Electrochemical Cells (Galvanic or Voltaic Cells)

See Chapter 21 of H & P

There are two types of electrical conduction:

1. Electron Conduction

This involves the flow of electrons through a conductor such as a metal wire or graphite (why? Explain in terms of structure of graphite). The reason the electricity flows through metals and semiconductors is that there is available delocalized electrons moving about the valence orbitals.

2. Electrolytic Conduction

This involves the passage of electricity through an *electrolyte* which contains mobile ions. The ions carry the electrical charge by moving through the solution. The electrolyte (acid, base or salt) must be dissolved (aqueous) or molten (liquid) for the ions to be mobile. *Galvani* and *Volta* were the discoverers of the electric cell.
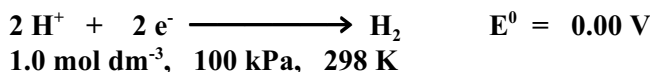
Standard Oxidation Potentials & Standard Reduction Potentials

There is an "order of oxidizability" of elements and compounds. The strongest reducing agents (active metals) are the most easily oxidized and are found at the top of the list, while non-metal ions are found at the bottom of the list (least easily oxidized). This table is also called the **electromotive series, emf** or the **displacement series**. The higher the metal is in the series, the easier it is for it to become an ion (be oxidized). Hydrogen appears as a "metal" since it loses electrons. Silver, Platinum and Gold are poor reducing agents and as such are not easily oxidized. (Called the Noble Metals).

A member of the series will displace (from solution) any metal below it on the table. Thus calcium will displace aluminum from a solution of aluminum ions. Copper can displace silver ions from solution, but not zinc ions. However, zinc metal can displace both silver and copper ions from solution.

The strongest oxidizing agents are found on the **bottom right** of an oxidation potential table (or the top left of a reduction potential table.) There is a large number of possible metals that can be combined in solution to measure their reduction potential relative to each other. How can the electrical potential of a metal alone may be determined?

It does not happen alone, there must be a subsequent oxidation. You can only measure the emf between two half-cells by combining them. Hence we use **standard Half-Cell potentials.** Scientists have chosen one half-cell as a reference and compared all other half-cells to it. The cell chosen is the **standard hydrogen electrode, (SHE)**:

$$2 \; H^+ \; + \; 2 \; e^- \longrightarrow H_2 \qquad E^0 \; = \; 0.00 \; V$$
$$1.0 \; mol \; dm^{-3}, \quad 100 \; kPa, \quad 298 \; K$$

The measured emf of a standard electrochemical cell containing a hydrogen half-cell is the standard potential, E^0 of the second half cell.

A **standard reduction potential** is the measure of the tendency to gain electrons from hydrogen.

A **standard oxidation potential** is the measure of the tendency to lose electrons relative to the hydrogen electrode. They are numerically equal but opposite in sign.

By convention, half cells are compared by reduction potentials.

Negative values – gain electrons less easily than hydrogen (i.e. reduced less easily than H_2)

Positive values – gain electrons more easily than hydrogen (more easily reduced than H_2)

Note: that standard potentials depend on concentration and do not change when the coefficients change.

Explain how you would measure the E^0 for:

1. A metal $M \, / \, M(NO_3)_{(aq)}$ 2. $Br_{2 \; (aq)} \, / \, Br^{-1}{}_{(aq)}$

There are **Electrochemical** and **Electrolytic** cells.

The Electrochemical Cells
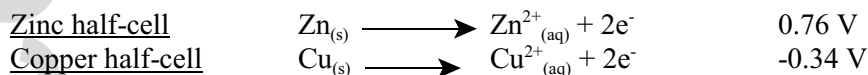(Produces electricity) (((Voltaic Cell)))

Two half cell reactions (one oxidation and one reduction) can be set up so that the spontaneous electron transfer must occur through an external electrical circuit (ie. so that electricity is produced). Galvanic cells can be considered to be constructed of **REDOX** couples, ie. two half reactions.

Spontaneous reaction
The electrochemical cell is produced by combining two half-cells. A half-cell consists of a metal bar immersed in a solution of that metal's ions (conc. of 1.0 mol/L). e.g. Zn/Zn^{2+}, Cu/Cu^{2+}, Ag/Ag^+ etc. The solutions are nitrates or sulphates of the metals, but any soluble salt will do.
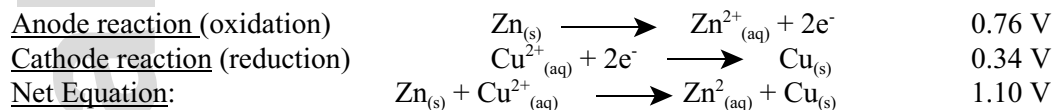When two half-cells are connected with wire and a **salt bridge** electricity will flow from the half-cell with the higher oxidation potential to the one with the lower oxidation potential. It is a spontaneous reaction.

