (for reduced species) is the sole product species under consideration. Of course, either O or R or both may be ions.

Sometimes, we shall address an even simpler class of electrode reaction in which there is only a single electroactive species of a variable activity. The simplest instance of this class is the reduction of metal ions on a cathode composed of that metal, for example



This reaction is the only one treated in Sect. 4 of this chapter.

It will be our custom to deal with cathodic electrode reactions, i.e. with reductions like (7) and (8), rather than with the equally important oxidation processes. For this reason, cathodic currents will be treated as positive*.

1.2 THE ELECTRODE SURFACE

The region extending from the phase boundary out to about 3 nm is quite unlike the solution beyond. Generalizations valid elsewhere in the solution do not necessarily apply here. In this inner zone, the so-called double-layer region [9], we may encounter a violation of the electro-neutrality condition (see Sect. 4.1) and large electric fields. Concentrations may be enhanced or depleted compared with the adjacent solution.

* This is the usual convention in electroanalytical chemistry, though it is at variance with the more logical IUPAC convention [8].

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