Applications of Spectroscopy, Part – V, M.Sc. IV Semester Chemistry

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This Presentation Includes

- **<u>Mass Spectroscopy</u>**
- Introduction
- Instrumentation
- Fragmentation
- Fragmentation Patterns
- Rearrangements/ McLafferty Rearrangement
- Nitrogen Rule
- Ring Rule
- Even Electron Rule
- Rule 13
- Isotope Effect
- Fragmentation Patterns for simple organic Compounds
- ✓ Alkanes
- ✓ Alkenes

- ✓ Alkynes
- ✓ Aromatic hydrocarbons
- ✓ Alcohols
- ✓ Phenol
- ✓ Ether
- ✓ Carbonyl Compounds
- ✓ Amines
- ✓ Nitriles
- ✓ Nitro compounds
- Assignment/ Set Of questions

Introduction

- **Mass spectrometry** (**MS**) is an analytical technique that measures the mass-to-charge ratio of ions. The results are typically presented as a mass spectrum, a plot of intensity as a function of the mass-to-charge ratio. Mass spectrometry is used in many different fields and is applied to pure samples as well as complex mixtures.

- A mass spectrum is a plot of the ion signal as a function of the mass-to-charge ratio. These spectra are used to determine the elemental or isotopic signature of a sample, the masses of particles and of molecules, and to elucidate the chemical identity or structure of molecules and other chemical compounds.

Introduction

- In a typical MS procedure, a sample, which may be solid, liquid, or gaseous, is ionized, for example by bombarding it with electrons. This may cause some of the sample's molecules to break into charged fragments or simply become charged without fragmenting. These ions are then separated according to their mass-to-charge ratio, for example by accelerating them and subjecting them to an electric or magnetic field: ions of the same mass-to-charge ratio will undergo the same amount of deflection. The ions are detected by a mechanism capable of detecting charged particles, such as an [electron multiplier]. Results are displayed as spectra of the signal intensity of detected ions as a function of the mass-to-charge ratio. The atoms or molecules in the sample can be identified by correlating known masses (e.g. an entire molecule) to the identified masses or through a characteristic fragmentation pattern.

Mass Spectrometer (Instrumentation)

- A mass spectrometer consists of three components: an ion source, a mass analyzer, and a detector. The *ionizer* converts a portion of the sample into ions. There is a wide variety of ionization techniques, depending on the phase (solid, liquid, gas) of the sample and the efficiency of various ionization mechanisms for the unknown species. An extraction system removes ions from the sample, which are then targeted through the mass analyzer and into the *detector*. The differences in masses of the fragments allows the mass analyzer to sort the ions by their mass-to-charge ratio. The detector measures the value of an indicator quantity and thus provides data for calculating the abundances of each ion present. Some detectors also give spatial information, e.g., a multichannel plate.

Mass Spectrometer (Instrumentation)
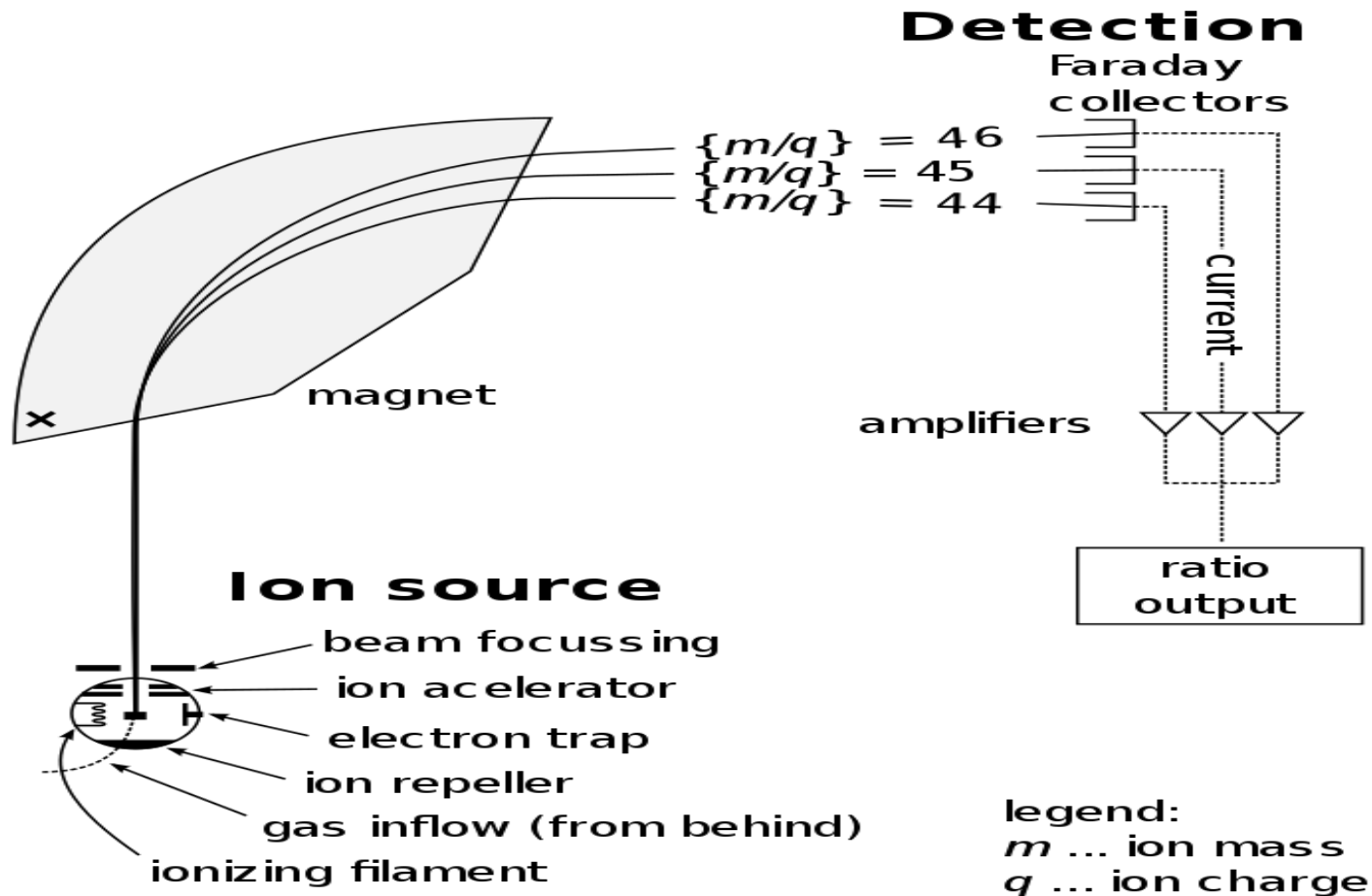
Fragmentation

- In mass spectrometry, **fragmentation** is the [dissociation](#) of energetically unstable molecular ions formed from passing the molecules in the ionization chamber of a mass spectrometer. The fragments of a molecule cause a unique pattern in the [mass spectrum](#). These reactions are well documented over the decades and fragmentation pattern is useful to determine the molar weight and structural information of the unknown molecule

Fragmentation (Example -Toluene)
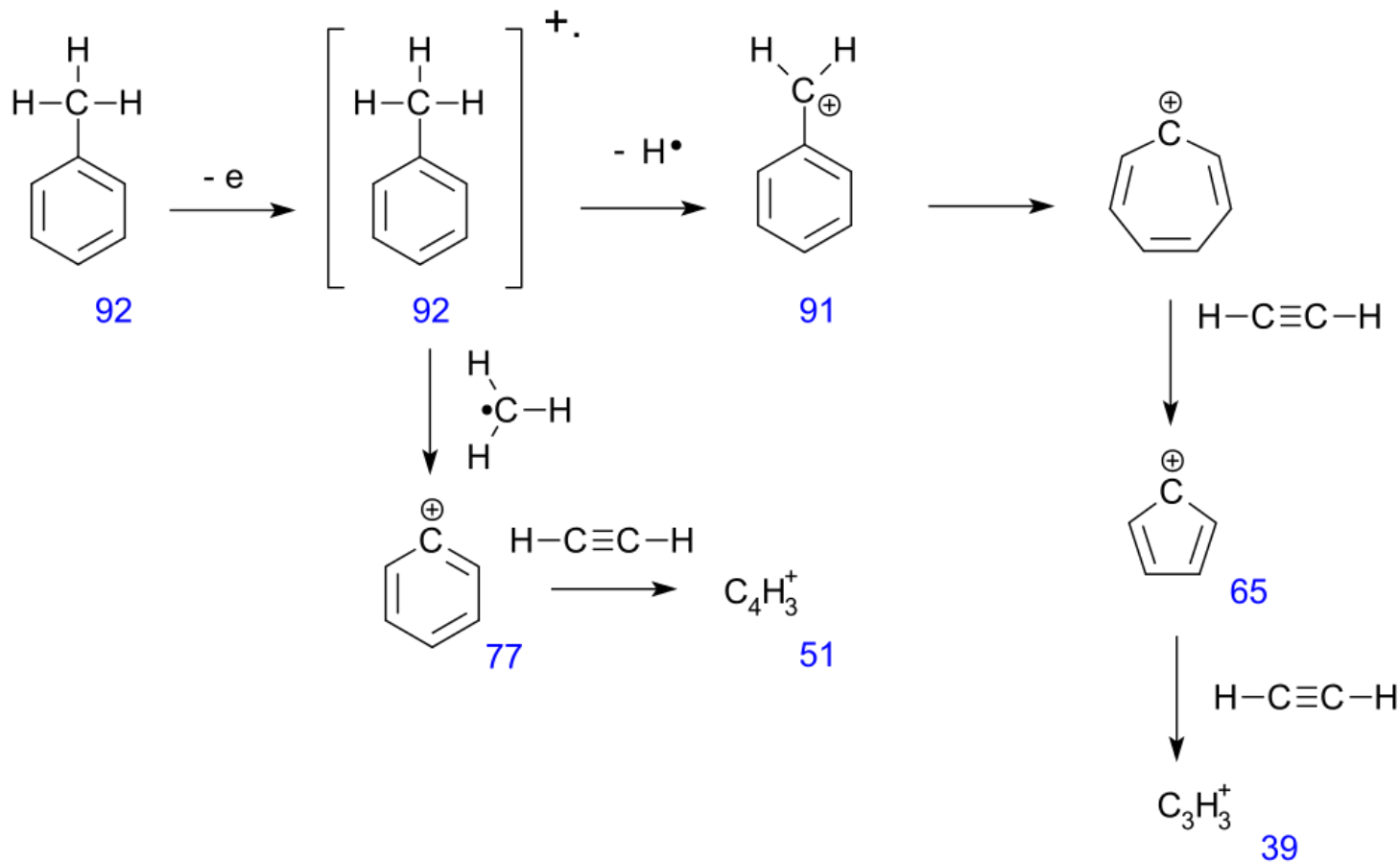
Fragmentation reactions

- Fragmentation is a type of chemical dissociation, in which removal of the electron from molecule result in ionization. Removal of electrons from either sigma bond, pi bond or nonbonding orbitals causes the ionization. That can take place by a process of homolytic cleavage/ homolysis or heterolytic cleavage/ heterolysis of the bond. Relative bond energy and the ability to undergo favorable cyclic transition states affect the fragmentation process. Rules for the basic fragmentation processes are given by Stevenson's Rule.

- Two major categories of bond cleavage patterns are simple bond cleavage reactions and rearrangement reactions.

Homolytic and Heterolytic Cleavage

$$A \text{—} B \longrightarrow A^{\bullet} + B^{\bullet}$$

$$A \text{—} B \longrightarrow A^{\oplus} + B^{\ominus}$$

$$A \text{—} B \longrightarrow A^{\ominus} + B^{\oplus}$$
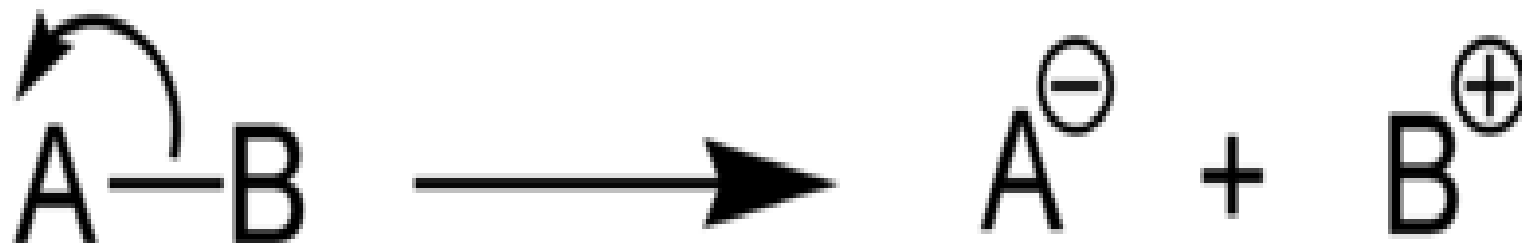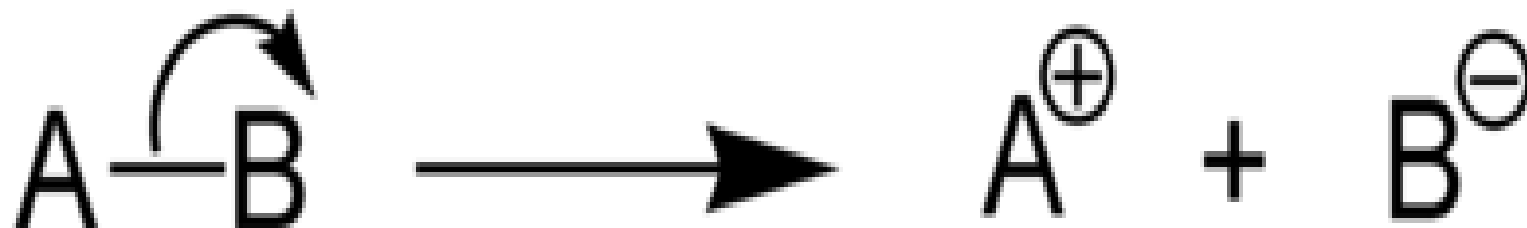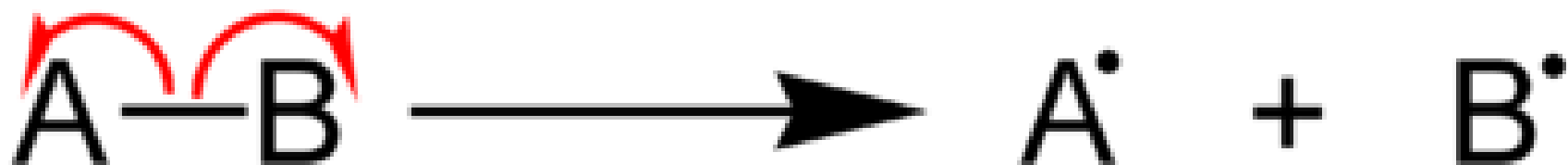
Simple bond cleavage reactions

- Majority of organic compounds undergo simple bond cleavage reactions, in which, direct cleavage of bond take place. Sigma bond cleavage, radical site-initiated fragmentation, and charge site-initiated fragmentation are few types of simple bond cleavage reactions
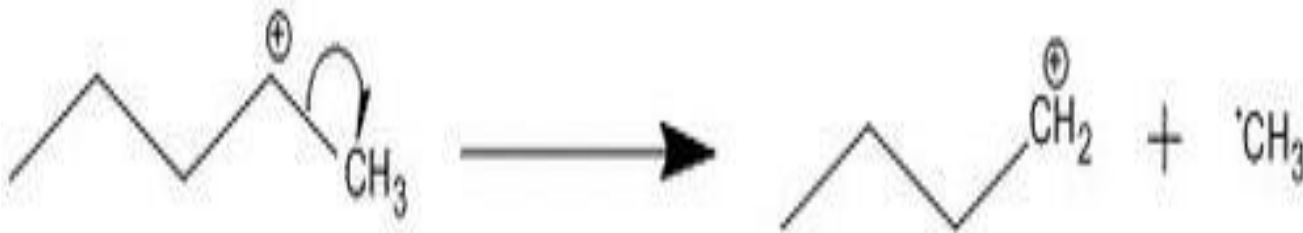
Sigma bond cleavage / σ-cleavage

- Sigma bond cleavage is most commonly observed in molecules, which can produce stable cations such as saturated [alkanes](#), secondary and tertiary [carbocations](#). This occurs when an alpha electron is removed. The C-C bond elongates and weakens causing fragmentation. Fragmentation at this site produces a charged and a neutral fragment.

