

Preface

These notes have arisen from a series of Journal Clubs held at Imperial College and King’s College London, beginning in 2018. The object was for a number of physicists to try and understand the puzzling language of electrochemistry. So I have whimsically ventured to call these “Electrophysics Notes”.

The approach is rather unorthodox because we assumed familiarity with electrostatics and density functional theory, but not with even elementary electrochemistry. The Appendix on thermodynamics, and in particular chemical potential, is adapted from my lecture notes to the MSE 307 class at Imperial College.

The notes are typeset in Plain \TeX , and the date is entered automatically. This means that readers can keep track of corrections and the addition of further sections; we don’t know how far these notes will evolve, or into what eventual form they will evolve.

Tony Paxton, King’s College London, 29 June 2019

1. The lemon lamp

We shall begin with the lemon lamp. I cut open a lemon and drive a zinc nail and a copper nail into the fruit without allowing them to touch. If I then use crocodile clips and wire to connect the two heads through a light bulb, the bulb will illuminate. See figure 1–1. I suggest you try this at home; you could use a galvanised nail and a brass screw.

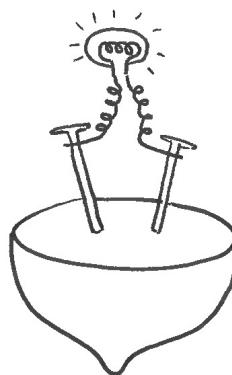


FIGURE 1–1

This is an electrochemical cell, as illustrated in figure 1–2. Zinc and copper metal “electrodes” are immersed in an acid solution; that is, an aqueous solution containing hydrogen ions (protons). A chemical reaction occurs spontaneously on the left hand electrode,



In this reaction a Zn atom at the surface of the electrode detaches itself into the solution, *but it leaves behind two electrons*. In this way it becomes a Zn^{++} “cation” free to wander in the liquid. Of course, this is corrosion of the zinc. The two electrons serve to reduce the charge carried by the electrode by $2e^-$ where, by convention, e is the fundamental constant—the charge on the proton, 1.602×10^{-19} Coulomb. Because of this spontaneous reaction this electrode is called the *electron sink*. Faraday called it the “anode”. In the terminology of Bockris, the zinc suffers “de-electronation”, also called “oxidation”. It is called that because its *oxidation state*—the number of plus signs in the superscript—is increased (from zero to two).

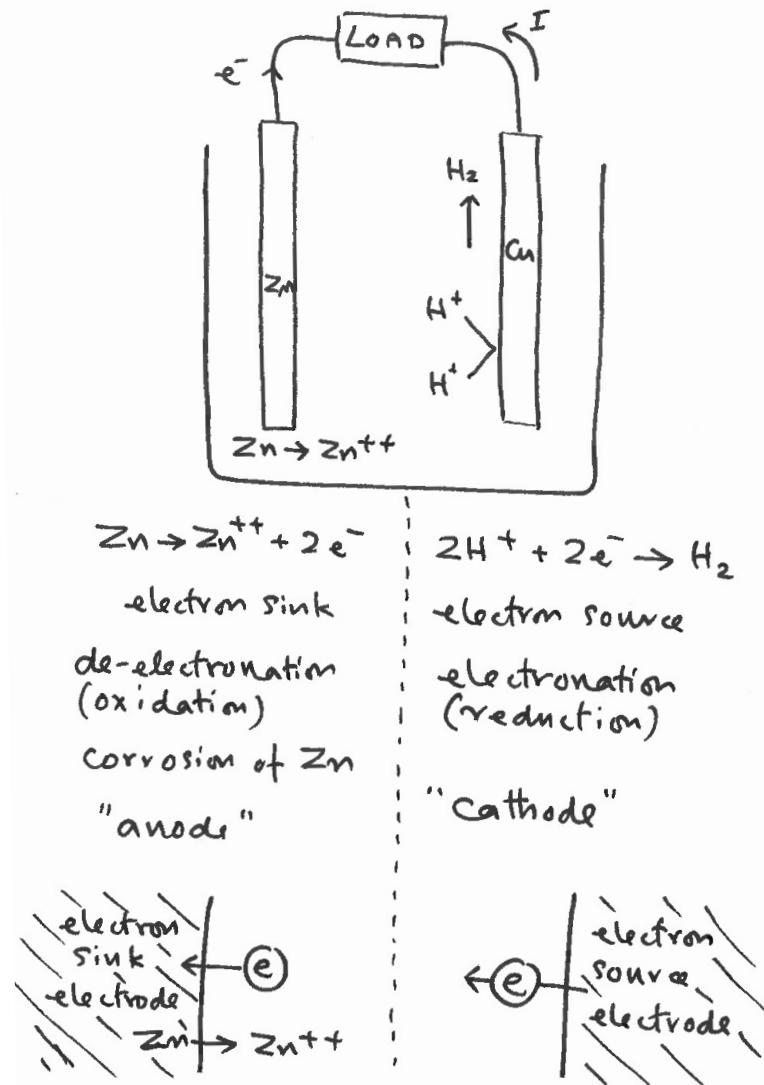
A second chemical reaction occurs spontaneously on the right hand electrode,



Two hydrogen ions in the acid solution swipe two electrons from the electron gas in the copper and combine to form hydrogen gas which bubbles off out of the liquid and into the air above. In this way this electrode, called the “cathode” by Faraday, is an *electron source* and the reaction is “electronation”, or “reduction” since the oxidation state of the H^+ ions are reduced from plus one to zero.[†]

[†] Note that you can easily tell an oxidation from a reduction reaction because in oxidation the electrons appear on the left of the arrow, while in reduction they appear on the right.

Because the two electrodes are connected by wire the electrons which are piling up on the zinc will repel each other because of the Coulomb force and will flow down the wire to the copper where they can serve the electronation reaction. In the process they can light up the bulb. Note that even if the wires are at open circuit so that electrons cannot flow, each reaction will proceed to some limited extent until the charge accumulating on the metals prevents any further reaction. A general conclusion is that if a metal is immersed in water containing some ions, the metal may become slightly charged.



2. The simplest electrochemical cell

The simplest electrochemical cell is illustrated in figure 2–1.

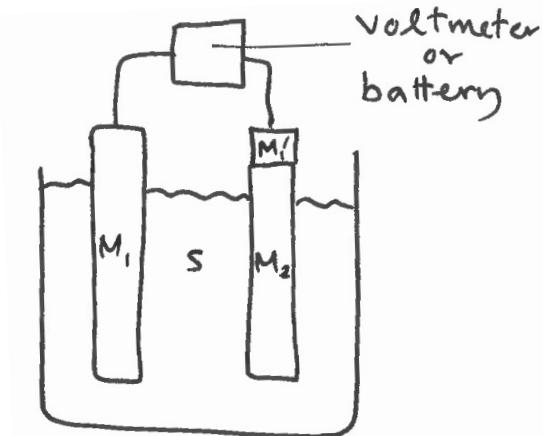


FIGURE 2–1

Two electrodes made of metal M_1 and metal M_2 are immersed in a solution, or *electrolyte*, S . They are connected so as to close the circuit through a battery or voltmeter. In the lemon lamp I glossed over the question of what metal the wires are made of. This is important all the same since the junction between dissimilar metals sets up an electric potential difference (see section 3.4) and this will contribute to the voltage at the voltmeter. In this simplest cell we take it that the wire is made of the same metal as one of the electrodes, say, M_1 . Because the wires on either side of the voltmeter (or battery) may be at a different electric potentials we indicate this in the cartoon by including a contact between wire of metal M'_1 and electrode of metal M_2 .

This cell can be illustrated more symbolically as in figure 2–2. This places the elements of the cell in line from left to right.

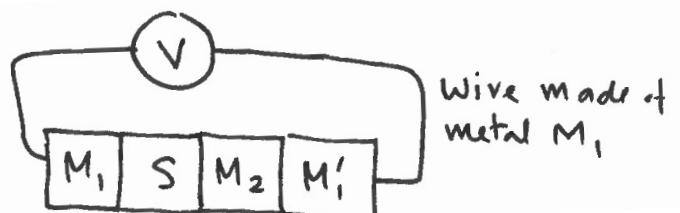


FIGURE 2–2

It is conventional to denote such cell in a formulaic way as follows, sometimes called the “cell diagram.”



The vertical bars indicate interfaces between the phases in contact. We assume that the electric potential is uniform within each phase but there may be an electric potential difference across each interface. The convention is to put the anode to the left where the reaction is de-electronation and the cathode on the right where the reaction is

electronation (reduction).

We anticipate by our experience with the lemon lamp that an electric potential difference (PD) will be set up between the terminals of the voltmeter. Since we assume that the electric potential is uniform within each phase then there may be an electric potential drop across each interface and the sum of these will make up the total PD across the voltmeter. This effect can be summarised in a *third* cartoon representation of the cell, namely the ladder diagram of figure 2–3.

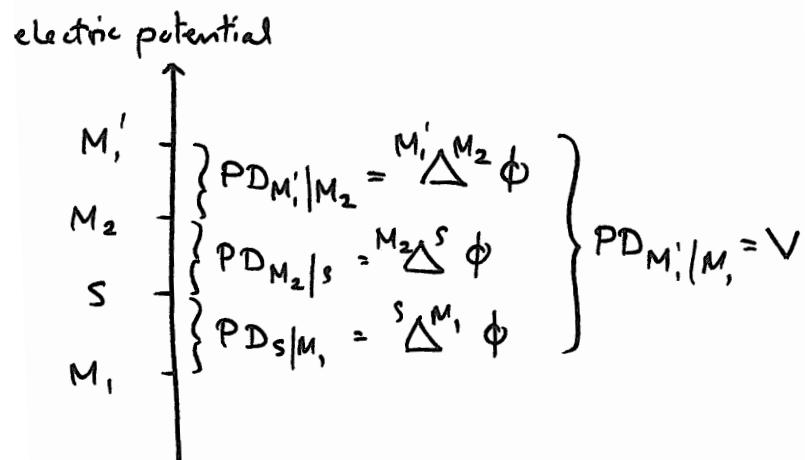


FIGURE 2–3

We concentrate for the present on the case where the circuit is closed through a high impedance voltmeter as we are interested in the electric potential difference that is set up by creating the sequence of interfaces. But keep in the back of your mind the thought that a battery in place of the voltmeter can be used to modify the PD. For example if the zinc electrode is made more positive it will drive the reaction (1.1) to the right and increase the tendency of the zinc to corrode. Hence the metallurgical dictum: “anodes are positive and they corrode.”

It is very important to appreciate what can and what cannot be measured. Clearly we can measure the total PD across the voltmeter; but thus far we have not established that we can measure any one of the electric potential drops across an interface. Generally we cannot because any such measurement necessarily introduces new electrodes and probes and new PDs that conspire to add to the one we’re trying to measure. As an exact statement we may assert that *it is not possible to measure a single electrode potential.*

3. The next simplest electrochemical cell

Immediately I have a counter response to that assertion. Figure 3–1 shows the *next* simplest electrochemical cell.

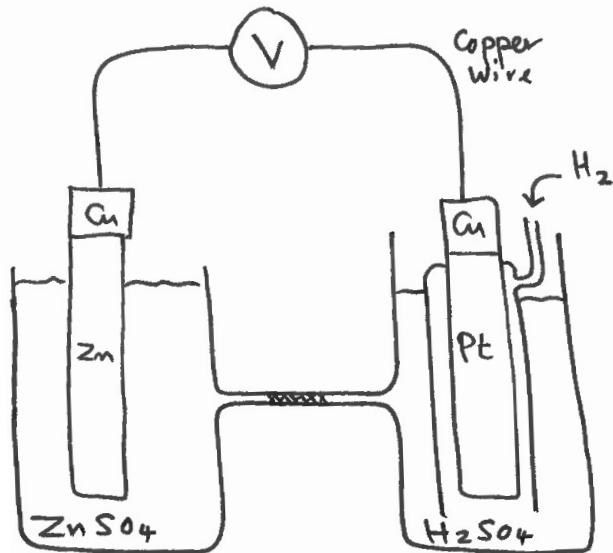
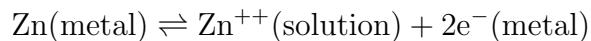


FIGURE 3–1

In this figure the single electrodes are separated by a narrow tube stuffed with some salt that allows ions to flow and complete the circuit but enables each electrode to be immersed in a different electrolyte. On the left is a Zn electrode immersed in a solution of zinc sulphate and so there can be an equilibrium of the reaction



The other cell is the famous “standard hydrogen electrode” (SHE) which consists of a platinum wire surrounded by hydrogen gas at exactly one bar pressure immersed in a solution of hydrochloric acid at such a strength that the hydrogen ion activity is exactly one. The zinc and platinum electrodes are connected through copper wires to a voltmeter or battery. Figure 3–2 shows the cell in the in-line cartoon form.

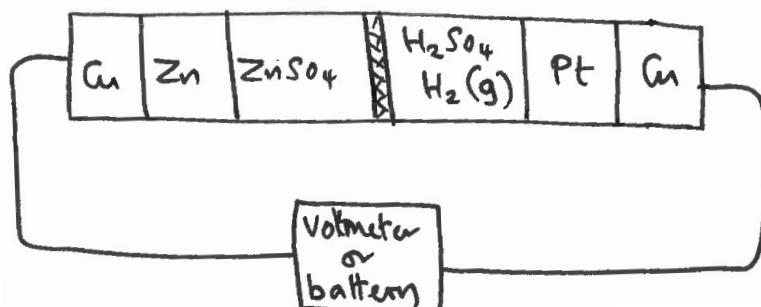


FIGURE 3–2

This set up does permit the measurement of a single electrode potential (as long as the Cu|Zn and Cu|Pt PDs are known) because the SHE is a so-called “non polarisable”,

reversible single electrode. This means that its single electrode potential is both known and unchanging as a result of it being connected to a second single electrode to form an electrochemical cell. A single electrode can be modelled in a first approximation as a capacitor and resistor connected in parallel, see figure 3–3. If the resistance is zero then the electrode is said to be “polarisable” so that if we try to change the electric potential on the electrode, current will leak out into the electrolyte and we find that the electric potential cannot be altered. Conversely, if the resistance is infinite then the interface acts as a capacitor and changes in electric potential are accommodated by charge accumulation across the interface. Therefore since all the electric potential drops are known except one, that at the Zn|S interface; then by varying the concentration of zinc sulphate and observing the voltmeter the single electrode potential may be inferred. This is only possible if the Zn|S interface is ideally polarisable.

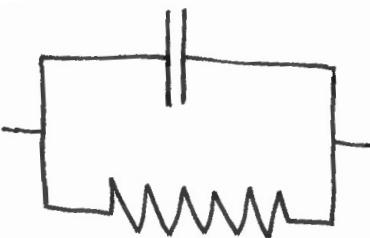


FIGURE 3–3

3. Inner potential, work function and contact potential

The surface of a metal has features absent in the bulk; in particular, since the electrons spill out into the vacuum there will exist an electric dipole pointing normal to the surface from the vacuum into the metal. Similarly for pure water: it has been established experimentally that water molecules at the surface are oriented with their oxygen atoms pointing into the vacuum; hence as for a metal surface, there is an electric dipole that points from the vacuum towards the water; the dipole potential at the surface of water is estimated from experiment to be 80mV. If a metal is immersed in an electrolyte it may become charged. The liquid close to the metal surface is bound to have a molecular structure that is different from the bulk. Not only are the water molecules differently oriented near the surface anyway, the additional charge will further modify the structure into what is called, loosely, the *double layer*. Pictures of the double layer are associated with the authors Helmholtz, Gouy and Chapman, and Stern. A common feature of the surfaces of both the metal and the electrolyte are the appearance of surface *electric dipoles*. After the interface between a metal and an electrolyte is established these dipoles will persist and the narrow region spanning the interface on either side is often referred to in the literature as the “interphase.” The purpose of the following few sections is to dissect the interphases such as indicated by a vertical bar in (2.1) in a semi-quantitative manner.

Now there needs to be some remark about the word “potential” which has two meanings in all the books and literature. I have carefully used “electric potential” where convenient to describe just that: a quantity calibrated in Volts or Joules per Coulomb in SI units.

Authors persistently use “potential” when they mean potential energy whose SI units are Joules. It is not really possible to write either “electric potential” or “potential energy” all the time without becoming prolix. And indeed quantities called chemical potential, or inner potential are so common that we must use them—although the former is in Joules and latter in Volts. The most egregious villains are in density functional theory: very confusing is Lang and Kohn on the work function, whose ϕ is called a potential and has the usual symbol of electric potential, but actually is a potential energy. At best I can warn you to be careful and hope that ambiguity doesn’t creep into these notes. Where possible, we will use lower case Greek, ϕ , ψ and χ for electric potentials and V or U for potential energy. For example if the electric potential somewhere is ϕ , then the potential energy of a charged object at the same place is $q\phi$ where q is the charge of the object. If the object is an electron then the potential energy is $-e\phi$ (measured in electron volts, eV). Finally recall that *all* instances of either electric potential or potential energy *must* be referenced to some arbitrary and agreed zero: it is always safest to mention potential differences rather than absolute potentials. For example in electrostatics we often take the electric potential as relative to a point at infinity out of range of all charges. In solid state physics if we treat only a bulk solid with no surfaces but periodic boundary conditions, then we choose a potential energy zero with reference to some mean energy within the solid (for example the average Hartree plus external potential energies).

3.1 Density functional theory

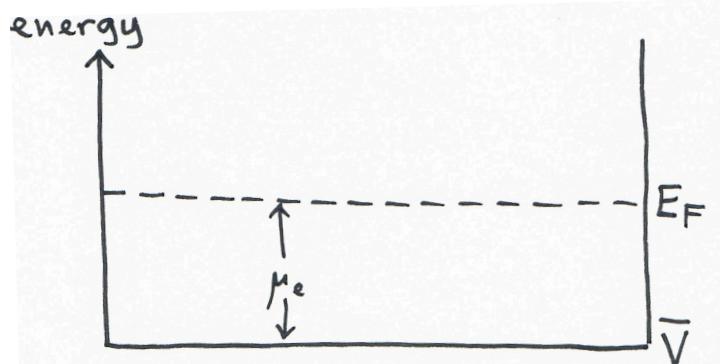


FIGURE 3–1

Figure 3–1 shows a sketch of the energy levels in a metal. The lower horizontal line indicates the average potential energy, $\bar{V} = -e\bar{\phi}$, of all the electrons in the metal. Because electrons are Fermions they occupy successively higher energy levels such that the energy of the highest occupied state is the Fermi energy, E_F . The bulk of the metal, far from its surfaces, must have its electronic structure exactly as described using periodic boundary conditions and as long as the metal is not charged we may describe the electronic levels using bulk density functional theory (DFT). A postulate of the DFT is that the total energy is formed of three terms, each a functional only of the ground state electron density, $n(\mathbf{r})$ (number of electrons per unit volume),

$$E_{\text{tot}}[n] = T[n] + V_{\text{en}}[n] + V_{\text{ee}}[n]$$

which are the expectation values of the the kinetic energy, electron–nucleus and electron–

electron operators. The number of electrons is

$$N = \int n(\mathbf{r}) d\mathbf{r}$$

Often we pull out the universal functional

$$F[n] = \left\langle \Psi \left| \hat{T} + \hat{V}_{ee} \right| \Psi \right\rangle$$

(Ψ is the ground state many-electron wavefunction) and write

$$E_{\text{tot}} = F + V_{\text{en}} = F + \int n(\mathbf{r}) v_{\text{ext}} d\mathbf{r}$$

where v_{ext} is the external potential (*i.e.*, that due to the nuclei). Note that v_{ext} is a potential energy, not an electric potential. In addition, we pull out from F the classical Coulomb self energy of the inhomogeneous electron gas, namely the Hartree energy,

$$F = E_{\text{H}} + G$$

which defines the universal functional, G , which contains all the contributions to the total energy from exchange and correlation, and the interacting part of the kinetic energy. The second Hohenberg–Kohn principle states that the ground state density is that which minimises the total energy: this requires a constrained minimisation,

$$\frac{\delta}{\delta n} \left\{ E_{\text{tot}}[n] - \mu \left(\int n(\mathbf{r}) d\mathbf{r} - N \right) \right\} = 0$$

in which μ is a Lagrange multiplier. This leads to the Euler–Lagrange equation

$$\begin{aligned} \frac{\delta E_{\text{tot}}}{\delta n} &= v_{\text{ext}} + V_{\text{H}} + \frac{\delta G}{\delta n} \\ &= \mu \end{aligned}$$

where, the $\delta/\delta n$ being a functional derivative with respect to the function $n(\mathbf{r})$,

$$V_{\text{H}} = \frac{\delta E_{\text{H}}}{\delta n}$$

is the “Hartree potential” (again, actually a potential energy) and

$$\begin{aligned} \mu &= v_{\text{ext}} + V_{\text{H}} + \frac{\delta G}{\delta n} \\ &= \left(\frac{\partial E_{\text{tot}}}{\partial N} \right)_{v_{\text{ext}}} \end{aligned} \tag{3.1.1}$$

is the zero temperature chemical potential, or variation of the total energy with respect to an infinitesimal change in electron number at fixed external potential.

In DFT the zero of energy is the energy of all the electrons and nuclei infinitely separated (the nuclei are not disassembled) so E_{tot} and μ are both referred to the DFT energy zero. On the other hand, if we make the choice that the zero of energy is the average potential energy of the electrons in the metal then we have

$$\bar{V} = \overline{v_{\text{ext}}} + \overline{V_H} = 0$$

and we may define

$$\mu_e = \mu - \bar{V} = \frac{\delta G}{\delta n} \quad (3.1.2)$$

as the “chemical potential of the electron in the metal.” The overbar denotes a spatial average, say, over a unit cell of the metal crystal. We shall adhere to the convention that we call μ_e the “chemical potential” and that it is always measured from the “mean inner potential”, \bar{V} .

