Chapter Two

2. Electrochemical Cells

2.1. Introduction

An **electrochemical cell** consists of two **electrodes**, or metallic conductors, in contact with an **electrolyte**, an ionic conductor (which may be a solution, a liquid, or a solid). An electrode and its electrolyte comprise **an electrode compartment**. The two electrodes may share the same compartment.

If the electrolytes are different, the two compartments may be joined by a **salt bridge**, which is a tube containing a concentrated electrolyte solution (for instance, potassium chloride in agar jelly) that completes the electrical circuit and enables the cell to function. Electrochemical cells mainly classified as **Galvanic cell** and **Electrolytic cell**. A **galvanic cell** is an electrochemical cell that produces electricity as a result of the spontaneous reaction occurring inside it. An **electrolytic cell** is an electrochemical cell in which a non-spontaneous reaction is driven by an external source of current.

Half-reactions and electrodes

A redox reaction is expressed as the difference of two reduction half-reactions; each one defines a redox couple.

oxidation is the removal of electrons from a species, a **reduction** is the addition of electrons to a species, and a **redox reaction** is a reaction in which there is a transfer of electrons from one species to another.

The **reducing agent** (or *reductant*) is the electron donor; the **oxidizing agent** (or *oxidant*) is the electron acceptor. It should also be familiar that any redox reaction may be expressed as the difference of two reduction **half-reactions**, which are conceptual reactions showing the gain of electrons.

Even reactions that are not redox reactions may often be expressed as the difference of two reduction half-reactions. The reduced and oxidized species in a half-reaction form a **redox couple**.

In general, a couple as Ox/Red and the corresponding reduction half-reaction can be write as

$$Ox + ve^- \rightarrow Red$$

Example

a) The dissolution of silver chloride in water $AgCl(S) \rightarrow Ag^{+}(S) + Cl^{-}(aq)$, which is not a redox reaction, can be expressed as the difference of the following two reduction half-reactions:

$$AgCl(S) + e^{-} \rightarrow Ag(S) + Cl^{-}(aq)$$

$$Ag^{+}(aq) + e^{-} \rightarrow Ag(S)$$

The redox couples are $AgCl/Ag\,, Cl^{-}\ and\ Ag^{+}/Ag$, respectively.

b) Express the formation of $H_2O\ from\ H_2\ and\ O_2$ in acidic solution (a redox reaction) as the difference of two reduction half-reactions

Answer - $4H^{+}(aq) + 4e^{-} \rightarrow 2H_2(g),\ O_2(g) + 4H^{+}(aq) + 4e^{-} \rightarrow 2H_2O(l)]$

The reduction and oxidation processes responsible for the overall reaction in a cell are separated in space: oxidation takes place at one electrode and reduction takes place at the other. As the reaction proceeds, the electrons released in the oxidation ($Red_1 \rightarrow Ox_1 + \nu e^-$) at one electrode travel through the external circuit and re-enter the cell through the other electrode. There they bring about reduction ($Ox_2 + \nu e^- \rightarrow Red_2$).

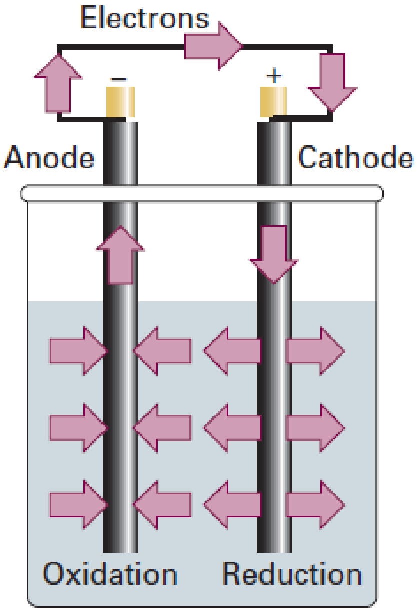


Fig.2.1 *When a spontaneous reaction takes place in a galvanic cell, electrons are deposited in one electrode (the site of oxidation, the anode) and collected from another (the site of reduction, the cathode), and so there is a net flow of current, which can be used to do work. Note that the + sign of the cathode can be interpreted as indicating the electrode at which electrons enter the cell, and the –sign of the anode as where the electrons leave the cell.*

The electrode at which oxidation occurs is called the **anode**; the electrode at which reduction occurs is called the **cathode**. In a galvanic cell, the cathode has a higher potential than the anode: the species undergoing reduction, Ox_2, withdraws electrons from its electrode (the cathode), so leaving a relative positive charge on it (corresponding to a high potential). At the anode, oxidation results in the transfer of electrons to the electrode, so giving it a relative negative charge (corresponding to a low potential).

2.2. Reversible electrodes

Reversible electrode is a metallic electrode that will dissolve when a current is passed from it into a solution and that will have plated on it metal from the solution when the current is passed in the reverse direction. Electrodes in a reversible cell are necessarily reversible electrodes. Seven types of such electrodes are frequently used.

