States of Matter

Lecture 1

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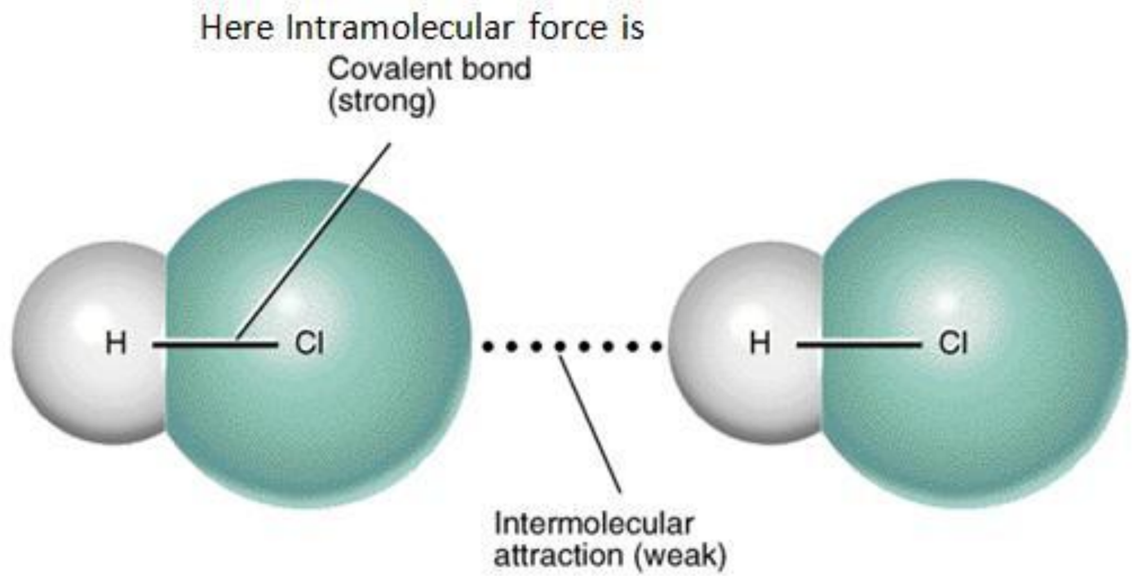
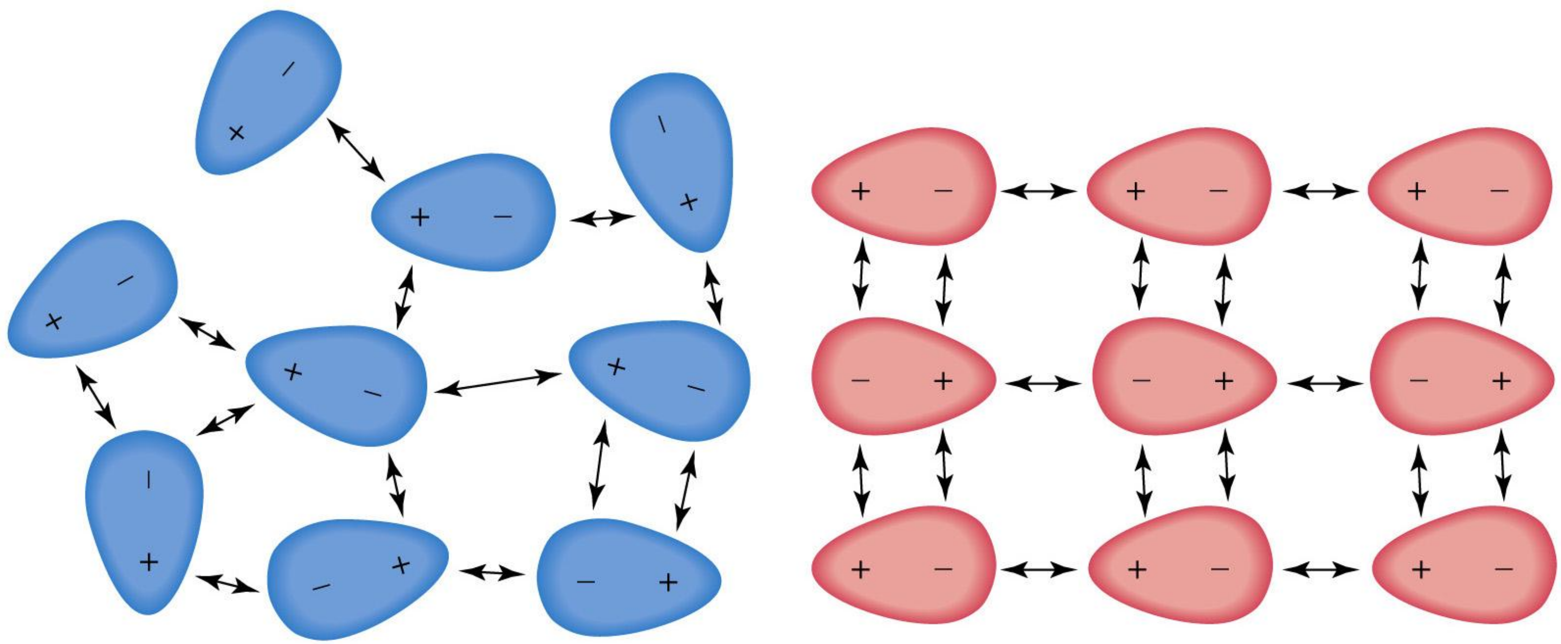
Physical pharmacy

