

## Ancillary Chemistry-II



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# STANDARD ELECTRODEPOTENTIAL

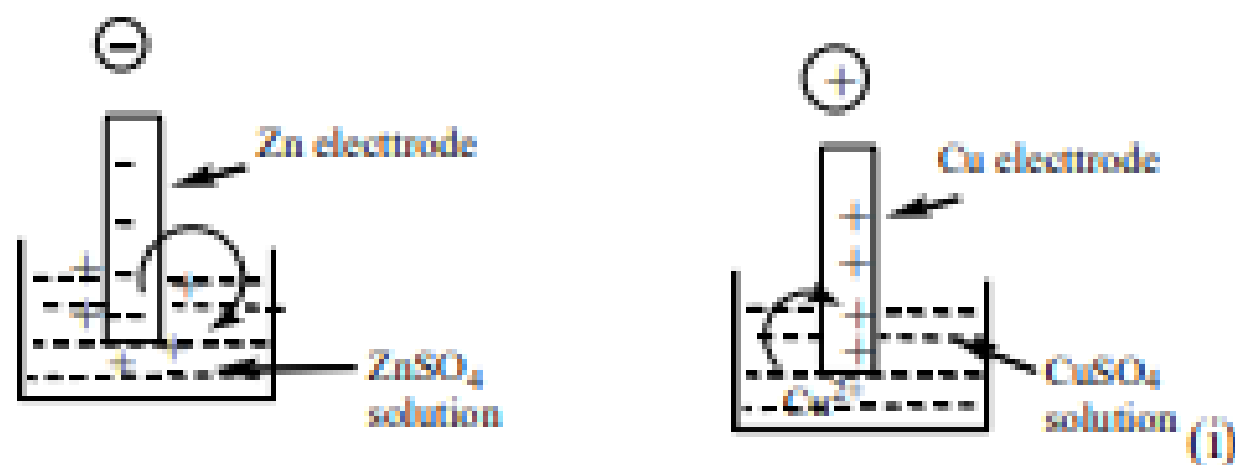
## Electrode Potential

When a metal (M) is placed in a solution of its own salt ( $M^{n+}$ ) one of the two processes are possible.

- (i) +ve metal ions may pass into solution



- (ii) +ve metal ions from solution may deposit on the metal



When Zn electrode is dipped in ZnSO<sub>4</sub> solution, Zn goes into solution as Zn<sup>2+</sup> ions.

A layer of + or - ve ions if formed on the metal, **Helmholtz electrical double layer** due to which a difference of potential is setup between the metal ions and the solution.

At equilibrium, the potential difference becomes a constant value (**Electrode potential of the metal**).

The tendency of the electrode to lose electrons is **Oxidation potential**.

Tendency of an electrode to gain electrons is **reduction potential**.

**Single electrode potential (E):** Tendency of a metallic electrode to lose or gain electrons when it is in contact with a solution of its own ions.

**Standard electrode potential ( $E^0$ ):** Tendency of a metallic electrode to lose or gain electrons when it is in contact with a solution of its own ions of 1M Concentration.

### **Nernst Equation for Electrode Potential**

Consider the redox reaction :  $M \longrightarrow M^{n+} + ne^{-}$

For such redox reversible reactions, the free energy change ( $\Delta G$ ) and its equilibrium constant ( $K$ ) are related by

$$\begin{aligned}\Delta G &= -RT \ln K + RT \ln \frac{[Product]}{[Reactant]} \\ &= \Delta G^0 + RT \ln \frac{[Product]}{[Reactant]} \quad (1)\end{aligned}$$

$\Delta G^0$  = Standard free energy change

The above equation is **Van't Hoff Isotherm**



The above equation is **Van't Hoff Isotherm**

In the cell, if the reaction involves the transfer of 'n' electrons, 'n' faraday of electricity will flow.

