Module II - Electrode potentials and Applications

Learning objectives

After reading this chapter, you will be able to

(i) comprehend the importance of Nernst equation

(ii) predict the occurrence of chemical reactions

(iii) employ Latimer and Frost diagrams for disproportionation reactions

Introduction

The analytical and physicochemical applications of the Nernst equation are exhaustive and hence an outline of various applications is provided below. At a preliminary stage, it is essential to acquire expertise in writing the Nernst equations for various types of half cells. It is customary to write both the half-cell reactions as reduction and cancelling the number of electrons when the complete cell reaction is considered. The terminology of anodes and cathodes will be different depending upon whether one considers galvanic or electrolytic cells. The galvanic cells are energy storage devices since they convert chemical energy into electrical energy, e.g (batteries, fuel cells etc). The electrolytic cells on the other hand, involve supplying electrical energy in order to bring about a chemical transformation. The synthesis of organic and inorganic compounds, extraction of metals from their respective ores etc are carried out in electrolytic cells. Thus, it is now customary to consider oxidation as occurring at anodes and reduction as a cathodic process. This nomenclature will be valid irrespective of whether one employs galvanic or voltaic cells.

Table 1: Half-cell reactions and corresponding Nernst equations

Half Cell	Reduction	Nernst Equation at 298K
Ag|AgCl| KCl	$AgCl + e^- \rightleftharpoons Ag + Cl^-$	$E = E^0 - 0.059\ log\ a_{Cl^-}$
$Hg\|Hg_2Cl_2\|KCl$	$Hg_2Cl_2 + 2e^- \rightleftharpoons 2Hg + 2Cl^-$	$E = E° - \frac{0.059}{2} log\ a_{Cl^-}^2$
$Hg\|Hg_2SO_4\|K_2SO_4$	$Hg_2SO_4 + 2e^- \rightleftharpoons 2Hg + SO_4^-$	$E = E^0 - \frac{0.059}{2} a_{SO_4^{2-}}$
$Pb\|PbSO_4\|H_2SO_4$	$PbSO_4 + 2e^- \rightleftharpoons Pb + 2SO_4^-$	$E = E^0 - \frac{0.059}{2} log\ a_{SO_4^{2-}}$
Hg/HgO/NaOH	$HgO + H_2O + 2e^- \rightleftharpoons Hg + 2OH^-$	$E = E^0 - \frac{0.059}{2} \frac{a_{OH^-}^2}{a_{H_2O}}$
$Ag\|Ag_2O\|NaOH$	$Ag_2O + H_2O + 2e^- \rightleftharpoons Ag + 2OH^-$	$E = E° - 0.059 \frac{a_{OH^-}^2}{a_{H_2O}}$
Sb|Sb₂O₃|NaOH	$Sb_2O_3 + 3H_2O + 6e^- \rightleftharpoons 2Sb + 6OH^-$	$E = E^0 - \frac{0.059}{6} \frac{a_{OH^-}^6}{a_{H_2O}^3}$
$Pt\|H_2\|HCl$	$2H^+ + 2e^- \rightarrow H_2$	$E = E° - \frac{0.059}{2} \frac{p_{H_2}}{a_{H^+}^2}$
$Pt\|Cl_2\|HCl$	$Cl_2 + 2e^- \rightarrow 2Cl^-$	$E = E° - \frac{0.059}{2} a_{Cl^-}^2$
$Pt\|Fe^{3+}, Fe^{2+}$	$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	$E = E^0 - .059. \frac{a_{F_e^{2+}}}{a_{F_e^{3+}}}$

$Cd - Hg$|CdSO4.$\frac{8}{3}H_2O$ |$CdSO_4$ (saturated)	$CdSO_4 + 2e^- \rightleftharpoons Cd^{2+} + 2SO_4^-$	$E = E° - \frac{0.059}{2}\frac{a_{Cd^{2+}}a_{SO_4}^{2-}}{a_{Cd^{2+}}}$
$Pt\|Q_{0x}, QH_2\|HCl$	$Q_{ox} + 2H^+ + 2e^- \rightleftharpoons QH_2$	$E = E^0 - \frac{.059}{2} log \frac{1}{2} a_{H^+}$

Sign Convention

The IUPAC (or Stockholm) convention employs the reduction potentials of both half cells. The net cell emf is positive and hence the reaction is spontaneous.

Consider the half-cell represented as Cd | Cd^{2+} and during the discharge of Cd^{2+}, the Cd electrode acquires positive charge and hence the reduction potential is positive while ΔG is negative. Analogously, in a complete cell when both half cell reactions are written as reduction, the sign of the overall cell potential will correspond to that of the r h s in the cell representation. The potential is calculated as the difference between the rhs and lhs of the cell representation. The important points in the construction of electrochemical cells are as follows:

1.Both half-cell reactions should be written as reductions;

E_0(rhs)-E_0(lhs) should be positive in the cell representation for any galvanic cells.

2. ΔG should be considered while manipulating cell reactions and not the electrode potentials.

Thermodynamic considerations underlying Nernst equation

Consider a general chemical equilibrium such as

aA + bB + ... = cC +dD+ .....(1)

The Gibbs free energy change (ΔG) is given by

$\Delta G = (c\,\Delta G_C + d\,\Delta G_D + ...) - (a\,\Delta G_A + b\,\Delta G_B + ...)$ ------ (2)

Further, ΔG under standard conditions (ΔG^0) becomes

$\Delta G = (c\,\Delta G^0_C + d\,\Delta G^0_D + ...) - (a\,\Delta G^0_A + b\,\Delta G^0_A + ...)$ ------ (3)

where μ_A, μ_B … denote the respective chemical potentials.

However, the chemical potentials are given by following general equations:

$$\mu_A = \mu_A^0 + RT\ ln\ a_A - - - (4)$$
$$\mu_B = \mu_B^0 + RT\ ln\ a_B - - - (5)$$
$$\mu_C = \mu_C^0 + RT\ ln\ a_C - - - (6)$$
$$\mu_D = \mu_D^0 + RT\ ln\ a_D - - - - (7)$$

Hence

$\Delta G - \Delta G^0 = RT\ ln \frac{a_C^c a_D^d}{a_A^a a_B^b}$ ----(8)

At equilibrium ΔG = 0

Hence, one can write

$$\Delta G^0 = -RT\ ln \frac{a_{C_1eq}^c a_{D_1eq}^d}{a_{A\ _1eq}^a a_{B_1eq}^b} - - - (9)$$

where the activities are now the values at equilibrium. Thus

$\Delta G^0 = -RT$ ln K_{eq}----- (10)

Furthermore, employing $\Delta G = -nFE$ and $\Delta G^0 = -nFE^0$, the familiar Nernst eqn follows as

$$E = E^0 - \frac{RT}{nF} ln \frac{a_C^c}{a_A^a} \frac{a_D^d}{a_B^b} \text{-----(11)}$$

Standard Chemical potentials

For a reduction reaction such as $Fe^{3+} + e^- = Fe^{2+}$, occurring at an inert electrode (Phase I) while the Phase II denotes an electrolyte, the equilibrium condition is given by

$\mu_{Fe^{3+}}, phase II + \mu_{e^-}, phase\ \text{I} = \mu_{Fe^{2+}}, phase\ \text{II}$

$$_{II}\mu_{Fe^{3+}}^0 + RT \ln\left(\frac{a_{Fe^{3+}}}{a^0_{Fe^{3+}}}\right) + nF\varphi_{II} + {}_I\mu_{e^-}^0 - F\varphi_I = {}_{II}\mu_{Fe^{2+}}^0 + RT \ln\left(\frac{a_{Fe^{2+}}}{a^0_{Fe^{2+}}}\right) + 2F\varphi_{II}$$