1. Metal – Metal ion Electrode; A metal in contact with a solution that contains its ions. It is the simplest type electrode. Such electrodes are generally represented by M/Mn^+ and the equilibrium that is established is

$$M \rightarrow M^{+n} + ne^- \text{ (Oxidation)}$$

Example,

$$Zn/Zn^{+2}(aq) \qquad Zn \rightarrow Zn^{+2} + 2e^-$$

$$Cu/Cu^{+2}(aq) \qquad Cu \rightarrow Cu^{+2} + 2e^-$$

$$\mathrm{Al}/Al^{+3}(aq) \qquad Al \rightarrow Al^{+3} + 3e^-$$

Note:- In this case the value of electrode potential depends on activity of metal ions. Zn in zinc sulphate solution, Cu in copper sulphate solution, etc are the examples. The electrodes are reversible with respect to the respective ions (Mn^+),

2. Metal sparingly soluble salt electrode: In this case the metal and its sparingly soluble salt is in contact with the electrolyte which contains same ions. E.g.

$$Ag, AgCl^-(s)Cl^- \qquad Ag + Cl^- \rightarrow AgCl(s) + e^-$$

$$Hg, Hg_2Cl_2(s)Cl^- \qquad Hg + Cl^- \rightarrow \frac{1}{2}Hg_2Cl_2(s) + e^-$$

Note:- The potential value of this electrode also depends on the activity of ions (Cl^-)

3. Gas electrode: There are several types of glass electrodes like hydrogen gas electrode, chlorine gas electrode, oxygen gas electrode etc. In case of hydrogen gas electrode, H_2 gas is bubbled through H^+ ion solution e.g. HCl and for electrical contact we insert platinium (Pt)

wire which is the inert metal in electrochemistry. Hydrogen gas electrode on paper is written as Pt, $H_2|H^+(aq)$ for oxidation, the reaction is

$$\frac{1}{2}H_2 \rightleftharpoons H^+ + e^-$$

The potential of this electrode depends on the pressure of hydrogen gas and the activity of H^+ ions.

4. Metal-Insoluble oxide of metal electrode: The electrode is obtained when metal and its insoluble oxide is in contact with OH^- ions.

Example

$Fe, FeO(s)\backslash OH^-(aq)$,

$$Fe + 2OH^- \rightleftharpoons FeO\ (s) + H_2O + 2e^-$$

$Sb, Sb_2O_3(s)\backslash OH^-(aq)$,

$$2Sb + 3OH^- \rightleftharpoons \frac{1}{2}Sb_2O_3 + \frac{3}{2}H_2O + 3e^-$$

$Pt, Mn_2O_3(s), Mn)O_2\backslash OH^-(aq)$,

$$Mn_2O_3 + 2OH^- \rightleftharpoons 2MnO_2(s)\ H_2O + 2e^-$$

5. Redox electrode: When two different oxidation state of same element are present in the same solution and if we insert a Pt wire for electrical contact redox electrode s formed, and potential developed across the Pt wire is known as Redox electrode potentioal.

Example

Pt, Fe^{+2}, Fe^{+3},

$$Fe^{+2} \rightleftharpoons Fe^{+3} + e^-$$

Pt, Sn^{+2}, Sn^{+4},

$$Sn^{+2} \rightleftharpoons Sn^{+4} + 2e^-$$

In this case the electrode potential depends on the ratio of the activity of ions in the oxidation and reduction state of metal.

2.3. Thermodynamics of electrochemical cells

In thermodynamics usually work defines in terms of pressure-volume work. But for work involving charges, the definition is different. The infinitesimal amount of electrical work, dw_{elect} is defined as the infinitesimal change in amount of charge,dQ, moving through some electric potential $\emptyset$:

$$dw_{elect} \equiv \emptyset \cdot dQ \tag{2.1}$$

Now considering to this kind of new work, this as part must include in the total change of internal energy under the first law of thermodynamics. That is, the infinitesimal change in the internal energy is now

$$dU = dw_{pv} + dq + dw_{elect} \tag{2.2}$$

This is not a *change* in the definition of internal energy. It is simply including another type of work. Other types of non-pV work include not just electrical (that is, potential-charge), but also surface tension–area, gravitational-mass, centrifugal-mass, and others. However, in this chapter, only electrical work will be considered.

Electrical work is performed by the movement of electrons, which are the charged particles that move around in the course of chemical reactions. Ions that have a positive charge of +z therefore represent $z \cdot F$ of positive charge per mole of ions, and ions having a negative charge of - z represent -$z \cdot F$ of negative charge per mole.

The infinitesimal change in charge dQ is related to the infinitesimal change in moles of ions, dn (where n is the number of moles of ions). Using the expressions from the previous paragraph, it can be stated as

$$dQ = z \cdot f \cdot dn \tag{2.3}$$

Substituting this expression for dQ into equation 2.1, the infinitesimal amount of work is

$$dw_{elect} = \emptyset \cdot z \cdot f \cdot dn \tag{2.4}$$

For multiple ions, the amount of work required to change the number of charged species labeled with an i subscript is

$$dw_{elect} = \sum_i \emptyset_i \cdot z_i \cdot f \cdot dn_i \tag{2.5}$$

In a system where there is a transfer of charge, the number of species having any particular charge is changing, dn_i, is not zero. Therefore, the infinitesimal change in *G* could be modified as the natural variable equation for *G*, given by

$$dG = -SdT + Vdp + \sum_i \mu_i dn_i \qquad (2.6)$$

to include the change in work due to the electric charges.

