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 **Application of EMF Measurements**

**i)** Determination of Equilibrium Constant

Measurement of the standard Emf of the cell, E°Cell, enables one to evaluate the equilibrium constant for the electrode reaction.

The relation between the standard free energy change and the equilibrium constant of a reaction is given by:

G0= -RT In K

But the standard free energy is related to the standard electrode potential by the expression:

G0 = -nE0F

 Hence

E0 = In K

At 298K

E0 = log K

Exercise 4

For the following electrochemical cell

Zn/Zn2+//Fe3+,Fe2+/Pt

Whose standard Emf is 1 .534V, the overall cell reaction is

Fe3 + + 1/2Zn  Fe2+ +1/2 Zn2+

**ii) Determination of Solubility Products**

This is a useful technique to evaluate the solubility product of sparingly soluble salt such as AgCI. The saturated solution of AgCl in water is so dilute that it is completely ionized as:

AgCl(s)Ag+(aq)+Cl-(aq)                                                                                        (9)

The solubility product is given by:

Ksp=aAg+ x aC1-                                                                                                 (10)

For solutions of high dilution   and activity may be replaced by concentration. Ksp for AgC1 may be determined from Emf measurements by employing a suitable cell whose overall cell reaction will be that given by eqn 9 above. A suitable cell would be

Ag(s)/Ag+(aq)//Cl-(aq)/AgCI(s)/Ag

Left electrode:                        Ag Ag+ + e                              E0= -0.799V

Right electrode:          AgCI + e  Ag + Cl- E° = +0.2225V

Overall:                       AgCl Ag+ + Cl- E°cell = -0.5765

The cell Emf is given by:

E=E0 - — In aAg+x aCl-

E=E0  - — In Ksp

At equilibrium the cell would not be able to perform any useful work and hence ECell = 0.

We also know that

G0 = -nE0F = -RT In Ksp

or

E0 = In Ksp

At 298K

E°=0.0591 log Ksp

Log Ksp =

Therefore Ksp = 1.76 x 10-10 mol2 dm-6

The solubility of AgCl may be evaluated from the solubility product. Since the concentration of Ag+ equals that of C1, we may write

[Ag+]= [Cl-] = (Ksp)1/2 = (1.76 x 10-10)1/2

Hence the solubility of AgCl is 1.32 x 10-5 mol dm-3

**iii) Determination of pH**

One of the most important applications of Emf measurements is the determination of the pH of solution. In principle, the activity of hydrogen ions or the concentration of hydrogen ions can be determined by setting a cell in which one of the electrodes is reversible to hydrogen ions.

In practice the hydrogen electrode is combined with another reference electrode such as standard hydrogen electrode (SHE) or a saturated calomel electrode (SCE) or any other reference electrode. ..

For the single hydrogen electrode Pt/H2(1atm)/H+, the electrode reaction is

1/2H2H++e

The electrode potential is given by

E=  In aH+                    since *E*° H+/H2 = 0

By definition pH = -log10aH+Hence the above equation becomes

E = + ()pH

At 298K

E=+0.0591pH                                                                                                 (11)

Thus the Emf of the cell is linearly dependent on the pH value of the solution. The hydrogen electrode may be combined with a reference calomel electrode to obtain the cell;

Pt/H2 (1atm)/H+(a1)//Cl-(a2)/Hg2Cl2/ Hg

As seen from above the potential of the hydrogen electrode is given by:

EH2=  In aH+

Since the calomel electrode is a reference electrode its potential will be constant and hence its potential may simply be referred to as reference potential written as E. The Emf of the cell is given by;

Ecell= ER – EL

        = Eref – EH2

 = Eref -0.0591 log aH+

       =Eref + 0.0591 pH

pH =  at 298K                                                                                                 (12)

Thus by measuring the Emf of a cell such as the one given above which has a reference electrode of known potential, the pH of the solution can be determined.

**iv) Determination of Activity Coefficients**

Consider a cell where a silver-silver chloride electrode is combined with a hydrogen electrode to give the following cell:

Pt/H2(1atm)/HCl(m)/AgCl/Ag

The overall cell reaction of the above cell is

1/2H2(g) + AgCl(s) Ag(s) + H+(aq) + Cl-(aq)

The Emf of the cell is:

E =ER –EL =E0Ag/AgCl – E0H+/H2 -                                           (13)

By definition E0H+/H2=0, and aAgCl =1

Also (PH2)1/2= 1 since PH2 =1 atm

Hence

E=E°Ag/AgCl -  In aH+aCl-(14)

The mean activity a± of HCl is defined as:

a±2 =aH+aCl-

and

a± =m+

where ± is the mean activity coefficient

E=E°Ag/AgCl -  In m-In±                                                                  (15)

Directly measurable quantities are rearranged on the left to give:

E + In m= E°Ag/AgCl -  In±                                                                                                                                                                                                                    (16)

At298K

E+0.1181og m=E°Ag/AgCl - 0.1181og±                                                 (17)

By measuring the Emf of the cell at different molalities of hydrochloric acid, the quantity (E+0.1181og m ) can be calculated at various molalities. If we plot(E+0.1181og m ) against m and extrapolate  to zero m, we determine the value of  E° because at zero m± is unity so ln± = 0. Once we know the value of  E°, the mean activity coefficient can be found at a particular value of m.