جامعة الزهراء للبنات

Lecture 1
States of matter

Qasim Allawi
Msc.Pharm.
Assistant professor
Lecturer in pharmaceutics
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Binding Forces Between Molecules

Repulsive and attractive forces
Intramolecular forces
Intermolecular forces
Bond energy

Repulsive and Attractive Forces

For molecules to exist as aggregates in gases, liquids, and solids, *inter*molecular forces must exist

These intermolecular forces involve both attractive and repulsive forces.

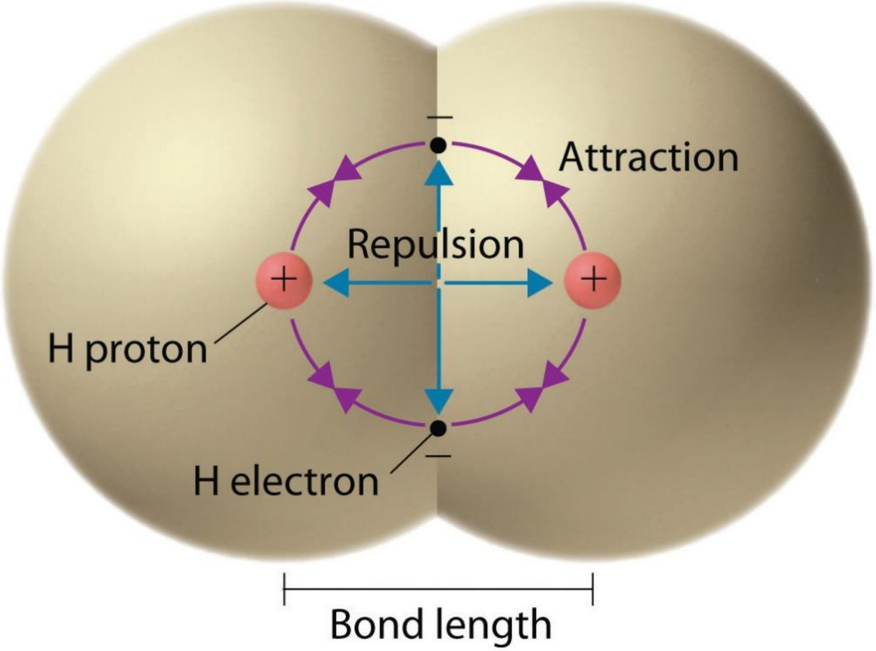
These forces must be balanced in an energetically favored arrangement for the molecules to interact.

Repulsive and Attractive Forces

When two atoms or molecules are brought closer together, the opposite charges and binding forces in the two molecules are closer together than the similar charges and forces, causing the molecules to attract one another.

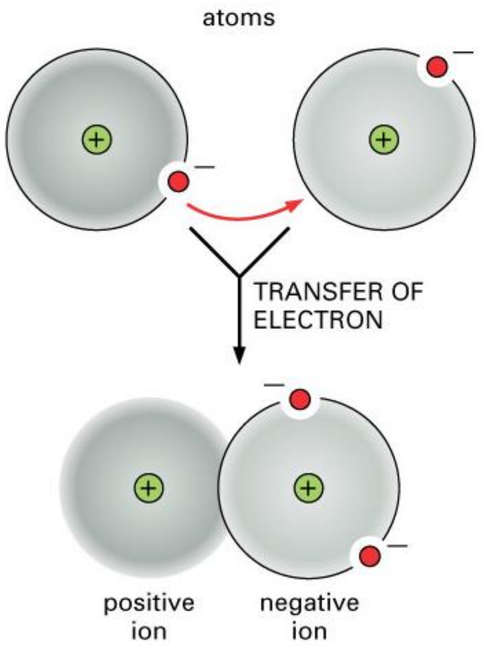
When the molecules are brought so close that the similar charges touch, they repel each other like rigid elastic bodies.

At a certain equilibrium distance, (about 3–4 Å), the repulsive and attractive forces are equal. At this position, the potential energy of the two molecules is a minimum and the system is most stable.

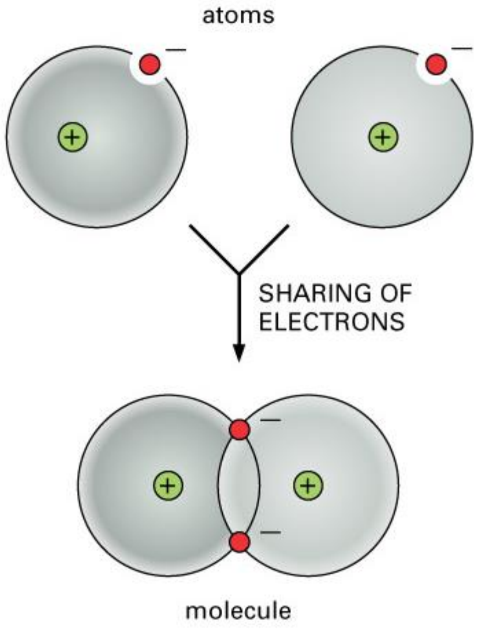


Intramolecular forces

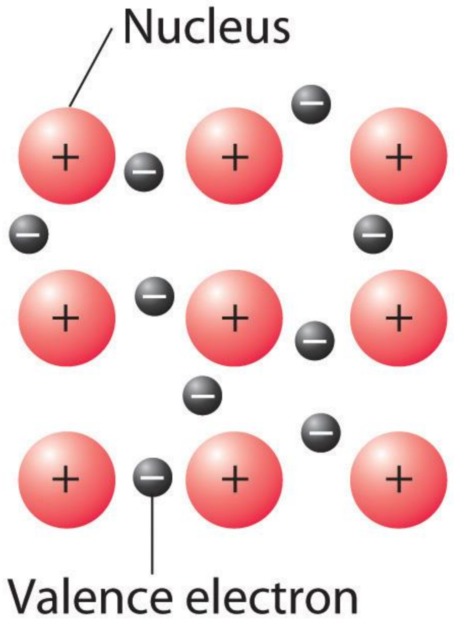
Atoms within a molecule are attracted to one another by sharing of electrons, it can be categorized into:



1. Ionic bonding:
between positively and negatively charged ions (metals and non-metals).



2. Covalent bonding:
between atoms that share the outer shell of electrons.



3. Metallic bonding:
between positively charged ions and delocalized outer electrons of metal elements, it is weaker than both ionic and covalent bonding.

