Module 5 : Electrochemistry
Lecture 24 : Applications of Electrode Potentials.

Objectives

In this lecture you will learn the following

- Determination of thermodynamic functions.

- Estimation of activities of electrolytes.

- Use emf measurements to determine the solubility product and the solubility of a sparingly soluble salt.

- The use of emf measurements to determine the pH of a solution.

- Determination of the end points using potentiometric titrations

- Determination of pK_a and pK_b

- Design of sensors.

24.1 Introduction

By measuring the emf of suitable galvanic cells, it is possible to calculate the changes in the thermodynamic functions $\triangle G$, $\triangle H$ and $\triangle S$, the solubility product, the pH of a solution, activities of electrolytes, and pK_a and pK_b. In analytical chemistry too, emf measurements have wide ranging applications.

$\triangle G$ and $\triangle S$ are determined from emf measurements and $\triangle H$ is evaluated from the Gibbs - Helmohltz equation. Emf measurements are normally made at constant temperature. Since emf is affected by changes in temperature, the temperature coefficient of emf viz., d /dT can be determined by measuring the emf at 2 or 3 different temperatures. It is related to $\triangle S$ as shown below. Differentiating $\triangle G$ = -nF   w.r.t. temperature (and replacing   by E for convenience),

d ($\triangle G$) /dT = - nF (dE /dT)

since d($\triangle G$) /dT = - $\triangle S$ we have

$\triangle S$ = nF [dE /dT]   (24.1)

$\triangle H$ at any given temperature can be either calculated from the Gibbs-Helmholtz equation or from the following standard relation for free energy.

$\triangle G$ = $\triangle H$ - T $\triangle S$ (24.2)

Example 24.1:

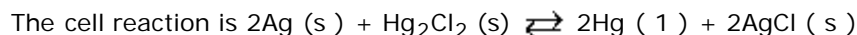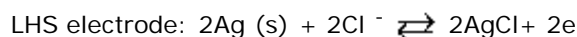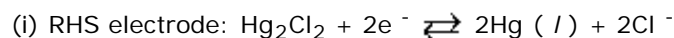The galvanic cell
Ag(s) | AgCl (s) | KCl (1.0 M) I Hg_2 Cl_2 (s) | Hg (l)
is an example of cell without a liquid junction since both the electrodes dip into the same electrolyte. The

emf of the cell is 0.058V at 298 K and 0.0614V at 308 K.

The electrode reaction are

(i) RHS electrode: $Hg_2Cl_2 + 2e^- \rightleftharpoons 2Hg\ (l) + 2Cl^-$

LHS electrode: $2Ag\ (s) + 2Cl^- \rightleftharpoons 2AgCl + 2e$

The cell reaction is $2Ag\ (s) + Hg_2Cl_2\ (s) \rightleftharpoons 2Hg\ (1) + 2AgCl\ (s)$

The thermodynamic function are calculated as shown below.

(ii) $\triangle G^O = -nFE^O = -2 \times 96500C \times 0.058\ V = -11194J\ mol^{-1}$

(iii) $dE^O /dT \cong \triangle E^O / \triangle T = (0.0614 - 0.058) / 10 = 3.40 \times 10^{-4}\ VK^{-1}$

(iv) $\triangle S^O = nF\ dE^O / dT = 2 \times 965000C \times 3.4 \times 10^{-4}\ VK^{-1} = 57.9\ JK^{-1}\ mol^{-1}$

(v) $\triangle G^O = \triangle H^O - T\triangle S^O$

$\triangle H^O = \triangle G^O + T\triangle S^O$

$= -11194 + 298 \times 57.9 = 6060\ J\ mol^{-1}$

These details have already been described in the earlier lecture 22 and are given here for completeness and continuity.

