

Electrochemical Cells and Buffer

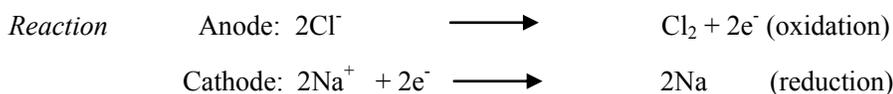
Part A Electrochemical Cells

Introduction

Device that produces electricity by virtue of chemical reaction and vice versa is called electrochemical cell. Electrochemical cells can be broadly classified into two major types: A) Electrolytic cells and B) Galvanic or Voltaic cells.

A) Electrolytic cells

Electrolytic cell is a device in which electric energy produces chemical reaction. Electrolysis is carried in an electrolytic cell. In an electrolytic cell two electrodes are dipped in a common electrolyte and the electrodes are connected to the positive and negative terminals of a battery as shown in the Figure 1. Molten NaCl comprises of Na^+ and Cl^- ions. When the circuit is completed, the positive ions (Na^+) travel towards negative electrode and gets reduced to sodium atom. Since, reduction takes place on the surface of a negative electrode it functions as cathode. Similarly, the negative ions (Cl^-) travel towards the positive electrode and gets oxidized by losing electrons to the electrode to form neutral chlorine atom. Two chlorine atoms then combine to form a chlorine molecule. Since, oxidation takes place on the surface of the positive electrode it is anode.



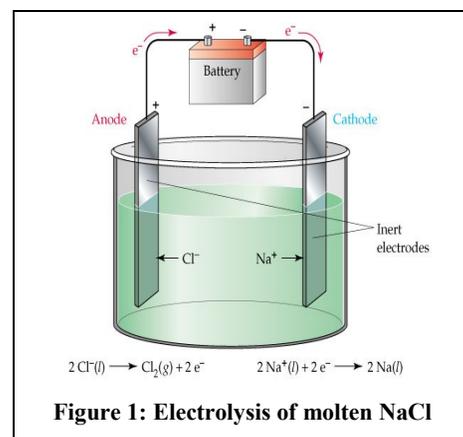
Electrolytic cells are used in electroplating, purifying metals like gold, silver, etc.

Question: What will form at anode and cathode if electrolysis of aqueous NaCl is carried out?

The product formed in electrolysis depends on factors like: the nature of the electrolyte used, the nature of electrodes used, and concentration of the electrolytes. Electrolytic cells are also used in many industrial processes including extraction of metallic sodium from fused NaCl, manufacture of caustic soda, purification of metals, electroplating etc.

B) Galvanic Cell

Galvanic cell is a device that produces electricity by virtue of chemical reaction. It consists of two half cells. Each half consists of an electrode dipped in an electrolyte having its reversible ions (example: zinc electrode is dipped in zinc sulphate solution, copper electrode dipped in copper sulphate solution, silver electrode dipped in silver nitrate solution, etc). Two different



electrolytes are connected by a salt bridge and the electrodes are connected by a metallic wire. When the circuit is completed, the electrons flow from anode to cathode.

Electrode Potential or Single electrode potential

When an electrode is dipped in a solution having its reversible ions or water, three types of interaction is observed.

- 1) Cations from the metal surface passes into the solution leaving electrons on the metal surface. This makes electrode negatively charged as Figure 2.
- 2) Cations from the solution diffuse into the surface of electrode making the electrode positively charged as Figure 3.
- 3) No interaction with the solution.

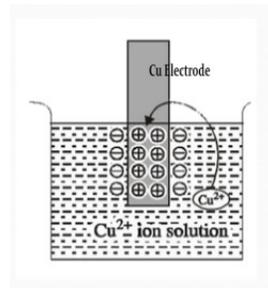
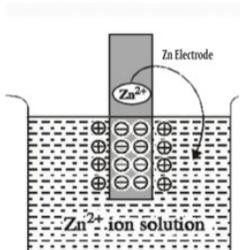


Figure 2: Cation from the electrode diffusing into the solution

Figure 3: Cation from the solution diffusing into the electrode

In case of first and second condition an electrical double layer is formed in the electrode electrolyte interface. In first case the electrode surface has negatively charged layer and the electrolyte at interface has positively charged layer. In second case, the electrode surface has positive charge layer and the electrolyte at interface has negatively charged layer. Due to this charge separation at interface due to the formation of electrical double layer, potential difference is developed at electric electrolyte interface. *The potential difference developed at electrode electrolyte interface at equilibrium due to charge separation i.e the formation electrical double layer is known as single electrode potential or simply electrode potential of that electrode.* It is denoted as E .

