Inorganic Chemistry

Second year
1st semester

Lecture 1

syllabus

1-Review on classification of periodic table

- Deviation of some d- and f- transition metals from n+1 rule

-Coordination number of elements, Sigma and pi bonding

-comparison, of f-elements with d-elements, Lanthanide contraction

- Uniqueness properties of 1st and 2nd period elements Diagonal effect

2- Oxidation state and oxidation no. of representative elements, d-block and f-block elements

3- Oxides of representative and transition metal elements

4-Colors and spectra of transition metal complexes, factors affecting absorption energy

5-Magnetism, temperature effect, magnetic moments, ESR

6- Electrode potential

-(review on cell potential, Nernst equation, relationship of $E^{o}cell$ to ΔG^{o} and K)

-Born-Harbor cycle of ΔGo

-oxidation – reduction in aq. Solutions as a function of pH,

-Latimer diagram

7- Symmetry

-Symmetry operations and Symmetry elements

-point group symbols from molecular shapes,

8- Solid State Chemistry

-(lattice points)

-Weiss and Miller indices

X- ray diffraction and Bragg's law examples

Structures of unit cells of some inorganic compounds

REFERENCES

1- G.E.Rodgers, Descriptive inorganic chemistry, coordination and solid state,2nd Ed, Brooks/ Cole, Thomson , (2002)

2- G.L.Miessler and D.A.Tarr , Inorganic chemistry . 2nd Ed, Prentice Hall

3- F.A.Cotton and G.Wilkinson Basic inorganic chemistry.3rd Ed,Wiley New york, (1995)

4- Whitten,Davis,Peck, Stanely, General chemistry, 7th Ed. , Brooks/ Cole, Thomson, (2003)

5- J.E.Huheey,E.A.keiter, R.L.Keiter, Inorganic Chemistry,4th Ed. Harper New York, (1993) ,Collins,

6- Shriver & Atkins, Inorganic chemistry, 4th Ed, Peter Atkins, Tina Overton, Oxford, University Press, (2006)

7- C.E.Housecroft and A.G.Sharpe, Inorganic chemistry, 3rd Ed., Prentice Hall, (2008)

8 - N.N.Greenwood and A.Earnshaw , Chemistry of elements, (1999)

To build up an atomic structure we should follow the rules:

1- Pauli principal : No two electrons in the same orbital can have the same four quantum no.s only electrons with opposite spin can occupy the same orbital.

2- Hund's rule : Electrons fill degenerate orbitals one at a time before doubling up in the same orbital"

The p,d,f,g orbitals sets are equivalent in energy but differ in orientation in space **ml=(2*l*+1)** p(3) , d(5) ,f(7), g(9) . So they should be half filled before any are filled to avoid electron-electron repulsion as repulsion means high energy

3- Aufbau Principle states that:

"The orbitals of lower energy are filled first with the electrons then the orbitals of high energy are filled."

The orbital energy does not depend on value of n only but also on ℓ , using (n + ℓ) rule , the lower energy orbital is that of lower value of (n + ℓ) . If (n + ℓ) values of different orbitals are equal the one with the lowest value of n fill first

The (n + ℓ) rule of orbital energies in a multielectron atom

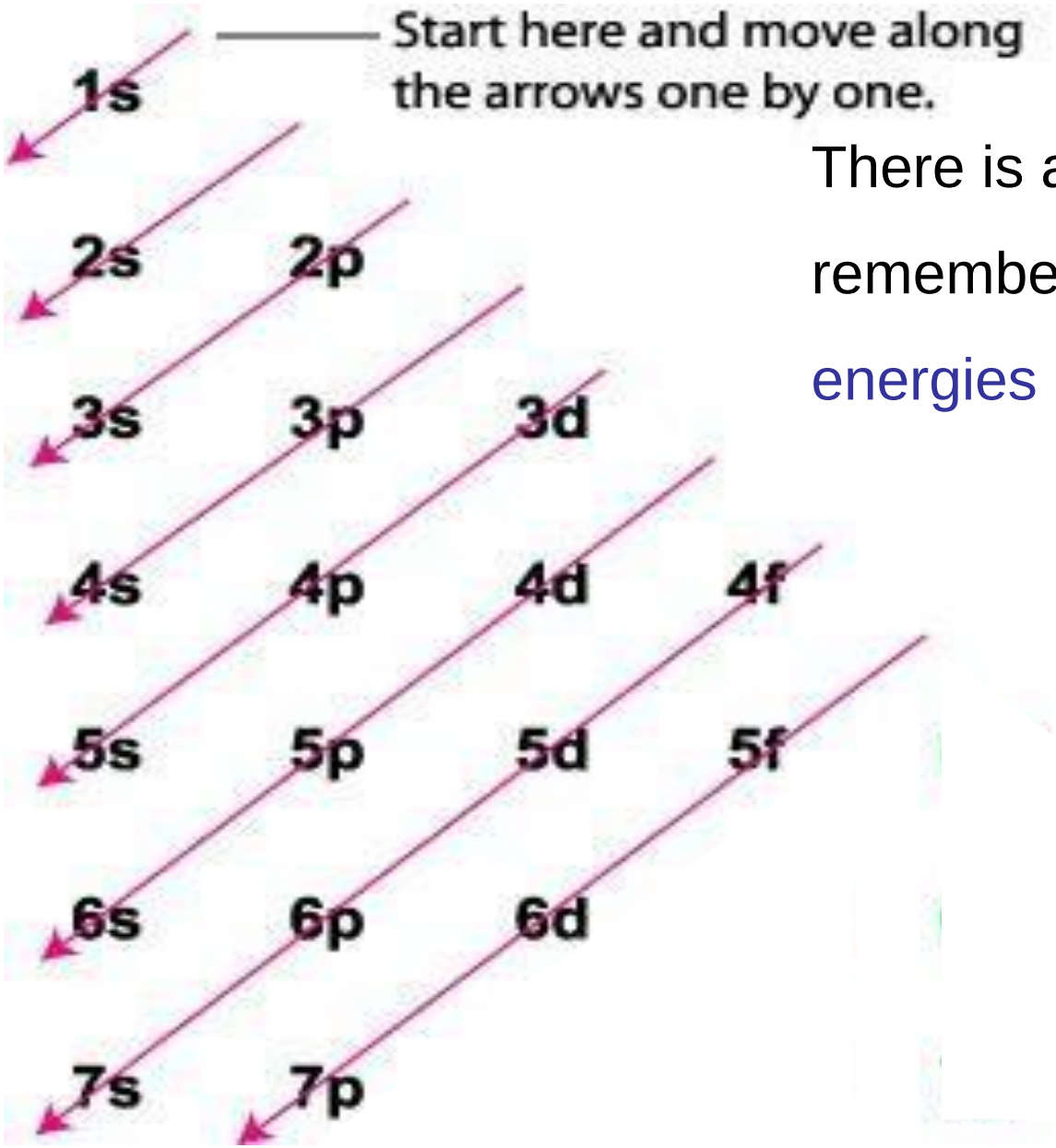
Electrons fill orbitals of different energies by filling the lowest energy first. The energies of orbitals of multielectron atoms follow the (n + ℓ) rule: the lowest value of (n + *l*) has the lowest energy.

