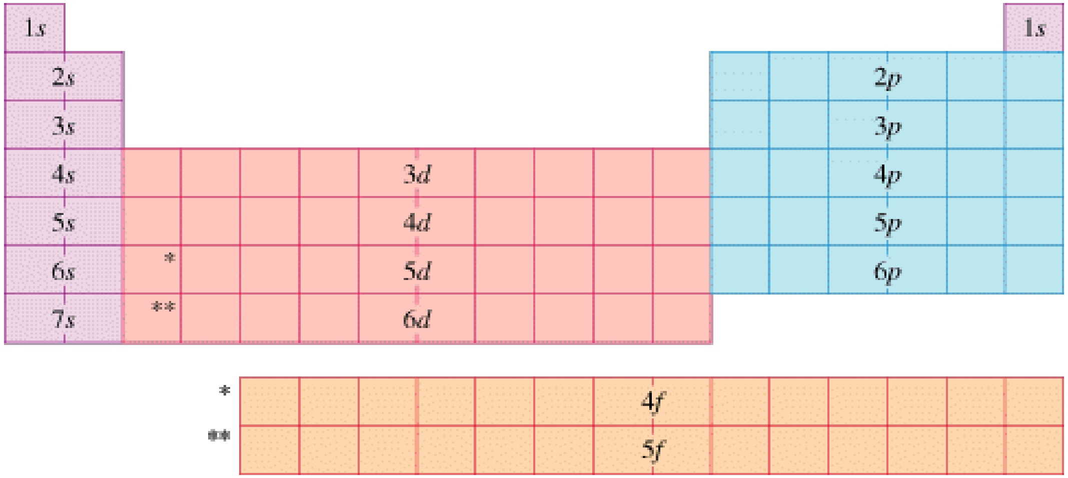
Periodic Properties

Dr. Bapan Saha
Assistant Professor, Chemistry
Handique Girls' College

Periodic Table

- Periodic Table is arguably the most important concept of Chemistry
- An awareness of Periodic Table is essential in Chemistry
- It is basically the classification of elements in a systematic way.
- Classification rationalizes the known chemical facts and helps in predicting the new.
- Contributors
  - Dobereiner
  - Newlands
  - Mendeleev
  - Meyer
  - Moseley



Periodic Table - Where and how did it come from?

- **Johann Dobereiner**

  - Triads (groups of 3 elements with similar characteristics, the middle one's mass is about equal to the average of the other two)

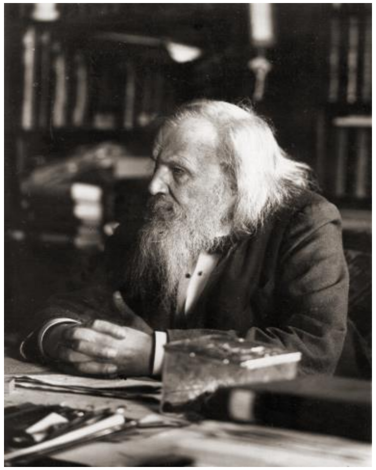
  - Seemed to work only for few elements.

- **John Newlands**

  - Law of Octaves (properties of the elements seemed to repeat every 8th element when the elements were ordered by atomic mass).

  - Seemed to be true only for elements upto Ca.

- **Dmitri Mendeleev** (1869)



- Periodic law (Physical and chemical properties of the elements are a periodic function of their atomic mass)
- Arranged the elements in horizontal rows and vertical columns.(63 elements)

- **Lothar Meyer** (1869) – unpublished as well as unlucky

- Plotted the physical properties (atomic volume, melting point, boiling point) against atomic mass and obtained a periodically repeated pattern.
- Developed a table of the elements that closely resembles the Modern Periodic Table.

- Dmitri Mendeleev and Lothar Meyer independently came to the **same conclusion** about how elements should be grouped.

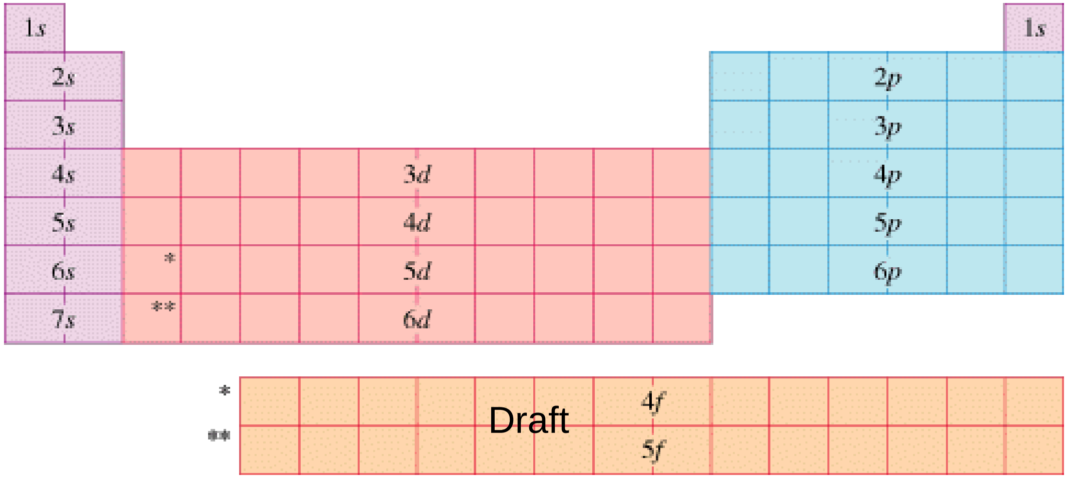
❖ **Henry Moseley** (1913) - Modern Periodic Law

- X-rays revealed that atoms of each element had a characteristic number of protons

- Moseley’s discovery allowed him to revise Mendeleev's Periodic Law.

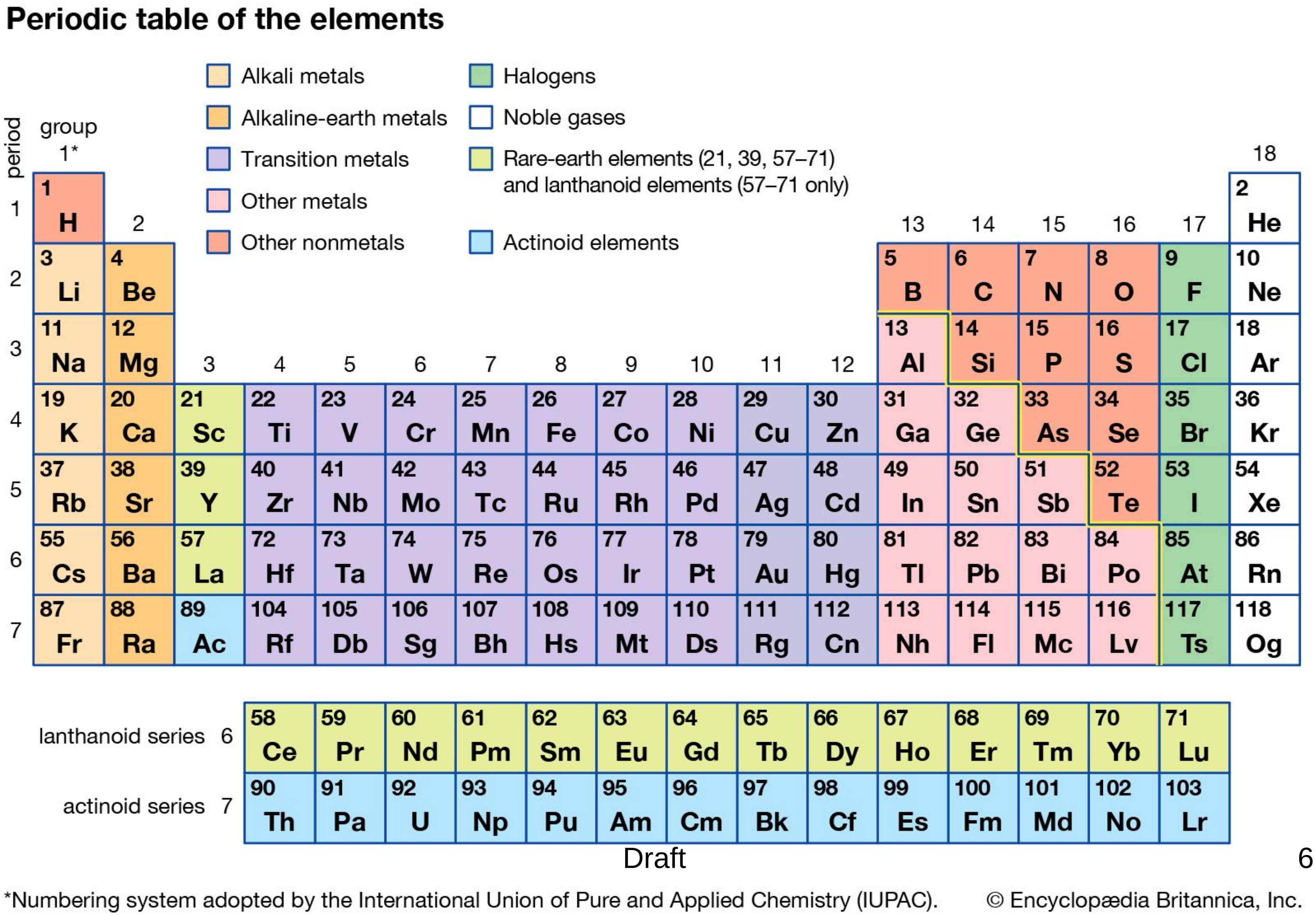
- He fixed all the inconsistencies by changing a single word: **Atomic Number**

- The physical and chemical properties of the elements are the periodic function of their **atomic number**



Modern Periodic table

- Group = vertical column of the Periodic Table = 18
- Period = horizontal column of the Periodic Table = 7
- Block = four (s, p, d and f)



