WEST BENGAL STATE UNIVERSITY
SYLLABUS FOR CHEMISTRY (HONOURS) ON ELECTROCHEMISTRY UNDER CHOICE BASED CREDIT SYSTEM
SEM IVH

Electrical Properties of molecules (20 Lectures) Marks: 18

Ionic equilibria: Chemical potential of an ion in solution; Activity and activity coefficients of ions in solution; Debye-Huckel limiting law-brief qualitative description of the postulates involved, qualitative idea of the model, the equation (without derivation) for ion-ion atmosphere interaction potential. Estimation of activity coefficient for electrolytes using Debye-Huckel limiting law; Derivation of mean ionic activity coefficient from the expression of ion-atmosphere interaction potential; Applications of the equation and its limitations

Electromotive Force: Quantitative aspects of Faraday‟s laws of electrolysis, rules of oxidation/reduction of ions based on half-cell potentials, applications of electrolysis in metallurgy and industry; Chemical cells, reversible and irreversible cells with examples; Electromotive force of a cell and its measurement, Nernst equation; Standard electrode (reduction) potential and its application to different kinds of half-cells. Application of EMF measurements in determining (i) free energy, enthalpy and entropy of a cell reaction, (ii) equilibrium constants, and (iii) pH values, using hydrogen, quinone-hydroquinone, glass and SbO/Sb_2O_3 electrodes

Concentration cells with and without transference, liquid junction potential; determination of activity coefficients and transference numbers; Qualitative discussion of potentiometric titrations (acid-base, redox, precipitation)

Books to follow:

- *Maron, S.H., Prutton, C. F., Principles of Physical Chemistry, McMillan*
- *Atkins, P. W. & Paula, J. de Atkins' Physical Chemistry, Oxford University Press*
- *Rakshit, P.C., Physical Chemistry, Sarat Book House*
- *Glasstone, S. An Introduction to Electrochemistry, East-West Press*
- *Castellan, G. W. Physical Chemistry, Narosa*

This course is taught by
Dr. Dipankar Mondal
Assistant Professor, Department of Chemistry,
BKC College, 111/2 B.T. Road, BonHoogly,
Dunlop, Kolkata-700108

Ionic equilibria:-

Chemical Potential:

For a substance "i" in a mixture, the chemical potential is defined as the partial molar Gibbs energy at constant pressure, temperature and other substances held constant except i^{th} component

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$

Proof:

The quantity G is a thermodynamic state function and called as Gibbs free energy can be written as

$$G = H - TS + \sum_j \mu_j n_j$$

where, H is enthalpy, S is entropy, T is temperature and "j" is no of component present in the mixture.

Now, we can write a general infinitesimal change in dG for a system of variable composition as

$$dG = dH - d(TS) + d\left(\sum_j \mu_j n_j\right)$$

$$dG = VdP - SdT + \mu_i dn_i + d\left(\sum_{j\neq i} \mu_j n_j\right)$$

Problem 1: Proof the following identities

$$\mu_J = \left(\frac{\partial U}{\partial n_j}\right)_{S,V,n_{i\neq j}}$$

$$\mu_J = \left(\frac{\partial H}{\partial n_j}\right)_{S,P,n_{i\neq j}}$$

$$\mu_J = \left(\frac{\partial A}{\partial n_j}\right)_{V,T,n_{i\neq j}}$$

When temperature, pressure and the amounts of the other substances held constant except i^{th} component in the mixture, then above equation become

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$

The chemical potential of Ideal and Real gas:

In an Ideal gas there are no forces acting between molecules. For an ideal gas i in an ideal gas mixture, the chemical potential

$$\mu_i = \mu_i^O + RT \ln p_i \qquad (1)$$

where μ_i^O is equal to the chemical potential of the ideal gas at unit partial pressure (1 atm). The value of μ_i, for the ideal gas is the same whether the ideal gas is pure gas at a pressure p_i or is in an ideal gas mixture at p_i partial pressure.

If the gas mixture is not ideal, the equation (1) no longer holds true. Various interaction forces come into operation, and the evaluation of μ_i needs to replace with effective pressure, which can be represented by "fugacity" f_i, therefore, chemical potential of a real gas or a real gas in a real gas mixture is

$$\mu_i = \mu_i^O + RT \ln f_i \qquad (2)$$

The chemical potential of Liquids:

In an Ideal gas there are no forces acting between molecules. But, in ideal solutions there are interactions, but the average energy of A-B interactions in the mixture is the same as the average energy of A-A and B-B interactions in the pure liquids. Now, when a pure liquid or a solution (mixture of liquids) is in equilibrium with its vapor, the chemical potential of any constituent in the liquid must be equal to that in the vapor.

$$\mu_i(vap) = \mu_i(liq) \qquad (3)$$

Now, if the vapor can be regarded as behaving ideally gas, the chemical potential of the constituent i of a solution can be written in the same form as equation (1), where p_i is now the partial pressure of the component "i" in the vapor in equilibrium with the solution. If the vapor is not ideal, " then equation (2) has to use.

Furthermore, according to Raoult’s law the partial vapor pressure of any constituent of an ideal solution is proportional to its mole fraction (x_i) in the solution, and hence it follows that the chemical potential in the liquid is given by

$$\mu_i = \mu_i^O + RT \ln x_i \qquad (4)$$

Thermodynamics of nonideal solutions: the activity Now, If the solution under consideration is not ideal, as is generally the case, especially for solutions of solid electrolytes, equation (3) is not applicable, and it is modified by writing

$$\mu_i = \mu_i^O + RT \ln \gamma_i x_i \qquad (5)$$

where, γ_i is a correction factor known as the activity coefficient of the constituent “i" in the given solution. The product $\gamma_i x_i$ is called the activity of the particular component and is represented by the symbol a_i, so that

$$\mu_i = \mu_i^O + RT \ln a_i \qquad (6)$$

For a system consisting of a solvent, designated by the suffix 1, and a solute, indicated by the suffix 2, the respective chemical potentials are

$$\mu_1 = \mu_1^O + RT \ln \gamma_1 x_1 \qquad (7a)$$

$$\mu_2 = \mu_2^O + RT \ln \gamma_2 x_2 \qquad (7b)$$

It is known that a solution tends towards ideal behavior more closely the greater the dilution; hence, it follows that

$$\gamma_1 \to 1 \; as \; x_1 \to 1 \; and \; \gamma_2 \to 0 \; as \; x_2 \to 0$$

Forms of the Activity Coefficient. The equations given above are satisfactory for representing the behavior of liquid solutes, but for solid solutes, especially electrolytes, a modified form is more convenient.

In a very dilute solution the mole fraction of solute is proportional both to its concentration (c), (moles per liter of solution) and to its molality (m), (moles per 1000 g. of solvent) hence for such solutions, which are known to approach ideal behavior, it is possible to write either

$$\mu = \mu_x^O + RT \ln x$$

$$or \quad \mu = \mu_c^O + RT \ln c_i$$

$$or \quad \mu = \mu_m^O + RT \ln m_i$$

Since solutions of appreciable concentration do not behave ideally, it is necessary to include the appropriate activity coefficients; thus

$$\mu = \mu_x^O + RT \ln a_x; \qquad where\ a_x = x\gamma_x$$

$$or \quad \mu = \mu_c^O + RT \ln a_c; \qquad where\ a_x = c\gamma_c$$

$$or \quad \mu = \mu_m^O + RT \ln a_m; \qquad where\ a_m = m\gamma_m$$

❖ Activities of Electrolytes:

Consider an electrolyte $M_{\nu_+}X_{\nu_-}$, which is ionized as

$$M_{\nu+}X_{\nu-} \rightleftharpoons \nu_+\, M^+ + \nu_-\, X^-$$

to yield the number ν_+ of M^+ ions and ν_- of X^- ions. Chemical potentials of these ions are given by the general equations

$$\mu_+ = \mu_+^O + RT \ln a_+ \qquad (8b)$$

$$\mu_- = \mu_-^O + RT \ln a_- \qquad (8b)$$

where a_+ and a_- are the activities of the ions M^+ and X^- respectively.

If μ_2 is the chemical potential of the undissociated portion of the electrolyte in a given solution and μ_2^O is the value in the standard state, then by the definition,

$$\mu_2^O = \nu_+\mu_+^O + \nu_-\mu_-^O$$

When the system of undissociated molecules and free ions in solution is in equilibrium, a small change at constant temperature and pressure produces no change in the free energy of the system; since one molecule of electrolyte produces ν_+ positive and ν_+ negative ions, it is seen that

$$\mu_2^O + RT \ln a_2 = \nu_+\mu_+ + \nu_-\mu_-$$

$$or \quad \mu_2^O + RT \ln a_2 = \nu_+(\mu_+^O + RT \ln a_+) + \nu_-(\mu_-^O + RT \ln a_-)$$

$$or \quad \mu_2^O + RT \ln a_2 = (\nu_+\mu_+^O + \nu_-\mu_-^O) + (\nu_+ RT \ln a_+ + \nu_- RT \ln a_-)$$

$$RT \ln a_2 = (\nu_+ RT \ln a_+ + \nu_- RT \ln a_-)$$

$$\ln a_2 = \ln {a_+}^{\nu_+}. + \ln {a_-}^{\nu_-})$$

$$a_2 = {a_+}^{\nu_+}.\, {a_-}^{\nu_-}$$

If the total number of ions produced by a molecule of electrolyte, $(\nu_+ + \nu_-)$, is represented by ν, then the mean activity $a_\pm$ of the electrolyte then

$$\nu(\mu_{\pm}^{O} + RT\ln a_{\pm)} = \nu_{+}(\mu_{+}^{O} + RT\ln a_{+}) + \nu_{-}(\mu_{-}^{O} + RT\ln a_{-})$$

$$a_{\pm}^{\nu} = a_{+}{}^{\nu_{+}}.a_{-}{}^{\nu_{-}}$$

Mean ionic activity coefficient, $\gamma_{\pm}$ of an electrolyte is defined by

$$\gamma_{\pm} = (\gamma_{+}{}^{\nu_{+}}.\gamma_{-}{}^{\nu_{-}})^{\frac{1}{\nu}}$$

where, γ_{+} and γ_{-} are ionic activity coefficient of cation and anion respectively.

And can consequently be represented by

$$\gamma_{\pm} = \left(\left(\frac{a_{+}}{m_{+}}\right)^{\nu_{+}}.\left(\frac{a_{-}}{m_{-}}\right)^{\nu_{-}}\right)^{\frac{1}{\nu}}$$

If m_2 is the molality of the electrolyte "i",

Then

$$m_{+} = \nu_{+}m_{2}$$

$$and \quad m_{-} = \nu_{-}m_{2}$$

Therefore,

$$\gamma_{\pm} = \left(\left(\frac{a_{+}}{\nu_{+}m_{2}}\right)^{\nu_{+}}.\left(\frac{a_{-}}{\nu_{-}m_{2}}\right)^{\nu_{-}}\right)^{\frac{1}{\nu}}$$

$$\gamma_{\pm} = \left(\frac{a_{+}^{\nu_{+}}.a_{-}^{\nu_{-}}}{\nu_{+}^{\nu_{+}}.\nu_{-}^{\nu_{-}}}.\frac{1}{m_{2}^{\nu}}\right)^{\frac{1}{\nu}}$$

$$\gamma_{\pm} = \frac{a_{\pm}}{m_{2}}\left(\frac{1}{\nu_{+}^{\nu_{+}}.\nu_{-}^{\nu_{-}}}\right)^{\frac{1}{\nu}}$$

The mean molality $m_{\pm}$ of the electrolyte is defined, in an analogous manner, by

$$m_{\pm} = (m_{+}{}^{\nu_{+}}.m_{-}{}^{\nu_{-}})^{\frac{1}{\nu}}$$

$$m_{\pm} = ((m_{2}\nu_{+})^{\nu_{+}}.(m_{2}\nu_{-})^{\nu_{-}})^{\frac{1}{\nu}}$$

$$m_{\pm} = m_{2}\left(\nu_{+}^{\nu_{+}}.\nu_{-}^{\nu_{-}}\right)^{\frac{1}{\nu}}$$

Now the equation mean ionic activity coefficient can be written as

$$\gamma_{\pm} = \frac{a_{\pm}}{m_{\pm}}$$

❖ Chemical Potential of an Electrolyte which is completely ionized in a solution

The partial molal or molar free energy is an important thermodynamic property in connection with the study of electrolytes; it can be represented either as $\bar{G}$ or by symbol μ, when it is referred as chemical potential.

