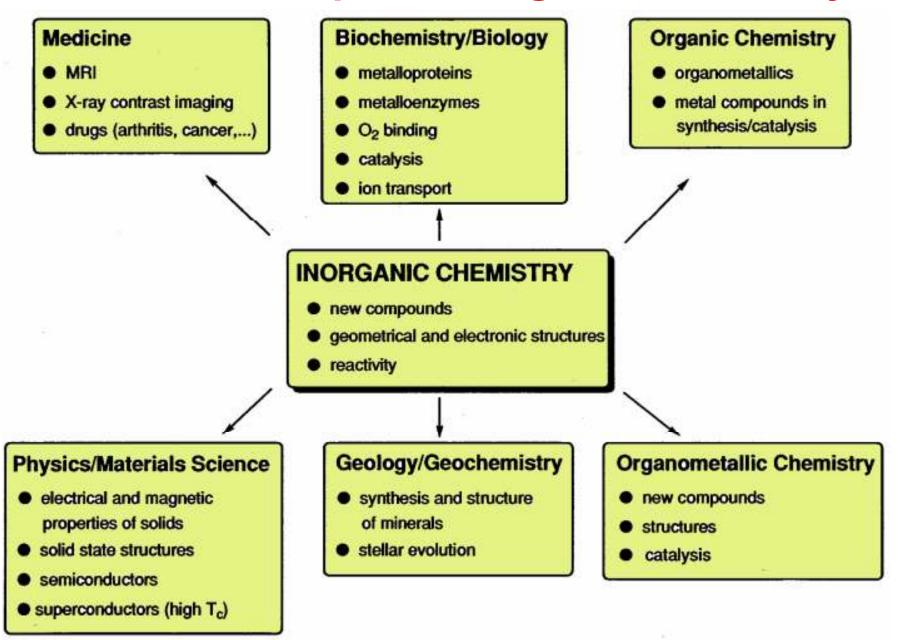
CH105(I)

Part I: Inorganic Chemistry

What is the scope of inorganic chemistry?



Modern Inorganic Chemistry

Inorganic Materials
Inorganic Biological Chemistry
Inorganic Drugs
Organometallic Chemistry
Catalysis
[These Influence life & life style]

These are built based on simple principles of chemistry in general and inorganic chemistry in particular

Modern Inorganic Chemistry: Vast & Vital

Electronic Configuration (s,p,d,f blocks)

Atoms (in elemental or metallic)
lons (in compounds or complexes)
Variable positive or negative charges or oxidation states

Size & charge, ionization potential, electron affinity, oxidation state, redox potential, polarisability, HSAB, coordination characteristics, CFSE,...

Modern Inorganic Chemistry: Vast & Vital

Coordination characteristics

- -Coordination number & geometry (CFSE),
- -Overall charge & size (Redox)
- -Ligating environment (HSAB)
- -Electron density & orbital orientations leading to bonding (covalent, non-covalent & ionic)
- -Ligand exchange & reactivity
- -Physical states (solid, liquid & gas)
- -Atoms (metals, nonmetals, metalloids) to molecules to supramolecules to materials
- -Properties at nano (nanosci. & Tech.) & bulk

Interpretations Explanations Substantiations

Are not necessarily reflected in the slides, but are reflected in the lecture.

Please Do Attend All the Classes.

Please DONOT miss any class

Course Coverage

- 1.Some properties of elements & compounds
- 2. Basic principles of extraction of metals from ores & purification
- 3. Transition metal chemistry & some applications
- 4. Magnetism & some applications
- 5. Biological inorganic chemistry & Inorganic compounds in medicine

