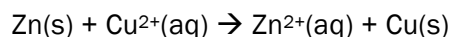
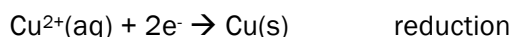
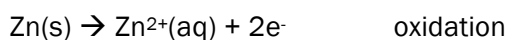


Electrochemistry

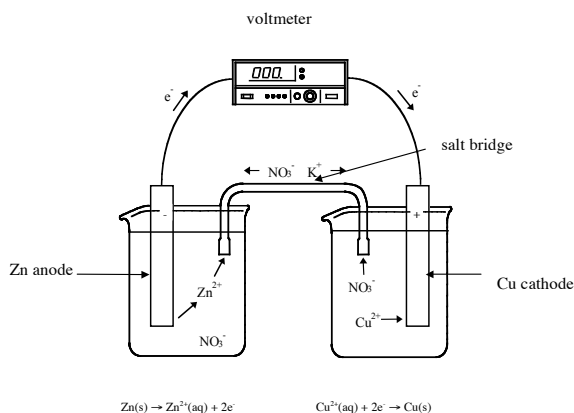
The reaction between solid Zn metal and ionic Cu(II) has a large equilibrium constant which means that when the reaction comes to equilibrium pretty much all the reactants have become products.



It is reasonable to think of this oxidation/reduction reaction as being the combination of separate oxidation and reduction steps.



Electrons are being removed from the Zn(s) and added to the Cu²⁺. Since electrons can be conducted through a wire it is possible to separate the sites of oxidation and reduction for this reaction and yet have the process occur. An appropriate design is shown below.



Both species involved in the oxidation process (Zn(s) and Zn²⁺) are present in one container (called the **oxidation half-cell**) while both species involved in the reduction process are present in the **reduction half-cell**. Electrons produced in the oxidation half-reaction are transported to the site of the reduction half-reaction via an electron conductor (a wire). A salt bridge of positive and negative ions also connects

the half-cells to ensure that there is no build up of charge in either cell. The tendency of the reaction to occur spontaneously produces what is called an **electromotive force**. A voltmeter can measure the electromotive force produced by the reaction. Electromotive force (measured in voltage) is a measure of the potential (ΔG) and thus the maximum amount of work that can be done per unit of charge passed through the cell. A volt is a joule (energy) per coulomb (charge). The voltage generated by a cell (often referred to as **E_{cell}**) is thus related to the change in Gibb's free energy necessary to reach equilibrium or how far the cell reaction is from equilibrium. The relationship between the voltage of a cell and the position of the equilibrium for the reaction that produces the electromotive force (emf) can be derived from the expression that relates the cell voltage to the concentrations of the products and reactants of the cell reaction.

It is reasonable there should be a dependence of cell voltage (or potential) on the concentration of reactants and products of the cell reaction. Increasing or decreasing the concentration of the reactants can control the direction of a chemical reaction. A non-spontaneous reaction can be made spontaneous by increasing the concentrations of reactants and decreasing the concentrations of products.

If we can determine the mathematical relationship between cell voltage (**E_{cell}**) and concentration of reactants and products we should be able to predict the concentrations that will give a cell voltage of zero. A cell voltage of zero suggests that there is no tendency for the cell reaction to go in either forward or reverse direction. This suggests that the reaction has reached equilibrium ($\Delta G = 0$). The relationship between the cell voltage and the concentrations of reactants and products in the cell is called the Nernst equation and is given by:

$$E_{cell} = E_{cell}^o - \frac{RT}{nF} \log Q \quad (1)$$

where E_{cell} is the measured voltage, E_{cell}^o is the voltage that would be measured if all concentrations were 1 M, R is the gas constant, T is the temperature in K, n is the moles of electrons transferred in the balanced cell reaction and F is Faraday's constant or the charge contained in a mole of electrons, 96,485 C/mol.

The value of E_{cell} is a measure of the potential for this reaction to come to equilibrium and thus is related to ΔG and the maximum amount of work that can be done by the cell reaction. Note that E_{cell} is measured in volts (V), an intensive unit of electromotive force that is equal to the energy per coulomb of charge transferred ($V = J/C$). Because the electromotive force is an intensive property, doubling the cell reaction stoichiometry (or halving it or doing any other multiple) will result in the same electromotive force. The amount of charge transferred in a given electrochemical cell reaction is equal to nF where n is the moles of electrons transferred in the balanced cell reaction and F is Faraday's constant. Thus the energy generated by the cell is

$$\Delta G = -nFE_{cell} \quad (2)$$

or

$$\Delta G = \Delta G^o + RT \ln Q \quad (3)$$

This change in free energy (ΔG) depends on the stoichiometric equivalents (n) used for the reaction and so it is an extensive property.

Both E_{cell} and ΔG are measures of the driving force of a process or chemical reaction to come to equilibrium. Thus, if these values are equal to zero, then the reaction is at equilibrium. The value of the reaction quotient at equilibrium is a very special value since it provides us with a measure of the relative proportions of reactants and products that will be in a solution when a chemical reaction comes to equilibrium. The larger K is, the more products we can hope to make from the chemical reaction. Setting either E_{cell} equal to zero in equation (1) or ΔG equal to zero in equation (3)

leads to equations (4) and (5). Note that these equations imply that we can calculate the equilibrium constant for a chemical reaction from a measurement of E_{cell} or a measurement of ΔG .

$$K = e^{-\Delta G^o/RT} \quad (4)$$

$$K = e^{nFE_{cell}^o/RT} \quad (5)$$