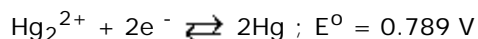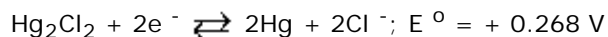## 24.2 Determination of Solubility Products of Sparingly Soluble Salts

The solubility product K_{sp} ($AB_n \rightarrow A^{n+} + n\ B^-$; K_{sp} is defined as $K_{sp} = [A^{n+}]\ [B^-]^n$) is an equilibrium constant and its value can be predicted from a knowledge of the standard electrode potentials. The electrodes are chosen in such a way , that the overall cell reaction is the solubility product equilibrium. A suitable galvanic cell is thus set up and its emf is determined experimentally. Even if measurements can not be made, it is possible to arrive at the approximate values of K_{sp} from appropriate half cell reaction potentials as shown below.

We will now illustrate the calculation of K_{sp} for Hg_2Cl_2 (s) at 298 K from data on electrode potentials.

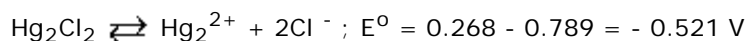$Hg_2Cl_2\ (s) \rightleftharpoons Hg_2^{2+} + 2Cl^-$;   (24.3)
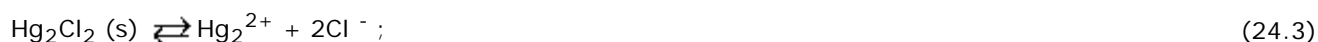
$K_{sp} = [Hg_2^{2+}]\ [Cl^-]^2$ (24.4)

We need to look for a reaction in which Hg_2Cl_2 takes part and another reaction in which Hg_2^{2+} and Cl^- take part. These reactions are

$Hg_2Cl_2 + 2e^- \rightleftharpoons 2Hg + 2Cl^-$; $E^O = +0.268\ V$

$Hg_2^{2+} + 2e^- \rightleftharpoons 2Hg$; $E^O = 0.789\ V$

Reaction (1) - Reaction (2) gives

$Hg_2Cl_2 \rightleftharpoons Hg_2^{2+} + 2Cl^-$; $E^O = 0.268 - 0.789 = -0.521\ V$

$\triangle G^O = -RT\ /n\ K_{eq} = -nFE^O$, $K_{eq} = [Hg_2^{2+}]\ [Cl^-]^2 / [Hg_2Cl_2]$ (24.5)

$= K_{sp}\ [Hg_2\ Cl_2]$ (24.6)

$= K_{sp}$ as the activity of the solid $[Hg_2Cl_2]$ is taken to be 1. We should be using activities all through. Since the concentrations of most of the ions of these sparingly soluble salts are less than 10^{-4} M, activities have been replaced by concentrations.

$$K_{sp} = \exp [nFE^o / RT] \text{ or } 10^{[nE^o / 0.051T]} = 1.355 \times 10^{-18} \qquad (24.7)$$

24.3 Determination of the pH of a Solution

The electrode reaction in the case of a hydrogen electrode is $H^+ + e^- = \frac{1}{2} H_2$. Nernst eqn. can be used to calculate the electrode potential of a hydrogen electrode.

$$E_H = E^o (SHE) - (0.0591/1) \log P_{H_2}^{1/2} / [H^+] \qquad (24.8)$$

Since $P_{H_2} = 1$ atm and E^o (SHE) = 0, this equation can be written as

$$E_H = 0 - 0.0591 (-\log [H^+] = -0.0591 P_{H_2} \qquad (24.9)$$

A hydrogen electrode (E_H) dipping into a solution of unknown pH is combined with a reference electrode like the saturated calomel electrode (SCE) and its emf is measured.

$$Pt \mid H_2 (1 \text{ atrn}) \mid [H^+] = x \parallel KCl \mid Hg_2Cl_2(s) \mid Hg$$
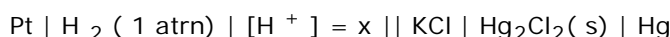
$$E_{cell} = E = E_R - E_L = 0.242 - E_H \qquad (24.10)$$

In the above equation, since E^o is known and the E^o (SCE) is + 0.242V, E_H can be calculated. This value is substituted in Eqn. (24.9) to obtain the pH of the solution. The commercial pH meters make use of a glass electrode - SCE assembly to measure pH. The glass electrode consists of a thin glass bulb of a special quality glass containing a solution of constant pH into which a reference electrode dips. The cell assembly can be represented as

$$Ag \mid AgCl (s) \mid 0.1N \; HCl \mid Glass \mid \text{experimental soln} \parallel Satd \; KCl \mid Hg_2Cl_2 (s) \mid Hg$$