The Galvani Potential (*vide infra*) is given by

$$\varphi_I - \varphi_{II} = \Delta\varphi^0 + \frac{RT}{F} \ln\left(\frac{a_{Fe^{3+}}}{a_{Fe^{2+}}} . \frac{a^0_{Fe2+}}{a^0_{Fe^{3+}}}\right)$$

where

$$\Delta\varphi^0 = \frac{{}_{II}\mu^0_{Fe^{3+}} - {}_{II}\mu^0_{Fe^{2+}} + {}_{II}\mu^0_{e^-}}{F}$$

Formal potentials

In general, the Nernst equation can be written in terms of the activities and hence

$$E = E^\circ - \frac{RT}{nF} ln \frac{\Pi a_{i,p}^{\gamma i}}{\prod a_{i,r}^{\gamma i}} - - - (12)$$

where $\prod$ refers to the multiplication symbol. A subtle distinction can be obtained by replacing the activities with concentrations so as to obtain

$$E = E_\circ' - \frac{RT}{nF} ln \frac{C_C^c C_D^d}{C_A^a C_B^b} - - - - (13)$$

$E_\circ'$ is designated as the *formal potential* and is related to E^0 as

$$E_\circ' = E^\circ - \frac{RT}{nF} ln \frac{\gamma_C^c \gamma_D^d}{\gamma_A^a \gamma_B^b} \text{------ (14)}$$

If all the activity coefficients are unity, the formal potential becomes identical to the standard electrode potential. The following Table provides a few formal potential values.

The Nernst equation, taking into account, the activity coefficients, stoichiometric coefficients and the formal potentials can be derived in the following manner:

Consider the reduction: $v_A + ne^- = v_B B$. The electrode potential E is given by

$$E = E^\circ - \frac{RT}{nF} ln \frac{a_B^{v_B}}{a_A^{v_A}} = E^\circ - \frac{RT}{nF} ln \frac{(C_B \gamma_B)}{(C_A \gamma_A)^{v_A}}^{v_B}$$

$E_\circ'$ is referred to as the *formal potential* and is related to E^0 as

$$E^{\circ\prime} = E^\circ - \frac{RT}{nF} ln \frac{\gamma_B^{v_B}}{\gamma_A^{v_A}}$$

Hence the Nernst eqn is given by

$$E = E^{\circ\prime} - \frac{RT}{nF} ln \frac{c_B^{v_B}}{c_A^{v_A}}$$

The single ionic activity coefficients cannot be experimentally obtained; but can be theoretically estimated using various theories such as Debye-Hückel theory, scaled particle theory, hypernetted chain approximation etc.

Table 2 : Formal electrode potentials at 25 ° C for a few compounds

Compound	E(V vs. SHE)
Ru $(NH_3)_5(py)^{2+}$	$E^{\circ\prime}$ = 0.299, 1M CF_3SO_3H
Thionine	$E^{\circ\prime}$ = 0.056, pH =7
$Ru(NH_3)_6^{3+}$	$E^{\circ\prime}$ = 0.051, 0.1M $NaBF_4$
Methylene blue	$E^{\circ\prime}$ = 0.011, pH = 7
Neutral Red	$E^{\circ\prime}$ = 0.325, pH = 7

Reference Electrodes

In order to measure the electrode potentials of any complete cell, it is essential to have a reference electrode. The standard hydrogen electrode (SHE) was originally chosen as the reference electrode, whose potential was assigned as Zero at 298K, unit activity of H^+ions and 1 atm pressure of $H_2(g)$. It is essential to point out that, by careful consideration of interfacial potentials and work functions, an absolute scale of electrochemical potentials can be constructed.

For an electrode to be employed as a reference electrode, the following requirements should be met: (i)long stability;(ii)non-polarizable;(iii) small temperature coefficient of the potential; (iv)ease of handling and (v) non-interference with the cell reaction. The requirement (i) is essential since the potential needs to be constant over long periods of time. A non-polarizable electrode ensures that its potential remains constant during the passage of current.

For electron transfer processes such as,

$Ox + ne^- \rightleftharpoons Red$

Nernst eqn becomes

$$E = E° - \frac{RT}{nF} ln \frac{a_{Red}}{a_{ox}}$$

For the electron transfer process Ox + ne^- - Red = 0, the equation for Affinity is given by

ν_A Ox + ne^- - ν_p Red = 0

Recognising that the stoichiometric number of the reactant is positive while that of the product is negative, the above eqn becomes

$$\sum_{i=1}^{m} \gamma_i c_i + ne^- = 0$$

where the summation index runs over all the species present in the system.

If a redox couple involves H^+ions, the above eqn. becomes more generalized as

$$Cr_2O_7^{2-} + 14H^+ - 2Cr^{3+} - 7H_2O + 6e^- = 0$$

The electrode potential depends upon concentrations of various species as well as pH of the solution.

Affinity of electrochemical reactions

We also note that the driving force for any (electro) chemical reaction is the affinity defined as

$$Affinity(A_r) = \sum_i \nu_i \mu_i$$

where μ_A is +ve for reactants and –ve for products.

For the equilibrium

$$aA + bB = cC + dD,$$

The affinity is,

$A = a\mu_A + b\mu_B - c\mu_C - d\mu_D$

and so on.

At this stage it is necessary to define various standard states(Table 3)

Table 3: Standard states of pure substances

Solid	Solid in its most stable and pure form at $\rho^{\theta} = 1\ bar\ (100kPa)$ and the specified temperature (T) (often at T=298.15K)
Liquid	Pure liquid in most stable form at $\rho^{\theta} = 1$ bar and T
Gas	Pure gas at unit fugacity

Common Reference electrodes

Normal (or standard) hydrogen electrode

In view of the reproducibility offered by Pt surface, the earliest known reference electrode was the Standard Hydrogen Electrode(SHE) or Normal Hydrogen Electrode(NHE) consisting of platinised Pt immersed in H_2SO_4. The reduction process in this half cell is

$$2H^+ + 2e^- \rightleftharpoons H_2$$

The Nernst eqn in this case is

$$E = E^\circ + \frac{RT}{2F} ln \left\{ \frac{(a_{H+})^2}{p_{H_2}} \right\}$$

As mentioned earlier, the potential of SHE is assigned zero at one atmosphere pressure of hydrogen, 298 K and unit activity of H+ ions.

Saturated calomel electrode (SCE)

It is probably the most widely used reference electrode. It consists of Hg electrode in contact with Hg_2Cl_2 in a saturated solution of KC1. In view of employing the saturated solution of KCl, the activity of Hg_2^{2+} ions remains constant through the solubility product Hg_2Cl_2 . The temperature-dependence of the electrode potential of the *aqueous* SCE versus SHE is given by

$$E\ (\text{in V}) = +0.242 - 7.6 \times 10^{-4} \times (T - 298)$$

The Normal Calomel Electrode (NCE) consists of 1N KC1 solution. The temperature-dependence in this case is given by the equation

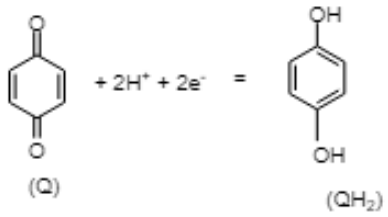
$$E\ (\text{in V}) = +0.280 - 2.4 \times 10^{-4} \times (T - 298)$$

Redox reactions and reference electrodes:

Quinone-Quinhydrone electrode

Symbol: Pt/Q, QH_2/H^+ (a= 1)

Reaction:



Nernst equation: $E_{Q|QH_2} = E^0_{Q|QH_2} - \frac{0.059}{2} log\left(\frac{a_{QH_2}}{a_Q.a^2_{H+}}\right)$

or $E_{Q/QH_2} = E^{\circ}_{Q/QH_2} - 0.059pH$ since $a_{QH2} = a_Q = 1$

As can be seen from the above, the Quinone-Quinhydrone electrode is convenient for pH measurements. However, several interesting pH dependences of this electrode can be envisaged as given below.