If E is the emf of the cell, the total electrical energy produced will be

$$\Delta G = nEF \quad (\text{or}) \quad \Delta G^\circ = nE^\circ F \quad (2)$$

$$\text{Comparing (1) \& (2)} \quad -nEF = -nE^\circ F RT \ln \frac{[M]}{[M^{n+}]} \quad (3)$$

Dividing (3) by  $-nF$  and knowing that  $[M] = 1$

$$E = E^\circ - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]} \quad (\text{or}) \quad E = E^\circ + \frac{RT}{nF} \ln [M^{n+}]$$

$$E = E^\circ + \frac{2.303RT}{nF} \log [M^{n+}] \quad (4)$$

When,  $R = 8.314 \text{ J/K/mole}$ ;  $F = 96,500 \text{ coulombs}$ ,  $T = 298 \text{ K}$  the above equation becomes

$$E = E^0 + \frac{0.0591}{n} \log [C] \quad (\text{Nernst equation for single electrode potential})$$

### Applications of Nernst equation

- i. To calculate unknown electrode potentials
- ii. Prediction of corrosion tendency of metals
- iii. To construct emf series

### Measurement of single electrode potential

It is not possible to evaluate the absolute value of a single electrode potential. Potential difference between two electrodes can be measured. For this purpose a **reference electrode** is used.

**Saturated hydrogen electrode (SHE)** is a common reference electrode whose potential is fixed as zero (**Primary reference electrode**)

The emf of the cell with SHE and the electrode under test as electrodes will be equal to the potential of the electrode

Setting up of SHE is difficult

**Saturated calomel electrode** is used as a secondary reference electrode

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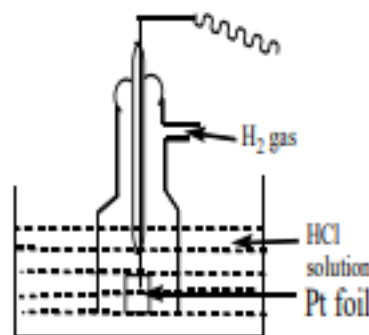
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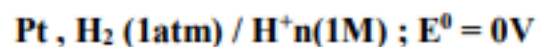
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### Primary reference electrode: Saturated hydrogen electrode (SHE)



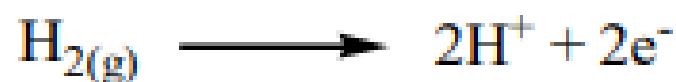
**Construction:** Hydrogen electrode consists of a Pt foil that is connected to a Pt wire sealed in a glass tube. Hydrogen gas is passed through the arm of the surrounding gas tube. The electrode dipped in 1N HCl and hydrogen is passed at 1 atm. is SHE





It is represented as

In the cell, when SHE acts as anode, the electrode reaction is



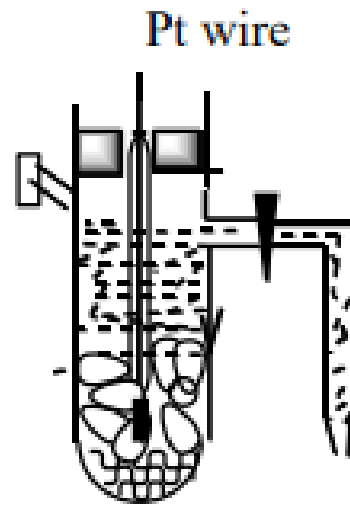
When it acts as cathode, the electrode reaction is



### **Limitations**

- i. requires hydrogen gas and is difficult to set up and transport
- ii. requires large volume of test solution
- iii. The solution may poison the surface of Pt electrode
- iv. Potential of the electrode is dependent on atmospheric pressure.

## Secondary reference electrode: Saturated calomel electrode (SCE)



**Construction:** Calomel electrode consists of a glass tube containing Hg at the bottom over which mercurous chloride paste is placed. The tube is filled with a saturated solution of KCl. A Pt electrode is dipped in. The side tube is for making contact via a salt bridge. The electrode potential of this electrode is +0.2422 V. It is represented as:  
**Hg, Hg<sub>2</sub>Cl<sub>2</sub>(s), KCl (sat. solution)**

In the cell, when SCE acts as anode, the electrode reaction is



When it acts as cathode, the electrode reaction is



The electrode potential (cathode) is given by

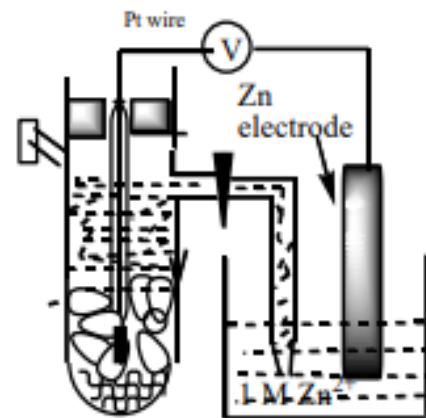
$$E_{(calomel)} = E_{(calomel)}^0 - \frac{RT}{2F} \ln a_{Cl^-}$$

