

In electrochemical cell anode is negatively charged and oxidation takes place at this electrode.  
L.H.S. (-) Anode oxidation takes place  
R.H.S. (+) Cathode reduction takes place

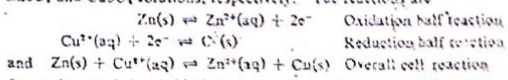
Electrochemical Cells

Topic - Electrical properties of Molecules

In an electrolytic cell, electrical energy is used to bring about a chemical reaction. The process may be reversed and electricity can be produced from chemical energy (released during a chemical reaction). Such devices, in which chemical energy is converted into electrical energy, are called electrochemical or galvanic cells. These cells are very important because of their many practical applications.

15.1 ELECTROCHEMICAL CELL

An electrochemical cell consists of two electrodes dipping into electrolyte solutions. These two electrodes are either dipping in the same solution or in different solutions separated by a salt bridge or porous material. Each compartment is called a half cell and the reaction occurring in each half cell is called a half cell reaction. Oxidation occurs at one electrode (anode) called oxidation half reaction and reduction occurs at the other (cathode) called reduction half reaction. The electrons released due to oxidation at the anode flow through the external wire to the cathode where reduction takes place. The overall cell reaction is the combination of the two half-cell reactions. For example, in the Daniell cell, the two electrodes of zinc and copper are dipped in ZnSO<sub>4</sub> and CuSO<sub>4</sub> solutions, respectively. The reactions are



It may be noted that oxidation takes place at the anode and reduction at the cathode, both in the electrolytic and galvanic cells. However, in the two cases, the signs of the electrodes are opposite. In an electrolytic cell the anode is positively charged and the anions migrate to it and get oxidized, whereas in the galvanic cell the anode is negatively charged as the constituents of the electrode get oxidized leaving the electrode rich in electrons, i.e. the anode becomes negatively charged.

15.2 TYPES OF SINGLE ELECTRODES OR HALF CELLS

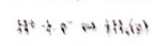
A single electrode consists of an electronic conductor (e.g. metal, gas adsorbed on metal, metal coated with sparingly soluble salt) in contact with an electrolytic conductor (electrolytic solution, inert salt, etc.)

Metal-Metal Ion Electrodes

This consists of a piece of metal dipped in a solution of its own ions. It is represented as  $M^{n+} | M$  (e.g.  $Zn^{2+} | Zn$ ). The electrode reaction is  $Zn^{2+} + 2e^- \rightleftharpoons Zn(s)$

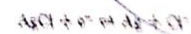
Gas Electrode

This consists of a gas bubbling over an inert metal dipping into a solution containing the corresponding ion. For example, the hydrogen electrode in which H<sub>2</sub> gas is bubbled over a platinum-platinum electrode dipped in an acid solution. It is represented as  $H^+ | H_2(g) | Pt$ . The reaction is



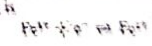
Metal-Metal Insoluble Salt Electrodes

These electrodes are prepared by coating a piece of metal with an insoluble salt of the same metal. For example, silver is coated with AgCl and dipped into a solution of Cl<sup>-</sup> ions, represented as  $Cl^- | AgCl | Ag$ . The reaction is



Inert Metal Electrodes

These consist of inert metal electrodes dipped in a solution containing ions with different oxidation states. For example, a platinum wire dipped in a solution of Fe<sup>2+</sup> and Fe<sup>3+</sup>, represented as  $Fe^{2+}, Fe^{3+} | Pt$ . The cell reaction is



Amalgam Electrodes

These consist of metal amalgam dipping in solutions of their ions. For example, lead amalgam dipping in a solution of Pb<sup>2+</sup> ions. It is represented as  $Pb(Hg) | Pb^{2+}$ . The reaction is  $Pb^{2+} + 2e^- \rightleftharpoons Pb$  (in Hg)

15.3 ELECTROMOTIVE FORCE OF A CELL

The difference of potential which causes a flow of current from the electrode of higher potential to that of lower potential is called the

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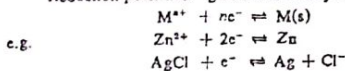
electromotive force of the cell. This is commonly abbreviated as e.m.f. and expressed in volts. The e.m.f. can be interpreted in terms of the difference of electrode potentials by writing

e.m.f. of the cell = Reduction potential of the right-hand-side electrode - reduction potential of the left-hand-side electrode

i.e., 
$$e.m.f. = E_R - E_L \quad (15.1)$$

Note: This is in accordance with the thermodynamic convention that the change in any thermodynamic quantity is the difference between the final state (products) and the initial state (reactants).

Reduction potentials\* give the tendency to gain electrons, i.e.



The e.m.f. of a cell cannot be measured with an ordinary voltmeter as the current drawn polarizes the electrodes. An unknown e.m.f. is opposed by another known e.m.f. until the two are equal, which is indicated by the galvanometer through a tap key (Poggendorf compensation method). However, these days VTVMs (vacuum tube voltmeters) are available, which draw very low currents and can be used for measuring the e.m.f. directly. A pH meter is actually a VTVM.