Now, if a change is made in a system at constant temperature and pressure, by adding n_2 moles of an electrolyte $M_{\nu_+}X_{\nu_-}$, which can completely ionized within n_1 moles of solvent

$$M_{\nu+}X_{\nu-} \rightleftharpoons \nu_+ \; M^+ + \nu_- \; X^-$$

number of moles of cation present in the solution, $n_+ = \nu_+ n_2$
number of moles of anion present in the solution, $n_- = \nu_- n_2$

Here, increase in free energy accompanying a change in a given system at constant temperature and pressure, is

$$(dG)_{T,P} = \sum_j \mu_j dn_j$$

Where j is number of constituent present in the solution

$$(dG)_{T,P} = \mu_1 dn_1 + \mu_+ dn_+ + \mu_- dn_-$$

$$(dG)_{T,P} = \mu_1 dn_1 + \mu_+ \nu_+ dn_2 + \mu_- \nu_+ dn_2$$

$$(dG)_{T,P} = \mu_1 dn_1 + (\mu_+ \nu_+ + \mu_- \nu_-) dn_2$$

Now, partial molar free energy, for the electrolyte present in the system, is defined by

$$\mu_2 = \left(\frac{dG}{dn_2}\right)_{T,P,n_1}$$

Thus, μ_2, chemical potential of the of the electrolyte ($M_{\nu_+}X_{\nu_-}$) in a given solution is

$$\mu_2 = \nu_+ \mu_+ + \nu_- \mu_-$$

$$\mu_2 = \nu_+(\mu_+^O + RT\ln a_+) + \nu_-(\mu_-^O + RT\ln a_-)$$

$$\mu_2 = \nu_+(\mu_+^O + RT\ln m_+\gamma_+) + \nu_-(\mu_-^O + RT\ln m_-\gamma_-)$$

$$\mu_2 = (\nu_+\mu_+^O + \nu_-\mu_-^O) + \ RT\ln(m_+\gamma_+)^{\nu_+} + RT\ln(m_-\gamma_-)^{\nu_-}$$

$$\mu_2 = \mu_2^O + \ RT\ln((m_+\gamma_+)^{\nu_+}.\,(m_-\gamma_-)^{\nu_-})$$

$$\mu_2 = \mu_2^O + \ RT\ln[(m_+{}^{\nu_+}.\,m_-{}^{\nu_-})(\gamma_+{}^{\nu_+}.\,\gamma_-{}^{\nu_-})]$$

$$\mu_2 = \mu_2^O + \ RT\ln\left(m_\pm^\nu\gamma_\pm^\nu\right)$$

$$\mu_2 = \mu_2^O + \ \nu RT\ln m_\pm\gamma_\pm$$

$$\mu_2 = \mu_2^O + \ \nu RT\ln\gamma_\pm + \nu RT\ln m_\pm$$

$$\mu_2 = \mu_2^O + \ \nu RT\ln\gamma_\pm + \nu RT\ln(\nu_\pm m_2)$$

$$\mu_2 = \mu_2^O + \ \nu RT\ln\gamma_\pm + \nu RT\ln\nu_\pm + \nu RT\ln m_2$$

$$\mu_2 = \mu_2^O + \ \nu RT\ln\gamma_\pm + RT\ln\left(\nu_+^{\nu_+}.\,\nu_-^{\nu_-}\right) + \nu RT\ln m_2$$

❖ Debye–Hückel Limiting law

Let mean ionic activity coefficient of an electrolyte ($M_{\nu+}X_{\nu-}$) is $\gamma_{\pm}$

$$M_{\nu+}X_{\nu-} \rightleftharpoons \nu_+ \, M^{Z+} + \nu_- \, X^{Z-}$$

And individual ionic activity coefficient of cation (M^{Z+}) and anion (X^{Z-}) are γ_+ and γ_- respectively.

we introduce the mean activity coefficient as the geometric mean of the individual coefficients, therefore

$$\gamma_{\pm} = \left(\gamma_+^{\nu_+}.\gamma_-^{\nu_-}\right)^{\frac{1}{\nu}}; \qquad where\ \nu = \nu_+ + \nu_-$$

$$\gamma_{\pm}^{\nu} = \left(\gamma_+^{\nu_+}.\gamma_-^{\nu_-}\right)$$

$$\text{or } \ln \gamma_{\pm}^{\nu} = \ln\left(\gamma_+^{\nu_+}.\gamma_-^{\nu_-}\right)$$

$$\text{or } \ \nu \ln \gamma_{\pm} = \nu_+ \ln \gamma_+ + \nu_- \ln \gamma_-$$

$$\text{or } \ln \gamma_{\pm} = \frac{\nu_+ \ln \gamma_+ + \nu_- \ln \gamma_-}{\nu} \qquad (1)$$

From *Debye-Hückel Theory* of Dilute Ionic Solution, Ionic activity coefficient of any ion “i” can be written as

$$\ln \gamma_i = -z_i^2 \left(\frac{e^2 N}{2DRT} \sqrt{\frac{4\pi e^2 N\rho}{D k_B T.1000}}\right) \sqrt{2I} \qquad (2)$$

$$\ln \gamma = -B z_A^2 \sqrt{I} \qquad (3)$$

Where,

$$B = \frac{\sqrt{2}}{DT^{3/2}} \left(\frac{e^2 N}{R} \sqrt{\frac{\pi e^2 N\rho}{k_B.1000}}\right) \qquad (4)\ \ and$$

Z= valency of the ion;

e=charge of an electron ($4.77\times10^{-10}\ e.s.u.$);

N=Avogadro number (6.023×10^{23});

ρ= Density of the solvent (water density is 0.997 at 25^{O}C);

D=Dielectric constant of the medium (78.54);

R=Universal gas constant ($8.31\times10^{7} erg.mole^{-1}K^{-1}$)

k_B=Boltzman constant ($1.38\times10^{-16} erg.K^{-1}$)

T=Temperature (25^{O}C or 298.13 K)

I=Ionic strength ($I = \frac{1}{2}\sum_i m_i z_i^2$)

Now using equation (3) in equation (1), we get

$$\ln \gamma_{\pm} = \frac{\nu_{+}(-Bz_{+}^{2}\sqrt{I}) + \nu_{-}(-Bz_{-}^{2}\sqrt{I})}{\nu}$$

$$\text{or} \quad \ln \gamma_{\pm} = -B\sqrt{I}\left[\frac{\nu_{+}z_{+}^{2} + \nu_{-}z_{-}^{2}}{\nu}\right]$$

$$\text{or} \quad \ln \gamma_{\pm} = -B\sqrt{I}\left[\frac{|\nu_{-}z_{-}z_{+}| + |\nu_{+}z_{+}z_{-}|}{\nu}\right]; as\ |\nu_{+}z_{+}| = |\nu_{-}z_{-}|$$

$$\text{or} \quad \ln \gamma_{\pm} = -B|z_{+}z_{-}|\sqrt{I}\,\frac{|\nu_{-} + \nu_{+}|}{\nu}$$

$$\text{or} \quad \ln \gamma_{\pm} = -B|z_{+}z_{-}|\sqrt{I}\,\frac{|\nu_{-} + \nu_{+}|}{\nu}$$

$$\text{or} \quad \ln \gamma_{\pm} = -B|z_{+}z_{-}|\sqrt{I}$$

$$\text{or} \quad \log_{10} \gamma_{\pm} = -\frac{B}{2.303}|z_{+}z_{-}|\sqrt{I}$$

$$\text{or} \quad \log_{10} \gamma_{\pm} = -A|z_{+}z_{-}|\sqrt{I}$$

At 25^{O} C considering all the parameter in equation (4), the value of A comes out to be 0.509

$$\text{or} \quad \log_{10} \gamma_{\pm} = -0.509|z_{+}z_{-}|\sqrt{I} \approx -0.5|z_{+}z_{-}|\sqrt{I}$$

This equation is often mentioned as the *Debye-Hückel Limiting Law* and it gives the method of calculation of the mean activity coefficient of very dilute solution of an electrolyte.

So, for different type of electrolyte, the mean ionic activity coefficient would be as follows

Electrolyte	$\log_{10} \gamma_{\pm}$
Uni-univalent (NaCl)	$-0.5\sqrt{I}$
Bi-univalent ($MgCl_2$)	$-1.0\sqrt{I}$
Bi-bivalent ($MgSO_4$)	$-1.5\sqrt{I}$

The linear graphs obtained on plotting $\log_{10}\gamma_{\pm}$ vs $\sqrt{I}$ are shown in Figure 1

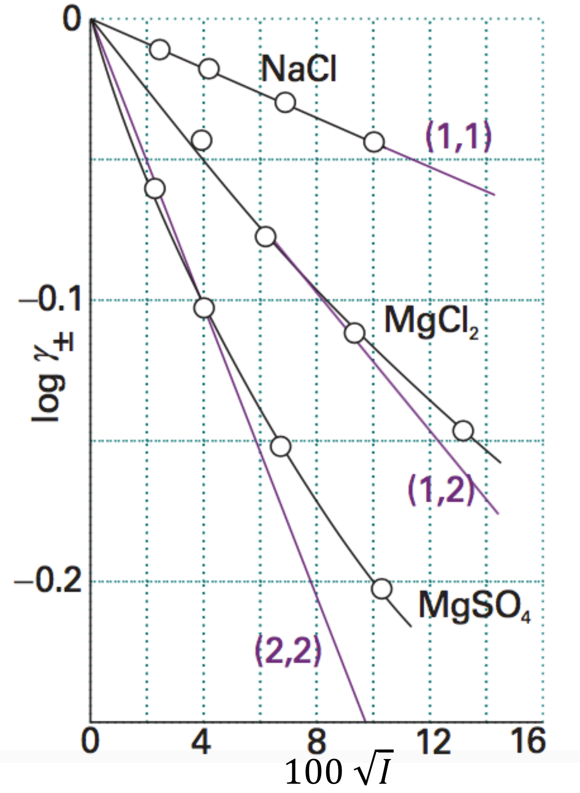


Figure 1: An experimental test of the *Debye–Hückel Limiting Law*. Although there are marked deviations for moderate ionic strengths, the limiting slopes as I → 0 are in good agreement with the theory, so the law can be used for extrapolating data to very low molalities. [*Black sphere and black line is experimental data and violet line is fitted line using Debye–Hückel Limiting Law*]

From the above plot it is evident that when the ionic strength of the solution is too high then *Debye–Hückel Limiting Law* would not be valid any more. Then activity coefficient may be estimated from the extended Debye–Hückel law

❖ Extended Debye–Hückel Law for concentrated Solution

$$\log_{10}\gamma_\pm = \frac{-A|z_+z_-|\sqrt{I}}{1+aB\sqrt{I}} + C\,I$$

$$\text{or}\quad \log_{10}\gamma_\pm = -A|z_+z_-|\sqrt{I}\left(1+aB\sqrt{I}\right)^{-1} + C\,I$$

$$\text{or}\quad \log_{10}\gamma_\pm = -A|z_+z_-|\sqrt{I}\left(1-aB\sqrt{I}\right) + C\,I$$

$$\text{or}\quad \log_{10}\gamma_\pm = (-A|z_+z_-|\sqrt{I}) + (A|z_+z_-|\sqrt{I}.aB\sqrt{I}) + C\,I$$

$$\text{or}\quad \log_{10}\gamma_\pm = \left(-A|z_+z_-|\sqrt{I}\right) + (A|z_+z_-|aB)\,I + C\,I$$

$$\text{or}\quad \log_{10}\gamma_\pm = \left(-A|z_+z_-|\sqrt{I}\right) + I(A|z_+z_-|aB + C)$$

$$\text{or}\quad \log_{10}\gamma_\pm = \left(-A|z_+z_-|\sqrt{I}\right) + C'I$$

where C' is a constant for the given electrolyte, equal to $A|z_+z_-|aB + C$.

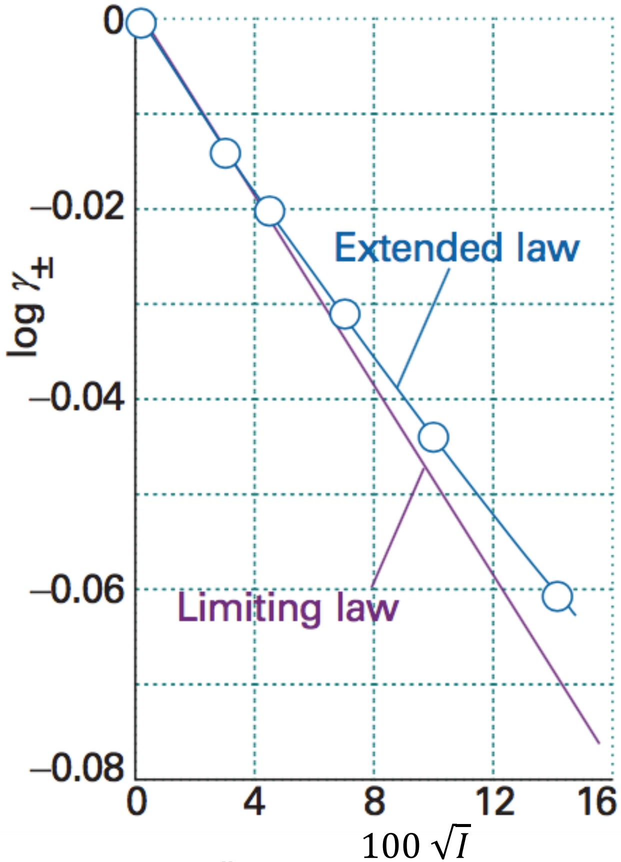


Figure 2: The extended Debye–Hückel law gives agreement with experiment over a wider range of molalities (as shown here for a 1,1-electrolyte), compared to Debye–Hückel Limiting law [*Cyan sphere is experimental data,*

Cyan line is fitted with extended Debye–Hückel law and violet line is fitted line using Debye–Hückel Limiting law].