Electrode potential depends on: 1) nature of the electrode 2) concentration of the electrolyte 3) temperature, and 4) pressure (only if gas is involved). Thus the electrode potential measured at 25°C, 1 atmospheric pressure (only if gas is involved), and when the concentration of electrolyte is 1M is known as standard electrode potential. It is denoted as E° .

Measurement of Standard Electrode Potential

Absolute electrode potential cannot be measured. The electrode potential values found in electrochemical series is actually the relative electrode potential of that electrode with respect to standard hydrogen electrode whose electrode potential is arbitrarily assigned as 0.00 V at all temperature.

Standard Hydrogen Electrode (SHE)

Standard hydrogen electrode (Figure 4) consists of hydrogen gas at 1 atmospheric pressure bubbled over 1M solution of H^+ ions (1 M HCl) at 25°C. As it is not possible to determine the absolute value of the electrode potential of a single electrode, SHE is used

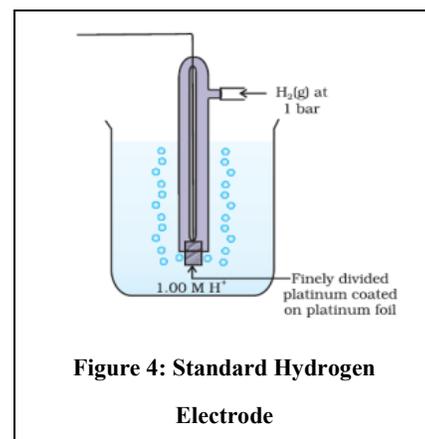


Figure 4: Standard Hydrogen Electrode

as a reference electrode to measure such. The inert metal (which often is Pt) act as a source or sink of electrons. The electrode whose electrode potential is to be determined is coupled with SHE forming a galvanic cell. While coupling SHE may act as an anode or cathode. The Emf of thus formed cell is measured using a potentiometer and the electrode potential of any electrode is determined as illustrated in following examples.

Measurement of Standard Electrode Potential of Zinc electrode using SHE

Note: Connection with potentiometer confirms that Zn is anode and SHE is cathode by giving positive Emf.

A zinc electrode is dipped in 1 M ZnSO₄ solution and maintained at 25°C so that the electrode potential measured for zinc is standard electrode potential. This half cell is coupled with SHE. The two electrolytes are connected through a salt bridge and the electrodes are connected to a potentiometer. On completing the circuit the potentiometer reads E^omf = 0.76 volt (Figure 5).

Now,

Since, $E^{\circ}mf = E^{\circ}cathode - E^{\circ}anode$ (Both are standard reduction potentials)

$$E^{\circ}mf = E^{\circ}SHE - E^{\circ}Zn^{++}/Zn$$

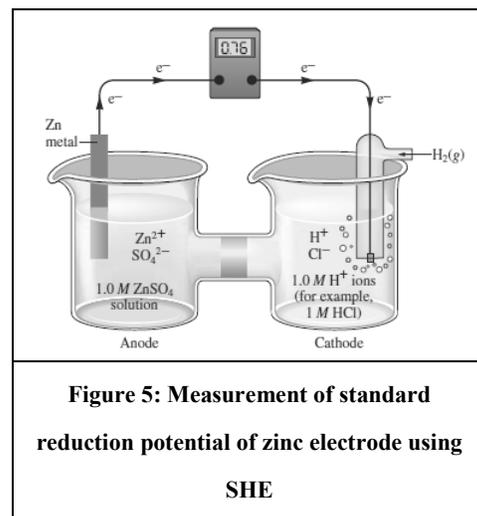
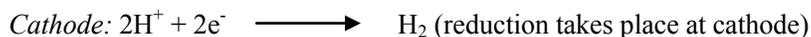
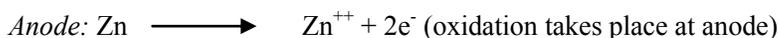
$$\text{Or, } 0.76 \text{ V} = 0.00 - E^{\circ}Zn^{++}/Zn$$

