

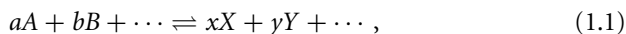
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Equilibrium Electrochemistry and the Nernst Equation

This chapter presents fundamental thermodynamic insights into electrochemical processes.

1.1 Chemical Equilibrium

Thermodynamics predicts the direction (but not the rate) of chemical change. Consider the chemical reaction,



where the reactants A, B, \dots and products X, Y, \dots may be solid, liquid, or gaseous. Thermodynamics tells us that the Gibbs energy of the system, G_{sys} , is minimised when it has attained equilibrium, as shown in Fig. 1.1.

Mathematically, at equilibrium, under conditions of constant temperature and pressure, this minimisation is given by

$$dG_{sys} = 0. \quad (1.2)$$

Consider the Gibbs energy change associated with dn moles of reaction (1.1) proceeding from left to right

$$dG = \{\text{Gain in Gibbs energy of products}\} \\ + \{\text{Loss of Gibbs energy of reactants}\}$$

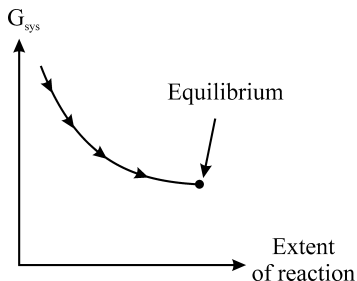


Fig. 1.1

$$\begin{aligned}
 &= \{x\mu_x \text{dn} + y\mu_y \text{dn} \dots\} - \{a\mu_A \text{dn} + b\mu_B \text{dn} + \dots\} \\
 &= \{x\mu_x + y\mu_y \dots - a\mu_A - b\mu_B\} \text{dn},
 \end{aligned} \tag{1.3}$$

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

$$a\mu_A + b\mu_B + \dots = x\mu_x + y\mu_y + \dots, \tag{1.5}$$

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

For an ideal gas,

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

where μ_j^o is the standard chemical potential of j , R is the universal gas constant ($8.313 \text{ J K}^{-1} \text{ mol}^{-1}$), P_j is the pressure of gas j and P^o is a standard pressure conventionally taken to be 10^5 Nm^{-2} approximating to 1 atmosphere (atm), although strictly speaking $1 \text{ atm} = 1.01325 \times 10^5 \text{ Nm}^{-2}$. It follows that μ_j^o is the Gibbs energy of one mole of j when it has a pressure of $1.01325 \times 10^5 \text{ Nm}^{-2}$. It follows

from Eqs. (1.5) and (1.6) that at equilibrium

$$x\mu_X^o + y\mu_Y^o + \dots - a\mu_A^o - b\mu_B^o = -xRT\ln\frac{P_X}{P^o} - yRT\ln\frac{P_Y}{P^o} + \dots + aRT\ln\frac{P_A}{P^o} + bRT\ln\frac{P_B}{P^o}, \quad (1.7)$$

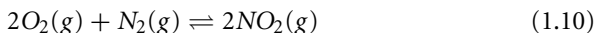
so that

$$\Delta G^o = -RT\ln K_p, \quad (1.8)$$

where $\Delta G^o = x\mu_X^o + y\mu_Y^o + \dots - a\mu_A^o - b\mu_B^o \dots$ is the standard Gibbs energy change accompanying the reaction and

$$K_p = \frac{\left(\frac{P_X}{P^o}\right)^x \left(\frac{P_Y}{P^o}\right)^y \dots}{\left(\frac{P_A}{P^o}\right)^a \left(\frac{P_B}{P^o}\right)^b \dots} \quad (1.9)$$

is a constant at a particular temperature, because the standard chemical potential μ^o depends only on this parameter (unless the gases are not ideal, in which case K_p may become pressure dependant). Thus, for the gas phase reaction



equilibrium is denoted by the equilibrium constant

$$K_p = \frac{\left(\frac{P_{NO_2}}{P^o}\right)^2}{\left(\frac{P_{O_2}}{P^o}\right)^2 \left(\frac{P_{N_2}}{P^o}\right)}. \quad (1.11)$$

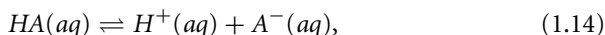
Note that if some of the reactants and/or products in reaction (1.10) are in solution, then the pertinent ideal expression for their chemical potentials are

$$\mu_j = \mu_j^o + RT\ln\frac{[j]}{[]^o}, \quad (1.12)$$

where $[]^o$ is a standard concentration taken to be one molar (one mole per cubic decimetre). Applied to Eq. (1.1) this leads to a general equilibrium constant

$$K_C = \frac{\left(\frac{[X]}{[]^o}\right)^x \left(\frac{[Y]}{[]^o}\right)^y}{\left(\frac{[A]}{[]^o}\right)^a \left(\frac{[B]}{[]^o}\right)^b}. \quad (1.13)$$

It follows that for the equilibrium



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

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

In common usage, Eqs. (1.11) and (1.1) take the more familiar forms of

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

where it is implicitly understood that pressure is measured in units of 10^5 Nm^{-2} (or strictly $1.01325 \times 10^5 \text{ Nm}^{-2}$) and concentrations in M (mol dm^{-3}) units.

In the case that the reactants in Eq. (1.1) are pure solids or pure liquids,

$$\mu_j \simeq \mu_j^0. \quad (1.16)$$

That is to say, the chemical potential approximates (well) to a standard chemical potential. Note that unlike gases or solutions, Gibbs energy *per mole* depends only on the temperature and pressure; changing the amount of material changes the total Gibbs energy, but not the Gibbs energy *per mole*.

It follows from Eq. (1.16) that, 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 participate. So for the general case

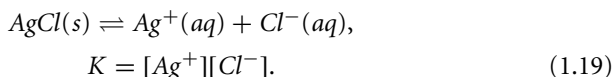


the equilibrium constant will be

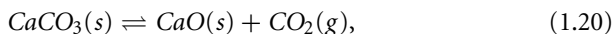
$$K = \frac{P_W^w [X]^x}{P_A^a [B]^b}, \quad (1.18)$$

where it is understood that the pressures are measured in units of 10^5 Nm^{-2} and the concentrations in units of moles dm^{-3} . The pure solids C and Y , and pure liquids D and Z do not appear. Illustrative real examples follow:

First, for

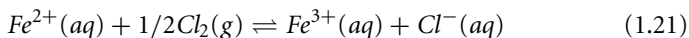


Second, for



$$K = P_{\text{CO}_2}.$$

Last,



leads to

$$K = \frac{[\text{Fe}^{3+}][\text{Cl}^-]}{[\text{Fe}^{2+}]P_{\text{Cl}_2}^{1/2}}.$$

1.2 Electrochemical Equilibrium: Introduction

In the previous section, we considered various forms of chemical equilibrium involving gaseous, liquid, solution phase and solid species. We now turn to electrochemical equilibrium and, as a paradigm case, focus on the following process



Such an equilibrium can be established by first preparing a solution containing both potassium hexacyanoferrate(II), $\text{K}_4\text{Fe}(\text{CN})_6$, and potassium hexacyanoferrate(III), $\text{K}_3\text{Fe}(\text{CN})_6$ dissolved in water and then inserting a wire (an “electrode”) made of platinum or another inert metal into the solution (Fig. 1.2).

The equilibrium in Eq. (1.22) is established at the surface of the electrode and involves the two dissolved anions and the electrons in the metal electrode. The establishment of equilibrium implies that the rate at which $\text{Fe}(\text{CN})_6^{4-}$ gives

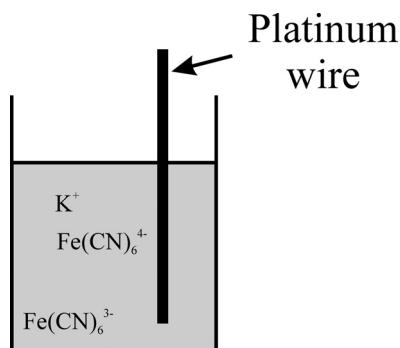


Fig. 1.2 A platinum wire immersed into an aqueous solution containing both ferrocyanide and ferricyanide.

up electrons to the metal wire or 'electrode' is exactly balanced by the rate at which electrons are released by the wire to the $Fe(CN)_6^{3-}$ anions, which are said to be 'reduced'. Correspondingly, the $Fe(CN)_6^{4-}$ ions losing electrons are said to be 'oxidised'. That a dynamic equilibrium of this type is established implies that, once established, no further change occurs. Moreover, the net number of electrons that are transferred in one direction or another is infinitesimally small, such that the concentrations of $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ are not measurably changed from their values before the electrode is introduced into the solution.

