مقرر الكيمياء التحليلية و غير العضوية
مقرر 434 ك

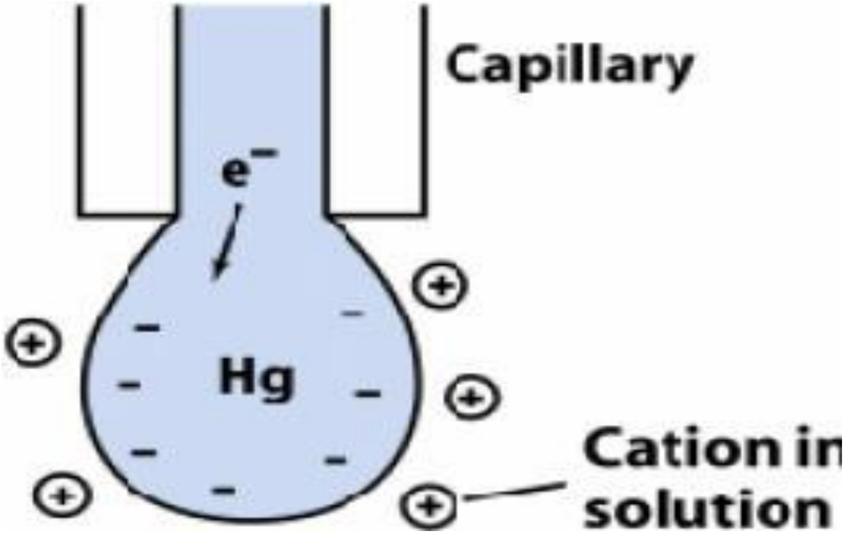
يحتوى على :

1. الجزء الخاص بالكيمياء التحليلية (التحليل الالى)
2. الجزء الخاص بالكيمياء غير العضوية
(عناصر الفئة F من الجدول الدورى)

اسم المقرر	الفرقة	الفصل الدراسي	الشعبه	لها عملي	النهاية العظمي للمقرر	النهاية الصغرى للمقرر	تحريري	درجة التحريري العظمى	درجة التحريري الصغرى	درجة العملي	درجة العملي الصغرى	درجة اعمال السنه	درجة الشفوي	مناقشة
تحليلية وغير عضوية	الفرقة الرابعه	الفصل الدراسي الثاني	الكيمياء	1	400	240	تحريري	240	72	80		40	40	

Polarography

Dropping Mercury Electrode (DME)



Polarography

❑ Polarography is one of the Voltametric methods of analysis;
electrochemical methods where current voltage curves obtained at the
surface of microelectrodes are studied.

❑In polarography the microelectrode is a dropping mercury
electrode (DME).

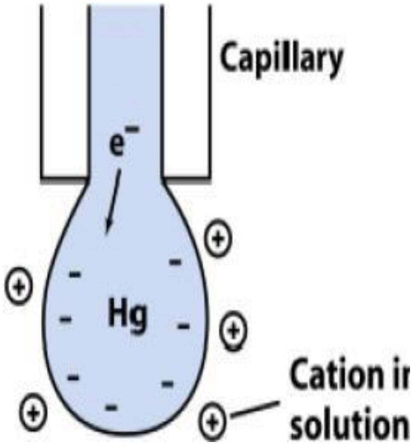
❑The method is used for the analysis of electroreducible or oxidizable
metal, ion or organic substance (electroactive species).

❑

Electroactive species is transferred into a polarographic cell
(electrolytic cell) where voltage is applied to the electrodes

- ❑ One of the electrodes is a polarizable microelectrode (DME) while the
other is reference non polarizable electrode

- -DME is the cathode
- (attached to the negative
- pole of the voltage supply)
- -upon applying the voltage,
- electroactive species will
- move towards DME,
- electron transfer occurs and
- a current flows.
- -The current produced is
- proportional to
- concentration of the
- electroactive species



Polarization:

Ohm's law : $E_{cell} = I R$

E □ I (current)

If the increase in cell potential is not accompanied by increase in current it is called Polarization.

Modes of Transport of Electroactive species to DME

1-By Convection:

by mechanical stirring or by heating, as it increases current increases . This type can be prevented by:

-avoiding stirring
-controlling the temperature.
-adding gelatin to increase viscosity of medium

2-By electrostatic attraction :

between positive species and the negative cathode; The current produced here is known by migration current, it can be minimized by:

-adding large excess of inert electrolyte (not reducible) known by supporting electrolyte (50- 100 time analyte concentration)

3-By diffusion:

-occurs due to concentration gradient of ions

-The rate of mass transport by diffusion depends on theconcentration and the diffusion coefficient (a constant

value characteristic for the analyte)

-the transport (current) will depend on concentration.

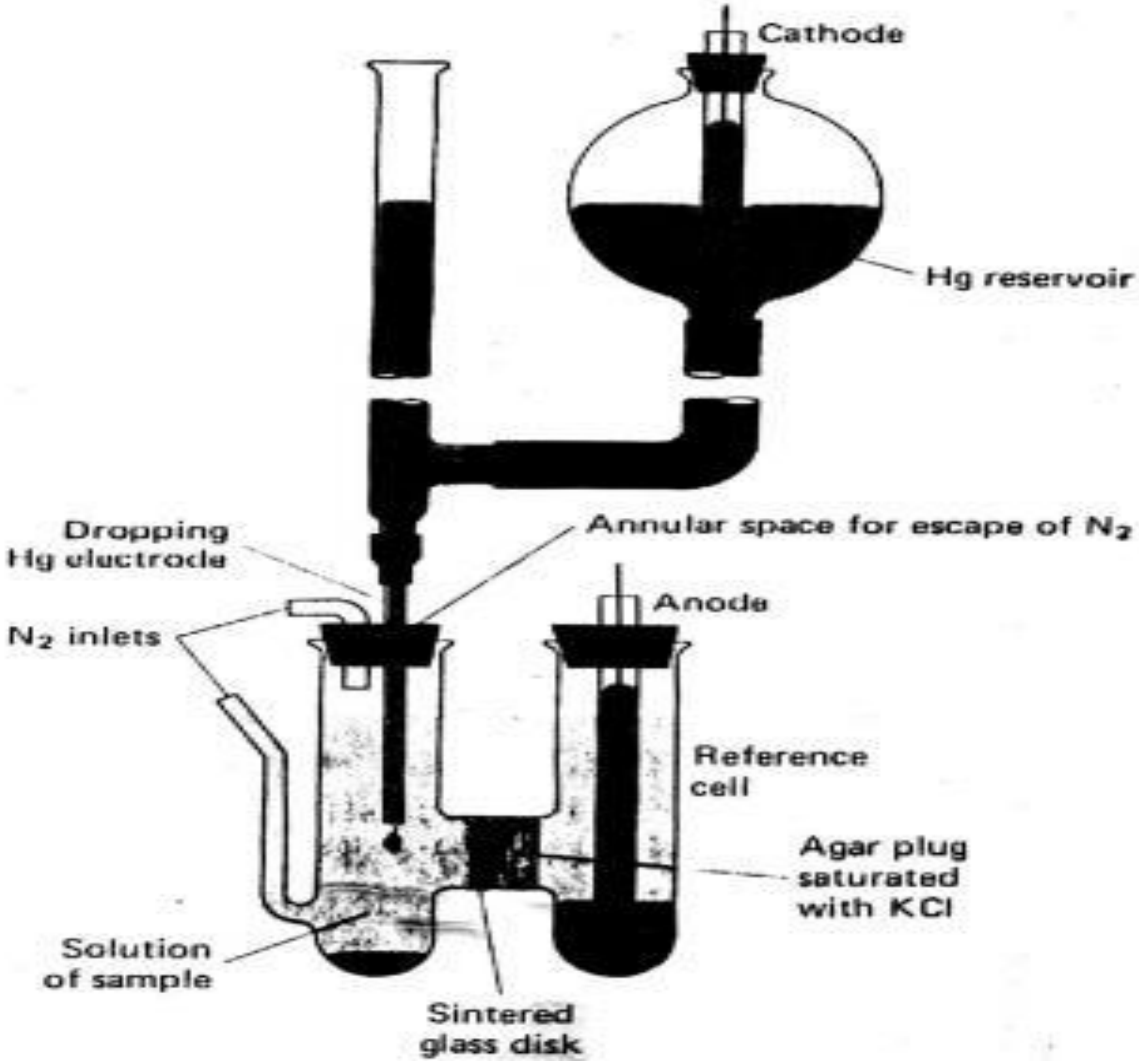
Small ion conc small inflection of curve

high ion conc large inflection of curve

in polarographic analysis the mode of mass transport should be only by diffusion.

- **Instrument (Polarograph):**
1-electric circuit
- 2-polarographic cell
- **1-electric circuit**
- -increasingly negative
- potential from
- +0.5 to -2.5 volt at a
- definite rate of
- millivolt.

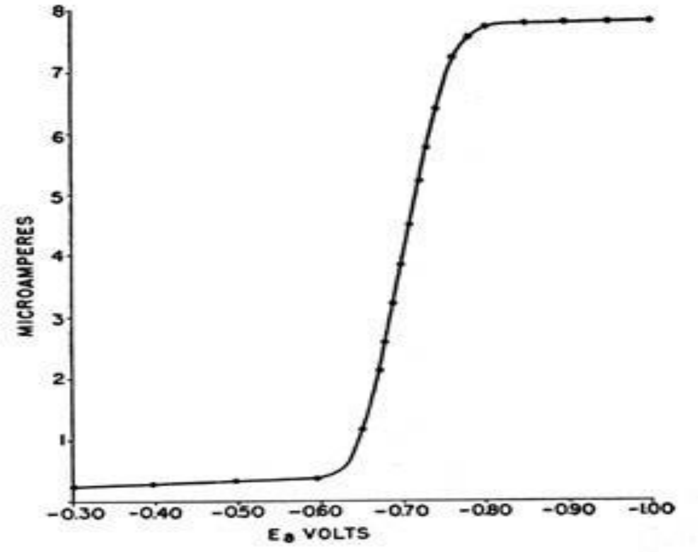
- **2-Polarographic cell**
- -lifetime of a drop
- from 2 to 6 seconds
- - Nitrogen is bubbled
- through the solution
- for five minutes to
- expel oxygen. Also
- kept at the surface

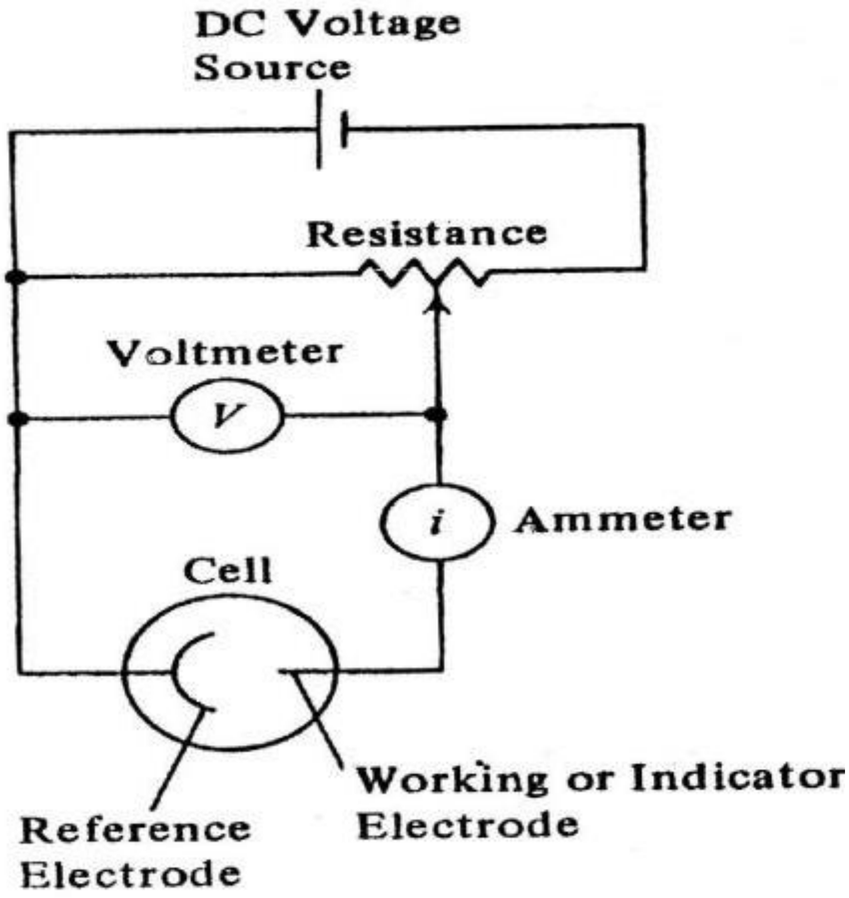

Cathode
Hg reservoir
Dropping
Hg electrode
Annular space for escape of N₂
Anode
N₂ inlets
Reference
cell
Agar plug
saturated
with KCl
Solution
of sample
Sintered
glass disk

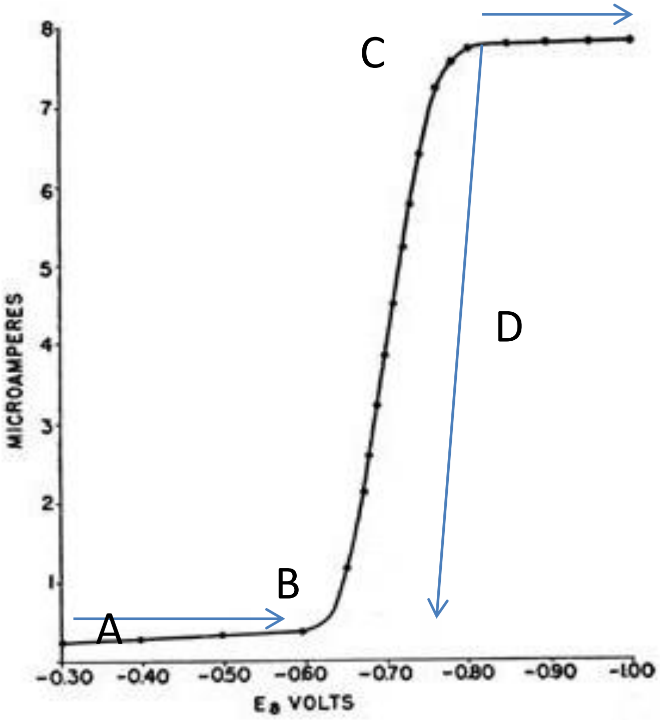
Polarogram •

I in •

-a plot of current as a •
function of applied •
potential •
-The applied •
potential is given a •
negative sign as the •
microelectrode is •
connected to the •
negative terminal of •
the power supply. •




DC Voltage Source
Resistance
Voltmeter
V
i
Ammeter
Cell
Working or Indicator Electrode
Reference Electrode


MICROAMPERES
8
7
6
5
4
3
2
1
−0.30
−0.40
−0.50
−0.60
−0.70
−0.80
−0.90
−1.00
E_a VOLTS
A
B
C
D

A-B : Activation polarization
Increase in volt not accompanied by increase incurrent , additional potential is needed to overcome the energy Barrier. **B : Decomposition potential**
Potential once exceeded, reduction begins
B-C : Increase in volt is accompanied by increase in current
(diffusion current)
small current passing through the cell is known by residual current i_r

Ilkovič Equation:

Id = 607 n D1/2 C m2/3 t1/6

Id average diffusion current

n number of electron in reduction of a molecule

D diffusion coefficient

C concentration

m rate of the mercury flow in capillary

t lifetime of a drop of mercury (2 to 7 sec.).

n,D,m and t are constants

(id = k C)

m2/3 t1/6 is known by the capillary characteristics it depends on

1- the mercury column height above the capillary tube

2- the internal capillary dimensions.

A) Advantages of DME

1-The current voltage curve shows only the process

2- can be done in acidic solutions as Large overvoltage is needed for reduction of H+

3- reproducible results are obtained as Mercury electrode surface is continuously renewed, smooth surface of the mercury drop which allows reproducible rapid electron transfer. .

4- several runs can be performed using the same solution
as the surface area of the electrode is very small the
amount electrolyzed is negligible and the concentration
of the original solution nearly remains the same

5- The reduced metals at the electrode surface form
amalgum

Disadvantage of the DME:

1) 
potential above 0.4

Hg metal is oxidized with a production of a wave that interferes with the analyte.

2-The drop surface area is changeable

3-The drop surface area change by of potential change

Application of polarography

organic
Polarography

In organic
Polarography
-Cations
-Anions
-Molecules

1- Cations

a- No interference in E1/2:

-Mixture of Cu+, Cu2+, Cd2+ Ni2+ Zn2+ Mn2+ is determined simultaneously in 0.5 M NH_4OH, O.5 M NH_4Cl as each cation has its characteristic E1/2 and shows separate wave.

b- interference in E1/2:

1-Pb2+, Ti+ and Sn2+ the same E1/2 (-0.5V) in neutral and acidic medium.

Use NaOH medium:

- Pb2+ form a complex with E1/2 -0.8 V
- Sn2+ can be oxidized to Sn4+ which is reduced at -0.35 V• Ti+ is reduced at -0.49.

2- Cu2+ and Bi3+ both are reduced at -0.25 in HNO3 .Use tartarate at pH 2 - 5 the potential is altered to -0.15 for Cu2+ and - 0.37 for Bi3+

Amperometry

Amperometry

Definition

Amperometry refers to the measurement of current under a constant applied voltage and under
these conditions it is the concentration of analyte which determine the magnitude of current.

In Amperometric titration the potential applied between the indicator electrode (dropping mercury electrode) and the appropriate depolarizing reference electrode (saturated calomel electrode) is kept constant and current through the electrolytic cell is then measured on the addition of each increment of titrating solution.

In these titrations the current passing through the cell between the indicator electrode and reference electrode at a suitable constant voltage is measured as a function of the volume of the titrating reagent.

By diffusion:

-occurs due to concentration gradient of ions

-The rate of mass transport by diffusion depends on the concentration and the diffusion coefficient (a constant value characteristic for the analyte)

-the transport (current) will depend on concentration.

=Small ion conc. small inflection of curve

=high ion conc. large inflection of curve

in polarographic analysis the mode of mass transport should be only by diffusion.

Ilkovič Equation:

Id = 607 n D1/2 C m2/3 t1/6

Id **average diffusion current**

n: number of electron in reduction of a molecule

D: diffusion coefficient

C: concentration

m rate of the mercury flow in capillary

t lifetime of a drop of mercury (2 to 7 sec.).

n,D,m and t are constants

(id = k C)

Principle:

According to Ilkovic equation
(Id= 607 X n X D1/2 X m2/3 X t 1/6 X C) ,
the diffusion current
(= limiting current - residual current) is
directly proportional to the concentration of
the electroactive
material in the solution.

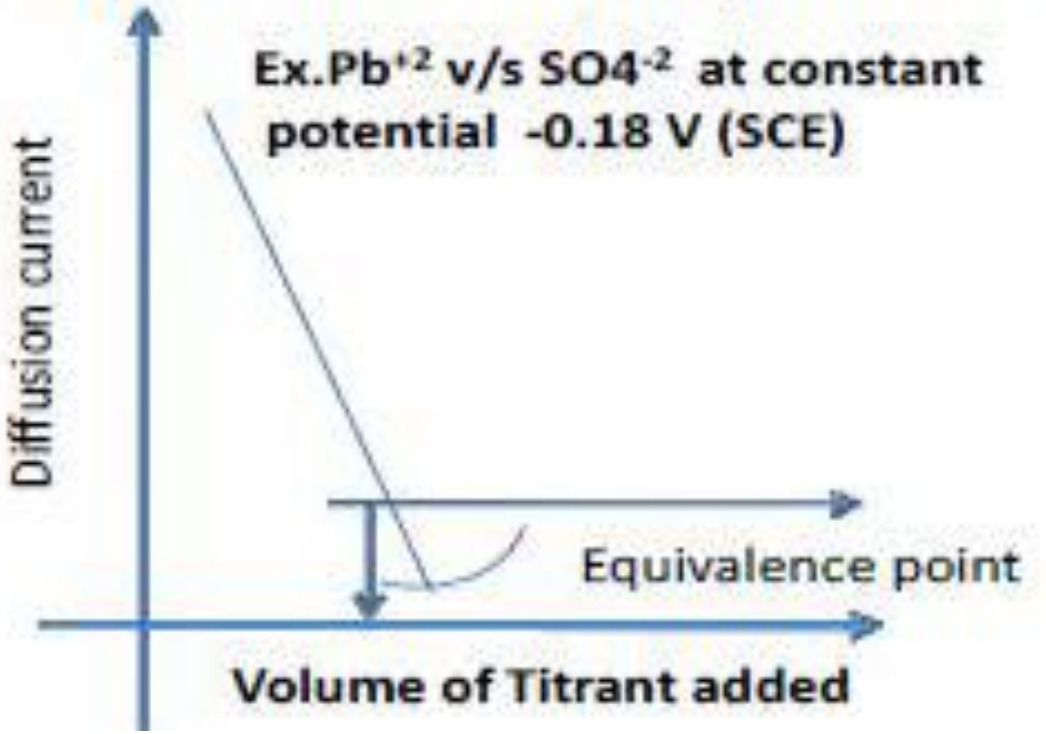
If some of the electro-active material is removed by interaction
with reagent, the diffusion current will decrease. This is the fundamental principle of
amperometric titrations. The observed diffusion current at a suitable applied voltage is measured
as a function of the volume of the titrating solution: the end point is the point of intersection of
two lines giving the change of current before and after the equivalence point

Titration Curves in Amperometry:

- **Titrand + Titrant -→-- Product.**

A) **Titrand is reducible but titrant and product not:** When solution containing Pb+2 ion is titrated against SO4-2 ion. A precipitate of PbSO4 is formed. The titration can be performed at fixed potential -0.8 Volt v/s saturated calomel electrode.

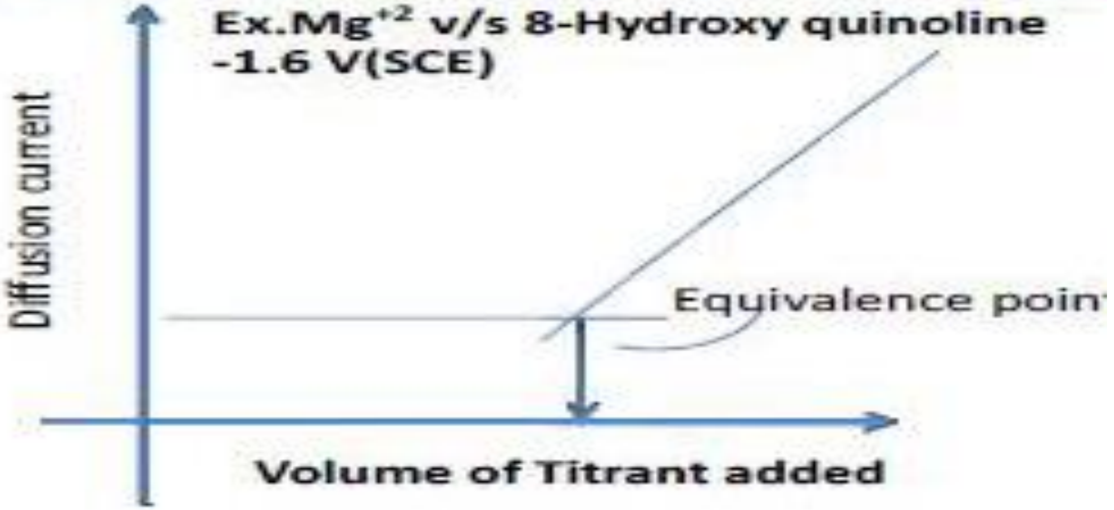
A) Ttrand is reducible but titrant and product not.



B) Titrant is reducible but titrand and product not : When solution containing Mg+2 ion is titrated against with the reducible species such as 8- hydroxy quinoline because Mg+2 ion does not undergoes reduction. Beyond the end point the 8- hydroxyl 4quinoline undergoes reduction.

As its concentration increases diffusion current also increases.

B) Titrant is reducible but titrand and product not

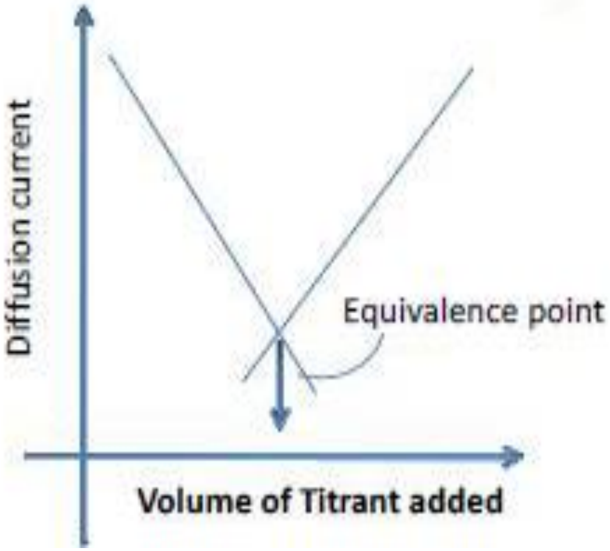


Ex.Mg^{+2} v/s 8-Hydroxy quinoline

-1.6 V(SCE)

C) Titrand and titrant both are reducible but product not : When solution containing Pb+2 ion is titrated against K2Cr2O7 . The titration is performed at potential of -0.8 Volt v/s SCE . Diffusion current is decreases due to removal of Pb+2 ion. The current is minimum at the end point. On further addition of the titrant the current once again increases. V shaped curve is obtained.

C) Ttrand and titrant both are reducible but product not Ex.Pb^{+2} v/s $K_2Cr_2O_7$ at constant potential -0.8 V (SCE)



CONDUCTOMETRY

CONDUCTOMETRY

- INTRODUCTION
- PRINCIPLE
- IMPORTANT DEFINITIONS & RELATIONS
- INSTRUMENTATIONS
- MEASUREMENT OF CONDUCTIVITY
- CONDUCTOMETRIC TITRATIONS
- ADVANTAGES & DISADVANTAGES OF CONDUCTOMETRIC TITRATIONS
- APPLICATIONS OF CONDUCTOMETRY

- INTODUCTION:

  - It is an electrochemical method of analysis concerned with electrical conductance through an electrolyte solution .

    (or)

  - It is defined has as determination or measurement of the electrical conductance of an electrolyte solution by means of a conductometer .

    - electric conductivity of an electrolyte solution depends on :

      1. Type of ions (cations, anions, singly or doubly charged
      2. Concentration of ions
      3. Temperature
      4. Mobility of ions

- PRINCIPLE:
  - Based on the conductance of electrical current through electrolyte solutions similar to metallic conductors
  - The electric conductance in accordance with ohms law which states that the stength of current(i)passing through conductor is directly porportional to potential difference & inversely to resistance.

$$i = V/R$$

- Important definitions & relations
  - Conductance
  - Specific conductance
  - Molar conductance
  - Equivalent conductance
  - Resistance
  - Specific resistance

- Conductance:(G)
  - ease with which current flows per unit area of conductor per unit potential applied & is reciprocal to resistance(R)

$$G = I/R$$

- Specific conductance (K):
  - conductance of the body of uniform length(l) &uniform area cross section(A)

$$K = 1/R \times 1/A$$

- Molar conductance: (^)
  - Conductance of a solution containing 1 mole of the solute in 1000 cm of the solution which placed between two parallel electrodes which are 1 cm apart

$$\wedge = 1000/C$$

- Equivalent conductance: ($\wedge_{eq}$)
  - specific conductance of the solution containing 1gm equivalent of solute in 1000cm^3 of solution.

$$\wedge_{eq} = 1000k/c_{eq}$$

- Resistance (r):
  - Is a measure of the conductors opposition to the flow of electric charge

$$R = 1/G$$

- Specific resistance:(ρ)
  - Is resistance offered by a conductor of unit length and having unit cross section

$$R \propto l/A$$

- Instrumentation

The instrument used for measurement of conductance are know as conductometers

It consists of :

1. Current source
    - Alternating current source
2. Conductivity cells
    - Wide mouthed cells
    - Cell for reactions producing precipitates
    - Dip type cells
3. Electrodes

CURRENT SOURCE:-

1. Mechanical high frequency AC generator by Washburn .
2. Vreeland oscillator by Taylor and Acree.
3. Vaccum tube oscillator by Hall & Adams.

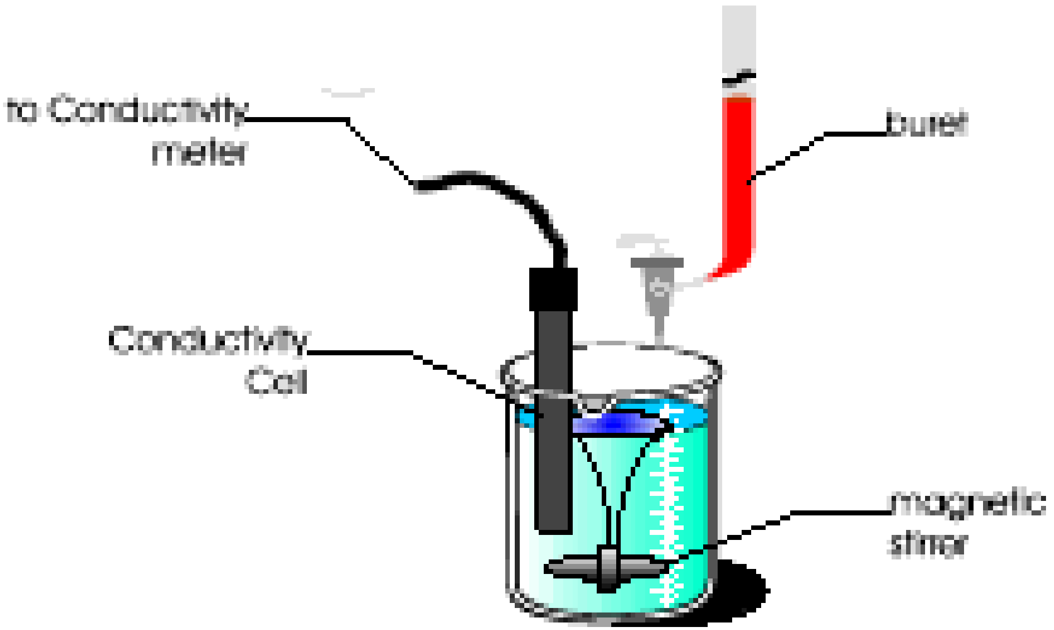
- ❖ When electical potential is applied across electrodes two process occurs.
- ➢ Ions accumulate near the electrodes.
- ➢ Transfer of charge through the interface.
- ➢ Note : DC current is not employed in conductance measurement because

1. Electrodes becomes polarised leading to high cell resistance.

- Conductivity cells:-
  - Made of pyrex or quartz and are fitted with two platinum electrodes.
  - Should be placed in vessel containing water to maintain constant temperature
  - Types :
    1. Wide mouthed cell
    2. Cell for reactions producing precipitation
    3. Dip type cells

- Wide mouthed cell:-
    - Measurement of low conductance
    - Wide mouthed fitted with an ebonite cover which has provisions for platinum electrodes and burettes

- Cell for reactions producing ppts:
  - Mainly used for ppt reactions
  - Also wide mouthed fitted with ebonite cover which has provisions for burette ,electrode , stirrer
  - Stirrer may be mechanical or magnetic



- Electrodes:
  - Platinum sheets, each of 1 cm^2 are fixed at distance of 1 cm
  - The surface is coated with platinum black to avoid polarization effects and increase effective surface area.
  - Platinisation of electrodes is done by coating solution of 3% chlorplatinic acid and lead acetate on it to get uniform coating
  - Electrodes usage depends on conductivity and concentration
  - If conc is low then electrodes should be largely and closely packed

- Measurement:-
  - The instrument used to measure conductance is called conductance bridge or conductometer
  - Classical circuit employed for measurement is wheatstone bridge
  - All other work on this principle
  - Various types are:
    1. Kohlrausch conductance bridge
    2. Direct reading conductance bridge
    3. Phillips conductance bridge
    4. Mullard's conductance bridge
    5. Pye's conductance bridge

- Kohlrausch conductance bridge:
  - Consists of a meter bridge XY with fixed resistors r’ & r” at both ends. One arm of bridge consists of resistance box ‘R’ & other arm with conductivity cell ’C’. Detector D is head phone while inductance coil ‘J’ is AC source which is operated by battery.
- Direct reading conductance bridge:-
  - In this head phone is replaced by magic eye which is electronic device

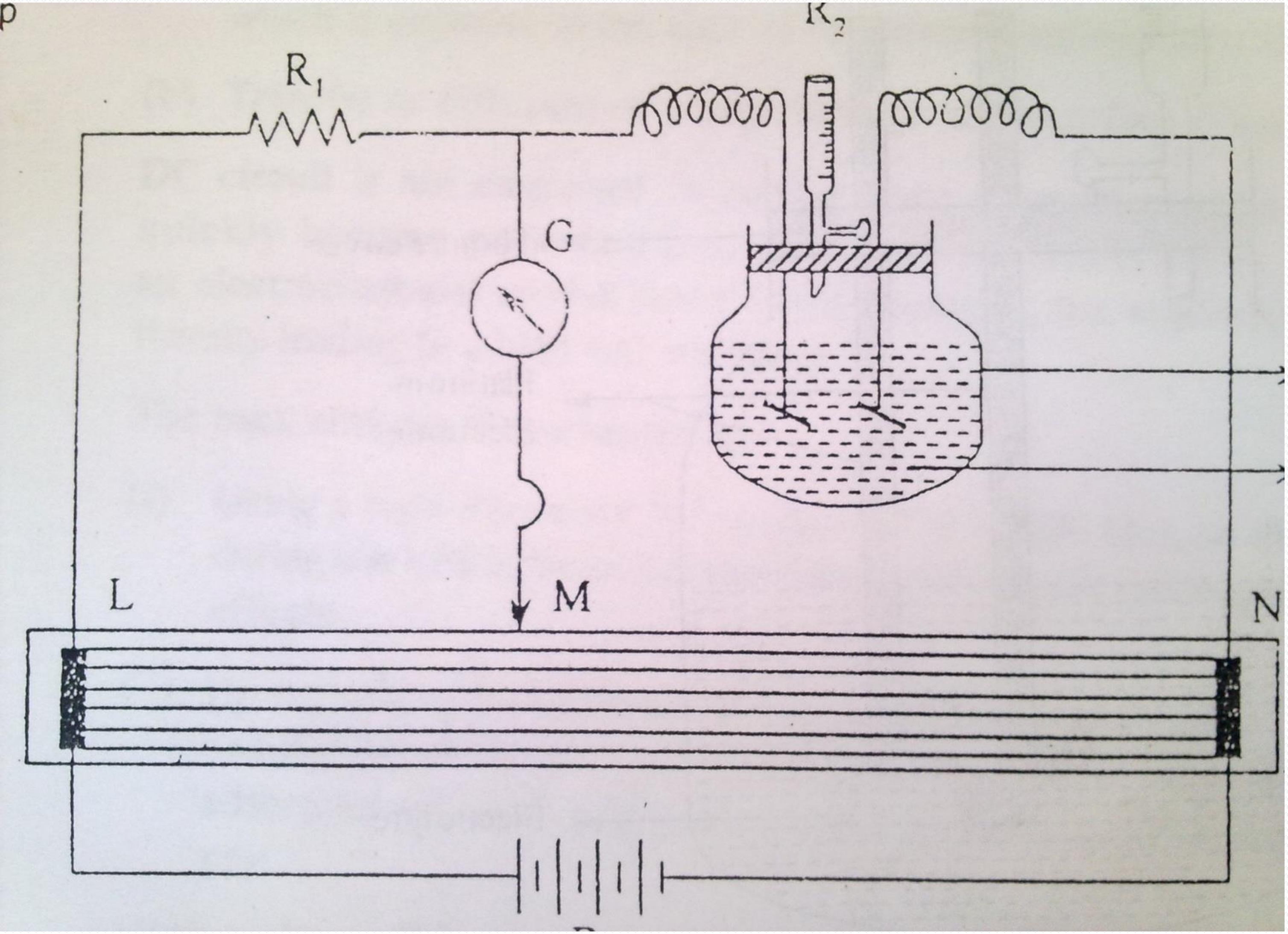
- The set up for Measurement :

  consists of meter bridge LN attached to standard resistance R1 & unknown resistance R2

  cell is connected to standard resistance to one side , meter bridge LN at other. The sliding contact with galvanometer (G) can be moved on the wire of meter bridge by means of jockey (M) so that resistance of unknown is balanced with that of standard. When galvanometer shows null deflection, the resistance of unknown is measured by following equation:

$$ML/NL = R_2/R_1$$

$$R_2 = ML/NL \times R_1$$



Conductivity cell

Solution

Meter bridge

- Hence conductivity of unknown solution:

$$1/R_2 = NL/ML \times R_1$$

The measured conductivity (1/R1) is not always equal to the specific conductivity of solution , because the physical configuration of platinum electrode i.e, length and area of electrodes varies from one another . Hence conductivity of solution is obtained by calculating a factor called “cell constant”.

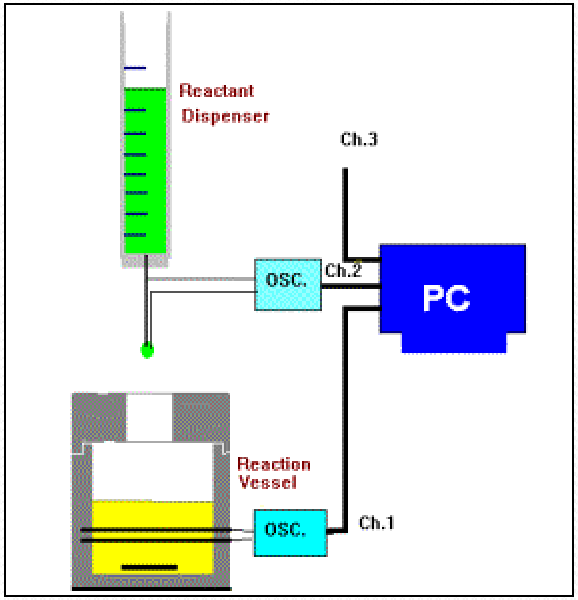
- Cell constant:

Defined as ratio of distance between the two electrodes(l) to the area of electrodes(A)

There fore,

$$\theta = 1 / A$$

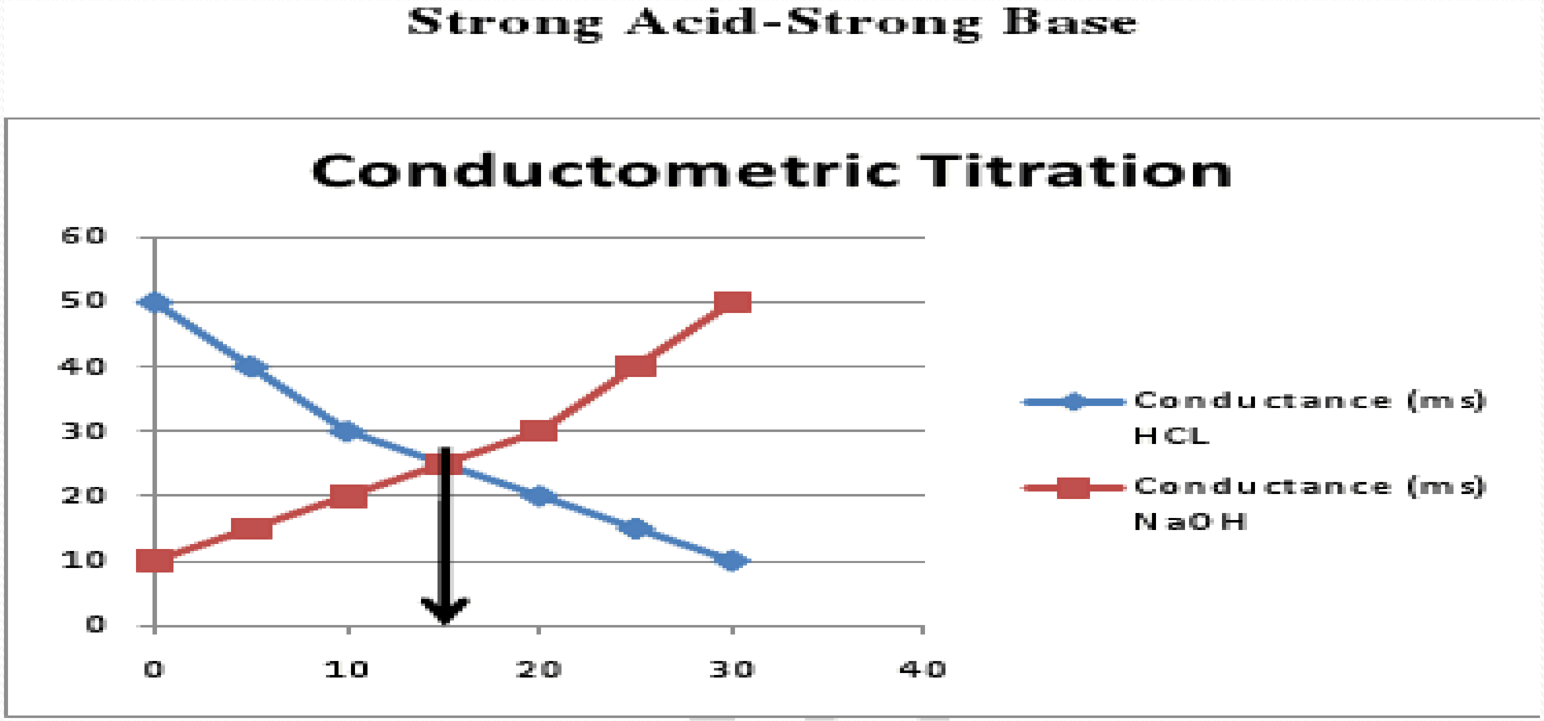
- CONDUCTOMETRIC TITRATIONS:
    - INTRODUCTION:
        - Is process of qualitative chemical analysis in which conc of sample is determined.Which is done by adding areagent(titrant) of known conc in measured volumes to the sample (anylate)



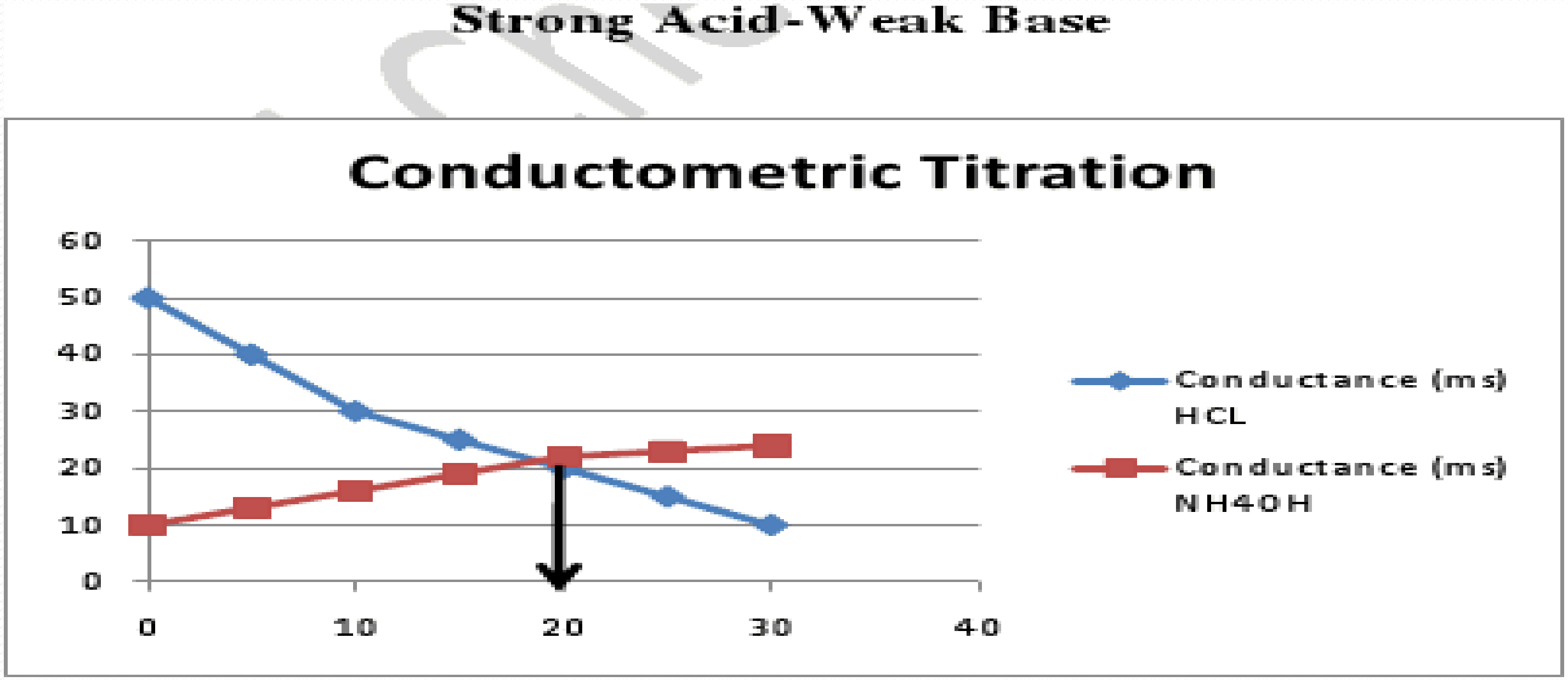
- TYRES OF CONDUCTOMETRIC TITRATIONS:
  - Acid –base or neutral titrations
  - Replacement or displacement titrations
  - Redox titrations
  - Precipitation titrations
  - Complexometric titrations
  - Non-aqueous titrations