Example:

Zinc half-cell	$Zn_{(s)} \longrightarrow$	$Zn^{2+}_{(aq)} + 2e^-$	0.76 V
Copper half-cell	$Cu_{(s)} \longrightarrow$	$Cu^{2+}_{(aq)} + 2e^-$	-0.34 V

Which half reaction becomes the anode (oxidation) reaction? The potential of the Zinc half-cell is higher and therefore it goes as written. Since this is the oxidation (loss of electrons), the copper half-cell works in reverse, as a reduction.
Thus, combining the two equations we get a voltage of 1.10 volts.

Anode reaction (oxidation)	$Zn_{(s)} \longrightarrow$	$Zn^{2+}_{(aq)} + 2e^-$	0.76 V
Cathode reaction (reduction)	$Cu^{2+}_{(aq)} + 2e^- \longrightarrow$	$Cu_{(s)}$	0.34 V
Net Equation:	$Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow$	$Zn^2_{(aq)} + Cu_{(s)}$	1.10 V

This zinc/copper cell is a battery with 1.10 volts.

Note: A piece of zinc metal will spontaneously react with a solution of copper ions to produce copper metal and zinc ions. What we do in the two half-cells is to send the electrons on a journey through a circuit rather than have oxidation-reduction taking place at the one spot. (Had they lived in the 20th Century, Galvani and Volta would of course get Nobel Prizes for their great work.)
A commercially viable cell known as the **Daniel Cell** has great historical significance and is based on the following arrangement:
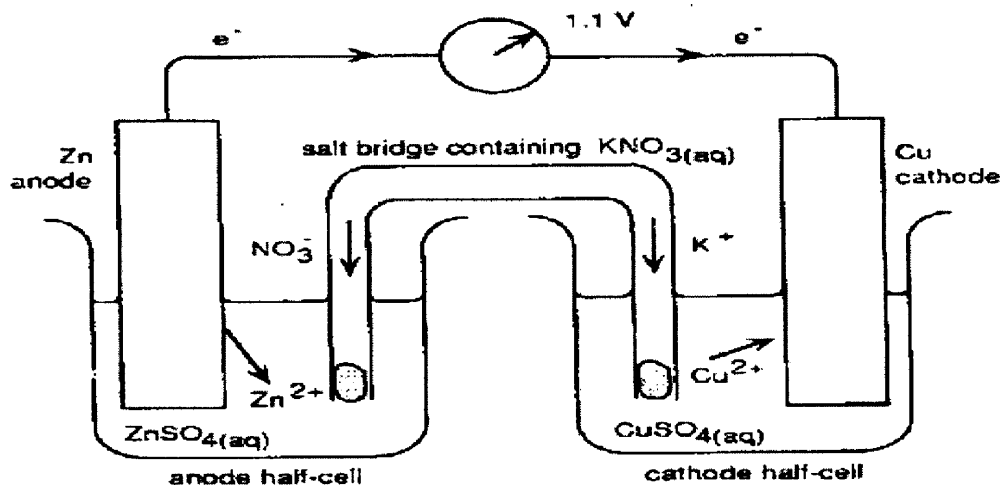
The cell may be written as: $Zn \mid Zn^{+2} \parallel Cu^{+2} \mid Cu$

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Rules to Remember

➢ One metal in the cell will be oxidized and the other will be reduced.
How do you know which metal to choose?
   1. Use an activity series
   2. Use a table of standard reduction potentials (see Table 15 in your Data Book). The half cell with the largest reduction potential contains the metal which will be reduced.

➢ Oxidation always occurs at the electrode called the ANODE (**an ox**). Similarly, reduction always occurs at the CATHODE (**red cat**).

➢ Electrons always flow from the anode to the cathode in an *external circuit of wire*. Thus, in galvanic cells, the **anode is labelled negative** because electrons build up there (by the half cell reaction of oxidation), and the **cathode is labelled positive** because electrons are depleted there (by reduction).

