

Gaseous State

For
B.Sc-II Chemistry(H&S)
Physical chemistry
Paper-III
Lecture-01



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Collision

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Collision theory

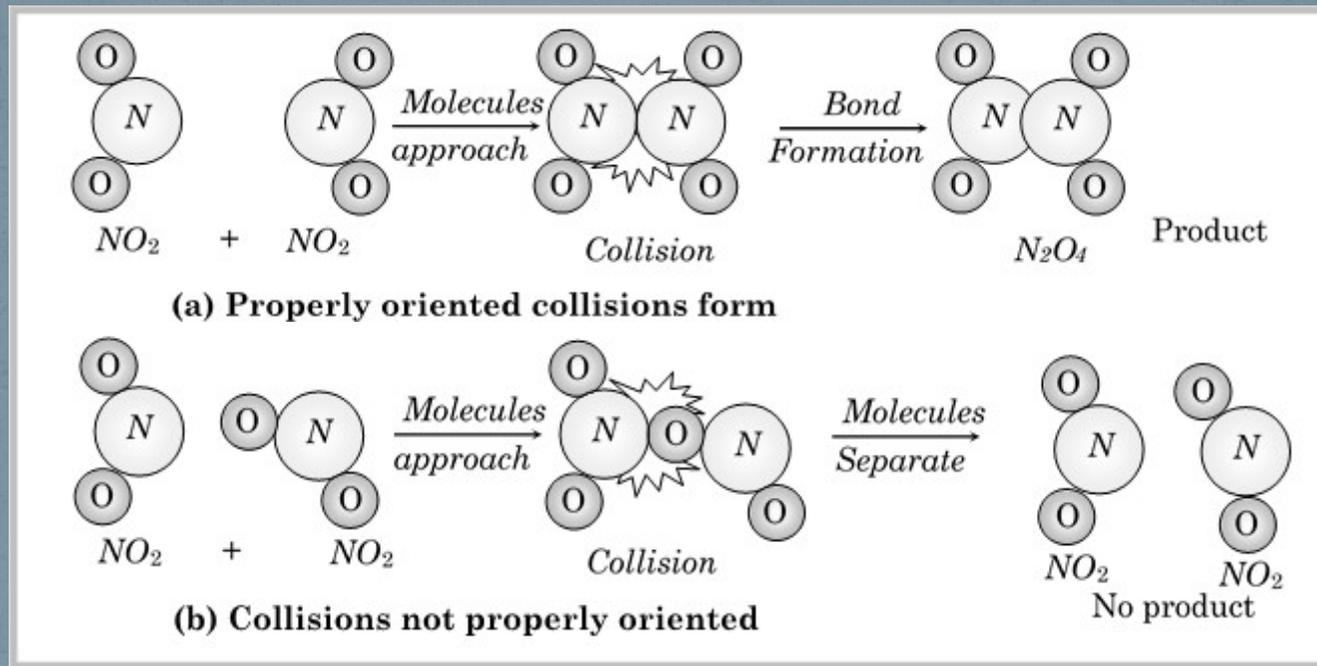
Used to predict the rates of chemical reactions, particularly for gases.

Based on the assumption that for a reaction to occur it is necessary for the reacting species (atoms or molecules) to come together or **collide** with one another.

Key point:

- Gas particles are constantly colliding with each other and the walls of their container.
- There is no net loss of energy from the collisions.
- Gas particles are small and the total volume occupied by gas molecules is negligible relative to the total volume of their container
- Collisions are perfectly elastic
- when two molecules collide, they change their directions and kinetic energies, but the total kinetic energy is conserved.
- Collisions are not sticky.
- The average kinetic energy of the gas molecules is directly proportional to the absolute temperature

Collisions



Collision number

The "**number of collisions**" per unit time.

The no of collision which a single molecules make with other molecules in one second

A **collision** is an interaction between two or more bodies in motion.

When one molecule involved, the average **number of collisions** per unit time nearly one second per moles of reactant between reacting molecules is called **collision number**

Collision model:

Reaction rate depends on

Collision frequency

Activation energy

Orientation factor

The reaction rate increases as the no of collision between reacting species increase

Temperature

concentration

Collision Model

Reaction rate depends on

- ❖ Collision frequency
- ❖ Activation energy
- ❖ Orientation factor

The reaction rate increases as the no of collision between reacting species increase

Temperature
concentration

Collision frequency

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A collision is an interaction between two or more bodies in motion. ... When one molecule involved, the average number of collisions per unit time nearly one second per moles of reactant between reacting molecules is called collision number

Collision frequency

The no of collision which takes place in one second among the molecule present in one cm cube of the gas .

Usually represented by Z

$$Z = \frac{1}{\sqrt{2}} \bar{V} \sigma^2 n^2$$

Z is directly proportional to

V- Average velocity of the gas molecules

σ^2 Square of the molecule diametr

n^2 Suare of the molecule per cm Cube

According to Kinetic Molecular Theory, the collision frequency is equal to the root-mean-square velocity of the molecules divided by their mean free path.