$$dG = -SdT + Vdp + \sum_i \mu_i dn_i + \sum_i \emptyset_i \cdot z_i \cdot f \cdot dn_i \qquad (2.7)$$

Under conditions of constant temperature and pressure, this equation becomes

$$dG = \sum_{ik} \mu_i dn_i + \sum_i \emptyset_i \cdot z_i \cdot f \cdot dn_i \qquad (2.8)$$

Rearranged algebraically

$$dG = \sum_i (\mu_i + \emptyset_i \cdot z_i \cdot f) dn_i \qquad (2.9)$$

If the quantity inside the parentheses redefines

$$\mu_{i,el} \equiv \mu_i + \emptyset_i \cdot z_i \cdot f \qquad (2.10)$$

Then

$$dG = \sum_i \mu_{i,el} \cdot dn_i \qquad (2.11)$$

$\mu_{i,el}$ is called the *electrochemical potential*, rather than the chemical potential. For electrochemical equilibrium, the equation analogous to $\sum \mu_i v_i = 0$ is

$$\sum_i n_i \cdot \mu_{i,el} = 0 \qquad (2.12)$$

This is the basic equation for electrochemical equilibrium.

Any reaction that involves a transfer of charge (that is, electrons) is an oxidation reduction reaction, or *redox* reaction. Because an oxidation process and a reduction process always occur together. The overall process is the sum of the two individual reactions (Hess's-law approach). Species A is being oxidized; the general chemical reaction can be represented as

$$A \rightarrow A^{n+} + ne^{-} \qquad (2.13)$$

where species A has lost *n* electrons, symbolized ne^{-}. Species B is being reduced. The general chemical reaction for this can be represented as

$$B^{n+} + ne^{-} \rightarrow B \qquad (2.14)$$

The overall chemical reaction is

$$A + B^{n+} \rightarrow A^{n+} + B \qquad (2.15)$$

Keeping in mind that the n_i values are negative for the reactants and positive for products, the above equation becomes

$$0 = \mu_{A^{n+},el} + \mu_{B,el} - \mu_{A,el} - \mu_{B^{n+},el} \qquad (2.16)$$

Using equation 2.10, and recognizing and requiring the same charge *n* on the ionic species, then

$$0 = \mu_{A^{n+}} + \mu_{B} - nf\emptyset_{ox} - \mu_{A} - \mu_{B^{n-}} + nf\emptyset_{red} \qquad (2.17)$$

Labeling each *f* as the potential from either the oxidation reaction ("ox") or the reduction reaction ("red"). The first ∅ term is negative and the second ∅ term is positive because *z*, the charge on electrons present in equation 2.10, is –1. The second ∅ term thus becomes positive because of two negative signs. Because the species A and B have no charge, there is no electrical work term (that is, equation 2.5 on their chemical potentials and so no *nF*∅ term associated with them.

The oxidation and reduction electric potential terms do *not* cancel from equation 2.17. The electric potential of A^{n+} is not going to be the same as the electric potential from B^{n+}.

Rearranging equation 2.17:

$$\left.\begin{aligned} nF\emptyset_{ox} - nF\emptyset_{red} &= \mu_{A^{n+}} + \mu_B - \mu_A - \mu_{B^{n+}} \\ nF(\emptyset_{ox} - \emptyset_{red}) &= \mu_{A^{n+}} + \mu_B - \mu_A - \mu_{B^{n+}} \end{aligned}\right\} \quad (2.18)$$

By convention, by substituting $(\emptyset_{red} - \emptyset_{ox})\, for\, (\emptyset_{ox} - \emptyset_{red})$ the left side of the equation rewrite as

$$-nF(\emptyset_{red} - \emptyset_{ox}) = \mu_{A^{n+}} + \mu_B - \mu_A - \mu_{B^{n+}} \qquad (2.19)$$

All of the terms on the right side of equation 2.19 are constant for a given state (pressure, temperature, and so on) of a system. Therefore, the entire right side of equation 2.19 is a constant. This means that the left side of equation 2.19 must be constant. The variables *n* and *F* are constants for the chemical reaction. Therefore, the expression $(\emptyset_{red} - \emptyset_{ox})$must also be a constant for the reaction. The *electromotive force, E,* defined as the difference between the reduction reaction's electric potential and the oxidation reaction's electric potential:

$$E \equiv \emptyset_{red} - \emptyset_{ox} \qquad (2.20)$$

Because $\emptyset$ values are expressed in units of volts, electromotive forces are expressed in units of volts. EMF stands for electromotive force. But EMFs are not true "forces" in the scientific sense. Rather, they are changes in electric potential.

Equation 2.19 becomes

$$-nFE = \mu_{A^{n+}} + \mu_B - \mu_A - \mu_{B^{n+}} \qquad (2.21)$$

Now consider the right side of equation 2.21. It is the chemical potential of the products minus the chemical potential of the reactants. This equals the change in the Gibbs energy of the reaction, $\Delta_{rxn}G$. Equation 2.21 can be rewritten as

$$\Delta_{rxn}G = -nFE \qquad (2.22)$$

Under standard conditions of pressure and concentration, this is

$$\Delta_{rxn}G^{o} = -nFE^{o} \tag{2.23}$$

This is the basic equation for relating changes in electric potential with changes in energy. This equation also takes advantage of the definition that 1 J = 1 V x C. The variable *n* represents the number of moles of electrons that are transferred in the balanced redox reaction. Because completed redox reactions do not usually show the balanced number of electrons explicitly. This might have to figure out from the redox reaction itself.