15.4 CONVENTIONS REGARDING CELL REACTIONS AND E.M.F.

An electrochemical cell consists of two electrodes. The e.m.f. of the cell depends upon the relative tendencies of oxidation and reduction at the two electrodes. The conventions regarding cells and cell reactions are:

1. In an electrochemical cell, oxidation occurs at the anode (or negative electrode), and reduction at the cathode (or positive electrode).
2. The cell is drawn in such a way that the reaction taking place at the left-hand-side electrode is oxidation and that on the right-hand-side electrode is reduction, i.e. in a cell the left-hand-side electrode acts as the negative electrode and the right-hand-side electrode acts as the positive electrode.
3. The e.m.f. of the cell is given as the electrode potential of the right-hand-side electrode ( $E_R$ ) minus that of the left-hand-side

\*The electrode potential arises due to charge separation between the electrode and the solution. Its magnitude and sign depend upon the ease with which the ion (to which it is reversible) is reduced.

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electrode ( $E_L$ ), i.e.

$$E_{cell} = E_R - E_L$$

According to IUPAC convention, the electrode potential is always taken as the reduction potential for both electrodes.

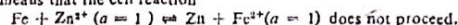
4. The cell reaction can be determined by writing the oxidation and reduction reactions with equal numbers of electrons and then adding the two reactions. It may be noted that, to equalise the electrons in oxidation and reduction reactions, the half reactions are multiplied by suitable integers. But the electrode potentials do not change for these half-cell reactions.
5. If the e.m.f. of the cell ( $E_R - E_L$ ) is positive, then the cell reaction is spontaneous in the forward direction, i.e. oxidation takes place at the LHS electrode and reduction at the RHS electrode.

Note: If the e.m.f. of the cell is negative, it means that reduction occurs at the left-hand electrode and oxidation at the right-hand electrode. For example, the e.m.f. of the cell

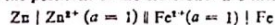
$$Fe | Fe^{2+}(a=1) || Zn^{2+}(a=1) | Zn$$

$$E_{cell}^\circ = E^\circ(Zn^{2+}, Zn) - E^\circ(Fe^{2+}, Fe) = -0.763 - (-0.440) = -0.323V$$

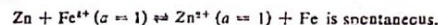
This means that the cell reaction



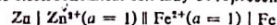
But, if the positions of the electrodes are interchanged,



so that  $E_{cell}^\circ = -0.440 - (-0.763) = 0.323V$  and the reaction



Thus, for a spontaneous cell reaction ( $E^\circ = +ve$ ), the electrode with the higher electrode potential is written on the right-hand-side (acts as cathode and reduction occurs) and the one with the lower electrode potential is written on the left-hand side (acts as anode and oxidation occurs). The electrochemical cell may be represented as



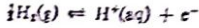
15.5 STANDARD ELECTRODE POTENTIAL

It is not possible to determine the potential of a single electrode because an electrochemical cell must contain two half cells suitably connected to each other. The problem can be solved by selecting an arbitrary reference electrode. For this purpose, a hydrogen electrode has been selected as the standard electrode and is assigned zero potential. It consists of a platinum foil coated with platinum black, dipped into an aqueous solution of  $H^+$  ions of unit activity in which hydrogen gas at 1 atm pressure (taken as unit fugacity) is constantly bubbled. The potential of all other electrodes are measured with respect to this reference electrode.



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- (a) If, in a cell, the standard hydrogen electrode acts as an anode, i.e. oxidation occurs,

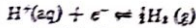


then reduction will occur at the other electrode and its electrode potential is positive. The e.m.f. of the cell is numerically equal to reduction potential of the other electrode, i.e.

$$E_{cell} = E_R - E_L$$

$$E_{cell} = E_R \quad (E_L = 0)$$

- (b) If the standard hydrogen electrode acts as a cathode, i.e. reduction occurs,



then the potential of the other electrode is negative.

$$E_{cell} = E_R - E_L$$

$$E_{cell} = -E_L \quad (E_R = 0)$$

Since

$$E_{cell} = +ve$$

$$\therefore E_L = -ve$$

All standard electrode potentials are taken as reduction potentials.

EXAMPLE 15.1 Write the half cell reactions and the overall cell reactions for the following electrochemical cells:

- (a)  $Pt | H_2 (1 \text{ atm}) | HCl (a_1) | Cu^{2+} (a_2) | Cu$  *cathode*  
 (b)  $Cd | CdSO_4 (a_1) | SO_4^{2-} (a_2) | H_2SO_4(l) | Hg(l)$   
 (c)  $Pt | CO_2 | H_2C_2O_4, H^+(a_1) | MnO_4^-, Mn^{2+}, H^+ | Pt$

Solution (a) The cell reactions can be written by writing the oxidation half reaction (L.H.S. electrode) and reduction half reaction (R.H.S. electrode) as:

- (a) Oxidation half reaction:  $H_2(g) = 2H^+(a_1) + 2e^-$   
 Reduction half reaction:  $Cu^{2+}(a_2) + 2e^- = Cu(s)$   
 Cell reaction:  $Cu^{2+}(a_2) + H_2(g) = Cu(s) + 2H^+(a_1)$   
 (b) Oxidation half reaction:  $Cd(s) = Cd^{2+}(aq) + 2e^-$   
 Reduction half reaction:  $H_2SO_4(l) + 2e^- = 2Hg(l) + SO_4^{2-}(aq)$   
 Cell reaction:  $Cd(s) + H_2SO_4(l) = Cd^{2+}(aq) + SO_4^{2-} + 2Hg(l)$   
 (c) Oxidation half reaction:  $[H_2C_2O_4 = 2CO_2 + 2H^+ + 2e^-] \times 5$   
 Reduction half reaction:  $[MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O] \times 2$   
 Cell reaction:  $2MnO_4^- + 5H_2C_2O_4 + 6H^+ = 2Mn^{2+} + 10CO_2 + 8H_2O$

EXAMPLE 15.2 Calculate the standard e.m.f. for the following:

- (a)  $Zn | Zn^{2+} (a=1) || Cu^{2+} (a=1) | Cu$   
 (b)  $Cr | Cr^{3+} (a=1) || Cu^{2+} (a=1) | Cu$   
 (c)  $Pt | I^-(a=1), I_2 | Fe^{2+} (a=1), Fe^{3+} (a=1) | Pt$

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The standard electrode potentials are:

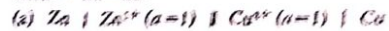
$$E^\circ(Zn^{2+}, Zn) = -0.763 \text{ V}, E^\circ(Cu^{2+}, Cu) = 0.337 \text{ V},$$

$$E^\circ(Cr^{3+}, Cr) = -0.774 \text{ V}, E^\circ(I_2, I^-) = 0.535 \text{ V},$$

$$E^\circ(Fe^{3+}, Fe) = 0.771 \text{ V}.$$

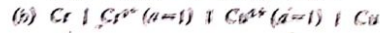
Solution The e.m.f. of the cell is,

$$E_{cell} = E_R - E_L$$



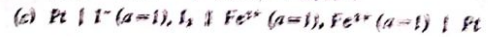
$$E_R = E^\circ(Cu^{2+}, Cu) = 0.337 \text{ V}, E_L = E^\circ(Zn^{2+}, Zn) = -0.763 \text{ V}$$

$$E_{cell} = 0.337 - (-0.763) = 1.1 \text{ V}$$



$$E_R = E^\circ(Cu^{2+}, Cu) = 0.337 \text{ V}, E_L = E^\circ(Cr^{3+}, Cr) = -0.774$$

$$E_{cell} = 0.337 - (-0.774) = 1.111 \text{ V}$$

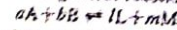


$$E_R = E^\circ(Fe^{3+}, Fe^{2+}) = 0.771 \text{ V}, E_L = E^\circ(I_2, I^-) = 0.535 \text{ V}$$

$$E_{cell} = 0.771 - 0.535 = 0.236 \text{ V}.$$

### 15.6 NERNST EQUATION: DEPENDENCE OF E.M.F. ON CONCENTRATION

The e.m.f. of a cell depends on both the standard e.m.f. ( $E^\circ$ ) as well as the activities (concentrations) of the species involved in the cell reaction. For a general reaction of the type



the e.m.f. of the cell is given by the equation

$$E = E^\circ - \frac{RT}{nF} \ln \frac{(a_A)^a (a_B)^b}{(a_L)^l (a_M)^m} \quad (15.2)$$

where  $a_A, a_B, a_L$  and  $a_M$  are the activities of the species A, B, L and M respectively,  $n$  is the number of electrons transferred if the chemical equation is expressed in two half-cell reactions,  $R$  is the gas constant and  $F$  is the Faraday (96500 C). Here  $E^\circ$  represents the standard e.m.f. and is the e.m.f. of the cell when all the reactants and products are in their standard states (unit activity). This equation is called the Nernst equation

Equation (15.2) may be written as

$$E = E^\circ - \frac{2.303 RT}{nF} \log \frac{(a_A)^a (a_B)^b}{(a_L)^l (a_M)^m} \quad (15.3)$$

(a)

Substituting the values of constants ( $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $T = 298 \text{ K}$ ,  $F = 96500 \text{ C mol}^{-1}$ ), the above equation becomes

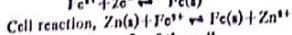
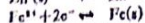
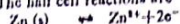
$$E = E^\circ - \frac{0.0591}{n} \log \frac{(a_1)^x (a_2)^y}{(a_A)^x (a_B)^y} \quad (15.4)$$

If the solutions behave ideally, the activities\* may be replaced by concentrations, i.e.

$$E = E^\circ - \frac{0.0591}{n} \log \frac{[A]^x [B]^y}{[A]^x [B]^y} \quad (15.5)$$

✓ EXAMPLE 15.3 What will be the e.m.f. of the cell  
 $\text{Zn} | \text{Zn}^{2+} (a = 0.01) || \text{Fe}^{2+} (a = 0.005) | \text{Fe}$   
 given that  $E^\circ(\text{Zn}^{2+}, \text{Zn}) = -0.763 \text{ V}$  and  $E^\circ(\text{Fe}^{2+}, \text{Fe}) = -0.44 \text{ V}$

