The Chemical forces / valence forces are responsible to hold the atoms and molecules together through the <u>Chemical bonds.</u>

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"Chemical bond defined as the force holding together two atoms or groups of atoms (molecules) forming an aggregate of ions, or molecular species such that there occurs a lowering of energy".

* Except the ionic and covalent forces, other chemical forces leading to Combining of different species are called "<u>weak chemical forces</u>. These are important in aggregation of species.
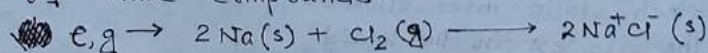
Different types of Chemical forces :

Types of force	Example	Equilibrium distance (pm).	Dissociation energy (kJmol).
1. Ion-ion interaction (ie ionic bond)	$Na^+ \cdots F^-$	230	670
2. Covalent bond (exchange interaction)	$H-H$	74	458
3. Ion-dipole interaction	$Na^+ \cdots O^{\delta-} \diagup H^{\delta+} \diagdown H$	240	84
4. Hydrogen bond (dipole-dipole int.)	$H^{\delta+} \diagdown \overset{\delta-}{O} \cdots H^{\delta+} \diagdown O^{\delta-} \diagup H$	280	20
5. Hydrophobic interaction	$\diagup CH_2 \cdots H_2C \diagdown$	~ 300	~ 4.0
6. Van-der Waals (dispersion force)	$Ne \cdots Ne$	~ 330	~ 0.3.

⊙ <u>Ionic Bond</u> : Defined as the electrostatic forces that bind together oppositely charged ions formed by the transfer of electrons from an electropositive metal to an electronegative non metal atom.

Every atom has a tendency to attain the nearest nobel gas electronic config. so attainment of nobel gas e.c is the clue of chemical reaction or forming a chemical Compounds.

The elements which have low I.P are the best candidates for forming +ive ions (cations). Similarly the elements which have high E.A are most likely to form negative ions (anions). <u>Factors</u> that influence I.P., E.A, and E.N also influence the formation of ionic compounds.

⊙ e,g → $2 Na(s) + Cl_2(g) \longrightarrow 2 Na^+Cl^-(s)$

The oppositely charged ions are held together by Coulombic forces.

Weak Interactions (Van-der Waals Fources):

Besides the primary fources responsible for the formation of molecules and ionic compounds there are secondary forces that operate between molecules. Though very weak in nature, this force is ultimately responsible for liquitaction and solidification of gases. Such intermolecular forces are popularly called Van-der waals forces.

Unlike Covalent bonding which is associated with orbital overlap at short internuclear distance van-der Waals forces may operate at longer distances where no orbital overlap can occur.

Examples:
Van-der Waals forces among the molecule mainly exist in the molecular Crystals. The mono atomic nobel gases consist of a cubic close packed structure in their solid state. In solid hydrogen, methane, halogens etc. the individual molecules provide the structural units of their respective Crystals. Molecular Crystals may also be formed by large and complex structural units. Rhombic sulpher consist of S_8 units while structural units in white phosphorous is the P_4 molecule. In graphite, the building unit is provided by infinite layers, of hexagonally arranged C-atoms. The c-atoms within a layers are linked by covalent bonds ($C-C$ distance $= 0.142$ nm) but the layers are held together by weak van-der Waals forces at large distance of 0.335 nm.

The Van-der Waals forces are very weak in comparision to other chemical forces. In solid ammonia, eg its amount to about 30 kJ mol^{-1} Vs the bond energy of $N-H$ covalent bonds equal to 389 kJ mol^{-1}. The forces are non directional.
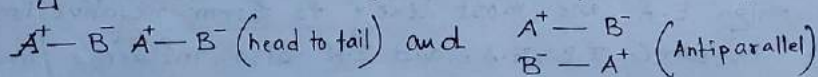
Origin : Intermolecular forces may have a wide variety of origin depending upon the environment. The different interactions involved may be classified as :

1. The attractive intermolecular forces

The following three types of interaction among the Covalent molecules

(i) Dipole-Dipole Interaction : "Keesom Forces"; E_k.