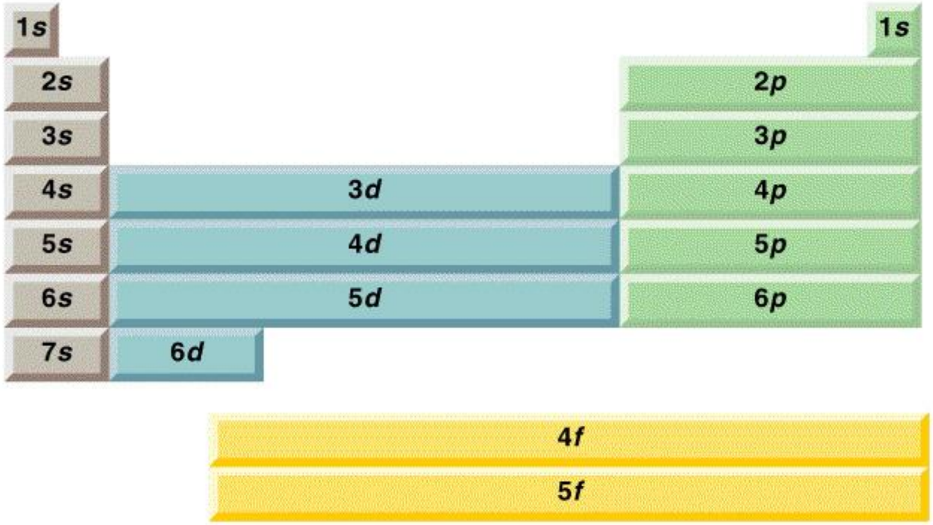
Periodic table of the elements

- ☐ Alkali metals
- ☐ Alkaline-earth metals
- ☐ Transition metals
- ☐ Other metals
- ☐ Other nonmetals
- ☐ Halogens
- ☐ Noble gases
- ☐ Rare-earth elements (21, 39, 57–71) and lanthanoid elements (57–71 only)
- ☐ Actinoid elements

period \ group	1*	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
1	1 H																	2 He	2
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne	8
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar	8
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr	18
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe	18
6	55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn	32
7	87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og	32

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

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



Classification of Elements According to the Type of Subshells Being Filled

- First, second and third are short periods
- Four to seven long periods
- Properties vary regularly in periods and groups with few exceptions
- Problems: position of H, Ln and An. Ele. conf of He.

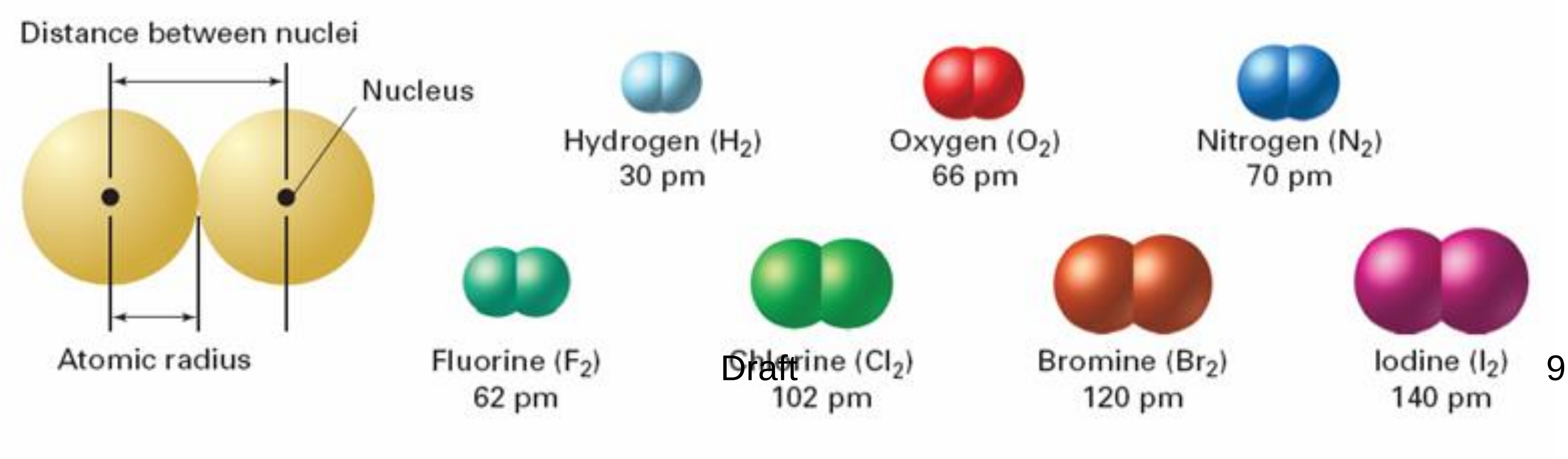
Trivial names	Elements	Trivial names	Elements
Alkali metals	Li, Na, K, Rb, Cs, Fr	Rare earth elements	Sc, Y, La-Lu
Alkaline earth metals	Be, Mg, Ca, Sr, Ba, Ra	Lanthanoids	Ce-Lu
Pnictogens	N. P, As, Sb, Bi	Actinoids	Th-Lw
Chalcogens	O, S, Se, Te, Po	Transuranium	beyond U
Halogens	F, Cl, Br, I, At	Coinage metals	Cu, Ag, Au
Noble gases	He, Ne, Ar, Kr, Xe, Rn	Noble metals	Pt, Au

Periodicity of elements

- Periodicity means recurring at regular interval.
- Similar elements get repeated after regular intervals and the intervals are 2, 8, 8, 18, 18, 32 called **Magic numbers**
- The repeated elements have similar electronic configurations.
- The properties of an element depend upon its atomic number and hence on its electronic configurations.
- The cause of the periodicity is the repetition of similar electronic configurations after regular intervals.
- Ln and An are placed separately (properties differ from others)
- The properties of new elements can be predicted prior to their discovery.

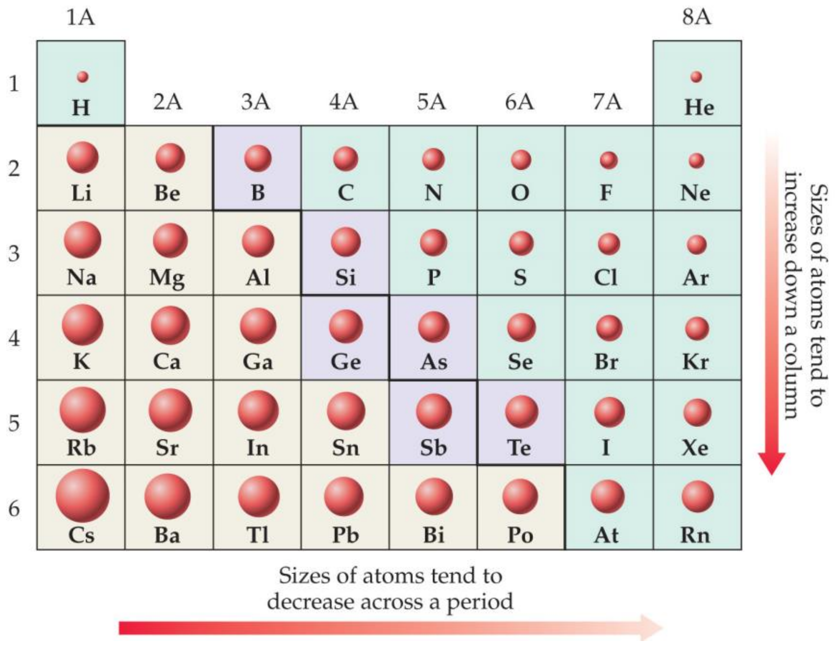
Atomic Radius

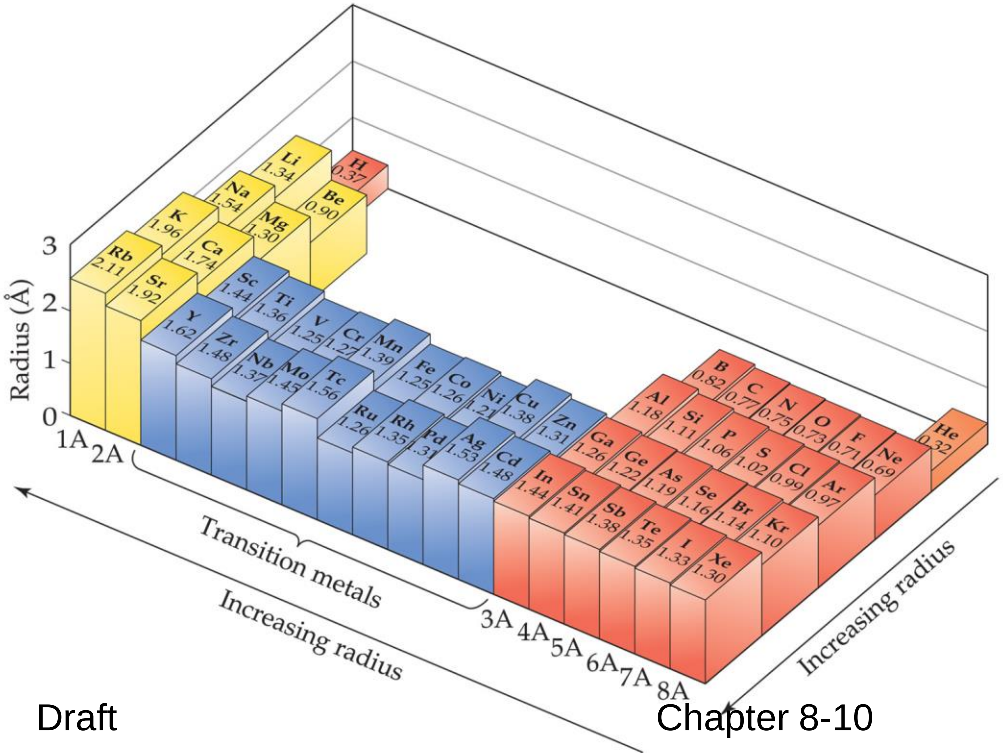
- Atomic Radius = size of an atom (distance between nucleus and outermost shell of e^-).
- The atomic radius is one half of the distance between the nuclei of two atoms of the same element when the atoms are joined, expressed in pm = 10^{-12} m, (Å is also used)
- Other than noble gases, all atoms/ions are almost unstable. so atomic/ionic radii cannot be measured directly.
- For the purpose, internuclear distance in crystals and in gaseous molecules are measured
- Atomic and ionic radius are bonded radii



Atomic radii: Periodic variation

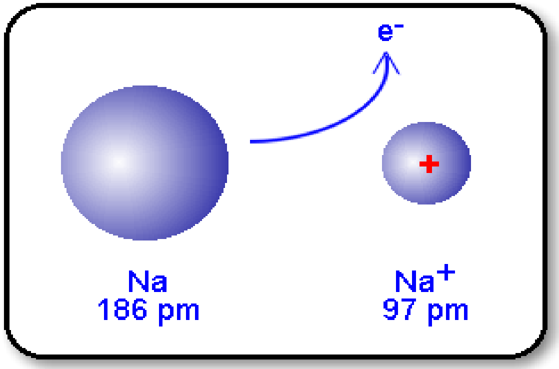
- Atomic radii decrease across a row (period) in the periodic table.
- Due to an increase in the effective nuclear charge (more protons in the nucleus).
- Within each group (vertical column), the atomic radius tends to increase down the groups.
- Down the groups, valence electrons are at higher energy levels and are loosely bound (screened or shielded by inner electrons).