......................glass.electrode...............................(S C E)

The potential of a glass electrode depends on the difference in pH on either side of the glass electrode. Since the solution in the glass electrode has a constant pH, the potential depends on the pH of the experimental solution. Before measuring the pH of a given solution, the glass electrode is immersed in a buffer solution (a solution of a constant pH, e.g., acetic acid and sodium acetate) and the pH meter adjusted so as to read the pH of this buffer solution. After washing and rinsing the glass electrode, it is next immersed in the experimental solution and the pH of the solution is read off from the instrument dial or the digital display of the pH meter. The glass electrode is an example of an ion selective electrode. By making suitable changes in the composition of glass, a glass electrode can be made selective to other cations like Na^+, K^+, NH_4^+, etc. Compacted discs of silver halides, Ag_2S or LaF_3 are found to be selective to the respective anions.

Ag/AgCl

0.1 M HCl (aq)
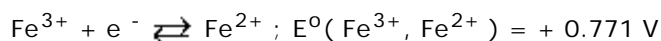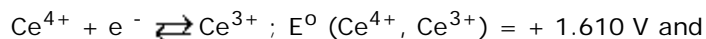
Glass membrane
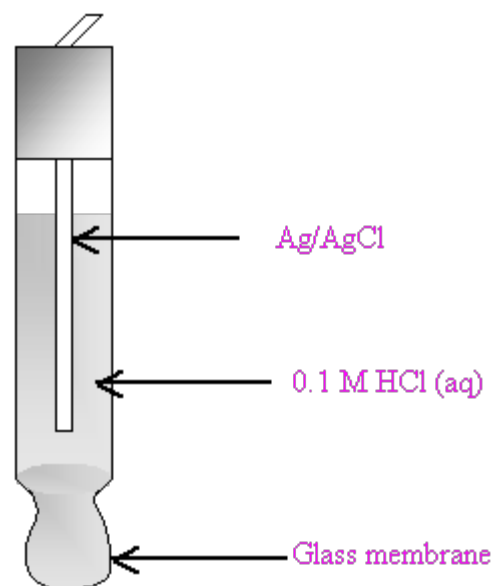
24.4 Potentiometric Titrations

One of the widely used applications of emf measurements is to detect the end point of a titration by measuring the emf of a cell consisting of an indicator electrode (electrode, whose potential depends on the concentration of the reactant ions) and a reference electrode (e.g., SCE) as the titration progresses. This is called a potentiometric titration (varying emf measured during the progress of titration). Since the electrode potential of the reference electrode is constant, the observed change in emf as the reaction progresses, is due to the change in the electrode potential of the indicator electrode.

During acid-base titrations, the pH of the solution changes. By monitoring the change in pH as the titration progresses, it is possible to detect the end point in acid-base titrations using a pH meter. Near the equivalence point, the change in pH is quite large, and at the end point the variation is the largest.

In a redox titration between Fe^{2+} and Ce^{4+}, the overall reaction is

$Ce^{4+} + Fe^{2+} \rightleftarrows Ce^{3+} + Fe^{3+}$
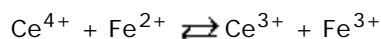
The overall reaction can be described in terms of the two half cell reactions

$Ce^{4+} + e^- \rightleftarrows Ce^{3+}$; E^o (Ce^{4+}, Ce^{3+}) = + 1.610 V and

$Fe^{3+} + e^- \rightleftarrows Fe^{2+}$; E^o(Fe^{3+}, Fe^{2+}) = + 0.771 V

Initially when no Ce^{4+} is added to the system, the potential of the electrode, is determined by the Fe^{3+}, Fe^{2+} couple, it is given by Eqn. (24.11)

$E_{Fe} = E^o_{Fe} - 0.059 \log [Fe^{2+}] / [Fe^{3+}]$ (24.11)

When all the Fe^{2+} has reacted, if a slight excess of Ce^{4+} is added, the potential is characteristic of the Ce^{4+}, Ce^{3+} system and is given by

$E_{Ce} = E^o_{Ce} - 0.059 \log [Ce^{3+}] / [Ce^{4+}]$ (24.12)

The variations in the reduction potential when 100 ml of 0.1N Fe^{2+} is titrated against 0.1N Ce^{4+} are tabulated in the following table (Table 24.1).