3.2 Inner potential difference

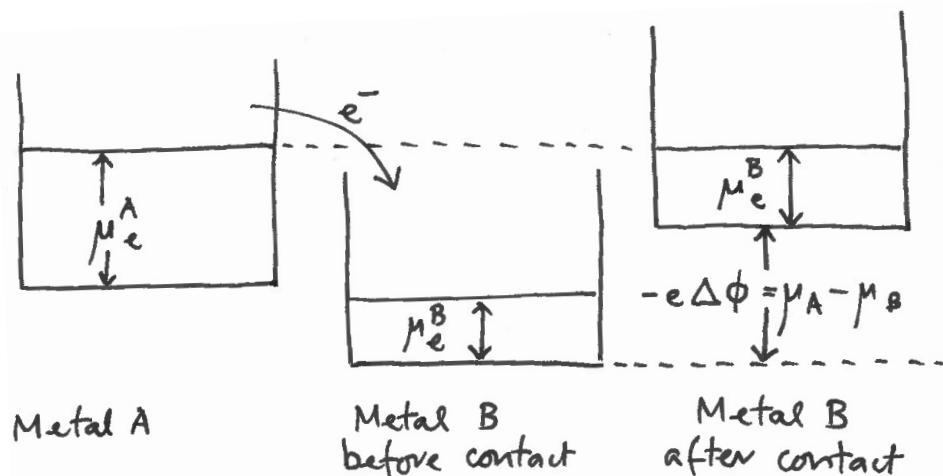


FIGURE 3-2

Consider two metals, A and B (figure 3-2). The Fermi energies of electrons in metals A and B will not be the same; therefore if I put specimens of the two metals into electrical contact, as for example at the $M_2|M'_1$ interface in (2.1) (or if I connect them with a wire) then if, say, $\mu_A > \mu_B$, relative to the DFT zero of energy, electrons will tend to flow from metal A to metal B. However in doing so, each metal will become charged, resulting in a shift in the potential energy, \bar{V} , of the electrons, and this will introduce an electric potential difference, $\Delta\phi = \phi_B - \phi_A$ between interior points in the two metals. As the electric potential in metal A becomes increasingly positive and in metal B negative then transfer will be resisted until the Fermi levels align by virtue of the shift in the potential energies in each metal. This is illustrated in figure 3-2. It is clear by construction that energy levels are shifted so that $-e\Delta\phi = \mu_e^A - \mu_e^B$. We therefore have, in equilibrium,[†]

$$\mu_e^A - e\phi_A = \mu_e^B - e\phi_B \quad (3.2.1)$$

[†] Suppose N electrons are transferred from metal A to metal B. If we refer the total energy to the average potential energy, \bar{V} , in each metal and hence define $\bar{E}(N) = E_{\text{tot}} - \bar{V}$ as

where $-e$ is the charge on the electron. The electric potential across the metal junction is sketched in figure 3–3. Because a metal is a conductor, all the excess charge resides at the interface.

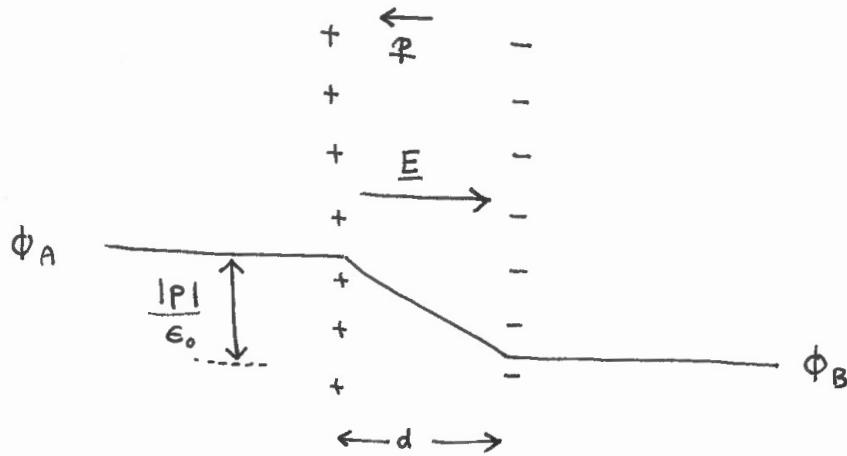


FIGURE 3–3

The charge averaged over the area of the interface forms a one dimensional distribution of charge density, $\delta\rho(x)$, if x is the cartesian component normal to the interface. This generates a dipole moment per unit area, \mathbf{p} . If we treat the double layer as a capacitor, as illustrated in figure 3–3, then the electric field is zero to either side and is constant and equal to σ/ϵ_0 in the gap of width d where σ is the charge per unit area. Therefore the electric potential drop acrosss the interface is

$$\phi_B - \phi_A = -\frac{1}{\epsilon_0} \sigma d = \frac{1}{\epsilon_0} p \quad (3.2.2)$$

in SI units. (Note that p is negative since \mathbf{p} points in the negative x -direction.) This is the “inner potential difference”, or “Galvani potential difference”. Following conventional, if cumbersome, notation we must write this as [†]

$$\phi_B - \phi_A = {}^B\Delta^A\phi \quad (3.2.3)$$

the total energy once N electrons have been added to the metal, then the total energy of the assembly is $\bar{E}_A(-N) + \bar{E}_B(N)$ plus the energy stored in the capacitor that is created by the charge dipole layer at the interface—figure 3–3. Then if C is the capacitance,

$$\begin{aligned} \bar{E}(N) &= \bar{E}_A(-N) + \bar{E}_B(N) + \frac{1}{2} \frac{e^2 N^2}{C} \\ &= \bar{E}_A(0) - N \frac{\partial \bar{E}_A}{\partial N} + \bar{E}_B(0) + N \frac{\partial \bar{E}_B}{\partial N} + \frac{1}{2} \frac{e^2 N^2}{C} \\ &= \bar{E}_A(0) - N \mu_e^A + \bar{E}_B(0) + N \mu_e^B + \frac{1}{2} \frac{e^2 N^2}{C} \end{aligned}$$

If this is minimised with respect to N we obtain (3.2.1) after noting that by comparison with a flat plate capacitor, $-eN/C = \phi_B - \phi_A$.

[†] Not only is it ugly, it is awkward and confusing; but it can be useful to shorten formulas

The result (3.2.2) is much more general than it seems. As long as the one dimensional charge density, $\delta\rho(x)$, is zero on both sides far from the interface and that it integrates to zero between these limits so that there is a dipole but the interface is not charged, then the work done in carrying an electron from left to right across the dipole layer is

$$W_{\text{dipole}} = -e(\phi_B - \phi_A) = -\frac{1}{\epsilon_0} ep \quad (3.2.4)$$

Briefly, the reasoning is this. The perturbation in charge density, $\delta\rho$, that creates the dipole layer is zero far to the left and far to the right of the interface and so is zero for all $x < a$ and $x > b$ where $x = a$ and $x = b$ are points in the interior of metals A and B respectively. The difference in potential $\phi_B - \phi_A$ is the work done in taking a unit test charge from $x = a$ to $x = b$ and this is minus the integral of the electric field, $E(x)$, between $x = a$ and $x = b$,

$$\begin{aligned} \phi(b) - \phi(a) &= - \int_a^b E dx = - \int_a^b E \left(\frac{d}{dx} x \right) dx \\ &= \int_a^b x \frac{dE}{dx} dx + [Ex]_a^b \\ &= \frac{1}{\epsilon_0} \int_a^b x \delta\rho(x) dx \\ &= \frac{1}{\epsilon_0} p \end{aligned}$$

We inserted a “one” in the first line and integrated by parts with the boundary term vanishing since there is no electric field in the interior of the metal. The third line follows from Poisson’s equation,

$$\frac{dE}{dx} = -\frac{d^2\phi}{dx^2} = \frac{1}{\epsilon_0} \delta\rho(x)$$

and the integral in the third line is by definition the dipole moment of the charge distribution.

It must be recalled that $\phi_B - \phi_A$ *cannot be measured*. It may have been sensible to call this the “contact potential”, and indeed Bockris does so, but this phrase is reserved for a subtly different electric potential difference between two metals in contact which *is* measurable and is the subject of the next section.

3.3 Contact potential

There is no doubt that the electric potential at a point “just outside” the surface of a metal, say 10^{-5} cm distant, is not the same as the electric potential at infinity (out of

when we add lots of PDs together. I am following Bockris and John West in putting the superscripts in the same order on both sides of (3.2.3). Fawcett, and Cheng and Sprik place them the other way around. This notation is probably best avoided: Schmickler and Santos don’t use it.

reach of all charges and fields). The reason for this is that as electrons spill out of the surface of the metal into the vacuum they create a charge dipole layer exactly as envisaged in figure 3–3 if metal B is replaced by vacuum. The details of the rearrangement of charge, both at the atomic level and as averaged over thousands of surface atoms depends on the indices of the crystal face and at the macroscopic level on the state of the surface—its roughness, contamination by adsorbates, oxidation products and so on. So each actual surface of a metal specimen will have a different distribution of polarisation (bound) charge which will give rise to stray electric fields outside the metal. These particularly arise at the corners of a single crystal or as “patch fields” which are external electric field lines connecting the surfaces of different grains in a polycrystalline sample. The existence of this electric potential is proved beyond doubt by experiments first made by Kelvin. The simplest realisation is to place the faces of two metals, or different faces of two single crystals of the same metal, into the form of a capacitor so that the two plane surfaces are parallel and separated by a distance d . If there exists an electric potential difference $\Delta\psi$ between points close to each surface then there must be an electric field, E , and surface charge densities $\pm\sigma$ such that

$$\Delta\psi = Ed = \frac{\epsilon_0\sigma}{d}$$

by analogy with a parallel plate capacitor. If the surfaces are moved further apart or closer together such that d changes but $\Delta\psi$ is to remain the same then the surface charge density must change and this will lead to a measurable current if the two metals are connected through an ammeter. This is indeed observed; and if in addition to the ammeter a battery and potentiostat are introduced into the circuit then a bias potential may be imposed. When this bias potential is exactly equal and opposite to $\Delta\psi$ then no current will flow when d is altered and this measured bias potential provides a *measurement* of $\Delta\psi$. This is the Kelvin probe. The bias potential that exactly opposes the contact potential is called the *compensation potential*. For two metals, A and B, the measured difference in outer electric potential, $\psi_B - \psi_A$ is called the *contact potential* difference. It is not the same as the inner potential difference (3.2.3) which is not measurable but which does contribute to the total PD measured across an electrochemical cell due to the use of different metal electrodes and electrical connectors.

3.4 Work function

The Kelvin probe can also be used to measure the work function (see Fawcett, section 8.7 for details of how this is done). It is easy to get confused by what is meant by work function and so here I will attempt to stay well grounded in either experiment or the density functional theory. However the two approaches actually give slightly different definitions of work function. Loosely stated the work function of a metal is the amount of work needed to remove an electron from the metal (as observed for example in thermionic emission or the photoelectric effect). Naturally an electron that has the highest (kinetic) energy will be the easiest to remove so the electron will originally be at the Fermi surface.

- Kittel defines the work function as “...the difference in potential energy of an electron between the vacuum level and the Fermi level”. The vacuum level, according to

Kittel is “...the energy of the electron at rest at a point sufficiently far outside the surface so that the electrostatic image force on the electron may be neglected—more than 100Å [10⁻⁶ cm] from the surface.” Different crystal surfaces have different work functions. For example tungsten has these work functions.

surface	work function (eV)
(100)	4.63
(110)	5.25
(111)	4.47

This table reflects the fact stated earlier that the electric potential is not the same just outside different faces of the same metal.

2. The definition of work function in DFT is,

$$W = [V(\infty) + E_{\text{tot}}(N - 1)] - E_{\text{tot}}(N) \quad (3.4.1)$$

In words: this is the difference in total energy between a piece of metal containing N electrons, and the same piece containing $N - 1$ electrons plus the potential energy of an electron at infinity. This definition can be made consistent with the first by replacing $V(\infty)$ with $-e\psi$ where ψ is the “outer electric potential” associated with the metal surface.

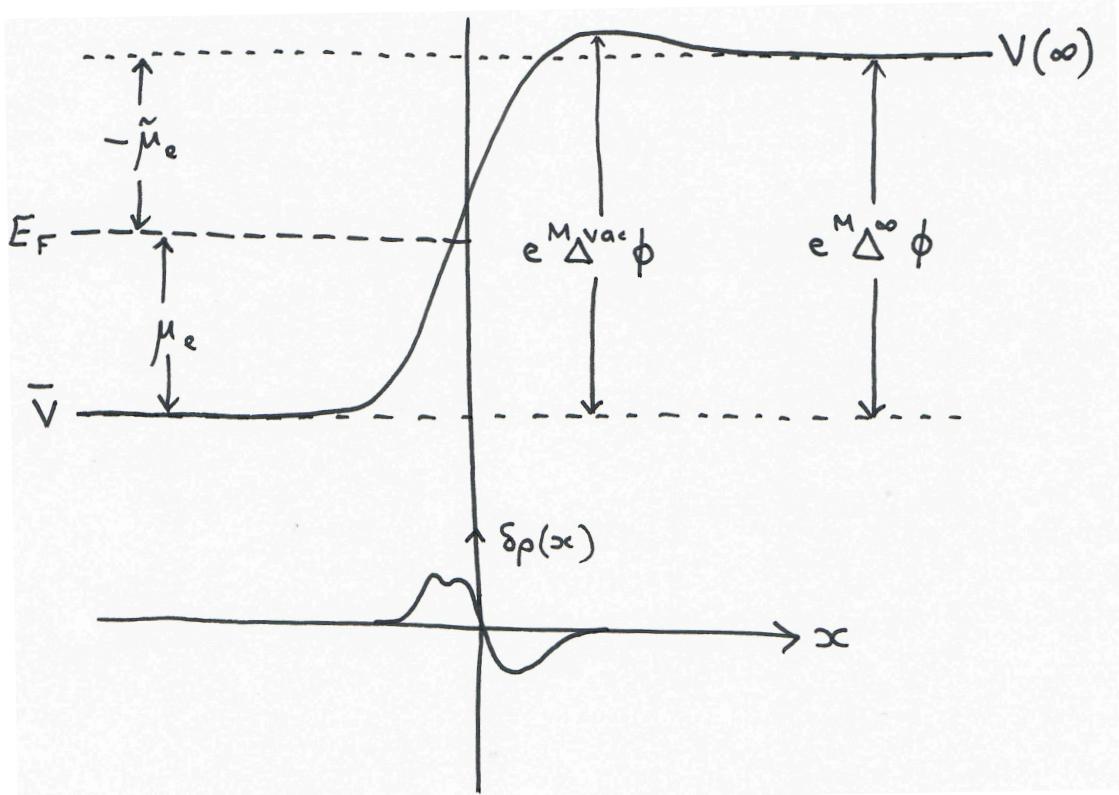


FIGURE 3-4

A way to picture the description embodied in (3.4.1) is to modify figure 3-1 to include the presence of a surface and vacuum.[†] Figure 3-4 shows the metal to the left with the

[†] By “vacuum” we really mean gas phase. In fact in the vacuum outside a metal there is

quantities \bar{V} , E_F and μ_e as in figure 3–1. To the right is the vacuum, and the potential energy of an electron is now sketched as increasing from left to right up to $V(\infty)$ as $x \rightarrow \infty$. Kohn and Lang show that without approximation in DFT, (3.4.1) is formally and exactly equal to

$$W = V(\infty) - \mu \quad (3.4.2)$$

in which μ is given by (3.1.1). Lang and Kohn then add and subtract \bar{V} and arrive at the formula

$$W = \underbrace{(V(\infty) - \bar{V})}_{\text{dipole potential}} - \underbrace{(\mu - \bar{V})}_{\mu_e} = e^m \Delta^\infty \phi - \mu_e \quad (3.4.3)$$

where ${}^m \Delta^\infty \phi = \phi_m - \phi_\infty$ (see equation (3.2.3) and footnote) is the difference in electric potential between the interior of the metal and infinity, and μ_e is the chemical potential as defined in (3.1.2). Note that ${}^m \Delta^\infty \phi$ is *positive* because the electric potential is more positive in the metal than outside (that's why the electrons are trapped inside). The first term in the last equation is $-e {}^\infty \Delta^M \phi = e {}^m \Delta^\infty \phi > 0$.

To make contact with experimental measurement and to allow for variations of work function with crystal orientation of the surface we may replace ${}^m \Delta^\infty \phi$ with

$${}^m \Delta^{\text{vac}} \phi = \phi - \psi = \chi > 0$$

where ψ is the electric potential at the vacuum level and $\phi = -\bar{V}/e$ is the electric potential in the interior of the metal. Both ϕ and ψ are relative to the electric potential at infinity. The “dipole (electric) potential” is (3.2.2)

$$\chi = -\frac{p}{\epsilon_0} \quad (p < 0)$$

and $q\chi$ is the work done in taking a test charge, q , from the vacuum level to the interior of the metal through the dipole layer of strength p per unit area which arises from the perturbation of the charge density from its bulk distribution due to the creation of the surface (figure 3–3). This difference in density is sketched in figure 3–4.

Finally, note that if $\phi \equiv {}^m \Delta^\infty \phi$ is the electric potential in the metal relative to infinity, then it is clear from figure 3–4 that we may define a quantity by construction

$$-\tilde{\mu}_e + \mu_e = e\phi$$

from which we define the “electrochemical potential” of the electron as

$$\tilde{\mu}_e = \mu_e - e\phi \quad (3.4.4)$$

It is then clear that since from (3.4.3) $W = e\phi - \mu_e$, the work function is equal to minus the electrochemical potential of the electron,

$$W = -\tilde{\mu}_e$$

a finite probability of finding an electron according to the Fermi–Dirac distribution. If there were not then there would be no possibility of equilibrium between the condensed and the gas phase.

It is also evident that (3.2.1) states that in equilibrium the electrochemical potentials of electrons in each metal are equal, which is the usual statement of equilibrium. It is very important to note that μ , μ_e and $\tilde{\mu}_e$ are *not* different quantities. They are the same quantity but referred to different zeros of energy. This is analogous to chemical potentials in chemical thermodynamics which are only defined with respect to some standard state.

3.4 Contact potential again

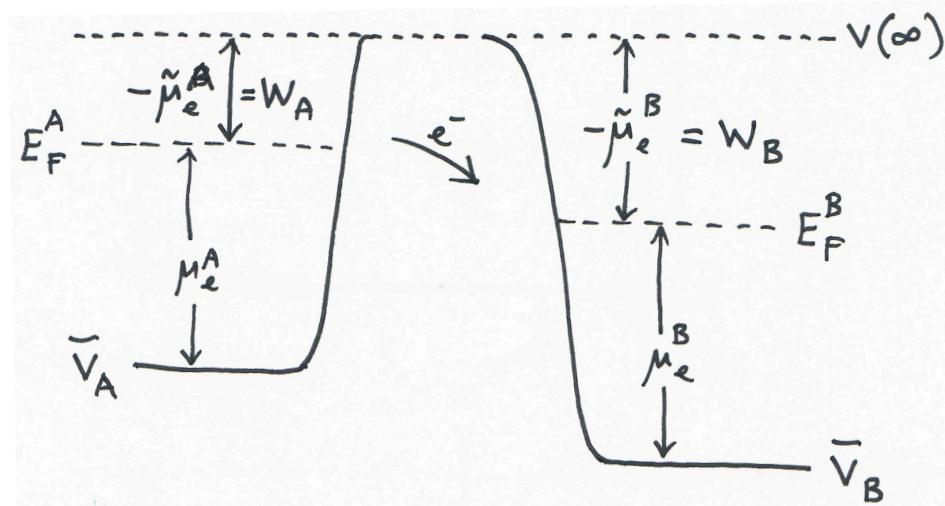


FIGURE 3-5

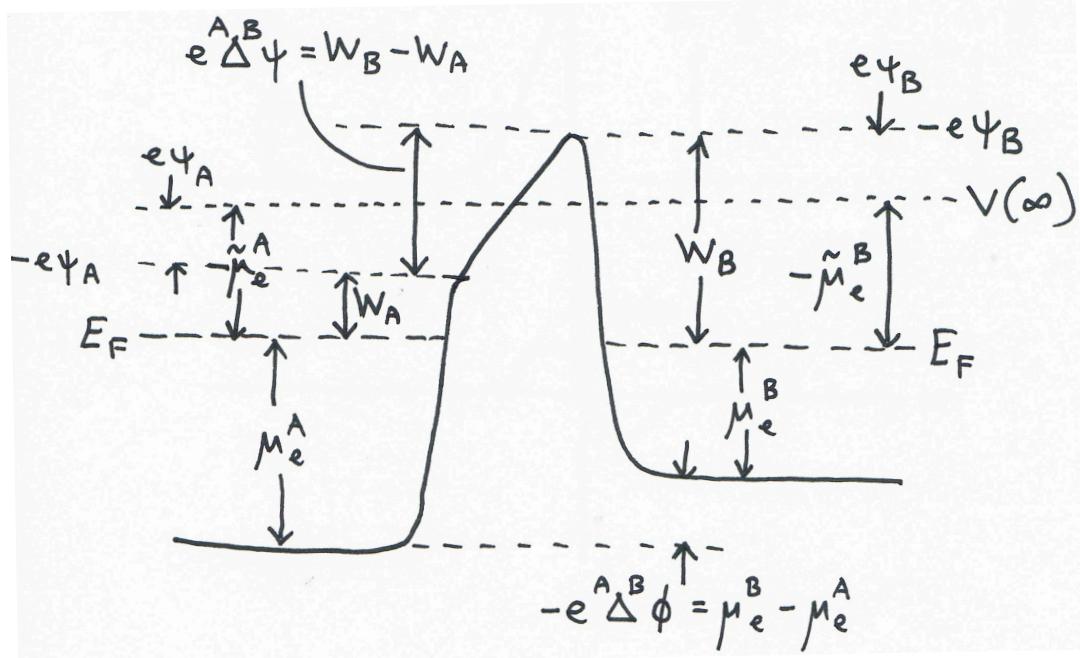


FIGURE 3-6

We can now return to the experiment in which two metals are electrically connected. Figure 3-5 shows energy diagrams for metals A and B before they are connected. These are two diagrams as figure 3-4 with energy levels for each metal referred to the vacuum zero of energy. Because the Fermi energy of metal A is higher than that of metal B we

expect that when they are connected electrically by a wire, electrons will flow so as to equalise the Fermi energies. This was already demonstrated to be the equilibrium condition in section 3.2. The condition for equilibrium is $\tilde{\mu}_e^A = \tilde{\mu}_e^B$ and this is demonstrated in Figure 3–6, adapted from Cusack, which is a cartoon of the energy levels once the metals are electrically in contact. The solid line shows $-e$ times the electric potential in the two metals and in the vacuum separating them. The slope in the electric potential is exactly the electric field that exists in the gap between two metal surfaces in Kelvin’s experiment. Because of the transfer of electrons both metals are charged, and so the electric potential in each metal is uniformly shifted. Metal A is positively charged and so its electric potential is raised and consequently its electronic energy levels are lowered. (It’s a real nuisance that electrons are negatively charged—should we blame JJ Thomson? On the other hand it does make you think—figures 3–4 and 3–5 would be “upside down” if we were plotting electric potential, or if you like, electrons flow uphill. The same issue crops up in semiconductor band diagrams in textbooks.)

It is clear now that the work function is *not* minus the electrochemical potential if the metal is charged. Instead as seen from figure 3–6, by construction, we have the more general formula

$$W = -e\psi - \tilde{\mu}_e \quad (3.4.5)$$

where ψ is the electric potential “just outside” the metal.

