

Intermolecular forces

Types of Bonding:-

Electropositive }
+
Electronegative } \rightarrow Ionic Bonding

Electronegative }
+
Electronegative } \rightarrow Covalent Bonding

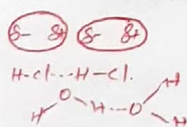
Electropositive }
+
Electropositive } \rightarrow Metallic Bonding

But intermolecular forces of attraction exist b/w polar as well as nonpolar molecules. These forces are called cohesive forces (or) Vander Waals forces.

It has originate from ① Dipole-Dipole interaction ② Dipole-Induced dipole interaction ③ Induced dipole-Induced dipole interaction.

① Dipole-Dipole Interactions:-

The molecules have permanent dipole moment, the van der Waals forces are mainly due to interaction between the dipoles known as dipole-dipole interaction. Ex:- NH_3 , SO_2 , HF , HCl .
Because of the attractive interaction, these gases can be easily liquified.



$$\text{Interaction Energy } \phi(r) = -\frac{2C}{r^6}$$

where $C = \frac{2}{3kT} \left[\frac{\mu_1 \mu_2}{4\pi\epsilon_0} \right]^2$

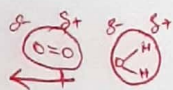
μ is their separation
 k Boltzmann const.
 $4\pi\epsilon_0 \rightarrow$ Permittivity factor of the medium.

② Dipole-Induced dipole Interaction:-

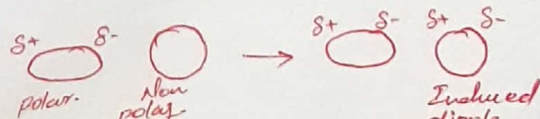
A polar molecule may sometime polarise a neutral molecule then interact with the dipole moment of the first molecule, and two molecules are attracted together.

$$C = \frac{\mu^2 \alpha}{4\pi\epsilon_0}$$

$\mu_1 \rightarrow$ permanent dipole moment



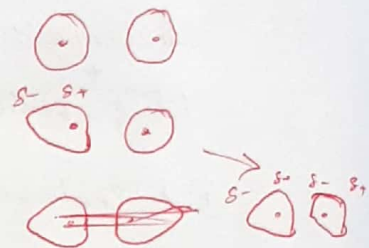
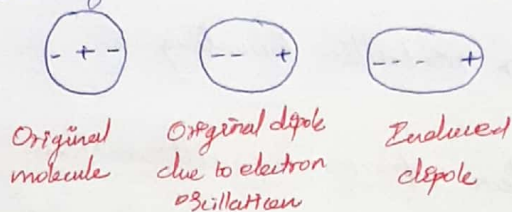
$$\text{Interaction Energy } \phi(r) = -\frac{C}{r^6}$$



(3) Induced dipole - Induced dipole Interaction.

(or) London forces (or) Dispersive forces.

The electrons of a neutral molecule keep on oscillating w.r.t the nuclei of the atoms. As a result positive charge may be concentrated in one region and -ve charge another region of the same molecule. i.e. Self polarised. These forces called dispersive forces (or) London forces.



$$\text{Interaction Energy } \phi(r) = -\frac{C}{r^6}$$

Eq. of state for real gases:

A number of eq of state have been suggested to describe the p-V-T relationship in real gases. The best known eq is that of van der Waals.

He modified the ideal gas eq by suggesting that the gas molecule were not mass points but behave like rigid spheres having a certain diameter and that there exist "Intermolecular forces of attraction between them."

Two correction made in that ① correction due to volume of gas molecules ② correction due to intermolecular forces of attraction. final equation is

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT.$$

for one mole of gas.

a, b → van der Waals constants.

Clausius Equation:-

Clausius accounting for the variation of the van der Waals constant 'a' with temperature, proposed the following eq:-

$$\left(P + \frac{a}{T(V_m + c)^2} \right) (V_m - b) = RT$$

c → new const

This eq is fairly satisfy to explain the P-V-T relationship in some but not in all gases.

Critical Temperature, pressure, Volume:-

Critical temperature of a gas may be defined as that temperature above which it cannot be liquefied ^{but in} ~~however~~ high ~~the~~ pressure may be.

