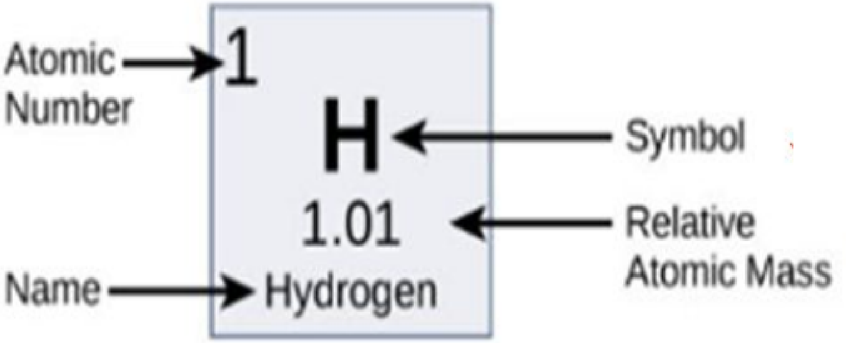
Inorganic Chemistry

Second year

1st semester

Lecture 2



Uniqueness Principle (1st and 2nd row anomlies)

H , He 1st row
Li ,Be ,B ,C, N, O , F, Ne 2nd row

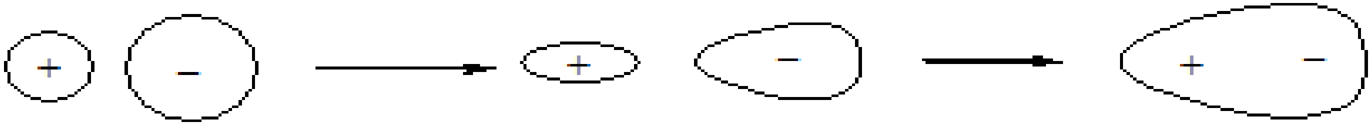
1- $H - e \rightarrow H^+$

it can behave like IA elements
e.g. HX (X=F H Cl Br I) ,O-H, S-H

2- $H + e \rightarrow H^-$ ≡ [He]
hydride anion

exothermic reaction behaves like halogens for having electron
With metals e.g. NaH, CaH_2

the size of H^- ion is larger than X^- (except I^-) because the proton of this anion cannot control the repulsing 2e which make it large and polarizable by small metal cations .It does not extend the trend of halogens (I– F) of decreasing size and increasing basicity and hardness



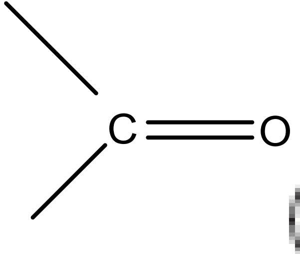
The uniqueness properties of **2nd row elements** are due to

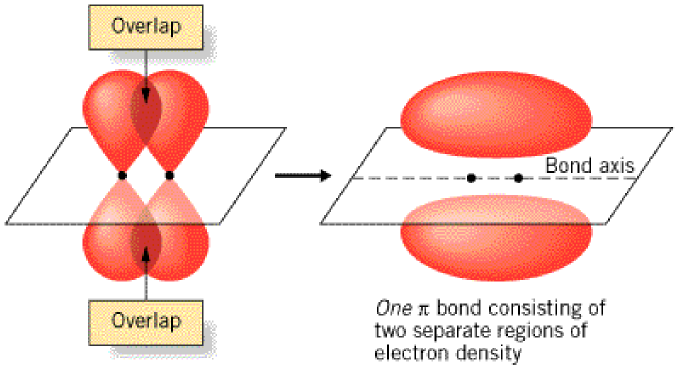
1 – Small size Small size leads to high IP, EA, and larger charge density e.g. F is most Electronegative than its group but EA of F is less than Cl , EA of O is less than S because adding e to these small atoms experience more e-e repulsion than larger atoms in their groups

high nuclear charge density Z*/r of Li, Be, B, C related to small size make covalent compounds of these elements because of high polarizing effect e.g. LiCl is more covalent because it polarizes the chloride anion cloud while NaCl is more ionic because Z*/r is lower and r Na^+> r Li^+ and hence polarizing effect of of Li cation is higher than that of Na cation

2- π (pi) bond formation

The small size of 2nd row elements increase the likelihood of π (pi) bond formation among them and with other elements in the form of **(p π-p π)** **-HC=CH-** $N\equiv N$





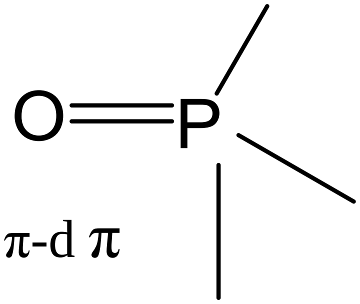
One π bond consisting of two separate regions of electron density

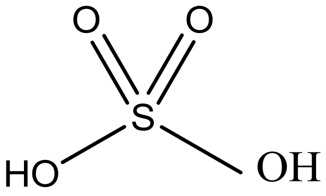
—C≡C—

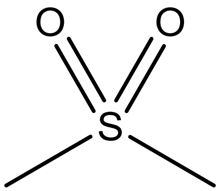
O=O

pπ- pπ

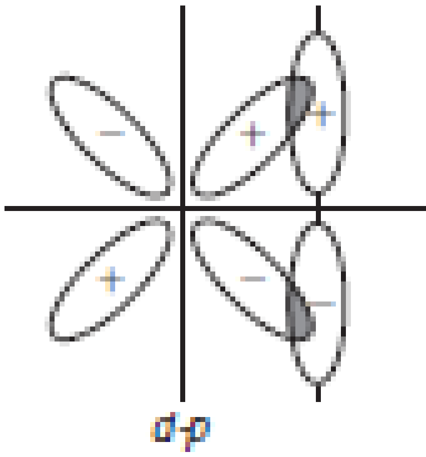
Or **p π-d π** with atoms containing empty d orbitals







Or p π-d π



dπ- pπ

3- The lack of *d* orbitals

It is an obvious fact that the elements Li to F are restricted to the set of 2*s* and 2*p* orbitals but their heavier congeners such as Na to Cl can use 3*s*, 3*p*, and 3*d* orbitals. This provides extra opportunities for bonding in the heavier elements that their lighter congeners do not enjoy.

