M. Sc. I Semester II

Paper I : Inorganic Chemistry

Chemistry of Non transition elements

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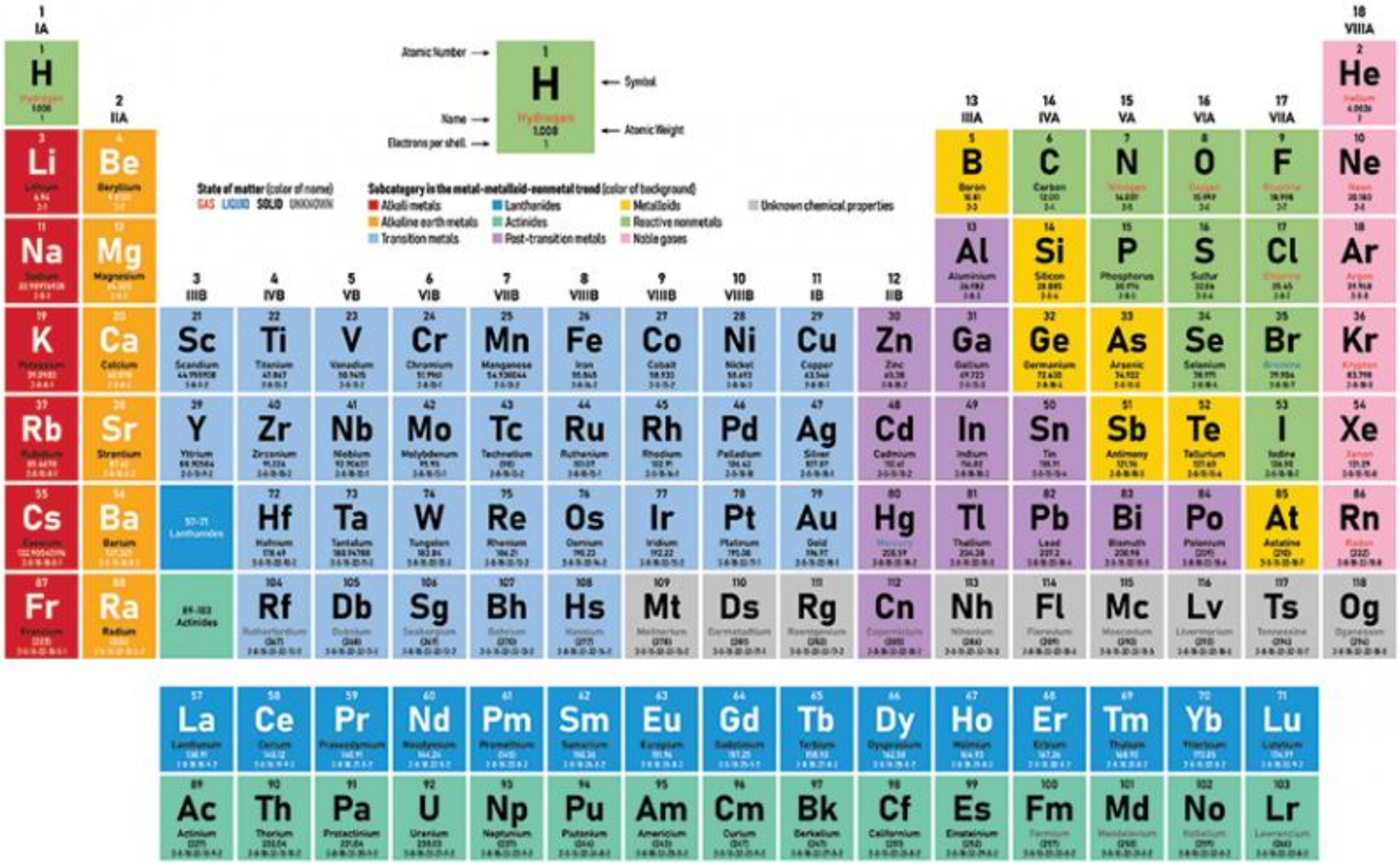
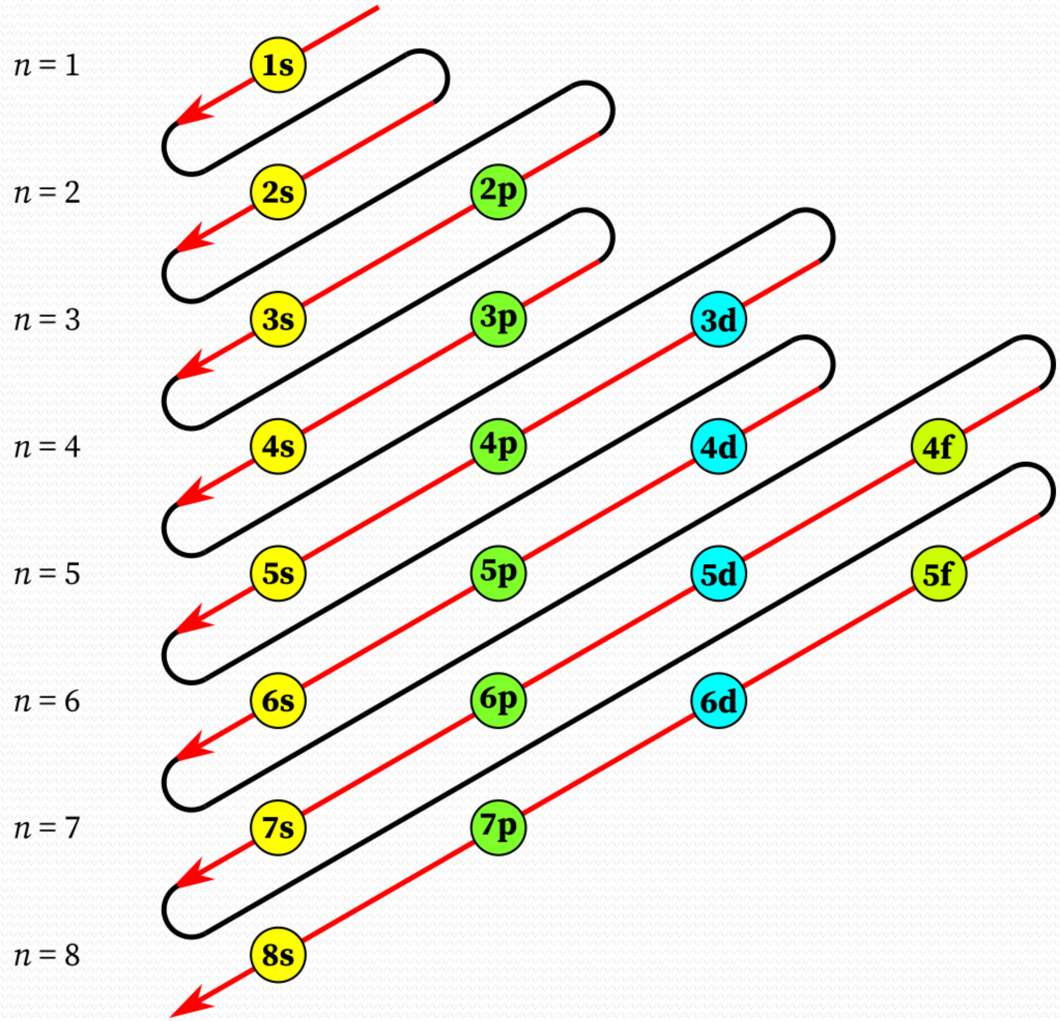
Periodic Table of the Elements



Periodic table

- Aufbau Principle



Periodic table

- Aufbau Principle

1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < 6d < 7p < 8s

Periodic table

- Aufbau Principle

1s <

2s < 2p <

3s < 3p <

4s < 3d < 4p <

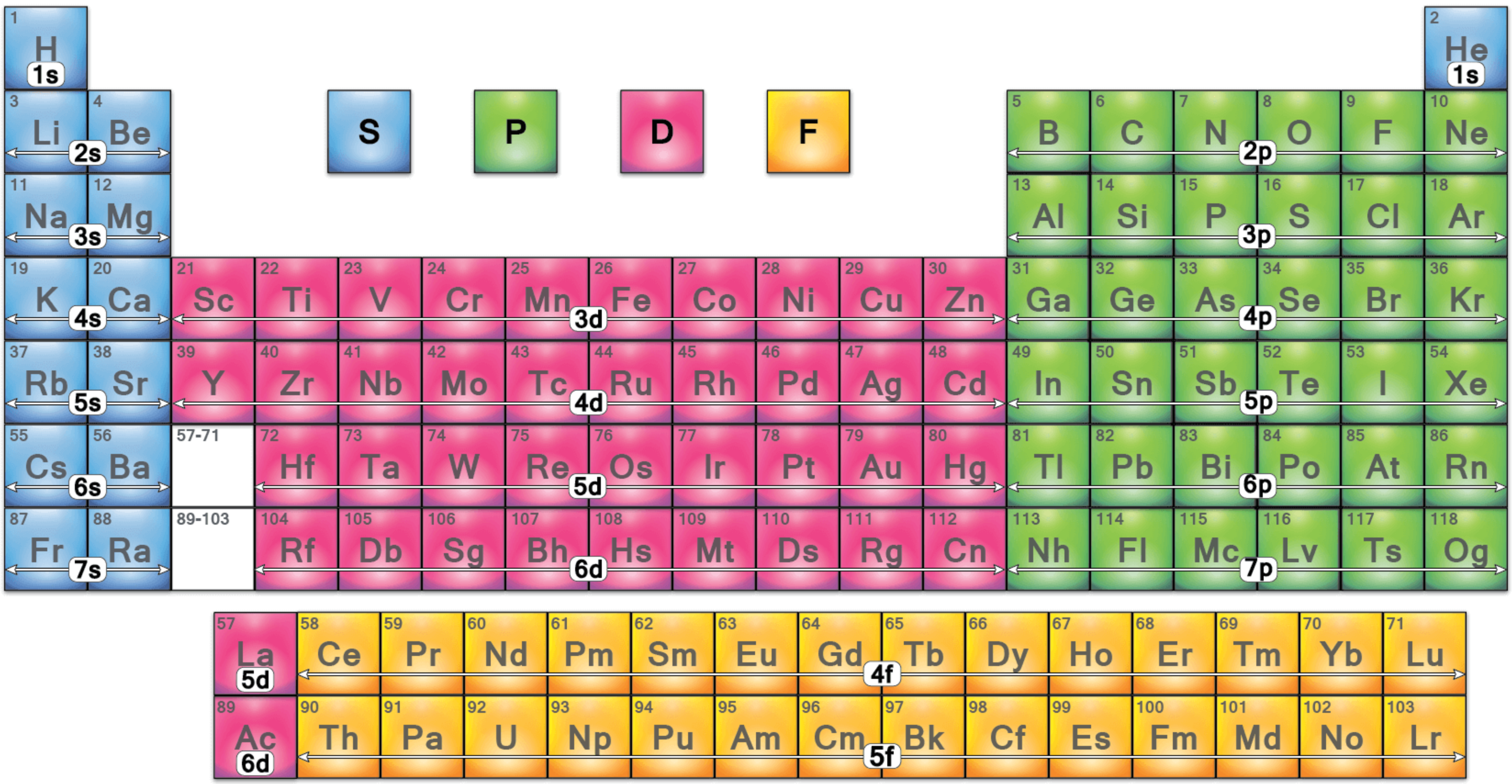
5s < 4d < 5p <

6s < 4f < 5d < 6p <

7s < 5f < 6d < 7p <

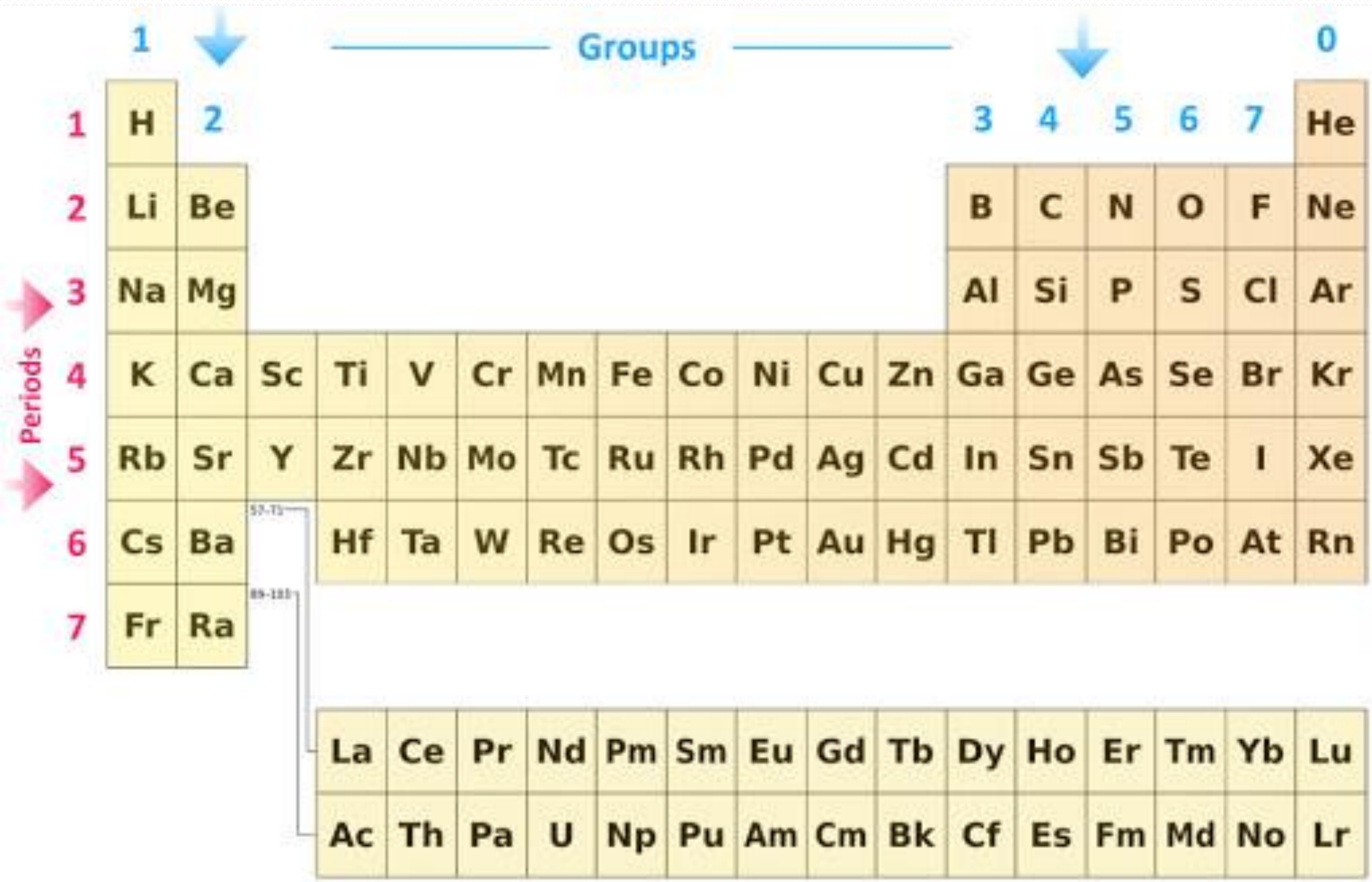
8s

Periodic table



Periodic table

- Atomic Numbers



Periodic table

- Electronic Configuration

$1s^1$																	$1s^2$
$2s^1$	$2s^2$											$2p^1$	$2p^2$	$2p^3$	$2p^4$	$2p^5$	$2p^6$
$3s^1$	$3s^2$											$3p^1$	$3p^2$	$3p^3$	$3p^4$	$3p^5$	$3p^6$
$4s^1$	$4s^2$	$3d^1$	$3d^2$	$3d^3$	$3d^5$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$3d^{10}$	$3d^{10}$	$4p^1$	$4p^2$	$4p^3$	$4p^4$	$4p^5$	$4p^6$
$5s^1$	$5s^2$	$4d^1$	$4d^2$	$4d^4$	$4d^5$	$4d^5$	$4d^7$	$4d^8$	$4d^{10}$	$4d^{10}$	$4d^{10}$	$5p^1$	$5p^2$	$5p^3$	$5p^4$	$5p^5$	$5p^6$
$6s^1$	$6s^2$		$5d^2$	$5d^3$	$5d^4$	$5d^5$	$5d^6$	$5d^7$	$5d^9$	$5d^{10}$	$5d^{10}$	$6p^1$	$6p^2$	$6p^3$	$6p^4$	$6p^5$	$6p^6$
$7s^1$	$7s^2$		$6d^2$	$6d^3$	$6d^4$	$6d^5$	$6d^6$	$6d^7$	$6d^8$	$6d^{10}$	$6d^{10}$	$7p^1$	$7p^2$	$7p^3$	$7p^4$	$7p^5$	$7p^6$

$5d^1$	$4f^1$	$4f^3$	$4f^4$	$4f^5$	$4f^6$	$4f^7$	$4f^7$	$4f^9$	$4f^{10}$	$4f^{11}$	$4f^{12}$	$4f^{13}$	$4f^{14}$	$4f^{14}$
$6d^1$	$6d^2$	$5f^2$	$5f^3$	$5f^4$	$5f^6$	$5f^7$	$5f^7$	$5f^9$	$5f^{10}$	$5f^{11}$	$5f^{12}$	$5f^{13}$	$5f^{14}$	$5f^{14}$

Periodic table

- Oxidation States

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
1 H +1 −1																	2 He
3 Li +1	4 Be +2											5 B +3	6 C +4 +2 −4	7 N +5 +4 +3 +2 +1 −3	8 O +2 −½ −1 −2	9 F −1	10 Ne
11 Na +1	12 Mg +2											13 Al +3	14 Si +4 −4	15 P +5 +3 −3	16 S +6 +4 +2 −2	17 Cl +7 +6 +5 +4 +3 +1 −1	18 Ar
19 K +1	20 Ca +2	21 Sc +3	22 Ti +4 +3 +2	23 V +5 +4 +3 +2	24 Cr +6 +5 +4 +3 +2	25 Mn +7 +6 +4 +3 +2	26 Fe +3 +2	27 Co +3 +2	28 Ni +2	29 Cu +2 +1	30 Zn +2	31 Ga +3	32 Ge +4 −4	33 As +5 +3 −3	34 Se +6 +4 −2	35 Br +5 +3 +1 −1	36 Kr +4 +2
37 Rb +1	38 Sr +2	39 Y +3	40 Zr +4	41 Nb +5 +4	42 Mo +6 +4 +3	43 Tc +7 +6 +4	44 Ru +8 +6 +4 +3	45 Rh +4 +3 +2	46 Pd +4 +2	47 Ag +1	48 Cd +2	49 In +3	50 Sn +4 +2	51 Sb +5 +3 −3	52 Te +6 +4 −2	53 I +7 +5 +1 −1	54 Xe +6 +4 +2
55 Cs +1	56 Ba +2	57 La +3	72 Hf +4	73 Ta +5	74 W +6 +4	75 Re +7 +6 +4	76 Os +8 +4	77 Ir +4 +3	78 Pt +4 +2	79 Au +3 +1	80 Hg +2 +1	81 Tl +3 +1	82 Pb +4 +2	83 Bi +5 +3	84 Po +2	85 At −1	86 Rn

Periodic table

- Periodic Trends
  - Atomic Size
  - Ionization Energy
  - Electronegativity
  - Metallic and nonmetallic character
  - Acidic and basic nature of oxides and hydroxides

Periodic Trends in Atomic Size

- As you go down a column of the periodic table, **the atomic radii increase**.

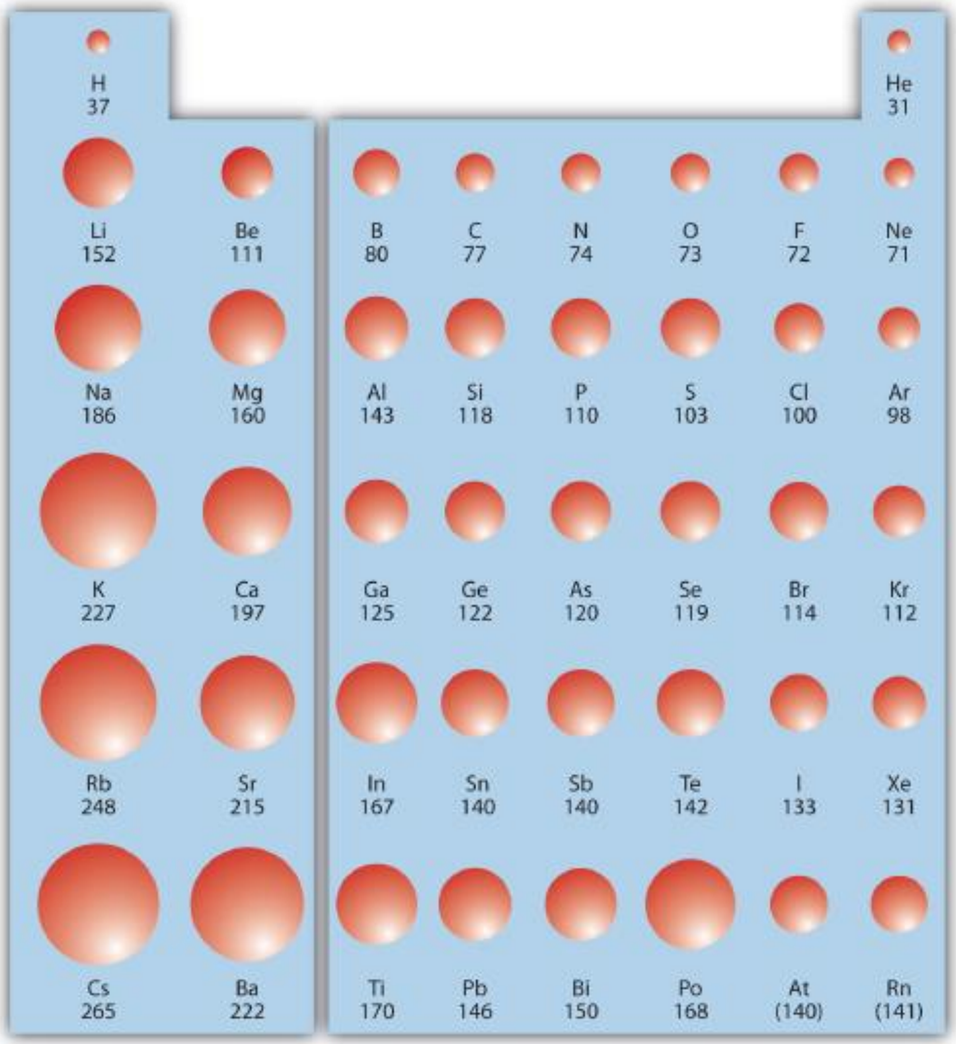
  This is because the valence electron shell is getting larger, so the valence shell lies farther away from the nucleus.

