1.2: Intermolecular Forces - Introduction and London Dispersion

Intermolecular forces are forces between molecules. Depending on its strength, intermolecular forces cause the forming of three physical states: solid, liquid and gas. The physical properties of melting point, boiling point, vapor pressure, evaporation, viscosity, surface tension, and solubility are related to the strength of attractive forces between molecules. These attractive forces are called Intermolecular Forces or Van der Waals forces.

Introduction

There are four types of intermolecular forces. The weakest of these are induced dipole forces (London Dispersion Forces). Most of the intermolecular forces are similar to bonding between atoms in a single molecule. Intermolecular forces just extend the thinking to forces between molecules and follows the patterns already set by the bonding within molecules.

Induced Dipole - London Dispersion Forces

London Dispersion Force is the weakest intermolecular force. It is the only attractive interaction between two nonpolar molecules.

The chance that an electron of an atom is in a certain area in the electron cloud at a specific time is called the "electron charge density." Since there is no way of knowing exactly where the electron is located and since they do not all stay in the same area 100 percent of the time, if the electrons all go to the same area at once, a dipole is formed momentarily. Even if a molecule is nonpolar, this displacement of electrons causes a nonpolar molecule to become polar for a moment, this is called an instantaneous dipole.

Since the molecule is now polar, this means that all the electrons are concentrated at one end and the molecule is partially negatively charged on that end. This negative end makes the surrounding molecules have an instantaneous dipole also, attracting the surrounding molecules' positive ends. This process is known as the London Dispersion Force of attraction.

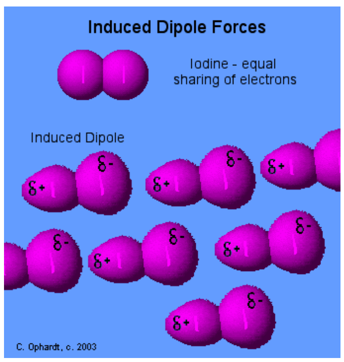


Figure 1: Induced dipoles between iodine molecules.

The ability of a molecule to become polar and displace its electrons is known as the molecule's "polarizability." The more electrons a molecule contains, the higher its ability to become polar. Polarizability increases in the periodic table from the top of a group to the bottom and from right to left within periods. This is because the higher the molecular mass, the more electrons an atom has. With more electrons, the outer electrons are easily displaced because the inner electrons shield the nucleus' positive charge from the outer electrons..

When the molecules become polar, the melting and boiling points are raised because it takes more heat and energy to break these intermolecular forces. Therefore, the greater the mass, the more electrons present, and the more electrons present, the higher the melting and boiling points of these substances.

London dispersion forces are stronger in those molecules that are not compact, but long chains of elements. This is because these molecules have greater surface area and therefore have more points of contact to interact with other molecules.

We can calculate the potential energy between the two identical nonpolar molecules using the following formula:

$$V = -\frac{3}{4}\frac{\alpha^2 I}{r^6} \tag{2}$$

- α is the polarizability of nonpolar molecule.

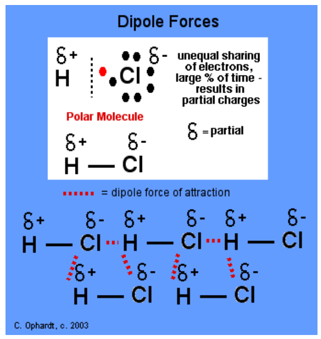
- r is the distance between the two molecule.
- I = the first ionization energy of the molecule.

Negative sign indicates the attractive interaction.

Dipole Forces

Molecular dipoles occur due to the unequal sharing of electrons between atoms in a molecule. Those atoms that are more electronegative pull the bonded electrons closer to themselves. The buildup of electron density around an atom or discreet region of a molecule can result in a molecular dipole in which one side of the molecule possesses a partially negative charge and the other side a partially positive charge. Molecules with dipoles that are not canceled by their molecular geometry are said to be polar.