If the molecules have diameter d, then we can use a circle of diameter $\sigma=2d$ to represent a molecule's effective collision area.

$$z = \frac{1}{\sqrt{2}} \bar{V} \pi d^2 n$$

Collision diameter

Collision diameter

The distance between the centers of two molecules taking part in a collision at the time of their closest approach.

What affects collision frequency:

Variables that **affect Collisional Frequency:**

If everything else remains constant, a single reactant comes in contact with more atoms in denser system.

Thus if density is increased, the collisional frequency must also increase.

Increasing the size of the reactants increases the collisional frequency.

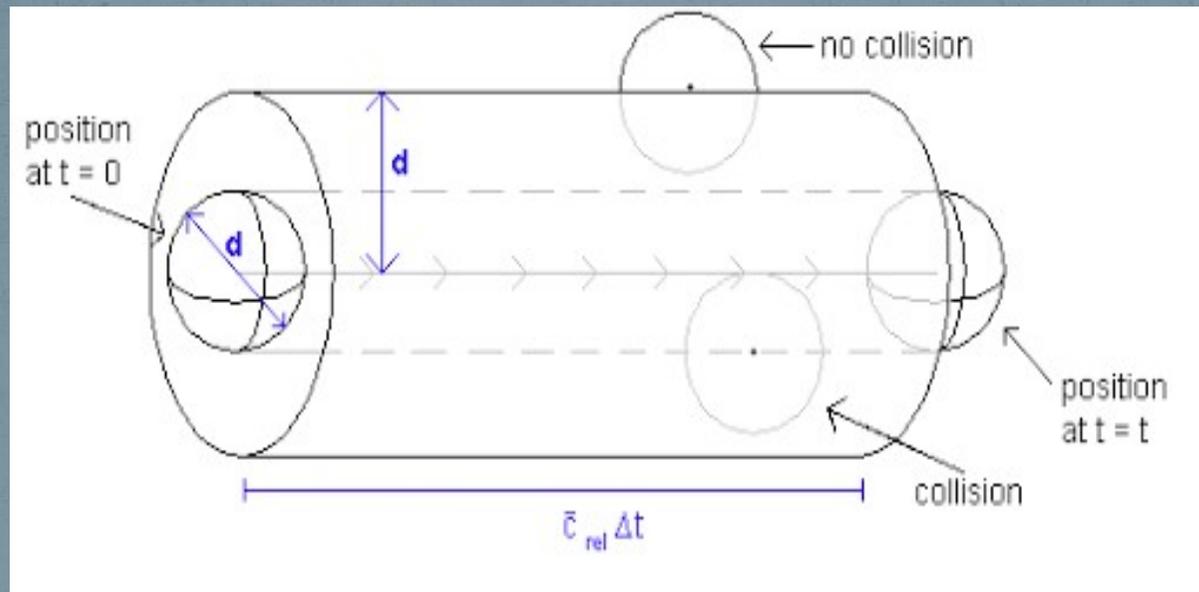
How can increase collision frequency:

Increasing the surface area of reactant increases the frequency of collisions and increases the reaction rate.

Several smaller particles have more surface area than one large particle.

The more surface area that is available for particles to collide, the faster the reaction will occur.

Collision frequency



Mean free path

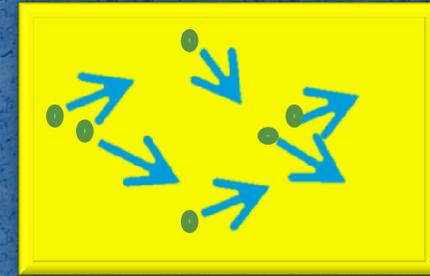
Mean free path: The average distance that a gas molecule can travel before colliding with another gas molecule.

Determined by :

Size of molecule

Temperature

Pressure



The factors on which the mean free path of a gas molecule depends are:

Density- Density increases when the no. of molecules increased or the volume is decreased. Radius of a molecule - When the radii of molecule are increased the space between them decreases.

Pressure, temperature, and other physical factors also affect the density of the gas and thus affect the mean free path.

Number of molecules: As the number of molecules increases the probability of collision increases and thus the mean free path decreases.

Van der Waals equation

The **van der Waals equation** of state approaches the ideal gas law $PV=nRT$ as the values of these **constants** approach zero. The **constant a** provides a correction for the intermolecular forces. **Constant b** is a correction for finite molecular size and its value is the volume of one mole of the atoms or molecules.