- Going across a row on the periodic table, left to right, **the atomic radii decrease.**

  Even though the valence shell maintains the same, the number of protons and hence the nuclear charge is increasing as you go across the row.

  The increasing positive charge holds the valence electrons strongly, so as you go across the periodic table, the atomic radii decrease.

Periodic Trends in Atomic Size



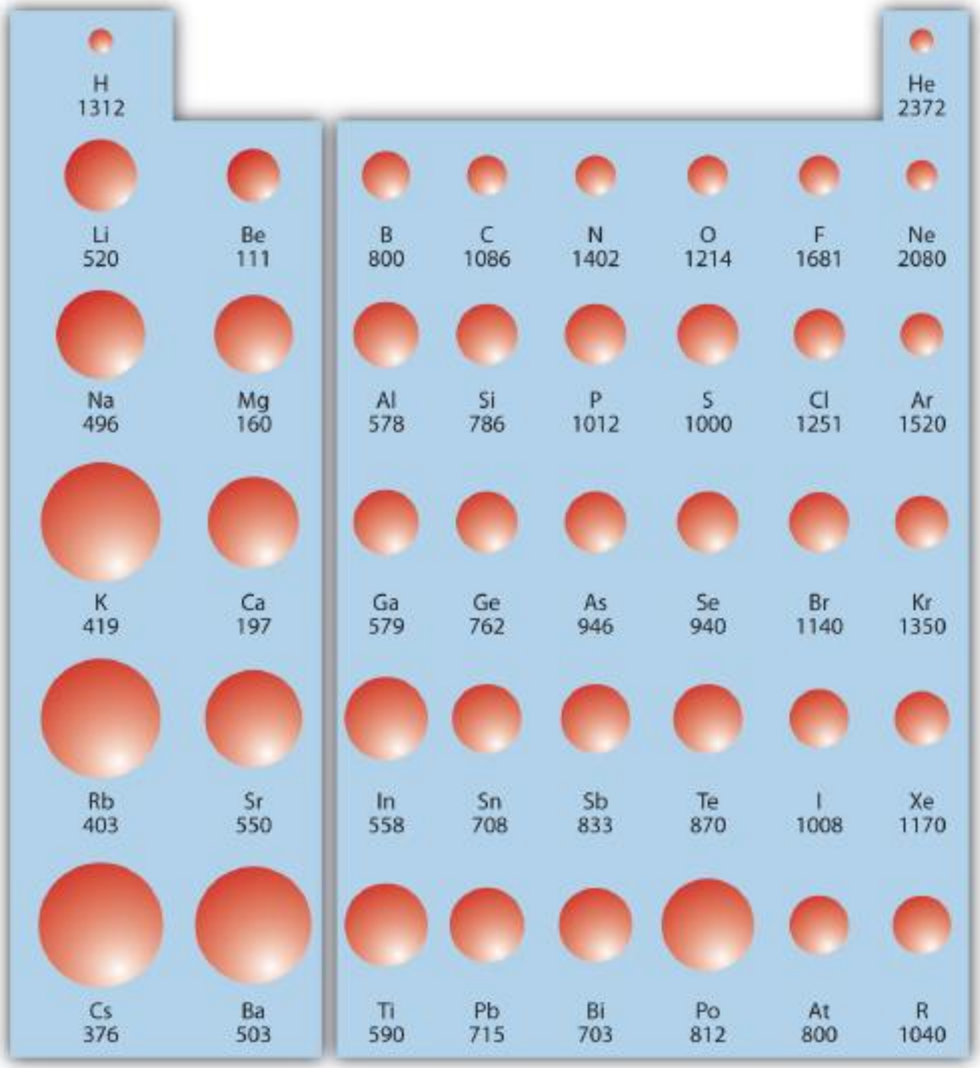
Periodic Trends in Ionization Energy

- It is the amount of energy required to remove an e from a neutral atom in its gaseous state.
- As you go down the periodic table, **IE decreases**.

  It becomes easier to remove an electron from an atom because the valence electron is farther away from the nucleus.
- As you go across the periodic table, **IE increases**.

  The electrons get drawn closer in, it takes more energy to remove an electron.

Periodic Trends in Ionization Energy



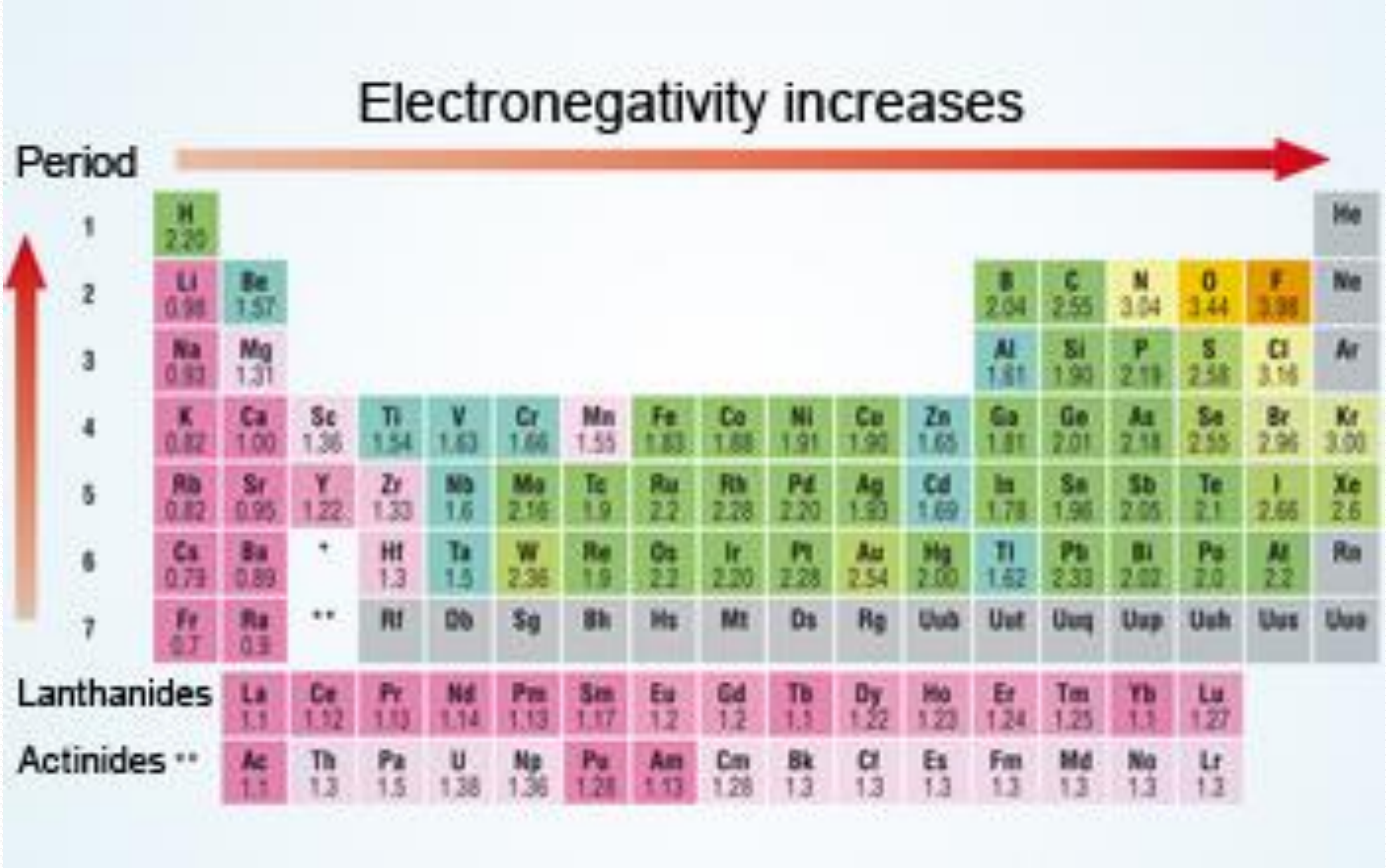
Periodic Trends in Electronegativity

- It is the tendency of an atom in its gaseous state to accept the electron.
- As you go down the periodic table, **Electronegativity decreases**.

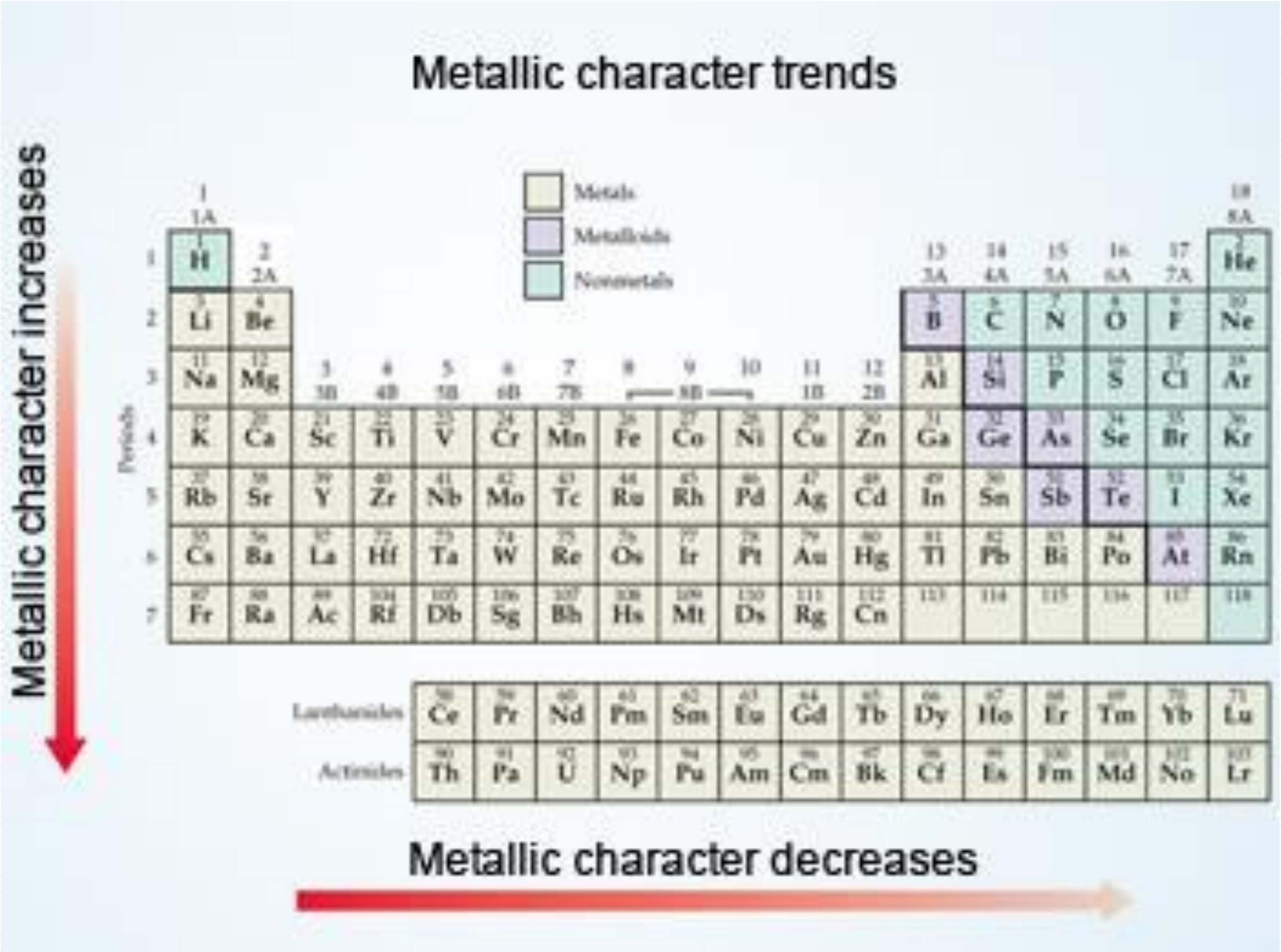
  As the valence shell is farther away from the nucleus.
- As you go across the periodic table, **Electronegativity increases**.

  As the valence shell is closer to the nucleus, nucleus attracts the electron.

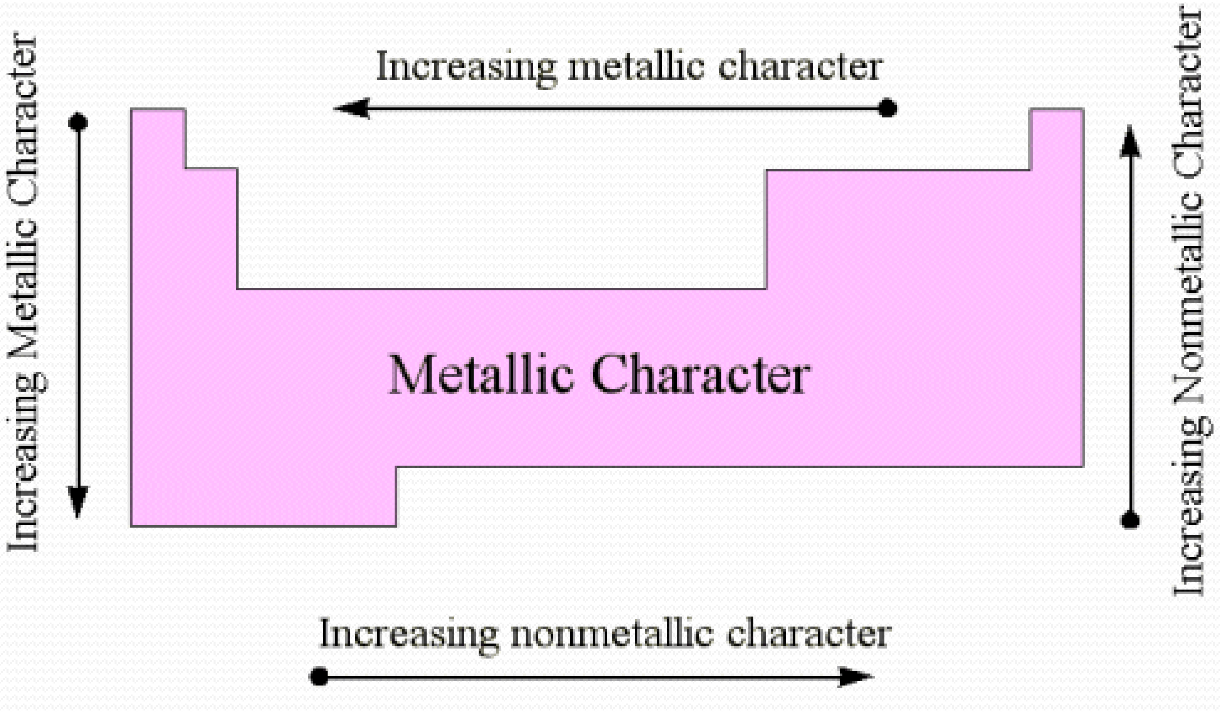
Periodic Trends in Electronegativity



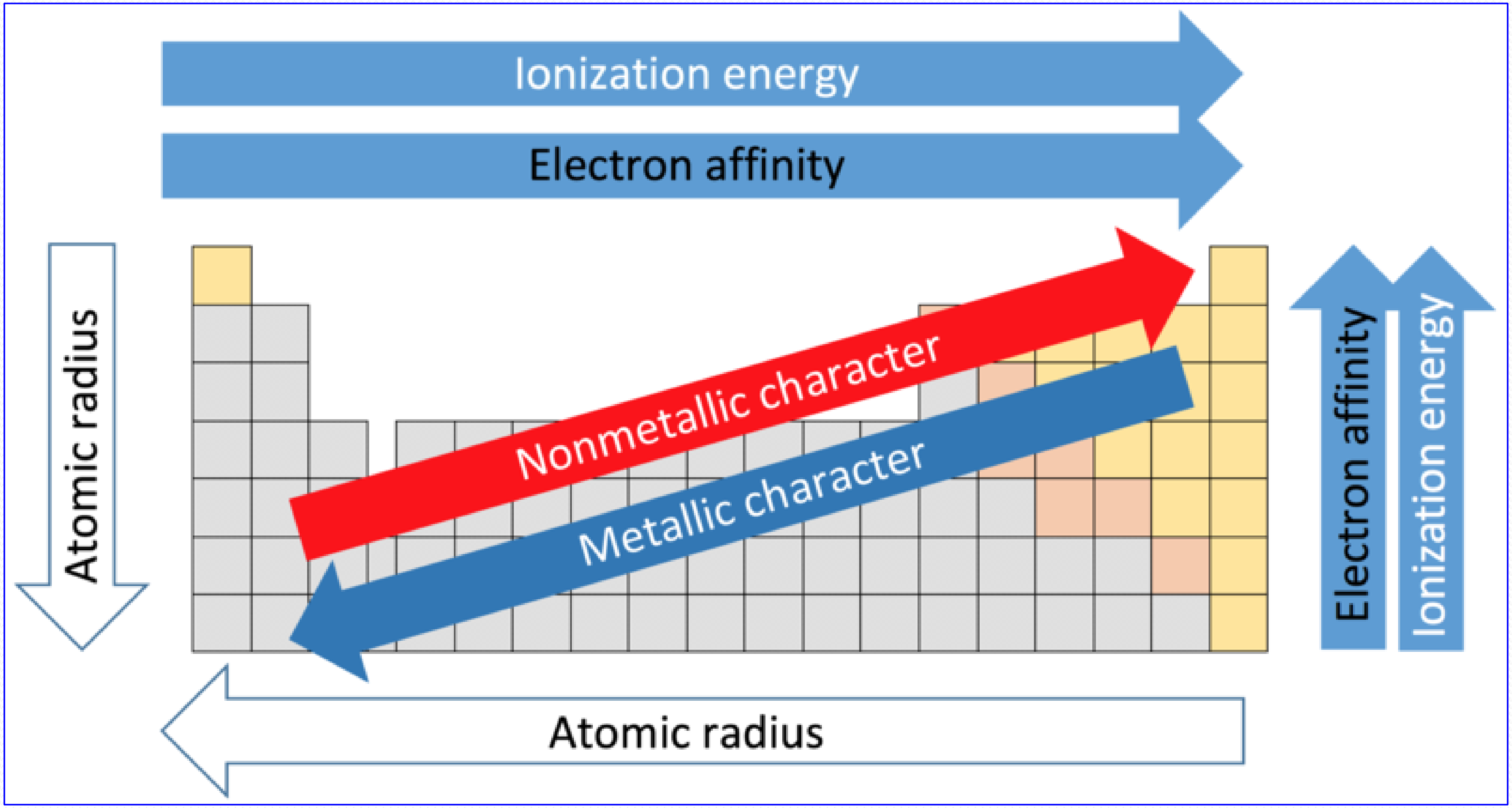
Periodic Trends in Metallic Character



Periodic Trends in Metallic Character



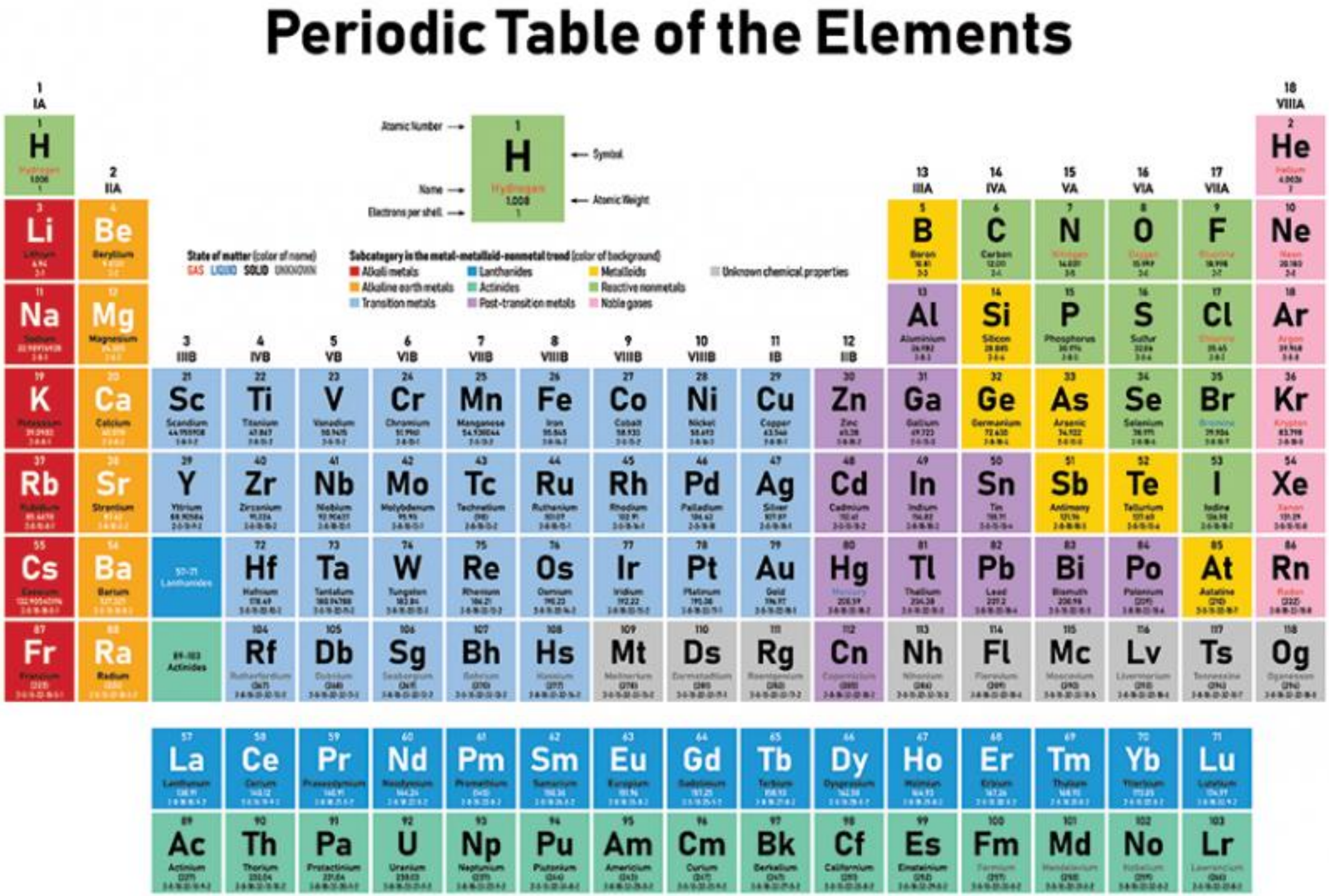
Periodic Trends in Periodic Properties



Chemistry of non–transition elements and their compounds

- General discussion on the properties of the non–transition elements,
- Polymorphism in carbon, phosphorous and sulphur,
- Synthesis, properties and structure of boranes, carboranes, silicates, carbides, phosphazenes, sulphur–nitrogen compounds,
- peroxo compounds of boron, carbon, sulphur,
- structure and bonding in oxyacids of nitrogen, phosphorous, sulphur and halogens
- interhalogens,
- pseudohalides