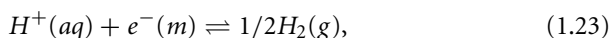
Equation (1.22) has a significant difference from the chemical equilibrium considered in section 1.1. In particular, the reaction involves the transfer of charged particles, electrons, between the metal and solution phases. As a result, when equilibrium is attained, there is likely to be a net electrical charge on each of these two phases. If reaction (1.22) lies to the left when equilibrium is reached, in favour of $Fe(CN)_6^{3-}$ 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 $Fe(CN)_6^{4-}$ 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 there will likely exist a charge separation between the electrode and the solution phases. Accordingly there will be a potential difference (difference in electrical potential) between the metal and the solution. In other words, an *electrode potential* has been established at the metal wire relative to the solution phase. The (electro)chemical reaction given in (1.22) is the basis of this electrode potential and it is helpful to refer to the chemical processes which establish electrode potentials as *potential determining equilibria*.

Other examples of electrochemical processes capable of establishing a potential on an electrode in aqueous solutions include the following:

(a) The hydrogen electrode, shown in Fig. 1.3, comprises a platinum black electrode dipping into a solution of hydrochloric acid.

The 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:



where (*m*) reminds us that the source of electrons resides in the *metal* electrode.

(b) The silver/silver chloride electrode comprises a silver wire coated with a porous layer of silver chloride. The latter is almost insoluble in water and can be formed

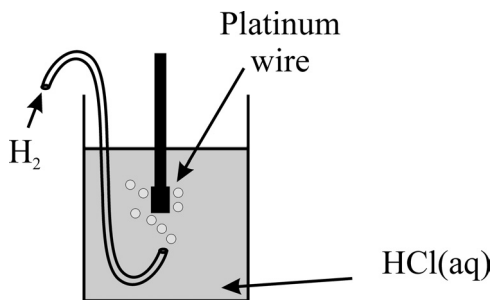
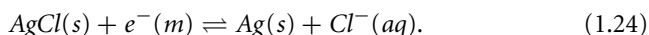


Fig. 1.3 A hydrogen electrode.

on the surface of the wire by electro-oxidation of the wire in a medium containing chloride ions such as an aqueous solution of KCl. The coated wire is then dipped into a fresh KCl solution, as shown in Fig. 1.4.

The following potential determining equilibrium is rapidly established:



The equilibrium is established at the silver/silver chloride boundary. It is crucial that the layer of silver chloride is porous so that the aqueous solution bathing the electrodes penetrates the layer allowing equilibrium to be established at the three-phase boundary comprising the silver metal, the solid silver chloride and the aqueous solution.

(c) The calomel electrode is depicted in Fig. 1.5. It comprises a column of liquid mercury, contacting insoluble di-mercury (I) chloride (known traditionally as 'calomel'). Both contact an aqueous solution containing chloride ions, usually in the form of KCl.

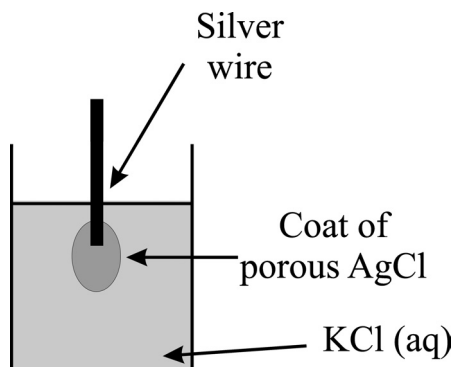


Fig. 1.4 A silver/silver chloride electrode.

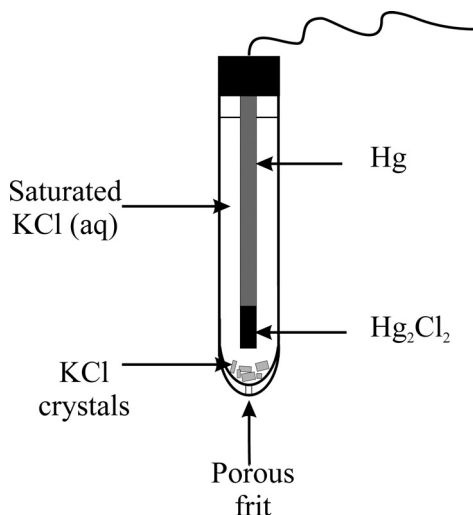


Fig. 1.5 A saturated calomel reference electrode (SCE).

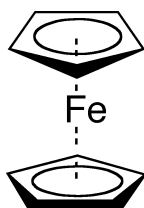
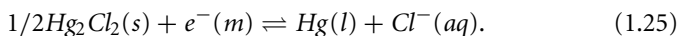


Fig. 1.6 The structure of ferrocene.

The potential determining equilibrium is established at the three-phase boundary:



(d) Finally, we consider an example of a potential determining equilibrium, which is not based on an aqueous solution but rather the aprotic solvent acetonitrile. The equilibrium involves an acetonitrile solution containing the molecule ferrocene, Cp_2Fe and a ferrocenium (Cp_2Fe^+) salt such as ferrocenium hexafluorophosphate, $\text{Cp}_2\text{Fe}^+\text{PF}_6^-$:

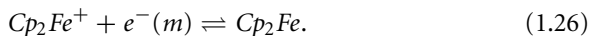
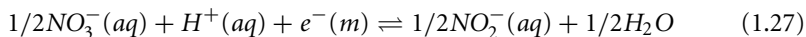


Figure 1.6 illustrates the structure of ferrocene, Cp_2Fe .

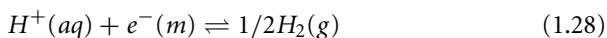
In all of the examples considered above, a dynamic equilibrium is rapidly established between the chemical species involved in the potential determining equilibrium, a charge separation established between the solution and the metal

wire, and an electrode potential is set up on the latter. We now consider one further example which is that of a platinum wire dipping into a solution containing nitrate (NO_3^-) and nitrite (NO_2^-) anions. At first sight, it is tempting to assume that the following potential determining equilibrium will be set up:



However, the *rates* of electron transfer in both the forward (reducing) and back (oxidising) directions are so slow that no equilibrium is set up. Accordingly, there is no charge separation at the solution–metal wire interface and no electrode potential is established.

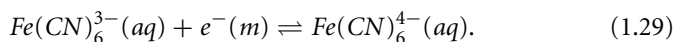
It is clear from the above discussion that fast rates of electron transfer between solution phase species and the electrode is *essential* for an electrode potential to be developed. In the absence of so-called ‘fast electrode kinetics’, no fixed potential is developed at any attempt at measurement of the potential discovers a floating variable value reflecting the failure to establish an electrode potential. The case of the hydrogen electrode discussed above nicely illustrates the importance of fast electrode kinetics. We have already noted that the electrodes are fabricated from platinised platinum rather than bright platinum metal. This difference is key to ensuring fast electrode kinetics. In particular the purpose of depositing a layer of fine platinum black is to provide catalytic sites, which ensures that the potential determining equilibrium



is *rapidly* established. In the absence of this catalysis, on a bright platinum electrode, the electrode kinetics are sluggish and cannot be guaranteed to establish the desired electrode potential. Figure 1.7 illustrates the effect of the platinum black in reducing the activation energy of the reaction and hence speeding up reaction (1.28). The catalyst binds the intermediate H^\bullet atoms leading to the transition state for the reaction being lowered in energy.

1.3 Electrochemical Equilibrium: Electron Transfer at the Solution–Electrode Interface

The ideas behind the development of electrode potentials at the solution–electrode interface can be usefully re-examined considering the energy levels associated with the species involved in the potential determining equilibrium. We return to our paradigm case,



The pertinent energy levels are shown in Fig. 1.8.

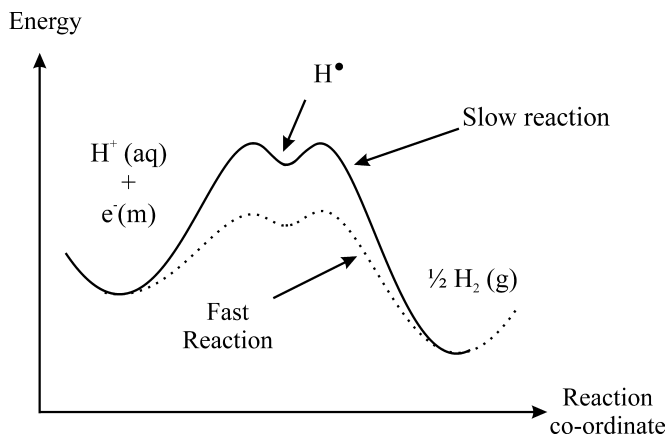
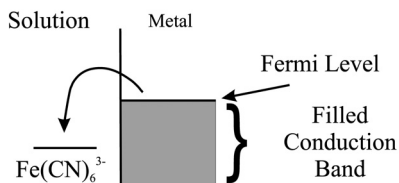


Fig. 1.7 The effect of platinum black on the H^+/H_2 equilibrium.