Intermolecular forces

Intermolecular forces occur between molecules. It can be divided into:

1. **Van der waals forces**
2. **Ion–dipole interaction**
3. **Ion–induced dipole interaction**
4. **Hydrogen bonds**

Intermolecular forces

Van der Waals Forces

Van der Waal interactions are weak forces that involve the dispersion of charge across a molecule called a dipole.

Van der Waal interactions can be classified into:

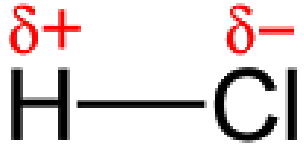
A. Dipole–dipole interaction, orientation effect, or **Keesom force**
B. Dipole-induced dipole interaction, induction effect, or **Debye force**
C. Induced dipole–induced dipole interaction, dispersion effect, or **London force**

Intermolecular forces

Van der Waals Forces: *Keesom forces*

Keesom forces occur between polar molecules in which the permanent dipoles interact with one another (***dipole-dipole* interactions**) or (**orientation effect**).

Polar molecules have polar covalent bonds which are unevenly distributed in space due to the difference in the electronegativity of the atoms forming the bond. e.g. HCl.

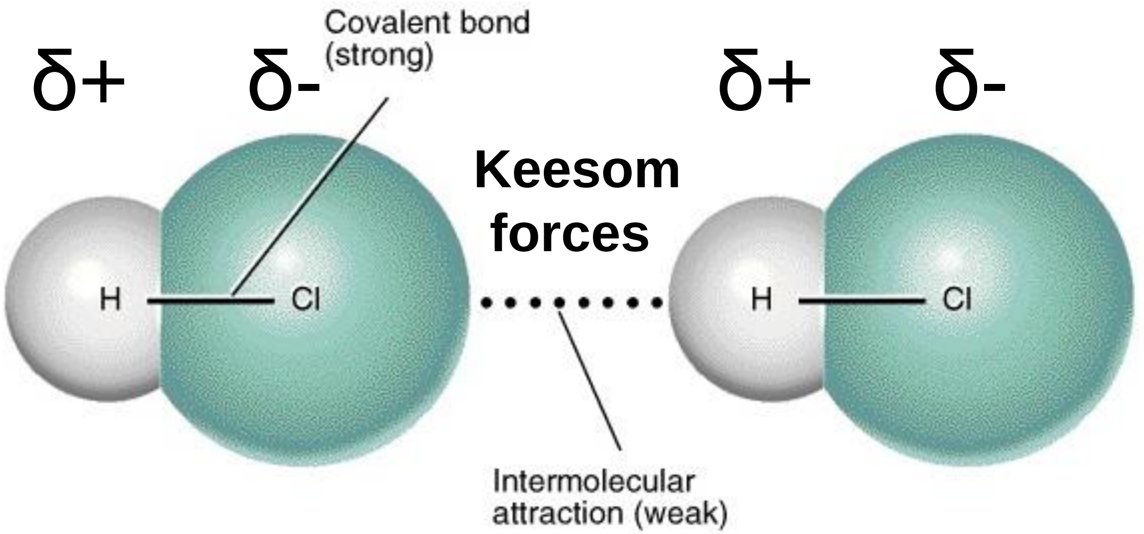


The nucleus of the chlorine atom pulls the electron pair involved in the chlorine–hydrogen bond closer to itself and creates a permanent partial positive charge on the hydrogen and a permanent partial negative charge on the chlorine (**Permanent dipole**),

Intermolecular forces

Van der Waals Forces: *Keesom forces*

The Partial opposite charges (permanent dipoles) attract one another (**dipole-dipole interactions**)



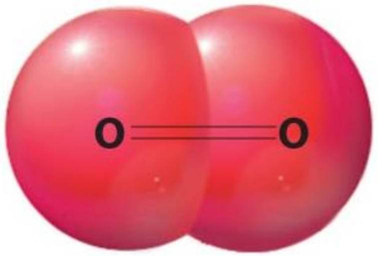
The dipole-dipole forces increases as the polarity of the molecule increases.

Keesom forces are much weaker than ionic bonds because the charges involved in bonding are partial.

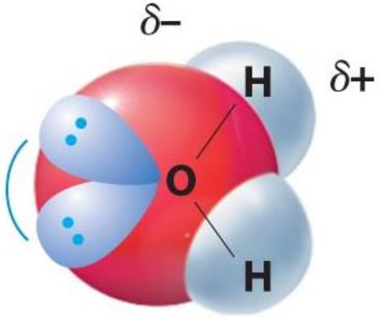
Intermolecular forces

Van der Waals Forces: *Debye forces*

Debye forces occur between a polar and a nonpolar molecule in which the permanent dipole in the polar molecule induce an electric dipole in the nonpolar one (***dipole-induced dipole* interactions**) or (**induction effect**). e.g. water and oxygen