<u>Notice:-</u>

Summary of spontaneity conditions

If ΔG is	If E is	Then the process is
Negative	Positive	Spontaneous
Zero	Zero	At equilibrium
Positive	Negative	Not spontaneous

E, the difference in electric potentials, is related to the change in the Gibbs energy of the reaction, equation 2.23. Furthermore, if some non-pressure-volume type of work is performed on or by the system, ΔG for that change represents a limit to the amount of non-*pV* work that can be performed:

$$\Delta G \leq w_{non-pV} \tag{2.24}$$

Because electrical work is a type of non-*pV* work, we can state that

$$\Delta G \leq w_{elect} \tag{2.25}$$

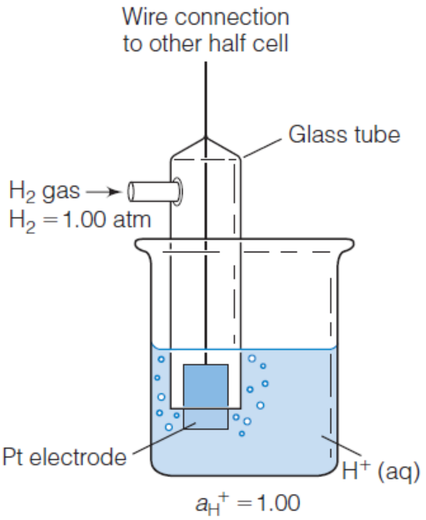
Because work done *by* the system has a negative numerical value and restate equation 2.25 by saying that ΔG for a redox reaction represents the maximum amount of electrical work that the system can do on the surroundings. These extracted with the consideration of oxidation and reduction *half-reactions*.

The two independent, physical systems that contain the reactions are called *half-cells*. The half-cell that contains the oxidation reaction is called the *anode*, and the half-cell containing the reduction reaction is called the *cathode*. The two half-cells together make up a system that, for a spontaneous reaction, is called a *voltaic cell* or *galvanic cell*. All batteries are voltaic cells, Systems in which nonspontaneous reactions are forced to proceed by the intentional introduction of electrons are called *electrolytic cells*. Such cells are used for electroplating metals onto jewelry and metal ware, among other uses. Keep in mind that the calculated value of dG for an electrochemical process represents the maximum amount of electric work that the reaction can do. In reality, less than that maximum is actually extracted. This is a consequence of the less than 100% efficiency of all processes.

2.4 Determination of standard electrode potential

Key point:-The standard potential of a couple is the cell potential in which it forms the right-hand electrode and the left-hand electrode is a standard hydrogen electrode.

A galvanic cell is a combination of two electrodes each of which can be considered to make a characteristic contribution to the overall cell potential. Although it is not possible to measure the contribution of a single electrode, we can define the potential of one of the electrodes as zero and then assign values to others on that basis. The specially selected electrode is the **standard hydrogen electrode** (SHE):



The standard hydrogen electrode.

$$|Pt(S)|H_2(g)|H^+(aq) \qquad E^o = 0 \qquad (2.26)$$

This is called convention standard potential

$$2H^+(aq) + 2e^- \rightarrow H_2(g) \qquad (2.27)$$

To achieve the standard conditions, the activity of the hydrogen ions must be 1 (that is, pH = 0) and the pressure (more precisely, the fugacity) of the hydrogen gas must be 1 bar. The **standard potential**, E^o, of another couple is then assigned by constructing a cell in which it is the right-hand electrode and the standard hydrogen electrode is the left-hand electrode.

The procedure for measuring a standard potential can be illustrated by considering a specific case, the silver chloride electrode. The measurement is made on the 'Harned cell':

$$\left.\begin{array}{c} Pt(s)|H_2(g)|HCl(aq)|AgCl(S)|Ag(S) \\ \\ \frac{1}{2}H_2(g) + AgCl(S) \ \rightarrow HCl(aq) + Ag(S) \\ \\ E^o_{cell} = \ E^i(AgCl/Ag\,, Cl^-) - \ E^o(SHE) = \ E^o(AgCl/Ag\,, Cl^-) \end{array}\right\} \qquad (2.28)$$

For which the Nernst equation is

$$E_{cell} = \ E^o(AgCl/Ag\,, Cl^-) - \frac{RT}{F}\ln\frac{a_{H^+}a_{Cl^-}}{a_{H_2}^{1/2}} \qquad (2.29)$$

But $a_{H_2} = 1$ for simplicity write the standard potential of the $AgCl/Ag\,, Cl^-\ electrode\ as\ E^o, then$

$$E_{cell} = E^o - \frac{RT}{F}\ln a_{H^+}a_{Cl^-} \qquad (2.30)$$

The activities can be expressed in terms of the molality b of HCl(aq) through
$a_{H^+} = \ \gamma_\pm b\ and\ a_{cl^-} = \ \gamma_\pm b.$ So,

$$E_{cell} = \ E^o - \frac{RT}{F}\ln b^2 - \frac{RT}{F}\ln\gamma_\pm^2 \qquad (2.31)$$

