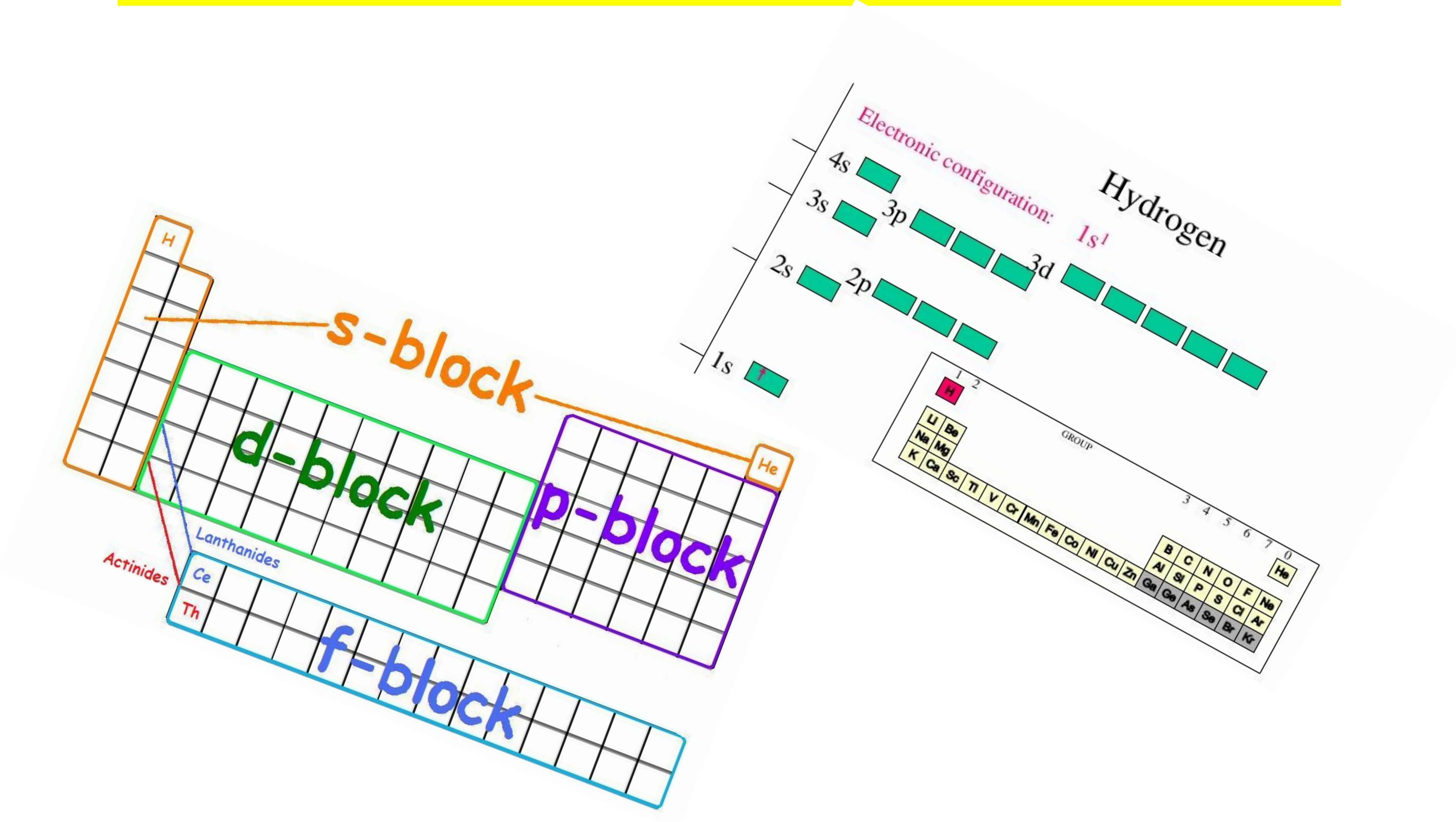
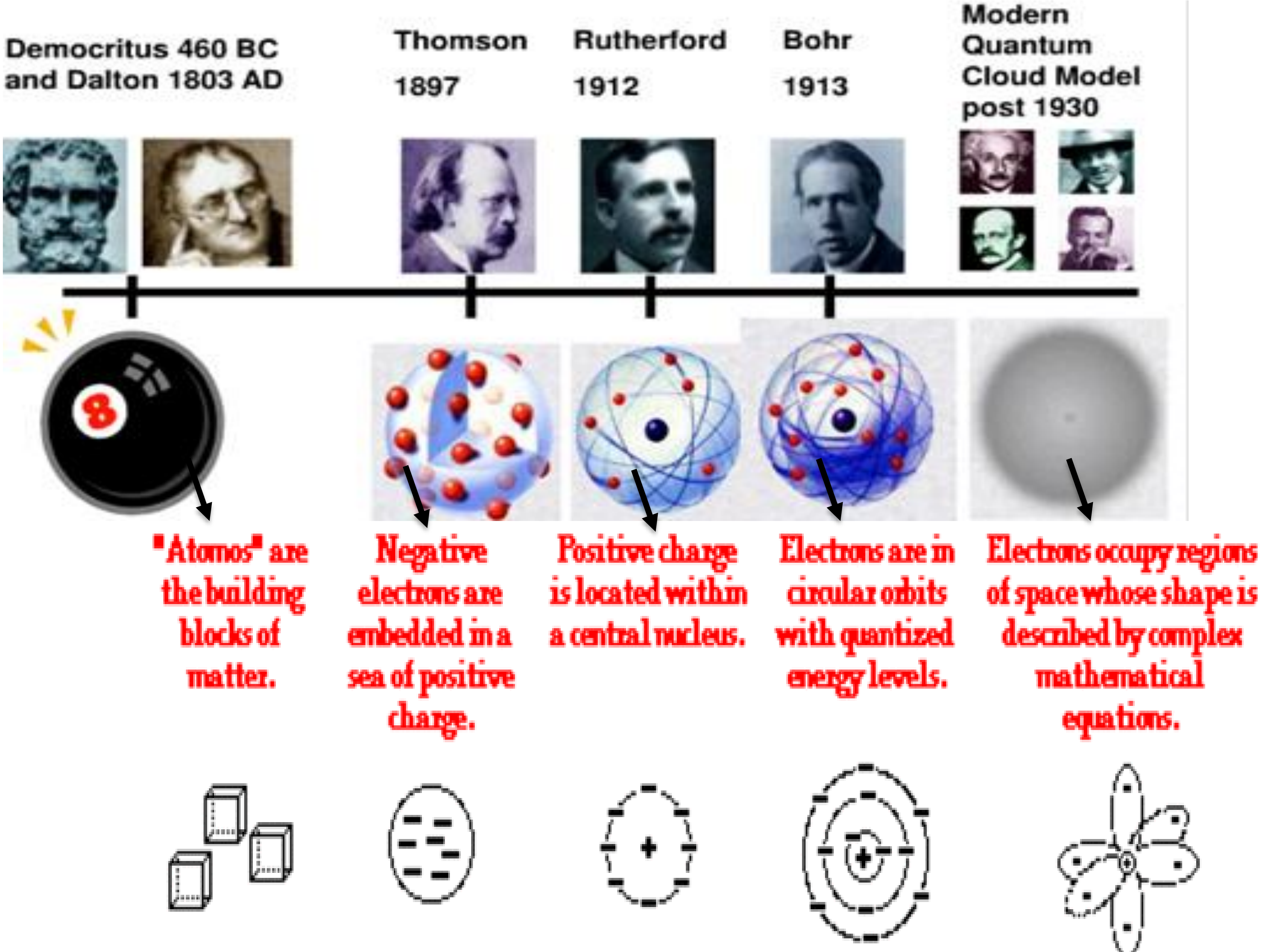
Chapter 1:

An Overview On The Electron Configuration Of Atoms and Ions And The Periodic Table of The Elements



❑ *HISTORICAL DEVELOPMENT OF THE ATOMIC MODEL*



"Atomos" are the building blocks of matter.

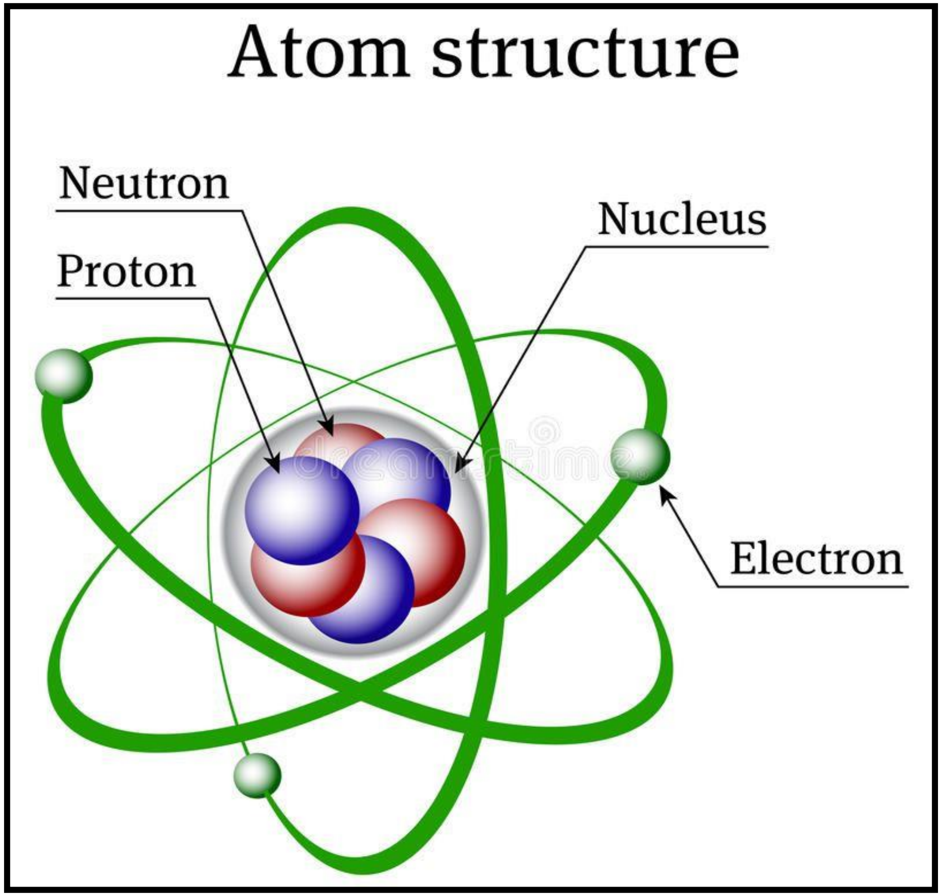
Negative electrons are embedded in a sea of positive charge.

Positive charge is located within a central nucleus.

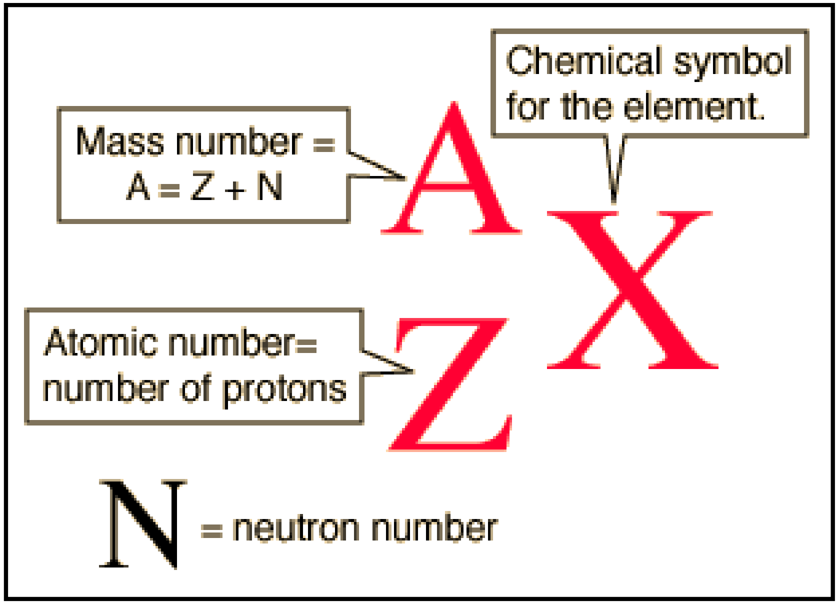
Electrons are in circular orbits with quantized energy levels.

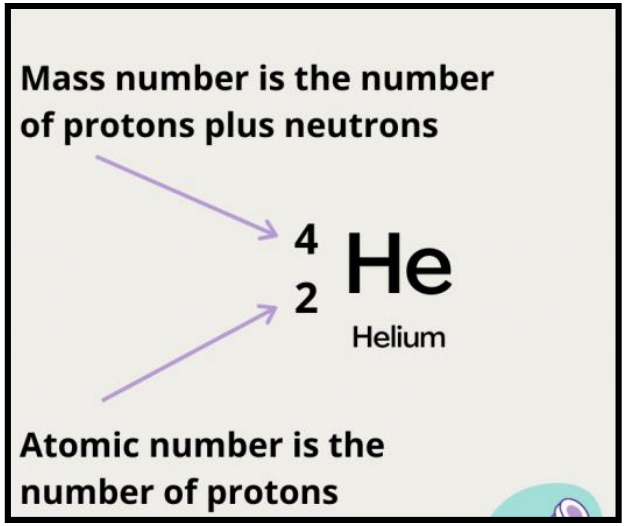
Electrons occupy regions of space whose shape is described by complex mathematical equations.

❑ THE MAIN CONSTITUENTS OF THE ATOM



The nuclear notation




Mass number is the number of protons plus neutrons

Atomic number is the number of protons

Property → Particle ↓	Mass (relative to p)	Charge (relative to p)	Description
Proton p	1.67 x10^{-27} kg 1 amu (u)	+ 1.6 x 10^{-19}C (+1e)	Nucleon (part of nucleus)
Neutron N	1.67 x10^{-27} kg 1 amu (u)	0	Nucleon
Electron e	9.1 x10^{-31} kg 1/1800 amu	- 1.6 x 10^{-19}C (-1e)	Found in a cloud around the nucleus

The atomic mass unit (a.m.u.)

It is defined as $\frac{1}{12}$ th of the mass of one ${}_6C^{12}$ atom

i.e.,

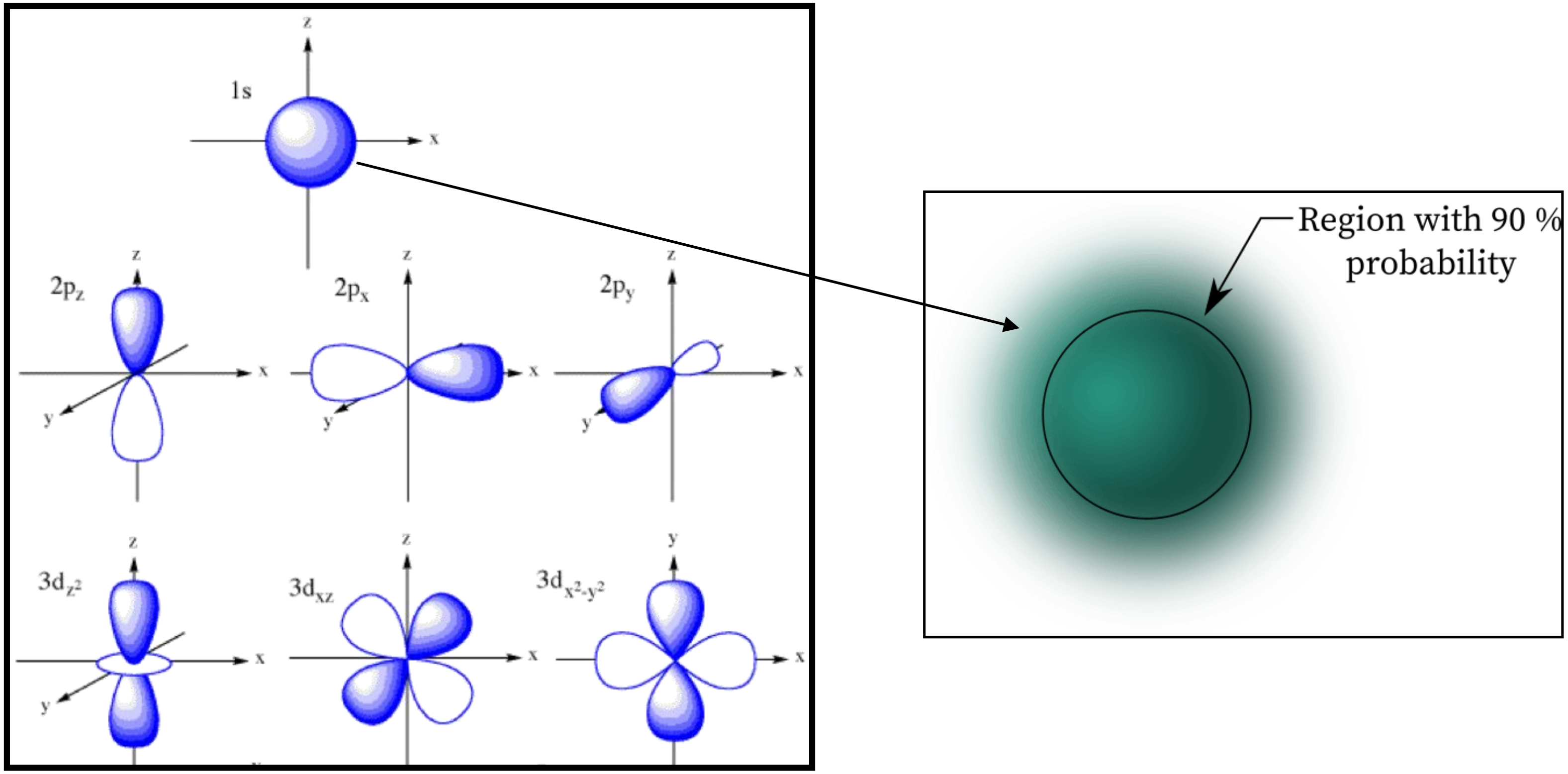
$$1 \text{ a.m.u.} = \frac{1}{12} \times \frac{12}{6.023 \times 10^{23}}$$

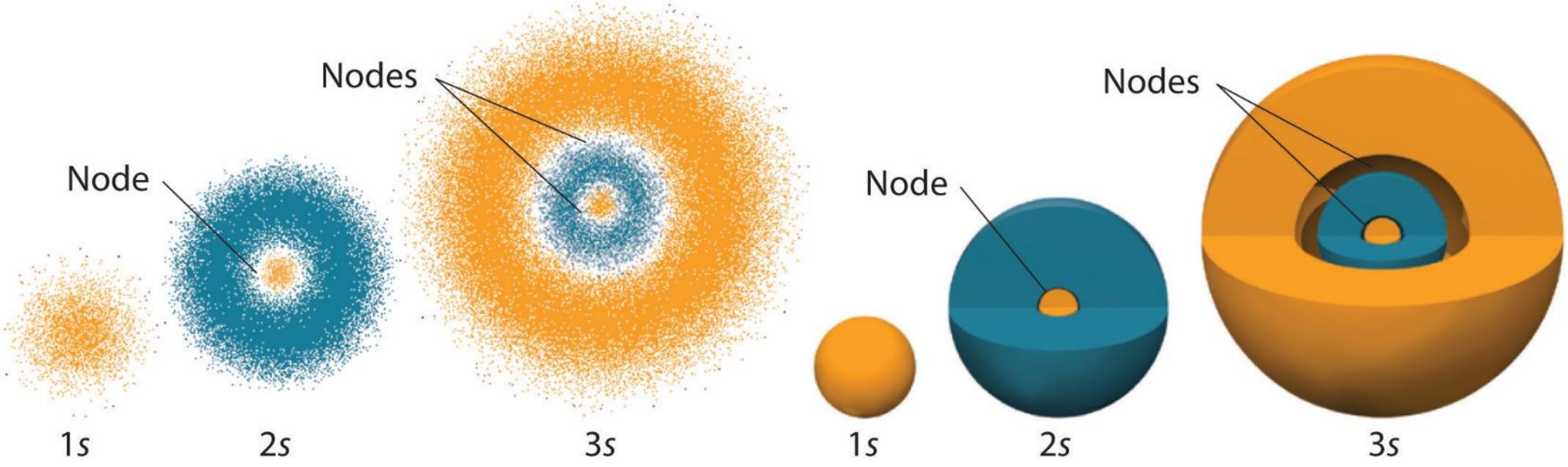
$$= 1.66 \times 10^{-27} \text{ kg.}$$

THE ATOMIC ORBITALS AND THE QUANTUM NUMBERS

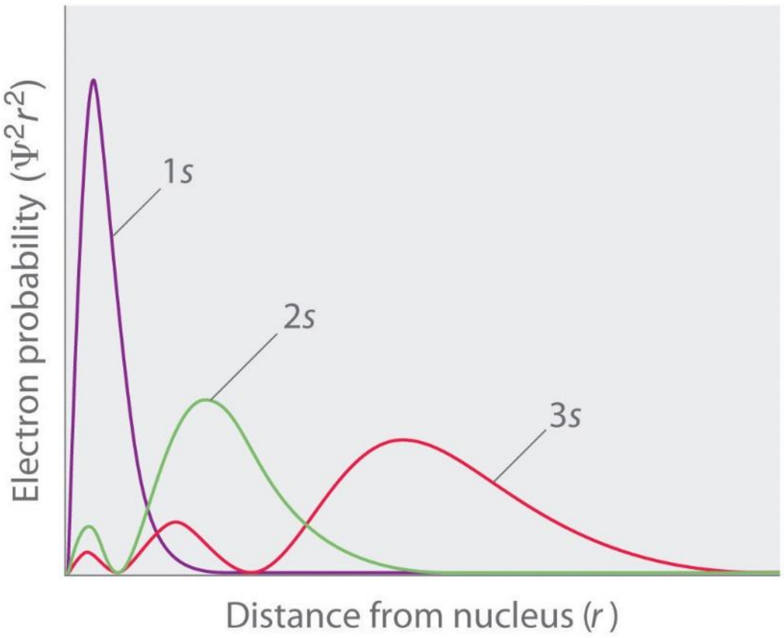
The atomic orbital (AO)

In atomic theory and quantum mechanics, an ***atomic orbital*** is a mathematical function that describes the wave-like behavior of either one electron or a pair of electrons in an atom. This function can be used to calculate ***the probability of finding any electron of an atom in any specific region around the atom's nucleus***.





(a) Electron probability **(b) Contour probability**



(c) Radial probability

- ***The quantum numbers***

Quantum mechanics have proven that the state of electron in an atom is fully described by ***4 different numbers called quantum numbers*** noted as:

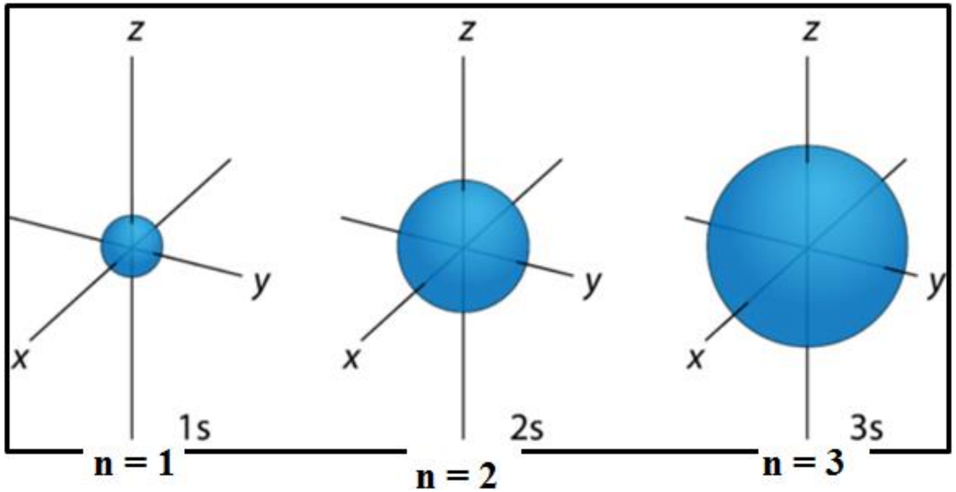
$\boldsymbol{n}$ $\boldsymbol{\ell}$ $\mathbf{m}_{\ell}$ $\mathbf{m}_{s}$

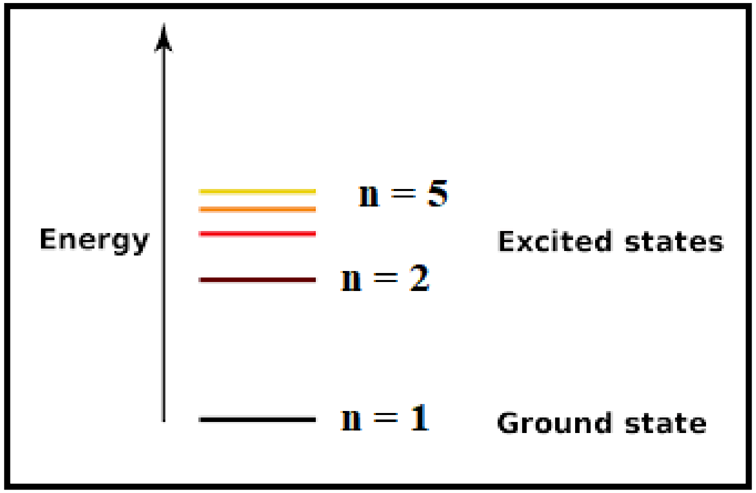
** The first three quantum numbers (n, ℓ, m_{ℓ}) specify the particular orbital's and the fourth quantum number (m_s) specifies the orientation of electrons spin around their own axes.

The Principal quantum number (n)

*The principal quantum number (**n**) specifies the **size** and quantifies the **energy** of an electron in a given of the orbital*. ***n is integer:*** ***n = 1, 2, 3,…∞***

*** the **size** and the **energy*** increase with increasing ***n***.





The angular momentum (or secondary) quantum number (ℓ)

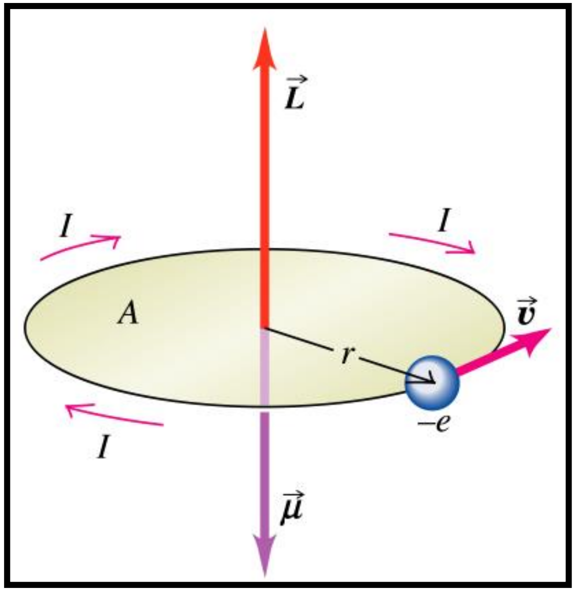
The *secondary quantum number* (**ℓ**) takes integer values:

$$\ell = 0, \quad 1, \quad 2, \quad 3, \ldots, (n-1)$$

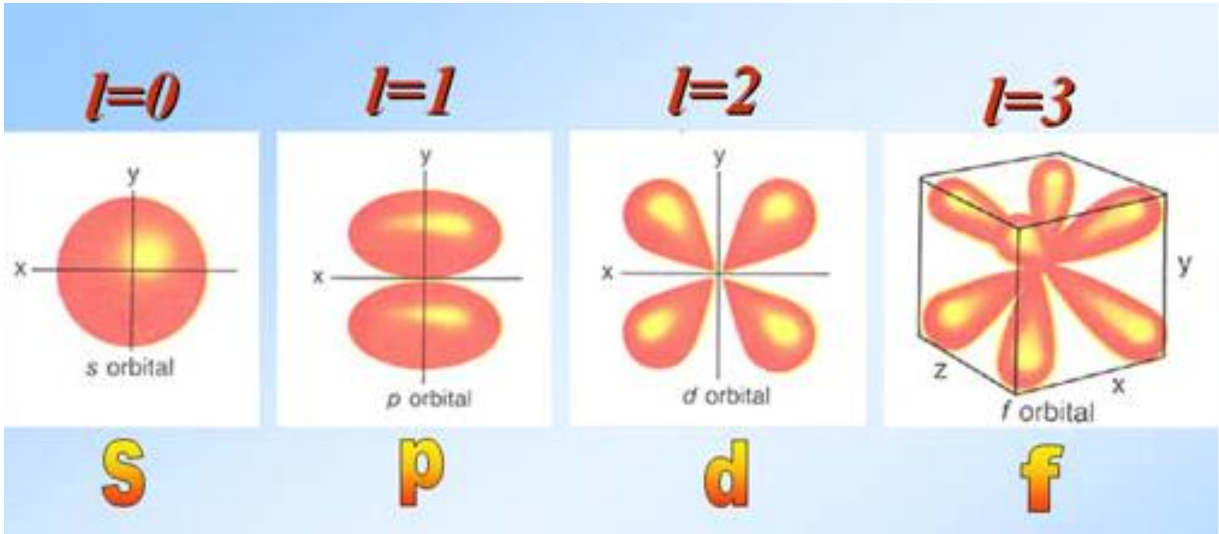
Usually, a small letter code is used to identify **ℓ** in order to avoid confusion with the principal quantum number, *n*.

ℓ	0	1	2	3
Letter code	**s**	**p**	**d**	**f**

*The Secondary quantum number (**ℓ**) quantifies the ***angular momentum*** of an electron in his motion around the nucleus.



It also specifies the ***shape* of an orbital at particular principal quantum number.

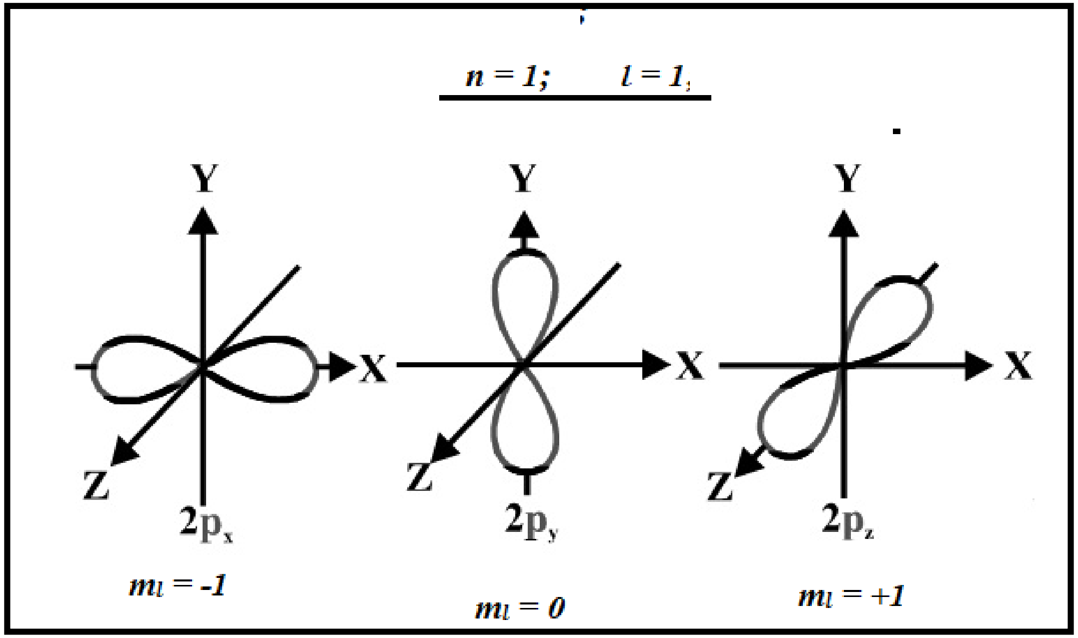


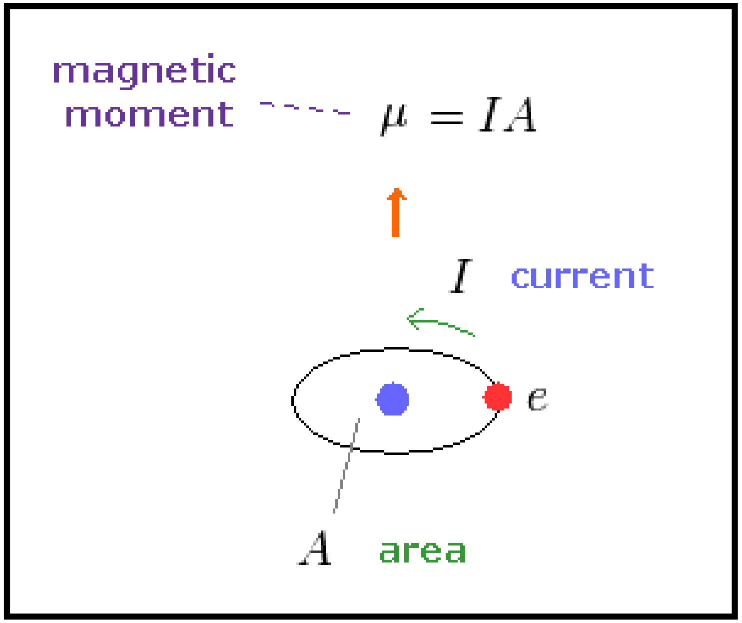
*The secondary quantum number divides the shells into smaller groups of orbitals called <u>*sub-shells*</u>.

n	**1**	**2**		**3**			**4**			
ℓ	0	0	1	0	1	2	0	1	2	3
Sub-shell notation	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f
Number of Sub-shells	1	2		3			4			

The magnetic quantum number (m_ℓ)

The magnetic quantum number (m_ℓ) *specifies the* ***<u>orientation</u>*** *of an orbital of a given energy (n) and shape (ℓ).*
It quantifies also the ***<u>magnitude of magnetic momentum</u>*** *of an electron in an atomic orbital in its motion around the nucleus.*





*For a given **ℓ**, the magnetic quantum number (m_ℓ) takes the values:

$$\mathbf{m_\ell} = -\ell, \ldots\ldots, 0, \ldots\ldots, +\ell.$$

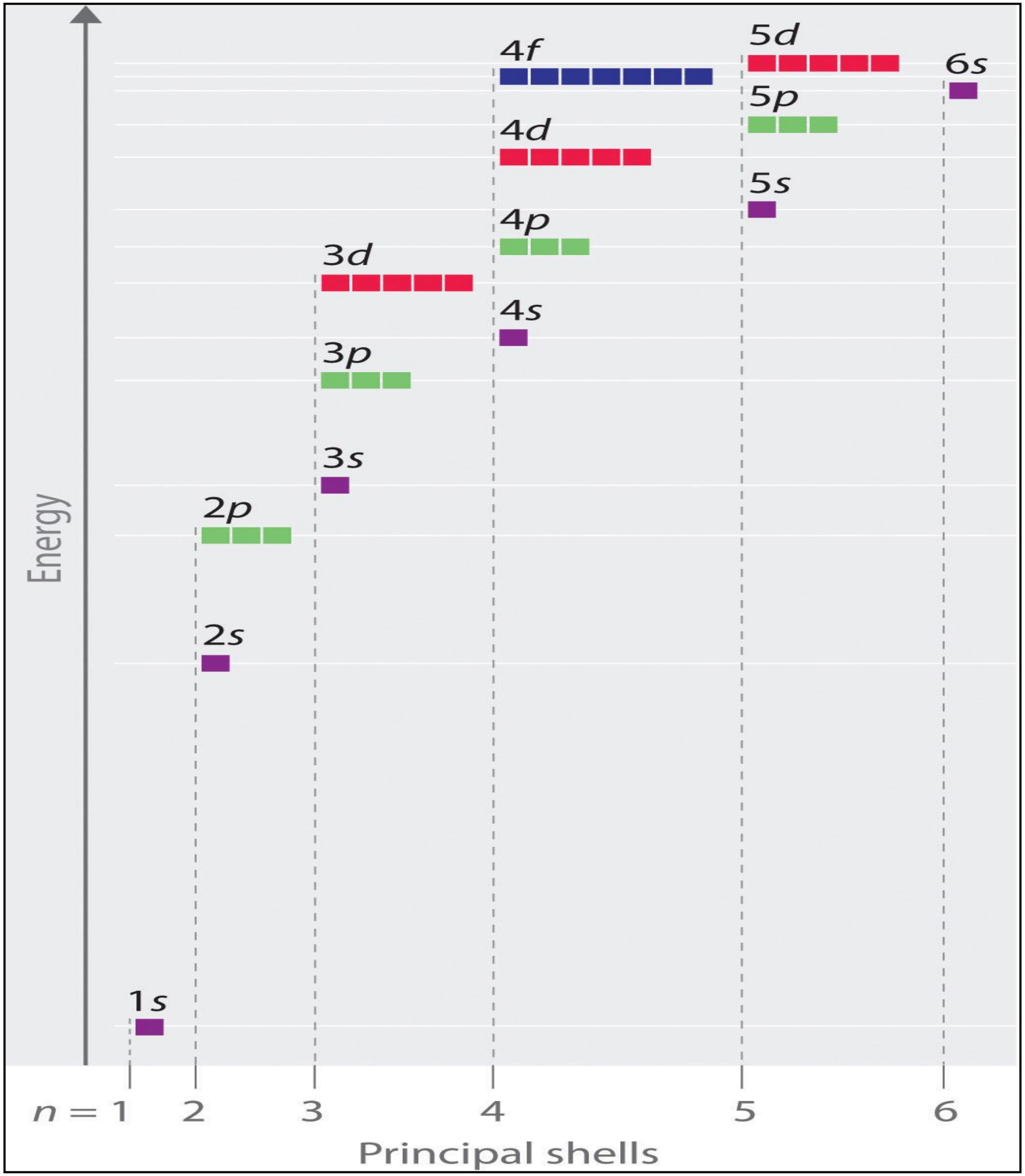
**This number $\mathbf{m_\ell}$ divides the subshell into <u>individual orbitals</u> in which electrons reside.

***There are (2ℓ+1) orbitals in each subshell.

For example the subshell p (ℓ = 1) consists of (2*1+1) orbitals = 3 orbitals

n	Possible values of ℓ	Subshell designation	Possible values of m_ℓ	Number of orbitals in a subs-hell	Total Number of atomic orbitals in a shell
1	0	1s	0	1	1
2	0	2s	0	1	4
	1	2p	-1, 0, 1	3	
3	0	3s	0	1	9
	1	3p	-1, 0, 1	3	
	2	3d	-2, -1, 0, 1, 2	5	
4	0	4s	0	1	16
	1	4p	-1, 0, 1	3	
	2	4d	-2, -1, 0, 1, 2	5	
	3	4f	-3, -2, -1, 0, 1, 2, 3	7	

Note. *For a given shell (energy Level **n**), the number of orbitals is equal to* $\underline{n}^2$

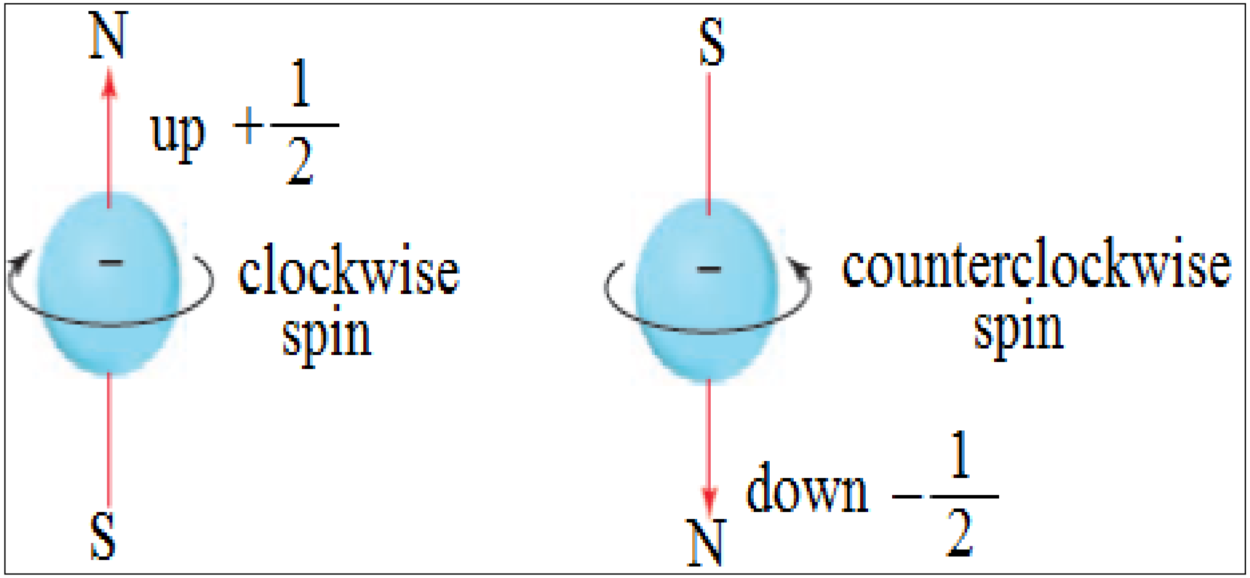

Energy
1s
2s
2p
3s
3p
3d
4s
4p
4d
4f
5s
5p
5d
6s
n = 1
2
3
4
5
6
Principal shells

The spin quantum number (*m_s*)

The ***spin quantum number*** (***m_s***) takes only 2 values:

$$m_s = +1/2 \text{ or } -1/2.$$

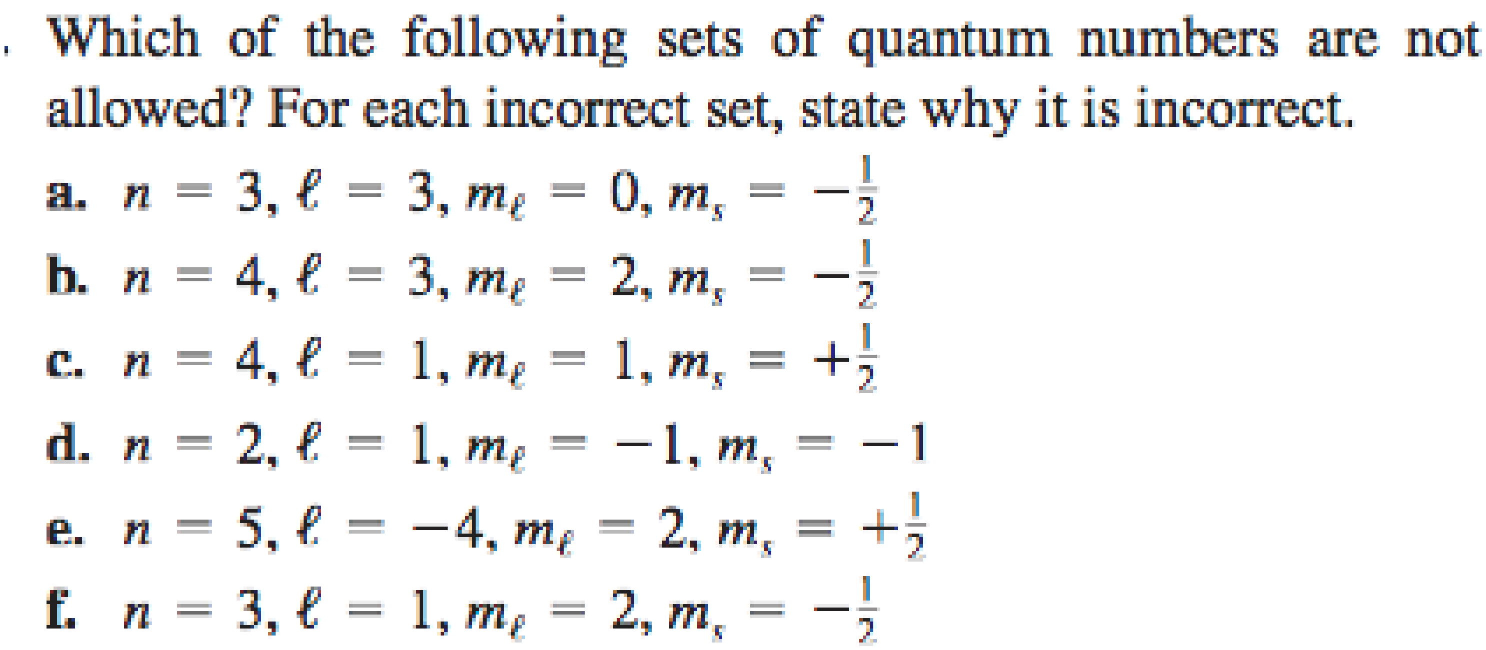
** It specifies the ***orientation*** of the spin axes of an electron and it quantifies the ***magnitude of magnetic momentum*** of the electron when spinning around its own axis.



** Electrons act like tiny magnets, if electrons are thought of as spinning on their own axes, as Earth does.

** The two possible spinning motions of an electron, one clockwise (up) and the other counterclockwise (down).

Exercise :



Which of the following sets of quantum numbers are not allowed? For each incorrect set, state why it is incorrect.

a. $n = 3, \ell = 3, m_\ell = 0, m_s = -\frac{1}{2}$

b. $n = 4, \ell = 3, m_\ell = 2, m_s = -\frac{1}{2}$

c. $n = 4, \ell = 1, m_\ell = 1, m_s = +\frac{1}{2}$

d. $n = 2, \ell = 1, m_\ell = -1, m_s = -1$

e. $n = 5, \ell = -4, m_\ell = 2, m_s = +\frac{1}{2}$

f. $n = 3, \ell = 1, m_\ell = 2, m_s = -\frac{1}{2}$

Answer :

The incorrect sets of quantum numbers are:

a. *Because* ℓ *should be less than n*

e. *Because* ℓ *is an integer and can't be negative*

f. *Because* $\mathbf{m}_\ell$ *can't be larger than* ℓ

❑ *THE ELECTRON CONFIGURATION OF ATOMS*

The distribution of electrons among the atomic orbitals is called electron configuration (or electron structure).

When assigning electrons to orbitals, we must follow a set of

three **rules**:

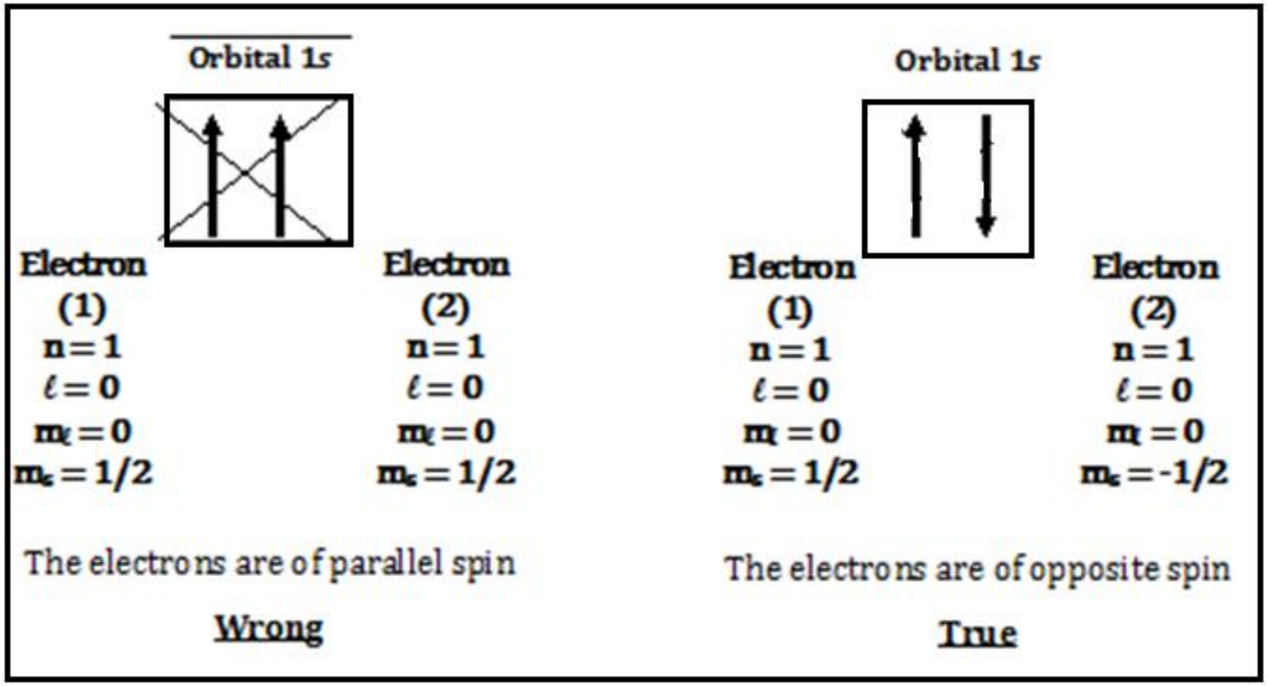
- ❑ the Pauli-Exclusion Principle
- ❑ the Hund's Rule
- ❑ the Aufbau Principle

The Pauli exclusion principale

The principle states that **No** two electrons can have the same **four** quantum numbers.

*It is important to note that according to Pauli principle, an orbital can at maximum hold 2 electrons with opposite spins, if one electron has $m_s = ½$, the second must has $m_s = -½$. The two electrons are said to have opposite spin or also said paired electrons.

**The maximum number of electrons in each shell and subshell is given in the table below.



The maximum number of electrons in each atomic shell and subshell

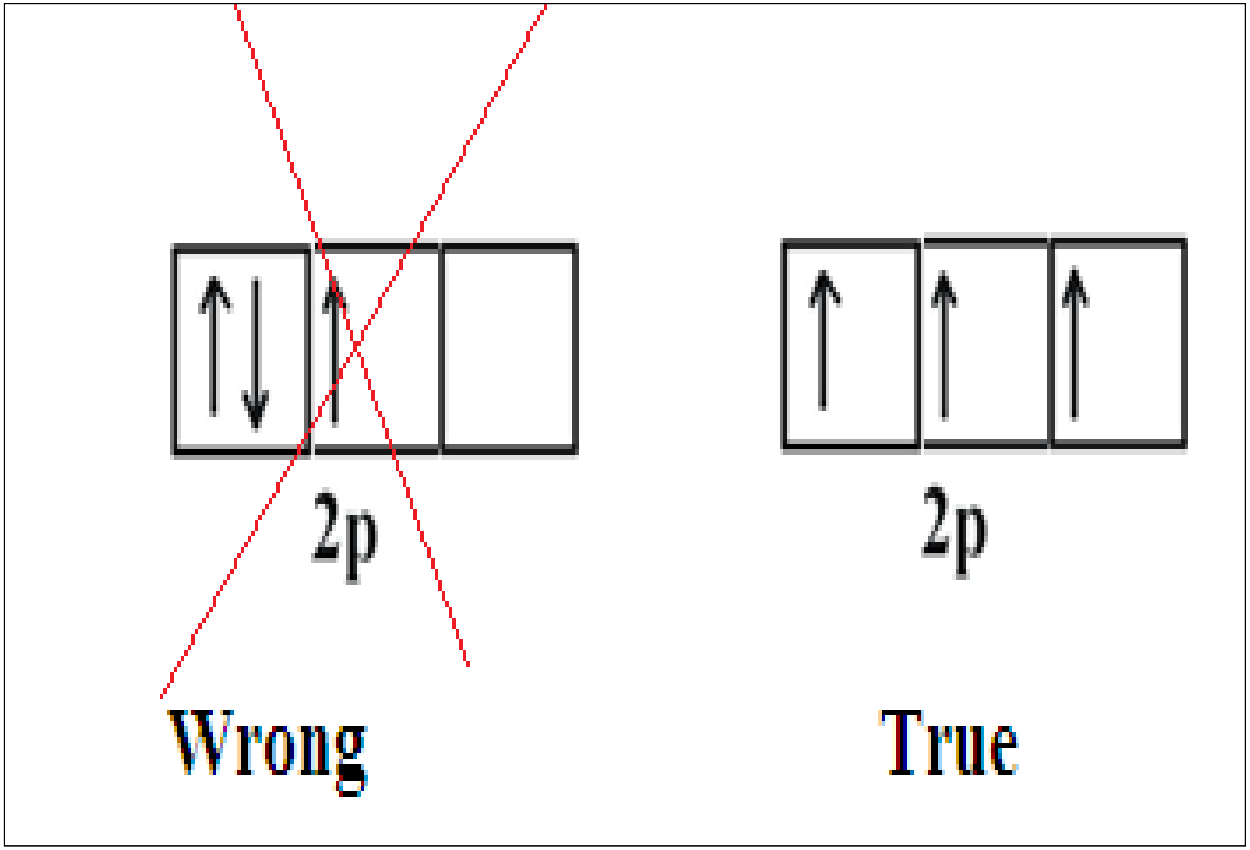
Shell	Subshell	Max electrons in a subshell	Max electrons in a shell
K (n = 1)	1s	2	2
L (n = 2)	2s	2	6 + 2 = 8
	2p	6	
M (n = 3)	3s	2	2 + 6 + 10 = 18
	3p	6	
	3d	10	
N (n = 4)	4s	2	2 + 6 + 10 + 14 = 32
	4p	6	
	4d	10	
	4f	14	

*** For a given shell (n), the number of electrons is equal to* $\boldsymbol{2n^2}$

❑ The Hund’s rule

Hund’s rule states that: when two or more orbitals of equal energy are available, electrons enter first **singly** with **parallel** spins.

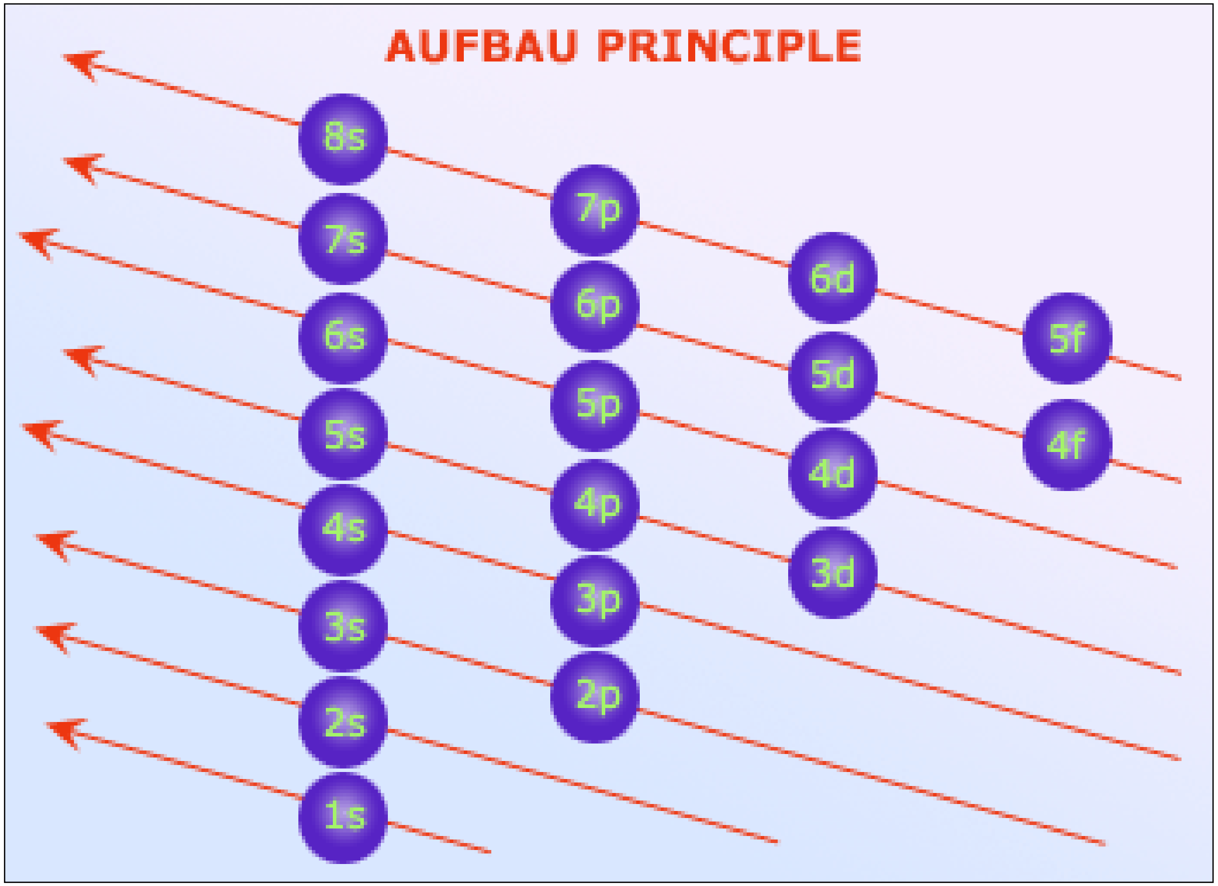
In other words, every orbital in a sublevel is singly occupied before any orbital is doubly occupied.



❑ The Aufbau principle

The atomic orbitals are filled in according to a scheme diagram known as Aufbau principle (‘’building up”) which corresponds (generally) to ***increasing energy*** of the subshells:

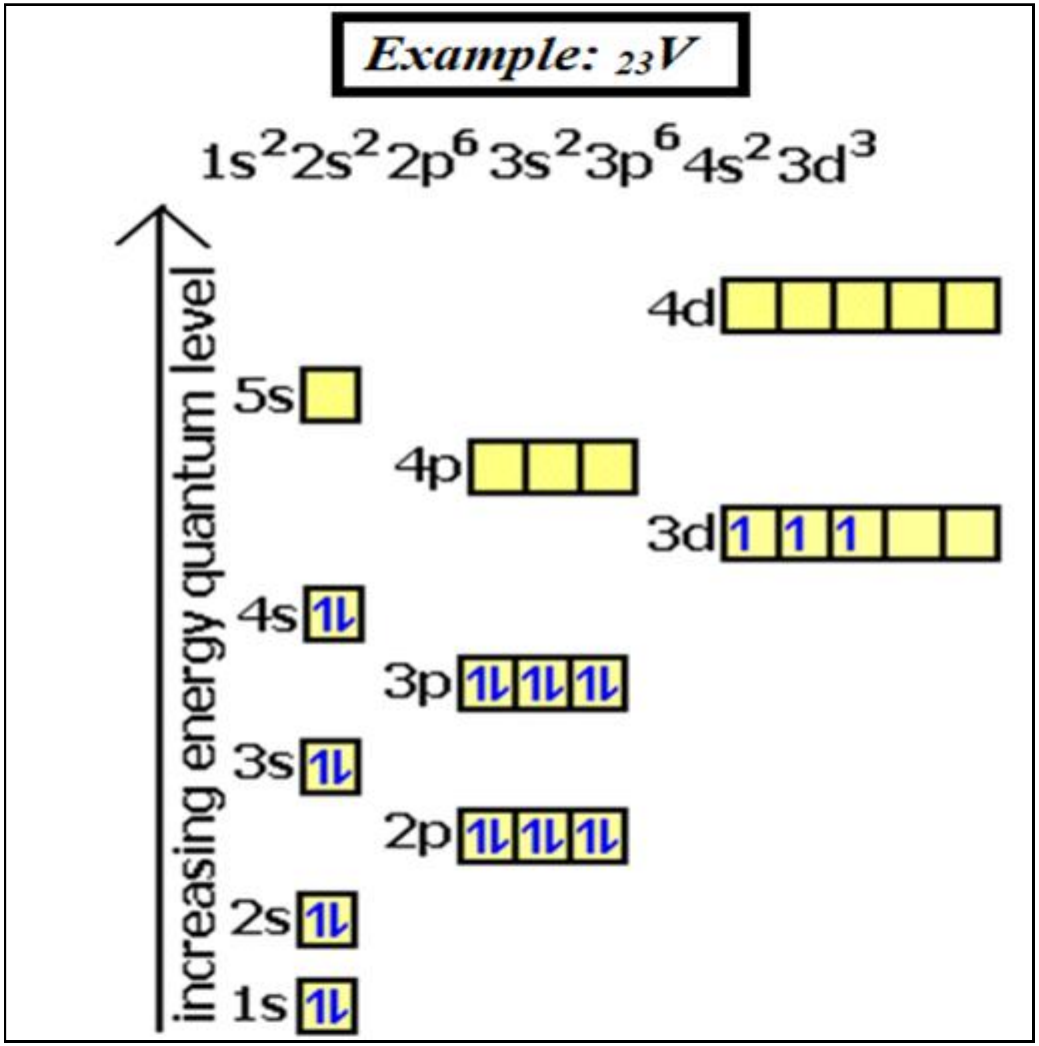
1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p…….etc

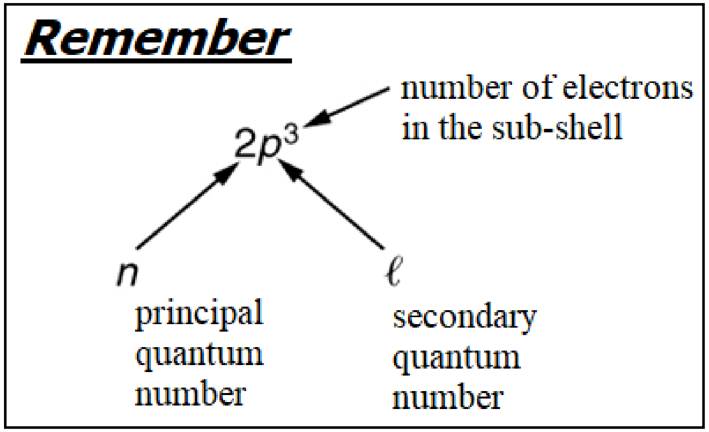


Writing the electron configuration of atoms

The atomic orbitals are filled in according to the three rules cited above for assigning electron orbitals given above. The order of filling is the following:

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ 6s^2\ 4f^{14}\ 5d^{10}\ 6p,...$

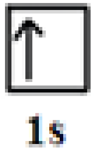
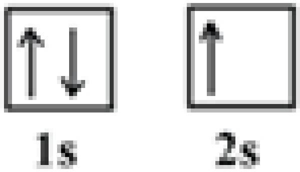
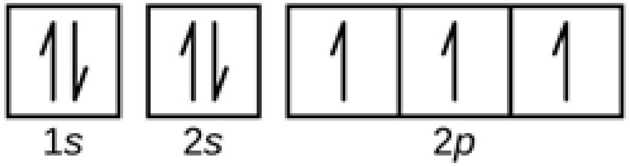
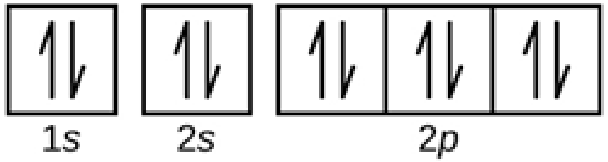


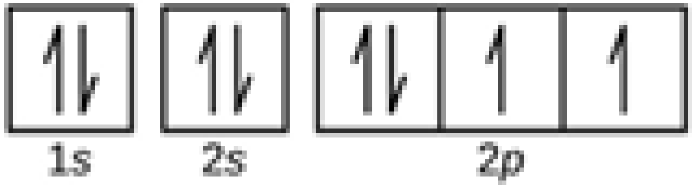
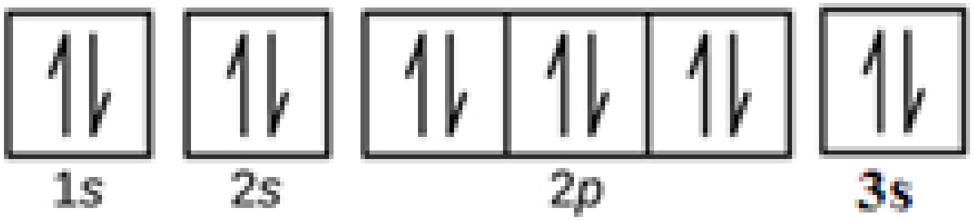
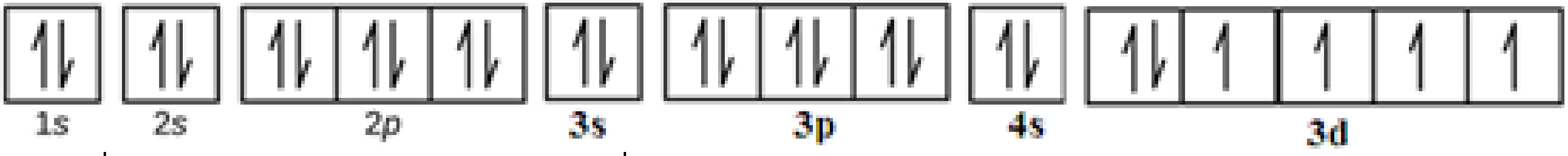


Exercise :

Write the electron configuration (*in spdf notation and orbital box diagram notation*) for the following atoms: $_{1}H$, $_{3}Li$, $_{7}N$, $_{10}Ne$, $_{8}O$, $_{12}Mg$, $_{26}Fe$

Answer :

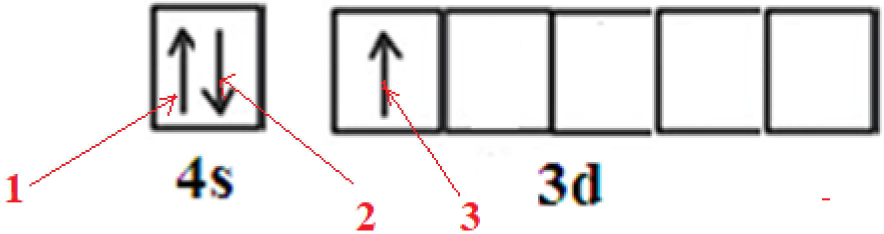
Atom	***spdf notation***	***Orbital box diagram notation***
$_{1}\mathbf{H}$	$1s^1$	
$_{3}\mathbf{Li}$	$1s^22s^1$	
$_{7}\mathbf{N}$	$1s^22s^22p^3$	
$_{10}\mathbf{Ne}$	$1s^22s^22p^6$	

$_{8}\mathrm{O}$	**$1s^22s^22p^4$**	
$_{12}\mathrm{Mg}$	$1s^22s^22p^63s^2$	
$_{26}\mathrm{Fe}$	$1s^22s^22p^63s^23p^64s^23d^6$	

Exercise :

Assign the four quantum numbers for the following electrons:

Answer :



	n	ℓ	m_ℓ	m_s
Electron 1	4	0	0	+1/2
Electron 2	4	0	0	-1/2
Electron 3	3	2	-2	+1/2

Exceptions to Aufbau principle

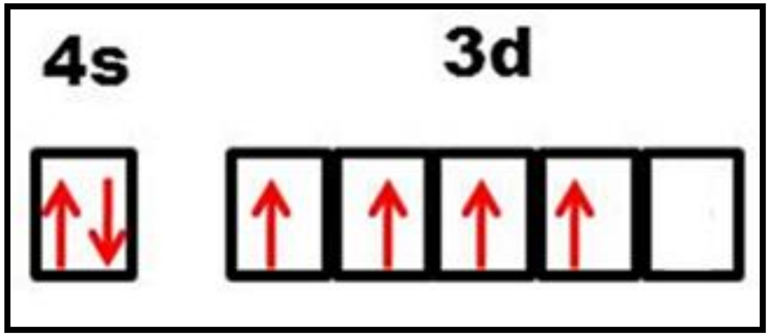
Although the Aufbau principle accurately predicts the electron configuration of most elements, there are ***notable exceptions*** among the transition metals (*d*-block) and heavier elements (*f*-block: The lanthanides and the actinides). The reason for these exceptions occur is that some elements are more stable with fewer electrons in some subshells and half or complete filled subshells by electrons.