Quinhydrone electrode

Consider the reduction of quinone to hydroquinone given by

Ox(Quinone) + 2e- ⇄Red(Hydroquinone $^{2-}$)

Nernst equation is

$$E_{qh} = E^{0'} + \frac{RT}{2F}\ln\frac{[quinone]}{[Hydroquinone^{2-}]}$$

where E_0' denotes the formal potential. The concentration of [hydroquinone $^{2-}$] is substituted from the equation for (i)the dissociation constant and (ii)overall concentration of hydroquinone.

The overall concentration of reduced form of hydroquinone [c_{red}] should be a sum of $[H_2\,Re\,d] + [HRed^-] + [Re\,d^{2-}]$. Thus

$$[\,c_{red}] = \frac{[H^+]^2[Re\,d^{2-}]}{K_1'K_2'} + \frac{[H^+][Re\,d^{2-}]}{K_2'} + [Re\,d^{2-}]$$

Employing K_1' and K_2' for the first two dissociation constants, it can be shown that

$$E_{qh} = E^{0'} + \frac{RT}{2F}\ln\frac{[Ox]}{c_{Red}} - \frac{RT}{2F}\ln K_1'K_2' + \frac{RT}{2F}\ln\left(\left[H^+\right]^2 + K_1'\left[H^+\right] + K_1'K_2'\right)$$

Since [Ox] = [c_{Red}] in this case, the second term on the right-hand side is zero while the first and third term together can be denoted as $E_{qh}^{0'}$. The fourth term varies with pH in the following manner:

In acidic solutions, $[H^+]^2 \gg K_1'K_2' + K_1'[H^+]$. Thus

$$E_{qh} = E_{qh}^{0'} - \frac{2.303RT}{F} pH$$

For alkaline solutions, $K_1'K_2' \gg (K_1'[H^+] + [H^+]^2)$, the potential becomes independent of pH:

$$E_{qh} = E_{qh}^{0'} + \frac{RT}{2F} \ln K_1^{'} K_2^{'}$$

It follows from the above considerations that the plot of E_{qh} with pH exhibits two linear regions with the respective slopes (at 298K) of 0.0591and 0.0295 and a parallel regime of pH impendence.

Antimony electrode (Sb_2O_3/Sb)

Reactions pertaining to antimony electrode

Hydrated Sb_2O_3 is in equilibrium with the solution in the following manner:

$Sb_2O_3 + 3H_2O \rightleftharpoons 2Sb^{3+} + 6OH^-$

The reduction of Sb^{3+} forming Sb yields the equilibrium $2Sb^{3+} + 6e^- \rightleftharpoons 2Sb$

The overall reaction is therefore,

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

Nernst equation for the above reduction is:

$E_{Sb_2O_3/Sb} = E°_{Sb_2O_3/Sb} - \frac{0.059}{6} \log[OH^-]^{\,6}$

$since\ a_{Sb} = a_{Sb_2O_3} = 1$

Hence

$$E_{Sb_2O_3/Sb} = E°_{Sb_2O_3/Sb} - 0.059\ log\ a_{OH-}$$

However, the ionic product of water K_w can be introduced and thus

$a_{OH-} = \frac{K_w}{a_{H+}}$ ------(22)

$E_{Sb_2O_3/Sb} = E°_{Sb_2O_3/Sb} - 0.059\ log\left(\frac{K_w}{a_{H+}}\right)$ ------ (23)

$$E_{Sb_2O_3/Sb} = \left(E°_{Sb_2O_3/Sb} - 0.059\ log\ 1\,0^{-14}\right) + 0.059\ log\ a_{H+}$$

$E°_{Sb_2O_3/Sb}$ = -0.6829 V vs SHE

The ionic product term yields +0.1431V

Hence the pH dependence of the potential of the antimony electrode (Sb_2O_3/Sb) yields

$E_{Sb_2O_3/Sb} = 0.1431 - 0.059pH$

This electrode provides accurate values if the pH of the solution is <7. In alkaline solutions, the above equation does not describe the variation of the potential with pH, on account of irreversible electrode reactions. The electrode is also not suitable in the case of solutions which lead to the formation of complexes.

Reference electrodes in non-aqueous solvents

When non-aqueous solvents are employed, the reference electrodes need to be carefully chosen. By a careful cell construction, SCE in aqueous solvents can often be used even for non-aqueous solvents. For example, SCE in aqueous solutions can be combined using KCl- agar bridge with the desired system in non-aqueous solvents, wherever chloride ions do not interfere with the potential and the potential window is not large. It is also possible to employ Ag/Ag+ electrodes as well as Pt/ I_3^-/ I^- in non-aqueous solvents. The use of non-aqueous solvents is of immense importance in view of the limitation offered by aqueous solvents in anodic and cathodic regions. In a variety of electro-organic reactions, such as the reduction of aromatic hydrocarbons, the *magnitude* of the reduction potential varies from 2.5 V to 3.2 V. In such cases, it is customary to employ ferrocene/ferrocenium as the reference electrode in suitable non-aqueous solvents.

<u>Conversion of potentials using reference electrodes</u>

It is straight forward to convert the potential from a given reference electrode (E Ref 1) to another (E Ref 2) using:

E (vs E Ref 2) = E (vs E Ref 1) + ERef 1- E Ref2

E (vs E Ref 2) denotes the required potential with respect to the desired electrode.

Determination of standard electrode potentials

It is easy to estimate the standard electrode potential of any electrode, by suitably combining it with a reference electrode. This is illustrated below using Ag/AgCl electrode dipped in HCl solution of different activities, using SHE as the reference electrode,

$$-ve\ Pt.H_2(g, 1\ atm\ pressure)|H^+Cl^-(activity\ a)|AgCl, Ag \quad +\text{ve}$$

Nernst eqn is

$$E(cell) = E^{\Theta}(cell) - \frac{2RT}{F} ln\ a_{\pm,HCl} = E^{\Theta}(cell) - \frac{2RT}{F} ln(m_{\pm}, \text{HCl}) - \frac{2RT}{F} ln(\gamma_{\pm,\text{HCl}})$$

where $m_{\pm}$ denotes mean molarity and $\gamma_{\pm}$ denotes mean ionic activity coefficient.

It is preferable to employ dilute solutions (<0.001m) so that Debye-Hückel theory is valid. A plot of [E(cell) + (2RT/F) ln $m_{\pm, HCl}$] against square root of the ionic strength ($I^{1/2}$) is linear and extrapolation to I = 0 yields the standard electrode potentials $E^{\Theta}(Ag/AgCl/Cl^-)$. Subsequently, employing this value, it is possible to estimate the mean ionic activity coefficient at various mean molalities.