1. ACID- BASE OR NEUTRAL TITRATIONS:
    - STRONG ACID-STRONG BASE
        - EG: HCL vs NaOH
    - STRONG ACID-WEAK BASE
        - EG: HCL vs NH_4OH
    - WEAK ACID-STRONG BASE
        - EG: CH_3COOH vs NaOH
    - WEAK ACID -WEAK BASE
        - EG: CH_3COOH vs NH_4OH

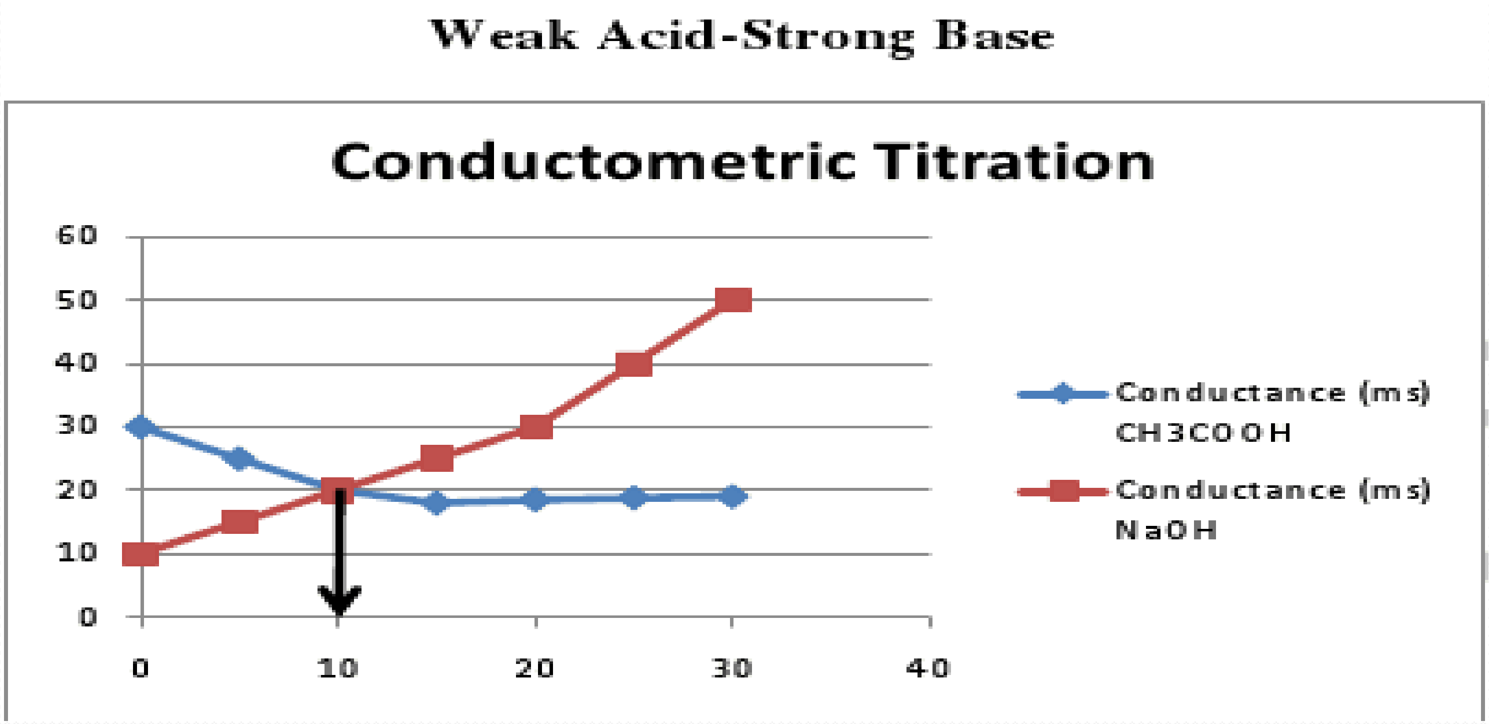
- Strong acid strong base:
  - Fall in conductance due to replacement of high conductivity Hydrogen ions by poor conductivity sodium ions
  - Rise in conductance due to increase in hydroxyl ions



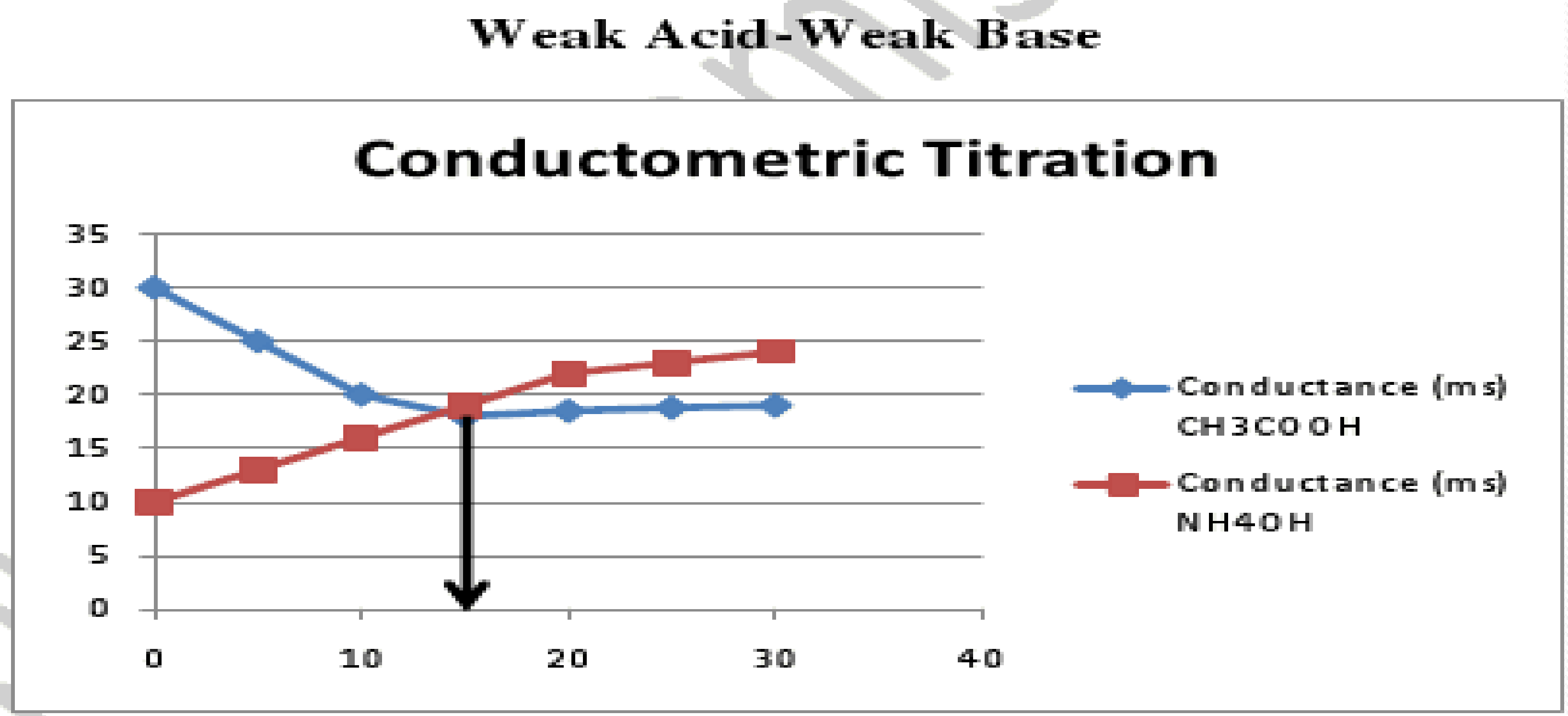
- Strong acid- weak base:
  - Fall in conductance due to replacement of hydrogen by ammonium ions
  - Conductance remain constant due to supression of NH4oH by NH4CL



- Weak acid –Strong base:
  - Initial decrease in conductance followed by increase due to NaOH
  - Steep rise due to excess of NaOH



- Weak acid- weak base:
  - Increase in conductance due to excess of CH3COOH
  - Constant conductance due to supression of NH4OH by CH3COOH



- ADVANTAGE OF CONDUCTOMETRIC TITRATIONS:

1. Does not require indicators since change in conductance is measured by conductometer
2. Suitable for coloured solutions
3. Since end point is determined by graphical means accurate results are obtained with minimum error
4. Used for analysis of turbid suspensions, weak acids, weak bases, mix of weak & strong acids

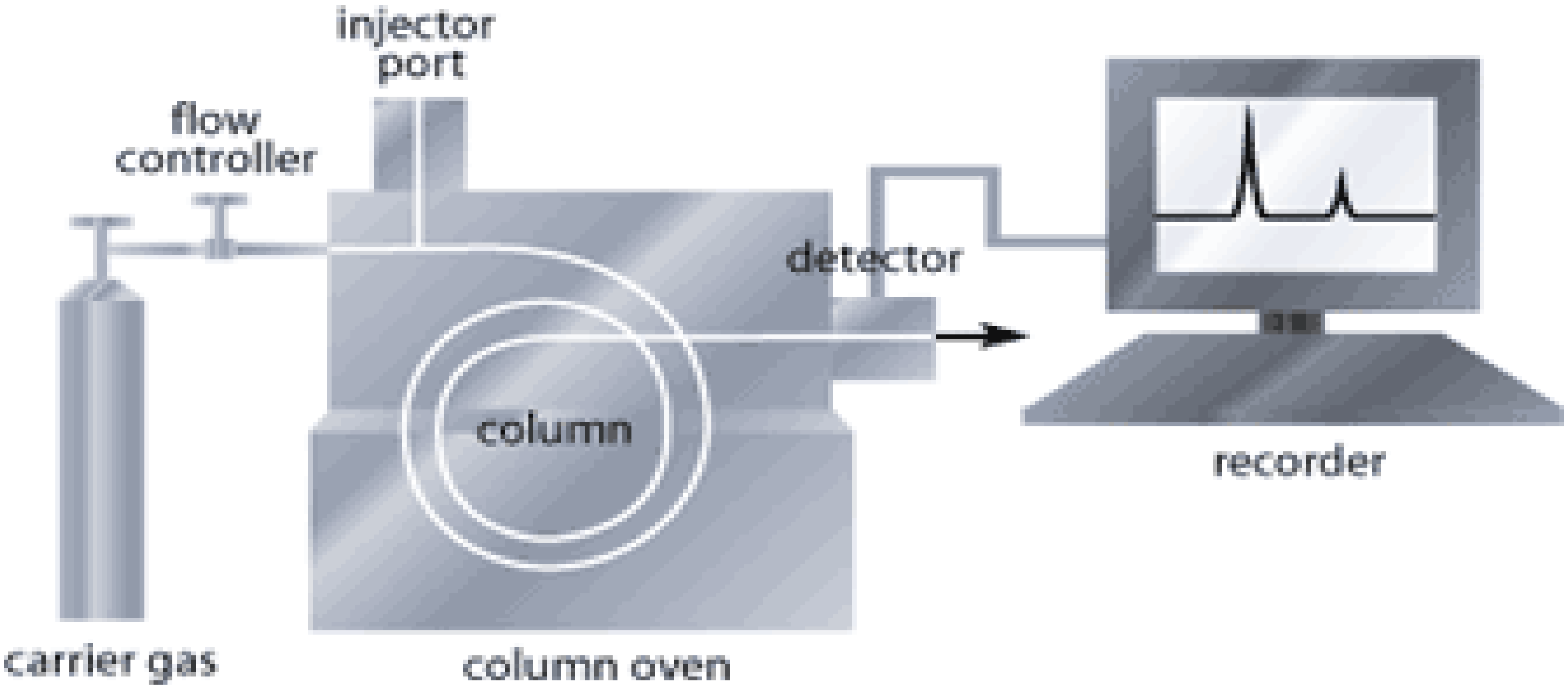
- Dis advantages of conductometric titration:
  1. Increased level of salts in solution masks the conductivity changes , in such cases it does not give accurate results
  2. Application of conductometric titrations to redox systems is limited because, high concentrations of hydronium ions in the solution tends to mask the changes in conductance

- Applications :
  1. Check water pollution in rivers and lakes
  2. Alkalinity of fresh water
  3. Salinity of sea water (oceanography)
  4. Deuterium ion concentration in water- deuterium mixture
  5. Food microbiology- for tracing micro organisms
  6. Tracing antibiotics
  7. Estimate ash content in sugar juices
  8. Purity of distilled and de - ionised water can determined
  9. Solubility of sparingly soluble salts like AgCl,BaSo4 can be detected
  10. Determination of atmospheric so_2,etimation of vanillin in vanilla flavour

References

- *Instrumental analysis* by *A. Skoog, F. James Holler and Stanly R. Crouch.*
- *Text book of pharmaceutical analysis*, third edition by *Dr.S.Ravi sankar.*

Gas Chromatography



What is Gas Chromatography?

- It is also known as…

Gas-Liquid Chromatography (GLC)

GAS CHROMATOGRAPHY

- Separation of gaseous & volatile substances
- Simple & efficient in regard to separation

GC consists of:

GSC (gas solid chromatography)

GLC (gas liquid chromatography

GSC principle is **ADSORPTION**

GLC principle is PARTITION

Sample to be separated is converted into vapour

And mixed with gaseous M.P

Component more soluble in the S.P → travels slower

Component less soluble in the S.P → travels faster

Components are separated according to their **Partition Co-efficient**

Criteria for compounds to be analyzed by G.C

1.VOLATILITY:

2.THERMOSTABILITY:

How a Gas Chromatography Machine
⸮Works⸮

– **First**, a vaporized sample is injected onto the *chromatographic column*.

– **Second**, the sample moves through the column through the flow of inert gas.

– **Third**, the components are recorded as a sequence of peaks as they leave the column.

Chromatographic Separation

– Deals with both the *stationary*
the *mobile phase*. *phase* and

- **Mobile** – inert gas used as carrier.
- **Stationary** – liquid coated on a solid
within a column. or a solid

Chromatographic Separation

Chromatographic Separation
– **In the mobile phase**, components of the sample are uniquely drawn to the stationary phase and thus, enter this phase at different times
–
The parts of the sample are separated within the column.
Compounds used at the stationary phase reach the detector at unique times and produce a series of peaks along a time sequence.

The peaks can then be read and analyzed by a forensic scientist to determine the exact components of the mixture.

– Retention time is determined by each component reaching the detector at a characteristic time.

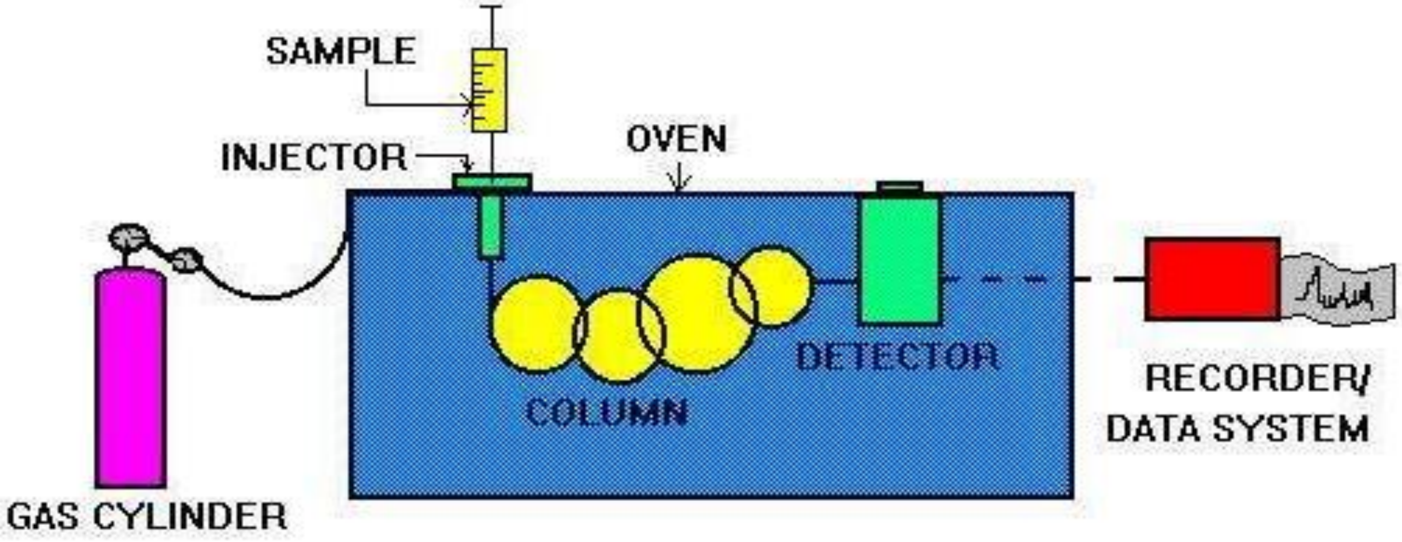
Chromatographic Analysis

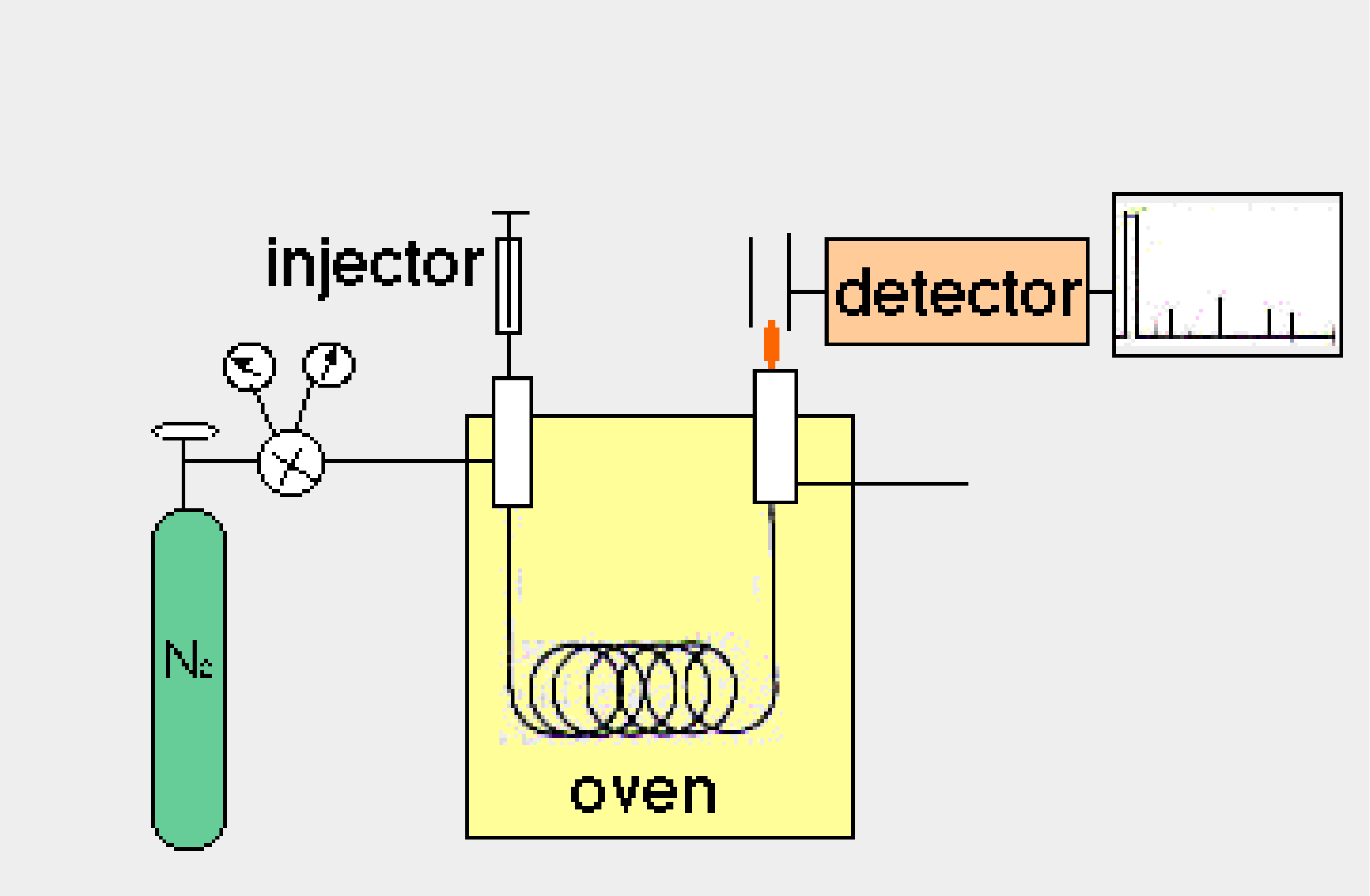
The number of components in a sample is determined by the number of peaks.

– The amount of a given component in a sample is determined by the area under the peaks.

– The identity of components can be determined by the given retention times.

GAS CHROMATOGRAPHY




injector
detector
N2
oven

PRACTICAL REQUIREMENTS

Carrier gas

- Flow regulators & Flow meters
- **Injection devices**
- **Columns**
- **Temperature control devices**
- **Detectors**
- **Recorders & Integrators**

Requirements of a carrier gas

- Inertness
- Suitable for the detector
- High purity
- Easily available
- Cheap
- Should not cause the risk of fire
- Should give best column performance

How to select a Carrier gas

Depending on	**priority**
Availability	first
Purity	Second
Coast	Third
Type of Detector	Fourth
consumption	Fifth

Required Gases Purities

Helium For carrier gas: 99.995% high purity, with •
less than 1.0 ppm each of

• water, oxygen, and total hydrocarbons after •
purification.

• Use water, oxygen, and hydrocarbon traps. •

Hydrogen For carrier or detector fuel gas: •
99.995% high purity, with <

• 1.0 ppm of total hydrocarbons after purification. •

• Use water, oxygen and hydrocarbon traps. •

Required Gases Purities

Air For detector fuel gas: 99.995% high purity. •

• Air compressors are not acceptable because • they do not

• meet pressure, water, and hydrocarbon • requirements.

Nitrogen For carrier or make-up gas: 99.995% • high purity, with less than 1.0

• ppm of total hydrocarbons after purification. •

Argon 5% Methane For ECD make-up gas: • 99.995% high purity.

Carrier Gas Control

The Flow mode has four options for the carrier •
gas control: •

- Constant flow •
- Constant pressure •
- Programmed flow •
- Programmed pressure •

Flow regulators & Flow meters

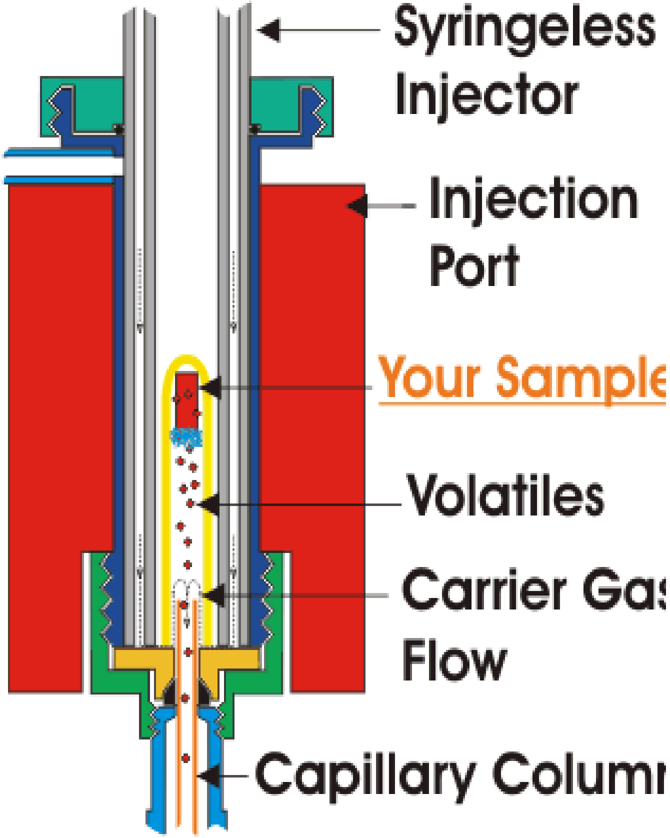
X□ deliver the gas with uniform pressure/flow rate

X□ **flow meters:-** Rota meter & Soap bubble **flow meter**

Injection Devices

Gases can be introduced into the column by valve devices

□ liquids can be injected through loop or septum devices



COLUMNS

- Important part of GC
- Made up of glass or stainless steel
- Glass column- inert , highly fragile

COLUMNS can be classified

□ Depending on its use

1. Analytical column

1-1.5 meters length & 3-6 mm d.m

2. Preparative column

3-6 meters length, 6-9mm d.m

Depending on its nature

1.Packed column: columns are available in a packed manner

S.P for GLC: polyethylene glycol, esters, amides, hydrocarbons, polysiloxanes…

2.Open tubular or Capillary column or Golay column

- Long capillary tubing 30-90 M in length
- Uniform & narrow d.m of 0.025 - 0.075 cm
- Made up of stainless steel & form of a coil
- Disadvantage: more sample cannot loaded

2. Column

The column •

• **Is where the chromatographic separation •**
of the sample occurs. •

• Several types of columns are available for •
different chromatographic applications: •

• The heart of the system. •

• It is coated with a stationary phase which •
greatly influences the separation of the •
compounds. •

Factors Affecting Column Separations

Volatility of compound: Low boiling (volatile) •
components will travel faster through the
column than will high boiling components •

• **Polarity of compounds**: Polar compounds •
will move more slowly, especially if the column is
polar. •

• **Column temperature**: Raising the column •
temperature speeds up All the compounds in a
mixture, “Columns have lower and upper •
temperature limits”.

Factors Affecting Column Separations

- **Column packing polarity**: Usually, all compounds will move slower on polar columns, but
- polar compounds will show a larger effect.
- **Flow rate of the gas through the column**: Speeding up the carrier gas flow increases the
- speed with which all compounds move through the column.
- **Length of the column**: The longer the column, the longer it will take all compounds to elute.
- Longer columns are employed to obtain better separation.

GLC

Carrier gas

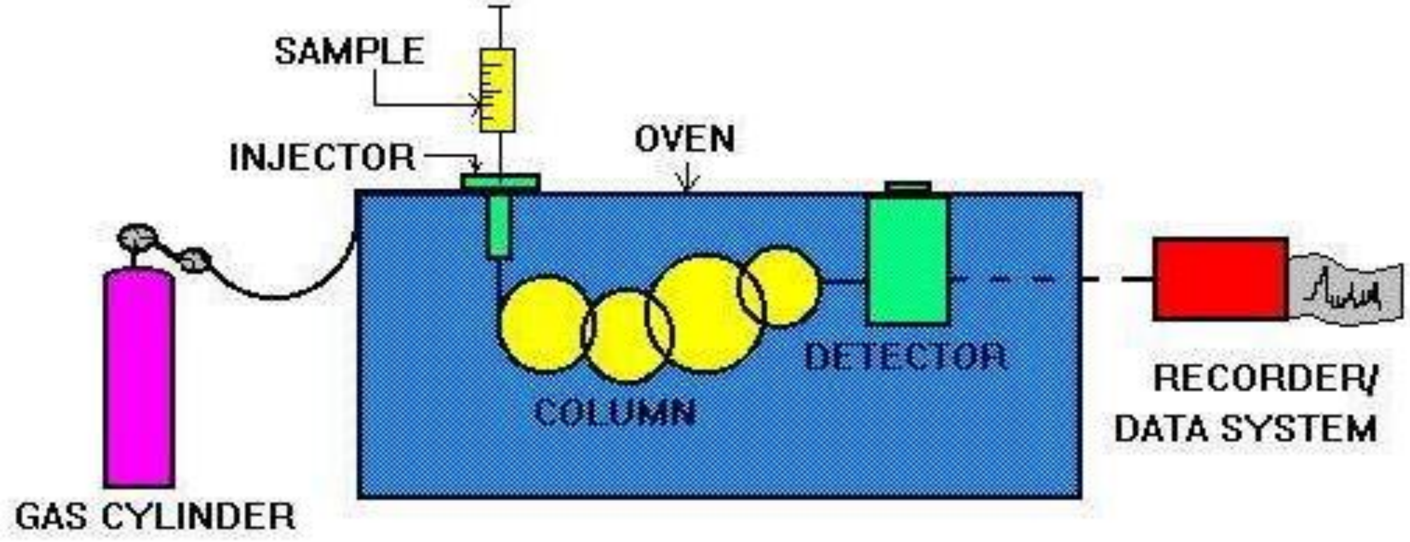
- Flow regulators & Flow meters
- **Injection devices**
- **Columns**
- **Temperature control devices**

- **Detectors**
- **Recorders & Integrators**

GC Part (2)

Gas Liquid Chromatography

GAS CHROMATOGRAPHY



GC

Carrier gas

- Flow regulators & Flow meters
- **Injection devices**
- **Columns**
- **Temperature control devices**

- **Detectors**
- **Recorders & Integrators**

Detector

- The part of a gas chromatograph
- which signals the change in
- composition of the mixture passing
- through it.

Detector types

- 1. Electron Capture Detector.
- 2. Flame ionization Detector.
- 3. Nitrogen Phosphors Detector.
- 4. Thermal Conductivity Detector.

Detector types

- 5. Flame Photometric Detector.
- 6. Photo ionization Detector.
- 7. Electrolytic Conductivity Detector.
- 8. Mass Spectrometric Detector.

1. Electron Capture Detector (ECD)

- **Mechanism:**
- • Electrons are supplied from a 63Ni foil lining the detector cell. A current is generated in the cell
- .Electronegative compounds capture electrons resulting in a reduction in the current.
- The amount of current loss is indirectly measured and a signal is generated.

ECD

- • **Selectivity**: Halogens, nitrates, conjugated carbonyls
- • **Sensitivity**: 0.1-10 pg (halogenated compounds);
- 1-100 pg (nitrates); 0.1-1 ng (carbonyls)
- Linear range: 1000-10000
- Gases: Nitrogen or argon/methane
- Temperature: 300-400°C

2. Flame ionization Detector (FID)

- **Mechanism:**
- • Compounds are burned in a hydrogen-air flame.
- • Carbon containing compounds produce ions that are attracted to the collector.
- • The No. of ions hitting the collector is measured and a signal is generated.

FID

- **Selectivity**: Compounds with C-H bonds.
- • **Sensitivity**: 0.1-10 ng
- Gases: Combustion hydrogen and air; Makeup He or N2
- Temperature: 250-300°C,and 400-450°C for high temp.

3. Nitrogen Phosphors Detector (NPD)

- **Mechanism:**
- • Compounds are burned • Nitrogen and phosphorous containing compounds
- produce ions that are attracted to the collector.
- • The number of ions hitting the collector is measured and a signal is generated.

NPD

- **Selectivity**: Nitrogen and phosphorous
- • **Sensitivity**: 1-10 pg
- Gases: Combustion - hydrogen and air; Makeup - Helium
- Temperature: 250-300°C

4. Thermal Conductivity Detector (TCD)

- **Mechanism:**
- • A detector cell contains a heated filament with an applied current.
- As carrier gas containing solutes passes through the cell, a change in the filament current occurs.
- • The current change is compared against the current in a reference cell.
- • The difference is measured and a signal is generated.

works by having two parallel tubes both containing gas and heating coils. The gases are examined by comparing the heat loss rate from the heating coils into the gas. Normally one tube holds a reference gas and the sample to be tested is passed through the other. Using this principle, a TCD senses the changes in the thermal conductivity of the column effluent and compares it to a reference flow of carrier gas. Most compounds have a thermal conductivity much less than that of the common carrier gases of hydrogen or helium.

TCD

- • **Selectivity**: All compounds except for the carrier gas
- • **Sensitivity**: 5-20 ng
- Linear range: 105 -106
- Gases: Makeup - same as the carrier gas
- Temperature: 150-250°C

5. Flame Photometric Detector (FPD)

- **Mechanism:**
- • Compounds are burned in a hydrogen-air flame.
- Sulfur and phosphorous containing compounds produce light emitting species (sulfur at 394 nm and phosphorous at 526 nm). A
- monochromatic filter allows only one of the wavelengths to pass. A photomultiplier tube is used to measure the amount of light and a signal is generated.
- A different filter is required for each detection mode.

FPD

- **Selectivity**: Sulfur or phosphorous containing compounds.
- • **Sensitivity**: 10-100 pg (sulfur); 1-10 pg (phosphorous)
- Linear range: Non-linear (sulfur); 103 -105 (phosphorous)
- Gases: Combustion - hydrogen and air; Makeup - nitrogen
- Temperature: 250-300°C

6. Photo ionization Detector (PID)

- **Mechanism:**
- • Compounds eluting into a cell are bombarded with high energy photons emitted from a lamp.
- Compounds with ionization potentials below the photon energy are ionized.
- The resulting ions are attracted to an electrode, measured, and a signal is generated.

PID

- • **Selectivity**: Depends on lamp energy. Usually used for aromatics and olefins (10 eV lamp).
- • **Sensitivity**: 25-50 pg (aromatics); 50-200 pg (olefins)
- Linear range: 105 -106
- Gases: Makeup - same as the carrier gas
- Temperature: 200°C

7. Electrolytic Conductivity Detector *(ELCD)*

- **Mechanism:**
- • Compounds are mixed with a reaction gas and passed through a high temperature reaction tube.
- Specific reaction products are created which mix with a solvent and pass through an electrolytic
- conductivity cell. The change in the electrolytic conductivity of the solvent is measured and a
- signal is generated. Reaction tube temperature and solvent determine which types of compounds are detected.

ELCD

- **Selectivity**: Halogens, sulfur or nitrogen containing compounds.
- • **Sensitivity**: 5-10 pg (halogens); 10-20 pg (S); 10-20 pg (N)
- Linear range: 105 -106 (halogens); 104 -105 (N); 103.5-104(S)
- Gases: Hydrogen (halogens and nitrogen); air (sulfur)
- Temperature: 800-1000 °C (halogens), 850-925 °C (N), 750-825 °C (S)

8. Mass Detector (MS)

- **Mechanism:**
- • Compounds are bombarded with electrons (EI) or gas molecules (CI). then fragmented into characteristic
- charged ions or fragments. The resulting ions are focused and accelerated into a mass filter.
- mass filter selectively allows all ions of a specific mass to pass through to the electron multiplier. All of the ions of the
- specific mass are detected. The mass filter then allows the next mass to pass

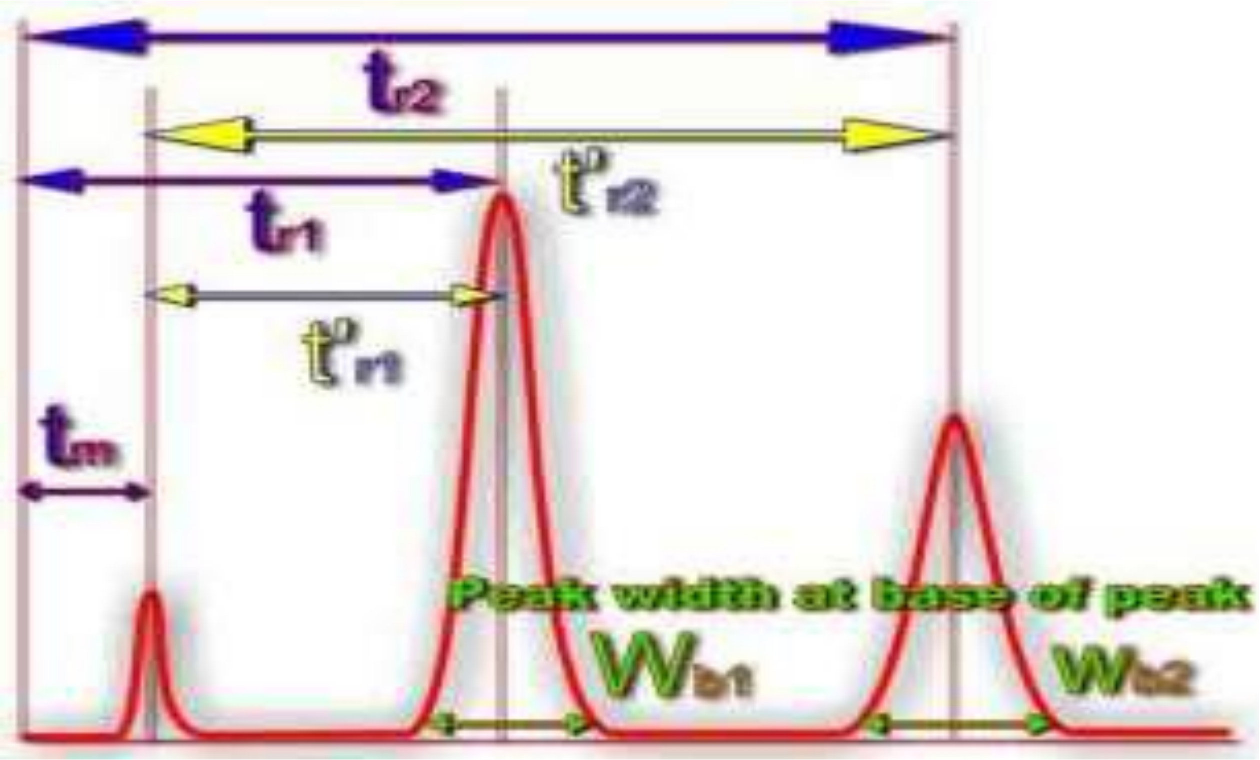
Good Detector

- 1.High sensitivity.
- 2. Rapidly respond to concentration changes.
- 3. Large linear range.
- 4. Stable with respect to noise and drift.
- 5. Low sensitivity to variation in flow,.
- 6. Possible selectivity.
- 8. Produces an easily handled signal.
- 9. A temperature range from room temperature to at least 400 C

Chromatogram

*The data recorder **plots the signal from the detector over time.**

- The retention time, is qualitatively indicative of the type of compound.
- The area under the peaks or the height of the peak is indicative of the amount of each component



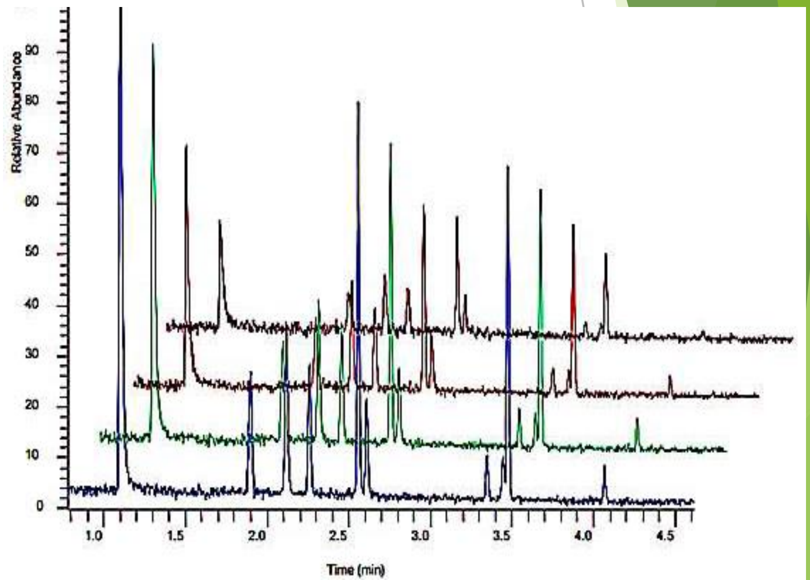
t_{r2}
t'_{r2}
t_{r1}
t'_{r1}
t_m
Peak width at base of peak
W_{b1}
W_{b2}

Retention Time (RT)

RT

- **RT, is the time it takes for a compound to travel**
- **from the injection port to the detector.**
- • Thousands of chemicals may have the same
- retention time, peak shape, and detector
- response.
- • For example, under certain conditions, DDT has
- the same retention time as PCBs
- (polychlorinated biphenyls).

Chromatogram



Applications

- the environmental
- • Testing or commercial laboratories
- • Industrial laboratories
- • Government laboratories
- • Research institutes
- **Petrochemical and Gas**
- • Refinery
- • Oil Industry
- • Gas suppliers

applications

- **Clean water analysis**
- **Pollutants in water**
- • Halocarbons
- • Acid priority pollutants: phenols,
- chlorophenols, nitrophenols
- • Pesticides
- **Other fields such as:** pharmaceutical
- foods

GC

Carrier gas

- Flow regulators & Flow meters
- **Injection devices**
- **Columns**
- **Temperature control devices**

- **Detectors**
- **Recorders & Integrators**

Solvent Extraction (part 2)

efficiency

The lecture is classified to:

- **1) Introduction**
- **2) Basic Principles of Solvent extraction Method**

3) The important of Solvent Extraction

- 4) Classification of Extraction Systems
- **5) methods of Extraction**
- **6)** Factors Influencing the Extraction Efficiency
- 7) Analytical Applications

Factors Influencing the Extraction Efficiency

- **Primary requirement of solvent extraction for** separation /removal purposes is a high distribution ratio of the solute of interest between the two liquid phases.
- It is useful to employ a number of different techniques for enhancing the distribution ratio.
- It depends on the nature of the species being
- extracted and extraction system.
- The attainment of selectivity in an extraction
- procedure is also very important.
- Some of the factors, which affect the
- distribution of solute of interest, are given below.

A) Choice of solvent

- safety, the toxicity and the flammability of the solvent must be considered.
- Use of a suitable solvent for effective separation is very important. Metal
- chelates and many organic molecules, being essentially covalent compounds do
- not impose many restrictions on the solvent and the general rules of solubility
- are the great use. In ion association systems and particularly in oxonium type
- ions, the role of solvents is very important. This is due to involvement of solvent
- in the formation of extractable species.

B) Acidity of an aqueous phase

- The extractability of metal complexes is greatly influenced by the acidity
- of an aqueous phase, so it is necessary to assure optimum concentration of H^+
- ions for maximum extraction. In the case of chelate extraction, the chelating
- reagent concentration is maintained constant; the distribution of the metal in a
- system is a function of pH. For this reason, curves of extractability versus pH at
- constant reagent concentration are of great analytical significance. Sometimes it
- is possible to achieve the desired characteristics of a solvent by employing a
- mixed solvent system.

C) Stripping

- Stripping is the removal of the extracted solute from the organic phase for
- further processing or analysis. In many colorimetric procedures and even
- radioactive techniques, the concentration of solute is determined directly in the
- organic phase. However, where further separation steps are required, it is
- necessary to remove the solute from the organic layer to more stable medium.

D) Use of masking agents

- In the extraction procedures for metal pairs that are difficult to separate;
- masking or sequestering agents are introduced to improve the separation factor.

E) Salting-out agents

- The term salting-out agent is applied to those electrolytes whose addition
- greatly enhances the extractability of complexes. The function of salting-out
- agent would be primarily of providing a higher concentration of complex and
- thus improve the extraction. Water is probably bound as a shell of oriented water
- dipoles around the ion and thus becoming unavailable as “free solvent”.
- Addition of salting-out agents decreases the dielectric constant

- Addition of salting-out agents decreases the dielectric constant of the
- aqueous phase, which favors the formation of the ion association complexes.
- Salting-out agents have been used with great success in separation involving the
- halide and thiocynate systems.

F) Backwashing

- Backwashing is an auxiliary technique used with batch extractions to
- influence quantitative separations of This technique is analogous in many respects to the re-precipitation step
- in a gravimetric precipitation procedure. With the proper conditions, most of the
- impurities can be removed by this backwashing operation, with neglisible loss of
- the main component, thereby attaining a selective operation.elements.