Two Examples of exceptions: Chromium and Copper

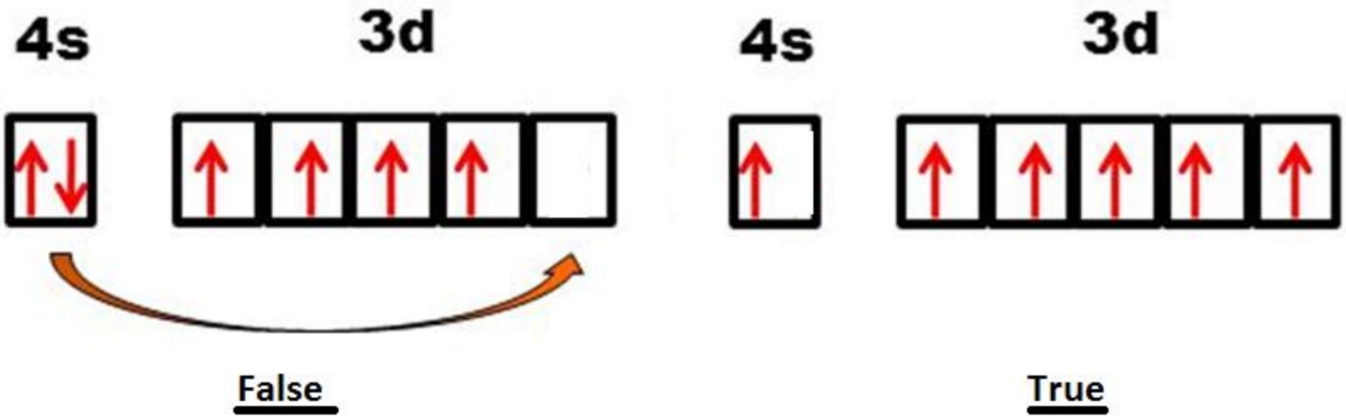
** **Chromium**: $_{24}Cr$

The expected electron configuration according to Aufbau rule is:

$1s^2 2s^2 2p^6 3s^2 3p^6 \underline{\mathbf{4s^2 3d^4}}$ **(False)**



The above electron configuration is in fact false; it should be corrected by taking an electron from $4s^2$ and putting it in the orbital $3d^4$.



The last orbital d is more stable when it is half filled, i.e. filled with 5 electrons.

The true electron configuration is therefore:

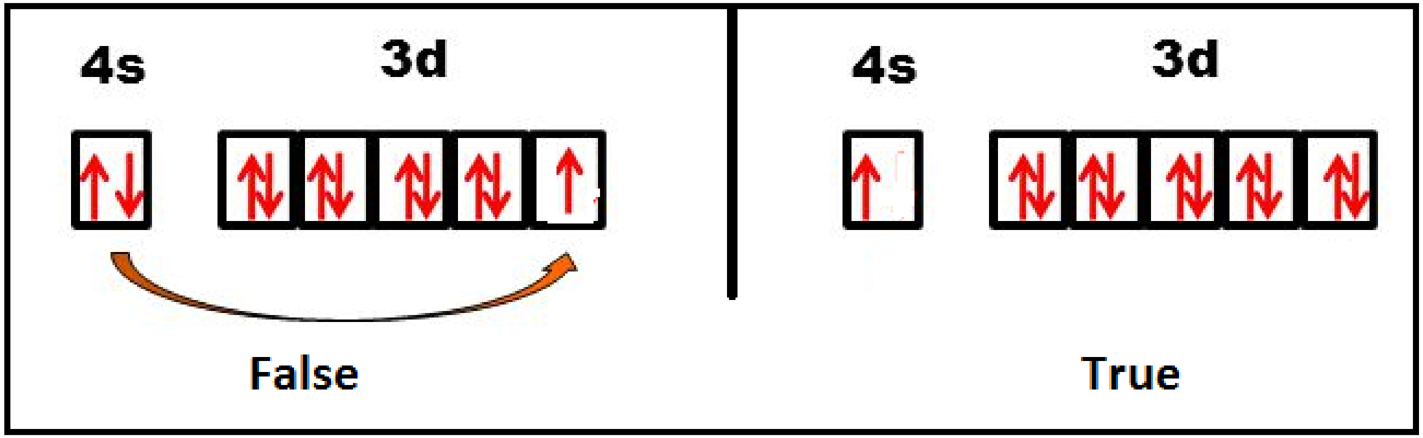
$1s^2 2s^2 2p^6 3s^2 3p^6 \underline{\mathbf{4s}}^{\mathbf{1}}\mathbf{3d^5}$ **(True)**

** **Copper**: $_{29}\mathrm{Cu}$

The expected electron configuration according to Aufbau rule is:

$1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}\underline{\mathbf{4s^{2}3d^{9}}}$ **(False)**

The above electron configuration is in fact false; it should be corrected by taking an electron from $4s^{2}$ and putting it in the orbital $3d^{9}$.



The last orbital d is more stable when it is completely filled, i.e. filled with 10 electrons.

The true electron configuration is therefore:

$1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}\underline{\mathbf{4s}}\mathbf{^{1}3d^{10}}$ **(True)**

The electron configuration of ions

Commonly, the electron configuration is used to describe the orbitals of an atom in its ground state, but it can also be used to represent an atom that has ionized into a cation or anion by compensating with the loss or gain electrons in their subsequent orbitals. The electrons are added or removed from the outer shell which corresponds to the largest principal quantum number, n, in the electron configuration of the neutral atom.

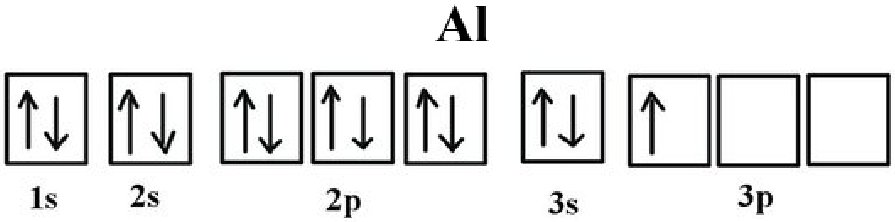
Exercise :

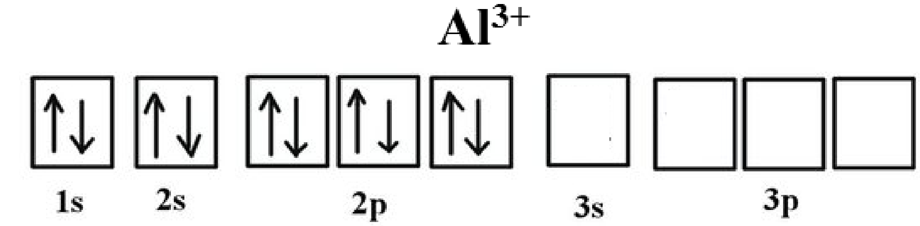
Write the electron configuration of $_{13}Al^{3+}$ and $_{16}S^{2-}$.

Answer :

** $_{13}Al^{3+}$

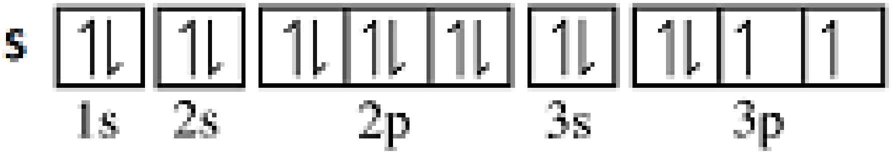
Al : $1s^2 2s^2 2p^6 3s^2 3p^1$ **Al^{3+}: $1s^2 2s^2 2p^6$**

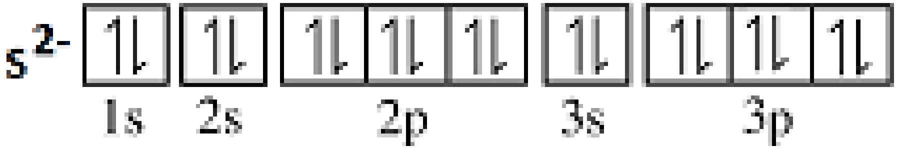




** $_{16}S^{2-}$

S : $1s^22s^22p^63s^23p^4$ **Al^{3+}: $1s^22s^22p^63s^23p^6$**





The valence electrons

The outermost electrons of an atom are called **valence electrons**. However, the inner electrons are called core electrons.

It is important to note that valence electrons of atoms play an important role in the chemical and physical properties of the elements and the compounds.

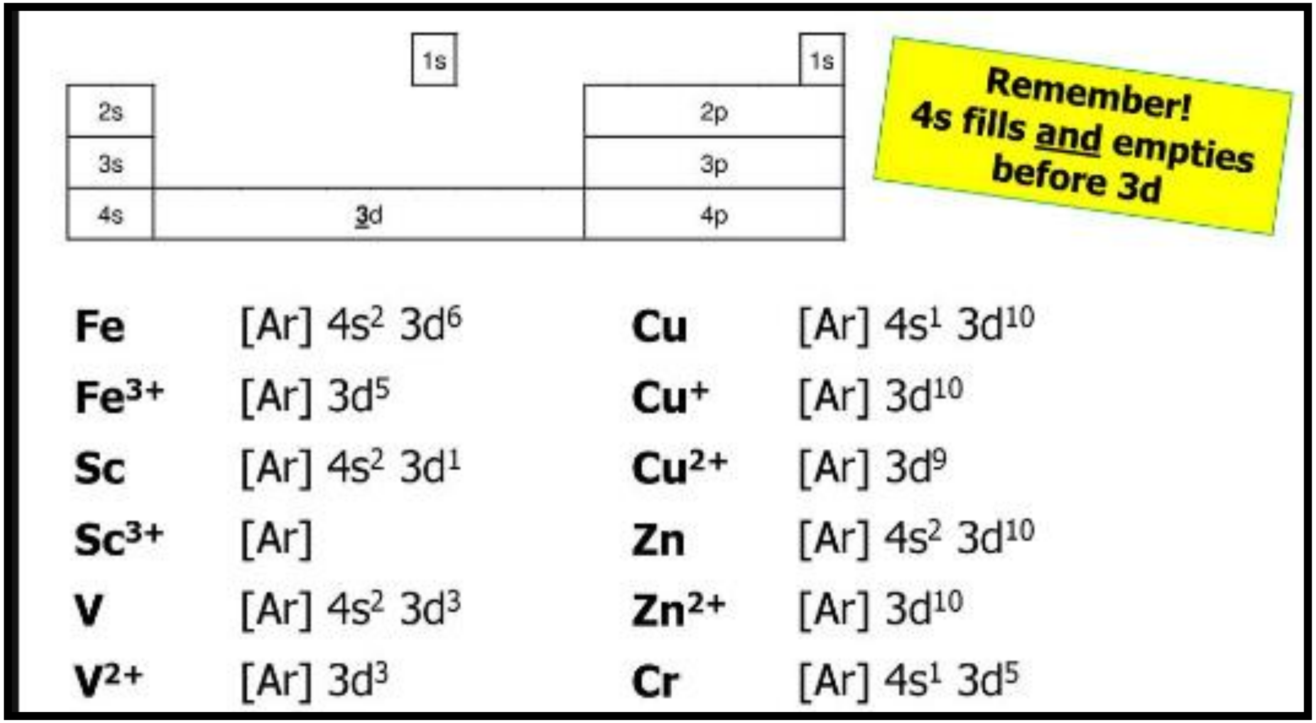
Besides, elements with the same valence electrons number show similar chemical properties.

Element	*Electron configuration in spdf notation*	Valence electrons	Valence electrons (In general)
$_{3}$Li	$1s^22s^1$	$2s^1$	*s*-Block: **ns^x** n = 1----7 x = 1 or 2
$_{11}$Na	$1s^22s^22p^63s^1$	$3s^1$	
$_{12}$Mg	$1s^22s^22p^63s^2$	$3s^2$	
$_{7}$N	$1s^22s^22p^1$	$2s^22p^1$	*p*-Block: **ns^2np^x** n = 2----7 x = 1 ----6
$_{8}$O	$1s^22s^22p^4$	$2s^22p^4$	
$_{51}$Sb	$1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^3$	$5s^24d^{10}5p^3$	
$_{26}$Fe	$1s^22s^22p^63s^23p^64s^23d^6$	$4s^23d^6$	*d*-Block: **$ns^x(n-1)d^y$** n = 4----7 x = 1 or 2 y = 1----10
$_{92}$U	$_{86}$[Rn] $5f^36d^17s^2$	$5f^36d^17s^2$	*f*-Block: **$(n-2)f^x(n-1)d^yns^2$** n = 6 or 7 x = 1----14 y = 0 or 1

The noble gas notation

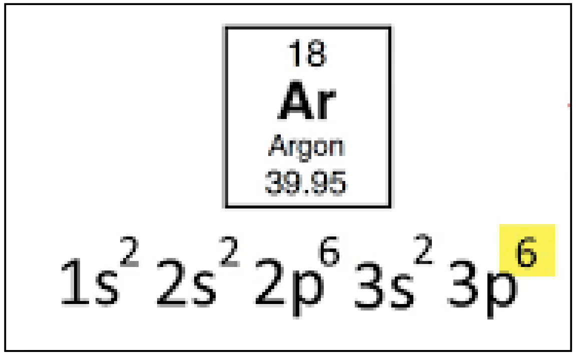
It is often useful to abbreviate the electron configuration of atoms and ions by indicating the <u>innermost electrons</u> with the symbol of the <u>preceding noble gas</u>. The resulting short electron configuration is called the <u>noble gas configuration</u> (or <u>noble gas notation</u>).

<u>Examples:</u>



Remember!
4s fills <u>and</u> empties
before 3d

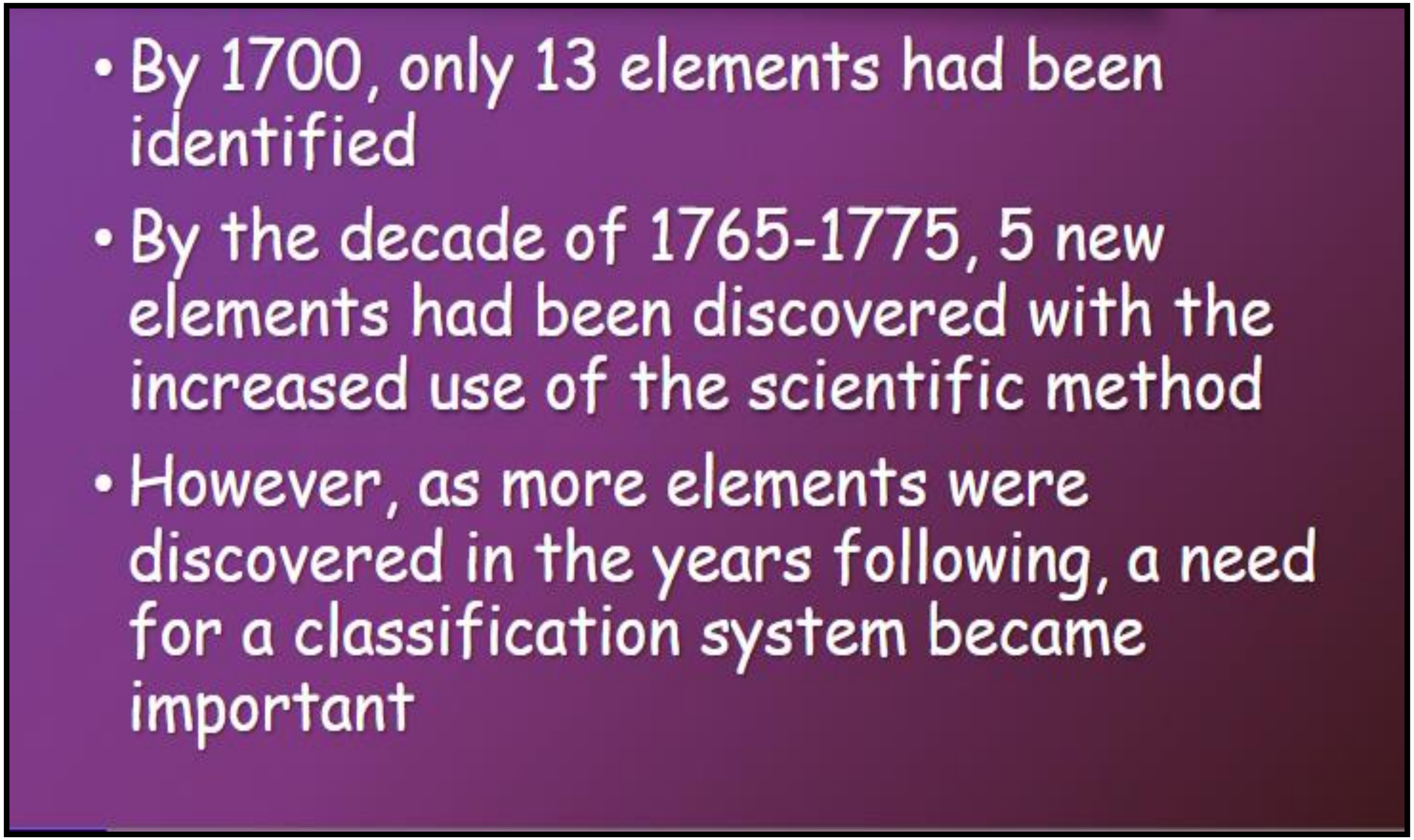
Fe	[Ar] $4s^2\ 3d^6$	**Cu**	[Ar] $4s^1\ 3d^{10}$
Fe^{3+}	[Ar] $3d^5$	**Cu^+**	[Ar] $3d^{10}$
Sc	[Ar] $4s^2\ 3d^1$	**Cu^{2+}**	[Ar] $3d^9$
Sc^{3+}	[Ar]	**Zn**	[Ar] $4s^2\ 3d^{10}$
V	[Ar] $4s^2\ 3d^3$	**Zn^{2+}**	[Ar] $3d^{10}$
V^{2+}	[Ar] $3d^3$	**Cr**	[Ar] $4s^1\ 3d^5$



$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

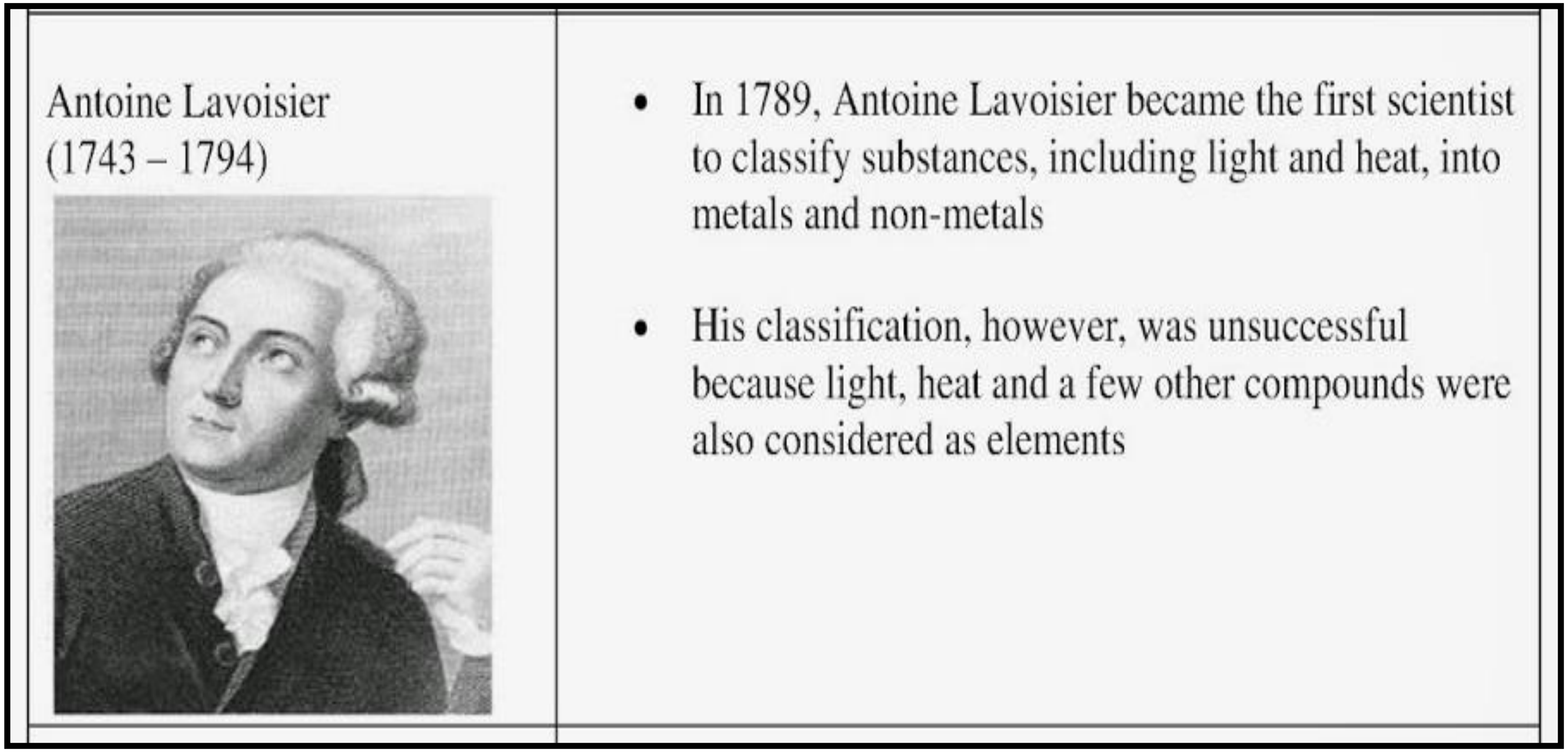
❑ *THE PERIODIC TABLE OF THE ELEMENTS*

❖ Historical Development Of The Periodic Table (A Short Overview)



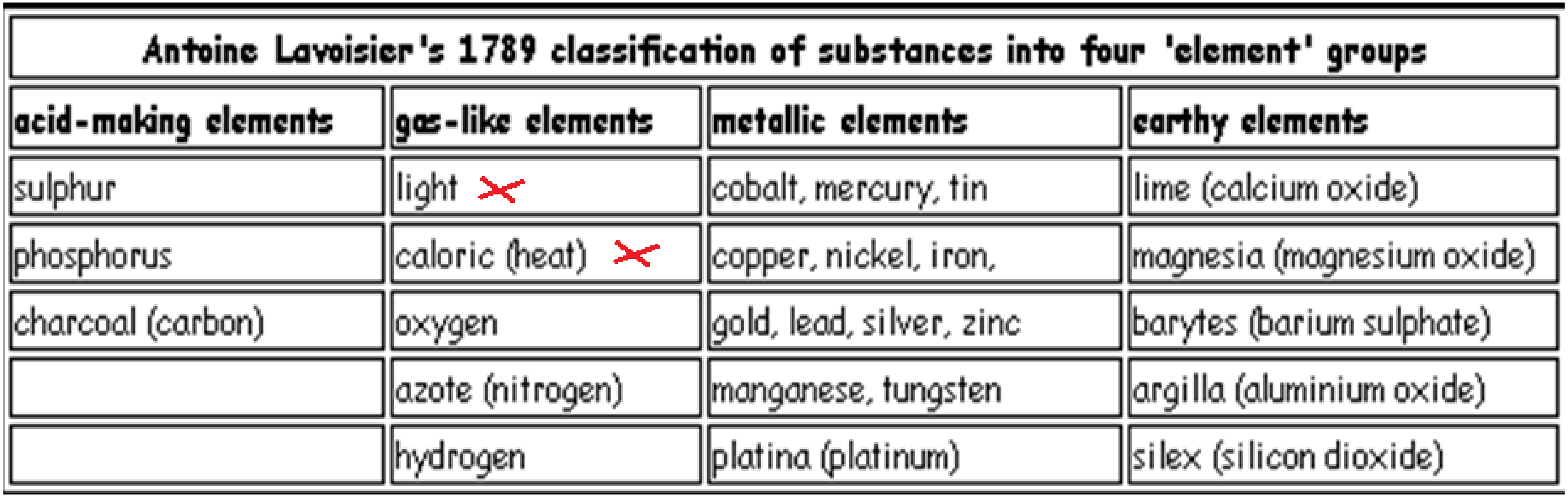
- By 1700, only 13 elements had been identified
- By the decade of 1765-1775, 5 new elements had been discovered with the increased use of the scientific method
- However, as more elements were discovered in the years following, a need for a classification system became important

The 13 elements discovered by 1700 (The Ancient discoveries) are:
Copper, Lead, Gold, Silver, Iron, Carbon, Tin,
Sulfur, Mercury, Zinc, Arsenic, Antimony, Bismuth

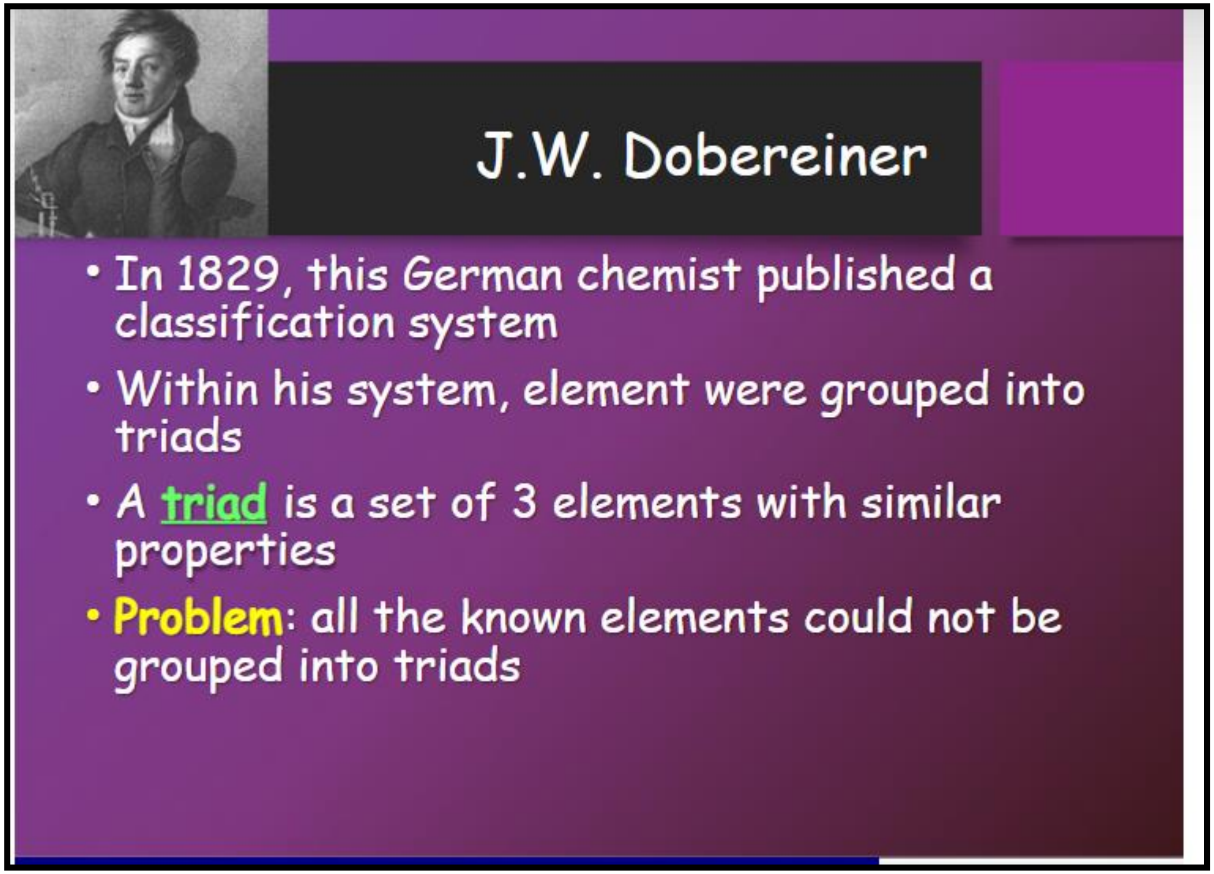


Antoine Lavoisier
(1743 – 1794)

- In 1789, Antoine Lavoisier became the first scientist to classify substances, including light and heat, into metals and non-metals
- His classification, however, was unsuccessful because light, heat and a few other compounds were also considered as elements

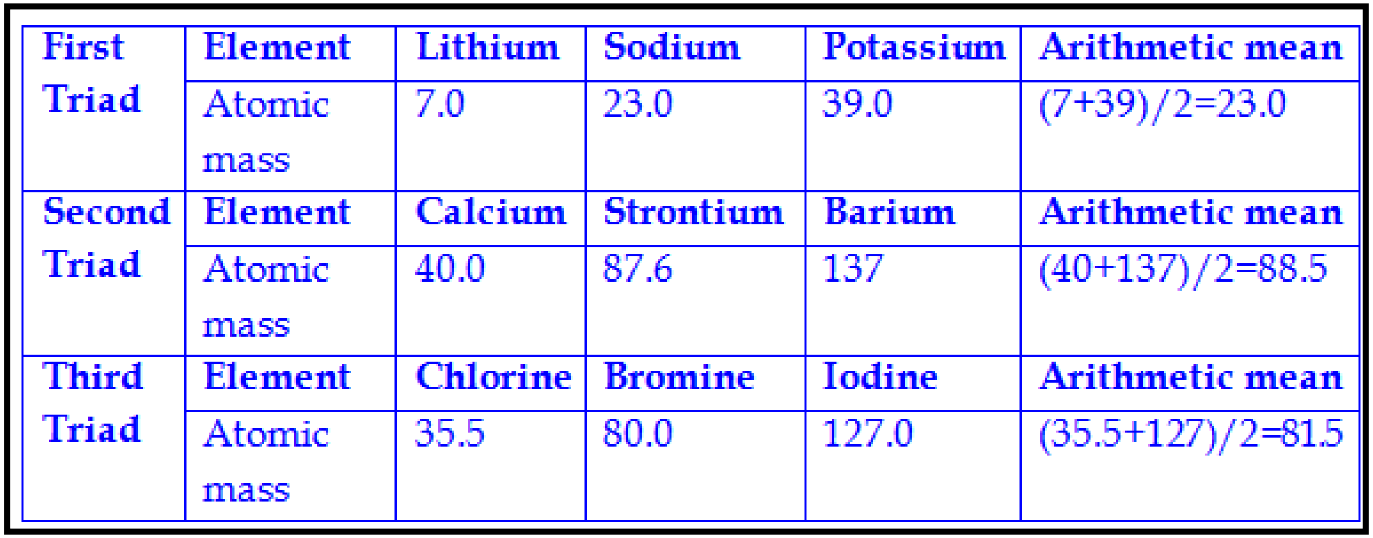


Antoine Lavoisier's 1789 classification of substances into four 'element' groups			
acid-making elements	**gas-like elements**	**metallic elements**	**earthy elements**
sulphur	light ✗	cobalt, mercury, tin	lime (calcium oxide)
phosphorus	caloric (heat) ✗	copper, nickel, iron,	magnesia (magnesium oxide)
charcoal (carbon)	oxygen	gold, lead, silver, zinc	barytes (barium sulphate)
	azote (nitrogen)	manganese, tungsten	argilla (aluminium oxide)
	hydrogen	platina (platinum)	silex (silicon dioxide)

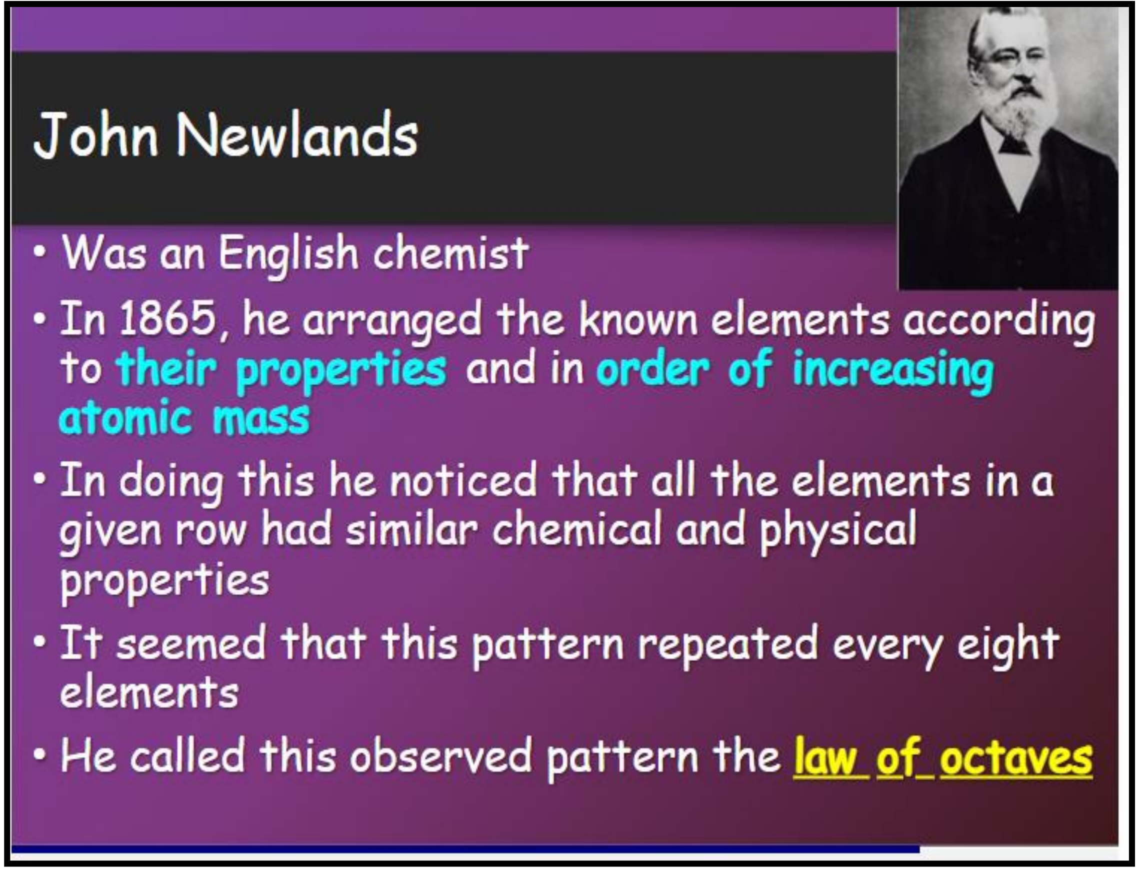


J.W. Dobereiner

- In 1829, this German chemist published a classification system
- Within his system, element were grouped into triads
- A triad is a set of 3 elements with similar properties
- **Problem**: all the known elements could not be grouped into triads

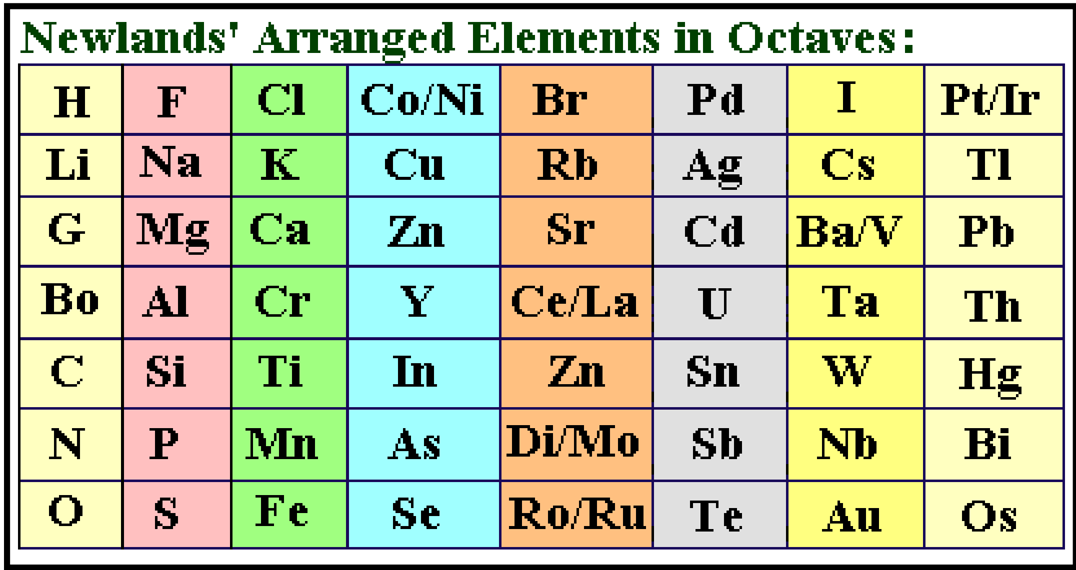


First Triad	**Element**	**Lithium**	**Sodium**	**Potassium**	**Arithmetic mean**
	Atomic mass	7.0	23.0	39.0	(7+39)/2=23.0
Second Triad	**Element**	**Calcium**	**Strontium**	**Barium**	**Arithmetic mean**
	Atomic mass	40.0	87.6	137	(40+137)/2=88.5
Third Triad	**Element**	**Chlorine**	**Bromine**	**Iodine**	**Arithmetic mean**
	Atomic mass	35.5	80.0	127.0	(35.5+127)/2=81.5



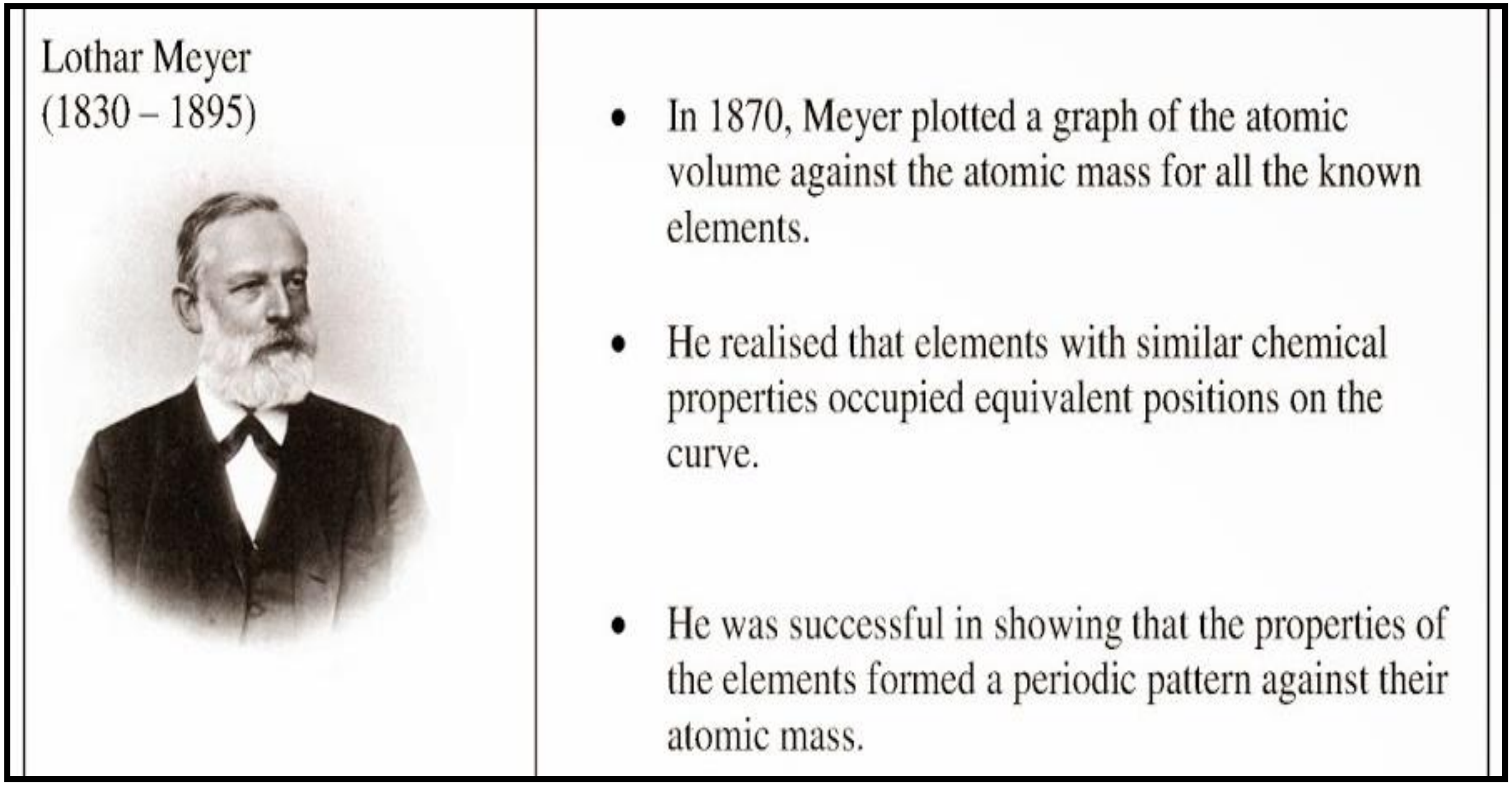
John Newlands

- Was an English chemist
- In 1865, he arranged the known elements according to **their properties** and in **order of increasing atomic mass**
- In doing this he noticed that all the elements in a given row had similar chemical and physical properties
- It seemed that this pattern repeated every eight elements
- He called this observed pattern the **law of octaves**



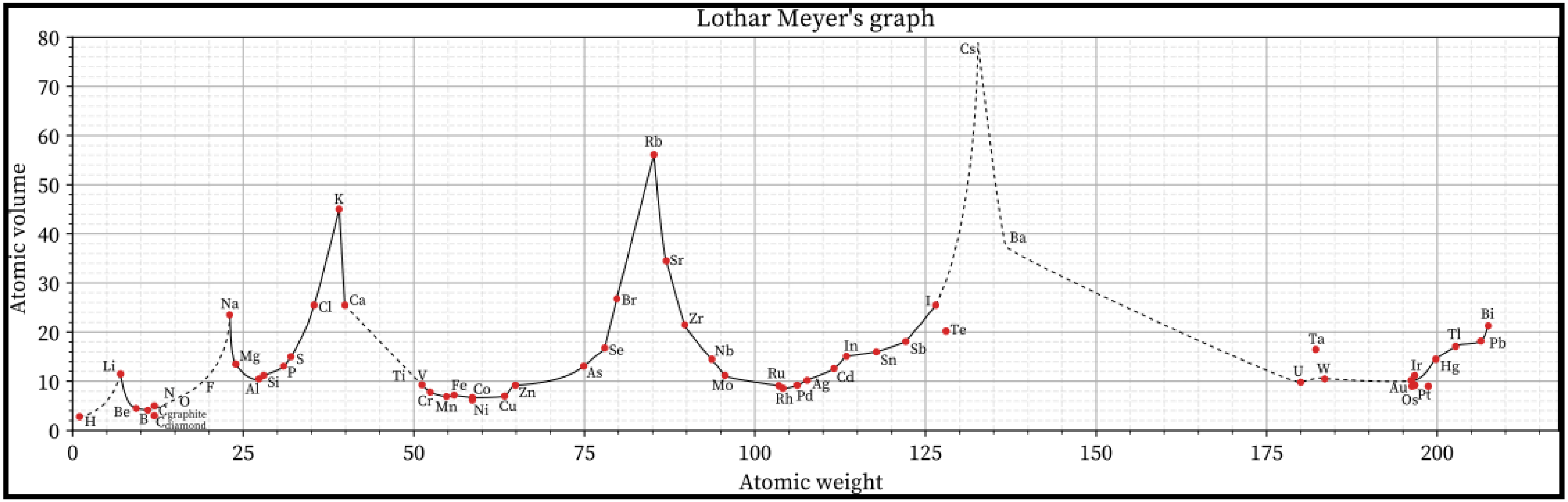
Newlands' Arranged Elements in Octaves:

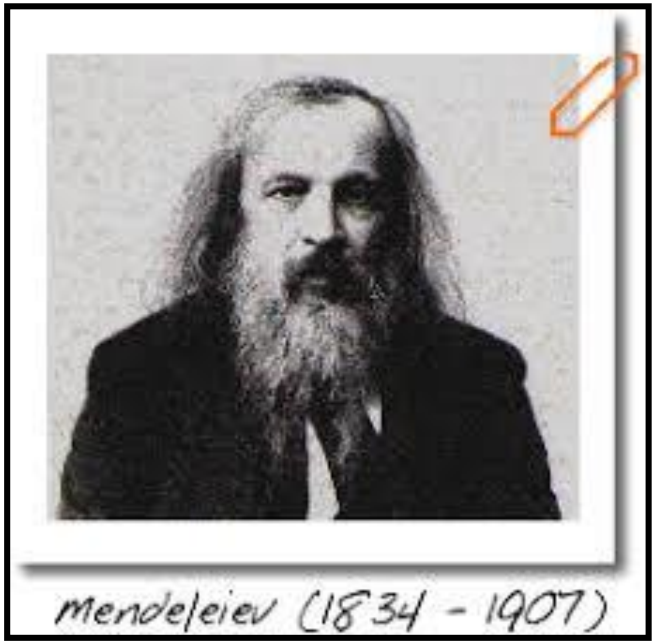
H	F	Cl	Co/Ni	Br	Pd	I	Pt/Ir
Li	Na	K	Cu	Rb	Ag	Cs	Tl
G	Mg	Ca	Zn	Sr	Cd	Ba/V	Pb
Bo	Al	Cr	Y	Ce/La	U	Ta	Th
C	Si	Ti	In	Zn	Sn	W	Hg
N	P	Mn	As	Di/Mo	Sb	Nb	Bi
O	S	Fe	Se	Ro/Ru	Te	Au	Os



Lothar Meyer
(1830 – 1895)

- In 1870, Meyer plotted a graph of the atomic volume against the atomic mass for all the known elements.
- He realised that elements with similar chemical properties occupied equivalent positions on the curve.
- He was successful in showing that the properties of the elements formed a periodic pattern against their atomic mass.



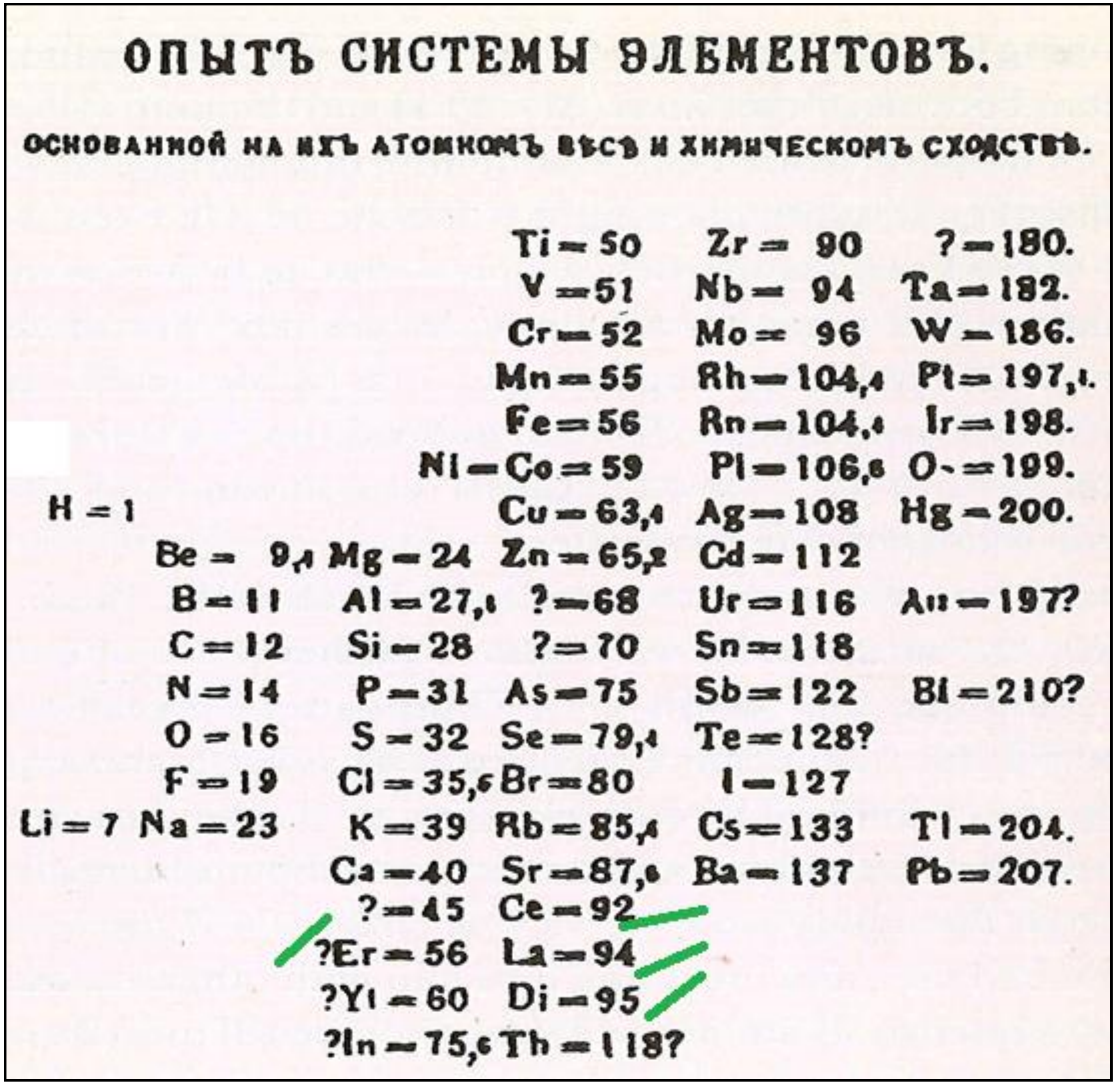


mendeleiev (1834 - 1907)

Dmitri Mendeleev was a Russian chemist and is widely known for the development of the periodic table. He not only corrected the properties of then-known elements but also predicted the properties of undiscovered elements, in fact, he was the 1st to do so. And he did this just knowing the location of the elements in the periodic table. He explicitly stated the periodic law and firmly stood for his predictions, which were eventually found to be true. It was his boldness and scientific approach to explain things earned him the title of the father of the modern periodic table.

To put some order into his study of chemical elements, Mendeleev made up a set of cards, one for each of the **63 elements** known at the time. Mendeleev wrote the atomic mass and the properties of each element on a card.

The first periodic table published by Mendeleev in March 6, 1869 in the German journal, Zeitschrift für Chemie



ОПЫТЪ СИСТЕМЫ ЭЛЕМЕНТОВЪ.

ОСНОВАННОЙ НА ИХЪ АТОМНОМЪ ВѢСѢ И ХИМИЧЕСКОМЪ СХОДСТВѢ.

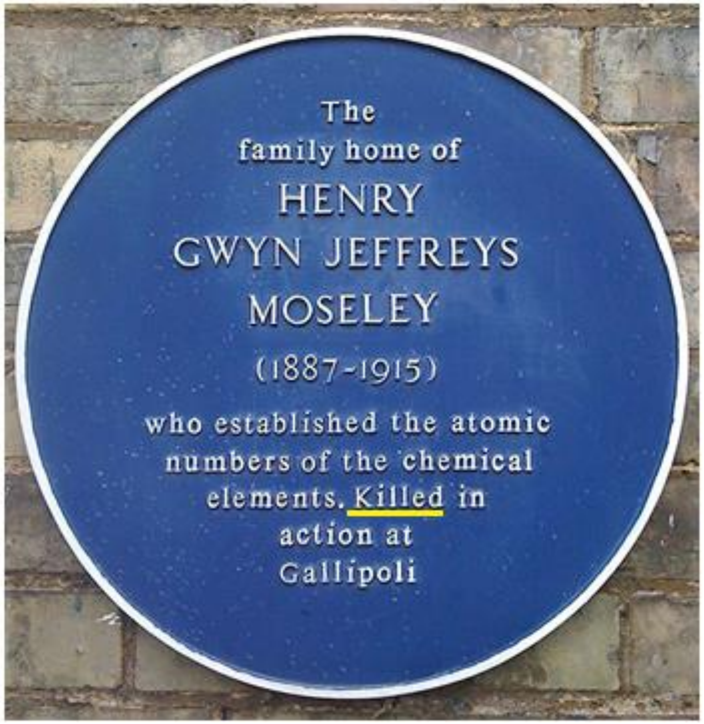
			Ti=50	Zr=90	?=180.
			V=51	Nb=94	Ta=182.
			Cr=52	Mo=96	W=186.
			Mn=55	Rh=104,4	Pt=197,4.
			Fe=56	Rn=104,4	Ir=198.
			Ni=Co=59	Pl=106,6	Os=199.
H=1			Cu=63,4	Ag=108	Hg=200.
	Be=9,4	Mg=24	Zn=65,2	Cd=112	
	B=11	Al=27,4	?=68	Ur=116	Au=197?
	C=12	Si=28	?=70	Sn=118	
	N=14	P=31	As=75	Sb=122	Bi=210?
	O=16	S=32	Se=79,4	Te=128?	
	F=19	Cl=35,5	Br=80	I=127	
Li=7	Na=23	K=39	Rb=85,4	Cs=133	Tl=204.
		Ca=40	Sr=87,6	Ba=137	Pb=207.
		?=45	Ce=92		
		?Er=56	La=94		
		?Yt=60	Di=95		
		?In=75,6	Th=118?		

- *When Mendeleev designed the first version of the periodic table in 1869, only 4 lanthanides (**La**, **Ce**, **Er**, and **Di**) were known. The chemical similarity of the lanthanides made their separation rather cumbersome and allocation into the periodic table of any later discovered lanthanide posed problems.*
- *In fact, later it was found that **Didymium** (**Di**) is a mixture of the rare earth elements praseodymium (Pr) and neodymium (Nd).*

- ***Note.** 2019 has been designated as the "International Year of the Periodic Table of Chemical Elements" (IYPT2019), celebrating the 150th anniversary of Mendeleev's discovery of the system which was in 1869.*

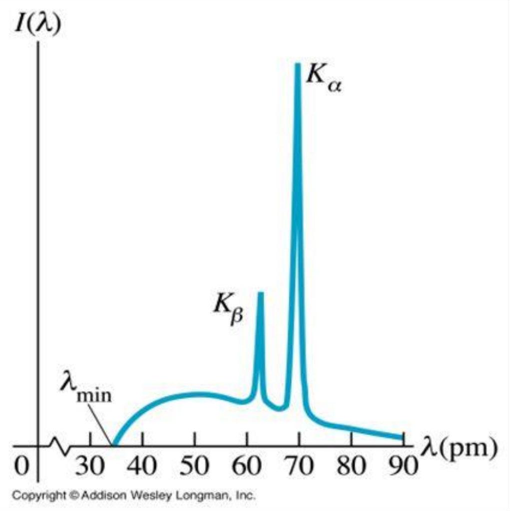
Henry Moseley – a young scientist - fixed the problem!

- 50 years after Mendeleev designed his table, Henry Moseley, a young British scientist determined each Element's atomic number (# of protons)
- By using atomic number instead of atomic mass, every element falls into place with similar physical and chemical properties without any exceptions!



The
family home of
HENRY
GWYN JEFFREYS
MOSELEY
(1887-1915)
who established the atomic
numbers of the chemical
elements. Killed in
action at
Gallipoli

X-ray spectra and Moseley law



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$$\lambda_{\min} = \frac{hc}{eV_{AC}}$$

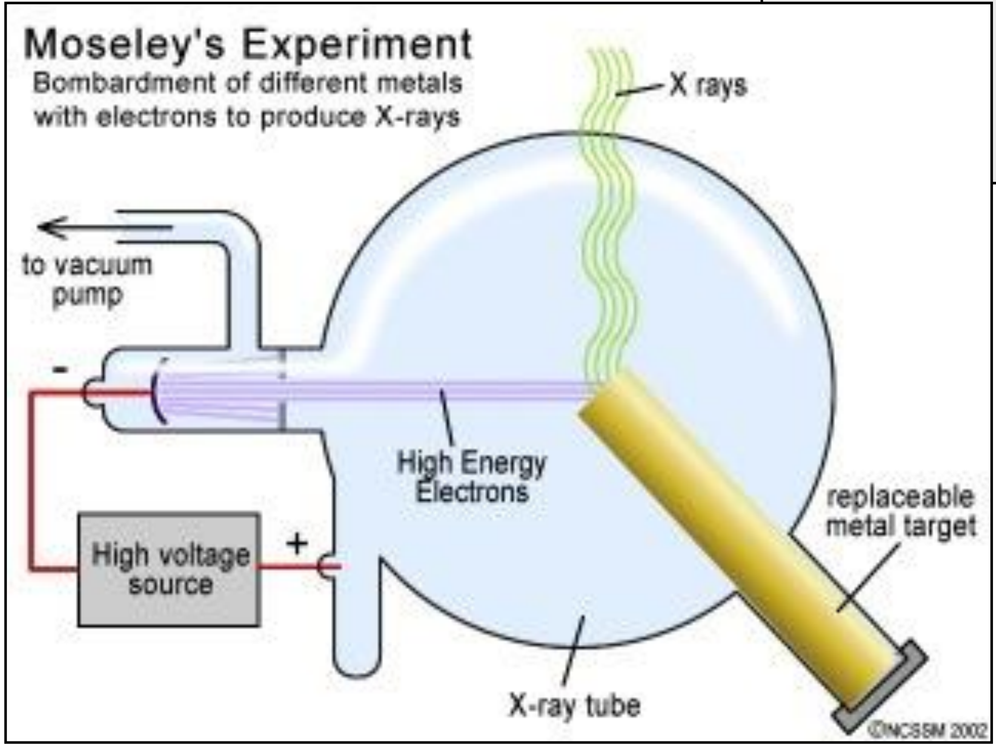
The continous –spectrum radiation is nearly independent of the target material.

Sharp peaks (characteristic spectra) depend on the accelerating voltage and the target element. Frequencies of the peaks as a function of the element's atomic number Z:

$$f = (2.48 \cdot 10^{15}\, Hz)(Z-1)^2$$

⇧

Moseley law



Moseley's Experiment

Bombardment of different metals with electrons to produce X-rays

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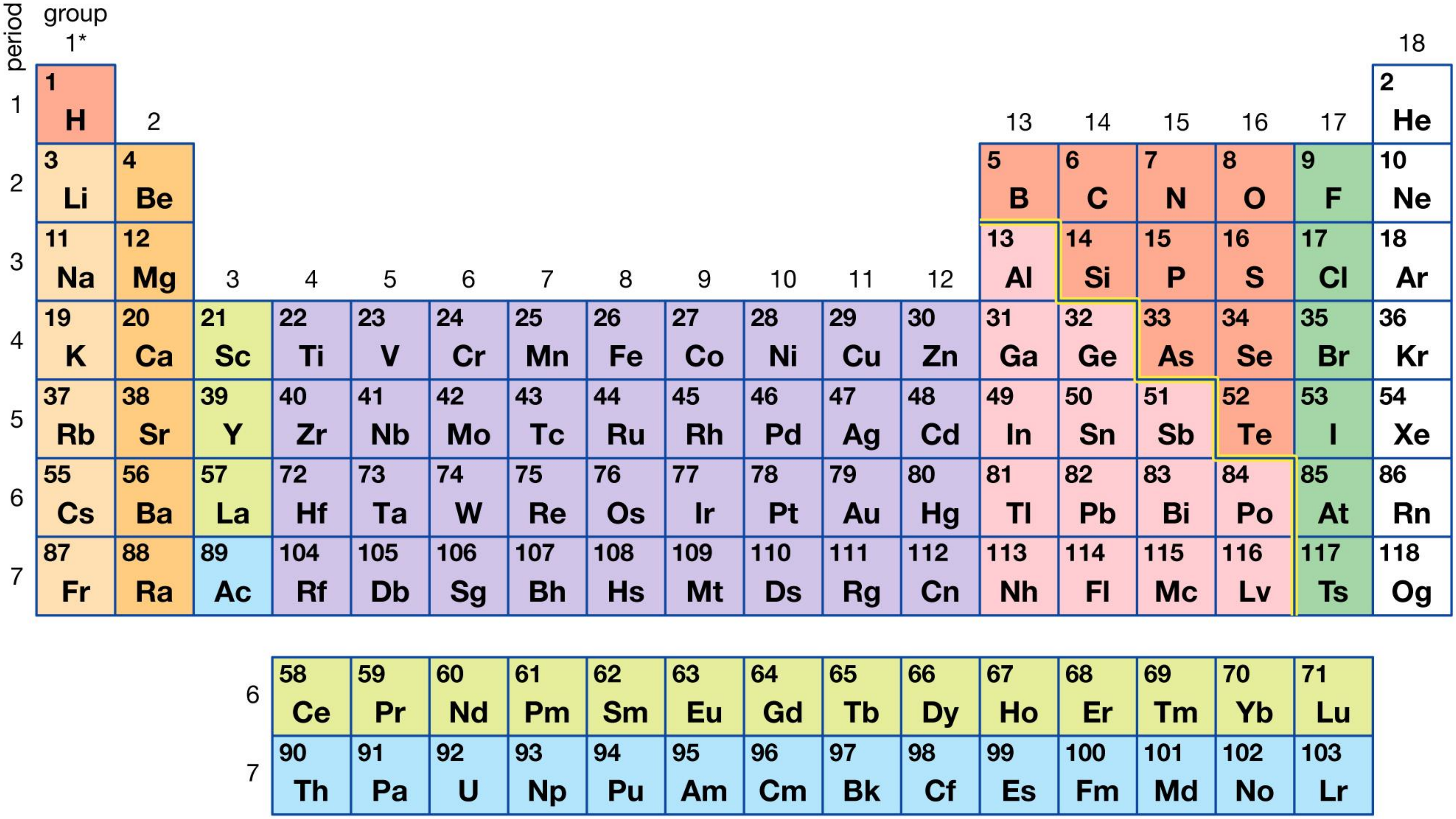
THE MODERN PERIODIC TABLE OF THE ELEMENTS

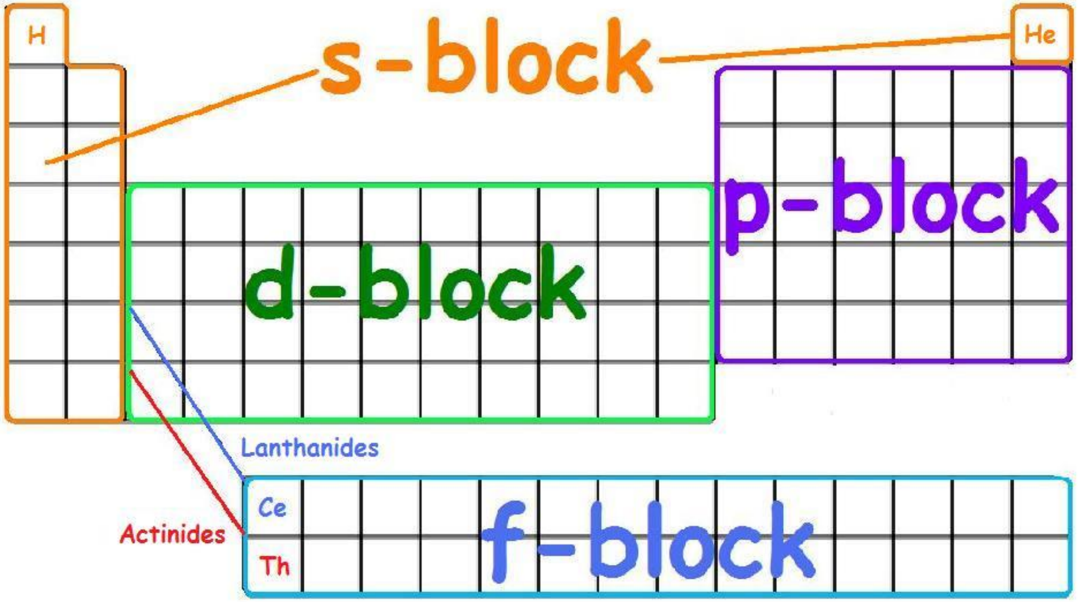


period	group 1*	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	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 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

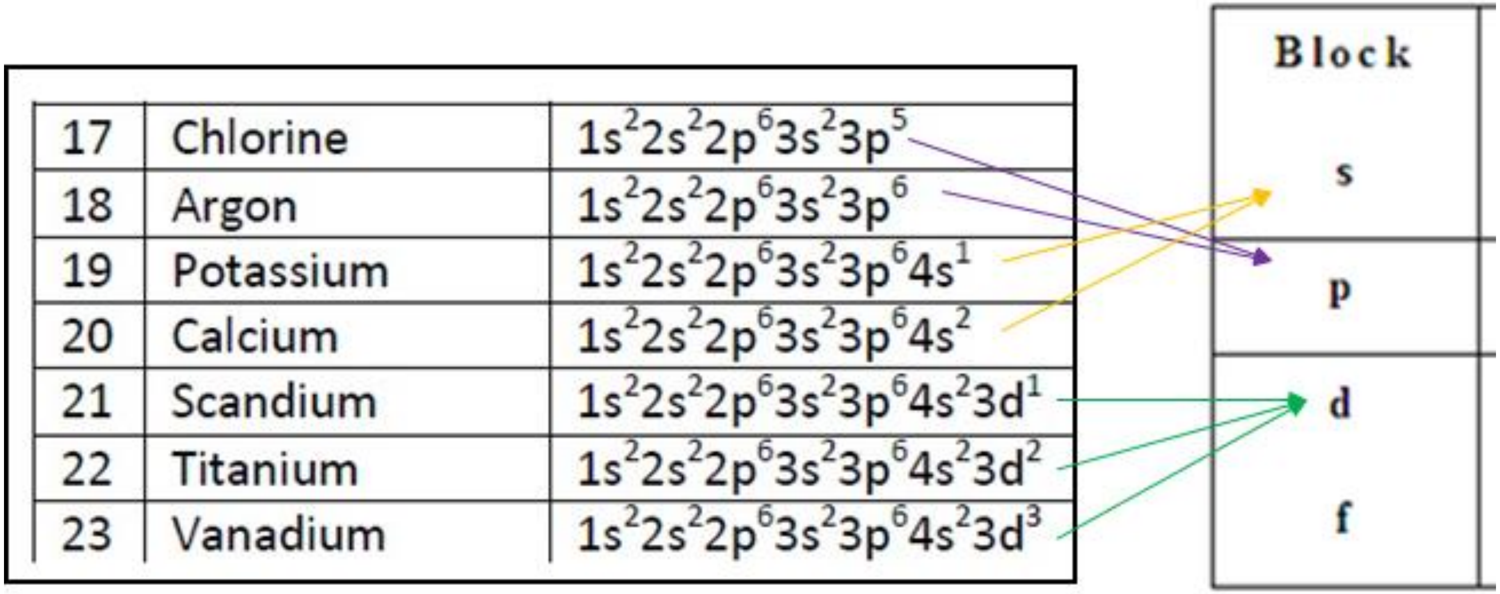
6	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
7	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

*Numbering system adopted by the International Union of Pure and Applied Chemistry (IUPAC).