❖ Relation Between ionic activity coefficient and temperature

$$\ln \gamma_i = -z^2 \left(\frac{e^2 N}{2DRT} \sqrt{\frac{4\pi e^2 N\rho}{Dk_B T.1000}} \right) \sqrt{2I}$$

$$\text{or} \quad \ln \gamma_i = -1.823 \times 10^6 \, z_i^2 \, \frac{\rho^{1/2}}{(DT)^{3/2}} \sqrt{I}$$

For a given electrolyte in a given solvent z_i (valency of cation and anion), ρ(density of the solvent), D(dielectric constant of the medium) and $\sqrt{I}$ (ionic strength of the electrolyte) are constant

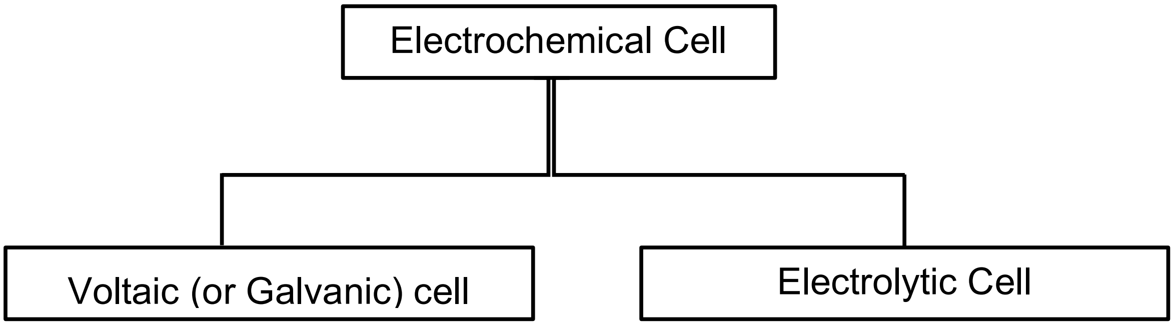
Therefore,

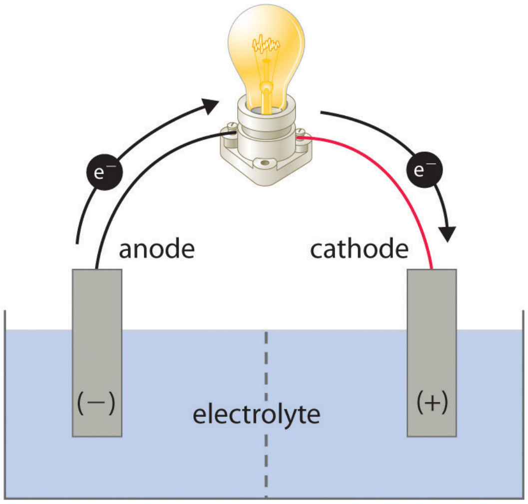
$$\ln \gamma_i \propto \frac{1}{(T)^{3/2}}$$

The above equation indicates that with increase in temperature activity coefficient of any ion will decrease.

❖ Electrochemical Cell:

This is a device in which free energy change due to chemical changes converts to electrical energy.





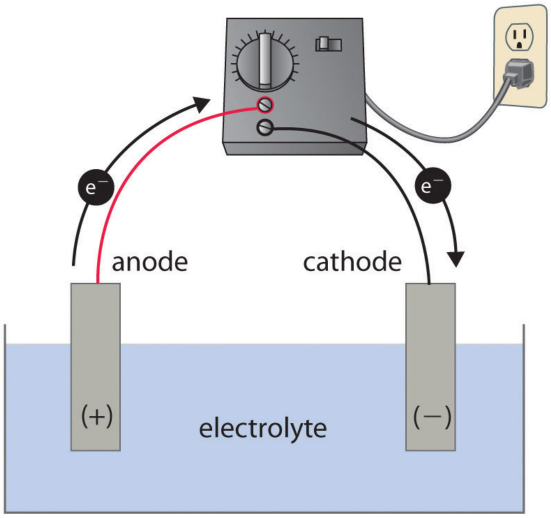
GALVANIC CELL

Energy released by spontaneous redox reaction is converted to electrical energy.

Oxidation half-reaction:
$Y \rightarrow Y^{+} + e^{-}$

Reduction half-reaction:
$Z + e^{-} \rightarrow Z^{-}$

Overall cell reaction:
$Y + Z \rightarrow Y^{+} + Z^{-}$ $(G < 0)$



ELECTROLYTIC CELL

Electrical energy is used to drive nonspontaneous redox reaction.

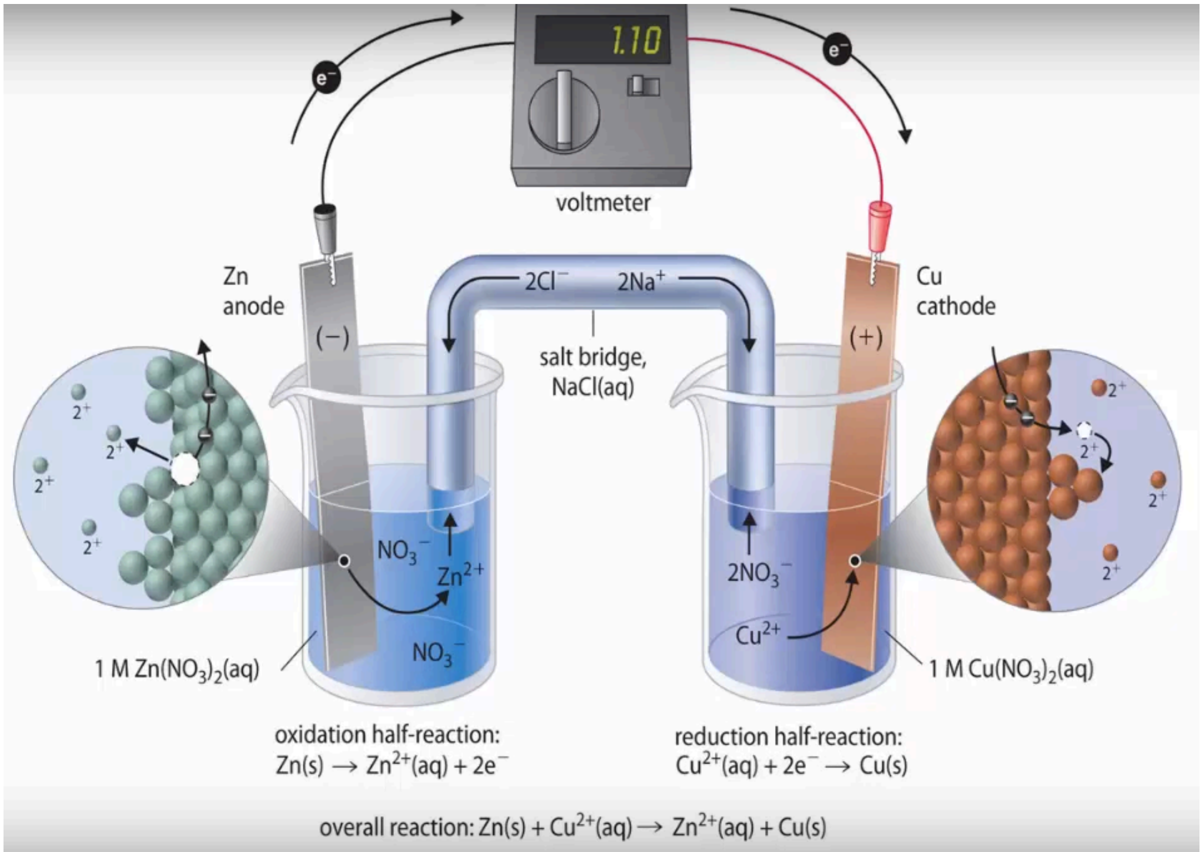
Oxidation half-reaction:
$Z^{-} \rightarrow Z + e^{-}$

Reduction half-reaction:
$Y^{+} + e^{-} \rightarrow Y$

Overall cell reaction:
$Y^{+} + Z^{-} \rightarrow Y + Z$ $(G > 0)$

Reversible cell: Daniel cell is a reversible cell

$$Zn \quad | \quad Zn^{2+}(aq) \quad \| \quad Cu^{2+}(aq) \quad | \quad Cu$$



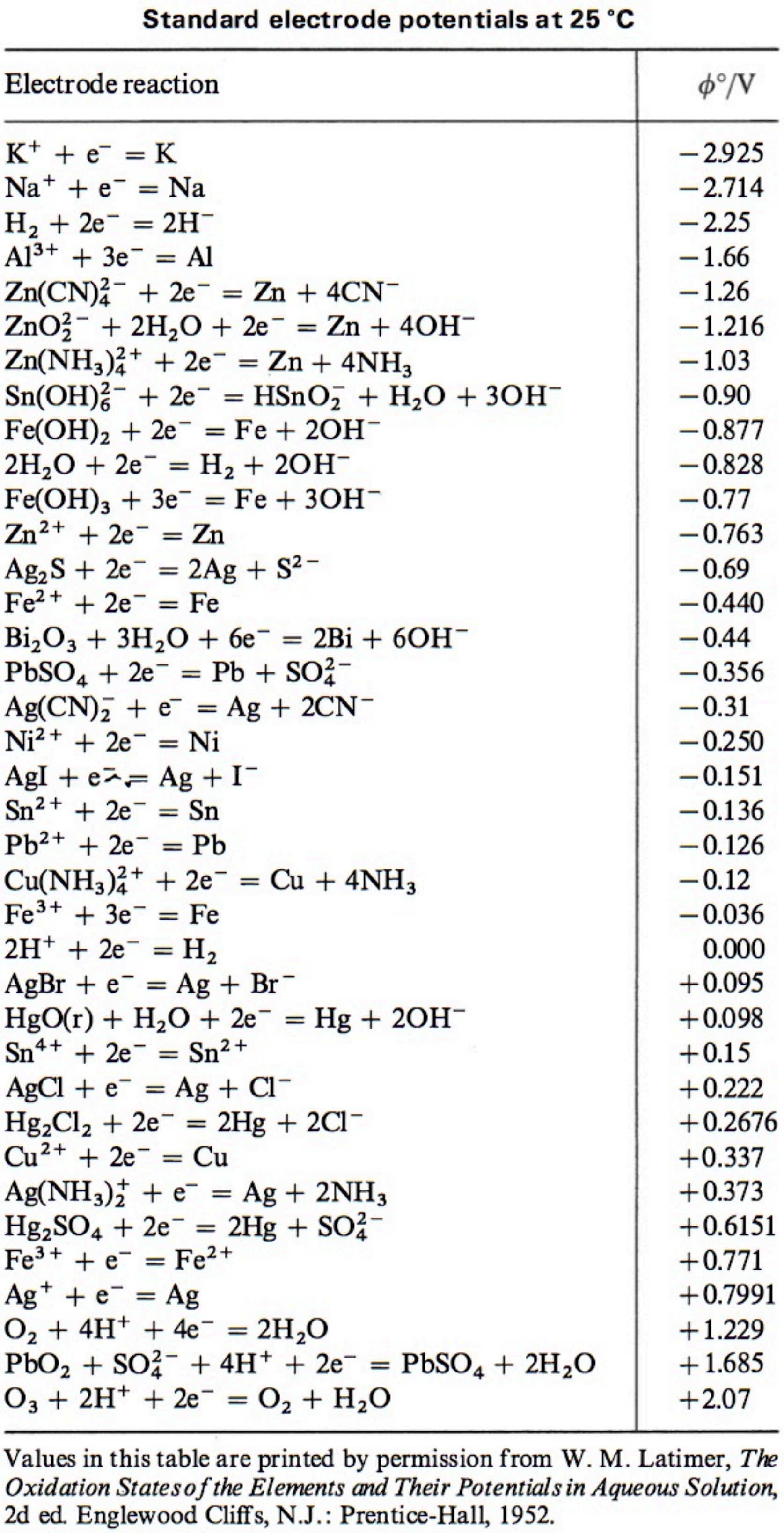
Zn: [Ar]$3d^{10}4s^2$
Cu: [Ar]$3d^{10}4s^1$

Irreversible cell: An example of irreversible cell is consisting of zinc and copper electrodes immersed in dilute sulfuric acid, viz

$$Zn \quad | \quad H_2SO_4 \quad | \quad Cu$$

When electrodes are externally connected by a metallic wire, a current flows from one electrodes to the another and inside the cell chemical changes occur. If 1 Faraday Current is produced, when 1 gm-equivalent Zinc goes into solution and one gm-equivalent hydrogen is liberated at Cu-cathode. If now 1 Farady current is passed through the cell in the opposite direction 1 gm-equivalent of copper goes into solution and 1 gm-equivalent of hydrogen is liberated at the Zn-electrode. The original state is not reproduced, the reaction is also not reversed, this is an irreversible cell.

Standard Reduction potential at 25^{O}C



Standard electrode potentials at 25 °C

Electrode reaction	$\phi°$/V
$K^+ + e^- = K$	−2.925
$Na^+ + e^- = Na$	−2.714
$H_2 + 2e^- = 2H^-$	−2.25
$Al^{3+} + 3e^- = Al$	−1.66
$Zn(CN)_4^{2-} + 2e^- = Zn + 4CN^-$	−1.26
$ZnO_2^{2-} + 2H_2O + 2e^- = Zn + 4OH^-$	−1.216
$Zn(NH_3)_4^{2+} + 2e^- = Zn + 4NH_3$	−1.03
$Sn(OH)_6^{2-} + 2e^- = HSnO_2^- + H_2O + 3OH^-$	−0.90
$Fe(OH)_2 + 2e^- = Fe + 2OH^-$	−0.877
$2H_2O + 2e^- = H_2 + 2OH^-$	−0.828
$Fe(OH)_3 + 3e^- = Fe + 3OH^-$	−0.77
$Zn^{2+} + 2e^- = Zn$	−0.763
$Ag_2S + 2e^- = 2Ag + S^{2-}$	−0.69
$Fe^{2+} + 2e^- = Fe$	−0.440
$Bi_2O_3 + 3H_2O + 6e^- = 2Bi + 6OH^-$	−0.44
$PbSO_4 + 2e^- = Pb + SO_4^{2-}$	−0.356
$Ag(CN)_2^- + e^- = Ag + 2CN^-$	−0.31
$Ni^{2+} + 2e^- = Ni$	−0.250
$AgI + e^- = Ag + I^-$	−0.151
$Sn^{2+} + 2e^- = Sn$	−0.136
$Pb^{2+} + 2e^- = Pb$	−0.126
$Cu(NH_3)_4^{2+} + 2e^- = Cu + 4NH_3$	−0.12
$Fe^{3+} + 3e^- = Fe$	−0.036
$2H^+ + 2e^- = H_2$	0.000
$AgBr + e^- = Ag + Br^-$	+0.095
$HgO(r) + H_2O + 2e^- = Hg + 2OH^-$	+0.098
$Sn^{4+} + 2e^- = Sn^{2+}$	+0.15
$AgCl + e^- = Ag + Cl^-$	+0.222
$Hg_2Cl_2 + 2e^- = 2Hg + 2Cl^-$	+0.2676
$Cu^{2+} + 2e^- = Cu$	+0.337
$Ag(NH_3)_2^+ + e^- = Ag + 2NH_3$	+0.373
$Hg_2SO_4 + 2e^- = 2Hg + SO_4^{2-}$	+0.6151
$Fe^{3+} + e^- = Fe^{2+}$	+0.771
$Ag^+ + e^- = Ag$	+0.7991
$O_2 + 4H^+ + 4e^- = 2H_2O$	+1.229
$PbO_2 + SO_4^{2-} + 4H^+ + 2e^- = PbSO_4 + 2H_2O$	+1.685
$O_3 + 2H^+ + 2e^- = O_2 + H_2O$	+2.07

Values in this table are printed by permission from W. M. Latimer, *The Oxidation States of the Elements and Their Potentials in Aqueous Solution*, 2d ed. Englewood Cliffs, N.J.: Prentice-Hall, 1952.