The electronic structure of a metal involves electronic conduction 'bands' in which the 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 which are filled up to an energy maximum known as the Fermi level. In contrast, the electronic energy levels associated with the solution phase $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ (aq) ions are discrete and relate to an unfilled molecular orbital in $Fe(CN)_6^{3-}$, which gains an electron to form $Fe(CN)_6^{4-}$. Note that, although not shown in Figure 1.8, adding an electron to $Fe(CN)_6^{3-}$ 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. Figure 1.8 shows that before electron transfer takes place between the electrode and the solution, the Fermi level is higher than the vacant orbital in the $Fe(CN)_6^{3-}$ ion. It is accordingly energetically favourable for electrons to leave the Fermi level and join the $Fe(CN)_6^{3-}$ species converting them to $Fe(CN)_6^{4-}$ ions. This energy difference is the driving force of the electron transfer discussed in the previous section. 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 Fig. 1.8 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 Fig. 1.8. Correspondingly, the generation of negative charge in the solution must raise the (electronic) energy levels of the solution phase species. 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

Before Electron Transfer



After Electron Transfer

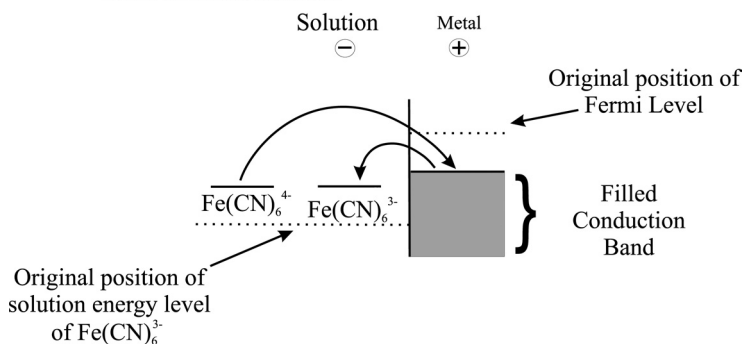


Fig. 1.8 The energy of electrons in the ions in solution and in the metal wire.

reduce $Fe(CN)_6^{3-}$ ions is exactly matched by the rate at which electrons join the metal from the $Fe(CN)_6^{4-}$ ions which become oxidised. As we have noted before, this situation corresponds to dynamic equilibrium and once it is attained, no further net charge is possible. However, at the point of equilibrium, there is a charge separation between the electrode and the solution, and this is the origin of the electrode potential established on the metal.

1.4 Electrochemical Equilibrium: The Nernst Equation

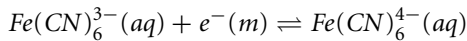
We saw in section 1.1 that the position of chemical equilibrium was controlled by the chemical potentials of the reactants and products. In the case of an electrochemical equilibrium such as reaction 1.29, the position of equilibrium represents a balance between chemical energies (quantified via the 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.

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

$$\bar{\mu}_j = \mu_j + Z_j F \phi, \quad (1.30)$$

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*.

Eq. (1.30) 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,



we note that this implies that at equilibrium

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

where $Fe(III)$ denotes $Fe(CN)_6^{3-}$ and $Fe(II)$ indicates $Fe(CN)_6^{4-}$. Applying Eq. (1.30) we obtain

$$(\mu_{Fe(III)} + 3F\phi_S) + (\mu_{e^-} - F\phi_M) = (\mu_{Fe(II)} + 2F\phi_S)$$

where ϕ_M and ϕ_S refer to the electrical potential of the metal electrode and of the solution respectively. Rearranging

$$F(\phi_M - \phi_S) = \mu_{Fe(III)} + \mu_{e^-} - \mu_{Fe(II)}.$$

But

$$\begin{aligned} \mu_{Fe(III)} &= \mu_{Fe(III)}^0 + RT \ln \left(\frac{[Fe(CN)_6^{3-}]}{[]^0} \right) \\ \mu_{Fe(II)} &= \mu_{Fe(II)}^0 + RT \ln \left(\frac{[Fe(CN)_6^{4-}]}{[]^0} \right) \end{aligned}$$

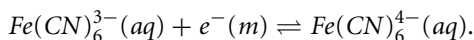
and hence

$$\phi_M - \phi_S = \frac{\Delta\mu^0}{F} + \frac{RT}{F} \ln \left(\frac{[Fe(CN)_6^{3-}]}{[Fe(CN)_6^{4-}]} \right) \quad (1.31)$$

where

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

which is a constant at a given temperature and pressure. Eq. (1.31) is the famous Nernst Equation written in a form appropriate to a single electrode–solution interface. It is helpful to examine Eq. (1.31) in the light of the electrochemical equilibrium (1.29). First the ions $\text{Fe}(\text{CN})_6^{4-}$ and $\text{Fe}(\text{CN})_6^{3-}$ feature in the potential determining equilibrium given in Eqs. (1.30) and (1.31). Unsurprisingly therefore they determine the magnitude and sign of the electrode potential established on the platinum wire shown in Fig. 1.2. Second, to explain this dependence, consider what happens if a further amount of $\text{Fe}(\text{CN})_6^{3-}$ is added to the solution shown in Fig. 1.2, whilst maintaining the *same* concentration of $\text{Fe}(\text{CN})_6^{4-}(\text{aq})$, so perturbing the equilibrium



The consequence of the addition may be thought of as a consequence of Le Chatelier's Principle. Henri Louis Le Chatelier (1850–1936), shown left, was an industrial chemist and is famous for his work on the principle of equilibrium. Le Chatelier was educated at the École Polytechnique followed by the École des Mines, and elected to the Académie des science.*



Bibliothèque de l'École
des mines de Paris

Le Chatelier originally stated the principle of equilibrium as:

*“Any system in stable chemical equilibrium, subjected to the influence of an external cause which tends to change either its temperature or its condensation (pressure, concentration, number of molecules in unit volume), either as a whole or in some of its parts, can only undergo such internal modifications as would, if produced alone, bring about a change of temperature or of condensation of opposite sign to that resulting from the external cause”*¹

Le Chatelier later changed this rather awkward statement to:

*“Every change of one of the factors of an equilibrium occasions a rearrangement of the system in such a direction that the factor in question experiences a change in a sense opposite to the original change.”*² Le Chatelier's Principle can

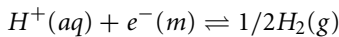
* A full biography can be found at www.anales.org/archives/x/lc.html

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 become relatively more negatively charged in comparison with the solution, thus making $\phi_M - \phi_S$ more negative (less positive). Both these shifts are qualitatively exactly as predicted by Eq. (1.31).

As a further illustration of the application of the electrochemical potential concept to the description of electrochemical equilibria, we consider the examples examined in the previous section.

(a) For the hydrogen electrode based on the equilibrium



at equilibrium

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

so that

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

Then, expanding the chemical potential terms using

$$\mu_{H^+} = \mu_{H^+}^0 + RT \ln \left(\frac{[H^+]}{[]^0} \right)$$

and

$$\mu_{H_2} = \mu_{H_2}^0 + RT \ln \left(\frac{P_{H_2}}{P^0} \right)$$

we obtain the Nernst equation:

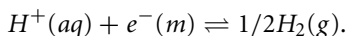
$$\phi_M - \phi_S = \frac{\Delta\mu^0}{F} + \frac{RT}{F} \ln \left(\frac{[H^+]}{P_{H_2}^{1/2}} \right), \quad (1.32)$$

where we have assumed that $[H^+]$ will be measured in units of M and P_{H_2} in units of 10^5 Nm^{-2} .