Electrochemical series

The most reactive *metals* have the largest *negative* standard reduction potentials and are capable of losing electrons in a facile manner. Upon reacting these metals which appear at the top of the electrochemical series with acids, H_2 (g) is liberated. Analogously, the metals with more positive standard reduction potentials are least reactive and appear at the bottom of the electrochemical series (with respect to zero as the reference potential value).(Table 4)

Table 4: Electrochemical series of metals

Metal	**E⁰ (V)**
Li	-3.05
K	-2.93
Ba	-2.91
Sr	-2.89
Ca	-2.87
Na	-2.71

Mg	-2.37
Al	-1.66
Mn	-1.18
Zn	-0.76
Cr	-0.74
Fe	-0.44
Cd	-0.40
Co	-0.28
Ni	-0.26
Sn	-0.14
Pb	-0.13
H_2	0.00
Bi	+0.32
Cu	+0.34
Ag	+0.80
Hg	+0.85
Pd	+0.92
Pt	+1.12

It is customary to classify electrodes into various types for convenience.

Electrodes of the **first kind** refer to metals dipped in the cations of their solutions (e.g Ni/Ni^{2+},Cu/Cu^{2+},Ag/Ag^{+} etc). Despite their simplicity and convenience, these are not practically useful on account of the non-selectivity and lack of specificity in reactions.

Electrodes of the **second kind** refer to metals which are coated with any of their own sparingly soluble compounds and dipped in the solution (having the anion of the compound). (e.g Ag/AgCl/KCl, Hg/Hg_2Cl_2/KCl). Occasionally, the terminology of electrodes of the **third kind** are employed .In this case, electrodes consist of metals which are involved in complexations selectively (e.g Hg electrodes involved in forming complexes with EDTA).Thus, this electrode responds to the concentration of other ions which do not form complexes with the complexing agent.

There are other types of electrodes such as (i) indicator and (ii) membrane electrodes. The indicator electrodes refer to inert metals dipped in a solution consisting of species existing in multiple valences (e.g Pt/Fe^{3+},Fe^{2+}; Ag/Ce^{4+},Ce^{3+}). The indicator electrodes are employed in potentiometric titrations.

Membrane electrodes respond selectively to specific ions by developing a potential difference between the analyte and reference solutions. The potential is directly proportional to the logarithm of the concentration of the analytes, thus enabling quantitative analysis. Similarly, on account of the specificity, the selective detection of ions is possible by the membrane electrodes.

Glass Electrodes

The glass electrode for the measurement of pH is a typical example of the membrane electrode. It consists of a thin (bulb-shaped) glass membrane, sealed onto a glass tube. The solution inside the electrode contains a solution with known pH .Since the pH of the solution within the membrane electrode is constant, the internal potential is a fixed value. An internal reference electrode is fixed inside the tube .The glass electrode is often used in combination with a reference electrode such as Ag/AgCl/KCl or SCE. By immersing this combination of the two electrodes in a solution of unknown pH, the measured potential yields the pH of the solution.

Galvani potential, Volta potential and surface potentials

In the foregoing derivation of the Nernst equation, we have not considered in a rigorous manner, the various potentials that contribute to E and E^0 . For this purpose, it is essential to provide a brief account of Galvani potential, Volta potential and surface potential, which are present at any metal/electrolyte interface. This is a non-trivial exercise in so far as there exist different contributions to the overall potential E when interfaces are considered. The electrochemical potential terms arising in the equation for the Gibbs free energy, involve the chemical contribution (chemical potential μ)and electrical contribution ($zF\Phi$) for a charged species of valence z .

Galvani potential

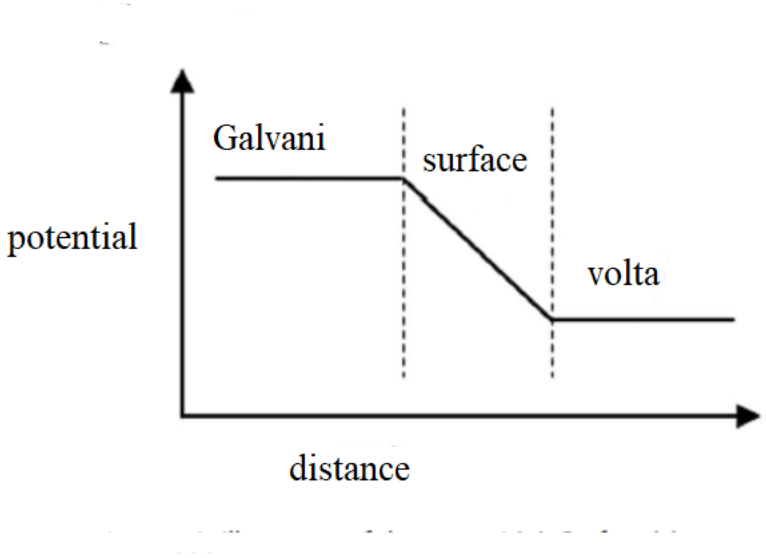
The Fermi level is associated with the Galvani potential difference ($\Phi m - \Phi s$) between a metal and an electrolyte solution.The absolute value of the standard redox potential (E_{abs}) is related to the Galvani potential difference and chemical potential of electrons in the metal. ($\Phi m - \Phi s$) is not an experimentally measurable quantity.

Volta potential

The difference in Volta potential ($\Delta\psi$) refers to the electrostatic potential between two different phases (either between two different metals or between a metal and an electrolyte) in thermodynamic equilibrium. In principle, the Volta potential is measurable.

Surface potential

The surface potential is associated with ions or dipoles adsorbed on the electrode surface and can often be estimated using statistical mechanical or electrostatic models. This value is of immense significance in the modelling of electrical double layer.



Schematic depiction of Galvani, volta and surface potentials

Electrochemical potential

It consists of the following components : (i) the outer, (or Volta) potential (Ψ) arising from the work done to transport a point charge from the bulk to a region near the surface in the absence of dipoles ; (ii) the surface potential (χ)associated with bringing the unit charge, across the (solvent)dipole layer, towards the neutral electrode surface and (iii) the inner, or (Galvani) potential (ϕ), arising from the work done to carry the test charge from the bulk of the solution towards the solvent dipole layer when the surface is charged. The outer (or Volta) potential can be in principle measured since it involves the same phase (from bulk solution to a region just outside the metal surface).The surface potential can be estimated theoretically but cannot be experimentally measured,

Galvani (or inner) potential = Volta (or outer) potential + surface potential.

Galvani (or inner) potential difference $\Delta\Phi = \Delta\Psi + \Delta\chi$

The term appearing in the electrochemical potential is the inner (or Galvani) potential difference ($\Delta\Phi$) and is a sum of $\Delta\chi$ and $\Delta\Psi$. The fact that the Galvani potential is not

measurable need not deter us since the use of an appropriate reference electrode obviates this limitation.

Absolute Electrode potentials

In order to obtain the absolute electrode potential of any system,various molecular parameters such as electron affinity, ionisation potential, lattice energy etc. can be invoked. It is of interest to enquire what will be the potential of the SHE if its value is not assigned zero. This value in terms of energies has been computed using solid state physics concepts as -4.5ev for the reduction of H^+.

$2H^+ + 2e^- \rightleftharpoons H_2$

Using this value, it is now possible to construct electrochemical series involving Fermi energy rather than E°.