Radical site-initiated fragmentation

- Sigma bond cleavage also occurs on radical cations remote from the site of ionization. This is commonly observed in alcohols, ethers, ketones, esters, amines,

alkenes and aromatic compounds with a carbon attached to ring. The cation has a radical on a heteroatom or an unsaturated functional group. The driving force of fragmentation is the strong tendency of the radical ion for electron pairing. Cleavage occurs when the radical and an odd electron from the bonds adjacent to the radical migrate to form a bond between the alpha carbon and either the heteroatom or the unsaturated functional group. The sigma bond breaks; hence this cleavage is also known as homolytic bond cleavage or α-cleavage

Charge site-initiated cleavage

- The driving force of charge site-initiated fragmentation is the inductive effect of the charge site in radical cations. The electrons from the bond adjacent to the charged-bearing atom migrate to that atom, neutralizing the original charge and causing it to move to a different site. This term is also called inductive cleavage and is an example of heterolytic bond cleavage

Rearrangement reactions

- Rearrangement reactions are fragmentation reactions that form new bonds producing an intermediate structure before cleavage. One of the most studied rearrangement reaction is the McLafferty rearrangement / γ-hydrogen rearrangement. This occurs in the radical cations with unsaturated functional groups, like ketones, aldehydes, carboxylic acids, esters, amides, olefins, phenylalkanes. During this reaction, γ-hydrogen will transfer to the functional group at first and then subsequent α, β-bond cleavage of the intermediate will take place. Other rearrangement reactions include heterocyclic ring fission (HRF), benzofuran forming fission (BFF), quinone methide (QM) fission or Retro Diels-Alder (RDA).[

# An Example of McLafferty Rearrangement
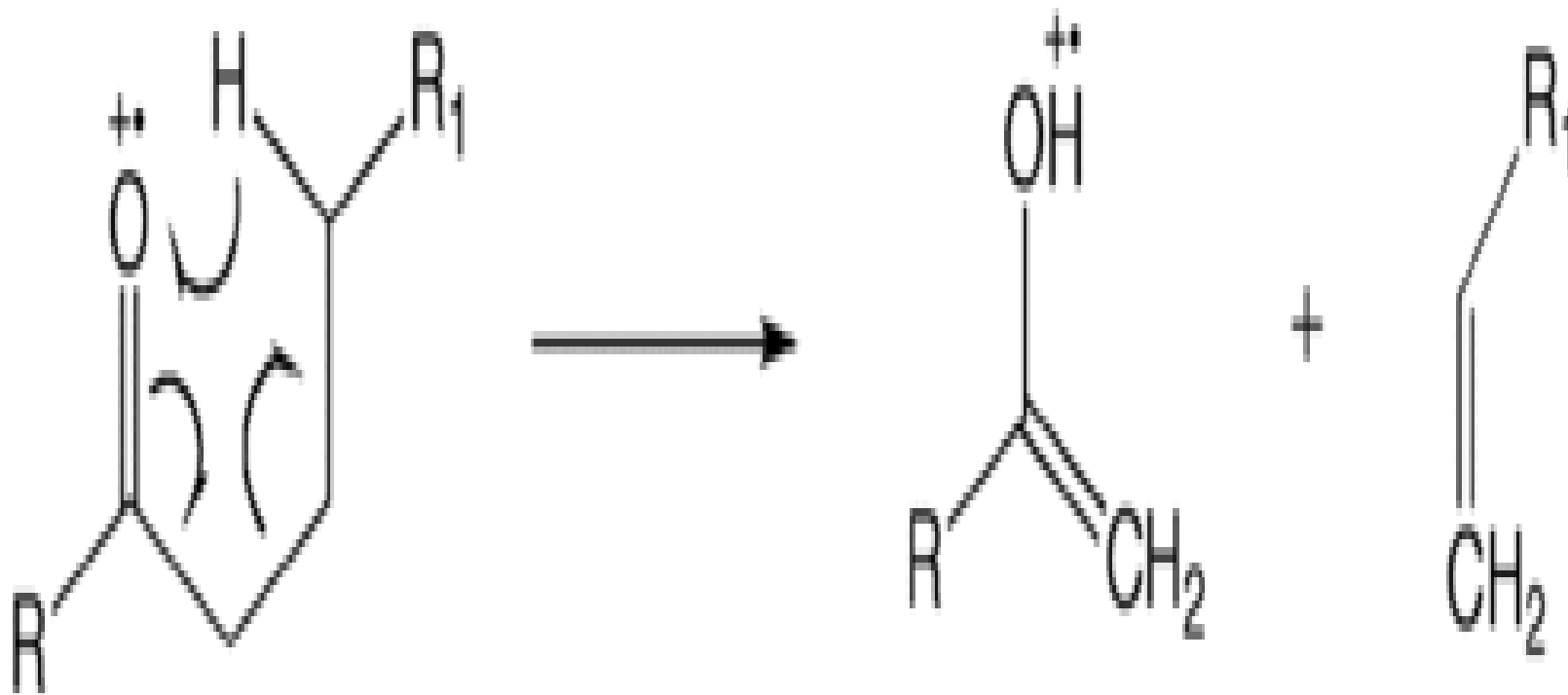
McLafferty rearrangement

- The **McLafferty rearrangement** is an [organic reaction](#) seen in [mass spectrometry](#). A mass spectrometer breaks apart the molecule being studied. The molecule breaks apart in consistent ways that chemists can predict. Most times, a carbon-carbon bond breaks and the atoms do not jump across the break between the fragments. The McLafferty rearrangement is an example of a hydrogen atom jumping to the other fragment as a part of the process of the bond breaking. It happens in an organic molecule containing a keto-group

McLafferty rearrangement

- The American chemist [Fred McLafferty](#) was the first to describe the reaction in 1959
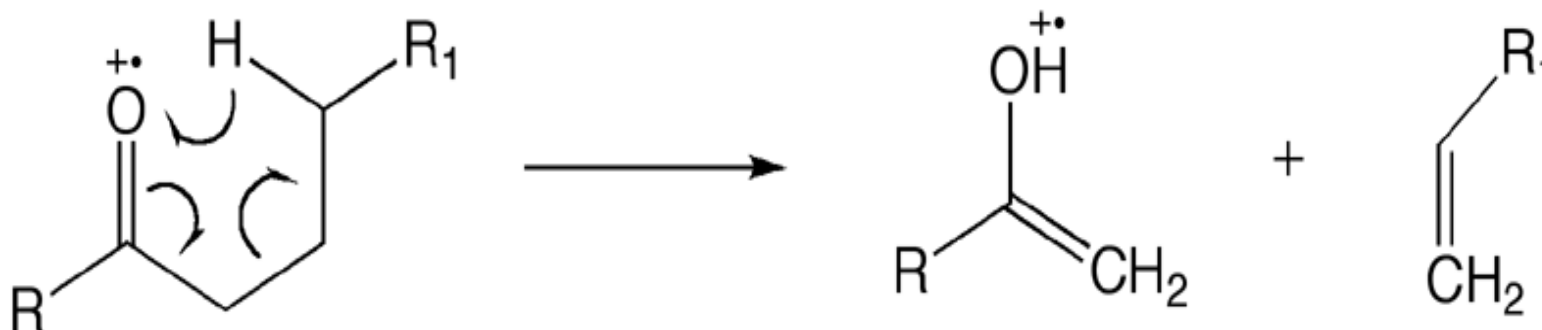
The keto-group undergoes β-cleavage, with the gain of the γ-hydrogen atom. This rearrangement may take place by a radical or ionic mechanism.

Nitrogen rule

- The nitrogen rule states that organic molecules that contain hydrogen, carbon, nitrogen, oxygen, silicon, phosphorus, sulfur, and the halogens have an odd nominal mass if they have an odd number of nitrogen atoms or an even mass if they have an even number of nitrogen atoms are present. The nitrogen rule is true for structures in which all of the atoms in the molecule have a number of covalent bonds equal to their standard valency, counting each sigma bond and pi bond as a separate covalent bond.

Rings rule

- From degree of unsaturation principles, molecules containing only carbon, hydrogen, halogens, nitrogen, and oxygen follow the formula

- Rings $+\pi$ bonds$=u=C-(H/2)-(X/2)+(N/2)+1$

- where C is the number of carbons, H is the number of hydrogens, X is the number of halogens, and N is the number of nitrogen.

Even electron rule

- The **even electron rule** states that ions with an even number of electrons (cations but not radical ions) tend to form even-electron fragment ions and odd-electron ions (radical ions) form odd-electron ions or even-electron ions. Even-electron species tend to fragment to another even-electron cation and a neutral molecule rather than two odd-electron species.

- $OE^{+\bullet} \rightarrow EE^{+} + R^{\bullet}$, $OE^{+\bullet} \rightarrow OE^{+\bullet} + N$

- **Stevenson's rules**

- The more stable the product cation, the more abundant the corresponding decomposition process. Several theories can be utilized to predict the fragmentation process, such as the electron octet rule, the resonance stabilization and hyperconjugation and so on

Rule of 13

- The **Rule of 13** is a simple procedure for tabulating possible [chemical formula](#) for a given molecular mass. The first step in applying the rule is to assume that only carbon and hydrogen are present in the molecule and that the molecule comprises some number of CH "units" each of which has a [nominal mass](#) of 13. If the molecular weight of the molecule in question is M, the number of possible CH units is n and

- $(M/13) = n + (r/13)$

- where r is the remainder. The base formula for the molecule is

- $C_n H_{n+r}$

- and the degree of unsaturation is

- $u = (n-r+2)/2$

- A negative value of u indicates the presence of heteroatoms in the molecule and a half-integer value of u indicates the presence of an odd number of nitrogen atoms. On addition of heteroatoms, the molecular formula is adjusted by the equivalent mass of carbon and hydrogen. For example, adding N requires removing CH_2 and adding O requires removing CH_4.

Isotope effects

- Isotope peaks within a spectrum can help in structure elucidation. Compounds containing halogens (especially chlorine and bromine) can produce very distinct isotope peaks. The mass spectrum of methylbromide has two prominent peaks of equal intensity at *m/z* 94 (M) and 96 (M+2) and then two more at 79 and 81 belonging to the bromine fragment.

- Even when compounds only contain elements with less intense isotope peaks (carbon or oxygen), the distribution of these peaks can be used to assign the spectrum to the correct compound. For example, two compounds with identical mass of 150 Da, $C_8H_{12}N_3^+$ and $C_9H_{10}O_2^+$, will have two different M+2 intensities which makes it possible to distinguish between them.

- Fragmentation patterns of specific compound classes

Alkanes

- For linear alkanes, molecular ion peaks are often observed. However, for long chain compounds, the intensity of the molecular ion peaks are often weak. Linear fragments often differ by 14 Da (CH_2 = 14). For example, hexane fragmentation patterns. The m/z=57 butyl cation is the base peak, and other most abundant peaks in the spectrum are alkyl carbocations at m/z=15, 29, 43 Da.
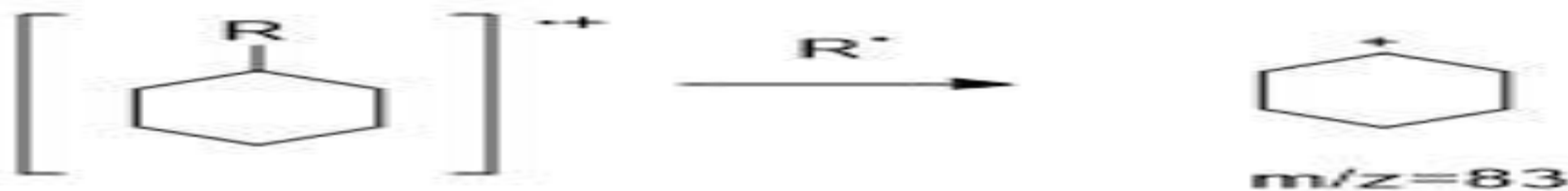
Alkanes
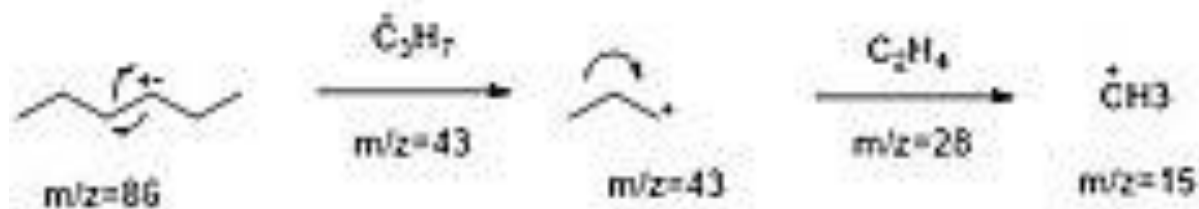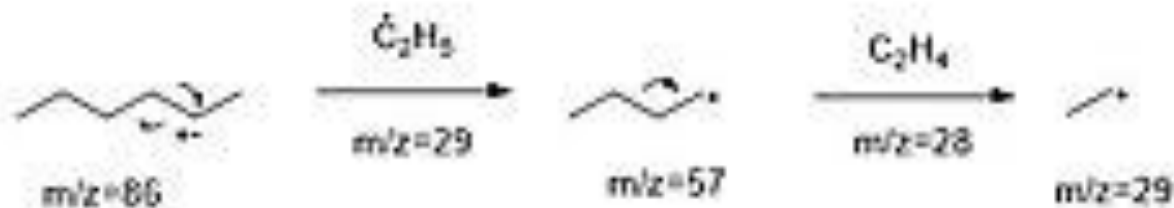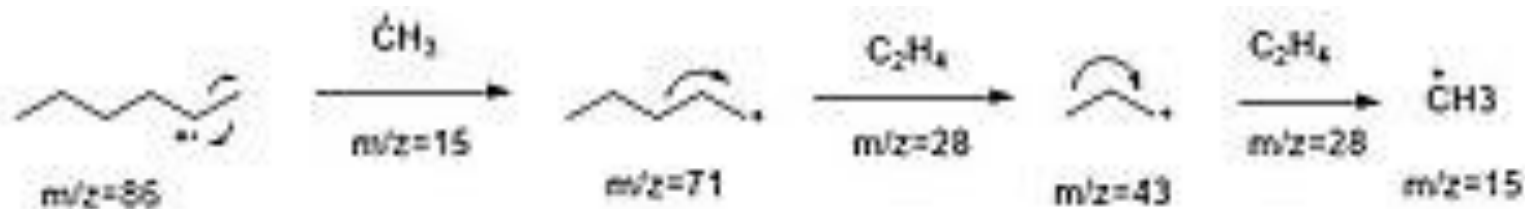
Alkanes