F-) Variation of oxidation state

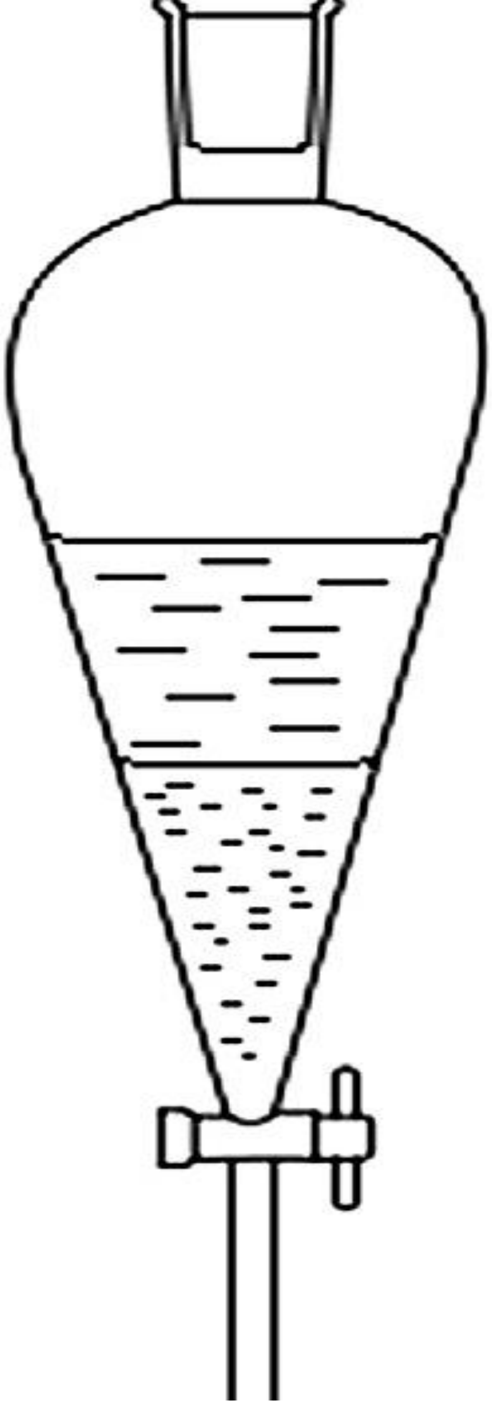
- The selectivity of an extraction is increased by the modification of
- oxidation states of the interfering ions present in solution, in order to prevent the
- formation of their extractable metal complexes e.g. reduction of Cerium(IV) to
- Cerium(III) prevents extraction of this element from nitrate media, the extraction
- of Iron(III) from chloride solutions can be prevented by reduction to Iron(II),
- which is not extractable. Similarly, Antimony(V) may be reduced to the
- tetravalent state to suppress its extraction.

G) Synergic Extraction

- Synergism is defined as the combined action of two complexing reagents,
- which is greater than the sum of the actions of the individual reagents used
- alone. An example of the synergic extraction of Ce(III) with picrolonic acid and benzo-15-crown-5.

H) Use of organic acid media

- Organic acid media are having ability of controlling the concentration of
- the complexing ligand, is one of the unique application, the ease of adjustment of
- pH and the wide difference in pH at which various metal ions form
- anionic complexes.



Removal of high boiling organics from wastewater

New technologies are developing day by day to reuse the water efficiently. Presence of micro pollutant such aniline, phenols, nitrate aromatics have adverse effect which renders the reuse of water. Solvent extraction method was reported as most effective method to remove and recover these chemicals from the wastewater. Several extractants including octanol, amines, cyanex, diethyl carbonate, ionic liquid etc. has been employed to remove high boiling organics especially phenol from wastewater. [5].

Removal of carboxylic acid

Acetic acid is produced during fermentation of yeast which is an important inhibiting agents [11]. This acetic acid as well as other carboxylic acids and dicarboxylic acids
such as formic acid, succinic acid, valeric acid etc. are removed from aqueous stream using LLE process. LLE process is more economical and less energy consuming process compared to the distillation process [6].

Essential oil extraction

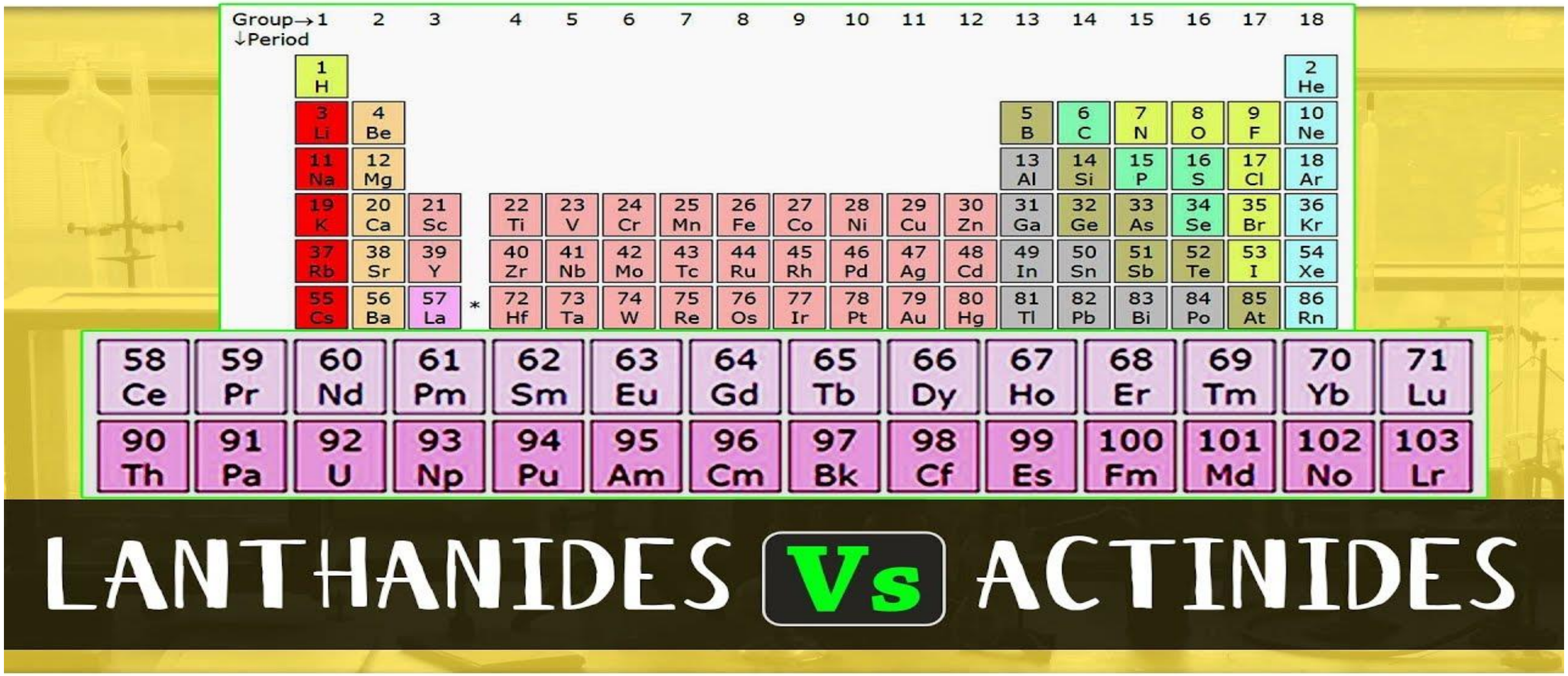
Bio-oil is produced from biomass pyrolysis. The end product is a complex mixture of different organic compounds. Due to high water content and high viscous property of bio-oil, LLE method is an efficient process to separate bio-oil according to their polarity and different chemical groups compared to the solid-phase extraction. The effect of extraction solvent and volume ratio is significant in case of LLE of bio-oil [8].

Agricultural chemical extraction

Agricultural chemicals such as herbicides and pesticides are extracted from the water using LLE method. Metals and mixture of organic compounds remains in the
agricultural waste are separated through the solvent extraction process [9].

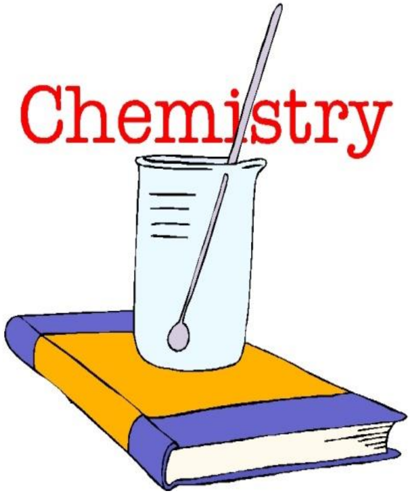
Food industry applications

LLE process is commonly used in food industries. As for example, separation and purification of a particular flavor or fragrance as well as caffeine extraction are done by this process [12].



Inorganic Chemistry

رابعة كيمياء خاص

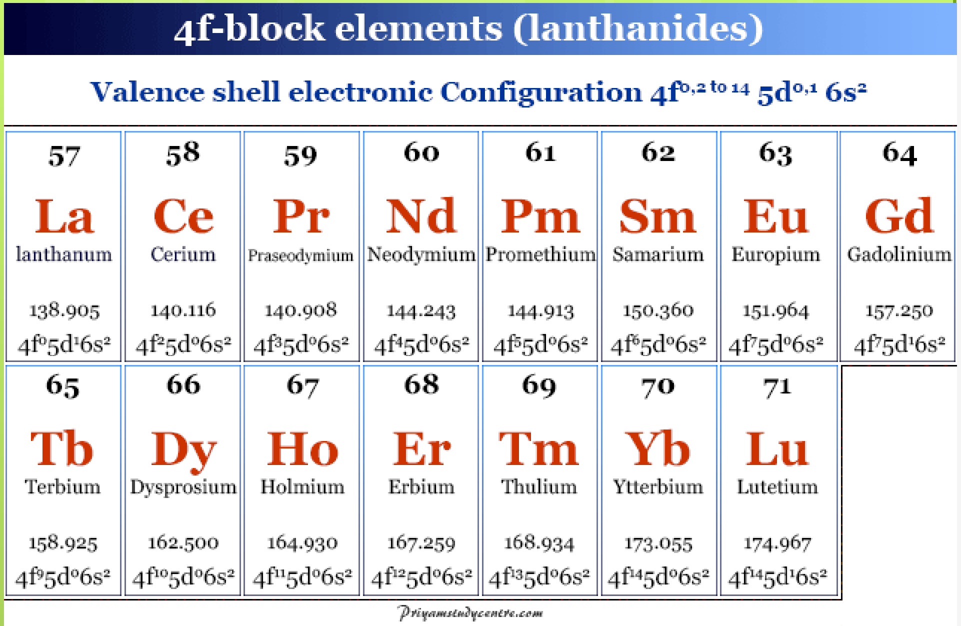


The Lanthanide and actinides Elements

د / صـــــفاء النحاس

The f - block elements

(inner transition elements).



4f-block elements (lanthanides)

Valence shell electronic Configuration $4f^{0,2\text{ to }14}\ 5d^{0,1}\ 6s^2$

57 **La** lanthanum 138.905 $4f^05d^16s^2$	58 **Ce** Cerium 140.116 $4f^25d^06s^2$	59 **Pr** Praseodymium 140.908 $4f^35d^06s^2$	60 **Nd** Neodymium 144.243 $4f^45d^06s^2$	61 **Pm** Promethium 144.913 $4f^55d^06s^2$	62 **Sm** Samarium 150.360 $4f^65d^06s^2$	63 **Eu** Europium 151.964 $4f^75d^06s^2$	64 **Gd** Gadolinium 157.250 $4f^75d^16s^2$
65 **Tb** Terbium 158.925 $4f^95d^06s^2$	66 **Dy** Dysprosium 162.500 $4f^{10}5d^06s^2$	67 **Ho** Holmium 164.930 $4f^{11}5d^06s^2$	68 **Er** Erbium 167.259 $4f^{12}5d^06s^2$	69 **Tm** Thulium 168.934 $4f^{13}5d^06s^2$	70 **Yb** Ytterbium 173.055 $4f^{14}5d^06s^2$	71 **Lu** Lutetium 174.967 $4f^{14}5d^16s^2$	

Priyamstudycentre.com

lanthanide series

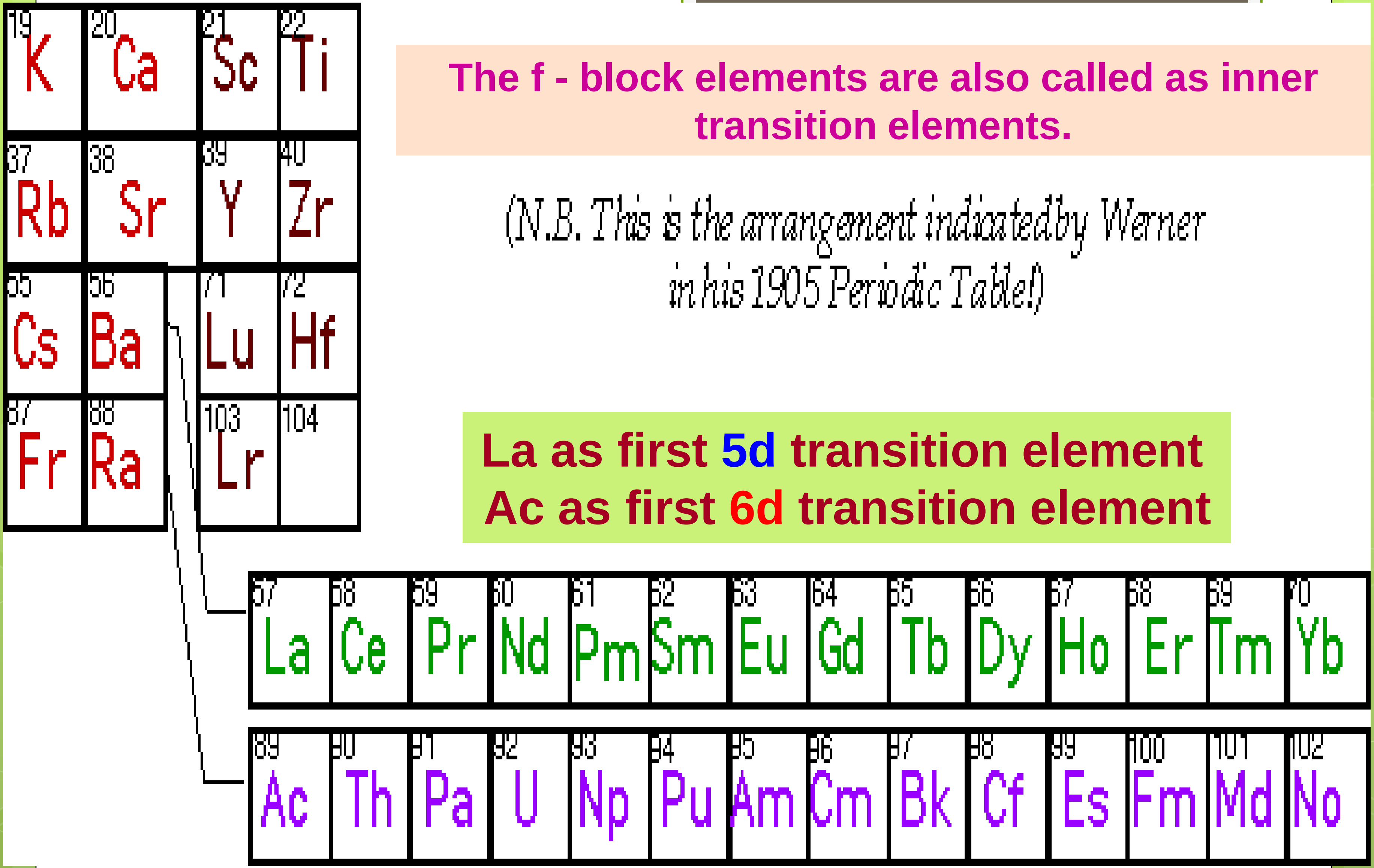
Rare-earth series

INTRODUCING THE LANTHANIDES

rare earth metals

Study.com

The f - block elements are also called as inner transition elements.



19 K	20 Ca	21 Sc	22 Ti
37 Rb	38 Sr	39 Y	40 Zr
55 Cs	56 Ba	71 Lu	72 Hf
87 Fr	88 Ra	103 Lr	104

57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb
89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No

(N.B. This is the arrangement indicated by Werner in his 1905 Periodic Table!)

La as first 5d transition element

Ac as first 6d transition element

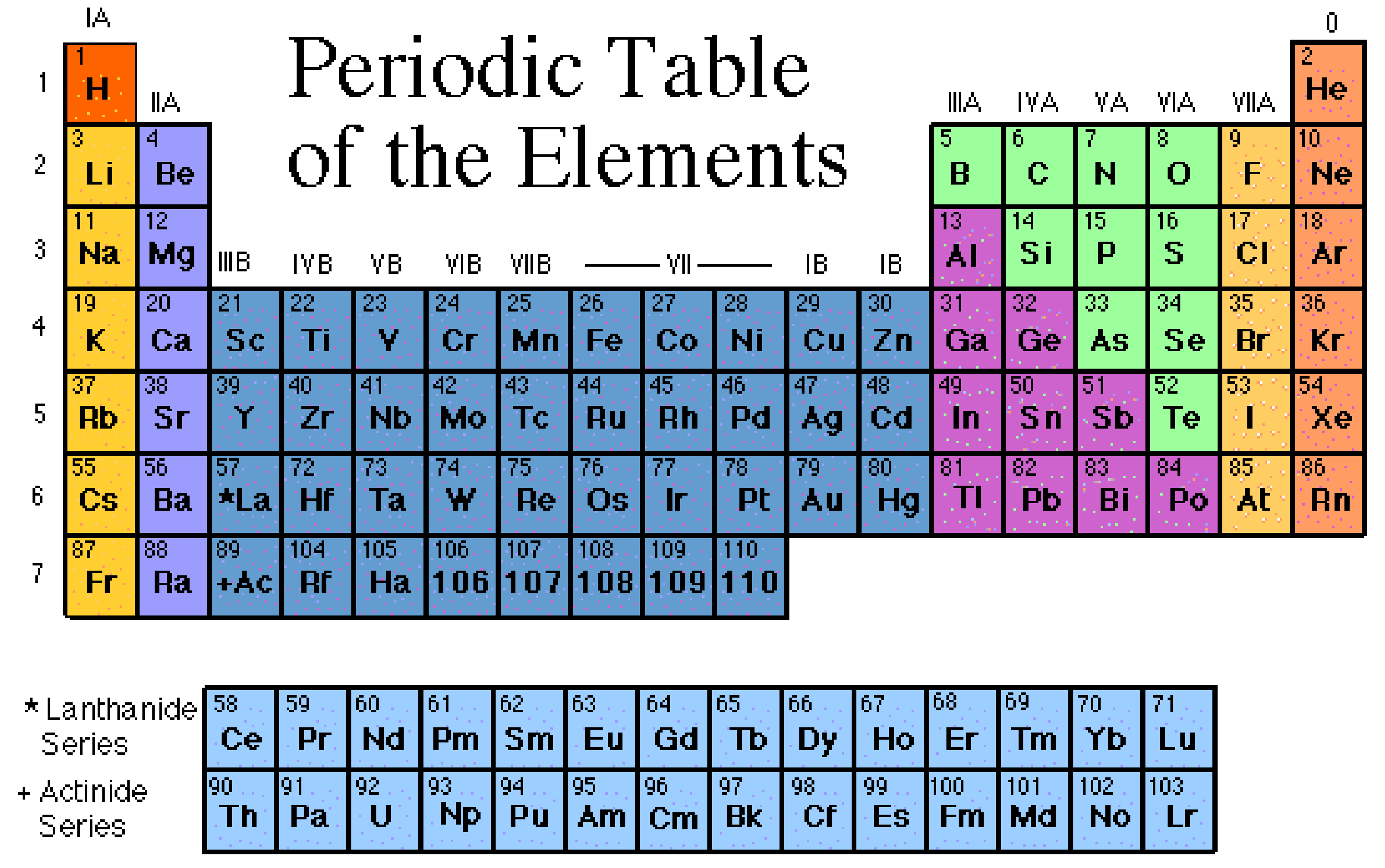
اكتشافها

- • تم اكتشاف عناصر اللانثانيدات في اواخر القرن الثامن عشر عند اكتشاف مادتي(اليتريا)و(السيريا.
- **حيث يحتوى خامة اكسيدالسيريا علي العناصر التالية:-**
- اللانثانيوم – (La
- االسيريوم -(Ce
- النيوديوم -(Nd
- البراسيديوم -(Pr
- السماريوم -(Sm
- الجادلينيوم -(Gd
- اليوربيوم -(Eu
- **يحتوى خامة اكسيداليتريا علي العناصر التالية:-**
- اليتريوم -(Y
- السكانديوم -(Sc
- التربيوم -(Tb
- الديسبروسيوم -(Dy
- الجادلينيوم -(Gd
- الهولميوم -(Ho
- اللوتيتيوم -(Lu
- ليتربيوم -(Yb
- الثاليوم -(Tm
- الاربيوم (Er

Position of Lanthanides

- The lanthanides belongs to III B group of the periodic table in the sixth period.
- These elements interrupt the third transition series of d- block elements in the sixth period.
- Only for the sake of convenience these elements are shown at the bottom of the periodic table.
- Their actual position is in between La (Z=57) and Hf (Z=72)together at one place.

Periodic Table of Elements

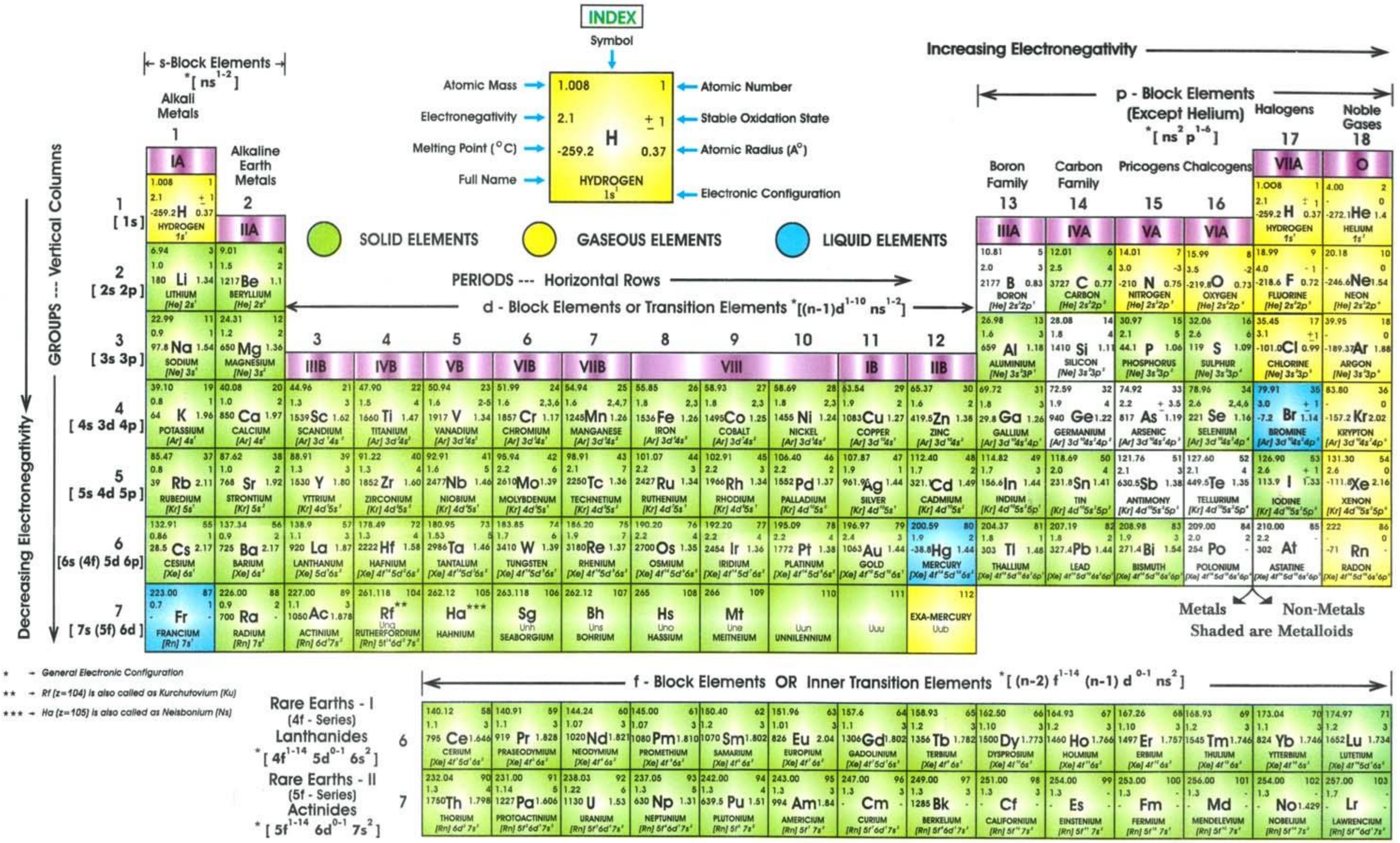


Periodic Table of the Elements

	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VII			IB	IB	IIIA	IVA	VA	VIA	VIIA	0
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 *La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 +Ac	104 Rf	105 Ha	106 106	107 107	108 108	109 109	110 110								

* Lanthanide Series	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
+ Actinide Series	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

LONG FORM OF PERIODIC TABLE



Atomic Number	Symbol	Full Name	Atomic Mass	Electronegativity	Melting Point (°C)	Atomic Radius (A°)
1	H	HYDROGEN	1.008	2.1	-259.2	0.37
2	He	HELIUM	4.00		-272.1	1.4
3	Li	LITHIUM	6.94	1.0	180	1.34
4	Be	BERYLLIUM	9.01	1.5	1217	1.1
5	B	BORON	10.81	2.0	2177	0.83
6	C	CARBON	12.01	2.5	3727	0.77
7	N	NITROGEN	14.01	3.0	-210	0.75
8	O	OXYGEN	15.99	3.5	-219.8	0.73
9	F	FLUORINE	18.99	4.0	-218.6	0.72
10	Ne	NEON	20.18		-246.6	1.54
11	Na	SODIUM	22.99	0.9	97.8	1.54
12	Mg	MAGNESIUM	24.31	1.2	650	1.36
13	Al	ALUMINIUM	26.98	1.6	659	1.18
14	Si	SILICON	28.08	1.8	1410	1.11
15	P	PHOSPHORUS	30.97	2.1	44.1	1.06
16	S	SULPHUR	32.06	2.6	119	1.09
17	Cl	CHLORINE	35.45	3.1	-101.0	0.99
18	Ar	ARGON	39.95		-189.3	1.88
19	K	POTASSIUM	39.10	0.8	64	1.96
20	Ca	CALCIUM	40.08	1.0	850	1.97
21	Sc	SCANDIUM	44.96	1.3	1539	1.62
22	Ti	TITANIUM	47.90	1.5	1660	1.47
23	V	VANADIUM	50.94	1.6	1917	1.34
24	Cr	CHROMIUM	51.99	1.6	1857	1.17
25	Mn	MANGANESE	54.94	1.6	1245	1.26
26	Fe	IRON	55.85	1.8	1536	1.26
27	Co	COBALT	58.93	1.8	1495	1.25
28	Ni	NICKEL	58.69	1.8	1455	1.24
29	Cu	COPPER	63.54	1.9	1083	1.27
30	Zn	ZINC	65.37	1.6	419.5	1.38
31	Ga	GALLIUM	69.72	1.8	29.8	1.26
32	Ge	GERMANIUM	72.59	1.9	940	1.22
33	As	ARSENIC	74.92	2.2	817	1.19
34	Se	SELENIUM	78.96	2.6	221	1.16
35	Br	BROMINE	79.91	3.0	-7.2	1.14
36	Kr	KRYPTON	83.80		-157.2	2.02
37	Rb	RUBEDIUM	85.47	0.8	39	2.11
38	Sr	STRONTIUM	87.62	1.0	768	1.92
39	Y	YTTRIUM	88.91	1.3	1530	1.80
40	Zr	ZIRCONIUM	91.22	1.3	1852	1.60
41	Nb	NIOBIUM	92.91	1.6	2477	1.46
42	Mo	MOLYBDENUM	95.94	2.2	2610	1.39
43	Tc	TECHNETIUM	98.91	2.1	2250	1.36
44	Ru	RUTHENIUM	101.07	2.2	2427	1.34
45	Rh	RHODIUM	102.91	2.2	1966	1.34
46	Pd	PALLADIUM	106.40	2.2	1552	1.37
47	Ag	SILVER	107.87	1.9	961.9	1.44
48	Cd	CADMIUM	112.40	1.7	321	1.49
49	In	INDIUM	114.82	1.7	156.6	1.44
50	Sn	TIN	118.69	2.0	231.8	1.41
51	Sb	ANTIMONY	121.76	2.1	630.5	1.38
52	Te	TELLURIUM	127.60	2.1	449.5	1.35
53	I	IODINE	126.90	2.6	113.9	1.33
54	Xe	XENON	131.30	2.6	-111.8	2.16
55	Cs	CESIUM	132.91	0.86	28.5	2.17
56	Ba	BARIUM	137.34	0.9	725	2.17
57	La	LANTHANUM	138.9	1.1	920	1.87
58	Ce	CERIUM	140.12	1.1	795	1.646
59	Pr	PRASEODYMIUM	140.91	1.1	919	1.828
60	Nd	NEODYMIUM	144.24	1.07	1020	1.821
61	Pm	PROMETHIUM	145.00	1.07	1080	1.810
62	Sm	SAMARIUM	150.40	1.2	1070	1.802
63	Eu	EUROPIUM	151.96	1.01	826	2.04
64	Gd	GADOLINIUM	157.6	1.1	1306	1.802
65	Tb	TERBIUM	158.93	1.2	1356	1.782
66	Dy	DYSPROSIUM	162.50	1.10	1500	1.773
67	Ho	HOLMIUM	164.93	1.2	1460	1.766
68	Er	ERBIUM	167.26	1.10	1497	1.757
69	Tm	THULIUM	168.93	1.2	1545	1.746
70	Yb	YTTERBIUM	173.04	1.1	824	1.746
71	Lu	LUTETIUM	174.97	1.2	1652	1.734
72	Hf	HAFNIUM	178.49	1.3	2222	1.58
73	Ta	TANTALUM	180.95	1.53	2986	1.46
74	W	TUNGSTEN	183.85	1.7	3410	1.39
75	Re	RHENIUM	186.20	1.9	3180	1.37
76	Os	OSMIUM	190.20	2.2	2700	1.35
77	Ir	IRIDIUM	192.20	2.2	2454	1.36
78	Pt	PLATINUM	195.09	2.2	1772	1.38
79	Au	GOLD	196.97	2.4	1063	1.44
80	Hg	MERCURY	200.59	1.9	-38.8	1.44
81	Tl	THALLIUM	204.37	1.8	303	1.48
82	Pb	LEAD	207.19	1.8	327.4	1.44
83	Bi	BISMUTH	208.98	1.9	271.4	1.54
84	Po	POLONIUM	209.00	2.0	254	
85	At	ASTATINE	210.00	2.2	302	
86	Rn	RADON	222		-71	
87	Fr	FRANCIUM	223.00	0.7		
88	Ra	RADIUM	226.00	0.9	700	
89	Ac	ACTINIUM	227.00	1.1	1050	1.878
90	Th	THORIUM	232.04	1.3	1750	1.798
91	Pa	PROTOACTINIUM	231.00	1.14	1227	1.606
92	U	URANIUM	238.03	1.22	1130	1.53
93	Np	NEPTUNIUM	237.05	1.3	630	1.31
94	Pu	PLUTONIUM	242.00	1.3	639.5	1.51
95	Am	AMERICIUM	243.00	1.3	994	1.84
96	Cm	CURIUM	247.00	1.3		
97	Bk	BERKELIUM	249.00	1.3	1285	
98	Cf	CALIFORNIUM	251.00	1.3		
99	Es	EINSTENIUM	254.00	1.3		
100	Fm	FERMIUM	253.00	1.3		
101	Md	MENDELEVIUM	256.00	1.3		
102	No	NOBELIUM	254.00	1.3		1.429
103	Lr	LAWRENCIUM	257.00	1.7		
104	Rf**	RUTHERFORDIUM (Unq)	261.118			
105	Ha***	HAHNIUM	262.12			
106	Sg	SEABORGIUM (Unh)	263.118			
107	Bh	BOHRIUM (Uns)	262.12			
108	Hs	HASSIUM (Uno)	265			
109	Mt	MEITNERIUM (Une)	266			
110	Uun	UNNILENNIUM				
111	Uuu					
112	Uub	EXA-MERCURY				

* - General Electronic Configuration

** - Rf (z=104) is also called as Kurchutovium (Ku)

*** - Ha (z=105) is also called as Neisbonium (Ns)

Values are taken from Lange's Handbook of Chemistry
12th Edition, McGraw Hill Book Company, New York
Edited by: John A. Dean

The lanthanides series elements

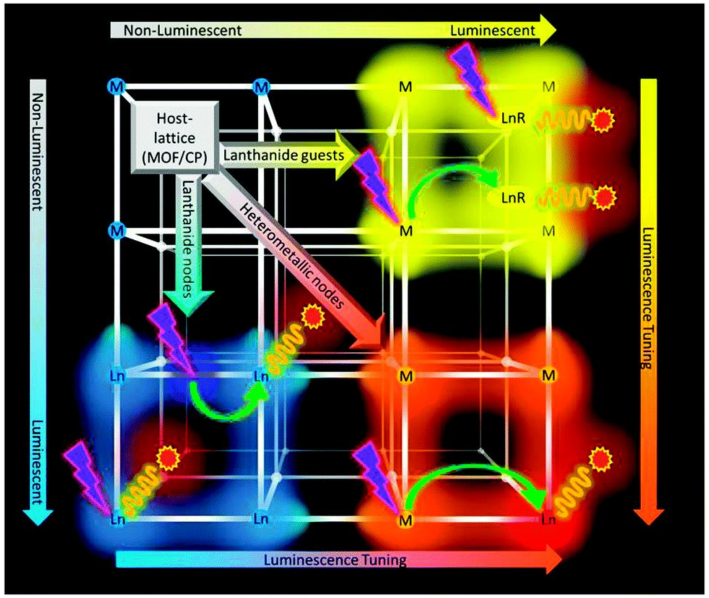
- Lanthanides are the elements in which the last electron enters into **4f - orbital**.
- These elements are also called as **Lanthanones** or **lanthanoids** or **4f-block elements.**
- Usually the symbol **Ln** is used to represent the lanthanide elements.

lanthanide series

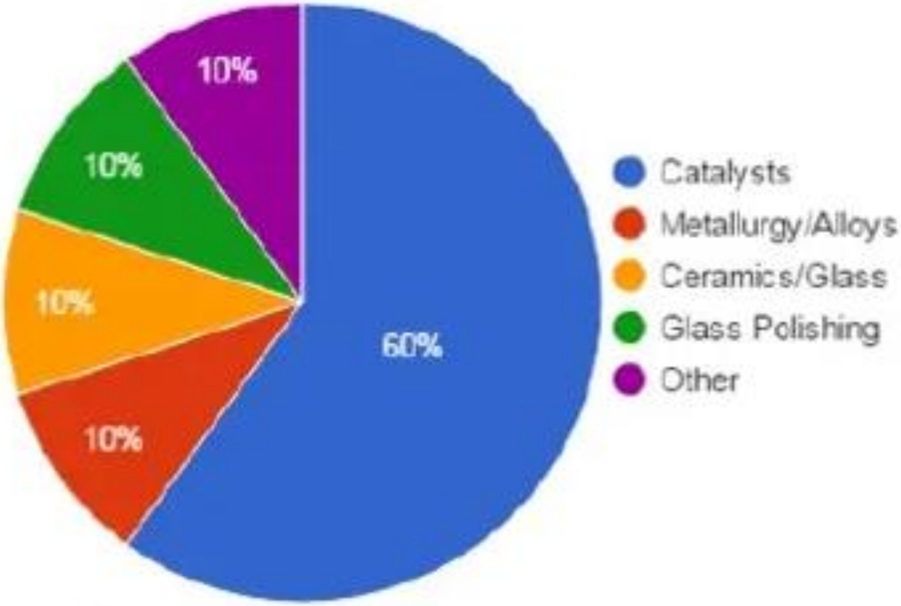
Rare-earth series

- At one time, the lanthanides were called the rare earth elements.
- The name suggests that chemists once thought that the elements were present in Earth's crust in only very small amounts.
- **That is NOT True**.
- The point of interest about the lanthanides, then, is not that they are so rare, **but that they are so much alike.**
- Most of the lanthanides occur together in nature,
- and they are very difficult to separate from each other.

Applications of lanthanides



Uses of Rare Earth Elements



Application of lanthanides elements

- One of the earliest uses involved an alloy of cerium and iron, called **Auer metal**, which produced a brilliant spark when struck.
- This has been widely used as a "flint" in cigarette and gas lighters.
- Auer metal is one of a series of mixed lanthanide alloys called misch metals (**cerium mischmetal**,) that have a variety of metallurgical applications.
- They have been used to impart strength, hardness, and inertness to structural materials. They have also been used to remove oxygen and sulfur impurities from systems.
- high coercivity magnets used in motorization (electric cars, wind turbines, hard diskdrives)
- lasers and telecommunications,
- biomedical analyses and imaging, and agriculture.
- They are classified as strategic materials by the military and several governments.

Application of lanthanides elements

The lanthanides are now used in a greater variety of applications.

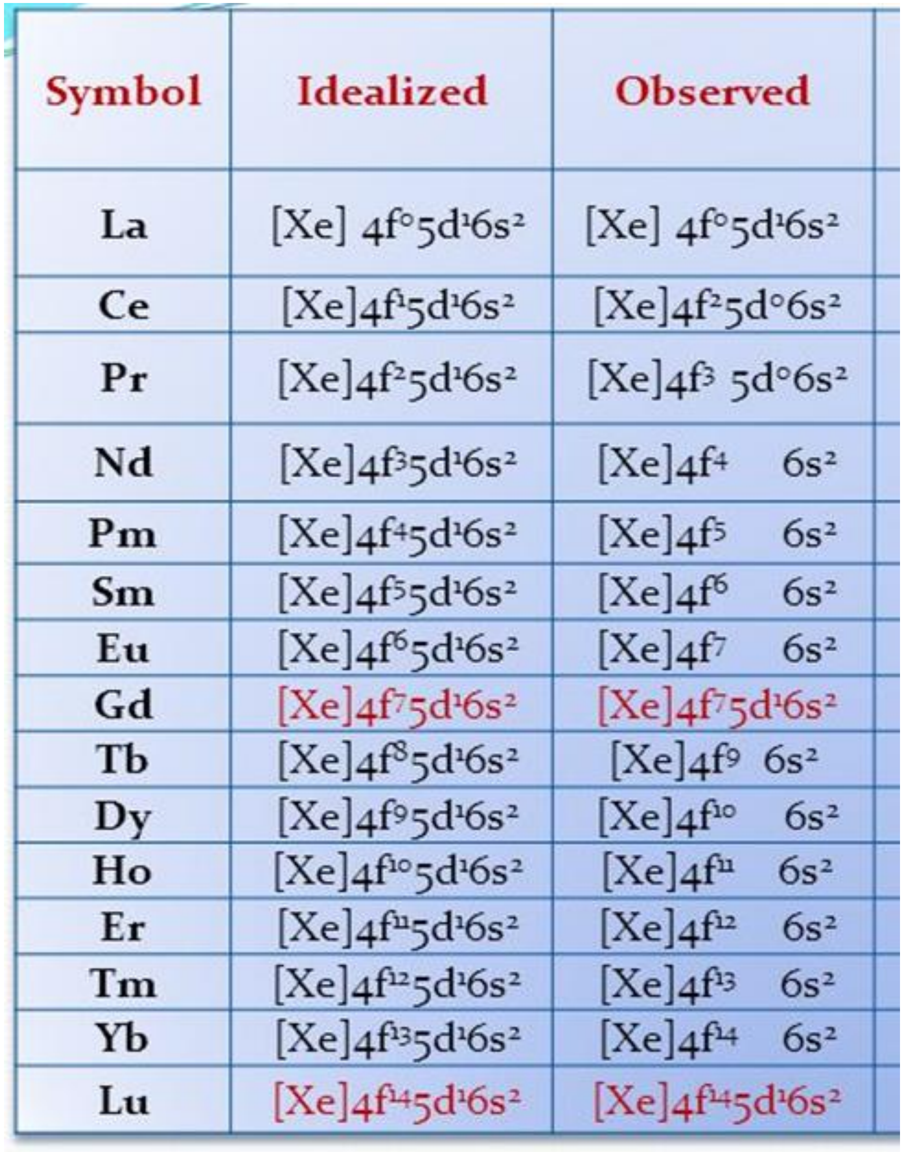
1. One such application is as catalysts in the refining industry, for example, the conversion of crude oil into gasoline, kerosene, diesel.

2. The lanthanides are also used as phosphors in color television sets.
3. Phosphors are chemicals that glow with various colors when struck by electrons.
4. For example, oxides of europium and yttrium are used to produce the red colors on a television screen.
5. Other lanthanide compounds are used in streetlights, searchlights, and in the high-intensity lighting present in sports stadiums.

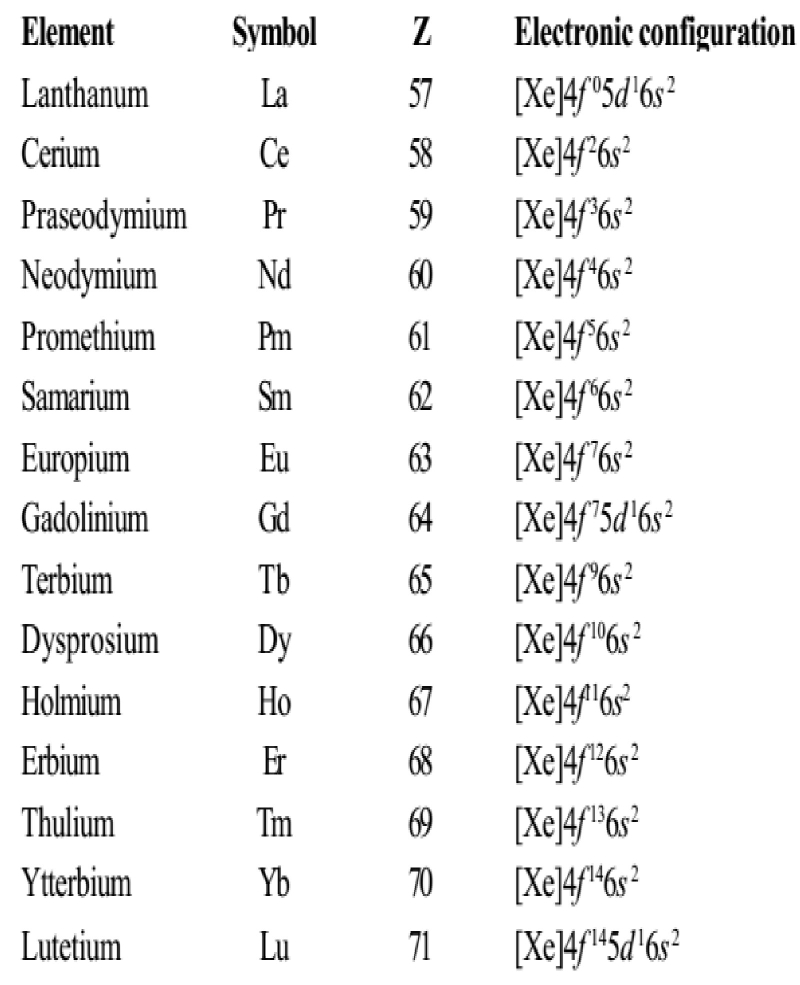
6. The ceramics industry uses lanthanide oxides to color ceramics and glasses.
7. Optical lenses made with lanthanum oxide are used in cameras and binoculars.
8. Compounds of praseodymium and neodymium are used in glass, such as in television screens, to reduce glare.
9. Cerium oxide has been used to polish glass.

10. The lanthanides also have a variety of nuclear applications. Because they absorb neutrons, they have been employed in control rods
11. They have also been used as shielding materials and as structural components in reactors.
12. Some lanthanides have unusual magnetic properties. For instance, cobalt-samarium magnets are very strong permanent magnets.

