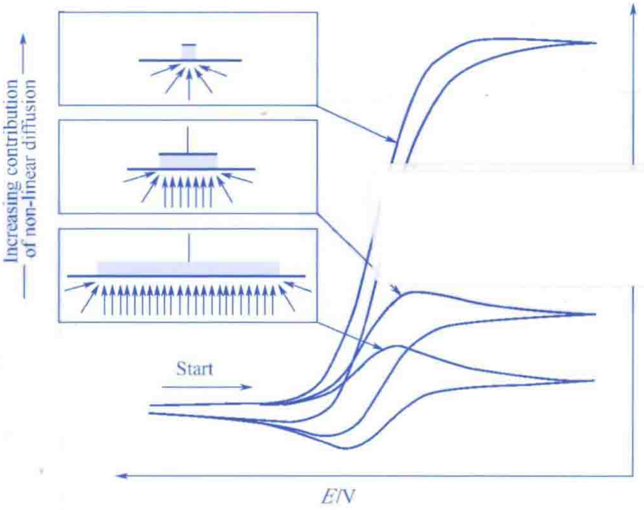
Voltammetric Principles

伏安原理

Xiaobo Ji Craig E Banks



Chemical Industry Press

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Preface

Electrochemistry, a powerful tool discipline, has extremely extensive application in many technical fields, such as corrosion and protection, chemical power sources, electrocatalysis, and so on. A range of electrochemical books exist, not only in Asia but worldwide. These range from encyclopedia versions through to dedicated books on very specific topics. What is missing is a book that will take students through from final undergraduate level, where traditional electrode potentials are introduced, through to undertaking masters level and early Ph.D. where more advanced techniques are required; the majority of books do not currently address this. This book, *Voltammetric Principles* tries to do exactly that and aims to explain concepts in a more concise way from the fundamentals of electrochemistry through to introducing current technology advantages and recent literature developments. This book features that integrate theory with practice, which elaborate in detail the basic principles of electrochemistry, a variety of methods and means of electrochemistry and their applications in various electrochemical fields. It analyzes the current application and development of electrochemical methods and principles in the current electrochemical frontier, highlights areas such as electrochemical analysis and carbon materials chemistry. With chapters, the book is addressed to scientists, researchers and graduate students interested in electroanalysis, electrocatalysis, materials for new energy.

I would like to express my sincere thanks to co-workers for their cooperations, the editorial and production staff of Chemical Industry Press for their help and support.This book is dedicated to Binghan Qiao, Hansen Ji and Alix.

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1

Equilibrium Electrochemistry

1.1 Chemical Equilibrium

Let us first consider fundamental thermodynamics that will allow insights into electrochemical processes. Thermodynamics predicts the direction, but not the rate of chemical change. Consider the general chemical reaction:

$$a\mathrm{A} + b\mathrm{B} + \cdots \rightleftharpoons x\mathrm{X} + y\mathrm{Y} + \cdots \qquad (1.1)$$

where the reactants A,B···and products X,Y,···, can be either solid, liquid, or gaseous forms. Thermodynamics informs us that the Gibbs energy of the system, G_{sys} is minimised when it has attained equilibrium, as shown in figure 1.1. At equilibrium, under constant temperature and pressure, this minimum may be defined mathematically as:

$$\mathrm{d}G_{sys} = 0 \qquad (1.2)$$

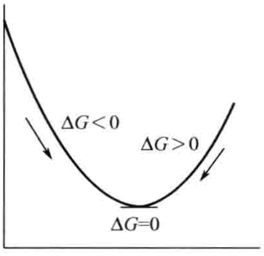

Figure 1.1 Extent of reaction

Consider equation (1.1), if there are n_{A} moles of A and n_{Y} moles of Y, $\mathrm{d}n_{\mathrm{A}}$ represents the change in the number of moles of A and $\mathrm{d}n_{\mathrm{Y}}$ represents the change in the number of moles of Y, and so forth. Since every molecule lost on the left hand side of equation (1.2) results in the production of molecule formed on the right hand side,

$$-\mathrm{d}n_{\mathrm{LHS}} = +\mathrm{d}n_{\mathrm{RHS}} = \mathrm{d}n$$

The associated Gibbs energy change is given by:

$$\partial G_{\text{sys}} = \{\text{Gain in Gibbs energy of products}\} + \{\text{Loss of Gibbs energy of reactants}\}$$

$$= \{x\mu_X\,\mathrm{d}n + y\mu_X\,\partial n \cdots\} - \{a\mu_A\,\mathrm{d}n + b\mu_B\,\partial n + \cdots\}$$
$$= \{x\mu_X + y\mu_Y \cdots - a\mu_A - b\mu_B\}\,\partial n \tag{1.3}$$

where

$$\mu_j = \left(\frac{\partial G}{\partial n_j}\right)_{T,\, n_i \neq n_j} \tag{1.4}$$

is the chemical potential of species j (j = A,B,...X,Y,...), T is the absolute temperature (K) and n_i is the number of moles of i ($i = A,B,\ldots X,Y,\ldots$). The chemical potential of j is therefore the Gibbs energy per mole of j. It follows at equilibrium that

$$a\mu_A + b\mu_B + \cdots = x\mu_X + y\mu_Y + \cdots \tag{1.5}$$

so that under conditions of constant temperature and pressure, the sum of the chemical potential of the reactants (weighted by their stoichiometric coefficients $a,b,\ldots x,y,\ldots$) equals that of the products. If this was not the case the Gibbs energy of the system would not be a minimum since the Gibbs energy could be furthered lowered by either more reactants turning into products or vice versa. For the case of an ideal gas,

$$\mu_j = \mu_j^0 + RT\ln\left(\frac{P_j}{P^0}\right) \tag{1.6}$$

Where μ_j^0 is the standard chemical potential of j, R is the universal gas constant (8.313J·K^{-1}·mol^{-1}), P_j is the pressure of gas j and P^0 is a standard pressure conventionally taken to be 1atm (1atm =1.01325×10^{5}N·m^{-2}). Under standard conditions and of pressure (1atm) μ_j^0 is the Gibbs energy of one mole of j. It follows from equation (1.5) and (1.6) that at equilibrium

$$x\mu_X^0 + y\mu_Y^0 + \cdots - a\mu_A^0 - b\mu_B^0 = -xRT\ln\frac{P_X}{P^0} - yRT\ln\frac{P_Y}{P^0} + \cdots + aRT\ln\frac{P_A}{P^0} + bRT\ln\frac{P_B}{P^0} \tag{1.7}$$

so that

$$\Delta G^0 = -RT\ln K_p \tag{1.8}$$

where $$\Delta G^0 = x\mu_X^0 + y\mu_Y^0 + \ldots - a\mu_A^0 - b\mu_B^0 \ldots$$

is the standard Gibbs energy change accompanying the reaction and

$$K_p = \frac{\left(\frac{P_X}{P^0}\right)^x \left(\frac{P_Y}{P^0}\right)^y \cdots}{\left(\frac{P_A}{P^0}\right)^a \left(\frac{P_B}{P^0}\right)^b \cdots} \tag{1.9}$$

is constant at particular temperatures. However, if the gases are not ideal, in which case K_p becomes pressure dependant, thus for the gas phase reaction involving $NO_2(g)$ in equilibrium:

$$2NO_2(g) \rightleftharpoons 2O_2(g) + N_2(g) \tag{1.10}$$

which is described by the equilibrium constant

$$K_p = \frac{\left(\frac{P_{NO_2}}{P^0}\right)^2}{\left(\frac{P_{O_2}}{P^0}\right)^2 \left(\frac{P_{N_2}}{P^0}\right)} \tag{1.11}$$

If some of the reactants and/or products in reaction (1.10) are solutions, the ideal expression for their chemical potentials are

$$\mu_j = \mu_j^0 + RT\ln\frac{[\mathrm{j}]}{[\ ]^0} \tag{1.12}$$

where $[\ ]^0$ is a standard concentration taken to be one molar, M (or $\mathrm{mol \cdot dm^{-3}}$, one mole per cubic decimetre). Applied to equation (1.1), this leads to a general equilibrium constant defined as:

$$K_c = \frac{\left(\frac{[X]}{[\ ]^0}\right)^x \left(\frac{[Y]}{[\ ]^0}\right)^y}{\left(\frac{[A]}{[\ ]^0}\right)^a \left(\frac{[B]}{[\ ]^0}\right)^b} \tag{1.13}$$

