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SOUTH VALLEY UNIVERSITY
جامعة جنوب الوادي

Physical and Inorganic chemistry
كيمياء فيزيائية وغير عضوية

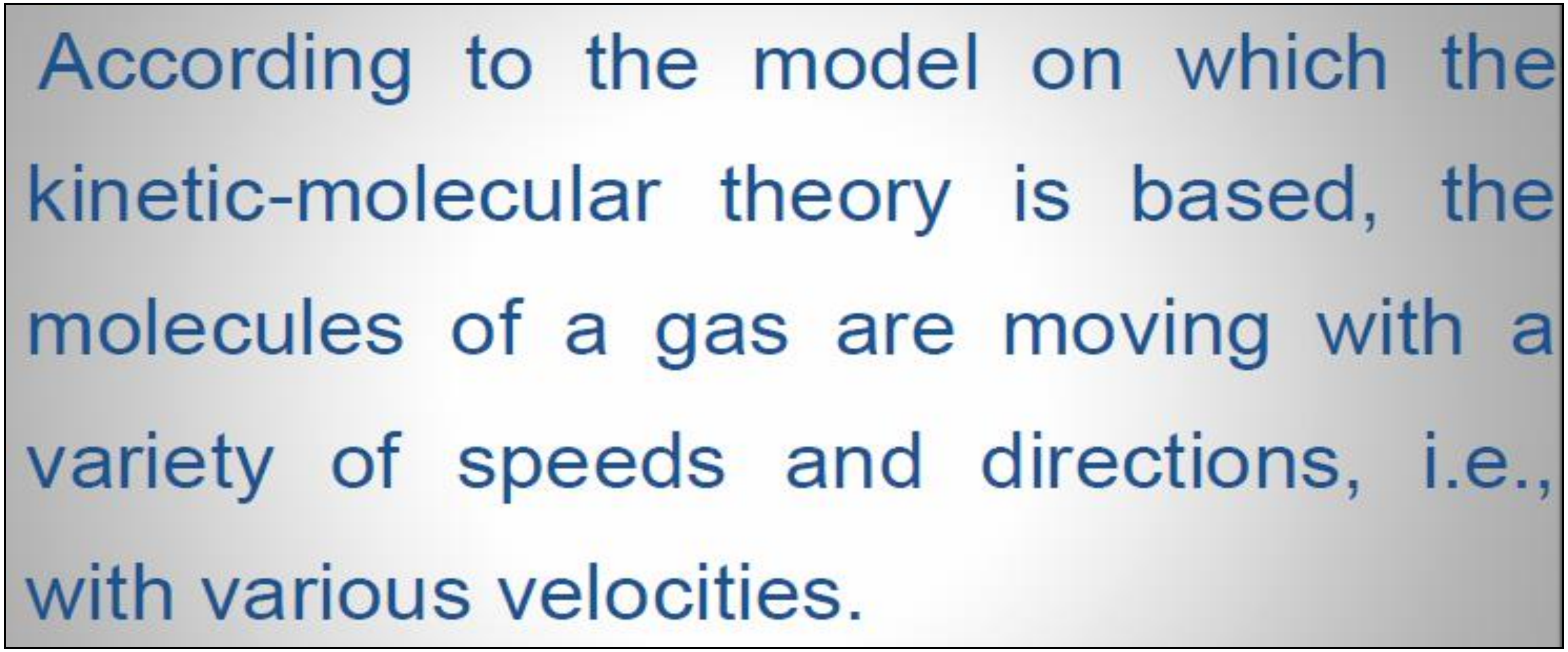
Code : 423Ch
For
4th year Students
(Chem/Microbiology, Chem/Zoology, Chem/Entomology,
Chem/Botany and Chem/Geology)

Kinetic Molecular Theory

Part 1

- Distribution of Velocities of Gas Molecules
- Speeds of Gas Molecules
- Molecular Collision
- Transport Phenomena In Gases

Distribution of Velocities of Gas Molecules in One Direction (Boltzmann Distribution)



According to the model on which the kinetic-molecular theory is based, the molecules of a gas are moving with a variety of speeds and directions, i.e., with various velocities.

Since gases behave similarly in all directions,

- We will investigate the distribution along a particular direction, say the x direction.

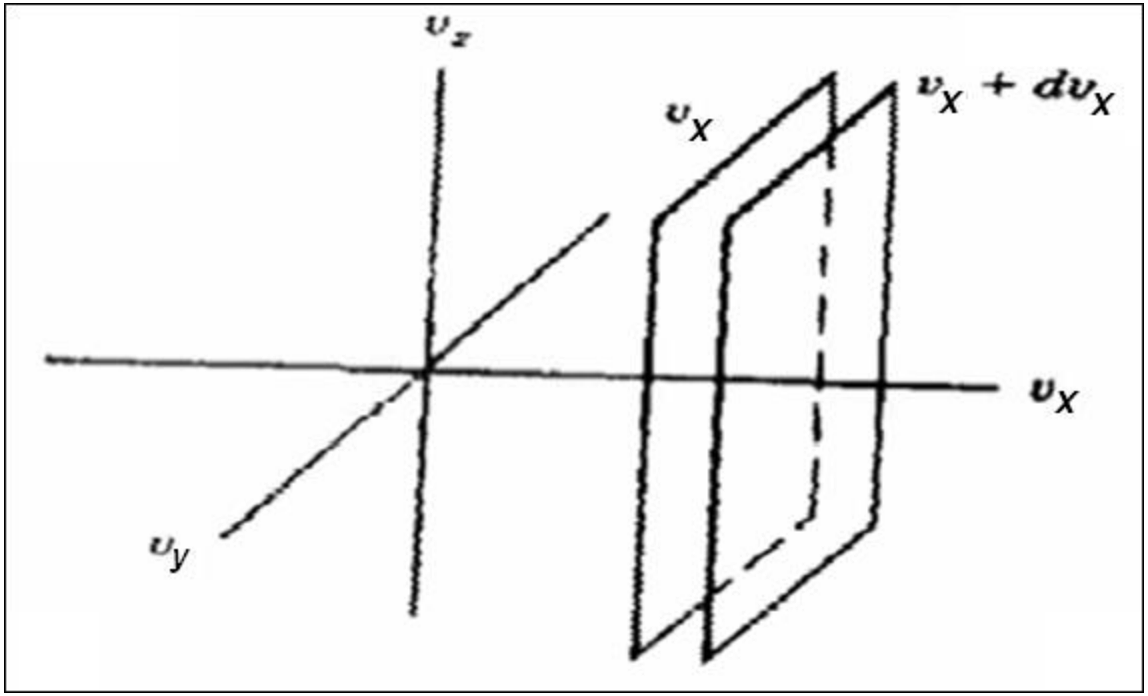
We assume that we have a sample of a gas of:

N total number of molecules .

dN probable number of molecules of velocities in the x direction between U_x and $U_x + dU_x$

dN/N fraction of molecules of velocities between U_x and $U_x + dU_x$ or the probability of finding molecules between the two planes.

This is also the probability of finding molecules with velocity components between two planes



- The probability is expressed also as $f(u_x)\,du_x$ component .

For each molecule $\varepsilon = \frac{1}{2} mU_x^2$

According to the Boltzmann distribution expression,

$$\frac{dN}{N} \alpha\ e^{-(1/2)mu_x^2/kT} du_x \qquad \therefore \frac{dN}{N} = Ae^{-(1/2)mu_x^2/kT} du_x \qquad (1)$$

- This constant can be evaluated by recognizing that integration of the right side of Eq. (1) over all possible values of u_x, that is, from $\mathbf{u_x = -\infty}$ **to** $\mathbf{u_x = +\infty}$, must account for all the velocity points. Thus we can write

$$A\int_{-\infty}^{+\infty} e^{-(1/2)mu_x^2/kT}\ \mathrm{du}_x = 1 \qquad (2)$$

$k = 1.380649\times10^{-23}$ J/K.

- so that the proportionality constant A is given by

$$A = \frac{1}{\int_{-\infty}^{+\infty} e^{-(1/2)mu_x^2/kT}du_x} \qquad (3)$$

- The value of the integral is seen from the table of integrals to be , $\sqrt{2\pi kT/m}$ and we obtain

$$A = \sqrt{\frac{m}{2\pi kT}} \qquad (4)$$

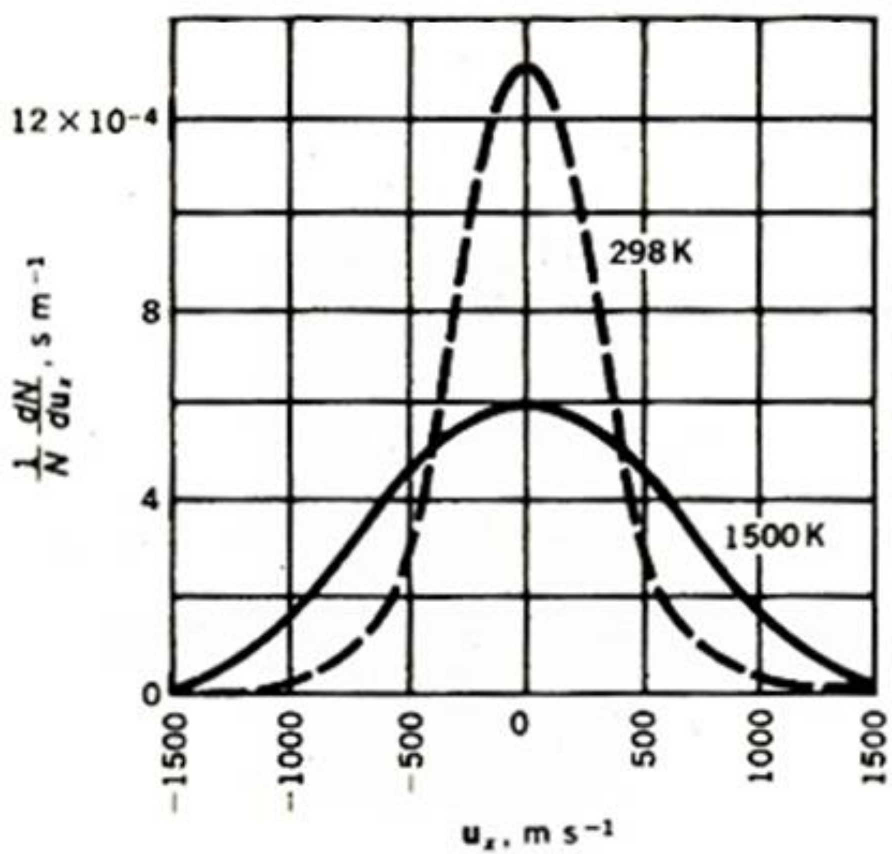
The relation between the Boltzmann constant and the universal gas constant is given by this equation: $R = N_A k$ where R is the ideal gas constant (sometimes called the universal gas constant) and N_A is the Avogadro constant (k is the Boltzmann constant of course).

- Finally, the equation for the distribution over the velocities along the x direction for a sample of N molecules can be written as

$$f(u_x) = \frac{dN/N}{dU_X} = \left(\frac{\mathrm{M}}{2\pi RT}\right)^{1/2} \exp\left(-\frac{\mathrm{M}u_x^2}{2RT}\right) \qquad (5)$$

•Note that **f(u$_x$)** is a velocity **probability density** so that the probability of finding a molecule with velocity components between u$_x$ and u$_x$+ du$_x$ is given by **f(u$_x$)du$_x$**.

•Graphs of this one-dimensional distribution function can be obtained



Probability density $F(U_x)$ for the velocity of N_2 gas in x direction at two different temperatures

Example 1

Calculate the probability density for u_x of N_2 molecules at 300 K.

$u_x = 300\ ms^{-1}$

Using equation (5)

$$f(u_x) = \left(\frac{M}{2\pi RT}\right)^{1/2} \exp\left(-\frac{Mu_x^2}{2RT}\right)$$

$$= \left[\frac{0.028\,kg\,mol^{-1}}{2\pi(8.314\,JK^{-1}mol^{-1})(300K)}\right]^{1/2} \exp\left[-\frac{(0.028\,kg\,mol^{-1})(300\,ms^{-1})^2}{2(8.314\,JK^{-1}mol^{-1})(300K)}\right]$$

$= 8.065 \times 10^{-4}\ s\ m^{-1}$

Exercise
Calculate the probability density of N2 at 0 and 600 K.

- The speed u of a molecule is related its component velocities by

$$u^2 = u_x^2 + u_y^2 + u_z^2$$

- Therefore, F(u) du is the probability of finding a molecule with a speed between u and u + du .
- The one-dimensional distribution can be combined to give the fraction of the molecules that have velocity components between u_x and u_x+du_x, u_x and u_y+du_y and u_z and u_z+du_z.

- It is given analytically ;

$$f(u_x, u_y, u_z)\, du_x du_y, du_z = \frac{dN}{N}$$

$$\therefore \frac{dN}{N} = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left[-\frac{m}{2kT}\left(u_x^2 + u_y^2 + u_z^2\right)\right] du_x du_y du_z$$

- The probability of finding a molecule with velocity components between u and u+ du is given by

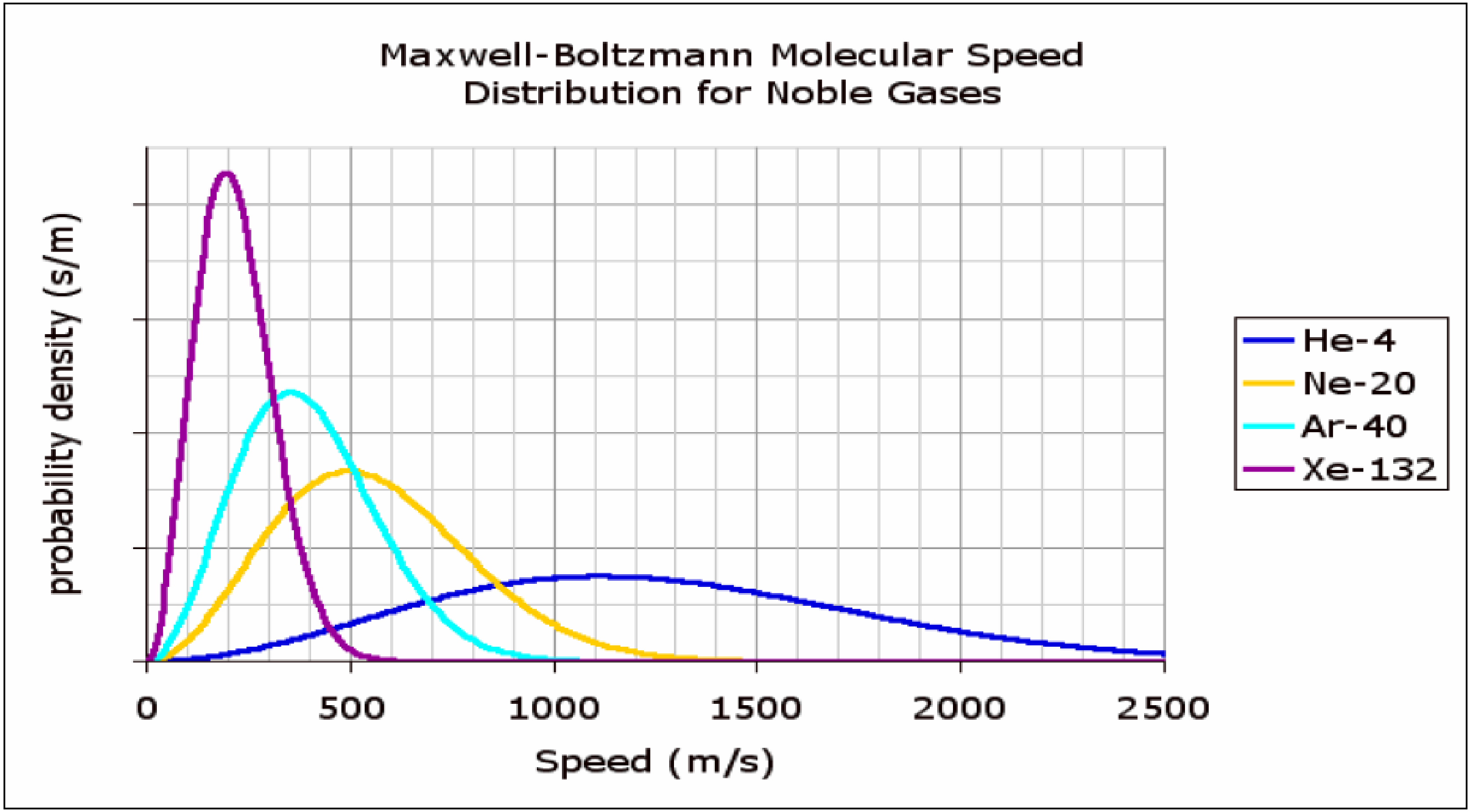
$$F(u)du = 4\pi u^2 \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(\frac{-mu^2}{2kT}\right) du$$

- The probability density F(u) is

$$F(u) = 4\pi u^2 \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(\frac{-mu^2}{2kT}\right)$$

- The probability density at a speed of 0 is zero.

- The probability density increases with the speed up to a maximum and then declines.


Maxwell-Boltzmann Molecular Speed
Distribution for Noble Gases
probability density (s/m)
0
500
1000
1500
2000
2500
Speed (m/s)
He-4
Ne-20
Ar-40
Xe-132

Example 2

A flask contains of N_2 molecules at 100 K. How many molecules have a velocity in the range 500.0-500.1 ms^{-1}?

Suppose that we have a sample of 1 mol of N_2

$$m = \frac{\text{mol. wt of } N_2}{\text{Avogadro number}}$$

$$m = \frac{28}{6.022x10^{23}} = 4.65x10^{-26} kg$$

$$\frac{dN}{N_A} = 4\pi u^2 \left(\frac{m}{2\pi kT}\right)^{1/2} \exp\left(-\frac{mu^2}{2kT}\right) du$$

$$= 4\pi(500ms^{-1})^2 \left(\frac{(4.65x10^{-26} kg)(T / kgm^2 s^{-2})}{2\pi(1.381x10^{-23} JK^{-1})(100K)}\right)^{1/2}$$

$$Exp\left(-\frac{(4.65x10^{-26} kg)(500\, ms^{-1})^2 (J / kgm^2 s^{-1})}{2\pi(1.38x10^{-23})(JK^{-1})(100\, K)}\right)(0.1\, \mathrm{ms}^{-1})$$

$$\frac{dN / N_A}{du} = 5.79x10^{-4} sm^{-1}$$

The number of molecules have velocities in the range 500.0-500.1 ms^{-1}

$$dN = (5.79x10^{-4})(6.022x10^{23})(0.1) = 3x10^{19} \text{ molecules}$$

and the percent of them is given as follows:

$$\frac{dN}{N}x100 = \frac{3x10^{19}}{6.02x10^{23}}x100 = 4.98x10^{-3}\%$$

Kinetic Molecular Theory

Part 2

The speed of the gas molecules is of three types:

- Most Probable Speed (u_p)

- Mean (average) Speed ($\bar{u}$)

- Root mean-square Speed (u_{rms}).

Speeds of Gas Molecules

Most probable speed u_p :

It is the speed at the maximum of F(u). By Differentiating and setting dF/du equal to zero, we find

$$F(u) = 4\pi u^2 \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(\frac{mu^2}{2kT}\right)$$

$$\frac{dF(u)}{du} = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mu^2/2kT}\left[8\pi u + 4\pi u^2\left(-\frac{mu}{kT}\right)\right] = 0$$

$$\therefore u_p = \left(\frac{2kT}{m}\right)^{1/2} = \left(\frac{2RT}{M}\right)^{1/2}$$

Mean speed ($\bar{u}$):

It is calculated as the average of (u) using the probability distribution F(u):

$$\bar{u} = \int_0^\infty uF(u)\,du$$

Substituting

$$F(u) = 4\pi u^2 \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(\frac{mu^2}{2kT}\right)$$

and performing the integral we find

$$\bar{u} = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\int_0^\infty \exp\left(-\frac{mu^2}{kT}\right)u^2 du$$

$$\therefore \bar{u} = \left(\frac{8kT}{\pi m}\right)^{1/2} = \left(\frac{8RT}{\pi M}\right)^{1/2}$$

Root-mean square speed (u_{rms}):

Which is defined as the square root of $\overline{u^2}$

$$u_{rms} = (\overline{u^2})^{1/2} = \left[\int_0^\infty u^2 F(u)du\right]^{1/2}$$

Substituting

$$F(u) = 4\pi u^2 \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(\frac{mu^2}{2kT}\right)$$

and using tables again, we find

$$u_{rms} = \left(\frac{3kT}{m}\right)^{1/2} = \left(\frac{3RT}{M}\right)^{1/2}$$

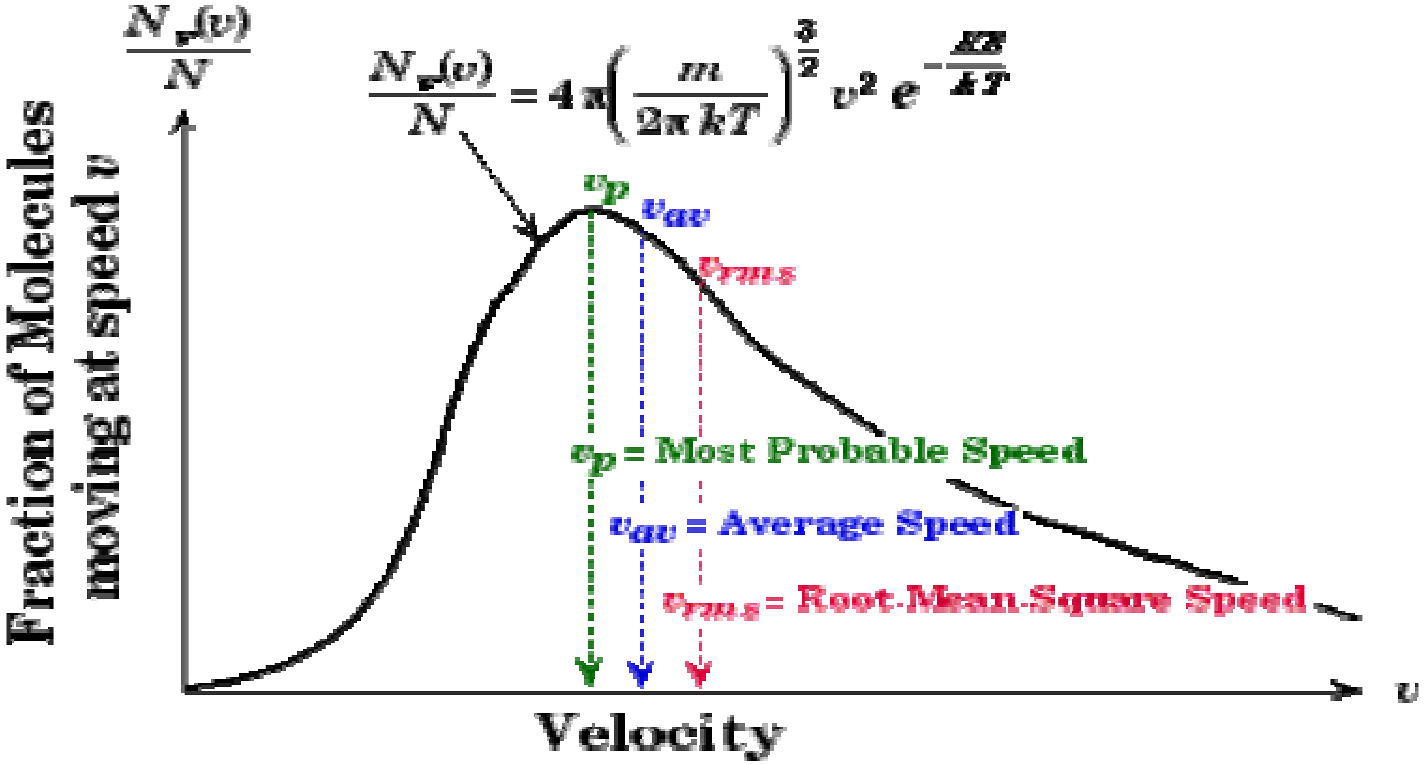
From these three calculations,

$$u_p = \left(\frac{2kT}{m}\right)^{1/2} = \left(\frac{2RT}{M}\right)^{1/2}$$

$$\overline{u} = \left(\frac{8kT}{\pi m}\right)^{1/2} = \left(\frac{8RT}{\pi M}\right)^{1/2}$$

$$u_{rms} = \left(\frac{3kT}{m}\right)^{1/2} = \left(\frac{3RT}{M}\right)^{1/2}$$

We can see that at any temperature $u_{rms} > \overline{\mathrm{u}} > \mathrm{u}_{\mathrm{p}}$



$$v_p = \sqrt{2\frac{kT}{m}} \qquad v_{av} = \sqrt{\frac{8}{\pi}\frac{kT}{m}} \qquad v_{rms} = \sqrt{3\frac{kT}{m}}$$

- ✓ Each of these speeds is proportional to $(T/M)^{1/2}$.
- ✓ Each increases with temperature
- ✓ Each decreases with molar mass. Lighter molecules therefore move faster than heavier molecules on average, as shown in the following table.

Various types of average speeds of gas molecules

Gas	$(u^2)^{1/2}$/m s^{-1}	(u)/m s^{-1}	u_p/m s^{-1}
H_2	1920	1769	1568
O_2	482	444	394
CO_2	411	379	336
CH_4	681	627	556

Example 1

Calculate the The different types of speeds of hydrogen molecules at 0°C.

$$u_p = \left(\frac{2RT}{M}\right)^{1/2} = \left[\frac{(2)(8.314\ Jk^{-1}mol^{-1})(273\ k)}{(2.016\ x10^{-3}\ kg\ \ \mathrm{mol}^{-1})}\right]^{1/2} = 1.50 \times 10^{3}\ \mathrm{m\ s^{-1}}$$

$$\bar{u} = \left(\frac{8RT}{\pi M}\right)^{1/2} = \left[\frac{(8)(8.314\ Jk^{-1}mol^{-1})(273\ k)}{(3.146)(2.016\ x10^{-3}\ kg\ \ \mathrm{mol}^{-1}}\right]^{1/2} = 1.69 \times 10^{3}\ \mathrm{m\ s^{-1}}$$

$$u_{rms} = \left(\frac{3RT}{M}\right)^{1/2} = \left[\frac{3(8.314 Jk^{-1} mol^{-1})(273.15k)^{1/2}}{2.06x10^{-3}\, kg\, \mathrm{mol}^{-1}}\right] = 1.84 \text{ x } 10^{3} \text{ m s}^{-1}$$

The root-mean square speed of a hydrogen molecule at 0°C is 6620 kmh^{-1}, but at ordinary pressures it travels only an exceedingly short distance before colliding with another molecule and changing direction.

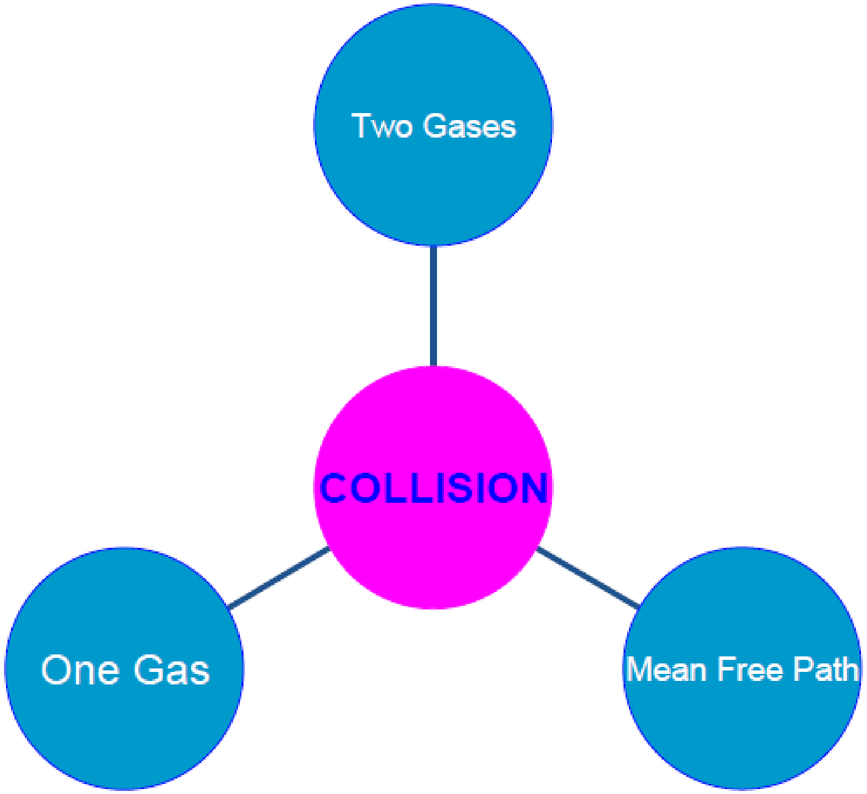
Exercise

How many molecules have a velocity exactly equal to 500 ms^{-1}?

Kinetic Molecular Theory

Part 3

Collision properties of gas molecules

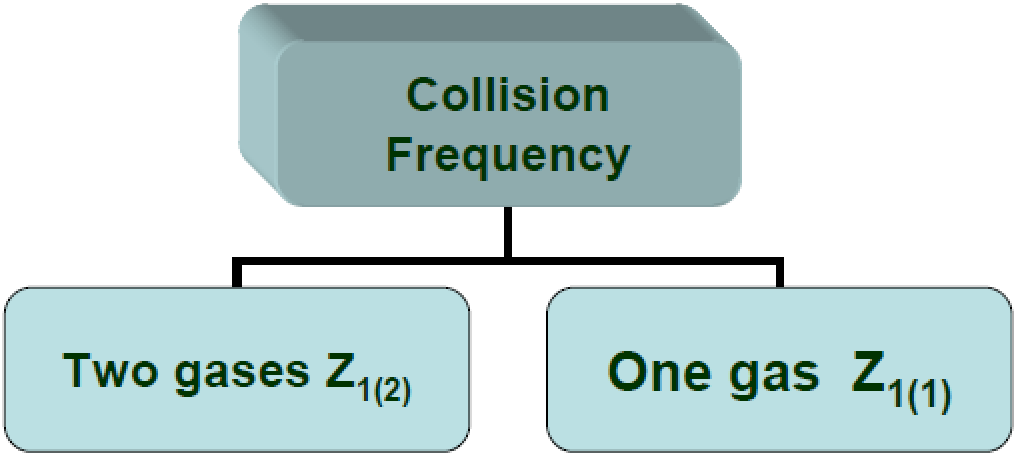


Two Gases

COLLISION

One Gas

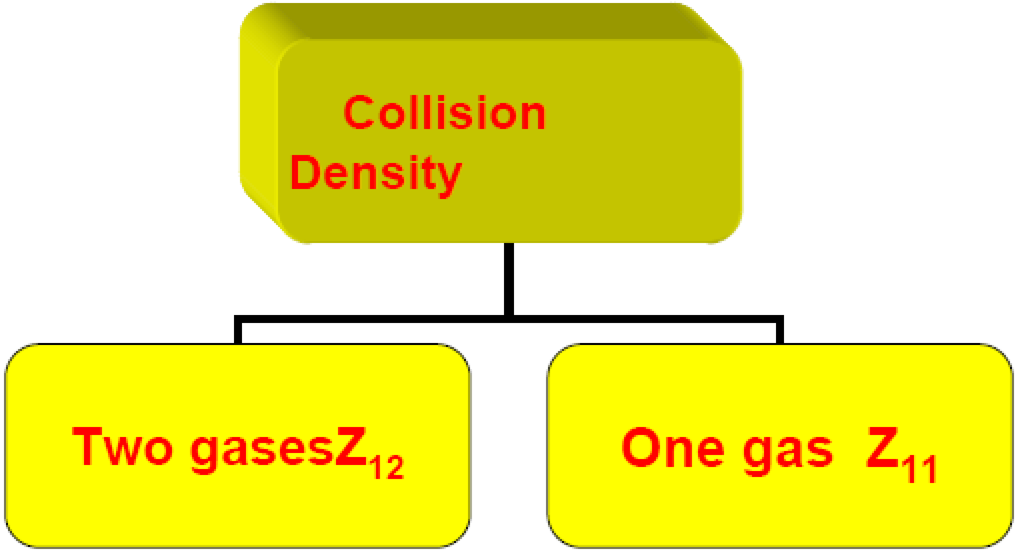
Mean Free Path



Collision Frequency

Two gases $Z_{1(2)}$

One gas $Z_{1(1)}$



Collision Density

Two gasesZ_{12}

One gas Z_{11}

Molecular Collision

Collision Frequency:

- The collision frequency is ***the number of collisions of molecules per unit time***, where
- $Z_{A(B)}$ for the collision between the molecules of two different gases A and B.
- $Z_{A(A)}$ for collision between identical molecules.
- let us consider a cylinder of length l (m) containing N_A and N_B molecules of gas A and gas B, respectively. These molecules have;
- Diameters d_A and d_B (m) and collision diamete

$$d_{AB} = (d_A + d_B)/2$$

- Atomic masses m_A and m_B (kg), molecular masses M_A and M_B (kg) and reduced mass .

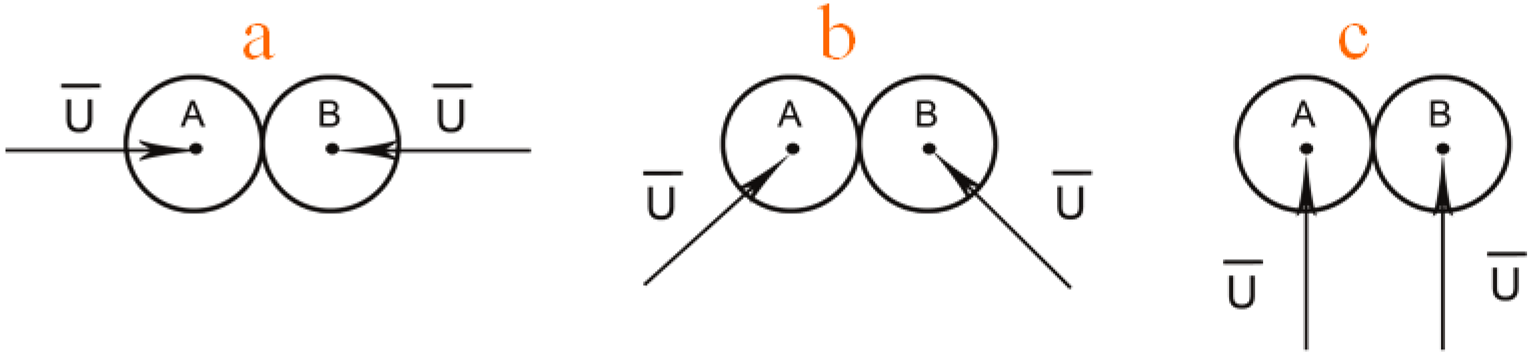
Reduced mass μ

$$\mu = \frac{1}{m_A} + \frac{1}{m_B} = \frac{N_A}{M_A} + \frac{N_A}{M_B} = N_A \frac{M_A + M_B}{M_A M_B}$$

- Densities ρ_A and ρ_B (m^{-3}), number of molecules per unit volume or $\rho = N/V$
- Velocities u_A and u_B (ms^{-1}) and mean relative velocity

$$\overline{u_{AB}} = \left(\frac{8RT}{\pi\mu}\right)^{1/2} \quad \longleftarrow \text{Why?}$$

The distribution of relative velocities between two molecules depends on the velocity of each one and the angle of approach:



$\overline{U}_{AB} = 2\overline{U}$

$U_{AB} = \sqrt{2}U$

$\overline{U}_{AB} = 0$

If the velocities of A equals that of B:

a) The two molecules move towards each other

$$\bar{U}_{AB}=\bar{U}_A+\bar{U}_B=2\bar{U}$$

b) The two molecules move together in the same way

$$\bar{U}_{AB}=\bar{U}_A-\bar{U}_B=0$$

c) The two molecules move with an angle of 90o (most probable case).

$$\bar{U}_{AB}=\sqrt{(\bar{U}_A)^2+(\bar{U}_B)^2}=[(\bar{U}_A)^2+(\bar{U}_B)^2]^{1/2}$$

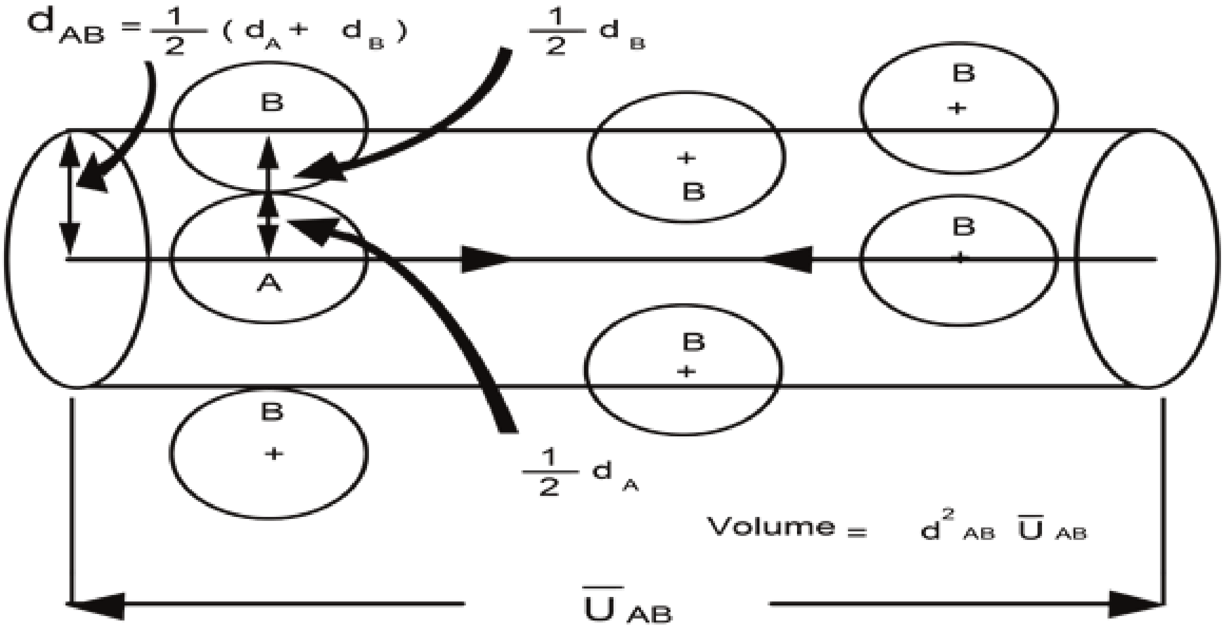
$$\bar{U}_A=\bar{U}_B$$

$$\bar{U}_{AB}=\sqrt{2}\bar{U}$$

$$\bar{U}_{AB} = \sqrt{(\bar{U}_A)^2 + (\bar{U}_B)^2} = [(\bar{U}_A)^2 + (\bar{U}_B)^2]^{1/2}$$

$$\bar{U} = \left(\frac{8RT}{\pi M}\right)^{1/2}$$

$$\bar{U}_{AB} = \left[\frac{8RT}{\pi.\mu_{AB}}\right]^{1/2}$$



- ☐ hard spherical molecules collide with each other if their centers come within a distance

  $d_{AB} = ½ (d_A+d_B)$, **the collision diameter.**

- Molecules of type B are stationary.
- A molecule of type A will collide in unit time with all molecules of type B that have their centers in a cylinder of

Volume = $\pi d_{AB}^{2} u_{A}$

- A molecule of type A would undergo a

number of collisions = $\pi d_{AB}^{2} u_{A} \rho_{B}$

per unit time.

❑ Molecules of type B are actually not stationary and so the relative speed $\mathbf{u}_{AB}$ should be used in calculating the rate of collisions $\mathbf{z}_{A(B)}$ of a molecule of type A with molecules of type B. Thus,

$$\mathbf{Z}_{A(B)} = \pi d_{AB}^2 \bar{u}_{AB} \rho_B \qquad (1)$$

or

$$Z_{A(B)} = \pi d_{AB}^2 \left(\frac{8RT}{\pi \mu} \right)^{1/2} \rho_B$$

- where $\mathbf{z}_{A(B)}$ is the **collision frequency** of molecules of type A with molecules of type B .

- The collision diameter $\mathbf{d}_{AB}$ has the unit m,
- The relative mean speed ($\mathbf{u}_{AB}$) has the unit m s^{-1},
- The collision frequency has the unit s^{-1}.

- Now a molecule of type A is moving through molecules of type A, rather than molecules of type B, Eq. (1) becomes

$$Z_{A(A)} = \pi d_A^2 \bar{u}_A \rho_A$$

Or

$$Z_{A(A)} = \pi d_A^2 \left(\frac{8RT}{\pi \mu} \right)^{1/2} \rho_A \qquad (2)$$

Example 1

What is the mean relative speed of **H_2** molecules with respect to **O_2**molecules (or oxygen molecules with respect to hydrogen molecules) at 298 ?

The molecular masses are:

$$m_1 = \frac{2.016\ x10^{-3}\ \text{kg mol}^{-1}}{6.022\ x10^{23}\ \text{mol}^{-1}} = 3.348\ x10^{-27}\ \text{kg}$$

$$m_2 = \frac{32.00\ x10^{-3}\ \text{kg mol}^{-1}}{6.022\ x10^{23}\ \text{mol}^{-1}} = 5.314\ x10^{-26}\ \text{kg}$$

$$\mu_{AB} = \frac{1}{m_A} + \frac{1}{m_B} = \frac{m_A + m_B}{m_A . m_B} = 6.022x10^{23}\,\frac{56.448x10^{-27}}{177.9x(10^{-27})^2} = 1.9x10^{50}$$

$$\bar{u}_{12} = \left(\frac{8kT}{\pi\mu}\right)^{1/2} = \left[\frac{8(1.381\ x10^{-23}\ Jk^{-1})(298\ k)}{\pi(3.150\ x10^{-17}\ kg)}\right] = 1824\ m\ s^{-1}$$

Note that the mean relative speed is closer to the mean speed of molecular hydrogen (1920 ms^{-1}) than to that of molecular oxygen (482 ms^{-1}) .

Kinetic Molecular Theory

Part 4

Collision Density

It is the number of collisions per unit tim per unit volume.

For two gases:

To calculate the number of collisions of molecules of type 1

with molecules of type 2 per unit time per unit volume of gas

$$Z_{12} = Z_{1(2)} x \rho_1$$

$$Z_{12} = \rho_1 . \rho_2 . \pi . d_{12}^2 . \bar{u}_{12}$$

For only one gas:

The number of collisions of molecules of type 1 with other molecules of type 1 per unit time per unit volume of gas will be reduced to

$$Z_{11} = \frac{1}{2}\rho^2 . \pi . d^2 . \bar{u}_{11}$$

The factor of 1/2 has been introduced to avoid double counting of the collisions. (so one A molecule colliding with another A molecule is counted as one collision regardless of their actual identities). For collisions of A and B molecules present at number densities ρ_A and ρ_B the collision density is

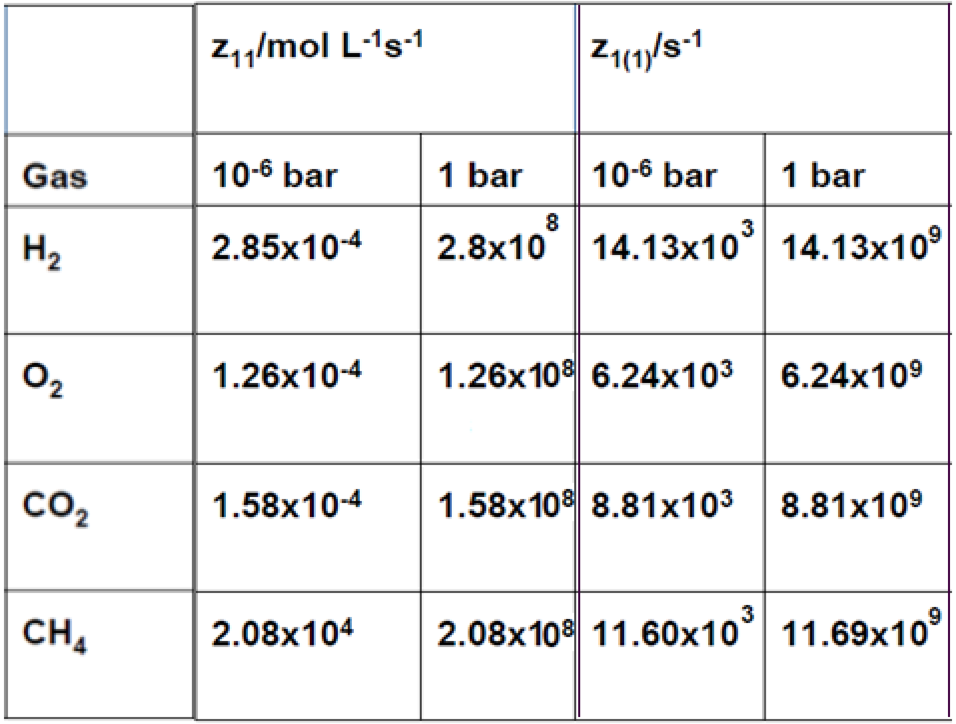
$$Z_{12} = \pi . d^2 . \bar{u}_{12} \rho_1 . \rho_2$$

The collision density is expressed in mol m^{-3} s^{-1}

The collision density is on interest because it sets an upper limit on the rate with which two gas molecules can react. Actual chemical reaction rates are usually much smaller than the collision rates, indicating that not every collision leads to reaction.

Collision frequencies z1(1) and collision densities z11 for four gases are given In next Table at 25 °C. The collision densities are expressed in mol $L^{-1} . s^{-1}$ because it is easier to think about chemical reactions in these units.

1 Pa = 1 N / m^2 = 10^{-5} bar = 7.5×10^{-3} Torr = 0.987 atm



	z_{11}/mol $L^{-1}s^{-1}$		$z_{1(1)}/s^{-1}$	
Gas	10^{-6} bar	1 bar	10^{-6} bar	1 bar
H_2	2.85×10^{-4}	2.8×10^{8}	14.13×10^{3}	14.13×10^{9}
O_2	1.26×10^{-4}	1.26×10^{8}	6.24×10^{3}	6.24×10^{9}
CO_2	1.58×10^{-4}	1.58×10^{8}	8.81×10^{3}	8.81×10^{9}
CH_4	2.08×10^{4}	2.08×10^{8}	11.60×10^{3}	11.69×10^{9}

Example 1

Calculate the collision frequency and collision density in ammonia, r=190pm, at 25°C and 100kPa. (M_{NH3} = 17.03 g/mol)

Note that he did not mention to ammonia concentration or volume (there is no n or V variables)

The collision frequency is

$$Z = \pi d_{NH_3}^2 \bar{U}_{A(A)} \rho_{NH_3}$$

$$\bar{U}_{A(A)} = \left(\frac{8kT}{\pi m} + \frac{8kT}{\pi m} \right)^{1/2} = 4\left(\frac{kT}{\pi m} \right)^{1/2}$$

$$\rho_{NH_3} = \frac{N}{V} = \frac{nN_A}{V} = \frac{PN_A}{RT} = \frac{P}{kT}$$

$$\pi d_{NH_3}^2 = \pi (2r_{NH_3})^2 = 4\pi r_{NH_3}^2$$

$$Z_{A(A)} = \pi d_{NH_3}^2 \bar{U}_{A(A)} \rho_{NH_3} = 4\pi r^2 . 4\left(\frac{kT}{\pi m} \right)^{1/2} . \frac{P}{kT}$$

$$Z_{A(A)} = 16Pr^2\left(\frac{\pi}{mkT}\right)^{1/2}$$

$$Z_{A(A)} = 16x(100x10^3 Pa)x(190x10^{-12} m)^2 x\left[\frac{\pi}{(17.03x1.66x10^{-27})^2 x(1.381x10^{-23})x298}\right]^{1/2}$$

$$;1u = 1.66x10^{-27}\ kg;\ u: atomic\ mass\ unit$$

$$Z_{A(A)} = 9.49x10^9 s^{-1}$$

The collision density $Z_{A(A)}$

$$Z_{AA} = Z_{AA}.\rho_{NH_3} = \frac{1}{2}Z_{A(A)}.\frac{P}{kT} = \frac{1}{2}x9.49x10^9 s^{-1}x\left(\frac{100x10^3 pa}{1.381x10^{-23} J.K^{-1}\times(298K)}\right)$$

$$Z_{AA} = 1.15x10^{15} s^{-1}.mol.m^{-3}$$

Mean Free Path

- The mean free path λ is the average distance traveled between collisions.
- It can be computed by dividing the average distance traveled per unit time by the collision frequency.
- For a molecule moving through like molecules.

$$\lambda = \frac{1}{2^{1/2} \rho \pi d^2}$$

Assuming that the collision diameter d is independent to temperature,

the temperature and pressure dependence of the mean free path may be obtained by substituting the ideal gas law in the form $\rho = P/kT$:

$$\lambda = \frac{1}{\sqrt{2}} \frac{kT}{P.\pi.d^2}$$

Thus, at constant temperature, the mean free path is inversely proportional to the pressure.

Example 2

For oxygen at 25 ^{o}C the collision diameter is 0.361 nm. What is the mean free path at 1.0 bar pressure, and (b) 0.1 Pa pressure?

a)

$$\rho = N/V = PN_{A}/RT = \frac{(1\ \text{bar})(6.022\ \text{x}10^{23})(10^{3}\ \text{Lm}^{-3})}{(0.083145\ \text{L bar K}^{-1}\text{mol}^{-1})(298\ \text{K})} = 2.43\ \text{x}\,10^{25}\ \text{m}^{-3}$$

$$\lambda = \frac{1}{2^{1/2}\rho\pi d^{2}}$$

$$\lambda = [(1.414)(2.43\text{x}10^{25}\text{m}^{-3})\pi(3.61\text{x}10^{-10}\text{m})^{2}]^{-1} = 7.11\text{x}10^{-8}\text{m}$$

Why he did not use Boltzmann constant k instead of gas constant?

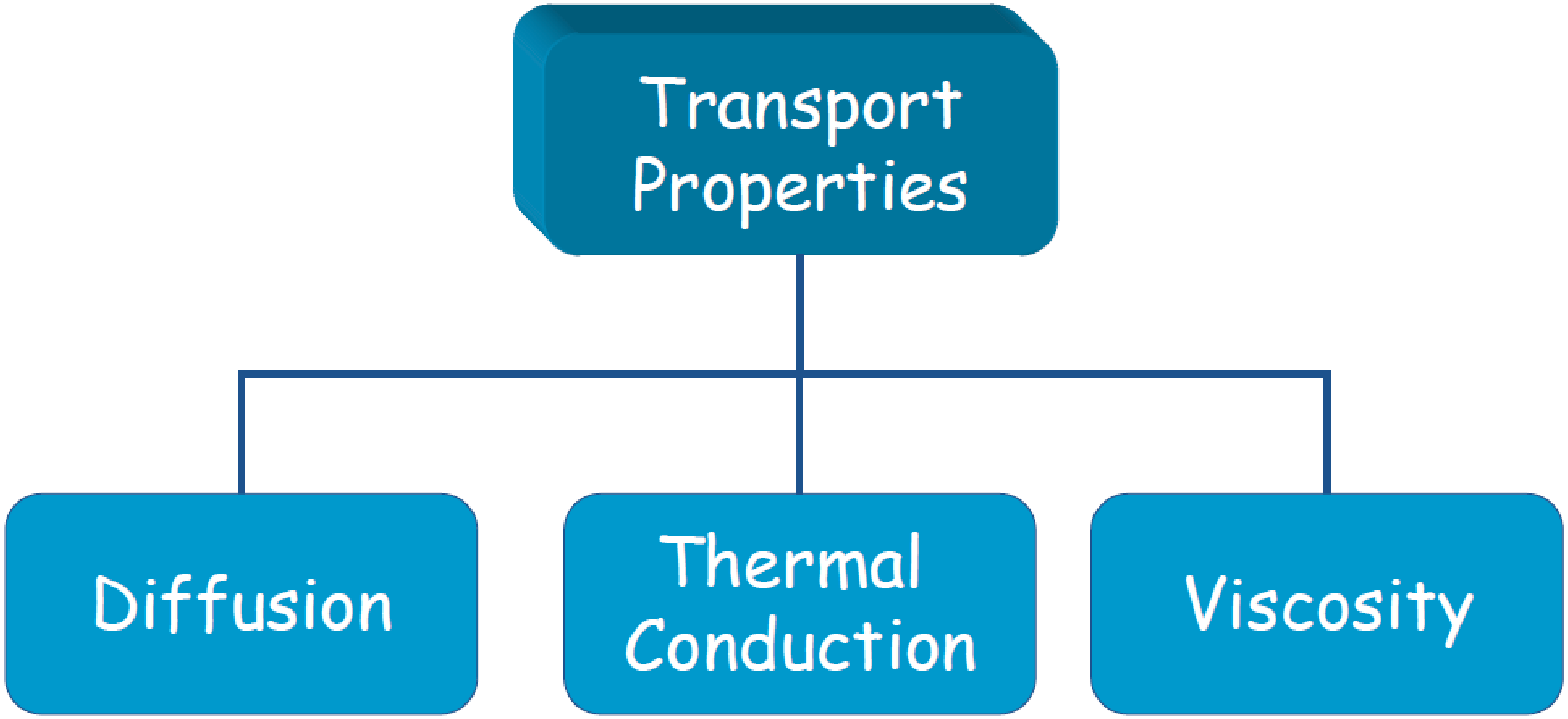
(b)

At pressure so low that the mean free path becomes comparable with the dimensions of the containing vessel, the flow properties of the gas become markedly different from those at higher pressures.

Kinetic Molecular Theory

Part 5

TRANSPORT PHENOMENA IN GASES



Transport Properties

- Diffusion
- Thermal Conduction
- Viscosity

If a gas is not uniform with respect to

- Composition
- temperature, and
- velocity,

transport processes occur until the gas becomes uniform.

Examples:

(1) Open a bottle of perfume at the front of a classroom:
Good smell moves from front row to rear (Diffusion).

(2) Metal bar, one end hot and one end cold:
Heat flows from hot to cold end until temperature becomes (Thermal Conduction)

TRANSORT PROPERTIES

TRANSPORT

PROPERTIES

OF GASES

DIFFUSION

Transport of (labelled) particles

THERMAL CONDUCTION

Transport of thermal energy

VISCOSITY

Transport of momentum in one direction through a gas in another direction

In each case,

- Rate of flow ∞ Rate of change of some property with distance, a so-called gradient
- All have same mathematical form:

Flow of____(per unit area, unit time) = (___x gradient___) (matter) (diffusion coefficient) (concentration)

J_{iz} $-D$ $\frac{dc_i}{dz}$

The flux of component i in the z direction due to diffusion is proportional to the concentration gradient dci/dz, according to Fick's law:

$$\boxed{J_{iz} = -D\frac{dc_i}{dz}}$$

Diffusion: Fick's Law

J_{iz} is the flux and

*Expressed in terms of quantity per unit area per unit time.

* J_{iz} has the units mol m^{-2} s^{-1},

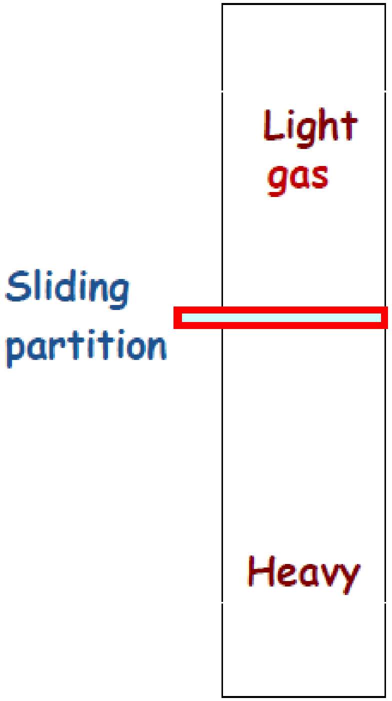
* dc_i/dz has the units of mol m^{-3}

* D has units of m^2 s^{-1}.

* The negative sign comes from the fact that if C_i increases in the positive z direction dCi/dz is positive, but the flux is in the negative z direction because the flow is in the direction of lower concentrations

Determination of D for the diffusion of one gas into another

- The sliding partition is withdrawn for a definite interval of time.
- From the average composition of one chamber or the other, After a time interval, D may be calculated.



Thermal Conduction: Fourier's Law

Transport of heat is due to a gradient in temperature.

(heat) (thermal conductivity) (temperature)

$q_z = - K_T \frac{dT}{dz}$

$$\therefore q_z = -K_T \frac{dT}{dz}$$

- K is the thermal conductivity.
- q_z has the units of J m^{-2} s^{-1} and
- d_T/d_z has the units of K m^{-1},
- K_T has the units of J m^{-1} s^{-1} K^{-1}.
- The negative sign indicates that if d_T/d_z is positive, the flow of heat is in the negative z direction, which is the direction toward lower temperature.

Viscosity: is a measure of the resistance that a fluid offers to an applied shearing force.

- Consider what happens to the fluid between parallel planes
- when the top plane is moved in the y direction at a constant speed relative to the bottom plane while maintaining a constant distance between the planes (coordinate z)
- The planes are considered to be very large, so that edge effects may be ignored.

- The layer of fluid immediately adjacent to the moving plane moves with the velocity of this plane.
- The layer next to the stationary plane is stationary; in between the velocity usually changes linearly with distance,.

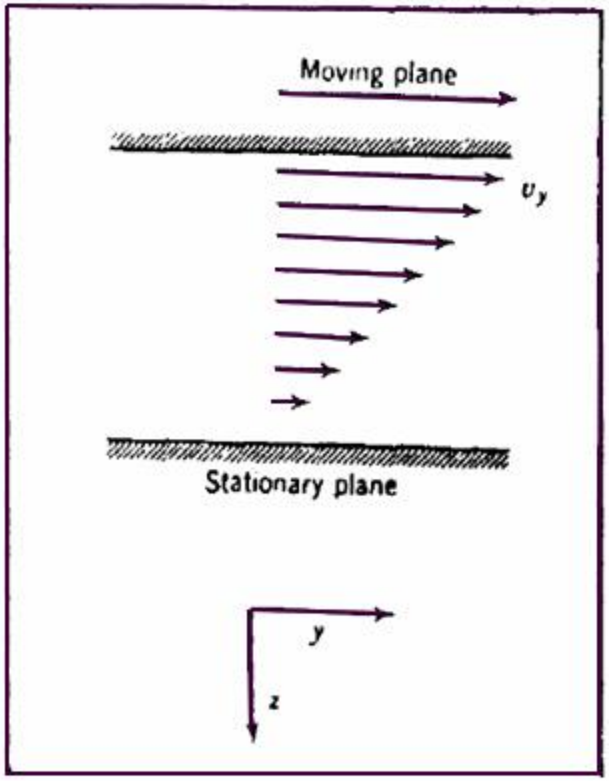
The velocity gradient

Rate of change of velocity with respect to distance measured perpendicular to the direction of flow is represented by

du_y / dz

The viscosity η is defined by the equation

$$F = -\eta \frac{du_y}{dz} \qquad (6.3)$$



- F is the force per unit area required to move one plane relative to the other.
- The negative sign comes from the fact that if F is in the +y direction, the velocity u_y decreases in successive layers away from the moving plane and du_y/dz is negative.