*Four Blocks



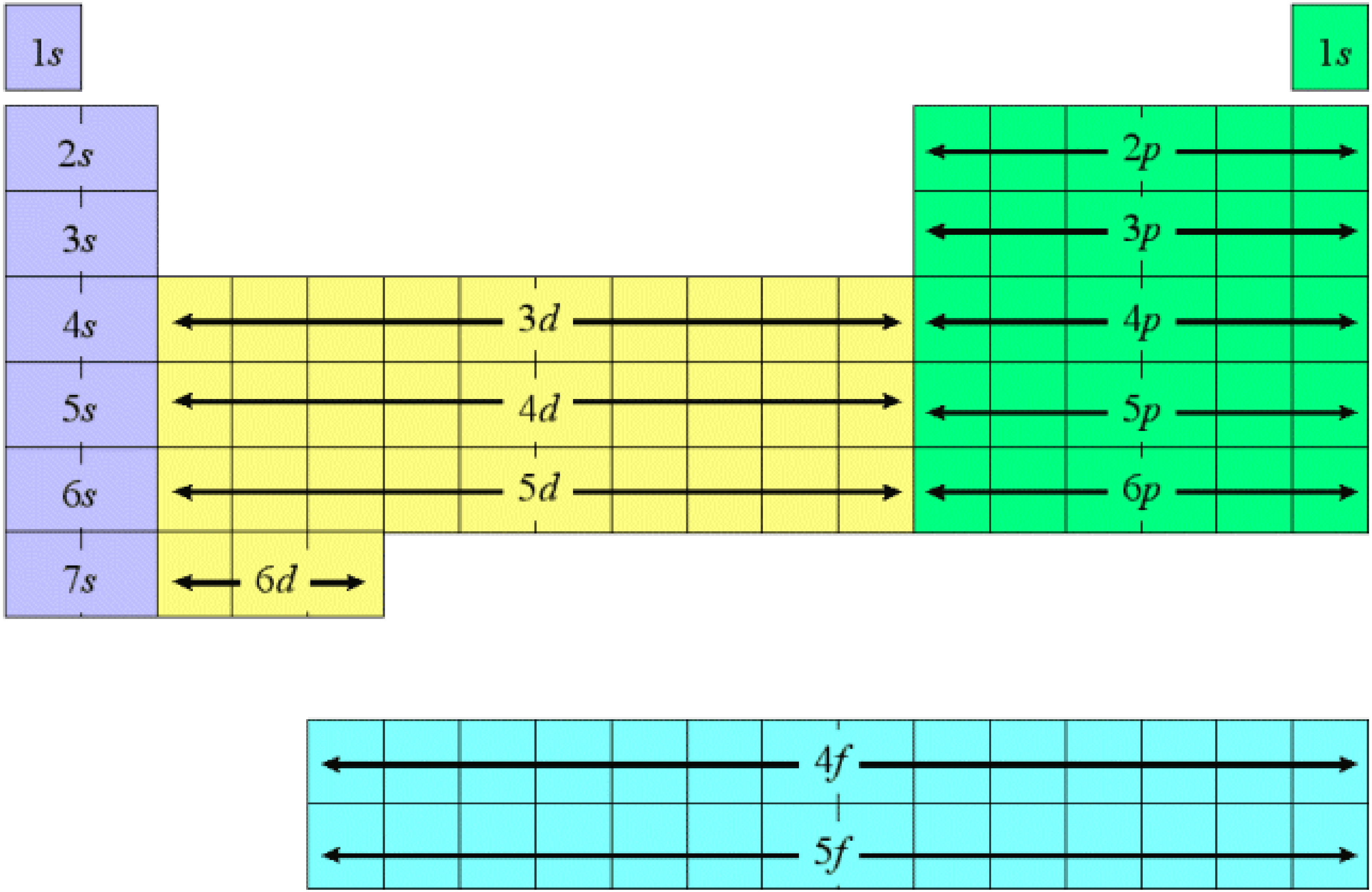
- *The naming of the blocks as s, p, d and f refers to the progressive filling of the outer atomic orbitals of the s, p, d and f, sub-shells, respectively.*

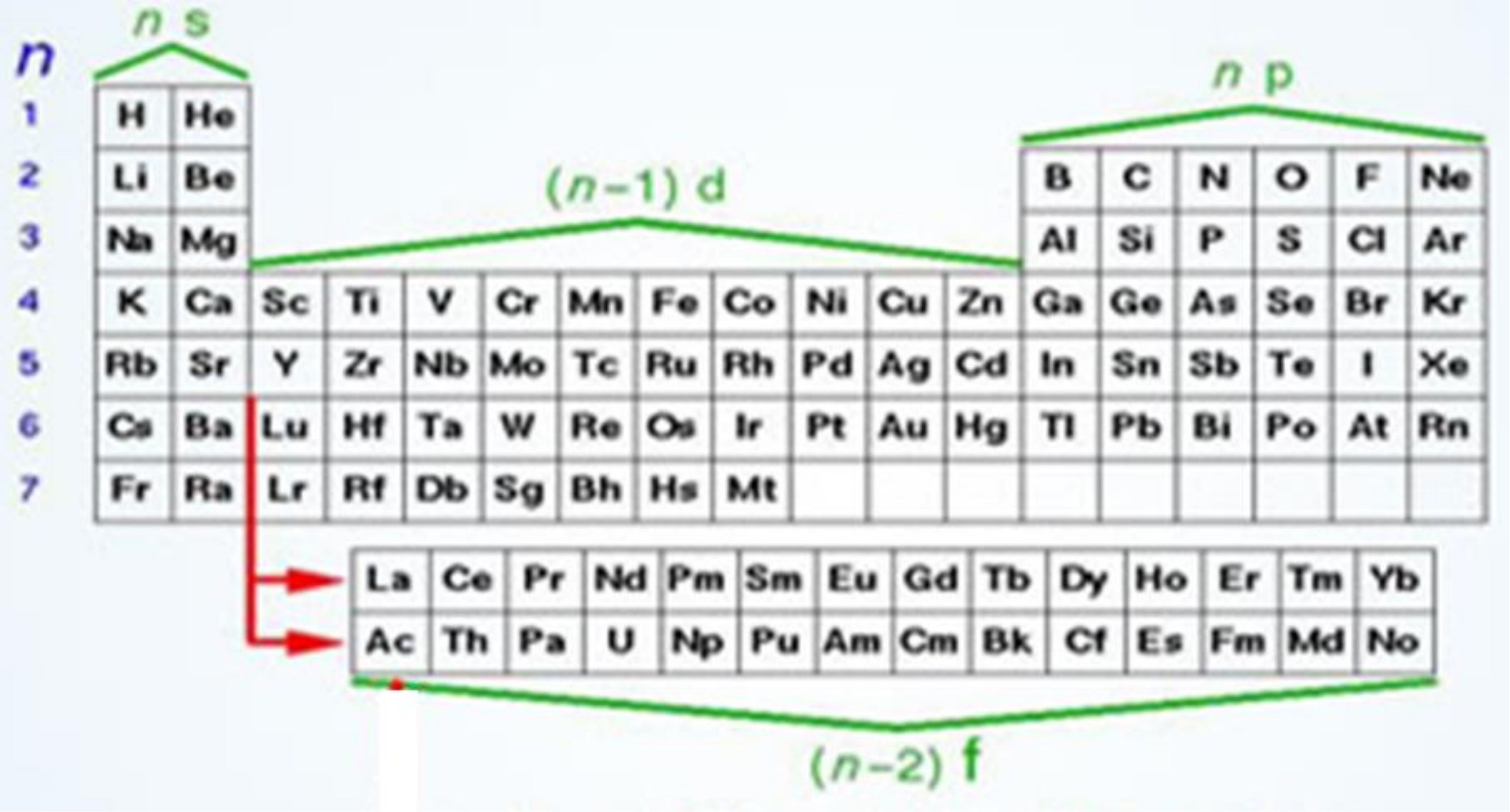


17	Chlorine	$1s^22s^22p^63s^23p^5$
18	Argon	$1s^22s^22p^63s^23p^6$
19	Potassium	$1s^22s^22p^63s^23p^64s^1$
20	Calcium	$1s^22s^22p^63s^23p^64s^2$
21	Scandium	$1s^22s^22p^63s^23p^64s^23d^1$
22	Titanium	$1s^22s^22p^63s^23p^64s^23d^2$
23	Vanadium	$1s^22s^22p^63s^23p^64s^23d^3$

Block
s
p
d f

- ***Distribution of the different sub-shells over the four blocks of the periodic table.***



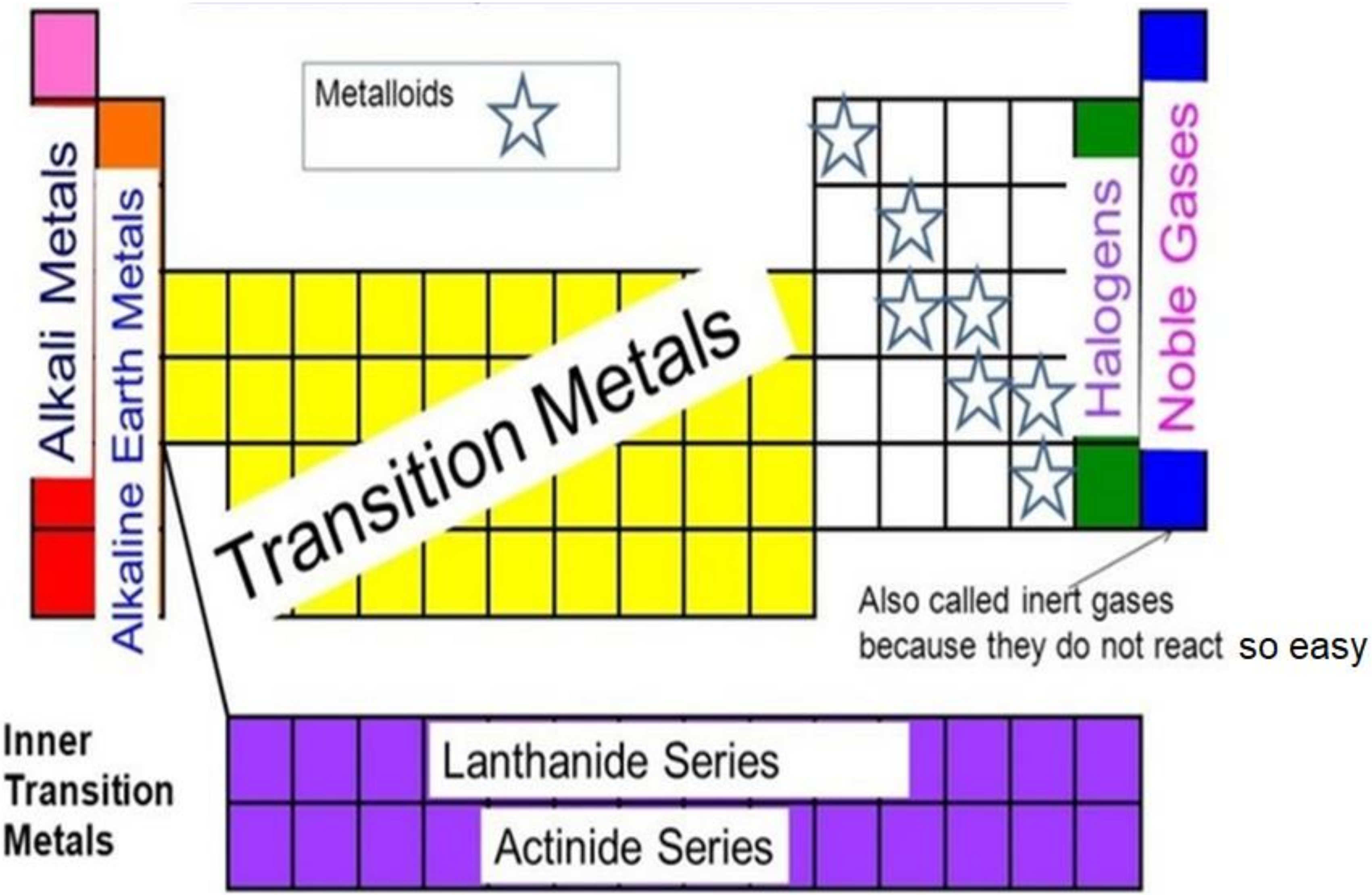


n																		
1	H	He																
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt									

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

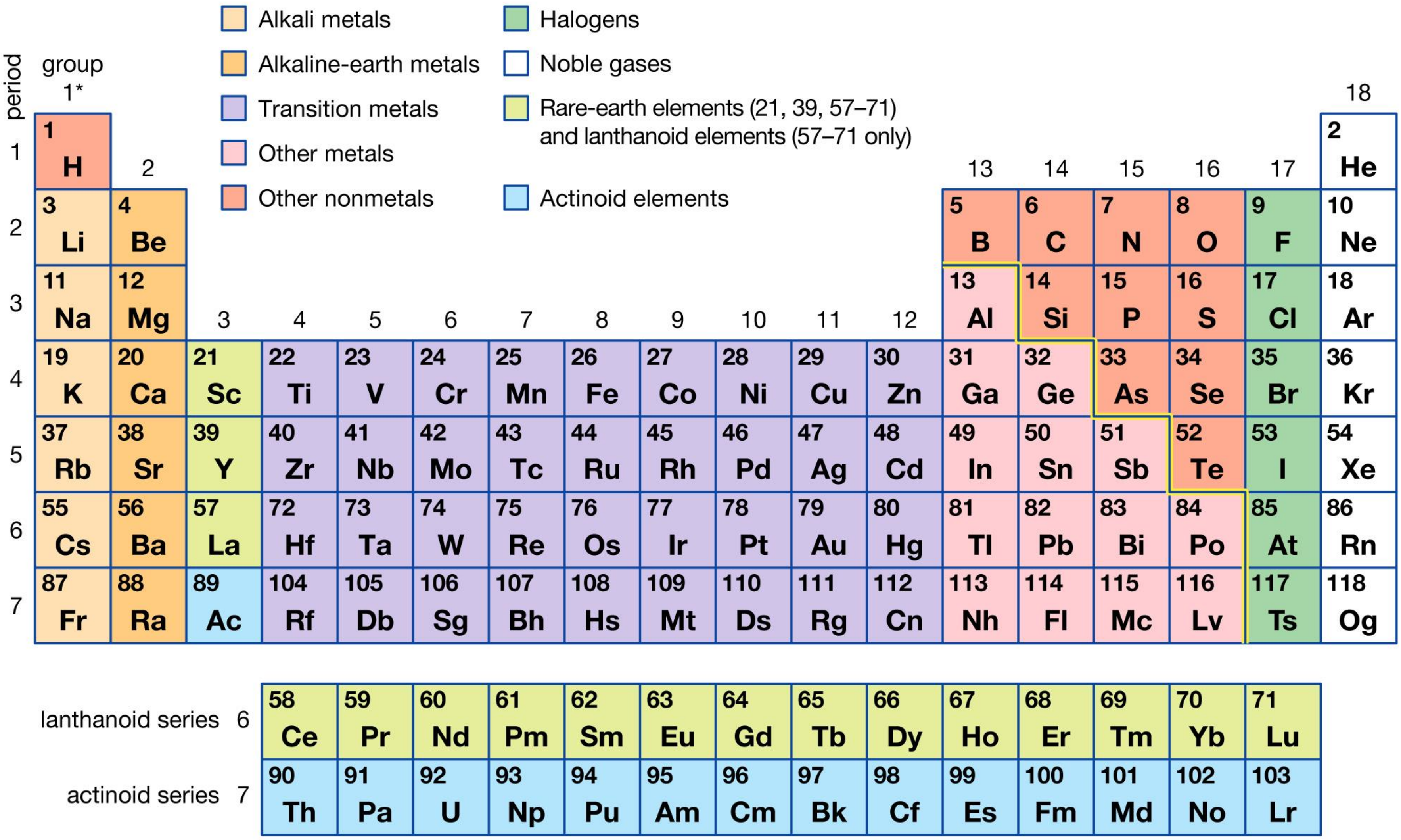
The naming of the blocks as s, p, d and f refers to the progressive filling of the outer atomic orbitals of the sub-shells, s, p, d and f, respectively.

*Groups Names



***Elements of blocks s and p (groups 1,2, and 13-18) are known as Representative Elements or Main Elements.**

*Groups Names



Periodic table of the elements

🟧 Alkali metals
🟧 Alkaline-earth metals
🟪 Transition metals
🟥 Other metals
🟥 Other nonmetals
🟩 Halogens
⬜ Noble gases
🟨 Rare-earth elements (21, 39, 57–71) and lanthanoid elements (57–71 only)
🟦 Actinoid elements

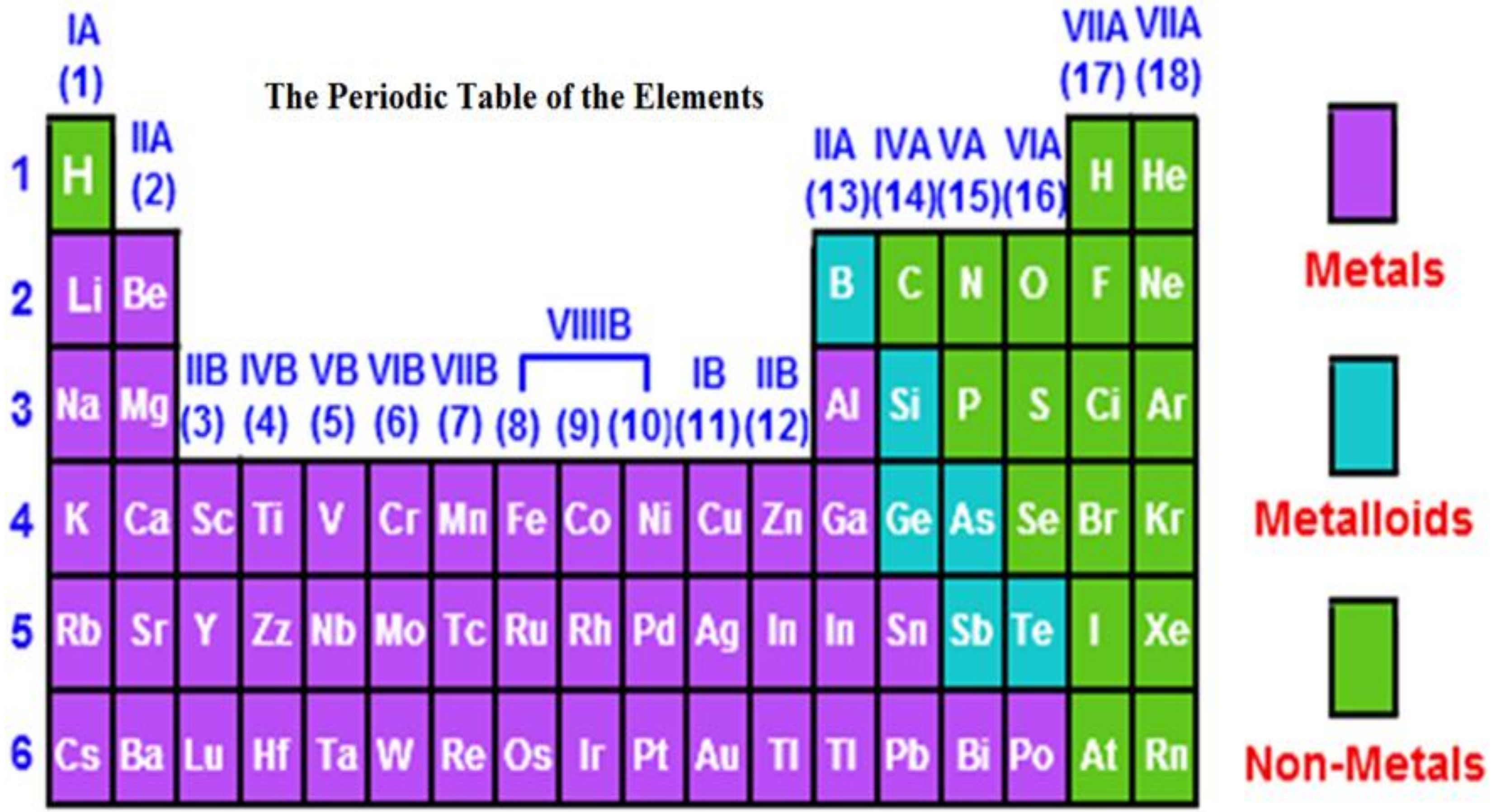
period	group 1*	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	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 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

lanthanoid series 6	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
actinoid series 7	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

*Numbering system adopted by the International Union of Pure and Applied Chemistry (IUPAC).

*****Elements of groups 1,2,13-17 are called Representative Elements or Main Elements.***

*Metals, Non-Metals and Metalloids



The Periodic Table of the Elements

	IA (1)	IIA (2)	IIB (3)	IVB (4)	VB (5)	VIB (6)	VIIB (7)	VIIIB (8)	(9)	(10)	IB (11)	IIB (12)	IIA (13)	IVA (14)	VA (15)	VIA (16)	VIIA (17)	VIIA (18)
1	H																H	He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Ci	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zz	Nb	Mo	Tc	Ru	Rh	Pd	Ag	In	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Tl	Tl	Pb	Bi	Po	At	Rn

🟪 Metals

🟦 Metalloids

🟩 Non-Metals

f-Block----4f: ***Lanthanides***

f-Block----5f: ***Actindes***

- About 80 percent of the elements are metals.
- About 15 percent of the elements are nonmetals.
- The remaining (about 5%) elements are metalloids.

- *A* **metal** (such as iron, Cupper, Sodium,…) is an element that has the characteristic properties:

- Luster, malleability and ductility.
- Good conductor of heat and electricity
- With the exception of mercury, all metals are solids at room temperature.
- Most of them possessed high meting temperature.
- Most of them are found as compounds in nature, but can exist freely once refined.

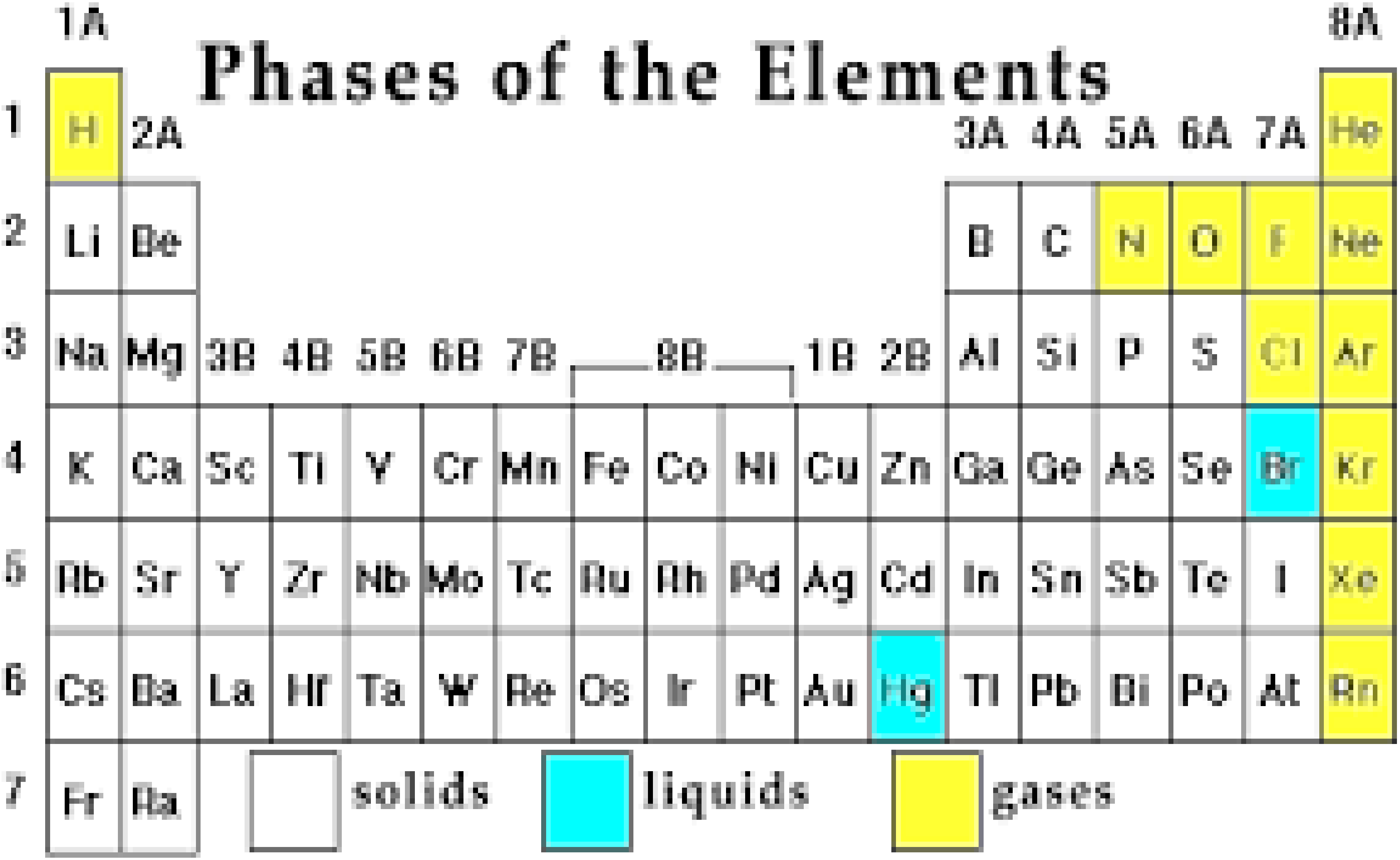
- *A* **non-metal** (such as Carbon, phosphor, Helium,…) is an element that has the characteristic properties:

- Absence of luster, malleability and ductility.
- Poor thermal and electrical conductivities.
- Many of the non-metals, such as oxygen, nitrogen and the noble gases, are gases.
- The only non-metal found as a liquid at room temperature is bromine.
- Solid non-metals include carbon, iodine, sulfur, and phosphorus.

- *A* **metalloid** (such as Boron, Silicon, Germanium,…) is an element that has properties that are intermediate between those of metals and non-metals.

Metalloids can also be called semimetals.

*Physical state of the Elements at 25 °C, P = 1atm



Phases of the Elements

	1A	2A	3B	4B	5B	6B	7B	8B			1B	2B	3A	4A	5A	6A	7A	8A
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	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra																

⬜ solids 🟦 liquids 🟨 gases

Exercise :

Referring to the periodic table, what is the chemical symbol of the element that fits each of the following descriptions?

- **a.** Located in both Period 3 and Group IVA
- **b.** The Period 4 noble gas
- **c.** The Period 2 alkaline earth metal
- **d.** The Period 3 halogen

Answer :

a. Period 3 is the third row of elements and Group IVA is the 5th column from the right side of the periodic table: The element that has this column–row (period–group) location is **Si** (silicon).

b. The noble gases are the elements of Group VIIIA (the right-most column in the periodic table). The Period 4 (fourth row) noble gas is **Kr** (krypton).

c. The *alkaline earth metals* are the elements of Group IIA (the second column from the left side of the periodic table). The Period 2 (second row) alkaline earth metal is **Be** (beryllium).

d. The halogens are the elements of Group VIIA (the second column from the right side of the periodic table). The Period 3 (third row) halogen is **Cl** (chlorine).

Exercise :

Referring to the periodic Table give the symbol and the name of the element that fits each of the following descriptions:

a. Located in both Period 4 and Group VIA

b. The Period 3 alkali metal

c. The Period 2 noble gas

d. The Period 4 halogen

Answer :

a. Se (selenium)

b. **b.** Na (sodium)

c. **c.** Ne (neon)

d. **d.** Br (bromine)

Exercise :

Write the electron configuration for following atoms, then determine if the element is a main element or transition metal element or a lanthanide metal element :

$_{1}$H, $_{2}$He, $_{23}$V, $_{20}$Ca, $_{10}$Ne, $_{11}$Na, $_{8}$O, $_{21}$Sc, $_{3}$Li, $_{30}$Zn, $_{34}$Se, $_{25}$Mn , $_{64}$Gd

Answer :

$_{1}$H	**$_{2}$He**	**$_{23}$V**
$1s^1$	$1s^2$	$1s^2\ 2s^2 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^3$
$_{20}$Ca	**$_{10}$Ne**	**$_{11}$Na**
$1s^2\ 2s^2 2p^6\ 3s^2\ 3p^6\ 4s^2$	$1s^2 2s^2 2p^6$	$1s^2 2s^2 2p^6 3s^1$
$_{8}$O	**$_{21}$Sc**	$_{3}$Li
$1s^2 2s^2 2p^4$	$1s^2\ 2s^2 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^1$	$1s^2\ 2s^1$
$_{30}$Zn	**$_{34}$Se**	**$_{25}$Mn**
$1s^2\ 2s^2 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}$	$1s^2\ 2s^2 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^4$	$1s^2\ 2s^2 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^5$
$_{64}$Gd		
$_{54}$[Xe] $4f^7 5d^1 6s^2$		

- Main elements are the elements belonging to ***s*** and p blocks. The electron configuration ends with unfilled **s** or **p subshells**.

- The transition elements are the elements belonging to ***d*** block. The electron configuration ends with unfilled ***d*** **subshells**.

- The lanthanide elements are the elements belonging to ***f*** block; The electron configuration ends with unfilled ***f*** **subshells**.

Main elements	**Transition metal elements**	**Lanthanide metal elements**
H, He, Li, O, N, Na, Ca, Se	Sc, V, Mn, Fe, Zn	Gd

Exercise :

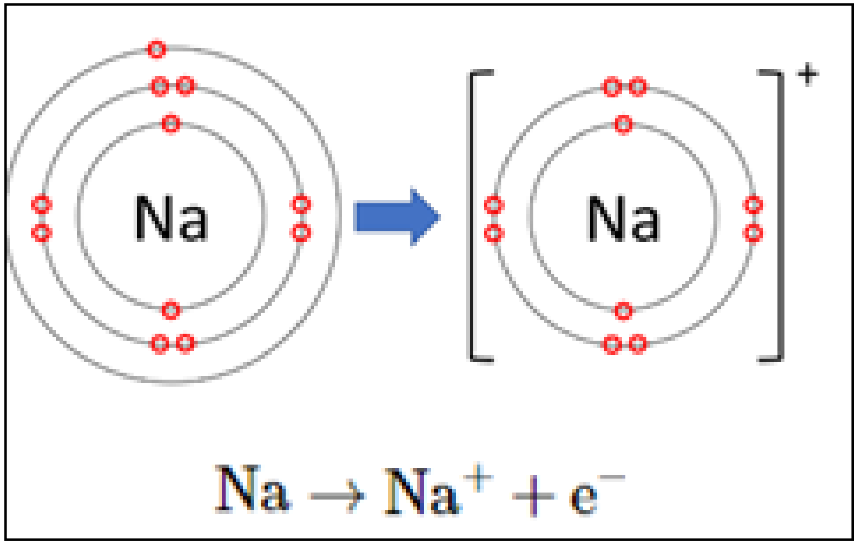
Without referring to the periodic table, complete the following table:

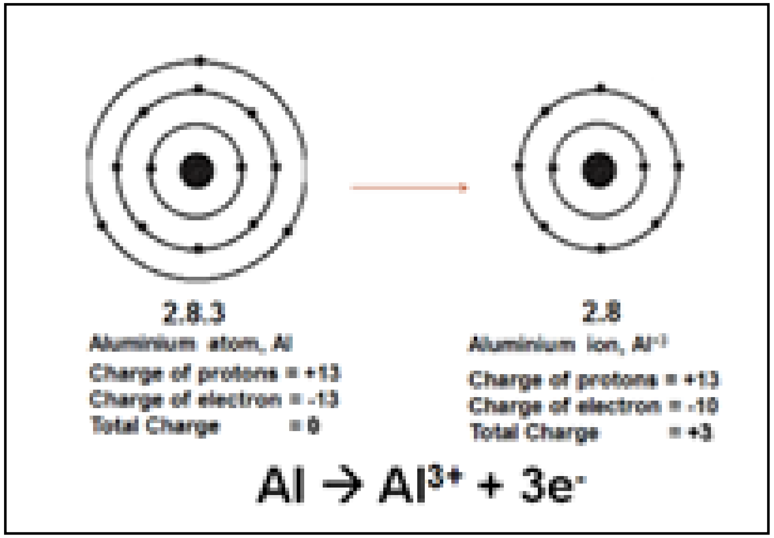
Answer :

	$_{12}$Mg	**$_{16}$S**	**$_{24}$Cr**
Electron configuration	$1s^2 2s^2 2p^6 3s^2$	$1s^2 2s^2 2p^6 3s^2 3p^4$	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$
Noble gas notation	$_{12}$Mg: $_{10}$[Ne]$\underline{3s^2}$	$_{16}$S: $_{10}$[Ne]$\underline{3s^2 3p^4}$	$_{24}$Cr: $_{18}$[Ar]$\underline{4s^1 3d^5}$
Block	s-block	p-block	d-block
Outer shell	$\underline{3s^2}$	$\underline{3s^2 3p^4}$	$\underline{4s^1 3d^5}$
Position (Period; Column)	$_{10}$[Ne]$\underline{3s^2}$ (P 3; Col $\underline{2A}$)	$_{10}$[Ne]$\underline{3s^2 3p^4}$ (P 3; Col $\underline{6A}$)	$_{18}$[Ar]$\underline{4s^1 3d^5}$ (P 4; Col $\underline{6B}$)
Number of unpaired electrons	0 (no unpaired electrons)	2 (it exists unpaired electrons)	6 it exists unpaired electrons)
Magnetism *(paramagnetic or diamagnetic)*	Diamagnetic	Paramagnetic	Paramagnetic

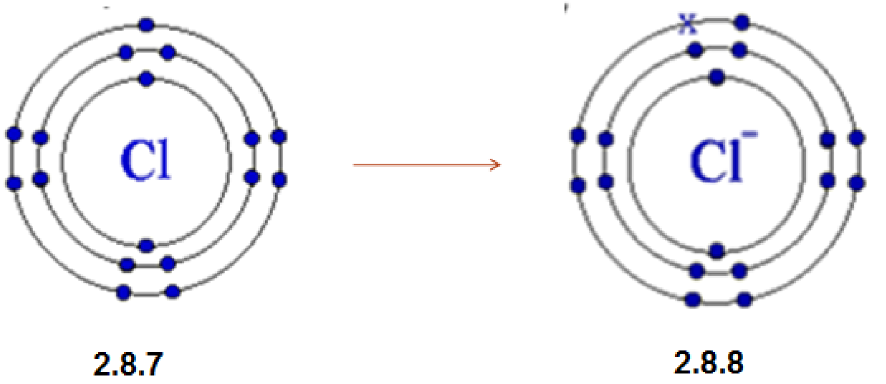
* *The ions*

- Most atoms do not have 8 electrons in their valence electron shell as the noble gases have.
- Some atoms have only a few electrons in their outer shell, while some atoms lack only 1 or 2 electrons to have an octet (8 electrons).
- In cases where an atom has 3 or fewer valence electrons (such as Na, Ca,…), the atom may lose those valence electrons quite easily until what remains is a lower shell that contains an octet. Atoms that lose electrons acquire a positive charge as a result because they are left with fewer negatively charged electrons to balance the positive charges of the protons in the nucleus. Positively charged ions are called <u>cations</u>. Most metals become cations when they make ionic compounds.





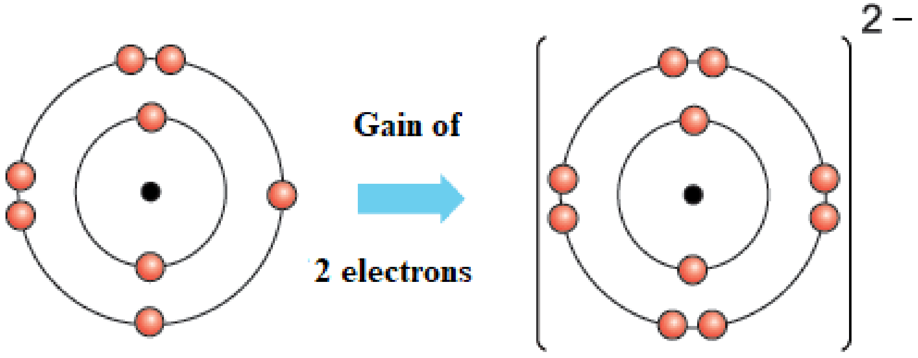
- Some other atoms have nearly 8 electrons in their valence shell (such as O, Cl,…)and can gain additional valence electrons until they have an octet. When these atoms gain electrons, they acquire a negative charge because they now possess more electrons than protons. Negatively charged ions are called anions. Most non-metals become anions when they make ionic compounds.



Chlorine atom, Cl
Charge of protons = + 17
Charge of electron = - 17
Total Charge = 0

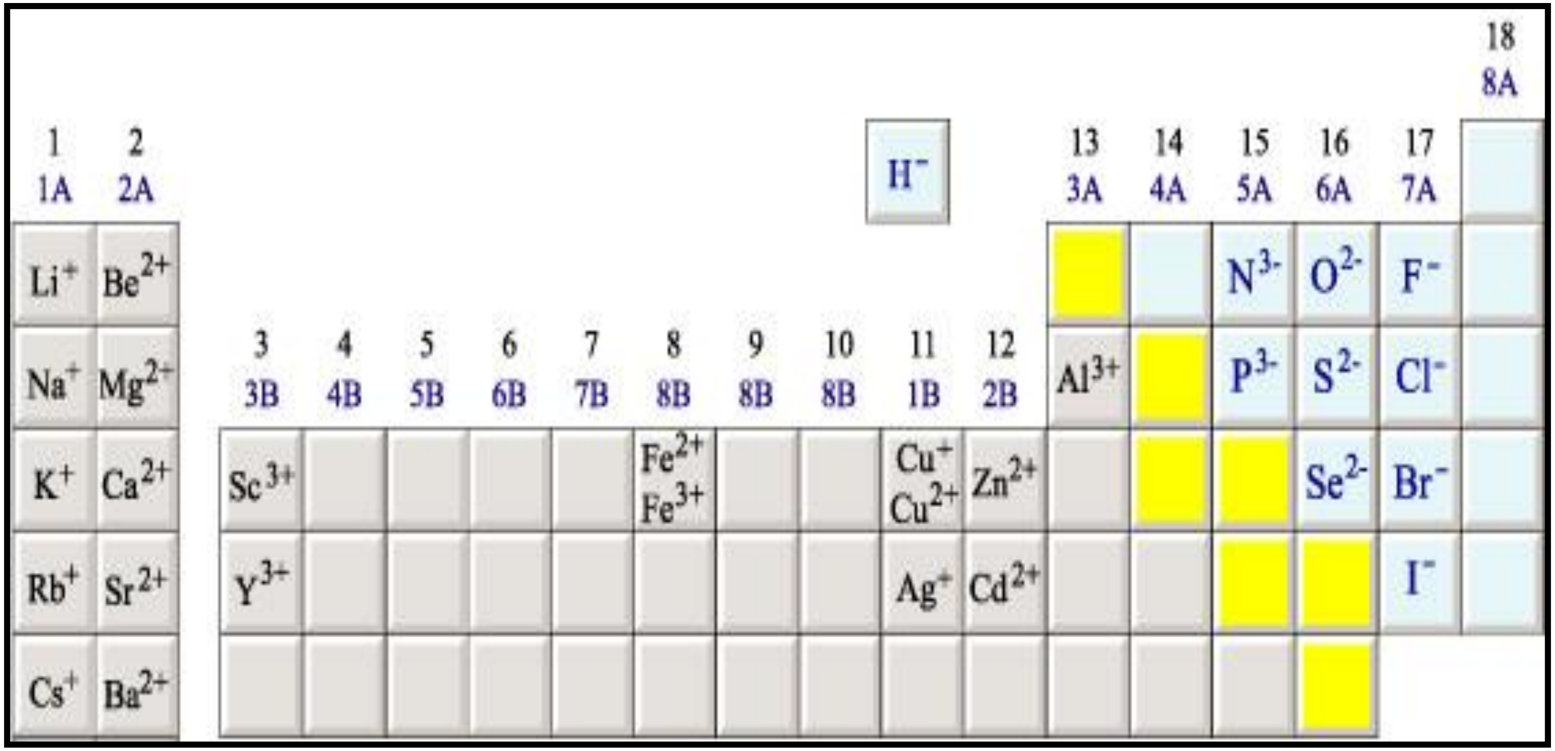
Chlorine ion, Cl-
Charge of protons = + 16
Charge of electron = - 17
Total Charge = - 1

$$Cl + e^- \rightarrow Cl^-$$



$$O + 2e^- \rightarrow O^{2-}$$

- In many cases, elements that belong to the same group (vertical column) on the periodic table form ions with the same charge because they have the same number of valence electrons (See the table below). Thus, the periodic table becomes a tool for remembering the charges on many ions. For example, all ions made from alkali metals (Li, Na,…), the 1st column on the periodic table, have a +1 charge. Ions made from alkaline earth metals (Be, Mg, Ca,…), the 2nd group on the periodic table, have a +2 charge. On the other side of the periodic table, the next-to-last column, the halogens (F, Cl,…), form ions having a -1 charge and the chalcogens (group 16 or 6A: O, S,…) form ions having a -2 charge.



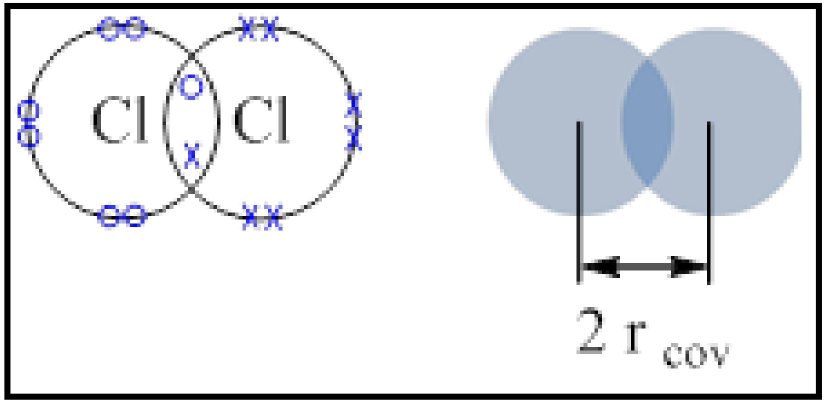
1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9 8B	10 8B	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
										H^-							
Li^+	Be^{2+}											🟨		N^{3-}	O^{2-}	F^-	
Na^+	Mg^{2+}											Al^{3+}	🟨	P^{3-}	S^{2-}	Cl^-	
K^+	Ca^{2+}	Sc^{3+}					Fe^{2+} Fe^{3+}			Cu^+ Cu^{2+}	Zn^{2+}		🟨	🟨	Se^{2-}	Br^-	
Rb^+	Sr^{2+}	Y^{3+}								Ag^+	Cd^{2+}			🟨	🟨	I^-	
Cs^+	Ba^{2+}														🟨		

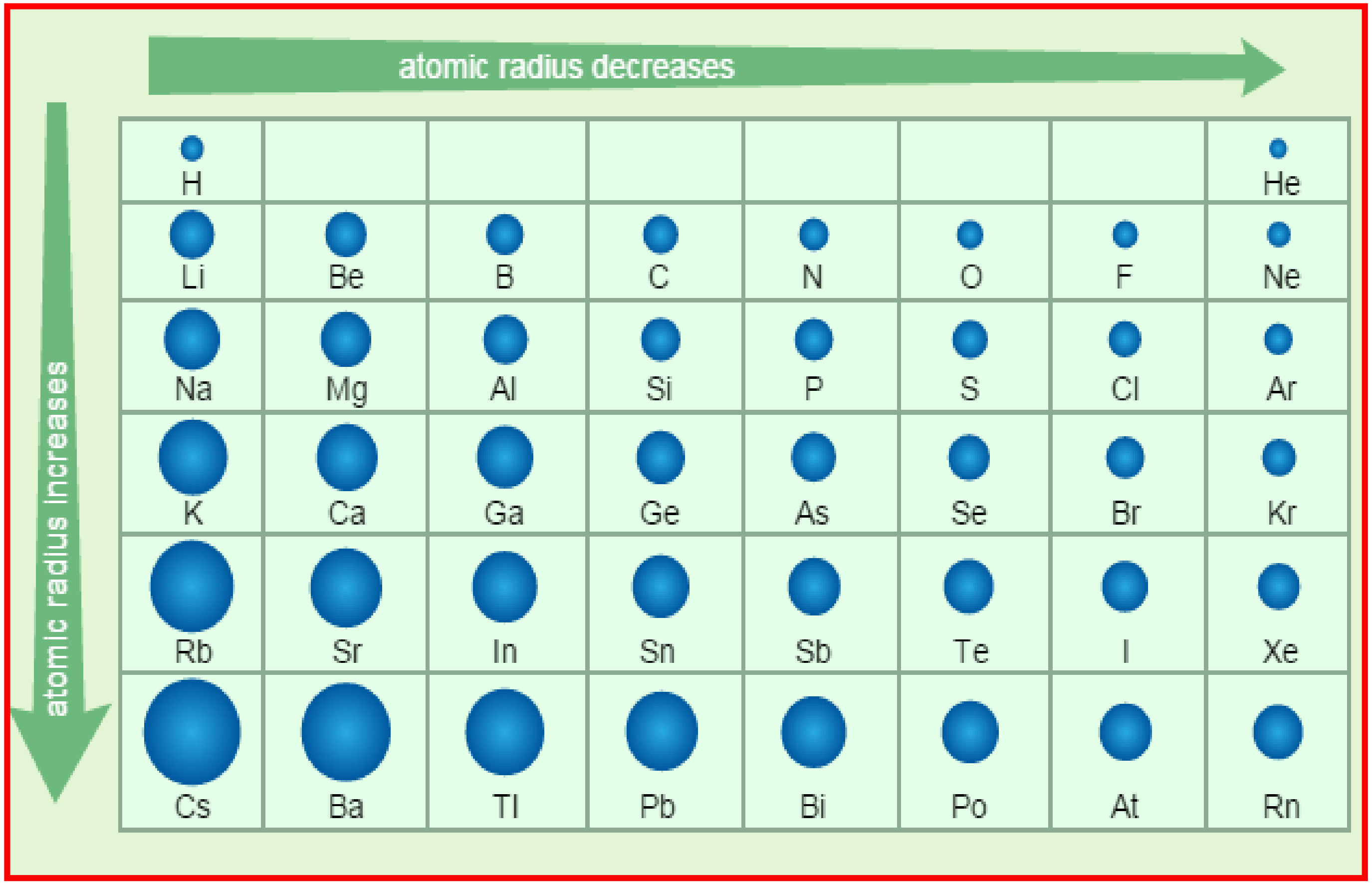
❑ THE PERIODIC TRENDS OF PROPERTIES OF THE ELEMENTS

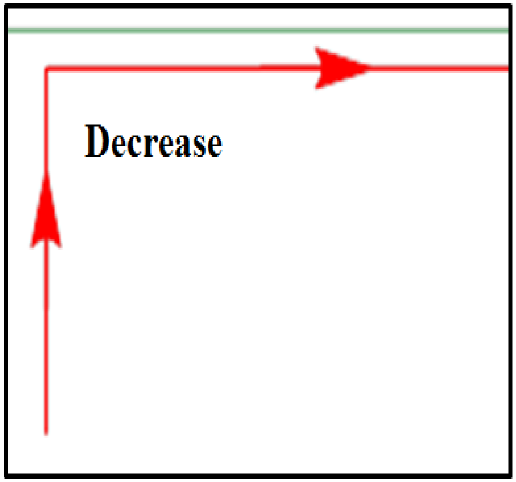
In the periodic table, the electron configuration of the elements shows a periodic variation with increasing atomic number, Z. Consequently there are also periodic variations in physical and chemical properties.

➢ THE ATOMIC RADIUS TRENDS

The atomic radius of an atom can be measured from its covalent atomic radius, r_{cov}, which is the half of the distance between the nuclei of two like atoms joined by a covalent bond in the same molecule, such as H_2, Cl_2, and O_2.



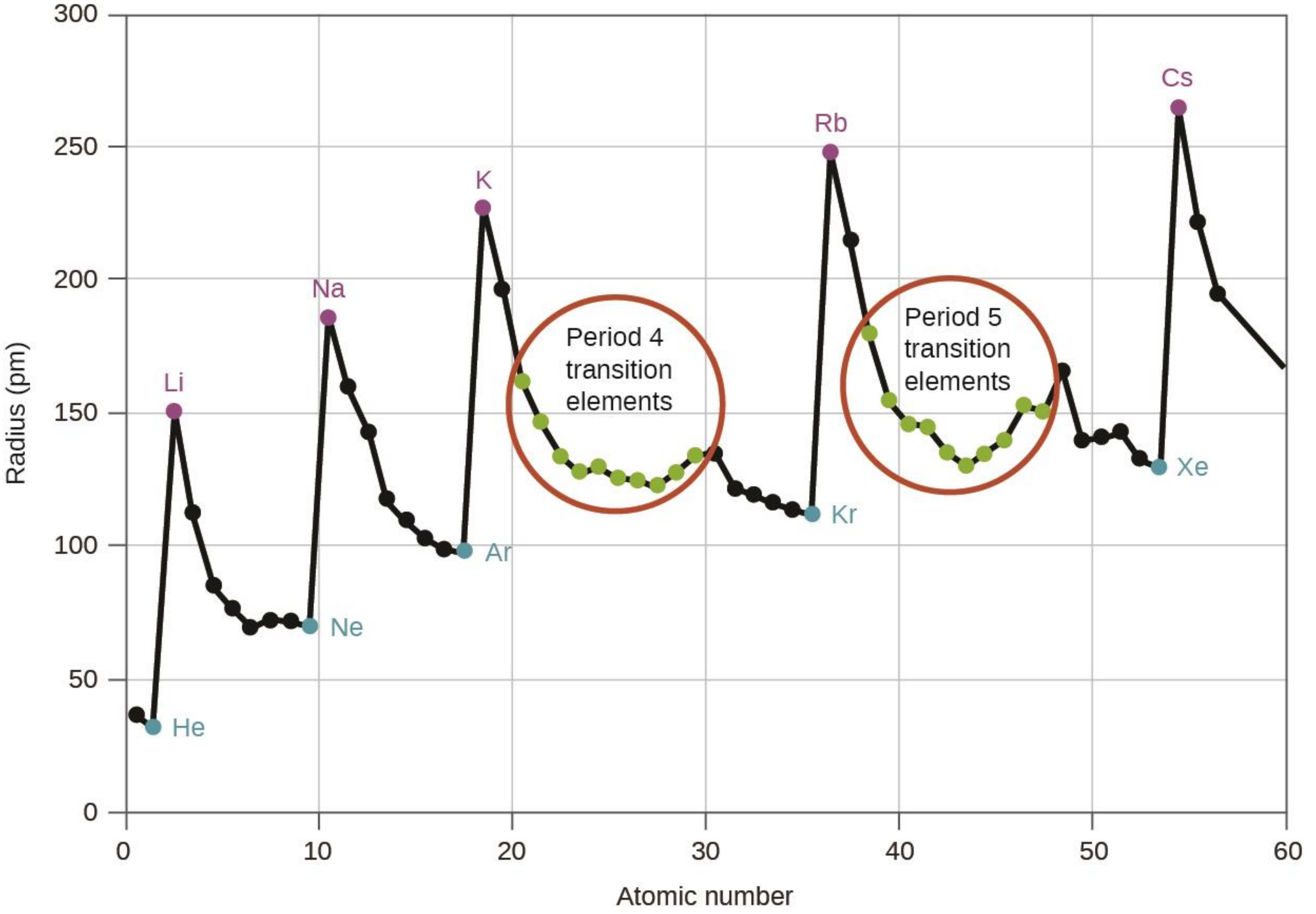




- Within a **group** of the period table, the **atomic radius increases** from **up to down.**

- Within a **period** of the period table, the atomic radius decreases from **left to right.**

✓The atomic radius exhibits periodicity on the periodic table.



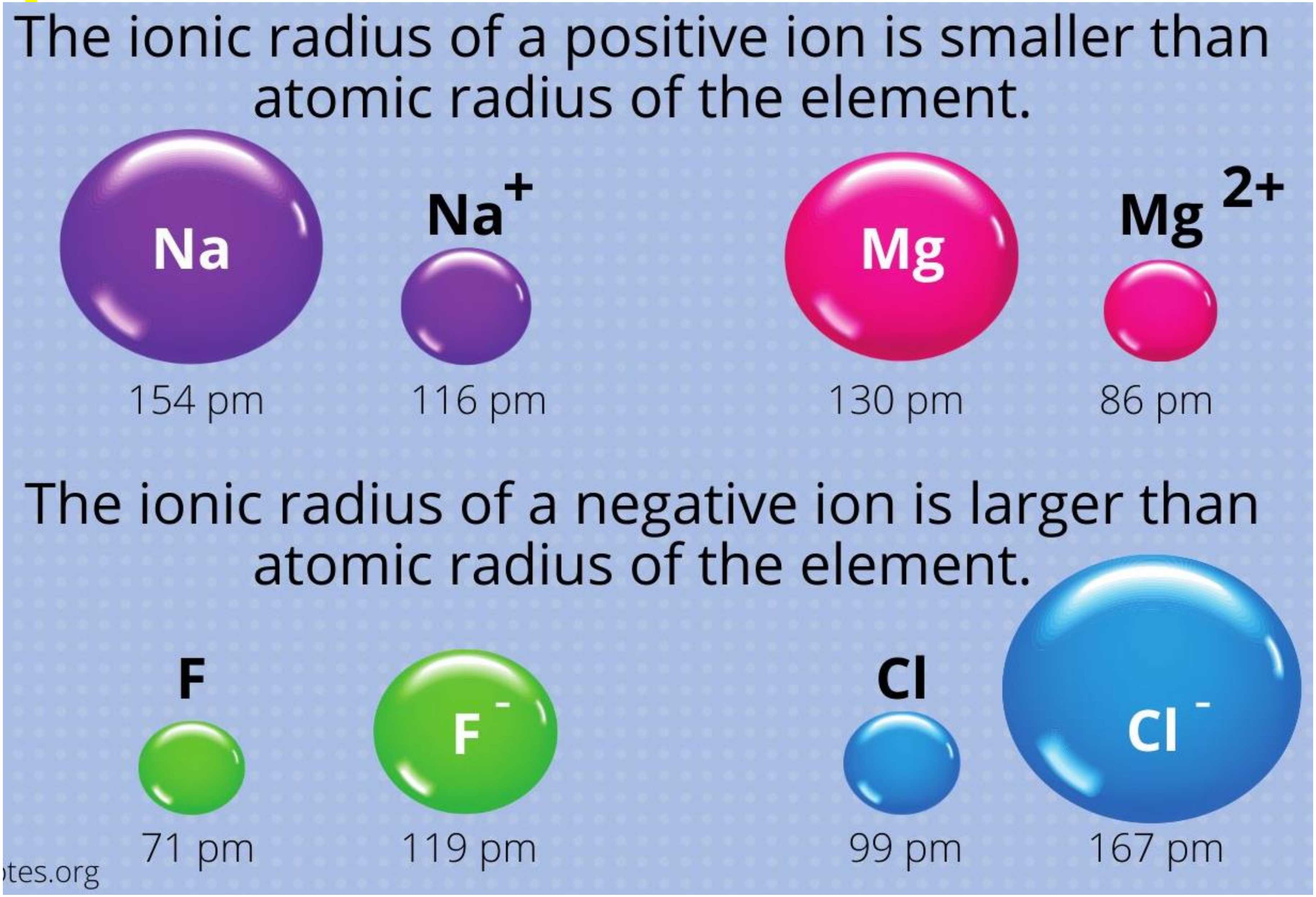
Exercise :

Referring to the periodic table, arrange the following elements by increasing atomic radius: P (Z = 15), N (Z = 7), O (Z = 8), F (Z = 9)

Answer :

F < O < N < P

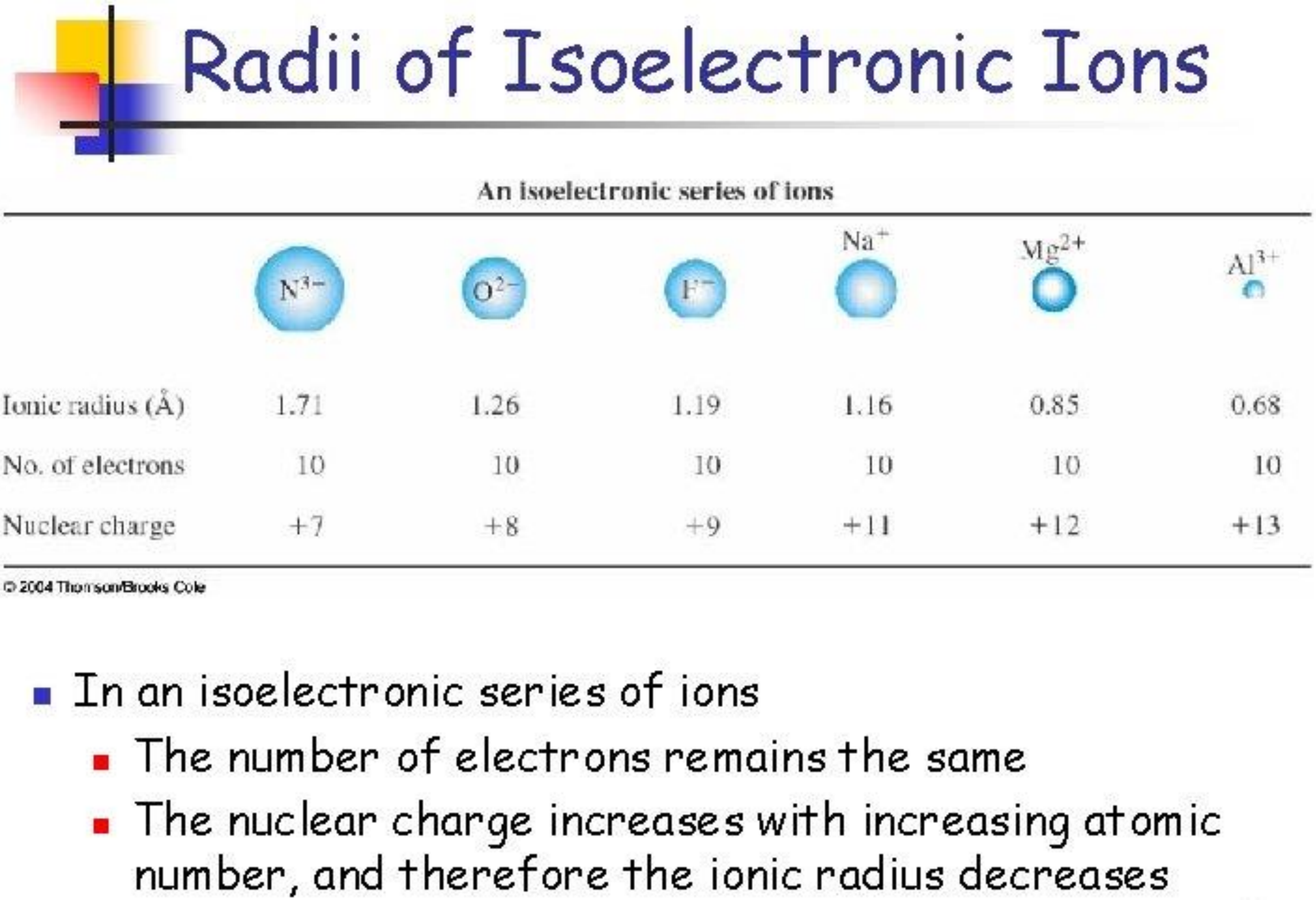
- **THE IONIC RADIUS TRENDS**



The ionic radius of a positive ion is smaller than atomic radius of the element.

The ionic radius of a negative ion is larger than atomic radius of the element.

An **Isoelectronic Series** is a group of atoms/ions that have the same number of electrons.



Radii of Isoelectronic Ions

An isoelectronic series of ions

	N^{3-}	O^{2-}	F^-	Na^+	Mg^{2+}	Al^{3+}
Ionic radius (Å)	1.71	1.26	1.19	1.16	0.85	0.68
No. of electrons	10	10	10	10	10	10
Nuclear charge	+7	+8	+9	+11	+12	+13

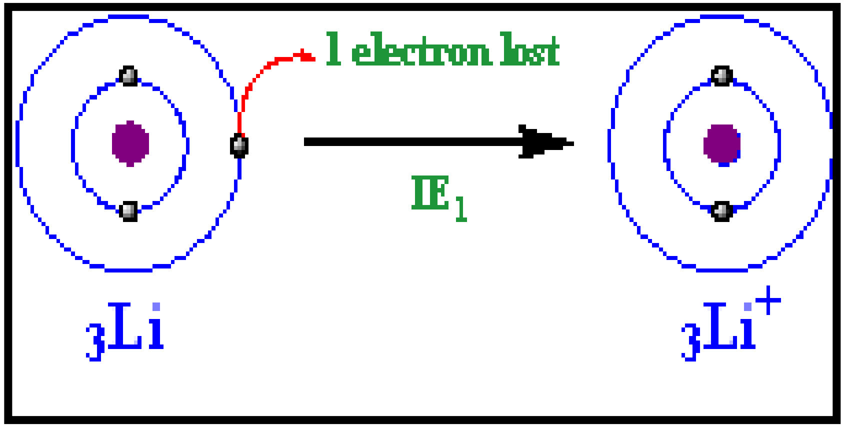
- In an isoelectronic series of ions
  - The number of electrons remains the same
  - The nuclear charge increases with increasing atomic number, and therefore the ionic radius decreases

➢ THE IONIZATION ENERGY (IE) TRENDS

By definition, the **first ionization energy** (IE_1) of an element (X) *is the energy needed to remove the outermost (or the most loosely held) electron from an isolated gaseous atom in its ground state:* $\mathbf{X_{(g)} \rightarrow X^+_{(g)} + e^-}$

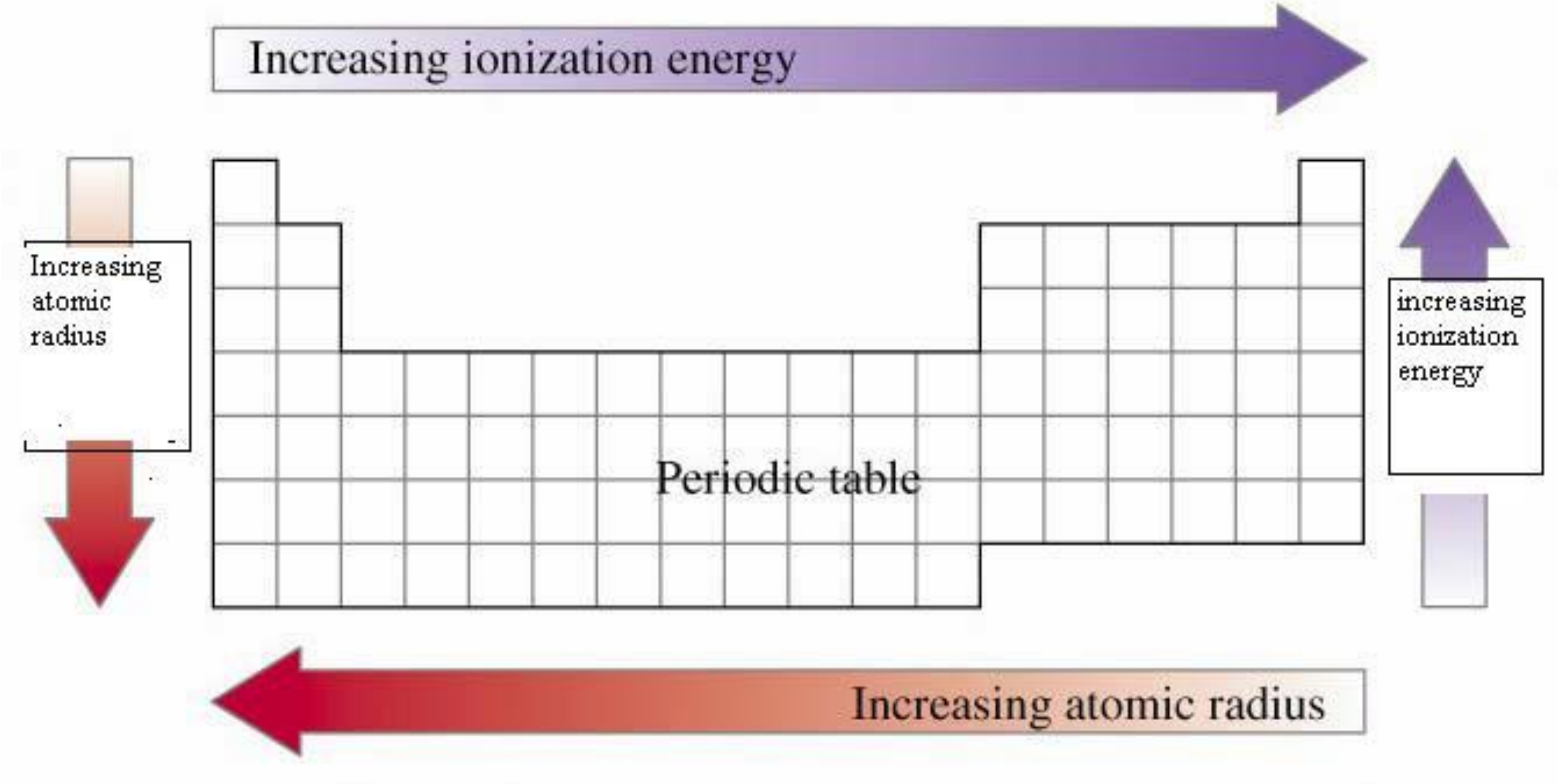
---For example for lithium atom ($_3Li$), the reaction associated for the first ionization energy is:

$$Li_{(g)} \rightarrow Li^+_{(g)} + e^-$$

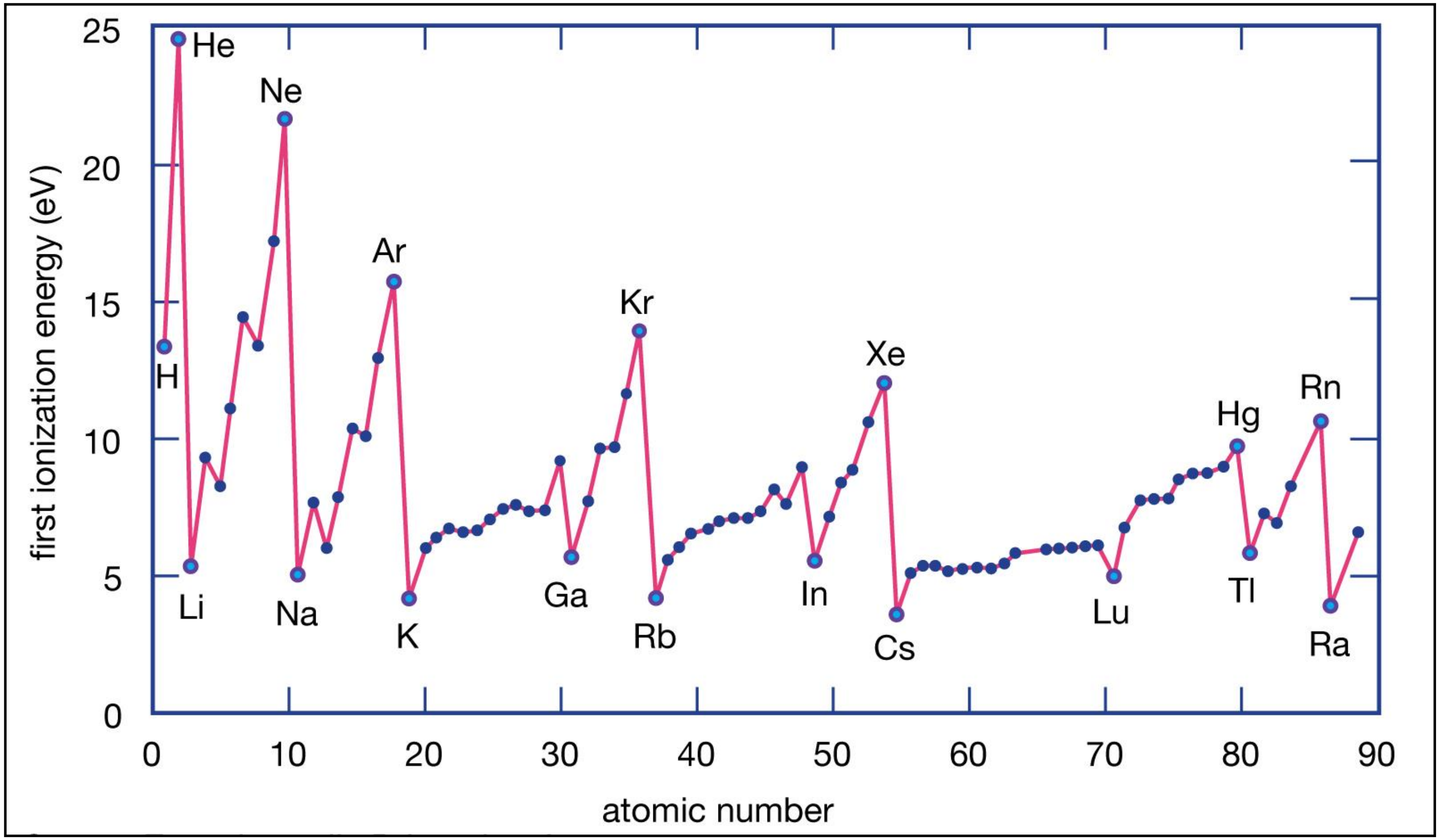


**The closer the electron to the nuclear the higher the attraction force, and thus the higher the energy required to overcome this attraction and remove the electron.

Therefore the smaller the radius the higher the ionization energy, and the bigger the radius the lower the energy need.