If we consider the following equilibrium:

$$\mathrm{HA(aq)} \rightleftharpoons \mathrm{H^+(aq) + A^-(aq)} \tag{1.14}$$

where HA is, say, a carboxylic acid and A^- a carboxylate anion, the equilibrium constant, K_c is given in terms of concentrations as:

$$K_c = \frac{\left(\frac{[H^+]}{[\ ]^0}\right)\left(\frac{[A^-]}{[\ ]^0}\right)}{\left(\frac{[HA]}{[\ ]^0}\right)} \tag{1.15}$$

In common usage equations (1.11) and (1.1) take the form of

$$K_p = \frac{P_X^x P_Y^y \ldots}{P_A^a P_B^b \ldots} \quad \text{and} \quad K_c = \frac{[X]^x [Y]^y \ldots}{[A]^a [B]^b \ldots}$$

In the case that the reactants in equation (1.1) are pure solids or pure liquids, the chemical potential approximates well to the standard chemical potential:

$$\mu_j \approx \mu_j^0 \tag{1.16}$$

Since the chemical potentials of pure liquids and solids are independent of the amount of material present, there are no corresponding terms in the expression for equilibrium constants in which these species are described. Let us consider the general case of the following equilibrium

$$a\mathrm{A(g)}+b\mathrm{B(aq)}+c\mathrm{C(s)}+d\mathrm{D(l)} \rightleftharpoons w\mathrm{W(g)}+x\mathrm{X(aq)}+y\mathrm{Y(s)}+z\mathrm{Z(l)} \tag{1.17}$$

and noting that pure solid (C and Y) and pure liquids (D and Z) do not appear in the equilibrium constant expression, we can write:

$$K = \frac{P_W^w \; [X]^x}{P_A^a \; [B]^b} \tag{1.18}$$

Worked Example

Let us consider the real example of silver chloride, AgCl (s), which is described as:

$$\mathrm{AgCl(s)} \rightleftharpoons \mathrm{Ag^+(aq)+Cl^-(aq)} \tag{1.19}$$

with the following equilibrium constant

$$K=[\mathrm{Ag^+}][\mathrm{Cl^-}]$$

Alternatively, for the case that the presence of a species in a gaseous phase such as:

$$\mathrm{CaCO_3(s)} \rightleftharpoons \mathrm{CaO(s)+CO_2(g)} \tag{1.20}$$

the equilibrium constant is simply defined as:

$$K=P_{\mathrm{CO_2}}$$

Last, for the case

$$Fe^{2+}(aq)+1/2Cl_2(g) \rightleftharpoons Fe^{3+}(aq)+Cl^-(aq) \tag{1.21}$$

the equilibrium constant is described as:

$$K=\frac{[Fe^{3+}][Cl^-]}{[Fe^{2+}]P_{Cl_2}^{1/2}}$$

1.2 An Introduction to Electrochemical Equilibrium

The introductory section considered chemical equilibrium and we now explore the case of electrochemical equilibrium. Let us first consider the case of a solution containing an iron (III) complex, such as potassium hexacyanoferrate (III), $K_3Fe(CN)_6$ and also an iron (II) complex, such as potassium hexacyanoferrate(II), $K_4Fe(CN)_6$ dissolved in water. Into this solution a wire constructed from platinum, *the electrode*, or another inert metal is inserted (figure 1.2) resulting in an equilibrium to be established which is described as

$$Fe^{3+}(aq)+e^-(m) \rightleftharpoons Fe^{2+}(aq) \tag{1.22}$$

Such an equilibrium can be established by first preparing a solution containing both potassium hexacyanoferrate(II), $K_4Fe(CN)_6$, and potassium hexacyanoferrate(III), $K_3Fe(CN)_6$ dissolved in an aqueous solution (water for example) and then inserting a wire *(the electrode*) made of platinum or another inert metal into the solution (figure 1.2).

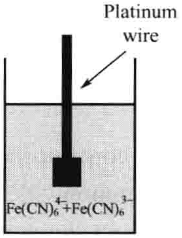

Figure 1.2 Schematic representation showing a platinum wire (the electrode) immersed into an aqueous solution containing both iron (II) and iron (III).Note that X^- will need to be present which is an anion present in the solution required for electroneutrality.