2nd row elements have octet Lewis structure

valency cannot have more than 4 bonds Maximum C.N=4(8e) or four electron pairs

the second row elements, Li to F, show a maximum covalence of 4, corresponding to a maximum hybridization of sp^3. In contrast, third row and heavier elements show 5, 6, and 7 coordination (Table 15.1) consistent with use of *d* orbitals.

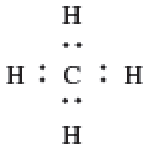


Table 15.1 Maximum Coordination Numbers of the Nonmetals

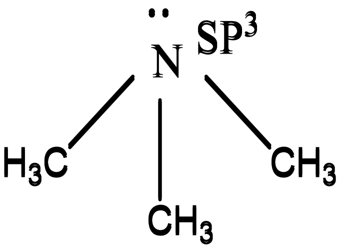
sp^3	CF_4 (**4**)	NF_3[a] (**3**)	OF_2[a] (**2**)	FF (**1**)
sp^3d^2	SiF_6^{-2}	PF_6^-	SF_6	ClF_5
	(**6**)			⋮
				IF_7 sp^3d^3
				(**7**)

electron pairs =4 octet rule,

High C.N=4,5,6,7 have empty d-oritals

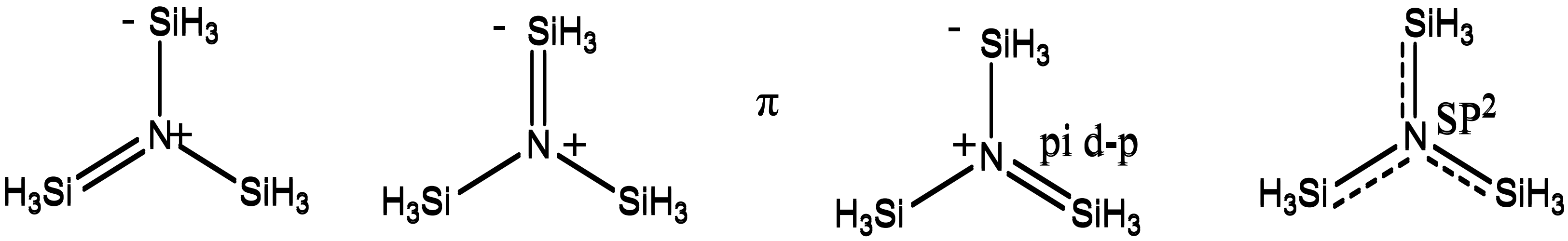
---

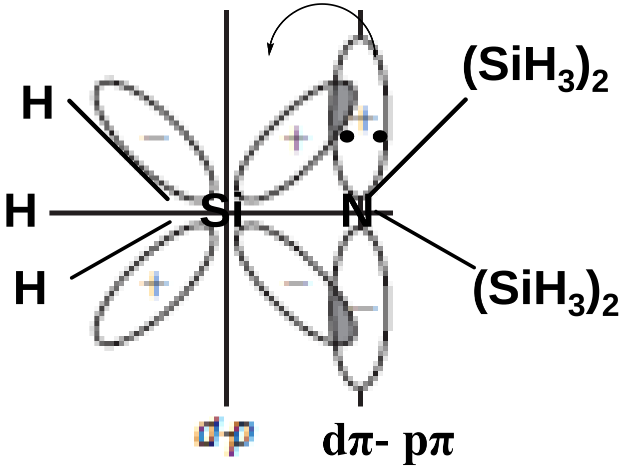
[a] N and O can achieve 4-coordination in onium salts, *e.g.*, NH_4^+.



Trimethyl amine
Lewis base

$N(SiH_3)_3$ is not a Lewis base because the lone pair of the nitrogen atom is of p type orbital which overlap with empty orbital of Si atom to form a Pi bond which is delocalized between the N atom and the 3 Si atoms and hybridization of N becomes SP^2