The difference between the electric potentials just outside the two metals is $\psi_B - \psi_A$ and is called the contact potential; either by construction or by subtracting (3.4.5) for two metals and noting that their electrochemical potentials are equal when in contact, we see that

$$W_B - W_A = -e(\psi_B - \psi_A)$$

In words: *the difference in “outer potential” of two electrically connected metals is equal to $-1/e$ times the difference in work function*. We also see that the difference in inner potentials is $+e$ times the difference in chemical potentials, which is consistent with (3.2.1).

The following table shows some Fermi energies, μ_e , (taken from Moruzzi, Janak and Williams) and work functions (taken from Ashcroft and Mermin). All are in eV; the inner potential difference in Volts is just the difference in Fermi levels, if two of the metals are in contact. The difference in outer potential in Volts is the difference in work functions.

	Li	Mg	Al	Ag	Cu	Zn	Fe	Ti
μ_e/eV	4.4	5.9	8.4	6.5	8.6	8.3	11.3	8.7
W/eV	2.4	3.6	4.3	4.3	4.4	4.3	4.3	4.3

Interestingly, as long as we know μ_e and W for two metals, we can infer both potential differences, ${}^A\Delta^B\phi$ and ${}^A\Delta^B\psi$, which appears in contradiction of the observation that only ${}^A\Delta^B\psi$ is *measurable*. The point is, I suppose, that μ_e is calculated, not measured.

4. Electrochemical potential; real potential

4.1 Electrochemical potential

The meaning of chemical potential is explained in some detail in the Appendix to these notes. At constant temperature and pressure, it is the infinitesimal change in free enthalpy with respect to the mole number of species i keeping the mole numbers of all other species unchanged,

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,p,n_j \neq i} \quad (\text{A2.7})$$

At constant temperature and volume, replace G with F , the free energy. Since G and F are always expressed with respect to some arbitrary zero of energy, the chemical potential is similarly undetermined to within a constant. This is usually expressed in terms of a standard chemical potential. For example, if you imagine taking a single atom or molecule from some reservoir and adding it to the body in question, then you may take the reservoir to be gas phase at standard temperature and pressure or pure substance; these two choices involve different amounts of reversible work and so the chemical potentials referred to these two standard states will not be the same. Just as in electrostatics, thermodynamics is about *changes* in energy; it is only necessary for consistency to keep to the same zero of energy when comparing energies. In electrolytes and solutions the chemical potential refers to a complicated process. Adding a molecule or atom to a solution involves much complex rearrangement of its environment as the host solvent molecules and preexisting solute molecules rearrange themselves to accommodate the new species. Indeed the work done will depend on the concentration of the species in question already present if the solute molecules are interacting. For example, we speak of the *free enthalpy of solvation* which includes the reversible work done by the solvent as its molecules create the so-called solvation shell (at constant T and p). Again, one defines a standard free enthalpy of solvation, for example at standard temperature and pressure and at unit activity (see the Appendix, section 3) of the solute.

If the species in question is *charged* then a polar solvent such as water will reorganise its molecular dipole moments the best to screen the electric field introduced by the charged species. Equation (A2.7) still defines the chemical potential but it is conventional to separate out from the chemical potential that part which is a result of the chemistry alone—solvation, effects of the concentration, temperature and pressure—and that part of the work done due to having to place the charge of the species i (namely $q_i = ez_i$ where z_i is called the “charge number” of the species) into the interior of a phase whose inner potential, ϕ , is different to that of the reservoir. If we agree that the species is at zero potential with respect to infinity in the reservoir, then we define the electrochemical potential as

$$\tilde{\mu}_i = \mu_i + Fz_i\phi \quad (4.1.1)$$

This introduces the *Faraday constant*, F , which is the charge on a mole of protons. It is $+e$ times the Avogadro number. You may ask, how can I redefine the chemical potential (A2.7) so as to somehow exclude all effects due to the charge on the species i ? After all the structure of the solvation shell will depend on the charge. This means that the new μ_i in (4.1) appears to be ill-determined. The only recourse is to recognise that $\tilde{\mu}_i$

in (4.1) is the same quantity as defined rigorously in (A2.7) and so the new μ_i in (4.1) is then uniquely determined by the operation of subtracting $Fz_i\phi$ from the chemical potential. I'm sorry—this is a horrible clash of notation: I have used μ_i to mean two different things in the same section. It shan't happen again... What I should have done is either written that (A2.7) is the chemical potential for an *uncharged* species, or to have used $\tilde{\mu}_i$ in the left hand side. To my mind, as in the case of the electron, μ and $\tilde{\mu}$ are anyway the same quantity, but referred to different zeros of energy.

4.2 Real potential

In the electrochemical literature it is common to introduce an additional potential energy, which is related to the work function and is useful when work functions are defined for chemical species. We start by rewriting (4.1.1)

$$\tilde{\mu}_i = \mu_i + Fz_i(\psi + \chi)$$

(see (5.1) in the following section). We have to ignore the subtle differences in potential between infinity, and the vacuum level where the electric potential is ψ (figure 3–4). Then if the phase is uncharged, we assert that $\psi = 0$ and give a new name to the electrochemical potential in those circumstances: the *real potential* of species i ,

$$\alpha_i = \mu_i + Fz_i\chi \tag{4.2.1}$$

The point is that this is a measurable thermodynamic property. In our definition number 1 of the work function in section 3.4, it should be clear that the work function of a metal is minus the real potential of an electron in the metal.

5. Outer electric potential

In electrochemistry the electrode and the solution are treated in their continuum electrostatics quite similarly. Certainly both are assumed perfect conductors in which the electric potential is uniform up to the surface or interphase and there is no electric field unless a current is flowing. For example we later will see that a work function can also be associated with the electrolyte; but this is a more involved quantity, firstly because the object withdrawn to the vacuum level is not usually an electron—it's an ion—and secondly because the work done depends on the state of solvation and the concentration of the ion in solution.

The inner electric potential difference (3.2.3) is called the difference in “Galvani potential”, always given the symbol ϕ . Whereas under some limiting circumstances as we have seen the Galvani potential difference can be measured (for example, for a polarisable single electrode connected to a reversible reference electrode) in principle the absolute Galvani potential within the bulk of an electrode or electrolyte cannot be measured. What *can* be measured is the so called outer electric potential, or “Volta potential” as we have seen in the Kelvin probe experiment. And so it is common to split up the

Galvani potential into two terms, the Volta potential, ψ , and the remainder called the dipole potential, χ . The latter is obviously not measurable. We have

$$\phi = \psi + \chi \quad (5.1)$$

Or, at an interface, A|B, (see equation (3.2.3) and footnote)

$${}^B\Delta^A \phi = {}^B\Delta^A \psi + {}^B\Delta^A \chi \quad (5.2)$$

The Volta potential difference, $\psi_B - \psi_A$, according to Bockris is “the contribution to the potential difference across an electrified interface arising from the charges on the two phases.” Imagine the process of taking a positive test charge from infinity where $\phi = 0$ and carrying it through the surface to the inside of an uncharged phase (electrode or electrolyte). We are asked to imagine first carrying the test charge to a certain point, P_B , just outside the surface where it is very close but still outside the range of the image potential. Now the image potential falls off like $1/r$ so rigorously speaking there is no such point; but this is also implicit in the definition of work function, above. For now, believe that this is possible and conclude that the electric potential at this point is still zero since the test charge has not encountered any electric field in its journey. Now suppose that the phase is charged. Again we imagine taking our test charge to P_B and now there will be positive or negative work done and the electric potential at P_B will not be zero. Because the point P_B is “outside the range of the image force” the work done is entirely due to moving the charge through the electric field of the charged phase. The electric potential thus defined at point P_B is the outer electric potential, or *Volta potential*, ψ . By construction, the Volta potential of an uncharged phase is zero. This procedure is illustrated both for solution and the electrode in figure 5–1.

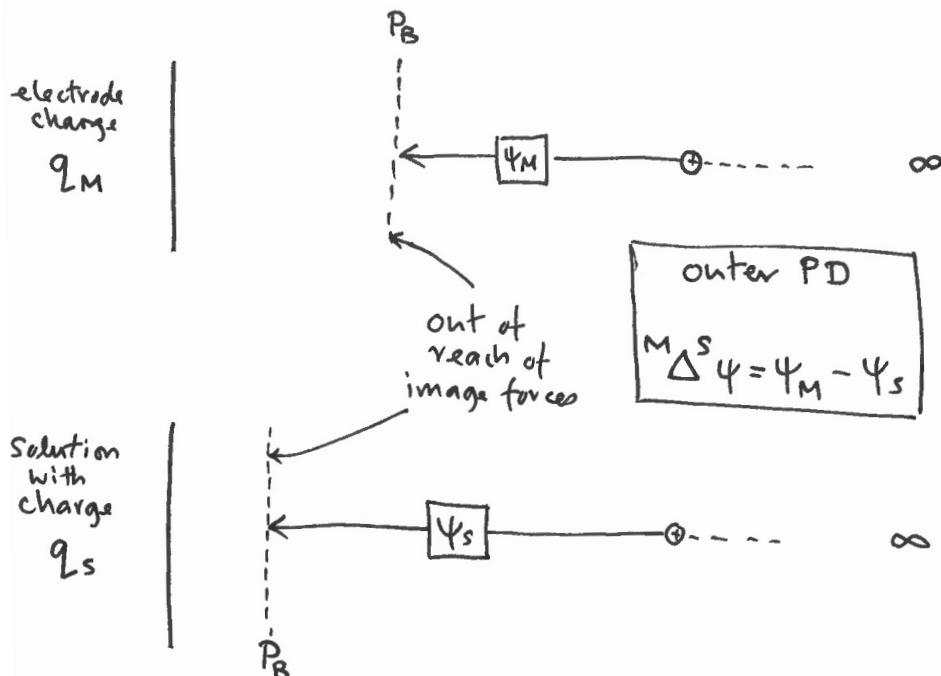


FIGURE 5–1

Bockris devised a thought experiment to clarify what is meant by the Volta potential difference across the interphase separating bulk metal (electrode) and bulk solution

(electrolyte). This is illustrated in figure 5–2. The entire assembly at the top of the figure shows the charged electrode on the left, carrying a charge q_M and possessing a dipole layer at its surface where it meets the solution carrying a charge q_s . This charge is distributed near the surface of the solution since we assume that the solution is a conductor and will not support an electric field. The possibly charged layer of solution abutting the interface may be quite wide before giving way to electrolyte with bulk properties; this layer is the Gouy–Chapman or Stern double (or triple) layer and as in the case of the metal we expect a complex rearrangement of molecules giving rise to dipole (and presumably higher multipole) moments. The simplest assumption as in the metal is to allow a one dimensional distribution, $\delta\rho(x)$, which integrates to zero so that the work done in taking a test charge across the double layer is equal to ϵ_0^{-1} times the dipole moment per unit area. Now Bockris imagines separating the interphase so that all the metal is exposed to vacuum as is all the solution. He then makes both halves neutral so that any dipole layer due to the charging or due to contact between the two phases vanishes. He then recharges the two phases to the original charges, q_M and q_s ; and uses a test charge as in figure 5–1 to find the outer potentials, ψ_m and ψ_s . Then the Volta potential difference across the interphase is ${}^m\Delta^s\psi$.

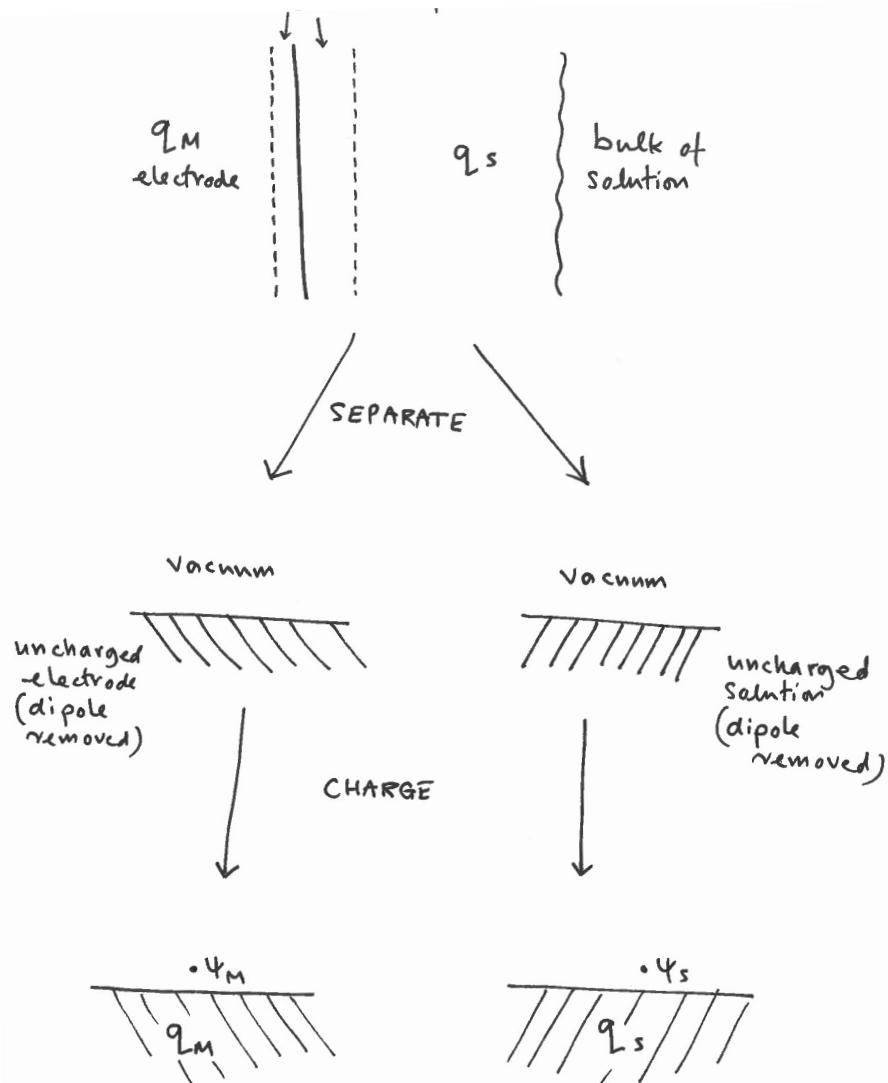


FIGURE 5–2

In order to clarify the dipole potential difference across the same interphase as in figure 5–2, Bockris devised a second thought experiment as illustrated in figure 5–3. The interphase is again dismantled and discharged; but this time the arrangement of molecules that made up the dipole, or “double”, layer in the solution is reassembled on the surface of the solution. Now the separated phases exposed to vacuum are uncharged but have the dipole layers reinstated.

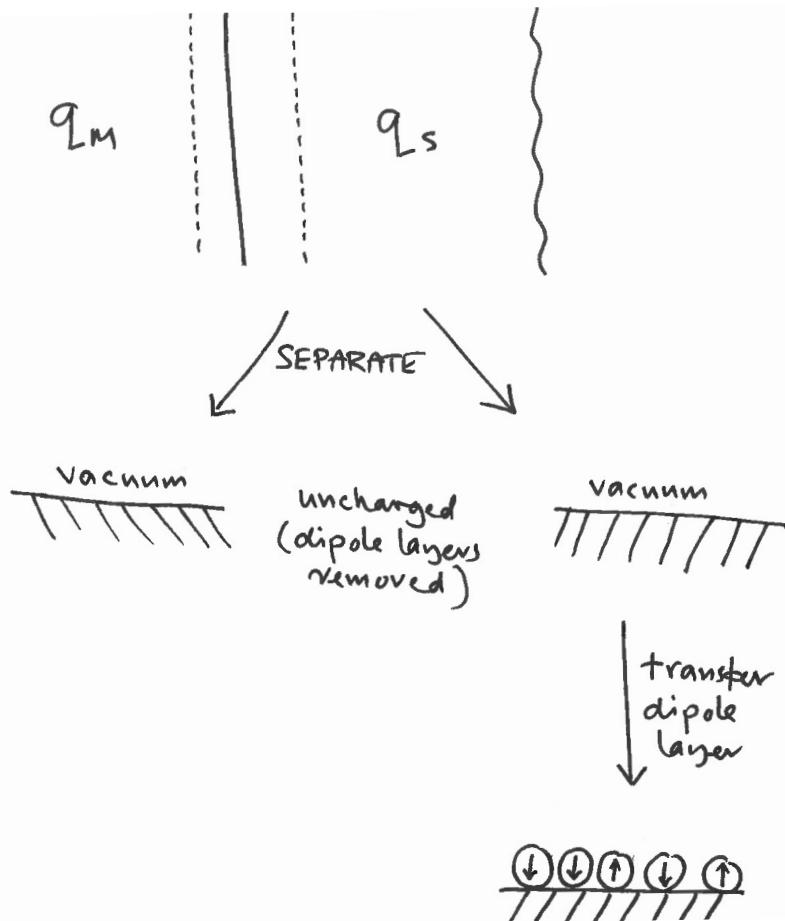


FIGURE 5–3

A positive test charge is now carried from infinity to the interior of the phase where it has bulk properties, see figure 5–4. This defines the χ -potential difference as ${}^m\Delta^s\chi$. In the case of the metal in figure 5–4 it is worthwhile to compare χ_m with the work function. There are two differences. Firstly, the test charge is positive and not negative and it travels in the other direction. A subtle point we'll come back to is that the test charge is not an electron so there will be no exchange contribution to the image force. Secondly in the second thought experiment we bring in the test charge from infinity and not from the vacuum level. The reason for the difference in electric potential between infinity and the vacuum level of a neutral metal described in section 3 is that a crystal naturally has several faces possibly with dissimilar dipole layers. Then the work required to move a test charge from infinity to the vacuum level just outside each face is affected by the electric fields produced by the changes in charge distribution at the corners of the crystal and as a result of differences in surface crystal orientation. *In all of Bockris's thought experiments and in electrochemical textbooks this subtle point is avoided. It is implicitly*

assumed that the extent of the surfaces and interfaces involved is infinite.[†] The process envisaged in Bockris's thought experiment number two is illustrated in figure 5–5. In the upper figure which illustrates the outer, Volta potential associated with the solution, ψ_s is only non zero because the solution carries a net charge $q_s \neq 0$. If the solution were uncharged then the implication is that the potential at infinity is the same as at the point P_B (which we may as well call the Bockris point); indicating that the surface is of infinite extent so there is no electric field.

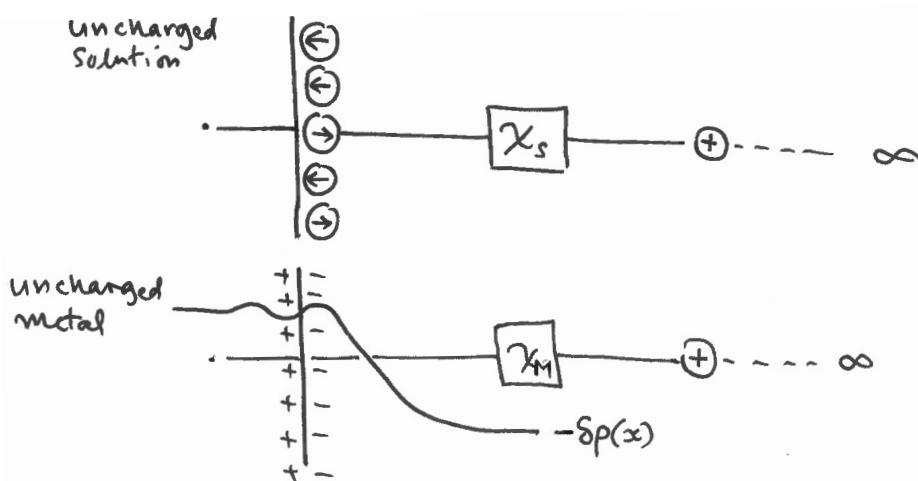


FIGURE 5-4

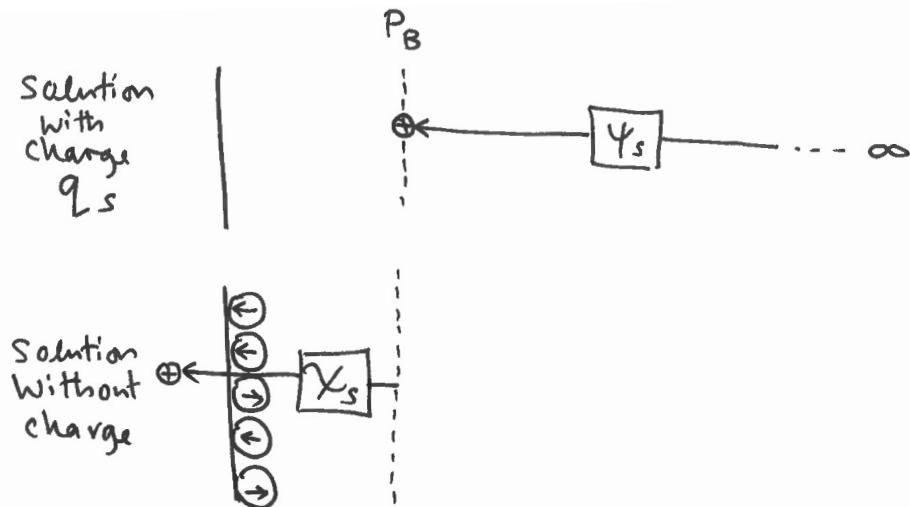


FIGURE 5-5

[†] Imagine two thin sheets of metal joined along their flat surfaces. If these really are infinite in the y and z directions in the sheet then to take a test charge from $-\infty$ to ∞ requires a journey through the three dipole layers and the associated work must be done: hence $\phi(-\infty) \neq \phi(\infty)$. On the other hand if the area of metal normal to x is large but not infinite then the test charge can be taken around the edge keeping essentially at infinity for the whole trip, in which case $\phi(-\infty) = \phi(\infty)$.

Figure 5–5 illustrates the construction of the inner potential from the outer potential and the dipole potential (5.1),

$$\phi_s = \psi_s + \chi_s \quad (5.3)$$

A test charge is taken from infinity to the Bockris point; the solution is discharged while retaining its dipole double layer and the test charge is carried across the double layer into the bulk of the solution where the electric potential is ϕ_s relative to infinity. In conclusion, for any of the interfaces indicated by vertical bars in, say, (2.1) the electric potential difference between two contiguous phases, figure 2–3, were it measurable, would be the difference in inner, or Galvani, potentials which is a sum of the differences of Volta and dipole potentials associated with each bulk phase.

