

1 Introduction

1.1 General Considerations

1.1.1 The Current–Potential Relationship

From a phenomenological point of view, the study of electrode kinetics involves the determination of the dependence of current on potential. It is therefore appropriate to start this book with a general qualitative description of such a relationship, as shown in Figure 1.1.

In the simplest case, E is the potential applied between two electrodes in solution and j is the current density. Curve a in Figure 1.1 represents the dependence of the purely activation-controlled current density on potential. Curve b is the actual current density measured, taking into account the effects of mass transport, represented by the limiting current density j_L . These concepts are explained in the following sections. In real experiments the potential E is always measured with respect to a suitable reference electrode and, instead of the current, one refers to the current density on the electrode being studied, but at this point we need not concern ourselves with these refinements.

It is immediately obvious from Figure 1.1 that Ohm's law does not apply, not even as a rough approximation. This observation is not as trivial as it may seem, when we recall that in the study of conductivity of electrolytic solutions, Ohm's law is strictly obeyed over a very large range of potentials and frequencies. The difference is that Figure 1.1 pertains to measurements conducted under direct current (DC) conditions, whereas ionic conductivity is measured, as a rule, with an alternating current or potential. The implication is that the impedance of the metal/solution interface is partially capacitive – a subject to be dealt with in considerable detail below.

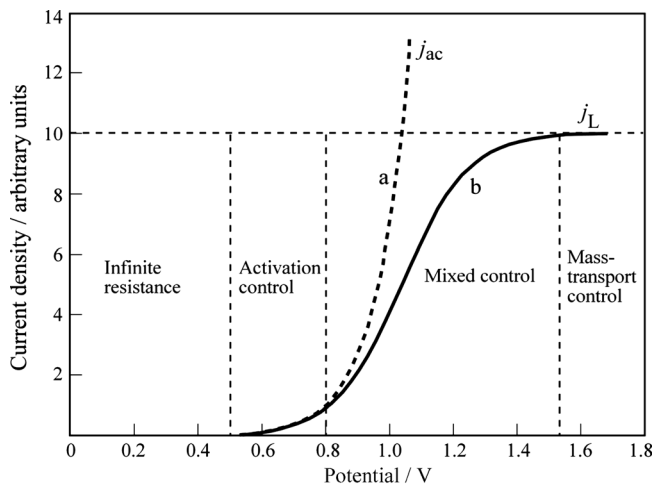
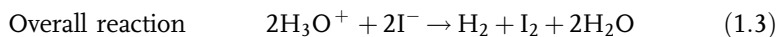
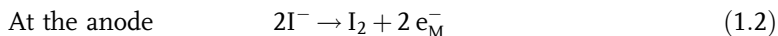
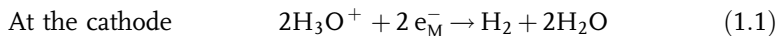


Figure 1.1 Schematic j/E plot for the electrolysis of a 1.0 M solution of KI in H_2SO_4 , employing two Pt electrodes. The minimum potential for DC current flow is 0.56 V.

1.1.2

The Resistance of the Interface Can Be Infinite

Looking at Figure 1.1 carefully, one observes that up to a certain potential the current is zero. This is not a matter of limited sensitivity of the measuring instrument. The current is *exactly* zero (ignoring minor background currents that may be caused by impurities), corresponding effectively to an infinite resistance of the interface. The reason for this behavior is to be found in the realm of thermodynamics. Thus, when a current flows through a cell, electrical energy is used to produce chemicals. The reactions taking place are



The reversible potential under standard conditions for this reaction is $E_{\text{rev}} = -0.56$ V, so this is the lowest potential that would allow passage of a current.

This is “up the Gibbs energy ladder”, (hence the potential is given a negative sign). Evidently this reaction proceeds spontaneously in the opposite direction (forming 2HI), and, therefore, electrical energy must be supplied to make the reaction happen, according to the well-known relation:

$$\Delta G = -nFE \quad (1.4)$$

The negative sign in this equation shows that when the Gibbs energy decreases, the potential is positive – the cell acts as a source of electrical energy, and vice versa.