- Branched alkanes have somewhat weaker molecular ion peaks in the spectra. They tend to fragment at the branched point. For the 2,3-dimethylbutane, an isopropyl cation peak (m/z=43) is very strong.
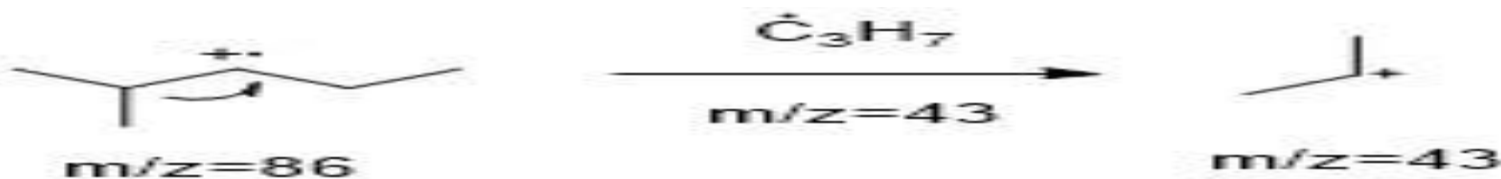
Alkanes

- Cycloalkanes have relatively intense molecular ion peaks (two bonds have to break). Alkene fragmentation peaks are often most significant mode. Loss of "CH_2CH_2" (= 28) is common, if present. However, for the substituted cycloalkanes, they prefer to form the cycloalkyl cations by cleavage at the branched points.
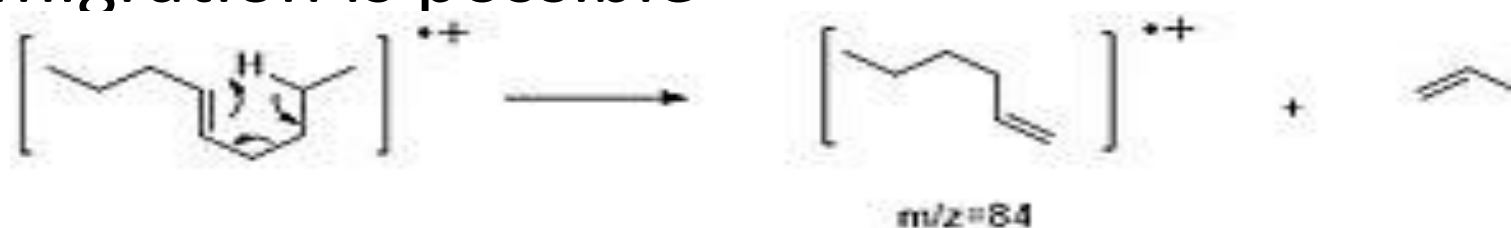
Alkenes

- Alkenes often produce stronger molecular ion peaks than alkanes due to the lower ionization energy of a pi electron than a σ electron. After the ionization, double bonds can migrate easily, resulting in almost impossible determination of isomers. Allylic cleavage is most significant fragmentation mode due to resonance stabilization.
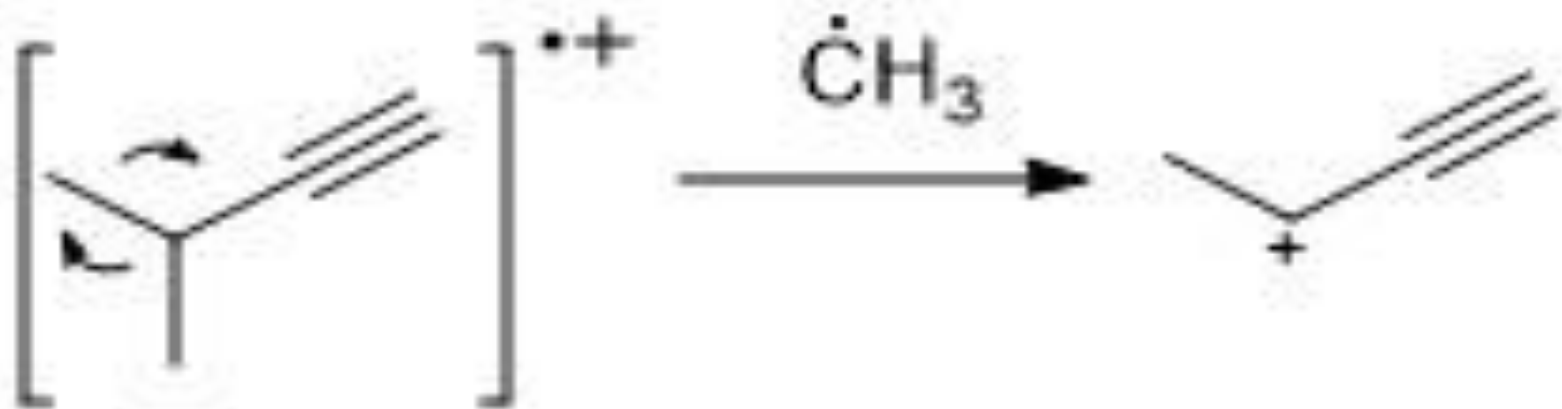
Alkenes

- McLafferty-like rearrangements are possible (similar to carbonyl pi bonds). Again, bond migration is possible

m/z=84

Cyclohexenes often undergo retro Diels-Alder reactions.

Alkynes

- Similar to alkenes, alkynes often show strong molecular ion peak. Propargylic cleavage is a most significant fragmentation mode.

Most possible ionization mechanism of alkyne

Aromatic hydrocarbons

- Aromatic hydrocarbons show distinct molecular ion peak. benzylic cleavage is pretty common. When alkyl groups are attached to the ring, a favorable mode of cleavage is to lose a H-radical to form the tropylium cation (m/z 91)
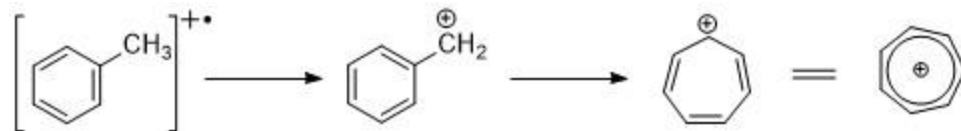
- Benzylic Cleavage

Aromatic Compounds

- Alkyl substituted benzenes can fragment via the kinetic controlled process to form $C_6H_5^+$, $C_6H_6^+$ ions

$m/z=77$ $m/z=78$ $m/z=79$
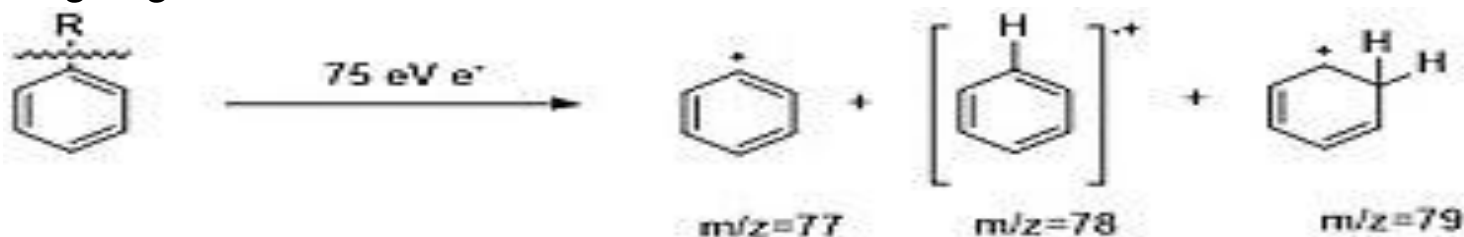
- Benzene derivatives fragmentation pattern

Aromatic Compounds

- Another common mode of fragmentation is the McLafferty rearrangement, which requires the alkyl chain length to be at least longer than 3 carbons.
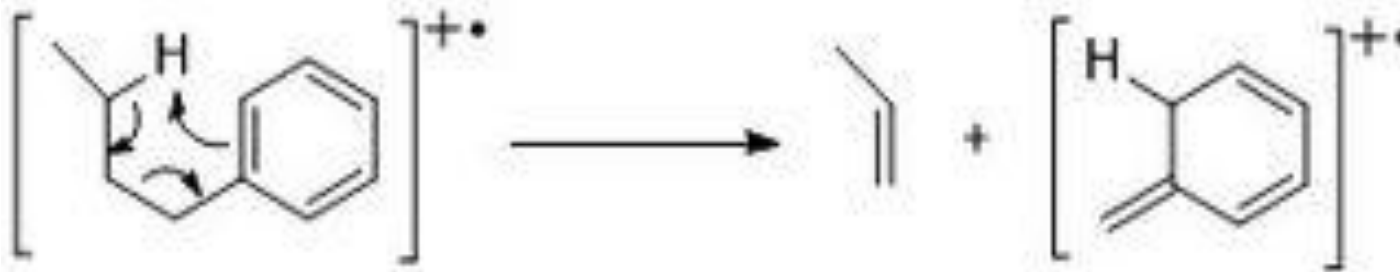
- Mclafferty Rearrangement in Aromatic Compounds

Alcohols

- Alcohols generally have weak molecular ion peaks due to the strong electronegativity of oxygen. "Alpha" cleavage is common due to the resonance stabilization. The largest alkyl group will be lost.
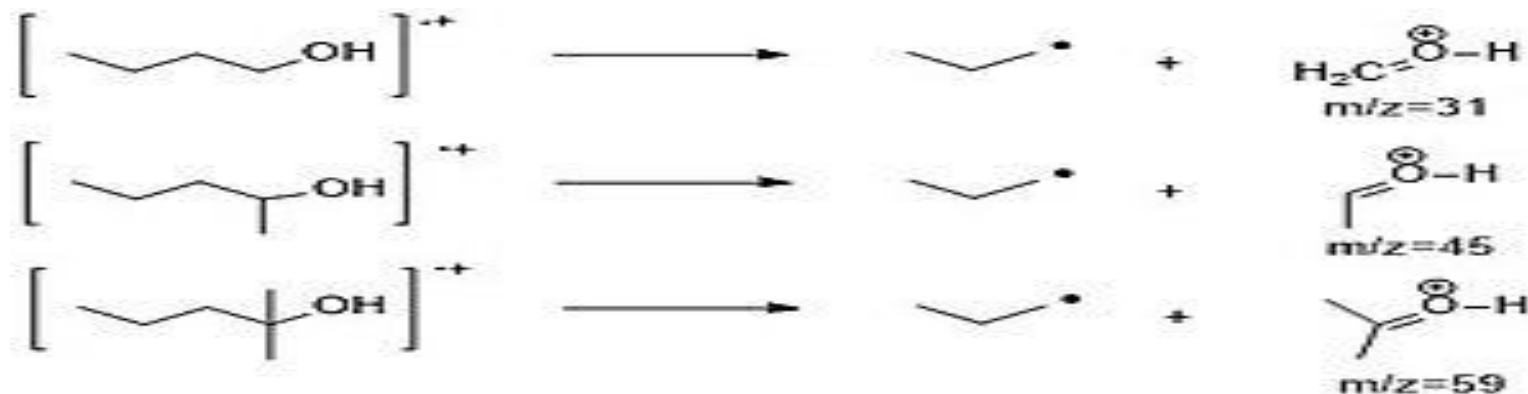
- Alpha –cleavage fragmentation of alcohols

Alcohols

- Another common fragmentation mode is dehydration (M-18). For longer chain alcohols, a McLafferty type rearrangement can produce water and ethylene (M -46).

Phenol

- Phenol exhibit a strong molecular ion peak. Loss of H· is observed (M – 1), CO (M – 28) and formyl radical (HCO·, M – 29) is common observed.
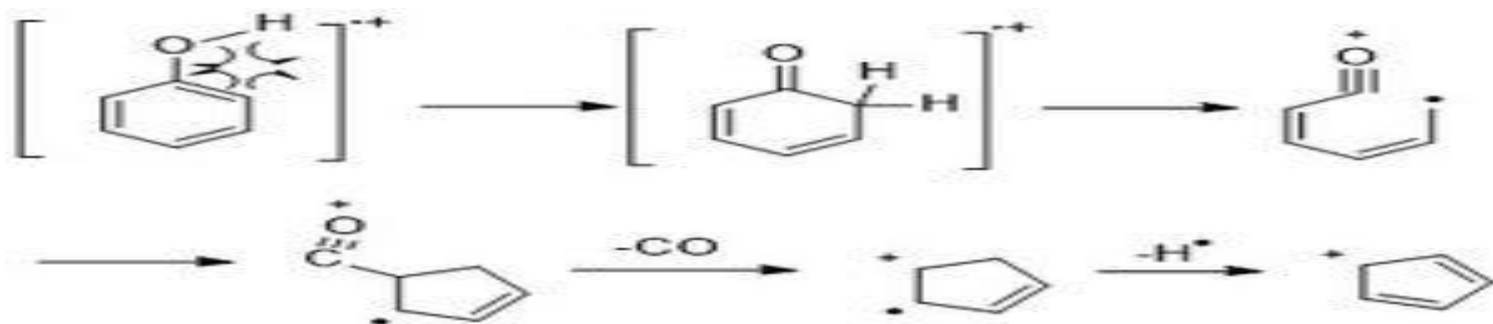
Ether

Ethers produce slightly more intense molecular ion peaks compared to the corresponding alcohols or alkanes. There are two common cleavage modes. α-cleavage and C-O bond cleavage.
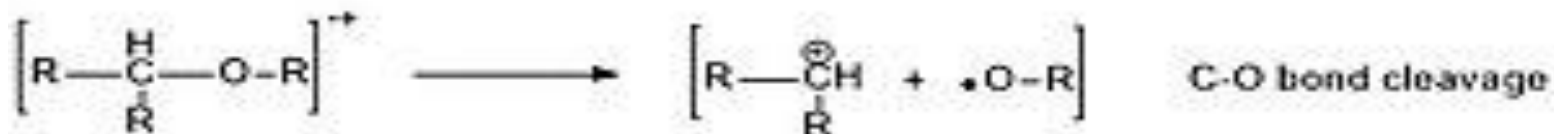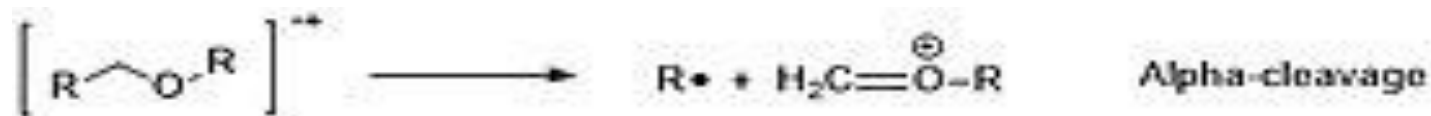
Ethers

- Aromatic ethers can generate the C6H5O+ ion by loss of the alkyl group rather than H; this can expel CO as in the phenolic degradation
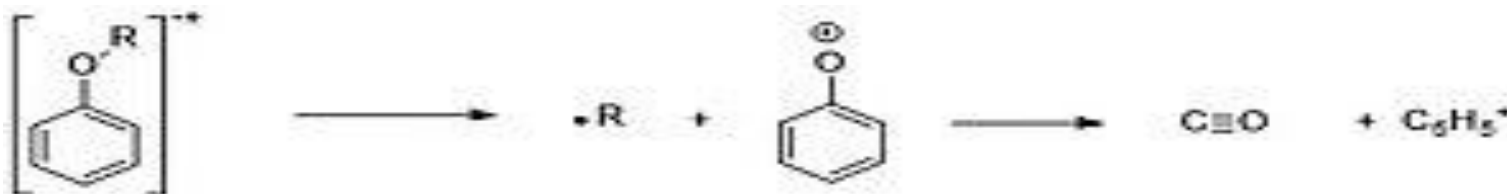
- Fragmentation for aromatic Ethers

Carbonyl compounds

- There are five types of carbonyl compounds, including aldehydes, ketones, carboxylic acids and esters. The principal fragmentation modes are described as follows:

- Alpha-cleavage can occur on either side of the carbonyl functional group since an oxygen lone pair can stabilize the positive charge.