- The thermal conductivity is determined by the hot wire method
- Determination of the rate of flow through a tube, the torque on a disk that is rotated in the fluid, or other experimental arrangement.
- The outer cylinder is rotated at a constant velocity by an electric motor.

- Since $1N = 1$ kg m s^{-2}, 1 Pa s = 1 kg m^{-1} s^{-1}. A fluid has a viscosity of 1 Pa s if a force of 1 N is required to move a plane of 1 m^2 at a velocity of 1 m s^{-1} with respect to a plane surface a meter away and parallel with it.

- The cgs unit of viscosity is the poise, that is, 1 $gs^{-1}cm^{-1}$
  0.1 Pa S = 1 poise.

Kinetic Molecular Theory

Part 6

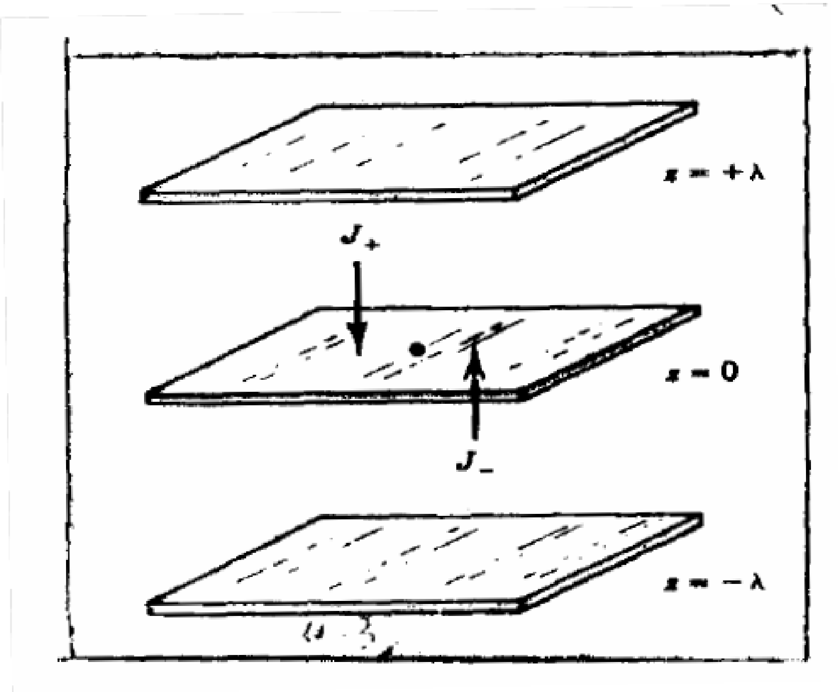
Calculation of Transport Coefficients

To calculate the transport coefficients

D, K_T, and η

even for hard-sphere molecules, needs to consider how the Maxwell-Boltzmann distribution is disturbed by a gradient of concentration, temperature or velocity.

Diffusion Coefficient



Planes constructed at distance ±λ (the mean free path) from the origin. The concentration gradient is in the z direction.

Where ρ_o is the number density of particles in the plane at $z = 0$.

The density of particles at $z = +\lambda$ is given by the term in brackets

- Consider the diffusion of molecules in a concentration gradient in the z direction and we are at $z = 0$.

- Imagine that we construct planes parallel to the xy plane at **x** = ±λ, where λ is the mean free path.

- We choose planes at the mean free path because molecules form more distant points will, on average, have suffered collisions before reaching $z = 0$.

- Calculate the flux of particles across z = 0 due to the molecules above (z>0) and below **(z<0)**. The flux across **z = 0** from above is

$$J_+ = \left[\rho_0 + \lambda \left(\frac{d\pi}{dz} \right) \right] \frac{\bar{u}}{4}$$

Similarly, the flux across z = 0 due to the molecules below z = 0 is

$$J_- = \left[\rho_o - \lambda\left(\frac{d\rho}{dz}\right)\right]\frac{\bar{u}}{4}$$

The net flux of particles across the plane z = 0 is then

$$J = -\frac{1}{2}(\bar{u})\frac{d\rho}{dz}$$

This equation can be compared with Eq. 5.1 to obtain

$$D_a = \frac{1}{2}(u)\lambda = \left(\frac{kT}{\pi m}\right)^{1/2}\frac{1}{\rho\pi d^2}$$

- where the subscript 'a' indicates approximate value.

- The exact theoretical expression for the diffusion coefficient of hard spheres is:

$$D = \frac{3\pi}{8}\left(\frac{kT}{\pi m}\right)^{1/2}\frac{1}{\rho\pi d^2} = \frac{3}{8}\left(\frac{RT}{\pi M}\right)^{1/2}\frac{1}{\rho d^2}$$

Example 1

Predict $D_{(O2,N2)}$ of an equimolar mixture of O_2 and N_2 gases at 1.00 atm and 0^0C using d_{O2} = 0.353 nm and d_{N2} = 0.373 nm.

$$\rho = \frac{N}{V} = \frac{nN_A}{V} = \frac{N_A P}{RT} \qquad \therefore \rho = \frac{(101.325\ \text{Pa})(6.022\text{x}\ 10^{23}\ mol^{-1})}{(8.314\ \text{m}^3 PaK^{-1} mol^{-1})(273K)} = 2.69\text{x}10^{25}\ m^{-3}$$

$d_{(O_2,N_2)}$ = (0.353 nm + 0.373 nm)/2 = 0.363 nm

$$d_{(O_2,N_2)} = \frac{3}{8}\left[\frac{(0.314\ \text{JK}^{-1} mol^{-1})(273\ \text{K})}{\pi(32.00\ x10^{-3}\ \text{kg mol}^{-1})}\right]^{1/2}$$

$$x\frac{1}{(3.63x10^{-10} m)^2(2.64x10^{-3} kg\ \text{mol}^{-1})} = 1.59x10^{-5} m^2 s^{-1}$$

A similar simplified model for thermal conductivity of hard spheres yield the approximate value

$$K_T = \frac{1}{T}\frac{\overline{C}u}{3N_A}\lambda(u)\rho = \frac{2\overline{C}u}{3N_A}\left(\frac{kT}{\pi m}\right)^{1/2}\frac{1}{\pi d^2}$$

The exact expression for hard sphere is:

$$K_T = \frac{25}{32}\left(\frac{kT}{\mu n}\right)^{1/2}\frac{C_v}{N_A d^2}$$

Example 2

Calculate the thermal conductivity coefficient for water vapor at 25°C assuming d = 0.50 nm and

$C_v = 25.26\ \mathrm{JK^{-1}\ mol^{-1}}$.

Substituting data into Eq. (4.11) gives

$$K_T = \frac{25}{32}\left[\frac{(1.381\mathrm{x}10^{-23}\ \mathrm{J.K^{-1}})(298\ \mathrm{K})}{\pi(18.02\mathrm{x}10^{-3}\ \mathrm{kg\ mol^{-1}}) / 6.022\mathrm{x}10^{23}\ \mathrm{mol^{-1}})}\right]^{1/2}$$

$$\mathrm{x}\ \frac{25.26\ \mathrm{JK^{-1}mol^{-1}}}{(6.022\mathrm{x}10^{23}\mathrm{mol})(5.0\mathrm{x}10^{-10}\mathrm{m})^2} = 0.027\ \mathrm{Jm^{-1}s^{-1}K^{-1}}$$

Finally, the approximate model for the viscosity of hard spheres yields:

$$\eta_a = \frac{1}{3}\rho(u)m\lambda = \frac{2}{3}\left(\frac{kT}{\pi m}\right)^{1/2}\frac{m}{\pi d^2}$$

whereas the exact expression for hard spheres is

$$\eta = \frac{3}{32\sqrt{2}}\left(\frac{kT}{\pi m}\right)^{1/2}\frac{m}{d^2}$$

Note that this does not imply that real molecules are hard spheres; in fact, we are forcing a model on the experiment. Nevertheless, the results in Table 6.1 show that a consistent set of molecular diameters result from this analysis of the data.

Example 3

Calculate the viscosity of molecular oxygen at 273.2K and 1 bar. The molecular diameter is 0.360 nm.

Using the exact equation for hard spheres, we find:

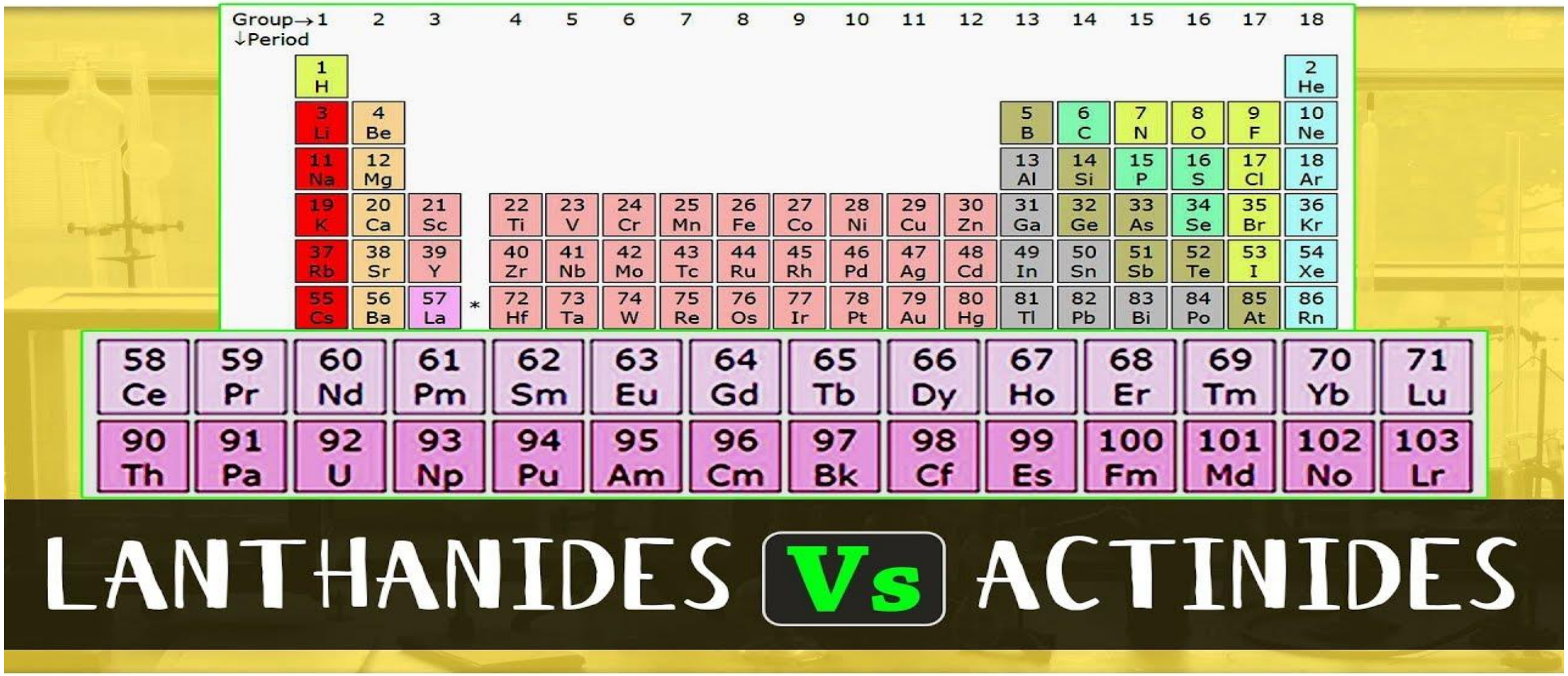
$$m = \frac{32.00 \times 10^{-3}\ \text{kg mol}^{-1}}{6.022 \times 10^{23}\ \text{mol}^{-1}}$$

$$= 5.314 \times 10^{-26}\ \text{kg}$$

$$\eta = \frac{5\pi}{16}\left(\frac{kT}{\pi m}\right)^{1/2} \frac{m}{\pi d^2}$$

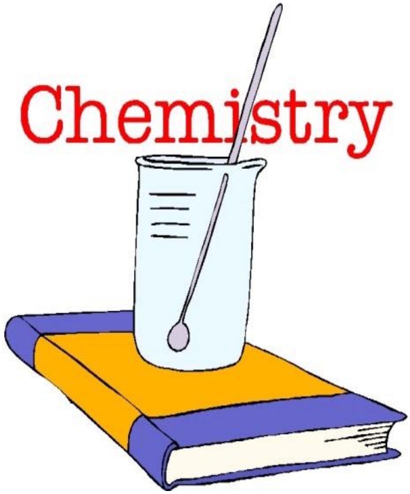
$$= \frac{5\pi}{16}\left[\frac{(1.380\text{x}10^{-23}\text{JK}^{-1}(273.2\text{K})}{\pi(5.314\text{x}10^{-26}\text{kg})}\right]^{1/2}\frac{5.314\text{x}10^{-26}\text{kg}}{\pi(0.360\text{x}10^{-9}\text{m})^2}$$

= 1.926 x 10-5 kg m^{-1} s^{-1}



Inorganic Chemistry

رابعة كيمياء مشترك



The Lanthanide and actinides Elements

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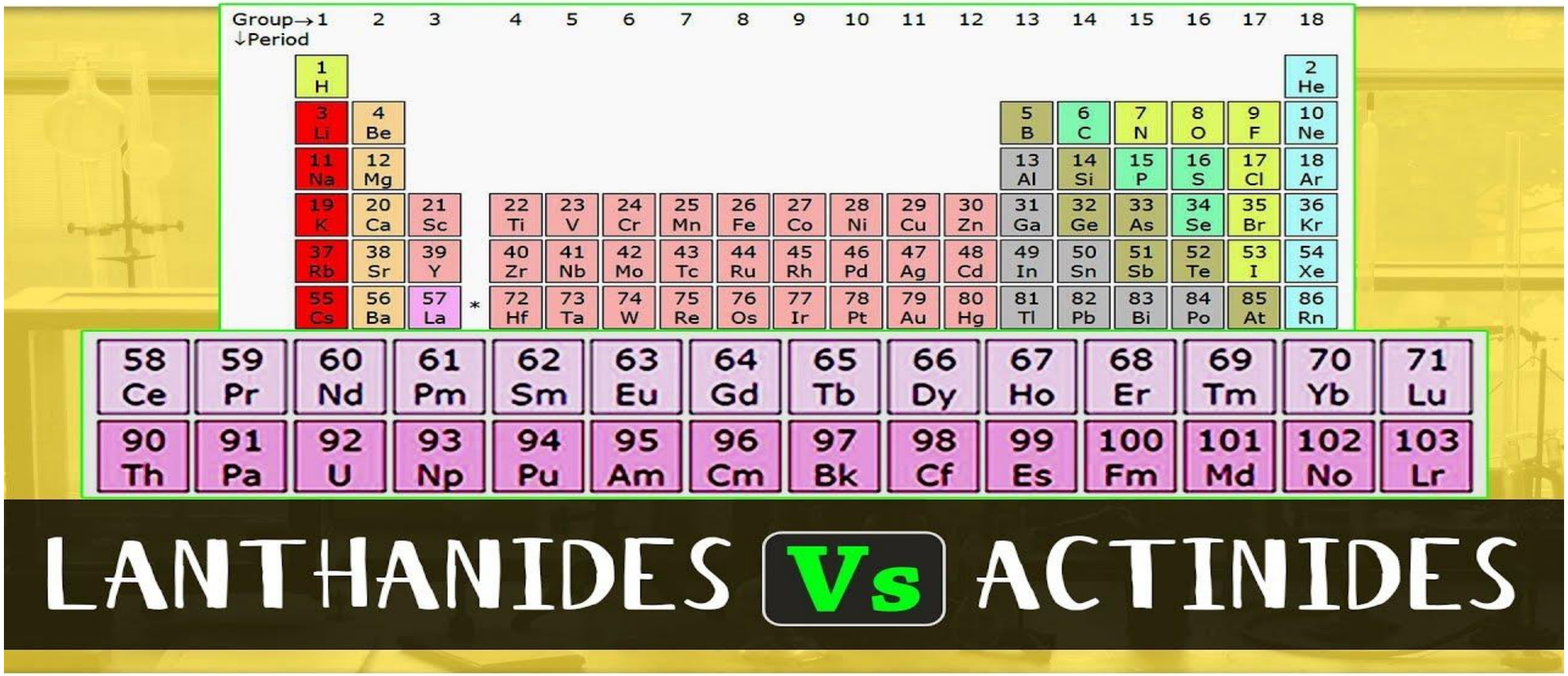
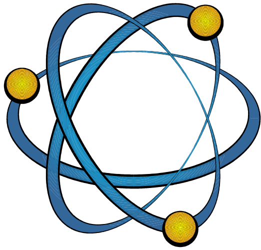
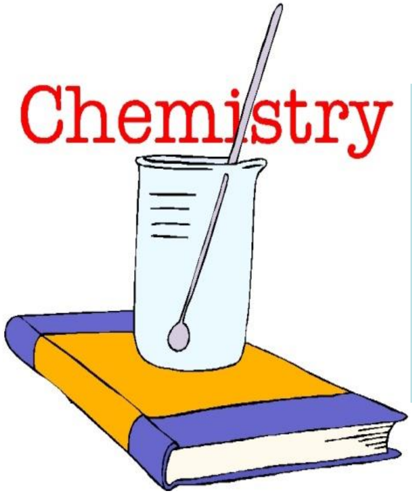




Inorganic Chemistry

The Periodic Table

The Lanthanide and actinides Elements



د / صـــــفاء النحاس

محتوى المقرر

☐ دراسة بعض خواص الجدول الدورى

☐ دراسة خواص عناصر الفئة S,P

☐ دراسة خواص عناصر مجموعات الفئة S (مجموعتين)

☐ دراسة خواص عناصر مجموعات الفئة P (5مجموعات)

☐دراسة خواص عناصر مجموعة الغازات النبيلة.

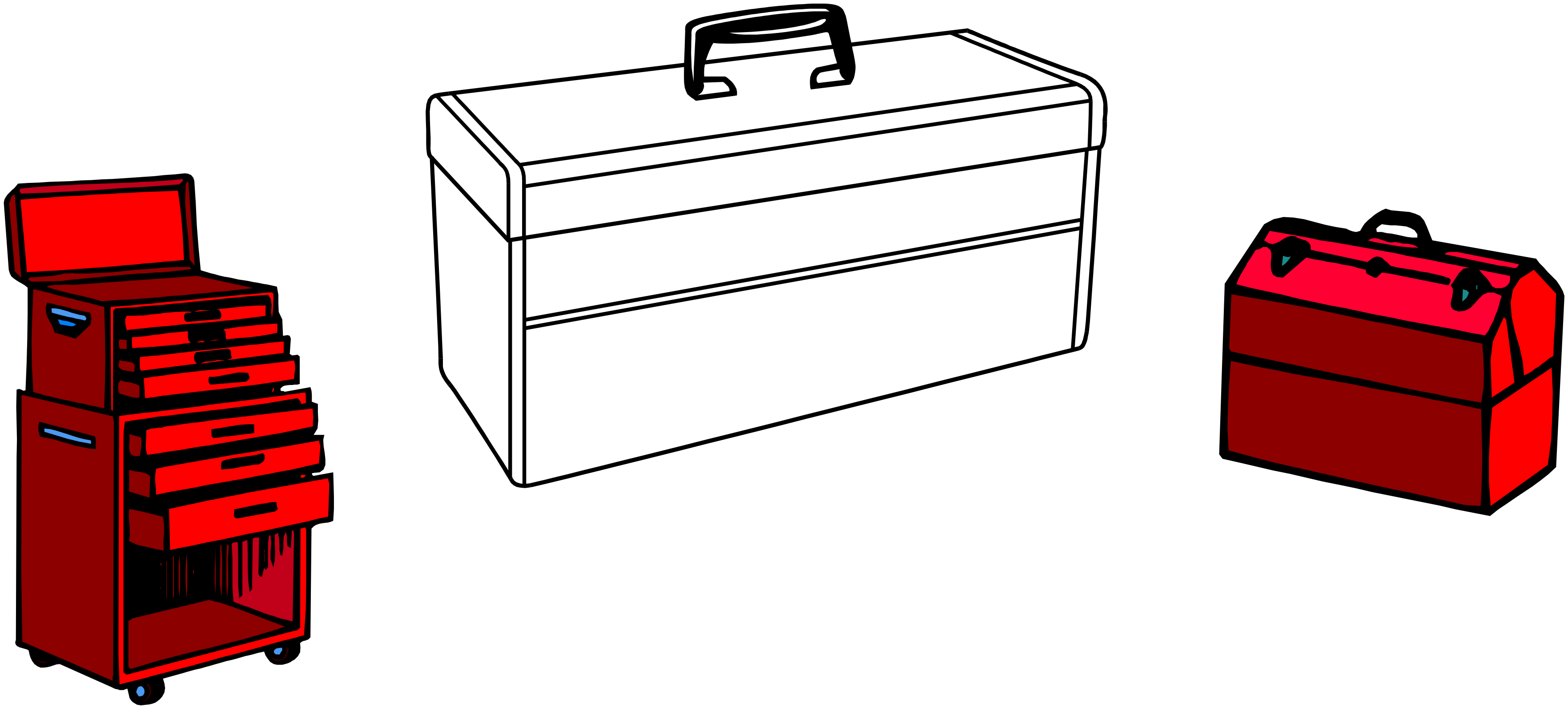
Representative elements:

- Groups 1A – 8A (filling *s* and *p* orbitals)

- Inorganic chemistry deals with many compounds formed by many Elements.
- It involves the study of the chemistry of more than 100 element that can form compounds such as gases, liquids or solids.
- The oldest and still most meaningful relies on the periodic table of the elements

The periodic table is the most important tool in the chemist’s toolbox!

الجدول الدورى هو أهم أداة فى شنطة أدوات الكيميائيين



Why is the Periodic Table important to me?

- The periodic table is the most useful tool to a chemist.
- You get to use it on every test.
- **It organizes lots of information about all the known elements**.

The History of the Modern Periodic Table

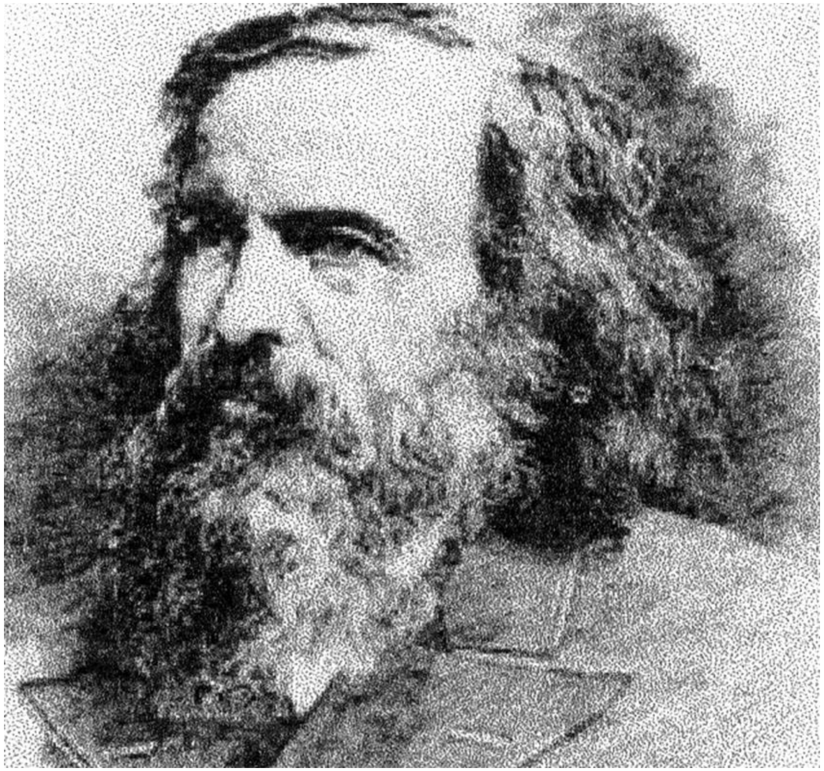
- **The periodic table is depend on:**

1- the electron structure of the gaseous atoms of different elements.

2- chemical properties of the elements

3- physical properties of the elements

Dmitri Mendeleev (1834-1907)



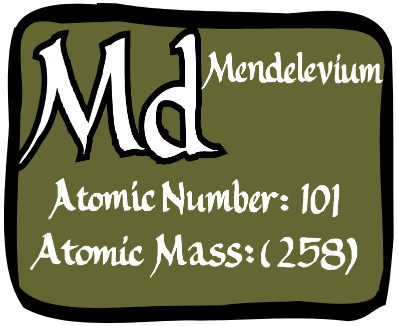
- Russian Chemist
- Published the first version of the period table in 1869
- Arranged elements according to increasing atomic mass
- His periodic table had gaps

Dmitri Mendeleev

The Father of the Table

HOW HIS WORKED…

- Put elements in rows by increasing atomic weight.
- Put elements in columns by the way they reacted.



SOME PROBLEMS…

- He left blank spaces for what he said were undiscovered elements. (Turned out he was right!)
- He broke the pattern of increasing atomic weight to keep similar reacting elements together.

Henry Moseley (1887-1915)

- Made improvements to Mendeleev's Periodic Table
- Arranged elements by **atomic number** instead of mass
- Realized that there were undiscovered elements

The Current Periodic Table

- Mendeleev wasn’t too far off.
- **Now** the elements are put in rows by increasing

ATOMIC NUMBER!!

- The horizontal rows are called periods and are labeled from 1 to 7.
- The vertical columns are called groups are labeled from 1 to 18.

Atomic Number (Z)

Atomic Number (Z): is the number of protons in the nucleus of the atom.

$$Z = p$$

- **Atomic Number (Z)** determine the identity of an element.
- the number of protons must = the number of electrons inside the atom.

Atomic Mass

is the weighted average

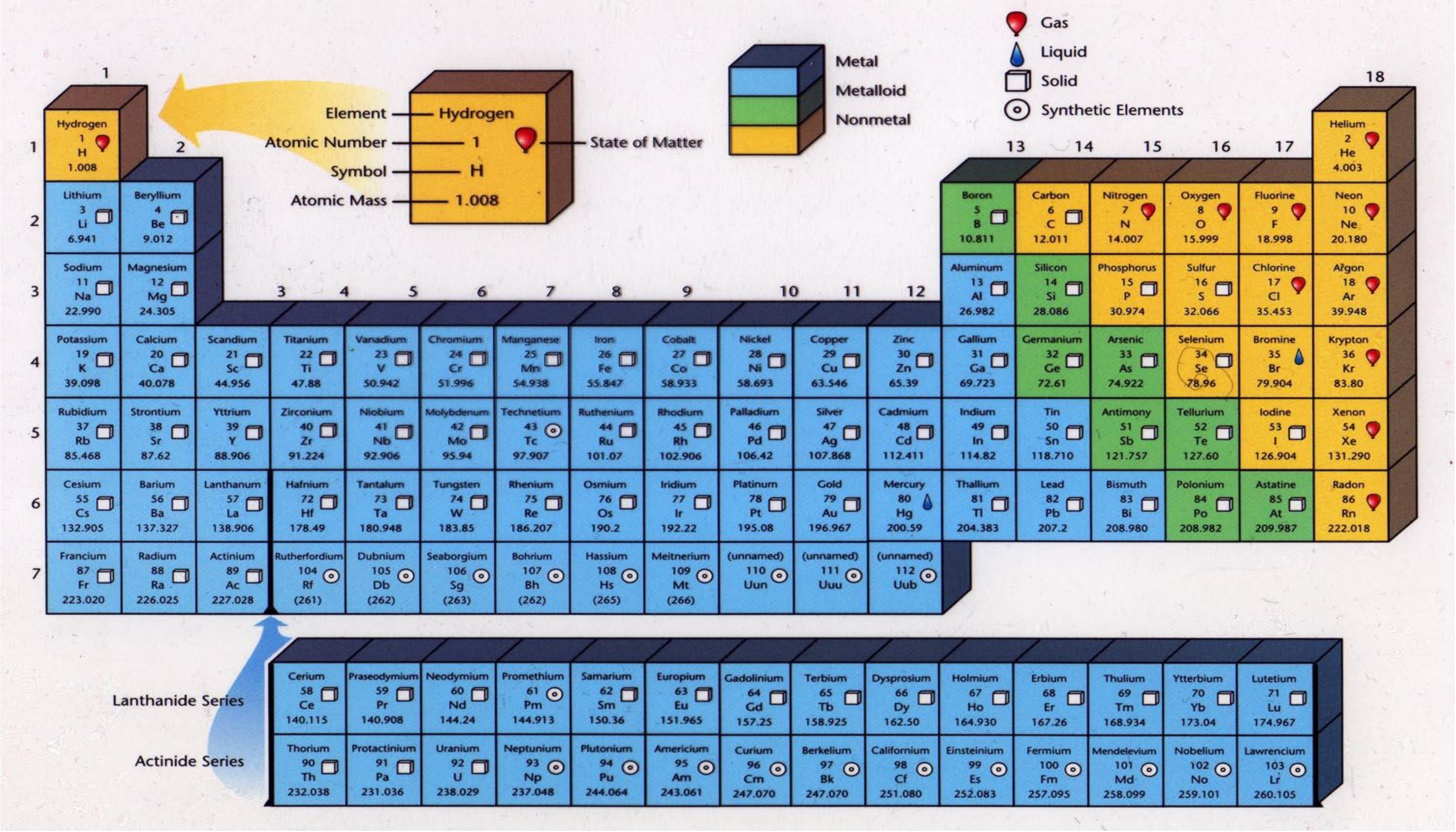
mass

of all the naturally occurring

isotopes

of that element.

The Modern Periodic Table



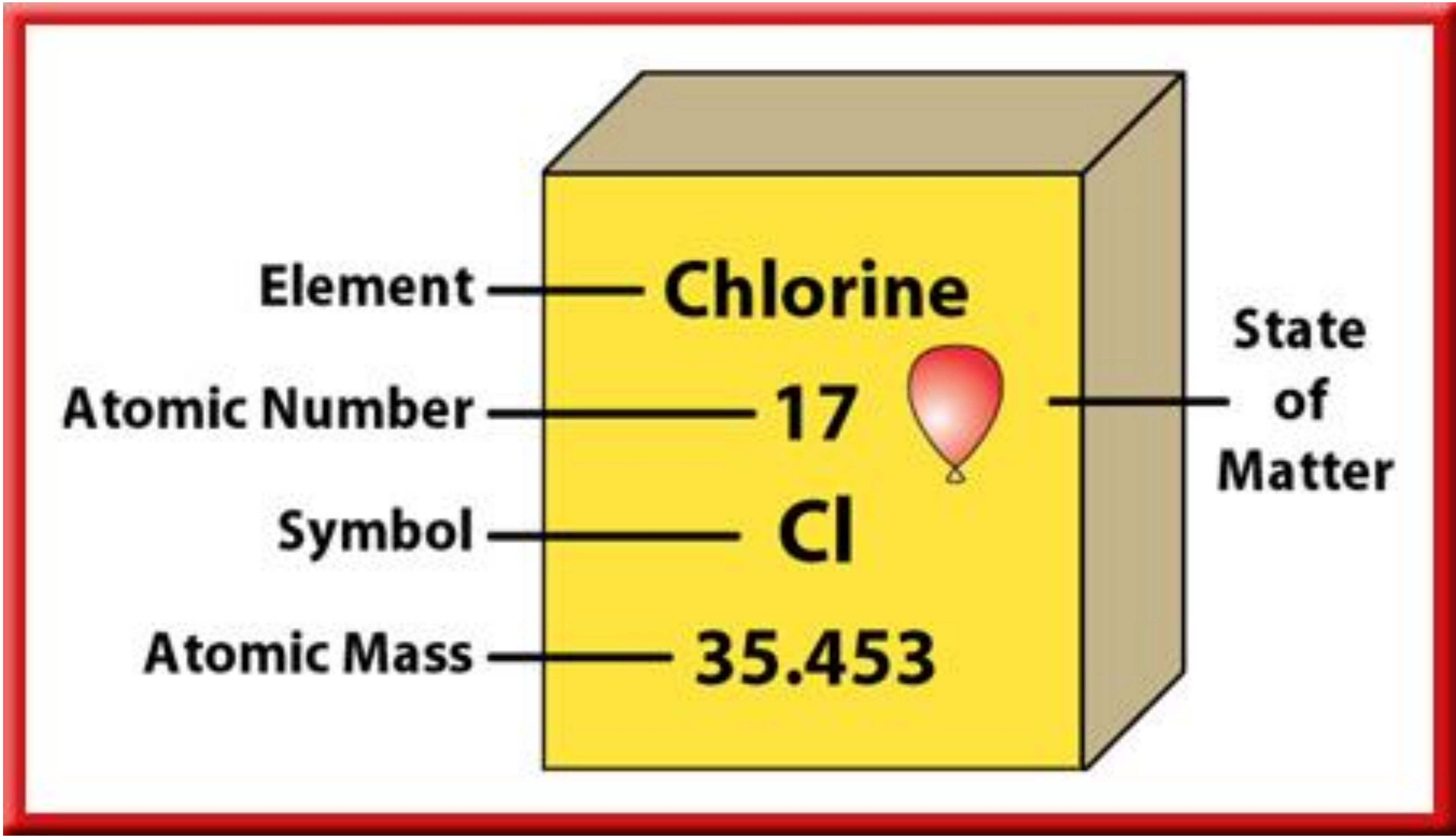
Element — Hydrogen
Atomic Number — 1
Symbol — H
Atomic Mass — 1.008
State of Matter

🟦 Metal
🟩 Metalloid
🟨 Nonmetal

🎈 Gas
💧 Liquid
☐ Solid
⊙ Synthetic Elements

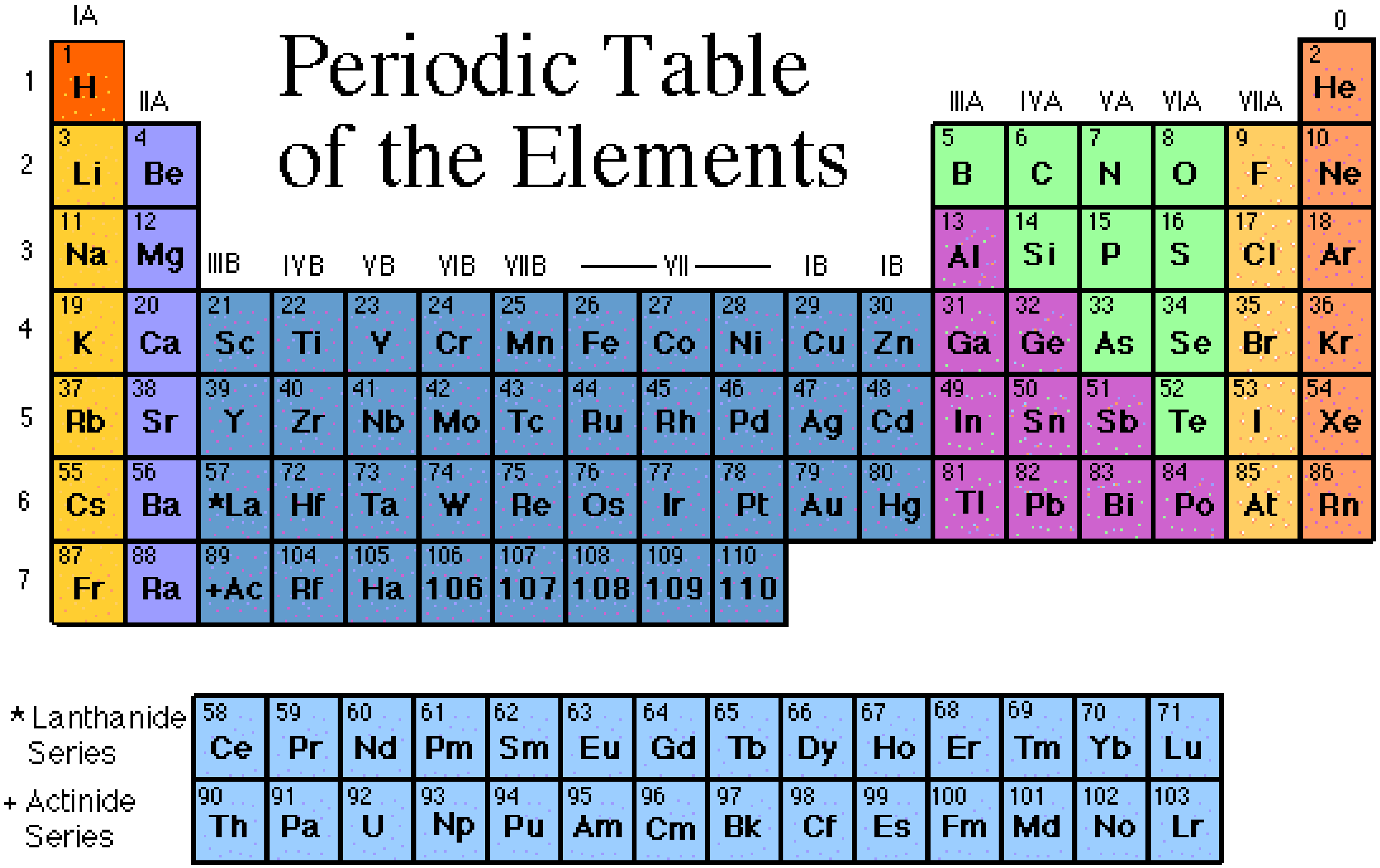
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	Hydrogen 1 🎈 H 1.008																	Helium 2 🎈 He 4.003
2	Lithium 3 ☐ Li 6.941	Beryllium 4 ☐ Be 9.012											Boron 5 ☐ B 10.811	Carbon 6 ☐ C 12.011	Nitrogen 7 🎈 N 14.007	Oxygen 8 🎈 O 15.999	Fluorine 9 🎈 F 18.998	Neon 10 🎈 Ne 20.180
3	Sodium 11 ☐ Na 22.990	Magnesium 12 ☐ Mg 24.305											Aluminum 13 ☐ Al 26.982	Silicon 14 ☐ Si 28.086	Phosphorus 15 ☐ P 30.974	Sulfur 16 ☐ S 32.066	Chlorine 17 🎈 Cl 35.453	Argon 18 🎈 Ar 39.948
4	Potassium 19 ☐ K 39.098	Calcium 20 ☐ Ca 40.078	Scandium 21 ☐ Sc 44.956	Titanium 22 ☐ Ti 47.88	Vanadium 23 ☐ V 50.942	Chromium 24 ☐ Cr 51.996	Manganese 25 ☐ Mn 54.938	Iron 26 ☐ Fe 55.847	Cobalt 27 ☐ Co 58.933	Nickel 28 ☐ Ni 58.693	Copper 29 ☐ Cu 63.546	Zinc 30 ☐ Zn 65.39	Gallium 31 ☐ Ga 69.723	Germanium 32 ☐ Ge 72.61	Arsenic 33 ☐ As 74.922	Selenium 34 ☐ Se 78.96	Bromine 35 💧 Br 79.904	Krypton 36 🎈 Kr 83.80
5	Rubidium 37 ☐ Rb 85.468	Strontium 38 ☐ Sr 87.62	Yttrium 39 ☐ Y 88.906	Zirconium 40 ☐ Zr 91.224	Niobium 41 ☐ Nb 92.906	Molybdenum 42 ☐ Mo 95.94	Technetium 43 ⊙ Tc 97.907	Ruthenium 44 ☐ Ru 101.07	Rhodium 45 ☐ Rh 102.906	Palladium 46 ☐ Pd 106.42	Silver 47 ☐ Ag 107.868	Cadmium 48 ☐ Cd 112.411	Indium 49 ☐ In 114.82	Tin 50 ☐ Sn 118.710	Antimony 51 ☐ Sb 121.757	Tellurium 52 ☐ Te 127.60	Iodine 53 ☐ I 126.904	Xenon 54 🎈 Xe 131.290
6	Cesium 55 ☐ Cs 132.905	Barium 56 ☐ Ba 137.327	Lanthanum 57 ☐ La 138.906	Hafnium 72 ☐ Hf 178.49	Tantalum 73 ☐ Ta 180.948	Tungsten 74 ☐ W 183.85	Rhenium 75 ☐ Re 186.207	Osmium 76 ☐ Os 190.2	Iridium 77 ☐ Ir 192.22	Platinum 78 ☐ Pt 195.08	Gold 79 ☐ Au 196.967	Mercury 80 💧 Hg 200.59	Thallium 81 ☐ Tl 204.383	Lead 82 ☐ Pb 207.2	Bismuth 83 ☐ Bi 208.980	Polonium 84 ☐ Po 208.982	Astatine 85 ☐ At 209.987	Radon 86 🎈 Rn 222.018
7	Francium 87 ☐ Fr 223.020	Radium 88 ☐ Ra 226.025	Actinium 89 ☐ Ac 227.028	Rutherfordium 104 ⊙ Rf (261)	Dubnium 105 ⊙ Db (262)	Seaborgium 106 ⊙ Sg (263)	Bohrium 107 ⊙ Bh (262)	Hassium 108 ⊙ Hs (265)	Meitnerium 109 ⊙ Mt (266)	(unnamed) 110 ⊙ Uun	(unnamed) 111 ⊙ Uuu	(unnamed) 112 ⊙ Uub						

Lanthanide Series	Cerium 58 ☐ Ce 140.115	Praseodymium 59 ☐ Pr 140.908	Neodymium 60 ☐ Nd 144.24	Promethium 61 ⊙ Pm 144.913	Samarium 62 ☐ Sm 150.36	Europium 63 ☐ Eu 151.965	Gadolinium 64 ☐ Gd 157.25	Terbium 65 ☐ Tb 158.925	Dysprosium 66 ☐ Dy 162.50	Holmium 67 ☐ Ho 164.930	Erbium 68 ☐ Er 167.26	Thulium 69 ☐ Tm 168.934	Ytterbium 70 ☐ Yb 173.04	Lutetium 71 ☐ Lu 174.967
Actinide Series	Thorium 90 ☐ Th 232.038	Protactinium 91 ☐ Pa 231.036	Uranium 92 ☐ U 238.029	Neptunium 93 ⊙ Np 237.048	Plutonium 94 ⊙ Pu 244.064	Americium 95 ⊙ Am 243.061	Curium 96 ⊙ Cm 247.070	Berkelium 97 ⊙ Bk 247.070	Californium 98 ⊙ Cf 251.080	Einsteinium 99 ⊙ Es 252.083	Fermium 100 ⊙ Fm 257.095	Mendelevium 101 ⊙ Md 258.099	Nobelium 102 ⊙ No 259.101	Lawrencium 103 ⊙ Lr 260.105


Element
Atomic Number
Symbol
Atomic Mass
Chlorine
17
Cl
35.453
State of Matter

Periodic Table of Elements

التسمية القديمة للجدول الدورى للعناصر

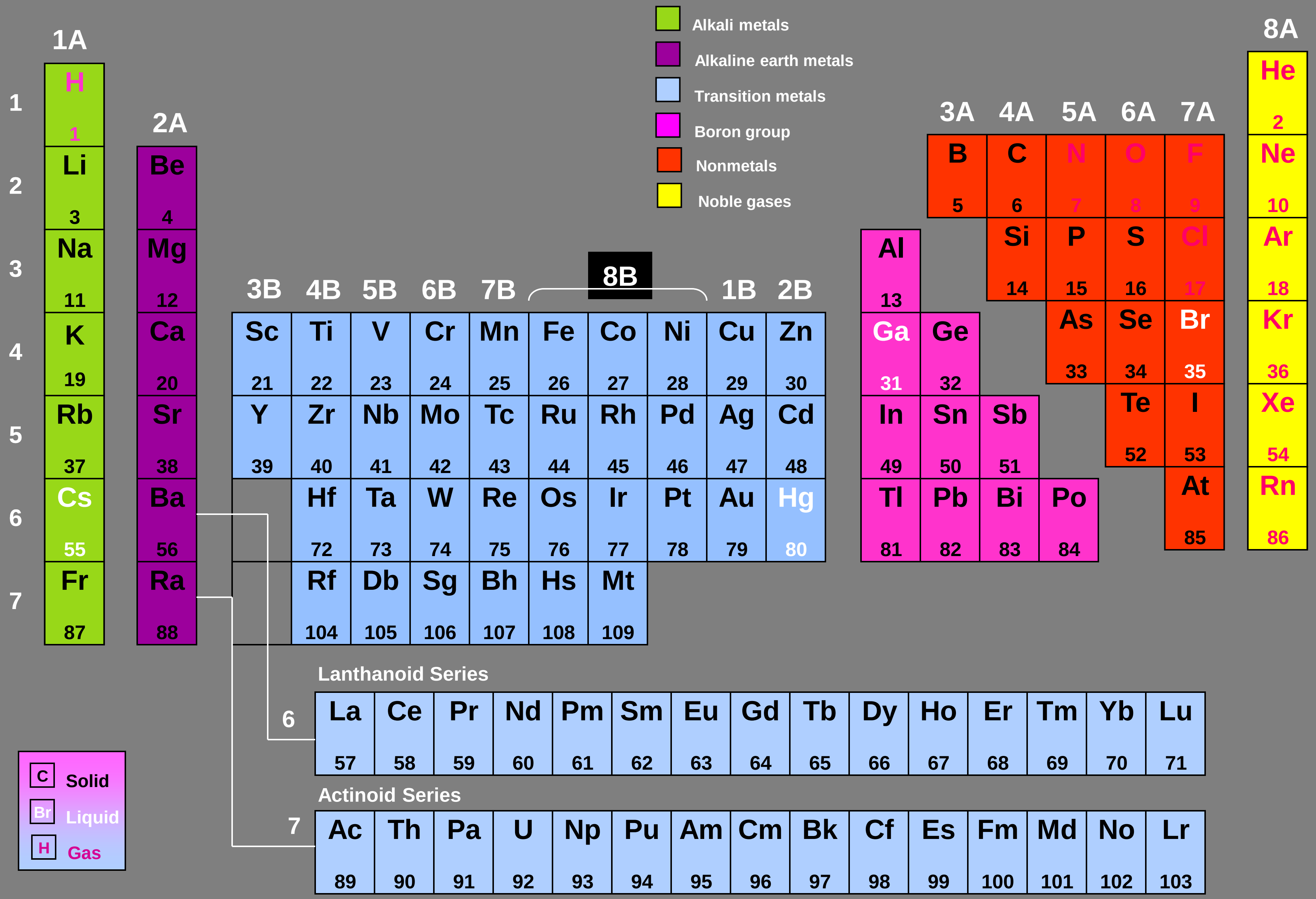


Periodic Table of the Elements

	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

Periodic Table



🟩 Alkali metals
🟪 Alkaline earth metals
🟦 Transition metals
▨ Boron group
🟥 Nonmetals
🟨 Noble gases

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

Lanthanoid Series

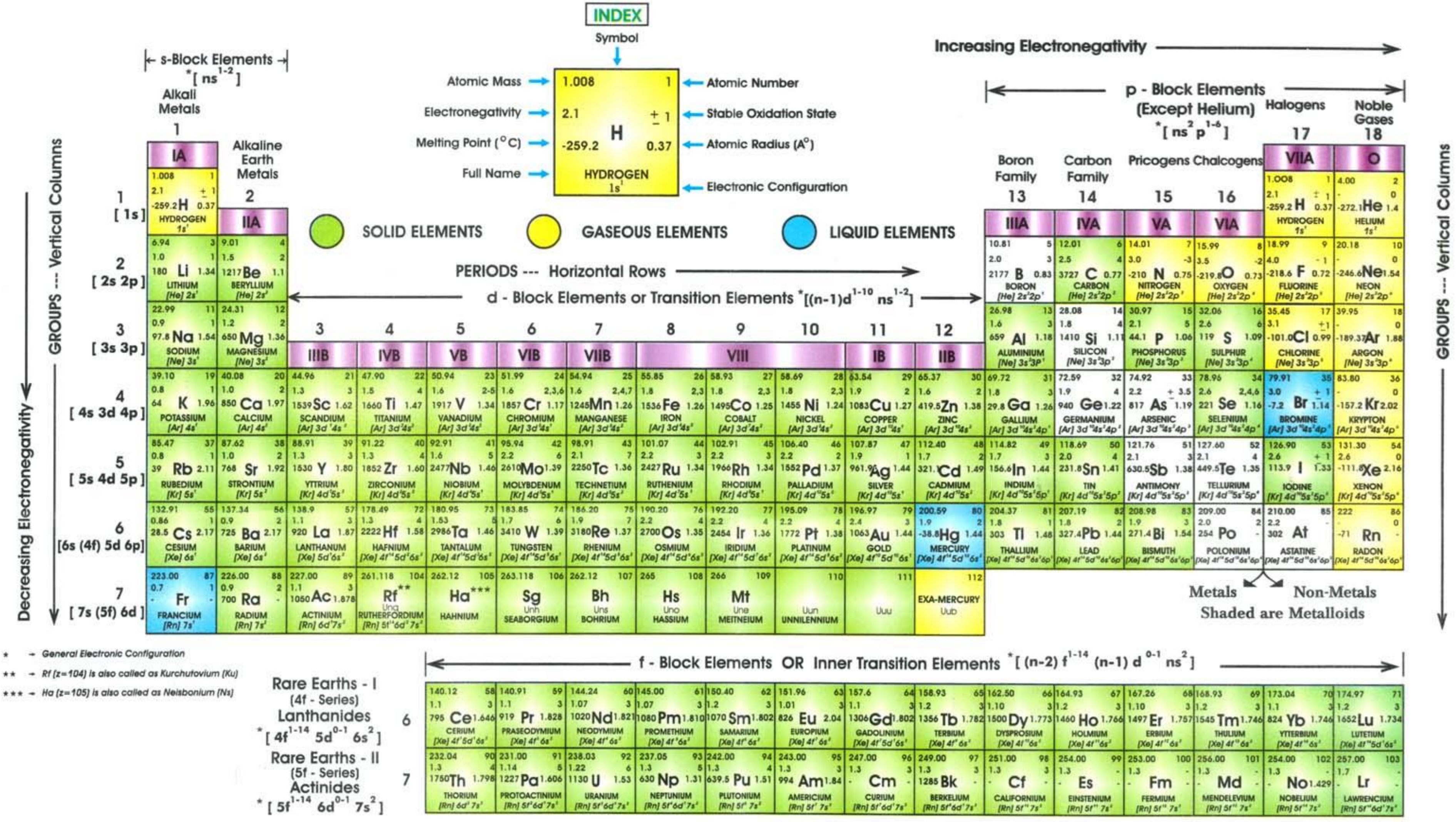
6	La 57	Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71

Actinoid Series

7	Ac 89	Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lr 103

C Solid
Br Liquid
H Gas

LONG FORM OF PERIODIC TABLE



INDEX

Symbol

Atomic Mass → 1.008 … 1 ← Atomic Number
Electronegativity → 2.1 … ±1 ← Stable Oxidation State
Melting Point (°C) → -259.2 H 0.37 ← Atomic Radius (A°)
Full Name → HYDROGEN
$1s^1$ ← Electronic Configuration

🟢 SOLID ELEMENTS 🟡 GASEOUS ELEMENTS 🔵 LIQUID ELEMENTS

Increasing Electronegativity →

Decreasing Electronegativity ↓

GROUPS --- Vertical Columns

PERIODS --- Horizontal Rows →

← s-Block Elements → $^*[ns^{1-2}]$

← d - Block Elements or Transition Elements $^*[(n-1)d^{1-10}\ ns^{1-2}]$ →

← p - Block Elements (Except Helium) $^*[ns^2 p^{1-6}]$ →

Period	1 Alkali Metals IA	2 Alkaline Earth Metals IIA
1 [1s]	1.008 1 2.1 ±1 -259.2 H 0.37 HYDROGEN $1s^1$	
2 [2s 2p]	6.94 3 1.0 1 180 Li 1.34 LITHIUM [He] $2s^1$	9.01 4 1.5 2 1217 Be 1.1 BERYLLIUM [He] $2s^2$
3 [3s 3p]	22.99 11 0.9 1 97.8 Na 1.54 SODIUM [Ne] $3s^1$	24.31 12 1.2 2 650 Mg 1.36 MAGNESIUM [Ne] $3s^2$
4 [4s 3d 4p]	39.10 19 0.8 1 64 K 1.96 POTASSIUM [Ar] $4s^1$	40.08 20 1.0 2 850 Ca 1.97 CALCIUM [Ar] $4s^2$
5 [5s 4d 5p]	85.47 37 0.8 1 39 Rb 2.11 RUBEDIUM [Kr] $5s^1$	87.62 38 1.0 2 768 Sr 1.92 STRONTIUM [Kr] $5s^2$
6 [6s (4f) 5d 6p]	132.91 55 0.86 1 28.5 Cs 2.17 CESIUM [Xe] $6s^1$	137.34 56 0.9 2 725 Ba 2.17 BARIUM [Xe] $6s^2$
7 [7s (5f) 6d]	223.00 87 0.7 1 - Fr - FRANCIUM [Rn] $7s^1$	226.00 88 0.9 2 700 Ra - RADIUM [Rn] $7s^2$

Period	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIII	9 VIII	10 VIII	11 IB	12 IIB
4 [4s 3d 4p]	44.96 21 1.3 3 1539 Sc 1.62 SCANDIUM [Ar] $3d^1 4s^2$	47.90 22 1.5 4 1660 Ti 1.47 TITANIUM [Ar] $3d^2 4s^2$	50.94 23 1.6 2-5 1917 V 1.34 VANADIUM [Ar] $3d^3 4s^2$	51.99 24 1.6 2,3,6 1857 Cr 1.17 CHROMIUM [Ar] $3d^5 4s^1$	54.94 25 1.6 2,4,7 1245 Mn 1.26 MANGANESE [Ar] $3d^5 4s^2$	55.85 26 1.8 2,3 1536 Fe 1.26 IRON [Ar] $3d^6 4s^2$	58.93 27 1.8 2,3 1495 Co 1.25 COBALT [Ar] $3d^7 4s^2$	58.69 28 1.8 2,3 1455 Ni 1.24 NICKEL [Ar] $3d^8 4s^2$	63.54 29 1.9 2 1083 Cu 1.27 COPPER [Ar] $3d^{10} 4s^1$	65.37 30 1.6 2 419.5 Zn 1.38 ZINC [Ar] $3d^{10} 4s^2$
5 [5s 4d 5p]	88.91 39 1.3 3 1530 Y 1.80 YTTRIUM [Kr] $4d^1 5s^2$	91.22 40 1.3 4 1852 Zr 1.60 ZIRCONIUM [Kr] $4d^2 5s^2$	92.91 41 1.6 5 2477 Nb 1.46 NIOBIUM [Kr] $4d^4 5s^1$	95.94 42 2.2 6 2610 Mo 1.39 MOLYBDENUM [Kr] $4d^5 5s^1$	98.91 43 2.1 7 2250 Tc 1.36 TECHNETIUM [Kr] $4d^5 5s^2$	101.07 44 2.2 3 2427 Ru 1.34 RUTHENIUM [Kr] $4d^7 5s^1$	102.91 45 2.2 3 1966 Rh 1.34 RHODIUM [Kr] $4d^8 5s^1$	106.40 46 2.2 2 1552 Pd 1.37 PALLADIUM [Kr] $4d^{10} 5s^0$	107.87 47 1.9 1 961.9 Ag 1.44 SILVER [Kr] $4d^{10} 5s^1$	112.40 48 1.7 2 321.1 Cd 1.49 CADMIUM [Kr] $4d^{10} 5s^2$
6 [6s (4f) 5d 6p]	138.9 57 1.1 3 920 La 1.87 LANTHANUM [Xe] $5d^1 6s^2$	178.49 72 1.3 4 2222 Hf 1.58 HAFNIUM [Xe] $4f^{14} 5d^2 6s^2$	180.95 73 1.53 5 2986 Ta 1.46 TANTALUM [Xe] $4f^{14} 5d^3 6s^2$	183.85 74 1.7 6 3410 W 1.39 TUNGSTEN [Xe] $4f^{14} 5d^4 6s^2$	186.20 75 1.9 7 3180 Re 1.37 RHENIUM [Xe] $4f^{14} 5d^5 6s^2$	190.20 76 2.2 4 2700 Os 1.35 OSMIUM [Xe] $4f^{14} 5d^6 6s^2$	192.20 77 2.2 4 2454 Ir 1.36 IRIDIUM [Xe] $4f^{14} 5d^7 6s^2$	195.09 78 2.2 4 1772 Pt 1.38 PLATINUM [Xe] $4f^{14} 5d^9 6s^1$	196.97 79 2.4 3 1063 Au 1.44 GOLD [Xe] $4f^{14} 5d^{10} 6s^1$	200.59 80 1.9 2 -38.8 Hg 1.44 MERCURY [Xe] $4f^{14} 5d^{10} 6s^2$
7 [7s (5f) 6d]	227.00 89 1.1 3 1050 Ac 1.878 ACTINIUM [Rn] $6d^1 7s^2$	261.118 104 Rf** Unq RUTHERFORDIUM [Rn] $5f^{14} 6d^2 7s^2$	262.12 105 Ha*** HAHNIUM	263.118 106 Sg Unh SEABORGIUM	262.12 107 Bh Uns BOHRIUM	265 108 Hs Uno HASSIUM	266 109 Mt Une MEITNEIUM	110 Uun UNNILENNIUM	111 Uuu	112 EXA-MERCURY Uub