Further rearrangement

$$E_{cell} + \frac{2RT}{F}\ln b = \ E^o - \frac{2RT}{F}\ln\gamma_\pm \qquad (2.32)$$

From the Debye–Hückel limiting law for a 1,1-electrolyte , a 1,1-electrolyte is a solution of singly charged M^+ and X^- ions), $\ln\gamma_\pm \propto -b^{1/2} \leftrightarrow \ ln\gamma_\pm = -Cb^{1/2}$. Therefore, with the constant of proportionality in this relation written as (*F*/2*RT*)*C*, the eqn becomes

$$E_{cell} + \frac{2Rt}{F}\ln b \ = \ E^o + Cb^{1/2} \qquad (2.33)$$

The expression on the left is evaluated at a range of molalities, plotted against $b^{1/2}$, and extrapolated to b = 0. The intercept at $b^{1/2} = 0$ is the value of E^o for the silver/silver chloride electrode. In precise work, the $b^{1/2}$ term is brought to the left, and a higher-order correction term from the extended Debye–Hückel law is used on the right.

Table 2.1 lists standard potentials at 298 K.

Couple	E^o/V
$Ce^{4+}\,(aq) + e^- \rightarrow Ce^{3+}\,(aq)$	+1.61
$Cu^{2+}\,(aq) + 2e^- \rightarrow Cu\,(S)$	0.34
$H\,(aq) + e^- \rightarrow \frac{1}{2}H_2\,(g)$	0
$AgCl\,(S) + e^- \rightarrow Ag\,(S) + Cl^-\,(aq)$	+0.22
$Zn^{2+}\,(aq) + 2e^- \rightarrow Zn\,(S)$	-0.76

A practical consequence is that a cell potential is independent of the physical size of the cell. In other words, the cell potential is an intensive property.

Example

Given that the standard potentials of the Cu^{2+}/Cu and Cu^+/Cu couples are +0.340 V and +0.522 V, respectively, evaluate $E^o(Cu^{2+}, Cu^+)$

Method

The reaction Gibbs energies may be added (as in a Hess's law analysis of reaction enthalpies). Therefore, the standard potentials should be converted to Gibbs energies using $\Delta_{rxn}G^o = nFE^o$ and then convert the overall standard Gibbs energy to the standard potential (E^o).

Answer - The electrode reactions are as follows:

$$a)\ Cu^{2+}(aq) + 2e^- \rightarrow Cu(S) \qquad E^o = +0.340\,V, \quad so\ \ \Delta_{rxn}G^0 = -2(0.340\,V)F$$

$$b)\ Cu^{+}(aq) + e^- \rightarrow Cu(S) \qquad E^o = +0.522\,V,\ so\ \ \Delta_{rxn}G^0 = -(0.522\,V)F$$

The required reaction is

$$c)\ Cu^{2+}(aq) + e^- \rightarrow Cu^{+}(aq) \qquad E^o = -\Delta_{rxn}G^0/F$$

Because $(c) = (a) - (b), the\ standard\ Gibbs\ energy\ of\ reaction\ (c) is$
$\Delta_r G^o = \Delta_r G^o(a) - \Delta_r G^o(b) = (-0.158\,V)F$

Therefore, $E^o = +0.158\ V$. Note that the generalization of the calculation we just performed is

$$v_c E^o(c) = v_a E^o(a) - v_b E^o(b)$$

with the v_r the stoichiometric coefficients of the electrons in each half-reaction.

2.5 Applications of standard potentials

a) The electrochemical series

For the redox couples, $Ox_1/Red_{1,}\ and\ Ox_2/Red_2$, and the cell

$$Red_1, Ox_1||Red_2, Ox_2 \qquad E^o_{cell} = E^o_2 - E^2_1 \qquad (2.34)$$

The cell reaction

$$Red_1 + Ox_2 \rightarrow Ox_1 + Red_2 \qquad (2.35)$$

has $k > 1$ as wriiten if $E^0_{cell} > 0, and$ therefore if $E^o_2 > E^o_1$. Because in the cell reaction $Red_1\ reduces\ Ox_2$ and this can be conclude as Red_1 has a thermodynamics tendency (in the sense $k > 1$) to reduce Ox_2 if $E^o_1 < E^o_2$

Example

$E^o(Zn^{2+}, Zn) = -0.76V < E^o(Cu^+, Cu) = +0.34V$ the reduction of Cu^{2+} by Zn is a reaction with $K > 1$, so zinc has a thermodynamic tendency to reduce Cu^{2+} ions in aqueous solution under standard conditions.

Note:- A metal low in the series (with a lower standard potential) can reduce the ions of metals with higher standard potentials.

b) The determination of activity coefficients

Once the standard potential of an electrode in a cell is known, It is possible to determine the mean activity coefficients by measuring the cell potential with the ions at the concentration of interest. Thus, the mean activity coefficient of the ions determined using the equation below if once the E_{cell} and the molality b is known

$$\ln \gamma_{\pm} = \frac{E^o - E_{cell}}{2RT/F} - lnb \qquad (2.36)$$

(c) The determination of equilibrium constants

The principal use for standard potentials is to calculate the standard potential of a cell formed from any two electrodes. To do so, we subtract the standard potential of the left-hand electrode from the standard potential of the right-hand electrode:

$$E^o_{cell} = E^o(right) - E^o\ (left) \qquad (2.37)$$

Because $\Delta_r G^o = -vFE^o_{cell}$, it then follows that, if the result gives $E^0_{cell} > 0$, then the corresponding cell reaction has $k > 1$.