Examples with (n + ℓ)

- **1s (1 + 0) < 2s (2 + 0) < 3s (3 + 0) < 3p (3+1) ,< 4s (4 + 0) < 3d (3 + 2) < 4p (4 + 1)**

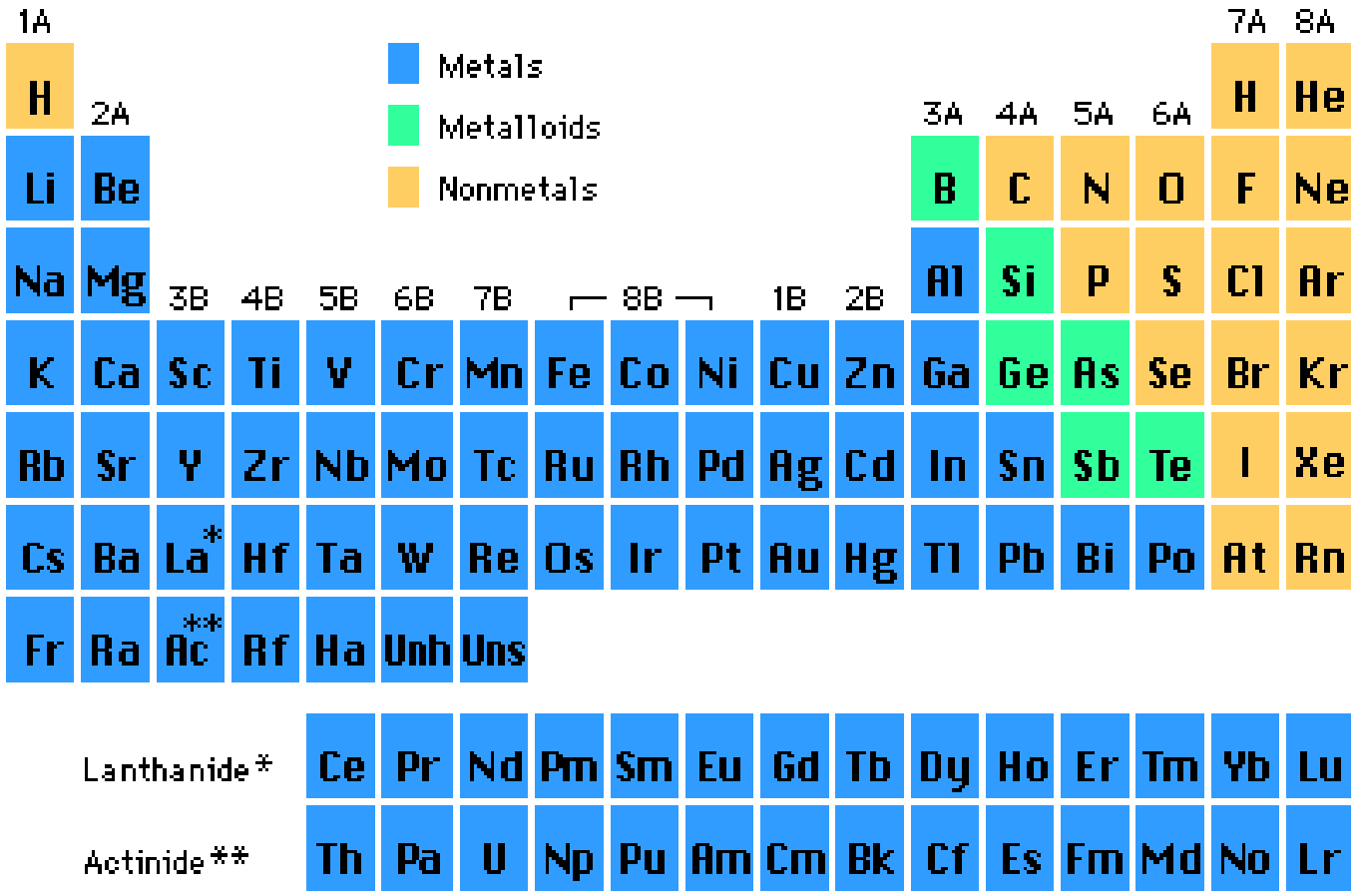
When n + ℓ is the same for two orbitals, the orbital with the higher value of n has the higher energy.