Solution The half cell reactions are



The standard e.m.f. of the cell

$$E^\circ = E^\circ(\text{Fe}^{2+}, \text{Fe}) - E^\circ(\text{Zn}^{2+}, \text{Zn}) \\ = -0.440 - (-0.763) = 0.323 \text{ V}$$

The cell e.m.f. is

$$E = E^\circ - \frac{0.0591}{n} \log \frac{a(\text{Zn}^{2+})}{a(\text{Fe}^{2+})}$$

$$n = 2, E^\circ = 0.323 \text{ V}, a(\text{Zn}^{2+}) = 0.01, a(\text{Fe}^{2+}) = 0.005$$

$$E = 0.323 - \frac{0.0591}{2} \log \frac{0.01}{0.005}$$

$$= 0.323 - 0.009 \\ = 0.314 \text{ V}$$

Thus, e.m.f. of the cell is 0.314 V.

EXAMPLE 15.4 Consider the cell reaction  
 $\text{Ag}(s) + \text{Cu}^{2+} (a = 0.48) + \text{Br}^- (a = 0.40) \rightleftharpoons \text{AgBr}(s) + \text{Cu}^+ (a = 0.32)$   
 given that the standard e.m.f. of the cell with the above cell reaction at 298 K is 0.058 V.

- Write the reactions occurring at the anode and cathode.
- Construct the cell.
- Calculate the e.m.f. of the cell.

Solution (a) At the anode (oxidation occurs),  
 $\text{Ag}(s) + \text{Br}^- \rightleftharpoons \text{AgBr}(s) + e^-$   
 At the cathode (reduction occurs),  
 $\text{Cu}^{2+} + e^- \rightleftharpoons \text{Cu}^+$

\*The electrode potential depends upon the activity of the ions towards which it is reversible. However, in case of dilute solutions, activities are equal to the concentrations (M).

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(b) The cell may be represented as  
 $\text{Ag} | \text{AgBr}(s), \text{Br}^- (a = 0.40) || \text{Cu}^+ (a = 0.32), \text{Cu}^{2+} (a = 0.48) | \text{Pt}$

(c) The e.m.f. of the cell is given by

$$E = E^\circ - \frac{0.0591}{1} \log \frac{[a(\text{Cu}^+)]}{[a(\text{Cu}^{2+})][a(\text{Br}^-)]}$$

$$= 0.058 - \frac{0.0591}{1} \log \frac{0.32}{0.48 \times 0.40}$$

$$= 0.058 - 0.013$$

$$= 0.045 \text{ V}$$

Thus, e.m.f. of the cell = 0.045 V.

### 15.7 THERMODYNAMICS AND E.M.F.

Thermodynamic functions, such as free energy, entropy and enthalpy changes, for cell reactions can be calculated from the e.m.f. and its temperature dependence.

Free energy change  
 $\Delta G = -nFE \quad (15.6)$

Differentiating  $\Delta G$  with respect to temperature at constant pressure, we get

$$\left( \frac{\partial \Delta G}{\partial T} \right)_p = -nF \left( \frac{\partial E}{\partial T} \right)_p$$

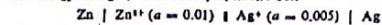
$$\text{but } \left( \frac{\partial \Delta G}{\partial T} \right)_p = -\Delta S$$

$$\therefore \Delta S = nF \left( \frac{\partial E}{\partial T} \right)_p \quad (15.7)$$

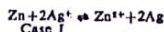
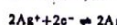
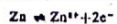
Now  $\Delta G = \Delta H - T\Delta S$  or  $\Delta H = \Delta G + T\Delta S$

$$\text{So that } \Delta H = -nFE + nFT \left( \frac{\partial E}{\partial T} \right)_p = nF \left[ T \left( \frac{\partial E}{\partial T} \right)_p - E \right] \quad (15.8)$$

Note: Half cells and cell reactions can be written with different numbers of electrons. It must be appreciated that the cell potential remains unchanged whereas free energy changes. For example, in the cell

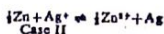
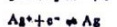
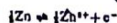


cell reactions may be written as



Case I

or



Case II

Handwritten notes:  
 $dg = v dp - s dt$   
 $dh_p = -s dt$   
 $\left( \frac{\partial g}{\partial T} \right)_p = -s$  (15.7)



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Substituting the values of constants ( $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $T = 298 \text{ K}$ ,  $F = 96500 \text{ C mol}^{-1}$ ), the above equation becomes

$$E = E^\circ - \frac{0.0591}{n} \log \frac{(a_1)^x (a_2)^y}{(a_3)^z (a_4)^w} \quad (15.4)$$

If the solutions behave ideally, the activities\* may be replaced by concentrations, i.e.

$$E = E^\circ - \frac{0.0591}{n} \log \frac{[L]^x [M]^y}{[A]^z [B]^w} \quad (15.5)$$

**EXAMPLE 15.3** What will be the e.m.f. of the cell  
 $\text{Zn} | \text{Zn}^{2+} (a = 0.01) || \text{Fe}^{2+} (a = 0.005) | \text{Fe}$   
 given that  $E^\circ(\text{Zn}^{2+}, \text{Zn}) = -0.763 \text{ V}$  and  $E^\circ(\text{Fe}^{2+}, \text{Fe}) = -0.44 \text{ V}$