Binding Forces Between Molecules

- For molecules to exist as aggregates in gases, liquids, and solids, **intermolecular** forces must exist.
- Cohesion: the attraction of like molecules
- adhesion: the attraction of unlike molecules are manifestations of intermolecular forces
- Repulsion is a reaction between two molecules that forces them apart.

- **Intermolecular** forces are forces between molecules
- Inter' means between, so these are the forces between molecules.
- **Intramolecular** forces act within molecules, which are the strong forces that keep a molecule together.
- Intra' means inside, so these are the inside forces in a molecule.
- Intermolecular forces are weaker than intramolecular forces.


Here Intramolecular force is
Covalent bond
(strong)
H
Cl
H
Cl
Intermolecular
attraction (weak)



(a) (b)

Repulsive and Attractive Forces

- When molecules interact, both repulsive and attractive forces operate.
- As 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.
- The negatively charged electron clouds of molecules largely govern the balance (equilibrium) forces between the two molecules .When the molecules are brought so close that the outer charge clouds touch, they repel each other like rigid elastic bodies.

- Thus, attractive forces are necessary for molecules to cohere, whereas repulsive forces act to prevent the molecules from interpenetrating and annihilating each other.
- Just as the actions of humans are often influenced by a conflict of loyalties, so too is molecular behavior governed by attractive and repulsive forces.

- Repulsion is due to the interpenetration of the electronic clouds of molecules and increases exponentially with a decrease in distance between the molecules. At a certain equilibrium distance, about (3-4)x 10^{-8} cm (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 in the following figure.

