Electrochemistry - Part 2

Objectives

After going through this lesson, the learners will be able to understand the following:

- Understand the concept of Nernst equation,
- Application of Nernst equation to calculate:
  - the standard electrode potential (E_0anode , E_0cathode),
  - cell EMF of a redox reaction occurring in an electrochemical cell (E_{cell}) ,
  - equilibrium constant (K) and
  - Gibbs free energy in an electrochemical cell reaction (ΔG).

Contents Outline

- Introduction
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Introduction

In the previous module, we learnt about calculating the EMF of a cell based upon its standard reduction potential values. In doing so, it was assumed that the concentration of all the species involved in the electrode reaction is unity. This need not always be true. The moment the two electrodes (anode and cathode) are connected, the concentration of ionic species changes and so the EMF. We require an equation that could calculate the EMF of the cell when ionic species involved have a concentration other than unity. This purpose is satisfied by Nernst Equation.

The Nernst equation has great utility in analytical chemistry as well as in important life processes such as nerve conduction and membrane potential. Electrochemical cells and hence Nernst equation are extensively used for calculating the pH of solutions, solubility product, equilibrium constant and other thermodynamic properties, potentiometric titrations and calculating resting potential of cell membranes. The Nernst equation gives the relation between the electrode potential and the standard electrode potential. Further, it is used to calculate the Gibbs free energy and to predict the spontaneity of an electrochemical reaction. A table of standard half-cell potentials (Table 1) expresses the relative powers of various substances to accept electrons from the reduction half-reaction potential. The module deals with the use of relative absolute potentials for calculating cell potentials.

Table 1 The standard electrode potentials at 298 K

Ions are present as aqueous species and H_2O as liquid; gases and solids are shown by g and s.

	Reaction (Oxidised form + ne^-	$\rightarrow$ Reduced form)		$E^\ominus$/V
Increasing strength of oxidising agent	$F_2(g) + 2e^-$	$\rightarrow 2F^-$	Increasing strength of reducing agent	2.87
	$Co^{3+} + e^-$	$\rightarrow Co^{2+}$		1.81
	$H_2O_2 + 2H^+ + 2e^-$	$\rightarrow 2H_2O$		1.78
	$MnO_4^- + 8H^+ + 5e^-$	$\rightarrow Mn^{2+} + 4H_2O$		1.51
	$Au^{3+} + 3e^-$	$\rightarrow Au(s)$		1.40
	$Cl_2(g) + 2e^-$	$\rightarrow 2Cl^-$		1.36
	$Cr_2O_7^{2-} + 14H^+ + 6e^-$	$\rightarrow 2Cr^{3+} + 7H_2O$		1.33
	$O_2(g) + 4H^+ + 4e^-$	$\rightarrow 2H_2O$		1.23
	$MnO_2(s) + 4H^+ + 2e^-$	$\rightarrow Mn^{2+} + 2H_2O$		1.23
	$Br_2 + 2e^-$	$\rightarrow 2Br^-$		1.09
	$NO_3^- + 4H^+ + 3e^-$	$\rightarrow NO(g) + 2H_2O$		0.97
	$2Hg^{2+} + 2e^-$	$\rightarrow Hg_2^{2+}$		0.92
	$Ag^+ + e^-$	$\rightarrow Ag(s)$		0.80
	$Fe^{3+} + e^-$	$\rightarrow Fe^{2+}$		0.77
	$O_2(g) + 2H^+ + 2e^-$	$\rightarrow H_2O_2$		0.68
	$I_2 + 2e^-$	$\rightarrow 2I^-$		0.54
	$Cu^+ + e^-$	$\rightarrow Cu(s)$		0.52
	$Cu^{2+} + 2e^-$	$\rightarrow Cu(s)$		0.34
	$AgCl(s) + e^-$	$\rightarrow Ag(s) + Cl^-$		0.22
	$AgBr(s) + e^-$	$\rightarrow Ag(s) + Br^-$		0.10
	$2H^+ + 2e^-$	$\rightarrow H_2(g)$		**0.00**
	$Pb^{2+} + 2e^-$	$\rightarrow Pb(s)$		–0.13
	$Sn^{2+} + 2e^-$	$\rightarrow Sn(s)$		–0.14
	$Ni^{2+} + 2e^-$	$\rightarrow Ni(s)$		–0.25
	$Fe^{2+} + 2e^-$	$\rightarrow Fe(s)$		–0.44
	$Cr^{3+} + 3e^-$	$\rightarrow Cr(s)$		–0.74
	$Zn^{2+} + 2e^-$	$\rightarrow Zn(s)$		–0.76
	$2H_2O + 2e^-$	$\rightarrow H_2(g) + 2OH^-(aq)$		–0.83
	$Al^{3+} + 3e^-$	$\rightarrow Al(s)$		–1.66
	$Mg^{2+} + 2e^-$	$\rightarrow Mg(s)$		–2.36
	$Na^+ + e^-$	$\rightarrow Na(s)$		–2.71
	$Ca^{2+} + 2e^-$	$\rightarrow Ca(s)$		–2.87
	$K^+ + e^-$	$\rightarrow K(s)$		–2.93
	$Li^+ + e^-$	$\rightarrow Li(s)$		–3.05

