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Sl. No	Name of Faculty	Programme Name	Youtube Channel
1	Dr. V. D. Naganuri	BA/BSC	https://youtube.com/channel/UCog2hHUgxZtyiMVHqAtsaQg
2	Shri. P. B. Burji	BSC	https://youtube.com/channel/UCsW2UCRJRAg_3Ti2yTLFHig
3	Shri. M. R. Patil	BSC	https://youtube.com/channel/UC8hEWFPi2OCUiqnMngcznQA
4	Shri. B. G. Patil	BA/BSC	https://youtube.com/channel/UCgPcdabItWx0yzgcqqxLIDg
5	Dr. D. S. Kamble	BA	https://youtube.com/channel/UCpI2bNarPPN_nmXf17I_EGQ
6	Shri. D. T. Sogalad	BA/BSC	https://youtube.com/channel/UCzJgaVn5ha91T8VgJ8N8M2w
7	Dr. H. Krishna	B.Sc	https://classroom.google.com/c/MTcwMjg0NDIwNzUw?cjc=3p3tmvz
8	Shri. M. L. Mang	BA	https://youtube.com/user/mangmaruti
9	Shri. Sunilkumar	BSC	https://youtube.com/channel/UCCN1NutD2udwVuPdVW1NJzg
10	Shri. K. B. Marathe	BA/BSC	https://youtube.com/channel/UC7rDMs8d9sPcbXXgDufSP2A
11	Dr. V. A. Edalli	BSC	https://youtube.com/channel/UCXWQeERlqNIDE3_BuM5shHQ
12	Shri N.R.Badiger	BA	https://youtube.com/channel/UCZq-FkR16PL3FQVhbgDvdQA
13	Miss. Laxmi Mudagal	BSC	https://youtube.com/channel/UC8ztP8DsugsRzoq-U4MYBUQ
14	Shri.L.D.Padmannavar	BSC	https://youtube.com/channel/UC61qGa-Ozey3YVaaH8z-CgQ
15	Miss. Shama Nadaf	BSC	https://youtube.com/channel/UCmpMAuxuygUy1gMMAiqbsCw
16	Miss. Megharani Patil	BSC	https://youtu.be/XIUg3hoV4z0
17	Miss. M. N. Waghi	BSC	https://youtube.com/channel/UCzcQPueDf-oX_9d-m7jByDA

UNIT–III - BATTERIES AND FUEL CELLS

BSC V SEMESTER PAPER – II, 5 HOURS

By

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India

UNIT – III BATTERIES AND FUEL CELLS

BSC V SEMESTER PAPER – II, 5 HOURS

- Primary and secondary batteries
- Construction and Applications of
  - Pb-acid battery,
  - Li-Battery,
  - Lithium-polymer cell, and
  - Nickel-cadmium cell.
- Fuel cells-

  - Hydrogen-oxygen and

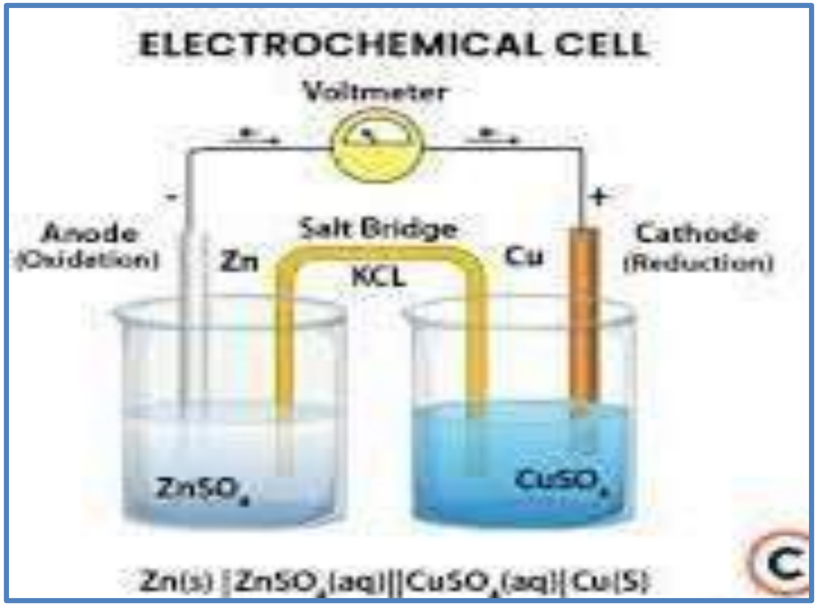
  - Hydrocarbon– Oxygen fuel cells and their applications.

ELECTROCHEMICAL CELLS

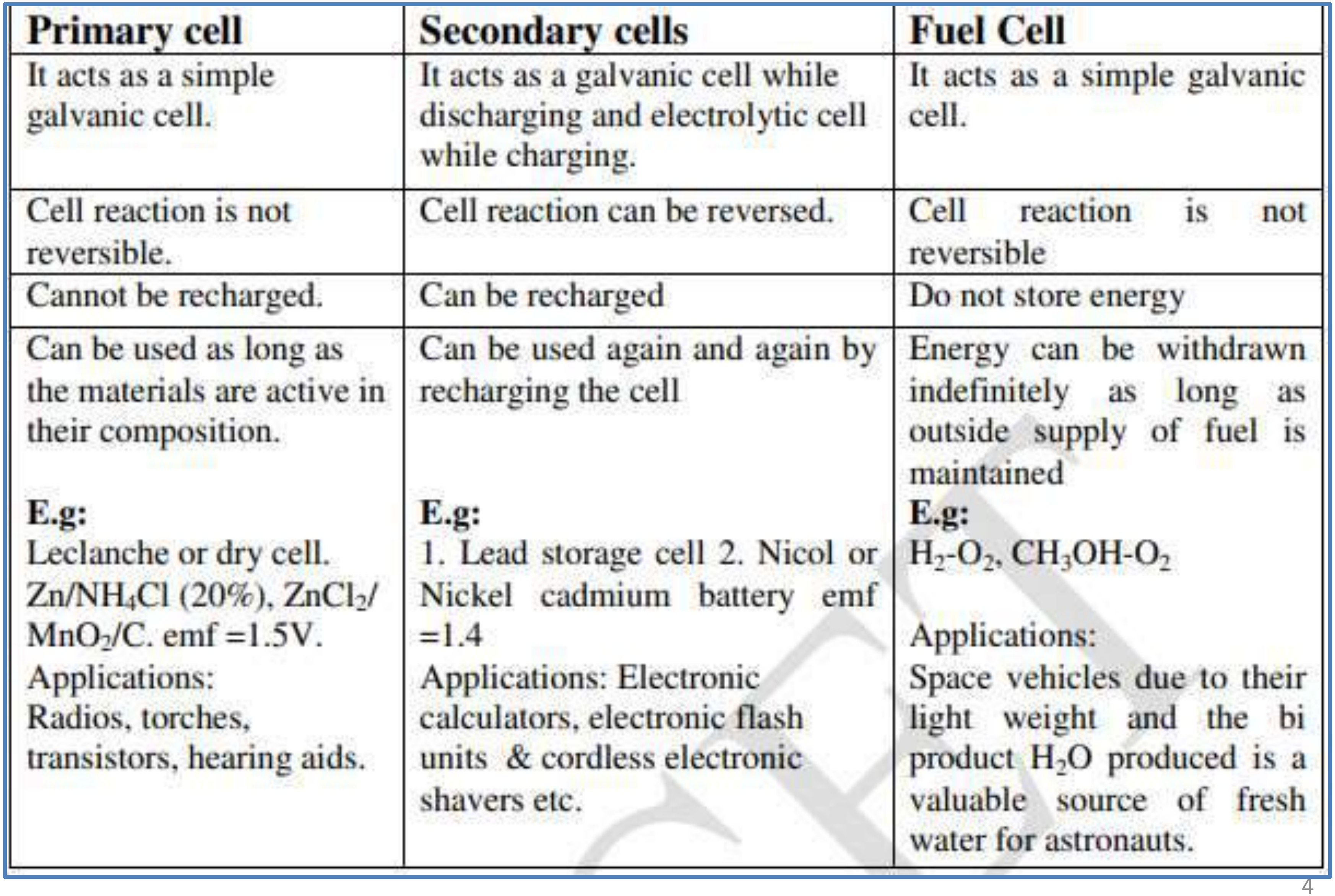
- An electrochemical cell is an electrochemical device which converts chemical energy into electrical energy.
- It consists of **two electrodes**, the **anode** and the **cathode**, separated by an electrolyte.

Electrolyte

- may be a **liquid** or a **solid**.

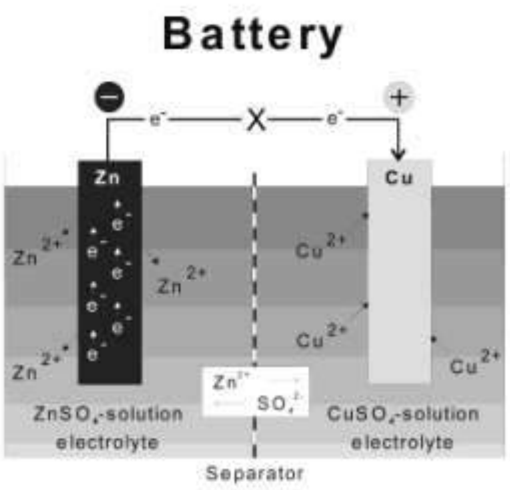


DIFFERENCES AMONG PRIMARY, SECONDARY AND FUEL CELLS



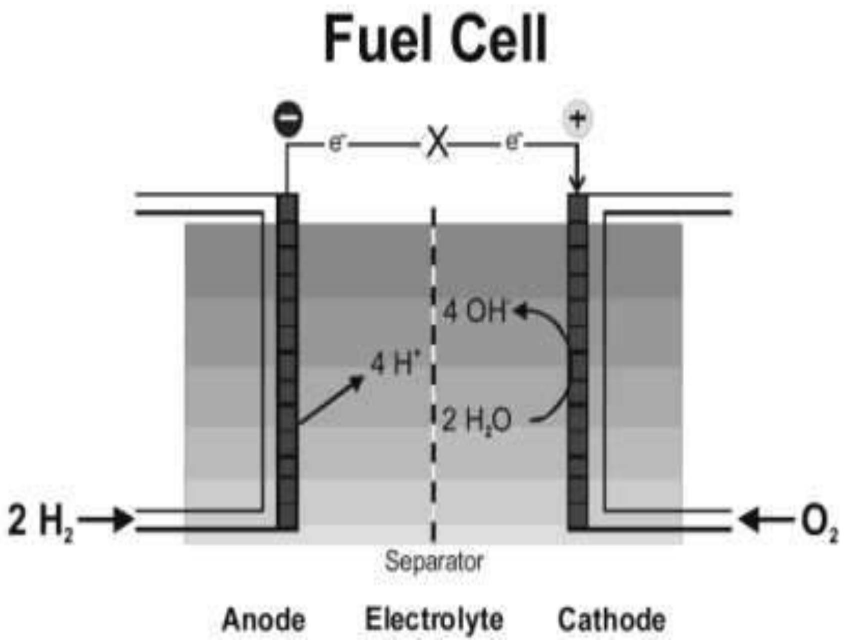
Primary cell	**Secondary cells**	**Fuel Cell**
It acts as a simple galvanic cell.	It acts as a galvanic cell while discharging and electrolytic cell while charging.	It acts as a simple galvanic cell.
Cell reaction is not reversible.	Cell reaction can be reversed.	Cell reaction is not reversible
Cannot be recharged.	Can be recharged	Do not store energy
Can be used as long as the materials are active in their composition. **E.g:** Leclanche or dry cell. Zn/NH_4Cl (20%), $ZnCl_2$/ MnO_2/C. emf =1.5V. Applications: Radios, torches, transistors, hearing aids.	Can be used again and again by recharging the cell **E.g:** 1. Lead storage cell 2. Nicol or Nickel cadmium battery emf =1.4 Applications: Electronic calculators, electronic flash units & cordless electronic shavers etc.	Energy can be withdrawn indefinitely as long as outside supply of fuel is maintained **E.g:** H_2-O_2, CH_3OH-O_2 Applications: Space vehicles due to their light weight and the bi product H_2O produced is a valuable source of fresh water for astronauts.

BATTERY VS FUEL CELLS



Requirements on	Anode	Electrolyte Separator	Cathode
electron conduction:	must	no	must
ion conduction:	can	must	can

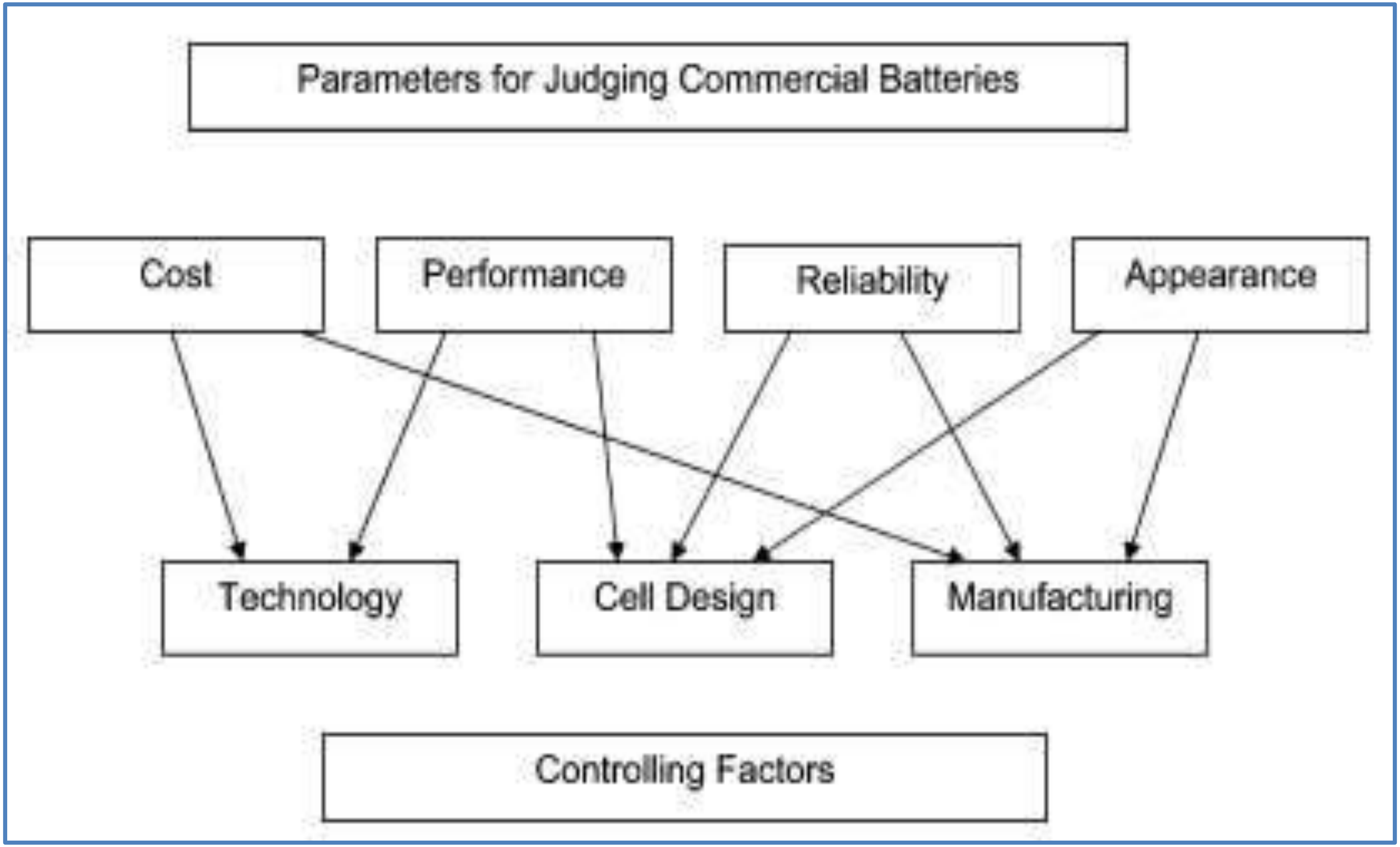
Figure 1. Representation of a battery (Daniell cell) showing the key features of battery operation and the requirements on electron and ion conduction.



interfaces, and (B, bottom) a fuel cell showing the continuous supply of reactants (hydrogen at the anode and oxygen at the cathode) and redox reactions in the cell.

Chemical Reviews, 2004, 104, 4245-4269

HOW BATTERIES ARE JUDGED BY USERS AND THE FACTORS THAT CONTROL THESE CRITERIA



BATTERIES TERMINOLOGIES

- **Battery:**
- **Primary batteries or primary cells:**
- **Secondary batteries or secondary cells:**
- **Electrolytes**

Two electrodes

- **Reductant** (anode) and
- **Oxidant** (cathode)
- **Separator (SPM)**

Separator is a critical component of lithium batteries, which plays a major role for flame retardance of LIBs.

BATTERIES AND FUEL CELLS

BATTERY

- It is a source which converts chemical energy into electrical energy and vice versa.
- A **cell** consists of **two electrodes** of **different metals** immersed in a **weak acid**.
- **Cell** is the **building block** of battery.
- Multiple cells can be stacked in series to make a battery.
- The **positive** terminal is called the **anode** and the **negative** terminal the **cathode**.
- Disposable and rechargeable batteries
- The lead acid battery

FUEL CELLS

- **Fuel cell** is a an **electrochemical device** that **converts energy** produced from a **chemical reaction** into **electrical energy**.
- More specifically, here **hydrogen** and **oxygen** combines to produce **electricity** with **water** and **heat** as **its by-product**.
- It **cannot store energy**, so they must be used in **conjunction** with a **storage battery**.

BATTERIES

PRIMARY BATTERIES

- Primary batteries, the **electrochemical reaction** is **not reversible**.
- Cannot be **recharged**.
- Chemical reaction totally destroy one of the metal after a period of time.
- Used as source of .**DC power**

Examples:

- **Dry cells (Leclanche cells)**
- (most) **alkaline batteries**
- **Mercury cells**.
- **Flash lights**, **radio batteries**

SECONDARY OR ACCUMULATORS BATTERIES

- The electrochemical reaction is **reversible**.
- Such cells can be **discharged** and **recharged many times**.
- Also known as **storage cell** or **accumulator**.

Examples:

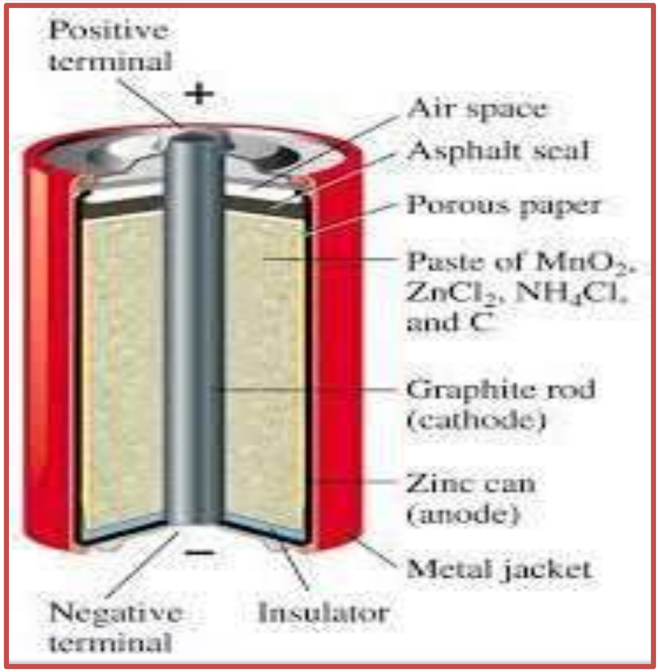
- **Nickel-Cadmium** (**NiCd – 1.2 v**),
- **Lead acid** (**2.0 v**), and
- **Lithium ion** (**3.3 v**) batteries.

IN SUMMARY MAJOR DIFFERENCE BETWEEN PRIMARY CELLS AND SECONDARY CELLS

PRIMARY CELLS	SECONDARY CELLS
Primary cells have **high energy density** and they get **discharged slowly**.	They have **low energy density** and made of **molten salts** therefore called as **wet cells**.
Since there is **no fluid** inside these cells are also known as **dry cells.**	**Internal resistance** is **low** and chemical reaction is **reversible**.
Internal resistance is **high** and chemical reaction is **irreversible** cell.	Cost is **high** and can be used through **large number of time** through **charging** and **discharging.**
Cost is **cheap** and **easy to use.**	

PRIMARY BATTERY – DRY CELL – LECLANCHE CELL, EMF = 1.5 V

Primary cell without fluid component.
Cylindrical **zinc** container – acts as **anode**.
Graphite rod – acts as a **cathode**.
The space between **anode** & **cathode** is packed with the paste of $\mathbf{NH_4Cl}$ and $\mathbf{ZnCl_2}$ and **graphite** is surrounded by **powdered** $\mathbf{MnO_2}$ & **carbon**.



At anode (Oxidation)

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

At cathode (Reduction)

$$2MnO_{2(S)} + H_2O + 2e^- \longrightarrow Mn_2O_{3(S)} + 2OH^-_{(aq)}$$

Net cell reaction:

$$Zn_{(s)} + MnO_{2(s)} + H_2O \longrightarrow Zn^{2+} + Mn_2O_3 + 2OH-$$

Zn-MnO_2 cell representation

$$Zn/Zn^{2+}, NH_4^+/MnO_2/C$$

The resulting OH^- ions react with NH_4Cl to produce NH_3 which is not liberated as gas but immediately combines with the Zn^{2+} and the Cl^- ions to form a complex salt $[Zn(NH_3)_2Cl_2]$ diamminedichlorozinc.

$$NH_4^+{}_{(aq)} + OH^-_{(aq)} \longrightarrow NH_{3(g)} + H_2O$$

$$2\,NH_4^+{}_{(aq)} + 2Cl^- + Zn^{2+} \longrightarrow [Zn(NH_3)_2Cl_2] + 2H^+$$

OVERALL CELL REACTION IS

$$Zn(s) + 2\,NH_4^+(aq) + Cl^-(aq) + 2MnO_2(s) \longrightarrow Mn_2O_3 + [Zn(NH_3)_2Cl_2] + H_2O$$

DRY CELL – LECLANCHE CELL

Advantages

- These cells voltage ranging from 1.25 V to 1.50 V.
- Primary cells are used in the torches, radios, transistors, calculators, hearing aids, pacemakers, watches etc.
- Price is low.

Disadvantages

- These cells does not have a long life, because the acidic NH_4Cl corrodes the container even when the cell is not in use.
- Zn metal dissolves slowly.
- When current is drawn rapidly from it, products build up on the electrodes thereby causing drop in voltage.

SECONDARY CELLS OR ACCUMULATOR BATTERIES

These cells can be **recharged** by passing an **electric current** through them and can be **used again** and **again**. **Examples include**:

A. lead acid storage battery

B. Nickel-cadmium battery

C. Lithium ion cell battery

Applications:
Widely used in cars, trains, motors, electric clocks, power stations, laboratories, emergency lights, telephone exchange, digital cameras, laptops etc.,

These are **reversible cells**,

A. Behave as GALVANIC CELLS while DISCHARGING.

B. Behave as ELECTROLYTIC CELL while CHARGING.

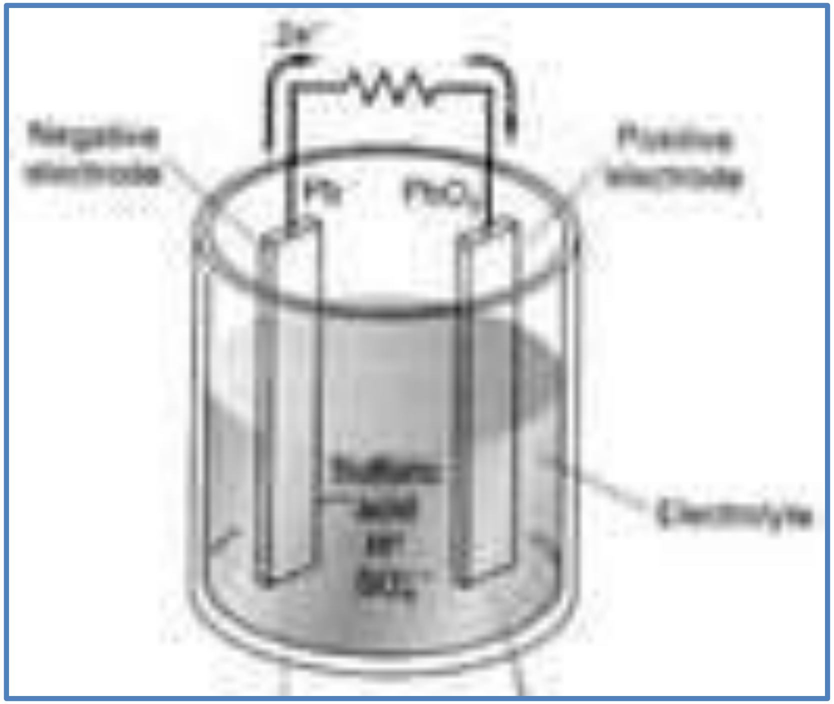
TO IMPROVE THE PERFORMANCE OF BATTERY FOR COMMERCIAL PURPOSE

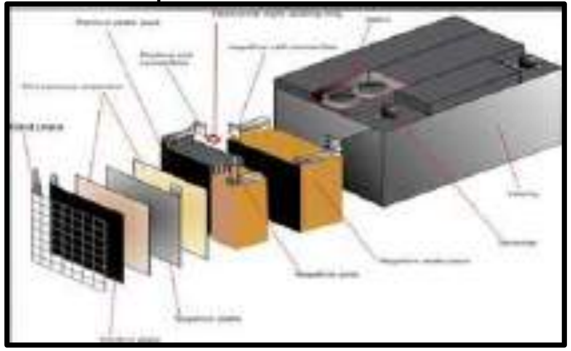
1. The **anodes** and **cathodes** with **very small separation** to conserve **space** are used.
2. **Current discharge** should be **high at low temperature**.
3. It should have **less variation in voltage** during **discharge**.
4. It should have **high energy efficiency**.
5. It should be **reliable**.
6. It should have **tolerance** to **shock**, **temperature** etc.
7. It should have no. of **charging** & **discharging** cycles before failure of battery (**Cycle life**).

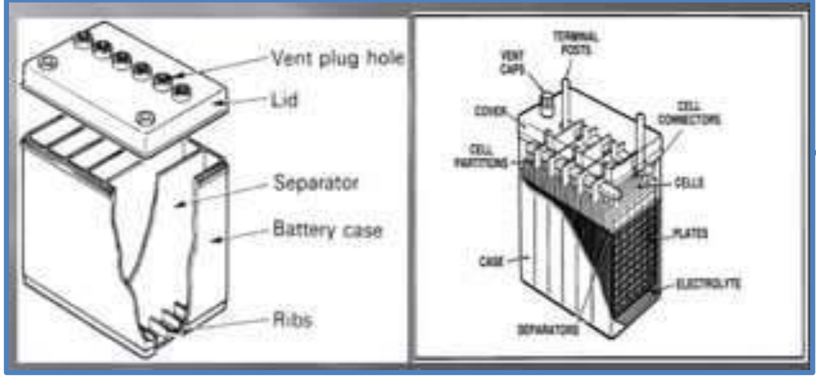
$$\% \text{ Energy Efficiency} = \frac{\text{Energy released on discharge}}{\text{Energy required for charge.}} \times 100$$

CONSTRUCTION OF LEAD-ACID BATTERY- INVENTED IN 19TH CENTURY

- Two electrode,
- One of **lead**, the other of **lead dioxide** (PbO_2) immersed in sulphuric acid
- **Lead** ions (Pb^{2+}) **dissolve**, leaving two electrons behind.
- Two electrons flow through the circuit and are used to help **lead dioxide dissolve**.







At Positive electrode

$$PbO_2 + SO_4^{2-} + 4\,H^+ + 2e^- \longrightarrow PbSO_4 + 2H_2O$$

At Negative electrode

$$Pb \longrightarrow Pb^{2+} + 2\,e^-$$

$$Pb^{2+} + SO_4^{2-} \longrightarrow PbSO_4$$

LEAD – ACID BATTERY (2V)

- Most common batteries used in automobiles.
- **12 V lead storage battery** is generally used which consists of **six cells** each providing **2 V**.
- Each cell consists of a lead anode and a grid of lead packed with lead oxide as the cathode.
- **Anode**: **Pb plates**
- **Cathode**: **PbO_2 plates coated with Pb-Sb alloy connected in parallel**.
- Anode & cathode immersed in **20 % dil. H_2SO_4 electrolyte** containing specific gravity about 1.2 to 1.3 V @ 25 °C.

LEAD ACID BATTERY

Discharging of cell

- Cell supplies electrical energy

Anode: Pb undergoes oxidation

At Anode: (Negative electrode)

$Pb \longrightarrow Pb^{2+} + 2\,e-$

$Pb^{2+} + SO_4^{2-} \longrightarrow PbSO_4$

- The 2e- released at anode flows to the PbO_2 electrode & reduce Pb^{4+} to Pb^{2+}.

At Cathode: (Positive electrode)

$PbO_2 + SO_4^{2-} + 4\,H^+ + 2e^- \longrightarrow PbSO_4 + 2H_2O$

- Net Reaction is

$Pb+PbO_2 + 2SO_4^{2-} +4\,H^+ + 2e^- \longrightarrow 2PbSO_4 + 2H_2O$

Charging of cell

- Discharging $PbSO_4$ is formed at the electrodes. While charging $PbSO_4$ will be removed.
- This can be done by applying **Ext EMF** greater than **2 volts** such that the reactions took place during **discharging are reversed**.

At Anode:

$2PbSO_4 + 2H_2O \longrightarrow PbO_2 + 2SO_4^{2-} +4\,H^+ + 2e^-$

At Cathode:

$PbSO_4 + 2\,e- \longrightarrow Pb^{2+} + SO_4^{2-}$

- Net Reaction is

$PbSO_4 + 2H_2O \longrightarrow Pb + PbO_2 + 2SO_4^{2-} + 4\,H^+$

Note: Usually with **decreasing temperature by 1 °C** leads to **decrease** in **voltage** by **1.5×10^{-4} volts**.
Due to this reason in the **Cold climate starting of car** is **difficult**. In such condition, the battery needs to be **heated to RT**.

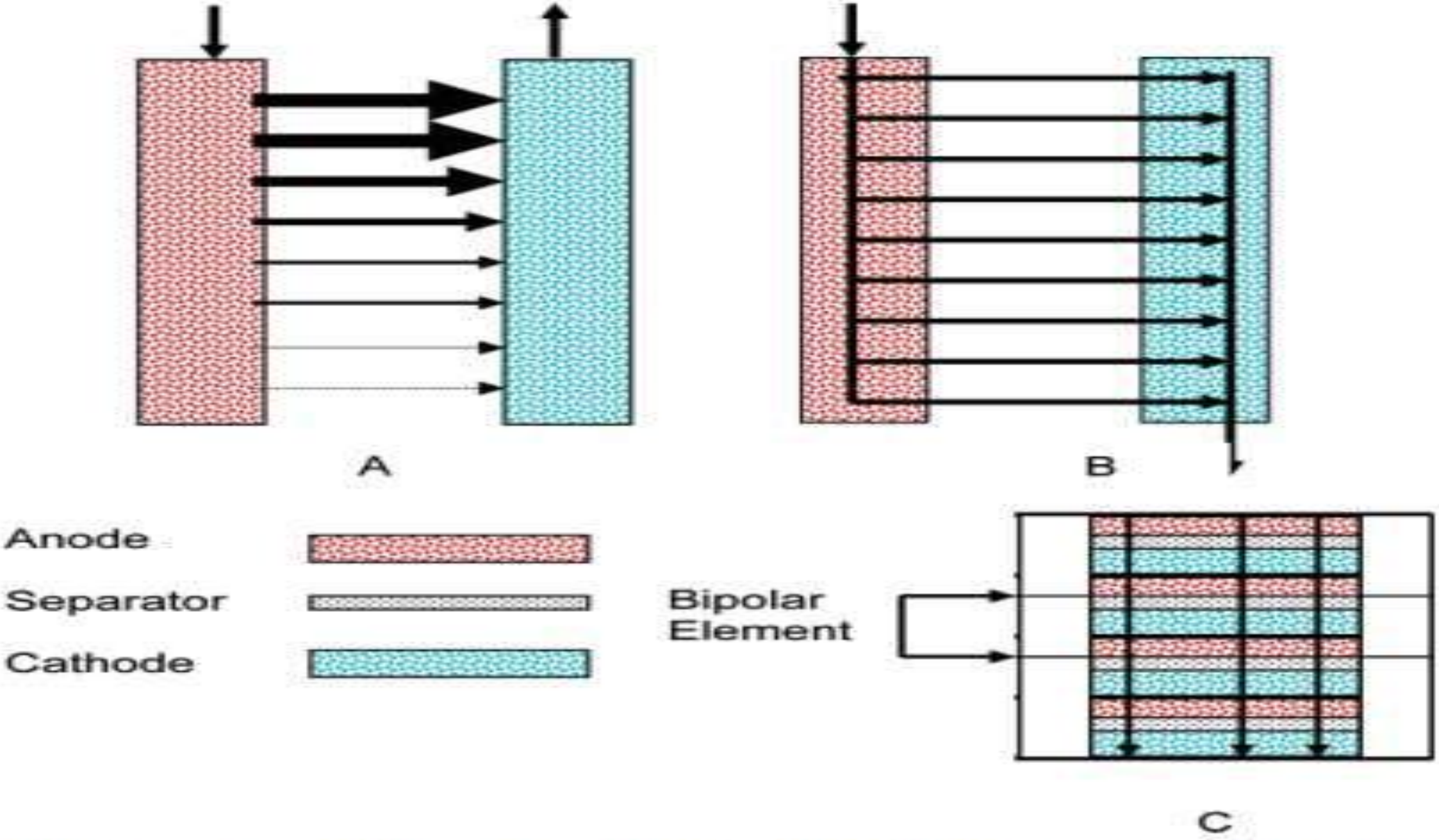


Figure 8. Primary current distribution on the front surface of the electrodes based on Kirkhof's law calculation for three different cell constructions: (A) Both connections to the cell are at the top. The higher resistance path at the bottom sections of the electrode reduces the current flow and results in a nonuniform current distribution. (B) All paths have equal resistance, and a uniform current distribution results. (C) The bipolar construction has equal resistance from one end to the other.

CHARACTERISTIC PROPERTIES OF ELECTRODES AND ELECTROLYTES

- The **negative electrode** is a **good reducing agent** (**electron donor**) such as **lithium**, **zinc**, or **lead**.
- The **positive electrode** is an **electron acceptor** such as **lithium cobalt oxide**, **manganese dioxide**, or **lead oxide**.
- The **electrolyte** is a **pure ionic conductor** that **physically separates** the **anode** from the **cathode**.
- In practice, a **porous electrically insulating material** containing the electrolyte is often placed between the anode and cathode to **prevent the anode from directly contacting the cathode.** Should the anode and cathode physically **touch**, **the battery will be shorted** and its full energy released as **heat** inside the battery.

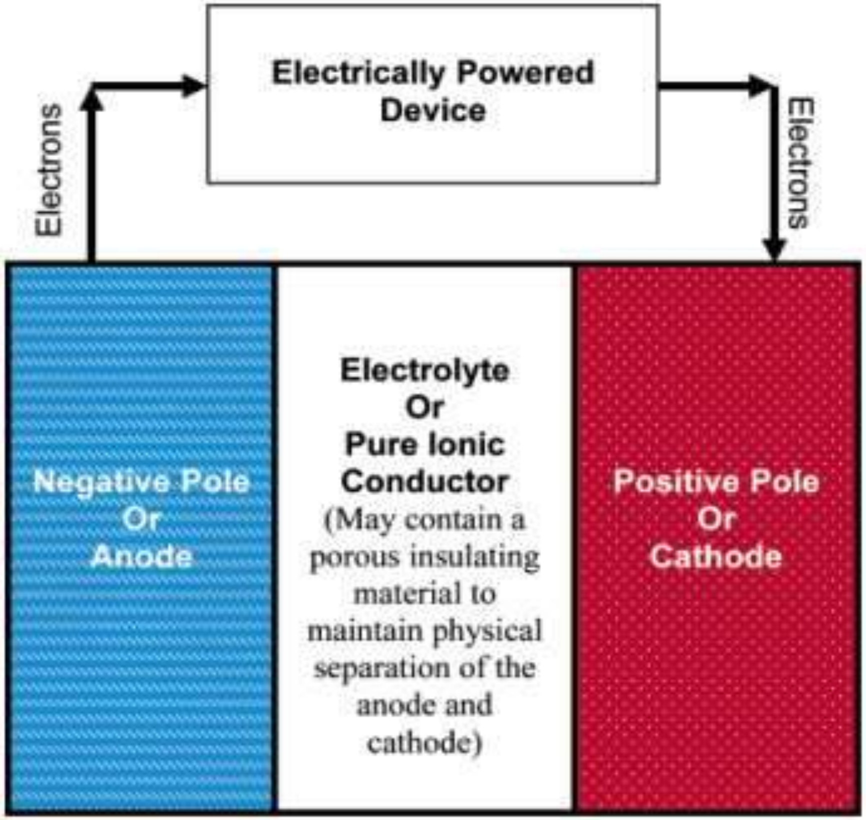


Figure 11. Block diagram of a cell or battery powering a device. If a battery is recharged, the load is replaced with an energy source that imposes a reverse voltage that is larger than the battery voltage and the flow of electrons is reversed.

ELECTROLYTES PHYSICAL PROPERTIES

- Battery electrolytes are usually liquid solvent based and can be subdivided into **aqueous**, **nonaqueous**, and **solid electrolytes**.
- **Aqueous electrolytes** are generally **salts of strong acids** and **bases** and are **completely dissociated** in solution into **positive** and **negative** ions.
- The electrolyte provides an ionic conduction path as well as a physical separation of the positive and negative electrodes needed for electrochemical cell operation. Each electrolyte is stable only within certain voltage ranges. Exceeding the electrochemical stability window results in its decomposition. The **voltage stability** range depends on the electrolyte **composition** and its **purity** level.
- The **high conductivity** of **aqueous solvent-based electrolytes** is due to their **dielectric constants**, which favor stable ionic species, and the **high solvating power**, which **favors** formation of **hydrogen bridge bonds** and allows the unique **Grotthus conductivity** mechanism for **protons**. **Thermodynamically**, aqueous electrolytes show an electrochemical stability window of **1.23 V**. **Kinetic** effects may expand the stability limit to **~2 V**.

In the **nonaqueous organic solvent-based** systems used for lithium batteries, the **conductivities** are of the order of 10^{-2}-10^{-3} S/cm^{-1}.

Compared to **water**, most **organic solvents** have a **lower solvating power** and a **lower dielectric constant**. This favors **ion pair formation**, even at **low salt concentration**.

Ion pair formation lowers the **conductivity** as the ions are **no longer free** and bound to each other.

Organic electrolytes show **lower conductivities** and **much higher viscosities** than aqueous electrolytes. Organic solvent based **electrolytes** (again with the help of kinetics) are limited to **~4.6 V**. Exceeding the voltage limit in the organic electrolytes results in **polymerization** or **decomposition** of the **solvent system**.

Solid electrolyte batteries have found limited use as the **power source** for **heart pacemakers** and for use in **military applications**. The basic principles described above apply to **fuel cells** and **electrochemical capacitors** as well as to **batteries**.

LEAD ACID BATTERY

Advantages:

- Rechargeability,
- Portability,
- Relatively constant potential and
- inexpensiveness.
-

Disadvantages:

- The use of concentrated sulphuric acid (dangerous) and use of lead.

APPLICATIONS OF LEAD ACID BATTERY

- **Stationary power sources** such as emergency back up power storage (UPS).
- Signaling stations for **railroads** and **telecommunication**.
- Used for supplying current to **electrical vehicles**, **railway**, **mines**, **laboratories**, **hospitals**, **automobiles**, **power stations** broadcasting stations in **telephone exchange**, **gas engine**, **automobiles**, **stand by suppliers** (UPS) etc.

LITHIUM BATTERY – WHY LITHIUM METAL?

- Li-ion batteries first proposed – **1970s**. But the **technology** to successfully create them wasn't **invented** until **1980s**. First **Li-ion commercial battery** was launched by **Sony** in late **1991**.
- **John** shared the Nobel Prize in Chemistry with **M. Stanley Whittingham** and **Akiro Yoshino** in **2019**
- Lithium cells are primary cells in which **lithium** acts as **anode** and the **cathode** may differ.
- Lithium metal is used as **anode** because of its **light weight**, **high standard oxidation** potential (≥3V) and **good conductivity**.
- As the **reactivity** of lithium in **aqueous solution is more**, lithium cells use **non-aqueous solvents** **as electrolyte**.
- **High capacity** of **storage** of **energy**: 370 -300 Wh/cm^3.
- **High** electrochemical **reduction potential**.
- **Highly reactive** material. Spread **thermal** range **– 25 °C to + 40 °C**.

PREFACE FOR THE SPECIAL ISSUE OF CHEMISTRY OF MATERIALS IN HONOR OF PROFESSOR JOHN B. GOODENOUGH ON HIS 100TH BIRTHDAY PUBLISHED AS PART OF THE VIRTUAL SPECIAL ISSUE "JOHN GOODENOUGH AT 100"

BRIEF HISTORY OF LITHIUM BATTERIES

Anthony K. Cheetham, Clare P. Grey, C. N. R. Rao,
Chem. Mater. 2022, 34, 6185−6187

- **Electrical conductivity**
- **Magnetism**
- **Superexchange** interaction between **transition metal oxides.**
- **Magnetism and electronic structure** to **ionic mobility** and **electrochemistry**.
- **High energy density**
- **$LiFePO_4$** in 1997, was **20 years ahead of its time**, but it has now been commercialized via, for example, the new **BYD Blade batteries** and in the **new** **Tesla 3 electric vehicles.**
- **$TiNb_2O_7$ Toshiba** battery commercialized .

(1) **Goodenough, J. B**. A Theory of the Deviation from **Close Packing in Hexagonal Metal Crystals**. Phys. Rev. 1953, **89, 282−294**.

(7) **Kanamori**, J. Superexchange Interaction and Symmetry Properties of Electron Orbitals. **J. Phys. Chem. Solids 1959, 10, 87−98**.

(11) Mizushima, K.; Jones, P. C.; Wiseman, P. **J.; Goodenough**, J. B. **Li_xCoO_2 (0 < x< 1)**: A new cathode material for batteries of high energy density. **Mater. Res. Bull. 1980, 15, 783−789**.

(12) **Whittingham, M. S.** The role of ternary phases in cathode reactions. **J. Electrochem. Soc. 1976**, 123, 315−320.

JOURNEY TOWARDS LITHIUM ION BATTERY DEVELOPMENT

- The **Nobel Prize in Chemistry 2019** is awarded to **John B. Goodenough**, **M. Stanley Whittingham** and **Akira Yoshino** for their contributions to the development of the **lithium-ion battery**. This **rechargeable battery laid the foundation** of **wireless electronics** such as **mobile phones** and **laptops**. It also makes a **fossil fuel-free** world possible, as it is used for everything from **powering electric cars** to **storing energy from renewable sources**.
- **They developed the world's most powerful battery**
- An element rarely gets to play a central role in a drama, but the story of **2019's** Nobel Prize in Chemistry has a clear protagonist: lithium, an ancient element that was created during the **first minutes of the Big Bang**.
- Humankind became aware of it in **1817**, when **Swedish chemists Johan August Arfwedson** and **Jöns Jacob Berzelius purified** it out of a mineral sample from **Utö Mine**, in the **Stockholm** archipelago.
- Berzelius named the new element after the **Greek word for stone**, **lithos**. Despite its heavy name, it is the **lightest solid element**, which is why we **hardly notice the mobile phones** we now carry around.

JOURNEY TOWARDS LITHIUM ION BATTERY DEVELOPMENT

- **Lithium's weakness** – its **reactivity** – is also its **strength**. In the early **1970s**, **Stanley Whittingham** used lithium's enormous drive to release its outer electron when he developed the **first functional lithium battery**.
- In **1980**, **John Goodenough** doubled the **battery's potential**, creating the right conditions for a vastly **more powerful** and **useful battery**.
- In **1985**, **Akira Yoshino** succeeded in **eliminating pure lithium** from the battery, instead basing it wholly on **lithium ions**, which are **safer than pure lithium**. This made the **battery workable in practice**.
- **Lithium-ion batteries** have brought the greatest benefit to humankind, as they have enabled the **development** of **laptop computers**, **mobile phones**, **electric vehicles** and the **storage of energy generated** by **solar** and **wind power**.
- He worked for many years at the Lincoln Laboratory at the **Massachusetts Institute of Technology, MIT**. While there, he contributed to the development of **random access memory (RAM)** which is still a **fundamental component** of **computing**.

HISTORY OF Li BATTERIES

John B Goodenough

- Lithium battery

Stanley Wittingham

- Lithium – tantalum to titanium disulfide
- (Metal sulphides) cathode = 2 V

John B Goodenough

- Lithium – Li + Metal oxide –
- Li + CoO = 4V

Akira Yoshino

- Lithium-cobalt oxide as the **cathode** and tried using various **carbon-based materials** as the anode. (**Graphite** to **petroleum coke**)
- **The lithium-ion battery – necessary for a fossil fuel-free society**
- The battery has enabled the development of **cleaner energy technologies** and **electric vehicles**, thus contributing to **reduced emissions** of **greenhouse gases** and **particulates**.
- Through their work, **John Goodenough**, **Stanley Whittingham** and **Akira Yoshino** have created the right conditions for a **wireless** and **fossil fuel-free society**, and so brought the greatest benefit to humankind.

LITHIUM CELLS ARE CLASSIFIED INTO TWO CATEGORIES

Lithium cells with solid cathode

- Most widely used cell is **Lithium-MnO_2 cell = 3 V.**
- MnO_2 should be heated to over 300°C to remove water before keeping it in the cathode, thereby the efficiency of the cell is increased.
- **Anode**: lithium metal
- **Cathode**: MnO_2 as an acctive material
- **Electrolyte**: $LiBF_4$ salt in a solution of propylene carbonate and 1,2-dimethoxy ethane.

At anode: $Li \longrightarrow Li^+ + e^-$

At Cathode: $MnO_2 + e^- \longrightarrow MnO_2^-$

Net reaction: $Li + MnO_2 \longrightarrow LiMnO_2$

- Applications:

1. **Coin** type cells are used in **watches** and **calculators**
2. **Cylindrical cells** are used in fully **automatic cameras.**

Lithium cells with liquid cathode

A. Lithium-sulphur dioxide cell is an example of lithium cathode. Co-solvents = acrylonitrile or propylene carbonate or mixture of two SO_2 in 50 % by volume.

Cell reaction: $2\ Li + 2SO_2 \longrightarrow LiS_2O_4$

B. Lithium thionyl chloride cell (3.3 – 3.5 V).

It consists of **high surface area carbon cathode**, **non-woven glass separator**.

Thionyl chloride acts as **electrolyte** & cathode.

At Anode: $4\ Li \longrightarrow Li^+ + 4\ e^-$

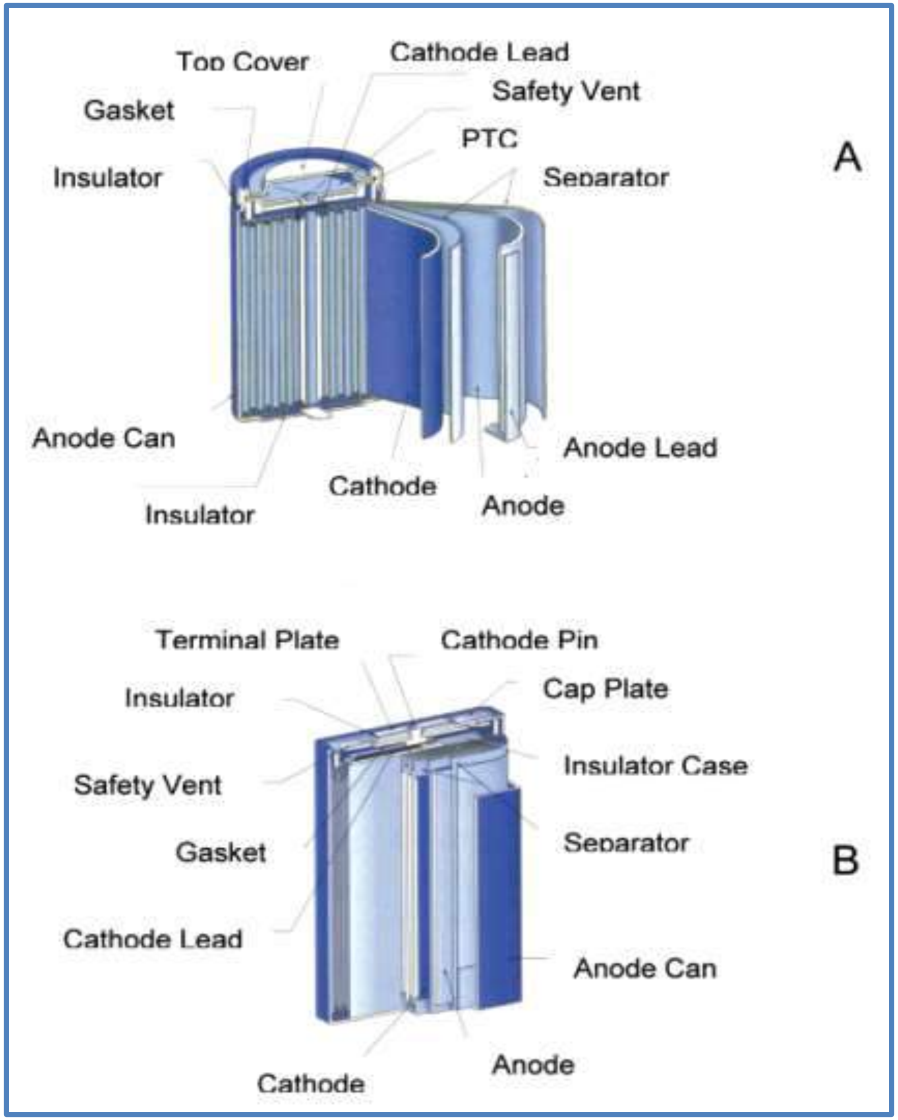
At Cathode: $4\ Li + 4\ e^- + 2\ SOCl_2 \longrightarrow 4\ LiCl + SO_2 + S$

Net reaction:

$4\ Li + 2\ SOCl_2 \longrightarrow 4\ LiCl + SO_2 + S$

Uses:

1. Used for **military** and **space** applications
2. Medicinal devices - **Neuro-stimulators** drug delivery system
3. **Electric circuit boards** for supplying **fixed voltage** for **memory protection** & **standby functions.**



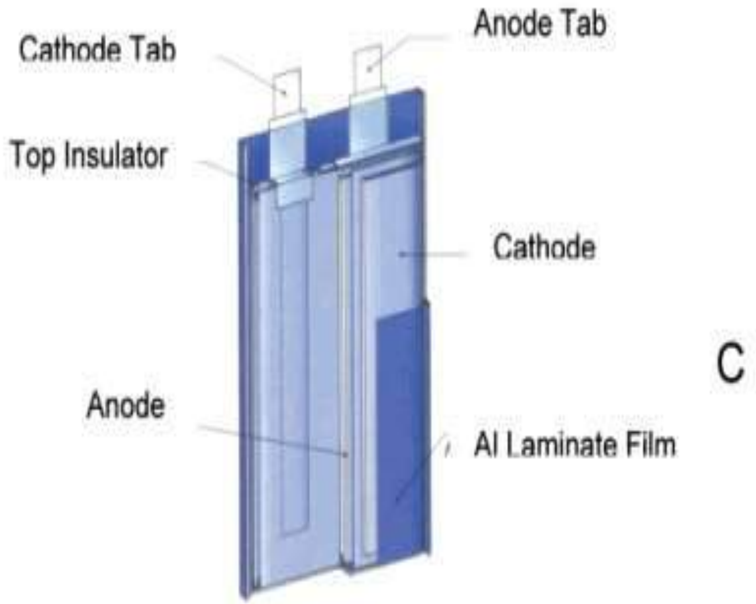


Figure 20. Construction of (A) cylindrical, (B) prismatic, and (C) polymer Li ion cells. (Reprinted with permission from a brochure by Sony Corporation).

Chem. Rev. 2004, 104, 4245−4269

SELECTION CRITERIA FOR COMMERCIAL BATTERY SYSTEMS

1. **Mechanical and Chemical Stability**
2. **Energy Storage Capability**.
3. **Temperature Range of Operation**. For military applications, the operational temperature range is from -50 to 85 °C.
4. **Self-Discharge**. Self-discharge is the loss of performance when a battery is not in use.
5. **Shape of the Discharge Curve**. The issue of a sloping versus a flat discharge depends on the intended use. For operation of an electronic device, a flat, unchanging, discharge voltage is preferred.
6. **Cost**. The cost of the battery is determined by the materials used in its fabrication and the manufacturing process. The manufacturer must be able to make a profit on the sale to the customer.
7. **Safety**. All consumer and commercial batteries must be safe in the normal operating environment and not present any hazard under mild abuse conditions. The cell or battery should not leak, vent hazardous materials, or explode.

ADDED CRITERIA FOR RECHARGEABLE BATTERIES ARE AS FOLLOWS:

1. **Ability To Recharge and Deliver Power**.
2. **Cycle Life**. It is not enough for a chemical system to be recharged and deliver power to qualify as a commercial rechargeable system.
3. **Charge Time**. The time it takes to recharge a battery completely relates to the use. For convenience, recharging in 15 min is accepted for many consumer applications. However, fast charging places a stress on the robustness of the electrode reactions and may result in shortened cycle life. Most batteries require 3-8 h to recharge completely and maintain their required cycle life. This slower charge rate allows time for the atoms and molecules to find their correct positions in the charged material.
4. 11. **Overcharge/Overdischarge Protection**. When a battery is forced outside its thermodynamic voltage levels, the reaction path becomes unstable; irreversible new reactions can occur, and new compounds can form. These events harm the active material and either reduce the capacity or render the system inoperable. In addition, unsafe battery conditions may occur under overcharge/overdischarge conditions. The Ni-Cd, Ni-MH, and lead acid have a built-in overcharge and overdischarge characteristic based on an oxygen recombination mechanism.

SEPARATOR MATERIALS FOR Li ION BATTERIES

- **Inorganic or ceramic particle coatings** are applied on either one side or two sides of traditional **polymer separators** to **improve** the
- **mechanical strength**,
- **porosity**,
- **electrolyte uptake**,
- **ionic conductivity**, and
- **flame retardance**.
- The inherently **nonflammable polymer separators** exhibit
- **high thermal stability**,
- **ionic conductivity**,
- **porosity**, and **flame retardance** as compared to **polyolefin separators**, but the **complex preparation process** and **high cost** impede their applications.

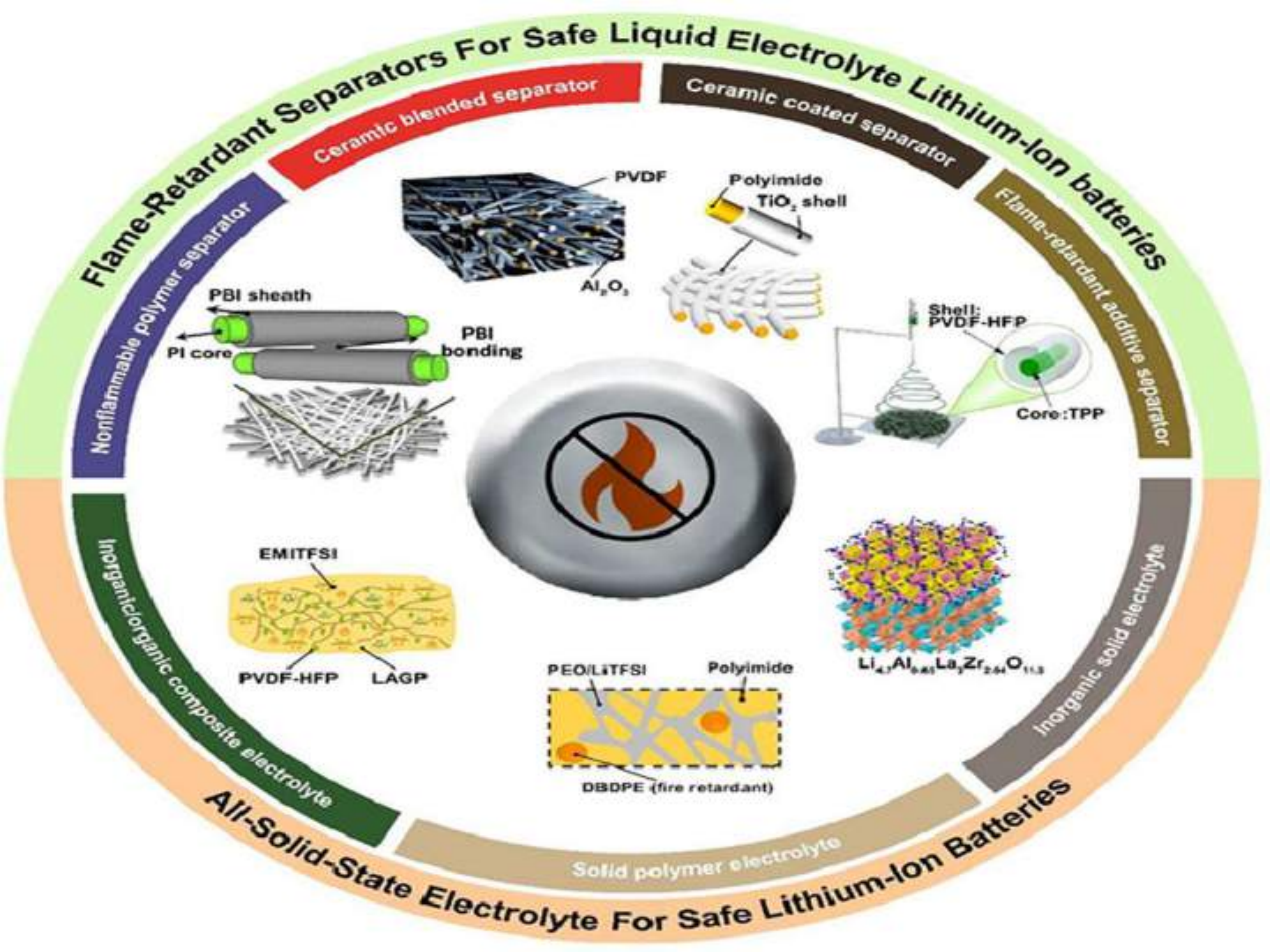
The **flame-retardant additive** can effectively improve the flame retardance of polymer separators, but most flame retardant additives cannot contact with the liquid electrolyte, otherwise the additives can increase the **viscosity of liquid electrolyte** or **react with electrode materials** during **charges** and **discharges**.

Therefore, the **additives** must be **encapsulated** by **polymers** or other components, and the **polymer shell** can be **melt under high temperature** to **release the flame retardants additives**.

RECENT PROGRESS IN FLAME-RETARDANT SEPARATORS FOR SAFE LITHIUM-ION BATTERIES

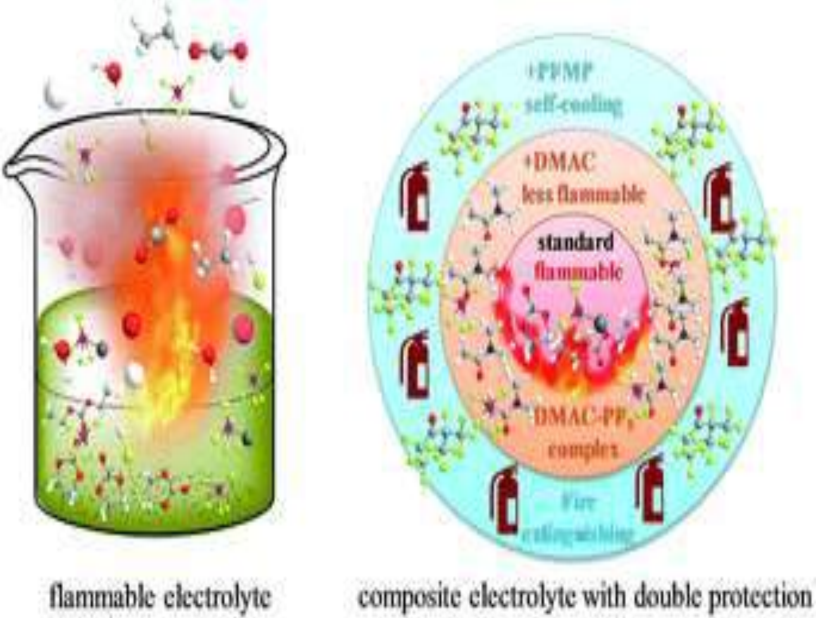
- The **composition**, **structure** and the **performance** of flame-retardant separators for liquid LIBs include
- **Inorganic particle** blended **polymer separators**,
- **Ceramic material** coated separators,
- inherently **nonflammable polymer** separators,
- Separators with **flame-retardant additives**.
- Then much attention is paid on the **solid-state electrolytes** including
- **inorganic solid electrolytes**,
- **solid polymer electrolytes**, and
- **inorganic/organic composite electrolytes**.