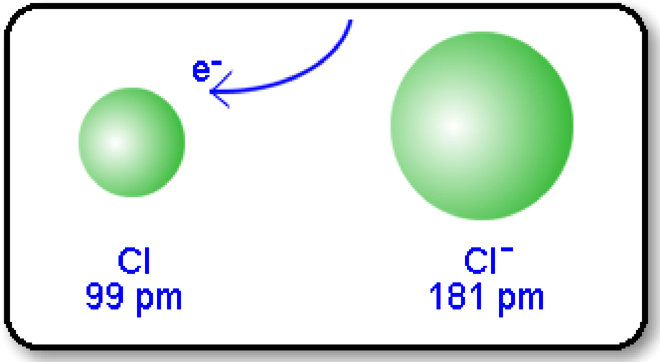




Ionic radii

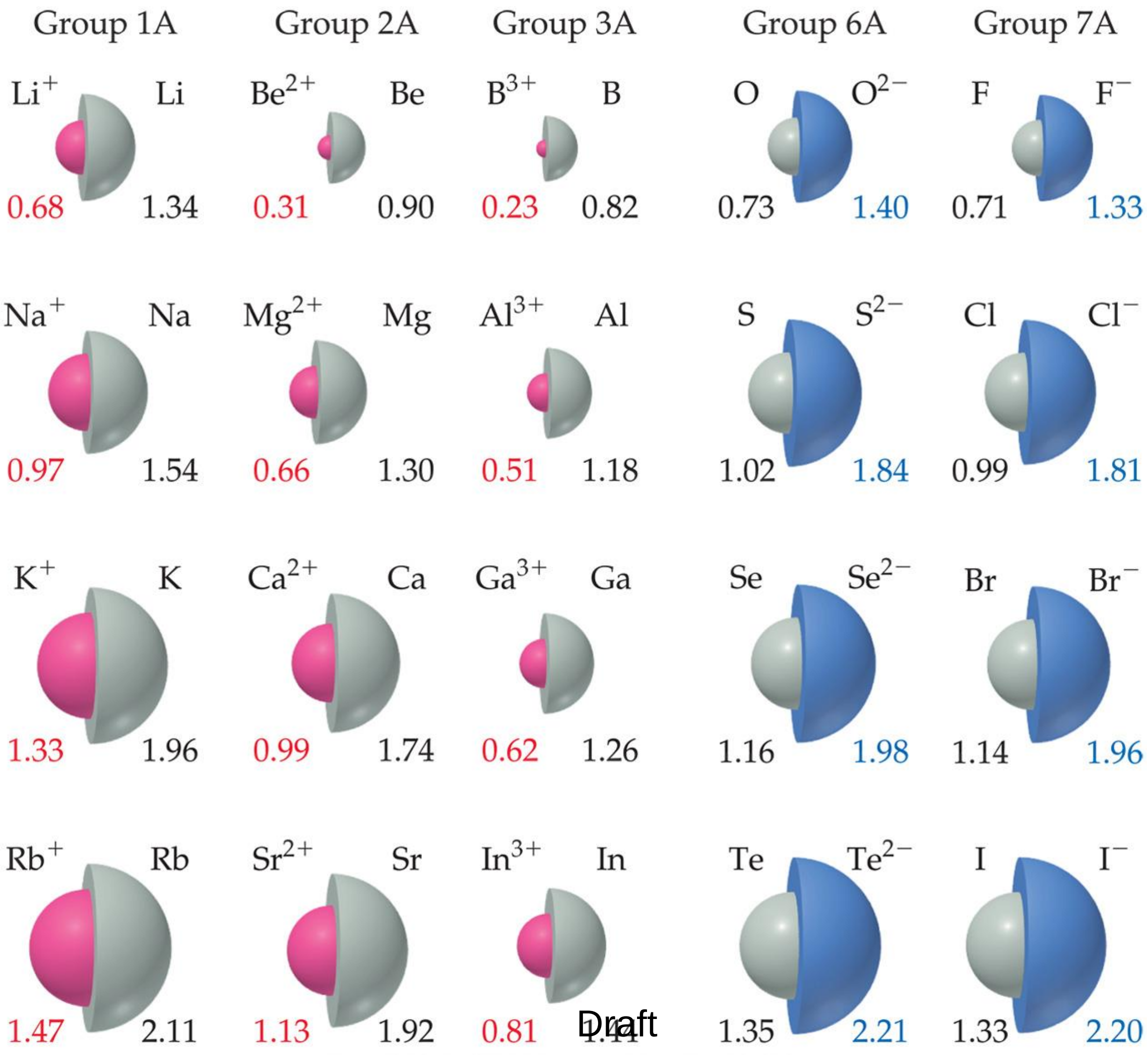
- Ionic radii is defined as the distance from the nucleus of an ion up to which it influences its electron charge cloud.
- This distance is taken as the sum of the radii of the two ions involved.
- Metals loose electrons while non-metals gain the same.
- Cations are smaller than parent atoms, electrons are removed and repulsions are reduced.
- Anions are larger than parent atoms, electrons are added and repulsions are increased.
- Ionic size depends on nuclear charge, number of electrons and orbitals in which electrons resides.





Ionic radii: Periodic variation

- Going from left to right there is a decrease in size of positive ions.
- Ionic size increases on moving down a column for both positive and negative ions.



red, blue – ionic radii

black – covalent radii

Factors effecting atomic/ionic size

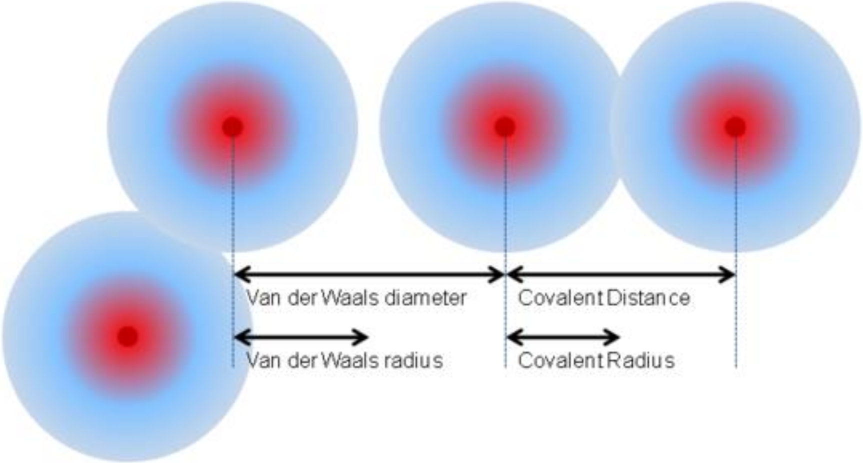
- **Hybridization**: Greater the s-character of an atom, smaller is the atomic/ionic radius. sp^3-C (77 pm) > sp^2-C (67 pm) > sp-C (60 pm)
- **Nuclear charge**: Greater the nuclear charge, smaller is the atomic/ionic radius.
- **Number of shell**: With increase in number of shell, atomic/ionic radius increases.
- **Bond order**: Higher the bond order, smaller is the atomic/ionic radius. C≡C (120 pm) < C=C (134 pm) < C-C (154 pm)
- **Oxidation number**: higher the oxidation state, smaller is the atomic/ionic radius, $Fe^{3+} < Fe^{2+}$

Metallic radii

- Metallic radii is defined as half of the inter nuclear distance between two adjacent atoms in a metallic bond.
- It helps to know the size of atoms of metallic elements
- Metallic radii of Na and K are 186 and 234 pm respectively.
- Metallic radius is larger than covalent radius, because no actual overlapping of atomic orbitals in metallic bond.
- It is measured by X-ray diffraction method (indicates how closely the metal atoms are packed).
- This close packing of atoms is called crystal lattice.
- For different elements the packing is different and hence different metallic radii.

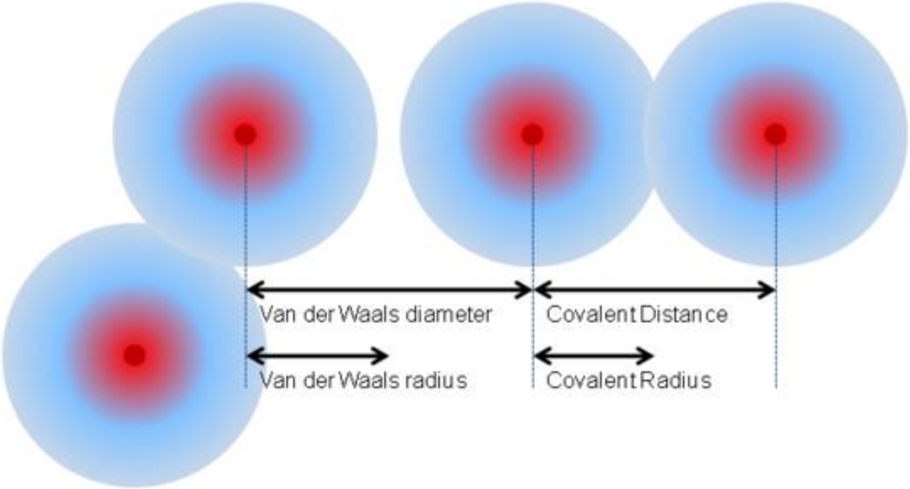
Covalent radii

- Covalent radius is defined as half the distance between two atoms (same) bound by a single bond (covalent) in a molecule.
- Distance between two different atoms is smaller than sum of individual's covalent radii.
- Electronegativity difference plays crucial role.
- Decreases from left to right in a period (electronic configuration and effective nuclear charge). Increases from top to bottom in a group (addition of extra shells).