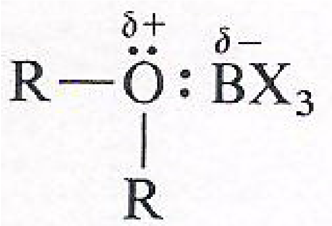




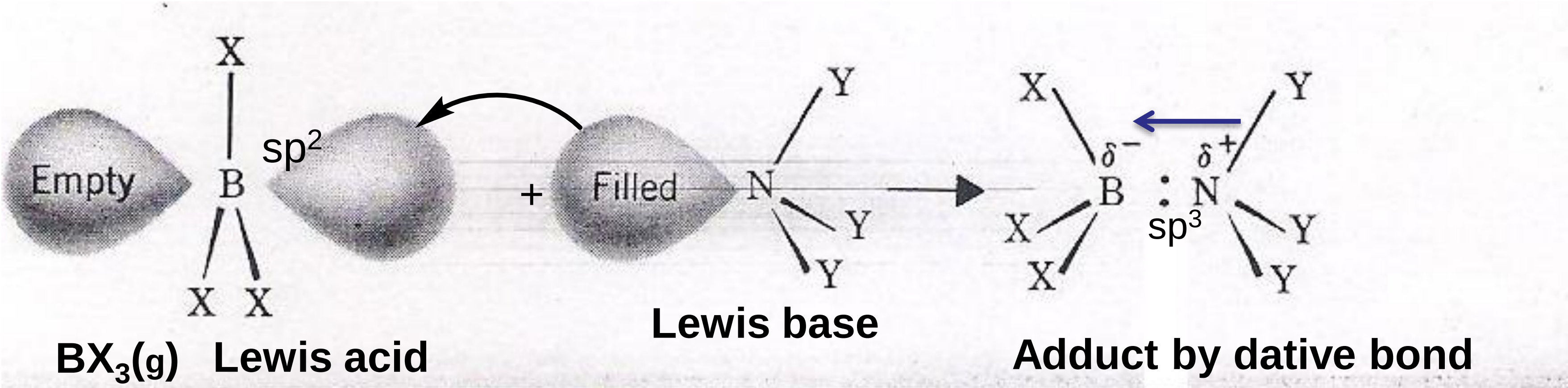
Electron deficient compounds of Gr. 13 act as (Lewis acids)

$BF_3\,(sp^2) + F^- \rightarrow BF_4^-\,(SP^3)$

$BCl_3 + :NH_3 \rightarrow Cl_3B:NH_3$



$R-\overset{\delta+}{\ddot{O}}:\overset{\delta-}{B}X_3$ with a second R on the O



The formation of a dative bond between boron in a BX_3 *acceptor and nitrogen in an* NY_3 *donor.*

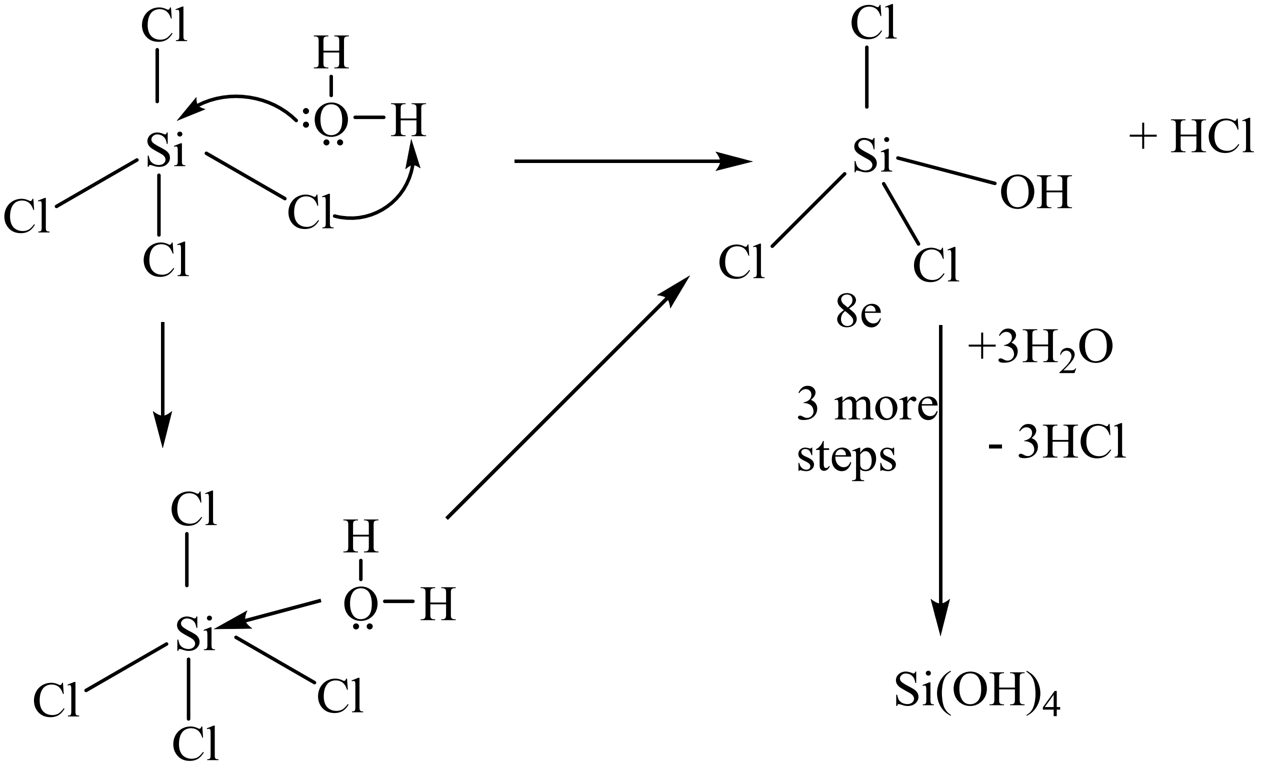
$CCl_4 + H_2O \longrightarrow$ N.R

8e

carbon atom (n=2) cannot exceed octet lewis structure, there is no empty d-orbitals

$SiCl_4 + 4H_2O \longrightarrow Si(OH)_4 + 4HCl$ rapid reaction

8e



Forms extended Lewis
valence structure(10 e)
there are empty d-orbitals (n=3)

* the difference in reactivity of second row elements

- **F** is a super halogen according to its difference from the remainders of gr. 17
- Li → F

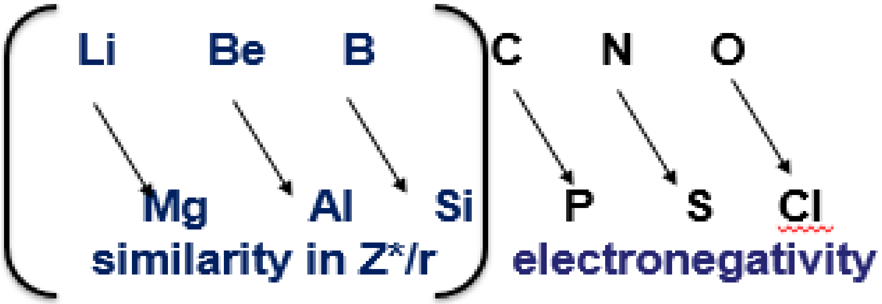
***F** is much **more** reactive than Cl , Br , I while **Li** is **less** reactive than its group

The great polarizing power of Li^+ cation is due to high ionic potential (z/ r) as a result of its **small size** so it destabilizes salts that are stable for other alkali metals .