The use the following equation

$$lnK = \frac{vFE^0_{cell}}{RT} \qquad (2.38)$$

<u>Example</u>

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

Right-hand electrode:

$$Cu(S)|Cu^{+}(aq) \qquad Cu^{+}(aq) + e^{-} \rightarrow Cu(aq) \qquad E^o = +0.52\ V$$

Left-hand electrode:

$$Pt(S)|Cu^{2+}(aq), Cu^{+}(aq) \quad Cu^{2+}(aq) + e^{-} \rightarrow Cu^{+}(S) \quad E^o = +0.16$$

The standard potential of the cell is therefore

$$E^0_{cell} = +0.52\ V - 0.16\ V = +0.36\ V$$

Thus, the equilibrium constant of the cell reaction calculated as follows since $v = 1$.

$$\ln K = \frac{0.36\ V}{0.025\ 693\ V} = \frac{0.36}{0.025693} \Leftrightarrow k = 1.2\ x\ 10^6$$

(d) The determination of thermodynamic functions

The standard potential of a cell is related to the standard reaction Gibbs energy through $\Delta_r G^o = -vFE^o_{cell}$, Therefore, by measuring E^o_{cell} cell this important thermodynamic quantity can be obtained. Its value can then be used to calculate the Gibbs energy of formation of ions. The temperature coefficient of the standard cell potential, dE^o_{cell}/dT, gives the standard entropy of the cell reaction. This conclusion follows from the thermodynamic relation $(\partial G/\partial T)_p = -S$ and $E^o_{cell} = -\frac{\Delta_r G^o}{vF}$, which combine to give

$$\frac{dE^o_{cell}}{dT} = \frac{\Delta_r S^o}{vF} \qquad (2.39)$$

The derivative is complete (not partial) because E^o, like $\Delta_r G^o$ is independent of the pressure. Hence an electrochemical technique is used for obtaining standard reaction entropies and through them the entropies of ions in solution. Finally, the results obtained so far combined and use them to obtain the standard reaction enthalpy:

$$\Delta_r H^o = \Delta_r G^o + T\Delta_r S^o = -vF\left(E^o_{cell} - T\frac{dE^o_{cell}}{dT}\right) \qquad (2.40)$$

This expression provides a non-calorimetric method for measuring $\Delta_r H^o$ and, through the convention $\Delta_f H^o(H^+, aq) = 0$, the standard enthalpies of formation of ions in solution. Thus, electrical measurements can be used to calculate all the thermodynamic properties.

Example

The standard potential of the cell $Pt(S)|H_2(g)|HBr(aq)|AgBr(S)|Ag(S)$ was measured over a range of temperatures, and the data were found to fit the following polynomial:

$$E^o_{cell}/V = 0.07131 - 4.99\ x\ 10^{-4}(T/K - 298) - 3.45\ x\ 10^{-6}(T/K - 298)^2$$

The cell reaction is $AgBr(S) + \frac{1}{2}H_2(g) \rightarrow Ag(S) + HBr(aq)$. Evaluate the standard reaction Gibbs energy, enthalpy, and entropy at 298 K. The standard Gibbs energy of reaction is obtained by using $E^o_{cell} = -\frac{\Delta_r G^o}{vF}$ after evaluating E^o_{cell} at 298 K and by using 1 V ·C = 1 J. The standard entropy of reaction is obtained by using

$$\frac{dE^o_{cell}}{dT} = \frac{\Delta_r S^o}{vF}$$

which involves differentiating the polynomial with respect to T and then setting T = 298 K. The reaction enthalpy is obtained by combining the values of the standard Gibbs energy and entropy.

Answer

At T = 298 K, $E^o_{cell} = +0.07131\ V$, So

$$\Delta_r G^o = -\nu F E^o_{cell} = -(1)x\ (9.6485\ x\ 10^4\ Cmol^{-1})x(+0.07131\ V)$$

$$= -\ 6.880\ KJ\ mol^{-1}$$

The temperature coefficient of the cell potential is

$$\frac{dE^o_{cell}}{dT} = -4.99\ x\ 10^{-4}\ VK^{-1} - 2(3.45\ x\ 10^{-6})(T/K - 298)VK^{-1}$$

At T = 298 K this expression evaluates to

$$\frac{dE^o_{cell}}{dT} = -4.99\ x\ 10^{-4}\ VK^{-1}$$

So, from equation (GGc), the reaction entropy is

$$\Delta_r S^o = 1\ x\ (9.6485\ x\ 10^4 Cmol^{-1})x\ (-4.99\ x\ 10^{-4} VK^{-1})$$
$$= -48.1\ JK^{-} mol^{-1}$$

The negative value stems in part from the elimination of gas in the cell reaction. It then follows that

$$\Delta_r H^o = \Delta_r G^o + T\Delta_r S^o = -6.880 KJmol^{-1} + (298\ K)x\ (-0.0482\ KJ\ K^{-1} mol^{-1})$$
$$= -21.2\ KJ\ mol^{-1}$$

One difficulty with this procedure lies in the accurate measurement of small temperature coefficients of cell potential. Nevertheless, it is another example of the striking ability of thermodynamics to relate the apparently unrelated, in this case to relate electrical measurements to thermal properties.