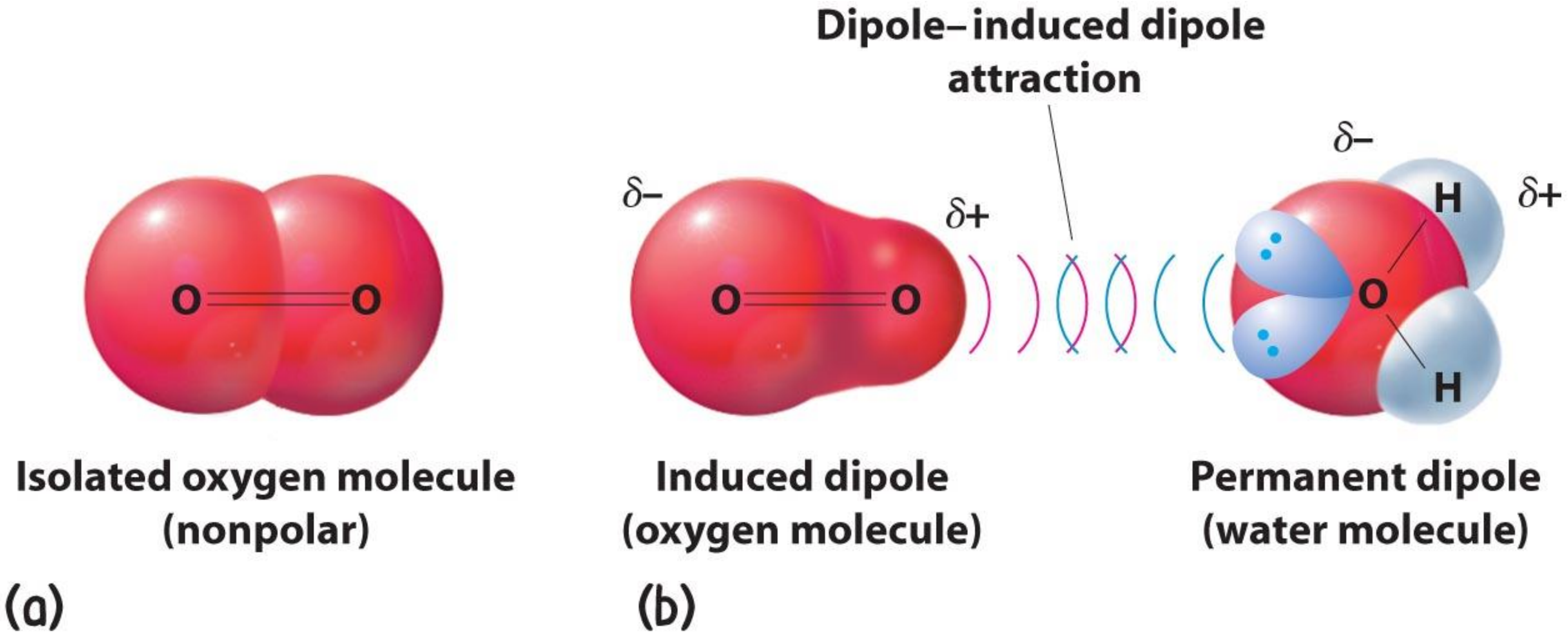
Oxygen molecule
(nonpolar)



Water molecule
(polar; permanent dipole)

Intermolecular forces

Van der Waals Forces: *Debye forces*



The oxygen molecule is nonpolar. However, when it comes close to the oxygen atom in a water molecule, the partial negative charge on the oxygen atom repels the electrons in the oxygen molecule. This causes (induces) a temporary partial positive charge in the end closest to the water molecule and a buildup of a partial negative charge in the end furthest away.

Intermolecular forces

Van der Waals Forces: *Debye forces*

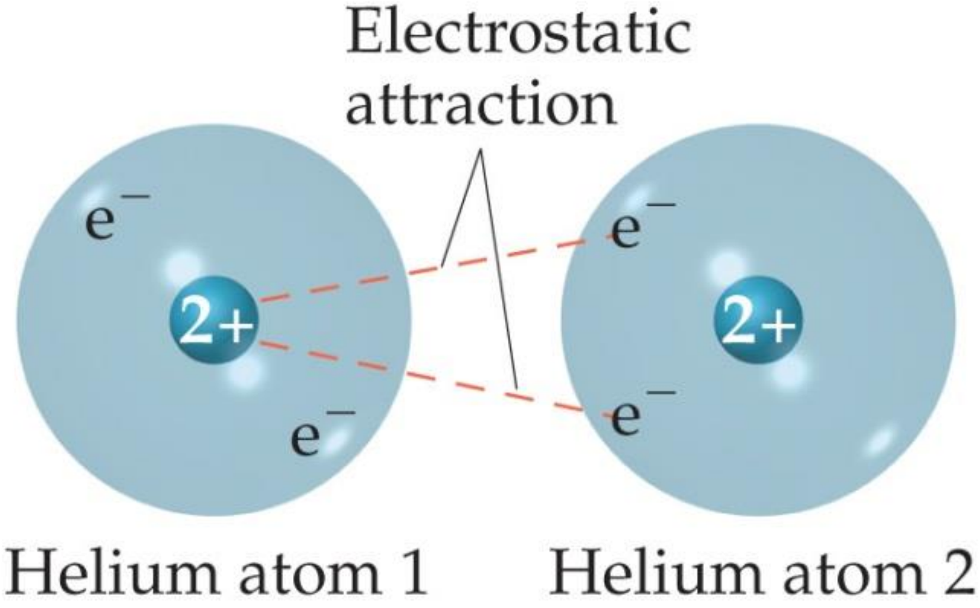
The strength of Debye forces increases with the ease of distortion of the electron cloud of the nonpolar molecule (i.e. polarizability of the molecule)

Debye forces is weaker than Keesom forces because the dipole in the nonpolar molecule is temporary (induced) and forms only when the two molecules is extremely close to each other.

Intermolecular forces

Van der Waals Forces: *London forces*

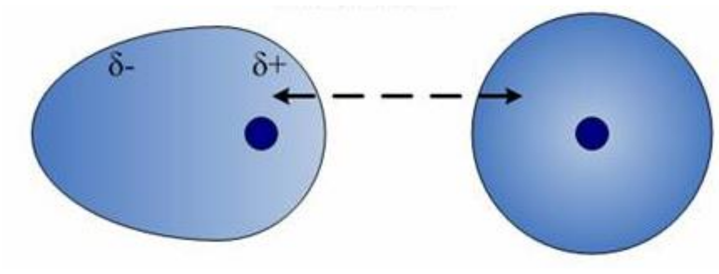
London forces occur between two nonpolar (neutral) molecules in which molecules can induce polarity on each other (***induced dipole-induced dipole* interactions**) or (**dispersion effect**). e.g. Helium



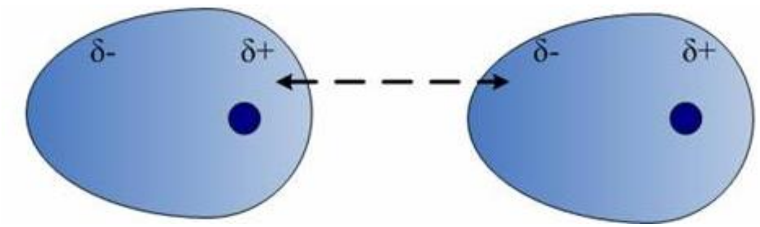
Intermolecular forces

Van der Waals Forces: *London forces*

Two Helium atoms are nonpolar and posses no dipoles. The average distribution of electrons around each nucleus is spherically symmetrical