1. A negative $E^\ominus$ means that the redox couple is a stronger reducing agent than the H^+/H_2 couple.
2. A positive $E^\ominus$ means that the redox couple is a weaker reducing agent than the H^+/H_2 couple.

Nernst Equation

Nernst showed that for the electrode reaction:

$M^{n+}(aq) + ne^{-} \rightarrow M(\mathrm{s})$

The electrode potential at any concentration measured with respect to standard hydrogen electrode can be represented by:

$$E_{M^{n+}/M} = E^{0}_{M^{n+}/M} - \frac{RT}{nF} ln \frac{[M]\,(s)}{[M^{n+}]\,(aq)}$$

but concentration of solid M is taken as unity and the above equation can be expressed as:

$$E_{M^{n+}/M} = E^{0}_{M^{n+}/M} - \frac{RT}{nF} ln \frac{1}{[M^{n+}]\,(aq)}$$

$E^{o}_{(Mn+\ /M)}$ has already been defined, R is gas constant (8.314J K^{-1} mol^{-1}), F is Faraday constant (96487 C mol^{-1}), T is temperature in Kelvin and $[M^{n+}]$ is the concentration of the species, M^{n+}.

In Daniel cell, the electrode potential for any given concentration of Cu^{2+} and Zn^{2+} ions, the above equation can be written as:

For Cathode:

$$E_{(cu^{2+}/cu)} = E^{0}_{(cu^{2+}/cu)} - \frac{RT}{2F} ln \frac{1}{[cu^{2+}\,(aq)]}$$

For Anode:

$$E_{(zn^{2+}/zn)} = E^{0}_{(zn^{2+}/zn)} - \frac{RT}{2F} ln \frac{1}{[zn^{2+}\,(aq)]}$$

The cell potential, $E_{cell} = E_{(cu^{2+}/cu)} - E_{(zn^{2+}/zn)}$

$$E_{cell} = E^{0}_{(cu^{2+}/cu)} - \frac{RT}{2F} ln \frac{1}{[cu^{2+}\,(aq)]} - E^{0}_{(zn^{2+}/zn)} + \frac{RT}{2F} ln \frac{1}{[zn^{2+}\,(aq)]}$$

$$E_{cell} = E^{0}_{(cu^{2+}/cu)} - E^{0}_{(zn^{2+}/zn)} - \frac{RT}{2F} \left\{ ln \frac{1}{[cu^{2+}\,(aq)]} - ln \frac{1}{[zn^{2+}\,(aq)]} \right\}$$

$$E_{cell} = E^{0}_{cell} - \frac{RT}{2F} ln \frac{[zn^{2+}]}{[cu^{2+}]}$$

From the above equation it is evident that $E_{(\mathrm{cell})}$ depends on the concentration of both Cu^{2+} and Zn^{2+} ions. It increases with increase in the concentration of Cu^{2+} ions and decrease in the concentration of Zn^{2+} ions. By converting the natural logarithm in above final $E_{(\mathrm{cell})}$ equation, to the base 10 and substituting the values of R, F and T = 298 K, it reduces to:

$$E_{cell} = E^{0}_{cell} - \frac{0.059}{2} \log K_C$$

The same number of electrons (n) for both the electrodes is to be used and thus for the following cell:

$Ni(s) \mid Ni^{2+}(aq) \parallel Ag^{+}(aq) \mid Ag(s)$

The cell reaction is $Ni\,(s) \; + \; 2Ag^{+}\,(aq) \rightarrow Ni^{2+}\,(aq) \; + \; 2Ag(s)$

The Nernst equation can be written as: $E_{cell} = E^{0}_{cell} - \frac{0.059}{2}\, ln\, \frac{[Ni^{2+}]}{[Ag^{+}]^{2}}$

For a general electrochemical reaction of the type: $a\,A + bB \xrightarrow{ne^{-}} cC + dD$

Nernst equation can be written as:

$$E_{cell} = E^{0}_{cell} - ln\, Q$$

$$E_{cell} = E^{0}_{cell} - ln \frac{[C]^{c}\,[D]^{d}}{[A]^{a}\,[B]^{b}}$$

Problem 1: Represent the cell in which the following reaction takes place. Calculate its $E_{(cell)}$ if $E^{0}_{cell} = 3.17$ V. $Mg\,(s) + 2Ag^{+}\,(0.0001M) \rightarrow Mg^{2+}\,(0.130M) + 2Ag\,(s)$,

Solution: The cell notation is: $Mg \mid Mg^{2+}\,(0.130M) \parallel Ag^{+}\,(0.0001M) \mid Ag$

And

$$E_{cell} = E^{0}_{cell} - \frac{RT}{2F}\, ln \frac{[Mg^{2+}]}{[Ag^{+}]^{2}}$$

$$E_{cell} = 3.17 - \frac{RT}{2F}\, ln \frac{[0.130]}{[0.0001]^{2}}$$

$$E_{cell} = 3.17 - \frac{0.059}{2} ln \frac{[0.130]}{[0.0001]^{2}}$$

$$E_{cell} = 3.17\,V - 0.21\,V$$

$$E_{cell} = 2.96\,V$$

Equilibrium Constant from Nernst Equation

$Zn(s)\ +\ Cu^{2+}(aq) \rightarrow Zn^{2+}(aq)\ +\ Cu(s$

If the circuit in Daniell cell (Fig.1) is closed then the reaction takes place as mentioned above and as time passes, the concentration of Zn^{2+} keeps on increasing while the concentration of Cu^{2+} keeps on decreasing. At the same time the voltage of the cell keeps on decreasing. After some time, there is no change in the concentration of Cu^{2+} and Zn^{2+} ions and at the same time, voltmeter gives zero reading. This indicates that equilibrium has been attained.

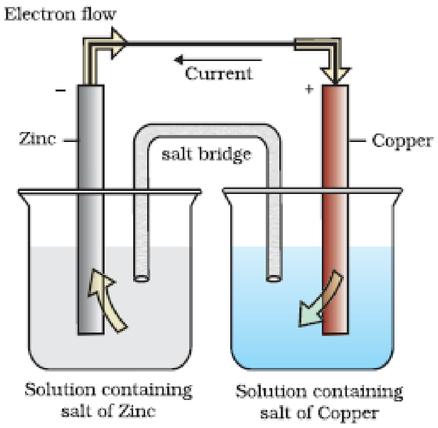


Fig.1: Daniell cell having electrodes of zinc and copper dipping in the solutions of their respective salts.

At equilibrium the Nernst equation may be written as:

$$E_{cell} = 0 = E^{0}_{cell} - \frac{2.303RT}{2F} log \frac{Zn^{2+}}{Cu^{2+} \vee E_{cell} = E^{0}_{cell} - \frac{2.303RT}{2F} log \frac{Zn^{2+}}{Cu^{2+}}}$$

But at equilibrium $\frac{Zn^{2+}}{Cu^{2+}} = K_c$ and at T = 298K the above equation can be written as:

$$E^{0}_{cell} = \frac{0.059}{2} log\ K_c = 1.1\ V \left(E^{0}_{cell} = 1.1V\right)$$

$$log\ K_c = \frac{[1.1V2]}{0.059V} = 37.228, K_c = 210^{37}\ at\ 298\ K$$

In general, $E^{0}_{cell} = \frac{2.303RT}{nF}\ logK_c$

This equation gives a relationship between equilibrium constant of the reaction and standard potential of the cell in which that reaction takes place. Thus, equilibrium constants of the reaction, difficult to measure otherwise, can be calculated from the corresponding E^{o} value of the cell.