$$\therefore E^{\circ}Zn^{++}/Zn = -0.76 \text{ V (standard reduction potential)}$$

$$\text{Or, } E^{\circ}Zn/Zn^{++} \text{ (standard oxidation potential)} = 0.76 \text{ V}$$

Cell Notation: Zn/Zn⁺⁺ (1 M) //H⁺ (1 M)/ H₂ (1 atm)/ Pt

Cell Reaction:



Measurement of Standard Electrode Potential of copper electrode using SHE

Note: Connection with potentiometer confirms that Cu is cathode and SHE is anode by giving positive Emf.

A copper electrode is dipped in 1 M CuSO₄ solution and maintained at 25°C so that the electrode potential measured for copper is standard electrode potential. This half cell is coupled with SHE to form a complete galvanic cell. The two electrolytes are connected through a salt bridge and the electrodes are connected to a potentiometer. On completing the circuit the potentiometer reads E^omf = 0.34 volt.

Now,

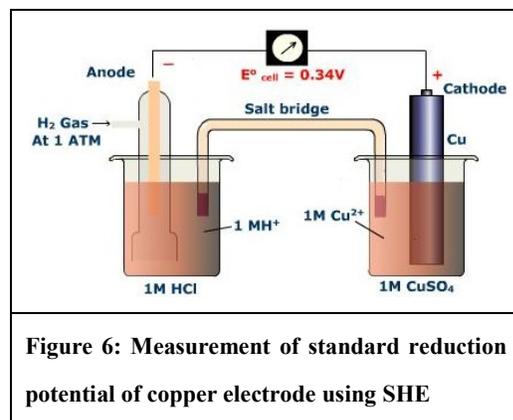
$$E^{\circ}mf = E^{\circ}Cu^{++}/Cu - SHE$$

$$\text{Or, } 0.34 \text{ V} = E^{\circ}Cu^{++}/Cu - 0.00 \text{ V}$$

$$\therefore E^{\circ}Cu^{++}/Cu = 0.34 \text{ V}$$

$$\text{And, } E^{\circ}Cu/Cu^{++} \text{ (standard oxidation potential)} = -0.34 \text{ V}$$

Cell Notation: Pt/ H₂ (1 atm)/ H⁺ (1M) // Cu⁺⁺ (1 M)/ Cu



Cell Reaction:



Electrochemical Series

The series in which the standard electrode potentials of various electrodes measured against standard hydrogen electrode is plotted in increasing order of the standard reduction potential is known as electrochemical series. By international convention, all standard electrode potential are listed as standard reduction potential.

Application of Electrochemical Series

a. *Predicting oxidizing and reducing strength:*

The higher the standard reduction potential, the greater the tendency of the oxidized form to be reduced. Similarly, higher the standard oxidation potential, the greater the tendency of the reduced form to be oxidized.

When comparing two electrode for example zinc and copper for oxidizing and reducing strength, the electrode (reduced form, Zn) higher in electro chemical series has higher tendency towards oxidation. Similarly, the electrode (oxidized form, Cu^{++}) lower in electro chemical series has greater tendency towards reduction. Therefore, in the reaction between Zn and copper sulphate solution, zinc oxidizes to Zn^{++} and Cu^{++} reduces to Cu.

b. *Predicting anode and cathode:* The electrode higher in electrochemical series functions as anode and the electrode lower in electro chemical series functions as cathode. For example in a cell having Zn and Cu, Zn functions as anode and Cu functions as cathode.

c. *Liberation of hydrogen from the acid:* Metals higher in electrochemical series than hydrogen can liberate hydrogen from the dilute acid solution. For example zinc can displace hydrogen from dilute acid but copper cannot.

d. *Predicting the displacement of metal form the salt solution:* Metals above in electro chemical series can displace metal below it from its aqueous salt solution. For example, zinc can displace copper from copper sulphate solution but copper cannot displace zinc from zinc sulphate solution.

e. *Predicting spontaneity of redox reaction:* If the E_{cell} is positive, the cell reaction is spontaneous.