At a given instant in time, the distribution of electrons around an individual atom may not be perfectly symmetrical (the electron cloud may be on one side of the nucleus). This atom will have an **instantaneous dipole** (temporary partial charges) causing a neighboring atom to distort due to the electrostatic attractions/repulsions of their electron clouds



Attraction between opposite partial charges of neighboring induced dipoles cause atoms to stick together for a very short time

Intermolecular forces

Van der Waals Forces: *London forces*

London forces occur between all atoms and molecules (between polar/polar and polar/nonpolar molecules as well)

The larger the atom or molecule, the ***greater*** its polarizability (***easier*** to induce a momentary dipole) and the ***stronger*** the dispersion forces become. This is because:

1. The electrons are farther from the positive nucleus and so are held less strongly
2. The number of electrons is greater

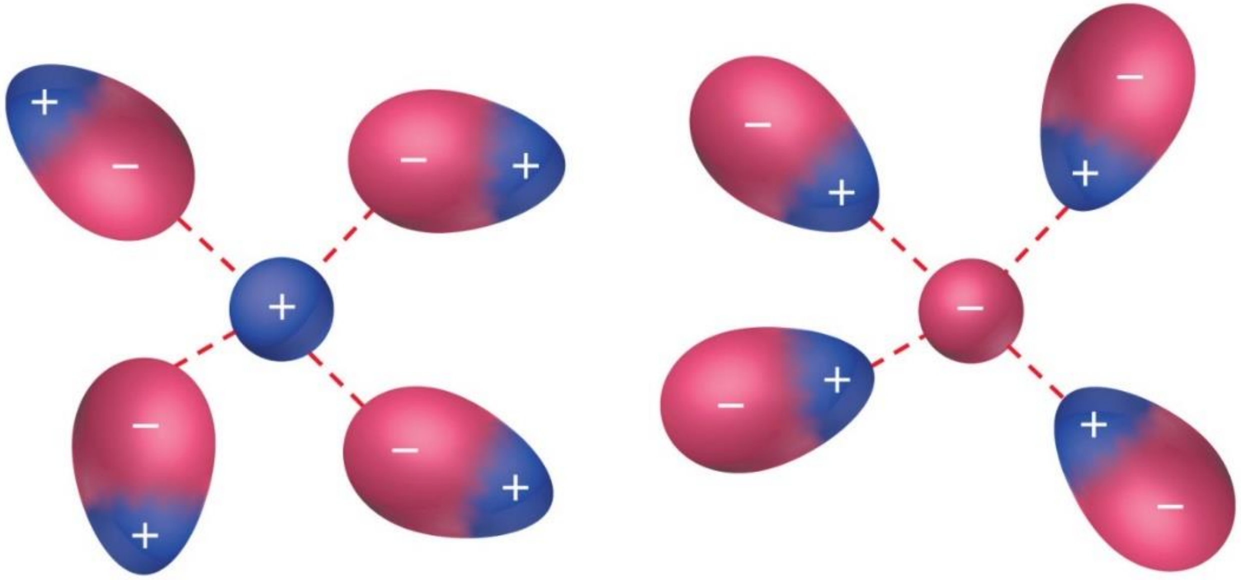
London Force is the weakest of all the intermolecular forces.

Intermolecular forces

Ion-dipole forces

Ion-dipole forces occur between a ***charged ion*** and a ***polar molecule*** (i.e. a molecule with a ***dipole***)

Cations are attracted to the negative end of a dipole, while anions are attracted to the positive end of a dipole

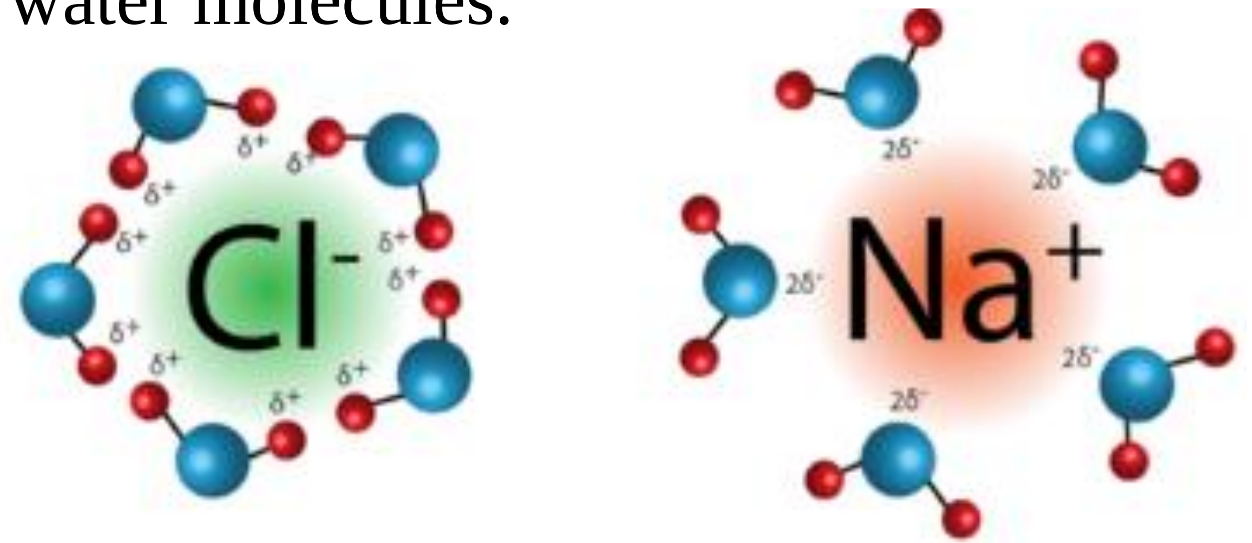


Cation–dipole attractions   Anion–dipole attractions

Intermolecular forces

Ion-dipole forces

These types of interactions account in part for the solubility of ionic crystalline substances in water; the cation, for example, attracts the relatively negative oxygen atom of water and the anion attracts the hydrogen atoms of the dipolar water molecules.