The electrode potential depends on the activity of  $Cl^-$  and Temperature.

a KCl	emf	a KCl	emf (V)	a KCl	emf (V)
0.1	0.3338	1.0	0.2800	Saturated	0.2422

Values at 298 K

### Measurement of single electrode potential of Zn using SCE



Zn electrode is coupled with calomel electrode. Since, the reduction potential of Zn electrode is less than  $E_{cal}^0$ ; calomel electrode will act as cathode and the reaction



$$E_{cell} = E_{right}^0 - E_{left}^0; E_{cell} = E_{cal}^0 - E_{Zn}^0$$

$$E_{Zn}^0 = E_{cal}^0 - E_{cell} = +0.2422 - 1.0025 = -0.7603V$$

**Electrode potentials of metals with respect to SHE**  
(Electrochemical series (or) EMF series)

***Electrochemical series***

Electrode	Electrode reaction	E <sup>0</sup> (V)	Nature
Li <sup>+</sup> /Li	Li <sup>+</sup> + e <sup>-</sup> ⇌ Li	-3.01	Anodic ↑
Mg <sup>2+</sup> /Mg	Mg <sup>2+</sup> + 2 e <sup>-</sup> ⇌ Mg	-2.37	
Pb <sup>2+</sup> /Pb	Pb <sup>2+</sup> + 2 e <sup>-</sup> ⇌ Pb	-1.12	
Zn <sup>2+</sup> /Zn	Zn <sup>2+</sup> + 2 e <sup>-</sup> ⇌ Zn	-0.76	
Fe <sup>2+</sup> /Fe	Fe <sup>2+</sup> + 2 e <sup>-</sup> ⇌ Fe	-0.44	
Sn <sup>2+</sup> /Sn	Sn <sup>2+</sup> + 2 e <sup>-</sup> ⇌ Sn	-0.136	Pt- Reference: ↓ Cathodic
H <sup>+</sup> /H <sub>2</sub>	2H <sup>+</sup> + 2e <sup>-</sup> ⇌ H <sub>2</sub>	0.00	
Cu <sup>2+</sup> /Cu	Cu <sup>2+</sup> + 2 e <sup>-</sup> ⇌ Cu	+0.34	
Ag <sup>+</sup> /Ag	Ag <sup>+</sup> + e <sup>-</sup> ⇌ Ag	+0.80	
Au <sup>+</sup> /Au	Au <sup>+</sup> + e <sup>-</sup> ⇌ Au	+1.50	
½ F <sub>2</sub> /F <sup>-</sup>	½ F <sub>2</sub> + e <sup>-</sup> ⇌ F <sup>-</sup>	+2.87	

**Significance of emf series (or) Application of electrochemical series (or) Applications of Nernst equation**

**i. Calculation of standard emf of the cell**

$E^0$  can be calculated if the standard electrode potential values are known

$$E_{cell} = E_{right}^0 - E_{left}^0$$

**ii. Relative ease of oxidation or reduction**

Higher (+ve) value of standard reduction potential, greater is the tendency for reduction.

Metals on the top (- value) are more easily oxidized.



Fluorine has higher +ve value of standard reduction potential (+2.87V) and shows higher tendency for reduction.

Lithium has highest – ve value (-3.02V) and shows higher tendency towards reduction.

### **iii. Displacement of one element by the other**

Metals which lie higher in the series can displace those which lie below them in the series.

Copper will displace silver from its solution.

Iron will displace copper from its solution.

### **iv. Determination of equilibrium constant (K) for a reaction**

$$-\Delta G^0 = RT \ln K = 2.303RT \log K$$

$$\log K = \frac{-\Delta G^0}{2.303RT} = \frac{nFE^0}{2.303RT} \quad \left[ \because -\Delta G^0 = nFE^0 \right]$$

From the value of  $E^0$ , the equilibrium constant for the reaction can be obtained


### **v. Hydrogen displacement behaviour**

Metals with – ve reduction potential (metals placed above  $H_2$ ) in emf series will displace hydrogen from acid solutions.