In the figure below, hydrochloric acid is a polar molecule with the partial positive charge on the hydrogen and the partial negative charge on the chlorine. A network of partial + and - charges attract molecules to each other.



$$V = -\frac{3}{2}\frac{I_A I_B}{I_A + I_B}\frac{\alpha_A \alpha_B}{r^6} \tag{3}$$

Dipole-Dipole Interactions

When a polar molecule encounters another polar molecule, the positive end of one molecule is attracted to the negative end of the other polar molecule. Many molecules have dipoles, and their interaction occur by dipole-dipole interaction. For example: $SO_2 \leftrightarrow SO_2$. (approximate energy: 15 kJ/mol). Polar molecules have permanent dipole moments, so in this case, we consider the electrostatic interaction between the two dipoles:

$$V = -\frac{2}{3}\frac{\mu_1^2 \mu_2^2}{(4\pi\epsilon_0)^2 r^6} \tag{4}$$

μ is the permanent dipole moment of the molecule 1 and 2.

Ion-Dipole Interactions

Ion-Dipole interaction is the interaction between an ion and polar molecules. For example, the sodium ion/water cluster interaction is approximately 50 KJ/mol.

$$Na^+ \leftrightarrow (OH_2)_n \tag{5}$$

Because the interaction involves in the charge of the ion and the dipole moment of the polar molecules, we can calculate the potential energy of interaction between them using the following formula:

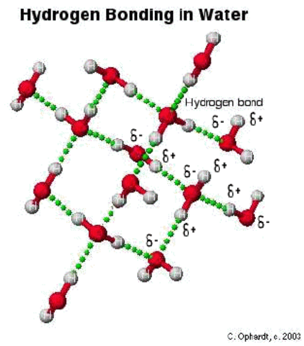
$$V = -\frac{q\mu}{(4\pi\epsilon_0)r^2} \tag{6}$$

- r is the distance of separation.
- q is the charge of the ion (only the magnitude of the charge is shown here.)
- μ is the permanent dipole moment of the polar molecule.

Hydrogen Bonding

The hydrogen bond is really a special case of dipole forces. A hydrogen bond is the attractive force between the hydrogen attached to an electronegative atom of one molecule and an electronegative atom of a different molecule. Usually the electronegative atom is oxygen, nitrogen, or fluorine. In other words - The hydrogen on one molecule attached to O or N that is attracted to an O or N of a different molecule.

In the graphic below, the hydrogen is partially positive and attracted to the partially negative charge on the oxygen or nitrogen. Because oxygen has two lone pairs, two different hydrogen bonds can be made to each oxygen. This is a very specific bond as indicated. Some combinations that are not hydrogen bonds include: hydrogen to another hydrogen or hydrogen to a carbon.



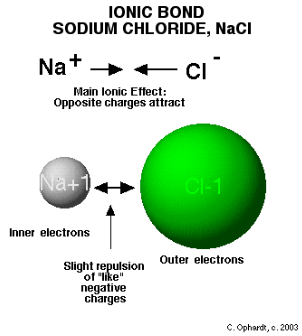
Coulombic Forces

The forces holding ions together in ionic solids are electrostatic forces. Opposite charges attract each other. These are the strongest intermolecular forces. Ionic forces hold many ions in a crystal lattice structure. According to Coulomb's law:

$$V = -\frac{q_1 q_2}{4\pi\epsilon r} \tag{1}$$

- q is the charges.
- r is the distance of separation.

Based on Coulomb's law, we can find the potential energy between different types of molecules.



References

1. Kotz, Treichel, Weaver. Chemistry and Chemical reactivity, sixth ed. Thompson, 2006.
2. Donald Allan McQuarrie, John Douglas Simon. Physical Chemistry: a molecular approach. University Science Books, 1997.
3. Petrucci, Ralph H., et al. General Chemistry: Principles and Modern Applications. Upper Saddle River, NJ: Prentice Hall, 2007

Contributors and Attributions

- Kathryn Rashe, Lisa Peterson, Seila Buth, Irene Ly