The dipoles with their opposite ends tend to be oriented in two ways — end to end (ie head to tail) and antiparallel arrangement

$A^- B \ A^- B$ (head to tail) and $\begin{array}{c} A^+ - B^- \\ B^- - A^+ \end{array}$ (Antiparallel)

[Simple electrostatic interaction among the dipoles in the liquid or solid state where the thermal agitation is not too high.]

eg→ H-bonding interaction is a special type of dipole-dipole interaction. Some examples of D-D interaction (without H-bonding)

NF_3 ($-129°c$, $\mu = 0.234 D$), OF_2 ($-145°c$, $\mu = 0.3D$), CF_4 ($-161°c$, $\mu = 0$).

Though the molar mass of CF_4 is higher than those of NF_3 and OF_2, but the lower boiling point of CF_4 arises from its zero dipole moment. NH_3 Vs NF_3 and H_2O Vs OF_2

(HIGHLY UNPOLAR) ($\mu = 0.234D$) ($\mu = 1.84D$) ($\mu = 0.3D$).
$\mu = 1.47D$

lower d.m of the fluoro compounds arise because of the contribution of opposing lone pair moment. and resulting lower boiling point.

* Nitroalkanes (RNO_2): Possess large dipole moments and enjoy more intermolecular attractive forces. Thus nitroalkanes show higher ~~from~~ b.p compared to alkanes of comparable molecular mass.

(ii) Dipole – Induced Dipole Interaction : "Debye Forces"; E_D

The electrical field of a dipole can induce a dipole moment in an adjacent molecule (which may be polar or nonpolar). Then the induced dipole can interact electrostatically with the polarising dipole. If both the interacting molecules are polar then both E_K and E_D exist.

eg→ Nobel gas hydrates; The solubility of the nobel gases in water is fairly high and it increases with the ~~with~~ increase of size, of the inert gases. Certain derivative of phenol; $Kr (Phenol)_2$, $Xe(Phenol)_2$, $Rn (Phenol)_2$ etc.

(iii) Instantaneous Dipole – Induced Dipole Interactions or Dispersion Forces : "London Forces"; E_L

An intermolecular attraction can exist even among the permanently nonpolar molecules (eg Cl_2, CH_4, Ar etc). To interpret the inner picture of this type of interaction, let us consider a nonpolar molecule. Here the time average electron distribution around the nuclei is spherical, but a particular moment an imbalance of the e-cloud distribution may be imagined to produce a dipole moment in a particular direction. There is an equal probability for the e-cloud to be polarised in the just opposite direction to produce a dipole moment of the same magnitude. Thus for each and every ~~with~~ instantaneous dipole moment due to the imbalance of the charge cloud distribution, there is an equal probability of having an instantaneous d.m of the same magnitude acting in the opposite direction. Thus on time average, the molecule is nonpolar but at a particular moment, it acts as a dipole which is equally probable in all directions.

eg— In H_2 molecule ; $\left[H_A^+ : H_B^- \longleftrightarrow H_A^- : H_B^+ \right]$
Each nonpolar molecule can be regarded as an instantaneous dipole.

* "London Force" works in all polar and nonpolar molecules but it becomes specially important for the nonpolar molecules when the other forces remain absent.

* **Intermolecular attractive force among the members of halogens and homologous series :**

For the larger molecules which are more polarisable, have the highest dispersion forces. Because of this fact, I_2 is solid, Br_2 is liquid, while Cl_2 and F_2 are gaseous at room temperature. The same trend also prevails among the inert gases. In a homologous series, the higher members show the higher m.p and b.p due to the same fact.

* **Physical states of BX_3 :**

For the boron halides, BF_3 and BCl_3 are gaseous, BBr_3 is volatile liquid while BI_3 is solid. In fact, the increased number of electrons enhances the polarisability of molecules.

