A few basic concepts

In this chapter we introduce and discuss a number of concepts that are commonly used in the electrochemical literature and in the remainder of this book. In particular we will illuminate the relation of electrochemical concepts to those used in related disciplines. Electrochemistry has much in common with *surface science*, which is the study of solid surfaces in contact with a gas phase or, more commonly, with ultrahigh vacuum (uhv). A number of surface science techniques has been applied to electrochemical interfaces with great success. Conversely, surface scientists have become attracted to electrochemistry because the electrode charge (or equivalently the potential) is a useful variable, which cannot be well controlled for surfaces in uhv. This has led to a laudable attempt to use similar terminologies for these two related sciences, and to introduce the concepts of the *absolute scale of electrochemical potentials* and the *Fermi level of a redox reaction* into electrochemistry. Unfortunately, there is some confusion of these terms in the literature, even though they are quite simple.

4.1 The electrochemical potential

In ordinary thermodynamics the chemical potential of a species $i$ is defined as:

$$\mu_i = \left( \frac{\partial G}{\partial N_i} \right)_{p,T}$$

where $G$ is the Gibbs energy of the phase under consideration, $p$ denotes the pressure, $T$ the temperature, and $N_i$ the number of particles of species $i$. So the chemical potential is the work required to add a particle to the system at constant pressure and temperature. Alternatively, one may define $\mu_i$ by taking the derivative with respect to $m_i$, the number of moles of species $i$. The two definitions differ by a multiplicative constant, Avogadro’s constant; we shall use the former definition.
If the particles of species $i$ in Eq. (4.1) are charged, one speaks of an 

electrochemical potential instead, and writes $\tilde{\mu}_i$. The usual thermodynamic 
equilibrium conditions are now in terms of the $\tilde{\mu}_i$. For example, if a species $i$ 

is present both in a phase $\alpha$ and in a phase $\beta$, and the interface between $\alpha$ 

and $\beta$ is permeable to $i$, then $\tilde{\mu}_{i,\alpha} = \tilde{\mu}_{i,\beta}$ at equilibrium.

In adding a charged particle work is done against the inner potential $\phi$, 

and it may be useful to separate this out and write:

$$\tilde{\mu}_i = \left( \frac{\partial G}{\partial N_i} \right)_{P,T} = \mu_i + z_i e_0 \phi$$

(4.2)

where $z_i$ is the charge number of species $i$, $e_0$ is the unit of charge, and $\mu_i$ 

is again called the chemical potential since it contains the work done against 

chemical interactions. For an uncharged species chemical and electrochemical 

potential are the same.

At zero temperature the electrons in a solid occupy the lowest energy levels 

compatible with the Pauli exclusion principle. As mentioned in Chapter 2, the 
highest energy level occupied at $T = 0$ is the Fermi level, $E_F$. For metals the 
Fermi level and the electrochemical potential are identical at $T = 0$, since any 
electron that is added to the system must occupy the Fermi level. At finite 
temperatures $E_F$ and the electrochemical potential $\tilde{\mu}$ of the electrons differ by 
terms of the order of $(kT)^2$, which are typically a fraction of a percent and are 

hence negligible for most purposes. Numerical values of $E_F$ or $\tilde{\mu}$ must refer 
to a reference point, or energy zero. Common choices are a band edge or the 

vacuum level, i.e. a reference point in the vacuum at infinity. Obviously, one 

to have to be consistent in the choice of the reference point when comparing the 

Fermi levels of different systems.

For electrons in a metal the work function $\Phi$ is defined as the minimum 

work required to take an electron from inside the metal to a place just outside 
(c.f. the preceding definition of the outer potential). In taking the electron 

across the metal surface, work is done against the surface dipole potential $\chi$.

So the work function contains a surface term, and it may hence be different 

diffrent surfaces of a single crystal. The work function is the negative 

of the Fermi level, provided the reference point for the latter is chosen just 

outside the metal surface. If the reference point for the Fermi level is taken 

to be the vacuum level at infinity instead, then $E_F = -\Phi - e_0 \psi$, since an 
extra work $-e_0 \psi$ is required to take the electron from the vacuum level to 

the surface of the metal. The relations of the electrochemical potential to the 
work function and the Fermi level are important because one may want to 

relate electrochemical and solid-state properties.