Bockris's thought experiments can be summarised in the diagram shown as figure 5–6 and taken from Fawcett. The difference in Galvani, or inner, potential, ${}^\alpha\Delta^\beta\phi$, between phases α and β , be they each either electrode or solution, can only be made rigorously by reference to a surface of each phase exposed to vacuum. For each phase a test charge is taken from infinity to the Bockris point and the work done per unit charge is the outer, or Volta, potential of each phase. If either phase is uncharged then this is zero for that phase. To avoid the complications of Bockris's second thought experiment we have to assume that all of the work against the electric field due to the charged phase has now been done so that as the test charge is now moved from P_B to the interior where the properties are uniform and bulk-like, the only work done is that against the dipole layer—this can be any charge distribution, $\delta\rho(x)$, as long as it integrates to zero between P_B and the interior point. The dipole potential is then just ϵ_0^{-1} times the dipole moment per unit area. The vertical arrows in the figure show the electric potential differences between the two Bockris points which is ${}^\alpha\Delta^\beta\chi$, and between the two interior points which is ${}^\alpha\Delta^\beta\phi$. This electric potential potential difference is the result of taking a test charge from the interior of the β phase to its Bockris point, on to infinity and then back to the Bockris point of the α phase and finally into the interior of that phase. This results in

$${}^\alpha\Delta^\beta\phi = -\chi_\beta - \psi_\beta + \psi_\alpha + \chi_\alpha$$

This confirms equation (5.2).

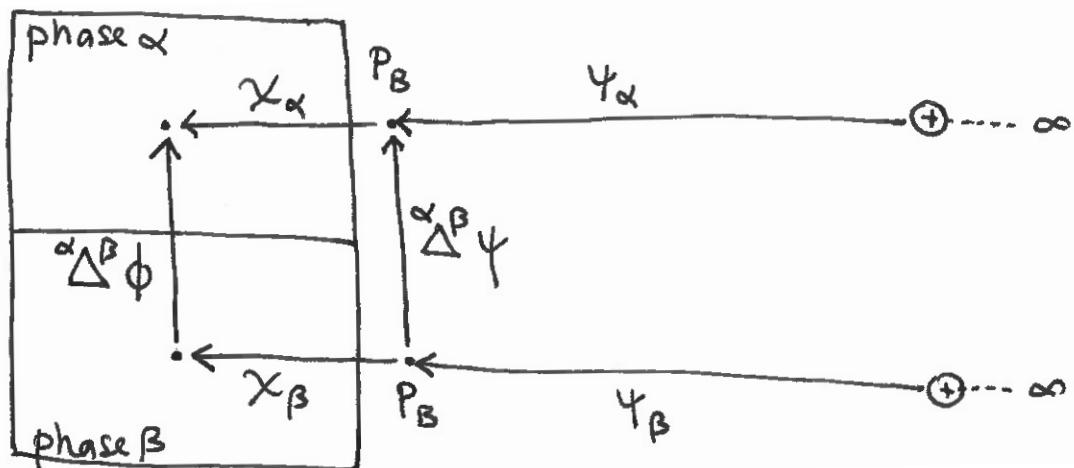


FIGURE 5–6

6. The Bockris point

How far is the Bockris point from the surface of a charged metal or electrolyte? Neglecting for the moment the image potential, suppose that the phase is in the shape of a sphere of radius r and carries a total charge Q . Then the outer electric potential with respect to a point at infinity at a distance s from the surface is

$$\psi_Q = \frac{1}{4\pi\epsilon_0} \frac{Q}{r+s}$$

Both Bockris and Fawcett assert that since $s \ll r$ we may write this as

$$\psi_Q = \frac{1}{4\pi\epsilon_0} \frac{Q}{r}$$

indicating that the outer potential is constant. Bockris argues that an appropriate distance is 10^{-5} cm; Fawcett suggests it is 10^{-4} cm. Both these are beyond the position of the vacuum level for a metal which Kittel states is greater than 10^{-6} cm. It seems unsatisfactory to neglect s altogether since an elementary Taylor expansion results in

$$\frac{1}{r+s} = \frac{1}{r} \left(1 - \frac{s}{r}\right)$$

to first order and this is not constant, but is linear in s . The image potential seen by a test charge q at s , with respect to infinity, if the sphere is conducting and grounded is (see Griffiths)

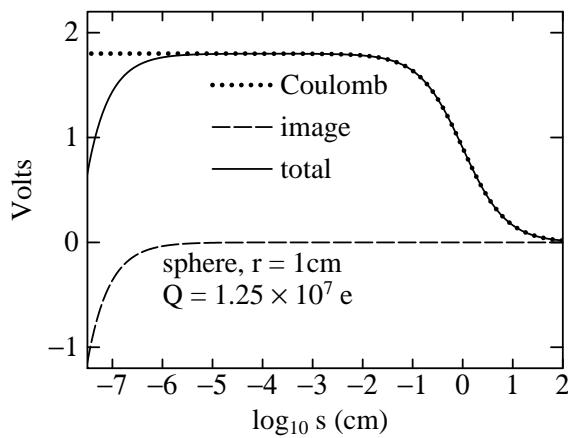
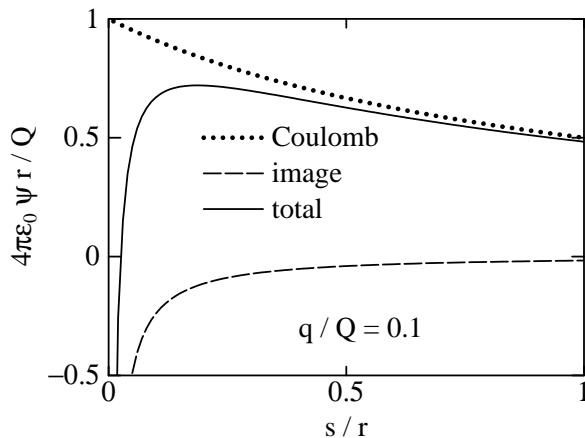
$$\psi_i = -\frac{1}{4\pi\epsilon_0} \frac{1}{2} \frac{qr}{s(s+2r)}$$

The total Volta potential, Coulomb plus image, is hence

$$\begin{aligned} \psi &= \frac{1}{4\pi\epsilon_0} \left(\frac{Q}{r+s} - \frac{1}{2} \frac{qr}{s(s+2r)} \right) \\ &= \frac{1}{4\pi\epsilon_0} \frac{Q}{r} \left(1 - \frac{s}{r} + \frac{q}{Q} \left(\frac{1}{8} - \frac{1}{4} \frac{r}{s} \right) \right) + \mathcal{O}\left(\frac{s}{r}\right)^2 \end{aligned}$$

It's not obvious that this function is constant for any $s \ll r$ and when plotted as in figure 6–1, it clearly is not.

However this plots the case when the test charge is as much as one tenth of the charge on the sphere. If we take a more realistic case of $q = e$, and $Q = 1.25 \times 10^7 e$ which will charge a sphere of $r = 1$ cm to about a volt, then we are rescued by making a plot against $\log s$. This is done in figure 6–2. Now there is quite a wide plateau, and indeed these calculations are consistent with similar plots shown by Bockris. In conclusion, the Bockris point, as asserted by Bockris, is no closer than 10^{-5} cm from the surface. Infinity is seen to be at about 10–100 cm. On the other hand the image potential is very short ranged and as Kittel states is negligible at about 10^{-6} cm from the surface.



Note that in figure 6-2 the test charge is taken to be a proton (or positron or anti-muon). This is to acknowledge that this a classical electrostatic calculation and the exchange contribution to the image potential is not included as it should be for an electron.

7. Electron work function of an electrolyte

In order to analyse the potential difference across an electrochemical cell, as well as asking about the work function of the metals involved we may ask about the solutions. Sometimes the work function for an ionic species is required, and usually that is expressed in terms of the real potential, say, of species i in phase α (Cheng and Sprik). In addition we may ask for the work done in withdrawing an electron from an electrolyte. An elegant thought experiment by Schmickler and Santos illustrates this procedure and comes up with an operational definition of work function for an electrolyte. These authors imagine a metal-electrolyte interface with both phases also being exposed to vacuum. The idea is to try and transfer an electron from the solution to the metal via the vacuum. The solution contains equal numbers of moles of Fe^{++} and Fe^{+++} ions. The electron transfer is accomplished in the following five steps.

1. Take an Fe^{++} ion out of the solution and into the vacuum just above the surface of the solution. The amount of work required is minus $\Delta_{\text{sol}}^r G(\text{Fe}^{++})$, which is the *real* free enthalpy of solvation of the Fe^{++} ion. This is a measurable real potential, and it includes the work done against the surface electric dipole belonging to the solution.
2. Remove an electron from the Fe^{++} ion,



The work done is the third ionisation potential of iron, I_3 .

3. Return the Fe^{+++} ion to the solution. This gains us the real free enthalpy of solvation of the Fe^{+++} ion.
4. Transfer the electron from the Bockris point of the electrolyte to the Bockris point of the metal. The work done is

$$-e(\psi_m - \psi_s)$$

5. Lastly put the electron into the metal and gain its work function, W_m .

The total work done should be zero if the electrons are in equilibrium in the assembly, so the energy budget is

$$0 = -\Delta_{\text{sol}}^{\text{r}} G(\text{Fe}^{++}) + I_3 + \Delta_{\text{sol}}^{\text{r}} G(\text{Fe}^{+++}) - e(\psi_m - \psi_s) - W_m$$

or

$$-e(\psi_m - \psi_s) = W_m - [\Delta_{\text{sol}}^{\text{r}} G(\text{Fe}^{+++}) - \Delta_{\text{sol}}^{\text{r}} G(\text{Fe}^{++}) + I_3]$$

Recall that for two metals, A and B the difference in work functions is $-e$ times the difference in outer potentials. This implies that the “work function” of the electrolyte is the sum of terms in brackets,

$$W^s = \Delta_{\text{sol}}^{\text{r}} G(\text{Fe}^{+++}) - \Delta_{\text{sol}}^{\text{r}} G(\text{Fe}^{++}) + I_3$$

all three quantities on the right being measurable. However this work function depends on many things. It is the work function of the $\text{Fe}^{++}/\text{Fe}^{+++}$ “redox couple” since we have used iron ions as the vehicle for carrying the electron away from the solution. The work function would of course be different if we used other cations. It also depends on temperature and on the composition. It is commonplace to construct *standard* real potentials and work functions based in unit activity and standard temperature and pressure.

8. Work function and real potential of a species in an electrolyte

8.1 Electrochemical potential of an ion

The chemical potential of a pure substance as described in the Appendix is nothing other than the partial molar free enthalpy, reflecting the fact that free enthalpy is an extensive state function which is homogeneous and of first order. This allows us to derive equation (A2.10) for the case of a substance made up of more than one component. Whereas G is only determined to within an arbitrary zero of energy, one might think that μ is independent of the choice of zero since the derivative implies a *difference* in free enthalpy which ought to cancel out the dependence on that choice. This is true for a pure substance. On the other hand the chemical potential of a species i in a multi-component substance as expressed in equation (A3.1) is still undefined because we need to refer it to a “standard” chemical potential which depends only on temperature and pressure. This is because the differentiation in (A2.7) still concerns a thought experiment whereby the number of moles of component i is varied while keeping T , p and the mole numbers of all other components fixed. We are reversibly adding an infinitesimal number of moles, dn , and so the total change in free enthalpy is

$$G(n_1 \dots, n_i + dn_i, \dots, n_N) - (G(n_1 \dots, n_i \dots, n_N) + \mu_i^\circ dn_i \text{ (moles of } i \text{ in a reservoir)})$$

So the chemical potential is not independent of the zero of energy because it depends on the nature of the reservoir and the molar free enthalpy, μ_i° , of species i in the reservoir—this is the standard chemical potential. It may be the free enthalpy per mole in the pure substance solid state, or the gas phase, at standard T and p ; or it may be the free enthalpy per mole in a dilute solution. In solution chemistry, we talk of Henrian

and Raoultian standard states, and molar and molal standard states meaning that the species is in unit concentration either in moles per litre or moles per kg of solvent. Nonetheless in the thought experiment, although we need to describe the nature of the reservoir, we do not need to consider the journey that the fraction of a mole of species takes when it leaves the reservoir and arrives in the system under study.

Everything changes when we have the complication that the species i and the system (electrode or electrolyte) may be charged. (In normal circumstances in electrochemistry, electrolytes are neutral however). In that case the reversible work done in carrying a charged component from infinity to the interior of a phase, as we have seen, depends on the details of the surface dipole layer and upon the Galvani potential within the bulk of the phase. It is completely unreasonable to assert that the system is in the shape of a thin specimen infinitely extended in the plane. If that object is charged then the electric field is constant and the electric potential is linear in the distance from the sheet, so it diverges to $\phi = \pm\infty$ at infinity so there can exist no field-free infinity. As Cheng and Sprik emphasise, the electrochemical potential is only defined for a system of finite spatial extent. What, as far as I have found, no textbook acknowledges, is that the electrochemical potential *depends on the shape of the phase*. Moreover, many authors omit to acknowledge the difference between the electric potential at infinity and the Volta potential of an uncharged phase. This is clearly a problem with the definition of the *real potential* (section 4.2) in Fawcett, which author also confuses himself in whether the electron work function is measured with respect to the potential energy of the electron at infinity or at the Bockris point (Fawcett, section 6.6).

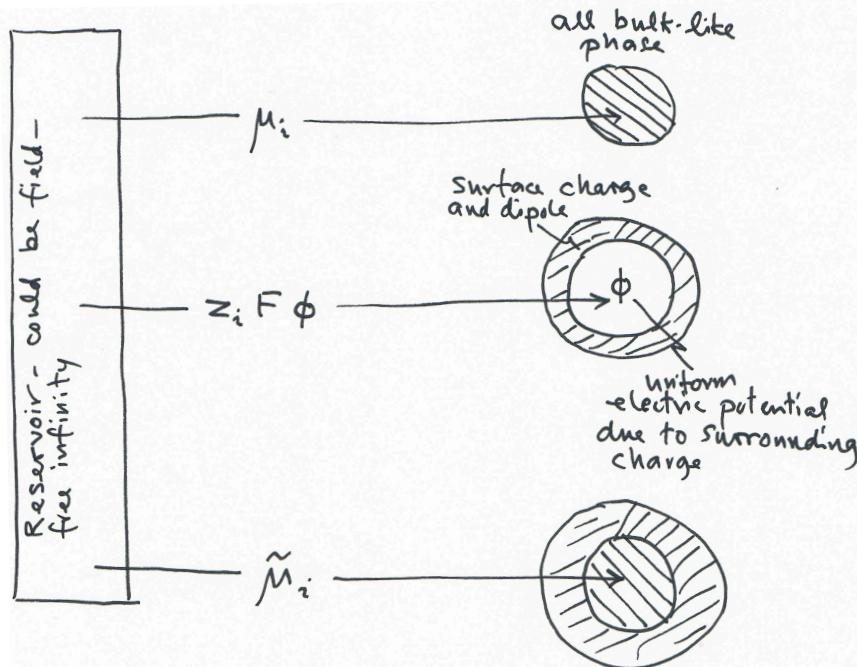


FIGURE 8-1

Figure 8-1 is adapted from Fawcett (and attributed to Parsons) to illustrate some of the points in this section. The upper cartoon is to illustrate the chemical potential. We imagine the system as being bulk-like and homogeneous up to its surface which is taken

as spherical. Since in the this case neither the phase nor the component is charged the shape is irrelevant. If however the phase *is* charged then the charge will reside at the surface (since we take electrolytes to be conducting) and there will be a charged surface dipole layer. The process shown in the lowest cartoon is the equivalent of the Bockris thought experiment in figure 5–5. Now instead of a test charge, we bring in the charged species i from infinity, past the Bockris point where the Volta electric potential is ψ , through the double layer and into the interior where the Galvani potential is ϕ . This serves to *define* the electrochemical potential, but it must be emphasised that this depends on, (*i*) the *shape* of the phase since the Volta potential depends on the distance from any corners and the presence of patch fields; and (*ii*) the details of the surface through which the component enters the phase if the surface is not isotropic. In the case of a liquid electrolyte the surface is almost certainly isotropic however. The centre cartoon is to illustrate how the electrochemical potential is divided, as in equation (4.1.1) into the electric work and the remainder. We imagine that the bulk has been excavated from the phase leaving the charged dipole layer surrounding empty space. The electric potential within the space is different from that at infinity due to the surface charge. Hence the reversible work per mole is $z_i F \phi$ where z_i is the charge number of component i and F is the Faraday constant.

Consider the case of one-to-one electrolyte, for example NaCl dissolved in water. The electrochemical potentials of the cation and anion, respectively are,

$$\tilde{\mu}_{\text{Na}^+} = \mu_{\text{Na}} + F\phi \quad ; \quad \tilde{\mu}_{\text{Cl}^-} = \mu_{\text{Cl}} - F\phi$$

Now the Galvani potential is in principle not measurable hence the *individual electrochemical potentials of ions are not measurable*; hence they are not proper thermodynamic quantities. This is a most important observation in electrochemistry, not to be ignored. What is measurable is the electrochemical potential of NaCl in the solution, since by addition the charge term cancels and we have

$$\tilde{\mu}_{\text{NaCl}} = \tilde{\mu}_{\text{Na}^+} + \tilde{\mu}_{\text{Cl}^-} = \mu_{\text{Na}} + \mu_{\text{Cl}} = \mu_{\text{NaCl}}$$

8.2 Ion work function of an electrolyte

The work function of an ion in an electrolyte is defined as the reversible work to remove one mole of ions from an *uncharged* solution, in which they are in a standard state of unit concentration and standard T and p , and taken to field-free infinity. The symbol for this normally is W_i^s for the work function of component i in a solution (superscript “s”) phase (Fawcett, Cheng and Sprik) but this fails to acknowledge that this is a standard state quantity as are the chemical potentials in its definition (8.2.1), so I will add a superscript to make this explicit,[†]

$$W_i^{\text{s},\circ} = \tilde{\mu}_i^{\text{g},\circ} - \tilde{\mu}_i^{\text{s},\circ} \quad (8.2.1)$$

[†] Instead of the superscript “s” meaning solution, Cheng and Sprik substitute a superscript α to distinguish possible different phases in a multiphase system. This won’t be necessary here and anyway I recoil from the symbol α_i^α which is hardly aesthetic.

Recall that the electrochemical potential of a component i in a phase depends on its concentration, T and p . The superscript \circ on $\tilde{\mu}_i^{\text{s},\circ}$ is to indicate that this is the electrochemical potential of component i when it finds itself in the solution phase at unit concentration and standard T and p . In all that follows we assume that the solution is uncharged (although the species i is not) then $\phi_s = \psi_s + \chi_s = \chi_s$ (5.3); and since the electric potential at infinity where the ion is in the gas phase is zero, we have,

$$W_i^{\text{s},\circ} = \mu_i^{\text{g},\circ} - \mu_i^{\text{s},\circ} - z_i F \chi_s = \mu_i^{\text{g},\circ} - \alpha_i^{\text{s},\circ} \quad (8.2.2)$$

where $\alpha_i^{\text{s},\circ}$ is the standard real potential (energy) of species i in the solution phase (4.2.1),

$$\begin{aligned} \alpha_i^{\text{s},\circ} &= \mu_i^{\text{s},\circ} + z_i F \chi_s = \tilde{\mu}_i^{\text{s},\circ} - z_i F \psi_s \\ &\equiv \tilde{\mu}_i^{\text{s},\circ} \end{aligned} \quad (8.2.3)$$

The first line follows because $\tilde{\mu} = \mu + q\phi$; the second because in the uncharged solution the Volta potential ψ_s is zero. Combining (8.2.2) and (8.2.3), we have

$$W_i^{\text{s},\circ} = \mu_i^{\text{g},\circ} - \tilde{\mu}_i^{\text{s},\circ} \quad (8.2.4)$$

If we write this as $W_i^{\text{s},\circ} = -\tilde{\mu}_i^{\text{s},\circ} + \mu_i^{\text{g},\circ}$, then an interpretation in words is that the ion work function in its standard state in an electrolyte is the work to remove the ion to the vacuum level plus the subsequent work to transfer it from vacuum into gas at standard T and p . I think that once it is in gas phase we must assume that it is accompanied by an equal number of ions of opposite charge so that the gas is neutral.

For an uncharged solute species, i , and an uncharged solvent, we define the standard free enthalpy of solvation as the reversible work at constant T and p needed to take a mole of solute molecules from the gas phase at standard T and p , and insert them into the solvent to achieve unit concentration at standard T and p ,

$$\Delta_{\text{sol}}G_i^\circ = \mu_i^{\text{s},\circ} - \mu_i^{\text{g},\circ} \quad (8.2.5)$$

Cheng and Sprik apply the same formula to define a standard free enthalpy of solvation for a charged species.[†] In that case we could write, using (4.1.1) and (8.2.4),

$$\begin{aligned} -\Delta_{\text{sol}}G_i^\circ &= \mu_i^{\text{g},\circ} - \mu_i^{\text{s},\circ} \\ &= \mu_i^{\text{g},\circ} - (\tilde{\mu}_i^{\text{s},\circ} - z_i F \phi_s) \\ &= W_i^{\text{s},\circ} + z_i F \phi_s \\ &= W_i^{\text{s},\circ} + z_i F \chi_s \end{aligned}$$

Therefore,

$$\Delta_{\text{sol}}G_i^\circ = -(W_i^{\text{s},\circ} + z_i F \chi_s) \quad (8.2.6)$$

[†] I have difficulty with this, because to me μ_i for a charged species is not physically motivated as I pointed out in comments after equation (4.1.1), above. To me, $\tilde{\mu}_i$ is well defined (although not directly measurable if the component is charged) and μ_i is just the *remainder* after the electric work has been subtracted.

which is equation (8) in Cheng and Sprik. We have already encountered the free enthalpy of solvation in section 7, above. There we were concerned with the *electron* work function of an electrolyte, but in order to remove an electron we used an iron ion as the carrier. However in that case since the ion is charged the correct quantity is the *real* solvation free enthalpy, which in contrast to (8.2.5) is,

$$\Delta_{\text{sol}}^{\text{r}} G_i^{\circ} = \tilde{\mu}_i^{\text{s},\circ} - \mu_i^{\text{g},\circ} \quad (8.2.7)$$

Then it follows from (8.2.3) and (8.2.2) that

$$\begin{aligned} \Delta_{\text{sol}}^{\text{r}} G_i^{\circ} &= \alpha_i^{\text{s},\circ} - \mu_i^{\text{g},\circ} \\ &\equiv -W_i^{\text{s},\circ} \end{aligned} \quad (8.2.8)$$

Finally since the quantities defined in this section are all standard free enthalpies, it is unsurprising that in the case that the solution is not at unit concentration, we use (A3.1),

$$\begin{aligned} \alpha_i^{\text{s}} &= \alpha_i^{\text{s},\circ} + RT \ln a_i \\ \Delta_{\text{sol}}^{\text{r}} G_i &= \Delta_{\text{sol}}^{\text{r}} G_i^{\circ} + RT \ln a_i \end{aligned} \quad (8.2.9)$$

where the activity is defined with respect to unit concentration. I don't think that people ever write $W_i^{\text{s},\circ} = W_i^{\text{s}} + RT \ln a_i$ which is probably why they don't put a superscript \circ on the ion work function.