Van der Waals radii

- It is the shortest distance to which two non bonded atoms can approach.
- It is defined as half of the distance between the nuclei of two adjacent identical atoms belonging to two neighbouring molecules in the solid state.
- Steric effect is primarily governed by van der Waals radii.
- Covalent radius (overlapping) < van der Waals radius (non bonded atoms, no overlapping)
- For noble gases, atomic radii = van der Waals radii (at the end of each period size increases)



Atomic/ionic size examples

Q. 1. Put the following in order of size, smallest to largest: Na, Na^+, Mg, Mg^{2+}, Al, Al^{3+}, S, S^{2-}, Cl, Cl^-

Solution:

- Al^{3+}, Mg^{2+}, Na^+, Cl, S, Al, Mg, Na, Cl^-, S^{2-}
- Start with atoms with no n = 3 electrons, order isoelectronic by nuclear charge.
- Next, neutral atoms highest Z* first
- Last, anions, highest Z* first

Q.2. Choose the Larger Atom in Each Pair

(a) C or O (b) Li or K (c) C or Al (d) Se or I?

Notes

- Metallic and covalent radii are subclass of atomic radii
- Covalent radius is generally shorter than its atomic/metallic radius
- Atomic radii should be used where atoms are bonded by metallic of a covalent bond.
- Size of a noble gas in its period is maximum (except alkali metals) due to presence of van der Waal forces
- For isoelectronic species, radius decreases with increase in number of protons or its atomic number.

Problem for practice

Q.1 Arrange in order and justify, N^{3-}, Na^{+}, Al^{3+}, O^{2-}, F^{-}, Mg^{2+}

Q.2 Arrange in increased order of size and justify Mg, Si and S

Q.3 Arrange in decreased order of size and justify C, Al and Si

Q.4 Arrange in increased order of size and justify P, As and Se

Q.5 Arrange in increased order of size and justify Si, P, Ge and As

Q.6 Arrange in decreased order of size and justify C, N, P and S

Q.7 Ne and Be, which one is larger and why?

Q.8 Arrange in decreased order of size and justify Ar, K^{+}, Cl^{-} and S^{2-}

Q.9 O, O^{+} and O^{2-} which one is larger and why?

Q.10 Which of the following substances has the largest radius: P^{3-}, S^{2-}, Cl^{-}, Ar, K^{+}, Ca^{2+} ? Explain.

Ionization Energy (Ionization potential)

- It is the amount of energy required to remove an electron from the ground state of an isolated gaseous atom.

$$M(g) + h\nu \rightarrow M^{+} + e^{-}; \text{IE}.$$

- Denoted by IE or IP. Unit is kJ/mol or kcal/mol
- Sign of the ionization energy is always positive, i.e., it requires energy for ionization to occur.
- First ionization energy (IE) is the energy required to remove first electron.
- Second ionization energy (IE_2) is that energy required to remove second electron.

$$M^{+}(g) + h\nu \rightarrow M^{2+} + e^{-}; IE_2.$$

- The third ionization energy is the energy required to remove an electron from an ion with a +2 charge.
- The energies for the subsequent loss of more electrons are increasingly higher, $IE_3 > IE_2 > IE$.
- It requires more energy to remove each successive electron.

Factors effecting IE

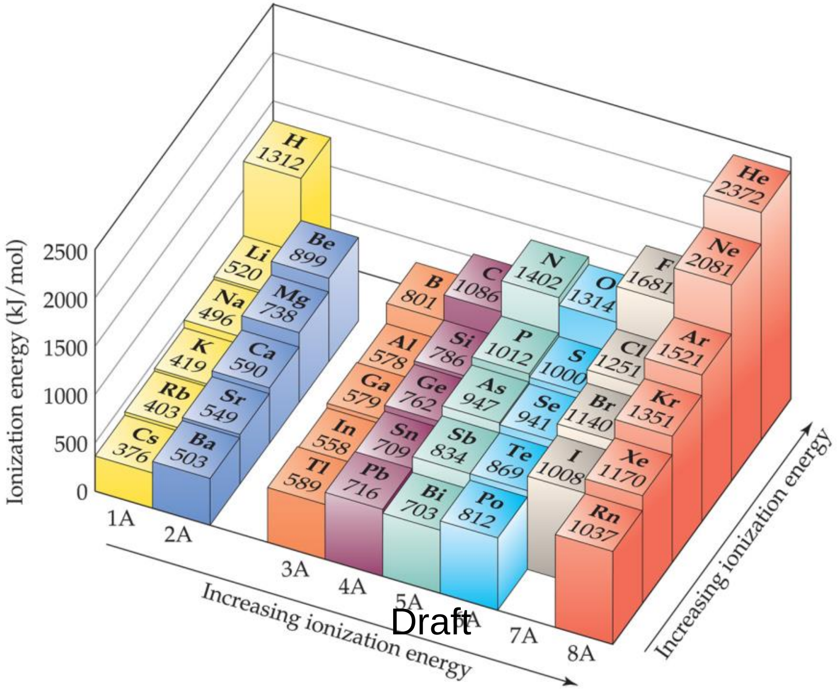
- **Stable electronic configuration**: Atoms with stable electronic configuration have higher first IE. Half filled and completely filled configurations have higher IE. Inert gas has higher IE although their size are relatively larger.
- **Size of atom:** Greater the size of the atom, less is the attraction between nucleus and electron and thereby less is the IE.
- **Magnitude of nuclear charge**: Greater the magnitude of nuclear charge or Z*, higher force of attraction between the nucleus and electron and hence larger is the IE
- **Screening effect**: Greater the number of shells between nucleus and valence electron, weaker will be the attraction between nucleus and electron and less would be the IE.
- **Penetration of sub shell**: Penetrating order s > p > d > f. Higher the penetrating power, greater is the IE.
- **Exceptions:**

  - IE of B, Al, Ga, etc. are less that of the element preceding them in their period.

  - Group 16 elements have less IE than group 15 elements.

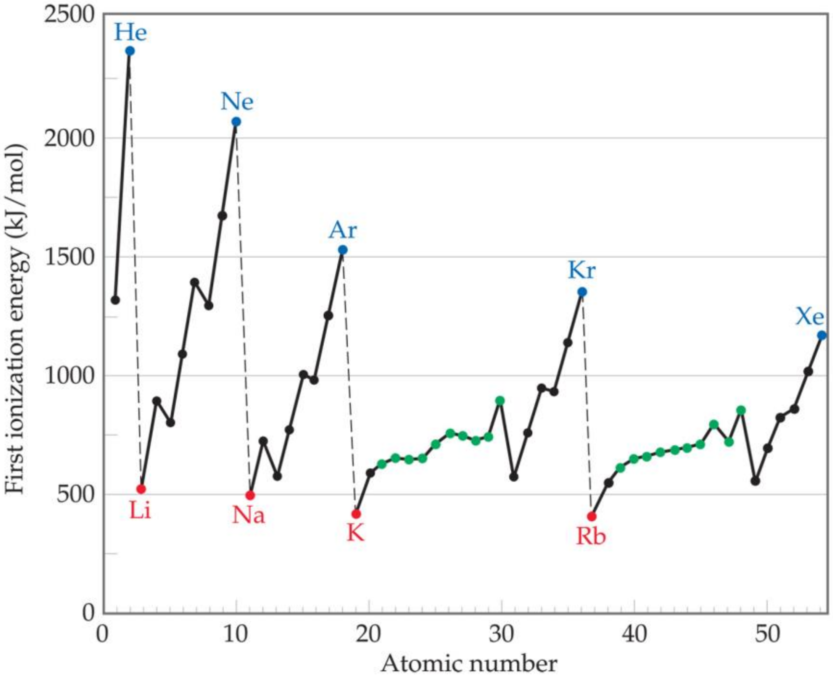
Ionization Energy-periodic variation

- Group Trend – Down the column (Top to Bottom), ionization energy decreases.
- On going down, atomic size is increasing, so easier to remove an e^-.
- Periodic Trend – Across a period (Left to Right), ionization energy increases.
- On going from left to right, atomic size is decreasing (more attraction), so more difficult to remove an e^-
- When all valence electrons have been removed, the ionization energy takes a quantum leap.

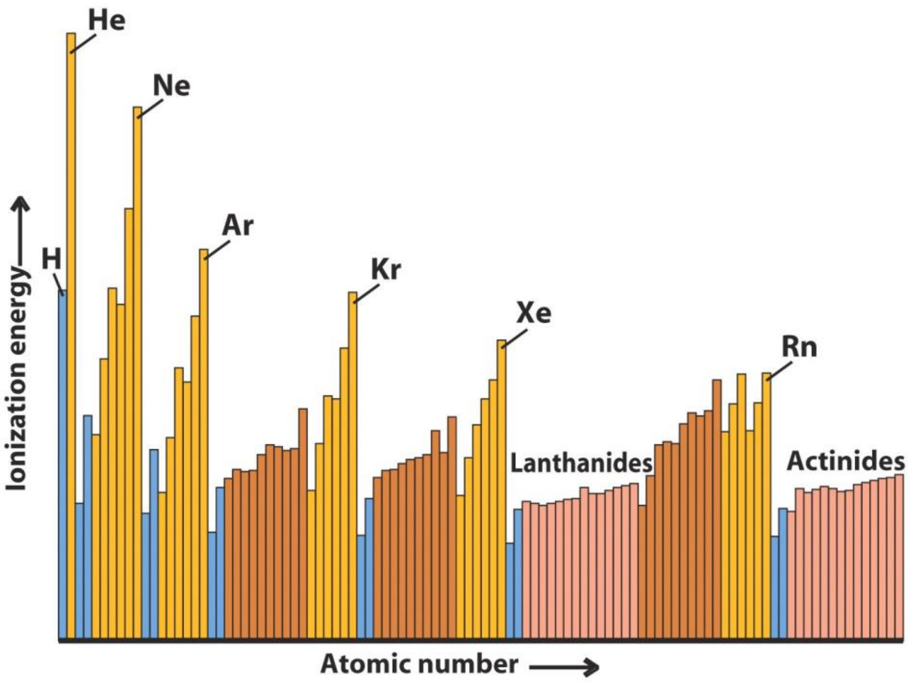


Trends in First Ionization Energies

- On a smaller scale, there are two jags in each line. Why?
- The first occurs between Groups IIA and IIIA.
- Electron removed from *p*-orbital rather than *s*-orbital
  - Electron farther from nucleus
  - Small amount of repulsion by *s* electrons
- The second occurs between Groups VA and VIA.
  - Electron removed comes from doubly occupied orbital.
  - Repulsion from other electron in orbital helps in its removal.