By plotting the potential against volume of Ce^{4+} added, Figure 24.1 is obtained. The equivalence point

corresponds to the point of inflection of the curve. A better procedure to obtain the equivalence point is to make use of the fact that the slope of $\triangle E/\triangle V$ is large in the vicinity of the equivalence point. If $\triangle E/\triangle V$ is plotted against V (Figure 24.2), the sharp maximum corresponds to the equivalence point.
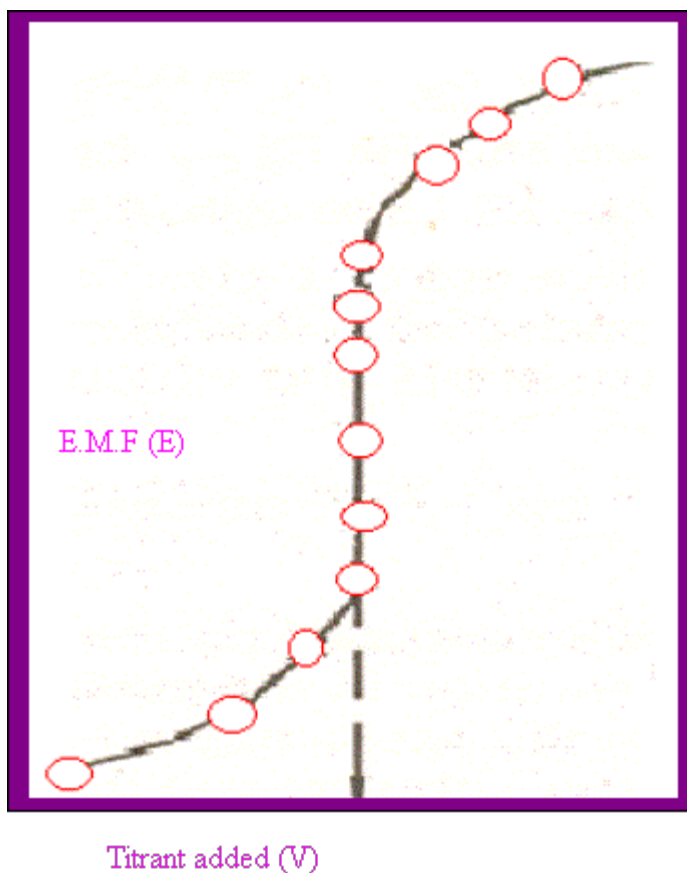

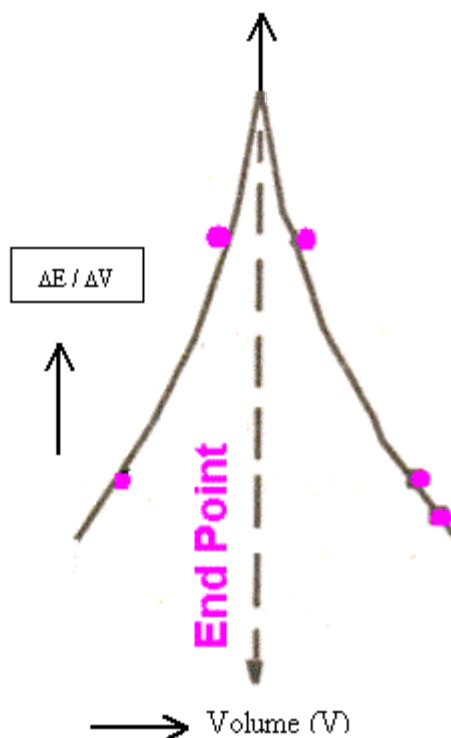**Figure 24.1 : A potentiometric titration curve.**

**Figure 24.2 : Determination of the equivalence point in a potentiometric titration**

Table 24.1 emf as a function of the titrant added in a potentiometric titration.