❖ Gibbs Energy and Cell Potential

Gibb’s free energy,

$$G = H - TS \qquad (1)$$

For free energy change of a system at constant temperature and constant pressure for a process that changes from initial state 1 to final state 2

$$\Delta G = \Delta G_2 - \Delta G_1 \qquad (2)$$

$$\Delta G = (H_2 - TS_2) - (H_1 - TS_1)$$

$$\Delta G = (H_2 - H_1) - T(S_2 - S_1)$$

$$\Delta G = \Delta H - T\Delta S \qquad (3)$$

This is known as Gibbs-Helmholtz equation.

Now, if such processes are preformed at various temperature but constant pressure separately then we can calculate how ΔG varies with respect to temperature.

So to calculate the change of ΔG at constant pressure we will have

$$\left(\frac{\partial \Delta G}{\partial T}\right)_P = \left(\frac{\partial \Delta H}{\partial T}\right)_P - T\left(\frac{\partial \Delta S}{\partial T}\right)_P - \Delta S \qquad (4)$$

However,

$$\left(\frac{\partial \Delta H}{\partial T}\right)_P = \Delta C_P \; and \; \left(\frac{\partial \Delta S}{\partial T}\right)_P = \frac{\Delta C_P}{T}$$

Hence equation (4) becomes

$$\left(\frac{\partial \Delta G}{\partial T}\right)_P = -\Delta S \qquad (5)$$

The relation between the reaction Gibbs energy and the e.m.f. of the cell is $\Delta G = -nFE$ also $\Delta G^O = -nFE^O$ (*for proof see Peter Atkins page 220*), where n is number of electron involved in the half cell reaction and F is eN_A, known as charge per mole of electron, which is 96500 coulomb ().

Hence,

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

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

$$and \qquad \Delta H^O = -nFE^O + nFT\left(\frac{\partial E^O}{\partial T}\right)_P$$

$$-\frac{\Delta H^O}{nF} = E^O - T\left(\frac{\partial E^O}{\partial T}\right)_P \qquad (6)$$

For an electrochemical reaction

$$\alpha A + \beta B \rightleftharpoons \gamma C + \delta D$$

$$\Delta G = \Delta G^O + RT\sum \nu \ln a$$

$$\Delta G = \Delta G^O + RT\; ln\frac{a_C^\gamma a_D^\delta}{a_A^\alpha a_B^\beta}$$

When $a_C = a_D = a_A = a_B = 1$ then $\Delta G = \Delta G^O$

We have $\Delta G = -nFE$ also $\Delta G^O = -nFE^O$

$$-nFE = -nFE^O + RT\; ln\frac{a_C^\gamma a_D^\delta}{a_A^\alpha a_B^\beta}$$

$$E = E^O - \frac{RT}{nF}\; ln\frac{a_C^\gamma a_D^\delta}{a_A^\alpha a_B^\beta} \qquad (7)$$

This is Nernst equation

$$or \quad E = E^O - \frac{RT}{nF}\ln Q\,, where\ Q = \frac{a_C^\gamma a_D^\delta}{a_A^\alpha a_B^\beta}$$

A special case of the Nernst equation has great importance in electrochemistry. Suppose the reaction has reached equilibrium; then $Q = K_{eq}$, where K_{eq} is the equilibrium constant of the cell reaction. However, a chemical reaction at equilibrium cannot do work, and hence it generates zero potential difference between the electrodes of a galvanic cell. Therefore, setting $E = 0$ and $Q = K_{eq}$ in the Nernst equation gives

$$or \quad E^O = \frac{RT}{nF}\ln K_{eq}$$

$$or \quad nFE^O = RT\ln K_{eq} \qquad (8)$$

Different Types of electrodes:

(1) ***Metal/Metal ion electrode*****:** In this type of electrode a metal is in equilibrium with its ions. Such as Zinc rod is dipped into a solution of Zinc sulfate solution. Or Cu rod is dipped into a Copper sulfate solution.

Electrode	Electrode process	*e.m.f.* of the half cell
Zn/Zn^{++}	$Zn \rightleftharpoons Zn^{++} + 2e$	$E = E^{O}_{Zn/Zn^{++}} - \frac{2.303RT}{2F} log \frac{a_{Zn^{++}}}{a_{Zn}}$

As metal electrode are in their pure form therefore their activity is considered as unity. Hence, e.m.f of the cell becomes

$$E = E^{O}_{Zn/Zn^{++}} - \frac{2.303RT}{2F} \log a_{Zn^{++}}$$

Some cases in metal-metal ion electrodes, pure metals are too active so to use them in aqueous solution of their ions, metal electrodes activities are controlled by using amalgamated electrode.

Electrode	Electrode process	*e.m.f.* of the half cell
$Pb\ (Hg)/Pb^{++}(aq)$	$Pb(Hg) \rightleftharpoons Pb^{++} + 2e$	$E_a = E^{O}_{Pb} - \frac{2.303RT}{2F} log \frac{a_{Pb^{++}}}{a_{Pb}}$

where $E^{O}_{Pb/Pb^{++}}$ standard electrode potential of the pure lead electrode. a_{Pb} is activity of the metallic lead in the amalgam, which is not unity in this case. (*For details see Prutton & Maron page 533*)

(2) ***Gas/ion electrode*****:** Gas electrode consist of a gas bubbling about an inert metal wire of foil immersed in a solution containing ions to which the gas is reversible. The function of the metal wire or foil, which is usually is platinized platinum, is to facilitate establishment of equilibrium between the gas and its ions and to serve as the electric contact for the electrode.

Electrode	Electrode process	*e.m.f.* of the half cell
$(Pt)H_2/H^+$	$\frac{1}{2}H_2(g, P_{H_2}) \rightleftharpoons H^+ + e$	$E_{\frac{1}{2}H_2/H^+} = E^{O}_{\frac{1}{2}H_2/H^+} - \frac{2.303RT}{F} log \frac{a_{H^+}}{p_{\frac{1}{2}H_2}}$

But $E^{O}_{\frac{1}{2}H_2/H^+}$ i.e. the e.m.f. of the hydrogen electrode at 1 atmosphere hydrogen pressure and at unit activity of hydrogen ion, is the reference of all e.m.f. measurement, and is taken by definition to be zero at all temperature. Consequently, the above equation becomes

$$E_{\frac{1}{2}H_2/H^+} = -\frac{2.303RT}{F}\log a_{H^+} + \frac{2.303RT}{F}\log p_{\frac{1}{2}H_2}$$

further when the pressure of hydrogen is 1 atmosphere $p_{\frac{1}{2}H_2} = 1$ then

$$E_{\frac{1}{2}H_2/H^+} = -\frac{2.303RT}{F}\log a_{H^+}$$

(3) ***Metal-Sparingly soluble salt/salt ion:*** The common characteristic of such electrodes is that they all consist of a metal in contact with one of its difficulty soluble salts, and a solution containing the ion present in the salt other than the metal. For instance, a silver-silver chloride electrode is composed of a silver wire coated with silver chloride and immersed in a solution of chloride ions (e.g. KCl solution)

Electrode	Electrode process	*e.m.f.* of the half cell
$Ag - AgCl \, / \, Cl^-$	$AgCl + e \rightleftharpoons Ag + Cl^-$	$E_{Ag-Agcl/Cl^-} = E^O_{Ag-AgCl/Cl^-} - \frac{2.303RT}{F} log \frac{a_{Ag}a_{Cl^-}}{a_{AgCl}}$

Since Silver and Silver chloride are in pure solid form therefore their activity is unity. Hence activity of AgCl and Ag do not appear in the equation. Therefore,

$$E_{Ag-Agcl/Cl^-} = E^O_{Ag-AgCl/Cl^-} - \frac{2.303RT}{F}\log a_{Cl^-}$$

(4) ***Oxidation/reduction electrode or Redox couple:*** Although every electrode involves oxidation and reduction, still the term oxidation-reduction electrodes is used to designate electrode in which the e.m.f. results from the presence of ions of a substance in two different stages of oxidation. In this type of electrodes an inert metal is dipping into a solution containing ions in two different oxidation state, e.g. ferric and ferrous ions in the following half cell

Electrode	Electrode process	*e.m.f.* of the half cell
$Pt \mid Fe^{++}, Fe^{+++}$	$Fe^{+++} + e \rightleftharpoons Fe^{++}$	$E_{Fe^{+++}/Fe^{++}} = E^O_{Fe^{+++}/Fe^{++}} - \frac{2.303RT}{F} log \frac{a_{Fe^{++}}}{a_{Fe^{+++}}}$

Since it is the function of the electrodes either to accept electrons from, or to donate electrons to ions in the solution, they are all in a sense oxidation-reduction electrode.

❖ Determination of Standard electrode potential of a cell:

The determination of the standard e.m.f. 's of cells is one of the most important procedure in electrochemistry. We shall illustrate a useful method by means of a typical example.

Consider a cell given below

$$Pt \quad | \quad H_2(g, 1\,atm) \quad | \quad HCl(\boldsymbol{m}) \quad | \quad AgCl - Ag$$

Here a hydrogen electrode and silver-silver chloride electrode are immersed in a solution of hydrochloric acid.

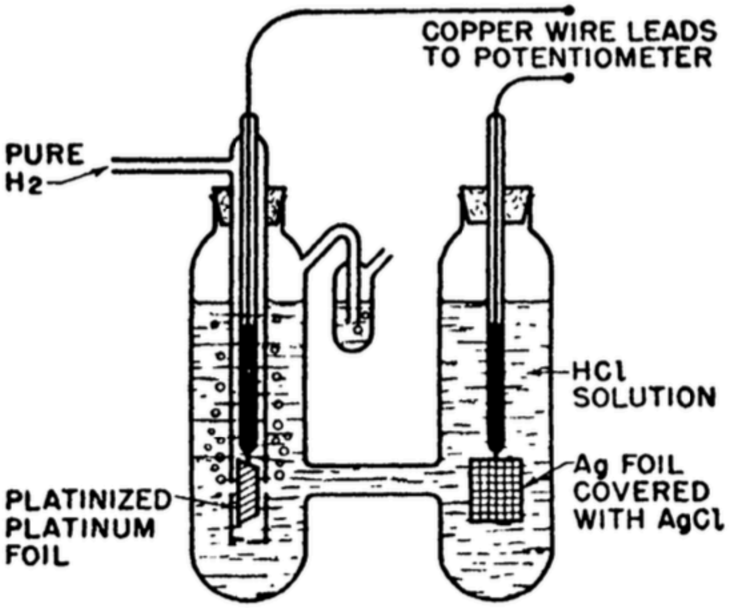


Figure 1. Hydrogen electrode and silver-silver chloride electrode in arrangement for standard e.m.f. determination.

The electrodes reactions are

$$\frac{1}{2}H_2(g) \quad \rightleftharpoons \quad H^+ + e \qquad\qquad at\ anode$$

$$AgCl(s) + e \;\rightleftharpoons\; Ag\ (s) + Cl^- \qquad\qquad at\ cathode$$

The over-all reaction is accordingly

$$AgCl(s) + \frac{1}{2}H_2(g) \quad \rightleftharpoons \quad Ag(s) + H^+ + Cl^-$$

Now, the e.m.f of the above cell can be written as

$$E_{cell} = E_{cathode}(reduction\ potential) - E_{anode}(reduction\ potential)$$

$$or \quad E_{cell} = E_{Agcl/Ag} - E_{H^+/\frac{1}{2}H_2}$$

$$or\ E_{cell} = \left(E^{O}_{AgCl/Ag} - \frac{2.303RT}{F} log \frac{a_{Cl^-} a_{Ag}}{a_{AgCl}}\right) - \left(E^{O}_{H^+/\frac{1}{2}H_2} - \frac{2.303RT}{F} log \frac{p_{H_2}^{1/2}}{a_{H^+}}\right)$$

Setting the activities of the solid phases equal to unity, and choosing the hydrogen pressure so that p_{H_2}= 1 (for ideal gas P 1 atm), we obtain the equation

$$or \quad E_{cell} = \left(E^{O}_{AgCl/Ag} - E^{O}_{H^+/\frac{1}{2}H_2}\right) - \frac{2.303RT}{F} log a_{H^+} a_{Cl^-}$$

$$or \quad E_{cell} = E^{O}_{cell} - \frac{2.303RT}{F} log a_{H^+} a_{Cl^-}$$

Here, $E^{O}_{cell} = E^{O}_{AgCl/Ag} - E^{O}_{H^+/\frac{1}{2}H_2}$

As we are using standard hydrogen electrode therefore, $E^{O}_{H^+/\frac{1}{2}H_2} = 0$

Hence, $E^{O}_{cell} = E^{O}_{AgCl/Ag}$

Now, introducing the mean ionic activity, we have

$$or \quad E_{cell} = E^{O}_{cell} - \frac{2.303RT}{F} log\, m^2 \gamma_{\pm}^2$$

$$or \quad E_{cell} = E^{O}_{cell} - \frac{2 \times 2.303RT}{F} \log m - \frac{2 \times 2.303RT}{F} log\, \gamma_{\pm}$$

According to Debye-Hückel theory, we know

$$\log_{10} \gamma_{\pm} = -A|z_+ z_-|\sqrt{I} + C'I$$

For HCl, $\log_{10} \gamma_{\pm} = -A\sqrt{I} + C'I$

$$or \quad E_{cell} = E^{O}_{cell} - \frac{2 \times 2.303RT}{F} \log m - \frac{2 \times 2.303RT}{F} \left(-A\sqrt{I} + C'I\right)$$

$$or \quad E_{cell} + 2K log\, m - 2KA\sqrt{I} = E^{O}_{cell} - 2KC'I \quad ; K = \frac{2 \times 2.303RT}{F}$$

$$or \quad E'_{cell} = E^{O}_{cell} - 2KC'I \quad ; E'_{cell} = E_{cell} + 2K log\, m - 2KA\sqrt{I}$$

E'_{cell} can be measured at different concentration of HCl (0.01 N to 0.1 N) using potentiometer. Then, the quantity on the left is plotted against ionic strength “I”, we will have a straight line. Then after extrapolated back to m=0, the intercept at m=0 gives the value of standard reduction potential of silver-silver chloride electrode.