Ionization energies as a graph: Periodic trends



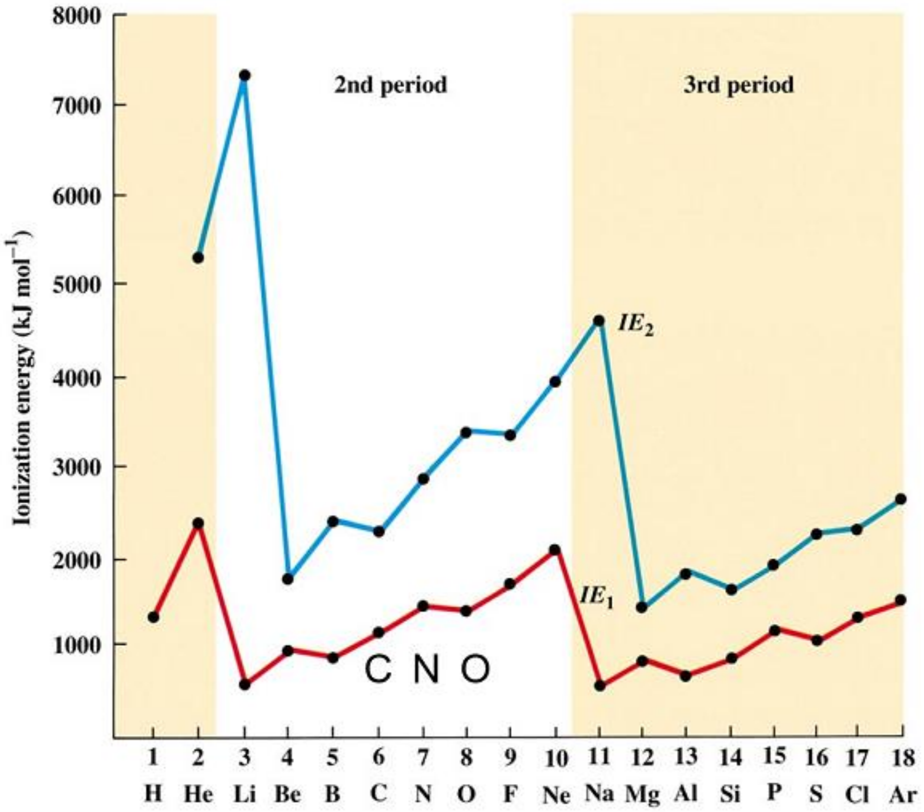
Why is the IE of H so much larger than the IE of Li?

Why are the IEs of the alkali metals so similar?

Why do noble gases have the highest IE?

Big drop after noble gases;

ns^2np^6 to $ns^2np^6(n+1)s^1$



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Why is the IE of N greater than that of C or O?

Which has lowest ionization energy?

Chlorine	Sodium
Magnesium	Argon

Problems for practice

Q.1 IE of Be is greater than Li

Q.2 IE of Be is greater than B

Q.3 IE of C is greater than B

Q.3 IE of N is greater than C

Q.4 IE of N is greater than O

Q.5 IE of F is greater than O

Q.6 IE of Ne is greater than F

Q.7 Write the increasing order of size of Mg, Si, S. Justify.

Q.8 Write the decreasing order of size of C, Al, Si. Explain.

Q.9 Write the increasing order of size of P, AS, Se. Justify.

Q.10 Arrange Si, P, Ge, As in the increasing order of their size and explain

Q.11 Arrange C, P, N, S in the increasing order of their size and explain

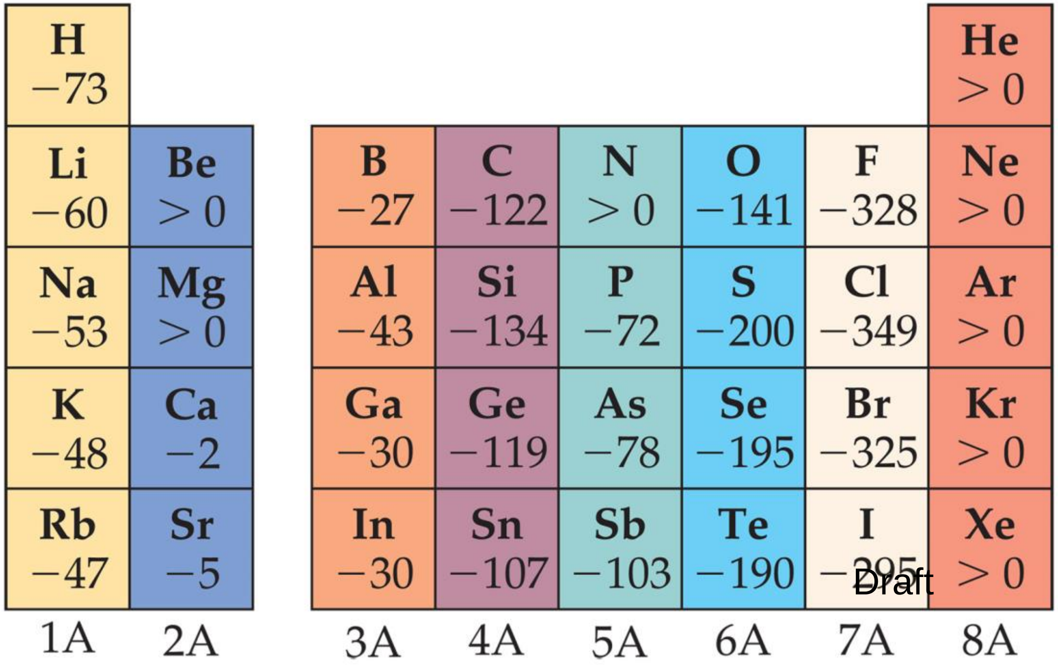
Q.12 Which out of Ne and Be has more size and why?

Q.13 Arrange Ar, K^+, Cl^-, S^{2-} in the increasing order of their size.

Q.14 Arrange the atoms and ions of oxygen atom in the increasing order of their size

Electron Affinity

- It is the energy change when an electron is added to an atom, $X(g) + e^- \rightarrow X^-(g)$
- Energy is released or required when an electron is added.
- Energy is often released during the process, more negative value favors the process
- Magnitude of released energy indicates the tendency of the atom to gain an electron.
- Electron affinity (EA) is defined as the amount of energy released when an extra electron is added to a neutral gaseous atom of an element
- Measured in terms of kcal/mol of kJ/mol or eV



H −73							He > 0
Li −60	Be > 0	B −27	C −122	N > 0	O −141	F −328	Ne > 0
Na −53	Mg > 0	Al −43	Si −134	P −72	S −200	Cl −349	Ar > 0
K −48	Ca −2	Ga −30	Ge −119	As −78	Se −195	Br −325	Kr > 0
Rb −47	Sr −5	In −30	Sn −107	Sb −103	Te −190	I −295	Xe > 0
1A	2A	3A	4A	5A	6A	7A	8A

- Halogens clearly have a strong tendency to become negatively charged
- Inert gases and group I & II elements are reluctant to add electron

Successive Electron affinity

- The phenomenon of adding the electrons to an atom one after the another i.e., in succession is defined as successive electron affinity.
- Generally, the first EA (electron is added to neutral gaseous atom) is negative

$$X(g) + e^- \rightarrow X^-(g)$$

- Second EA (electron is added to mono-negative ion, EA_2) is positive (energy is required).

$$X^-(g) + e^- \rightarrow X^{2-}(g)$$

- Similarly, third EA (electron is added to di-negative ion, EA_3) is also positive.

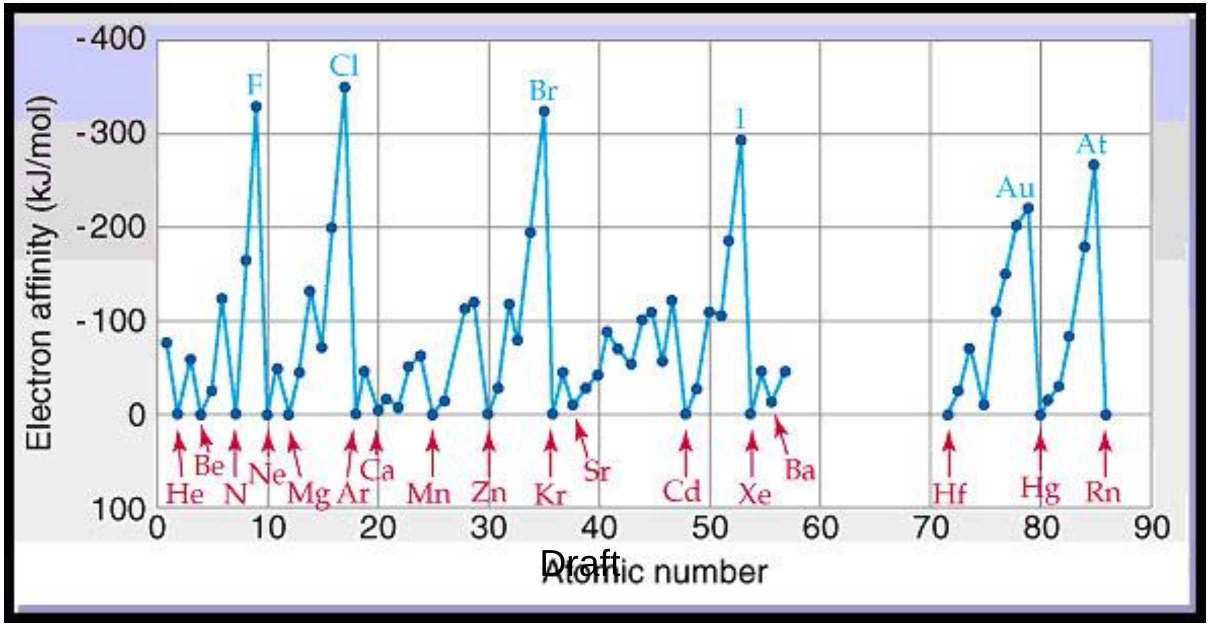
$$X^{2-}(g) + e^- \rightarrow X^{3-}(g)$$

- A positive electron affinity (EA) means a resistance to gaining another electron.
- The more negative the EA, the more strongly the atom attracts another electron.
- F (EA=-328 kJ/mol) attracts electrons more strongly than O (EA=-141 kJ/mol).