Vol of Ce^{4+} added	Excess ml of		$[Fe^{2+}]/[Fe^{3+}]$	$[Ce^{3+}]/[Ce^{4+}]$	E in volt	
	Fe^{2+}	Ce^{4+}				
1	99	-	99/1	-	0.771- 0.59 log (99/1)	= 0.652
10	90	-	90 /10	-	0.771- 0.059 log (9)	= 0.715
50	50	-	1			0.771
91	9	-	9/ 91	-	0.771- 0.059 log (9/ 91)	= 0.830
99	1	-	1/ 99	-	0.771- 0.059 log (1/ 99)	= 0.889
99.9	0.1	-	0.1 / 99.9	-	0.771 – 0.059 log (1/999)	= 0.948
100.0	-	-	-	-	Equivalence point	1.19
100.1	-	0.1	-	100 /0.1	1.61-0.059 log (100/0.1)	1.433
101.0	-	1.0	-	100 /1	1.61 – 0.059 log (100/1)	1.492
110.0	-	10.0	-	100/10	1.61 – 0.059 log (10)	1.551
120.0	-	20	-	100/20	1.61- 0.059 log (5)	1.668

It will be seen that the change in potential within 0.1 ml of the equivalence point is quite high. i.e.. 0.485V (1.433 - 0.948)

24.5 Measurement of pK

In the Bronsted – Lowry classification scheme, an acid is a proton donor and a base is a proton acceptor. The dissociation equilibrium of acid HA in water may be written as

$HA (aq) + H_2O (l) \rightleftharpoons H_3O^+ (aq) + A^- (aq)$
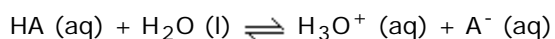
The equilibrium constant (in this case, an ionization constant) K_a is defined as

$K_a = \{a_{H_3O^+} \, a_{A^-} / a_{HA}\}_{aq}$

The activity of water, a_{H_3O} is taken to be unity. The value of pK_a is defined as

$pK_a = - \log_{10} K_a$

A⁻ is called the conjugate base of acid HA.

For a base B which is a proton acceptor, BH^+ is the conjugate acid and equilibria as above can be easily written. For diprotic acids, we can define two equilibria, with the first ionization constant K_{a1} and a second ionization constant K_{a2}. pK_a values measure the strengths of acids . The pK_{a2} value of H_2SO_4 is 1.925. Smaller the pK_a, stronger the acid.

In the acid base titration of a strong acid with strong base, the end point has a pH of 7, at 25°C. For the titration of strong acid with weak base or weak acid with strong base the end point lies at different pH values (other than 7) due to solvolysis (association of solvent molecules with ionic or other species). We need to know the pH of the solution at each stage of titration of say weak acid with strong base to determine the pK_a of the acid. We need to consider the following three criteria.

1) The two equilibria associated with the dissociation of a weak acid are,

$HA(aq) + H_2O (l) \rightleftharpoons A^- (aq) + H_3O^+ (aq)$, and

$2H_2O (l) \rightleftharpoons OH^- (aq) + H_3O^+ (aq)$
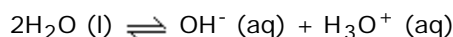
$K_a = [H^+] [A^-] / [HA], K_w = [H^+] [OH^-]$

2) The overall electroneutrality of the solution,

$[H^+] + [M^+] = [A^-] + [OH^-]$

Here MOH is the strong base (fully dissociating) and $[M^+]$ = amount of base added = [MOH] added, and

3) Constant value of the number of A groups (i.e., in HA and the salt MA)

$[HA] + [A^-] = [A] + [S]$

where [A} and [S] are the concentrations of the acid and the salt respectively.

Using the above three points the following relation between $[H^+]$, [A], K_a, K_w (=10^{-14}) and [S] can be derived.

