Forces of Physical adsorption

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Physical adsorption, on the surface of a solid, takes place due to the **intermolecular forces** between the adsorbing molecules. Unlike chemisorption, where a chemical bond is established between the solid surface and the molecules, physisorption does not involve the formation of chemical bonds. The intermolecular forces are called as **Vander Waals forces** or **Cohesive forces.** Depending on the nature of these forces, they are classified into:

1. Dipole-Dipole interaction
2. Dipole-Induced dipole interaction
3. Induced dipole-Induced dipole (London forces or Dispersive forces)

1. Dipole-Dipole Interaction:

In case of polar molecules, though neutral, have permanent dipoles. Here the intermolecular force is the **electrostatic interaction** between the dipoles. Gases like ammonia have permanent dipoles which allow them to be liquified easily due to the attractive interaction.

The interaction energy, however, depends on the dipole moment of the molecules. Typical example is NH_3 (b.pt: -33.34 C) and NF_3 (b.pt: -129 C). The dipole moment of Ammonia is **1.46 D** and for Nitrogen trifluoride it is **0.24 D**. As discussed above, molecules with a larger dipole moment tend to interact and condense easily compared to molecules with a lower dipole moment. So, ammonia condenses at relatively higher temperature than nitrogen trifluoride.

The average interaction energy between two molecules with permanent dipole moments $\boldsymbol{\mu_1}$ and $\boldsymbol{\mu_2}$ separated by distance **r** is given by:

$$\boldsymbol{\phi(r) = -2c \,/\, r^6}$$

Where, $\mathbf{c} = \frac{2}{3kT}\left[\frac{\mu_1\mu_2}{4\pi\varepsilon_0}\right]^2$.

ε_0 is the dielectric constant.

2. **Dipole-Induced dipole interactions:**

Sometimes a polar molecule polarizes a neutral molecule which lies in the vicinity and thereby induces dipolarity in that molecule. The induced dipole thereby interacts with the dipole moment of the first molecule and the two molecules are attracted together. Unlike the first case, where the interaction energy depends only on the dipole moments of the two molecules, here the interaction energy depends on the dipole moment of the polar molecule and also on the polarizability of the neutral molecule.

The average interaction energy is given by:

$$\phi(r) = -c\,/\,r^6$$

Where $c = \mu_1^2\alpha_2\,/\,(4\pi\varepsilon_0)$

α_2 is the polarizability of the neutral molecule.

3. **Induced dipole-Induced dipole (London or Dispersive forces):**

The Vander waals forces also exists even in non-polar molecules like Nitrogen, oxygen and even in monoatomic molecules like Helium, Neon etc. This attraction is evident from the condensation of these gases at sufficiently low temperatures and high pressure. The reason for the existence of these forces in a non-polar molecule could not be understood for years. In **1930**, **F. London** provided a satisfactory explanation for this.

According to him, electrons of a neutral molecule keep on oscillating with respect to the nuclei of the atoms. As a result of this, at a given instant positive charge may be concentrated in one region and the negative charges in the other region of the same molecule. Thus, a non-polar molecule can become momentarily polarized. This polarized molecule may induce a dipole moment in the neighboring molecule with antiparallel orientation.

The electrostatic forces of attraction between the induced dipole and the original dipole (due to electron oscillation) are known as **London forces.** Therefore, the Vander waals attraction between non-polar molecules is solely due to the London forces.

Dispersion forces are present between **all** molecules, whether they are polar or nonpolar.

- Larger and heavier atoms and molecules exhibit stronger dispersion forces than smaller and lighter ones.
- In a larger atom or molecule, the valence electrons are, on average, farther from the nuclei than in a smaller atom or molecule. They are less tightly held and can more easily form temporary dipoles.
- The ease with which the electron distribution around an atom or molecule can be distorted is called the ***polarizability***.

London dispersion forces tend to be:

- stronger between molecules that are easily polarized.
- weaker between molecules that are not easily polarized.