Alpha Cleavage of carbonyl compounds

Carbonyl Compounds

- β-cleavage is a characteristic mode of carbonyl compounds' fragmentation due to the resonance stabilization.
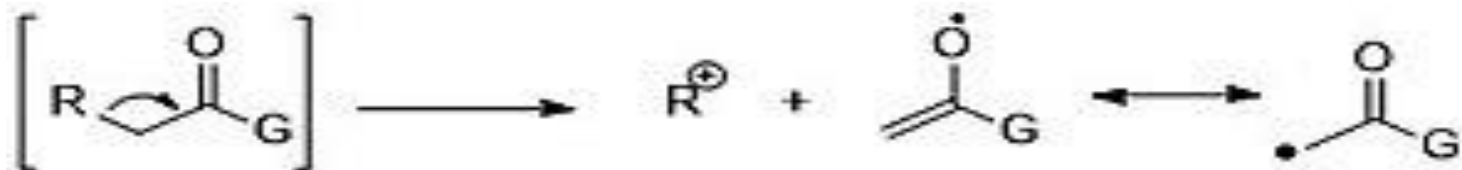
McLafferty rearrangements in Carbonyl Compounds

- For longer chain carbonyl compounds (carbon number is bigger than 4), McLafferty rearrangements are dominant.
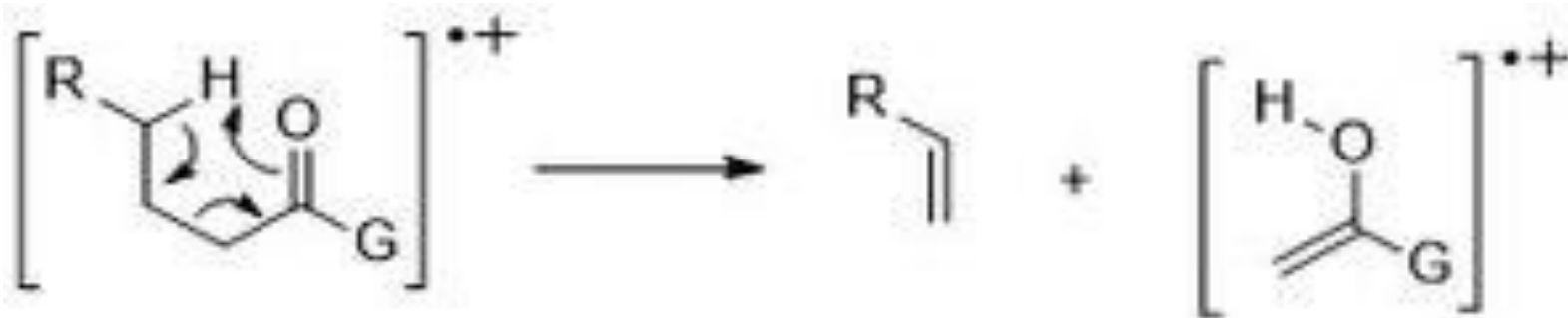
Aromatic Carbonyl Compounds

• For aromatic carbonyl compounds, Alpha-cleavages are favorable primarily to lose G· (M – 1,15, 29…) to form the C6H5CO+ ion (m/z=105), which can further lose CO (m/z= 77) and HCCH (m/z=51).
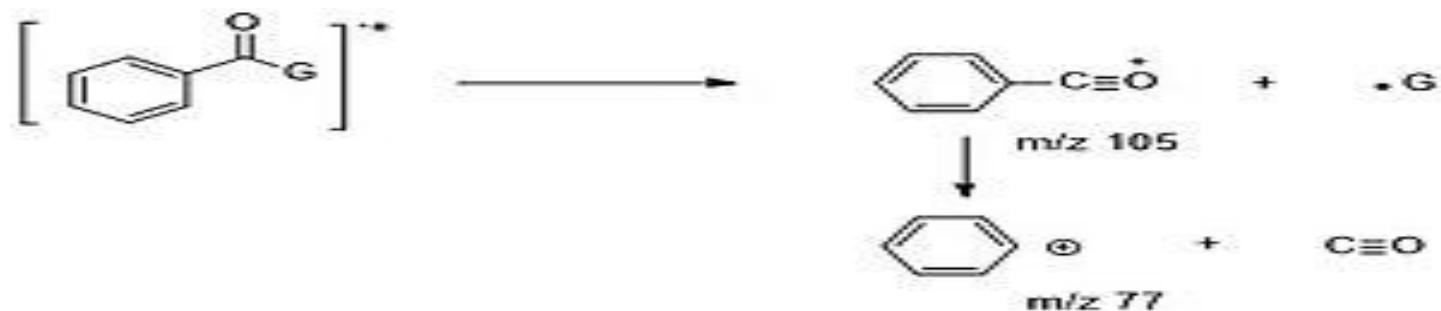
Amines

- Amines follow nitrogen rule. Odd molecular ion mass-to-charge ratio suggests existence of odd numbers of nitrogens. Nonetheless, molecular ion peaks are weak in aliphatic amines due to the ease of fragmentation next to amines. Alpha-cleavage reactions are the most important fragmentation mode for amines; for 1° n-aliphatic amines, there is an intense peak at m/z 30.

- Aromatic amines have intense molecular ion peaks. For anilines, they prefer to lose a hydrogen atom before the expulsion of HCN.

Amines
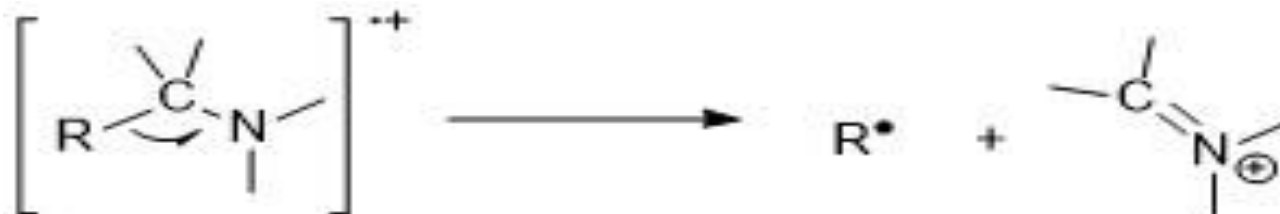
Alpha cleavage of amines
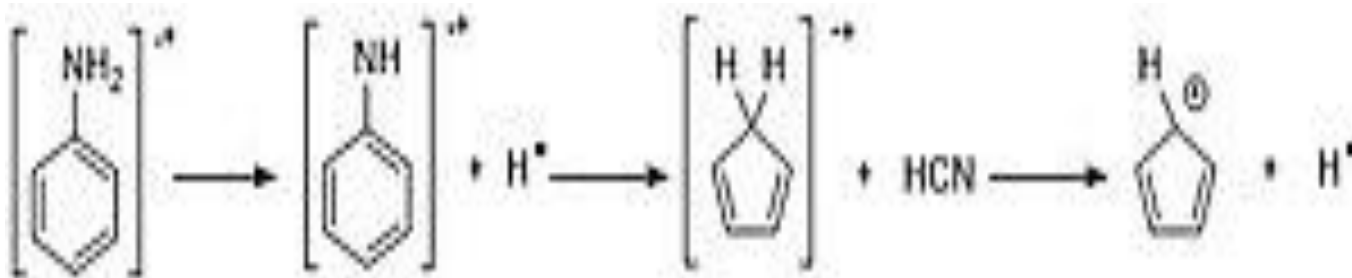
Aniline fragmentation
mechanism

Nitriles

- The principle fragmentation mode is the loss of an H-atom (M − 1) from the carbon next to the CN group due to the resonance stabilization. McLafferty rearrangement can be observed when they have longer chain lengths.

$$\left[\begin{array}{c} R \\ \diagdown\text{—}C\equiv N \end{array}\right]^{\cdot+} \longrightarrow H\cdot \;+\; R\text{—}\underset{H}{C}\text{=}C\text{=}\overset{\oplus}{N}$$
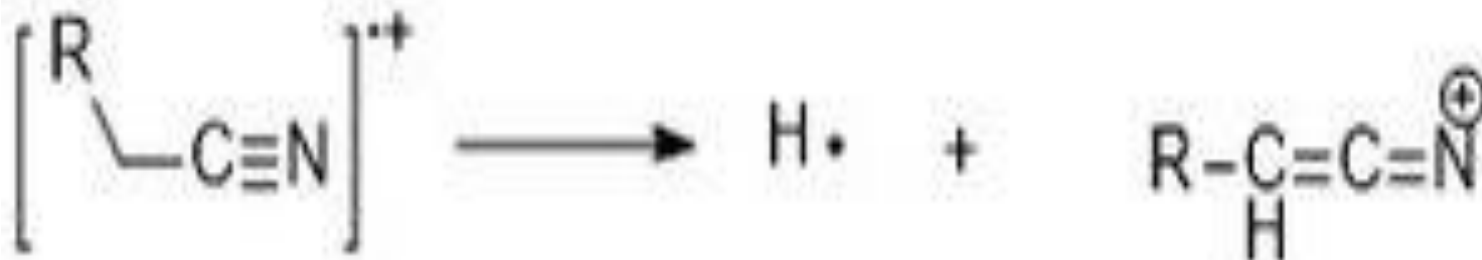
Nitro compounds

- The aliphatic nitro compounds normally show weak molecular ion peaks, while the aromatic nitro compounds give a strong peak. Common degradation mode is loss of NO^+ and NO^{2+}
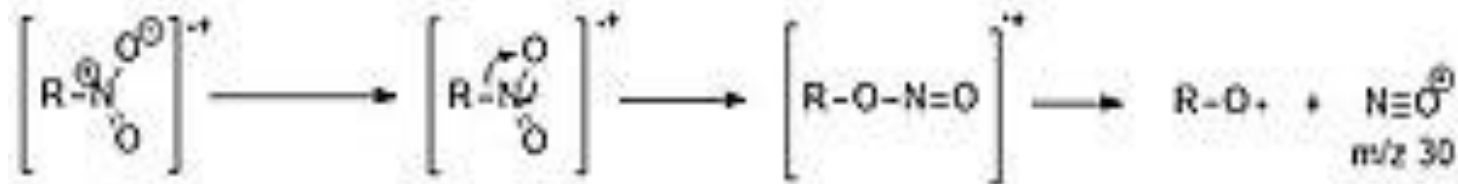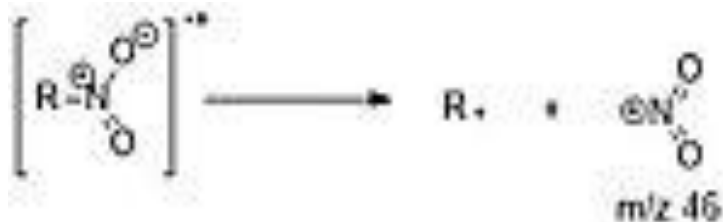
Assignment/ Set of Questions

- Q1. Explain the principle of Mass spectroscopy.
- Q2. Explain the instrumentation involved in mass spectroscopy.
- Q3. Write a note on fragmentation as observed in mass spectroscopy.
- Q4. What do yu understand by rearrangements? Explain McLafferty rearrangement.
- Q5. Write a note on nitrogen rule
- Q6. Write a note on even electron rule
- Q7. Write a note on rule 13.
- Q8. Write a note on rings rule

Assignment/ Set of quetions

- Q9. Write an explicit note on application of mass spectroscopy.
- Q10. Explain fragmentation pattern in the following compounds:
❑ Alkanes
❑ Alkenes
❑ Alkynes
❑ Aromatic compounds
❑ Alcohols
❑ Phenol
❑ Ether
❑ Carbonyl Compounds
❑ Amines
❑ Nitriles
❑ Nitro Compounds

- Best of Luck

Electro chemistry – II, B.Sc. II year , Paper -I

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This presentation Includes

- Conductance
- It's relation with resistance
- Ohm's Law
- Equivalent conductance
- Molar conductance
- Variation of conductance with concentration
- Strong and weak electrolytes
- Kohlarausch Law
- It's applications
- DHO equation
- Transport number
- Moving boundary method
- Hittorff's method
- Assignment and set of questions

Conductance and Resistance

- The **electrical resistance** of an object is a measure of its opposition to the flow of electric current. The inverse quantity is **electrical conductance**, and is the ease with which an electric current passes. Electrical resistance shares some conceptual parallels with the notion of mechanical friction. The SI unit of electrical resistance is the ohm (Ω), while electrical conductance is measured in siemens (S).

- The resistance of an object depends in large part on the material it is made of. Objects made of electrical insulators like rubber tend to have very high resistance and low conductivity, while objects made of electrical conductors like metals tend to have very low resistance and high conductivity. This relationship is quantified by resistivity or conductivity. The nature of a material is not the only factor in resistance and conductance, however: it also depends on the size and shape of an object because these properties are extensive rather than intensive. For example, a wire's resistance is higher if it is long and thin, and lower if it is short and thick. All objects resist electrical current, except for superconductors, which have a resistance of zero.

Ohm's Law

- **Ohm's law** states that the current through a conductor between two points is directly proportional to the voltage across the two points. Introducing the constant of proportionality, the resistance, one arrives at the usual mathematical equation that describes this relationship:

- $V = IR$

Specific Conductivity

Conductivity (or **specific conductance**) of an electrolyte solution is a **measure** of its ability to conduct electricity.

Specific conductance, $\kappa = \dfrac{1}{\rho}$

But $\rho = \dfrac{a}{\ell}R$

$\therefore K = \dfrac{\ell}{aR}$

$K = \left(\dfrac{\ell}{a}\right) \times$ Conductance

l/a is known as cell constant
The SI unit of Specific Conductance is Sm^{-1}

Equivalent Conductance

- It is the conductance of all ions furnished when one gram equivalent of an electrolyte is dissolved in V cc of the solution. Equivalent conductance is represented by λ_{eq}

Mathematically, $\lambda_{eq} = \kappa \times V$

$$\lambda_{eq} = \frac{\kappa \times 1000}{\text{Normality}}$$

Where, κ = Specific conductivity

   V = Volume of solution in "cc" containing one gram equivalent of the electrolyte.