The equilibrium as described in equation (1.22) is established at the surface of the electrode and involves the two dissolved anions and electrons from the inserted metal (electrode). The presence of the equilibrium as described by equation (1.22) implies that the rate at which Fe^{2+} gives up electrons to the metal wire or "electrode" (noted by the presence of (m) in equation 1.22 to represent this fact) is exactly balanced by the rate at which electrons are released by the wire to the Fe^{3+}, which are said to be "reduced". Correspondingly the Fe^{2+} ions losing electrons are said to be "oxidised". This is known as a dynamic equilibrium and once established, no further change occurs. Note that the total number of electrons which are transferred in one direction (or another) is so small that the concentrations of Fe^{2+} and Fe^{3+} are not significantly changed from their values before the electrode was inserted into the solution.

Inspection of equation (1.22) reveals that the reaction involves the transfer of charged particles (electrons) between the metal and solution phases. This results, when equilibrium is attained, that a net electrical charge is established on each of these two phases. If the reaction described in equation (1.22) lies to the left when equilibrium is reached, in favour of Fe^{3+} and electrons then the *electrode* will bear a net *negative* charge and the solution a net positive charge of equal magnitude. Conversely if the equilibrium favours Fe^{2+} and lies to the right, then the *electrode* will be *positive* and the solution negatively charged.

Irrespective of the position of the equilibrium of reaction (1.22) it can be recognised that a charge separation will exist between the electrode and the solution phases. Accordingly there will be a potential difference, that is, a difference in electrical potential, between the inserted metal and the solution known as an *electrode potential.* The basis of this electrode potential is the (electro)chemical process described in equation(1.22) which is referred to as *potential determining equilibria.* Later in the text we explore other pertinent examples.

1.3 Electron Transfer at the Solution | Electrode Interface

Let us return to the potential determining equilibrium as described earlier:

$$Fe^{3+}(aq)+e^{-}(m) \rightleftharpoons Fe^{2+}(aq) \qquad (1.23)$$

If we consider the energy of electrons contained in the metal wire (m) which involves electronic conduction ‘bands’ which is commonly described as the "electron sea" model in which electrons are free to move throughout the solid binding the (metal) cations rigidly together. The energy levels in these bands form an effective continuum of levels or ‘bands’ where an effective continuum of energy levels are available. These are filled up to an energy maximum known as the Fermi level. The electronic energy levels associated with the solution phase Fe^{3+} and Fe^{2+} ions are discrete and relate to an unfilled molecular orbital in Fe^{3+} which gains an electron (reduces) to form Fe^{2+}. It is important to note that iron will exist in a hydrated form surrounded by, in these cases, probably six tightly bound water molecules (inner hydration shell) with a corresponding outer hydration shell which not depicted in figure 1.3, the addition of an electron to Fe^{3+} alters the solvation of the ion so that the electron energy has a different value in the two complexes even though the same molecular orbital is involved. The pertinent energy levels involved in this process are shown in figure 1.3.

Figure 1.3 shows that before electron transfer takes place between the electrode and the solution the Fermi level is higher than the vacant orbital in the Fe^{3+} ion. It is accordingly energetically favourable for electrons to leave the Fermi level and join the Fe^{3+} species converting them to Fe^{2+} ions. This energy difference is the 'driving force' for electron transfer discussed in the case of potential determining equilibria. As this electron transfer proceeds, positive charge must build up on the electrode (metal) and corresponding negative charge in the solution phase. Accordingly since the energy scale in figure 1.3 measures that of the electron, then the electronic energy in the metal must be lowered and so the Fermi level becomes progressively lower in the diagram, as shown in figure 1.3. Correspondingly the generation of negative charge in the solution must raise the (electronic) energy levels of the solution phase species.

