



## CHM 213 (INORGANIC CHEMISTRY): Applications of Standard Reduction Potentials

Compiled by

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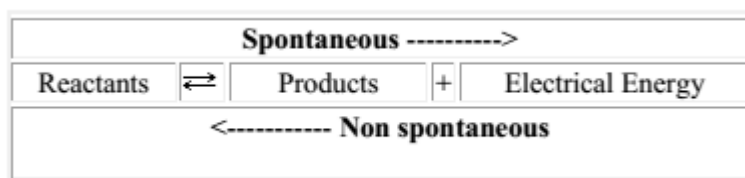
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### Electrochemical Cell

- Electrochemical cell is a device which converts chemical energy into electrical energy in an indirect redox reaction.
- An electrochemical cell can either drive an external electrical device (load) or be driven by it (power supply), depending upon the relative electromotive forces applied by the cell and the device.
- Oxidation and reduction half-reactions are kept separate in **half-cells**.
- Electron flow through a wire along with ion flow through a solution constitutes an electric circuit.
- It requires a conductive solid **electrode** to allow the transfer of electrons.
- Through external circuit
- Metal or graphite
- Requires ion exchange between the two half-cells of the system.

### Electrochemical Reactions

The general form of the reaction can be written as:



### Spontaneity of Electrochemical Reactions

A chemical reaction may or may not have a natural tendency to occur. If it has this tendency *i.e.*, if it takes place spontaneously, it means, the net Gibbs' Free Energy ( $\Delta G$ ) of the reaction (at that temperature and pressure) is negative. The spontaneity of any chemical reaction is well explained by thermodynamics.

At any given temperature and pressure, a negative Gibbs Energy change implies that the reaction will be spontaneous. Gibbs Free Energy, G is a state function (depends only on the thermodynamic state of the system, defined by quantities like P, T and composition).

$$\Delta G = \Delta H - T\Delta S$$

For any “spontaneous reaction”, at any temperature and pressure,  $\Delta G$  is negative. This means, the driving force is the tendency to move towards lower Gibbs energy. This is favoured naturally by lower enthalpy (lowering of H *i.e.*, negative  $\Delta H$  favours negative value of  $\Delta G$ ). Similarly, higher entropy (+ve  $\Delta S$ ) is helpful in achieving lower G at a particular temperature and pressure.

$\Delta G$  is also related to the equilibrium constant of the reaction, K:

$$\Delta G = -RT \ln K$$

$\Delta G$  is related to electrode potential, E

$$\Delta G = -nFE$$

where, n is the number of electrons being transferred in the electrode reaction (reduction or oxidation) and F is faraday.

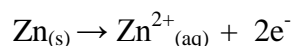
### **Redox Reaction**

A redox reaction is an electrochemical reaction in which both reduction and oxidation take place together. The redox potential data are extensively used for prediction of the direction of a redox reaction under a given set of conditions. For the same, one needs to understand some basic terms.

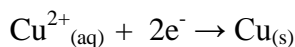
### **Redox Half Reaction**

Redox half reaction or the half-cell reaction is the chemical reaction taking place around one electrode of a cell. Consider the two parts of a complete redox system. In one part, oxidation is taking place and in the other, reduction is taking place. The electron is transferred from one part to the other.

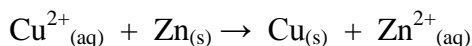
### **Oxidation half reaction**



### **Reduction half reaction**



### **The Overall Reaction**



$\text{Cu}_{(s)}$ : from +2 to 0 reduced (oxidizing agent)

$\text{Zn}_{(s)}$ : from 0 to +2 oxidized (reducing agent)

*Oxidation (electron loss) is always accompanied by reduction (electron gain)*

*Oxidizing agent is reduced the reducing agent is oxidized*

*The total number of e- gained by the oxidizing agent is always equal to the total number lost by the reducing agent*

In order to bring out such a complete redox system,

- a) the two parts (and the two species, the one undergoing oxidation and the other undergoing reduction) may form the bulk together (and electron transfer will be random) or,
- b) the two parts may be kept separated and connected by a conducting wire such that the electron released in one process, to the wire is collected by the other species and utilized in the reduction process there.