Diagonal Rule

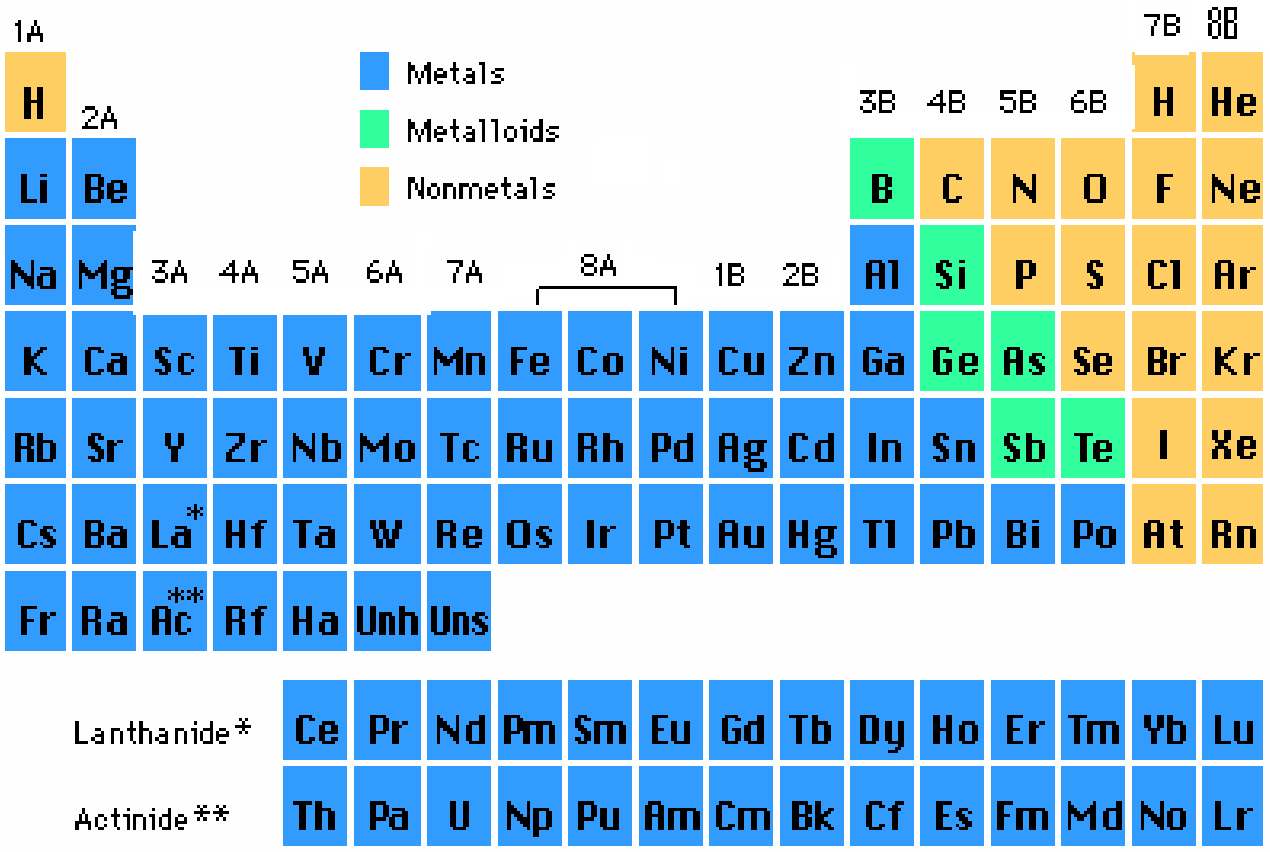


There is an easy way to remember the sequence of the energies of the subshells.