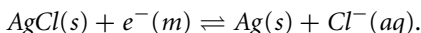
Note that the constant

$$\Delta\mu^0 = \mu_{H^+}^0 + \mu_{e^-} - 1/2\mu_{H_2}^0.$$

Further note that Eq. (1.32) predicts that $\phi_M - \phi_S$ will become more positive as the H^+ concentration increases and/or the H_2 pressure decrease: both of these and/or predictions are consistent with the application of Le Chatelier's Principle to the potential determining equilibrium



(b) The silver/silver chloride electrode is based on the equilibrium



Equating the electrochemical potential of the reactants and products,

$$\bar{\mu}_{AgCl} + \bar{\mu}_{e^-} = \bar{\mu}_{Ag} + \bar{\mu}_{Cl^-}$$

so that

$$(\mu_{AgCl}) + (\mu_{e^-} - F\phi_M) = (\mu_{Ag}) + (\mu_{Cl^-} - F\phi_S),$$

noting that

$$\mu_{Cl^-} = \mu_{Cl^-}^o + RT \ln \left(\frac{[Cl^-]}{[]^o} \right)$$

but for the pure solids AgCl and Ag,

$$\mu_{AgCl} = \mu_{AgCl}^o$$

and

$$\mu_{Ag} = \mu_{Ag}^o,$$

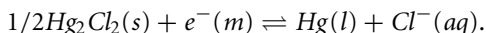
we obtain the Nernst equation:

$$\begin{aligned} \phi_M - \phi_S &= \frac{\Delta\mu^o}{F} + \frac{RT}{F} \ln \left(\frac{1}{[Cl^-]} \right) \\ &= \frac{\Delta\mu^o}{F} - \frac{RT}{F} \ln[Cl^-], \end{aligned}$$

where we are presuming that $[Cl^-]$ is measured in unit of moles dm^{-3} . The constant

$$\Delta\mu^o = \mu_{Ag}^o + \mu_{Cl^-}^o - \mu_{e^-} - \mu_{AgCl}^o.$$

(c) The calomel electrode is based on the equilibrium



The application of the electrochemical potential concept together with the chemical potentials of the pure solids and liquids,

$$\mu_{\text{Hg}_2\text{Cl}_2} = \mu_{\text{Hg}_2\text{Cl}_2}^{\circ}$$

and

$$\mu_{\text{Hg}} = \mu_{\text{Hg}}^{\circ}$$

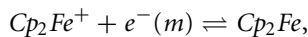
leads to

$$\phi_M - \phi_S = \frac{\Delta\mu^{\circ}}{F} - \frac{RT}{F} \ln [\text{Cl}^-],$$

as the Nernst equation for this electrode, where

$$\Delta\mu^{\circ} = \mu_{\text{Hg}}^{\circ} + \mu_{\text{Cl}^-}^{\circ} - \mu_{e^-} - 1/2\mu_{\text{Hg}_2\text{Cl}_2}^{\circ}.$$

(d) For the ferrocene/ferrocenium couple in acetonitrile



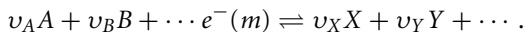
analogy with the $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$ equilibrium discussed fully above shows

$$\phi_M - \phi_S = \frac{\Delta\mu^{\circ}}{F} + \frac{RT}{F} \ln \left(\frac{[\text{Cp}_2\text{Fe}^+]}{[\text{Cp}_2\text{Fe}]} \right),$$

where $[\text{Cp}_2\text{Fe}^+]$ is measured in M and

$$\Delta\mu^{\circ} = \mu_{\text{Cp}_2\text{Fe}}^{\circ} - \mu_{e^-}^{\circ} - \mu_{\text{Cp}_2\text{Fe}^+}^{\circ}.$$

Having established the Nernst equation for several specific examples, we consider the general case and focus on the following electrochemical equilibrium



The terms ν_j ($j = A, B, \dots, X, Y, \dots$) are the so-called stoichiometric coefficients. Since the reaction is assumed to be equilibrium

$$\nu_A \bar{\mu}_A + \nu_B \bar{\mu}_B + \cdots \bar{\mu}_{e^-} = \nu_X \bar{\mu}_X + \nu_Y \bar{\mu}_Y + \cdots$$

or,

$$\begin{aligned} \nu_A(\mu_A + Z_A F \phi_S) + \nu_B(\mu_B + Z_B F \phi_S) + \cdots (\mu_{e^-} - F \phi_M) \\ = \nu_X(\mu_X + Z_X F \phi_S) + \nu_Y(\mu_Y + Z_Y F \phi_S) + \cdots, \end{aligned}$$

where Z_j is the charge on the species j . Conservation of electrical charge requires that

$$\nu_A Z_A + \nu_B Z_B + \dots - 1 = \nu_X Z_X + \nu_Y Z_Y + \dots .$$

Hence,

$$F(\phi_M - \phi_S) = \nu_A \mu_A + \nu_B \mu_B + \dots + \mu_{e^-} - \nu_X \mu_X - \nu_Y \mu_Y - \dots .$$

We now write

$$\mu_j = \mu_j^o + RT \ln a_j,$$

where, if j is the solution phase

$$a_j = \frac{[j]}{[]^o},$$

but

$$a_j = \frac{P_j}{p^o}$$

if j is gaseous, whilst if j is a pure solid or liquid

$$a_j = 1,$$

and we obtain

$$\phi_M - \phi_S = \frac{\Delta\mu^o}{F} + \frac{RT}{F} \ln \left(\frac{a_A^{\nu_A} a_B^{\nu_B} \dots}{a_X^{\nu_X} a_Y^{\nu_Y} \dots} \right), \quad (1.33)$$

which is a general statement of the Nernst equation with

$$\Delta\mu^o = \nu_A \mu_A^o + \nu_B \mu_B^o + \dots + \mu_{e^-} - \nu_X \mu_X^o - \nu_Y \mu_Y^o - \dots .$$

1.5 Walther Hermann Nernst

Walther Hermann Nernst was born in Briesen, West Prussia (now Wabrzezno, Poland) on the 25th June 1864. Nernst studied physics and mathematics at the universities of Zurich, Berlin and Graz (Ludwig Boltzmann and Albert von Ettingshausen). Whilst at Graz, he worked with von Ettingshausen and published work in 1886 which formed part of the experimental foundation of the modern electronic theory of metals (the Nernst–Ettingshausen effect).



NERNST, Walther Hermann
Nobel Laureate CHEMISTRY 1920
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He undertook his PhD at Wurzburg with Friedrich Kohlrausch and graduated in 1887 with a thesis on electromotive forces produced by magnetism in heated metal plates. Nernst then joined Ostwald at Leipzig University, where Van't Hoff and Arrhenius were already established. In 1888, Nernst developed work on the theory of electromotive force of voltaic cells. He devised methods for measuring dielectric constants and first showed that solvent of high dielectric constant promote the ionisation of substance. Nernst also proposed the theory of solubility products, generalised the distribution law and offered a theory of heterogeneous reactions. In 1889, he elucidated the theory of galvanic cells via assuming an 'electrolytic pressure of dissolution', which

forces ions from electrode into solution and which was opposed to the osmotic pressure of the dissolved ions.

In 1894, Nernst received invitations to the Physics Chairs in Munich and in Berlin, as well as to the Physical Chemistry Chair in Göttingen. He accepted this latter invitation, and founded the *Physikalisch-Technisches Reichsanstalt* in Göttingen (now the Institute for Physical Chemistry and Electrochemistry) and became its Director in 1922, a position he retained until his retirement in 1933. His transition to chemistry actually began in Leipzig, but developed fully in his subsequent position as an associate professor of physics at Göttingen.

By 1900, Nernst realised that interfacial potential differences between different phases were not individually measurable and concluded that electrochemical potential could only be measured relative to another and proposed the hydrogen electrode as the standard. This allowed Nernst to formulate his equation for the potential of a general cell.

In 1906, Nernst developed his heat theorem, known as the Third Law of Thermodynamics; in addition to its theoretical implications, the theorem was soon applied to industrial problems, including calculations in ammonia synthesis. In 1918, his studies of photochemistry led him to his atom chain reaction theory. Nernst was awarded the Nobel prize for his heat theorem work of 1906.

Nernst, as well as his substantial contributions to the physical sciences developed an improved electric light, the Nernst Lamp, which was commercialised by George Westinghouse. The ‘Nernst Lamp Company’ was founded in 1901 in Pittsburg, USA and by 1904, 130,000 Nernst glowers had been sold. However, the Nernst lamp, which contained oxides such as Y_2O_3 , lost competition when the more convenient incandescent light bulbs containing metal (tungsten) filaments became available. Nernst also conceived an electric piano, the “Neo-Bechstein-Flügel” in 1930 in association with the Bechstein and Siemens companies, replacing the sounding board with radio amplifiers. The piano used electromagnetic pickups to produce electronically modified and amplified sound.