Molar Conductance

- It is defined as the conducting power of all the ions produced by 1 mole of an electrolyte in the given solution.

- It is represented as μ.

$$\mu = K \times V$$

K= specific conduction of the solution

V= volume in cc containing 1mole of the electrolyte

If M is the molarity of the solution then-

$$\mu = K \times 1000/M$$

- SI unit is Siemen metre square per mol.

Variation in molar conductivities with concentration

Molar Conductivities (Cont'd)

- Molar conductivities as a function of electrolyte concentration.

Λ_m

Strong electrolytes

Weak electrolytes

$C^{1/2}$
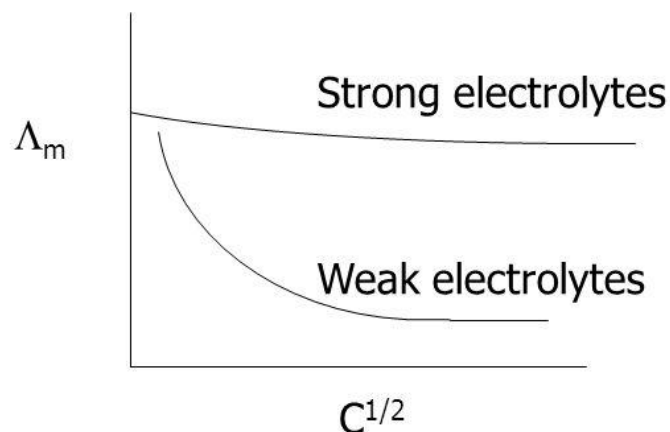
Variation of equivalent conductance with concentration
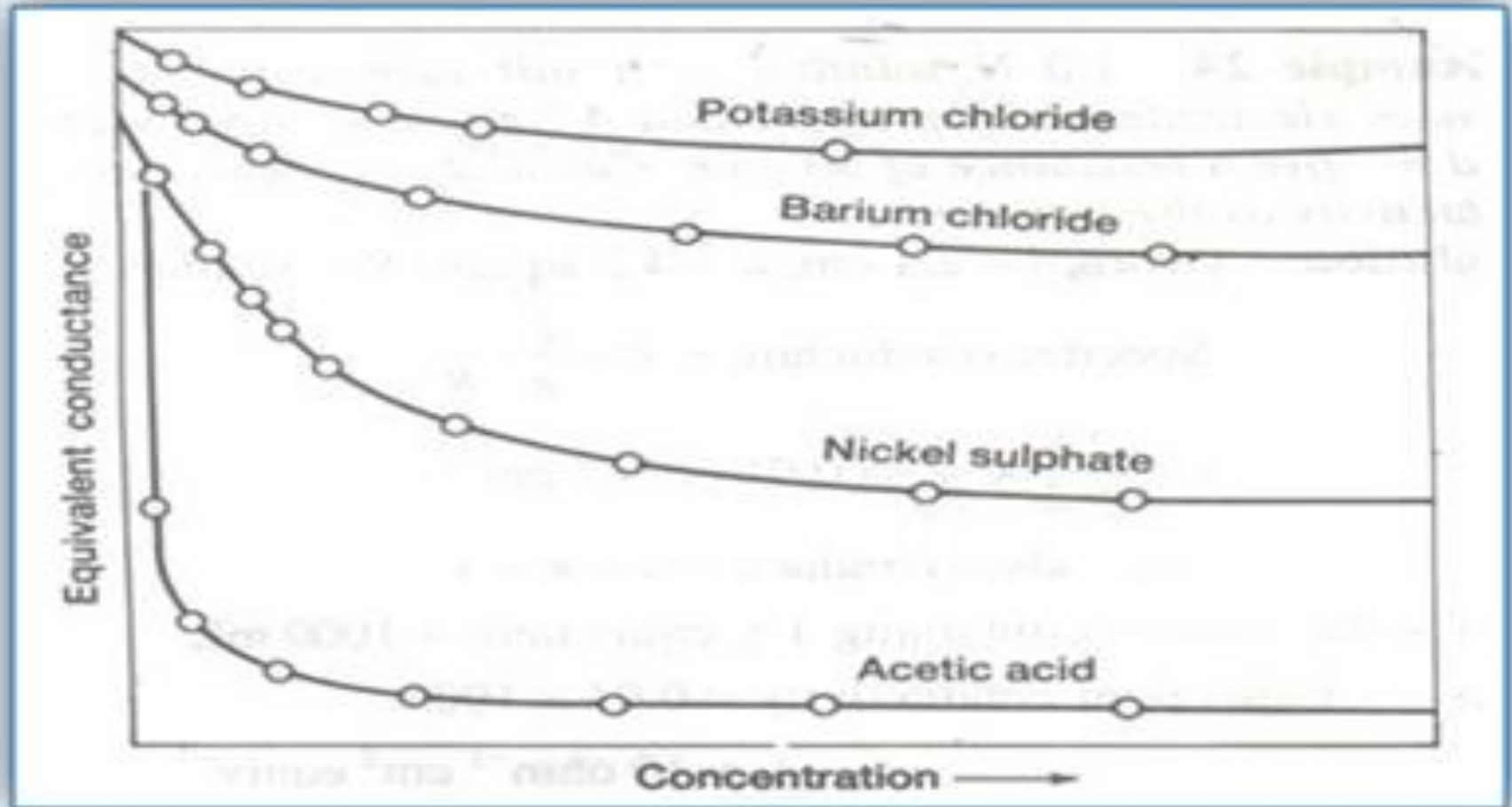
Strong and weak electrolytes

- A **strong electrolyte** is a solution/solute that completely, or almost completely, ionizes or dissociates in a solution. These ions are good conductors of electric current in the solution.

- Originally, a "strong electrolyte" was defined as a chemical that, when in aqueous solution, is a good conductor of electricity. With a greater understanding of the properties of ions in solution, its definition was replaced by the present one.

- A concentrated solution of this strong electrolyte has a lower vapor pressure than that of pure water at the same temperature. Strong acids, strong bases and soluble ionic salts that are not weak acids or weak bases are strong electrolytes.

- A substance whose aqueous solution or molten state decomposed into ions by passing electricity is known as electrolytes.

Strong and weak electrolytes

- For strong electrolytes, a single reaction arrow shows that the reaction occurs completely in one direction, in contrast to the dissociation of weak electrolytes, which both ionize and re-bond in significant quantities.

- Strong electrolyte$(aq) \rightarrow$ Cation$^+$$(aq)$ + Anion$^-$$(aq)$

- Strong electrolytes conduct electricity *only* when molten or in aqueous solutions. Strong electrolytes break apart into ions completely.

- The stronger an electrolyte the greater the voltage produced when used in a galvanic cell.

Strong and weak electrolytes

Strong Electrolytes

- **Strong Acids**
- **Strong Bases**
- Salts

Weak Electrolytes

- **Weak Acids**
- **Weak Bases**
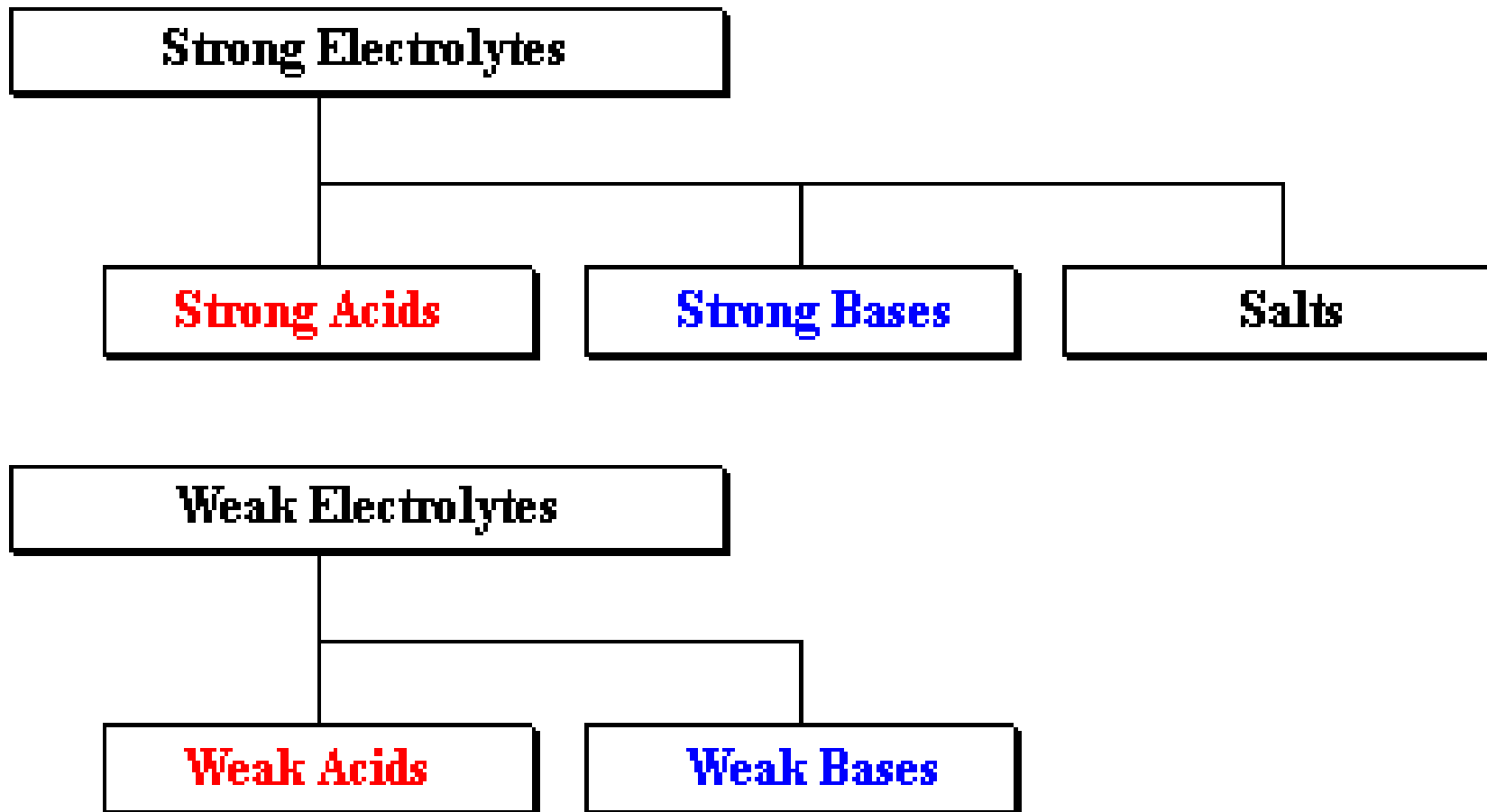
TYPES OF ELECTROLYTES

A **weak electrolyte** dissociates partially.

• Weak electrolyte solutions are poor conductors.

• Different weak electrolytes dissociate to different extents.

Weak electrolytes include:

• Weak acids and weak bases (NH_4OH)

• A few insoluble ionic compounds

• A water H_2O

A **strong electrolyte** dissociates completely.

• A strong electrolyte is present in solution almost exclusively as **ions**.

• Strong electrolyte solutions are good conductors.

Strong electrolytes include:

• Strong acids (HCl, HBr, HI, HNO_3, H_2SO_4, $HClO_4$)

• Strong bases (IA and IIA metals hydroxides)

• Most water-soluble ionic compounds (salts)

Always USE → arrow	Always USE ⇆ arrow	
Strong Electrolyte	Weak Electrolyte	Nonelectrolyte
HCl	CH_3COOH	$(NH_2)_2CO$ (urea)
HBr		
HI	HF	CH_3OH (methanol)
HNO_3		
$HClO_4$	HNO_2	C_2H_5OH (ethanol)
$H_2SO_4{}^*$	NH_3	$C_6H_{12}O_6$ (glucose)
All 1A: (LiOH, NaOH,		
KOH, RbOH, CsOH)	H_2O^*	$C_{12}H_{22}O_{11}$ (sucrose)
2A: $Ba(OH)_2$ & $Sr(OH)_2$		
$Ca(OH)_2$	(all of the above loose	
Ionic Compounds	an H^+ ion when dissociated)	The strong/weak parts of this chart should be memorized because it will help you to memorize your strong/weak acids and bases.
•H_2SO_4 has 2 ionizable H^+ ions, the second form, $HSO_4{}^-$ is a weak electrolyte.	*Pure water is an extremely weak electrolyte	

Ostwald's Dilution Law

- [Wilhelm Ostwald](#)'s **dilution law** is a relationship proposed in 1888 between the [dissociation constant](#) K_d and the [degree of dissociation](#) α of a weak [electrolyte](#). The law takes the form

Ostwald's Dilution Law

simplifying:	HB(aq)	$\rightleftarrows$	H^+(aq)	+	B^-(aq)
molarity @ start:	c		zero		zero
molarity @ equilm:	c - αc		αc		αc
	i.e. c(1-α)				

$$K_a = \frac{[H^+][B^-]}{[HB]}$$

i.e.
$$K_a = \frac{\alpha c \times \alpha c}{c(1-\alpha)}$$

i.e.
$$K_a = \frac{\alpha^2 c}{1-\alpha}$$

DEBYE-HUCKEL-ONSAGER EQUATION

Debye and huckel (1923)derived a mathematical expression for the variation of equivalent conductance with concentration. This equation was further improved by Onsager(1926-1927) and is known as Debye-Huckel-Onsager equation.

$$\Lambda_c = \Lambda_0 - [82.4/(DT)^{1/2} \acute{\eta} + 8.20 \times 10^5/(DT)^{3/2} \lambda_0]\sqrt{C}$$

Where Λ_c =Equivalent conductance at concentration c.
Λ_0 =Equivalent conductance at infinite dilution.
D = Diectric constant of the medium.
$\acute{\eta}$ =Coefficient of viscosity of the medium.
T =Temperature of the solution in degree absolute.
c = Concentration of the solution in moles/litre.

As D and ή are constant for a particular solvent.Therefore,at constant temperature, the above equation can be written in the form:

$$\Lambda_c = \Lambda_0 - (A + B\Lambda_0)\sqrt{c}$$ where A and B are constants for a particular solvent

KOHLRAUSCH'S LAW

- At infinite dilution the ions **act completely independently**, and the $\Lambda°$ <u>obeys a rule of additivity</u>:

$$\Lambda°(AX) = \Lambda°(AY) + \Lambda°(BX) - \Lambda°(BY)$$

where AX, AY, BX and BY are strong electrolytes.