❖ Determination of mean activity coefficient ($\gamma_{\pm}$) of an electrolyte:

Let we have HCl solution at m (molal) concentration, whose mean activity coefficient needs to be measured.

$$Pt \quad | \quad H_2(g, 1\,atm) \quad | \quad HCl(\boldsymbol{m}) \quad | \quad AgCl - Ag$$

The cell reaction of the above cell

$$AgCl(s) + e \quad \rightleftharpoons \quad Ag\ (s) + Cl^-$$

$$\frac{1}{2}H_2(g) \quad \rightleftharpoons \quad H^+ + e$$

$$AgCl(s) + \frac{1}{2}H_2(g) \quad \rightleftharpoons \quad Ag(s) + H^+ + Cl^-$$

The e.m.f. of the cell is

$$E_{cell} = E_{cathode}^{reduction} - E_{anode}^{reduction}$$

$$or \qquad E_{cell} = \left(E_{AgCl/Ag,Cl^-}^{O} - E_{H^+/\frac{1}{2}H_2}^{O}\right) - \frac{2.303RT}{F}\log a_{H^+}a_{Cl^-}$$

$$or \qquad E_{cell} = E_{AgCl/Ag,Cl^-}^{O} - \frac{2.303RT}{F}\log\ (m_{H^+}\gamma_{H^+})(m_{Cl^-}\gamma_{Cl^+})$$

$$or \qquad E_{cell} = E_{AgCl/Ag,Cl^-}^{O} - \frac{2.303RT}{F}\log\ m_{H^+}m_{Cl^-} - \frac{2.303RT}{F}\log\ \gamma_{H^+}\gamma_{Cl^-}$$

$$or \qquad E_{cell} = E_{AgCl/Ag,Cl^-}^{O} - \frac{2\times 2.303RT}{F}\log m_{HCl} - \frac{2\times 2.303RT}{F}\log \gamma_{\pm}$$

$$or \qquad E_{cell} + 0.118\log m_{HCl} = E_{AgCl/Ag,Cl^-}^{O} - 0.118\log \gamma_{\pm} \qquad at\ 25^{O}C$$

Now, if we know the standard electrode potential of Ag-AgCl electrode, we can easily elucidate the mean activity coefficient ($\gamma_{\pm}$) by measuring e.m.f. of the cell.

Additionally, this method can be applied to measure the standard electrode potential of the $Ag - AgCl/Cl^-$ half cell.

❖ Determination of ionic product of water (K_W)

The most satisfactory method for determining the ionic product of water makes use of cells without liquid junction, similar to those employed for the evaluation of dissociation constants. The e.m.f. of the cell

$$Pt \quad | \quad H_2(g, 1\,atm) \quad | \; KOH(\boldsymbol{m_1})\ ,\ KCl(\boldsymbol{m_2}) \quad | \quad AgCl - Ag$$

$$or \;\; E_{cell} = \left(E^{O}_{AgCl/Ag,Cl^-} - E^{O}_{H^+/\frac{1}{2}H_2}\right) - \frac{2.303RT}{F}\log a_{H^+}a_{Cl^-}$$

$$or \;\; E_{cell} = E^{O}_{AgCl/Ag,Cl^-} - \frac{2.303RT}{F}\log a_{H^+}a_{Cl^-}$$

Ionic product of water, $K_W = a_{H^+}a_{Cl^-}$, the activity of water being assumed constant, it follows that

$$or \quad E_{cell} = E^{O}_{AgCl/Ag,Cl^-} - \frac{2.303RT}{F}\log\frac{K_W}{a_{OH^-}}a_{Cl^-}$$

$$or \quad E_{cell} = E^{O}_{AgCl/Ag,Cl^-} - \frac{2.303RT}{F}\log K_W - \frac{2.303RT}{F}\log\frac{a_{Cl^-}}{a_{OH^-}}$$

$$or \quad E_{cell} = E^{O}_{AgCl/Ag,Cl^-} - K\log K_W - K\log\frac{m_{Cl^-}}{m_{OH^-}} - K\log\frac{\gamma_{Cl^-}}{\gamma_{OH^-}}$$

and after rearrangement gives,

$$or \quad E_{cell} - E^{O}_{AgCl/Ag,Cl^-} + K\log\frac{m_{Cl^-}}{m_{OH^-}} = -K\log K_W - K\log\frac{\gamma_{Cl^-}}{\gamma_{OH^-}}$$

Debye-Hückel theory,

$$\log\gamma_i = -A\sqrt{I} + C'I$$

$$or \quad \log\frac{\gamma_{Cl^-}}{\gamma_{OH^-}} = (C'_{Cl^-} - C'_{OH^-})I = B'I$$

$$or \quad E_{cell} - E^{O}_{AgCl/Ag,Cl^-} + K\log\frac{m_{Cl^-}}{m_{OH^-}} = -K\log K_W - KB'I$$

$$or \quad \frac{E_{cell} - E^{O}_{AgCl/Ag,Cl^-}}{K} + \log\frac{m_{Cl^-}}{m_{OH^-}} = -\log K_W - B'I$$

$$or \quad \frac{E_{cell} - E^{O}_{AgCl/Ag,Cl^-}}{K} + \log\frac{m_{Cl^-}}{m_{OH^-}} = PK_W - B'I$$

$$or \quad PK'_W = PK_W - B'I$$

The activity coefficient fraction $\gamma_{Cl^-}/\gamma_{OH^-}$ is unity at infinite dilution, and so the value of the right-hand side of above equation becomes equal to $-\log K_W$ under these conditions. It follows therefore, that if the left hand side of this equation , for various concentrations of alkali hydroxide and chloride, is plotted against the ionic strength, the intercept of infinite dilution gives $-\log K_W$.

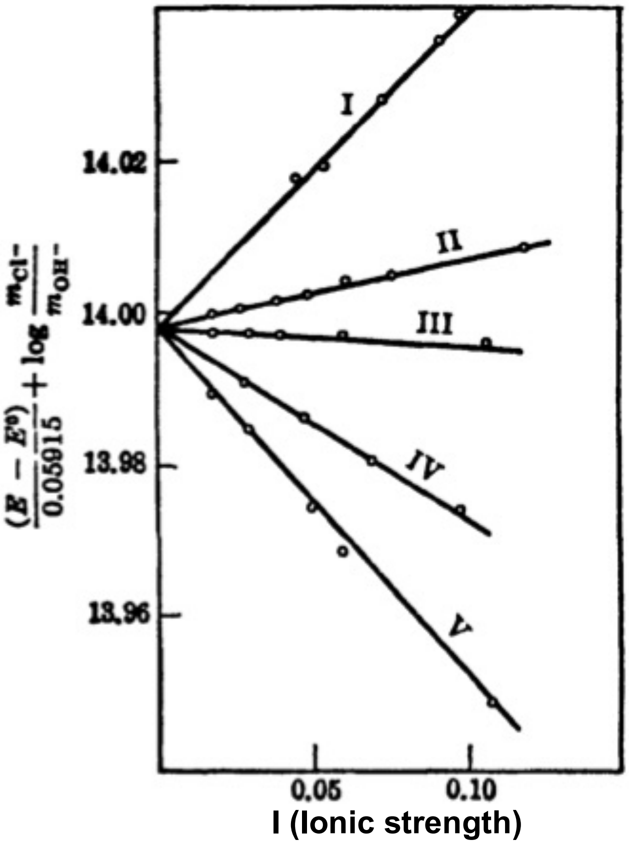


Figure 2: Determination of the ionic product of water (Harned, et al.)

The results shown in Figure 2 are for a series of cells containing cesium (I), potassium (II), sodium (III), barium (IV), and lithium (V) chlorides together with the corresponding hydroxides; the agreement between the values extrapolated to infinite dilution is very striking. The value of $-\log K_W$ is found to be 13.9965 at 25^{O}C, so that $K_W = 1.008 \times 10^{-14}$ (*see S. Glasstone, Introduction to electrochemistry, P-341-342*).

❖ Determination of dissociation constant (K_A) of CH_3COOH:

The evaluation of dissociation constants, can be accurately performed using the cells without liquid junction. The chemical cell reaction occurring in the cell

$$Pt \quad | \; H_2(g, 1\,atm) \; | \; HA\,(\boldsymbol{m_1}), MA(\boldsymbol{m_2}), \mathrm{MCl}\,(\boldsymbol{m_3})| \; AgCl - Ag$$

Where, HA is an acid, whose molality is m_1 in the solution, and MA is its metal salt, of molality m_2, is

$$AgCl(s) + \frac{1}{2}H_2(g) \quad \rightleftharpoons \quad Ag(s) + H^+ + Cl^-$$

for the passage of one Faraday, the *e.m.f.* of the cell is therefore given by

$$or \;\; E_{cell} = E^O_{AgCl/Ag,Cl^-} - \frac{2.303RT}{F}\log a_{H^+}a_{Cl^-}$$

The dissociation constant of the acid HA is

$$K_A = \frac{a_{H^+}a_{A^-}}{a_{HA}} \; as \; HA \rightleftharpoons H^+ + Cl^-$$

$$or \;\; E_{cell} = E^O_{AgCl/Ag,Cl^-} - 0.05915\log\frac{K_A a_{HA} a_{Cl^-}}{a_{A^-}}; \qquad at\; 25^O C$$

$$or \;\; E_{cell} = E^O_{AgCl/Ag,Cl^-} - 0.05915\log K_A - 0.0591\log\frac{a_{HA}a_{Cl^-}}{a_{A^-}}$$

$$or \quad \frac{E_{cell} - E^O_{AgCl/Ag,Cl^-}}{0.05915} = -\log K_A - \log\frac{a_{HA}a_{Cl^-}}{a_{A^-}}$$

$$or \quad \frac{E_{cell} - E^O_{AgCl/Ag,Cl^-}}{0.05915} = -\log K_A - \log\frac{m_{HA}m_{Cl^-}}{m_{A^-}}\frac{\gamma_{HA}\gamma_{Cl^-}}{\gamma_{A^-}}$$

$$or \quad \frac{E_{cell} - E^O_{AgCl/Ag,Cl^-}}{0.05915} + \log\frac{m_{HA}m_{Cl^-}}{m_{A^-}} = -\log K_A - log\frac{\gamma_{HA}\gamma_{Cl^-}}{\gamma_{A^-}}$$

The right hand side of the above equation may be set to $-\log K'_A$, where K'_A becomes identical with K_A at infinite dilution, for then the activity coefficient $\gamma_{HA}\gamma_{Cl^-}/\gamma_{A^-}$ becomes unity and the term $\log\gamma_{HA}\gamma_{Cl^-}/\gamma_{A^-}$ becomes zero.

In dilute solution,

(i) MCl (NaCl) may be assumed to be completely dissociated so that the molality of the chloride ion can be taken as equal to that of MCl (NaCl)., i.e., $m_{Cl^-} = m_3$.

(ii) The acid HA (CH_3COOH) will be partly in the undissociated form and partly dissociated into hydrogen ion and A^- ions.. The stoichiometric molality of HA is m_1, and if m_{H^+} is the molality of the hydrogen ion resulting from the dissociation, the molality of of undiccociated HA molecules in the above equation is $m_{HA} = m_1 - m_{H^+}$.

(iii) Finally, it is required to know m_{A^-}: The A^- ions are produced by the dissociation of MA ($NaOOCCH_3$), which may be assumed to be complete, and also by the small dissociation of the acid HA (CH_3COOH); it follows, therefore, that $m_{A^-} = m_2 + m_{H^+}$

$$or \quad \frac{E_{cell} - E^{O}_{AgCl/Ag,Cl^-}}{0.05915} + \log\frac{(m_1 - m_{H^+})m_3}{(m_2 + m_{H^+})} = -\log K_A - log\frac{\gamma_{HA}\gamma_{Cl^-}}{\gamma_{A^-}}$$

Now if hydrogen ion concentration is known then the values of the left hand side of the equation are plotted against the ionic strength of the solution and extrapolated to infinite dilution, the intercept gives $-\log K_A$, from which the dissociation constant K_A can be readily obtained (*see S. Glasstone, Introduction to electrochemistry, P-313-316*).