Therefore in 2nd row elements , the first element is not most representative of the gr.it will be better to choose the second element in each gr.(Na ,Mg , Al , Si , P , S, Cl , Ar) are more representative

Diagonal effect: the top element in each group tends to resemble the second element of the group on the right in chemical and physical properties .

Elements of 2nd row differ in behavior from elements of their groups : Li is resembles Mg rather than its group Na → Cs , Be is closely related to Al than to its group ….etc (diagonal effect) here is related to resemblance in Z*/r of metals . Diagonal effect on non metals is related to resemblance in EN

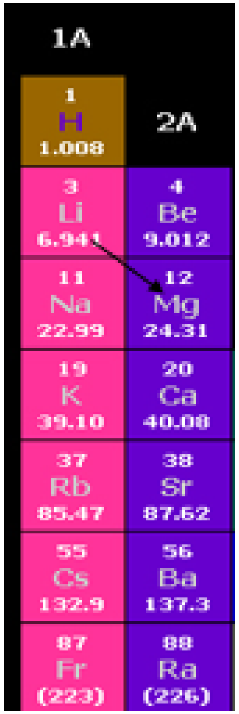


Li Be B C N O

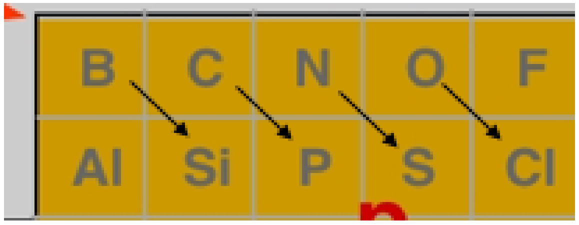
Mg Al Si P S Cl

similarity in Z*/r electronegativity

- Li_2CO_3 + heat → $Li_2O + CO_2$
- $MgCO_3$+ heat → $MgO + CO_2$
- Na_2CO_3 + heat → stable



1A	
1 H 1.008	2A
3 Li 6.941	4 Be 9.012
11 Na 22.99	12 Mg 24.31
19 K 39.10	20 Ca 40.08
37 Rb 85.47	38 Sr 87.62
55 Cs 132.9	56 Ba 137.3
87 Fr (223)	88 Ra (226)



Comparsion of f- elements with d- elements

The transition metal of d-block elements are d-partially filled shells (3d , 4d , 5d , 6d) . The d-orbital is projected well out to the periphery of the atoms and ions . So that the (e) occupying them are strongly influenced by the surrounding of the ion and in turn are able to influence on the environment very significantly . Thus many of the properties of an ion with partially filled d-orbitals are quite sensitive to the number and arrangement of d-electrons .

In marked contrast to this the (4f) orbitals in the lanthanoid elements are **rather deeply buried in the atom and ions**. The electrons that occupy them are largely screened from the surrounding by overlying shell **(5s , 5p)** electrons and therefore reciprocal interaction of (4f) electrons and surroundings of atom or ion are of little chemical importance. As a result the **chemical properties of all Lanthanoids are homologous whereas there are irregular variation in chemical properties of d-block elements**

The behavior of actinides (5f) lies between the two types because the (5f) orbitals are **not so well shielded** as are the 4f orbitals although they are **not so exposed** as are the d-orbital elements , so they **show resemblence to the main transition elements** e.g.

$_{90}Th \longrightarrow {}_{97}Bk$ are available for bonding allowing up to (+7) oxidation state

$_{90}Th$ (+4) $_{91}Pa$ (+5) $_{92}U$ (+6)

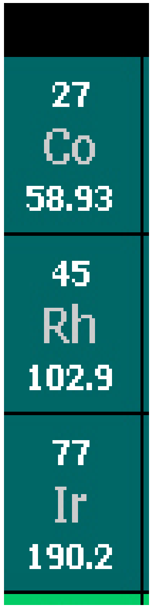
Lanthanoid contraction

There is a general **decrease** from left to right in the **radii** of main tr. metals as well as Lanthanoids this is called **Lanthanoid contraction**

Atomic weight of Rhodium (Rh) = 103 (n = 5 , 4d)
Atomic weight of Iridium (Ir) = 190 (n = 6 , 5d

But the metallic radii of Rh and Ir are almost identical

$_{40}Zr^{4+}$ n=5 (4d) and $_{72}Hf^{4+}$ n=6(5d) have almost identical radii and so are $_{48}Cd(II)$ (n=5)and $_{80}Hg$ (II) ions (n=6) because of weak shielding effect of d & f elements



The metallic radii of the elements of the 3rd transition series are about the same as of the 2nd tr. series in spite of additional shell as a result of lanthanide contraction

Lanthanoid contraction

The effective nuclear charge **Z***(?) experienced by 4f electrons **increases from left to right with increasing atomic numbers** , this is because the **shielding effect** of one (f) electron on the other from the effect of nuclear charge is **quite weak on account of the shapes of the f- orbitals. As a result** effective nuclear charge **Z*** **increases** and hence causes a **shrinkage in the radii** of atoms or ions as one proceeds from **La → Lu** which goes further to d-block of 2nd and third transition series.