Application of Kohlrausch Law

1) Λ_m^0 of weak electrolyte

$$\Lambda_{m(A^+B^-)}^0 = \Lambda_{m(A^+C^-)}^0 - \Lambda_{m(D^+C^-)}^0 + \Lambda_{m(D^+B^-)}^0$$

AB $\longrightarrow$ Weak electrolyte

AC, DC, DB $\longrightarrow$ Strong electrolyte

2) K_a of weak electrolyte

$$\propto = \frac{\Lambda_m^c}{\Lambda_m^0} \qquad K_a = \frac{c(\Lambda_m^c)^2}{\Lambda_m^0(\Lambda_m^0 - \Lambda_m^c)}$$

3) Solubility of sparingly soluble salt

$$S = \frac{\kappa \times 1000}{\Lambda_m^0}$$

Application of Kohlrausch Law

$$\Lambda^{\circ}_{m(CH_3-COOH)} = \lambda^{\circ}_{CH_3-COO^-} + \lambda^{\circ}_{H^+}$$

$$= \left[\lambda^{\circ}_{CH_3-COO^-} + \lambda^{\circ}_{Na^+} \right] + \left[\lambda^{\circ}_{H^+} + \lambda^{\circ}_{Cl^-} \right] - \left[\lambda^{\circ}_{Na^+} + \lambda^{\circ}_{Cl^-} \right]$$

i.e. $\Lambda^{\circ}_{m(CH_3-COOH)} = \Lambda^{\circ}_{m(CH_3-COONa)} + \Lambda^{\circ}_{m(HCl)} - \Lambda^{\circ}_{m(NaCl)}$

Application of Kohlrausch Law

Λ^{o}_{m} (CH$_3$COOH) = ?

Λ^{o}_{m} (HCl) = 426 S cm^2 mol^{-1}

Λ^{o}_{m} (NaCl) = 126 S cm^2 mol^{-1}

Λ^{o}_{m} (CH$_3$COONa) = 91 S cm^2 mol^{-1}

Λ^{o}_{m} (CH$_3$COOH) = Λ^{o}_{m} (HCl) + Λ^{o}_{m} (CH$_3$COONa) − Λ^{o}_{m} (NaCl)

$$= 426 + 91 - 126$$

$$= 391 \text{ S cm}^2 \text{ mol}^{-1}$$

TRANSPORT NUMBER

The fraction of the total current carried by an ion is called its transport number or Hittorf's number.

Transport number of anion $n_a = \dfrac{u_a}{u_a + u_c}$

Transport number of cation $n_c = \dfrac{u_c}{u_a + u_c}$

Transport numbers of cations in various electrolytes

Electrolyte	t^+	Electrolyte	t^+
HCl	0.823	$ZnSO_4$	0.395
LiCl	0.338	$CuSO_4$	0.397
NaCl	0.395	$BaCl_2$	0.449
KCl	0.490	$AgNO_3$	0.461
KBr	0.488	K_2SO_4	0..483

Moving Boundary method

The moving boundary method

- The concentrations of the solutions are so adjusted that hydrochloric acid floats over cadmium chloride, since HCl is lighter than the cadmium chloride solution.

- A sharp boundary appears between the two solutions. The selection of the indicator electrolyte is done carefully, so that its cation do not move faster than the cation whose transport number is to be determined, and it should have the same anion as the principal electrolyte; cadmium chloride fulfills both the requirements.

- The mobility of cadmium ions is less than that of hydrogen ions and it has a common anion with hydrochloric acid.

The moving boundary method

- This method is based on the direct observation of migration of ions in an electric field. The conductivity cell, in this method consists of a vertical tube filled with cadmium chloride and hydrochloric acid.

- HCl is the principal electrolyte, and $CdCl_2$ serves as the indicator electrolyte to enable formation of a boundary.
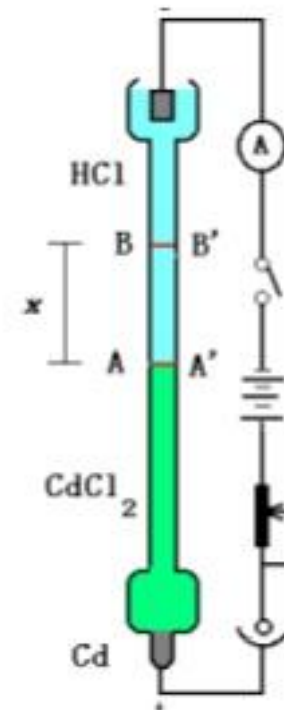
measurement of transport number by the moving boundary method
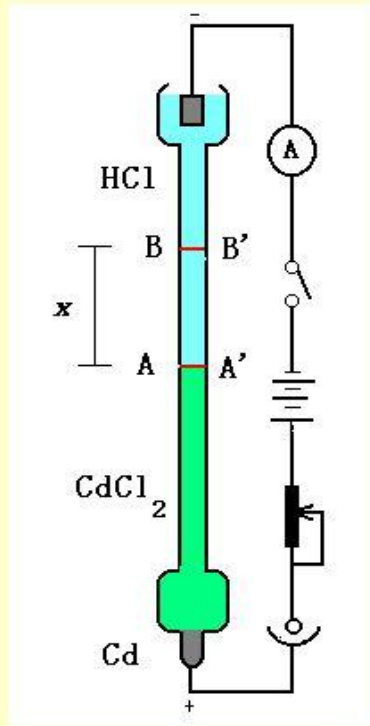
Suppose the boundary moves a distant x from AA' to BB' for the passage of Q coulombs. All the ions, H^+, passed through the boundary AA'.

The amount of substances transported is then Q/F, of which t_+Q/F are carried by the positive ion. If the volume between the boundaries AA' and BB' is V, and the concentration of HCl is c, then

$$t_+ Q / F = Vc$$

$$t_+ = \frac{FVc}{Q}$$

Hittorff's Method

DETERMINATION OF TRANSPORT NUMBERS BY HITTORF'S METHOD

Hittorf's method:-

Principle:- The method is based upon the principle that the fall in concentration around an electrode is proportional to the speed of the ion moving away from it.

n_c = $\dfrac{\text{Number of gram equivalent lost from the anodic compartment}}{\text{Number of gram equivalent deposited in the voltameter}}$

Hittorf's Method (Experimental procedure)

- Hittorf's apparatus consists of a two limbed vessel, connected by a narrow U-tube in the middle. Both limbs as well as the U-tube are provided with stop-cocks at the bottom for the withdrawal of the solution.
- The two limbs are provided with Pt electrodes. To determine the transport numbers of Ag^+ in $AgNO_3$ the electrodes are either of Pt or pure Ag.
- The apparatus is filled with a standard solution of $AgNO_3$ (usually 0.1N) and the cell is connected in series with a source of direct current (like battery).

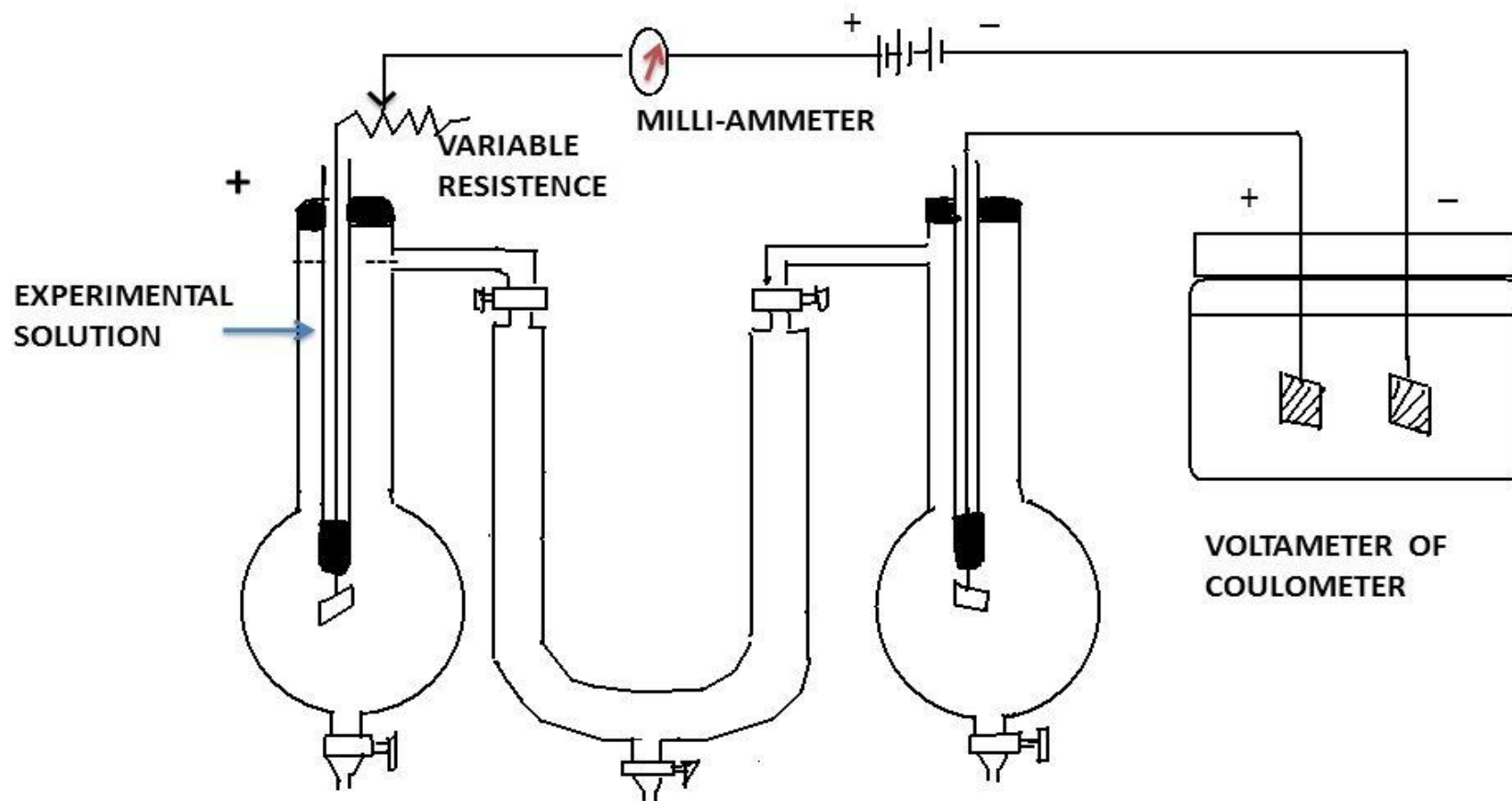# APPARATUS FOR THE DETERMINATION OF TRANSPORT NUMBER

FIG:7

Assignment/ Set of Questions

- Q1. What is conductance?
- Q2. How is conductance related to resistance?
- Q3.Define specific conductance.
- Q4. Define equivalent conductance.
- Q5. What is molar conductance?
- Q6.Explain the variation of conductance with concentration.
- Q7. What are strong and weak electrolytes? Enlist the differences between them.

Assignment/ Set of questions

- Q8. Write and explain DHO equation.
- Q9. What is Kohlarausch law?
- Q10. Explain the applications of Kohlarausch law.
- Q11. What do you understand by transport number of any electrolyte?
- Q12. Explain Moving boundary method to estimate transport number.
- Q13. Explain Hittorff's Method to estimate the transport number.
- Q14. State and explain Ohm's law
- Q15. Calculate equivalent conductance of acetic acid.
- Q16. State and derive Ostwald's dilution law

- Best of Luck

ELECTROCHEMISTRY,

B.SC. II YEAR

Kishor Arora

Professor- Chemistry,

Govt. P.G. College, (Auto.); Datia (M.P.) 475 661

Reversible Electrodes

- Electrodes reversible w.r.t. positive ions [Metal dipped in metal salt solution e.g. Zn|ZnSO4]

- Electrodes reversible w.r.t. to negative ions [Metal in contact with one of its insoluble salts immersed in a solution of a soluble salt of the same anion; $Cl^-(4M)\left|Hg_2Cl_2(s)\right|Hg(l)\left|Pt\right.$]

- Oxidation- reduction electrodes; [metal (usually Pt)in contact with a solution containing ions in two valency states]

Reversible Electrodes

- Gas-metal ion electrode
- Metal- Metal ion electrode
- Metal -metal insoluble salt anion electrode
- Redox Electrode
- Amalgam Electrode
- Non-metal, Non gas electrode
- Metal- insoluble oxide electrode

GAS – METAL ION ELECTRODE

- A **reversible hydrogen electrode** (RHE) is a <u>reference electrode</u>, more specific a subtype of the <u>standard hydrogen electrodes</u>

$Pt_{(s)}$ | H_2 (1 atm) | H^+ (1 M)

$$2\,H_3O^+ + 2\,e^- \rightleftarrows H_2 + 2\,H_2O$$
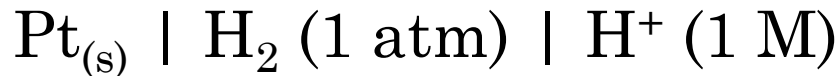
$$E = E_{00} + \frac{R\,T}{F}\left(\ln\left(a[H_3O^+]\right) - \frac{1}{2}\ln\left(p[H_2]\right)\right)$$

$$E_0 = 0.000 - 0.059 * pH$$

METAL- METAL ION ELECTRODE

- Zn/Zn2+ :
  $Zn_{(s)}$ | Zn^{2+} (1M)

- Cu/Cu2+:
  Cu^{2+} (1M) | $Cu_{(s)}$

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$$

$$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$$
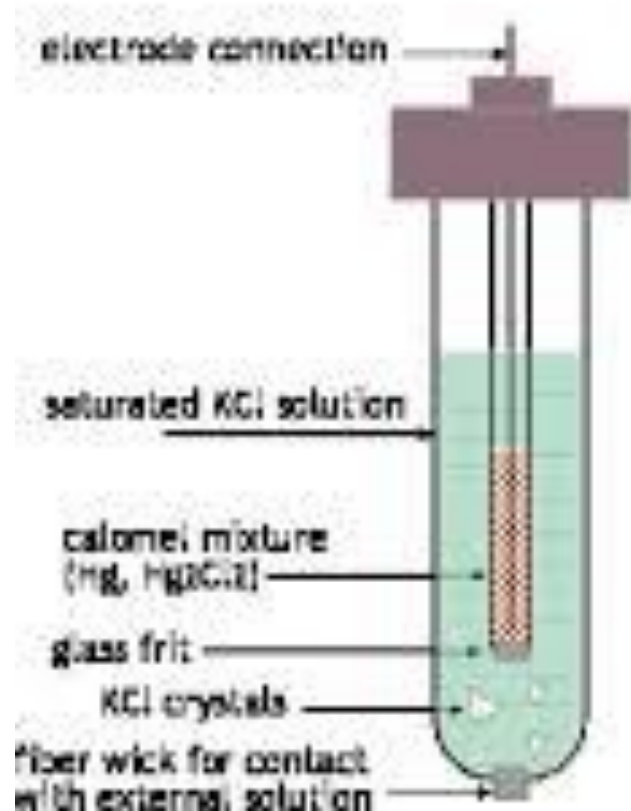
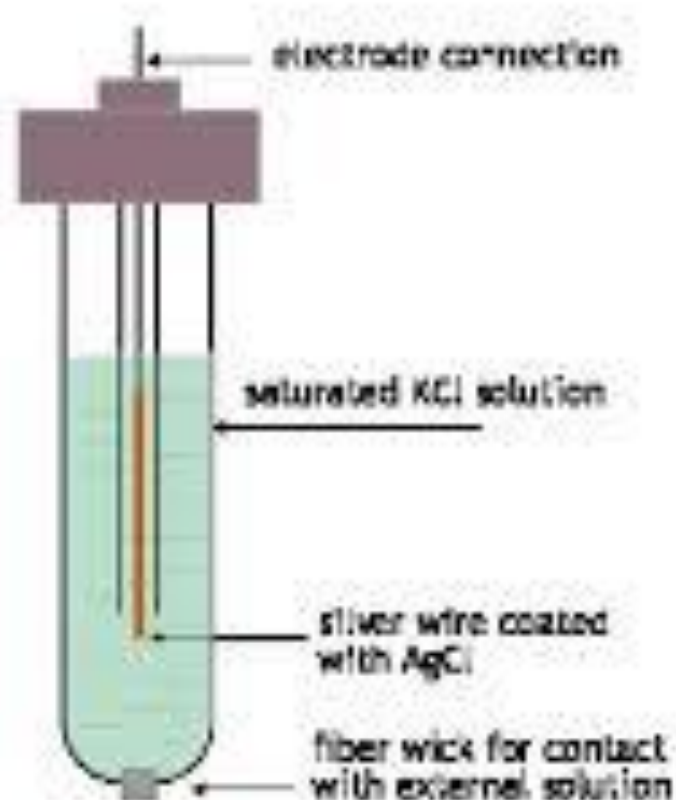# METAL- METAL INSOLUBLE SALT- ANION ELECTRODES