Elements	Electrode Reaction	E_{red}° (volts)
<i>Oxidised Form + ne⁻ → Reduced Form</i>		
Li	$\text{Li}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Li}(\text{s})$	-3.05
K	$\text{K}^+(\text{aq}) + \text{e}^- \longrightarrow \text{K}(\text{s})$	-2.93
Ba	$\text{Ba}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Ba}(\text{s})$	-2.90
Ca	$\text{Ca}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Ca}(\text{s})$	-2.87
Na	$\text{Na}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Na}(\text{s})$	-2.71
Mg	$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Mg}(\text{s})$	-2.37
Al	$\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \longrightarrow \text{Al}(\text{s})$	-1.66
Zn	$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Zn}(\text{s})$	-0.76
Cr	$\text{Cr}^{3+}(\text{aq}) + 3\text{e}^- \longrightarrow \text{Cr}(\text{s})$	-0.74
Fe	$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Fe}(\text{s})$	-0.44
	$\text{H}_2\text{O}(\text{l}) + \text{e}^- \longrightarrow \frac{1}{2}\text{H}_2(\text{g}) + \text{OH}^-(\text{aq})$	-0.41
Cd	$\text{Cd}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Cd}(\text{s})$	-0.40
Pb	$\text{PbSO}_4(\text{s}) + 2\text{e}^- \longrightarrow \text{Pb}(\text{s}) + \text{SO}_4^{2-}(\text{aq})$	-0.31
Co	$\text{Co}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Co}(\text{s})$	-0.28
Ni	$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Ni}(\text{s})$	-0.25
Sn	$\text{Sn}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Sn}(\text{s})$	-0.14
Pb	$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Pb}(\text{s})$	-0.13
H₂	$2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2(\text{g})$ (standard electrode)	0.00
Cu	$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Cu}(\text{s})$	+0.34
I ₂	$\text{I}_2(\text{s}) + 2\text{e}^- \longrightarrow 2\text{I}^-(\text{aq})$	+0.54
Fe	$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \longrightarrow \text{Fe}^{2+}(\text{aq})$	+0.77
Hg	$\text{Hg}_2^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow 2\text{Hg}(\text{l})$	+0.79
Ag	$\text{Ag}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Ag}(\text{s})$	+0.80
Hg	$\text{Hg}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Hg}(\text{l})$	+0.85
N ₂	$\text{NO}_3^- + 4\text{H}^+ + 3\text{e}^- \longrightarrow \text{NO}(\text{g}) + 2\text{H}_2\text{O}$	+0.97
Br ₂	$\text{Br}_2(\text{aq}) + 2\text{e}^- \longrightarrow 2\text{Br}^-(\text{aq})$	+1.08
O ₂	$\text{O}_2(\text{g}) + 2\text{H}_3\text{O}^+(\text{aq}) + 2\text{e}^- \longrightarrow 3\text{H}_2\text{O}$	+1.23
Cr	$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \longrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	+1.33
Cl ₂	$\text{Cl}_2(\text{g}) + 2\text{e}^- \longrightarrow 2\text{Cl}^-(\text{aq})$	+1.36
Au	$\text{Au}^{3+}(\text{aq}) + 3\text{e}^- \longrightarrow \text{Au}(\text{s})$	+1.42
Mn	$\text{MnO}_4^- + 8\text{H}_3\text{O}^+(\text{aq}) + 5\text{e}^- \longrightarrow \text{Mn}^{2+}(\text{aq}) + 12\text{H}_2\text{O}(\text{l})$	+1.51
F ₂	$\text{F}_2(\text{g}) + 2\text{e}^- \longrightarrow 2\text{F}^-(\text{aq})$	+2.87

Zn-Cu cell (Daniel cell)

Zn-Cu cells consists of two half cells. Oxidation half cell consists of a zinc electrode dipped in zinc sulphate solution and the reduction half cell consists of copper electrode dipped in copper sulphate solution. The solutions of two half cells are connected by a salt bridge and the electrodes are connected with a metallic wire as shown in the Figure 7.