Period	13 Boron Family IIIA	14 Carbon Family IVA	15 Pricogens VA	16 Chalcogens VIA	17 Halogens VIIA	18 Noble Gases O
1 [1s]					1.008 1 2.1 ±1 -259.2 H 0.37 HYDROGEN $1s^1$	4.00 2 - 0 -272.1 He 1.4 HELIUM $1s^2$
2 [2s 2p]	10.81 5 2.0 3 2177 B 0.83 BORON [He] $2s^2 2p^1$	12.01 6 2.5 4 3727 C 0.77 CARBON [He] $2s^2 2p^2$	14.01 7 3.0 -3 -210 N 0.75 NITROGEN [He] $2s^2 2p^3$	15.99 8 3.5 -2 -219.8 O 0.73 OXYGEN [He] $2s^2 2p^4$	18.99 9 4.0 -1 -218.6 F 0.72 FLUORINE [He] $2s^2 2p^5$	20.18 10 - 0 -246.6 Ne 1.54 NEON [He] $2s^2 2p^6$
3 [3s 3p]	26.98 13 1.6 3 659 Al 1.18 ALUMINIUM [Ne] $3s^2 3P^1$	28.08 14 1.8 4 1410 Si 1.11 SILICON [Ne] $3s^2 3p^2$	30.97 15 2.1 5 44.1 P 1.06 PHOSPHORUS [Ne] $3s^2 3p^3$	32.06 16 2.6 6 119 S 1.09 SULPHUR [Ne] $3s^2 3p^4$	35.45 17 3.1 ±1 -101.0 Cl 0.99 CHLORINE [Ne] $3s^2 3p^5$	39.95 18 - 0 -189.37 Ar 1.88 ARGON [Ne] $3s^2 3p^6$
4 [4s 3d 4p]	69.72 31 1.8 3 29.8 Ga 1.26 GALLIUM [Ar] $3d^{10} 4s^2 4p^1$	72.59 32 1.9 4 940 Ge 1.22 GERMANIUM [Ar] $3d^{10} 4s^2 4p^2$	74.92 33 2.2 ±3.5 817 As 1.19 ARSENIC [Ar] $3d^{10} 4s^2 4p^3$	78.96 34 2.6 2,4,6 221 Se 1.16 SELENIUM [Ar] $3d^{10} 4s^2 4p^4$	79.91 35 3.0 ±1 -7.2 Br 1.14 BROMINE [Ar] $3d^{10} 4s^2 4p^5$	83.80 36 - 0 -157.2 Kr 2.02 KRYPTON [Ar] $3d^{10} 4s^2 4p^6$
5 [5s 4d 5p]	114.82 49 1.7 3 156.6 In 1.44 INDIUM [Kr] $4d^{10} 5s^2 5p^1$	118.69 50 2.0 4 231.8 Sn 1.41 TIN [Kr] $4d^{10} 5s^2 5p^2$	121.76 51 2.1 3 630.5 Sb 1.38 ANTIMONY [Kr] $4d^{10} 5s^2 5p^3$	127.60 52 2.1 4 449.5 Te 1.35 TELLURIUM [Kr] $4d^{10} 5s^2 5p^4$	126.90 53 2.6 ±1 113.9 I 1.33 IODINE [Kr] $4d^{10} 5s^2 5p^5$	131.30 54 2.6 0 -111.8 Xe 2.16 XENON [Kr] $4d^{10} 5s^2 5p^6$
6 [6s (4f) 5d 6p]	204.37 81 1.8 1 303 Tl 1.48 THALLIUM [Xe] $4f^{14} 5d^{10} 6s^2 6p^1$	207.19 82 1.8 2 327.4 Pb 1.44 LEAD [Xe] $4f^{14} 5d^{10} 6s^2 6p^2$	208.98 83 1.9 3 271.4 Bi 1.54 BISMUTH [Xe] $4f^{14} 5d^{10} 6s^2 6p^3$	209.00 84 2.0 2 254 Po - POLONIUM [Xe] $4f^{14} 5d^{10} 6s^2 6p^4$	210.00 85 2.2 - 302 At ASTATINE [Xe] $4f^{14} 5d^{10} 6s^2 6p^5$	222 86 - 0 -71 Rn - RADON [Xe] $4f^{14} 5d^{10} 6s^2 6p^6$

Metals ↙ ↘ Non-Metals
Shaded are Metalloids

← f - Block Elements OR Inner Transition Elements $^*[(n-2)f^{1-14}\ (n-1)d^{0-1}\ ns^2]$ →

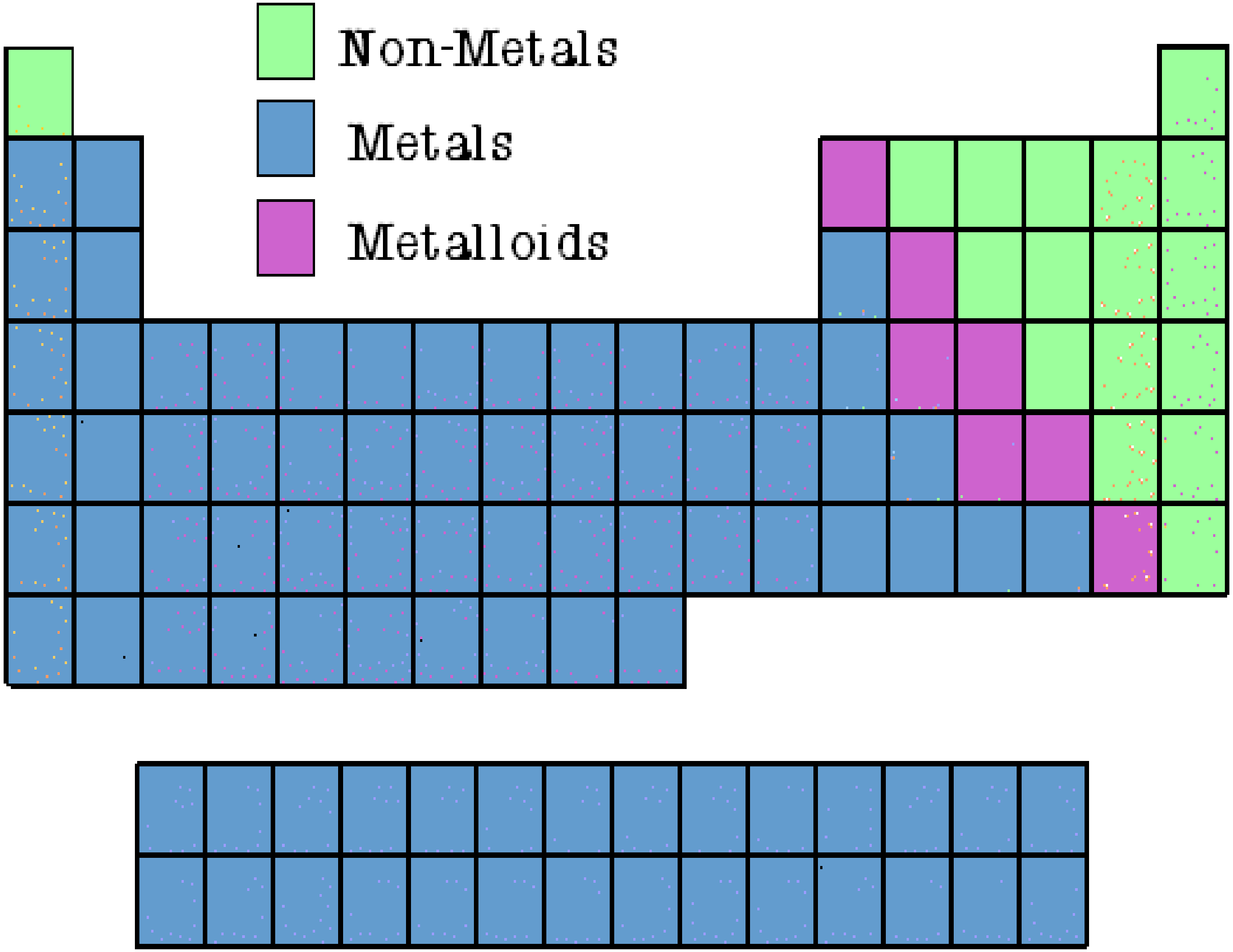
Rare Earths - I (4f - Series) Lanthanides $^*[4f^{1-14}\ 5d^{0-1}\ 6s^2]$	6	140.12 58 1.1 3 795 Ce 1.646 CERIUM [Xe] $4f^1 5d^1 6s^2$	140.91 59 1.1 3 919 Pr 1.828 PRASEODYMIUM [Xe] $4f^3 6s^2$	144.24 60 1.07 3 1020 Nd 1.821 NEODYMIUM [Xe] $4f^4 6s^2$	145.00 61 1.07 3 1080 Pm 1.810 PROMETHIUM [Xe] $4f^5 6s^2$	150.40 62 1.2 3 1070 Sm 1.802 SAMARIUM [Xe] $4f^6 6s^2$	151.96 63 1.01 3 826 Eu 2.04 EUROPIUM [Xe] $4f^7 6s^2$
Rare Earths - II (5f - Series) Actinides $^*[5f^{1-14}\ 6d^{0-1}\ 7s^2]$	7	232.04 90 1.3 4 1750 Th 1.798 THORIUM [Rn] $6d^2 7s^2$	231.00 91 1.14 5 1227 Pa 1.606 PROTOACTINIUM [Rn] $5f^2 6d^1 7s^2$	238.03 92 1.22 6 1130 U 1.53 URANIUM [Rn] $5f^3 6d^1 7s^2$	237.05 93 1.3 5 630 Np 1.31 NEPTUNIUM [Rn] $5f^4 6d^1 7s^2$	242.00 94 1.3 4 639.5 Pu 1.51 PLUTONIUM [Rn] $5f^6 7s^2$	243.00 95 1.3 3 994 Am 1.84 AMERICIUM [Rn] $5f^7 7s^2$

6	157.6 64 1.1 3 1306 Gd 1.802 GADOLINIUM [Xe] $4f^7 5d^1 6s^2$	158.93 65 1.2 3 1356 Tb 1.782 TERBIUM [Xe] $4f^9 6s^2$	162.50 66 1.10 3 1500 Dy 1.773 DYSPROSIUM [Xe] $4f^{10} 6s^2$	164.93 67 1.2 3 1460 Ho 1.766 HOLMIUM [Xe] $4f^{11} 6s^2$	167.26 68 1.10 3 1497 Er 1.757 ERBIUM [Xe] $4f^{12} 6s^2$	168.93 69 1.2 3 1545 Tm 1.746 THULIUM [Xe] $4f^{13} 6s^2$	173.04 70 1.1 3 824 Yb 1.746 YTTERBIUM [Xe] $4f^{14} 6s^2$	174.97 71 1.2 3 1652 Lu 1.734 LUTETIUM [Xe] $4f^{14} 5d^1 6s^2$
7	247.00 96 1.3 3 - Cm - CURIUM [Rn] $5f^7 6d^1 7s^2$	249.00 97 1.3 3 1285 Bk - BERKELIUM [Rn] $5f^8 6d^1 7s^2$	251.00 98 1.3 3 - Cf - CALIFORNIUM [Rn] $5f^{10} 7s^2$	254.00 99 1.3 - - Es - EINSTENIUM [Rn] $5f^{11} 7s^2$	253.00 100 1.3 - - Fm - FERMIUM [Rn] $5f^{12} 7s^2$	256.00 101 1.3 - - Md - MENDELEVIUM [Rn] $5f^{13} 7s^2$	254.00 102 1.3 - - No 1.429 NOBELIUM [Rn] $5f^{14} 7s^2$	257.00 103 1.7 - - Lr - LAWRENCIUM [Rn] $5f^{14} 6d^1 7s^2$

* → 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 elements of the periodic table can be divided into three main categories: Metals, Non-Metals, and Metalloids.



The physical properties for metal

1- high reflectivity

2- high electrical conductance

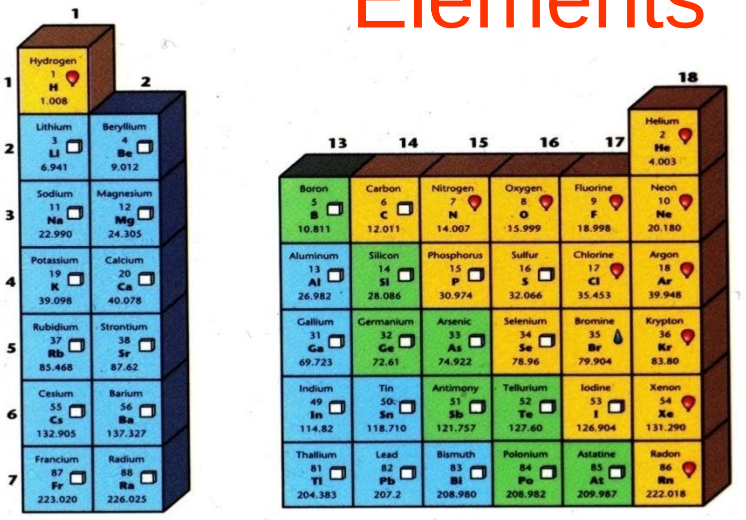
3- high thermal conductance

4- mechanical properties (strength, ductility,…..)

Metals vs. Nonmetals

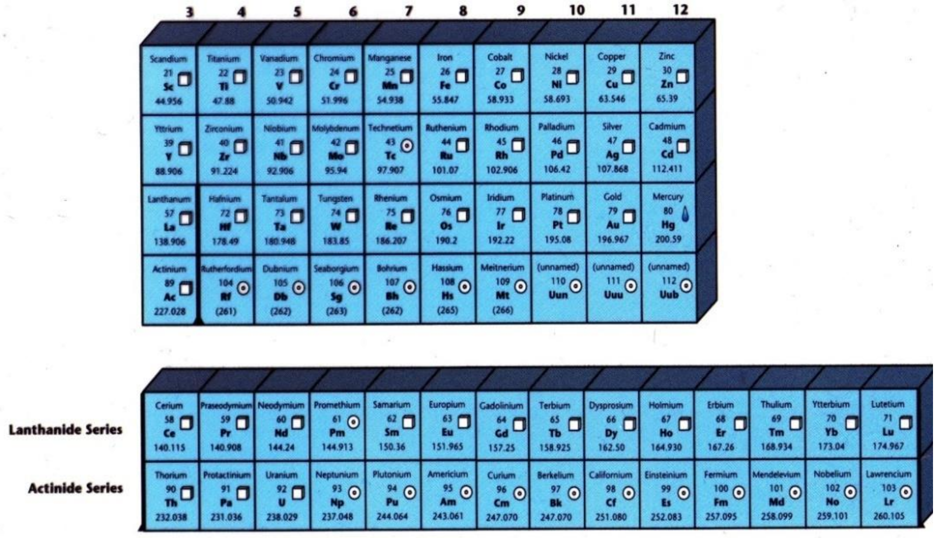
- Metals tend to lose valence electrons to form cations
- Nonmetals tend to gain valence electrons to form anions
- Metallic character increases going down a group (I.E. Decreases going down a group)

Non-Transition Elements



- Groups 1-2 & 13-18
- Alkali Metals
- Alkaline Earth Metals
- The Boron Family
- The Carbon Group
- The Nitrogen Group
- The Oxygen Group
- The Halogens
- The Noble Gases

Transition Elements



- Groups 3-12
- All transition elements are metals.
- Group 11 (The Coinage Metals)
- The Lanthanides
- The Actinides

التركيب الكترونى للدورات الافقية

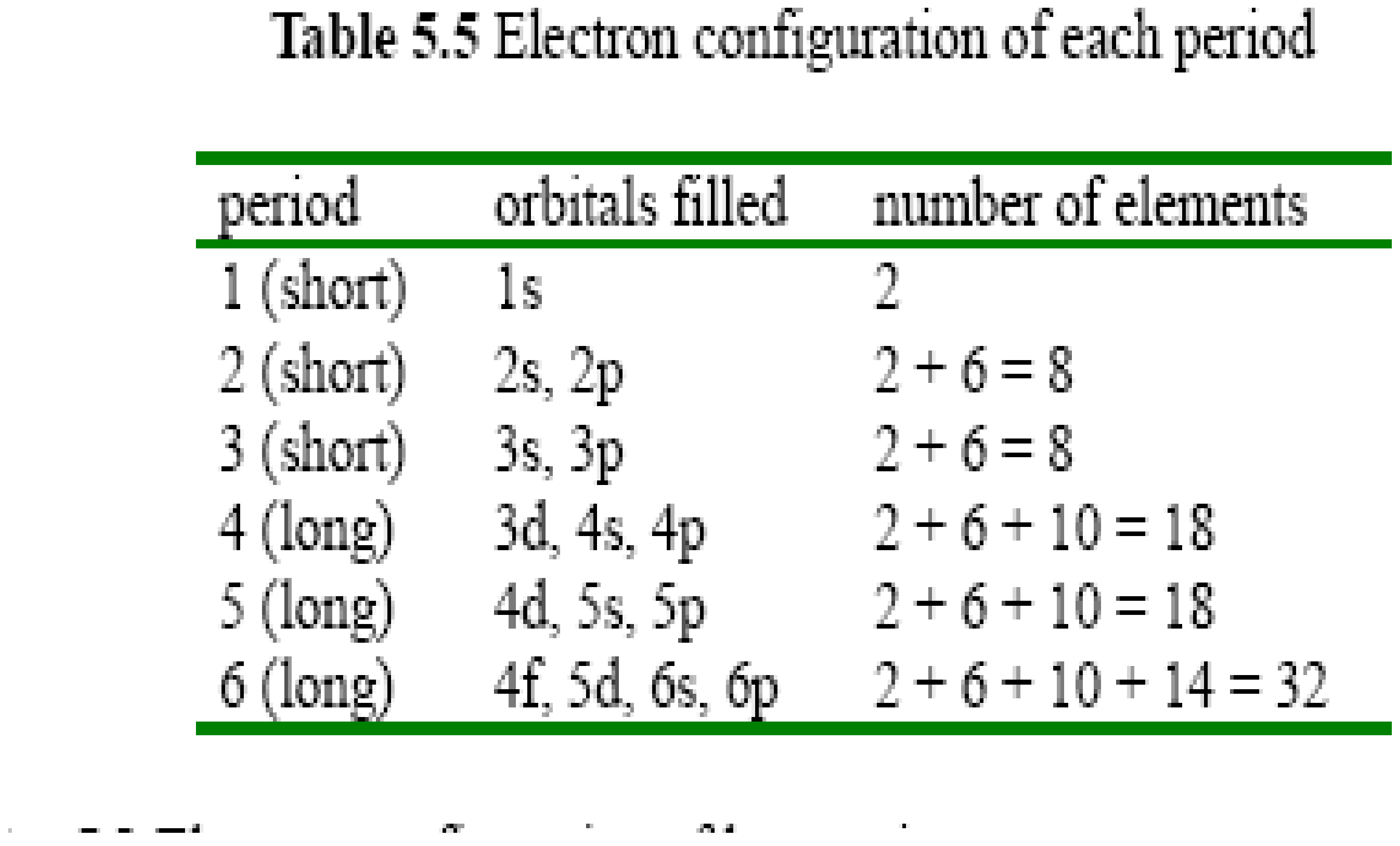
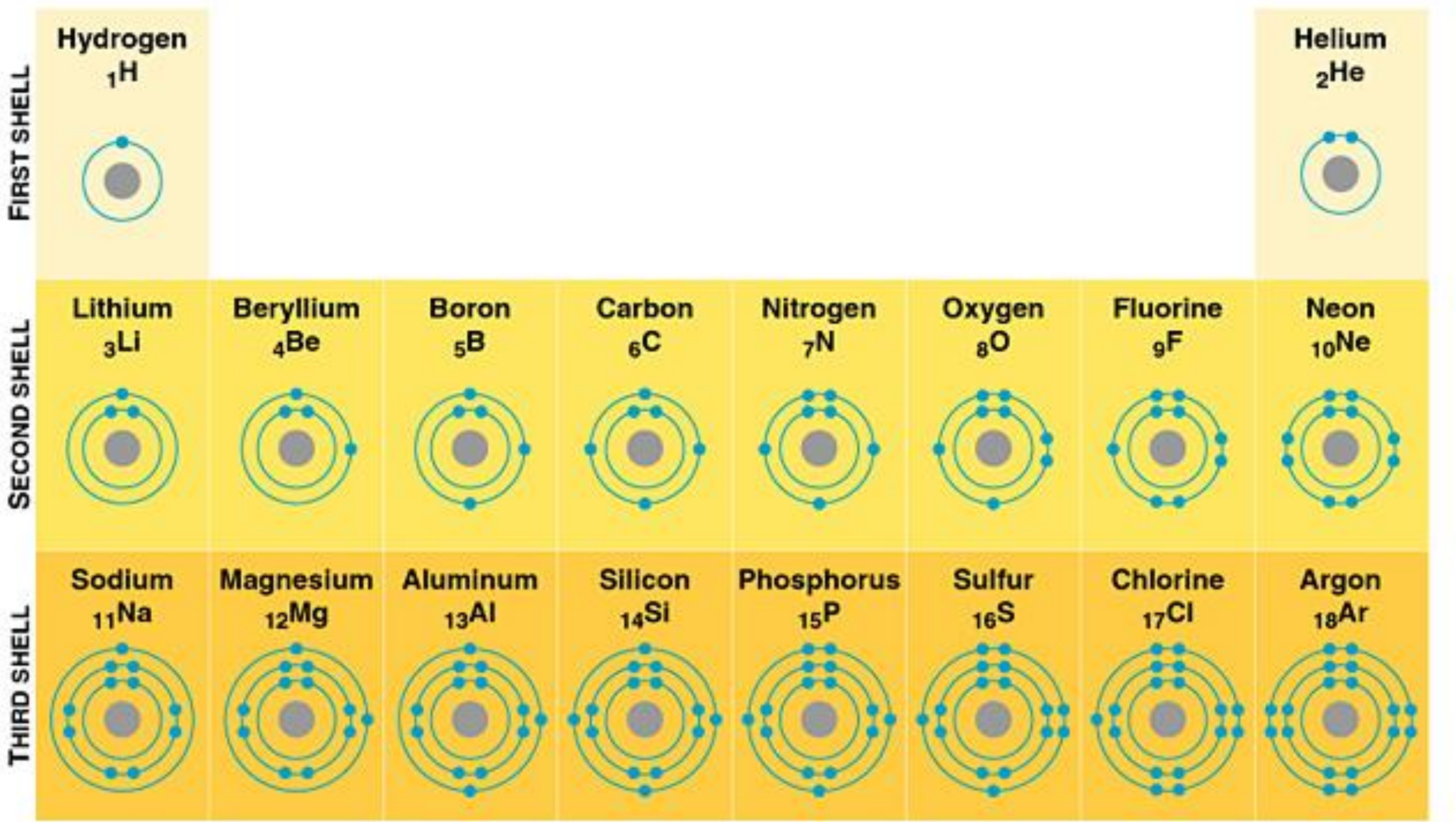


Table 5.5 Electron configuration of each period

period	orbitals filled	number of elements
1 (short)	1s	2
2 (short)	2s, 2p	$2 + 6 = 8$
3 (short)	3s, 3p	$2 + 6 = 8$
4 (long)	3d, 4s, 4p	$2 + 6 + 10 = 18$
5 (long)	4d, 5s, 5p	$2 + 6 + 10 = 18$
6 (long)	4f, 5d, 6s, 6p	$2 + 6 + 10 + 14 = 32$

Electron Orbits
ملئ الاروبيتالات

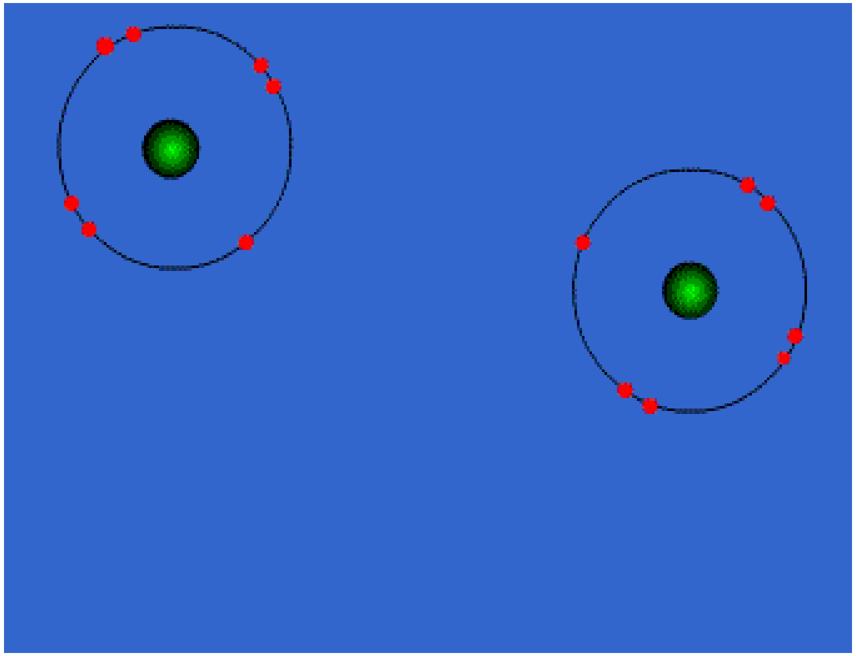


Valence Electrons

الكترونات التكافؤ

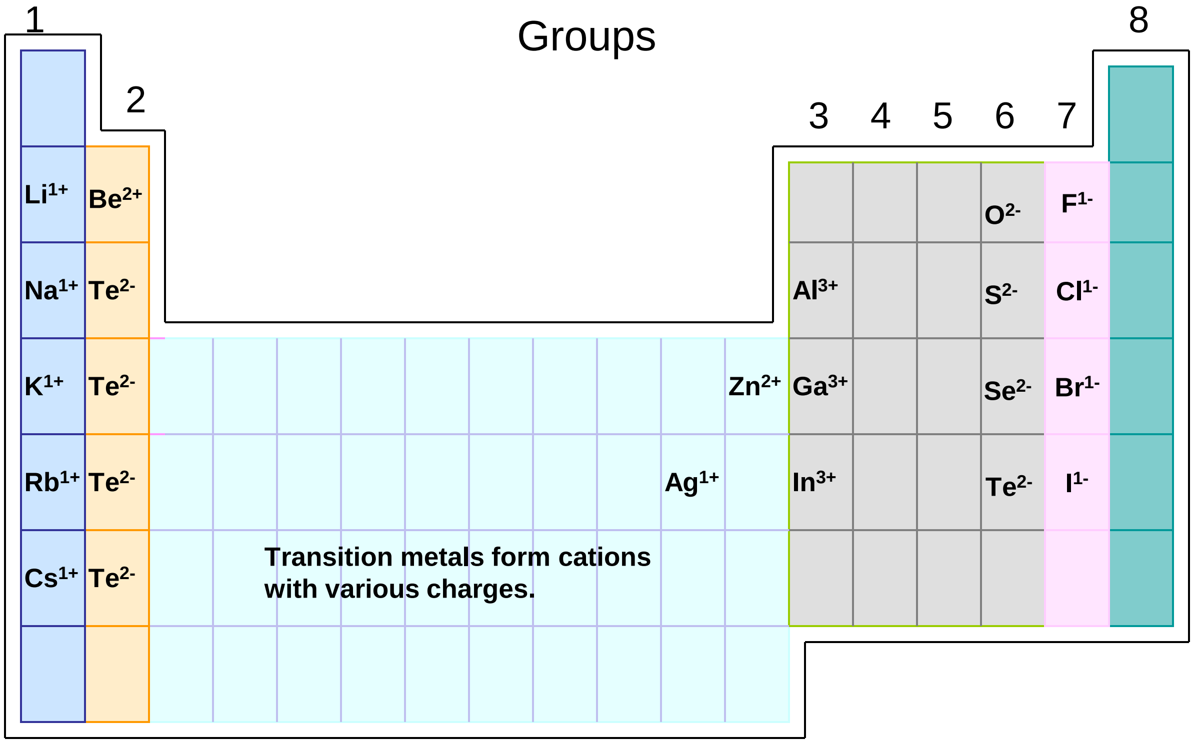
- Valence electrons are the electrons in the outer energy level of an atom.
- These are the electrons that are transferred or shared when atoms bond together.

- الكترونات التكافؤ هى تلك الكترونات الموجودة فى الغلاف الاخير فى الذرة .
- التكافؤ هو عدد الكترونات التى تفقدها أو تكتسبها أو تشارك بها الذرة فى الترابط عند تكوين مركبات.



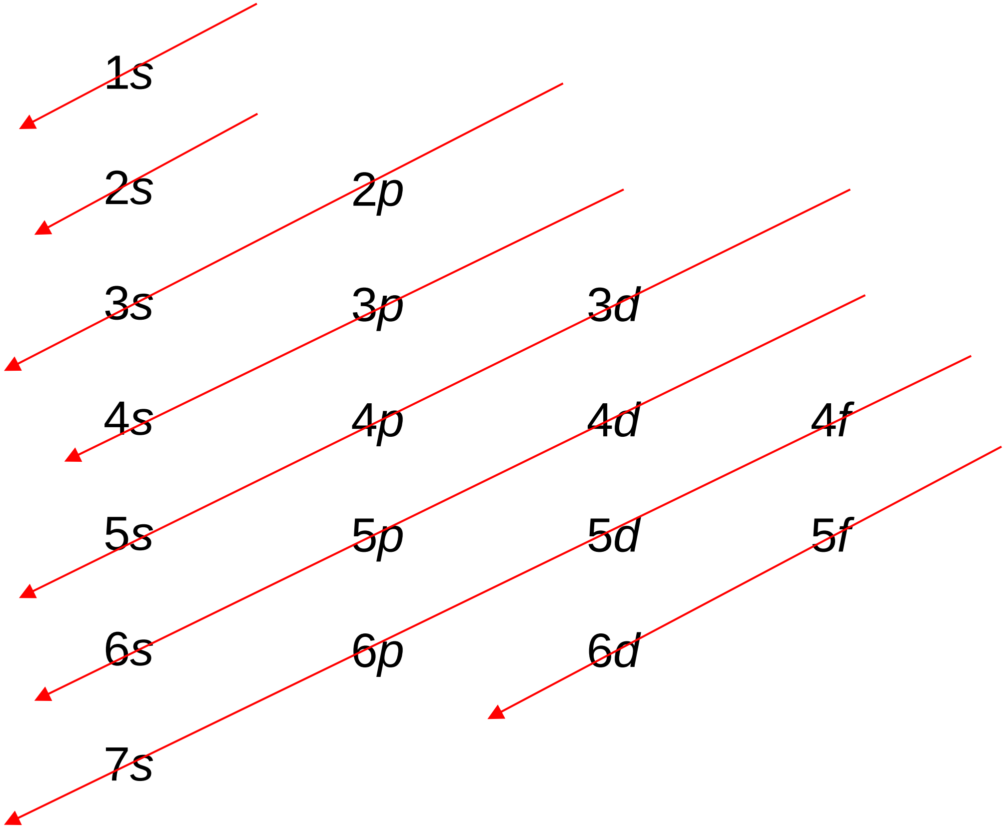
Orbitals Being Filled

كيفية ملئ الاروبيتالات



Transition metals form cations with various charges.

Order in which subshells are filled with electrons



1*s*

2*s* 2*p*

3*s* 3*p* 3*d*

4*s* 4*p* 4*d* 4*f*

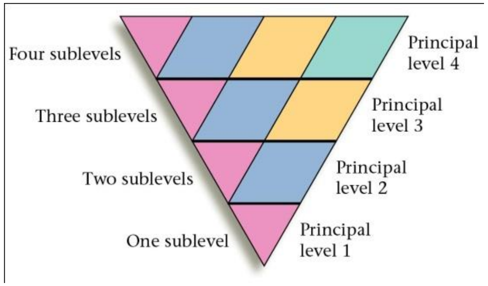
5*s* 5*p* 5*d* 5*f*

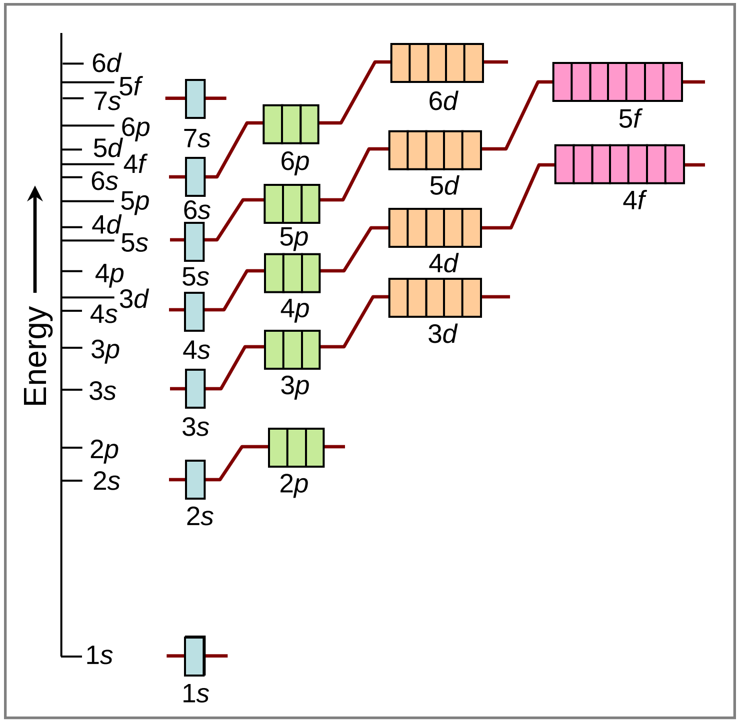
6*s* 6*p* 6*d*

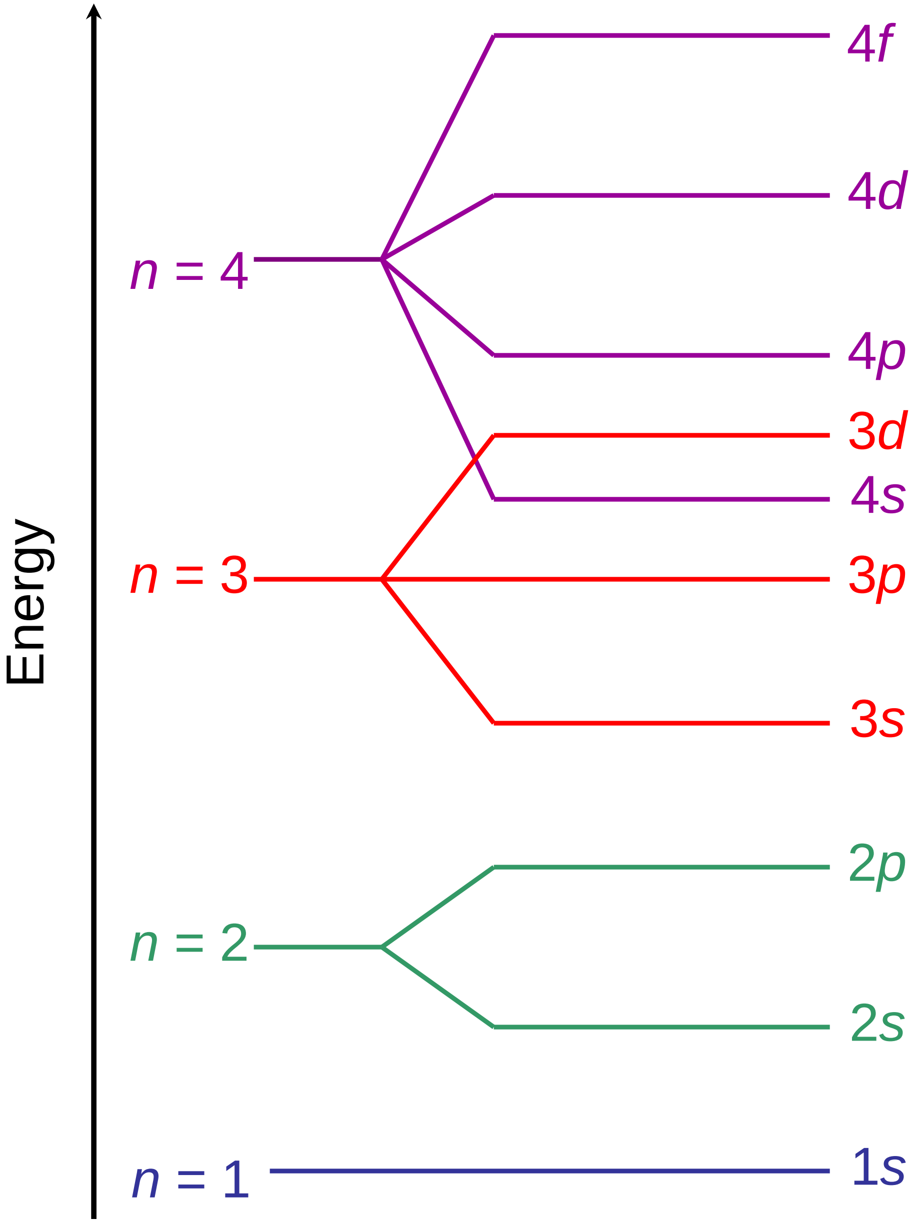
7*s*

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10}$…

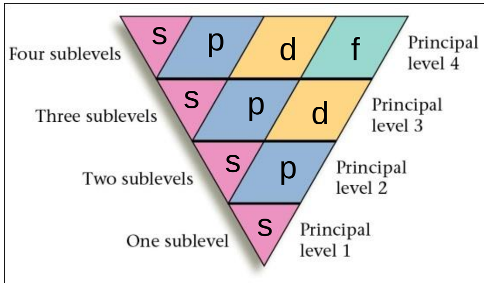
Sublevels


Four sublevels
Principal level 4
Three sublevels
Principal level 3
Two sublevels
Principal level 2
One sublevel
Principal level 1

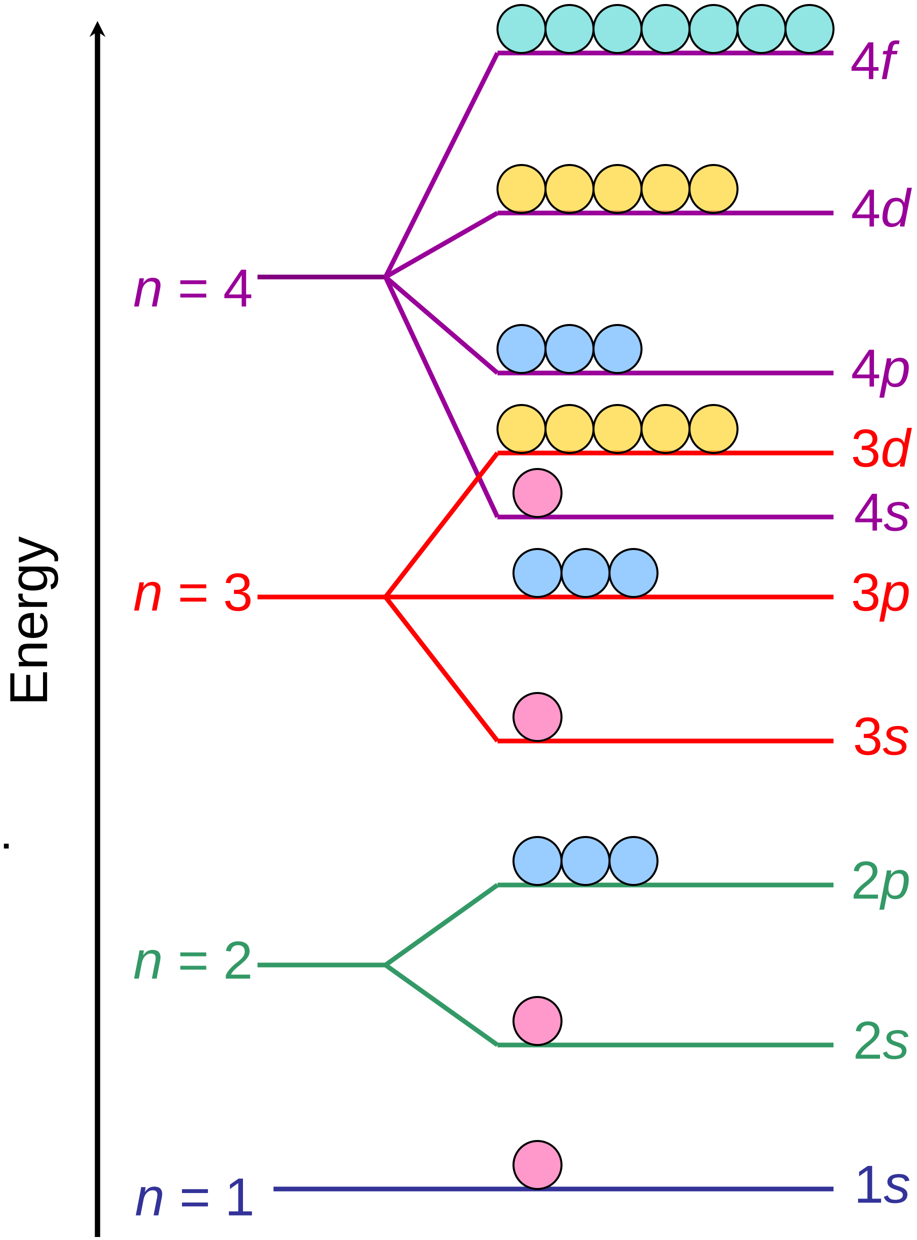

Energy
6d
5f
7s
6p
5d
4f
6s
5p
4d
5s
4p
3d
4s
3p
3s
2p
2s
1s
7s
6p
6d
5f
6s
5p
5d
4f
5s
4d
4s
4p
3d
3s
3p
2s
2p
1s


Energy
4f
4d
n = 4
4p
3d
4s
n = 3
3p
3s
n = 2
2p
2s
n = 1
1s

Sublevels



$1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}\ldots$



																	H 1	**He** 2
1	**H** 1																	
2	**Li** 3	**Be** 4											**B** 5	**C** 6	**N** 7	**O** 8	**F** 9	**Ne** 10
3	**Na** 11	**Mg** 12											**Al** 13	**Si** 14	**P** 15	**S** 16	**Cl** 17	**Ar** 18
4	**K** 19	**Ca** 20	**Sc** 21	**Ti** 22	**V** 23	**Cr** 24	**Mn** 25	**Fe** 26	**Co** 27	**Ni** 28	**Cu** 29	**Zn** 30	**Ga** 31	**Ge** 32	**As** 33	**Se** 34	**Br** 35	**Kr** 36
5	**Rb** 37	**Sr** 38	**Y** 39	**Zr** 40	**Nb** 41	**Mo** 42	**Tc** 43	**Ru** 44	**Rh** 45	**Pd** 46	**Ag** 47	**Cd** 48	**In** 49	**Sn** 50	**Sb** 51	**Te** 52	**I** 53	**Xe** 54
6	**Cs** 55	**Ba** 56	*	**Hf** 72	**Ta** 73	**W** 74	**Re** 75	**Os** 76	**Ir** 77	**Pt** 78	**Au** 79	**Hg** 80	**Tl** 81	**Pb** 82	**Bi** 83	**Po** 84	**At** 85	**Rn** 86
7	**Fr** 87	**Ra** 88	Ω	**Rf** 104	**Db** 105	**Sg** 106	**Bh** 107	**Hs** 108	**Mt** 109									
				La 57	**Ce** 58	**Pr** 59	**Nd** 60	**Pm** 61	**Sm** 62	**Eu** 63	**Gd** 64	**Tb** 65	**Dy** 66	**Ho** 67	**Er** 68	**Tm** 69	**Yb** 70	**Lu** 71
				Ac 89	**Th** 90	**Pa** 91	**U** 92	**Np** 93	**Pu** 94	**Am** 95	**Cm** 96	**Bk** 97	**Cf** 98	**Es** 99	**Fm** 100	**Md** 101	**No** 102	**Lr** 103

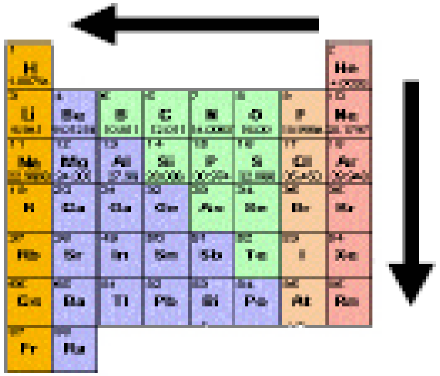
Some factors

نصف قطر الذره

هو نصف المسافة بين مركزى ذرتين متماثلتين متجاورتين للعنصر

أو هو المسافة بين مركز النواة و اخر الكترون فى غلاف التكافؤ

Atomic Radii: Half the distance between the centers of neighboring atoms in a solid or a homonuclear molecule.



Why: Going across a period the effective nuclear charge increases therefore the pull on the electrons increases and the atomic radii decrease. Going down a group the effective nuclear charge decreases therefore the atomic radii increases.

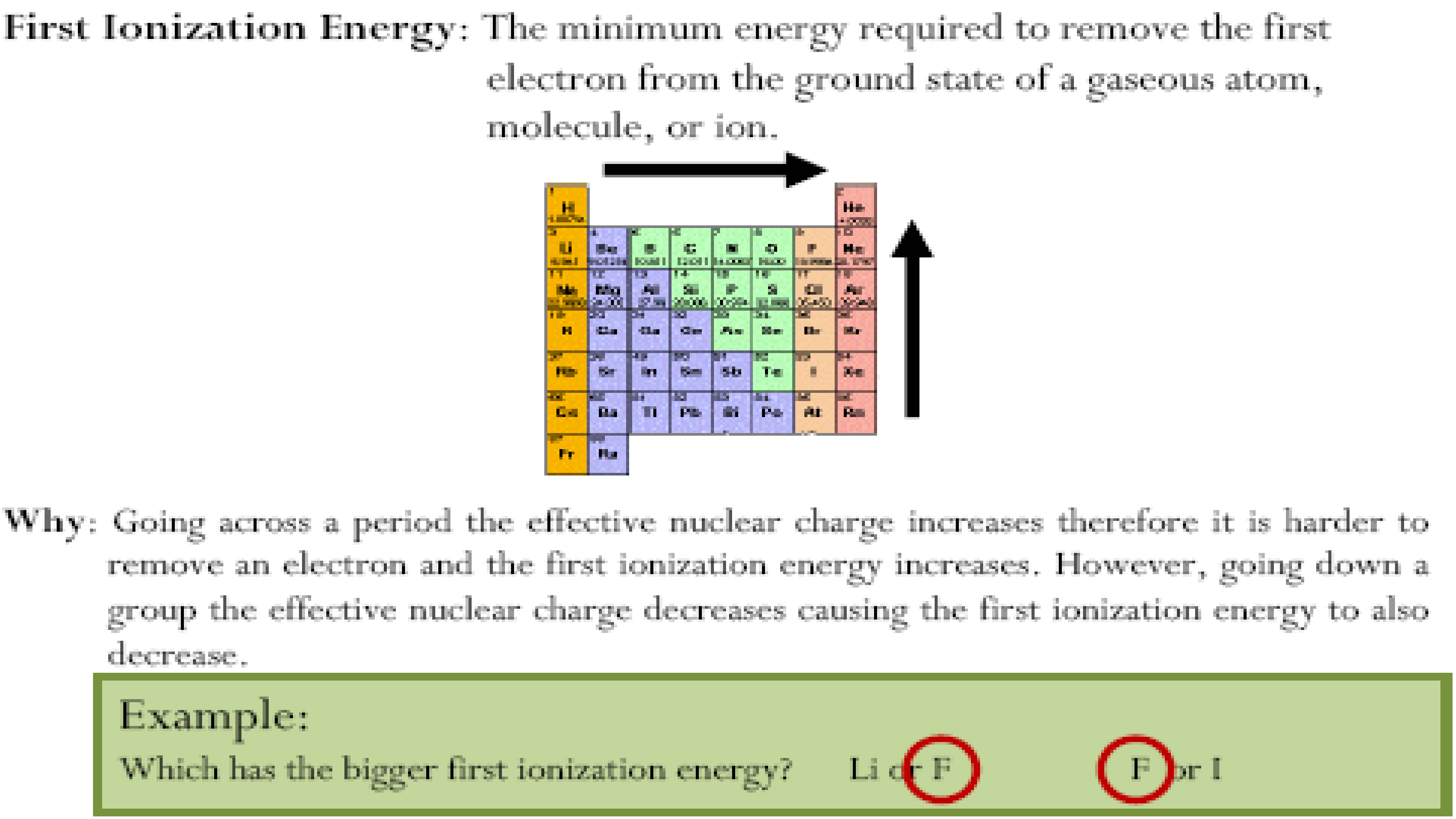
Example:

Which has the bigger atomic radii? [✓ Li] or F F or [✓ I]

جهد التأين

هو أقل طاقة لازمة لانتزاع الكترون من الذرة فى الحالة المستقرة لتتحول الى أيون

هناك جهد التأين الاول و الثانى و الثالث



First Ionization Energy: The minimum energy required to remove the first electron from the ground state of a gaseous atom, molecule, or ion.

Why: Going across a period the effective nuclear charge increases therefore it is harder to remove an electron and the first ionization energy increases. However, going down a group the effective nuclear charge decreases causing the first ionization energy to also decrease.

Example:

Which has the bigger first ionization energy? Li or [✓ F] [✓ F] or I

ما هى العوامل التى تؤثر على جهد التأين؟

- الحجم الذرى أو نصف قطر الذرة
- الشحنة النووية داخل النواة
- عدد الكترونات فى الأغلفة و بالتالى نوع المدار S,P,D,F
- التشبع النصفى والكامل للمدارات الداخلية

Ionization Energies

جهود التأين

Mg
738

Symbol

First Ionization Energy (kJ/mol)

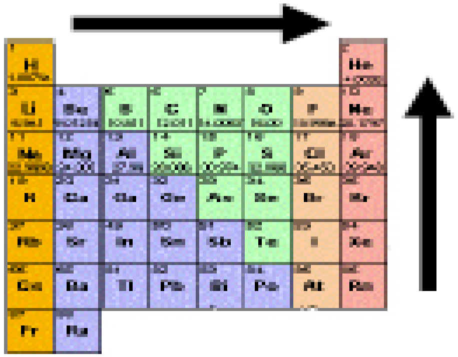
Period	Group 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 1312																	He 2372
2	Li 520	Be 900											B 801	C 1086	N 1402	O 1314	F 1681	Ne 2081
3	Na 496	Mg 738											Al 578	Si 787	P 1012	S 1000	Cl 1251	Ar 1521
4	K 419	Ca 590	Sc 633	Ti 659	V 651	Cr 653	Mn 717	Fe 762	Co 760	Ni 737	Cu 746	Zn 906	Ga 579	Ge 762	As 947	Se 941	Br 1140	Kr 1351
5	Rb 403	Sr 550	Y 600	Zr 640	Nb 652	Mo 684	Tc 702	Ru 710	Rh 720	Pd 804	Ag 731	Cd 868	In 558	Sn 709	Sb 834	Te 869	I 1008	Xe 1170
6	Cs 376	Ba 503	La* 538	Hf 659	Ta 761	W 770	Re 760	Os 839	Ir 878	Pt 868	Au 890	Hg 1007	Tl 589	Pb 716	Bi 703	Po 812	At --	Rn 1038
7	Fr --	Ra 509	Acψ 490	Rf --	Db --	Sg --	Bh --	Hs --	Mt --	Ds --	Uuu --	Uub --	Uut --	Uuq --	Uup --			Uuo --

* Lanthanide series	Ce 534	Pr 527	Nd 533	Pm 536	Sm 545	Eu 547	Gd 592	Tb 566	Dy 573	Ho 581	Er 589	Tm 597	Yb 603	Lu 523
ψ Actinide series	Th 587	Pa 570	U 598	Np 600	Pu 585	Am 578	Cm 581	Bk 601	Cf 608	Es 619	Fm 627	Md 635	No 642	Lr --

القابلية الكترونية

هى الطاقة المنطلقة عند اكتساب الذرة للأكترون

Electron Affinity: (E_{ea}) The energy released when an electron is added to a gas-phase atom.



Why: Going across a period the effective nuclear charge increases therefore the atom has a larger positive charge and releases more energy when an electron is added to the atom. Going down a group the effective nuclear charge decreases and therefore the atom has a smaller positive charge and the electron affinity decreases.

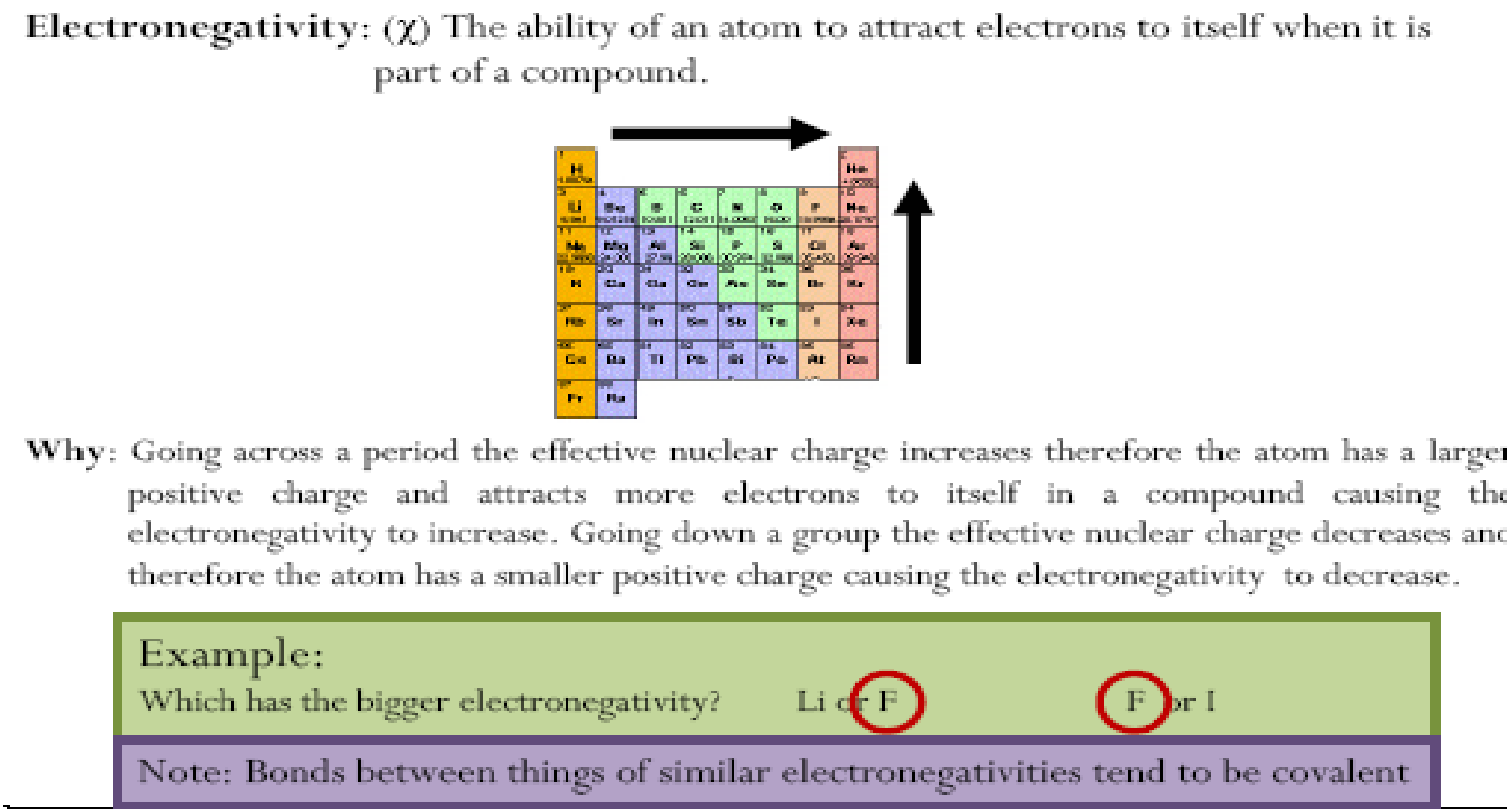
Example:

Which has the bigger electron affinity? Li or [✓ F] [✓ F] or I

Note: This trend has the most atoms that do not obey the trend

السالبية الكهربية

هى قدرة الذرة على جذب الكترونات عندما تكون جزء من مركب



Electronegativity: (χ) The ability of an atom to attract electrons to itself when it is part of a compound.

Why: Going across a period the effective nuclear charge increases therefore the atom has a larger positive charge and attracts more electrons to itself in a compound causing the electronegativity to increase. Going down a group the effective nuclear charge decreases and therefore the atom has a smaller positive charge causing the electronegativity to decrease.

