ELECTROCHEMISTRY NOTES

The Origin of Electrode Potentials

An equilibrium of reduction and oxidation is set up in a solution of M^{n+} and M^{m+} when a source of electrons (e.g. metal wire) is introduced.

$$\text{e.g. } Fe^{3+}(aq) + e^{-}(metal) \Leftrightarrow Fe^{2+}(aq)$$

Regardless of the favoured direction, it is expected that at equilibrium there will exist a charge separation between the electrode and solution, and hence a potential difference between the two will exist.

Using Le Chatelier's Principle, we can expect that the concentration of metal ions will influence the equilibrium, and hence the potential. In fact, that ratio of the concentrations of e.g. Fe^{3+} and Fe^{2+} is crucial:

$$\phi_M - \phi_S = \text{constant} - {}^{RT}/_F \ln ([Fe^{2+}]/[Fe^{3+}])$$

Where ϕ denotes the electrical potential, and F is the Faraday Constant.
This is the **Nernst Equation**.

Thermodynamic Description of Equilibrium

Consider the gas phase reaction:

$$A(g) \Leftrightarrow B(g)$$

The simplest way of keeping track of this system is to note that at equilibrium the reactants and products must have identical chemical potentials:

$$\mu_A = \mu_B$$

These can in turn be related to partial pressures, as:

$$\mu_A = \mu_A^o + RT \ln p_A$$

At equilibrium:

$$K_p = p_B/p_A = \exp [(\mu_A^o - \mu_B^o)/RT]$$

Applying this now to the case where A and B are in solution:

$$\mu_A = \mu_A^o + RT \ln x_A = \mu_A^o + RT \ln [A]$$

where the solutions are assumed to be ideal. Also,

$$x_A = n_A/(n_A+n_B) \text{ and } [A] = n_A/V$$

This gives rise to two alternative standard states:

(i) when mole fractions are used, μ^o is the chemical potential when $x = 1$ and so relates to a pure liquid, and
(ii) when considering concentrations, μ^o is the chemical potential of a solution of A of unit concentration.

Thermodynamic Description of Electrochemical Equilibrium

The above must be modified for two phases (solution and electrode). Also, it involves the transfer of a charge particle (electrical energy must also be considered). The latter adds a factor of $z_AF\phi$ to the chemical potential, where z_A is the charge on the molecule A.

Deriving the Nernst Equation for the Fe^{2+}/Fe^{3+} system above, the starting point for this is that at equilibrium, total electrochemical potential of reactants = total electrochemical potential of products. This gives us:

$$(\mu_{Fe3+} + 3F\phi_s) + (\mu_{e-} - F\phi_M) = (\mu_{Fe2+} + 2F\phi_s)$$

From the revised equation for chemical potential. Rearranging, and applying:

$$\mu_{Fe3+} = \mu^o_{Fe3+} + RT \ln [Fe^{3+}] \text{ (and similar for } Fe^{2+})$$

we obtain:

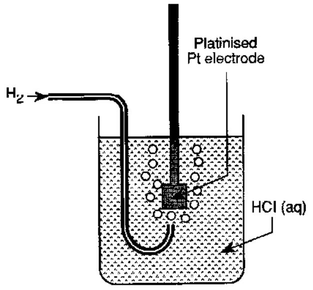
$$\phi_M - \phi_s = \Delta\phi^o - {}^{RT}/_F \ln ([Fe^{2+}]/[Fe^{3+}])$$

$\Delta\phi^o$ is a constant, containing the two standard chemical potentials + the chemical potential of an electrode in the electrode.

The Nernst Equation and some other electrode/solution Interfaces

The Hydrogen Electrode

$$H^+(aq) + e^-(metal) \Leftrightarrow \tfrac{1}{2}H_2(g) \qquad (1)$$



We can derive the Nernst Equation as above:

$$(\mu_{H+} + F\phi_s) + (\mu_{e-} - F\phi_M) = \tfrac{1}{2}\,\mu_{H2}$$

Rearrangement as above gives:

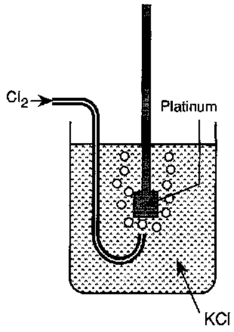
$$\phi_M - \phi_S = \Delta\phi^o + {}^{RT}/_F \ln([H^+]/p_{H2}^{1/2})$$

where $p_{H2}^{1/2}$ is equivalent to the "concentration" of H_2 gas in terms of chemical potentials.

The Nernst Equation thus predicts that increasing $[H^+]$ should make the electrode more positive relative to the solution. This is exactly what we would predict on the basis of the potential determining equilibrium written for this electrode above (i.e. equation (1) is the right way round). Applying Le Chatelier's Principle, adding H^+ shifts the equilibrium to the right. This removes electrons from the electrode, so makes it more positively charged.

The Chlorine Electrode

$$\tfrac{1}{2}\,Cl_2(g) + e^-(metal) \Leftrightarrow Cl^-(aq)$$



Deriving the Nernst Equation exactly as above gives:

$$\tfrac{1}{2}\,\mu_{Cl2} + (\mu_{e-} - F\phi_M) = (\mu_{Cl-} - F\phi_s)$$

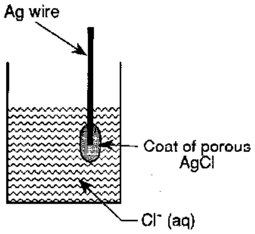
i.e.

$$\phi_M - \phi_S = \Delta\phi^o + {}^{RT}/_F \ln(p_{Cl2}^{1/2}/[H^+])$$

This predicts that the quantity $\phi_M - \phi_s$ becomes more positive if the partial pressure of chlorine gas is increased, or if the concentration of Cl^- is decreased (i.e. the opposite way round to the Hydrogen Electrode).

The Silver/Silver Chloride Electrode

$$AgCl(s) + e^-(metal) \Leftrightarrow Ag(metal) + Cl^-(aq)$$



The equilibrium is established at the silver/silver chloride boundary. It is therefore important that the silver chloride coat is porous so that the aqueous solution containing the chloride ions penetrates to the boundary to establish equilibrium. We obtain:

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

Both AgCl and Ag are present as pure solids, hence no terms of the form RT ln [A] appear in their chemical potential equations (only for solutions / gases). This gives:

$$\phi_M - \phi_S = \Delta\phi^o - {}^{RT}/_F \ln([Cl^-])$$

Concentrations or Activities?

Activities are introduced to account for non-ideality. More on this below. For now, we can say that activities approximate to concentrations in chemical potential terms, i.e.

$$\phi_M - \phi_S = \Delta\phi^o - {}^{RT}/_F \ln([a_{Cl-}])$$

is the most accurate way to express the above. The activity terminology will be used from now on.

Generalising the Nernst Equation for arbitrary potential determining equilibria

For any electrode process:

$$v_A A + v_B B + \ldots + e^-(\text{metal}) \Leftrightarrow v_C C + v_D D + \ldots$$

The v_J terms are the stoichiometric amounts of each component.

Using the same methodology as for the Fe^{2+}/Fe^{3+} (and subsequent examples) we find that the Nernst Equation generalises to:

$$\phi_M - \phi_S = \Delta\phi^o - {}^{RT}/_F \ln (a_A{}^{vA} a_B{}^{vB} \ldots / a_C{}^{vC} a_D{}^{vD} \ldots)$$

For gaseous components, the activity is replaced by the partial pressures, p_J as above.