The average interaction energy for London forces is given by:

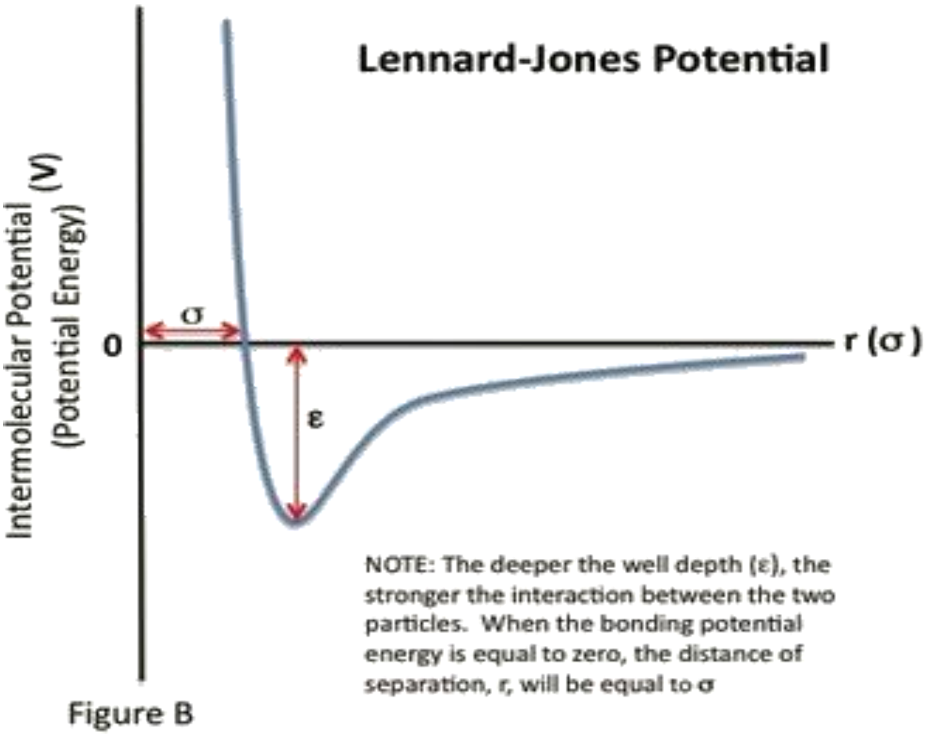
$$\boldsymbol{\phi(r) = -c\ /\ r^6}$$

Where $\boldsymbol{c = \frac{3}{2}\alpha_1\alpha_2\left[\frac{IE_1 \cdot IE_2}{IE_1 + IE_2}\right]}$

Where **IE** is the ionization energy.

The nature of these interactions can be used to understand the physical significance of vander waals constants. When two molecules are far away, there exists an attractive energy between the positively charged nucleus and the negative electron cloud. But as they approach closer, they repel due to the negative electron clouds.

So, the intermolecular potential energy consists of a long-range attractive term and a short-range repulsive term.



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$$\boldsymbol{\phi(r) = 4\varepsilon[(\sigma\,/\,r)^{12} - (\sigma\,/\,r)^{6}]}$$

Here $\boldsymbol{\varepsilon,}$ is the bond energy and $\boldsymbol{\sigma}$ is the bond length corresponding to zero potential energy. For **r**> $\boldsymbol{\sigma,}$ the attractive term predominates (second term) while for **r**< $\boldsymbol{\sigma,}$ the repulsive term predominates (first term).

At the minimum potential energy, $\boldsymbol{\frac{d\phi}{dr} = 0,}$ and **r** = $\mathbf{r_{min}}$

We get, $\boldsymbol{r_m = (2)^{1/6}\sigma.}$ Substituting this value in the Lennard jones potential, we get:

$$\boldsymbol{\phi(r_m) = -\varepsilon}$$