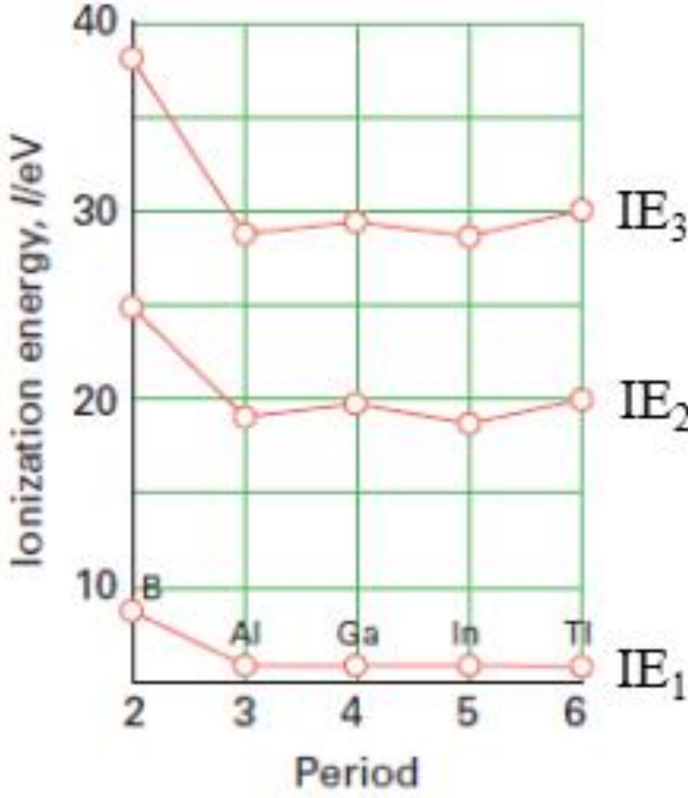


- In general, within a **group** of the period table, the ionization energy **increases** from **down to up** (the opposite of the atomic radius trend).
- In general, within a **period** of the period table, the ionization energy **increases** from **left to right** (the opposite of the atomic radius trend).



- ✓ Ionization energy exhibits periodicity on the periodic table.
- ✓ The *IE* of noble gases is the largest, therefore they are the most stable elements.
- ✓ The *IE* of Be, Mg, Zn, Cd, Hg, are higher than the elements that follow because each of them has filled s-subshell (ns^2).
- ✓ The IE of the p-block elements with the valence shell ns^2np^3, have higher value than the elements that follow because each of them has half-filled p-subshell (np^3).

- ✓ Some elements have several ionization energies; thes varying energies are referred to as the first ionizatio energy (IE_1), the second ionization energy (IE_2), thir ionization energy (IE_3), etc. The first ionization energ is the energy required to remove the outermost, c highest, energy electron, the second ionization energ is the energy required to remove any subsequent higł energy electron from a gaseous cation, etc.



The first, second, and third ionization energies of the elements of Group 13. Successive ionization energies increase, but there is no clear pattern of ionization energies down the group.

Another important pattern is that successive ionizations c an element require increasingly higher energies;

$$IE_n > IE_{n-1} > \ldots.\ IE_3 > IE_2 > IE_1$$

Exercise :

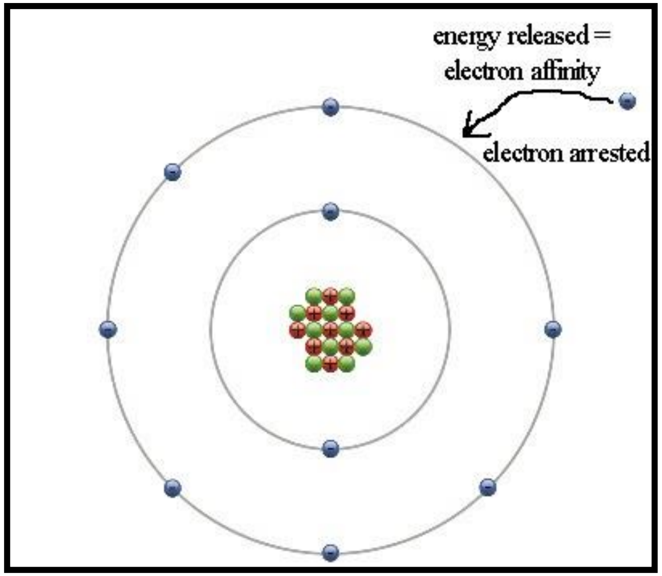
Referring to the periodic table, arrange the following elements by decreasing first ionization energy: P (Z = 15), N (Z = 7), O (Z = 8), F (Z = 9)

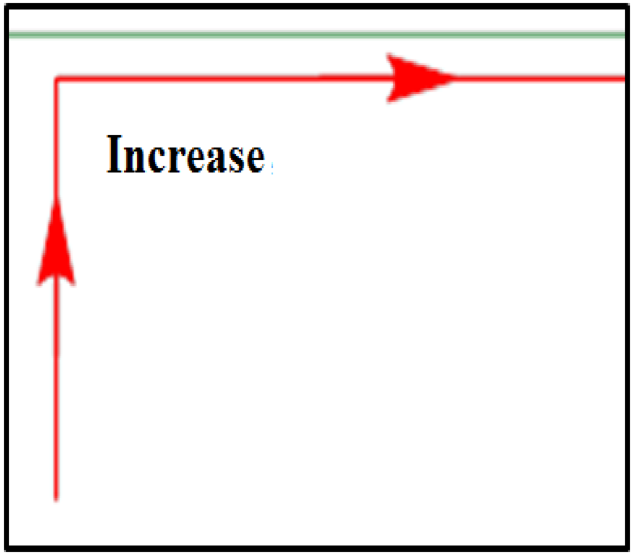
Answer :

F > N > O > P

➢ The Electron Affinity (EA) TRENDS

It is the energy associated with the process in which an electron is added to an isolated gaseous atom in its ground state: $X(g) + e^- \rightarrow X^-(g)$





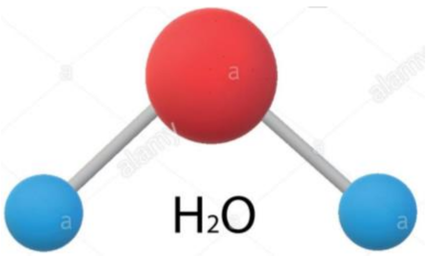
- In general, within a **group**, the EA **increases** from **down to up**.
- In general, within a **period**, the EA **increases** from **left to right**.

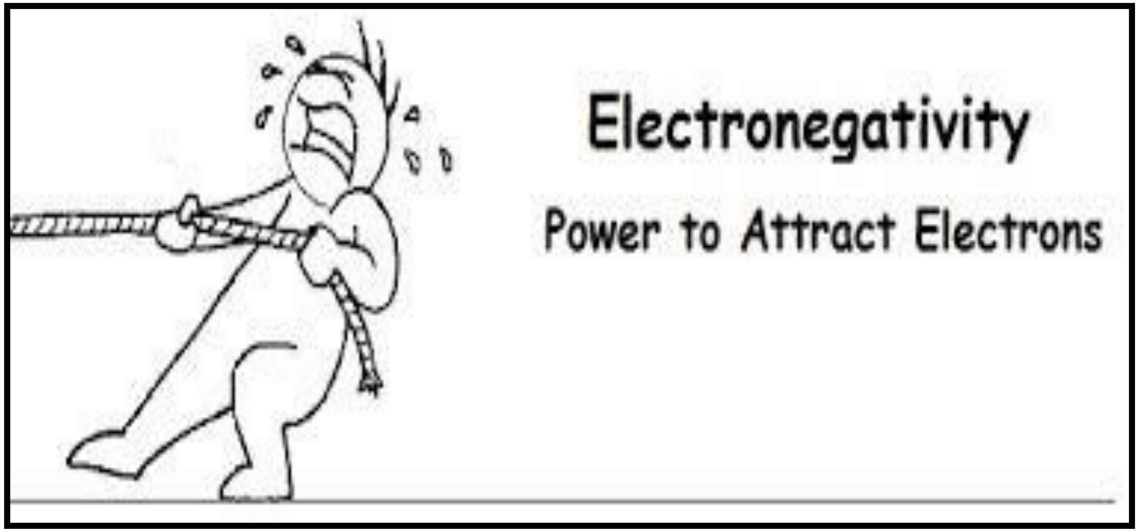
- The Group IIA elements, the alkaline earths, have low electron affinity values. These elements are relatively stable because they have filled *s* subshells.
- Group VIIA elements, the halogens, have high electron affinities because the addition of an electron to an atom results in a completely filled shell.
- Group VIII elements, noble gases, have electron affinities near zero since each atom possesses a stable octet and will not accept an electron readily.

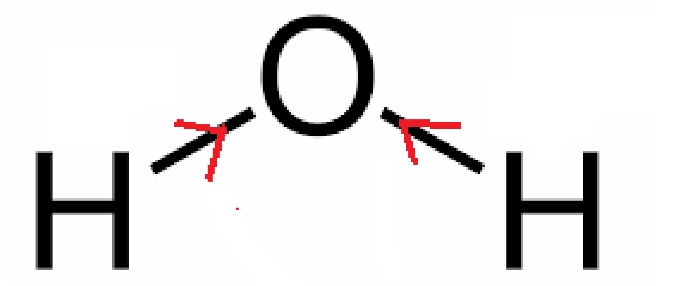
➢ THE ELECTRONEGATIVITY (EN) TRENDS

The Electronegativity (EN) is a chemical property that describes the tendency of an atom or a functional group to attract electrons towards itself.

Electronegativity determines how the shared electrons are distributed between the two atoms in a bond. The more strongly an atom attracts the electrons in its bonds, the larger its electronegativity.

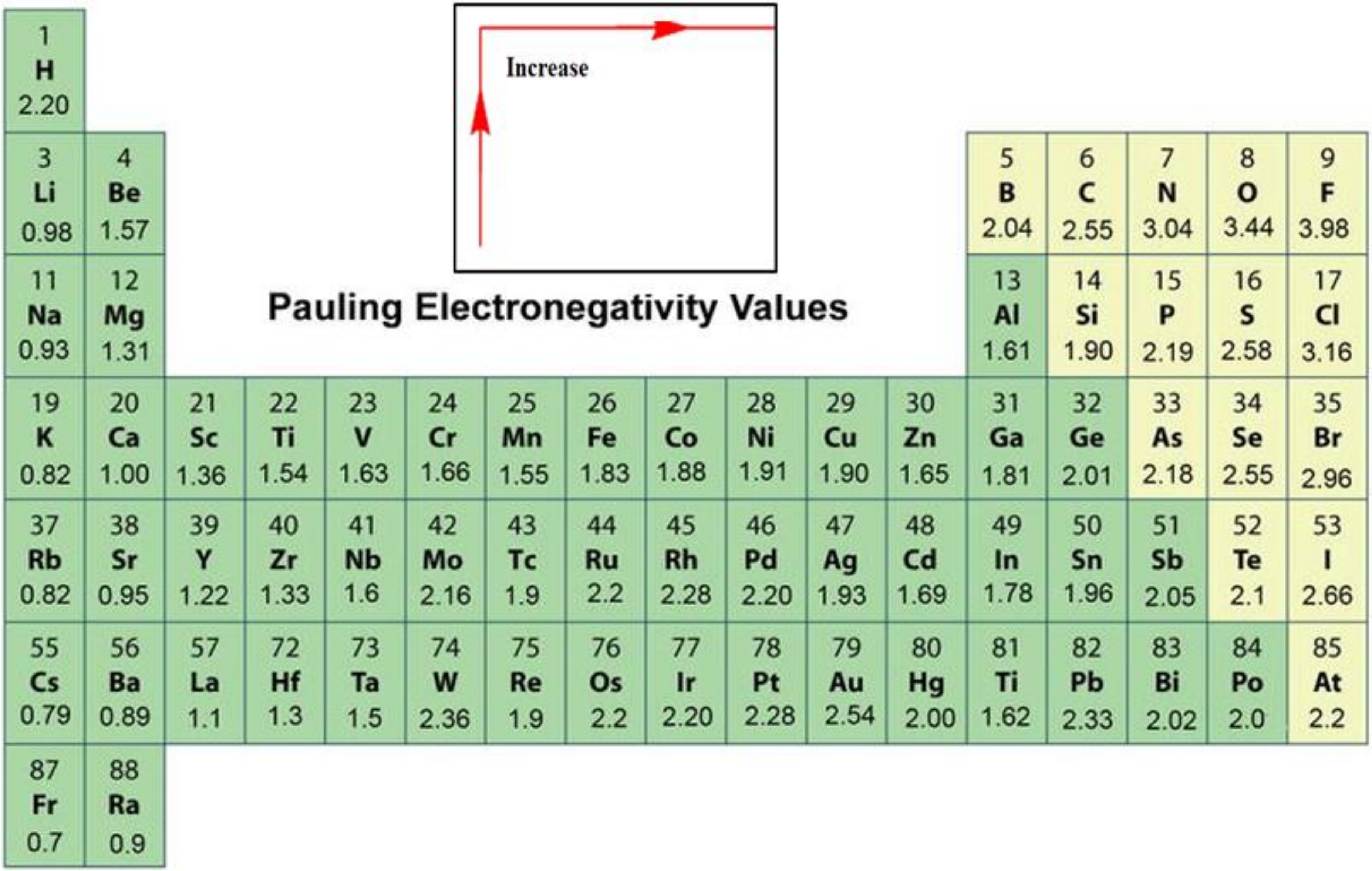






Oxygen atom is more electronegative than hydrogen atom.

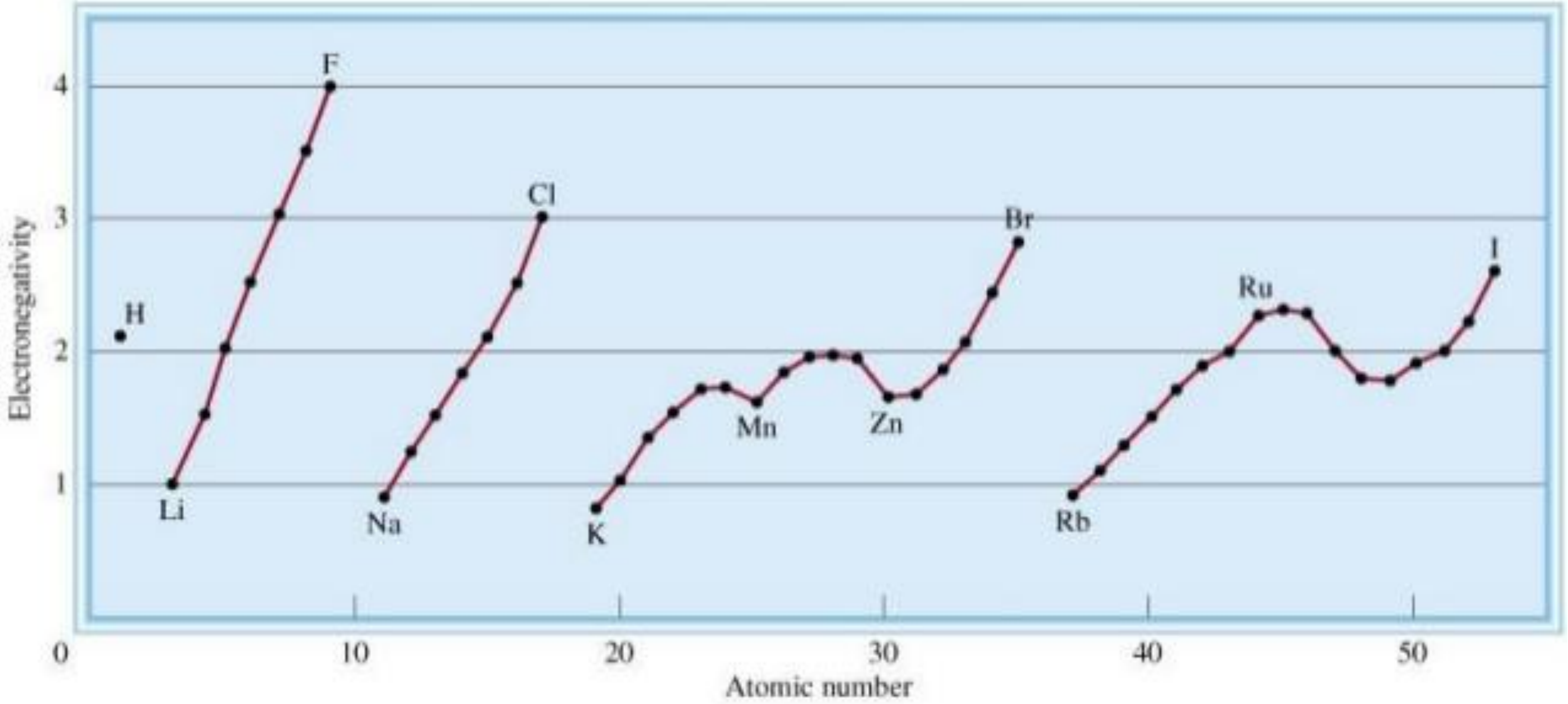
- In general, within a **group**, the EA **increases** from **down to up**.
- In general, within a **period**, the EA **increases** from **left to right**.



Pauling Electronegativity Values

1 H 2.20																
3 Li 0.98	4 Be 1.57											5 B 2.04	6 C 2.55	7 N 3.04	8 O 3.44	9 F 3.98
11 Na 0.93	12 Mg 1.31											13 Al 1.61	14 Si 1.90	15 P 2.19	16 S 2.58	17 Cl 3.16
19 K 0.82	20 Ca 1.00	21 Sc 1.36	22 Ti 1.54	23 V 1.63	24 Cr 1.66	25 Mn 1.55	26 Fe 1.83	27 Co 1.88	28 Ni 1.91	29 Cu 1.90	30 Zn 1.65	31 Ga 1.81	32 Ge 2.01	33 As 2.18	34 Se 2.55	35 Br 2.96
37 Rb 0.82	38 Sr 0.95	39 Y 1.22	40 Zr 1.33	41 Nb 1.6	42 Mo 2.16	43 Tc 1.9	44 Ru 2.2	45 Rh 2.28	46 Pd 2.20	47 Ag 1.93	48 Cd 1.69	49 In 1.78	50 Sn 1.96	51 Sb 2.05	52 Te 2.1	53 I 2.66
55 Cs 0.79	56 Ba 0.89	57 La 1.1	72 Hf 1.3	73 Ta 1.5	74 W 2.36	75 Re 1.9	76 Os 2.2	77 Ir 2.20	78 Pt 2.28	79 Au 2.54	80 Hg 2.00	81 Ti 1.62	82 Pb 2.33	83 Bi 2.02	84 Po 2.0	85 At 2.2
87 Fr 0.7	88 Ra 0.9															

✓ Electronegativity exhibits periodicity on the periodic table. Except for the noble gas elements.

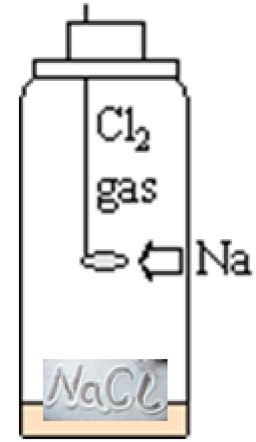


** Elements with high EN tend to acquire electrons in chemical reactions and are found in the upper right corner of the periodic table.

**Elements with low EN, however tend to lose electrons in chemical reactions and are found in the lower left corner of the periodic table. They are said electropositive.

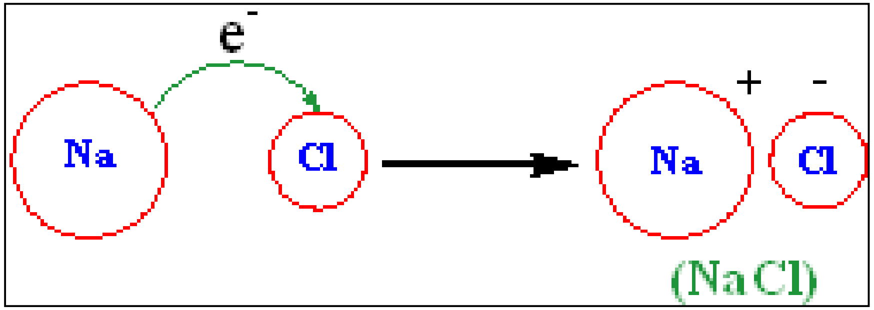
-- For example, at gaseous sate sodium ($_{11}$Na) reacts with chorine ($_{17}$Cl) to yield sodium chloride salt (the table salt), NaCl(s) according to:

$$\mathbf{Na(s) + 1/2\ Cl_2(g) \longrightarrow NaCl(s)}$$



**NaCl(s) is an ionic compound. It is formed of Na^+ and Cl^- ions held together by electrostatic forces.

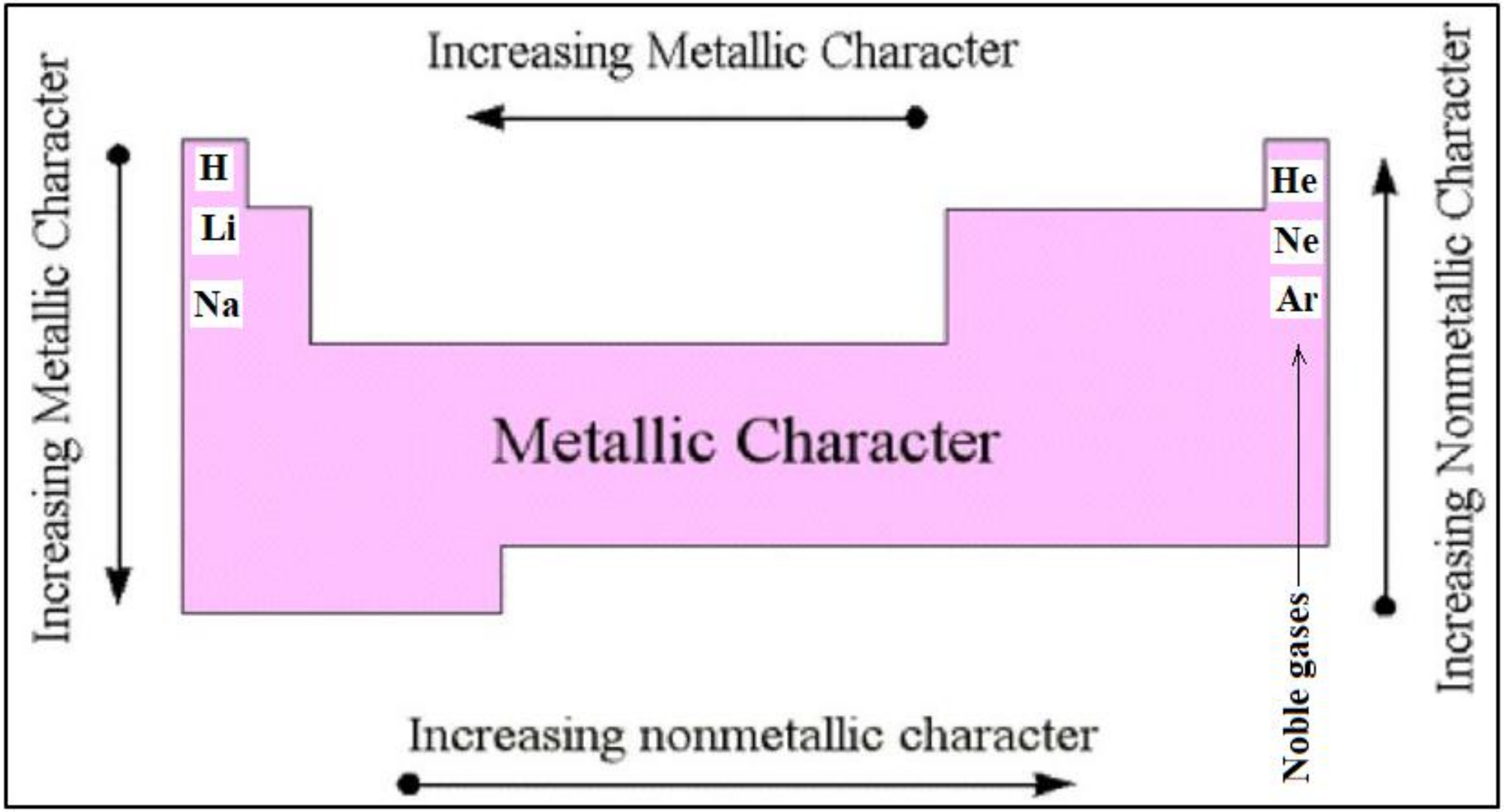
**In the reaction given above, a Na loses an electron, whereas a Cl atom gains the electron. Cl is said to be more electronegative than Na and vice-versa.



➢ THE METALLIC CHARACTER TRENDS

The metallic character of an element can be defined as how readily an atom can lose an electron.

- In general, within a **group**, the metallic character **increases** from **up to down**.
- In general, within a **period**, the metallic character **increases** from **right to left**.



Exercise :

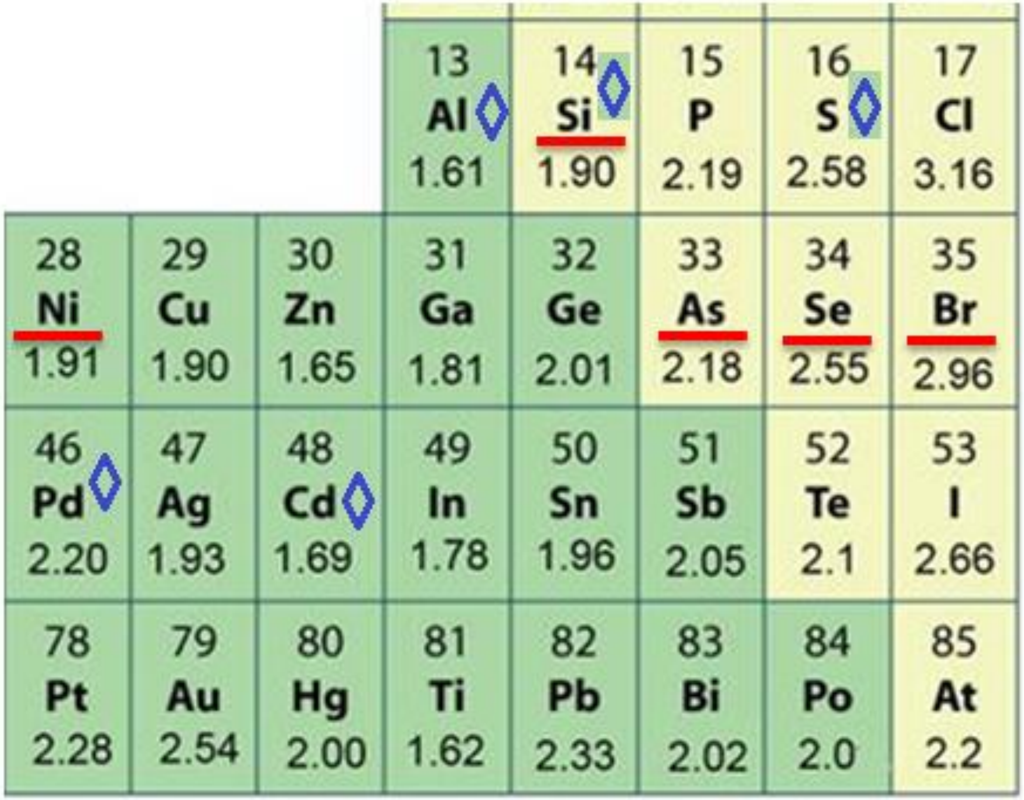
Referring to the periodic table, specify which of these elements has the greatest metallic character: Br, Se, Ni, As, Si

Answer : Ni

Exercise :

Referring to the periodic table, specify which of these elements has the greatest non-metallic character: Pd, Si, Al, S, Cd

Answer : S



			13 Al 1.61	14 Si 1.90	15 P 2.19	16 S 2.58	17 Cl 3.16
28 Ni 1.91	29 Cu 1.90	30 Zn 1.65	31 Ga 1.81	32 Ge 2.01	33 As 2.18	34 Se 2.55	35 Br 2.96
46 Pd 2.20	47 Ag 1.93	48 Cd 1.69	49 In 1.78	50 Sn 1.96	51 Sb 2.05	52 Te 2.1	53 I 2.66
78 Pt 2.28	79 Au 2.54	80 Hg 2.00	81 Ti 1.62	82 Pb 2.33	83 Bi 2.02	84 Po 2.0	85 At 2.2

➢ THE OXIDATION STATE

The oxidation state to which is associated an oxidation number, is an indicator of the degree of oxidation (loss of electrons) of an atom.

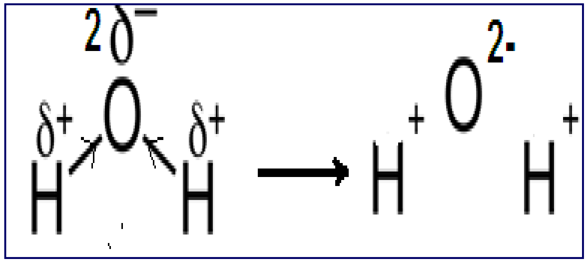
The oxidation number, which may be positive, negative or zero, is the formal (hypothetical) or actual (real) charge that an atom would have if all bonds to atoms of different elements were 100% ionic.

In the hypothetical ions which formed, the more electronegative atom gains the electron(s) of the chemical bond(s), whereas the less electronegative losses it (them).

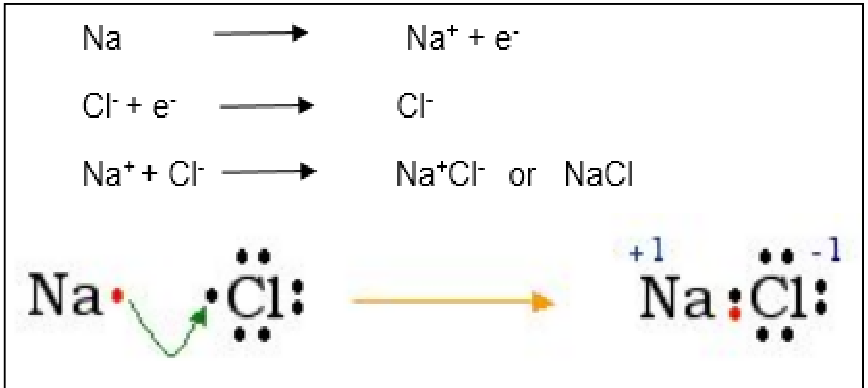
Examples:

* For H_2O since O is more electronegative than H, the oxidation number of H and O are +1 and -2, respectively.

In H_2O which is a covalent compound, the charges +1 and -2 are hypothetical and not real.



** For NaCl which is an ionic compound (Na^+Cl^-), the oxidation number of Na and Cl are +1 and -1, respectively. Here the charges are real and not formal.

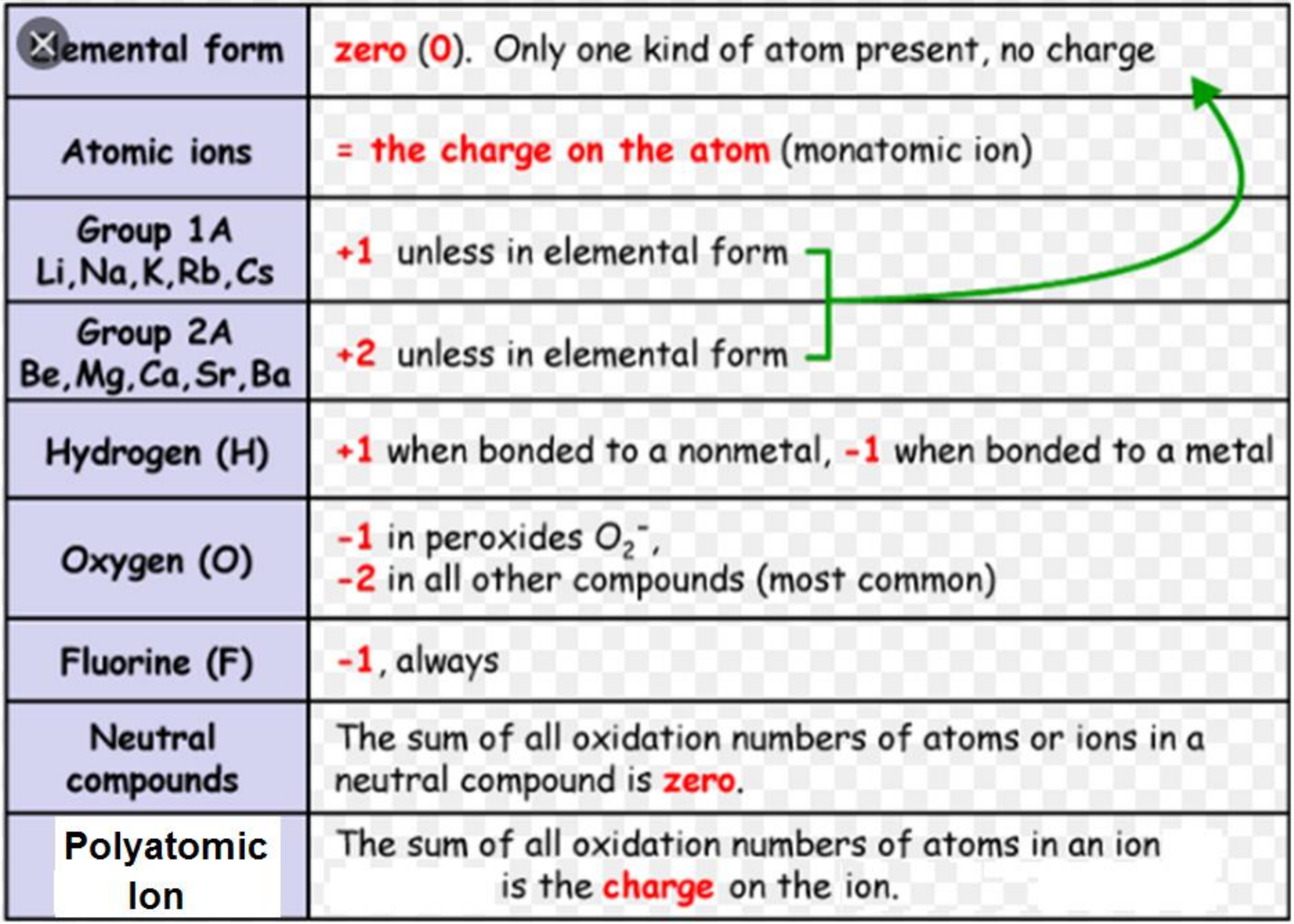


$Na \longrightarrow Na^+ + e^-$

$Cl + e^- \longrightarrow Cl^-$

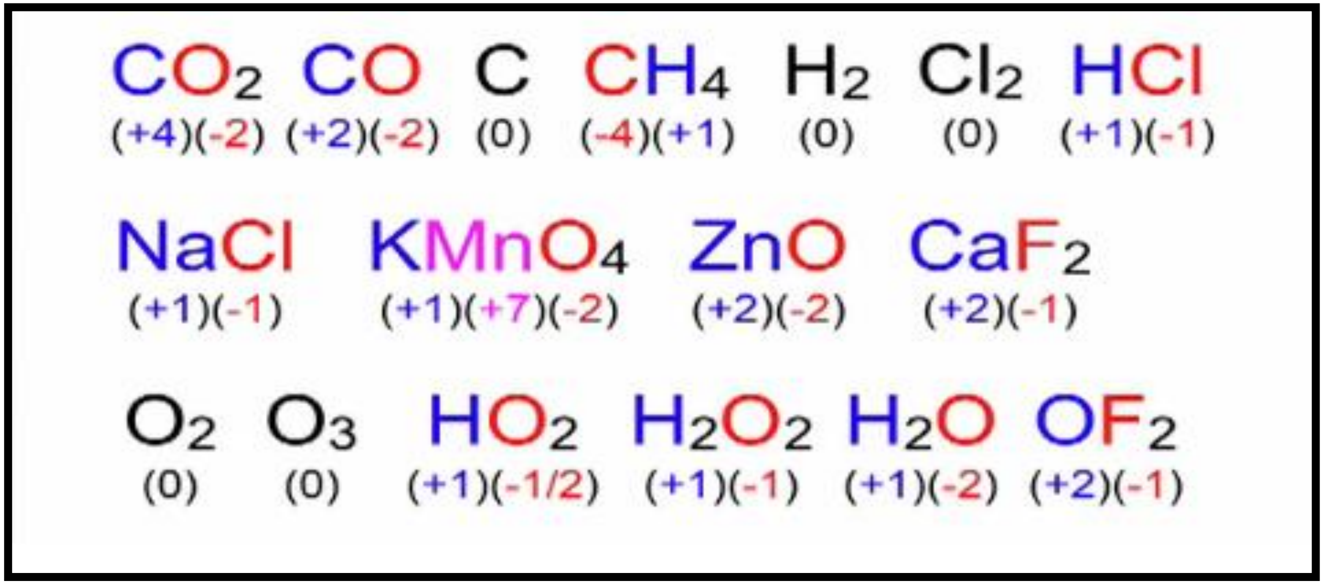
$Na^+ + Cl^- \longrightarrow Na^+Cl^-$ or $NaCl$

** *Rules of Oxidation Number Assignment*

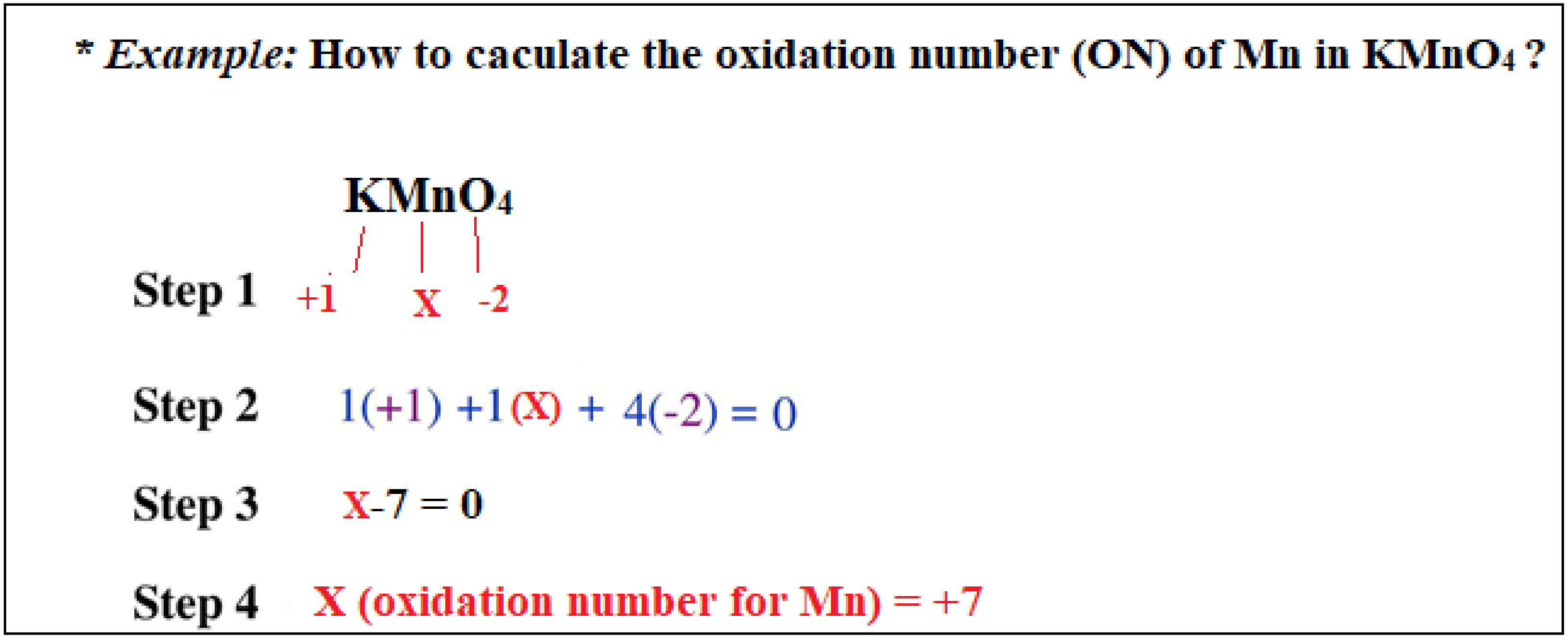


Elemental form	zero (0). Only one kind of atom present, no charge
Atomic ions	= the charge on the atom (monatomic ion)
Group 1A **Li, Na, K, Rb, Cs**	+1 unless in elemental form
Group 2A **Be, Mg, Ca, Sr, Ba**	+2 unless in elemental form
Hydrogen (H)	+1 when bonded to a nonmetal, -1 when bonded to a metal
Oxygen (O)	-1 in peroxides O_2^-, -2 in all other compounds (most common)
Fluorine (F)	-1, always
Neutral compounds	The sum of all oxidation numbers of atoms or ions in a neutral compound is zero.
Polyatomic Ion	The sum of all oxidation numbers of atoms in an ion is the charge on the ion.

** *Examples of Oxidation Number Calculation*



CO_2	CO	C	CH_4	H_2	Cl_2	HCl
(+4)(-2)	(+2)(-2)	(0)	(-4)(+1)	(0)	(0)	(+1)(-1)
$NaCl$	$KMnO_4$	ZnO	CaF_2			
(+1)(-1)	(+1)(+7)(-2)	(+2)(-2)	(+2)(-1)			
O_2	O_3	HO_2	H_2O_2	H_2O	OF_2	
(0)	(0)	(+1)(-1/2)	(+1)(-1)	(+1)(-2)	(+2)(-1)	



* ***Example:*** **How to caculate the oxidation number (ON) of Mn in $KMnO_4$?**

$KMnO_4$

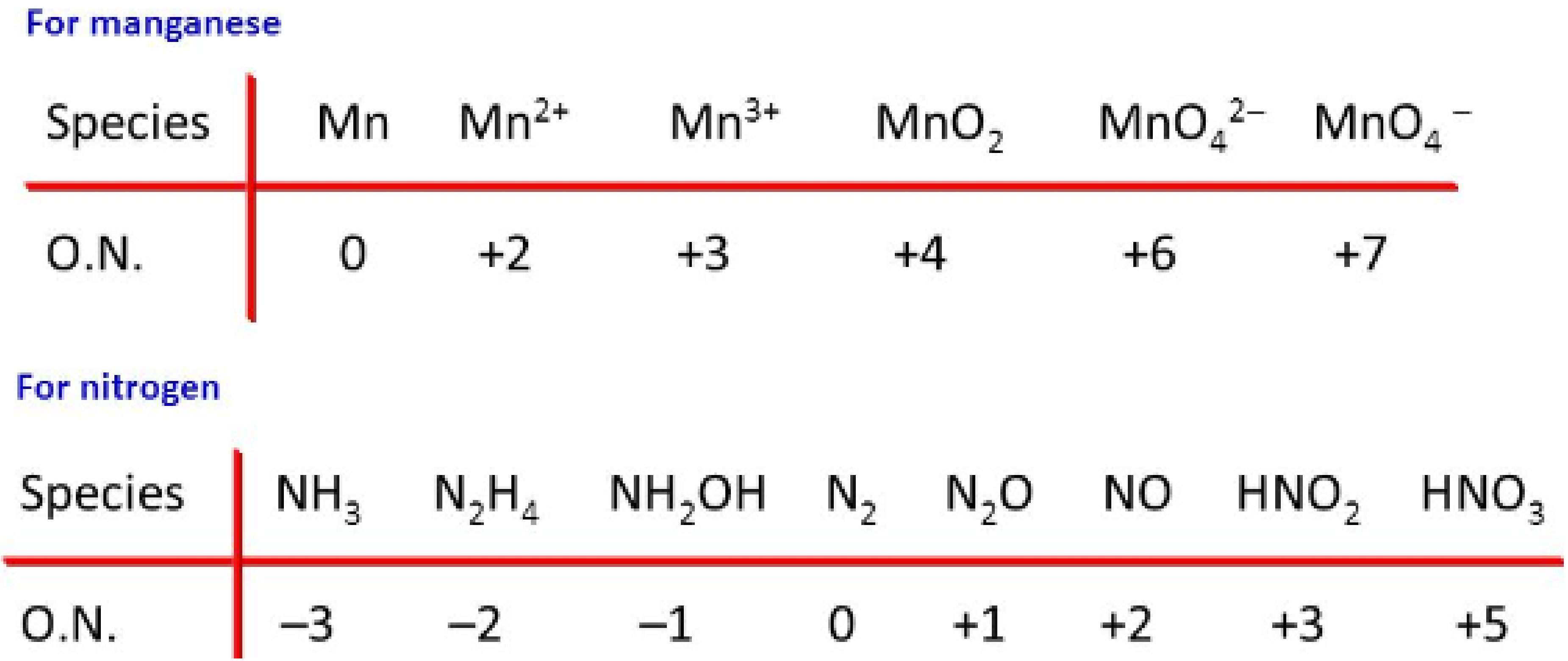
Step 1 $+1 \quad X \quad -2$

Step 2 $1(+1) + 1(X) + 4(-2) = 0$

Step 3 $X - 7 = 0$

Step 4 X (oxidation number for Mn) = +7

***** Other Examples: The Oxidation Number of Mn and N in different chemical species***



For manganese

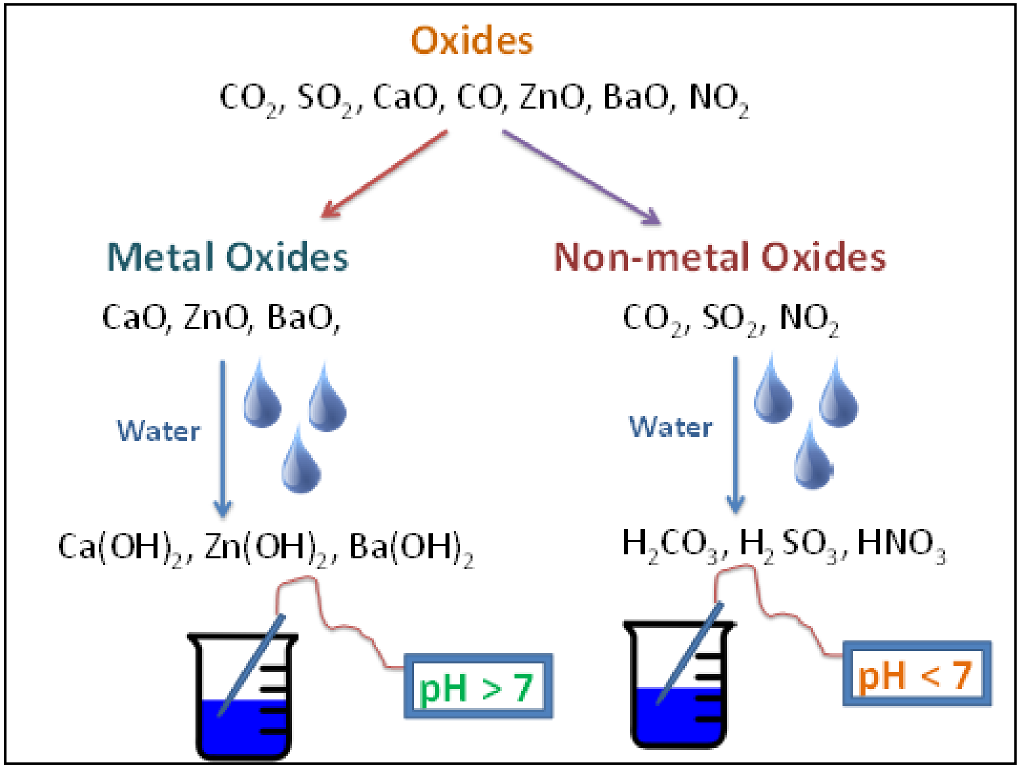
Species	Mn	Mn^{2+}	Mn^{3+}	MnO_2	MnO_4^{2-}	MnO_4^{-}
O.N.	0	+2	+3	+4	+6	+7

For nitrogen

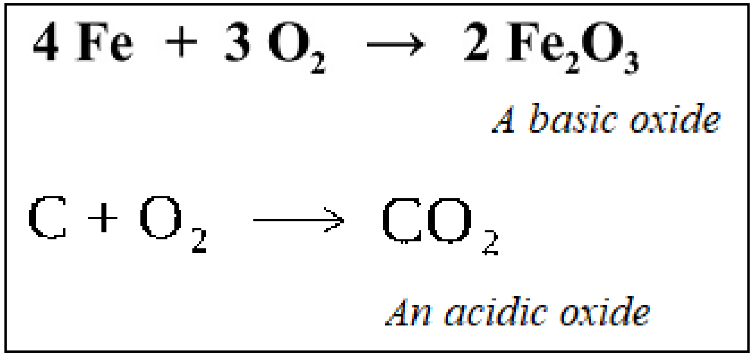
Species	NH_3	N_2H_4	NH_2OH	N_2	N_2O	NO	HNO_2	HNO_3
O.N.	−3	−2	−1	0	+1	+2	+3	+5

THE ACIDE-BASE CHARACTER TRENDS

- Metal oxides that dissolve in water react to form alkaline (or basic) solutions with a pH more than 7 are called basic oxides.
- Water soluble non-metal oxides react with water forming acidic solution with a pH less than 7. The non-metal oxides are called acidic oxides.



- Metals react with oxygen gas to form metal oxides (basic oxides).
- Non-metals react with oxygen gas to produce non-metal oxides (acidic oxides).
- The more basic the oxide is, the less acidic it is and vice-versa.



$$4\,Fe + 3\,O_2 \rightarrow 2\,Fe_2O_3$$

A basic oxide

$$C + O_2 \longrightarrow CO_2$$

An acidic oxide

- In a given period of the period table, from left to right, oxides progress from strongly basic, through weakly basic, amphoteric, and weakly acidic, to strongly acidic. That is for the following oxides, the basicity decreases as:

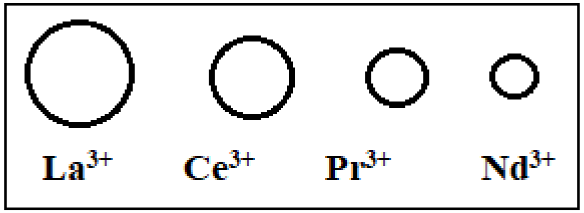
$$Na_2O > MgO > A1_2O_3 > SiO_2 > P_4O_{10} > SO_3 > C1O_2.$$

- Basicity of oxides decreases with increasing oxidation state. As example:

$$MnO > Mn_2O_3 > MnO_2 > Mn_20_7.$$

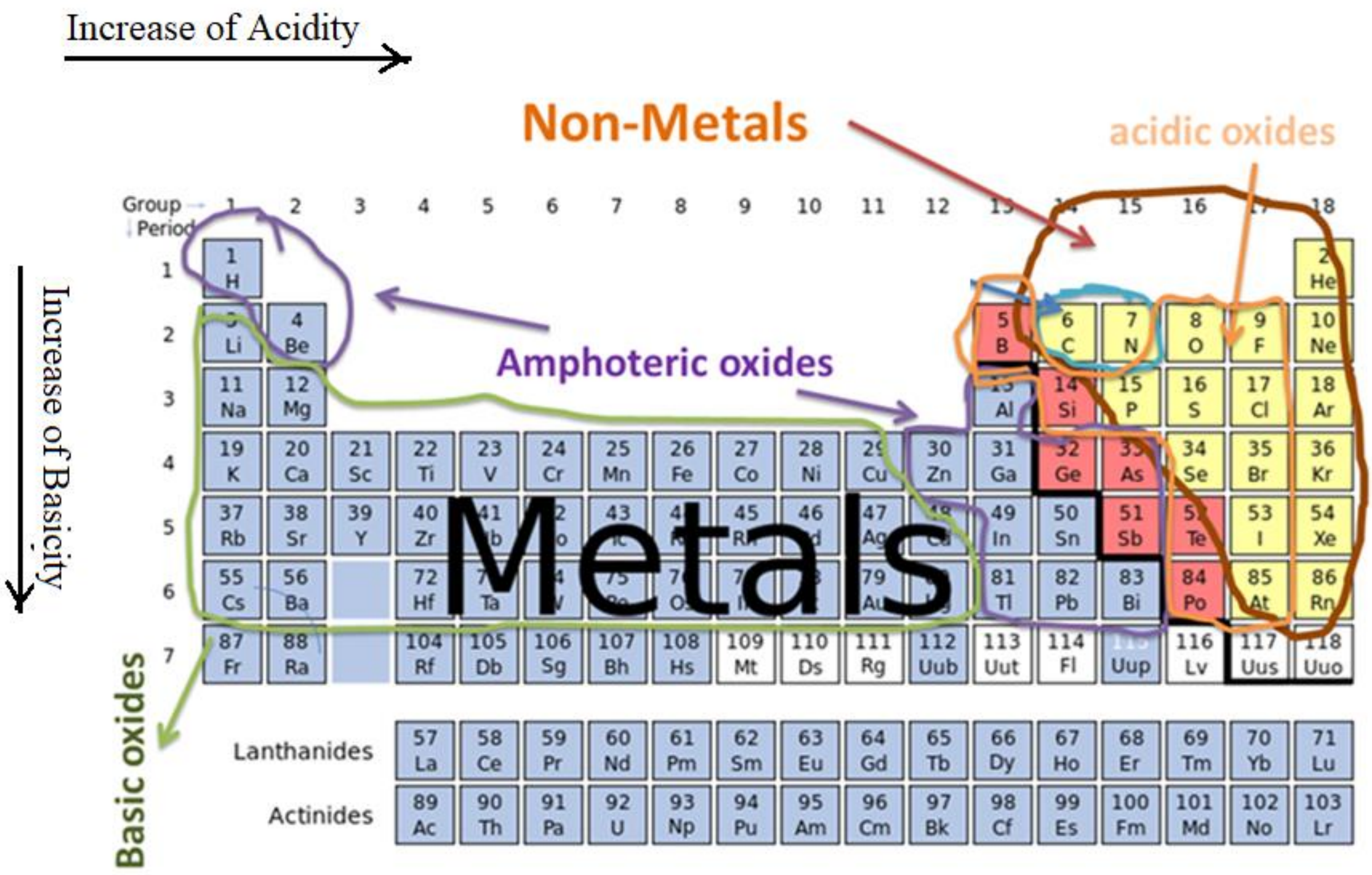
- A similar trend is the decrease in basicity of the lanthanide oxides (Ln_2O_3) from left to right (from La to Lu) consequence of the decrease of ionic radius :

$La_2O_3 > Ce_2O_3 > Pr_2O_3 > Nd_2O_3 > ...$



- In the main groups 1 and 2, basicity of the oxides increases from top to down. For example for Group 2 oxides, the basicity varies in the order: $BeO < MgO < CaO < SrO < BaO$.
- The oxides of the elements between the pure metals and the pure non-metals can chemically react as either acid or base. They are called amphoteric oxides. Examples are:

$$ZnO, Fe_2O_3, Al_2O_3, SnO_2$$



Increase of Acidity

Increase of Basicity

Non-Metals

acidic oxides

Amphoteric oxides

Metals

Basic oxides

non-metals + oxygen = non-metal oxides (mostly acidic oxides)

metals + oxygen = metal oxides (mostly basic oxides)

Exercise :

Classify the following oxides into three types and name the types:

Al_2O_3, CaO, MgO, CO_2, SO_3, Na_2O, ZnO, Fe_2O_3

Answer :

Oxides are of three types: :

- Acidic Oxides: CO_2 (Carbon dioxide), SO_3 (Sulfur trioxide) because C and S are non-metals
- Basic Oxides: CaO (Calcium oxide), MgO (Magnesium oxide), Na_2O (Sodium oxide)

because Na, Ca and Mg are metals at the left or the periodic table.

- Amphoteric Oxides: ZnO (Zinc oxide), Al_2O_3 (Aluminium oxide), Fe_2O_3 (Ferric oxide)

Because Zn, Al and Fe are considered in the middle of the periodic table.

➢ THE MELTING POINT TRENDS

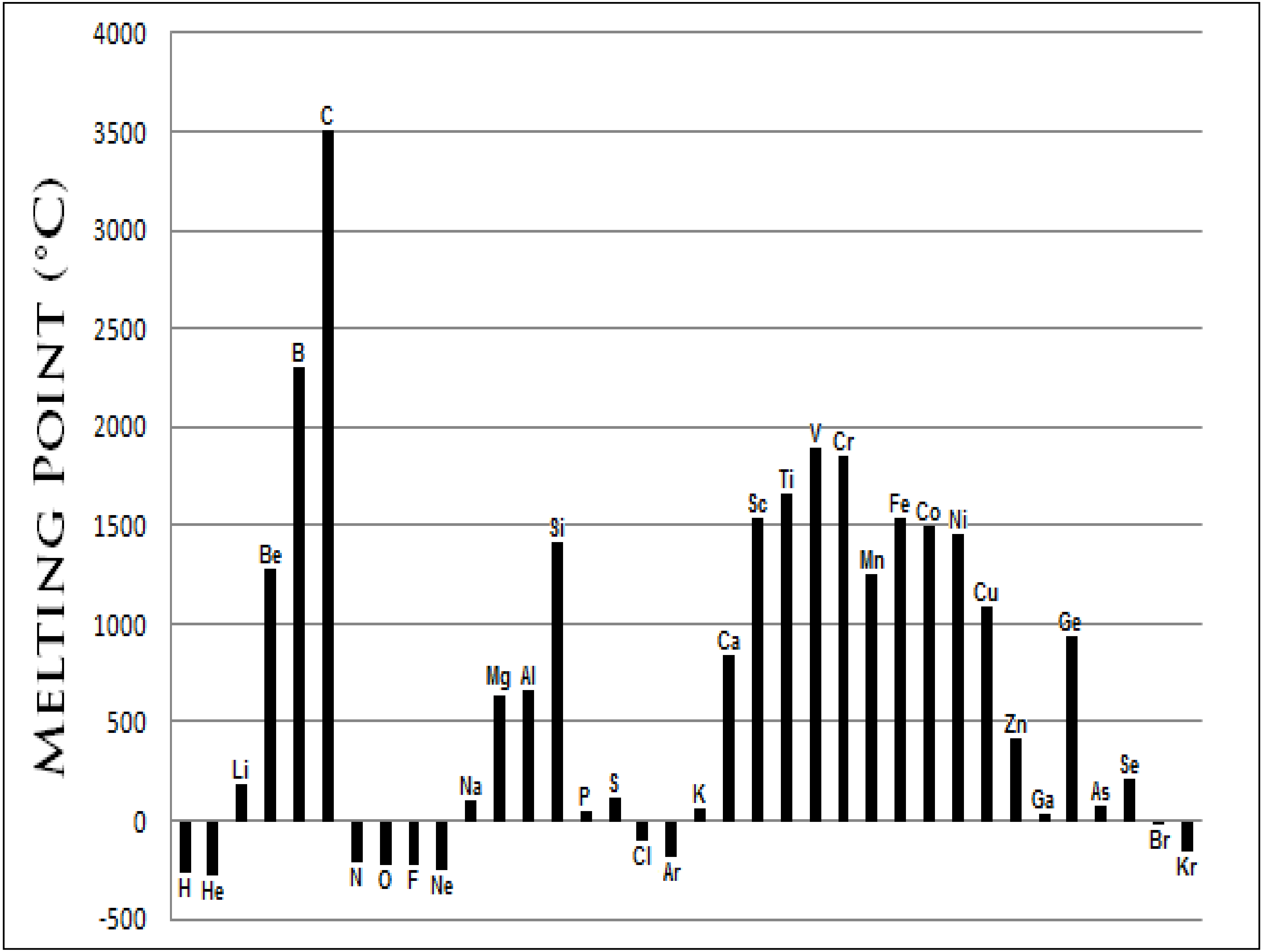
- The melting point (or, rarely, liquefaction point) of a substance is the temperature at which it changes state from solid to liquid.
- At the melting point the solid and liquid phase exist in equilibrium.
- The melting point of a substance depends on pressure and is usually specified at a standard pressure such as 1 atmosphere or 100 kPa.
- Generally, the stronger the bond between the atoms of an element, the more energy required to break that bond.
- Because temperature is directly proportional to energy, a high bond dissociation energy correlates to a high melting temperature.
- Melting points are varied and do not generally form a distinguishable trend across the periodic table. However, certain conclusions can be drawn:

✓ Metals generally possess a high melting point.

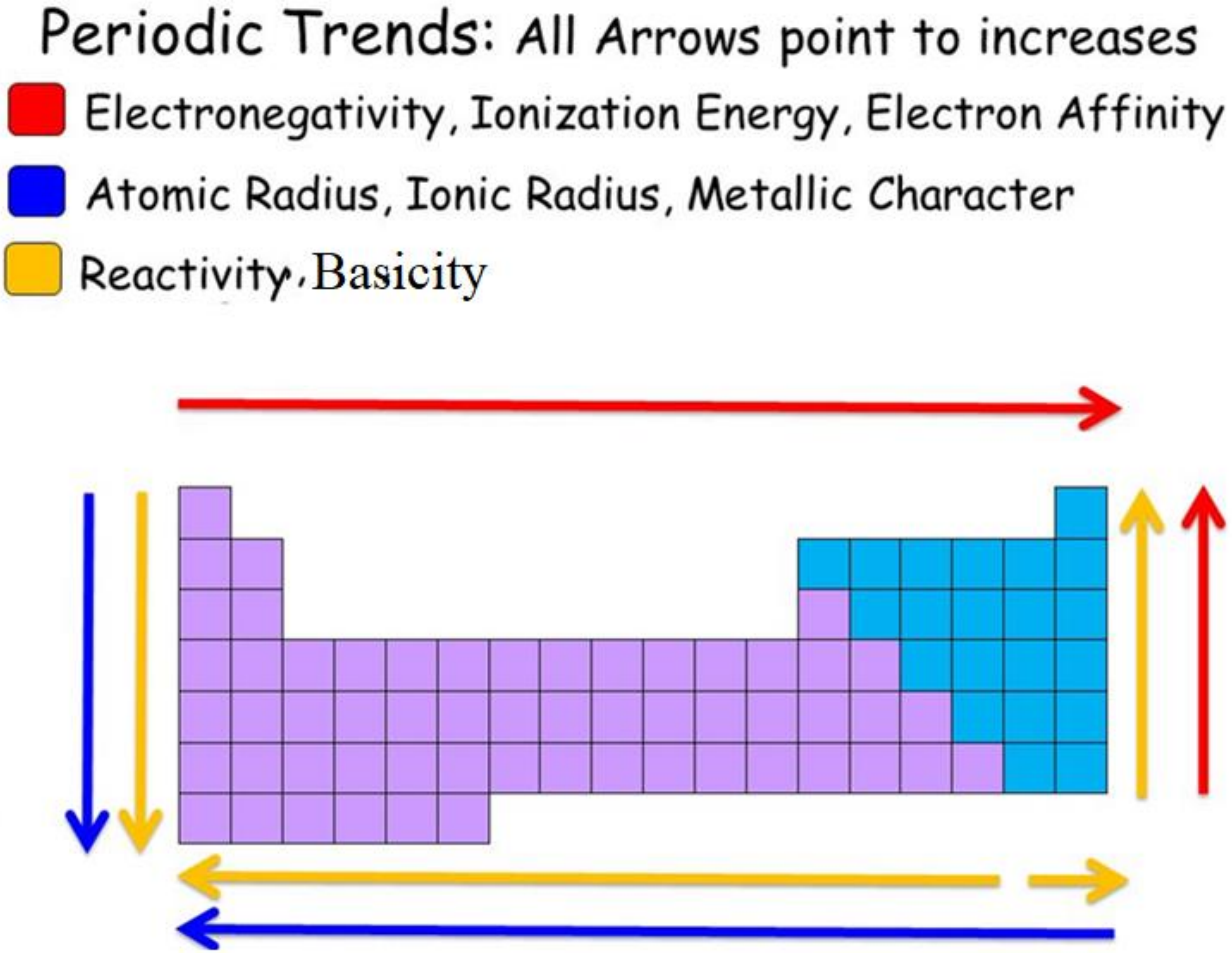
✓ Most non-metals possess low melting points.

✓ The non-metal carbon possesses the highest melting point of all the elements.

✓ The semi-metal boron also possesses a high melting point.

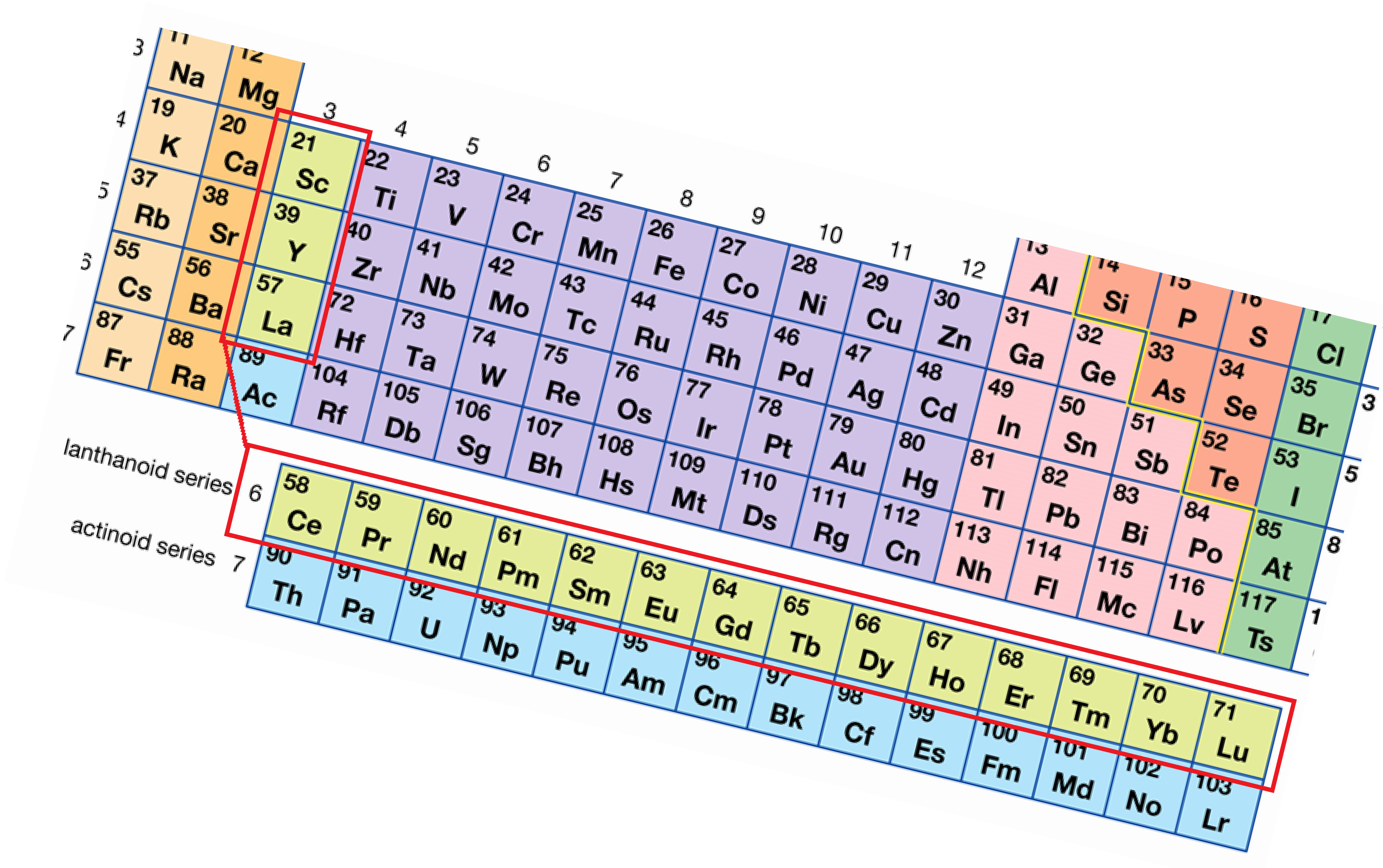

MELTING POINT (°C)
4000
3500
3000
2500
2000
1500
1000
500
0
-500
H
He
Li
Be
B
C
N
O
F
Ne
Na
Mg
Al
Si
P
S
Cl
Ar
K
Ca
Sc
Ti
V
Cr
Mn
Fe
Co
Ni
Cu
Zn
Ga
Ge
As
Se
Br
Kr

❖ The Periodic Trends of Properties of The Elements: A summary

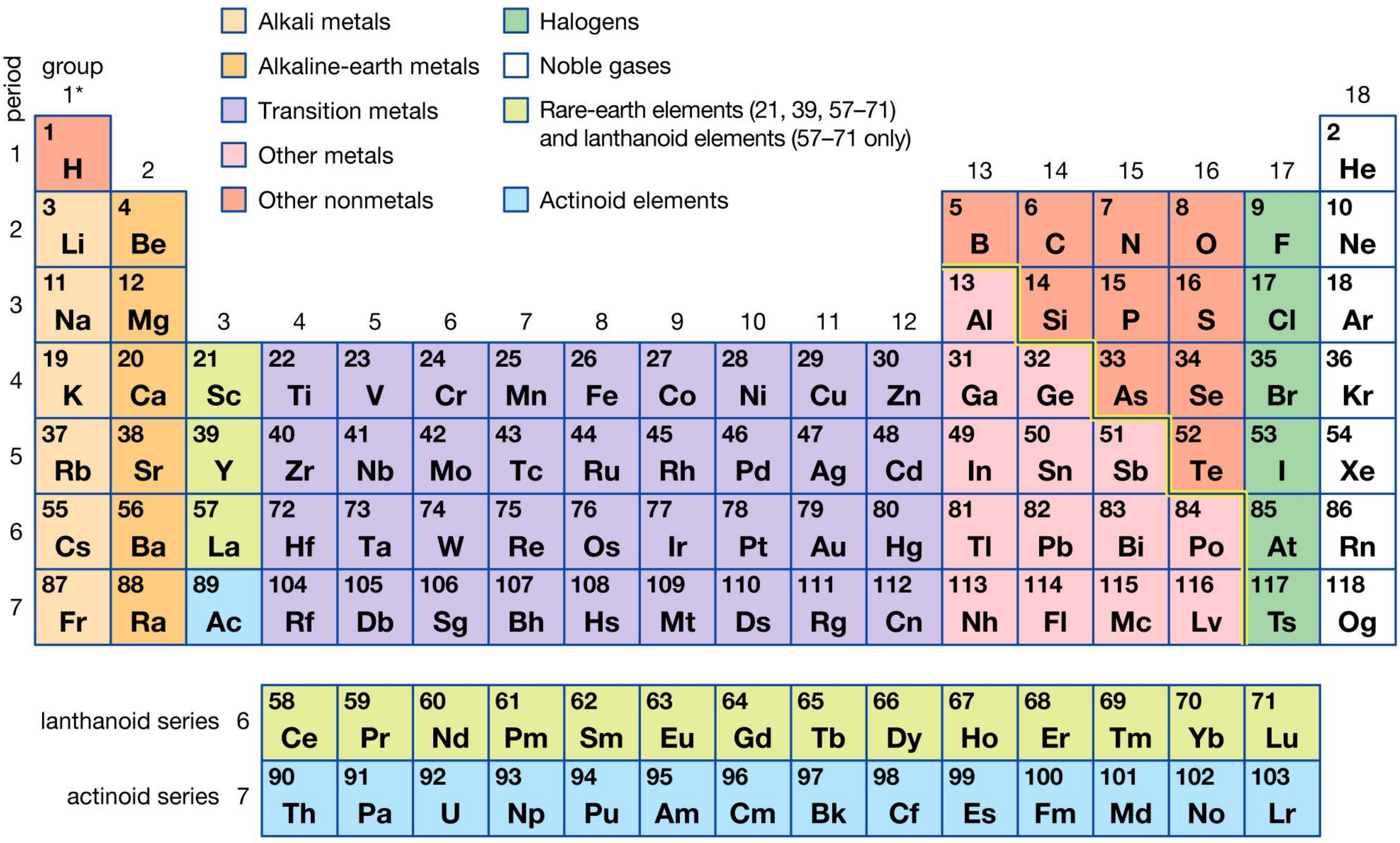


Chapter 2:

Introduction To The Lanthanides



❑ ***The Modern Periodic Table Of The Elements***



🟧 Alkali metals

🟫 Alkaline-earth metals

🟪 Transition metals

▨ Other metals

🟥 Other nonmetals

🟩 Halogens

⬜ Noble gases

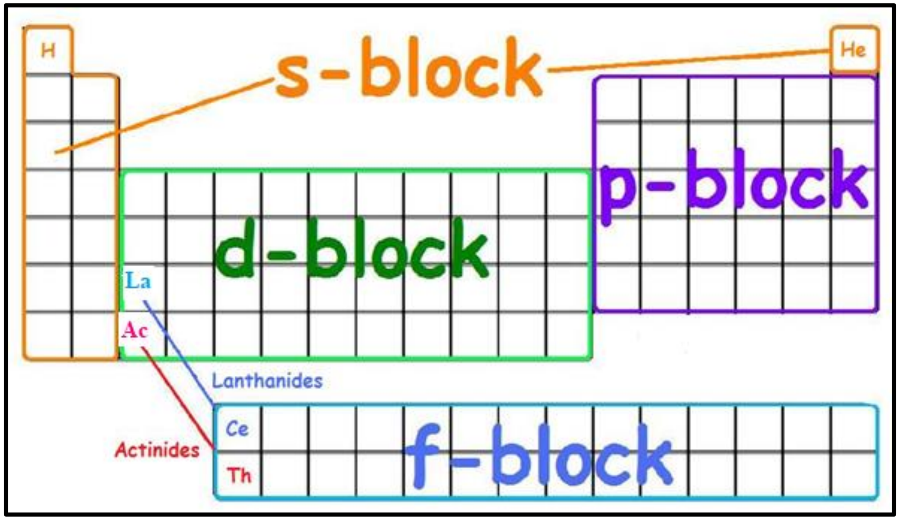
🟨 Rare-earth elements (21, 39, 57–71) and lanthanoid elements (57–71 only)

🟦 Actinoid elements

period	group 1*	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
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 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
lanthanoid series 6				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	
actinoid series 7				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	

*Numbering system adopted by the International Union of Pure and Applied Chemistry (IUPAC).