After winning the highest scientific accolade possible, Nernst also received the Benjamin Franklin Medal in Chemistry (1928) and was elected a Fellow of the Royal Society (London) in 1932. Nernst retired in 1933 to breed carp and to hunt. Nernst died in 1941 and a tomb was erected at Göttingen Stradtfriedhof. Post-mortem events include a crater on the far side of the moon (coordinates $35.3^\circ N/94.8^\circ W$, diameter 116 km) and several roads named after Nernst.³

1.6 Reference Electrodes and the Measurement of Electrode Potentials

Equation (1.33) is the Nernst equation for an arbitrary electrochemical equilibrium involving an electrode and the reaction components, $A, B, \dots X, Y, \dots$. It relates the quantity $\phi_M - \phi_S$ to the concentrations and/or pressures of these species. However, a little thought shows that although this quantity can be discussed conceptually, *it is impossible to measure an absolute value for the quantity $\phi_M - \phi_S$ relating to a single electrode–solution interface.*

Measurements of potential are usually carried out using a digital voltammeter (‘DVM’), a device which measures the potential between the two test leads as shown in Fig. 1.9.

It does so by passing a tiny current (\sim pico-amperes, $10^{-12}A$) through the external circuit under test. Measurement of the potential drop $\phi_M - \phi_S$ at a single electrode–solution interface such as that developed at a platinum wire dipping into a solution of $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ ions is clearly impossible, since there will necessarily be two metal solution interfaces created if the measurement is attempted

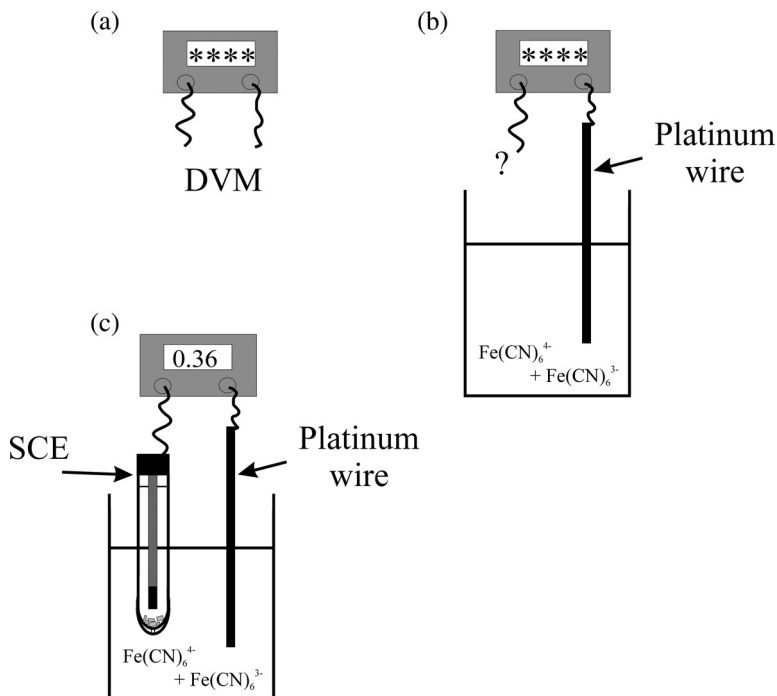


Fig. 1.9 Measurement of electrode potentials.

(Fig. 1.9). However, if a second electrode, for example a calomel electrode, is introduced into the solution (Fig. 1.9c) the measurement becomes feasible and the DVM records the difference of two quantities of the form $\phi_M - \phi_S$ pertaining to the two electrodes:

$$\text{Measured potential difference} = (\phi_M - \phi_S)_{Pt \text{ wire}} - (\phi_M - \phi_S)_{calomel}.$$

On the basis of the discussion in the previous two sections we can recognise that, for a fixed temperature and pressure,

$$(\phi_M - \phi_S)_{Pt \text{ wire}} = A + \frac{RT}{F} \ln \left(\frac{[Fe(CN)_6^{3-}]}{[Fe(CN)_6^{4-}]} \right),$$

where A is a constant.

Also,

$$(\phi_M - \phi_S)_{calomel} = B - \frac{RT}{F} \ln ([Cl^-]),$$

where B is another constant. The measured potential difference is then

$$(\phi_M - \phi_s)_{Pt\text{wire}} - (\phi_M - \phi_s)_{calomel} = C + \frac{RT}{F} \ln \left(\frac{[Fe(CN)_6^{3-}][Cl^-]}{[Fe(CN)_6^{4-}]} \right),$$

where C is a further constant, equal to $(A - B)$.

The observed potential difference thus depends on the concentrations $[Cl^-]$, $[Fe(CN)_6^{4-}]$ and $[Fe(CN)_6^{3-}]$. The introduction of the second electrode, the calomel electrode, has facilitated the successful measurement in contrast to the hopeless situation of Fig. 1.9b.

In the above measurement, the calomel electrode can be thought of as acting as a reference electrode. If the concentration of chloride ions inside the calomel electrode (see Fig. 1.9) is maintained constant, then $(\phi_M - \phi_s)_{calomel}$ is also constant, so that

$$(\phi_M - \phi_s)_{Pt\text{wire}} = D + \frac{RT}{F} \ln \left(\frac{[Fe(CN)_6^{3-}]}{[Fe(CN)_6^{4-}]} \right),$$

where D is yet a further constant, equal to $C + (\phi_M - \phi_s)_{calomel} + \frac{RT}{F} \ln [Cl^-]$.

Accordingly, the reference electrode allows us to establish changes in the electrode potential of the platinum wire, for examples induced by changes in the concentration of $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$. Since we can write

$$(\phi_M - \phi_s)_{Pt\text{ wire}} = D + \frac{2.3RT}{F} \text{Log}_{10} \left(\frac{[Fe(CN)_6^{3-}]}{[Fe(CN)_6^{4-}]} \right) \quad (1.34)$$

and the ratio $2.3RT/F$ has the value of *ca.* 59 mV at room temperature, it follows that if the concentration of $Fe(CN)_6^{3-}$ is changed by a factor of ten whilst the concentration of $Fe(CN)_6^{4-}$ is kept constant, then the measured potential on the DVM will change by 59 mV. Note however that because of the constant term, D , in Eq. (1.34) we can only measure *changes* in the electrode potential, not absolute values.

It is instructive to consider what is happening when the DVM in Fig. 1.10 makes the measurement of the difference in potential between the platinum wire and the calomel electrode.

As already discussed, this requires a tiny current to be passed through the meter and hence, through the external circuit involving our two electrodes, the calomel and the platinum wire. The tiny current corresponds to an almost infinitesimal flow of electrons around the external circuit. Suppose that this is in the direction shown in Fig. 1.10. Then, the way the charge is passed through the two electrode–solution interfaces is by the occurrence of an almost infinitesimal amount of the following two reactions:

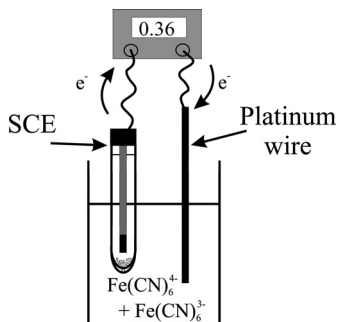
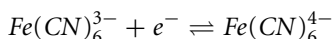
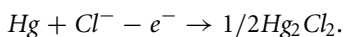


Fig. 1.10 A tiny flow of electrons (current) is required to measure the potential difference between the two electrodes.

At the Pt wire



and at the calomel electrode



In practice, the magnitude of the current passed is so small that the concentrations of the species in the cell are effectively unperturbed from the values pertaining before the measurement was conducted, but enough current flows to secure the measurement. Given that the reactions above allow charge to pass through the two solution interfaces the passage of the measuring current through the bulk solution is carried by the 'conduction' of the ionic species (K^+ , Cl^- , $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$) in the solution phases, both inside the calomel electrode and inside the solution bathing the platinum wire.

The term 'conduction' implies that there is an electric field (potential drop) within the solution phased to 'drive' ion motion. However, since the current, I , being passed is so tiny, this is almost negligible. Algebraically,

$$\begin{aligned} \text{Measured potential difference} &= \lim_{I \rightarrow 0} [(\phi_M - \phi_S)_{Pt \text{ wire}} \\ &\quad + IR - (\phi_M - \phi_S)_{calomel}] \\ &= (\phi_M - \phi_S)_{Pt \text{ wire}} - (\phi_M - \phi_S)_{calomel}, \end{aligned}$$

where R corresponds to the resistance of the electrolyte solution.