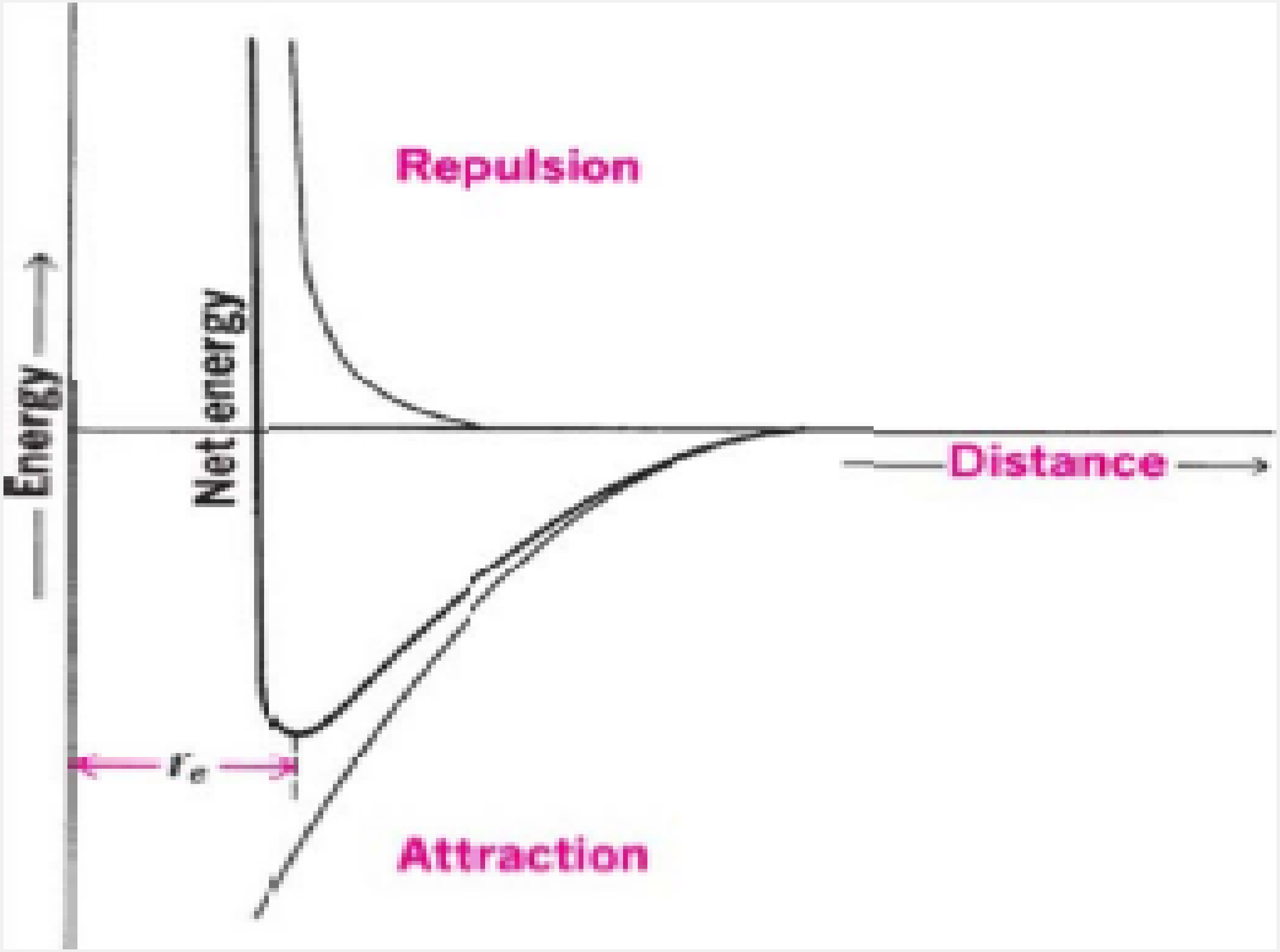
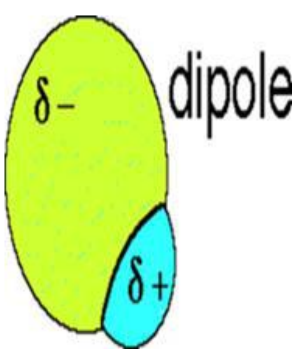


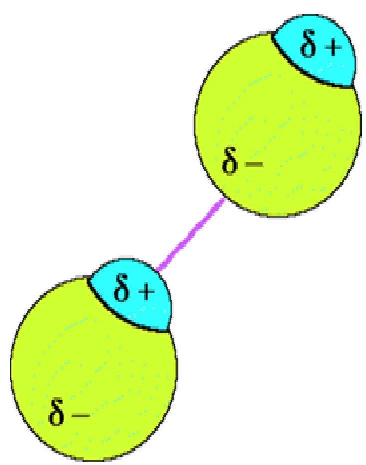
Fig. 2-1. Repulsive and attractive energies and net energy as a function of the distance between molecules. Note that a minimum occurs in the net energy because of the different character of the attraction and repulsion curves.