Problem 2: Calculate the equilibrium constant of the reaction:

$Cu\,(s)\ +\ 2Ag^{+}(aq) \rightarrow Cu^{2+}(aq)\ +\ 2Ag(s)$ $\qquad E^{0}_{cell} = 0.46\ V$

Solution: $E^{0}_{cell} = \frac{2.303RT}{nF} logK_{c} = 0.46$ V

$log\ K_{c} = \frac{[0.46 \times 2\ V]}{0.059\ V} = 15.6$

$K_{c} = 3.92 \times 10^{15}$

Electrochemical Cell and Gibbs Energy of the Reaction

Electrical work done in one second is equal to electrical potential multiplied by total charge passed. If we want to obtain maximum work from a galvanic cell then charge has to be passed reversibly. The reversible work done by a galvanic cell is equal to decrease in its Gibbs energy and therefore, if the emf of the cell is $E_{(cell)}$ and nF is the amount of charge passed and $\Delta_r G$ is the Gibbs energy of the reaction, then

$$\Delta_{r}G = -nFE_{(cell)}$$

It may be remembered that $E_{(cell)}$ is an intensive parameter but $\Delta_r G$ is an extensive thermodynamic property and the value depends on *n value*. Thus, if we write the reaction

$Zn\,(s)\ +\ Cu^{2+}\,(aq) \rightarrow Zn^{2+}\,(aq)\ +\ Cu\,(s)$ $\qquad \Delta_r G = -2FE_{(cell)}$

but when we write the reaction

$2Zn\,(s)\ +\ 2Cu^{2+}\,(aq) \rightarrow 2\,Zn^{2+}(aq)\ +\ 2Cu\,(s)$ $\qquad \Delta_r G = -4FE_{(cell)}$

If the concentration of all the reacting species is unity, then $E_{(cell)} = E^{o}_{(cell)}$ and we have

$$\Delta_{r}G^{o} = -nFE^{o}_{(cell)}$$

Thus, from the measurement of $E^{o}_{(cell)}$ we can obtain an important thermodynamic quantity, $\Delta_r G^{o}$, standard Gibbs energy of the reaction.

From the latter, we can calculate equilibrium constant by the equation:

$$\Delta_{r}G^{o} = -RT\ lnK$$

Problem 3: The standard electrode potential for Daniel cell is 1.1 V. Calculate the standard Gibbs energy for the reaction:

$$Zn(s)\ +\ Cu^{2+}(aq) \rightarrow Zn^{2+}\,(aq)\ +\ Cu(s)$$

Solution: $\Delta_{r}G^{o} = -nFE^{o}_{(cell)}$

n in the above equation is 2, F = 96487 C mol^{-1} and $E^{o}_{(cell)} = 1.1$ V

Therefore, $\Delta_r G^o = -2 \times 1.1\ \text{V} \times 96487\ \text{C mol}^{-1} = -21227\ \text{J mol}^{-1} = -212.27\ \text{kJ mol}^{-1}$

Problem 4:

Problem For the following cell,

$Cu(s)|Cu^{2+}_{(aq)}||Ag^{+}_{(aq)}|Ag(s)$ at 298 K:

(i) State the cell reaction.

(ii) Give the Nernst equation for the cell.

(iii) Calculate the cell EMF when the ions are present at concentration of

(a) 1.0 M and (b) 0.1 M.