Example:

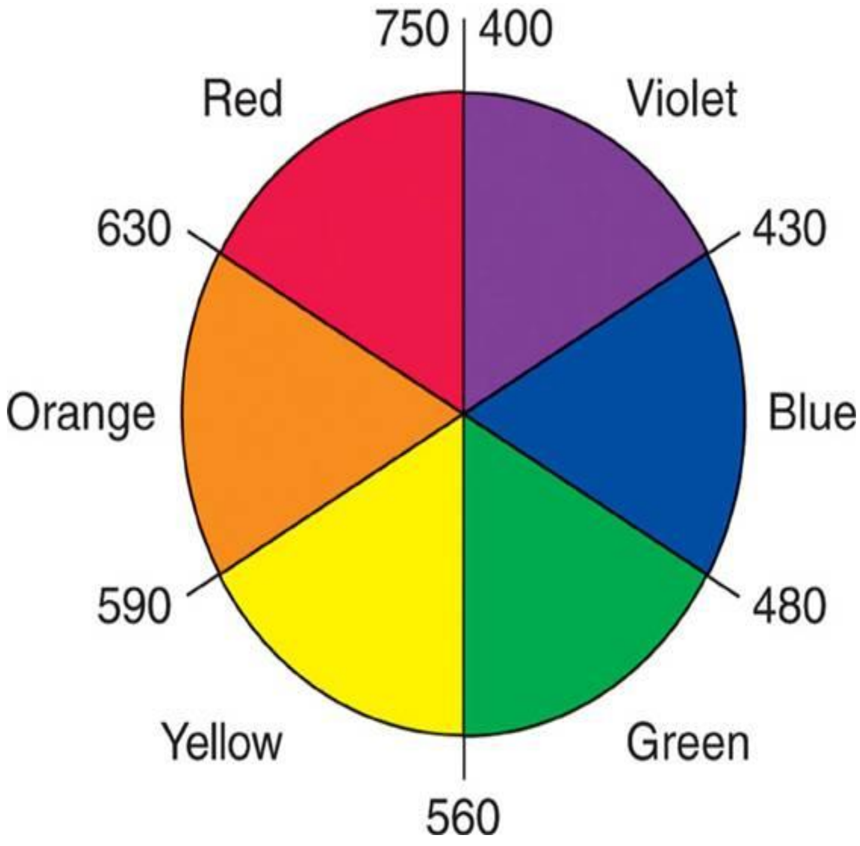
Which has the bigger electronegativity? Li or [✓ F] [✓ F] or I

Note: Bonds between things of similar electronegativities tend to be covalent

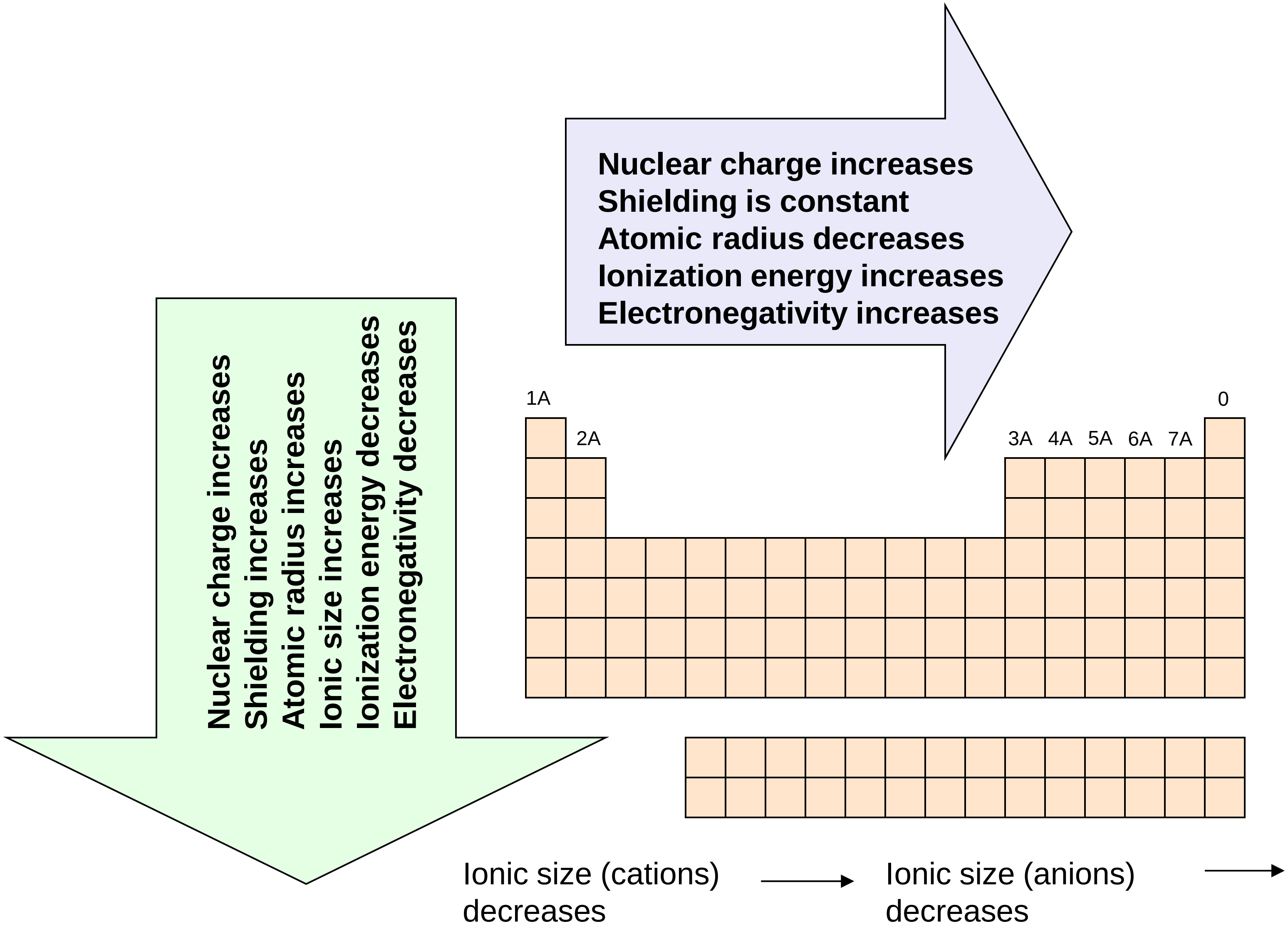
خاصية اللون

- معظم مركبات عناصر الفئة S, P تكون غير ملونة

- يعزى لون أيون الى اثارة الكترونات المستويات الداخليةd,f داخل نفس المستوى يعرف بانتقالات (d-d), (f-f)



Summary of Periodic Trends



Nuclear charge increases
Shielding is constant
Atomic radius decreases
Ionization energy increases
Electronegativity increases

Nuclear charge increases
Shielding increases
Atomic radius increases
Ionic size increases
Ionization energy decreases
Electronegativity decreases

Ionic size (cations) decreases →

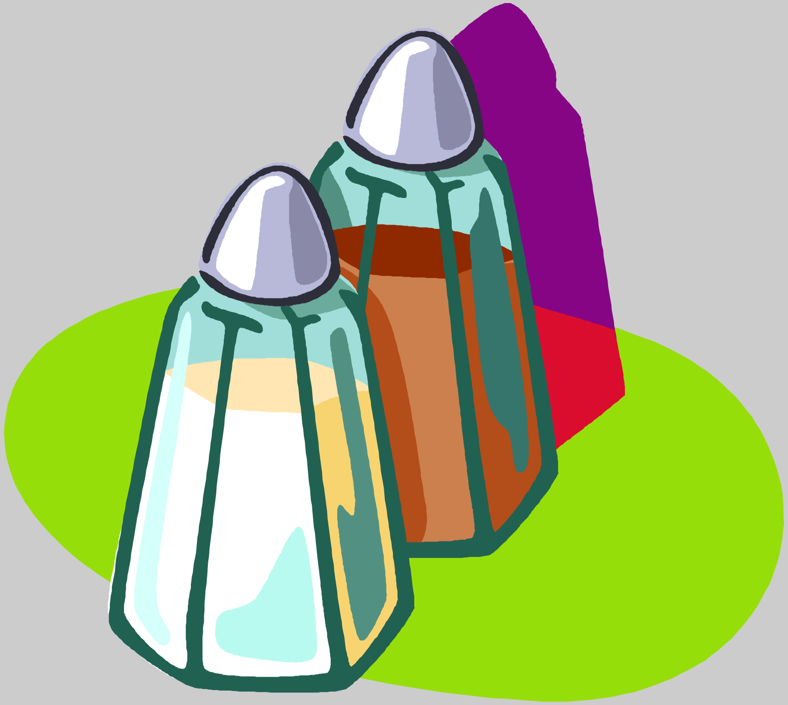
Ionic size (anions) decreases →

Hydrogen

- Hydrogen belongs to a family of its own.
- Hydrogen is a diatomic, reactive gas.
- Hydrogen was involved in the explosion of the Hindenberg.
- Hydrogen is promising as an alternative fuel source for automobiles

Alkali Metals

- 1st column on the periodic table (Group 1) not including hydrogen.
- Very reactive metals, always combined with something else in nature (like in salt).
- Soft enough to cut with a butter knife

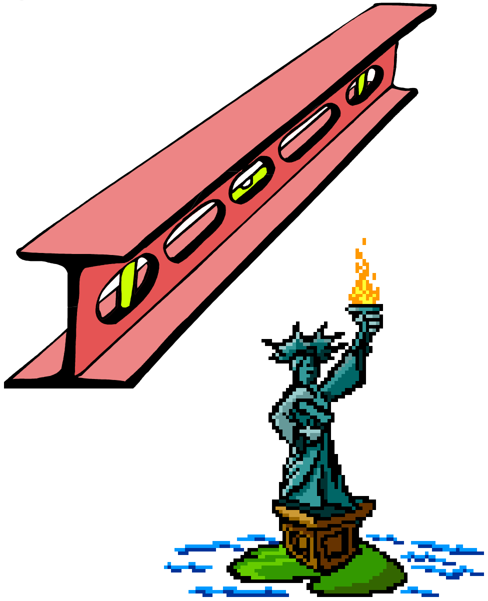


Alkaline Earth Metals

- Second column on the periodic table. (Group 2)
- Reactive metals that are always combined with nonmetals in nature.
- Several of these elements are important mineral nutrients (such as Mg and Ca

Transition Metals

- Elements in groups 3-12
- Less reactive harder metals
- Includes metals used in jewelry and construction.
- Metals used “as metal.”



Boron Family

- Elements in group 13
- Aluminum metal was once rare and expensive, not a “disposable metal.”

Carbon Family

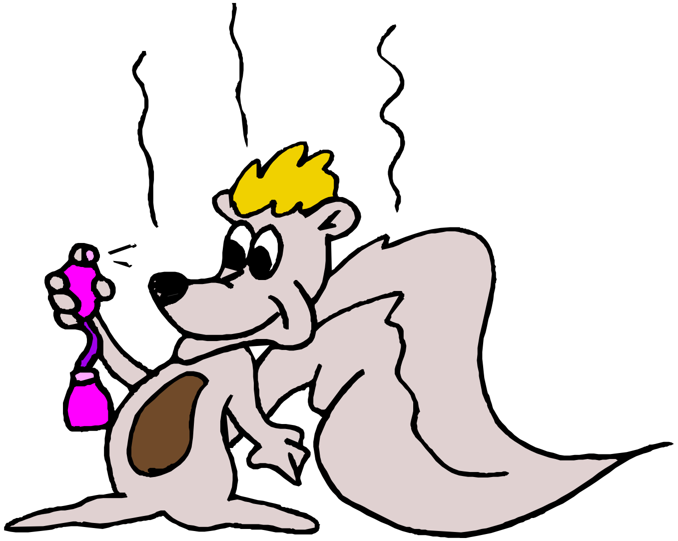
- Elements in group 14
- Contains elements important to life and computers.
- Carbon is the basis for an **entire branch** of chemistry.
- Diamond and Graphite are two forms of carbon.
- Silicon and Germanium are important semiconductors.

Nitrogen Family

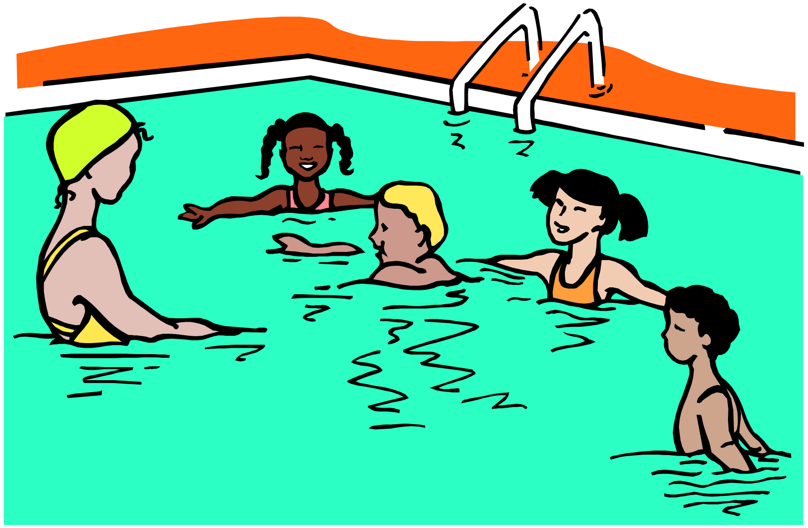
- Elements in group 15
- Nitrogen makes up over ¾ of the atmosphere.
- Nitrogen and phosphorus are both important in living things.
- Most of the world’s nitrogen is not available to living things.
- The red stuff on the tip of matches is phosphorus.

Oxygen Family

- Elements in group 16
- Oxygen is necessary for respiration.
- Many things that stink, contain sulfur (rotten eggs, garlic, skunks,etc.)



Halogens

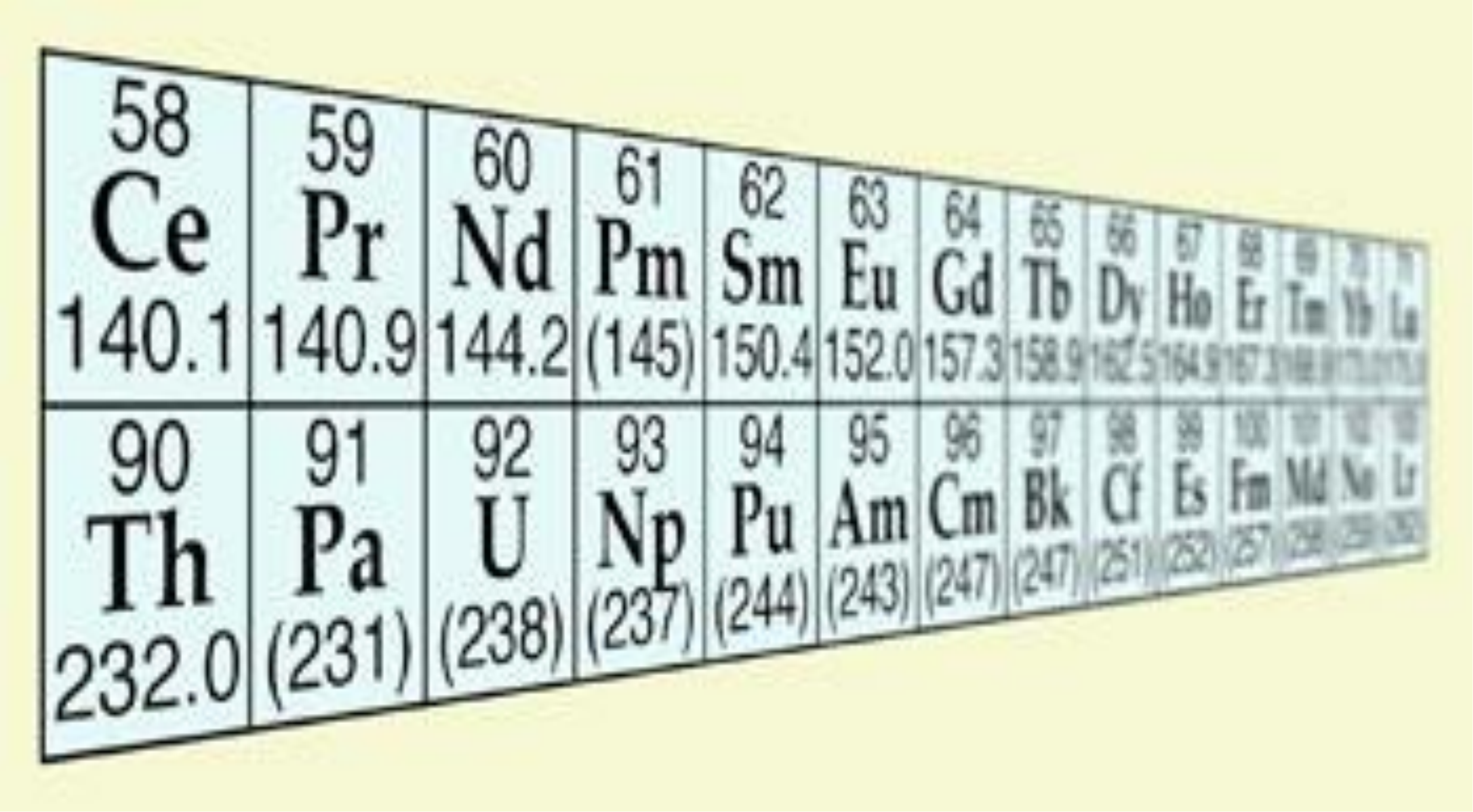


- Elements in group 17
- Very reactive, volatile, diatomic, nonmetals
- Always found combined with other element in nature .
- Used as disinfectants and to strengthen teeth.
- Fluorine is an active ingredient in toothpaste

The Noble Gases

- Elements in group 18
- VERY unreactive, monatomic gases
- Used in lighted “neon” signs
- Have a full valence shell.
- Helium is used to fill balloons

Lanthanides & Actinides



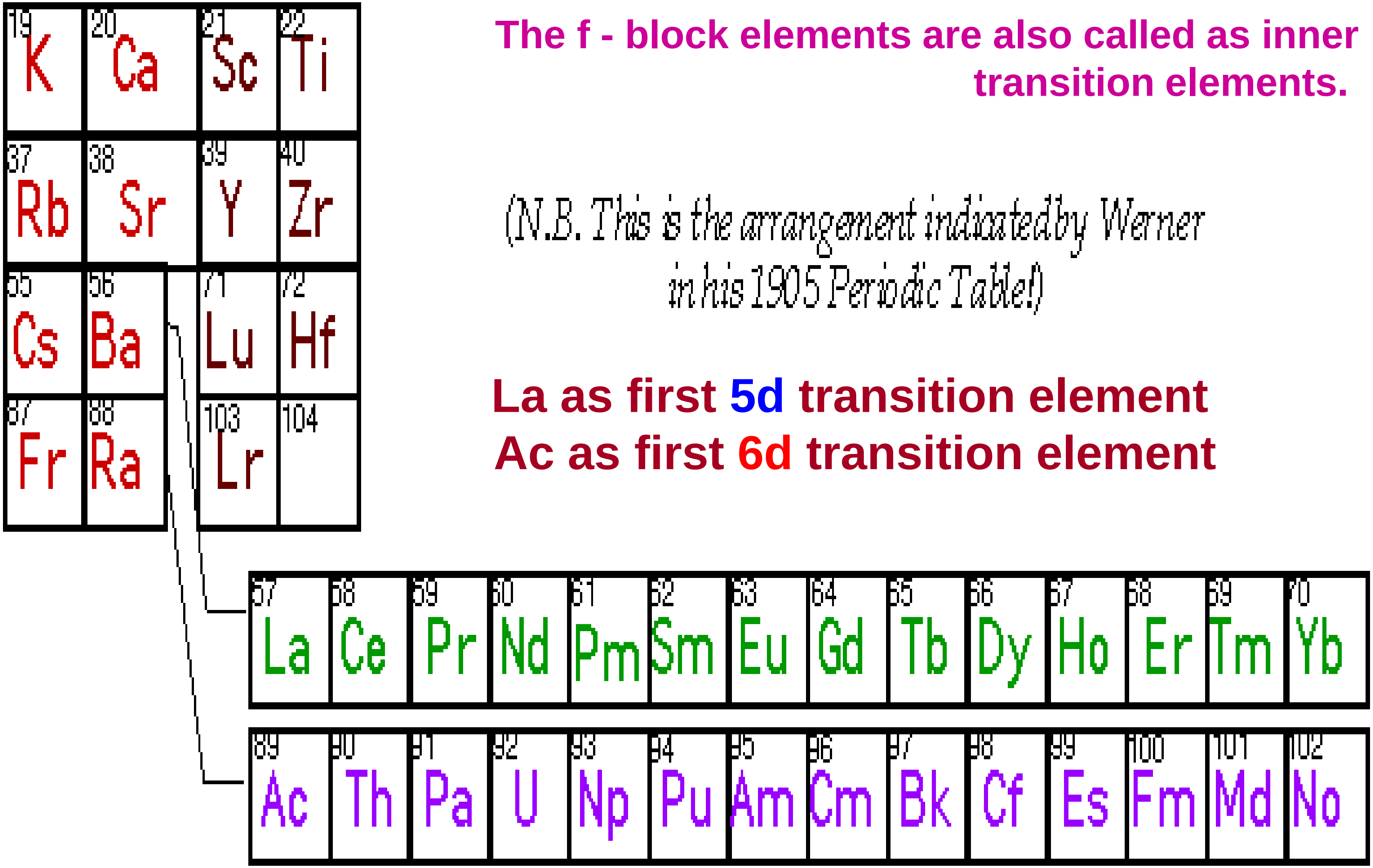
58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	[illegible] Tm [illegible]	[illegible] Yb [illegible]	[illegible] Lu [illegible]
90 Th 232.0	91 Pa (231)	92 U (238)	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	[illegible] Md [illegible]	[illegible] No [illegible]	[illegible] Lr [illegible]

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

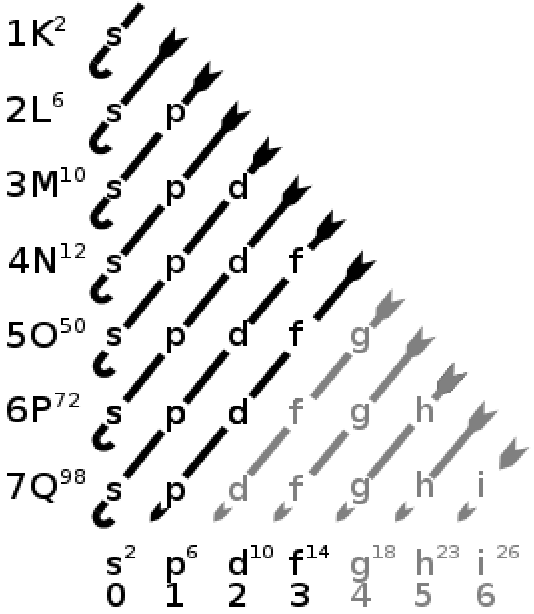
(N.B. This is the arrangement indicated by Werner in his 1905 Periodic Table!)

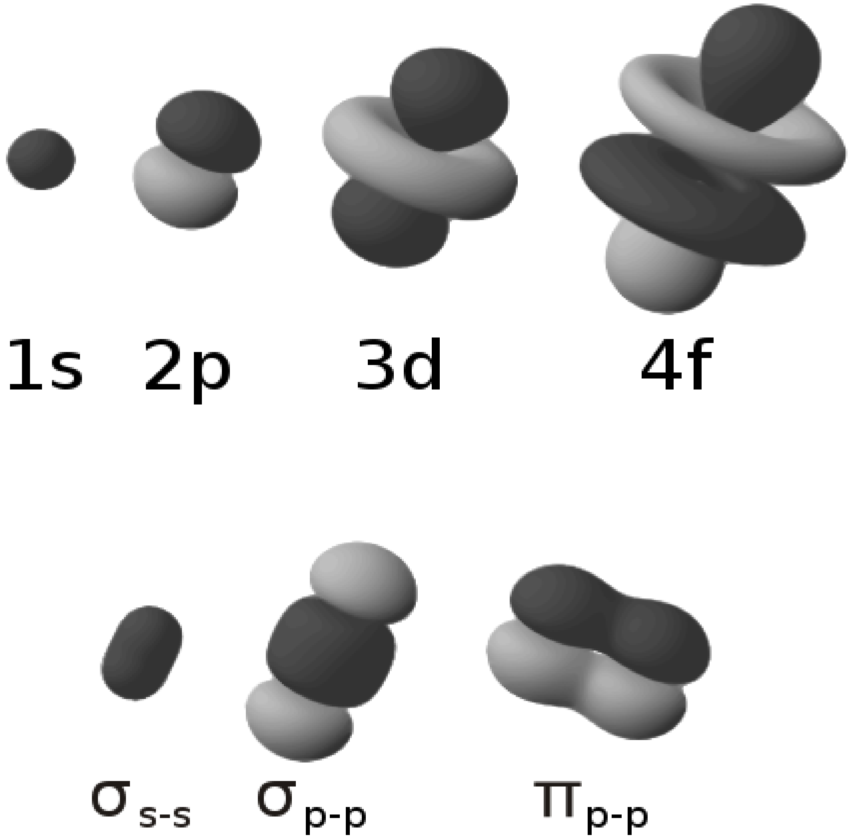
La as first 5d transition element

Ac as first 6d transition element



F- configuration





$1s^2_2 2s^2_4 2p^6_{10} 3s^2_{12} 3p^6_{18} 4s^2_{20} 3d^{10}_{30} 4p^6_{36} 5s^2_{38} 4d^{10}_{48} 5p^6_{54} 6s^2_{56} 4f^{14}_{70} 5d^{10}_{80} 6p^6_{86} 7s^2_{88} 5f^{14}_{102} 6d^{10}_{112} 7p^6_{118}$

Inner Transition Elements

- ☐ The elements in which the additional electrons enters (n-2)f orbitals are called **inner transition elements**.

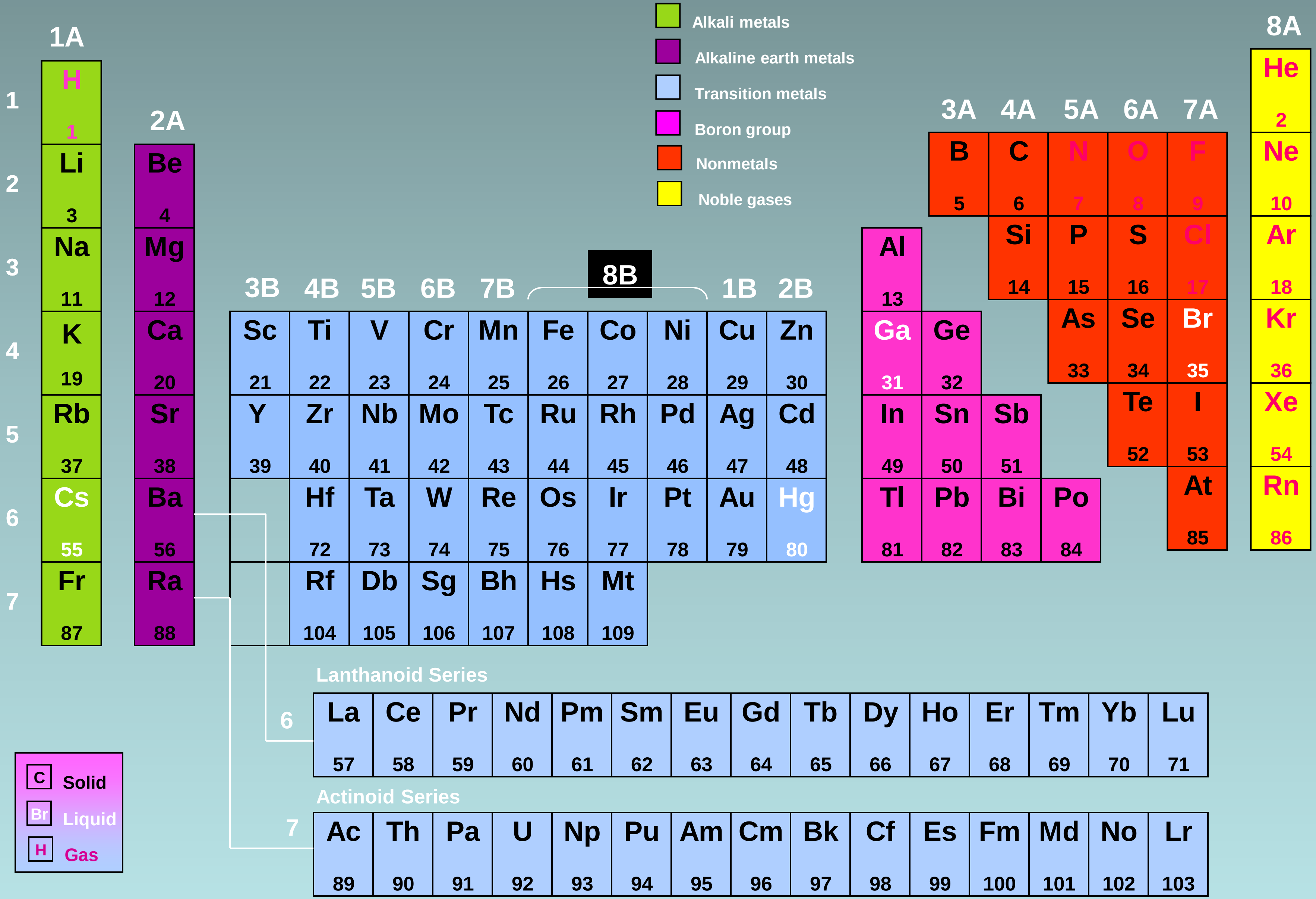
- ☐ The valence shell electronic configuration of these elements can be represented as **$(n-2)f^{0\text{-}14}(n-1)d^{0\text{-}1}ns^2$.**

- ✓ 4f inner transition metals are known **as lanthanides** because they come immediately after lanthanum.

- ✓ 5f inner transition metals are known as actinoids because they come immediately after actinium.

Periodic Table

- 🟩 Alkali metals
- 🟪 Alkaline earth metals
- 🟦 Transition metals
- 🟪 Boron group
- 🟥 Nonmetals
- 🟨 Noble gases



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

Lanthanoid Series

6	La 57	Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71

Actinoid Series

7	Ac 89	Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lr 103

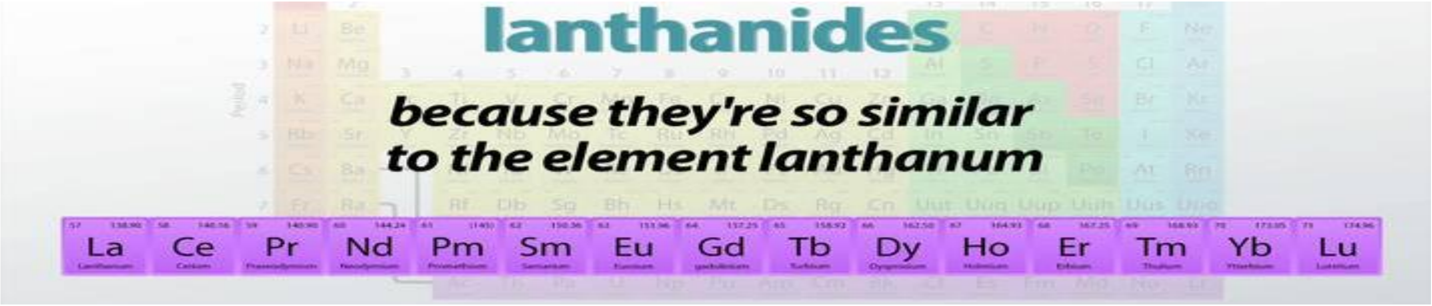
- C Solid
- Br Liquid
- H Gas

4f-block elements (lanthanides)

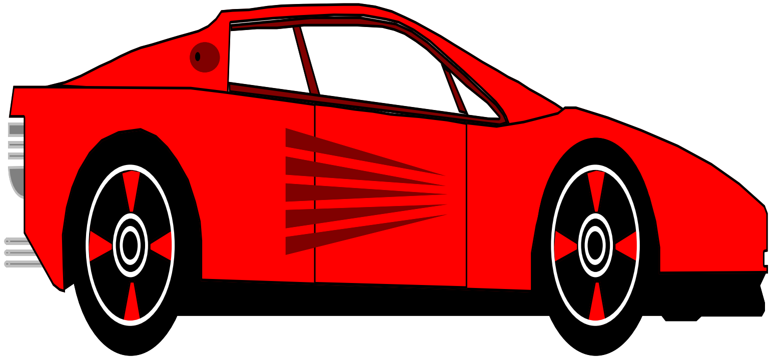
Valence shell electronic Configuration $4f^{0,2\text{ to }14}\,5d^{0,1}\,6s^2$

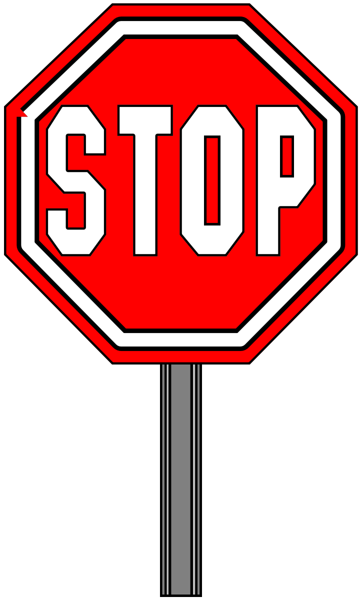
57	58	59	60	61	62	63	64
La	**Ce**	**Pr**	**Nd**	**Pm**	**Sm**	**Eu**	**Gd**
lanthanum	Cerium	Praseodymium	Neodymium	Promethium	Samarium	Europium	Gadolinium
138.905	140.116	140.908	144.243	144.913	150.360	151.964	157.250
$4f^0 5d^1 6s^2$	$4f^2 5d^0 6s^2$	$4f^3 5d^0 6s^2$	$4f^4 5d^0 6s^2$	$4f^5 5d^0 6s^2$	$4f^6 5d^0 6s^2$	$4f^7 5d^0 6s^2$	$4f^7 5d^1 6s^2$

65	66	67	68	69	70	71
Tb	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**
Terbium	Dysprosium	Holmium	Erbium	Thulium	Ytterbium	Lutetium
158.925	162.500	164.930	167.259	168.934	173.055	174.967
$4f^9 5d^0 6s^2$	$4f^{10} 5d^0 6s^2$	$4f^{11} 5d^0 6s^2$	$4f^{12} 5d^0 6s^2$	$4f^{13} 5d^0 6s^2$	$4f^{14} 5d^0 6s^2$	$4f^{14} 5d^1 6s^2$



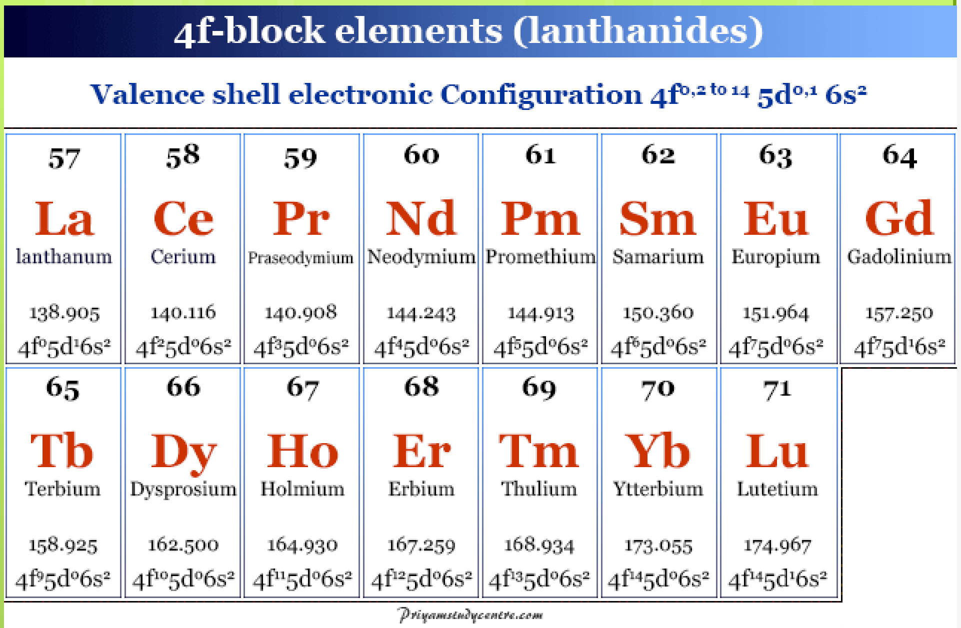
The End





The f - block elements

(inner transition elements).



4f-block elements (lanthanides)

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

57 **La** lanthanum 138.905 $4f^{0}5d^{1}6s^{2}$	58 **Ce** Cerium 140.116 $4f^{2}5d^{0}6s^{2}$	59 **Pr** Praseodymium 140.908 $4f^{3}5d^{0}6s^{2}$	60 **Nd** Neodymium 144.243 $4f^{4}5d^{0}6s^{2}$	61 **Pm** Promethium 144.913 $4f^{5}5d^{0}6s^{2}$	62 **Sm** Samarium 150.360 $4f^{6}5d^{0}6s^{2}$	63 **Eu** Europium 151.964 $4f^{7}5d^{0}6s^{2}$	64 **Gd** Gadolinium 157.250 $4f^{7}5d^{1}6s^{2}$
65 **Tb** Terbium 158.925 $4f^{9}5d^{0}6s^{2}$	66 **Dy** Dysprosium 162.500 $4f^{10}5d^{0}6s^{2}$	67 **Ho** Holmium 164.930 $4f^{11}5d^{0}6s^{2}$	68 **Er** Erbium 167.259 $4f^{12}5d^{0}6s^{2}$	69 **Tm** Thulium 168.934 $4f^{13}5d^{0}6s^{2}$	70 **Yb** Ytterbium 173.055 $4f^{14}5d^{0}6s^{2}$	71 **Lu** Lutetium 174.967 $4f^{14}5d^{1}6s^{2}$	

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lanthanide series

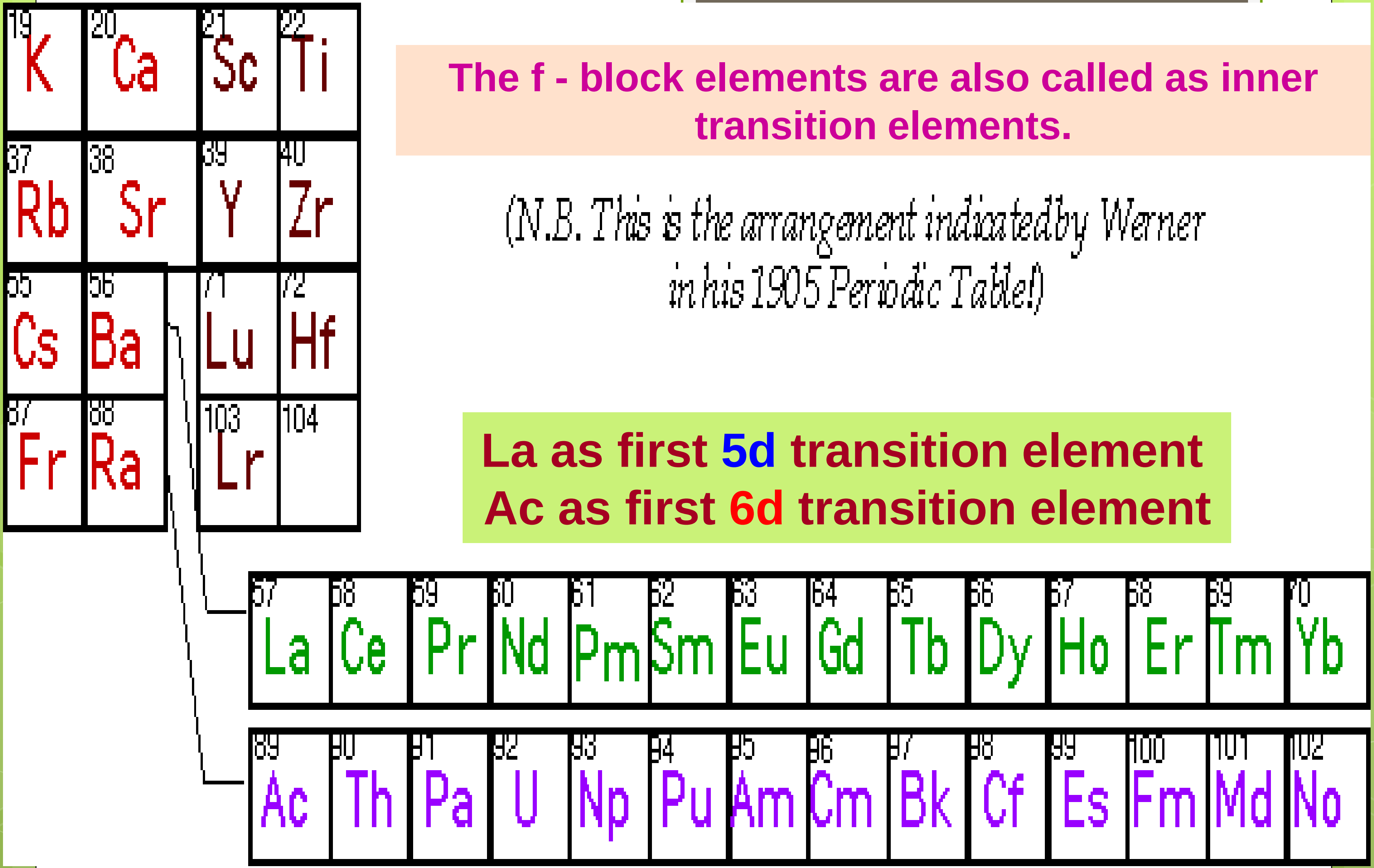
Rare-earth series


INTRODUCING THE LANTHANIDES
rare earth metals
fact
Study.com

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

(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



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

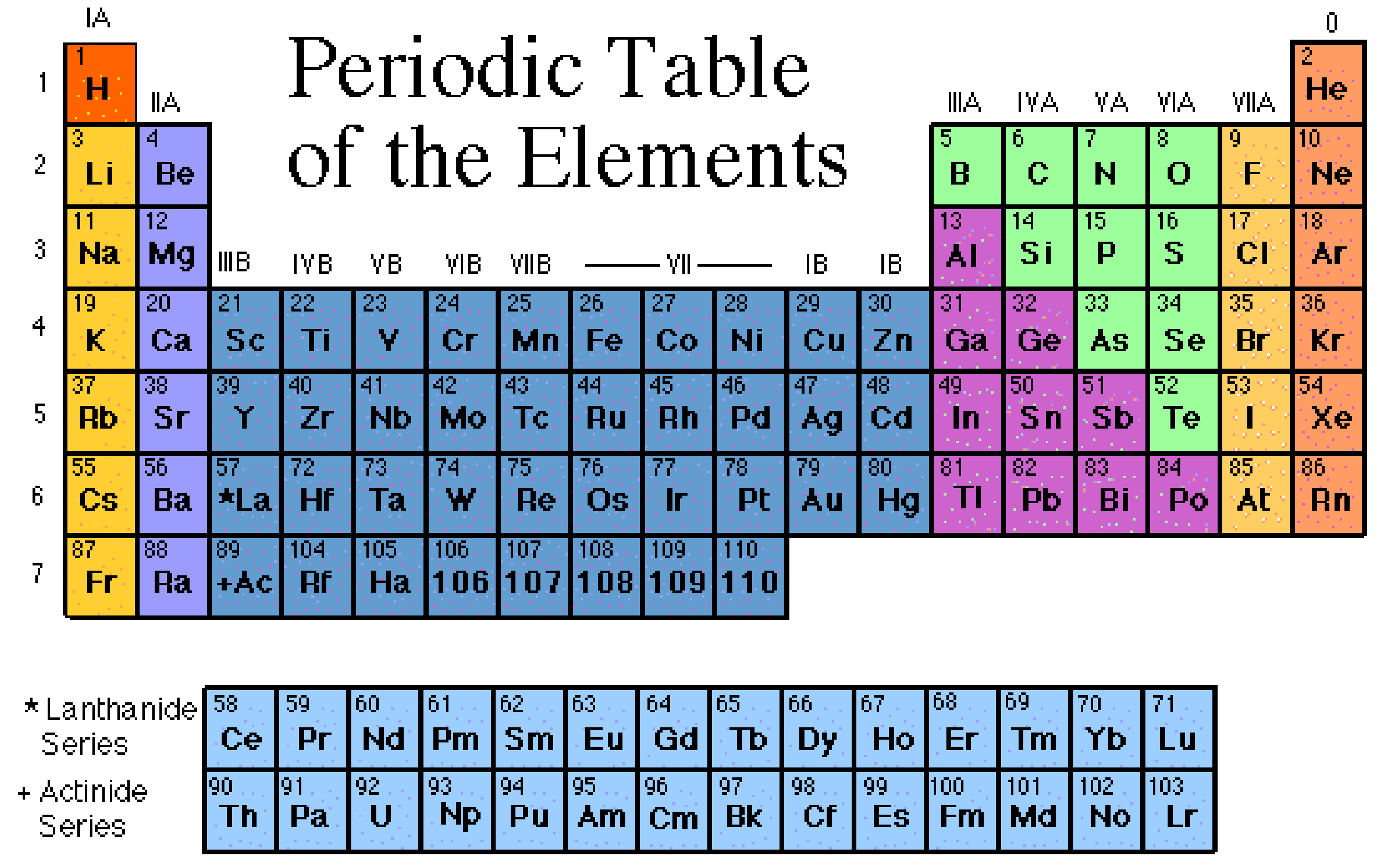
اكتشافها

- • 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

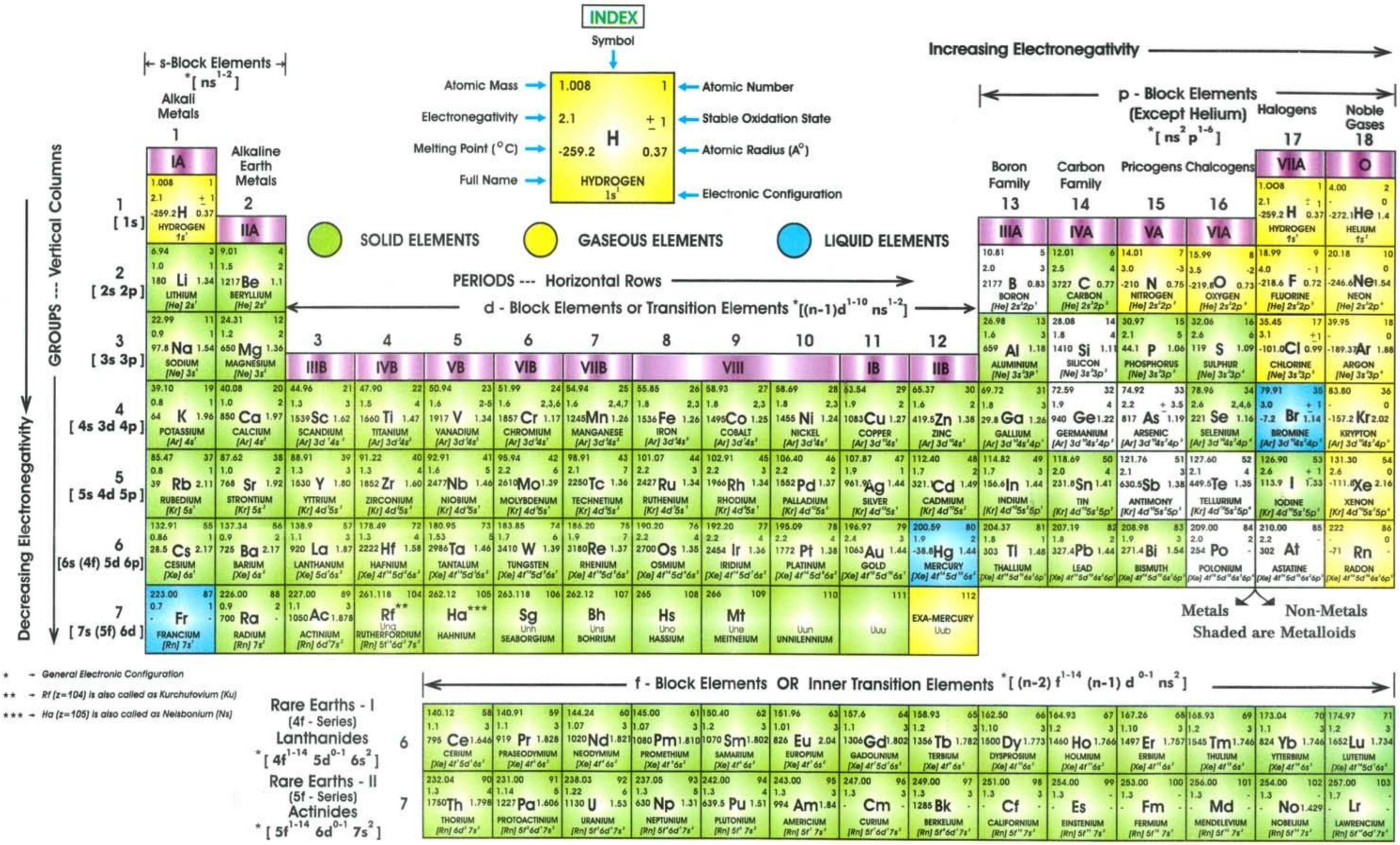


Periodic Table of the Elements

	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



INDEX

Symbol

Atomic Mass → 1.008 | 1 ← Atomic Number

Electronegativity → 2.1 | ± 1 ← Stable Oxidation State

Melting Point (°C) → -259.2 | H | 0.37 ← Atomic Radius (A°)

Full Name → HYDROGEN

$1s^1$ ← Electronic Configuration

🟢 SOLID ELEMENTS 🟡 GASEOUS ELEMENTS 🔵 LIQUID ELEMENTS

Increasing Electronegativity →

Decreasing Electronegativity ↓

PERIODS --- Horizontal Rows →

GROUPS --- Vertical Columns

← s-Block Elements → *[ns^{1-2}]

← d - Block Elements or Transition Elements *[$(n-1)d^{1-10}$ ns^{1-2}] →

← p - Block Elements (Except Helium) *[ns^2p^{1-6}] →

← f - Block Elements OR Inner Transition Elements *[$(n-2)f^{1-14}$ $(n-1)d^{0-1}$ ns^2] →

Group	Label	Family
1	IA	Alkali Metals
2	IIA	Alkaline Earth Metals
3	IIIB	
4	IVB	
5	VB	
6	VIB	
7	VIIB	
8	VIII	
9	VIII	
10	VIII	
11	IB	
12	IIB	
13	IIIA	Boron Family
14	IVA	Carbon Family
15	VA	Pricogens
16	VIA	Chalcogens
17	VIIA	Halogens
18	O	Noble Gases

Period	Orbitals
1	[1s]
2	[2s 2p]
3	[3s 3p]
4	[4s 3d 4p]
5	[5s 4d 5p]
6	[6s (4f) 5d 6p]
7	[7s (5f) 6d]

Atomic Number	Symbol	Full Name	Atomic Mass	Electronegativity	Stable Oxidation State	Melting Point (°C)	Atomic Radius (A°)	Electronic Configuration
1	H	HYDROGEN	1.008	2.1	± 1	-259.2	0.37	$1s^1$
2	He	HELIUM	4.00	-	0	-272.1	1.4	$1s^2$
3	Li	LITHIUM	6.94	1.0	1	180	1.34	[He] $2s^1$
4	Be	BERYLLIUM	9.01	1.5	2	1217	1.1	[He] $2s^2$
5	B	BORON	10.81	2.0	3	2177	0.83	[He] $2s^22p^1$
6	C	CARBON	12.01	2.5	4	3727	0.77	[He] $2s^22p^2$
7	N	NITROGEN	14.01	3.0	-3	-210	0.75	[He] $2s^22p^3$
8	O	OXYGEN	15.99	3.5	-2	-219.8	0.73	[He] $2s^22p^4$
9	F	FLUORINE	18.99	4.0	- 1	-218.6	0.72	[He] $2s^22p^5$
10	Ne	NEON	20.18	-	0	-246.6	1.54	[He] $2s^22p^6$
11	Na	SODIUM	22.99	0.9	1	97.8	1.54	[Ne] $3s^1$
12	Mg	MAGNESIUM	24.31	1.2	2	650	1.36	[Ne] $3s^2$
13	Al	ALUMINIUM	26.98	1.6	3	659	1.18	[Ne] $3s^23P^1$
14	Si	SILICON	28.08	1.8	4	1410	1.11	[Ne] $3s^23p^2$
15	P	PHOSPHORUS	30.97	2.1	5	44.1	1.06	[Ne] $3s^23p^3$
16	S	SULPHUR	32.06	2.6	6	119	1.09	[Ne] $3s^23p^4$
17	Cl	CHLORINE	35.45	3.1	± 1	-101.0	0.99	[Ne] $3s^23p^5$
18	Ar	ARGON	39.95	-	0	-189.37	1.88	[Ne] $3s^23p^6$
19	K	POTASSIUM	39.10	0.8	1	64	1.96	[Ar] $4s^1$
20	Ca	CALCIUM	40.08	1.0	2	850	1.97	[Ar] $4s^2$
21	Sc	SCANDIUM	44.96	1.3	3	1539	1.62	[Ar] $3d^14s^2$
22	Ti	TITANIUM	47.90	1.5	4	1660	1.47	[Ar] $3d^24s^2$
23	V	VANADIUM	50.94	1.6	2-5	1917	1.34	[Ar] $3d^34s^2$
24	Cr	CHROMIUM	51.99	1.6	2,3,6	1857	1.17	[Ar] $3d^54s^1$
25	Mn	MANGANESE	54.94	1.6	2,4,7	1245	1.26	[Ar] $3d^54s^2$
26	Fe	IRON	55.85	1.8	2,3	1536	1.26	[Ar] $3d^64s^2$
27	Co	COBALT	58.93	1.8	2,3	1495	1.25	[Ar] $3d^74s^2$
28	Ni	NICKEL	58.69	1.8	2,3	1455	1.24	[Ar] $3d^84s^2$
29	Cu	COPPER	63.54	1.9	2	1083	1.27	[Ar] $3d^{10}4s^1$
30	Zn	ZINC	65.37	1.6	2	419.5	1.38	[Ar] $3d^{10}4s^2$
31	Ga	GALLIUM	69.72	1.8	3	29.8	1.26	[Ar] $3d^{10}4s^24p^1$
32	Ge	GERMANIUM	72.59	1.9	4	940	1.22	[Ar] $3d^{10}4s^24p^2$
33	As	ARSENIC	74.92	2.2	± 3.5	817	1.19	[Ar] $3d^{10}4s^24p^3$
34	Se	SELENIUM	78.96	2.6	2,4,6	221	1.16	[Ar] $3d^{10}4s^24p^4$
35	Br	BROMINE	79.91	3.0	± 1	-7.2	1.14	[Ar] $3d^{10}4s^24p^5$
36	Kr	KRYPTON	83.80	-	0	-157.2	2.02	[Ar] $3d^{10}4s^24p^6$
37	Rb	RUBEDIUM	85.47	0.8	1	39	2.11	[Kr] $5s^1$
38	Sr	STRONTIUM	87.62	1.0	2	768	1.92	[Kr] $5s^2$
39	Y	YTTRIUM	88.91	1.3	3	1530	1.80	[Kr] $4d^15s^2$
40	Zr	ZIRCONIUM	91.22	1.3	4	1852	1.60	[Kr] $4d^25s^2$
41	Nb	NIOBIUM	92.91	1.6	5	2477	1.46	[Kr] $4d^45s^1$
42	Mo	MOLYBDENUM	95.94	2.2	6	2610	1.39	[Kr] $4d^55s^1$
43	Tc	TECHNETIUM	98.91	2.1	7	2250	1.36	[Kr] $4d^55s^2$
44	Ru	RUTHENIUM	101.07	2.2	3	2427	1.34	[Kr] $4d^75s^1$
45	Rh	RHODIUM	102.91	2.2	3	1966	1.34	[Kr] $4d^85s^1$
46	Pd	PALLADIUM	106.40	2.2	2	1552	1.37	[Kr] $4d^{10}5s^0$
47	Ag	SILVER	107.87	1.9	1	961.9	1.44	[Kr] $4d^{10}5s^1$
48	Cd	CADMIUM	112.40	1.7	2	321.1	1.49	[Kr] $4d^{10}5s^2$
49	In	INDIUM	114.82	1.7	3	156.6	1.44	[Kr] $4d^{10}5s^25p^1$
50	Sn	TIN	118.69	2.0	4	231.8	1.41	[Kr] $4d^{10}5s^25p^2$
51	Sb	ANTIMONY	121.76	2.1	3	630.5	1.38	[Kr] $4d^{10}5s^25p^3$
52	Te	TELLURIUM	127.60	2.1	4	449.5	1.35	[Kr] $4d^{10}5s^25p^4$
53	I	IODINE	126.90	2.6	± 1	113.9	1.33	[Kr] $4d^{10}5s^25p^5$
54	Xe	XENON	131.30	2.6	0	-111.8	2.16	[Kr] $4d^{10}5s^25p^6$
55	Cs	CESIUM	132.91	0.86	1	28.5	2.17	[Xe] $6s^1$
56	Ba	BARIUM	137.34	0.9	2	725	2.17	[Xe] $6s^2$
57	La	LANTHANUM	138.9	1.1	3	920	1.87	[Xe] $5d^16s^2$
72	Hf	HAFNIUM	178.49	1.3	4	2222	1.58	[Xe] $4f^{14}5d^26s^2$
73	Ta	TANTALUM	180.95	1.53	5	2986	1.46	[Xe] $4f^{14}5d^36s^2$
74	W	TUNGSTEN	183.85	1.7	6	3410	1.39	[Xe] $4f^{14}5d^46s^2$
75	Re	RHENIUM	186.20	1.9	7	3180	1.37	[Xe] $4f^{14}5d^56s^2$
76	Os	OSMIUM	190.20	2.2	4	2700	1.35	[Xe] $4f^{14}5d^66s^2$
77	Ir	IRIDIUM	192.20	2.2	4	2454	1.36	[Xe] $4f^{14}5d^76s^2$
78	Pt	PLATINUM	195.09	2.2	4	1772	1.38	[Xe] $4f^{14}5d^96s^1$
79	Au	GOLD	196.97	2.4	3	1063	1.44	[Xe] $4f^{14}5d^{10}6s^1$
80	Hg	MERCURY	200.59	1.9	2	-38.8	1.44	[Xe] $4f^{14}5d^{10}6s^2$
81	Tl	THALLIUM	204.37	1.8	1	303	1.48	[Xe] $4f^{14}5d^{10}6s^26p^1$
82	Pb	LEAD	207.19	1.8	2	327.4	1.44	[Xe] $4f^{14}5d^{10}6s^26p^2$
83	Bi	BISMUTH	208.98	1.9	3	271.4	1.54	[Xe] $4f^{14}5d^{10}6s^26p^3$
84	Po	POLONIUM	209.00	2.0	2	254	-	[Xe] $4f^{14}5d^{10}6s^26p^4$
85	At	ASTATINE	210.00	2.2	-	302	-	[Xe] $4f^{14}5d^{10}6s^26p^5$
86	Rn	RADON	222	-	0	-71	-	[Xe] $4f^{14}5d^{10}6s^26p^6$
87	Fr	FRANCIUM	223.00	0.7	1	-	-	[Rn] $7s^1$
88	Ra	RADIUM	226.00	0.9	2	700	-	[Rn] $7s^2$
89	Ac	ACTINIUM	227.00	1.1	3	1050	1.878	[Rn] $6d^17s^2$
104	Rf** (Unq)	RUTHERFORDIUM	261.118					[Rn] $5f^{14}6d^27s^2$
105	Ha***	HAHNIUM	262.12					
106	Sg (Unh)	SEABORGIUM	263.118					
107	Bh (Uns)	BOHRIUM	262.12					
108	Hs (Uno)	HASSIUM	265					
109	Mt (Une)	MEITNEIUM	266					
110	Uun	UNNILENNIUM						
111	Uuu							
112	Uub	EXA-MERCURY						

Metals ↙ ↘ Non-Metals

Shaded are Metalloids

Rare Earths - I (4f - Series) Lanthanides *[$4f^{1-14}$ $5d^{0-1}$ $6s^2$] — 6

Atomic Number	Symbol	Full Name	Atomic Mass	Electronegativity	Stable Oxidation State	Melting Point (°C)	Atomic Radius (A°)	Electronic Configuration
58	Ce	CERIUM	140.12	1.1	3	795	1.646	[Xe] $4f^15d^16s^2$
59	Pr	PRASEODYMIUM	140.91	1.1	3	919	1.828	[Xe] $4f^36s^2$
60	Nd	NEODYMIUM	144.24	1.07	3	1020	1.821	[Xe] $4f^46s^2$
61	Pm	PROMETHIUM	145.00	1.07	3	1080	1.810	[Xe] $4f^56s^2$
62	Sm	SAMARIUM	150.40	1.2	3	1070	1.802	[Xe] $4f^66s^2$
63	Eu	EUROPIUM	151.96	1.01	3	826	2.04	[Xe] $4f^76s^2$
64	Gd	GADOLINIUM	157.6	1.1	3	1306	1.802	[Xe] $4f^75d^16s^2$
65	Tb	TERBIUM	158.93	1.2	3	1356	1.782	[Xe] $4f^96s^2$
66	Dy	DYSPROSIUM	162.50	1.10	3	1500	1.773	[Xe] $4f^{10}6s^2$
67	Ho	HOLMIUM	164.93	1.2	3	1460	1.766	[Xe] $4f^{11}6s^2$
68	Er	ERBIUM	167.26	1.10	3	1497	1.757	[Xe] $4f^{12}6s^2$
69	Tm	THULIUM	168.93	1.2	3	1545	1.746	[Xe] $4f^{13}6s^2$
70	Yb	YTTERBIUM	173.04	1.1	3	824	1.746	[Xe] $4f^{14}6s^2$
71	Lu	LUTETIUM	174.97	1.2	3	1652	1.734	[Xe] $4f^{14}5d^16s^2$

Rare Earths - II (5f - Series) Actinides *[$5f^{1-14}$ $6d^{0-1}$ $7s^2$] — 7

Atomic Number	Symbol	Full Name	Atomic Mass	Electronegativity	Stable Oxidation State	Melting Point (°C)	Atomic Radius (A°)	Electronic Configuration
90	Th	THORIUM	232.04	1.3	4	1750	1.798	[Rn] $6d^27s^2$
91	Pa	PROTOACTINIUM	231.00	1.14	5	1227	1.606	[Rn] $5f^26d^17s^2$
92	U	URANIUM	238.03	1.22	6	1130	1.53	[Rn] $5f^36d^17s^2$
93	Np	NEPTUNIUM	237.05	1.3	5	630	1.31	[Rn] $5f^46d^17s^2$
94	Pu	PLUTONIUM	242.00	1.3	4	639.5	1.51	[Rn] $5f^67s^2$
95	Am	AMERICIUM	243.00	1.3	3	994	1.84	[Rn] $5f^77s^2$
96	Cm	CURIUM	247.00	1.3	3	-	-	[Rn] $5f^76d^17s^2$
97	Bk	BERKELIUM	249.00	1.3	3	1285	-	[Rn] $5f^86d^17s^2$
98	Cf	CALIFORNIUM	251.00	1.3	3	-	-	[Rn] $5f^{10}7s^2$
99	Es	EINSTENIUM	254.00	1.3	-	-	-	[Rn] $5f^{11}7s^2$
100	Fm	FERMIUM	253.00	1.3	-	-	-	[Rn] $5f^{12}7s^2$
101	Md	MENDELEVIUM	256.00	1.3	-	-	-	[Rn] $5f^{13}7s^2$
102	No	NOBELIUM	254.00	1.3	-	-	1.429	[Rn] $5f^{14}7s^2$
103	Lr	LAWRENCIUM	257.00	1.7	-	-	-	[Rn] $5f^{14}6d^17s^2$

* → 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

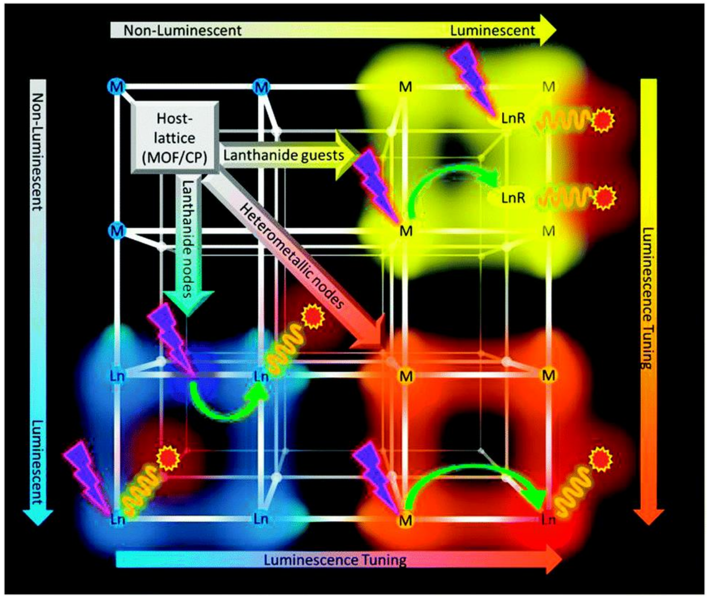
- Lanthanides are the elements in which the last electron enters into **4f - orbital**.
- These elements are also called as **Lanthanones** or **lanthanoids** or **4f-block elements.**
- Usually the symbol **Ln** is used to represent the lanthanide elements.

lanthanide series

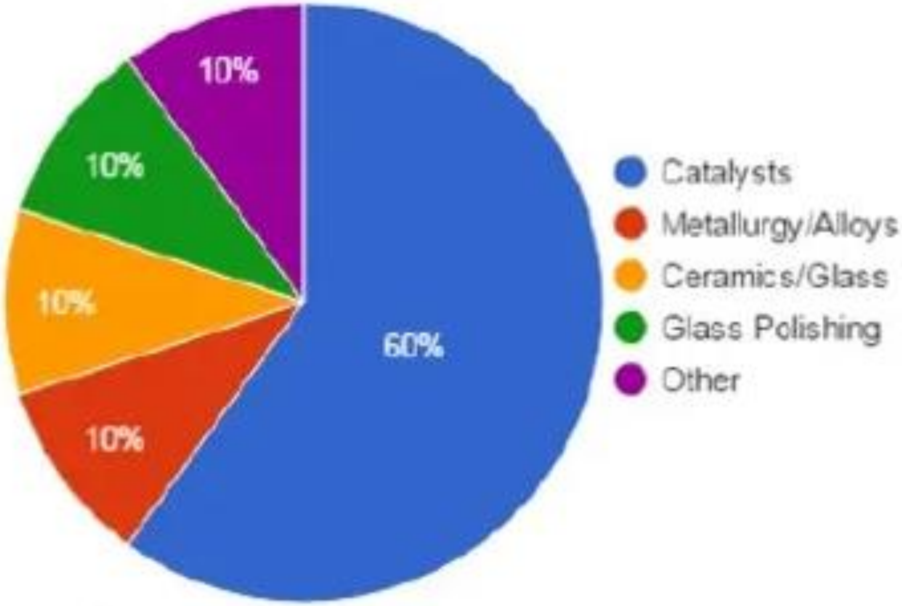
Rare-earth series

- 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.