**Solution** The half cell reactions are  
 $\text{Zn}(s) \rightleftharpoons \text{Zn}^{2+} + 2e^-$   
 $\text{Fe}^{2+} + 2e^- \rightleftharpoons \text{Fe}(s)$   
 Cell reaction,  $\text{Zn}(s) + \text{Fe}^{2+} \rightleftharpoons \text{Fe}(s) + \text{Zn}^{2+}$   
 The standard e.m.f. of the cell  
 $E^\circ = E^\circ(\text{Fe}^{2+}, \text{Fe}) - E^\circ(\text{Zn}^{2+}, \text{Zn})$   
 $= -0.440 - (-0.763) = 0.323 \text{ V}$   
 The cell e.m.f. is

$$E = E^\circ - \frac{0.0591}{n} \log \frac{a(\text{Zn}^{2+})}{a(\text{Fe}^{2+})}$$

$n = 2, E^\circ = 0.323 \text{ V}, a(\text{Zn}^{2+}) = 0.01, a(\text{Fe}^{2+}) = 0.005$

$$E = 0.323 - \frac{0.0591}{2} \log \frac{0.01}{0.005}$$

$$= 0.323 - 0.009$$

$$= 0.314 \text{ V}$$

Thus, e.m.f. of the cell is 0.314 V.

**EXAMPLE 15.4** Consider the cell reaction  
 $\text{Ag}(s) + \text{Cu}^{2+}(a = 0.48) + \text{Br}^-(a = 0.40) = \text{AgBr}(s) + \text{Cu}^+(a = 0.32)$   
 given that the standard e.m.f. of the cell with the above cell reaction at 298 K is 0.058 V.

- (a) Write the reactions occurring at the anode and cathode.
- (b) Construct the cell.
- (c) Calculate the e.m.f. of the cell.

**Solution** (a) At the anode (oxidation occurs).  
 $\text{Ag}(s) + \text{Br}^- \rightleftharpoons \text{AgBr}(s) + e^-$   
 At the cathode (reduction occurs).  
 $\text{Cu}^{2+} + e^- \rightleftharpoons \text{Cu}^+$

\*The electrode potential depends upon the activity of the ions towards which it is reversible. However, in case of dilute solutions, activities are equal to the concentrations (M).

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- (b) The cell may be represented as  
 $\text{Ag} | \text{AgBr}(s), \text{Br}^-(a = 0.40) || \text{Cu}^+(a = 0.32), \text{Cu}^{2+}(a = 0.48) | \text{Pt}$
- (c) The e.m.f. of the cell is given by

$$E = E^\circ - \frac{0.0591}{1} \log \frac{[a(\text{Cu}^+)]}{[a(\text{Cu}^{2+})][a(\text{Br}^-)]}$$

$$= 0.058 - \frac{0.0591}{1} \log \frac{0.32}{0.48 \times 0.40}$$

$$= 0.058 - 0.013$$

$$= 0.045 \text{ V}$$

Thus, e.m.f. of the cell = 0.045 V.

15.7 THERMODYNAMICS AND E.M.F.

Thermodynamic functions, such as free energy, entropy and enthalpy changes, for cell reactions can be calculated from the e.m.f. and its temperature dependence.

Free energy change  
 $\Delta G = -nFE$  (15.6)

Differentiating  $\Delta G$  with respect to temperature at constant pressure, we get

$$\left(\frac{\partial \Delta G}{\partial T}\right)_P = -nF \left(\frac{\partial E}{\partial T}\right)_P$$

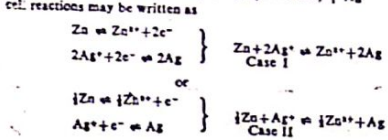
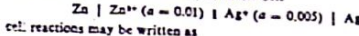
$$\text{But } \left(\frac{\partial \Delta G}{\partial T}\right)_P = -\Delta S$$

$$\therefore \Delta S = nF \left(\frac{\partial E}{\partial T}\right)_P$$

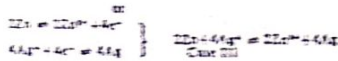
Now  $\Delta G = \Delta H - T\Delta S$  or  $\Delta H = \Delta G + T\Delta S$

So that  $\Delta H = -nFE + nFT \left(\frac{\partial E}{\partial T}\right)_P = nF \left[ T \left(\frac{\partial E}{\partial T}\right)_P - E \right]$  (15.8)

Note: Half cells and cell reactions can be written with different numbers of electrons. It must be appreciated that the cell potential remains unchanged whereas free energy changes. For example, in the cell



$dg = v dp - s dt$   
 $d \ln p = -s dt$   
 $\left(\frac{\partial g}{\partial T}\right)_P = -s$  (15.7)



According to Nernst equation

$$E = E^\circ - \frac{RT}{nF} \ln \left[ \frac{a_{\text{Zn}^{2+}}}{a_{\text{Cu}^{2+}}} \right]^{2/2}$$

where  $n_{\text{Zn}^{2+}}$  and  $n_{\text{Cu}^{2+}}$  represent the number of ions of zinc and copper, respectively. If we put these variables according to the overall reaction:

$$E = E^\circ - \frac{RT}{nF} \ln \left[ \frac{a_{\text{Zn}^{2+}}}{a_{\text{Cu}^{2+}}} \right] \quad \text{Case I}$$

$$= E^\circ - \frac{RT}{nF} \ln \left[ \frac{a_{\text{Zn}^{2+}}}{a_{\text{Cu}^{2+}}} \right] \quad \text{Case II}$$

Case III

Thus, e.m.f. in all three cases is the same. However, free energies, given by the relation  $\Delta G^\circ = -nFE^\circ$ , are different in all three cases. This is because e.m.f. is an intensive quantity (difference of potentials) whereas  $\Delta G^\circ$  is an extensive quantity.