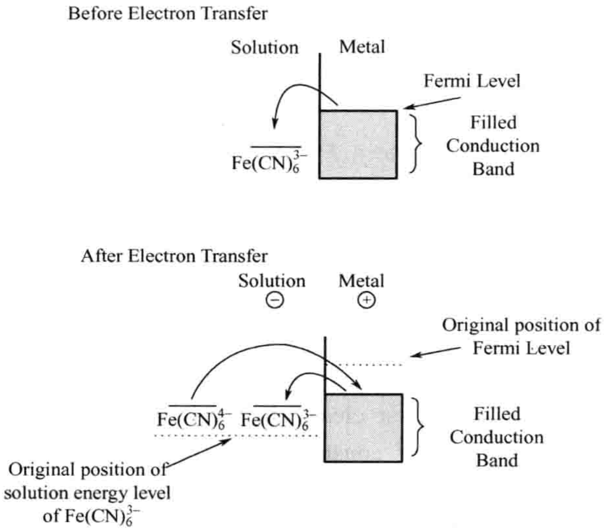

Figure 1.3 The energy of electrons in the ions in solution and in the metal wire (electrode)

Ultimately a situation is reached when the Fermi level lies in between the energy levels of the two ions so that the rate at which electrons leave the electrode and reduce Fe^{3+} ions is exactly matched by the rate at which electrons join the metal from the Fe^{2+} ions which become oxidised. At this point there will be a difference of charge and hence of potential between the metal and solution solutions. This situation corresponds to *dynamic equilibrium* and once it is attained, no further net charge is possible. This is the origin of the Nernst equation which we explore in the next section.

1.4 The Nernst Equation and Electrode | Solution Interfaces

We observed in section 1.1 that the position of chemical equilibrium was controlled by the chemical potentials of the reactants and products. In the case of an electrochemical equilibrium such as reaction 1.22 then the position of equilibrium represents a balance between chemical energies (quantified via the chemical potentials) and electrical energies. The reason for this is that electrochemical equilibrium involves the transfer of a charged particle, the electron, between two phases, the solution and the electrode, which may have two different electrical potentials. Accordingly the electrical energy of the electrons differs from one phase to another.

1.4.1 One Phase to Another

In order to account for both chemical and electrical energies we introduce the electrochemical potential, $\overline{\mu_j}$, of a species, *j*,

$$\overline{\mu_j} = \mu_j + Z_j F \phi \tag{1.24}$$

where Z_j is the charge on molecule *j*, *F* is the Faraday constant corresponding to the charge on one mole of electrons (96487 Coulombs) and ϕ is the potential of the particular phase – electrode or solution – in which species *j* is found. The electrochemical potential of *j* is thus comprised of two terms. The first is the chemical potential, μ_j. The second term, $Z_j F \phi$, describes the electrical energy of species *j*. The latter is of the form of charge (Z_j) multiplied by potential ϕ and the constant *F* puts the electrical energy on a 'per mole' basis in the same way that the chemical potential is Gibbs energy per mole.

Equation (1.24) allows us to analyse electrochemical equilibrium recognising that when this is attained under conditions of constant temperature and pressure there will be a balance (equality) between the electro-chemical potentials of the reactants and those of the products. Returning to the example we have considered throughout this chapter,

$$\mathrm{Fe^{3+}(aq) + e^-(m) \rightleftharpoons Fe^{2+}(aq)}$$

we note that this implies that at equilibrium

$$\overline{\mu}_{\mathrm{Fe\ (III)}} + \overline{\mu}_{\mathrm{e^-}} = \overline{\mu}_{\mathrm{Fe\ (II)}}$$

where Fe(III) denotes $\mathrm{Fe(CN)_6^{3-}}$ and Fe(II) indicates $\mathrm{Fe(CN)_6^{4-}}$. Applying equation (1.24) we obtain

$$(\mu_{\mathrm{Fe(III)}} + 3F\phi_{\mathrm{S}}) + (\mu_{\mathrm{e-}} - F\phi_{\mathrm{M}}) = (\mu_{\mathrm{Fe(II)}} + 2F\phi_{\mathrm{S}})$$

where ϕ_{M} and ϕ_{S} refer to the electrical potential of the metal electrode and of the solution respectively. Rearranging

$$F(\phi_{\mathrm{M}} - \phi_{\mathrm{s}}) = \mu_{\mathrm{Fe\ (III)}} + \mu_{\mathrm{e^-}} - \mu_{\mathrm{Fe\ (II)}}$$