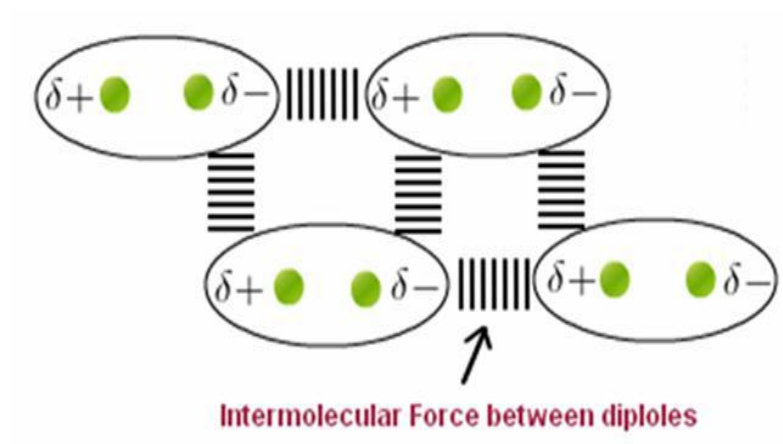
Van der Waals Forces

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

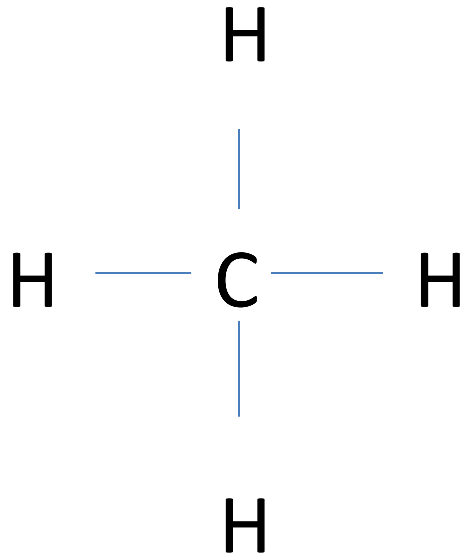
A. In a permanent dipole, called keesom forces

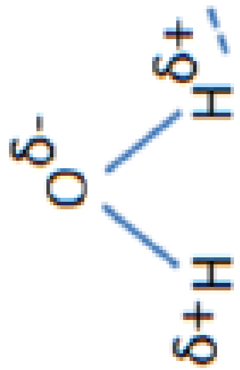






B. **Debye forces** show the ability of a permanent dipole to polarize charge in a neighboring molecule.

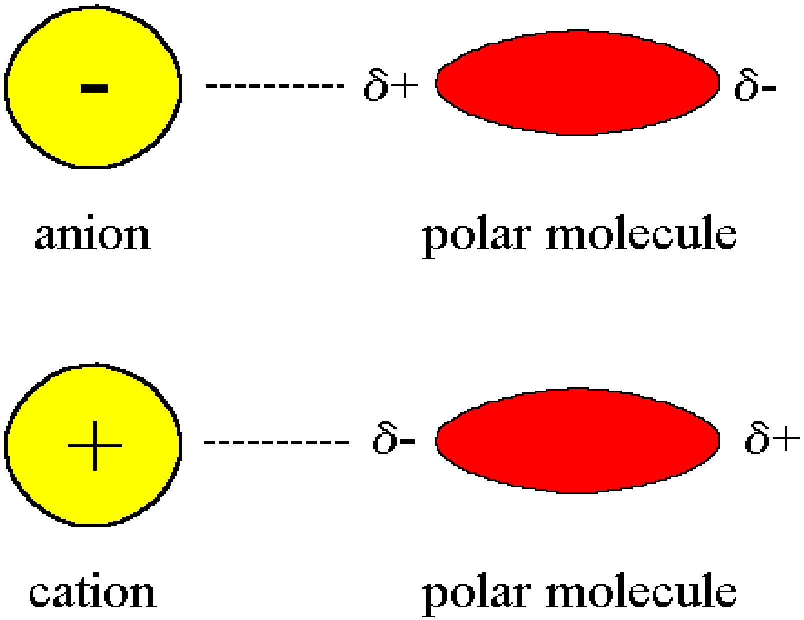


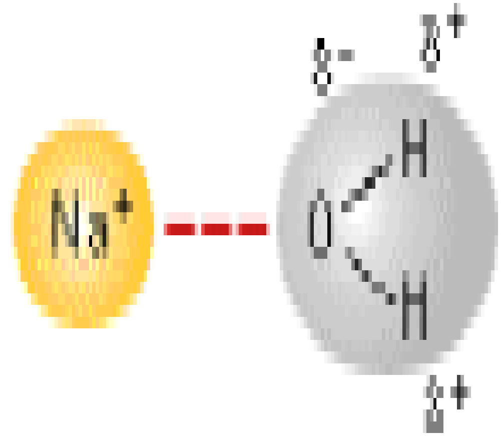


C. **In London forces**, two neighboring neutral molecules, for example, aliphatic hydrocarbons, induce partial charge distributions. Without this polarization, the membrane interior would be destabilized and lipid bilayers might break down. Therefore, London forces give rise to the fluidity and cohesiveness of the membrane under normal physiologic conditions.