The standard electrode potentials are: $E^0_{Ag|Ag+} = +0.80$ V and $Cu|Cu^{2+} = +0.34$ V

Solution

(i) At cathode we have

$$2Ag^{+}(aq) + 2e^{-} \leftrightharpoons 2Ag(s)$$

At anode we have

$$Cu^{2+}(aq) + 2e^{-} \leftrightharpoons Cu(s)$$

Adding gives the cell reaction

$$2Ag^{+}(aq) + Cu(s) \leftrightharpoons 2Ag(s) + Cu^{2+}(aq)$$

(ii) The Nernst equation for the cell is:

$$E_{(cell)} = E^0_{(cell)} - RT/F\ ln\ [Cu^{2+}]/[Ag^{+}]^2$$

$$E^0_{(cell)} = E^0_{Ag^{+}/Ag} - E^0_{Cu/Cu^{2+}} = 0.80\ \text{V} - 0.34\ \text{V} = 0.46\ \text{V}$$

(iii) Substituting $[Ag^{+}] = [Cu^{2+}] = 1$ in above gives $E_{(cell)} = 0.46$ V

Similarly for $[Ag^{+}] = [Cu^{2+}] = 0.1$ we find $E_{(cell)} = 0.43$ V

Example 5:

A. Calculate the potential of hydrogen electrode in contact with a solution of pH 10.

Solution: Concentration of $[H^{+}]$ of the solution with pH =10 is:

$[H^{+}] = 10^{-pH}$, Therefore $[H^{+}] = 10^{-10}$ Molar

For Hydrogen electrode the reaction is: $H^{+} + e^{-} \rightarrow \frac{1}{2}[H_2]$

The EMF of the cell using a hydrogen electrode can be calculated from Nernst Equation:

$$E_{cell} = E^{0}_{cell} - \frac{0.0591}{n} log \frac{1}{H^{+}}$$

$$E_{cell} = 0 - \frac{0.0591}{n} log \frac{1}{10^{-10}}$$

$$E_{cell} = \frac{-0.0591}{n}(10)$$

$$E_{cell} = \quad - 0.591V$$

The potential of a hydrogen electrode in contact with a solution of pH 10 is – 0.591 V.

B. Calculate the emf of the cell in which the following reaction takes place

$Ni(s) \ + \ 2Ag^{+}\,(0.002\ M) \rightarrow Ni^{2+}\,(0.160\ M) \ + \ 2Ag(s)$ Given that E°$_{(cell)}$ = 1.05 V

Solution: Given:

Concentration of [Ag^{+}] = 0.002 M; Concentration of [Ni^{2+}] = 0.160 M

$n = 2$

E°$_{(cell)}$ = 1.05 V

On Applying the Nernst equation,

$$E_{cell} = E^{0}_{cell} - \frac{0.0591}{n} log \frac{\left[Ni^{2+}\right]}{\left[Ag^{+}\right]^{2}}$$

Substitute the given values and calculate:

$$E_{cell} = 1.05\ V - \frac{0.0591}{2} log \frac{[0.160]}{[0.002]^{2}}$$

$$=1.05\ V - \frac{0.0591}{2} log\left(410^{4}\right)$$

$$= 1.05\ V - 0.02954.6021$$

$$= 1.05\ V - 0.14\ V = 0.91V$$

C. Calculate the standard Gibbs energy and the equilibrium constant of the cell reaction given below:

$$2Fe^{3+}(aq) \ + \ 2I^{-}(aq) \rightarrow 2Fe^{2+}\,(aq) \ + \ I_{2}(s)$$

given E^{o}_{cell} = 0.236 V at 298 K.

Solution: Given: Number of moles involved in the reaction n= 2,

Temperature, T= 298 K and E^{o}_{cell} = 0.236 V

Formula used: $\Delta_{r}G^{o} = -nFE^{o}_{cell}$ (i)

$\Delta_{r}G^{0} = -2.303RT\ \log K_{c}$ (ii)

On substituting the values of n, E^{0}_{cell} and F in (i)

$$\Delta_r G^o = -\ 2 \times 96487 \times 0.236$$

$$\Delta_r G^o = -\ 45541.86\ J\ mol^{-1}$$ (Divide by 1000 to convert into KJ)

$$\Delta_r G^o = -\ 45.54\ kJ\ mol^{-1}$$

Substitute values of R, $\Delta_r G^0$, T in (ii) and solve:

$$= -45541.86\ \mathrm{J\ mol^{-1}} = -2.303 \times 8.314 \times 298 \log K_c$$

$\log K_c = 7.98$

Take antilog on both sides: $K_c = \text{Antilog}\ (7.98)$

$K_c = 9.6 \times 10^7$

Analytical Applications of Nernst Equation

Various areas of Chemistry, either directly or indirectly are concerned with the determination of concentrations of ions in solution. And with the use of the Nernst equation, cell potentials can be measured easily. The Nernst equation relates them to ionic activities rather than to concentrations and the difference between them is negligible in solutions where the total ionic concentration is less than about 10^{-3} M.