Thus,

Fermi energy of Fe^{3+}/Fe^{2+} ~ -5.3 eV

Fermi energy of Zn^{2+}/Zn ~ -3.7 eV

Fermi energy of Hg_2^{2+}/Hg ~ -4.7 eV

Fermi energy of H^+/H_2 ~ -4.5 eV

Lest one may underestimate the importance of the Nernst eqn, the concentration dependence of the species is immense importance in (i) fabricating ion-selective electrodes ;(ii) choosing the concentration of H_2SO_4 in lead acid batteries;(iii) optimising the activity of CH_3OH in methanol fuel cells and (iv) for simultaneous electrodeposition of different metals etc.

Ion selective electrodes

In the case of ion selective electrodes, by merely combining two half cells, one of which contains a suitable electrode dipped in the solution of an unknown concentration, the measured electrode potential can lead to the quantitative detection of ions. Furthermore, since the standard reduction cell potential varies with the analytes, simultaneous as well as selective detection is made possible.

<u>Thermodynamic functions from e.m.f measurements</u>

As mentioned earlier, the change in the Gibbs free energies are given by the equations

$\Delta G = -nFE$ and $\Delta G^0 = -nFE^0$,

Hence it follows that by measuring EMF of a cell at various temperatures, the thermodynamic parameters ΔG°, ΔH° and ΔS° can be effortlessly estimated. The energy costs are related closely to the cell voltage. The specific energy (Joules per unit weight) can be obtained using

$$w(Jg^{-1}) = \frac{z.F.E_{cell}}{n.M}$$

where z denotes the valence of the species and M is the (atomic or molecular)weight of the reactants, with n being the number of electrons.The above eqn assumes 100% efficiency of the faradaic reaction.

Consider the reduction reactions and corresponding standard electrode potentials

$A + ne^- = B$ $(E^o_{A/B})$

and

$B + me^- = C$ $(E^\circ_{B/C})$

The standard reduction potential ($E^\circ_{A/C}$) for the net cell reaction can be derived in the following manner:

$A + (n+m)e^- = C$

$$\Delta G^0_{A/C} = \Delta G^0_{A/B} + \Delta G^0_{B/C}$$

$$\Delta G^0_{A/C} = -(n+m)FE^0_{A/C}$$

$$\Delta G^0_{A/B} = -nFE^0_{A/B}$$

$$\Delta G^0_{B/C} = -mFE^0_{B/C}$$

$$-(n+m)FE^0_{A/C} = -FE^0_{A/B} - mFE^0_{A/B}$$

$$\therefore E^0_{A/C} = \frac{nE^0_{A/B} + mE^0_{B/C}}{n+m}$$

This implies that the calculation of E^0 from the two constituent reactions is dependent upon the precise values of n and m. We note that $E^0_{A/C}$ is a **weighted arithmetic mean of $E^0_{A/B}$ and $E^0_{B/C}$**

pH measurements

Since the measured potential depends upon the logarithm of activity (or concentrations) even extremely small analyte concentrations can be measured. The glass electrode, often employed for pH measurements has the lowest detection limit as picomolar. However such ion-selective electrodes (or potentiometric sensors) suffer from the limitation of interfering ions which also yield a potential response.

There are several methods of obtaining the hydrogen ion activities of the solutions. One of the most facile methods consists in constructing two different cells as given below:

The potential E(X) and E (S) of the following electrochemical cells are measured at 298K.

$$-ve\ \mathrm{Pt,H_2}(g, 1\ atm)|\text{unknown pH (solution X) | SCE } + \text{ve}$$

$$-\ \text{ve Pt,H}_2\text{(g, 1 atm) known pH (solution S) SCE} + \text{ve}$$

$$E(X) = E(SCE) - (RT/F)\ln\,[a(H_3O^+)_X] + LJP(X)$$

$$E(S) = E(SCE) - \frac{RT}{F} ln\,[a(H_3O^+)_S] + LJP(S)$$

Assuming that LJP(X) and LJP(S) values are nearly identical,

$$E(X) - E(S) = \frac{RT}{F} ln\ \ a(H_3O^+)_S - \frac{RT}{F} ln\ \ a(H_3O^+)_X$$

$$= \frac{2.303\ RT}{F}[pH(X) - pH(S)]$$

$$\text{pH}(X) = \text{pH}(S) + \frac{F[E(X) - E(S)]}{2.303\ \text{RT}}$$

Equilibrium constants

The estimation of equilibrium constants using standard electrode potential data is a straight-forward exercise, *albeit* with the help of standard Gibbs free energies. For example, the Gibbs free energies for the two electron transfer reactions are as follows:

$Ox_1 + n_1\,e^- \longrightarrow Red_1 \quad \Delta G^\circ_1 = -n_1FE_1^\circ$

$Red_1 + n_2\,e^- \longrightarrow Red_2 \quad \Delta G^\circ_2 = -n_2FE_2^\circ$

The subtraction yields

$Ox_1 + Red_2 \longrightarrow 2Red_1 \quad \Delta G^\circ_3 = -\,(n_1 - n_2)\,FE_3^\circ$

$$\Delta G_1^0 - \Delta G_2^0 = \Delta G_3^0$$

Substituting Eqns (29) and (30) in Eqn (31)

$$-n_1 F E_1^0 + n_2 F E_2^0 = (n_1 - n_2) F E_3^0$$
$$= RT\ ln\ K_{eq}$$

$$ln\ K_{eq} = \frac{n_1 F E_1^{\circ} - n_2 F E_2^{\circ}}{RT}$$

Thermodynamic equilibrium constants

The estimation of the true and apparent equilibrium constants can be illustrated using the following example:

$$Fe^{2+} + Ag^{+} \rightleftarrows Fe^{3+} + Ag(s)$$

$$E^{\Theta}(cell) = \frac{RT}{F} ln\ \ K_{therm} = \frac{RT}{F} ln\ \ \left(\frac{a(Fe^{3+})}{a(Fe^{2+})a(Ag^{+})}\right)_e$$

$$= E^{\Theta}\left(Ag^{+}, Ag\right) - E^{\Theta}\left(Fe^{3+}, Fe^{2+}\right)$$

The value of K_c depends upon the equilibrium *concentrations* of Fe^{2+}, Fe^{3+} and Ag^{+} while the thermodynamic equilibrium constant K_{therm} incorporates the *activity coefficients* in the following manner:

$$K_{therm} = K_c \times \frac{\gamma(Fe^{3+})}{\gamma(Fe^{2+})\gamma(Ag^{+})}$$

Employing the Debye-Hückel limiting law for ionic activity coefficients, a plot of log K_c vs square root of the ionic strength of the solution can yield the thermodynamic(true) dissociation constant.In an analogous manner, the true and apparent dissociation constants of weak electrolytes can be estimated.