Electron Configuration



Symbol	Idealized	Observed
La	$[\mathrm{Xe}]\ 4f^{0}5d^{1}6s^{2}$	$[\mathrm{Xe}]\ 4f^{0}5d^{1}6s^{2}$
Ce	$[\mathrm{Xe}]4f^{1}5d^{1}6s^{2}$	$[\mathrm{Xe}]4f^{2}5d^{0}6s^{2}$
Pr	$[\mathrm{Xe}]4f^{2}5d^{1}6s^{2}$	$[\mathrm{Xe}]4f^{3}\ 5d^{0}6s^{2}$
Nd	$[\mathrm{Xe}]4f^{3}5d^{1}6s^{2}$	$[\mathrm{Xe}]4f^{4}\quad 6s^{2}$
Pm	$[\mathrm{Xe}]4f^{4}5d^{1}6s^{2}$	$[\mathrm{Xe}]4f^{5}\quad 6s^{2}$
Sm	$[\mathrm{Xe}]4f^{5}5d^{1}6s^{2}$	$[\mathrm{Xe}]4f^{6}\quad 6s^{2}$
Eu	$[\mathrm{Xe}]4f^{6}5d^{1}6s^{2}$	$[\mathrm{Xe}]4f^{7}\quad 6s^{2}$
Gd	$[\mathrm{Xe}]4f^{7}5d^{1}6s^{2}$	$[\mathrm{Xe}]4f^{7}5d^{1}6s^{2}$
Tb	$[\mathrm{Xe}]4f^{8}5d^{1}6s^{2}$	$[\mathrm{Xe}]4f^{9}\ 6s^{2}$
Dy	$[\mathrm{Xe}]4f^{9}5d^{1}6s^{2}$	$[\mathrm{Xe}]4f^{10}\quad 6s^{2}$
Ho	$[\mathrm{Xe}]4f^{10}5d^{1}6s^{2}$	$[\mathrm{Xe}]4f^{11}\quad 6s^{2}$
Er	$[\mathrm{Xe}]4f^{11}5d^{1}6s^{2}$	$[\mathrm{Xe}]4f^{12}\quad 6s^{2}$
Tm	$[\mathrm{Xe}]4f^{12}5d^{1}6s^{2}$	$[\mathrm{Xe}]4f^{13}\quad 6s^{2}$
Yb	$[\mathrm{Xe}]4f^{13}5d^{1}6s^{2}$	$[\mathrm{Xe}]4f^{14}\quad 6s^{2}$
Lu	$[\mathrm{Xe}]4f^{14}5d^{1}6s^{2}$	$[\mathrm{Xe}]4f^{14}5d^{1}6s^{2}$



Element	Symbol	Z	Electronic configuration
Lanthanum	La	57	$[\mathrm{Xe}]4f^{0}5d^{1}6s^{2}$
Cerium	Ce	58	$[\mathrm{Xe}]4f^{2}6s^{2}$
Praseodymium	Pr	59	$[\mathrm{Xe}]4f^{3}6s^{2}$
Neodymium	Nd	60	$[\mathrm{Xe}]4f^{4}6s^{2}$
Promethium	Pm	61	$[\mathrm{Xe}]4f^{5}6s^{2}$
Samarium	Sm	62	$[\mathrm{Xe}]4f^{6}6s^{2}$
Europium	Eu	63	$[\mathrm{Xe}]4f^{7}6s^{2}$
Gadolinium	Gd	64	$[\mathrm{Xe}]4f^{7}5d^{1}6s^{2}$
Terbium	Tb	65	$[\mathrm{Xe}]4f^{9}6s^{2}$
Dysprosium	Dy	66	$[\mathrm{Xe}]4f^{10}6s^{2}$
Holmium	Ho	67	$[\mathrm{Xe}]4f^{11}6s^{2}$
Erbium	Er	68	$[\mathrm{Xe}]4f^{12}6s^{2}$
Thulium	Tm	69	$[\mathrm{Xe}]4f^{13}6s^{2}$
Ytterbium	Yb	70	$[\mathrm{Xe}]4f^{14}6s^{2}$
Lutetium	Lu	71	$[\mathrm{Xe}]4f^{14}5d^{1}6s^{2}$

- Lanthanum has the electron configuration [Xe],4f0,5d1,6s2. It does not possess any 4f electron. This is definite.

- The next electron after lanthanum does not enter the expected 5d sublevel but enters 4f sublevel.

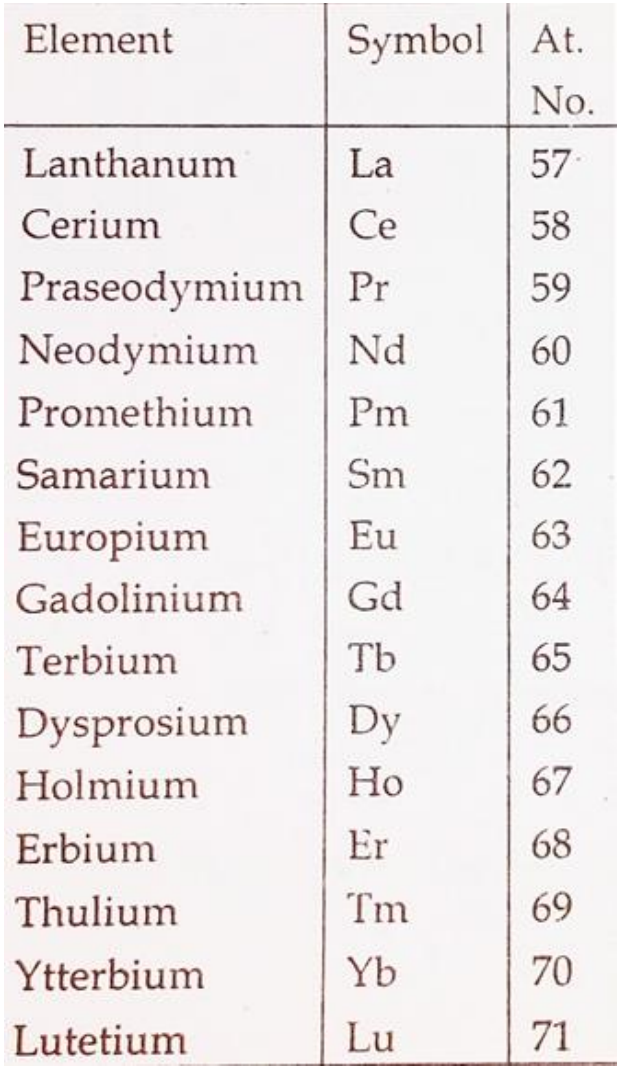
- Successive filling of electrons In 4f orbital takes place in the 14 elements which follow lanthanum, i.e. cerium onwards.

- Strictly speaking lanthanum is not a member of this series. The 14 elements from cerium (Z=58) to lutetium (Z=71) constitute lanthanides.

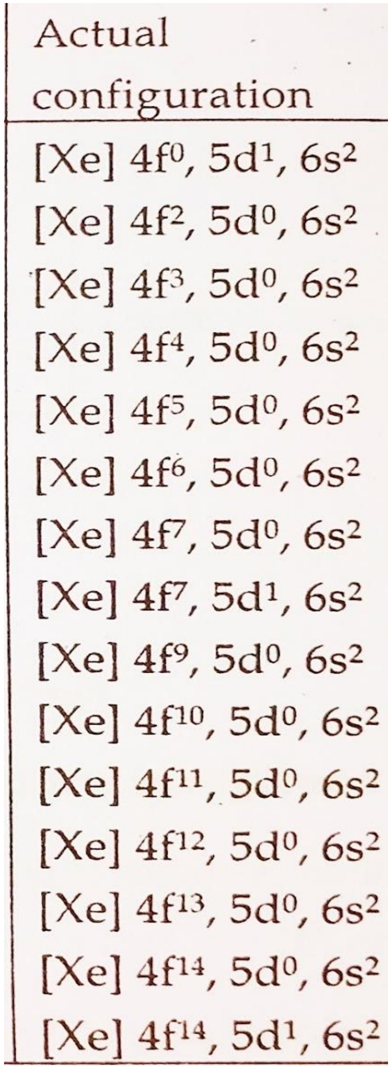
- These elements are called Lanthanides because many physical and chemical properties of these elements are similar to those of lanthanum.

Oxidation States

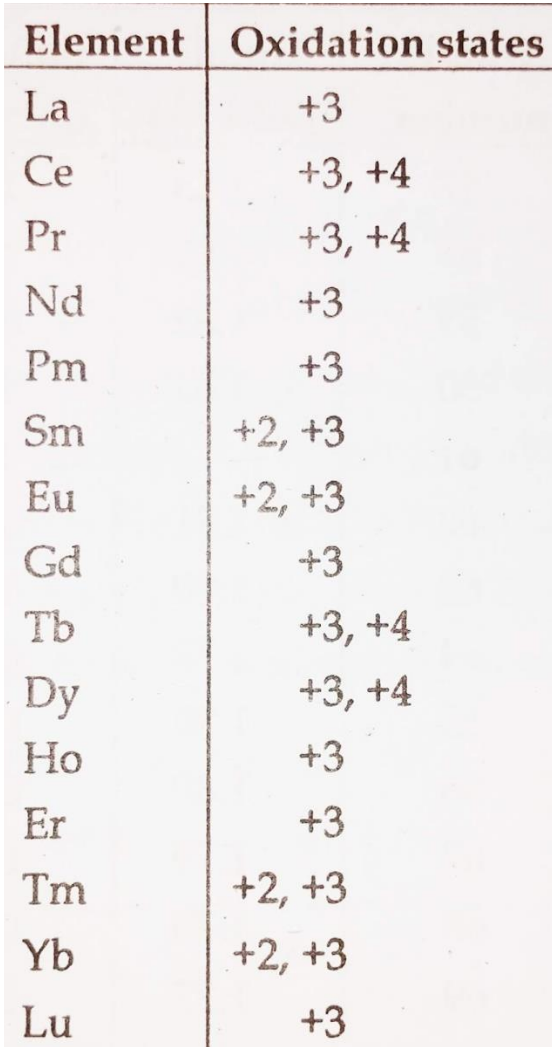
- Lanthanides exhibit different oxidation states like +2, +3 and +4.
- Among these +3 is the most stable oxidation state.
- The elements that attain stable electronic configuration by losing 2 or 4 electrons exhibit +2 and +4 oxidation states.
- Example: Europium and ytterbium exhibits +2 and +3 oxidation states –
- cerium exhibits +4 oxidation state.



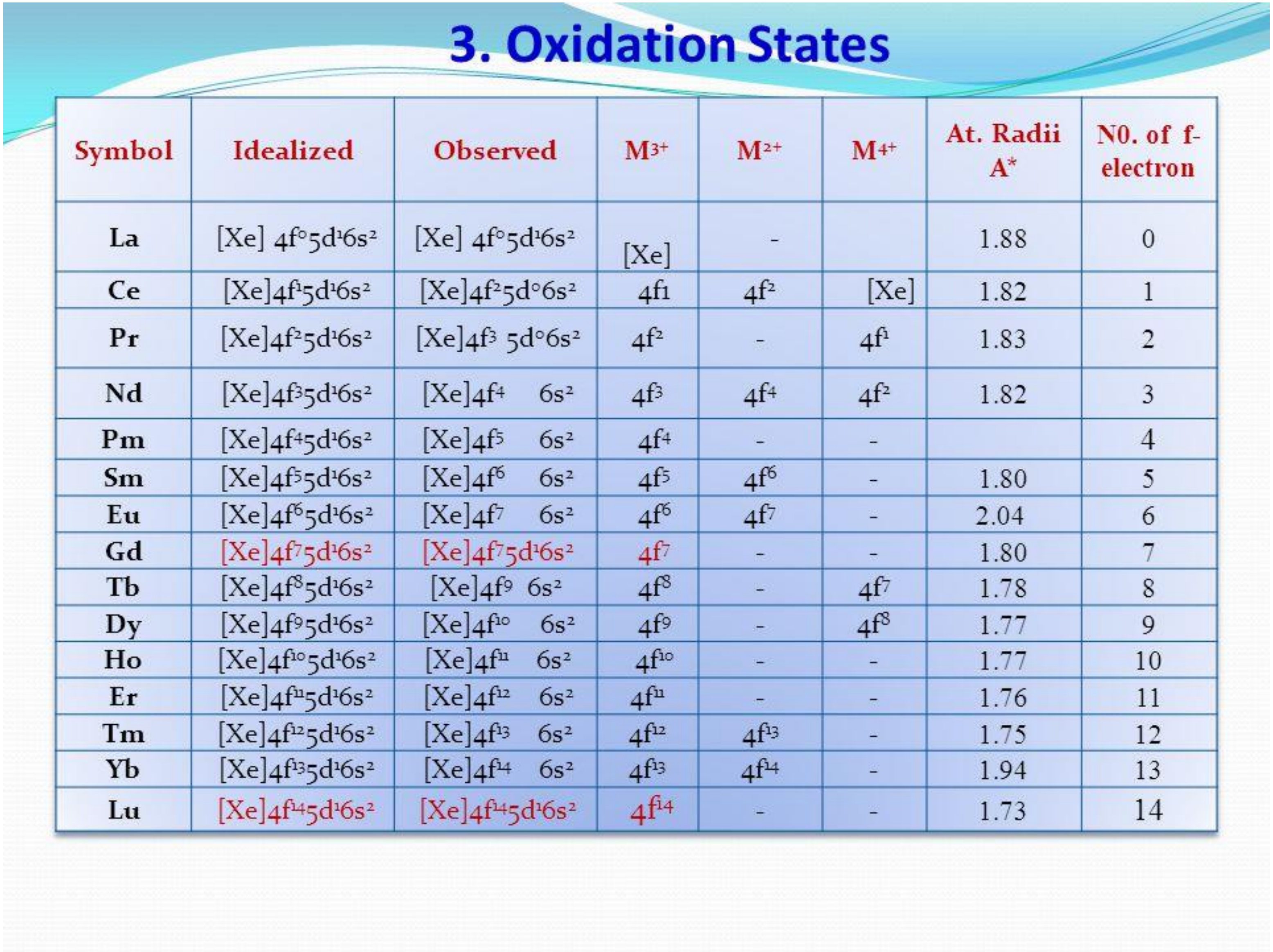
Element	Symbol	At. No.
Lanthanum	La	57
Cerium	Ce	58
Praseodymium	Pr	59
Neodymium	Nd	60
Promethium	Pm	61
Samarium	Sm	62
Europium	Eu	63
Gadolinium	Gd	64
Terbium	Tb	65
Dysprosium	Dy	66
Holmium	Ho	67
Erbium	Er	68
Thulium	Tm	69
Ytterbium	Yb	70
Lutetium	Lu	71



Actual configuration
[Xe] $4f^0, 5d^1, 6s^2$
[Xe] $4f^2, 5d^0, 6s^2$
[Xe] $4f^3, 5d^0, 6s^2$
[Xe] $4f^4, 5d^0, 6s^2$
[Xe] $4f^5, 5d^0, 6s^2$
[Xe] $4f^6, 5d^0, 6s^2$
[Xe] $4f^7, 5d^0, 6s^2$
[Xe] $4f^7, 5d^1, 6s^2$
[Xe] $4f^9, 5d^0, 6s^2$
[Xe] $4f^{10}, 5d^0, 6s^2$
[Xe] $4f^{11}, 5d^0, 6s^2$
[Xe] $4f^{12}, 5d^0, 6s^2$
[Xe] $4f^{13}, 5d^0, 6s^2$
[Xe] $4f^{14}, 5d^0, 6s^2$
[Xe] $4f^{14}, 5d^1, 6s^2$



Element	**Oxidation states**
La	+3
Ce	+3, +4
Pr	+3, +4
Nd	+3
Pm	+3
Sm	+2, +3
Eu	+2, +3
Gd	+3
Tb	+3, +4
Dy	+3, +4
Ho	+3
Er	+3
Tm	+2, +3
Yb	+2, +3
Lu	+3



3. Oxidation States

Symbol	Idealized	Observed	M3+	M2+	M4+	At. Radii A*	N0. of f-electron
La	$[Xe]\ 4f^0 5d^1 6s^2$	$[Xe]\ 4f^0 5d^1 6s^2$	[Xe]	-		1.88	0
Ce	$[Xe]4f^1 5d^1 6s^2$	$[Xe]4f^2 5d^0 6s^2$	4f1	$4f^2$	[Xe]	1.82	1
Pr	$[Xe]4f^2 5d^1 6s^2$	$[Xe]4f^3\ 5d^0 6s^2$	$4f^2$	-	$4f^1$	1.83	2
Nd	$[Xe]4f^3 5d^1 6s^2$	$[Xe]4f^4\ 6s^2$	$4f^3$	$4f^4$	$4f^2$	1.82	3
Pm	$[Xe]4f^4 5d^1 6s^2$	$[Xe]4f^5\ 6s^2$	$4f^4$	-	-		4
Sm	$[Xe]4f^5 5d^1 6s^2$	$[Xe]4f^6\ 6s^2$	$4f^5$	$4f^6$	-	1.80	5
Eu	$[Xe]4f^6 5d^1 6s^2$	$[Xe]4f^7\ 6s^2$	$4f^6$	$4f^7$	-	2.04	6
Gd	$[Xe]4f^7 5d^1 6s^2$	$[Xe]4f^7 5d^1 6s^2$	$4f^7$	-	-	1.80	7
Tb	$[Xe]4f^8 5d^1 6s^2$	$[Xe]4f^9\ 6s^2$	$4f^8$	-	$4f^7$	1.78	8
Dy	$[Xe]4f^9 5d^1 6s^2$	$[Xe]4f^{10}\ 6s^2$	$4f^9$	-	$4f^8$	1.77	9
Ho	$[Xe]4f^{10} 5d^1 6s^2$	$[Xe]4f^{11}\ 6s^2$	$4f^{10}$	-	-	1.77	10
Er	$[Xe]4f^{11} 5d^1 6s^2$	$[Xe]4f^{12}\ 6s^2$	$4f^{11}$	-	-	1.76	11
Tm	$[Xe]4f^{12} 5d^1 6s^2$	$[Xe]4f^{13}\ 6s^2$	$4f^{12}$	$4f^{13}$	-	1.75	12
Yb	$[Xe]4f^{13} 5d^1 6s^2$	$[Xe]4f^{14}\ 6s^2$	$4f^{13}$	$4f^{14}$	-	1.94	13
Lu	$[Xe]4f^{14} 5d^1 6s^2$	$[Xe]4f^{14} 5d^1 6s^2$	$4f^{14}$	-	-	1.73	14

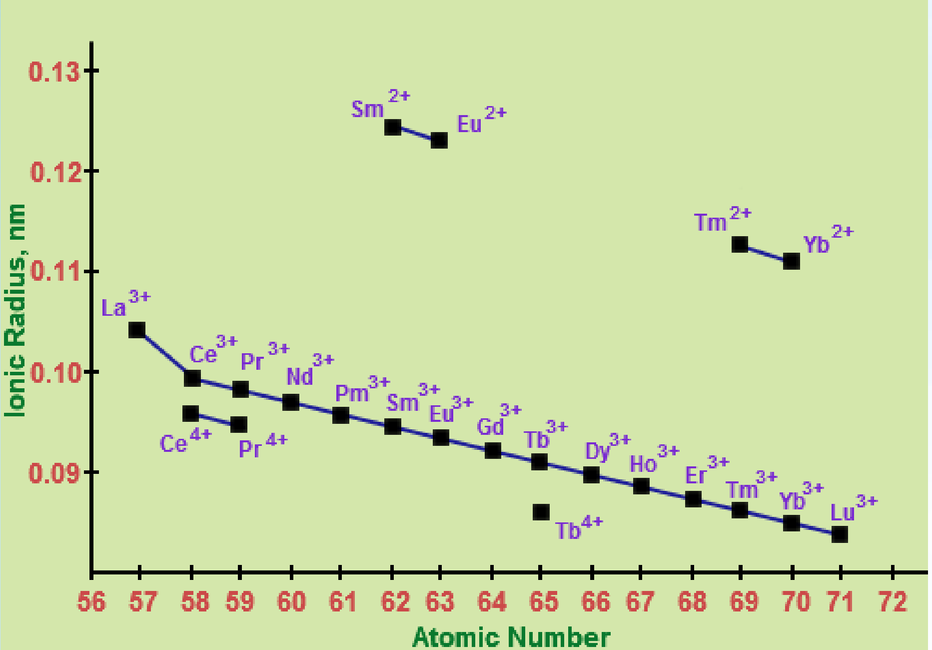
*Lanthanides properties

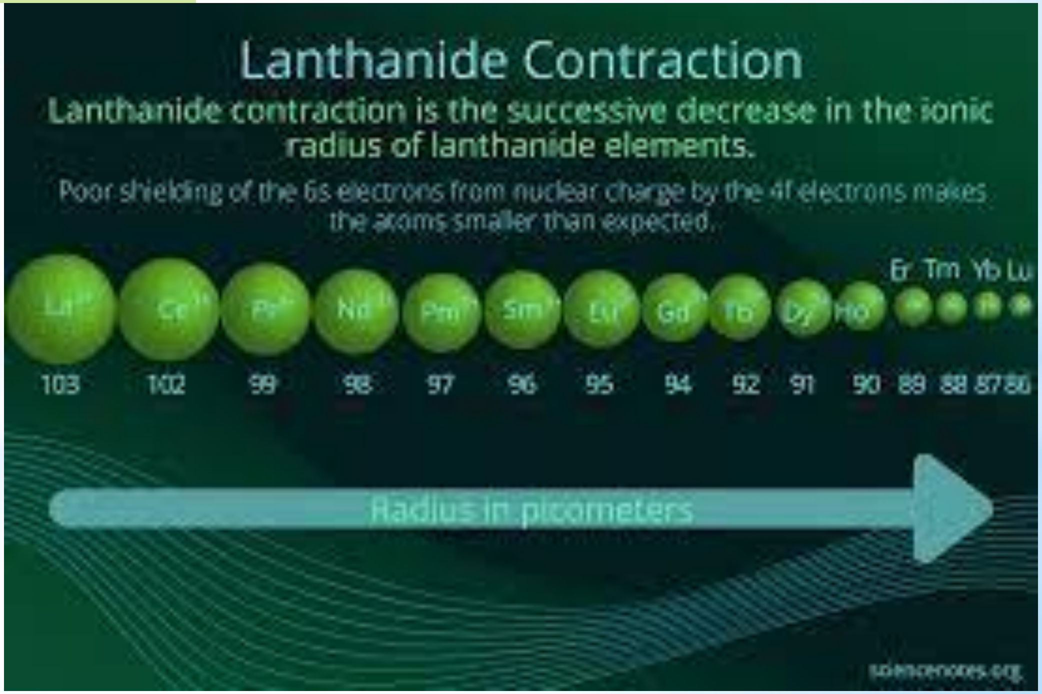
*lanthanide contraction

- الانكماش اللانثانيدي هو تناقص أكثر مما هو متوقع في نصف القطر الأيوني للعناصر في سلسلة اللانثانيدات انطلاقاً من العنصر ذي العدد الذري 57 لانثانوم إلى العنصر 71 لوتيشيوم.

- As the atomic number increases, each succeeding element contains one more electron in the 4f orbital and one proton in the nucleus.
- The 4f electrons are ineffective in screening the outer electrons from the nucleus causing imperfect shielding.
- As a result, there is a gradual increase in the nucleus attraction for the outer electrons.
- Consequently gradual decrease in size occur.
- This is called lanthanide contraction

Element name	**Symbol**	**Z**	**Ln**	**Ln^{3+}**	**Radius Ln^{3+}/ pm**
Lanthanum	La	57	$[Xe]6s^2 5d^1$	$[Xe]4f^0$	116
Cerium	Ce	58	$[Xe]4f^1 6s^2 5d^1$	$[Xe]4f^1$	114
Praesodymium	Pr	59	$[Xe]4f^3 6s^2$	$[Xe]4f^2$	113
Neodymium	Nd	60	$[Xe]4f^4 6s^2$	$[Xe]4f^3$	111
Promethium	Pm	61	$[Xe]4f^5 6s^2$	$[Xe]4f^4$	109
Samarium	Sm	62	$[Xe]4f^6 6s^2$	$[Xe]4f^5$	108
Europium	Eu	63	$[Xe]4f^7 6s^2$	$[Xe]4f^6$	107
Gadolinium	Gd	64	$[Xe]4f^7 6s^2 5d^1$	$[Xe]4f^7$	105
Terbium	Tb	65	$[Xe]\ 4f^9 6s^2$	$[Xe]4f^8$	104
Dysprosium	Dy	66	$[Xe]\ 4f^{10} 6s^2$	$[Xe]4f^9$	103
Holmium	Ho	67	$[Xe]\ 4f^{11} 6s^2$	$[Xe]4f^{10}$	102
Erbium	Er	68	$[Xe]\ 4f^{12} 6s^2$	$[Xe]4f^{11}$	100
Thulium	Tm	69	$[Xe]\ 4f^{13} 6s^2$	$[Xe]4f^{12}$	99
Ytterbium	Yb	70	$[Xe]\ 4f^{14} 6s^2$	$[Xe]4f^{13}$	99
Lutetium	Lu	71	$[Xe]\ 4f^{14} 6s^2 5d^1$	$[Xe]4f^{14}$	98





Lanthanide Contraction

Lanthanide contraction is the successive decrease in the ionic radius of lanthanide elements.

Poor shielding of the 6s electrons from nuclear charge by the 4f electrons makes the atoms smaller than expected.

The reason of lanthanoid contraction

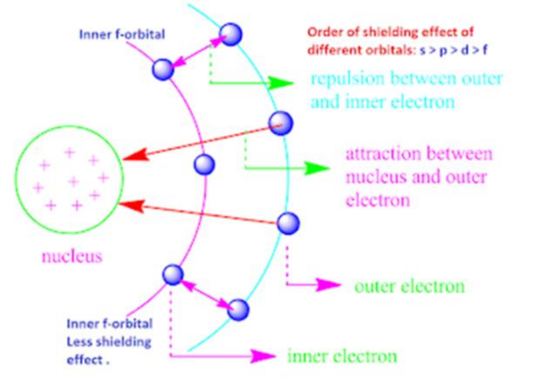
- The reason of lanthanoid contraction is:
- **The poor shielding effect of f-electrons is cause of lanthanoid contraction.**

- Two consequences of lanthanoid contraction

1. There is close resemblance between 4d and 5d transition series.

- Ionization energy of 5d transition series is higher than 3d and 4d transition series.

2. Difficulty in separation of lanthanides



Explain why the Size of trivalent lanthanoid cation decreases with increase in atomic number.

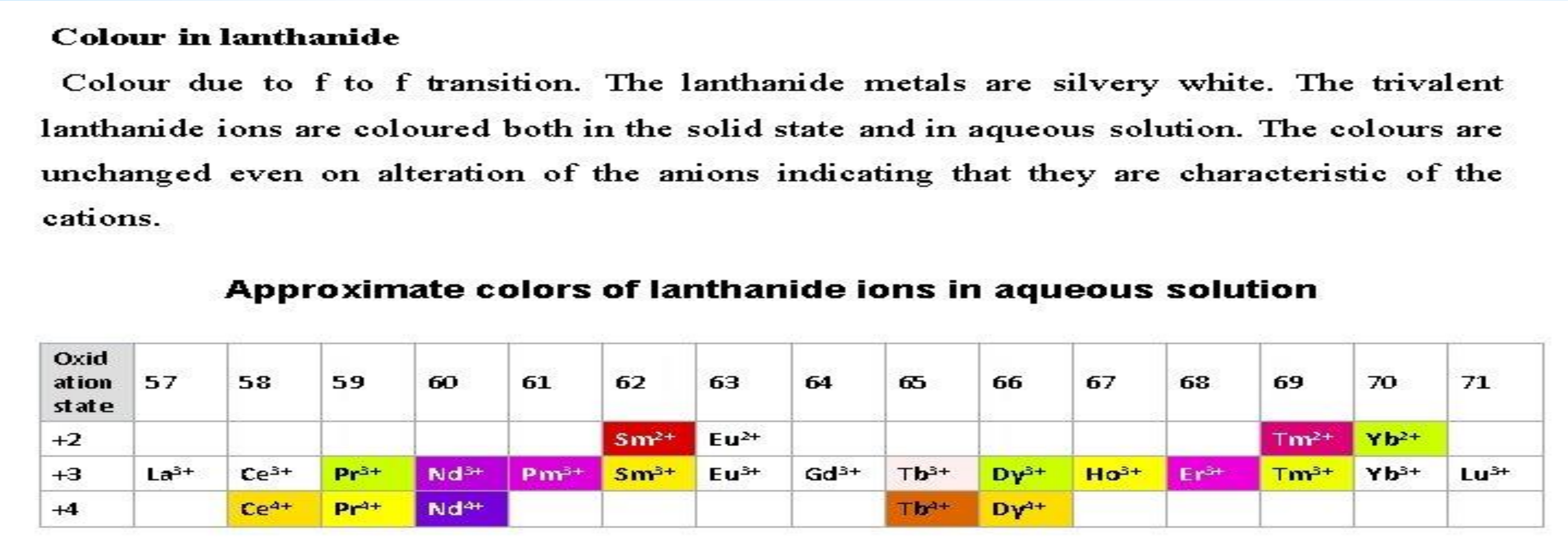
- ☐ It is due to poor shielding effect of f-electrons,
- ☐ valance electrons are strongly attracted towards nucleus,
- ☐ therefore, effective nuclear charge increases,
- ☐ hence ionic size decreases.

Colours in lanthanoid

- Colours of these ions may be attributed to the presence of f electrons.

- Absorption bands are narrow, probably because of the excitation within f level.
- Neither La3+ nor Lu3+ ion shows any colour but the rest do so.

Lanthanum	[Xe]$6s^2 5d^1$	[Xe]$4f^0$
Lutetium	[Xe] $4f^{14} 6s^2 5d^1$	[Xe]$4f^{14}$



Colour in lanthanide

Colour due to f to f transition. The lanthanide metals are silvery white. The trivalent lanthanide ions are coloured both in the solid state and in aqueous solution. The colours are unchanged even on alteration of the anions indicating that they are characteristic of the cations.

Approximate colors of lanthanide ions in aqueous solution

Oxidation state	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
+2						Sm^{2+}	Eu^{2+}						Tm^{2+}	Yb^{2+}	
+3	La^{3+}	Ce^{3+}	Pr^{3+}	Nd^{3+}	Pm^{3+}	Sm^{3+}	Eu^{3+}	Gd^{3+}	Tb^{3+}	Dy^{3+}	Ho^{3+}	Er^{3+}	Tm^{3+}	Yb^{3+}	Lu^{3+}
+4		Ce^{4+}	Pr^{4+}	Nd^{4+}					Tb^{4+}	Dy^{4+}					

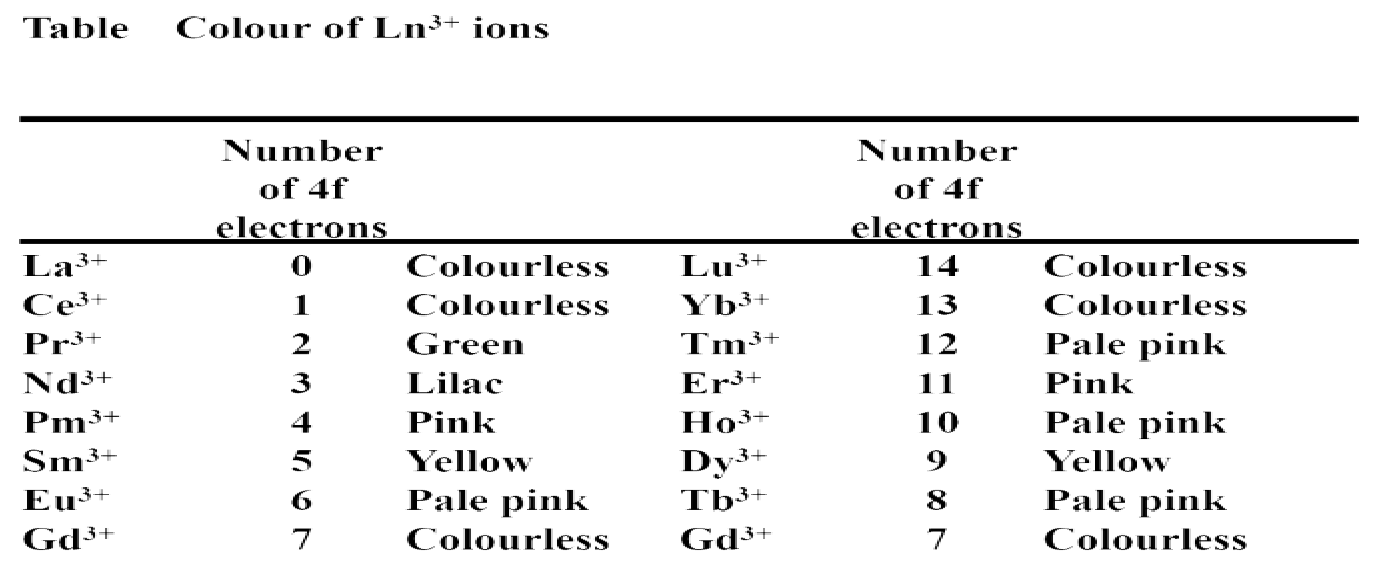


Table Colour of Ln^{3+} ions

	Number of 4f electrons			Number of 4f electrons	
La^{3+}	0	Colourless	Lu^{3+}	14	Colourless
Ce^{3+}	1	Colourless	Yb^{3+}	13	Colourless
Pr^{3+}	2	Green	Tm^{3+}	12	Pale pink
Nd^{3+}	3	Lilac	Er^{3+}	11	Pink
Pm^{3+}	4	Pink	Ho^{3+}	10	Pale pink
Sm^{3+}	5	Yellow	Dy^{3+}	9	Yellow
Eu^{3+}	6	Pale pink	Tb^{3+}	8	Pale pink
Gd^{3+}	7	Colourless	Gd^{3+}	7	Colourless

COLOUR OF IONS

❖ Lanthanides ions can have electrons in f-orbital and also empty orbitals like the d-block elements.

❖When a frequency of light is absorbed, the light transmitted ***exhibit a colour complementary to the frequency absorbed***.

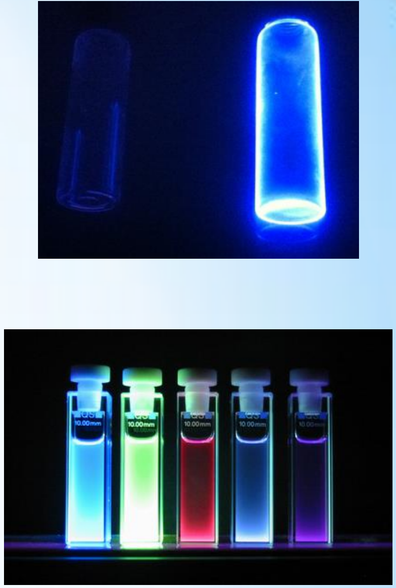
❖Inner transition element ions can absorb the ***frequency in the visible region*** to use it for f-f electron transition and produce visible colour.

❖Many of the ***lanthanide metals are silver-white***.

❖ The lanthanide ions with +3 oxidation state are coloured both in solid-state and in aqueous solutior

❖The colour of a cation depends on the number of unpaired f electrons Lanthanides, with ***xf electrons, have the same colour as of (14-x) electron elements.***

Luminescence of lanthanoid complexes



Irradiation of some Lanthanide(III) complexes with UV light causes them to fluoresce

The origin of fluorescence is 4*f*-4*f* transitions.

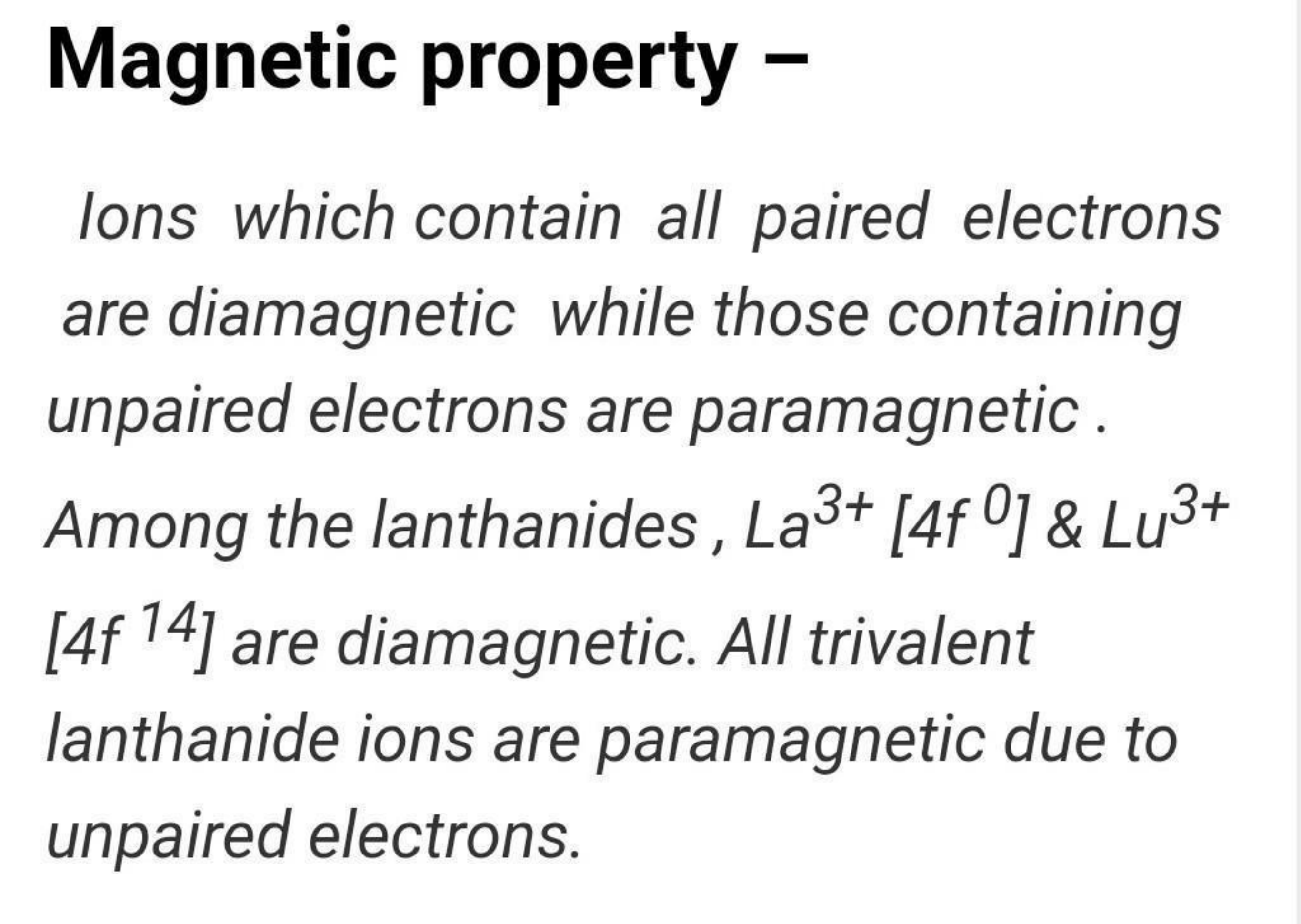
–the excited state produced decays to the ground state with emission of energy.

Some examples are Eu^{3+} (red) and Tb^{3+} (green)

They can be used as phosphors in television sets and fluorescent lighting.

These applications are specific to lanthanoid ions because of the sharp transitions observed.

Magnetic properties

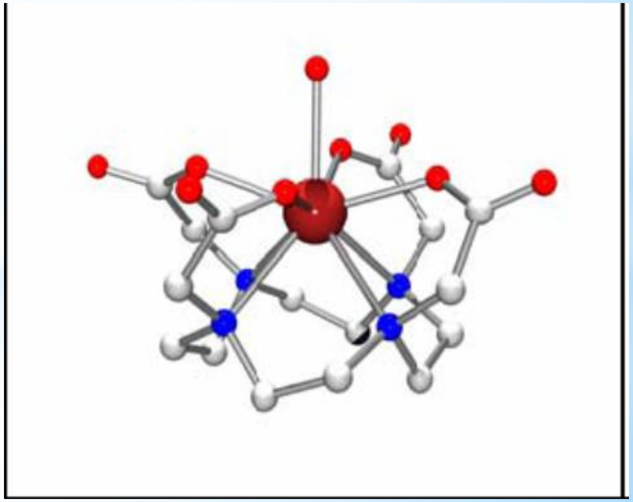


Magnetic property –

Ions which contain all paired electrons are diamagnetic while those containing unpaired electrons are paramagnetic . Among the lanthanides , La^{3+} $[4f^{0}]$ *&* Lu^{3+} $[4f^{14}]$ *are diamagnetic. All trivalent lanthanide ions are paramagnetic due to unpaired electrons.*

- Lanthanides have very high magnetic susceptibilities due to their large numbers of unpaired f-electrons.
- The strongest known magnets contain lanthanides (eg. Nd-Fe-B, Sm-Fe-N, and Sm-Co).

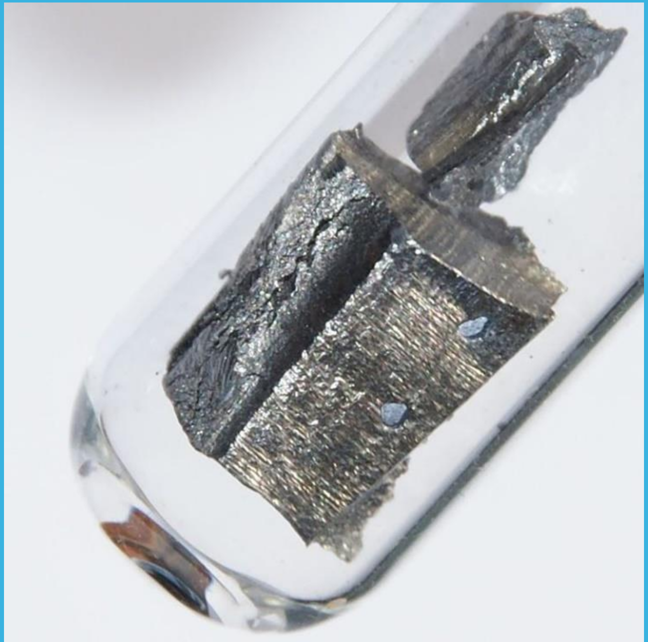
- Lanthanide complexes are used in MRI (medical
- resonance imaging), eg. [Gd(III)(dtpa)]2-



Magnetic properties

- Another interesting feature of lanthanides is the magnetic properties of some of their ions,
- which makes them useful as contrast agents in Magnetic Resonance Imaging (MRI) applications.
- MRI is an imaging technique widely used in the clini for the diagnosis of disease and visualisation of injuries,
- which utilises magnetic fields and electromagnetic radiation to create images of the physiology within the body.
- Contrast agents are normally needed to enhance the signal obtained from MRI and improve the quality of the images obtained, and the most popular contrast agent currently used is **the lanthanide ion gadolinium(III).**

❑ CHEMICAL PROPERTIES



COMMON OXIDATION STATES

Ln, Pm, Ho, Eb, Lu	+3
Ce, Pr, Tb, Dy	+3, +4
Sm, Eu, Tm, Yb	+2, +3
Nd,	+2, +3, +3

Lanthanides exhibits a principal oxidation state of +3 which contain an outer shell containing 8 electrons and an underlying layer containing up to 14 electrons. The +3 ions of La, Gd and Lu which contain respectively an empty, a half-filled, and a completely filled 4f level are especially stable. Ce can exhibit an oxidation state of +4 in which it has the same electronic structure with La^{+3} i.e. an empty 4f level-noble gas configuration). Also, Tb^{4+} exists which has the same electronic structure as Gd^{3+} i.e. a half-filled 4f level. An empty, a half-filled and a completely filled 4f shell confers some extra stability on a particular oxidation state.

La^{3+} $4f^{0}5s^{2}5p^{6}$	Ce^{4+} $4f^{0}5s^{2}5p^{6}$	(empty 4f level)
Gd^{3+} $4f^{7}5s^{2}5p^{6}$	Tb^{4+} $4f^{7}5s^{2}5p^{6}$	(half-filled 4f level)

Also, Eu^{+2} is isoelectronic with Gd^{+3} i.e. half-filled 4f level and Yb^{+2} is isoelectronic with Lu^{+3}

Gd^{3+} $4f^{7}5s^{2}5p^{6}$	Eu^{2+} $4f^{7}5s^{2}5p^{6}$	(half-filled 4f level)
Lu^{3+} $4f^{14}5s^{2}5p^{6}$	Yb^{2+} $4f^{14}5s^{2}5p^{6}$	(completely filled 4f level)

COMMON OXIDATION STATES

In addition, +2and +4 states exist for elements that are close to these states. For example, Sm^{2+} and Tm^{2+}occur with f^6 and f^{13} arrangements and Pr^{4+} and Nd^{4+} have f^1 and f^2 arrangements.