4.2 Absolute electrode potential

The standard electrode potential [10] of an electrochemical reaction is commonly 
measured with respect to the standard hydrogen electrode (SHE) [11],
and the corresponding values have been compiled in tables. The choice of this reference is completely arbitrary, and it is natural to look for an absolute standard such as the vacuum level, which is commonly used in other branches of physics and chemistry. To see how this can be done, let us first consider two metals, I and II, of different chemical composition and different work functions $\Phi_I$ and $\Phi_{II}$. When the two metals are brought into contact, their Fermi levels must become equal. Hence electrons flow from the metal with the lower work function to that with the higher one, so that a small dipole layer is established at the contact, which gives rise to a difference in the outer potentials of the two phases (see Fig. 4.1). No work is required to transfer an electron from metal I to metal II, since the two systems are in equilibrium. This enables us calculate the outer potential difference between the two metals in the following way. We first take an electron from the Fermi level $E_F$ of metal I to a point in the vacuum just outside metal I. The work required for this is the work function $\Phi_I$ of metal I. We then take the electron in the vacuum to a point just above metal II; this requires the work $-e_0(\psi_{II} - \psi_I)$. We then take the electron to the Fermi level of metal II, and gain the energy $-\Phi_{II}$. Since the total work for this process must be zero, we obtain:

$$\psi_I - \psi_{II} = \frac{- (\Phi_I - \Phi_{II})}{e_0}$$

(4.3)

so that the outer potential difference can be calculated from the metal work function. By the same reasoning different faces of a single metal crystal have different outer potentials if their work functions are not equal.

We should like to define a “work function” of an electrochemical reaction which enables us to calculate outer potential differences in the same way for a metal-solution interface, and this work function should also refer to the vacuum. For this purpose we consider a solution containing equal amounts of $\text{Fe}^{3+}$ and $\text{Fe}^{2+}$ ions in contact with a metal $M$, and suppose that the reaction is at equilibrium. We now transfer an electron from the solution via the vacuum to the metal in the following way:
1. Take an Fe\(^{2+}\) ion from the solution into the vacuum above the solution; the work required is the negative of \(\Delta G^r_{\text{sol}}(\text{Fe}^{2+})\), the real Gibbs energy of solvation of the Fe\(^{2+}\) ion. Real Gibbs energies of solvation are measurable; they include the work done against the surface potential of the solution.

2. Take an electron from the Fe\(^{2+}\) ion: Fe\(^{2+}\) $\rightarrow$ Fe\(^{3+}\) + e\(^-\); the work required is the third ionization energy \(I_3\) of Fe.

3. Put the Fe\(^{3+}\) back into the solution, and gain \(\Delta G^r_{\text{sol}}(\text{Fe}^{3+})\).

4. Take the electron from just outside the solution across to a position just outside the metal; the work required is \(-e_0(\psi_m - \psi_s)\); the index \(m\) denotes the metal, \(s\) the solution.

5. Take the electron to the Fermi level of the metal, and gain \(-\Phi_m\) in energy.

Adding up all the energies, we obtain:

\[-\Delta G^r_{\text{sol}}(\text{Fe}^{2+}) + I_3 + \Delta G^r_{\text{sol}}(\text{Fe}^{3+}) - e_0(\psi_m - \psi_s) - \Phi_m = 0\]  
(4.4)

or

\[e_0(\psi_m - \psi_s) = \left[\Delta G^r_{\text{sol}}(\text{Fe}^{3+}) - \Delta G^r_{\text{sol}}(\text{Fe}^{2+}) + I_3\right] - \Phi_m\]  
(4.5)

Comparison with Eq. (4.3) suggests that we identify the expression in the square brackets, which depends only on the properties of the redox couple Fe\(^{3+}\)/Fe\(^{2+}\) in the solution, with the work function of this couple and define:

\[\Phi(\text{Fe}^{3+}/\text{Fe}^{2+}) = \Delta G^r_{\text{sol}}(\text{Fe}^{3+}) - \Delta G^r_{\text{sol}}(\text{Fe}^{2+}) + I_3\]  
(4.6)