For convenience, we have denoted the concentration of H^+ by [H].
$[H] = [A] / \{ 1+ [H] / K_a\} + K_w / [H] - [S] / \{1 + K_a / [H]\}$
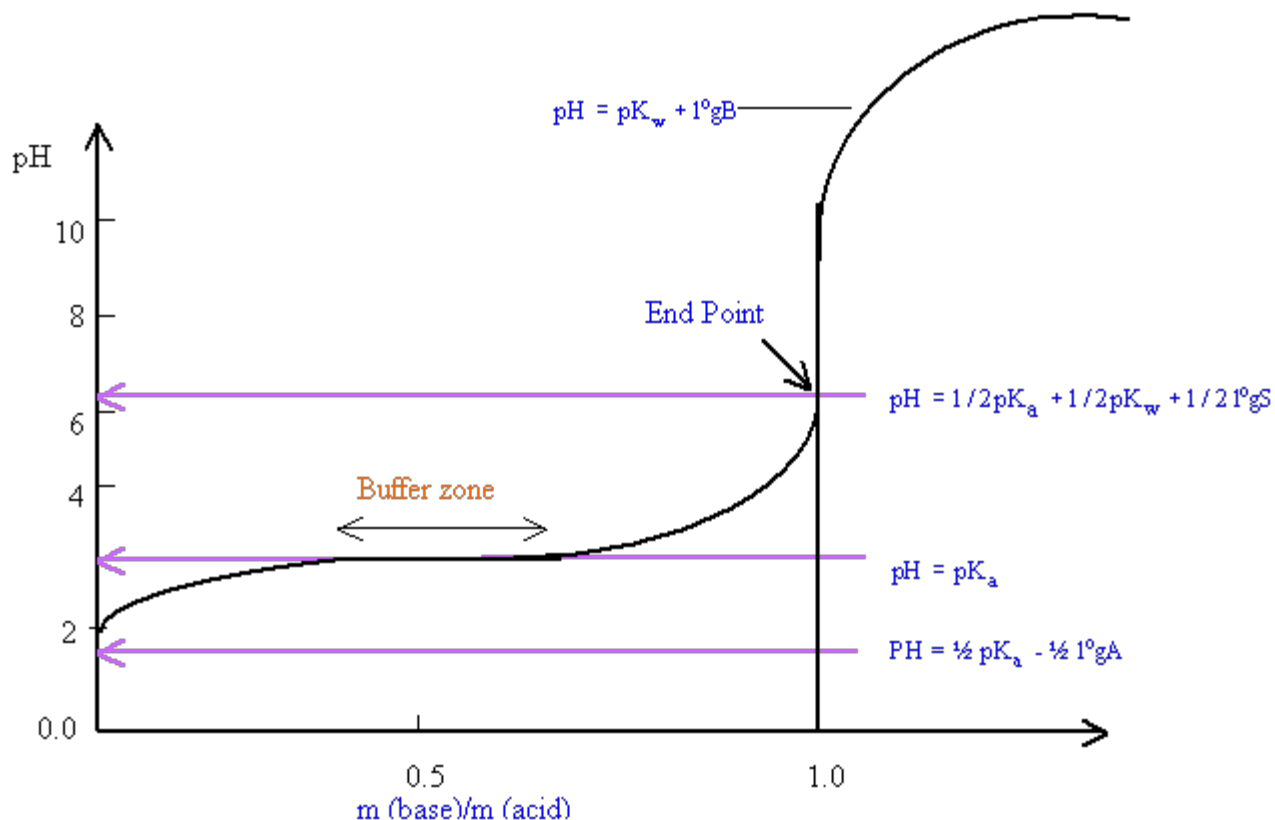
This equation reduces to simpler forms when a) no base is added, b) near the end point of the titration and c) when excess base is added beyond the end point.
a) $pH = \frac{1}{2} pK_a - \frac{1}{2} \log [A]$

b) $pH = \frac{1}{2} pK_a + \frac{1}{2} pK_w + \frac{1}{2} \log [S]$

c) $pH = pK_w + \log [B]$

When the pH hardly changes when the base is added (a region before reaching the end point) the solution is referred to as the buffer solution. In this buffer zone, pH = pK_a. The full titration curve for the titration of a weak acid against a strong base is shown in the following figure (24.3). You can see that pKa can be readily determined from the graph.