Heavy metals and inert valence s^2 electron pair effect

The heavy metals of post transition metals of (period 6) (representative elements) located at at the end of groups :

13	($_{81}$Tl)	$[Xe]4f^{14}\,5d^{10}\,6s^2\,6p^1$
14	($_{82}$Pb)	$[Xe]4f^{14}\,5d^{10}\,6s^2 6p^2$
15	($_{83}$Bi)	$[Xe]4f^{14} 5d^{10}\,6s^2 6p^3$
16	($_{84}$Po)	$[Xe]4f^{14}\,5d^{10} 6s^2 6p^4$

are characterized of low activity of the electron pair of 6s orbitals of valence shell they are more stable when losing the p electrons only to form cations of valence lower than their groups by 2e and their compounds are more stable at low oxidation state and unstable at high oxidation state e.g.

G13 prefer (+3) state but on going down the group Tl is more stable as(+1)
G14 prefer (+4) state but on going down the group Sn, Pb is more stable as(+2)
G15 prefer (+5) state but on going down the group Bi is more stable as(+3)
G16 prefer (+6) state but on going down the group Po is more stable as(+4)

This means that A high ionization potential is required to remove the s electrons from the valence shell because the band gap between 6s and 6p is higher than in smaller elements .The second reason is the low shielding effect of d and f orbitals that increase the nuclear charge Z* on 6s and 5s very high so elements follow filling of d and f orbitals prefer lower ox. state than their groups
Shielding effect s> p>d> f

Oxidation states and oxidation number

* (metals)

Elements farther to the left and down, highly electropositive, High shielding effect, low EN,EA, IP & large r

they intend to lose electrons)Assigned (+) ox. states

* (non metals)

Elements farther to the right and higher up

have high EN,EA, IP,Z* and smaller r)

Assigned a (–) ox. States , so they intend to gain electron

(H = +1, -1)

Gr. IA (1) Li ⟶ Cs [N. g] $ns^1 \rightarrow$ +1 stable

Gr.IIA (2) Be ⟶ Ba [N. g] $ns^2 \rightarrow$ +2 stable

Gr.IIIA(13) B ⟶ Tl [N. g] $ns^2np^1 \rightarrow$ * (+1 , +3)

B Al Ga In *Tl

$\longrightarrow$

increased stability of +1, decreased stability of +3

Gr. IV A (14) [N.g] ns^2np^2

C	Si	Ge	Sn	Pb
+2, **+4**	+2, **+4**	+2, **+4**	+2, **+4**	**+2,** +4

Increased stability of (+2) , decreased stability of (+4)

Increased difficulty to lose ns^2 electron (6s^2)

Gr. VA(15)   [N.g]ns^2np^3

N (−3) with metals

(+1, +2, +3, +4, +5) with nonmetals especially oxygen, and F e.g. NF_3 (+3)

P (−3) with metals

(+3, +5) with oxygen and halogens

As (−3 with IA , +3, +5 with oxygen and halogens)

Sb (+3, +5)

Bi (+3, +5) +5 (unstable, oxidizing agent)

P As Sb Bi

→

Increased stability of (+3) ,Increased difficulty of losing ns^2 electrons

Gr. VIA (16) [N.g] ns^2np^4

O (-2 , -1 , -½ , -⅓) with metals and low EN elements

(-2)	**oxide**	O^{2-}	
(-1)	**peroxide**	O_2^{2-}	
(-½)	**superoxide**	O_2^-	
(-⅓)	**ozonide**	O_3^-	
(+1 , +2)		F_2O , F_2O_2	**only with Fluorine**

S , Se , (−2, +4, +6)

Te −2 (unstable) , +4 , +6

Po <u>(+4</u> , +6)

Gr. VIIA (17) [N.g] $ns^2\ np^5$ (Halogens)

F (-1) with metals & nonmetals
Cl , Br , I (-1) with metals & H

Ox. States +1 , +3 , +5 , +7 with F & oxygen

ClO^-, ClO_2^-, ClO_3^-, ClO_4^-

Gr. IIIA (18) [N.g] ns^2np^6 (noble gases)

He , Ne , Ar **(Inert)**

Kr Xe Rn

$\longrightarrow$

Increased reactivity with oxygen and F

(+2) KrF_2 , XeF_2 , RnF_2

(+4) XeF_4 , (to a less degree $XeCl_4$)

(+6) XeF_6 , XeO_3

(+8) XeO_4 , XeO_6^{4-}

Oxidation states of d- block elements

The *highest* oxidation state of the first five or six elements in each series is equal to the total number of *d* and *s* electrons in the two outer shells.

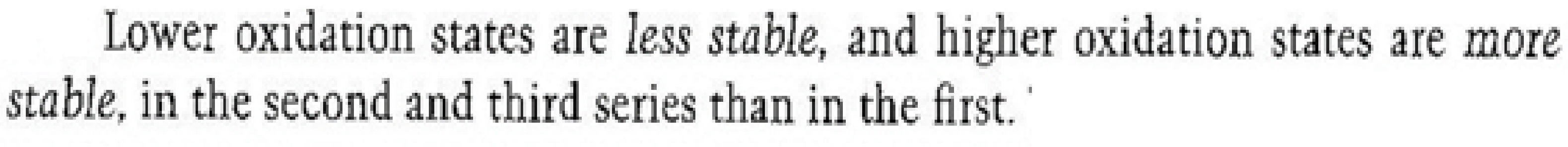
d- block elements with maximum oxidation state