**EXAMPLE 15.5** The standard e.m.f. of the cell

Pt | H<sub>2</sub> (1 atm), H<sup>+</sup> (a = 1) | KCl (a = 1), AgCl | Ag at 298 K is 0.222 V. The temperature coefficient of the e.m.f. at constant pressure has been found to be -0.45 mV K<sup>-1</sup>.

- Write the cell reaction for the cell.
- Calculate  $\Delta G^\circ$ ,  $\Delta F^\circ$  and  $\Delta S^\circ$  for the cell reaction.

**Solution**

(a) Oxidation half reaction:  $\frac{1}{2}\text{H}_2(\text{g}) = \text{H}^+ (\text{a} = 1) + e^-$

Reduction half reaction:  $\text{AgCl}(s) + e^- = \text{Ag} + \text{Cl}^- (\text{a} = 1)$

Cell reaction:  $\frac{1}{2}\text{H}_2(\text{g}) + \text{AgCl}(s) = \text{Ag}(s) + \text{H}^+(\text{a} = 1) + \text{Cl}^-(\text{a} = 1)$

(b) The Gibbs free energy change for the reaction at 298 K

$$\Delta G^\circ = -nFE^\circ$$

$$n = 1, F = 96500 \text{ C mol}^{-1}, E^\circ = 0.222 \text{ V}$$

$$\therefore \Delta G^\circ = -(1) \times (96500 \text{ C mol}^{-1}) \times (0.222 \text{ V})$$

$$= -21.521 \times 10^3 \text{ J mol}^{-1}$$

$$= -21.521 \text{ kJ mol}^{-1} \quad [\text{C.V.} = 10^3]$$

$$\Delta S^\circ = nF \left( \frac{\partial E^\circ}{\partial T} \right)_P$$

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The temperature coefficient of the e.m.f. at constant pressure

$$\left( \frac{\partial E^\circ}{\partial T} \right)_P = -0.45 \text{ mV K}^{-1} = -0.45 \times 10^{-3} \text{ V K}^{-1}$$

$$\text{Thus, } \Delta S^\circ = (1) \times (96500 \text{ C mol}^{-1}) \times (-0.45 \times 10^{-3} \text{ V K}^{-1})$$

$$= -43.275 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\text{Now, } \Delta S^\circ = \frac{\Delta G^\circ}{T} + nF \left( \frac{\partial E^\circ}{\partial T} \right)_P$$

$$= -21.521 \text{ kJ mol}^{-1} + (298 \text{ K}) \times (-43.275 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$= -21.521 - 12.895$$

$$= -34.416 \text{ kJ mol}^{-1}$$

### 15.8 EQUILIBRIUM CONSTANT AND E.M.F.

The e.m.f. of the cell may be used to calculate the equilibrium constant for the cell reaction.

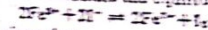
$$-\Delta G^\circ = RT \ln K = nFE^\circ$$

$$RT \ln K = nFE^\circ$$

(15.9)

$$\text{or } \log K = \frac{nFE^\circ}{2.303 RT}$$

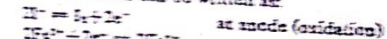
**EXAMPLE 15.6** Calculate the equilibrium constant for the reaction



at 298 K, given that

$$E^\circ(\text{I}_2/\text{I}^-) = 0.536 \text{ V and } E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) = 0.771 \text{ V}$$

**Solution** The cell reaction can be written as:



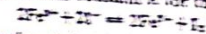
So the e.m.f. =  $E_2 - E_1$

$$= E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) - E^\circ(\text{I}_2/\text{I}^-)$$

$$= 0.771 - 0.536$$

$$= 0.235 \text{ V}$$

The equilibrium constant  $K$  for the reaction



is given by the relation

$$\log K = \frac{nFE^\circ}{2.303 RT}$$

$$n = 2, F = 96500 \text{ C mol}^{-1}, E^\circ = 0.235 \text{ V}, R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}, T = 298 \text{ K}$$

$$\log K = \frac{2 \times (96500 \text{ C mol}^{-1}) \times (0.235 \text{ V})}{2.303 \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})}$$

$$= 7.95$$

$$K = 8.3 \times 10^7$$





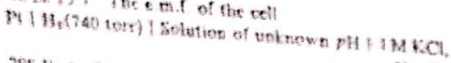
Sem-4, Lec-8 (H) Theo

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Specific Ion Electrodes

In recent years a number of electrodes have been developed whose potentials depend on the ratio of activities of a particular ion across suitable type of membranes. These electrodes are called specific ion electrodes and are used conveniently for determining the activity of a given ion using a sensitive pH meter.