24.3 Titration curve for the titration of a weak acid against a strong base i.

Figure labels:
- pH
- $pH = pK_w + 1^\circ gB$
- End Point
- $pH = 1/2 pK_a + 1/2 pK_w + 1/2 1^\circ gS$
- Buffer zone
- $pH = pK_a$
- $PH = \frac{1}{2} pK_a - \frac{1}{2} 1^\circ gA$
- m (base)/m (acid)

24.6 Electrochemical sensors

Sensors are beginning to play an increasingly important role in our daily lives, particularly in chemical, biochemical, optical and mechanical applications. We will comment here on some features of electrochemical and biochemical sensors. Electrochemical sensors employ potentiometric, amperometric and conductometric measurements. Among the major potentiometric sensors are ion selective electrodes and electrodes that depend on the concentration differences in electrolytes (e.g. potentionmetric solid electrolyte sensor).

The ion selective electrodes (ISEs) are sensitive to ions such as Na^+, K^+, Li^+, Ca^{2+}, Cl^-, HS^-, HPO_4^- and pH. Some of them use coated wire electrodes wherein the coating can be an ion selective polymer membrane. These sensors can be miniaturized. In biomedical monitoring (immunosensors) ion selective field effect transistors have been used. Multisensors that are capable of detecting multiple ions use microelectronics. These can be used in vivo. The sensitivity required in these sensors is 10^{-4} V. Some of the techniques that are useful in the development of sensors are cyclic voltametry, linear sweep voltametry, chronoamperometry, chronopotentionmetry and electrochemical impedance spectroscopy. You may read about these from your technical libraries.

24.7 Problems

24.1) What are the galvanic cells that you will set up for measuring the solubility products of $BaSO_4$ AgI, Ag_2CrO_4 an Fe $(OH)_3$. Can you estimate the values of the solubility products?

24.2) During a potentiometric titration such as the one discussed in the present lecture, after the addition of some Ce^{4+}, two equilibria, $Ce^{4+} + e^- \rightleftharpoons Ce^{3+}$ and $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ are present in the solution. Both equilibria are "sensed" at the electrode dipping in the solution. Are the electrode potentials for these two equilibria equal?

24.3) List two examples of reactions that can be studied using potentiometric titrations.

24.4) List the pK_a and pK_b values of 3 to 4 organic acids and bases. Try to rationalise the differences in their pK_a (or pK_b) values in terms of the differences in the bond strengths/reactivities of the functional groups in the molecules.

24.5) List the names of five sensors that are used commonly in daily life. How many of them are electrochemical sensors?

24.6) Which are some common electrodes (other than the Calomel electrode) that can be used as a reference electrode for measuring pH?

24.7) The solubility of AgBr is 1.5×10^{-6} mol/kg at $20^{\circ}C$. What is the emf of the cell Ag | AgBr (aq) | AgBr,Ag at this temperature?

24.8) At $25^{\circ}C$, the cell Pt, H_2(1atm)| HCl (aq) |AgCl, Ag has an emf of 0.332 at $25^{\circ}C$. What is the pH of this solution? If the H_2 | H^+ cell is replaced by a calomel electrode, what would be the resulting emf ?

Recap

In this Lecture you have learnt the following

Summary

Galvanic cells in which the electrode potential of one of the electrodes depends on hydrogen ion concentration, $[H^+]$, form the basis of pH measurements. Commercial pH meters make use of a glass electrode and a reference electrode like the saturated calomel electrode (SCE) to measure pH. Acid-base and redox titrations can be carried out more accurately using potentiometry than by using indicators. Determination of solubility products, pK_a and pK_b has also been described in this lecture. The elcetrochemical basis for the design of sensors has been given. The determination of thermodynamic functions and activities using emf has been illustrated in this and the earlier two lectures.