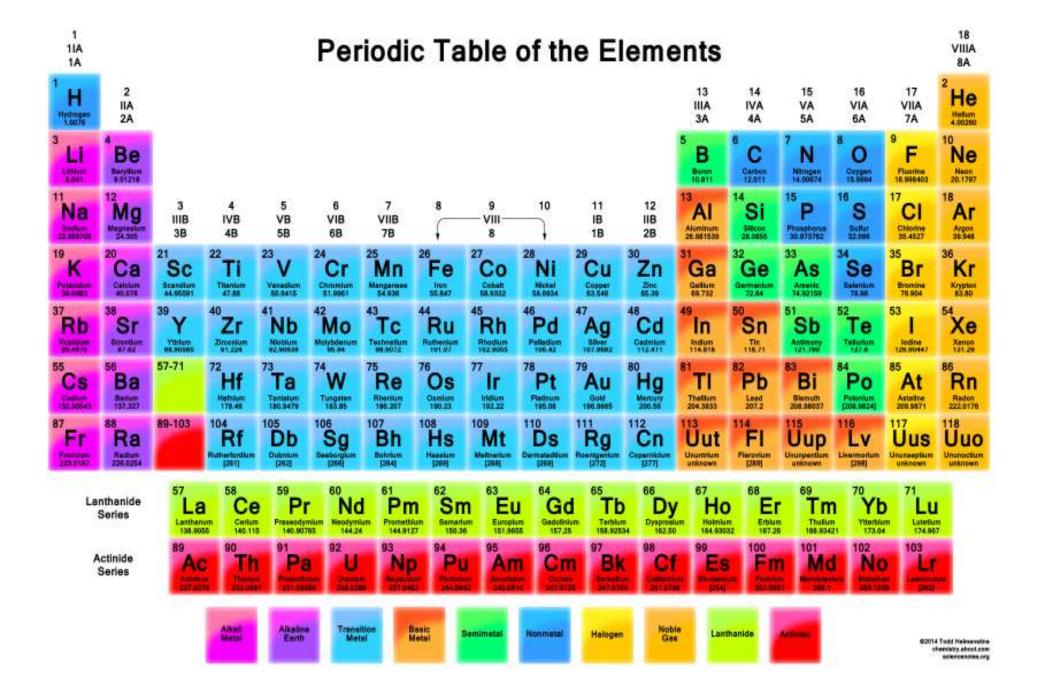
Recommended Text Books

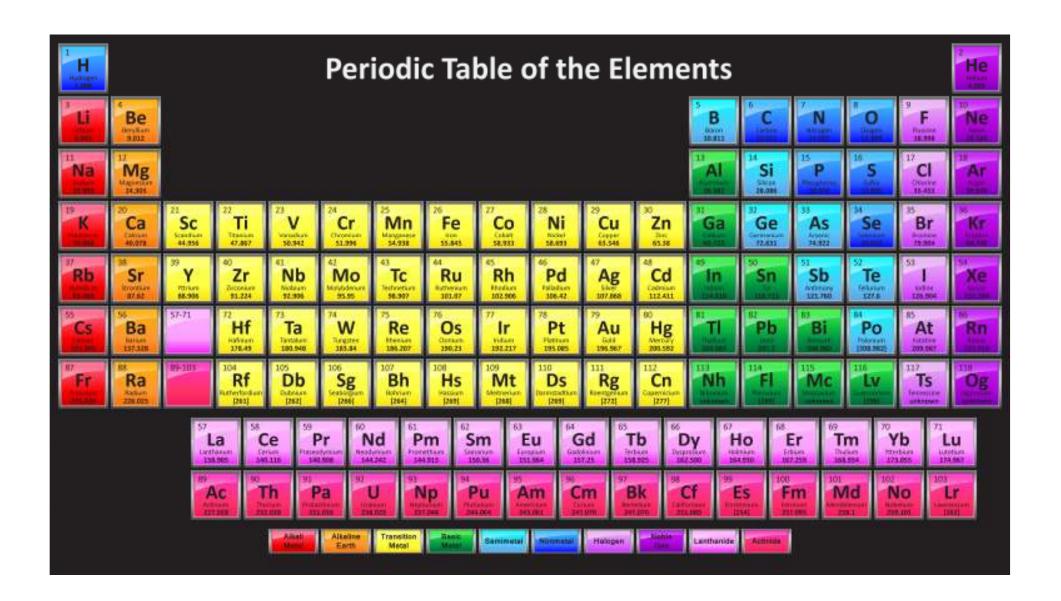
(1) Concise Inorganic Chemistry - J.D. Lee

- (2) Shriver & Atkins' Inorganic Chemistry
- P. Atkins, T. Overton, J. Rourke, M. Weller, F. Armstrong

Topic I

Some properties of elements & compounds





Few concepts which are important in explaining the trends in the properties of atoms (you have already studied)

Effective nuclear charge

Penetration of orbitals

Nuclear influence on electrons

Shielding/Screening

The energy order of orbitals for a given quantum number depends on shielding effects (σ), effective nuclear charge (Z^* or Z_{eff}) & penetration of orbitals

$$Z^* = Z - \sigma$$

How to estimate the Z*? (tutorial) {If the electron resides in s or p orbital}

- 1. Electrons in principal shell higher than the e⁻ in question: contribute 0 to σ
- 2. Each e^{-} in the same principal shell: contribute 0.35 to σ
- 3. Electrons in (n-1) shell: each contribute 0.85 to σ
- 4. Eelectrons in deeper shell: each contribute 1.00 to σ

P.S.: There may be other ways of calculating these as given in the literature. Please stick to this procedure as far as this course is concerned.

How to estimate the Z*? (tutorial) Example: Calculate the Z* for the 2p electron Fluorine (Z = 9) $1s^2 2s^2 2p^5$ Screening constant for one of the outer electron (2p): 6 (six) (two 2s e- and four 2p e-) = 6 X 0.35

= 2.10
2 (two)1s e- = 2 X 0.85 = 1.70

$$\sigma$$
 = 1.70+2.10 = 3.80 & Z* = 9 - 3.80 =

5.20

P.S.: There may be other ways of calculating these as given in the literature. Please stick to this procedure as far as this course is concerned.

How to estimate the Z*? (tutorial) {If the e⁻ resides in a 'd' or 'f' orbital}

- 1. All e⁻'s in higher principal shell contribute 0
- 2. Each e⁻ in the same shell contributes 0.35
- 3. All inner shells in (n-1) and lower contributes 1.00

P.S.: There may be other ways of calculating these as given in the literature. Please stick to this procedure as far as this course is concerned.