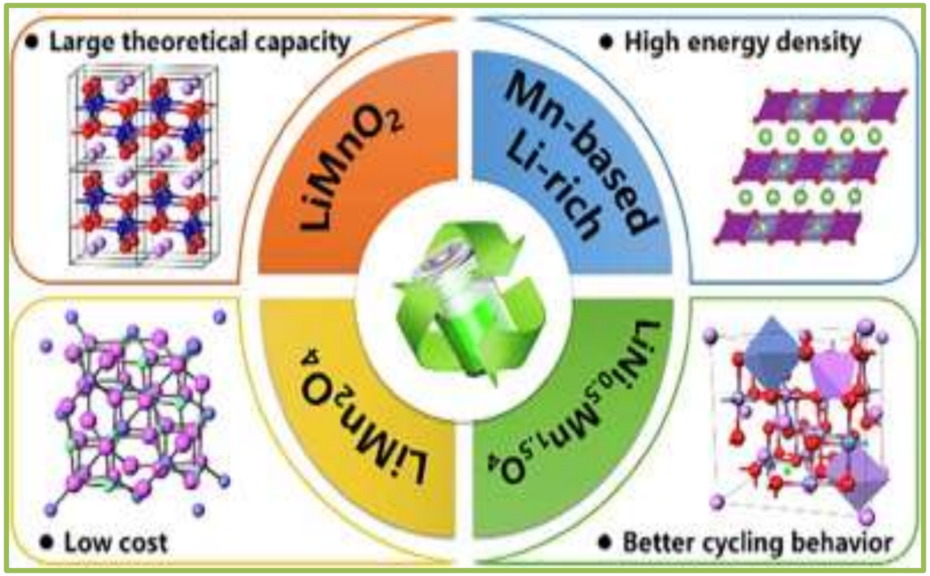
Energy Storage Materials 37 (2021) 628–647

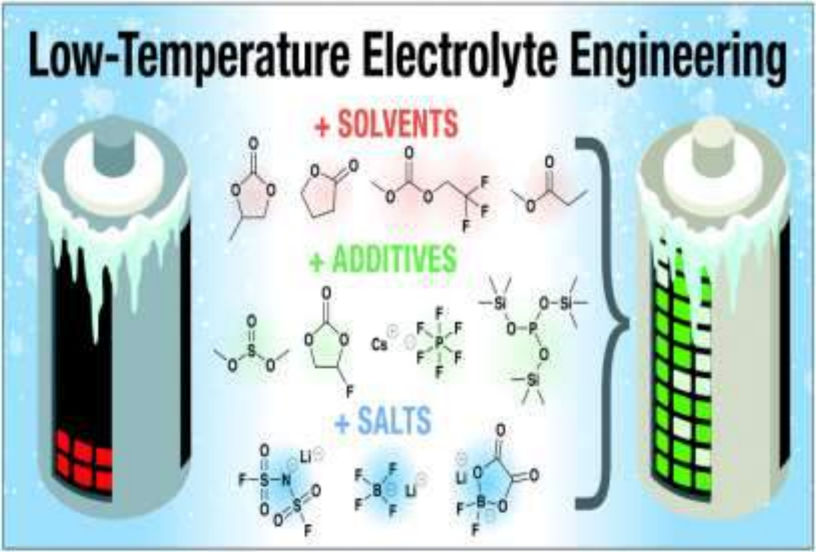

Flame-Retardant Separators For Safe Liquid Electrolyte Lithium-Ion batteries
Ceramic blended separator
Ceramic coated separator
Flame-retardant additive separator
Nonflammable polymer separator
PVDF
Al_2O_3
Polyimide
TiO_2 shell
PBI sheath
PI core
PBI bonding
Shell: PVDF-HFP
Core:TPP
EMITFSI
PVDF-HFP
LAGP
$Li_{4.7}Al_{0.43}La_3Zr_{2.64}O_{11.3}$
PEO/LiTFSI
Polyimide
DBDPE (fire retardant)
Inorganic/organic composite electrolyte
Solid polymer electrolyte
Inorganic solid electrolyte
All-Solid-State Electrolyte For Safe Lithium-Ion Batteries

COMPONENTS OF LITHIUM BATTERIES

- Electrolytes
- Liquid electrolyte
- Molten lithium salt
- Amorphous polymer electrolytes
- Crystalline polymers







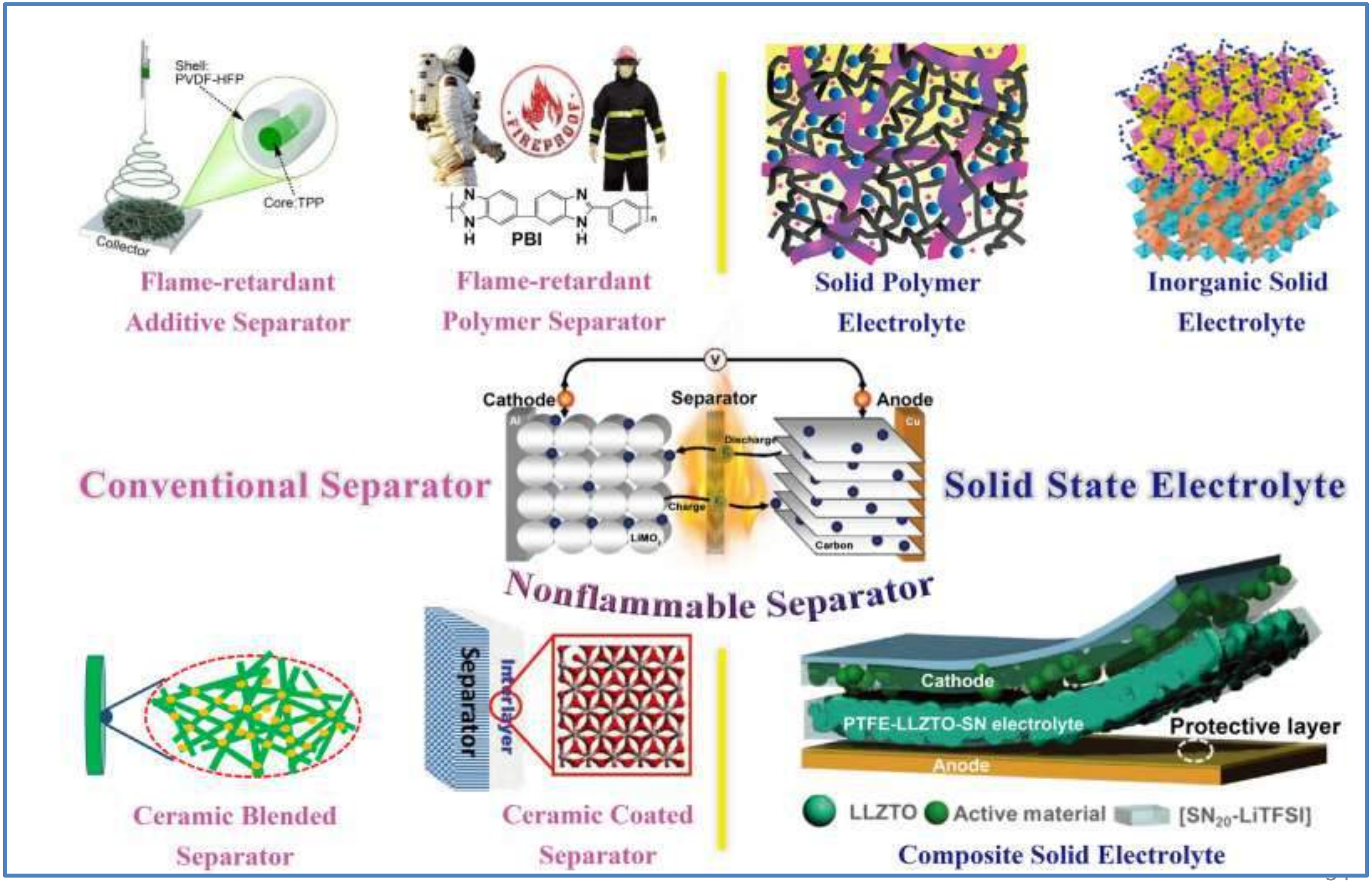
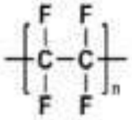
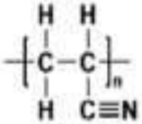
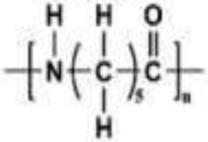
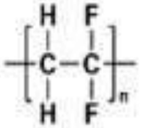
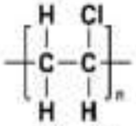
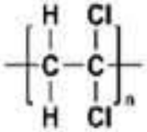
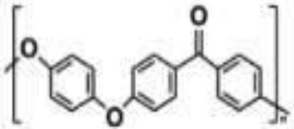

Shell: PVDF-HFP
Core:TPP
Collector
Flame-retardant Additive Separator
FIREPROOF
PBI
Flame-retardant Polymer Separator
Solid Polymer Electrolyte
Inorganic Solid Electrolyte
V
Cathode
Separator
Anode
Al
Cu
Discharge
Charge
LiMO$_2$
Carbon
Conventional Separator
Solid State Electrolyte
Nonflammable Separator
Separator
Interlayer
Ceramic Blended Separator
Ceramic Coated Separator
Cathode
PTFE-LLZTO-SN electrolyte
Protective layer
Anode
LLZTO
Active material
[SN$_{20}$-LiTFSI]
Composite Solid Electrolyte

TABLE 1: IMPORTANT CHARACTERISTICS OF TYPICAL NONFLAMMABLE POLYMERS FOR LIBS

Material	Structure	Melting points [°C]	Thermal degradation temperature [°C]	Limiting oxygen index [%]	Ignition temperature [°C]	Tensile strength [MPa]
Poly(tetrafluoroethylene) (PTFE)		327	543	95	630	19.6–35.2
Poly(acrylonitrile) (PAN)		320	293	18	460	2.2–3.8
Polyamide 6 (PA 6)		260	424	25	432	64.7
Poly(vinylidene fluoride) (PVDF)		160–170	438	43–65	643	35
Polyvinyl chloride (PVC)		189	273	50	395	52
Poly(vinylidene chloride) (PVDC)		195	225	42	-	-
Poly(ether-ether-ketone) (PEEK)		340	570	37	570	100

CONTINUATION ………………

TABLE 1: IMPORTANT CHARACTERISTICS OF TYPICAL NONFLAMMABLE POLYMERS FOR LIBS

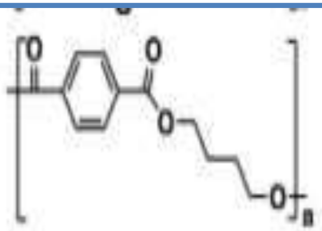
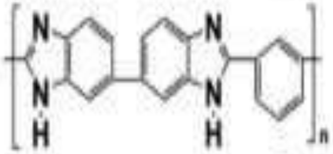
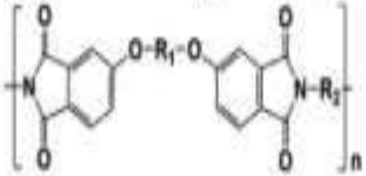
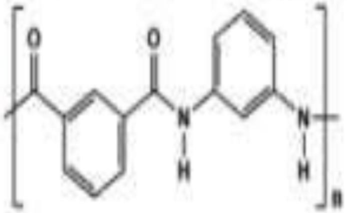
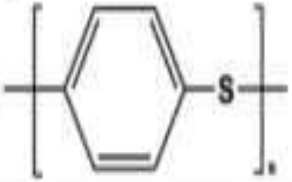
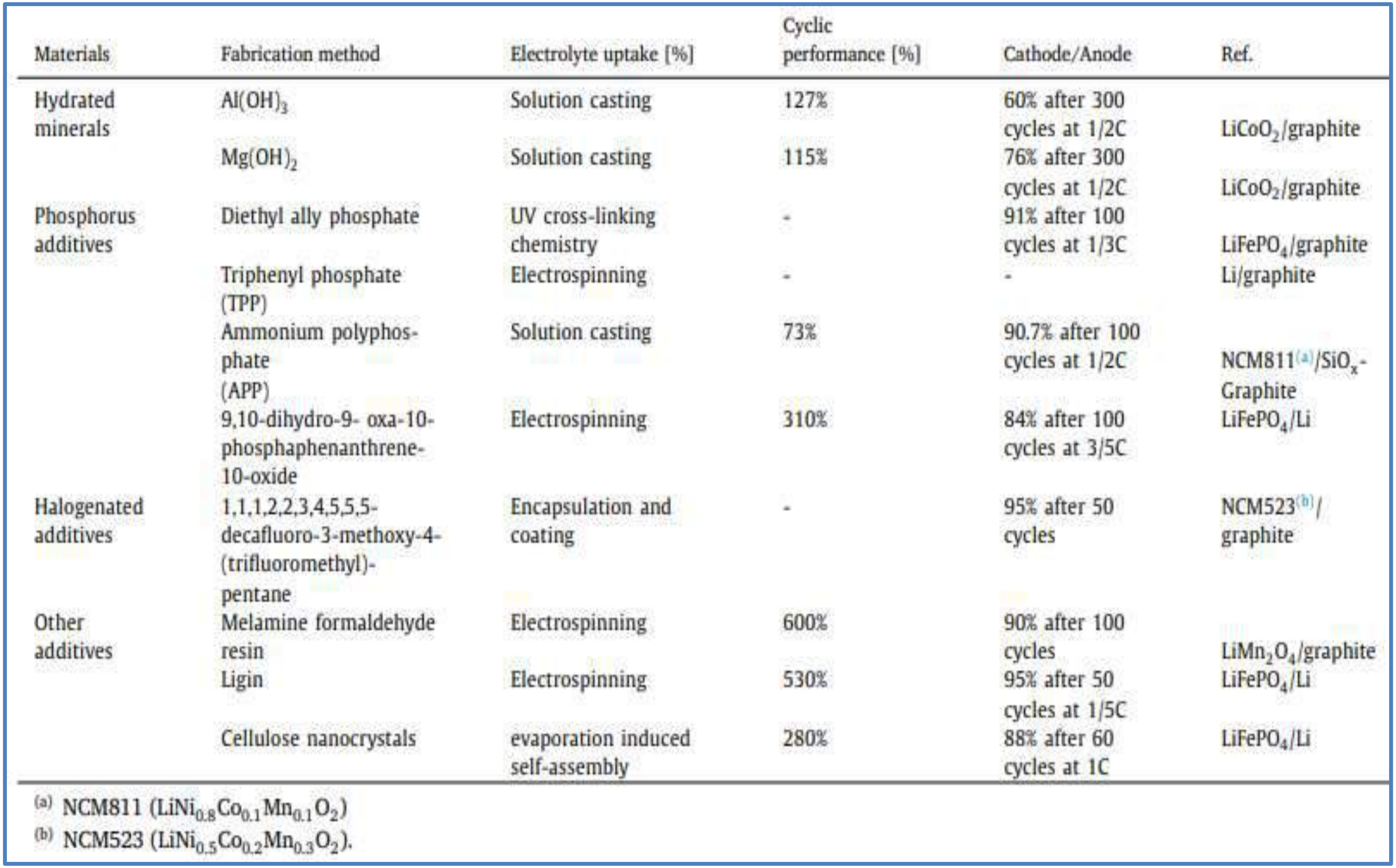
Material	Structure	Melting points [°C]	Thermal degradation temperature [°C]	Limiting oxygen index [%]	Ignition temperature [°C]	Tensile strength [MPa]
Polybutylene terephthalate (PBT)		237	382	20-24	382	34-60
Polybenzimidazoles (PBI)		-	584	42	-	160
Polyetherimide (PEI)		-	527	47	528	85
Poly(m-phenyleneisophthalamide) (NOMEX)		407	-	29	-	-
Polyphenylene sulfide (PPS)		287	504	44	575	45-172

TABLE: THE TYPICAL FLAME-RETARDANT ADDITIVES FOR LIB SEPARATORS



Materials	Fabrication method	Electrolyte uptake [%]	Cyclic performance [%]	Cathode/Anode	Ref.
Hydrated minerals	$Al(OH)_3$	Solution casting	127%	60% after 300 cycles at 1/2C	$LiCoO_2$/graphite
	$Mg(OH)_2$	Solution casting	115%	76% after 300 cycles at 1/2C	$LiCoO_2$/graphite
Phosphorus additives	Diethyl ally phosphate	UV cross-linking chemistry	-	91% after 100 cycles at 1/3C	$LiFePO_4$/graphite
	Triphenyl phosphate (TPP)	Electrospinning	-	-	Li/graphite
	Ammonium polyphosphate (APP)	Solution casting	73%	90.7% after 100 cycles at 1/2C	NCM811[a]/SiO_x-Graphite
	9,10-dihydro-9- oxa-10-phosphaphenanthrene-10-oxide	Electrospinning	310%	84% after 100 cycles at 3/5C	$LiFePO_4$/Li
Halogenated additives	1,1,1,2,2,3,4,5,5,5-decafluoro-3-methoxy-4-(trifluoromethyl)-pentane	Encapsulation and coating	-	95% after 50 cycles	NCM523[b]/graphite
Other additives	Melamine formaldehyde resin	Electrospinning	600%	90% after 100 cycles	$LiMn_2O_4$/graphite
	Ligin	Electrospinning	530%	95% after 50 cycles at 1/5C	$LiFePO_4$/Li
	Cellulose nanocrystals	evaporation induced self-assembly	280%	88% after 60 cycles at 1C	$LiFePO_4$/Li

[a] NCM811 ($LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$)

[b] NCM523 ($LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$).

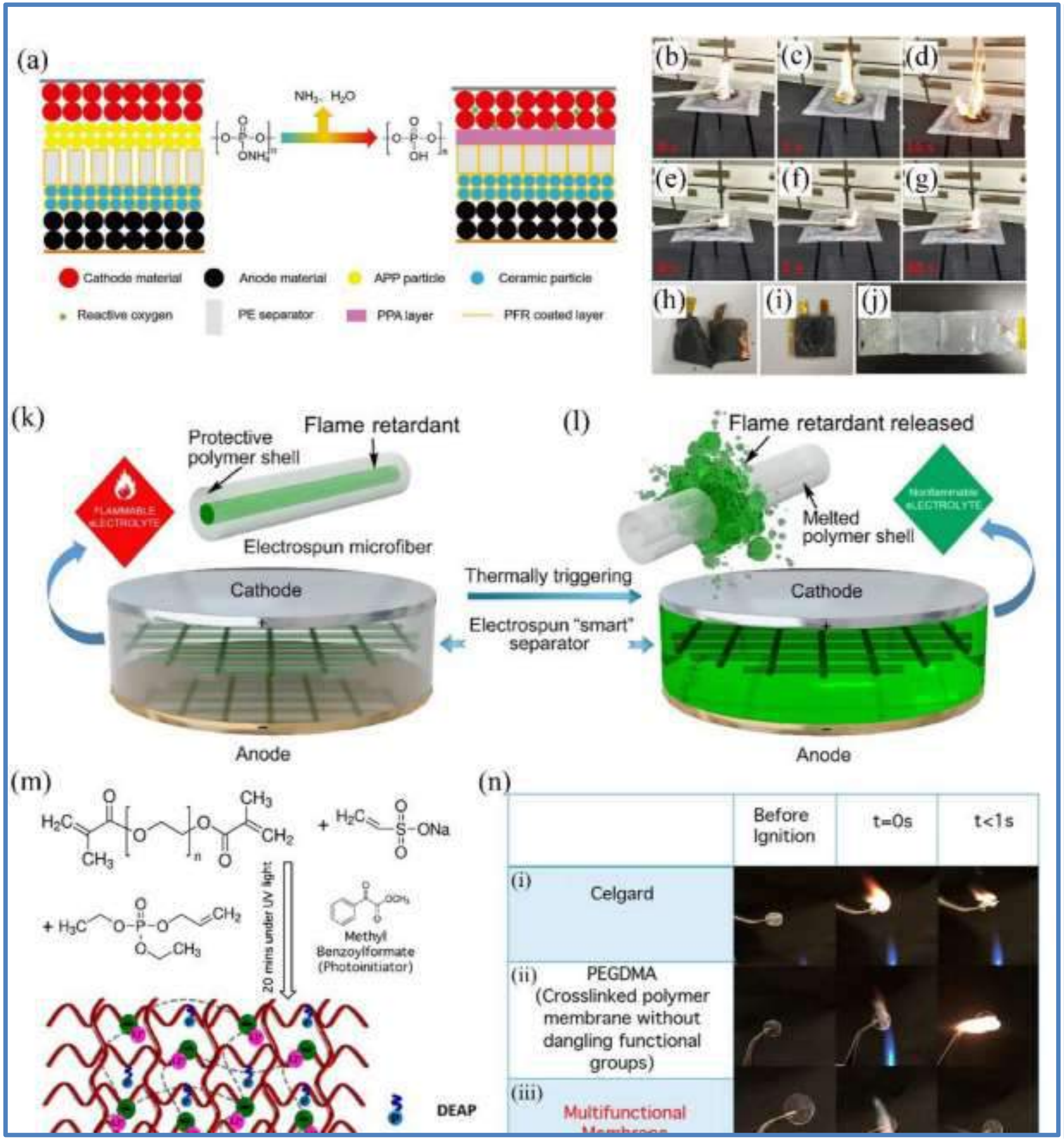


Fig. 9. (a) The safety mechanism of APP-CCS@PFR for LIBs. (b-d) The combustion tests at various times of $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2|SiO_x$-Gr full cells assembled with PE separator and (e-g) APP-CCS@PFR, respectively. (h-i) The cells assembled with PE separator and APP-CCS@PFR after combustion test, respectively. (j) Photograph of APP-CCS@PFR taken apart from the cell that after combustion test. Reproduced with permission [94]. Copyright 2020, Wiley-VCH. (k) The free-standing separator composed of microfibers with a core-shell structure, where the polymer is the shell and the flame-retardant additive is the core. (l) The polymer shell melted during thermal runaway inside of battery, the encapsulated flame retardant is released into the electrolytes and suppressing the combustion of the electrolytes. Reproduced with permission [6]. Copyright 2017, Sci. Adv. (m) Schematic diagram depicting the synthesis procedure for cross-linked PEGDMA membranes with pendant sulfonate and phosphate groups, with ionic crosslinks between the sulfonate chains. (n) Flame-retardant properties of soaked multifunctional membranes compared to commercial separator; (i) Celgard, (ii) pure cross-linked PEGDMA, (iii) multifunctional membrane, and (iv) multifunctional membrane as a coating on the commercial separator. Reproduced with permission [93].

LI-ION RECHARGEABLE BATTERY

- The Li-ion rechargeable battery (LIB) has enabled the wireless revolution of
- Cell phones,
- Laptop computers,
- Digital cameras, and
- iPads
- that has transformed global communication.

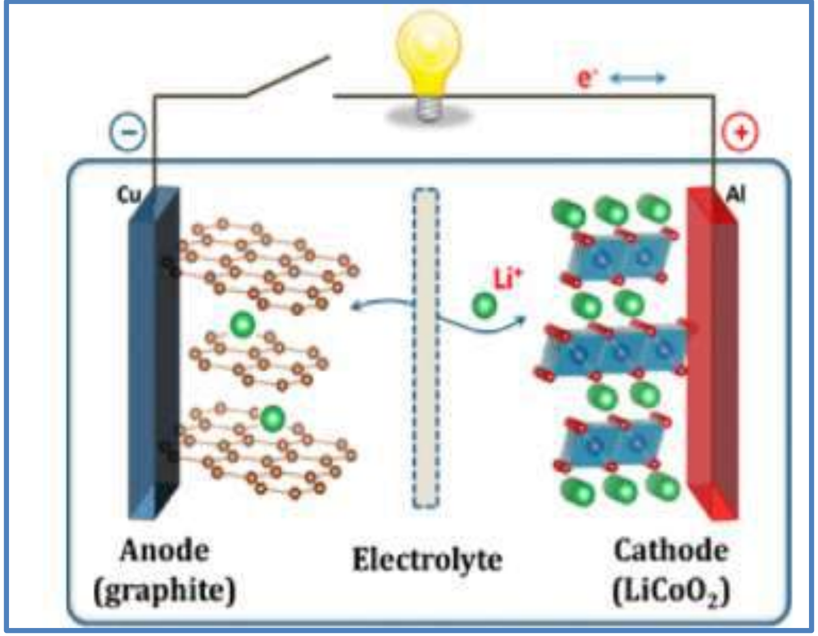


Figure 1. Schematic illustration of the first Li-ion battery (LiCoO2/Li+ electrolyte/graphite).

CONSTRUCTION AND APPLICATIONS OF LITHIUM-POLYMER CELL

- To ensure optimum adhesion of active materials to these metal surfaces, **poly(vinylidene difluoride) (PVdF)** and **carboxymethyl cellulose** or **styrene−butadiene latex** materials were identified as effective binders for **cathode** and **anode** materials, respectively.
- Chem. Rev. 2018, 118, 11433−11456

DIFFERENCE BETWEEN LITHIUM AND LITHIUM ION BATTERY

Lithium batteries

- Not rechargeable
- Pure Li metallic form (Anode)
- Primary battery
- Instantly react with H_2O or even moisture in the air.
- Examples: pacemakers, implantable electronic medical devices
- Lithium iron disulfide primary battery

Lithium ion batteries

- Rechargeable
- Li compounds used are much more stable than elemental Li.
- Higher energy density (can store more energy)
- Lower self discharge rate ie., they retain their charge for a longer time.
- Will retain most of their charge even after months of storage – **high shelf life**
- Li in Li-ion batteries is in a less reactive compound
- **Li ion** move from **negative electrode** to the **positive electrode** during **discharge** and back when **charging**.
- Ex: $LiCoO_2$, $LiMn_2O_4$, $LiNiMnCoO_2$, $LiFePO_4$

NICKEL-CADMIUM CELL – (1.4 V)

- **Waldemer Junger** – 1899 prepared the **first Ni-Cd battery**.
- Alkaline storage batteries because the electrical energy is desired by the reaction of alkaline solution.

Rechargeable Ni-Cd batteries:

- **Anode** (Negative plate): Cadmium as its main active material
- **Anode compartment**:
- The composition of the active material of the anode are spongy Cd with 78% $Cd(OH)_2$, 18% Fe, 1% Ni and 1% graphite which are pressed into the tablet form and wrapped in nickel wire gauge.
- **Cathode** (Positive electrode): Nickel oxy hydroxide NiO(OH) active material
- **Cathode active material**:
- The outer cup contains a mixture of 80% NiO(OH) and $Ni(OH)_2$, 2% $Cd(OH)_2$, 18% graphite and very minute quantities of **barium compounds** to increase the **efficiency** of **active materials** and also the **cycle life**.
- **Electrolyte**: KOH solution
- **Separator**: made of a thin **non-woven fabric**, an **alkaline electrolyte**. A cell cup made up of steel coated with nickel.

HALF CELL REACTIONS OF Ni-Cd CELL

Anode compartment

- When the cell is supplying current to a external circuit, electrons flow from this electrode and reaction proceeds to form cadmium hydroxide-the cadmium is oxidized to cadmium hydroxide.

At anode (oxidation):

$Cd_{(s)} + 2OH^-_{(aq)} \longrightarrow Cd(OH)_{2\,(s)} + 2e^-$

- When the cell is being charged this reaction is reversed. Electrons are supplied to the cadmium electrode and the hydroxide is reduced back to metallic cadmium.

Cathode compartment

- The positive electrode is a hydrated oxide of nickel. During discharge it is reduced to divalent nickel hydroxide.

At Cathode (Reduction):

$2NiO(OH)_{(s)} + 2H_2O + 2e^- \longrightarrow 2\,Ni(OH)_{2\,(s)} + 2OH^-_{(aq)}$

- When the cell is supplying current to an external circuit, electrons are supplied into the cathode from the external circuit and the reaction proceeds to form nickel hydroxide.

Net cell reaction:-

$$2NiO(OH)_{(s)} + Cd_{(s)} + 2H_2O \longrightarrow 2Ni(OH)_{2\,(s)} + Cd(OH)_{2\,(s)}$$

ADVANTAGES OF Ni-Cd BATTERY

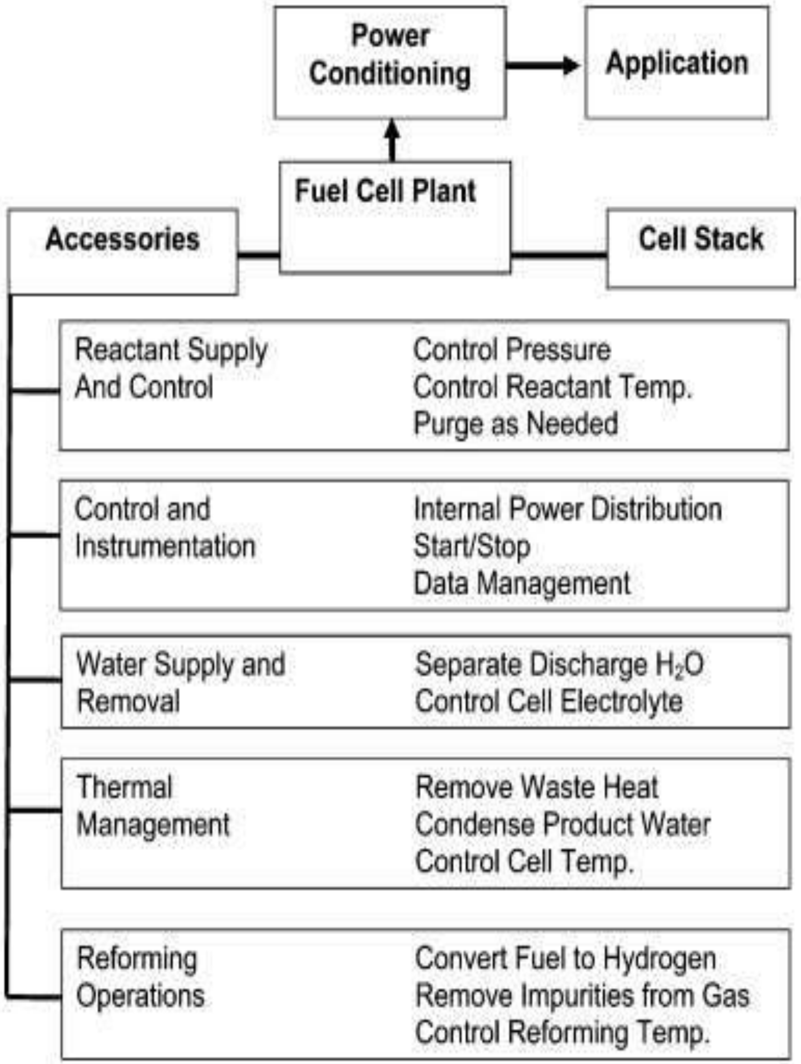
- The **potential** of **Cd anode** is **below the hydrogen electrode**.
- Therefore the cadmium battery is completely **inert** to the **electrolyte**.
- These batteries are **suitable** to **very high rate discharge** and **low temperature**.
- They have **long shelf life** without any **maintenance**.
- It requires almost **no current to keep charged**, and consequently the **water consumption** and **float charge current** are extremely **low**.

APPLICATIONS OF Ni-Cd BATTERY

They are used for aircraft and diesel engine starting, train flights, emergency power supply and many military applications.

FUEL CELLS

- Fuel cells are galvanic cells in which chemical energy of fuels is directly converted into electrical energy
- Fuel cells convert about 75 % of the available chemical energy into electrical energy.
- In fuel cell hydrogen is “burned” by mixing with oxygen in such a way that it creates a voltage across two electrodes.
- Only water and heat is produced as a by-product
- Hydrogen can be fed in directly or as part of larger molecules such as methane (natural gas).



Power Conditioning → Application

Fuel Cell Plant

Accessories

Cell Stack

Reactant Supply And Control	Control Pressure Control Reactant Temp. Purge as Needed
Control and Instrumentation	Internal Power Distribution Start/Stop Data Management
Water Supply and Removal	Separate Discharge H_2O Control Cell Electrolyte
Thermal Management	Remove Waste Heat Condense Product Water Control Cell Temp.
Reforming Operations	Convert Fuel to Hydrogen Remove Impurities from Gas Control Reforming Temp.

Figure 22. Block diagram of the component parts of a functioning fuel cell.

anode: $H_2 - 2e^- = 2H^+$ (19)

cathode: $O_2 + 2H^+ + 2e^- = H_2O_2$ (20)

$H_2O_2 + 2H^+ + 2e^- = 2H_2O$ (21)

overall: $O_2 + 4H^+ + 4e^- = 2H_2O$ (22)

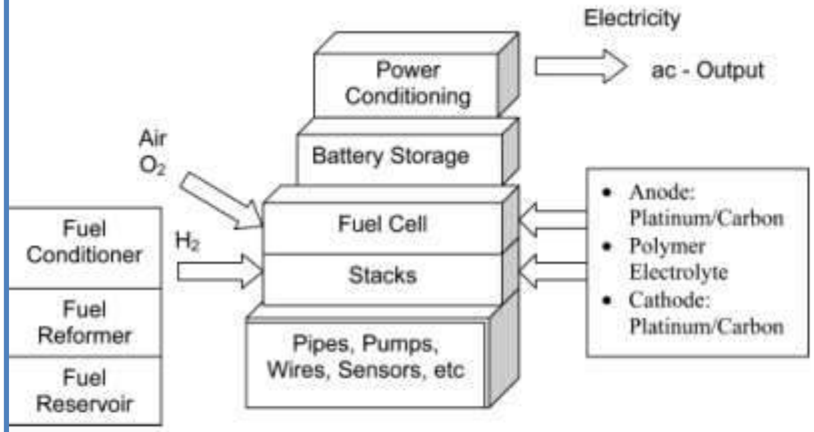


Figure 23. Depiction of the components of a complete fuel cell system including the re-former and power conditioning unit.

advantages	disadvantages
efficient energy conversion	complex to operate
modular construction	best as primary energy source
nonpolluting	impurities in gas stream shorten life
low maintenance	pulse demands shorten cell life
silent	expensive
safe	limited availability
high energy density	low durability
	low power density per volume

BASIC PRINCIPLE OF FUEL CELLS

- The **basic principle** of a **fuel cell** are **identical** to those of the well known **electrochemical cell (galvanic cell)**.
- Like any other electrochemical cell the fuel cell has **two electrodes** and an **electrolyte**.
- The **fuel** and the **oxidizing agents** are **continuously** and **separately** supplied to the **two electrodes** of the cell, at which they undergo reaction.
- The fuel cells are capable of supplying the current **as long as they supplied with the reactants**.
- A fuel consists of the following arrangement:
- **Fuel/electrode/electrolyte/electrode/oxidant**

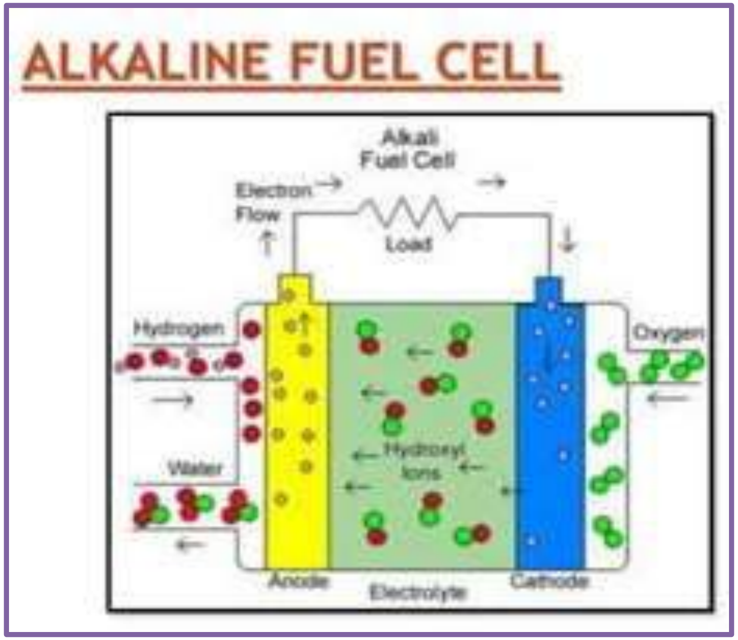
ADVANTAGES OF FUEL CELLS:

- **Theoretically** the **efficiency** can be **100%**.
- But actually it is about **50-80%**, owing to **over potential** and **resistance** of the cell.
- They have **high efficiency**
- Their **noise level** is very **low**
- They are **free** from **vibration**, **heat transfer** and **thermal pollution**.
- They are **modular** and hence they can be built in a wide range of **power requirements**.
- **No need** of **charging**.

COMPONENTS OF FUEL CELLS

- **Electrode**
  - – Anode and Cathode
- **Electrolyte**
  - – proton exchange membrane.
  - - Specially treated material, only conducts positively charged ions.
  - - Membrane blocks electrons.
- **Catalyst**
  - – facilitates chemical reactions,
  - - Usually Pt powder very thinly coated onto carbon paper or cloth.
  - - Maximizes surface area

HYDROGEN -OXYGEN FUEL CELL



- Introduced in early 1960's.
- **Electrolyte**:

  Alkaline KOH – expensive electricity generation
- Common type of fuel cell is based on the combustion of hydrogen to form water.

$$\begin{array}{lcll} 2H_{2(g)} & + & O_{2(g)} & \longrightarrow & 2H_2O_{(l)} \\ \text{Fuel} & & \text{Oxidant} & & \text{Water} \end{array}$$

- Compressed **hydrogen** and **oxygen fuel** (Continuously fed into the cell).
- Under a pressure of about **50 atmosphere**.
- **Electrodes**: porous **graphite impregnated** with a **catalyst** (**Pt, Ag or a metal oxide**). Inner sides of the graphite electrodes are in contact with an aqueous solution of **KOH or NaOH**.
- **Gases diffuse** onto the **electrode pores** and so does the electrolyte solution.
- **EMF = 1 V, 70 % efficiency**
- **150 – 200 °C** operating temperature.

H_2-O_2 FUEL CELL CHEMICAL REACTIONS

At Anode: Oxidation half cell reaction

- **Hydrogen is oxidized to H+ ions** which are **neutralized by the OH- ions** of the electrolyte:

$$H_2 \longrightarrow 2H^+ + 2e^-$$

$$2H^+ + 2OH^- \longrightarrow 2H_2O$$

- The net **oxidation half-cell reaction** is

$$2H^+ + 2OH^- \longrightarrow 2H_2O + 2e^-$$

At Cathode: Reduction half cell reaction

- **Reduction** of **oxygen** to **OH-** ions:

$$O_2 + 2H_2O + 2e^- \longrightarrow 4OH^-$$

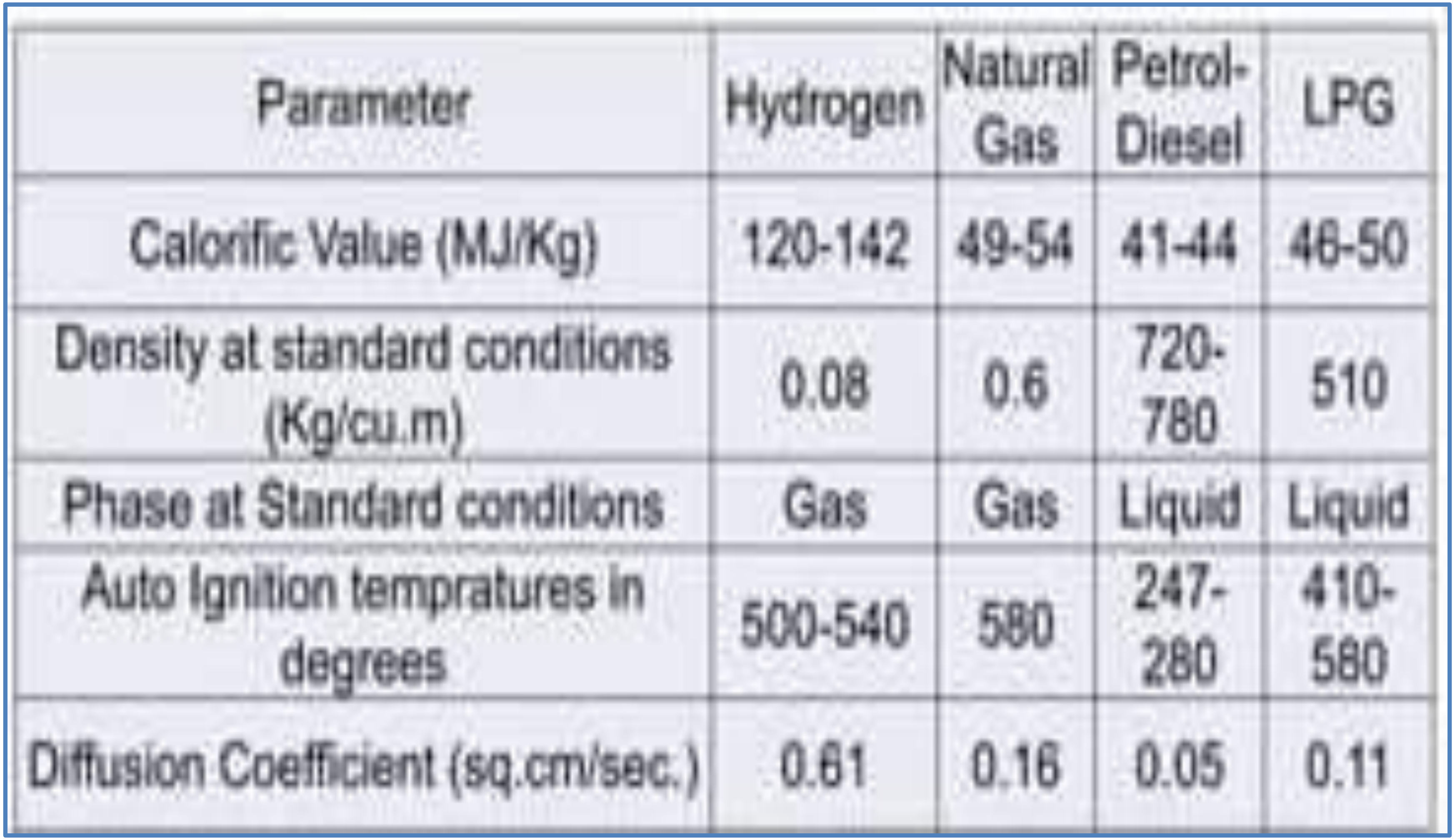
- The overall fuel cell reaction is

$$2H_{2(g)} + 2O_{2(g)} \longrightarrow 2H_2O$$

- EMF = 1 V.
- The water produced vaporizes off since the cell is operated at temperature above 100 ºC. this can be condensed and used.

Note: In place of KOH or NaOH, **phosphoric acid can** be also be used as an **electrolyte**. Operated at **200 ºC**, at this temperature H_3PO_4 polymerizes to **pyrophosphoric** acid which has considerably **higher ionic conductivity** than the parent acid. **Pt-Co-Cr alloy** is used as the **catalyst**.

COMPARISON OF HYDROGEN WITH OTHER FUELS



Parameter	Hydrogen	Natural Gas	Petrol-Diesel	LPG
Calorific Value (MJ/Kg)	120-142	49-54	41-44	46-50
Density at standard conditions (Kg/cu.m)	0.08	0.6	720-780	510
Phase at Standard conditions	Gas	Gas	Liquid	Liquid
Auto Ignition tempratures in degrees	500-540	580	247-280	410-580
Diffusion Coefficient (sq.cm/sec.)	0.61	0.16	0.05	0.11

H_2 AND O_2 FUEL CELL

Advantages

- **Clean and environmentally benign fuel. Water** is the only **discharge.**
- **Higher efficiency** than **conventional engines**.
- Hydrogen can substitute petrol and diesel and **reduce** our **dependence** on **imports** of **fossil fuels**.
- Hydrogen is used as a fuel in aeronautical industry (Rockets).
- **Zero emission**.
- **Negligible noise pollution**.
- They are very **light**, individual cells can be **stacked** and connected in **series** to **generate higher voltage**.
- About 75 % of chemical energy can be converted into electrical energy.

Disadvantages

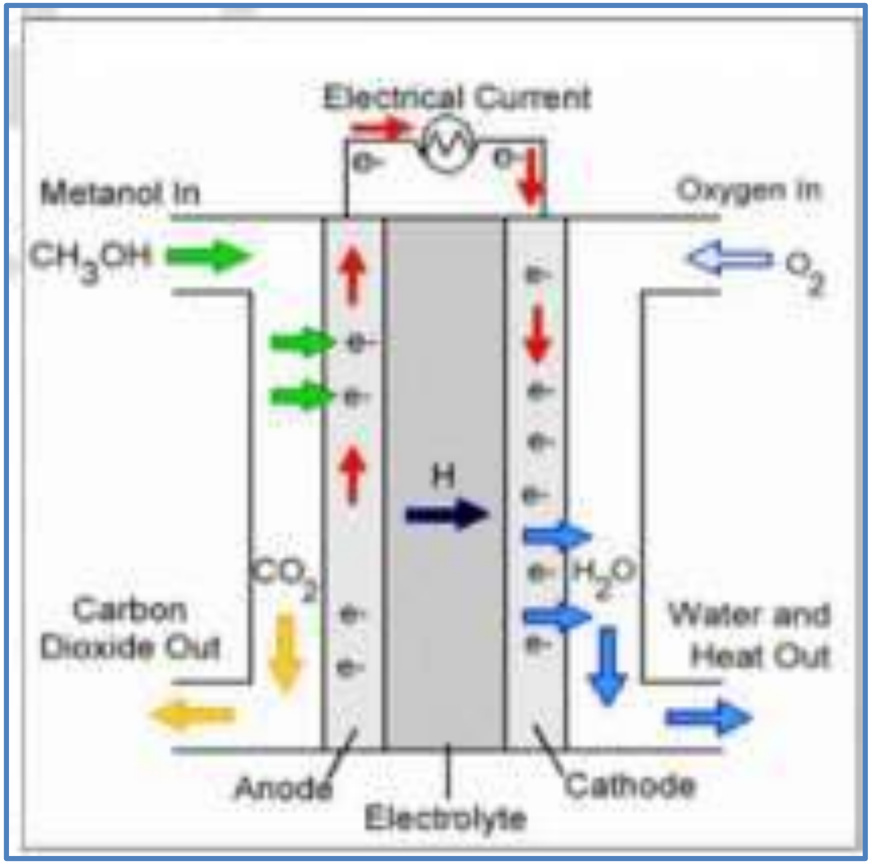
- **CO_2** discharged with methanol reform.
- Little more efficient than alternatives.
- **Technology currently expensive**. Many design issues still in progress.
- Hydrogen often created using "dirty" energy (e.g., coal)
- **Pure hydrogen is difficult to handle**.
- Main disvantage would be the elimination of hazardous air pollutants such as CO, NOx, SO_2 etc. which are inherently associated with the internal combust engine.

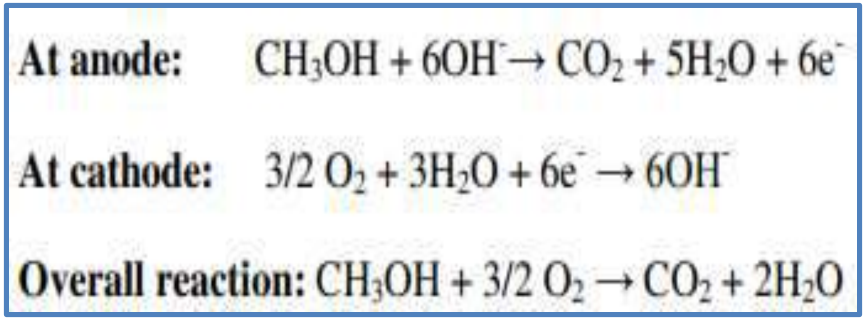
HYDROCARBON – OXYGEN FUEL CELLS

- Fuel cells based on the combustion of **hydrocarbons** such as **CH_4, C_2H_6, C_3H_8** etc., in the presence of catalyst have also been operated.
- **Catalyst**: **Platinum** this makes the fuel cell operation **highly expensive**.

METHYL ALCOHOL- OXYGEN (ALKALINE FUEL CELL):

- In this fuel cell, **CH_3OH** is used as a **fuel** and **O_2 as oxidant** to generate electrical energy.
- The **methyl alcohol–oxygen** fuel cell has two electrodes.
- The **anode** consists of **porous nickel electrode impregnated with Pt/Pd catalyst**.
- **Porous nickel electrode coated with silver catalyst** constitutes a **cathode** of the cell.
- The **electrolyte**, **KOH**, is taken in between the two electrodes.
- **CH_3OH** and **O_2** are sent continuously into their respective electrodes as shown in Fig. and the electrical energy is produced with the continuous replenishment of the fuel, CH_3OH at the anode.





At anode: $CH_3OH + 6OH^- \rightarrow CO_2 + 5H_2O + 6e^-$

At cathode: $3/2\ O_2 + 3H_2O + 6e^- \rightarrow 6OH^-$

Overall reaction: $CH_3OH + 3/2\ O_2 \rightarrow CO_2 + 2H_2O$

ADVANTAGES OF METHYL ALCOHOL-OXYGEN FUEL CELL:

1. **Methanol fuel cells** are reasonably stable at all environmental conditions.
2. Easy to transport .
3. **Do not require complex steam reforming operation**.
4. These fuel cells are targeted to **portable applications**.
5. Because of high hydrogen concentration in methanol. it is an excellent fuel.
6. **Methanol poses less risk to aquatic plants, animals and human beings than gasoline**.
7. Because methanol possess **lower inflammability** limit than gasoline it poses less fire risk than gasoline.
8. There is **zero emission** by the cells hence the **fuel cells are eco friendly**.

APPLICATION OF ALCOHOL-OXYGEN FUEL CELL:

The major application of methyl alcohol oxygen fuel cells is a fuel for fuel cell motor vehicles like NECAR-5 in Japan, USA etc.

HYDROCARBON – OXYGEN FUEL CELLS – PROPYL GAS AS HC

Oxidation half-cell reactions

$C_3H_8 + 6H_2O \longrightarrow 3CO_2 + 2OH^- + 20e^-$

$[H^+ + OH^- \longrightarrow H_2O] \times 20$

The net oxidation half-cell reaction is

$C_3H_8 + 20(OH^-) \longrightarrow 3CO_2 + 14H_2O + 20e^-$

Reduction half-cell reactions

$O_2 + 2H_2O + 4e^- \longrightarrow 4(OH^-)] \times 5$

- Overall fuel cells reaction

$C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$

FUEL CELLS – APPLICATIONS

- They are used as auxiliary energy sources in **space vehicles**, **submarines** or other **military vehicles**.
- H_2 and O_2 fuel cells in **manned space flights**. (Electrolyte used in these cells is an **ion-exchange material**). (Solid oxide fuel cells electrolyte – Yttrium stabilized zirconia)
- They have very **high efficiency** than the **internal combustion engine**.
- For **space craft**, they are preferred due to their **lightness** and product **water** is a valuable source of **fresh water for astronauts**.
- Can be used as **power sources** in **remote areas**.
- Can be used to **produce off-grid power** supplies.
- Can be applicable in both **hybrid** and **electric vehicles**.
- **Waste water treatment plant** and **landfill**. Etc..,

CONCLUSION

To meet energy demands and for the sustainable development.

- **Battery** characteristic property should have the following key points or **basic requirements**
- High energy density
- Should have Long shelf life
- No ecological problems
- Low cost
- Easy portability
- Should be compact and light weight.
- Should provide economically priced continuous electric supply.
- Should be capable of recharging.

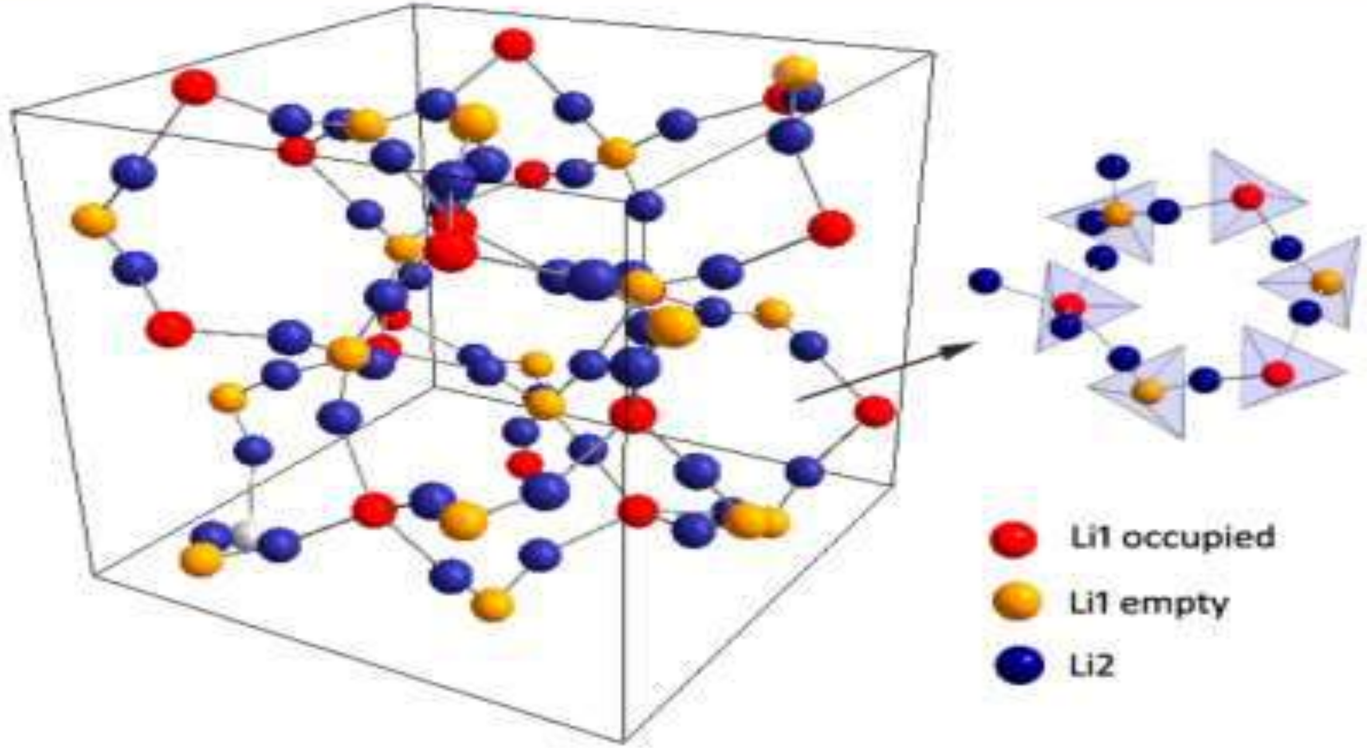


Figure 8. 3D connection of Li sites within the interstitial space of the garnet framework with 7.5 Li per formula unit. Loop structure and the separations of Li atoms are also displayed.

ICT enabled tools for effective teaching and learnng process

Sl. No	Name of Faculty	Programme Name	Youtube Channel
1	Dr. V. D. Naganuri	BA/BSC	https://youtube.com/channel/UCog2hHUgxZtyIMVHqAtsaQg
2	Shri. P. B. Burji	BSC	https://youtube.com/channel/UCsW2UCRJRAg_3Ti2yTLFHig
3	Shri. M. R. Patil	BSC	https://youtube.com/channel/UC8hEWFPI2OCUIqnMngcznQA
4	Shri. B. G. Patil	BA/BSC	https://youtube.com/channel/UCgPcdabitWx0yzgcqgxLIDg
5	Dr. D. S. Kamble	BA	https://youtube.com/channel/UCpl2bNarPPN_nmXf17l_EGQ
6	Shri. D. T. Sogalad	BA/BSC	https://youtube.com/channel/UCzJgaVn5ha91T8VgJ8N8M2w
7	Dr. H. Krishna	B.Sc	https://classroom.google.com/c/MTcwMjg0NDIwNzUw?cjc=3p3tmvz
8	Shri. M. L. Mang	BA	https://youtube.com/user/mangmaruti
9	Shri. Sunilkumar	BSC	https://youtube.com/channel/UCCN1NutD2udwVuPdVW1NJzg
10	Shri. K. B. Marathe	BA/BSC	https://youtube.com/channel/UC7rDMs8d9sPcbXXgDufSP2A
11	Dr. V. A. Edalli	BSC	https://youtube.com/channel/UCXWQeERIqNIDE3_BuM5shHQ
12	Shri N.R.Badiger	BA	https://youtube.com/channel/UCZq-FkR16PL3FQVhbgDvdQA
13	Miss. Laxmi Mudagal	BSC	https://youtube.com/channel/UC8ztP8DsugsRzoq-U4MYBUQ
14	Shri.L.D.Padmannavar	BSC	https://youtube.com/channel/UC61qGa-Ozey3YVaaH8z-CgQ
15	Miss. Shama Nadaf	BSC	https://youtube.com/channel/UCmpMAuxuygUy1gMMAiqbsCw
16	Miss. Megharani Patil	BSC	https://youtu.be/XIUg3hoV4z0
17	Miss. M. N. Waghi	BSC	https://youtube.com/channel/UCzcQPueDf-oX_9d-m7jByDA

PRINCIPAL
S. S. Arts College & T.P. Science Institute
SANKESHWAR

Acids and Bases

B.Sc VI semester - NEP

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Content – Acids and Bases topic

- Arrhenius concepts of acids and bases
- Bronsted-Lowry concepts of acids and bases
- Lux-Flood concepts of acids and bases
- Solvent system
- Lewis concepts of acids and bases
- Hard and Soft acids and bases (HSAB)
- Classification of acids and bases as hard and soft,
- Pearson’s HSAB concept

Textbooks for reference

- NCERT PUC textbooks
- IIT-JEE main Chemistry, Arihanth publishers
- **Inorganic Chemistry** 3rd Edition (Donald A. Tarr, Gary Miessler)
- **Principles of Inorganic Chemistry**, by B. R. Puri and L. R. Sharma & K. C. Kalia
- **Shriver and Atkins' Inorganic Chemistry**, 5th Edition, Peter Atkins, Tina Overton, Jonathan Rourke, Mark Weller, Fraser Armstrong

Some of the common examples of acid-base reactions

- For instance, production of acid rain begins with a very simple reaction between sulfur dioxide and water:

$$2SO_2(g) + H_2O(l) \rightarrow HOSO_2^-(aq) + H^+(aq)$$

- Saponification is the process used in soapmaking:

$$NaOH(aq) + RCOOR'(aq) \rightarrow RCO_2Na(aq) + R'OH(aq)$$

This too is a type of acid–base reaction.

Early concepts of acids and bases

Characteristic properties are

1. **Taste** –

Sour taste for acid

Bitter taste for base

2. Color change of the pigments

For acids – litmus turns to **red**

For bases – litmus turns to **blue**

3. Neutralization reaction

Reaction between acids and bases results in the formation of salts

4. Displacement of hydrogen gas

When acid reacts with compounds containing hydrogen, in which the hydrogen can be replaced by a metal

Arrhenius concept of acids and bases

- **1880-1890**
- Acid-base chemistry was first satisfactorily explained in molecular terms after **Ostwald** and **Arrhenius** established the existence of ions in aqueous solution.
- After much controversy and professional difficulties, Arrhenius received the **1903 Nobel Prize in Chemistry** for this theory

Arrhenius – a narrow definition of acids and bases

- An **acid** is a substance that when dissolved in water increases the concentration of hydrogen ions (H^+)
- A **base** is a substance that increases the hydroxide (OH^-) concentration.