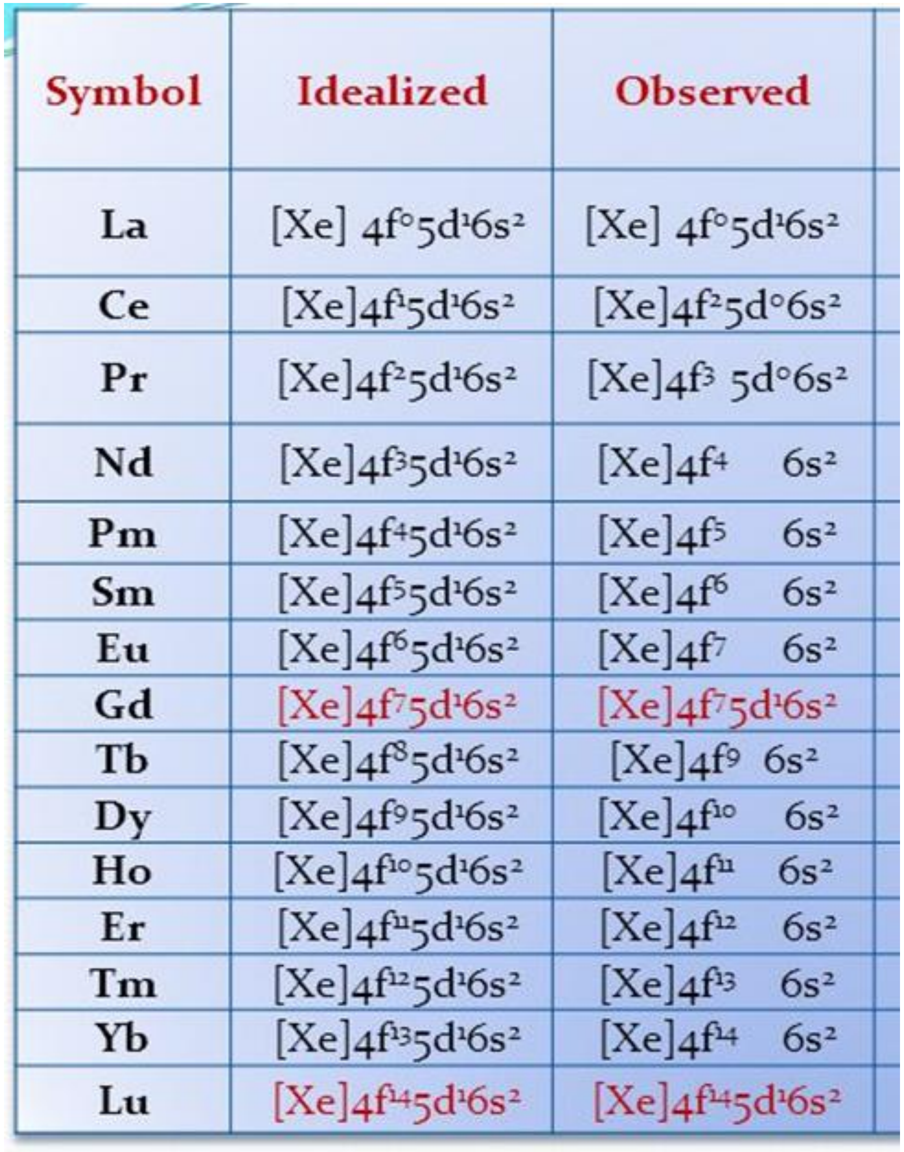
1. One such application is as catalysts in the refining industry, for example, the conversion of crude oil into gasoline, kerosene, diesel.

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.

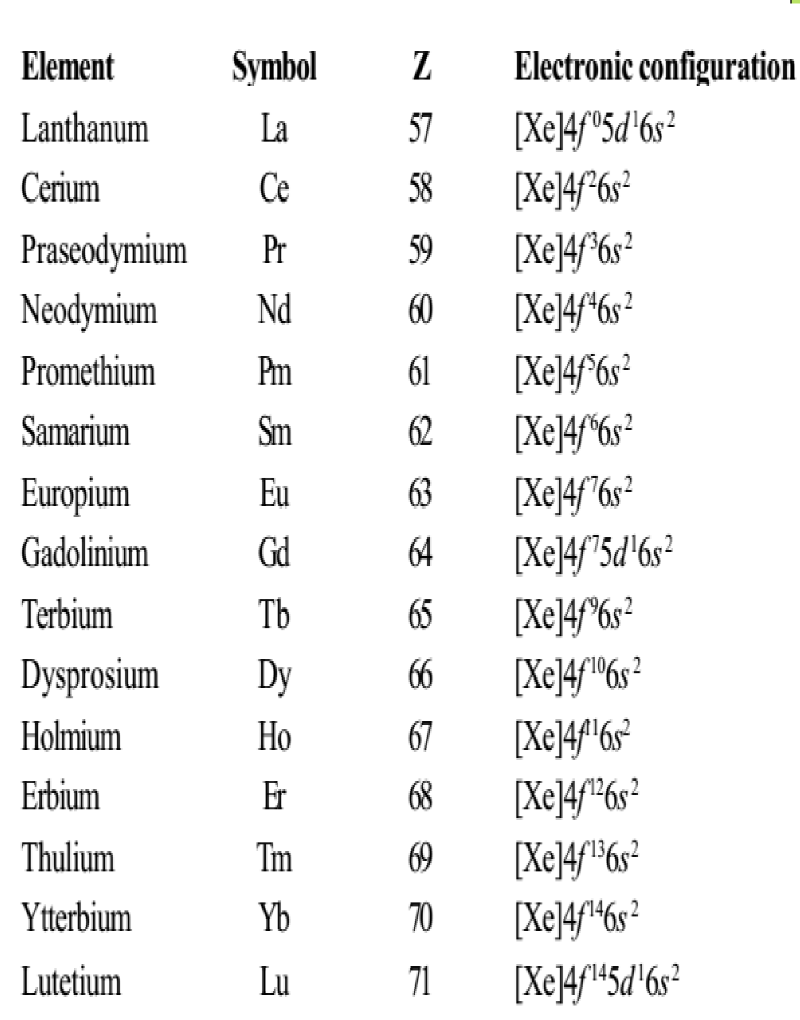
6. The ceramics industry uses lanthanide oxides to color ceramics and glasses.
7. Optical lenses made with lanthanum oxide are used in cameras and binoculars.
8. Compounds of praseodymium and neodymium are used in glass, such as in television screens, to reduce glare.
9. Cerium oxide has been used to 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	[Xe] $4f^0 5d^1 6s^2$	[Xe] $4f^0 5d^1 6s^2$
Ce	[Xe]$4f^1 5d^1 6s^2$	[Xe]$4f^2 5d^0 6s^2$
Pr	[Xe]$4f^2 5d^1 6s^2$	[Xe]$4f^3$ $5d^0 6s^2$
Nd	[Xe]$4f^3 5d^1 6s^2$	[Xe]$4f^4$ $6s^2$
Pm	[Xe]$4f^4 5d^1 6s^2$	[Xe]$4f^5$ $6s^2$
Sm	[Xe]$4f^5 5d^1 6s^2$	[Xe]$4f^6$ $6s^2$
Eu	[Xe]$4f^6 5d^1 6s^2$	[Xe]$4f^7$ $6s^2$
Gd	[Xe]$4f^7 5d^1 6s^2$	[Xe]$4f^7 5d^1 6s^2$
Tb	[Xe]$4f^8 5d^1 6s^2$	[Xe]$4f^9$ $6s^2$
Dy	[Xe]$4f^9 5d^1 6s^2$	[Xe]$4f^{10}$ $6s^2$
Ho	[Xe]$4f^{10} 5d^1 6s^2$	[Xe]$4f^{11}$ $6s^2$
Er	[Xe]$4f^{11} 5d^1 6s^2$	[Xe]$4f^{12}$ $6s^2$
Tm	[Xe]$4f^{12} 5d^1 6s^2$	[Xe]$4f^{13}$ $6s^2$
Yb	[Xe]$4f^{13} 5d^1 6s^2$	[Xe]$4f^{14}$ $6s^2$
Lu	[Xe]$4f^{14} 5d^1 6s^2$	[Xe]$4f^{14} 5d^1 6s^2$



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

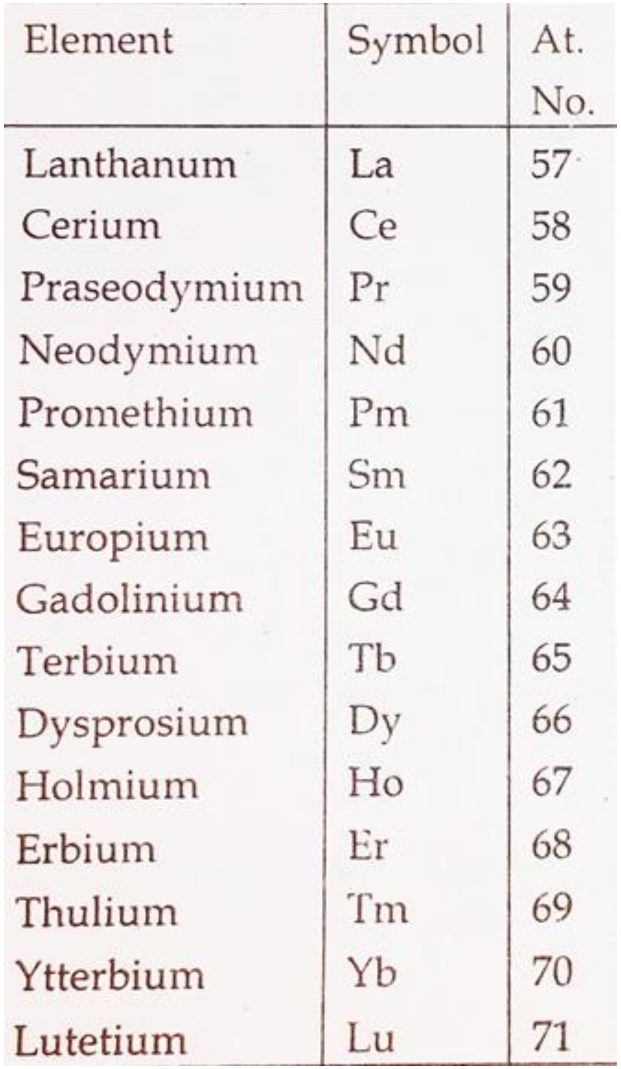
- Successive filling of electrons In 4f orbital takes place in the 14 elements which follow lanthanum, i.e. cerium onwards.

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

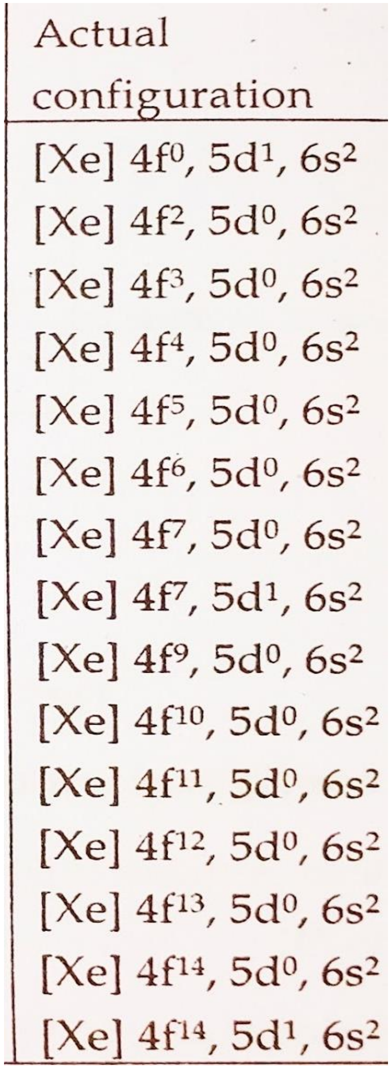
- These elements are called Lanthanides because many physical and chemical properties of these elements are similar to those of lanthanum.

Oxidation States

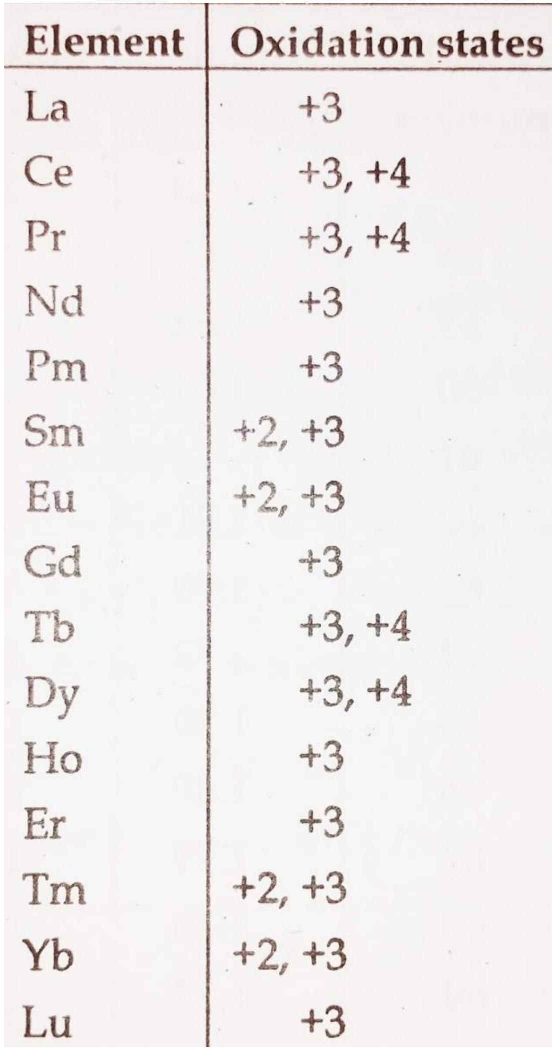
- Lanthanides exhibit different oxidation states like +2, +3 and +4.
- Among these +3 is the most stable oxidation state.
- The elements that attain stable electronic configuration by losing 2 or 4 electrons exhibit +2 and +4 oxidation states.
- Example: Europium and ytterbium exhibits +2 and +3 oxidation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



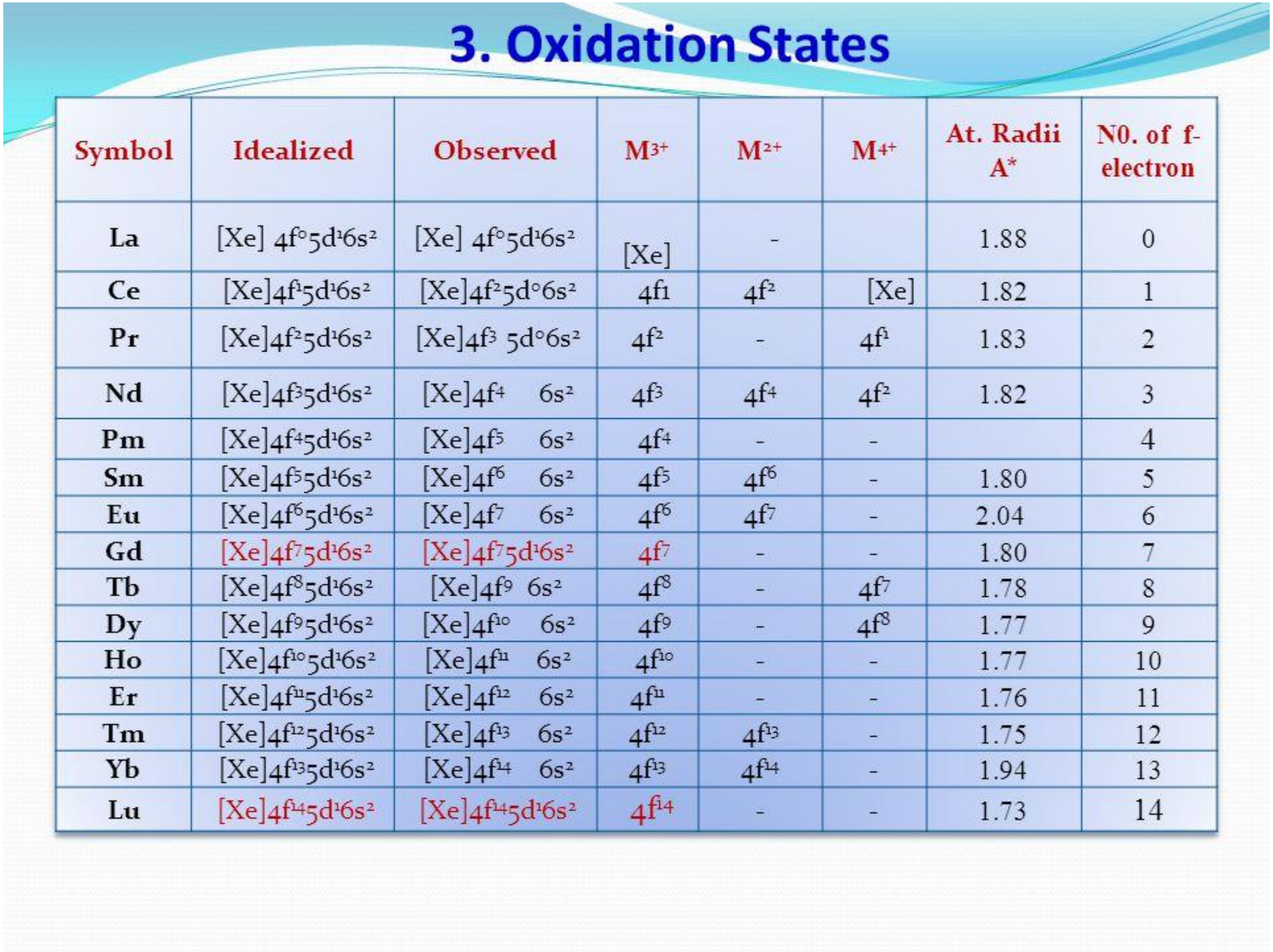
Element	Symbol	At. No.
Lanthanum	La	57
Cerium	Ce	58
Praseodymium	Pr	59
Neodymium	Nd	60
Promethium	Pm	61
Samarium	Sm	62
Europium	Eu	63
Gadolinium	Gd	64
Terbium	Tb	65
Dysprosium	Dy	66
Holmium	Ho	67
Erbium	Er	68
Thulium	Tm	69
Ytterbium	Yb	70
Lutetium	Lu	71



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	M^{3+}	M^{2+}	M^{4+}	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

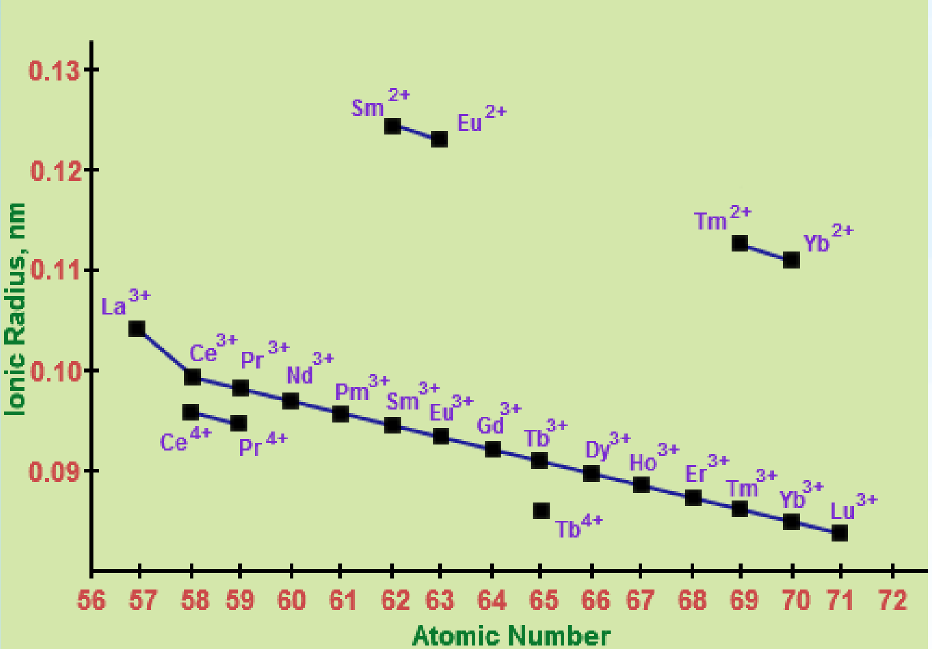
Lanthanides properties

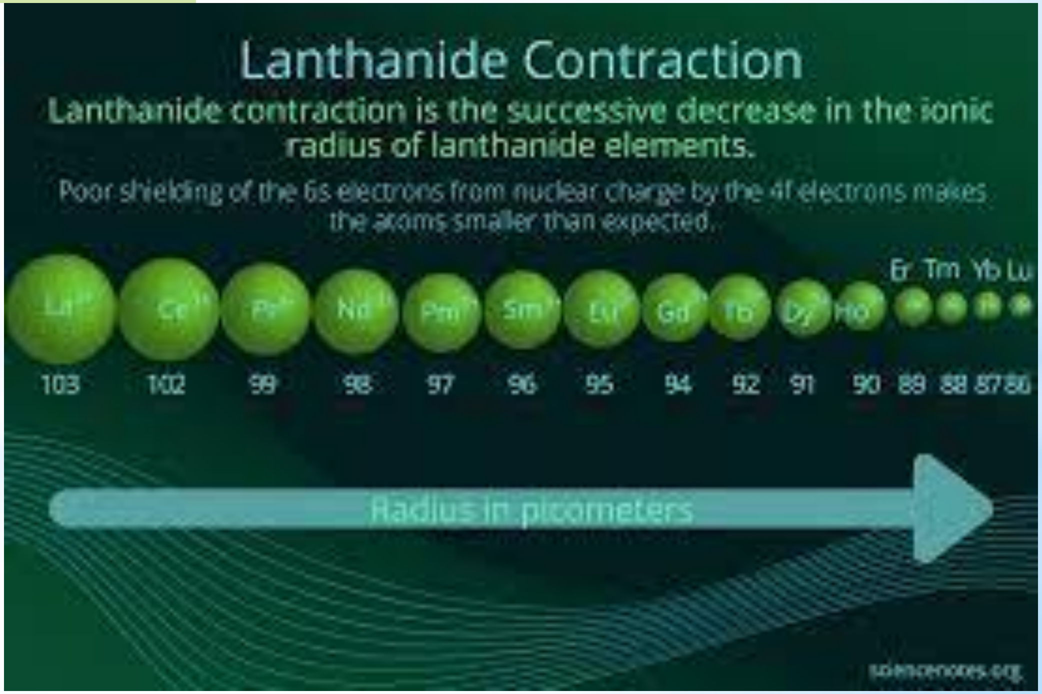
lanthanide contraction

- 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.

sciencenotes.org

The reason of lanthanoid contraction

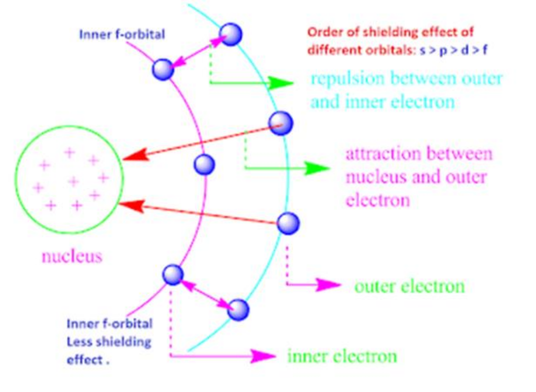
- The reason of lanthanoid contraction is:
- **The poor shielding effect of f-electrons is cause of lanthanoid contraction.**

- 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,

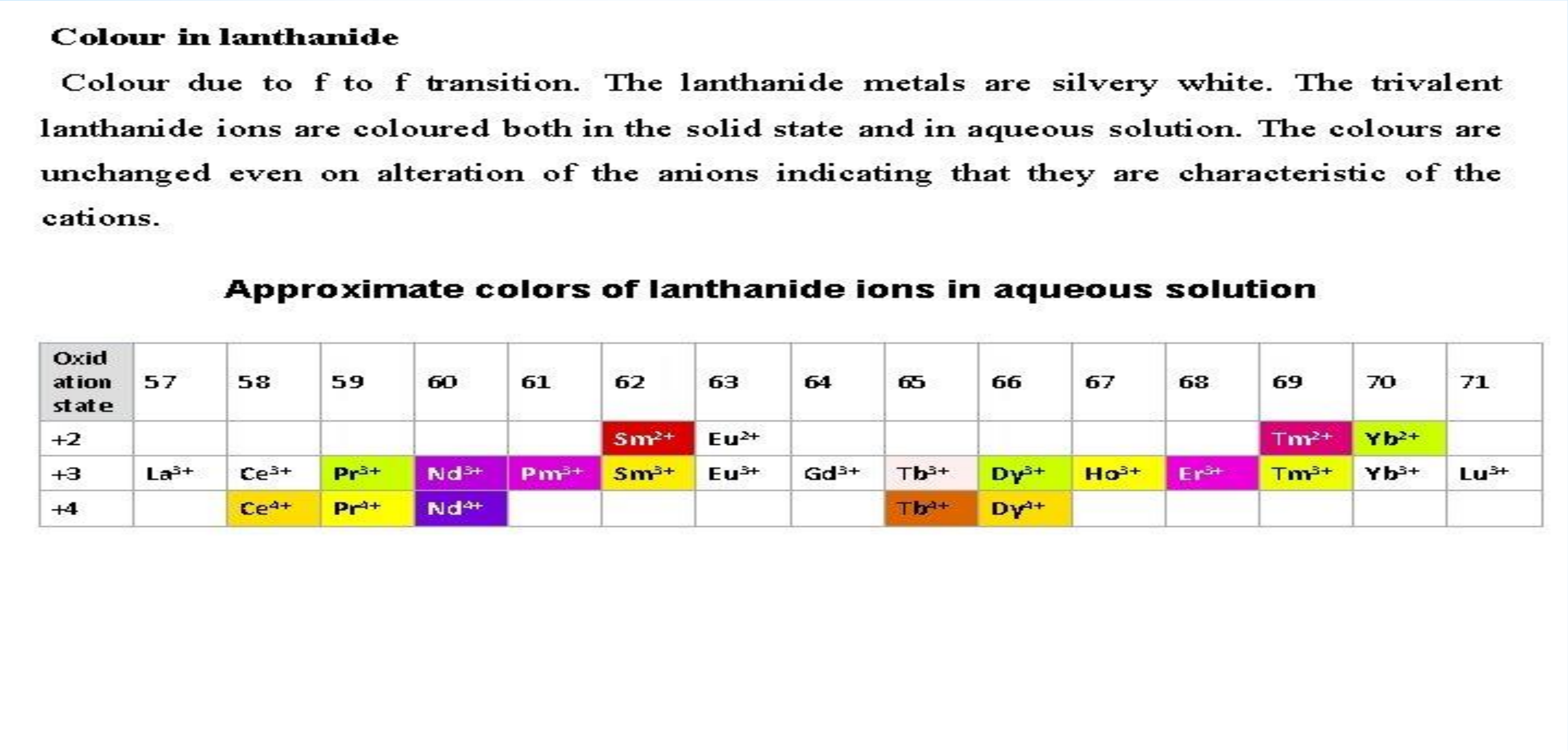
☐ hence ionic size decreases.

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+}					

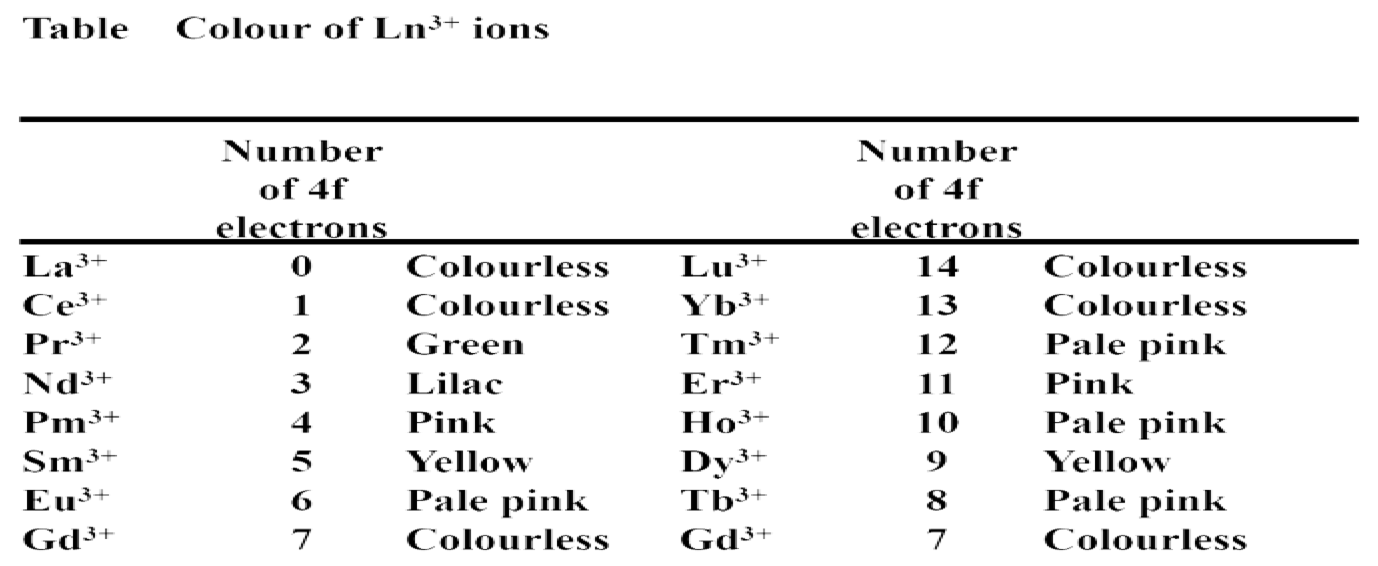


Table Colour of Ln^{3+} ions

	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.

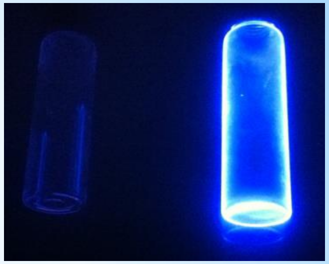
- When a frequency of light is absorbed, the light transmitted ***exhibit a colour complementary to the frequency absorbed***.

- 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 solution
- 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.

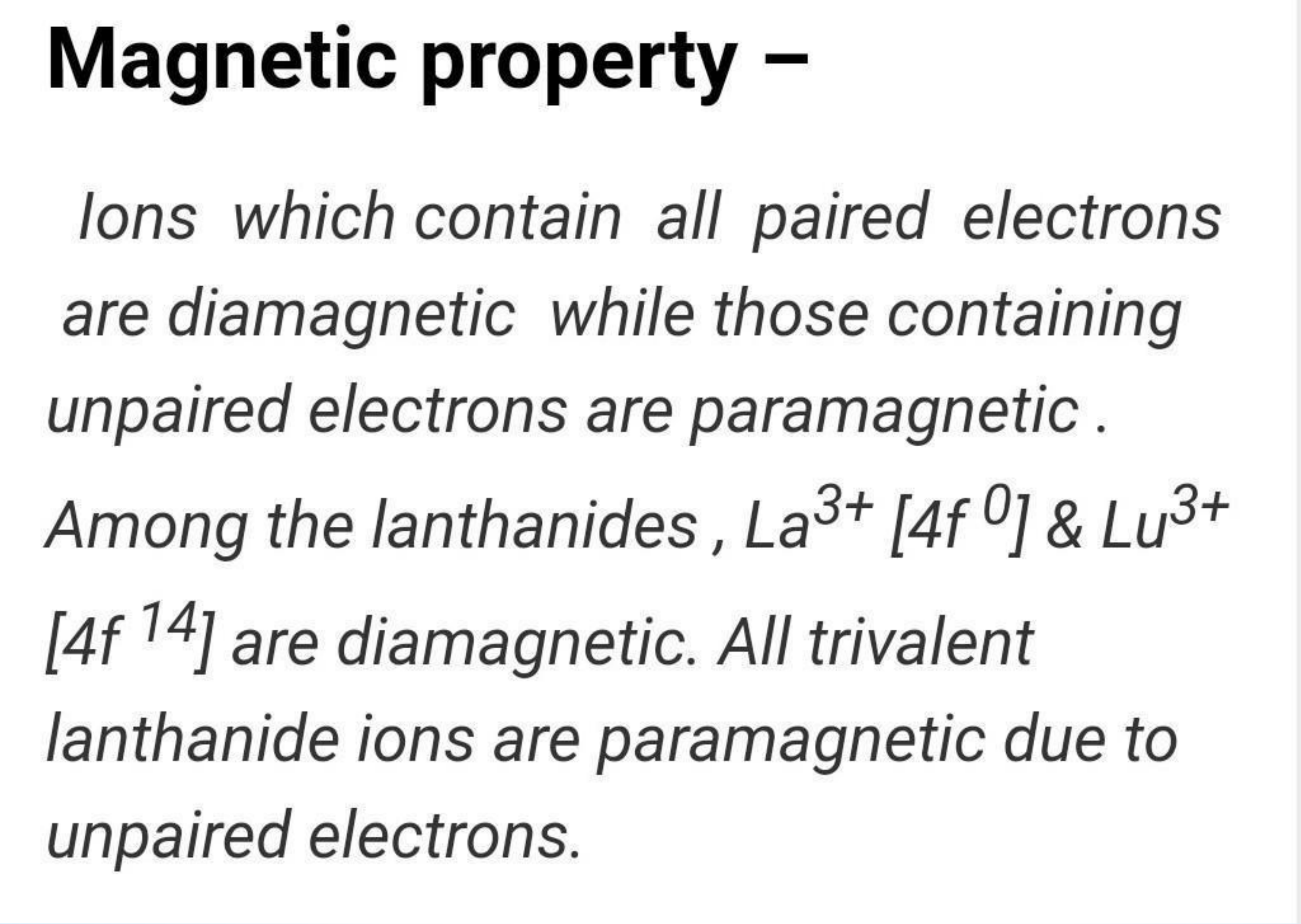
–the excited state produced decays to the ground state with emission of energy.

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

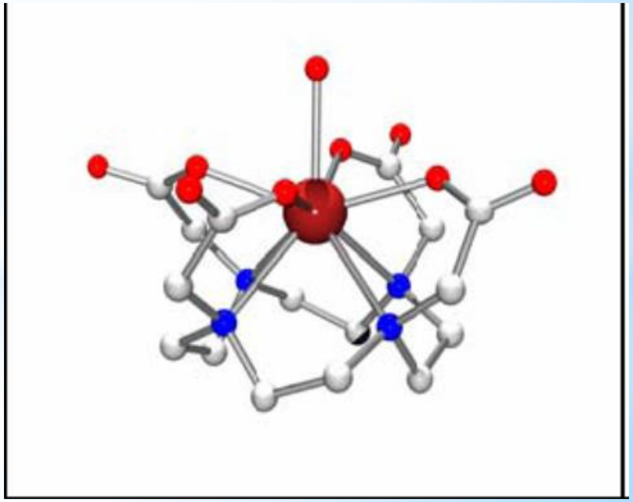


Magnetic property –

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).

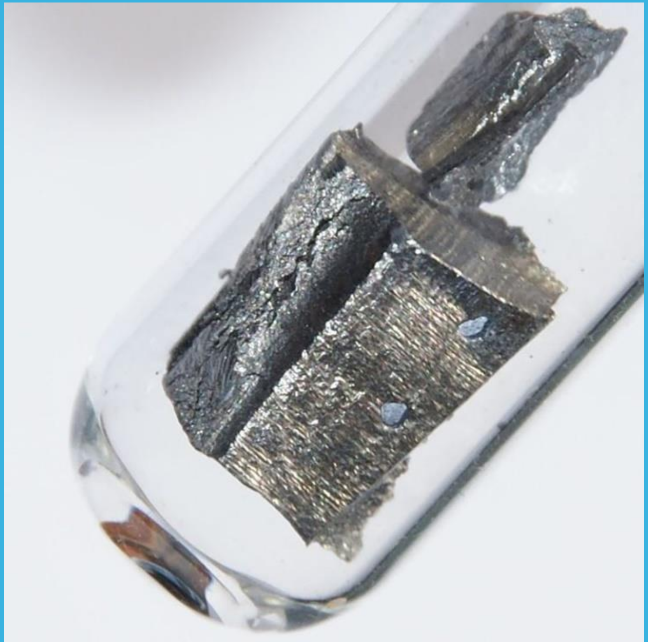
- Lanthanide complexes are used in MRI (medical
- resonance imaging), eg. [Gd(III)(dtpa)]2-



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

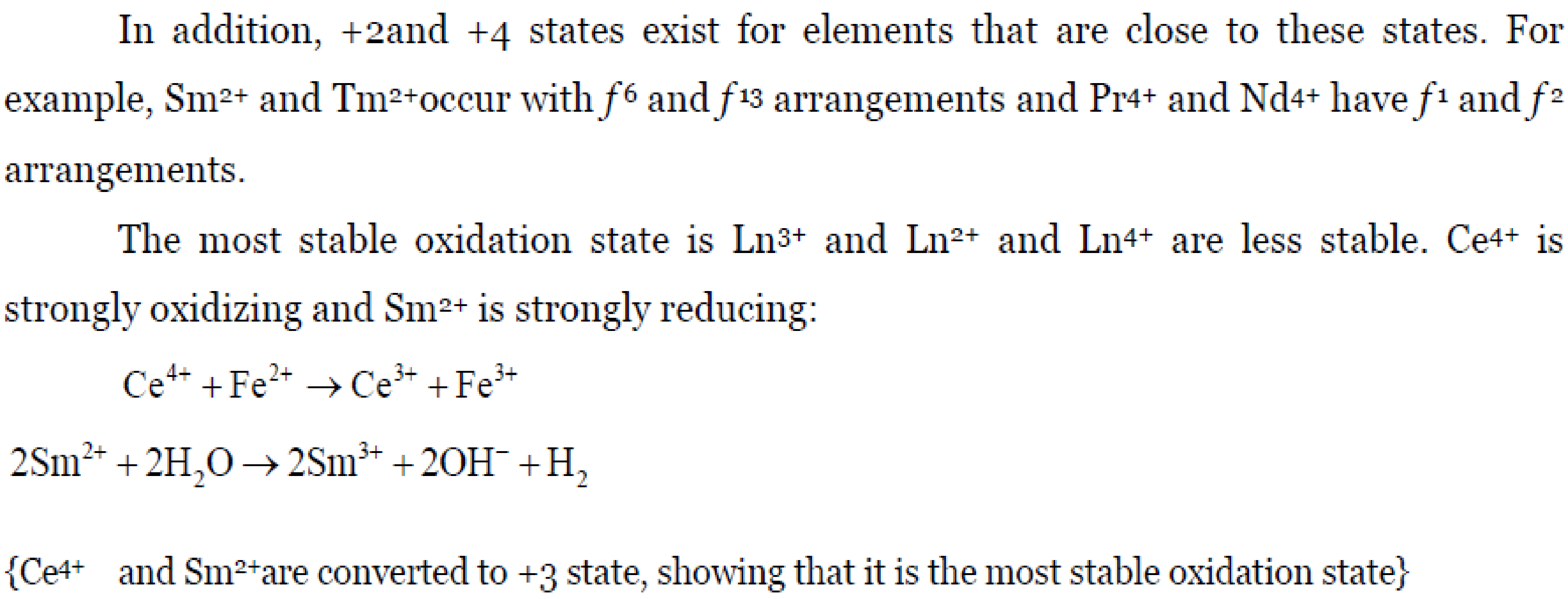
Lanthanides exhibits a principal oxidation state of +3 which contain an outer shell containing 8 electrons and an underlying layer containing up to 14 electrons. The +3 ions of La, Gd and Lu which contain respectively an empty, a half-filled, and a completely filled 4f level are especially stable. Ce 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



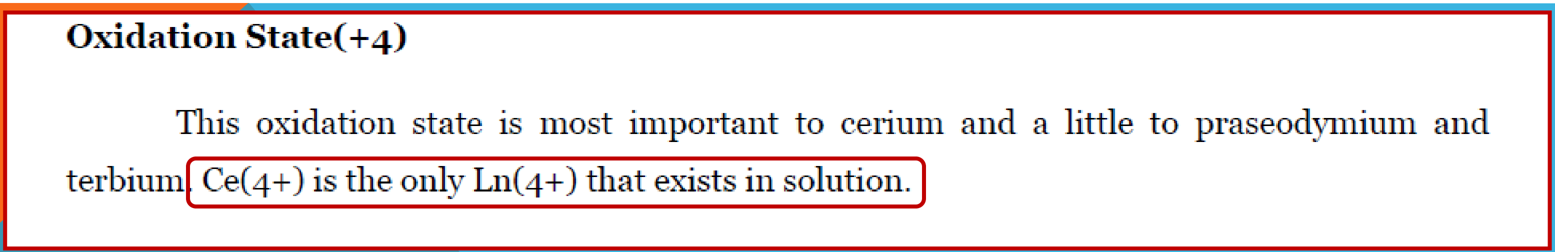
In addition, +2and +4 states exist for elements that are close to these states. For example, Sm^{2+} and Tm^{2+}occur with f^6 and f^{13} arrangements and Pr^{4+} and Nd^{4+} have f^1 and f^2 arrangements.

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^{0}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.

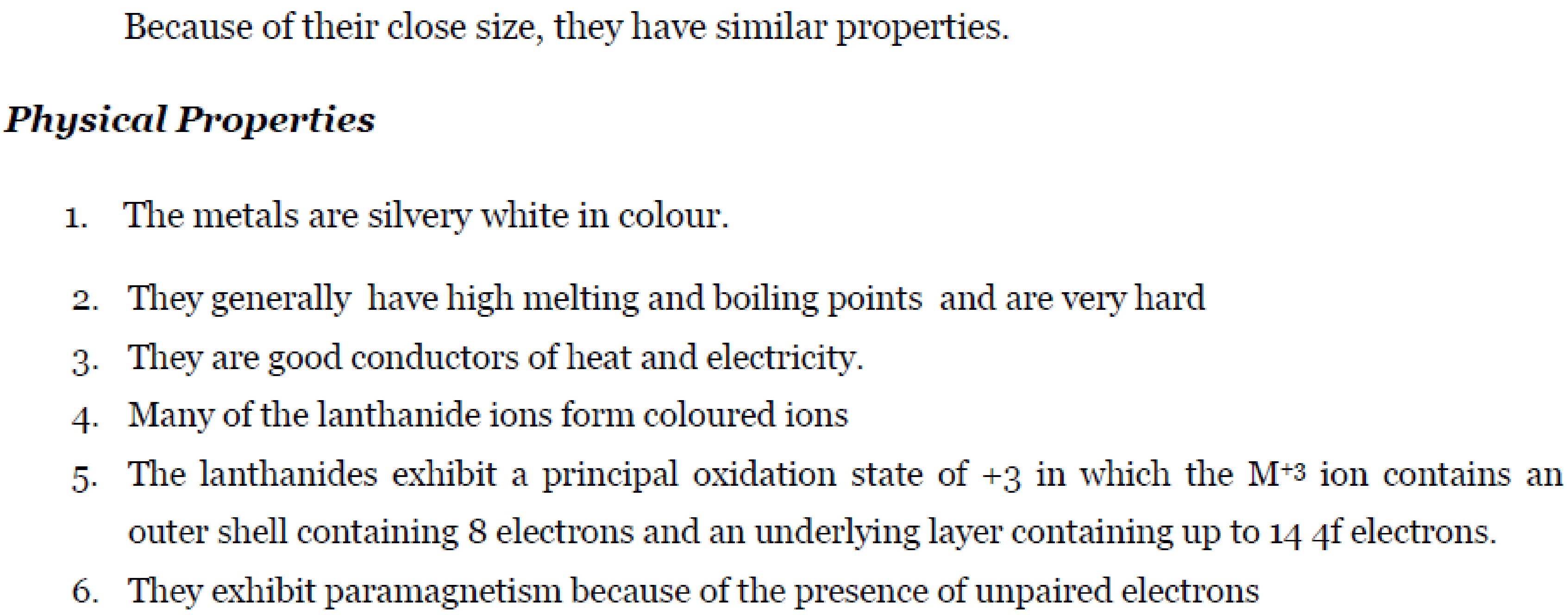
Halides (LnX_3): Fluorides are pptd. by the addition of HF to Ln^{+3} salt solution. The fluorides of heavier lanthanides are sparingly soluble in HF to Ln^{+3} salt solutions. The fluorides of heavier lanthanides are sparingly soluble in HF due to formation of fluoro complexes.

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

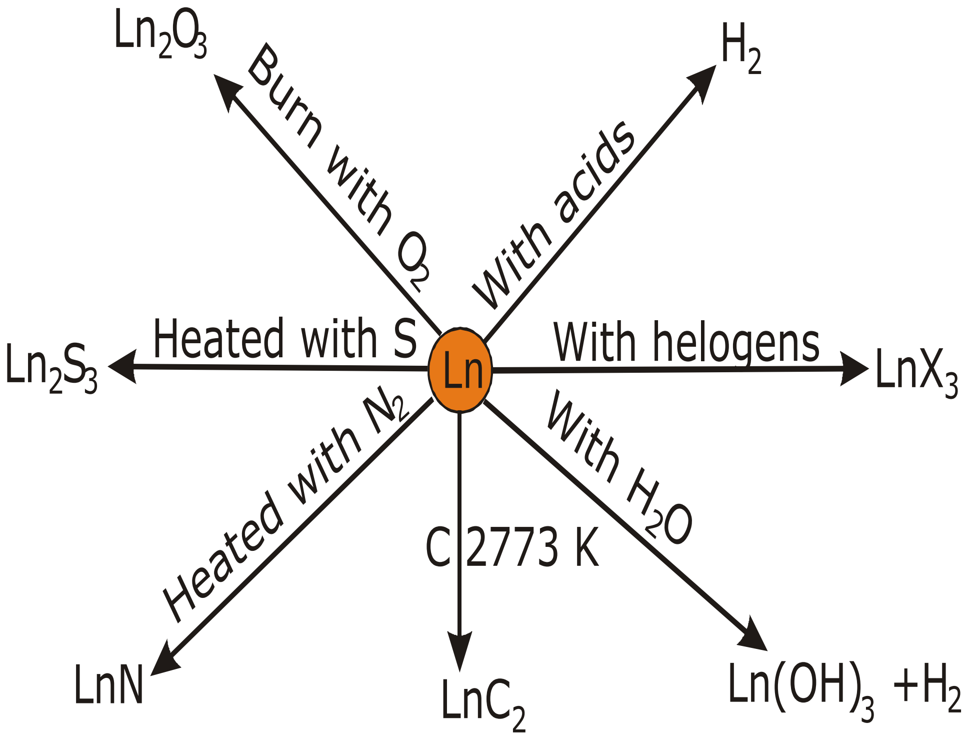
CHEMICAL PROPERTIES

- ✓ 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)

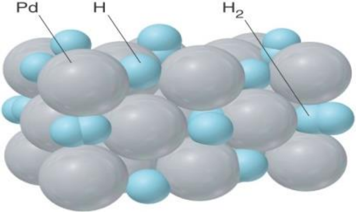
ويكون هيدريدات تساهمية مثل p-block كما يمكن للهيدروجين ان يشارك بالكترون مع عناصر الفئة : CH_4 NH_3 H_2O HF

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

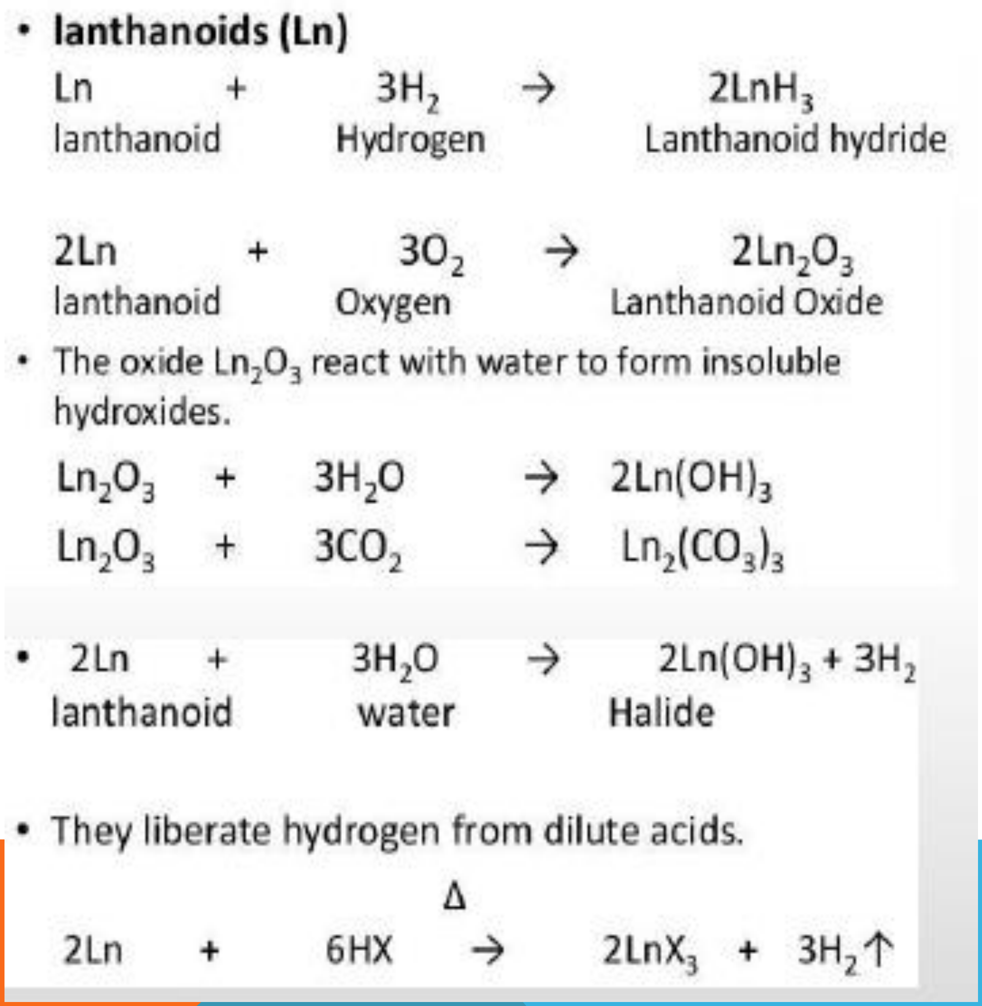
3- Metallic (interstitial) hydrides

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.

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

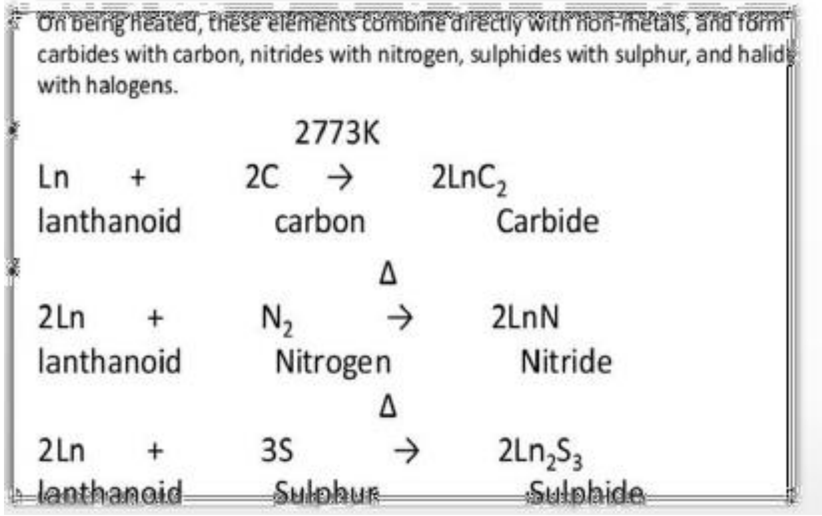
  $Ln_2O_3 + 3CO_2 \rightarrow Ln_2(CO_3)_3$

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

  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 X, P, S, O, N)

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

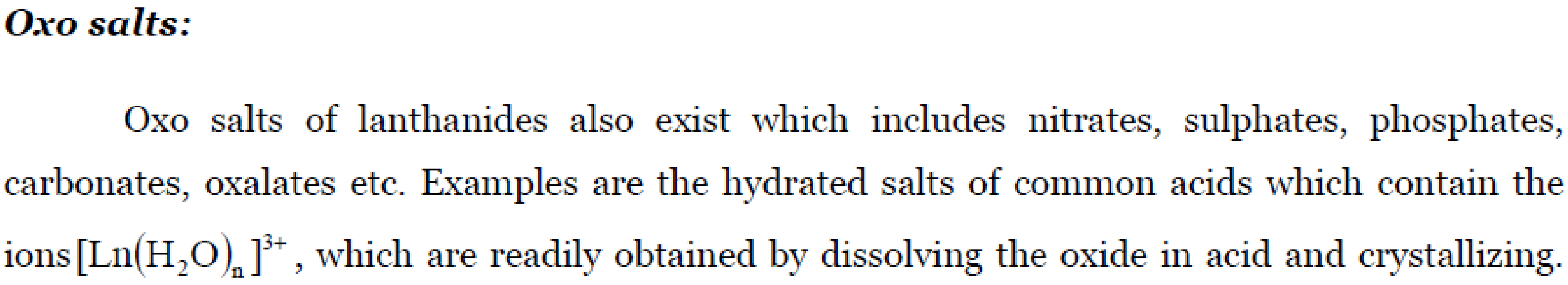
In chemical reactivity, they resemble calcium.

