

## 1. Details of Module and its structure

Module Detail	
Subject Name	Chemistry
Course Name	Chemistry 03 (Class XII, Semester 01)
Module Name/Title	Electrochemistry: Part 2_Nernst Equation, Equilibrium Constant, Gibbs Energy.
Module Id	lech_10302
Pre-requisites	Knowledge about difference between Galvanic cell & Electrochemical cell, Calculation of electrode potential
Objectives	After going through this module, the learners will be able to: <ol style="list-style-type: none"><li>1. Understand the concept of Nernst equation,</li><li>2. Application of Nernst equation to calculate:<ol style="list-style-type: none"><li>a) the standard electrode potential (<math>E^0_{\text{anode}}</math> , <math>E^0_{\text{cathode}}</math>),</li><li>b) cell EMF of a redox reaction occurring in an electrochemical cell (<math>E_{\text{cell}}</math>) ,</li><li>c) equilibrium constant (<math>K</math>) and</li><li>d) Gibbs free energy in an electrochemical cell reaction (<math>\Delta G</math>).</li></ol></li></ol>
Keywords	Electrochemical cell, Nernst equation, Electrode potential, EMF of a cell, Equilibrium constant, Gibbs free energy.

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### 1. 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 be always 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**

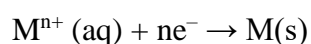
Ions are present as aqueous species and H<sub>2</sub>O as liquid; gases and solids are shown by g and s.

Reaction (Oxidised form + ne <sup>-</sup> → Reduced form)	E <sup>o</sup> /V
F <sub>2</sub> (g) + 2e <sup>-</sup> → 2F <sup>-</sup>	2.87
Co <sup>3+</sup> + e <sup>-</sup> → Co <sup>2+</sup>	1.81
H <sub>2</sub> O <sub>2</sub> + 2H <sup>+</sup> + 2e <sup>-</sup> → 2H <sub>2</sub> O	1.78
MnO <sub>4</sub> <sup>-</sup> + 8H <sup>+</sup> + 5e <sup>-</sup> → Mn <sup>2+</sup> + 4H <sub>2</sub> O	1.51
Au <sup>3+</sup> + 3e <sup>-</sup> → Au(s)	1.40
Cl <sub>2</sub> (g) + 2e <sup>-</sup> → 2Cl <sup>-</sup>	1.36
Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> + 14H <sup>+</sup> + 6e <sup>-</sup> → 2Cr <sup>3+</sup> + 7H <sub>2</sub> O	1.33
O <sub>2</sub> (g) + 4H <sup>+</sup> + 4e <sup>-</sup> → 2H <sub>2</sub> O	1.23
MnO <sub>2</sub> (s) + 4H <sup>+</sup> + 2e <sup>-</sup> → Mn <sup>2+</sup> + 2H <sub>2</sub> O	1.23
Br <sub>2</sub> + 2e <sup>-</sup> → 2Br <sup>-</sup>	1.09
NO <sub>3</sub> <sup>-</sup> + 4H <sup>+</sup> + 3e <sup>-</sup> → NO(g) + 2H <sub>2</sub> O	0.97
2Hg <sup>2+</sup> + 2e <sup>-</sup> → Hg <sub>2</sub> <sup>2+</sup>	0.92
Ag <sup>+</sup> + e <sup>-</sup> → Ag(s)	0.80
Fe <sup>3+</sup> + e <sup>-</sup> → Fe <sup>2+</sup>	0.77
O <sub>2</sub> (g) + 2H <sup>+</sup> + 2e <sup>-</sup> → H <sub>2</sub> O <sub>2</sub>	0.68
I <sub>2</sub> + 2e <sup>-</sup> → 2I <sup>-</sup>	0.54
Cu <sup>+</sup> + e <sup>-</sup> → Cu(s)	0.52
Cu <sup>2+</sup> + 2e <sup>-</sup> → Cu(s)	0.34
AgCl(s) + e <sup>-</sup> → Ag(s) + Cl <sup>-</sup>	0.22
AgBr(s) + e <sup>-</sup> → Ag(s) + Br <sup>-</sup>	0.10
2H <sup>+</sup> + 2e <sup>-</sup> → H <sub>2</sub> (g)	0.00
Pb <sup>2+</sup> + 2e <sup>-</sup> → Pb(s)	-0.13
Sn <sup>2+</sup> + 2e <sup>-</sup> → Sn(s)	-0.14
Ni <sup>2+</sup> + 2e <sup>-</sup> → Ni(s)	-0.25
Fe <sup>2+</sup> + 2e <sup>-</sup> → Fe(s)	-0.44
Cr <sup>3+</sup> + 3e <sup>-</sup> → Cr(s)	-0.74
Zn <sup>2+</sup> + 2e <sup>-</sup> → Zn(s)	-0.76
2H <sub>2</sub> O + 2e <sup>-</sup> → H <sub>2</sub> (g) + 2OH <sup>-</sup> (aq)	-0.83
Al <sup>3+</sup> + 3e <sup>-</sup> → Al(s)	-1.66
Mg <sup>2+</sup> + 2e <sup>-</sup> → Mg(s)	-2.36
Na <sup>+</sup> + e <sup>-</sup> → Na(s)	-2.71
Ca <sup>2+</sup> + 2e <sup>-</sup> → Ca(s)	-2.87
K <sup>+</sup> + e <sup>-</sup> → K(s)	-2.93
Li <sup>+</sup> + e <sup>-</sup> → Li(s)	-3.05