The most stable oxidation state is Ln^{3+} and Ln^{2+} and Ln^{4+} are less stable. Ce^{4+} is strongly oxidizing and Sm^{2+} is strongly reducing:

$$Ce^{4+} + Fe^{2+} \rightarrow Ce^{3+} + Fe^{3+}$$

$$2Sm^{2+} + 2H_2O \rightarrow 2Sm^{3+} + 2OH^- + H_2$$

{Ce^{4+} and $Sm^{2+}$are converted to +3 state, showing that it is the most stable oxidation state}

Oxidation State(+4)

This oxidation state is most important to cerium and a little to praseodymium and terbium. Ce(4+) is the only Ln(4+) that exists in solution.

Chemistry of +2 state :

This is an anomalous oxidation state. The lanthanides showing oxidation state can be divided into +2 two categories:

(a) Sm, Eu, and Yb : The dipositive ions of these lanthanides (i.e. Sm^{+2},Eu^{+2} and Yb^{+2}) exist in solution. The standard oxidation potentials at 25°C, in acid solution, of these cations are given below:

$Sm^{+3}_{(aq)} + e^- \leftrightarrow Sm^{+2}_{(aq)}$ – 1.55 volts

$Eu^{+3}_{(aq)} + e^- \leftrightarrow Eu^{+2}_{(aq)}$ – 0.43 volts

$Yb^{+3}_{(aq)} + e^- \leftrightarrow Yb^{+2}_{(aq)}$ – 1.15 volts

These values indicate that Sm^{+2}, Eu^{+2} and Yb^{+2} ions are strong reducing agents and their reducing strength is in the order: $Sm^{+2} > Yb^{+2} > Eu^{+2}$

Sm^{+2} and Yb^{+2} ions are rapidly oxidised by H_3O^+ ion, while Eu^{+2} ion is fairly stable and is only slowly oxidized by H_3O^+ ion.

$2Sm^{+2}(\text{or } Yb^{+2}) + 2H_3O^+ \rightarrow 2Sm^{+3}(\text{or } 2Yb^{+3}) + 2H_2O + H_2$

All these cations are rapidly oxidized in presence of oxygen.

e.g. $4Ln^{+2} + 4H_3O^+ + O_2 \rightarrow 4Ln^{+3} + 6H_2O$, where Ln^{+2} may be Sm^{+2}, Eu^{+2} or Yb^{+2}.

The compounds of Sm^{+2}, Eu^{+2} and Yb^{+2} which are insoluble in H_2O are not oxidized by H_2O, while hydrated water soluble compounds of Sm^{+2} and Yb^{+2} are oxidized by their water. Hydrated water soluble compounds of Eu^{+2} are more stable.

(b) Ce, Nd and Tm: The compounds having these elements in +2 oxidation state are known only as solid halides. These are immediately oxidized with air.

Of the divalent compounds of lanthanides, those of Eu^{+2} ion are more stable. The compounds of Ln^{+2} ion are not stable in solution. All the Ln^{+2} compounds decompose water with evolution of H_2.

$2Ln^{+2} + 2H_2O \rightarrow 2Ln^{+3} + 2OH^- + H_2 \uparrow$

Chemistry of +4 state:

This oxidation state is also an anomalous oxidation state. Double salts like $Ce(NO_3)_4.2NH_4NO_3$ and $Ce(SO_4)_2.2(NH_4)2SO_4.2H_2O$ have also been prepared.

The standard oxidation potentials at 25^0C, in acid solution, of Ce^{+4} and Pr^{+4} ions are given as under:

$Ce^{+4} + e^- \leftrightarrow Ce^{+3} + 1.74$ volts

$Pr^{+4} + e^- \leftrightarrow Pr^{+3} + 2.86$ volts

There values show that Ce(IV) and Pr(IV) are strong oxidizing agents. $Ce(SO_4)_2$ is generally used in volumetric analysis. Ce^{+4} ion is readily reduce to Ce^{+3} ion.

The tetravalent ions of Ce are stable in the solid state as well as in solution. Pr^{IV}, Nd^{IV}, Tb^{IV} and Dy^{IV} are stable only in solution.

Chemistry of +3 state:

All known anion form compounds with Ln^{+3} cation. These compounds are stable in solid as well as in solution state. Compounds of Ln^{+3} with anions such at OH^-, CO_3^{-2}, SO_4^{-2} etc. decompose on heating gives first basic salt and finally oxides.

Compounds of Ln^{+3} cation with the anions Cl^-, Br^- , I^- , NO_3^-, CH_3COO^-, BO_3^{-3} are generally soluble in H_2O, While of F^-,OH^-,O^{-2},$C_2O_4^-$ etc. are generally insoluble in H_2O.

OXIDES: The oxides Ln_2O_3 are formed by heating the metal in O_2 or by decomposition of $Ln(OH)_3$ or oxy salts like $Ln_2(CO_3)_3$ and $Ln(NO_3)_3$. Oxides are similar to alkaline earth oxides. All are insoluble in water. They absorb CO_2 and H_2O from air to form carbonates and hydroxides respectively.

Hydroxides[$Ln(OH)_3$]: The hydroxides are precipitated as gelatinous precipitates from aqueous solution by the addition by ammonia of dilute alkali to soluble salts of Ln^{+3} ion in solution.

The hydroxides are not amphoteric. They have hexagonal structure. They absorb CO_2 to give carbonate. Oxides and hydroxides are basic. The basicity decreases with increasing atomic number. La_2O_3 and $La(OH)_3$ are most basic, while Lu_2O_3 and $Lu(OH)_3$ are least basic.

Carbonates ($Ln_2(CO_3)_3$): The normal carbonates can be prepared by passing CO_2 into aq. solution of $Ln(OH)_3$. They can be prepared by adding Na_2CO_3 solution to Ln^{+3} salt solution. The CO_3^{-2} are insoluble in H_2O but dissolve in acids with liberation of CO_2 and forming Ln^{+3} salts.

Halides (LnX_3): Fluorides are pptd. by the addition of HF to Ln^{+3} salt solution. The fluorides of heavier lanthanides are sparingly soluble in HF to Ln^{+3} salt solutions. The fluorides of heavier lanthanides are sparingly soluble in HF due to formation of fluoro complexes.

Chlorides are obtained by direct combination of element on heating. It is obtained by heating oxides with $COCl_2$ or NH_4Cl.

$$Ln_2O_3 + 3COCl_2 \longrightarrow 2LnCl_3 + 3CO_2$$

$$Ln_2O_3 + 6NH_4Cl \xrightarrow{300\ C} 2LnCl_3 + 3H_2O + 6NH_3$$

PHYSICAL PROPERTIES

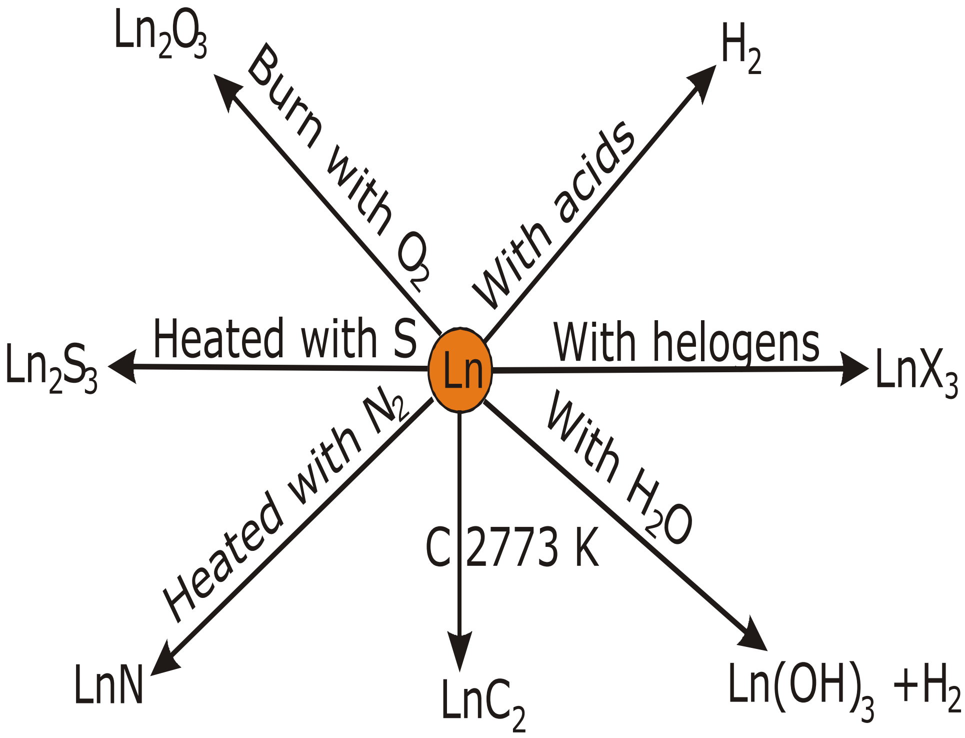
Because of their close size, they have similar properties.

Physical Properties

1. The metals are silvery white in colour.
2. They generally have high melting and boiling points and are very hard
3. They are good conductors of heat and electricity.
4. Many of the lanthanide ions form coloured ions
5. The lanthanides exhibit a principal oxidation state of +3 in which the M^{+3} ion contains an outer shell containing 8 electrons and an underlying layer containing up to 14 4f electrons.
6. They exhibit paramagnetism because of the presence of unpaired electrons

CHEMICAL PROPERTIES

- ✓ Metal combines with hydrogen when gently heated in the gas.
- ✓ The carbides, Ln_3C, Ln_2C_3 and LnC_2 are formed when the metals are heated with carbon.
- ✓ They liberate hydrogen from dilute acids and burn in halogens to form halides.
- ✓ They form oxides and hydroxides, M_2O_3 and $M(OH)_3$, basic like alkaline earth metal oxides and hydroxides.



HYDRIDES الهيدريدات

1- Ionic (salt like) hydrides

Hydrogen combines with many elements to form binary hydrides – (contain H and one other element)

Hydrogen gains an electron to form ionic hydrides containing H^- (s-block elements except Be and Mg)

مثال: ويكون هيدريدات ايونية s-block يكتسب الهيدروجين الكترون واحد من عناصر الفئة

$2Li(s) + H_2(g) \rightarrow 2LiH(s)$

2-Covalent hydrides

Hydrogen shares electrons in the covalent hydrides (p-block elements)

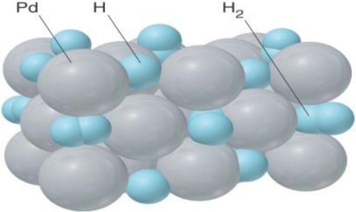
ويكون هيدريدات تساهمية مثل p-block كما يمكن للهيدروجين ان يشارك بالكترون مع عناصر الفئة : CH_4 NH_3 H_2O HF

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

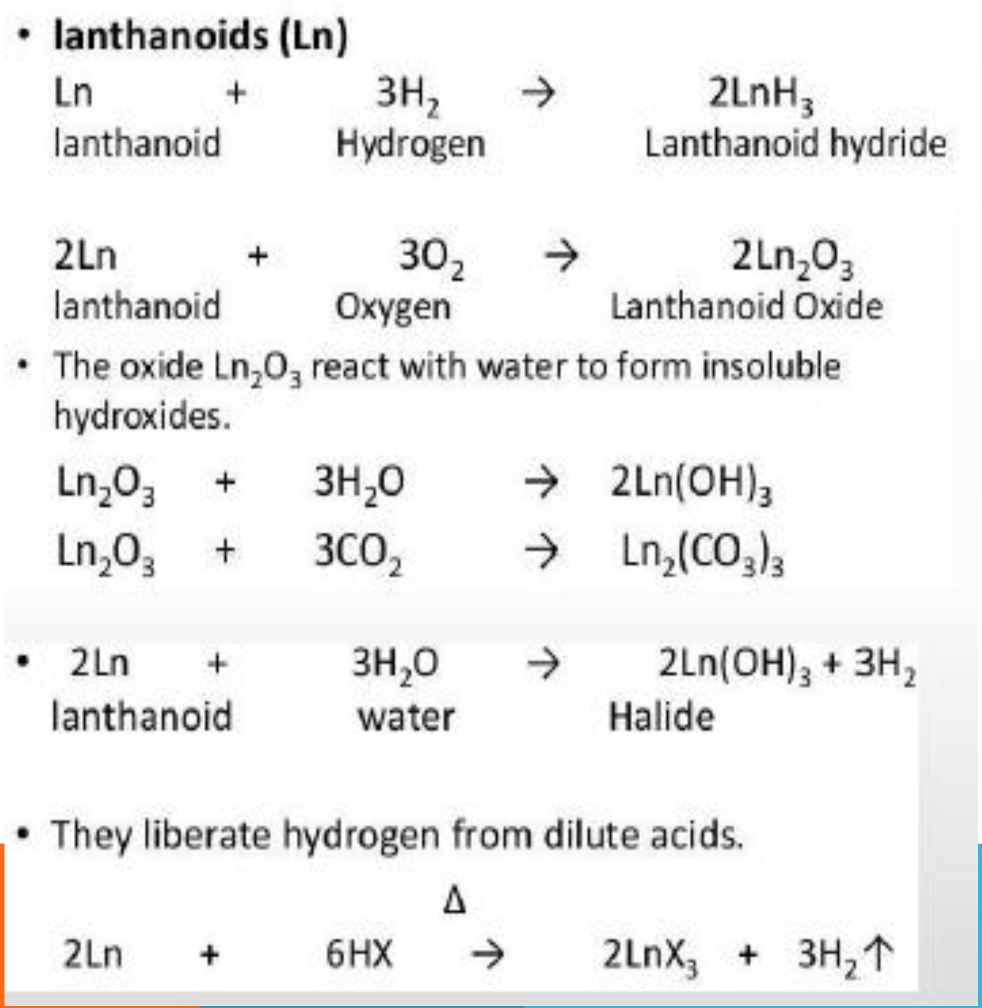
3- Metallic (interstitial) hydrides

Hydrogen is involved in metallic bonding in the interstitial or metallic hydrides (transition metals)

أيضا يكون الهيدروجين هيدريدات فلزية مع العناصر الانتقالية



CHEMICAL PROPERTIES



- **lanthanoids (Ln)**

  $Ln + 3H_2 \rightarrow 2LnH_3$

  lanthanoid Hydrogen Lanthanoid hydride

  $2Ln + 3O_2 \rightarrow 2Ln_2O_3$

  lanthanoid Oxygen Lanthanoid Oxide

- The oxide Ln_2O_3 react with water to form insoluble hydroxides.

  $Ln_2O_3 + 3H_2O \rightarrow 2Ln(OH)_3$

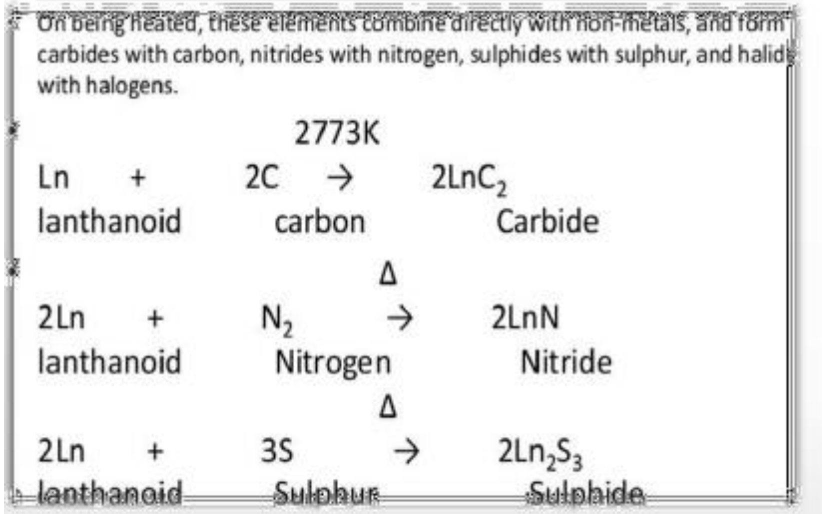
  $Ln_2O_3 + 3CO_2 \rightarrow Ln_2(CO_3)_3$

- $2Ln + 3H_2O \rightarrow 2Ln(OH)_3 + 3H_2$

  lanthanoid water Halide

- They liberate hydrogen from dilute acids.

  $2Ln + 6HX \xrightarrow{\Delta} 2LnX_3 + 3H_2\uparrow$



On being heated, these elements combine directly with non-metals, and form carbides with carbon, nitrides with nitrogen, sulphides with sulphur, and halid with halogens.

$Ln + 2C \xrightarrow{2773K} 2LnC_2$

lanthanoid carbon Carbide

$2Ln + N_2 \xrightarrow{\Delta} 2LnN$

lanthanoid Nitrogen Nitride

$2Ln + 3S \xrightarrow{\Delta} 2Ln_2S_3$

lanthanoid Sulphur Sulphide

الكربيدات

هى مركبات الكربون مع عناصر أخرى أقل منة فى السالبية الكهربية (وليس تتضمن N, O, S, P, X)

تنقسم الكربيدات الى ثلاثة انواع:

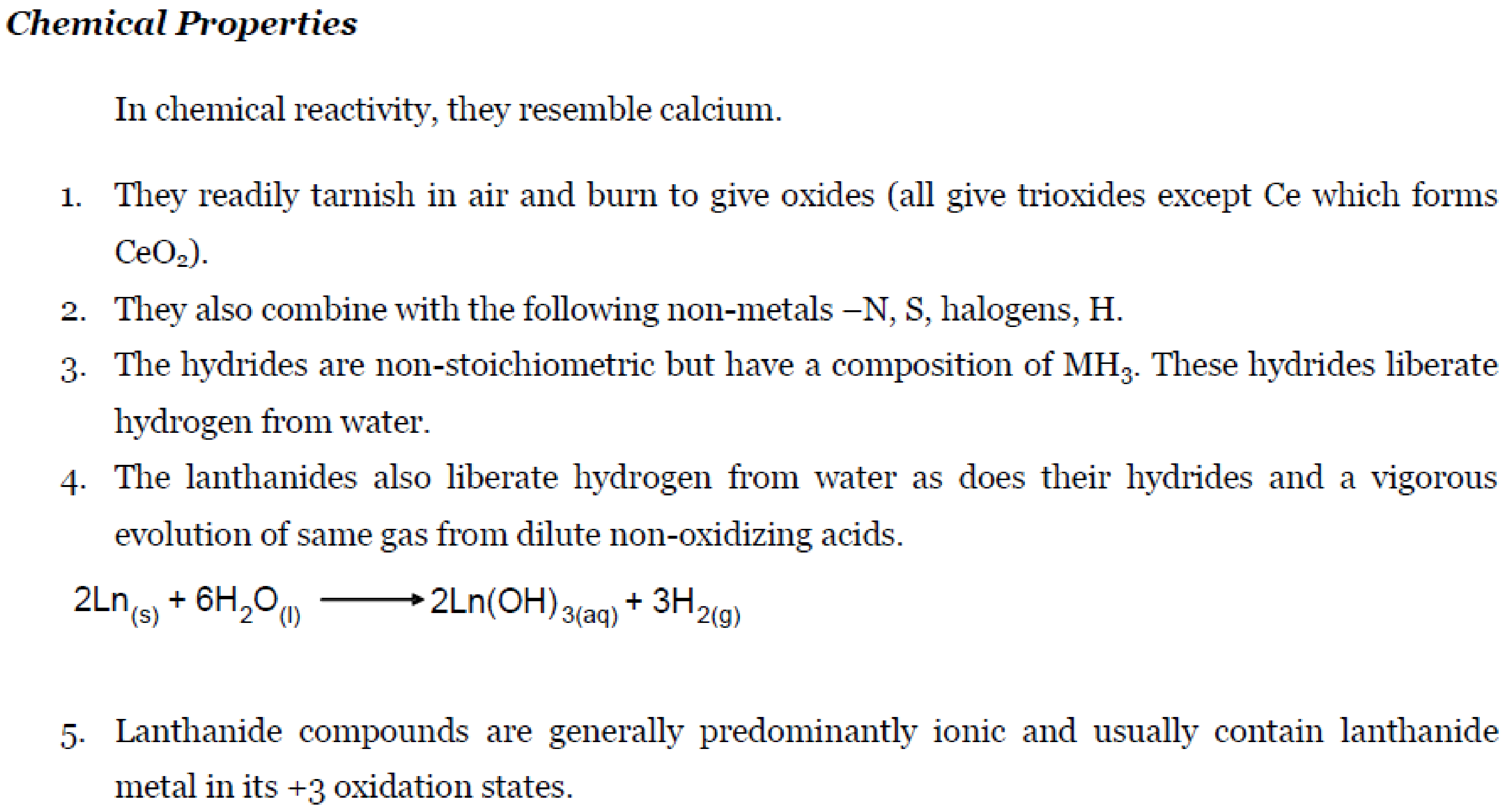
الكربيدات الأيونية : التى تتكون من اتحاد الكربون بعناصر المجموعات الأولى و الثانية و الثالثة

$$CaC_2(s) + 2H_2O(g) \rightarrow Ca(OH)_2(aq) + C_2H_2(g)$$

الكربيدات البينية: التى تتكون غالبا بواسطة العناصر الانتقالية و خاصة الكروم

الكربيدات التساهمية: مثل كربيد السليكون و كربيد البورون

CHEMICAL PROPERTIES



Chemical Properties

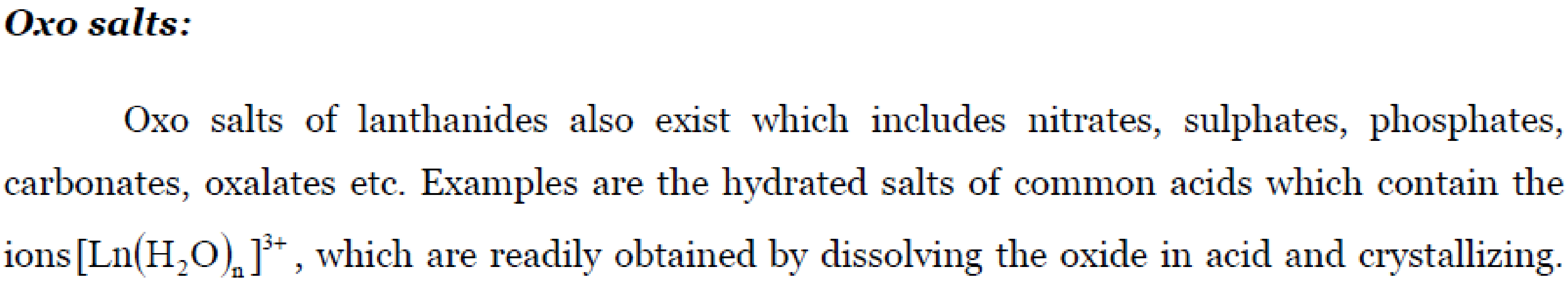
In chemical reactivity, they resemble calcium.

1. They readily tarnish in air and burn to give oxides (all give trioxides except Ce which forms CeO_2).
2. They also combine with the following non-metals –N, S, halogens, H.
3. The hydrides are non-stoichiometric but have a composition of MH_3. These hydrides liberate hydrogen from water.
4. The lanthanides also liberate hydrogen from water as does their hydrides and a vigorous evolution of same gas from dilute non-oxidizing acids.

$$2Ln_{(s)} + 6H_2O_{(l)} \longrightarrow 2Ln(OH)_{3(aq)} + 3H_{2(g)}$$

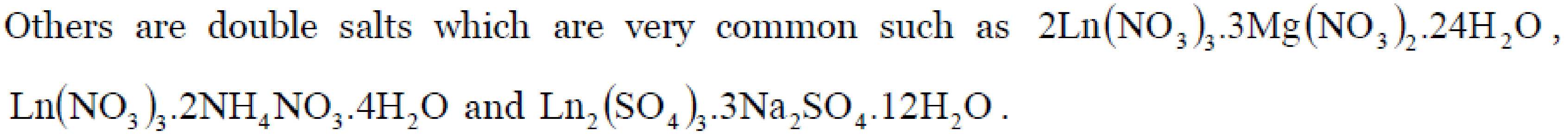
5. Lanthanide compounds are generally predominantly ionic and usually contain lanthanide metal in its +3 oxidation states.

OXO SALTS



Oxo salts:

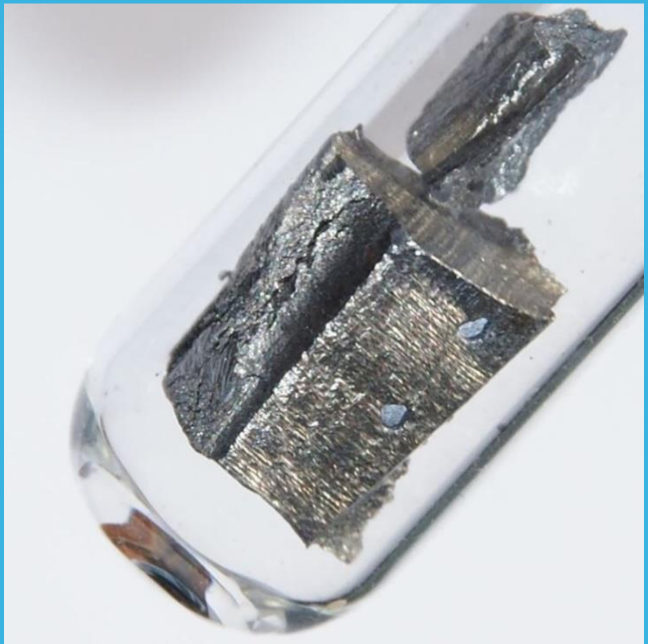
Oxo salts of lanthanides also exist which includes nitrates, sulphates, phosphates, carbonates, oxalates etc. Examples are the hydrated salts of common acids which contain the ions $[Ln(H_2O)_n]^{3+}$, which are readily obtained by dissolving the oxide in acid and crystallizing.



Others are double salts which are very common such as $2Ln(NO_3)_3.3Mg(NO_3)_2.24H_2O$, $Ln(NO_3)_3.2NH_4NO_3.4H_2O$ and $Ln_2(SO_4)_3.3Na_2SO_4.12H_2O$.


Any
Questions

❑ LANTHANIDE OCCURRENCE IN NATURE



LANTHANIDE OCCURRENCE IN NATURE

- Each known Lanthanide mineral contains all the members of the series.
- However, each mineral contains different concentrations of the individual Lanthanides.
- The three main mineral sources are the following:

1. Monazite: contains mostly the lighter Lanthanides.
2. Xenotime: contains mostly the heavier Lanthanides
3. Euxenite: contains a fairly even distribution of the Lanthanides

MONAZITE

- ✓ Monazite is a primarily reddish-brown phosphate mineral that contains rare-earth elements. Due to variability in composition, monazite is considered a group of minerals.[
- ✓ The most common species of the group is monazite-(Ce):
- ✓ monazite-(Ce), (Ce,La,Nd,Th) PO4 (the most common member),
- ✓ monazite-(La), (La,Ce,Nd)PO4,
- ✓ monazite-(Nd), (Nd,La,Ce)PO4,
- ✓ monazite-(Sm), (Sm,Gd,Ce,Th)PO4,
- ✓ monazite-(Pr), (Pr,Ce,Nd,Th)PO4.

MONAZITE
OCCURRENCE IN NATURE

- The most important source of the lanthanides is monazite,
- The heavy dark sand found in Brazil, India, Australia, South Africa, and the United States.
- The composition of monazite varies depending on its location,
- but it generally contains about 50 percent of lanthanide compounds by weight.
- Because of the similarity of their properties and their occurrence together in nature, the lanthanides can be separated from each other and purified only with considerable effort.

- Consequently, commercial production of the lanthanides tends to be expensive.

- Monazite: A mineral that constitutes the major source of the lanthanides.

XENOTIME

- Xenotime is used chiefly as a source of yttrium
- and heavy lanthanide metals (dysprosium, ytterbium, erbium and gadolinium).
- the major component of which is yttrium orthophosphate (YPO_4).

EUXENITE

It contains calcium, niobium, tantalum, cerium, titanium, yttrium, and typically uranium and thorium, with some other metals. The chemical formula is (Y, Ca, Ce, U, Th)(Nb, Ta, Ti) $_2O_6$.
It is commonly partially amorphous due to radiation damage.

Euxenite forms a continuous series with the titanium rich polycrase-(Y) having the formula $(Y,Ca,Ce,U,Th)(Ti,Nb,Ta)_2O_6$.

EXTRACTION OF LANTHANIDES FROM MONAZITE MINERAL

- Monazite is the chief mineral from which lanthanides are extracted.
- While extracting thorium from monazite, the lanthanides are obtained as byproducts.

Following operations are carried out in the extraction:

1) Concentration of mineral:

- The concentration of monazite is started with gravity separation using Wilfley tables.
- The monazite sand being heavier gets caught up on the riffles while the remaining lighter material gets washed off.
- This heavier portion is then subjected to magnetic separator whereby the monazite being less magnetic gets separated from other magnetic material.
- At the end of this operation, a refined monazite with a rough composition of ThO_2 =7.5%, Ce_2O_3 =30%, P_2O_5=29%, SiO_2 = 1.5% and 32% of other rare earths is obtained.

EXTRACTION OF LANTHANIDES FROM MONAZITE MINERAL

2)Cracking/ processing or opening up of the mineral:

This chemical treatment may be applied by either

(a) Acidic method using H_2SO_4 or

(b) (b) Alkaline method using NaOH.

EXTRACTION OF LANTHANIDES FROM MONAZITE MINERAL

(a) Acidic method using H2SO4:

- First of all the refined monazite obtained from the concentration process is heated with 93% H2SO4 at 2100C in cast iron vessels having mechanical stirrers. After about four hours, a viscous paste is obtained. This paste contains sulfates of lanthanides and thorium.
- This paste is leached with water for about 15 hours when all these sulfates go into solution.
- Only insoluble SiO2, unreacted mineral and traces of TiO2 and ZrSiO4 are left behind. This residue is then crushed and returned for recycle.
- The leached solution is acidic because of formation of phosphoric acid.

$$\mathrm{P2O5 + 3H2O \rightarrow 2H3PO4 \rightarrow 2H+ + 2H2PO4}$$

- This solution is treated with sodium pyrophosphate(Na2P2O7) to precipitate thorium as Th(P2O7)2.
- The remaining filtrate is treated with oxalic acid to precipitate a mixture of oxalates of lanthanides and little amount of thorium and zirconium oxalates.
- This mixture is then boiled with ammonium oxalates to dissolve the thorium and zirconium oxalate.
- The residue is then ignited carefully with concentrated sulfuric acid. Sodium sulfate is added to the clear solution of sulfates of lanthanides so that the lighter lanthanides (La 57 to Eu 63) precipitate as double sulfates while the heavier ones remain in the solution as single sulfates.
- The addition of hot sodium hydroxide to the precipitates yields a mixture of hydrated oxides.
- Upon drying this mixture in air at 100 0C mixture of oxides of lighter lanthanides with a rough composition of La2O3 = 17%, CeO2 = 5%, Pr2O3 = 8% Nd2O3= 20%, Sm2O3=5% and little Eu2O3 is obtained.

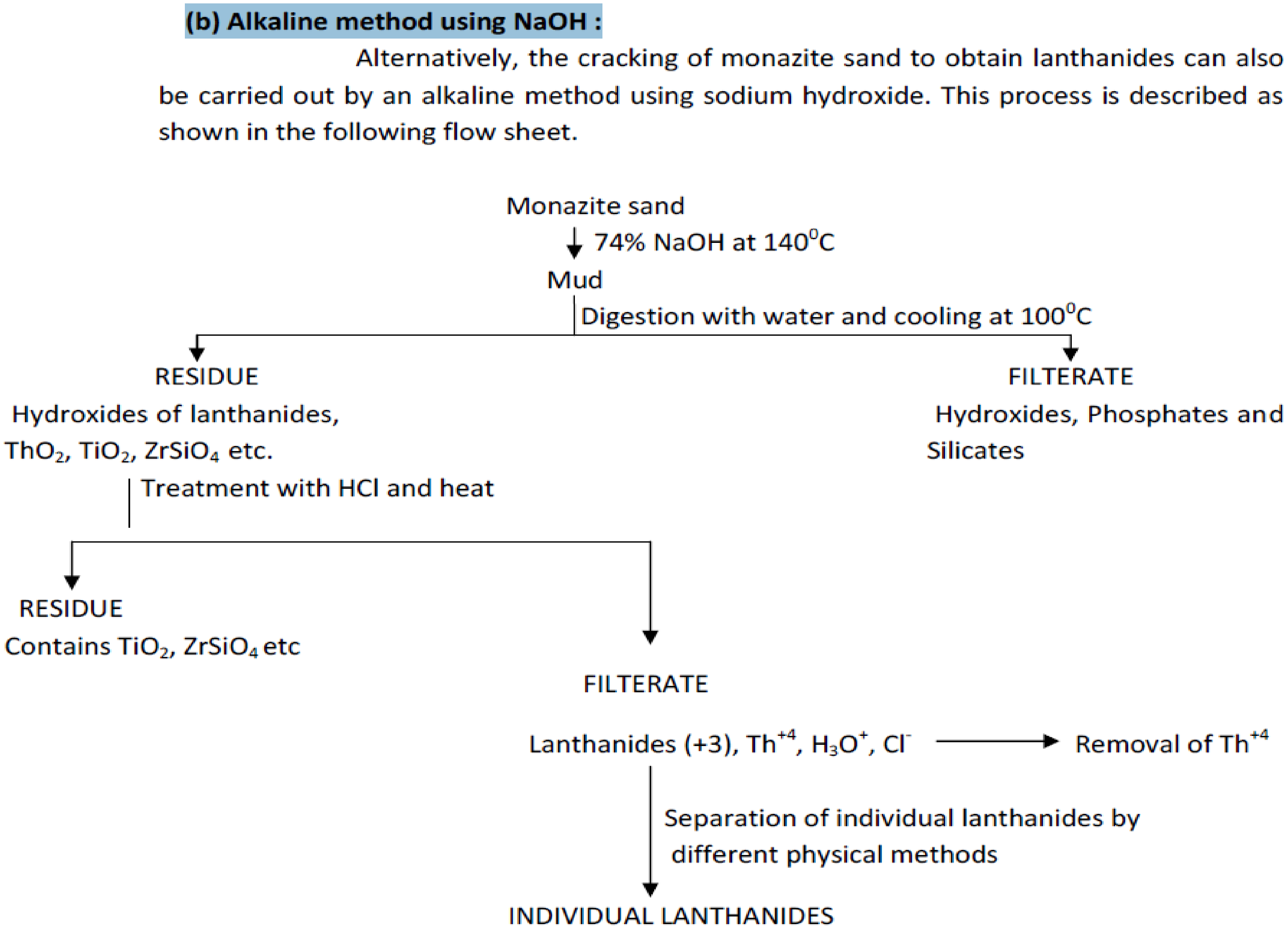
EXTRACTION OF CERIUM :

- Upon treatment of this mixture with dilute nitric acid, all the lanthanide oxides except that of Ce gets dissolved.
- The residual $CeO2$ is dissolved in 85% nitric acid to make crude $Ce(NO3)4$ which is further converted into red basic nitrate $Ce(OH)(NO3)3\cdot 3H2O$ by reacting with dilute sulfuric acid.
- The solution containing nitrates of the remaining lanthanides is then subjected to

different methods for further separation.

- The solution containing heavier lanthanides is also similarly subjected to different methods for separation of individual lanthanides

(B) ALKALINE METHOD USING SOD. HYDROXIDE



(b) Alkaline method using NaOH :

Alternatively, the cracking of monazite sand to obtain lanthanides can also be carried out by an alkaline method using sodium hydroxide. This process is described as shown in the following flow sheet.

Monazite sand

↓ 74% NaOH at 140^{0}C

Mud

Digestion with water and cooling at 100^{0}C

RESIDUE

Hydroxides of lanthanides, ThO_2, TiO_2, $ZrSiO_4$ etc.

Treatment with HCl and heat

FILTERATE

Hydroxides, Phosphates and Silicates

RESIDUE

Contains TiO_2, $ZrSiO_4$ etc

FILTERATE

Lanthanides (+3), Th^{+4}, H_3O^+, Cl^- → Removal of Th^{+4}

Separation of individual lanthanides by different physical methods

INDIVIDUAL LANTHANIDES

METHODS USED FOR THE SEPARATION OF LANTHANIDES:

The methods of separation of lanthanides are broadly classified into two classes:

(a) old classical methods:

(i) Fractional crystallization (ii) Fractional precipitation method

(ii) (iii) Fractional thermal decomposition of oxy- salts

(iii) (iv) Change of oxidation states by selective oxidation or reduction procedures.

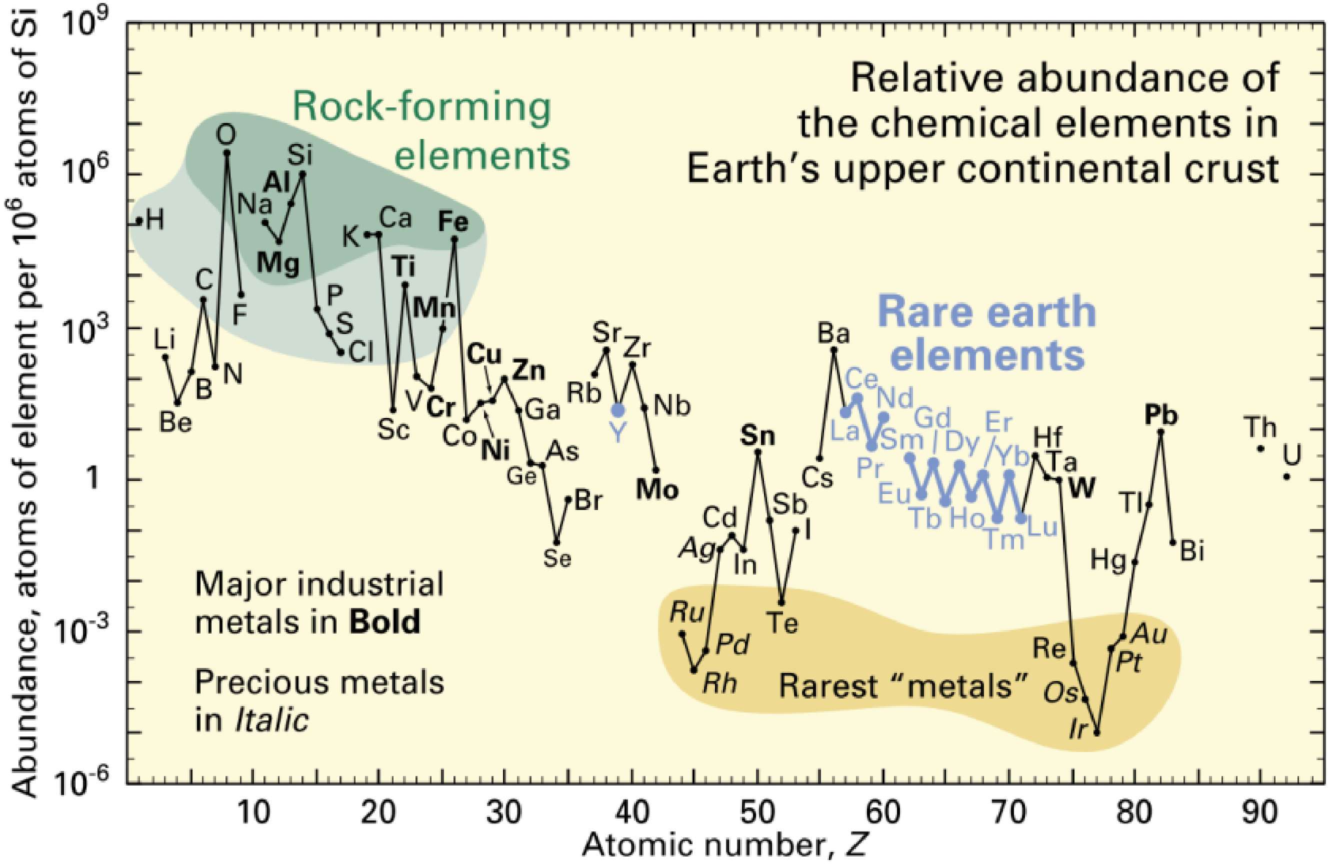
(b) Modern methods:

1. Ion – exchange method
2. Solvent (liquid-liquid) extraction method
3. Paper chromatography
4. Gas chromatography
5. Thin layer chromatography
6. Complex formation

LANTHANIDES SEPARATION

- In all the ores, the atoms with a even atomic number are more abundant.
- This allows for more nuclear stability, as explained in the Oddo-Harkins rule.
- The Oddo-Harkins rule simply states that the abundance of elements with an even atomic number is greater than the abundance of elements with an odd atomic number.
- In order to obtain these elements, the minerals must go through a separating process, known as separation chemistry.
- This can be done with selective reduction or oxidation. Another possibility is an ion-exchange method.

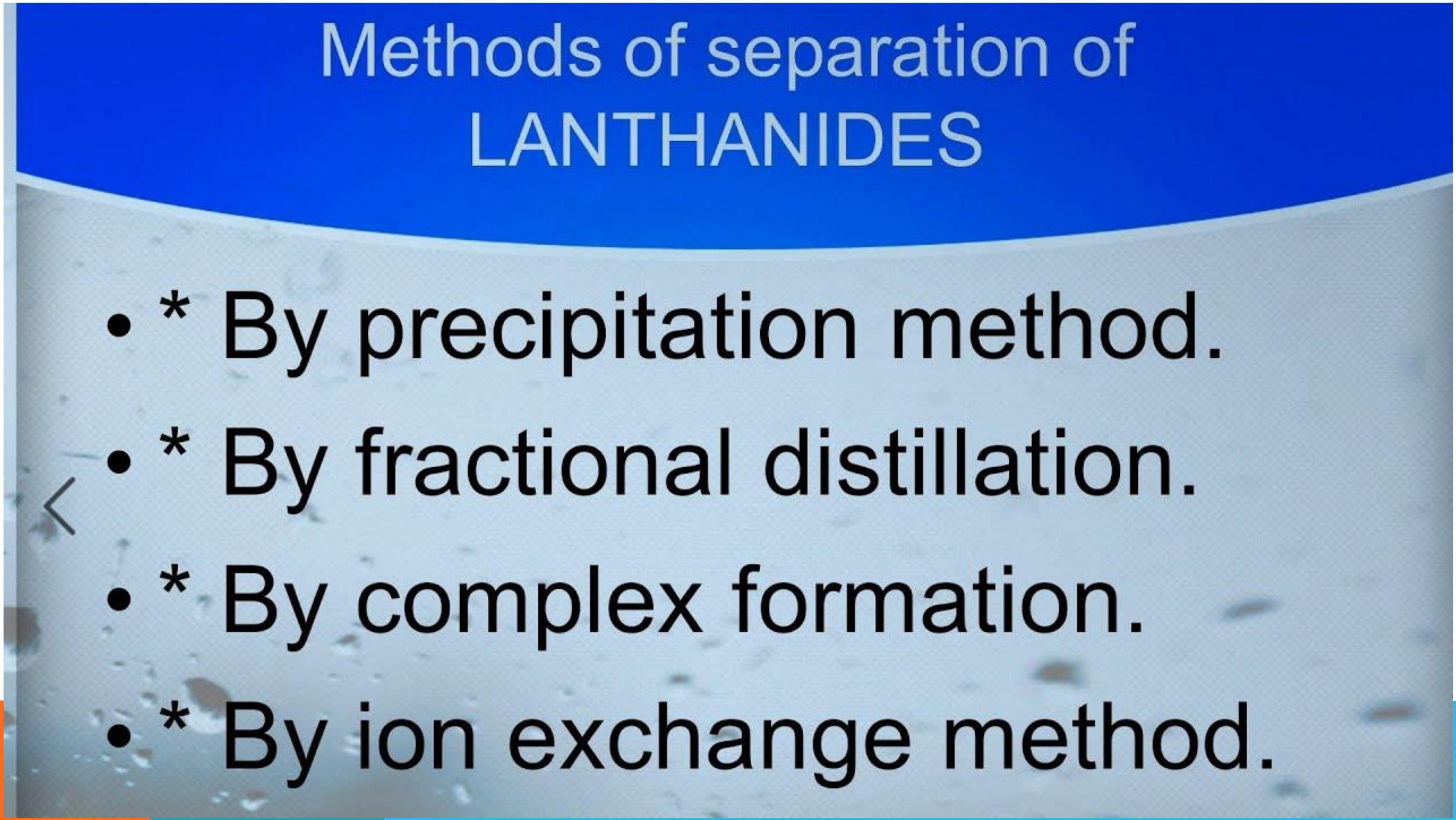
Oddo-Harkins rule



SEPARATION OF LANTHANIDES:

Except promethium, they occur together in earth's crust in various forms and very difficult to separate from each other because all the lanthanides have the same size and charge (of +3 unit). The chemical properties of these elements which depend on the size and charge are, therefore, almost identical. Hence, their isolation from one another is quite difficult. However, the following methods have been used to separate them from one another.