➢ Ions in solution flow through a **Salt Bridge** or a porous cup in an *internal circuit*. Each metal is placed in a container in a solution of its own salt (so that it will not react with anything until connected to the other half cell). The ions in solution in the salt bridge serve to help maintain electrical neutrality within the cell and therefore make it last longer. The salt bridge maintains the balance in each cell, ie. the salt bridge allows migration of ions to prevent accumulation of charge in each beaker.
The electrolyte in the salt bridge is generally an ionic compound in solution therefore cations and anions are present:
Cations (+) flow towards the Cathode to counteract the pool of electrons arriving from the anode.
Anions (-) flow towards the Anode to counteract the loss of electrons occurring at this electrode as they leave the site of oxidation and flow through the external circuit to the cathode.

➢ Overtime:
   1. The **anode loses mass** because its metal is entering the solution.
   2. The **cathode gains mass** because its ions are coming out of solution
   (**fat red cat**).
   3. The cell loses its ability to generate electricity.

➢ **Standard** half cells refers to the following conditions: the ion concentrations are 1.0 mol dm^{-3}, the temperature is 25°C and any gases are a 100 kPa pressure. By international agreement, the standard hydrogen electrode is chosen as the reference electrode for measuring standard electrode potentials.
$$2 H^+ + 2 e^- \longrightarrow H_2 \qquad E^0 = 0.00 \text{ V}$$
1.0 mol dm^{-3},   100 kPa,   298 K

➢ A **voltmeter of high resistance** rather than one of low resistance is used to prevent electrons from travelling continuously from one half cell to the other. Under these conditions the cell reaction cannot occur to any significant extent and the voltmeter registers the **maximum** potential difference which the cell can produce.

➢ The overall cell potential, E^0_{cell}, is the difference between the two electrode potentials:

$$\textbf{E}^0_{\textbf{cell}} = \textbf{ standard electrode potential } - \textbf{ standard reduction potential}$$
   of the substance reduced   **of the substance oxidized**

> The electrode potential of the cell is independent of the physical dimensions of the cell, it depends **only** on the *intensive* properties of the cell, eg. The concentrations of the solutions, the nature of the electrode and, of course, the temperature.

> There is a convenient method of representing a cell than by drawings, ie. by using a **cell diagram**. A vertical bar (|) represents the phase boundary between the electrode and the solution. The centre double vertical line (‖) indicates the salt bridge. In all cell diagrams, the more reduced forms are written to the outside while the more oxidised forms are written closer to the salt bridge.
> By international convention the **sign of the electrode potential of the cell is the polarity of the right-hand electrode in the cell diagram.**
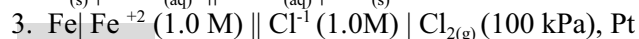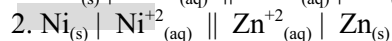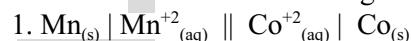
Anode | anode electrolyte ‖ cathode electrolyte | cathode

Summarising for the general cell: **A | B ‖ C | D**

If the E^0_{cell} is positive, then the cell reaction is: $A + C \longrightarrow B + D$
If the E^0_{cell} is negative, then the cell reaction is: $B + D \longrightarrow A + C$

For each of the following cells calculate the magnitude and the sign of the E^0_{cell}, write the overall cell reaction and draw the cell diagram (label all relevant parts fully):
1. $Mn_{(s)} | Mn^{+2}_{(aq)} \; \| \; Co^{+2}_{(aq)} | Co_{(s)}$
2. $Ni_{(s)} | Ni^{+2}_{(aq)} \; \| \; Zn^{+2}_{(aq)} | Zn_{(s)}$
3. $Fe | Fe^{+2} (1.0 \; M) \| Cl^{-1} (1.0M) | Cl_{2(g)} (100 \; kPa), Pt$

Using E^0 values to predict spontaneous reactions

This now provides the capacity to make predictions (and calculate voltages) for combinations of half reactions.
1. To proceed, electrons must be on opposite sides.
2. The larger the voltage total, generally speaking, the more vigorous the overall reaction.
3. Standard voltages are not changed by the multiplication required to balance the electrons.

One can predict the outcome of chemical reactions.
For example, will there be a reaction between Potassium metal and Chlorine gas?
Calculate the E^0_{cell} for the reaction, if a substantial potential is obtained, therefore leading to the prediction that a vigorous reaction is likely.