8.3 Confused and confusing remarks

The object in taking the notes in this direction and to this stage is to put us in a position to follow the authoritative paper by Cheng and Sprik which takes central importance since it provides a qualitative link between experimental electrochemistry and electronic structure theory. There remain for me at least two outstanding questions which have led me into confusion.

1. We insist in accord with electrochemical practice that solutions and electrolytes are globally uncharged. This is implicit in the development from equation (5) to (8) in Cheng and Sprik although they do not state explicitly that $\psi_s = 0$. In that case (8.2.3) and (8.2.8) are *identities*. This means that there is *absolutely no point* in inventing either the real potential or the ion work function. The real potential of charged species i is identical to its electrochemical potential when it's in an uncharged solution. The ion work function is minus the (real) standard free enthalpy of solution. In my view we needn't call this "real" because for a charged species, the free enthalpy of solution (8.2.5) is unphysical so we can use the term "free enthalpy of solution" for the measurable quantity (8.2.9) and (8.2.7).
2. Cheng and Sprik state, "The electrochemical potential, $\tilde{\mu}_i$, is the negative of the reversible work for transferring a particle from solution all the way to infinity. A separate potential $[\alpha_i]$ is introduced for the [negative of the] work of bringing the particle to just outside the surface of a phase. This is the real potential..." This seems to me to be unnecessarily complicated because it is then assumed that the solution is uncharged and hence $\psi_s = 0$ and $\alpha_i = \tilde{\mu}_i$. For even an uncharged

metal the electric potential at the vacuum level (Bockris point) is not the same as at infinity. In an extreme case like tungsten the difference in outer potentials at different crystal faces is as much as 0.75 V. In the case of an electrolyte this difference is apparently ignored in electrochemistry. I think I can see the justification for this. Firstly a liquid has isotropic surfaces; as long as it is uncharged then the outer potential is unlikely to depend on its shape. However if the electrolyte is in physical contact with a metal electrode at an interphase then surely the molecular structure and dipole moment will be very different to that at the surface of the electrolyte. In that case can we continue to imagine that the electrolyte surface is isotropic? It is interesting that the difference in inner potential between two metals in contact can be found from bulk properties, namely the Fermi level, μ_e , *independent of reference to the vacuum* as we've seen in section 3.2. On the other hand in the Bockris thought experiments and the developments in later sections, we have exploited the decomposition of the inner potential into outer and surface (or dipole) potentials (5.3). In that sense the inner potential difference is accessible by reference to the vacuum level. Perhaps this rescues us from the issue that with an interphase the electrolyte boundaries are not isotropic: by constructing the inner potential difference by reference to the surface that faces vacuum (or presumably that part of the electrolyte exposed to air in an electrochemical cell) we avoid the need to worry about the molecular structure of the interphase (figure 5–6).

9. Equilibrium and reversible work of the electrochemical cell

9.1 Standard reaction free enthalpy

Suppose we are interested in a chemical reaction



in which n_A moles of a substance A and n_B moles of a substance B react to form n_C moles of a substance C and n_D moles of a substance D. On the left are *reactants*, and on the right are *products*. If this reaction occurs spontaneously then the change in free enthalpy is, in view of (A2.10),

$$\Delta G = (n_C \mu_C + n_D \mu_D) - (n_A \mu_A + n_B \mu_B) < 0$$

If we use (A3.1) to expand the chemical potentials we get

$$\begin{aligned} \Delta G &= (n_C \mu_C^\circ + n_C RT \ln a_C + n_D \mu_D^\circ + n_D RT \ln a_D) \\ &\quad - (n_A \mu_A^\circ + n_A RT \ln a_A + n_B \mu_B^\circ + n_B RT \ln a_B) \end{aligned}$$

Gathering terms, we have

$$\begin{aligned} \Delta G &= (n_C \mu_C^\circ + n_D \mu_D^\circ) - (n_A \mu_A^\circ + n_B \mu_B^\circ) \\ &\quad + (n_C RT \ln a_C + n_D RT \ln a_D) - (n_A RT \ln a_A + n_B RT \ln a_B) \\ &= \Delta G^\circ + RT \ln \frac{a_C^{n_C} a_D^{n_D}}{a_A^{n_A} a_B^{n_B}} \\ &= \Delta G^\circ + RT \ln K \end{aligned}$$

This serves to define for us the *standard free enthalpy change* of the reaction (9.1.1)

$$\Delta G^\circ = (n_C \mu_C^\circ + n_D \mu_D^\circ) - (n_A \mu_A^\circ + n_B \mu_B^\circ) \quad (9.1.2)$$

and the *equilibrium constant*,

$$K = \frac{a_C^{n_C} a_D^{n_D}}{a_A^{n_A} a_B^{n_B}} \quad (9.1.3)$$

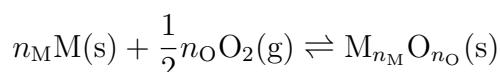
It is easy enough to generalise (9.1.2) and (9.1.3) to the case of any number of reactants and products using summation and product signs. If the reaction (9.1.1) is in equilibrium, that is the rate of reaction to the right is equal to the rate of reaction to the left, then $\Delta G = 0$ and we have

$$K = e^{-\Delta G^\circ / RT}$$

This is called the “van’t Hoff isotherm” and given the standard free enthalpy of the reaction allows us to calculate the equilibrium activities of the component species. Observe that the equilibrium constant is not constant at all—it depends exponentially on the temperature.

I have used the generic superscript \circ to indicate the standard state. But once we specify a reaction I can use for example \bullet if the component is in the pure substance standard state, or $^\ominus$ if the substance is in the one bar gaseous state; and I can mix these in the formula-pair (9.1.2) and (9.1.3) as long as I use the same standard for μ° and the activity.

In electrochemistry, and in corrosion in particular, we are interested in the oxidation of metals. For a metal M, the reaction of interest is



where “s” stands for solid phase and “g” stands for gas phase. The standard free enthalpy of formation of the oxide is (9.1.2)

$$\Delta_f G^\circ = \mu_{M_{n_M} O_{n_O}}^\bullet - n_M \mu_M^\bullet - \frac{1}{2} n_O \mu_{O_2}^\ominus$$

We are free to choose zeros of energy such that the free energy of a pure substance in its standard state is zero. Some measured standard free enthalpies of formation (in kilojoule per mole) with respect to the pure reactants are in the following table.

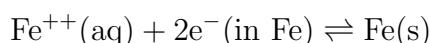
MgO	TiO ₂	NiO	Al ₂ O ₃	FeO	Fe ₂ O ₃	Fe ₃ O ₄	ZnO	H ₂ O
-300	-90	-245	-1700	-270	-820	-1120	-350	-285
Au ₂ O ₃	MnO	Mn ₂ O	HgO	SiO ₂	AgO	V ₂ O ₃	RuO ₂	
-2	-360	-460	-60	-860	-10	-65	-250	

All these are negative, which reflects Humankind’s struggle through the copper, bronze and iron ages to win metals from their ores and the fight to prevent these returning to

the oxide—that is, corroding and oxidising. The only metal found in its noble state in the earth is gold (apart from some meteoric iron) which is why it is highly prized. At the end of civilisation when Gaia returns to her natural owners there will be no trace of the metals that were won from their ores during the disastrous evolutionary experiment of combining a large fore-brain with opposable thumbs (with acknowledgment to Amory Lovins).

9.2 Inner potential difference across a metal–solution interface

In section 3.2 we calculated the inner potential difference across a metal–metal interface: it's the difference in Fermi levels. Now we are in a position to do the same at an electrode–electrolyte interface. Consider the “half-cell” in which Fe metal is immersed in a solution of Fe^{++} ions. The following chemical reaction will occur,



“aq” means in aqueous solution. The free enthalpy change is

$$\begin{aligned}\Delta G &= \mu_{\text{Fe}} - 2\tilde{\mu}_{\text{e}} - \tilde{\mu}_{\text{Fe}^{++}} \\ &= (\mu_{\text{Fe}}^\bullet + RT \ln a_{\text{Fe}}) - (\mu_{\text{Fe}^{++}}^\infty + RT \ln h_{\text{Fe}^{++}} + 2F\phi_s) - 2(2\mu_{\text{e}}^{\text{Fe}} - F\phi_m)\end{aligned}$$

$h_{\text{Fe}^{++}} = x_{\text{Fe}^{++}}$ is the Henrian activity (mole fraction) of iron ions (Appendix, section 3.2) and the superscript ∞ indicates the infinite dilution standard state. $\mu_{\text{e}}^{\text{Fe}}$ is the (standard) chemical potential of the electron in the metal, (3.4.4), $\tilde{\mu}_{\text{e}} = \mu_{\text{e}} - F\phi_m$. [†] Having immersed the metal in the electrolyte, when the half-cell comes to equilibrium $\Delta G = 0$ and we have,

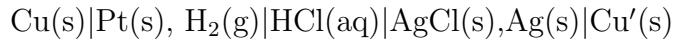
$$\begin{aligned}2F(\phi_m - \phi_s) &= (\mu_{\text{Fe}^{++}}^\infty - \mu_{\text{Fe}}^\bullet + 2\mu_{\text{e}}^{\text{Fe}}) + RT \ln \frac{h_{\text{Fe}^{++}}}{a_{\text{Fe}}} \\ &= \mu_{\text{Fe}^{++}}^\infty + 2\mu_{\text{e}}^{\text{Fe}} + RT \ln x_{\text{Fe}^{++}} \quad (9.2.1a) \\ &= \mu_{\text{Fe}^{++}}^m + 2\mu_{\text{e}}^{\text{Fe}} + RT \ln m_{\text{Fe}^{++}} \quad (9.2.1b)\end{aligned}$$

The second line follows because the standard free enthalpy of the pure solid iron is zero. The last line re-expresses the chemical potential in the unimolar standard state (Appendix, section 3.3 (A3.12b)) in which m_i is the normalised concentration in moles per kilogram of solvent. Equation (9.2.1) should allow us to deduce ${}^m\Delta^s\phi$ from the concentration of iron ions in the electrolyte. However this can only be known relative to some other half cell: the absolute value of $\mu_{\text{Fe}^{++}}^m$ can only be measured relative to another ion as the electrochemical potential of a charged ion is not measurable (section 8.1). Relative to the hydrogen ion, the standard (unimolar) chemical potential of the Fe^{++} ion is -85 kJ/mol . We could complicate the problem by imagining an iron alloy; in which case we'd need to know the standard free energy of formation of the alloy, its iron content and the activity coefficient of Fe in the alloy.

[†] Compare this with (3.4.4). I will not distinguish in the notation between free enthalpy *per mole* and free enthalpy *per particle*. It will be obvious from the context.

9.3 Open circuit voltage—electromotive force

Consider the electrochemical cell shown in figure 9–1. On the left is a hydrogen electrode; the electrolyte is hydrochloric acid, HCl; the right hand electrode is silver on which silver chloride has been deposited in lumps by the action of the acid. The “cell diagram” is



The Pt and Ag electrodes are connected via copper wire through a high impedance voltmeter, so that no current flows but the electric potential difference, $\overset{\text{Cu}'}{\Delta}\overset{\text{Cu}}{\phi}$ can be measured. We wish to calculate this “open circuit” voltage and determine how much useful work can be done by the cell if a current is allowed to flow. By convention the oxidation reaction is placed on the left, the reduction reaction on the right, and if current is allowed to flow then positive charge will flow from left to right through the electrolyte and negative charge (electrons) will flow from left to right through the external circuit.

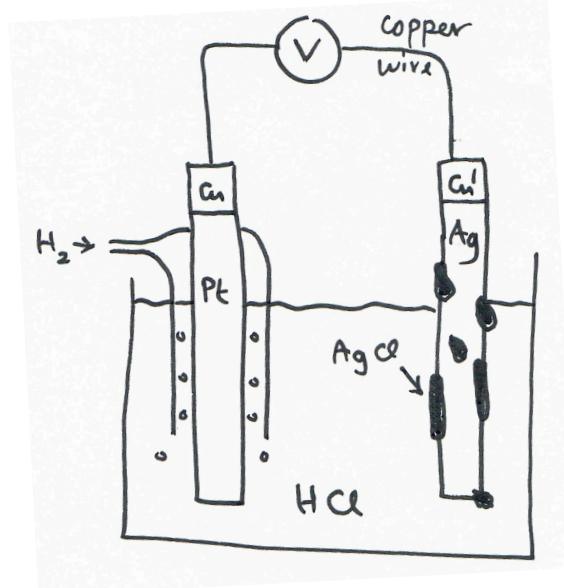
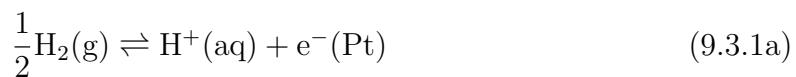


FIGURE 9–1

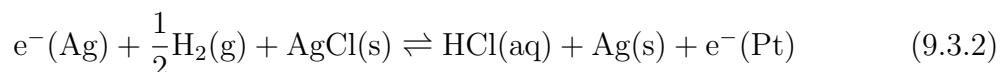
The oxidation reaction at the anode is



and the reduction reaction at the cathode is



The combined reaction is



The change in free enthalpy is

$$\begin{aligned} \Delta G &= \mu_{\text{HCl}} + \mu_{\text{Ag}} + \tilde{\mu}_{\text{e}}(\text{Pt}) - \left(\frac{1}{2}\mu_{\text{H}_2} + \mu_{\text{AgCl}} + \tilde{\mu}_{\text{e}}(\text{Ag}) \right) \\ &= \mu_{\text{HCl}}^m + \mu_{\text{Ag}}^\bullet - \frac{1}{2}\mu_{\text{H}_2}^\ominus - \mu_{\text{AgCl}}^\circ + RT \ln \frac{m_{\text{HCl}}}{p^{1/2}} + (\tilde{\mu}_{\text{e}}(\text{Pt}) - \tilde{\mu}_{\text{e}}(\text{Ag})) \quad (9.3.3\text{a}) \\ &= \Delta G^\circ + RT \ln m_{\text{HCl}} + (\tilde{\mu}_{\text{e}}(\text{Pt}) - \tilde{\mu}_{\text{e}}(\text{Ag})) \quad (9.3.3\text{b}) \end{aligned}$$

in which μ_{HCl}^m is the concentration of the acid in moles per kg of water in the electrolyte and p is the pressure of hydrogen as measured in bar. The molar free enthalpies of the pure hydrogen and silver can be taken as zero and the pressure of hydrogen is adjusted to one bar. The activities of the solid components are taken as one. In this way we have the *standard free enthalpy* for the reaction (9.3.2),

$$\Delta G^\circ = \mu_{\text{HCl}}^m - \mu_{\text{AgCl}}^\circ$$

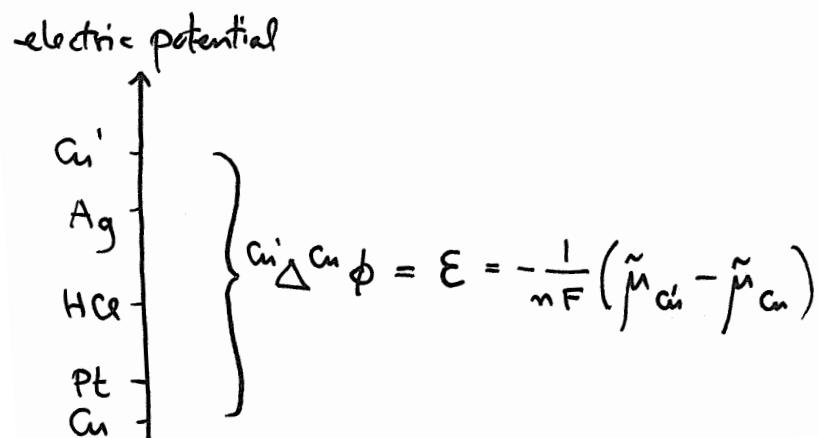


FIGURE 9-2

When both the reduction and oxidation reactions (9.3.1) come to equilibrium then at open circuit the free enthalpy change is zero, $\Delta G = 0$, even though the electrons in the electrodes are not at equilibrium. However since each electrode is in contact with its copper wire the electrons across these junctions will have the same electrochemical potential and while

$$\tilde{\mu}_e(\text{Pt}) = \tilde{\mu}_e(\text{Cu}) ; \quad \tilde{\mu}_e(\text{Ag}) = \tilde{\mu}_e(\text{Cu}') \quad (9.3.4)$$

the electrochemical potentials in the two wires connected across the voltmeter are not the same. At this stage it's helpful to draw a ladder diagram as in figure 2-3. This is shown in figure 9-2. The electric potential of the anode is negative compared to the electric potential of the cathode. That is, $\phi_{\text{Cu}'} < \phi_{\text{Cu}}$. Conventionally represented as the electrode on the left, the anode is the electron sink (figure 1-2) so a metal atom is losing an electron to become a cation which will migrate to the right through the electrolyte ("cations" migrate to the "cathode"). The electrons left behind being negatively charged serve to *lower* the electric potential on the anode.[†] The right hand electrode, the

[†] This is confusing because we learn, "anodes are positive and they corrode". True. If I turn the voltmeter into a battery and connect the positive terminal to the left hand electrode, this will remove electrons from the electrode, make its electric potential more positive and drive the oxidation (corrosion) of the electrode metal. In this case, the platinum is not corroding. The de-electronation reaction is the oxidation of hydrogen gas to hydrogn ions (protons).

cathode, is conversely more positive than the left hand electrode. The total potential difference across the electrochemical cell, as indicated in figure 9–2, is $\mathcal{E} = {}^{\text{Cu}'}\Delta^{\text{Cu}}\phi > 0$ and is called the “electromotive force” of the cell. It is measured in Volts. The existence of this non zero e.m.f. is due entirely to the difference in electrochemical potentials on the two electrodes. It must be true therefore that

$$\mathcal{E} = -\frac{1}{F}(\tilde{\mu}_e(\text{Ag}) - \tilde{\mu}_e(\text{Pt})) = -\frac{1}{F}(\tilde{\mu}_e(\text{Cu}') - \tilde{\mu}_e(\text{Cu}))$$

Putting this fact into (9.3.3) with $\Delta G = 0$ at open circuit, and using (9.3.4) we arrive at the formula we are looking for, namely,

$$-F\mathcal{E} = \Delta G^\circ + RT \ln m_{\text{HCl}} \quad (9.3.5)$$

All the quantities in (9.3.5) can be measured: the concentration of HCl is ours to control and the standard molar free enthalpies can be looked up in tables of data to obtain the standard free enthalpy change, ΔG° , for the cell reaction.

As to the amount of work that the cell might do, we note that at open circuit the cell reactions (9.3.1) are in equilibrium even though the electrochemical potentials of the electrons in the Pt and Ag electrodes are not. If we were to allow some current to flow through the external circuit, but *slowly*: then we may allow the cell to do some reversible work. If one mole of reactants is permitted to become one mole of products, then the change in free enthalpy is ΔG . If in the process n moles of positive charge are transferred from left to right through the electrolyte then an equal and opposite electronic charge, $-nF$, is transferred from left to right through the copper wire across an electric potential difference of $\Delta\phi = \mathcal{E}$, which will do an amount of work equal to $-nF\mathcal{E}$. *This statement lies at the heart of electrochemistry, batteries, fuel cells...* This is exactly how *chemical energy* is converted into *electrical energy*; and of course the reverse is also true: if the charge on $-nF$ moles of electrons is carried from right to left by a power source then one mole of product will be converted to one mole of reactant in the cell. This is how electricity is stored as chemical energy in a battery. Perhaps the most important equation in electrochemistry is the one that expresses the equivalence of chemical and electrical work—from the above argument it is clear that

$$\Delta G = -nF\mathcal{E} \quad (9.3.6)$$

The meaning of the number, n , can be a bit confusing. It is the number of electrons involved in the combined “redox” reaction. So in the case of (9.3.2), $n = 1$.

9.4 The electrochemical series

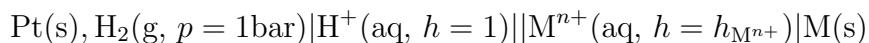
We've seen that we cannot measure a single electrode potential. Nevertheless it is very useful to rank them by comparing different metal single electrodes to a reference electrode under standard conditions. The reference usually used is the standard hydrogen electrode (SHE). It is evident from figure 9–2 that at least formally we can divide the electric potential drop across the cell into that due to the silver half cell and that due to the SHE.

$$(\phi_{\text{Ag}} - \phi_{\text{Pt}}) = (\phi_{\text{Ag}} - \phi_{\text{HCl}}) + (\phi_{\text{HCl}} - \phi_{\text{Pt}})$$

or

$${}^{\text{Ag}}\Delta^{\text{Pt}}\phi = {}^{\text{Ag}}\Delta^{\text{HCl}}\phi - {}^{\text{Pt}}\Delta^{\text{HCl}}\phi \quad (9.4.1)$$

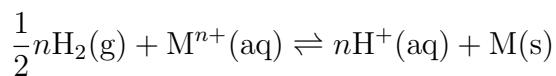
Suppose I am interested in a particular metal, M, which may be oxidised in an electrolyte, S, containing M^{n+} metal ions having a charge of ne . I can construct an electrochemical cell just as shown in figure 3–1, but with the SHE on the left,



For this cell I will have that the e.m.f. according to (9.4.1) is

$$\mathcal{E} = {}^{\text{m}}\Delta^{\text{s}}\phi - {}^{\text{m}}\Delta^{\text{s}}\phi = \mathcal{E}_{\text{M}}$$

essentially the difference between two half-cell potentials. By definition, \mathcal{E}_{M} is the *single potential* of the $\text{M}^{n+}(\text{aq})|\text{M(s)}$ electrode *on the SHE scale*. The cell reaction is



for which the free enthalpy change is

$$\begin{aligned}\Delta G &= \mu_{\text{M}}^\bullet + n\mu_{\text{H}^+}^m - \frac{1}{2}n\mu_{\text{H}_2}^\bullet - (\mu_{\text{M}^{n+}}^m + RT \ln h_{\text{M}^{n+}}) \\ &= -(\mu_{\text{M}^{n+}}^m + RT \ln h_{\text{M}^{n+}})\end{aligned}$$

(pure substance standard chemical potentials being zero). Since we arbitrarily set the e.m.f. of the SHE to zero, we have, using (9.3.6)

$$\begin{aligned}\mathcal{E}_{\text{M}} &= -\frac{\Delta G}{nF} \\ &= \frac{\mu_{\text{M}^{n+}}^m}{nF} + \frac{RT}{nF} \ln h_{\text{M}^{n+}}\end{aligned} \quad (9.4.2a)$$

$$= \mathcal{E}_{\text{M}}^\circ + \frac{RT}{nF} \ln h_{\text{M}^{n+}} \quad (9.4.2b)$$

We have also set $\mu_{\text{H}^+}^m = 0$, which means that the standard unimolar chemical potential of the metal ion is implicitly referred to that of the hydrogen ion. Below is a table of μ^m for some cations in kilojoule per mole.