### **Electrodes**

An electrode is solid electric conductor through which an electric current enters or leaves an electrolytic cell or other medium.

In electrochemical reactions, oxidation or reduction reaction takes place at the electrodes. These are called electrode reactions, or half-reactions.

A half-reaction can be either a reaction in which electrons appear as products (oxidation) or a reaction in which electrons appear as reactants (reduction).

A combination of two half reaction forms the complete reaction.

### ***Anode***

- Electrode where oxidation occurs
- Anions attracted to it
- Connected to positive end of battery in an electrolytic cell
- Loses weight in electrolytic cell

### ***Cathode***

- Electrode where reduction occurs
- Cations attracted to it
- Connected to negative end of battery in an electrolytic cell
- Gains weight in electrolytic cell
- Electrode where plating takes place in electroplating

### **TYPES of Electrochemical Cells**

The cell could be of two types *viz.*:

**Galvanic Cell:** The overall reaction corresponds to a decrease in  $G$  (-ve  $\Delta G$ ) and spontaneous reduction and oxidation are taking place in the two respective half cells. The cell reaction is unaided and spontaneous. It could be used as a source of electrical energy.

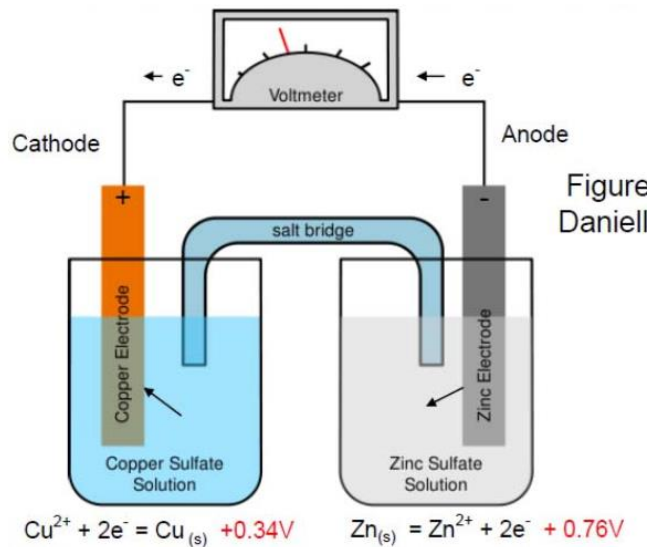
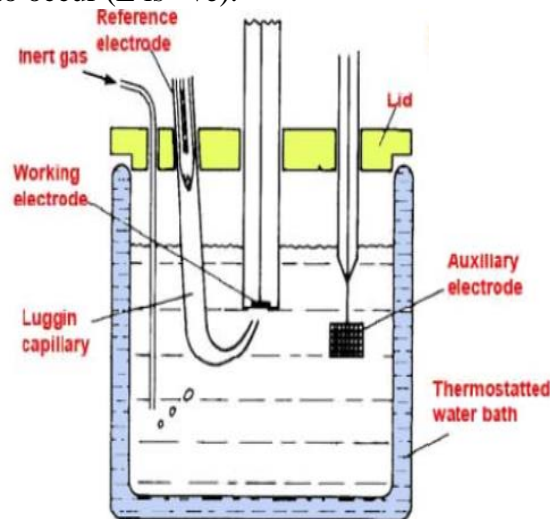


Figure Daniell

**Electrolytic Cell:** The  $\Delta G$  for the overall redox reaction is +ve and energy from outside is essential for the reaction to occur ( $E$  is -ve).



### Electrode Potential

When an electrode is in contact with the solution of its ions in a half-cell, it has a tendency to lose or gain electrons which is known as electrode potential. It is expressed in volts. It is an intensive property, i.e. independent of the amount of species in the reaction. It is denoted as  $E$ .