(+3)	Sc	[Ar]	$3d^14s^2$	(+3)	Y	[Kr]	$4d^15s^2$	(+3)	La	[Xe]	$5d^16s^2$
(+4)	Ti	[Ar]	$3d^24s^2$	(+4)	Zr	[Kr]	$4d^25s^2$	(+4)	Hf	[Xe]	$5d^26s^2$
(+5)	V	[Ar]	$3d^34s^2$	(+5)	Nb	[Kr]	$4d^45s^1$	(+5)	Ta	[Xe]	$5d^36s^2$
(+6)	Cr	[Ar]	$3d^54s^1$	(+6)	Mo	[Kr]	$4d^55s^1$	(+6)	W	[Xe]	$5d^46s^2$
(+7)	Mn	[Ar]	$3d^54s^2$	(+7)	Tc	[Kr]	$4d^65s^1$	(+7)	Re	[Xe]	$5d^56s^2$
	Fe	[Ar]	$3d^64s^2$	(+8)	Ru	[Kr]	$4d^75s^1$	(+8)	Os	[Xe]	$5d^66s^2$
	Co	[Ar]	$3d^74s^2$		Rh	[Kr]	$4d^85s^1$		Ir	[Xe]	$5d^76s^2$
	Ni	[Ar]	$3d^84s^2$		Pd	[Kr]	$4d^{10}$		Pt	[Xe]	$5d^96s^1$
	Cu	[Ar]	$3d^{10}4s^1$		Ag	[Kr]	$4d^{10}5s^1$		Au	[Xe]	$5d^{10}6s^1$

Maximum ox. State never exceed the family number in **gr. 3** → **gr.7** by which the elements reach the configuration of noble gas

(+2) oxidation states for 3d metals is unstable for Ti→Cr (reducing) then it becomes more stable starting from Mn→Cu .Beyond Mn the lower ox. State(+2) becomes more stable Fe , Co (+2 , +3) , Ni (+2).

For 4d and 5d transition metals (+2) is not very stable until Pd and Pt are reached .Then it becomes unstable at Ag(+1) nd Au(+1,+3)



Lower oxidation states are *less stable*, and higher oxidation states are *more stable*, in the second and third series than in the first.

Descending down the group from **1st to 2nd to 3rd** transition series the **stability of lower oxidation states decreases** and **Higher oxidation states become more stable** especially in fluorides and oxides

V^{5+} Cr^{6+} Mn^{7+} ← **more Oxidizing**

Nb^{5+} Mo^{6+} Tc^{7+} } **less oxidizing**

Ta^{5+} W^{6+} Re^{7+}

↓ **Increased stability of higher oxidation states**

3d	(VO_3^{-})	$(CrO_4^{=})$	(MnO_4^{-})
4d	(NbO_3^{-})	$(MoO_4^{=})$	(TcO_4^{-})
5d	(TaO_3^{-})	$(WO_4^{=})$	(ReO_4^{-})

↓ **Increased stability of higher oxidation states**

3d << 4d < 5d

←

Decrease stability of high ox. state

$(CrO_4^{=}) > (MoO_4^{=}) > (WO_4^{=})$

←

Increased oxidizing strength

Oxidation states of d- block

3d

21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn
+3	+4 +3 +2 red	+5 ox. +4 +3 +2	+6 ox. +5 +4 +3 +2 red	+7 ox. +6 +5 +4 +3 +2	+6 ox. +4 +3 +2	+4 +3 +2	+4 +3 +2	+3 ox. +2 +1	+2

4d

39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd
+3	+4 +3	+5 +4	+6 +5 +4 +3	+7 +6 +5 +4	+8 | +4 +3 +2	+6 +5 +4 +3 +2	+4 +2	+3 +2 +1	+2

5d

57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg
+3	+4 +3	+5 +4	+6 +5 +4	+7 +6 +5 +4	+8 | +5 +4 +3	+6 +5 +4 +3 +2	+4 +2	+3 +2 +1	+2 +1 $[Hg\text{-}Hg]^{2+}$

Increased stability of high oxidation states

Inner transition elements (rare earth) f-block

Lanthanoids

(+3) is the most stable ox. State for all elements

(+2) exists in $_{63}Eu$ **[Xe]4f ^{7} (half filled shell)**

(+4) exists in $_{58}Ce$ **[Xe]**

Actinoids They show greater variation of oxidation states other than(+3) i.e.