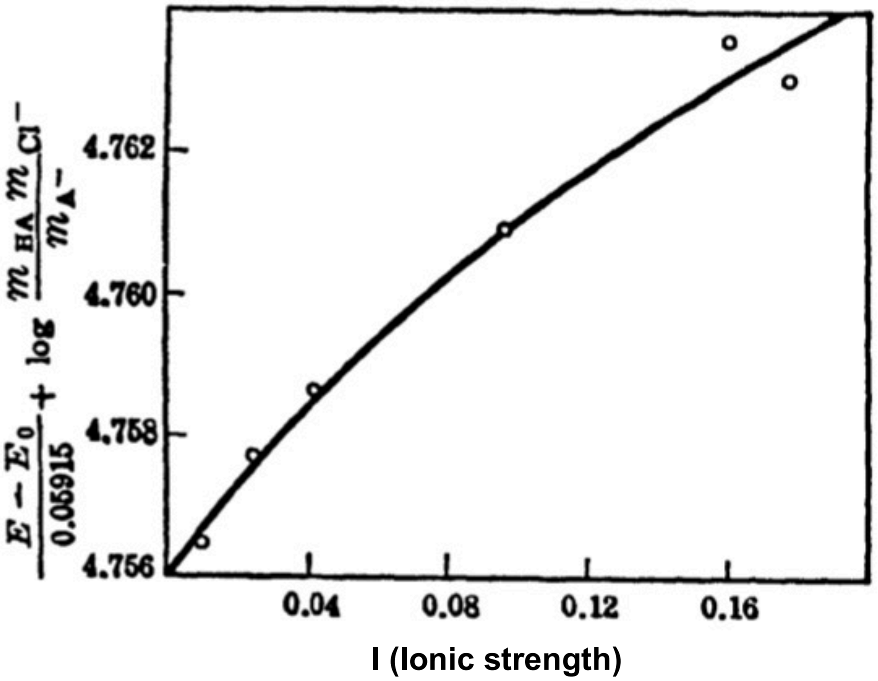


Figure 3: Dissociation constant of acetic acid (Harned and Ehlers)

❖ Determination of pH

(i) By using a Hydrogen electrode

The potential of a hydrogen electrode in contact with a solution of H^+ ion involving the reaction

$$H^+ + e \rightleftharpoons \frac{1}{2}H_2(1\,atm)$$

and

$$E_{H^+/\frac{1}{2}H_2} = E^O_{H^+/\frac{1}{2}H_2} - \frac{2.303RT}{F}\log\frac{p_{H_2}^{1/2}}{a_{H^+}}$$

$$E_{H^+/\frac{1}{2}H_2} = E^O_{H^+/\frac{1}{2}H_2} + \frac{2.303RT}{F}\log[H^+]\ \ for\ dilute\ acid\ concentration$$

As standard electrode potential pf hydrogen electrode is zero, therefore,

$$E_{H^+/\frac{1}{2}H_2} = \frac{2.303RT}{F}\log[H^+]$$

$$E_{H^+/\frac{1}{2}H_2} = -0.0591\,pH \quad at\ 25^O C$$

If is evident from the above equation that potential of hydrogen electrode depends on pH of the solution. So to determine the pH of solution we can make the following complete cell by using a reference electrode.

$$Pt\ |\ H_2(g, 1\,atm)\ |\ HCl(\boldsymbol{unknwon})\ \|\ \mathrm{KCl\ (sat.solution)}, Hg_2Cl_2(\mathrm{s})\ |\ Hg$$

The e.m.f of the cell is determined potentiometrically and that can be written as follows

$$E_{cell} = E^{reduction}_{cathode} - E^{reduction}_{anode}$$

$$E_{cell} = E_{calomel} - E_{H^+/\frac{1}{2}H_2}$$

$$E_{cell} = E_{calomel} + 0.0591\,pH$$

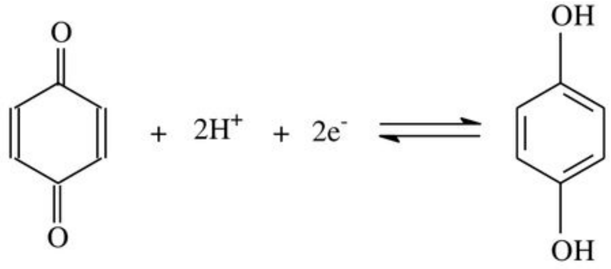
$$pH = \frac{E_{cell} - E_{calomel}}{0.0591}$$

E_{cell} can be obtained from potentiometer, and $E_{calomel}$ is 0.242 volt

Therefore,

$$pH = \frac{E_{cell} - 0.242}{0.0591}\quad at\ 25^O C$$

(ii) By using quinone-hydroquinone



Q = quinone H$_2$Q = hydroquinone

For the reduction reaction given above, the potential developed at the platinum electrode that is immersed in the system is given by the Nernst equation

$$E_{Q/QH_2} = E^{O}_{Q/QH_2} - \frac{2.303RT}{2F}\log\frac{a_{QH_2}}{a_Q . a^2_{H^+}}$$

$$or \quad E_{Q/QH_2} = E^{O}_{Q/QH_2} - \frac{2.303RT}{2F}\log\frac{a_{QH_2}}{a_Q} + \frac{2.303RT}{2F} log a^2_{H^+}$$

In such electrode instead of taking quinone (Q) and hydroquinone (QH$_2$), a small amount of quinohydrone is taken, which is equimolar mixture of quinone and hydroquinone. Since the QH$_2$ is a weak acid therefore, it's ionization is very small if the pH of the solution is less than 7. Therefore, the concentration of hydroquinone is as same as quinone. Thus, the quantity $\frac{a_{QH2}}{a_Q}$ is unity.

So,

$$E_{Q/QH_2} = E^{O}_{Q/QH_2} + \frac{2.303RT}{2F} log a^2_{H^+}$$

$$E_{Q/QH_2} = E^{O}_{Q/QH_2} - \frac{2.303RT}{F} pH$$

$$E_{Q/QH_2} = 0.6996 - 0.0591\, pH \;\; at\ 25^{O}C$$

If is evident from the above equation that potential of quinohydrone electrode depends on pH of the solution. So to determine the pH of solution we can make the following complete cell by using a reference electrode

$$Pt\ |Hg|\ Hg_2Cl_2(\mathrm{s})\ |\ \mathrm{KCl\ (sat.\,soln.)}\ ||\ HCl(\textbf{unknwon}), \mathrm{Sat.\,with\ quinohydrone}\ |\ pt$$

The e.m.f of the above cell is determined potentiometrically and that can be written as follows

$$E_{cell} = E_{Q/QH_2} - E_{SCE}; SCE: Standard\ calomel\ electrode$$

$$or \quad E_{cell} = E^{O}_{Q/QH_2} - \frac{2.303RT}{F} pH - E_{SCE}$$

$$or \quad pH = \frac{E^{O}_{Q/QH_2} - E_{SCE} - E_{cell}}{0.0591} \quad at\ 25^{O}C$$

$$or \quad pH = \frac{0.6996 - 0.242 - E_{cell}}{0.0591} \quad at\ 25^{O}C$$

(iii) By using Glass electrode

Fritz Haber and Z. Klemensiewicz first showed that, when two solution of different pH are separated by a glass membrane, a potential is established across the membrane, whose magnitude depends on the difference in pH of the two solutions. Since then it has been found that when the pH of one of these solutions is held constant while that of the second is varied, the e.m.f. of the glass electrode follows the equation

$$E_{Glass} = E^{O}_{Glass} - \frac{2.303RT}{F} \log a_{H^+}$$

$$E_{Glass} = E^{O}_{Glass} + 0.0591pH \quad at\ 25^{O}C$$

The glass electrode is immersed directly into the solution whose pH to be determined, consists of a thin bulb constructed usually of a special glass (Corning 015 glass composed of 72% silica, 22% sodium monoxide, 6% calcium oxide). On the inside of this bulb is placed a 0.1 N HCl and Silver-Silver Chloride electrode. The hole combination, namely

$$Ag - \mathrm{AgCl(s)} \ | \ 0.1N\ \mathrm{HCl} \ | \ glass \ | \ \text{Unknown solution } (H^+)$$

constitute the glass electrode. When combined with the calomel the resulting cell is

$$Ag - \mathrm{AgCl(s)} \ | \ 0.1N\ \mathrm{HCl} \ | \ glass \ | \ \text{Unknown solution } (H^+) \ | \ Calomel$$

The *e.m.f.* of the above cell will be

$$E_{cell} = E^{Oxidation}_{anode} - E^{oxidation}_{cathode}$$

$$E_{cell} = E_{Glass} - E_{SCE}$$

$$E_{cell} = \left(E^{O}_{Glass} + \frac{2.303RT}{F} pH \right) - E_{SCE}$$

(iv) By Antimony Electrode

The antimony electrode is really an electrode consisting of antimony and its trioxide, the reaction being

$$Sb_2O_3 + 6H^+ + 6e \rightleftharpoons 2Sb + 3H_2O$$

So the potential of the above half cell is

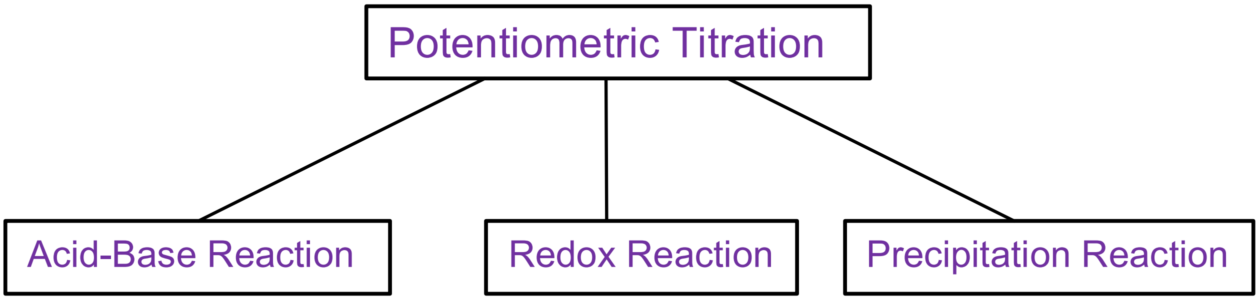
$$E_{Sb_2O_3/Sb} = E^O_{Sb_2O_3/Sb} - \frac{2.303RT}{6F} log \frac{a^2_{Sb}}{a_{Sb_2O_3} a^6_{H^+}}$$

$$E_{Sb_2O_3/Sb} = E^O_{Sb_2O_3/Sb} - \frac{2.303RT}{6F} log \frac{a^2_{Sb}}{a_{Sb_2O_3}} - \frac{2.303RT}{6F} log \frac{1}{a^6_{H^+}}$$

$$E_{Sb_2O_3/Sb} = E^O_{Sb_2O_3/Sb} + \frac{2.303RT}{F} log a_{H^+}$$

$$E_{Sb_2O_3/Sb} = E^O_{Sb_2O_3/Sb} - \frac{2.303RT}{F} pH$$

the activities of the solid antimony and antimony trioxide, being taken as unity. The potential of the Sb, Sb_2O_3 electrode should thus depend on the hydrogen ion activity of the solution in which it is placed.



There are number of advantages of potentiometric titrations over the ordinary titration involving the use of indicators. Potentiometric titration can be carried out into colored solution while indicator can not be used in such cases. Also, in ordinary titrations we need to know the relative strength of the acids and bases before a proper indicator is chosen. However, no such information is needed for potentiometric titration.

Acid-Base Titration:- If we want to titrate a unknown strength HCl solution against NaOH, any electrode whose potential depends on H^+ concentration (e.g. Hydrgen electrode, Quinohydrone electrode, Glass electrode) can be used. Then it can be connected to a reference electrode (e.g. Calomel electrode, Ag, AgCl electrode) to form a galvanic cell. One such example is

$$Pt \mid H_2(g, 1\ atm) \mid HCl(\textbf{unknwon}) \parallel \text{KCl (sat. solution)} \mid Hg_2Cl_2(\text{s}) \mid Hg \mid Pt$$

The *e.m.f.* of the above cell will be

$$E_{cell} = E_{cathode}^{reduction} - E_{anode}^{reduction}$$

$$or \quad E_{cell} = E_{SCE} - E_{Hydrogen}; \qquad SCE: Standard\ calomel\ electrode$$

$$or \quad E_{cell} = 0.242 - 0.0591 \log H^+ \qquad at\ 25^O C$$

$$or \quad E_{cell} = 0.242 + 0.0591\, pH \qquad at\ 25^O C$$

Let 100 ml of unknown HCl solution is to be titrated against 1 M NaOH. The concentration of titrant is to be taken always much higher concentration than that of the solution to be titrated so that the volume change is as small as possible.