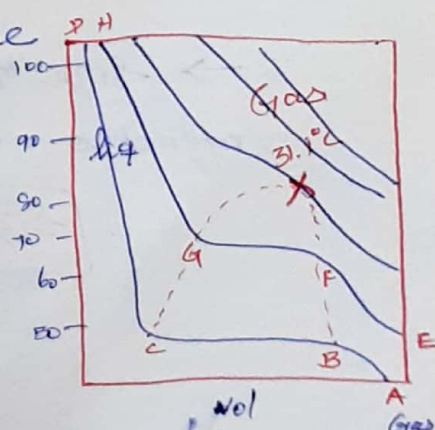
$\text{CO}_2 \rightarrow CT \Rightarrow 31.1^\circ\text{C}$

At the critical temp, a certain pressure is needed to liquefy the gas. This pressure is called the critical pressure.

$\text{CO}_2 \Rightarrow CP \Rightarrow 72.9 \text{ atm}$

The volume occupied by one mole of a gas at its critical temp and critical pressure is known as the critical volume.

$\text{CO}_2 \rightarrow CV \Rightarrow 940 \text{ ml per mole}$



Effective Nuclear charge (~~EAN~~ ^{EAN state}).

"The attractive force ^{of} experience by an electron from its nucleus is known as effective nuclear charge".

→ All electron in an atom does not experience the same extent of attractive force.

→ 2nd electron of Li is ~~experience~~ less effective charge (Z_{eff}) than 1st electron. because the nucleus is shielded by 1st electron. This is known as "Screening effect" (or) Shielding effect.

→ Order of Screening effect. $s > p > d > f$

→ When Screening effect decrease the EAN increase.

→ The EAN increase with increasing charge of the nucleus (\uparrow No. of protons) decreasing Shielding effect.

Ex:- No. of e^- = No. of proton \Rightarrow No. of Z_{eff} (Neutral atom)

No. of e^- > No. of proton \Rightarrow Less Z_{eff} (Negative ion).

No. of e^- < No. of proton \Rightarrow High Z_{eff} (positive ions).

→ Size of ions is inversely proportional to the effective nuclear charge of ions.

$$\boxed{\text{Size of ions} \propto \frac{1}{\text{Effective Nuclear charge}}}$$

Calculation of Z_{eff} : Slater Rules:-

$$Z_{eff} = Z - S$$

where $Z \rightarrow$ Atomic Number

$S \rightarrow$ Screening const

Values of S can be calculated by using the following rules.

\rightarrow Write the electronic configuration of the element in the following order and grouping.

(1s) (2s, 2p) (3s, 3p) (3d), (4s, 4p) (4d) (4f) (5s, 5p) etc.,

\rightarrow Electrons in any group higher in this sequence than the electron under consideration contribute nothing to S .

\rightarrow Consider a particular electron in ns or np orbital.

(i) Each of the other electrons in the (ns, np) group contributes $S = 0.35$

(ii) Each of the electrons in the (n-1) shell contributes $S = 0.85$

(iii) Each of the electron in the (n-2) (or) lower shells contributes $S = 1.00$

(iv) Consider a particular electron in an nd (or) nf orbital

(a) each of the other electrons in the (nd, nf) groups contributes $S = 0.35$

Ex:-1

The Effective nuclear charge experienced by the 4s electron of potassium.

Electronic configuration: K is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$

$$\begin{aligned} Z_{eff} &= Z - S \\ &= 19 - [(8 \times 0.85) + (10 \times 1.00)] \\ &= 2.20 \end{aligned}$$

Periodic properties - Trends:-

From Left to Right:-

Increasing →

- 1) melting point
- 2) Boiling point
- 3) Electronegativity
- 4) Electron affinity
- 5) Ionisation potential
- 6) Oxidising power.
- 7) Non metallic character.
- 8) Acidity.