If the flow of current is negligible between the two electrodes, the potentials difference is equal to the electromotive force (e.m.f.) of the cell, which is referred to as the absolute value of the difference of two individual electrode potentials,  $E_1$  and  $E_2$ .

$$\text{e.m.f.} = |E_1 - E_2|$$

These electrode potentials are potential differences themselves, which are formed between the electrode (solid phase) and the electrolyte (liquid phase). Their occurrence can be most easily interpreted by the formation of double layers on the phase boundaries. If a piece of metal is immersed in a solution, which contains its own ions, say, Zn in a solution of  $\text{ZnSO}_4$ , two processes will immediately start. First, the atoms of the outside layer of the metal will

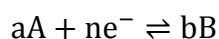
dissolve, leaving electrons on the metal itself, and slowly diffuse into the solution as metal ions. Secondly, metal ions from the solution will take up electrons from the metal and get deposited in the form of metal atoms.

These two processes have different initial rates. If the rate of dissolution is higher than the rate of deposition, the net result of this process will be that an excess of positively charged ions will get into the solution, leaving behind an excess of electrons on the metal. Thus, the electrostatic attraction between the oppositely charged particles, that is, the electrons in the metal phase and the ions in the solution, will accumulate at the phase boundary, forming an **electric double layer**. Once this layer is formed, the rate of dissolution becomes slower, because of the repulsion of the ionic layer at the phase boundary while the rate of deposition increases, because of the electrostatic attraction forces between the negatively charged metal and the positively charged ions. Soon the rate of the two processes will become equal and an equilibrium state will come into being, when, in a given time, the number of ions discharged equals the number of ions produced.

The potential difference established between a metal and a solution of its salt will depend on:

1. The nature of the metal; and
2. The concentration of the ions in the solution

Generally, for a half reaction,



the half-cell potential (at 25 °C), E, is given by

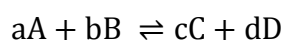
$$E = E^\circ - \frac{RT}{nF} \ln \left( \frac{[B]^b}{[A]^a} \right)$$

Or

$$E = E^\circ - \frac{0.05916}{n} \log_{10} \left( \frac{[B]^b}{[A]^a} \right)$$

where, E = half-cell potential,  $E^\circ$  = standard electrode potential, R = gas constant =  $8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ , F = Faraday constant =  $96487 \text{ Cmol}^{-1}$ , T = absolute temperature (K), [A] = concentration of chemical species, A, [B] = concentration of chemical species, B, a and b are the stoichiometric coefficients of A and B respectively and n = number of moles of electrons.

For the overall reaction,



The potential at 25 °C is given by

$$E = E^\circ - \frac{RT}{nF} \ln \left( \frac{[C]^c [D]^d}{[A]^a [B]^b} \right)$$

Or

$$E = E^\circ - \frac{0.05916}{n} \log_{10} \left( \frac{[C]^c [D]^d}{[A]^a [B]^b} \right)$$

This is called Nernst Equation.

### Standard Reduction Potentials

The driving force for a spontaneous reaction is measured by the cell voltage. This is an intensive property, independent of the number of electrons passing through the cell.

It is dependent on the:

1. nature of the redox reaction and
2. the concentrations of the species involved.

The standard cell potential,  $E^\circ_{\text{cell}}$ , is measured at a:

- i temperature of 25°C,
- ii with the concentrations of all species in solution at 1M and
- iii all gases at 1 atm pressure.

However, it is not possible to determine the absolute value of electrode potential. For this a reference electrode is required. The electrode potential is only the difference of potentials between two electrodes that we can measure by combining them to give a complete cell.

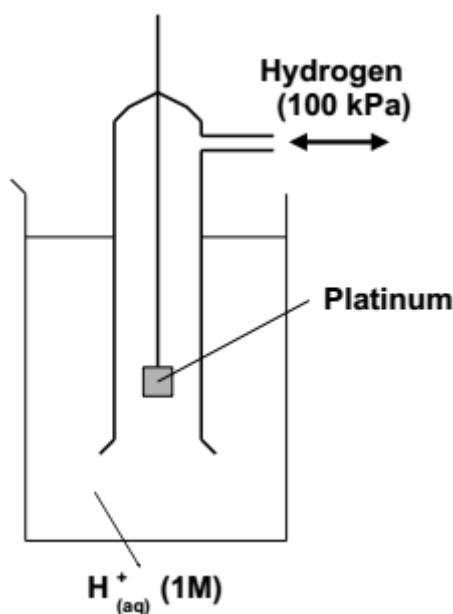
### Reference Electrodes

The electrode of known potential is called reference electrode. It may be primary reference electrode like hydrogen electrode or secondary reference electrode like calomel electrode. Standard hydrogen electrode (SHE) also known as normal hydrogen electrode (NHE), consists of platinum wire, carrying platinum foil coated with finely divided platinum black. The wire is sealed into a glass tube placed in beaker containing 1 M HCl. The hydrogen gas at 1 atm pressure is bubbled through the solution at 298K. The electrode potential of SHE has been fixed as zero at all temperatures.