Non transition Elements

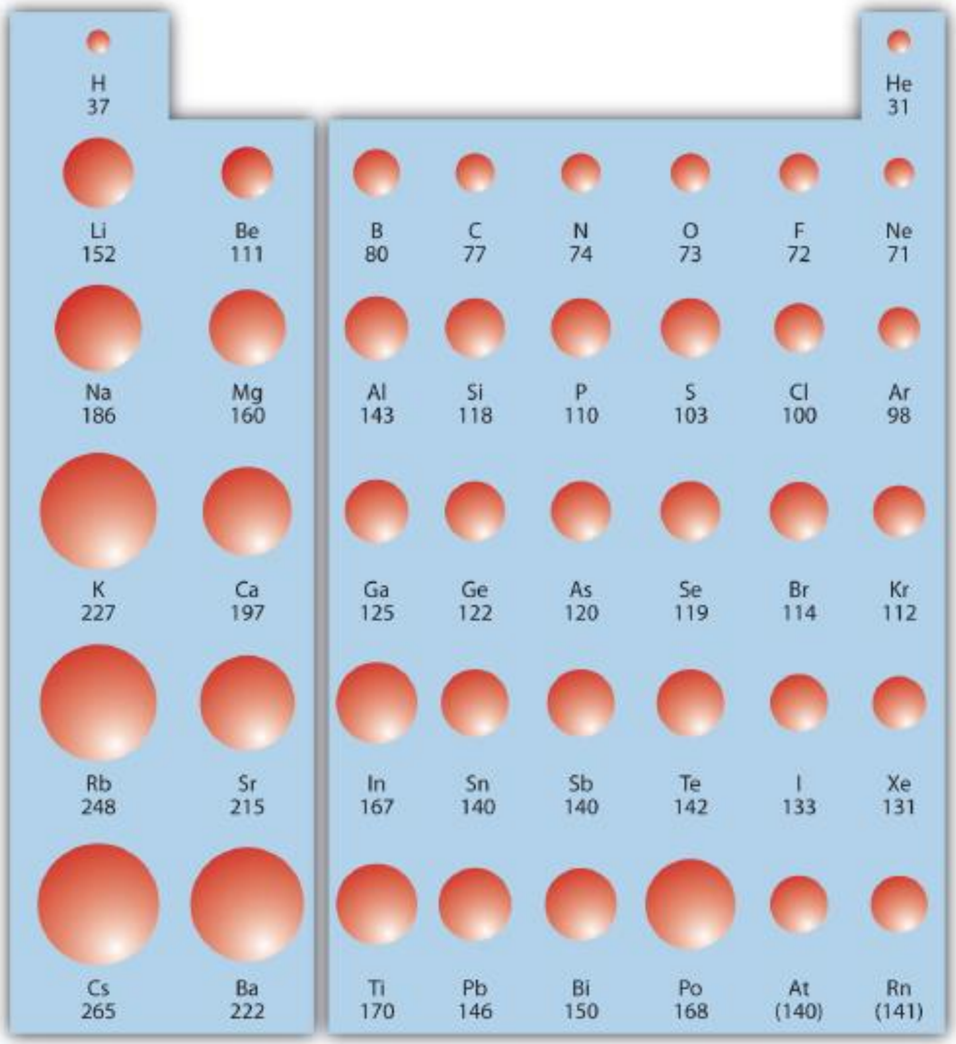


Electronic Configuration

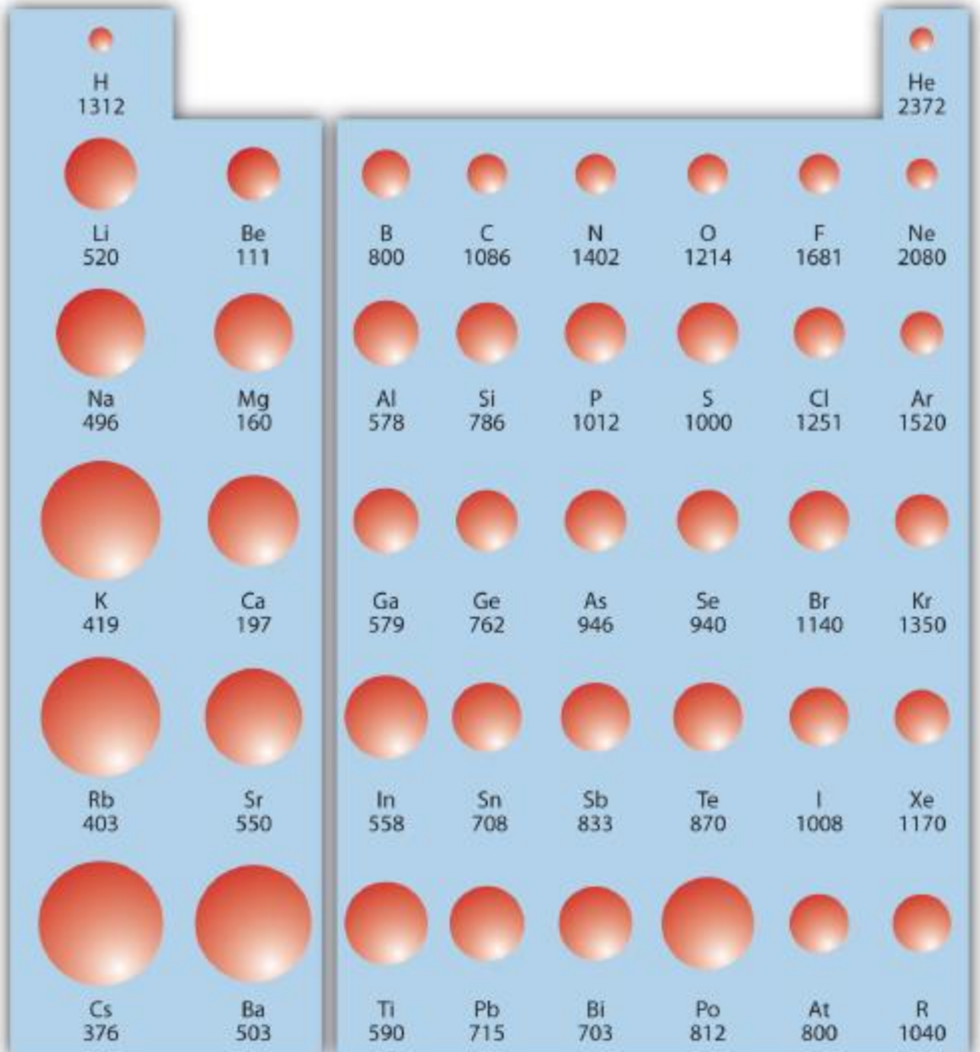
$1s^1$																	$1s^2$
$2s^1$	$2s^2$											$2p^1$	$2p^2$	$2p^3$	$2p^4$	$2p^5$	$2p^6$
$3s^1$	$3s^2$											$3p^1$	$3p^2$	$3p^3$	$3p^4$	$3p^5$	$3p^6$
$4s^1$	$4s^2$	$3d^1$	$3d^2$	$3d^3$	$3d^5$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$3d^{10}$	$3d^{10}$	$4p^1$	$4p^2$	$4p^3$	$4p^4$	$4p^5$	$4p^6$
$5s^1$	$5s^2$	$4d^1$	$4d^2$	$4d^4$	$4d^5$	$4d^5$	$4d^7$	$4d^8$	$4d^{10}$	$4d^{10}$	$4d^{10}$	$5p^1$	$5p^2$	$5p^3$	$5p^4$	$5p^5$	$5p^6$
$6s^1$	$6s^2$		$5d^2$	$5d^3$	$5d^4$	$5d^5$	$5d^6$	$5d^7$	$5d^9$	$5d^{10}$	$5d^{10}$	$6p^1$	$6p^2$	$6p^3$	$6p^4$	$6p^5$	$6p^6$
$7s^1$	$7s^2$		$6d^2$	$6d^3$	$6d^4$	$6d^5$	$6d^6$	$6d^7$	$6d^8$	$6d^{10}$	$6d^{10}$	$7p^1$	$7p^2$	$7p^3$	$7p^4$	$7p^5$	$7p^6$

$5d^1$	$4f^1$	$4f^3$	$4f^4$	$4f^5$	$4f^6$	$4f^7$	$4f^7$	$4f^9$	$4f^{10}$	$4f^{11}$	$4f^{12}$	$4f^{13}$	$4f^{14}$	$4f^{14}$
$6d^1$	$6d^2$	$5f^2$	$5f^3$	$5f^4$	$5f^6$	$5f^7$	$5f^7$	$5f^9$	$5f^{10}$	$5f^{11}$	$5f^{12}$	$5f^{13}$	$5f^{14}$	$5f^{14}$

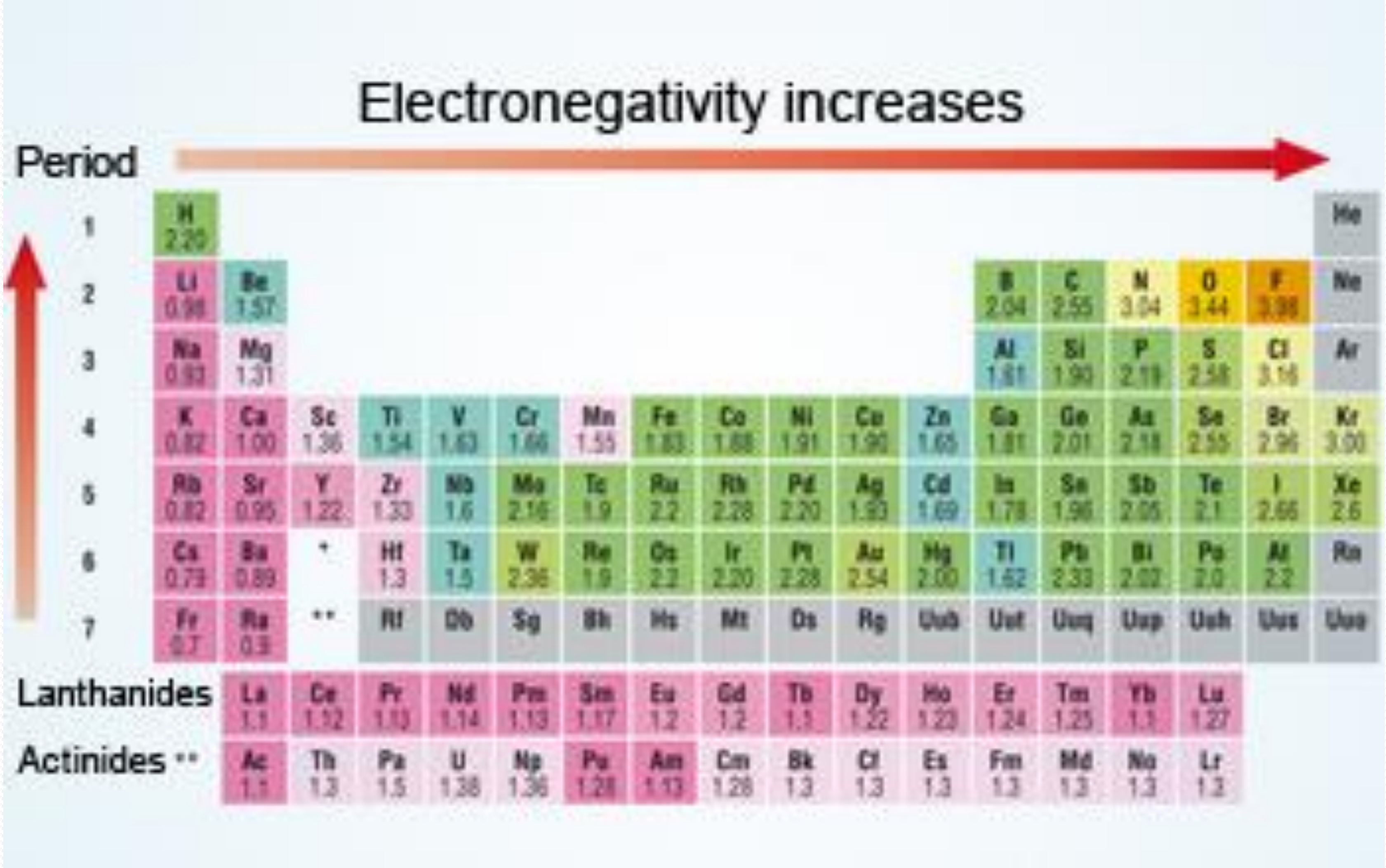
Atomic Radius



Ionization Energy



Electronegativity



Oxidation State

1	H +1, -1							He
2	Li +1	Be +2	B +3	C +4 +2 -4	N +5 +4 +3 +2 +1 -3	O +2 -1 -2	F -1	Ne
3	Na +1	Mg +2	Al +3	Si +4 -4	P +5 +3 -3	S +6 +4 +2 -2	Cl +7 +6 +5 +4 +3 +1 -1	Ar
4	K +1	Ca +2	Ga +3	Ge +4 -4	As +5 +3 -3	Se +6 +4 -2	Br +5 +3 +1 -1	Kr +4 +2
5	Rb +1	Sr +2	In +3 +1	Sn +4 +2	Sb +5 +3 -3	Te +6 +4 -2	I +7 +5 +1 -1	Xe +6 +4 +2
6	Ba +1	Ba +2	Tl +3 +1	Pb +4 +2	Bi +5 +3	Po +2	At -1	Rn

Group 1 / IA

Property	Li	Na	K	Rb	Cs
Atomic Number	3	11	19	37	55
Electronic Configuration	$[He]2s^1$	$[Ne]3s^1$	$[Ar]4s^1$	$[Kr]5s^1$	$[Xe]6s^1$
Covalent radius (pm)	123	156	203	216	235
Ionic radius (M^+) (pm)	60	95	133	148	169
Ionization Energy ($KJmol^{-1}$)	520	496	419	403	376
Electron Affinity ($KJmol^{-1}$)	60	53	48	47	46
Electronegativity	0.912	0.869	0.734	0.706	0.659
Melting Point (^0C)	180.5	97.8	63.2	39.0	28.5
Boiling Point (^0C)	1347	881	766	688	705

Group 2 / IIA

Property	Be	Mg	Ca	Sr	Ba	Ra
Electronic Configuration	$[He]2s^2$	$[Ne]3s^2$	$[Ar]4s^2$	$[Kr]5s^2$	$[Xe]6s^2$	$[Rn]7s^2$
Ionic radius (pm)	31	65	99	113	135	-
Covalent radius (pm)	89	136	174	191	198	-
Ionization Energy ($KJmol^{-1}$) (I)	900	738	590	549	502	509
Electron Affinity ($KJmol^{-1}$)	-50	-40	-30	-30	-30	-30
Melting Point (^0C)	1287	649	839	768	727	700*
Boiling Point (^0C)	2500	1105	1494	1381	1850*	1700*
Electronegativity	1.576	1.293	1.034	0.963	0.881	0.9

Group 13 / IIIA

Property	B	Al	Ga	In	Tl
Electronic Configuration	$[He]2s^2 2p^1$	$[Ne]3s^2 3p^1$	$[Ar]3d^{10} 4s^2 4p^1$	$[Kr]4d^{10} 5s^2 5p^1$	$[Xe]4f^{14} 5d^{10} 6s^2 6p^1$
Atomic radius (pm)	85	143	135	167	170
Ionization Energy (I) ($KJmol^{-1}$)	801	578	579	558	589
Electronegativity	2.05	1.61	1.75	1.65	1.79
Melting Point (^0C)	2180	660	29.8	157	304
Boiling Point (^0C)	3650	2467	2403	2080	1457

Group 14 / IVA

Property	C	Si	Ge	Sn	Pb
Electronic Configuration	$[He]2s^2 2p^2$	$[Ne]3s^2 3p^2$	$[Ar]3d^{10} 4s^2 4p^2$	$[Kr]4d^{10} 5s^2 5p^2$	$[Xe]4f^{14} 5d^{10} 6s^2 6p^2$
Covalent radius (pm)	77	118	122	140	146
Ionization Energy (I) ($KJmol^{-1}$)	1086	786	762	709	716
Electronegativity	2.54	1.92	1.99	1.82	1.85
Melting Point (^0C)	4100	1420	945	232	327
Boiling Point (^0C)	Sublimes	3280	2850	2623	1751

Group 15 / VA

Property	N	P	As	Sb	Bi
Atomic Number	7	15	33	51	83
Electronic Configuration	$[He]2s^2 2p^3$	$[Ne]3s^2 3p^3$	$[Ar]3d^{10} 4s^2 4p^3$	$[Kr]4d^{10} 5s^2 5p^3$	$[Xe]4f^{14} 5d^{10} 6s^2 6p^3$
Covalent Radius (pm)	70	110	121	141	148
Ionization Energy ($KJ\ mol^{-1}$)	1402	1012	947	834	703
Electron Affinity ($KJmol^{-1}$)	-7	72	78	103	91
Electronegativity	3.06	2.05	2.21	1.98	2.01
Melting Point (^0C)	-210	44	*	631	271
Boiling Point (^0C)	-195.8	280.5	*	1587	1564

Group 16 / VIA

Property	O	S	Se	Te	Po
Atomic Number	8	16	34	52	84
Electronic Configuration	$[He]2s^2 2p^4$	$[Ne]3s^2 3p^4$	$[Ar]3d^{10} 4s^2 4p^4$	$[Kr]4d^{10} 5s^2 5p^4$	$[Xe]4f^{14} 5d^{10} 6s^2 6p^4$
Covalent radius (pm)	66	104	117	137	146
Ionization Energy (I^{st}) ($KJmol^{-1}$)	1314	1000	941	869	812
Electron Affinity ($KJmol^{-1}$)	141	200	195	190	180
Electronegativity	3.61	2.58	2.42	2.15	2.10
Melting Point (^0C)	-218.8	112.8	217.0	452.0	250.0
Boiling Point (^0C)	-183.0	444.7	685.0	990.0	962.0

Group 17 / VIIA

Property	F	Cl	Br	I
Atomic Number	9	17	35	53
Electronic Configuration	$[He]2s^2 2p^5$	$[Ne]3s^2 3p^5$	$[Ar]3d^{10} 4s^2 4p^5$	$[Kr]4d^{10} 5s^2 5p^5$
Covalent radius (pm)	64	99	114	133
Ionization Energy (I^{st}) ($KJmol^{-1}$)	1681	1251	1140	1008
Electron Affinity ($KJ\ mol^{-1}$)	333	349	325	295
Electronegativity	4.19	2.87	2.68	2.36
Melting Point (^0C)	-218.6	-101.0	-7.25	113.6 *
Boiling Point (^0C)	-188.1	-34.0	59.5	185.2

Group 18 / VIIIA

Property	He	Ne	Ar	Kr	Xe	Rn
Atomic Number	2	10	18	36	54	86
Electronic Configuration	$1s^2$	$[He]2s^22p^6$	$[Ne]3s2\ ^3p^6$	$[Ar]3d^{10}\ 4s^2\ 4p^6$	$[Kr]4d^{10}\ 5s^25p^6$	$[Xe]4f^{14}\ 5d^{10}6s^2\ 6p^6$
Vander Waal's radius (pm)	-	131	174	189	210	215
Ionization Energy ($KJmol^{-1}$)	2372	2081	1521	1351	1170	1037
Melting Point (^0C)	-	-248.6	-189.4	-157.2	-111.8	-71.0
Boiling Point (^0C)	-268.9	-246.1	-185.9	-153.4	-108.1	18.1

POLYMORPHISM

- **Polymorphism** is defined as the ability of a solid material to exist in more than one form or crystal structure.
- The more general term, used for any crystalline material, is **polymorphism**.
- The term **allotropy** is used for elements only, not for compounds.
- Allotropy refers only to different forms of an element within the same phase.