Had we removed KI from the solution, the reaction taking place would be the electrolysis of water, forming molecular oxygen and hydrogen. The standard Gibbs energy for water electrolysis at room temperature is $+237.16 \text{ kJ mol}^{-1}$, corresponding to -1.229 V . The positive value of ΔG^0 and the corresponding negative value of the standard potential E^0 show that this reaction will not occur spontaneously. A positive potential of at least 1.229 V has to be applied for it to occur. In this case the resistance of the cell shown in Figure 1.1 would be infinite up to this potential.

Replacing the platinum electrodes with copper, and adding some CuSO_4 , changes the situation radically. Passing a current between the electrodes causes no net chemical change (copper is dissolved off the anode and deposited on the cathode). In this case current is observed as soon as a potential, small as it may be, is applied between the electrodes.

1.1.3

The Transition from Electronic to Ionic Conduction

If one were to describe the essence of electrode kinetics in one short phrase, it would be: the transition from electronic to ionic conduction, and the phenomena associated with, and controlling it. Conduction in the solution is ionic, whereas in the electrodes and the connecting wires it is electronic. The transition from one mode of conduction to the other requires charge transfer across the interfaces. This is a kinetic process. Its rate is controlled by the catalytic properties of the surface and adsorption on it, the concentration and the nature of the reacting species and all other parameters that control the rate of heterogeneous chemical reactions. In addition, the potential plays an important role. This is not surprising, since charge transfer is involved, which may be accelerated by applying a potential difference of the right polarity across the interface.

The current would continue to rise exponentially with potential, along line a in Figure 1.1, were it not for mass-transport limitation, represented by the horizontal part of line b. In the initial rising part of the curve, the reaction is said to be “charge-transfer controlled” or “activation controlled”. The detailed dependence of current on potential in this region is discussed later.

1.1.4

Mass-Transport Limitation

The rate of charge transfer can be greatly increased by increasing the potential, but charge can be transferred across the interface only over a very short distance (of the order of 0.5 nm). Another process is required to bring the reacting species close enough to the surface, and to remove the species formed at the surface into the bulk of the solution. This process is called *mass transport*.

Mass transport and charge transfer are two consecutive processes. It is therefore always the slower of the two that determines the overall rate observed experimentally. When the potential applied is low, barely above the minimum value needed to pass a current, charge transfer is slow and one can ignore mass-transport limitation. The

bottleneck is in transferring the charge across the interface to the electroactive species, not in getting the species to the surface. At high potentials, charge transfer becomes the faster process and ceases to influence the overall rate. Increasing the potential further will increase the rate of charge transfer, but this will have no effect on the observed current, which will be limited by mass transport. The result is a current density that is independent of potential, which is referred to as *the limiting current density*, j_L .

For the observed current density j , one can write the simple equation:

$$\frac{1}{j} = \frac{1}{j_{ac}} + \frac{1}{j_L} \quad (1.5)$$

Clearly, the smaller of the two currents is dominant. The mass-transport-limited current density can be written as

$$j_L = \frac{nFDc_b}{\delta} \quad (1.6)$$

in which nF is the charge transferred per mol ($C \text{ mol}^{-1}$), D is the diffusion coefficient ($\text{cm}^2 \text{ s}^{-1}$), c_b is the bulk concentration (mol cm^{-3}), and δ is the Nernst-diffusion-layer thickness (cm). Calculated in these units, the current density is obtained in A cm^{-2} .

The corresponding equation for the activation controlled current density is

$$j_{ac} = nFk c_b \quad (1.7)$$

Where the rate constant k is a function of potential. From a comparison of the two equations it is seen that the ratio D/δ in Eq. (1.6) has the same role as the rate constant k in Eq. (1.7), except that it is independent of potential. This ratio may be regarded as the specific rate for diffusion.

Now, the essence of mass transport is the quantity δ . In certain favorable cases it has been calculated theoretically, in others it can only be determined experimentally. Sometimes it is a function of time, while under different circumstances it is essentially constant during an experiment. Stirring the solution and transporting it towards, past, or through the electrode all decrease the value of δ , and hence increase j_L . Moving the electrode (rotation, vibration) has a similar effect. In quiescent solutions δ increases linearly with $t^{1/2}$, hence j_L can be increased by taking measurements at short times.