$E^0_{Positive}$ Spontaneous Reaction
Products Predominate

Thus: a positive sum of electrode potentials = spontaneous reaction
          a negative sum of electrode potentials = non- spontaneous reaction

Example: predict if the following reaction will work:
1. $Cl_{2(g)}$ will oxidize $Br^{-1}_{(aq)}$
2. $H_2SO_3 + Br_2 + H_2O \longrightarrow SO_4^{-2} + 2 Br^{-1} + 4 H^{+1}$
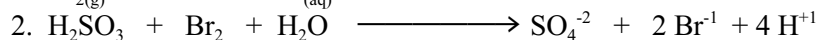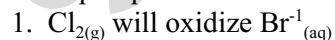
Predictions about whether a reaction can occur or not can also be obtained from calculating ΔG^0 for a reaction:
$$\Delta G^0 = - n F E^0_{cell}$$
See Notes Below:

Predictions for Reactions, E^0 and ΔG^0

The standard potential E^0 is a quantitative measure of the tendency of the reactants in their standard states to proceed to products in their standard states and so is the standard free energy change for a reaction, ΔG^0_{rxn}.. The exact relation between them is:

$$\Delta G^0_{rxn} = -nFE^0_{cell}$$

Where n is the number of moles of electrons transferred between oxidizing and reducing agents in a balanced redox reaction, and F is the **Faraday Constant, 96 485.31 C/mol**.

Thus, if E^0_{cell} is positive, then ΔG^0_{rxn} will be negative, so a spontaneous reaction if possible, i.e. a galvanic cell will run in the direction that gives a positive value for E^0_{cell}, hence giving a negative value for ΔG^0 which is a condition for spontaneity.

Reactant-favoured reaction have a negative E^0, hence positive ΔG^0, non-spontaneous.

Note: when a reaction is reversed, the magnitude of ΔG^0 and E^0 remain the same, but their signs are reversed.

Summary

|	ΔG^0	E^0
Spontaneous reaction (ECcells)	-	+
Equilibrium	0	0
Non-spontaneous (electrolytic cells)	+	-

Example 1
The reaction of zinc metal with copper(II) ions has a standard cell potential E^0 of +1.10 V at 25 C. Calculate ΔG^0 for the reaction...
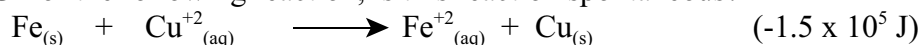$$Zn_{(s)} + Cu^{+2}_{(aq)} \longrightarrow Cu_{(s)} + Zn^{+2}_{(aq)} \qquad (\text{-212 kJ})$$
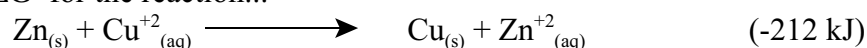
Example 2
The following reaction has an E^0 value of –0.76 V. Calculate ΔG_{rxn}, and tell whether the reaction is product-favoured or reactant-favoured.
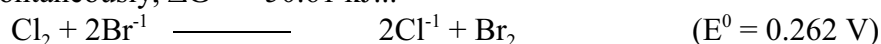$$H_{2(g)} + 2H_2O_{(l)} + Zn^{+2}_{(aq)} \longrightarrow Zn_{(s)} + 2H_3O^+_{(aq)}$$
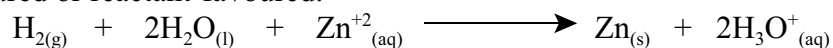
Example 3
Calculate ΔG^0 for the following reaction, is this reaction spontaneous?
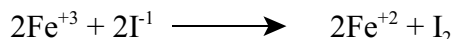$$Fe_{(s)} + Cu^{+2}_{(aq)} \longrightarrow Fe^{+2}_{(aq)} + Cu_{(s)} \qquad (\text{-1.5 x } 10^5 \text{ J})$$

Example 4
Find the standard cell potential for an electrochemical cell in which the following cell reaction takes place spontaneously, $\Delta G^0 = $ -50.61 kJ...
$$Cl_2 + 2Br^{-1} \longrightarrow 2Cl^{-1} + Br_2 \qquad (E^0 = 0.262 \text{ V})$$

Example 5
The cell potential for an electrochemical cell in which the following reaction occurs is 0.236 V...
$$2Fe^{+3} + 2I^{-1} \longrightarrow 2Fe^{+2} + I_2$$
Calculate ΔG^0. $\qquad\qquad\qquad$ (- 45.5 kJ)