**Free energy and EMF**

Objectives After studying this Lecture you will be able to Distinguish between electrolytic cells and galvanic cells. Write the cell representation for electrochemical reactions. Derive the Nernst equation. Use the Nernst equation for calculating the electromotive force (emf) of a cell for any combination of activities of solution species. Evaluate ∆rG, ∆rH and ∆rS form dE /dT.

**Introduction :**

Both electrolytic cells and galvanic cells provide wonderful examples of conversion of one form of energy into another. In an electrolytic cell, a current is passed through a fluid medium (solutions, molten salts) causing migration of ions towards electrodes and the charge deposition by the ions at the electrodes. For example, if a current is passed through a solution of sodium chloride, the following reactions occur at the cathode and anode.

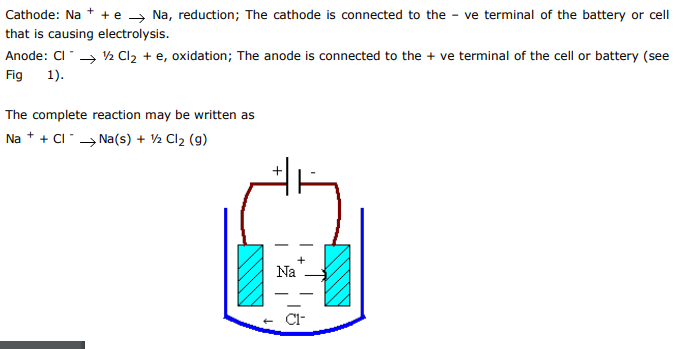
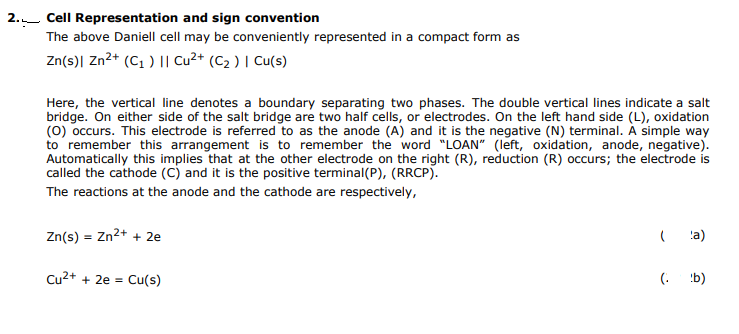
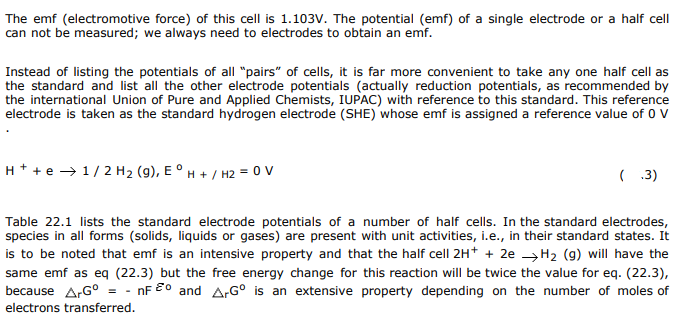


Figure 1: An electrolytic cell showing the migration of cations and anions.

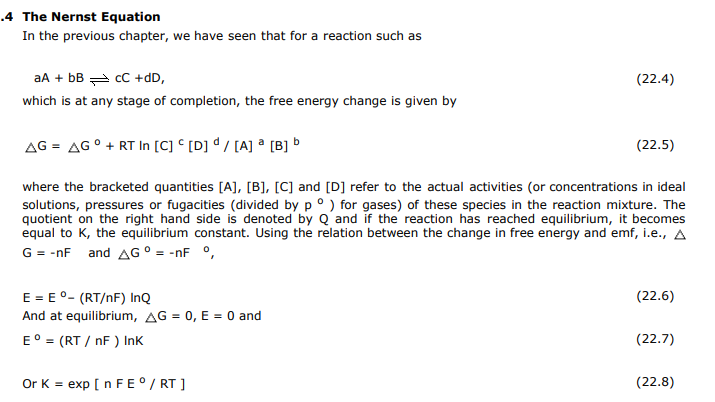
In a galvanic cell on the other hand, the two electrodes are present in differing chemical environments with different chemical potentials / free energies. We have already seen in the earlier chapter that a decrease in the Gibbs free energy is equal to the maximum non pressure volume work obtainable from the system.

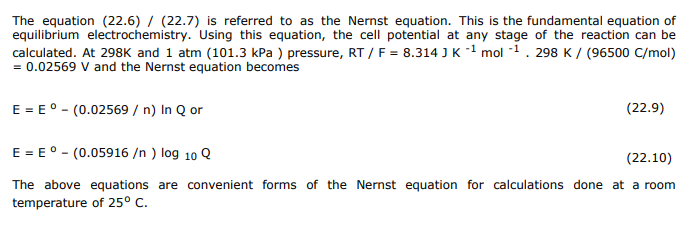
**∆r Go = - n F ξo**





(Note):Table 22.1 Standard electrode potentials at 298.15 K

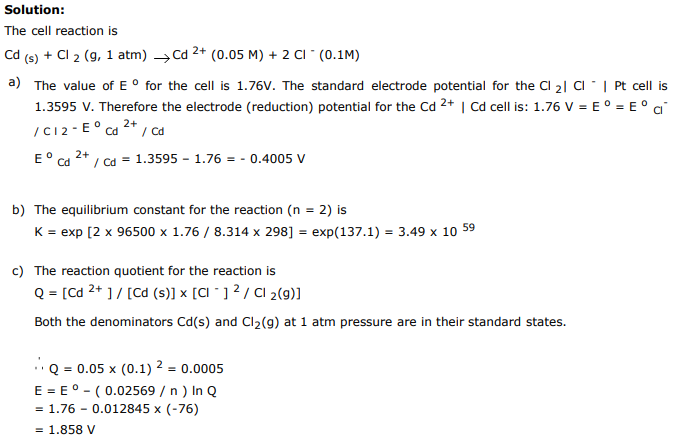




**Example (1 )**

For the galvanic cell Cd | Cd 2+ (0.05 M) || Cl - (0.10 M ) | Cl 2(1 atm ) | Pt, E o = 1.76 V. Calculate

a) the standard electrode potential of the cadmium electrode, b) the equilibrium constant for the cell reaction and c) the emf at 25 oC.



Standard reduction potentials The standard reduction potential for a given electrode is defined to be the zero-current potential for the galvanic cell that contains the standard hydrogen electrode (SHE) as the left-hand electrode and the given electrode as the right-hand electrode. All of the reacting species must be at unit activity. For example, for the Zn|Zn2+ electrode, the cell is