Measurement of Electrode Potentials: The Need For A Reference Electrode

Impossible to measure an absolute value for the potential drop at a single electrode solution interface. Need a test electrode and a reference electrode to compare to (to complete the circuit). This is depicted in shorthand notation as:

Reference Electrode | Solution | Test Electrode

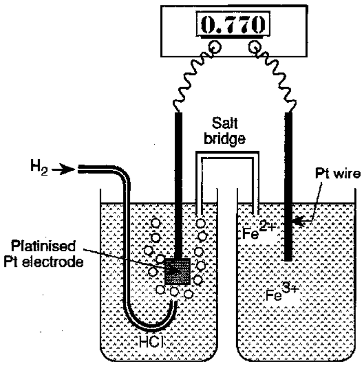
The vertical line notates a boundary between two separate phases. The measured potential by the cell is then given by $(\phi_{test} - \phi_s) - (\phi_{ref} - \phi_s)$. This works best when $(\phi_{ref} - \phi_s)$ is constant. We can then measure any changes in measured potential directly.

A successful reference electrode must display the following properties:

- The chemical composition of the electrode and the solution to which the electrode is directly exposed must be held fixed. This is because the reference electrode potential will be established by some potential-determining equilibrium and the value of this potential will depend on the relative concentrations of the chemical species involved. If these concentrations change the electrode potential also changes.
- One very important consequence of the requirement for a fixed chemical composition is that it would be disastrously unwise to pass a large electric current through the reference electrode since the passage of this current would induce electrolysis to take place and this would inevitable perturb the concentrations of the species involved in the potential-determining equilibrium.
- It is also experimentally desirable that potential term $(\phi_{ref} - \phi_s)$ attains its thermodynamic equilibrium value rapidly. In other words the potential determining equilibrium should display *fast electrode kinetics*.

The Standard Hydrogen Electrode

The standard Hydrogen Electrode (SHE) fits the above well. For example, to measure the Fe^{2+}/Fe^{3+} potential we would use:



<u>The Salt Bridge</u> – tube containing KCl which places the two half cells in electrical contact. One purpose of this is to stop the two different solutions required for the two half cells from mixing. Otherwise, for example, the Pt electrode forming part of the SHE would be exposed to Fe^{2+}/Fe^{3+} and its potential accordingly disrupted.

- In the SHE the pressure of hydrogen gas is fixed at one atmosphere and the concentration of protons in the aqueous HCl is exactly 1.18M (unity activity of H^+). The temperature is fixed at 298K.
- The digital voltmeter draws negligible current so that no electrolysis of the solution occurs during measurement.
- The reference electrode is fabricated from platinised platinum rather than bright platinum metal to ensure fast electrode kinetics. The purpose of depositing a layer of fine platinum black onto the surface is to provide catalytic sites which ensure that the potential determining equilibrium is rapidly established.

Using the Nernst Equation we obtain:

$$\phi_{Pt} - \phi_S = \Delta\phi^o_{Fe2+/Fe3+} - {}^{RT}/_F \ln (a_{Fe2+}/a_{Fe3+})$$

$$\phi_{ref} - \phi_S = \Delta\phi^o_{H2/H+} - {}^{RT}/_F \ln (a_{H+}/p_{H2}{}^{1/2})$$

The measured potential is:

$$\Delta\phi = \phi_{Pt} - \phi_{ref}$$

And can be obtained from the above by simple subtraction:

$$\Delta\phi = (\phi_{Pt} - \phi_s) - (\phi_{Pt} - \phi_s)$$

$$\Delta\phi = \Delta\phi^o_{Fe2+/Fe3+} - \Delta\phi^o_{H2/H+} + {}^{RT}/_F \ln (a_{Fe3+}p_{H2}{}^{1/2}/a_{Fe2+}a_{H+})$$

Which is often written as:

$$E = E^o + {}^{RT}/_F \ln (a_{Fe3+}p_{H2}{}^{1/2}/a_{Fe2+}a_{H+})$$

The value of E^o is known as the "standard electrode potential" of the Fe^{2+}/Fe^{3+} couple. This is the measured potential with the SHE ($a_{H+} = 1$, $p_{H2} = 1$atm) when all the chemical species contributing to the potential determining equilibrium are present at unity activity.

Standard Electrode Potentials (SEP)

A further example is the Cu/Cu^{2+} couple.

$$Pt \mid H_2(g)\ (p = 1atm) \mid H^+(aq)\ (a=1) \parallel Cu^{2+}(aq)\ (a=1) \mid Cu$$

(The symbol || denotes the salt bridge).

The SEP of the Cu/Cu^{2+} couple is given by:

$$E^o_{Cu/Cu2+} = \phi_{Cu} - \phi_{Pt}$$

When measured the potential difference between the copper and platinum electrodes is found to be 0.34V with the copper electrode positively charged and the platinum negatively charged. In writing down potentials a convention is essential so that the correct polarity is assigned to the cell. This is done as follows: *with reference to a cell diagram, the potential is that of the right hand electrode relative to that of the left hand electrode, as the diagram is written down*. Thus for:

$$Cu \mid Cu^{2+}(aq)\ (a=1) \parallel H^+(aq)\ (a=1) \mid H_2(g)\ (p=1atm) \mid Pt$$

$$E_{cell} = -0.34V = \phi_{Pt} - \phi_{Cu}$$

$$Pt \mid H_2(g)\ (p = 1atm) \mid H^+(aq)\ (a=1) \parallel Cu^{2+}(aq)\ (a=1) \mid Cu$$

$$E_{cell} = +0.34V = \phi_{Cu} - \phi_{Pt}$$

Tabulated values allow the prediction of the potential of any cell formed from any pair of half cells. For example, the cell,

$$Cu \mid Cu^{2+}(aq)\ (a=1) \parallel Zn^{2+}(aq)\ (a=1) \mid Zn$$

$$E_{cell} = \phi_{Zn} - \phi_{Cu}$$

$$E^o_{cell} = E^o_{Zn/Zn2+} - E^o_{Cu/Cu2+}$$

Note also that it is possible to calculate cell potentials when the activity is non-unity. For example,

$$Cu \mid Cu^{2+}(aq)\ (a_{Cu2+}) \parallel Zn^{2+}(aq)\ (a_{Zn2+}) \mid Zn$$

$E_{cell} = \phi_{Zn} - \phi_{Cu} = (\phi_{Zn} - \phi_s) - (\phi_{Cu} - \phi_s)$
$E_{cell} = (\Delta\phi^o_{Zn/Zn2+} + {}^{RT}/_{F} \ln a_{Zn2+}^{1/2}) - (\Delta\phi^o_{Cu/Cu2+} + {}^{RT}/_{F} \ln a_{Cu2+}^{1/2})$
$E_{cell} = (\Delta\phi^o_{Zn/Zn2+} - \Delta\phi^o_{Cu/Cu2+}) + {}^{RT}/_{F} \ln (a_{Zn2+}^{1/2}/a_{Cu2+}^{1/2})$
$E_{cell} = E^o_{Zn/Zn2+} - E^o_{Cu/Cu2+} + {}^{RT}/_{2F} \ln (a_{Zn2+}/a_{Cu2+})$

This is the Nernst Equation for the cell.

The Nernst Equation Applied to General Cell
Following the procedure below (generalised strategy of preceding section):

(i) Write down the cell in shorthand notation.

(ii) Write the reactions at the two electrodes as reductions involving **one electron only**. Writing the reaction as a reduction means that the electron appears in the left hand side of the equation in each case.

(iii) Subtract the reaction at the left hand electrode (in the cell as written down) from the reaction at the right hand electrode to find a “formal cell reaction”:

$$\sum_i v_i R_i \rightarrow \sum_j v_j P_j$$

where R_i represents the reactants, P_j the products, and v_i and v_j are their stoichiometries.

(iv) The resulting Nernst Equation is given by:

$$E_{cell} = E^o{}_{cell} + \frac{RT}{F} \ln \frac{\prod_i a_{R_i}^{v_i}}{\prod_j a_{P_j}^{v_j}}$$

Where $E^o_{cell} = E^o_{right} + E^o_{left}$ (the SEPs of the half-cell reactions as drawn).