Ion-Dipole and Ion-Induced Dipole Forces:

- They occur between polar or non-polar molecules and ion.
- These types of interactions account in part for the solubility of ionic crystalline substances in water, the cation for example attracting the relatively negative oxygen atom of water and the anion attracting the hydrogen atoms of the dipolar water molecules.


δ+
δ-
anion
polar molecule
δ-
δ+
cation
polar molecule


δ-
δ+
Na^+
O
H
H
δ+

- Ion-induce dipole forces are involved in the formation of iodide complex and accounts for solubility of iodide in a solution of potassium iodide.

$$I_2 + K^+I^- = K^+I_3^-$$

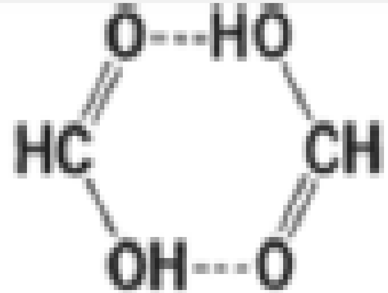
Hydrogen Bonds

- The interaction between a molecule containing a **hydrogen atom** and a strongly electronegative atom such as **fluorine, oxygen, or nitrogen** is of particular interest.
- Such a bond, exists in ice and in liquid water; it accounts for many of the unusual properties of water including its high dielectric constant, abnormally low vapor pressure, and high boiling point.
- The structure of ice is an open but well ordered three-dimensional array of regular tetrahedra with oxygen in the center of each tetrahedron and hydrogen atoms at the four corners.

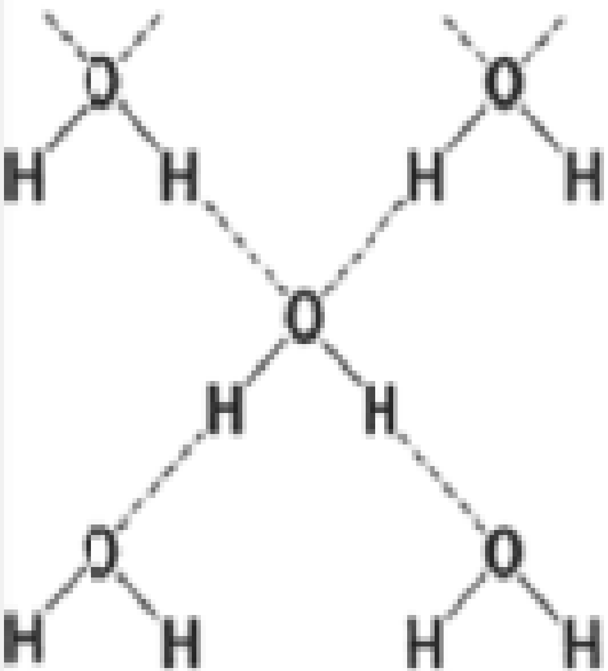
- Hydrogen bonds can also exist between alcohol molecules, carboxylic acids, aldehydes, esters, and polypeptides.
- The hydrogen bonds of formic acid and acetic acid are sufficiently strong to yield dimers (two molecules
- attached together), which can exist even in the vapor state. Hydrogen fluoride in the vapor state exists
- as a hydrogen-bonded polymer (F—H …)n, where n can have a value as large as 6. This is largely due
- to the high electronegativity of the fluorine atom interacting with the positively charged

- It will be noticed that intra- as well as intermolecular hydrogen bonds may occur (as in salicylic acid).