A salt bridge consists of U shaped glass tube filled with a semisolid paste prepared by adding agar-agar or gelatin to the aqueous solution of strong electrolyte as KCl, KNO₃, K₂SO₄, etc,. The strong electrolyte should be chemically inert. The main function of salt bridge is to keep the solutions in the two half cells electrically neutral. Anode is the source of electrons and cathode is the sink of electrons.

In case of zinc half cell (oxidation half), the Zinc atoms on the surface of the electrode dissociates to Zn⁺⁺ and electrons. The Zn⁺⁺ (cation) from the surface of the electrode enters the solution leaving the electrode negatively charged. This continues till the equilibrium is achieved. Similarly, in case of copper half cell (reduction half), the Cu⁺⁺ cations from the solution enter the copper electrode surface till the equilibrium is achieved and making the electrode positive charge. On the completion of the circuit, the electrons from zinc electrode (anode) are transferred to the copper electrode, where Cu⁺⁺ ions on the surface of the electrode get reduced to Cu.

Cell Notation: Zn/ Zn⁺⁺ (xM) // Cu⁺⁺ (yM)/Cu

At standard state the concentration of each electrolyte is 1 M and the temperature is 25°C.

Cell Notation: Zn/Zn⁺⁺ (1M) // Cu⁺⁺ (1M)/Cu

Cell reaction:

At anode: Zn \longrightarrow Zn⁺⁺ + 2e⁻ (oxidation)

At cathode: Cu⁺⁺ + 2e⁻ \longrightarrow Cu (reduction)

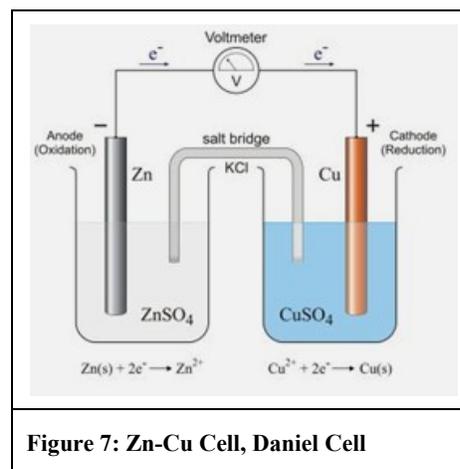
Net reaction: Zn + Cu⁺⁺ \longrightarrow Zn⁺⁺ + Cu

At standard state the emf of the cell (E^omf) is

$$E^{\circ}mf = E^{\circ}Cu^{++}/Cu - E^{\circ}Zn^{++}/Zn$$

$$= 0.34 \text{ V} - (-0.76\text{V})$$

$$= 1.1 \text{ V}$$



Cu-Ag Cell

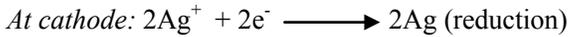
Cu-Ag cells consists of two half cells. Oxidation half cell consists of a copper electrode dipped in aqueous copper sulphate solution and the reduction half cell consists of silver electrode in aqueous silver nitrate solution. The solutions of two half cells are connected by a salt bridge and the electrodes are connected with a metallic wire as shown in the Figure 8.

Cell Notation: Cu/Cu⁺⁺ (xM) // Ag⁺ (yM)/Ag

At standard state the concentration of each electrolyte is 1 M and the temperature is 25°C.