In an aqueous solution, acids ionizes/behaves as

$$HCl(g) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq) \qquad (9.1)$$

$$HNO_3(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq) \qquad (9.2)$$

Arrhenius acid-base reaction can be written as

acid + base ⟶ salt + water

For example

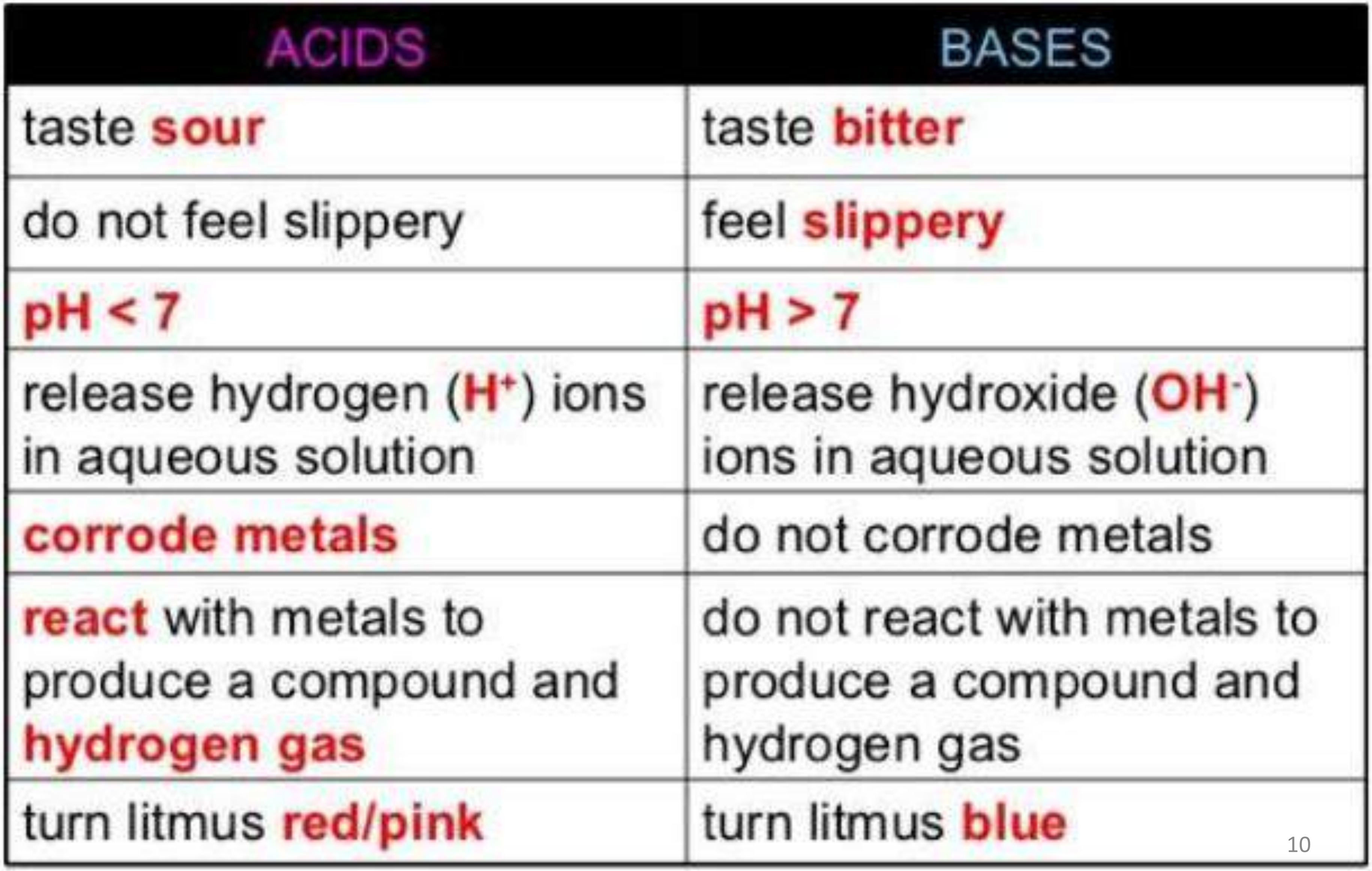
hydrochloric acid + sodium hydroxide ⟶ sodium chloride + water

$$H^+ + Cl^- + Na^+ + OH^- \longrightarrow Na^+ + Cl^- + H_2O$$

Limitation of Arrhenius theory

- The concept is limited to aqueous solutions only
- This theory fails for gas phase reactions
- This theory fails for solid phase reactions
- It can not explain the acidic character of certain salts like $AlCl_3$, BF_3 and basic character of NH_3, PH_3.
- It cannot be applied to compounds which do not contain free H^+ and OH^- ions i.e., in non-aqueous solvent conditions.

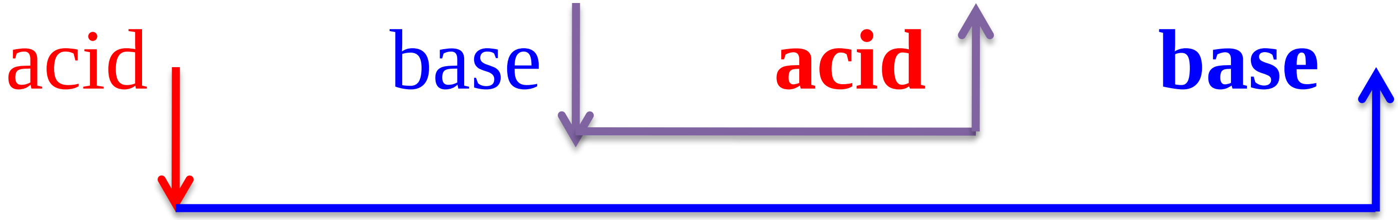
Properties of Acids and Bases



ACIDS	BASES
taste **sour**	taste **bitter**
do not feel slippery	feel **slippery**
pH < 7	**pH > 7**
release hydrogen (**H^+**) ions in aqueous solution	release hydroxide (**OH^-**) ions in aqueous solution
corrode metals	do not corrode metals
react with metals to produce a compound and **hydrogen gas**	do not react with metals to produce a compound and hydrogen gas
turn litmus **red/pink**	turn litmus **blue**

Bronsted (Denmark)-**Lowry** (London) **concept - 1923**

- A Bronsted – Lowry acid
  - a substance that can donate a hydrogen ion
  - Or tendency to lose a hydrogen ion (H^+)
- A Bronsted-Lowry base
  - a substance that can accept a hydrogen ion
  - Or tendency to gain a hydrogen ion (H^+)
- Examples
- $CH_3COOH_{(aq)} + H_2O_{(l)} \leftrightarrow H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$



acid base **acid** **base**

The usefulness of the Bronsted-Lowry definition lies in its ability to handle any protonic solvent such as liquid ammonia or sulphuric acid.

In addition, other proton-transfer reactions that would not normally be called neutralization reactions but which are obviously acid-base in character may be treated as readily

Reactions such as the above proceed in the direction of forming weaker species.
The stronger acid and the stronger base of each conjugate pair react to form the weaker acid and base.

Chemical species that differ from each other only to the extent of the transferred proton are termed conjugates (connected by brackets)

Example 2

$$\underset{\text{acid 1}}{H_3O^+} + \underset{\text{base 2}}{NO_2^-} \longrightarrow \underset{\text{base 1}}{H_2O} + \underset{\text{acid 2}}{HNO_2}$$

- This definition Bronsted-Lowry theory expanded the Arrhenius list of acids and bases to include the gases HC1 and NH_3, along with many other compounds.

- This definition also introduced the concept of **conjugate acids and bases,** differing only in the presence or absence of a proton,

- It described all reactions as occurring between a stronger acid and base to form a weaker acid and base.

Conjugate acid-base pairs:

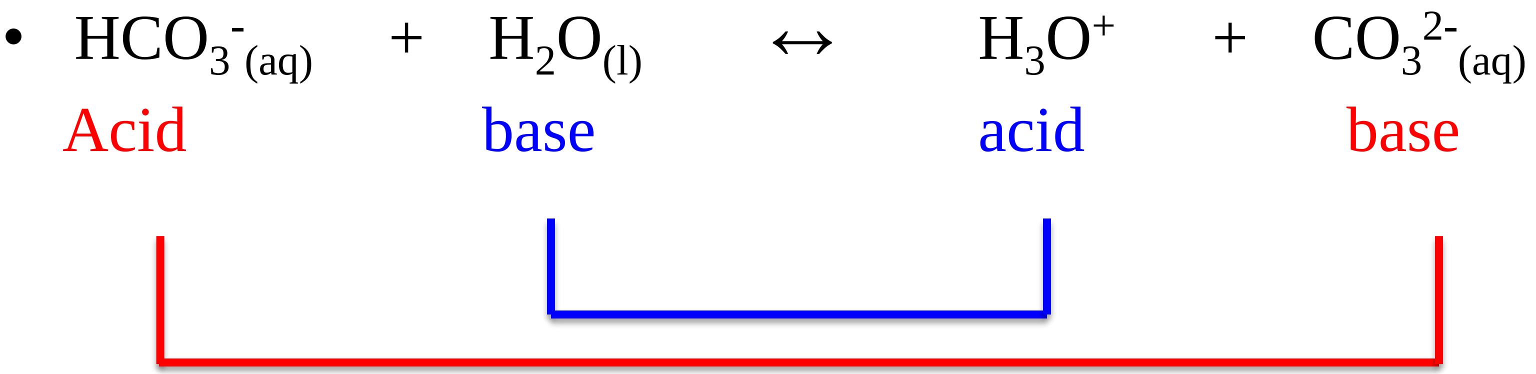
Acid	Base
H_3O^+	H_2O
HNO_2	NO_2^-

Conjugate acid-base pairs

- The conjugate base of an acid is the base that is formed when the acid has donated a hydrogen ion.

- The conjugate acid of a base is the acid that forms when base accepts a hydrogen ion.

- CH_3COOH and CH_3COO^- are a pair
- H_2O and H_3O^+ are a pair.



- $HCO_3^-{}_{(aq)} + H_2O_{(l)} \leftrightarrow H_3O^+ + CO_3^{2-}{}_{(aq)}$

  Acid base acid base

Amphoteric – molecules that can function either as acids or bases depending on the reaction conditions.

Example: H_2O

Case I: Water behaving as acid

Case II: Water behaving as base

Limitations of Bronsted-Lowry concept

- The protonic definition cannot be used to explain the reactions occurring in the non-protonic solvents such as $COCl_2$, SO_2, N_2O_4 etc.

- This concept cannot explain the reaction between some acidic oxides (such as CO_2, SO_2, SO_3) and basic oxides (such as CaO, BaO, MgO) which take place even in the absence of the solvent, e.g.,

- $AlCl_3$, BF_3 etc., do not have any hydrogen, and hence, cannot give a proton but are known to behave as acids

Summary of Bronsted-Lowry concept

- Proton donor = acid
- Proton acceptor = base
- Conjugate acid base pairs
- It has been observed that acid-base reactions proceed in a direction to form the weak acid and weak base and
- Hence in these reactions a strong acid reacts with a strong base to form weak acid and weak base.

Lux-Flood concept of acid - base theory

- Definition proposed by Lux - German chemist Hermann **Lux** in 1939
- Flood further improved/extended by Håkon **Flood** circa (Norwegian chemist) professor of Inorganic Chemistry at the Norwegian Institute of Technology in Trondheim, Norway 1947

- Revival of oxygen **theory** of **acids** and **bases**
- **Acid is a substance which accepts the oxide ion.**
- **Base is a substance which donates the oxide ion.**

- Acid – oxide ion acceptor

  Examples – SiO_2, CO_2, P_4O_{10}, etc
- Base – oxide ion donor

  Examples – CaO, BaO, PbO, etc

- The concept was advanced to treat non-protonic systems which were not amenable to the Bronsted-Lowry definition
- This concept is used to explain reactions which takes place at high temperatures.
- For example, in high-temperature inorganic melts, reactions such as the following taking place:

Base	**Acid**	**Salt**
CaO +	SiO_2 $\longrightarrow$	$CaSiO_3$
PbO +	SO_3 $\longrightarrow$	$PbSO_4$
BaO +	CO_2 $\longrightarrow$	$BaCO_3$
$6Na_2O$ +	P_4O_{10} $\longrightarrow$	$4Na_3PO_4$
TiO_2 +	$Na_2S_2O_7$ $\longrightarrow$	$TiOSO_4 + Na_2SO_4$

This approach emphasizes the acid- and basic-anhydride aspects of acid-base chemistry.

The Lux-Flood base is a **basic anhydride**

$$Ca^{2+} + O^{2-} + H_2O \longrightarrow Ca^{2+} + 2OH^-$$

And the **Lux-Flood acid** is an **acid anhydride**

$$SiO_2 + H_2O \longrightarrow H_2SiO_3$$

This reaction is very slow and is of more importance in the reverse, dehydration reaction

The characterization of these metal and nonmetal oxides as acids and bases is of help in rationalizing the working
for instance of a basic Bessemer convertor in steelmaking

Limitations

- This concept only has limited scope
- The usefulness of this system is limited to systems such as molten oxides.

Amphoteric oxides

Amphoteric are those which have tendency to loose and gain an oxide ion

Example 1. $$ZnO \xrightleftharpoons{+\ O^{2-}} ZnO_2^{2-}$$

Amphoteric

$$ZnO \xrightleftharpoons{-\ O^{2-}} Zn^{2+} + O^{2-}$$

Example 2. $$Al_2O_3 \xrightleftharpoons{+\ O^{2-}} 2AlO_2-$$

Amphoteric

$$Al_2O_3 \xrightleftharpoons{-\ 3\ O^{2-}} 2Al^{3+} + 3\ O^{2-}$$

Summary of Lux-Flood concept of acid - base theory

- Acid – oxide ion acceptor
- Base – oxide ion donor

- **Merits**
- Non-protonic systems where Bronsted-Lowry concept or Arrhenius concepts failed
- Successfully explained for the inorganics of molten conditions reactions involving at very high temperatures
- Explained to some extent of acid and base anhydrides properties in few reactions

- **Demerits**
- System applied to only oxide ion reaction conditions.

Solvent system (or autoionization) concept of acid-base theory

The **concept was introduced** by Franklin in **1905** and was extended by Cady- Esley in **1928**.

Edward Curtis **Franklin** - American experimentalist chemists - studied the **acid–base** reactions in liquid ammonia in 1905 and pointed out the similarities to the water-based Arrhenius theory

The **definition** of acids and bases **given** by this **concept** can be applied for **protonic** as well as for **non-protonic solvents**.

The solvent system applies to any solvent that can dissociate into a cation and an anion (**autodissociation**)

Solvent system acid	**Solvent system base**
Cation resulting from auto-dissociation of the solvent	Anions resulting from auto-dissociation of the solvent
Species that increases the concentration of the cation characteristics of that solvent	Species that increases the concentration of the anion characteristics of that solvent

The solvent system acid base concept generalizes the Arrhenius acid base concept by focusing on cation and anion generation in solution.

The Brønsted-Lowry concept seeks to generalize Arrhenius acidity in ways that allow all hydrogen ion transfers

The solvent system definition also allows for autoionizations which involve the transfer of an ion other than hydrogen

- Autoionization of water and autoionization of liquid ammonia, are represented as

Thus, in water, substances giving H_3O^+ ions are acids and those giving OH^- ions are bases

Thus, in ammonia, substances giving NH_4^+ ions acts as acids and those giving NH_2^- act as bases.

Another example: ammonium chloride and potassium amide in liquid ammonia behaving as acid and base respectively

- The acid-base neutralization reaction of NH_4Cl and KNH_2 in liquid NH_3 is analogous to that of HCl and NaOH in water

The solvent system approach can also be used with solvents that do not contain hydrogen.

Consider the autoionization of liquid nitrogen tetraoxide **(non-aqueous solvents)**

Nitrosyl ions (NO^+) behave as acids

Nitrate ions (NO_3^-) behave as bases

For example,

BrF_3 (**non-aqueous solvents**) also undergoes autodissociation

Advantages of solvent system concept:

- 1. The definition of acids and bases given by solvent system concept can be used for both protonic (e.g. H_2O, NH_3 etc.) as well as non-protonic (e.g. SO_2, $SOCl_2$ etc.) solvents.

- 2. The definition is applicable for aqueous (H_2O) as well as non-aqueous solvents (NH_3, HF, H_2SO_4 etc).

Limitations of solvent system concept

- Mainly focussed on ionic reaction and chemical properties of solvent. Ignores physical properties of solvent.
- Only applies when ionic species formed in solution is confirmed.
- Could not be applicable for solvents which are not conducive toward ion formation
- In the absence of solvent, it cannot explain the acid base phenomenon
- It can not explain the neutralization reactions occurring without the presence of ions.
- The concept can’t account for the acid-base reaction occurring in non- ionizing solvents like C_6H_6, $CHCl_3$ etc.

Lewis Acid and Base – more general definition

- Applies to reactions that don’t involve a hydrogen ion.
- Lewis base –
  - species that donates lone-pair electrons
- Lewis acid –
  - species that accepts such electrons

Lewis concept (electron donor-acceptor concept)

Acid	**+**	**: Base**	→	**[Acid Base]**
Lewis acid		Lewis base		Adduct
Electrophile		Nucleophile		
Electron deficient		Electron rich		

Lewis acids	**Examples**
Positively charged ions	H^+, RCO^+, ..
Metal cations	Co^{3+}, Fe^{3+}, …
Molecules	CO_2, BF_3, SO_2,
Lewis bases	**Examples**
Negatively charged ions	OH^-, F^-, NH_2^-
Electron rich	NH_3, H_2O

Neutralization reaction

According to Lewis concept, the formation of co-ordinate covalent bond between an acid and the donor atom of base is called neutralization

Types of Lewis acids

1. Incomplete octet atoms/elements/molecules
2. Molecules containing a central atom with vacant d-orbitals
3. Simple cations
4. Molecules having a multiple bond between atoms of dissimilar electronegativity
5. Elements with an electron sextet

Types of Lewis acids

- Molecules containing a central atom with incomplete octet, e.g., $AlCl_3$, BF_3, $GaCl_3$, $MgCl_2$, $BeCl_2$, etc.

- Molecules containing a central atom with vacant d-orbitals, e.g.,

  PF_3, PF_5, SF_4, SeF_4, $TeCl_4$, GeX_4, $SnCl_4$ etc.

- All simple cations like Na^+, Cu^{2+}, Ag^+, Al^{3+}, Fe^{3+}, Ca^{2+}, H^+, etc. However, Na^+, K^+, Ca^{2+}, etc., have very little tendency to accept electrons.

Lewis acid strength or co-ordinating ability increases with

a. Increase in positive charge of cation
b. Increases in nuclear charge for atoms in any period
c. Decrease in ionic radius
d. Decrease in number of shielding electron shells.

Evidently the acid strength of cations increases for the elements on moving from left to right in a period and from bottom to top in a group

$Fe^{2+} < Fe^{3+}$ "+ve charge ↑ from 2 to 3"
$K^{+} < Na^{+}$ from bottom to top
$Li^{+} < Be^{2+}$ from left to right

------ strength of Lewis acid increasing →

- Molecules with multiple bonds between dissimilar atoms, e.g., O=C=O, O=S=O, SO_3 etc.
  - Here O-atom is more electronegative than C or S as a result the electron density of π-electrons is displaced away from carbon or sulphur atoms
  - As a result the carbon or sulphur becomes electron deficient hence acts as electrophile.

Lewis acid

Lewis base

Bicarbonate ion

Bisulphate ion

- Elements with an electron sextet, e.g., O, S, etc.

Type of Lewis bases

- All simple anions like Cl^-, F^-, OH^-, CN^-, etc.

- Molecules with one or two unshared (lone) pairs,
- e.g.,

  pyridine, etc.

- Multiple bonded compounds which form co-ordination compounds with transition metals,

  e.g., CO, NO, ethylene, acetylene etc.

Limitations of Lewis concept

- The strength of Lewis acids and bases is found to depend on the type of reaction, it is not possible to arrange them in any order of their relative strength. Example:
  - F^- complex with Be^{2+} is more stable than Cu^{2+} because Be^{2+} is more acidic than Cu^{2+}
  - But amine complex with Cu^{2+} is more stable than Be^{2+} indicating that Cu^{2+} is more acidic than Be^{2+}
- It does not explain the behaviour of protonic acids such as HNO_3, HCl, H_2SO_4 etc.

- Catalytic activity of Lewis acid can’t be explained because the catalytic activity of many acids is due to their tendency to furnish H^+. Lewis acid does not do so.
- Lewis acids and Lewis base reactions are slow
- The Lewis concept includes all reactants which can form coordination bonds. Even metals in their zero oxidation (e.g., Fe, Ni, Co, Mn) are termed as Lewis acids in their complexes with pi acceptor ligands such as CO, cyclopentadiene and olefins

Table 18.1 Some Common Acids and Bases and Their Household Uses

Substance	Use
Acids	
Acetic acid, CH_3COOH	Flavoring, preservative
Citric acid, $H_3C_6H_5O_7$	Flavoring
Phosphoric acid, H_3PO_4	Rust remover
Boric acid, H_3BO_3	Mild antiseptic, insecticide
Aluminum salts, $NaAl(SO_4)_2 \cdot 12H_2O$	In baking powder, with sodium hydrogen carbonate
Hydrochloric acid (muriatic acid), HCl	Brick and ceramic tile cleaner
Bases	
Sodium hydroxide (lye), $NaOH$	Oven and drain cleaners
Ammonia, NH_3	Household cleaner
Sodium carbonate, Na_2CO_3	Water softener, grease remover
Sodium hydrogen carbonate, $NaHCO_3$	Fire extinguisher, rising agent in cake mixes (baking soda), mild antacid
Sodium phosphate, Na_3PO_4	Cleaner for surfaces before painting or wallpapering

ICT based teaching on the topic of Vermicompost.
by. Dr. Honnur Krishna, Placement cell chairman.

SANKESHWAR
591313

PRINCIPAL
S. S. Arts College & T.P. Science Institute
SANKESHWAR.

Sankeshwar, Karnataka, India
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Long 74.476558°
19/01/24 11:05 AM GMT +05:30

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Paper – II

Nuclear Chemistry

BSc VI semester – NEP

Unit – I
8 hours

Dr. Honnur Krishna
Assistant Professor
Department of Chemistry,
S. D. V. S. Sangh's, S. S. Arts College and T. P. Science Institute,
(*Affiliated to Rani Channamma University*)
Sankeshwar, Hukkeri Taluk,
Belagavi District – 591313, Karnataka,
India

Contents - Paper – II Unit – I – 8 hour

- **Nuclear Chemistry- 8 hr**
- Nuclear particles (positron, neutrino, mesons, pions, and quarks),
- Nuclear instability,
- Nuclear fission and
- Nuclear fusion,
- Nuclear reactors,
- Different types of nuclear reactors,

- Nuclear reactions
- (α, n), (n, α), (α, p), (p, α), (p, n) and (n, p).
- Applications of radioisotopes in tracer technique,
- Neutron activation analysis and
- Carbon dating.

LIST OF REFERENCES FOR NUCLEAR CHEMISTRY

- Inorganic chemistry – Puri Sharma,
- Radiation and Nuclear Chemistry – B. K. Sharma
- Radiochemistry and Nuclear Chemistry - Gregory Choppin, Jan-olov liljenzin, Jan Rydberg, Christian Ekber
- Nuclear and Radiochemistry : Fundamentals and Applications, Karl Heinrich Lieser
- Modern Nuclear Chemistry - Water Loveland
- Inorganic Chemistry, Madan Malik and G. D. Tuli
- NUCLEAR AND RADIOCHEMISTRY 3rd Edition, Gerhart Friedlander Joseph W. Kennedy Edward s. Macias Julian Malcolm Miller
- Some internet sources
- Review articles
- Vedanta
- Chemistry libre texts,

TERMINOLOGIES IN NUCLEAR CHEMISTRY

Structure of the atom

- **Bonding – Electrostatic force of attraction,**
- **Nuclides**, parent nuclides, daughter nuclides, subatomic particles
- Radiations – ionizing and non-ionizing radiations
- **Radioactivity** - unit of radioactivity

  The phenomenon of spontaneous emission of powerful penetrating radiations (which are not influenced by any external factors) from some heavy elements – natural **radioactivity** and such elements are called naturally occurring **radioactive** elements.
- **Unstable nucleus – N/P ratios**
  - The nuclei of radioactive substances are unstable due to an **unstable ratio of protons to neutrons.**
- **Nuclear forces –**
- **Nuclear particles - alpha, beta and gamma emissions**
  - **Nucleons - Fermions - Quarks, Hadrons, mesons, muons, kaons, baryons**
  - **Leptons – Bosons**
- **Nuclear particles properties-**

  Charge, Mass, Spin – Wavefunctions, Pauli principle,

- **Electron volt** – energy gained by an electron when it is accelerated through a potential difference of one volt.
- The electron volt is defined as the energy necessary to raise one electron through a potential difference of 1 V.
- Atomic mass unit (a.m.u), nuclear fuel
- Half-life
- Rate
- Decay constant
- Mass defect
- Binding energy
- Nuclear fission
- Nuclear fusion
- Nuclear Reactors - Characteristic features of nuclear reactors are **Reactor core , Nuclear fuel , Moderators, Coolants, Control rods, Reflector, Pressure vessel, Shielding**
- Moderators, coolants,
- Nuclear drop model
- C-14 dating
- Radio isotopes
- Isotones
- Isobars
- Particle accelerators
- NAA

APPLICATIONS OF RADIOISOTOPES

- ^{131}I is used in the diagnosis and treatment of thyroid disorders; in brain scanning.
- ^{32}P is used in
  - i. Bone metastasis to control the pain
  - ii. In agriculture and synthesis of nucleotides
  - iii. In studying blood circulation.
- ^{60}Co is used in treatment of brain tumours.
- ^{24}Na is used in detecting the location of pipeline leaks
- $^{99}Tc^{m}$: (metastable nuclear isomer of Tc) Brain, heart, lung, thyroid, gall bladder, skin, lymph, node, bone, liver, spleen, and kidney imaging.
- ^{11}C, ^{13}N, ^{15}O, ^{18}F are used in PET (Positron Emission Tomography) – metabolic activity of the cells of body tissues.
- ^{2}H, ^{13}C, ^{15}N, ^{18}O are used as tracers in chemical and biological reactions to find out the mechanisms and pathways.
- ^{35}S in heart diagnosis.

Nuclear science journey

Physicists

- **William Conrad Roentgen** in **1895**
- **Henri Becquerel**
- **Rutherford – gold foil experiments**
- **Marie curie**
- **Hideki Yukawa** - 1935 - Japanese theoretical physicist
- Nuclear forces – mesons theory

Indian

- Prof. Homi J. Baba
- Prof. Raja Ramanna

Nuclear chemistry has found essential uses and applications in a broad variety of applied disciplines

Why Nuclear chemistry?

- In addition to frontier research, nuclear chemistry has found essential uses and applications in a broad variety of applied disciplines, such as
- Nuclear medicine and isotope production,
- Radio-pharmaceutical preparation,
- Nuclear stockpile stewardship and security,
- Surveillance of clandestine nuclear activities,
- Nuclear power,
- Separation science,
- Nuclear waste processing and minimization,
- Waste isolation and remediation of nuclear-contaminated sites, and
- Prediction and monitoring of behavior of actinides in the environment, to name only a few.

Importance

- Nuclear science is crucial to **understanding** our **universe**, our **world**, and **ourselves** at the **atomic level**.
- Interactions of atoms, existence of atoms – Efficient materials & medicines development.

Nuclear waste contains radioactive material and requires safe disposal.

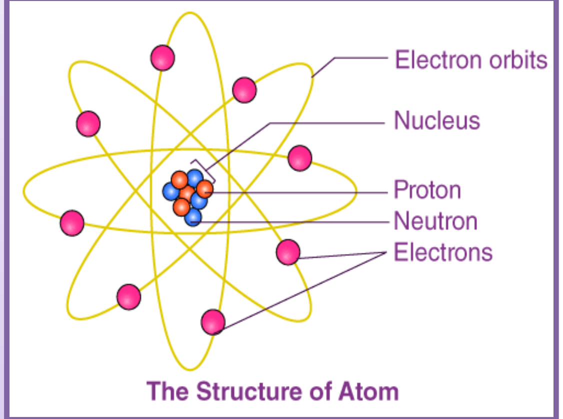
Source: https://pixabay.com/photos/nuclear-waste-radioactive-trash-1471361/

STRUCTURE OF THE ATOM

Composition of the atom

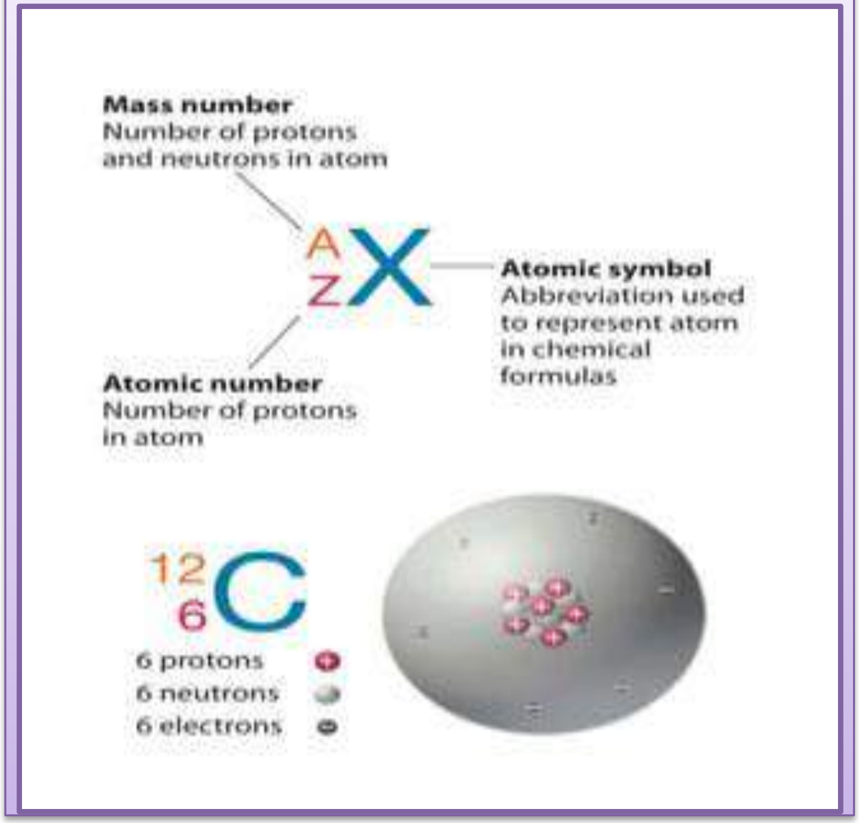
- Nucleus
- Proton
- Electron
- Positron
- Neutrino
- Fermions – quarks – hadrons
- Mesons

Nuclide OR Nucliede : Nucleus with known composition



The Structure of Atom

Structure of the C-atom



Standard model

PARTICLES

All the *matter* in the Universe, including atoms, stars, rocks, plants and animals is made of...

The particles *carrying* the forces between the matter are...

Fermions

2 TYPES

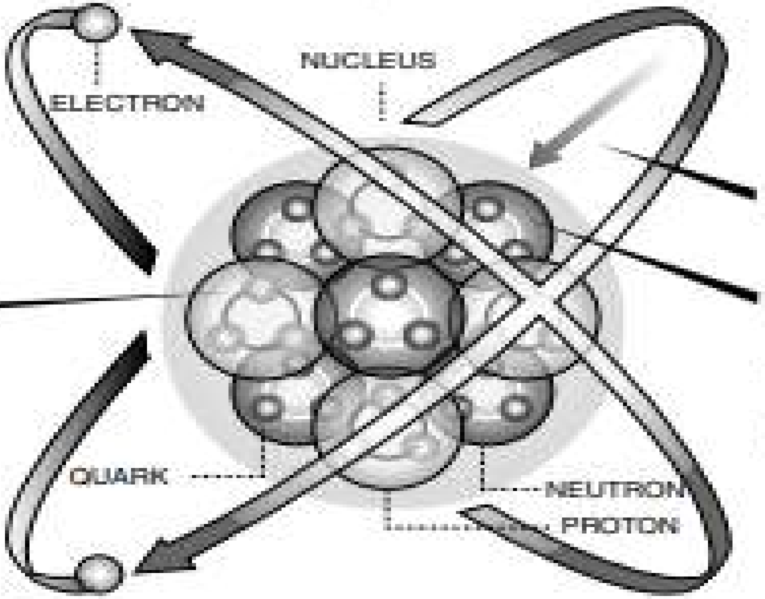
QUARKS

The **protons** and **neutrons** of an atom's nucleus are themselves complex structures, made up of groups of three basic particles called **quarks.** Quarks can also bind with **antiquarks** to make other particles called **mesons.**

LEPTONS

Leptons are not made of quarks, and include the **electrons** that orbit the atomic nucleus, and their more esoteric relatives, like **muons, taus** and **neutrinos.**

STRUCTURE OF THE ATOM



Bosons

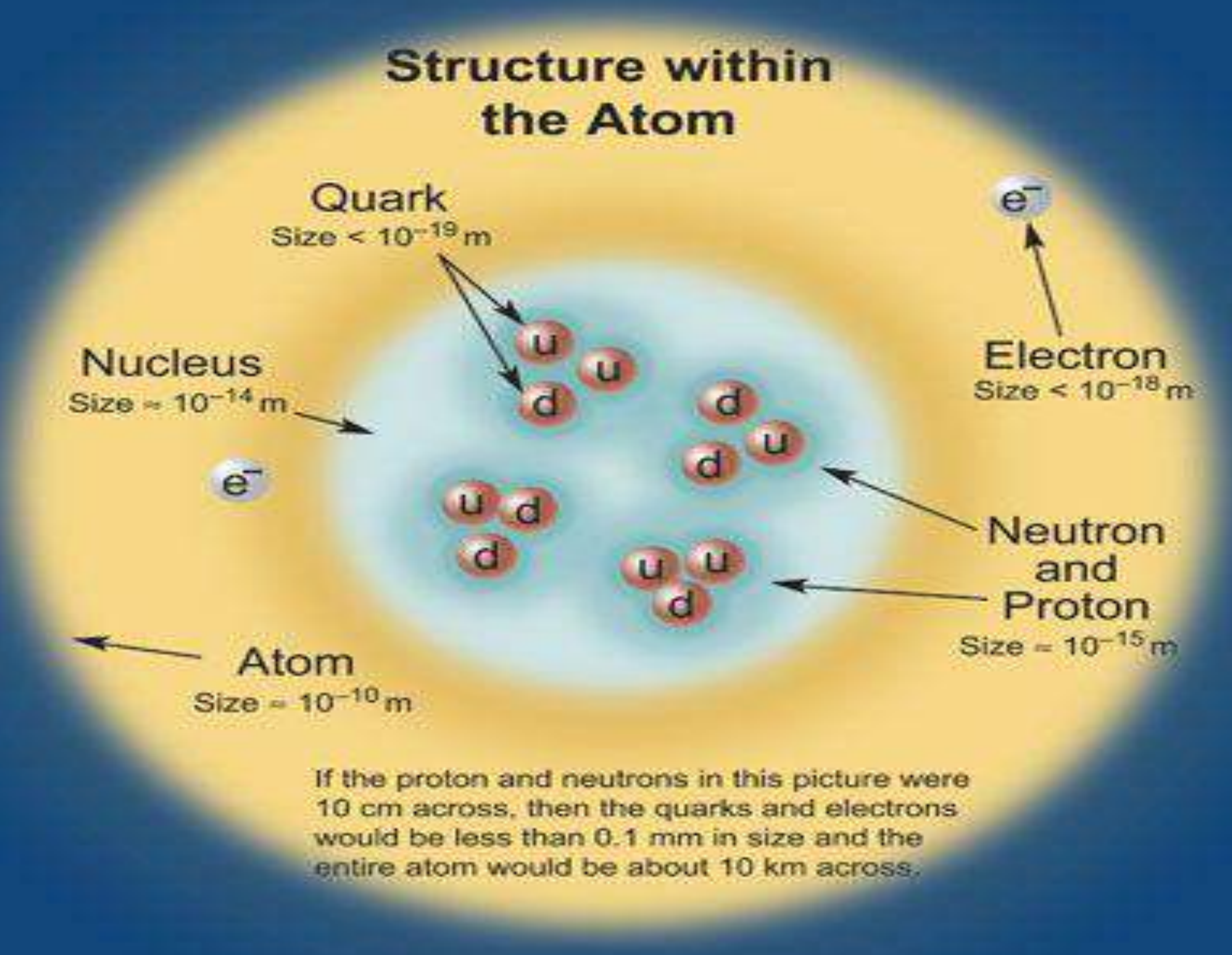
A family of particles called **gauge bosons** transmit the forces between the fermions. There is a different kind of particle for each force:

- **Photons** (the particles of light) carry the electromagnetic force;
- **Gluons** carry the strong force;
- **W** and **Z** bosons carry the weak force;
- **Gravitons**—not yet observed—are believed to be responsible for gravity, which is not a part of the Standard Model.

FORCES

There appear to be four basic forces at work:

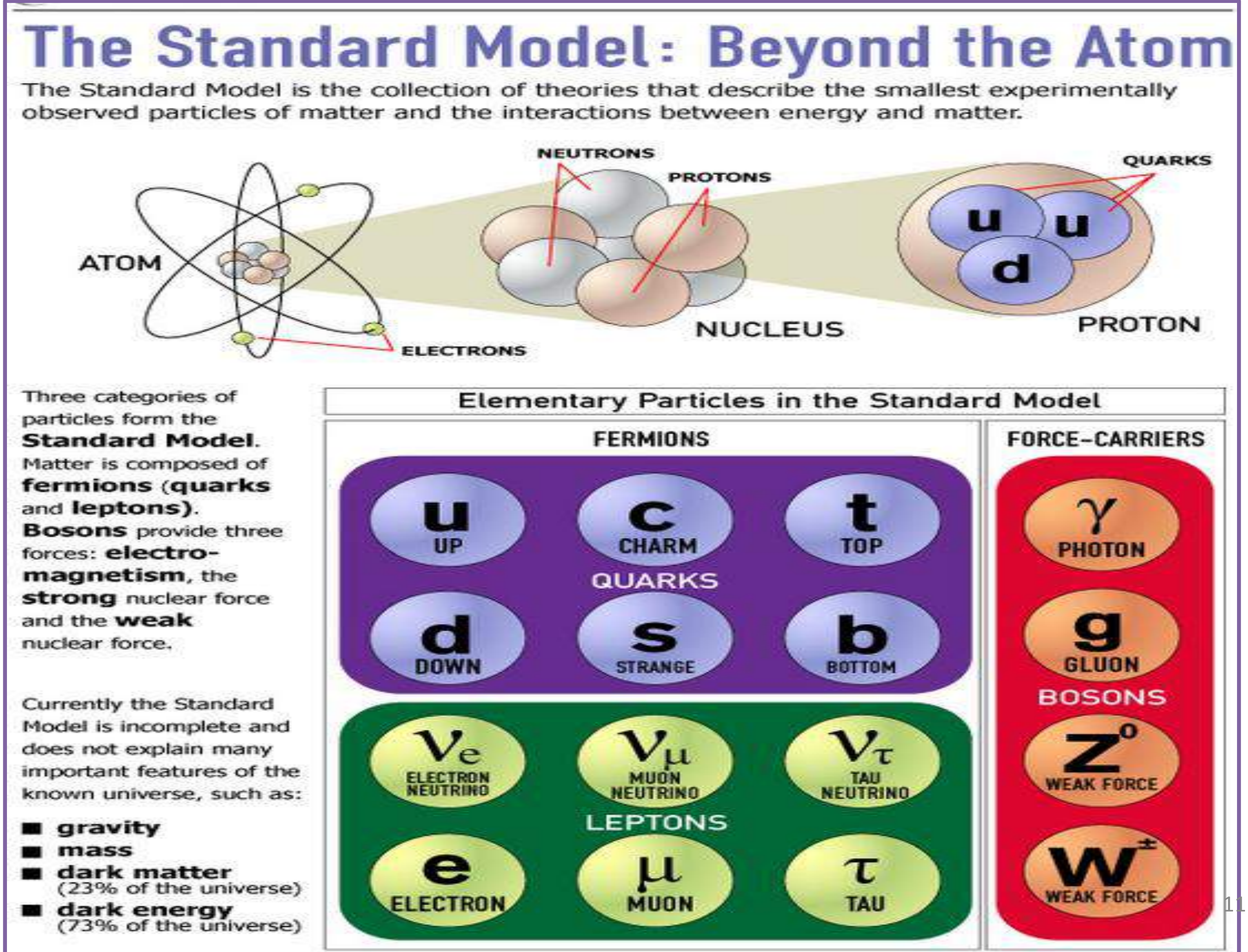
- **Strong force** is responsible for holding together protons and neutrons.
- **Weak force** causes certain forms of radioactivity.
- **Electromagnetic force** holds atoms and molecules together.
- **Gravity** is responsible for the large-scale structure of the Universe, binding stars and galaxies together.



Structure within the Atom

If the proton and neutrons in this picture were 10 cm across, then the quarks and electrons would be less than 0.1 mm in size and the entire atom would be about 10 km across.

Fundamental particles



The Standard Model: Beyond the Atom

The Standard Model is the collection of theories that describe the smallest experimentally observed particles of matter and the interactions between energy and matter.

Three categories of particles form the **Standard Model**. Matter is composed of **fermions (quarks** and **leptons)**. **Bosons** provide three forces: **electro-magnetism**, the **strong** nuclear force and the **weak** nuclear force.

Currently the Standard Model is incomplete and does not explain many important features of the known universe, such as:

- **gravity**
- **mass**
- **dark matter** (23% of the universe)
- **dark energy** (73% of the universe)

Elementary Particles in the Standard Model

FERMIONS

QUARKS

- u UP
- c CHARM
- t TOP
- d DOWN
- s STRANGE
- b BOTTOM

LEPTONS

- ν_e ELECTRON NEUTRINO
- ν_μ MUON NEUTRINO
- ν_τ TAU NEUTRINO
- e ELECTRON
- μ MUON
- τ TAU

FORCE-CARRIERS

BOSONS

- γ PHOTON
- g GLUON
- Z^0 WEAK FORCE
- $W^\pm$ WEAK FORCE

TYPES OF PARTICLES:

Elementary particles can be divided into fermions and bosons

Fermions:

e.g. Neutrons, protons, electrons etc

- **Obey Pauli principle**
- **Have anti symmetric wave functions**
- **Have half integer spin values**

Fermions are again divided into

1. **Leptons:**

e.g. electron, which cannot interact by strong interactions.

2. **Hadrons:**

e.g. neutron and proton, which can have strong nuclear interactions.

Bosons:

e.g. **Photons**

- **Do not obey Pauli principle**
- **Have symmetric wave functions**
- **Have integer spin values.**

Note:

- MeV:
- 1eV = 1.6 x 10^{-19} joules
- 1 MeV = 10^{6} eV
- 1 amu = 931.46 MeV (approximately 931 MeV)

Nuclear chemistry - Introduction

- ***Discovery of Particles***
- The **discovery** of **x-rays** by **William Conrad Roentgen** in **1895** excited the imagination of a generation of scientists who rushed to study this phenomenon.
- Within a few months, **Henri Becquerel** found that both **uranium** metal and **salts** of this element gave off a different form of **radiation**, which could also pass through **solids**.
- By **1898**, **Marie Curie** found that compounds of **thorium** were also "**radioactive**." After pain-staking effort she eventually isolated two more radioactive elements **polonium** and **radium** from **ores** that contained **uranium**.

Henri Becquerel
(1852-1908)

Pierre Curie and Mme
Curie

All three awarded **Nobel Prize in physics** for the **discovery** of the **radioactivity** in chemistry **1903**.

History of nuclear science

- The **discoveries** and **inventions** made until today are based on two aspects. The first one is made on a purpose, most often to fulfill a need. The second one is rather a quite interesting one, that is, accidental discoveries and inventions.
- Accidental discoveries have been probably path-breaking inventions in the history of mankind. The invention of X-ray is also one such accidental invention.
- Until this invention was made, **health care professionals** treated all **ailments** related to the **musculoskeletal** system mostly on instinct.

Wilhelm Roentgen was the first Physicist ever to win a Nobel Prize in 1901 for his accidental discovery of the X-ray.

Milestones in the basic science

Fundamental particles discoveries	Nuclear particles
• α – alpha particle • β – beta particle • γ – gamma particle	• Positron • Neutrino • Mesons • Pions and • Quarks

Nuclear particles - Positron

Positron: the antimatter counterpart of the electron.

- Positron is also known as the **positive electron**;
- It is a positively charged subatomic particle having the same or equal mass and magnitude of charge as the electron and creates the **antiparticle** of a **negative electron**.
- It is formed when a **proton** is converted into a **neutron**. Hence the atomic number (Z) is decreased by one and again without any change in mass number.

  Proton → neutron + positron (β^+) + neutrino **or** ${}^{1}_{+1}p \rightarrow {}^{1}_{0}n + {}^{0}_{+1}e + {}^{0}_{0}\nu_e$

NOTE:

- ❖ Positron emission is observed for nuclides in which the n:p ratio is low.
- ❖ These nuclides lie below the band of stability.
- ❖ **Oxygen-15** is an example of a nuclide that undergoes **positron emission**:
- **Example** 1: and **Example** 2:

$${}^{15}_{8}O \rightarrow {}^{15}_{7}N + {}^{0}_{+1}e$$

$${}^{40}_{19}K \rightarrow {}^{40}_{18}Ar + {}^{0}_{+1}e$$

Nuclear particles - Neutrino

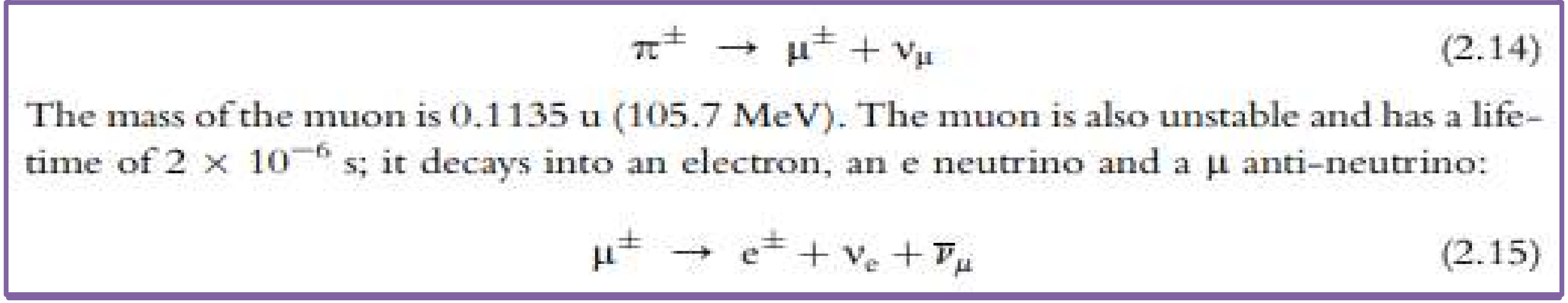
- Studies of beta decay also led to the discovery of **neutrino**.
- A neutrino is a fermion particle! (Pg No. 23, **Jan Rydberg** book)
- The existence of the electron neutrino was predicted by Pauli in 1927 but it was not proven until **1956** when **Reines and Cowan** detected them in experiments at the Savannah River (USA) nuclear reactor.
- This low or no mass neutral particle was named neutrino (little neutron) by **Enrico Fermi**.
- While **electrons** have a **negative** charge, **neutrinos have no charge** at all.
- Neutrinos are also incredibly small and light.
- ~~They have some mass, but not much.~~
- They are the lightest of all the subatomic particles that have mass.
- **β-decay** is accompanied by the emission of **neutrinos**.
- But these are very difficult to detect.

Nuclear particles - Neutrino cont…

- Several types of neutrino called **flavors**
- β^- decay results in **anti-neutrino**
- β^+ decay results in **neutrino**
- Both these neutrinos are now referred as **electron neutrinos** $^{-}\nu_e$ and ν_e

Nuclear particles - Pions or pi meson

- Pions or pi meson is any of three subatomic particles ie., π^0, π^+, π^-
- Each pion consists of a quark and an antiquark & is therefore a meson.
- ~~Pions are the **hightest** mesons and more generally the **hightest** hadrons.~~
- Pions formed in nuclear particle reactions are unstable and decay with a life-time of $3\text{x}10^{-8}$ s into a **muon** and a μ **neutrino**:
- The neutral pion decaying lifetime = 85 attoseconds.
- Mass of the muon is 0.1135 u (105.7 MeV)
- Muon is also unstable and has a life-time of $2\text{x}10^{-6}$ s
- It decays into an electron, a neutrino, and anti-neutrino.



$$\pi^{\pm} \rightarrow \mu^{\pm} + \nu_{\mu} \tag{2.14}$$

The mass of the muon is 0.1135 u (105.7 MeV). The muon is also unstable and has a life-time of 2×10^{-6} s; it decays into an electron, an e neutrino and a μ anti-neutrino:

$$\mu^{\pm} \rightarrow e^{\pm} + \nu_e + \bar{\nu}_{\mu} \tag{2.15}$$

Nuclear particles - Mesons

- Nuclear physicist **Yukawa** in **1935**.
- Fundamental or the elementary particles.
- The mesons are the **hadronic** subatomic particles composed of a combination of **quark** and an **antiquark**.
- Carrying unit charge and possessing mass intermediate between the mass of the electron (m_e) and the mass of the proton (m_p).
- The most common type of **mesons** are the **pions** (pi mesons), **kaons** (K mesons) and the eta **meson** (η-meson).
- The π^+ and π^- mesons are of special importance in nuclear science.
- The quark/antiquark pairs in the π mesons couple to have zero spin, and thus these **mesons** are **bosons**
- Pions are of charge +1, -1, and 0 are denoted π^+ (^+e charge), π^-(^-e charge), and π^0 (neutral charge), respectively.
- All have zero spins

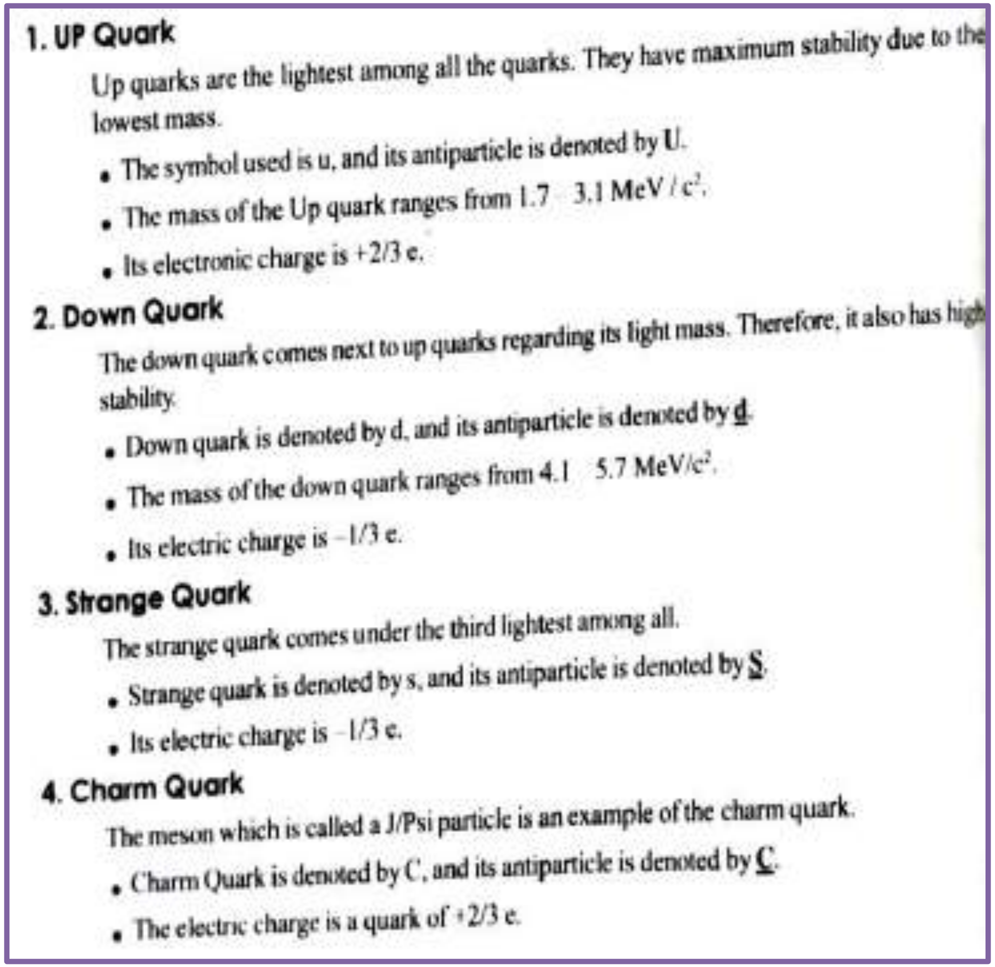
Kaons or K Mesons

- **Kaons or K Mesons**
- A **kaon** or **k** meson is a meson that contains one ordinary quark, either an *up quark* or a *down quark* and *one strange quark*.
- The K mesons were first discovered in **1947**. The k mesons are abbreviated as **kaon** or the **k meson** came into use in about **1958**.
- The k mesons or Kaons come in two varieties: **positively** charged (K^+) and **neutral** (K^0)and their **antiparticles** K^- and .
- They are spin 0 particles, the weight of kaons is about half as much as nucleons, and decay by means of weak interactions.

Quarks

- Fundamental constituent of matter and is defined as an elementary particle.
- **Quarks combine** to form **composite particles** called **hadrons.**
- **Quarks cannot exist independently but as a constituent part of the matter.**
- The most stable of which are protons and neutrons, components of atomic nuclei.
- **Examples**:
- 1. **Protons** consist of two up quarks and one down quark.
- 2. **Neutron** is made up of two down quarks and one up quark.
- The quark model was independently proposed by physicists Murray Gell-Mann and George Zweig in 1964.
- Quarks were introduced as parts of an ordering scheme for hadrons, and there was little evidence for their physical existence until deep inelastic scattering experiments at the Stanford Linear Accelerator Center in 1968.
- There are six types, known as flavors, of quarks: up, down, charm, strange, top, and bottom.
- Quarks have various intrinsic properties, including electric charge, mass, color charge, and spin.

Types of quarks



1. UP Quark

Up quarks are the lightest among all the quarks. They have maximum stability due to the lowest mass.

- The symbol used is u, and its antiparticle is denoted by $\underline{U}$.
- The mass of the Up quark ranges from 1.7 3.1 MeV / c^2.
- Its electronic charge is +2/3 e.

2. Down Quark

The down quark comes next to up quarks regarding its light mass. Therefore, it also has high stability.

- Down quark is denoted by d, and its antiparticle is denoted by $\underline{d}$.
- The mass of the down quark ranges from 4.1 5.7 MeV/c^2.
- Its electric charge is –1/3 e.

3. Strange Quark

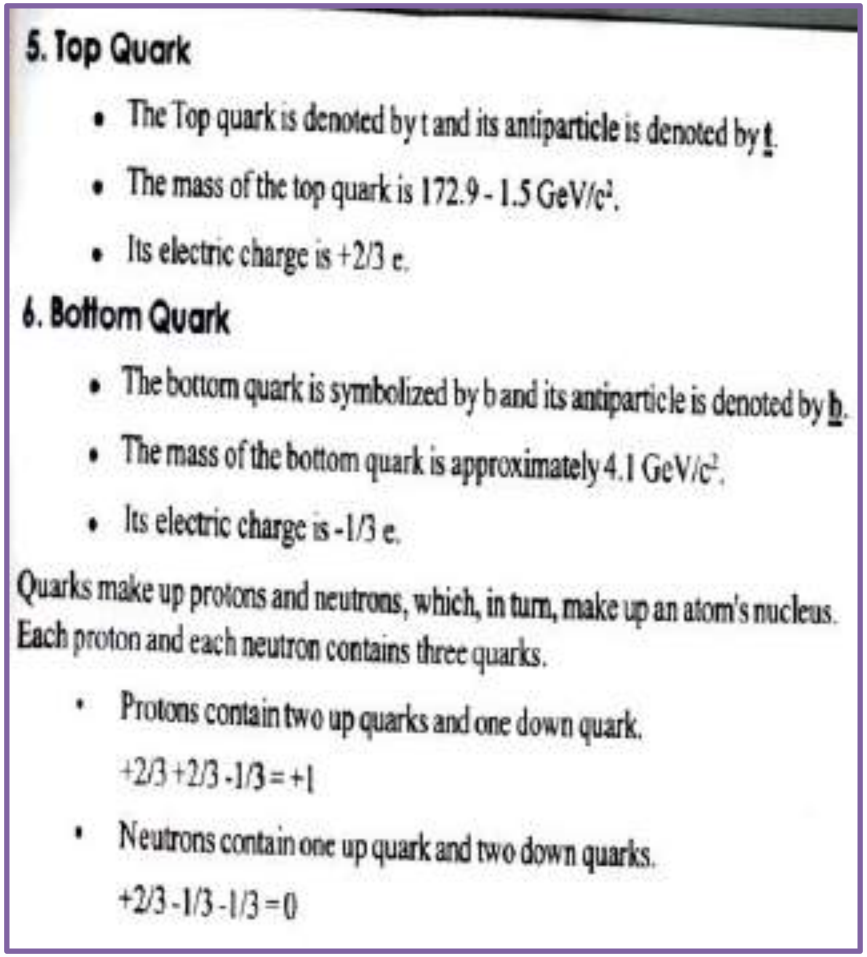
The strange quark comes under the third lightest among all.

- Strange quark is denoted by s, and its antiparticle is denoted by $\underline{S}$.
- Its electric charge is –1/3 e.

4. Charm Quark

The meson which is called a J/Psi particle is an example of the charm quark.

- Charm Quark is denoted by C, and its antiparticle is denoted by $\underline{C}$.
- The electric charge is a quark of +2/3 e.



5. Top Quark

- The Top quark is denoted by t and its antiparticle is denoted by $\underline{t}$.
- The mass of the top quark is 172.9 - 1.5 GeV/c^2.
- Its electric charge is +2/3 e.

6. Bottom Quark

- The bottom quark is symbolized by b and its antiparticle is denoted by $\underline{b}$.
- The mass of the bottom quark is approximately 4.1 GeV/c^2.
- Its electric charge is -1/3 e.

Quarks make up protons and neutrons, which, in turn, make up an atom's nucleus. Each proton and each neutron contains three quarks.

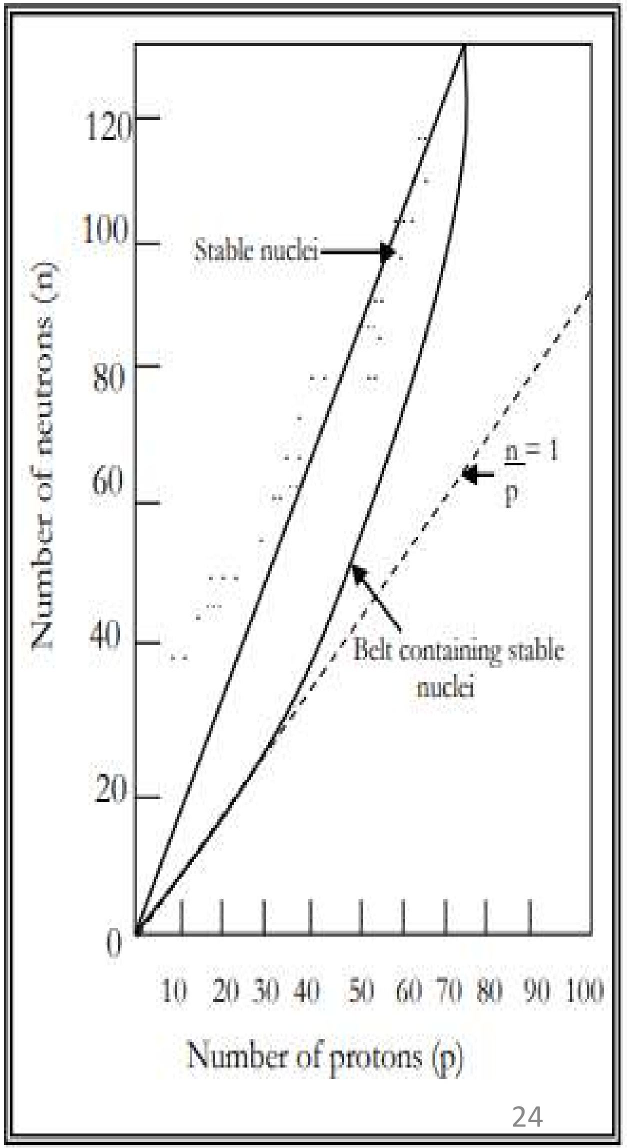
- Protons contain two up quarks and one down quark.

  +2/3 +2/3 -1/3 = +1
- Neutrons contain one up quark and two down quarks.

  +2/3 -1/3 -1/3 = 0

Nuclear instability or Nuclear stability – N/P ratio:

- The neutron-proton ratio explains the stability of a nucleus.
- A plot of the number of neutrons against the number of neutrons for various elements gives a well defined belt in which the stable nuclei lie.
- Nuclei whose N/P ratio lies outside the belt are unstable and, therefore, undergo spontaneous radioactive disintegration.
- For nuclei with atomic number 20 or less the **N/P ratio** for stability lies close to **unity**.
- However, as the nuclear charge exceeds 20, the ratio N/P for stability exceeds unity, i.e., the number of neutrons is larger than that of protons.
- The nuclei with N/P ratio lying below or above the belt are unstable.
- The N/P ratio rises from 146/92 to 144/90, i.e., from 1.58 to 1.60. The unstable nucleus continues to emit alpha or beta particles until a stable arrangement is reached.