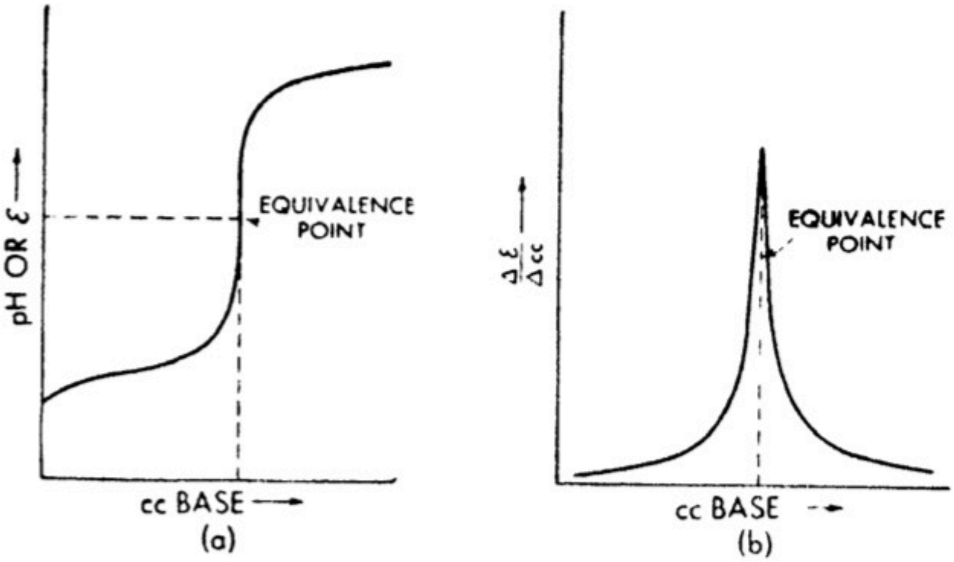


Figure 4: (a) Potentiometric titration of an acid with base (b) Determination of end-point in potentiometric titration

As the titration proceeds the concentration of H^+ goes on decreasing i.e. pH of the solution goes on increasing hence *e.m.f.* of the cell goes on increasing. Initially, it will be observed that the pH of the solution raises slowly, then more rapidly, until at the equivalent point there is a very sharp increase in pH for a very small quantity of added base. Once past the equivalence point, the curve again tapers off, indicating that the pH increases only slightly on the addition of excess base. (*Prutton and Maron, Fundamental Principles Of Physical Chemsitry, page-566*)

Precipitation Reaction: We can estimate of chlorides by potentiometric titration with silver nitrate solution. A known volume of NaCl solution is taken in a beaker in which a clean silver wire is inserted to act as an electrode, called "indicator" electrode. From a burette the titrant $AgNO_3$ is added in small amounts. As silver chloride is formed there, we have a reversible electrode $Ag \mid AgCl\,(s)\,|Cl^-$. This is coupled with a reference electrode say a standard calomel electrode, i.e.,

$$Ag \mid AgCl\,(s)\,|Cl^- \parallel \;\; Calomel\ electrode$$

The cell *e.m.f.*

$$E_{cell} = E_{Cathode}^{reduction} - E_{Anode}^{reduction}$$

$$E_{cell} = E_{SCE} - E_{AgCl/Ag}$$

$$E_{cell} = E_{SCE} - \left(E_{AgCl/Ag}^{O} - \frac{RT}{F}\ln\frac{a_{Ag}a_{Cl^-}}{a_{AgCl}}\right)$$

$$E_{cell} = E_{SCE} - E_{AgCl/Ag}^{O} + \frac{RT}{F}\ln\frac{a_{Ag}}{a_{AgCl}} + \frac{RT}{F}\ln a_{Cl^-}$$

$$E_{cell} = E_{SCE} - E_{AgCl/Ag}^{O} + \frac{RT}{F}\ln\frac{K_{sp}}{a_{Ag^+}}$$

$$E_{cell} = E_{SCE} - E_{AgCl/Ag}^{O} + \frac{RT}{F}\ln K_{sp} - \frac{RT}{F}\ln a_{Ag^+}$$

$$E_{cell} = C - \frac{RT}{F}\ln a_{Ag^+}\,; \quad C = E_{SCE} - E_{AgCl/Ag}^{O} + \frac{RT}{F}\ln K_{sp}$$

The solubility of $AgCl$ is quiet small, the concentration of Ag^+ ions in solution will change very slightly with the progress of titration and hence *e.m.f.* of the cell change but little. But when the equivalence point is reached, even a drop of $AgNO_3$ added would bring about a large increase in the silver ion concentration and therefore sharp change *e.m.f.* This sharp of change of *e.m.f.* indicates, the end point is reached.

A plot of *e.m.f.* of the cell against the volume of $AgNO_3$ solution is added is shown below., from which the sudden change in slope is clearly noticed. The end-point is thus easy to detect. If the differential in *e.m.f.* with volume

$\left({}^{\Delta E}/_{\Delta V}\right)$ be plotted against the volume the titre added, a still better indication of the end point is obtained that is shown in figure (b). This method can be easily extended to other titrations where precipitation occur. The indicator electrode has to be suitably chosen. (*P.C.Rakshit Page-619*).

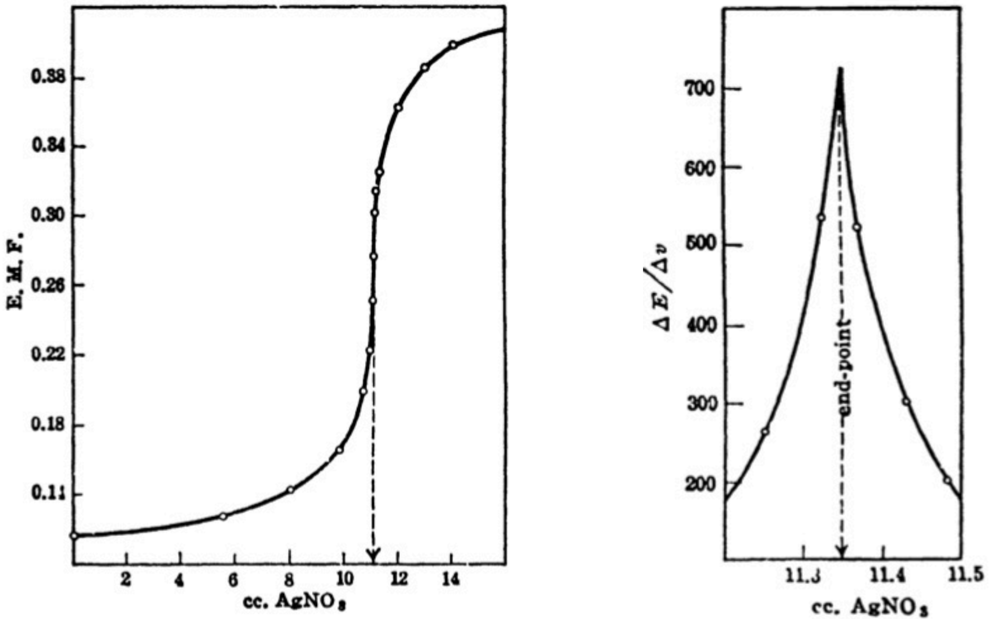


Figure 5: (a) Potentiometric titration (b) Determination of end-point in potentiometric titration

Redox Reaction: Let consider the titration of an acidified ferrous sulphate solution with an oxidizing agent, e.g. Potassium dichromate solution. A known volume of ferrous salt solution is taken in a beaker and a Pt-wire is inserted into the solution. The titre $K_2Cr_2O_7$ solution is added from a burette. At any instant during the titration, we have a mixture of Fe^{2+} and Fe^{3+} ions. With a Pt-wire in it and this forms a reversible electrode. This electrode is coupled with a reference electrode, namely calomel electrode to form the complete cell.

$$Pt|\ Hg(liq)|Hg_2Cl_2(s)|KCl(sat., aq)||\ Fe^{2+}(aq), Fe^{3+}(aq)\ \ |\quad Pt$$

Electrode process can be represented as

Anode (LHE) $2Hg(l) + 2Cl^- \rightleftharpoons Hg_2Cl_2 + 2e$

Anode (RHE) $Fe^{3+} + e \rightleftharpoons Fe^{2+}$

Net process: $2Hg(l) + 2Cl^-(aq) + 2Fe^{3+}(aq) \rightleftharpoons Hg_2Cl_2(s) + 2Fe^{2+}(aq)$

The e.m.f of the above cell,

$$E_{cell} = E_{Fe^{3+}/Fe^{2+}} - E_{SCE};\qquad SCE: standard\ calomel\ electrode$$

$$or \quad E_{cell} = E^{O}_{Fe^{3+}/Fe^{2+}} - \frac{2.303RT}{F} \log \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}} - E_{SHE}$$

$$or \quad E_{cell} = E^{O}_{Fe^{3+}/Fe^{2+}} - E_{SHE} + \frac{2.303RT}{F} \log \frac{a_{Fe^{3+}}}{a_{Fe^{2+}}}$$

$$or \quad E_{cell} = C + \frac{2.303RT}{F} \log \frac{a_{Fe^{3+}}}{a_{Fe^{2+}}}; \quad C = E^{O}_{Fe^{3+}/Fe^{2+}} - E_{SHE}$$

At a constant temperature C is constant. Therefore, The progressive addition of oxidizing agent $K_2Cr_2O_7$ will cause a change in the e.m.f. of the cell as the ratio ${}^{a_{Fe^{3+}}}/_{a_{Fe^{2+}}}$ increases. The concentration of Fe^{2+} ions will be ultimately extremely small but not zero. If the *e.m.f.* of the cell is plotted against the volume of $K_2Cr_2O_7$ added, the curve will show its greatest slope when the equivalence point is reached. From an observation of the sharp change in the *e.m.f.*, the end point of the reaction can be detected.

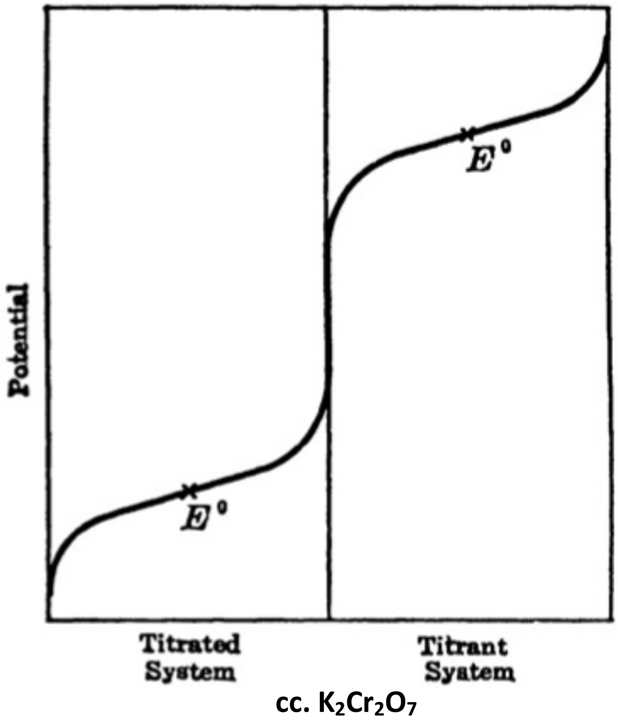
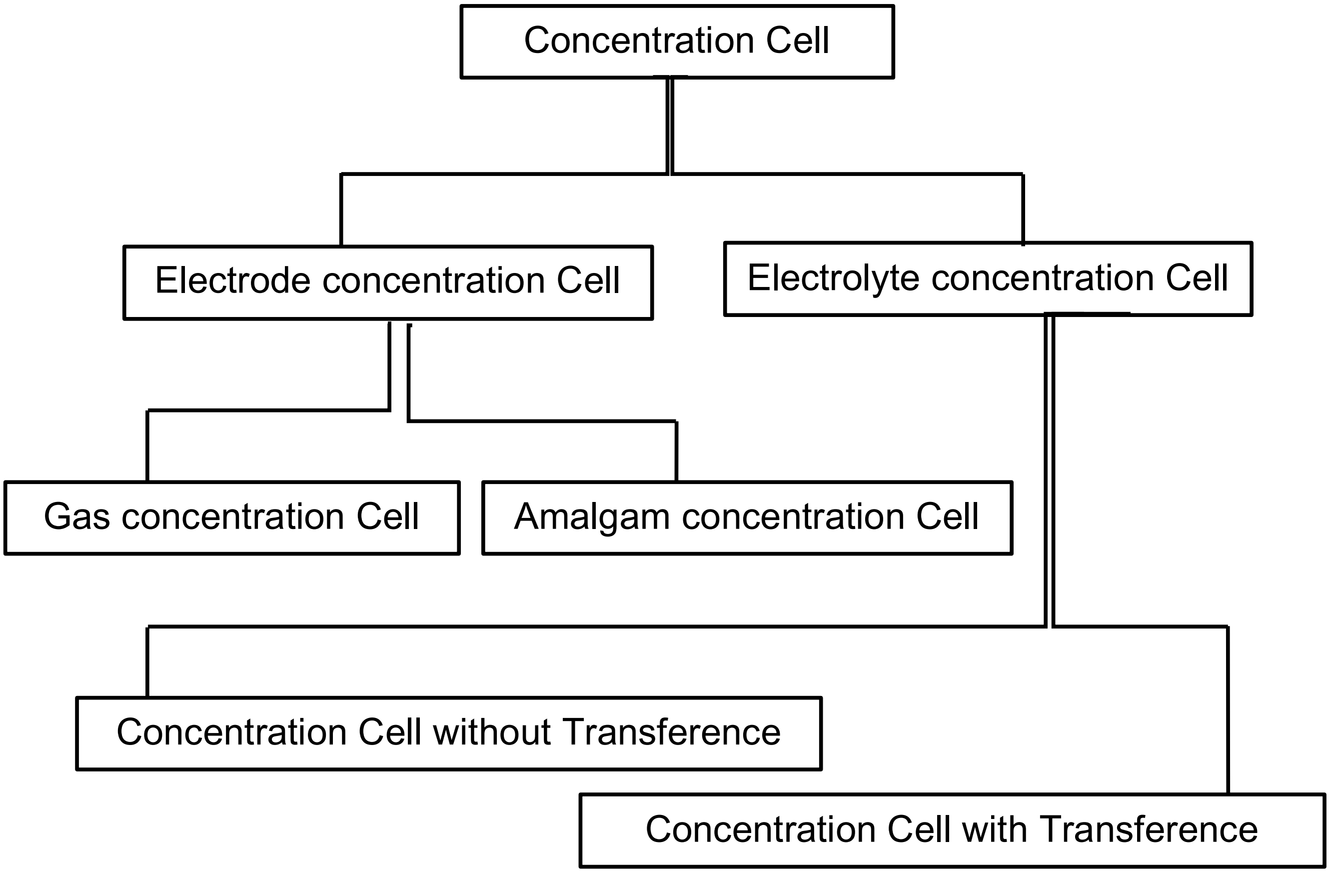


Figure 6: (a) Potentiometric titration of a redox system with an oxidizing agent

It is evident that before the end point is reached, the potential is governed by the titrated system ($Fe^{2+}, Fe^{3+}\ system$). But when equivalence point is passed and the excess of $K_2Cr_2O_7$ is added, the potentials are mainly determined by the titrant system ($Cr^{2+}, Cr_2O_7^{2-}\ system$).