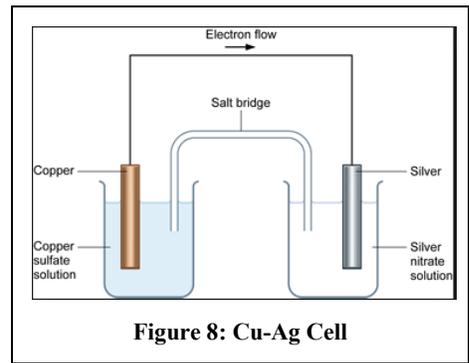
Cell Notation: Cu/Cu⁺⁺ (1M) // Ag⁺ (1M)/Ag

Cell reaction:



At standard state the emf of the cell (E°_{mf}) is

$$\begin{aligned} E^\circ_{mf} &= E^\circ_{\text{Ag}^+/\text{Ag}} - E^\circ_{\text{Cu}^{++}/\text{Cu}} \\ &= 0.80 \text{ V} - 0.34 \text{ V} \\ &= 4.6 \text{ V} \end{aligned}$$



Nernst Equation

Nernst Equation can be used to measure the electrode potential of a single electrode or Emf of the cell with the change in concentration of the electrolytes. Electrode potential at nonstandard condition is calculated as:

$$E_{\text{red}} = E^\circ_{\text{red}} - \frac{2.303 RT}{nF} \log Q$$

Where, Q is the reaction quotient equivalent to the law of mass action, E°_{red} = standard reduction potential of the electrode, R = Universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T = temperature in Kelvin scale ($273.15 + ^\circ\text{C}$), F = Faraday Constant 96500 C mol^{-1} , and n = number of moles of electron transferred in the balanced chemical equation.

Similarly, Emf of the cell can be measured as:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{2.303 RT}{nF} \log Q$$

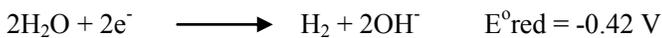
Where $E^\circ_{\text{Cell}} = E^\circ_{\text{red cathode}} - E^\circ_{\text{red Anode}}$

Corrosion

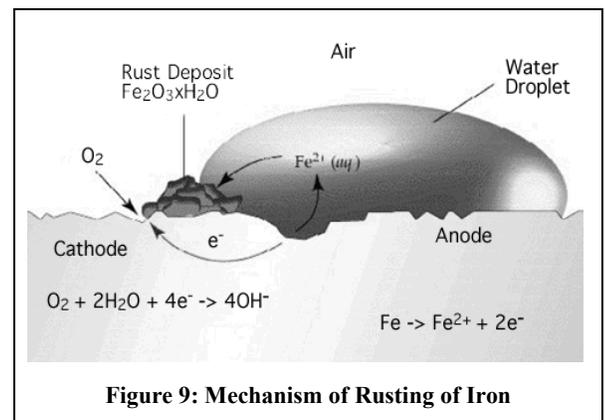
Disintegration or degradation of metal from its surface is known as corrosion. Rusting of iron, formation of green film on the surface of copper, black coating of silver, etc are some examples of corrosion.

Mechanism of Corrosion

When the iron comes in contact with oxygen and water, oxidation starts in its surface, starting of the rusting process.

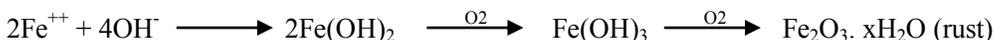


The reduction potential values of the above systems suggest that iron in presence of moisture i.e. water and oxygen acts as anode and thus undergo oxidation. The iron surface having crack or irregularities (depression) acts as anode and the wet area close to it function as cathode. At anode, the iron gets oxidized, the electrons travel through the water or metal surface to the cathode where the system of water and oxygen is reduced to hydroxide. The hydroxide and ferrous ions



The hydroxide and ferrous ions

combine to give ferrous hydroxide which signifies the starting of the rusting process. The ferrous hydroxide in presence of excess of oxygen oxidizes to ferric hydroxide and finally to rust as shown below.



Control of Corrosion

- By polishing and painting the surface.
- By coating with metals lying above it in electrochemical series. For example, iron can be coated with zinc. If iron is exposed to moisture by the formation of crack or due to injury, iron still functions as cathode and is protected from oxidation
- By coating with metal lying below it in electrochemical series. For example, iron can be coated with tin. However, if iron is exposed to moisture by the formation of crack or due to injury, iron will function as anode and will oxidize with higher rate.
- Connecting the metal directly to a sacrificial anode. It is not possible to galvanize structures as large as ships, underground pipe lines, storage tanks and bridges. In such cases, iron is connected to a strip of Mg or Zn, more active metal. The more active metal is preferentially oxidized than iron so that zinc or magnesium functions as sacrificial anode.