Nuclear fission

- The splitting of a heavy nucleus into two or more smaller nuclei of comparable masses is known as **nuclear fission**.
- There is **mass defect** during **fission**, i.e., the total mass of products of fission is less than the total mass of substances undergoing fission. The loss of mass appears in the form of energy according to Einstein's mass energy relationship, $E = mc^2$.

$${}^{235}_{92}U + {}^{1}_{0}n \rightarrow \left({}^{236}_{92}U\right) \rightarrow {}^{141}_{56}Ba + {}^{92}_{36}Kr + 3\,{}^{1}_{0}n$$

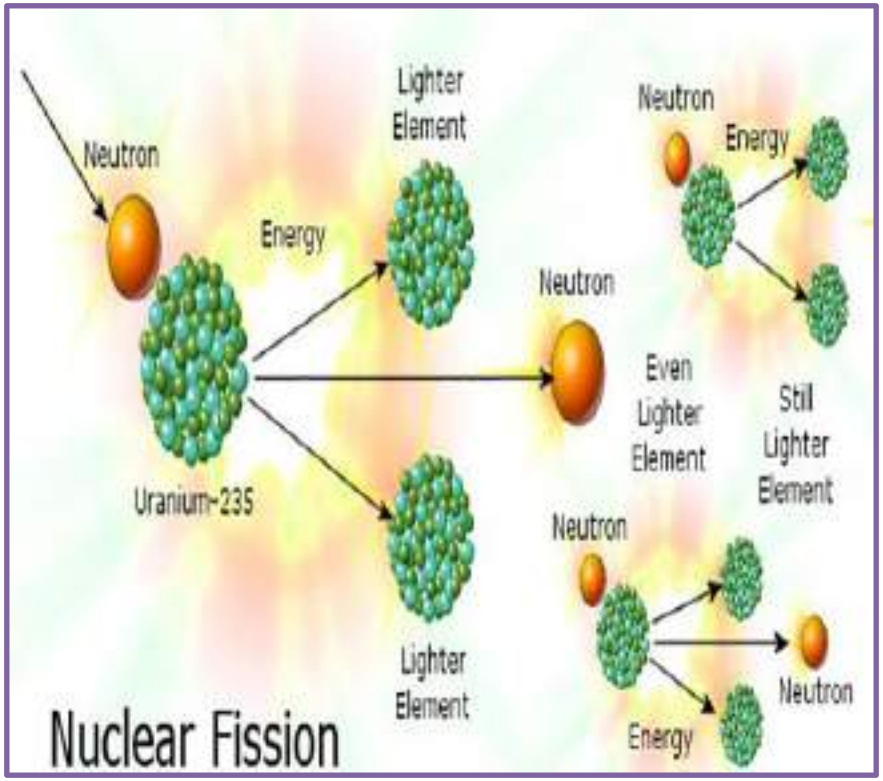
- The neutrons liberated in the fission may then combine other atoms to undergo further fission. Thus it becomes a **chain reaction**.

Calculation of energy released in nuclear fission:

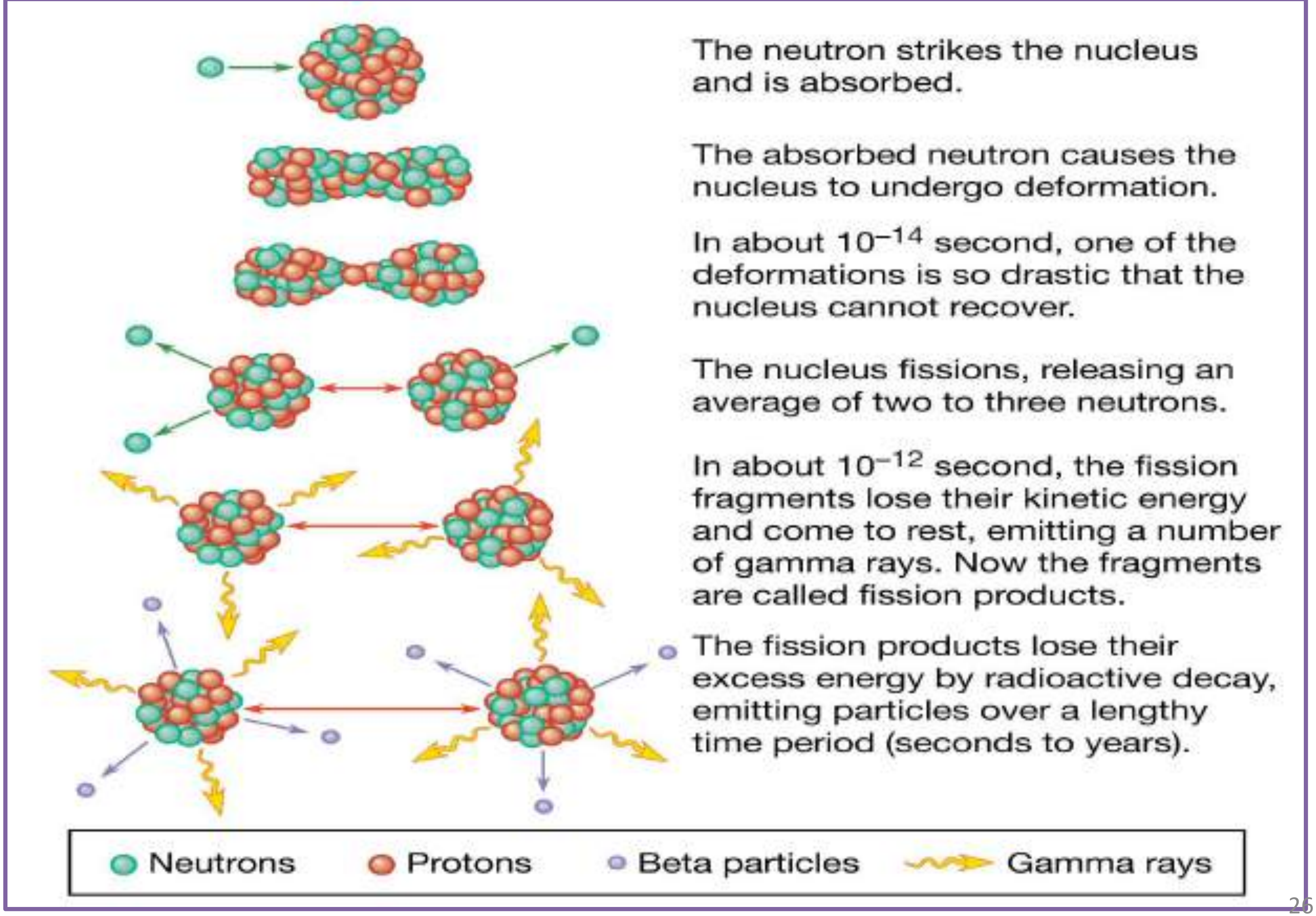
1. Calculation of energy release from binding energies:
2. Calculation of energy release from mass defect:

Modes of release of fission energy:

1. Uncontrolled release of fission energy: Production of an atom bomb.
2. Controlled release of Fission energy:
3. Plutonium as fissionable material.



Nuclear fission reaction mechanism



The neutron strikes the nucleus and is absorbed.

The absorbed neutron causes the nucleus to undergo deformation.

In about 10^{-14} second, one of the deformations is so drastic that the nucleus cannot recover.

The nucleus fissions, releasing an average of two to three neutrons.

In about 10^{-12} second, the fission fragments lose their kinetic energy and come to rest, emitting a number of gamma rays. Now the fragments are called fission products.

The fission products lose their excess energy by radioactive decay, emitting particles over a lengthy time period (seconds to years).

Nuclear fusion

- The origin of the word "**fusion**" to describe **light-nucleus exothermic nuclear reactions** is itself interesting.
- It appears to have been introduced at a relatively late date, by Bethe and Louis Ridenour in 1950,[5–7] when writing about the **H-bomb** after President Harry Truman's announcement that the United States would pursue the bomb, following the Soviet Union's first **A-bomb test** in **1949**.
- **George Gamow** introduced the word "**thermonuclear**" in 1937–1938[11] to mean reactions induced by **hot ions** with a thermalized distribution of kinetic energies.

Nuclear fusion

- The formation of a heavier nucleus from two or more lighter nuclei with liberation of energy is known as **nuclear fusion**.

$$ {}_{1}^{2}H + {}_{1}^{3}H \rightarrow {}_{2}^{4}He + {}_{0}^{1}n + 17.6\,MeV $$

- The energy release during fusion reaction is four times greater than fission reaction.
- Fusion reaction takes place at high temperature (4 x 10^6 ºC) and high pressure hence called as **thermonuclear reaction**.
- Fusion reaction are not suitable for man-made experiment.
- **Hydrogen bomb** works on this principle.

Examples of nuclear reactions:

1. Thorium is used as blanket as it fertile material (do not undergo fission). In the atomic transmutation take place to form fissionable product as

$$ {}_{90}^{232}Th + {}_{0}^{1}n \xrightarrow{(n,\gamma)} {}_{90}^{233}Th \xrightarrow{-\beta} {}_{91}^{233}Pa \xrightarrow{-\beta} {}_{92}^{233}U $$

Nuclear fusion

2. ^{233}U and ^{235}U are fissionable nuclides, ^{233}U is obtained from ^{232}U.

3. Plutonium is not occurring naturally. The fissile plutonium obtained from natural uranium.

$$_{92}^{238}U \xrightarrow{(n,\gamma)} {}_{92}^{239}U \xrightarrow{-\beta} {}_{93}^{239}Np \xrightarrow{-\beta} {}_{94}^{239}Pu$$

- Thus, ^{233}U, ^{235}U, & ^{239}Pu are fissile and used atomic fuel.

Nuclear fusion – examples combination of 2 H and 2 n

$${}_1^2H + {}_1^3H \rightarrow {}_2^4He + {}_0^1n + 17.6MeV$$

- The formation of a heavier nucleus from two or more lighter nuclei with liberation of energy is known as **nuclear fusion**.
- Considering the formation of helium nucleus.
- It contains 2 protons and 2 neutrons in the nucleus and 2 electrons outside the nucleus. In other words, it is formed by the combination of two hydrogen atoms (i.e., 2 protons and 2 electrons) and two neutrons. Its atomic mass (M') should be given by
- $M' = 2m_H + 2m_n$

  $= 2 \times 1.007825 + 2 \times 1.008665$

  $= 4.03298$ a.m.u.

- Actual mass of helium atom (M) on the same scale = 4.00260 a.m.u.

∴ Mass defect,

$\Delta M = M' - M$

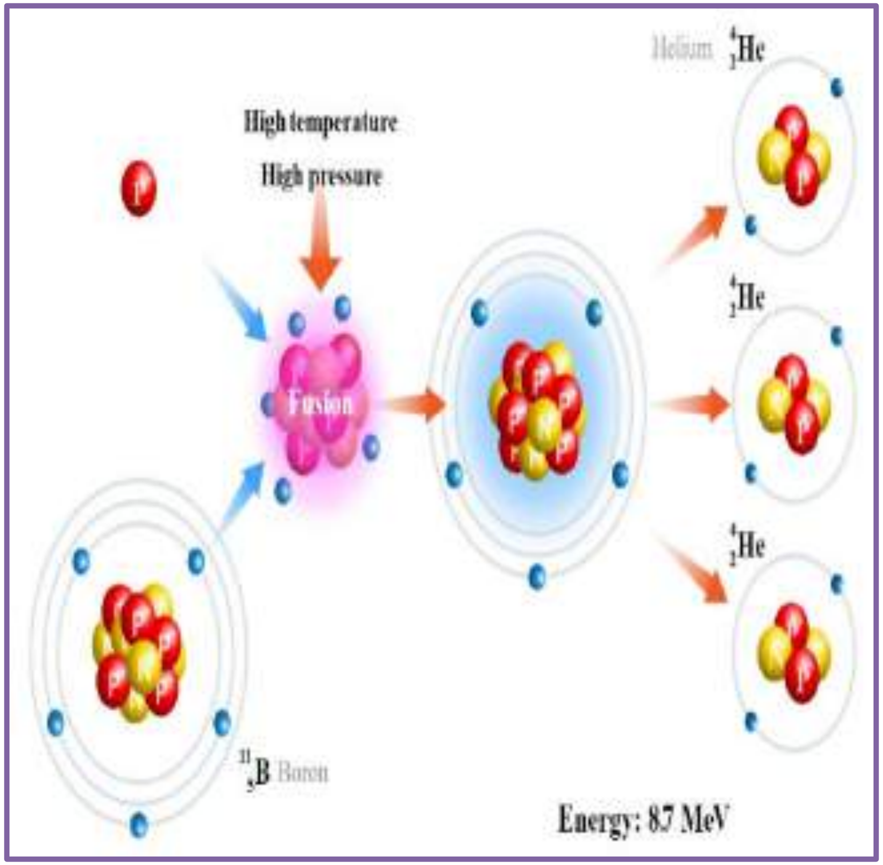
$= 4.03298 – 4.00260 = 0.3038$ a.m.u.

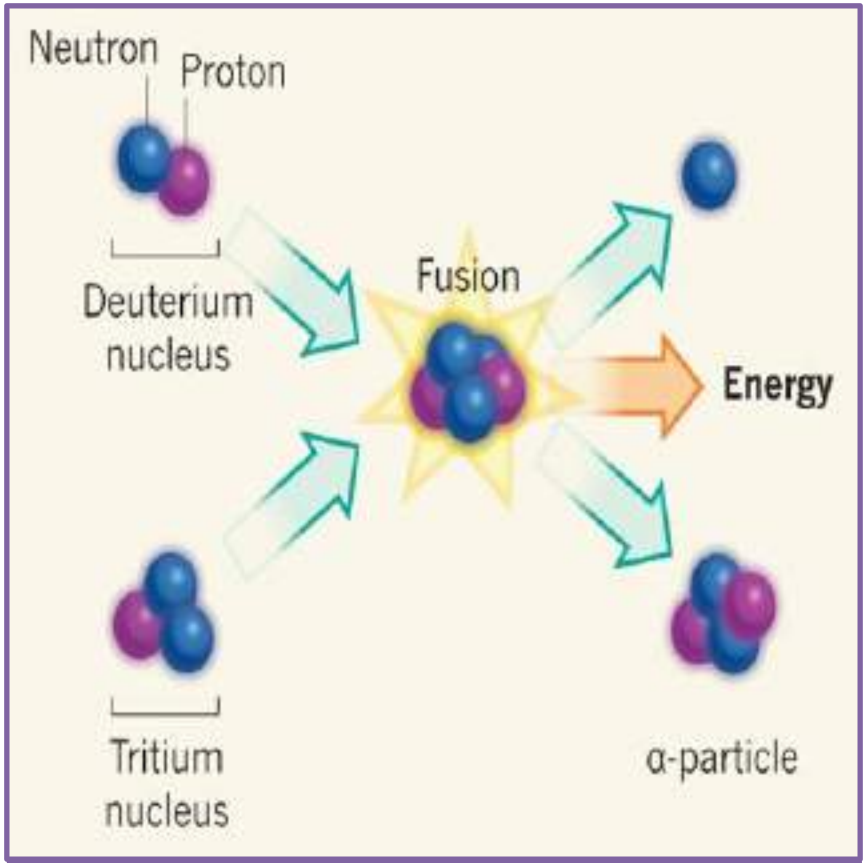
∴ Energy released in the formation of helium nucleus = 0.3038 a.m.u. × 931.5 MeV/a.m.u.

- Hence, energy released in the formation of 1 mole of helium nuclei = 0.03038 × 931.5 × 6.022 × 10^{23} MeV = 170.42 × 10^{23} MeV.
- Thus, an enormous amount of energy is released by the formation of a heavier nucleus from those of lighter elements on account of the mass defect.

Thermonuclear fusion

Formidable challenges face the decades long quest to achieve **nuclear fusion — the power source of stars — in the laboratory**. For a plasma to undergo self heating nuclear fusion (ignition), it must be both **hot** and **well confined**. The facilities that hope to accomplish this goal are technological **marvels**, but are dauntingly **expensive** to **build** and **operate**

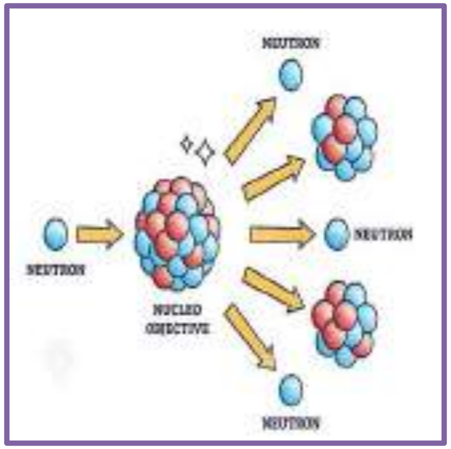


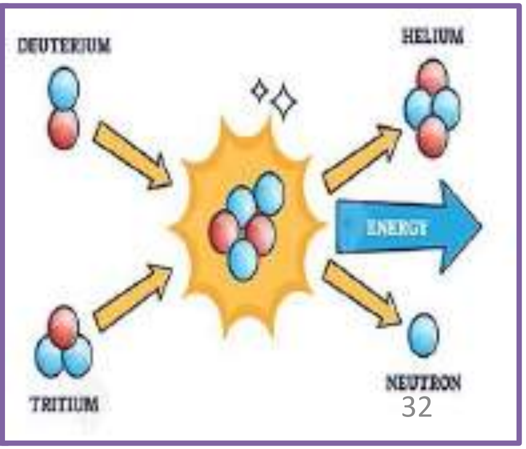


Hurricane et. Al.,
20 FEBRUARY 2014 | VOL 506 | NATURE | 343

Difference between Nuclear Fission and Nuclear Fusion reactions

Sl. No.	Nuclear fission	Nuclear fusion
1	A heavy nucleus breaks up to form two lighter nuclei.	Two nuclei combine to form a heavy nucleus.
2	It involves a chain reaction.	Chain reaction is not involved.
3	The heavy nucleus is bombarded with neutrons.	Light nuclei are heated to an extremely high temp.
4	We have proper mechanisms to control fission reaction for generating electricity.	Proper mechanisms to control fusion reaction are yet to be developed.
5	Disposal of nuclear waste is a great environmental problem.	Disposal of nuclear waste is not involved.
6	Raw material is not easily available and is costly.	Raw material is comparatively cheap and easily available.



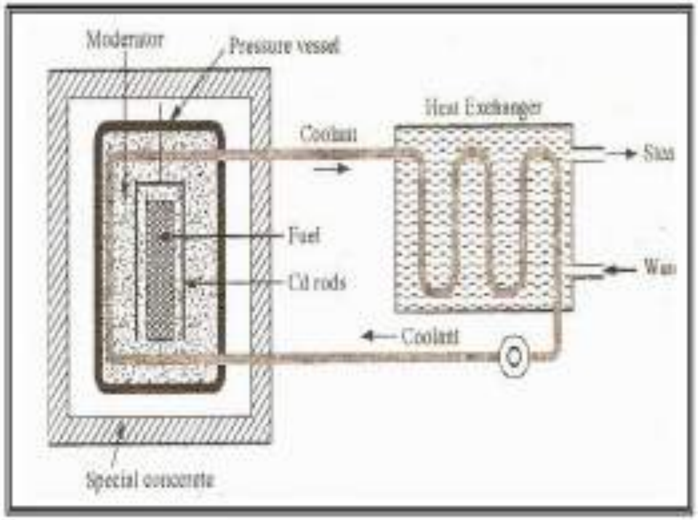


Nuclear reactors

Different types of Nuclear Reactors

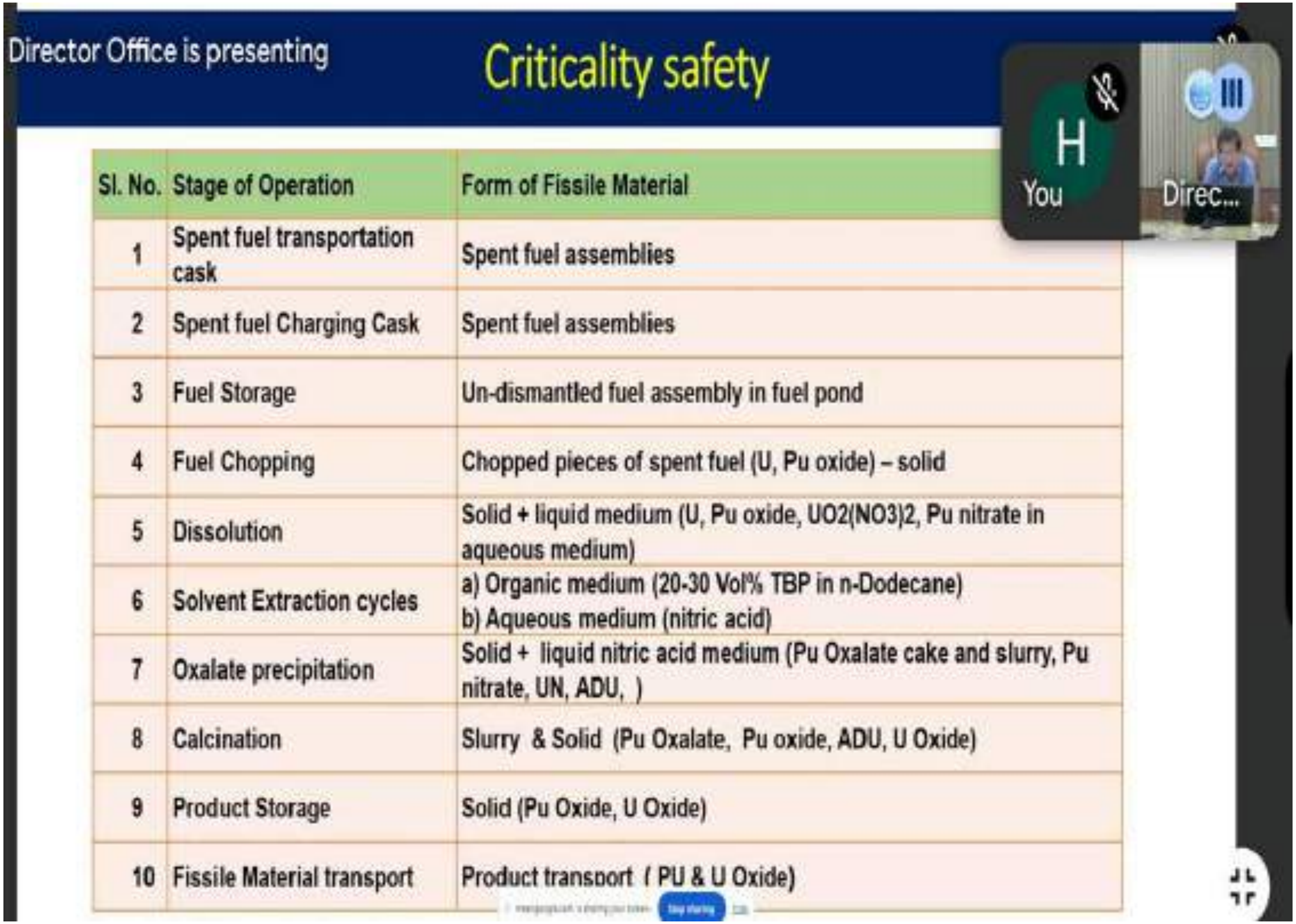
Nuclear reactors

- The release of energy by nuclear fission is the basis of nuclear reactor. In a nuclear reactor, the fission material (U^{235} or Pu^{239}) is stacked with **heavy water** or **graphite** called **moderator**. The neutrons produced in the fission pass through the moderator and lose some of their energy. Resulting slow neutrons can be captured to initiate the new fission.
- **Cadmium** or **boron rods** are inserted in the moderator and these have the **ability to absorb neutrons** and thus **control** the **rate** of the **chain reaction**.
- The energy released in this controlled chain reaction appears mainly as **heat** and can be removed by circulating a **coolant**, **water** around the reactor. **Steam** produced is used in **steam turbines** for generating **power**.
- It has been estimated that the **fission of 1 Kg of U^{235}** liberates as much **heat** as produced by burning **2,000 tonnes of coal.**



Nuclear reactor is a device for carrying out **fission reaction** at a diluted and controlled rate, so that the **heat liberated** can be converted into **electrical energy** by the fission of U-235.

The nuclear reactor works on the **slow neutron chain** which is achieved with natural uranium of high purity by the use of **graphite**, which acts as a **moderator** to **slow down** the **neutrons** to such a velocity that they would be more easily captured by the surrounding uranium.



Criticality safety

Sl. No.	Stage of Operation	Form of Fissile Material
1	Spent fuel transportation cask	Spent fuel assemblies
2	Spent fuel Charging Cask	Spent fuel assemblies
3	Fuel Storage	Un-dismantled fuel assembly in fuel pond
4	Fuel Chopping	Chopped pieces of spent fuel (U, Pu oxide) – solid
5	Dissolution	Solid + liquid medium (U, Pu oxide, UO2(NO3)2, Pu nitrate in aqueous medium)
6	Solvent Extraction cycles	a) Organic medium (20-30 Vol% TBP in n-Dodecane) b) Aqueous medium (nitric acid)
7	Oxalate precipitation	Solid + liquid nitric acid medium (Pu Oxalate cake and slurry, Pu nitrate, UN, ADU,)
8	Calcination	Slurry & Solid (Pu Oxalate, Pu oxide, ADU, U Oxide)
9	Product Storage	Solid (Pu Oxide, U Oxide)
10	Fissile Material transport	Product transport (PU & U Oxide)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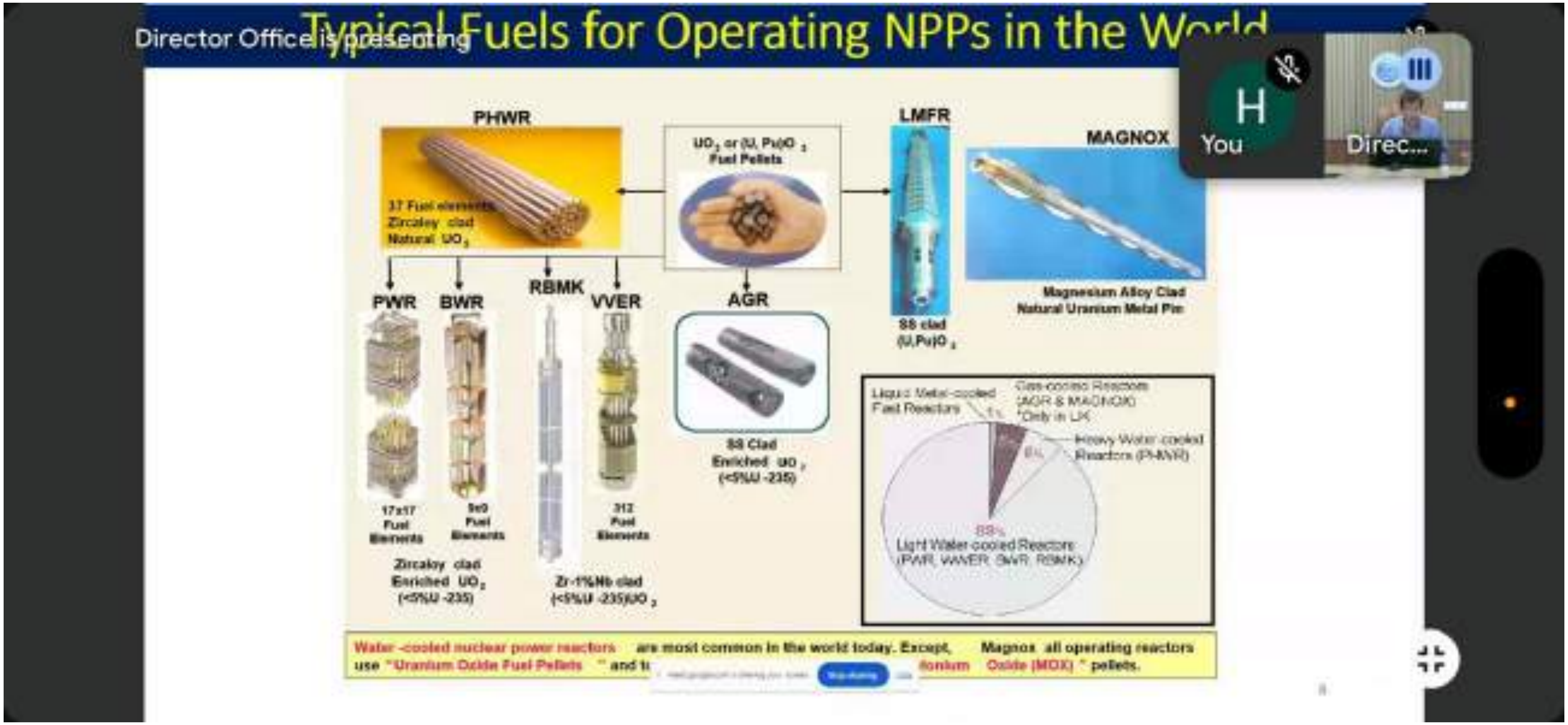
Storage of Spent Fuel

Major Activities in Reprocessing Plants

- Spent fuel shipment to the reprocessing plant
- Spent fuel storage
- Fuel charging, chopping and dissolution
- Separation Process
- Process Sampling and Analytical work in laboratory
- Plutonium Reconversion laboratory
- Reconversion of Uranyl nitrate solution to Oxide form
- Waste management
  - Interim Storage of high level and intermediate level liquid
  - Solid radioactive wastes
  - Gaseous Waste
- Maintenance

Spent Fuel Generatio

Reactor	Spent fuel (Te/year)	Fuel
Dhruva	15	Nat. U metal
PHWR-220	40	Nat. U Oxide
PHWR-540	90	Nat. U Oxide
PHWR- 700	120	Nat U Oxide
BWR -160	10	LEU Oxide
LWR -1000	25	LEU Oxide



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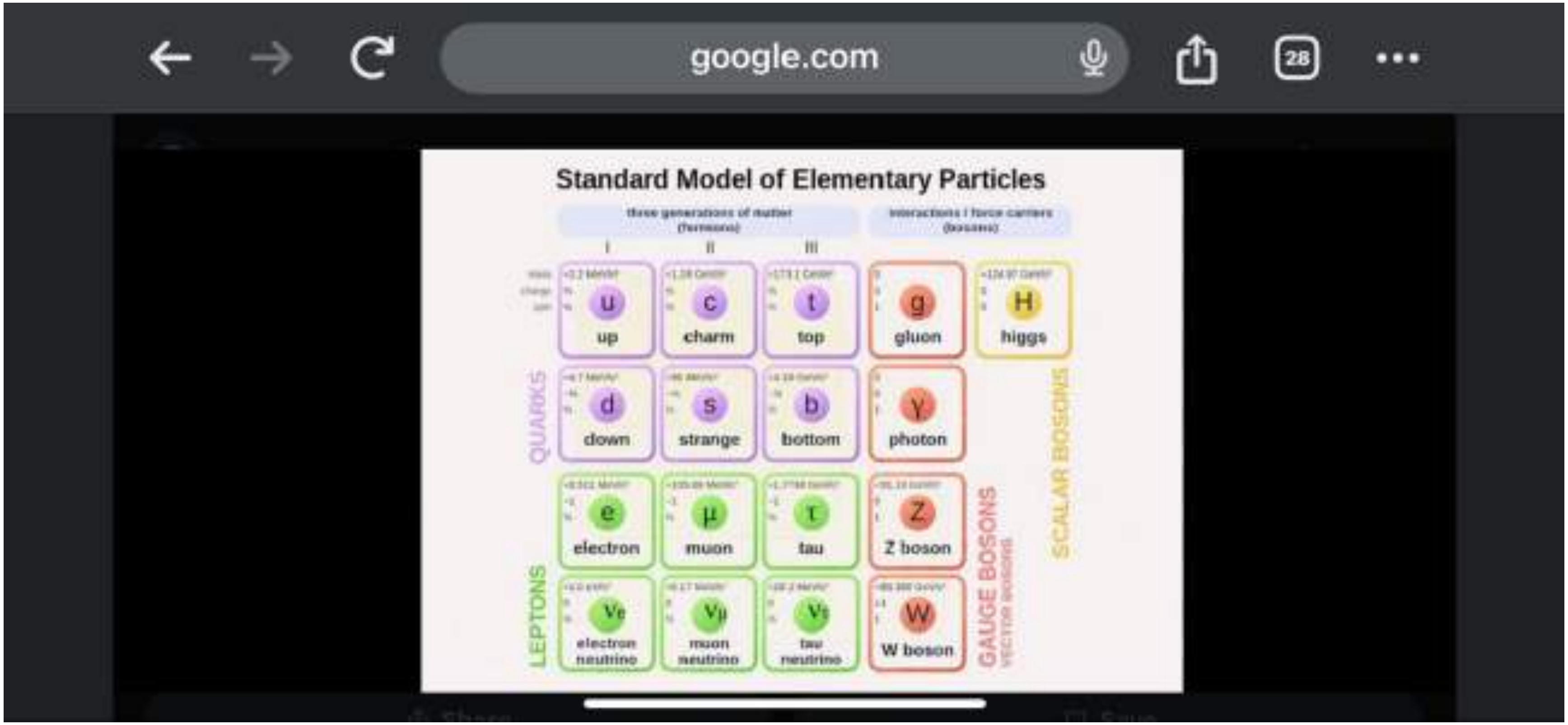
Typical Fuels for Operating NPPs in the World

Water -cooled nuclear power reactors are most common in the world today. Except, Magnox all operating reactors use "Uranium Oxide Fuel Pellets " and t [illegible] tonium Oxide (MOX) " pellets.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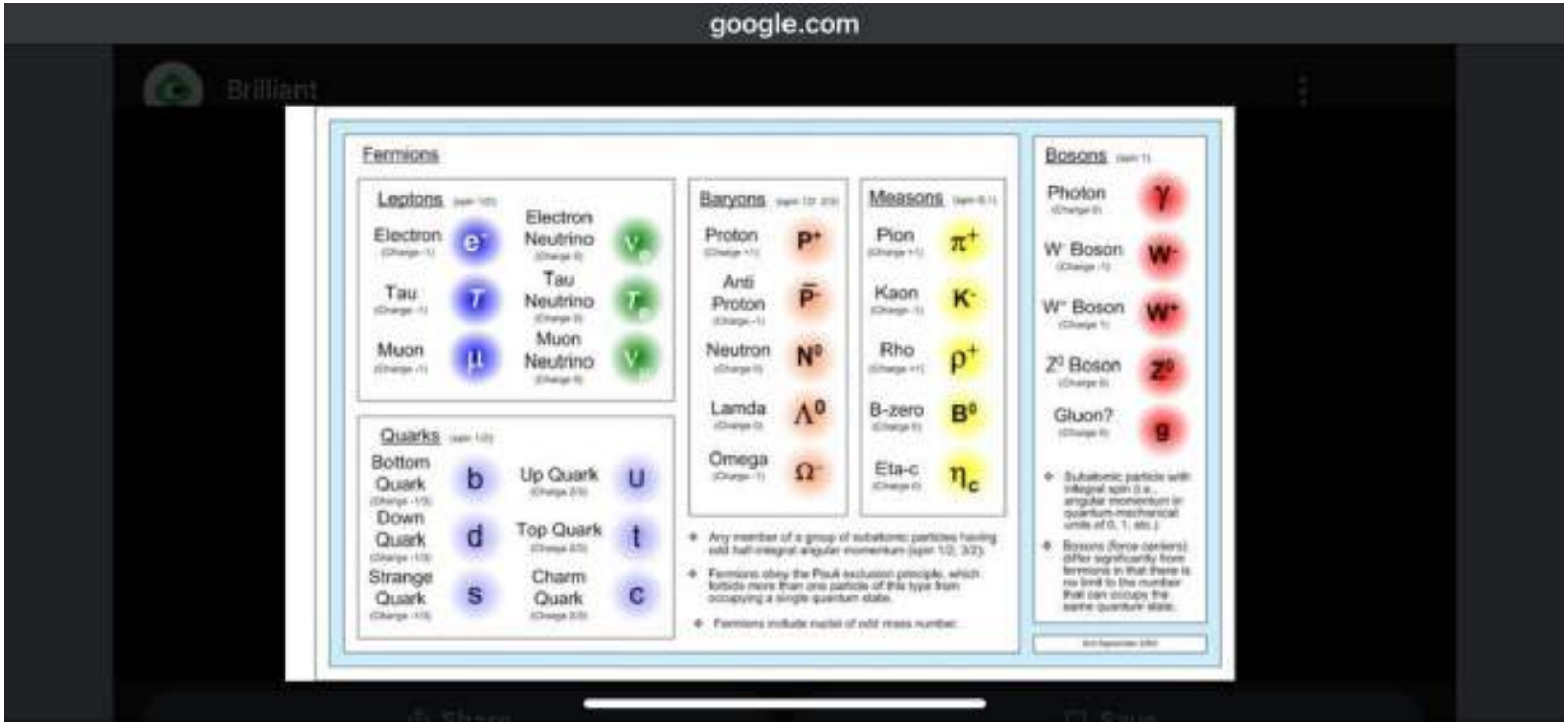
28
Standard Model of Elementary Particles
I
II
III
u
up
c
charm
t
top
g
gluon
H
higgs
d
down
s
strange
b
bottom
γ
photon
e
electron
μ
muon
τ
tau
Z
Z boson
νe
electron neutrino
νμ
muon neutrino
ντ
tau neutrino
W
W boson
QUARKS
LEPTONS
GAUGE BOSONS
SCALAR BOSONS



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Brilliant

Fermions

Leptons (spin 1/2)

Electron (Charge -1)	e^-	Electron Neutrino (Charge 0)	ν_e
Tau (Charge -1)	τ	Tau Neutrino (Charge 0)	τ_e
Muon (Charge -1)	μ	Muon Neutrino (Charge 0)	ν_μ

Quarks (spin 1/2)

Bottom Quark (Charge -1/3)	b	Up Quark (Charge 2/3)	u
Down Quark (Charge -1/3)	d	Top Quark (Charge 2/3)	t
Strange Quark (Charge -1/3)	s	Charm Quark (Charge 2/3)	c

Baryons (spin 1/2, 3/2)

Proton (Charge +1)	P^+
Anti Proton (Charge -1)	$\bar{P}^-$
Neutron (Charge 0)	N^0
Lamda (Charge 0)	Λ^0
Omega (Charge -1)	Ω^-

Measons (spin 0, 1)

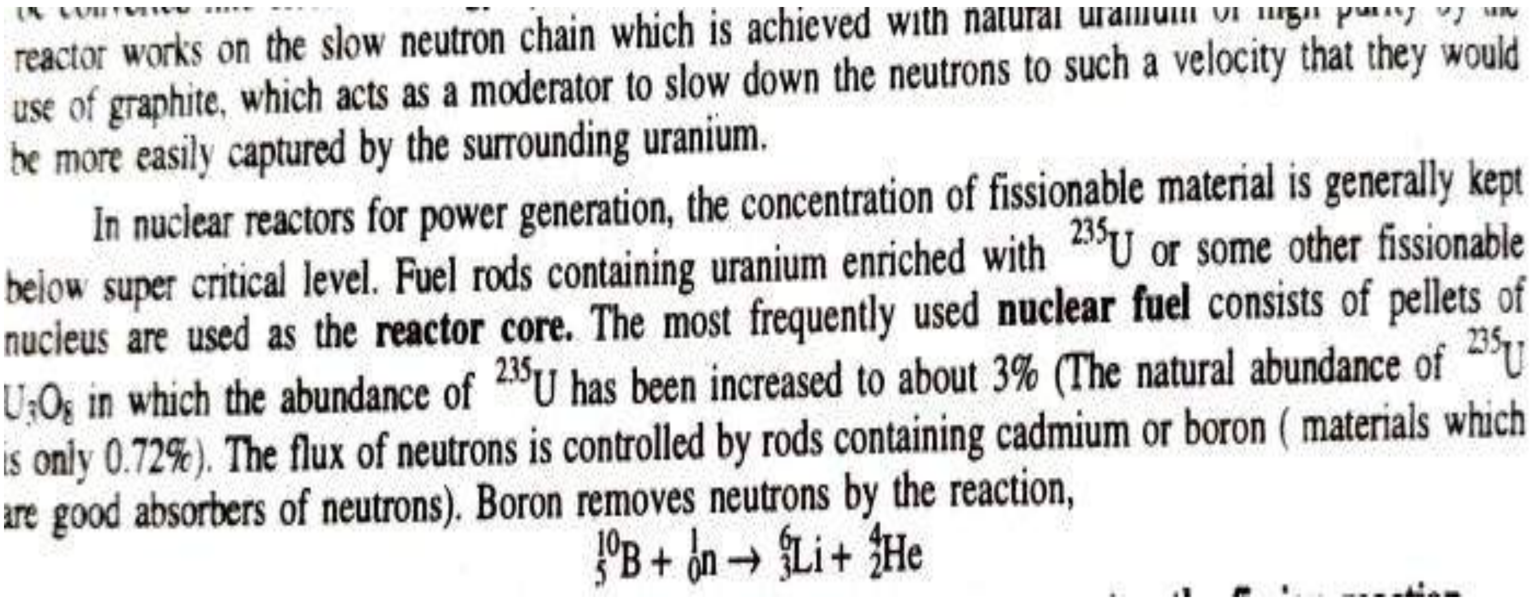
Pion (Charge +1)	π^+
Kaon (Charge -1)	K^-
Rho (Charge +1)	ρ^+
B-zero (Charge 0)	B^0
Eta-c (Charge 0)	η_c

- Any member of a group of subatomic particles having odd half-integral angular momentum (spin 1/2, 3/2).
- Fermions obey the Pauli exclusion principle, which forbids more than one particle of this type from occupying a single quantum state.
- Fermions include nuclei of odd mass number.

Bosons (spin 1)

Photon (Charge 0)	γ
W^- Boson (Charge -1)	W^-
W^+ Boson (Charge 1)	W^+
Z^0 Boson (Charge 0)	Z^0
Gluon? (Charge 0)	g

- Subatomic particle with integral spin (i.e., angular momentum in quantum-mechanical units of 0, 1, etc.)
- Bosons (force carriers) differ significantly from fermions in that there is no limit to the number that can occupy the same quantum state.



reactor works on the slow neutron chain which is achieved with natural uranium of high purity by the use of graphite, which acts as a moderator to slow down the neutrons to such a velocity that they would be more easily captured by the surrounding uranium.

In nuclear reactors for power generation, the concentration of fissionable material is generally kept below super critical level. Fuel rods containing uranium enriched with ^{235}U or some other fissionable nucleus are used as the **reactor core.** The most frequently used **nuclear fuel** consists of pellets of U_3O_8 in which the abundance of ^{235}U has been increased to about 3% (The natural abundance of ^{235}U is only 0.72%). The flux of neutrons is controlled by rods containing cadmium or boron (materials which are good absorbers of neutrons). Boron removes neutrons by the reaction,

$$^{10}_{5}B + ^{1}_{0}n \rightarrow ^{6}_{3}Li + ^{4}_{2}He$$

Breeder reactor:

- U^{235} is used as a reactor fuel for producing electricity.
- But it's predicted that the amount of U^{235} available may last for another fifty years. However, **non-fissionable U^{238}** is about 100 times more plentiful in nature.
- This is used as a **source of energy** in the so-called **breeder reactors** which can supply energy to the world for **5,000 years** or more.
- Here the U^{235} core is covered with a layer or 'blanket' of U^{238}.
- The neutrons released by the core are absorbed by the blanket of uranium-238. This is then converted to fissionable plutonium-239.
- It undergoes a chain reaction, producing more neutrons and energy.

$${}^{238}_{92}U + {}_0n^1 \rightarrow {}^{239}_{94}Pu + 2\,{}_{-1}e^0 \qquad {}^{238}_{94}Pu + {}_0n^1 \rightarrow {}^{90}_{38}Sr + {}^{147}_{56}Ba + {}_0n^1$$

Nuclear reactors

Characteristic features of nuclear reactors

- Reactor core
- Nuclear fuel -
- Moderators – Graphite, deuterium, heav
- Coolants – Benzene, polyphenols
- Control rods
- Reflector
- Pressure vessel
- Shielding

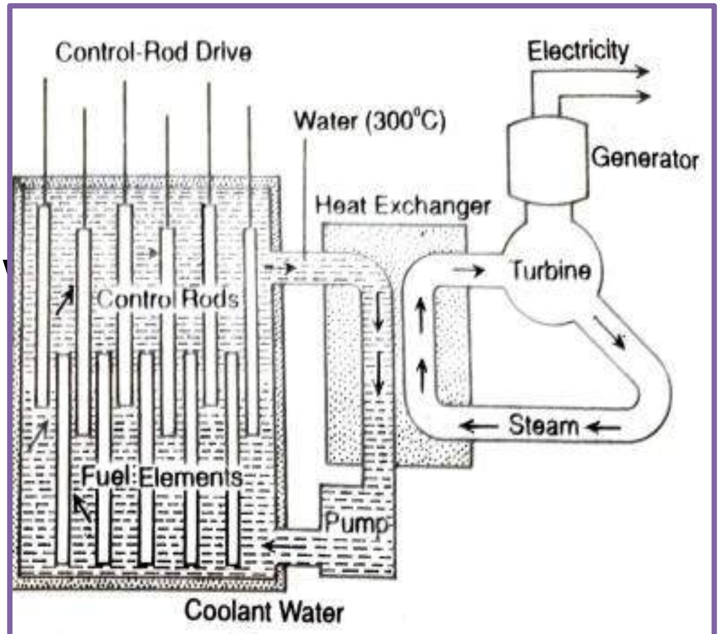


Fig. 1. Nuclear reactor.

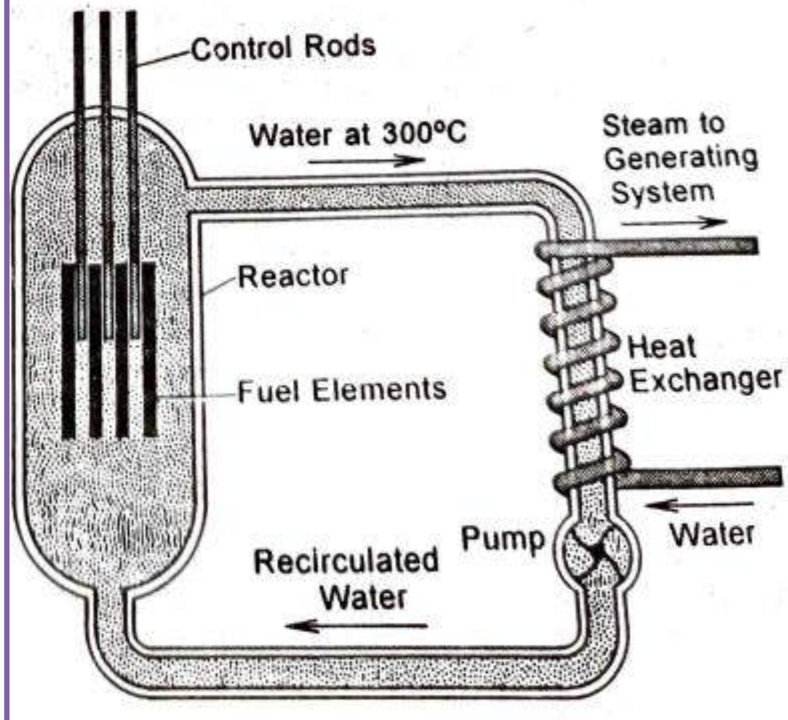


Fig. 2. Pressurised water type nuclear reactor.

Nuclear reactions (α, n), (n, α), (α, p), (p, α), (p, n) and (n, p).

- Nuclear transmutation reaction induced by alpha, neutron, and proton particles.

APPLICATIONS OF RADIOISOTOPES

- ^{131}I is used in the diagnosis and treatment of thyroid disorders; in brain scanning.
- ^{32}P is used in
  - i. Bone metastasis to control the pain
  - ii. In agriculture and synthesis of nucleotides
  - iii. In studying blood circulation.
- ^{60}Co is used in treatment of brain tumours.
- ^{24}Na is used in detecting the location of pipeline leaks
- $^{99}Tc^{m}$: (metastable nuclear isomer of Tc) Brain, heart, lung, thyroid, gall bladder, skin, lymph, node, bone, liver, spleen, and kidney imaging.
- ^{11}C, ^{13}N, ^{15}O, ^{18}F are used in PET (Positron Emission Tomography).
- ^{2}H, ^{13}C, ^{15}N, ^{18}O are used as tracers in chemical and biological reactions to find out the mechanisms and pathways.
- ^{35}S in heart diagnosis.

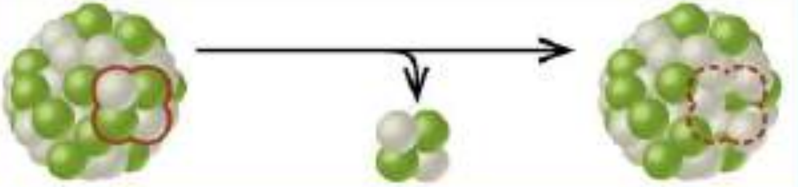
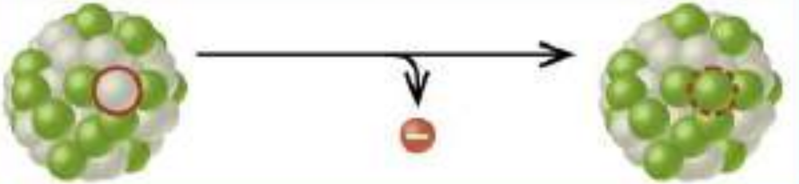
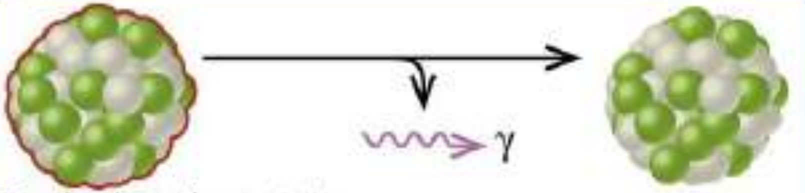
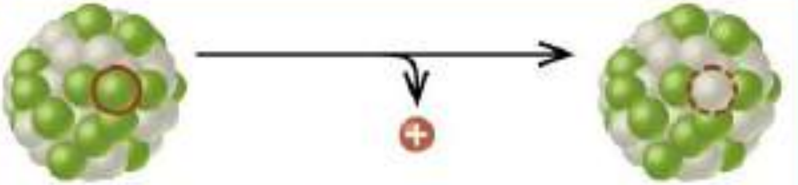
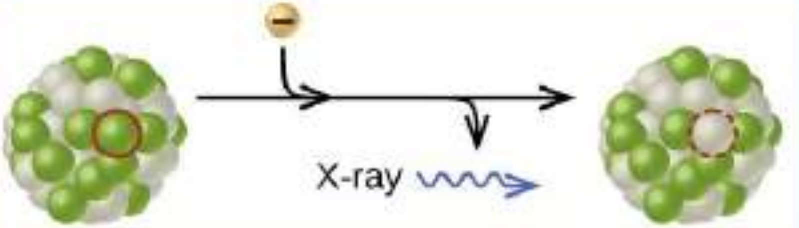
Ernest Rutherford experiments

- In 1899 Ernest Rutherford found that there were at least two different forms of radioactivity when he studied the absorption of radioactivity by thin sheets of metal foil. One, which he called *alpha () particles*, were absorbed by metal foil that was a few hundredths of a centimeter thick.
- The other, *beta (particles*, could pass through 100 times as much metal foil before they became absorbed. Shortly thereafter, a third form of radiation, *gamma () rays*, was discovered that could penetrate as much as several centimeters of lead.
- The results of early experiments on these three forms of radiation are shown in the figure below. The direction in which -particles were deflected by an electric field suggested that they were positively charged. The magnitude of this deflection suggested that they had the same charge-to-mass ratio as an He^{2+} ion. To test the equivalence between -particles and He^{2+} ions, Rutherford built an apparatus that allowed -particles to pass through a very thin glass wall into an evacuated flask that contained a pair of metal electrodes. After a few days, he connected these electrodes to a battery and noted that the gas in the flask did indeed give off the characteristic emission spectrum of helium.

LEARNING OUTCOMES FOR NUCLEAR CHEMISTRY

- Students will be able to…
- Explain the macroscopic observables associated with nuclear change and the microscopic or chemists view of nuclear change.
- Identify and define various types of nuclear transmutation including fission, fusion and decay reactions.
- Use proper isotopic notation to write down and balance a nuclear reaction.
- State and compare the differences and similarities between a nuclear change and a chemical change.
- Recall and properly use Einstein's theory of relativity equation, $E = mc^2$, to calculate the amount of energy released upon a nuclear change.
- Define binding energy and mass defect and be able to calculate each for a given nucleus.
- Understand and explain the concept of ionizing radiation and distinguish between the three different types of radiation.
- Understand and explain the concept of isotopic stability including the band of stability.
- Be familiar with the units used to quantify nuclear decay
- Understand the concept of rate of change and half life in the context of nuclear decay.
- Understand the basics of nuclear chemistry applications: nuclear power, medical treatment, isotopic labeling, and carbon dating.

Figure: summarizes these types of decay, along with their equations and changes in atomic and mass numbers.

Type	Nuclear equation	Representation	Change in mass/atomic numbers
Alpha decay	$^{A}_{Z}\mathrm{X} \qquad ^{4}_{2}\mathrm{He} + ^{A-4}_{Z-2}\mathrm{Y}$		A: decrease by 4 Z: decrease by 2
Beta decay	$^{A}_{Z}\mathrm{X} \qquad ^{0}_{-1}\mathrm{e} + ^{A}_{Z+1}\mathrm{Y}$		A: unchanged Z: increase by 1
Gamma decay	$^{A}_{Z}\mathrm{X} \qquad ^{0}_{0}\gamma + ^{A}_{Z}\mathrm{Y}$	 Excited nuclear state	A: unchanged Z: unchanged
Positron emission	$^{A}_{Z}\mathrm{X} \qquad ^{0}_{+1}\mathrm{e} + ^{A}_{Y-1}\mathrm{Y}$		A: unchanged Z: decrease by 1
Electron capture	$^{A}_{Z}\mathrm{X} \qquad ^{0}_{-1}\mathrm{e} + ^{A}_{Y-1}\mathrm{Y}$		A: unchanged Z: decrease by 1

NUCLEAR AND CHEMICAL PROPERTIES OF RADIONUCLIDES

- **Nuclear** and **chemical properties** of **radionuclides**
- Currently used in nuclear imaging and therapy.
- Nuclear forensics is a relatively new branch of nuclear chemistry that combines radiochemistry, nuclear physics, and material science to identify the origin of clandestine nuclear materials.
- The earlier actinides (**U, Np, Pu, Am, and Cm**) display a very rich redox chemistry. They can exist in a variety of oxidation states, ranging from +3 to +7 for neptunium and plutonium, from +3to +6 for americium, and from +3 and +4 for curium. It is noteworthy that Pu(IV), Pu(V), and Pu(VI) can coexist in oxic aqueous solutions due to their similar redox potentials.

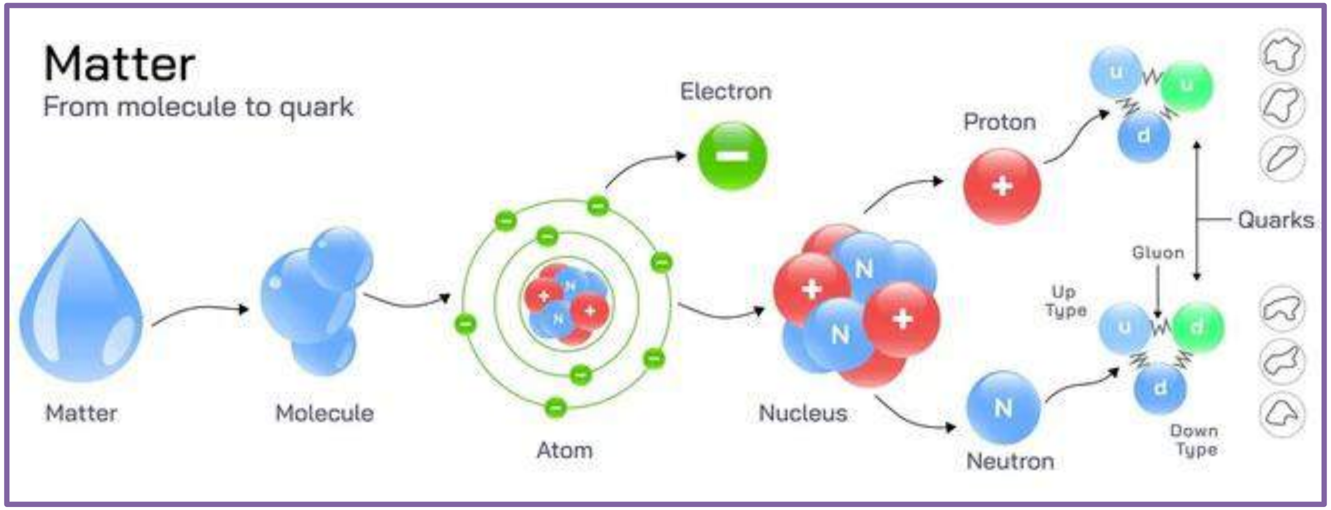
Neutron activation analysis

- NAA was discovered in 1936 by **George Charles de Hevesy** (Hungary) **and Hilde Levi** (Denmark).
- The analytical technique in which radioactive emissions are monitored from a sample that has been bombarded with neutrons is NAA.
- NAA is a sensitive multi-element analytical technique used for both qualititative and quantitative analysis of **major**, **minor**, **trace** and **rare** elements.
- NAA is a method for both qualititative and quantitative determination of elements based on the measurement of characteristic radiation from radionuclide's formed directly or indirectly by neutron irradiation of the material.