Its main drawbacks are:

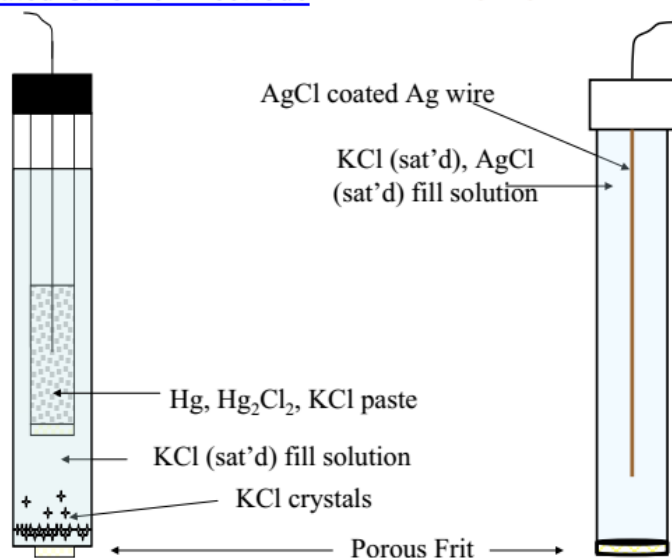
1. It is difficult to maintain 1 atm pressure of H<sub>2</sub> gas.
2. It is difficult to maintain H<sup>+</sup> ion concentration 1 M.
3. The platinum electrode is easily poisoned by traces of impurities.

Hence, calomel electrodes are conveniently used as reference electrodes. Calomel electrode consists of mercury in contact with Hg<sub>2</sub>Cl<sub>2</sub> (calomel) paste in a solution of KCl.



### Saturated Calomel Electrode

### Ag/AgCl Electrode



### **Electrochemical Series**

The standard electrode potential values of common systems when arranged in descending order make a series. Thus, the one with the highest  $E^{\circ}$  value is on the top (high positive value means the element has strong tendency to undergo reduction and so it is a strong oxidizing agent). Similarly, the low  $E^{\circ}$  value (more on the negative side) signifies tendency to get converted to its oxidized form and hence it is a strong reducing agent. This series is called electrochemical series.

Some of the general features of this series are:

1. The oxidized form of the couple is stronger oxidizing agent than the one below it in the series.
2. The reduced form of the couple is stronger reducing agent than the one above it in the series.
3. The reduced form of the couple that is below the  $H^{+}/H_2$  couple in the series, will have a natural tendency to liberate  $H_2$  from acidic solutions.
4. The reduced form of the couple below in the list will reduce the oxidized form of a couple above it in the series.
5. The oxidized form of the couple above in the list will oxidize the reduced form of a couple below it in the series.
6. The half-reaction with the greater reduction potential will drive the other half-reaction in the direction of oxidation.
7. The difference between the two reduction potentials provides a quantitative description of the electromotive force of the cell.

In simple terms, the electrochemical series is an arrangement of metals in their increasing reducing power such that the one in lower position in the series will reduce ions  $(aq)$  of metal in higher position.