H^+	Ti^{++}	Ni^+	Al^{+++}	Fe^{++}	Fe^{+++}	Zn^{++}
0	-160	-50	-480	-85	-11	-150
Au^{+++}	Mg^{++}	Hg^+	Sn^{++}	Ag^+	Cu^+	Cu^{++}
+410	-450	+160	-25	+75	+50	+65

The more negative is the standard chemical potential, the more work can the cation do at the anode of an electrochemical cell.

$\text{Au}^{3+} + 3e^- \rightarrow \text{Au}$	1.50
$\text{Pd}^{2+} + 2e^- \rightarrow \text{Pd}$	0.987
$\text{Hg}^{2+} + 2e^- \rightarrow \text{Hg}$	0.854
$\text{Ag}^+ + e^- \rightarrow \text{Ag}$	0.800
$\text{Hg}_2^{2+} + 2e^- \rightarrow 2\text{Hg}$	0.789
$\text{Cu}^+ + e^- \rightarrow \text{Cu}$	0.521
$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$	0.337
$2\text{H}^+ + 2e^- \rightarrow \text{H}_2$	(Reference) 0.000
$\text{Pb}^{2+} + 2e^- \rightarrow \text{Pb}$	-0.126
$\text{Sn}_2^+ + 2e^- \rightarrow \text{Sn}$	-0.136
$\text{Ni}^{2+} + 2e^- \rightarrow \text{Ni}$	-0.250
$\text{Co}^{2+} + 2e^- \rightarrow \text{Ni}$	-0.277
$\text{Tl}^+ + e^- \rightarrow \text{Tl}$	-0.336
$\text{In}^{3+} + 3e^- \rightarrow \text{In}$	-0.342
$\text{Cd}^{2+} + 2e^- \rightarrow \text{Cd}$	-0.403
$\text{Fe}^{2+} + 2e^- \rightarrow \text{Fe}$	-0.440
$\text{Ga}^{3+} + 3e^- \rightarrow \text{Ga}$	-0.53
$\text{Cr}^{3+} + 3e^- \rightarrow \text{Cr}$	-0.74
$\text{Cr}^{2+} + 2e^- \rightarrow \text{Cr}$	-0.91
$\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn}$	-0.763
$\text{Mn}^{2+} + 2e^- \rightarrow \text{Mn}$	-1.18
$\text{Zr}^{4+} + 4e^- \rightarrow \text{Zr}$	-1.53
$\text{Ti}^{2+} + 2e^- \rightarrow \text{Ti}$	-1.63
$\text{Al}^{3+} + 3e^- \rightarrow \text{Al}$	-1.66
$\text{Hf}^{4+} + 4e^- \rightarrow \text{Hf}$	-1.70
$\text{U}^{3+} + 3e^- \rightarrow \text{U}$	-1.80
$\text{Be}^{2+} + 2e^- \rightarrow \text{Be}$	-1.85
$\text{Mg}^{2+} + 2e^- \rightarrow \text{Mg}$	-2.37
$\text{Na}^+ + e^- \rightarrow \text{Na}$	-2.71
$\text{Ca}^{2+} + 2e^- \rightarrow \text{Ca}$	-2.87
$\text{K}^+ + e^- \rightarrow \text{K}$	-2.93
$\text{Li}^+ + e^- \rightarrow \text{Li}$	-3.05

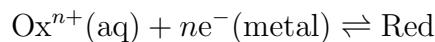
Electrochemical, or *electromotive force*, series.

\mathcal{E}_M° is the *standard single cell potential on the SHE scale*. These may be compiled into a ranked table called the *electrochemical series* or the *electromotive force series*. If at the first page of these notes, the lemon lamp, you asked how is it that the zinc corrodes and not the copper; the answer is in the electrochemical series. When the two half cells $\text{Zn}^{++}(\text{aq})|\text{Zn}(\text{s})$ and $\text{Cu}^{++}(\text{aq})|\text{Cu}(\text{s})$ are connected electrically, and they share the same electrolyte (lemon juice which is acidic) then the $\text{Zn}^{++}(\text{aq})|\text{Zn}(\text{s})$ electrode having a more negative standard electrode potential (-0.76V, compared to +0.34V) becomes the anode and de-electronation occurs at the Zn electrode and electronation at the Cu electrode. As expressed in (9.4.2) $\mathcal{E}_{\text{Zn}} < \mathcal{E}_{\text{Cu}}$ because $\mu_{\text{Zn}^{n+}}^m < \mu_{\text{Cu}^{n+}}^m$, that is, the Zn ion has the more negative standard chemical potential in solution in water. Evidently the system can gain more free enthalpy if the Zn dissolves, rather than the Cu. This

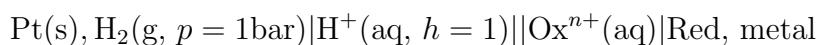
to my mind does not really *explain* why the Zn chooses to corrode. You may gaze at the electrochemical series and wonder how Nature has organised metals in this way. To a physicist, the noble metals are Cu, Ag and Au. To the chemist the noble metals are those at the top of the electrochemical series, Au, Pt, Pd; they call Cu, Ag, Au the *coinage metals*. (The $\text{Pt}^{++}(\text{aq})|\text{Pt}(\text{s})$ single electrochemical potential is +1.2V—it's missing from the table I found.) The metals with a large negative \mathcal{E}_M are called *base metals*. To a corrosion scientist the fact that a metal of interest, for example Mg, is a base metal can be depressing. In the design of Mg alloys poor corrosion resistance is one of the principal reasons why this least dense of engineering alloys is less ubiquitous than you may expect. But there is almost nothing that can be done to combat the fundamental fact that $\mathcal{E}_{\text{Mg}} = -2.37\text{V}$. I have no deep insight as to why the metals are ordered as they are. Fawcett gives three factors that determine the position of a metal in the series: (i) the free enthalpy of solvation of the metal ion in water; (ii) the free enthalpy of the metal, which depends on its crystal and electronic structure; (iii) the ionisation energy of the metal atom. I don't imagine that this is the last word on the matter.

9.5 Nernst equation

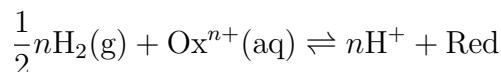
The half cell reaction can be generalised to consider a substance “Ox”, which is reduced by acquiring an electron from the electrode and become the reduced substance, “Red”,



The half cell single potential can be measured as in section 9.4 by connecting to a SHE



The cell reaction is



The e.m.f. is

$$\mathcal{E} = \mathcal{E}^\circ + \frac{RT}{nF} \ln \frac{h_{\text{Ox}}}{h_{\text{Red}}} \quad (9.5.1)$$

The standard e.m.f. is

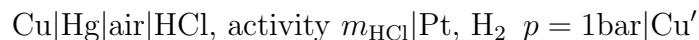
$$\mathcal{E}^\circ = \frac{1}{nF} (\mu_{\text{Ox}}^m - \mu_{\text{Red}}^m)$$

(9.5.1) is called the *Nernst equation*.

10. Relative and absolute ion work function and real potential

10.1 Measurement the proton work function and real potential in water

The electrochemical potential of a charged species is *in principle* not measurable. However measurements can be made if assumptions are made that extend beyond the scope of equilibrium thermodynamics. Many measurements are made using a device called “Kenrick’s apparatus.” The idea is create an air gap between a metal electrode and an electrolyte and create conditions in which the Volta potential difference between the two surfaces is zero. This is done as already described in section 3.4 using the Kelvin probe. There, a bias potential is applied of an amount just to prevent any current flowing if the surfaces are moved closer to each other or further away. That so called *compensation potential*, denoted $\Delta_c\phi$, is equal to minus the difference in Volta potential, permitting the measurement of the Volta potential difference between two surfaces (see Fawcett, section 8.7 for details). In Kenrick’s apparatus, rather than applying a bias potential, it is arranged that the Volta potential difference is zero by design. This is done using a liquid mercury electrode that is arranged to flow rapidly past a flowing stream of electrolyte in the opposite direction with an air gap between. Because the two opposing surfaces are in rapid flow it is assumed that charge cannot distribute in time so that the Volta potential difference across the air gap is zero (see Fawcett, section 8.7). I have to say I do not find this convincing: the time taken for charge to distribute in a metal must be roughly the inverse plasma frequency; I don’t know what it is in an electrolyte. But if the system is in steady state, or worse, then I don’t see how we can apply thermodynamic principles. However, it’s been around a long time and it works. (You really can abuse thermodynamics if you don’t mind offending the ghost of Josiah Willard Gibbs—when I was a metallurgy undergraduate doing problems, they occasionally required the student to “assume equilibrium in the blast furnace.”) Using this apparatus, and making one very reasonable and not at all serious non-thermodynamic assumption it is possible to measure the *work function of the proton in water*. The assumption is necessary because the activity of a proton cannot be measured. So in hydrochloric acid, HCl, in the dilute limit it is assumed that $m_{H^+} = m_{HCl}$ (see (A3.13) in the appendix). The Kenrick apparatus for this experiment uses streams of mercury and HCl, the electrolyte being connected to a standard hydrogen electrode. The cell diagram is



The potential measured across the copper leads is a compensation potential by virtue of

$${}^s\Delta^{\text{Hg}}\psi = 0$$

and is given by

$$\begin{aligned} F\Delta_c\phi &= \tilde{\mu}_{\text{e}}(\text{Cu}) - \tilde{\mu}_{\text{e}}(\text{Cu}') \\ &= \tilde{\mu}_{\text{e}}(\text{Hg}) - \tilde{\mu}_{\text{e}}(\text{Pt}) \\ &= \mu_{\text{e}}^{\text{Hg}} - \mu_{\text{e}}^{\text{Pt}} - F(\phi_{\text{Pt}} - \phi_{\text{Hg}}) \end{aligned} \tag{10.1.1}$$

By considering the equilibrium of the SHE half cell, using procedures just as in section 9,

one finds for ${}^{\text{HCl}}\Delta^{\text{Pt}}\phi$,

$$F(\phi_s - \phi_{\text{Pt}}) = \frac{1}{2}\mu_{\text{H}_2}^{\text{g},\circ} - \mu_{\text{H}^+}^{\text{s},\circ} - \mu_{\text{e}}^{\text{Pt}} - RT \ln m_{\text{H}^+}$$

Combining this with (10.1.1) to eliminate Pt potentials in favour of Hg potentials results in

$$F\Delta_c\phi = F(\chi_s - \chi_{\text{Hg}}) + RT \ln m_{\text{H}^+} - \Delta G^\circ$$

where

$$\Delta G^\circ = \frac{1}{2}\mu_{\text{H}_2}^{\text{g},\circ} - \mu_{\text{H}^+}^{\text{s},\circ} - \mu_{\text{e}}^{\text{Hg}}$$

Here the dipole potential difference enters since in view of the air gap and the flowing electrode and electrolyte the Volta potential difference is zero and ${}^s\Delta^{\text{Hg}}\phi = {}^s\Delta^{\text{Hg}}\chi$. The experimenter measures the voltage across the copper leads with a very high impedance voltmeter as a function of the strength of the acid. Assuming that the activity of H^+ is equal to the activity of Cl^- (this is the “extrathermodynamic” input) then plotting $\Delta_c\phi - RT \ln m_\pm$ (where $m_\pm = \sqrt{m_{\text{H}^+}m_{\text{Cl}^-}}$ is the geometric mean ionic activity) against the square root of the HCl concentration and extrapolating to zero concentration yields a value of **-56.3mV** in the infinitely dilute limit (see Fawcett, section 8.7). Because it's constant we don't yet need to know what ΔG° is.

Next, employ the fact that in this limit the dipole potential of the infinitely dilute acid is the same as that of water, $\chi_{\text{H}_2\text{O}}$. Then,

$$\begin{aligned} F\Delta_c\phi - RT \ln m_\pm (m_\pm \rightarrow 0) &= -56.3\text{mV} \times F \\ &= \mu_{\text{H}^+}^{\text{s},\circ} + F\chi_{\text{H}_2\text{O}} + \mu_{\text{e}}^{\text{Hg}} - F\chi_{\text{Hg}} - \frac{1}{2}\mu_{\text{H}_2}^{\text{g},\circ} \\ &= \alpha_{\text{H}^+}^{\text{s},\circ} + \alpha_{\text{Hg}}^{\text{s},\circ} - \frac{1}{2}\mu_{\text{H}_2}^{\text{g},\circ} \end{aligned} \quad (10.1.2)$$

using, in the second line, the definition of the real potential (4.2.1) and remembering that the charge on the electron is negative. Now, the real potential of the electron in a metal is the same as minus its work function, which for mercury is 4.5eV. The last term in (10.1.2) is the standard chemical potential of hydrogen in the gas phase which is zero for the pure substance. Hence (see equation (3.2.3) and footnote),

$$\alpha_{\text{H}^+}^{\text{s},\circ} = -0.056 + 4.5 = 4.44\text{eV} \quad (10.1.3)$$

The proton work function is (8.2.8)

$$W_{\text{H}^+}^{\text{s},\circ} = \mu_{\text{H}^+}^{\text{g},\circ} - \alpha_{\text{H}^+}^{\text{s},\circ}$$

The first term, $\mu_{\text{H}^+}^{\text{g},\circ}$, is the standard free enthalpy of formation of a proton in the gas phase. Relative to the standard free enthalpy of the hydrogen molecule, this is half the dissociation (bond) energy (4.52eV) plus the ionisation energy (13.6eV), namely 15.9eV. The work function of the proton in water then comes out as 11.4eV (1103 kJ/mol). Once that is known, then using (8.2.6) and the measured standard free enthalpy of solvation of hydrogen ions (again not strictly measurable, but using sensible extrathermodynamic

assumptions) it is possible to deduce from experiment that the electric dipole potential at the surface of water is 80mV. This presents a challenge to DFT to try and calculate it.

10.2 Absolute electrode potential

The electrochemical series ranks electrode potentials and provides a single electrode potential *relative to the standard hydrogen single electrode potential*. This is inevitable because thermodynamics does not furnish us with an absolute zero of energy. Hence we choose the one most convenient to us. So far we have encountered up to five choices. (i) In the DFT using periodic boundary conditions and hence with no reference to the surfaces of the substance or the world beyond it, we use the average potential energy seen by an electron, \bar{V} , as a convenient reference (section 3.1). (ii) The DFT total energy, E_{tot} , is calculated with reference to the situation where all the electrons and nuclei are scattered, each to its own field-free infinity (the nuclei are not disassembled into nucleons or quarks however). (iii) We have used the electric potential at infinity or at the vacuum level (“Bockris point”) as convenient zeros of potential. (iv) The reader may be bemused and sceptical of our conveniently setting certain standard chemical potentials to zero. We can do this if we allow that the zero of energy is somewhat similar to the DFT zero, but instead we envisage a number of reservoirs of pure substance, solid or ideal gas at one bar and 298K, infinitely far from each other and from which we are drawing our components to make up the substance under study. (v) We have used the single SHE potential as a zero of electric potential. Electrochemists also use other standards such as the standard calomel electrode, but they can easily be calibrated to the SHE by constructing a suitable electrochemical cell.

The question now is, can we find an *absolute* single electrode potential for the SHE relative to the thermodynamic reference (iv)? This cannot be done without using assumptions beyond the equilibrium thermodynamics, but in fact there is an argument first put forward by Sergio Trassati in the 1980s.

We start by looking at section 9.3 in a different way. There we used the fact that the e.m.f. of the cell in figure 9–1 was the difference in electrochemical potentials of the electrons in the right and left hand leads. Instead, pursue the following line of argument. The equilibrium in the left hand cell (9.3.1a) implies equality of the electrochemical potentials,

$$\begin{aligned}\frac{1}{2}\mu_{\text{H}_2} &= \tilde{\mu}_{\text{H}^+} + \tilde{\mu}_{\text{e}}^{\text{Pt}} \\ &= \mu_{\text{H}^+} + F\phi_s + \mu_{\text{e}}^{\text{Pt}} - F\phi_{\text{Pt}} \\ &= \mu_{\text{H}^+}^m + RT \ln m_{\text{H}^+} + F\phi_s + \mu_{\text{e}}^{\text{Pt}} - F\phi_{\text{Pt}}\end{aligned}$$

This is the *standard* hydrogen electrode, so we'll have unit activity of H^+ and 1 bar pressure of hydrogen gas. Then after rearranging,

$$F(\phi_{\text{Pt}} - \phi_s) = -\frac{1}{2}\mu_{\text{H}_2}^\ominus + \mu_{\text{H}^+}^m + \mu_{\text{e}}^{\text{Pt}} \quad (10.2.1)$$

Equilibrium of the right hand cell (9.3.1b) similarly implies the equality of electrochemical potentials on either side of the reaction,

$$\mu_{\text{AgCl}} + \tilde{\mu}_e^{\text{Ag}} = \mu_{\text{Ag}} + \tilde{\mu}_{\text{Cl}^-}$$

and after expanding the electrochemical potentials and rearranging exactly as above,

$$\begin{aligned} F(\phi_s - \phi_{\text{Ag}}) &= -\mu_{\text{AgCl}}^\bullet + \mu_{\text{Ag}}^\bullet + \mu_{\text{Cl}^-}^m + RT \ln m_{\text{Cl}^-} - \mu_e^{\text{Ag}} \\ &= \mu_{\text{Cl}^-}^m + RT \ln m_{\text{Cl}^-} - \mu_e^{\text{Ag}} \end{aligned} \quad (10.2.2)$$

since the Ag and AgCl are in their pure substance standard states. The open circuit e.m.f. is

$$\begin{aligned} \mathcal{E} &= \phi_{\text{Cu}'} - \phi_{\text{Cu}} \\ &= (\phi_{\text{Pt}} - \phi_{\text{Cu}}) + (\phi_s - \phi_{\text{Pt}}) + (\phi_{\text{Ag}} - \phi_s) + (\phi_{\text{Cu}'} - \phi_{\text{Ag}}) \end{aligned} \quad (10.2.3)$$

In view of (3.2.1) and its footnote we have,

$$\begin{aligned} \phi_{\text{Pt}} - \phi_{\text{Cu}} &= \frac{1}{F} (\mu_e^{\text{Pt}} - \mu_e^{\text{Cu}}) \\ \phi_{\text{Cu}'} - \phi_{\text{Ag}} &= \frac{1}{F} (\mu_e^{\text{Cu}'} - \mu_e^{\text{Ag}}) \end{aligned}$$

A key point is that the Fermi levels in both copper leads are the same even though their electrons are at different electrochemical potentials. This is because the Fermi level is the same as the bandwidth (figure 3–1). So $\mu_e^{\text{Cu}'} = \mu_e^{\text{Cu}}$ and (10.2.3) becomes

$$\begin{aligned} \mathcal{E} &= \left((\phi_{\text{Ag}} - \phi_s) - \frac{1}{F} \mu_e^{\text{Ag}} \right) - \left((\phi_{\text{Pt}} - \phi_s) - \frac{1}{F} \mu_e^{\text{Pt}} \right) \\ &= \mathcal{E}_{\text{Ag}|\text{AgCl}} - \mathcal{E}_{\text{H}^+|\text{Pt}} \end{aligned} \quad (10.2.4)$$

Two points are worth noting.

- (i) Comparing (10.2.4) with (10.2.1) and (10.2.2) it is clear that the Fermi levels in each metal cancel. This will always happen in a formula for the full cell e.m.f. but not in the formula for a half cell such as (9.2.1). However because of this cancellation you will see in textbooks such as John West's a statement like, “we assume that electrons in metals are in their standard state so their standard chemical potentials can be set to zero.”
- (ii) In spite of this we leave (10.2.4) in the form that it is because it has separated the e.m.f. into single electrode potentials, each depending only on the properties of its own electrode.

Because of point (ii) we could imagine adding and subtracting a constant, K_{abs} , to (10.2.4) as an attempt to identify an *absolute* electrode potential,

$$\begin{aligned} \mathcal{E}_{\text{Ag}|\text{AgCl}}^{\text{abs}} &= (\phi_{\text{Ag}} - \phi_s) - \frac{1}{F} \mu_e^{\text{Ag}} + K_{\text{abs}} \\ \mathcal{E}_{\text{H}^+|\text{Pt}}^{\text{abs}} &= \mathcal{E}_{\text{SHE}}^{\text{abs}} = (\phi_{\text{Pt}} - \phi_s) - \frac{1}{F} \mu_e^{\text{Pt}} + K_{\text{abs}} \end{aligned}$$

Now, Trassatti's idea is to modify the cell in section 9.3 so as to introduce an air gap into the electrolyte,



This is a thought experiment so maybe it doesn't matter how to realise this in practice, but it is imagined that the Volta potential difference across the air gap can be made to be zero, presumably by some streaming of the electrolyte as in Kenrick's apparatus (section 10.1). In that case the e.m.f. at open circuit is a compensation potential (section 10.1) and in the manner of (10.2.3) this can be written as a sum of potential differences across the phase boundaries indicated by ']' in the cell diagram,

$$\begin{aligned}\Delta_c\phi &= (\phi_{\text{Cu}'} - \phi_{\text{Cu}}) \\ &= (\phi_{\text{Pt}} - \phi_{\text{Cu}}) + (\phi_s - \phi_{\text{Pt}}) + (\phi_{\text{air}} - \phi_s) + (\phi_s - \phi_{\text{air}}) + (\phi_{\text{Ag}} - \phi_s) + (\phi_{\text{Cu}'} - \phi_{\text{Ag}})\end{aligned}$$

Because of zero Volta potential difference across the air gap, we have

$$(\psi_{\text{air}} - \psi_s) = (\psi_s - \psi_{\text{air}}) = 0$$

and so the Galvani potential potential difference is just the dipole potential between the water and air (we know that the surface dipole potential of water is about 80mV, section 10.1, but we don't need to use this number in what follows),

$$(\psi_{\text{air}} - \psi_s) = -(\psi_s - \psi_{\text{air}}) = \chi_s$$

Going through the same steps leading to equations (10.2.1), (10.2.2) and (10.2.4), we arrive at

$$\begin{aligned}\mathcal{E} &= \left((\phi_{\text{Ag}} - \phi_s) - \frac{1}{F}\mu_e^{\text{Ag}} + \chi_s \right) - \left((\phi_{\text{Pt}} - \phi_s) - \frac{1}{F}\mu_e^{\text{Pt}} + \chi_s \right) \\ &= \mathcal{E}_{\text{Ag}|\text{AgCl}}^{\text{abs}} - \mathcal{E}_{\text{H}^+|\text{Pt}}^{\text{abs}}\end{aligned}$$

We can assert that we have now found the absolute single SHE potential because the air gap and the high impedance across the voltmeter have isolated the two half cells. In this case using $K_{\text{abs}} = \chi_s$ identifies the constant needed to refer the SHE to the "thermodynamic" zero of energy. Now using (10.2.1) we get

$$\begin{aligned}\mathcal{E}_{\text{SHE}}^{\text{abs}} &= \phi_{\text{Pt}} - \phi_s - \frac{1}{F}\mu_e^{\text{Pt}} + \chi_s \\ &= \frac{1}{F} \left(\mu_{\text{H}^+}^m - \frac{1}{2}\mu_{\text{H}_2}^\ominus + \mu_e^{\text{Pt}} \right) - \frac{1}{F}\mu_e^{\text{Pt}} + \chi_s \\ &= \mu_{\text{H}^+}^m + \frac{1}{F}\chi_s \\ &= \frac{1}{F}\alpha_{\text{H}^+}^{s,o}\end{aligned}$$

In the second line the Fermi energy of Pt has cancelled as promised. We also take the chemical potential of hydrogen gas in its standard state of one bar pressure and 298K

as zero. The last line follows from (4.2.1) and leaves us with the remarkably simple result that the absolute e.m.f. of the standard hydrogen electrode is the real potential of the proton in the electrolyte. Assuming that this is the same as for water, $\chi_{\text{H}_2\text{O}} = \chi_s$ (and I don't see how we can assume this) then we have already calculated the answer in (10.1.3),

$$\mathcal{E}_{\text{SHE}}^{\text{abs}} = 4.44V$$

This should be a great help in computer simulations of half cells, when comparing to measurements against the SHE. An alternative derivation and a refinement of the answer to 4.42V can be found in Cheng and Sprik.