Next we illustrate the above procedure for the cell:

$Cd \mid Cd^{2+}(aq)\ (a_{Cd2+}) \parallel Pb^{2+}(aq)\ (a_{Pb2+}) \mid Pb$

Step (ii) gives the reaction at the right hand electrode as:

$½Pb^{2+}(aq) + e^- \rightarrow ½Pb(s)$

At the left hand electrode the reaction is:

$½Cd^{2+}(aq) + e^- \rightarrow ½Cd(s)$

Step (iii) and subtracting gives:

$½Pb^{2+}(aq) + ½Cd(s) \rightarrow ½Pb(s) + ½Cd^{2+}(aq)$

This is the formal cell reaction.
Step (iv) gives:

$$E_{cell} = E^o{}_{cell} + \frac{RT}{F} \ln \frac{a_{Pb2+}^{1/2}}{a_{Cd2+}^{1/2}}$$

Where $E^o_{cell} = E^o_{Pb/Pb2+} + E^o_{Cd/Cd2+}$.

Tables give $E^o_{Pb/Pb2+} = -0.126V$ and $E^o_{Cd/Cd2+} = -0.403V$:

$E^o_{cell} = (-0.126) - (-0.403) = +0.277V$

$$E_{cell} = 0.277 + \frac{RT}{2F} \ln \frac{a_{Pb^{2+}}}{a_{Cd^{2+}}}$$

It should be noted that the formal cell reaction, as introduced in step (iii), depends on how the cell is written down in step (i). For example, the cell:

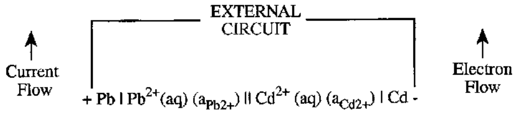
$Cd \mid Cd^{2+}(aq)\ (a_{Cd2+}) \parallel Pb^{2+}(aq)\ (a_{Pb2+}) \mid Pb$
$½Pb^{2+}(aq) + ½Cd(s) \rightarrow ½Pb(s) + ½Cd^{2+}(aq)$
$E^o_{cell} = +0.277V$

In contrast the cell:

$$\mathrm{Pb}\,|\,\mathrm{Pb}^{2+}(aq)\,(a_{Pb2+})\,||\,\mathrm{Cd}^{2+}(aq)\,(a_{Cd2+})\,|\,\mathrm{Cd}$$
$$\tfrac{1}{2}\mathrm{Cd}^{2+}(aq) + \tfrac{1}{2}\mathrm{Pb}(s) \rightarrow \tfrac{1}{2}\mathrm{Cd}(s) + \tfrac{1}{2}\mathrm{Pb}^{2+}(aq)$$
$$E^{o}_{cell} = -0.277\mathrm{V}$$

It is thus helpful to distinguish the formal cell reaction from the spontaneous cell reaction. The latter is the reaction that would occur if the cell were shortcircuited. That is, the two electrode were directly connected to each other.

The nature of the spontaneous reaction can be readily deduced since in reality, electrons will flow from a negative electrode to a positive electrode through an external circuit as is illustrated:



Notice that this predicts the Cadmium electrode to be negatively charged and the Lead to carry a positive charge. Electrons therefore pass from the Cd to the Pb. This implies that oxidation occurs at the right hand electrode:

$$\tfrac{1}{2}\,\mathrm{Cd} \rightarrow \tfrac{1}{2}\,\mathrm{Cd}^{2+} + e^{-}$$

And reduction at the left hand electrode:

$$\tfrac{1}{2}\,\mathrm{Pb}^{2+} + e^{-} \rightarrow \tfrac{1}{2}\,\mathrm{Pb}$$

It follows that the spontaneous reaction is:

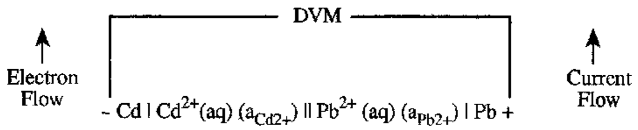
$$\tfrac{1}{2}\mathrm{Pb}^{2+}(aq) + \tfrac{1}{2}\mathrm{Cd}(s) \rightarrow \tfrac{1}{2}\mathrm{Pb}(s) + \tfrac{1}{2}\mathrm{Cd}^{2+}(aq)$$

In general, the spontaneous cell reaction that occurs when the two electrodes are shortcircuited may be established using the protocol set out earlier, and tables of electrode potentials decide which electrode is positive charged and which negatively charged. Electron flow in the external current will always be from the negative to the positive electrode so that an oxidation process will occur at the former and a reduction at the latter.

The relation of Electrode Potentials to the Thermodynamics of the Cell Reaction

Due to the negligible current, electrons are transferred under essentially thermodynamically reversible conditions.

Consider,



If dn moles of electrons flow from the negative electrode, then dn moles of the following reaction will occur:

$$\tfrac{1}{2}\mathrm{Pb}^{2+}(aq) + \tfrac{1}{2}\mathrm{Cd}(s) \rightarrow \tfrac{1}{2}\mathrm{Pb}(s) + \tfrac{1}{2}\mathrm{Cd}^{2+}(aq)$$

Associated with this will be a change dG in the Gibbs Free Energy of the cell.

$$dG = dw_{additional}$$

where dw_{add} corresponds to the work done (other than pdV work) in the process. In the above scheme the only contribution to this quantity is the work done in transferring the charge (-Fdn Coulombs) through the external circuit across a potential difference of E_{cell}volts. It follows that:

$$dG = dw_{add} = (-Fdn)E_{cell}$$

For each mole transferred:

$$\Delta G = -\,FE_{cell}$$

Where ΔG refers to the reaction:

$$\frac{1}{2}Pb^{2+}(aq) + \frac{1}{2}Cd(s) \rightarrow \frac{1}{2}Pb(s) + \frac{1}{2}Cd^{2+}(aq)$$

If the cell components are at unit activity, then:

$$\mathbf{\Delta G^o = - FE^o}$$

It can therefore be seen that the measurement of cell potentials provides information about free energy changes. Furthermore, since:

$$dG = Vdp - SdT$$

It can be concluded that:

$$F\left(\frac{\partial E}{\partial T}\right)_p = \Delta S$$

Combining this with ΔH^o with $\Delta G^o + T\Delta S^o$ gives:

$$\Delta H^o = - FE^o + TF\left(\frac{\partial E^o}{\partial T}\right)_p$$

i.e. the entropy and enthalpy of a cell reaction can be obtained from the cell potential and its variation with temperature.

Standard Electrode Potentials and the Direction of Chemical Reactions

$$\sum_i v_i R_i \rightarrow \sum_j v_j P_j$$

$$E^o_{cell} = E^o_{right} + E^o_{left}$$

$$\mathbf{\Delta G^o = - FE^o = - RT \ln K}$$

Hence we obtain,

$$E^o = (RT/F) \ln K$$

We can thus conclude that if E^o is greater than zero K will be greater than one, and if E^o is negative K will be less than unity for the cell reaction. For example, we consider the SEP of a metal/metal ion couple as noted:

$$Pt \mid H_2(g)\ (p=1atm) \mid H^+(aq)\ (a=1),\ M^{n+}(aq)\ (a=1) \mid M$$

The formal cell reaction will be:

$$^1/_n\ M^{n+}(aq) + \frac{1}{2}H_2(g) \rightarrow {}^1/_n\ M(s) + H^+(aq)$$

and so the SEP of the metal/metal ion couple indicates whether or not the metal will react with $H^+(aq)$ to give hydrogen gas. Thus for example in the case of gold, we consider have a SEP for the above of +1.83V and so $\Delta G^o = - 1.83F$. It follows that gold will not react with acid under standard conditions to form H_2.

Conversely, considering the reaction with Li^+, the SEP is -3.04V so that for the above reaction $\Delta G^o = +3.04F$, showing reaction of Li with acid is strongly favoured in thermodynamic terms.

The inertness of gold and the reactivity of lithium in aqueous acid predicted in this way is well known.