All the quantities on the right-hand side of this equation are measurable; so this work function is well defined. Fortunately, it is not necessary to calculate the work function for every electrode reaction: The difference between the work functions of two electrode reactions (measured in eV) equals the difference between their standard potentials on the conventional hydrogen scale (measured in V) – this can be easily seen by constructing electrochemical cells with the SHE (standard hydrogen electrode) as a counter electrode. So it is sufficient to know the work function of one particular reaction in a given solvent. For the SHE (i.e. the couple H\(_2\)/H\(^+\)), the work function is currently estimated as 4.5 ± 0.2 eV; so one obtains the work function of any electrochemical reaction by simply adding this number to the standard potential (in volts) on the SHE scale. By dividing the resulting scale of work functions by the unit charge (or expressing quantities in volts instead of electron volts) one obtains the absolute scale of electrochemical potentials.

Since the absolute and the conventional electrode potentials differ only by an additive constant, the absolute potential depends on the concentration of the reactants through the familiar Nernst’s equation. This dependence is implicitly contained in Eq. (4.6): the real Gibbs energies of solvation contain an entropic term, which depends on the concentration of the species in the solution.

For a metal, the negative of the work function gives the position of the Fermi level with respect to the vacuum outside the metal. Similarly, the negative of the work function of an electrochemical reaction is referred to as the
Fermi level $E_F^{\text{redox}}$ of this reaction, measured with respect to the vacuum; in this context *Fermi level* is used as a synonym for electrochemical potential. If the same reference point is used for the metal and the redox couple, the equilibrium condition for the redox reaction is simply: $E_F^{\text{metal}} = E_F^{\text{redox}}$. So the notion of a Fermi level for a redox couple is a convenient concept; however, this terminology does not imply that there are free electrons in the solution which obey Fermi-Dirac statistics, a misconception sometimes found in the literature.

The scale of electrochemical work functions makes it possible to calculate the outer potential difference between a solution and any electrode provided the respective reaction is in equilibrium. A knowledge of this difference is often important in the design of electrochemical systems, for example, for electrochemical solar cells. However, in most situations one needs only relative energies and potentials, and the conventional hydrogen scale suffices.

### 4.3 Three-electrode configuration

Generally electrochemists want to investigate one particular interface between an electrode and an electrolyte. However, to pass a current through the system at least two electrodes are needed. Further, one needs a reference electrode to determine the potential of the working electrode. Since the potential of the reference electrode must remain constant, no current should flow through it. So in practice one takes three electrodes: the working electrode, which one wants to investigate, a counter electrode, which takes up the current, and a reference electrode (see Fig. 4.2). The potential of the working electrode is then measured with respect to that of the reference electrode. It is important that the ohmic potential drop between the working and the reference electrode is as small as possible. One procedure is to keep the reference electrode in a separate compartment, and link it to the main cell with a so-called *Luggin capillary*, whose tip is placed very close to the working electrode. Since no current passes between the working and the reference electrode, the ohmic drop between the two is limited to the region between the capillary tip and the working electrode. There is an additional problem caused by the *junction potential* at the Luggin capillary; a small potential drop is established in the region where two electrolytes of different composition meet [12]. However, in practice these junction potentials can be kept very small and, more importantly, constant, and can be disregarded.

What is actually measured as electrode potential in such a configuration? Consider a metal electrode ($M$) in equilibrium with a solution containing a redox couple red/ox with a standard hydrogen electrode attached. One measures the electrode potential by taking the two leads of a voltmeter and attaching one to the working and the other to the reference electrode. The latter is made of platinum, and to avoid unnecessary complications we assume that the two leads of the voltmeter are also made of platinum. According to Ohm's
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**Fig. 4.2.** Electrochemical cell with a three-electrode configuration.