Slightly positive hydrogen are attracted to chlorine anions

Slightly negative oxygen are attracted to sodium cations

Intermolecular forces

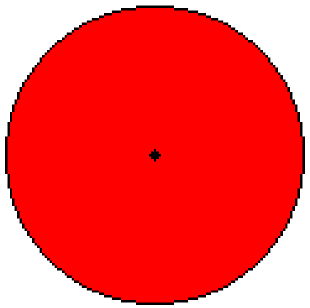
Ion-induced dipole forces

Ion-Induced dipole forces occur between a charged ion and a nonpolar molecule.

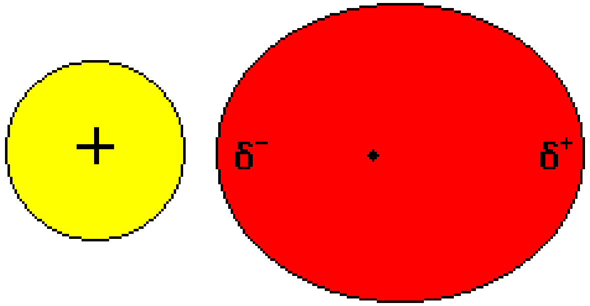
Theses forces result when the approach of an ion induces a dipole in an atom or in a nonpolar molecule by disturbing the arrangement of electrons

Ion-induced dipole forces are presumably involved in the formation of the potassium iodide complex

$$I^2 + K^+I^- = K^+\ I_3^-$$



Spherical atom with no dipole. The dot indicates the location of the nucleus.

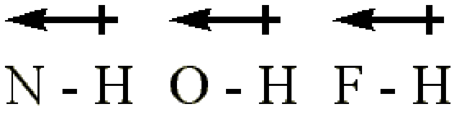


Upon approach of a charged ion, electrons in the atom respond and the atom develops a dipole.

Intermolecular forces

Hydrogen bond

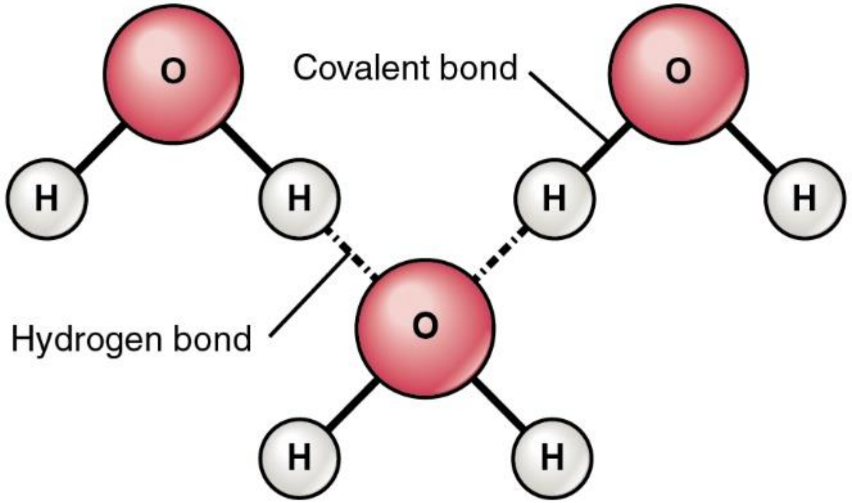
Hydrogen bond is a strong type of dipole-dipole interaction that occurs between a molecule containing a hydrogen atom and a strongly electronegative atom such as fluorine, oxygen, or nitrogen



In order to create the bond, the hydrogen atom must be covalently attached to another electronegative atom.

A perfect example of hydrogen bond is ***water***.

Hydrogen bonds can also exist between alcohol molecules, carboxylic acids, aldehydes, esters, and polypeptides.

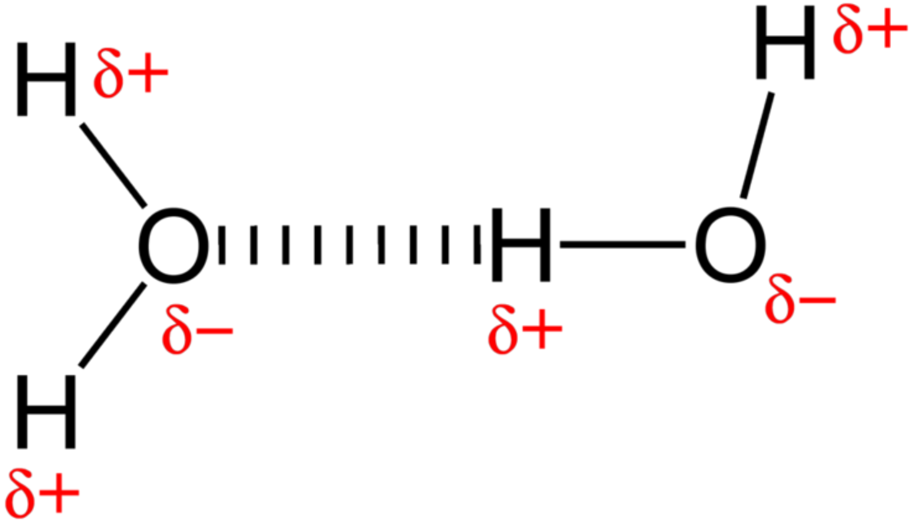


Intermolecular forces

Hydrogen bond

In a water molecule, the hydrogen lone electron is pulled by the covalently attached oxygen atom, creating a naked nucleus on the side of the hydrogen atom facing away (partial positive charge).

This side of the hydrogen atom can get close to neighboring oxygen atom (with a partial negative charge) and interact strongly with it.



Intermolecular forces

Hydrogen bond

Hydrogen bonds are responsible for many unusual physical properties of water including its abnormally low vapor pressure, high boiling point, and the greater volume of ice water.

Hydrogen bonding is stronger than all Van der Waals intermolecular forces (they are given their own classification), but are still weaker than ionic and covalent bonds.

Bond energy

Bond energy is a measure of bond strength.