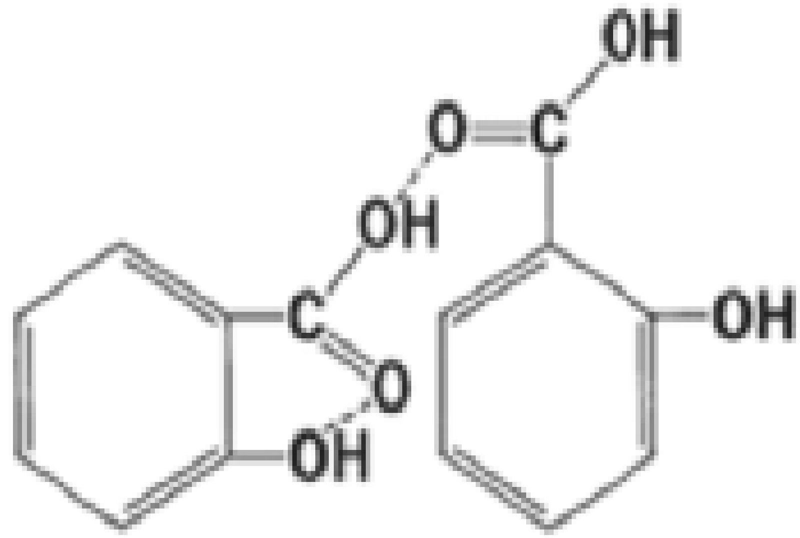
Hydrogen fluoride



Formic acid dimer



Water



Salicylic acid showing intermolecular and intramolecular hydrogen bonding

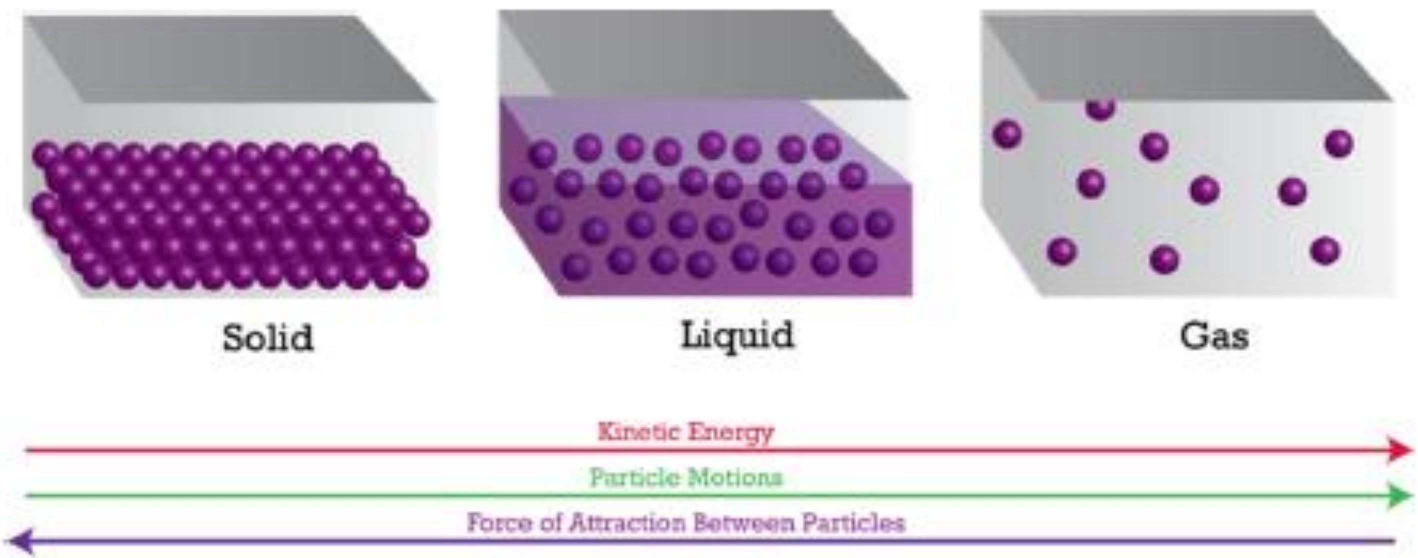
Table 2-1 Intermolecular Forces and Valence Bonds

Bond Type	Bond Energy (approximately) (kcal/mole)
Van der Waals forces and other intermolecular attractions	
Dipole–dipole interaction, orientation effect, or Keesom force	
Dipole–induced dipole interaction, induction effect, or Debye force	1–10
Induced dipole–induced dipole interaction, dispersion effect, or London force	
Ion–dipole interaction	
Hydrogen bonds: O—H· · ·O	6
C—H· · ·O	2–3
O—H· · ·N	4–7
N—H· · ·O	2–3
F—H· · ·F	7
Primary valence bonds	
Electrovalent, ionic, heteropolar	100–200
Covalent, homopolar	50–150

States of Matter

- Gases , liquids and crystalline solids are the three primary states of matter .
- The molecules , atoms ,ions in the solid state are held in close proximity by intermolecular , interatomic or ionic forces.
- The atoms in the solid can oscillate only about fixed positions.
- As the temperature of a solid is raised, the atoms acquire sufficient energy to disrupt the ordered arrangement of lattice and pass into the liquid form.