2.6. Liquid junction potentials

In a cell with two different electrolyte solutions in contact, as in the Daniell cell)Fig.2.2(a), there is an additional source of potential difference across the interface of the two electrolytes. This potential is called the **liquid junction potential**, E_{lj}. Another example of a junction potential is that between different concentrations of hydrochloric acid. At the junction, the mobile H^+ ions diffuse into the more dilute solution. The bulkier Cl^- ions follow, but initially do so more slowly, which results in a potential difference at the junction. The potential then settles down to a value such that, after that brief initial period, the ions diffuse at the same rates. Electrolyte concentration cells always have a liquid junction; electrode concentration cells do not. The contribution of the liquid junction to the potential can be reduced (to about 1 to 2 mV) by joining the electrolyte compartments through a salt bridge (Fig. 2.2(b)). The reason for the success of the salt bridge is that, provided the ions dissolved in the jelly have similar mobilities, then the liquid junction potentials at either end are largely independent of the concentrations of the two dilute solutions, and so nearly cancel.

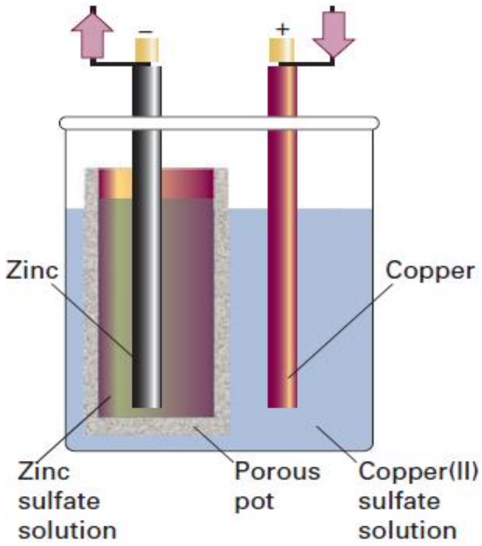


Fig. 2.2 (a) one version of the Daniell cell. The copper electrode is the cathode and the zinc electrode is the anode. Electrons leave the cell from the zinc electrode and enter it again through the copper electrode.

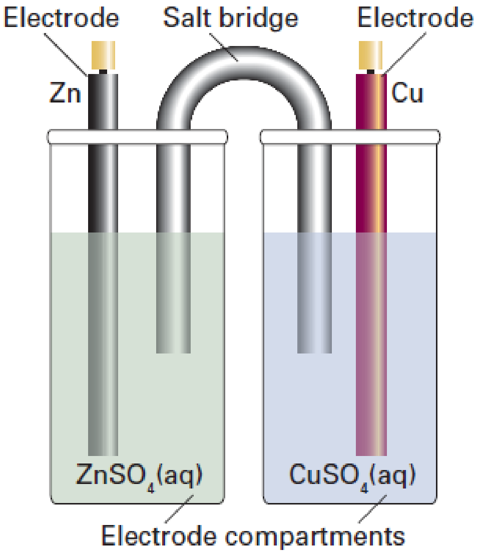


Fig.2.2 (b) the salt bridge, essentially an inverted U-tube full of concentrated salt solution in a jelly, has two opposing liquid junction potentials that almost cancel.

Notation of cells

Phase boundaries are denoted by a vertical bar

$$Pt(S)|H_2(g)|HCl(aq)|AgCl(S)|Ag(S)$$

A liquid junction is denoted by ⋮, So the cell in Fig.2.2(a) is denoted

$$Zn(S)|ZnSO4(aq) \vdots CuSO4(aq)|Cu(S)$$

A double vertical line, ||, denotes an interface for which it is assumed that the junction potential has been eliminated. Thus the cell in Fig. 2.2(a) is denoted

$$Zn(S)|ZnSO4(aq)||CuSO4(aq)|Cu(S)$$

An example of an electrolyte concentration cell in which the liquid junction potential
is assumed to be eliminated is

$$Pt(S)|H_2(g)|HCl(aq,b_1)||HCl(aq,b_2)|H_2(g)|Pt(S)$$

2.7 Measurement of pH

The concentrations of hydrogen ions in aqueous solutions range from about 1 mol $^{-L}$ in 1 mol $^{-L}$ HCl to about 10^{-14} mol $^{-L}$ in 1 mol $^{-L}$ NaOH. pH as the negative exponent of 10 that gives the hydrogen ion concentration. Now the pH is defined to be as close as possible to the negative base 10 logarithm of the hydrogen ion activity:

$$pH = -\log a_{H^+} \qquad (2.41)$$

Strictly speaking, the activity of a single ion cannot be determined, but pH meters are calibrated with buffers for which the pH has been calculated using the extended Debye–Huckel equation. The pH may be measured with a hydrogen electrode connected with a calomel electrode through a salt bridge:

$$Pt\left|H_2\left(P_{H_2}\right)\right|H^+(a_{H^+}) \mathrel{::} Cl^-|Hg_2Cl_2|Hg \qquad (2.42)$$

The electromotive force of this cell may be considered to be made up of three contributions:

$$E = 0.2802 - 0.0591\log\left[\frac{a_{H^+}}{\left(P_{H_2}/P^o\right)^{1/2}}\right] + E_{liquid\ junction} \qquad (2.43)$$

where the contribution by the normal calomel electrode is 0.2802 V at 25°C. Although the activities of single ions cannot be determined, Equation 2.43 is often used with the assumption that $E_{liquid\ junction} = 0$. If $P_{H_2} = 1\ bar$,1 then

$$E - 0.2802 = -0.0591\ \log a_{H^+} \qquad (2.44)$$

Hydrogen ion activities obtained in this way are of great practical use, even though they are based on an approximation.