It is the heat required to break one mole of molecules into their individual atoms

The relative strength of forces from strongest to weakest:

Intramolecular forces

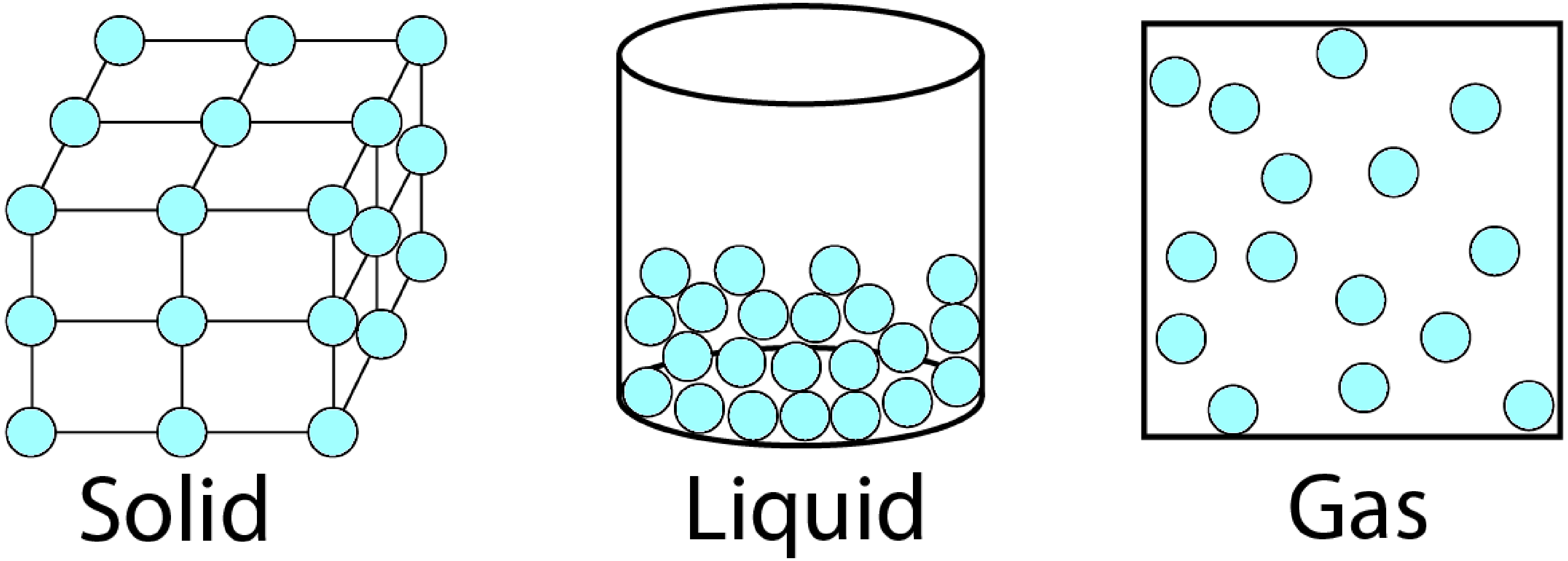
1. Ionic
2. Covalent
3. Metallic

Intermolecular forces

1. Ion-dipole forces
2. Ion-induced dipole
3. Hydrogen Bond
4. Van der Waals’ forces (Keesom forces > Debye forces > London forces)

States of matter

1. Gaseous state
2. Liquid state
3. Solid and crystalline state
4. Liquid crystalline state



The gaseous state

Gas general properties

Ideal gas

Real gas

Gas general properties

Gases can be expanded infinitively, therefore gases can fill containers and take their volume and shape.

Gases diffuse and mix evenly and rapidly.

Gases have much lower densities than liquids and solids (There is a lot of free space in a gas, therefore; It is the most compressible state of matter).

Gas general properties

Gas molecules travel in random paths and collide with one another and with the walls of the container in which they are confined

A gas exerts a **pressure** (a force per unit area) expressed in dynes/cm^2, atmospheres or in mmHg (1 atm = 760 mmHg).

Gases have **volumes** that is expressed in liters or cubic centimeters (1 cm^3 = 1 mL).

The **temperature** involved in the gas equations is expressed by the *absolute* or *Kelvin* scale (0°C=273.15 K (Kelvin)).

Ideal gas

Ideal gas is a gas where **no intermolecular interactions** exist and collisions are **perfectly elastic**, and thus no energy is exchanged during collision.

The properties of the ideal gas can be described by the *general ideal gas law,* which are derived from Boyle, Charles and Gay-Lussac laws