but

$$\mu_{\mathrm{Fe(III)}} = \mu^0_{\mathrm{Fe(III)}} + RT\ln\left(\frac{[\mathrm{Fe(CN)}_6^{3-}]}{[\ \ ]^0}\right)$$

$$\mu_{\mathrm{Fe(\,II)}} = \mu^0_{\mathrm{Fe(III)}} + RT\ln\left(\frac{[\mathrm{Fe(CN)}_6^{4-}]}{[\ \ ]^0}\right)$$

and hence

$$\phi_{\mathrm{M}} - \phi_{\mathrm{S}} = \frac{\Delta\mu^0}{F} + \frac{RT}{F}\ln\left(\frac{[\mathrm{Fe(CN)}_6^{3-}]}{[\mathrm{Fe(CN)}_6^{4-}]}\right) \tag{1.25}$$

where

$$\Delta\mu^0 = \mu^0_{\mathrm{Fe(III)}} + \mu_{\mathrm{e^-}} - \mu^0_{\mathrm{Fe(II)}}$$

which is a constant at a given temperature and pressure. Equation (1.25) is the famous Nernst Equation written in a form appropriate to a single electrode | solution interface. It is helpful to examine equation (1.25) in the light of the electrochemical equilibrium:

$$\mathrm{Fe^{3+}(aq) + e^-(m) \rightleftharpoons Fe^{2+}(aq)}$$

First the ions $\mathrm{Fe^{2+}}$ and $\mathrm{Fe^{3+}}$ feature in the potential determining equilibrium given in equation (1.25). Unsurprisingly therefore they determine the magnitude and sign of the electrode potential established on the platinum wire shown in figure 1.2. Second, to explain this dependence, consider what happens if a further amount of $\mathrm{Fe^{3+}}$ is added to the solution shown in figure 1.2, whilst maintaining the *same* concentration of $\mathrm{Fe^{2+}}$(aq), so disturbing the equilibrium.

This addition may be thought of as a consequence of *Le Chatelier's Principle*[1]. The French chemist Henri Le Chatelier in 1884 deduced that if a chemical system at equilibrium is disturbed, the system would adjust itself to minimize the effect of the disturbance. In more scientific terms, Le Chatelier's Principle can be summarised as "*if a change (of temperature, pressure, concentration,...) is imposed on a system previously at* *chemical equilibrium, then the system will respond in a way so as to oppose or counteract the imposed perturbation*".

Applying the principle to the electrochemical equilibrium of interest this equilibrium will become "pushed" to the right and electrons will be taken from the electrode. Consequently the metal electrode will become more positive relative to the solution and the potential difference $\phi_M - \phi_S$ will similarly be more positive. Conversely addition of $Fe(CN)_6^{4-}$ will shift the equilibrium to the left and the electrode will gain electrons and so becomes relatively more negatively charged in comparison with the solution so making $\phi_M - \phi_S$ more negative (less positive). Both these shifts are qualitatively exact as predicted by equation (1.25).

We now explore other examples of electrochemical processes capable of establishing a potential on an electrode in aqueous solutions. The first is the hydrogen electrode, as shown in figure 1.4, which comprises a platinum black electrode submersed into a solution of hydrochloric acid.

The hydrogen electrode

Such an electrode may be formed by taking a bright platinum 'flag' electrode and electro-depositing a fine deposit of 'platinum black' from a solution containing a soluble platinum compound, typically K_2PtCl_6. Hydrogen gas is bubbled over the surface of the electrode and the following potential determining equilibrium is established:

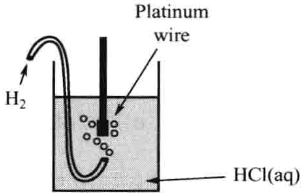

Figure 1.4 A schematic representation of a hydrogen electrode

$$H^+(aq)+e^-(m) \rightleftharpoons \frac{1}{2}H_2(g) \tag{1.26}$$

where (m) reminds us that the source of electrons resides in the metal electrode. At equilibrium we can write

$$\bar{\mu}_{H^+} + \bar{\mu}_{e^-} = \frac{1}{2}\bar{\mu}_{H_2}$$

such that

$$(\mu_{H^+} + F\phi_S) + (\mu_{e^-} - F\phi_M) = \frac{1}{2}\mu_{H_2}$$