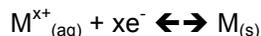**Revised August 2011**

HONORS TOPIC 14: Electrochemistry

- **Electrode potentials and half-cells**

When a metal comes into contact with a solution containing its own ions an equilibrium is set up.

$$M^{x+}_{(aq)} + xe^- \longleftrightarrow M_{(s)}$$

Some reactive metals such as Mg will lose electrons readily and the equilibrium lies relatively to the left. A large number of electrons are released which collect on the surface of the metal giving a negative charge.

$$Mg^{2+}_{(aq)} + 2e^- \longleftarrow\longleftarrow\longleftarrow\longleftarrow\longrightarrow Mg_{(s)}$$

A less reactive metal such as silver will show less tendency to ionize, and the equilibrium lies relatively to the right. Fewer electrons will collect on the metal and the charge will be much less negative. In fact, if the aqueous ions remove electrons from the metal it will develop a positive charge.

$$Ag^{+}_{(aq)} + e^- \longleftarrow\longrightarrow\longrightarrow\longrightarrow\longrightarrow Ag_{(s)}$$

Non-metals can also be considered, for example;

$$H^{+}_{(aq)} + e^- \longleftrightarrow \tfrac{1}{2}H_{2(g)}$$

So whenever an element is placed in contact with a solution containing its own ions, an electric charge will develop on the metal, or in the case of a non-metal on the inert conductor placed in solution. The charge is called the electrode potential and the system is called a half-cell. The sign and size of the charge will depend on the ability of the element to lose or gain electrons.

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- **Electrochemical series and electrode potentials**

Species that appear at the top of the series **gain electrons most readily** and therefore **have the most positive $E^\ominus$ values**, are **easily reduced** and are the best oxidizing agents.

Species that appear at the bottom of the series **lose electrons most readily** and therefore **have the most negative $E^\ominus$ values**, are **easily oxidized** and are the best reducing agents.

STANDARD REDUCTION POTENTIALS IN AQUEOUS SOLUTION AT 25°C

| Half-reaction			$E^0(V)$
$F_2\,(g) + 2e^-$	→	$2F^-$	2.87
$Co^{3+} + e^-$	→	Co^{2+}	1.82
$Au^{3+} + 3e^-$	→	$Au(s)$	1.50
$Cl_2\,(g) + 2e^-$	→	$2Cl^-$	1.36
$O_2\,(g) + 4H^+ + 4e^-$	→	$2H_2O(l)$	1.23
$Br_2\,(l) + 2e^-$	→	$2Br^-$	1.07
$2Hg^{2+} + 2e^-$	→	Hg_2^{2+}	0.92
$Hg^{2+} + 2e^-$	→	$Hg(l)$	0.85
$Ag+ + e^-$	→	$Ag(s)$	0.80
$Hg_2^{2+} + 2e^-$	→	$2Hg(l)$	0.79
$Fe^{3+} + e^-$	→	Fe^{2+}	0.77
$I_2\,(s) + 2e^-$	→	$2I^-$	0.53
$Cu^+ + e^-$	→	$Cu(s)$	0.52
$Cu^{2+} + 2e^-$	→	$Cu(s)$	0.34
$Cu^{2+} + e^-$	→	Cu^+	0.15
$Sn^{4+} + 2e^-$	→	Sn^{2+}	0.15
$S\,(s) + 2H^+ + 2e^-$	→	$H_2S(g)$	0.14
$2H^+ + 2e^-$	→	$H_2(g)$	0.00
$Pb^{2+} + 2e^-$	→	$Pb(s)$	-0.13
$Sn^{2+} + 2e^-$	→	$Sn(s)$	-0.14
$Ni^{2+} + 2e^-$	→	$Ni(s)$	-0.25
$Co^{2+} + 2e^-$	→	$Co(s)$	-0.28
$Tl^+ + e^-$	→	$Tl(s)$	-0.34
$Cd^{2+} + 2e^-$	→	$Cd(s)$	-0.40
$Cr^{3+} + e^-$	→	Cr^{2+}	-0.41
$Fe^{2+} + 2e^-$	→	$Fe(s)$	-0.44
$Cr^{3+} + 3e^-$	→	$Cr(s)$	-0.74
$Zn^{2+} + 2e^-$	→	$Zn(s)$	-0.76
$Mn^{2+} + 2e^-$	→	$Mn(s)$	-1.18
$Al^{3+} + 3e^-$	→	$Al(s)$	-1.66
$Be^{2+} + 2e^-$	→	$Be(s)$	-1.70
$Mg^{2+} + 2e^-$	→	$Mg(s)$	-2.37
$Na^+ + e^-$	→	$Na(s)$	-2.71
$Ca^{2+} + 2e^-$	→	$Ca(s)$	-2.87
$Sr^{2+} + 2e^-$	→	$Sr(s)$	-2.89
$Ba^{2+} + 2e^-$	→	$Ba(s)$	-2.90
$Rb^+ + e^-$	→	$Rb(s)$	-2.92
$K^+ + e^-$	→	$K(s)$	-2.92
$Cs^+ + e^-$	→	$Cs(s)$	-2.92
$Li^+ + e^-$	→	$Li(s)$	-3.05