Part B Buffer

A solution that resists the change in its pH on the addition of small amount of strong acid or base is known as buffer solution. When strong acid is added, the buffer function as a base and when strong base is added, the buffer functions as an acid. Therefore, buffer has reserve acidity and basicity. Buffers are of two types:

Acidic Buffer: pH less than 7, acidic buffer solution consists of a mixture of weak acid and ionic salt of the same acid. For example a mixture of CH_3COOH and CH_3COONa makes an acidic buffer.

Basic Buffer: pH more than 7, basic buffer solution consists of a mixture of a weak base and ionic salt of the same base. For example, a mixture of NH_4OH and NH_4Cl makes basic buffer.

Acidic Buffer	Basic Buffer
$\text{HCOOH} + \text{HCOONa}$	$\text{NH}_4\text{OH} + \text{NH}_4\text{NO}_3$, blood, etc.

Mechanism of Buffer (Buffer Action)

How the buffer resists the change in its pH even on the addition of small amount of strong acid or base is known as mechanism of buffer or buffer action. Buffer works on Le-Chatlier principal and common ion effect.

Le-Chatlier Principal

When a system in equilibrium is subjected to stress, the equilibrium will shift in the direction to minimize or nullify the stress.

For Example: $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$

In this case if C or D is added, the reaction will proceed in back ward direction to minimize the addition of C or D. Similarly, if A or B is added, the reaction will proceed in forward direction to consume the addition of A or B.

Common Ion Effect

Degree of ionization of weak electrolyte is highly suppressed by the addition of a strong electrolyte have a common ion of the weak electrolyte. For example the addition of sodium acetate in the solution of acetic acid highly suppresses the ionization of acetic acid.



In the above example, the addition of acetate ions to the solution of acetic acid shifts the equilibrium in equation (i) in backward direction, i.e. combination of acetate ions and hydronium ions will take place to give acetic acid. Thus the ionization of acetic acid is suppressed.

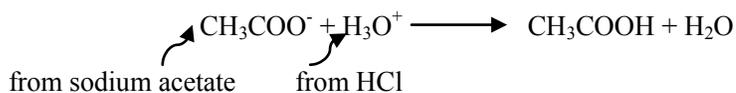
Mechanism of Acidic Buffer

Let us take an example of acidic buffer with acetic acid (weak acid) and sodium acetate (ionic salt of acetic acid). Acetic acid ionizes partially and sodium acetate ionizes completely in the buffer solution. Moreover, the ionization of acetic acid is highly suppressed by the presence of excess of acetate ions in the solution as according to common ion effect.

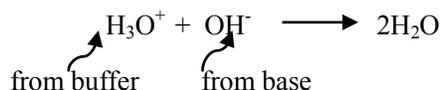


The pH of the solution depends on the concentration of hydronium ion in the solution. For the buffer solution to work, the concentration of the hydronium ion should not change on the addition of small amount of strong acid or base.

On addition of HCl: When HCl is added, it adds hydronium ions to the solution, which according to the Le-Chatlier principal combines with excess of acetate ions to give acetic acid. The formed acetic acid is almost prevented from ionization due to common ion effect, keeping the concentration of hydronium ion almost the same. Hence, there is no significant change in pH on the addition of HCl.



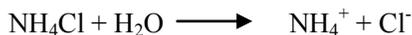
On addition of NaOH: When NaOH is added, it gives hydroxide ions in the solution, which immediately combines with the hydronium ions of the solution to give water. Due to the consumption of hydronium ions, the equilibrium in equation (i) shifts in forward direction keeping the concentration of hydronium ion almost same. Thus there is no change in pH on the addition of NaOH.



Mechanism of Basic Buffer:

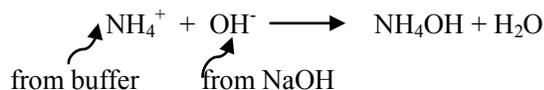
Let us take an example of basic buffer with ammonium hydroxide (weak base) and ammonium chloride (ionic salt of ammonia or ammonium hydroxide). Ammonium hydroxide ionizes partially and ammonium chloride ionizes completely in the buffer

solution. Moreover, the ionization of ammonium hydroxide is highly suppressed by the presence of excess of ammonium ions in the solution as according to common ion effect.