Determination of Solubility Products

The Nernst equation can be used with minimum error where the concentrations of ions which are in equilibrium with a sparingly soluble salt are sufficiently low. Instead of directly measuring the concentration of the relevant ions, the more common and easier method would be to set up a cell in which one of the electrodes involves the insoluble salt which has a net cell reaction as just the dissolution of the salt. For example, to determine the *Ksp* for silver chloride, we could use the *silver-silver chloride electrode* in the cell: The question mark represents the concentration of the silver ions in terms of molarity.

$\mathrm{Ag(s)\ |\ Ag^+\ ?\ M\ ||\ Cl^-\ |\ AgC}l\mathrm{\ (s)\ |\ Ag\ (s)}$

$$AgCl\,(s) + e^- \rightarrow Ag\,(s) + Cl^-\,(aq) \qquad E^0 = +0.22\ \mathrm{V}$$

$$\underline{\mathrm{Ag\ (s)} \rightarrow \mathrm{Ag^+\ (aq)} + e^- \qquad E^0 = (+\ 0.799)\ \mathrm{V}}$$

$$AgCl\,(s) \rightarrow Ag^+ + Cl^- \qquad E^0 = 1.019\ \mathrm{V}$$

From the measured value of cell emf, E_{cell}, the concentration of Ag^+ ions can be calculated with the help of Nernst equation and used for calculation of K_{sp}.

Potentiometric Titrations:

In many cases, the accurate determination of an ion concentration by direct measurement of the potential of the cell is not possible, because of the presence of other ions and a lack of information on activity coefficients of these ions. Therefore, in such situations, the concentration of the ions can be determined indirectly by titration with some other ion. For example, the initial concentration of an ion like the Fe^{2+} ion can be found by titration with a strong oxidizing agent like the Ce^{4+} ion containing solution. The titration is carried out in the left half-cell which has a reference electrode in the right half-cell:

$Pt(s) \mid Fe^{2+}, Fe^{3+} \parallel$ reference electrode

Initially the left cell contains only Fe^{2+}. As the titrant Ce^{4+} is added, the ferrous ion is oxidized to Fe^{3+} ions as the reaction comes to a completion:

$Fe^{2+} + Ce^{4+} \parallel Fe^{3+} + Ce^{3+}$

The cell potential is measured as the Ce^{4+} is added in small amounts/drops. The potential of the left half-cell is controlled by the ratio of oxidized and reduced iron ion concentrations according to the Nernst equation:

$$E = 0.68 - 0.059\, log$$

On reaching the equivalence point, the Fe^{2+} are completely consumed (the large equilibrium constant ensures it to be so), and the cell potential is now controlled by concentration ratio of Ce^{3+}/Ce^{4+}. This is based on the concept that *both* species of a redox couple must be present in reasonable amounts so as to let the concentration of the ions in solution to control the potential of an electrode. Considering the actual cell potentials for various concentrations of all these species, the resulting titration curve (Fig. 2) looks like the acid-base titration curve. The end point is calculated by finding the volume of titrant that gives the steepest part of the curve and not by measuring the cell emf/voltage.