1. A negative E<sup>o</sup> means that the redox couple is a stronger reducing agent than the H<sup>+</sup>/H<sub>2</sub> couple.
2. A positive E<sup>o</sup> means that the redox couple is a weaker reducing agent than the H<sup>+</sup>/H<sub>2</sub> couple.

## 2. Nernst Equation:

Nernst showed that for the electrode reaction:



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

$$E_{\frac{M^{n+}}{M}} = E_{\frac{M^{n+0}}{M}} - \frac{RT}{nF} \ln [M]$$

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

$$E_{\frac{M^{n+}}{M}} = E_{\frac{M^{n+0}}{M}} - \frac{RT}{nF} \ln 1$$

$E^{\circ}_{(M^{n+}/M)}$  has already been defined,  $R$  is gas constant ( $8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ ),  $F$  is Faraday constant ( $96487 \text{ C mol}^{-1}$ ),  $T$  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  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions, the above equation can be written as:

For Cathode:

$$E_{\frac{\text{Cu}^{2+}}{\text{Cu}}} = E_{\frac{\text{Cu}^{2+0}}{\text{Cu}}} - \frac{RT}{2F} \ln 1$$

For Anode:

$$E_{\frac{\text{Zn}^{2+}}{\text{Zn}}} = E_{\frac{\text{Zn}^{2+0}}{\text{Zn}}} - \frac{RT}{2F} \ln 1$$

The cell potential,  $E_{\text{cell}} = E_{\frac{\text{Cu}^{2+}}{\text{Cu}}} - E_{\frac{\text{Zn}^{2+}}{\text{Zn}}}$

$$E_{\text{cell}} = E_{\frac{\text{Cu}^{2+0}}{\text{Cu}}} - \frac{RT}{2F} \ln 1$$

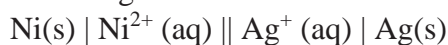
$$E_{\text{cell}} = E_{\frac{\text{Cu}^{2+0}}{\text{Cu}}} - E_{\frac{\text{Zn}^{2+0}}{\text{Zn}}} - \frac{RT}{2F} \ln 1$$

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{RT}{2F} \ln 1$$

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

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.059}{2} \ln$$

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



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

The Nernst equation can be written as:  $E_{cell} = E_{cell}^0 - \frac{0.059}{2} \ln \frac{2+}{}$

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

Nernst equation can be written as:

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

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

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

**Solution:** The cell notation is:  $\text{Mg} | \text{Mg}^{2+} (0.130\text{M}) || \text{Ag}^+ (0.0001\text{M}) | \text{Ag}$

And

$$E_{cell} = E_{cell}^0 - \frac{RT}{2F} \ln$$

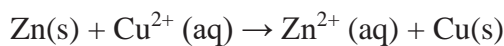
$$E_{cell} = 3.17 - \frac{0.059}{2} \ln$$

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

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

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

### 3. Equilibrium Constant from Nernst Equation:



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  $\text{Zn}^{2+}$  keeps on increasing while the concentration of  $\text{Cu}^{2+}$  keeps on decreasing. At the same time voltage of the cell keeps on decreasing. After some time, there is no change in the concentration of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions and at the same time, voltmeter gives zero reading. This indicates that equilibrium has been attained.