ELECTROYSIS OF TYPICAL ELECTROYTES

As mentioned earlier, the galvanic cells serve as energy storage devices while electrolytic cells require supplying energy to a system for bringing about a desired transformation. The rules involved in the analysis of electrochemical cells are far more complex than the study of energy storage devices in so far as the anodic and cathodic reactions depend upon (i) nature

of anodes and cathodes;(ii) quantity of electricity;(iii) conductivity of the medium (iv) solvents and (v) pH of the solution. .Table 5 provides a few typical electrolytic processes

Table 5: Electrolysis of compounds in various solvents, using different working electrodes

Electrolyte or Solute	Solvent	Electrodes	cell reaction
$CuSO_4$	H_2O	Cu	Cu(anodic)------->Cu(Cathodic)
$CuSO_4$	H_2O	Pt	$2CuSO_4 + 2H_2O = 2Cu + 2H_2SO_4 + O_2 \uparrow$
H_2SO_4	H_2O	Pt	$2H_2O = 2H_2 \uparrow + O_2 \uparrow$
H_2SO_4	H_2O	Pb anode	$PbO_2+Pb+2H_2SO_4=2PbSO_4+2H_2O$
K_2SO_4	H_2O	Pt	$2H_2O=2H_2 \uparrow +O_2 \uparrow$
NaOH	H_2O	Pt	$2H_2O=2H_2 \uparrow +O_2 \uparrow$
NaOH	H_2O	Pt anode,Hg,Cathode	$4NaOH+Hg=4Na/Hg+2H_2O$
NaOH	H_2O	Zn anode, C cathode	$2Zn+4NaOH+O_2=2Na_2ZnO_2+2H_2O$
NaOH(molten)	none	Pt	$4NaOH=4Na+2H_2O+O \uparrow$
$NaCl$	H_2O	c anode, Hg cathode	$2NaCl+Hg=2Na/Hg+Cl_2 \uparrow$
$NaCl(molten)$	none	c	$2NaCl=2Na+Cl_2 \uparrow$
Al_2O_3	molten Cryolite	C anode Al cathode	$2Al_2O_3+3C=4Al+3CO_2 \uparrow$
CH_3COOH	H_2O	Pt	$2CH_3COOH=H_2 \uparrow 2CO_2 \uparrow +C_2H_6$

Latimer and Frost Diagrams

One of the important applications of the Latimer and Frost diagrams consists in predicting the species capable of undergoing disproportionation or comproportionation reaction. This is accomplished by ascertaining the compound which is lower in the abscissa in the volt equivalent vs oxidation state diagram.The volt equivalent is essentially – ΔG and hence any species which has more negative ΔG will form as a result of either reaction.

Disproportionation and comproportionation reactions

Disproportionation:

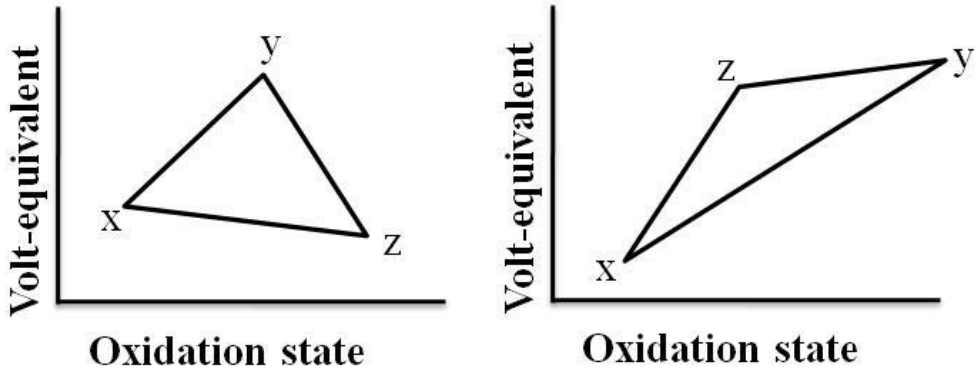
A redox reaction in which a reactant undergoes simultaneous oxidation and reduction.

Comproportionation:

A redox reaction in which an element in a higher oxidation state reacts with the same element in a lower oxidation state to yield the element in an intermediate oxidation state

The volt equivalent vs oxidation state diagram is shown below for comproportionation and disproportionation reactions.

(a) Comproportionation (b)disproportionation



The species lower on the volt equivalent vs oxidation state diagram is more stable and hence in (a) the formation of z is favourable and in (b)the disproportionation of z is more favourable.

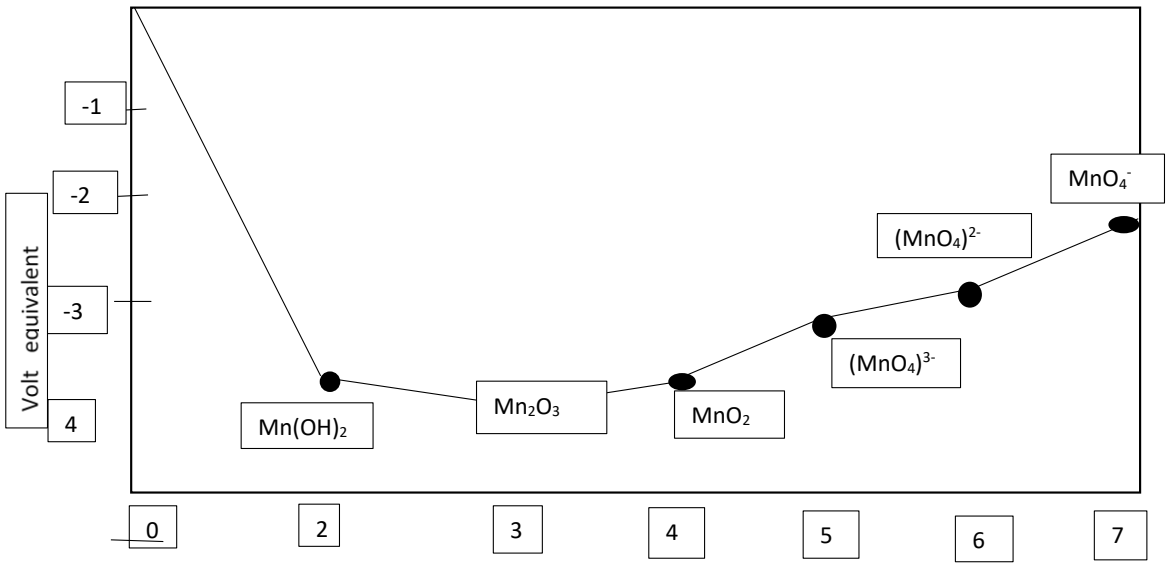
Both Latimer and Frost diagrams essentially contain the same information viz (i) stability of species in acidic and alkaline media; (ii) tendency for disproportionation and comproportionation reactions and (iii) prediction of electrode potentials. While Latimer diagrams represent the standard reduction potentials connecting various oxidation states of an element(Mn, N, P, Cl, Co, Cr etc), Frost diagrams postulate a quantity called the volt equivalent defined as $\Delta G/nF$, where n denotes the number of electrons and F indicates Faraday. By merely looking at the Frost diagram, it is possible to predict the stability of compounds in their respective oxidation states, using the sign of $\Delta G/nF$. The species which appear lower in the Frost diagram has more negative Gibbs free energy and are more stable than those occurring above them .

Illustration of Latimer diagram for Mn

$$MnO_4 \xrightarrow{0.564} MnO_4^{2-} \xrightarrow{0.274} MnO_4^{1-} \xrightarrow{4.27} MnO_2 \xrightarrow{0.95} Mn^{3+} \xrightarrow{1.51} Mn^{2+} \xrightarrow{-1.18} Mn \downarrow$$

Latimer diagram for Mn in various oxidation states

Using such diagrams for elements with varying oxidation states, it is possible to predict the standard reduction potentials for the desired compound.



Consider the line connecting the species MnO_2 and $(MnO_4)^{2-}$. It is easy to notice that the point corresponding to $(MnO_4)^{3-}$ lies above the line. Hence it is inferred that the formation of MnO_2 and $(MnO_4)^{2-}$ from $(MnO_4)^{3-}$ is thermodynamically feasible.