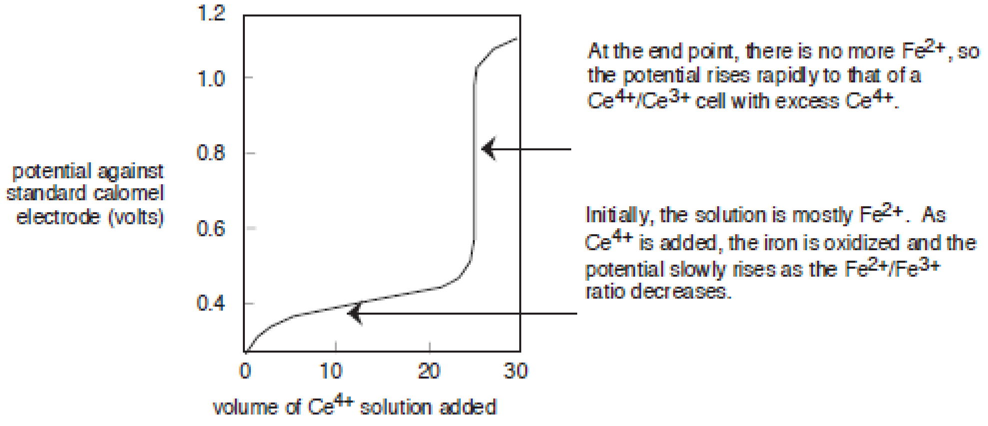


Figure 2: Curve for the potentiometric titration of $FeSO_4$ with $Ce(SO_4)_2$

Measurement of pH:

The pH of a solution is actually defined in terms of hydrogen ion *activity* and not its concentration. A hydrogen electrode allows a direct measure of activity of hydrogen ions (a_{H+}), thus pH = -log a_{H+}. The molarity of H+ ions is represented by a question mark which is also a measure of the concentration of hydrogen ions.

$$H_2(g,\ 1atm)\ |\ Pt\ |\ H^+(?\ M)\ ||\ \text{reference electrode}$$

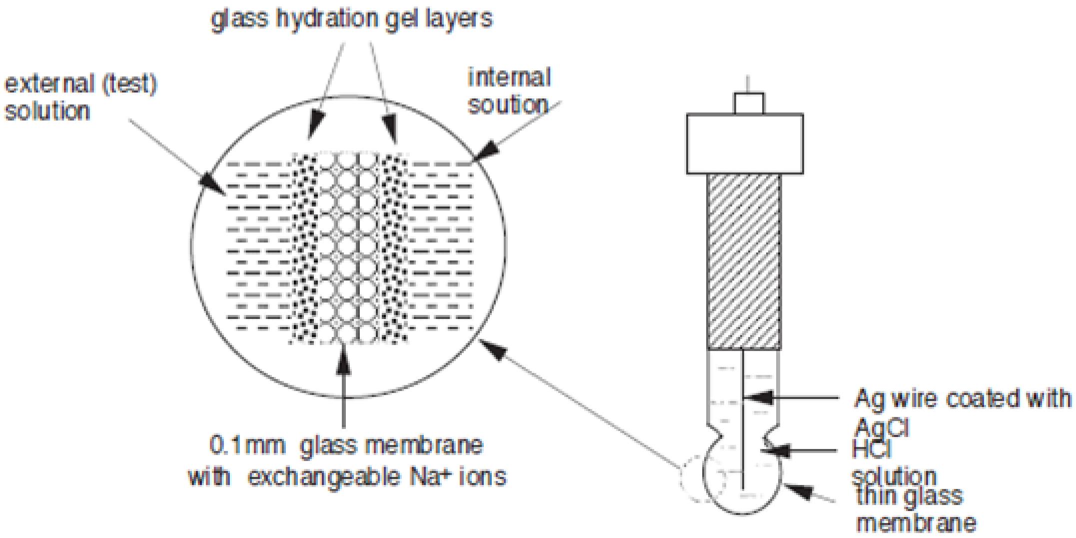


Figure 3 : The glass electrode for pH measurements

This arrangement (in which the reference electrode could be a standard hydrogen electrode) has been used for high-precision, but it would not be practical for routine pH measurements, especially outside the laboratory. The discovery of glass electrodes in

1914 changed everything. This electrode has a solution of HCl enclosed in a thin glass membrane and it can produce a potential that varies with $[H^+]$ in the same way as the hydrogen electrode. Glass electrodes (Fig. 3) since then are manufactured in huge numbers for both laboratory and field use. They contain a built-in Ag-AgCl reference electrode in contact with the HCl solution enclosed in a thin glass membrane. The potential of a glass electrode is given by the Nernst equation in a form very similar to that of an ordinary hydrogen electrode, but without the H_2 gas:

$$E_{membrane} = constant + \frac{RT}{F} ln$$

The reason being that the H+ ions diffuse through the glass and push out a corresponding number of Na^+ ions which are present in most glasses. These sodium ions diffuse to the side of the membrane that has the lower H^+ concentration and remain confined to the surface of the glass, which is porous and gelatinous by nature. The excess charge due to these positive ions gives rise to the pH-dependent potential.