Trends in Z* (Z_{eff}): Down a group

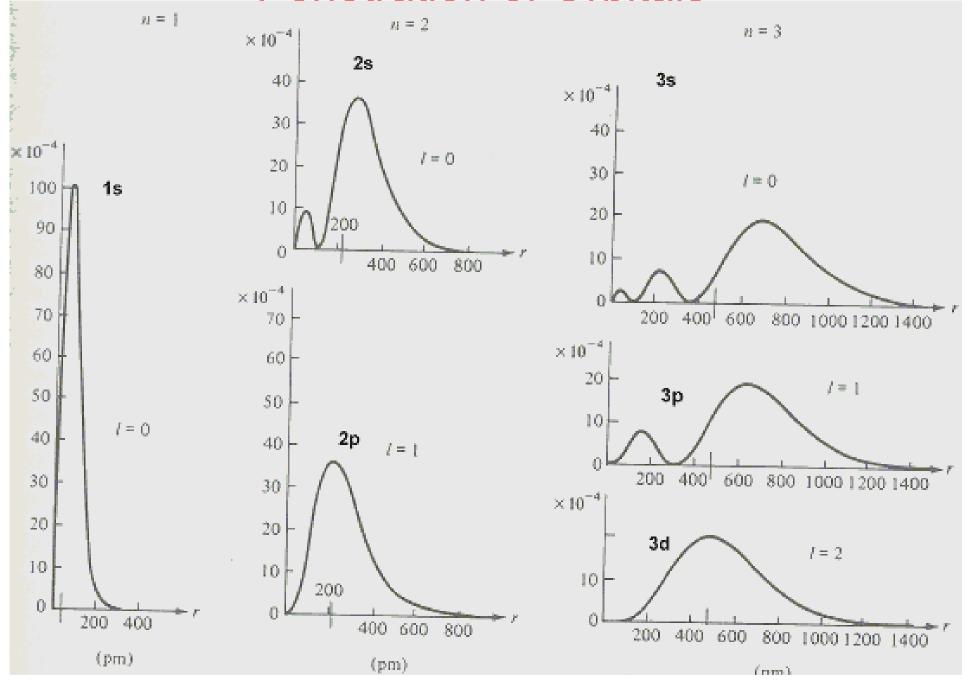
	n	Z	Z *	Effective nuclear
н	1	1	1.0	charge Z* increases
Li	2	3	1.3	very slowly down a
Na	3	11	2.5	group for the
K	4	19	2.2	"valence electron".
Rb	5	37	2.2	Example of Valence
Cs	6	55	2.2	configuration as 'ns ¹ '

Consequence of this?

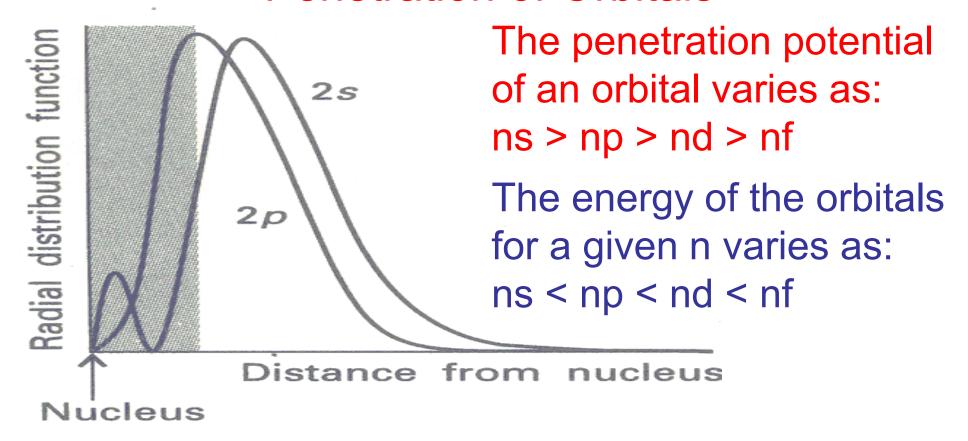
Trends in Z* (Z_{eff}): Across a period

Effective nuclear charge Z* increases rapidly along a period. For example, take period two

Penetration of Orbitals



Penetration of Orbitals



The penetration of 2s electron through the inner core is greater than that of a 2p electron because the latter vanishes at the nucleus. Therefore, the 2s electrons are less shielded than the 2p electrons.

Consequence:Influence of nucleus on e's

Two electrons present in the same d-orbital repel each other more strongly than do two electron in the same s-orbital.

The electrons present in f are much less influenced by the nucleus as compared to d, those present in d much less influenced as compared to p, than s, etc.

It is essential to consider all contributions to the energy of a configuration, and just not one-electron orbital energies.

On going from

Atom → **Molecule** → **Compound** or **Material**

The following properties are important in order to address the compounds formed

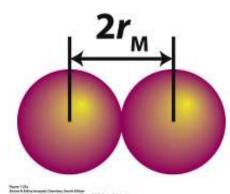
- Atomic size (radius)
- Ionic size (radius)
- Ionization energy
- Electron affinity
- Electronegativity
- Hard soft acid base (HSAB)
- Polarizability
- Oxidation states
- Redox properties

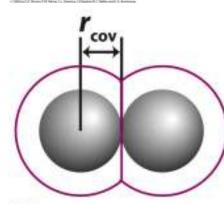
Size (Radius)

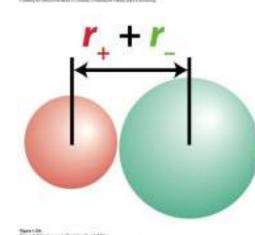
The METALLIC RADIUS is half of the experimentally determined distance between the nuclei of nearest neighbors in the solid

The COVALENT RADIUS of a non-metallic element is half of the experimentally determined distance between the nuclei of nearest neighbors in the solid

The IONIC RADIUS of an element is related to the distance between the nuclei of neighboring cations and anions Ionic radius of O²⁻ is 1.40 Å; What is the ionic radius for Mg²⁺? Measure the Mg-O distance in MgO and subtract 1.40 Å







Trend in Size (Radius)

In a period, left to right: atomic radius decreases

- 1. n (number of shells) remain constant.
- 2. Z increases (by one unit)
- 3. Z* increases (by 0.65 unit)
- 4. Electrons are pulled close to the nucleus by the increased Z*

In a group, top to bottom: atomic radius increases

- 1. n increases
- 2. Z increases
- 3. No dramatic increase in Z* almost remains constant