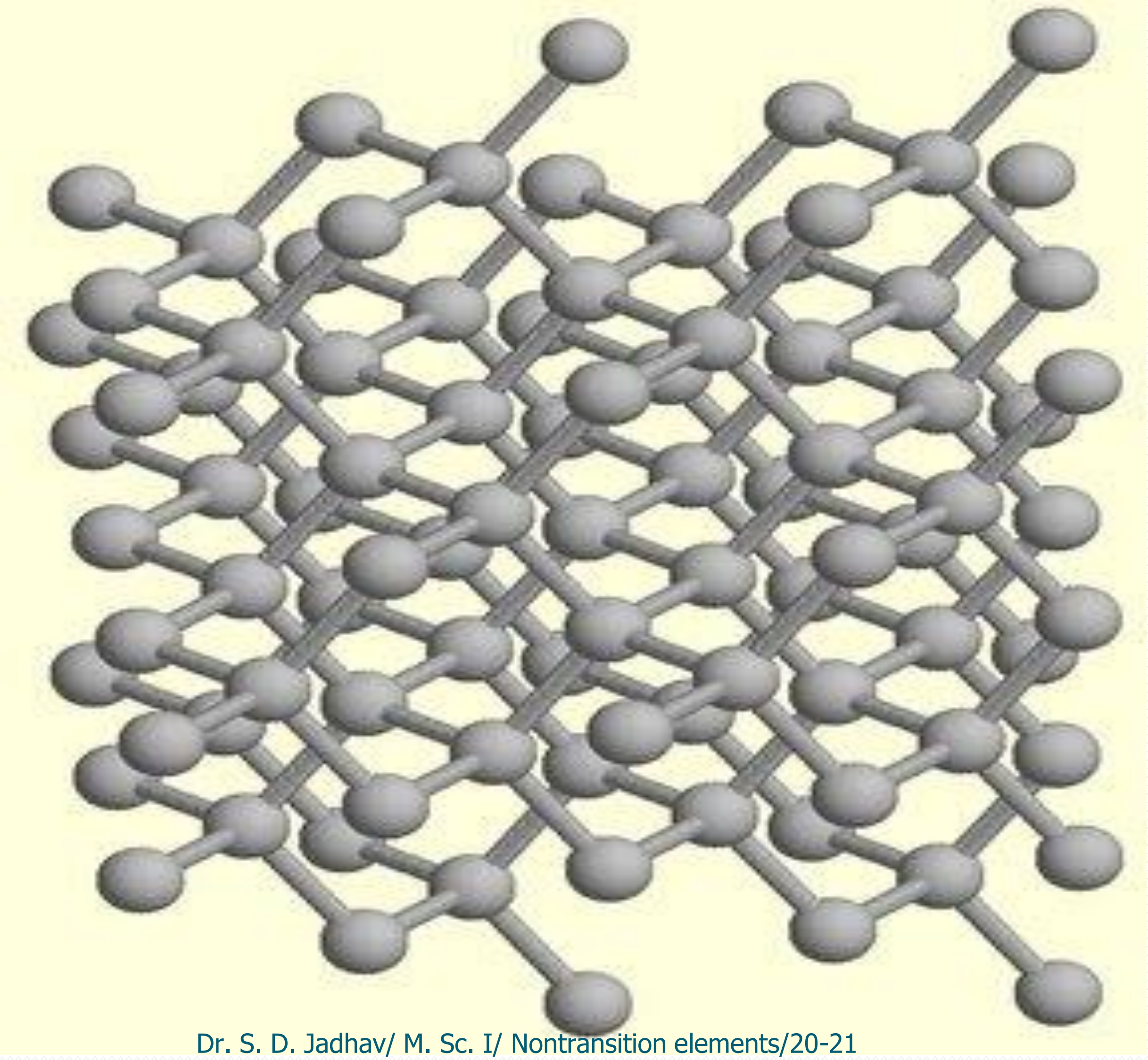
Allotropy

- The existence of an element in two or more forms, which are different in physical properties but have similar chemical properties.

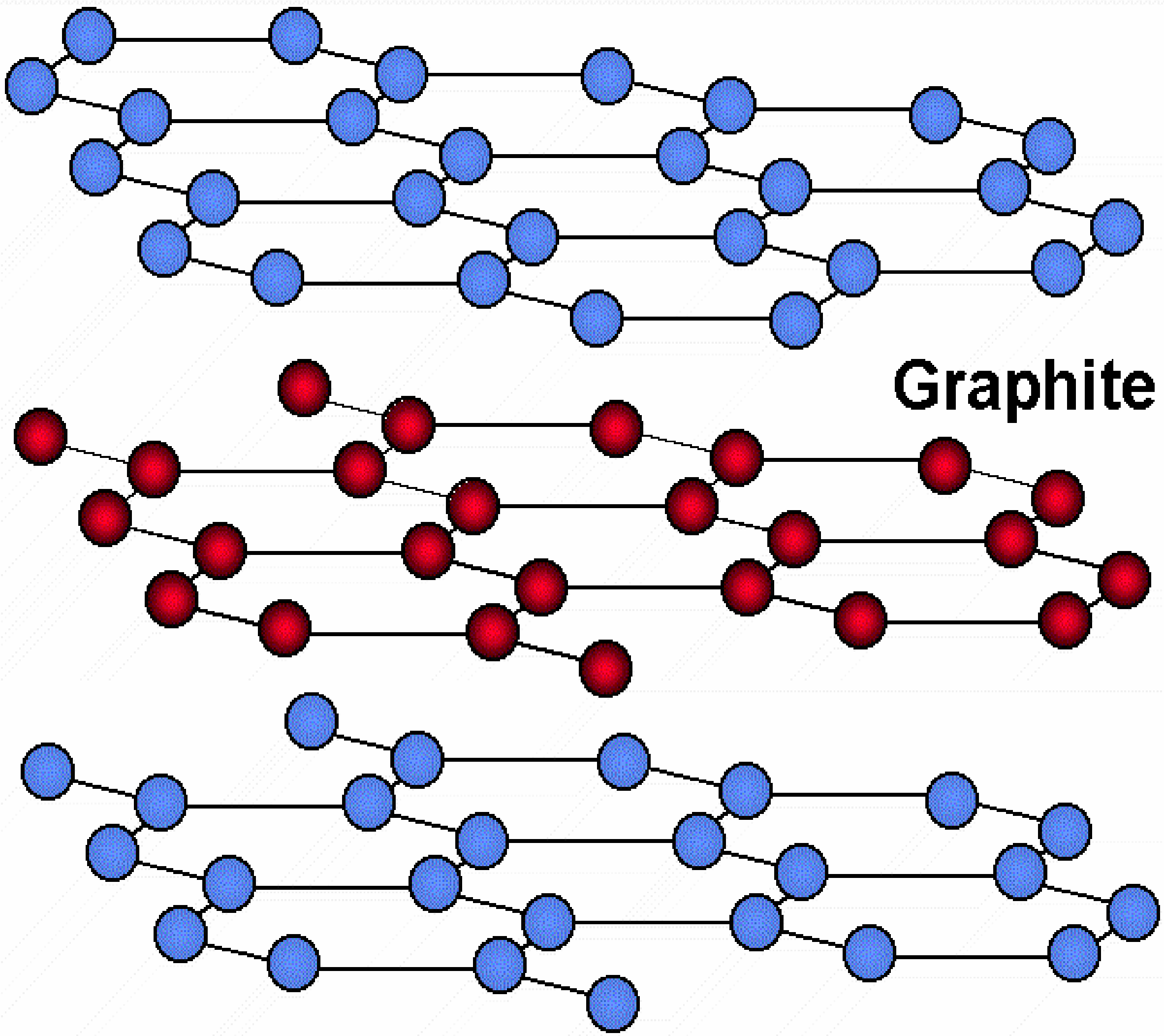
Carbon

- Diamond
- Graphite
- Amorphous carbon
- Fullerene
- Carbon nanotube

Diamond



Graphite



Amorphous carbon

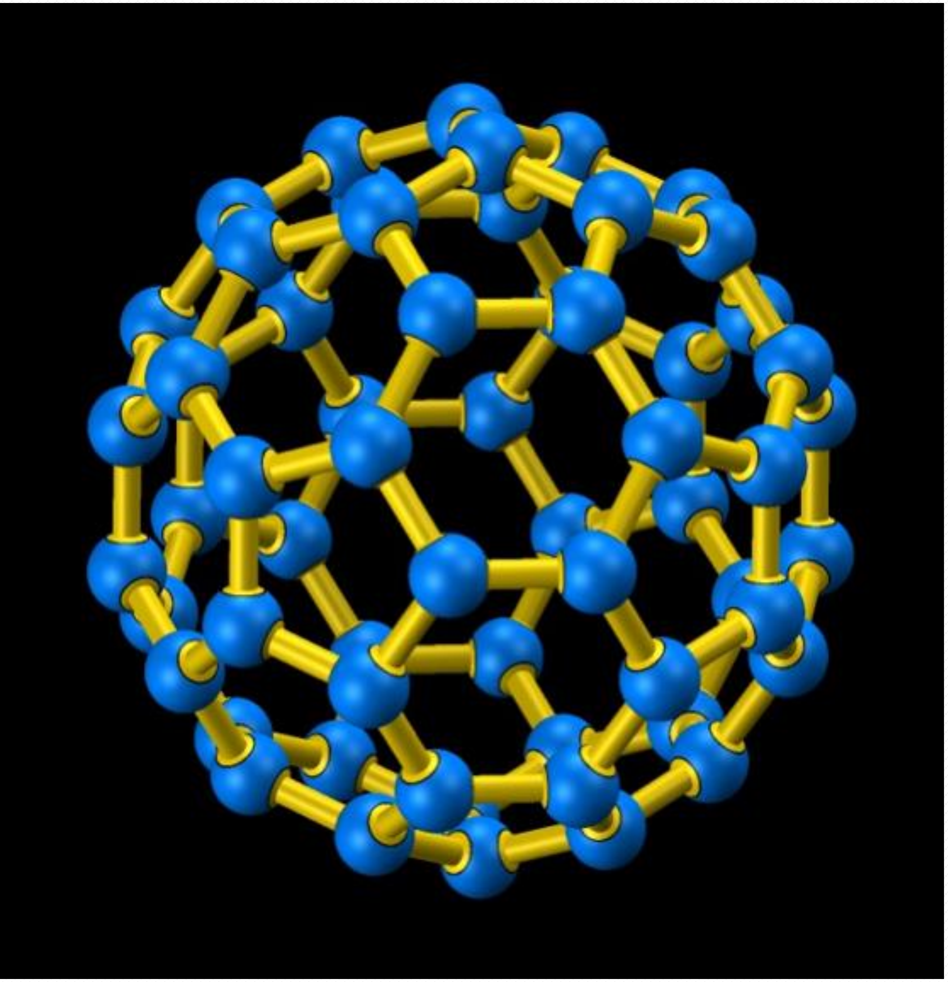
- Examples : Coal
- Highest grade coals –
  - Anthracite (90% carbon)
  - Bituminous coal (75-90% carbon)
  - Lignite (55% carbon)
- Do not show definite crystal structure

Fullerenes

- Discovered in 1985
- General formula C_{2n}
- Examples : C_{60} Buckminsterfullerene / Bucky ball
- Other Ex. :C_{32}, C_{50}, C_{70}, C_{76}, C_{84}.

  Preparation – By passing high voltage current through graphite rods, in inert atm. of Helium.

C_{60} Buckminsterfullerene



Structure :

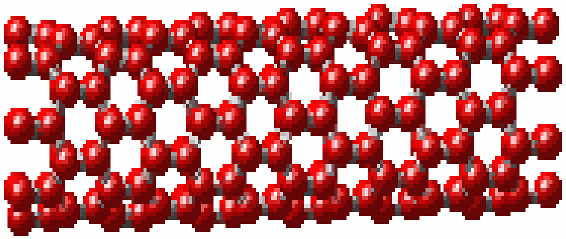
- Spherical molecule
- 20 hexagons
- 12 pentagons
- C-C bond lengths 1.48 & 1.38 A^{o}
- Covalent bonding

- Decomposes at 700°C
- Soluble in organic solvents
- Reacts with Gr. I metals to form solid M_3C_{60}
- Become superconductors below 18K
- Forms complexes with metals like Pt, Os, etc.
- Medicinal uses

Nanotubes

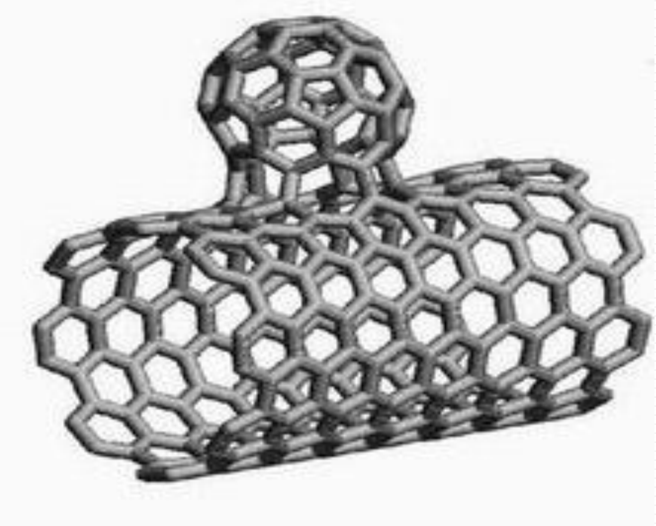
- Cylindrical carbon molecules
- Diameter- in order of few nanometers
- Length- several cms
- Types: Single walled nanotubes (SWNT)
  Multi walled nanotubes (MWNT)
- Useful in nanoelectronics, optics, etc.

Structure:



- Cylindrical tubes of carbon
- one end typically capped with a hemisphere of buckyball structure.

Carbon Nanobuds

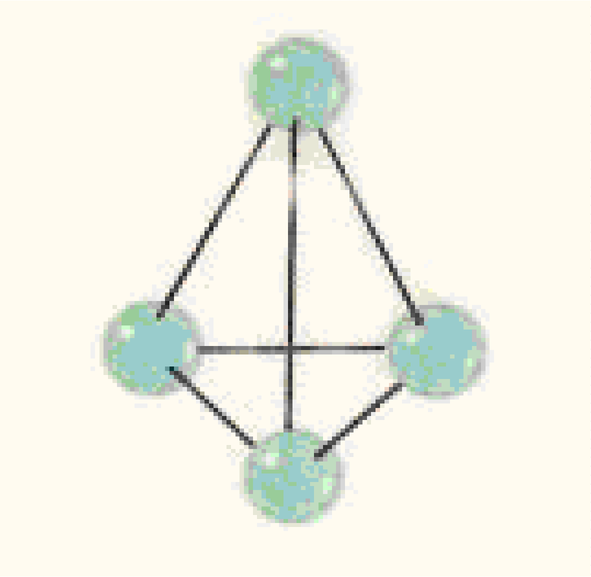


- Newly discovered allotrope
- Fullerene like buds are attached to the outer walls of nanotubes
- Show properties of both fullerenes and nanotubes

Phosphorus

- White Phosphorus
- Red Phosphorus
- Metallic Phosphorus/α-Black
- β-Black Phosphorus
- Scarlet Phosphorus
- Violet Phosphorus

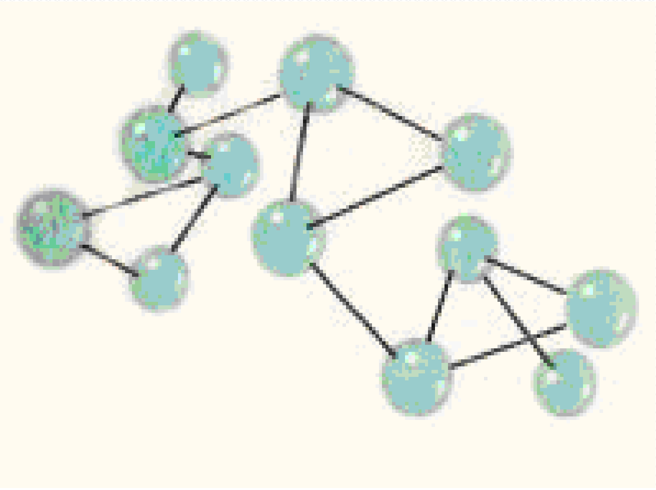
White Phosphorus



- Prepared by rapid cooling vapours of Phosphorus
- Exists as discrete tetrahedral P_4 molecules
- Covalent bonds P-P 2.21A^o
- Highly reactive
- Glows in air, emitting greenish yellow light : Phosphorescence

- Readily soluble in CS_2
- Soft, waxy in nature
- Extremely poisonous
- M.P. 44^{o}C B.P. 280^{o}C
- Above 800^{o}C, dissociates to P_2 molecules
- When exposed to air, temperature raises gradually & catches fire after 30^{o}C. So kept under water.

Red Phosphorus



- Violet-Red powder
- Obtained by heating White P in absence of air
- Stable under ordinary conditions
- Does not ignite in air
- Not poisonous
- Has minute crystalline structure
- Does not show phosphorescence

Metallic Phosphorus / α-Black

- Prepared by dissolving Red Phosphorus in molten Phosphorus at 400^{o}C in a sealed tube.On cooling black P is obtained
- Stable at ordinary condition
- Does not oxidize in air unless heated strongly.

β-Black Phosphorus

- Obtained by heating white phosphorus at 2000^{o}C & 4000 atm.
- Crystalline structure
- Consists of sheets, in which each P is bonded to three neighbouring P-atoms
- Stable & donot burn upto 400^{o}C
- Good conductor of electricity

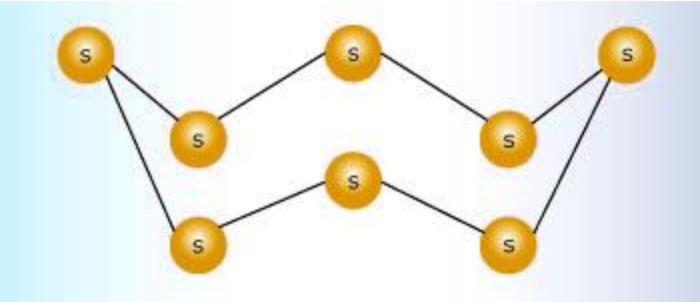
Allotropy of Sulphur

- Rhombic / α-Sulfur
- Monoclinic / β-Sulfur
- Colloidal Sulfur
- Plastic Sulfur

Rhombic / α-Sulfur

- Common allotrope
- Stable below 95.6^{o}C
- Soluble in CS_2
- Sp. Gravity : 2.06 M.P. 114^{o}C
- When solution of sulfur in CS_2 is evaporated slowly – rhombic sulfur is formed
- Crystal structure : S_8 molecules arranged as puckered rings

Monoclinic / β-Sulfur



- Stable above 95.6^{o}C
- Soluble in CS_2
- Sp. Gravity : 1.96 M.P. 120^{o}C
- By melting Rhombic sulfur
- Crystal structure : needle like crystals containing S_8 molecules arranged in different manner.

Colloidal Sulfur

- When H_2S is passed through an oxidizing solution such as HNO_3, $KMnO_4$, sulfur separates out in colloidal state
- It is obtained by passing H_2S through water containing SO_2.

Plastic Sulfur

- Molten sulfur is heated to 350^oC & poured into cold water. Soft rubber like mass is formed – Plastic sulfur
- It hardens on standing & changes gradually to Rhombic sulfur.
- Sp. Gravity : 1.95
- Contains rings & long helical chains containing large no. of S-atoms.
- Can be converted into fibres, when heated in atm. of Nitrogen at 300^oC.