**Fig. 4.3.** Shift of the metal Fermi level on application of an overpotential.

law the current is proportional to the difference in the driving force, which is the difference in the electrochemical potential. So the voltmeter connected to two phases measures the difference in the electrochemical potential; hence the measured voltage $\Delta V$ is given by:

$$-e_0 \Delta V = \mu_1 - \mu_2 = \mu_1 - e_0 \phi_1 - \mu_2 + e_0 \phi_2$$

(4.7)

When the two phases have the same chemical composition, the chemical potentials are equal, and then $\Delta V = \phi_1 - \phi_2$, which was already pointed out in section 1. In our case both leads are made of the same material, platinum; so the measured electrode potential, which is the equilibrium potential $\phi_0$ of the redox couple, is:

$$\phi_0 = \phi_1 - \phi_2 = (\phi_1 - \phi_M) + (\phi_M - \phi_{\text{sol}}) + (\phi_{\text{sol}} - \phi_2)$$

(4.8)

Generally, when two phases are in electronic equilibrium, $e_0(\phi_1 - \phi_2) = \mu_1 - \mu_2$. In our case, the wire I is in equilibrium with the metal $M$, the latter is in equilibrium with the redox couple, and the platinum electrode II is in
equilibrium with the reference couple (index “ref”). So we can rewrite Eq. (4.8) as:
\[ ε_0 φ_0 = (μ_1 - μ_M) + (μ_M - μ_{\text{redox}}) + (μ_{\text{ref}} - μ_{\text{II}}) = -μ_{\text{redox}} + μ_{\text{ref}} \] (4.9)

Since the redox couple and the reference system experience the same inner potential $φ_{\text{sol}}$, we have:
\[ ε_0 φ_0 = -μ_{\text{redox}} + μ_{\text{ref}} = Φ_{\text{redox}} - Φ_{\text{ref}} \] (4.10)

since the work function is the negative of the electrochemical potential. So one actually measures the difference in the work functions between the redox couple and the reference electrode, and this is independent of the electrode material for a redox couple not involving a reaction with the electrode $M$.

In the preceding derivation we presumed that equilibrium prevails, so that the Fermi levels of the metal and of the redox couple are equal. This equilibrium can be disturbed by the application of an external electrode potential $φ$, which lowers the electronic energies in the metal, and in particular the Fermi level, by an amount $-ε_0 η$, where $η = φ - φ_0$ is called the overpotential (see Fig. 4.3). Thus the application of an overpotential leads to a difference $-ε_0 η$ in the Fermi levels of the metal and the solution. However, as the equilibrium is disturbed, the reaction proceeds in one direction; current flows and the concentrations of the reactants at the interface will change unless they are kept constant by fast transport processes. Experimental methods for dealing with this difficulty will be discussed in Chapters 19 and 20. Until then we will generally assume that the concentrations of the reactants are kept constant.

4.4 Surface tension

The correct thermodynamic function to describe the energetics of a system depends on the external conditions. Thus, for a bulk system held at constant temperature and pressure it is the Gibbs energy $G$, and for constant temperature and volume it is the Helmholtz energy $F$. Electrochemical interfaces have an extra variable, the electrode potential $φ$. Commonly, they are held at constant temperature, pressure and potential, and are described by the surface tension $γ$, which we will treat in greater detail in Chapter 8. For liquid electrodes, the surface tension can be measured directly as the Gibbs energy required to increase the surface area. For solid electrodes, the absolute value of $γ$ cannot be measured, but, as we shall demonstrate below, changes in $γ$ can.

With the recent advances in computation is has become possible to calculate the energetics of surfaces and interfaces. Leaving the question of the accuracy of such calculations aside, which obviously depends on the complexity of the system considered, we want to relate the quantities calculated to the surface tension. For every type of energy, we can define a surface excess
in the following way. We calculate the actual energy of the system, subtract the energy that the system would have if each of the adjoining phases had bulk properties, and divide the result by the area of the surface or interface. Quantum chemical calculations are usually performed at constant temperature, volume, and surface charge density \( \sigma \) on the solid electrode, and thus give the surface Helmholtz energy \( F_s \) per unit area. To obtain the surface tension, we perform what is technically known as a Legendre transformation. This is familiar from ordinary thermodynamics: The internal energy \( U \) describes a system at constant volume and entropy; by the transformation \( F = U - TS \) one obtains the Helmholtz energy, which has temperature and volume as natural variables.