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.

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

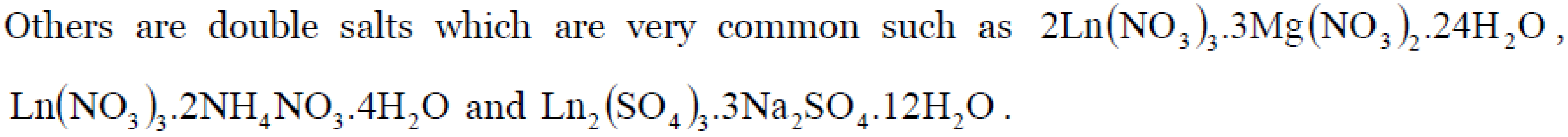
5. Lanthanide compounds are generally predominantly ionic and usually contain lanthanide metal in its +3 oxidation states.

OXO SALTS



Oxo salts:

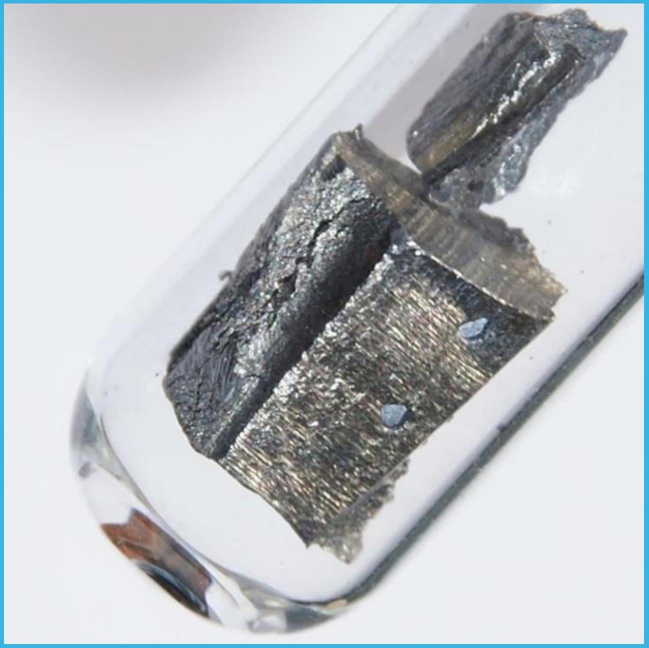
Oxo salts of lanthanides also exist which includes nitrates, sulphates, phosphates, carbonates, oxalates etc. Examples are the hydrated salts of common acids which contain the ions $[Ln(H_2O)_n]^{3+}$, which are readily obtained by dissolving the oxide in acid and crystallizing.



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.


The Arkenstone, iRocks.com

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 $ThO2$ =7.5%, $Ce2O3$ =30%, $P2O5$=29%, $SiO2$ = 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 H_2SO_4:

- First of all the refined monazite obtained from the concentration process is heated with 93% H_2SO_4 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 SiO_2, unreacted mineral and traces of TiO_2 and $ZrSiO_4$ are left behind. This residue is then crushed and returned for recycle.
- The leached solution is acidic because of formation of phosphoric acid.

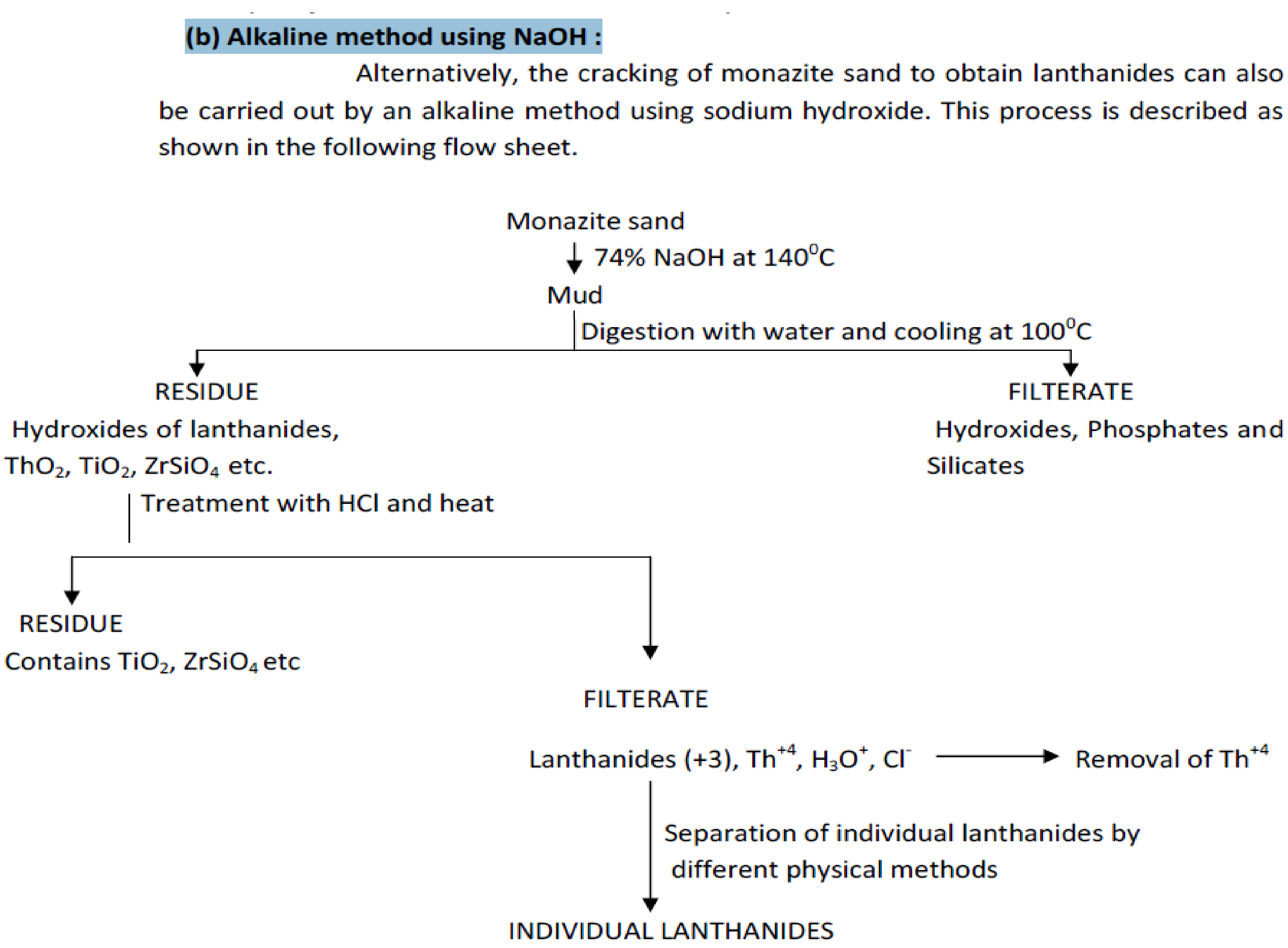
$$P_2O_5 + 3H_2O \rightarrow 2H_3PO_4 \rightarrow 2H^+ + 2H_2PO_4$$

- This solution is treated with sodium pyrophosphate($Na_2P_2O_7$) to precipitate thorium as $Th(P_2O_7)_2$.
- 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 La_2O_3 = 17%, CeO_2 = 5%, Pr_2O_3 = 8% Nd_2O_3= 20%, Sm_2O_3=5% and little Eu_2O_3 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 $Ce(OH)(NO3)3\cdot3H2O$ 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.

FILTERATE

Hydroxides, Phosphates and Silicates

Treatment with HCl and heat

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.

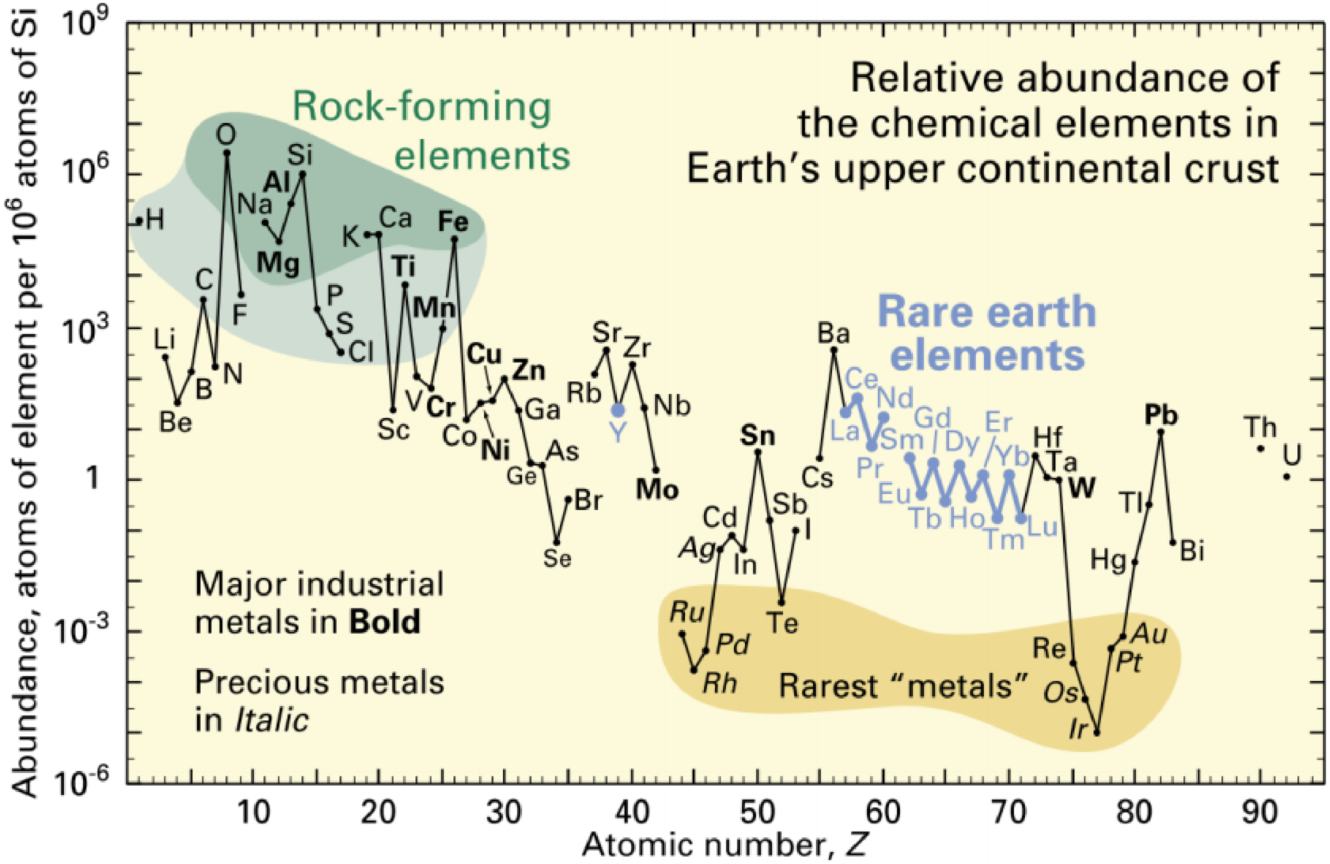
(b) Modern methods:

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.

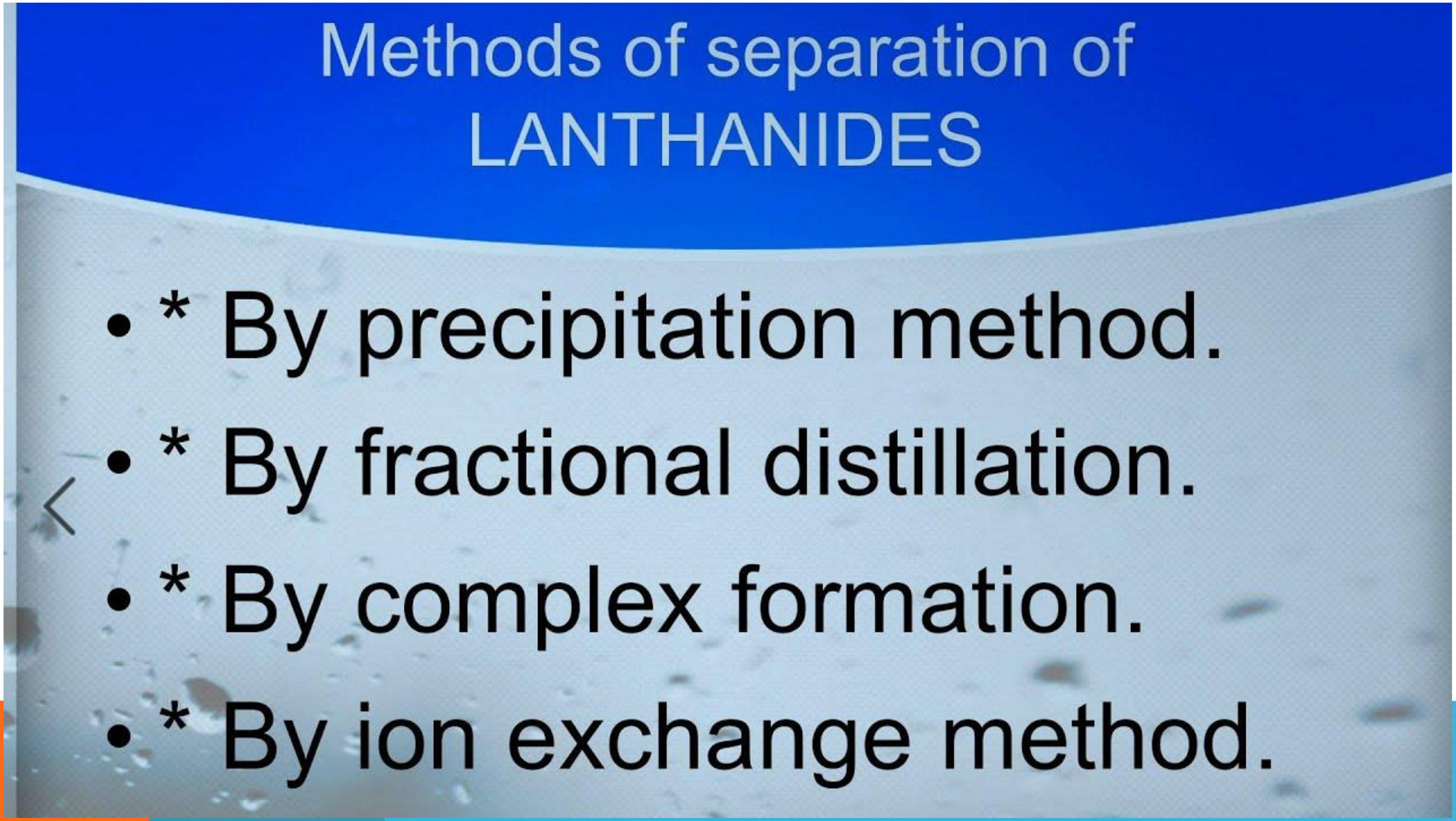
Oddo-Harkins rule



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

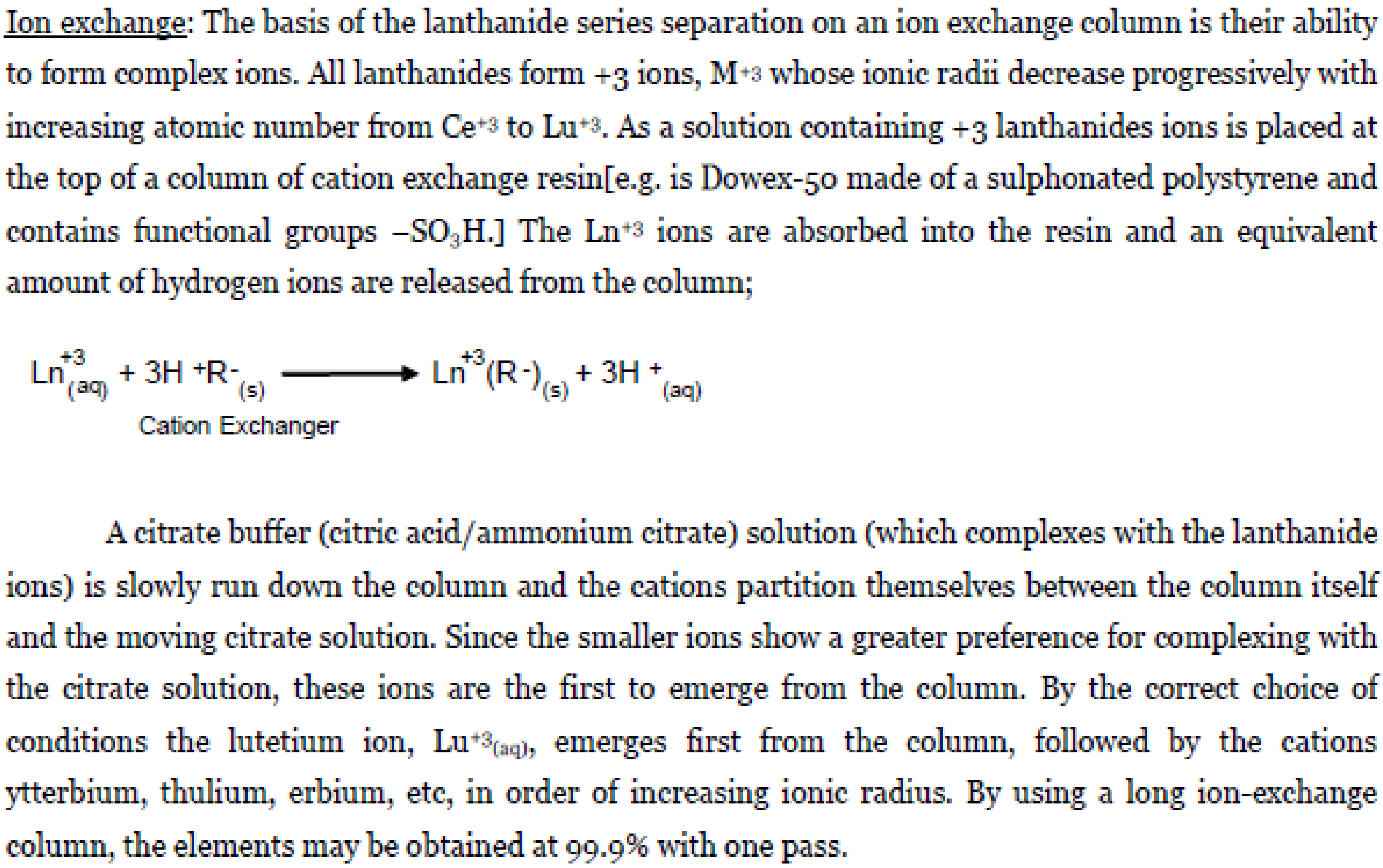
is reduced electrolytically using a Hg cathode or Zn amalgam, then Eu^{2+} is produced. If H_2SO_4 is present, $EuSO_4$ which is insoluble will be precipitate. This can be filtered off.

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 $-SO_3H$ 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 $-SO_3H$ or $-COOH$ group of the resin and get fixed on the resin.

$$Ln^{+3}\,(aq) + 3HR\,(solid) \leftrightarrow LnR_3(solid) + 3H^+\,(aq)$$

- In order to remove Ln^{+3} ions fixed as LnR_3(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 NH_4^+ ions of the eluating agent replace Ln^{+3} ions from LnR_3(solid) to give Ln^{+3} ions which reacts with citrate ion to form the Ln-citrate complex.

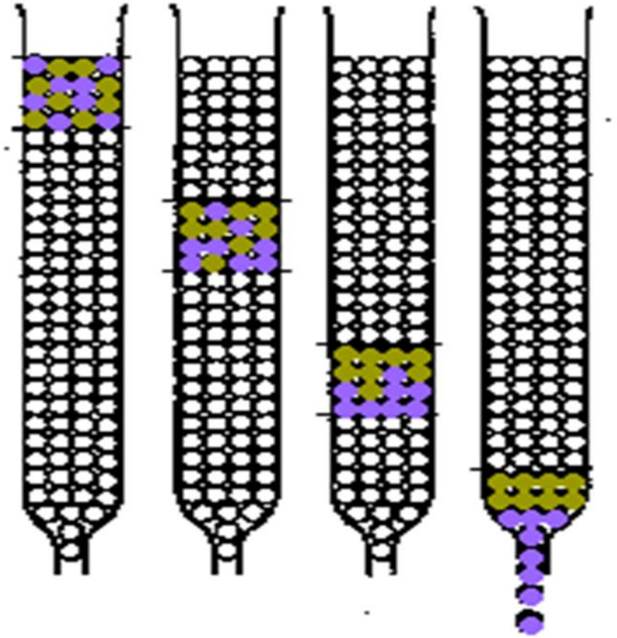
$$LnR_3 + NH_4^+ \longrightarrow NH_4R + Ln^{+3}$$

$$Ln^{+3} + \text{citrate ion} \longrightarrow \text{Ln-citrate complex}$$

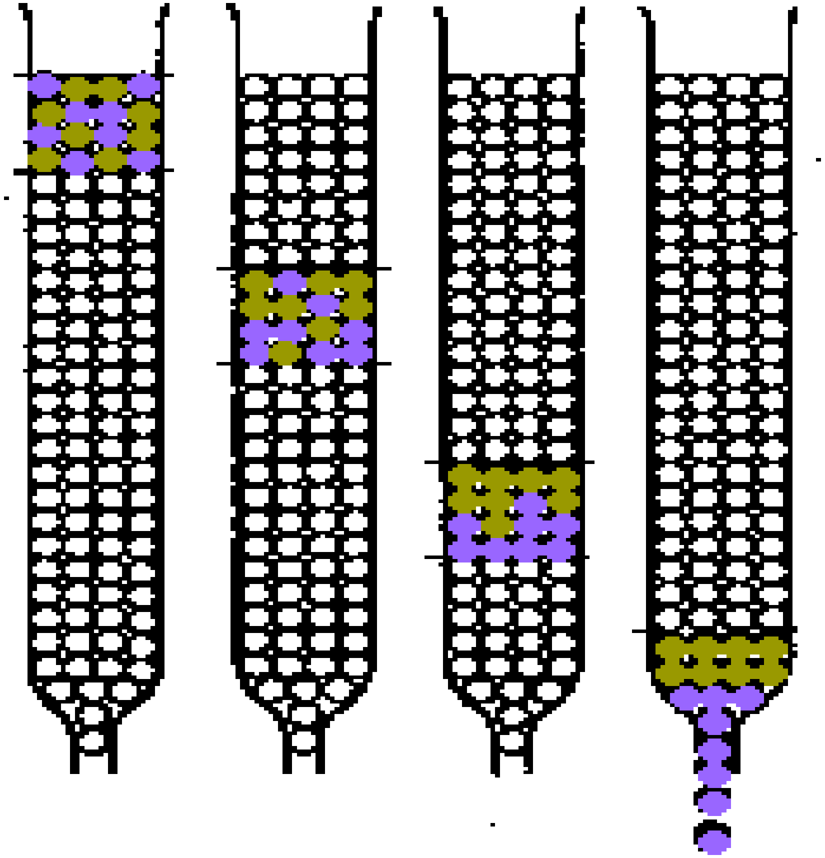
- We have seen that since La^{+3} (aq) is attached to resin with maximum and Lu^{+3} (aq) with minimum firmness, Lu-citrate complex comes out of the column first and La-citrate complex comes out last.
- In actual practice the process of elution is to be repeated several times by careful control of concentration 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.* $Ln(NO_3)_3.2NH_4NO_3.4H_2O$ or $Ln(BrO_3)_3$
- Fractional Thermal Decomposition of *e.g.* $Ln(NO_3)_3$

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.

$$\text{Ln+3(aq) + 3 NO3- (aq) +3TBP (org)} \leftrightarrow \underset{\text{Complex}}{\text{Ln(NO3)3(TBP)3(org)}}$$

- 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.

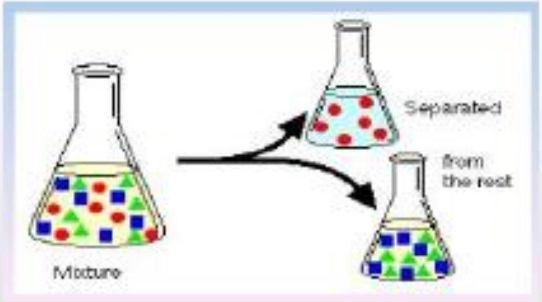
The major uses of solvent extraction process for separation of Ln+3 from Ln+4, ions such as Ce+4

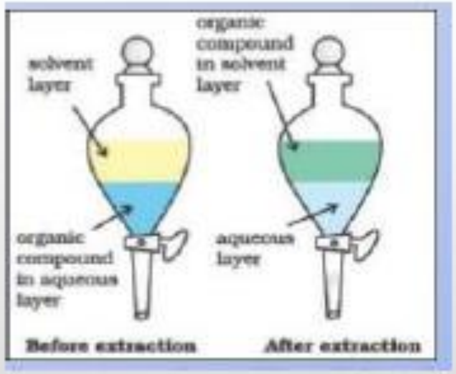
and Th+4 and in the purification of Ce, Th, and La.

Solvent extraction method: Separation of Lanthanides

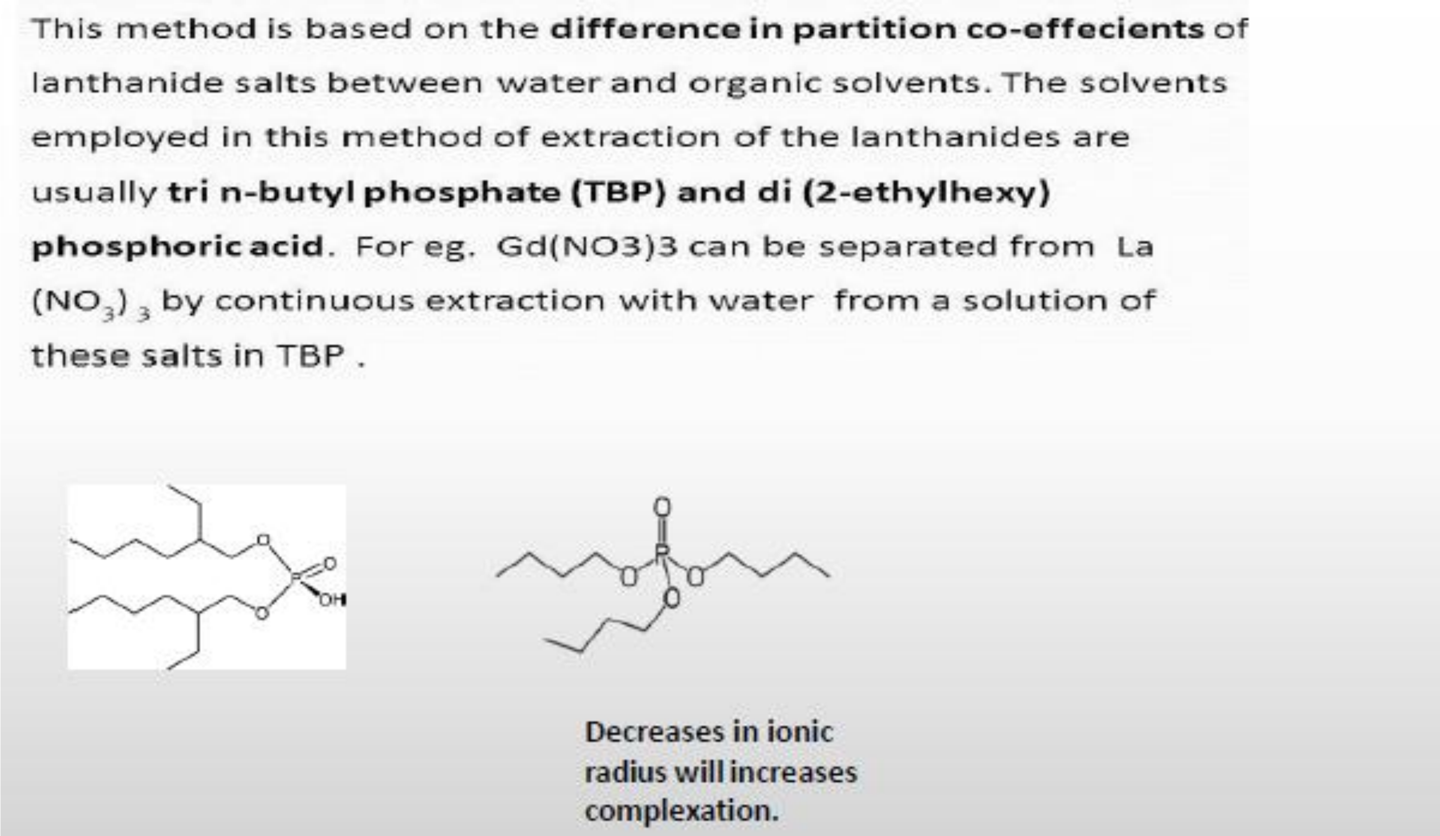
What is Solvent Extraction ?

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

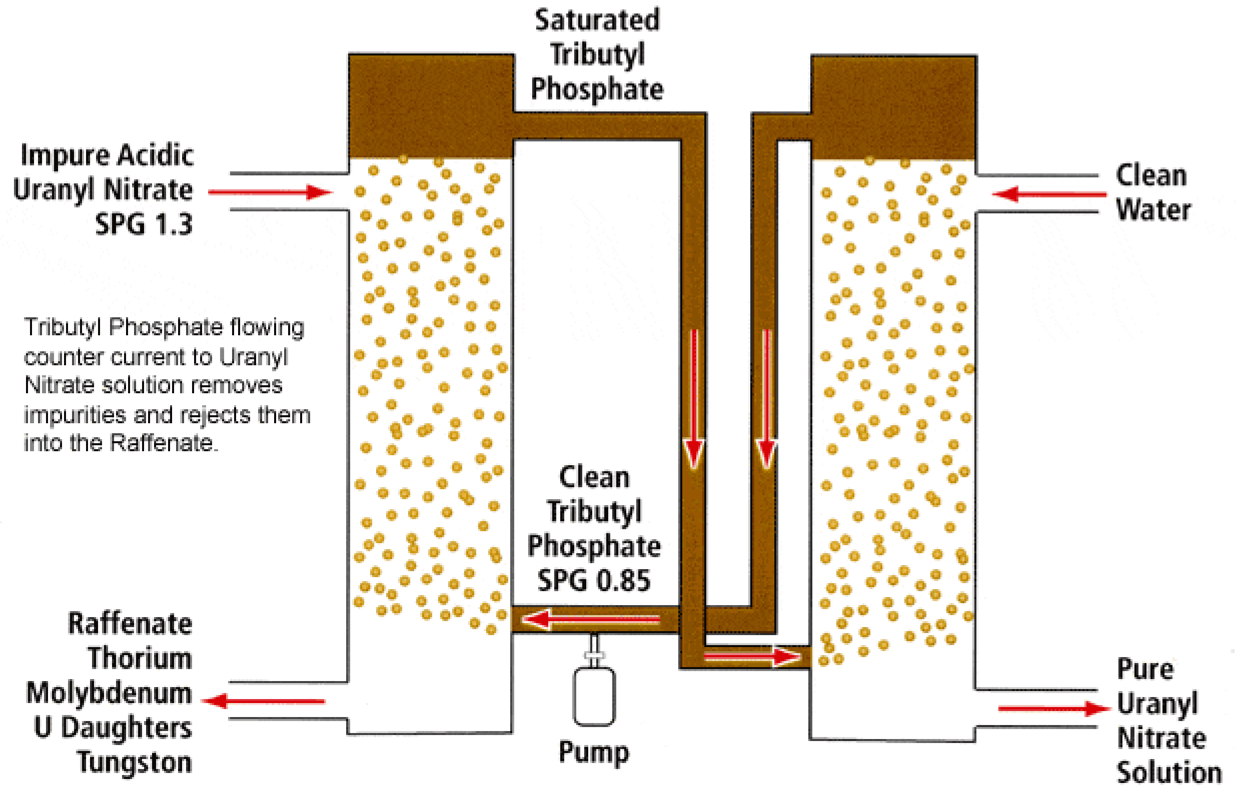
- tri-*n*-butylphosphine oxide (**TBPO**) (nBu3O)3PO

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

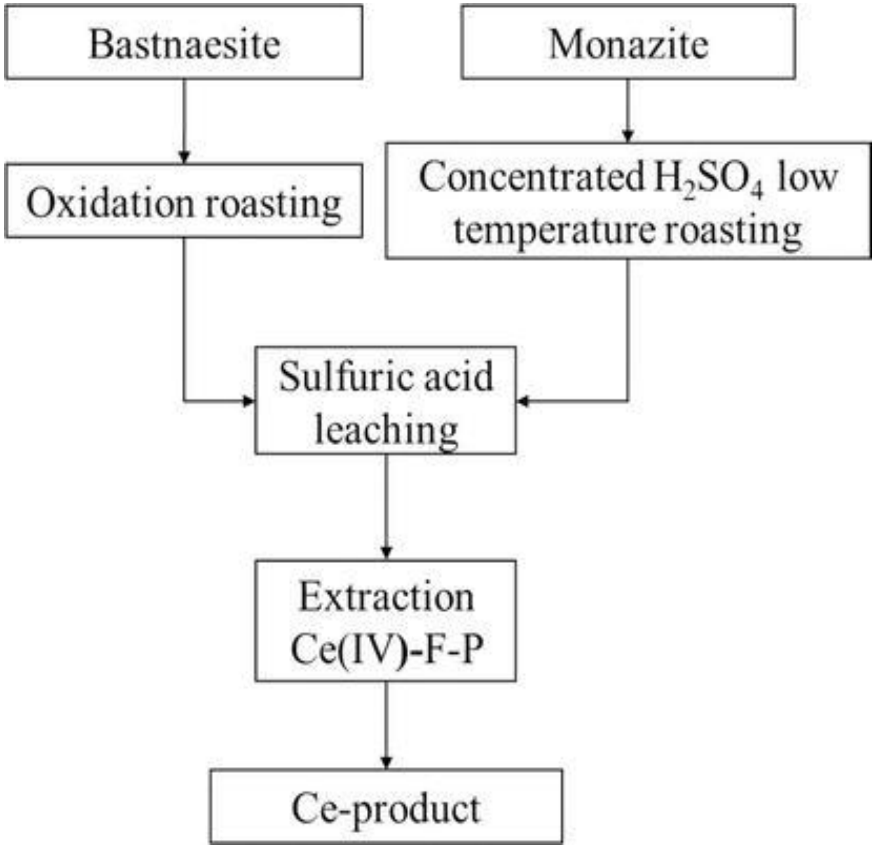


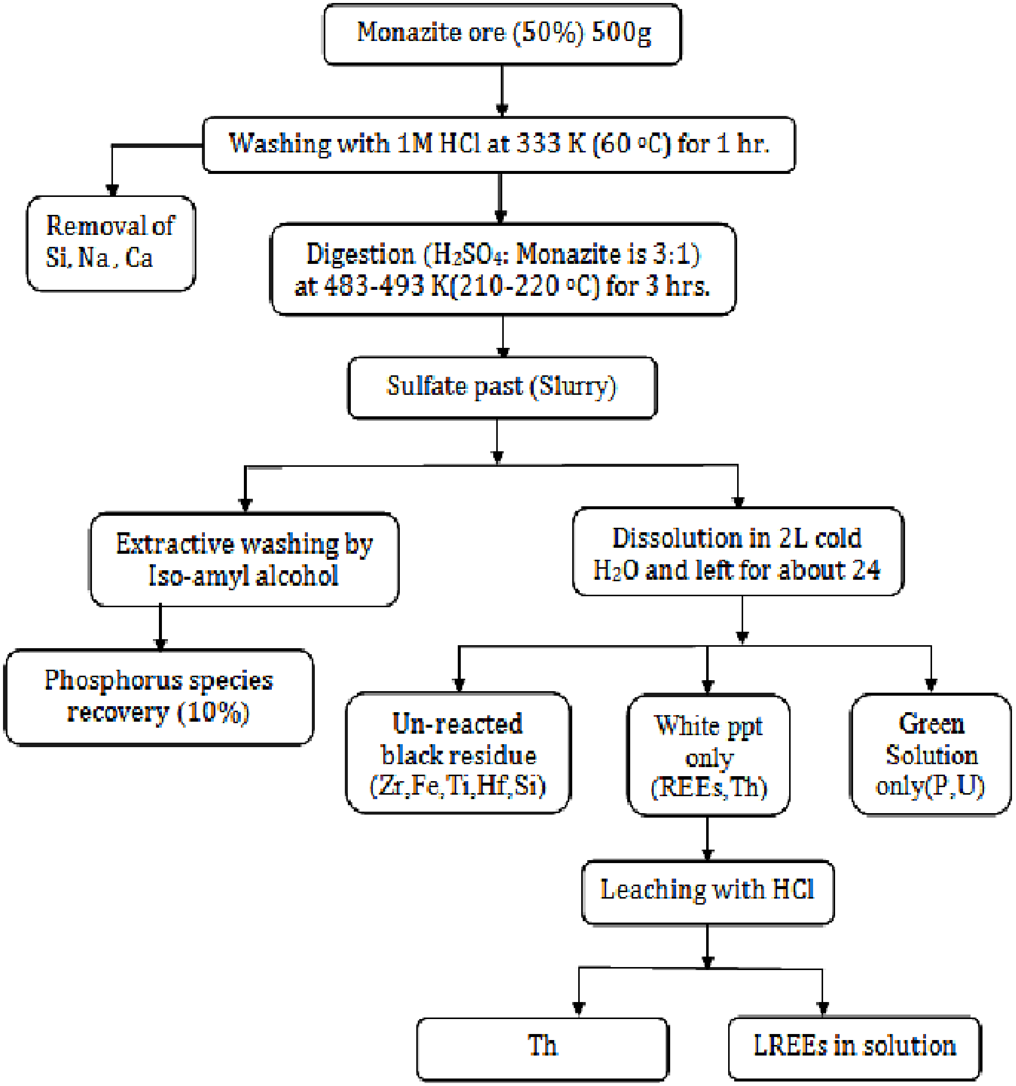
Tributyl Phosphate flowing counter current to Uranyl Nitrate solution removes impurities and rejects them into the Raffenate.

EXTRACTION PLANT

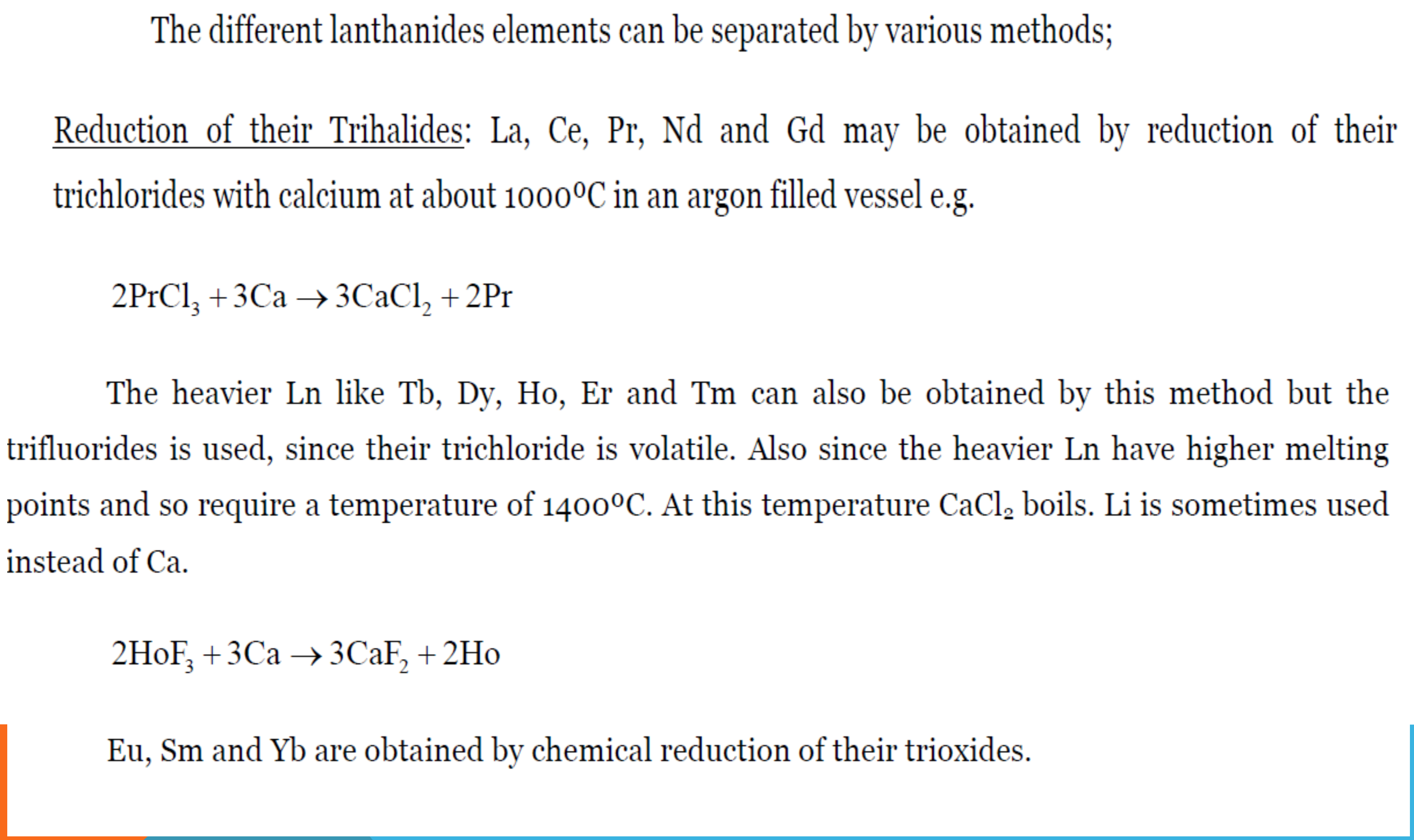
EXTRACTION PLANT

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
Dissolution in 2L cold H_2O and left for about 24
Phosphorus species recovery (10%)
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 1000°C in an argon filled vessel e.g.

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

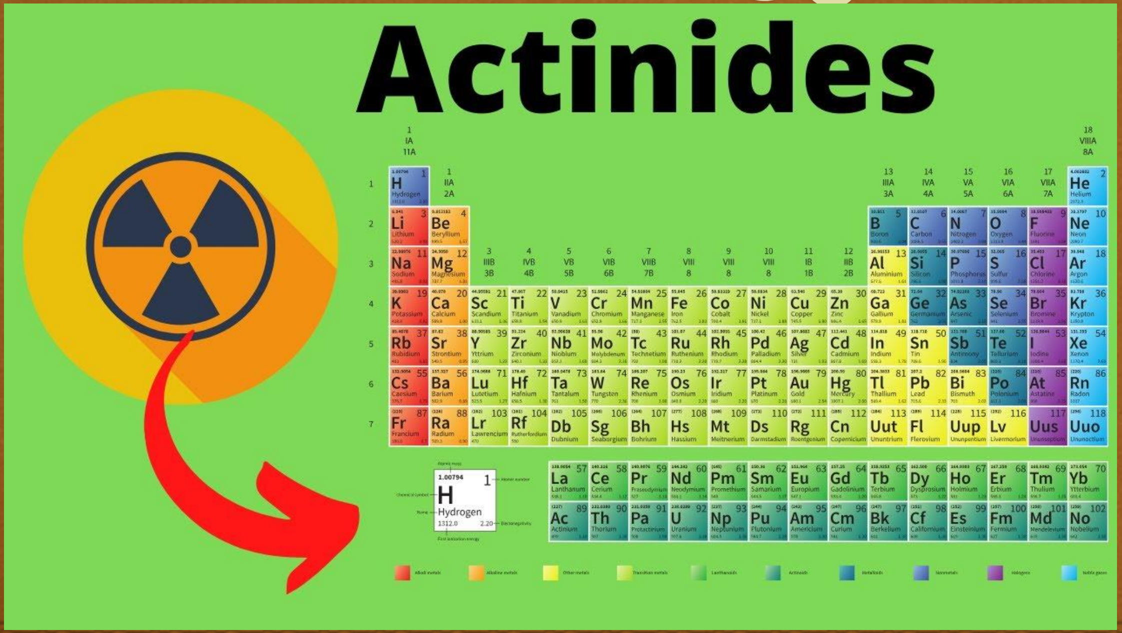
The heavier Ln like Tb, Dy, Ho, Er and Tm can also be obtained by this method but the trifluorides is used, since their trichloride is volatile. Also since the heavier Ln have higher melting points and so require a temperature of 1400°C. At this temperature $CaCl_2$ boils. Li is sometimes used instead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

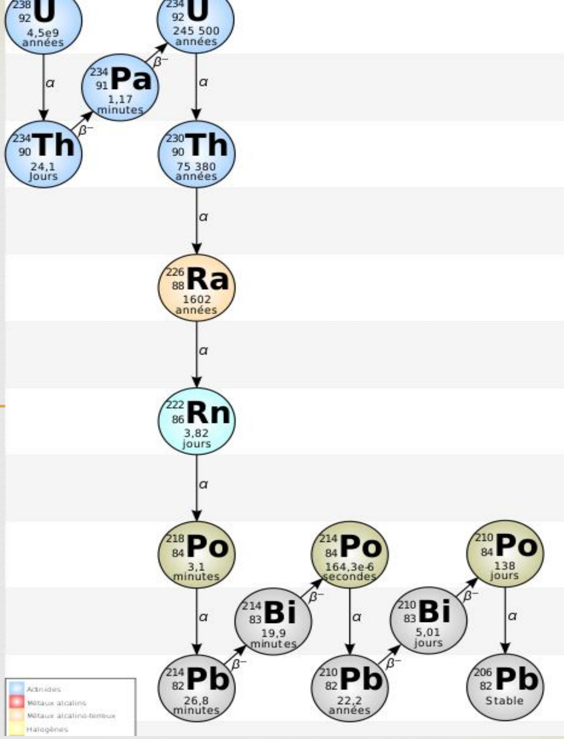
- •Only **Actinium**, **Thorium**, **Protactinium** &**Uranium** occur naturally (*i.e.*$Z =< 92$) in Uranium minerals.
- •all the remaining actinides are unstable and made artificially by nuclear transmutations.
- •The actinides elements lying **beyond Uranium,** are called **trans-uranium** or **trans-Uranic**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

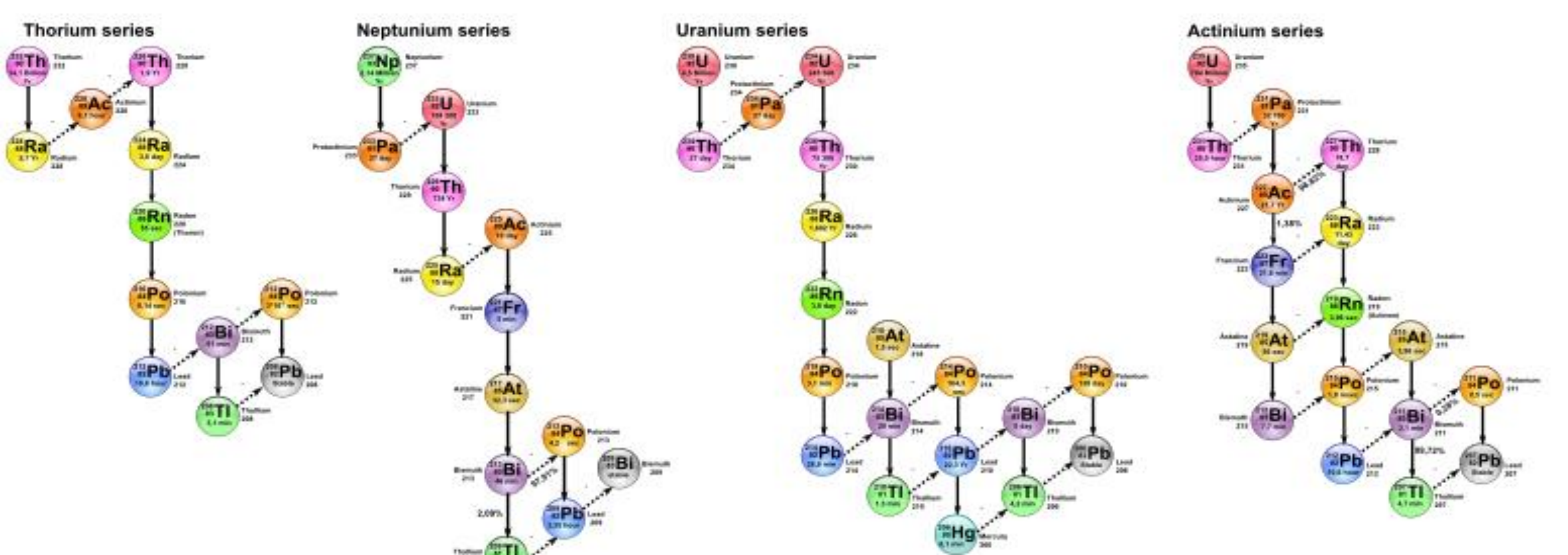
4. Radioactive Decay

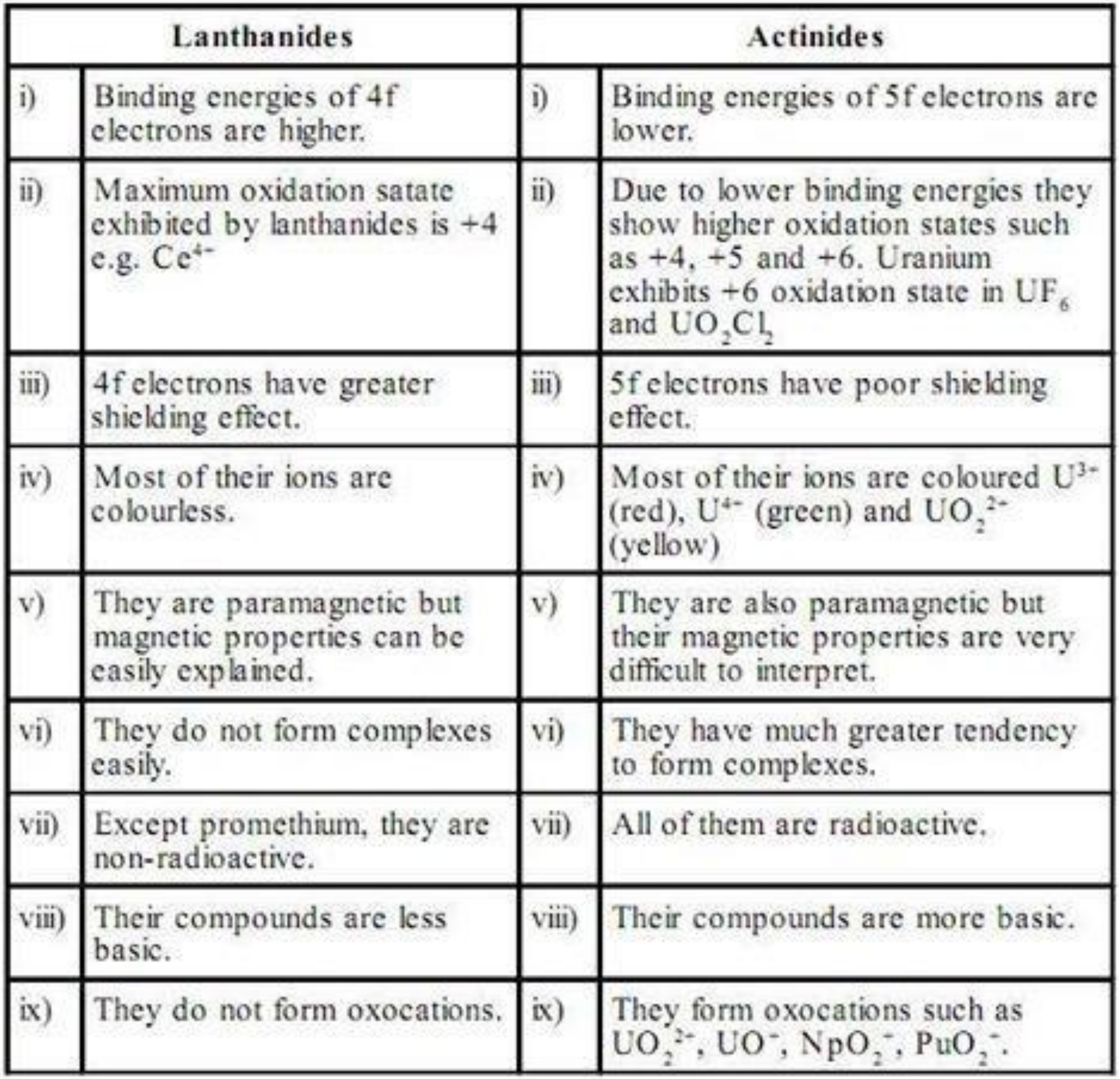
4.1 Decay Series

- 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.

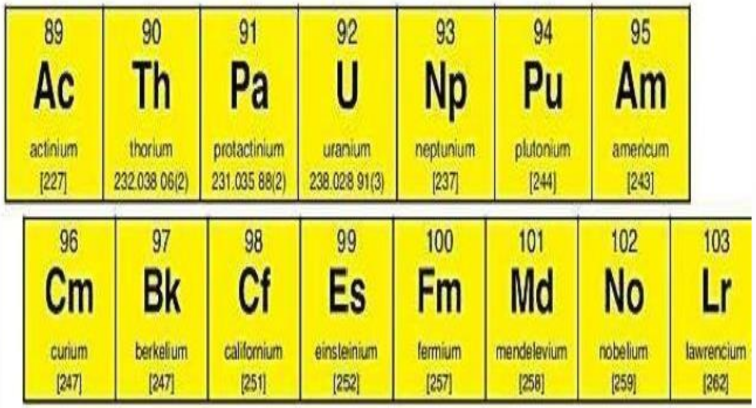
Differences

- ✓ 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.