Generalising the above, it can be seen that if a metallic element M has a SEP for M/M^{n+} couple which is negative, then it is possible for M to react with acid under standard conditions to evolve hydrogen. If the SEP is positive then it will be impossible thermodynamically.

A further useful example is seen when taking Cu^+ and Cu^{2+} in aqueous solution. If we consider the disproportionation reaction of Cu(I):

$$2Cu^+(aq) \Leftrightarrow Cu(s) + Cu^{2+}(aq)$$

This can be broken down into two separate reactions:

$$Cu^+(aq) + e^- \rightarrow Cu(s)$$
$$Cu^{2+}(aq) + e^- \rightarrow Cu^+(aq)$$

We find that E^o for the former reaction is +0.52V and for the latter is +0.16V. It follows that for the reaction:

$$Cu^+(aq) + \tfrac{1}{2} H_2(g) \Leftrightarrow Cu(s) + H^+(aq)$$
$$\Delta G^o = -0.52F$$

Likewise,

$$Cu^{2+}(aq) + \tfrac{1}{2} H_2(g) \Leftrightarrow Cu^+(aq) + H^+(aq)$$
$$\Delta G^o = -0.16F$$

The two reactions may be subtracted to give the disproportionation reaction:

$$\begin{array}{llcl} & Cu^+(aq) + \tfrac{1}{2} H_2(g) & \Leftrightarrow & Cu(s) + H^+(aq) \\ \text{minus} & Cu^{2+}(aq) + \tfrac{1}{2} H_2(g) & \Leftrightarrow & Cu^+(aq) + H^+(aq) \\ \text{gives} & 2Cu^+(aq) & \Leftrightarrow & Cu(s) + Cu^{2+}(aq) \end{array}$$

For which $\Delta G^o = (-0.52F) – (-0.16F) = -0.36F$

And so:

$$K = a_{Cu2+}/a_{Cu}a_{Cu+} = 1.2 \times 10^6 \text{ mol dm}^{-3}$$

We conclude that the disproportionation reaction is very likely to occur. Indeed Cu(I) disproportionates very rapidly in water, with a lifetime typically of less than one second, forming metallic copper and copper(II) ions.

Standard Electrode Potentials and Disproportionation

Extending the above Copper example to generalise for the reaction:

$$(a+b)\ M^{x+}(aq) \Leftrightarrow aM^{(x+b)+}(aq) + bM^{(x-a)+}(aq)$$

If we consider the separate reactions:

$$^1/_b\ M^{(x+b)+}(aq) + \tfrac{1}{2} H_2(g) \Leftrightarrow {^1/_b}\ M^{x+}(aq) + H^+(aq) \quad \Delta G^o = -FE^o(M^{x+}/M^{(x+b)+})$$
$$^1/_a\ M^{x+}(aq) + \tfrac{1}{2} H_2(g) \Leftrightarrow {^1/_a}\ M^{(x-a)+}(aq) + H^+(aq) \quad \Delta G^o = -FE^o(M^{(x-a)+}/M^{x+})$$

Thus,

$$\begin{array}{ll} \text{(ab) times:} & ^1/_a\ M^{x+}(aq) + \tfrac{1}{2} H_2(g) \Leftrightarrow {^1/_a}\ M^{(x-a)+}(aq) + H^+(aq) \\ \text{minus (ab) times:} & ^1/_b\ M^{(x+b)+}(aq) + \tfrac{1}{2} H_2(g) \Leftrightarrow {^1/_b}\ M^{x+}(aq) + H^+(aq) \\ \text{gives:} & (a+b)\ M^{x+}(aq) \Leftrightarrow aM^{(x+b)+}(aq) + bM^{(x-a)+}(aq) \end{array}$$

So that:

$$\Delta G^o = -abF\ [\ E^o(M^{(x-a)+}/M^{x+}) – E^o(M^{x+}/M^{(x+b)+})\ ]$$

It follows that the ΔG^o will be negative and the disproportionation favourable if:

$$E^o(M^{x+}/M^{(x+b)+}) < E^o(M^{(x-a)+}/M^{x+})$$

In the case of copper, $E^o(Cu^+/Cu^{2+}) < E^o(Cu/Cu^+)$, and thus disproportionation is favourable.

Standard Electrode Potentials and pH

$$pH = -\log_{10} a_{H3O+}$$

Consider the disproportionation of bromine:

$$2Br_2(aq) + 3H_2O(l) \rightarrow BrO_3^-(aq) + 6H^+(aq) + 5Br^-(aq)$$

Since $E^o(Br_2/BrO_3^-) = +1.48V$ and $E^o(Br^-/Br_2) = +1.06V$, it follows that $\Delta G^o = +2.10F$ kJ mol^{-1}.

Hence,

$$K = \frac{a_{H+}^6 . a_{BrO_3^-} . a_{Br-}^5}{a_{Br2}^3} = \exp(\frac{-2.10F}{RT})$$

Thus, at pH = 0, where a_{H+} = 1 the disproportionation is unfavourable. However, at pH = 9, we can deduce that:

$$\frac{a_{BrO_3^-} . a^5_{Br-}}{a^3_{Br2}} = 3.06x10^{-36} \times (10^9)^6 = 3.06 \times 10^{18}$$

So that in weakly basic solution the disproportionation becomes thermodynamically possible. Whenever protons or hydroxide ions appear for particular redox couples, the equilibria involved in these couples will be sensitive to the solution pH and by varying this quantity the equilibrium may be shifted in favour of products or reactants.

Thermodynamics vs. Kinetics

We have illustrated the use of electrode potentials in predicting the position of chemical equilibria. The predictions are subject, however, to kinetic limitations.

A classic example of this is Mg(s) dipped in water. Calculations predict this is favourable by -1.53F kJ mol^{-1}, but in practice little or no reaction is observed since a thin film of MgO on the metal surface prevents the reaction taking place. This is also seen for Titanium and Aluminium in water.

Electrode Potentials tell us **nothing** about the likely rate of the reaction.

Allowing for Non-Ideality – Activity Coefficients

Non-ideal solutions have a chemical potential given by $\mu_A = \mu_A^o + RT \ln a_A$, where a_A is the effective concentration of A in the solution or the activity of A. It is related to the concentration of the solution by the coefficient γ, such that $a_A = \gamma_A[A]$.

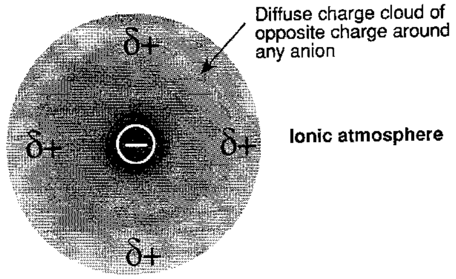
Clearly, if γ_A is unity, then the solution is ideal. Deviations from unity by γ_A are a measure of non-ideality. For dilute electrolytic solutions it is possible to calculate γ_A, involving the use of the Debye-Huckel Theory.

In approaching this topic, it is useful to have some grounding in the Thermodynamics of Solutions, found in the **Thermodynamics Notes**.

Debye Huckel Theory

For a dilute electrolytic solution the activity coefficient, γ, is usually less than 1. This implies that the solution is more stable, by an amount RT ln γ_I, as compared to the hypothetical situation where the ionic charge is "off". The physical origin of this stabilisation arises from the fact that the anion "sees" more oppositely charged ions than like-charged ions as it moves about in solution. Let us consider the distribution of charge around an ion.

On a time average this must be spherically symmetrical and reflect the fact that there will be a build up of opposite charge around the ion. The magnitude of the opposite charge decreases in a radial direction away form the ion in question. Far away from the ion the charge becomes zero corresponding to bulk solution, sufficiently remote that the ion's electroneutrality is unperturbed. These are referred to as *ionic atmospheres*.



We can calculate the charge distribution in the ionic atmosphere around a particular ion, j, and then use this to quantify the stabilisation of the ion. When scaled up for one mole of ions this should be equal to RT ln γ_j.