Illustration of Frost diagram for Br_2

The efficacy of Frost diagrams can be illustrated with the redox couple Br_2/Br^-. The standard reduction potential for

$Br_2 + 2\ e^- = 2\ Br^-$ (1.065 V).

The volt equivalent for the above reaction is -1.065.

Analogously, consider the reduction potential for HBrO to Br_2

$2H^+ + 2HBrO + 2\ e^- = Br_2 + 2H_2O$ (1.574V)

The corresponding volt equivalent is -1.574V.

The difference in the potentials is -0.509 V for the reaction

$Br_2 + H_2O = Br^- + H^+ + HBrO$

Since the electrode potential is negative, the volt equivalent is positive. Hence Br_2 will not undergo disproportionation to yield Br^- and HBrO.

Consider the reactions

$$X + e \rightleftarrows Y \quad \text{and } Y + e \rightleftarrows Z \qquad (3.2.25)$$

The disproportionation reaction is

$$2Y \rightleftarrows X + Z, \qquad K = \frac{X_X X_Z}{X_Y^2} \qquad (3.2.26)$$

where K is the equilibrium constant for disproportionation. At equilibrium, the electrode potential E is

$$E = E^0_{X,Y} + \frac{RT}{F} ln \frac{X_X}{X_Y} = E^0_{Y,Z} + \frac{RT}{F} ln \frac{X_Y}{X_Z}$$

Worked out examples

1.Consider the reaction

$$A + 2\ e^- + 2\ H^+ \rightarrow AH_2$$

Estimate the magnitude of (∂E/∂pH) at 298 K in millivolts.

At 298 K, it is possible to write the corresponding Nernst eqn as

$E = E^0 - (0.059/2) \log_{10} [AH_2]/ [A] [H+]^2 = E^0 + 0.059$ pH

Hence the slope (∂E/∂pH) is 59 millivolts.

2.Consider the cell reaction represented as

$$Zn(s) + 2NH_4^+(eq) + 2MnO_2(s) = Zn^{2+}(eq) + 2MnOOH(s) + 2NH_3$$

The standard electrode potential is 1.26V, and the temperature coefficient of the reaction is -0.0012 VK^{-1}. Estimate ΔG°, ΔS°, ΔH° at 298K. What is the thermodynamic efficiency?

$\Delta S° = nF\left(\frac{\partial E}{\partial T}\right)_p = (2)(96500)(-0.0012)$= - 231.6 JK^{-1}

ΔG° = -nFE° = (-2)(96500)(1.26)

= -243.18kJmol^{-1}

$\Delta H^\circ = \Delta G^\circ + T\Delta S^\circ$

= -243.18×1000+ (298)(-231.6)

= -312.19 kJ mol^{-1}

Thermodynamic efficiency = 0.78

3.Consider the following Latimer series for nitrogen:

$$\overbrace{NO_3^- \xrightarrow{0.79V} NO_2 \xrightarrow{1.12V} H\underbrace{NO_2 \xrightarrow{1.00V} NO}}^{x} \underbrace{\xrightarrow{1.59V} N_2O \xrightarrow{1.77V} N_2}_{y}$$

Estimate the potential for the reduction of NO_3^- to NO and HNO_2 to N_2.

(*i*) Using ΔG^0 values, we note that

$$-3FE^0 = -F(0.79+1.12+1.00)$$
$$E^0 = 0.97V$$
$$\therefore x=0.97V$$

(ii) $-3FE^0 = -F(1.00+1.59+1.77)$

$E^0 = 1.12V$

y = 1.12V

4.When one mole of methane was employed in a fuel cell, the thermodynamic efficiency was estimated as 0.92. If the enthalpy change in the reaction was 890 $kJmol^{-1}$, calculate (i)the standard electrode potential of the overall cell reaction and (ii)capacity (in kWh) of 120 cells connected in series when the charge stored is nearly 10^6 coulombs

(i) Thermodynamic efficiency is given by the ratio between ΔG^0 and ΔH^0. Hence

$$0.92 = \frac{\Delta G^0}{\Delta H^0} = \frac{\Delta G^0}{-890kJ/mol}$$

$$\Delta G^0 = -818.8kJ/mol$$
$$-nFE^0 = (-8)(96500cmol^{-1})E_0$$
$$E^0 = 1.06V$$

(ii) Capacity of 120 cells in series = 127.2 x 10^6 J = 35.33 kWh

5.The standard reduction potentials are given below

Zn^{2+}/Zn $\Delta E^0 = -0.76V$
Cu^{2+}/Cu $\Delta E^0 = +0.34V$
Ag^+/Ag $\Delta E^0 = 0.80V$
Mg^{2+}/Mg $\Delta E^0 = -2.37V$

Construct the cell which yields the most spontaneous reaction as well as indicate the polarity of the cell.

Since $\Delta G^\circ = -nFE^\circ$, the most positive value from the two half cells should be chosen.

Hence $Mg|Mg^{2+}||Ag^+|Ag$ is suitable

The double vertical line denotes the salt bridge, essential to minimise the liquid junction potential. The positive pole corresponds to Ag/Ag+ half cell.

6.Using H+ or OH-, balance the following eqn

$x[Cr_2O_7]^{2-} + yI_2 + z[H^+] = x1[Cr]^{3+} + y1[IO_3]^- + z1[H_2O]$

and write the Nernst eqn for the cell reaction.

It is easy to see that for dichromate ions, the required reaction is

$$Cr_2O_7^{2-} + 14H^+ + 6e^- = 2Cr^{3+} + 7H_2O$$

The other reaction involves the oxidation of I_2 to IO_3^-

$I_2 + 6H_2O = 2IO_3^- + 12H^+ + 10e^-$

Upon cancelling the number of electrons for both reduction and oxidation, the balanced reaction is

$5Cr_2O_7^{2-} + 34H^+ + 3I2 = 10Cr^{3+} + 6IO_3^- + 17\,H_2O$

Nernst eqn can be written as

E = $E^{\theta}(cell) - \frac{RT}{30F} ln\ \ Q$

where

Q = $[Cr^{3+}]^{10}[IO_3^-]^6 / Cr_2O_7^{2-}]^5 [H^+]^{34} [I_2]^3$

7.The following values are the standard reduction potentials with respect to the same reference electrode in non-aqueous solvents. Identify the most suitable oxidant using this data:

Reactant	Reduction potential (V)
(a) O_2	-0.8
(b) I_2	+0.7
(c) 1,4 benzoquinone	-0.5
(d) tetra cyanoquinodimethane	+0.2

The most suitable oxidant will have most negative reduction potential. Hence O_2 is the best oxidant Ans: (a)

8.Calculate ΔG^0 for the complexation reaction

$Zn^{2+} + 4NH_3 \longrightarrow [Zn(NH_3)_4]^{2+}$

using $E^{\circ}_{Zn2+/Zn}$ = -0.763 V and $E^{\circ}[_{Zn(NH3)4}]^{2+}/_{Zn}$ = -1.03 V

A complete cell where the above reaction occurs should be constructed from two appropriate half cells.