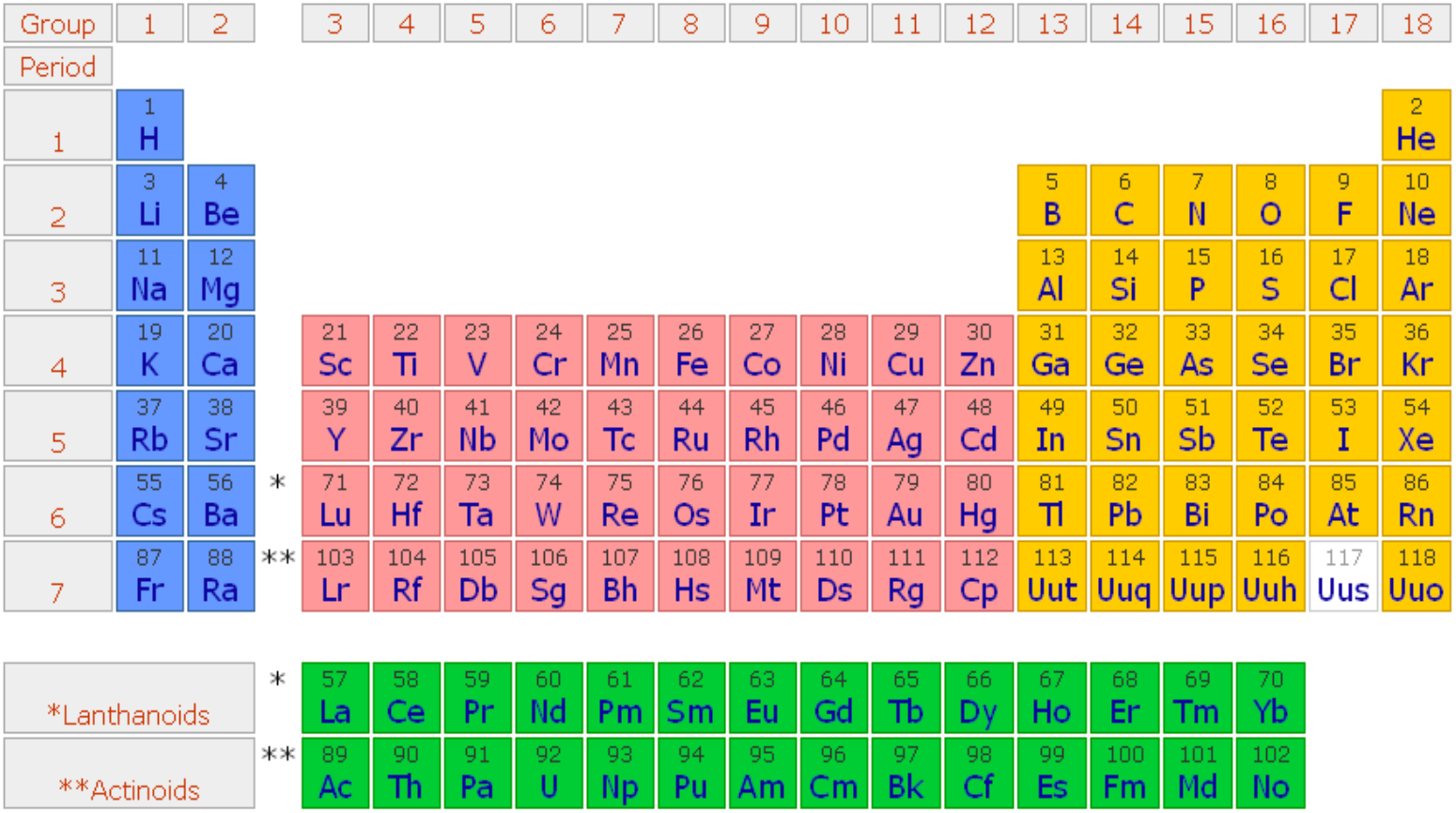
American Classification

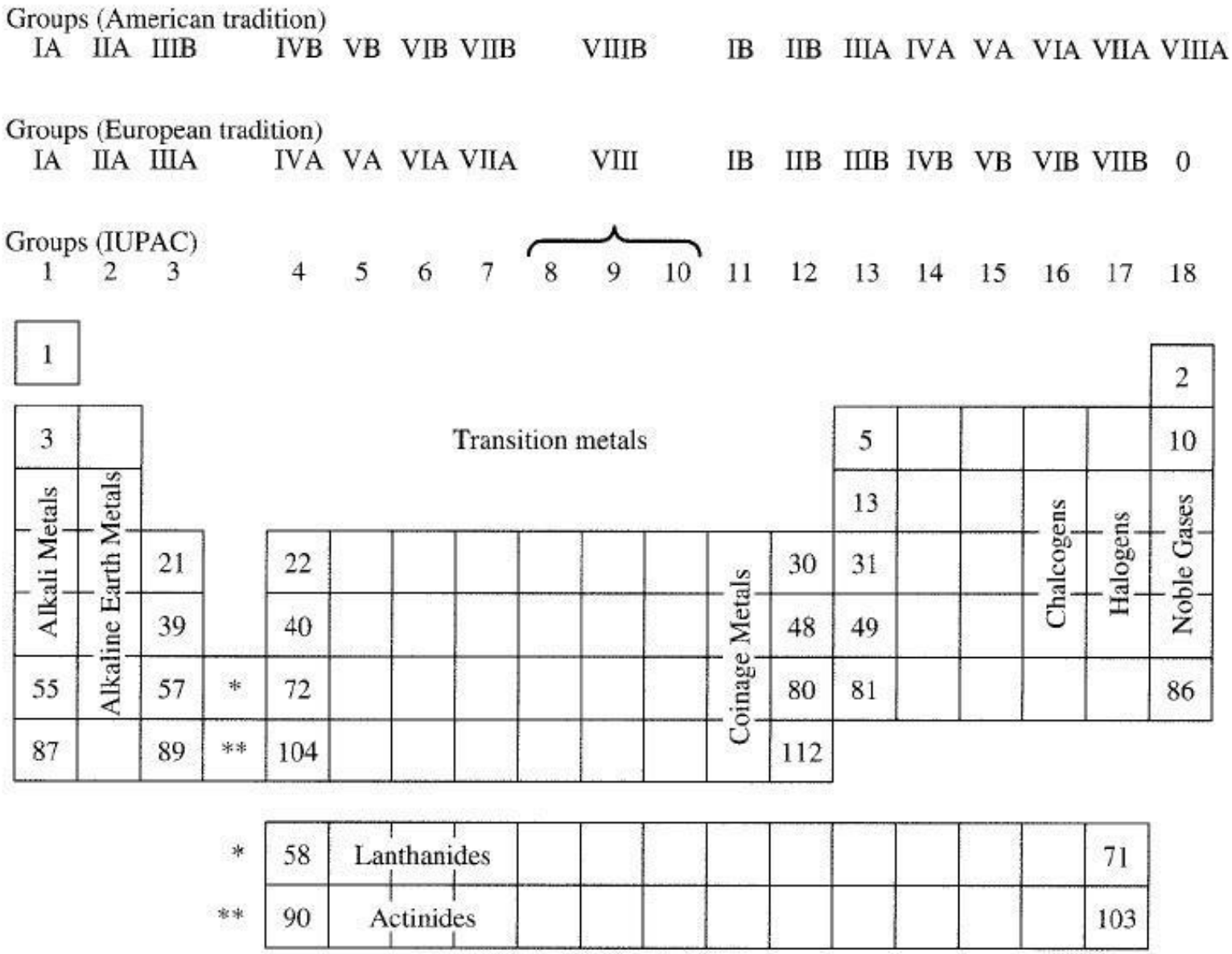


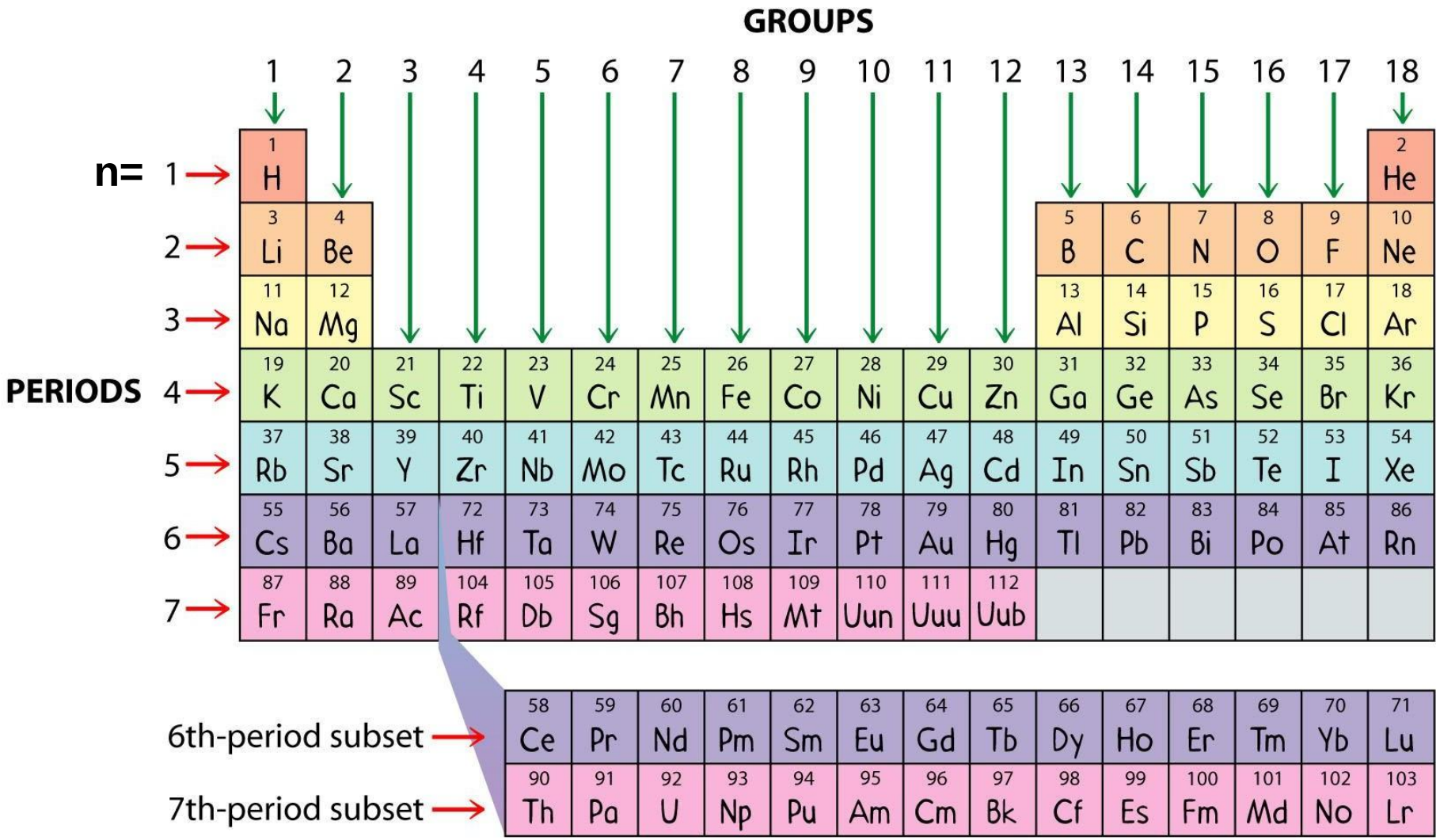
European Classification



IUPAC Classification




Groups (American tradition)
IA IIA IIIB IVB VB VIB VIIB VIIIB IB IIB IIIA IVA VA VIA VIIA VIIIA
Groups (European tradition)
IA IIA IIIA IVA VA VIA VIIA VIII IB IIB IIIB IVB VB VIB VIIB 0
Groups (IUPAC)
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
Transition metals
Alkali Metals
Alkaline Earth Metals
Coinage Metals
Chalcogens
Halogens
Noble Gases
Lanthanides
Actinides



Classification of periodic table according to groups(families)(1-18)(**IUPAC**):

1- Main or representative groups

a- s-Block (1,2) alkali metals(IA)	$_{3}Li$- $_{87}Fr$	ns^1	GI
alkali earth metals(IIA)	$_{4}Be$- $_{88}Ra$	ns^2	GII
b- p- Block(13) boron group or family	$_{5}B$- $_{81}Tl$	$ns^2\ np^1$	GIII
carbon group(14) or family	$_{6}C$- $_{82}Pb$	$ns^2\ np^2$	GIV
15 nitrogen group or family(pnictogens)	$_{7}\mathbf{N}$- $_{\mathbf{83}}\mathbf{Bi}$	$ns^2\ np^3$	GV
16 oxygen family(Chalcogens)	$_{8}O$- $_{84}Po$	$ns^2\ np^4$	GVI
17 Halogens	$_{9}F$- $_{85}At$	$ns^2\ np^5$	GVII
18 noble gases	$_{2}He$ – [$_{10}Ne$- $_{86}Rn$]	$ns^2\ np^6$	GVIII

2- Main Transition metals d-Bolck (3-12) 3d 1st transition series, 4d (2nd transition series, 5d (3rd transition series)…..