Zn will displace  $H_2$  from dilute acids whereas, silver cannot.

vi. Predicting the spontaneity of redox reactions If  $E^0$  of a cell is +ve the reaction is spontaneous  
If  $E^0$  of a cell is -- ve the reaction is not possible

### Galvanic series

Magnesium	
Magnesium alloys	
Zinc	
Aluminium	
Aluminium alloys	
Copper	
Copper – nickel alloys	
Gold	
Platinum	

Oxidation potential of various metals alloys are measured by immersing them in sea water. SCE is used as the reference electrode. The values are arranged in decreasing order of activity and the series is **Galvanic series**

This series provide more practical information on the relative corrosion tendencies of different metals and alloys. The speed of corrosion depends on the difference in potential between the anodic and cathodic metals in contact.

## Potentiometric titration

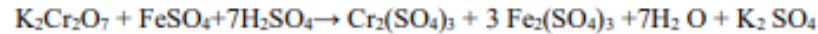
- Potentiometric titration is a volumetric method in which the changes in the emf between two electrodes (referent and indicator electrode) on the addition of titrant of known concentration (titrant) to a solution of unknown (analyte).
- The indicator electrodes is reversible with respect to one of the ions of analyte taking part in the titration reaction but does not take part in the reaction. They are inert electrode made up of Pt or Au.
- During the course of the titration, the concentration of active ion in the analyte changes thereby electrode potential of indicator electrode changes.
- Types of potentiometric titration for the determination of analytes in solutions include acid-base, redox, precipitation, and complexometric.

## I) Redox Titration: $\text{Fe}^{2+}$ against dichromate

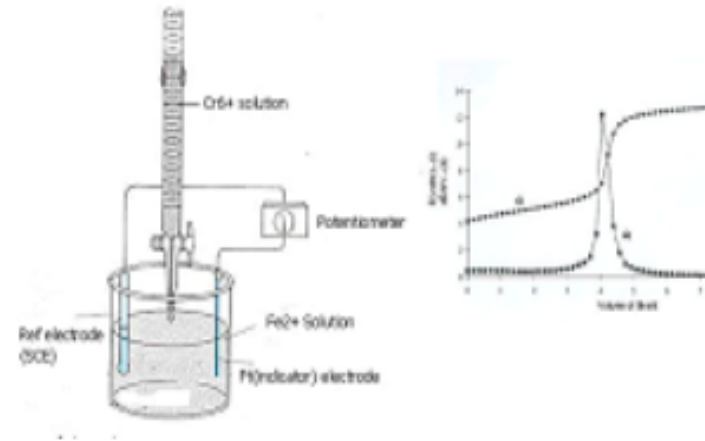
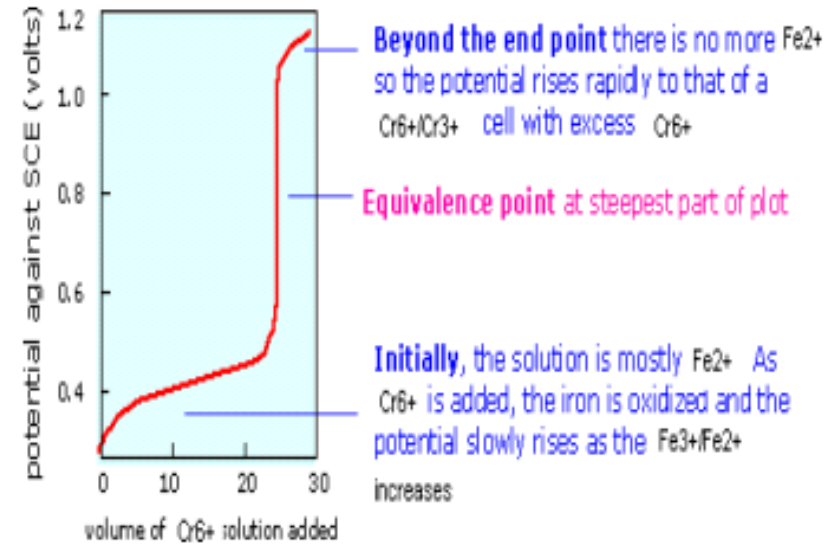
- The concentration of an ion such as  $\text{Fe}^{2+}$  can be found by titrating with a strong oxidizing agent such as  $\text{KMnO}_4$  ( $\text{Mn}^{7+}$ ) or  $\text{K}_2\text{Cr}_2\text{O}_7$  ( $\text{Cr}^{6+}$ ).
  - The titration is carried out in one side of a cell whose other half is a reference electrode: Calomel electrode,  
 $\text{Pt} | \text{Hg} | \text{Hg}^{2+} (\text{aq}) | \text{KCl} ||$
-