EXAMPLE 15.7 The e.m.f. of the cell

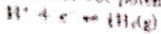


at 298 K is 0.480. The electrode potential of the reference calomel electrode is 0.280 V. Calculate the pH of the solution.

Solution The e.m.f. of the cell is

$$E_{\text{cell}} = E_{\text{reference}} - E_{\text{hydrogen}}$$

The electrode potential for the hydrogen electrode,



$$E = - \frac{RT}{f} \ln \frac{1/(\text{H}_2)}{a(\text{H}^+)} = \frac{2.303 RT}{2F} \log p_{\text{H}_2} - \frac{2.303 RT}{F} \text{pH}$$

$$p_{\text{H}_2} = \frac{740}{760} = 0.974 \text{ atm}$$

$$\text{At } 298 \text{ K, } E = - \frac{0.0591}{2} \log 0.974 - 0.0591 \text{ pH}$$

Thus,  $E_{\text{cell}} = E_{\text{reference}} - E_{\text{hydrogen}}$

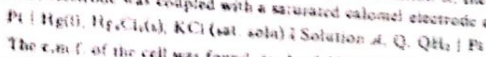
$$0.480 = 0.280 + \frac{0.0591}{2} \log 0.974 + 0.0591 \text{ pH}$$

$$\text{or } 0.480 = 0.280 - 0.0003 + 0.0591 \text{ pH}$$

$$0.0591 \text{ pH} = 0.2003$$

$$\text{or pH} = \frac{0.2003}{0.0591} = 3.39$$

EXAMPLE 15.8 To calculate the pH of a given solution a quinhydrone electrode was coupled with a saturated calomel electrode as

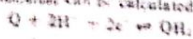


The e.m.f. of the cell was found to be 0.123 V at 298 K. Calculate the pH of the solution.  $E_{\text{reference}} = 0.2415 \text{ V}$  and  $E^\circ(\text{H}^+, \text{Q}, \text{QH}_2) = 0.6996 \text{ V}$ .

Solution The e.m.f. of the cell,

$$E_{\text{cell}} = E_{\text{quinhydrone}} - E_{\text{reference}}$$

$E_{\text{quinhydrone}}$  can be calculated from the reaction,



$$E_{\text{quinhydrone}} = E_{\text{quinhydrone}}^\circ - \frac{RT}{2F} \ln \frac{1}{[a(\text{H}^+)]^2}$$

$$= 0.6996 - \frac{2.303 RT}{F} \text{pH}$$

At 298 K,

$$E_{\text{quinhydrone}} = 0.6996 - 0.0591 \text{ pH}$$

and  $E_{\text{reference}} = 0.2415 \text{ V}$

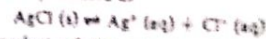
$$\text{Now, } E_{\text{cell}} = E_{\text{quinhydrone}} - E_{\text{reference}}$$

$$0.123 = 0.6996 - 0.0591 \text{ pH} - 0.2415$$

$$\text{pH} = \frac{0.3351}{0.0591} = 5.67$$

15.10 SOLUBILITY PRODUCT FROM E.M.F. DATA

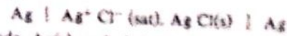
In a saturated solution of a sparingly soluble salt such as  $\text{AgCl}$ , equilibrium is represented as



The product of the activities of  $\text{Ag}^+$  and  $\text{Cl}^-$  ions is the solubility product

$$K_{sp} = [a(\text{Ag}^+)] \times [a(\text{Cl}^-)]$$

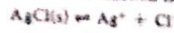
Since the solubility product is the equilibrium constant, it must be related to the e.m.f. of the selected cell having an overall reaction as above. For example, for determining the solubility product of  $\text{AgCl}$ , the cell is



At anode,  $\text{Ag}(\text{s}) = \text{Ag}^+ + e^-$

At cathode,  $\text{AgCl}(\text{s}) + e^- = \text{Ag} + \text{Cl}^-$

So that the overall reaction is



$$\text{and } E_{\text{cell}}^\circ = \frac{RT}{nF} \ln [a(\text{Ag}^+)] [a(\text{Cl}^-)]$$

$$= \frac{RT}{nF} \ln K_{sp}$$

Knowing the value of  $E^\circ$ ,  $K_{sp}$  can be calculated.

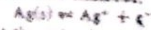
EXAMPLE 15.9 Calculate  $K_{sp}$  of  $\text{AgCl}$  by forming a suitable cell, given that  $E^\circ(\text{AgCl}, \text{Ag}, \text{Cl}^-) = 0.2224 \text{ V}$  and  $E^\circ(\text{Ag}^+, \text{Ag}) = 0.7991 \text{ V}$ .