G. Hevesy

Hilde Levi

Extra information



Radiochemistry and Nuclear Chemistry - Gregory Choppin, Jan-olov liljenzin, Jan Rydberg, Christian Ekber

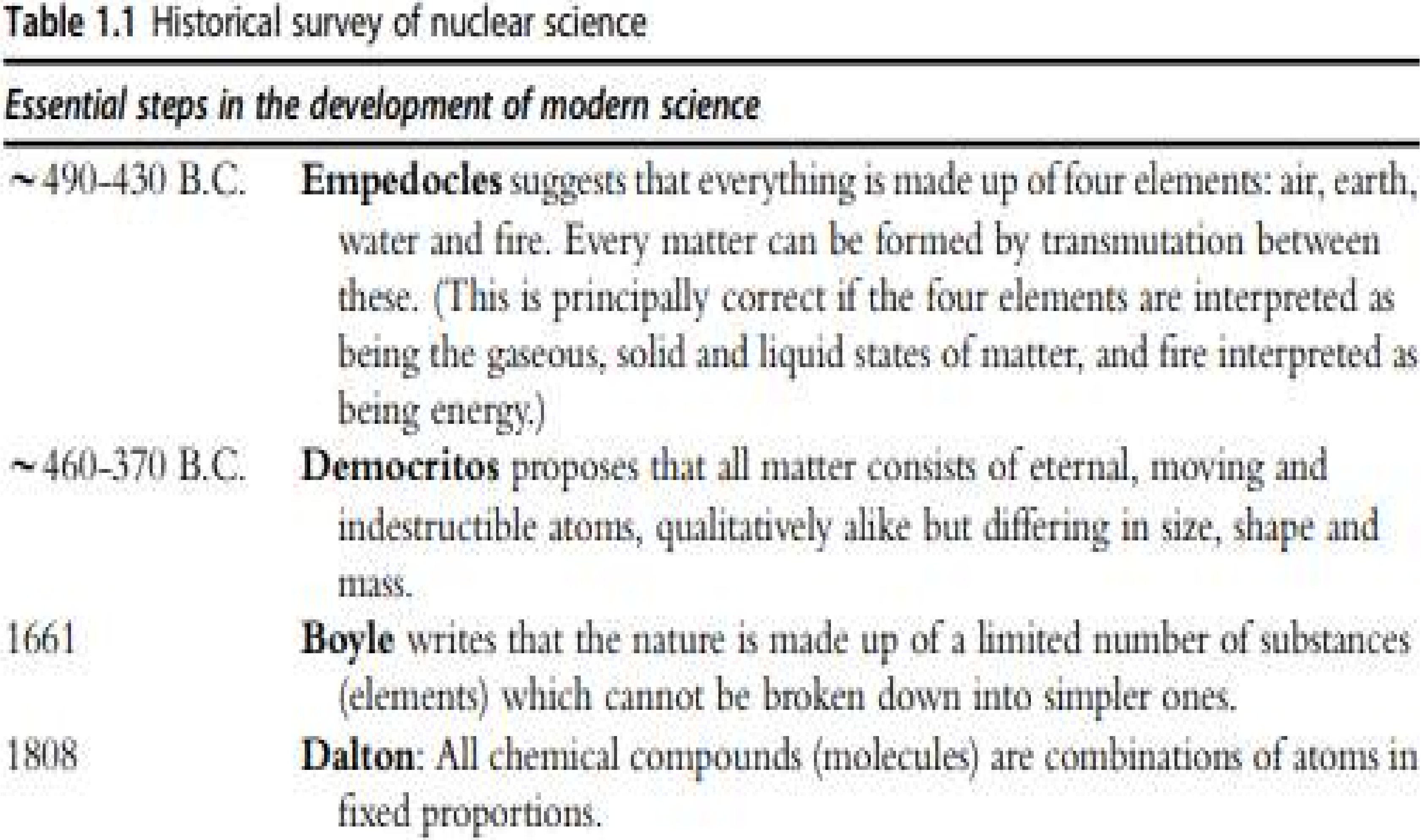
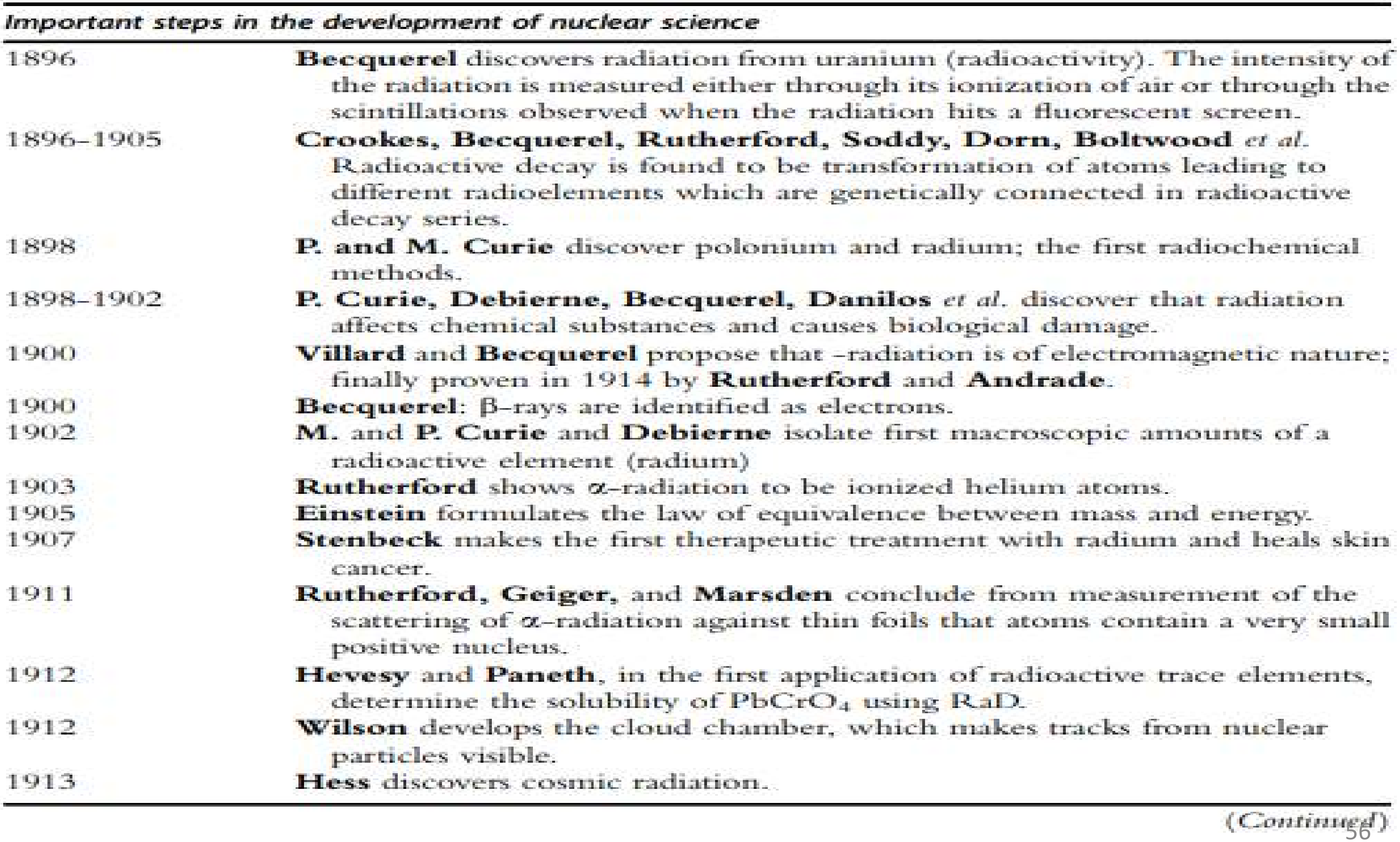


Table 1.1 Historical survey of nuclear science

Essential steps in the development of modern science	
~490-430 B.C.	**Empedocles** suggests that everything is made up of four elements: air, earth, water and fire. Every matter can be formed by transmutation between these. (This is principally correct if the four elements are interpreted as being the gaseous, solid and liquid states of matter, and fire interpreted as being energy.)
~460-370 B.C.	**Democritos** proposes that all matter consists of eternal, moving and indestructible atoms, qualitatively alike but differing in size, shape and mass.
1661	**Boyle** writes that the nature is made up of a limited number of substances (elements) which cannot be broken down into simpler ones.
1808	**Dalton**: All chemical compounds (molecules) are combinations of atoms in fixed proportions.



Important steps in the development of nuclear science

1896	**Becquerel** discovers radiation from uranium (radioactivity). The intensity of the radiation is measured either through its ionization of air or through the scintillations observed when the radiation hits a fluorescent screen.
1896–1905	**Crookes, Becquerel, Rutherford, Soddy, Dorn, Boltwood** *et al.* Radioactive decay is found to be transformation of atoms leading to different radioelements which are genetically connected in radioactive decay series.
1898	**P. and M. Curie** discover polonium and radium; the first radiochemical methods.
1898–1902	**P. Curie, Debierne, Becquerel, Danilos** *et al.* discover that radiation affects chemical substances and causes biological damage.
1900	**Villard** and **Becquerel** propose that -radiation is of electromagnetic nature; finally proven in 1914 by **Rutherford** and **Andrade**.
1900	**Becquerel**: β-rays are identified as electrons.
1902	**M.** and **P. Curie** and **Debierne** isolate first macroscopic amounts of a radioactive element (radium)
1903	**Rutherford** shows α-radiation to be ionized helium atoms.
1905	**Einstein** formulates the law of equivalence between mass and energy.
1907	**Stenbeck** makes the first therapeutic treatment with radium and heals skin cancer.
1911	**Rutherford, Geiger,** and **Marsden** conclude from measurement of the scattering of α-radiation against thin foils that atoms contain a very small positive nucleus.
1912	**Hevesy** and **Paneth**, in the first application of radioactive trace elements, determine the solubility of $PbCrO_4$ using RaD.
1912	**Wilson** develops the cloud chamber, which makes tracks from nuclear particles visible.
1913	**Hess** discovers cosmic radiation.

(*Continued*)

Table 1.1 Historical survey of nuclear science—cont'd

1913	**Fajans** and **Soddy** explain the radioactive decay series by assuming the existence of isotopes. This is proven by **J. J. Thomson** through deflection of neon ions in electromagnetic fields. **Aston** separates the isotopes of neon by gas diffusion.
1913	**N. Bohr** shows that the atomic nucleus is surrounded by electrons in fixed orbitals.
1919	**Rutherford**: first nuclear transformation in the laboratory, $^{4}He + {}^{14}N \rightarrow {}^{17}O + {}^{1}H$.
1919	**Aston** constructs the first practical mass spectrometer and discovers that isotopic weights are not exactly integers.
1921	**Hahn** discovers nuclear isomers: $^{234m}Pa(UX_2) \xrightarrow[1.2\ min]{\gamma} {}^{234}Pa(UZ)$
1924	**de Broglie** advances the hypothesis that all moving particles have wave properties.
1924	**Lacassagne** and **Lattes** use radioactive trace elements (Po) in biological research.
1925–1927	Important improvements of the Bohr atomic model: Pauli exclusion principle, Schrödinger wave mechanics, Heisenberg uncertainty relationship.
1928	**Geiger** and **Müller** construct the first GM tube for single nuclear particle measurements.
1931	**van de Graaff** develops an electrostatic high voltage generator for accelerating atomic ions to high energies.
1931	**Pauli** postulates a new particle, the neutrino, to be formed in β–decay.
1932	**Cockcroft** and **Walton** develop the high voltage multiplier and use it for the first nuclear transformation in the laboratory with accelerated particles (0.4 MeV $^{1}H + {}^{7}Li \rightarrow 2\ {}^{4}He$).
1932	**Lawrence** and **Livingston** build the first cyclotron.
1932	**Urey** discovers deuterium and obtains isotopic enrichment through evaporation of liquid hydrogen.
1932	**Chadwick** discovers the neutron.
1932	**Andersson** discovers the positron, e^{+} or β^{+}, through investigation of cosmic rays in a cloud chamber.
1933	**Urey** and **Rittenberg** show isotopic effects in chemical reactions.
1934	**Joliot** and **I. Curie** discover artificial radioactivity: $^{4}He + {}^{27}Al \rightarrow {}^{30}P + n$; $^{30}P \xrightarrow[2.5\ min]{\beta^{+}} {}^{30}Si$.
1935	**DeHevesy** develops neutron activation analysis.
1935	**Yukawa** predicts the existence of mesons.
1935	**Weizsäcker** derives the semiempirical mass formulae.
1937	**Neddermeyer** and **Andersson** discover μ–mesons in cosmic radiation using photographic plates.
1938	**Bethe** and **Weizsäcker** propose the first theory for energy production in stars through nuclear fusion: $3\ {}^{4}He \rightarrow {}^{12}C$.
1938	**Hahn** and **Strassman** discover fission products after irradiation of uranium with neutrons.

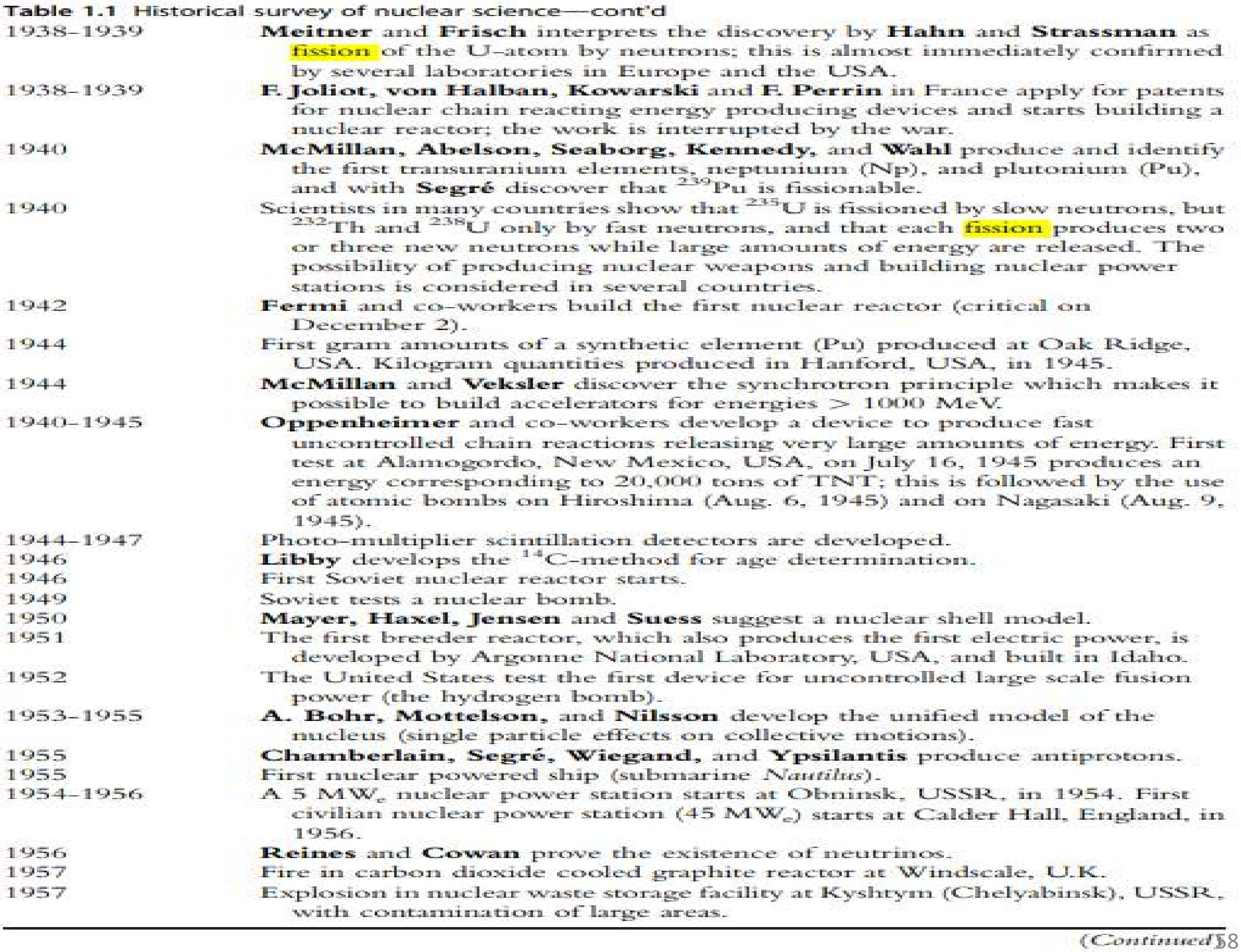


Table 1.1 Historical survey of nuclear science—cont'd

1938–1939	**Meitner** and **Frisch** interprets the discovery by **Hahn** and **Strassman** as fission of the U-atom by neutrons; this is almost immediately confirmed by several laboratories in Europe and the USA.
1938–1939	**F. Joliot, von Halban, Kowarski** and **F. Perrin** in France apply for patents for nuclear chain reacting energy producing devices and starts building a nuclear reactor; the work is interrupted by the war.
1940	**McMillan, Abelson, Seaborg, Kennedy,** and **Wahl** produce and identify the first transuranium elements, neptunium (Np), and plutonium (Pu), and with **Segré** discover that ^{239}Pu is fissionable.
1940	Scientists in many countries show that ^{235}U is fissioned by slow neutrons, but ^{232}Th and ^{238}U only by fast neutrons, and that each fission produces two or three new neutrons while large amounts of energy are released. The possibility of producing nuclear weapons and building nuclear power stations is considered in several countries.
1942	**Fermi** and co-workers build the first nuclear reactor (critical on December 2).
1944	First gram amounts of a synthetic element (Pu) produced at Oak Ridge, USA. Kilogram quantities produced in Hanford, USA, in 1945.
1944	**McMillan** and **Veksler** discover the synchrotron principle which makes it possible to build accelerators for energies > 1000 MeV.
1940–1945	**Oppenheimer** and co-workers develop a device to produce fast uncontrolled chain reactions releasing very large amounts of energy. First test at Alamogordo, New Mexico, USA, on July 16, 1945 produces an energy corresponding to 20,000 tons of TNT; this is followed by the use of atomic bombs on Hiroshima (Aug. 6, 1945) and on Nagasaki (Aug. 9, 1945).
1944–1947	Photo-multiplier scintillation detectors are developed.
1946	**Libby** develops the ^{14}C-method for age determination.
1946	First Soviet nuclear reactor starts.
1949	Soviet tests a nuclear bomb.
1950	**Mayer, Haxel, Jensen** and **Suess** suggest a nuclear shell model.
1951	The first breeder reactor, which also produces the first electric power, is developed by Argonne National Laboratory, USA, and built in Idaho.
1952	The United States test the first device for uncontrolled large scale fusion power (the hydrogen bomb).
1953–1955	**A. Bohr, Mottelson,** and **Nilsson** develop the unified model of the nucleus (single particle effects on collective motions).
1955	**Chamberlain, Segré, Wiegand,** and **Ypsilantis** produce antiprotons.
1955	First nuclear powered ship (submarine *Nautilus*).
1954–1956	A 5 MW$_e$ nuclear power station starts at Obninsk, USSR, in 1954. First civilian nuclear power station (45 MW$_e$) starts at Calder Hall, England, in 1956.
1956	**Reines** and **Cowan** prove the existence of neutrinos.
1957	Fire in carbon dioxide cooled graphite reactor at Windscale, U.K.
1957	Explosion in nuclear waste storage facility at Kyshtym (Chelyabinsk), USSR, with contamination of large areas.

(*Continued*)

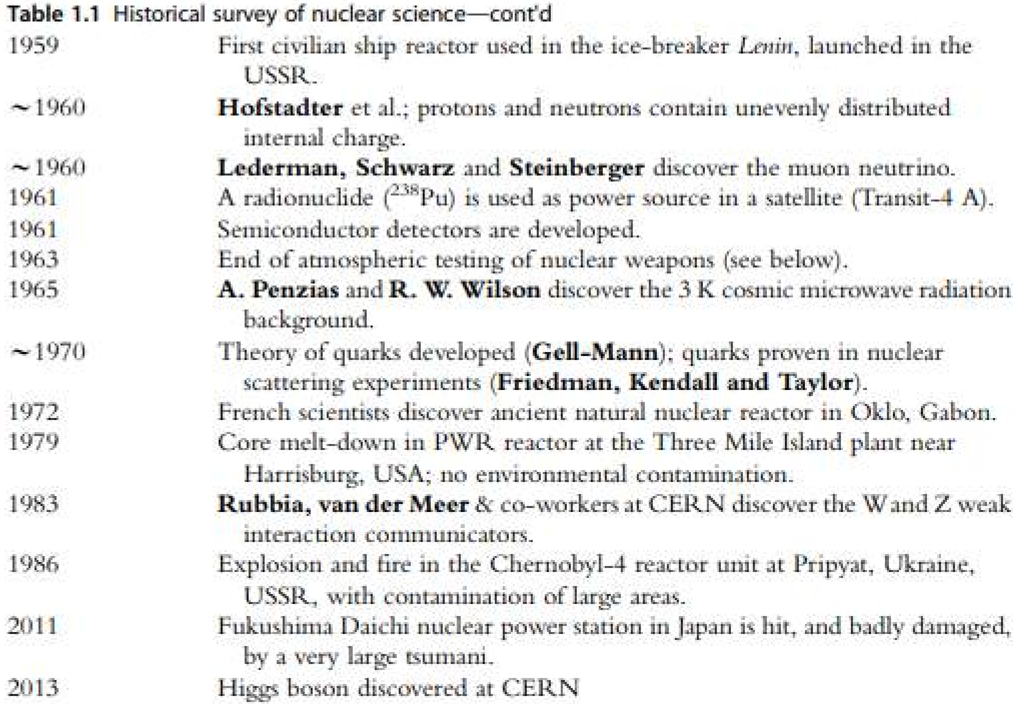
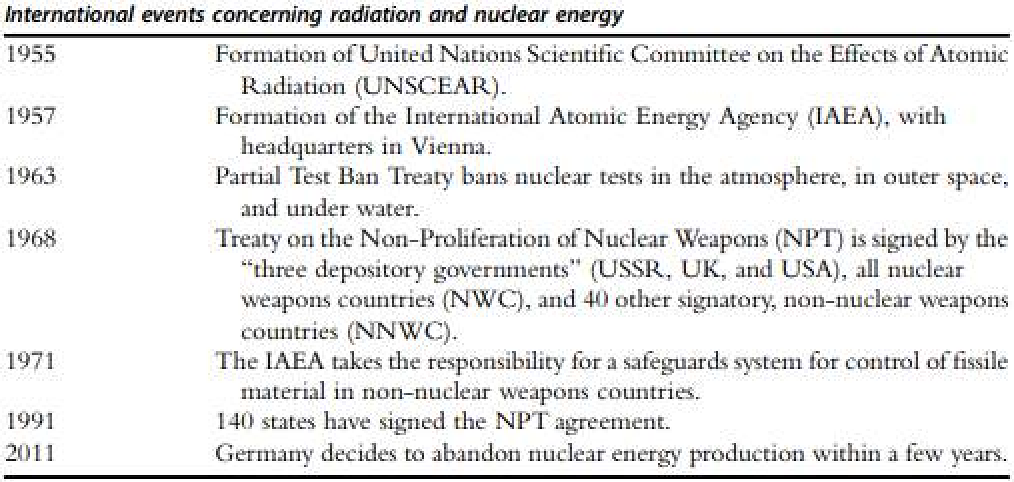


Table 1.1 Historical survey of nuclear science—cont'd

1959	First civilian ship reactor used in the ice-breaker *Lenin*, launched in the USSR.
~1960	**Hofstadter** et al.; protons and neutrons contain unevenly distributed internal charge.
~1960	**Lederman, Schwarz** and **Steinberger** discover the muon neutrino.
1961	A radionuclide (^{238}Pu) is used as power source in a satellite (Transit-4 A).
1961	Semiconductor detectors are developed.
1963	End of atmospheric testing of nuclear weapons (see below).
1965	**A. Penzias** and **R. W. Wilson** discover the 3 K cosmic microwave radiation background.
~1970	Theory of quarks developed (**Gell-Mann**); quarks proven in nuclear scattering experiments (**Friedman, Kendall and Taylor**).
1972	French scientists discover ancient natural nuclear reactor in Oklo, Gabon.
1979	Core melt-down in PWR reactor at the Three Mile Island plant near Harrisburg, USA; no environmental contamination.
1983	**Rubbia, van der Meer** & co-workers at CERN discover the W and Z weak interaction communicators.
1986	Explosion and fire in the Chernobyl-4 reactor unit at Pripyat, Ukraine, USSR, with contamination of large areas.
2011	Fukushima Daichi nuclear power station in Japan is hit, and badly damaged, by a very large tsumani.
2013	Higgs boson discovered at CERN



International events concerning radiation and nuclear energy

1955	Formation of United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR).
1957	Formation of the International Atomic Energy Agency (IAEA), with headquarters in Vienna.
1963	Partial Test Ban Treaty bans nuclear tests in the atmosphere, in outer space, and under water.
1968	Treaty on the Non-Proliferation of Nuclear Weapons (NPT) is signed by the "three depository governments" (USSR, UK, and USA), all nuclear weapons countries (NWC), and 40 other signatory, non-nuclear weapons countries (NNWC).
1971	The IAEA takes the responsibility for a safeguards system for control of fissile material in non-nuclear weapons countries.
1991	140 states have signed the NPT agreement.
2011	Germany decides to abandon nuclear energy production within a few years.

Standard Model of

FUNDAMENTAL PARTICLES AND INTERACTIONS

FERMIONS

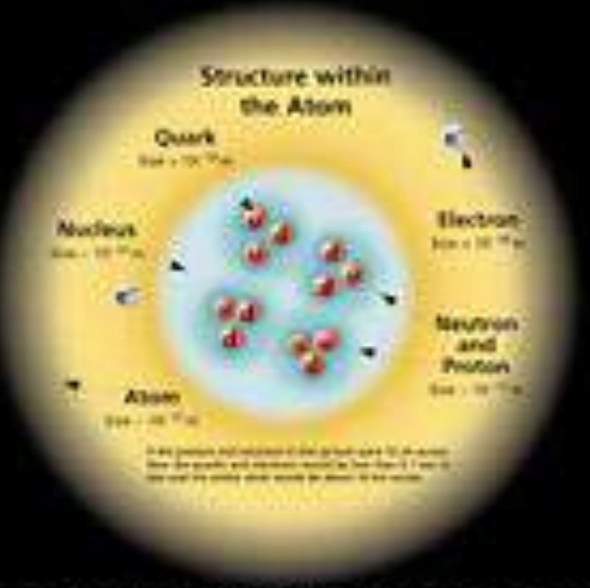
matter constituents
spin = 1/2, 3/2, 5/2, ...

Leptons spin = 1/2

Flavor	Mass GeV/c²	Electric charge
ν_e electron neutrino	<1×10⁻⁸	0
e electron	0.000511	−1
ν_μ muon neutrino	<0.0002	0
μ muon	0.106	−1
ν_τ tau neutrino	<0.02	0
τ tau	1.7771	−1

Quarks spin = 1/2

Flavor	Approx. Mass GeV/c²	Electric charge
u up	0.003	2/3
d down	0.006	−1/3
c charm	1.3	2/3
s strange	0.1	−1/3
t top	175	2/3
b bottom	4.3	−1/3



BOSONS

force carriers
spin = 0, 1, 2, ...

Unified Electroweak spin = 1

Name	Mass GeV/c²	Electric charge
γ photon	0	0
W^-	80.4	−1
W^+	80.4	+1
Z^0	91.187	0

Strong (color) spin = 1

Name	Mass GeV/c²	Electric charge
g gluon	0	0

Color Charge

Quarks Confined in Mesons and Baryons

Residual Strong Interaction

PROPERTIES OF THE INTERACTIONS

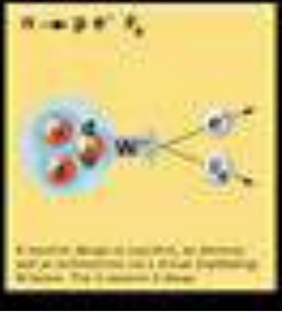
Property \ Interaction	Gravitational	Weak	Electromagnetic	Strong: Fundamental	Strong: Residual
Acts on:	Mass – Energy	Flavor	Electric Charge	Color Charge	[illegible]
Particles experiencing:	All	Quarks, Leptons	Electrically charged	Quarks, Gluons	Hadrons
Particles mediating:	Graviton	W^+ W^- Z^0	γ	Gluons	Mesons
Strength [illegible]	10^{-41}	0.8	1	25	Not applicable to quarks
[illegible]	10^{-41}	10^{-4}	1	60	
[illegible]	10^{-36}	10^{-7}	1	Not applicable to hadrons	20

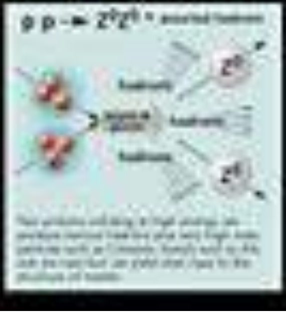
Baryons qqq and Antibaryons q̄q̄q̄

Mesons qq̄

Matter and Antimatter

Figures





The Particle Adventure

Sponsors

UNIT – IV - MASS SPECTROSCOPY
PAPER - II

By
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MASS SPECTROMETRY 5 HOURS

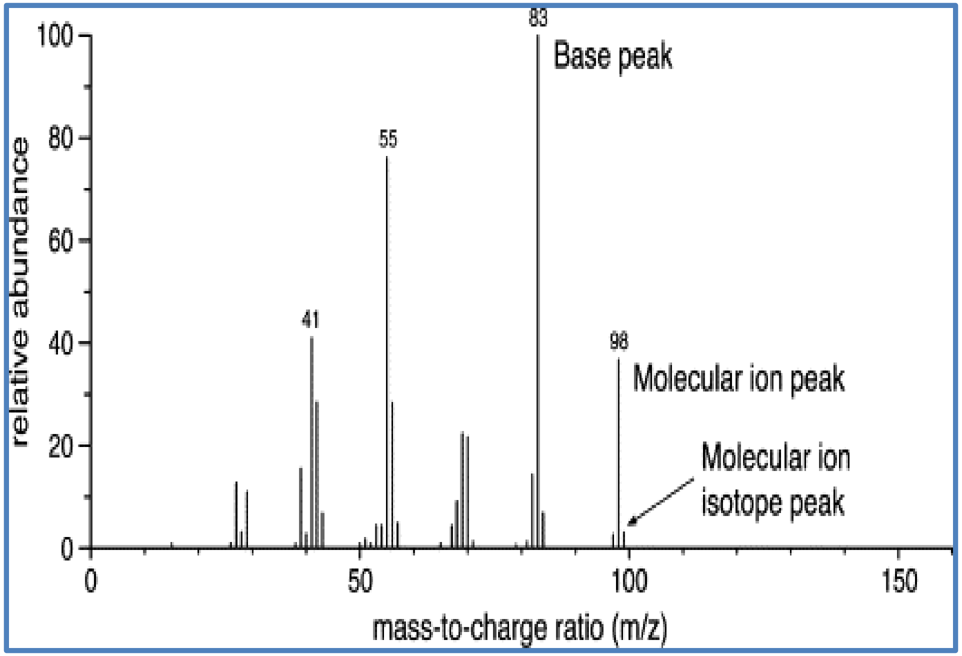
- Principle,
- Determination of m/e ratio,
- Instrumentation
- Determination of molecular mass and isotopic abundance.
- Molecular ion peak and base peak,
- McLafferty rearrangement with respect to
  - 2- hexanone,
  - Hexenoic acid and
  - Methyl hexanoate.

WHAT IS MASS SPECTROMETRY?

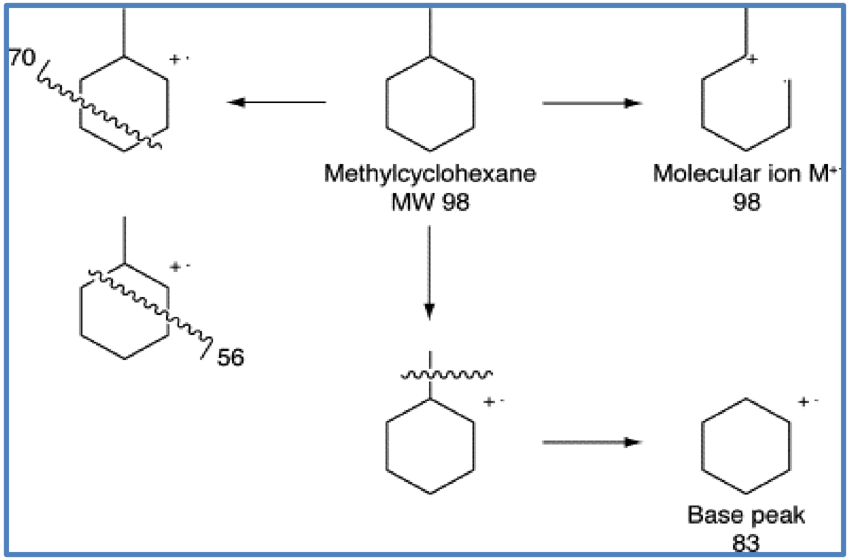
Mass spectrometry is an instrumental technique in which sample is converted to rapidly moving positive ions by electron bombardment and charged particles are separated according to their masses.

WHAT IS MASS SPECTRUM?

Mass spectrum is a plot of relative abundance against the ratio of mass/charge (m/e).



Mass spectrum of methylcyclohexane



APPLICATIONS OF MASS SPECTROSCOPY

Specific applications of mass spectrometry include

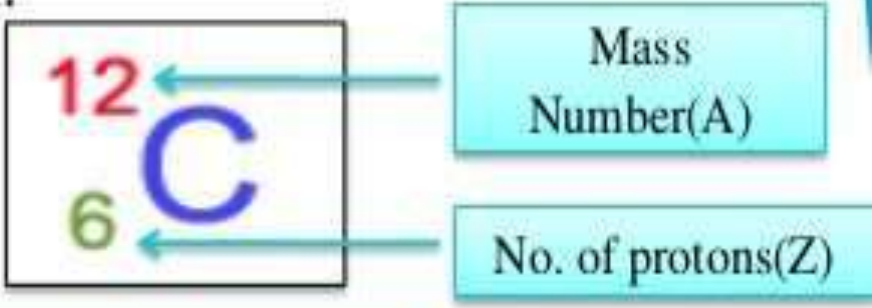
- Elucidation of the structure of the organic and biological molecules
- Determination of molecular mass of peptides, proteins and oligonuleotides
- Drug testing and identification metabolites of drugs in blood, urine, and saliva.
- Analysis of aerosol particles.
- Food contamination detection,
- Determination pesticide residues analysis.
- Isotope ratio determination, protein identification, and carbon dating.

MS INSTRUMENT AT NCBS

Example:-

Carbon atom have 6 protons and 6 neutrons in the centre of the nucleus, 2 electrons situated in the inner orbital where as other 4 electrons are outside the orbital.

We can represent carbon atom like

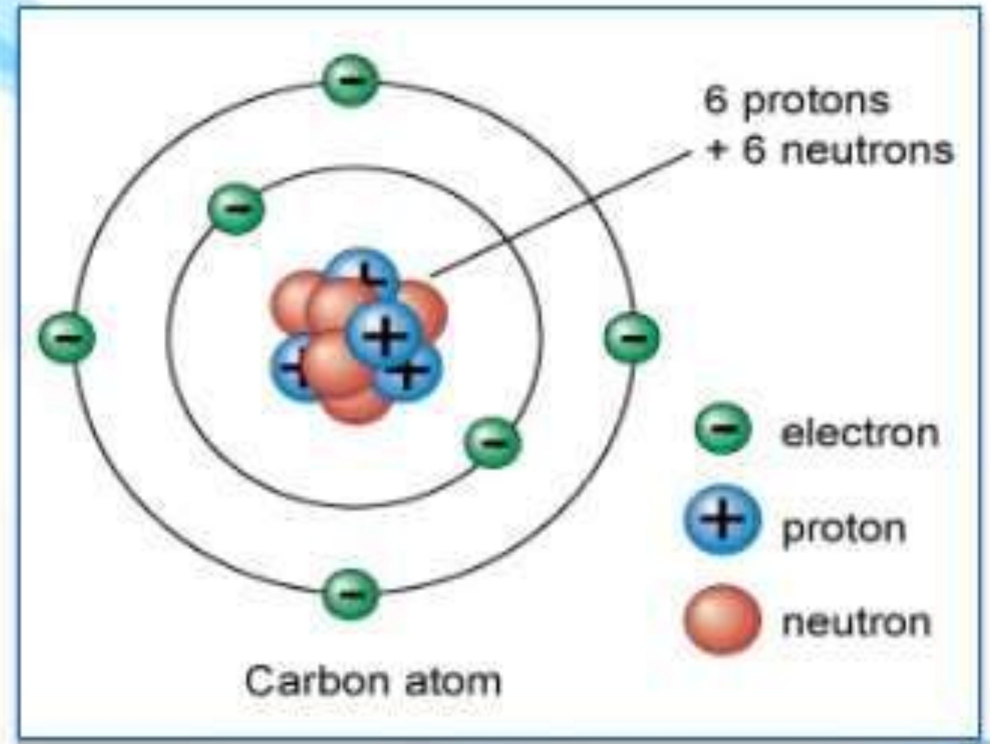


$^{12}_{6}\mathrm{C}$

Mass Number(A)

No. of protons(Z)

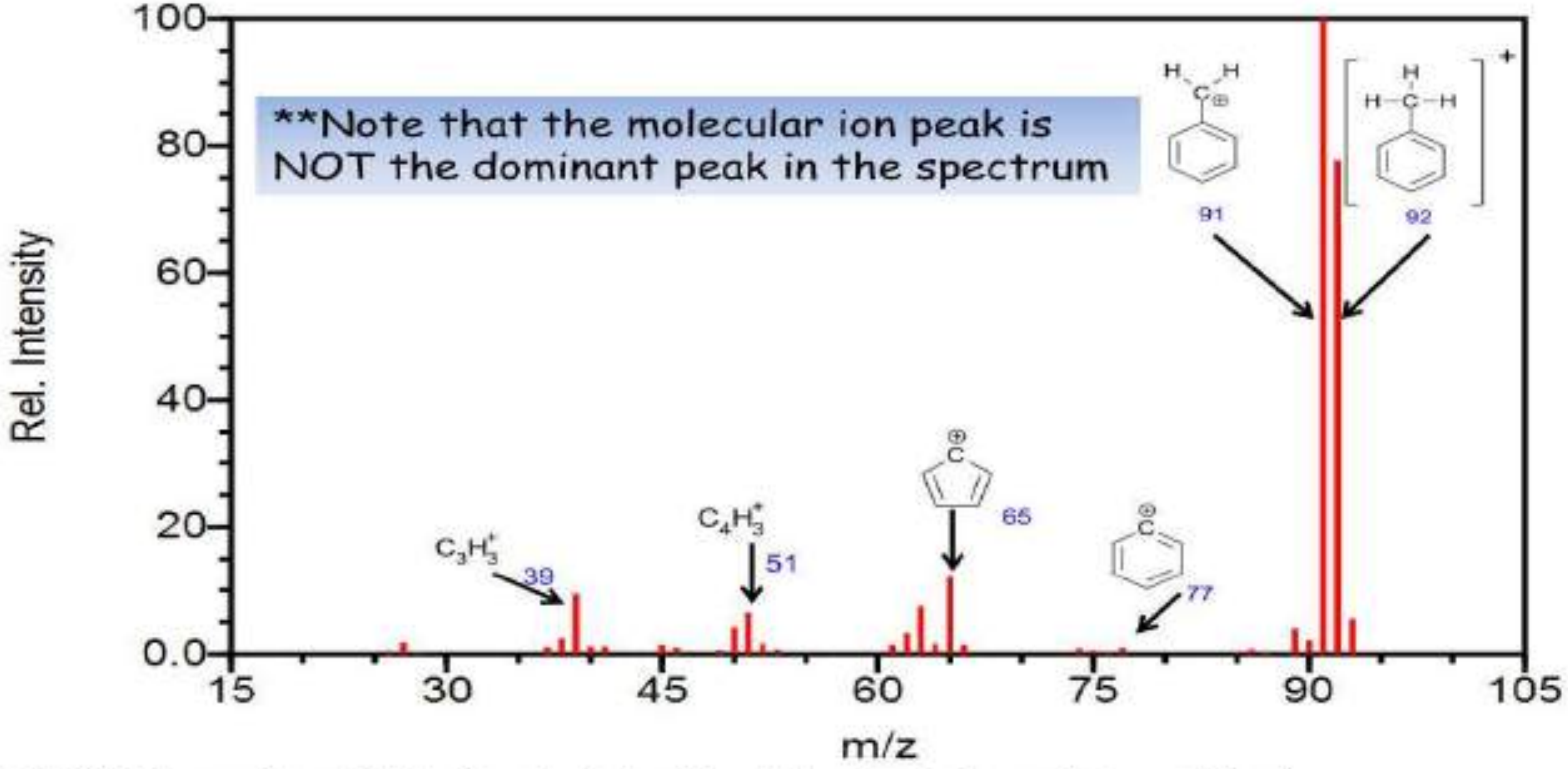
Carbon Atom:-



Carbon atom

MASS SPECTRUM OF TOLUENE

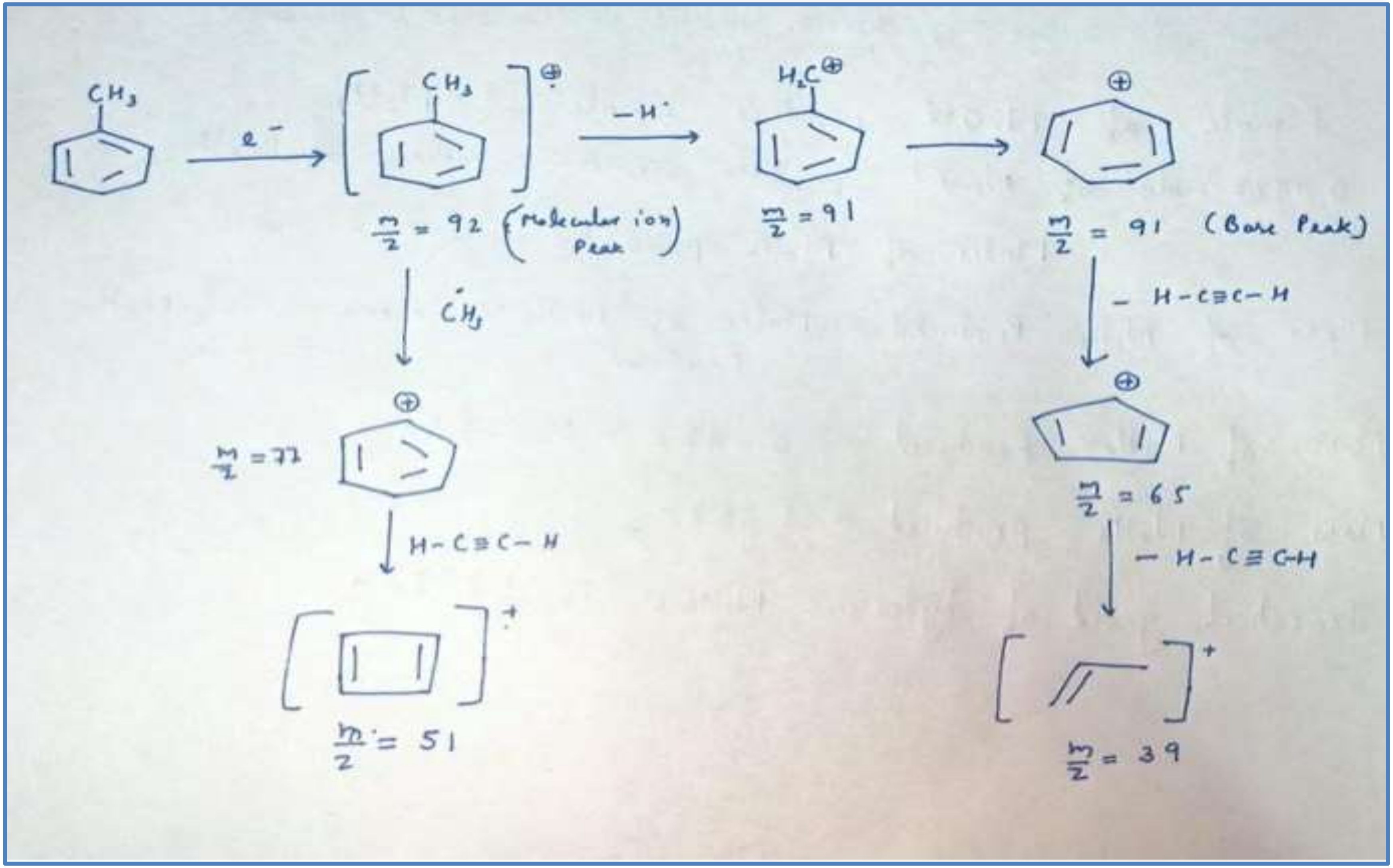
Toluene (C_7H_8) Fragmentation



**Note that the molecular ion peak is NOT the dominant peak in the spectrum

NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

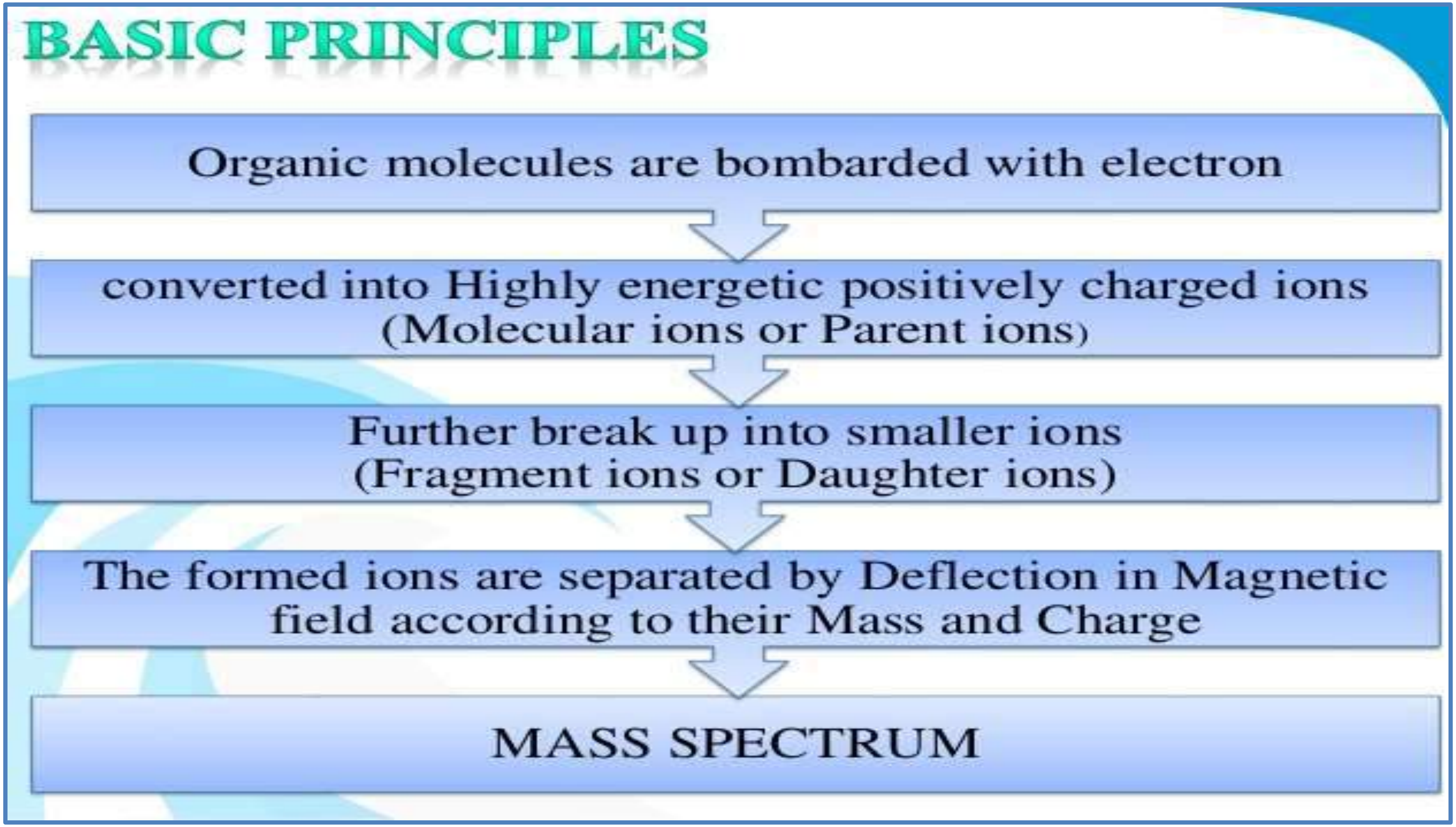
MASS SPECTRUM OF TOLUENE



39 – allylic carbocation, 51 – butyl cationcation, 91 – tropylium carboation

THREE PRINCIPLE BEHIND MASS

- To measure relative molecular masses
- To know the fragmentation of the molecules.
- Comparison of mass spectra with known compounds



BASIC PRINCIPLES

Organic molecules are bombarded with electron

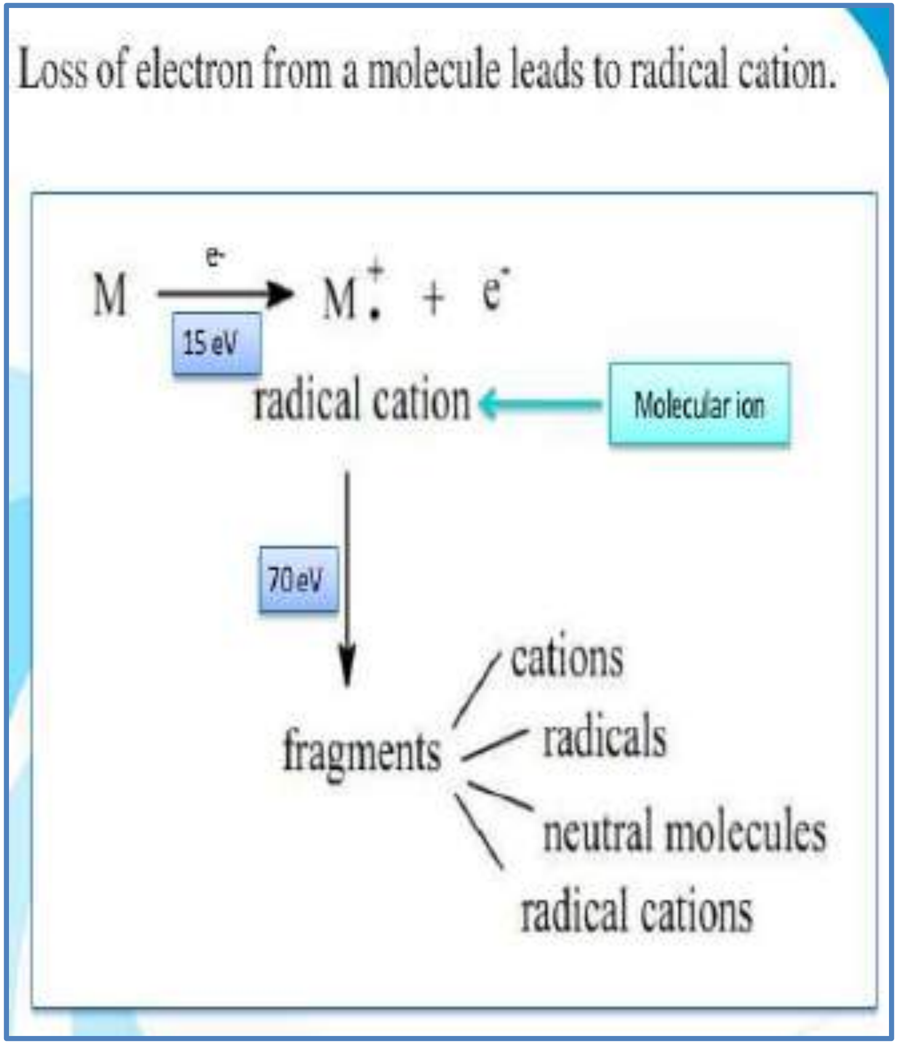
converted into Highly energetic positively charged ions (Molecular ions or Parent ions)

Further break up into smaller ions (Fragment ions or Daughter ions)

The formed ions are separated by Deflection in Magnetic field according to their Mass and Charge

MASS SPECTRUM

THEORY OF MS AND ENERGY CONSIDERATIONS



Loss of electron from a molecule leads to radical cation.

$$M \xrightarrow[15\ eV]{e^-} M^{+\bullet} + e^-$$

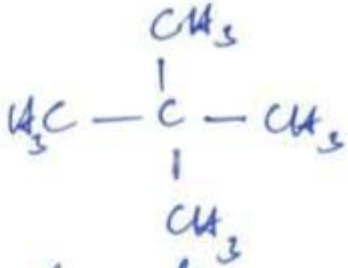
- Electron removed from molecule orbital having lowest ionization potential (IP).
- In general $n < \pi < \sigma$

Compounds	Ionization potential
CH_4	12.6 eV
C_2H_4	10.52 eV
CH_3NH_2	10.3 eV

1 eV = 23 Kcal/mol

CONSIDER AN EXAMPLE – NEOPENTANE

- Mass spectroscopy (MS) is used to determine ① mol. mass of the compounds. & ② its elemental composition.
- It is most accurate method amongst all other spectroscopic techniques.



$$CH_3-C(CH_3)_2-CH_3$$

Neopentane

$$C_5H_{12} \longrightarrow (12\times5)+(1\times12)$$

$$= 60+12 = 72. \quad (\text{M. wt.})$$

- Signal will appear in the form of mass to charge ratio (m/e or m/z)
- Generally charge will be +1 in most of the cases; rarely it will be +2.
- $72/_{+1} = \boxed{72} \longrightarrow$ Molecular weight.

FRAGMENTATION OF THE NEOPENTANE

- Molecular ions will be fragmented.

molecular ion

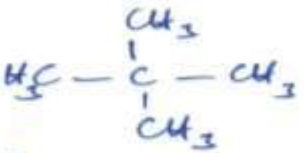
$M + e^- \longrightarrow \dot{M}^{+\cdot} + 2e^-$ — e^-, e^-

$\dot{m}_1^+ + \dot{m}_2$ $\quad$ $\dot{m}_1 + m_2^+$] Fragment ions

→ stable ions ←

why free radicals are not detected by M.S

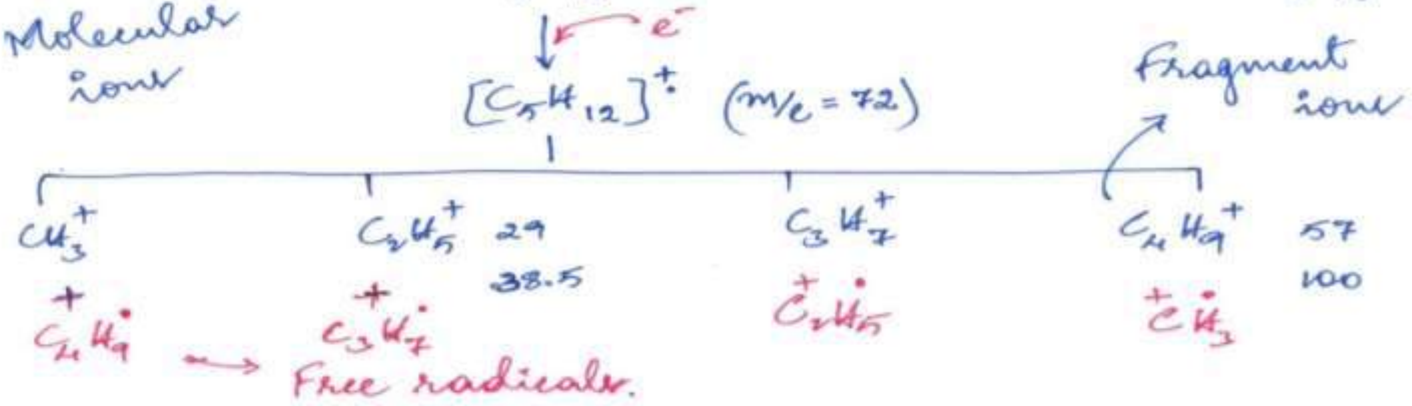
$M^+ , m_1^+ , m_2^+ \longrightarrow$ Detected in M.S.



Neopentane $\longrightarrow C_5H_{12}$

Relative intensity

M/e	= 72	$(C_5H_{12})^+$	
	= 57	$(C_4H_9^+)$	Base 100 peak
	= 41	$(C_3H_5^+)$	41.
	= 29	$(C_2H_5^+)$	38.
	= 27	$(C_2H_3^+)$	15.
	= 15	(CH_3^+)	



Molecular ion

$C_5H_{12} \xrightarrow{e^-} [C_5H_{12}]^{+\cdot}$ $(m/e = 72)$

Fragment ions

$CH_3^+ + C_4H_9^\cdot$

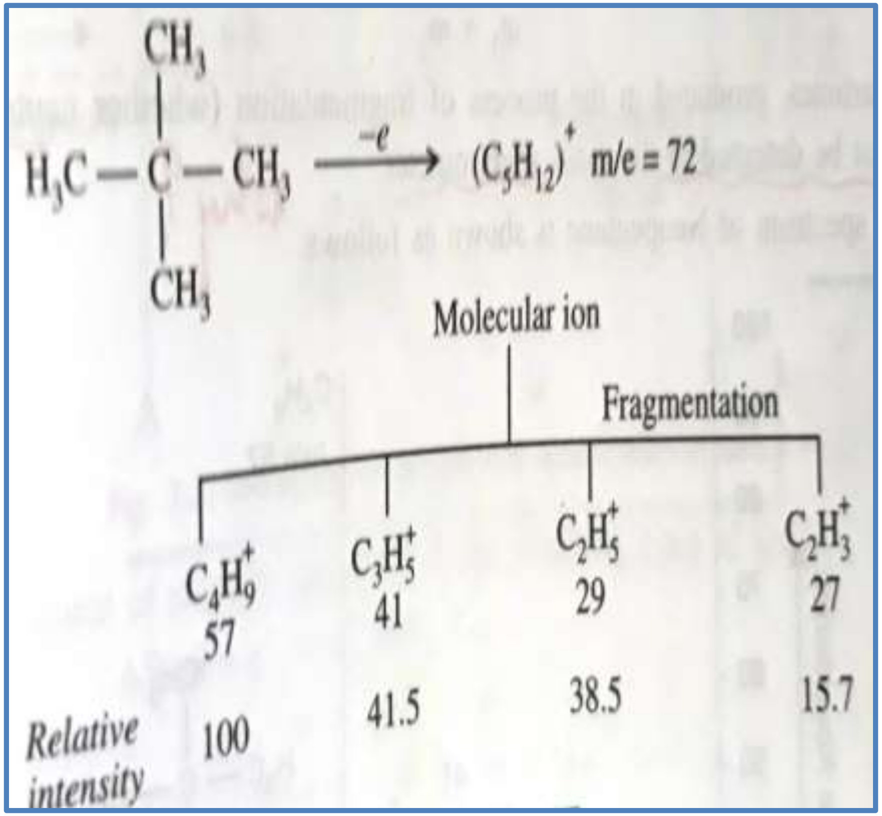
$C_2H_5^+$ 29, 38.5, $+ C_3H_7^\cdot$

$C_3H_7^+ + C_2H_5^\cdot$

$C_4H_9^+$ 57, 100 Relative intensity, $+ CH_3^\cdot$

→ Free radicals.

NEOPENTANE



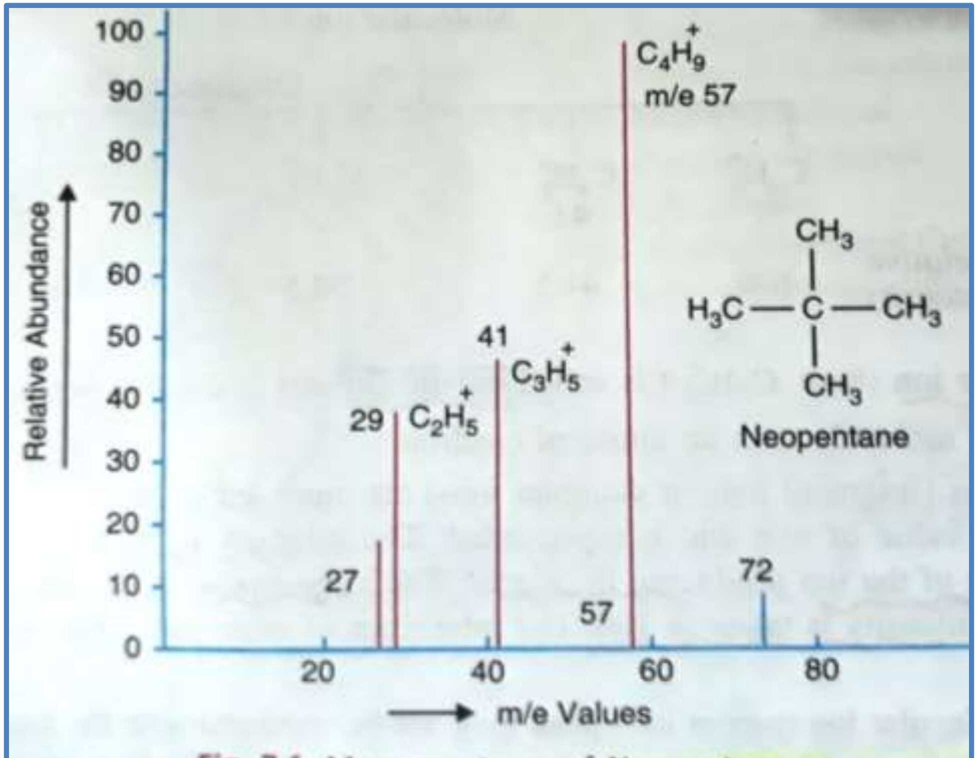
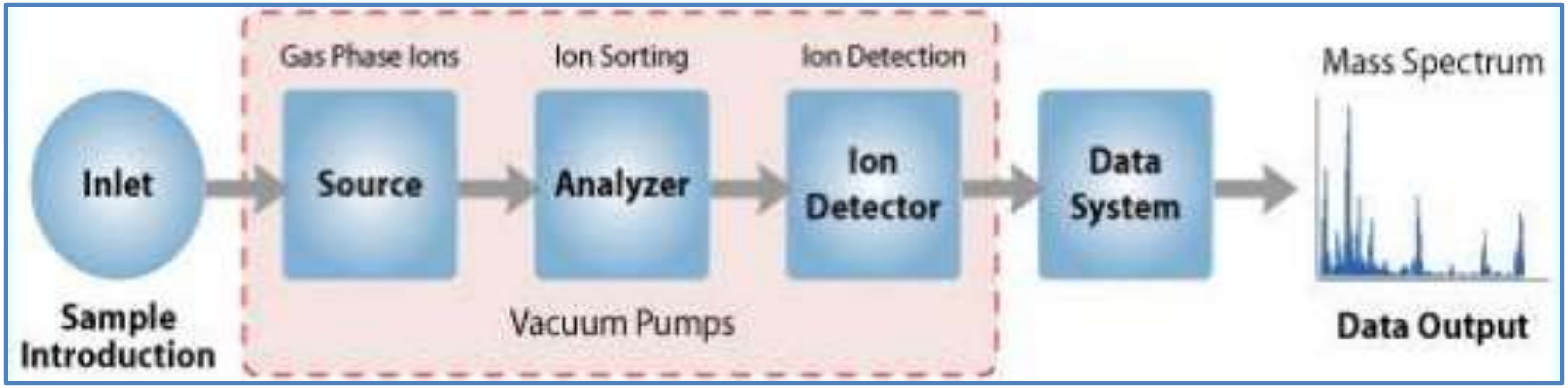


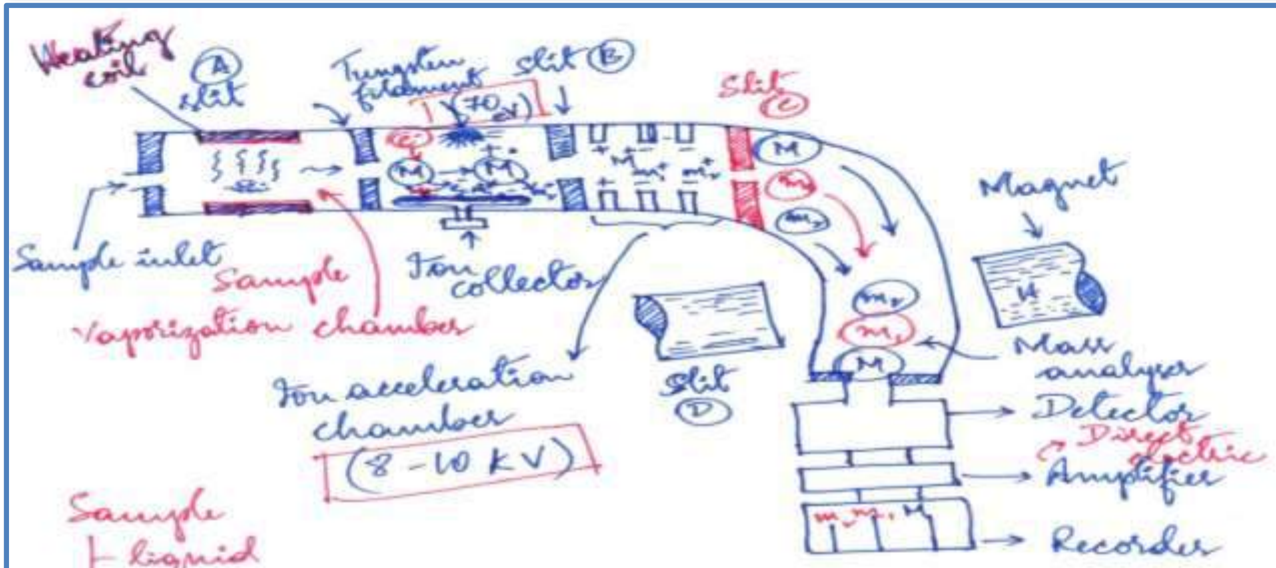
Fig. 7.1. Mass spectrum of Neopentane.