- **Electrochemical cells**

An electrochemical cell is the apparatus for generating electrical energy from a spontaneous REDOX reaction. Connecting two half-cells that have different electrode potentials forms an electrochemical cell (battery).

A high resistance voltmeter is used to measure the voltage since it draws no current and will not affect the reading.

A salt bridge connects the two half-cells. It can be made from a piece of filter paper soaked in a suitable ionic solution, often potassium chloride or potassium nitrate. The ionic solution used in the salt bridge must not interfere with the equilibrium of the two half cells, e.g., KCl could not be used if one of the half cells was contained Ag^+ ions as they would react with the Cl^- ions (the Ag^+ would be precipitated out and the concentration of Ag^+ in solution would drop). The salt bridge allows the transfer of **ions** between the two solutions, thus completing the circuit. Ions will flow in order to balance the charge.
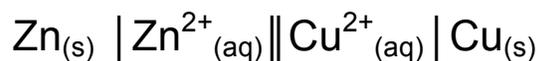
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For example, a zinc and copper cell;
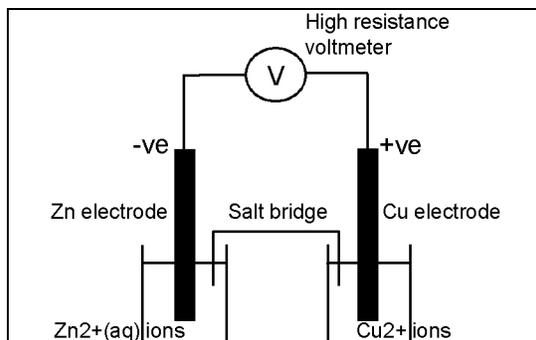
The **electrons** will flow through the **wire**, toward the more positive half-cell, in this case from zinc to copper. As a result, the copper ions gain electrons and are therefore reduced. A **"cell diagram"** can be written thus;

$$Zn_{(s)} \mid Zn^{2+}{}_{(aq)} \parallel Cu^{2+}{}_{(aq)} \mid Cu_{(s)}$$

As Zn^{2+} ions are produced in the zinc half-cell there will be a build up of positive charge. This is balanced by negative ions migrating from the salt bridge into the zinc half-cell. 'Cell diagrams' have a number of standard features;

- The reduced species is placed on the RHS (right hand side) – this is the **CATHODE**
- The oxidized species is placed on the LHS (left hand side) – this is the **ANODE**
  N.B. RHS/LHS apply to the 'cell diagram' not to any *drawing* of apparatus
- The vertical line │ represents the different phases present in each electrode
- The double vertical line ‖ represents the salt bridge connecting the two electrodes
- Different species in the same phase are separated by a comma, e.g., $Fe^{2+}{}_{(aq)}$, $Fe^{3+}{}_{(aq)}$
- The presence of an inert conductor (**required when no SOLID metal is present**) may also be shown inside parentheses ( ). E.g., for the hydrogen half-cell, (Pt) │ $\frac{1}{2}H_{2(g)}$ │ $H^+{}_{(aq)}$

Task 14a

Using the SERP table on page 2, write cell diagrams for the following combinations of electrodes. Remember to include state symbols and inert electrodes where appropriate.