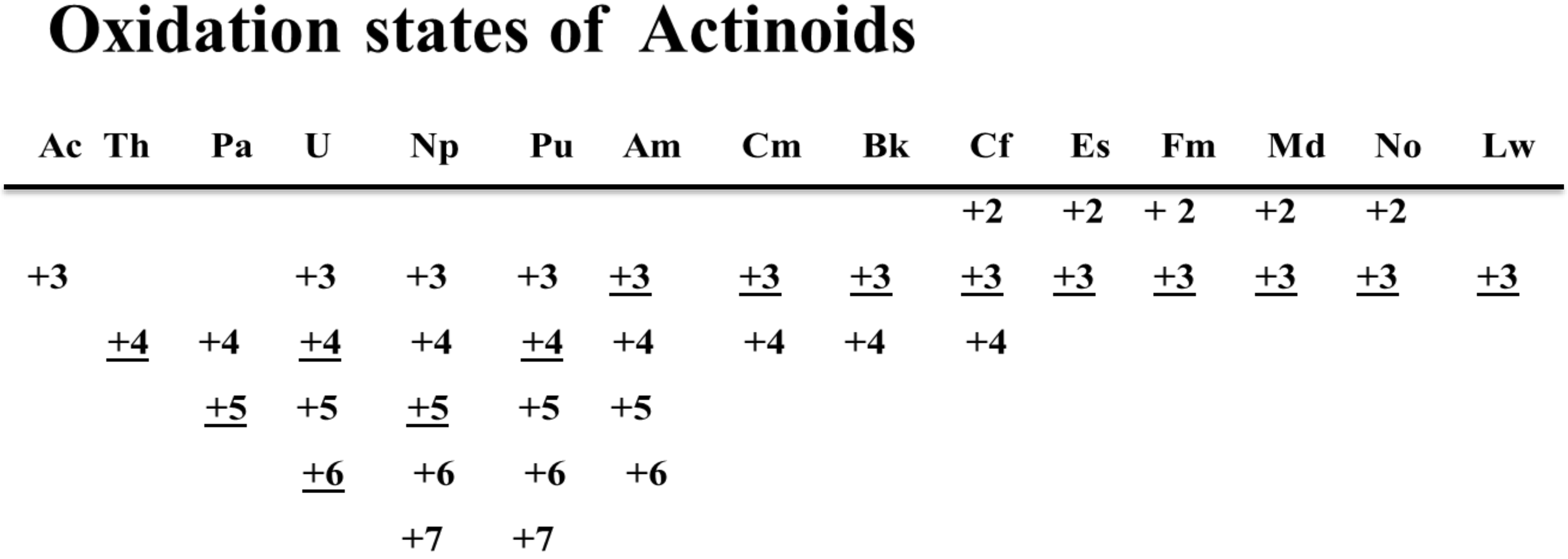
(+4) →(+6) especially from $_{90}Th \longrightarrow {}_{92}U$

until we reach Americium (**$_{95}Am$ [Rn] 5f^7 7s^2**)

where the (+3) become more stable to the end of series

Oxidation states of Lanthanoides

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
-	-	+2	-	+2	+2	-	-	-	-	-	+2	+2	-
+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3
+4	+4	+4					+4	+4					



Oxidation states of Actinoids

Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw
									+2	+2	+ 2	+2	+2	
+3			+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3
	+4	+4	+4	+4	+4	+4	+4	+4	+4					
		+5	+5	+5	+5	+5								
			+6	+6	+6	+6								
				+7	+7									

Fajans rule

1-The ease of ion formation and stability of oxidation state increase with decreased number of gained or lost electrons to reach noble gas configuration

2-Atoms capable of losing electrons are metals(low IP) .The larger the size (r) the more electropositive is the metal the easier to form cations

3- Atoms capable of gaining electrons are non metals(high **Z* , IP , EN , EA)** .The smaller sizes (r) are the more electronegative atoms and the easier to form anions

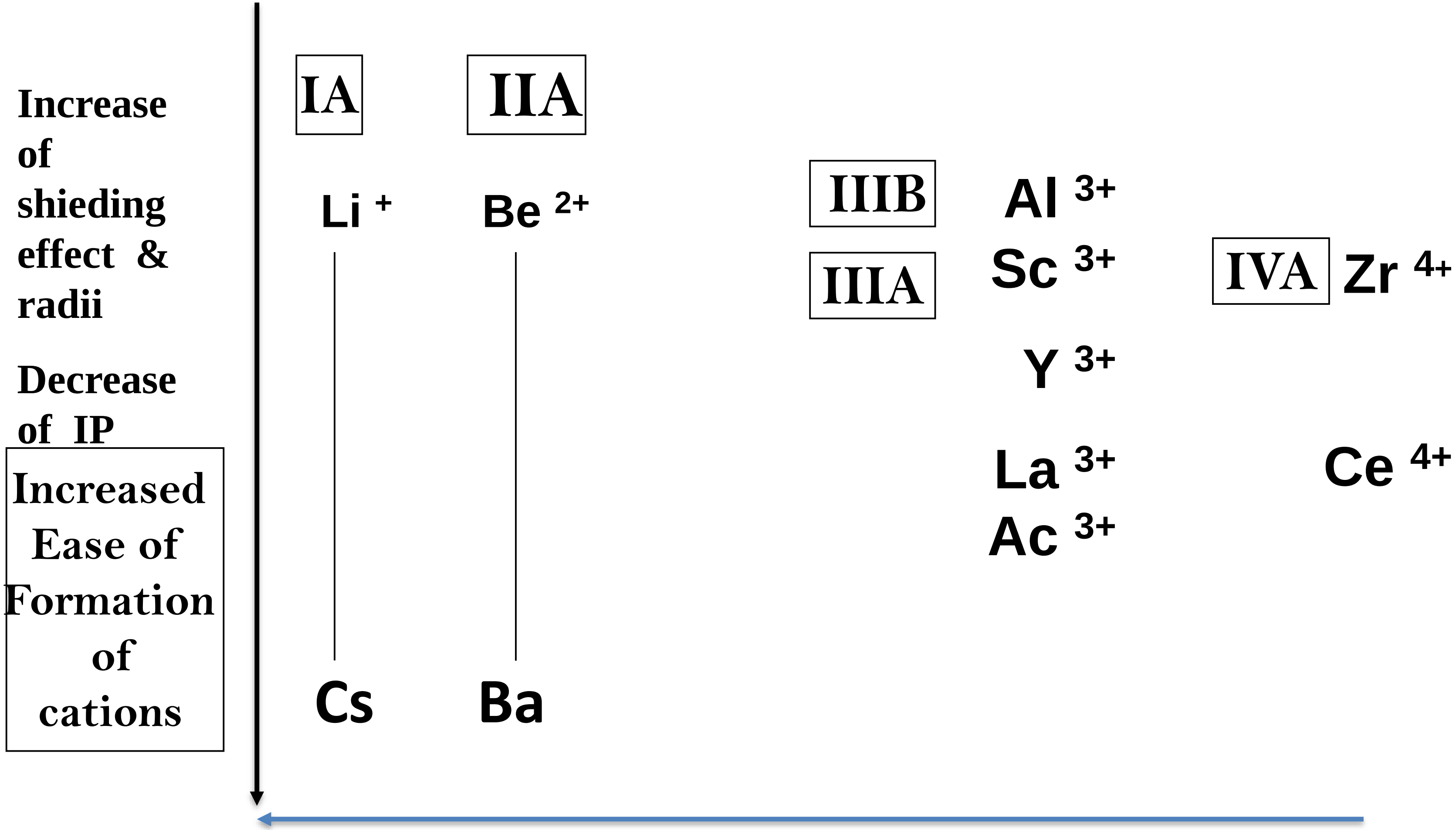
4-losing electrons decrease the size of atom .The **more electrons lost the smaller the sizes of cations**