Solution

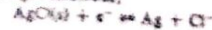
The cell can be represented as



At the left electrode,



At the right electrode,



$\Delta G^\circ = -RT \ln K = -nFE^\circ$   
 $\ln K = \frac{-nFE^\circ}{-RT}$   
 $\ln K = \frac{nFE^\circ}{RT}$   
 $\ln K_{sp} = \frac{1 \times 96485 \times 0.2224}{8.314 \times 298}$

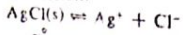
P-8/9



Sem-4, CC-8

(CH), Theo. P-9/9

Overall reaction:



$$E_{\text{cell}}^{\circ} = E_R - E_L$$

$$= 0.2224 - 0.7990$$

$$= -0.5766 \text{ V}$$

Now,  $E^{\circ} = \frac{RT}{nF} \ln K_{sp}$

or  $\ln K_{sp} = \frac{nFE^{\circ}}{RT}$

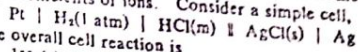
$$\log K_{sp} = \frac{(1) \times (96500 \text{ C mol}^{-1}) \times (-0.5766 \text{ V})}{2.303 \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})}$$

$$= -9.75$$

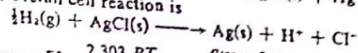
$$K_{sp} = 5.6 \times 10^{-9}$$

15.11 DETERMINATION OF ACTIVITY COEFFICIENTS FROM E.M.F.

E.m.f. measurements provide the most convenient method of determining activity coefficients of ions. Consider a simple cell,



The overall cell reaction is



$$E_{\text{cell}} = E^{\circ} - \frac{2.303 RT}{nF} \log \frac{a(\text{H}^+) a(\text{Cl}^-)}{[f(\text{H}_2)]^{1/2}}$$

The activities of solid Ag and AgCl are taken constant and the fugacity of hydrogen at 1 atm is also unity, so that

$$E = E^{\circ} - 0.0591 \log a(\text{H}^+) a(\text{Cl}^-)$$

Now  $a(\text{H}^+) = \gamma_+ m(\text{H}^+); a(\text{Cl}^-) = \gamma_- m(\text{Cl}^-)$

For HCl,  $m_+ = m_- = m$ , so that

$$E = E^{\circ} - 0.0591 \log m^2 - 0.0591 \log \gamma_+ \gamma_-$$

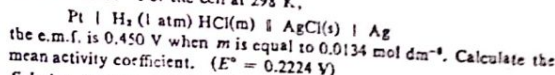
For each ion, the activity coefficient  $\gamma_+ \gamma_- = \gamma_{\pm}^2$  where  $\gamma_{\pm}$  is called the mean activity coefficient.

$$E = E^{\circ} - 2 \times 0.0591 \log m - 0.0591 \log \gamma_{\pm}^2$$

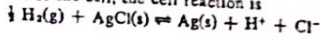
or  $E = E^{\circ} - 0.1182 \log m - 0.1182 \log \gamma_{\pm}$

Thus, knowing the value of E at a particular concentration m, and E°, the mean activity coefficient can be calculated.

EXAMPLE 15.10 For the cell at 298 K,



Solution For the cell, the cell reaction is



$$E = E^{\circ} - \frac{2.303RT}{nF} \log a(\text{H}^+) a(\text{Cl}^-)$$

$$= E^{\circ} - 0.0591 \log m^2 - 0.0591 \log \gamma_{\pm}^2$$

$$= E^{\circ} - 0.1182 \log m - 0.1182 \log \gamma_{\pm}$$

$$E = 0.45 \text{ V}, E^{\circ} = 0.2224 \text{ V}, m = 0.0134$$

$$\therefore 0.1182 \log \gamma_{\pm} = E^{\circ} - 0.1182 \log m - E$$

$$= 0.2224 - 0.1182 \log (0.0134) - 0.450$$

$$= 0.2224 + 0.2214 - 0.450$$

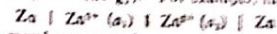
$$= -0.0062$$

$$\log \gamma_{\pm} = -0.052$$

$$\gamma_{\pm} = 0.887$$

15.12 CONCENTRATION CELLS

Electrical energy can also be obtained by the concentration difference of the solutions in which the electrodes are dipping. These cells are called concentration cells. In these cells, the free energies of solutions are different at two concentrations, and electrical energy arises from the transfer of substance from the solution of higher activity around one electrode (higher energy) to that of lower activity around the other electrode (lower energy). For example, in the case of a cell

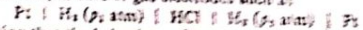


e.m.f. may be expressed as

$$E = - \frac{RT}{nF} \ln \frac{a_1}{a_2}$$

For a cell to be positive,  $a_1 > a_2$ , so that the reaction proceeds in the direction indicated.

However, in case of gas electrodes such as:



assuming that the behaviour of hydrogen is nearly ideal, e.m.f. may be written as

$$E = - \frac{RT}{nF} \ln \frac{p_1}{p_2}$$

15.13 JUNCTION POTENTIAL

A liquid junction between the solutions in a cell gives rise to a junction potential. The e.m.f. of the cell will depend on the transference numbers of the ions. Such cells are called concentration cells with transference. The e.m.f. of the cell will be equal to  $E_{\text{cell}} - E_j$  where  $E_{\text{cell}}$  is the potential of the cell that would be observed in the absence of junction potential and  $E_j$  is the junction potential.  $E_j$  can be calculated as  $E_j = E - (E_R - E_L)$ .

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