Factors effecting Electron Affinity

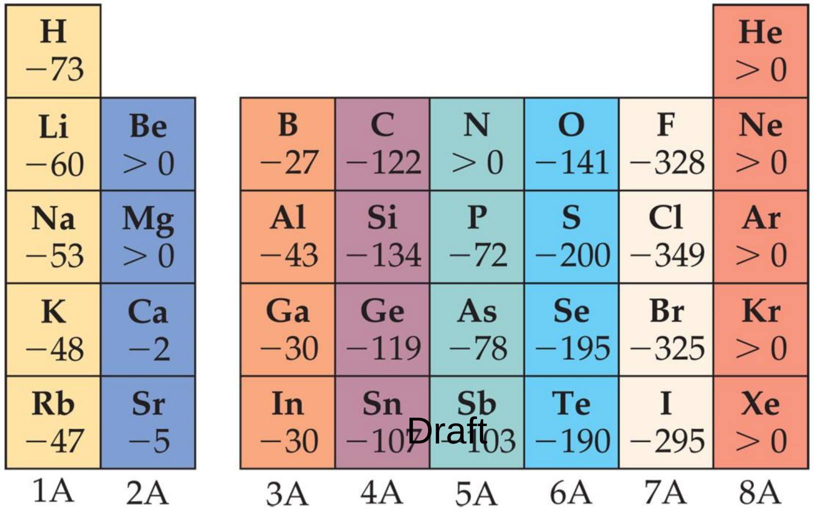
- **Size of the atom**: Smaller the size of the atom, greater would be the attraction of its nucleus for the added electrons and hence higher is the EA. For example, C is smaller than B and hence EA of C is more than B.
- **Magnitude of effective nuclear charge**: Greater the magnitude of effective nuclear charge, stronger is the attraction for added electrons and hence higher is the EA. For example, C has higher Z* than B and hence EA of C is more than B.
- **Electronic configuration**: Atom with stable (half or completely filled) configuration has little tendency to gain electrons and hence lower is the EA (even energy is required in some cases)
- Halogens have most negative EA values, addition of an e^- leads to noble gas configuration, very favorable.

- Group 15 elements have half filled shell discourages addition of an electron, EA values less negative than neighbors (Groups 14 & 16 elements).
- Alkaline Earths metals have filled s-subshell discourages addition of an electron, EA values nearly zero.
- Noble gases have completely filled shell strongly discourages addition of an electron, EA values are positive.



Electron Affinity-Periodic variation

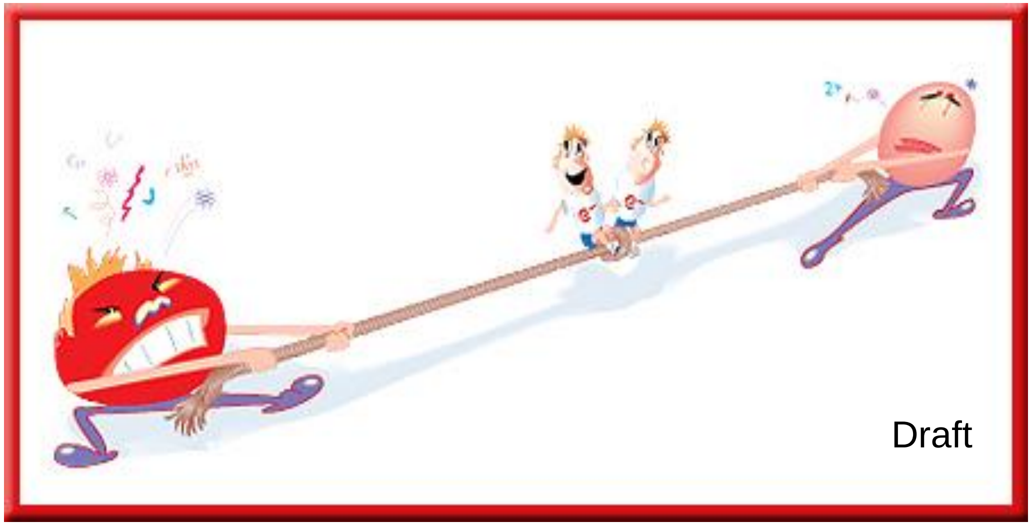
- Electron affinity becomes more negative (exothermic), increases from left to right across a period.
- Due to increase in Z* and decrease in size of atoms
- Not regular, in case of half or completely filled electronic arrangement
- Electron affinity decreases down the group.
- Due to predominant role increasing atomic size over increased nuclear charge.
- Exception: the first member of every family has a lower electron affinity the next heavier member of the group, attributed to very small size (large repulsion between electrons)

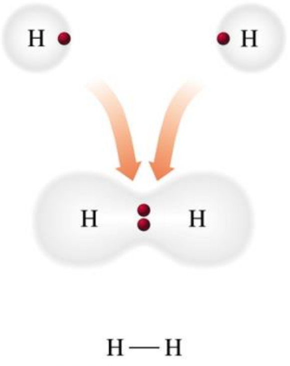


1A	2A	3A	4A	5A	6A	7A	8A
H −73							**He** > 0
Li −60	**Be** > 0	**B** −27	**C** −122	**N** > 0	**O** −141	**F** −328	**Ne** > 0
Na −53	**Mg** > 0	**Al** −43	**Si** −134	**P** −72	**S** −200	**Cl** −349	**Ar** > 0
K −48	**Ca** −2	**Ga** −30	**Ge** −119	**As** −78	**Se** −195	**Br** −325	**Kr** > 0
Rb −47	**Sr** −5	**In** −30	**Sn** −107	**Sb** −103	**Te** −190	**I** −295	**Xe** > 0

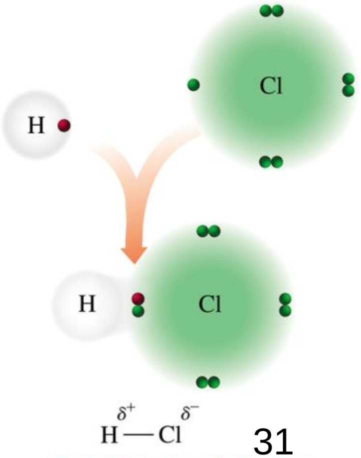
Electronegativity

- Electronegativity is the tendency of an element in a molecule to attract shared electron pair towards itself.
- It is purely qualitative and can be quantify by different methods.
- It has no unit
- If the bonded atoms are identical (same electronegativity), the shared electron pair is equally attracted, the molecule is non polar.
- If the bonded atoms are different, the shared electron pair is attracted by higher electronegative element, the molecule is polar.





Equal sharing of electrons in a nonpolar covalent bond



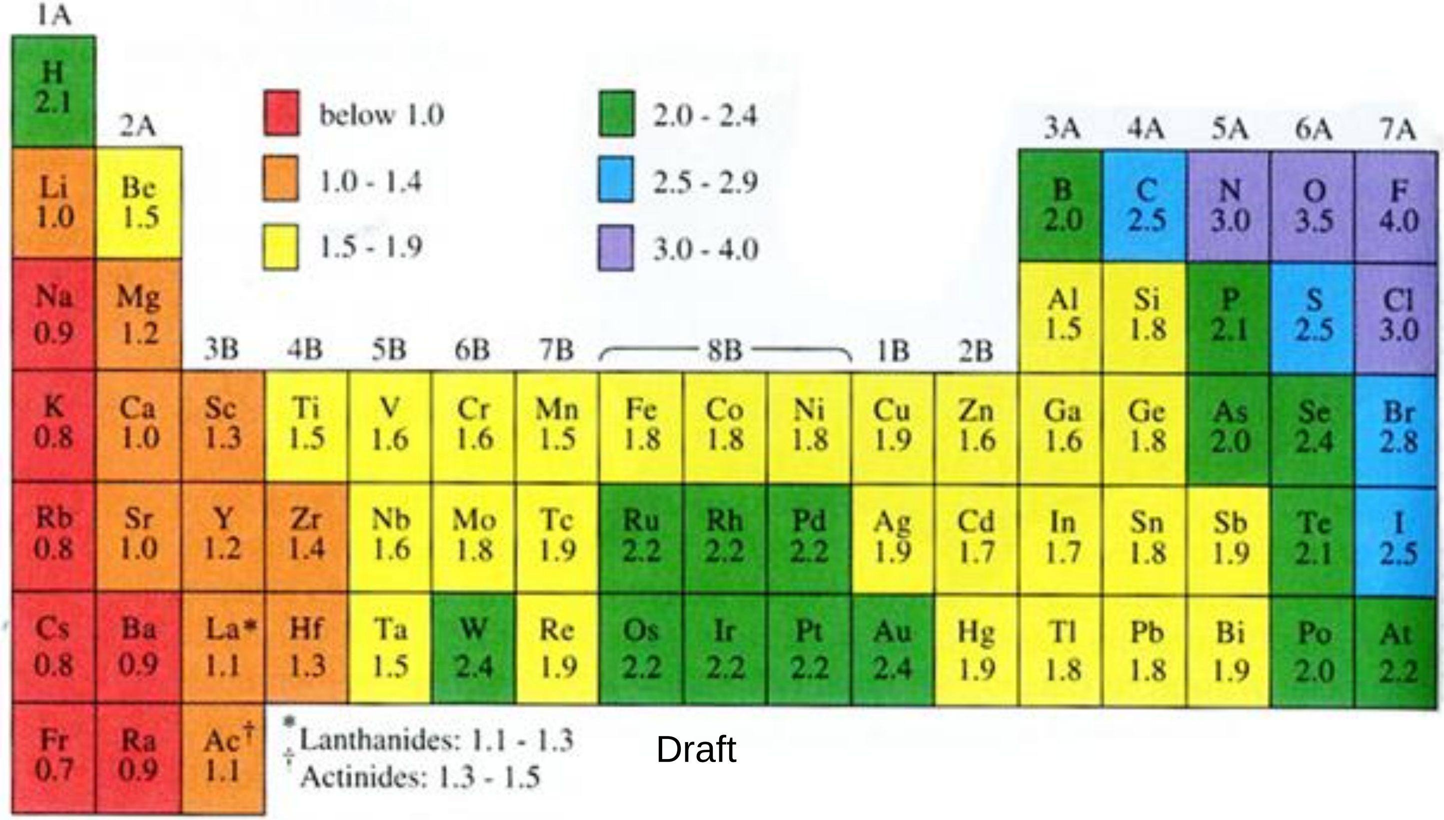
Unequal sharing of electrons in a polar covalent bond