Finally, it is instructive to consider the liquid-liquid interface formed at the frit of the calomel electrode, where it enters the solution bathing the platinum wire electrode. On one side of this interface is a high concentration of aqueous KCl (see

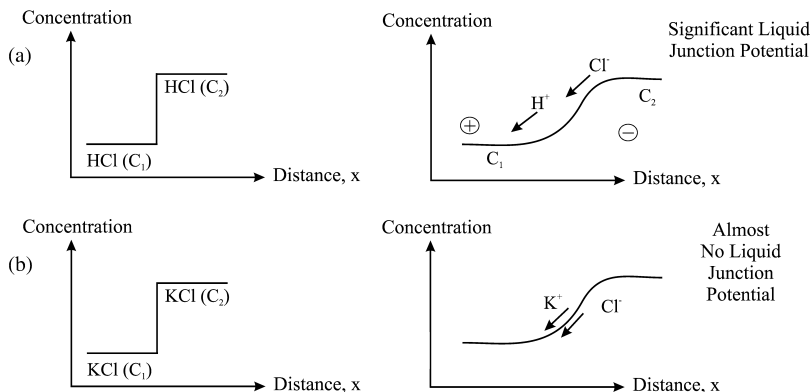


Fig. 1.12 Interfacial diffusion between two phases can lead to liquid junction potentials.

which both ions move at a steady state through the liquid–liquid interface across which the steady state charge separation leads to a potential difference, known as a *liquid junction potential*. Typically, these potentials are no more than some tens of millivolts.

Next, consider Fig. 1.12(b), in which two solutions of KCl of different concentrations are put in contact. Again, there will be diffusion of K^+ and Cl^- ions from the higher to the lower concentration. However, as we noted above, these two ions move with almost exactly the same speed and so now the diffusion leads to no charge separation and hence, no liquid junction potential is established.

It follows from the above that if a charge is carried through a liquid–liquid interface by ions of closely similar mobility, then no liquid junction potentials will be established. In contrast, if the ions have different mobilities, a significant liquid junction potential may be established. Table 1.1 reports the single ion conductivities for various cations and anions at 25°C. These can be thought to represent the relative speeds of movement of the species under the same potential gradient (electric field).

It is evident that liquid–liquid interfaces between solutions of different concentrations of HCl, Li_2SO_4 or NaOH will experience significant liquid junction potentials, whereas electrolytes such as NH_4NO_3 or KCl will be relatively liquid junction potential free.

We next return to the measurement of the potential difference between the platinum wire and the calomel electrode shown in Fig. 1 and focus on the transport of current through the liquid–liquid interface formed at the frit of the calomel electrode (see Fig. 1.13).

Table 1.1. Single ion conductivities in water (25°C) / $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$.

Ion	Λ_+	Ion	Λ_-
H^+	350	$Fe(CN)_6^{4-}$	442
Ba^{2+}	127	OH^-	199
Ca^{2+}	119	SO_4^{2-}	158
Mg^{2+}	106	Br^-	78
NH_4^+	74	I^-	77
K^+	74	Cl^-	76
Ag^+	62	NO_3^-	71
Na^+	50	F^-	55
Li^+	39	CH_3COO^-	41

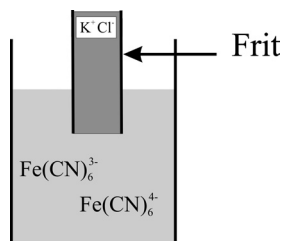


Fig. 1.13 The liquid–liquid interface formed at the frit of the calomel electrode shown in Fig. 1.10.

This interface is depicted in Fig. 1.13. The solution above the frit inside the calomel electrode is of very high concentrations ($> 1\text{ M}$), since it is saturated with KCl. The concentrations outside of the frit are typically much smaller. Accordingly, the dominant diffusive fluxes across the liquid–liquid interfaces are from K^+ and Cl^- ions, rather than from $Fe(CN)_6^{4-}$ or $Fe(CN)_6^{3-}$ ions. For this reason, no significant liquid junction potentials will be established unless unusually large ($\sim\text{M}$) concentrations of $Fe(CN)_6^{4-}$ or $Fe(CN)_6^{3-}$ ions are being studied.

To summarise, the measurement of the potential difference between the platinum wire electrode shown in Fig. 1.10 and the calomel electrode acting as a reference electrode gives the following result:

$$\text{Measured potential difference} = A' + \frac{RT}{F} \ln \left(\frac{[Fe(CN)_6^{3-}]}{[Fe(CN)_6^{4-}]} \right),$$

where A' is a constant.

Key features of the experiment are as follows:

- The passage of tiny currents through the DVM and hence the external circuit means that the 'IR' term in the bulk solution is negligible.
- The presence of a saturated solution of KCl inside the calomel electrode caused by the presence of solid KCl inside the electrode, coupled with the passage of tiny currents only, leads to the pinning of the quantity $(\phi_M - \phi_s)_{\text{calomel}}$ at a constant value since the chloride ion concentration is constant. Under these conditions, the calomel electrode acts as a suitable 'reference' electrode.
- The use of KCl inside the calomel electrode ensures that negligibly small liquid junction potentials are established at the liquid–liquid interface at the tip of the frit unless extremely high concentrations of $\text{Fe}(\text{CN})_6^{4-}$ and/or $\text{Fe}(\text{CN})_6^{3-}$ are used.

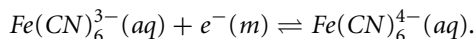
1.7 The Hydrogen Electrode as a Reference Electrode

The discussion in the previous section identified the key features required of a 'reference' electrode and showed the merits of the calomel electrode for this purpose. Indeed, the calomel electrode is a widely employed reference electrode. However, the primary reference electrode against which data is conveniently reported is the standard hydrogen electrode. This is shown in Fig. 1.3 and for the electrode to be 'standard' the pressure of hydrogen gas, P_{H_2} , must be close to 10^5 Nm^{-2} and the concentration of protons, $[\text{H}^+]$ to be close to 1 mol dm^{-3} . In practice, because the solution is not ideal, Eq. 1.32 does not hold exactly, so that a concentration of 1.18 M is required at 25°C for the protons to behave as if they were an ideal solution of 1 M. The origins of this deviation lie in Debye–Huckel theory and its extension to concentrated solutions.^{4,5} However, for our present purpose, it is sufficient to note that provided $P_{\text{H}_2} = 1.01325 \times 10^5 \text{ Nm}^{-2}$ and $[\text{H}^+] = 1.18\text{M}$ at 25°C , then the hydrogen electrode is 'standard', and it is this particular reference electrode against which the International Union of Pure and Applied Chemistry (IUPAC) formally require that potentials are reported.⁶

If a measurement such of the type shown in Fig. 1.10 is carried out, in which the potential of a calomel electrode containing saturated KCl is measured with respect to the standard hydrogen electrode (SHE), it is found to be 0.242 V positive of the SHE. Accordingly, measurements made relative to the saturated calomel electrode are readily correlated to the SHE by adding this value to the number measured. For example, returning to Fig. 1.10, it is found experimentally that the measured potential difference on the DVM for case when $[\text{Fe}(\text{CN})_6^{4-}] = [\text{Fe}(\text{CN})_6^{3-}]$ is 0.118 V (at 25°C). On the SHE scale, this becomes $0.118 \text{ V} + 0.242 \text{ V} = 0.36 \text{ V}$.