- Cell configuration:  
 $Pt(s) | Hg^+ (aq) | Hg_2 Cl_2 (s) | KCl || Fe^{3+}(aq) | Fe^{2+}(aq) | Pt(s)$
- $E_{meas} = E_{ind} - E_{SCE}$
- $E_{ind}$   
 $(E_{Fe^{3+}/Fe^{2+}}) = E^0_{Fe^{3+}/Fe^{2+}} + 0.0591 \log \frac{Fe^{3+}}{Fe^{2+}}$   
 where  $E^0_{Fe^{3+}/Fe^{2+}} = 0.77V$
- Initially the left cell contains only  $Fe^{2+}$ . As the titrant is added, the ferrous ion is oxidized to  $Fe^{3+}$
- according to the reaction.

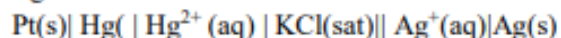


- Once the first drop of  $Cr^{6+}$  ( $K_2Cr_2O_7$ ) titrant has been added, the potential of the indicator electrode is controlled by the ratio of oxidized and reduced iron which causes the potential to rise as more iron becomes oxidized.
- Near the end-point the ratio changes very rapidly since a small quantity of added  $Mn^{7+}$  or  $Cr^{6+}$  removes considerable proportion of the few remaining  $Fe^{2+}$  ions.
- When the equivalence point is reached, the  $Fe^{2+}$  will have been totally consumed and the potential will then be controlled by the concentration ratio of cell couple  $Cr^{6+} / Cr^{3+}$
- The end point is found not by measuring a particular cell voltage, but by finding what volume of titrant gives the steepest part of the curve.
- A titration curve has a characteristic sigmoid curve. The part of the curve that has the maximum change marks the equivalence point of the titration.
- The first derivative,  $\Delta E / \Delta V$ , is the slope of the curve, and the endpoint occurs at the volume,  $V'$ , where  $\Delta E / \Delta V$  has the maximum value.



## II) Precipitation Titration- $\text{Ag}^+$ Vs $\text{Cl}^-$ titrants

- Titration involving precipitation can be followed potentiometrically by the use of active metal (Ag) electrode.
- For the measurement of  $\text{Ag}^+$ , Ag electrode dipping in unknown  $\text{AgNO}_3$  solution is coupled with calomel electrode.
- Cell configuration:



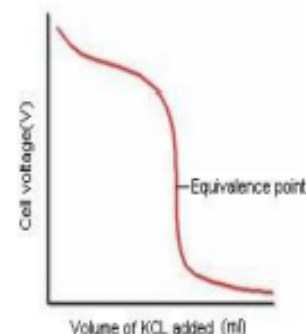
- $E_{\text{meas}} = E_{\text{Ag}^+ / \text{Ag}} - E_{\text{SCE}}$   
 $E_{\text{meas}} = E_{\text{Ag}^+ / \text{Ag}} - 0.246 \text{ V},$   
 $E_{\text{Ag}^+ / \text{Ag}} = E^0_{\text{Ag}^+ / \text{Ag}} + 0.0591 \log [\text{Ag}^+]$
- Initially the cell contains excess  $\text{Ag}^+$  ions. As the titrant KCl or NaCl is added, concentration of  $\text{Ag}^+$  ion decreases due to the precipitation of  $\text{Ag}^+$  ions as AgCl according to the equation  

$$\text{AgNO}_3 + \text{KCl} \rightarrow \text{AgCl} \downarrow + \text{KNO}_3$$
- The reduction potential of active electrode goes on decreasing progressively on the addition of KCl.
- At the end point the concentration change of  $\text{Ag}^+$  is quite rapid and its concentration becomes very small due to slight solubility of AgCl.
- After the end point, further addition of KCl or NaCl does not affect the concentration of  $\text{Ag}^+$  due to common ion effect.
- A titration curve has a characteristic sigmoid curve. The part of the curve that has the maximum change marks the equivalence point of the titration.
- The first derivative,  $\Delta E / \Delta V$ , is the slope of the curve, and the endpoint occurs at the volume,

$V'$ , where  $\Delta E / \Delta V$  has the maximum value

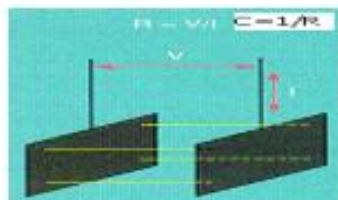
### Advantages of potentiometric titration

- They are more accurate and precise.
- Can be used with colored or opaque solutions and ionic concentration down to  $10^{-3} \text{ N}$
- No interference due to other ions.