MASS SPECTROMETER – COMPONENTS

- Sample inlet
- Sample vaporization chamber - Source
- Ion collector
- Ion acceleration chamber
- Mass analyzers – Magnetic coils deflector
- Ion detectors
- Detector - Amplifier – MS spectrum



INSTRUMENTATION SET UP



Sample
- liquid
- Gas
- Solid

Ionization chamber

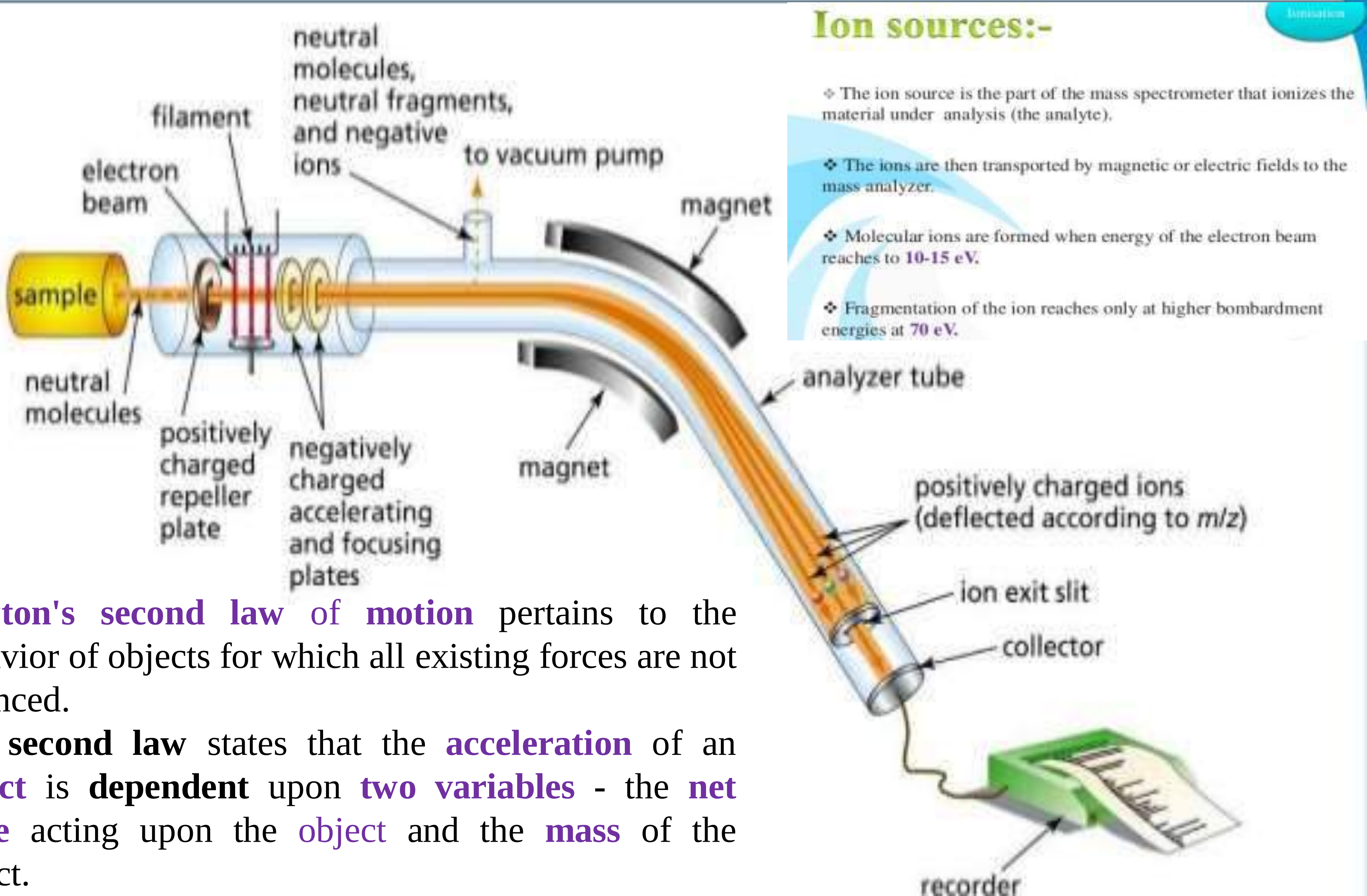
* Ionization potential

↳ minimum potential required to convert M to M^+, approximate value is 8 to 15 eV

* Types of mass analyser

① Magnetic field deflection
② Double focussing
③ Quadrupole
④ Time of flight
⑤ FT - ICR.
Fourier transform ion cyclotron resonance.

INSTRUMENTATION



Ion sources:-

- The ion source is the part of the mass spectrometer that ionizes the material under analysis (the analyte).
- The ions are then transported by magnetic or electric fields to the mass analyzer.
- Molecular ions are formed when energy of the electron beam reaches to **10-15 eV.**
- Fragmentation of the ion reaches only at higher bombardment energies at **70 eV.**

Newton's second law of motion pertains to the behavior of objects for which all existing forces are not balanced.

The **second law** states that the **acceleration** of an **object** is **dependent** upon **two variables** - the **net force** acting upon the object and the **mass** of the object.

THE TERM M/E OR M/Z VALUE

$$\frac{1}{2}mv^2 = eV \quad \text{———} \quad ①$$

m = mass of the ion

v = velocity of the ion

e = charge on the ion

V = Potential difference or potential applied.

From Newton's second law of motion

$$HeV = \frac{mv^2}{r} \quad \text{———} \quad ②$$

H = applied magnetic field

r = radius of the path

squaring both the sides in eqn. ②.

$$H^2e^2\cancel{v^2} = \frac{m^2 v^{\overset{2}{\cancel{4}}}}{r^2} \quad \text{———} \quad ③$$

$$H^2e^2 = m^2\frac{v^2}{r^2} \quad \text{———} \quad ④.$$

Rearrange eqn ①

$$mv^2 = 2eV \quad \text{———} \quad ⑤$$

Put the value of mv^2 from eqn ⑤ to ④.

$$H^2e^{\cancel{2}} = m.\frac{2\cancel{e}V}{r^2} \quad ; \quad H^2e = \frac{2mV}{r^2}$$

$$(\text{or}) \quad \boxed{\frac{m}{e} = \frac{H^2r^2}{2V}} \quad \text{———} \quad ⑥$$

IONIZATION TECHNIQUES

- Mass spectrum is significantly depended upon the ionization method.
- Variations in the spectrum is introduced in terms of
  - Number of peaks
  - Intensity of peaks (specially molecular ions)

Ionization Technique can be categorised into three parts

- Methods

① Gas phase
- EI e⁻ impact ionization
- CI chemical ionization

② Desorption
- Field desorption
- FAB
- MALDI

③. Evaporation
- Thermospray
- ESI electron spray ionization
- APCI
- APPI

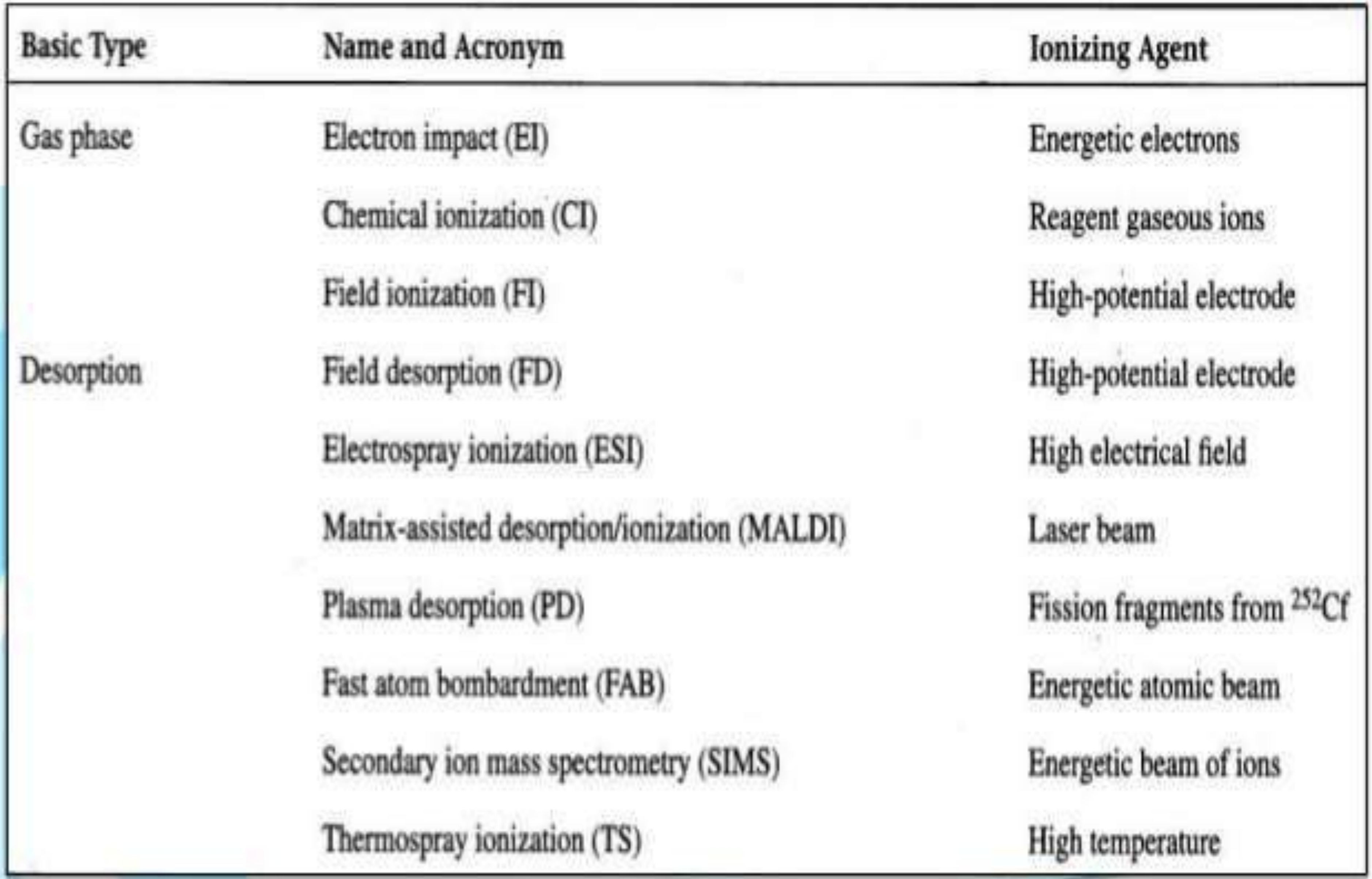
① * Gas phase ionization
- oldest and most popular method.
- Sample is vaporised before ionized

(EI) Electron Ionization – direct ionization thro' e⁻ beam

(CI) chemical ionization
- carrier gas will be ionised, then secondary ions will be produced & ions will be transferred to the analytes

② * Desorption Ionization Method
- Liquid/solid samples will be directly converted into gaseous ions

IONIZING AGENT IN MS



Basic Type	Name and Acronym	Ionizing Agent
Gas phase	Electron impact (EI)	Energetic electrons
	Chemical ionization (CI)	Reagent gaseous ions
	Field ionization (FI)	High-potential electrode
Desorption	Field desorption (FD)	High-potential electrode
	Electrospray ionization (ESI)	High electrical field
	Matrix-assisted desorption/ionization (MALDI)	Laser beam
	Plasma desorption (PD)	Fission fragments from ^{252}Cf
	Fast atom bombardment (FAB)	Energetic atomic beam
	Secondary ion mass spectrometry (SIMS)	Energetic beam of ions
	Thermospray ionization (TS)	High temperature

IONIZATION METHOD IN MS

IONISATION METHOD	COMPOUNDS	MASS RANGE
Electron impact ionisation	Thermally volatile and stable	500 Da
Chemical ionisation	Thermally volatile and Stable	500 Da
Electro spray ionisation	Polar and Basic	70000 Da
Fast atom bombardment	Peptides	7000 Da
Field ionisation	Thermally volatile	1000 Da
MALDI	Large Biomolecules	3,00,000 Da
Plasma desorption	Neutral compounds	500 Da
APCI	Thermally liable	1000 Da
SIMS	Same as FAB	300-13000 Da
Laser desorption	Elemental analysis	500 Da

TYPES OF PEAKS IN MS

- Molecular ion peak
- Fragment ions peak
- Rearrangement ions peak
- Metastable ion peaks
- Multicharged ions
- Base peak
- Negative ion peak

Molecular ion Peak:-

When a sample is bombarded with electrons of 9 to 15 eV energy, the molecular ion is produced, by loss of single electron.

$$M \xrightarrow{e^-} M^+ + 2e^-$$

Fragment ions Peak:-

when an energy is given further more upto 70 eV, fragment ions produced, it have lower mass number.

Rearrangement ion Peak:-

Recombination of fragment ion is known as Rearrangement Peaks.

Metastable ion Peak:-

The ions resulting from the decomposition between the source region and magnetic analyser are called as Meta stable ions.These appear as broad peaks called Metastable ion Peaks.

Multicharged ions:-

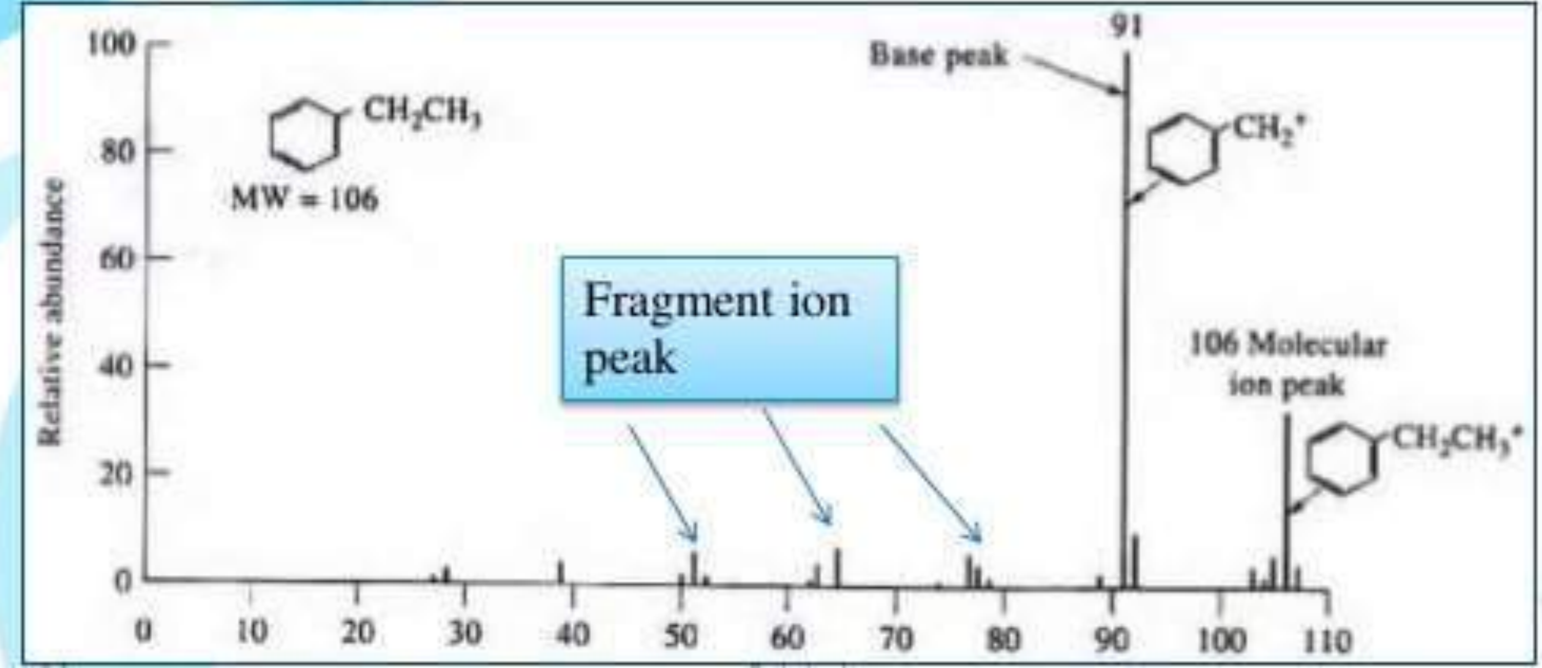
Ions may exist with 2 or 3 charges instead of usual single charge.The peaks due to these charged ions are known as Multicharged ion peaks.

Base Peak:-

The largest peak in the mass spectrum corresponding to the most abundant ion or most intense peak in the spectrum is called as Base Peak.

Negative ion Peak:-

Negative ions are formed from electron bombardment of sample. These results due to the capture of electron by a molecule during collision of molecules

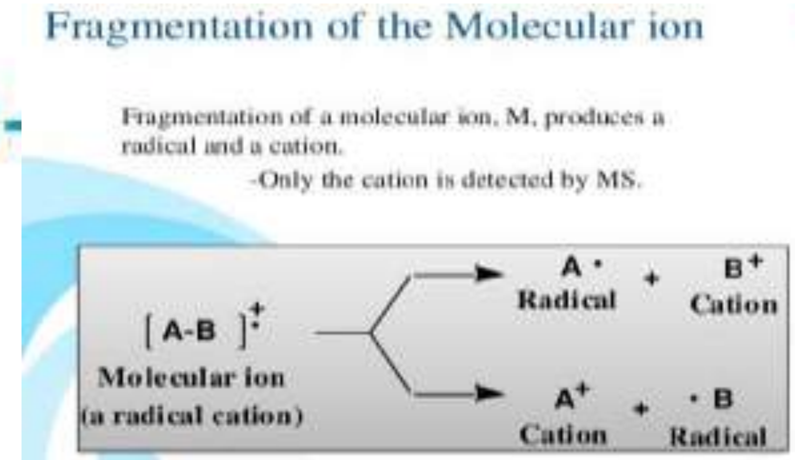


FRAGMENTATION

Fragmentation is a type of chemical dissociation.
Fragmentation takes place by a process of heterolysis or homolysis.

Types of Fragmentation:-

- Collision induced dissociation(CID)
- Electron capture dissociation(ECD)
- Electron transfer dissociation(ETD)
- Electron detachment dissociation(EDD)
- Photo dissociation
  - Infrared multiphoton dissociation(IRMPD)
  - Blackbody infrared radiative dissociation(BIRD)
- Surface induced dissociation(SID)
- Charge remote fragmentation
- Higher energy C-trap dissociation(HCD)



Fragmentation of the Molecular ion

Fragmentation of a molecular ion, M, produces a radical and a cation.

-Only the cation is detected by MS.

MASS INTERPRETATION

- Fragmentation rules
- **McLafferty rearrangement**
- Alpha cleavage
- Beta cleavage
- Nitrogen rule
- Retro diels alder reaction
- IHD – index of hydrogen deficiency

MCLAFFERTY REARRANGEMENT

⑤
M-S

Mclafferty Rearrangement

- It involves the migration of γ-hydrogen atom followed by the cleavage of a β-bond. The rearrangement leads to the elimination of neutral molecules from aldehydes, ketones, amines, unsaturated compounds, substituted aromatic compounds etc. The rearrangement proceeds thro' a sterically hindered six membered transition state.

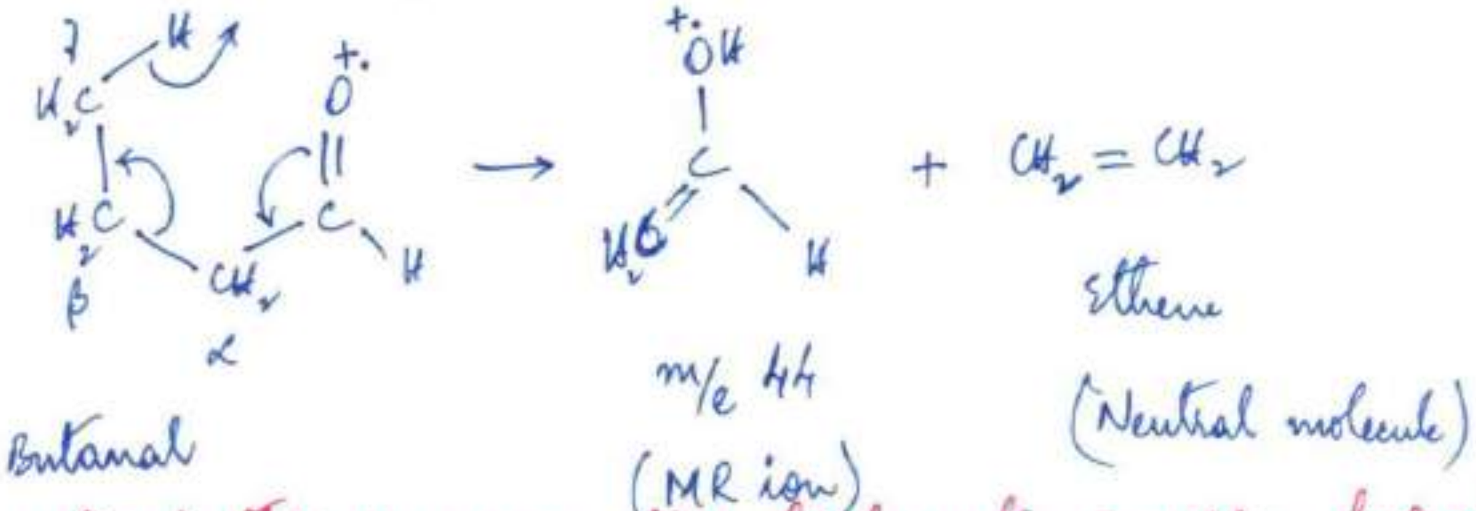
Ex: consider a general compound (ketone).

M.R ion = Mclafferty rearrangement ion.

Note: * In this rearrangement, radical centre in M ion derived from a lone pair or π-bond
* removes H from γ position
* π bond is formed b/w β & γ position
* a bond is broken b/w α & β position.

CONSIDER AN EXAMPLE

Ex: Butyraldehyde/Butanal.



Butanal

m/e 44

(MR ion)

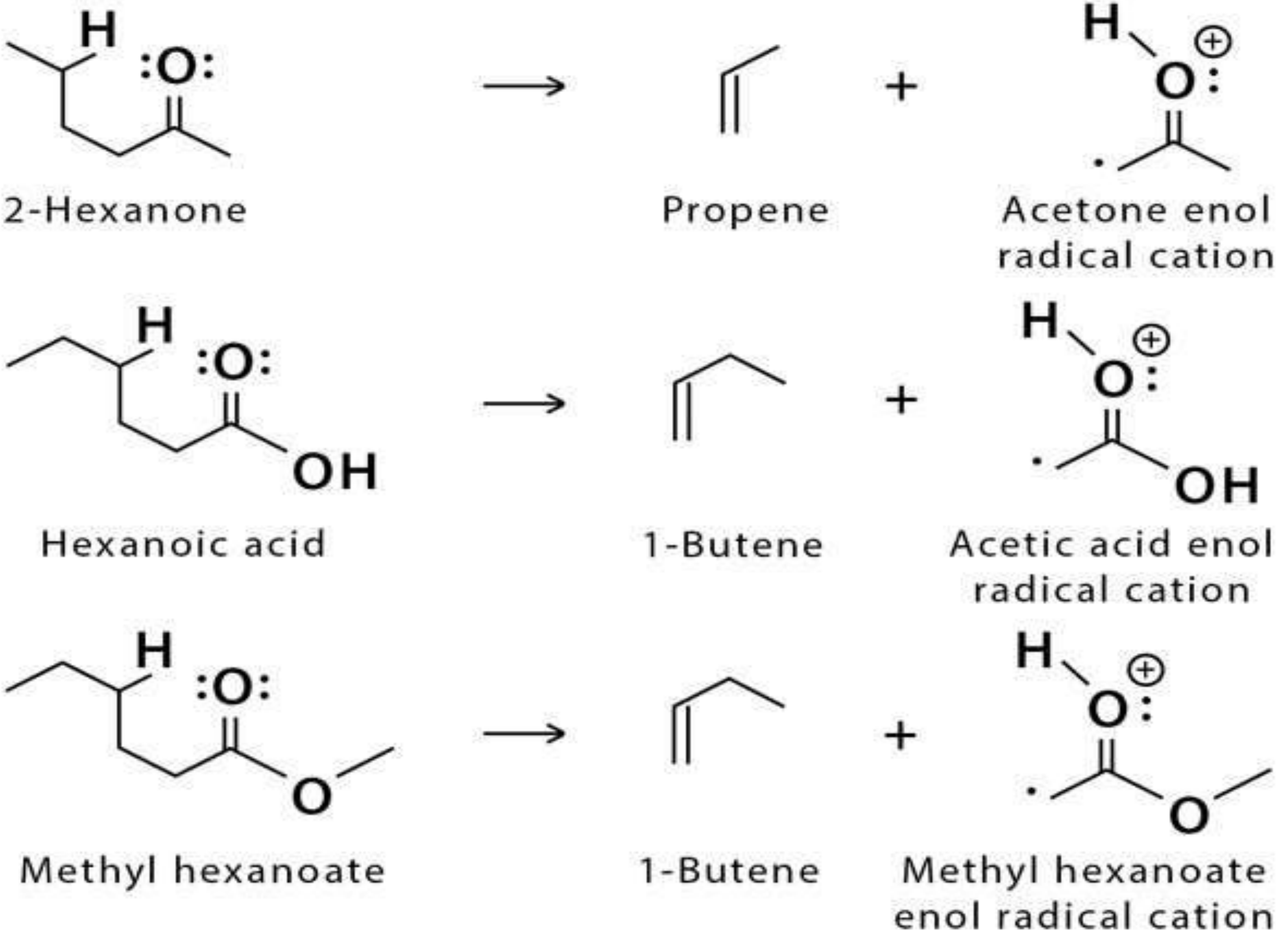
ethene

(Neutral molecule)

Note: * In this rearrangement, radical centre in M ion derived from a lone pair or π-bond

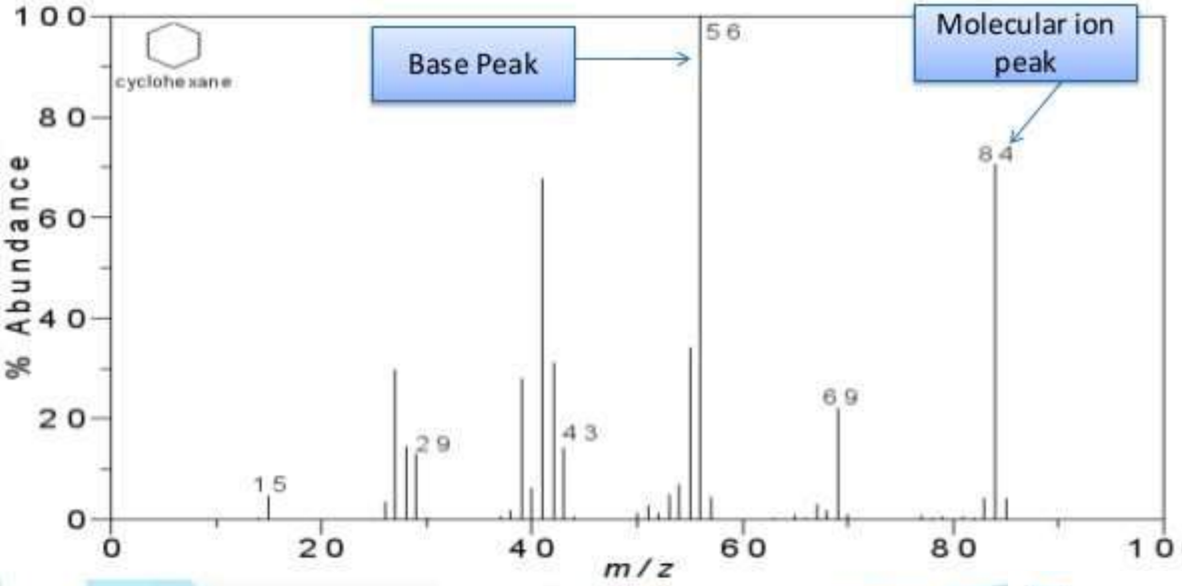
- * removes H from γ position
- * π bond is formed b/w β & γ position
- * a bond is broken b/w α & β position.

MCLAFFERTY REARRANGEMENT EXAMPLES



Mass Spectrum of compounds:-

Alkane:-



Fragmentation of Cyclo Hexane:-

$C_6H_{12}^+$ = 84 (**Molecular ion Peak**),
$C_4H_8^+$ = 56 (**Base Peak**), (M-28)

$C_6H_9^+$ = 69 (Fragment ion Peak), (M-15)
$C_3H_7^+$ = 43 (Fragment ion Peak), (M-41)

$C_2H_5^+$ = 29 (Daughter ion Peak),
CH_3^+ = 15 (Daughter ion Peak).

Tandem MS:-

What is Tandem MS:-

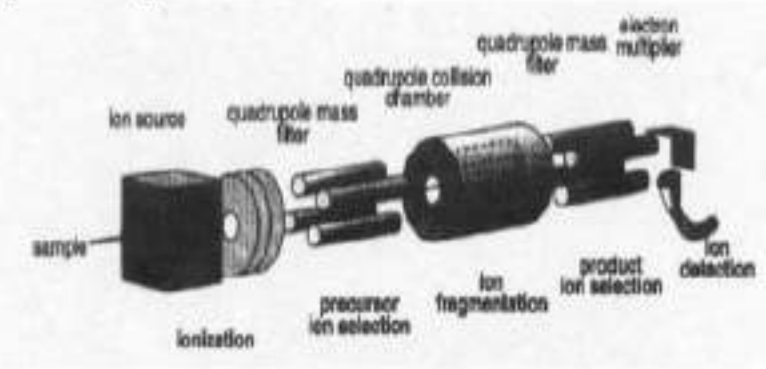
-Uses 2 (or more) mass analyzers in a single instrument.

-One purifies the analyte ion from a mixture using a magnetic field.

-The other analyzes fragments of the analyte ion for identification and quantification.

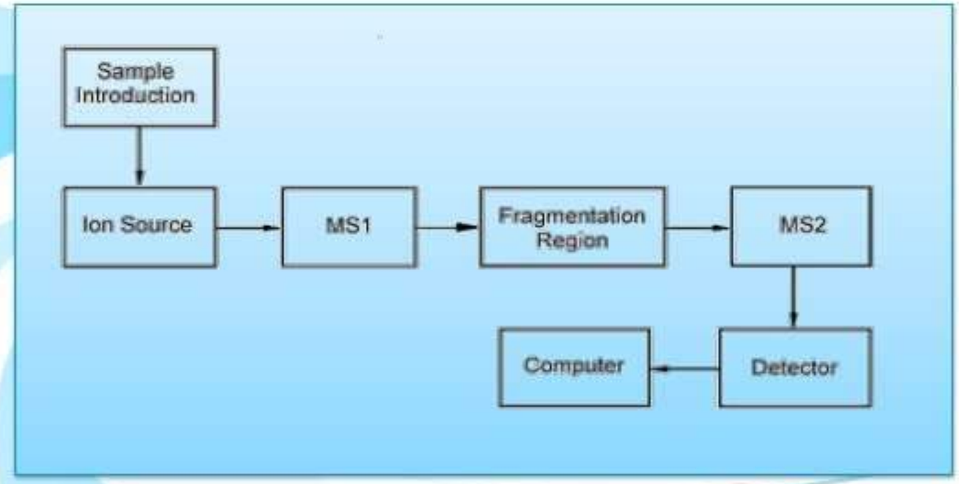
TANDEM Mass Spectrometry

Tandem mass spectrometry uses two stages of mass analysis, one to preselect an ion and the second to analyze fragments induced by collision with an inert gas like argon or helium.



Triple Quadrupole Mass Spectrometer

Tandem mass spectrometry, also known as **MS/MS** or **MS²**, involves multiple steps of mass spectrometry selection, with some form of fragmentation occurring in between the stages.



Applications of Tandem MS

Biotechnology & Pharmaceutical

- To determine chemical structure of drugs and drug metabolites.
- Detection/quantification of impurities, drugs and their metabolites in biological fluids and tissues.
- Analysis of liquid mixtures
- Fingerprinting

Nutraceuticals/herbal drugs/tracing source of natural products or drugs

Clinical testing & Toxicology

- Inborn errors of metabolism, cancer, diabetes, various poisons, drugs of abuse, etc.

MALDI-MS

Matrix-assisted laser desorption/ionization (MALDI) is a soft ionization technique used in mass spectrometry allowing the analysis of biomolecules (biopolymers such as DNA, proteins, peptides and sugars) and large organic molecules (such as polymers, dendrimers and other macromolecules).

Common matrix in MALDI

Matrix	Solvent	Applications
2,5-dihydroxy benzoic acid	Acetonitrile,water,methanol,acetone,CHcl$_3$	Peptides,Nucleotides, oligo nucleotides
3,5-dimethoxy-4-hydroxycinnamic acid	Acetonitrile, water,acetone, CHcl$_3$	Peptides,proteins,lipids
4-hydroxy-3-methoxycinnamic acid	Acetonitrile, water, propanol	Proteins
Picolinic acid	Ethanol	Oligo nucleotides

- ➢ MALDI is based on the bombardment of sample molecules with a laser light to bring about sample ionisation.
- ➢ The sample is pre-mixed with a highly absorbing matrix compound for the most consistent and reliable results.
- ➢ The matrix transforms the laser energy into excitation energy for the sample, which leads to sputtering of analyte and matrix ions from the surface of the mixture.
- ➢ Most commercially available MALDI mass spectrometers now have a pulsed nitrogen laser of wavelength 337 nm.

Applications of MS:-

- Elucidation of the structure of the organic and biological molecules.
- Determination of molecular mass of peptides, proteins, and Oligonucleotides.
- Monitoring gases in patients breath during surgery.
- Identification of drugs abuse and metabolites of drugs of abuse in blood, urine, and saliva.
- Analyses of aerosol particles.
- Determination of pesticides residues in food.

REFERENCES

- Organic spectroscopy by William Kemp
- Elements of Organic spectroscopy by Y R Sharma
- Instrumental analysis by Skoog, West & Holler
- Research articles and review articles.

Nephelometry & Turbidometry

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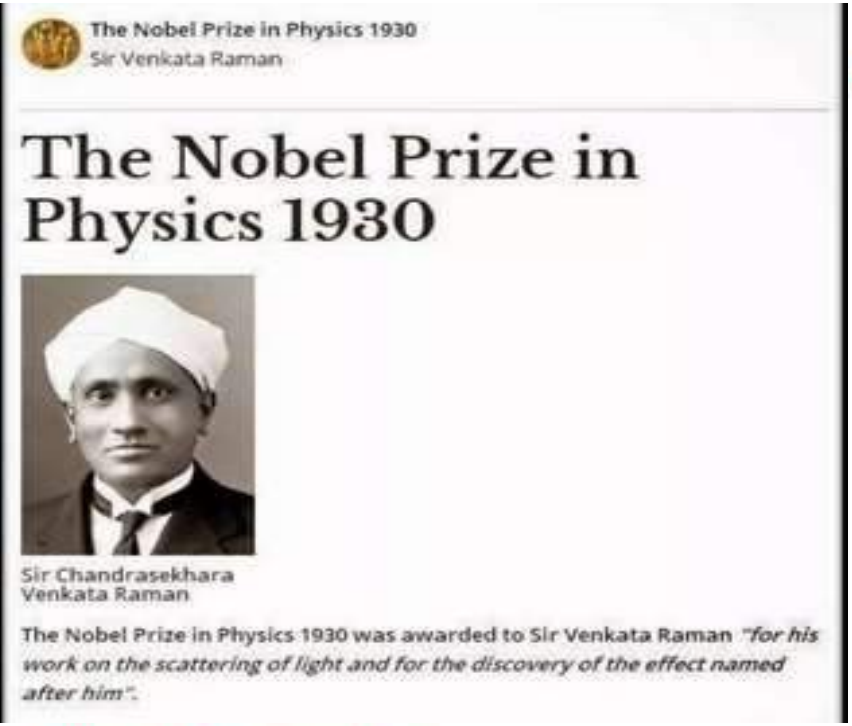
Content - 4 hrs

- **Nephelometry and Turbidometry**:
- Introduction
- Principle
- Instrumentations of nephelometry and turbidometry
- Effects of concentration
- Particle size and wavelength on scattering
- Choice between nephelometry and turbidometry
- Applications of nephelometry and turbidimetry
- Determination of $SO_4^{2-}$and PO_4^{3-}



The Nobel Prize in Physics 1930
Sir Venkata Raman

The Nobel Prize in Physics 1930

Sir Chandrasekhara Venkata Raman

The Nobel Prize in Physics 1930 was awarded to Sir Venkata Raman *"for his work on the scattering of light and for the discovery of the effect named after him".*

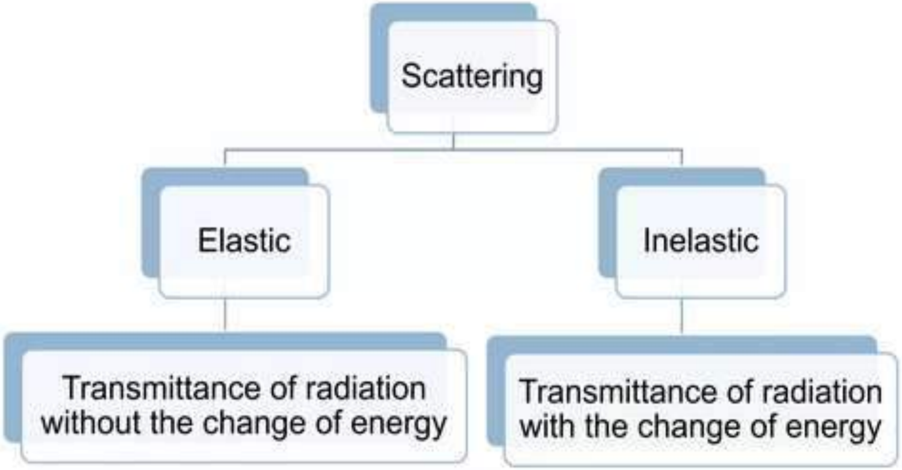
Introduction

- Transmission and diffraction of electromagnetic radiation.
- Amount of light scattered is directly proportional to the concentration or the density of the insoluble particles → k/as Tyndall Effect
- Scattering is defined as: The phenomenon where, beams of light when impinges with particulate matter change its direction of propagation from one to multiple planes without changing net radiating power of energy.

Scattering of light depends on:

The amount of radiation removed or deviated from the primary radiation beam depends on the following factors:

- Concentration of particles
- Wavelength
- Particle size (geometry)
- RI difference
- Molecular weight of particles and
- Distance of observation



Scattering

Elastic

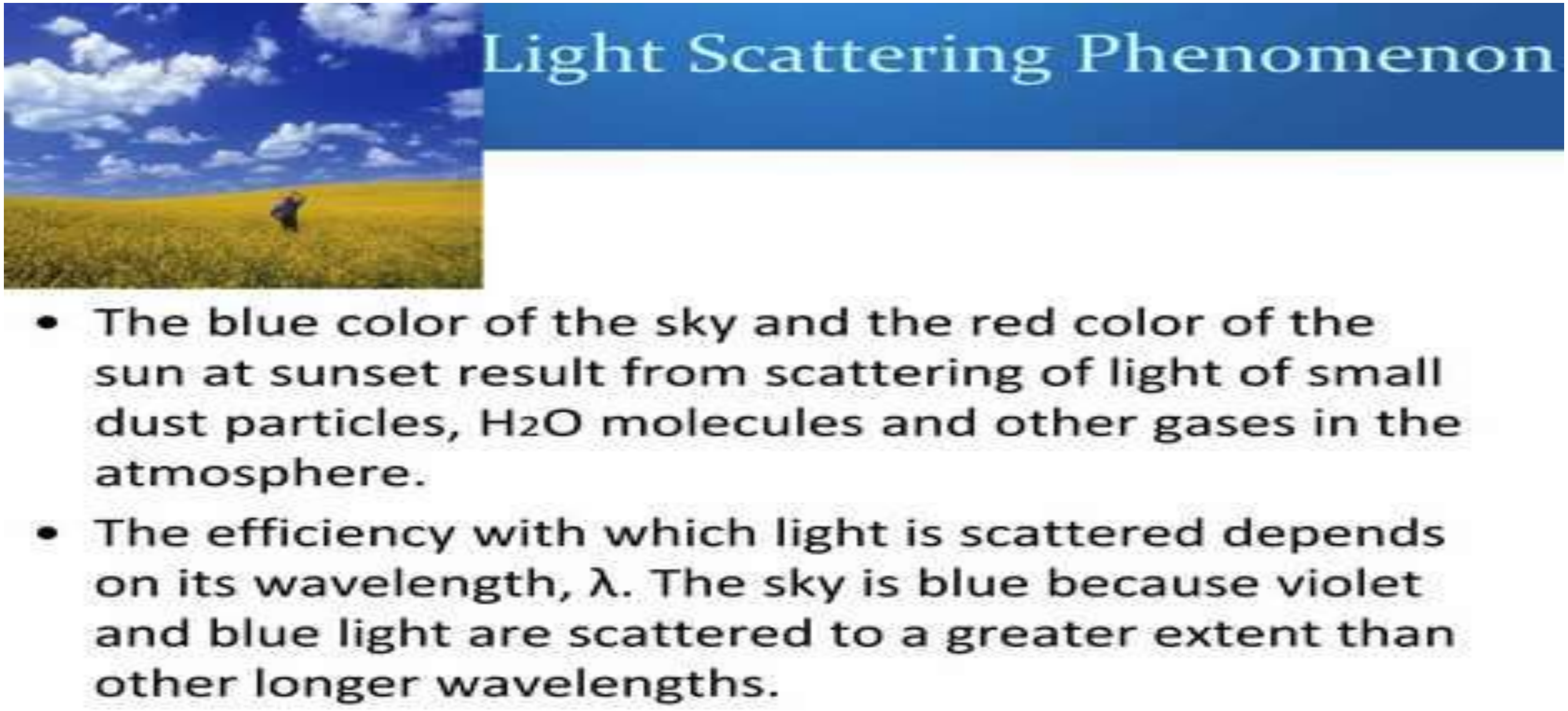
Inelastic

Transmittance of radiation without the change of energy

Transmittance of radiation with the change of energy

Introduction:

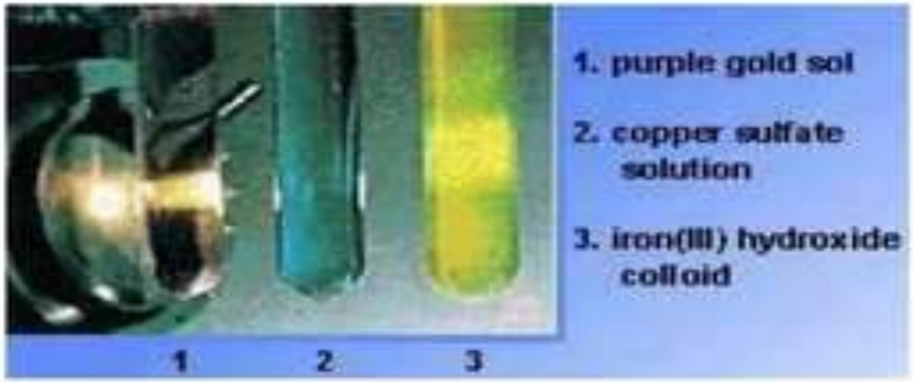
- Blue and red colour-day and sunset-scattering of dust, water and gases
- Efficiency of scattering depends on the wavelength
- During the day time blue is efficiently scattered
- Red-less efficient scattering and hence transmitted to a greater extent than others

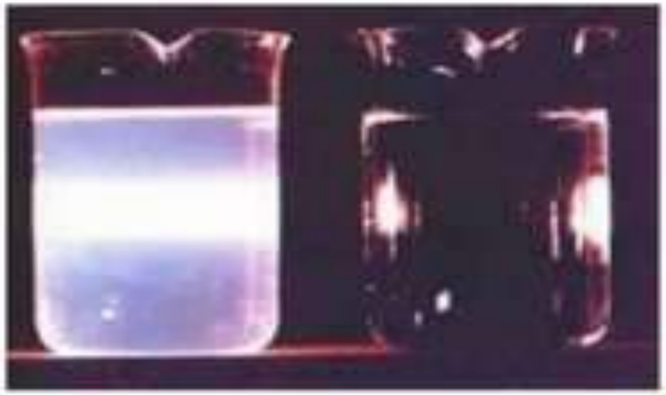


Light Scattering Phenomenon

- The blue color of the sky and the red color of the sun at sunset result from scattering of light of small dust particles, H_2O molecules and other gases in the atmosphere.
- The efficiency with which light is scattered depends on its wavelength, λ. The sky is blue because violet and blue light are scattered to a greater extent than other longer wavelengths.

- Scattering of light- by particles in a colloid or suspension.
- the longer-wavelength light is more transmitted while the shorter-wavelength light is more reflected via scattering.





Origin of scattering:

- Scattering is a function of size of the particle size and wavelength of incident light
- A monochromatic radiation of wavelength, λ, can scattered light whose dimensions are less than (3/2) λ. For eg a radiation of wavelength 500 nm can be scattered by particle size less than 750 nm
- Elastic (similar wavelength) and inelastic (different wavelength)
- Rayleigh (small particle scattering and large particle scattering)
- Rayleigh scattering occurs when particle size is less than 5% of the radiation wavelength
- Intensity is proportional to 4th power of frequency
- Small particle, scattering is evenly distributed. Large particles, scattering increases in forward direction and decreases in back ward direction as

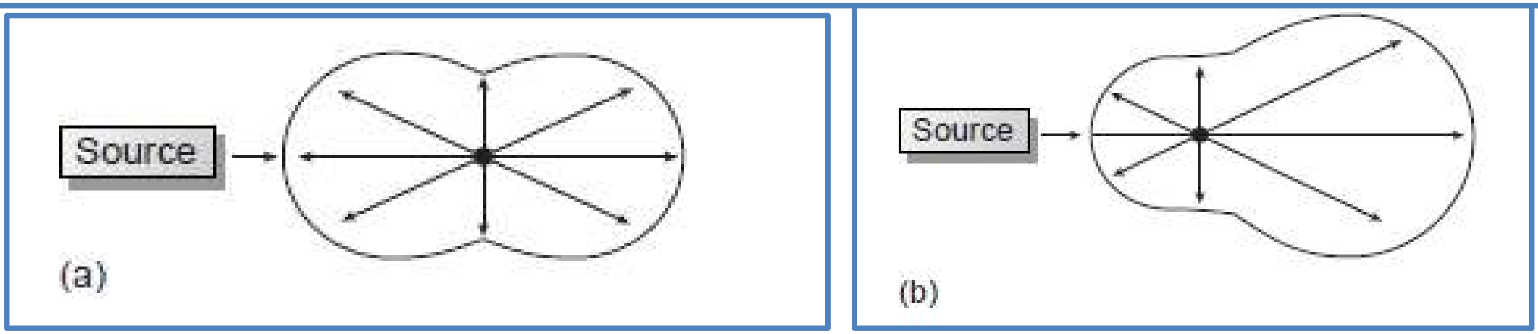
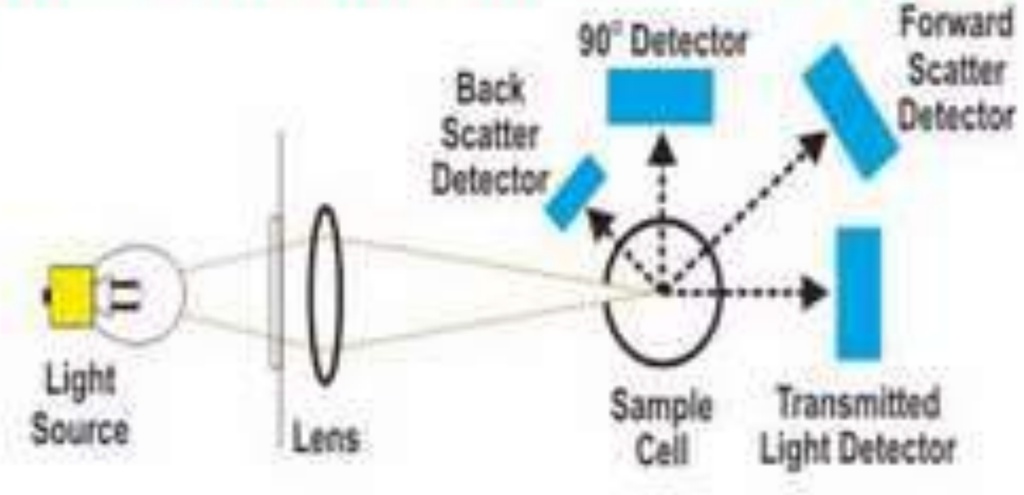


Figure: Distribution of the radiation for (a) Rayleigh scattering and (b) large-particle scattering

Theory

Scattered light may be measured by

- Turbidimetry
- Nephelometry
- In turbidimetry, the intensity of light transmitted through the medium, the unscattered light, is measured.



TURBIDIMETER

An instrument used to measure the relative clarity of a fluid by measuring the amount of light scattered by particles suspended in a fluid sample.

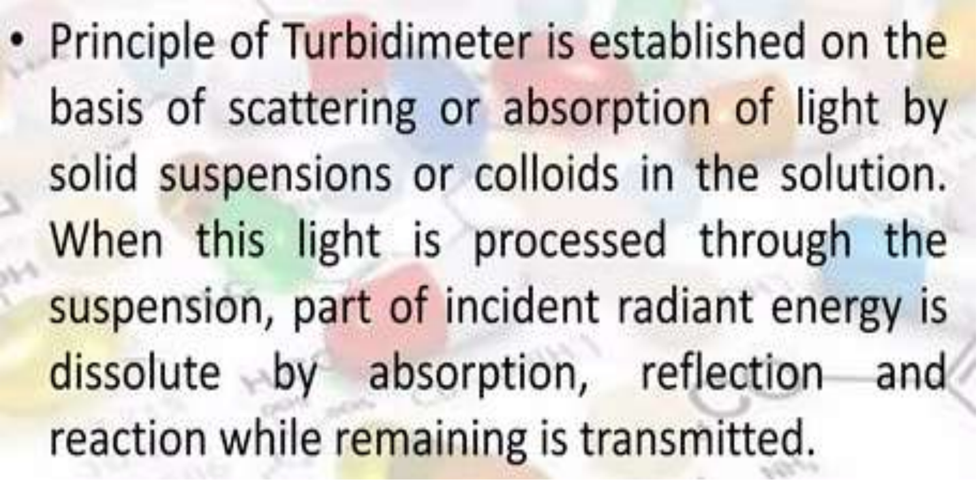
TURBIDITY

- **Turbidity** is the cloudiness or haziness of a fluid.
- The turbidity of a sample may be due to a single chemical substance or a combination of several.

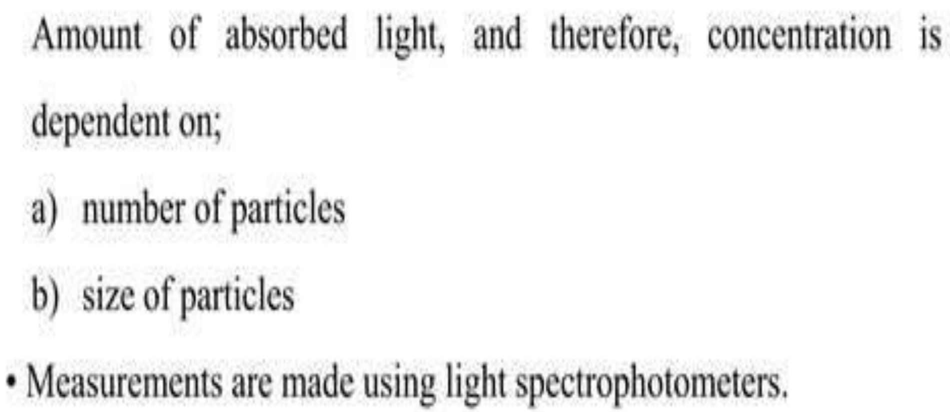
- Turbidity can be measured on most routine analysers by a spectrophotometer (absorbed light)
  - Reduced sensitivity and precision.
- Extent of light scattering increases as wavelength increases
- The intensity of scattered light is normally measured by Nephelometer.

- A turbidimeter measures obstruction to determine the haziness, or intensity of light, in a sample
- Measured in: nephelometric turbidity units (NTU).

Principle



- Principle of Turbidimeter is established on the basis of scattering or absorption of light by solid suspensions or colloids in the solution. When this light is processed through the suspension, part of incident radiant energy is dissolute by absorption, reflection and reaction while remaining is transmitted.

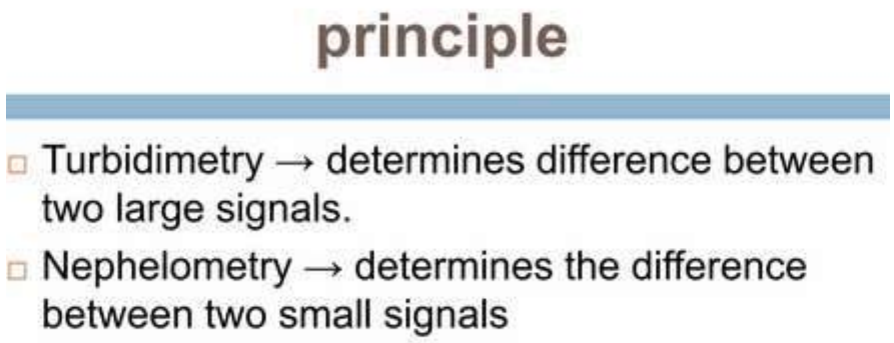


Amount of absorbed light, and therefore, concentration is dependent on;

a) number of particles

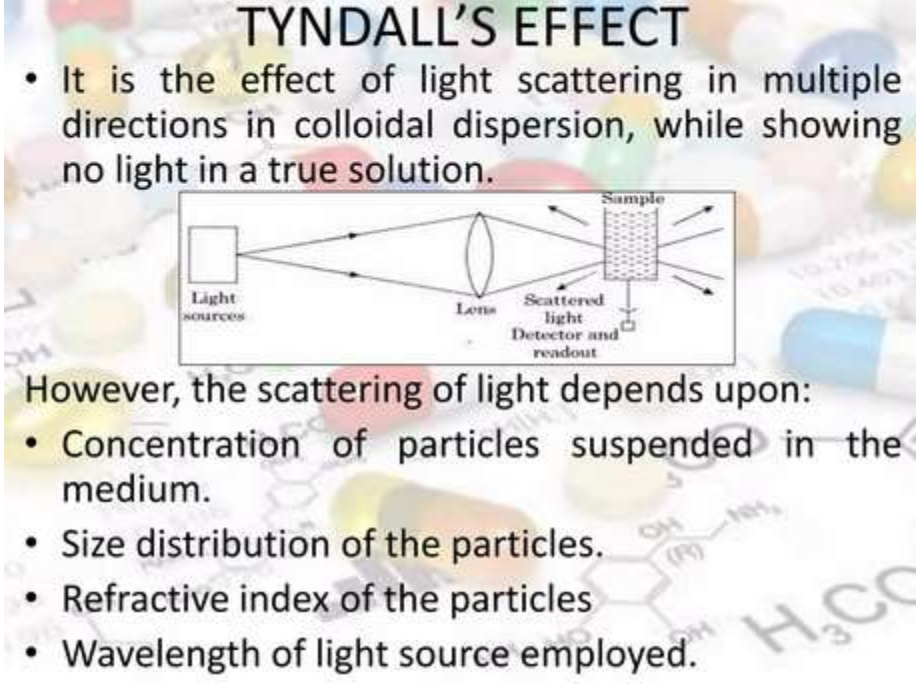
b) size of particles

- Measurements are made using light spectrophotometers.



principle

- ☐ Turbidimetry → determines difference between two large signals.
- ☐ Nephelometry → determines the difference between two small signals

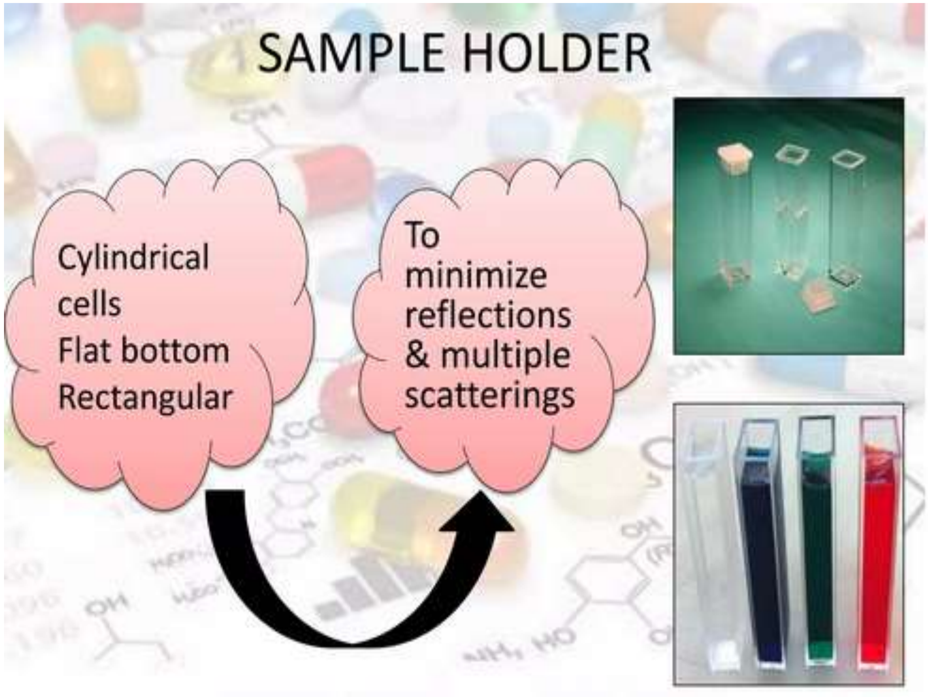


TYNDALL'S EFFECT

- It is the effect of light scattering in multiple directions in colloidal dispersion, while showing no light in a true solution.