LANTHANIDES SEPARATION

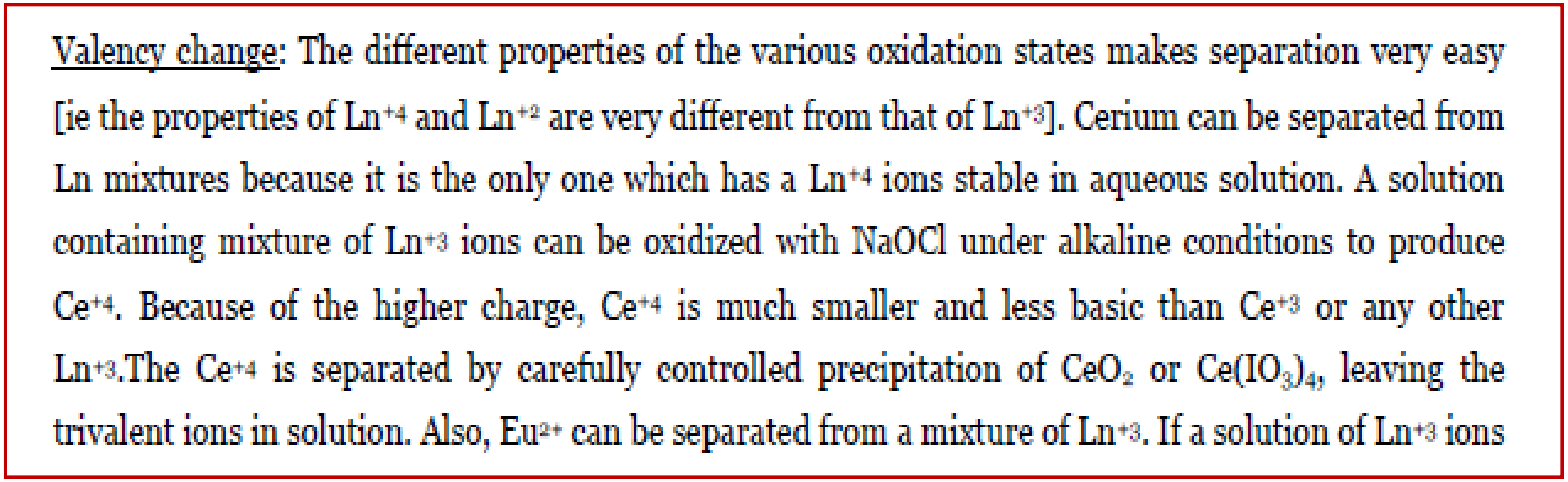


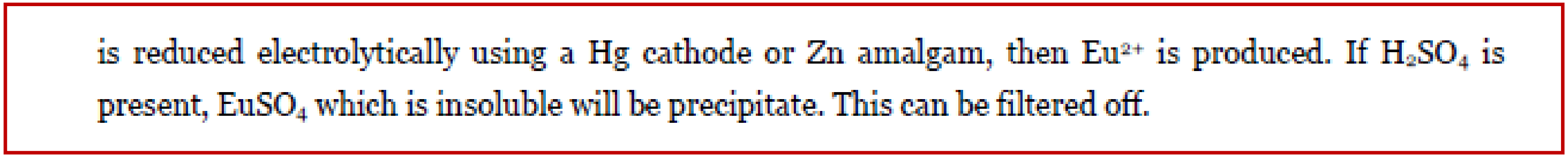
Methods of separation of LANTHANIDES

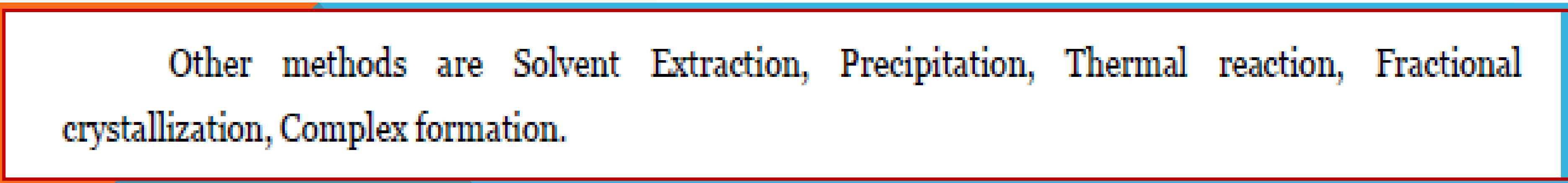
- * By precipitation method.
- * By fractional distillation.
- * By complex formation.
- * By ion exchange method.

- * SOLVENT EXTRACTION METHOD

LANTHANIDES SEPARATION


Valency change: The different properties of the various oxidation states makes separation very easy [ie the properties of Ln^{+4} and Ln^{+2} are very different from that of Ln^{+3}]. Cerium can be separated from Ln mixtures because it is the only one which has a Ln^{+4} ions stable in aqueous solution. A solution containing mixture of Ln^{+3} ions can be oxidized with NaOCl under alkaline conditions to produce Ce^{+4}. Because of the higher charge, Ce^{+4} is much smaller and less basic than Ce^{+3} or any other Ln^{+3}.The Ce^{+4} is separated by carefully controlled precipitation of CeO_2 or $Ce(IO_3)_4$, leaving the trivalent ions in solution. Also, Eu^{2+} can be separated from a mixture of Ln^{+3}. If a solution of Ln^{+3} ions

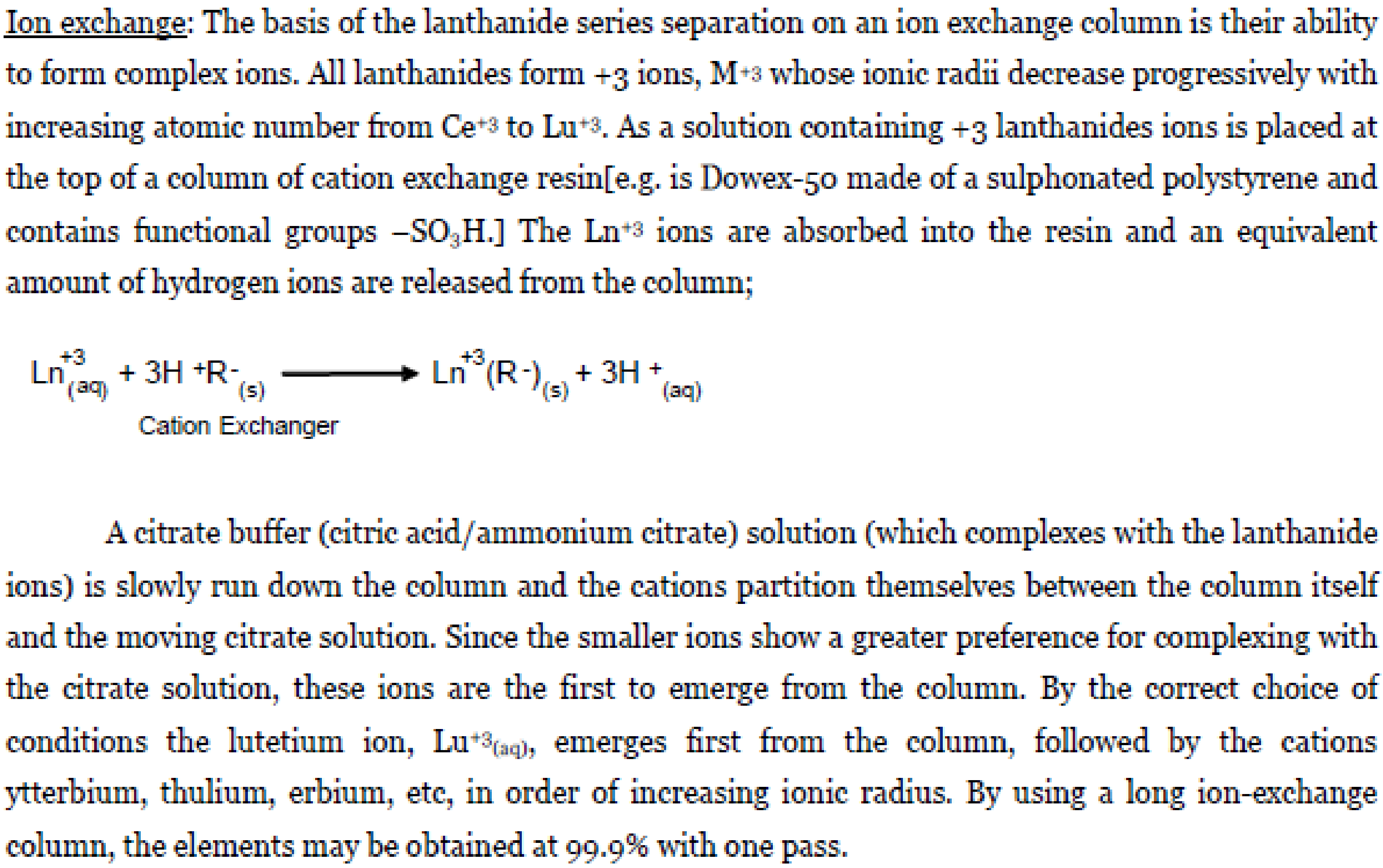

is reduced electrolytically using a Hg cathode or Zn amalgam, then Eu^{2+} is produced. If H_2SO_4 is present, $EuSO_4$ which is insoluble will be precipitate. This can be filtered off.


Other methods are Solvent Extraction, Precipitation, Thermal reaction, Fractional crystallization, Complex formation.

ROLES FOR LANTHANIDES SEPARATION

- They are extracted from the earlier mentioned ores.
- Monazite is treated with hot concentratedH_2SO_4.
- Th, La and the Ln dissolve as sulphates and are separated from insoluble material.
- Th is precipitated as ThO_2 by partial neutralization with NH_4OH.
- Na_2SO_4 is used to salt out La and the lighter Ln as sulphates, leaving the heavy lanthanides in solution.
- The light Ln are oxidized with bleaching powder $Ca(OCl)_2$. Ce^{2+} is oxidized to Ce^{4+} which is precipitated as $Ce(IO_3)_4$ and removed.
- The extraction process from bastnaesite is slightly simpler since it does not contain Th.

ION-EXCHANGE DISPLACEMENT COLUMN



Ion exchange: The basis of the lanthanide series separation on an ion exchange column is their ability to form complex ions. All lanthanides form +3 ions, M^{+3} whose ionic radii decrease progressively with increasing atomic number from Ce^{+3} to Lu^{+3}. As a solution containing +3 lanthanides ions is placed at the top of a column of cation exchange resin[e.g. is Dowex-50 made of a sulphonated polystyrene and contains functional groups $-SO_3H$.] The Ln^{+3} ions are absorbed into the resin and an equivalent amount of hydrogen ions are released from the column;

$$Ln^{+3}_{(aq)} + \underset{\text{Cation Exchanger}}{3H^+R^-_{(s)}} \longrightarrow Ln^{+3}(R^-)_{(s)} + 3H^+_{(aq)}$$

A citrate buffer (citric acid/ammonium citrate) solution (which complexes with the lanthanide ions) is slowly run down the column and the cations partition themselves between the column itself and the moving citrate solution. Since the smaller ions show a greater preference for complexing with the citrate solution, these ions are the first to emerge from the column. By the correct choice of conditions the lutetium ion, $Lu^{+3}_{(aq)}$, emerges first from the column, followed by the cations ytterbium, thulium, erbium, etc, in order of increasing ionic radius. By using a long ion-exchange column, the elements may be obtained at 99.9% with one pass.

(1) ION – EXCHANGE METHOD:

- This is the most modern method for the separation of lanthanide elements.
- In this method synthetic cation resins are used. These resins contain –SO3H or –COOH groups, the hydrogen of which are replaced by cations.
- The aqueous solution containing a mixture of trivalent positive Lanthanide ions, Ln+3 is allowed to pass down a column filled with cation – exchange resin. The Ln+3 ions replaced H+ ions of –SO3H or –COOH group of the resin and get fixed on the resin.

Ln+3 (aq) + 3HR (solid) ↔ LnR3(solid) + 3H+ (aq)

- In order to remove Ln+3 ions fixed as LnR3(solid) on the resin, the column is leached with a complexing agent in aqueous solution like buffer solution of Ammonium citrate- citric acid (PH= 4 to 7).
- Such complexing agents called eluants or eluates or eluating agents. During elution process NH4+ ions of the eluating agent replace Ln+3 ions from LnR3(solid) to give Ln+3 ions which reacts with citrate ion to form the Ln-citrate complex.

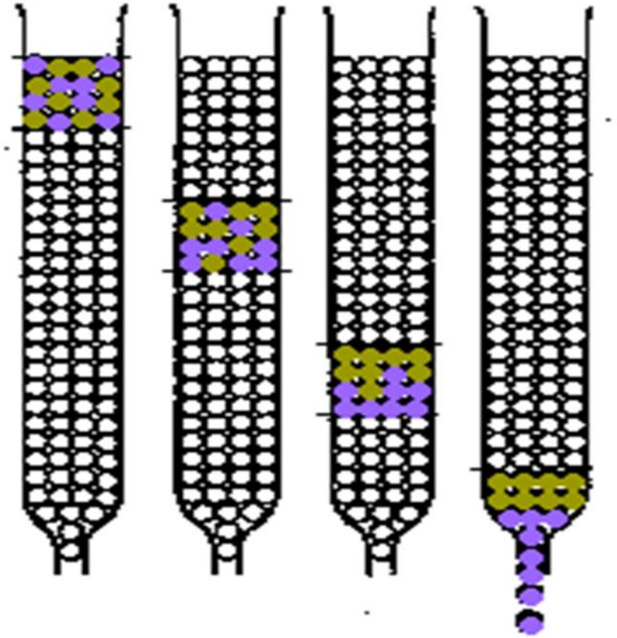
LnR3 + NH4+ ⟶ NH4R + Ln+3

Ln+3 + citrate ion ⟶ Ln-citrate complex

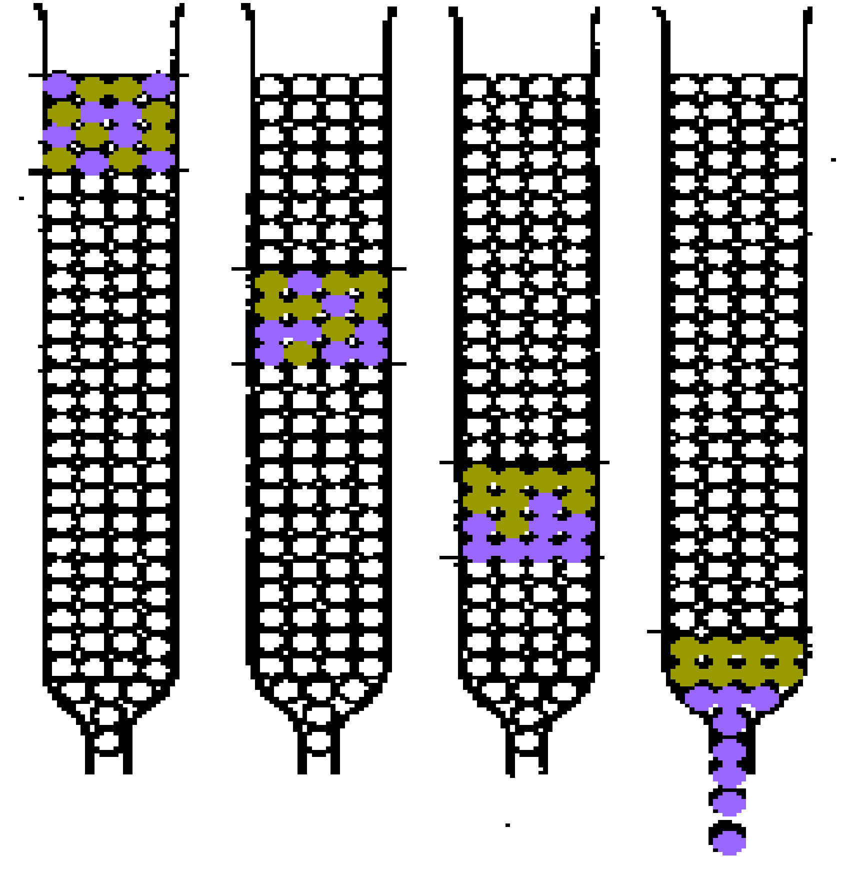
- We have seen that since La+3 (aq) is attached to resin with maximum and Lu+3 (aq) with minimum firmness, Lu-citrate complex comes out of the column first and La-citrate complex comes out last.
- In actual practice the process of elution is to be repeated several times by careful control of concentration of Ammonium Citrate- Citric Acid solutions.
- By using this method 99.99% pure rare-earth elements can be isolated.

ION-EXCHANGE DISPLACEMENT COLUMN

- Ln3+(aq) are strongly adsorbed by a cation-exchange resin
-
- add an *eluant* ligand typically *chelating* ligands e.g. EDTA , or 2-hydroxy-EDTA *e.g.* HIB{[[alpha]]-hydroxyisobutyric acid}
- Ligand binds most strongly to smallest ion *e.g.* the binding constants of the Ln(EDTA) complexes



THE PROCESS OF SEPARATION IS INDICATED



LANTHANIDES SEPARATION

2/3 of world production is actually used mixed in the proportions occurring naturally in the ore

1. Cerium & Europium may be extracted Chemically:

- Oxidize only Ce to M^{4+} by HOCl or $KMnO_4$, then precipitate as CeO_2 or $Ce(IO_3)_4$
- On action of Zn/Hg only Eu forms a stable M^{2+} that doesn't reduce H_2O, then isolate by precipitation as $EuSO_4$.

SEPARATION BY FRACTIONATION:

Small Scale methods used originally:

- Fractional Crystallization of *e.g.* $\mathrm{Ln(NO3)3.2NH4NO3.4H2O}$ or $\mathrm{Ln(BrO3)3}$
- Fractional Thermal Decomposition of *e.g.* $\mathrm{Ln(NO3)3}$

Current Small Scale Lab. Separation:

(2) SOLVENTS (LIQUID-LIQUID) EXTRACTION METHOD:

- This method was first reported by fischer. The method is based on the difference in the solubility of Lanthanides salts in water and immiscible organic solvents.
- These organic solvents are called extracting solvent. This method is used on both tracer and micro scales. In this process the aqueous solution of lanthanide salts pass through the organic solution, in which lanthanide extract from water.
- The most widely used extracting solvent is tri-n-butyl phosphate (TBP), in an inert medium like kerosene or xylene to extract the lanthanides from nitric acid solutions.
- TBP forms complexes with Ln+3 (aq) ions in presence of NO3 - ions.

$$Ln+3(aq) + 3\ NO3-\ (aq) + 3TBP\ (org) \leftrightarrow Ln(NO3)3(TBP)3(\ org)$$

Complex

- Kilogram quantities of 95% pure lanthanides have been prepared by solvent extraction technique.
- Another organic solvent which is a better extractant than TBP is Di-(2-ethyl hexyl) phosphoric acid.

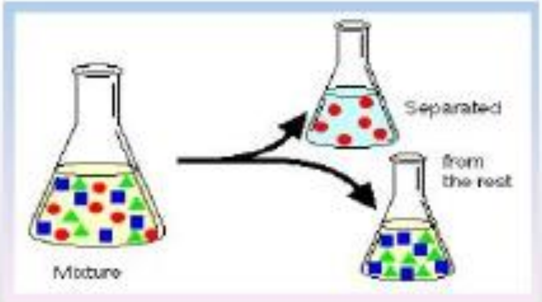
The major uses of solvent extraction process for separation of Ln+3 from Ln+4, ions such as Ce+4

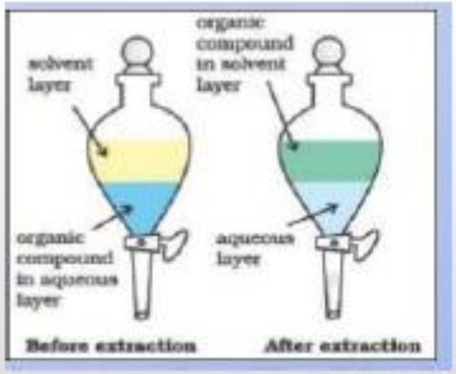
and Th+4 and in the purification of Ce, Th, and La.

Solvent extraction method: Separation of Lanthanides

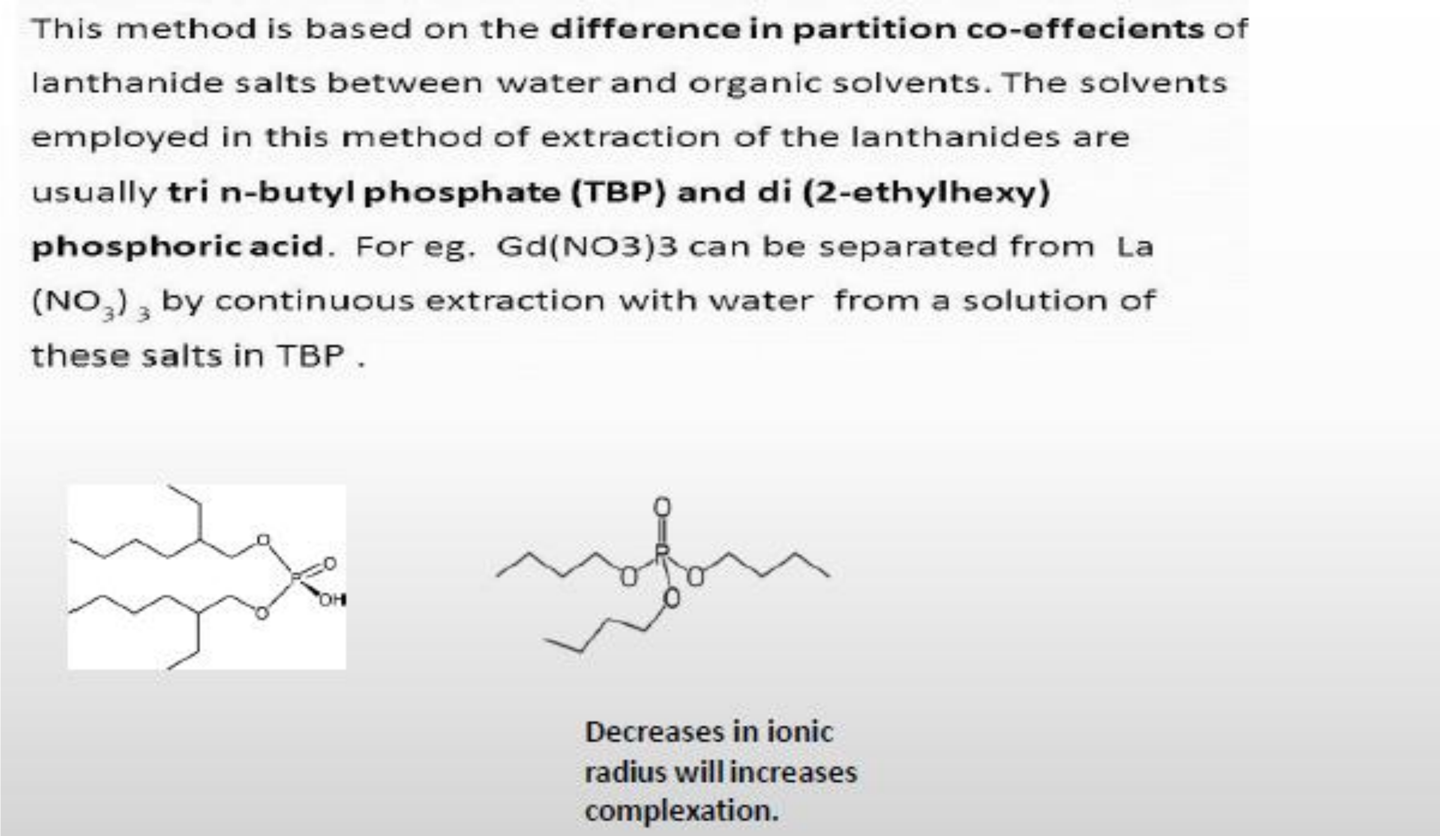
What is Solvent Extraction ?

Solvent Extraction, also known as liquid-liquid extraction, is a method to separate compounds based on their relative solubilities in two different immiscible liquids, usually water and an organic solvent.





SOLVENT EXTRACTION



This method is based on the **difference in partition co-effecients** of lanthanide salts between water and organic solvents. The solvents employed in this method of extraction of the lanthanides are usually **tri n-butyl phosphate (TBP) and di (2-ethylhexy) phosphoric acid**. For eg. Gd(NO3)3 can be separated from La (NO$_3$)$_3$ by continuous extraction with water from a solution of these salts in TBP .

Decreases in ionic radius will increases complexation.

SOLVENT EXTRACTION

Ln3+(aq) is extracted in a continuous counter-current process into a non-polar organic liquid (*e.g.* kerosene)

the kerosene contains ca. 10% of

- bis(2-ethylhexyl)phosphinic acid (**DEHPA**)

or

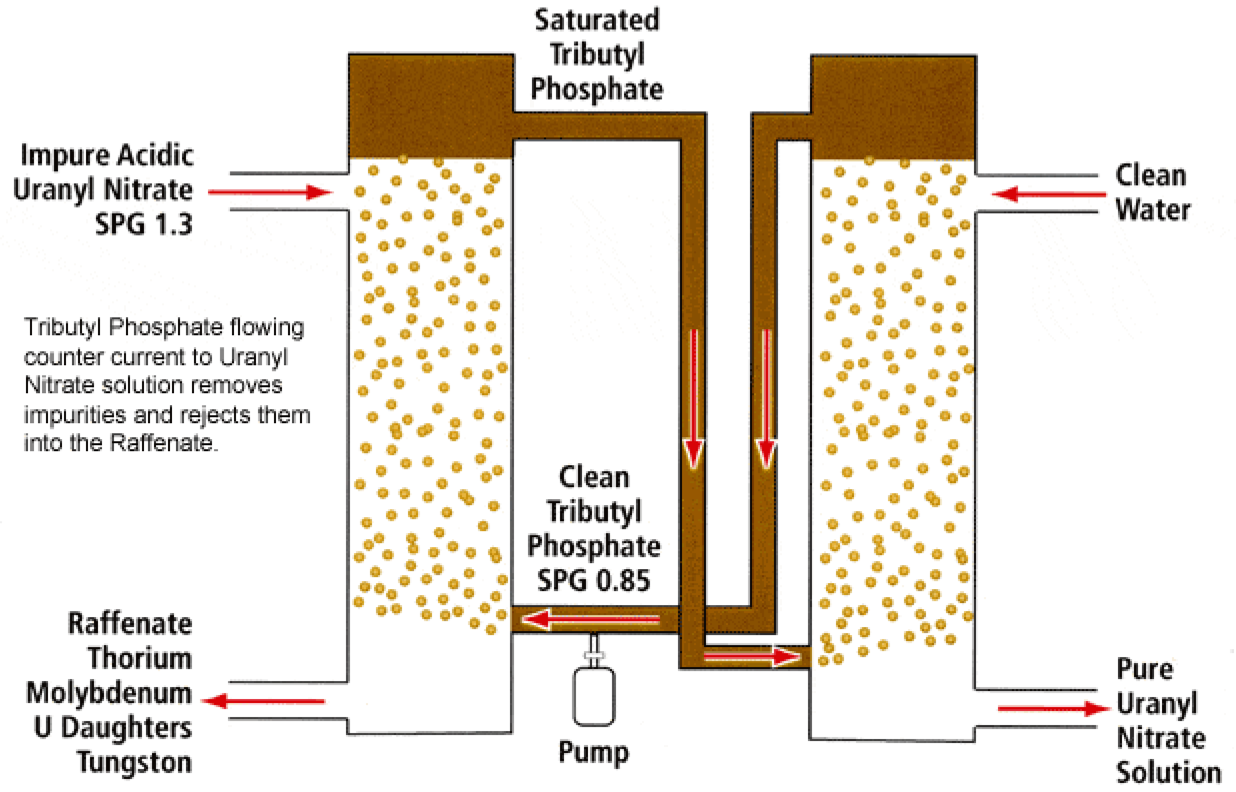
- tri-*n*-butylphosphine oxide (**TBPO**) (nBu3O)3PO

solubility of Ln3+ in organic solvent increases with its RAM

separation factor for adjacent rare earths = 2.5

automatic multistep, counter-current conditions Æ 99.9% purity Ln

SOLVENT EXTRACTION PROCESS

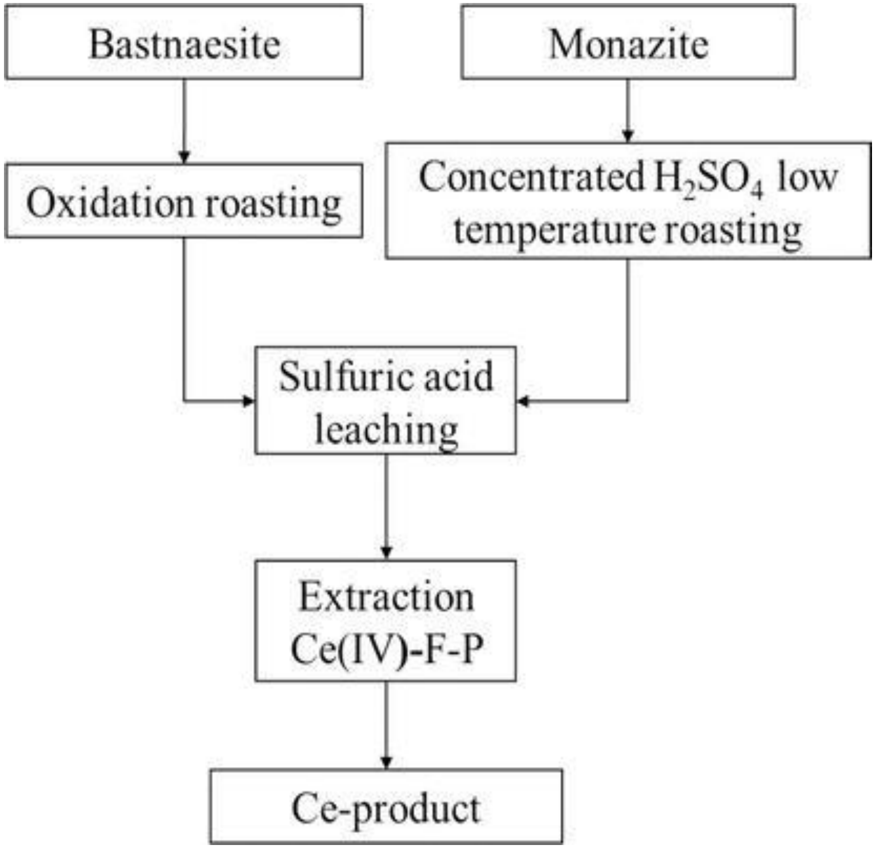


Tributyl Phosphate flowing counter current to Uranyl Nitrate solution removes impurities and rejects them into the Raffenate.

EXTRACTION PLANT

EXTRACTION PLANT

SCHEMES' FOR SEPARATION


Bastnaesite

Monazite

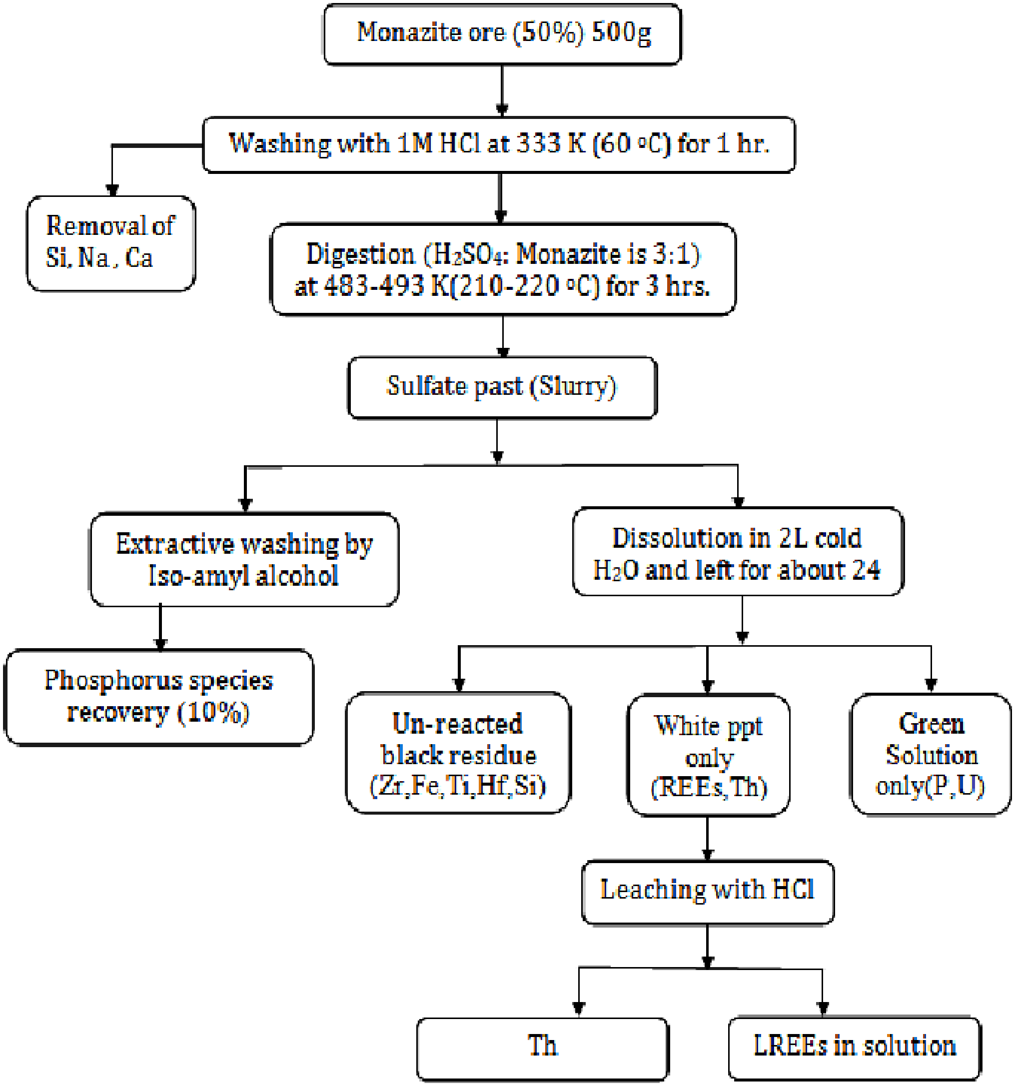
Oxidation roasting

Concentrated H_2SO_4 low temperature roasting

Sulfuric acid leaching

Extraction Ce(IV)-F-P

Ce-product


Monazite ore (50%) 500g

Washing with 1M HCl at 333 K (60 °C) for 1 hr.

Removal of Si, Na, Ca

Digestion (H_2SO_4: Monazite is 3:1) at 483-493 K(210-220 °C) for 3 hrs.

Sulfate past (Slurry)

Extractive washing by Iso-amyl alcohol

Phosphorus species recovery (10%)

Dissolution in 2L cold H_2O and left for about 24

Un-reacted black residue (Zr,Fe,Ti,Hf,Si)

White ppt only (REEs,Th)

Green Solution only(P,U)

Leaching with HCl

Th

LREEs in solution

LANTHANIDES SEPARATION

The different lanthanides elements can be separated by various methods;

Reduction of their Trihalides: La, Ce, Pr, Nd and Gd may be obtained by reduction of their trichlorides with calcium at about 1000ºC in an argon filled vessel e.g.

$$2PrCl_3 + 3Ca \rightarrow 3CaCl_2 + 2Pr$$

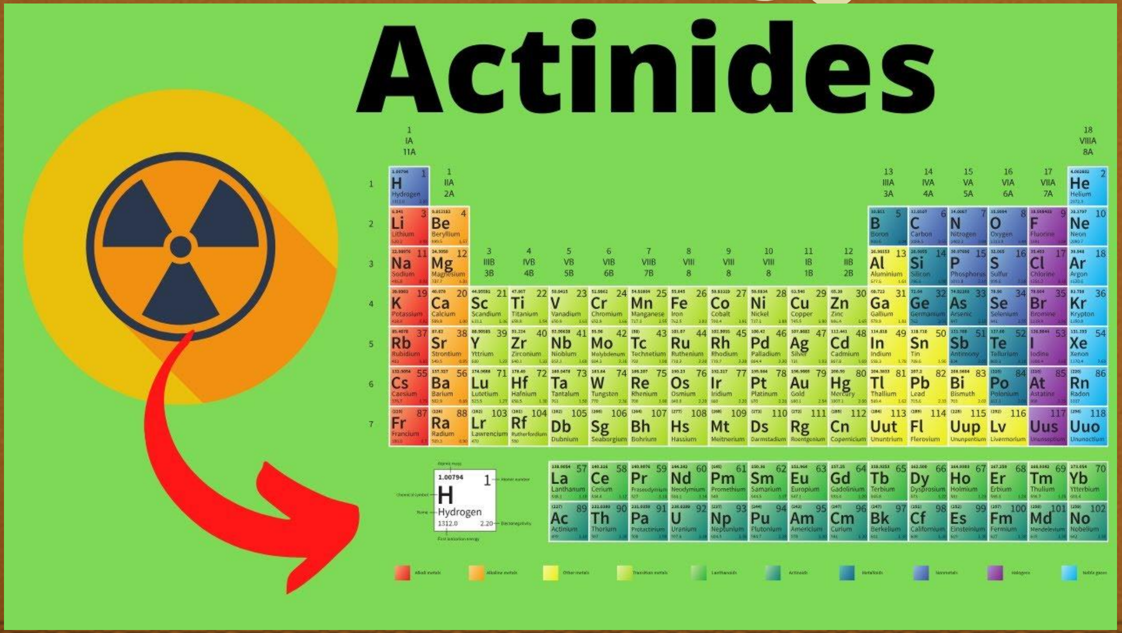
The heavier Ln like Tb, Dy, Ho, Er and Tm can also be obtained by this method but the trifluorides is used, since their trichloride is volatile. Also since the heavier Ln have higher melting points and so require a temperature of 1400ºC. At this temperature $CaCl_2$ boils. Li is sometimes used instead of Ca.

$$2HoF_3 + 3Ca \rightarrow 3CaF_2 + 2Ho$$

Eu, Sm and Yb are obtained by chemical reduction of their trioxides.


Any
Questions

Introduction of Actinides



Actinides Elements

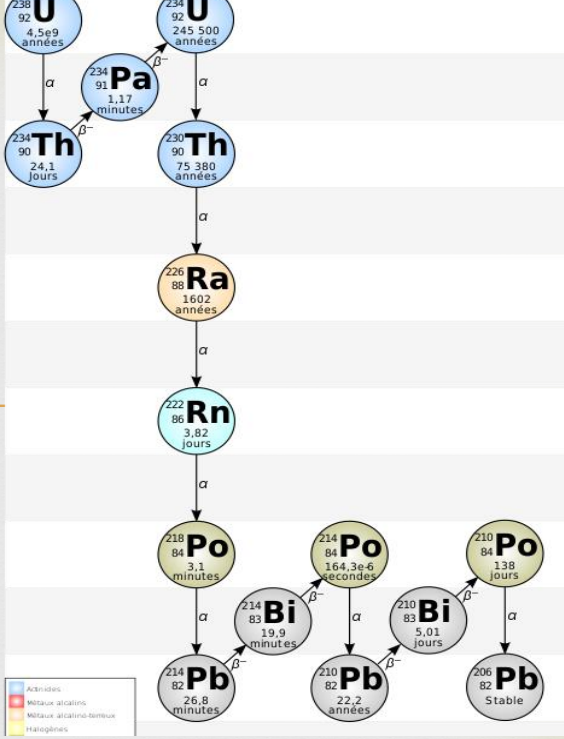
- •Only **Actinium**, **Thorium**, **Protactinium** &**Uranium** occur naturally (*i.e.*$Z=<92$) in Uranium minerals.
- •all the remaining actinides are unstable and made artificially by nuclear transmutations.
- •The actinides elements lying **beyond Uranium,** are called **trans-uranium** or **trans-Uranic** elements
- •All the actinides are **radioactive.**

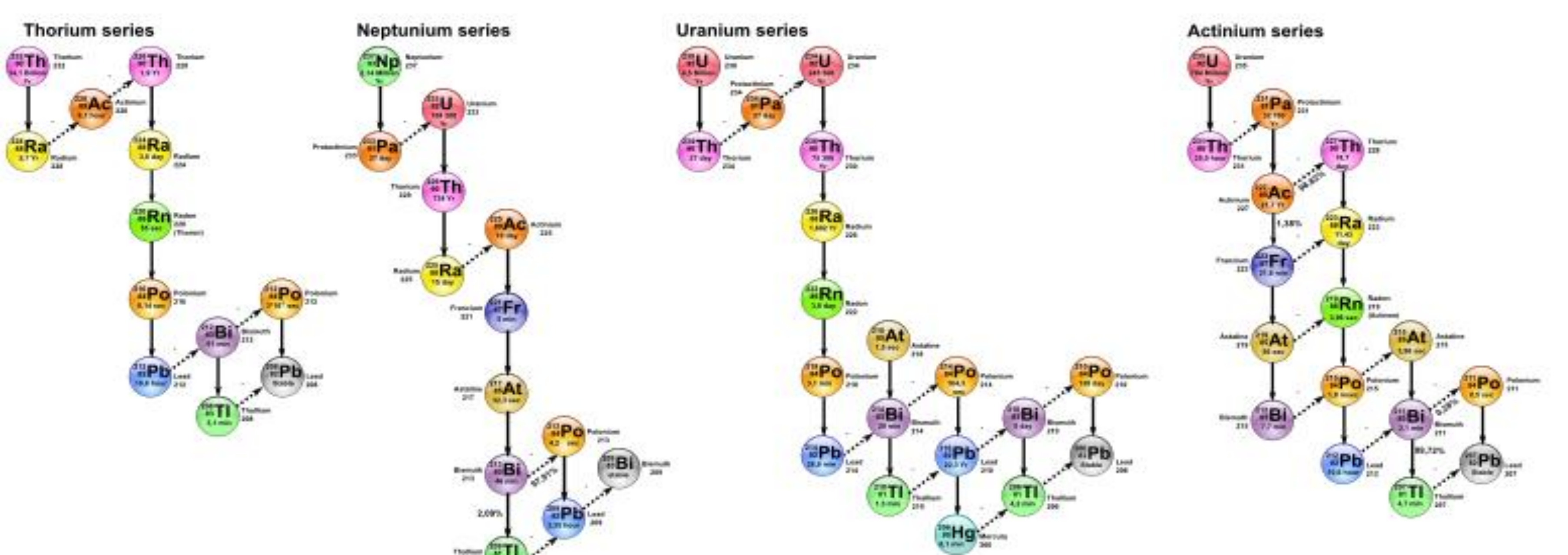
4. Radioactive Decay

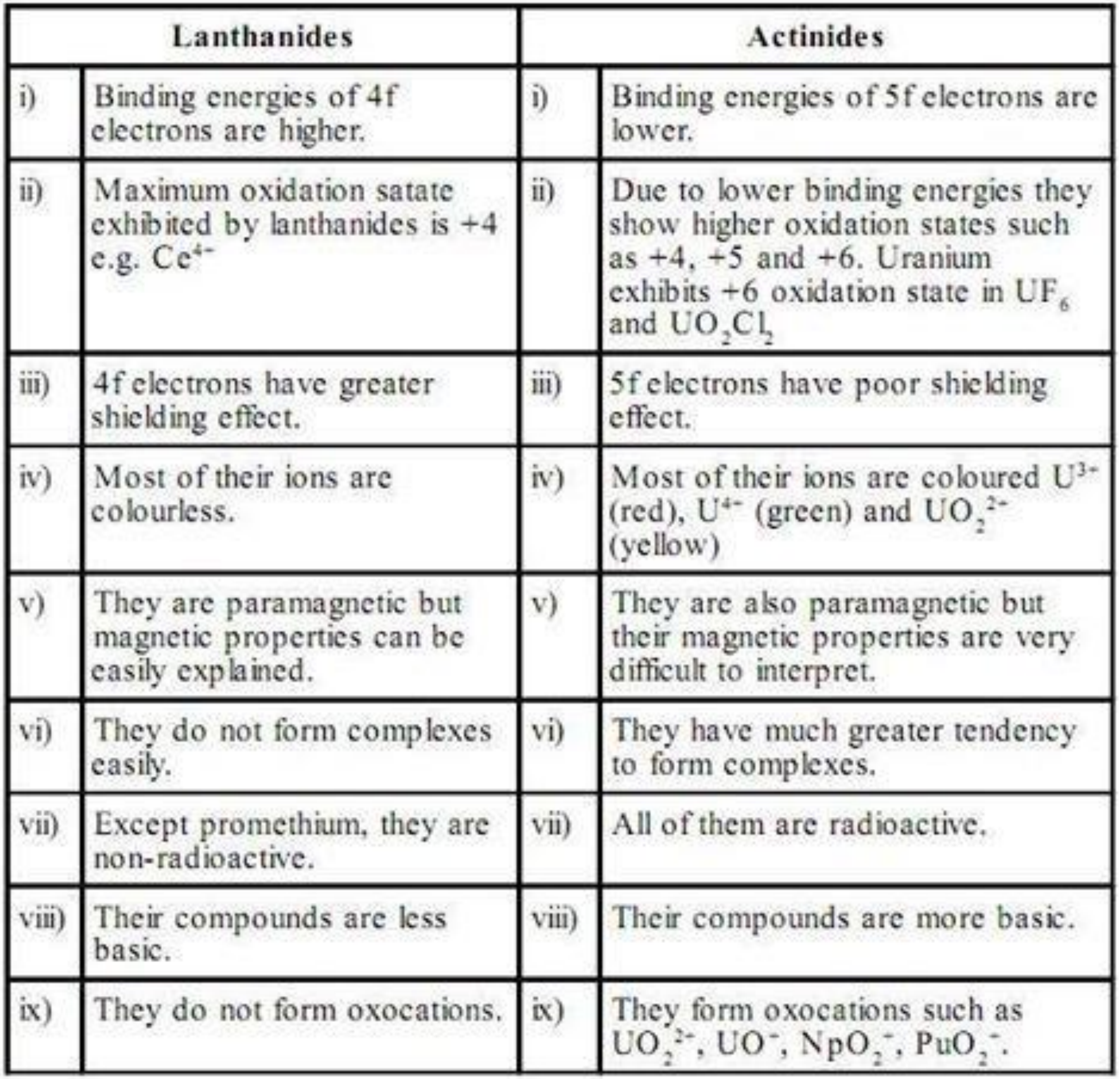
4.1 Decay Series

- radioactive transmutation and decay are synonymous expressions
- 4 main series

4n	^{232}Thorium
4n + 2	^{238}Uranium-Radium
4n + 3	^{235}Actinium
4n + 1	^{237}Neptunium







Lanthanides		Actinides	
i)	Binding energies of 4f electrons are higher.	i)	Binding energies of 5f electrons are lower.
ii)	Maximum oxidation satate exhibited by lanthanides is +4 e.g. Ce^{4+}	ii)	Due to lower binding energies they show higher oxidation states such as +4, +5 and +6. Uranium exhibits +6 oxidation state in UF_6 and UO_2Cl_2
iii)	4f electrons have greater shielding effect.	iii)	5f electrons have poor shielding effect.
iv)	Most of their ions are colourless.	iv)	Most of their ions are coloured U^{3+} (red), U^{4+} (green) and UO_2^{2+} (yellow)
v)	They are paramagnetic but magnetic properties can be easily explained.	v)	They are also paramagnetic but their magnetic properties are very difficult to interpret.
vi)	They do not form complexes easily.	vi)	They have much greater tendency to form complexes.
vii)	Except promethium, they are non-radioactive.	vii)	All of them are radioactive.
viii)	Their compounds are less basic.	viii)	Their compounds are more basic.
ix)	They do not form oxocations.	ix)	They form oxocations such as UO_2^{2+}, UO^+, NpO_2^+, PuO_2^+.