## Conductometric Titrations

- Method of volumetric analysis based on the change in conductance of the solution at the equivalence point or end point during titration.
- Conductance (C) is the reciprocal of electrical resistance (R).  $[C = 1/R]$ . It is a measure of the ability of a solution to conduct electricity.
- The conductance of a solution depends upon the number of free ions in the solution, the charge on the ions, and the mobility of the ions. The conductance of a solution is the sum of the conductances of all of the ions that are in the solution.  $C = \sum C_i$
- The unit of conductance is the Siemens (S), which is the reciprocal of resistance  $\Omega$ .
- Specific conductance (K) is the conductance of one cm cube of material and is usually measured with an alternating current between two identical, platinized platinum electrodes.
- Specific conductance is obtained by multiplying measured conductance by cell constant of the conductivity cell.  $K = \text{cell constant} \times \text{measured conductance}$



**Conductivity Cell:** Specially designed cells in which two plates of inert metal (Pt or Au) are provided to serve the flow in and flow out of electron.

#### Titration of strong acid vs strong base (hydrochloric acid with sodium hydroxide)

- The reaction that takes place in the titration vessel is  

$$\text{H}^+ + \text{Cl}^- + \text{Na}^+ \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{Na}^+ \text{Cl}^-$$
- Before the end point,  $\text{H}^+$  is removed from the solution by reaction with  $\text{OH}^-$ , and  $\text{Na}^+$  is added to the solution.
- Since the relative conductance of  $\text{H}^+$  is about seven times that of  $\text{Na}^+$ , the conductance of the solution decreases prior to the end point.
- After the end point, no  $\text{H}^+$  is available to react, and the conductance of the solution increases as a result of the addition of  $\text{Na}^+$  and  $\text{OH}^-$ .
- Consequently the titration curve has a V-shape as shown in the figure.

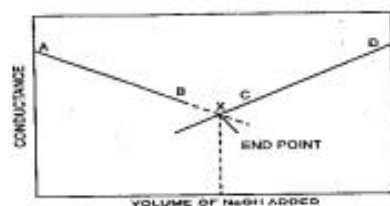
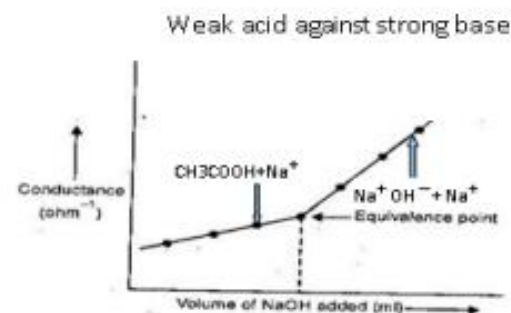


Fig. Plot of conductance versus volume of NaOH.

- $\text{Na}^+ \text{OH}^-$  The end point of the titration corresponds to the intersection of the extrapolated linear portions of the titration curve.

#### Titration of weak acid vs strong base (Acetic acid with NaOH)

- Since acetic acid is dissociated slightly ( $K_a = 1.8 \times 10^{-5}$ ) in aqueous solution, the conductance of the acetic acid solution is initially small.
- As sodium hydroxide is added, the hydroxide reacts with the acid to form water and acetate.  $\text{CH}_3\text{COOH} + \text{NaOH} \rightarrow \text{H}_2\text{O} + \text{Na}^+ \text{CH}_3\text{COO}^- + \text{H}^+ + \text{CH}_3\text{COO}^-$
- The addition of  $\text{CH}_3\text{COO}^-$  and  $\text{Na}^+$  ions to the solution causes the conductance of the solution to increase.



After the end point,  $\text{Na}^+$  and  $\text{OH}^-$  are added to the solution. Since the relative conductance of  $\text{OH}^-$  is nearly five times that of  $\text{C}_2\text{H}_3\text{O}_2^-$ , the conductance of the solution after the end point increases more rapidly than it did before the end point.