$\underrightarrow{V^{2+} < V^{3+} V^{4+} < V^{5+}}$ decreased size **of cations**

5-gaining electrons increase the size. The **more electron gaining the larger the size of anions**

$\underrightarrow{O < O^{-} < O^{2-}}$ **increased size of anions**

Ease formation of cations (Fajans rule)



Increase of shieding effect & radii

Decrease of IP

Increased Ease of Formation of cations

IA

Li^{+}

Cs

IIA

Be^{2+}

Ba

IIIB

IIIA

Al^{3+}

Sc^{3+}

Y^{3+}

La^{3+}

Ac^{3+}

IVA

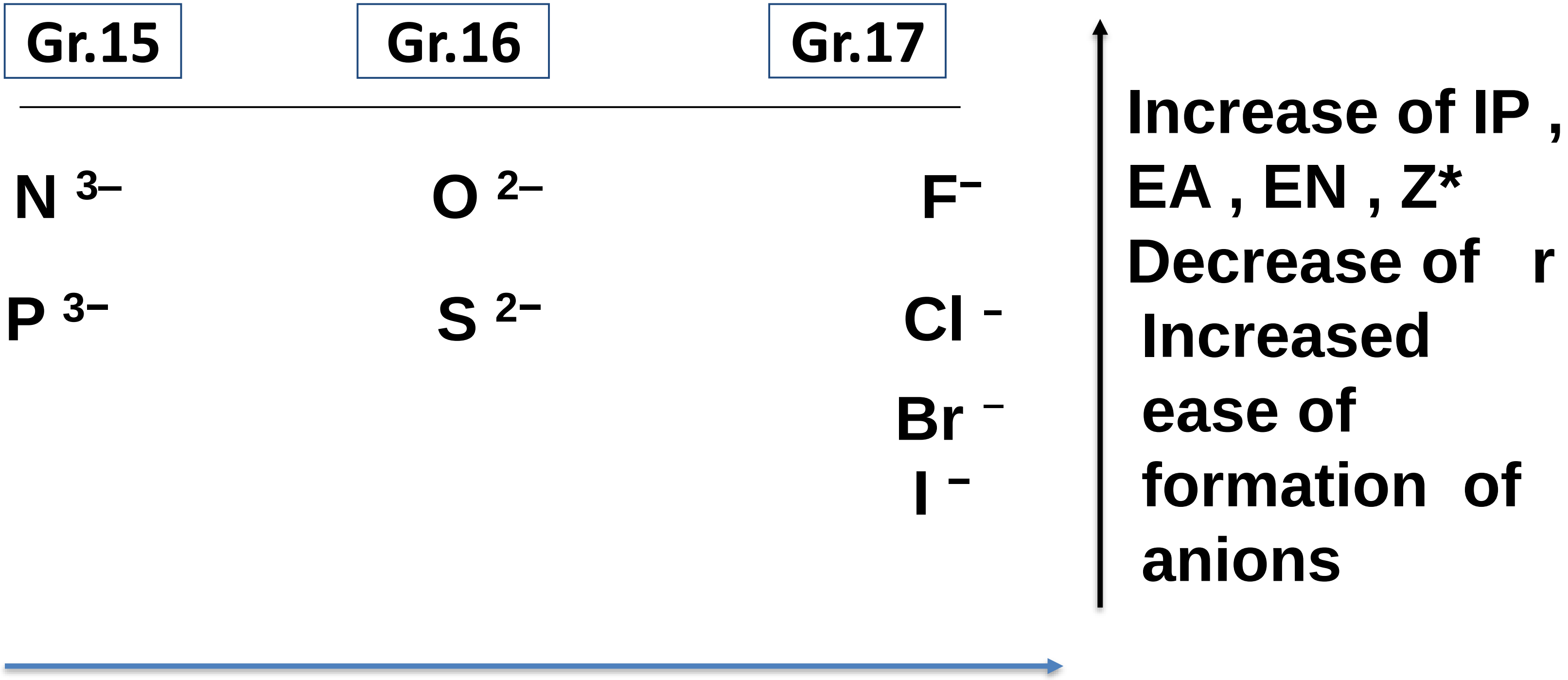
Zr^{4+}

Ce^{4+}

Decrease of lost electrons to reach noble gas configuration

Decrease of IP , increase of r Increased ease of formation of cation

Ease formation of anions with change of r (Fajans rule)



Gr.15 | **Gr.16** | **Gr.17**

N^{3-} O^{2-} F^{-}

P^{3-} S^{2-} Cl^{-}

Br^{-}

I^{-}

Increase of IP , EA , EN , Z*

Decrease of r

Increased ease of formation of anions

Decrease of gained electrons to reach noble gases configuration .

Increase of Z* , IP , EN , EA .

Decrease of r

Increased ease of formation of anions