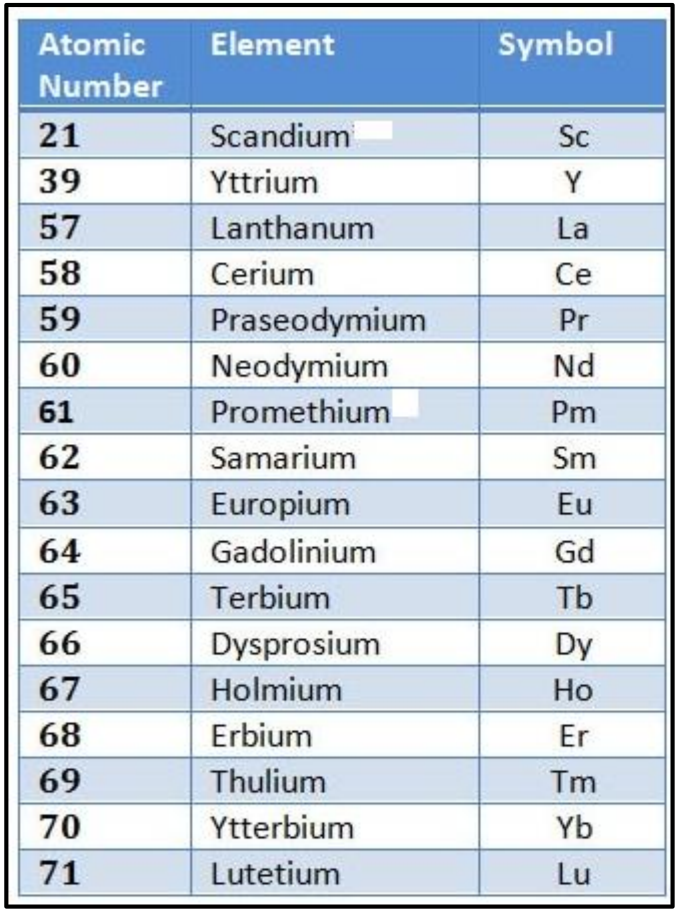
❑ *The Position in the Periodic Table and the Electron Configuration*



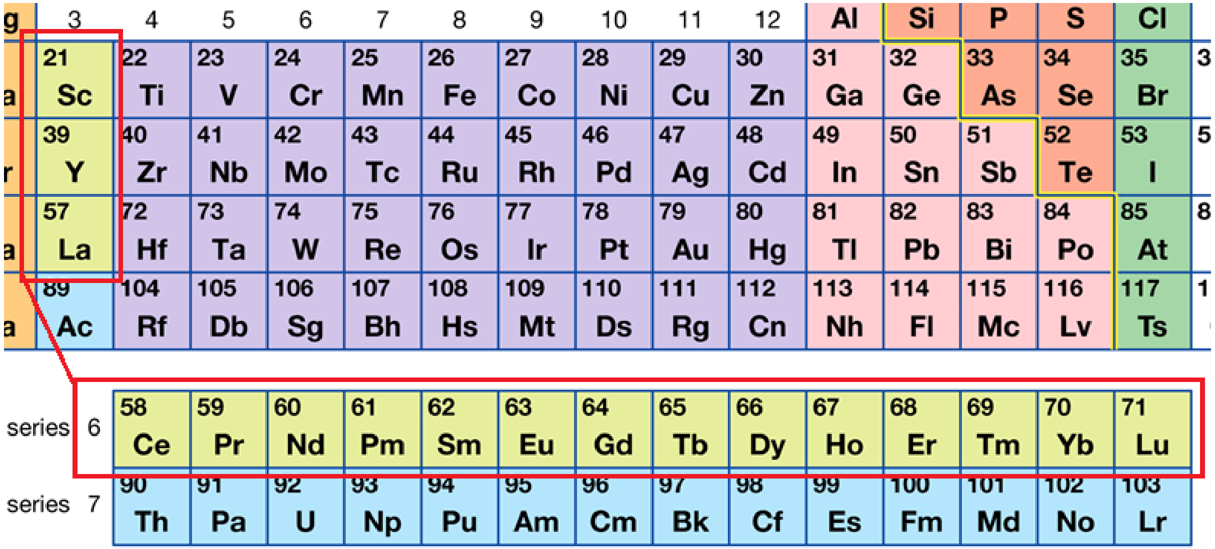
- The naming of the blocks as *s*, *p*, *d* and *f* refers to the progressive filling of the outer atomic orbitals of the sub-shells, *s*, *p*, d and *f*, respectively.
- The elements constituting the *f* block are those in which the *4f* and *5f* orbitally progressively filled.
- Elements of bloc *f* are the member of group 3 (Scandium, Yttrium, Lanthanum and Actinium).
- The *f* block elements are termed as ‘’inner transition’’ elements. It is because literally speaking they constitute transition series within transition series (*d*-block elements).

- In addition to incomplete *d*-subshell, their *f*-subshell is also incomplete. There are seven *f* orbitals in a given shell. As much as 14 electrons can be occupied in a given *f* block series.
- The “lanthanides”, “lanthanons” and “lanthanoids” series is present in the period 6 of the periodic Table of the elements. The word “lanthanides” comes from the Greek “lanthanein” meaning “to be hidden.” The name probably arose because these elements all hide behind one another in the periodic table.
- The lanthanides series comprises the 14 elements from ${}_{58}$Ce to ${}_{71}$Lu, but are commonly taken to include ${}_{57}$La and sometimes ${}_{21}$Sc and ${}_{39}$Y as well. ${}_{21}$Sc and ${}_{39}$Y, both of which are actually elements above ${}_{57}$La in the periodic table and the all the three elements belong to the group number 3.
- The 17 elements including the 14 elements from ${}_{58}$Ce to ${}_{71}$Lu plus the 3 elements scandium (${}_{21}$Sc), yttrium (${}_{39}$Y) and lanthanum (${}_{57}$La) are commonly named as ‘’Rare Earth Elements” (REEs).
- ${}_{21}$Sc and ${}_{39}$Y were added to the 15 elements (${}_{57}$La to ${}_{71}$Lu) because they have similar physicochemical properties to the these elements.
- The REEs are all metals, and they are also referred to as "rare earth metals’’ (*REMs*).

The Rare Earth Elements (REEs)



Atomic Number	Element	Symbol
21	Scandium	Sc
39	Yttrium	Y
57	Lanthanum	La
58	Cerium	Ce
59	Praseodymium	Pr
60	Neodymium	Nd
61	Promethium	Pm
62	Samarium	Sm
63	Europium	Eu
64	Gadolinium	Gd
65	Terbium	Tb
66	Dysprosium	Dy
67	Holmium	Ho
68	Erbium	Er
69	Thulium	Tm
70	Ytterbium	Yb
71	Lutetium	Lu

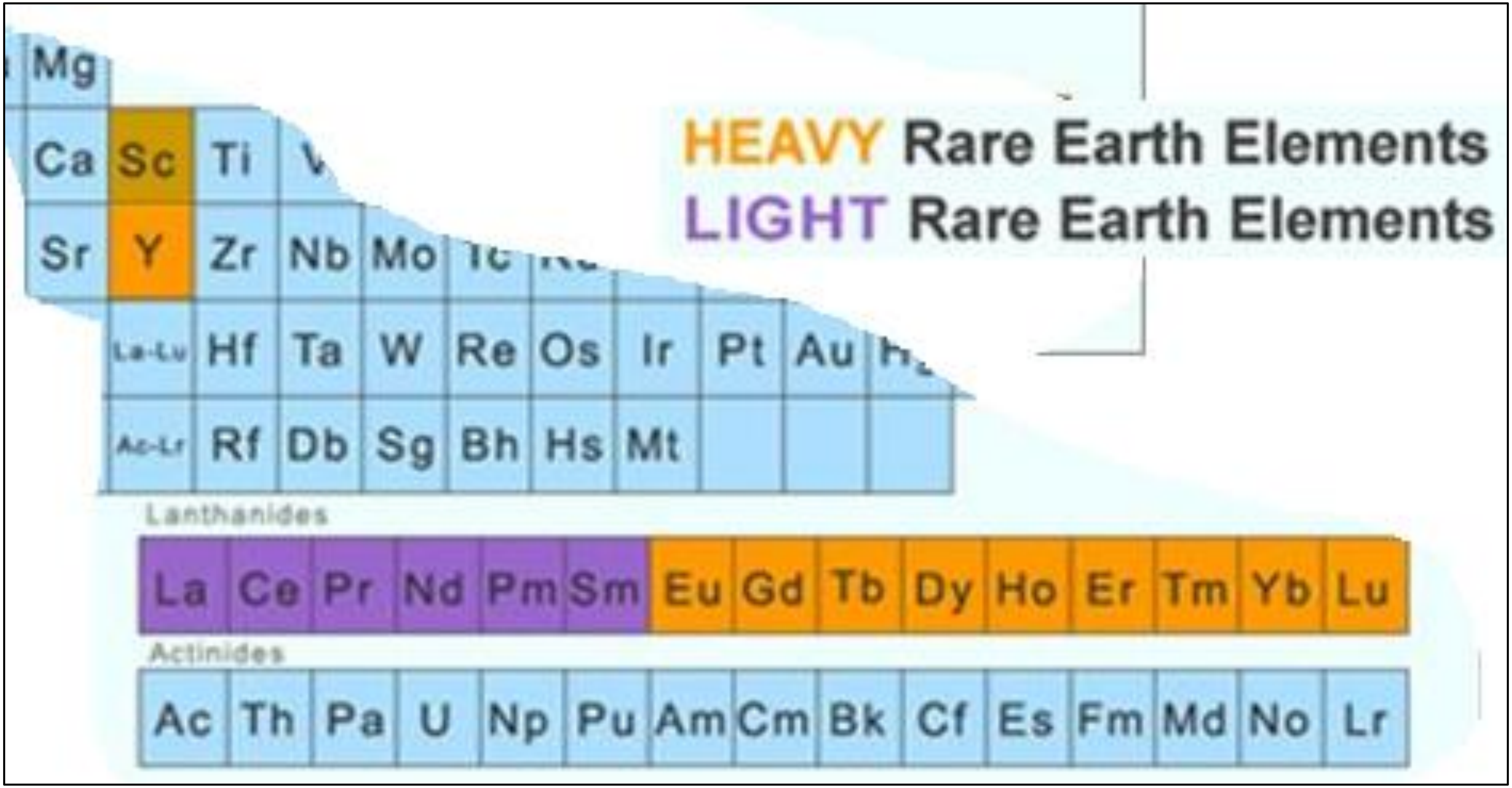


- Originally these elements were termed as ‘’rare-earths’’, because they are spread very evenly over the earth, so it is hard to find a lot in one place. Such an occurrence is the culmination of their similar chemical behavior.
- So, the term ‘’rare earth’’ is actually a misnomer. However, the REEs concentration range from ten to a few hundred parts per million by weight. Therefore, finding them where they can be economically mined and processed presents a real challenge.
- When Mendeleev designed the first version of the periodic table in 1869, only 3 lanthanide elements (La, Ce, Er) were known in their isolated form. The chemical similarity of the lanthanides made their separation rather cumbersome and allocation into the periodic table of any later discovered lanthanide posed problems.

- There was no way of predicting how many of these elements there would be until Henry Moseley (1887–1915) analyzed the X-ray spectra of elements and gave meaning to the concept of atomic number. He showed that there were 15 elements from lanthanum (*La*) to lutetium (*Lu*), which had only been identified in 1907. The discovery of radioactive promethium had to wait until after World War 2.

- In the extractive metallurgy processing, the 16 elements form ${}_{39}$Y to ${}_{71}$Lu are often grouped into light rare earth elements (LREEs) and heavy rare earth elements (HRREs) (See the next slide):

- LREEs beginning at atomic number 57 and ending with 62. They constitute approximately 98% of all RE ores.
- HRREs includes the elements with atomic numbers from 63 to 71 and ${}_{39}$Y. Elements in that group include Eu and Gd. Yttrium (${}_{39}$Y) is grouped with the HRREs even though its atomic numbers is low. Scientists place it in the heavy group because its properties resemble those of the HRREs.


HEAVY Rare Earth Elements
LIGHT Rare Earth Elements
Mg
Ca Sc Ti V
Sr Y Zr Nb Mo Tc
La-Lu Hf Ta W Re Os Ir Pt Au
Ac-Lr Rf Db Sg Bh Hs Mt
Lanthanides
La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Actinides
Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr

- Generally the REEs follow Aufbau principle (‘’building up’’).
- For the Lanthanides the electron configuration of the free atoms are determined only with difficulty because of the complexity of their atomic spectra, but it is generally agreed that they are nearly all (See Table below):

$$_{54}[\mathrm{Xe}]4f^{0\text{-}14}5d^{0\text{-}1}6s^{2}$$

- Only 3 elements for which the *d* subshell contains 1 electron (d^1). The exceptions are:
    - Cerium ($_{58}$Ce), for which the sudden contraction and reduction in energy of the *4f* orbitals immediately after lanthanum ($_{57}$*La*) is not yet sufficient to avoid occupancy of the ***5d*** orbitals.
    - Gadolinium ($_{64}$Gd), which reflects the stability of the half-filled *4f* shell with 7 electrons;
    - Lutetium ($_{71}$Lu), at which point the *4f* shell has been filled with 14 electrons.

- The general valence electron configuration of the lanthanide elements is (See Table below):

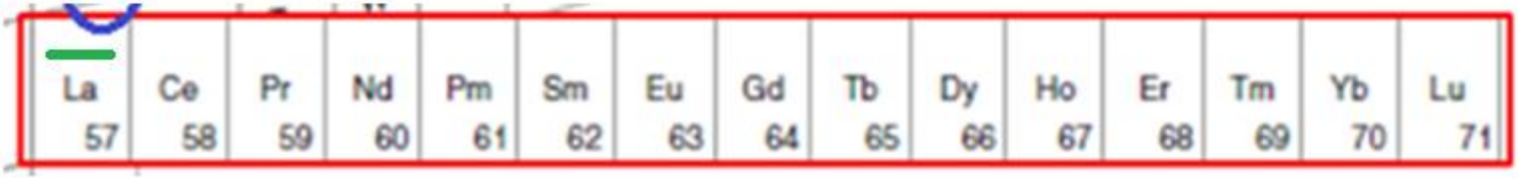
$$\mathbf{4f^{0\text{-}14}5d^{0\text{-}1}6s^{2}}$$

- *The electron configuration (in box diagram notation) of selected REEs is presented below.*
- It is interesting to note that the *f* block elements (lanthanides and actinides) are placed outside the body of the periodic table. The reason for this is the remarkable similarities among the chemical properties of the lanthanides.
- ${}_{21}Sc$, ${}_{39}Y$ and the ${}_{57}La$ are the elements that begin 3 successive series of transition elements. Their valence electron configurations are, respectively:

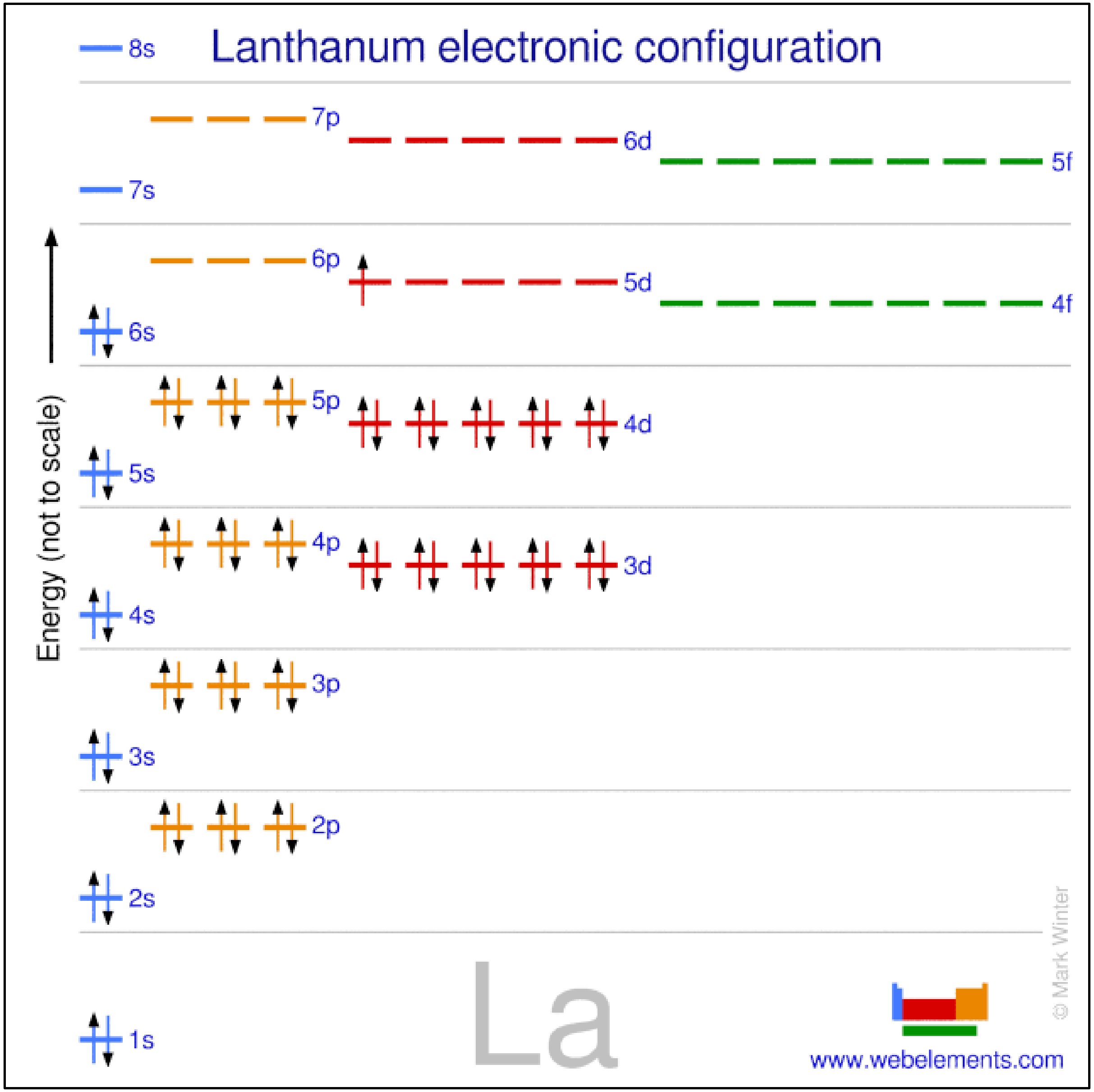
$$\mathbf{ns^{2}(n-1)d^{1} \qquad \text{with } n = 4, 5, \text{ and } 6}$$

- The similarities in properties, in turn, is due to the similar electronic configuration of the outermost shell. These elements differ only in the number of *f*-electrons which do not take part in chemical bonding (difference from *d*-block elements in which differentiating *d*-electrons are involved in chemical interaction).

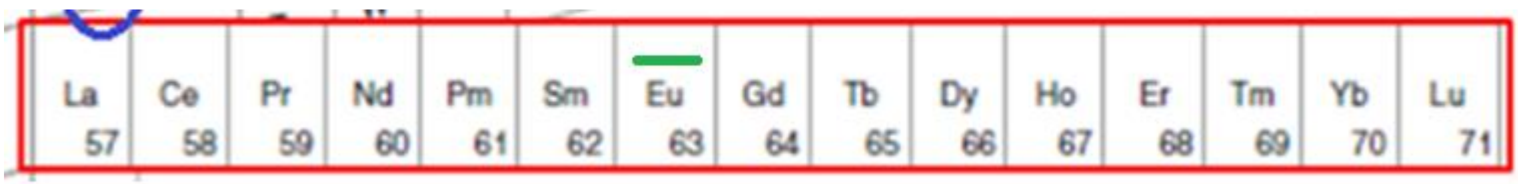
Element	Symbol	Atomic Number	Expected electronic configuration	Observed electronic configuration
Lanthanum	La	57	[Xe] $4f^0\ 5d^1\ 6s^2$	[Xe] $4f^0\ 5d^1\ 6s^2$
Cerium	Ce	58	[Xe] $4f^1\ 5d^1\ 6s^2$	[Xe] $4f^1\ 5d^1\ 6s^2$
Praseodymium	Pr	59	[Xe] $4f^2\ 5d^1\ 6s^2$	[Xe] $4f^3\ 5d^0\ 6s^2$
Neodymium	Nd	60	[Xe] $4f^3\ 5d^1\ 6s^2$	[Xe] $4f^4\ 5d^0\ 6s^2$
Promethium	Pm	61	[Xe] $4f^4\ 5d^1\ 6s^2$	[Xe] $4f^5\ 5d^0\ 6s^2$
Samarium	Sm	62	[Xe] $4f^5\ 5d^1\ 6s^2$	[Xe] $4f^6\ 5d^0\ 6s^2$
Europium	Eu	63	[Xe] $4f^6\ 5d^1\ 6s^2$	[Xe] $4f^7\ 5d^0\ 6s^2$
Gadolinium	Gd	64	[Xe] $4f^7\ 5d^1\ 6s^2$	[Xe] $4f^7\ 5d^1\ 6s^2$
Terbium	Tb	65	[Xe] $4f^8\ 5d^1\ 6s^2$	[Xe] $4f^9\ 5d^0\ 6s^2$
Dysprosium	Dy	66	[Xe] $4f^9\ 5d^1\ 6s^2$	[Xe] $4f^{10}\ 5d^0\ 6s^2$
Holmium	Ho	67	[Xe] $4f^{10}\ 5d^1\ 6s^2$	[Xe] $4f^{11}\ 5d^0\ 6s^2$
Erbium	Er	68	[Xe] $4f^{11}\ 5d^1\ 6s^2$	[Xe] $4f^{12}\ 5d^0\ 6s^2$
Thulium	Tm	69	[Xe] $4f^{12}\ 5d^1\ 6s^2$	[Xe] $4f^{13}\ 5d^0\ 6s^2$
Ytterbium	Yb	70	[Xe] $4f^{13}\ 5d^1\ 6s^2$	[Xe] $4f^{14}\ 5d^0\ 6s^2$
Lutetium	Lu	71	[Xe] $4f^{14}\ 5d^1\ 6s^2$	[Xe] $4f^{14}\ 5d^1\ 6s^2$



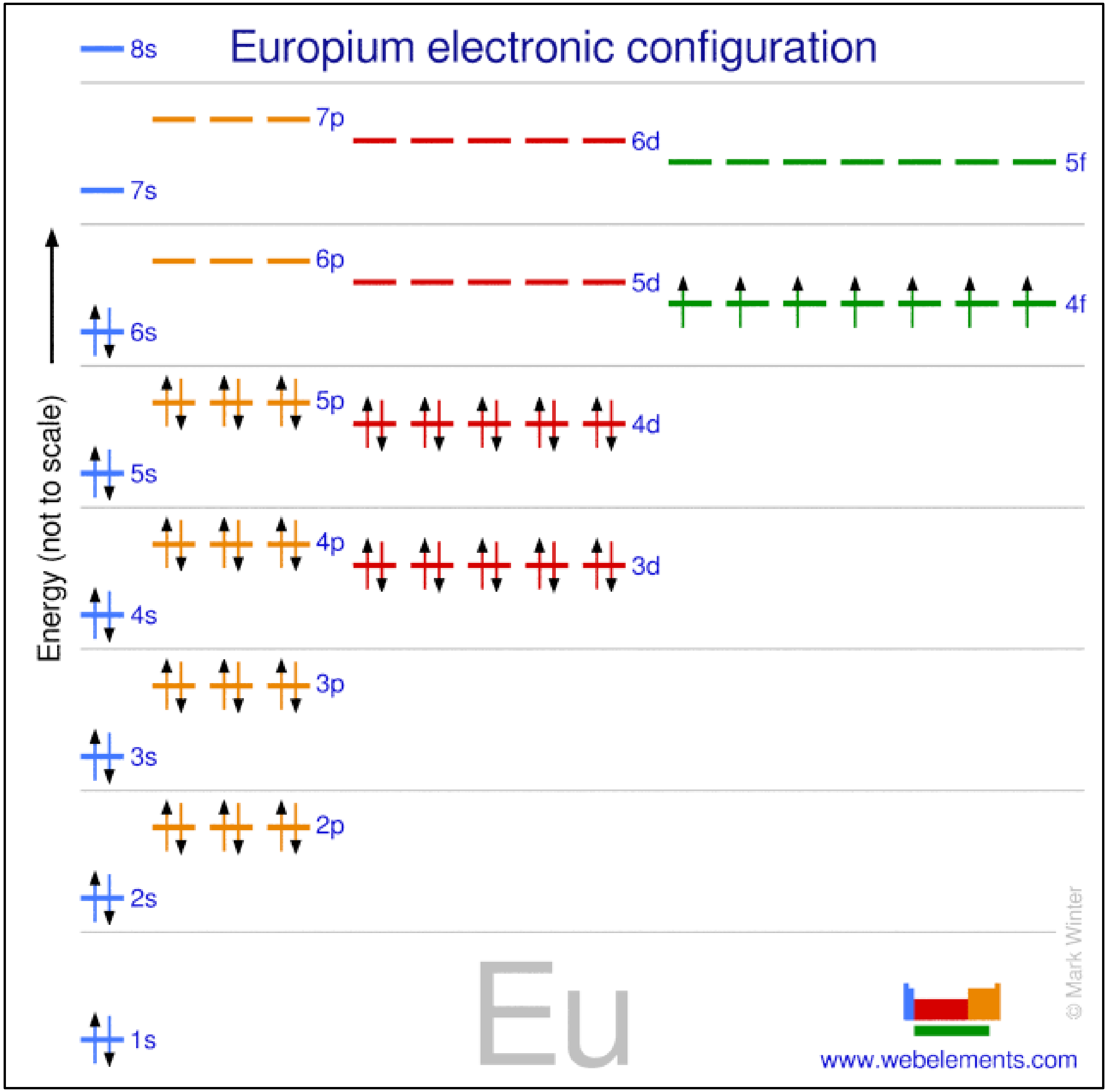
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
57	58	59	60	61	62	63	64	65	66	67	68	69	70	71

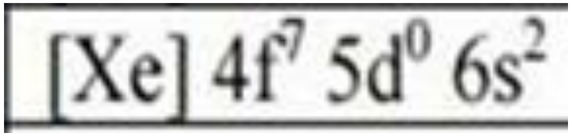


$[Xe]\ 4f^0\ 5d^1\ 6s^2$



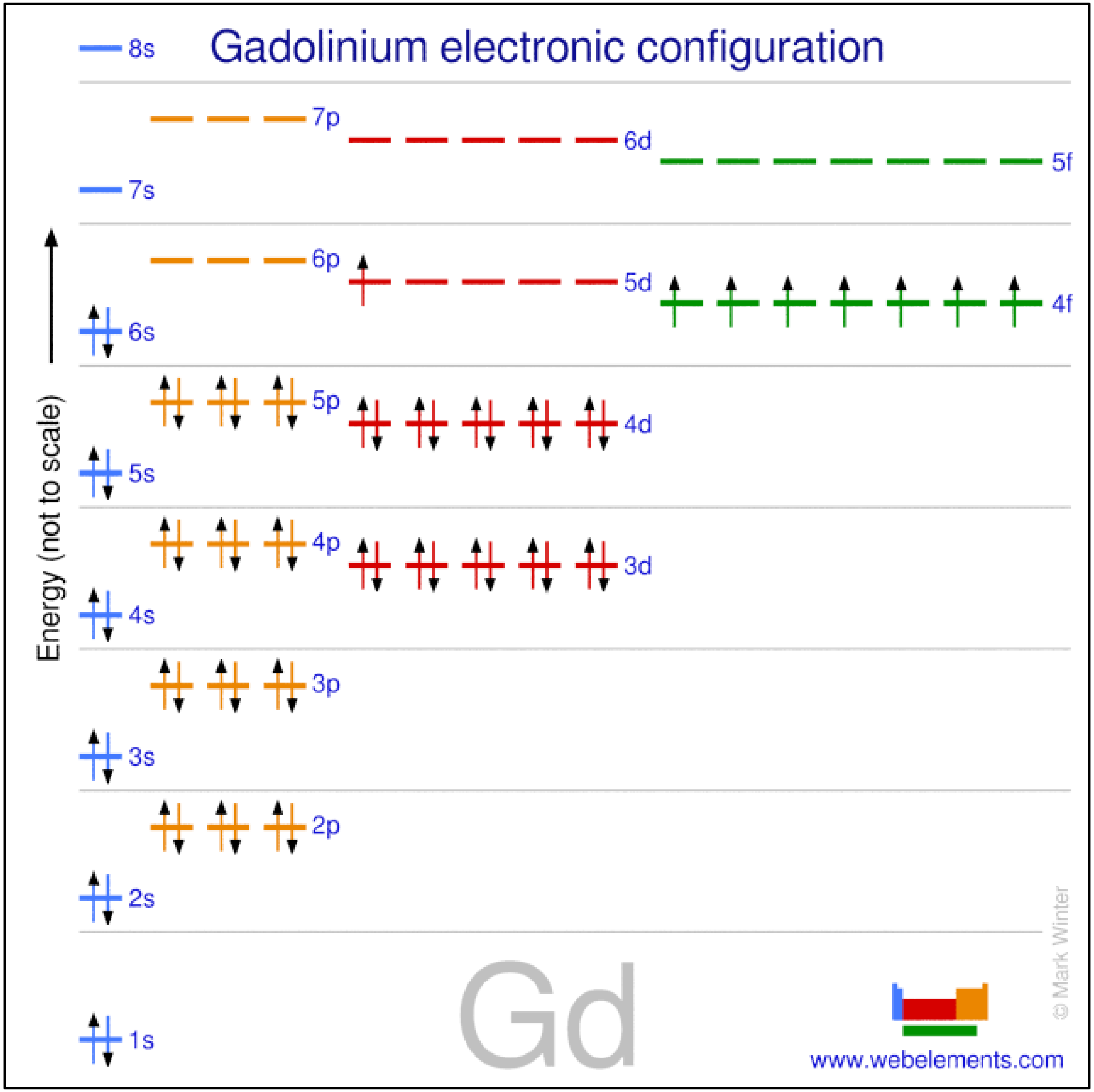
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
57	58	59	60	61	62	63	64	65	66	67	68	69	70	71

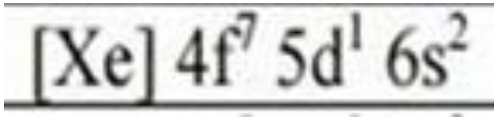




$[Xe]\ 4f^7\ 5d^0\ 6s^2$

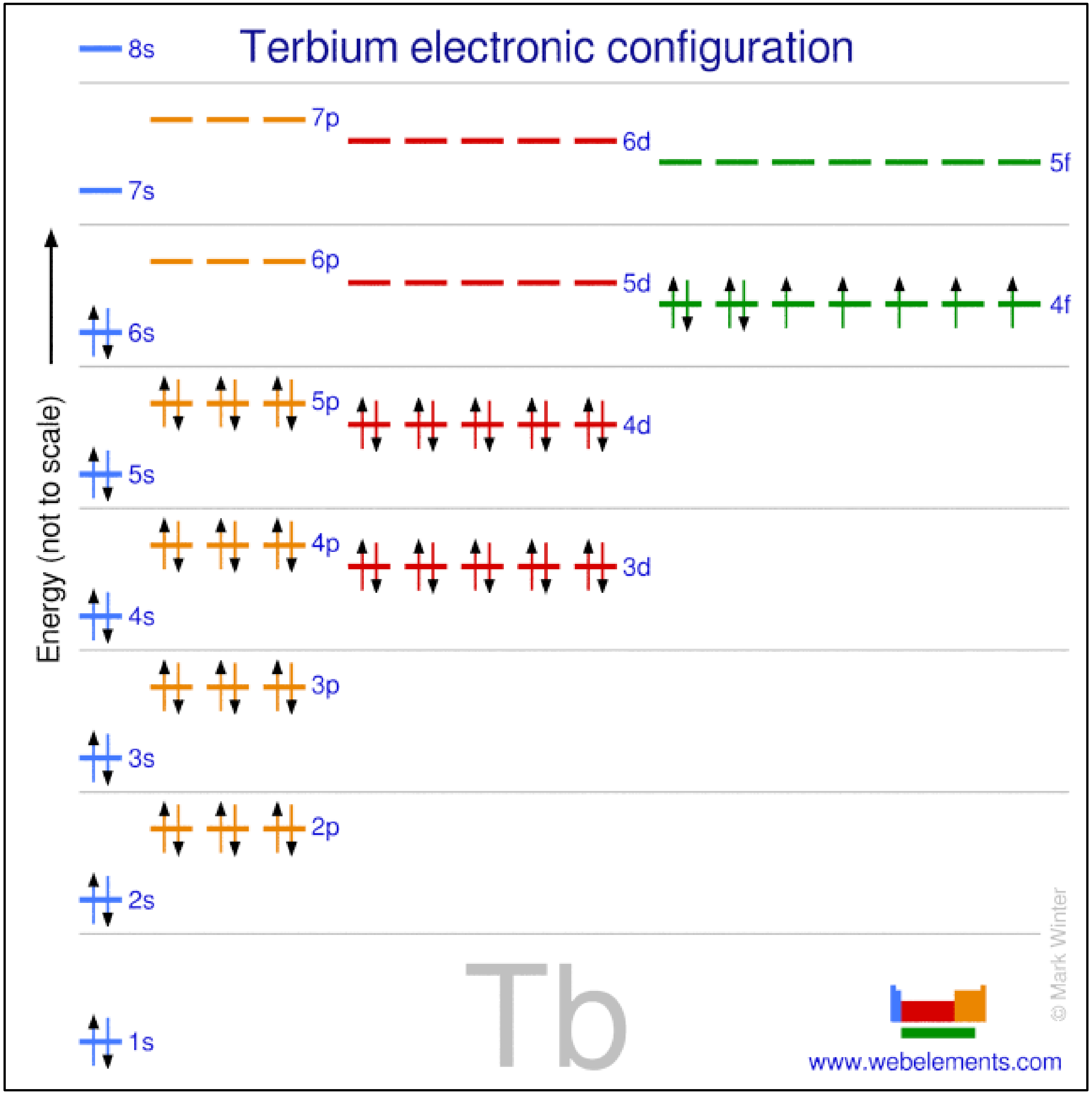
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
57	58	59	60	61	62	63	64	65	66	67	68	69	70	71

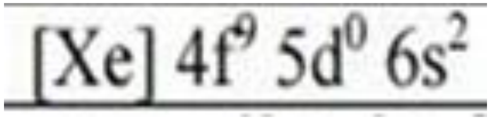




$[Xe]\ 4f^7\ 5d^1\ 6s^2$

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





$[Xe]\ 4f^9\ 5d^0\ 6s^2$

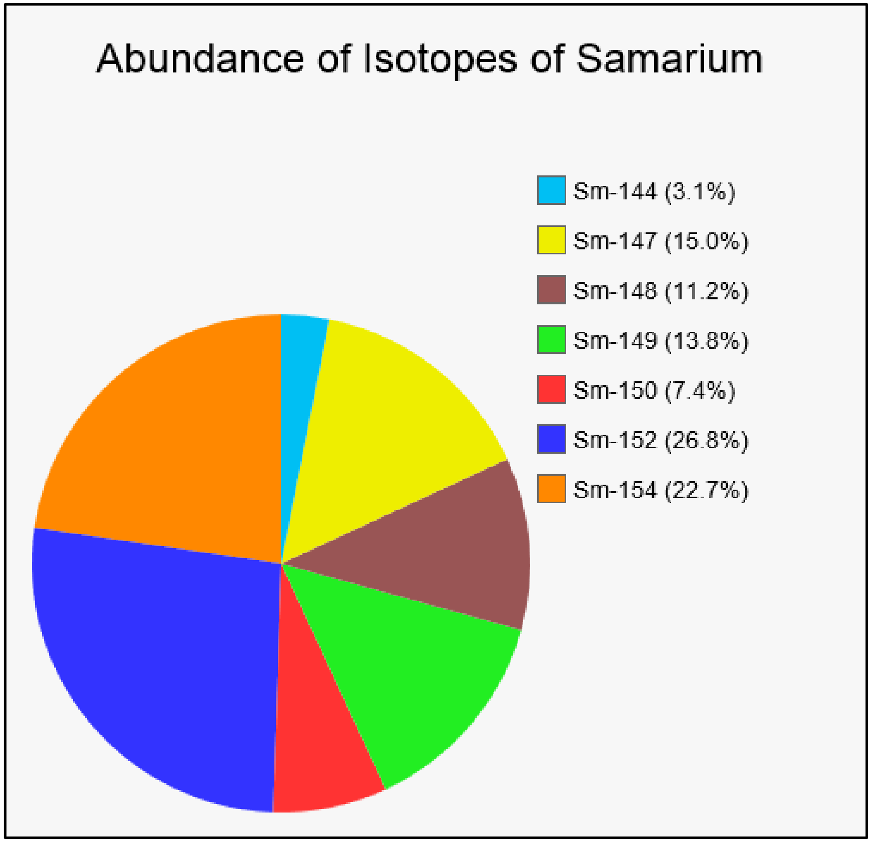
❑ *The Isotopes*

- Isotopes are two or more types of atoms of the same chemical element that have the same atomic number (number of protons in their nuclei) and position in the periodic table but they differ in nucleon numbers (mass numbers) due to different numbers of neutrons in their nuclei.
- As a group, the REEs are rich in the total numbers of isotopes, ranging from 24 for Sc to 42 for Ce and averaging about 35 each without counting nuclear isomers.
- The elements with odd atomic numbers have only 1, or at most 2, stable (or very long-lived) isotopes, but those with even atomic numbers have from 4 to 7 stable isotopes.

Ce	Pr	Nd		Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
1	1	5		7	2	5	1	4	1	4	1	5	1

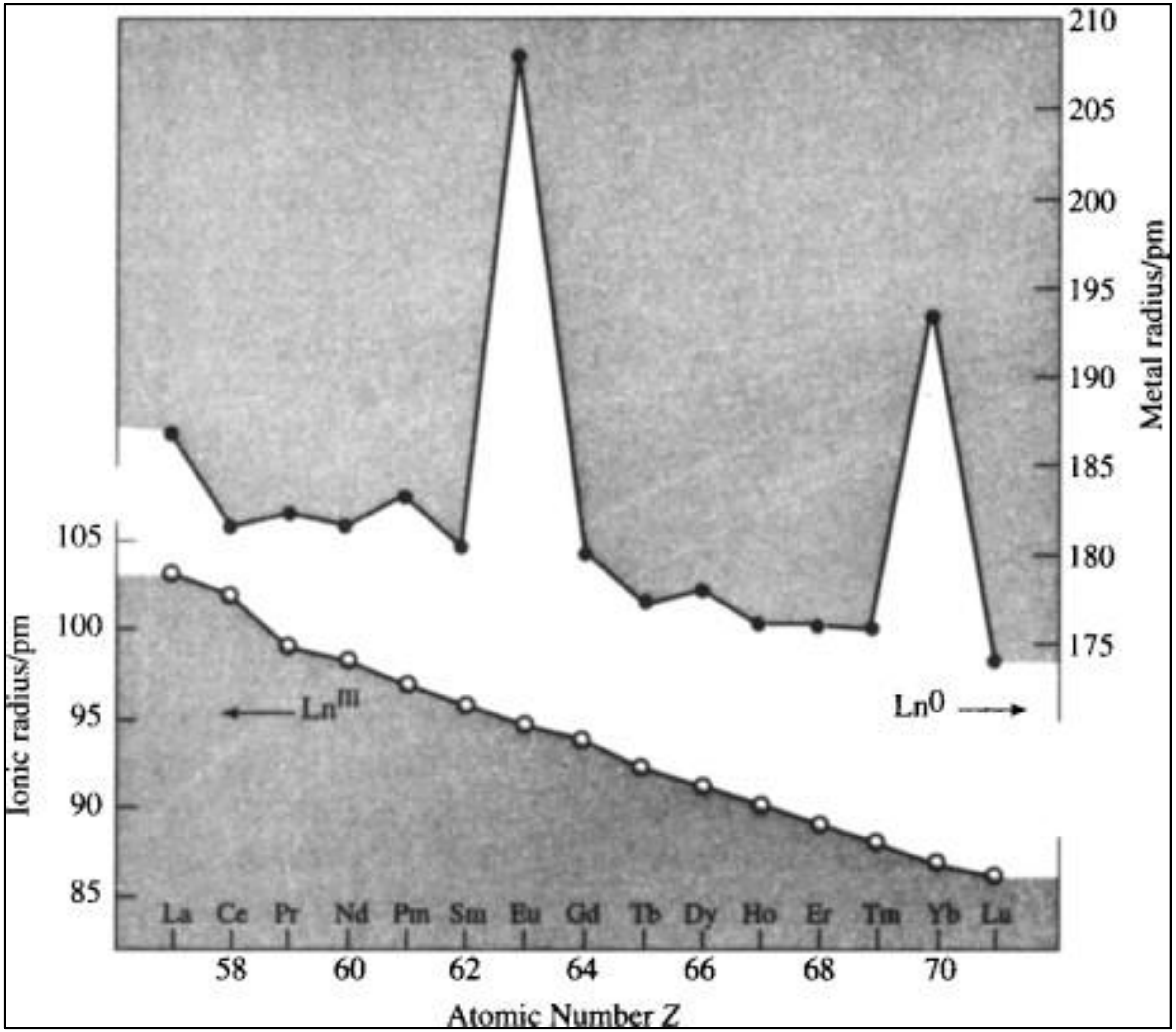
- All lanthanides have stable isotopes, except $_{61}$Pm, which is radioactive. For example, the 7 stable isotopes of Sm and their abundance in nature is shown in the figure below. ^{152}Sm being the most abundant isotope.

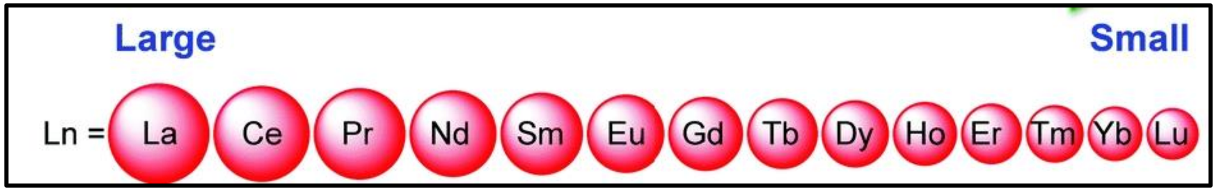
- Promethium ($_{61}$Pm) is radioactive and does not have any stable isotopes. ^{145}Pm has the longest half-life, 17.7 years.
- Some of the unstable isotopes are feebly radioactive, having extremely long half-lives. The unstable radioactive isotopes are produced in many ways—e.g., by fission, neutron bombardment, radioactive decay of neighboring elements, and bombardment of neighboring elements with charged particles.



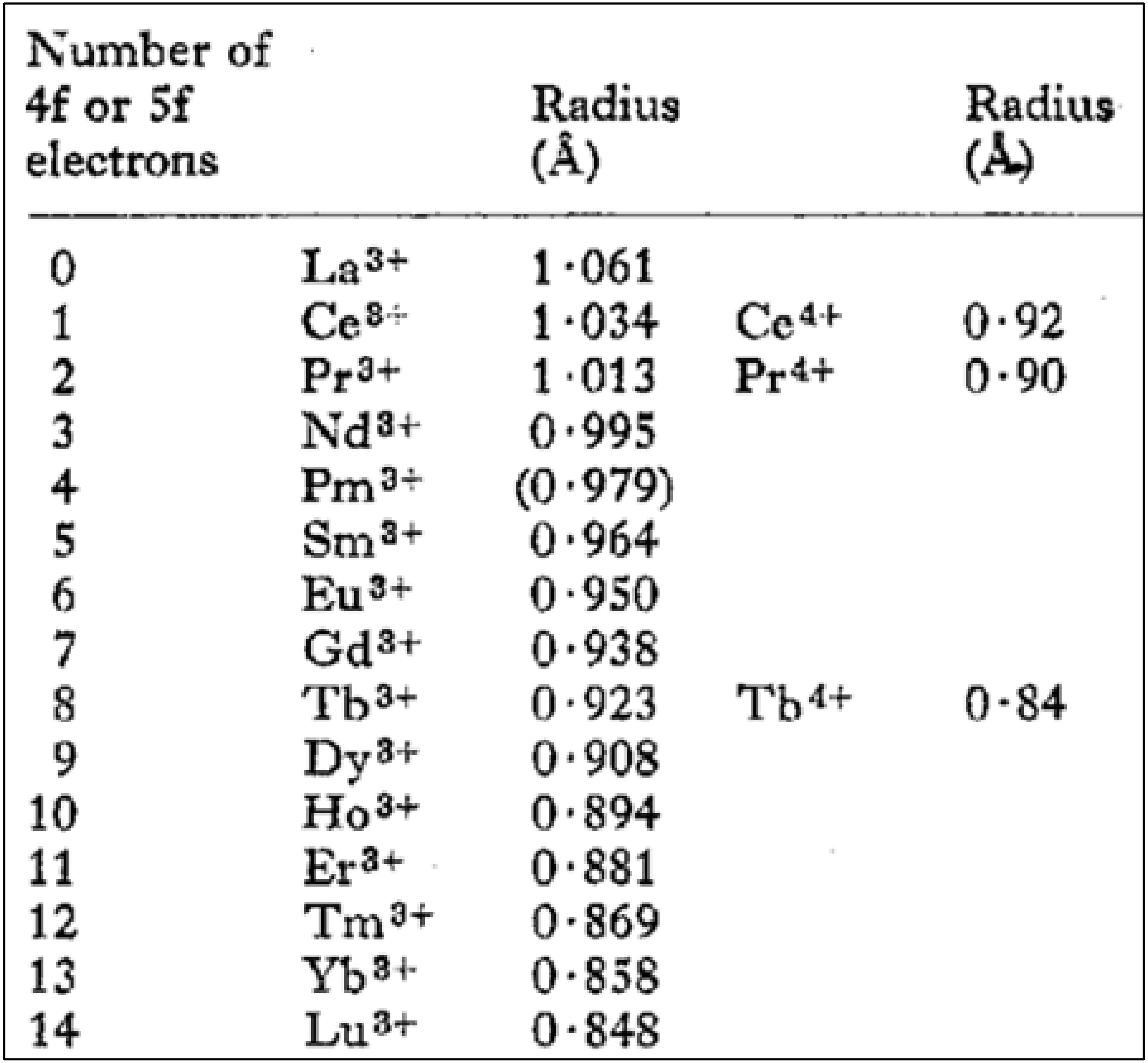
❑ *The Atomic and the Ionic Radii of the Elements*

- The size of the atomic and ionic radii is determined by both the nuclear charge and by the number of electrons that are in the electronic shells. Within those shells, the degree of occupancy will also affect the size.
- In the Lanthanide series, there is a gradual decrease in atomic and ionic size from $_{57}$La to $_{71}$Lu (i.e. on moving in the series from left to right). The steady decrease in all is about 22pm (1pm = 10^{-12} m) (see the figure and table given below).
- It is important to note that because the lanthanide contraction keeps these ions about the same size and because they all generally exhibit the +3 oxidation state, their chemical properties are very similar, with the result that at least small amounts of each one are usually present in every RE mineral. This renders the separation and purification processes of individual compounds (which are mostly in the form of oxides) from each others an extremely difficult task.





- *Variation of the* Ln^0 *atomic (metal) radius and the* Ln^{3+} *ionic radius for the lanthanide series.*



Number of 4f or 5f electrons		Radius (Å)		Radius (Å)
0	La^{3+}	1·061		
1	Ce^{3+}	1·034	Ce^{4+}	0·92
2	Pr^{3+}	1·013	Pr^{4+}	0·90
3	Nd^{3+}	0·995		
4	Pm^{3+}	(0·979)		
5	Sm^{3+}	0·964		
6	Eu^{3+}	0·950		
7	Gd^{3+}	0·938		
8	Tb^{3+}	0·923	Tb^{4+}	0·84
9	Dy^{3+}	0·908		
10	Ho^{3+}	0·894		
11	Er^{3+}	0·881		
12	Tm^{3+}	0·869		
13	Yb^{3+}	0·858		
14	Lu^{3+}	0·848		

- *Ln^{3+} and Ln^{4+} ionic radius (in angström, 1 Å = 10-10 m) of the lanthanide series.*

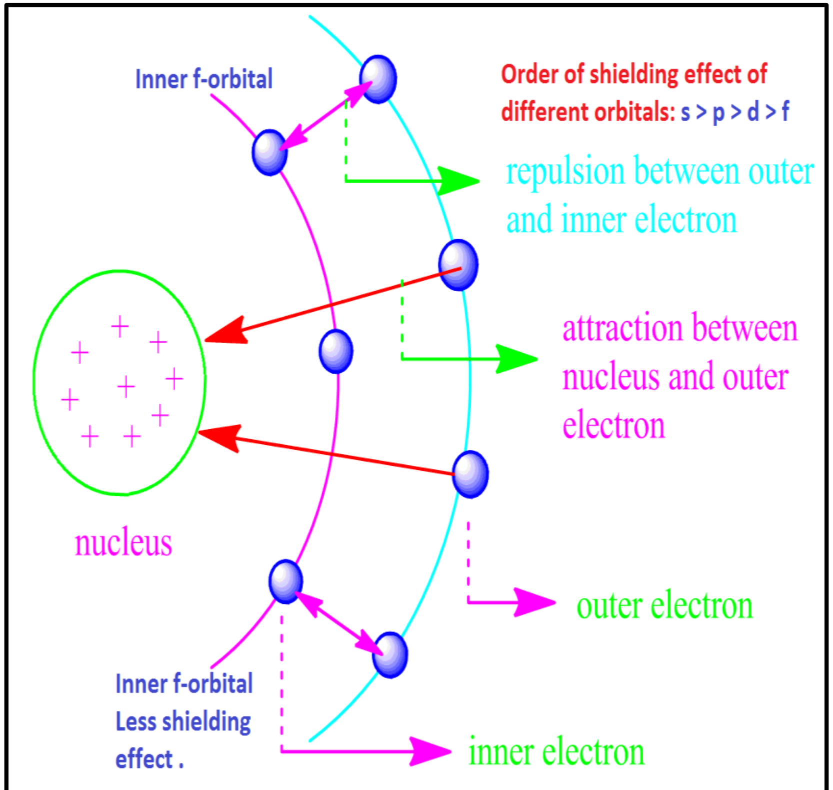
- The decrease in ionic size is known as the Lanthanide Contraction. It is very much regular for the lanthanide ions, Ln^{3+}. This is due to the increase of the effective nuclear charge (Z*) which pulls the orbital electrons close to the nuclear. The increase of Z* is a consequence of the so-called ‘’poor shielding (or screening) effect’’ of electrons of *f* orbitals.
- It is very important to note that although the close chemical similarity of the REs, the Lanthanide Contraction consists the fundamental parameter on which are based the separation methods of lanthanides from one another in a mixture of them.

○ *Note. The explanation of the Lanthanide Contraction is given in an ulterior page.*

- While, irregularity in size is seen for metals; the atomic size of Eu and Yb are spectacularly irregular and are larger than expected by the Lanthanide Contraction trend.

- ✓ *Explanation of the Lanthanide Contraction:*

For each consecutive atom, the nuclear charge is more positive by one unit, accompanied by a corresponding increase in the number of electrons present in the 4f orbitals surrounding the nucleus. Due to the shape of f atomic orbitals, the 4f electrons experience poor shielding (screening) effect on each others (see figure below) from the increased positive charge of the nucleus. So that the effective nuclear charge (Z) attracting each electron steadily increases through the lanthanide elements, resulting in successive reductions of the atomic and ionic radii with increasing atomic number from* $_{57}La$ *to* $_{71}Lu$*.*

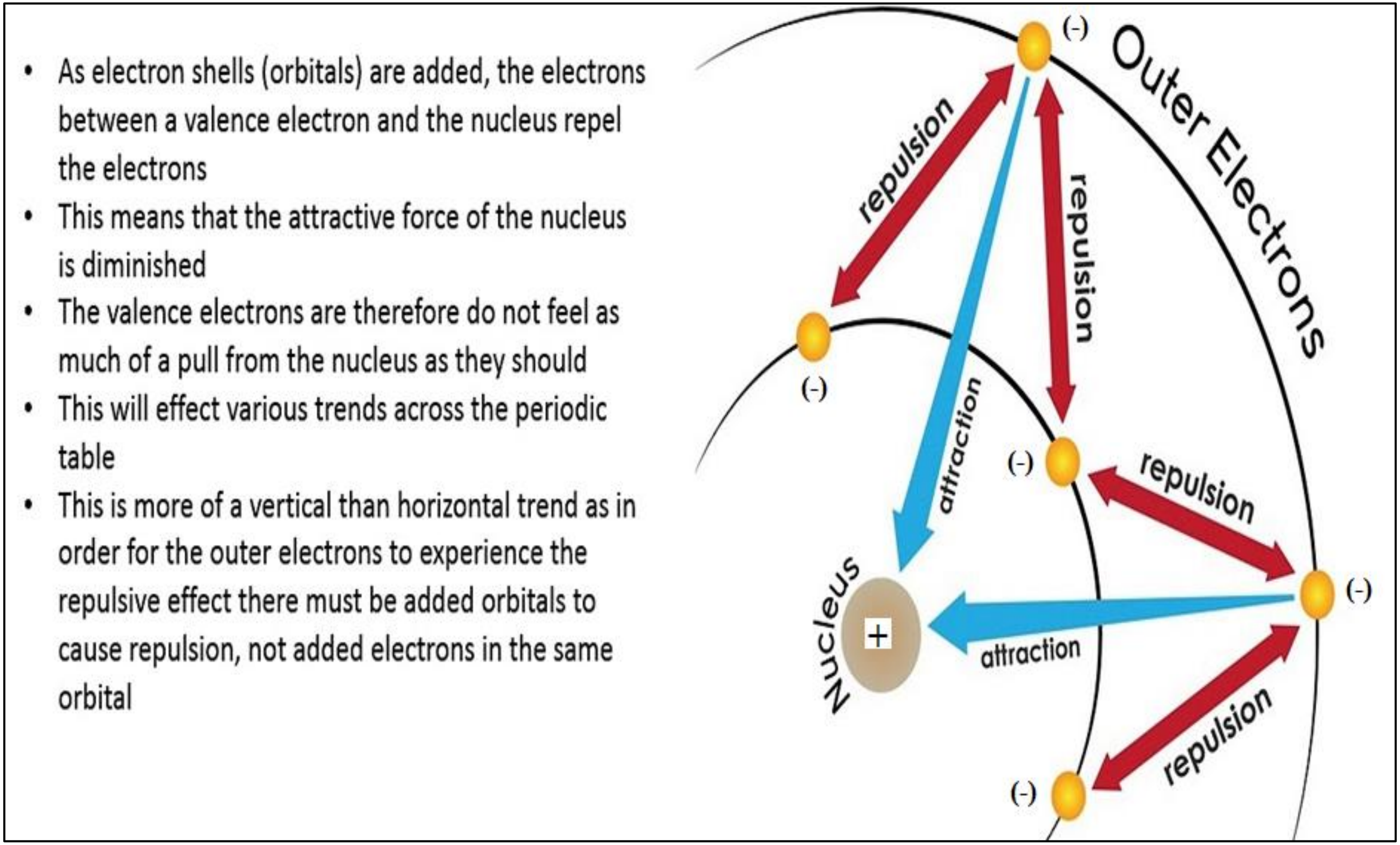


- ○ *Schematic illustration of the weak electron shielding effect (or the screening effect) of the 4f electrons.*

- ***What is Electron Shielding***?

Shielding effect (or screening effect) can be defined as a reduction in the effective nuclear charge on the electron cloud, due to a difference in attraction forces of the electrons on the nucleus.

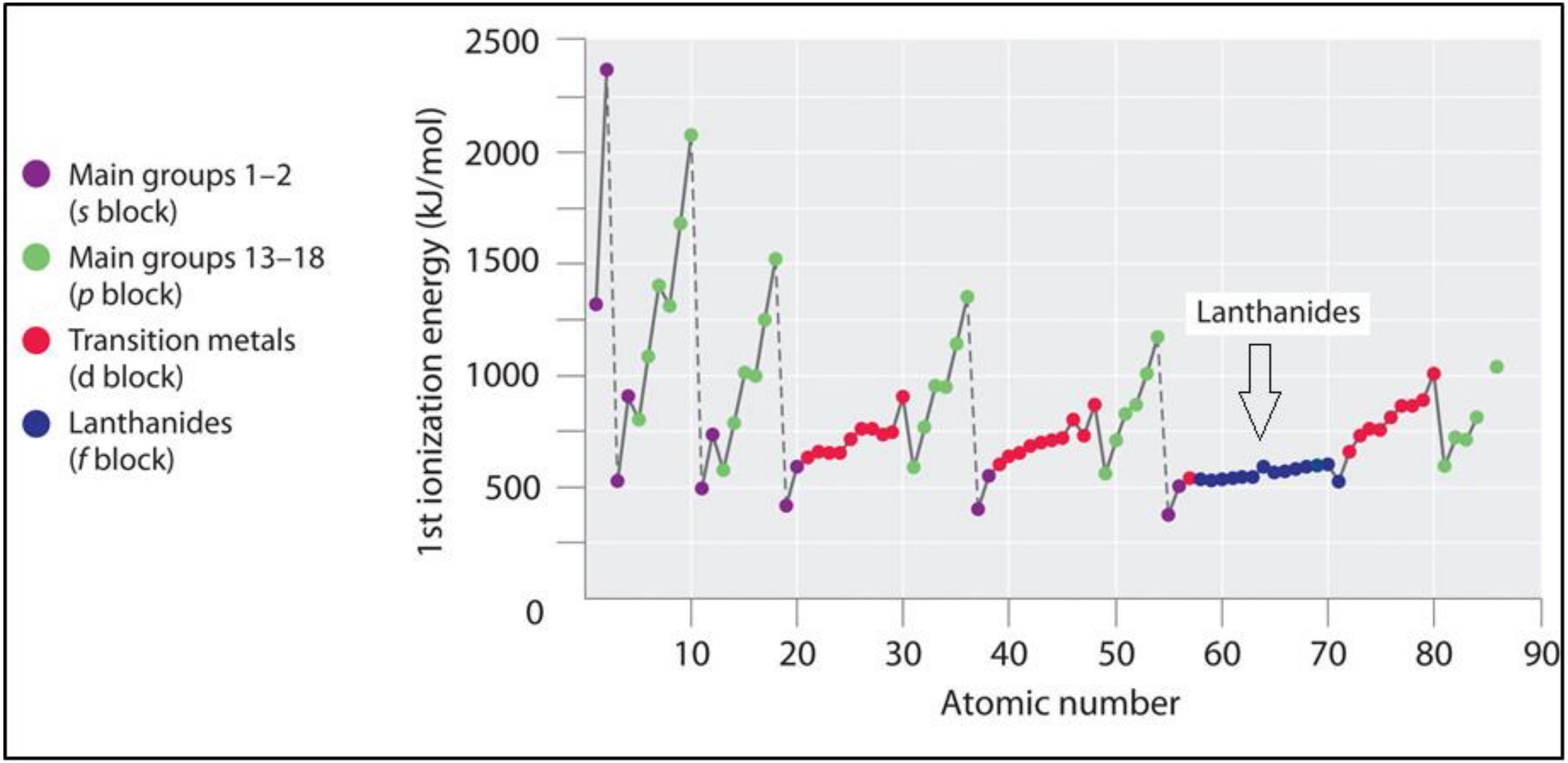
- *The shielding effect of different orbitals is as follows:* *s > p > d > f.*



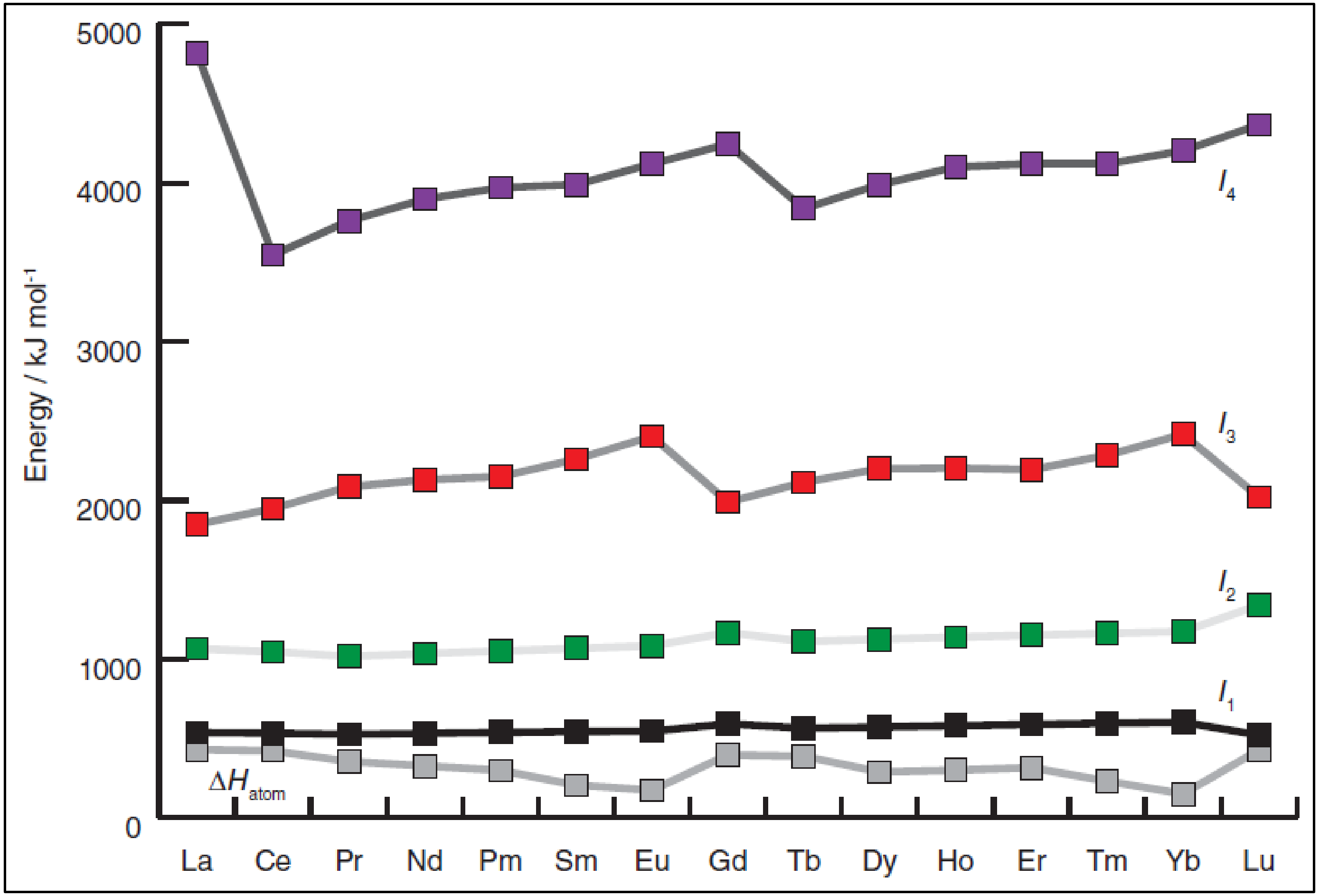
- As electron shells (orbitals) are added, the electrons between a valence electron and the nucleus repel the electrons
- This means that the attractive force of the nucleus is diminished
- The valence electrons are therefore do not feel as much of a pull from the nucleus as they should
- This will effect various trends across the periodic table
- This is more of a vertical than horizontal trend as in order for the outer electrons to experience the repulsive effect there must be added orbitals to cause repulsion, not added electrons in the same orbital

❑ *The Ionization Energy*

- Except the group 1 elements, the 1st ionization energy of lanthanides is low as compared to the other elements of the periodic table.