Half-reaction (couple)	$E^\circ$ (volts)
$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$	0.34
$\text{Hg}_2\text{Cl}_2 + 2e^- \rightarrow 2\text{Hg} + 2\text{Cl}^-$	0.34
$\text{AgCl} + e^- \rightarrow \text{Ag} + \text{Cl}^-$	0.22
$\text{SO}_4^{2-} + 4\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{SO}_3 + \text{H}_2\text{O}$	0.20
$\text{Cu}^{2+} + e^- \rightarrow \text{Cu}^+$	0.16
$2\text{H}^+ + 2e^- \rightarrow \text{H}_2$	0.00
$\text{Pb}^{2+} + 2e^- \rightarrow \text{Pb}$	-0.13
$\text{Sn}^{2+} + 2e^- \rightarrow \text{Sn}$	-0.14
$\text{Ni}^{2+} + 2e^- \rightarrow \text{Ni}$	-0.23
$\text{PbSO}_4 + 2e^- \rightarrow \text{Pb} + \text{SO}_4^{2-}$	-0.35
$\text{Cd}^{2+} + 2e^- \rightarrow \text{Cd}$	-0.40
$\text{Cr}^{3+} + e^- \rightarrow \text{Cr}^{2+}$	-0.41
$\text{Fe}^{2+} + 2e^- \rightarrow \text{Fe}$	-0.41
$\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn}$	-0.76
$\text{Mn}^{2+} + 2e^- \rightarrow \text{Mn}$	-1.03
$\text{Al}^{3+} + 3e^- \rightarrow \text{Al}$	-1.71
$\text{H}_2 + 2e^- \rightarrow 2\text{H}^-$	-2.23
$\text{Mg}^{2+} + 2e^- \rightarrow \text{Mg}$	-2.37
$\text{La}^{3+} + 3e^- \rightarrow \text{La}$	-2.37
$\text{Na}^+ + e^- \rightarrow \text{Na}$	-2.71
$\text{Ca}^{2+} + 2e^- \rightarrow \text{Ca}$	-2.76
$\text{Ba}^{2+} + 2e^- \rightarrow \text{Ba}$	-2.90
$\text{K}^+ + e^- \rightarrow \text{K}$	-2.92
$\text{Li}^+ + e^- \rightarrow \text{Li}$	-3.05

### Applications of Electrochemical Series (ECS)

- The lower the value of  $E^\circ$ , the greater the tendency to form cation.  

$$\text{M} \rightarrow \text{M}^{n+} + ne^-$$
- Metals placed below hydrogen in ECS replace hydrogen from dil. acids but metals placed above hydrogen cannot replace hydrogen from dil. acids.
- Oxides of metals placed below hydrogen are not reduced by  $\text{H}_2$ , but oxides of iron and metals placed above iron are reduced by  $\text{H}_2$ .
  - $\text{SnO}$ ,  $\text{PbO}$ ,  $\text{CuO}$  are reduced by  $\text{H}_2$
  - $\text{CaO}$ ,  $\text{K}_2\text{O}$  are not reduced by  $\text{H}_2$
- Reducing character increases down the series.
- Reactivity increases down the series.
- Determination of emf; emf is the difference of reduction potentials of two half-cells.

$$E_{\text{emf}} = E_{\text{RHS}} - E_{\text{LHS}}$$

If the value of emf is positive, then reaction take place spontaneously, otherwise not.

- Greater the reduction potential of a substance, oxidising power. (e.g.  $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$ )
- A negative value of standard reduction potential shows that it is the site of oxidation.
- Oxides of metals having  $E^\circ_{\text{red}} \geq 0.79$  will be decomposed by heating to form  $\text{O}_2$  and metal.



### Use of Redox Potentials

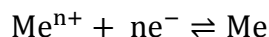


Although oxidation-reduction potentials can be treated in a general way, there are four broad classes of treating reduction potentials of redox systems. These are:

1. Metal electrodes
2. Simple redox system
3. Combined redox and acid-base systems, and
4. Gas electrodes

### Metal Electrodes

The half-cell reaction on which their operation is based can be written as

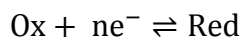


and the electrode potential can be calculated from the expression:

$$E = E^{\circ} + \frac{0.05916}{n} \log_{10} [\text{Me}^{n+}]$$

### Simple Redox System

The half-cell reaction can be symbolized in general terms as

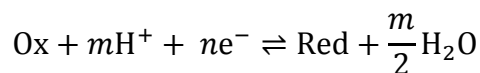


Ox represents the oxidized form and Red the reduced form of the redox couple. Both the oxidized and reduced forms are in the dissolved phase.