Factors effecting Electronegativity

- Electronegativity depends on the nature of atom with which it is bonded.
- **Size of the atom**: the smaller the size of an atom, greater is the attraction for bonding electron and hence higher is the electronegativity.
- **Type of the ion**: Cations are more electronegative than the parent while anions are less electronegative from the same.
- **Hybridization**: Greater the s-character of hybrid orbitals, greater is the electronegativity.
- **Effect of substituent**: More electronegative substituent withdraws the electron density from the central atom, making it more positive and thus increasing its electronegativity.
- **EA and IE**: Higher the EA and IE, higher is the electronegativity (Mulliken)
- **Effective nuclear charge**: Higher the Z*, higher is the electronegativity (Allred-Rochow)

Electronegativity-Periodic variation

- Along a period, electronegativity increases (effective nuclear charge increases > screening effect)
- Down the group, electronegativity decreases (effective nuclear charge < screening effect)
- Helium, Neon and Argon are excluded from this trend. Since they do not bond with anything, they do not have electronegativity.



🟥 below 1.0
🟧 1.0 - 1.4
🟨 1.5 - 1.9
🟩 2.0 - 2.4
🟦 2.5 - 2.9
🟪 3.0 - 4.0

1A	2A	3B	4B	5B	6B	7B	8B			1B	2B	3A	4A	5A	6A	7A
H 2.1																
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
Cs 0.8	Ba 0.9	La* 1.1	Hf 1.3	Ta 1.5	W 2.4	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2
Fr 0.7	Ra 0.9	Ac† 1.1														

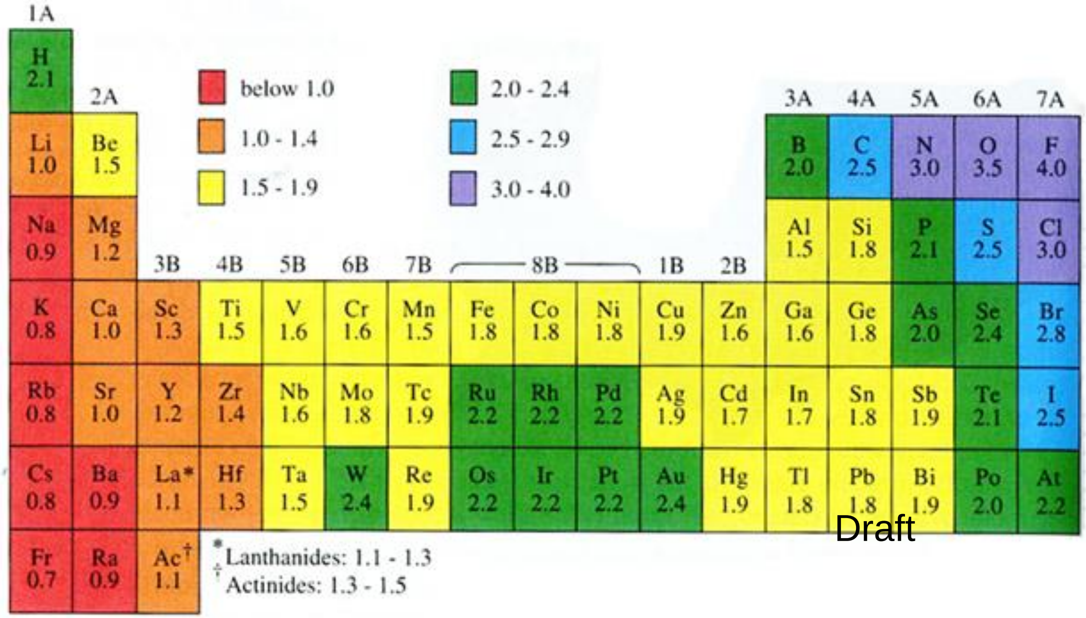
*Lanthanides: 1.1 - 1.3
†Actinides: 1.3 - 1.5

Pauling scale

- According to Pauling, electronegativity difference between two bonded atoms is given by

  $(\chi_A - \chi_B) = 0.208\ (\Delta \text{ in kcal/mol})^{1/2} = 0.102\ (\Delta \text{ in kJ/mol})^{1/2}$
- Δ = Resonance energy = Actual bond energy - Energy for 100% covalent bond
- Actual bond energy is measured experimentally.
- Energy of 100% covalent bond is calculated as

  Energy of 100% covalent (A-B) bond, $E_{A\text{-}B} = (E_{A\text{-}A}E_{B\text{-}B})^{½}$; $E_{A\text{-}B}$, $E_{A\text{-}A}$ and $E_{B\text{-}B}$ are the bond energies of A-B, A-A and B-B bond respectively.
- The Pauling scale is the most commonly used



🟥 below 1.0
🟧 1.0 - 1.4
🟨 1.5 - 1.9
🟩 2.0 - 2.4
🟦 2.5 - 2.9
🟪 3.0 - 4.0

1A	2A	3B	4B	5B	6B	7B	8B			1B	2B	3A	4A	5A	6A	7A
H 2.1																
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
Cs 0.8	Ba 0.9	La* 1.1	Hf 1.3	Ta 1.5	W 2.4	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2
Fr 0.7	Ra 0.9	Ac† 1.1														

*Lanthanides: 1.1 - 1.3
†Actinides: 1.3 - 1.5

Element	Pauling scale
F	4.0
Cl	3.0
O	3.5
N	3.0
S	2.5
C	2.5
H	2.1
Na	0.9
Cs	0.7

- Let us consider the process (formation of A-B is exothermic mostly)

$$\text{A-A} + \text{B-B} \longrightarrow 2\text{A-B}$$

- If A-B is purely covalent, the bond A-B would not get this extra stability (due to unequal sharing of bonding electrons i.e., induced ionic character)
- The extent of this ionic character (unequal sharing of electrons) measures the extra stability of A-B
- Pauling termed this property as electronegativity and correlated the extra stability of A-B bond to the difference in electronegativity between them.
- In terms of bond energy it is termed as resonance energy (Δ), it is the difference between actual bond energy of A-B and hypothetical energy of 100% covalent A-B molecule.
- $\Delta = E_{A\text{-}B} - E_{A\text{-}B(cov)}$
- $E_{A\text{-}B(cov)}$ is defined as the geometric mean of the covalent bond energies in A-A ($E_{A\text{-}A}$) and B-B ($E_{B\text{-}B}$) molecules. Thus, $E_{A\text{-}B(cov)} = (E_{A\text{-}A}.E_{B\text{-}B})^{½}$
- Therefore, $\Delta = E_{A\text{-}B} - (E_{A\text{-}A}.E_{B\text{-}B})^{½}$

- The final expression of electronegativity difference thus becomes

$$\chi_A - \chi_B = 0.102\ [(E_{A\text{-}B} - (E_{A\text{-}A}.E_{B\text{-}B})^{1/2}]^{1/2}$$

Merits:

1. The approach is straightforward and involves simple calculations based on available data
2. The scale offers good first hand knowledge of bond polarity and helps in predicting reaction courses with reasonable accuracy.

Demerits:

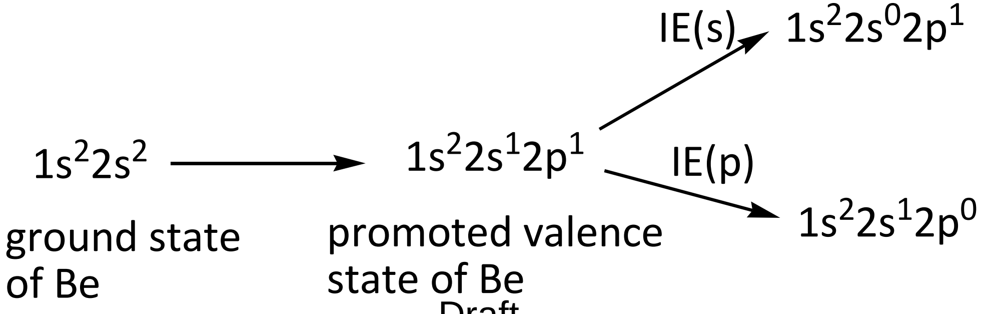
1. The idea of a single invariant electronegativity value for an element. Because oxidation state, hybridization and nature of orbitals play significant role in controlling electronegativity.
2. The bond enthalpy values calculated by electronegativity obtained using this method is uncertain.