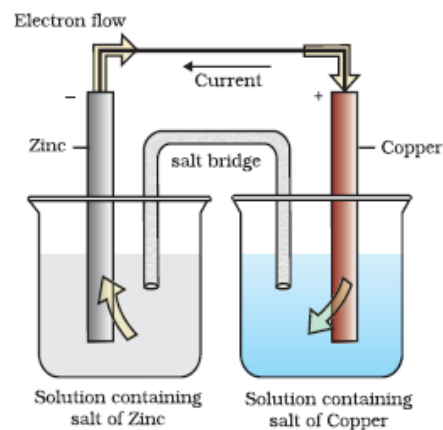


Fig.1: Daniell cell having electrodes of zinc and copper dipping in the solutions of their respective salts.

At equilibrium the Nernst equation may be written as:

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

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

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

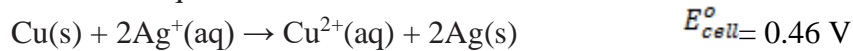
$$E_{cell}^0 = \frac{0.059}{2} \log K_c = 1.1V (E_{cell}^0 = 1.1V)$$

$$\log K_c = \frac{[1.1V \cdot 2]}{0.059V} = 37.228, \wedge K_c = 210^{37} \text{ at } 298K$$

In general,  $E_{cell}^0 = \frac{2.303RT}{nF} \log K_c$

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  $E^0$  value of the cell.

**Problem 2:** Calculate the equilibrium constant of the reaction:



**Solution:**  $E_{cell}^0 = \frac{2.303RT}{nF} \log K_c = 0.46 V$

$$\log K_c = \frac{[0.46V \cdot 2]}{0.059V} = 15.6$$

$$K_c = 3.9210^{15}$$

#### 4. Electrochemical Cell and Gibbs Energy of the Reaction

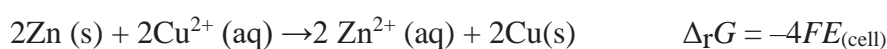
Electrical work done in one second is equal to electrical potential multiplied by total charge passed. If we want to obtain maximum work from a galvanic cell then charge has to be passed reversibly. The reversible work done by a galvanic cell is equal to decrease in its Gibbs energy and therefore, if 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  $n$ . Thus, if we write the reaction



but when we write the reaction



If the concentration of all the reacting species is unity, then  $E_{(cell)} = E_{(cell)}^0$  and we have

$$\Delta_r G^0 = -nFE_{(cell)}^0$$

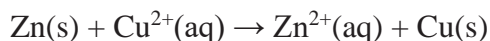
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Thus, from the measurement of  $E^\circ_{(\text{cell})}$  we can obtain an important thermodynamic quantity,  $\Delta_r G^\circ$ , standard Gibbs energy of the reaction.

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

$$\Delta_r G^\circ = -RT \ln K.$$

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



**Solution:**  $\Delta_r G^\circ = -nFE^\circ_{(\text{cell})}$

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

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

#### Problem 4:

Problem For the following cell,

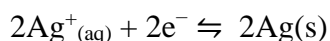
$\text{Cu(s)}|\text{Cu}^{2+}_{(\text{aq})}||\text{Ag}^{+}_{(\text{aq})}|\text{Ag(s)}$  at 298 K:

- (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.

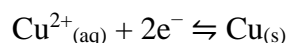
The standard electrode potentials are:  $E^\circ_{\text{Ag}|\text{Ag}^+} = +0.80 \text{ V}$  and  $E^\circ_{\text{Cu}|\text{Cu}^{2+}} = +0.34 \text{ V}$

#### Solution

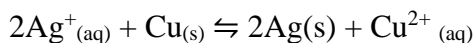
- (i) At cathode we have



At anode we have



Subtracting gives the cell reaction



- (ii) The Nernst equation for the cell is:

$$E_{(\text{cell})} = E^\circ_{(\text{cell})} - \frac{RT}{F} \ln \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2}$$

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

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

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

**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:

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

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:

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

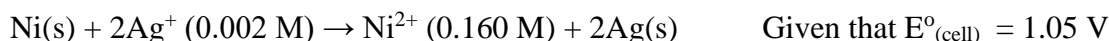
$$E_{cell} = 0 - \frac{0.0591}{n} \log \frac{1}{10^{-10}}$$

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

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

The potential of 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



**Solution:** Given:

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

$$n = 2 \quad E^0_{(cell)} = 1.05 V$$

On Applying the Nernst equation,

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

Substitute the given values and calculate:

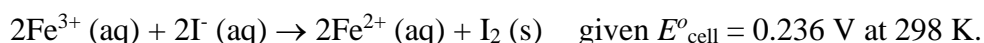
$$E_{cell} = 1.05V - \frac{0.0591}{2} \log \frac{[0.160]}{[0.002]^2}$$

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

$$1.05V - 0.02954.6021$$

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

c) Calculate the standard Gibbs energy and the equilibrium constant of the cell reaction given below:



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

Temperature  $T= 298$  K and  $E^0_{cell} = 0.236$  V

Formula used:  $\Delta_r G^0 = -nFE^0_{cell}$  (i)



$$\Delta_r G^0 = -2.303RT \log K_c \quad (\text{ii})$$

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

$$\Delta_r G^0 = -2 \times 96487 \times 0.236$$

$$\Delta_r G^0 = -45541.86 \text{ J mol}^{-1} \quad (\text{Divide by 1000 to convert into KJ})$$

$$\Delta_r G^0 = -45.54 \text{ kJ mol}^{-1}$$

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

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

$$\log K_c = 7.98$$

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

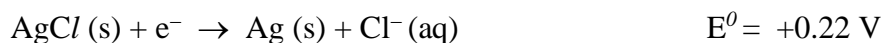
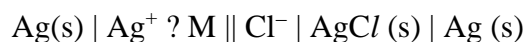
$$K_c = 9.6 \times 10^7$$

## 5. 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  $10^{-3} M$ .

### I. 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  $K_{sp}$  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.

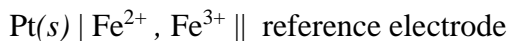


From the measured value of cell emf,  $E_{cell}$ , the concentration of  $\text{Ag}^+$  ions can be calculated with the help of Nernst equation and used for calculation of  $K_{sp}$ .

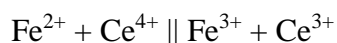
### II. Potentiometric titrations:

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  $\text{Fe}^{2+}$  ion can be found by titration with a strong oxidizing agent like the  $\text{Ce}^{4+}$  ion containing solution. The titration is carried out in the left half-cell which has a reference electrode in the right half-cell:



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



The cell potential is measured as the  $\text{Ce}^{4+}$  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  $\text{Fe}^{2+}$  are completely consumed (the large equilibrium constant ensures it to be so), and the cell potential is now controlled by concentration ratio of  $\text{Ce}^{3+}/\text{Ce}^{4+}$ . 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.

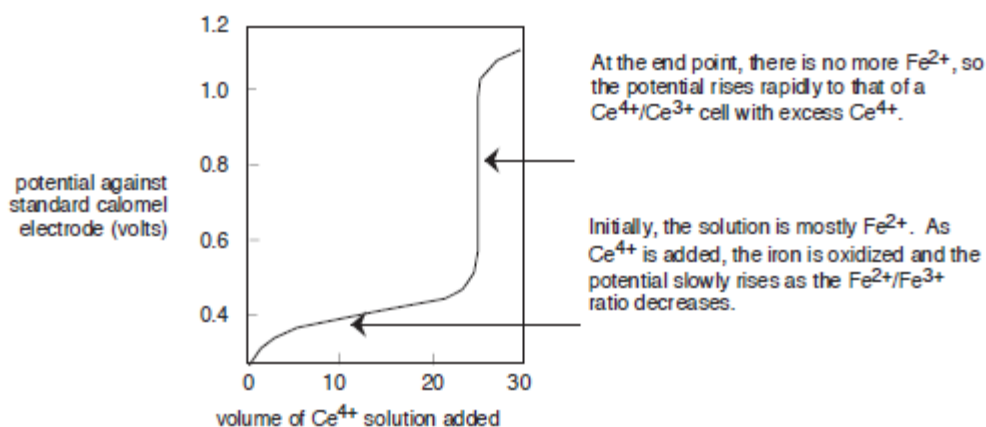


Figure 2: Curve for the potentiometric titration of  $\text{FeSO}_4$  with  $\text{Ce}(\text{SO}_4)_2$

### III. 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

( $a_{\text{H}^+}$ ), thus  $\text{pH} = -\log a_{\text{H}^+}$ . The molarity of  $\text{H}^+$  ions is represented by a question mark which is also a measure of the concentration of hydrogen ions.