* **Polarisability depending on the molar mass and the chemical environment :**

"London Forces" increase with the increasing polarisability (i.e softness) and the molar vol^m among the comparable species. ~~PARAMI~~ $(I_2, Br_2, Cl_2, F_2$; Inert gases ; $PbH_4, SnH_4, GeH_4, SiH_4, CH_4$; Organic homologous series).

The Boiling point sequence is $BF_3 < BMe_3$; $NF_3 < NMe_3$.

Comparable molecular weight ; but substitution of nonpolarisable (i.e hard) F by softer CH_3 increases the polarisability of the methyl derivatives. Thus in the respective methyl derivatives, the 'London Force' is largely to increase the boiling point.

* Polarisability largely depends on the chemical environment or nature of the compounds. substituents of the compound under consideration.

* **Solubility $Me_4N^+Cl^-$ Vs $NH_4^+Cl^-$.**

more soluble in nonpolar solvent. Because the charge is shielded by the hydrophobic groups. Cation is stabilised in nonpolar solvents through the hydrophobic interaction. (i.e L.Force).

No such stabilization is possible for $NH_4^+Cl^-$. in nonpolar solvents.

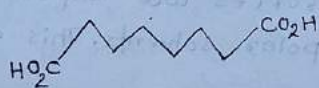* **$SiCl_4$ Vs CCl_4 :** $SiCl_4$ with a higher m.w shows the lower b.p than CCl_4.

Because : Lower e.n of Si than that of C, in $SiCl_4$ the Cl atoms bear a higher negative charge. Consequently the -ive charge cloud density at the periphery of the $SiCl_4$ molecule is higher than that of the CCl_4 molecule. It establishes a higher electrostatic repulsion among the $SiCl_4$ than that among the CCl_4. It leads to the lower density of $SiCl_4$.
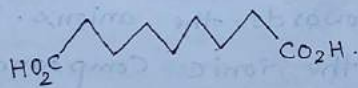
Secondly; Due to the $Si(d\pi) \leftarrow Cl(p\pi)$ bonding there is an effective decrease in the intermolecular forces in $SiCl_4$ to lower its boiling point. This type of π-bonding is not possible in CCl_4. The π-bonding in $SiCl_4$ reduces the nonbonding electron cloud density on the periphery of the molecule. Consequently, the overall polarisability of $SiCl_4$ is decreased and thus the dispersion force is reduced. The π-bonding effectively reduces the +ive charge on Si and Consequently, the intermolecular attraction among the $SiCl_4$ molecule is also reduced.

* Intermolecular attractive forces within the Covalent Crystal increase with the increase of symmetry of the molecules to enhance the m.p and reduce the solubility. For the Covalent molecules, the magnitude of this force depends on the degree of packing of the molecules within the crystal.

m.p of dicarboxylic acids $HO_2C-(CH_2)_n^- CO_2H$; hydro carbon
Chain is oriented in a zig-zag fashion.

HO₂C .... CO₂H

even acid (more symmetrical)
'Trans' Config.

HO₂C .... CO₂H
Odd acid
"Cis" Config.

The trans Config. is more symmetrical and Consequently, the dicarboxylic acid with the even no. of C atoms experience the closer packing in the Crystal. It leads to the higher intermolecular attractive forces among the chains (i. force) of the dicarboxylic acids. of even no. of C atoms; and hence higher m.p than which mxs. with dicarboxylic acid with odd no. of C-atoms.

⊘ Total Intermolecular Attractive Forces (Van-der Wahl Forces):

The sum of the three attractive forces i.e kee som forces, Debye forces, and London forces is called the Van-der Waals forces. Some authors Consider only the 'London forces' as the Van-der Waals forces.

$$E_{attractive} = E_K + E_D + E_L$$

E_K = It arises due to the proper orientation of the parmanent d.m of the molecules.

E_D = " Interaction between an induced dipole moment of one molecule and with the parmanent d.m of the polarising molecule.