Holding the electrode at constant potential is equivalent to holding the electrons at constant electrochemical potential \( \bar{\mu}_e \). The excess charge \( \sigma \) per area is related to the number of electrons \( N_e \) through
\[
\sigma = -e_0 \frac{N_e - zN_a}{A},
\]
where \( N_a \) is the number of atoms, which is constant, and \( z \) their charge number; \( A \) is the surface area. Therefore, we obtain the elecrochemical potential of the electrons through
\[
-\bar{\mu}/e_0 = \frac{\partial F_s}{\partial \sigma} \quad (4.11)
\]
The surface tension is then defined as:
\[
\gamma = F_s + \sigma \bar{\mu}/e_0 \quad (4.12)
\]
and has the electrode potential as its natural variable, since \( d\bar{\mu}/e_0 = -d\phi \).

In fact, keeping all other variables constant, we have:
\[
dF_s = -\frac{\bar{\mu}}{e_0} d\sigma \quad d\gamma = dF + \frac{\sigma}{e_0} d\bar{\mu} + \frac{\bar{\mu}}{e_0} d\sigma = -\sigma d\phi \quad (4.13)
\]
which also shows that the surface tension has an extremum for \( \sigma = 0 \), the point or potential of zero charge (pzc). Differentiating again gives:
\[
\frac{d^2 \gamma}{d\phi^2} = -\frac{d\sigma}{d\phi} = -C \quad (4.14)
\]
where \( C \) is the differential capacity per unit area, which will be treated in more detail in the following chapter. Since the capacity must be positive – otherwise the interface would charge spontaneously – the extremum at the pzc is a maximum. The second part of eq. (4.13) shows, that changes in the surface tension can be measured by integrating the charge density over the electrode potential.

For liquid electrodes, the equations derived above are exact; on solid electrodes, there is an extra term involving the surface stress. However, this extra term is negligible for all practical purposes, so that the above equations are excellent approximations for solid metals – see Chapter 8 for details.

In the literature there is some confusion concerning the use of the surface tension and the Helmholtz surface energy. In surface science, often \( F_s/A \) is
called the surface tension. Note that $\gamma$ and $F_s/A$ agree only at the pzc (see eq. (4.12)), and the latter does not have a maximum at the pzc, but a positive slope which, because of the relation between $\mu$ and $\Phi$ gives the work function. Therefore, using the wrong form of energy can entail qualitative errors.

Problems

1. Consider a monolayer of water molecules arranged in a square lattice with a lattice constant of 3 Å. The dipole moment of a single molecule is $6.24 \times 10^{-30}$ Cm. (a) Calculate the potential drop across the monolayer if all dipole moments are parallel and perpendicular to the lattice plane. (b) If the potential drop across the layer is 0.1 V, what is the average angle of the dipole moment with the lattice plane?

2. Following the ideas of Section 4.2, devise a suitable cycle to derive the work function of a metal deposition reaction; this will involve the energy of sublimation of the metal.

3. In a simple model for sp metals known as jellium the ionic charge is smeared out into a constant positive background charge (see also Fig. 1.5). If the metal occupies the region $-\infty < z \leq 0$, the positive charge distribution is given by:

$$n_+(z) = \begin{cases} n_0 & \text{for } z \leq 0 \\ 0 & \text{for } z > 0 \end{cases}$$

In a simple approximation the distribution of the electrons takes the form:

$$n_-(z) = \begin{cases} n_0(1 - A \exp \alpha z) & \text{for } z \leq 0 \\ n_0B \exp -\alpha z & \text{for } z > 0 \end{cases}$$

Show that for an uncharged metal surface: $A = B = 1/2$, and derive a formula for the surface dipole potential. Cesium has an electronic density of $6.9 \times 10^{22}$ cm$^{-3}$ and $\alpha \approx 2$ Å$^{-1}$. Calculate its surface dipole potential.