This turns out to be a straightforward but tedious exercise in electrostatics, provided some assumptions are made. The result is quite simple.

The deviation from ideality depends on a quantity known as the ionic strength, I, of the solution. This is defined as:

$$I = \frac{1}{2}\sum_i c_i {z_i}^2$$

where the sum is over all the ions, i, in solution, c_i is the concentration of ion i and z_i its charge.

For example, consider a 0.1M solution of $MgCl_2$:

$$I = ½ [\ 0.1 \times (+2)^2 + 0.2 \times (-1)^2\ ] = 0.3M$$

The ionic strength here is greater than the concentration.

As a second example consider a 0.1M solution of NaCl:

$$I = ½ [\ 0.1 \times (+1)^2 + 0.1 \times (-1)^2\ ] = 0.1M$$

In this case the ionic strength equals the concentration. This is a general result for species of the formula M^+X^-.

The basic equation of Debye-Huckel Theory is:

$$\mathbf{\log_{10} \gamma_j = - A{z_j}^2 \sqrt{I}}$$

where z_j is the charge on the ion and A is a temperature and solvent dependent parameter. For water at 25°C, A ≈ 0.5.

In calculating the electrostatic stabilisation conferred on an ion by its atmosphere so as to establish this equation, several assumptions are made:

(i) The cause of the solution non-ideality resides exclusively in coulombic interactions between the ions, and not at all, for example, in ion-solvent interactions.

(ii) The ionic interactions are quantitatively described by Coulomb's Law for point charge. This presumes that the effects of the solvent is solely to reduce inter-ionic forces by means of the dielectric constant.

(iii) The electrolyte is fully dissociated and no significant numbers of ion pairs exist. This implies that the external forces between the ions are weaker than the thermal forces in the solution moving ions around, together and apart.

These assumptions work well in dilute solutions, so that for ionic concentrations below ~ 10^{-2} M the Debye-Huckel Limiting Law works quantitatively.

The Debye-Huckel Limiting Law predicts that the deviation from ideality increases with the square root of the ionic strength, I. It is interesting to consider why this should be, and to focus on the size of the ionic atmosphere. The effective size is the latter is measured by its Debye length, which gives an indication of the distance between any ion and the average location of the charge in its ionic atmosphere. The higher the concentration, the shorter the Debye length, i.e. Debye length $\propto 1/\sqrt{I}$.

It follows that as the ionic strength increases the distance between the central ion and the charge in the ionic atmosphere shrinks. Accordingly Coulomb's Law leads us to expect that the electrostatic stabilisation of the ion conferred by the ionic atmosphere increases so that γ_j becomes smaller and the solution more non-ideal.

Limits of Debye-Huckel Theory

Works well in dilute solution – up to concentrations around 10^{-2}M, but overestimates the deviation from ideality at higher concentrations.

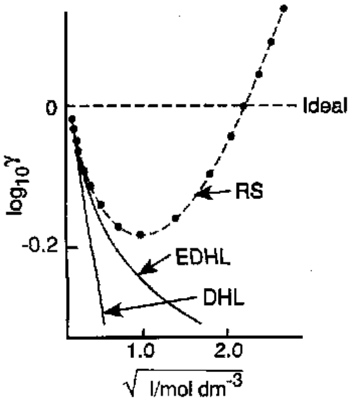
The Extended Debye-Huckel Law is given by the equation:

$$\log_{10}\gamma_j = \frac{-Az_j^{\,2}\sqrt{I}}{1+Ba\sqrt{I}}$$

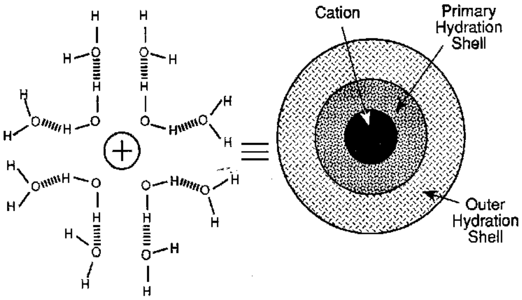
The constant B is, like A, a solvent and temperature specific parameter, whilst a is the radius of the ion, j. Hence, it is derived without the need to assume point charges (uses spheres of radius a instead). This works at higher concentrations.

Neither of these laws can predict the upturn seen at higher concentrations however. Physically this is because both equations attribute the deviation from ideality to electrostatic forces stabilising each ion and these increase – and the ionic atmospheres shrink – as the ionic strength increases. Some new factor must become important at higher concentrations.

This is because the y-axis no longer relates to the activity coefficient of a single ion, but is the mean activity coefficient, $\gamma_\pm$, defined as $\gamma_\pm = (\gamma_+\gamma_-)^{1/2}$ for an electrolyte of stoichiometry MX.



It can be seen that the deviation of experiment from the Debye-Huckel Limiting Law is faster for e.g. LiCl when compared to KCl. This implies that the new factor influencing deviation is greatest for Li^+. This can be attributed to charge density, which is higher on Li^+. As a consequence, Li^+ is more strongly hydrated in solution, i.e. deviation from the Debye-Huckel Limiting Law at higher concentrations is due to ion-solvent effects.



Can actually add a cI term to the Extended Debye-Huckel Law to account for this, where c is a solute and solvent specific parameter characterising the salvation of the ions.

Applications of the Debye-Huckel Limiting Law

Solubilities

The solubility of sparingly soluble salts can be slightly enhanced by an increase in ionic strength. For example the solubility product of silver chloride is $K_{sp} = a_{Ag+}a_{Cl-} = 1.7\times10^{-10}$ mol^2 dm^{-6} so that in pure water the solubility is approximately 1.3×10^{-5} mol dm^{-3}. The solubility of AgCl is promoted, a little, by the addition of KNO_3.

$$M^{z+}M^{z-}(s) \Leftrightarrow M^{z+}(aq) + M^{z-}(aq)$$

$$K_{sp} = a_M a_X = \gamma_M[M^{z+}].\gamma_x[X^{z-}]$$

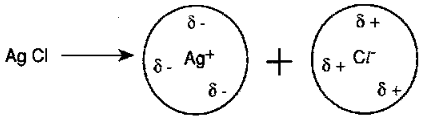
$$= \gamma_\pm^{2}[M^{z+}][X^{z-}]$$

The cation and anion concentrations will equal one another (=c), so that:

$$\log_{10} K_{sp} = 2\log_{10}\gamma_\pm + 2\log_{10}c.$$

Applying the Debye-Huckel Limiting Law then gives:

$$\log_{10}c = ½\log_{10}K_{sp} + z^2A\sqrt{I}.$$



Low ionic strength
Diffuse ionic atmosphere
Weak ionic stabilisation

High ionic strength
Tight ionic atmosphere
Strong ionic stabilisation

This shows that as the ionic strength is increased the solubility of MX is promoted. It is helpful to ask the physical reason for this, and to focus on the specific case of silver chloride. When AgCl is dissolved into a solution to which KNO_3 is progressively added, the Ag^+ and Cl^- ions will develop ionic atmospheres around themselves which will serve to stabilise the ions. Considering the equilibrium, stabilisation will pull it to the right hand side, so promoting solubility of the silver halide. As the ionic strength of the solute rises, the Debye length of the ionic atmosphere will shrink so that each ion will become closer to the (opposite) charge surrounding it and so the stabilisation is enhanced. Remember though that it will only apply quantitatively to dilute solutions.