From Top to bottom

Increasing ↓

- 1) ionic radii
- 2) Atomic radii
- 3) Atomic volume
- 4) Lattice energy
- 5) Basic nature of oxides of elements increases due to the increase in the electropositive character of element.
- 6) Thermal stability of carbonates, sulphates, nitrates of metal increases down the gp due to Metal oxygen bond strength.
- 7) Reducing character of elements increases with increasing A.No of element in group.
- 8) metallic character increases
- 9) Acidity increases.

Electronic configuration:

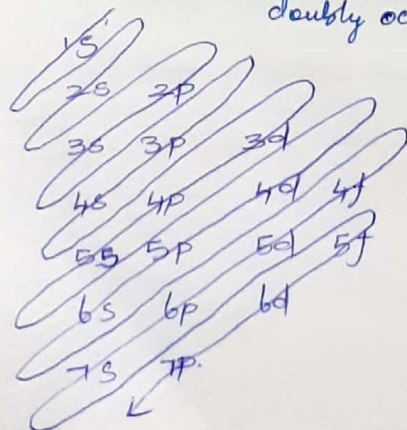
electrons are filled in orbital by following

Rules.

→ Pauli's exclusion principle (Two identical fermion cannot occupy the same quantum with in a orbital.)

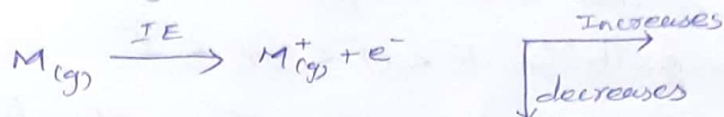
→ Aufbau principle

→ Hund's rule (every orbital in a subshell is singly occupied with one electron before any one orbital is doubly occupied)



Ionisation Energies:-

The energy necessary to remove an electron from an atom in the gas phase is called I.E.



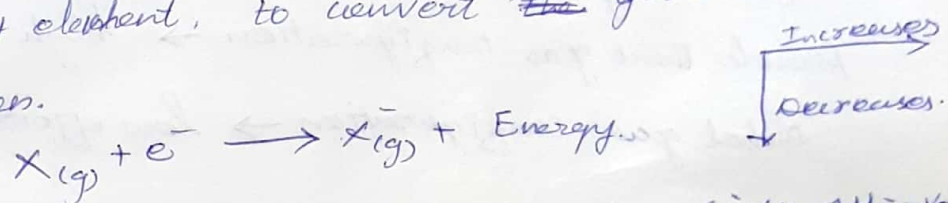
→ I.E is always endothermic

→ Bcz of effective nuclear charge increases along a period

$$IE_1 < IE_2 < IE_3.$$

Electron Affinity:-

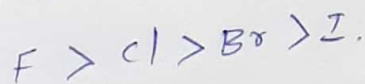
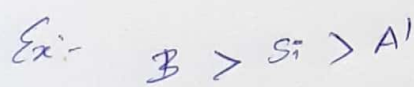
The amount of energy released, when an electron is added to the valence shell of an isolated gaseous atom of that element, to convert ~~the~~ gaseous into negative ion.



→ It is always an exothermic reaction since $\Delta H = -ve$

Electronegativity:-

Electronegativity of bonded atom is defined as its relative tendency (or) ability to attract the shared electron pair toward itself.



↑ Increase
↓ Decrease.

Polarization (Fajan's rule).

The extent of polarization depends on the polarising power of the cation and anion.
The rules regarding ~~the~~ polarization are known as Fajan's Rule.

→ The cations with smaller size have higher polarizing power. $\text{Li}^+, \text{Na}^+, \text{K}^+, \text{Rb}^+$

→ The anion with large size have higher polarizability. $\text{F}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$

→ For effective polarisation, there should be high charge on cation (or) anion.

→ Cations with pseudo inert gas configuration $ns^2 np^6 d^10$ with inert pair configuration viz d^10 have higher polarizing power while cation with noble gas configuration viz $ns^2 p^6$ have low polarizing power.

Pseudo inert gas configuration → high effective nuclear charge.
Noble gas configuration → low effective nuclear charge.

Coordination number :-

The total number of ligands attached to the central metal ion is called coordination number. otherwise it is equals to the sigma bond between the ligands and central metal atom. π bonds are considered in determining the coordination number.