Ion-Selective Electrodes The function of the membrane in the glass electrode is to allow hydrogen ions to pass through and cause a change in potential, while preventing other cations from doing the same thing. Thus, the glass electrode is one form of *ion selective* electrode. Since 1970, various other membranes which show similar selectivity's to certain other ions have been developed. These have wide use in industrial, biochemical, and environmental applications.

Membrane Potentials:

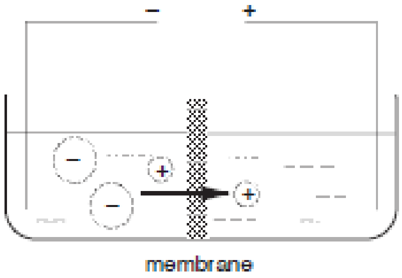
The phenomena of osmosis and osmotic pressure are observed when two solutions having different solute concentrations are separated by a thin film or membrane which has a porosity that allows small ions and molecules to diffuse through and holds back larger particles. If one of the solutions has a pair of oppositely-charged ionic species with large difference in sizes, the smaller ions will pass through the semipermeable membrane but the larger ones will not be able to pass through. This will cause a charge imbalance between the two solutions, with the original solution having the charge sign of the larger ion. Eventually the system settles into an equilibrium state in which a constant potential difference is maintained which is termed as the *membrane potential*. Fig. 4 shows a system containing the potassium salt of a protein on one side of the membrane, and potassium chloride on the other side. The proteinate anion is too large to diffuse through the membrane thus it gets collected on one side giving rise to the potential difference. The membrane potential can be expressed in terms of the ratio of the K^+ or Cl^- ion activities as given below and the potential difference can be determined using the Nernst equation:

$$\Delta\Phi = \frac{RT}{nF} ln$$

The membrane surrounding the living cells contains sites or “channels" which selectively transport K^+ ions so as to maintain 10-30 times the concentration of K^+ ions inside the cell as compared to that in the intracellular fluid. If the activity ratio is taken as 20, the potential difference $\phi_{\text{inside}} - \phi_{\text{outside}}$ as predicted by the equation given below is consistent with the observed values.

$$\Delta\Phi = 0.059 log_{10}\left[\frac{1}{20}\right] = 70\ mV$$

Transport of an ion such as K^+ from a region of low concentration to the region of higher concentrated intercellular fluid requires energy, which is supplied by ATP under enzymatic control. The metabolic processes governing this action are often referred to as “ion pumps".



If the smaller ions are able to diffuse through the membrane but the larger ones cannot, a potential difference will develop between the two solutions. This membrane potential can be observed by introducing a pair of Pt electrodes.

Figure 4: Origin of a membrane potential

Summary

The EMF of a cell under standard conditions can be obtained by taking the difference of the standard reduction potentials of cathode and anode [$E^0_{\text{(cell)}} = E^0_{\text{cathode}} - E^0_{\text{anode}}$]. But Standard Electrode potential values in themselves are not sufficient to calculate the EMF of a cell when ionic species involved have a concentration other than unity.

Concentration dependence of the potentials of the electrodes and the cells are given by Nernst equation. For any reaction of form M^{n+} (aq) + ne^- → M(s) , The electrode potential at any concentration measured with respect to standard hydrogen electrode can be represented by:

$$E_{M^{n+}/M} = E^{0}_{M^{n+}/M} - \frac{RT}{nF} ln\frac{1}{[M^{n+}]\,(aq)}$$

Here concentration of solid M is taken as unity. Nernst equation are extensively used for calculating the pH of solutions, solubility product, equilibrium constant and other thermodynamic properties

The standard potential of the cells are related to standard Gibbs energy

([$\triangle_r G^o = -nFE^o_{(cell)}$] and **equilibrium constant** ($\triangle_r G^o = -RTlnK$) of the reaction taking place in the cell.