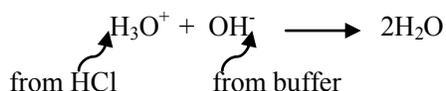


The pH of the solution depends on the concentration of hydroxide ion in the solution. For the buffer solution to work, the concentration of the hydroxide ion should not change on the addition of small amount of strong acid or base.

On addition of NaOH: When NaOH is added, it adds hydroxide ions to the solution, which according to the Le-Chatelier principle combines with excess of ammonium ions to give ammonium hydroxide. The formed ammonium hydroxide is almost prevented from ionization due to common ion effect, keeping the concentration of hydroxide ion almost the same. Hence, there is no significant change in pH on the addition of NaOH.



On addition of HCl: When HCl is added, it gives hydronium ions in the solution, which immediately combines with the hydroxide ions of the buffer solution to give water. Due to the consumption of hydroxide ions, the equilibrium will shift in forward direction keeping the concentration of hydroxide ion almost same. Thus there is no change in pH on the addition of HCl.



Henderson's Equation

Henderson's equation is used to calculate the pH of the buffer when the concentrations of acid/base and salt are known.

Henderson's equation for Acidic Buffer



Applying law of mass action in equation (i)

$$K_e = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}][\text{H}_2\text{O}]} \quad \text{where, } K_e \text{ is equilibrium constant}$$

$$\text{Or } K_e [\text{H}_2\text{O}] = K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} \quad \text{where, } K_a \text{ is ionization constant of weak acid}$$

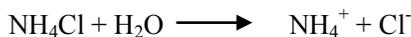
$$\text{Or, } [\text{H}_3\text{O}^+] = K_a \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}, \text{ then taking } -\log \text{ both side we get}$$

$$-\log [\text{H}_3\text{O}^+] = -\log \left\{ K_a \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} \right\} \quad \text{or, } \text{pH} = -\log K_a - \log \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} \quad \text{or, } \text{pH} = \text{p}K_a + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

The concentration of acetate ions is entirely contributed by sodium acetate as ionization of acetic acid is highly suppressed by common ion effect, Therefore, the concentration of acetate ions equals to the concentration of sodium acetate.

Therefore, $\text{pH} = \text{pK}_a + \log \frac{[\text{CH}_3\text{COONa}]}{[\text{CH}_3\text{COOH}]}$ or, $\text{pH} = \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$

Henderson's equation for Basic Buffer



Applying law of mass action in equation (i)

$$K_e = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}][\text{H}_2\text{O}]} \quad \text{where, } K_e \text{ is equilibrium constant}$$

$$\text{Or } K_e [\text{H}_2\text{O}] = K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} \quad \text{where, } K_b \text{ is ionization constant of weak base}$$

$$\text{Or, } [\text{OH}^-] = K_b \frac{[\text{NH}_4\text{OH}]}{[\text{NH}_4^+]}, \text{ then taking } -\log \text{ both side we get}$$

$$-\log [\text{OH}^-] = -\log \left\{ K_b \frac{[\text{NH}_4\text{OH}]}{[\text{NH}_4^+]} \right\} \quad \text{or, } \text{pOH} = -\log K_b - \log \frac{[\text{NH}_4\text{OH}]}{[\text{NH}_4^+]} \quad \text{or, } \text{pOH} = \text{pK}_b + \log \frac{[\text{NH}_4^+]}{[\text{NH}_4\text{OH}]}$$

Since the concentration of ammonium ions is entirely contributed by ammonium chloride as ionization of ammonium hydroxide is highly suppressed by the common ion effect, the concentration of ammonium ions equals to the concentration of ammonium chloride.

$$\text{Therefore, } \text{pOH} = \text{pK}_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

Buffer Capacity

The buffer capacity is defined as the number of moles of acid or base added per liter of buffer required to cause a unit change in pH.

Or, Buffer capacity = No. of mole of acid or base added per liter of the buffer/ Change in pH