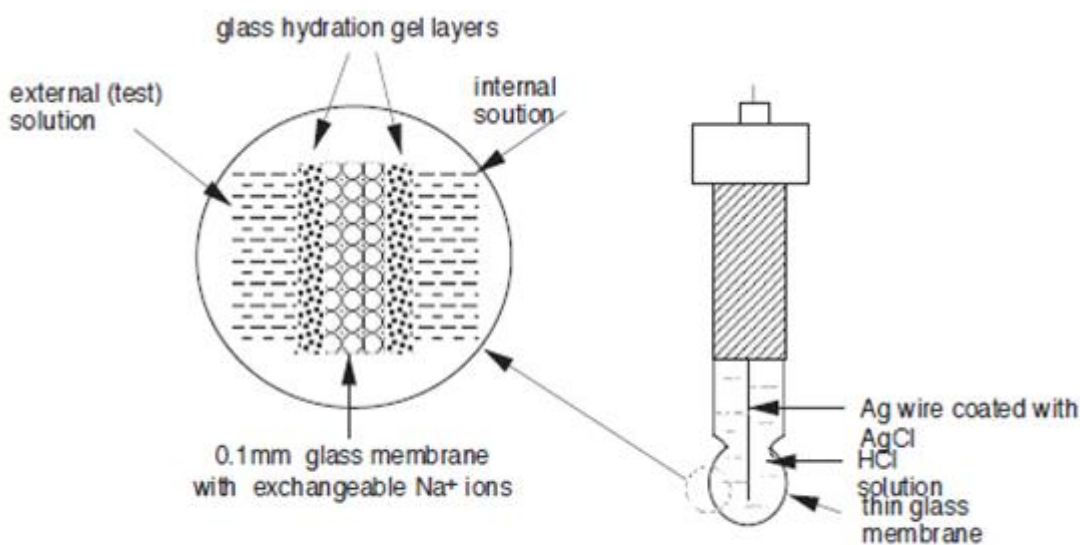
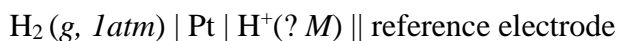


Figure 3 : The glass electrode for pH measurements

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  $[\text{H}^+]$  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  $\text{H}_2$  gas:

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

The reason being that the  $\text{H}^+$  ions diffuse through the glass and push out a corresponding number of  $\text{Na}^+$  ions which are present in most glasses. These sodium ions diffuse to the side of the membrane that has the lower  $\text{H}^+$  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:

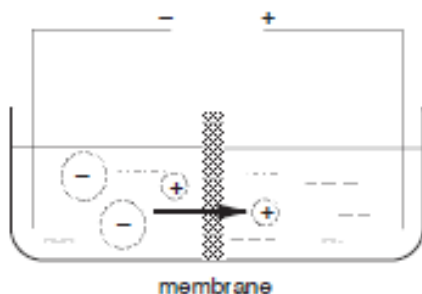
The phenomena of osmosis and osmotic pressure observed when two solutions having different solute concentrations are separated by a thin film or membrane which has a porosity that allows small ions and molecules to diffuse through and holds back larger particles. If one of the solutions has a pair of 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.

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

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

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## 6. 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  $M^{n+}(\text{aq}) + ne^- \rightarrow M(\text{s})$ , The electrode potential at any concentration measured with respect to standard hydrogen electrode can be represented by:  $E_{M^{n+}/M} = E^0_{M^{n+}/M} - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]}$  where 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 ( $[\Delta_r G^0 = -nFE^0_{(\text{cell})}]$ ) and **equilibrium constant** ( $\Delta_r G^0 = -RT \ln K$ ) of the reaction taking place in the cell.