BORANES

- Chemical compounds of B & H
- General formula : BxHy
- Types & Formulae :
  - Nidoboranes B_nH_{n+4}
  - arachnoboranes B_nH_{n+6}
  - closoboranes $B_nH_n^{-2}$
  - hyphoboranes B_nH_{n+8}

- B_2H_6 : diborane
- B_5H_9 : pentaborane-9
- B_6H_{10} : hexaborane-10
- B_8H_{12} : octaborane-12
- $B_{10}H_{14}$: dodecaborane
- B_4H_{10} : tetraborane
- B_5H_{11} : pentaborane-11
- B_6H_{12} : hexaborane-12
- B_8H_{14} : octaborane-14
- B_9H_{15} : nonaborane/enneaborane

- Synthesis :

1. By the reaction of sodium borohydrate and iodine in solvent diglyme.

$$2NaBH_4 + I_2 \longrightarrow B_2H_6 + 2NaI + H_2$$

2. By reduction of BCl_3 with Li-Aluminium hydride

$$4BCl_3 + 3LiAlH_4 \longrightarrow 2B_2H_6 + 3AlCl_3 + 3LiCl$$

3. Magnesium boride Mg_3B_2 react with H_3PO_4 to give mixture of boranes which on heating gives diborane

Properties :

Reactions of Diborane :

1) $B_2H_6 \longrightarrow 2\ BH_3$

2) $B_2H_6 + 3\ O_2 \longrightarrow B_2O_3 + 3H_2O$

3) $B_2H_6 + 6\ H_2O \longrightarrow 2B(OH)_3 + 3H_2$ (boric acid)

4) $B_2H_6 + 6\ ROH \longrightarrow 2B(OR)_3 + 3H_2$ (borate ester)

5) $B_2H_6 + 6\ H_2C{=}CH_2 \longrightarrow 2BEt_3$

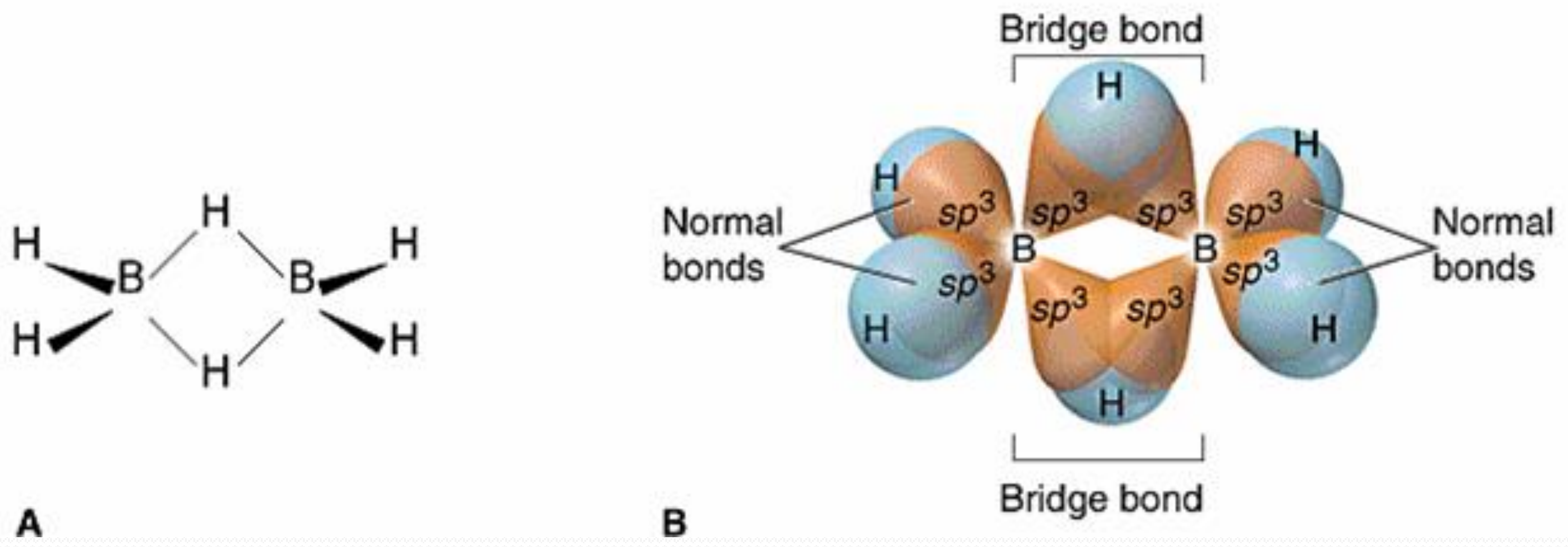
6) $B_2H_6 + 2\ MH \longrightarrow 2M[BH_4]$ (M = Li or Na)

7) $B_2H_6 + 2\ NR_3 \longrightarrow 2R_3N{\bullet}BH_3$ (R = alkyl)

8) $B_2H_6 + 2\ NH_3 \longrightarrow [BH_2\ (NH_3)\ _2][BH_4]$

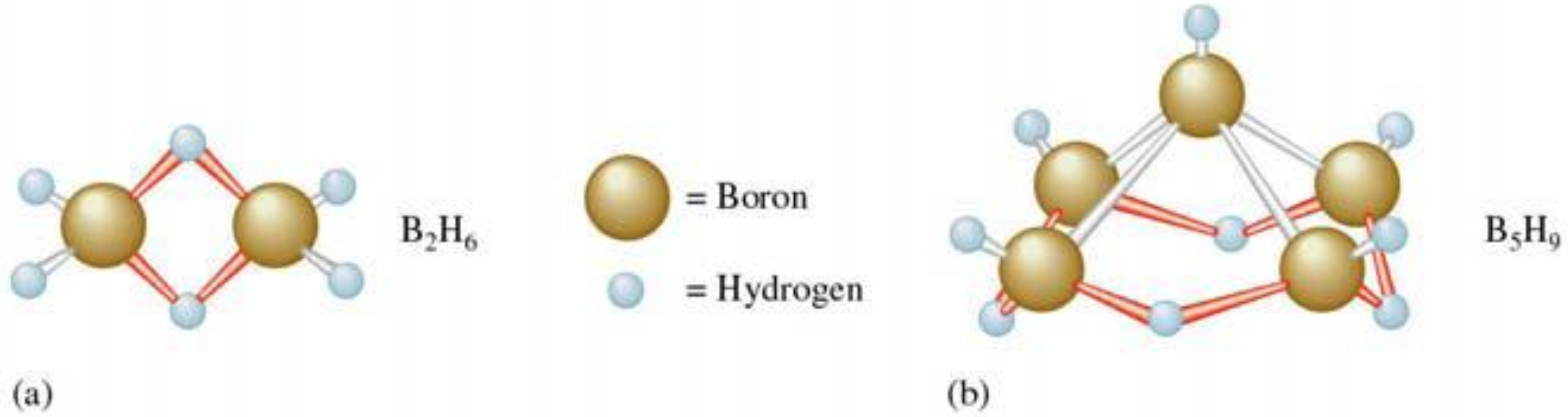
9) $Me_2O{\bullet}BH_3 + NH_3 \longrightarrow H_3N{\bullet}BH_3 + Me_2O$

Bonding in Diborane

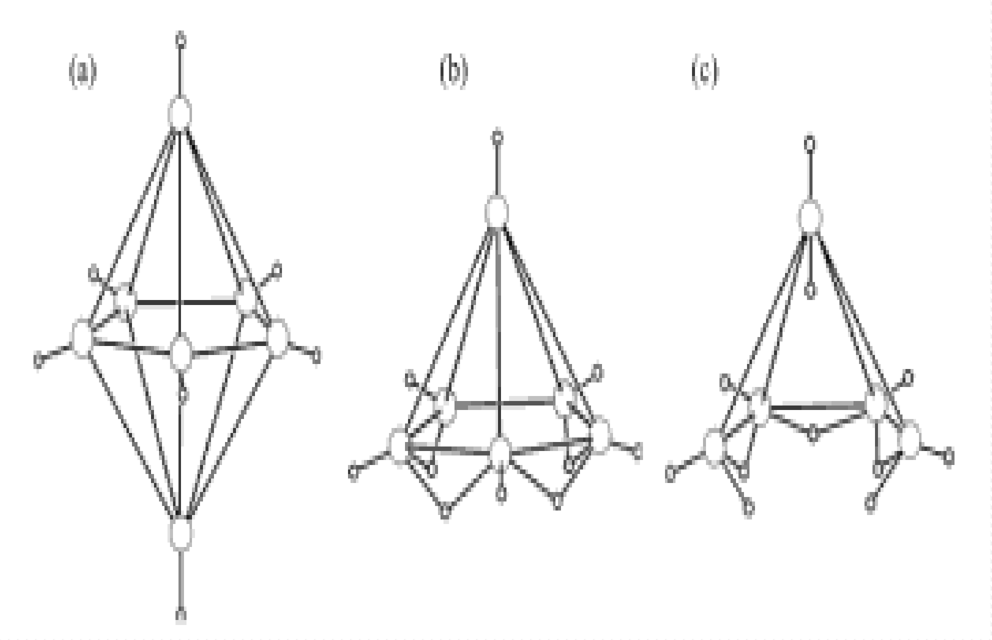


Electron deficient- "bridge bonds" require unusual 3-center, 2-electron bonding

Structures of Boranes



Bonding in Boranes

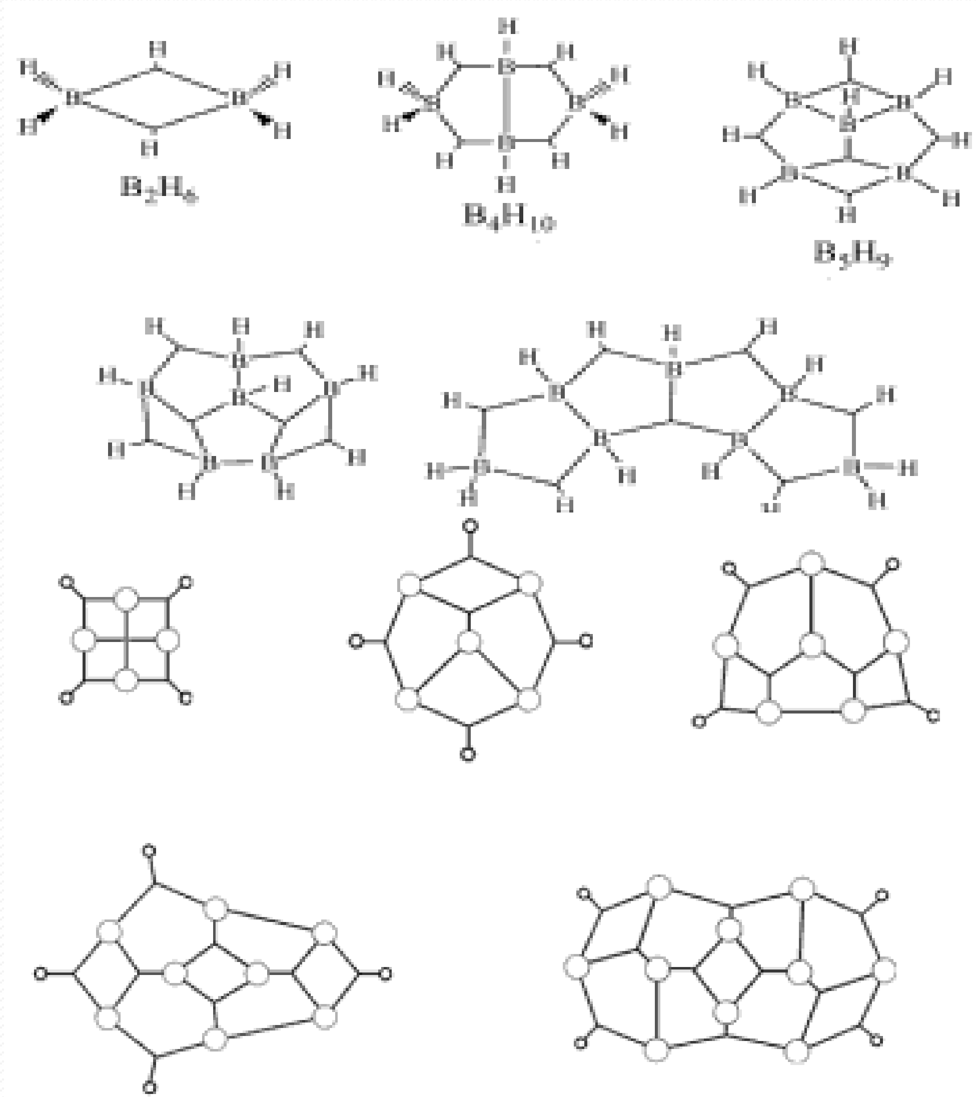


(a) Closoboranes : closed polyhedral structure in which all vertices are occupied.

(b) Nidoboranes : derived from polyhedral structure of closoboranes, by the removal of one of the vertices of the polyhedron

(c) Arachnoboranes : derived from the structure of nidoboranes, by removal of one of the vertices.

B-H-B, B-H, B-B, B-B-B bonds: 2e-s each



Cluster Valence Electron Theory

- This is a method for determining the geometry of a borane.
- To use this method, the total number of valence electrons used in cluster binding must be determined. There are

  3 valence electrons for each B atom,

  1 valence electron for each H atom, and

  the total charge on the complex must be added in.

- The structure is determined according to the following equations:
- ***closo* - 4n + 2 valence electrons**
- ***nido* - 4n + 4 valence electrons**
- ***arachno* - 4n + 6 valence electrons**

  n = number of boron atoms in the cluster

Wade's Rule

- Each B-H unit contributes $2e^{-}$s
- -ve charge : $1e^{-}$
- Additional H-atom : $1e^{-}$

Wade's Rule

Boron hydride	Name	No. of skeletal electron pairs	Examples
$[B_nH_n]^{2-}$ or B_nH_{n+2}	Closo	n+1	$B_6H_6^{2-}$, $B_{12}H_{12}^{2-}$
B_nH_{n+4}	Nido	n+2	B_2H_6, B_5H_9, $B_{10}H_{14}$
B_nH_{n+6}	Arachno	n+3	B_4H_{10}
B_nH_{n+8}	Hypho	n+4	$B_5H_{12}^{-}$

- **$B_6H_6^{-2}$**

14 electrons

7 e^- pairs

(n+1) e^- pairs n = total no. of B atoms

n = 6

Closoborane

- **B_5H_9 :**

14 electrons

7 e^- pairs

(n+2) e^- pairs n = 5

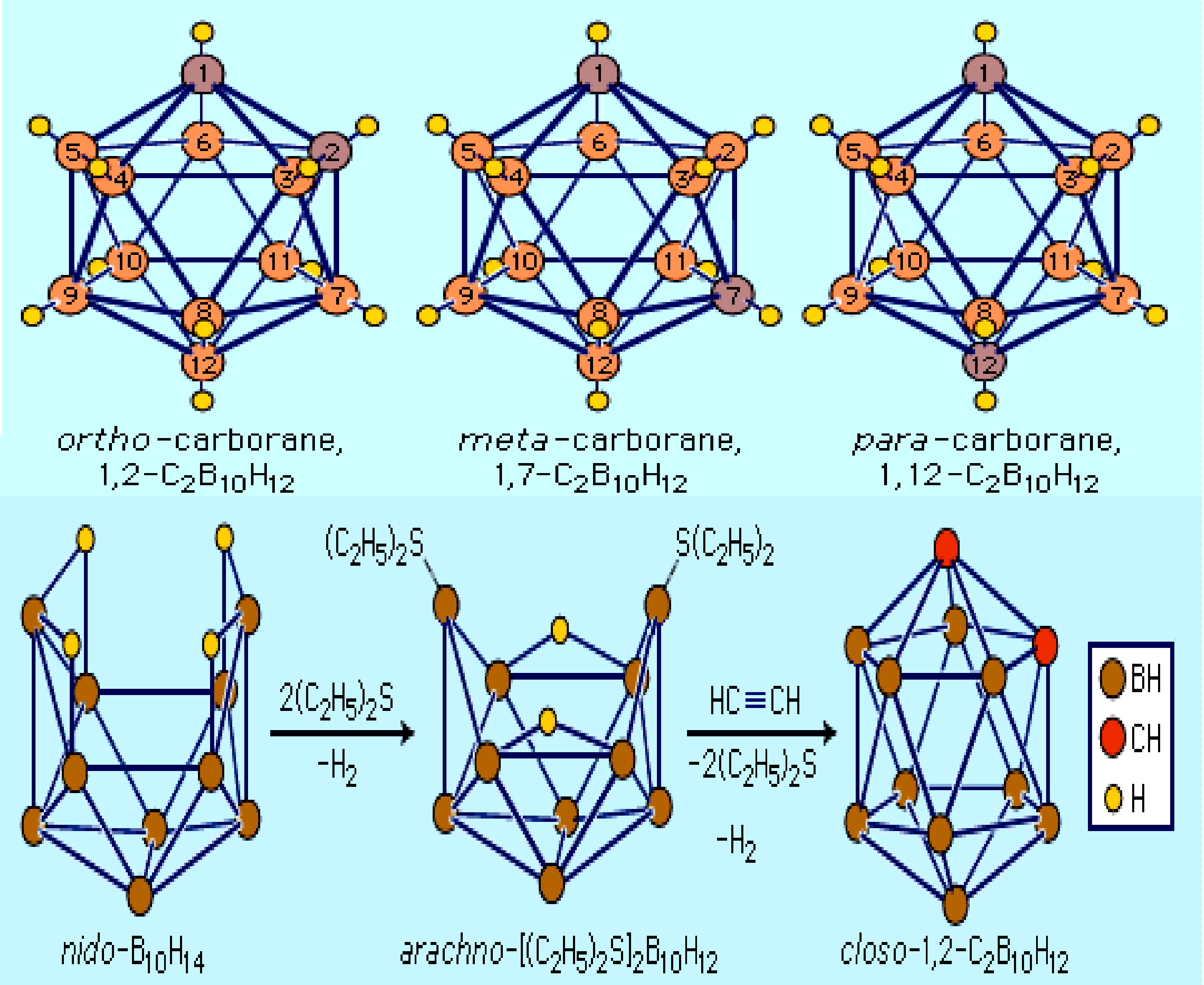
Nidoboranes

- **B_5H_{11} :**
  16 electrons
  8 e^- pairs
  (n+3) e^- pairs n = 5
  Arachnoborane

- **$B_5H_{12}^-$:**
  18 electrons
  9 e^- pairs
  (n+4) e^- pairs n = 5
  Hypoborane

CARBORANES

- Chemical compounds of C, B & H.
- B and C occupy vertices of triangular polyhedron B-H units of boranes are replaced by C-H units



ortho-carborane,
1,2-C2B10H12
meta-carborane,
1,7-C2B10H12
para-carborane,
1,12-C2B10H12
(C2H5)2S
S(C2H5)2
2(C2H5)2S
-H2
HC≡CH
-2(C2H5)2S
-H2
BH
CH
H
nido-B10H14
arachno-[(C2H5)2S]2B10H12
closo-1,2-C2B10H12

Wade's Rule

- Each B-H unit contributes $2e^{-}$s
- -ve charge : $1e^{-}$
- Additional H-atom : $1e^{-}$
- Each C-H unit : $3e^{-}$s

- **$C_2B_{10}H_{12}$:**
  closed triangular polyhedral structure in which all 3 vertices are occupied by C-atoms.
  (m+1) e- pairs m = total no. of B & C atoms
  m = 2 + 10 = 12 **13 e-pairs**
  Closocarboranes
- **$C_2B_4H_8$:**
  derived from closotriangular polyhedral structure of closocarboranes, by the removal of one of the vertices of the polyhedron
  (m+2) e- pairs m = 2 + 4 = 6 **8 e-pairs**

Nidocarboranes

- **$C_2B_7H_{13}$:**
  derived from the structure of nidocarboranes, by the removal of one of the vertices.
  (m+3) e- pairs m = 2 + 7 = 9 **12 e-pairs**
  Arachnocarboranes

CARBIDES

A class of chemical compounds in which carbon is combined with a metallic or semimetallic element.

Preparation:

- Carbides are prepared from carbon and metal or metal oxide, at temperatures of 1,000 to 2,800 °C.

$$BeO + 3\,C \longrightarrow Be_2C + 3CO$$

$$CaO + 3\,C \longrightarrow CaC_2 + 2CO$$

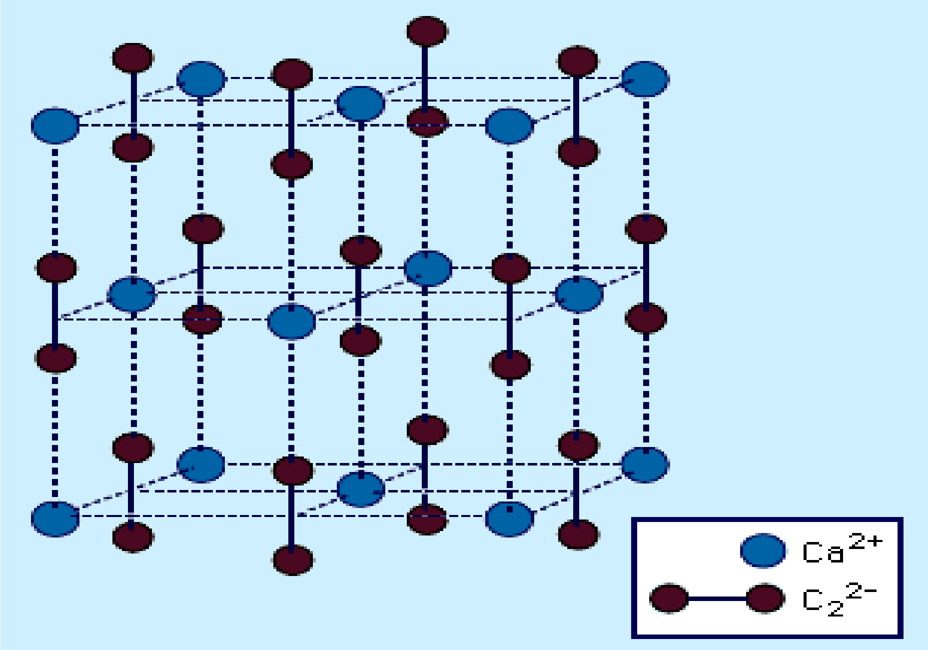
Classification of Carbides

- The most electropositive metals form ionic/saltlike carbides.
- The transition metals tend to form interstitial carbides.
- The nonmetals of electronegativity similar to that of carbon form covalent or molecular carbides.

Ionic / saltlike carbides

Ionic carbides have carbon anions like C^{4-}, C_2^{-2}, C_3^{-4}

- Methanoids : Al_4C_3,Be_2C on hydrolysis give CH_4
- Acetylides : MgC_2, BeC_2,CaC_2 on hydrolysis give C_2H_2
- Allylides : Mg_2C_3 on hydrolysis gives allylene $CH_3C.CH$



- They react with water.