E_L = Interaction between the instantaneous developed d.m through the synchronization of Charge cloud imbalance.
(to occur at the same time)

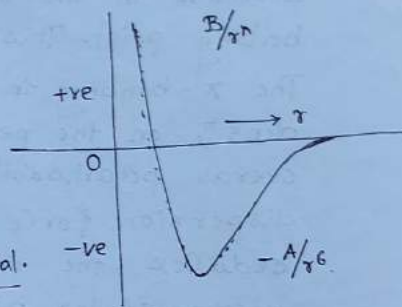$$\boxed{E_{attractive} = -\frac{A}{r^6} \quad \text{(at a fixed temp)}}$$

* Lennard - Jones Potential

$$E_{total} = E_{attractive} + E_{repulsion}.$$

$$= -\frac{A}{r^6} + \frac{B}{r^n}$$

(due to e-e and n-n) repulsion)

For $n = 12$, it is Called a 6-12 potential.

Interaction Between Ionic And Covalent Compounds:

1. Ion - Dipole Interaction:

When an ionic Compound is dissolved in a polar solvent, the polar solvent moleCule are oriented towards the electrical field of the ions in such a way that the -ve ends of the dipole are oriented towards the Cations and the +ve ends of the dipoles are projected towards the anions. These forces are important in dissolving the ionic Compounds in polar solvents. This actually leads to the solvation energy.

eg $\longrightarrow$ NaCl in water is hydrated as $Na(OH_2)_x^+$ and $Cl(H_2O)_y^-$.

For the transition metal Cations, the ion dipole interaction is so strong that it leads to the discrete aqua-metal Complex in water and ammine-metal Complex in liq. ammonia solvent.
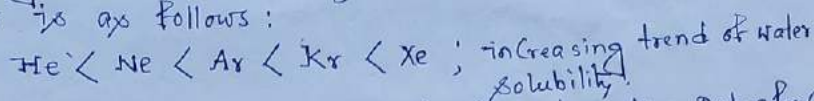
2. Ion- Induced dipole Interaction:

When the electrical field of an ion Can polarise a moleCule (which may be polar or non polar) to induce a dipole moment in the moleCule due to the distortion polarisation. Thus the induced dipole Can interact electrostatically with the polarising ion. The extent of polarisation depends on the electrical field intensity.

eg $\longrightarrow$ The interaction of the halide ions with the halogen moleCule $(I^- + I_2 \longrightarrow I_3^-)$ giving rise to the polyhalide ions is Considered to be this type. The stability sequence, $I_3^- > Br_3^- > Cl_3^-$ Can be explained from the Consideration of polarisability of the halogen moleCules. The larger moleCules are more polarisable, if $I_2 > Br_2 > Cl_2$. Thus the larger moleCules form the more stable Compounds.

** Write down the solubility order of nobel gases in water and explain this observation.

In Creasing order of solubility of nobel gases in polar solvent like water is as follows :

$$He < Ne < Ar < Kr < Xe \; ; \; \text{increasing trend of water solubility}.$$

This can be explained by Dipole - induced dipole interaction, Debye force. As size increases in the order $He < Ne < Ar < Kr < Xe$, so polarisability due to the dipole (water) increasing in the same trend. Thus for the larger atom (Xe) which are more polarisable, have the highest and the smallest atom He among the nobel gases have the lowest Debye force (D - ID interaction). As a result, the solubility of the nobel gases in water increases with the increase of size of the inert gases.

** Explain the trend of stability of the polyhalide ion $I_3^- > Br_3^- > Cl_3^-$.

Larger molecules are more polarisable, so the order of polarisability of the halogen molecule is $I_2 > Br_2 > Cl_2$; and the stability of the polyhalides based on the interaction of the halide ions with the halogen molecules ($X^- + X_2 \rightarrow X_3^-$). Larger molecules, I_2 which are more polarisable interact better with the, I^- to form stable polyhalide (I_3^-) and least ion - dipole induced dipole -interaction between Cl_2 and Cl^- to form less stable polyhalide (Cl_3^-) and intermediate stability in case of Br_3^-. So the order of stability of the polyhalide ions; $I_3^- > Br_3^- > Cl_3^-$.