Trends in atomic radii

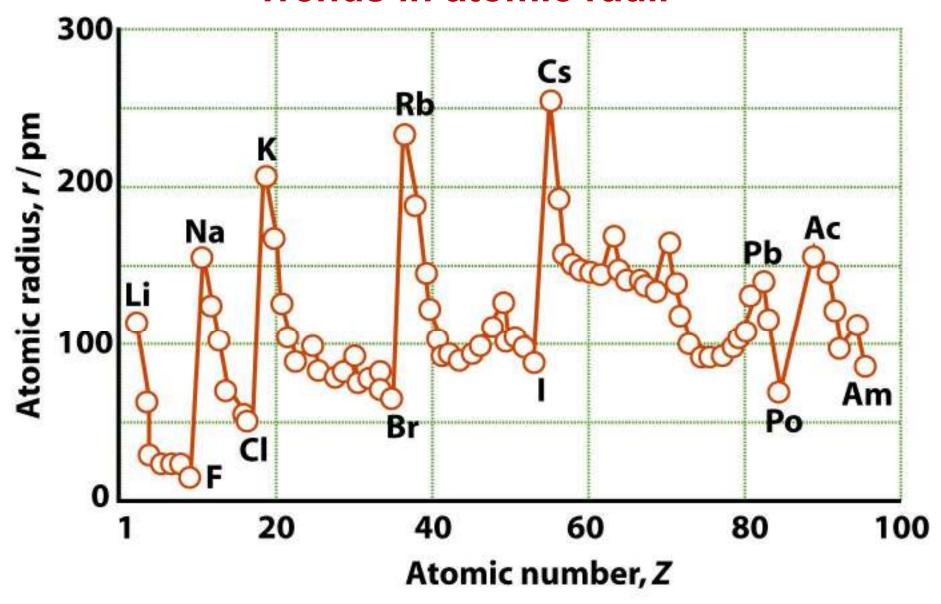


Figure 1-24

Shriver & Atkins Inorganic Chemistry, Fourth Edition

© 2006 by D. F. Shriver, P. W. Atkins, T. L. Overton, J. P. Rourke, M. T. Weller, and F. A. Armstrong

Table of atomic radii

Li	Be											В	C	N	0	F
157	112											88	77	74	66	64
Na	Mg											Al	Si	P	S	CI
191	160											143	118	110	104	99
(Ca	Sc	Ti	٧	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	В
235	197	164	147	135	129	137	126	125	125	128	137	153	122	121	117	11
Rb	Sr	Y	Zr	Nb	Мо	Tc	Ru	Rh	Pd	Ag	Cd	ln	Sn	Sb	Te	1
250	215	182	160	147	140	135	134	134	137	144	152	167	158	141	137	13
Cs	Ba	Lu	Hf	Ta	w	Re	Os	lr	Pt	Au	Hg	Τl	Pb	Bi		
272	224	172	159	147	141	137	135	136	139	144	155	171	175	182		

Decreases with increase in Z in a period Increases moving down a group

Metallic Radius in 5d- elements

Metallic radii of 5d- block elements are expected to be larger than that of the 4d- elements, but found that these are not larger. Of course these are larger than 3d- block elements.

Lanthanide Contraction f-orbitals have poor shielding properties; low penetrating power.

Li+	Be ²⁺	B ³⁺			N^{3-}	0 ²⁻	F ⁻
59(4)	27(4)	11(4)			146	135(2)	128(2)
76(6)						138(4)	131(4)
						140(6)	133(6)
						142(8)	
Na ⁺	Mg ²⁺	Al ³⁺			P ³⁻	S ²⁻	Cl ⁻
99(4)	49(4)	39(4)			212	184(6)	181(6)
102(6)	72(6)	53(6)					
118(8)	89(8)						
K ⁺	Ca ²⁺	Ga ³⁺			As ³⁻	Se ²⁻	Br ⁻
138(6)	100(6)	62(6)			222	198(6)	196(6)
151(8)	112(8)						
159(10)	123(10)						
160(12)	134(12)						
Rb ⁺	Sr ²⁺	In ³⁺	Sn ²⁺	Sn ⁴⁺		Te ²⁻	-
152(6)	118(6)	79(6)	83(6)	69(6)		221(6)	220(6)
160(8)	125(8)	92(8)	93(8)				
173(12)	144(12)						
Cs ⁺	Ba ²⁺	T(3+					
167(6)	149(6)	88(6)					
174(8)	156(8)	Tl ⁺					
188(12)	175(12)	164(6)					

Table of ionic radii

All anions are larger than their parent atoms

The cations are smaller than their parent atoms

^{*} Numbers in parentheses are the coordination number of the ion. For more values, see Resource section 1.

Ionisation Energy (IE)

The minimum energy needed to remove an electron from a gas phase atom

Depends on: (a) Size of the atom - IE decreases as the size of the atom increases; (b) Nuclear Charge - IE increases with increase in nuclear charge; (c) The type of electron - Shielding effect

1st IE: H =1312 KJ mol⁻¹ Li =520 KJ mol ⁻¹

Reasons: (1) Average distance of 2s electron is greater than that of 1s; (2) Penetration effect; 3. Electronic configuration

Trends in Ionisation Energy (IE)

On moving down the group: IE decreases

- 1. nuclear charge increases
- 2. Z* due to screening is (very small) & almost constant down the group
- 3. number of shells increases, hence atomic size increases.
- 4. there is an increase in the number of e's which shield the valence electrons from the nucleus.