Comparison of Lanthanides and Actinides

Similarities

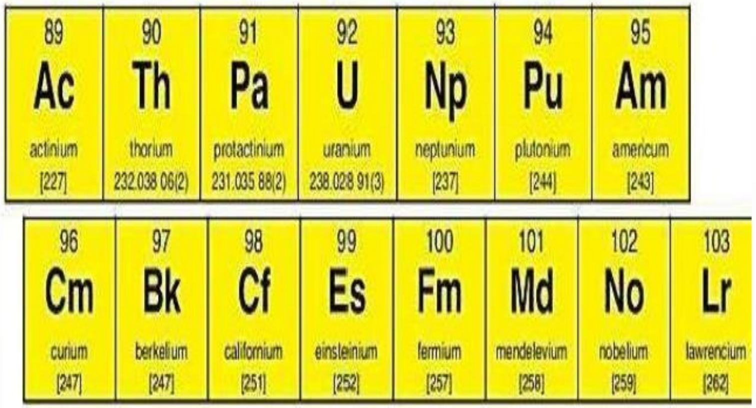
- ❑ Lanthanides and actinides involve filling of f-orbitals and thus are similar in many respects.
- ❑ The most common oxidation state is +3 for both lanthanides and actinides.
- ❑ Both are electropositive in nature and thus very reactive.
- ❑ Magnetic and spectral properties are exhibited by both lanthanides and actinides.
- ❑ Actinides exhibit actinide contraction just like lanthanides.

Differences

- ✓ Besides +3, lanthanides also show oxidation states of +2 and +4 while actinides show higher oxidation states of +4, +5, +6 and + 7 as well.
- ✓ Lanthanide ions are colourless while most of the actinide ions are coloured.
- ✓ Actinides have a greater tendency towards complex formation as compared to lanthanides.
- ✓ Lanthanide compounds are less basic while actinide compounds have appreciable basicity
- ✓ Actinides form few important oxocations such as UO_2^{2+}, PuO_2^{2+}, etc, while such oxocations are not known for lanthanides.
- ✓ Almost all actinides are radioactive while lanthanides, except promethium, are non-radioactive.
- ✓ The magnetic properties of actinides can be easily explained while it is difficult to do so in the case of lanthanides.

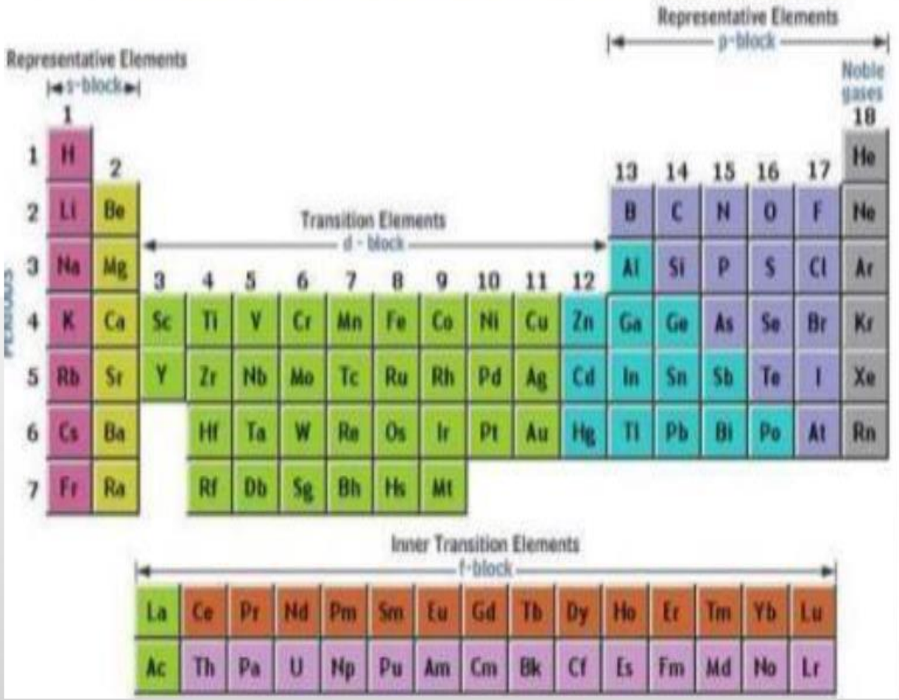
Actinoids

- 7 period and actinide series.
- Electron enter in 5f orbital.
- Many physical and chemical property are similar to actinium(actinoids).
- Second inner transition element.
- Outermost and penultimate shell remain the same.
- General E.C **$5f^{1-10}$ $6d^{0-1}$ $7s^2$**
- First 4 member occur in nature.
- Others are made artificially.
- All are toxic to humans.



89 Ac actinium [227]	90 Th thorium 232.038 06(2)	91 Pa protactinium 231.035 88(2)	92 U uranium 238.028 91(3)	93 Np neptunium [237]	94 Pu plutonium [244]	95 Am americum [243]

96 Cm curium [247]	97 Bk berkelium [247]	98 Cf californium [251]	99 Es einsteinium [252]	100 Fm fermium [257]	101 Md mendelevium [258]	102 No nobelium [259]	103 Lr lawrencium [262]



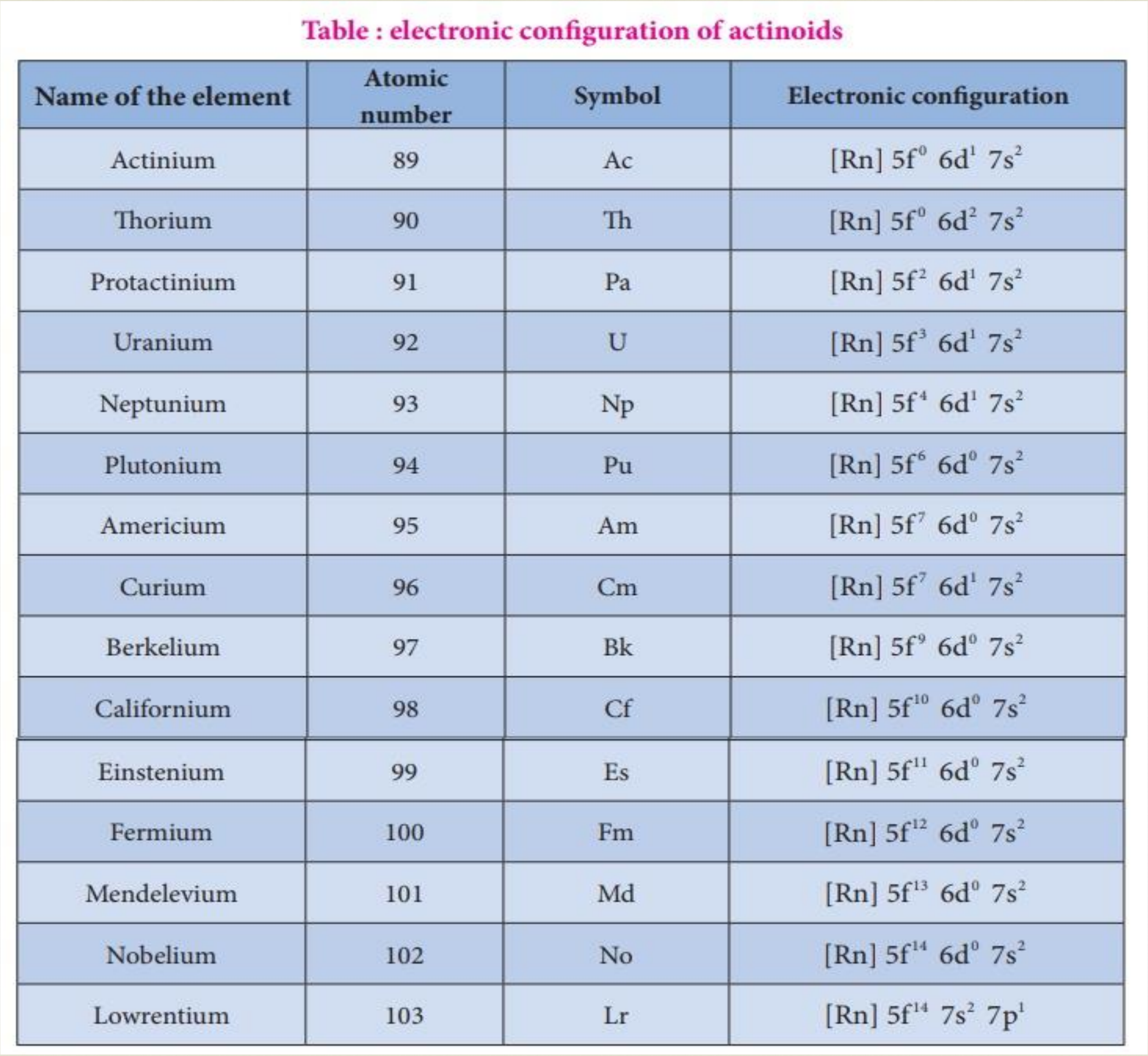
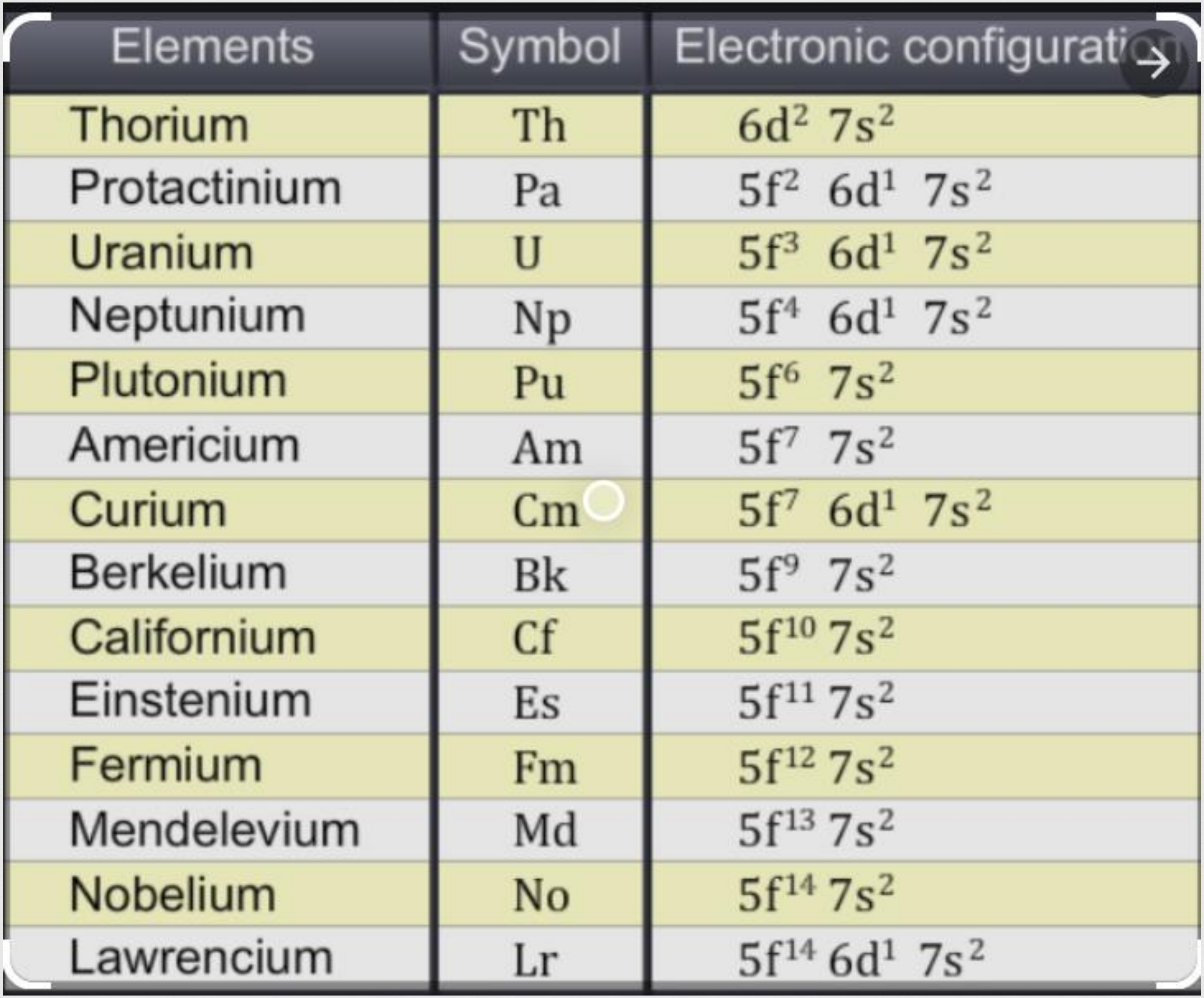
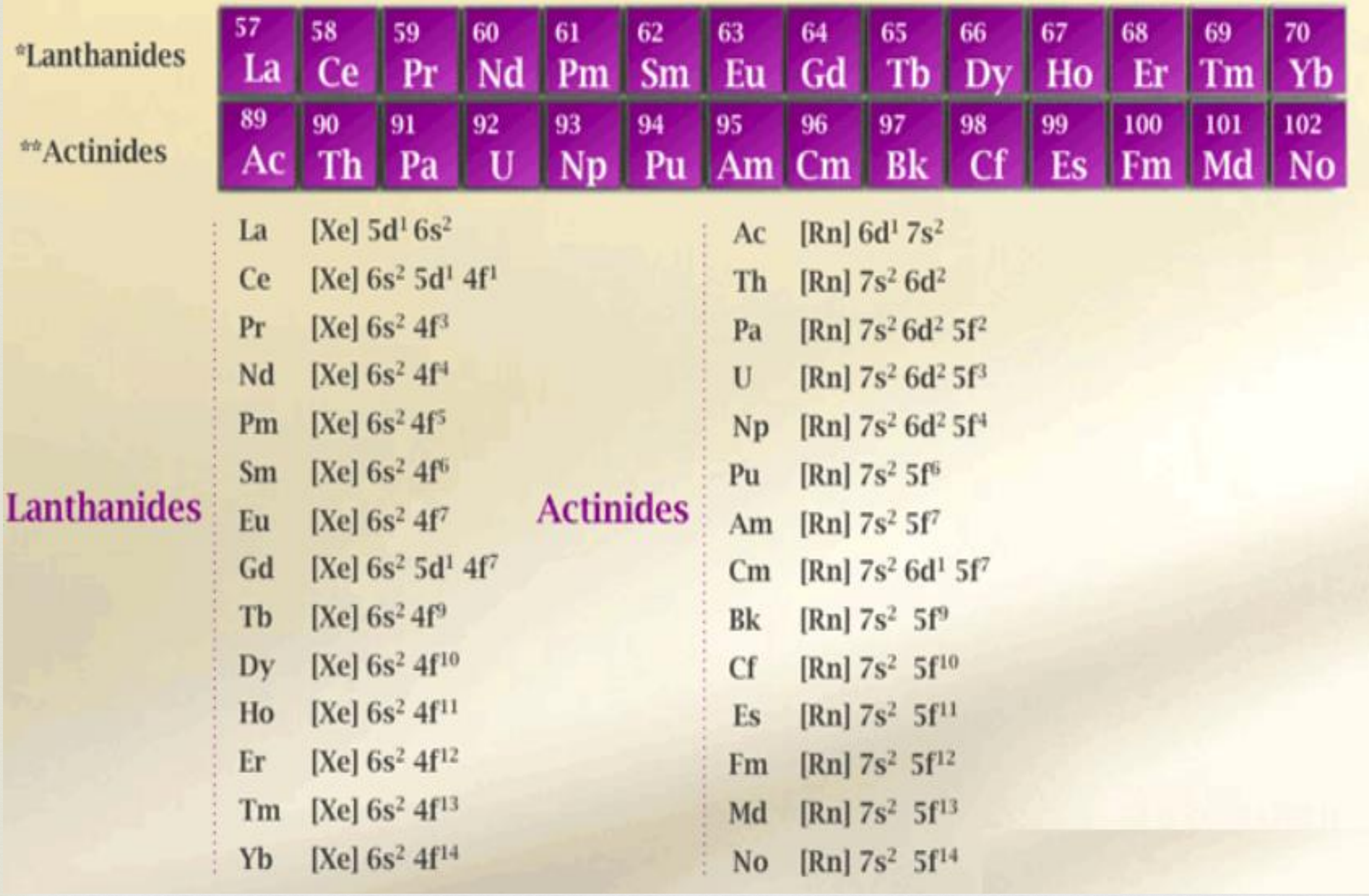


Table : electronic configuration of actinoids

Name of the element	Atomic number	Symbol	Electronic configuration
Actinium	89	Ac	[Rn] $5f^0\ 6d^1\ 7s^2$
Thorium	90	Th	[Rn] $5f^0\ 6d^2\ 7s^2$
Protactinium	91	Pa	[Rn] $5f^2\ 6d^1\ 7s^2$
Uranium	92	U	[Rn] $5f^3\ 6d^1\ 7s^2$
Neptunium	93	Np	[Rn] $5f^4\ 6d^1\ 7s^2$
Plutonium	94	Pu	[Rn] $5f^6\ 6d^0\ 7s^2$
Americium	95	Am	[Rn] $5f^7\ 6d^0\ 7s^2$
Curium	96	Cm	[Rn] $5f^7\ 6d^1\ 7s^2$
Berkelium	97	Bk	[Rn] $5f^9\ 6d^0\ 7s^2$
Californium	98	Cf	[Rn] $5f^{10}\ 6d^0\ 7s^2$
Einstenium	99	Es	[Rn] $5f^{11}\ 6d^0\ 7s^2$
Fermium	100	Fm	[Rn] $5f^{12}\ 6d^0\ 7s^2$
Mendelevium	101	Md	[Rn] $5f^{13}\ 6d^0\ 7s^2$
Nobelium	102	No	[Rn] $5f^{14}\ 6d^0\ 7s^2$
Lowrentium	103	Lr	[Rn] $5f^{14}\ 7s^2\ 7p^1$



Elements	Symbol	Electronic configuration
Thorium	Th	$6d^2\ 7s^2$
Protactinium	Pa	$5f^2\ 6d^1\ 7s^2$
Uranium	U	$5f^3\ 6d^1\ 7s^2$
Neptunium	Np	$5f^4\ 6d^1\ 7s^2$
Plutonium	Pu	$5f^6\ 7s^2$
Americium	Am	$5f^7\ 7s^2$
Curium	Cm	$5f^7\ 6d^1\ 7s^2$
Berkelium	Bk	$5f^9\ 7s^2$
Californium	Cf	$5f^{10}\ 7s^2$
Einstenium	Es	$5f^{11}\ 7s^2$
Fermium	Fm	$5f^{12}\ 7s^2$
Mendelevium	Md	$5f^{13}\ 7s^2$
Nobelium	No	$5f^{14}\ 7s^2$
Lawrencium	Lr	$5f^{14}\ 6d^1\ 7s^2$



*Lanthanides	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb
**Actinides	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No

Lanthanides

La	[Xe] $5d^1 6s^2$
Ce	[Xe] $6s^2 5d^1 4f^1$
Pr	[Xe] $6s^2 4f^3$
Nd	[Xe] $6s^2 4f^4$
Pm	[Xe] $6s^2 4f^5$
Sm	[Xe] $6s^2 4f^6$
Eu	[Xe] $6s^2 4f^7$
Gd	[Xe] $6s^2 5d^1 4f^7$
Tb	[Xe] $6s^2 4f^9$
Dy	[Xe] $6s^2 4f^{10}$
Ho	[Xe] $6s^2 4f^{11}$
Er	[Xe] $6s^2 4f^{12}$
Tm	[Xe] $6s^2 4f^{13}$
Yb	[Xe] $6s^2 4f^{14}$

Actinides

Ac	[Rn] $6d^1 7s^2$
Th	[Rn] $7s^2 6d^2$
Pa	[Rn] $7s^2 6d^2 5f^2$
U	[Rn] $7s^2 6d^2 5f^3$
Np	[Rn] $7s^2 6d^2 5f^4$
Pu	[Rn] $7s^2 5f^6$
Am	[Rn] $7s^2 5f^7$
Cm	[Rn] $7s^2 6d^1 5f^7$
Bk	[Rn] $7s^2 5f^9$
Cf	[Rn] $7s^2 5f^{10}$
Es	[Rn] $7s^2 5f^{11}$
Fm	[Rn] $7s^2 5f^{12}$
Md	[Rn] $7s^2 5f^{13}$
No	[Rn] $7s^2 5f^{14}$

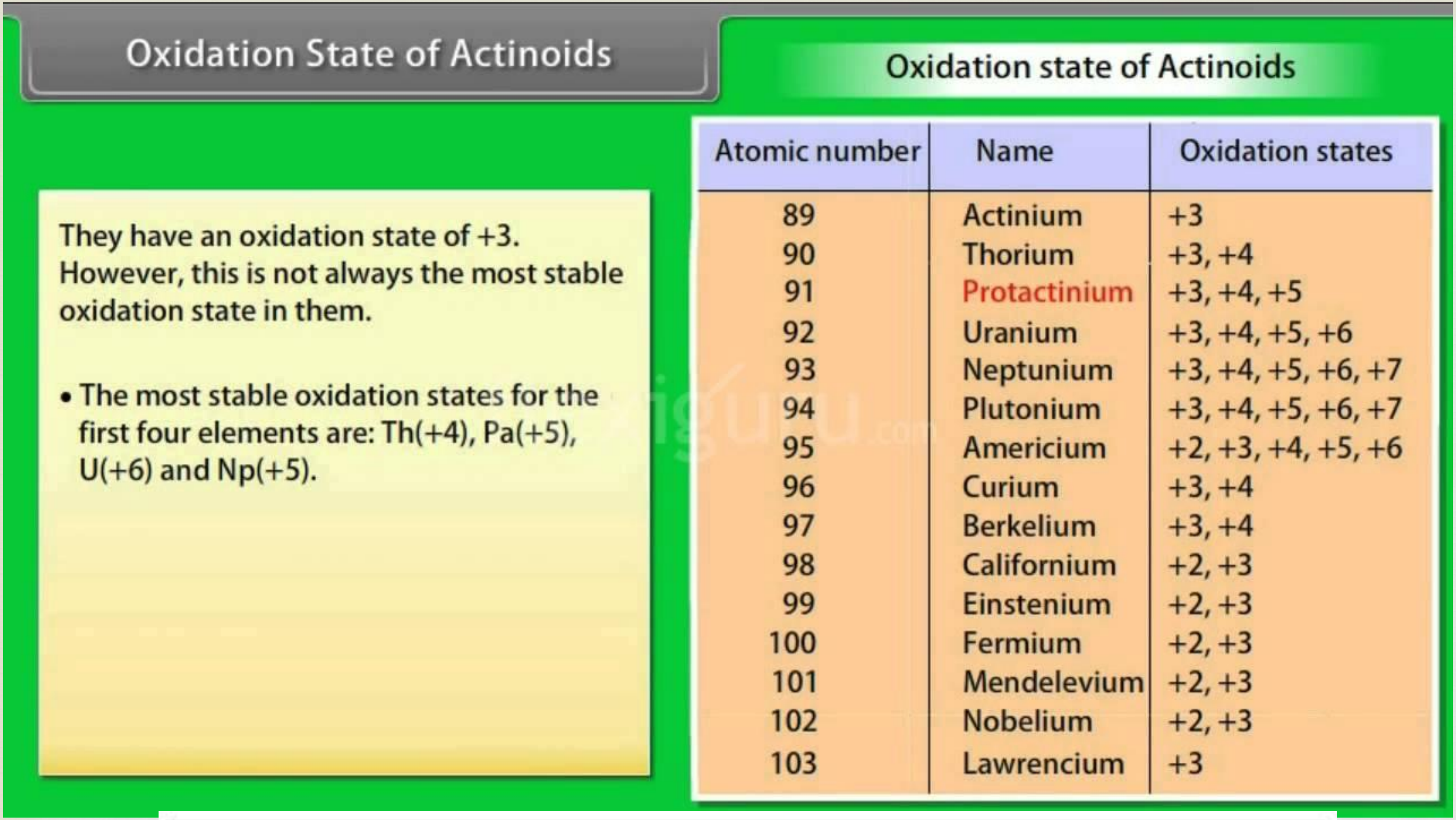
Electronic Configuration

- **The electron configurations of the actinides are due to the following:**

1. The energy in the 6d orbitals is lower in energy than in the 5f orbitals.
2. They fill 5f orbital, 6d orbital, then 7s orbital.
3. The 5f orbitals are not shielded by the filled 6s and 6p subshells.
4. There is a small energy gap between the $5f^n\ 7s^2$ and $5f^{n-1}\ 6d\ 7s^2$ configurations.
5. The 5f orbitals do not shield each other from the nucleus effectively.
6. The energies of the 5f orbital drop rapidly with increasing atomic number.

Electronic Configuration

- As there is not much difference between 5f and 6d, it becomes difficult to know whether the electron has entered 5f or 6d. This makes predicting electronic configuration difficult.
- •The ground state electronic configuration of actinium, **[Rn]$6d^1 7s^2$** is identical to that of lanthanum and certainly the two elements possess alike chemical properties.
- •The difference in energy between 5f and 6d orbitals in the starting of the actinide series is less than that between the 4f and 5d orbitals for the lanthanides.
- •Thus, both 5f and 6d orbitals are comprised in accommodating successive electrons.
- •Therefore the filling of 5f orbitals in actinides is not quite so regular as the filling of 4f orbitals in case of the lanthanides.
- •By the time plutonium and following members of the series are reached, the 5f orbitals seem evidently to be of lower energy than the 6d orbitals, and therefore the electrons preferably fill the former.
- Actinides show higher oxidation states than Lanthanides



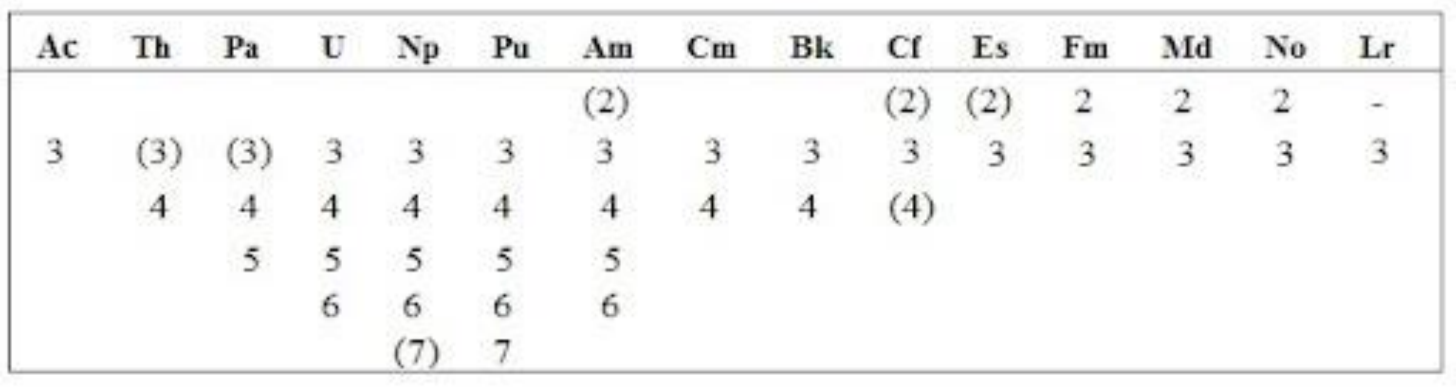
Oxidation State of Actinoids

They have an oxidation state of +3. However, this is not always the most stable oxidation state in them.

- The most stable oxidation states for the first four elements are: Th(+4), Pa(+5), U(+6) and Np(+5).

Oxidation state of Actinoids

Atomic number	Name	Oxidation states
89	Actinium	+3
90	Thorium	+3, +4
91	Protactinium	+3, +4, +5
92	Uranium	+3, +4, +5, +6
93	Neptunium	+3, +4, +5, +6, +7
94	Plutonium	+3, +4, +5, +6, +7
95	Americium	+2, +3, +4, +5, +6
96	Curium	+3, +4
97	Berkelium	+3, +4
98	Californium	+2, +3
99	Einstenium	+2, +3
100	Fermium	+2, +3
101	Mendelevium	+2, +3
102	Nobelium	+2, +3
103	Lawrencium	+3



Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
						(2)			(2)	(2)	2	2	2	-
3	(3)	(3)	3	3	3	3	3	3	3	3	3	3	3	3
	4	4	4	4	4	4	4	4	(4)					
		5	5	5	5	5								
			6	6	6	6								
				(7)	7									

Different Oxidation States

- We can observe from the table which almost all the actinides show **at least two stable oxidation states**
- and **oxidation states higher than +3 are simply accessible** in the early actinides.
- For thorium, protactinium and uranium **the highest accessible oxidation state is the most stable** one as well in aqueous solution.
- This might be as 5f orbitals extend further from the nucleus than the 4f orbitals
- and 5f electrons are more efficiently shielded from the nuclear charge than are the 4f electrons of the corresponding lanthanides.
- As the **5f electrons are less firmly held**, they are **all available for bonding in the early actinides.**
- Though, as the later actinides are approached, the build-up of nuclear charge **causes-contraction of the 5f orbitals** in such a way that the metal-ligands overlap reduces and the **+3 state becomes predominant**.
- Interestingly, the +2 state that is achievable in case of mendelevium and nobelium is more stable than Eu^{2+}.

Oxidation States

- Up to Uranium, stable oxidation states of the elements is the one involving all the valence electrons.

- •Neptunium forms the +7 state using all the valence electrons but this is oxidizing and **the most stable state is +5**.

- •Plutonium also shows states up to +7 and Americium up to +6 but the **most stable state drops to Pu (+4) and Am(+3).**

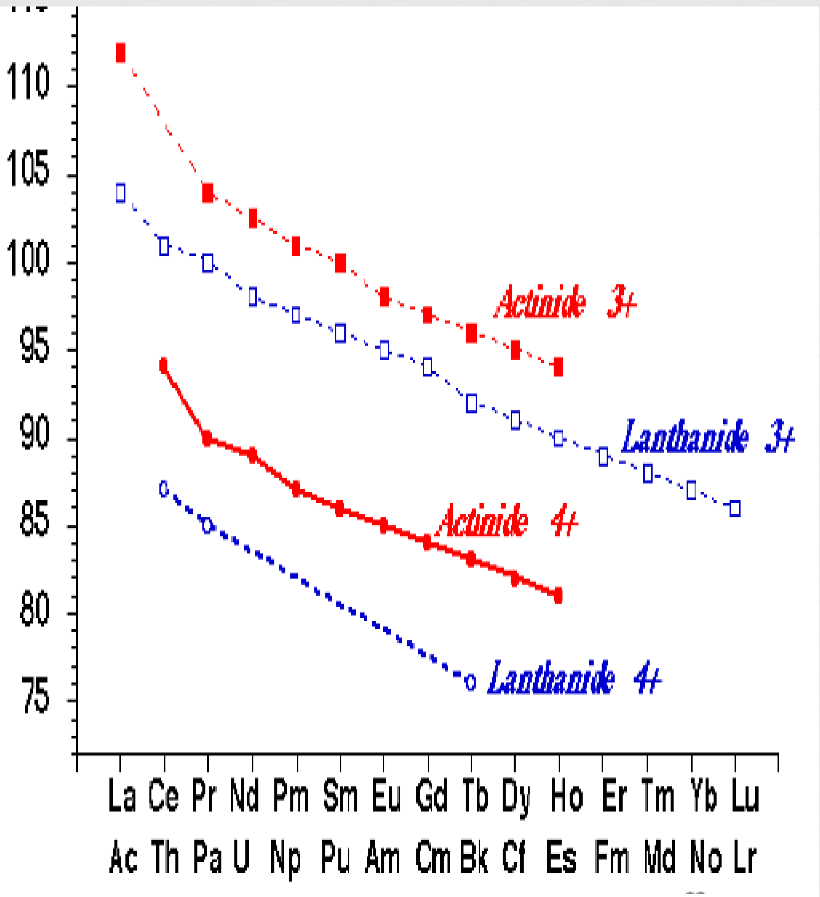
- •**Berkeliumin+4 state is strongly oxidizing** but is more stable than curium and americium in +4 stated up to f7 configuration.

- •Similarly, nobelium is **markedly stable in +2** stated up to its f14 configuration

Ionic Radius

Ionic radius

The ionic radius of actinides decreases regularly along the series. The decrease in ionic radius of actinides is called ***actinides contraction***, and is due to the poor screening effect of the nuclear charge by the *f* electrons.



Actinide Contraction

- The size of atoms or M^{3+} ions decrease regularly along the actinides series with increase in atomic number from Th to Lr.
- The steady decrease in ionic radii with increase in atomic number is referred to as actinide contraction just like lanthanide contraction.

Magnetic properties

- All actinides are **paramagnetic** in nature which depends on the presence of unpaired electrons.
- •Magnetic properties are more complex than those of lanthanoids.
- •Ligand field effects are expected where 5f orbitals are involved in bonding.
- 5f electrons are closer to the surface of the atom and is simply affected by the chemical environment; however not to the similar extent as do the d electrons.
- •The less sharply stated distinctions between the 5f and 6d electrons as compared by 4f and 5d electrons.

- The magnetic properties of actinide ions are more complex than those of the lanthanide ions.
- •5 f electrons are closer to the surface of the atom and is simply affected by the chemical environment; however not to the similar extent as do the d electrons.
- •The less sharply stated distinctions between the 5f and 6d electrons as compared by 4f and 5d electrons.

Colour of Ions

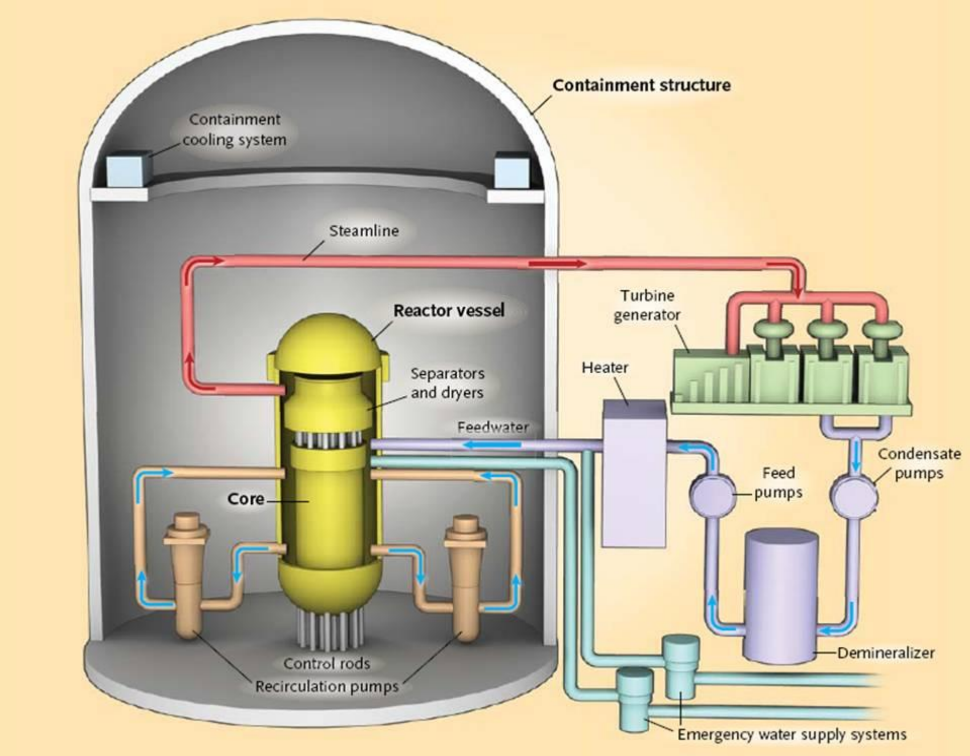
- The ions of lanthanides and actinides are colored in the solid state and also in aqueous solution, as is the case with the ions of transition metals.
- We know that the colours of transition metal ions occur due to absorption of light because of d-d electronic transitions.
- As there are no electrons in the d-orbitals, the colours of lanthanide and actinide ions occur because of electronic transitions in the 4f and 5f orbitals.
- The colours of hydrated lanthanide and actinide ions are illustrated in the first and second table, correspondingly.

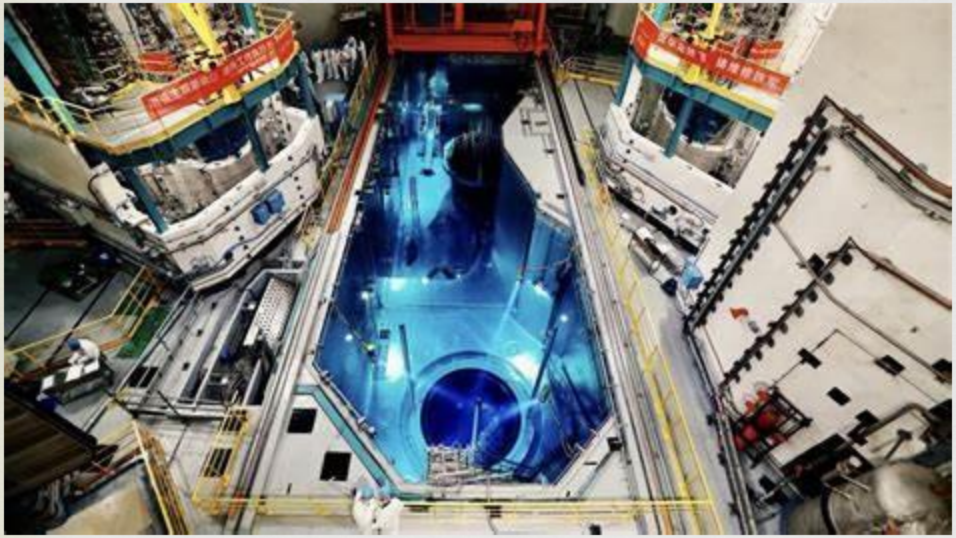
Common Properties

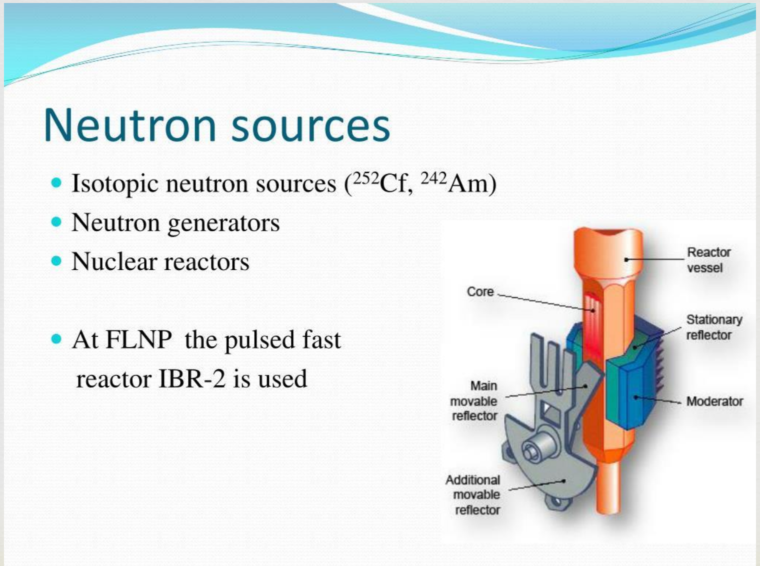
- **Actinides share the following properties:**
- All are radioactive. These elements have no stable isotopes.
- Actinides are highly electropositive.
- The metals tarnish readily in air. These elements are pyrophoric (spontaneously ignite in the air), particularly as finely divided powders.
- Actinides are very dense metals with distinctive structures. Numerous allotropes can be formed—plutonium has at least six allotropes. The exception is actinium, which has fewer crystalline phases.
- They react with boiling water or dilute acid to release hydrogen gas.
- Actinide metals tend to be fairly soft. Some can be cut with a knife.
- These elements are malleable and ductile.
- All the actinides are paramagnetic.
- All these elements are silver-colored metals that are solid at room temperature and pressure.

Uses

- For the most part, we don't often encounter these radioactive elements in daily life.
- Americium is found in smoke detectors.
- Thorium is found in gas mantles.
- Actinium is used in scientific and medical research as a neutron source, indicator, and gamma source.
- Actinides may be used as dopants to make glass and crystals luminescent.
- The bulk of actinide use goes to energy production and defense operations.
- The primary use of the actinide elements is as nuclear reactor fuel and in the production of nuclear weapons.
- The actinides are favored for these reactions because they readily undergo nuclear reactions, releasing incredible amounts of energy.
- If the conditions are right, the nuclear reactions can become chain reactions.







Neutron sources

- Isotopic neutron sources (^{252}Cf, ^{242}Am)
- Neutron generators
- Nuclear reactors

- At FLNP the pulsed fast reactor IBR-2 is used

ACTINIDES CHEMISTRY

CHEMISTRY ACTINIDE METALS

- ***Preparation***

- **General method for all Actinides**:

1. Reduction of AnF_3 or AnF_4 with vapours of Li, Mg, Ca or Ba at 1100 - 1400 °C
2. Highly **Electropositive**.
3. Typically react with:
4. air → tarnishing
5. boiling water or dilute acid → releasing Hydrogen
6. most non-metals in direct combination

- ***Structures***

- Very dense metals (e.g. U = 19 g cm^{-3}) with distinctive structures, e.g. Plutonium has at least 6 allotropes and forms numerous alloys.