saturated calomel electrode

silver-silver chloride electrode

electrode connection

saturated KCl solution

calomel mixture (Hg, Hg2Cl2)

glass frit

KCl crystals

fiber wick for contact with external solution

electrode connection

saturated KCl solution

silver wire coated with AgCl

fiber wick for contact with external solution

CALOMEL ELECTRODE

- Notation $\quad Cl^-(4M)|Hg_2Cl_2(s)|Hg(l)|Pt$

- Reaction $\quad Hg_2^{2+} + 2e^- \rightleftharpoons 2Hg(l)$

- Equation

$$E = E^o_{Hg_2^{2+}/Hg} - \frac{RT}{2F}\ln\frac{1}{a_{Hg_2^{2+}}}$$

- This activity can be found from the <u>solubility product</u> of the reaction

$$Hg_2^{2+} + 2Cl^- \rightleftharpoons Hg_2Cl_2(s), \qquad K_{sp} = a_{Hg_2^{2+}}a_{Cl^-}^2$$
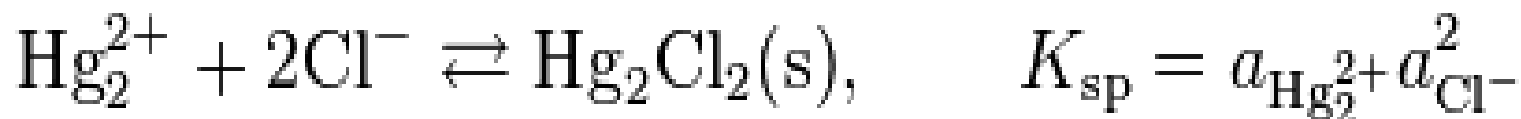
- By replacing the activity in the Nernst equation with the value in the solubility equation, we get

$$E = E^0_{Hg_2^{2+}/Hg} + \frac{RT}{2F}\ln K_{sp} - \frac{RT}{2F}\ln a_{Cl^-}^2$$

CALOMAL ELECTRODE

- The electrode is based on the redox reaction
- The Nernst equation for this reaction is shown in the previous slide
- where E^0 is the standard electrode potential for the reaction and a_{Hg} is the activity for the mercury cation (the activity for a liquid of 1 Molar is 1). This activity can be found from the solubility product of the reaction
- The only variable in this equation is the activity (or concentration) of the chloride anion. But since the inner solution is saturated with potassium chloride, this activity is fixed by the solubility of potassium chloride. When saturated the redox potential of the calomel electrode is +0.2444 V vs. SHE at 25 °C, but slightly higher when the chloride solution is less than saturated. For example, a 3.5M KCl electrolyte solution increases the reference potential to +0.250 V vs. SHE at 25 °C, and a 0.1 M solution to +0.3356 V at the same temperature

Silver – Silver Chloride Electrode

- The corresponding equations can be presented as follows:-

$$Ag^+ + e^- \rightleftharpoons Ag(s)$$
$$AgCl(s) \rightleftharpoons Ag^+ + Cl^-$$

an overall reaction can be written

$$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-$$

Silver- Silver Chloride Electrode

- The Nernst equation shows the dependence of the potential of the silver-silver(I) chloride electrode on the activity or effective concentration of chloride-ions

$$E = E^0 - \frac{RT}{F} \ln a_{Cl^-}$$

- **Reference Electrode Potentials** Electrode Potential $E^0 + E_{lj}$Temperature Coef.(V) at 25 °C(mV/°C) at around 25

Ag/AgCl/Sat. KCl+0.197-1.01

REDOX ELECTRODE

- Electordes with reactions

Electrode	Electrode Reactions
1. Pt	Fe^{3+}, Fe^{2+}	Fe^{3+} (aq) + e^- ⇌ (aq) Fe^{2+}
2. Pt	Sn^{4+}, Sn^{2+}	Sn^{4+} (aq) + $2e$ ⇌ (aq) Sn^{2+}
3. Pt	Ce^{3+}, Ce^{2+}	Ce^{3+} (aq) + e^- ⇌ (aq) Ce^{2+}

... reaction for all electrodes of the redox type ma

$$E = E^\circ - \frac{RT}{nF} \ln \frac{a_2}{a_3}$$

Redox Electrode

- Many electrode reactions involve only ionic species, such as Fe2+ and Fe3+. If neither of the electroactive species is a metal, some other metal must serve as a conduit for the supply or removal of electrons from the system. In order to avoid complications that would arise from electrode reactions involving this metal, a relatively inert substance such as platinum is commonly used. Such a half cell would be represented as

- Pt(s) | Fe^{3+}*(aq)*, Fe^{2+}*(aq)* || …..

and the half-cell reaction would be

- $Fe2+(aq) \rightarrow Fe3+(aq) + e-$

GAS ELECTRODE

- Some electrode reactions involve a gaseous species such as H_2, O_2, or Cl_2. Such reactions must also be carried out on the surface of an electrochemically inert conductor such as platinum. A typical reaction of considerable commercial importance is
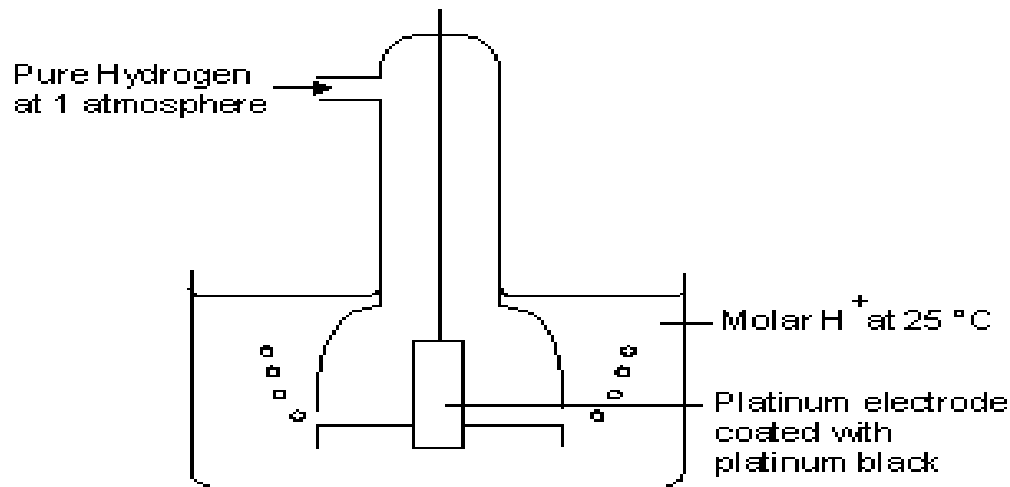
  $Cl^-(aq) \rightarrow \frac{1}{2} Cl_2(g) + e^-$
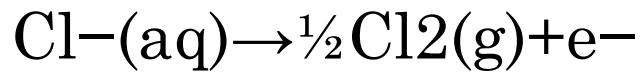
- Similar reactions involving the oxidation of Br_2 or I_2 also take place at platinum surfaces.

REFERENCE ELECTRODE

- Primary Reference Electrode (SHE)
- Secondary reference Electrode (Calomel Electrode)

Pure Hydrogen at 1 atmosphere

Molar H^+ at 25 °C

Platinum electrode coated with platinum black

NERNST EQUATION

- Nernst equation may be expressed as

$$E_{\text{red}} = E^{\ominus}_{\text{red}} + \frac{RT}{zF} \ln \frac{a_{\text{Ox}}}{a_{\text{Red}}}$$

- For a half cell reaction

$$Ox + ze^- = Red$$

DERIVATION OF NERNST EQUATION

- **Using Boltzmann factors**
- For simplicity, we will consider a solution of redox-active molecules that undergo a one-electron reversible reaction

$$Ox + e^- \rightleftharpoons Red$$

- and that have a standard potential of zero. The chemical potential of this solution is the difference between the energy barriers for taking electrons from and for giving electrons to the working electrode that is setting the solution's electrochemical potential.

DERIVATION OF NERNST EQUATION

- The ratio of oxidized to reduced molecules, [Ox]/[Red], is equivalent to the probability of being oxidized (giving electrons) over the probability of being reduced (taking electrons), which we can write in terms of the Boltzmann factor for these processes:

$$\frac{[\text{Red}]}{[\text{Ox}]} = \frac{\exp\left(-[\text{barrier for losing an electron}]/kT\right)}{\exp\left(-[\text{barrier for gaining an electron}]/kT\right)} = \exp\left(\mu_c/kT\right).$$

- Taking the natural logarithm of both sides gives

$$\mu_c = kT \ln \frac{[\text{Red}]}{[\text{Ox}]}.$$

- If $\mu_c \neq 0$ at [Ox]/[Red] = 1, we need to add in this additional constant:

$$\mu_c = \mu_c^0 + kT \ln \frac{[\text{Red}]}{[\text{Ox}]}.$$

- Dividing the equation by e to convert from chemical potentials to electrode potentials, and remembering that $k/e = R/F$, we obtain the Nernst equation for the one-electron process :

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

DERIVATION OF NERNST EQUATION

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

$$E = E^o + \frac{kT}{e} \ln \frac{[\text{Red}]}{[\text{Ox}]}$$

$$= E^o - \frac{RT}{F} \ln \frac{[\text{Ox}]}{[\text{Red}]}.$$

STANDARD ELECTRODE POTENTIAL

- In electrochemistry, the **standard electrode potential**, abbreviated $E°$ or $E^{\ominus}$ (with a superscript character, pronounced "standard" or "nought"),

- It is the measure of individual potential of a reversible electrode at standard state, which is with solutes at an effective concentration of 1 mol dm^{-3}, and gases at a pressure of 1 atm.

- The reduction potential is an intensive property.

- The values are most often tabulated at 25 °C.

- The basis for an electrochemical cell such as the galvanic cell is always a redox reaction which can be broken down into two half-reactions:

  oxidation at anode (loss of electron) and

  reduction at cathode (gain of electron).

Electrochemical Series

- Shows the ease/tendency of species to accept/lose electrons
- Written as standard reduction potential

WEAK Oxidising Agent   **STRONG Reducing Agent**

- Species on TOP left
- Low ↓ tendency to gain e
- $Li^+ + e \rightarrow Li$
- E^0 Li = - 3.04V
- WEAK oxidising Agent
- Reduction NOT favourable

- Species on TOP right
- High ↑ tendency to lose e
- $Li \rightarrow Li^+ + e$
- E^0 Li = +3.04V
- STRONG reducing Agent
- Oxidation favourable

Oxidized species		Reduced species	E^0 / V
$Li^+(aq) + e^-$	⇌	Li(s)	-3.04
$K^+(aq) + e^-$	⇌	K(s)	-2.93
$Ca^{2+}(aq) + 2e^-$	⇌	Ca(s)	-2.87
$Na^+(aq) + e^-$	⇌	Na(s)	-2.71
$Mg^{2+}(aq) + 2e^-$	⇌	Mg(s)	-2.37
$Al^{3+}(aq) + 3e^-$	⇌	Al(s)	-1.66
$Mn^{2+}(aq) + 2e^-$	⇌	Mn(s)	-1.19
$H_2O(l) + e^-$	⇌	$\frac{1}{2}H_2(g) + OH^-(aq)$	-0.83
$Zn^{2+}(aq) + 2e^-$	⇌	Zn(s)	-0.76
$Fe^{2+}(aq) + 2e^-$	⇌	Fe(s)	-0.45
$Ni^{2+}(aq) + 2e^-$	⇌	Ni(s)	-0.26
$Sn^{2+}(aq) + 2e^-$	⇌	Sn(s)	-0.14
$Pb^{2+}(aq) + 2e^-$	⇌	Pb(s)	-0.13
$H^+(aq) + e^-$	⇌	$\frac{1}{2}H_2(g)$	0.00
$Cu^{2+}(aq) + e^-$	⇌	$Cu^+(aq)$	+0.15
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$	⇌	$H_2SO_3(aq) + H_2O(l)$	+0.17
$Cu^{2+}(aq) + 2e^-$	⇌	Cu(s)	+0.34
$\frac{1}{2}O_2(g) + H_2O(l) + 2e^-$	⇌	$2OH^-(aq)$	+0.40
$Cu^+(aq) + e^-$	⇌	Cu(s)	+0.52
$\frac{1}{2}I_2(s) + e^-$	⇌	$I^-(aq)$	+0.54
$Fe^{3+}(aq) + e^-$	⇌	$Fe^{2+}(aq)$	+0.77
$Ag^+(aq) + e^-$	⇌	Ag(s)	+0.80
$\frac{1}{2}Br_2(l) + e^-$	⇌	$Br^-(aq)$	+1.07
$\frac{1}{2}O_2(g) + 2H^+(aq) + 2e^-$	⇌	$H_2O(l)$	+1.23
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$	⇌	$2Cr^{3+}(aq) + 7H_2O(l)$	+1.33
$\frac{1}{2}Cl_2(g) + e^-$	⇌	$Cl^-(aq)$	+1.36
$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	⇌	$Mn^{2+}(aq) + 4H_2O(l)$	+1.51
$\frac{1}{2}F_2(g) + e^-$	⇌	$F^-(aq)$	+2.87

-ve reduction potential

+ve reduction potential

- Species on BOTTOM left
- High ↑ tendency to gain e
- $F_2 + 2e \rightarrow 2F^-$
- E^0 F_2 = +2.87V
- STRONG oxidising Agent
- Reduction favourable

- Species on BOTTOM right
- Low ↓ tendency to lose e
- $F^- \rightarrow 1/2 F_2 + e$
- E^0 F_2 = -2.87V
- WEAK reducing Agent
- Oxidation NOT favourable