3- Inner transition metals(rare earth metals) –f-Block 4f(lanthanides) 5f(Actinides)

Classification according to periods(1-7)(n)

n=1 (2e) 2 elements H He $1s^{1-2}$
n=2 (8e) 8 elements Li Be B C N O F Ne [He]$2s^{1-2}$ $2p^{1-6}$
n=3 (8) elements Na Mg Al Si P S Cl Ar [Ne]$3s^{1-2}$ $3p^{1-6}$

n=4 (18) [Ar] $3d^{1-10}$ (n+l =5) $4s^{1-2}$ (n+l =4)$4p^{1-6}$ (n+l=5)
n=4 K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr

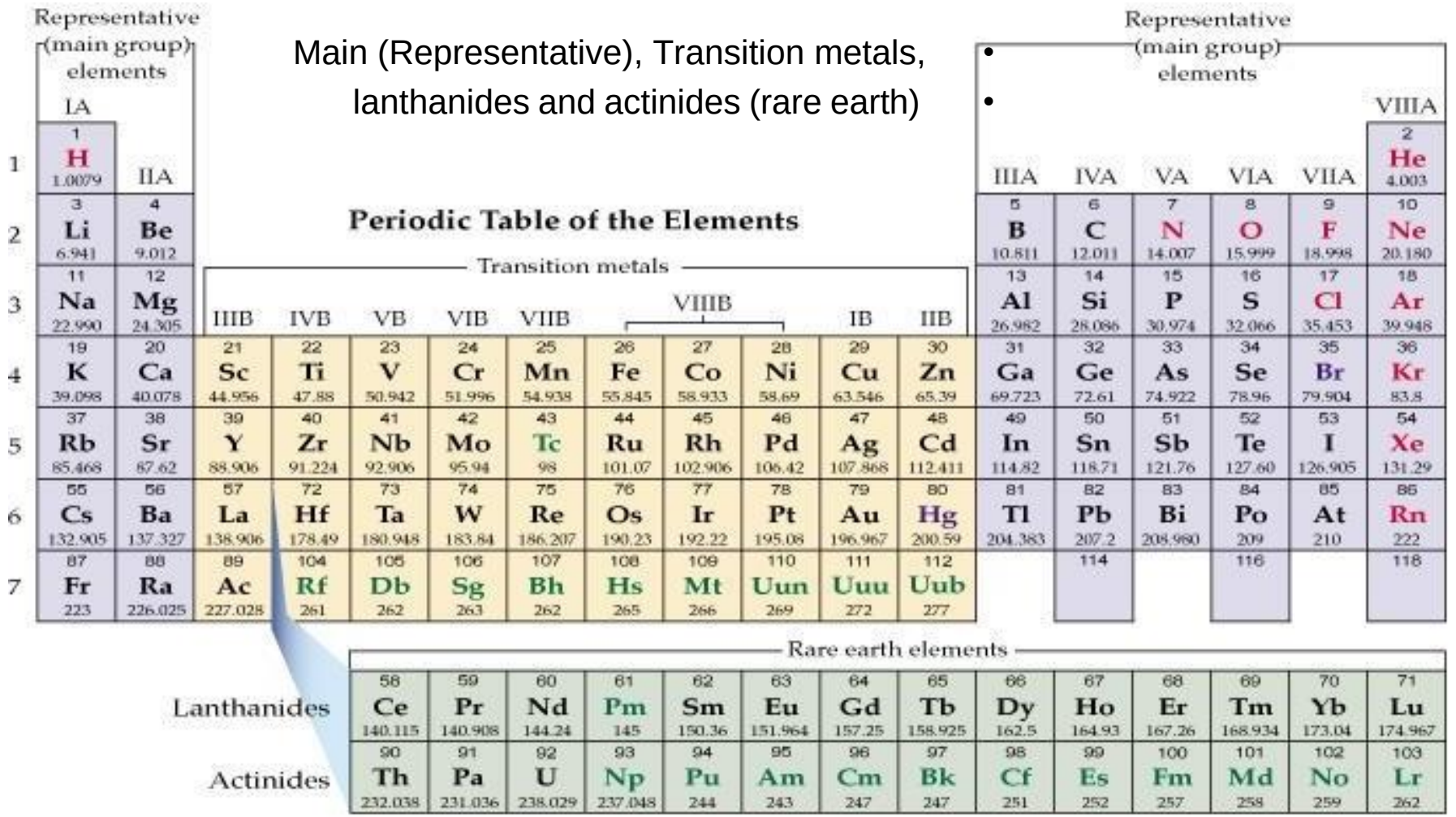
n=5 (18) [Kr] $4d^{1-10}$(n+l=6) $5s^{1-2}$(n+l=5) $5p^{1-6}$ (n+l=6)
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Pt Ag Cd In Sn Sb Te I Xe