1.8 Standard Electrode Potentials and Formal Potentials

The potential of 0.36 V obtained at the end of the previous section is the standard electrode potential of the following potential determining equilibrium:



In order to understand this quantity more generally, it is necessary to briefly address the issue of solvent non-ideality. In establishing the Nernst equation of the form of Eqs. (1.31), (1.32) and (1.33) for single electrode–solution interfaces, we relied on the following relationship between chemical potential and concentration, which is correct for an ideal solution:

$$\mu_j = \mu_j^o + RT \ln \left(\frac{[j]}{[]^o} \right). \quad (1.35)$$

However, concentrated solutions of electrolytes in particular, are not ideal. Accordingly, it is necessary to introduce the ‘activity coefficient’. In order to modify Eq. (1.34) to allow for non-ideality, we write

$$\mu_j = \mu_j^o + RT \ln \left(\frac{\gamma_j [j]}{[]^o} \right),$$

where γ_j is the activity coefficient of species j . For electrolyte solutions

$$\gamma_j \rightarrow 1,$$

as the solute becomes highly dilute, *viz*

$$[\gamma_j] \rightarrow 0.$$

Accordingly, under these conditions the solution becomes ideal. For more concentrated solutions, γ_j deviates from unity and the extent of the deviation measures the degrees of non-ideality reflecting ion–ion and ion–solvent interactions in the electrolyte. We saw in section 1.6 that, for the hydrogen electrode to be standard, it was necessary that

$$[\text{H}^+] = 1.18 \text{ M},$$

implying under these conditions that

$$\gamma_{\text{H}^+} = \frac{1}{1.18} = 0.85.$$

The standard electrode potential of the $[\text{Fe}(\text{CN})_6^{4-}]/[\text{Fe}(\text{CN})_6^{3-}]$ couple involves an arrangement similar to that of Fig. 1.10, except that the reference electrode must

be the *standard* hydrogen electrode and the concentrations of the two anions must be chosen carefully, so that

$$\mu_{Fe(III)} = \mu_{Fe(III)}^o$$

and

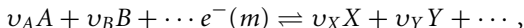
$$\mu_{Fe(II)} = \mu_{Fe(II)}^o.$$

That is the terms,

$$\frac{\gamma_{Fe(II)}[Fe(II)]}{[\]^0} = \frac{\gamma_{Fe(III)}[Fe(III)]}{[\]^0} = 1.$$

Under these conditions, the 'activity' of the ions is said to be unity and the 'In' term in the expression for the chemical potentials disappears (Eq. 1.33). Extensive tables of standard electrode potentials exist; Table 2.1 provides a fragment of the data that is available.

Each of the entries in the table relate to the standard electrode potential of the redox couple shown, measured relative to a standard hydrogen electrode under conditions where all the species involved in the potential determining equilibrium are at unit activity. These potentials are given the symbol E^0 . For the general electrochemical equilibrium



it follows that for arbitrary concentrations of A, B, \dots, X, Y, \dots , we have

$$E = E^0(A, B, \dots / X, Y, \dots) + \frac{RT}{F} \ln \left(\frac{\gamma_A^{\nu_A} \gamma_B^{\nu_B} \dots [A]^{\nu_A} [B]^{\nu_B}}{\gamma_X^{\nu_X} \gamma_Y^{\nu_Y} \dots [X]^{\nu_X} [Y]^{\nu_Y}} \right),$$

where E is again measured against the standard hydrogen electrode and $E^0(A, B, \dots / X, Y, \dots)$ is the standard electrode potential of the $A, B, \dots / X, Y, \dots$ couple. It is evident that $E = E^0(A, B, \dots / X, Y, \dots)$ when the 'In' term vanishes corresponding to each ion having unit activity. Needless to say, however, that it is far from trivial to arrange this situation experimentally since a knowledge of the relevant activity coefficients, γ_j , and their concentration dependence is typically lacking. Accordingly, the concept of the formal potential, E_f^0 is introduced where

$$E_f^0(A, B, \dots / X, Y, \dots) = E^0(A, B, \dots / X, Y, \dots) + \frac{RT}{F} \ln \left(\frac{\gamma_A^{\nu_A} \gamma_B^{\nu_B} \dots}{\gamma_X^{\nu_X} \gamma_Y^{\nu_Y} \dots} \right),$$

so that

$$E = E_f^0(A, B, \dots / X, Y, \dots) + \frac{RT}{F} \ln \left(\frac{[A]^{\nu_A} [B]^{\nu_B} \dots}{[X]^{\nu_X} [Y]^{\nu_Y} \dots} \right).$$

Table 1.2. Standard Electrode Potentials for Aqueous Solutions (25°C).

Half Reaction	E / V
$\text{Li}^+ + \text{e}^- \rightarrow \text{Li}$	-3.04
$\text{K}^+ + \text{e}^- \rightarrow \text{K}$	-2.92
$1/2\text{Ca}^{2+} + \text{e}^- \rightarrow 1/2\text{Ca}$	-2.76
$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$	-2.71
$1/2\text{Mg}^{2+} + \text{e}^- \rightarrow 1/2\text{Mg}$	-2.37
$1/3\text{Al}^{3+} + \text{e}^- \rightarrow 1/3\text{Al}$ (0.1 M NaOH)	-1.71
$1/2\text{Mn}^{2+} + \text{e}^- \rightarrow 1/2\text{Mn}$	-1.18
$\text{H}_2\text{O} + \text{e}^- \rightarrow 1/2\text{H}_2 + \text{OH}^-$	-0.83
$1/2\text{Zn}^{2+} + \text{e}^- \rightarrow 1/2\text{Zn}$	-0.76
$1/2\text{Fe}^{2+} + \text{e}^- \rightarrow 1/2\text{Fe}$	-0.44
$1/3\text{Cr}^{3+} + \text{e}^- \rightarrow 1/3\text{Cr}$	-0.41
$1/2\text{Cd}^{2+} + \text{e}^- \rightleftharpoons \text{Cd}$	-0.40
$1/2\text{Co}^{2+} + \text{e}^- \rightarrow 1/2\text{Co}$	-0.28
$1/2\text{Ni}^{2+} + \text{e}^- \rightarrow 1/2\text{Ni}$	-0.23
$1/2\text{Sn}^{2+} + \text{e}^- \rightarrow 1/2\text{Sn}$	-0.14
$1/2\text{Pb}^{2+} + \text{e}^- \rightarrow 1/2\text{Pb}$	-0.13
$1/3\text{Fe}^{3+} + \text{e}^- \rightarrow 1/3\text{Fe}$	-0.04
$\text{H}^+ + \text{e}^- \rightarrow 1/2\text{H}_2$	0.00
$1/2\text{Sn}^{4+} + \text{e}^- \rightarrow 1/2\text{Sn}^{2+}$	+0.15
$\text{Cu}^{2+} + \text{e}^- \rightarrow \text{Cu}^+$	+0.16
$1/2\text{Cu}^{2+} + \text{e}^- \rightarrow 1/2\text{Cu}$	+0.34
$2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^- \rightarrow 4\text{OH}^-$	+0.40
$\text{Cu}^+ + \text{e}^- \rightarrow \text{Cu}$	+0.52
$1/2\text{I}_2 + \text{e}^- \rightarrow \text{I}^-$	+0.54
$1/2\text{O}_2 + \text{H}^+ + \text{e}^- \rightarrow 1/2\text{H}_2\text{O}_2$	+0.68
$\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$	+0.77
$1/2\text{Hg}^{2+} + \text{e}^- \rightarrow 1/2\text{Hg}$	+0.79
$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	+0.80
$1/3\text{NO}_3^- + 4/3\text{H}^+ + \text{e}^- \rightarrow 1/3\text{NO} + 2/3\text{H}_2\text{O}$	+0.96
$1/2\text{Br}_2(\text{l}) + \text{e}^- \rightarrow \text{Br}^-$	+1.06
$1/4\text{O}_2 + \text{H}^+ + \text{e}^- \rightarrow 1/2\text{H}_2\text{O}$	+1.23
$1/2\text{MnO}_2 + 2\text{H}^+ + \text{e}^- \rightarrow 1/2\text{Mn}^{2+} + \text{H}_2\text{O}$	+1.21
$1/2\text{Cl}_2 + \text{e}^- \rightarrow \text{Cl}^-$	+1.36
$1/3\text{Au}^{3+} + \text{e}^- \rightarrow 1/3\text{Au}$	+1.52
$\text{Co}^{3+} + \text{e}^- \rightarrow \text{Co}^{2+}$ (3M HNO ₃)	+1.84

The formal potentials will depend on temperature and pressure, as do the standard potentials, but will also have a dependence on electrolyte concentrations, not only on these of the species involved in the potential determining equilibrium but also on other electrolytes present in the solution bathing the electrode on which the potential is established, since these influence ion activities.

The formal potential loses the thermodynamic generality of the standard potential being only applicable to very specific conditions, but enables the experimentalist to proceed with meaningful voltammetric measurements.

1.9 Formal Potentials and Experimental Voltammetry

For practical purposes, *viz* voltammetry, the Nernst equation can be written for the general electrochemical equilibrium of section 1.4,

$$E = E_f^0(A, B, \dots / X, Y, \dots) + \frac{RT}{F} \ln \left(\frac{[A]^{v_A} [B]^{v_B} \dots}{[X]^{v_X} [Y]^{v_Y} \dots} \right)$$

or

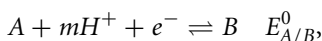
$$\left(\frac{[A]^{v_A} [B]^{v_B} \dots}{[X]^{v_X} [Y]^{v_Y} \dots} \right) = e^{\Theta},$$

where

$$\Theta = \frac{F}{RT} [(E - E_f^0(A, B, \dots / X, Y, \dots))].$$

The formal potential, E_f^0 will *approximate* to the standard potentials given in Table 2 but will typically show differences reflecting the precise composition of the solution under study which leads to deviations from solution validity.