Where $pH = -\log a_{H^+}$, Then Equation 2.44 become

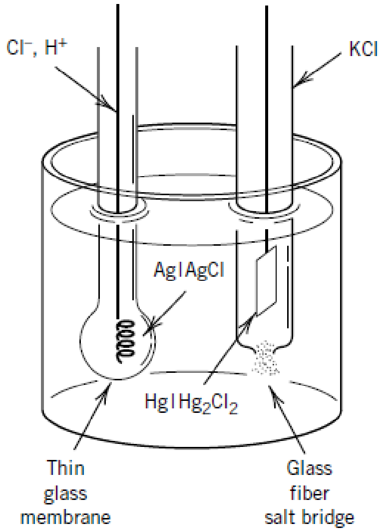
$$E - 0.2802 = 0.0591pH$$

Or

$$pH = \frac{E - 0.2802}{0.0591} \tag{2.45}$$

Usually the pH is measured with a glass electrode because this avoids the use of hydrogen and the possibility of poisoning the platinized platinum surface. A glass electrode consists of a reversible electrode, such as a calomel or Ag-AgCl electrode, in a solution of constant pH inside a thin membrane of a special glass. The thin glass bulb of this electrode is immersed in the solution to be studied along with a reference calomel electrode to form the cell indicated by

$$Ag|AgCl|Cl^-, H^+|glass\ memberane|solution :: Calomelelectrode$$



Glass electrode and calomel electrode for pH meters

It is found experimentally that the potential of such a glass electrode varies with the activity of hydrogen ions in the same way as the hydrogen electrode, that is, 0.0591 V per pH unit at 25 °C. An ordinary potentiometer cannot be used to measure the voltage of such a cell because of the high resistance of the glass membrane, so an electronic voltmeter must be employed. Electronic devices using the glass electrode have been developed that make it possible to measure pH values to $\pm 0.01\ pH$ unit with an easily portable apparatus. The pH meter, as it is often called, is calibrated by means of a buffer of known pH before it is used to measure the pH of an unknown solution.

The glass electrode has become the most useful electrode for determining the pH of a solution. It is not affected by oxidizing or reducing agents and is not easily poisoned. It is especially useful in biochemical investigations.

2.8. MEMBRANE POTENTIAL

If two different electrolyte solutions are separated by a membrane, a potential difference will be set up between the two solutions if the membrane is permeable to some ions and impermeable to others. For example, consider two KCl solutions separated by a membrane permeable to K^+but impermeable to Cl^-. If solution α is more concentrated than solution β , K^+ ions will diffuse through the membrane from α to β. This will cause solution β to become positively charged relative to solution α and to have a higher electric potential. Actually, the amount of K^+ that has to diffuse through the membrane to produce the potential difference is chemically insignificant. As K^+diffuses through the membrane, the electrical potential difference that is set up across the membrane retards the diffusion of more K^+, and eventually equilibrium is reached.

At equilibrium

$$\mu_i'(\alpha) + z_i F\emptyset(\alpha) = \mu_i'(\beta) + z_i F\emptyset(\beta) \qquad (2.46)$$

The transformed chemical potential depends on the activity as the chemical potential does, so we have

$$\mu_i' = \mu_i'^{o} + RT \ln a_i \qquad (2.47)$$

Substituting equation 2.47, in equation 2.46 and obtain

$$\mu_i'^{o}(\alpha) + RT\, lna_i(\alpha) + z_i F\emptyset(\alpha) = \mu_i'^{o}(\beta) + RT\ \ln a_i(\beta) + z_i F\emptyset(\beta)$$

Since the solvent is the same on both sides of the membrane and the electric potentials have to be the same in the definition of the standard states for the transformed chemical potential of $i, \mu_i'^{o}(\alpha) = \mu_i'^{o}(\beta)$, equation 2.46 becomes

$$RT\ \ln a_i\,(\alpha) + z_i F\emptyset(\alpha) = RT\, lna_i(B) + z_i F\emptyset(\beta) \quad (2.48)$$

Thus,

$$\Delta\emptyset = \emptyset(\beta) - \emptyset(\alpha) = -\frac{RT}{z_i F}\ln\frac{a_i(\beta)}{a_i(\alpha)} \qquad (2.49)$$

Where $\Delta\emptyset$ is referred to as the membrane potential.

This equation may be written in terms of molal concentrations if the activity coefficients of ion i are nearly the same in solutions $\alpha\ and\ \beta$. The membrane potential $\Delta\emptyset$ may be measure by placing identical reversible electrode in solution $\alpha\ and\ \beta$.