- Finally when sufficient energy is supplied , the atoms or molecules pass into the gaseous state.



The Gaseous State

Owing to vigorous and rapid motion and resultant collisions ,gas molecules travel in random paths and collide not only with one another but with the walls of containers in which they are confined. Hence, they exert a **pressure** –a force per unit area- expressed in dyne $/\mathrm{cm}^2$. Pressure is also recorded in atmosphere or in milliliters of mercury.

Another characteristic is **volume** which is expressed in liters or cubic centimeters .

- The **temperature** is measured in absolute or kelvin scale .Zero degrees of centrigrade is equal to 273.15 K.

Ideal Gas Equation

Refer to ideal situation where no intermolecular interaction exist and no energy is exchanged upon collision

$$\boxed{PV = nRT}$$

n is moles

R is the **gas constant**

- The conditions 0 ^{0}C and 1 atm are called **standard temperature and pressure (STP).**

- Experiments show that at STP, 1 mole of an ideal gas occupies 22.414 L.

$$PV = nRT$$

$$R = \frac{PV}{nT} = \frac{(1\ \text{atm})(22.414\text{L})}{(1\ \text{mol})(273.15\ \text{K})}$$

$$R = 0.082057\ \text{L} \bullet \text{atm} / (\text{mol} \bullet \text{K})$$

Example

- What is volume of 2 moles of ideal gas at 25 °C and 780 mmHg? (**1 atm =760 mmHg** and **R = 0.08205 L • atm / (mol • K)**

P= 780/760 = 1.026 atm

V= ?

n=2 mole

T= 25 °C+273= 298 k

$$PV = n\,R\,T$$

$$1.026\ \cancel{\text{atm}} \times V = 2\cancel{\text{moles}} \times \frac{0.08205\ \text{L} \bullet \cancel{\text{atm}}}{\cancel{\text{mole}}.\cancel{\text{K}}} \times 298\cancel{\text{K}}$$

V= 47.65 liter

Molecular Weight

The approximate molecular weight of a gas can be determined by use of the ideal gas law. The number of moles of gas *n* is

P.24

replaced by its equivalent *g/M*, in which *g* is the number of grams of gas and *M* is the molecular weight:

$$PV = \frac{g}{M}RT \qquad (2\text{–}7)$$

or

$$M = \frac{gRT}{PV} \qquad (2\text{–}8)$$

Example 2-3

Molecular Weight Determination by the Ideal Gas Law

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? Assume that the vapor behaves as an ideal gas. Write

$$M = \frac{0.30 \times 0.082 \times 373}{1 \times 0.2}$$

$$M = 46.0 \text{ g/mole}$$

The van der Waals Equation for Real Gases

The fundamental kinetic equation (2-9) is found to compare with the ideal gas equation because the kinetic theory is based on the assumptions of the ideal state. However, real gases are not composed of infinitely small and perfectly elastic nonattracting spheres. Instead, they are composed of molecules of a finite volume that tend to attract one another. These factors affect the volume and pressure terms in the ideal equation so that certain refinements must be incorporated if equation (2-5) is to provide results that check with experiment. A number of such expressions have been suggested, the *van der Waals equation* being the best known of these. For 1 mole of gas, the van der Waals equation is written as

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \qquad (2\text{–}13)$$

For the more general case of *n* moles of gas in a container of volume *V*, equation (2-13) becomes

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \qquad (2\text{–}14)$$

The term a/V^2 accounts for the *internal pressure* per mole resulting from the intermolecular forces of attraction between the molecules; *b* accounts for the incompressibility of the molecules, that is, the *excluded volume*, which is about four times the molecular volume. This relationship holds true for all gases; however, the influence of nonideality is greater when the gas is compressed. Polar liquids have