

FUNDAMENTALS OF ADSORPTION & CATALYSIS



Assignment on Forces of Physical Adsorption

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Introduction

Physical adsorption from an adsorbent molecule occurs when the inter-molecular attractive forces between molecules of the solid adsorbent and the gas are greater than those between molecules of the adsorbent itself. Unlike chemisorption, where a chemical bond is established between the solid surface and the molecules, physisorption does not involve any bond formation. The intermolecular forces which come into action for physical adsorption are called Van der Waals forces. These forces are classified into different types:

- Keesom Interactions (Permanent dipole- Permanent dipole interaction)
- Debye Interactions (Permanent dipole-Induced dipole interaction)
- London forces or Dispersive forces (Induced dipole- Induced dipole)

Of the three forces mentioned above, the London force is always present (like the gravitational force) because it does not require the existence of permanent polarity or charge-induced polarity in the molecules. Even neutral atoms or molecules such as helium or hydrocarbons give rise to the London interaction. It influences physical adsorption and surface tension; in addition, it is important in adhesion, wetting phenomena, structure of macromolecules such as proteins and other biological and nonbiological polymer molecules, and stability of foams and thin films. It also plays a very important part in determining the strengths of solids, properties of gases and liquids, heat of melting and vaporization of solids, and the like.

Some of the important features of Van der Waals forces are:

- 1. *The Van der Waals forces are always attractive in nature.***
- 2. *They are relatively long ranged compared to other atomic or molecular-level forces and can have an interval of influence ranging from about 0.2 nm to over 10 nm.***
- 3. *The London force is also often called the dispersion force. The word dispersion here has nothing to do with the role of the London force in colloidal dispersions, but is the result of the role this type of interaction force plays in the dispersion of light in the visible and ultraviolet wavelengths.***
- 4. *The dispersion force between two atoms, molecules, or large bodies is influenced by the presence of other nearby particles. Nevertheless, we consistently add pairwise interactions between the atoms in separate bodies as our procedure for scaling up the interactions. This must be viewed as an approximation since perturbations by neighbouring atoms***

limit the additivity of these forces.

Keesom Interactions (Permanent Dipole-Permanent Dipole)

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 liquefied easily due to the attractive interaction.

The interaction energy, however, depends on the dipole moment of the molecules. Typical example is NH₃ (B.P.: -33.34 °C) and NF₃ (B.P.: -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 μ_1 and μ_2 separated by distance r is given by:

$$\phi(r) = -2\frac{c}{r^6}$$

$$\text{Where, } c = \frac{2}{3kT} \left[\frac{\mu_1 \mu_2}{4\pi\epsilon_0} \right]^2, \epsilon_0 \text{ is the dielectric constant.}$$

One thing which can be noted from the above equation is that the interaction energy is directly dependent on absolute temperature of the system.

Debye Interactions (Permanent Dipole-Induced Dipole)

The second contribution is the induction (also termed polarization) or Debye force, arising from interactions between rotating permanent dipoles and from the polarizability of atoms and molecules (induced dipoles). These induced dipoles occur when one molecule with a permanent dipole repels another molecule's electrons. A molecule with permanent dipole can induce a dipole in a similar neighbouring molecule and cause mutual attraction. Debye forces cannot occur between atoms. The forces between induced and permanent dipoles are not as temperature dependent as Keesom interactions because the induced dipole is free to shift and rotate around the polar molecule. The Debye induction effects and Keesom orientation effects are termed polar interactions.

The induced dipole forces appear from the induction (also termed polarization), which is the attractive interaction between a permanent multipole on one molecule with an induced (by the former di/multi-pole) on another. This interaction is called the *Debye force*, named after Peter J. W. Debye.

One example of an induction interaction between permanent dipole and induced dipole is the interaction between HCl and Argon. In this system, Argon experiences a dipole as its electrons are attracted (to the H side of HCl) or repelled (from the Cl side) by HCl. The average interaction energy is given by the following equation:

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

where $c = \frac{\mu_1 \mu_2 \alpha_2}{4\pi \epsilon_0}$ & $\alpha_2 = \text{polarizability}$.

This kind of interaction can be expected between any polar molecule and non-polar/symmetrical molecule. The induction-interaction force is far weaker than dipole-dipole interaction, but stronger than the London dispersion force.

London/Dispersion Force (Induced Dipole-Induced Dipole)

Finally, we turn our attention to the third contribution to Van der Waals attraction, *London* (or *dispersion*) forces between a pair of induced dipoles. It will be noted that (at least) one permanent dipole is needed for the preceding sources of attraction to be operative. No such restriction is present for the London component. Therefore, this latter quantity is present between molecules of all substances, whether or not they have a permanent dipole. The Van der 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, Fritz 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 neighbouring molecule with antiparallel orientation.

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, further from the nuclei than in a smaller atom or molecule. They are less tightly held and can more easily form temporary dipoles. London force is strong between molecules that are easily polarisable but weak between molecules that are not easily polarisable.

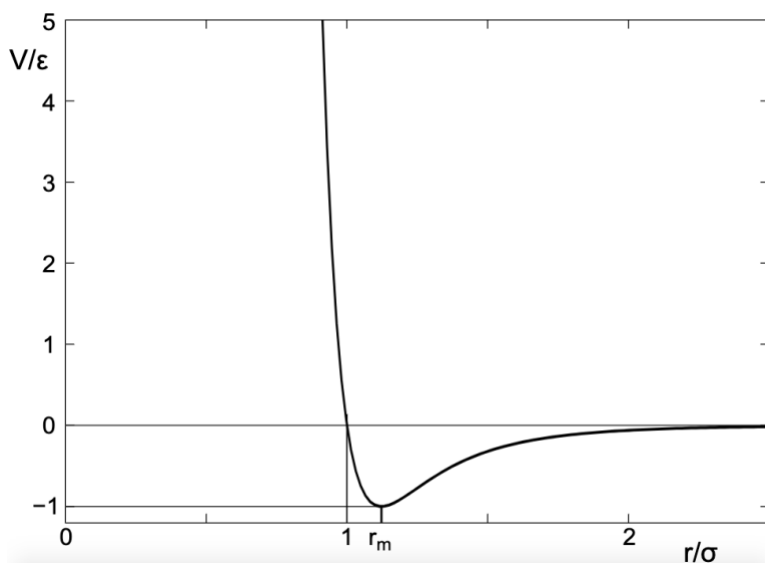
The nature of these interactions can be used to understand the physical significance of Van der Waals constants. When two molecules are far away, there exists an attractive energy between the positively charged nucleus and the negative electron cloud. But as they approach closer, they repel due to the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

So, the intermolecular potential energy consists of a long-range attractive term and a short-range repulsive term. To quantify the London forces, Lennard Jones Potential comes into picture.

$$\phi(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

where σ is the bond length, ϵ is the bond energy and r is the distance between particles or molecules and r_m is the distance at which the potential reaches its minimum.

$$\left. \frac{d\phi(r)}{dx} \right] = 0 \Rightarrow r_m = 2^{1/6} \sigma = 1.122\sigma$$



Lennard Jones Potential