**STRONG Oxidising Agent**   **WEAK Reducing Agent**

Significance of Electro Chemical Series

- Knowledge of relative tendency of formation of positive ions by the metals
- Calculation of Standard e.m.f.
- Determination of Change in free energy of cell reaction or determination of feasibility of a cell reaction
- To predict if metal displaces hydrogen gas from acids
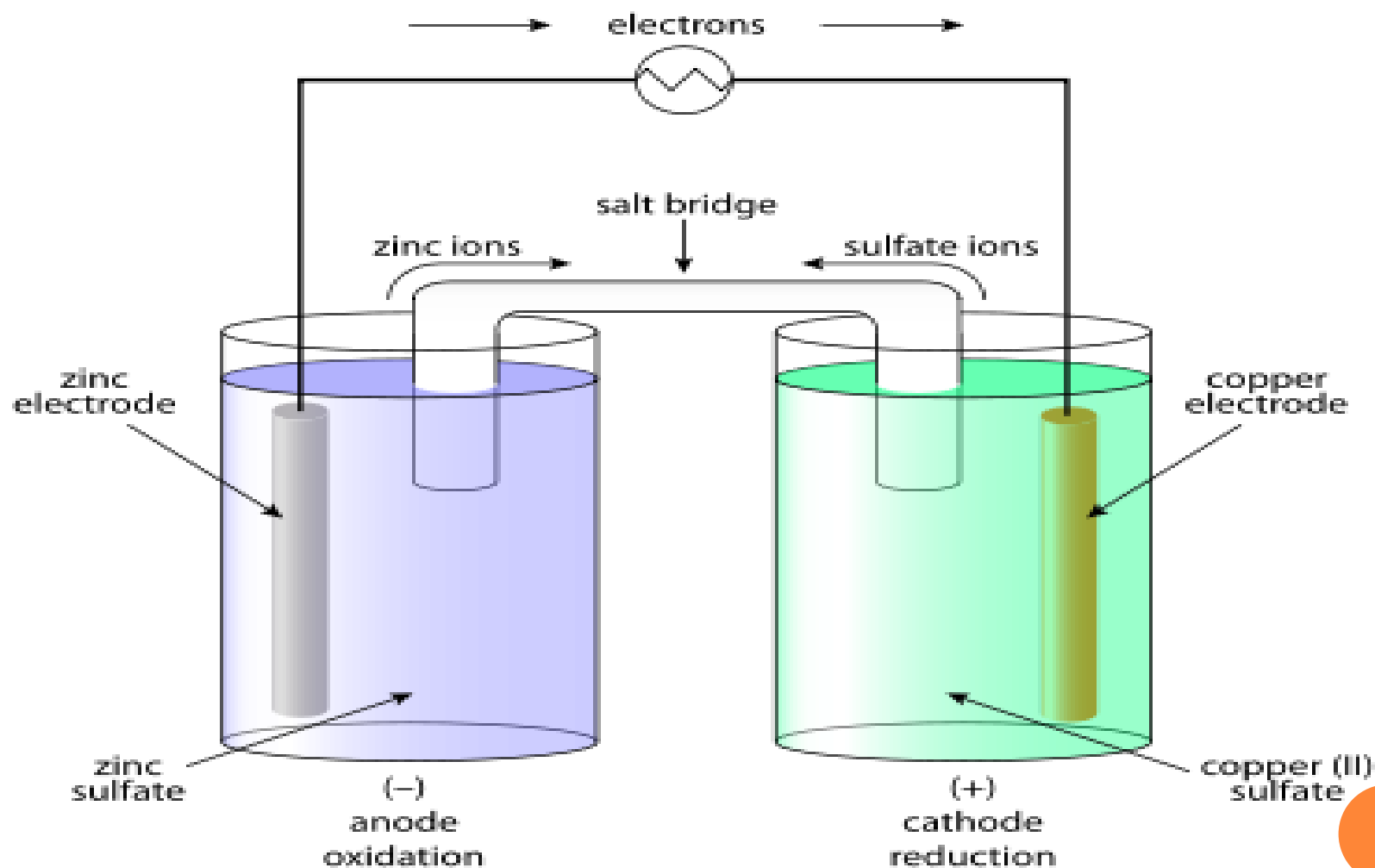- Determination of equilibrium constant of a cell reaction

ELECTROLYTIC CELL
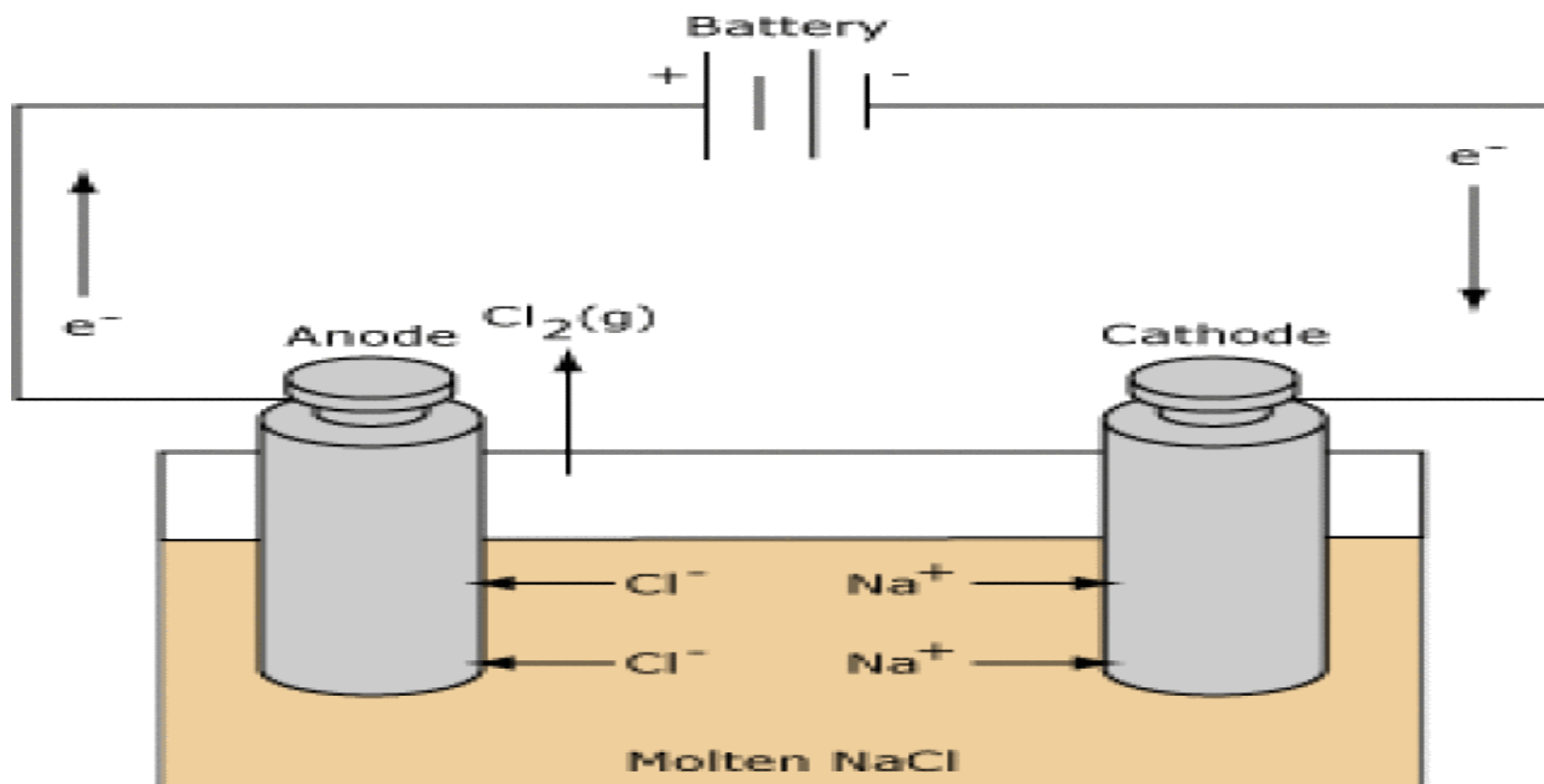
Electrolytic Cell

GALVANIC CELL

CELL NOTATIONS AND CELL REACTIONS

- Cell notations:-

  Zn*(s)* | Zn²⁺*(aq)* || Cu²⁺*(aq)* | Cu*(s)*

- Cell reactions:

$$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$$

$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$$

E.M.F. AND SPONTANEITY OF REACTION

- In a galvanic cell, where a spontaneous redox reaction drives the cell to produce an electric potential, Gibbs free energy $\Delta G°$ must be negative, in accordance with the following equation:

- $\Delta G°_{cell} = -nFE°_{cell}$ where n is number of moles of electrons per mole of products and F is the Faraday constant, ~96485 C/mol. As such, the following rules apply:

E.M.F. AND SPONTANEITY OF REACTION

- If $E°_{cell} > 0$, then the process is spontaneous ([galvanic cell](#))If $E°_{cell} < 0$, then the process is non spontaneous ([electrolytic cell](#))Thus in order to have a spontaneous reaction ($\Delta G° < 0$), $E°_{cell}$ must be positive, where:

- $E°_{cell} = E°_{cathode} - E°_{anode}$ where $E°_{anode}$ is the standard potential at the anode and $E°_{cathode}$ is the standard potential at the cathode as given in the table of standard electrode potential.
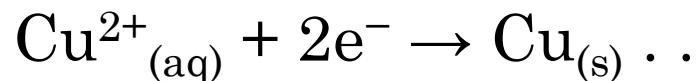
EMF OF DANIELL CELL

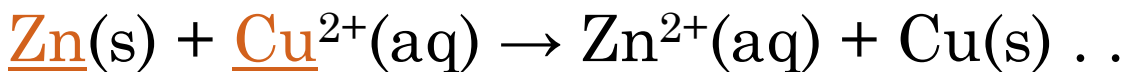- At the anode, zinc is oxidized per the following half reaction:

  $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$ . .
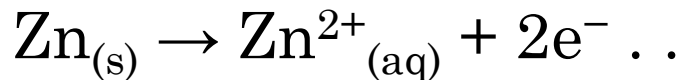
(Standard electrode potential -0.7618 V)

- At the cathode, copper is reduced per the following reaction:

  $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$ . .

(Standard electrode potential +0.340 V)

- The total reaction being:

Zn(s) + Cu^{2+}(aq) $\rightarrow$ Zn^{2+}(aq) + Cu(s) . .

(Open-circuit voltage 1.1018 V)

EMF AND THERMODYNAMIC PARAMETERS

- The energy referred to as <u>electrical work</u> and is expressed by the following equation:

$$W_{max} = W_{electrical} = -nFE_{cell}$$

- And free energy

$$\Delta G = -nFE_{cell}$$

- The relation between the <u>equilibrium constant</u>, K, and the Gibbs free energy for an electrochemical cell is expressed as follows:

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

EMF AND THERMODYNAMIC PARAMETERS

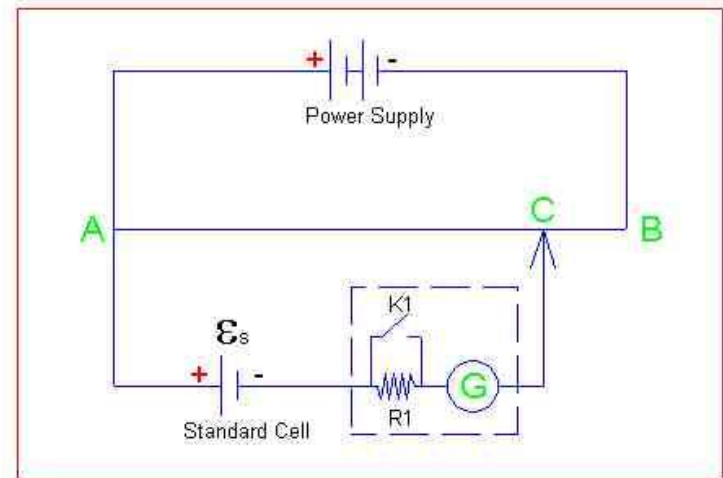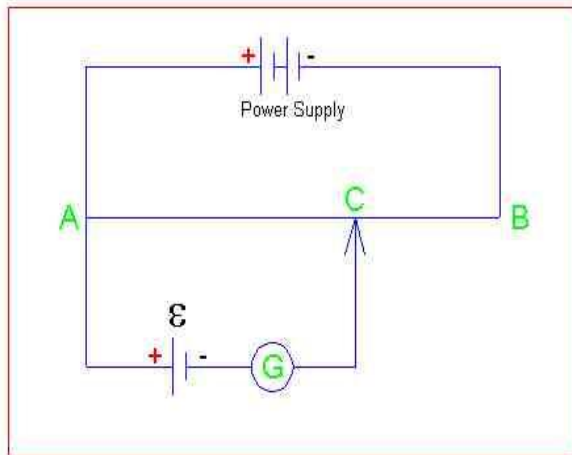○ Rearranging to express the relation between standard potential and equilibrium constant yields

$$E^o_{cell} = \frac{RT}{nF} \ln K$$

○ The previous equation can use [Briggsian logarithm](#) as shown below:

$$E^o_{cell} = \frac{0.0591\,\mathrm{V}}{n} \log K$$

MEASUREMENT OF EMF

Measurement of EMF

$$\frac{\varepsilon_x}{\varepsilon_s} = \frac{L_x}{L_s}$$

$$\varepsilon_x = \frac{L_x}{L_s}\varepsilon_s$$

OVER POTENTIAL

- In electrochemistry, **overpotential** is the potential difference (voltage) between a half-reaction's thermodynamically determined reduction potential and the potential at which the redox event is experimentally observed.

- The term is directly related to a cell's *voltage efficiency*.

- In an electrolytic cell the overpotential requires more energy than thermodynamically expected to drive a reaction.

- In a galvanic cell overpotential means less energy is recovered than thermodynamics predicts. In each case the extra/missing energy is lost as heat.

- Overpotential is specific to each cell design

- It is used more practically to define the current density (typically small) at which the overpotential is measured.

HYDROGEN OVERVOLTAGE

- Hydrogen overvoltage is the potential difference that can be found between an electrode and a reversible hydrogen electrode within a single solution. This is where hydrogen (H_2) undergoes formation from ions of hydrogen.

- At constant temp., Change of hydrogen overvoltage with current density is given by

$\varepsilon_0 = a + b\log I$

Fig. 2.22. Hydrogen over voltage on various metals.
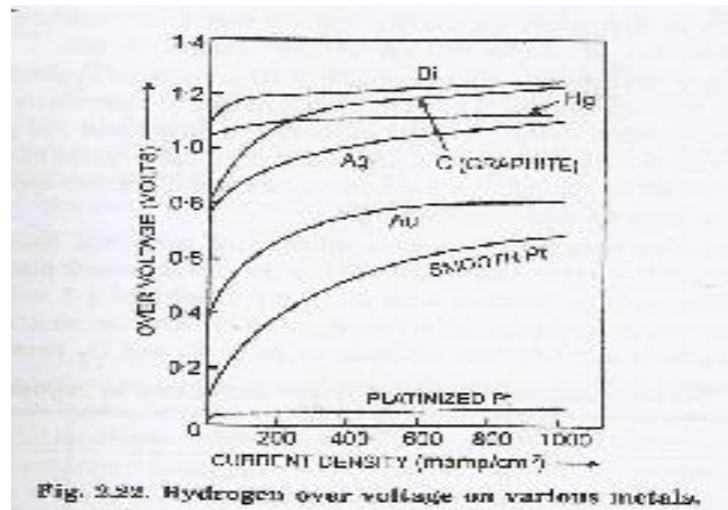
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Thanks