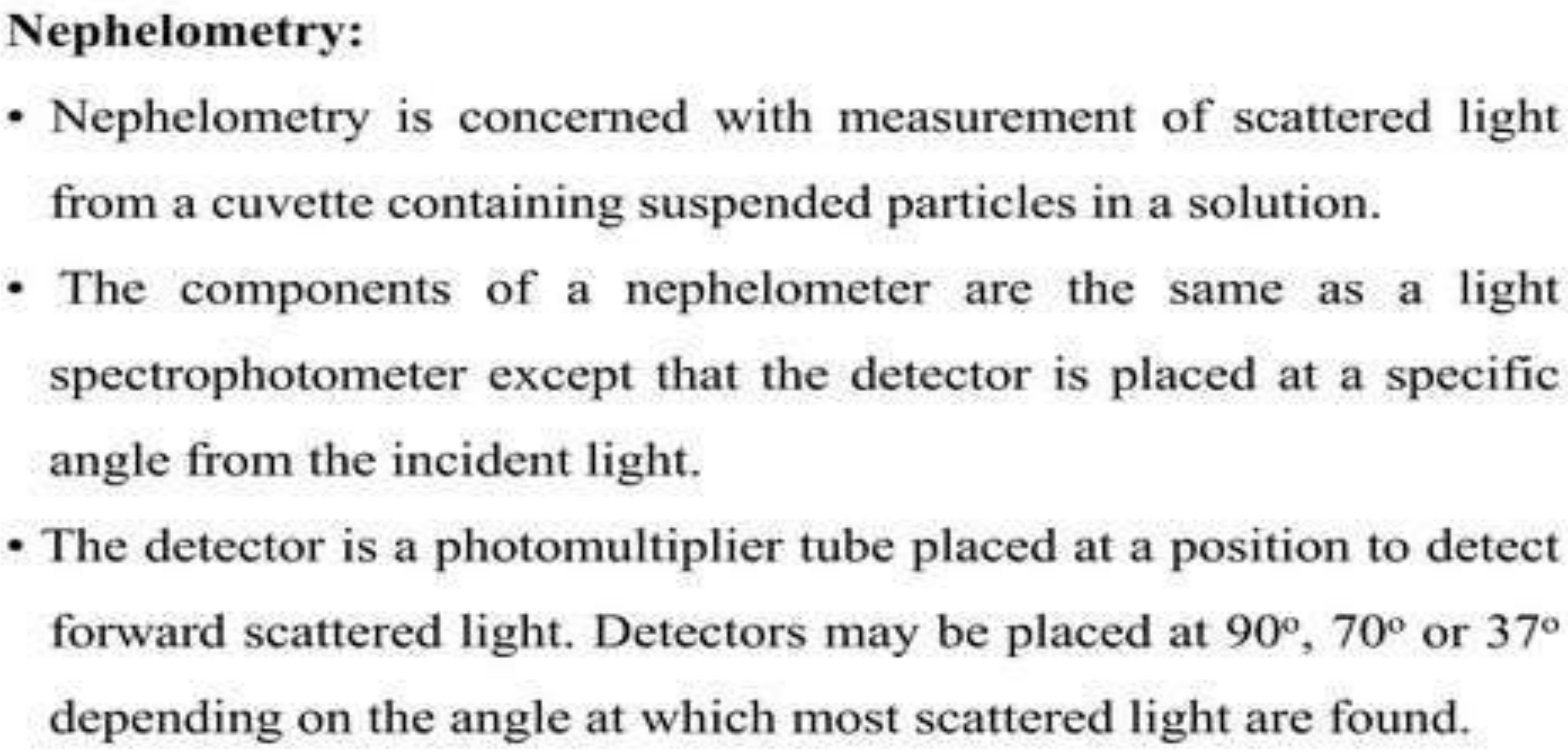
However, the scattering of light depends upon:

- Concentration of particles suspended in the medium.
- Size distribution of the particles.
- Refractive index of the particles
- Wavelength of light source employed.



SAMPLE HOLDER

Nephelometry



Nephelometry:

- Nephelometry is concerned with measurement of scattered light from a cuvette containing suspended particles in a solution.
- The components of a nephelometer are the same as a light spectrophotometer except that the detector is placed at a specific angle from the incident light.
- The detector is a photomultiplier tube placed at a position to detect forward scattered light. Detectors may be placed at 90°, 70° or 37° depending on the angle at which most scattered light are found.

Instrumentation

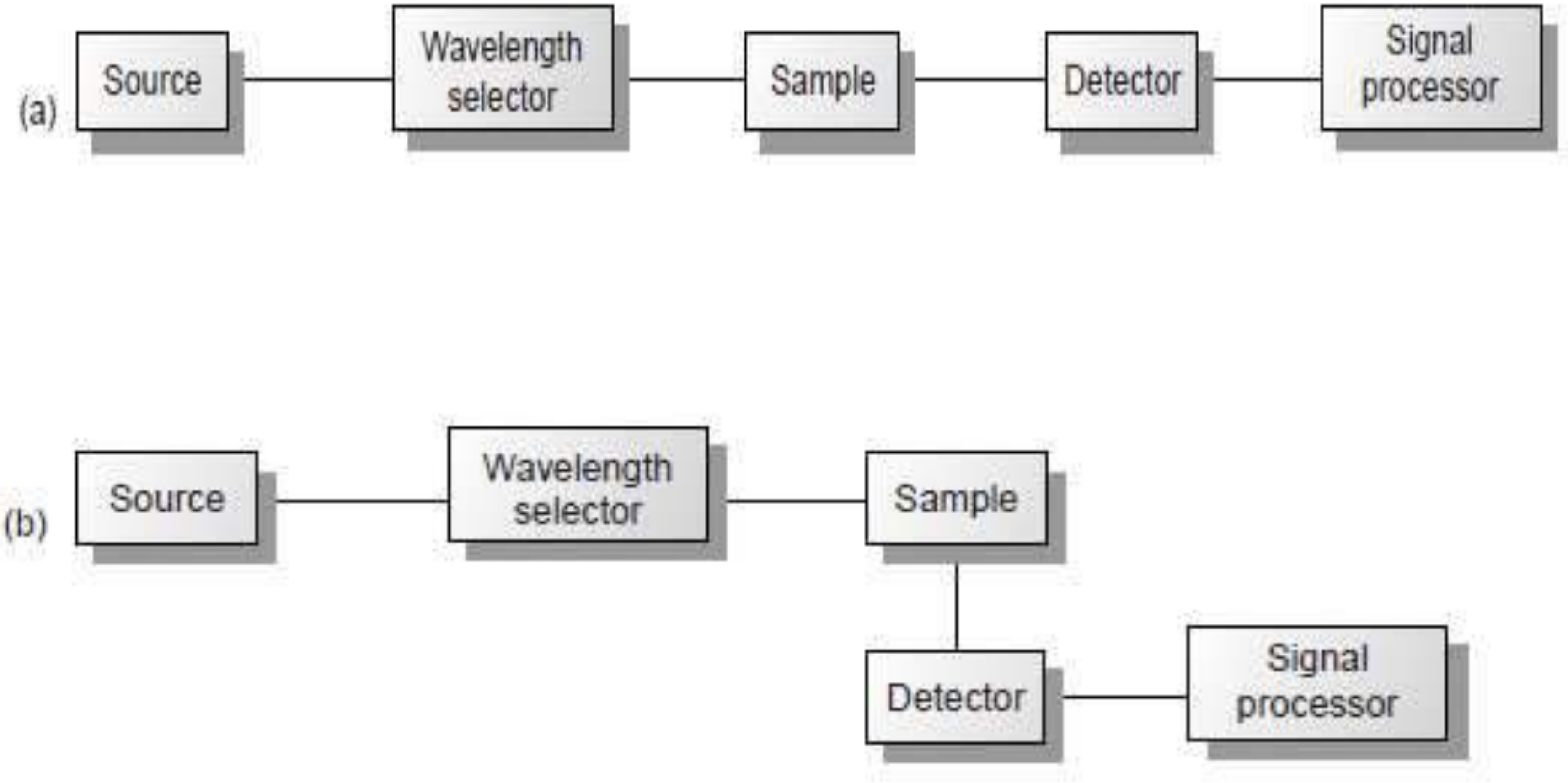


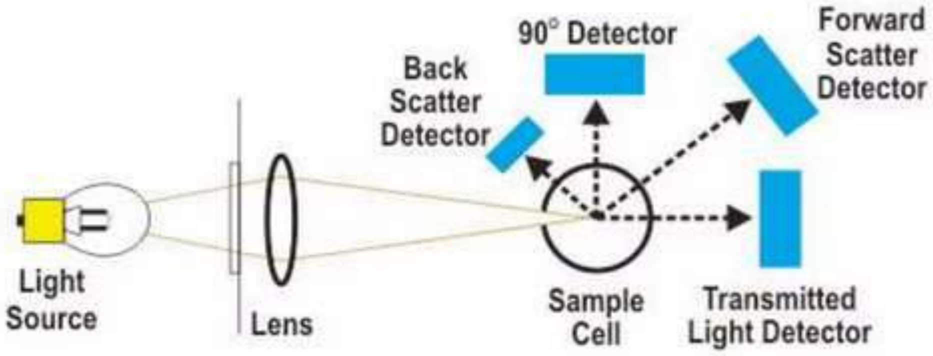
Figure: Block diagrams for (a) Turbidimetry (b) Nephelometry

Instrumentation

- Sources
- Wavelength selector
- Sample holder
- Detector
- Signal processor

The basic instrument contains,

- **Light Source**
  Tungsten its relatively low intensity makes it less useful for samples with low light scattering.
  Alternatives are: Quartz halogen lamp, mercury arc, xenon lamp and laser which have higher intensities than tungsten lamp.
- **Filters**
  There is provision for the insertion of filter between the sample and source of light
- **Sample cells (Cuvette)**
- **Detectors**
  It is shielded to minimize interference from stray light.
- **Read out device**
  Light intensity is converted to an electrical signal by the detector .



Schematic Representation for Nephelo-turbidimetric Measurement

Radiation source

Mercury Arc Lamp

Tungsten Lamp

Filters and monochromators

- Monochromatic light.
- As per the feasibility → colorimeter with a blue filter (530nm) is turbidimeter; fluorimeter with a visible secondary filter is a nephelometer.
- Absorption filters and Interference filters → used in Nepheloturbidimetry.
- Absorption filters → made up of glass or coated with pigment that absorbs unwanted light.
- Interference filters → dielectric spacer films → made up of CaF_2, MgF_2 between two silver films.

Sample cell

- Cuvette or sample cells → made up of transperent glasses.
- Shape → Cylindrical / Rectangular or Special cells with path length 1cm.
- Special Cell → Measure light scattering → at 45°, 90° and 135° → employed in nepheloturbidimetric analysis.

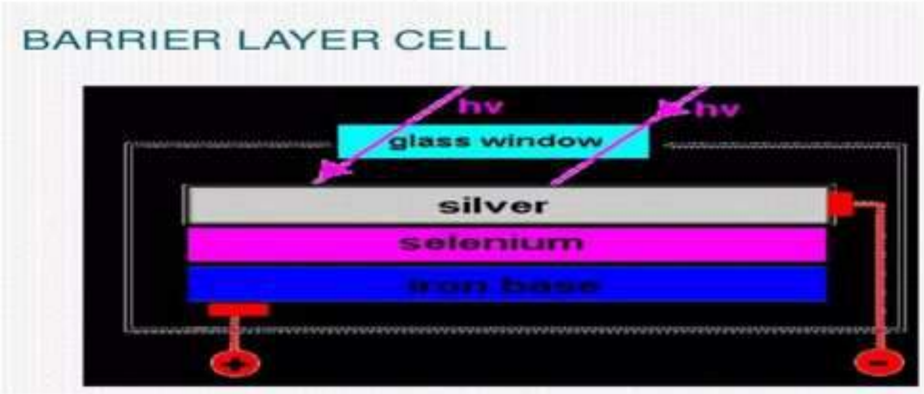
Detectors

Photovoltaic cell

light → selenium → electrons generated → photocathode → potential difference

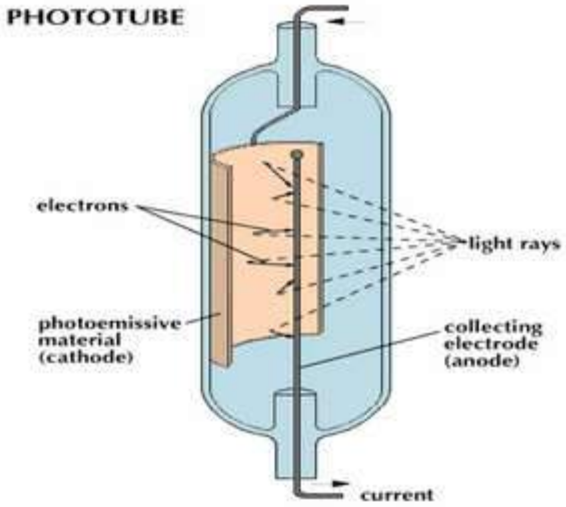
↓

Intensity of radiation ← deflection In galvanometer ← electric current

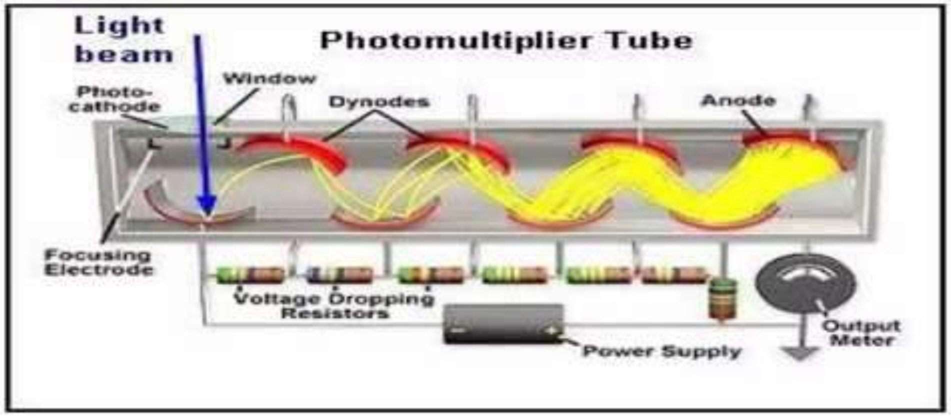


Phototubes

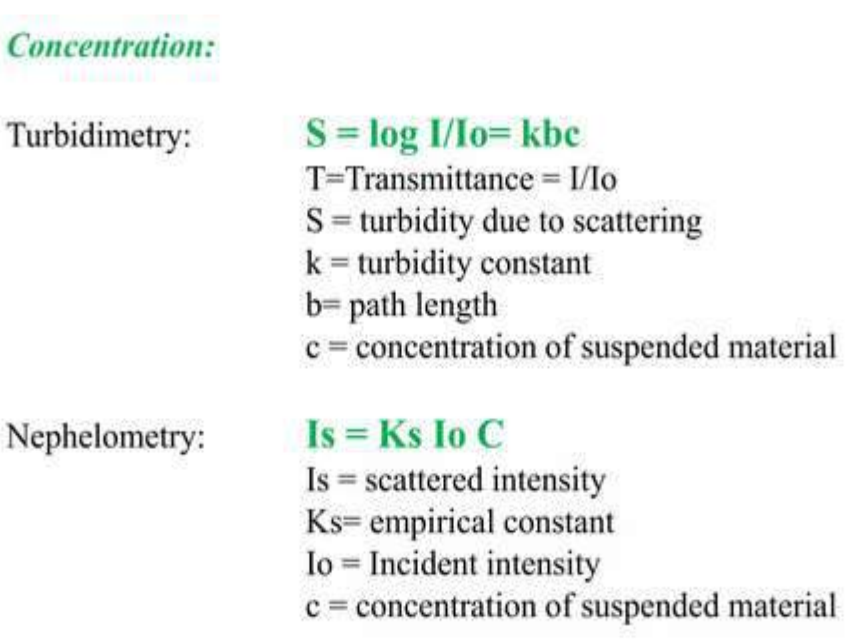
Light → photocathode → electrons generated → anode → current → intensity of radiation



Photomultiplier tubes (PMT)



Effects of concentration



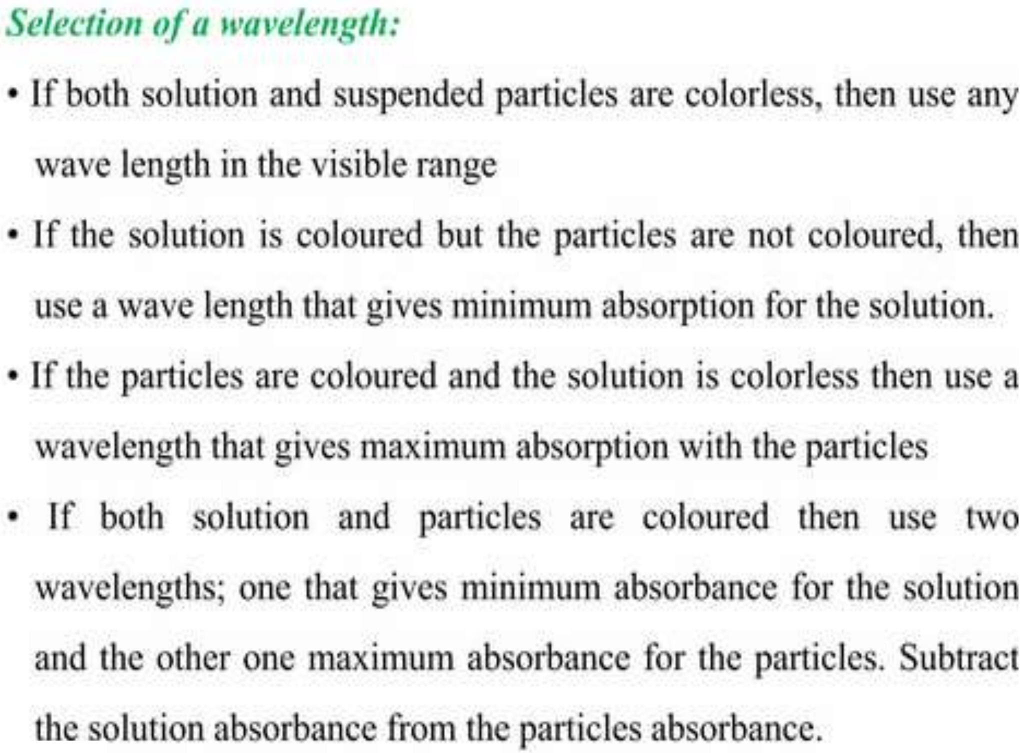
Concentration:

Turbidimetry: **$S = \log I/Io = kbc$**

T=Transmittance = I/Io
S = turbidity due to scattering
k = turbidity constant
b= path length
c = concentration of suspended material

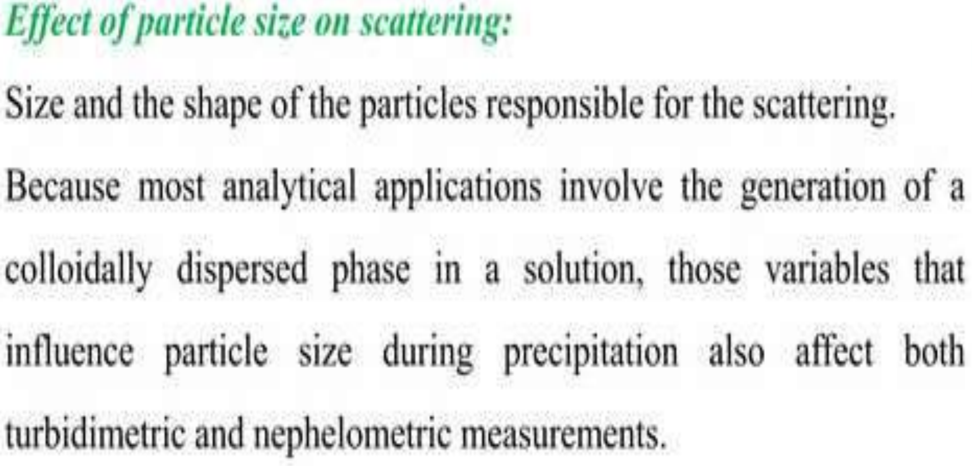
Nephelometry: **$Is = Ks\ Io\ C$**

Is = scattered intensity
Ks= empirical constant
Io = Incident intensity
c = concentration of suspended material



Selection of a wavelength:

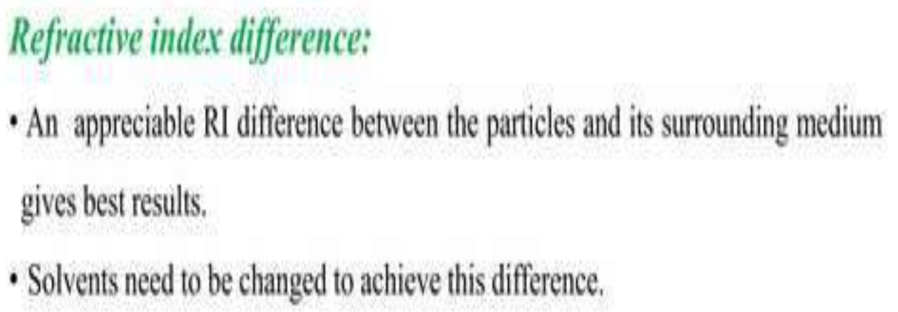
- If both solution and suspended particles are colorless, then use any wave length in the visible range
- If the solution is coloured but the particles are not coloured, then use a wave length that gives minimum absorption for the solution.
- If the particles are coloured and the solution is colorless then use a wavelength that gives maximum absorption with the particles
- If both solution and particles are coloured then use two wavelengths; one that gives minimum absorbance for the solution and the other one maximum absorbance for the particles. Subtract the solution absorbance from the particles absorbance.



Effect of particle size on scattering:

Size and the shape of the particles responsible for the scattering.

Because most analytical applications involve the generation of a colloidally dispersed phase in a solution, those variables that influence particle size during precipitation also affect both turbidimetric and nephelometric measurements.

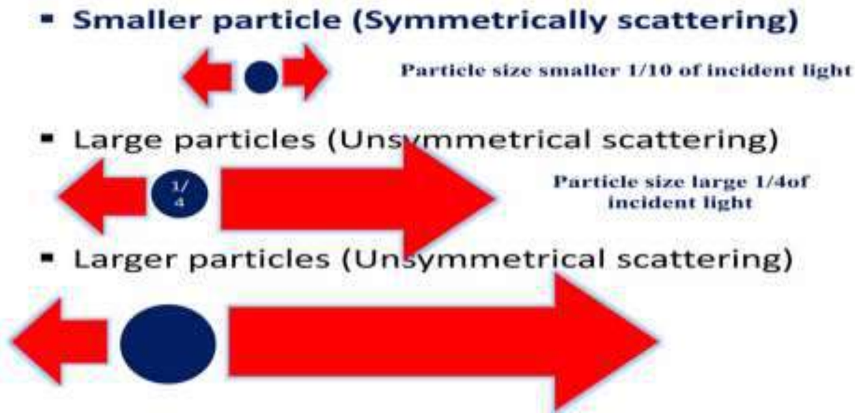


Refractive index difference:

- An appreciable RI difference between the particles and its surrounding medium gives best results.
- Solvents need to be changed to achieve this difference.

Particle size and wavelength on scattering

- ***Raman*** and ***Rayleigh scattering*** occur when the dimensions of the scattering particles are less than 5 percent of the wavelength of the incident radiation.
- Both Rayleigh and Raman scattering are caused by the effect on the analyte of the fluctuating electromagnetic field that is associated with the passing incident radiation.
- The fluctuating field induces an electric dipole (separation of charges equal in size but opposite in sign) within the scattering particles that oscillates at the same frequency as the incident radiation. The oscillating dipole behaves as a point source of emitted radiation.



- **Smaller particle (Symmetrically scattering)**

- Large particles (Unsymmetrical scattering)

- Larger particles (Unsymmetrical scattering)

Particle Size

- **The fraction of light scattered at any angle depends upon size and shape of particles.**
- **The amount of scattering (S) α proportional to square of effective radius of the particle.**
- **To control the particle size and shape, sample solutions and standards must be prepared under identical conditions.**
- ***Following care must be taken:***

i) Concentrations of two ions forming ppt.

ii) Ratio of concentration of the solutions.

iii) Order of mixing of ppt.

iv) Temperature at which suspension is prepared.

Wavelength

- The intensity of scattered radiation depends upon wavelength of the incident light.
- Shorter wavelength are scattered to greater extent than the longer one.
- Wavelength of light is chosen in such a way that analyte solution does not absorbs strongly.
- ***Turbimetric & Nephelometric measurements are carried using white light.***

NEPHELOMETRY

↓ concentration, uniform scattering, intensity of scattered lig

proportional to conc. measured at 90^0

TURBIDIMETRY

↑ concentration, scattering not uniform, intensity of transmitted lig

measured at 180^0

CHOICE OF THE METHOD

Depends upon the amount of light scattered by suspended particl

present in solution.

TURBIDIMETRY - high concentrated suspensions

NEPHELOMETRY - low concentrated suspensions - more accurate results.

Turbidimetry

↕

Colorimetry

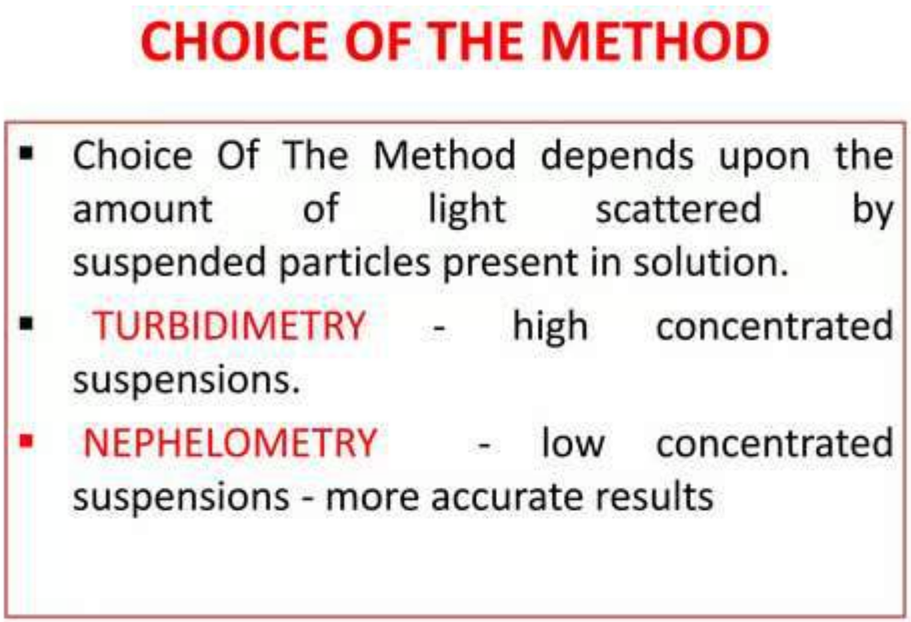
- Measurement of the intensity of light transmitted through a medium, light intensity is decreased.

Nephelometry

↕

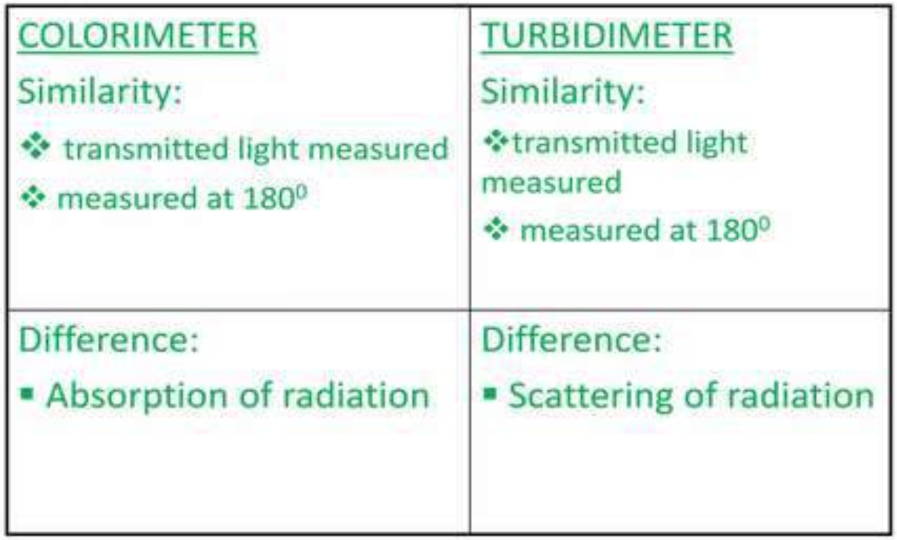
Fluorimetry

- Measurement of scattered light at 90^0



CHOICE OF THE METHOD

- Choice Of The Method depends upon the amount of light scattered by suspended particles present in solution.
- TURBIDIMETRY - high concentrated suspensions.
- NEPHELOMETRY - low concentrated suspensions - more accurate results



COLORIMETER	TURBIDIMETER
Similarity: ❖ transmitted light measured ❖ measured at 180^0	Similarity: ❖transmitted light measured ❖ measured at 180^0
Difference: ▪ Absorption of radiation	Difference: ▪ Scattering of radiation

FLOURIMETRY	NEPHELOMETRY
Similarity: ❖ Emergent radiation measured at 90^0	Similarity: ❖ Emergent radiation measured at 90^0
Difference: » emitted radiation measured » emitted radiation – longer WL than incident light	Difference: » Scattered radiation measured » emitted radiation – same WL as that of incident light

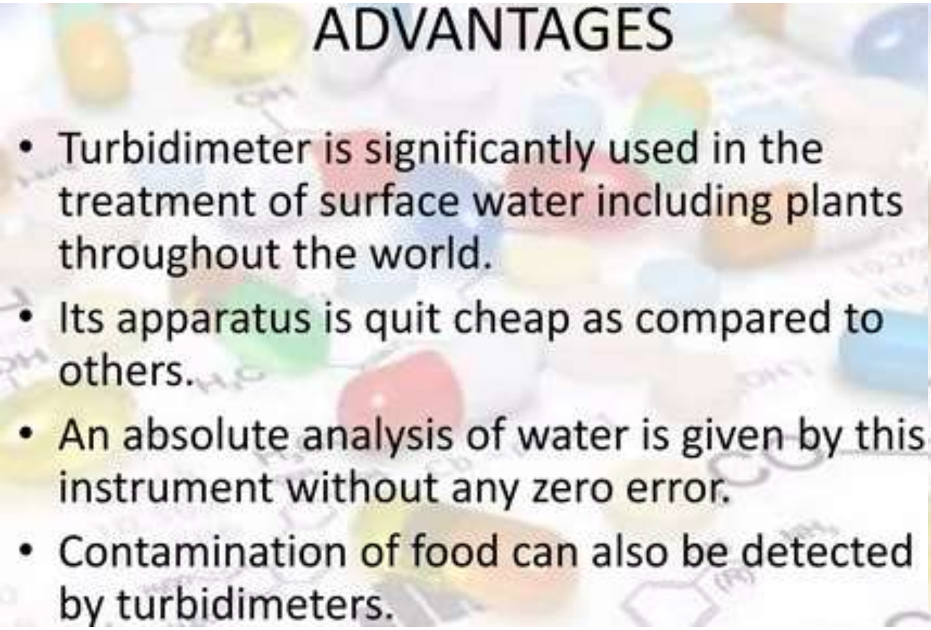
Nephelometric Turbidity Units (NTU)

- Turbidity is a measure of the cloudiness of water. The higher the turbidity, the harder it is to see through the water.
- Turbidity measurements are reported in nephelometric turbidity units (NTU) or Jackson turbidity units (JTU).
- Different units are used depending on which method is chosen to measure turbidity. These two units are roughly equivalent.
- **Drinking Water Standard:**

Drinking water should have a turbidity of ≤ 5 NTU

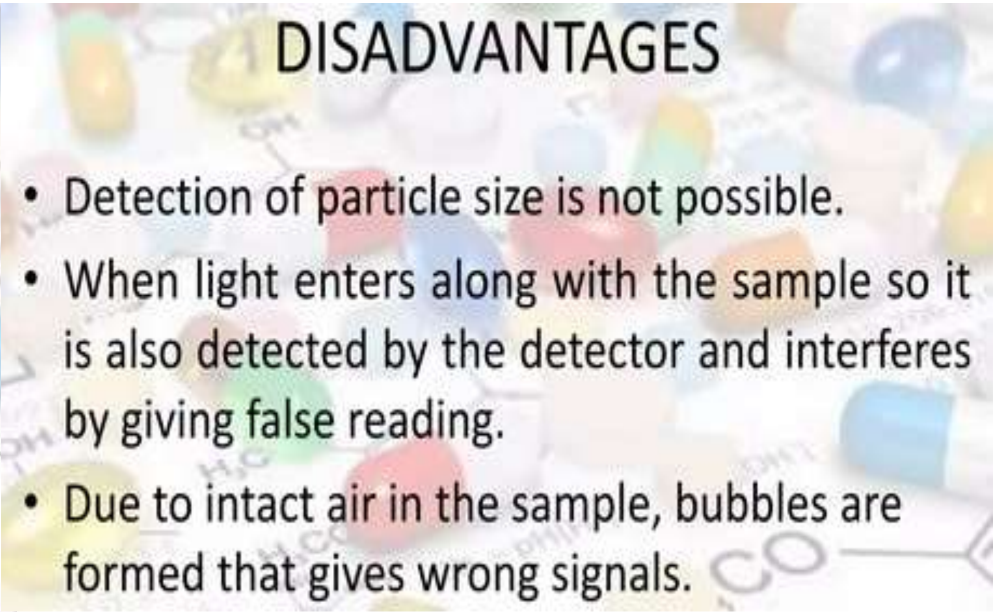
Reason: Turbidity becomes visible at approximately 5 NTU, and water with any visible turbidity may be rejected in favour of a clearer.

Advantages & Disadvantages of TURBIDIMETRY



ADVANTAGES

- Turbidimeter is significantly used in the treatment of surface water including plants throughout the world.
- Its apparatus is quit cheap as compared to others.
- An absolute analysis of water is given by this instrument without any zero error.
- Contamination of food can also be detected by turbidimeters.



DISADVANTAGES

- Detection of particle size is not possible.
- When light enters along with the sample so it is also detected by the detector and interferes by giving false reading.
- Due to intact air in the sample, bubbles are formed that gives wrong signals.


Application of turbidimetry
Purity of water
Food and beverage industry
Air and water pollution
End point in precipitati0n
Immuno-assay
Densities of microbes
Complexion of human serum
Presence of ions

Applications:

- Analysis of water (water pollution)- clarity, conc. of ions
- Determination of CO_2 (Air pollution)
- Determination of inorganic substances (Turbidimetric titrations)
  - Sulphate – barium chloride
  - Ammonia – Nesslers reagent (KI, KOH, $HgCl_2$)
  - Phosphorus – Strychine molybedate
  - Fluoride- calcium
  - Bromide- Silver
- Determination of inorganic substances
- Biochemical Analysis
- Quantitative Analysis (Turbidimetric titrations) – (ppm level)
- Determination of mole. wt of high polymers

. Miscellaneous

Water treatment plants, sewage work, refineries, paper industry

. Atmospheric pollution

smokes & fogs

. Determination of mole. Wt of high polymers

. Phase titration

Beverages and food products.

- ☐ Determination of particle size.
- ☐ Determination of average molecular weight.
- ☐ Measuring of atmospheric pollutants.
- ☐ Determination of concentration of solution.
- ☐ Growth of bacterial cell in liquid nutrient medium.
- ☐ Determination of end point of precipitation titration., etc

Differenctiate bet^n

Nephelometry	Turbidimetry
Suspended particles < 100 mg/L	Suspended particles > 100 mg/L
Intensity of scattered light is measured	Intensity of unscattered light is measured
Low concentration suspension is used	High concentration suspension is used
Scattering is uniform	Scattering is not uniform
Intensity of scattered light → proportional to the concentration	Intensity of transmitted light → inversely proportional to the concentration
Measured at 90°	Measured at 180°
Detector: Sensitive Photomultiplier	Detector: Photocell

NEPHLOTURBIDIMETER

Two detectors

Turbidimetry versus Nephelometry:

- The selection of the instrumentation depends upon two principle factors: **intensity** and **size** of the scattering particles. The intensity of the transmitted or scattered radiation relative to the intensity of the radiation from the source. When the solution contains **small concentration** of scattering particles, the intensity of the transmitted radiation, I_T, will be very similar to the intensity of the incident light, I_o. Determination of small difference in the intensity of the two signals is a subject of substantial uncertainty. Thus, **Nephelometry** is more appropriate choice of samples containing **few scattering particles**. On the other hand, **Turbidimetry** is a better choice for samples containing **high concentration** of scattering particles.
- For Nephelometry, the intensity of the scattering radiation at 90^0 will be greatest if the size of the particles are small enough accompanying Rayleigh scattering. For large particles, scattering intensity is diminished at 90^0. When using an UV-Vis source of radiation, the optimum particle size is in the range 0.1 – 1.0 μm. The size of the particles are less important in the Turbidimetric measurements because signal is the relative decrease in the transmitted radiation. In fact, Turbidimetric measurements are still feasible even when the size of the scattering particles results in an increase in reflection and refraction.

FACTORS:

- Depends on **intensity** and **size** of scattering particles
- Small concentration of scattering particles- intensity of transmitted light is similar to incident light thus
  - **Nephelometry** is appropriate choice for sample of **few scattering particle**
  - **Turbidimetry** is suitable for samples containing **large concentration** of **scattering particles**.
  - for **small particle** intensity will be greatest at **90^0**
  - for **large particle** intensity will be **diminished** at **90^0**

- **Determination of concentration:**
- **In Turbidimetry**, decrease in intensity of light is measured
- $$T = \frac{I_T}{I_o}$$
- $$-\log T = kbC$$
- B = path length, k = a constant (depends on size shape and wavelength of radiation source), C = concentration
- **In Nephelometry**, scattered radiation is measured,
- $$I_s = K_s I_o C$$
- K_s = constant-determined by calibration graph, I_o= intensity of incident radiation, C = concentration

DETERMINATION OF SO_4^{2-} BY NEPHELOMETRY

Principle

- The most widely used determination is that of sulphate after addition of $BaCl_2$ to form a suspension of $BaSO_4$ in the concentration range 0.2 to 100 ppm. **NaCl** and **HCl** are added before the precipitation in order to inhibit the growth of micro crystals of $BaSO_4$. Optimum pH is maintained. A **glycerol ethanol** solution helps to **stabilize** the **turbidity**. The reaction vessel is shaken gently to obtain a uniform particle size. The unknown should be treated exactly like the standard solution.

Reagents required.

- (i). **Standard sulphate solution**: Dissolve 1.814 g dry K_2SO_4 in distilled water and dilute to 1 L. This solution contains 1000 mg of SO_4^{2-} ion per mL.
- (ii). **NaCl – HCl reagent**. Dissolve 60 g NaCl in 200 mL distilled water. Add 5 mL pure conc. HCl and dilute to 250 mL.
- (iii). **Glycerol-ethanol solution**. Dissolve 1 volume of glycerol in 2 volumes of absolute ethanol.
- (iv). **$BaCl_2$ crystals**.

PROCEDURE

- Transfer 0, 0.25, 0.5, 0.75, 1.0, 1.25, and 1.5 mL of the standard potassium sulphate (1000 ppm of sulphate) solution from a calibrated burette to separate **50 mL standard flasks**.
- To each flask, add 5 mL of the NaCl-HCl reagent, 10 mL of the glycerol-ethanol solution and dilute to 50 mL with distilled water. Add 0.15 g of $BaCl_2$ to each flask and dissolve it completely. Stopper the flasks and shake each flask for 1 min by inverting each flask one per second, all the $BaCl_2$ should be dissolved.
- Allow to stand for 2 -3 min and measure the turbidity in the nephelometer.
- Take care to avoid small air bubble adhering to the wall of the matched test tube.
- Use the most concentrated solution as standard and by means of the sensitivity control, adjust the micro-ammeter reading to 100 divisions.
- Prepare a blank solution. Repeat the above sequence of operations but do not add any sulphate solution. Place the blank solution in the nephelometer and adjust to zero reading scale by means of the zero control.
- Check the reading of the most turbid solution and adjust any deviation from 100 by means of sensitivity control.
- Repeat the measurement with the five other standard sulphate solutions.
- Plot the reading against the sulphate ion content per mL. Determine the sulphate-ion content of an unknown solution, 0.15 mg per mL using the calibration curve.

- Table and calculations
- Graph
- Result:
- The conc. of sulphate in the given unknown solution is

Determination of PO_4^{3-} by Nephelometry

Principle

The phosphate ion is determined as a white coloured fine particles of strychnine phosphomolybdate by nephelometric measurements. The unnecessary agitation of the precipitate results in its agglomeration. The precipitate is sensitive to temperature change.

Reagents required.

(i). Standard Phosphate solution. Dissolve 1.721 g KH_2PO_4 in 1 L of water in a flask. Pipette 10 mL of this solution into 1 L graduated flask and dilute to the mark. This dilute solution contains 0.001 mg P_2O_5 per mL.

(ii). Molybdate Strychnine reagent. The reagent is prepared in two parts and mixed just before use, since the addition of acid and molybdate solution to the strychnine sulphate solution produces a precipitate after 24 hours.

Solution A (Acid molybdate solution). To 30 g of molybdenum trioxide in a 500 mL flask and 10 g Na_2CO_3 and 200 mL water. Mixture is boiled until a clear solution. Add 200 mL of 5 M H_2SO_4, cool and dilute it to 500 mL.

(iii). Solution B. Dissolve 1.6 g of strychnine sulphate in 100 mL of warm distilled water, cool and dilute to 500 mL.

Prepare the reagent by mixing equal volumes of A and B. Shake well and discard the bluish white precipitate. The clear solution can be kept for 20 hours.

(iv). Prepare saturated aqueous solution of sodium sulphate at 50 °C and cool to room temperature.

(v). 1 M $H_2SO_{4.}$ .Dilute 27 mL of conc. sulphuric acid to 500 mL.

PROCEDURE

- Run 1.0, 2.0, 4.0, 6.0, 8.0 and 10.0 mL of the standard phosphate solution into separate 100 mL graduated flask.
- To each flask add 18 mL of 1 M H_2SO_4 and 16 mL of saturated sodium sulphate solution and dilute to 95 mL with distilled water.
- Add **2.0 mL of molybdate strychnine reagent** and dilute to 100 mL. Mix the contents by gently inverting the flask several times but do not shake.
- A blank is prepared similarly **without** the addition of phosphate solution. Use the most concentrated solution as the initial standard and adjust the microammeter reading to 100 divisions.
- Check the standard solution for a galvanometer reading of 100.
- Plot galvanometer reading against **mg P_2O_5 per mL**.
- Now the unknown solution is used and its concentration determined.

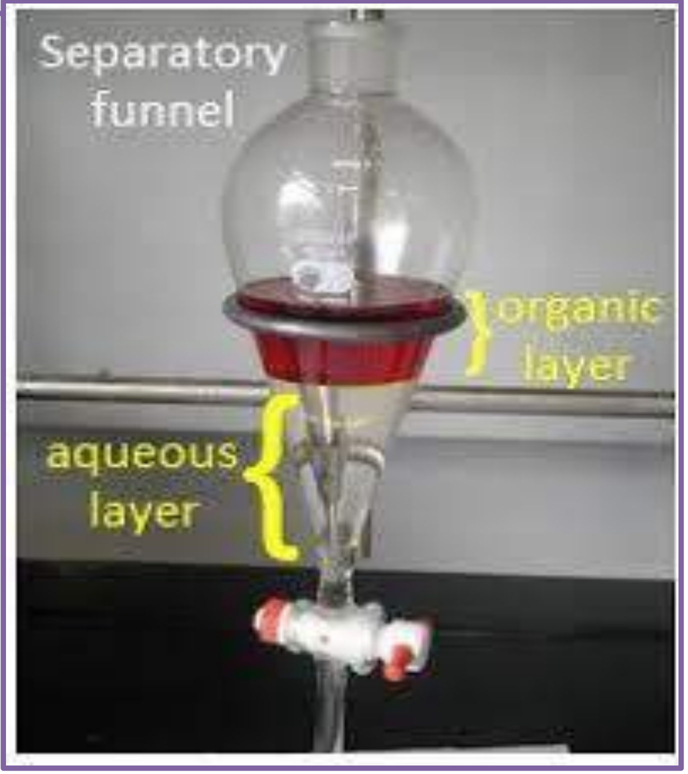
Turbidimetric titrations

- Turbidimetric titrations are carried out in a manner analogous to photometric titrations. Read the turbidity in any appropriate quantity after each increment of titrant and plot the titration curve. The end point is determined from the titration curve. The appearance of a turbidity is sometimes utilized to mark the equivalence point of a reaction. Equal increments of the titrant should be used and a fixed procedure of adding titrant and shaking should be followed. With the increase in the volume of titrant the concentration of the precipitate increases and hence the absorbance increases. When the whole substance is precipitated, absorbance becomes constant. An abrupt change in the slope shows the end point.
- In the below figure, the Turbidimetric titration curve A is an ideal curve. Curves B and C are due to particles of mixed size in the precipitate, poor stirring etc. which result in an inaccurate result. The relative error is ±5%. The concentration curve for titration is 10^{-5} to 10^{-6} F.
- Turbidimetric titrations are of particular interest because no general indicators have been developed as in neutralization or redox titrations. Examples of such titrations are: SO_4 as $CaSO_4$, Ag as AgX, Ca as CaC_2O_4 or CaF_2 etc. Turbidimetry can also be used for titrating a mixture of two liquids by a third which is miscible with one but not with the other. Addition of a sufficient quantity of the third liquid will result in separation of phases causing turbidity. The results can be interpreted on the basis of knowledge of **three component phase** diagram or one should titrate unknown with known mixtures. These titrations are particularly termed as **phase titrations.**.

Questions.......

SOLVENT EXTRACTION

BSc – IV SEM
NEP Syllabus



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CONTENT - SOLVENT EXTRACTION: 4 H

Syllabus

- Types-batch, continuous,
- Efficiency
- Selectivity
- Distribution coefficient,
- Factors affecting the partition,
- Relationship between % extraction and volume fraction,
- **Numerical problems** on solvent extraction.
- Solvent extraction of iron and copper.

Important

- Terminologies
- Introduction -
- Principle of working – Gibb's phase rule
- Nernst distribution law
- Extraction procedures
  - Simple Extraction
  - Multiple extractions & its importance.
- Applications of solvent extractions

Terminologies

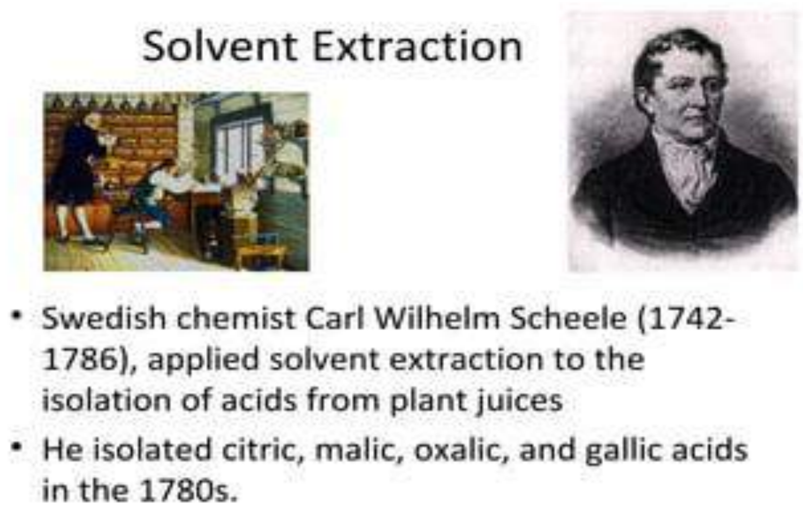
- Solvent extraction – liquid-liquid extraction.
- inorganic species
- organic solvents as extractants.
- chelating,
- ion-pair, or organic reagents
- extraction
- hydrophobic,
- hydrophilic, or
- weak bonds.
- **Tributyl phosphate solvent** – nuclear chemistry for the extraction of uranium
- Extraction – transfer of solute from one phase to another.

- **Equilibrium at two phases.**
- **Partition co-efficient (P)** – conc. ratio of unionized species of compound.
- **Distribution coefficient (D)**– conc. ratio of all species of the compound (ionized+unionized).
- This ratio is a **measure** of the **difference** in **solubility** of the **compound** in these **two phases**.

APPLICATIONS OF SOLVENT EXTRACTIONS OR WHY WE NEED TO STUDY THE SOLVENT EXTRACTIONS??

Historical importance

- Important and powerful technique to solve the separation, purification and recovery problems.



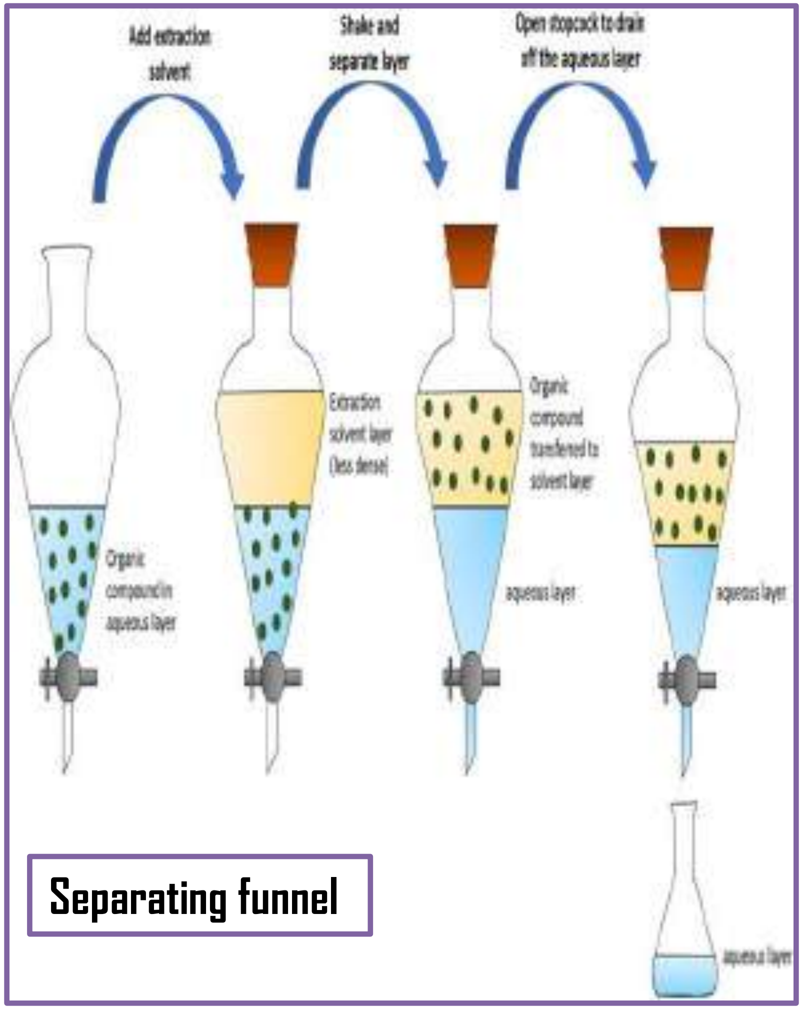
Solvent Extraction

- Swedish chemist Carl Wilhelm Scheele (1742-1786), applied solvent extraction to the isolation of acids from plant juices
- He isolated citric, malic, oxalic, and gallic acids in the 1780s.

Applications

- Solvent extractions find many applications in different fields.
- Nuclear science & technology.
- Rare earth elements extractions
- Petroleum industry
- Food industry – edible oil extraction
- Hydrometallurgy
- Extraction and Isolation of metal atoms. Transuranium elements,

SOLVENT EXTRACTION – INTRODUCTION



Separating funnel

✓**Solvent extraction**, also called **liquid-liquid extraction** (LLE) and **partitioning**, is a method to separate compounds based on their relative **solubilities** in two different **immiscible liquids**.

✓**Working principle: Nernst Distribution Law or principle.**

✓Immiscible liquids are ones that cannot get mixed up together and separate into layers when shaken together.

✓Ex: **water (**aqueous medium **)** and an **organic solvent**.

✓**LLE** is an extraction of a substance from one liquid into another liquid phase.

✓Employed in a **laboratory** or in **large scale manufacturing**.

✓Organic solvents (**non-aqueous layer**) - **benzene**, **chloroform**, and **ether**, than in **water** and these solvents are **immiscible** with **water**.

✓Upon shaking, these **separate into two layers**.

✓. Finally this non-aqueous layer is removed and **distilled** to obtain the **purified compound**.

✓Solvent extraction is a widely used method for the extraction of various **inorganic species** from various samples using **organic solvents** as **extractants**.

✓In this method, usually the solvent contains **chelating**, **ion-pair**, or **organic** (**hydrophobic** or **hydrophilic**) **reagents** for the extraction of inorganic species through **ion-pair**, **hydrophobic**, **hydrophilic**, or **weak bonds**.

PRINCIPLE OF SOLVENT EXTRACTION:

- As per the **Gibb's phase rule**:

$$P + V = C + 2.$$

- Where P = no. of phases, C = no. of components, V = degree of freedom.
- In solvent extraction we have two phases namely the aqueous & the organic phase, the component is (C = 1) solute, in solvent and water phase and at constant temperature and pressure V = 1, thus we have,

$$2 + 1 = 1 + 2$$

$$\text{i.e., } P + V = C + 2$$

PRINCIPLE OF SOLVENT EXTRACTION:

- ✓ According to **Nernst distribution law**, if $[X_1]$ and $[X_2]$ are the concentration of solute in phase 1 and 2, then at equilibrium,
  - ❖ The **partition** or **distribution coefficient** is given by the equation
  - ❖ $K_D = [X_2]/[X_1]$. K_D is the partition co-efficient.
  - ❖ K_D is **independent** of the **total solute concentration** in either of the **two phases**.
- In the above equation, the **activity co-efficient** of the species in **organic** as well as **aqueous** phase is not considered.
- The value of **distribution ratio** (D) to account for the **total concentration** of **species** in **two phases** is given by
- $$D = \frac{\text{Total concentration of species in the organic phase}}{\text{Total concentration of species in the aqueous phase.}}$$

Now assuming there is no **association**, **dissociation** or **polymerization** in both the phases then, under idealized conditions, **K_D would be equal to D.**

NERNST DISTRIBUTION LAW, CONTINUATION..

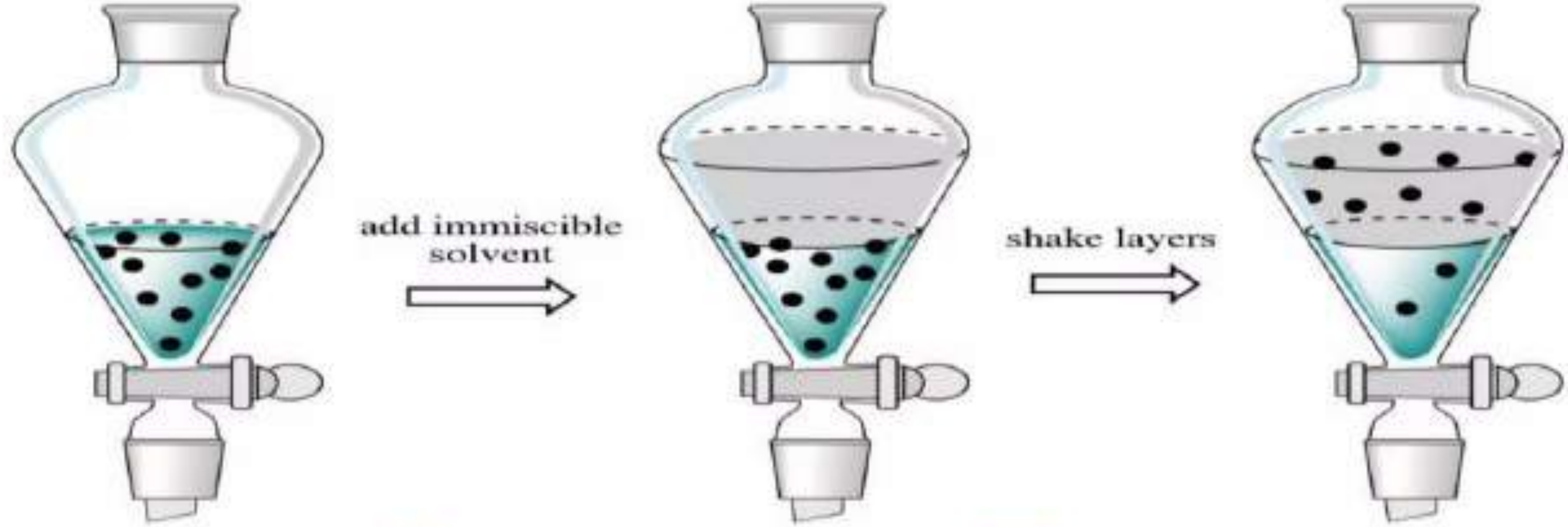
- In practical work, instead of using the terms K_D or D one prefer to use the term percentage extraction (E).
- This is related to distribution ratio (D) by the expression
- $D = \frac{(V_w/V_O)E}{100-E}$

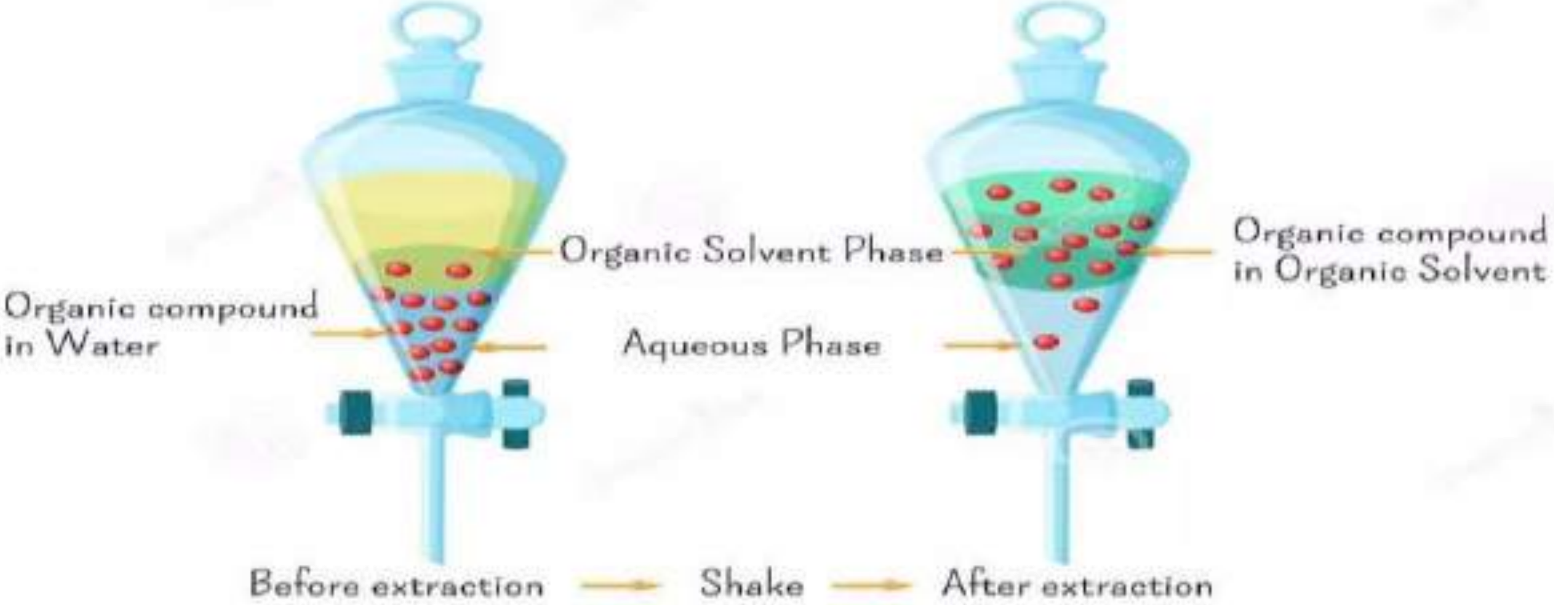
Where, V_w = Volume of the Aqueous phase.

V_O = Volume of Organic phase.

E = % of Extraction.