On moving across the period: IE increases

- 1. the atomic size decreases
- 2. nuclear charge increases (does not decrease as much as it happens down ar)

Trends in Ionisation Energy (IE)

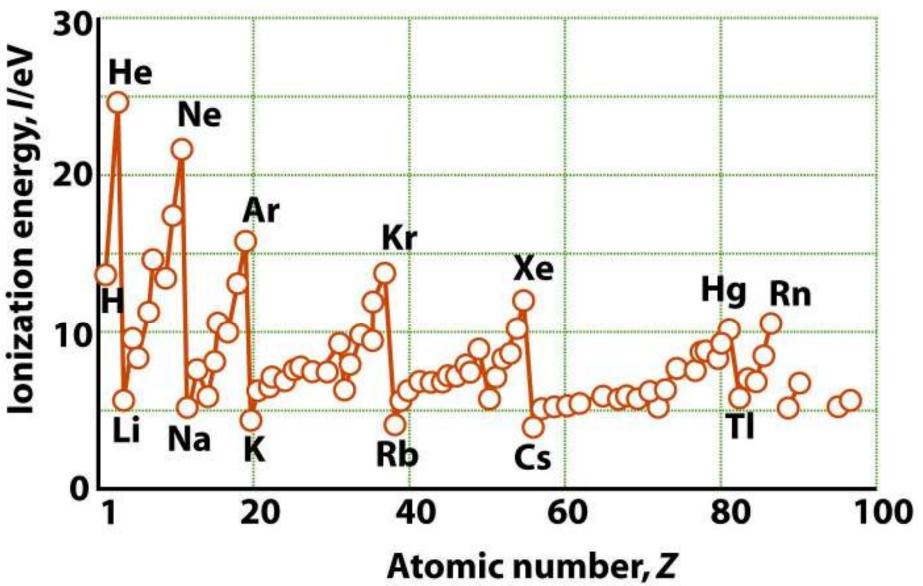


Figure 1-25

Shriver & Atkins Inorganic Chemistry, Fourth Edition

© 2006 by D. F. Shriver, P.W. Atkins, T. L. Overton, J. P. Rourke, M. T. Weller, and F. A. Armstrong

Table 1.6	First and se	cond (and so	me higher)	ionization e	nergies of t	he elements	,
Н							He
1312							2373
							5259
Li	Ве	В	C	N	0	F	Ne
513	899	801	1086	1402	1314	1681	2080
7297	1757	2426	2352	2855	3386	3375	3952
11809	14844	3660	4619	4577	5300	6050	6122
		25018					
Na	Mg	Al	Si	P	S	Cl	Ar
495	737	577	786	1011	1000	1251	1520
4562	1476	1816	1577	1903	2251	2296	2665
6911	7732	2744	3231	2911	3361	3826	3928
		11574					
K	Ca	Ga	Ge	As	Se	Br	Kr
419	589	579	762	947	941	1139	1351
3051	1145	1979	1537	1798	2044	2103	3314
4410	4910	2963	3302	2734	2974	3500	3565
Rb	Sr	In	Sn	Sb	Те	1	Xe
403	549	558	708	834	869	1008	1170
2632	1064	1821	1412	1794	1795	1846	2045
3900	4210	2704	2943	2443	2698	3197	3097
Cs	Ва	π	Pb	Bi	Po	At	Rn
375	502	590	716	704	812	926	1036
2420	965	1971	1450	1610	1800	1600	
3400	3619	2878	3080	2466	2700	2900	
SHOW WELVE			- And Annual Continues	A	will be as all		e was

Table of ionization energies

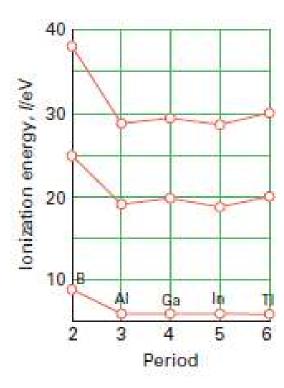


Figure 1.26 The first, second, and third ionization energies of the elements of Group 13. Successive ionization energies increase, but there is no clear pattern of ionization energies down the group.

Electron affinity (EA)

- the amount of energy associated with the gain of electrons

The greater the energy released in the process of taking up the extra electron, greater is the EA

The EA of an atom is a measure of the tightness with which it binds an additional electron to itself.

Trends in Electron affinity (EA)

On moving across a period,

- -As the size decreases, the force of attraction by the nucleus increases. Consequently, the atom has a greater tendency to attract added electron, i.e., EA electron affinity increases
- -Generally the EA's of metals are low while those of non-metals are high
- -Halogens have high EA. This is due to their strong tendency to change their configuration to ns²np⁶

On moving down a group,

- the atomic size increases and therefore, the effective nuclear attraction decreases and thus electron affinity decreases

Thus, electron affinity follows the left-right trend of electronegativity but not the up-down trend.

The following data are quoted in kJ/mol. Elements marked with an asterisk are expected to have negative or near-zero electron affinities on quantum mechanical grounds.

Be -231 Mg *	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
-231 Mg																
-231 Mg																
-231 Mg																He -189
Mg											В	С	N	0	F	Ne
200											27	122	-134	141	328	*
*											Al	Si	Р	S	CI	Ar
											42	134	72	200	349	-110
Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
2	18	8	51	65	(-96)	15	64	112	119		41	119	79	195	324	*
Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	ln	Sn	Sb	Te	1	Хe
5	30	41	86	72	*	101	110	54	126	**:	39	107	101	190	295	(-5
Ва	1200	Hf	Ta	W	Re	Os	lr .	Pt	Au	Hg	TI	Pb	Bi	Po	At	Rr
14	*	(11)	31	79	14	104	150	205	223		36	35	91	(127)	(269)	*
Ra		Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	FI	Mc	Lv	Ts	Og
(10)	**											<u>[</u>			(173)	(5)
	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu	
*		55	93	(16)	(12)	(16)	11	(13)	(42)	(34)	(33)	(30)	99	0	33	
**	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	<u>k</u>
		* 45 Ac	* 45 55 Ac Th	* 45 55 93 ** Ac Th Pa	* 45 55 93 (16) Ac Th Pa U	* 45 55 93 (16) (12) ** Ac Th Pa U Np	* 45 55 93 (16) (12) (16) Ac Th Pa U Np Pu	* 45 55 93 (16) (12) (16) 11 Ac Th Pa U Np Pu Am	* 45 55 93 (16) (12) (16) 11 (13) Ac Th Pa U Np Pu Am Cm	* 45 55 93 (16) (12) (16) 11 (13) (42) Ac Th Pa U Np Pu Am Cm Bk	* 45 55 93 (16) (12) (16) 11 (13) (42) (34) Ac Th Pa U Np Pu Am Cm Bk Cf	* 45 55 93 (16) (12) (16) 11 (13) (42) (34) (33) Ac Th Pa U Np Pu Am Cm Bk Cf Es	* 45 55 93 (16) (12) (16) 11 (13) (42) (34) (33) (30) Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm	* 45 55 93 (16) (12) (16) 11 (13) (42) (34) (33) (30) 99 Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md	* 45 55 93 (16) (12) (16) 11 (13) (42) (34) (33) (30) 99 0 Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No	* 45 55 93 (16) (12) (16) 11 (13) (42) (34) (33) (30) 99 0 33 Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr

The number mentioned is Electron affinity in kJ/mol (rounded)

For the equivalent value in eV, see: Electron affinity (data page)

* Denotes elements that are expected to have negative or near-zero electron affinities on quantum mechanical grounds Parentheses denote predictions

Electronegativity

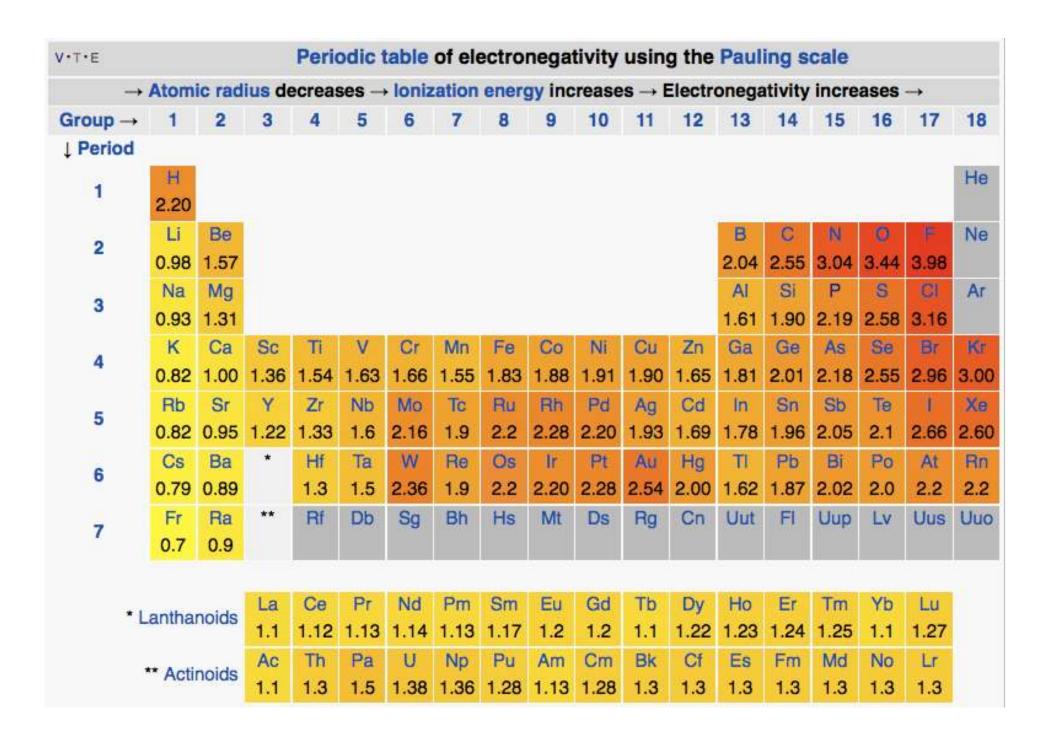
measure of the tendency of an element to attract electrons to itself (from its neighbour)

On moving down the group: EN decreases

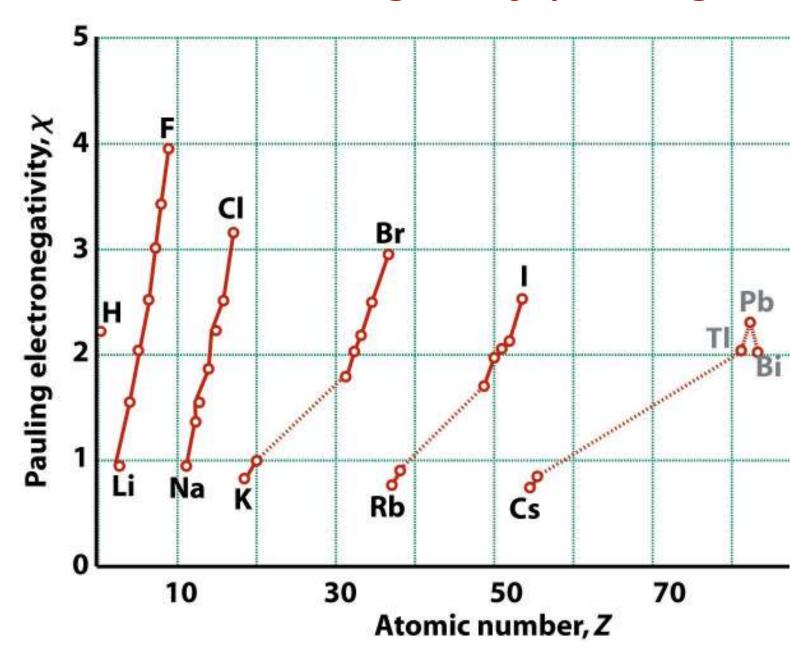
- -Z increases but Z* almost remains constant
- -number of shells (n) increases
- -atomic radius increases
- -force of attraction between added electron and nucleus decreases

On moving across a period: EN increases

- -Z and Z* increases
- -number of shells remains constant
- -atomic radius decreases
- -force of attraction between added electron and nucleus increases



Trends in electronegativity (Pauling scale)



Polarizability

The polarizability of an atom is its willingness to be distorted by the electric field generated by the neighbouring atom or ion.