In using Table 2 as a guide for approximate values of formal potentials, it should be noted that if protons (or hydroxide ions) are involved in the potential determining equilibrium, then the values are only relevant near $\text{pH} = 0$ corresponding to unit activity of protons. Therefore, if the solution under study deviates from this pH value, then the estimate of the formal potential must be correspondingly adjusted. For the general reaction



it follows that

$$E = E^0(A/B) + \frac{RT}{F} \ln \left(\frac{\gamma_A}{\gamma_B} (\gamma_{\text{H}^+})^m \frac{[A][\text{H}^+]^m}{[B]} \right)$$

becomes

$$E = E^0(A/B) + \frac{RT}{F} \ln \frac{\gamma_A}{\gamma_B} + m \frac{RT}{F} \ln(\gamma_{H^+})[H^+] + \frac{RT}{F} \ln \frac{[A]}{[B]}$$

$$E = E_f^0(A/B) + \frac{RT}{F} \ln \frac{[A]}{[B]} - 2.303m \frac{RT}{F} pH,$$

since

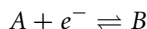
$$E_f^0(A/B) = E^0(A/B) + \frac{RT}{F} \ln \frac{\gamma_A}{\gamma_B},$$

$$\log_{10} N = \frac{\ln N}{\ln 10} = \frac{\ln N}{2.303} \quad \text{and}$$

$$pH = -\log_{10} \gamma_{H^+}[H^+],$$

and pH is defined by IUPAC in terms of the single ion activity of H^+ .

From an experimental point of view, in buffered media especially, the electrochemical equilibrium can be rewritten as



for which the *effective* formal potential is

$$E_{f,eff}^0(A/B) = E_f^0(A/B) - 2.303m \frac{RT}{F} pH,$$

so that

$$E = E_{f,eff}^0(A/B) + \frac{RT}{F} \ln \frac{[A]}{[B]}.$$

The above equation shows that at 25°C the formal potential will change by m times 0.059 mV per pH unit. Accordingly, for a pH shift from 0 (corresponding to standard conditions) to 7 (neutral) the formal potential will change by a little more than 400 mV if one proton is taken up per electron in the electrochemical equilibrium. This is a very large change given the size of potential windows typically explored in voltammetry.

To summarise:

- The most useful form of the Nernst equation, relating to a process $A + e^- \rightleftharpoons B$ for voltammetry is of the form:

$$\frac{[A]}{[B]} = e^{\Theta},$$

where $\Theta = \frac{F}{RT}(E - E_f^\ominus)$ and E_f^\ominus is the *formal* electrode potential of the A/B couple.

- Standard electrode potentials provide approximate values for formal potentials. Helpful extensive tables of standard potentials are available, most notably and authoritatively “Standard potentials in aqueous solutions”.^{*} The latter are reported on the standard hydrogen electrode scale so, if for example, your reference electrode is a saturated calomel electrode or a saturated silver/silver chloride electrode then you need to *subtract* a value of 0.242 V or 0.197 V to put the estimate derived from the tables on the correct scale.
- If working in aqueous media at a pH different from the ‘standard’ condition of pH 0, estimates of formal potentials need to be corrected by 59 mV per proton per pH unit (at 25°C).

Finally, it must be stressed the estimates of the formal potential are thermodynamic quantities and presume electrochemical equilibration and hence, fast electrode kinetics. This is often not a correct assumption. We address this issue in the next section.

1.10 Electrode Processes: Kinetics vs. Thermodynamics

Classically, electrode potentials were measured using a potentiometer such as that shown schematically in Fig. 1.14.

The principle of the method is as follows. A battery C, of constant voltage larger than any to be measured, is connected across a wire AB of high electrical resistance. The cell X under study is connected to the point A and then through a current measuring device, G, to a sliding contact, D, which can be moved along the wire AB. The position of D is adjusted so that no current flows through G. At this point,

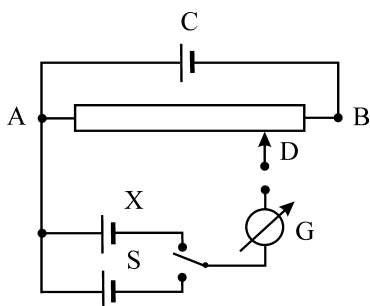


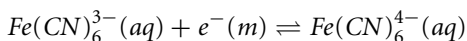
Fig. 1.14 Schematic diagram of a Poggendorf potentiometer.

^{*} By A.J. Bard, R. Parsons and J. Jordan, Marcel Dekker, New York, 1985.

the drop of potential along AD due to the cell, C, is exactly compensated by the voltage of X, E_x . By means of a switch, the cell X is then replaced by a standard cell, S of known voltage E_s . The point of contact D is re-adjusted to a new point, D' until no current flows, The drop of voltage across AD' then matches E_s . It follows then that the unknown voltage

$$E_x = \frac{AD}{AD'} \times E_s.$$

A merit of the potentiometer approach is that the electrode kinetics of the electrochemical equilibrium of interest rapidly becomes apparent. For example, let us consider the following two electrode processes:



and

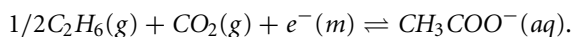


Figure 1.15 shows possible experimental arrangements of their study using a calomel electrode as a reference electrode. Also shown is the current measured on a potentiometer such as that shown in Fig. 1.14. In the case of the $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ process, true electrochemical equilibrium is rapidly established at the platinum wire electrode.

If the sliding contact is moved either side of the balance point then significant current will flow, since the applied potential no longer balances the potential from the cell under study and either $Fe(CN)_6^{4-}$ ions are oxidised or $Fe(CN)_6^{3-}$ ions are reduced, depending on which direction the contact is shifted. The fact that significant currents flow in both the oxidising and reducing senses when there is only a slight imbalance of the potentiometer shows that the electrode kinetics are fast and hence, that a true electrochemical equilibrium has been set up on the platinum wire. In contrast in the case of acetate/ CO_2/C_2H_6 , no current flows at any point of contact with the potentiometer. This reflects the fact that the electrode kinetics in this case are very slow, so that no electrochemical equilibrium is established on the platinum wire and, even if significant positive or negative potentials are applied to the cell (by varying the contact point), no current flows.

In conclusion, electrode potentials are only established when an electrochemical equilibrium is truly established at the electrode and this requires fast electrode kinetics. The next chapter first considers a model by which electrode kinetics can be interpreted and then sets out to rationalise why some electrode processes are fast and some slow.

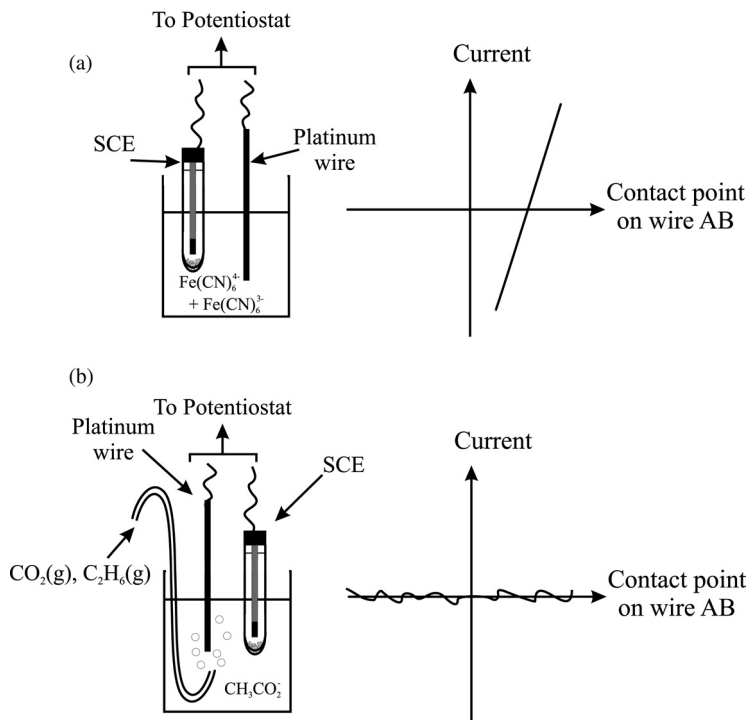


Fig. 1.15 Potentiometric measurements of systems with (a) fast electron kinetics and (b) slow electrode kinetics.

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