n=6 (32) [Xe] $4f^{1-14}$ (n+l=7 lanthanoids) $5d^{1-10}$(n+l=7) $6s^{1-2}$(n+l=6) $6p^{1-6}$
$_{55}Cs$ $_{56}Ba$ $_{57}La$ (lanthanoids $_{58}Ce$- $_{71}Lu$) $_{72}Hf$ $_{73}Ta$ $_{74}W$ $_{75}Re$ $_{76}Os$ $_{77}Ir$ $_{78}Pt$
$_{79}Au$ $_{80}Hg$ $_{81}Tl$ $_{82}Pb$ $_{83}Bi$ $_{84}Po$ $_{85}At$ $_{86}Rn$

n=7 (32) [Rn] $5f^{1-14}$(n+l=8 actinoids) $6d^{1-10}$(n+l=8) $7s^{1-2}$(n+l=7) $6d^{1-10} \rightarrow 7p^{1-6}$
$_{87}Fr$ $_{88}Ra$ $_{89}Ac$(Actinoids $_{90}Th$ -$_{103}Lr$(w)) $\rightarrow 4^{th}$ transition series

Periodic Table: The three broad Classes Main, Transition, Rare Earth

Main (Representative), Transition metals, lanthanides and actinides (rare earth)



Valence Electrons

- Every element has both **core** electrons and **valence** electrons, e.g. Magnesium: Mg Z=12 $\rightarrow$ 12 electrons:

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

core electrons valence electrons

- Core electrons are electrons in **fully filled shells**
- Valence electrons are electrons in the outermost shell that is not fully filled with the exception of the **noble gases** that all have fully filled shells

He: $1s^2$,

Ne: {He} $2s^2\ 2p^6$,

Ar: {Ne} $3s^2\ 3p^6$,

Kr: {Ar} $4s^2\ 3d^{10}\ 4p^6$,

Xe: {Kr} $5s^2\ 4d^{10}\ 5p^6$.

Rn: {Xe} $6s^2\ 4f^{14}\ 5d^{10}\ 6p^6$.

core electrons

S- block elements
IA and IIA

Group 1 - elements with only one valence electron: These are called the Alkali-Metal Group

		Electronic configuration
^{3}Lithium	Li	{He}2s^{1}
^{11}Sodium	Na	{Ne}3s^{1}
^{19}Potassium	K	{Ar}4s^{1}
^{37}Rubidium	Rb	{Kr}5s^{1}
^{55}Cesium	Cs	{Xe}6s^{1}
^{87}Francium	Fr	{Rn}7s^{1}

Physical Properties
metals i.e good conductors, soft, low melting point and boiling point

S- block elements
IA and IIA

Group 2 - The Alkaline Earth Metals(IIA)

			electron configuration
beryllium	Be	Z= 4	[He] $2s^2$
magnesium	Mg	12	[Ne] $3s^2$
calcium	Ca	20	[Ar] $4s^2$
strontium	Sr	38	[Kr] $5s^2$
barium	Ba	56	[Xe] $6s^2$
radium	Ra	88	[Rn] $7s^2$

The last element, radium, is radioactive and will not be considered here.

Deviation from (n+ *l*) rule

In some main transition elements and inner transition elements some deviation from (n + l) rule is observed

The interaction between the two Cr and Cu in 1^{st} tr. Series electrons in 4S orbital is of high energy (paring energy) this effect places an extra electron to 3d level and remove from 4s causing

$_{24}Cr$ [Ar] $3d^5$ $4s^1$(half-filled orbitals)

$_{29}Cu$ [Ar] $3d^{10}$ $4s^1$(half-filled s-orbitals and full d-orbitals)

The difference in energy between an orbital of 2e and 1e can be explained as the pairing energy is higher than energy gap between ns & (n-1)d as the value of Z* increase the energy of shells decreases

Controlling factors on limitation of Aufbau principle

1-Stability with half filled & completely filled

2-The energies of neighboring subshells e.g. (4s, 3d), (5s, 4d), (4f, 5d), (5f, 6d) etc are quite close together (low energy gap)

3- Electron-electron repulsion (high pairing energy)

Main transition elements (d-block)

•Main transition elements (d-block) take their collective name from their role as a bridge between the chemically active metals of gr. IA & IIA and much less active metals of gr. 12(Zn family) , 13(Boron family) , 14(Carbon family) .

•As s-block elements are metallic in nature and p-block elements are non-metallic, hence d-block elements show a transition from metallic to non-metallic nature. In other words, they show a transition from most electropositive s-block elements to least electropositive or most electronegative p-block elements.

•The elements $_{30}Zn$, $_{48}Cd$, $_{80}Hg$ (gr. 12) have unique properties , while they resemble the alkaline earth metals IIA in giving oxidation state of (+2) , they differ from IIA of having higher Z* and more polarizing effect

1st transition element series : A part of (Period 4)

[Ar] $3d^{1-10}$ $4s^{1-2}$ This is also called as 3d series

Sc	**(Z = 21)**	**[Ar] $3d^1$ $4s^2$**
Ti	**(Z = 22)**	**[Ar] $3d^2$ $4s^2$**
V	**(Z = 23)**	**[Ar] $3d^3$ $4s^2$**
Cr	**(Z = 24**	*** [Ar] $3d^5$ $4s^1$**
Mn	**(Z = 25)**	**[Ar] $3d^5$ $4s^2$**
Fe	**(Z = 26)**	**[Ar] $3d^6$ $4s^2$**
Co	**(Z = 27)**	**[Ar] $3d^7$ $4s^2$**
Ni	**(Z = 28**	**[Ar] $3d^8$ $4s^2$**
Cu	**(Z = 29)**	***[Ar] $3d^{10}$ $4s^1$**
Zn	**(Z = 30)**	**[Ar] $3d^{10}$ $4s^2$ (non Tr.)**