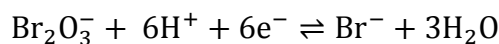
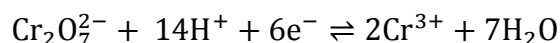
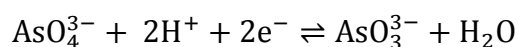
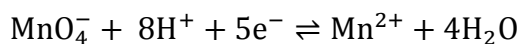
$$E = E^{\circ} + \frac{0.05916}{n} \log_{10} \left( \frac{[\text{Ox}]}{[\text{Red}]} \right)$$

### Combined Redox and Acid-Base Systems

The half-cell reaction of such system can be written as



Such half-cells are



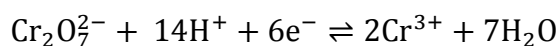
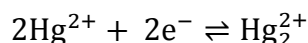
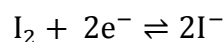
The Nernst Equation for such half-cells can be expressed as

$$E = E^{\circ} + \frac{0.05916}{n} \log_{10} \left( \frac{[\text{Ox}][\text{H}^{+}]^m}{[\text{Red}]} \right)$$

From this expression, it can be seen clearly that the oxidation-reduction potential of such systems depends as well on the hydrogen-ion concentration (pH) of the solution.

However, in cases of heterogeneous redox systems, where is change in the number of molecules (or ions) when a substance is reduced or oxidized, the general equations would be too complex to quote, but the potential can be easily expressed, if the half-cell reaction is known.

Such systems are



The oxidation-reduction potentials of these systems can be expressed as

$$E = E^\circ - \frac{0.05916}{2} \log_{10} \left( \frac{[I^-]^2}{[I_2]} \right)$$

$$E = E^\circ - \frac{0.05916}{2} \log_{10} \left( \frac{[Hg_2^{2+}]}{[Hg^{2+}]^2} \right)$$

$$E = E^\circ - \frac{0.05916}{2} \log_{10} \left( \frac{[Cr^{3+}]^2}{[Cr_2O_7^{2-}][H^+]^{14}} \right)$$

and

$$E = E^\circ - \frac{0.05916}{6} \log_{10} \left( \frac{[Cr^{3+}]^2}{[Cr_2O_7^{2-}][H^+]^{14}} \right)$$

### Gas Electrodes

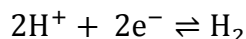
Gaseous substances, when donating or accepting electrons, may act as electrons. As the gases themselves do not conduct electricity, a suitable inert electrode e.g. platinum or graphite must be used as a link to the electrical circuit.

There are three gas electrodes of practical importance:

1. Hydrogen electrode
2. Oxygen electrode
3. Chlorine electrode

#### *Hydrogen Electrode*

It operates on the basis of the half-cell reaction:



This can be regarded as a simple redox system and its potential expressed as

$$E = E^\circ - \frac{0.05916}{2} \log_{10} \left( \frac{[H_2]}{[H^+]^2} \right)$$

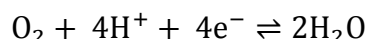
However, the concentration of hydrogen gas cannot be easily measured. Thus, its pressure value is used.

Hence,

$$E = E^\circ - \frac{0.05916}{2} \log_{10} \left( \frac{P_{H_2}}{[H^+]^2} \right)$$

### ***Oxygen Electrode***

It operates based on the half-cell reaction



The system is considered as a combined redox and acid-base reaction, and its potential can be expressed as

$$E = E^\circ - \frac{0.05916}{4} \log_{10} \left( \frac{[\text{H}_2\text{O}]^2}{[\text{O}_2][\text{H}^+]^4} \right)$$

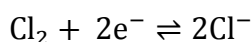
Likewise, the concentration of oxygen, being a gas, cannot be easily measure. Thus, its pressure value is used. The concentration of water is taken as constant in dilute aqueous solutions.