The polarizability is greater when the electron cloud can be easily distorted, which is common with the atoms having unfilled atomic orbitals which lie close to the highest energy filled orbitals.

Small & highly charged cations have greater polarizing ability Large & highly charged anions are easily polarized Cations not possessing noble-gas e- configuration are easily polarized

Ionization limit Zin (a) (b)

(for example, heavy atoms & ions)

Figure 1.28 The interpretation of the electronegativity and polarizability of an element in terms of the energies of the frontier orbitals (the highest filled and lowest unfilled atomic orbitals). (a) Low electronegativity and polarizability; (b) high electronegativity and polarizability.

- E denotes the strength of the electric field and
- α is the polarizability constant with units of C m²V⁻¹.

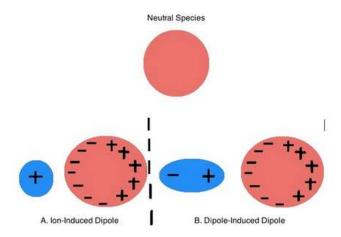


Figure 1.1: A neutral nonpolar species's electron cloud is distorted by A.) an Ion and B.) a polar molecule to induce a dipole moment.

In general, polarizability correlates with the interaction between electrons and the nucleus. The amount of electrons in a molecule affects how tight the nuclear charge can control the overall charge distribution. Atoms with less electrons will have smaller, denser electron clouds, as there is a strong interaction between the few electrons in the atoms' orbitals and the positively charged nucleus. There is also less shielding in atoms with less electrons contributing to the stronger interaction of the outer electrons and the nucleus. With the electrons held tightly in place in these smaller atoms, these atoms are typically not easily polarized by external electric fields. In contrast, large atoms with many electrons, such as negative ions with excess electrons, are easily polarized. These atoms typically have very diffuse electron clouds and large atomic radii that limit the interaction of their external electrons and the nucleus.

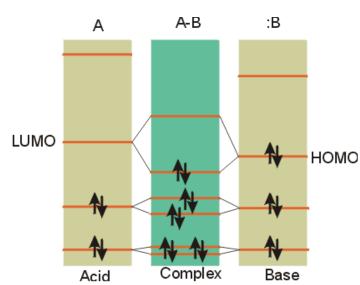
Hardness and Softness [Chemical but not mechanical] An important concept (HSAB) of compounds formed

Chemical Hardness or Softness of an atom can be correlated with ionization energy (IE), electron affinity (EA), size and polarizability. If the IE > EA, the EA can be ignored.

High IE, smaller size, low polarizability -- makes Harder

Low IE, larger size, high polarizability -- makes softer

The lighter atoms of a group are chemically harder The heavier atoms of a group are chemically softer

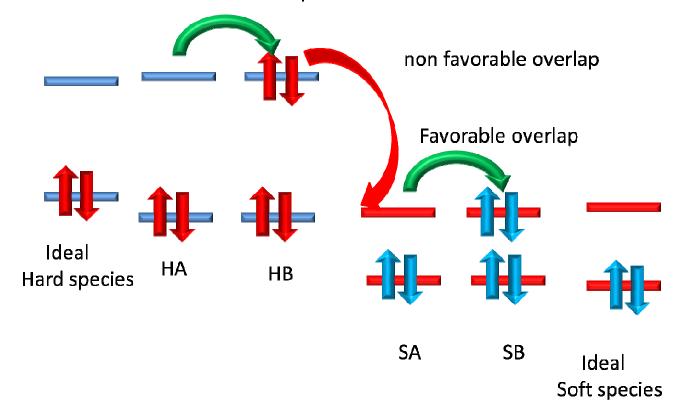


HSAB: Conceptual

The LUMO and HOMO are called frontier orbitals.

If there is a net lowering of energy, the adduct is stable.

Favorable overlap



Hardness and Softness

The difference between the IE of a neutral atom and its anion: If it is more, the hardness is more & if it is less, the hardness is less or it will be softer.

Pearson's Absolute Hardness $\eta = \frac{I - A}{2}$

Same as saying that the separation between the two frontier orbitals is large it is hard and if small it is soft. .ie. I= HOMO energy and A=LUMO energy

Therefore,

Hard acids tend to bind to hard bases preferentially Soft acids tend to bind to soft bases preferenctially

Example for HSAB

SCN⁻ can bind through either S or N depending upon the HSAB nature of the metal ion.

For eg., Si or Pt

N will prefer Si due to Hard ... Hard type interactions, since 'N' is hard Lewis base, & 'Si' is hard Lewis Acid.

S will prefer Pt due to Soft ... Soft type interactions, since 'S' is soft Lewis base & 'Pt' is soft Lewis Acid

Trends are exhibited,

By keeping the metal same and changing the anion/ligand

By keeping the anion/ligand same and changing the metal

Bonding/Interction types: Covalent, Non-covalent, Ionic

Non-covalent interactions are WEAK Interactions (between atoms & between molecules)

Atoms → **Molecules** → **Supramolecules** → **Materials or Solids**

Hydrogen bonding interactions lon – molecular interactions Vander Waal's interactions

Van der Waal's Interactions

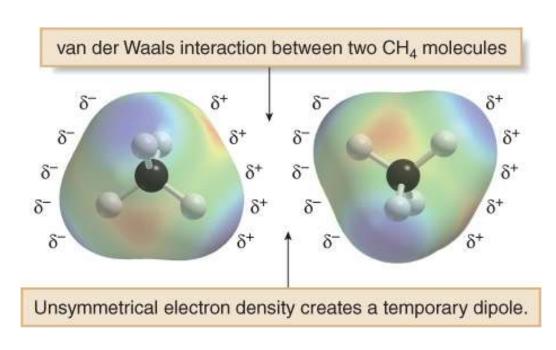
Three types of Van der Waal's interactions:

- (a) Dipole Dipole Interactions
- (b) Dipole Induced Dipole Interactions
- (c) Induced Dipole Induced Dipole Transient Dipole – Transient Dipole (London Dipersion Forces)

van der Waals Forces (self reading)

- van der Waals forces are also known as London forces.
- They are weak interactions caused by momentary changes in electron density in a molecule.
- They are the only attractive forces present in nonpolar compounds.