(i)   *Zn/Zn^{2+} and fluorine*

(ii)   *Sn/Sn^{2+} and hydrogen*

(iii)   *Cu/Cu^{2+} and Fe/Fe^{2+}*

(iv)   *Fe^{2+}/Fe^{3+} and hydrogen*

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- **Measurement of Electromotive Force (EMF) or E_{cell}**

The EMF or E_{cell} is the voltage measured when no current is being drawn from the cell and is determined using a high resistance voltmeter. It can be calculated by applying the following relationship to the cell diagram.

$$E_{cell} = E_{RHS} - E_{LHS} \qquad \text{or} \qquad E_{cell} = E_{reduced} - E_{oxidized}$$

Since the half reactions are reversible they are subject to change according to Le Chatelier's principle. In order to make meaningful comparisons it is necessary to stipulate a set of standard conditions under which the electrode potential of a given half-cell is measured.

- **Standard Electrode Reduction Potential**

The Standard Electrode Reduction Potential of a half cell, $E^{\ominus}$ (SERP), is defined as, the electrode potential of a half cell, measured relative to a standard hydrogen electrode, which has a value of 0.00 V, measured under standard conditions, which are set as, a temperature of 25 ^{o}C (298 K), any gases at a pressure of 1.0 atm and all solutions at concentrations of 1.0 M. The diagram below shows the standard hydrogen electrode being used to determine the $E^{\ominus}$ for electrode under test.
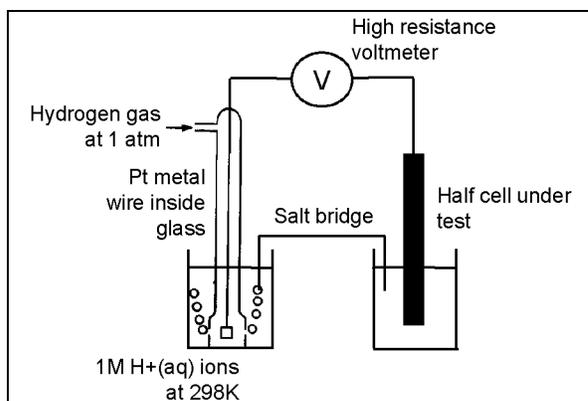
The practical use of the hydrogen half-cell for determining $E^{\ominus}$ values suffers from three main problems.

- It is difficult to set up the $H_{2(g)}$ at precisely 1.0 atm pressure
- It is fragile and non-portable
- The equilibrium $H^{+}_{(aq)} + e^{-} \leftrightarrow \frac{1}{2}H_{2(g)}$ is only established slowly

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Task 14b

A cell formed from a silver standard electrode and a hydrogen standard electrode generates a voltage of + 0.80 V. Hydrogen is the more negative electrode and has a value of 0.00 V.

      (i)   Write the cell diagram and calculate the standard potential of the silver electrode.

      (ii)   When the silver electrode is combined with a standard aluminum electrode the voltage of the cell is +2.46 V and aluminum is the more negative electrode. Write the cell diagram and calculate the standard electrode potential of the aluminum electrode.

      (iii)   If the beaker containing aluminum ions has distilled water added to it, what would happen to the voltage of the cell? Explain.

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- **The Nernst Equation**

The Nernst equation can be used to calculate the voltage generated by the combination of two half-cells when the conditions are **NOT** standard and can take two forms.

$$E_{cell} = E^{\theta} - \left(\frac{RT}{nF}\right) \ln Q \quad \text{or} \quad E_{cell} = E^{\theta} - \left(\frac{0.0592}{n}\right) \log Q$$

In both equations;

R is the gas constant (8.314 J/K mol), T = Kelvin temp, n = # of electrons transferred, F = Faraday constant, E^{θ} = voltage generated **IF** the conditions **WERE** standard, ln = natural log and Q = the reaction quotient (remember to raise to stoichiometric numbers and omit pure solids & liquids).

The first form is used if BOTH the temperature and concentrations are non-standard; the second form can be used if it is only the concentrations of ions that have changed but the temperature is STILL standard, i.e., 298 K

e.g., If the reaction $Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Cu_{(s)} + Zn^{2+}_{(aq)}$ is carried out using solutions that are 5.0 M Zn^{2+} and 0.3 M Cu^{2+} at 298 K, what is the actual cell voltage?