Hence, we have

$$E = E^\circ + \frac{0.05916}{4} \log_{10}(P_{\text{O}_2}[\text{H}^+]^4)$$

### ***Chlorine Electrode***

The operation of chlorine electrode is based on the half-reaction,



The electrode potential is expressed as

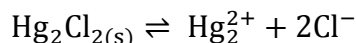
$$E = E^\circ - \frac{0.05916}{2} \log_{10} \left( \frac{[\text{Cl}^-]^2}{P_{\text{Cl}_2}} \right)$$

### **Other Applications**

#### **Determination of Solubility Products of Sparingly Soluble Salts**

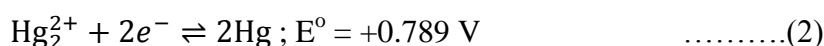
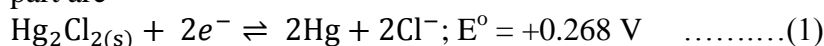
The solubility product  $K_{\text{sp}}$  ( $\text{AB}_n \rightarrow \text{A}^{n+} + n\text{B}^-$ ;  $K_{\text{sp}}$  is defined as  $K_{\text{sp}} = [\text{A}^{n+}][\text{B}^-]^n$ ) is an equilibrium constant and its value can be predicted from a knowledge of the standard electrode potentials. The electrodes are chosen in such a way, that the overall cell reaction is the solubility product equilibrium.

We will now illustrate the calculation of  $K_{\text{sp}}$  for  $\text{Hg}_2\text{Cl}_{2(\text{s})}$  at 298 K from data on electrode potentials.

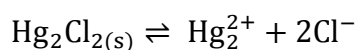


$$K_{\text{sp}} = [\text{Hg}_2^{2+}][\text{Cl}^-]^2$$

The half-cell reactions in which  $\text{Hg}_2\text{Cl}_2$  takes part and another reaction  $\text{Hg}_2^{2+}$  and  $\text{Cl}^-$  take part are



Eqn. (1) – Eqn. (2):



$$\Delta E^\circ = 0.268 - 0.789 \text{ V} = -0.521 \text{ V}$$

But,

$$\Delta G^\circ = -RT \ln K_{\text{eq}} = -nF\Delta E^\circ$$

where,

$$K_{\text{eq}} = \frac{[\text{Hg}_2^{2+}][\text{Cl}^-]^2}{[\text{Hg}_2\text{Cl}_2]}$$

Since  $[\text{Hg}_2\text{Cl}_2] = 1$ , then,

$$K_{\text{eq}} = [\text{Hg}_2^{2+}][\text{Cl}^-]^2 = K_{\text{sp}}$$

Hence,

$$\ln K_{\text{sp}} = \frac{nF\Delta E^\circ}{RT}$$

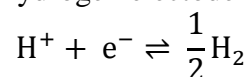
$$K_{\text{sp}} = e^{\frac{nF\Delta E^\circ}{RT}}$$

where,  $n = 2$ ,  $F = 96485 \text{ C}$ ,  $\Delta E^\circ = -0.521 \text{ V}$ ,  $R = 8.314 \text{ JK}^{-1}$  and  $T = 298 \text{ K}$

$$K_{\text{sp}} = 2.38 \times 10^{-18}$$

### Determination of pH of Solution

The electrode reaction in the case of hydrogen electrode is



The electrode potential is expressed as

$$E_H = E_{\text{SHE}}^\circ - \frac{0.05916}{1} \log \left( \frac{P_{\text{H}_2}}{[\text{H}^+]} \right)$$

Since  $P_{\text{H}_2} = 1 \text{ atm}$ ,  $E_{\text{SHE}}^\circ = 0$ , then we have

$$E_H = 0 - \frac{0.05916}{1} \log \left( \frac{1}{[\text{H}^+]} \right)$$

$$E_H = 0 - 0.05916 (-\log[\text{H}^+])$$

$$E_H = -0.05916 \text{ pH}$$

### Potentiometric Titrations

One of the widely used applications of e.m.f. measurements is to detect the endpoint of a titration by measuring the e.m.f. of a cell consisting of an indicator electrode (electrode, whose potential depends on the concentration of the reactant ions) and a reference electrode (e.g., SCE) as the titration progresses. This is called a potentiometric titration (varying e.m.f.

measured during the progress of titration). Since the electrode potential of the reference electrode is constant, the observed change in e.m.f. as the reaction progresses, is due to the change in the electrode potential of the indicator electrode.

During acid-base titrations, the pH of the solution changes. By monitoring the change in pH as the titration progresses, it is possible to detect the end point in acid-base titrations using a pH meter. Near the equivalence point, the change in pH is quite large, and at the end point the variation is the largest.