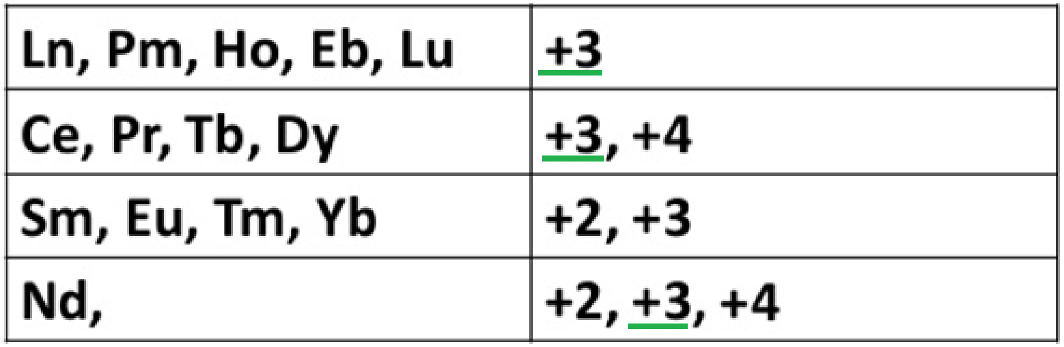


- The lanthanides have very small 2nd ionization energies (as compared to the other elements of the periodic table), and these can also be easily compensated for by bonding or ion-dipole interactions in solution.
- The predominance of the +3 oxidation state (*Ln*$^{3+}$) for the lanthanides is therefore simply a consequence of $IE_1 + IE_2 + IE_3$ being sufficiently small, and IE_4 being way too large.



❑ *The Oxidation State*

- The REEs display variable oxidation states (+2 (also noted +II); +3 (also noted +III); +4 (also noted +IV)) but much less than those displayed by the transition elements (block *d*).
- The characteristic and the most stable oxidation state of the lanthanides is **+3** (REE^{3+}) in their compounds and ions (see the table below).



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

- The lanthanide ions (Ln^{2+}, Ln^{3+} and Ln^{4+}) formed by loosing the two 6s electrons, the one *d* electrons or one *f* electron.
- The electron configuration of valence electrons of the lanthanide ions in their possible oxidation states is given in the table below. It is of the form ${}_{54}[\text{Xe}]4f^{n}$ ($n = 0$–14)

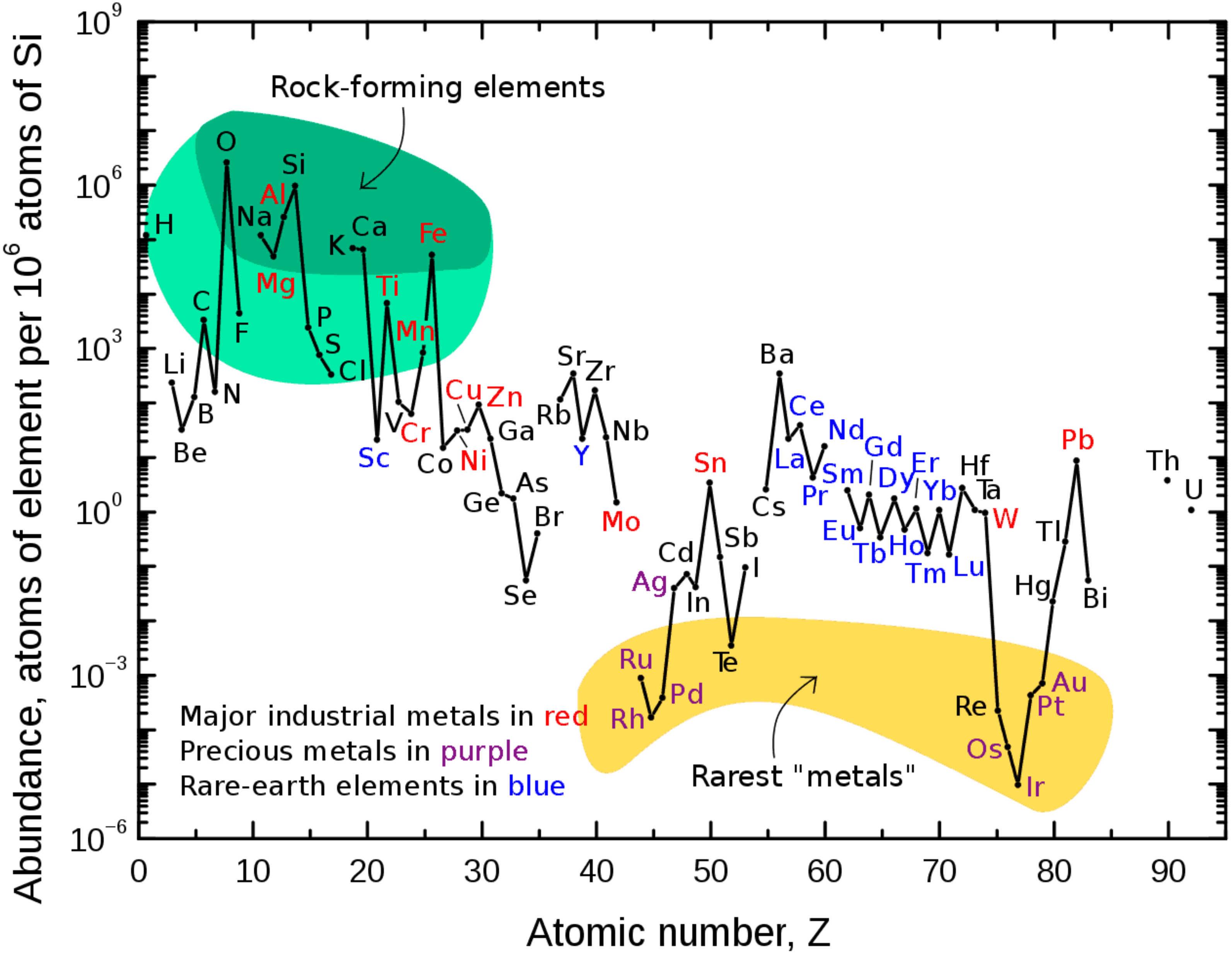
Oxidation States

Symbol	Idealized	Observed	Ln^{3+}	Ln^{2+}	Ln^{4+}	N0. of f-electron
La	[Xe] $4f^05d^16s^2$	[Xe] $4f^05d^16s^2$	[Xe]	-		0
Ce	[Xe]$4f^15d^16s^2$	[Xe]$4f^25d^06s^2$	4f1	$4f^2$	[Xe]	1
Pr	[Xe]$4f^25d^16s^2$	[Xe]$4f^3$ $5d^06s^2$	$4f^2$	-	$4f^1$	2
Nd	[Xe]$4f^35d^16s^2$	[Xe]$4f^4$ $6s^2$	$4f^3$	$4f^4$	$4f^2$	3
Pm	[Xe]$4f^45d^16s^2$	[Xe]$4f^5$ $6s^2$	$4f^4$	-	-	4
Sm	[Xe]$4f^55d^16s^2$	[Xe]$4f^6$ $6s^2$	$4f^5$	$4f^6$	-	5
Eu	[Xe]$4f^65d^16s^2$	[Xe]$4f^7$ $6s^2$	$4f^6$	$4f^7$	-	6
Gd	[Xe]$4f^75d^16s^2$	[Xe]$4f^75d^16s^2$	$4f^7$	-	-	7
Tb	[Xe]$4f^85d^16s^2$	[Xe]$4f^9$ $6s^2$	$4f^8$	-	$4f^7$	8
Dy	[Xe]$4f^95d^16s^2$	[Xe]$4f^{10}$ $6s^2$	$4f^9$	-	$4f^8$	9
Ho	[Xe]$4f^{10}5d^16s^2$	[Xe]$4f^{11}$ $6s^2$	$4f^{10}$	-	-	10
Er	[Xe]$4f^{11}5d^16s^2$	[Xe]$4f^{12}$ $6s^2$	$4f^{11}$	-	-	11
Tm	[Xe]$4f^{12}5d^16s^2$	[Xe]$4f^{13}$ $6s^2$	$4f^{12}$	$4f^{13}$	-	12
Yb	[Xe]$4f^{13}5d^16s^2$	[Xe]$4f^{14}$ $6s^2$	$4f^{13}$	$4f^{14}$	-	13
Lu	[Xe]$4f^{14}5d^16s^2$	[Xe]$4f^{14}5d^16s^2$	$4f^{14}$	-	-	14

- In just the same way as for other elements, the higher oxidation states (+4) occur in the fluorides (Example: the Terbium(IV) fluoride, TbF_4) and oxides (Example: the Cerium(IV) oxide, CeO_2), and the lower oxidation states (+2) occur in the other halides, particularly bromides (example: the Samarium (II) bromide, $SmBr_2$) and iodides (Example: the Samarium (II) iodide SmI_2).
- Oxidation numbers (+2) and (+4) do occur, particularly when they lead to:
  - A noble gas configuration. e.g. Ce^{4+} (f^0)
  - A half-filled *f* shell e.g. Eu^{2+} and Tb^{4+} (f^7)
  - A completely filled *f* level. e.g. Yb^{2+} (f^{14})
- In addition (+2) and (+4) states exist for elements that are close to these states. Thus 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 only (+4) and (+2) states which have any aqueous chemistry are Ce^{4+}, Sm^{2+}, Eu^{2+} and Yb^{2+}.

❑ *Resources and Abundance*

- REEs *(with the exception of promethium ($_{61}$Pm))* are relatively abundant in the Earth's crust, but minable concentrations are less common than for most other ores.
- In all the ores, the atoms with an even *(any integer that can be divided exactly by 2)* 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 *(any integer that cannot be divided exactly by 2)* atomic number.
- The REEs are actually not rare. For example, Cerium (64*ppm* in the earth's crust) is the 26th most abundant of all elements, being half as abundant as Chlorine (Cl) and 5 times as abundant as Lead (Pb) (See the figure in the next slide).
- Even Thulium (Tm) (0.33ppm), the rarest after Promethium (Pm), is rather more abundant in the earth's crust than is iodine (I). Further, samarium ($_{62}$Sm) is the 40th most plentiful element found in the Earth's mineral deposits and Neodymium ($_{60}$Nd), like other REEs occurs in small, less accessible ore deposits. However, this REE is nearly as common as copper and more plentiful than gold ($_{79}$Au).



- *The abundance of the REEs in the earth crust in comparison with some other metals and non-metals.*

- After China, the major RE countries based on reserve volume are Vietnam, Brazil, and Russia.
- Numerically, most of the deposits are located in the United States, followed by Australia, Brazil, China, Canada, India, Russia, and South Africa. These deposits belong to both the placers and hard-rock types.
- Promethium ($_{61}Pm$) occurs as traces in uranium ores and is separated from fission products produced in nuclear reactors. It is unstable with a half-life of 2.623 years.
- While scandium ($_{21}Sc$) and yttrium ($_{39}Sc$) occur mainly in uranium ores, the other members occur in over 100 minerals (Monazite, Bastnasite, Euxenite, Gadolinite, Xenotime, Apatite, Loparite, China’s ion-adsorption ore,…) but the only 3 minerals of commercial importance are:

- The **monazite** sand, which is a RE phosphate, $\underline{\mathit{RE}PO_4}$
- The **bastnasite**, which is a RE fluorocarbonate, $\underline{\mathit{RE}CO_3F}$
- The **Xenotime**, which is a RE phosphate ore with the major component of which is yttrium orthophosphate (YPO_4).

- There are 5 different most common species of **monazite**, depending on the relative amounts of the REEs in the mineral:
    - Monazite-(Ce), (Ce, La, Nd, Th)PO_4 (the most common member)
    - Monazite-(La), (La, Ce, Nd)PO_4,
    - Monazite-(Nd), (Nd, La, Ce)PO_4,
    - Monazite-(Sm), (Sm, Gd, Ce, Th)PO_4,
    - Monazite-(Pr), (Pr, Ce, Nd, Th)PO_4.

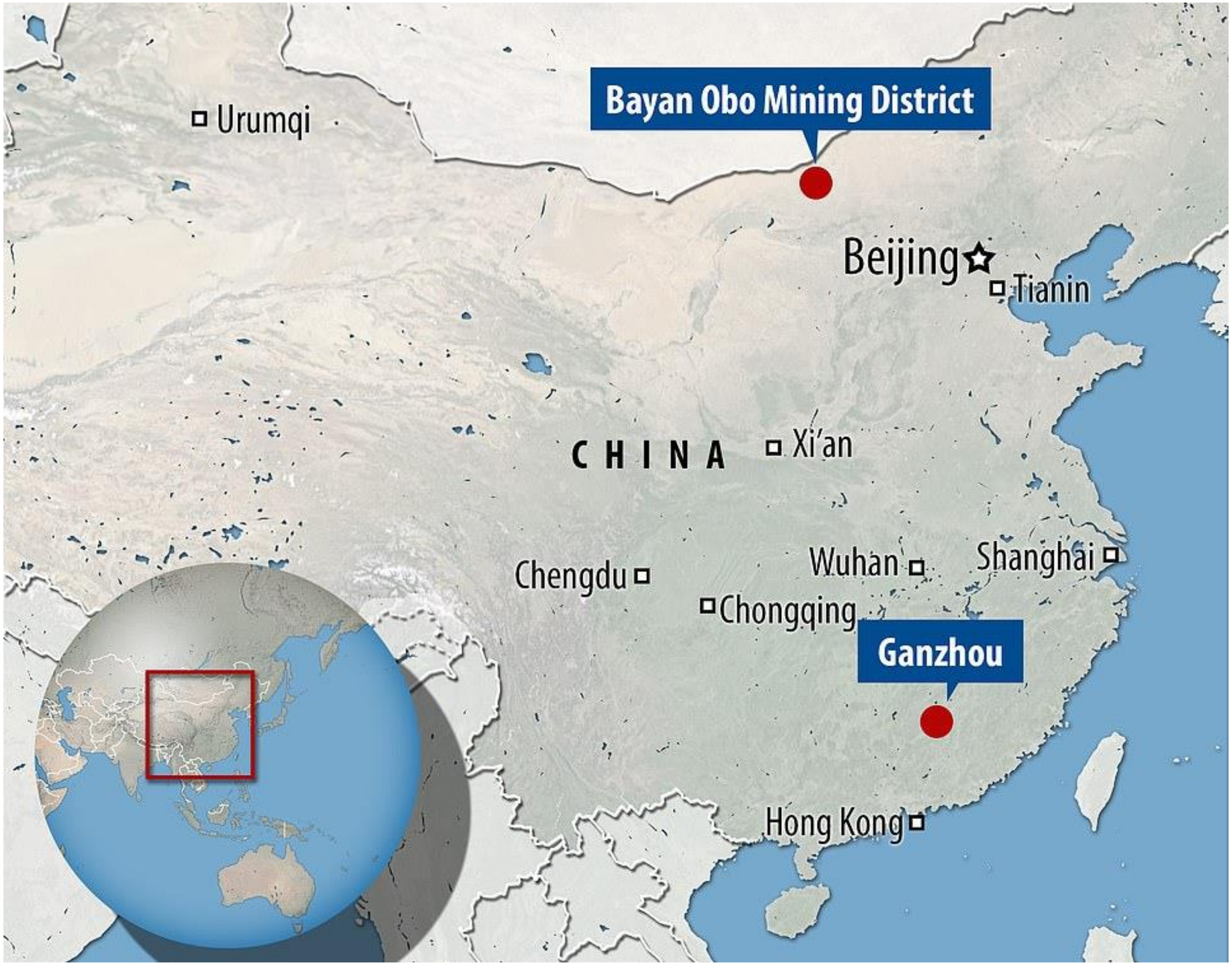
✓ *Note. In the compositions given above, the elements in parentheses are listed in the order of their relative proportion within the mineral. For example, Cerium (Ce) is the most abundant REE in monazite-(Ce).*

- The mineral **bastnasite** is one of a family of 3 carbonate-fluoride minerals, which includes:
    - Bastnasite-(Ce) with a formula of (Ce,La)CO_3F,
    - Bastnasite-(La) with a formula of (La,Ce)CO_3F,
    - Bastnasite-(Y) with a formula of (Y,Ce)CO_3F.

- *Monazite-(Ce) specimen from Siglo XX mine, Bolivia-the orange mineral is monazite, and the clear one quartz.*

- *Bastnasite (Ce) named for the type locality at the Bastnas mines in Vastmanland, Sweden and for the dominance of cerium (Ce) over the other rare earth elements in the composition.*

- Although the number of identified deposits in the world may be over 850, the actual operating mines are only handful. Prominent currently operating mines are Bayan Obo (the world’s largest RE mine) in China, Mountain Pass in the US and recently opened Mount Weld in Australia.
- The advent of the Chinese era (mid 1980s) was marked by availability of REs at prices that undercut most other mining operations, resulting in closure of many mines outside of China. At this point, the Chinese have around 55% of all known RE deposits and control 95% of world supply through integrated mining, refining and supply chains.

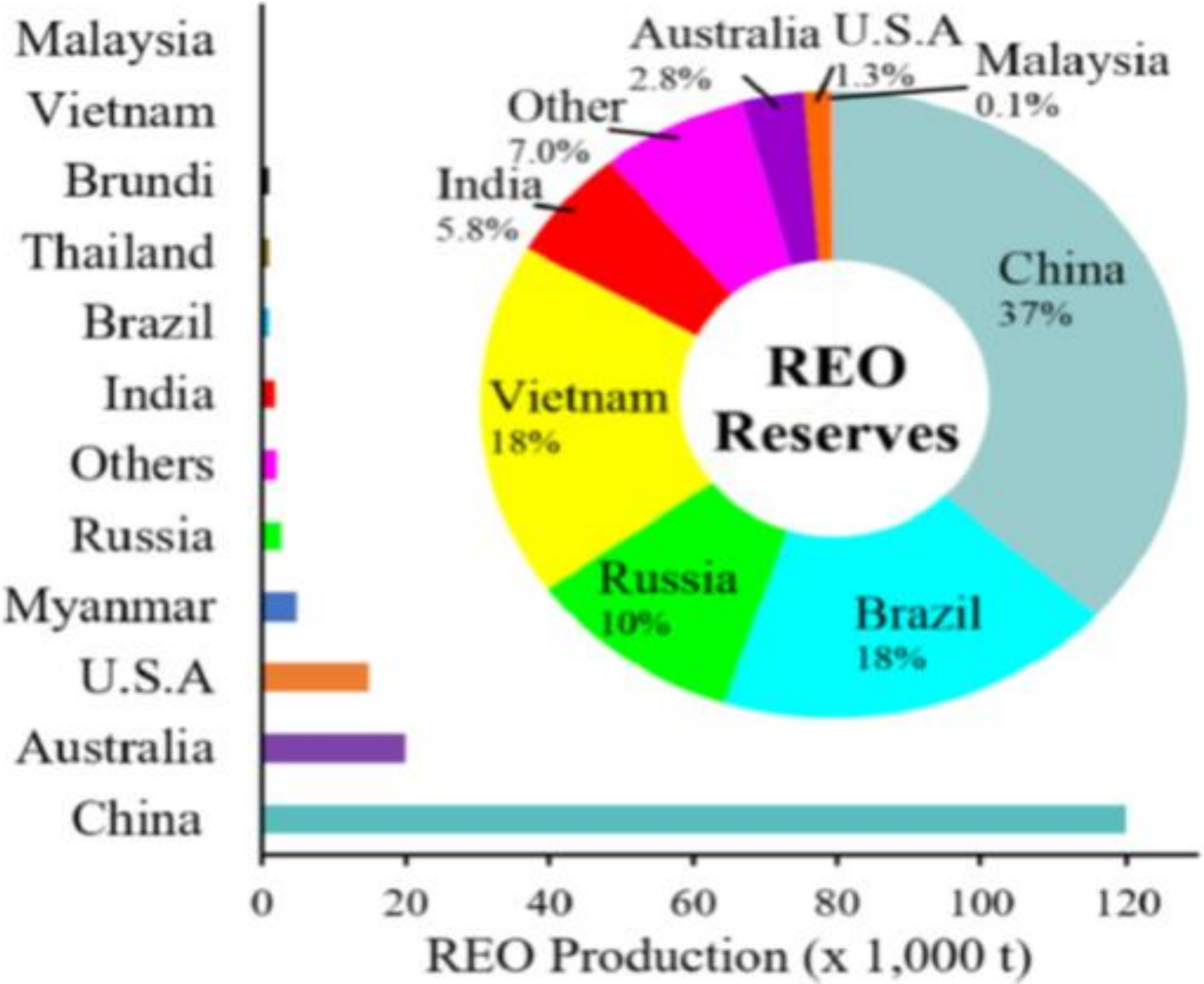


- *Bayan Obo* is *the world's largest RE mine which is a mining town in the west of Inner Mongolia.*
- *The 2nd largest RE mine in china is located in Ganzhou, south china.*

❑ *Worldwide Reserves and Production*

- Although REs are distributed around the world, their ores are mainly extracted in China. Milling, floating, separation, and purification processes are carried out in China as well.

This country shows a strategic position in RE production and market in the world. According to the production and reserve data of 2018 (see figure below), the world’s total RE reserve is 120 million tons. China retains 37% of these reserves and dominates the RE oxides (REO) production. The REO production amount of China for 2018 was 120,000 tons. Australia was in second place with 20,000 tons of REO.

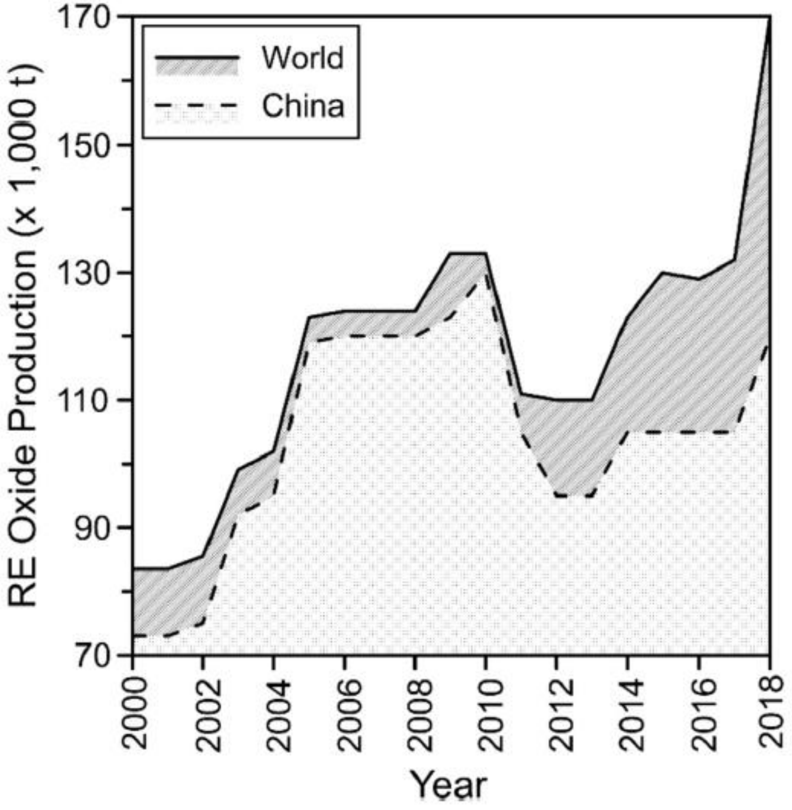


Doughnut chart shows the percentage of rare earth oxide (REO) reserves by countries. The bar chart shows the amount of REO production by countries.

Data refer to 2018

- World REO production has shown an increasing tendency driven by China until 2010. Global financial crisis affected the production from 2010 to 2013 (see figure opposite).

The trend has started increasing again from 2013 again. Simultaneously with the worldwide financial crisis, commercial tensions between China and Japan resulted in China’s cessation of RE trade to Japan on 2010. The prices of metallic lanthanide have been strictly affected by the aforementioned crises: the lanthanide prices decreased after 2010. Thus, the importance of lanthanides and their domestic production have been progressively understood in the rest of the world too. This is evidenced really the increasing world production of REO respect to that of China (see figure opposite).



World production of rare earth oxide (REO) from 2000 to 2018, and the production in China.

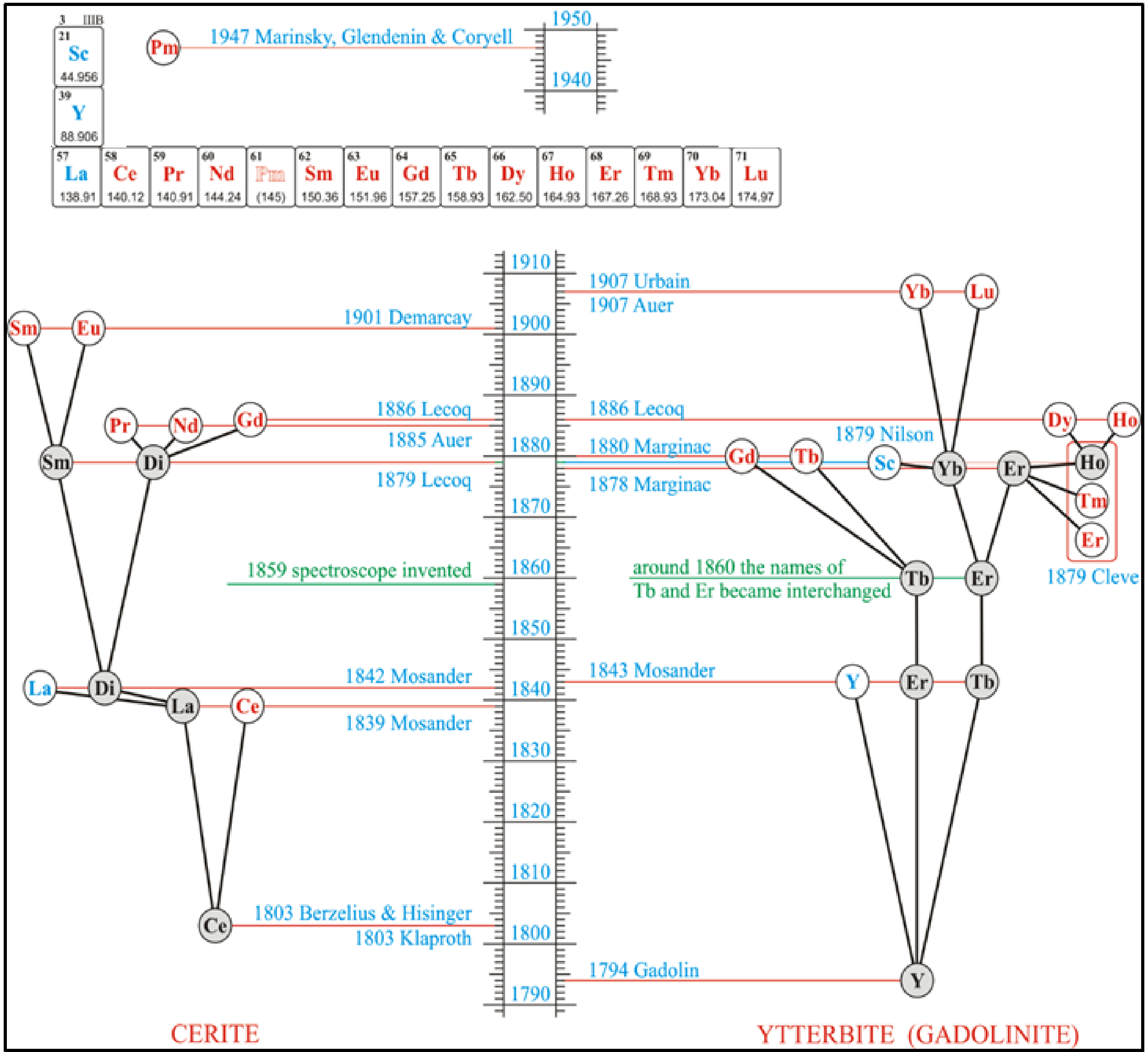
❑ *Discovery of the REEs (A Short History) : 196 years of REs History*

- The history of RE minerals begins in the year 1751, when the Swedish mineralogist and chemist Axel Fredrik Cronstedt (1722-1765) described an unusually heavy, reddish mineral (later named ***cerite***) which he had found in the quarry of Bastnäs, near Eyddarhyttan, Sweden.

The famous Swedish chemist Carl Wilhelm Scheele (1742-1786) analyzed it and came to the conclusion that it was only an iron aluminum silicate and the mineral was more or less forgotten for next 5 decades.

- In 1787, the story continued when a Swedish chemist Lieutenant Carl Axel Arrhenius (1757-1824) found an interesting, very dense black mineral which he named ***ytterbite*** in a small feldspar and quartz mine near the village of *Ytterby*, Sweden. The first scientific description of the mineral was performed by Swedish mineralogist Bengt Reinhold Geijer (1758-1851) who speculated that the mineral might contain the recently discovered element tungsten.

- The complex compositions of the two starting minerals cerite and ytterbite (later renamed gadolinite) are revealed in the flow chart of discoveries of the elements (see the figure below).



○ *The complex compositions of the 2 starting minerals, cerite and gadolinite (ytterbite) are revealed in the flow chart of discoveries of the elements.*

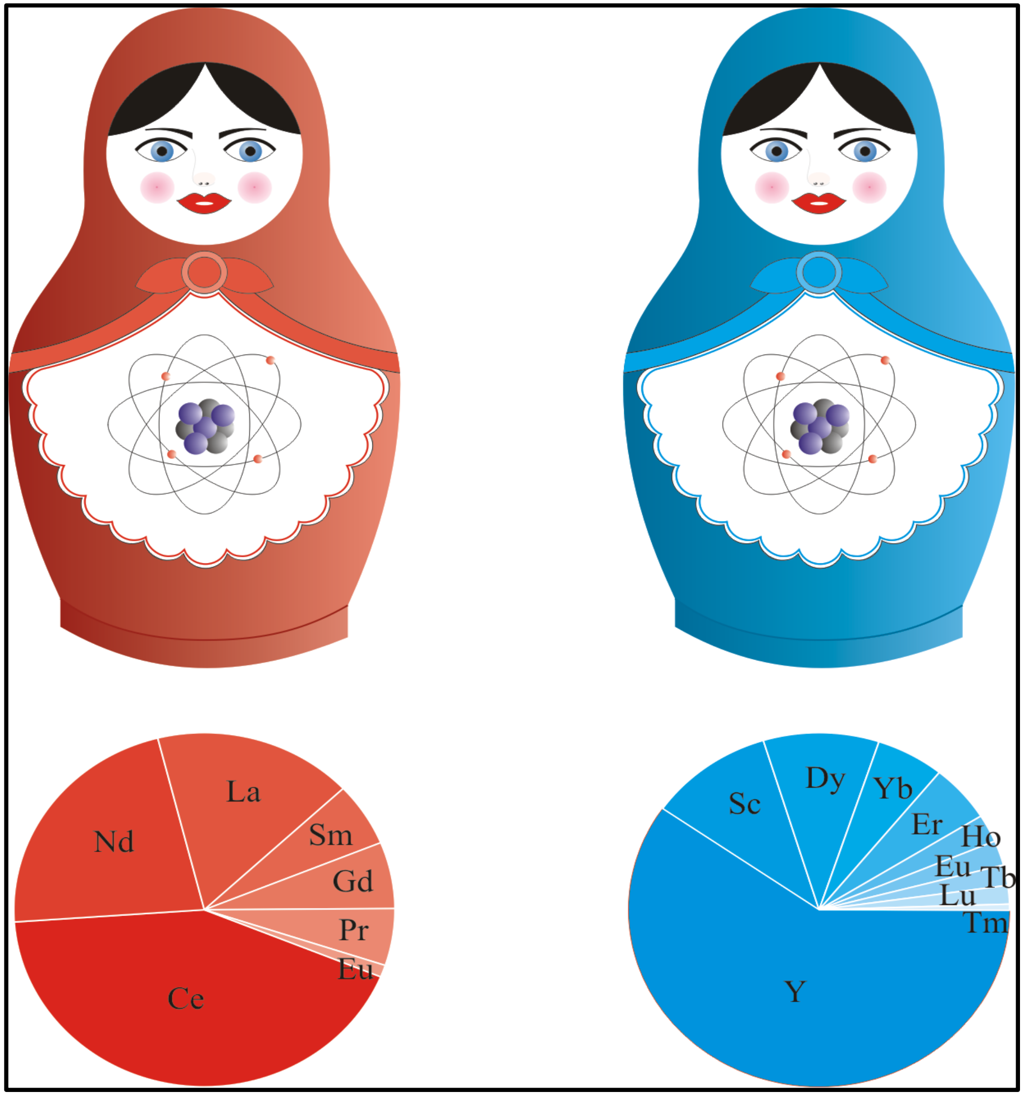
- Whilst then cerite was the first of the RE minerals to be discovered, it was in ytterbite (later renamed gadolinite) that new elements were first recognized, and the chemistry of the REs began in 1794 with Gadolin's observation. The Finnish chemist Johan Gadolin (1760-1852), while examining an Arrhenius' rock, was able to show that the new mineral contained 23 % silicon dioxide, 4.5 % beryllium oxide, 16.5 % iron oxide, and about 55.5 % of a new oxide he called ytterbia.
- 3 years later the Swedish chemist and mineralogist Anders Gustaf Ekeberg (1767-1813) had confirmed Gadolin's analysis and he shortened the name ytterbia to yttria.
- The early Greeks defined earths as materials that could not be changed further by the sources of heat then available. This Greek conception remained strong in chemistry, and oxides of metals such as calcium, aluminum, and magnesium were known as earths and were thought to be elements. Not until 1808 did the English chemist Sir Humphry Davy (1778-1829) demonstrate that the earths as a class were not elements themselves but were compounds of oxygen and metallic elements.

- After discovery of yttria, the chemists looked closely at Cronstedt's *'heavy stone from Bastanäs'*. In 1803, the Swedish ironmaster and scientist Wilhelm Hisinger (1766-1852) together with the young chemist Jöns Jakob Berzelius (1779-1848) analyzed a sample of the 'tungsten (heavy stone) of Bastanäs', and isolated an earth similar to yttria but recognized it was distinct. The Swedish chemists named new earth ceria, from the asteroid Ceres, discovered two years previous, in 1801, between Mars and Jupiter by the Italian monk and astronomer Guiseppe Piazza (1746-1826).
- At the same time and independently of Hisinger and Berzelius the German chemist Martin Klaproth (1743-1817) also analyzed tungsten from Bastanäs and come to the same conclusion: it contained a new element which he called ochroite (from the Greek *ochra* meaning yellow brown) due to the light brown color of the pure substance. Hisinger, Berzelius and Klaproth are usually named as co-discovers of cerium.

- But no one was aware that new elements are like a Russian matryoshka dolls (See next slide).
- Then, in 1839, Berzelius' student, the Swedish chemist Carl Gustav Mosander (1797-1858) separated ceria into pure ceria and an earth which he named lanthana (from the Greek word *lanthanein*, to lie hidden, because it lay hidden in the mineral cerite for 36 years after ceria was discovered in 1803). In 1842 he showed that lanthana contained another earth, which he called didymia (from the Greek *didymos* meaning twins because it closely resembled lanthana).

❖ ***’’Yttria matryoshka’’***

- Next year, Mosander took *'yttria matryoshka'* into his own hands. He separated yttria into three fractions: the first one, an oxide with a yellow color, he named erbia, the second one with a rosy color he named terbia, and the final fraction, a colorless oxide he continued to call yttria. Given that he separated the two new earths from yttria, Mosander derived the names of terbia and erbia from the name of the village Ytterby.



- *REEs as a Russian nesting dolls (matryoshka or babushka dolls): red is 'ceria matryoshka' and blue is ‘Yttria matryoshka'.*

Babushka meaning "grandmother" or "old woman”

✓ *Matryoshka dolls (Russian: матрёшка) also known as babushka dolls, stacking dolls, nesting dolls, Russian tea dolls, or Russian dolls are a set of wooden dolls of decreasing size placed one inside another. The name matryoshka, literally "little matron", is a diminutive form of the Russian female first name "Matryona" (Матрёна) or "Matryosha".*

- However, in the confusion arising from the similarity in the properties of the REEs, the names of two, terbium and erbium, became interchanged (around 1860).
- After Mossander's work, other chemists attempted to isolate other REs, but there were proved to be a hard nut to crack. It was not until the invention of the spectroscope by the German chemist Robert Wilhelm Bunsen (1811-1899) and physicist Gustav Robert Kirchhoff (1824-1887) in 1859 and the development of spectral analysis that the tools for studying REs were finally provided.
- In 1878, the Swiss chemist Jean-Charles Galissard de Marignac (1817-1894) finally split one of the *'rare earth matryoshkas'* triggering an avalanche of discoveries. He showed that Mosander's terbia, now erbia, could be separated into two earths: the rose-colored earth he continued to call erbia and the colorless one he named ytterbia.

- ***Note:*** *This small village on the Swedish island of Resarö, in the Stockholm archipelago is now celebrated in the names of no less than four elements: yttrium (Y), terbium (Tb), erbium (Er), and ytterbium (Yb).*

- This erbia was, however, still not a pure oxide. In the following year the Swedish chemist Per Theodor Cleve (1840-1905) split erbia into a purified erbia and two new earths: the brownish precipitate he named holmia (the Latin name of his native city Stockholm) and the greenish one he named thulia (after *Thule*, the old name for Scandinavia).
- One of these new earths was also impure and, in 1886, the French chemist Paul-Émile Lecoq de Boisbaudran (1838-1912) separated a new oxide from holmia, which he named dysprosia (according Greek verb *dysprositos*, hard to get at).
- In 1879, during a routine procedure for isolating very pure ytterbia (ytterbium oxide, Yb_2O_3) from the RE mineral euxenite, the Swedish chemist Lars Fredrik Nilson (1840-1899) found traces of an unknown earth which he named scandia (this time after the Latin name for Scandinavia, *Scandia*)

- In 1880 Galissard de Marignac discovered that one fraction of gadolinite, known as terbia, contained a previously unknown element which he tentatively called Yα.
- Six years later, in 1886, de Boisbaudran separated a pure form of the earth Yα from Mosander's didymia. Boisbaudran proposed and Marignac agreed to rename Yα to gadolinium after the mineral in which it was found.
- Finally in 1907, the French chemist Georges Urbain (1872-1938) and the Austrian chemist and engineer Carl Auer (1858-1929), who later became Baron von Welsbach, independently demonstrated that ytterbia contains one more oxide. Urbain's designation of the new element as lutecium, after the ancient name for his native city, Paris, was accepted by most, although Auer's name cassiopium, after the constellation Cassiopeia, was used in German-speaking countries for many years.

❖ ***‘’Ceria matryoshka’’***

- On the other hand, *'ceria matryoshka'* revealed even more hidden dolls within. In 1879, during analysis of the mineral samarskite, Boisbaudran found that ammonium hydroxide has caused a new precipitate to form before the dydimia formation. He called the new earth samaria according to its mineral source.

➢ ***Note:*** *Mineral samarskite was named after the Russian mining engineer, Colonel Vasilij Evgrafovič Samarskij-Byhovec (1803-1870) who supported the development of geology and mining in the Ural mountains. This rather unknown person was the first person by which one chemical element is named.*

- In 1885 von Welsbach succeeds to separate new didymia into two new earths which he named praesodymia (green didymia its leek-green salts) and neodymia (new didymia), breaking the tradition of keeping the old name. So, after 40 years of being known as the element with the symbol Di, didymium was removed from the periodic table of Mendeleev.

- Further spectroscopic analysis in 1886 of samaria by the French chemist Eugène-Anatole Demarçay (1852-1904) yielded new spectroscopic lines which were indicating an unknown element. 5 years later, Demarçay had improved his separation technique that enabled him to isolate some suitably pure samples of the new colorless earth, closely associated with samaria, which he named europium.

❖ ***<u>The last element discovered</u>*: The promethium ($_{61}$Pm)**

- When the British physicist Henry Gwyn Jeffreys Moseley (1887-1915) developed the present-day scheme for assigning atomic numbers to the elements in 1912, it became apparent that one RE metal was missing between neodymium ($_{60}$Nd) and samarium ($_{62}$Sm).
- During the years several groups claimed to have produced the element 61, but they could not confirm their discoveries because of the difficulty of separating it from other elements.
- The isolation and identification of element 61 was finally made in 1947 by the American chemists Jacob Akiba Marinsky (1918-2005), Lawrence Elgin Glendenin (1918-2008), and Charles DuBois Coryell (1912-1971) from the fission products of uranium fuel irradiated in a nuclear reactor at Oak Ridge, USA.
- The element <u>promethium</u> ($_{61}$Pm) was appropriately named after the Prometheus, son of Iapetus, who stole fire from Zeus' lightning and brought it to humans, because it was created in the one of first atomic fires lighted by human hand.

Chapter 3:

Properties And Resources Processing Of The Elemental Rare Earth Metals

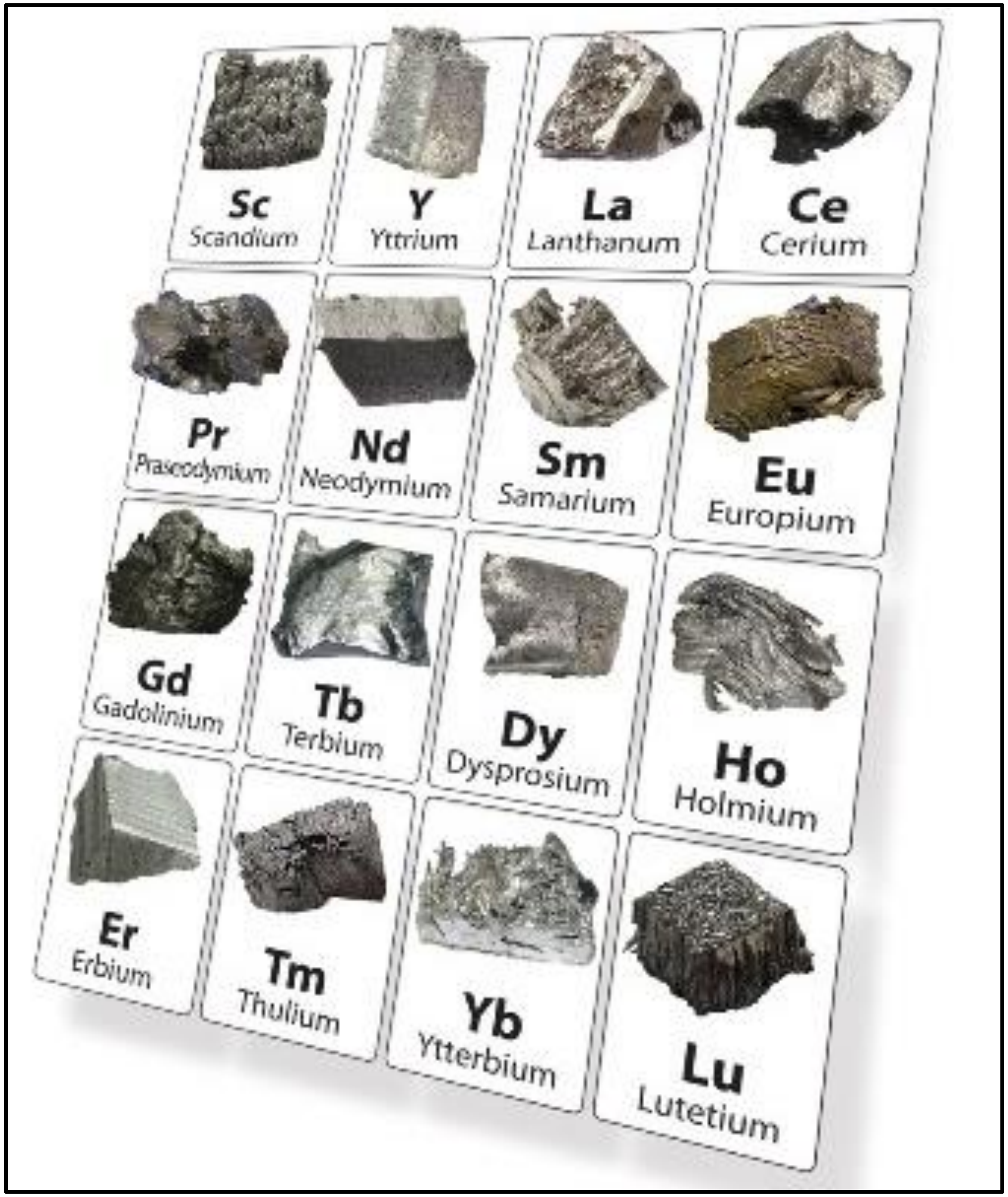
❑ ***The Physical Properties***

- The rare earth elements (*REEs*) (17 elements: Sc, Y, La, and the lanthanide series from Ce to Lu) have many similar chemical properties, and that often causes them to be found together in geologic deposits. They are also referred to as "rare earth oxides" (*REOs*) because many of them are typically sold as oxide compounds.
- However, there are extraordinary diversity in physical properties of the pure metallic elements as well as the *REEs* containing compounds and alloys. For example, their melting points differ by nearly a factor of 2, and the vapor pressures differ by a factor of more than one billion.

❖ ***The Metallicity, Color and Hardness***

- The *REEs* are all metals, and the group is often referred to as the "rare earth metals." (*REMs*)
- *REMs* have a high luster and a silvery white color (except for Eu and Yb which are pale yellow). But, they tarnish readily when exposed to air, especially Ce, La and Eu, forming a surface layer of their oxides, RE_2O_3.

- They are rather soft, but become harder across the series.
- They are malleable and ductile.

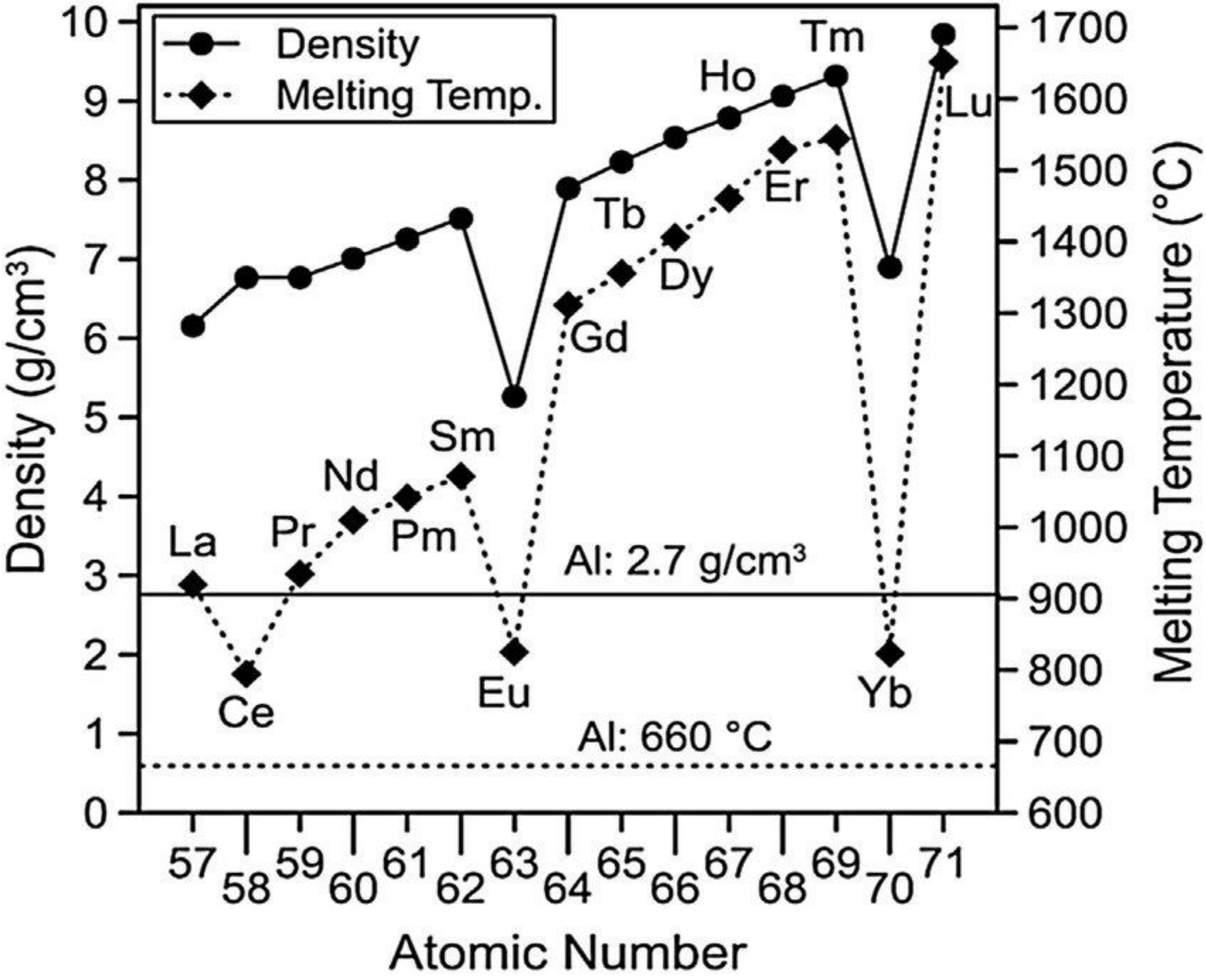


❖ ***The Melting Point***

Melting, or fusion, is a physical process that results in the phase transition of a substance from a solid to a liquid. In a pure crystalline solid, this process occurs at a fixed temperature called the melting point (or melting temperature). However, an impure solid generally melts over a range of temperatures below the melting point of the principal component.

For the *REMs* , the melting point increases in a regular manner across the series from $_{57}$La to $_{71}$Lu with the exception of $_{58}$Ce, $_{63}$Eu, and $_{70}$Yb (see figure below). The melting point of Lu is almost twice that of La. While considering the increase in the melting point by as much as 750 °C, as the RE series is traversed from La to Lu, as unusual for a group of nearly identical elements.

The change in the melting point is attributed to the extent of hybridization of the *4f* and *5d6s* orbitals. The hybridization is the largest for Ce (with the lowest-melting point) and decreases along the series from light lanthanides to heavy lanthanides. A lower melting point is associated with a greater amount of hybridization.



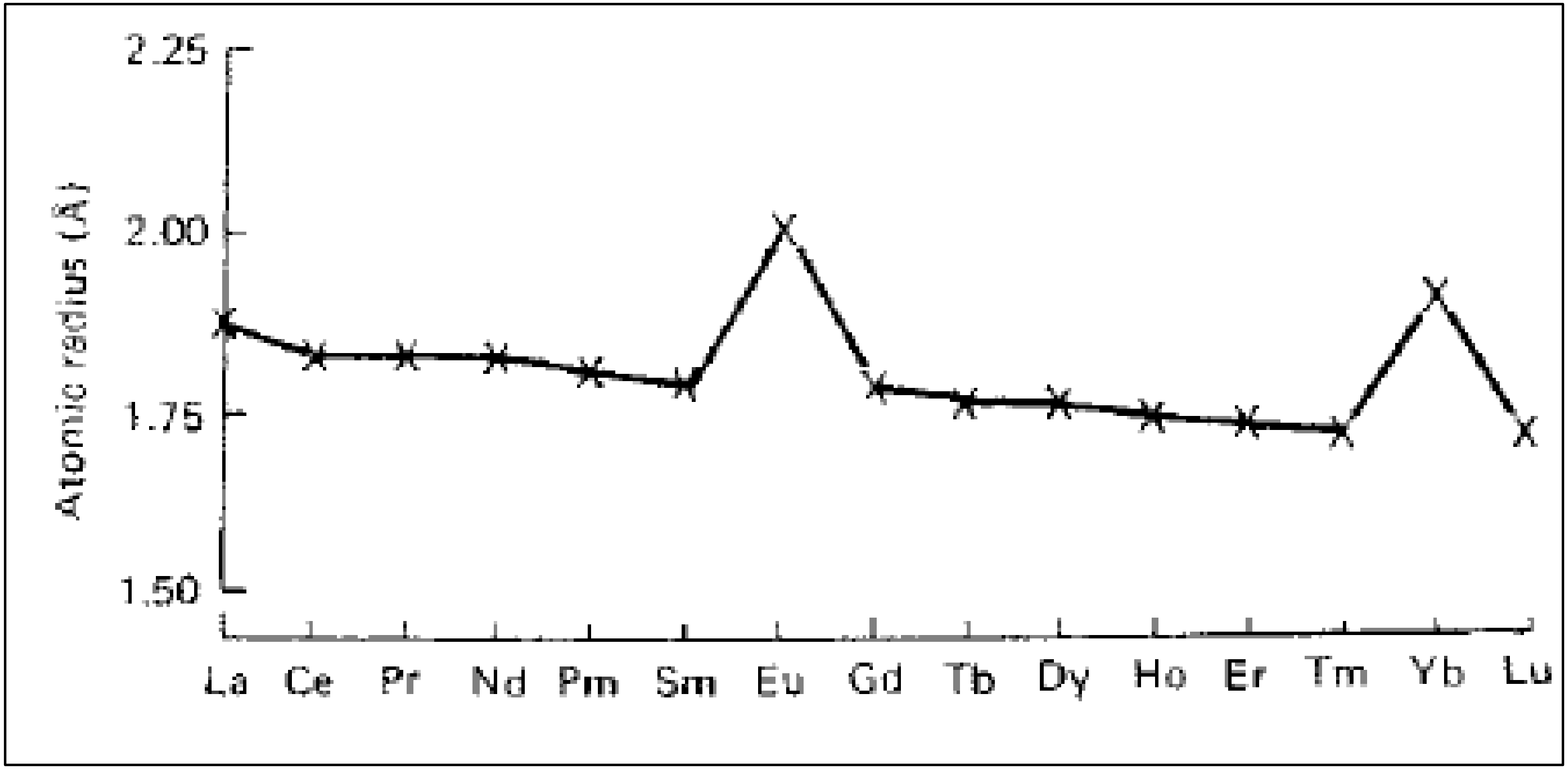
- *Density and melting temperature of lanthanide elements.*

❖ ***The Density***

The density shows a similar trend as the meting point. It increases with the increase of atomic number from La to Lu. While, Eu and Yb interrupt this trend showing the lower densities of 5.26 and 6.90 g.cm^{-3}, respectively (see last slide).

- ***The metallic (atomic) radius***

The atomic radius shows a similar trend as the density. It shows smooth transition across the series, except the discontinuities observed for the metals europium and ytterbium. Thus the atomic radii of europium and ytterbium are about 20 pm greater than might be predicted by interpolation from values for the flanking lanthanides (see figure below).



- *The atomic radius of lanthanide elements.*

❖ ***The Boiling Point***

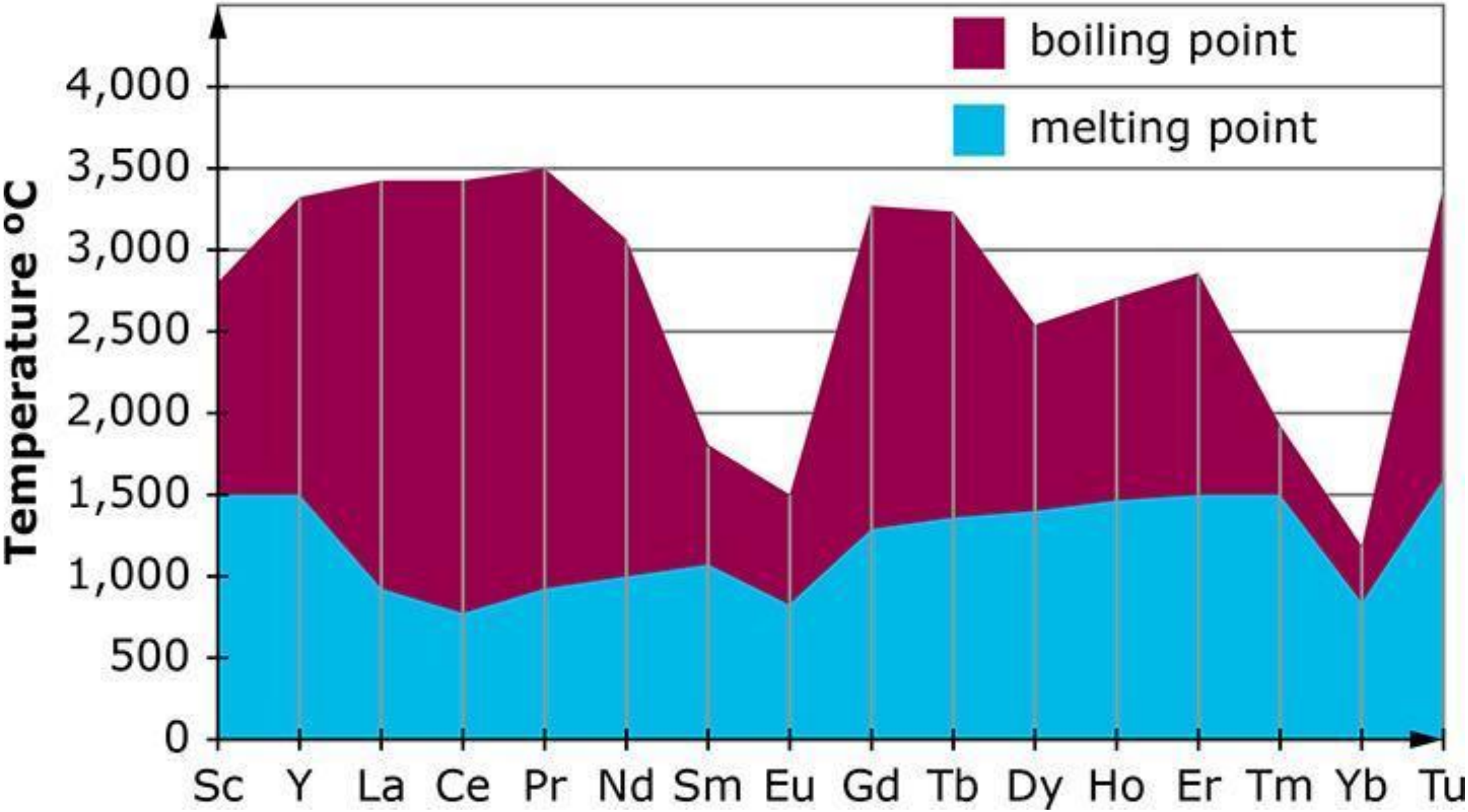
Boiling is the rapid vaporization (phase transition of a substance from a liquid to a gas) of a liquid, which occurs when a liquid is heated to its boiling point.

Boiling point is the temperature at which the vapor pressure of the liquid is equal to the pressure exerted on the liquid by the surrounding atmosphere.

The boiling points of *REMs* do not exhibit a trend, even to the extent, the melting points displayed, across the series (see figure below).

$_{57}$La metal, which is among the four lowest-melting-point *REs*, has the highest boiling point. In other words, it has the lowest vapor pressure at its melting point for any *REM*. The most volatile *REM* is $_{70}$Yb. At 1000 °C, for example, the vapor pressure of $_{57}$La is one-billionth of the vapor pressure of $_{70}$Yb.

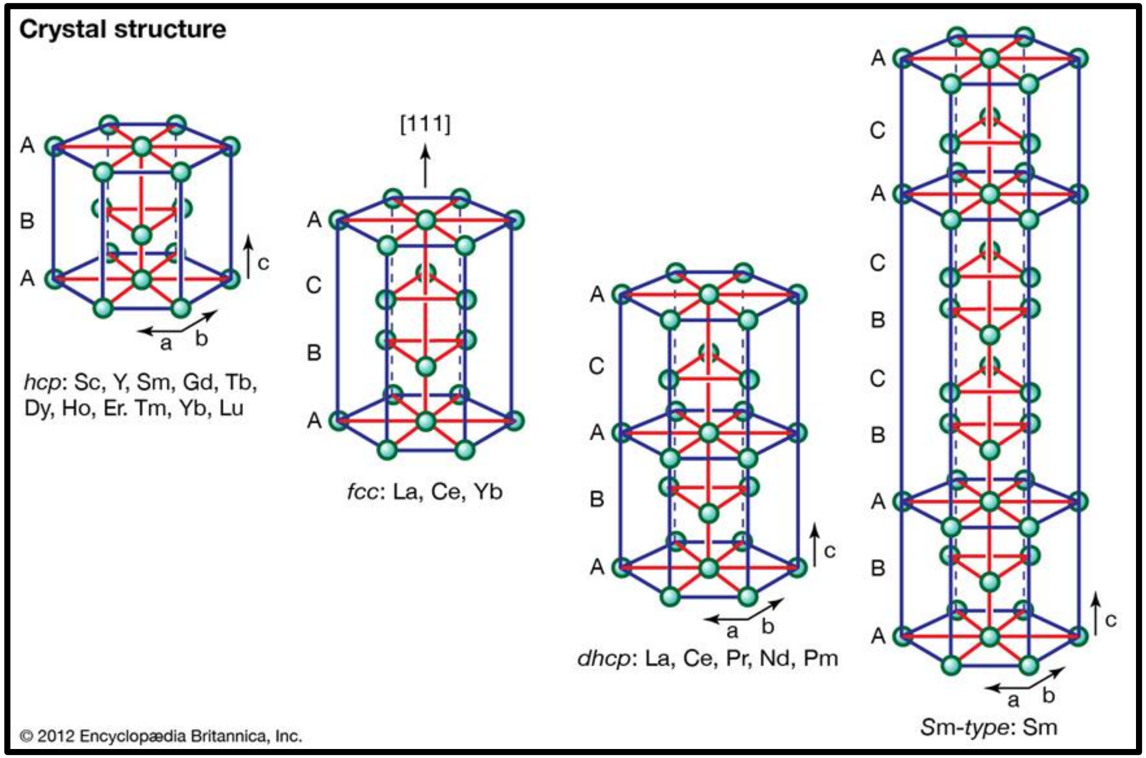
The boiling point of a *REM* strongly influences the method used for its preparation and purification of the metal. For example, the most volatile metals—europium, samarium, and ytterbium—are prepared by the reduction–distillation process.

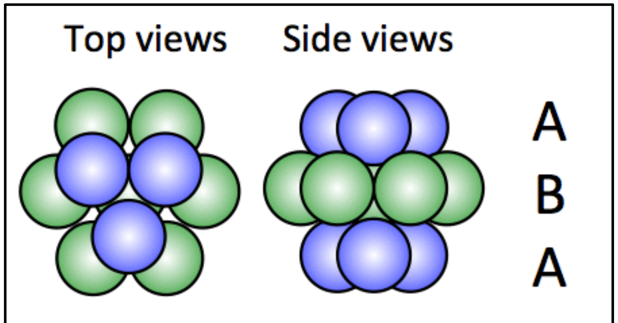


Melting and Boiling Points of Some Rare Earth Element

❖ *The Crystal Structure*

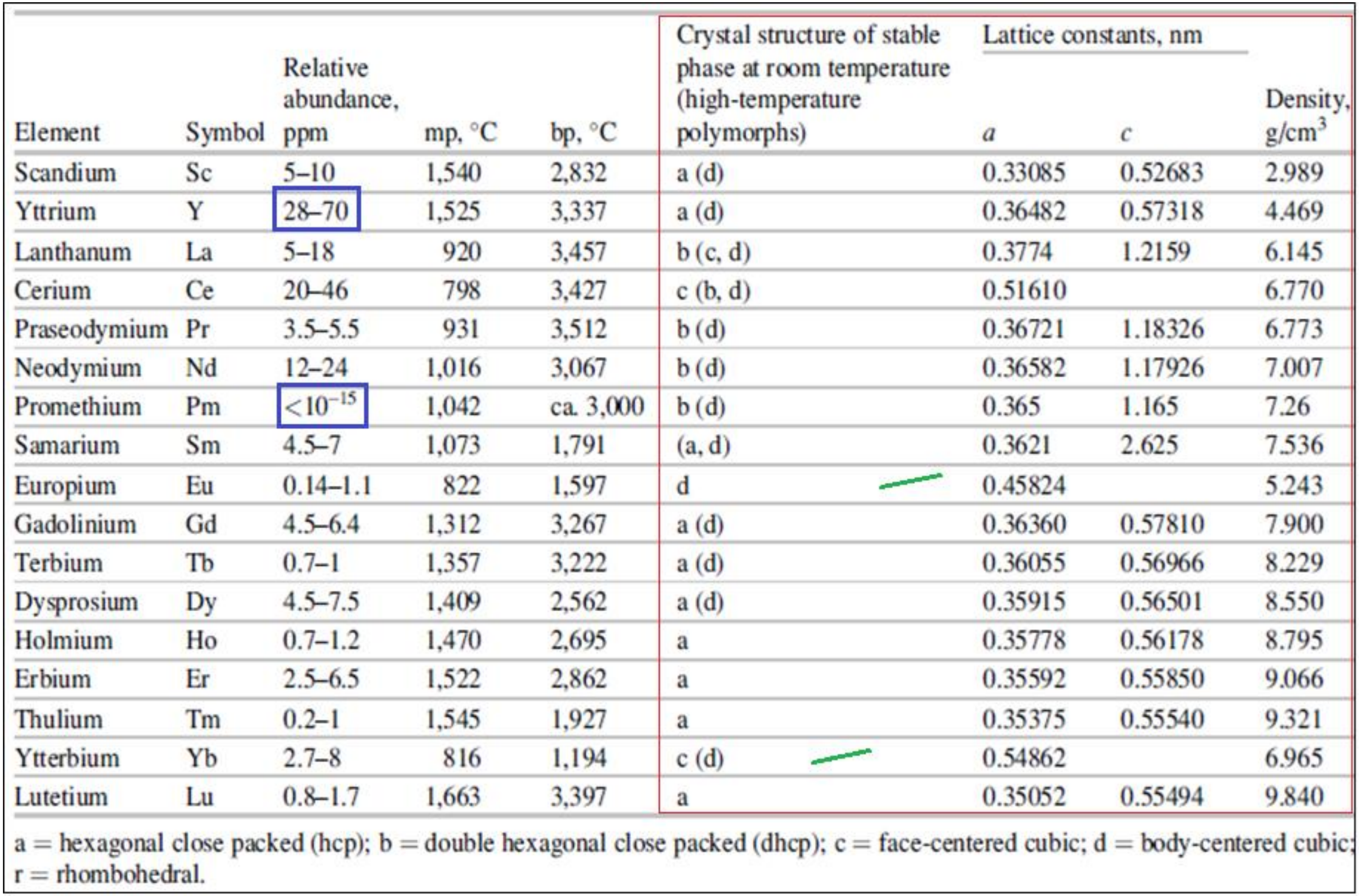
- Crystal structure is a description of the ordered arrangement of atoms, ions or molecules in a crystalline material.
- Most of *REEs* exist in more than one crystallographic form, of which the hexagonal close packing crystal structure (*hcp)* is the most common; all are based on typically metallic close-packed arrangements.





The *hcp* crystal structure

➢ The abundance, selected physical characteristics and the crystal structure of *REEs* are depicted in the table given below. From the Table it can be noted that the lattice parameters of Eu and Yb are larger than expected due to their larger atomic radii.