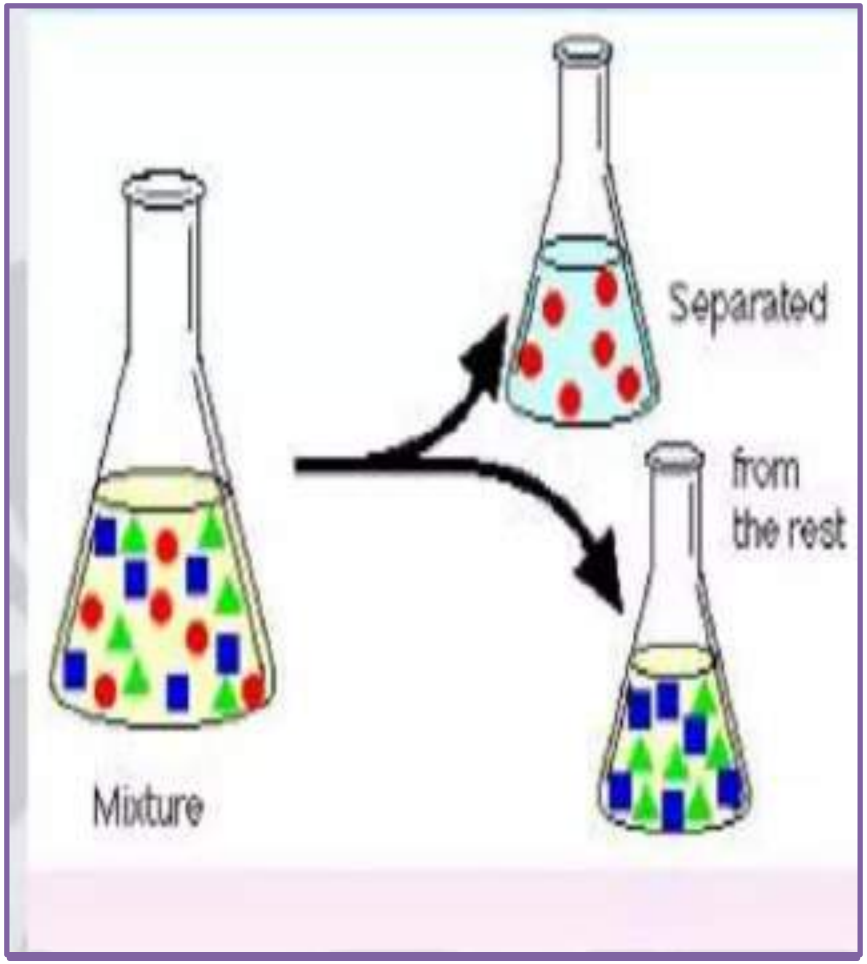
SOLVENT EXTRACTION PROCEDURE





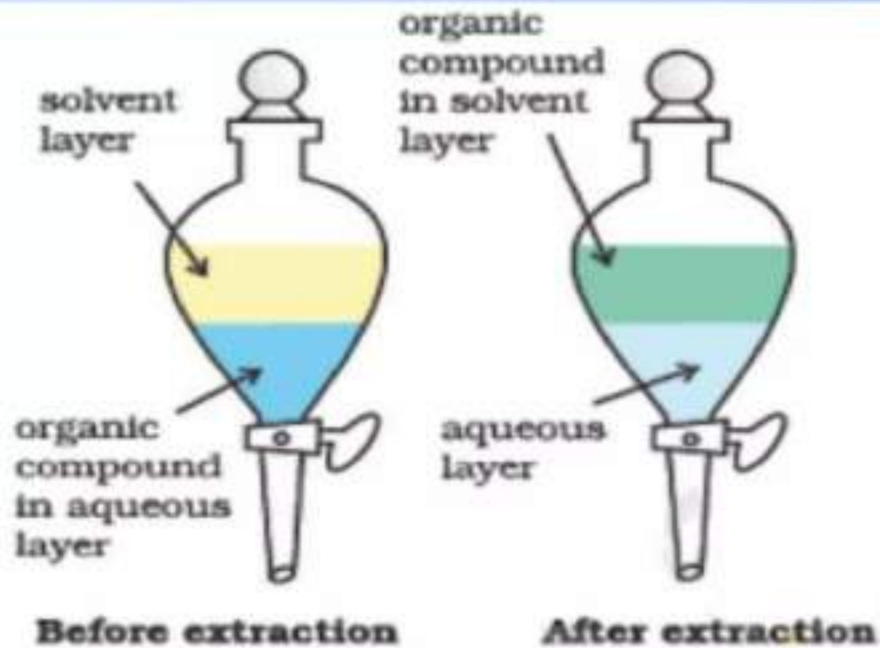
SOLVENT EXTRACTION PROCEDURE

- Solvent extraction is a method to separate compounds based on their **relative solubilities** in two **immiscible liquids**, usually **water** and an **organic solvent**.
- Simple extractions



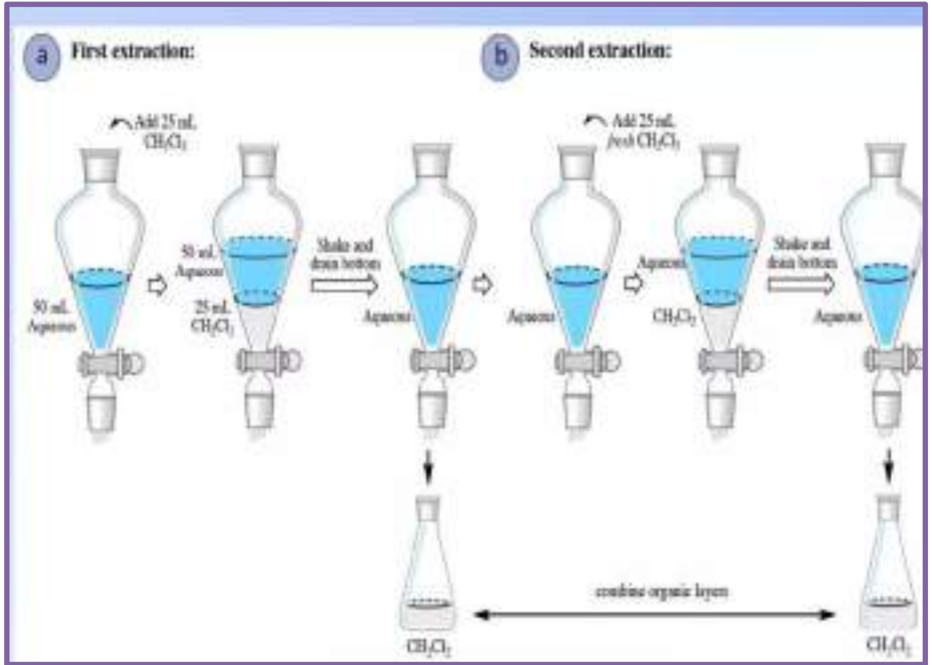
SOLVENT EXTRACTION PROCEDURE - TWO STEPS

Simple extraction



The extraction process when carried out with the total amount of given organic solvent in a single step is known as **simple extraction**.

Multiple extraction



When the extraction is carried out in **more number of steps** by using small amounts of organic solvent from total solvent with same aqueous solution is known as **multiple extraction**.

Multiple extraction gives more extraction of organic substance than single step extraction by using same amount of extracting solvent.

TYPES-BATCH, CONTINUOUS,

- Solvent extraction is considered to be the most versatile and popular method of separation.

EXTRACTION TECHNIQUES

1. Batch extraction
2. Stripping extraction
3. Continuous extraction

1. BATCH EXTRACTION:

- Batch extraction is employed where a large distribution ratio for the desired separation is readily obtainable.
- A separating funnel is the simplest and most suitable apparatus for a single – batch type of extraction.
- The two immiscible liquids are taken in the funnel; the system is rigorously shaken to provide the most intimate contact between the two phases.
- On standing for some time the two liquids separate and the dense liquid is withdrawn through the stop cock.
- Eg., NaCl + Cholesterol.

2. STRIPPING OR BULK EXTRACTION:

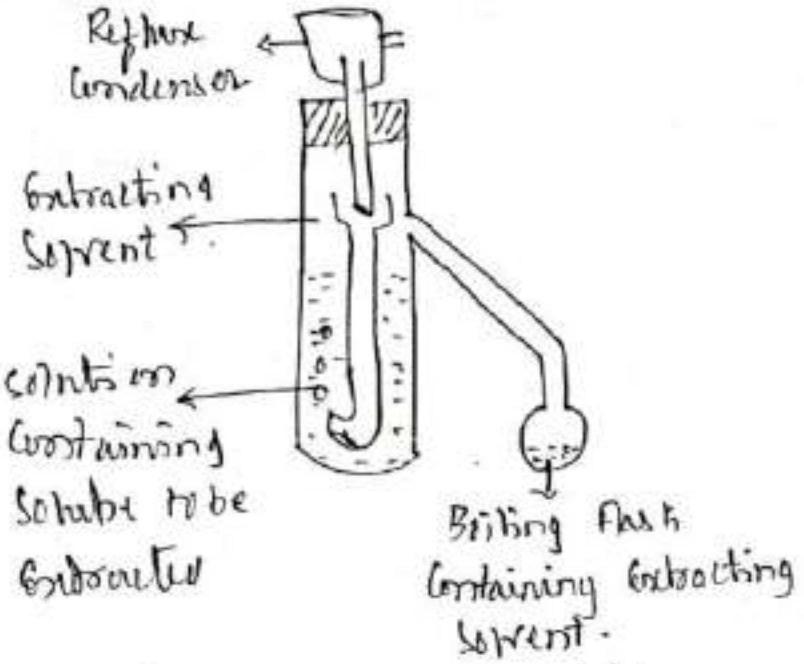
- Stripping is the removal of extracted solute from the organic phase to more suitable medium for further determination.
- If the solvent is volatile the simplest procedure is to add a small volume of water and evaporate the solvent.
- Care should be taken to avoid loss of a volatile solute during evaporation.
- Sometimes adjustment of pH of solution, change in valence state or the use of competitive water-soluble complexing reagents may be employed to prevent loss of water.

3. CONTINUOUS EXTRACTION

- The process of extraction can be accelerated by the use of an apparatus known as continuous extractor. A design for such an extractor is shown in the below figure in which the solvent used for extraction is lighter than the solvent initially containing the solute.
- The heavier liquid containing the sample is placed in lower part of a long vertical table.
- A funnel tube which is U-shaped at lower end is inserted and also a reflux condenser at the top.
- The lighter solvent is boiled in a flask connected to a side arm. Its vapors which enter the extractor are converted back to the liquid state in the reflux condenser which then pass downward through the U-shaped end and percolated upward through the solution containing the solute to be extracted.
- Finally, the extracting solvent now containing solute, overflows back into the boiling flask.
- The solute should be non-volatile and thermally stable.

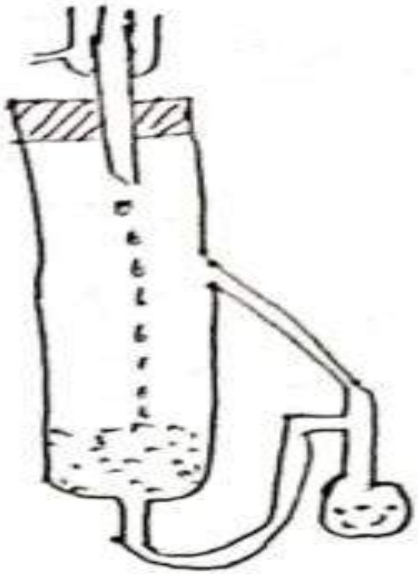
3. CONTINUOUS EXTRACTION

Organic solvent lighter than water



ⓐ Organic solvent lighter than water

Organic solvent heavier than water



ⓑ Organic Solvent Heavier than water.

SELECTIVITY OF SOLVENT EXTRACTION

- If the initial solvent contains two solutes A and B. it often happens that, when A is completely extracted, and undesired amount of B is also extracted.
- The effectiveness of the separation increases with the increase in the value of separation coefficient or separation factor 'β', which is related to individual distribution coefficient as follows

$$\beta = \left(\frac{[A]_2 / [A]_1}{[B]_2 / [B]_1} \right) = \left(\frac{K_{D(A)}}{K_{D(B)}} \right)$$

- The equilibrium distribution of each solute, A and b is largely dependent on the presence of each other unless, there is some chemical interaction involving both A and B takes place.
- Separation of A from B the value of should be as high as possible and that of as low as possible.

EFFICIENCY OF SOLVENT EXTRACTION

- The efficiency of an extraction depends on the magnitude of 'D' and on the relative volumes of the liquid phases. The percentage of extraction is given by

$$E=\left(\frac{100D}{\left[D+\left(\frac{V_W}{V_0}\right)\right]}\right)$$

- Where V_w and V_0 are the volume of the aqueous phase and volume of organic phase respectively, or , $E=\left(\frac{100D}{(D+1)}\right)$
- where D= distribution ratio.
- When the phases are of equal volumes.

- **Efficiency of extraction depends on**
    - Coordinating ability of solvent.
    - Acidity of the aqueous solution (pH)
    - Oxidation state/charge of metal ions
    - Use of appropriate solvent.

DISTRIBUTION COEFFICIENT

- The distribution ratio which is the ratio of the concentrations of all the species of the solute in each phase.

$$D = \left(\frac{K_D}{1 + K \frac{K_a}{[H^+]_a}} \right)$$

- Or

$$D = \left(\frac{\frac{V_W}{V_0} . E}{100 - E} \right)$$

- Where, K_D = equilibrium distribution; $[H^+]_a$ = concentration of H^+ ions; K_a acidity constant.

FACTORS AFFECTING THE PARTITION IN SE

- Effect of **temperature** and inert solutes.
- Effect of **pH**
- Molarity of the acid.
- Presence of **salting out agents** (To enhance extraction, small size, high charge – ammonium salts, ferric salts, aluminum salts)
- Effect of metal ion concentration.
- Presence of **masking** (sequestering) **agents**. E.g., CN-, tartarate, citrate, fluoride, EDTA (At highly acidic conditions – Masking agents do not work effectively).
- Concentration of the **extractants**.
- The nature of **diluents**.
- Nature of **solute**
- Nature of **solvent**

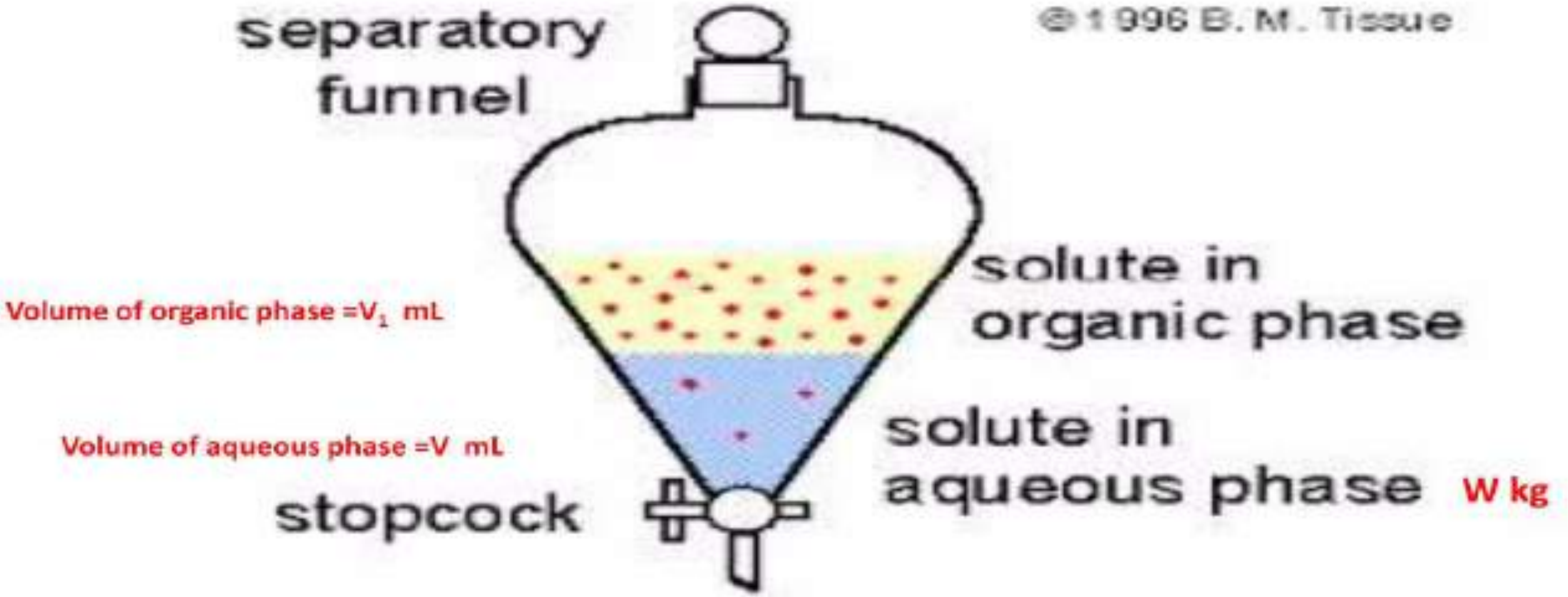
Choice of solvents for extraction

- High D for solute and low D for undesirable impurities.
- Low solubility in aqueous phase.
- Sufficient low viscosity and density difference from aqueous phase to avoid formation of emulsions.
- Low toxicity and inflammability
- Ease of recovery of solute from the solvent for subsequent analytical processing.

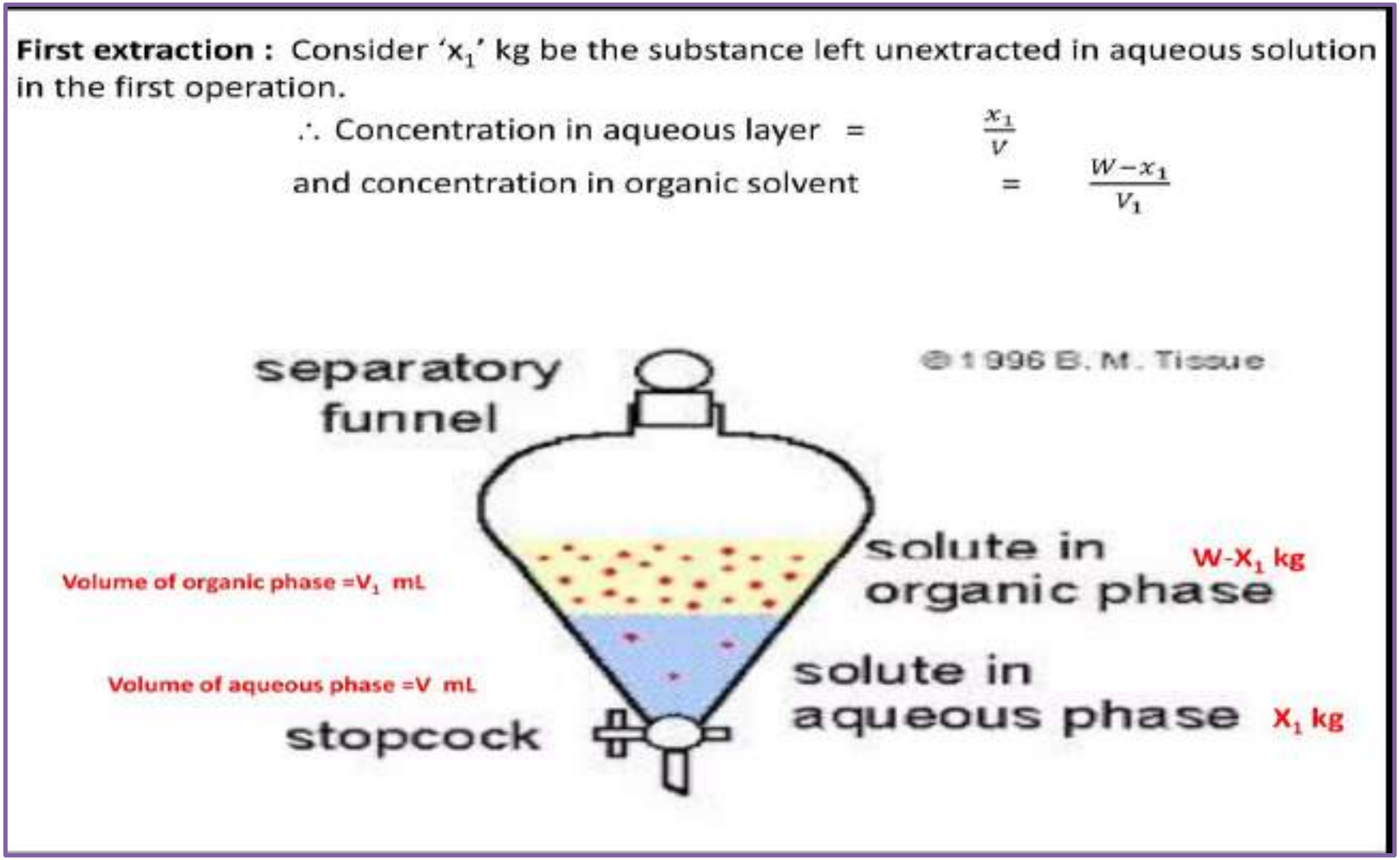
RELATIONSHIP BETWEEN % EXTRACTION AND VOLUME FRACTION

Equation for the solute left unextracted after nth extraction

Suppose V ml of an aqueous solution contain 'W' kg of an organic substance. Let V_1 ml of given organic solvent is used for extraction in each step.



RELATIONSHIP BETWEEN % EXTRACTION AND VOLUME FRACTION



First extraction : Consider 'x_1' kg be the substance left unextracted in aqueous solution in the first operation.

$\therefore$ Concentration in aqueous layer $= \frac{x_1}{V}$

and concentration in organic solvent $= \frac{W-x_1}{V_1}$

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RELATIONSHIP BETWEEN % EXTRACTION AND VOLUME FRACTION

From distribution law

$$K = \frac{Concentration\ in\ aqueous\ phase}{Concentration\ in\ organic\ phase}$$

$$= \frac{\frac{x_1}{V}}{\frac{W - x_1}{V_1}}$$

$$= \frac{x_1 V_1}{V(W - x_1)}$$

OR $$KVW - KVx_1 = x_1 V_1$$

$$KVW = x_1 V_1 + KVx_1$$

$$KVW = x_1 (V_1 + KV)$$

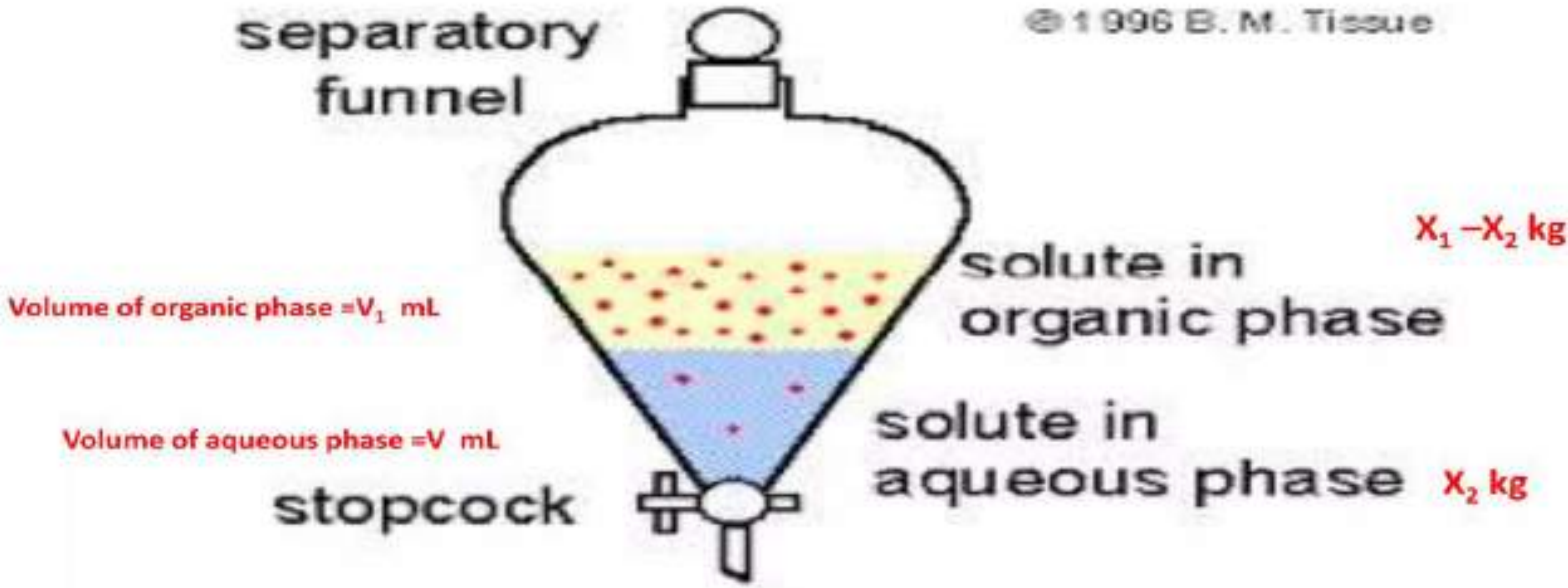
$$x_1 = W \quad \left(\frac{KV}{V_1 + KV}\right) \qquad .....(1)$$

RELATIONSHIP BETWEEN % EXTRACTION AND VOLUME FRACTION

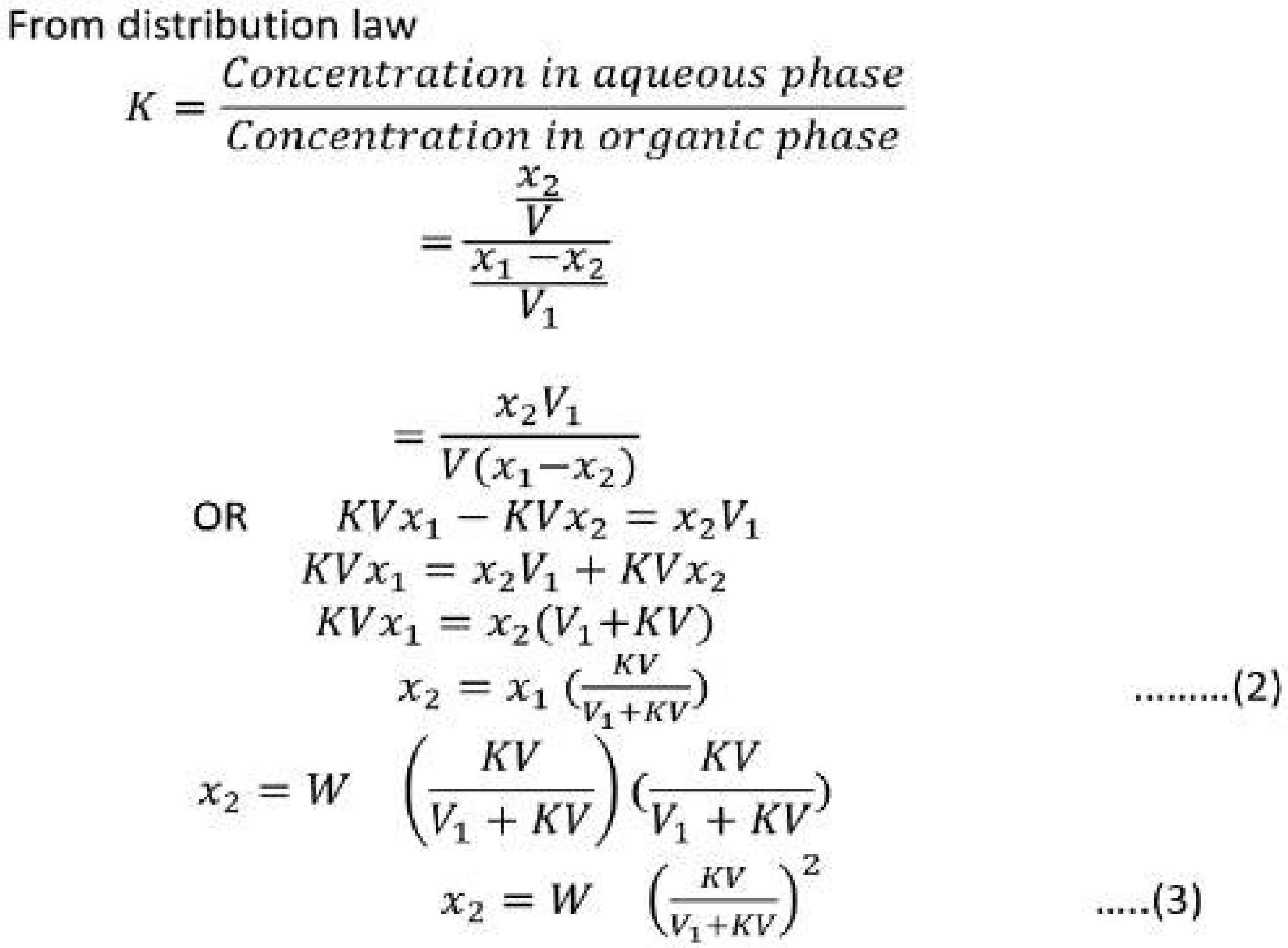
Second extraction : Second extraction is carried by using same V_1 ml of fresh solvent from aqueous solution remained after first extraction. Let 'x_2' kg be the substance unextracted in aqueous layer.

$\therefore$ Concentration in aqueous layer $= \frac{x_2}{V}$

and concentration in organic solvent $= \frac{x_1 - x_2}{V_1}$



RELATIONSHIP BETWEEN % EXTRACTION AND VOLUME FRACTION



From distribution law

$$K = \frac{Concentration\ in\ aqueous\ phase}{Concentration\ in\ organic\ phase}$$

$$= \frac{\frac{x_2}{V}}{\frac{x_1 - x_2}{V_1}}$$

$$= \frac{x_2 V_1}{V(x_1 - x_2)}$$

OR $$KVx_1 - KVx_2 = x_2V_1$$

$$KVx_1 = x_2V_1 + KVx_2$$

$$KVx_1 = x_2(V_1 + KV)$$

$$x_2 = x_1\left(\frac{KV}{V_1 + KV}\right) \qquad \text{.........(2)}$$

$$x_2 = W\left(\frac{KV}{V_1 + KV}\right)\left(\frac{KV}{V_1 + KV}\right)$$

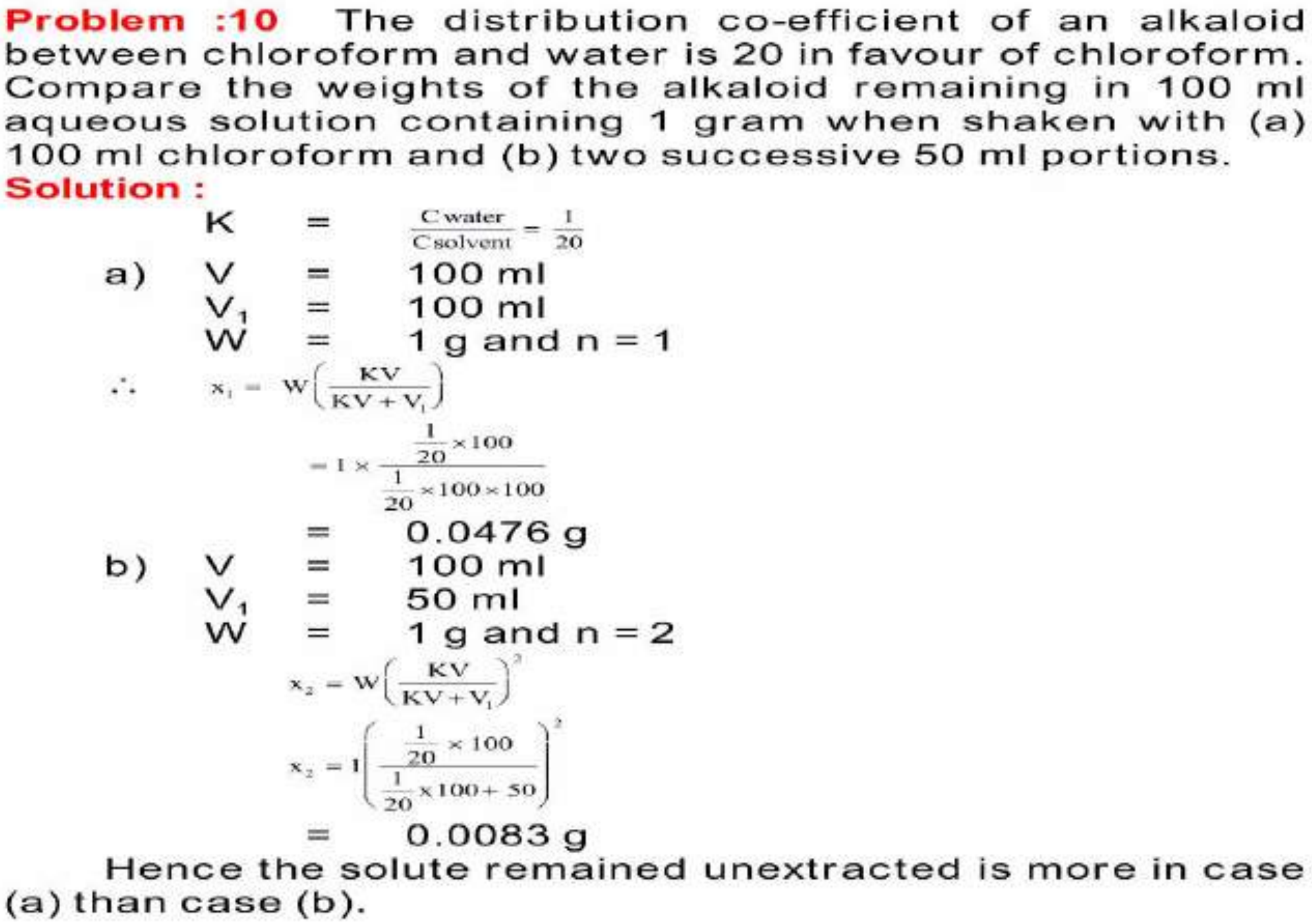
$$x_2 = W\left(\frac{KV}{V_1 + KV}\right)^2 \qquad \text{.....(3)}$$

RELATIONSHIP BETWEEN % EXTRACTION AND VOLUME FRACTION

3) nth extraction : Similar to 2nd extraction, n-extractions are carried out. Let ‘x_n’ kg be the solute unextracted, then we get,

$$x_n = W \left(\frac{KV}{V_1+KV}\right)^n \qquad \text{.........(4)}$$

NUMERICAL PROBLEMS ON SOLVENT EXTRACTION.



Problem :10 The distribution co-efficient of an alkaloid between chloroform and water is 20 in favour of chloroform. Compare the weights of the alkaloid remaining in 100 ml aqueous solution containing 1 gram when shaken with (a) 100 ml chloroform and (b) two successive 50 ml portions.

Solution :

$$K = \frac{C\,\text{water}}{C\,\text{solvent}} = \frac{1}{20}$$

a) V = 100 ml
V_1 = 100 ml
W = 1 g and n = 1

$$\therefore \quad x_1 = W\left(\frac{KV}{KV+V_1}\right)$$

$$= 1 \times \frac{\frac{1}{20}\times 100}{\frac{1}{20}\times 100 \times 100}$$

= 0.0476 g

b) V = 100 ml
V_1 = 50 ml
W = 1 g and n = 2

$$x_2 = W\left(\frac{KV}{KV+V_1}\right)^2$$

$$x_2 = 1\left(\frac{\frac{1}{20}\times 100}{\frac{1}{20}\times 100 + 50}\right)^2$$

= 0.0083 g

Hence the solute remained unextracted is more in case (a) than case (b).

NUMERICAL PROBLEMS RELATED TO SE

Problem : 11 An aqueous 0.1 dm^3 solution of organic compound contains 0.01 Kg of compound would be extracted in five instalments of 0.02 dm^3 each of ether. If the partition coefficient is 5 in favour of ether, calculate the amount extracted.

Solution :

$$K = \frac{\text{Concentration of water}}{\text{Concentration in ether layer}} = \frac{1}{5} = 0.2$$

Given : $W = 0.01$ Kg

$V = 0.1\ dm^3$

$V_1 = 0.02\ dm^3$

$n = 5$

$$\therefore \quad \text{Amount un extracted} = W\left(\frac{KV}{KV + V_1}\right)$$

$$= 0.01\left(\frac{0.2 \times 0.1}{0.2 \times 0.1 + 0.02}\right)$$

$$= 3.125 \times 10^{-4}\ \text{Kg}$$

Hence the amount extracted $= 0.01 - 3.125 \times 10^{-4}$ Kg.

$= 9.6874 \times 10^{-3}$ Kg

APPLICATIONS OF SOLVENT EXTRACTION:

- This technique is used predominantly for the isolation of a single chemical species prior to a determination.
- Most widespread application is in the determination of metals as minor and trace elements in variety of inorganic and organic materials.
- The analysis of metallurgical and geological samples
- Analysis of petrochemical products.
- Analysis of food stuffs.
- Analysis of plant extractions.
- Analysis of extraction of animal tissues and body fluids.
- Separation of compounds such as hydrocarbons, acids, fats, waxes etc.

SOLVENT EXTRACTION OF IRON.

- Iron (III) can be separated from most of the mono and divalent cations by extraction it from 6 N HCl into diethyl ether, diisopropyl ether or dichlorodiethyl ether.
- In the presence of HCl, following equilibria exist, though its parent form is represented as $[FeCl_4][Fe(H_2O)_6]^{3+}$

- $[Fe(H_2O)_6]^{3+} + Cl^- \longleftrightarrow [Fe(H_2O)_5Cl]^{2+} + H_2O$
- $[Fe(H_2O)_5Cl]^{2+} + Cl^- \longleftrightarrow [Fe(H_2O)_4Cl_2]^{+} + H_2O$
- $[Fe(H_2O)_4Cl_2]^{+} + Cl^- \longleftrightarrow [Fe(H_2O)_3Cl_3] + H_2O$
- $[Fe(H_2O)_3Cl_3] + Cl^- \longleftrightarrow [Fe(H_2O)_2Cl_4]^- + H_2O$
- If HCl conc is 4 N or greater the last equilibria is dominant.

PROCEDURE - SOLVENT EXTRACTION OF IRON.

- Dissolve a 0.5 g sample of steel in 2.5 ml of 6 N HCl and 4 mL of conc HNO_3 by heating the mixture on a water bath.
- Evaporate the solution, to dryness and dissolve the contents in 15 mL of 1:2 HCl.
- Transfer the solution to continuous extractor.
- Extract the solution with diethyl ether until ether layer above the solution is colorless; this layer is put in a separating funnel.
- Remove the iron from ethereal layer by successive washings with an H_2O, titrate the solution for its iron contents against 0.1 N $K_2Cr_2O_7$ solutions by reducing it to Fe^{2+} state prior to titration.

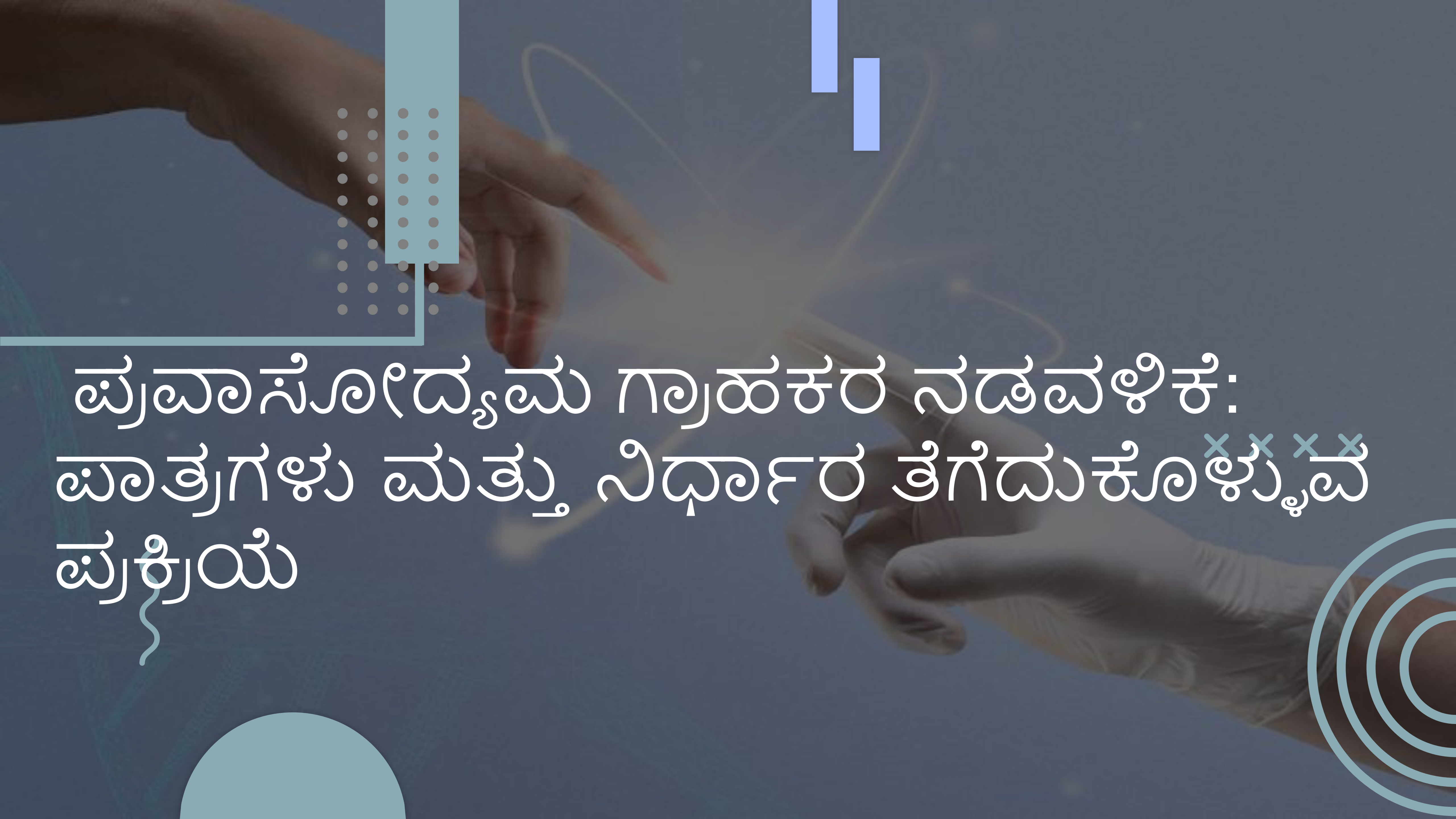
DETERMINATION OF COPPER BY OXINE:

- Oxine or 8hydroxyquinoline exists as zwitter ion. Trivalent metal ions from neutral complexes with three molecule of oxine while only two molecules of the reagents are required for divalent metal like Cu^{2+}.
- Cu2+ + 2 8-HQ === complex + 2H+
- The selectivity of the extraction is enhanced by using EDTA or cyanides as masking agents.

THANK YOU

Pending works

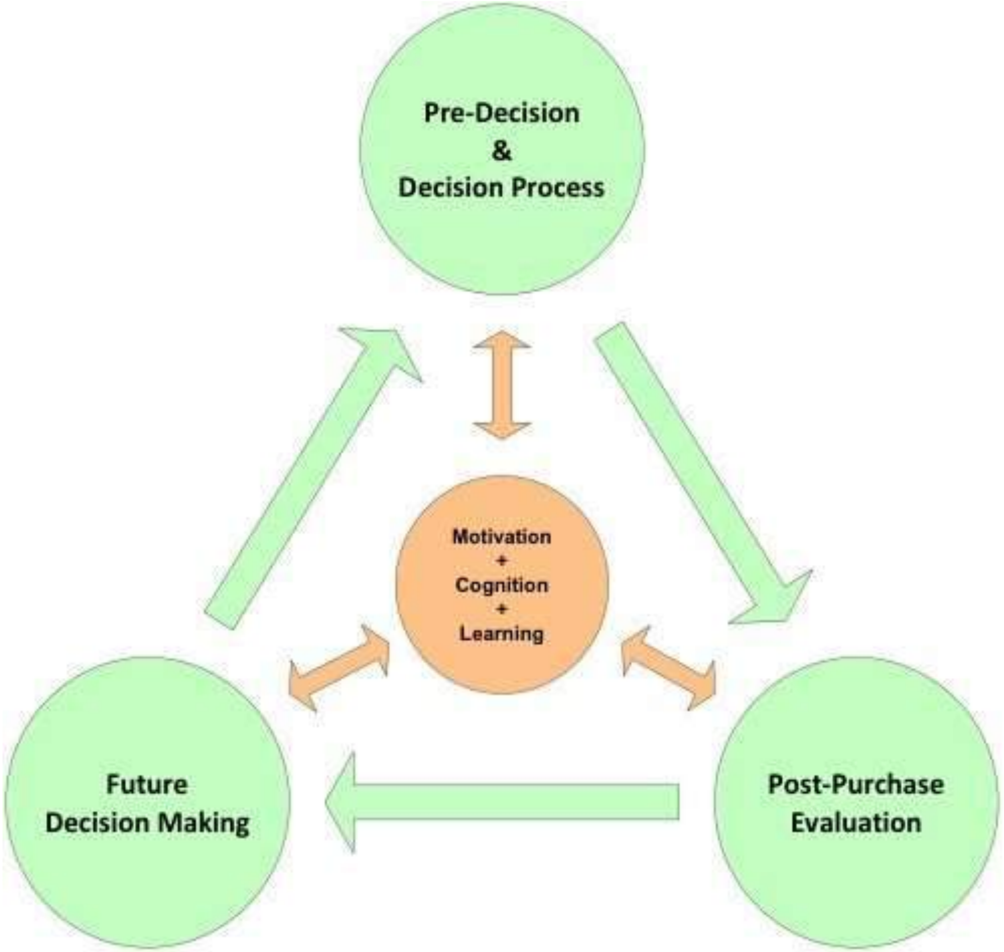
- Chromatography – PPT for I BSc SEP
- https://www.slideshare.net/0673504457/history-of-drug-discovery#3
- SE – PPT informations



ಪ್ರವಾಸೋದ್ಯಮ ಗ್ರಾಹಕರ ನಡವಳಿಕೆ: ಪಾತ್ರಗಳು ಮತ್ತು ನಿರ್ಧಾರ ತೆಗೆದುಕೊಳ್ಳುವ ಪ್ರಕ್ರಿಯೆ

ಪರಿಚಯ:

ಪ್ರವಾಸೋದ್ಯಮ ಗ್ರಾಹಕರ ನಡವಳಿಕೆ ಎನ್ನುವುದು ಪ್ರವಾಸೋದ್ಯಮ ಉದ್ಯಮದ ಪ್ರಮುಖ ಅಂಶವಾಗಿದೆ. ಪ್ರವಾಸೋದ್ಯಮ ಗ್ರಾಹಕರು ಯಾರು, ಅವರು ಯಾವ ರೀತಿಯ ನಿರ್ಧಾರಗಳನ್ನು ತೆಗೆದುಕೊಳ್ಳುತ್ತಾರೆ ಮತ್ತು ಅವರ ನಿರ್ಧಾರಗಳನ್ನು ಯಾವ ಅಂಶಗಳು ಪ್ರಭಾವಿಸುತ್ತವೆ ಎಂಬುದನ್ನು ಅರ್ಥಮಾಡಿಕೊಳ್ಳುವುದು ಪ್ರವಾಸೋದ್ಯಮ ವ್ಯವಹಾರಗಳನ್ನು ಯಶಸ್ವಿಯಾಗಿಸಲು ಸಹಾಯ ಮಾಡುತ್ತದೆ.



ಪ್ರವಾಸೋದ್ಯಮ ಗ್ರಾಹಕರ ನಡವಳಿಕೆಯನ್ನು ಅರ್ಥಮಾಡಿಕೊಳ್ಳಲು, ಅವರನ್ನು ವಿವಿಧ ಪಾತ್ರಗಳಲ್ಲಿ ವಿಂಗಡಿಸಬಹುದು. ಈ ಪಾತ್ರಗಳು ಒಬ್ಬ ವ್ಯಕ್ತಿಯು ಪ್ರವಾಸದ ಯೋಜನೆ ಮತ್ತು ನಿರ್ವಹಣೆಯಲ್ಲಿ ವಹಿಸುವ ವಿಭಿನ್ನ ಕಾರ್ಯಗಳನ್ನು ಪ್ರತಿನಿಧಿಸುತ್ತವೆ.

1. ಪ್ರಾಥಮಿಕ ಗ್ರಾಹಕರು ಎನ್ನುವುದು ಪ್ರವಾಸದ ಪ್ರಯೋಜನವನ್ನು ಪಡೆಯುವ ಜನರು. ಇವುಗಳಲ್ಲಿ ಪ್ರವಾಸಿಗರು, ಅವರ ಕುಟುಂಬ ಮತ್ತು ಸ್ನೇಹಿತರು ಸೇರಿದ್ದಾರೆ.

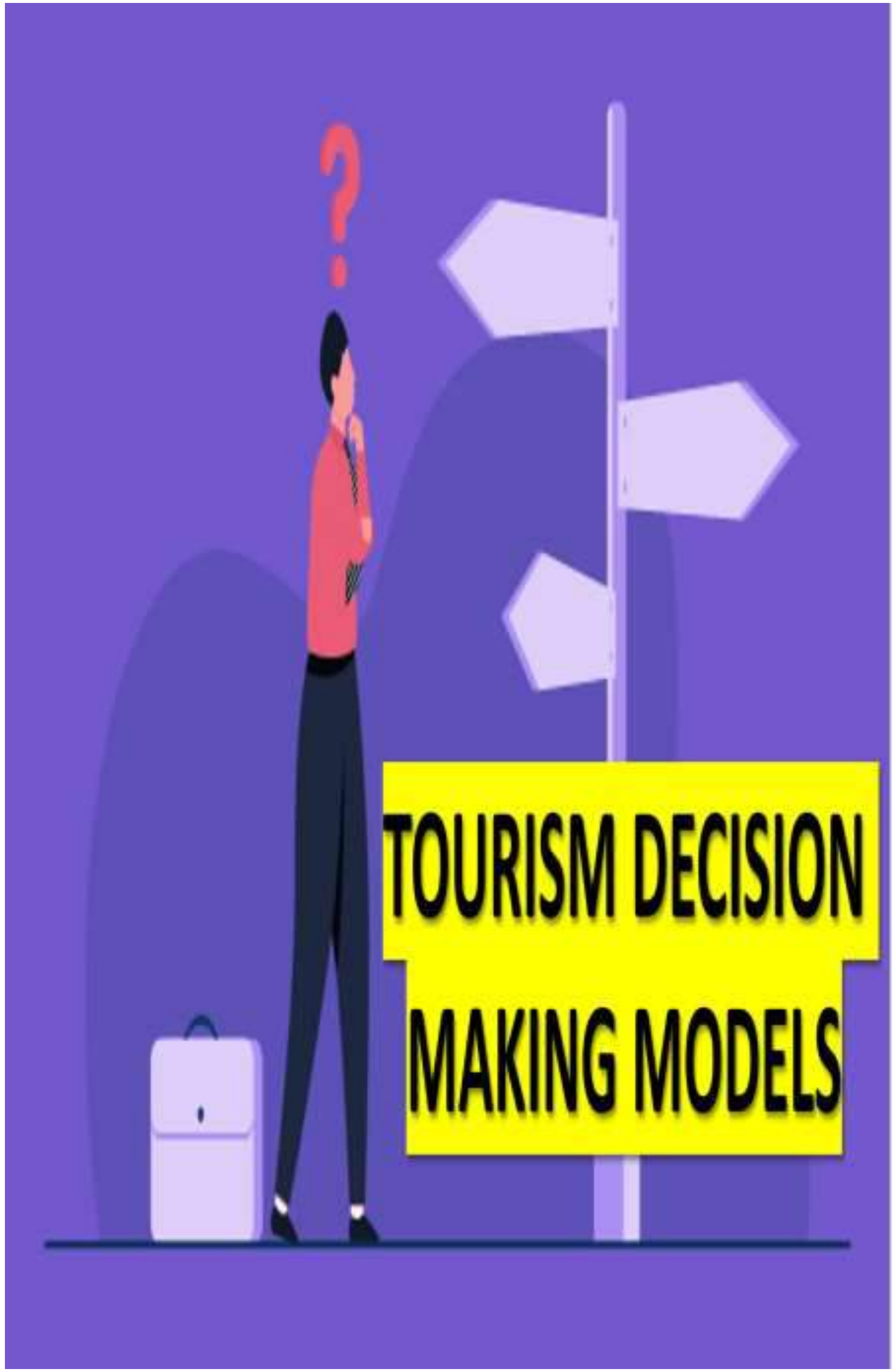
2. ದ್ವಿತೀಯಕ ಗ್ರಾಹಕರು ಎನ್ನುವುದು ಪ್ರವಾಸದ ಯೋಜನೆ ಮತ್ತು ನಿರ್ವಹಣೆಯಲ್ಲಿ ಸಹಾಯ ಮಾಡುವ ಜನರು. ಇವುಗಳಲ್ಲಿ ಪ್ರವಾಸೋದ್ಯಮ ಏಜೆಂಟ್‌ಗಳು, ಟ್ರಾವೆಲ್ ಬ್ಲಾಗರ್‌ಗಳು ಮತ್ತು ಸಾಮಾಜಿಕ ಮಾಧ್ಯಮ ಪ್ರಭಾವಕರು ಸೇರಿದ್ದಾರೆ.

3. ಆಂತರಿಕ ಗ್ರಾಹಕರು ಎನ್ನುವುದು ಪ್ರವಾಸೋದ್ಯಮ ಉದ್ಯಮದಲ್ಲಿ ಕೆಲಸ ಮಾಡುವ ಜನರು. ಇವುಗಳಲ್ಲಿ ಪ್ರವಾಸೋದ್ಯಮ ಕಂಪನಿಗಳ ನೌಕರರು, ಪ್ರವಾಸೋದ್ಯಮ ಸೇವೆಗಳನ್ನು ಒದಗಿಸುವ ಉದ್ಯಮಗಳು ಮತ್ತು ಸಾರ್ವಜನಿಕ ವಲಯದ ಪ್ರವಾಸೋದ್ಯಮ ಸಂಸ್ಥೆಗಳು

ಪ್ರವಾಸೋದ್ಯಮ ಗ್ರಾಹಕರ ನಡವಳಿಕೆಯನ್ನು ಅರ್ಥಮಾಡಿಕೊಳ್ಳಲು, ಅವರ ನಿರ್ಧಾರ ತೆಗೆದುಕೊಳ್ಳುವ ಪ್ರಕ್ರಿಯೆಯನ್ನು ಅರ್ಥಮಾಡಿಕೊಳ್ಳುವುದು ಸಹ ಮುಖ್ಯವಾಗಿದೆ. ಈ ಪ್ರಕ್ರಿಯೆಯು ಸಾಮಾನ್ಯವಾಗಿ ಈ ಹಂತಗಳನ್ನು ಒಳಗೊಂಡಿರುತ್ತದೆ

1. ಅಗತ್ಯತೆಗಳು ಮತ್ತು ಆಸಕ್ತಿಗಳನ್ನು ಗುರುತಿಸುವುದು
2. ಬಜೆಟ್ ಮತ್ತು ಸಮಯದ ಮಿತಿಯನ್ನು ನಿರ್ಧರಿಸುವುದು
3. ಗುರಿಗಳನ್ನು ಹೊಂದಿಸುವುದು
4. ಆಯ್ಕೆಗಳನ್ನು ಪರಿಗಣಿಸುವುದು
5. ನಿರ್ಧಾರ ತೆಗೆದುಕೊಳ್ಳುವುದು

Tourist Decision-Making Process



1. ಅಗತ್ಯತೆಗಳು ಮತ್ತು ಆಸಕ್ತಿಗಳನ್ನು ಗುರುತಿಸುವುದು

ಪ್ರವಾಸೋದ್ಯಮ ಗ್ರಾಹಕರು ತಮ್ಮ ಪ್ರವಾಸದಿಂದ ಏನು ಪಡೆಯಲು ಬಯಸುತ್ತಾರೆ ಎಂಬುದನ್ನು ಮೊದಲು ಅರ್ಥಮಾಡಿಕೊಳ್ಳುವುದು ಮುಖ್ಯವಾಗಿದೆ. ಅವರ ಅಗತ್ಯತೆಗಳು ಮತ್ತು ಆಸಕ್ತಿಗಳು ವೈಯಕ್ತಿಕ ಮತ್ತು ವೈಯಕ್ತಿಕವಾಗಿರಬಹುದು. ಕೆಲವು ಪ್ರಮುಖ ಅಗತ್ಯತೆಗಳು ಮತ್ತು ಆಸಕ್ತಿಗಳಲ್ಲಿ ಇವು ಸೇರಿವೆ.

- ಮನರಂಜನೆ ಮತ್ತು ವಿಶ್ರಾಂತಿ
- ಶೈಕ್ಷಣಿಕ ಅನುಭವ
- ಸಾಂಸ್ಕೃತಿಕ ಅನುಭವ
- ಖರೀದಿಯ ಅವಕಾಶಗಳು
- ನೈಸರ್ಗಿಕ ಸೌಂದರ್ಯ

2. ಬಜೆಟ್ ಮತ್ತು ಸಮಯದ ಮಿತಿಯನ್ನು ನಿರ್ಧರಿಸುವುದು

ಪ್ರವಾಸದ ಬಜೆಟ್ ಮತ್ತು ಸಮಯದ ಮಿತಿಯು ಗ್ರಾಹಕರು ಮಾಡಬಹುದಾದ ಆಯ್ಕೆಗಳನ್ನು ನಿರ್ಧರಿಸುತ್ತದೆ. ಬಜೆಟ್ ಕಡಿಮೆಯಿದ್ದರೆ, ಪ್ರವಾಸಿಗರು ಹೆಚ್ಚು ಕೈಗೆಟುಕುವ ಸ್ಥಳಗಳು ಮತ್ತು ಚಟುವಟಿಕೆಗಳನ್ನು ಆಯ್ಕೆ ಮಾಡಬೇಕಾಗುತ್ತದೆ. ಸಮಯದ ಮಿತಿಯು ಕಡಿಮೆಯಿದ್ದರೆ, ಪ್ರವಾಸಿಗರು ಹೆಚ್ಚು ಒತ್ತಡದ ಪ್ರಯಾಣವನ್ನು ಮಾಡಬೇಕಾಗುತ್ತದೆ.

3. ಗುರಿಗಳನ್ನು ಹೊಂದಿಸುವುದು

ಪ್ರವಾಸದ ಗುರಿಗಳು ಗ್ರಾಹಕರು ಏನು ಸಾಧಿಸಲು ಬಯಸುತ್ತಾರೆ ಎಂಬುದನ್ನು ನಿರ್ಧರಿಸುತ್ತದೆ. ಕೆಲವು ಪ್ರಮುಖ ಗುರಿಗಳಲ್ಲಿ ಇವು ಸೇರಿವೆ:

- ಹೊಸ ಸ್ಥಳಗಳನ್ನು ಅನ್ವೇಷಿಸುವುದು
- ಸ್ನೇಹಿತರು ಮತ್ತು ಕುಟುಂಬದೊಂದಿಗೆ ಸಮಯ ಕಳೆಯುವುದು
- ವಿಶ್ರಾಂತಿ ಪಡೆಯುವುದು
- ಆರೋಗ್ಯವನ್ನು ಸುಧಾರಿಸುವುದು

4. ಆಯ್ಕೆಗಳನ್ನು ಪರಿಗಣಿಸುವುದು

ಪ್ರವಾಸದ ಅಗತ್ಯತೆಗಳು, ಬಜೆಟ್ ಮತ್ತು ಗುರಿಗಳನ್ನು ಆಧರಿಸಿ, ಪ್ರವಾಸಿಗರು ಹಲವಾರು ಆಯ್ಕೆಗಳನ್ನು ಪರಿಗಣಿಸಬೇಕಾಗುತ್ತದೆ. ಈ ಆಯ್ಕೆಗಳಲ್ಲಿ ಇವು ಸೇರಿವೆ:

- ವೇಳಾಪಟ್ಟಿ
- ಸ್ಥಳಗಳು
- ಹೋಟೆಲ್‌ಗಳು
- ವಾಹನಗಳು
- ಚಟುವಟಿಕೆಗಳು

5. ನಿರ್ಧಾರ ತೆಗೆದುಕೊಳ್ಳುವುದು

ಅಂತಿಮವಾಗಿ, ಪ್ರವಾಸಿಗರು ತಮ್ಮ ಅಗತ್ಯತೆಗಳು, ಬಜೆಟ್ ಮತ್ತು ಗುರಿಗಳಿಗೆ ಸೂಕ್ತವಾದ ನಿರ್ಧಾರವನ್ನು ತೆಗೆದುಕೊಳ್ಳಬೇಕಾಗುತ್ತದೆ. ಈ ನಿರ್ಧಾರವು ಸಂಕೀರ್ಣ ಮತ್ತು ವೈಯಕ್ತಿಕವಾಗಿರಬಹುದು.ಈ ಪ್ರಕ್ರಿಯೆಯನ್ನು ಅರ್ಥಮಾಡಿಕೊಳ್ಳುವುದು ಪ್ರವಾಸೋದ್ಯಮ ವ್ಯವಹಾರಗಳಿಗೆ ಗ್ರಾಹಕರ ಅಗತ್ಯತೆಗಳನ್ನು ಉತ್ತಮವಾಗಿ ಪೂರೈಸಲು ಸಹಾಯ ಮಾಡುತ್ತದೆ.

Thank You!