❖ Concentration Cell

The cell so far we have described where *e.m.f.* of chemical cells is a consequence of the chemical reaction occurring in the cell. There is also an important class of cells in which no net chemical change occurs. They owe their *e.m.f.* due to concentration change either in the electrolyte or in the electrodes (pressure change for gas electrode). These types of cells are called concentration cells.



❖ Electrode-concentration cells:

(i) Gas Concentration cell: An example of a gas electrode concentration cell would be one consisting of two hydrogen electrodes operating at different pressures and dipping into a hydrochloric-acid solution:

$$Pt \mid H_2\,(g, p_1) \mid HCl\,(aq, a) \mid H_2\,(g, p_2) \mid Pt$$

Anode process

$$\frac{1}{2}H_2(p_1) \rightleftharpoons H^+ + e$$

Therefore

$$E_{anode}^{oxidation} = -\frac{RT}{F} ln\frac{a_{H^+}}{\sqrt{p_1}}$$

$$E_{anode}^{reduction} = \frac{RT}{F} ln\frac{a_{H^+}}{\sqrt{p_1}}$$

Cathode process

$$H^+ + e \rightleftharpoons \frac{1}{2}H_2(p_2)$$

Then

$$E_{cathode}^{reduction} = -\frac{RT}{F} ln\frac{\sqrt{p_2}}{a_{H^+}}$$

The complete cell process

$$\frac{1}{2}H_2(p_1) \rightleftharpoons \frac{1}{2}H_2(p_2)$$

The *e.m.f.* of the complete cell is

$$E_{cell} = E_{cathode}^{reduction} - E_{anode}^{reduction}$$

$$E_{cell} = -\frac{RT}{F} ln\frac{\sqrt{p_2}}{a_{H^+}} - \frac{RT}{F} ln\frac{a_{H^+}}{\sqrt{p_1}}$$

$$E_{cell} = \frac{RT}{F} ln\frac{\sqrt{p_1}}{\sqrt{p_2}} = \frac{RT}{2F}\ln\frac{p_1}{p_2}$$

The *e.m.f.* depends on the the pressure of the gas at the two electrodes. For spontaneous process E_{cell} must be positive, therefore $\ln\frac{p_1}{p_2}$ should be positive hence $p_1 > p_2$. Therefore, where the gas pressure is higher would be the negative terminal of the cell or anode.

(ii) Amalgam Concentration cell: This is an electrode concentration cell. The activities of Cadmium in the two amalgam are different. Let cadmium activity in left hand cell is a_1 and that in right hand cell is a_2.

$$Cd - Hg\ (a_1) \quad |\ \mathrm{CdSO_4} \quad |\ Cd - Hg\ (a_2)$$

Anode process

$$Cd(a_1) \rightleftharpoons Cd^{++} + 2e$$

$$E_{anode}^{oxidation} = E_{Cd/Cd^{++}}^{O} - \frac{RT}{2F}\ln\frac{a_{Cd^{++}}}{a_1}$$

$$E_{anode}^{reduction} = E_{Cd^{++}/Cd}^{O} + \frac{RT}{2F}\ln\frac{a_{Cd^{++}}}{a_1}$$

Cathode process

$$Cd^{++} + 2e \rightleftharpoons Cd(a_2)$$

$$E_{cathode}^{reduction} = E_{Cd^{++}/Cd}^{O} - \frac{RT}{2F}\ln\frac{a_2}{a_{Cd^{++}}}$$

The complete cell process

$$Cd(a_1) \rightleftharpoons Cd(a_2)$$

The *e.m.f.* of this cell arises from the net work obtained in transferring cadmium from an amalgam where its activity is a_1 to one with activity a_2. The *e.m.f.* is therefore:

$$E_{cell} = E_{cathode}^{reduction} - E_{anode}^{reduction}$$

$$E_{cell} = \left(E_{Cd^{++}/Cd}^{O} - \frac{RT}{2F}\ln\frac{a_2}{a_{Cd^{++}}}\right) - \left(E_{Cd^{++}/Cd}^{O} + \frac{RT}{F}\ln\frac{a_{Cd^{++}}}{a_1}\right)$$

$$E_{cell} = -\frac{RT}{2F}\ln\frac{a_2}{a_{Cd^{++}}} - \frac{RT}{F}\ln\frac{a_{Cd^{++}}}{a_1}$$

$$E_{cell} = \frac{RT}{2F}\ln\frac{a_1}{a_2}$$

For spontaneous process E_{cell} must be positive, therefore $\ln\frac{a_1}{a_2}$ should be positive hence $a_1 > a_2$. Therefore, the amalgam with higher concentration of Cd act as the negative electrode or anode.

❖ Electrolyte concentration cell

(i) Concentration cell without transference: In this type of cells, the both electrodes on the two sides are dipped into same electrolyte solution.

$$Pt \ \ | \ H_2(g, 1\,atm) \ \ \big| HCl(aq, \ \boldsymbol{a_1}), \mathrm{AgCl\ (S)} \ \big| \ \ \mathrm{Ag}\ (S)$$

For this cell the cell reaction will be

$$\frac{1}{2} H_2(g, 1\,atm) + AgCl\ (s) \rightleftharpoons Ag(s) + HCl\ (a_1)$$

The cell *e.m.f.* can be written as

$$E_{a_1} = E^O_{a_1} - \frac{RT}{F} \ln a_1$$

Again for the same but with different activity of HCl, namely

$$Pt \ | \ H_2(g, 1\,atm) \ \ | \ \ HCl(aq, \ \boldsymbol{a_2}) \,| \ \mathrm{AgCl\ (S) - Ag}\ (S)$$

For this cell the cell reaction will be

$$\frac{1}{2} H_2(g, 1\,atm) + AgCl\ (s) \rightleftharpoons Ag(s) + HCl\ (a_2)$$

and the cell *e.m.f.* will be

$$E_{a_2} = E^O_{a_2} - \frac{RT}{F} \ln a_2$$

If these two cells are connected together so as to oppose each other, i.e.

$$Pt \,|\, H_2(g, 1\,atm) \,|\, \ HCl(\ a_1), \mathrm{AgCl\ (S)} \,|\, \ \mathrm{Ag} - Ag \ \,|\, \mathrm{AgCl\ (S)}, HCl(\ a_2) \,|\, H_2(g, 1\,atm) \,|\, Pt$$

The overall reaction of the combination cell

$$\left(\frac{1}{2} H_2(g, 1\,atm) + AgCl\ (s)\right) - \left(\frac{1}{2} H_2(g, 1\,atm) + AgCl\ (s)\right)$$

$$\rightleftharpoons \big(Ag(s) + HCl\ (a_1)\big) - \big(Ag(s) + HCl\ (a_2)\big)$$

$$or\ HCl\ (a_1) \rightleftharpoons HCl\ (a_1)$$

Similarly, the *e.m.f.* of the cell is

$$E_{cell} = E_{a_1} - E_{a_2}$$

$$E_{cell} = \left(E^O_{a_1} - \frac{RT}{F} \ln a_1\right) - \left(E^O_{a_2} - \frac{RT}{F} \ln a_2\right)$$

$$E_{cell} = -\frac{RT}{F}\ln\frac{a_1}{a_2} = \frac{RT}{F}\ln\frac{a_2}{a_1}$$

For this cell, e.m.f to be positive in above equation a_2 must be grater than a_1. In other wards the transfer process is spontaneous for passage of electrolyte from the more concentrated to the more dilute solution, as is to be expected.

(ii) Concentration cell with transference: A typical concentration cell with transference is given below, where two identical hydrogen electrode immersed in two HCl solution of different concentration in and the two solutions of hydrochloric acid are in contact, and direct transfer from one to the other is possible. The presence of a liquid junction, as the region where the two solutions are brought into contact. For this cell total e.m.f. is composed of two single electrode potentials and the potential at the junction. There is a direct transfer of HCl from more concentrated solution (a_2) to the less concentrated one (a_1).

$$Pt \mid H_2\,(g, 1\,atm) \mid HCl\,(a_1) \,\vdots\, HCl\,(a_2) \mid H_2\,(g, 1\,atm) \mid Pt$$

Anode process

$$\frac{1}{2}H_2 \rightleftharpoons H^+(a_1) + e$$

Cathode process

$$H^+(a_2) + e \rightleftharpoons \frac{1}{2}H_2$$

The overall cell process

$$H^+(a_2) \rightleftharpoons H^+(a_1)$$

When electricity flow externally from left to right, they must complete circuit by passing through the cell from right to left, i.e. electrons must pass across the liquid junction from right to left. The electron current in the cell is composed of course not of free electron but of negative ions, namely chloride (Cl^-), moving from right to left and positive ion or H^+, moving across the junction from left to right.

Let t_- be the transference number of Cl^- and then for every Faraday passing through the cell t_- equivalent Cl^- will be transported from the solution where the activity is a_2 to the solution where the activity is a_1.

$$or \quad t_-Cl^-(a_2) = t_-Cl^-(a_1)$$

again $t_+ = (1 - t_1)$ equivalent of H^+ will be transferred from the solution of activity a_1 to the solution of activity a_2.

$$or \quad (1 - t_-)H^+(a_1) = (1 - t_-)H^+(a_2)$$

Therefore, in order to obtain the net transfer of material, we will have

$$H^+(a_2) + t_-Cl^-(a_2) + (1 - t_-)H^+(a_1) \rightleftharpoons H^+(a_1) + t_-Cl^-(a_1) + (1 - t_-)H^+(a_2)$$

$$t_-H^+(a_2) + t_-Cl^-(a_2) \rightleftharpoons t_-H^+(a_1) + t_-Cl^-(a_1)$$

$$t_-HCl(a_2) \rightleftharpoons t_-HCl(a_1)$$

Application of the Nernst *e.m.f.* equation to the above process gives immediately for the cell *e.m.f.*

$$E'_{cell} = -\frac{RT}{F}\ln\frac{a_1^{t_-}}{a_2^{t_-}}$$

$$E'_{cell} = \frac{t_-RT}{F}\ln\frac{a_2}{a_1}$$

$$E'_{cell} = 2t_-\frac{RT}{F}\ln\frac{a_{\pm 2}}{a_{\pm 1}}$$

Where a_1, a_2 are the activities of the two HCl solution and $a_\pm$ denotes the mean ionic activity and

$$a_1 = a_{\pm 1}^2 \; and \; a_2 = a_{\pm 2}^2$$

❖ Transference number from *e.m.f.* measurement

Science concentration cell with transference involve transport numbers in their cell and *e.m.f.* equations, such cells can be used to utilize for estimating these quantities from *e.m.f.* data. It is also possible to arrive at t_+ or t_- alone without a knowledge of the activity coefficients.

For any concentration cell with transference in which the electrodes are reversible to the cation, as

$$M \;|\; \mathrm{MX}\,(a_1) \;|\; MX\,(a_2) \;|\; M$$

The above equation gives the *e.m.f.* as

$$E_{wt} = t_- \frac{RT}{F} \ln \frac{a_2}{a_1} \qquad (i)$$

again for a concentration cell involving the same concentrations of the electrolyte but without transference, namely

$$M \;|\; \mathrm{MX}\,(a_1) \;|\; X - X \;|\; MX\,(a_2) \;|\; M$$

The overall cell reaction would be

$$MX(a_2) \rightleftharpoons MX(a_1)$$

and *e.m.f.* of the equation would be

$$E_{wot} = \frac{RT}{F} \ln \frac{a_2}{a_1} \qquad (ii)$$

Now diving equation (i) by equation (ii)

$$\frac{E_{wt}}{E_{wot}} = \frac{t_- \frac{RT}{F}}{\frac{RT}{F}} \frac{\ln \frac{a_2}{a_1}}{\ln \frac{a_2}{a_1}} = t_-$$

Hence t_- follows as the ratio of the *e.m.f.* of the cell with transference and the same cell without transference.

Similarly, for a concentration cell with transference reversible to anion, as

$$X| \;\; \mathrm{MX}\,(a_1) \;|\; MX\,(a_2) \;|\; X$$

This equation yields the *e.m.f.*

$$E_{wt} = t_+ \frac{RT}{F} \ln \frac{a_1}{a_2} \qquad (iii)$$

while the same cell without transference, i.e.

$$M \;|\; \mathrm{MX}\,(a_1) \;|\; M - M \;|\; MX\,(a_2) \;|\; M$$

and the *e.m.f.* is

$$E_{wot} = \frac{RT}{F} \ln \frac{a_1}{a_2} \quad where \quad a_1 > a_2 \quad (iv)$$

Now diving equation (iii) by equation (iv)

$$\frac{E_{wt}}{E_{wot}} = \frac{t_+ \dfrac{RT}{F}}{\dfrac{RT}{F}} \frac{\ln \dfrac{a_1}{a_2}}{\ln \dfrac{a_1}{a_2}} = t_+$$

Hence + follows as the ratio of the *e.m.f.* of the cell with transference and the same cell without transference.