The Kinetic Salt Effect

Consider the reaction between two charged species, M and X:

$$M + X \Leftrightarrow \{ M,X \} \rightarrow \text{products}$$

Where { M,X } is an activated complex or transition state denoted ‡ below. Assuming a pre-equilibrium with reactants M and X prior to reaction to the former with rate constant k, then:

$$K = a_{\ddagger} / a_M a_X = (\gamma_{\ddagger}/\gamma_M\gamma_X)([\ddagger]/[M][X])$$

The rate of reaction will be given by rate = k[‡]
Combining gives:

$$\text{rate} = kK(\gamma_M\gamma_X/\gamma_{\ddagger})$$

Or,

$$\log_{10}k_{app} = \log_{10}kK + \log_{10}\gamma_M + \log_{10}\gamma_X - \log_{10}\gamma_{\ddagger}$$

When expanding taking into account the Debye-Huckel Limiting law this gives:

$$\log_{10}k_{app} = \log_{10}kK - Az_M^2\sqrt{I} - Az_X^2\sqrt{I} + A(z_M+z_X)^2\sqrt{I}$$
$$\log_{10}k_{app} = \log_{10}kK + 2Az_Mz_X\sqrt{I}$$

Or,

$$\log_{10}\left(\frac{k_{app}}{k_{0\rightarrow1}}\right) = 2Az_M z_X \sqrt{I}$$

where $k_{0\rightarrow1}$ is the measured second order rate constant at infinite dilution.

This equation predicts that if we change the ionic strength, I, of a solution by adding an inert electrolyte containing no M or X, and which plays no part in the reaction other than to change the ionic strength, nevertheless the rate of the reaction between M and X can be altered. Bizarrely, if M and X have the same charge, increasing the ionic strength is predicted to increase the rate, while opposite charges gives an anticipated decrease in rate!

The clue to this behaviour lies in the effect of ionic atmospheres, not just on the reactants M and X, but also now on the transition state.

Considering a pair of divalent anions and cations reacting, adding an inert salt supplies ions which provide the reactants with an ionic atmosphere. This will stabilise the ions. In contrast, the transition state, which is neutral, will have no ionic atmosphere and hence its energy will be essentially unchanged. The barrier to the reaction is thus increased.

Two divalent cations reacting, however, means that the transition state carries charge. In this case both the reactants and transition state are stabilised by the ionic atmosphere, and the reaction barrier is now lowered.

More on Electrode Potentials

Suppose we wanted to obtain the value of the standard electrode potential of the cell:

$$\text{Pt} \mid H_2(g)\ (p=1\text{atm}) \mid H^+(aq)\ (a=1)\ Cl^-(aq)\ (a=1) \mid \text{AgCl} \mid \text{Ag}$$

This cell is know as the Harned Cell.

That is equivalent to investigating the standard electrode potential of the Ag/AgCl couple:

$$E^o_{Ag/AgCl} = \phi_{Ag} - \phi_{Pt}$$

In order to proceed with measurement we need to know how to obtain the concentration for unit solution activity. It is necessary to proceed as follows:

The potential of the cell is given by:

$$E = E^o_{Ag/AgCl} – (RT/F) \ln [\, a_{H+}a_{Cl-} \,]$$

Where the activities are related to the concentrations by means of activity coefficients γ. If the solution is suitably dilute the Debye-Huckel Limiting Law can be used to predict the ionic activity coefficients:

$$\log_{10} \gamma_+ = - A\, z_+^2 \sqrt{I}$$

In our example $z_+ = z_- = 1$ and $A = 0.509$, which gives:

$$E = E^o_{Ag/AgCl} – (RT/F) \ln [HCl]^2 – (RT/F) \ln \gamma_\pm^2$$

On relating the activity coefficient to the ionic strength we finally obtain:

$$E + (2RT/F) \ln [HCl] = E^o_{Ag/AgCl} + (2.34RT/F) \sqrt{[HCl]}$$

Consequently if we measure the cell potential, E, as a function of the HCl concentration in the region where the Debye-Huckel limiting law applies, a plot of $E + (2RT/F) \ln [HCl]$ against $\sqrt{[HCl]}$ should give a straight line with an intercept equal to the standard electrode potential of the Ag/AgCl couple.

The above experiment is a little special in the sense that both electrodes dip into the same electrolyte solution. The latter contains H^+ ions which participate (with the hydrogen gas) in establishing the potential at the platinum electrode and also Cl^- ions which help produce the potential on the silver/silver chloride electrode. In other cases it is simply not possible to use a single solution. For example, suppose we wished to measure the standard electrode potential of the Fe^{2+}/Fe^{3+} couple. A single solution cell,

$$\text{Pt} \mid H_2(g)\ (p=1) \mid H^+(aq)\ (a=1),\ Fe^{2+}(aq)\ (a=1),\ Fe^{3+}(aq)\ (a=1) \mid \text{Pt}$$

is inappropriate since both platinum electrodes are exposed to the Fe^{2+} and Fe^{3+} ions. Thus at one of the two electrodes both the Fe^{2+}/Fe^{3+} and the H^+/H_2 couples will try to establish their potentials. This is why salt bridges are used.

Worked Examples

Equilibrium Constants

Calculate the equilibrium constants for the following reactions at 25°C in aqueous solutions,

- *a)* $Sn(s) + CuSO_4(aq) \Leftrightarrow Cu(s) + SnSO_4(aq)$
- *b)* $2H_2(g) + O_2(g) \Leftrightarrow 2H_2O(l)$

Given the following standard electrode potentials:

$\frac{1}{2} Sn^{2+}(aq) + e^- \Leftrightarrow \frac{1}{2} Sn(s)$	*-0.136V*
$\frac{1}{2} Cu^{2+}(aq) + e^- \Leftrightarrow \frac{1}{2} Cu(s)$	*+0.337V*
$\frac{1}{4} O_2(g) + H^+(aq) + e^- \Leftrightarrow \frac{1}{2} H_2O$	*+1.229V*

We consider first equilibrium (a) and begin by noting that definition of the standard electrode potential of the Sn/Sn^{2+} couple implies for the following cell:

$$Pt \mid H_2(g)\ (p=1atm) \mid H^+(aq)\ (a=1) \parallel Sn^{2+}(aq)\ (a=1) \mid Sn$$

the cell potential is $E^o_{Sn/Sn2+} = -0.136V = \phi_{Sn} - \phi_{Pt}$

The strategy from earlier allows us to associate a formal cell reaction with the above cell as follows. The potential determining equilibrium at the right hand electrode is:

$$\tfrac{1}{2} Sn^{2+} + e^- \Leftrightarrow \tfrac{1}{2} Sn(s)$$

And at the left hand electrode:

$$H^+(aq) + e^- \Leftrightarrow \tfrac{1}{2} H_2(g)$$

Subtracting gives:

$$\tfrac{1}{2} Sn^{2+}(aq) + \tfrac{1}{2} H_2(g) \Leftrightarrow \tfrac{1}{2} Sn(s) + H^+(aq)$$

For this last reaction:

$$\Delta G^o = -FE^o_{Sn/Sn2+} = +0.136F$$

Likewise for the Cu cell,

$$Pt \mid H_2(g)\ (p=1atm) \mid H^+(aq)\ (a=1) \parallel Cu^{2+}(aq)\ (a=1) \mid Cu$$

$$E^o_{Cu/Cu2+} = +0.337V$$

The potential determining equilibria at each electrode are:

Right Hand Electrode: $\tfrac{1}{2} Cu^{2+}(aq) + e^- \Leftrightarrow \tfrac{1}{2} Cu(s)$
Left Hand Electrode: $H^+(aq) + e^- \Leftrightarrow \tfrac{1}{2} H_2(g)$

This enables the formal cell reaction to be deduced:

$$\tfrac{1}{2} Cu^{2+}(aq) + \tfrac{1}{2} H_2(g) \Leftrightarrow \tfrac{1}{2} Cu(s) + H^+(aq)$$

For which:

$$\Delta G^o = -FE^o_{Cu/Cu2+} = -0.337F$$

From these two reactions, subtracting:

$$\tfrac{1}{2} Cu^{2+}(aq) + \tfrac{1}{2} Sn(s) \Leftrightarrow \tfrac{1}{2} Cu(s) + \tfrac{1}{2} Sn^{2+}(aq)$$

For which,
$\Delta G^o = (-0.337F) – (+0.136F) = -0.463F$
and $\Delta G^o = -RT \ln K_c$
K_c here $= [Sn^{2+}]/[Cu^{2+}] = 1 \times 10^8$, so for the original question (1 mol, not ½), the equilibrium constant $= 1 \times 10^{16}$.