Element	Symbol	Relative abundance, ppm	mp, °C	bp, °C	Crystal structure of stable phase at room temperature (high-temperature polymorphs)	Lattice constants, nm		Density, g/cm^3
						a	*c*	
Scandium	Sc	5–10	1,540	2,832	a (d)	0.33085	0.52683	2.989
Yttrium	Y	28–70	1,525	3,337	a (d)	0.36482	0.57318	4.469
Lanthanum	La	5–18	920	3,457	b (c, d)	0.3774	1.2159	6.145
Cerium	Ce	20–46	798	3,427	c (b, d)	0.51610		6.770
Praseodymium	Pr	3.5–5.5	931	3,512	b (d)	0.36721	1.18326	6.773
Neodymium	Nd	12–24	1,016	3,067	b (d)	0.36582	1.17926	7.007
Promethium	Pm	$<10^{-15}$	1,042	ca. 3,000	b (d)	0.365	1.165	7.26
Samarium	Sm	4.5–7	1,073	1,791	(a, d)	0.3621	2.625	7.536
Europium	Eu	0.14–1.1	822	1,597	d	0.45824		5.243
Gadolinium	Gd	4.5–6.4	1,312	3,267	a (d)	0.36360	0.57810	7.900
Terbium	Tb	0.7–1	1,357	3,222	a (d)	0.36055	0.56966	8.229
Dysprosium	Dy	4.5–7.5	1,409	2,562	a (d)	0.35915	0.56501	8.550
Holmium	Ho	0.7–1.2	1,470	2,695	a	0.35778	0.56178	8.795
Erbium	Er	2.5–6.5	1,522	2,862	a	0.35592	0.55850	9.066
Thulium	Tm	0.2–1	1,545	1,927	a	0.35375	0.55540	9.321
Ytterbium	Yb	2.7–8	816	1,194	c (d)	0.54862		6.965
Lutetium	Lu	0.8–1.7	1,663	3,397	a	0.35052	0.55494	9.840

a = hexagonal close packed (hcp); b = double hexagonal close packed (dhcp); c = face-centered cubic; d = body-centered cubic; r = rhombohedral.

- *The Abundance, selected physical characteristics and the crystals structure of REEs.*

❖ ***The Electrical Resistivity***

- Electrical resistivity is a fundamental property of a material that measures how strongly it resists electric current. Its inverse, called electrical conductivity, quantifies how well a material conducts electricity. A low resistivity indicates a material that readily allows electric current. The SI unit of electrical resistivity is the ohm-meter (Ω·m).
- The *REMs* are relatively poor electrical conductors as compared to other metals (for example some metals of the transition metals). For example, at 20 ^{o}C, the electrical resistivity of copper is of 1.7 μΩ.cm while the electrical resistivity of *REMs* vary from 25 to 131 μΩ.cm.
- Room temperature resistivities are highest in the middle of the series.
- They also show anisotropy; Resistivity measured along the c-axis of a *REM*s single crystal differs from that measured along the a- or b-axis in the basal plane.
- REs are self-resistance heated during their purification by solid-state electrotransport.
- The electrical resistivity of the *REMs* vary from 25 to 131 microohms.cm (μΩ.cm), which fall into the middle of the electrical resistance values of the metallic elements (*s, d and f block*s).

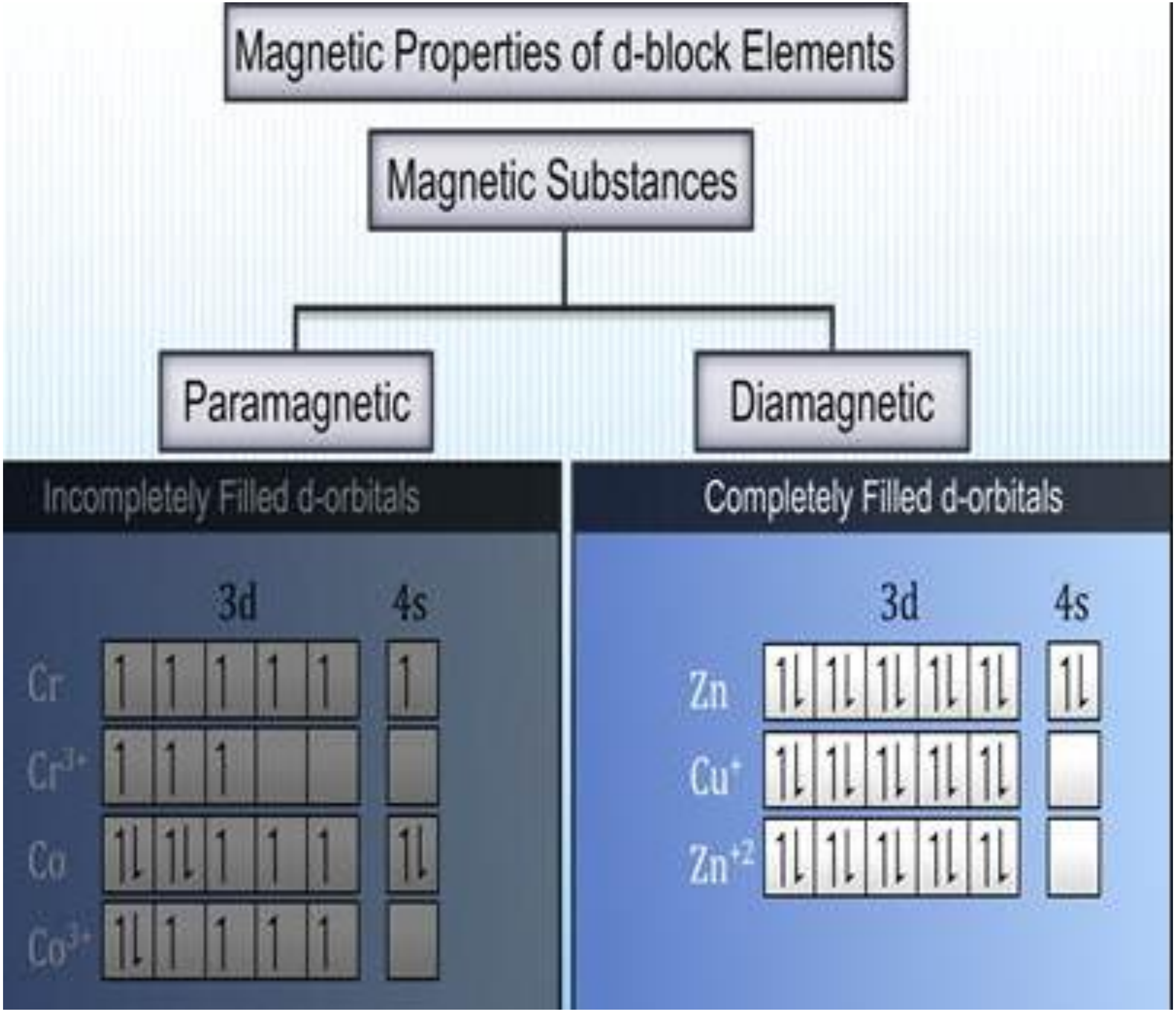
- Most trivalent *REMs* have electrical resistivity values at room temperature ranging from about 60 to 90 μΩ.cm. The low value of 25 μΩ.cm is for divalent *fcc Yb* metal, while the two largest values, *Gd* (131 μΩ.cm) and Tb (115 μΩ.cm), are due to a magnetic contribution to the electrical resistivity that occurs near the magnetic ordering temperature of a material.
- *La* metal is the only superconducting (i.e., no electrical resistance) *REM* at atmospheric pressure. While Sc, Y, Ce, and Lu are also superconducting but at high pressure.
- The *fcc* modification of *La* becomes superconducting at Ts = 6.0 K (−267.2 °C), while the *dhcp* polymorph has a Ts of 5.1 K (−268.1 °C).
- The resistivity of the metal at 4K is sensitive to the presence of impurities, particularly oxygen, nitrogen, and hydrogen, to the extent that it can be used for denoting the metal purity. A well-known method for estimating the total purity of a metal is to measure the ratio of its resistivities at 298 K and at 4 K, or even at 1 K. The impurities will be very low if the resistivity ratio obtained is very high.

❖ ***The Magnetic Properties***

- All materials can be classified in terms of their magnetic behavior falling into one of **five categories** (See Table below).
- The two most common types of magnetism are diamagnetism and paramagnetism, which account for the magnetic properties of most of the periodic table of elements at room temperature (see the periodic Table below).
- Substances that are attracted by the magnetic field and are called **paramagnetic**. This phenomenon is called paramagnetism. Paramagnetic property is only shown when the substance contains one or more unpaired electrons.
- When a substance acquires a permanent magnetic moment, it is known as **ferromagnetic** and the phenomenon is called ferromagnetism. Ferromagnetic materials, like paramagnetic ones, are also attracted to a magnetic field; however, the magnitude of the interaction for a ferromagnetic substance with a magnetic field is approximately a million times stronger than it is with paramagnetic materials.

In the periodic table of elements, only Fe, Co and Ni are ferromagnetic at and above room temperature (See table below).

- There are substances which are weakly repelled by magnetic field. They are called **diamagnetic** substances. A diamagnetic substance contains only paired electrons.



Magnetic Properties of d-block Elements

Magnetic Substances

Paramagnetic

Diamagnetic

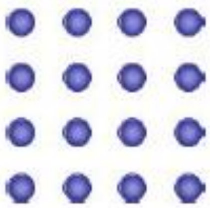
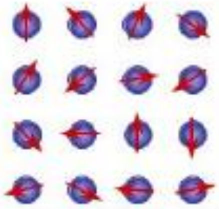
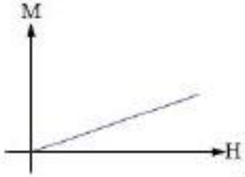
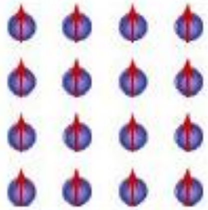
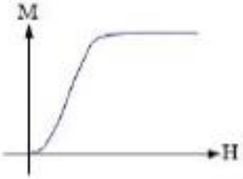
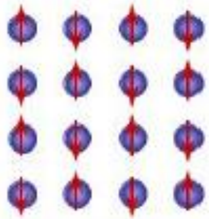
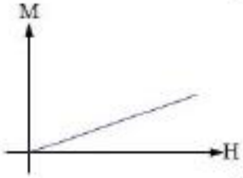
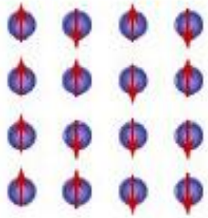
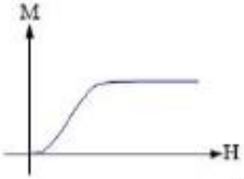
Incompletely Filled d-orbitals

	3d					4s
Cr	↑	↑	↑	↑	↑	↑
Cr^{3+}	↑	↑	↑			
Co	↑↓	↑↓	↑	↑	↑	↑↓
Co^{3+}	↑↓	↑	↑	↑	↑	

Completely Filled d-orbitals

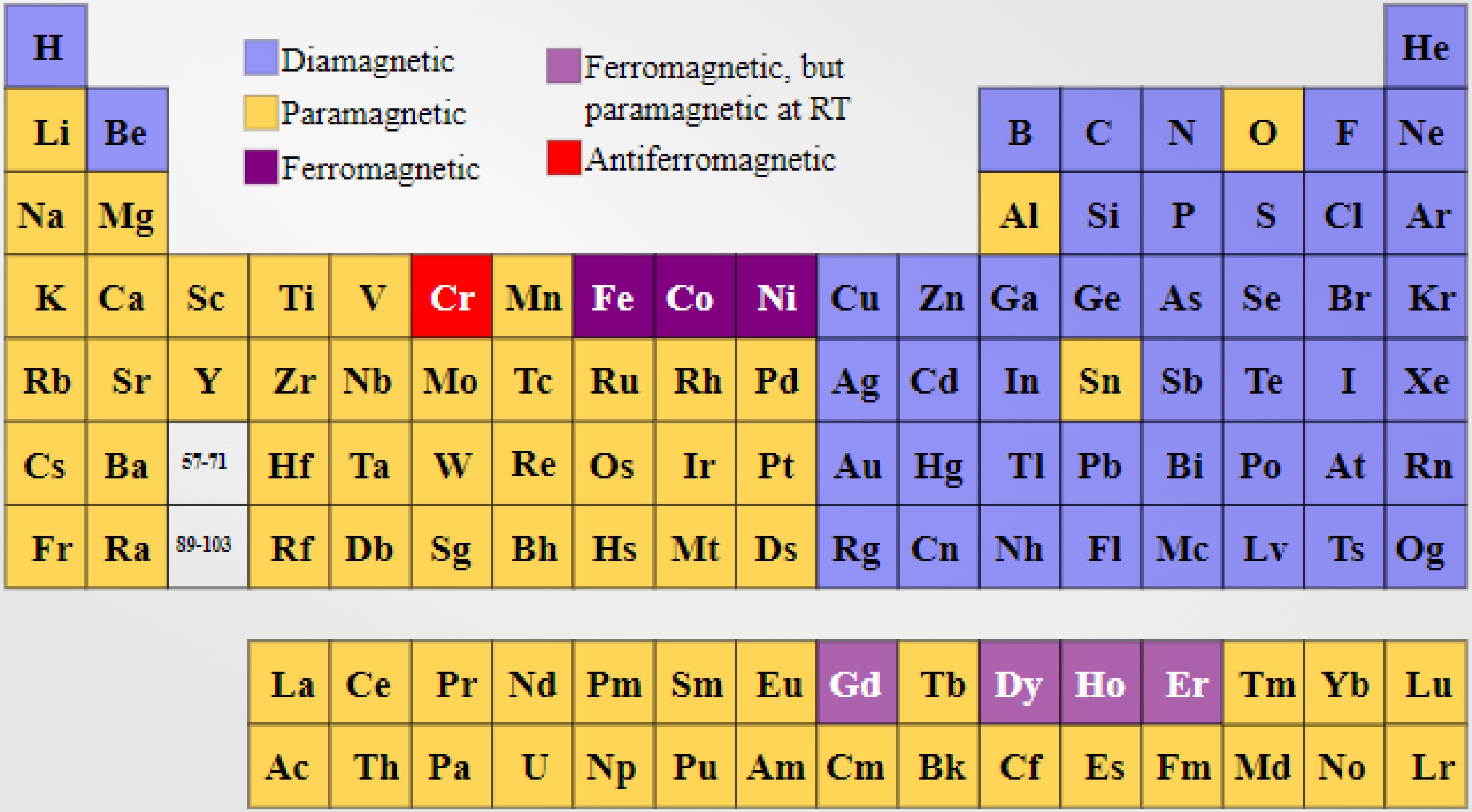
	3d					4s
Zn	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓
Cu^{+}	↑↓	↑↓	↑↓	↑↓	↑↓	
Zn^{+2}	↑↓	↑↓	↑↓	↑↓	↑↓	

- **The five categories** of all materials classified in terms of their magnetic behavior.

Type	Example	Atomic/Magnetic Behaviour		
Diamagnetism	Inert gases; many metals eg Au, Cu, Hg; non-metallic elements e.g. B, Si, P, S; many ions e.g. Na^+, Cl^- & their salts; diatomic molecules e.g. H_2, N_2; H_2O; most organic compounds	Atoms have no magnetic moment. Susceptibility is small & negative, -10^{-6} to -10^{-5}		
Paramagnetism	Some metals, e.g. Al; some diatomic gases, e.g. O_2, NO; ions of transition metals and rare earth metals, and their salts; rare earth oxides.	Atoms have randomly oriented magnetic moments. Susceptibility is small & positive, $+10^{-5}$ to $+10^{-3}$		
Ferromagnetism	Transition metals Fe, H, Co, Ni; rare earths with $64 \leq Z \leq 69$; alloys of ferromagnetic elements; some alloys of Mn, e.g. MnBi, Cu_2MnAl.	Atoms have parallel aligned magnetic moments. Susceptibility is large (below T_C)		
Antiferromagnetism	Transition metals Mn, Cr & many of their compound, e.g. MnO, CoO, NiO, Cr_2O_3, MnS, MnSe, $CuCl_2$.	Atoms have anti-parallel aligned magnetic moments. Susceptibility is small & positive, $+10^{-5}$ to $+10^{-3}$		
Ferrimagnetism	Fe_3O_4 (magnetite); γ-Fe_2O_3 (maghemite); mixed oxides of iron and other elements such as Sr ferrite.	Atoms have mixed parallel and anti-parallel aligned magnetic moments. Susceptibility is large (below T_C)		

A summary of the different types of magnetic behaviour.

PERIODIC TABLE



🟦 Diamagnetic

🟨 Paramagnetic

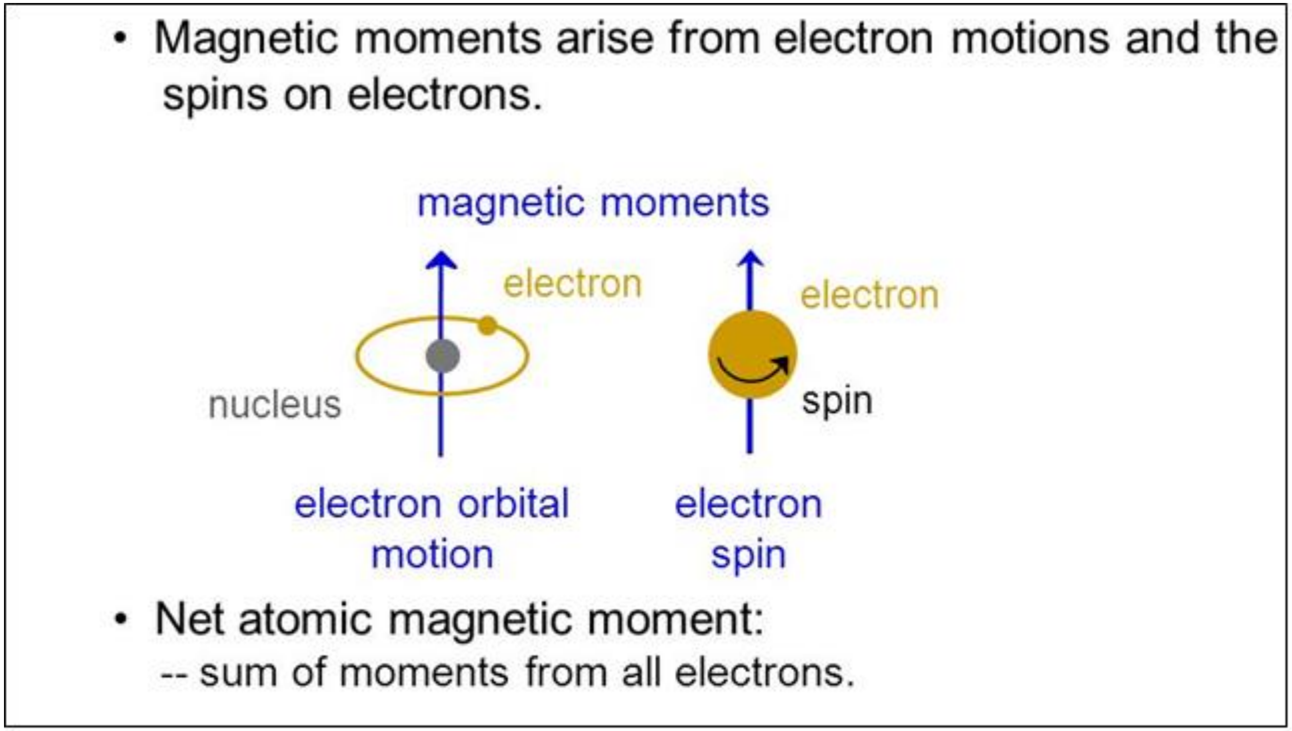
🟪 Ferromagnetic

▨ Ferromagnetic, but paramagnetic at RT

🟥 Antiferromagnetic

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	57-71	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	89-103	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og
			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

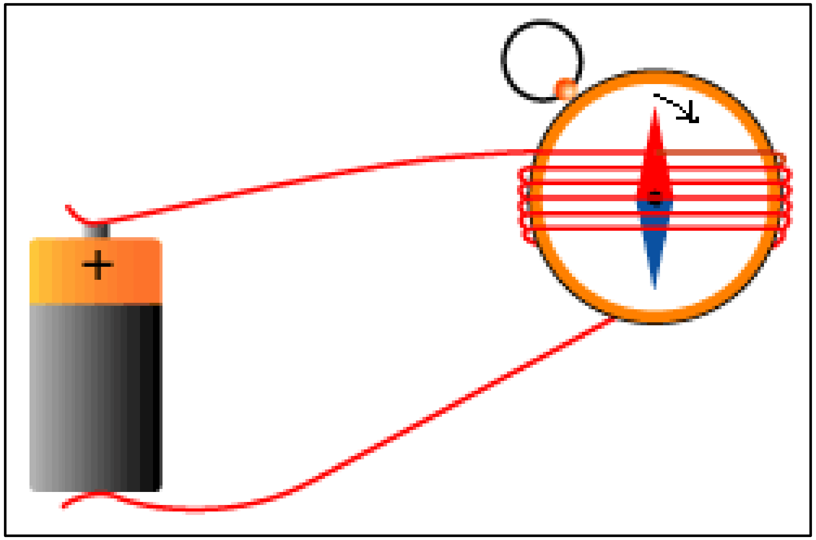
Microscopic Origin of Magnetism



- Magnetic moments arise from electron motions and the spins on electrons.

- Net atomic magnetic moment:
  -- sum of moments from all electrons.

- *The origin of magnetism arising from electron' motion around the nucleus has an analogous with a current-carrying loop which creates a magnetic field at around; The electron' motion in loop compares the electron motion around the nucleus.*



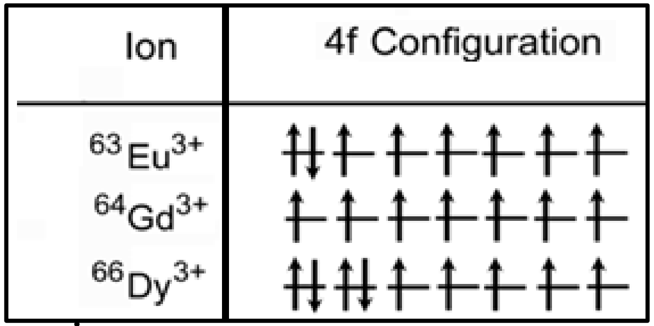
- The two most common types of magnetism are diamagnetism and paramagnetism, which account for most of the periodic table of elements at room temperature. These elements are usually referred to as **non-magnetic**.
- whereas those which are referred to as magnetic are actually classified as ferromagnetic. The only other type of magnetism observed in pure elements at room temperature is **antiferromagnetism**.

In the periodic table the only element exhibiting antiferromagnetism at room temperature is chromium (Cr).

- Finally, magnetic materials can also be classified as **ferrimagnetic** although this is not observed in any pure element but can only be found in compounds, such as the mixed oxides (such as the magnetite (Fe_3O_4), cobalt ferrite ($CoFe_2O_4$)), known as ferrites, from which ferrimagnetism derives its name.

➢ ***Magnetic Properties of the REMs***

- The 4*f* electrons determine the magnetic behavior of the *REMs*.
- In the completed 4*f* subshell, the magnetic effects of different electrons cancel each other out, but in the incomplete 4*f* subshell, they do not.



Ion	4f Configuration
$^{63}Eu^{3+}$	↑↓ ↑ ↑ ↑ ↑ ↑ ↑
$^{64}Gd^{3+}$	↑ ↑ ↑ ↑ ↑ ↑ ↑
$^{66}Dy^{3+}$	↑↓ ↑↓ ↑ ↑ ↑ ↑ ↑

- All *REMs*, except Sc, Y, La and Lu, are strongly paramagnetic.
- On cooling, many of them become antiferromagnetic, and on cooling further, a number of these elements become ferromagnetic.
- If a magnetic field of sufficient strength is applied, all paramagnetic *REMs* become ferromagnetic at low temperatures.
- The *REMs* display strong magnetic anisotropy; their magnetic behavior depends on the crystal axis.
- Gd metal orders ferromagnetically at room temperature and is the only element other than the 3*d* electron elements (Fe, Co, and Ni) to do so.
- The magnetic behavior of the *REMs* are strongly sensitive of their purity and microstructure (porosity, grain size an shape).

Magnetic moments of La^{3+} and the lanthanide^{3+} ions

Element		Electronic structure of M^{3+}	Magnetic moment	
			Calculated (BM)	Observed (BM)
Lanthanum	La	[Xe] $4f^{0}$	0	0
Cerium	Ce	[Xe] $4f^{1}$	2.54	2.3–2.5
Praseodymium	Pr	[Xe] $4f^{2}$	3.58	3.4–3.6
Neodymium	Nd	[Xe] $4f^{3}$	3.62	3.5–3.6
Promethium	Pm	[Xe] $4f^{4}$	2.68	2.7
Samarium	Sm	[Xe] $4f^{5}$	0.84	1.5–1.6
Europium	Eu	[Xe] $4f^{6}$	0	3.4–3.6
Gadolinium	Gd	[Xe] $4f^{7}$	7.94	7.8–8.0
Terbium	Tb	[Xe] $4f^{8}$	9.72	9.4–9.6
Dysprosium	Dy	[Xe] $4f^{9}$	10.63	10.4–10.5
Holmium	Ho	[Xe] $4f^{10}$	10.60	10.3–10.5
Erbium	Er	[Xe] $4f^{11}$	9.57	9.4–9.6
Thulium	Tm	[Xe] $4f^{12}$	7.63	7.1–7.4
Ytterbium	Yb	[Xe] $4f^{13}$	4.50	4.4–4.9
Lutetium	Lu	[Xe] $4f^{14}$	0	0

❑ *The Chemical Reactivity*

❖ ***General properties***

- The REs are very electropositive (the opposite of electronegative, i.e. they readily lose their valence electrons) and reactive metals.
- Lanthanide contraction (which keeps similar ionic size) and the common +3 oxidation state fro all REEs, cause very similar chemical properties of the REs.
- With the exception of Yb, their reactivity apparently depends on atomic size. So that Eu which has the largest atomic radius is the most reactive.
- Their reactivity is especially pronounced at elevated temperature or when they are finely divided.
- The chemical reactivity of *REMs* is greater than the transition metals and comparable to those group 2 metals (the alkaline metal earth metals: Be, Mg, Ca,…).
- Mineralogically (in the ores), *REEs* form oxides, halides, carbonates, phosphates and silicates, borates or arsenates, but not sulphides.

- The *REEs* form tens of thousands of compounds and alloys with all the elements to the right of the periodic table and including the group 7 metals (manganese (Mn), technetium (Tc), and rhenium (Re)) in the periodic table, plus beryllium (Be) and magnesium (Mg), which lie on the far left-hand side in group 2.
- Unlike the transition metals (elements of *d*-block), *REMs* do not form carbonyls and have almost no chemistry in the 0 oxidation state.

❖ ***Reaction with oxygen***

- *REMs* tarnish in air and, if ignited in air or O_2, they burn readily and oxidize to give rare earth oxides (REOs).
    - *Example:* $4La(s) + 3O_2(g) \rightarrow 2La_2O_3(s)$
- The largest family of inorganic RE compounds studied to date is the REOs and the most common stoichiometry is RE_2O_3 in which the oxidation state of the REE is +3.
- But, because a few lanthanide elements have other valence states in addition to +3, other stoichiometries exist. For instance, cerium(IV) oxide (CeO_2), europium(II) oxide (EuO), europium(II, III) oxide (Eu_3O_4), praseodymium oxide (Pr_6O_{11}), terbium oxide (Tb_4O_7),...
- The light lanthanides (Ln to Nd) oxidize much more rapidly in air than the heavy lanthanides (Gd through Lu), Sc, and Y. Because of this, the light lanthanides must be stored in vacuum or in an inert gas atmosphere. While the heavy lanthanides and Sc and Y can be left out in the open air for years without any oxidation.

- Eu metal, which has a *bcc* (body-centered cubic) crystal structure, oxidizes the most rapidly of any of the *REMs* with moist air and needs to be handled at all times in an inert gas atmosphere. The reaction product of Eu when exposed to moist air is a hydrate hydroxide, $Eu(OH)_2.H_2O$, which is an unusual reaction product because all the other *REMs* form oxides.

Reaction with hydrogen

- At temperatures 300-350 ^{o}C, the REs readily react with hydrogen gas to form the blacks solid hydrides of REH_2. Under strong hydriding conditions, they form the trihydrides REH_3, except Sc, which does not form a trihydride.
  - *Example:* $2Sm(s) + 3H_2(g) \rightarrow 2SmH_3(s)$

Reaction with halogens

- Except Eu, when heated in halogens, *REMs* burn producing the trihalides REX_3 (X = Cl, F, Br, I).
  - *Example:* $2Sm(s) + 3Cl_2(g) \rightarrow 2SmCl_3(s)$
- The only tetrahalides known are the REF_4 phases, where RE = Ce, Pr, and Tb.
- The dihalides REX_2, where RE = Sm, Eu, and Yb, have been known for a long time, are stable compounds, and are easily prepared.

Reaction with nitrogen

- At elevated temperatures *REMs* react with nitrogen gas as:
  - $2RE(s) + N_2(g) \rightarrow 2REN(s)$

❖ ***Reaction with water***

- Generally, *LREMs* react with water (hydrolysis) slowly at room temperature and vigorously at higher temperatures. Whereas H*REMs* react very slowly. In all case they produce an hydroxide with the release of hydrogen gas.

Example: $2Ce(s) + 6H_2O(l) \rightarrow 2Ce(OH)_3(s) + 3H_2(g)$

- However, even with cold water, europium reacts to form $Eu(OH)_2.H_2O$, liberating hydrogen.

❖ ***Reaction with sulfur, selenium and phosphorus***

- The R*EMs* react exothermically with sulfur (S), selenium (Se), and phosphorus (P).

On heating a *REM* with these elements, the reaction sets off and, if precautions are not taken, could seriously damage the crucible, furnace, vacuum enclosures, etc.

The strong exothermicity may afford preparation of sufides (examples: LaS, LaS_2, La_2S_3, La_3S_4), selenides, and phosphides of REs by self-propagating high-temperature synthesis.

❖ ***Reaction with inorganic acids***

- The *REMs* readily dissolve in dilute strong inorganic acids such as HCl, HNO_3 and H_2SO_4 releasing H_2 gas and forming the corresponding salts. Concentrated sulfuric acid has a somewhat smaller effect on them.
    - *Example:* $2Gd(s) + 6HCl(aq) \rightarrow 2GdCl_3(aq) + 3H_2(g)$
    - *Example:* $2Y(s) + 6HNO_3(aq) \rightarrow 2Y(NO_3)_3(aq) + 3H_2(g)$
- The RE metals resist attach by the weak hydrofluoric acid, HF, because a thin layer of REF_3 forms on the metal, preventing further dissolution.

❖ ***Reaction with carbon***

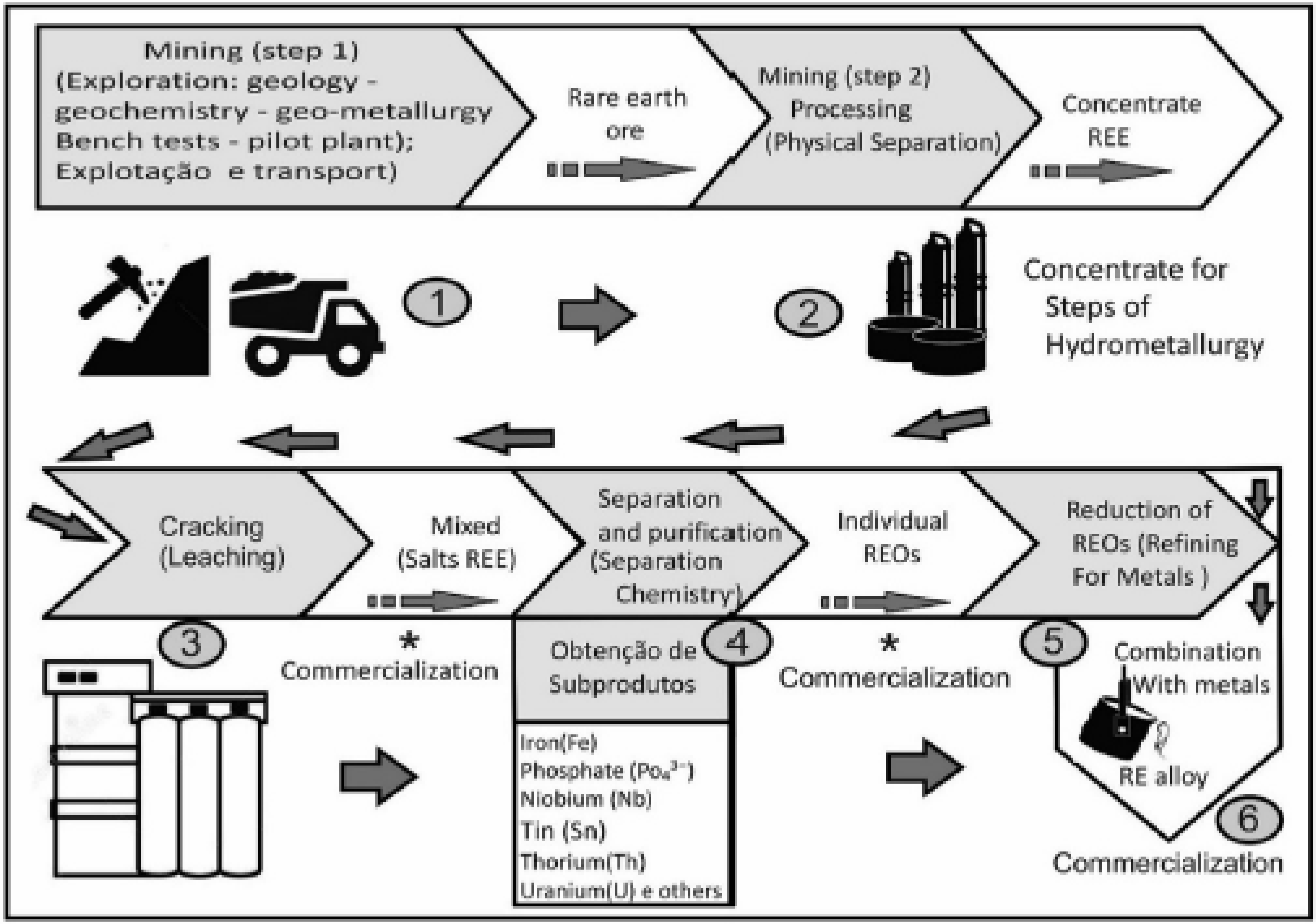
- At high reaction temperatures (about 2500 ^oC), All *REMs* form dicarbides (REC_2) with carbon.
- Several of them (La–Sm and Gd– Ho) also form sesquicarbides (RE_2C_3).
- Solid solubility of carbon in *REMs* also occurs easily. The carbides also form solid solutions with nitrogen and oxygen.

❑ ***Resources Processing of the REs***

- Much of the actual extraction of *REs* is principally from the minerals Bastnasite, Monazite, Xenotime and the special resource, China's ion adsorption ore.
- The largest worldwide *REs* deposits (ores) are located in China and then in Brazil.
- It is important to emphasize that all the *REs* generally occur together in all the minerals with large variations in relative proportions. Such an occurrence is the culmination of their similar chemical behavior, and it is this chemical similarity that has, in the past made separation of *REs* from one another a daunting task. Thus, the discovery of the *REs* themselves occurred over a period of nearly 160 years (1787–1941) and their resources processing for isolating them all took around 100 years.
- The processing is also sometimes dangerous in some cases because some of the *REEs* are occurring with radioactive elements such as Thorium (Th).
- Usually, these processes accomplish sequential removal of impurity compounds from the material being processed.

- In the case of *REs*, the resource processing involves not only the operations that result in such impurity removal but also special operations that achieve the difficult task of separating the considerable number of naturally co-occurring *REEs* from one another.
- In the overall *REs* extraction flow sheet, the term ***resource processing*** refers to the group of unit operations, comprising both physical and chemical processing, used to obtain from the as-mined ore a compound that is either an end-product in itself or an inter-process intermediate for the subsequent processing to the metal or alloy or other compounds.
- The productive chain of the *REEs* consists of several steps (1—6). Everything will depend on the type of mineral deposit to be explored and exploited. The figure below (see next slide) shows a simplified schematic drawing of the main steps involved in the productive process of *REE* in hard rock deposits.

The steps (2—6) gather the resource processing operations.



Simplified schematic drawing of the main steps involved in the REE production process (for hard rock deposits). Source: self elaboration. Note: *The commercialization of rare earths in mixed stage or in separate REO stage may occur, depending on the objective of the granted project.

- Briefly, the productive chain (step 1) starts with mineral exploration (geology, geochemistry/mineralogy and, specially, geo-metallurgy), exploitation and transport.

After the results of the surveys, which among other important information provide data on the quality and tonnage of the target deposit, many studies are required regarding the type of deposit and its mineralogy/geochemistry, aiming to determine the best technological route of resource utilization with the best economic performance possible. Only after proven the economic viability of the deposit, the stage of exploitation of the RE ore starts.

In the mining phase (steps 1─2), Exploitation/Mining and Processing, operations are widely dependent on the nature of the deposit. The results of the economic feasibility studies will determine, in addition to the method of mining (exploitation), the technological route for the use of RE ore more adequate to the information obtained in the exploration stage.

One of the most important information to the viability of the project is whether the future mine will be built by the open or underground method, or whether the two methods will be used during the mining project (depending on the shape of the mineralized body and thickness of the soil layer−capping−on the material of interest, which translates into the sterile/mineral ratio). However, the location of the reservoir, the local infrastructure (water, energy and access), the method of exploitation (open or underground), are variables that can have a great impact in the increase of costs and consequently the viability of the project, especially in step of the productive chain. The main factors affecting the selection of *RE* ore treatment processes are: type and nature of the deposit (e.g., beach sand), type of vein (intrusion of eruptive rocks into crevices), igneous or complex ores and their complexity, type and nature of other valuable minerals present with *REO* and their complexity, type and nature of other valuable minerals present with *REOs*, type and nature of the gang minerals (e.g., clay, soluble gang), type and composition of the minerals (individual rare earth oxides), and the social and environmental acceptability of the process.

After the exploitation phase (mining of the ore), the mineral material begins to be processed, which is fragmented (crushed) and milled (in the case of hard rock deposits).

Then, generally, the material is subjected to a physical separation (Mining (step(2)). Conventional methods of physical separation are:

- gravity separation,
- magnetic separation,
- electrostatic separation, and
- flotation.

These methods are used to concentrate RE ore, obtaining a concentrate containing REE with a minimum economic content necessary for the following steps.

The physical processing method will heavily depend on the mineralogy of the deposit.

- The concentrated ore goes to the next steps (steps 3–6) and is subsequently leached in chemical solution (obtaining a mixture of REE) in a process commonly called ‘’cracking’’. The individual elements are selectively removed from the mixed solution of REE by hydro-metallurgical techniques, such as, for example, solvent extraction and ion-exchange. The precipitated products (in the extraction step) may be marketed in the form of pure metal oxides or reduced to pure metal products, that is, the product of this primary processing step is subjected to a further step, the refining step, wherein the REOs, already separated, are refined and converted into metals, which are then combined with other metals to produce RE-containing alloys (light alloys of REE). The final product of the venture will depend on the final objective (the market for which the project of exploitation of the deposit was conceived, production of concentrate, REO, RE alloy, etc.).

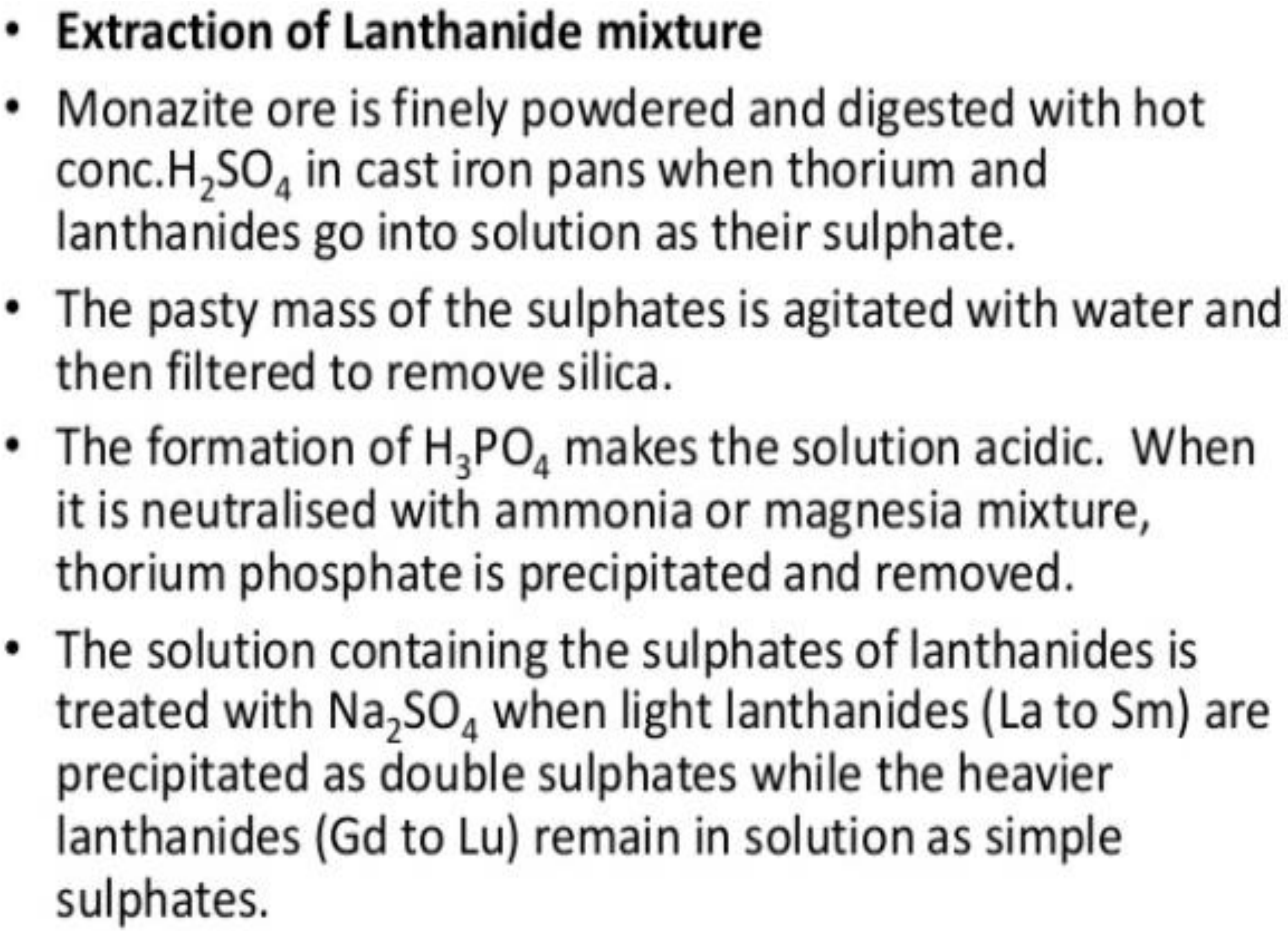
The different steps of the REE production chain are interrelated as shown in the figure above.

After obtaining the REE concentrate, in the step of mineral processing (physical separation), it is worth to highlight this step, where currently the projects in the production step, and the most promising ones (in the economic feasibility step), work with the prospect of obtaining a mineral concentrate of competitive content, that is, of a content greater than 30% REO. In this sense, deposits that have mineralogy and distribution of favorable REOs can guarantee a more promising concentrate, making the deposit/project more competitive, since in the processing and processing step smaller amounts of chemical substances will be used, once the high costs of these substances are those that considerably increase the production process. After the mineral concentration step, the next step is the dissolution, separation and purification of the metals (chemical separation). Thus, the mineral concentrates are separated into usable oxides (blends of REE metals of high purity). For this, hydro-metallurgical techniques (for instance: leaching, extraction, precipitation) are typically used, as hydro-metallurgy is one of the most important and expensive stages of the production chain.

In a complete hydro-metallurgical treatment of the *RE* ores concentrates, three unit operations should be considered: dissolution of REs in acid, sometimes high pressure and temperature; separation of different *REE* in pure and concentrated solutions, with solvent extraction or extraction of ionic liquid and ion-exchange; and generation of individual *REEs*.

The use of known extraction techniques is possible thanks to the ***differences in basicity*** resulting from the reduction of the ionic radius of light rare earth elements (*LREE*) to heavy rare earth elements (*HREE*) among the different *REs*, since this property influences the solubility of the salts, the hydrolysis of ions, and the formation of complex species. In addition to a trivalent oxidation state, cerium, praseodymium and terbium may also occur in the tetravalent state, and europium, samarium, and ytterbium in a divalent state. Thus, the selective oxidation and reduction of these *REEs* are useful in an efficient separation procedure, because in the divalent and tetravalent state it indicates that *REEs* have a different physico-chemical behavior, compared to the trivalent state. Organophosphoric acids are the typical cation exchange reagents used in the separation of *REEs*. However, these properties are based on separation techniques. ***Extraction techniques*** such as ion-exchange, fractional crystallization and liquid- liquid extraction, were developed in the 1950s and 1960s, after understanding the chemistry of the lanthanides, which was the key to lanthanides metallurgy.

❖ *Example of Extraction: Extraction of REs from the Monazite sand ore*

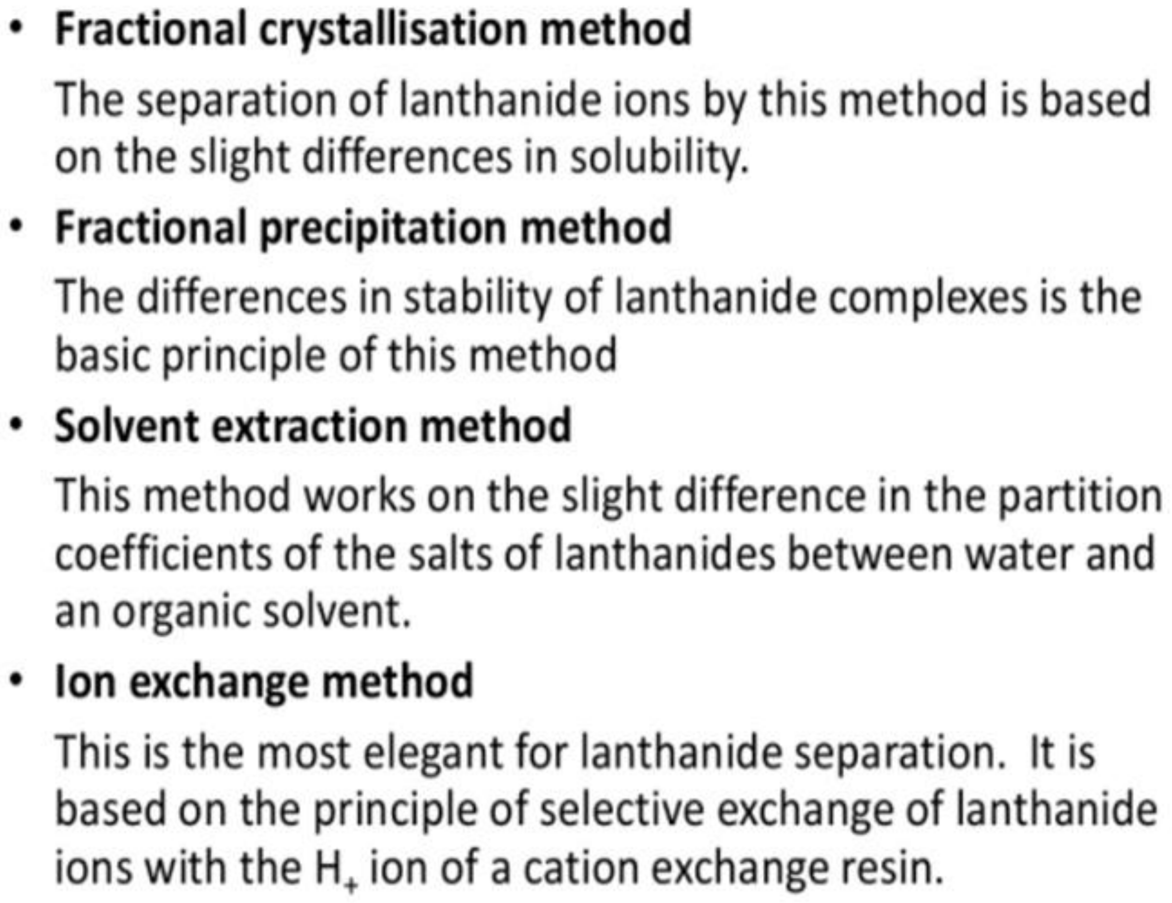


- **Extraction of Lanthanide mixture**
- Monazite ore is finely powdered and digested with hot conc.H_2SO_4 in cast iron pans when thorium and lanthanides go into solution as their sulphate.
- The pasty mass of the sulphates is agitated with water and then filtered to remove silica.
- The formation of H_3PO_4 makes the solution acidic. When it is neutralised with ammonia or magnesia mixture, thorium phosphate is precipitated and removed.
- The solution containing the sulphates of lanthanides is treated with Na_2SO_4 when light lanthanides (La to Sm) are precipitated as double sulphates while the heavier lanthanides (Gd to Lu) remain in solution as simple sulphates.

- The precipitated double sulphates ae treated with hot NaOH when hydroxides of light lanthanides are formed.
- The hydroxides ae washed and dried in air at 100^0C to get oxides of light lanthanides.
- The oxides are treated with dil. HNO_3 when cerium is precipitated as CeO_2.
- The solution contains nitrated of La, Pr, Nd and Sm. From this, the individual lanthanides are separated by a suitable method

❖ *4 Major separation methods of REEs one from another*

There are 4 major separation methods of *REEs*. Separation of the lanthanides by the two classical methods: the fractional crystallization and the fractional precipitation was difficult and time consuming. But currently, the solvent extraction and the ion exchange methods are the methods of choice.



- **Fractional crystallisation method**

  The separation of lanthanide ions by this method is based on the slight differences in solubility.

- **Fractional precipitation method**

  The differences in stability of lanthanide complexes is the basic principle of this method

- **Solvent extraction method**

  This method works on the slight difference in the partition coefficients of the salts of lanthanides between water and an organic solvent.

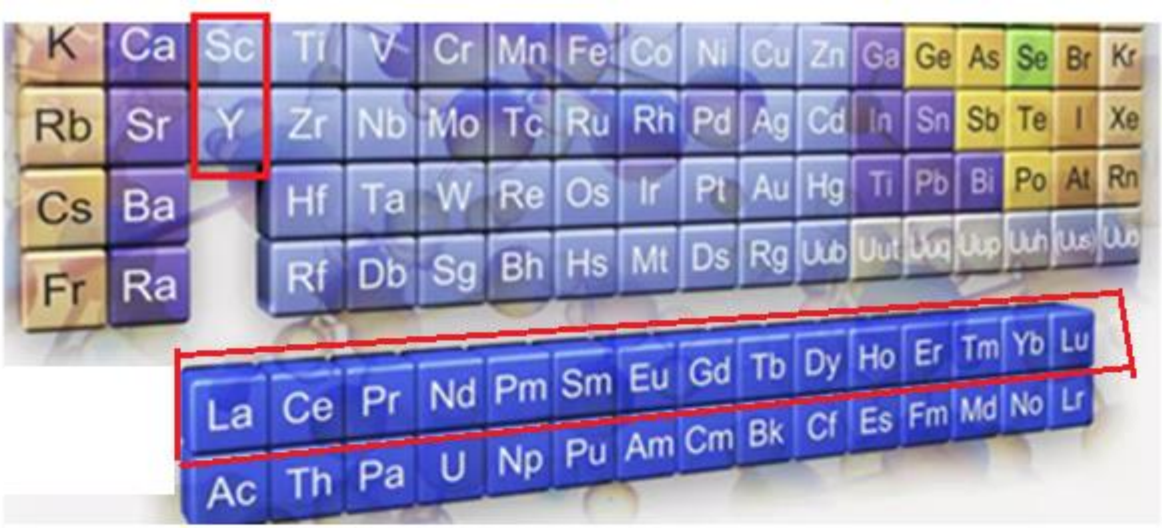
- **Ion exchange method**

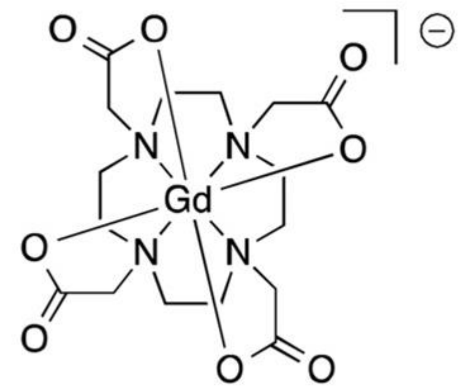
  This is the most elegant for lanthanide separation. It is based on the principle of selective exchange of lanthanide ions with the H_+ ion of a cation exchange resin.

- ***Selected powders of isolated pure REOs (RE= Er; Pr; Gd; Nd).***

Chapter 4:

Compounds And Alloys Of The Rare Earth Elements: Chemistry ,Selected Physical Properties And Uses





Gd-DOTA$^-$

❑ *Synthesis/Elaboration and Chemical Reactivity of RE-Containing Compounds and Alloys*

❖ ***The oxides***

- Despite the metals burn easily, rather like Group 2 metals, forming oxides, as already mentioned (see Chapter 3), the oxides are best made by thermal decomposition of compounds like the nitrates or the carbonates.

For example, the thermal decomposition of nitrates occurs as:

$$4RE(NO_3)_3(s) \rightarrow 2RE_2O_3(s) + 12NO_2(g) + 3O_2(g)$$

And the thermal decomposition of lanthanum carbonate at 600 ^{o}C occurs as:

$$La_2(CO_3)_3(s) \rightarrow La_2O_3(s) + 3CO_2(g)$$

- The oxides of *REEs* are strongly basic. The *LREEs* (from $_{57}$La to $_{61}$Pr) are more basic, with a basicity resemble the oxides of group 2 (Mg, Ca, Ba, Sr).

Thus, *REOs* react with water (hydrolysis) to form insoluble hydroxides:

$$RE_2O_3(s) + H_2O \rightarrow 2RE(OH)_3(s)$$

- The oxides react with carbon dioxide to form insoluble carbonates:

$$RE_2O_3(s) + 3CO_2(g) \rightarrow RE_2(CO_3)_3(s)$$

- Certain *REOs* react with boron trioxide. An example:

$$La_2O_3(s) + 3B_2O_3(s) \rightarrow 2La(BO_2)_3(s)$$

❖ ***The halides***

- Most halides are LnX_3 (Ln = lanthanide; X = F, Cl, I, Br) but a number of LnX_2 are known, as are a handful of tetrafluorides, LnX_4.
- As already mentioned (see Chapter 3), the metals burn in a halide gas to produce a trihalide, LnX_3 according to:

$$2RE(s) + 3X_2(g) \rightarrow 2REX_3(s)$$

But there are also other methods for the synthesis of LnX_3. For example, a route that works well in practice involves thermal decomposition of ammonium halogenometallates. Adding ammonium chloride to a solution of the metal oxides in hydrochloric acid, followed by evaporation gives halogenometallate salts. These can be dehydrated by heating with excess of ammonium chloride in a stream of gaseous HCl, the resulting anhydrous salt being decomposed by heating *in vacuo* at about 300 °C.

$$\boxed{\begin{array}{c} Ln_2O_3 + 9\,NH_4Cl + 3\,HCl \rightarrow 2\,(NH_4)_3LnCl_6 + 3\,NH_3 + 3\,H_2O \\ 2\,(NH_4)_3LnCl_6 \rightarrow 2\,LnCl_3 + 6\,NH_4Cl \end{array}}$$

- The *RE* trihalides (*REX*$_3$) react readily with various chemicals. As examples:

- In high temperature, samarium (III) chloride hexahydrate ($SmCl_3.6H_2O$) reacts with a mixture of elemental sulfur (S), and hydrogen gas (H_2) to produce samarium sulfide according to the reaction:

$$2SmCl_3 \cdot 6H_2(s) + 3S(g) + 3H_2(g) \rightarrow Sm_2S_3(s) + 6HCl(g) + 6H_2O(g)$$

- $SmCl_3.6H_2O$ reacts with phosphoric acid (H_3PO_4) to produce samarium (III) phosphate according to:

$$SmCl_3.6H_2(s) + H_3PO_4(aq) \rightarrow SmPO_4(s) + 3HCl(aq) + 6H_2O(l)$$

- A number of *RE* dihalides (*RE*X$_2$) is also known. These are most common for metals with a stable (+2) state, such as Eu, Yb, and Sm.

These compounds (e.g. EuX_2, YbX_2, or SmI_2) are usually made by reduction using hydrogen gas or reproportionation:

$$2\,EuCl_3 + H_2 \rightarrow 2\,EuCl_2 + 2\,HCl$$ **Reduction by hydrogen gas**

$$2\,DyCl_3 + Dy \rightarrow 3\,DyCl_2$$ **Reproportionation**

- Europium difluoride (EuF_2), the most stable *RE* difluoride, may be prepared by the reaction of $EuSO_4$ dissolved (suspended) in boiling NaOH/NaF solution following the equation:

$$EuSO_4 + 2NaF \rightarrow EuF_2 + Na_2SO_4$$

❖ *The borides*

- A number of stoichiometries *RE* borides such as REB_2, REB_4, REB_6, REB_{12}, and REB_{66} are known.

The most important are REB_6, in particular lanthanum hexaboride (LaB_6). LaB_6 is important ceramic used as a source of electrons in electron microscopes and many other applications.

RE borides are obtained by heating the corresponding elements (*RE* and *B*) together at 2000 ^oC or by heating the lanthanide oxide (RE_2O_3) with boron (*B*) or born carbide (BC_4) at 1800 ^oC.

❖ *The nitrides*

These can be made by direct synthesis from the elements at 1000 ^oC according to:

$$2RE(s) + N_2(g) \rightarrow 2REN(s)$$

❖ *The sulfides*

These are quite important compounds. A number of stoichiometries exist, the most important being RE_2S_3. These can be made by direct synthesis, heating the elements together (See chapter 3), or by passing the gas hydrogen disulfide (H_2S) over heated $RECl_3$ according to:

$$2RECl_3 + 3H_2S \rightarrow RE_2S_3 + 6HCl$$

Note. Eu_2S_3 cannot be prepared by this latter route.

❖ ***The Carbonates***

- *RE* carbonates can be produced via reactions between a *RE* oxide and carbon dioxide:

$$RE_2O_3(aq) + 3CO_2(g) \rightarrow RE_2(CO_3)_3(s)$$

- *RE* carbonates can be also produced via reactions between solutions of a *RE* salt (chloride, acetate, nitrate) and sodium bicarbonate, $NaHCO_3$.

As an example, is the synthesis of lanthanum carbonate according to the following overall acid-base equation:

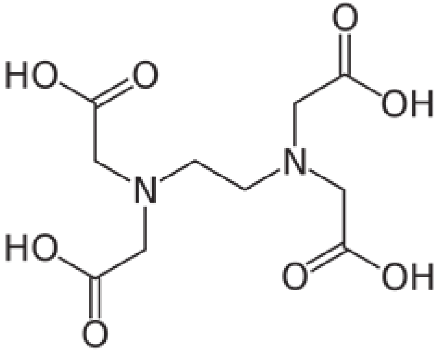
$$2LaCl_3(aq) + 6NaHCO_3(aq) \rightarrow La_2(CO_3)_3(s) + 6NaCl(aq) + 3H_2O(l) + 3CO_2(g)$$

❖ ***The coordination complexes***

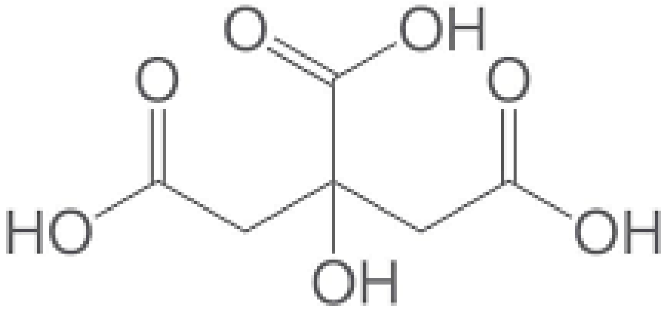
- The formation of complex species is an important feature of tripositive RE^{3+} ions. A great number of RE^{3+} complexes is currently known.

The RE^{3+} complexes are being exploited in many applications, including catalysis, biomedical diagnosis and therapy, and environmental chemistry.

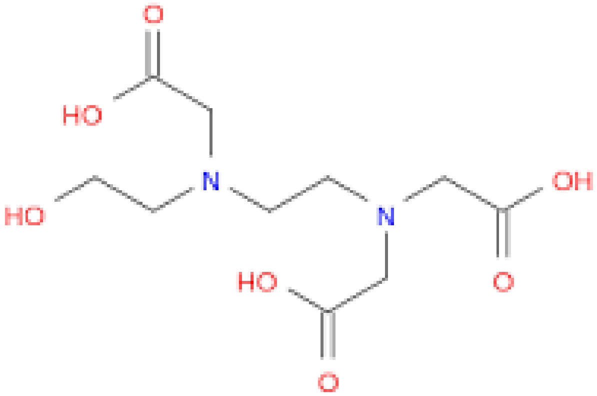
The complexes formed by tripositive RE^{3+} ions include complexes of the ligands: citric acid, ethylenediamine tetraacetic acid (EDTA), hydroxyl ethylenediamine triacetic acid (HEDTA) (The molecular structure of some ligands is provide in next page) and much more ligands such as F^-, Cl^-, NO_3^-, OH^-, H_2O, glycine,…).



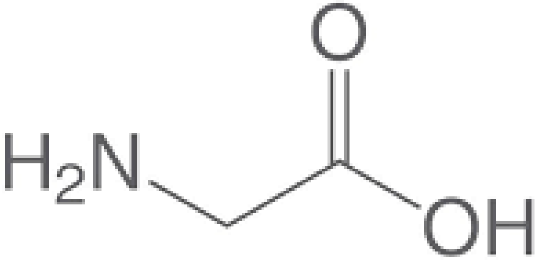
EDTA



Citric acid



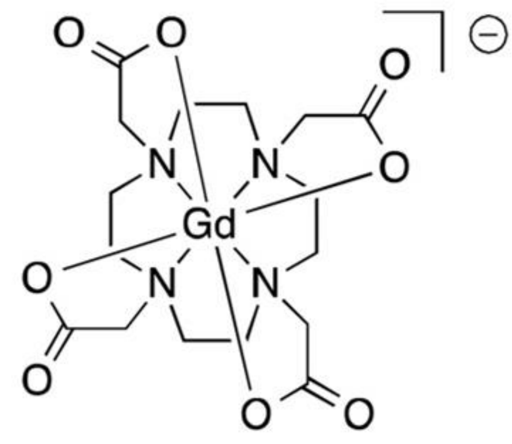
hydroxy ethylenediamine triacetic acid



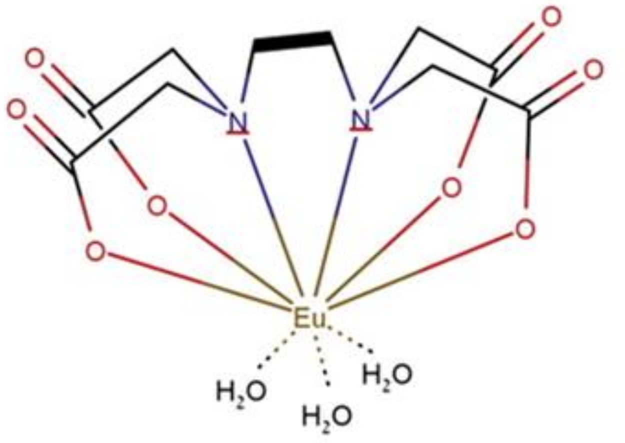
Glycine

- With water, RE^{3+} ions form aqua complexes $[Ln(H_2O)_n]^{3+}$. The coordination number (CN) is believed to be 9 for the early lanthanides (La–Eu) and 8 for the later ones (Dy–Lu), with the intermediate metals exhibiting a mixture of species.
- Gadolinium(III), like most lanthanide ions, forms complexes with high CN. This tendency is illustrated by the use of the chelating agent DOTA, an octadentate (CN = 8) ligand.

Salts of $[Gd(DOTA)]^-$ (See below) are useful in magnetic resonance imaging (MRI). The CN in the complexes is high and it is usually 7, 8, 9, or 10.



Gd-DOTA$^-$



$[Eu(EDTA)(H_2O)_3]$

❖ ***The organometallic compounds***

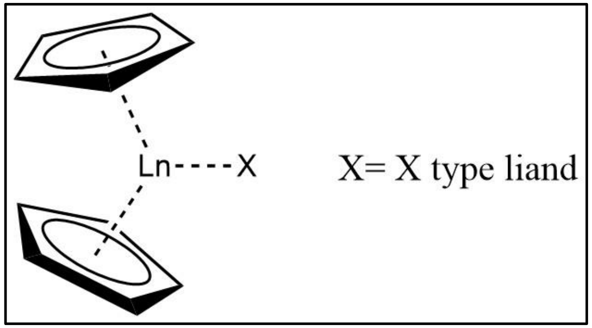
An Organometallic compound (or Organometallic complex) is a compound containing at least one direct carbon-metal bond (*C-M*) with a high covalent character.

RE compounds reacts with a variety of organic ligands to produce organometallic compounds.

- For example alkyls of samarium (SmR_3) (*R = alkyl or aryl group such as* CH_3, C_2H_5, *Phenyl,..*) can be obtained through a metathesis reaction of samarium chloride ($SmCl_3$) and an organolithium (LiR) in tetrahydrofuran or ether solvent according to:

$$SmCl_3 + 3LiR \rightarrow SmR_3 + 3LiCl$$

- Another important class of organometallic compounds is the lanthanocenes which are a type of metallocene compounds that contain an element from the lanthanide series. The most common lanthanocene complexes contain two cyclopentadienyl anions $C_5H_5^-$ (Cp^-) and an X type ligand, usually a hydride or an alkyl ligand.



The first step of the reaction involves the synthesis of the lanthanocene chloride complex according to:

$$LnCl_3 + 2MC_5H_5 \rightarrow [\,Ln(C_5H_5)_2Cl] + 2MCl \qquad M = Na, Ti$$

❖ ***The Alloys***

An *alloy* is an admixture of metals, or a metal combined with one or more other non-metallic elements.

For example, combining the metallic elements gold and copper produces red gold, gold and silver becomes white gold, copper and zinc gives the alloy brass, copper and tin gives the alloy bronze, iron and a small amount of carbon gives the steel,...

✓ ***The Mischmetal***

The pure *RE* metals alone have little use. However, the alloys of the metals can be very useful.

RE metals form a large variety of alloys with each other as well as with other metals, or with non-metals or even with metalloids.

As examples of alloy is the *Mischmetal*. The Mischmetal (from German: *Mischmetall*–"mixed metal") is an alloy of *REEs*. A typical composition of a *Mischmetal* includes approximately 55% Ce, 25% Ln, and 15-18% Nd with traces of other *REMs*; It contains 95% lanthanides and 5% iron. Its most common use is in the pyrophoric ferrocerium "flint" ignition device of many lighters and torches.

Mischmetal is often produced starting from mixed-*RE* oxides (RE_2O_3) by various processes. One of them is the called the thermal reduction process.

Thermal reduction is accomplished in 3 steps:

- Step 1: $RE_2O_3 + 4NH_4HF \rightarrow 2REF{\cdot}NH_4F + 2NH_3 + 3H_2O$
- Step 2: $REF_3.NH4F \rightarrow REF_3 + NH_4F$
- Step 3: $2REF_3 + 3Ca \rightarrow 2RE + 3CaF_2$ *where RE represents the desired Mischmetal*

✓ *pyrophoric Mischmetal (”ferrocerium” "flint“) ignition device of many lighters,....*

✓ ***The Magnetic Materials (The Permanent Magnets)***

- There is another important class of *RE*-containing alloys. The class is the permanent magnets. Along with the *RE*, the alloy can contain metals such as Co and Fe, and metalloids such as B.
- In general, there are two main different types of useful magnets, the permanent magnets and the electromagnets. A permanent magnet is called a permanent magnet because its magnetism is ‘always on’, it generates its own persistent magnetic field unlike an electromagnet which is made from a coil of wire wrapped around a ferrous core and requires an electric current to generate a magnetic field.
- In general, the industrial processing of *RE*-containing alloys permanent magnets involves two major stages: The first is the preparation of the alloy, and the next is the production of the magnets from the alloy.

\- *Example 1:* Manufacture of permanent magnet alloy $SmCo_5$:

Many routes can be applied to process the *RE*–Co alloy. One of the processing routes of the *RE*-Co alloy production is the ‘’Reduction–Diffusion’’.

One of the well known alloys for strong permanent magnets production is $SmCo_5$.