* Deviate from($n+l$)

Second transition series: A part of (period 5) : [Kr] $4d^{1-10}\ 5s^{1-2}$

This is also called as 4d series

Element	Atomic Number	Symbol	Electronic configuration
Yttrium	39	Y	[Kr] $4d^1\ 5s^2$
Zirconium	40	Zr	[Kr] $4d^2\ 5s^2$
Niobium	41	Nb	*[Kr] $4d^4\ 5s^1$
Molybdenum	42	Mo	*[Kr] $4d^5\ 5s^1$
Technetium	43	Tc	?[Kr] $4d^5\ 5s^2$
Ruthenium	44	Ru	*[Kr] $4d^7\ 5s^1$
Rhodium	45	Rh	*[Kr] $4d^8\ 5s^1$
Palladium	46	Pd	*[Kr] $4d^{10}\ 5s^0$
Silver	47	Ag	*[Kr] $4d^{10}\ 5s^1$
Cadmium(non Tr.)	48	Cd	[Kr]$4d^{10}\ 5s^2$

* Deviate from$(n+l)$; ? May have [Kr] $4d^6\ 5s^1$

Third Transition Series

It is a part of period 6 : [Xe] $4f^{14}$ $5d^{1-10}$ $6s^{1-2}$ except La [Xe] $4f^{0}$ $5d^{1}$ $6s^{2}$? Lanthanum and Hafnium to Mercury This is also called as 5d series

Element	Atomic number	Symbol	Electronic configuration
Lanthanum	57	La	*[Xe] $4f^{0}$ $5d^{1}$ $6s^{2}$
Hafnium	72	Hf	[Xe] $4f^{14}$ $5d^{2}$ $6s^{2}$
Tantalum	73	Ta	[Xe] $4f^{14}$ $5d^{3}$ $6s^{2}$
Tungsten	74	W	[Xe] $4f^{14}$ $5d^{4}$ $6s^{2}$
Rhenium	75	Re	[Xe] $4f^{14}$ $5d^{5}$ $6s^{2}$
Osmium	76	Os	[Xe] $4f^{14}$ $5d^{6}$ $6s^{2}$
Iridium	77	Ir	[Xe] $4f^{14}$ $5d^{7}$ $6s^{2}$
Platinum	78	Pt	*[Xe] $4f^{14}$ $5d^{9}$ $6s^{1}$
Gold	79	Au	*[Xe] $4f^{14}$ $5d^{10}$ $6s^{1}$
Mercury(non Tr.)	80	Hg	[Xe] $4f^{14}$ $5d^{10}$ $6s^{2}$

* Deviate from($n+\ell$)

Inner transition elements

The elements in which the additional electrons enters (n-2)f orbitals are called **inner transition elements**. The valence shell electronic configuration of these elements can be represented as **$(n-2)f^{0-14}\ (n-1)d^{0-1}\ ns^{2}$.**

4f inner transition metals are known as lanthanides because they come immediately after lanthanum and 5f inner transition metals are known as actinoids because they come immediately after actinium.

Electronic Configuration of Lanthanoids (part of period 6)

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

- Or [Xe]$4f^2\ 6s^2$ *deviates from $(n+\ell)$

The Actinoids

Result from the filling of the 5f orbitals.

All isotopes are radioactive, with only ^{232}Th, ^{235}U, ^{238}U and ^{244}Pu having long half-lives.

Only Th and U occur naturally-both are more abundant in the earth's crust than tin.

The others must be made by nuclear processes.

Electronic configuration of Actinoids (part of period 7

Element name	Symbol	Z	M
Actinium	Ac	89	*[Rn] $6d^1 7s^2$
Thorium	Th	90	*[Rn]5f $6d^2$ $7s^2$
Protactinium	Pa	91	*[Rn]$5f^2 6d^1 7s^2$
Uranium	U	92	*[Rn]$5f^3 6d^1 7s^2$
Neptunium	Np	93	*[Rn]$5f^4 6d^1 7s^2$
Plutonium	Pu	94	[Rn]$5f^6 7s^2$
Americium	Am	95	[Rn]$5f^7 7s^2$
Curium	Cm	96	*[Rn]$5f^7 6d^1 7s^2$
Berkelium	Bk	97	[Rn]$5f^9 7s^2$
Californium	Cf	98	*[Rn]$5f^{10} 7s^2$
Einsteinium	Es	99	[Rn]$5f^{11} 7s^2$
Fermium	Fm	100	[Rn]$5f^{12} 7s^2$
Mendelevium	Md	101	[Rn]$5f^{13} 7s^2$
Nobelium	No	102	[Rn]$5f^{14} 7s^2$
Lawrencium	Lr	103	[Rn]$5f^{14} 6d^1 7s^2$

Or *[Rn]$5f^9 6d^1 7s^2$, *deviates from (n+l)

Electric property of elements

Metallic character increase in going down a column and decrease from left to right , they have low IP

Non metal character increase in a column by going upward and increase in a period from left to right , they have high IP

Metalloids : they have both metallic and non metallic properties and they are semiconductive . We recognize 8 elements:

B , Si , Ge , As , Sb , Te , Po , At lined by a heavy zigzag line

Noble gas do not behave like metals or non metals

H cannot be classified as any

Reading the Periodic Table: Classification

- **Nonmetals, Metals, Metalloids, Noble gases**