Further Reading

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Appendix—outline of thermodynamics

1. Closed systems

1.1 State functions

All thermodynamic thinking begins with a definition of the portion of the universe under study, i.e., the system.

John O'M. Bockris

I will not start right at the beginning but I will try and introduce what we will need in thermodynamics using just what you have already learned about the first and second laws.

The first law states that for a “closed” system changes in the heat content and the amount of work done *on* the system amount to a change in *internal energy*[†] written as

$$dU = \delta q + \delta w \quad (\text{A1.1})$$

If this is combined with the second law then this becomes

$$dU = T dS - p dV \quad (\text{A1.2})$$

This is true as long as the only work done involves a change in volume, V , against an external pressure, p . The absolute temperature is T and S is the entropy. A *closed* system is one that does not exchange matter with its surroundings (although it may transfer heat). We will come on to *open* systems in a while.

Before that, we note that (A1.2) is a complete statement of the combined first and second laws for a closed system if only pV -work is done.[‡] However it may not be the most convenient. For example, we may like to simplify things by doing experiments so that one of the two terms on the right hand side of (A1.1) is zero. So if we want to know just the result of the system doing some work, then working with the internal energy as a function of entropy and volume, $U(S, V)$, requires us to do experiments adiabatically, that is under the condition $\delta q = 0$, and this is not very easy.

[†] From a mechanical point of view we often state that the total energy of a body, say a sphere of Cu–Ni alloy, is equal to its potential energy, E_{pot} , if it's in a gravitational field, say, plus its kinetic energy, E_{kin} , if it's moving relative to some inertial frame. This neglects the *internal* state of the body, that is to say, what its atoms are doing and whether any diffusion, phase transformations or chemical reactions are taking place, whether it is expanding or getting hotter or colder. So in thermodynamics as opposed to mechanics we express the total energy as $E_{\text{tot}} = E_{\text{pot}} + E_{\text{kin}} + U$ and since thermodynamics concerns only *changes* in total energy we consider systems for which the potential and kinetic energies are unchanging, for example that the body is not in motion, and focus purely on the internal energy.

[‡] We have to extend this in cases where there is surface tension, non uniform stress, changes in electric or magnetic state and so on. For example work done on a body by a non hydrostatic stress is $\sigma_{ij} d\varepsilon_{ij}$, or work done on a body by increasing the area, A , of an internal interface of energy γ per unit area (say between the ferrite and austenite phases in steel) is γdA .

So without making any additional postulates we devise a number of *auxiliary functions*. These are,

$$\begin{array}{ll} \text{enthalpy,} & H = U + pV \\ \text{Helmholtz function,} & F = U - TS \\ \text{Gibbs function,} & G = H - TS \end{array}$$

G is also known as the *free enthalpy* or *Gibbs free energy*; F is also known as the *free energy* or *Helmholtz free energy*. We are most interested in the Gibbs function so I'll show you how we get it from equation (A1.2). We do it in two steps. First we have that U is a function of S and V as indicated by (A1.2). Can we find an auxiliary function that depends on T and V instead? What is the relation between T and S ? From (A1.2) we have

$$T = \left(\frac{\partial U}{\partial S} \right)_V$$

We say that S and T are “conjugate variables”, and we invent the new function

$$F = U - TS \quad (\text{A1.3})$$

that is, the first function, U , take away the product of the two conjugate variables (the one we are trying to get rid of and replace with the other). Now by taking the total derivative (that means, asking what does a change in F result in?)

$$\begin{aligned} dF &= dU - d(TS) = dU - TdS - SdT \\ &\quad = -SdT - pdV \end{aligned} \quad (\text{A1.4})$$

using (A1.2). Now we have a function F which depends on T and V rather than U which depends on S and V so that we can more readily interpret experiments done at constant volume or constant temperature. Suppose we are working at constant pressure rather than constant volume, then we need yet another auxiliary function, which we obtain from F by replacing the variable V with its conjugate $-p$. Indeed we know from (A1.4) that

$$p = - \left(\frac{\partial F}{\partial V} \right)_T$$

so $-p$ and V are conjugate variables, meaning that I can find a function that depends on p and T by writing down

$$\begin{aligned} G &= F + pV \\ &= H - TS \end{aligned} \quad (\text{A1.5})$$

(the original function take away the product of the two conjugate variables[†]). Then similar to before,

$$\begin{aligned} dG &= dF + pdV + Vdp \\ &= dU - TdS - SdT + pdV + Vdp \\ &= TdS - pdV - TdS - SdT + pdV + Vdp \\ &= -SdT + Vdp \end{aligned} \quad (\text{A1.6})$$

[†] In mathematics, this is called a *Legendre transformation*. Note that for a pair of conjugate variables, one is intensive and the other extensive.

and is thereby shown to be the required auxiliary function of T and p .

1.2 Conditions for equilibrium in closed systems

According to the second law, in an *isolated system* (one that can exchange neither matter nor energy with the environment) if any change takes place it must be such that the entropy increases or remains constant,[†]

$$dS \geq 0$$

Strictly in thermodynamics when we write

$$d(\text{something})$$

we really mean

$$\frac{d(\text{something})}{dt}$$

but we accept that the “arrow of time” always runs in the positive direction even if we don’t quite understand why and we leave out the dt denominator. If the isolated system is made up of one or more parts then we have

$$\sum_m dS_m \geq 0$$

each part being labelled by a subscript m . So some part may suffer a decrease in entropy as long as the total entropy does not decrease. So we can think of a closed system as an isolated system made up of two parts—the part we are interested in (say, a block of alloy) and a large reservoir of heat at a fixed temperature T . In this way we can keep our body at constant temperature if it is kept in contact with the reservoir. So if the entropy of our body is S and that of the reservoir is S_r then, for a natural process,

$$dS + dS_r \geq 0 \quad (\text{A1.7})$$

Now for an infinitesimal change in heat content of the body, δq , at a temperature T , the change in entropy is $\delta q/T$; [‡] this means that the change in entropy of the reservoir where the heat came from is $dS_r = -\delta q/T$ (because that amount of heat has been taken out of the reservoir at constant temperature T) and so putting this into (A1.7) the second law has it that

$$dS - \frac{\delta q}{T} \geq 0$$

[†] We believe that the Universe is an isolated system, hence the famous statement of Rudolf Clausius, *Die Energie der Welt ist konstant. Die Entropie der Welt strebt einem Maximum zu*: The energy of the world is constant. The entropy of the world is striving to a maximum. This will of course lead to the “heat death” of the universe, but don’t worry the sun will have grown into a red giant and swallowed the earth by then.

[‡] You can think of this as the *definition* of entropy if you like: if an infinitesimal quantity of heat, δq , is added to a body reversibly and at constant temperature T , then the body’s entropy increases by the amount $\delta q/T$.

Now using (A1.2) we have

$$dS - \frac{dU - \delta w}{T} \geq 0$$

I multiply through by T , rearrange and note that since this change is at constant temperature $d(U - TS) = dU - TdS$ and I get

$$d(U - TS) \leq \delta w \quad (\text{A1.8})$$

By comparison with (A1.3) we have $dF \leq \delta w$ so that if the body does work ($\delta w < 0$) then the Helmholtz function may increase, but otherwise and especially if no work is done either by or on the body, then the Helmholtz function can only decrease during a natural change, or remain constant. Thus when all changes have happened and the body is in equilibrium then the Helmholtz free energy is at a minimum. This is a condition for equilibrium.

I can add $d(pV)$ to both sides of equation (A1.8) and I get

$$d(U + pV - TS) = dG \leq \delta w + d(pV)$$

If as well as working at constant temperature, my body is maintained under a constant external pressure, p , then $d(pV) = pdV$ and so if I define $\delta w' = \delta w + pdV$ as the work done not including work done, pdV , by the body against the external pressure[†] then the condition for equilibrium is that the Gibbs free energy of a body at constant temperature and pressure is a minimum if no work other than that either *against* or *by* the external pressure is done either on or by the body,

$$dG \leq \delta w' \quad \text{in a closed system}$$

If no such work is done ($\delta w' = 0$) then $dG \leq 0$ in which case the Gibbs free energy can only decrease or remain constant. This means that when all changes have happened that are going to happen the system is in equilibrium and G is a minimum, $dG = 0$. This is the condition for equilibrium of a closed system at constant temperature and pressure.

In metallurgy when we deal with solids the amount of work done say by the thermal expansion of a body against atmospheric pressure is so tiny as to be negligible, and we can regard the Helmholtz and Gibbs functions to be interchangeable and both minimal at equilibrium; but since we usually work at constant pressure and not constant volume the focus is always on the Gibbs free energy.

[†] In these notes δw is the work done on the body, not the work done by the body. The latter convention is commonly used by engineers who are interested in, say, an internal combustion engine for which pdV is the work done by the explosion of a fuel moving a piston against the external pressure p . So for us, if the body does work against the external pressure then the work done *on* the body is $-pdV$. So $\delta w' = \delta w - (-pdV) = \delta w + pdV$.

2. Open systems, chemical potential

An “open” system, such as the lump of metal that we have been thinking about, can exchange both energy and matter with its surroundings. Under these circumstances we must modify our statement of the combined first and second laws (A1.2). We have to ask about the chemical composition of our body and to identify how many different “components” it is made up from. It is sufficient for our purposes to identify each chemical element as one of the components, so that for example a piece of Cu–Ni alloy has two components. In addition to components the body may be divided into phases. For example a piece of Fe–C alloy at equilibrium within the $\alpha + \gamma$ field of the Fe–C phase diagram may have a certain volume fraction of ferrite, having a very small concentration of carbon and a certain volume fraction of austenite with a much larger concentration of dissolved carbon. These two phases will be intimately in contact sharing one or more interfaces which divide the body into its phases. For now we consider a homogeneous, single phase body having N components and we will use a subscript i to label these in our mathematical formulas. The internal energy is now no longer a function of only the two variables S and V it is also a function of the number of moles,[†] n_i , of each component that currently make up the body,

$$U = U(S, V, n_1, n_2 \dots n_N)$$

The total differential of the internal energy is, now,

$$dU = \left(\frac{\partial U}{\partial S} \right)_{V, n_i} dS + \left(\frac{\partial U}{\partial V} \right)_{S, n_i} dV + \sum_{i=1}^N \left(\frac{\partial U}{\partial n_i} \right)_{S, V, n_j \neq i} dn_i \quad (\text{A2.1})$$

In the case of constant composition, this is obviously still valid, and so from (A1.2)

$$\left(\frac{\partial U}{\partial S} \right)_{V, n_i} = T \quad (\text{A2.2})$$

and

$$\left(\frac{\partial U}{\partial V} \right)_{S, n_i} = -p \quad (\text{A2.3})$$

We now define the *chemical potential* of component i as the term under the summation sign in (A2.1)

$$\mu_i = \left(\frac{\partial U}{\partial n_i} \right)_{S, V, n_j \neq i} \quad (\text{A2.4})$$

and here the partial derivative is taken of U with respect to the number of moles of component i while keeping all other variables constant: namely the volume and entropy

[†] If you’re a physicist you tend to think in terms of the number of particles or number of atoms of each component, but since we deal with macroscopically sized bodies, in metallurgy and chemistry we use the number of moles to keep the numbers of reasonable size. A mole is nothing other than an Avogadro number of objects and the Avogadro number is $N_A = 6.023 \times 10^{23}$. Physicists use the Boltzmann constant, k_B , while we use the gas constant $R = N_A k_B$.

and the numbers of moles of all the other components. You might ask how can I do this in practice? The answer is to imagine that to the body in question you take an infinitesimal number of moles of component i (from a reservoir in which its chemical potential has some standard value—more on that later) and add it to the body. While the body's volume necessarily changes you readjust that by application of an infinitesimal increase in pressure. Since the added quantity of matter may bring with it some heat, to ensure that the entropy doesn't change in this process it is necessary then to remove that heat, say by placing it in contact with a heat bath at the appropriate temperature.

Maybe you'd like to think of the chemical potential as the reversible work done in bringing an infinitesimal amount of matter from a reservoir to the body in question. Sometimes I like the analogy with electrostatics; the *electric potential* is the work done in taking a positive test charge from infinity (the reservoir) to a place in space where there is an electric field—that is, the influence of other charges. Loosely speaking if the electric potential is large and negative then positive charges are attracted to that place and the work done in bringing the test charge from infinity is negative; conversely, if the electric potential $\phi(\mathbf{r})$ is positive at position \mathbf{r} , then I need to do work to bring in extra positive charges. In this vein if the chemical potential of, say, carbon in Fe–C is large and positive then I need to expend energy to increase its concentration. If the concentration, or rather the chemical potential, of C in Fe varies from place to place then if the carbon is mobile it will diffuse from regions of high chemical potential to regions of low chemical potential. This is rather obvious if we equate chemical potential with concentration. Later we'll see how these two are actually related. Whereas in standard diffusion theory you are told that the carbon will travel down a concentration gradient, to be properly precise you should say that if diffuses down the gradient in *chemical potential*.

In view of equations (A2.1)–(A2.4) we have for the total differential of the internal energy of a body,

$$dU = TdS - pdV + \sum_{i=1}^N \mu_i dn_i \quad (\text{A2.5})$$

which is the modification of the combined first and second laws (A1.2) for the case of an open system.

Now let me begin this argument again, but this time starting with the modification of the Gibbs function (A1.5) for an open system. The Gibbs free energy is a function of temperature, pressure and the numbers of moles of each of the components,

$$G = G(T, p, n_1, n_2 \cdots n_N)$$

and so its total differential is

$$dG = \left(\frac{\partial G}{\partial T} \right)_{p,n_i} dT + \left(\frac{\partial G}{\partial p} \right)_{T,n_i} dp + \sum_{i=1}^N \left(\frac{\partial G}{\partial n_i} \right)_{T,p,n_j \neq i} dn_i \quad (\text{A2.6})$$

We now define the *chemical potential* of component i as

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,p,n_j \neq i} \quad (\text{A2.7})$$

and (A2.6) being still valid in the special case of all the dn_i being zero (that is, fixed composition) equation (A1.6) gives

$$\left(\frac{\partial G}{\partial T}\right)_{p,n_i} = -S \quad ; \quad \left(\frac{\partial G}{\partial p}\right)_{T,n_i} = V \quad (\text{A2.8})$$

which when put into (A2.6) results in

$$dG = -SdT + Vdp + \sum_{i=1}^N \mu_i dn_i \quad (\text{A2.9})$$

with μ_i defined by equation (A2.7). This is the modification of (A1.6) for an open system. Have I now made two different definitions of the chemical potential? That would be a real mess. Well, luckily, no! If I add to both sides of (A2.5) the quantity $d(pV - TS)$ then this equation is transformed into equation (A2.9) by virtue of the fact that $G = U + pV - TS$.

We will use equation (A2.7) as our expression for the chemical potential (numerically it is identical to (A2.4), but we are concerned in metallurgy with the Gibbs function whose independent variables are p and T which are easily controlled—it's not easy to measure let alone control the entropy!). In the case of there being a single component then the chemical potential is the “partial free energy per mole”. Usually for all extensive state functions we define a partial amount, being the amount per mole. We use lower case for these. In this way, we have for a single component homogeneous body,

$$\begin{aligned} \text{partial molar volume, } & v = V/n \\ \text{partial molar enthalpy, } & h = H/n \\ \text{partial molar free energy, } & f = F/n \\ \text{partial molar free enthalpy, } & g = G/n \end{aligned}$$

Equation (A2.7) is the more general expression of the partial free enthalpy of component i when it finds itself in a body having mole numbers n_1, n_2, \dots, n_N .

Finally in this section let's find a way to express the total Gibbs free energy of a body in terms of the mole numbers and chemical potentials of the components, equation (A2.10) below. Now, the Gibbs free energy is an *extensive* property so if I know $G(T, p, n_1, n_2, \dots, n_N)$ for a body and then I assemble some number λ of these bodies together then p and T do not change as these are intensive properties and the mole numbers are all multiplied by λ and the total Gibbs free energy is also multiplied by λ (because it is an extensive property),

$$G(T, p, \lambda n_1, \lambda n_2, \dots, \lambda n_N) = \lambda G(T, p, n_1, n_2, \dots, n_N)$$

(actually λ does not need to be a whole number—if I extend the body by an amount λ then the free energy is increased in the same ratio). We now invoke Euler's theorem for homogeneous functions of first order. Suppose a function f of N variables satisfies

$$f(\lambda x_1, \lambda x_2, \dots, \lambda x_N) = \lambda f(x_1, x_2, \dots, x_N)$$

We first exchange left and right hand sides and write $u_i = \lambda x_i$

$$\lambda f(x_1, x_2, \dots, x_N) = f(u_1, u_2, \dots, u_N)$$

then differentiate each side with respect to λ , using the rule for differentiating a function of a function for the right hand side,

$$\begin{aligned} f(x_1, x_2, \dots, x_N) &= \sum_{i=1}^N \frac{\partial f}{\partial u_i} \frac{du_i}{d\lambda} \\ &= \sum_{i=1}^N \frac{\partial f}{\partial u_i} x_i \\ &= \sum_{i=1}^N \frac{1}{\lambda} \frac{\partial f}{\partial x_i} x_i \end{aligned}$$

This is true for any λ but if I choose $\lambda = 1$ then I get

$$f(x_1, x_2, \dots, x_N) = \sum_{i=1}^N \frac{\partial f}{\partial x_i} x_i$$

This is Euler's theorem which I now apply to the Gibbs function,

$$G(T, p, n_1, n_2, \dots, n_N) = \sum_{i=1}^N \left(\frac{\partial G}{\partial n_i} \right)_{T, p, n_j \neq i} n_i$$

and by comparison with (A2.7) I get

$$G = \sum_{i=1}^N \mu_i n_i \tag{A2.10}$$

This states that the total free energy of a phase having N components is equal to the sum of the number of moles of each component times its chemical potential.

From this I can obtain the famous *Gibbs-Duhem equation*. If I take the total differential of (A2.10),

$$dG = \sum_{i=1}^N \mu_i dn_i + \sum_{i=1}^N n_i d\mu_i$$

and if I compare this with (A2.9) there results

$$-SdT + Vdp - \sum_{i=1}^N n_i d\mu_i = 0$$

This is the Gibbs-Duhem equation which you can use to prove the *Gibbs phase rule* which is central to the interpretation of phase diagrams (but for brevity I'll leave that out of these notes). At constant T and p , we then find

$$\sum_{i=1}^N n_i d\mu_i = 0 \tag{A2.11}$$

2.1 Conditions for equilibrium in open systems

Possibly the most significant statement in metallurgical thermodynamics that you need to remember is this, *in equilibrium the chemical potential of each component is the same in all phases*. That is to say, if the body comprises more than one phase (and we will label the phases with subscripts α , β , ...) and the components are distributed among the phases so that the number of moles of component i in phase α is $n_{i\alpha}$, then as long as the phases are in contact and each component can diffuse throughout the body, then at equilibrium the chemical potential μ_i for component i is the same in each phase. This makes sense because it implies that if the chemical potential of component i is the same everywhere then there's no gradient to drive diffusion and so all atoms stay where they are—equilibrium is reached. For example a piece of Fe–C alloy at equilibrium within the $\alpha + \gamma$ field of the Fe–C phase diagram has a particular volume fraction of ferrite, having a very small concentration of carbon and a certain volume fraction of austenite with a large concentration of dissolved carbon. The concentrations of C in the two phases is very different because of the big difference in solubility of C in α -Fe and γ -Fe, but in equilibrium $\mu_{C\alpha} = \mu_{C\gamma}$ —the chemical potential of carbon is the same everywhere.

For the curious, I will try and prove this for you. Suppose in a multiphase, multicomponent body I take an infinitesimal amount of component i , $dn_{i\alpha}$, from phase α and transfer it reversibly into phase β .[†] The amount of increase of component i in the β phase is, rather obviously, $dn_{i\beta} = dn_{i\alpha}$ while the change of mole number of component i in phase α is negative *viz.*, $-dn_{i\alpha}$. If I do this at constant temperature and pressure, then according to equation (A2.9) the change in Gibbs free energy is

$$dG = -\mu_{i\alpha}dn_{i\alpha} + \mu_{i\beta}dn_{i\beta} = (\mu_{i\beta} - \mu_{i\alpha})dn_{i\alpha}$$

since (A2.9) must hold separately in each phase as each phase may be regarded as an open system and a part of the whole body. If the system was originally in equilibrium and the transfer is done reversibly then

$$dG = 0 = (\mu_{i\beta} - \mu_{i\alpha})dn_{i\alpha}$$

and so, since $dn_{i\alpha} \neq 0$, it must be true that

$$\mu_{i\alpha} = \mu_{i\beta}$$

[†] For example I could have some Fe–C at the temperature at which austenite and ferrite are in equilibrium (at the “no name” line in the Fe–C phase diagram). Then keeping T , p and the carbon concentrations fixed, I could take $dn_{Fe\alpha}$ moles of body centred cubic Fe (ferrite) and transfer them across the α / γ interface and rearrange them into the face centred cubic austenite. Alternatively I could reversibly move the α / γ interface in such a way that $dn_{Fe\alpha}$ moles of ferrite are rearranged into austenite. Actually there is a complication in this thought experiment because once I have transformed some ferrite into austenite I will have to also transfer an amount of carbon so that the austenite retains the carbon concentration appropriate to the tie line in the phase diagram; I gloss over this somewhat here, but as long as the amount I am transferring is *infinitesimal* in the sense of the differential calculus then I can neglect the need to re-equilibrate the carbon in this process.

if the two phases are in equilibrium. We can extend this argument to any number of phases.