Ideal gas
Boyle’s law

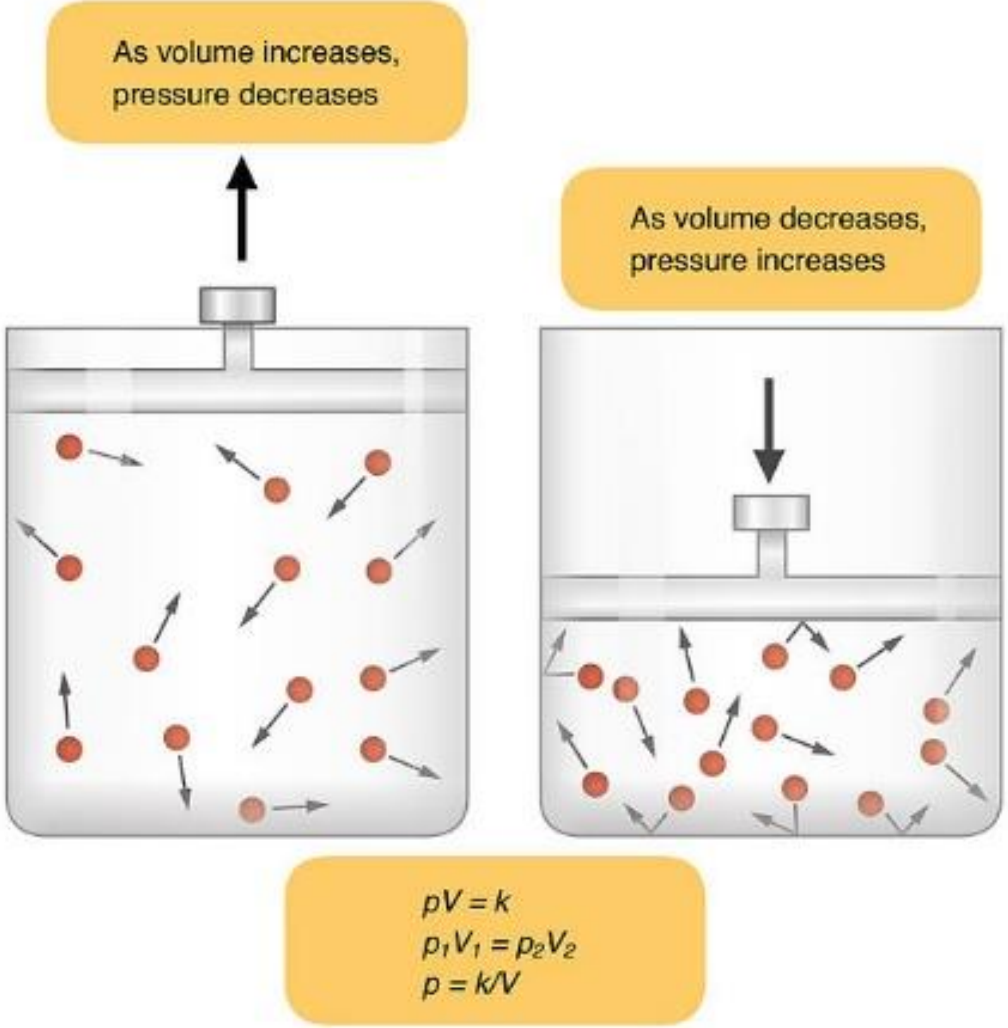
Boyle’s law states that the volume and pressure of a given mass of gas is inversely proportional (i.e. when the pressure of a gas increases, its volume decreases).

$$\mathbf{P}\ \boldsymbol{\alpha}\ \frac{\mathbf{1}}{V} \quad or \quad \mathbf{P} = \frac{K}{V}$$

$$\mathbf{P_1V_1 = P_2V_2}$$

P: pressure, **K**: constant,

V: volume



As volume increases, pressure decreases

As volume decreases, pressure increases

$pV = k$
$p_1V_1 = p_2V_2$
$p = k/V$

Ideal gas

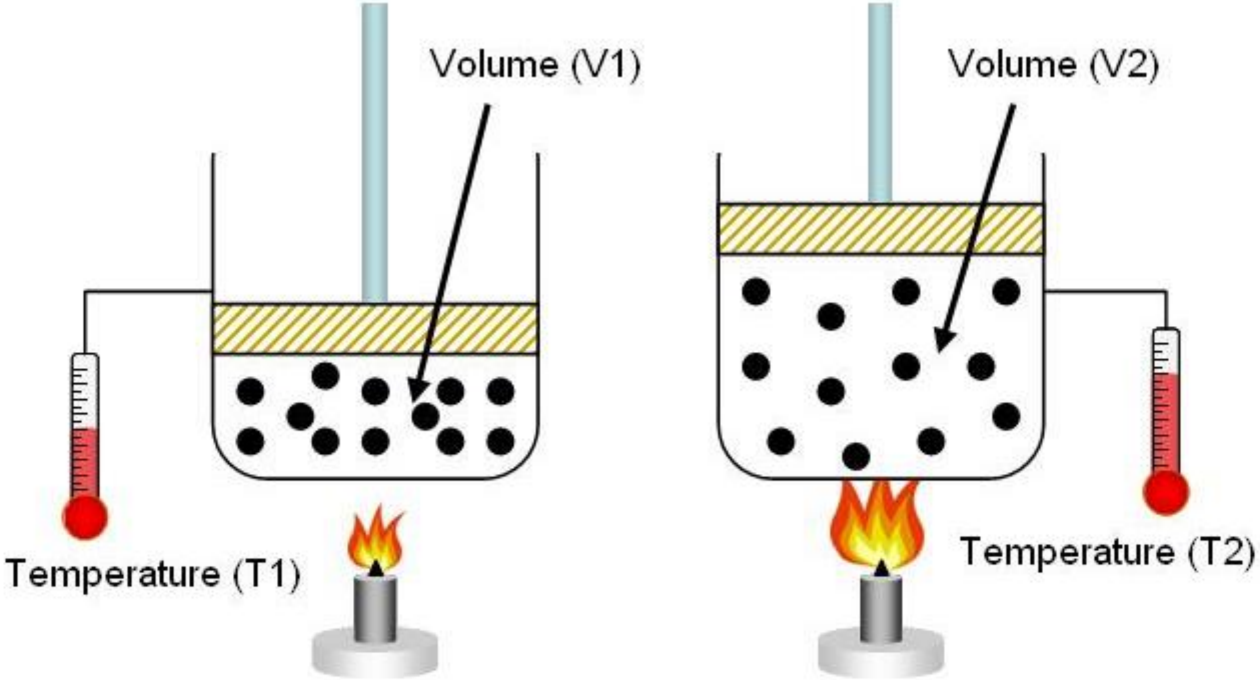
Charles law

Charles law states that the volume and absolute temperature of a given mass of gas at constant pressure are directly proportional (i.e when the temperature of a gas increases, its volume increases as well).

V α T *or* **V = k T**

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

T: temperature in Kelvin



Ideal gas

Gay-Lussac law

The law of Gay-Lussac states that the pressure and absolute temperature of a given mass of gas at constant volume are directly proportional (i.e when the temperature of a gas increases, its pressure increases as well).