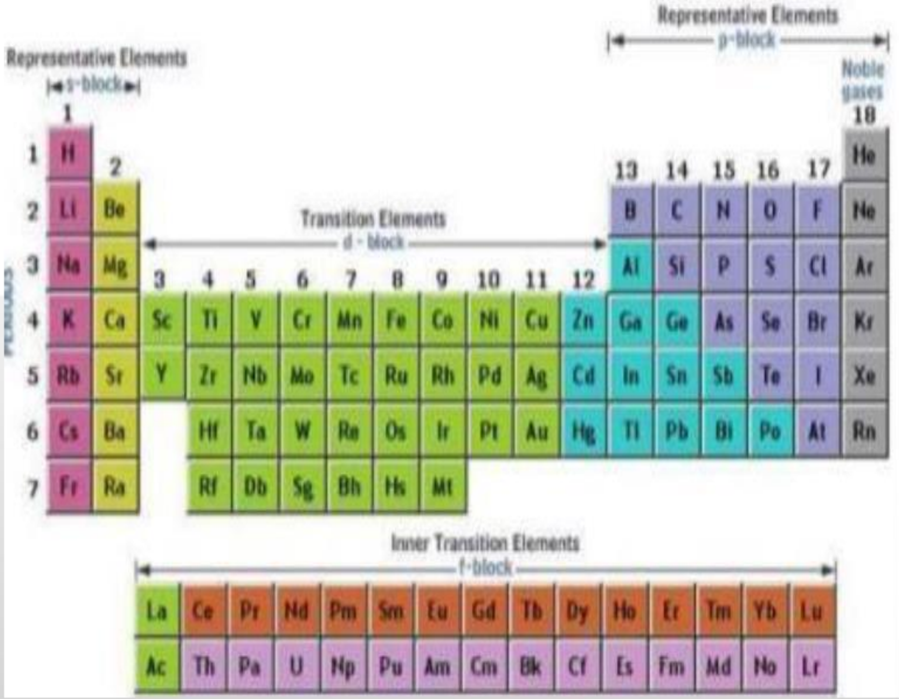
Actinoids

- 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]



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H																	He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra		Rf	Db	Sg	Bh	Hs	Mt									

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

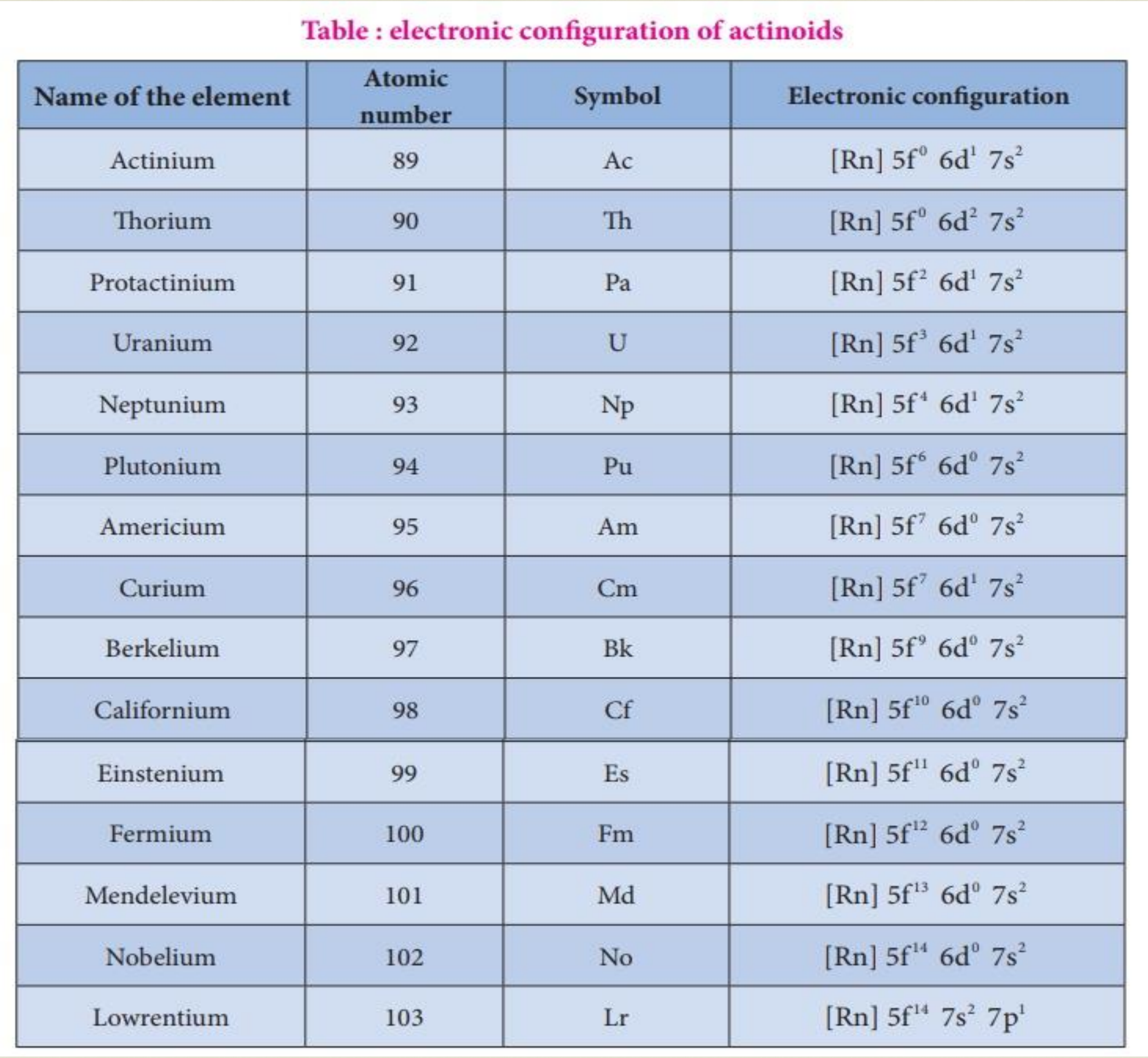
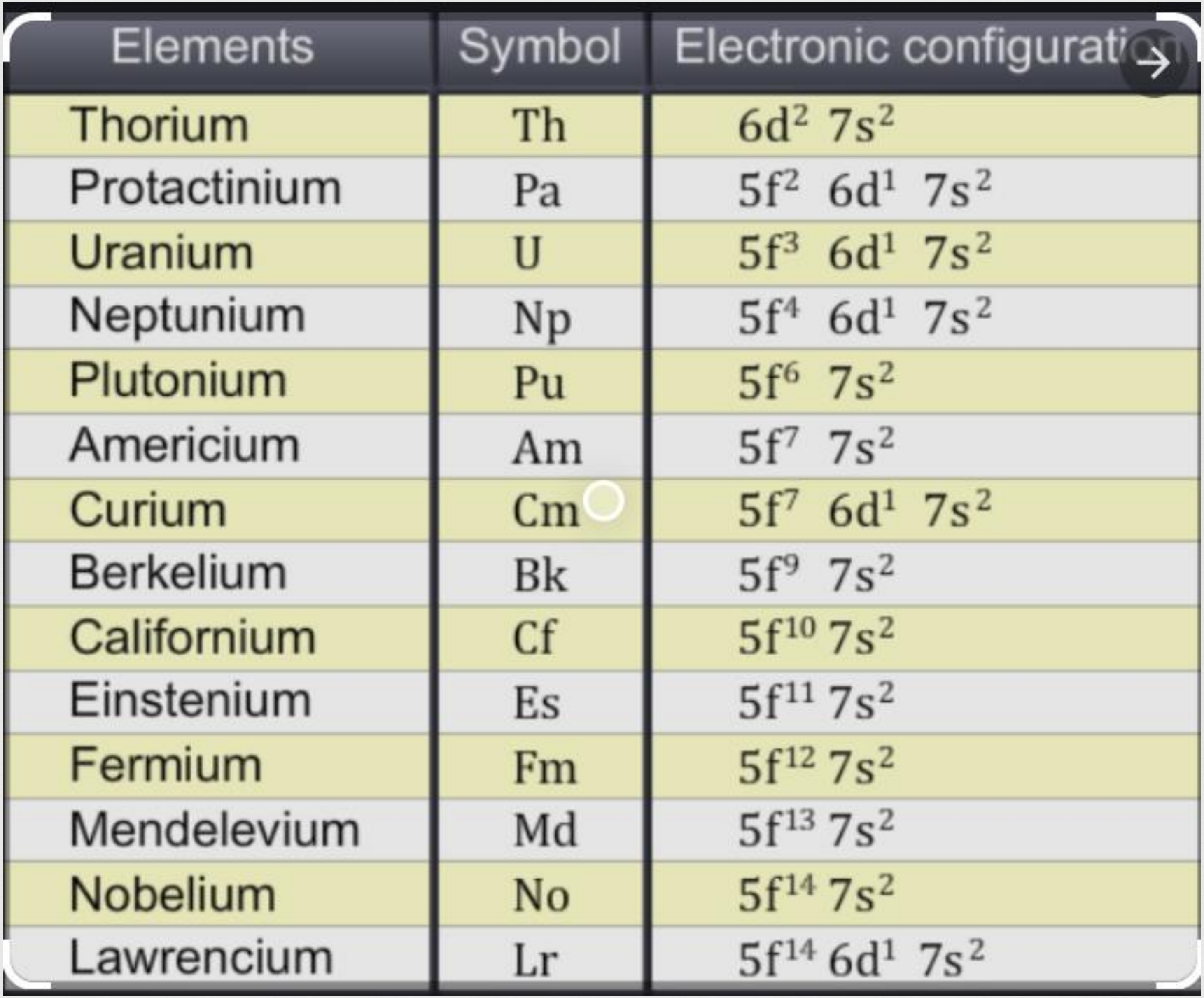
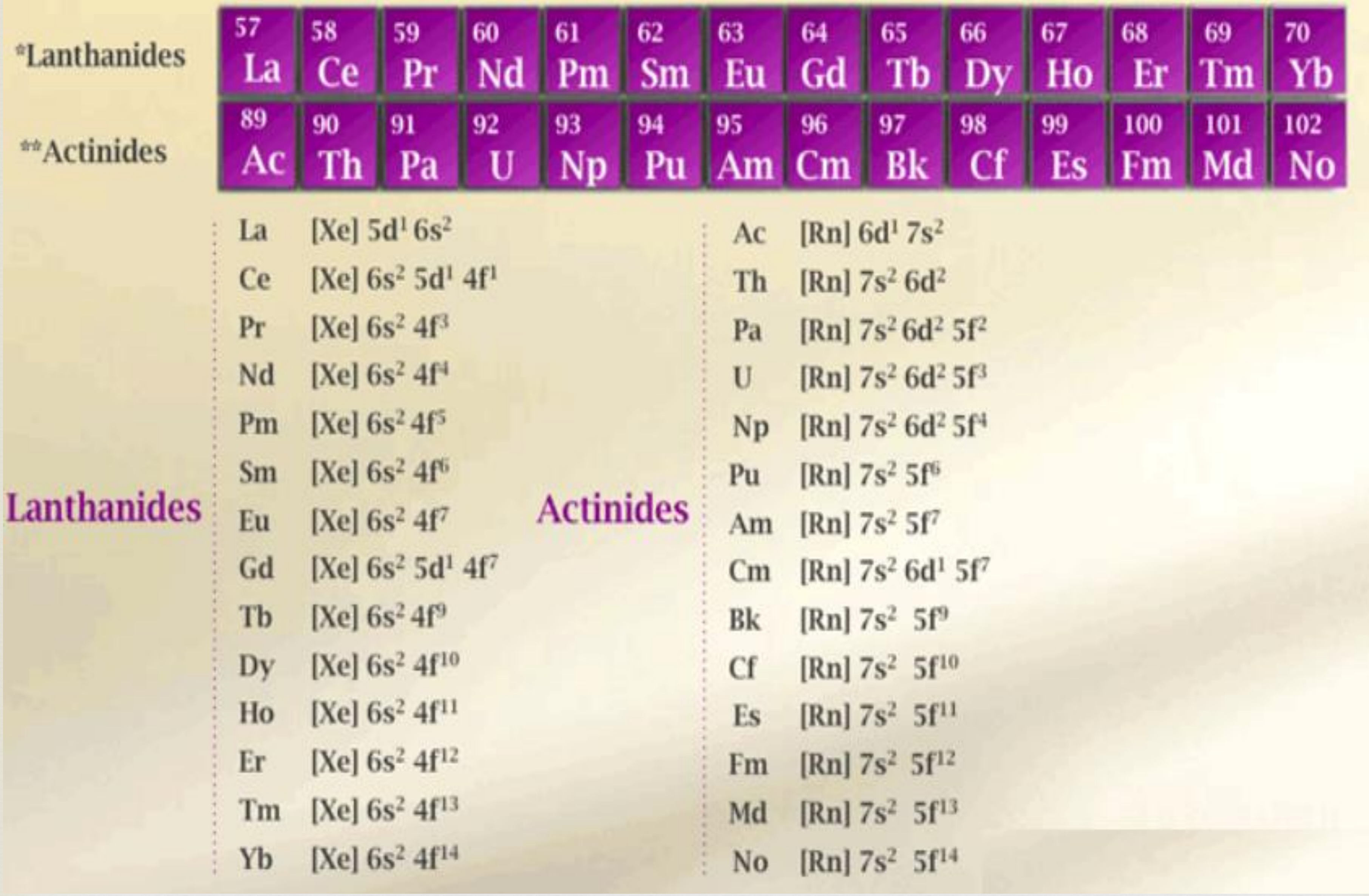


Table : electronic configuration of actinoids

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.

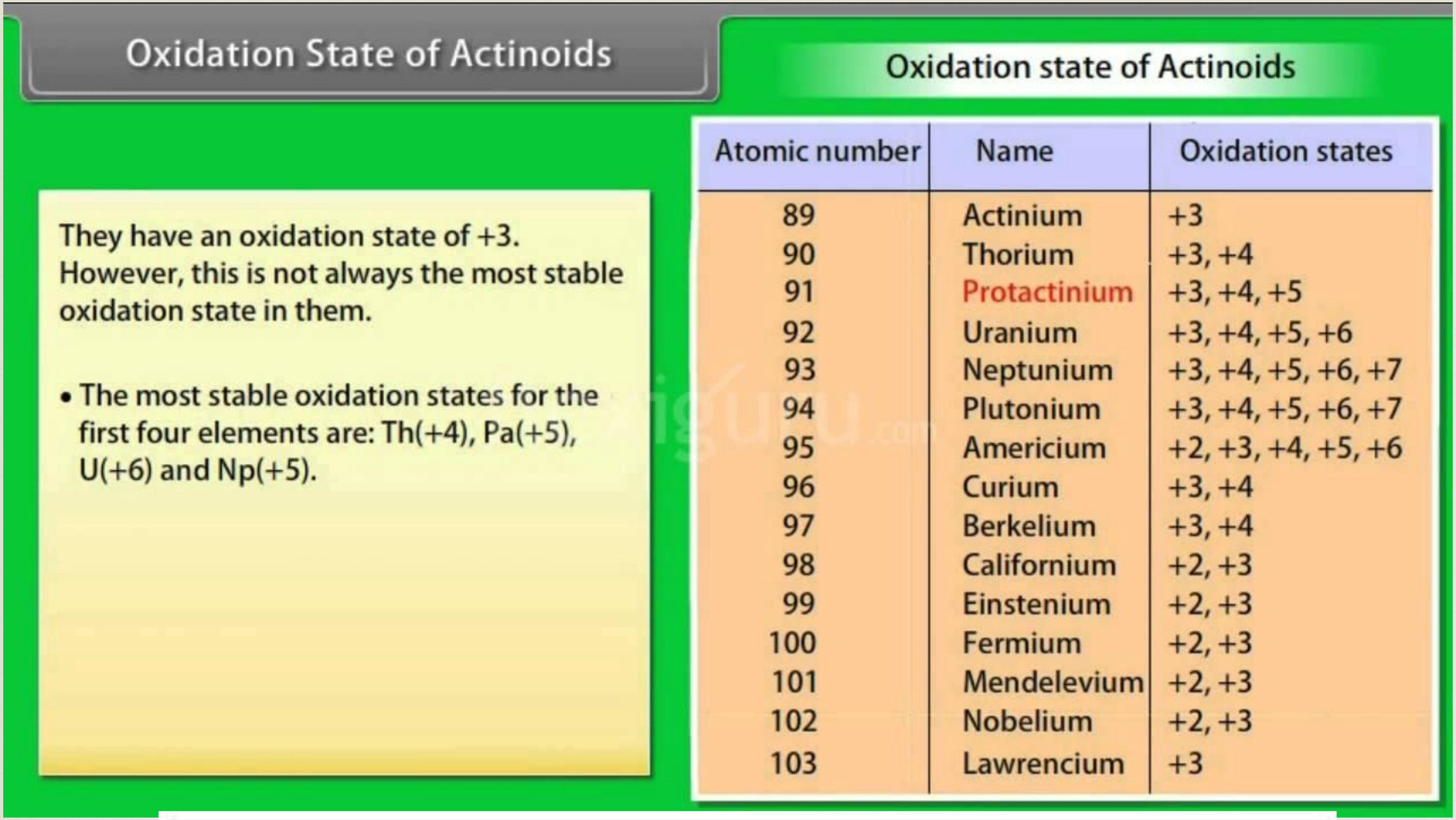
4. There is a small energy gap between the $5f^n\ 7s^2$ and $5f^{n-1}\ 6d\ 7s^2$ configurations.

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



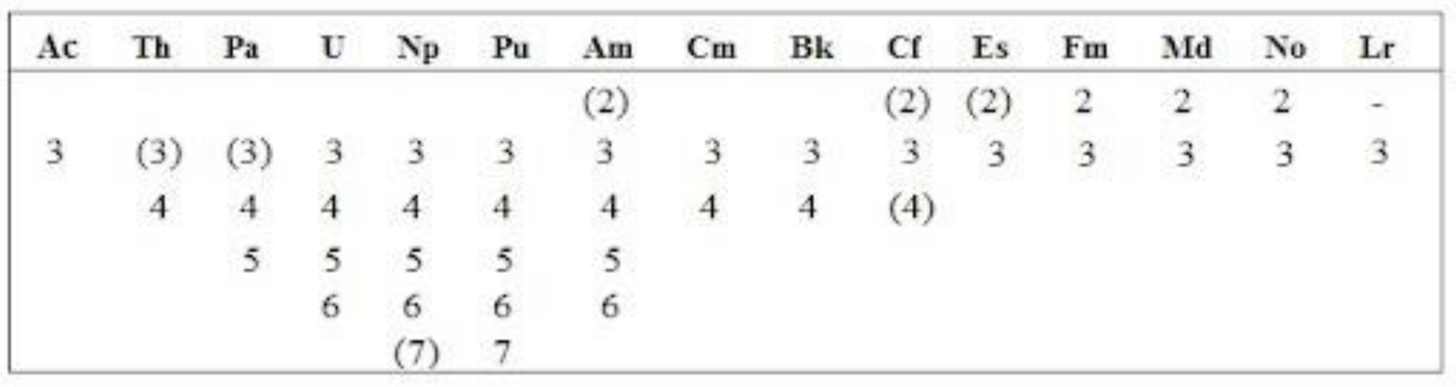
Oxidation State of Actinoids

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).**

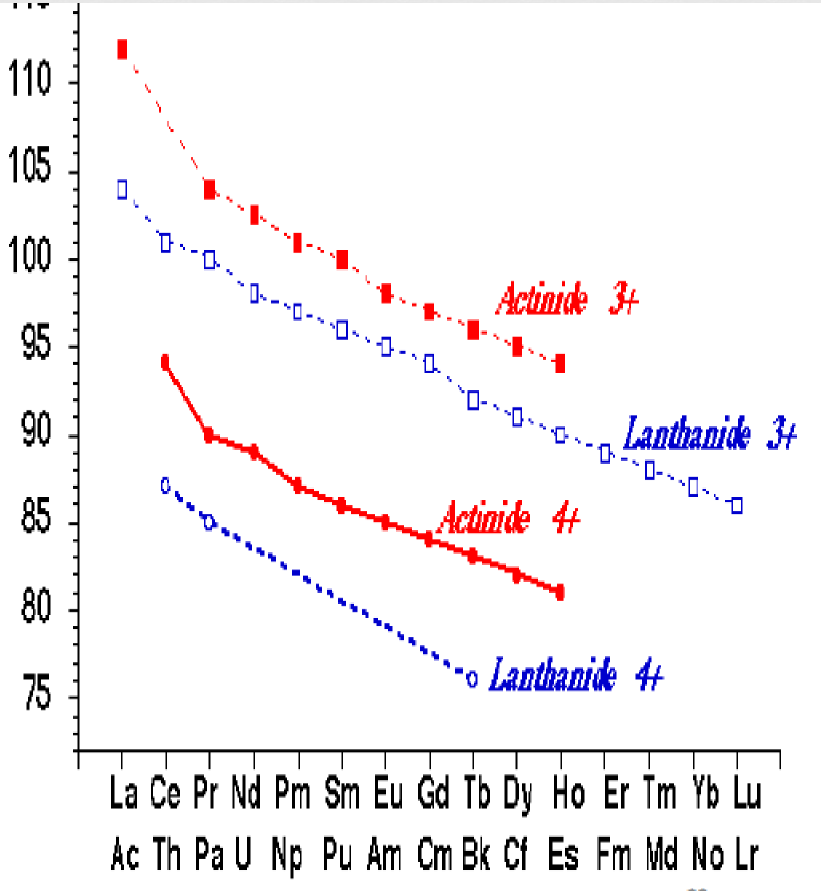
- •**Berkeliumin+4 state is strongly oxidizing** but is more stable than curium and americium in +4 stated up to f7 configuration.

- •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

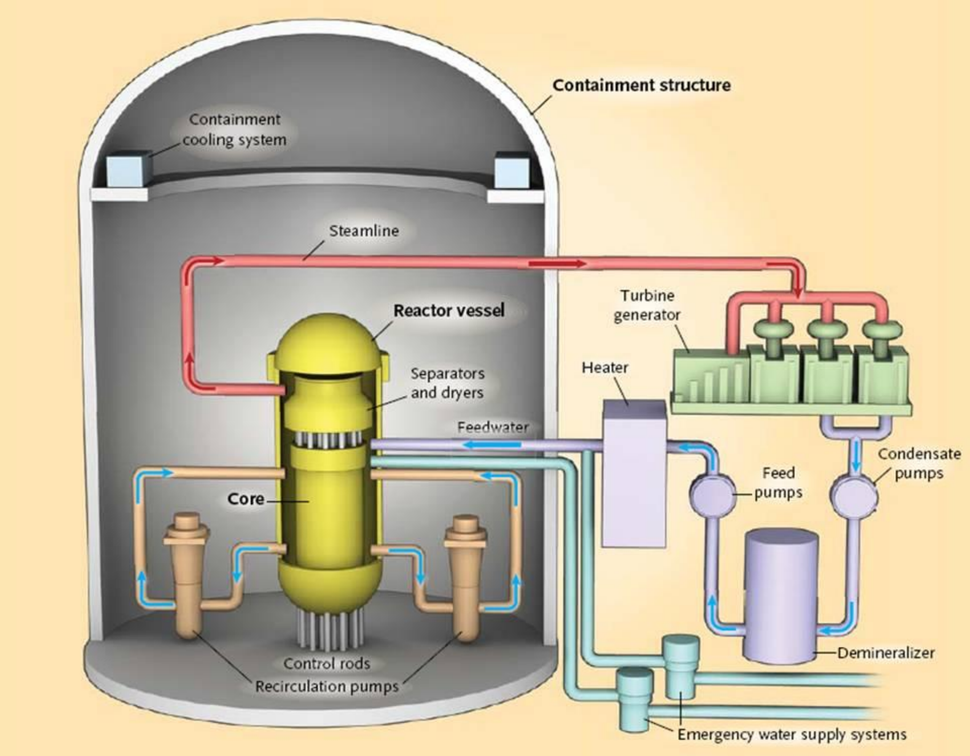
- The ions of lanthanides and actinides are colored in the solid state and also in aqueous solution, as is the case with the ions of transition metals.
- We know that the colours of transition metal ions occur due to absorption of light because of d-d electronic transitions.
- As there are no electrons 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.

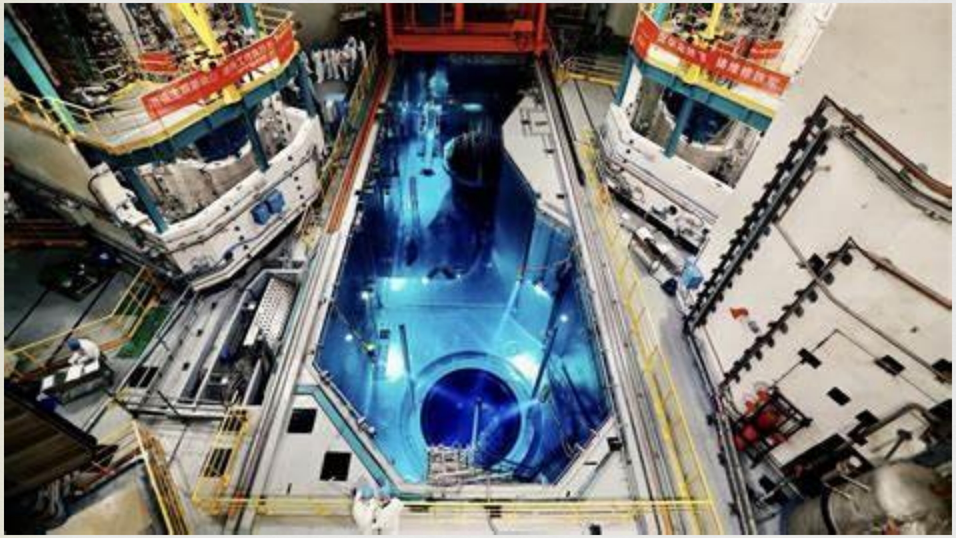
Common Properties

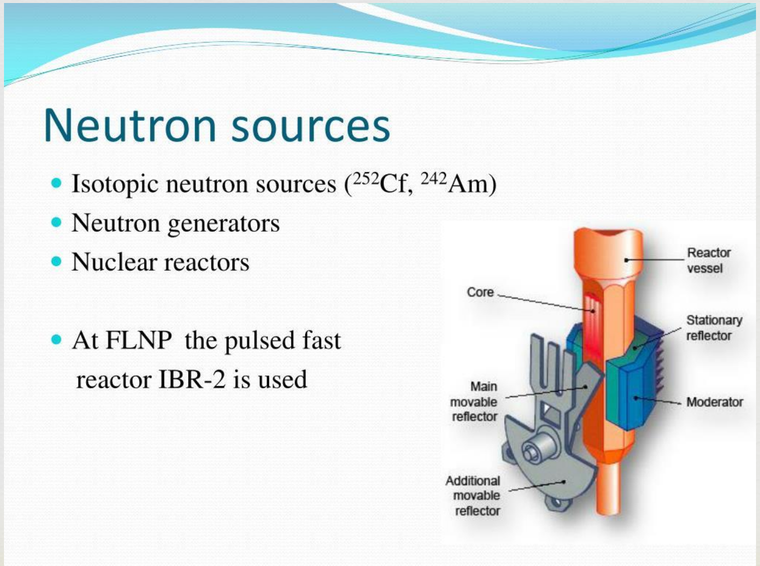
- **Actinides share the following properties:**
- All are radioactive. These elements have no stable isotopes.
- Actinides are highly electropositive.
- The metals tarnish readily in air. These elements are pyrophoric (spontaneously ignite in the air), particularly as finely divided powders.
- Actinides 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

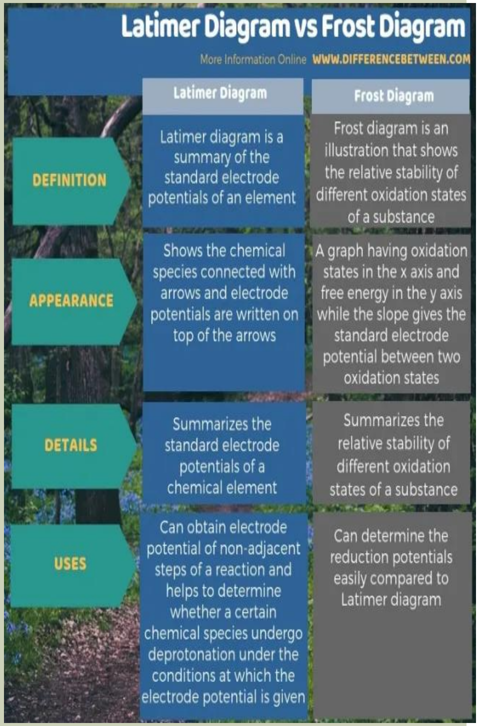
- Only the marginally stable oxo-anions of Np and Pu, e.g. $(AnO_5)^{3-}$.

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

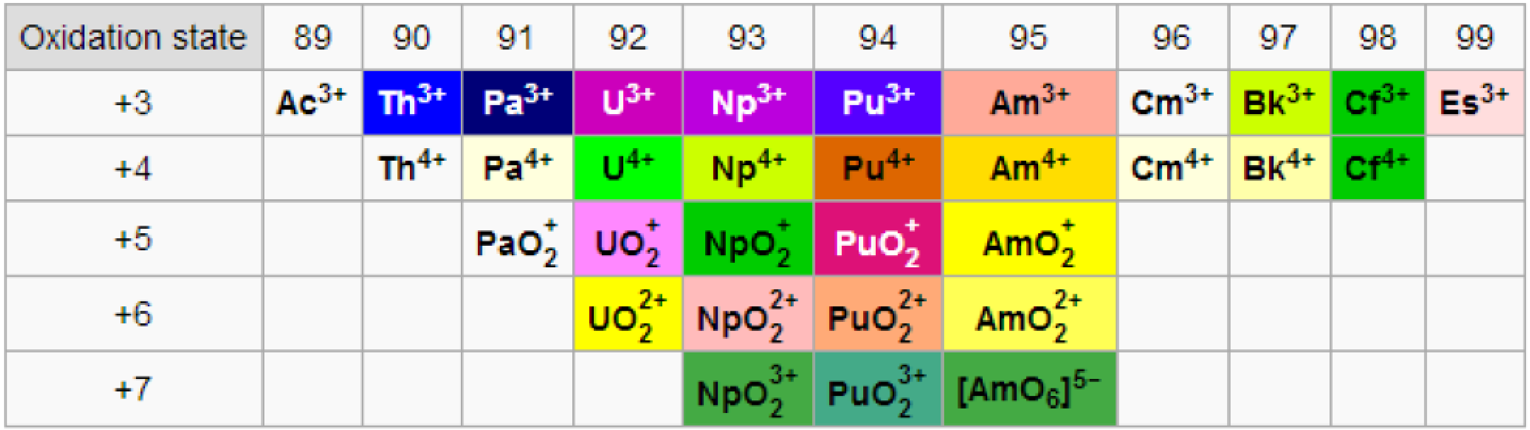
5. Color

- 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

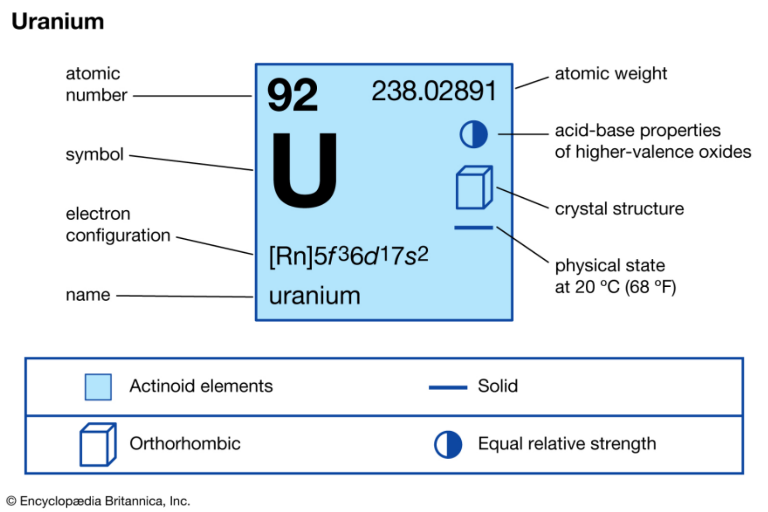
- A wide range of complexes with monodentate and chelating ligands.
- Complexing ability:- $[M^{5+}] > M^{4+} > (MO_2)^{2+} > M^{3+} > MO^{2+}$
- Geometry may be strongly influenced by covalent bonding effects, e.g. MO_2^{2+} unit is always linear
- $UO_2(\eta2\text{-}NO_3)_2(H2O)_2$ is hexagonal bipyramidal.

- **Compounds**

- Actinide Hydrides, Halides, Oxides, Oxyhalides …

Uranium Chemistry

اليورانيوم



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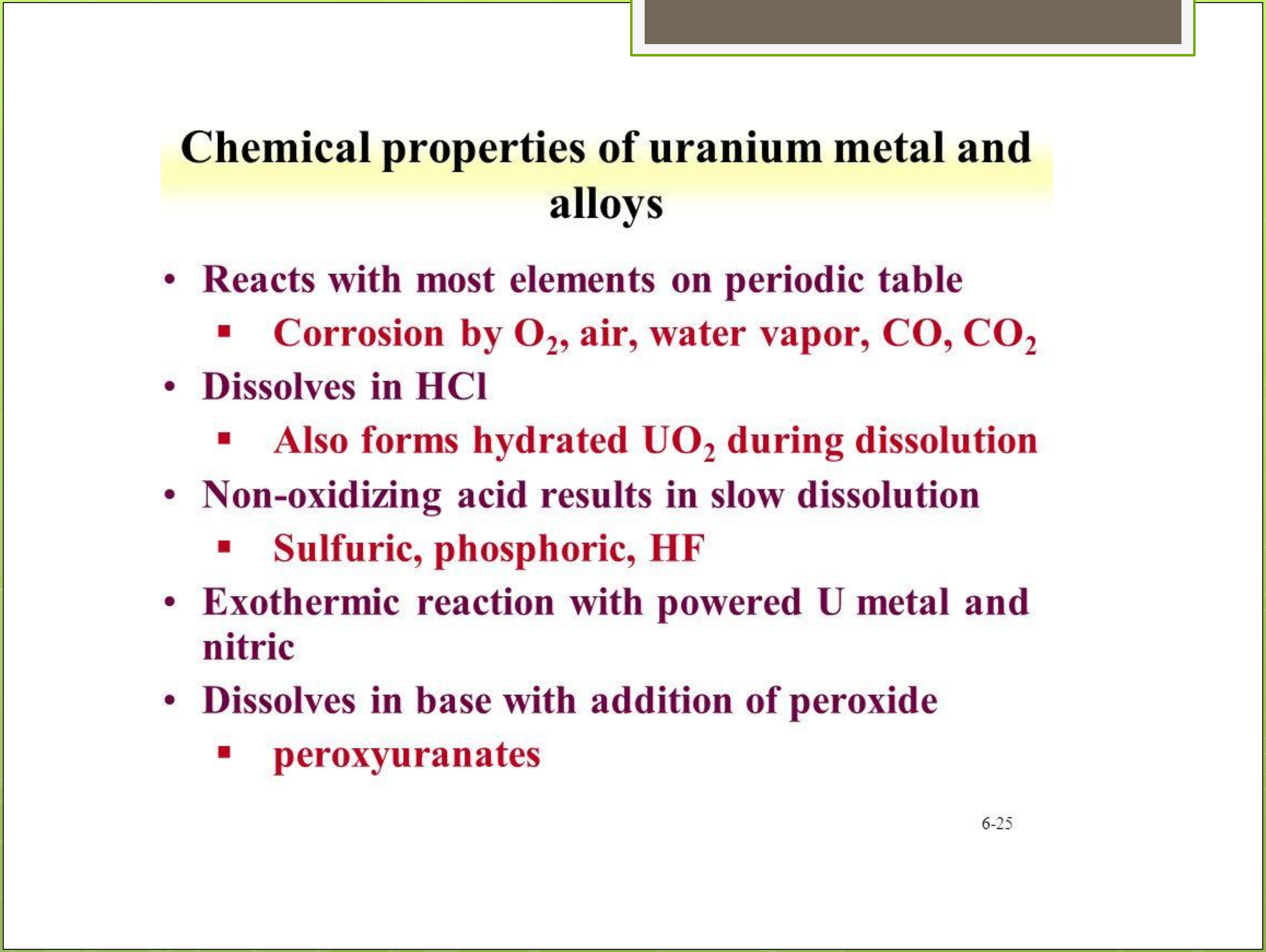


Chemical properties of uranium metal and alloys

- 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

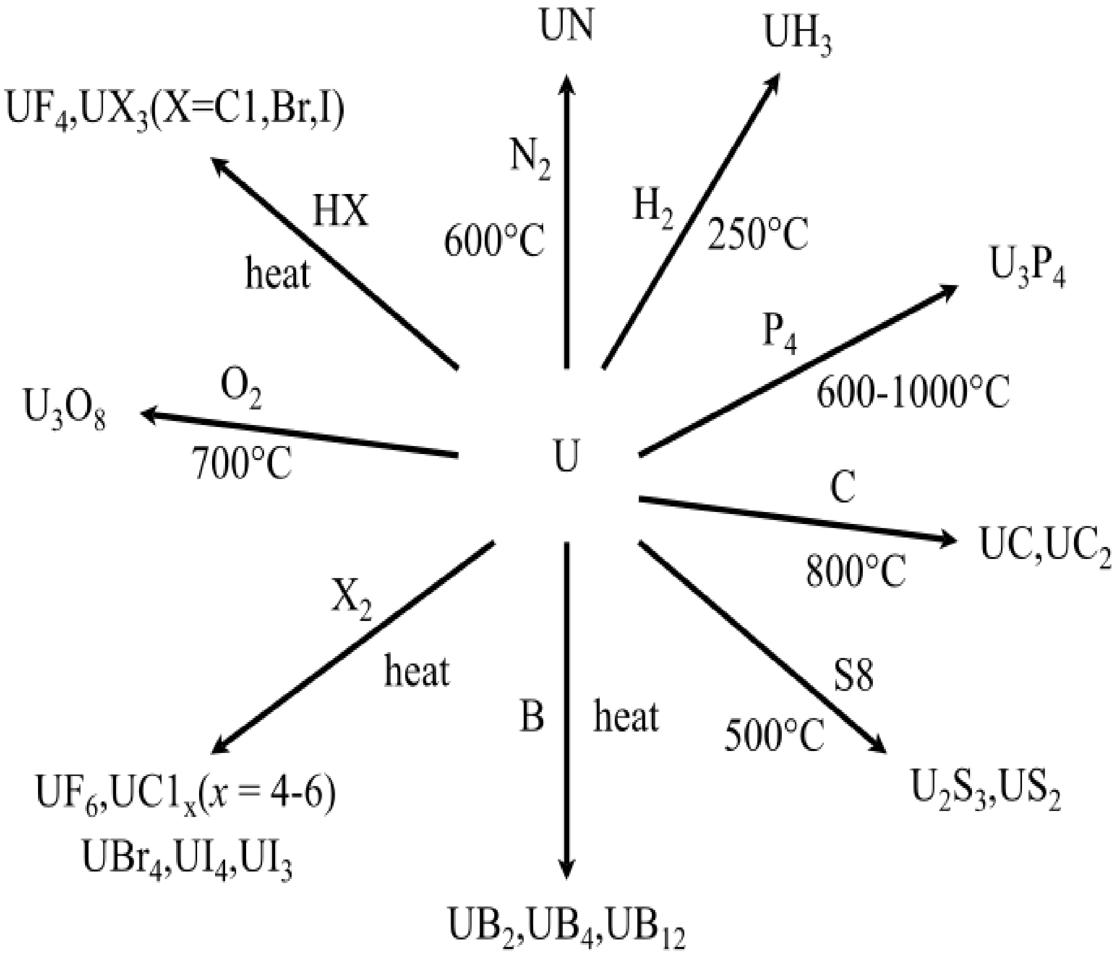
- Uranium metal reacts with almost all non-metal elements (with the exception of the noble gases) and their compounds, with reactivity increasing with temperature.

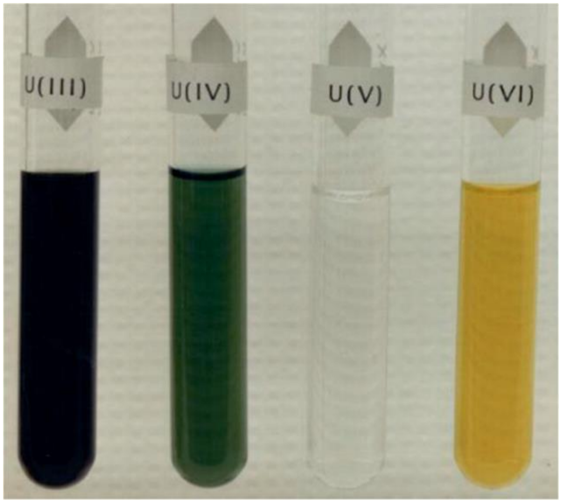
- Hydrochloric and nitric acids dissolve uranium,
- but non-oxidizing acids other than hydrochloric acid attack the element very slowly.

- 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:

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

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

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

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

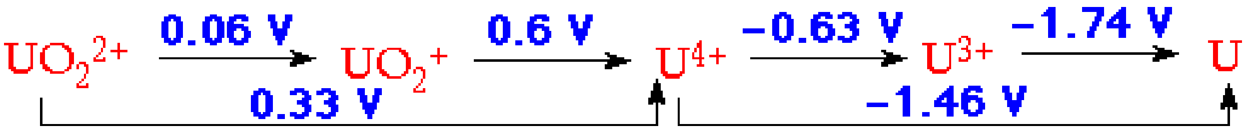
$$UO_2(NO_3)_2 \xrightarrow[400\text{–}600^\circ C]{O_2} UO_3 \qquad (NH_4)_2U_2O \xrightarrow[500^\circ C]{O_2} UO_3$$

Uranates

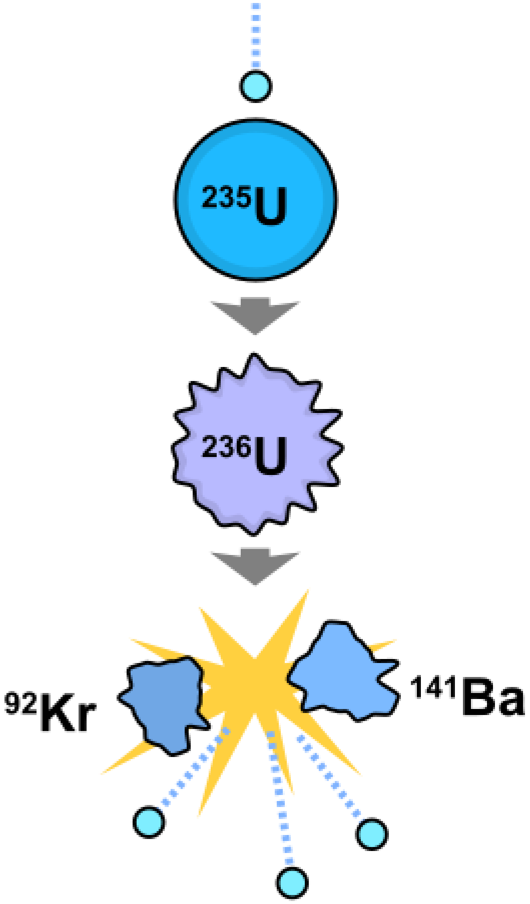
- Fusion of uranium oxides with alkali or alkaline earth carbonates
- chemical formula is **$M_xU_yO_z$**
- orange/yellow/brown mixedoxides,
- **Uranates:**
- Na_2UO_4......oxidation state+6
- CaU_2O_7......oxidation state+4
- Ca_3UO_6 ......oxidation state+4
- $NaUO_3$......oxidation state+5
- Ca_3UO_6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



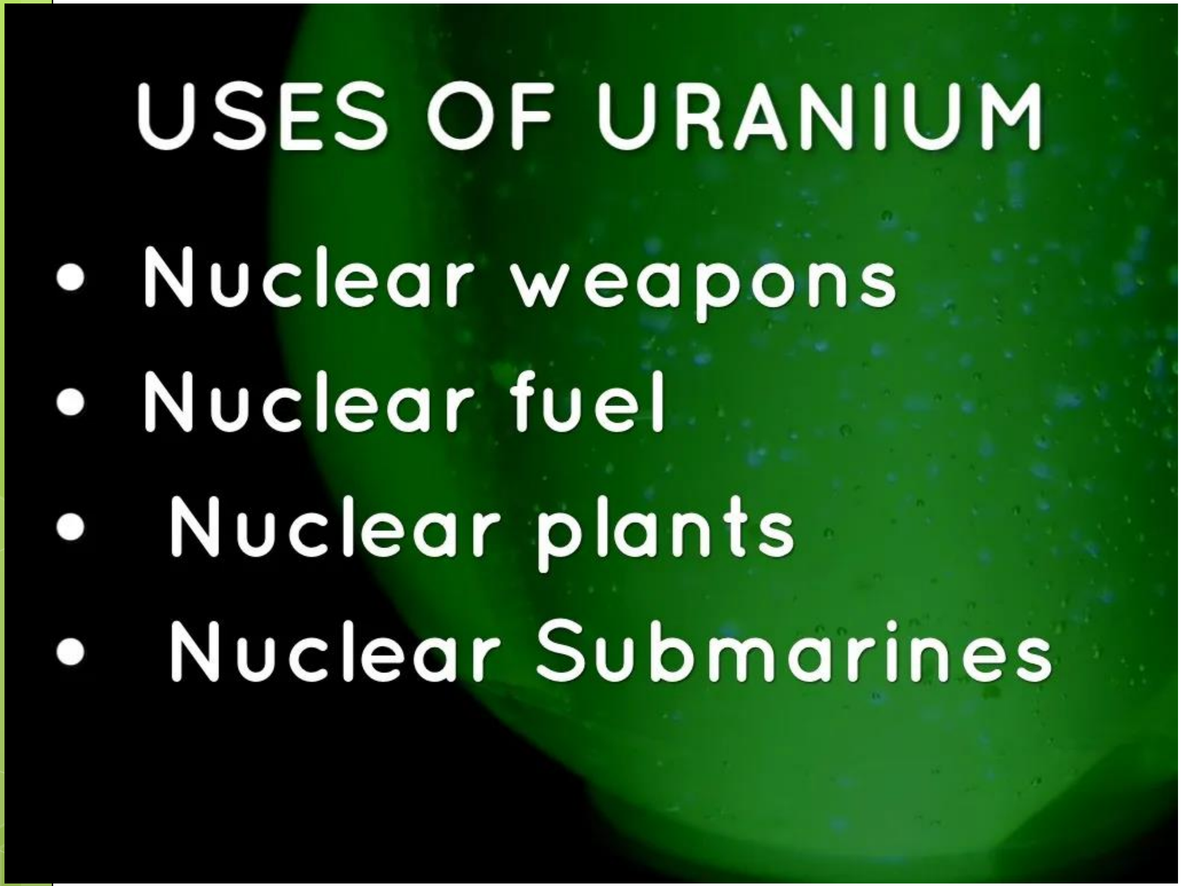
- Uranium-235 was the first isotope that was found to be fissile.
- Other naturally occurring isotopes are fissionable, but not fissile.
- On bombardment with slow neutrons, its uranium-235 isotope will most of the time divide into two smaller nuclei, releasing nuclear binding energy and more neutrons.



Modern Nuclear Reactors

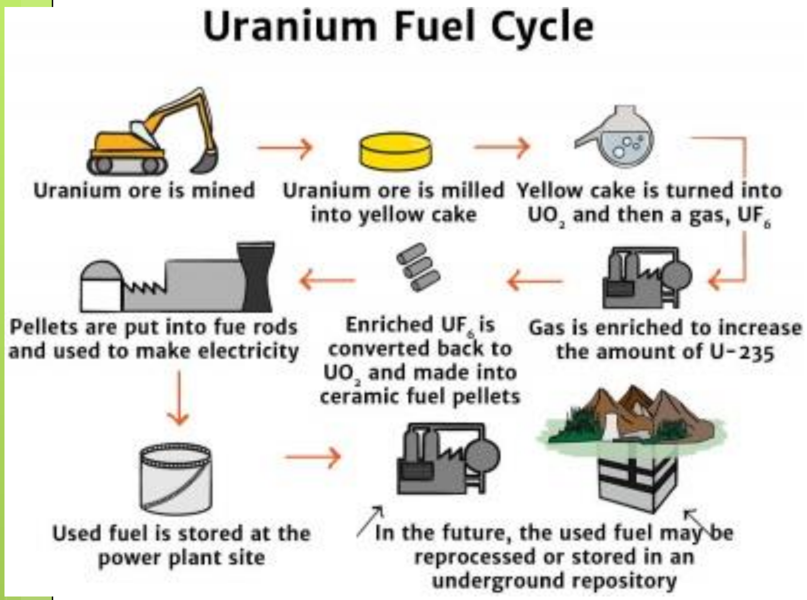
- Current nuclear reactors use UO_2 fuel – less reactive than U metal.
- Enrichment is by fractional gaseous centrifugation of UF_6 (easily sublimed).
- Neutron capture by ^{238}U results in formation of ^{239}Pu, which is fissile. Significant amounts of Pu will only be produced in an unmoderated reactor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

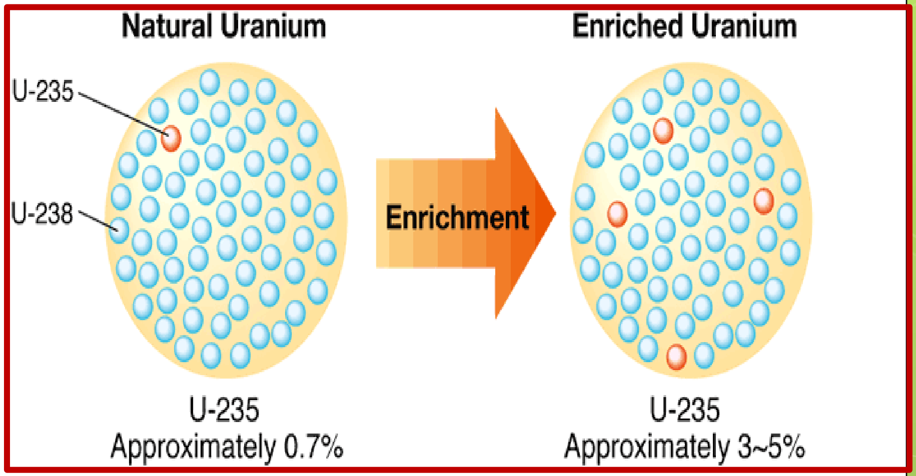
$$\underset{4.468\times10^{9}\,y}{^{238}U} \xrightarrow{(n,\gamma)} \underset{23.45m}{^{239}U} \xrightarrow{\beta^-} \underset{2.356d}{^{239}Np} \xrightarrow{\beta^-} \underset{2.411\times10^{4}\,y}{^{239}Pu}$$



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
Gas is enriched to increase the amount of U-235
Enriched UF6 is converted back to UO2 and made into ceramic fuel pellets
Pellets are put into fue rods and used to make electricity
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:

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

- 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:

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

- 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.**

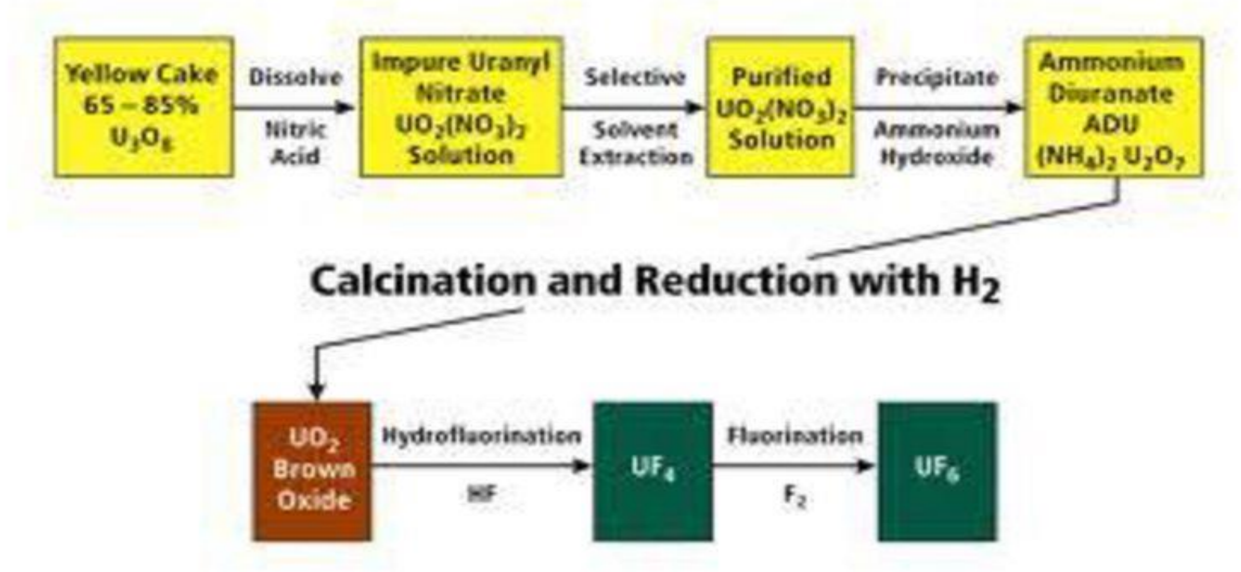
Converting UO_3 to UF_6

- 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:

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

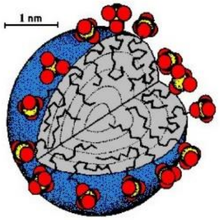
- The hexafluoride is now suitable feedstock for the gaseous diffusion process (Enrichment), i.e., to increase the percentage of ^{235}U in uranium.

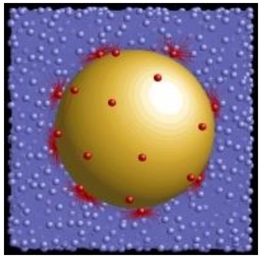
Refining and Converting U_3O_8 to UF_6

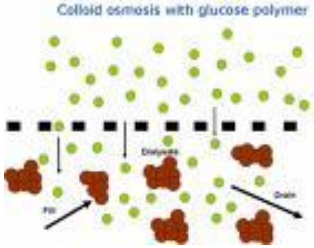


Introduction to

Colloid & Surface Chemistry



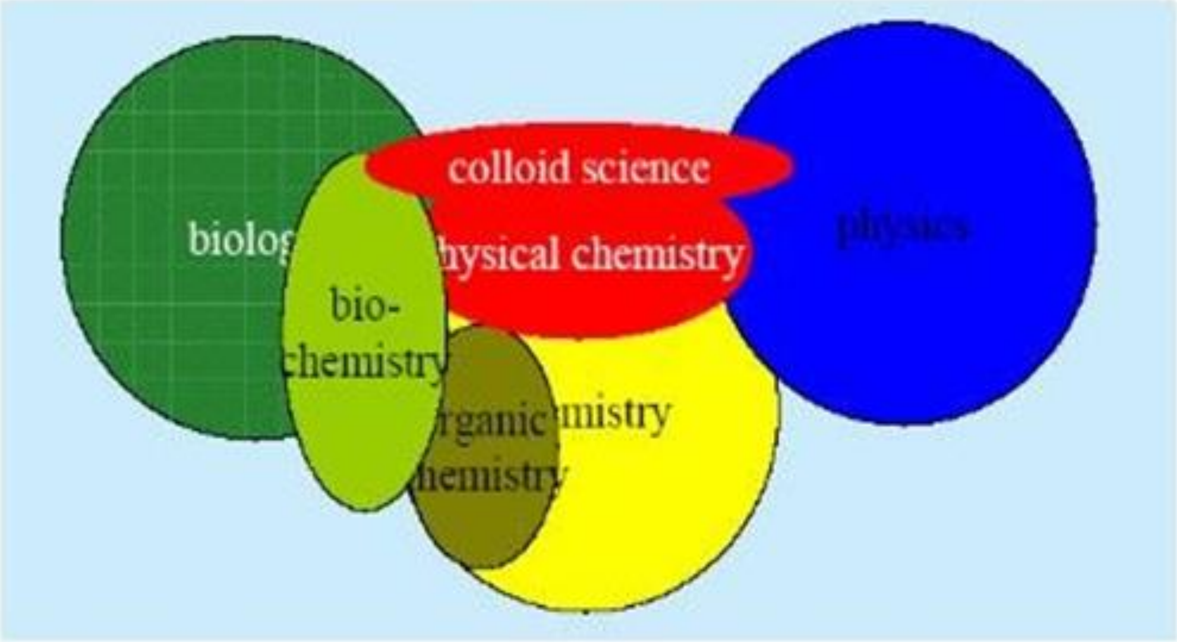




Part 1
Colloidal state

Colloid science is interdisciplinary

1. partly physical chemistry
   - it is not the chemical composition which is important
   - the state is independent of the composition
2. partly physics
   - the physical properties are of great importance
   - basic law of physics can be applied
3. partly biology
   - biological materials are colloids
   - the mechanisms of living systems are related to colloid- and interfacial chemistry



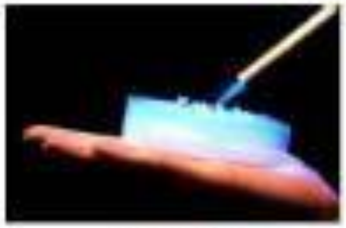
Examples of colloidal systems from daily life


Foams


Milk


Fog, smoke

Detergents


Aerogel


Blood


Paints

Cosmetics

Background (Old and new conceptions of colloids)

- In 1861, Thomas Graham divided soluble substances into two classes according to diffuse into water across a permeable membrane:

Thomas Graham

- He observed that crystalline substances such as sugar, urea, and sodium chloride passed through the membrane, while others like glue, gelatin and gum did not.
- He called the former **crystalloids** and the latter **colloids** (Greek, kolla = glue). Graham thought that the difference in the behavior of 'crystalloids' and 'colloids' was due to the particle size.

Crystalline

Crystalloids:

Diffuse rapidly across vegetable or animal membranes such as salt, sugar and urea.

amorphous

Colloids:

Exhibit little or no tendency to diffuse across vegetable or animal membranes such as gelatin, starch and gum.

Greek: *kola*= glue and *eiods*= like

Background (Old and new conceptions of colloids)

- According to Graham NaCl is crystalloid but it has been obtained in the colloidal state in benzene.
- Soap behaves as colloid in water and as crystalloid in alchohol

Later it was realized that (New conception):

►The difference in the rate of diffusion between crystalloids and colloids is due to the difference in the particle size

►Any substance, regardless of its nature, could be converted into a colloid by subdividing it into particles of colloidal size.

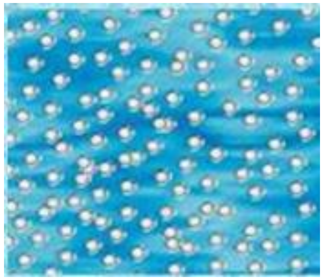
►We should speak of the colloidal state of matter as we speak of the gaseous, liquid or solid state of matter rather than to call a particular material as colloid or crystalloid

Nature of colloidal solutions (What are colloids)?

Sugar + water

True solution

1- 10 A^{o}



Sand + water

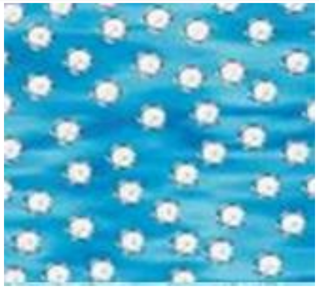
Suspension

>1000 A^{o}

Starch + water

Colloidal solution

10- 1000 A^{o}



Nature of colloidal solutions (What are colloids) ?

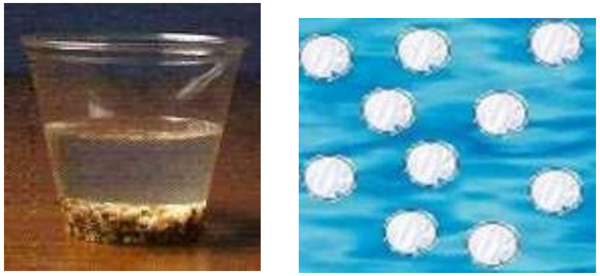
In **a true solution** as sugar or salt in water, the solute particles are dispersed in the solvent as single molecules with diameter less than 1 nm

Sugar + water (true solution(

< **1 nm**

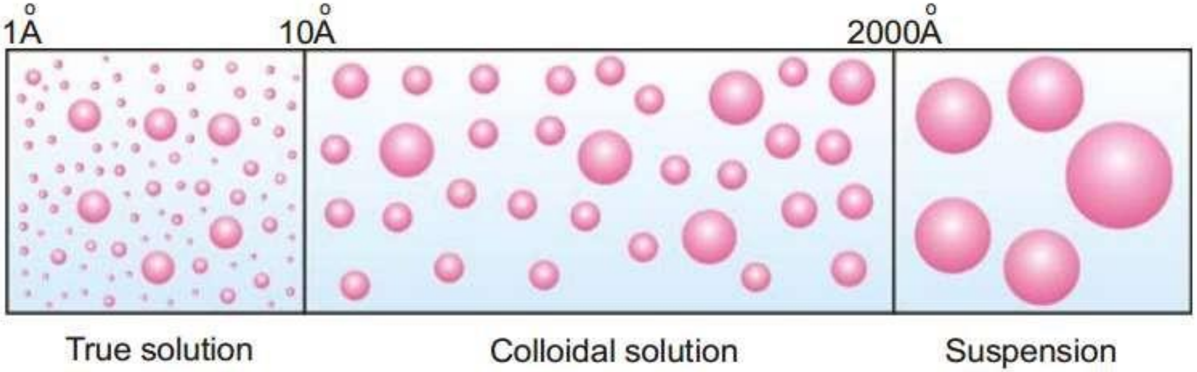
On the other hand, if **a suspension** as sand stirred into water, the dispersed particles are aggregates of millions of molecules. The diameter of these particles is of the order 1 000،Å or more

Sand + water (suspension(



<1 000Å

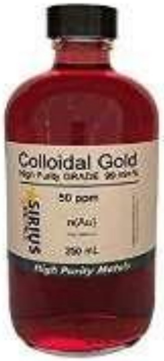
The colloidal solutions or colloidal dispersions are intermediate between true solutions and suspensions. In other words, the diameter of the dispersed particles in a colloidal dispersion is more than that of the solute particles in a true solution and smaller than that of a suspension.



Examples of colloidal solutions

Ink

Paint



Colloidal Gold

Nature of colloidal solutions (What are colloids) ?

True solution	**Suspension**	**Colloidal solution**
1- 10 A°	>1000 A°	10- 1000 A°
Transparent to light	Not transparent to light	Not transparent to light

Nature of colloidal solutions (What are colloids) ?