First, calculate E^{θ}_{cell} assuming standard conditions. $Zn_{(s)} \mid Zn^{2+}_{(aq)} \parallel Cu^{2+}_{(aq)} \mid Cu_{(s)}$

$Zn^{2+}_{(aq)} + 2e^- \leftrightarrow Zn_{(s)} \qquad E^{\theta} = -0.76$ V
$Cu^{2+}_{(aq)} + 2e^- \leftrightarrow Cu_{(s)} \qquad E^{\theta} = +0.34$ V
$E^{\theta} = E_{RHS} - E_{LHS} = +0.34$ V $- (-0.76$ V$) = 1.10$ V

Secondly, calculate Q. Since zinc and copper metals are solids, they are omitted from Q.

$$Q = \frac{[Zn^{2+}]}{[Cu^{2+}]} = \frac{5.0}{0.3} = 16.7$$

and since 2 electrons are transferred, $E_{cell} = 1.10 - \left(\frac{0.0592}{2}\right) \log (16.7) = \mathbf{1.06 \ V}$

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- **Electrolysis**

Electrolysis is the process in which electrical energy is used to cause a non-spontaneous REDOX reaction to occur. **It _is the opposite of an electrochemical cell_**. An electrolytic cell is one that is used to carry out electrolysis. A typical electrolytic cell is shown below;
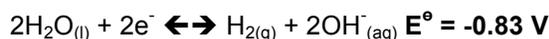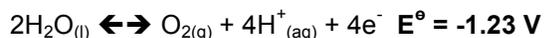

Anions in the electrolyte solution are attracted towards the anode where they under go a process of oxidation. Electrons flow from the anode to the cathode where cations undergo a process of reduction.
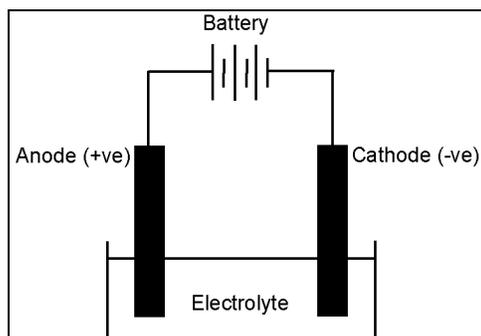
e.g., the electrolysis of **molten** potassium chloride will produce these reactions;

ANODE: $Cl^-_{(aq)} \rightarrow \frac{1}{2} Cl_{2(g)} + e^-$
CATHODE: $K^+_{(aq)} + e^- \rightarrow K_{(s)}$
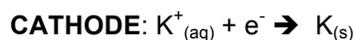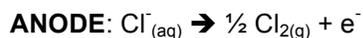
The electrolysis of **aqueous solutions** can be more complicated since water is present that can ALSO undergo REDOX processes, e.g.,

$2H_2O_{(l)} \leftrightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-$ **$E^\ominus$ = -1.23 V**
$2H_2O_{(l)} + 2e^- \leftrightarrow H_{2(g)} + 2OH^-_{(aq)}$ **$E^\ominus$ = -0.83 V**

When this is the case, decisions based upon SERP values must be made about the relative likelihood of one process over another.

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Quantitative aspects of electrolysis

The amount of a substance produced in an electrolytic cell can be calculated using Faradays law. One method is;

1. Calculate the number of Faradays passed in the electrolysis by using these expressions;

    a. Firstly, calculate the amount of charge (coulombs) that has been passed.

$$q = I\,t$$

Where I = current in amps, q = charge in coulombs and t is time in Seconds.

    b. Secondly, convert this to Faradays.

$$\text{Number of Faradays} = \text{Charge in coulombs (q)} \times \frac{1\ \text{Faraday}}{96500\ \text{Coulombs}}$$

2. Then, use the stoichiometry of the electrode process to determine the mass of product deposited at the electrode, remembering that a process that produces **one mol of product** by the transfer of **one electron** will require **one Faraday** to produce that one mol, and that a process that produces **one mol of product** by the transfer of **two electrons** will require **two Faraday's** to produces that one mol etc.

    For example, in the processes below, 1 mole of Cu solid can be produced from the reduction of 1 mol of Cu^{2+} ions by the passage of 2 Faradays, and ½ a mol of chlorine gas can be produced by the oxidation of 1 mol of chloride ions by the passage of 1 Faraday.

    $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$
    $Cl^-_{(aq)} \rightarrow \tfrac{1}{2}Cl_{2(g)} + e^-$
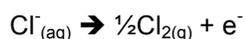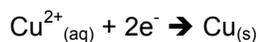
    When the number of Faraday's is less (or more) that the required stoichiometric amount demanded by the half-reaction, ratio can be applied.