P α T *or* **P = k T**

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

Ideal gas

Combined gas law

Boyle, Gay-Lussac and Charles law can be combined to obtain the familiar relationship:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Ideal gas

Combined gas law: *Example 1*

A gas occupies a volume of 30.0 mL at a temperature of 20°C and a pressure of 740 mm Hg. Assuming the gas is ideal, what is the volume at 0°C and 760 mm Hg?

$$\frac{\mathbf{P_1\ V_1}}{\mathbf{T_1}} = \frac{\mathbf{P_2\ V_2}}{\mathbf{T_2}}$$

$$\frac{740 \times 30}{273 + 20} = \frac{760\ \times\ \mathbf{V_2}}{273}$$

$$\mathbf{V_2} = 27.2\ \mathrm{mL}$$

Ideal gas

Combined gas law: *Example 2*

A sample of methane CH4 has a volume of 7.0 dm^3 at a temperature of 4°C and a pressure of 0.848 atm. Calculate the volume of methane at a temperature of 11°C and a pressure of 1.52 atm.

$$\frac{\mathbf{P_1\ V_1}}{\mathbf{T_1}} = \frac{\mathbf{P_2\ V_2}}{\mathbf{T_2}}$$

$$\frac{0.848 \times 7}{273 + 4} = \frac{1.52 \times \mathbf{V_2}}{273 + 11}$$

$$\mathbf{V_2} = 4\ \mathrm{dm}^3$$

Ideal gas

General ideal gas law

General ideal gas law (also called *equation of state*) relates the specific conditions, that is, the **pressure**, **volume**, and **temperature** of a given mass of gas.

$$\frac{\mathbf{P_1\ V_1}}{\mathbf{T_1}} = \frac{\mathbf{P_2\ V_2}}{\mathbf{T_2}} \quad \Longrightarrow \quad \frac{\mathbf{P\ V}}{\mathbf{T}} = \mathbf{R}$$

R: the *molar gas constant* value for the **PV/T** ratio of an ideal gas.

For **n** moles it becomes:

$$\mathbf{PV = nRT}$$

Ideal gas

General ideal gas law: *Molar gas constant*

The volume of 1 mole of an ideal gas under *standard conditions* of temperature and pressure (i.e., at 0°C and 1 atm) has been found by experiment to be 22.414 liters.

Substituting this value in general ideal gas law:

*Q/ How can you find **R** value?*

$$\mathbf{R = \frac{P\,V}{T} = \frac{1 \times 22.414}{273.16} = 0.08205\ atm\ L/mole\ K}$$

The molar gas constant can also be expressed by energy units:

R = 8.314 Joules/mole K or

R = 8.314×10^{7} erg/mole K 1 joule = 10^{7} erg

Ideal gas

General ideal gas law: *Example*

What is the volume of 2 moles of an ideal gas at 25°C and 780 mm Hg?

780 mmHg / 760 mmHg = 1.0263 atm

25 °C + 273 = 298 K

PV = nRT

$$\mathbf{V} = \frac{\mathbf{nRT}}{\mathbf{P}} = \frac{2 \times 0.08205 \times 298}{1.\ 062} = 47.65\ \text{L}$$

Ideal gas

General ideal gas law: *Molecular weight*

The approximate molecular weight of a gas can be determined by use of the ideal gas law:

$\mathbf{PV = nRT}$ since $\mathbf{n = g/M}$

Then

$$\mathbf{PV = \frac{g}{M}RT}$$

$$\mathbf{M = \frac{gRT}{PV}}$$

Ideal gas

General ideal gas law: *Molecular weight*

Example

If 0.30 g of ethyl alcohol in the vapor state occupies 200 mL at a pressure of 1 atm and a temperature of 100°C, what is the molecular weight of ethyl alcohol?

100 °C + 273 = 373 K

200 mL ÷ 1000 mL = 0.2 L

$$\mathbf{M} = \frac{\mathbf{gRT}}{\mathbf{PV}} = \frac{0.3 \times 0.082 \times 373}{1 \times 0.2} = 46\,\frac{\mathrm{g}}{\mathrm{mole}}$$

Ideal gas

Kinetic Molecular Theory

Kinetic molecular theory explains the behavior of gases according to the ideal gas law:

1. Gases are composed of particles called atoms or molecules, the total volume of which is so small (negligible) in relation to the volume of the space in which the molecules are confined.
2. Gas molecules exert neither attractive nor repulsive forces on one another.

Ideal gas

Kinetic Molecular Theory

3. The particles exhibit continuous random motion. The average kinetic energy, *E*, is directly proportional to the absolute temperature of the gas, or **$E = (3/2) RT$**.
4. The molecules exhibit perfect elasticity; there is no net loss of speed or transfer of energy after they collide with one another and with the walls of the confining vessel.

Real gas

Real gases do not interact without energy exchange, and therefore do not follow the laws of Boyle, Charles, and Gay-Lussac.

Real gases are not composed of infinitely small and perfectly elastic non-attracting spheres.

They are composed of molecules of a finite volume that tend to attract one another.

The significant molecular volume and the intermolecular attractions between gas molecules affect both the <u>volume</u> and the <u>pressure</u> of a real gas respectively.

Real Gas

Van der Waals Equation

The *van der Waals equation* is a modified ideal gas equation that takes into account the factors that affect the volume and pressure of a real gas.

For 1 mole of gas: $\left(\boldsymbol{P} + \frac{\boldsymbol{a}}{\boldsymbol{V}^2}\right)(\boldsymbol{V} - \boldsymbol{b}) = \boldsymbol{RT}$

For **n** moles of gas: $\left(\boldsymbol{P} + \frac{\boldsymbol{a}\boldsymbol{n}^2}{\boldsymbol{V}^2}\right)(\boldsymbol{V} - \boldsymbol{nb}) = \boldsymbol{nRT}$

The term $\boldsymbol{a/V^2}$ accounts for the *internal pressure* per mole resulting from the intermolecular forces of attraction between the molecules;

b accounts for the *excluded volume*, which is about four times the molecular volume.

Real Gas

Van der Waals Equation

The influence of non-ideality is greater when the gas is compressed (At high pressure and low temperature).

When the volume of a gas is large (At low pressure and high temperature), the molecules are well dispersed and far apart. Under these conditions, a/V^2 and b become insignificant with respect to P and V, respectively, and the van der Waals equation for the real gas reduces to the ideal gas equation:

$$PV = nRT$$

At these conditions, real gases behave in an ideal manner.

Q/ when can we notice a real gas with ideal manner?

References

Sinko, P. J. M. A. N. 2006. *Martin's physical pharmacy and pharmaceutical sciences: physical chemical and biopharmaceutical principles in the pharmaceutical sciences*, Philadelphia, Lippincott Williams & Wilkins.