- The end point corresponds to the intersection of the extrapolated linear portions of the curve.

### **Advantages of conductometric titration**

- No special care is necessary near the end point as the end point is ascertained graphically.
- Colored solution which cannot be titrated by ordinary volumetric methods with the help of indicators can be titrated
- The titrations of weak acid against weak bases can be performed, they cannot be measured in volumetric titration because they do not produce sharp color change of indicators.
- Very dilute solutions can be titrated
- The method is very accurate in dilute solutions
- It can even be used in colored or turbid solution.

# How to calculate Electrode potential?

The standard reduction potential can be determined by subtracting the standard reduction potential for the reaction occurring at the anode from the standard reduction potential for the reaction occurring at the cathode. The minus sign is needed because oxidation is the reverse of reduction.



$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$\begin{aligned} E^\circ_{\text{Cu}^{2+}/\text{Cu}} - E^\circ_{\text{H}^+/\text{H}_2} &= E^\circ_{\text{Cu}^{2+}/\text{Cu}} - 0 = E^\circ_{\text{Cu}^{2+}/\text{Cu}} \\ &= +0.34\text{V} \end{aligned}$$



# Electrochemical Series

- The standard reduction potentials of ~~elements are arranged in order of~~

The arrangement of elements in order of increasing reduction potential values is called **electrochemical series**. It is also called **activity series**, of some typical electrodes.

Table 1: Electrochemical Series		
	Equilibrium (Oxidants ↔ Reductants)	E° (volts)
Metal Reducing Activity Increasing ↑	Lithium: $\text{Li}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{Li}(\text{s})$	-3.03
	Potassium: $\text{K}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{K}(\text{s})$	-2.92
	Calcium: $\text{Ca}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Ca}(\text{s})$	-2.87
	Sodium: $\text{Na}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{Na}(\text{s})$	-2.71
	Magnesium: $\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Mg}(\text{s})$	-2.37
	Aluminum: $\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \leftrightarrow \text{Al}(\text{s})$	-1.66
	Zinc: $\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Zn}(\text{s})$	-0.76
	Iron: $\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Fe}(\text{s})$	-0.44
	Lead: $\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Pb}(\text{s})$	-0.13
	Hydrogen: $2\text{H}^+(\text{aq}) + 2\text{e}^- \leftrightarrow \text{H}_2(\text{g})$	0.00
	Copper: $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Cu}(\text{s})$	+0.34
	Silver: $\text{Ag}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{Ag}(\text{s})$	+0.80
	Gold: $\text{Au}^{3+}(\text{aq}) + 3\text{e}^- \leftrightarrow \text{Au}(\text{s})$	+1.50
↓ Metal Oxidizing Activity Increasing		

# Reduction Potential & Extraction Methods

Table 1: Electrochemical Series

Equilibrium (Oxidants $\leftrightarrow$ Reductants)	$E^\circ$ (volts)
Lithium: $\text{Li}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{Li}(\text{s})$	-3.03
Potassium: $\text{K}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{K}(\text{s})$	-2.92
Calcium: $\text{Ca}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Ca}(\text{s})$	-2.87
Sodium: $\text{Na}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{Na}(\text{s})$	-2.71
Magnesium: $\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Mg}(\text{s})$	-2.37
Aluminum: $\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \leftrightarrow \text{Al}(\text{s})$	-1.66
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Lead: $\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Pb}(\text{s})$	-0.13
Hydrogen: $2\text{H}^+(\text{aq}) + 2\text{e}^- \leftrightarrow \text{H}_2(\text{g})$	0.00
Copper: $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Cu}(\text{s})$	+0.34
Silver: $\text{Ag}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{Ag}(\text{s})$	+0.80
Gold: $\text{Au}^{3+}(\text{aq}) + 3\text{e}^- \leftrightarrow \text{Au}(\text{s})$	+1.50

## Extraction Methods

- Electrolysis of fused salts, usually chlorides
- Electrolysis of  $\text{MgCl}_2$  High temp. reduction with Carbon Electrolysis of  $\text{Al}_2\text{O}_3$  dissolved in  $\text{Na}_3[\text{AlF}_6]$
- Chemical reduction of oxides with Carbon
- Found as native metal or compounds easily decomposed by heat.