Next we turn to equilibrium (b).

$$Pt \mid H_2(g)\ (p=1atm) \mid H^+(aq)\ (a=1),\ H_2O\ (a=1) \mid O_2(g)\ (p=1atm) \mid Pt$$

The formal cell reaction can be deduced by subtracting the potential determining equilibria at each electrode, as follows:

Right Hand Electrode: $\tfrac{1}{4} O_2(g) + H^+(aq) + e^- \Leftrightarrow \tfrac{1}{2} H_2O(l)$
Left Hand Electrode: $H^+(aq) + e^- \Leftrightarrow \tfrac{1}{2} H_2(g)$
To Give: $\tfrac{1}{4} O_2(g) + \tfrac{1}{2} H_2(g) \Leftrightarrow \tfrac{1}{2} H_2O(l)$

For this reaction, $\Delta G^o = -1.229F$
And the associated equilibrium constant:

$$K = \frac{1}{P_{H_2}^{1/2} P_{O_2}^{1/4}} = \exp(-\Delta G^o / RT) = 6 \times 10^{20}\ atm^{-3/4}$$

Note that the activity of water is absent from the definition of K.

The Nernst Equation

For the following cell:

$$Al \mid Al^{3+}(aq) \parallel Sn^{4+}(aq),\ Sn^{2+}(aq) \mid Pt$$

State or calculate at 25°C:

(a) *the cell reaction*
(b) *the cell EMF when all concentrations are 0.1M and 1.0M (ignore activity coefficients).*
(c) *ΔG^o for the cell reaction in (a)*
(d) *K for the cell reaction in (a)*

(e) *The positive electrode and the direction of electron flow in an external circuit connecting the two electrodes.*

The standard potentials are $E^o_{Sn2+/Sn4+} = 0.15V$ *and* $E^o_{Al/Al3+} = -1.61V$

The potential determining equilibria are:

Right Hand Electrode: $\frac{1}{2} Sn^{4+}(aq) + e^- \Leftrightarrow \frac{1}{2} Sn^{2+}(aq)$
Left Hand Electrode: $\frac{1}{3} Al^{3+}(aq) + e^- \Leftrightarrow \frac{1}{3} Al(s)$
Formal cell reaction: $\frac{1}{2} Sn^{4+}(aq) + \frac{1}{3} Al(s) \Leftrightarrow \frac{1}{2} Sn^{2+}(aq) + \frac{1}{3} Al^{3+}(aq)$

When all the potential determining species in the cell are present at unit activity the cell potential is:

$$E^o_{cell} = E^o_{Sn2+/Sn4+} - E^o_{Al/Al3+} = (0.15) - (-1.66) = 1.81V$$

So that for the reaction above: $\Delta G^o = -1.81F = -175 kJ\ mol^{-1}$
It follows that the reaction is thermodynamically downhill and is the process which would occur if the cell was short-circuited.

The cell EMF will be given by the appropriate Nernst Equation:

$$E = 1.81 - \frac{RT}{F}\ln\left(\frac{[Al^{3+}]^{\frac{1}{3}}[Sn^{2+}]^{\frac{1}{2}}}{[Sn^{4+}]^{\frac{1}{2}}}\right)$$

So that when all the concentrations are 1.0M the cell EMF is 1.81V.
When the concentrations are 0.1M,

$$E = 1.81 - \frac{RT}{F}\ln\left(\frac{0.1^{\frac{1}{3}}0.1^{\frac{1}{2}}}{0.1^{\frac{1}{2}}}\right) = 1.81 + 0.02 = 1.83V$$

The equilibrium constant for the reaction is:

$$K = [Al^{3+}]^{\frac{1}{3}}[Sn^{2+}]^{\frac{1}{2}}/[Sn^{4+}]^{\frac{1}{2}} = \exp(1.81F/RT) = (4\times10^{30}\ mol\ dm^{-3})^{1/2}$$

Last we note the cell polarity will always be:

$$(-)\ Al \mid Al^{3+}(aq) \parallel Sn^{4+}(aq), Sn^{2+}(aq) \mid Pt\ (+)$$

unless tremendous extremes of concentration ratios occur ($[Al^{3+}] >> [Sn^{4+}]$ and $[Sn^{2+}] >> [Sn^{4+}]$). It follows that if the cell is short-circuited then electrons would leave the aluminium, which would oxidise, and that at the platinum electrode Sn^{4+} ions would be reduced.

Concentration Cells

Consider the following cell:

$$Pt \mid H_2(g)\ (p_1) \mid HCl(aq)\ (m_1) \parallel HCl(aq)\ (m_2) \mid H_2(g)\ (p_2) \mid Pt$$

Where the hydrogen gas pressures are p_1 *and* p_2 *atmospheres respectively and the two hydrochloric acid concentrations are* m_1 *and* m_2 *in mol* dm^{-3}*. At 25°C calculate or state:*

a) *an expression for the cell EMF in terms of* m_1, m_2, p_1 *and* p_2 *(ignoring activity coefficients).*
b) *The cell EMF when* $m_1 = 0.1M$, $m_2 = 0.2M$ *and* $p_1 = p_2 = 1$ *atm.*
c) *The cell EMF when the hydrogen pressure* p_2 *is increased to 10atm, all other concentrations remaining the same*
d) *The cell reaction*

As in the previous examples the strategy is first to identify the potential determining equilibria which in this case are:

Right Hand Electrode: $H^+(aq, m_2) + e^- \Leftrightarrow \frac{1}{2} H_2(g, p_2)$
Left Hand Electrode: $H^+(aq, m_1) + e^- \Leftrightarrow \frac{1}{2} H_2(g, p_1)$

Formal Cell Reaction: $H^+(aq, m_2) + \frac{1}{2} H_2(g, p_1) \Leftrightarrow H^+(aq, m_1) + \frac{1}{2} H_2(g, p_2)$

The Nernst Equation is therefore:

$$E = 0 - \frac{RT}{F} \ln\left(\frac{p_2^{\ 1/2} m_1}{m_2 p_1^{\ 1/2}} \right)$$

When $p_1 = p_2 = 1$, and $m_1 = 0.1$ but $m_2 = 0.2$:

$$E = (-RT/F) \ln (0.1/0.2) = 0.018V$$

It p_2 is changed to 10 atm we have:

$$E = (-RT/F) \ln (0.1x10^{1/2}/0.2) = -0.012V$$

The formal cell reaction in this example was established above. The spontaneous cell reaction – that occurring when the cell is short-circuited – can be seem from the above to depend on the cell concentrations. When $p_1 = p_2 = 1$ then the spontaneous reaction is the same as the formal cell reaction since:

$$\Delta G = -0.018F < 0$$

When p_2 is increased to 10 atm, $\Delta G = +0.012F > 0$, so that the direction of the spontaneous cell reaction is reversed.

Solubility Products

Given the standard electrode potentials:

$$E^o_{Ag/Ag+} = +0.799V \text{ and } E^o_{Ag/AgI} = -0.152V$$

Calculate the solubility product, K_{sp}, and solubility of silver iodide at 25°C.