Zn^{2+} (aq) + $2e^-$ = Zn(s) E° = -0.763V

$[Zn(NH_3)_4]^{2+} + 2e^-$ = Zn(s) + $4NH_3$ E = -1.030 V

The net cell reaction is

$Zn^{2+}(aq) + 4NH_3 = [Zn(NH_3)_4]^{2+}$ $E^{\circ} = E_R - E_L$ = 1.030V- 0.763V = 0.267V

$\Delta G^{\circ} = -nFE^{\circ} = -RT \ln K$

ΔG° = -(2)(96500)(0.267)

= - 51.531 $kJmol^{-1}$

9.The standard reduction potential of NO_3^- to NO_2^- in acidic solution is 0.955V while its value is 0.015V in alkaline solutions. Estimate the apparent dissociation constant of HNO_2 using the ionic product of water as 10^{-14}

$$NO_3^- + 3H^+ + 2e^- \rightarrow HNO_2 + H_2O \quad E^0 = 0.955V$$

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^- \quad E^0 = 0.015V$$

$$\Delta G_2^0 - \Delta G_1^0 = +(2)(F)(0.955V) - (2)(F)(0.015V)$$

This value corresponds to the reaction

$$2H_2O + HNO_2 \rightarrow 3H^+ + NO_2^- + 2OH^-$$

The above eqn can be written as,

$$2H_2O \rightarrow 2H^+ + 2OH^- \quad K_w = 10^{-14}$$

$$and$$

$$HNO_2 \rightarrow H^+ + NO_2^- \qquad K_a = ?$$

Hence

$$2 \times 96500C \times 0.955V - (2)\ (96500\text{C})\ (0.015\text{V})$$

$$= -2\text{RTln}K_w - RT\ \ ln\ Ka$$

$$\frac{(2F)(.955V) - 2F(0.015V)}{RT} = -2\ ln\ K_w - ln\ K_a$$

$$\left(\frac{F}{RT}\right)(1.88V) = -2\ ln(10^{-14}) - ln\ K_a$$

$$\frac{1.88}{0.02569} + 2\ (-32.236) = -\ ln\ K_a\ ;\ ln\ K_a = -8.708$$

Apparent dissociation constant= Ka =1.65×10^{-4}

10.Estimate the solubility product of Ag_2CrO_4 using the appropriate standard reduction potentials.

The solubility product of Ag_2CrO_4 can be estimated using the cell

$Ag|Ag+, CrO_4^{2-}|| Ag_2CrO_4 |Ag$

r h s $Ag_2CrO_4 + 2e^- = 2Ag + CrO_4^{2-}$ $E^0 = 0.447$; $\Delta G^0 = -2F(0.447)$

l h s $2Ag^+ + 2e^- = 2Ag$ $E^0 = 0.799$; $\Delta G^0 = -2F(0.799)$

r h s – l h s yields

$Ag_2CrO_4 = 2Ag^+ + CrO_4^{2-}$ ΔG^0 (cell reaction) = -2F (0.447-0.799) = -2F(-0.352)

$\Delta G^0 = - RT \ln (K_{sp}) = +0.704F$

$\ln (K_{sp}) = - (F/RT)(0.704) = -(0.704/0.0256)$.

K_{sp} of $Ag_2CrO_4 = 1.13 \times 10^{-12}$

11.The cell potential is measured in a galvanic cell as 0.75 V vs SHE.

What will be the potential if the reference electrode is changed to SCE (the potential of SCE is 0.244V vs SHE)?

E (vs E Ref 2) = E (vs E Ref 1) + ERef 1- E Ref2 = 0.75 +0 -0.244 = 0.506V

12.From one mole of Ni_2O_3 in the Edison storage cell, the electrical energy released is 245.11 KJ

If the standard reduction potential of

Ni_2O_3 (s) + H_2O (l) + $2e^-$ + 2 NiO (s) + $2OH^-$ is 0.4V, estimate E°_{red} of the half-cell Fe/FeO/KOH

Since the electrical energy released is 24.511 KJ/mol, we can write

$\Delta G^o = -nFE^o$

$-245.11\ kJmol^{-1} = -(2)(96500)VC\ mol^{-1}E^o$

$\therefore E^o_{Cell} \sim 1.27V$

$E^o_{Cell} = E^o_{right} - E^o_{left}$

1.27V = 0.4 V- E^o_{left}

$\therefore E^o_{left}$ = -0.87V

$\therefore E^o_{Fe/FeO/KOH}$ = -0.87V

13.In the bulk electrolysis of $[Ru(NH_3)_6]^{3+}$ to $[Ru(NH_3)_6]^{2+}$ using graphite electrodes, a potential of 0.32V vs SHE was applied for a duration of 300 minutes. If the initial concentration of $[Ru(NH_3)_6]^{3+} is\ 0.015M$, estimate (i)the final concentration of $[Ru(NH_3)_6]^{3+}$ and (ii) mass transfer rate constant (in cm sec $^{-1}$). The diffusion coefficient of the reactant is 10^{-5} cm^2 sec $^{-1}$ while the diffusion layer thickness is 0.01 cm. ($E^0_{[Ru(NH_3)6]^{4+/3+}} = 0.10V$).

$$(i) \quad [Ru(NH_3)_6]^{3+} + e^- \rightarrow [Ru(NH_3)_6]^{2+}$$

$$E = E^0 - \frac{RT}{F} \ln \frac{[Ru(NH_3)_6]^{2+}}{[Ru(NH_3)_6]^{3+}}$$

$$0.32 = 0.10 - .0257 \ln \frac{[Ru(NH_3)_6]^{2+}}{0.015}$$

$$\ln \left[\frac{[Ru(NH_3)_6]^{2+}}{.015}\right] = -\frac{0.22}{0.0257}$$

$$\left[Ru(NH_3)_6{}^{2+}\right] = 2.87 \times 10^{-6} M$$

Final concentration of the reactant = 0.01499 M

mass transfer rate constant = Diffusion coefficient/ diffusion layer thickness = 10^{-7} cm sec $^{-1}$

14.Indicate the cathodic and anodic reactions arising in the chlor-alkali process.

The electrolysis of brine (NaCl solutions) is employed in chlor-alkali industry in order to produce Cl_2 (g) (at cathode) , H_2 (g) at anode and NaOH solution.

15.Among the following, which is true for the glass electrodes?

(i) Not suitable for pH < 7

(ii) Suitable for all pH values

(iii) Not suitable for pH > 7

(iv) Not suitable for weak electrolytes

Answer (iii)

16.The following Latimer diagram for Mn is acidic solutions is well known:

$$\underline{MnO_4 \xrightarrow{0.564} MnO_4^{2-} \xrightarrow{0.274} MnO_4^{1-} \xrightarrow{4.27} MnO_2} \xrightarrow{0.95} Mn^{3+} \xrightarrow{1.51} Mn^{2+} \xrightarrow{-1.18} Mn$$

Estimate the potential corresponding to the reduction of Mn^{7+} to Mn^{2+}.

$$E^0_{Mn^{7+}/Mn2+} = \frac{0.564 + 0.274 + 4.27 + 0.95 + 1.51}{5} = 1.51\text{V}$$

17.Which of the following is correct regarding the experimentally observed equilibrium constant? It is a measure of the difference between

(a) Volta potentials
(b) Work functions
(c) Galvani potentials
(d) Surface potentials

Answer (c)

Exercises

1.Estimate the absolute redox potential of the standard hydrogen electrode.

2. What are the requirements for a system to be chosen as a reference electrode?

3. Using an illustrative example, describe the estimation of the mean ionic activity coefficients of electrolytes using Nernst equations.

4. Distinguish between true and apparent solubility products.

Summary

The salient features of Nernst equation are pointed out.

Typical applications of Nernst equation were highlighted.

The significance of Latimer and Frost diagrams is indicated.