True solution	Suspension	Colloidal solution
1- 10 A°	>1000 A°	10- 1000 A°
Transparent to light	Not transparent to light	Not transparent to light
Can not be seen by the naked eyes or even under a microscope	Can be seen by the naked eye	Can not be seen by the naked eye or with ordinary microscope

Nature of colloidal solutions (What are colloids) ?

True solution	**Suspension**	**Colloidal solution**
1- 10 A°	>1000 A°	10- 1000 A°
Transparent to light	Not transparent to light	Not transparent to light
Can not be seen by the naked eyes or even under a microscope	Can be seen by the naked eye	Can not be seen by the naked eye or with ordinary microscope
Not influenced by the gravitational pull and remain suspended in the solvent all the time	They are influenced by the gravitational pull and settle down automatically on standing	Not influenced by the gravitational pull and remain suspended in the solvent all time

Nature of colloidal solutions (What are colloids) ?

True solution	Suspension	Colloidal solution
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Not influenced by the gravitational pull and remain suspended in the solvent all the time	They are influenced by the gravitational pull and settle down automatically on standing	Not influenced by the gravitational pull and remain suspended in the solvent all time
Pass through an ordinary filter paper	Retained by an ordinary filter paper	Pass through an ordinary filter paper

Colloidal particles under microscope

Light microscope

Ultra- microscope

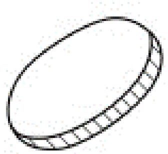
Electron microscope

The colloidal particles are smaller than the wavelength of the visible light. Thus, they are unable to reflect light and hence cannot be seen by ordinary microscope

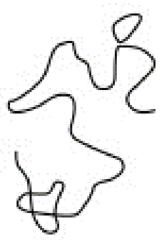
Note that

The colloidal particles are not necessarily corpuscular in shape. In fact, these may be rod-like, disc-like, thin films, or long filaments. For matter in the form of corpuscles, the diameter gives a measure of the particle size .

Rod



Disc



Random coil

However, in other cases one of the dimensions (length, width and thickness) has to be in the colloidal range for the material to be classed as colloidal .

Thus in a broader context we can say:

“A system with at least one dimension (length, width, or thickness) of the dispersed particles in the range 10 Å to 1 000‹Å, is classed as a colloidal dispersion”

Classification of colloids

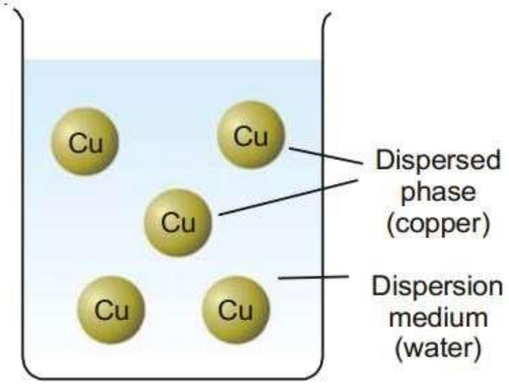
Classification is based on following criteria:

1. Physical state of dispersed phase and dispersion medium.
2. Nature of interaction between dispersed phase and dispersion medium.
3. Types of particles of the dispersed phase.

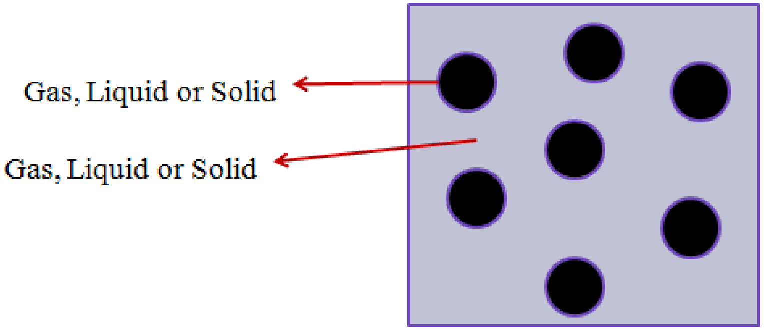
Classification based on physical state of dispersed phase and dispersion medium

Any colloidal system is made of two phases. The substance distributed as the colloidal particles is called the **Dispersed Phase** and the second continuous phase in which the colloidal particles are dispersed is called the **Dispersion Medium.**

For example, for a colloidal solution of copper in water, copper particles constitute the dispersed phase and water the dispersion medium.



Either the dispersed phase or the dispersion medium can be a gas, liquid or solid



A colloidal dispersion of one gas in another is not possible since the two gases would give a homogeneous molecular mixture. So that, there are **Eight** possible types of colloidal systems

X

Dispersed phase	Gas	Gas	Gas	Liquid	Liquid	Liquid	Solid	Solid	Solid
Dispersion medium	Gas	Liquid	Solid	Gas	Liquid	Solid	Gas	Liquid	Solid

1 Foam

Dispersed phase: Gas **Dispersion medium:** Liquid

Examples


Whipped cream


Shaving cream


Soda water


Soap Solution

2 Solid Foam

Dispersed phase: Gas **Dispersion medium:** Solid

Examples


Cork stoppers


Pumice stone


Foam rubber


Marshmallow

3 Aerosol

Dispersed phase: Liquid **Dispersion medium:** Gas

Examples


Cloud


Aerosol spray


Mist


Fog

4 Emulsion

Dispersed phase: Liquid **Dispersion medium:** Liquid

Examples


Milk

Hair cream


Mayonnaise


Emulsified water

5 Solid Emulsion (Gel)

Dispersed phase: Liquid

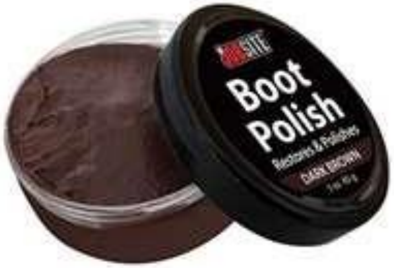
Dispersion medium: Solid

Examples

Butter

Cheese

Jelly



Boot Polish

6 Smoke

Dispersed phase: Solid **Dispersion medium:** Gas

Examples

7 Sol (Colloidal Solutions)

Dispersed phase: Solid
Dispersion medium: Liquid

Examples

Ink

Paint

Colloidal Gold

8 Solid Sol

Dispersed phase: Solid
Dispersion medium: Solid

Examples

Colored Glass

Metal Alloys

Classification of colloids

Classification is based on following criteria:

1. Physical state of dispersed phase and dispersion medium.
2. Nature of interaction between dispersed phase and dispersion medium.
3. Types of particles of the dispersed phase.

Classification based on nature of interaction

Solid dispersed in liquid (Sols(

Lyophilic (solvent-loving) **and Lyophobic** (solvent-hating) **sols**

Lyophilic sols: are those in which the dispersed phase exhibits a definite affinity for the medium or the solvent.

The examples of Lyophilic sols are dispersions of starch, gum, and protein in water.

Lyophobic sols: are those in which the dispersed phase has no attraction for the medium or the solvent.

The examples of Lyophobic sols are dispersion of gold, iron (III) hydroxide and sulphur in water.

Solid dispersed in liquid (Sols(

Lyophilic (solvent-loving) **and Lyophobic** (solvent-hating) **sols**

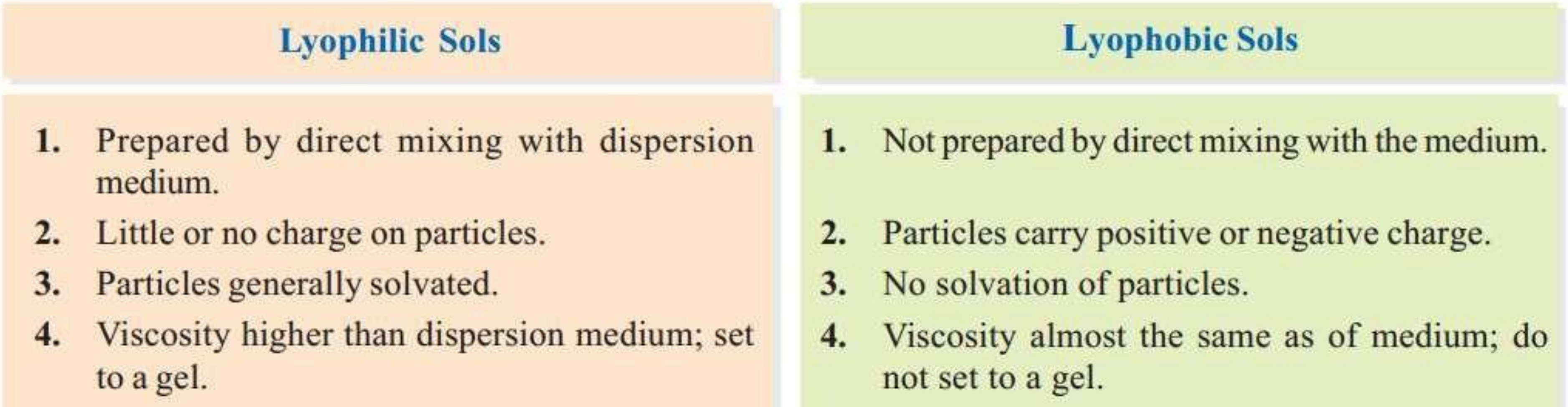
- The affinity or attraction of the sol particles for the medium, in a lyophilic sol, is due to hydrogen bonding with water .

- If the dispersed phase is a protein (as in egg) hydrogen bonding takes place between water molecules and the amino groups ($–NH–$, $–NH_2$) of the protein molecule.

- In a dispersion of starch in water, hydrogen bonding occurs between water molecules and the – OH groups of the starch molecule.

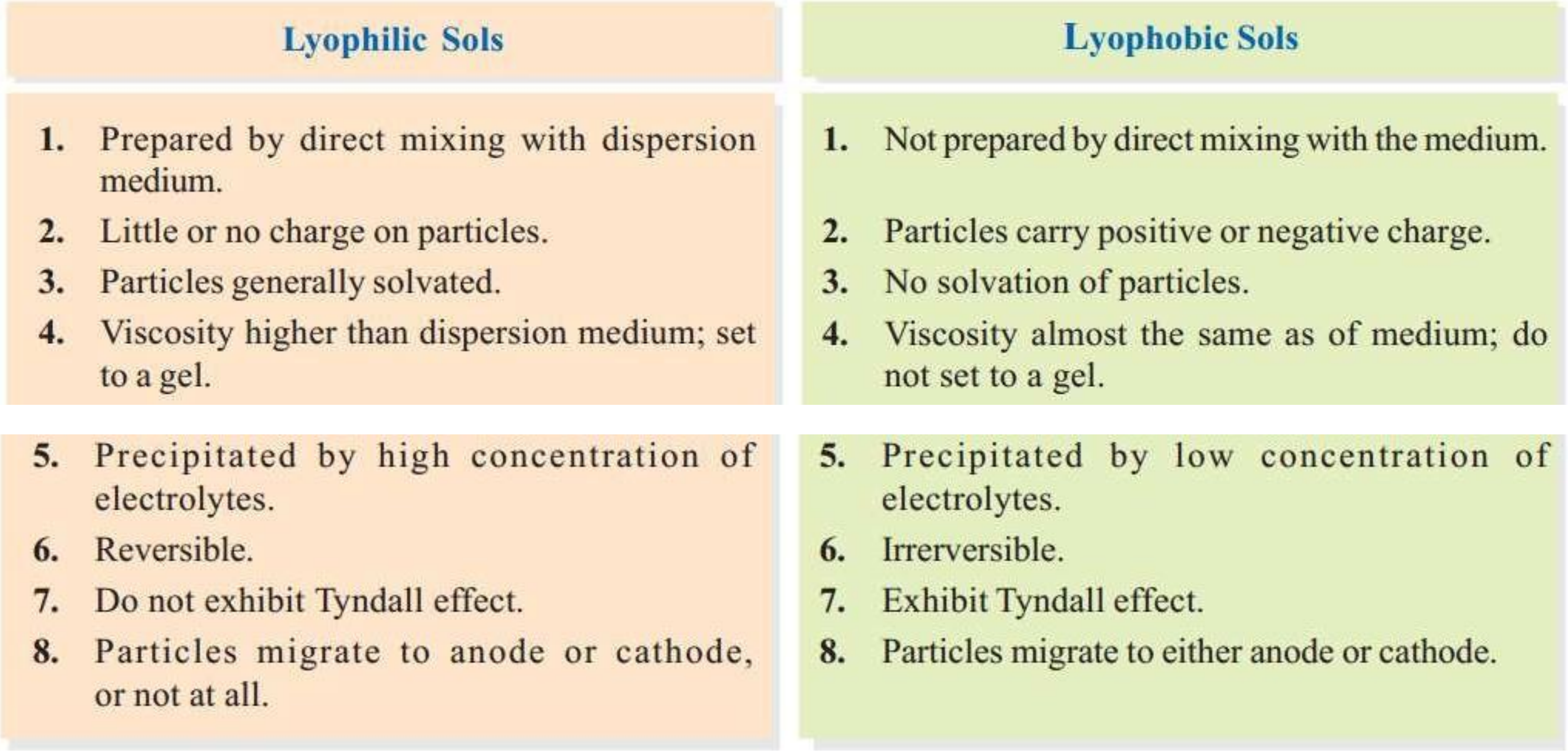
- There are no similar forces of attraction when sulphur or gold is dispersed in water.

Differences between lyophilic and lyophobic sols



Lyophilic Sols	Lyophobic Sols
1. Prepared by direct mixing with dispersion medium.	**1.** Not prepared by direct mixing with the medium.
2. Little or no charge on particles.	**2.** Particles carry positive or negative charge.
3. Particles generally solvated.	**3.** No solvation of particles.
4. Viscosity higher than dispersion medium; set to a gel.	**4.** Viscosity almost the same as of medium; do not set to a gel.

Differences between lyophilic and lyophobic sols



Lyophilic Sols	Lyophobic Sols
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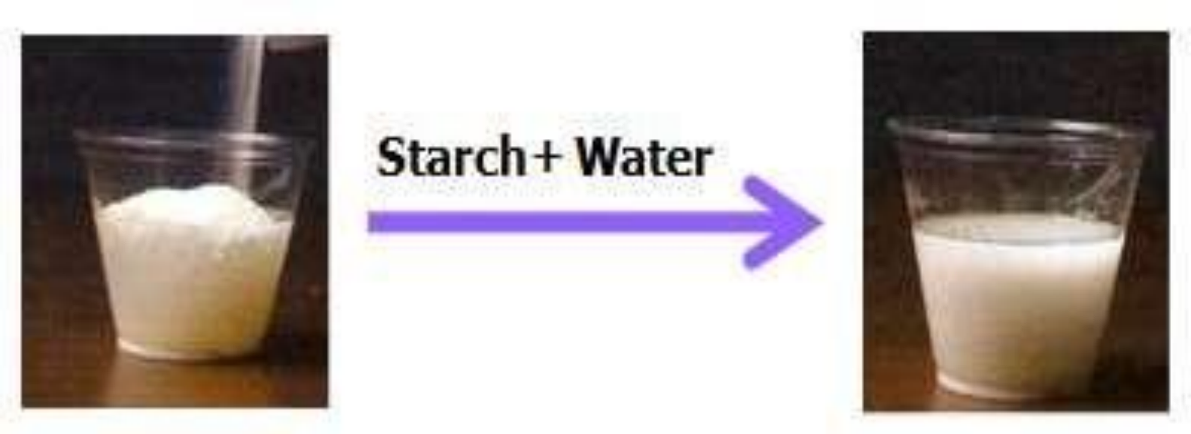
3. Particles generally solvated.	**3.** No solvation of particles.
4. Viscosity higher than dispersion medium; set to a gel.	**4.** Viscosity almost the same as of medium; do not set to a gel.
5. Precipitated by high concentration of electrolytes.	**5.** Precipitated by low concentration of electrolytes.
6. Reversible.	**6.** Irrerversible.
7. Do not exhibit Tyndall effect.	**7.** Exhibit Tyndall effect.
8. Particles migrate to anode or cathode, or not at all.	**8.** Particles migrate to either anode or cathode.

Preparation of sols

Lyophilic sols may be prepared by simply warming the solid with the liquid dispersion medium e.g., starch with water.



Preparation of sols

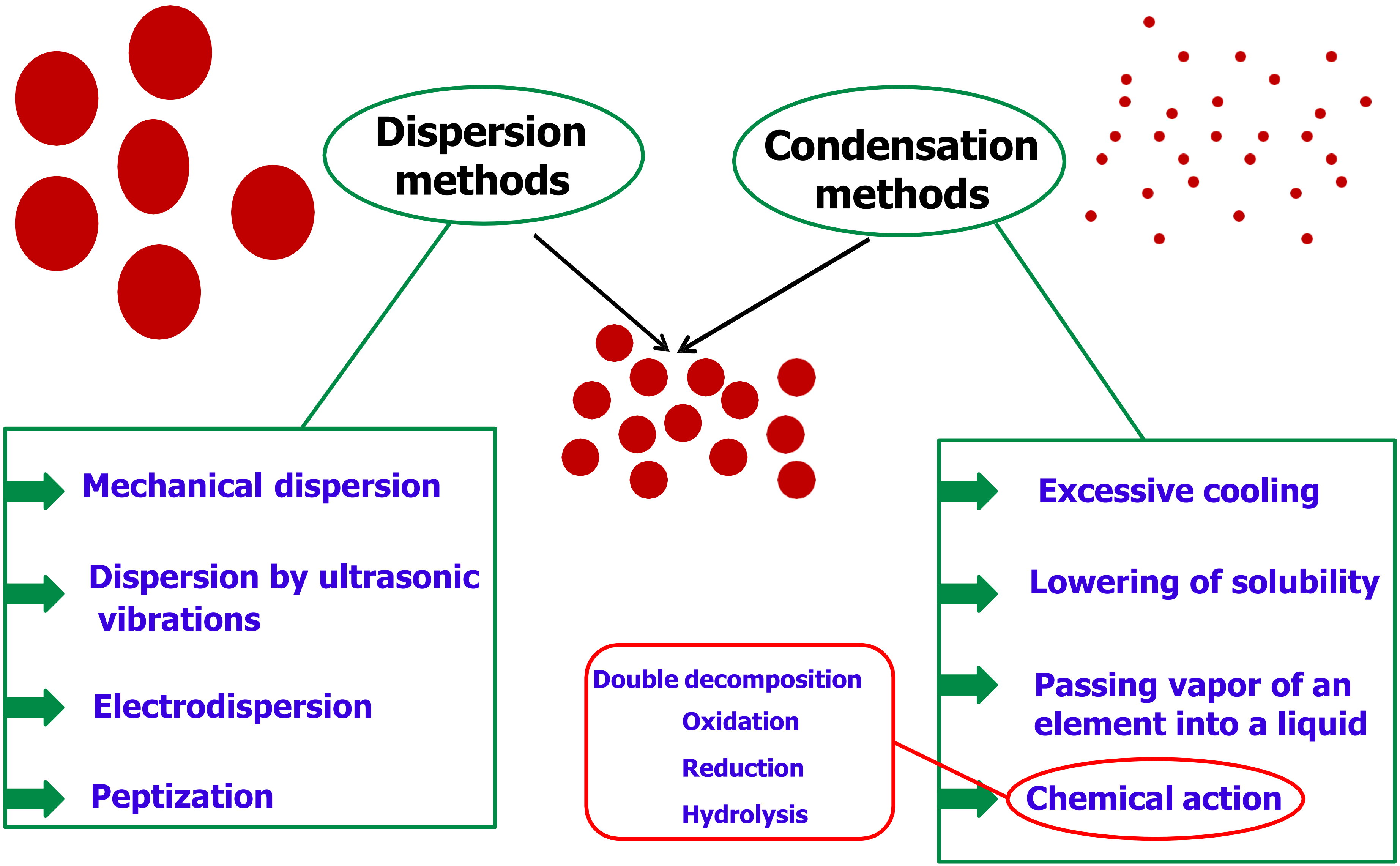
Lyophobic sols

Have to be prepared by special methods. These methods fall into two categories :

Dispersion Methods:in which larger macro-sized particles are broken down to colloidal size.

Aggregation (Condensation) Methods: in which colloidal size particles are built up by aggregating single ions or molecules of true solution

Preparation of colloidal solutions



Dispersion methods

- Mechanical dispersion
- Dispersion by ultrasonic vibrations
- Electrodispersion
- Peptization

Condensation methods

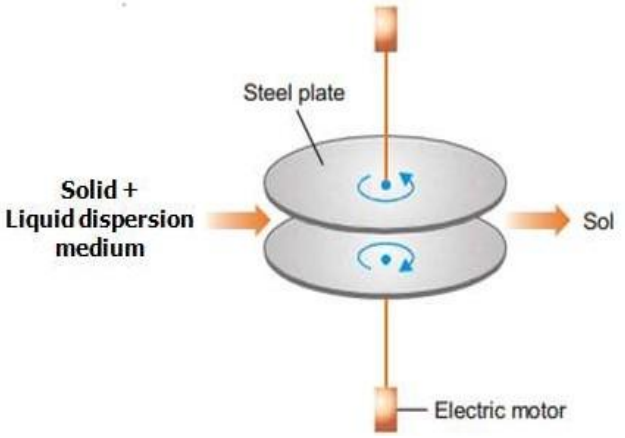
- Excessive cooling
- Lowering of solubility
- Passing vapor of an element into a liquid
- Chemical action

Double decomposition
Oxidation
Reduction
Hydrolysis

A- Dispersion Methods

-1Mechanical dispersion using colloid mill

- The solid along with the liquid dispersion medium is fed into a Colloid disk mill.
- The mill consists of two steel plates nearly touching each other and rotating in opposite directions with high speed.
- The solid particles are ground down to colloidal size and are then dispersed in the liquid to give the sol.
- Colloidal graphite and printing inks are made by this method.

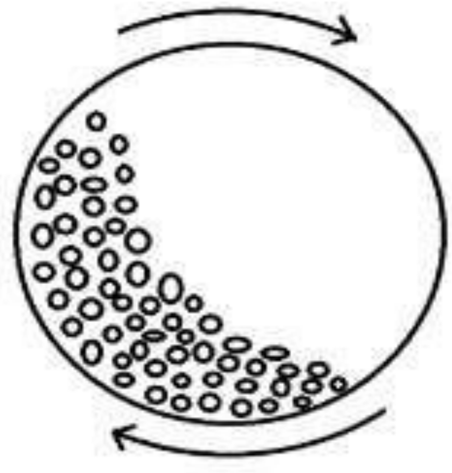


Disk mill

A- Dispersion Methods

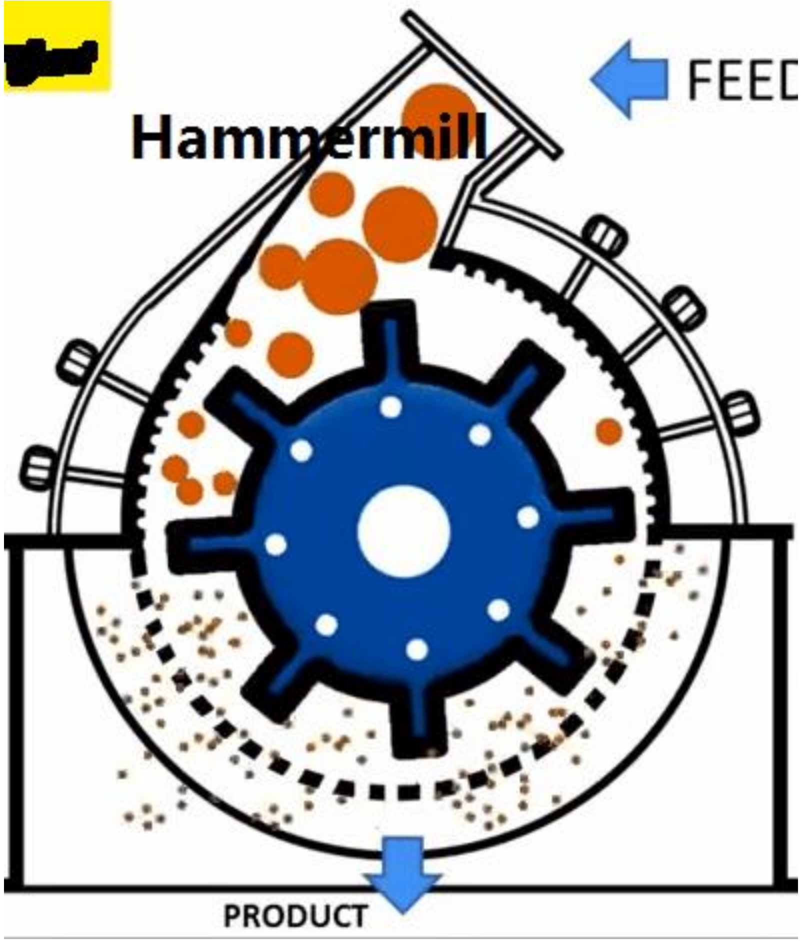
-1Mechanical dispersion using colloid mill

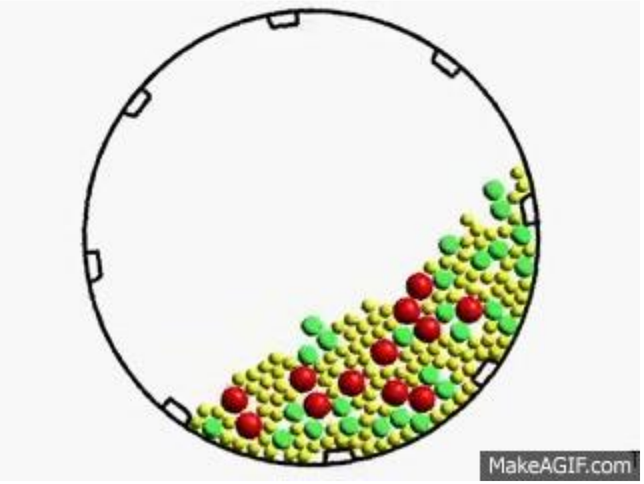
- A colloidal ball mill can also employed to obtain a colloidal solution from suspension .
- Due to the high speed rotation of the mill the coarse particles roll over one another to form fine particles of the colloidal size.



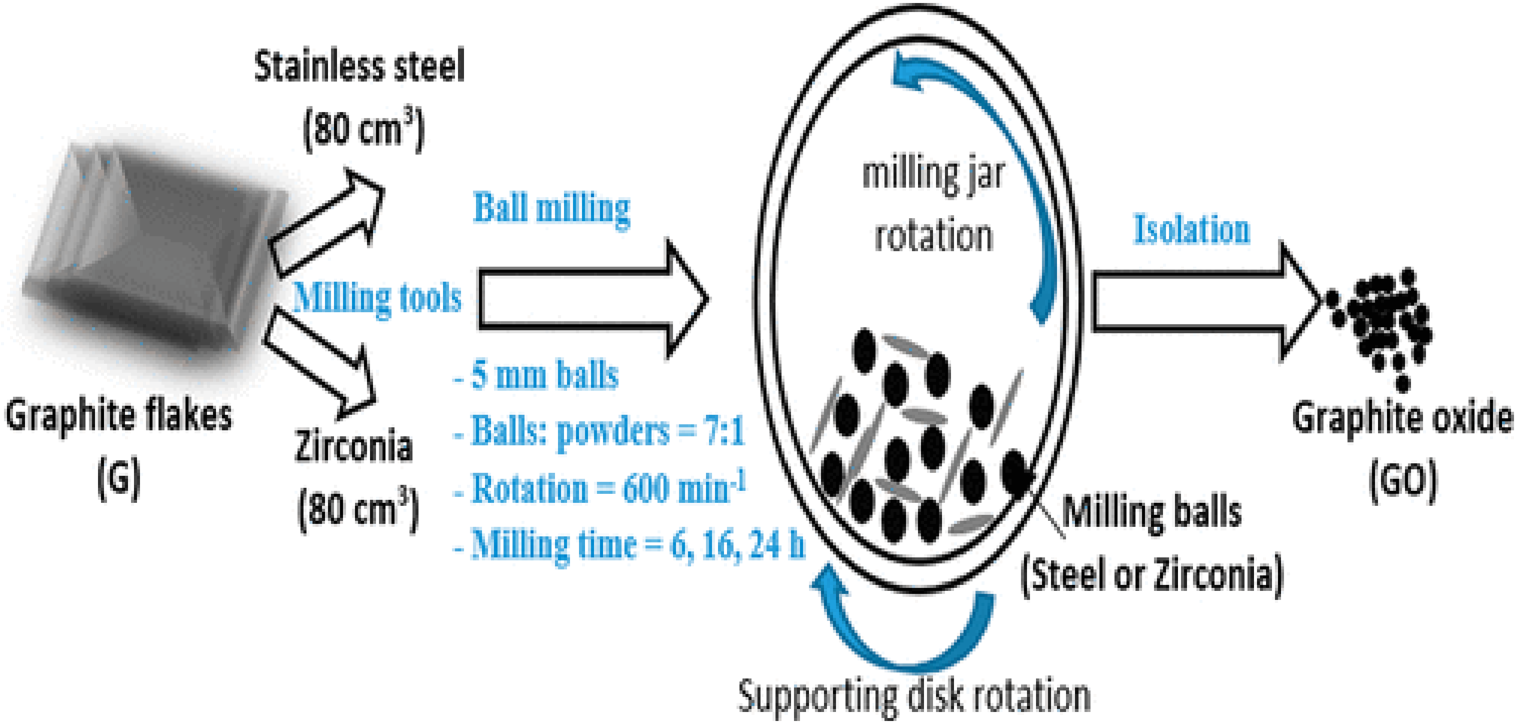
Ball mill

1- Mechanical dispersion using colloid mill





-1Mechanical dispersion using colloid mill



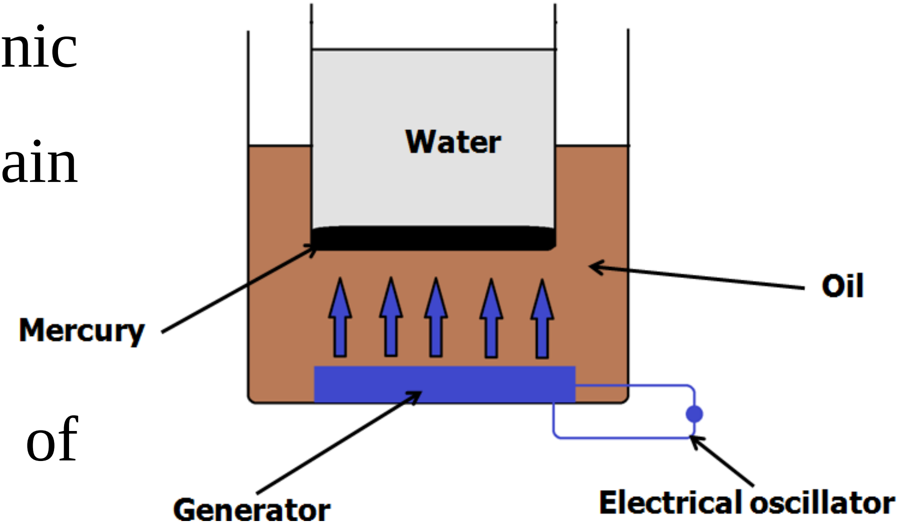
Ref: Sustainable Synthesis of High-Surface-Area Graphite Oxide via Dry Ball Milling, Alaa El Din Mahmoud, Achim Stolle, and Michael Stelter, *ACS Sustainable Chem. Eng.* 2018, 6, 5, 6358–6369.

-2Dispersion by ultrasonic vibrations

- In this case, the transformation of coarse particles to the colloidal size is carried out using the ultrasonic vibrations produced by a certain generator.

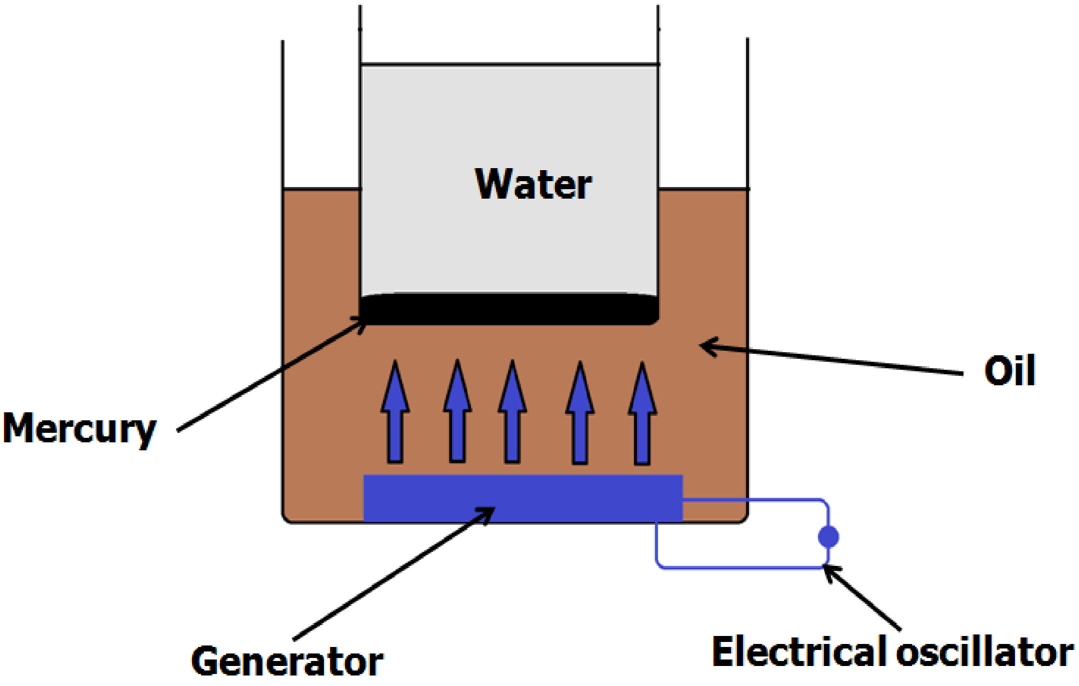
- The figure shows the formation of colloidal solution of mercury in water.

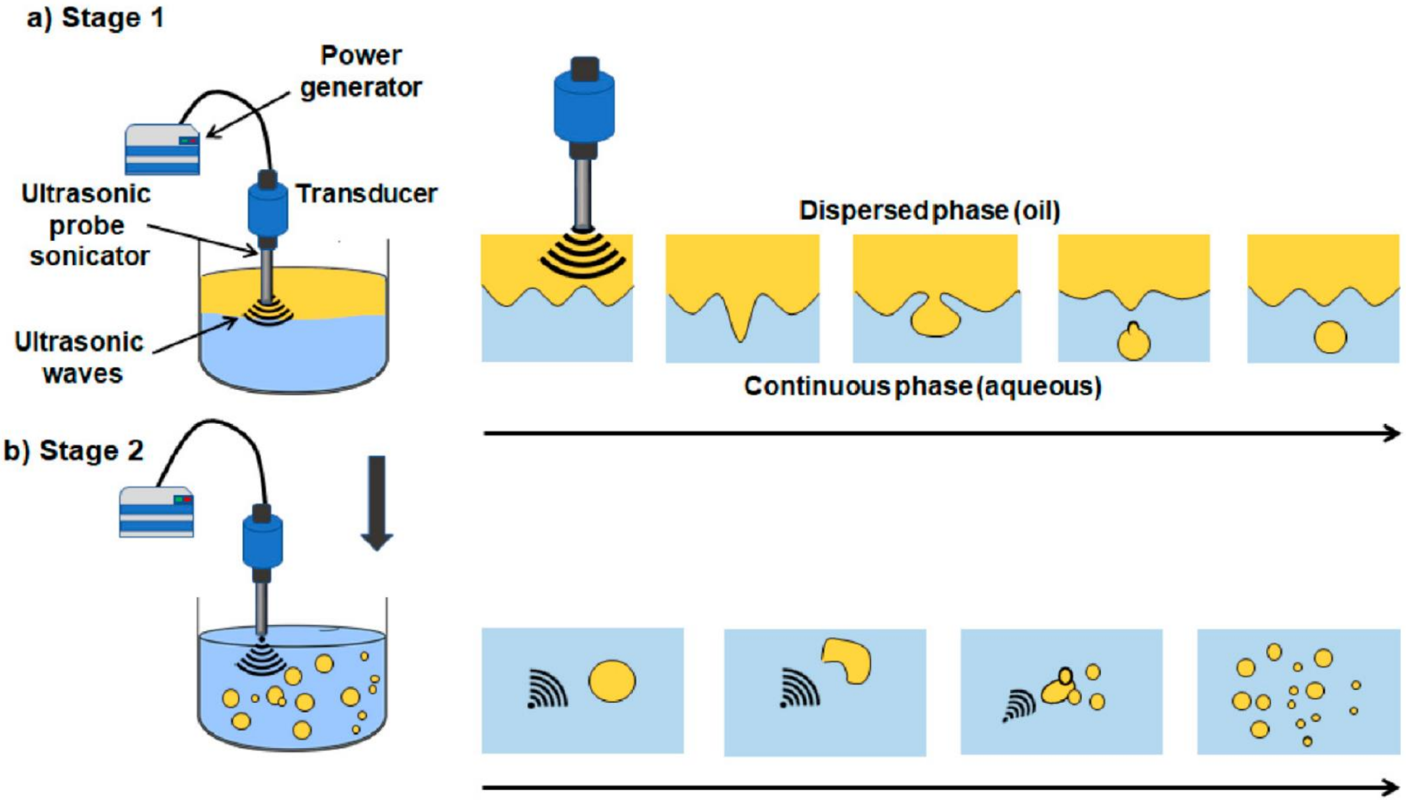
- Ultrasonic vibrations spread through the oil and hit the vessel having mercury under water .



-2Dispersion by ultrasonic vibrations

- The ultrasonic vibrations travels through the walls of the mercury container and produce clouds of mercury which form the mercury sol.





Schematic representation of ultrasonic emulsification.

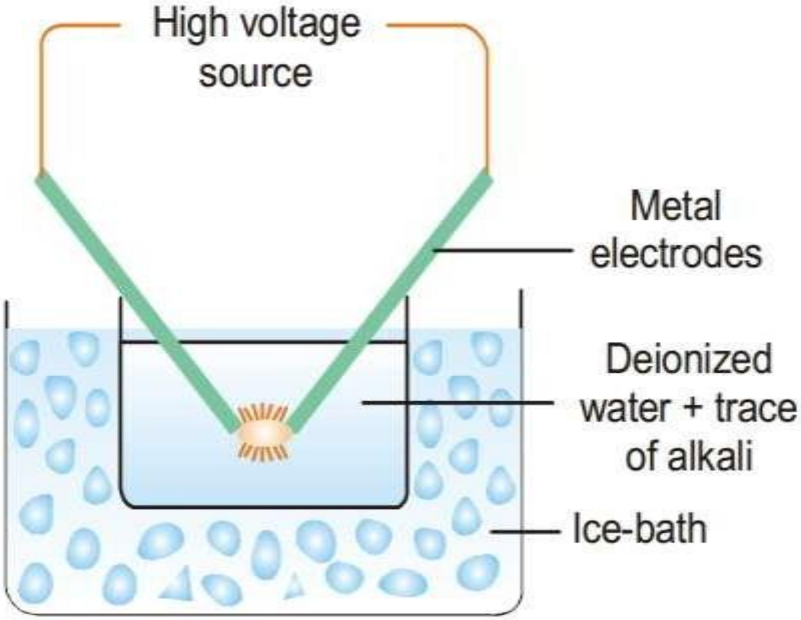
(a) The shear forces generated during acoustic cavitation near the interface between the aqueous phase and oil phase promote the eruption of large oil drops (dispersed phase) in the continuous aqueous phase.

(b) The oil droplets formed in the first stage are reduced to smaller droplets as a consequence of the shock waves generated during cavitation

(adapted from Perdih et al., 2019 and Plüisch and Wittemann, 2016).

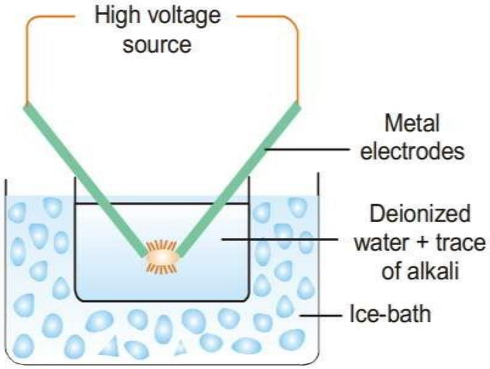
-3Bredig's Arc Method (electrical disintegration)

- It is used for preparing hydrosols of metals e.g., silver, gold and platinum .
- An arc is struck between the two metal electrodes held close together in de- ionized water with trace of alkali .
- The water is kept cold by immersing the container in ice/water bath.
- The intense heat of the spark across the electrodes vaporizes some of the metal and the vapor condenses under water.

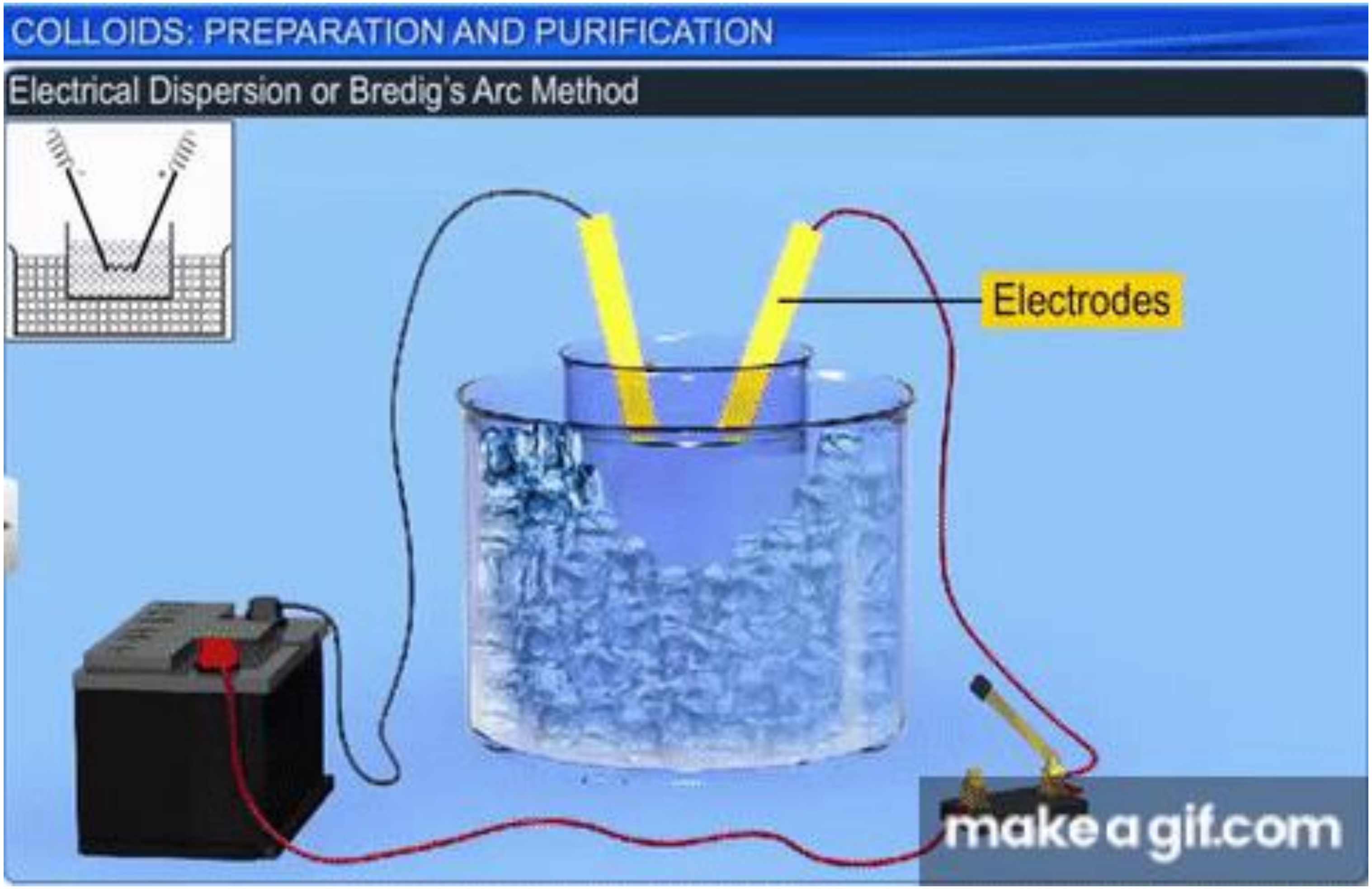


-3Bredig’s Arc Method

- Thus the atoms of the metal present in the vapour aggregate to form colloidal particles in water .
- Since the metal has been ultimately converted into sol particles (via metal vapour), this method has been treated as of dispersion method also.
- Non-metal sols can be made by suspending coarse particles of the substance in the dispersion medium and striking an arc between iron electrodes.
- This method is not suitable when the dispersion medium is an organic liquid as considerable charring occurs.



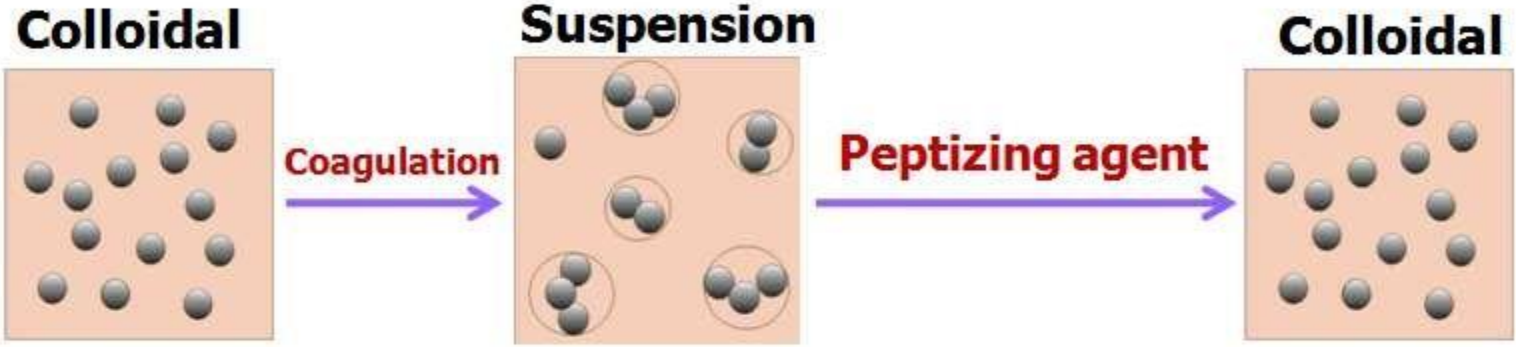
3- Bredig’s Arc Method



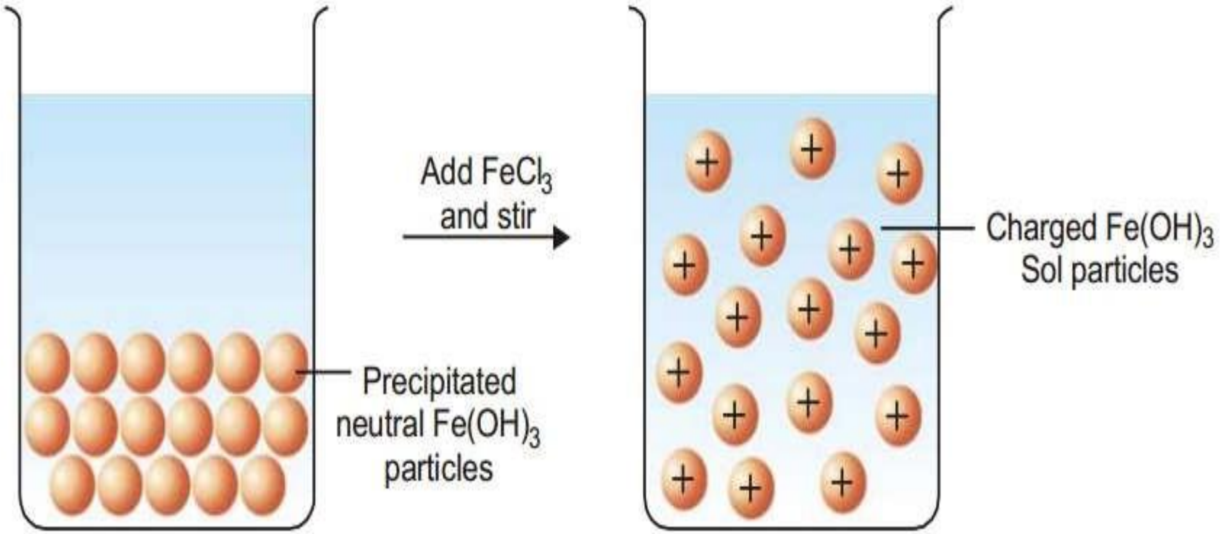
-4Peptization

- Some freshly precipitated ionic solids are dispersed into colloidal solution in water by the addition of small quantities of electrolytes, particularly those containing a common ion .

- The precipitate particles adsorbs the common ions to be electrically charged particles, then split from each other to form colloidal solution.



Sol of ferric hydroxide is obtained by stirring fresh precipitate of ferric hydroxide with a small amount of $FeCl_3$

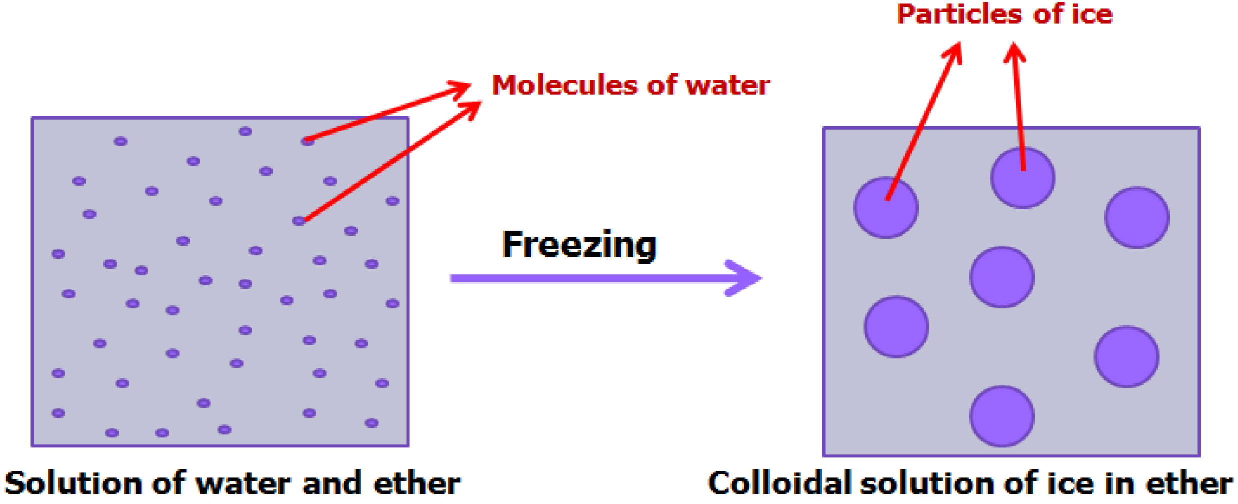


- The transformation of a precipitated material to colloidal solution by the action of an electrolyte in solution, is termed **peptization** which is the reverse of **coagulation** and the electrolyte used is called a peptizing agent.
- Another examples of preparation of sols by peptization is silver chloride, AgCl which can be converted into a sol by adding hydrochloric acid

B- Aggregation Methods

The more important aggregation methods are:

-1Extensive cooling



- The colloidal solution of ice in an organic solvent like ether is obtained by freezing a solution of water in the solvent .
- As a result of the sudden freezing of the solution, the molecules of water held together to form particles in the colloidal size dispersed in the organic solvent (ether(

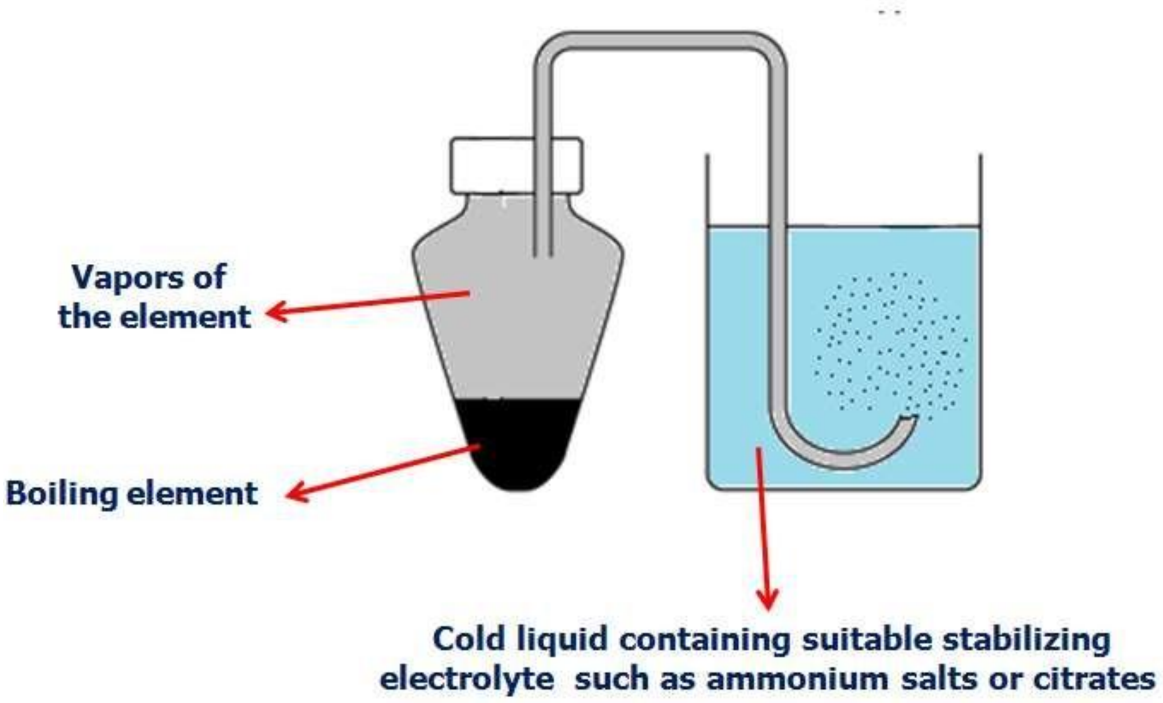
-2Lowering of solubility by exchange of solvent

- Substances like **sulphur**, **phosphorous**, etc., which are more soluble in alcohol than in water give a hydrosol by pouring a small amount of their alcoholic solution in excess of water .

- By the transference from alcohol to water, the substance is transformed from the **molecular state (true solution)** to the **colloidal state** by the coagulation of molecules together to form particles in the colloidal range.

- Phenolphthalein indicator, for example, is soluble in alcohol and not in water, so that, it is supplied to laboratory as alcoholic solution. If water is added to this solution, a milky liquid of colloidal phenolphthalein in water is produced.

-3Passing vapor of an element into a liquid



- If the vapors of a boiling element are conducted into a cold liquid, condensation takes place. Sometimes, this condensation resulted in the formation of a stable sol .
- Mercury and sulphur sols can be prepared by this method.

-4Chemical action

a- Double decomposition

- An arsenic sulphide (As_2S_3) sol is prepared by passing a slow stream of hydrogen sulphide gas through a cold solution of arsenious oxide (As_2O .($_3$

$$As_2O_3 \quad + \quad 3\,H_2S \rightarrow As_2S_{3(\text{yellow sol })} \quad + \; 3\,H_2O$$

- This is continued till the yellow colour of the sol attains maximum intensity.

-4Chemical action

b- Reduction

Silver sols and gold sols can be obtained by treating dilute solutions of silver nitrate or gold chloride with suitable reducing agents

$$AgNO_3 \xrightarrow{\text{Reducing agent}} \text{Ag sol}$$

$$AuCl_3 \xrightarrow{\text{Reducing agent}} \text{Au sol}$$

Reducing agents could be organic reducing agents like tannic acid or formaldehyde or others.

c- Oxidation

A sol of sulphur is produced by passing hydrogen sulphide into a solution of sulphur dioxide.

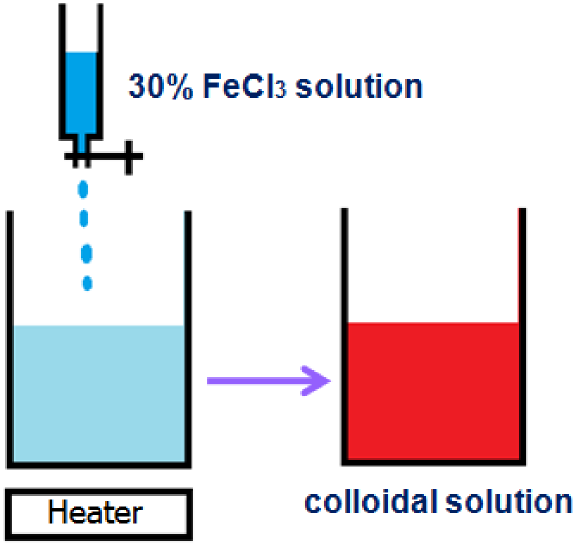
$$2H_2S + SO_2 \longrightarrow 2H_2O + S\downarrow$$

Or exploring H_2S to air for a long time

$$H_2S + O \rightarrow H_2O + S$$

d- Hydrolysis

- Sols of the hydroxides of **iron**, **chromium** and **aluminium** are readily prepared by the hydrolysis of salts of the respective metals .



- In order to obtain a red sol of ferric hydroxide, a few drops of 30% ferric chloride solution is added to a large volume of almost boiling water and stirred with a glass rod.

$$FeCl_3 + 3H_2O \longrightarrow \underset{\text{red sol}}{Fe(OH)_3} + 3HCl$$

Condensation method

Normal crystals are formed in two stages:

1. The Nucleation (formation of crystallization centers) in a supersaturated solution (like in chemical reaction that yields a slightly soluble compound.(
2. The growth of nuclei leading to the formation of sufficiently large crystals.

The nucleation rate (U) can be expressed as:

$$U = K\,(C_{sup} - C_s)/C_s$$

Condensation method

$$U = K\,(C_{sup} - C_s)/C_s$$

Where K is constant

C_{sup} = conc. of supersaturated solution

C_s = conc. of a saturated solution.

$(C_{sup}-C_s)$ is an excess of a substance which is able to form crystals, then can serve as a measure of the rate of liberation from the solution.

Cs can serve a measure of resistance to the liberation (interaction between the solute and solvent).

Condensation method

So, the grater the (C_{sup}-C_s) and the smaller Cs, the more rapidly the nuclei formed and the larger is the no. of crystallization centers, hence the smaller are colloidal particles because the liberated substance will be distributed between a large n. of crystallization centers.