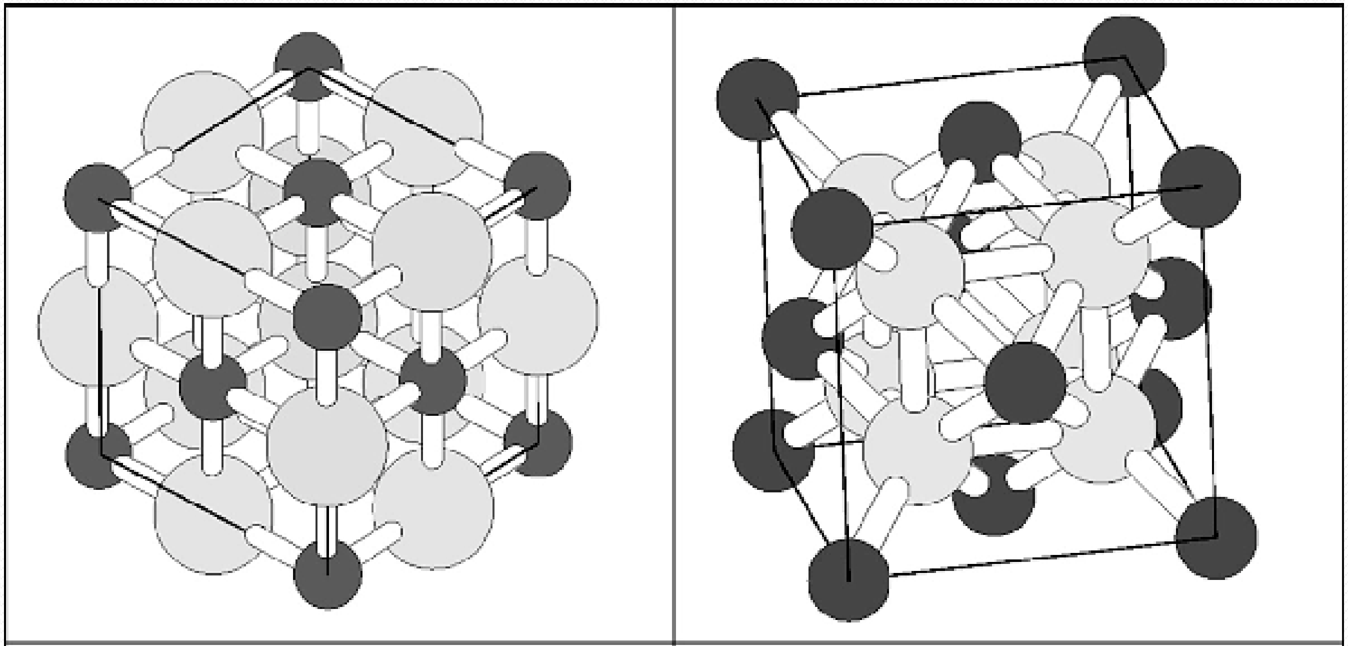
CaC_2

Interstitial carbides

- Carbon atoms occupy the interstices of the close-packed crystal structure of metal atoms. (Transition metals are large and carbon atoms are comparatively smaller)
- They show properties of metals, like high M.P., high conductivity, malleability.
- Do not react with water.
- Examples : WC, TaC, Fe_3C

Fe_3C

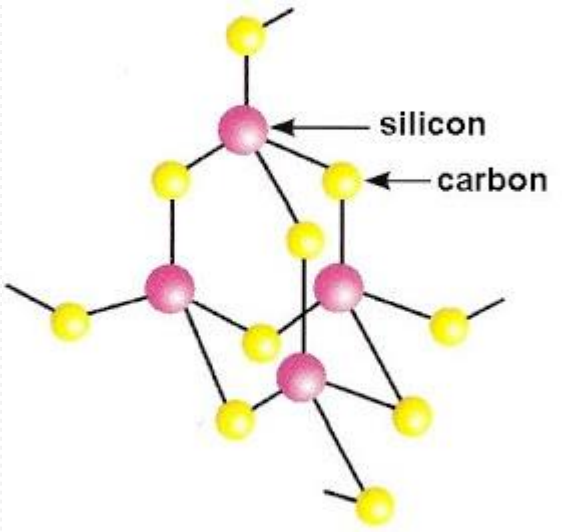
Interstitial carbides



NaCl type of structure | CaF_2 type of structure

Covalent carbides

- These carbides are formed with the elements that are most similar to carbon in size and electronegativity.
- **Silicon carbide (SiC)** is known as carborundum and is prepared by the reduction of SiO_2 with elemental carbon in an electric furnace.



Covalent carbides

- **Boron carbide**
- B_4C It is prepared by the reduction of boron oxide (B_2O_3) with carbon in an electric furnace.

  It is also extremely hard and inert. In the structure of B_4C, the boron atoms occur in icosahedral groups of 12, and the carbon atoms occur in linear chains of three.
- BC_3 a graphite like structure, is produced from the reaction of benzene (C_6H_6) and boron trichloride (BCl_3) at 800°C.
- B_4C is harder than SiC and used as abrasive and used as shields from radiations.

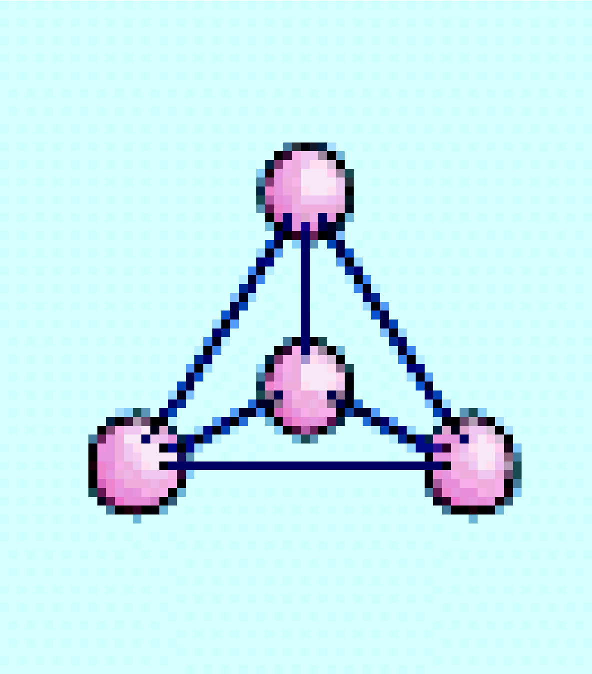
SILICATES

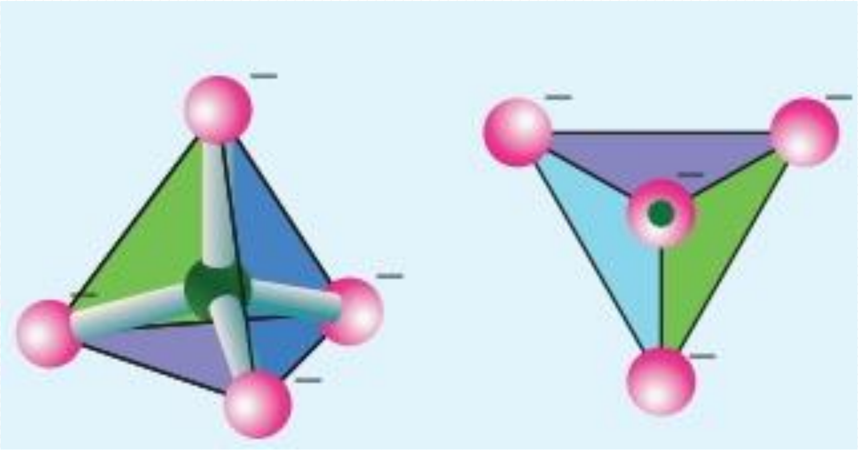
Silicates

- Silicates are salts containing anions of silicon and oxygen.
- Silicates occur in earth's crust in the form of silicate minerals
- In all silicates, silicon is always tetravalent, Silicon atoms are found at the centers of tetrahedrons with oxygen atoms at the corners.
- Na_2SiO_3 is soluble in water.
- Most silicates are insoluble in water.
- Electronegativity of Si is 1.8 & O is 3.5
- Si–O bond has ionic character.

Silicates

- In silicates Si undergoes sp^3 hybridization, 4O-atoms are bonded with Si-atoms. O-atoms picks up one electron from metals to complete octet.
- $(SiO_4)^{-4}$ tetrahedral unit





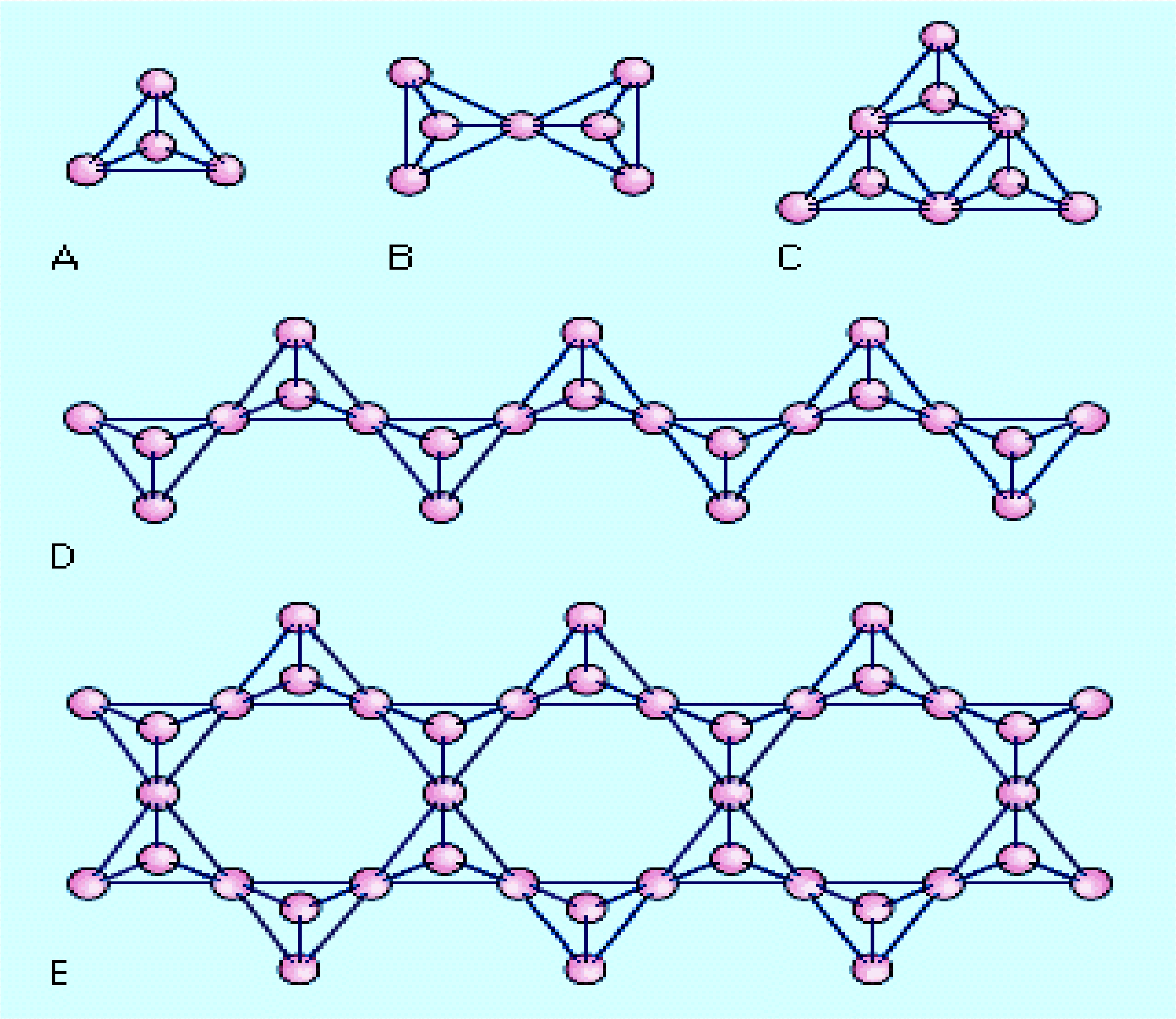
Silicates

- In silicates, severals $(SiO_4)^{-4}$ tetrahedral units are bridged together through O-atoms of the units. Bonding oxygen atom is bonded covalently with 2Si-atoms. Thus complex silicates are formed.

Types of Silicates

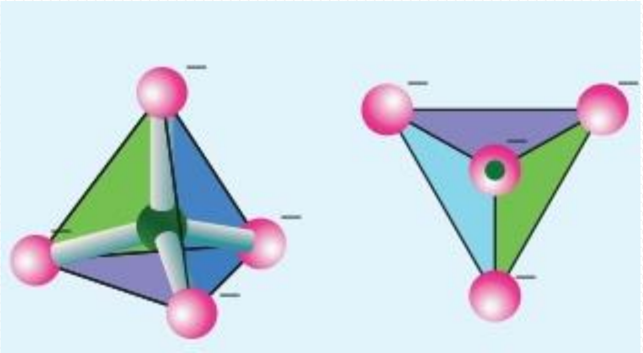
- Depending upon linkage of $(SiO_4)^{-4}$ tetrahedral units, silicates are classified as,

Orthosilicates	$(SiO_4)^{-4}$	discrete units	Zn_2SiO_4 Willemite, Be_2SiO_4 Phenacite
Pyrosilicates	$(Si_2O_7)^{-6}$	discrete anions	$Sc_2Si_2O_7$ Thortveitite
Chain silicates (Pyroxene)	$(SiO_3)_n^{-2n}$	2 bridging O-atoms per unit	$Mg_2(SiO_3)_2$ enstatite, $LiAl(SiO_3)_2$ spodumene
Chain silicates (Amphibole)	$(Si_4O_{11})_n^{-6n}$	double chain structures	$Ca_2Mg_5Si_4O_{11}(OH)_2$ tremolite


A
B
C
D
E

Types of Silicates

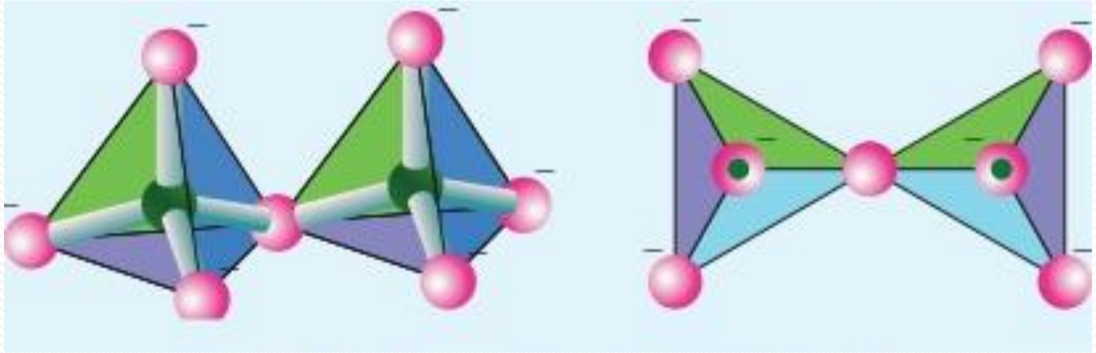
- Orthosilicates (Nesosilicates)
- $(SiO_4)^{-4}$



- Zn_2SiO_4 Willemite,
- Be_2SiO_4 Phenacite

Types of Silicates

- Pyrosilicates (Sorosilicates)
- $(Si_2O_7)^{-6}$



- $Sc_2Si_2O_7$ Thortveitite

Types of Silicates

- Cyclic silicates (Cyclosilicate)
- $(SiO_3)_n^{-2n}$

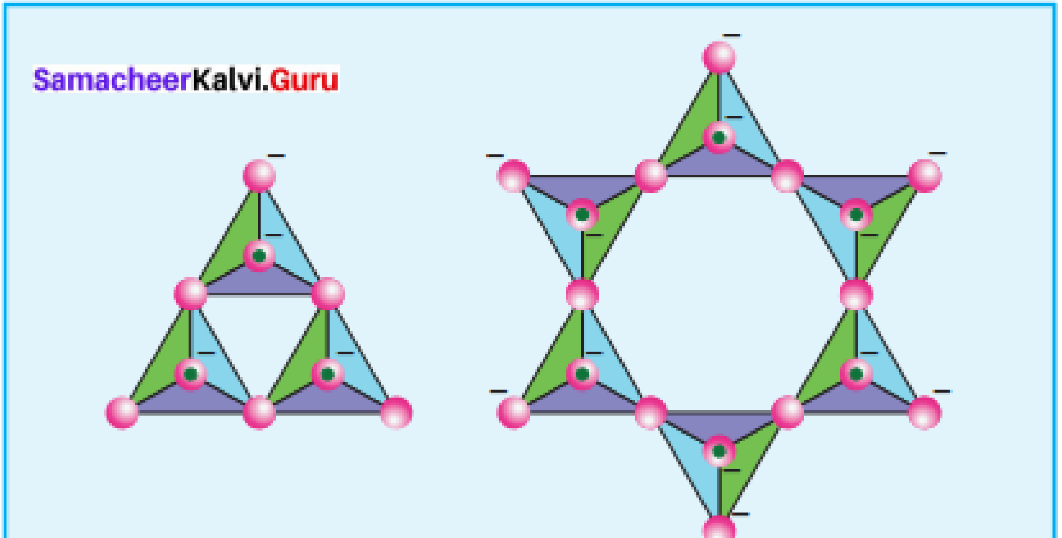


Figure 2.13 Structure of Cyclic silicates

- $Be_3Al_2(SiO_3)_6$ Beryl

Types of Silicates

- Chain silicates (Pyroxene) (Inosilicates)
- $(SiO_3)_n^{-2n}$

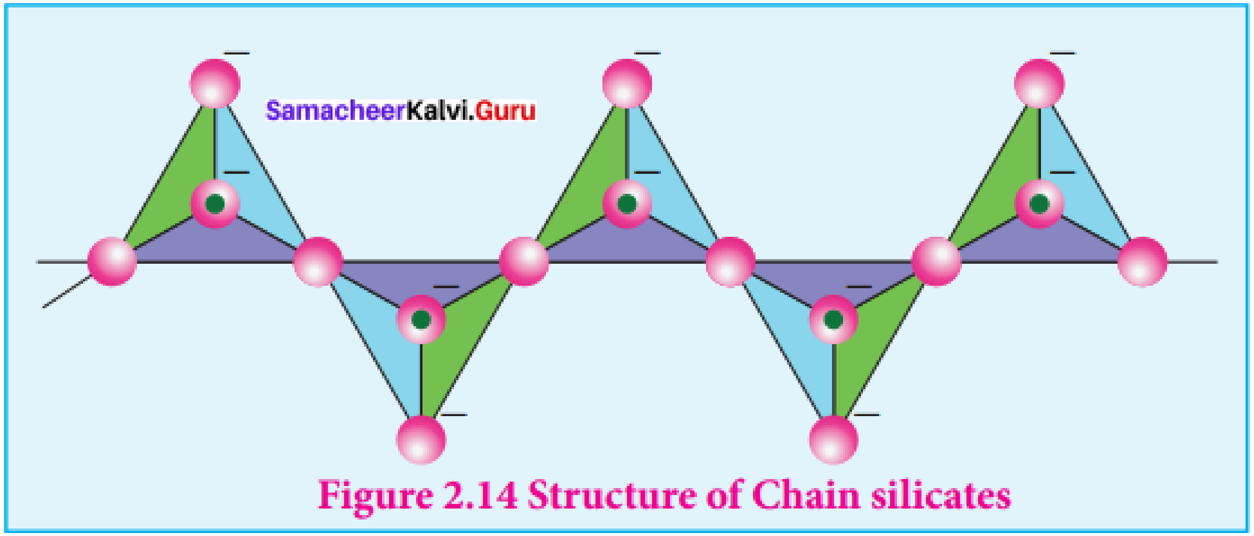


Figure 2.14 Structure of Chain silicates

- $Mg_2(SiO_3)_2$ Enstatite,
- $LiAl(SiO_3)_2$ Spodumene

Types of Silicates

- Chain silicates (Amphibole) (Inosilicates)
- $(Si_4O_{11})_n^{-6n}$

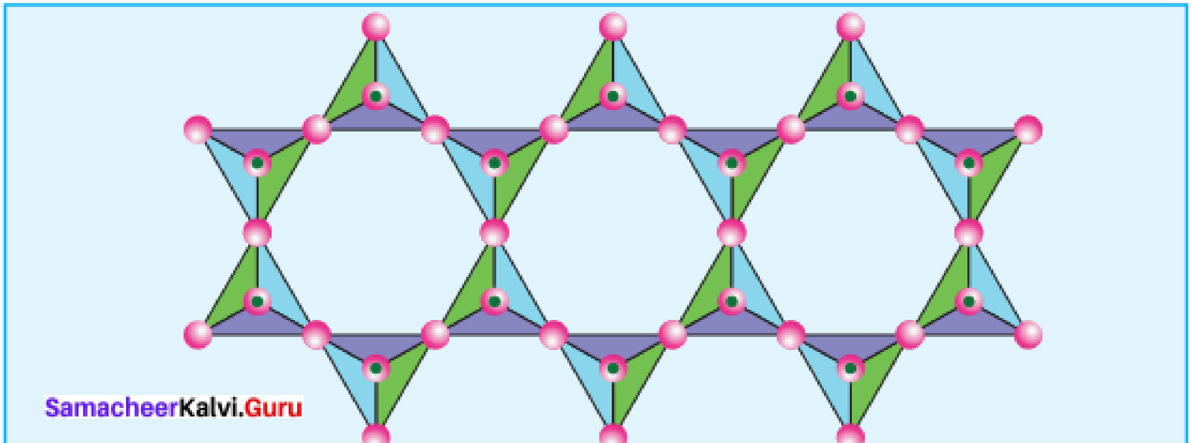


Figure 2.15 Structure of Double chain silicates

- $Ca_2Mg_5Si_4O_{11}(OH)_2$ Tremolite, Asbestos

Types of Silicates

- Sheet silicates
- $(Si_2O_5)_n^{-2n}$

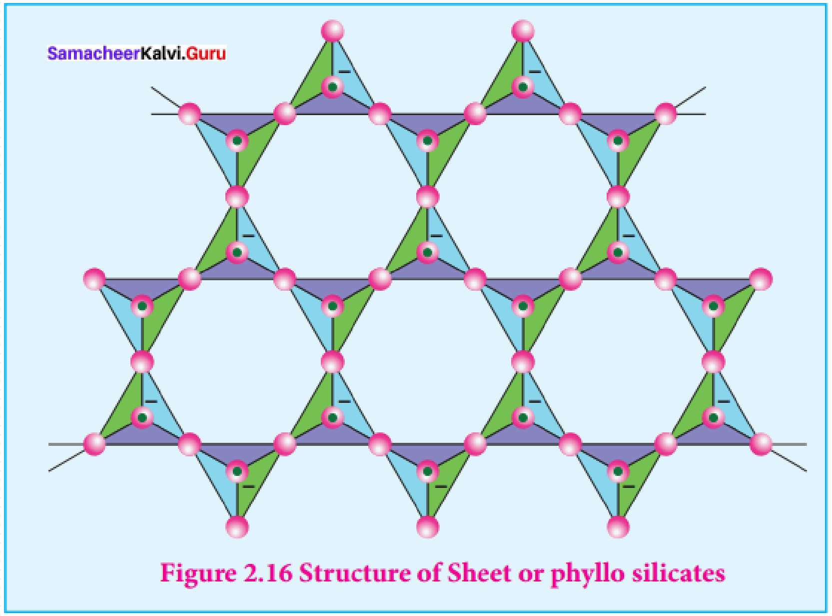
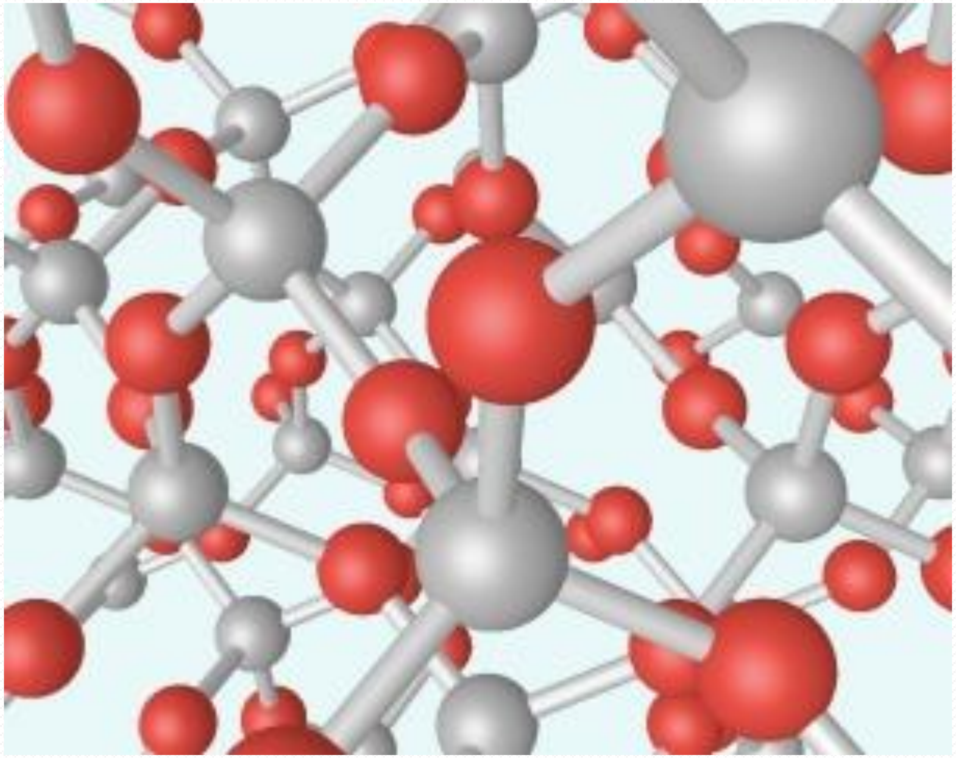