In typical electrochemical measurements, the Nernst-diffusion-layer thickness attains values in the range 10^{-3} – 10^{-1} cm. Since in aqueous solutions at room temperature the diffusion coefficient is of the order of $10^{-5} \text{ cm}^2 \text{ s}^{-1}$, this yields limiting current densities in the range 0.01 – 1.0 mA cm^{-2} , when $n=1$ and the concentration of the electroactive species in solution is 1.0 mM .

The two most important things to notice in Eq. (1.6) are (i) that the limiting current density is independent of potential, and (ii) that it depends linearly on the bulk concentration. A less obvious, but equally important, consequence of this equation is that j_L is independent of the kinetics of the reaction (i.e., of the nature of the surface and its catalytic activity). These characteristics make it an ideal tool for probing the concentration of species in solution. This is why most electroanalytical methods

depend, in one way or another, on measurements of the mass-transport-limited current density.

1.1.5

The Capacitance at the Metal/Solution Interface

When a metal is dipped in solution, a discontinuity is created. This affects both phases to some degree, so that their properties near the contact are somewhat different from their bulk properties. The exact position of the interface on the atomic scale is hard to define. “Where does the metal end?” we may ask. Is it the plane going through the center of the outermost layer of atoms, is it one atomic radius farther out, or is it even farther out, where the charge-density function of the free electrons in the metal has decayed to essentially zero? Fortunately, we do not need to know the position of this plane for most purposes, when we discuss the properties of the interface.

One distinct property of the metal/solution interface is a capacitance, called *the double-layer capacitance*, C_{dl} . It is a result of the charge separation between the two phases in contact. The double-layer capacitance observed depends on the structure of a very thin region near the interface, extending about 1–10 nm, called *the double layer*. If the surface is rough, the double layer will follow its curvature down to atomic dimensions, and the capacitance measured under suitably chosen conditions is proportional to the *real* surface area of the electrode.

The double-layer capacitance is rather large, of the order of $10\text{--}30\ \mu\text{F cm}^{-2}$. This presents a serious limitation on our ability to study fast electrode reactions. Thus, a $10\ \mu\text{F}$ capacitor coupled with a $10\ \Omega$ resistor yield a time constant of $R \times C_{dl} = \tau_c = 0.1\ \text{ms}$. It is possible to take measurements at shorter times by applying special techniques, but even so, the lower limit at present seems to be about $0.05\ \mu\text{s}$, six orders of magnitude slower than that currently achievable in the gas phase.

The double-layer capacitance depends on the potential, the composition of the solution, the solvent and the metal. It has been the subject of numerous investigations, some of which are discussed later.

1.2

Polarizable and Nonpolarizable Interfaces

1.2.1

Phenomenology

When a small current or potential is applied, the response is in many cases linear. The effective resistance can, however, vary over a wide range. When this resistance is high, we have a polarizable interface, meaning that a small current generates a high potential across it (i.e., the interface is polarized to a large extent).

When the effective resistance is low, the interface is said to be nonpolarizable. In this case a significant current can be passed with only minimal change in the

potential across the interface. A nonpolarizable electrode is, in effect, a reversible electrode. The reversible potential is determined by the electrochemical reactions taking place and the composition of the solution, through the Nernst equation. For a copper electrode in a solution containing CuSO_4 this is

$$E_{\text{rev}} = E^0 + (2.3RT/nF)\log(a_{\text{Cu}^{2+}}) \quad (1.8)$$

in which $E^0 = +0.34 \text{ V}$ is the standard potential for the Cu^{2+}/Cu couple, on the standard hydrogen electrode (SHE) scale, and $a_{\text{Cu}^{2+}}$ is the activity of cupric ions in solution. In aqueous solutions that are not very concentrated, ($c_b \leq 1.0 \text{ M}$) the error introduced by replacing the activity by the concentration is rather small, and often considered negligible.