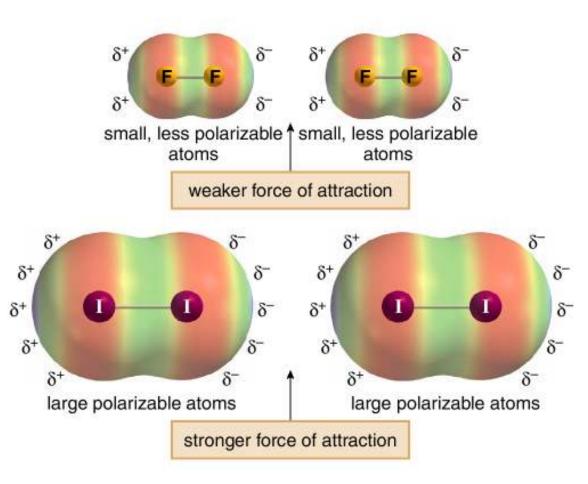
Even though CH₄ has no net dipole, at any one instant its electron density may not be completely symmetrical, resulting in a temporary dipole. This can induce a temporary dipole in another molecule. The weak interaction of these temporary dipoles constitutes van der Waals forces.



van der Waals Forces (self reading)

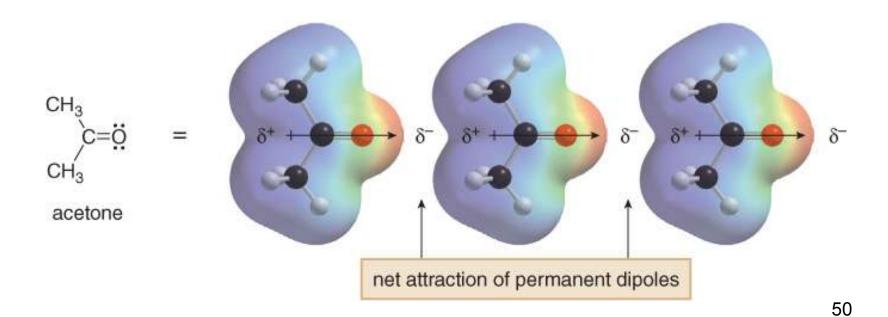
- van der Waals forces are also affected by polarizability.
- Polarizability is a measure of how the electron cloud around an atom responds to changes in its electronic environment.

Larger atoms, like iodine, which have more loosely held valence electrons, are polarizable than more smaller atoms like fluorine, which have more tightly held electrons. Thus, two F₂ have little molecules attractive force between δ⁺ them since the electrons 8+ tightly held are and dipoles temporary are difficult to induce.



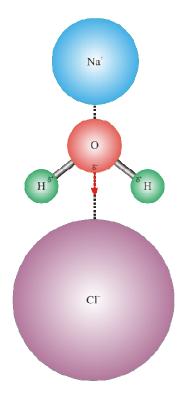
Dipole-Dipole Interactions (self reading)

- Dipole—dipole interactions are the attractive forces between the permanent dipoles of two polar molecules.
- Consider acetone (below). The dipoles in adjacent molecules align so that the partial positive and partial negative charges are in close proximity. These attractive forces caused by permanent dipoles are much stronger than weak van der Waals forces.



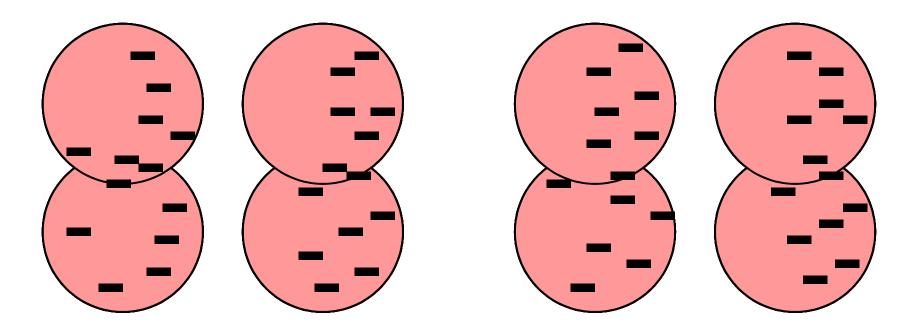
Ion-Dipole (self reading)

- Permanent dipole interacts with an ion.
- This explains for example the solubility of NaCl in water.
- The figure below shows the interaction of Na⁺ and Cl⁻ ions interacting with the permanent dipoles in a water molecule.



London forces (self reading)

Instantaneous dipole: Induced dipole:



are situated so that tiny dipoles form

Eventually electrons A dipole forms in one atom or molecule, inducing a dipole in the other

IUPAC Nomenclature of elementsWith atomic number above 100 (tutorial)

Digit	Name	Abbreviation	
• 0	nil	n	
• 1	un	u	E. g.,
• 2	bi	b	114
• 3	tri	t	
• 4	quad	q	Ununquadium
• 5	pent	р	Uuq
• 6	hex	h	118
• 7	sept	S	Ununoctium
• 8	oct	Ο	
• 9	enn	е	Uuo