NATURALLY OCCURRING ACTINIDES

- **Only Actinium, Thorium, Protactinium & Uranium occur naturally** (i.e. $Z \leq 92$).
- **Actinium** & **Protactinium** occur only in trace amounts.
- **Neptunium** & **Plutonium** occur in uranium minerals in minute amounts - not appreciated
- until after they had been synthesized that the synthesis route might occur naturally!
- **All isotopes of all the actinides are radioactive**.
- Most of the longer-lived isotopes decay by α-emission.
- Both Thorium and Uranium are far from rare.

NATURALLY OCCURRING ACTINIDES

ThO_2

- ***Thorium***
- Widely dispersed, accounts for > 3ppm of the earth's crust.
- Natural Thorium is essentially 100% ^{232}Th.
- Occurs in **monazite** [with the rare earths] and in **uranothorite** [a mixed Th, U silicate].
- Obtained as ThO2, **Thoria**, from mineral extraction process.
- **Thorianite** is a rare thorium oxide mineral,
- Used as 99% ThO_2 / 1% CeO2 in thoria gas mantles.
- ***Uranium***
- Widely distributed - found scattered in the faults of old igneous rocks.
- Natural Uranium is 99.27% 238U & 0.72% 235U.
- Obtained usually as UO2.
- Used for nuclear fuel, and on a smaller scale for colouring glass/ceramics.

OXIDATION STATES

Element	Symbol	A.N	Electronic configuration	An^{3+}	Other Oxidation states
Actinium	Ac	89	[Rn] 6d^{1}7s^2	[Rn]4f^0	
Thorium	Th	90	[Rn]5f^{1}6d^{1}7s^2	[Rn]4f^1	IV
Protactinium	Pa	91	[Rn]5f^2 6d^{1}7s^2	[Rn]4f^2	IV, V
Uranium	U	92	[Rn]5f^{3}6d^{1}7s^2	[Rn]4f^3	IV, V, VI
Neptunium	Np	93	[Rn]5f^{4}6d^{1}7s^2	[Rn]4f^4	IV, V, VI, VII
Plutonium	Pu	94	[Rn]5f^{6}7s^2	[Rn]4f^5	IV, V, VI, VII
Americium	Am	95	[Rn]5f^{7}7s^2	[Rn]4f^6	IV,VI
Curium	Cm	96	[Rn]5f^{7}6d^{1}7s^2	[Rn]4f^7	IV
Berkelium	Bk	97	[Rn]5f^{9}7s^2	[Rn]4f^8	IV
Californium	Cf	98	[Rn]5f^{10}7s^2	[Rn]4f^9	IV
Einsteinium	Es	99	[Rn]5f^{11}7s^2	[Rn]4f^{10}	II
Fermium	Fm	100	[Rn]5f^{12}7s^2	[Rn]4f^{11}	II
Mendelevium	Md	101	[Rn]5f^{13}7s^2	[Rn]4f^{12}	II
Nobelium	No	102	[Rn]5f^{14}7s^2	[Rn]4f^{13}	II

OXIDATION STATE +2

- **Unusual** oxidation state.
- Common only for the heaviest elements.
- Nobelium (No^{2+}) & Mendelevium (Md^{2+}) are more stable than Lanthanide element (Eu^{2+})
- **Actinide (An^{2+})ions have similar properties to Lanthanide Ln^{2+} and to Ba^{2+} ions.**

OXIDATION STATE +3

- **The most common oxidation state.**
- The most stable oxidation state for all trans-Americium elements (except No).
- Of marginal stability for early actinides Th, Pa, U (But: Group oxidation state for Ac).
- General properties resemble Ln3+ and are size-dependent.
- Stability constants of complex formation are similar for same size An3+ & Ln3+.
- Isomorphism is common.
- Later An3+ & Ln3+ must be separated by ion-exchange/solvent extraction.
- Binary Halides, MX3 easily prepared, & easily hydrolysed to MOX.
- Binary Oxides, M2O3 known for Ac, Th and trans-Am elements.

OXIDATION STATE +4

- **Principal oxidation state for Th.**
- Th^{4+} chemistry shows resemblance to Zr^{4+} / Hf^{4+} - like a transition metal.
- **Very important, stable state for Pa, U, Pu.**
- Am, Cm, Bk & Cf are increasingly easily reduced - only stable in certain complexes, e.g.
- Bk^{4+} is more oxidizing than Ce^{4+}.
- **MO_2 known from Th to Cf (fluorite structure).**
- MF_4 are isostructural with lanthanide tetrafluorides.
- MCl_4 only known for Th, Pa, U & Np.
- Hydrolysis / Complexation / Disproportionation are all important in (aq).

OXIDATION STATE +5

- **Principal state for Pa**.
- Pa^{5+} chemistry resembles that of Nb^{5+} / Ta^{5+} - like a transition metal.
- For U, Np, Pu and Am the AnO_2^+ ion is known (i.e. quite unlike Nb/Ta).
- Comparatively few other An(V) species are known.e.g. fluorides, PaF_5, NbF_5, UF_5; fluoro-anions, $(AnF_6)^-$, $(AnF_7)^{2-}$, $(AnF_8)^{3-}$.
- e.g. oxochlorides, $PaOCl_3$, $UOCl_3$; uranates, $NaUO_3$

OXIDATION STATE +6

- $(AnO_2)^{2+}$ ions are important for U, Np, Pu, Am.
- **uranyl ion** $(UO_2)^{2+}$ is the most stable.
- Few other compounds e.g. AnF_6 (An = U, Np, Pu), UCl_6, UOF_4 etc…, $U(OR)_6$.

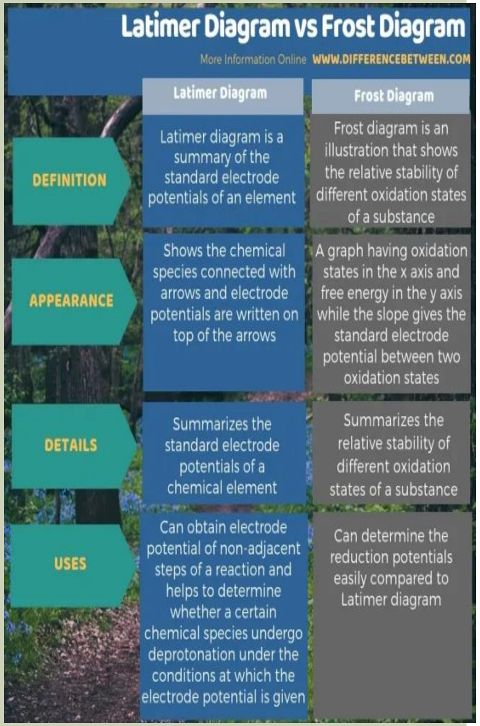
OXIDATION STATE +7

- Only the marginally stable oxo-anions of Np and Pu, e.g. $(AnO_5)^{3-}$.

ACTINIDE AQUEOUS CHEMISTRY

- Latimer & Frost Diagrams for elements in acid & alkaline (aq) indicate actinides **are quite electropositive**.
- Pa - Pu show significant redox chemistry, e.g. all 4 oxidation states of Pu can co-exist in appropriate conditions in (aq).
- **Stability of high oxidation states peaks at U (Np).**
- An^{3+} is the maximum oxidation state for (Cf)Es – Lr.
- No^{2+}(aq) is especially stable ~ most stable state for No in (aq).
- Redox potentials show strong dependence on pH (data for Ac - Cm).
- **High oxidation states are more stable in basic conditions**.
- Even at low pH hydrolysis occurs - formation of polymeric ions. When hydrolysis leads to precipitation measurement of potentials is difficult, e.g. Pa5+ hydrolyses easily; potentials that indicate it to be the most **stable oxidation state are recorded in presence of F$^-$ or $(C_2O_4)^{2-}$**.
- Tendency to disproportionation is particularly dependent on pH, e.g. at high pH

  $$3Pu^{4+} + 2H_2O \rightarrow (PuO_2)^{2+} + 2Pu^{3+} + 4H^+.$$
- Early actinides have a tendency to form complexes - complex formation influences reduction potentials, e.g. Am^{4+}(aq) only exists when complexed by fluoride (15 M NH_4F(aq)).
- Radiation-induced solvent decomposition produces H$^\bullet$ and OH$^\bullet$ radicals, which lead to reduction of higher oxidation states e.g. Pu V/VI, Am IV/VI



Latimer Diagram vs Frost Diagram

More Information Online WWW.DIFFERENCEBETWEEN.COM

	Latimer Diagram	Frost Diagram
DEFINITION	Latimer diagram is a summary of the standard electrode potentials of an element	Frost diagram is an illustration that shows the relative stability of different oxidation states of a substance
APPEARANCE	Shows the chemical species connected with arrows and electrode potentials are written on top of the arrows	A graph having oxidation states in the x axis and free energy in the y axis while the slope gives the standard electrode potential between two oxidation states
DETAILS	Summarizes the standard electrode potentials of a chemical element	Summarizes the relative stability of different oxidation states of a substance
USES	Can obtain electrode potential of non-adjacent steps of a reaction and helps to determine whether a certain chemical species undergo deprotonation under the conditions at which the electrode potential is given	Can determine the reduction potentials easily compared to Latimer diagram

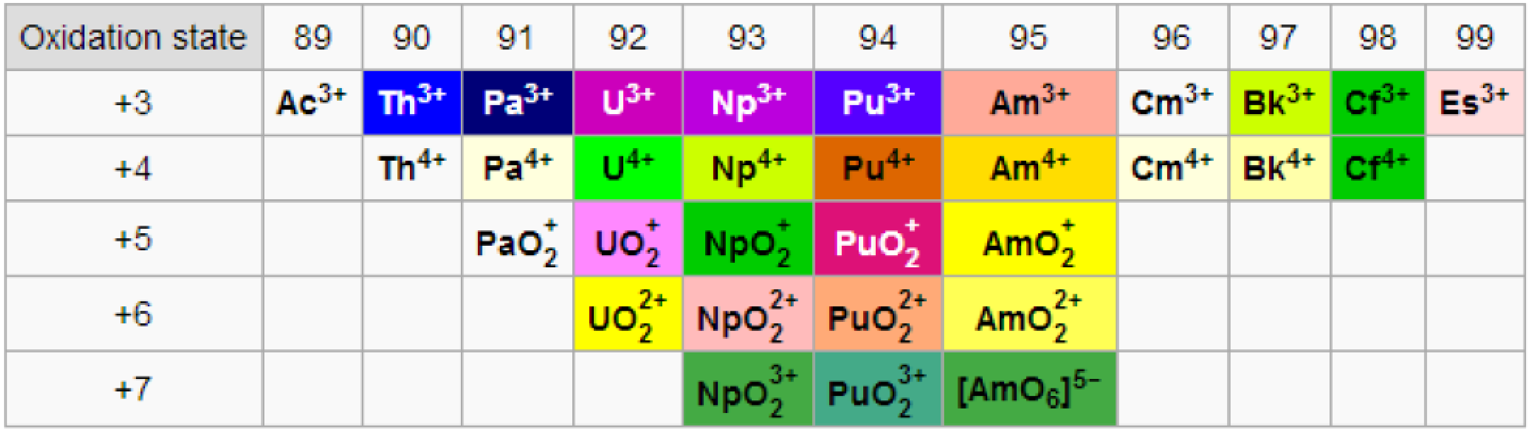
5. Color

- Actinides ions are usually colored.
- The color depends upon the number of 5f electrons,
- ions with $5f^0$ electrons and $5f^{14}$ electrons are colorless.
- The color is due to f-f electronic transitions.
- Most of the tri positive and tetra positive (3+ and 4+) ions are colored.

Example:

Ac^{3+}-colorless ,
Np^{3+} - Purple,
Am^{3+} - pink,
Cm^{3+} - colorless, U^{4+} - Green,
Np^{4+} - Yellow-green.

Approximate colors of actinide ions in aqueous solution[82]



Oxidation state	89	90	91	92	93	94	95	96	97	98	99
+3	Ac^{3+}	Th^{3+}	Pa^{3+}	U^{3+}	Np^{3+}	Pu^{3+}	Am^{3+}	Cm^{3+}	Bk^{3+}	Cf^{3+}	Es^{3+}
+4		Th^{4+}	Pa^{4+}	U^{4+}	Np^{4+}	Pu^{4+}	Am^{4+}	Cm^{4+}	Bk^{4+}	Cf^{4+}	
+5			PaO_2^+	UO_2^+	NpO_2^+	PuO_2^+	AmO_2^+				
+6				UO_2^{2+}	NpO_2^{2+}	PuO_2^{2+}	AmO_2^{2+}				
+7					NpO_2^{3+}	PuO_2^{3+}	$[AmO_6]^{5-}$				

6. Complex formation

- The degree of complex formation decreases in the following order:

$M^{4+} > MO_2^{2+} > MO^{2+}$

- The complexing power of different singly charged and doubly charged anions following order.

$F^- > NO_3^- > Cl^-$ (mono-dentate ligands)

$CO_3^{2-} > C_2O_4^{2-} > SO_4^{2-}$ (bi-dentate ligands)

COMPLEXES & COMPOUNDS

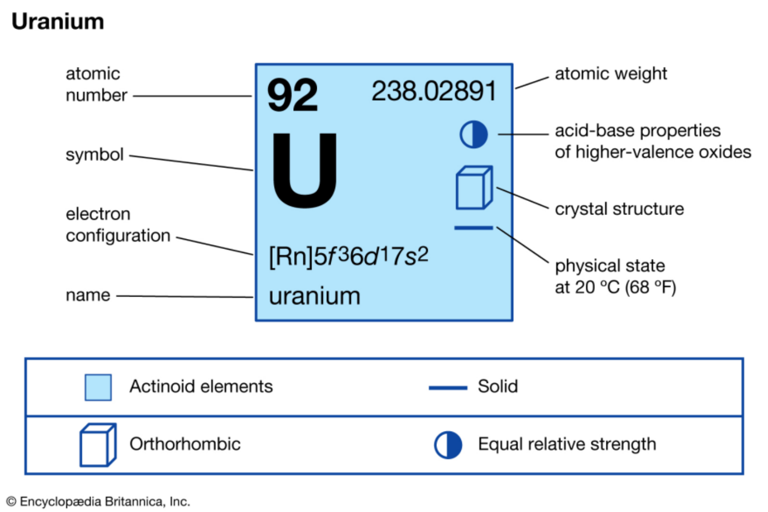
- A wide range of complexes with monodentate and chelating ligands.
- Complexing ability:- $[M^{5+}] > M^{4+} > (MO_2)^{2+} > M^{3+} > MO^{2+}$
- Geometry may be strongly influenced by covalent bonding effects, e.g. MO_2^{2+} unit is always linear
- $UO_2(\eta 2\text{-}NO_3)_2(H2O)_2$ is hexagonal bipyramidal.

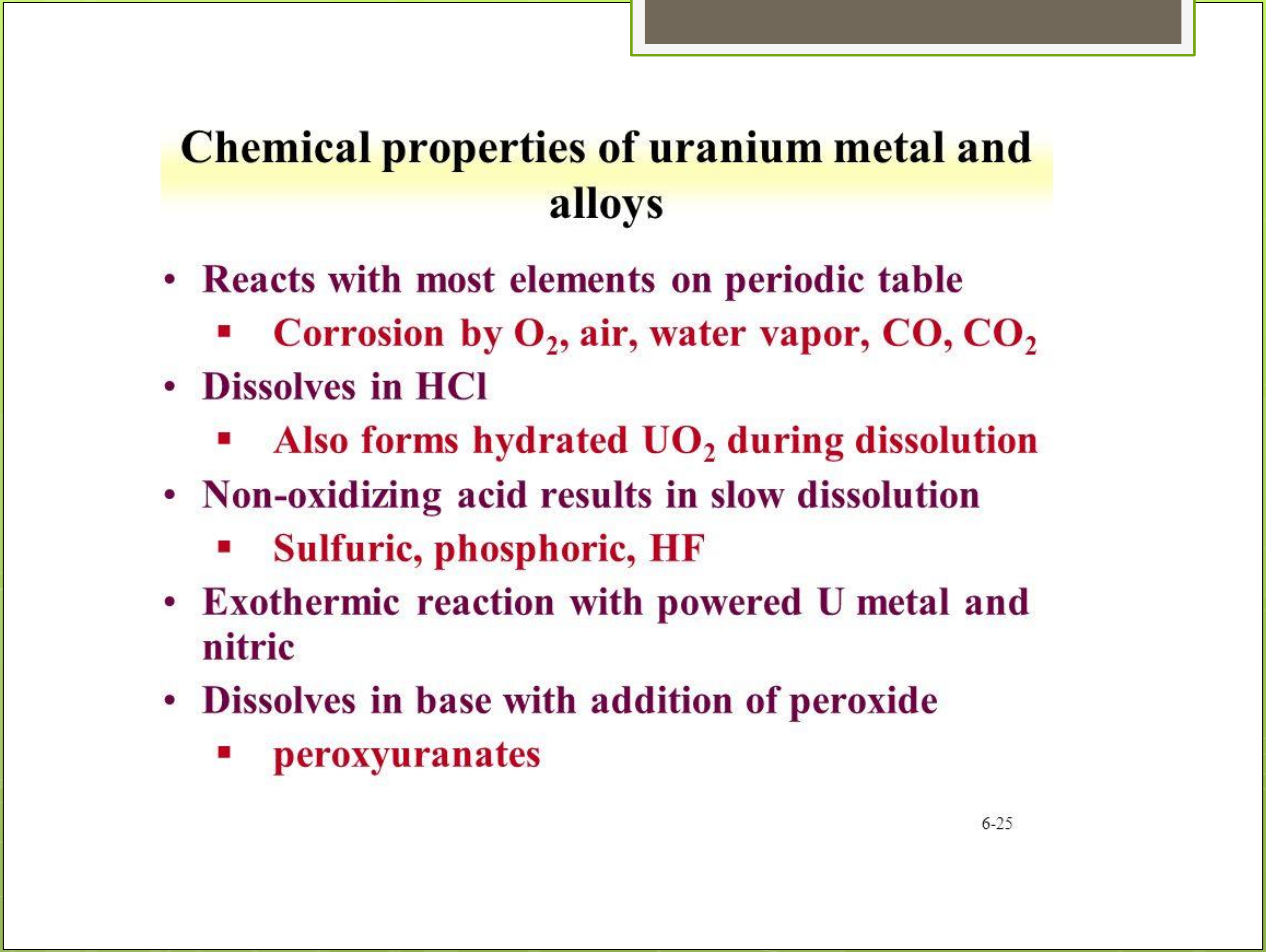
- **Compounds**

- Actinide Hydrides, Halides, Oxides, Oxyhalides …

Uranium Chemistry

اليورانيوم





Chemical properties of uranium metal and alloys

- Reacts with most elements on periodic table
    - Corrosion by O_2, air, water vapor, CO, CO_2
- Dissolves in HCl
    - Also forms hydrated UO_2 during dissolution
- Non-oxidizing acid results in slow dissolution
    - Sulfuric, phosphoric, HF
- Exothermic reaction with powered U metal and nitric
- Dissolves in base with addition of peroxide
    - peroxyuranates

Chemical reaction of Uranium

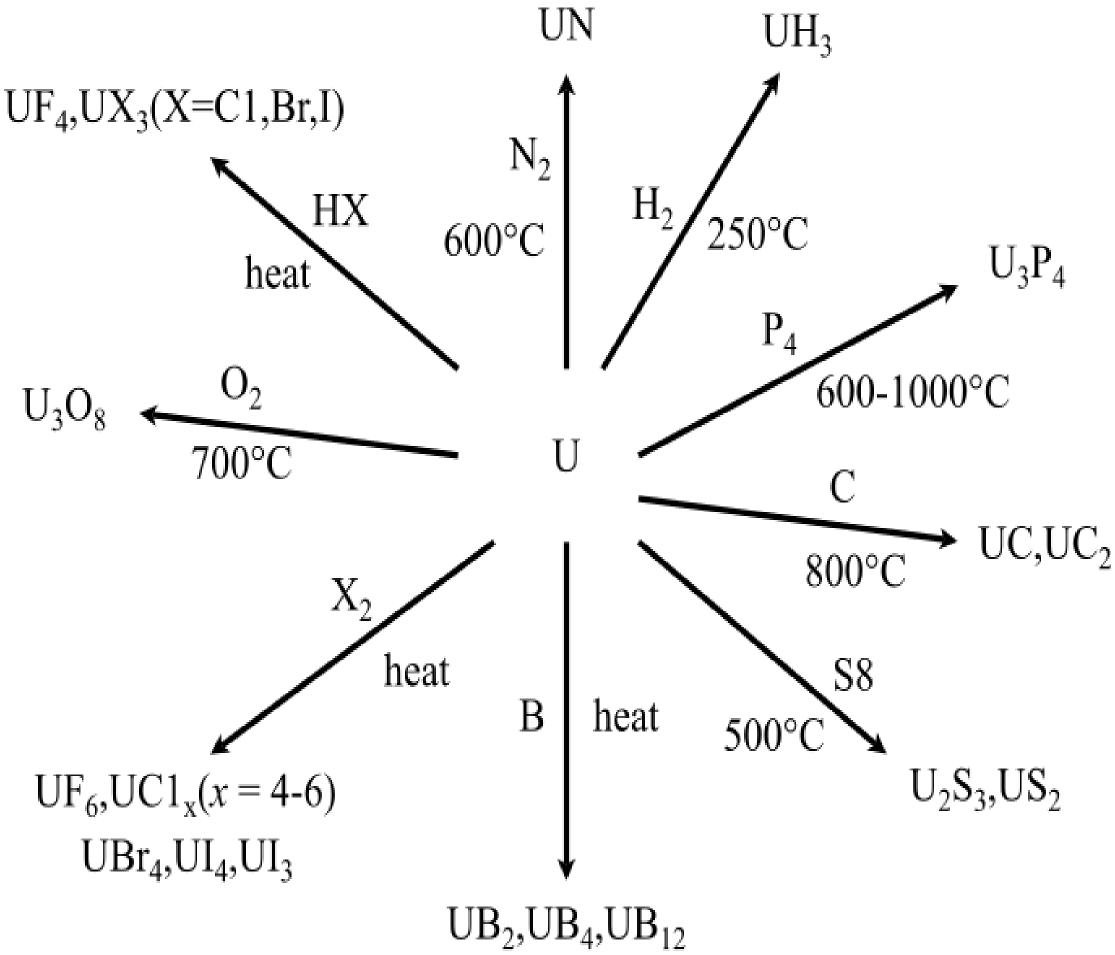
- Uranium metal reacts with almost all non-metal elements (with the exception of the noble gases) and their compounds, with reactivity increasing with temperature.

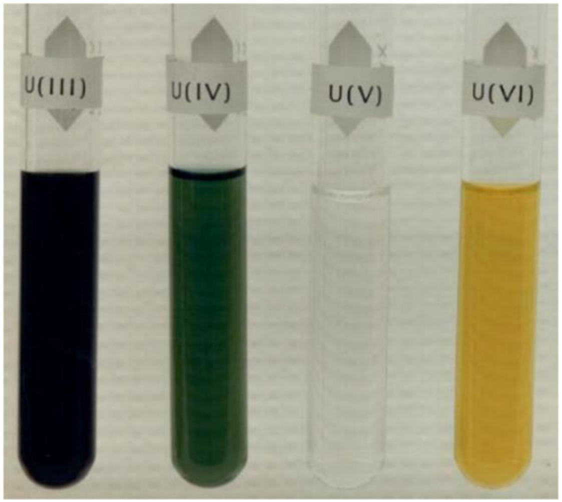
- Hydrochloric and nitric acids dissolve uranium,
- but non-oxidizing acids other than hydrochloric acid attack the element very slowly.

- When finely divided, it can react with cold water.
- in air, uranium metal becomes coated with a dark layer of uranium oxide.

- Uranium in ores is extracted chemically and converted into uranium dioxide or other chemical forms usable in industry.

Chemical reactions





Halides

Fluorides

- UF6 - the most important fluoride.
  - *Preparation:*
  - $UO2 + 4HF \rightarrow UF_4 + 2H2O$.
  - $3UF4 + 2ClF3 \rightarrow 3UF_6 + Cl_2$.
- *Properties*:
- mp. 64°C, vapour pressure = 115 mmHg at 25°C.
- **Made on a large scale to separate uranium isotopes.**
- **Gas diffusion or centrifugation separates $^{235}UF_6$ from $^{238}UF_6$.**
- Uranium richer in 235-U is termed enriched, richer in 238-U is depleted.
- Powerful **fluorinating** agent.
  - Other Fluorides

$$UF6 + Me_3SiCl \rightarrow Me_3SiF + \frac{1}{2}Cl_2 + UF_5$$

- (melts to an electrically-conducting liquid).

$$UF6 + 2Me_3SiCl \rightarrow 2Me_3SiF + Cl2 + UF_4 \rightarrow 500\text{-}600°C \text{ gives } UO_2 + CFCl_2CFCl_2.$$

- Mixed-Valence fluorides such as U2F9 also form.
- Reduction of $UF4 + \frac{1}{2}H_2 \rightarrow UF_3$.

Halides

Chlorides

- UCl_4 – is the usual starting material for the synthesis of other U(IV) compounds.
- **Preparation:**
- Liquid-phase chlorination of UO3 by refluxing hexachloropropene.
- ***Properties***:
- Soluble in polar organic solvents & in water.
- Forms various adducts (2 - 7 molecules) with O and N donors.
- **UCl_3**
- Usually encountered as UCl3(thf)x (a rather intractable material). *THF = tetrahydrofuran*)
- Unsolvated binary gives its name to the UCl3 structure!
- Actinide trihalides form a group with strong similarities (excepting redox behaviour) to the Lanthanides.

UCl_6

- From chlorination of U_3O_8 + C.
- Highly oxidising.
- Moisture-sensitive :

  $UCl_6 + 2H_2O \rightarrow UO_2Cl_2$ (Uranyl Chloride) + 4HCl.

- In CH_2Cl_2 solution UCl_6 decomposes to U_2Cl_{10}

Oxides

- Many binary phases UO_x have been reported.
- Many are not genuine phases.
- Genuine phases show range of O-content.
- The most important genuine phases are **UO_2, U_4O_9, U_3O_8, UO_3**.

Oxides

- **UO_2** (black-brown) has the Fluorite structure. Stoichiometric material is best obtained from:

$$UO_3 \xrightarrow[300\text{–}600°C]{H_2 \text{ or } CO} UO_2 + H_2O \text{ (or } CO_2\text{)}$$

- **U_3O_8** is dark green.
- conveniently made by heating uranyl nitrate or ethanoate in air.

$$3UO_2(NO_3)_2 \xrightarrow[650\text{–}800°C]{O_2} U_3O_8 + 6NO_2 + 2O_2$$

- **UO_3** is orange-yellow.
- Produced by a variety of methods:

$$UO_2(NO_3)_2 \xrightarrow[400\text{–}600°C]{O_2} UO_3 \qquad (NH_4)_2U_2O \xrightarrow[500°C]{O_2} UO_3$$

Uranates

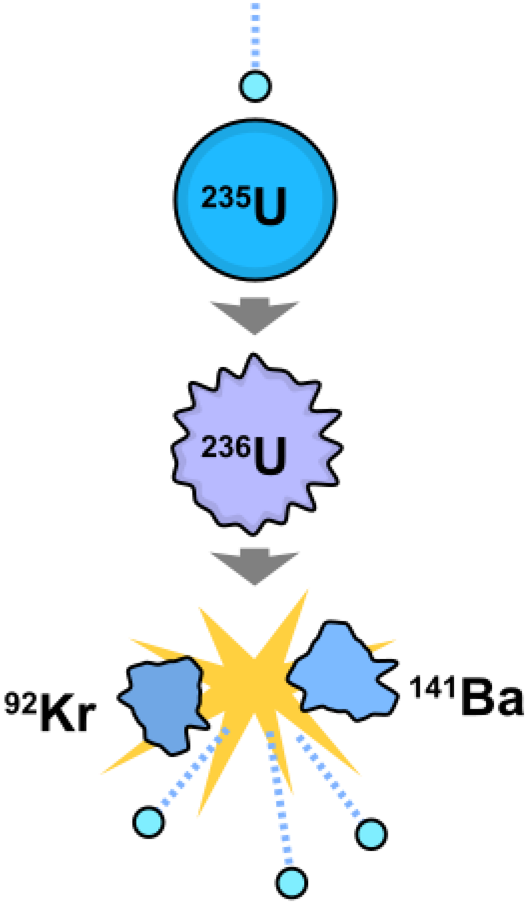
- Fusion of uranium oxides with alkali or alkaline earth carbonates
- chemical formula is **$M_xU_yO_z$**
- orange/yellow/brown mixedoxides,
- **Uranates:**
- Na_2UO_4......oxidation state+6
- CaU_2O_7......oxidation state+4
- Ca_3UO_6 ......oxidation state+4
- $NaUO_3$......oxidation state+5
- Ca_3UO_6 ......oxidation state+6

Aqueous Chemistry of uranium

- Complex aqueous chemistry due to extensive possibilities for complexation, hydrolytic reactions,
- often leading to polymeric ion species.
- Reduction Potentials appropriate for 1M HClO4 indicate:

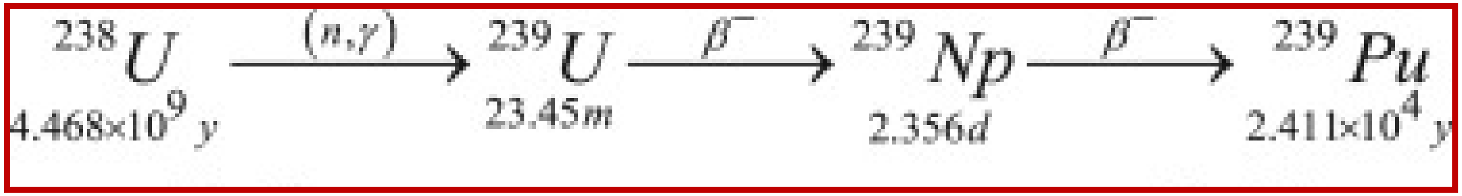
$$\begin{tikzcd}
UO_2^{2+} \arrow[r, "0.06\ \text{V}"] \arrow[rr, bend right, "0.33\ \text{V}"'] & UO_2^{+} \arrow[r, "0.6\ \text{V}"] & U^{4+} \arrow[r, "-0.63\ \text{V}"] \arrow[rr, bend right, "-1.46\ \text{V}"'] & U^{3+} \arrow[r, "-1.74\ \text{V}"] & U
\end{tikzcd}$$

- Uranium-235 was the first isotope that was found to be fissile.
- Other naturally occurring isotopes are fissionable, but not fissile.
- On bombardment with slow neutrons, its uranium-235 isotope will most of the time divide into two smaller nuclei, releasing nuclear binding energy and more neutrons.

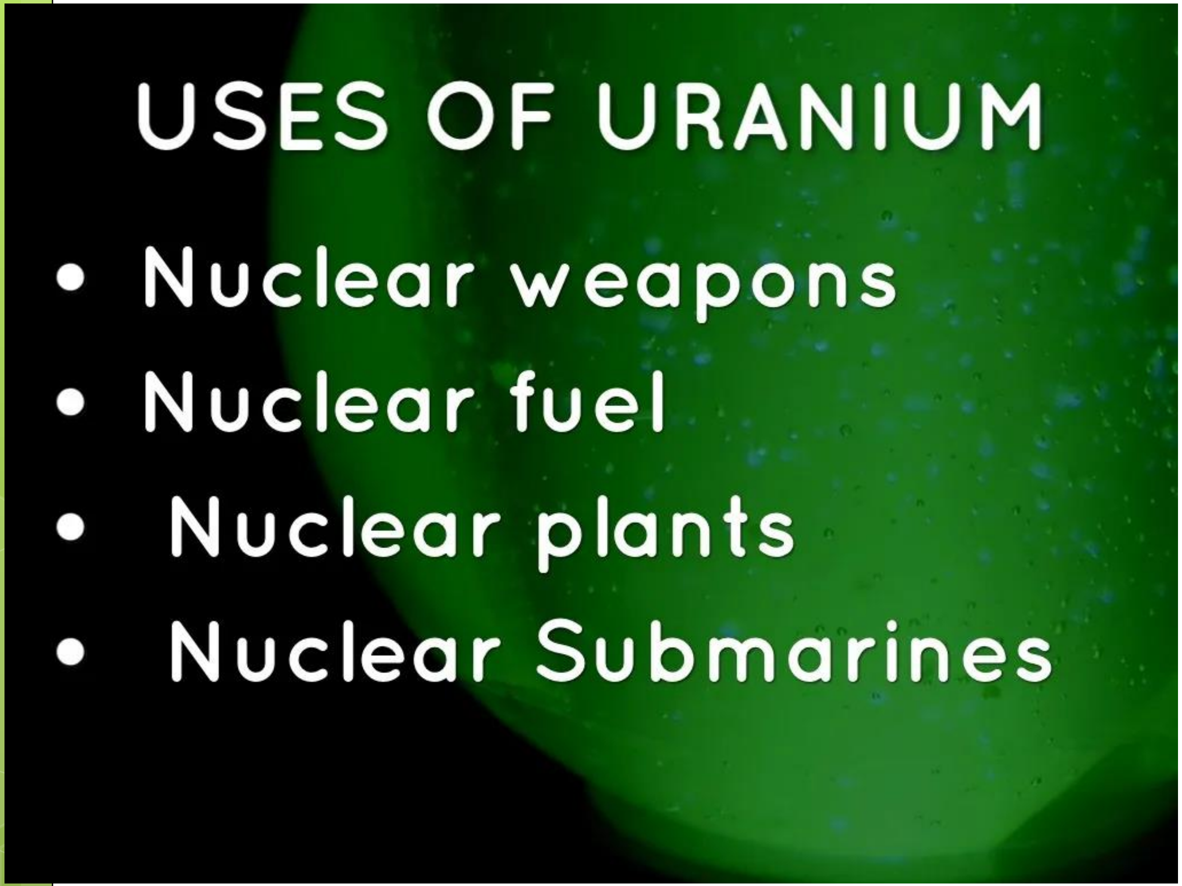


Modern Nuclear Reactors

- Current nuclear reactors use UO_2 fuel – less reactive than U metal.
- Enrichment is by fractional gaseous centrifugation of UF_6 (easily sublimed).
- Neutron capture by ^{238}U results in formation of ^{239}Pu, which is fissile. Significant amounts of Pu will only be produced in an unmoderated reactor (fuel reprocessing more dangerous!

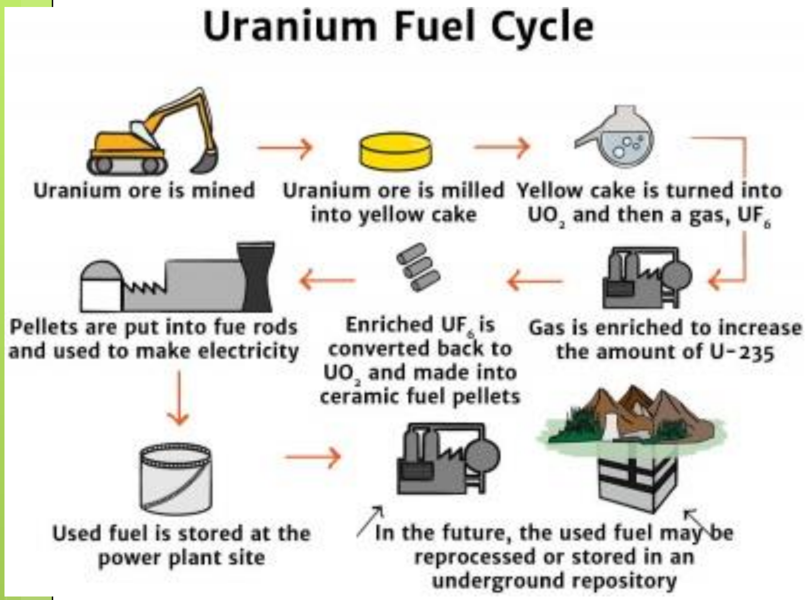


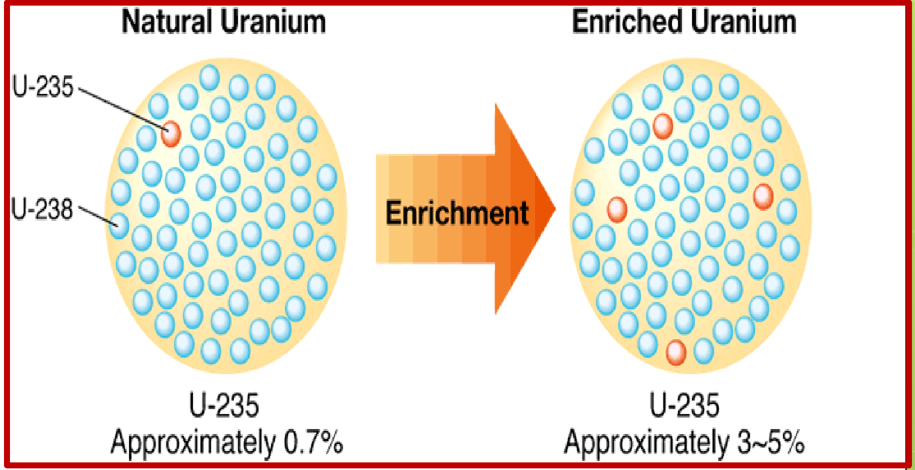
$$\underset{4.468\times10^{9}\,y}{^{238}U} \xrightarrow{(n,\gamma)} \underset{23.45m}{^{239}U} \xrightarrow{\beta^-} \underset{2.356d}{^{239}Np} \xrightarrow{\beta^-} \underset{2.411\times10^{4}\,y}{^{239}Pu}$$



USES OF URANIUM

- Nuclear weapons
- Nuclear fuel
- Nuclear plants
- Nuclear Submarines


Uranium Fuel Cycle
Uranium ore is mined
Uranium ore is milled into yellow cake
Yellow cake is turned into UO₂ and then a gas, UF₆
Pellets are put into fue rods and used to make electricity
Enriched UF₆ is converted back to UO₂ and made into ceramic fuel pellets
Gas is enriched to increase the amount of U-235
Used fuel is stored at the power plant site
In the future, the used fuel may be reprocessed or stored in an underground repository


Natural Uranium
Enriched Uranium
U-235
U-238
Enrichment
U-235
Approximately 0.7%
U-235
Approximately 3~5%


Mining
Milling
Conversion

Preparation of Yellow Cake, U_3O_8 (s) Uranite or Pitchblende ($UO_2 + UO_3$)

- Extraction of uranium is often difficult and the metallurgical procedures vary with the geological environment of the ore. The ore is first crushed and ground to liberate mineral particles.
- The amphoteric oxide (UO_3) is then leached with sulphuric acid.

$$UO_3 + 2H^+ (aq) \longrightarrow UO_2^{2+} (aq) + H_2O$$

$$UO_2^{2+} (aq) + 3SO_4^{2-} (aq) \longrightarrow UO_2(SO_4)_3^{4-} (aq)$$

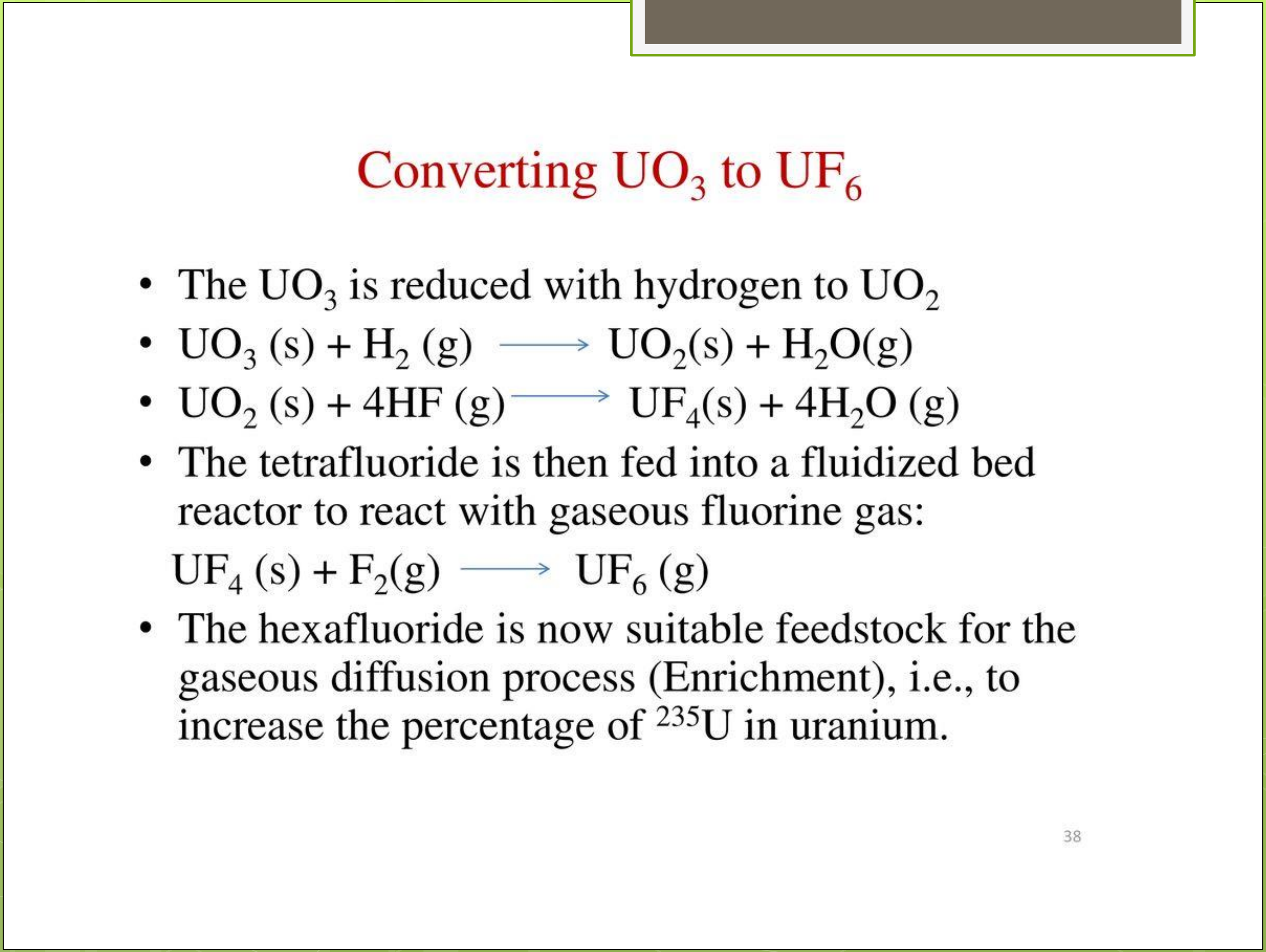
- The basic oxide is converted by a similar process to that of a water soluble $UO_2(CO_3)_3^{4-}$ (aq) ion.
- Two methods are used to concentrate and purify the uranium (ion exchange and solvent extraction). The common method is solvent extraction, uses tertiary amines in an organic kerosene solvent in a continuous process.
- First the amines, R_3N, react with sulfuric acid:

$$2R_3N\text{ (org)} + H_2SO_4\text{ (aq)} \longrightarrow (R_3NH)_2SO_4\text{ (org)}$$

- Then the amine sulphate extracts the uranyl ions into the organic phase while the impurities remain in the aqueous phase. In the case of the uranyl sulfate ion, the following reactions occur:

$$2(R_3NH)_2SO_4\text{ (org)} + UO_2(SO_4)_3^{4-}\text{(aq)} \longrightarrow (R_3NH)_4UO_2(SO_4)_3\text{ (org)} + 2SO_4^{2-}\text{ (aq)}$$

- The solvents are removed by evaporating in a vacuum and ammonium di-uranate, $(NH_4)_2U_2O_7$, is precipitated by adding ammonia to neutralize the solution. The di-uranate is then heated to yield a purified, solid U_3O_8, known as **yellow cake.**



Converting UO_3 to UF_6

- The UO_3 is reduced with hydrogen to UO_2
- $UO_3\,(s) + H_2\,(g) \longrightarrow UO_2(s) + H_2O(g)$
- $UO_2\,(s) + 4HF\,(g) \longrightarrow UF_4(s) + 4H_2O\,(g)$
- The tetrafluoride is then fed into a fluidized bed reactor to react with gaseous fluorine gas:

$UF_4\,(s) + F_2(g) \longrightarrow UF_6\,(g)$

- The hexafluoride is now suitable feedstock for the gaseous diffusion process (Enrichment), i.e., to increase the percentage of ^{235}U in uranium.

Refining and Converting U_3O_8 to UF_6