A good reference electrode is always a reversible electrode. The inverse is not necessarily true. Not every reversible electrode is suitable as a reference electrode. For example, the correct thermodynamic reversible potential of a metal/metal-ion electrode may be hard to reproduce, because of impurities in the metal or complexing agents in the solution, even when the interface is highly nonpolarizable.

Polarizable interfaces behave differently. Their potential is not fixed by the solution composition, and it can be changed at will over a certain range, depending on the metal and the composition of the solution in contact with it. For such a system the potential may be viewed as an additional degree of freedom in the thermodynamic sense, as used in the Gibbs phase rule. To be sure, a so-called nonpolarizable interface can be polarized by passing a significant current through it. This, however, alters the concentration of both the reactant and the product *at the electrode surface* (without changing significantly their bulk concentrations). The potential developed across the interface will be in agreement with the Nernst equation, as long as the concentrations used are the surface concentrations, which depend on the current passing across the interface.

1.2.2

The Equivalent Circuit Representation

We have already seen that the metal/solution interface has some capacitance associated with it, as well as a (nonohmic) resistance. Also, the solution has a finite resistance that must be taken into account. Thus, a cell with two electrodes can be represented by the equivalent circuit shown in Figure 1.2.

Usually one considers only the part of the circuit inside the dashed line, since the experiment is set up in such a way that only one of the electrodes is studied at a time.

The equivalent circuit shown in Figure 1.2 represents a gross oversimplification, and interfaces rarely behave exactly like it. It does, nevertheless, help us gain some insight concerning the properties of the interface.

The combination of the double-layer capacitance C_{dl} and the Faradaic resistance R_{F} (also referred to as the charge-transfer resistance, R_{ct}) represents the interface. How do we know that C_{dl} and R_{F} must be put in a parallel rather than in a series combination? Simply because we can observe a steady direct current flowing when

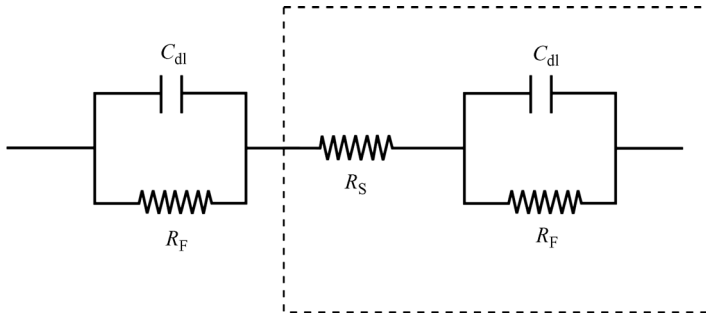


Figure 1.2 Equivalent circuit for a two-electrode cell. A single interface is usually represented by the elements inside the dashed rectangle. C_{dl} , R_F and R_S represent the double-layer capacitance, the Faradaic resistance and the solution resistance, respectively.

the potential is high enough (above the minimum prescribed by thermodynamics). Also when the resistance is effectively infinite under DC conditions, we can still have an AC signal going through.

The equivalent circuit just described also makes it clear why conductivity measurements are routinely done by applying a small AC signal. If the appropriate frequency is chosen, the capacitive impedance associated with C_{dl} can be made negligible compared to the Faradaic resistance R_F , which is thus effectively shorted, leaving the solution resistance R_S as the only measured quantity.

As pointed out earlier, the equivalent circuit shown in Figure 1.2 is meant to represent the simplest situation only. It does not take into account factors such as mass transport, heterogeneity of the surface and the occurrence of reaction intermediates absorbed on it. Some of these factors are discussed later. Even in the simplest cases, in which this circuit does represent the response of the interface to an electrical perturbation reasonably well, one should bear in mind that both C_{dl} and R_F depend on potential and, in fact, R_F depends on potential exponentially over a wide range, as will be discussed later.

The difference between polarizable and nonpolarizable interfaces can be easily understood in terms of this equivalent circuit. A high value of R_F is associated with a polarizable interface, whereas a low value of R_F represents a non-polarizable interface.