Chemically speaking the reduction–diffusion process for the preparation of $SmCo_5$ consisted of 2 steps both performed in high temperature furnaces:

- Step 1: $10Co + Sm_2O_3 + CaH_2 \rightarrow 2SmCo_5O + CaO + H_2$ (850 ºC)
- Step 2: $2SmCo_5O + 2CaH_2 \rightarrow 2SmCo_5 + 2CaO + 2H_2$ (1050 ºC

- *Example 2:* Manufacture of the permanent magnet alloy $Nd_{15}Fe_{77}B_8$:

The strongest permanent magnets in the world are neodymium (Nd) magnets, they are made from magnetic material made from an alloy of neodymium–iron–boron (*Nd–Fe–B*).

Many methods have been developed for the production of *Nd–Fe–B* alloys. They include direct melting, co-reduction, and several special techniques that make use of reduction extraction or thermit-type processes for directly making the *Nd–Fe* or *Nd–Fe–B* alloys.

One of the processing routes is the ‘’co-reduction’’. The co-reduction process leads to the direct preparation of the *Nd-Fe-B* alloy from the *RE* and Fe oxides and using a ferroboron ($Fe_{44}B_{56}$) as a source of boron and calcium metal as the reductant.

Co-reduction is based on the following overall reaction:

$$7.5Nd_2O_3 + 50.7Fe + Fe_2O_3 + 0.143Fe_{44}B_{56} + 52.5Ca$$

$$\xrightarrow[\text{vacuum, 4 h}]{1100\text{–}1200°C} Nd_{15}Fe_{77}B_8 + 52.5Cao$$

❖ ***The Luminescent Materials***

- Luminescence is an emission of photons which is not due to heat. It is the opposite of incandescence.
- *REs* have greatly contributed to improving the performance of luminescent materials (phosphors) and finally the devices using them, due to their unique intrinsic properties, which derive from unpaired *4f* electrons (partially filled *4f* subshell).

FIG. 15.1

(Left) Schematic energy levels involved in luminescence process. (Right) Fluorite natural fluorite (CaF_2:Eu^{2+}) before and after UV excitation.

- The routes for the synthesis of the *RE* -based luminescent materials can be arranged in two classes:

- the “solid-state” route from separated elements (generally from oxides or carbonates)
- the “precursor” route, which consists of an improvement over the solid-state route, starting from precipitated mixed compounds (called “precursors”).

Whatever the route, phosphors need to have a high crystallinity. Usually, this implies a high temperature calcination step (greater than 1000 ^{o}C) with the assistance of a few mass % of melting agent (‘’flux’’). The flux helps with the fusion-recrystallization mechanism and reduces the firing temperature. For each phosphor, optimization of firing temperature and flux (nature and amount) are required. The flux is usually fluoride (NaF, LiF, NH_4F), chloride ($BaCl_2$), or borate ($Li_2B_4O_7$, H_3BO_3).

○ ***The solid-state route***

In Brief, the solid-state route consists of 3 steps:

- **Step 1.** Mix the raw materials and the “flux” well in an adequate blender. The “flux” is added in small quantity (less than few percent) to the mixture, which helps to melt the blend at lower temperature, and enables a better control of particle shape.

- **Step 2.** Fire the raw materials with the ‘’flux’’. The firing step is generally performed in a tunnel furnace, in small crucibles (few kilograms maximum).

The temperature profile in each region of the furnace needs also to be very carefully adjusted, as well as the crucible type, shape, and filling rate.

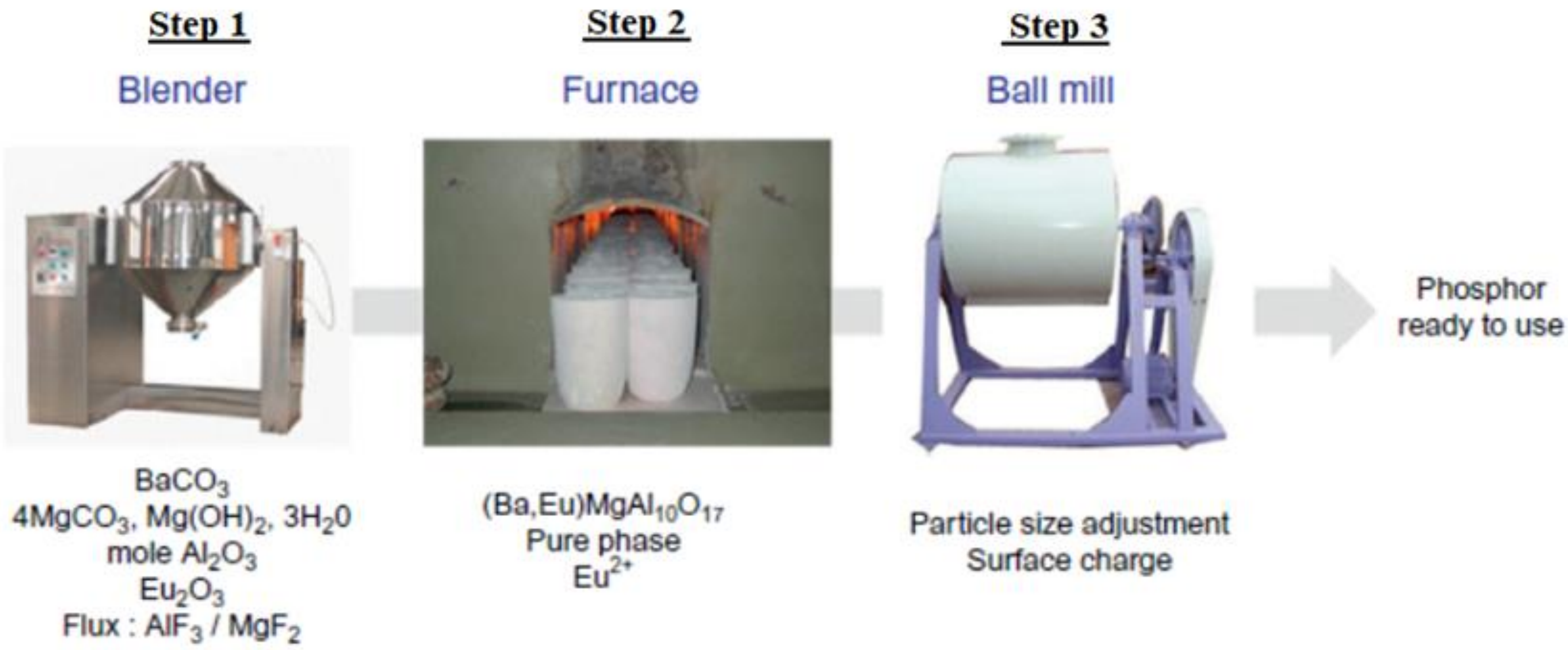
The firing step can be performed under air (to eliminate excess of oxygen carbonate). Some additional firing under reducing atmosphere is often necessary to control the oxidation state of the *RE* (Eu^{2+}, Ce^{3+}, Tb^{3+}).

Step 3. Crush the *RE* doped material obtained in the firing step.

A crusher helps to manage the cake grinding into smaller parts (ten to several hundred mm).

Some post washing is used to help cake softening, as well as to remove some noncrystalline residues, or impurities.

The equipment for grinding is adjusted depending on cake hardness and targeted grain sizes (jet-milling, wet and dry ball milling).



Step 1

Blender

$BaCO_3$
$4MgCO_3$, $Mg(OH)_2$, $3H_20$
mole Al_2O_3
Eu_2O_3
Flux : AlF_3 / MgF_2

Step 2

Furnace

$(Ba,Eu)MgAl_{10}O_{17}$
Pure phase
Eu^{2+}

Step 3

Ball mill

Particle size adjustment
Surface charge

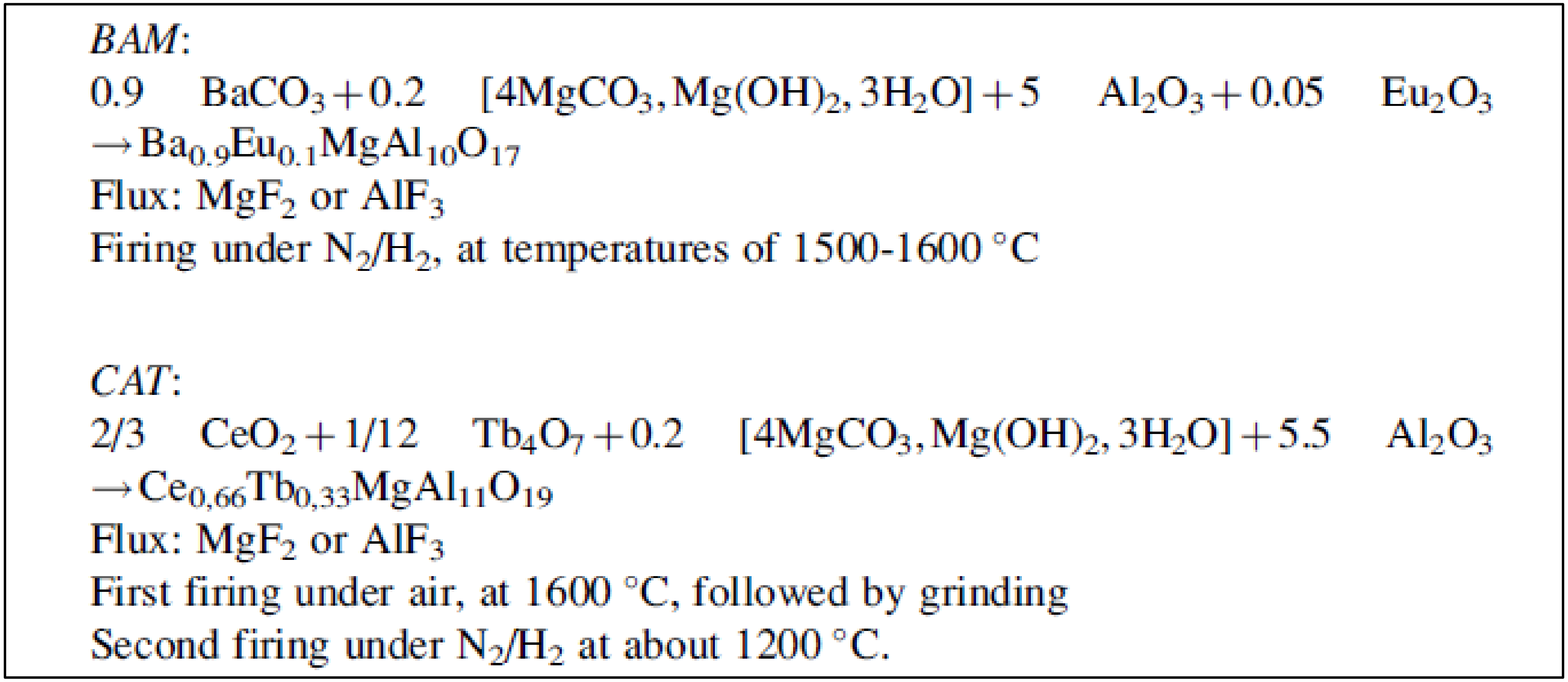
Phosphor ready to use

Classical steps and equipment used in the solid-state route of phosphor manufacture.

- This synthesis route (the “solid-state” route) was used in the past for all lighting phosphors, but is used today mainly for *BAM* (barium magnesium aluminate: $Ba_{0,9}Eu_{0,1}MgAl_{10}O_{17}$), *CAT* ($Ce_{0,66}Tb_{0,33}MgAl_{11}O_{19}$), and *YAG* (yttrium aluminum garnet: $Y_3Al_5O_{12}$) phosphors.

Nowadays *YAG* is used as host matrix in a Nd^{3+} doped *YAG* material (*Nd:YAG*) as a lasing media for solid state lasers. The dopant Nd^{3+}, typically replaces a small fraction (1%) of the Y^{3+} ions in the host crystal structure of the yttrium aluminum garnet (*YAG*).

The chemical reactions and the starting materials for the elaboration of *BAM* and *CAT* are the following (for simplicity, off-gases have been omitted):



BAM:

$0.9 \quad BaCO_3 + 0.2 \quad [4MgCO_3, Mg(OH)_2, 3H_2O] + 5 \quad Al_2O_3 + 0.05 \quad Eu_2O_3 \rightarrow Ba_{0.9}Eu_{0.1}MgAl_{10}O_{17}$

Flux: MgF_2 or AlF_3

Firing under N_2/H_2, at temperatures of 1500-1600 °C

CAT:

$2/3 \quad CeO_2 + 1/12 \quad Tb_4O_7 + 0.2 \quad [4MgCO_3, Mg(OH)_2, 3H_2O] + 5.5 \quad Al_2O_3 \rightarrow Ce_{0,66}Tb_{0,33}MgAl_{11}O_{19}$

Flux: MgF_2 or AlF_3

First firing under air, at 1600 °C, followed by grinding

Second firing under N_2/H_2 at about 1200 °C.

- The improved solid-state route is able to produce high-quality phosphors such as *BAM* and *CAT*, with mean particle sizes in the range of 5-15 mm.
- Some major improvements in terms of particle size reduction (down to 2.5 mm) and in terms of brightness have been made for *YOX* (Europium Yttrium Oxide: $(Y,Eu)_2O_3$) and *LAP* (Cerium Lanthanum oxide doped with terbium ion, Tb^{3+}: $(La,Ce)_2O_{3:}Tb^{3+}$) phosphors, by the use of the precursor route (see next section).

The precursor route

- The objective of the precursor route is to replace the blend of oxides and carbonates raw materials used in the traditional solid-state route by an advanced materials called a “precursors”
- “precursor” is a fine mixture of all the elements with suitable stoichiometry, a strict homogeneity of the dopant concentration, and a fine particle size (close to the target phosphor size). It often already has the appropriate crystal structure. This advanced precursor is obtained by wet chemistry. This allows lowering the firing temperature and duration, thus giving much better control of the sintering step. Gentle post treatments are thus used, which lead to many fewer defects in the final product, and hence to better luminescence properties.

The main steps and equipment for the finishing steps of the precursor route are similar to those used in the solid-state route. This innovation relies in good management of the precursor precipitation step.

- *Example 1:* The manufacture of the ‘’*YOX*’’ Phosphor

Today, due to the technology evolution, the “*YOX*” phosphor, namely, $(Y,Eu)_2O_3$ is used in almost all applications. Some fine tuning of particle size, *Eu* content, and minor co-doping have also been developed to improve its properties. Another very important advantage is its high chemical stability.

The wet chemistry route for manufacturing the oxide *YOX* entails:

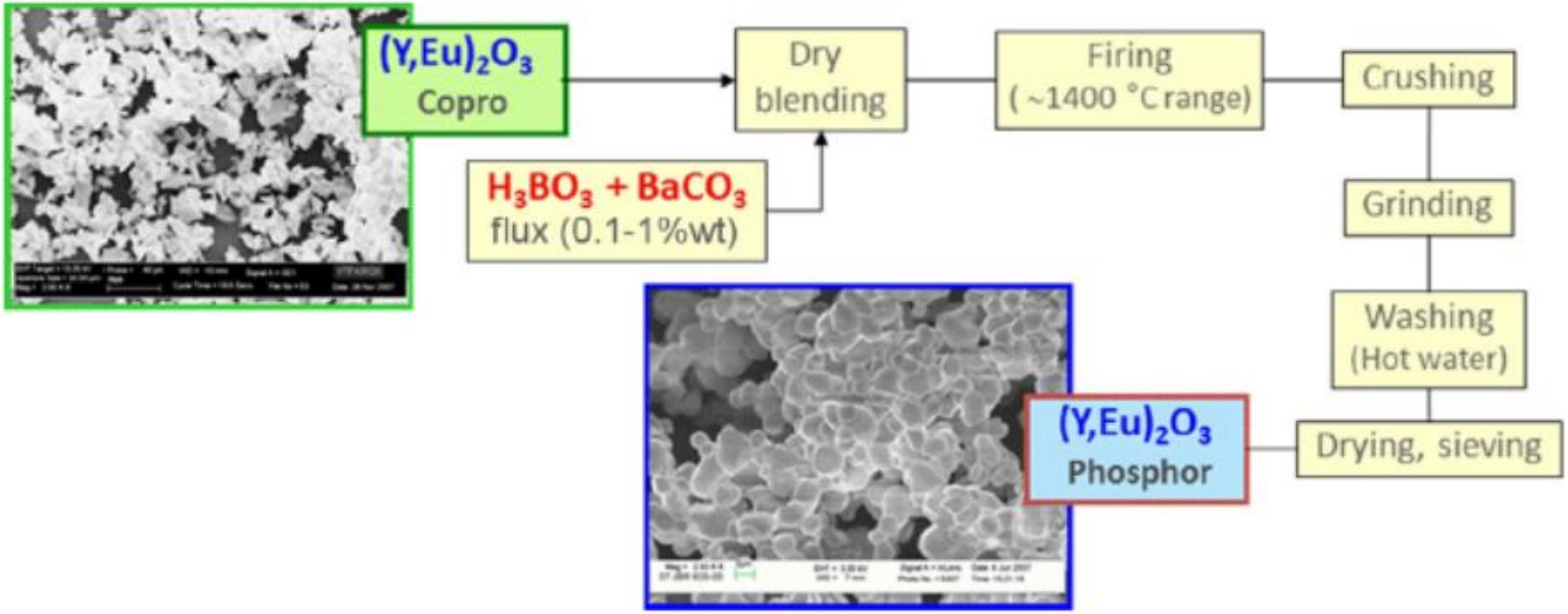
- Preparation of a co-nitrate (or co-chloride) of Y/Eu solution
- Precipitation of the precursor with oxalic acid, under controlled acidity conditions
- Filtering and washing to eliminate residual salts
- Firing at medium temperature (700-900 ^{o}C) to decompose the oxalate and obtain the final *YOX* oxide precursor.

Many variations of the precipitation conditions permit control of the particle size and morphology of the precursor. At this step, the crystalline structure is suitable but the crystallinity is too low. Brightness is then limited.

In a second step, the precursor is usually carefully blended with a flux (based on barium carbonate ($BaCO_3$) and boric acid (H_3BO_3) and further re-fired at between 1400 and 1500 °C in air, to enhance crystallinity.

The post crushing, grinding, and washing steps are much gentler than for the classical solid-state route.

The success of the precursor relies in perfect distribution of *Eu* in the *Y* lattice.



Wet YOX phosphor route.

- *Example 2:* The manufacture of the ‘’*LAP*’’ Phosphor

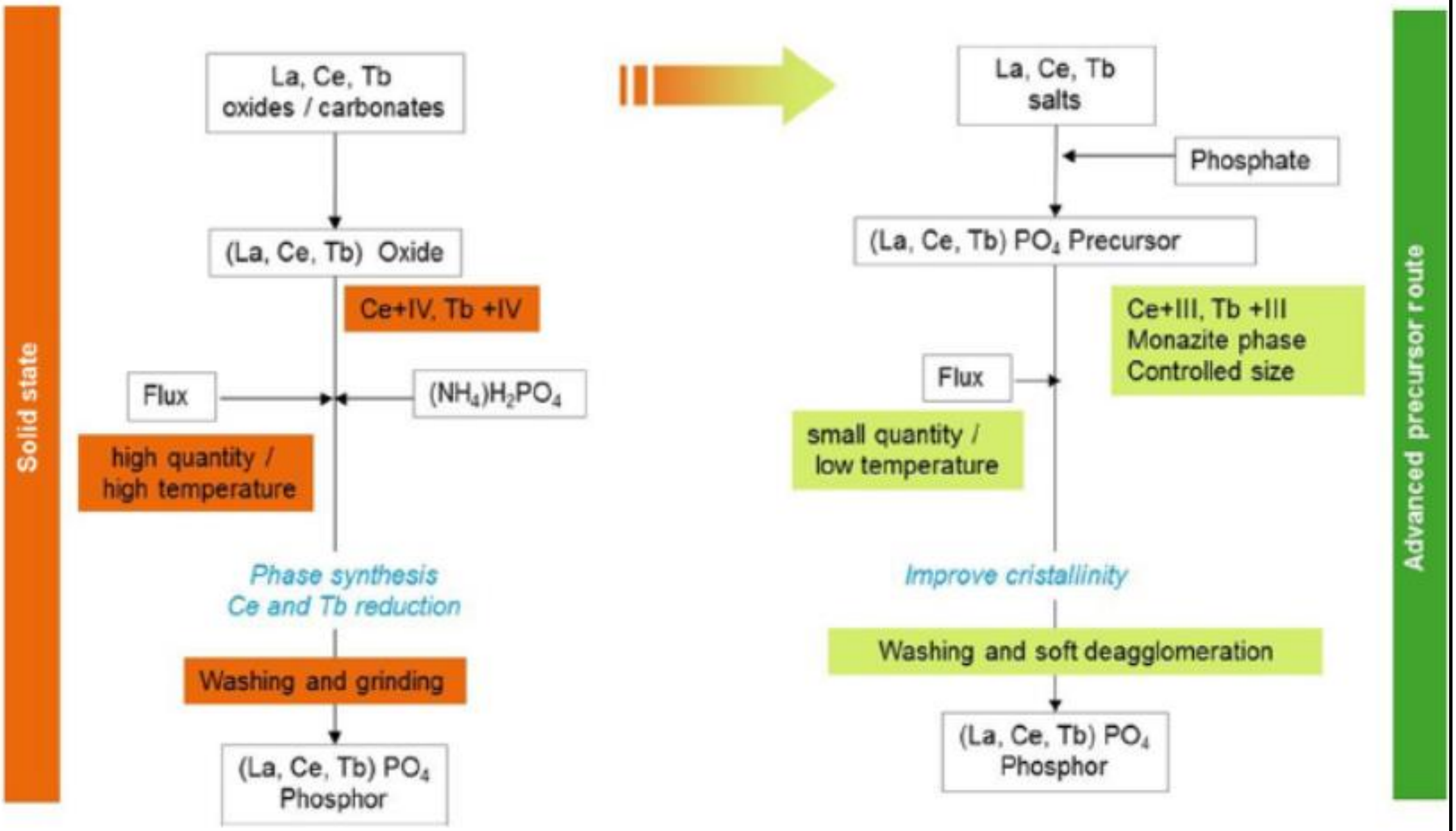
The ‘’*LAP*’’ phosphor ($(La,Ce)PO_4:Tb^{3+}$) is a Lanthanum-cerium phosphate doped with the trivalent terbium, Tb^{3+}. *LAP* is used in many devices including *LCD* screens, lamps,…

When the *LAP* formula is made through a purely solid-state route, it is quite impossible to manage the oxidation state of all the Ce at the +3 oxidation state. It is also difficult to manage particle size and avoid phasic impurities. Thus, the precursor route was developed in the 1990s, which greatly improved the product and made it possible to use *LAP* widely in lighting applications.

The precursor is synthesized through precipitation from *RE* salts and a phosphate source in water, then washing and firing in air, in order to obtain monazite $(La,Ce,Tb)PO_4$, with controlled particle size, and an oxidation state of Ce and Tb oxidation state which is mostly at +3.

Second, a blend with small quantity of borate flux is added before the firing at medium temperature (around 1100 ^{o}C) under a gentle reducing atmosphere (N_2/H_2) in order to consolidate the crystallinity of the phase and perform full reduction of the *REs*.

Gentle grinding and washing are used to obtain a final high performance phosphor.



Wet LAP phosphor route.

➢ *Further Details On the Optical Properties of the RE-Containing Compounds*

✓ *The color*

- Many trivalent lanthanide RE^{3+} ions are strikingly colored both in the solid state and in aqueous solution (See figures in the next page).
- The color seems to depend on the number of unpaired *f e*lectrons. Depending on the atomic number, the *4f* orbitals of the RE^{3+} ion are more or less filled, the electron number varying from 0 (La^{3+} or Ce^{3+}) to 14 (Lu^{3+}).
- Elements with (n)*f* electrons often have a similar color to those with (14 – n)*f* electrons.

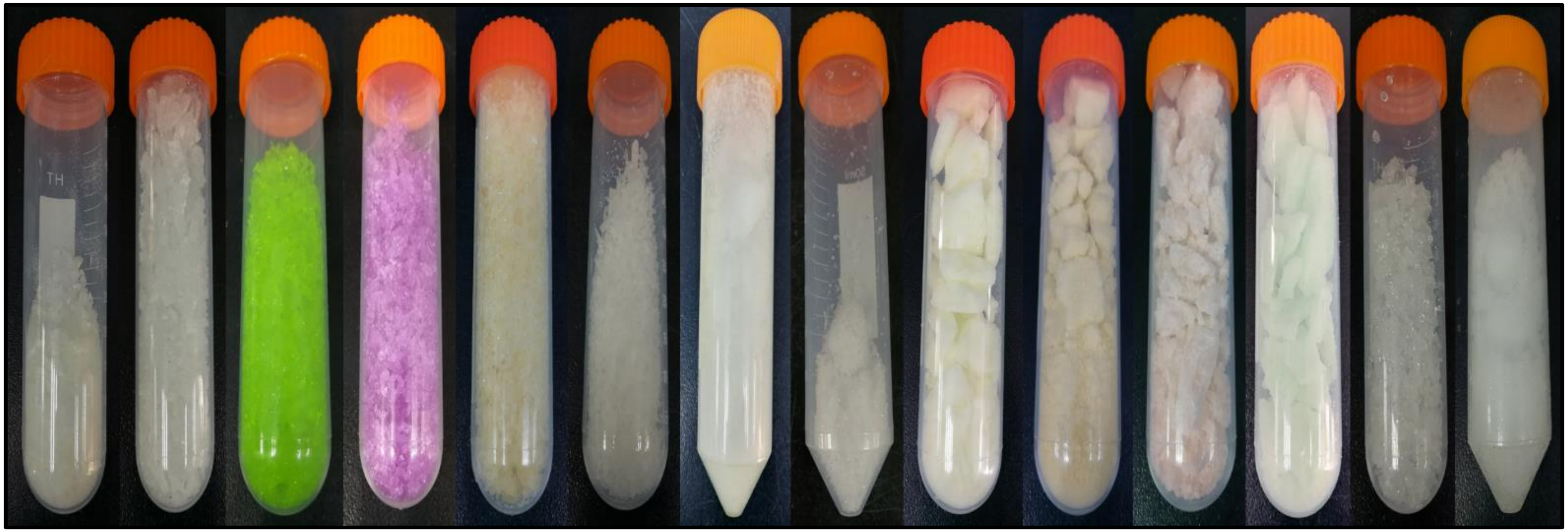
However, the elements in other valence states do not all have colors similar to their isoelectronic RE^{3+} counterparts.

- The trivalent RE^{3+} ions, except Ce^{3+} and Yb^{3+}, exhibit very sharp absorption bands in the visible and ultraviolet (UV) regions (see figure below). These bands are caused by *f–f* transitions, and the sharpness comes because the electrons in the *4f* inner shell of the *REs* are shielded from the chemical environment by the $5s^2p^6$ octet. The spectra are similar to those for free atoms and quite unlike the broad bands observed for the *d-d* transitions (see figure below).

Therefore, optical spectra are virtually independent of environment and are useful fingerprinting and quantitation of lanthanides ions (Ln^{3+}).

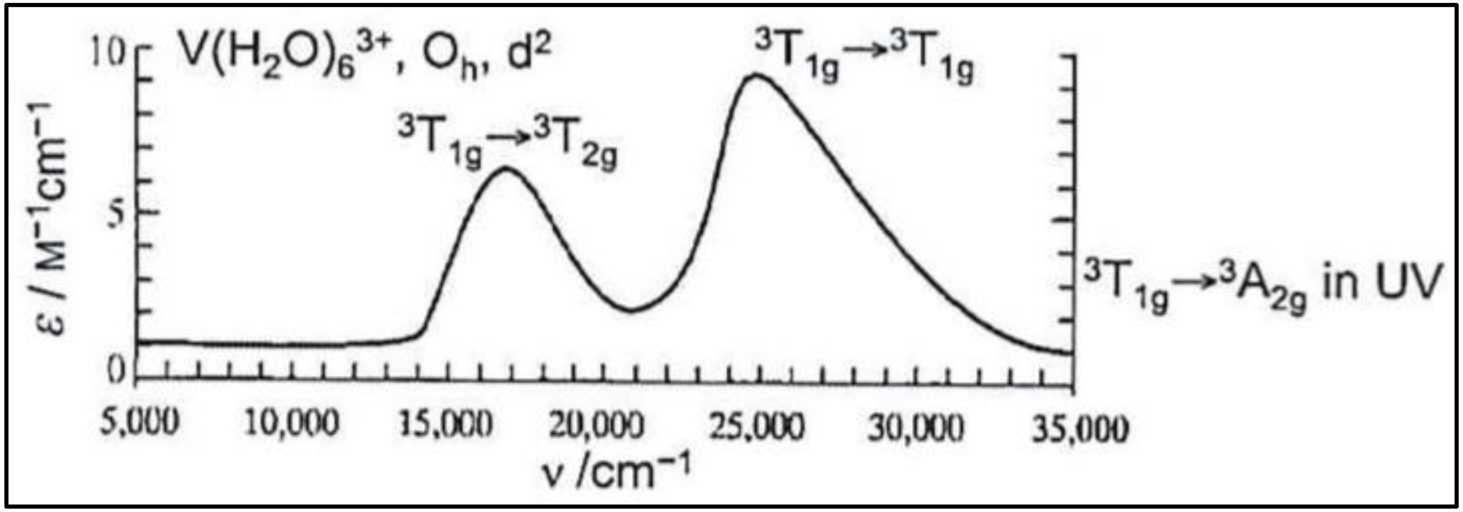
- *The color of solids of lanthanide nitrates in their hexahydrate form ($Ln(NO_3)_3).6H_2O$).*

From left to right: La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu.

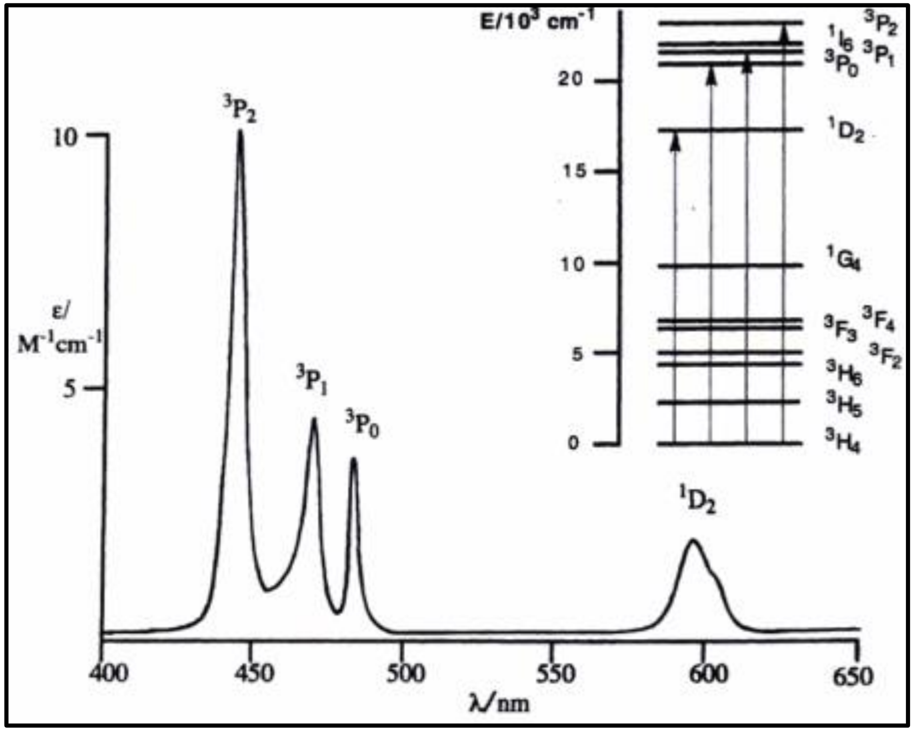


- *The approximate colors of lanthanide ions in aqueous solutions.*

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+}					



- ***UV-visible spectrum of the hexaaquavanadium $[V(H_2O)_6]^{3+}$ complex ion.***



- ***UV-visible spectrum of***
a Praseodymium (Pr^{3+}) complex ion.

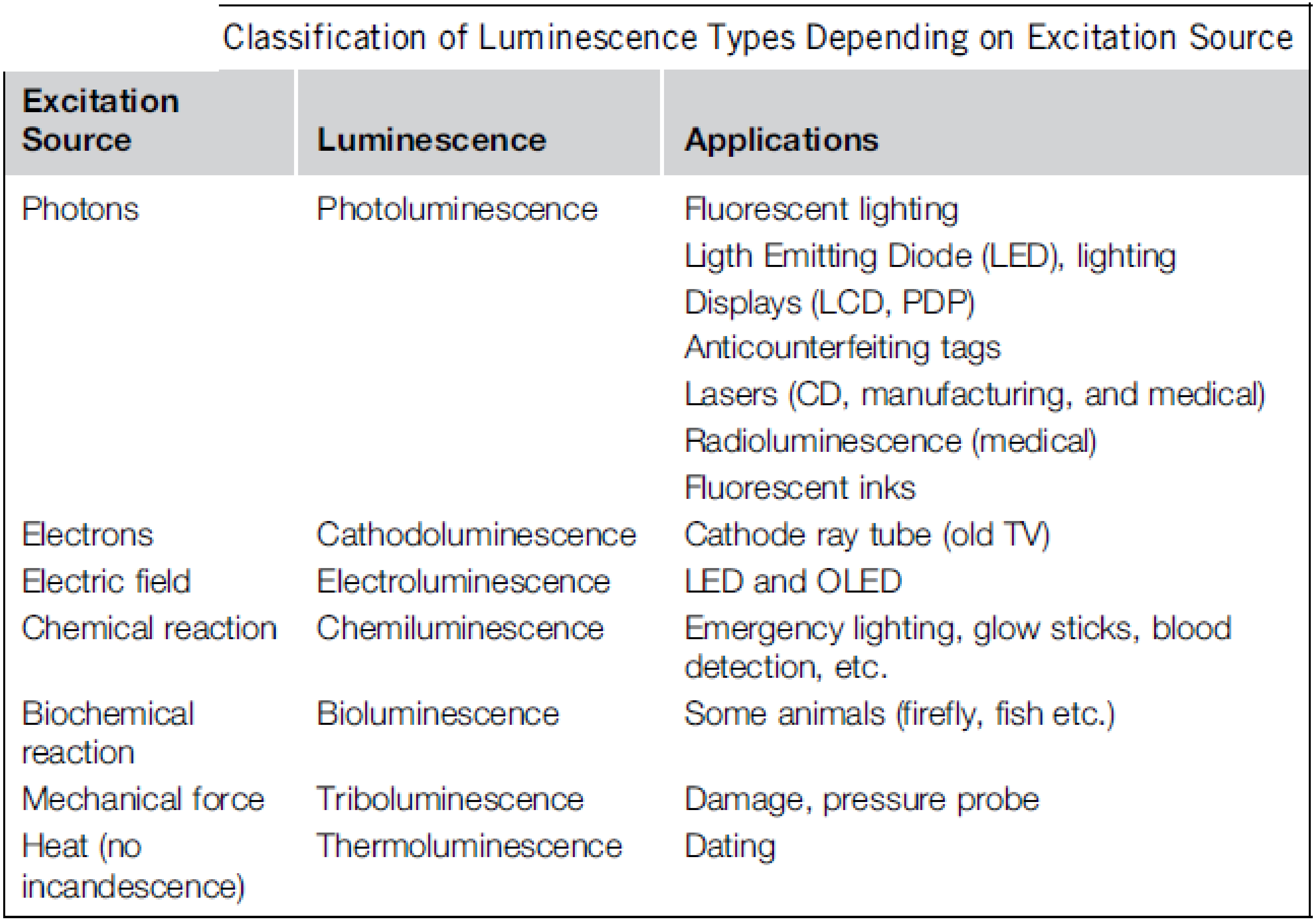
✓ *The Luminescence*

- Luminescence is an emission of photons which is not due to heat. It is the opposite of incandescence.
- Due to their electronic structure, some materials are able to absorb energy after external excitation, even at low temperature. If the absorbed energy is high enough, an electron can be "excited" from its fundamental state in an upper electronic layer (see figure below). The de-excitation to its fundamental level is made either by non-radiative de-excitation (emission of heat through vibrational energy levels) or by radiative emission corresponding to the emission of a photon (example see the figure below for the natural mineral, fluorite $CaF_2:Eu^{2+}$). This phenomenon is called "Luminescence" (*from Latin lumen*, *meaning light*).

FIG. 15.1

(Left) Schematic energy levels involved in luminescence process. (Right) Fluorite natural fluorite ($CaF_2:Eu^{2+}$) before and after UV excitation.

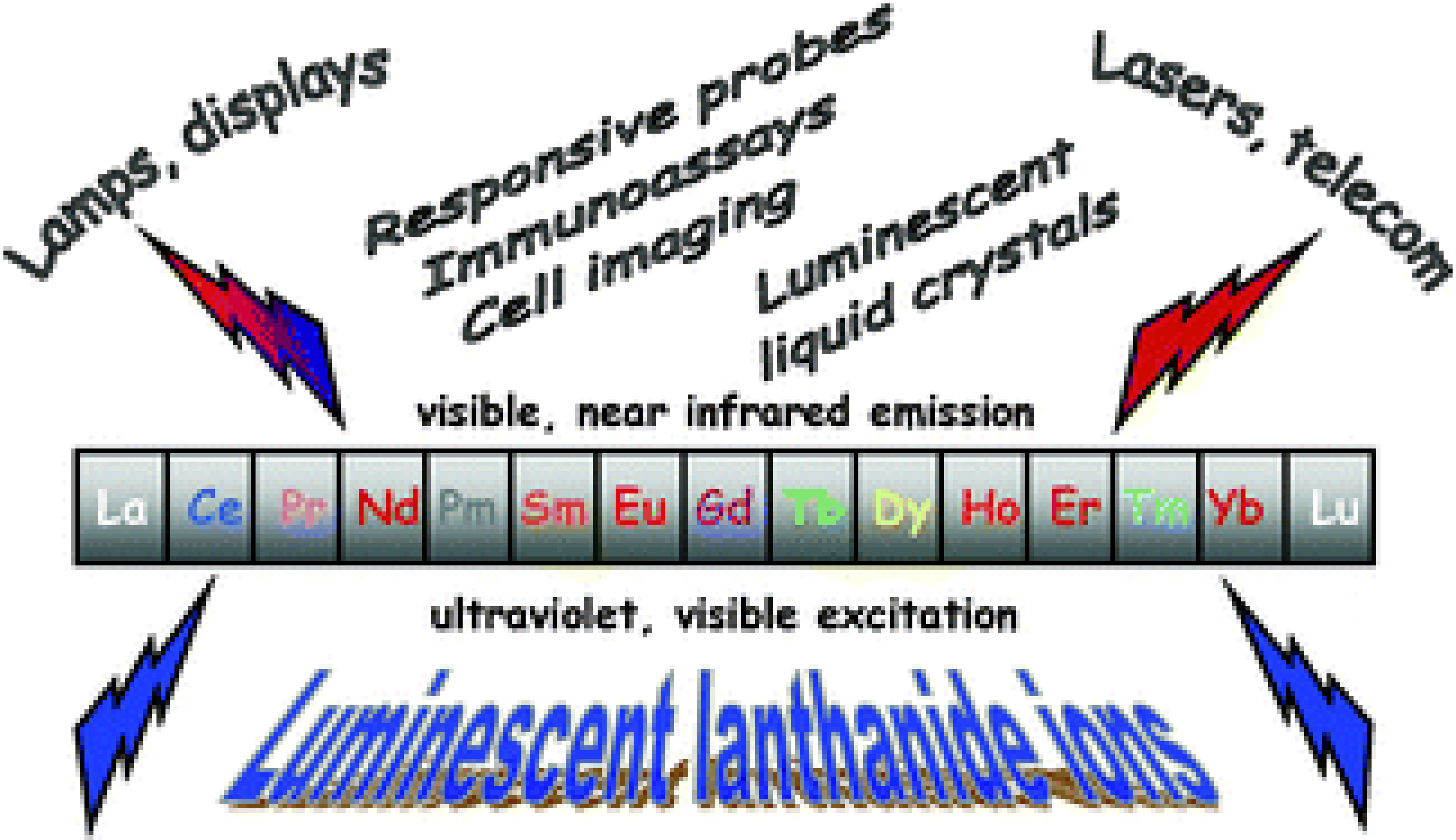
- The nature of excitation can be very diverse, leading to subcategories of luminescence types (See Table below). As an example, if the excitation source is photonic, the science is called photoluminescence.



Classification of Luminescence Types Depending on Excitation Source

Excitation Source	**Luminescence**	**Applications**
Photons	Photoluminescence	Fluorescent lighting Ligth Emitting Diode (LED), lighting Displays (LCD, PDP) Anticounterfeiting tags Lasers (CD, manufacturing, and medical) Radioluminescence (medical) Fluorescent inks
Electrons	Cathodoluminescence	Cathode ray tube (old TV)
Electric field	Electroluminescence	LED and OLED
Chemical reaction	Chemiluminescence	Emergency lighting, glow sticks, blood detection, etc.
Biochemical reaction	Bioluminescence	Some animals (firefly, fish etc.)
Mechanical force	Triboluminescence	Damage, pressure probe
Heat (no incandescence)	Thermoluminescence	Dating

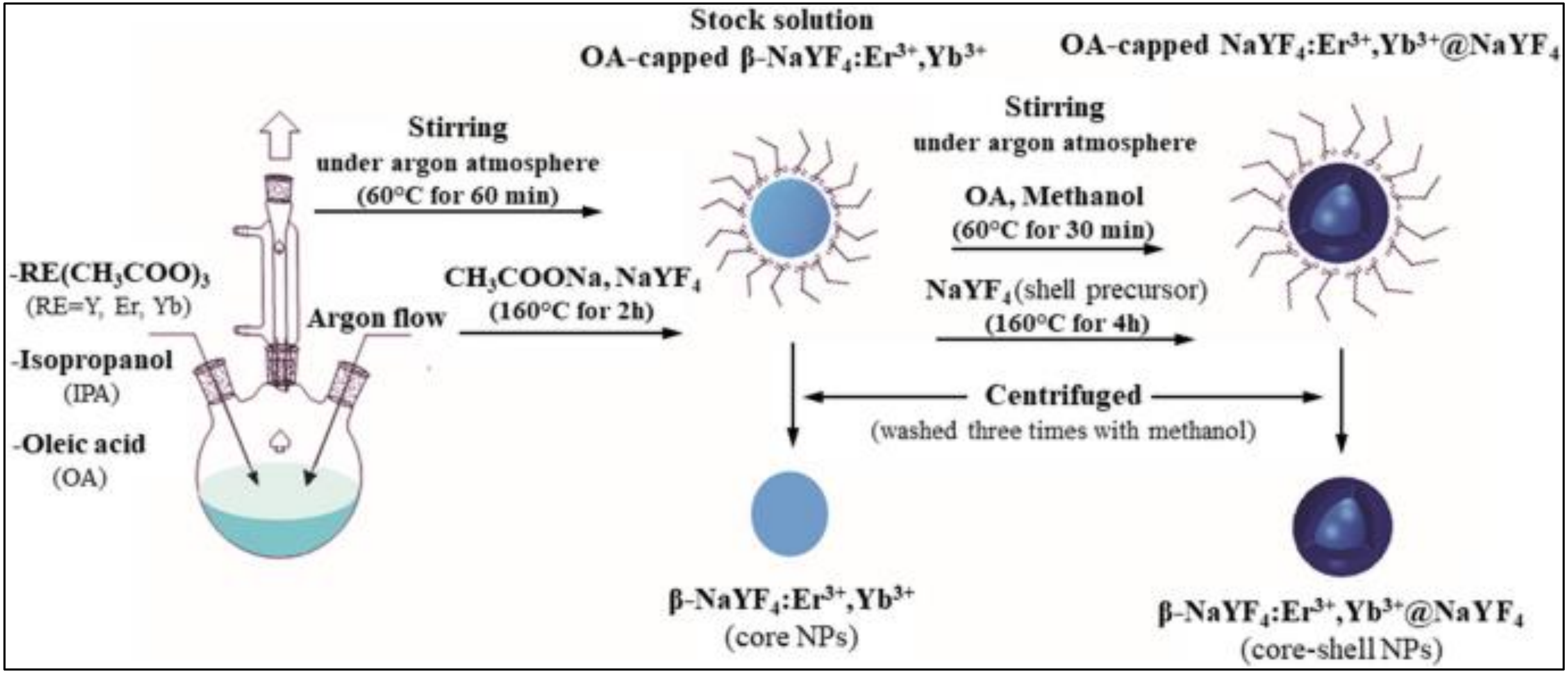
- Luminescent materials are widely used in everyday life, for example, for lighting (energy saving lamps), displays (laptop, cathode ray tube (*CRT*) *TV*, liquid crystal display (*LCD*) TV, Plasma TV (PDP)), *DVD* player (laser), diagnosis (X-rays, tomography), or manufacture of devices and materials (by laser). The common point for all these technologies is mastering of the photon source, or generally speaking, of light.
- In most of the above examples, *REs* have faced a major development in the past 50 years. They have greatly contributed to improving the performance of luminescent materials and finally the devices using them, due to their unique intrinsic properties, which derive from unpaired *4f* electrons.
- Most *RE*-based phosphors are inorganic compounds, a few are organic. These materials are composed of a matrix, where *RE* ions substitute some cations. Notice that the substitution ratio is generally low, below 10%.


Lamps, displays
Responsive probes
Immunoassays
Cell imaging
Luminescent
liquid crystals
Lasers, telecom
visible, near infrared emission
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
ultraviolet, visible excitation
Luminescent lanthanide ions

- The nature of the matrixes is very wide: oxides, phosphates, borates, silicates, nitrides, and sulfides. In order to manage *RE* substitution, matrixes are composed of cations with similar ionic radii as lanthanides.
- For trivalent RE^{3+}, the matrix host could have La^{3+} and Y^{3+} (sometimes Gd^{3+}) as inactive host cations; this is the case of $Y_{2-x}Eu_xO_3$ (Eu^{3+} in 6-fold coordination) or $La_{1-x-y}Ce_xTb_yPO_4$ (Ce^{3+} and Tb^{3+} in 9-fold coordination).
- For divalent *REs*, alkaline earths are mainly used; e.g., Ba^{2+}, Sr^{2+}, and Ca^{2+} are used in phosphors. The most famous case is $Ba_{1-x}Eu_xMgAl_{10}O_{17}$ (Eu^{2+} in 9-fold coordination).

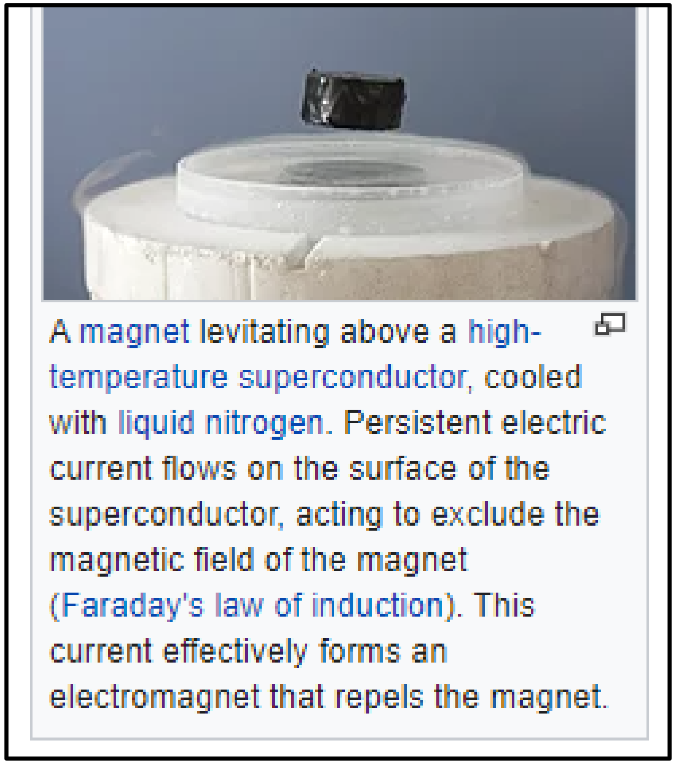
- Lanthanide (*Ln* = Eu, Er, Yb, Ho, …) doping in inorganic matrices such as sodium *RE* tetrafluorides ($\mathrm{Na}\mathit{RE}\mathrm{F}_4$; *RE* = Y, Gd,..,), perovskites (ABX_3 such as $CsPbCl_3$),…have demonstrated extremely excellent optical properties and great application potentials.

Chemical synthesis often involves the use *RE* salts (such acetates), organic solvents (such as alcohols) and surfactants (such as oleic acid) in a controlled atmosphere and temperature. The surfactant permits the stabilization of the inorganic core in a colloidal state.



❖ ***The Superconducting Materials***

- Superconductivity is a set of physical properties observed in certain materials where electrical resistance vanishes and magnetic flux fields are expelled from the material. Any material exhibiting these properties is a superconductor.



A magnet levitating above a high-temperature superconductor, cooled with liquid nitrogen. Persistent electric current flows on the surface of the superconductor, acting to exclude the magnetic field of the magnet (Faraday's law of induction). This current effectively forms an electromagnet that repels the magnet.

- Superconductor material classes include chemical elements (e.g. mercury or lead), alloys (such as niobium–titanium, germanium–niobium, and niobium nitride), ceramics (Yttrium barium copper oxide (*YBCO*),…), superconducting pnictides (like fluorine-doped *LaOFeAs*) or organic superconductors (fullerenes and carbon nanotubes; though perhaps these examples should be included among the chemical elements, as they are composed entirely of carbon)

- *Example :* Synthesis of the *YBCO* ($YBa_2Cu_3O_{7-x}$)

Yttrium barium copper oxide (*YBCO*) is a family of crystalline chemical compounds, famous for displaying high-temperature superconductivity.

It includes the first material ever discovered to become superconducting above the boiling point of liquid nitrogen (77 K) at about 92 K.

Many *YBCO* compounds have the general formula $YBa_2Cu_3O_{7-x}$ (also known as *Y123*), although materials with other Y:Ba:Cu ratios exist, such as $YBa_2Cu_4O_y$ (Y124) or $Y_2Ba_4Cu_7O_y$ (Y247).

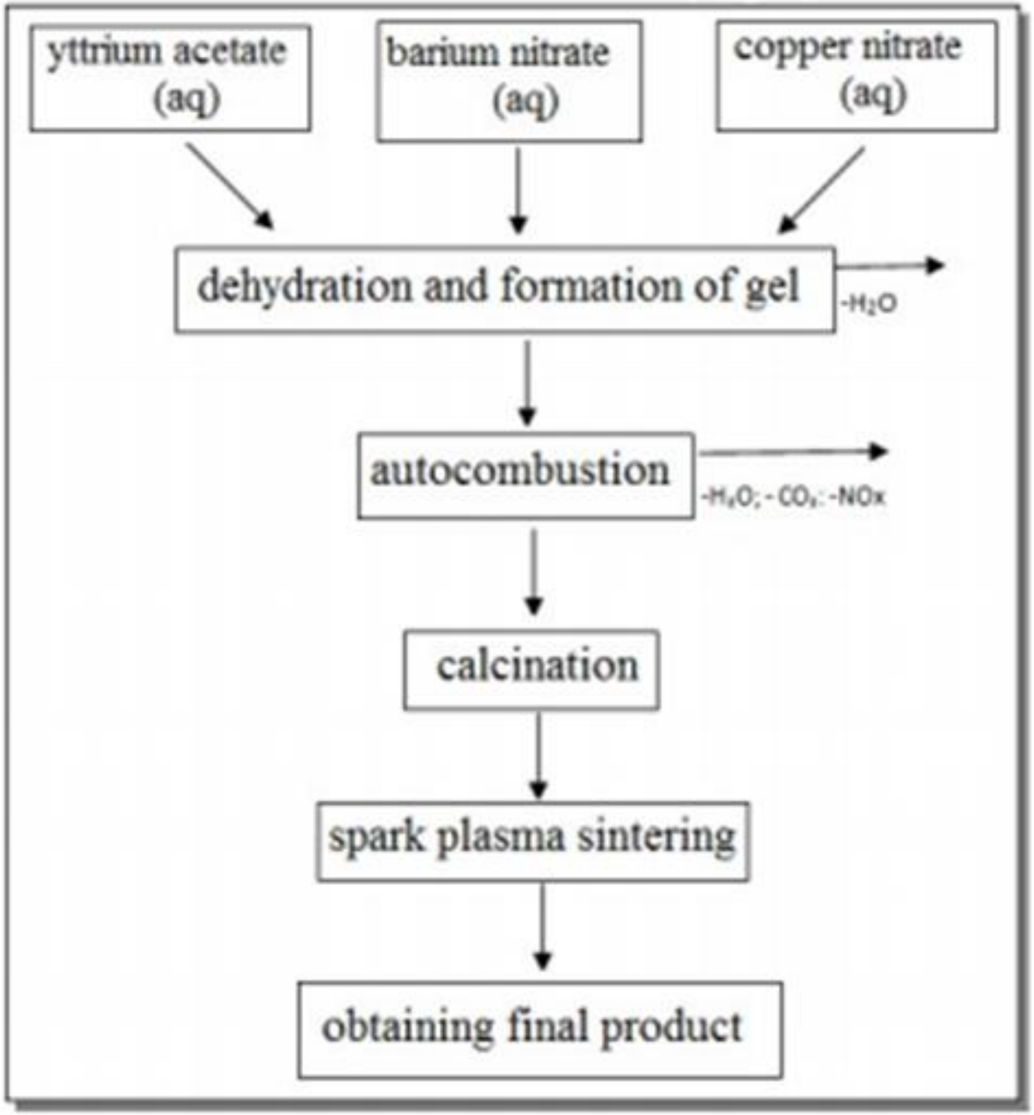
Relatively pure *YBCO* (*Y123*), was first synthesized by heating a mixture of the metal carbonates at temperatures between 1000 and 1300 K in presence of oxygen:

$$4BaCO_3 + Y_2(CO_3)_3 + 6CuCO_3 + (1/2-x)O_2 \rightarrow 2YBa_2Cu_3O_{7-x} + 13CO_2$$

- \Various modern syntheses routes of *YBCO* were subsequently performed using the corresponding oxides, nitrates, acetates,...

An example of processing synthesis of *YBCO* from the yttrium acetate and barium and copper nitrates is given in the flow chart below.

$$\mathbf{8}Y(CH_3COO)_3+\mathbf{16}Ba(NO_3)_2+\mathbf{24}Cu(NO_3)_2 \longrightarrow \mathbf{8}YBa_2Cu_3O_7+\mathbf{50}NO_2+\mathbf{48}CO_2+\mathbf{36}H_2O+\mathbf{15}N_2$$



Flow chart of the process for obtaining sintered YBCO

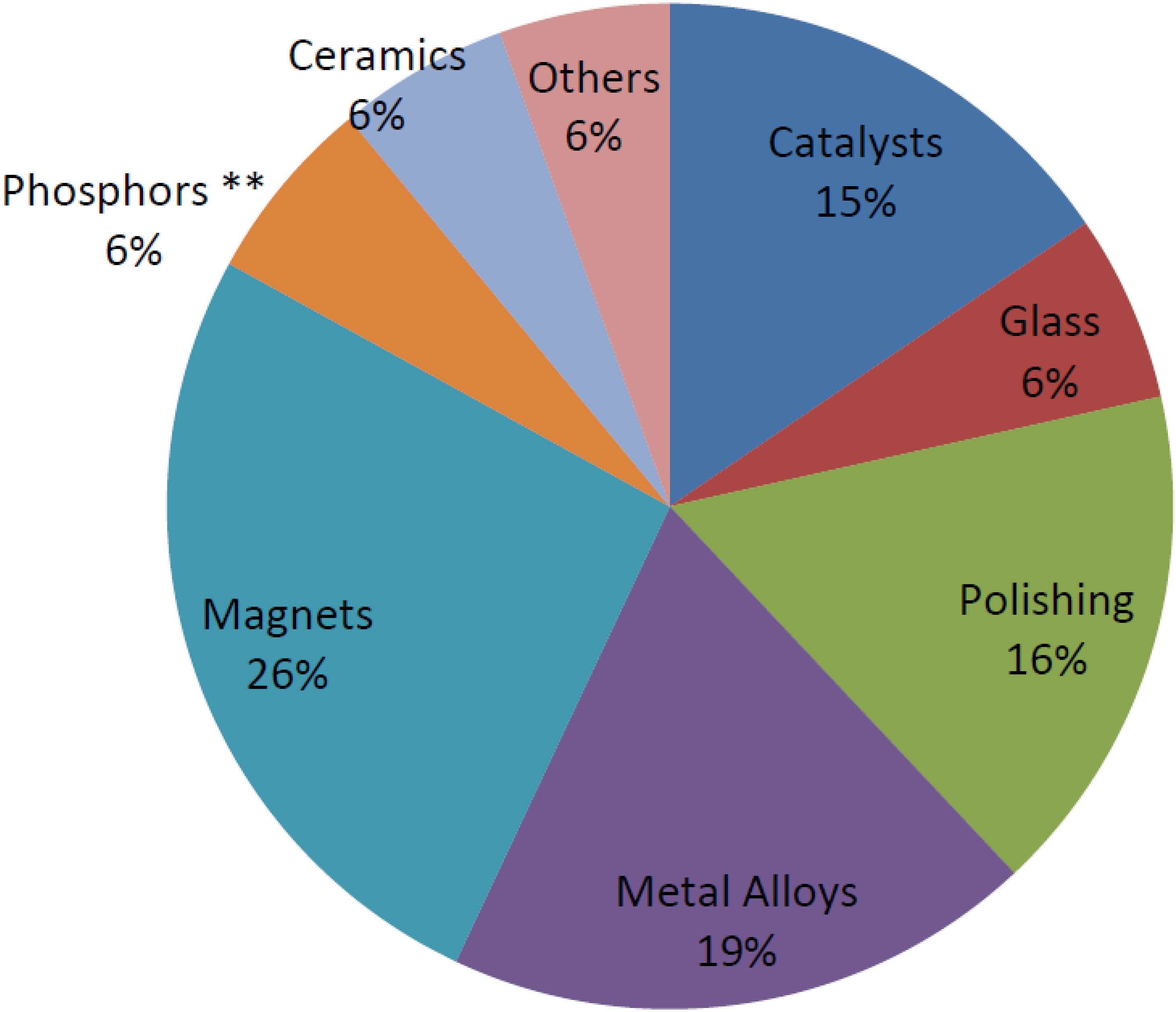
❑ *Other Uses of REs-Containing End-Product Materials*

- *REs*-containing end-product materials destined for commercial use or for research applications are numerous. These materials can be basically divided into two groups:

* One group comprises commercially used *RE* compounds, alloys, and metals,

* while the other group comprises *RE*-bearing products obtained using *RE* compounds, alloys, and metals as the interprocess intermediates.

- Some of the largest uses of *REs* are in catalysts (15%, largely Ce and La), *RE* magnets (26%, largely Nd, Sm and Dy), alloys (19%), powder production (16%) and phosphors (6%). Catalyst applications are for both industrial and auto catalysts (see figure below).
- Phosphors are important for a range of applications particularly for visual display in screens and low energy lighting. This is a likely growth area and will put pressure particularly on Eu and Tb reserves.
- *REs* containing end-product materials are used as laser producing ceramics. For example neodymium-doped yttrium aluminum garnet (Nd:YAG) lasers are used in a variety of applications including medicine, manufacturing, military,…


Others
6%
Catalysts
15%
Glass
6%
Polishing
16%
Metal Alloys
19%
Magnets
26%
Phosphors **
6%
Ceramics
6%

Rare earth minerals

- 17 metals
- Key components in high-tech products
- China supplies at least 95% of world's rare earths

Examples of products containing rare earth elements:

Smartphones
scandium
yttrium
lanthanum
neodymium

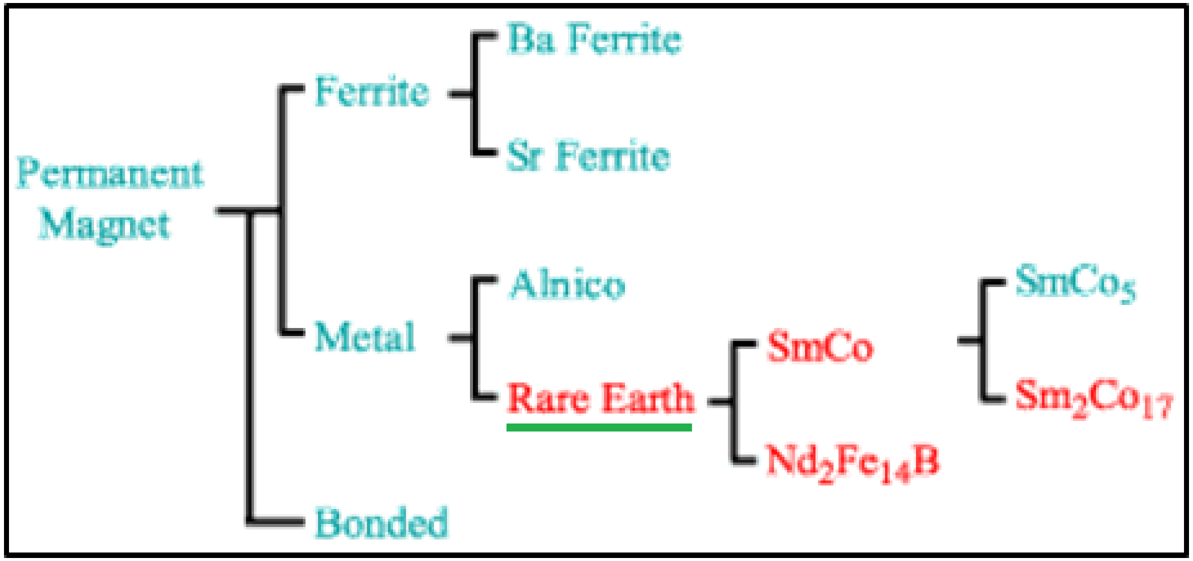
Wind turbines
dysprosium
neodymium
praseodymium
terbium

Energy-efficient fluorescent light bulbs
europium
terbium
yttrium

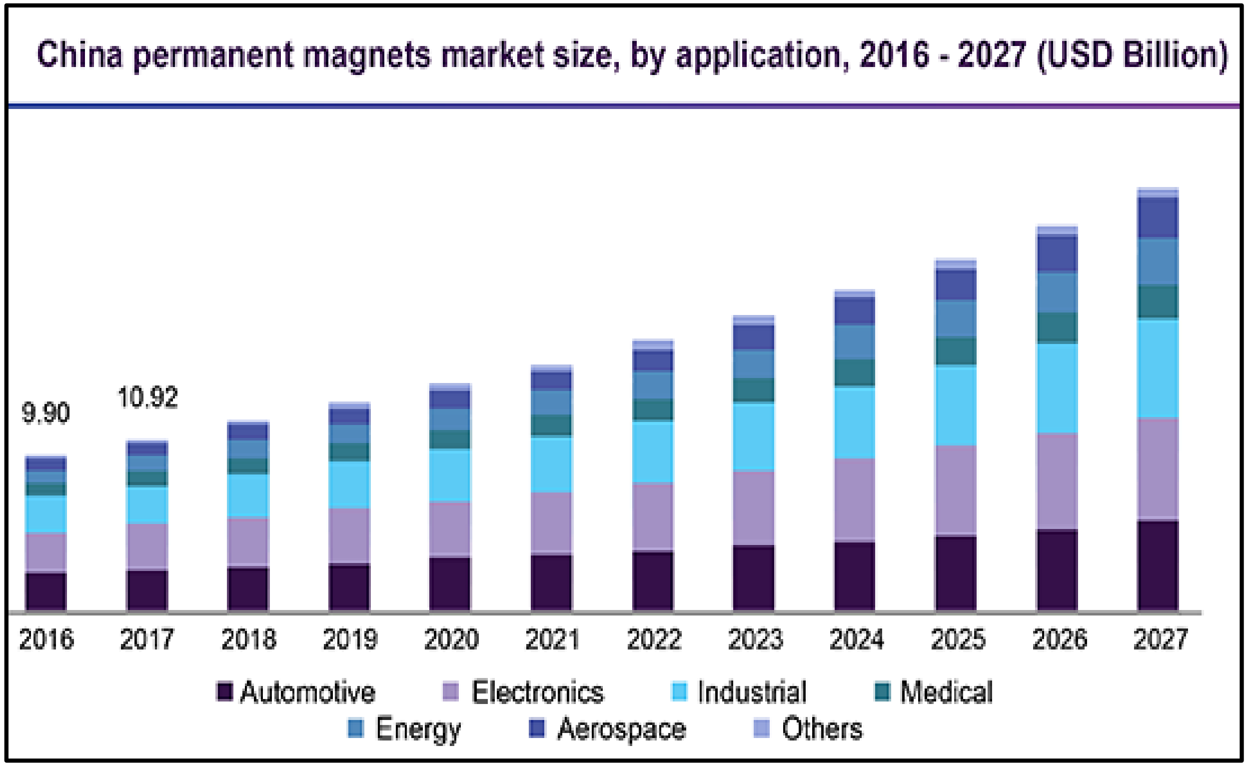
Hybrid vehicles
dysprosium
lanthanum
neodymium
praseodymium

Fibre optics
erbium
europium
terbium
yttrium

- Another area for expansion will be *RE* magnets (Nd, Pr, Sm and Dy) particularly for alternative energies. These will find widespread application in wind turbines, the auto industry (electric and hybrid cars) and defense industry (*i.e.*, missile guidance systems).
- *RE*-containing (Er) glasses are important for fiber optical amplifiers required in high speed optical communication networks.
- Improving the efficiency of solar energy conversion is another area of probable expansion for *REs*.
- The *REs* Er, Y and Ho show promise for up-conversion (converting low energy photons into higher energy photons by increasing the wavelength *i.e.*, infrared photons to visible) and Yb, Tm and Tb for down-conversion (converting high energy photons to lower energy).
- Some novel areas for *REs* include refrigeration using either laser cooling or the magnetocaloric effect. In laser cooling, vibrational energy is removed by emission of photons with a higher average energy than the absorbing photons in various materials that may include Y, Yb, La, Nd and Tm. In the magnetocaloric effect, a material has its magnetic domains aligned under a strong magnetic field and when the field is removed the domains can unalign using phonons energy causing cooling. Room temperature magneto-caloric materials (e.g., $Gd_5(Si_xGe(_{1-x}))$ may offer an alternative to current vapor compression cycles used with current refrigerants.



○ *Strong Permanent $Nd_2F_{14}B$ Magnets*



- Some more mundane uses include flints for cigarette lighters (Ce), polishing agents (CeO_2), rechargeable batteries (La) and carbon arc lamps (La).
- Some of the *RE* salts are used in the titration of chemical species through Redox reactions.

For example Cerium (IV) sulfate ($Ce(SO_4)_2$) is an oxidizing agent used in the in volumetric chemical analysis of ferrous ions, Fe^{2+}. The titration reaction occurs according to:

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

The end point can be seen by indicators such as orthophenanthroline or by instrumental methods such as potentiometry.

- *REs* underpin technologies that are seen as critical for clean energy economies, such as in photovoltaic devices, battery technologies for transport and wind energy, and phosphors for lighting. High speed optical fiber communication (Praseodymium: ${}_{59}Pr$) is another likely growth area.

- *REEs* such as Sc, Ce, Nd and Pr, have been widely used as alloys to impart strength and hardness to metals. For example, aluminium scandium alloys (2.0 wt % Sc) can be used in the form of sheet and plate for aerospace applications. Other applications for Al-Sc alloys include blades for wind-mills and sporting goods like bicycle frames, baseball bats and golf clubs.
- *REEs* are also widely used in the petroleum industry for refining of crude oil into gasoline products.
- Erbium ($_{68}$Er) and other lanthanides are widely used in some optical devices, such as night vision goggles, laser beams, and phosphorescent materials.

- *REs* are now especially important, and used extensively, in the **defense industry**. Some of their specific defense applications include: anti-missile defense, aircraft parts, communications systems, electronic countermeasures, jet engines, rockets, underwater mine detection, missile guidance systems and space-based satellite power.
- Gadolinium-based contrast agents (*GBCAs*) help doctors see abnormal tissues in magnetic resonance imaging (**MRI**) scans with more detail. They help doctors **diagnosis** inflammation, tumors and blood clots by providing them with clearer, brighter images from inside the body.