Figure 2.16 Structure of Sheet or phyllo silicates

- Talc $Mg_3Si_4O_{10}(OH)_2$
- Mica

Types of Silicates

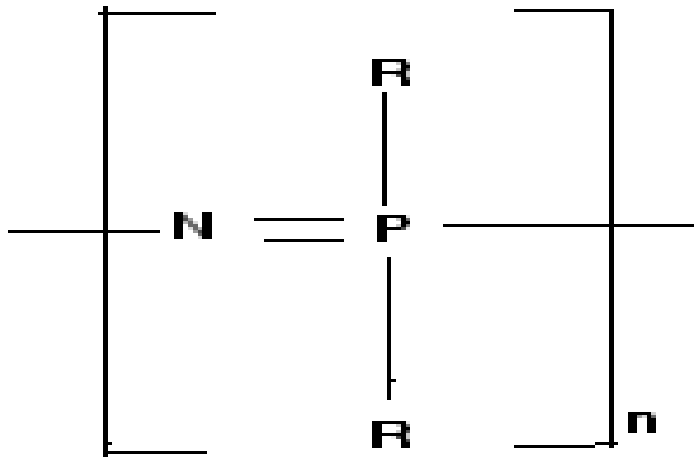
- Three dimensional silicates
- $(SiO_2)_n$



- Quartz

PHOSPHAZENES

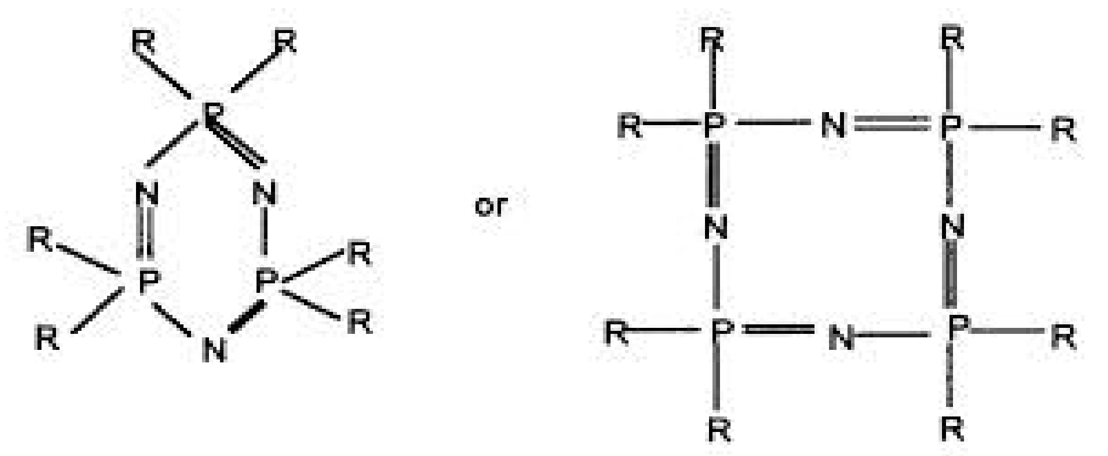
- Inorganic polymers containing alternate phosphorous and nitrogen atoms with two substituent on each phosphorous atom.



Cyclophosphazenes

- Form an extensive homologous series $(NPR_2)_n$ (n = 3–40)

- The six-membered rings are usually planar (or close to planar), whereas the larger ring systems adopt puckered conformations, with the exception of the tetramer $(NPR_2)_4$, which is almost planar.

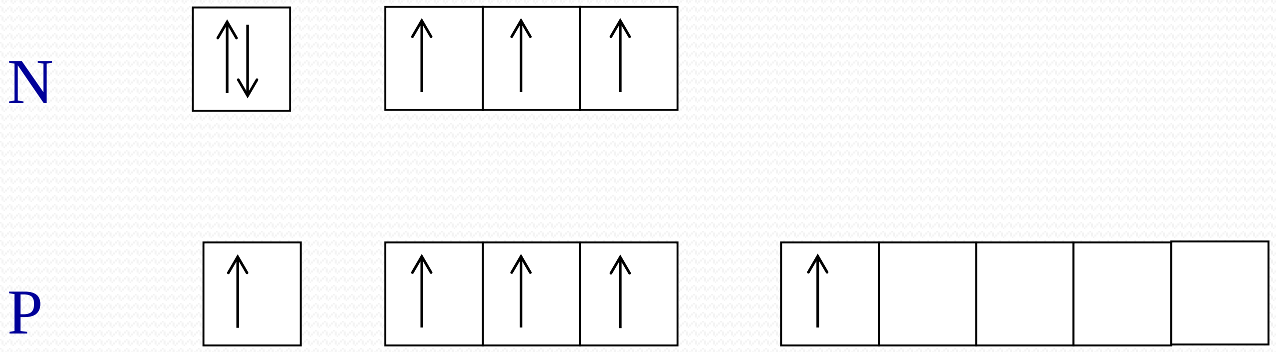


- **The parent system (R = H) is not known**, but a wide variety of derivatives where R = Cl, F, CF_3, alkyl, OR, NR_2

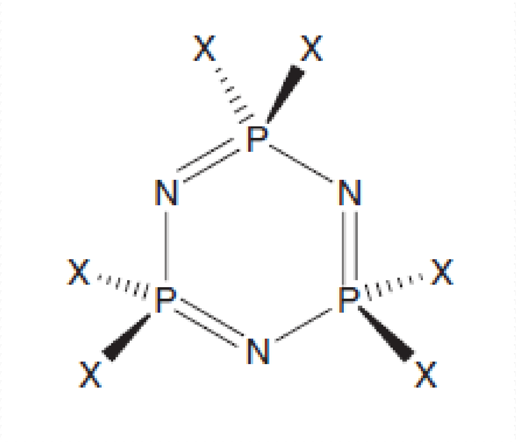
P undergoes sp^3 hybridization while N undergoes sp^2 hybridization. The P atoms in cyclophosphazenes use four valence electrons in forming σ-bonds to their four nearest neighbours, **leaving one electron available for π-bonding**.

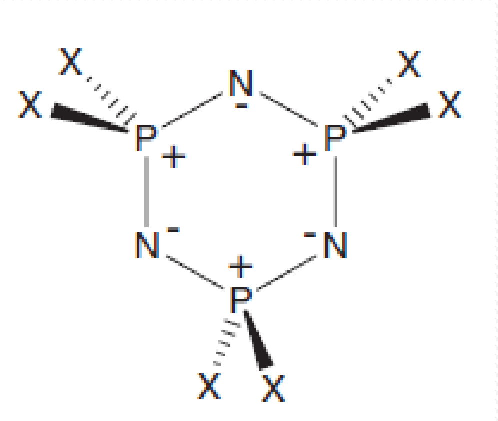
The N atoms utilize two electrons to bond to the two adjacent phosphorus atoms and also accommodate a lone pair of electrons in an 'sp^2' orbital in the plane of the P_3N_3 ring

Thus, **each N atom has one electron available for π-bonding** in a p-orbital perpendicular to the plane of the ring.



The cyclotriphosphazenes, $(NPX_2)_3$ are **π-electron precise systems** with six π-electrons for six ring atoms.





PREPARATIONS OF PHOSPHAZENES

(A) Methods for polyphosphazene

1. $N\ PCl_5 + n\ NH_4Cl \longrightarrow (PNCl_2)_n + 4n\ HCl$
   phosphonitrilic chloride
2. $(P_3N_5)_n + nCl_2 \longrightarrow (PNCl_2)_n$
3. $S_4N_4 + 6SOCl_2 + 12\ PCl_3 \longrightarrow 4\ (PNCl_2)_3$
4. $5PCl_5 + 3NH_3 \longrightarrow (PNCl_2)_3 + 9\ HCl$
5. $(PNCl_2)_3 + 6KSO_2F \longrightarrow (PNF_2)_3 + 6\ KCl + 5\ SO_2$
6. $(PNCl_2)_3 + PbF_2 \longrightarrow (PNFCl)_4 + PbCl_2$

PROPERTIES

1. PHYSICAL PROPERTIES : on heating $(NPCl_2)_3$ and $(NPCl_2)_4$ polymerise to elastic product of high molecular weight and on heating the product gets depolymerised.

2. SUBSTITUTION REACTIONS :
The chlorine atom in phosphonitrilic chloride is very reactive and it can be easily replaced by monovalent groups like F, Br, OH, OR, SH, SR, SCN, NH_2 , NR_2 etc.

3. HYDROLYSIS : The trimer can be hydrolysed to trimetaphosphamic acid which undergoes isomeric change totrimetaimido phosphoric acid.

4. REACTION WITH AMMONIA : $(NPCl_2)_3$ reacts with ammonia to give various substituted products by replacing chlorine. However in presence of excess ammonia P_3N_5 formed.

USES OF PHOSPHAZENES

1. The phosphonitrilic halides are used as rigid plastics, fibers because they are water proof and fire proof and unaffected by oil and petrol.
2. They are used as catalysts in manufacture of silicones.
3. Thin films of poly(aminophosphazene) are used to cover severe burns because they prevent the loss of body fluids and keep germs out.

Sulphur-Nitrogen Compounds

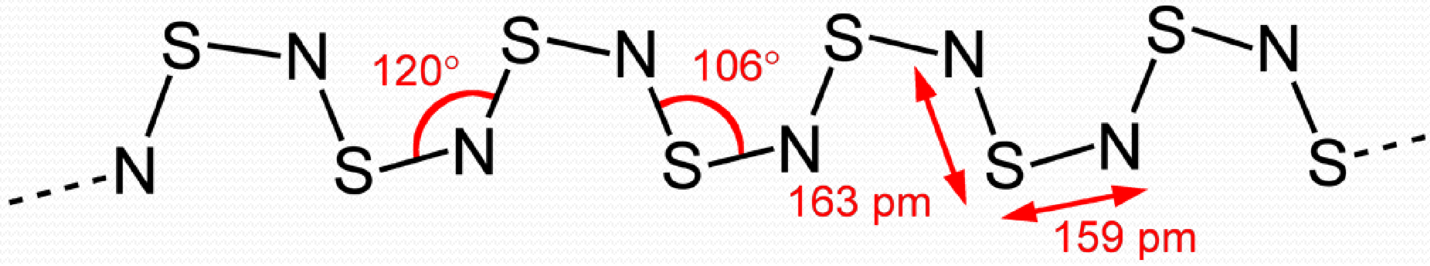
- S–N heterocycles belong to 'electron-rich aromatic compounds' which obey the **Huckel 4n+2 π-electron rule.**

- Each S and each N atom uses **two valence e^-s** for bonding in the σ-system and there is **a lone pair** on each atom.

- **two electrons from each S** and **one electron from each N** form the π-system.

Polythiazyl

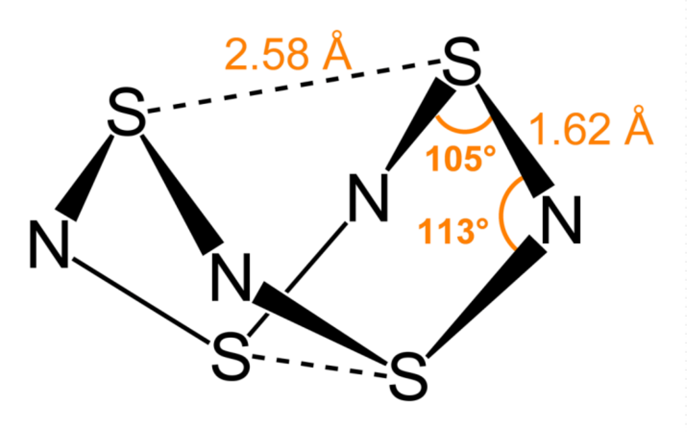
- **Polythiazyl** (polymeric sulfur nitride), $(SN)_x$
- It is an electrically conductive polymer with metallic luster.



Polythiazyl is synthesized by the polymerization of S_2N_2.
Conversion of cyclic tetramer S_4N_4 to dimer S_2N_2 is catalyzed with silver wool.

$$S_4N_4 \rightarrow n\ S_2N_2 \rightarrow (SN)_x$$

Tetrasulfur tetranitride



Tetrasulfur tetranitride S_4N_4.

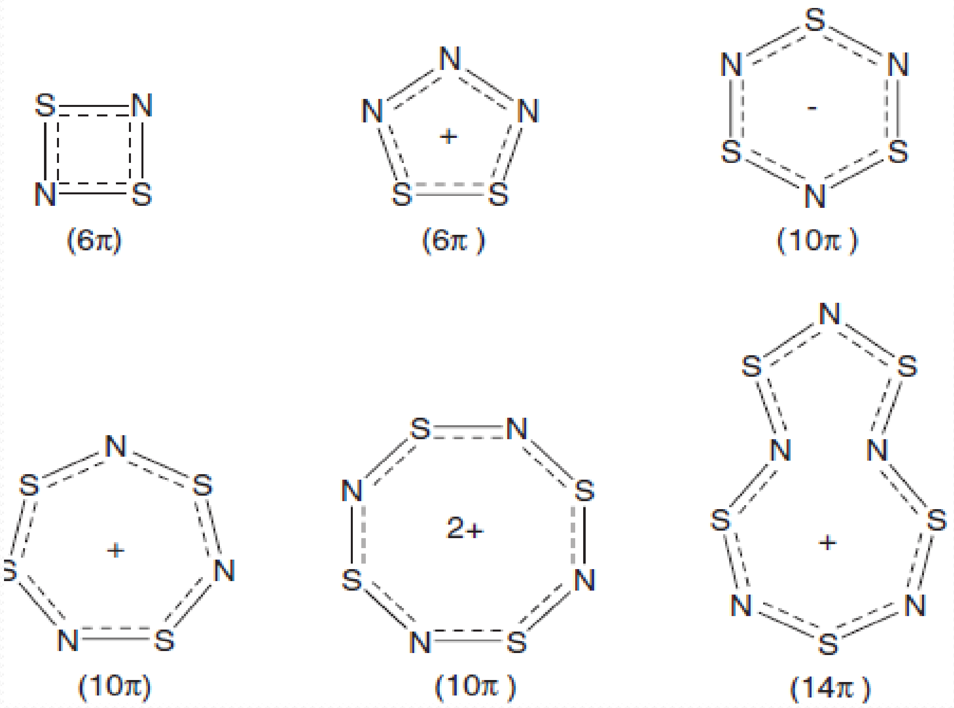
It has cradle structure.

It is a precursor to many S-N compounds

$$4\ NH_4Cl + 6\ S_2Cl_2 \rightarrow S_4N_4 + 16\ HCl + S_8$$

$$24\ SCl_2 + 64\ NH_3 \rightarrow 4\ S_4N_4 + S_8 + 48\ NH_4Cl$$

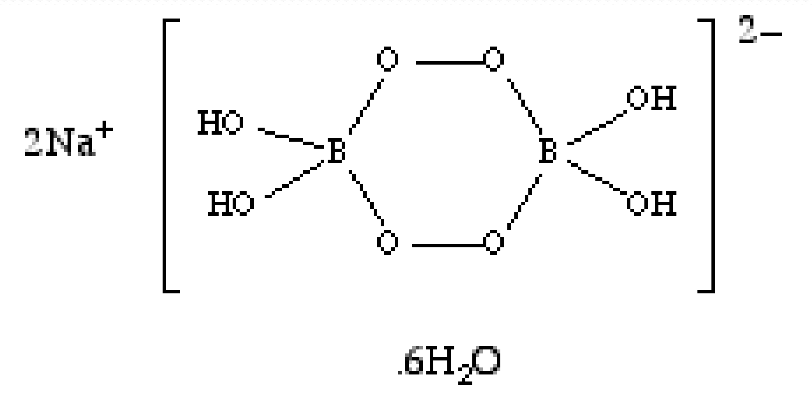
Sulfur-Nitrogen Rings



Peroxo Compounds

Peroxo Compounds of Boron

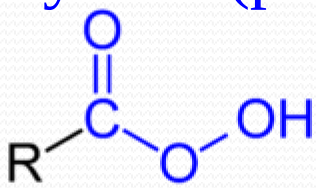
- Sodium perborate (used as bleach)
- $Na_2[B_2(O_2)_2\ (OH)_4].6H_2O$



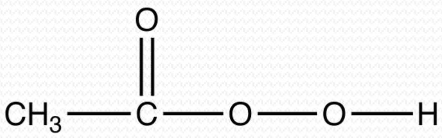
- contains peroxide anion O_2^{-2}
- peroxoanion $[B_2(O_2)_2\ (OH)_4]^{-2}$
- Two tetrahedral units are joined by O-O linkages
- It is stable and liberates oxygen at elevated temperatures.

Peroxo Compounds of Carbon

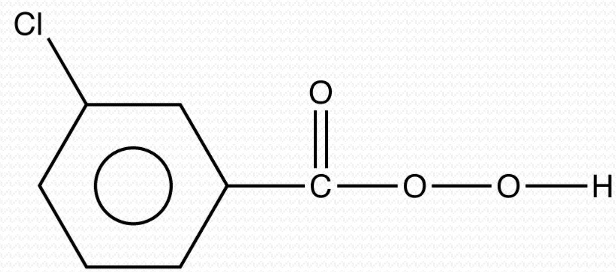
- A peroxy acid (peracid) contains –O–O– linkage.



- $RCOOH + H_2O_2 \longrightarrow RCOOOH + H_2O$
- Peroxycarboxylic acids are about 1000 times weaker than the parent carboxylic acid.



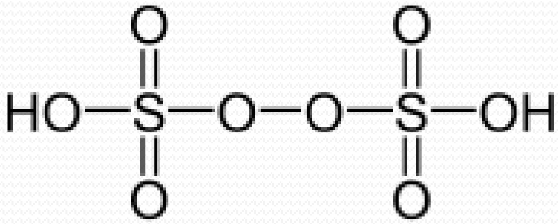
peracetic acid
(peroxyacetic acid)



m–chloroperbenzoic acid
(*m*CPBA)

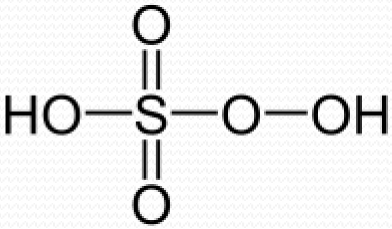
Peroxo Compounds of Sulphur

- **Peroxydisulfuric acid** $H_2S_2O_8$.
- **Marshall's acid.**
- It contains sulfur in its +6 oxidation state.
- Its salts are commonly known as persulfates and are industrially important as powerful oxidizing agents.
- The acid is prepared by the reaction of chlorosulfuric acid with hydrogen peroxide:
- $2ClSO_3H + H_2O_2 \rightarrow H_2S_2O_8 + 2\ HCl$



- **Peroxymonosulfuric acid**, (H_2SO_5), also known as **persulfuric acid**, **peroxysulfuric acid** or **Caro's acid.**
- It contains sulfur in its +6 oxidation state.
- It is one of the strongest oxidants known and is highly explosive.
- The laboratory scale preparation of Caro's acid involve the combination of chlorosulfuric acid and hydrogen peroxide.