Mulliken scale (1934)

- Mulliken suggested that electronegativity of an element is the average of its first IE and first EA.
- He determined the electronegativity by using the following relationships
- When IE and EA are measured in eV, $\chi = (IE + EA)/2$
- When IE and EA are measured in kcal/mol, $\chi = [(IE + EA)/2] \times (1/62.5)$
- **Disadvantage:** Difficult to obtain reliable EA values and, IE and EA values changes with change in valence state.
- **Relation between Pauling and Mulliken scale**:

$$\chi_P = 1.35\, \chi_M^{1/2} - 1.37$$

- The IE and EA values are not the experimentally observed values for the isolated gaseous atom. These are calculated values for the atom in the valence state i.e., when the atoms forms a part of a molecule.
- In BeF_2, the IE of Be atom used in Mulliken's formula is not the one which is experimentally observed for an isolated Be atom having $1s^22s^2$ configuration but is the hypothetical energy required to remove an electron from an sp hybrid of the Be atom. In other words, it is the average of energies IE(s) and IE(p) required to remove 2s and 2p electrons from the promoted valence state of Be atom in BeF_2 molecule.



$$\begin{tikzcd}
 & & 1s^22s^02p^1 \\
1s^22s^2 \arrow[r] & 1s^22s^12p^1 \arrow[ur, "IE(s)"] \arrow[dr, "IE(p)"] & \\
 & & 1s^22s^12p^0
\end{tikzcd}$$

ground state of Be

promoted valence state of Be

Allred and Rochow scale

- Allred and Rochow defined electronegativity as the electrostatic force exerted by the nucleus on the valence electrons.
- According to Allred and Rochow, electronegativity of an element is defined as,

$$\chi = 0.359\,(Z^*/r^2) + 0.744$$

- Z^* is the effective nuclear charge felt by the electron and r is the covalent radius (in Å) for the same.
- 0.359 and 0.744 are arbitrarily chosen constants.
- Electronegativity values calculated by this method is remarkably close to those reported by Pauling.
- **Advantage**: The parameters like electron affinity, bond energies are not required
- **Disadvantage**: Calculated Z^* by Slater's rule is empirical and covalent radii are known for few elements only.

Mulliken-Jaffe's Approach

- Jaffe and co-workers proposed a new definition for electronegativity according to which $\chi = dE/dq$; where, E is the total energy of an atom and related to partial ionic charge, q by $E = \alpha q + \beta q^2$
- On differentiating E with respect to q, $\chi = \alpha + 2\beta q$; $\chi = a + bq$. A corresponds to the electronegativity of neutral atom (q=0) and b is the coefficient of electronegativity.
- This definition is identical to Mulliken's definition upto singly occupied orbitals.
- For small and hard atoms like F, b has large value while for large and soft atoms like S, b has small value.
- Jaffe's concept gives a clear understanding of ionic character in terms of charge transferred between the bond forming orbitals.

Sanderson’s scale

- Sanderson suggested electronegativity scale based on stability ratio (SR).
- The stability ratio is defined as the ratio of average electron density (ED) around the nucleus and its ideal electron density (ED_i) calculated for inert atom having same number of electrons. $SR = ED/ED_i$
- According to Sanderson, SR is a measure of electronegativity, $\chi_S = ED/Ed_i$
- ED is a measure of compactness of the atom (average electron density) and is given by $ED = 3Z/4\pi r^3 = Z/4.19r^3$ d; Z is nuclear charge and r is covalent radius of an atom
- ED_i is is obtained by interpolating the electron density of inert gas atoms against atomic numbers.
- **Relation between Pauling and Sanderson scale**: $\chi_P^{1/2} = 0.21\ \chi_S + 0.77$

Group Electronegativity

- Group electronegativity is the electronegativity of elements in presence of substituents (such as -OH, -CN, -COOH etc.)
- Group electronegativity is calculated from electronegativity of atoms, dipole moments, kinetic data etc.

CH_3 = 2.3, OH = 3.5 – 3.9, CF_3 = 3.35, CCl_3 =3.0,
COOH = 2.85, C_6H_5 = 3.0, NO_2 = 3.4, CN = 3.3

- **Effect of substituent**: Electronegativity of an atom depends upon the nature of the substituents attached to it. For instance, the C-atom in CF_3I acquires a greater positive charge than in CH_3I. Hence, the C-atom in CF_3I is more electronegative (more electron pulling) than in CH_3I. The difference in the electronegativities of an atom caused by the substituents results in different chemical behaviour of that atom. For instance, CF_3I and CH_3I yield different products on hydrolysis.

$$CF_3I + OH^- \longrightarrow CF_3H + IO^- \qquad CH_3I + OH^- \longrightarrow CH_3OH + I^-$$

Applications of electronegativity

- **Calculation of partial ionic character of a covalent bond**:

  According to Pauling, Percent ionic character = $[1 - e^{-(\chi A - \chi B)/4}]$x 100 where $\chi_A - \chi_B$ is the electronegativity difference between A and B.

  Pauling also suggested another equation according to which, Percent ionic character = $18 (\chi_A - \chi_B)^{1.4}$

  According to Hanny Smith equation, Percent ionic character = $16(\chi_A - \chi_B) + 3.5 (\chi_A - \chi_B)^2$

- **Calculation of bond length**:

  Bond length (A-B) = Covalent radius of a + Covalent radius of B (in angstrom).

  Schomaker and Stevenson proposed the following empirical relationship for calculating bond length between A and B, $d_{A-B} = r_A + r_B - 0.09 (\chi_A - \chi_B)$

- **Calculation of magnitude of bond angle**:

  If the electronegativity of central atom is larger than that of surrounding, the bonding pairs will shift towards the former, increases the bp-bp repulsion and thereby the bond angle.

- **Calculation of enthalpy of formation**:

  Pauling has proposed the following empirical formula for calculating enthalpy of formation, $\Delta H_f = 23 \epsilon (\chi_A - \chi_B)^2 - 55.4 n_N - 26.0 n_O$; ϵ is the number of bonds in the molecule, n_N and n_O are the number of N and O-atoms respectively.

- **Prediction of polarity (nature) of a bond**: Nature of the bond between two atoms can be predicted from the electronegativity difference of the two atoms.

  (a) $\chi_A - \chi_B = 0$, the bond is purely covalent.

  (b) $\chi_A - \chi_B$ is small, the bond is polar covalent.

  (c) $\chi_A - \chi_B$ is 1.7, the bond is 50% covalent and 50% ionic.

  (d) $\chi_A - \chi_B$ is very high, the bond is predominantly ionic.

- **Predication of acidity of oxides**:

  $(X_O - X_A)$ difference predicts the nature of the oxides formed by the element A. X_O is the electronegativity of oxygen.

  $\chi_O - \chi_A$ is large, the oxide shows basic nature, (e.g. Na_2O,).

  $\chi_O - \chi_A$ is small, the oxide shows acidic nature, (e.g.SO_2,).

- **Colour of the salt**: Compounds having percentage ionic character less than 20% were found coloured. Lower the percentage ionic character, darker will be the colour.

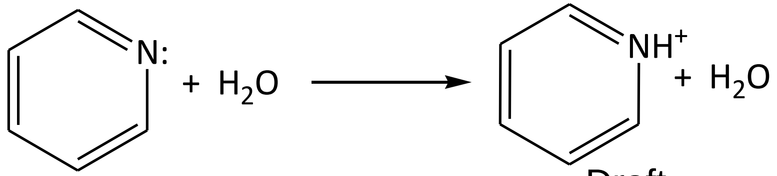
AgCl	AgBr	AgI	Ag2S
22%	18%	11%	8%
White	Light yellow	Dark yellow	Black

- **Acidic and basic character of XOH molecule**

1. When $\chi_O - \chi_X < \chi_O - \chi_H$, the O-H bond will be more polar than X-O bond and hence the ionisation of XOH molecule will take place at O-H and XOH will behave as an acid.
2. When $\chi_O - \chi_X > \chi_O - \chi_H$, the X-O bond will be more polar than O-H bond and hence the ionisation of XOH molecule will take place at X-O bond and XOH will behave as a base.

- The basicity of amines is a function of the hybridization of N-atom. More the electronegative N-atom, less readily it will share its lone pair electrons and act as a base.

$$Me_3N: + H_2O \longrightarrow Me_3NH+ \; OH^-$$



$$MeCN: + H_2O \longrightarrow \text{No reaction}$$

Basicity trends: aliphatic amine (sp^3)> aromatic amine (sp^2)> nitrile (sp)

Applications of electronegativity

❖ **Reaction mechanism**

1. In the first reaction, presence of F-atoms induces a partial positive charge on the C-atom and effectively increases its electronegativity. Finally, C-atom becomes more electronegative than I, inducing a positive charge on the I-atom. Nucleophilic attack by OH^- ion now takes place at positively charged I, giving OI^-

$$CF_3I + OH^- \longrightarrow CF_3H + IO^- \qquad CH_3I + OH^- \longrightarrow CH_3OH + I^-$$

2. A similar situation also arises in the following reactions. In the first reaction, I atom in CH3I has more electronegativity the C. Thus C attains positive charge and experience the nucleophilic attack. In the second reaction, C atom in CF3I has more electronegativity than I because of presence of highly electronegative F-atoms. Thus, I-atom attains a partial positive charge and experiences the nucleophilic attack.

$$CH_3I + Na^+[Mn(CO)_5]^- \longrightarrow NaI + CH_3Mn(CO)_5$$

$$CF_3I + Na^+[Mn(CO)_5]^- \longrightarrow NaI + Mn(CO)_5I + C_2F_6$$

Problems for practice

Q.1 EA of Be, Mg, N and noble gases are positive. Explain

Q.2 Halogens have highest EA. Explain

Q.3 Electron gain enthalpy of F is less than that of Cl. Explain

Q.4 Calculate the χ of C in C-H bond if $E_{C\text{-}H}$, $E_{H\text{-}H}$ and $E_{C\text{-}C}$ bonds are 98, 104 and 83 kcal/mol respectively.

Q.5 Find the electronegativity of Zn with covalent radius 125pm

Q.6 Calculate the χ of N, if B-F, N-N and F-F bond energies are 56, 32 and 37.8 kcal/mol respectively. Electronegativity of F is 4.0

Q.7 Calculate the H-Cl distance. Given, covalent radii of H (0.37 A) and Cl (0.99 A) and χ of H (2.1) and Cl (3.0)

Q.8 Calculate the enthalpy of formation of H-Cl if χ of H and Cl are 2.1 and 3.0 respectively.

Summary of periodic variations

Shielding is constant →

Atomic Radius decreases →

Ionization energy increases →

More negative electron affinity →

Electronegativity increases →

Nuclear charge increases →

Nuclear charge increases ↓

Shielding increases ↓

Atomic radius increases ↓

Ionic size increases ↓

Ionization energy decreases ↓

Electronegativity decreases ↓