The first SEP quoted relates to the cell:

$$Pt \mid H_2(g)\ (p=1atm) \mid H^+(aq)\ (a=1) \parallel Ag^+(aq)\ (a=1) \mid Ag(s)$$

For which the formal cell reaction is:

$$Ag^+(aq) + \tfrac{1}{2} H_2(g) \Leftrightarrow Ag(s) + H^+(aq)$$

$$\Delta G^o = -0.799F$$

Likewise the second SEP is that of the cell:

$$Pt \mid H_2(g)\ (p=1atm) \mid H^+(aq)\ (a=1), I^-(aq)\ (a=1) \mid AgI \mid Ag(s)$$

The potential determining equilibria at the two electrodes are:

RHS: $AgI(s) + e^- \Leftrightarrow Ag(s) + I^-(aq)$
LHS: $H^+(aq) + e^- \Leftrightarrow \frac{1}{2} H_2(g)$
Formal: $AgI(s) + \frac{1}{2} H_2(g) \Leftrightarrow Ag(s) + I^-(aq) + H^+(aq)$
Which has $\Delta G^o = +0.152F$

Subtracting the two reactions gives:

$$AgI(s) \Leftrightarrow Ag^+(aq) + I^-(aq)$$

For which:
$\Delta G^o = (+0.152F) - (-0.799F) = 0.951F = -RT \ln K_{sp}$
$K_{sp} = 8.5x10^{-17}\ mol^2\ dm^{-6}$.

Weak Acids

The EMF of each of the following Harned cells is measured at two temperatures:

$$Pt \mid H_2(g)\ (p=1atm) \mid HCl\ (10^{-5}M) \mid AgCl \mid Ag\ (E_1)$$

$$Pt \mid H_2(g)\ (p=1atm) \mid HA\ (10^{-2}M), KA\ (10^{-2}M), KCl\ (10^{-5}M) \mid AgCl \mid Ag\ (E_2)$$

Where HA is a weak acid and KA is its potassium salt. The results are as follows:

	293K	***303K***
E_1 / V	*0.820*	*0.806*
E_2 / V	*0.878*	*0.866*

Calculate K_a and ΔH^o for the dissociation of the weak acid, pointing out any assumptions you make. Do not ignore activity coefficients, but assume in the second cell that [HA] >> $[H^+]$.

We start by identifying the potential determining equilibria in the two cells. In both cases these are:

RHS: $AgCl(s) + e^- \Leftrightarrow Ag(s) + Cl^-(aq)$
LHS: $H^+(aq) + e^- \Leftrightarrow ½\, H_2(g)$
Formal: $AgCl(s) + ½\, H_2(g) \Leftrightarrow Ag(s) + Cl^-(aq) + H^+(aq)$

The corresponding Nernst Equation is:

$$E = E^o - (RT/F) \ln [a_{H+}a_{Cl-}]$$

This applies to both cells although the a-values will differ.
Now,

$$a_{H+} = \gamma_{H+}[H^+] \text{ and } a_{Cl-} = \gamma_{Cl-}[Cl^-]$$

Consider the first cell and apply the Nernst Equation at the lower temperature:

$$0.820 = E^o_{Ag/AgCl} - (293R/F) \ln [\ \gamma_{H+}\gamma_{Cl-}10^{-5}.10^{-5}\ ]$$

At concentrations as low as 10^{-5}M the solutions are effectively ideal to a high degree of approximation. Physically this arises since the ions are so far apart that the ion-ion interactions are negligible. We can therefore put: $\gamma_{H+} = \gamma_{Cl-} \approx 1$, and so deduce that:

$$E^o_{Ag/AgCl} = 0.240V \text{ (at 293K)}$$

At the higher temperature, but the same method:

$$E^o_{Ag/AgCl} = 0.206V \text{ (at 303K)}$$

We next turn to the second cell and note that the hydrogen ion activity, a_{H+}, "seen" by the hydrogen electrode will be governed by the dissociation of the weak acid,

$$HA(aq) \Leftrightarrow H^+(aq) + A^-(aq)$$

For which we can write the acid dissociation constant:

$$K_a = \frac{a_{H+}a_{A-}}{a_{HA}} = \frac{\gamma_{H+}\gamma_{A-}}{\gamma_{HA}}\frac{[H^+][A^-]}{[HA]}$$

Now HA is uncharged so that we can safely assume $\gamma_{HA} \approx 1$ is a very good approximation. However, the ionic strength, I, of the solution is in excess of 10^{-2} mol dm^{-3} so we expect that $\gamma_{Cl-} < 1$ and $\gamma_{A-} < 1$.

Returning to the Nernst Equation:

$$E_2 = E^o_{Ag/AgCl} - (RT/F) \ln [a_{H+}\gamma_{Cl-}10^{-5}]$$

At the lower temperature of 293K:

$$0.878 = 0.240 - 0.058 \log [a_{H+}\gamma_{Cl-}10^{-5}]$$

So that:

$$\log [a_{H+}\gamma_{Cl-}] = -6.00 \text{ (at 293K)}$$

At the higher temperature,

$$\log [a_{H+}\gamma_{Cl-}] = -6.00 \text{ (at 303K)}$$

it follows that at both temperatures:

$$a_{H+}\gamma_{Cl-} = 10^{-6}$$

Now,

$$K_a = a_{H+}a_{Cl-}(\gamma_{A-}/\gamma_{Cl-})([A^-]/[HA])$$
$$= 10^{-6}(\gamma_{A-}/\gamma_{Cl-})(10^{-2}/10^{-2}) = 10^{-6}M$$
$$\text{(if } \gamma_{A-} = \gamma_{Cl-})$$

The last assumption is a good one since the Debye-Huckel Limiting Law predicts the same value for the activity coefficients of ions with the same charge experiencing the same ionic strength.

We have shown that K_a has the same value at both 293 and 303K. We can find ΔH for the acid dissociation by using the Van't Hoff Ischore:

$$d \ln K / dT = \Delta H^o / RT^2$$

Which shows that $\Delta H^o \approx 0$.

Thermodynamic Quantities

The EMF of the cell

$$Ag \mid AgCl \mid HCl\ (10^{-5}M) \mid Hg_2Cl_2 \mid Hg$$

is 0.0421V at 288K and 0.0489V at 308K. Use this information to calculate the enthalpy, free energy and entropy changes that accompany the cell reaction at 298K.

The potential determining equilibria at the electrodes are:

RHS:	$\frac{1}{2} Hg_2Cl_2(s) + e^- \Leftrightarrow Hg(l) + Cl^-(aq)$
LHS:	$AgCl(s) + e^- \Leftrightarrow Ag(s) + Cl^-(aq)$
Formal:	$\frac{1}{2} Hg_2Cl_2(s) + Ag(s) \Leftrightarrow Hg(l) + AgCl(s)$

$$\Delta G^o = -FE^o$$

So,

$$\Delta G^o_{288} = -0.421F = -4.062 \text{ kj mol}^{-1} \text{ at 288K.}$$

While

$$\Delta G^o_{308} = -0.0489F = -4.719 \text{ kJ mol}^{-1} \text{ at 308K}$$

Linearly interpolating between 288K and 308K we find:

$$\Delta G^o_{298} = -4.390 \text{ kJ mol}^{-1} \text{ at 298K}$$

Note that the reaction involves the pure solid metal chlorides and pure elements in their standard states so that the free energies evaluated above are standard free energies, regardless of the concentration of HCl in the cell – the latter does not enter the net formal cell reaction, or influence the cell EMF. It does however play the vital role of establishing the potentials on the two electrodes through the potential determining equilibria given above.

The entropy change be found from:

$$\Delta S^o_{298} = F \left(\frac{\partial E^o}{\partial T} \right)_p$$

$$= F\,[\,(-0.0489 - 0.0421)/20\,]$$

$$= 32.8 \text{ J K}^{-1} \text{ mol}^{-1} \text{ at 298K}$$

The enthalpy change may be readily estimated from $\Delta H^o = \Delta G^o + T\,\Delta S^o$

$$\Delta H^o_{298} = -4.390 + [298 \times 32.8/10^3] = +5.387 \text{kJ mol}^{-1} \text{ at 298K.}$$

It is apparent that the cell reaction is thermodynamically downhill, but that it is entropy drive, the process being enthalpically unfavourable (ΔH > 0). The positive ΔS value reflects the increase in disorder in converting the solids Hg_2Cl_2 and Ag into solid AgCl and *liquid* Hg.