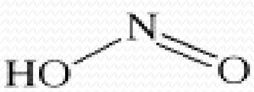
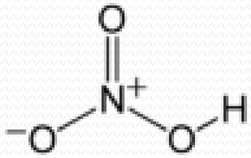
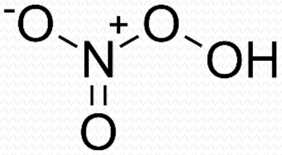
- $H_2O_2 + ClSO_2OH \rightleftharpoons H_2SO_5 + HCl$
- $H_2O_2 + H_2SO_4 \rightleftharpoons H_2SO_5 + H_2O$



Oxyacids

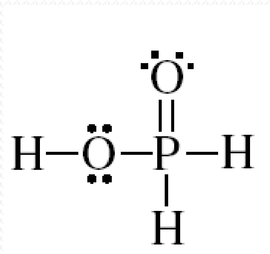
Oxyacids of Nitrogen

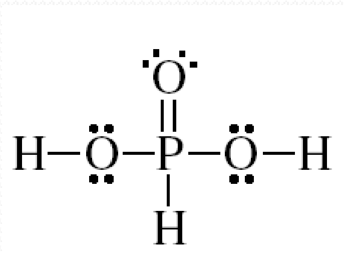
Hyponitrous acid	$H_2N_2O_2$	+1	$2NaNO_2 + 4H_2 \longrightarrow Na_2N_2O_2 \longrightarrow H_2N_2O_2$
Nitrous acid	HNO_2	+3	$Ba(NO_2)_2 + H_2SO_4 \longrightarrow HNO_2 + BaSO_4$
Nitric acid	HNO_3	+5	$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$
Pernitric acid	HNO_4	+5	$H_2O_2 + N_2O_5 \longrightarrow HNO_4 + HNO_3$

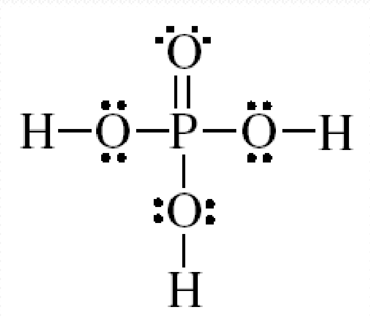





Oxyacids of Phosphorus

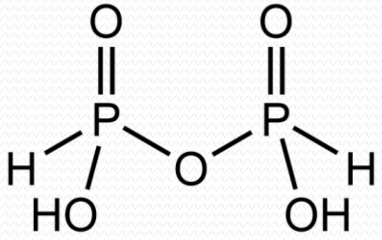
Hypophosphorous acid (Phosphinic acid)	H_3PO_2	+1	$2P_4 + 3Ba(OH)_2 + 6H_2O$
Orthophosphorous acid (Phosphonic acid)	H_3PO_3	+3	$PCl_3 + P_2O_6$
Orthophosphoric acid (Phosphoric acid)	H_3PO_4	+5	$P_4O_{10} + 6H_2O$

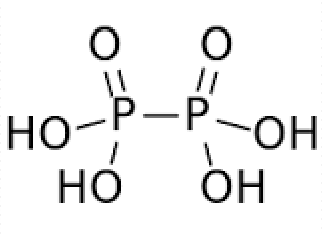


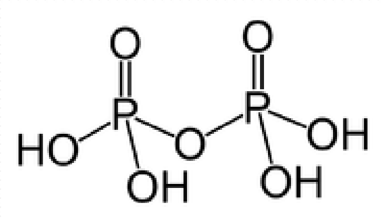




Pyrophosphorous acid	$H_4P_2O_5$	+3	$PCl_3 + H_3PO_3$
Hypophosphoric acid	$H_4P_2O_6$	+4	Oxidation of red P with Na-chlorite solution at RT to form Na-salt and salt passed through cation exchanger.
Pyrophosphoric acid	$H_4P_2O_7$	+5	By heating H_3PO_4 to 250^0C.



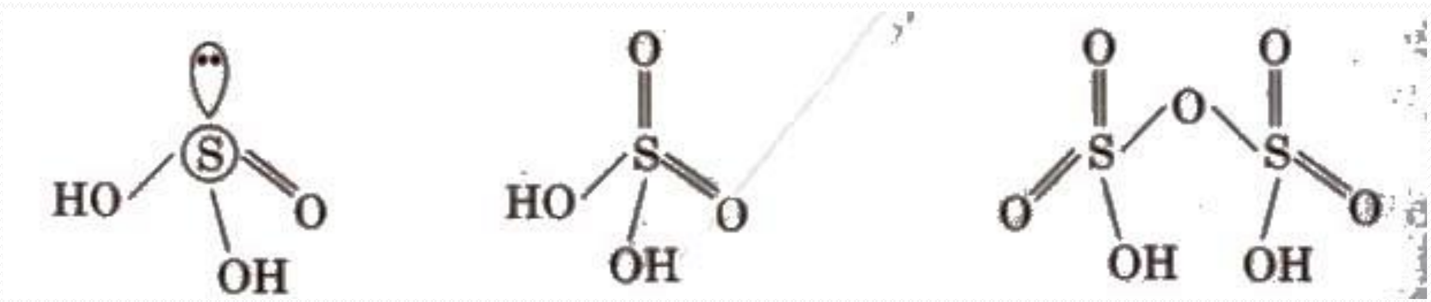




Oxyacids of Sulphur

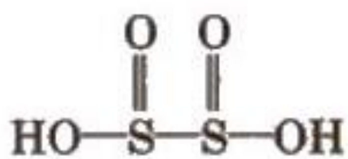
- Sulphurous acid

Sulphurous acid	H_2SO_3	+4	$SO_2 + H_2O$	Pyramidal
Sulphuric acid	H_2SO_4	+6	$SO_3 + H_2O$	tetrahedral
Pyrosulphuric acid	$H_2S_2O_7$	+6	$SO_3 + H_2SO_4$	

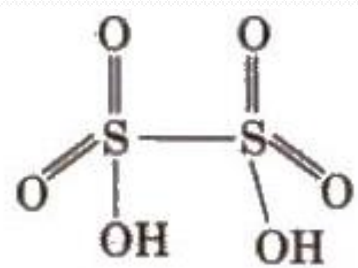


- Thionic acid

Dithionous acid	$H_2S_2O_4$	+3
Dithionic acid	$H_2S_2O_6$	+5

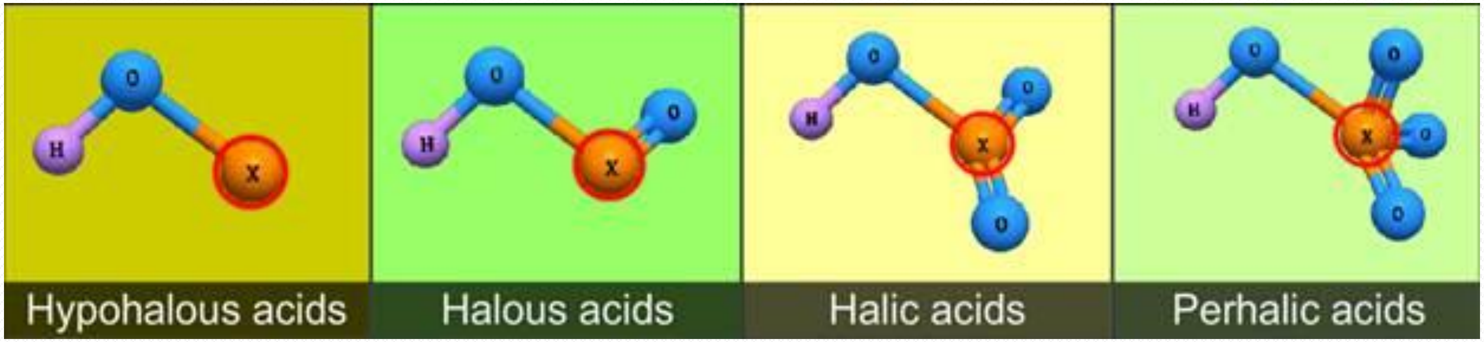


dithionous acid
($H_2S_2O_4$)

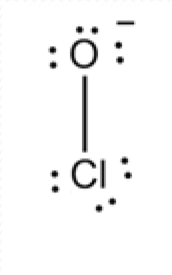


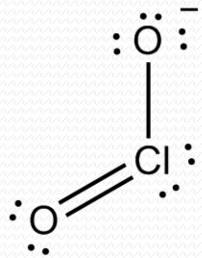
Oxyacids of Halogens

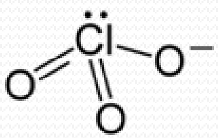
Hypohalous acid	HOX	+1	$2HgO + 2Cl_2 + H_2O$	Linear
Halous acid	HOXO	+3	$Ba(ClO_2)_2 + H_2SO_4$	Angular (V-shape)
Halic acid	$HOXO_2$	+5	$Ba(ClO_3)_2 + H_2SO_4$	pyramidal
Perhalic acid	$HOXO_3$	+7	$KClO_4 + H_2SO_4$	Tetrahedral

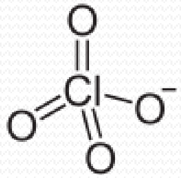


- Hypohalous ions:









hypochlorous	chlorous	chloric	perchloric
linear	angular	pyramidal	tetrahedral

Interhalogens

AX	AX_3	AX_5	AX_7
ClF BrF BrCl ICl IBr	ClF_3 BrF_3 ICl_3	BrF_5 IF_5	IF_7

$$Cl_2 + F_2 \text{ (equal volume)} \xrightarrow{473K} 2ClF \text{ (AX type)}$$

$$I_2 + Cl_2 \text{ liquid (equi molar)} \rightarrow 2ICl \text{ (AX type)}$$

$$Cl_2 + 3F_2 \text{ (excess)} \xrightarrow{573K} 2\,ClF_3 \text{ (}AX_3\text{ type)}$$

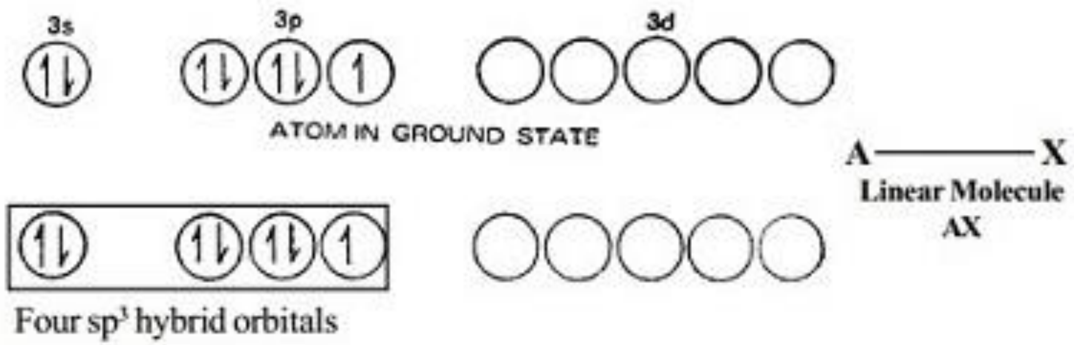
$$Br_2 + 3F_2 \text{ (diluted with nitrogen)} \rightarrow 2BrF_3$$

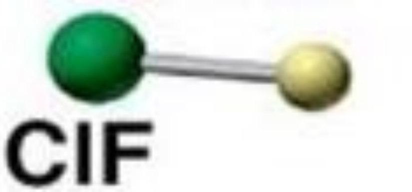
$$Br_2 + 5F_2 \text{ (excess)} \rightarrow 2BrF_5 \text{ (}AX_5\text{ Type)}$$

$$I_2 + 5F_2 \text{ (Excess)} \rightarrow 2IF_5 \text{ (}AX_5\text{ Type)}$$

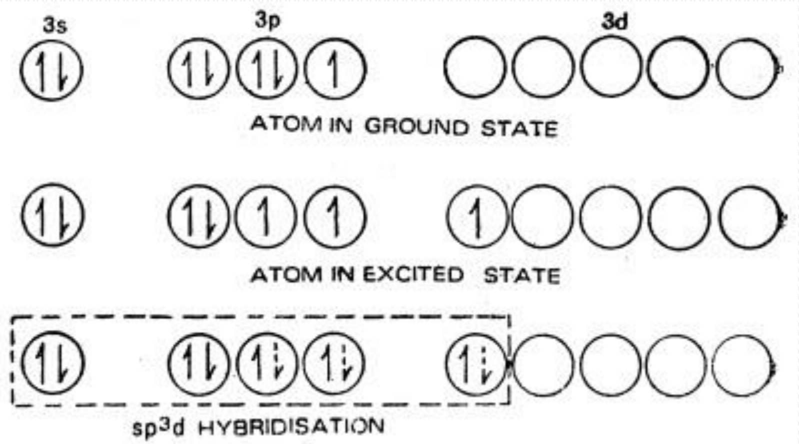
$$IF_5 + F_2 \text{ (Excess)} \xrightarrow{573K} IF_7 \text{ (}AX_7\text{ Type)}$$

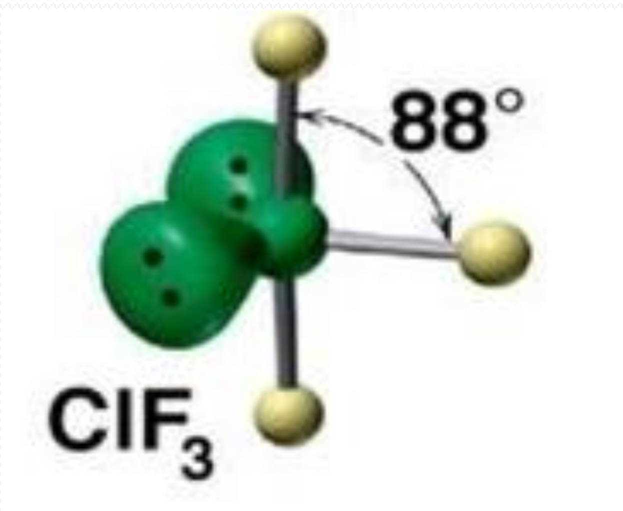
- AX

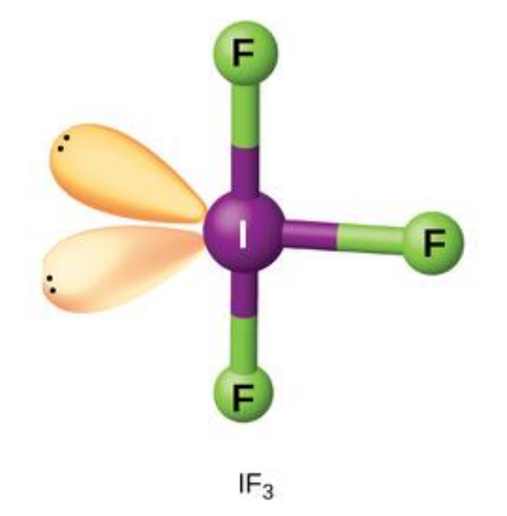

3s
3p
3d
ATOM IN GROUND STATE
A——X
Linear Molecule
AX
Four sp³ hybrid orbitals


ClF

- AX_3

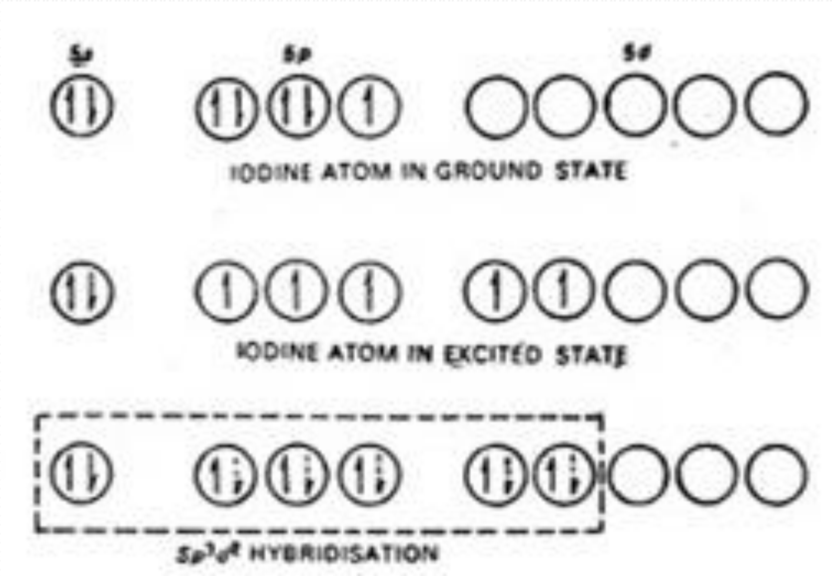

3s
3p
3d
ATOM IN GROUND STATE
ATOM IN EXCITED STATE
sp3d HYBRIDISATION

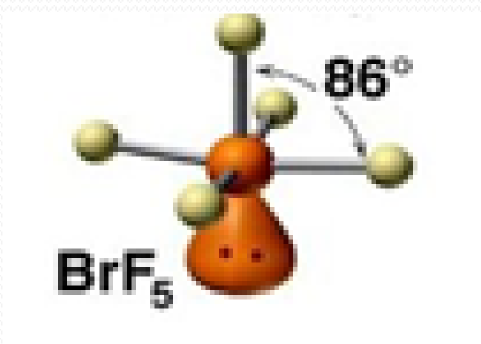

88°
ClF3

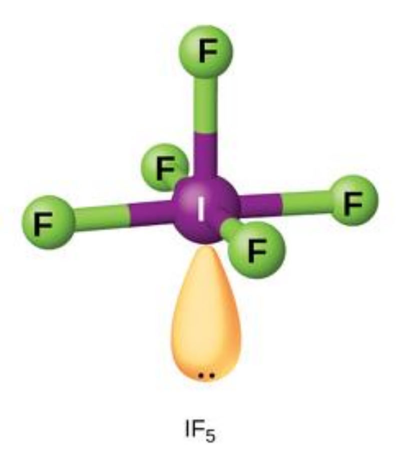

F
F
F
I
IF3

T-shaped

- AX_5

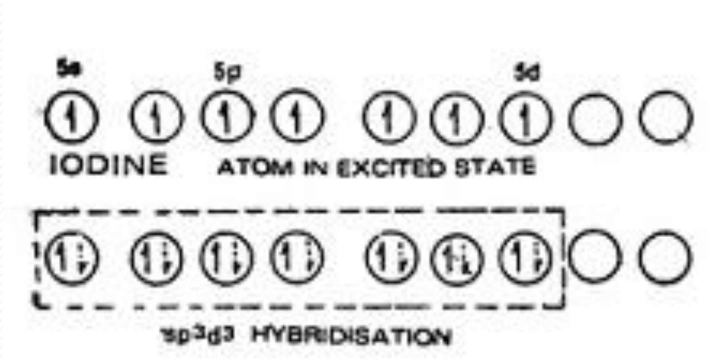


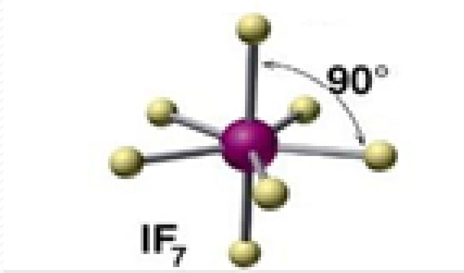


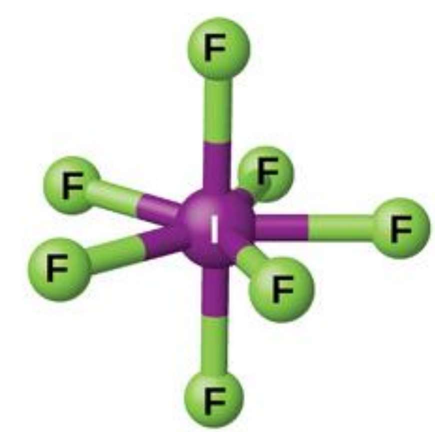


Square pyramidal

- AX_7





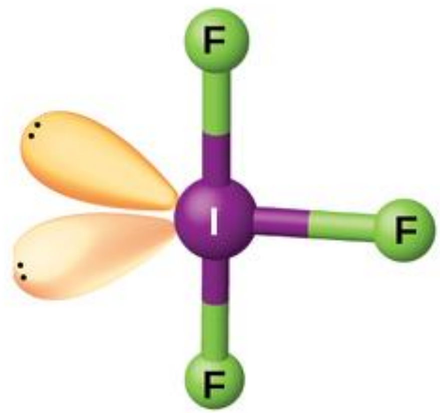


IF_7

Pentagonal bipyramidal

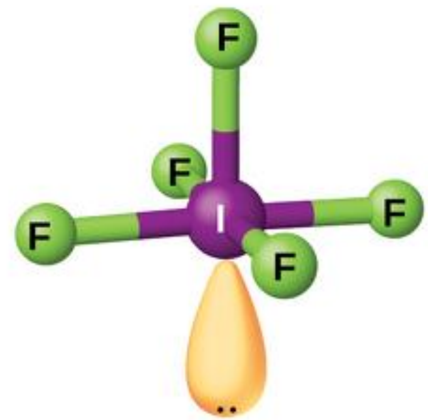
Cl—F

Linear



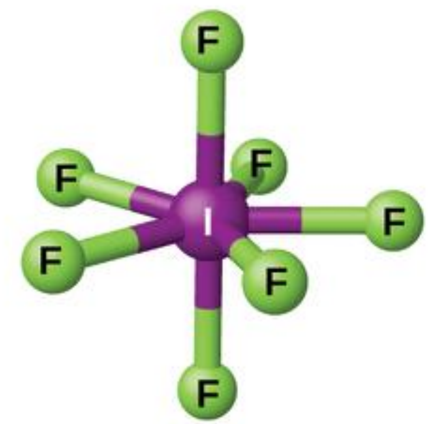
IF_3

T-shaped



IF_5

Square pyramidal



IF_7

Pentagonal bipyramidal

Pseudohalogens

- Polyatomic species resembling to halogens.
- Similar to halogens they form
  - Diatomic molecules.
  - Acids
  - Complexes
  - Salt with Ag

Cl^-	Cl_2	HCl	$[Co(Cl)_6]^{-3}$	AgCl
Pseudohalide	**Pseudohalogen**	**Acid**	**Complex**	**Salt**
CN^- cyanide	$(CN)_2$ cyanogen	HCN Hydrogen cyanide	$[Co(CN)_6]^{-3}$	AgCN
SCN^- Thiocyanate	$(CN)_2$ dithiocyanogen	HSCN Hydrogen thiocyanate	$[Co(SCN)_6]^{-3}$	AgSCN
OCN^- cyanate		HOCN Isocyanic acid		
N_3^- azide		HN3 Hydrazoic acid		

THANK YOU