3. Activity

Next, we need to know how does the chemical potential relate to the concentration. Obviously we design and process metal alloys using concentrations of the components but as we have seen what controls the thermodynamics and the kinetics at the fundamental level is the chemical potential. The best way to start this is simply to write down the answer. The chemical potential of component i in a particular phase (I'll leave out the subscript α unless it's needed) is

$$\mu_i = \mu_i^\circ + RT \ln a_i \quad (\text{A3.1})$$

μ_i° is the chemical potential in some “standard state” (mathematically it's an integration constant) and depends only on temperature and pressure; and a is the “activity”. Where does this equation come from? At the most shallow level it's simply a *definition* of activity, and still we need to find the connection between activity, a_i and concentration, x_i expressed as the mole fraction, n_i/n . This is most generally expressed like this,

$$a_i = \gamma_i x_i$$

which may be a very complicated function since the so called “activity coefficient” γ_i is a function of temperature, pressure and the concentrations of all the components, not just component i ,

$$\gamma_i = \gamma_i(T, p, x_1, x_2, \dots, x_N)$$

Thermodynamics can tell us nothing about how the activity depends on the concentrations. Ultimately it is up to experiment or detailed atomic-scale theory to determine the relationship. For example, it follows from the Gibbs-Helmholtz equation that[†]

$$R \left(\frac{\partial \ln \gamma_i}{\partial (1/T)} \right)_{p, n_j \neq i} = h_i - h_i^\circ \quad (\text{A3.2})$$

where h_i° is the partial molar enthalpy in the same standard state as is applied to μ_i° . For an ideal solution, $\gamma = \text{constant}$ and so the left hand side is zero, implying that the enthalpy of the component in solution is the same as in the pure substance at the same T and p , if the pure substance standard state is used. By integration of the

[†] Combine (A1.5) with (A2.8),

$$G = H + T \left(\frac{\partial G}{\partial T} \right)_{p, n_i}$$

which can be recast as follows,

$$\left(\frac{\partial (G/T)}{\partial T} \right)_{p, n_i} = -\frac{H}{T^2}$$

which is the Gibbs-Helmholtz equation. Just divide G and H by the number of moles and insert (A3.1) with $a_i = \gamma_i x_i$ to get (A3.2).

Gibbs-Helmholtz equation, activity coefficients can be inferred from measured heats of solution.

The results of such experiments are shown in figure 1. You can see that the activity does not at all show a straightforward relationship to the concentration, except to say that as the concentration increases so does the activity. However you see two very clear limits: for large concentrations we see that

$$a_i = x_i \quad (x_i \rightarrow 1)$$

meaning that in the concentrated limit the activity of the *solvent* is equal to its concentration, the activity coefficient being one; and

$$a_i = \gamma_i^\infty x_i \quad (x_i \rightarrow 0)$$

with γ_i^∞ constant, that is, in the infinitely dilute limit the activity of the *solute* is proportional to its concentration. In this limit the activity coefficient is a proportionality constant. These two limits are statements of, respectively, Raoult's law and Henry's law (first stated to refer to the partial pressures of gasses).

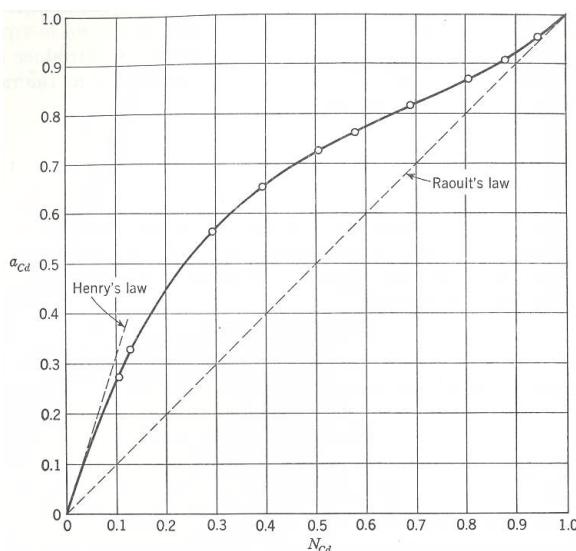


FIG. 10-5. Activity of cadmium in the Cd-Pb system at 500°C.

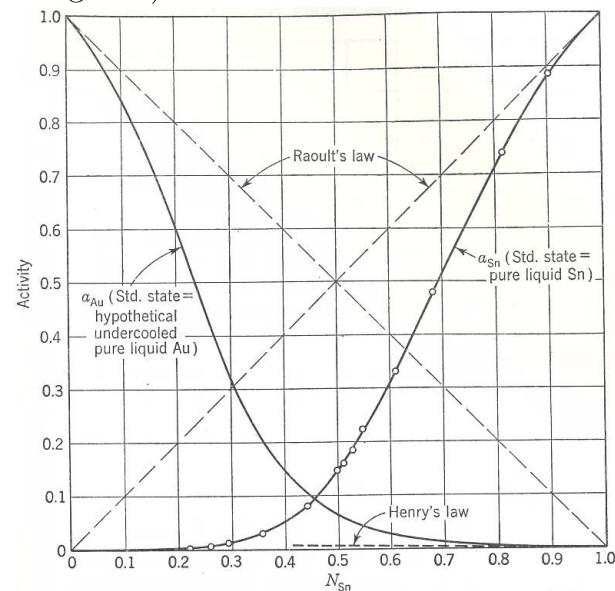


FIG. 10-10. Activity of tin and gold in the Sn-Au system at 600°C.

Figure A1. Activity for some liquid binary alloys as functions of concentration. The left hand figure shows a *positive* deviation from Raoult's law and the right hand figure shows *negative* deviation. When the concentration of a component tends to one we then call this component the *solvent* for obvious reasons.

In solid solutions with positive deviation, $a_i > x_i$, the solute behaves as if it were in a greater concentration than it actually is, and *vice versa*. Equation (A3.2) indicates that if $a_i > x_i$ (activity coefficient greater than one) then the mixing of the solute in the solvent is endothermic, meaning that the solute doesn't want to form a solid solution

and the mixture has a tendency to phase separation or possibly spinodal decomposition. Conversely if $\gamma_i < 1$ then the mixing is exothermic, very roughly meaning that the component i likes to form bonds with the atoms of the solvent.

Incidentally a consequence of the Gibbs-Duhem equation (A2.11) is that

$$\sum_{i=1}^N x_i d \ln a_i = 0$$

This can often be used to find the activity of one component if the activity of the others is known.

3.1 Ideal mixture

The “ideal mixture” or ideal solution, or ideal solid solution, like the ideal gas, is an idealisation but which fits the facts in many cases. They are characterised by a special form of the entropy of mixing, namely this: if the two components are initially separated into two containers and subsequently allowed to mix at constant temperature then the change in entropy is

$$\begin{aligned}\Delta S &= R \sum_{i=1}^N n_i \ln \frac{n}{n_i} \\ &= R \left(n \ln n - \sum_{i=1}^N n_i \ln n_i \right)\end{aligned}\tag{A3.3}$$

Here, n is the total number of moles and n_i is the number of moles of component i . For an ideal gas, we have from the ideal gas law (Dalton’s Law) that $n/n_i = p/p_i$ where p is the total pressure and p_i is the partial pressure of component i . So you can define the ideal solution as one whose entropy of mixing is taken by analogy with the ideal gas. You can see (A3.3) derived in a textbook on thermodynamics (look up “Gibbs’s paradox”).†

† In the case of a binary mixture you can derive (A3.3) from a statistical point of view. If the N atoms are arranged on the lattices of two perfect crystals then the number of ways of arranging the atoms into two separated bodies is exactly **one**. When the atoms are randomly mixed on a common lattice in the alloy body then the number of ways of arranging the N_a A-atoms and the N_b B-atoms is

$$W = \frac{(N_a + N_b)!}{N_a! N_b!} = \frac{N!}{N_a! N_b!}$$

So from the Boltzmann formula for the entropy, $S = k_B \ln W$ the entropy of mixing is

$$\begin{aligned}\Delta S &= k_B \ln \frac{W}{\text{one}} = k_B (\ln N! - \ln N_a! - \ln N_b!) \\ &= -k_B \left(N_a \ln \frac{N_a}{N} - N_b \ln \frac{N_b}{N} \right)\end{aligned}$$

using Sterling’s approximation $\ln x! \approx x \ln x - x$ for large x , and this is consistent with (A3.3).

So when I take n_i moles of each of N components in the pure state at a given temperature and pressure, and I mix them to produce an *ideal* homogeneous single phase mixture of atoms, then the total Gibbs free energy of the body that I have created is the sum of the numbers of moles times the molar free energies, $\mu_i^{\alpha,\bullet}$, of the pure substances in phase α plus the free enthalpy of mixing which is $-T\Delta S$ since the solution is ideal. Hence,

$$G(T, p) = \sum_{i=1}^N n_i \left(\mu_i^{\alpha,\bullet}(T, p) - RT \ln \frac{n}{n_i} \right)$$

By comparison with equation (A2.10) I see that the chemical potential of component i in the ideal mixture is

$$\begin{aligned} \mu_i &= \mu_i^{\alpha,\bullet}(T, p) + RT \ln \frac{n_i}{n} \\ &= \mu^\bullet + RT \ln \frac{n_i}{n} \end{aligned} \quad (\text{A3.4})$$

so that μ^\bullet is the chemical potential of component i in its reference state: that is, in the pure substance in phase α (presumably but not necessarily the crystal structure adopted by the pure substance) at the temperature and pressure specified. So you can at least see where the structure of (A3.1) comes from: x_i is n_i/n and we replace x_i with a_i to recognise that not all mixtures are ideal in real life. In the case of the ideal gas, we have

$$dG = Vdp - SdT$$

and so at constant temperature

$$dG = Vdp = nRT d\ln p ; \quad \text{using the ideal gas law } pV = nRT$$

which on integration results in

$$\left(\frac{\partial G}{\partial n} \right)_{T,p} = \mu = \mu^\ominus + RT \ln \frac{p}{p^\ominus} \quad (\text{A3.5})$$

in which if the pressure is measured in bar ($p^\ominus = 10^5 \text{ N/m}^2$) then μ^\ominus is the chemical potential (free enthalpy per mole) in the standard state of one bar pressure and the temperature in question, and the pressure p is measured in units of one bar.

3.2 Non ideal mixture

Up to now I have used the superscript \circ applied to μ to denote some unspecified “standard state”. In the case of the ideal gas once we have integrated dG then the integration constant will depend on the boundary condition. If we choose to measure the pressure in bar, then (A3.5) indicates that μ^\ominus is the chemical potential of the ideal gas at one bar pressure and the temperature in question. We could have chosen different units of pressure, atmospheres or Pascal, in which case the integration constant would be different. We are transferring weight from the constant term to the log term without altering the chemical potential in the right hand side of (A3.5). This is called “choosing a standard state.” Then, rather than the generic superscript \circ we use the superscript \ominus to indicate

that we are using the “one-bar standard state.” The only restriction on the choice of standard state is that the standard chemical potential (the integration constant) should depend *only* on temperature and pressure.

In (A3.4) we used the superscript \bullet to denote the “pure substance standard state” so we rewrite (A3.1),

$$\mu_i = \mu_i^\bullet + RT \ln \gamma_i x_i = \mu_i^\bullet + RT \ln a_i \quad (\text{A3.6})$$

In the limit that the mixture tends to pure component i , γ_i tends to one,

$$\begin{aligned} \mu_i &= \mu_i^\bullet + RT \ln \gamma_i x_i \\ \rightarrow \underbrace{\mu_i}_{\text{Raoult's law}} &= \mu_i^\bullet + RT \ln x_i \quad (x_i \rightarrow 1) \end{aligned}$$

At $x_i = 1$, the last term is zero ($\log 1 = 0$) and so $\mu_i = \mu_i^\bullet$ which identifies μ_i^\bullet as the chemical potential of pure substance i at the temperature and pressure of interest. From now on, we will refer to a_i as the *Raoultian activity* of component i , understanding that the Raoultian activity is referred to the pure solvent standard state.

$$a_i = \gamma_i x_i \quad \longleftarrow \text{Raoultian activity}$$

In the *infinitely dilute limit*, $x_i \rightarrow 0$, the activity coefficient becomes a constant, independent of concentration.[†]

$$\begin{aligned} \mu_i &= \mu_i^\bullet + RT \ln \gamma_i x_i \\ \rightarrow \underbrace{\mu_i}_{\text{Henry's law}} &= \mu_i^\bullet + RT \ln \gamma_i^\infty x_i \quad (x_i \rightarrow 0) \end{aligned}$$

It is useful therefore to create a new, infinitely dilute, standard state in order to describe the activity of dilute solutes. To this end we write

$$\begin{aligned} \mu_i &= \mu_i^\bullet + RT \ln \gamma_i x_i \\ &\approx \mu_i^\bullet + RT \ln \gamma_i^\infty x_i \quad (x_i \rightarrow 0) \\ &= \mu_i^\bullet + RT \ln \gamma_i^\infty + RT \ln x_i \\ &= \mu_i^\infty + RT \ln x_i \\ &= \mu_i^\infty + RT \ln h_i \end{aligned} \quad (\text{A3.7})$$

where

$$\mu_i^\infty = \mu_i^\bullet + RT \ln \gamma_i^\infty$$

is the chemical potential in the *Henrian* standard state and, since γ_i^∞ does not depend on composition, depends only on T and p . We also introduce the *Henrian activity* of component i ,

$$h_i = x_i = \frac{a_i}{\gamma_i^\infty} \quad \longleftarrow \text{Henrian activity}$$

[†] The mathematically astute will notice that as x_i goes to zero so μ_i goes to minus infinity.

We have

$$\text{Henrian activity} = \frac{\text{Raoultian activity}}{\text{infinite dilution activity coefficient}}$$

Rewriting (A3.6) for the *same chemical potential*,

$$\mu_i = \mu_i^* + RT \ln a_i \quad a_i = \gamma_i x_i \quad \text{Raoultian std. state} \quad (\text{A3.8a})$$

$$= \mu_i^\infty + RT \ln \frac{\gamma_i}{\gamma_i^\infty} x_i$$

$$\approx \mu_i^\infty + RT \ln h_i \quad h_i = x_i \quad \text{Henrian std. state—dilute limit only} \quad (\text{A3.8b})$$

so we have exploited the freedom of choosing a standard chemical potential to transfer mathematically weight between the two terms, and then made the approximation $\gamma_i = \gamma_i^\infty$ in the dilute limit. For the solvent it is convenient to express the concentration in terms of Raoultian activity and use the corresponding standard chemical potential; for the solute it is usually convenient to use the Henrian activity.

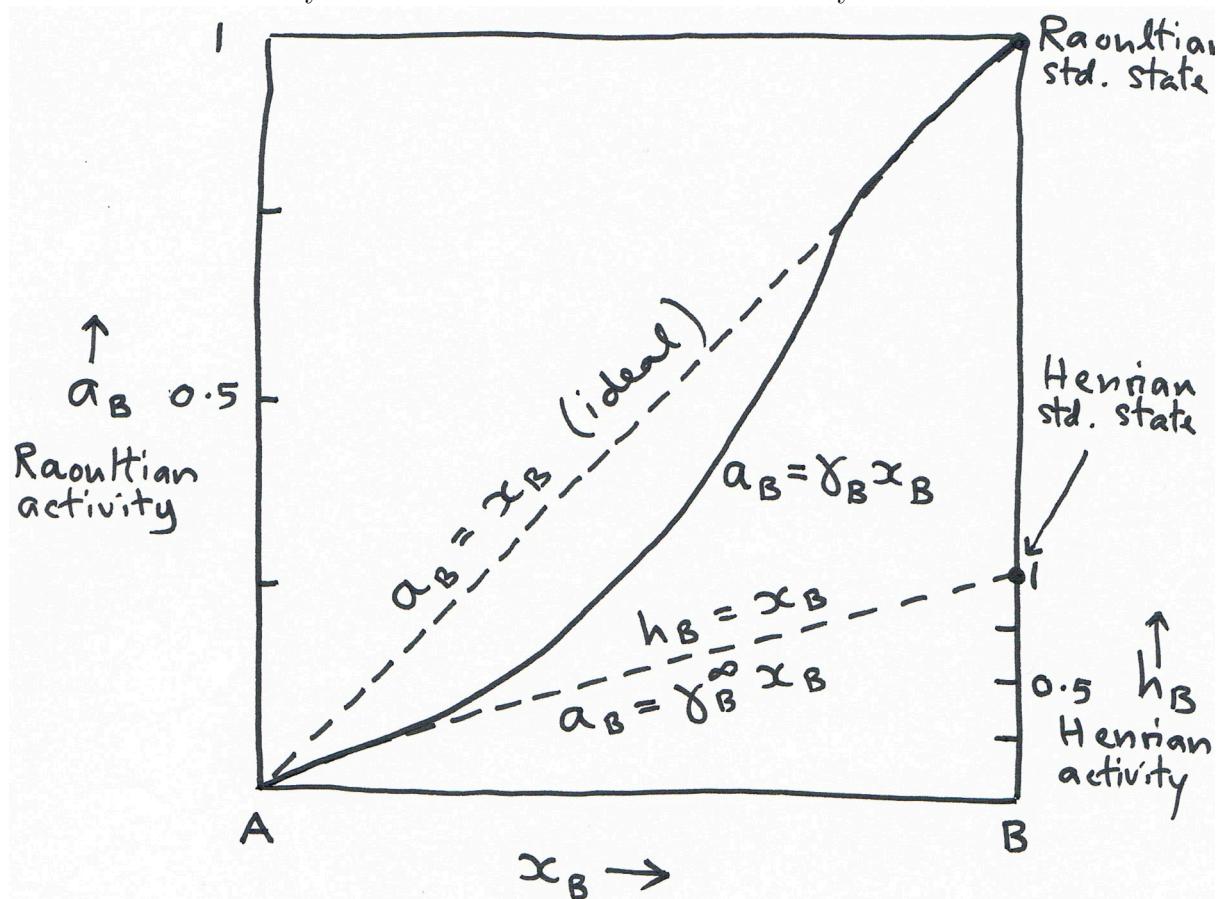


Figure A2. (After John West) Cartoon of the activity as a function of concentration (solid line) for a binary AB solution. An ideal solution has $a = x$. The Raoultian activity, a , is equal to the concentration, x in the limit as $x \rightarrow 1$. The Henrian activity h is equal to x as $x \rightarrow 0$. Because the width of the abscissa is one, the slope of the Henrian activity as a function of x is γ^∞ and the straight line intersects the right hand ordinate at the Henrian standard state.

These concepts are illustrated in figure A2. The Raoultian standard state (A3.8a) may be used over the whole range of concentration since the Raoultian activity, $a_i = \gamma_i(T, p, x_1, x_2, \dots, x_N)x_i$ describes the whole solid curve and contains all of the non ideality of the mixture. On the other hand the Henrian standard state (A3.8b) is very convenient because we can use concentration directly as a surrogate for activity, but it is *only correct as long as the component is sufficiently dilute* for Henry's law to be valid; that is, the solid curve in figure A2 must coincide with the Henry's law straight line. This is due to the \approx sign in (A3.7). Also the Henrian standard chemical potential, μ^∞ , is impossible to visualise: it is the chemical potential for a solute at a concentration of one—at which point it has become pure solvent! On the other hand the Raoultian standard chemical potential is clearly the molar free enthalpy of the pure substance, which may be conveniently be set to zero at standard temperature and pressure.

3.3 Unimolar standard state

The mole fraction, x_i , is the same as the atom fraction and is the number of moles (or atoms) of component i divided by the total number of moles (or atoms) in a substance. This is obviously a good measure of concentration in physical or metallurgical thermodynamics, but in electrochemistry and solution chemistry it is usual to measure concentrations in moles per litre or moles per kilogram of solvent. By definition one mole of a substance has a mass equal to its relative molar mass (molecular weight), M_W , in grams. Hence one kg of solvent contains $10^3/M_W$ moles. The mole fraction is

$$x_i = \frac{n_i}{n} \quad (\text{A3.9})$$

and the concentration in moles per kg is

$$c_i = \frac{n_i}{M} \quad (\text{A3.10})$$

where M is the mass of the solvent in kg. As there are n moles of solvent the mass of the solvent in kg is

$$M = 10^{-3} \times n M_W$$

and hence

$$c_i = \frac{10^3}{M_W} \frac{n_i}{n} = x_i \frac{10^3}{M_W} \quad (\text{A3.11})$$

This is not dimensionless and so we finally define a modified, “unimolar” Henrian activity

$$m_i = \frac{c_i}{c^\circ} = x_i \frac{10^3}{c^\circ M_W}$$

in which c° is the standard concentration of one mole per kilogram.

There is a small error which I have overlooked in comparing x_i and c_i . In (A3.9) the denominator is the *total number of moles* $\sum_j n_j$ including the component i , whereas in (A3.10) the denominator is just the mass of the solvent. So (A3.10) is only correct in the dilute limit. This is also the limit in which (A3.8b) is true and we can take

that equation and, as before, move weight from the log term to the standard chemical potential term, and introduce the *unimolar standard state*,

$$\mu_i \approx \mu_i^\infty + RT \ln x_i \quad (\text{A3.12a})$$

$$= \mu_i^m + RT \ln m_i \quad (\text{A3.12b})$$

where

$$\mu_i^m = \mu_i^\infty + RT \ln \frac{10^3}{c^\circ M_W}$$

in which M_W is the molecular weight of the solvent and $c^\circ = 1$ if the activity is expressed in moles per kg of solvent. We can reintroduce an activity coefficient, f_i , to describe the departure from Henry's law, so that the chemical potential with respect to the unimolar standard state is

$$\mu_i = \mu_i^m + RT \ln f_i m_i$$

In the case of a dissolved salt, such as sodium chloride, this will be completely ionised in water to its constituent ions, Na^+ and Cl^- . We cannot measure their activities or chemical potentials separately so it's conventional to write the chemical potentials of the cations and anions as,

$$\mu_+ = \mu_+^m + RT \ln f_\pm m_+ \quad (\text{A3.13a})$$

$$\mu_- = \mu_-^m - RT \ln f_\pm m_- \quad (\text{A3.13b})$$

and f_\pm is the "mean molal activity coefficient. Here they are for NaCl to show how deviation from Henry's law is observed as the concentration of NaCl increases.

m_{NaCl}	0.001	0.003	0.01	0.03	0.1	0.3	1	3
x_{NaCl}	1.8×10^{-5}	5.4×10^{-4}	1.8×10^{-4}	5.4×10^{-3}	0.0018	0.0054	0.018	0.054
f_\pm	0.97	0.94	0.90	0.85	0.78	0.71	0.66	0.71

Further Reading

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