The **van der Waal's equation of state for a real gas is:**

$$(P + n^2a / V^2)(V - nb) = nRT$$

P-Pressure

n- no of moles

R-Ideal gas constant

V-Volume

T-temperature

A & b constant

To convert '**a**' into atm L²/mol² multiply by 0.986 atm/bar
To convert '**a**' into kPa L²/mol² multiply by 100.0 kPa/bar

Van der Waals constant

Gas	<i>a</i> (bar·L²/mol²)	<i>a</i> (atm·L²/mol²)	<i>b</i> (L/mol)
CH ₄	2.303	2.273	0.0431
CO ₂	3.658	3.610	0.0429
Cl ₂	6.343	6.260	0.0542
NH ₃	4.225	4.170	0.0371
H ₂ O	5.537	5.465	0.0305
Xe	4.192	4.137	0.0516

Boltzmann distribution

- Boltzmann distribution, that the assumption of a single speed in the Kinetic Theory is over simplified!
- In fact there are three kinds of average or characteristic speed that we can identify from the Boltzmann distribution

1. The Root Mean Square Speed:

$$c_{rms} = (3RT/M)^{1/2}$$

If N is the total number of atoms, If N is the total number of atoms, c_1 is the speed of atom 1, and c_2 the speed of atom 2, etc

$$c_{rms} = [(1/N)(c_1^2 + c_2^2 + c_3^2 + \dots)]^{1/2}$$

2. The Average Speed:

$$C_{average} = [(1/N)(c_1 + c_2 + c_3 + \dots)]$$

$$C_{average} = (8RT/\pi M)^{1/2}$$

3. The Most Probable Speed:

c_{mp} is the value of c that gives $(\Delta N/N)$ in the Boltzmann distribution which is the largest value.

Maxwell's distribution

The no of molecules moving with velocity between v & $v+dv$ is:

$$f(v) = N \left(\frac{m}{2\pi kT} \right)^{3/2} \exp \left[-\frac{mv^2}{2kT} \right]$$

Where, m = mass of a molecule

N = Total no of molecules

k = Boltzmann constant

T = Absolute temperature

Critical phenomena

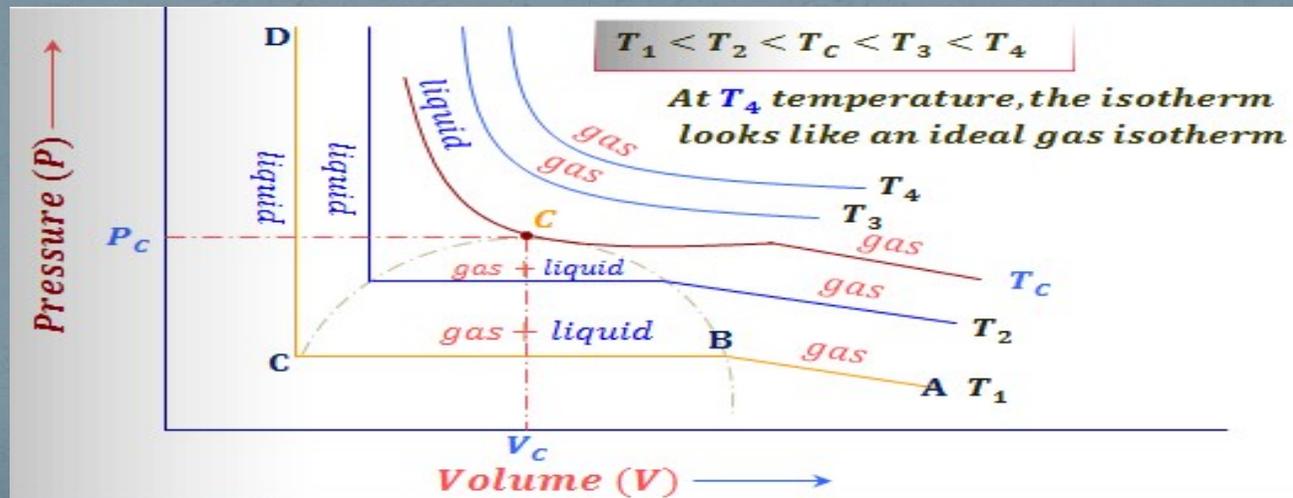
The **phenomenon** of a smooth merging of a gas into its liquid state under a **critical** state or **critical** point

The density of the gas at the **critical** point is called the **critical** density

The essential condition for the liquefaction of the **gas** is described by the study of **critical** temperature, **critical** pressure and **critical** volume and their inter relationships.

When a **gaseous** system is transformed to its liquid state, there is a tremendous decrease in the volume.

In 1869, Thomas Andrews carried out an experiment in which P - V relations of carbon dioxide gas were measured at different temperatures.



Andrews experiment

Thomas Andrews carried out an experiment in which P - V relations of carbon dioxide gas were measured at different temperatures In 1869.

- Following are observed from the P-V graph
- At high temperatures, such as T_4 , the isotherms look like those of an ideal gas.
- At low temperatures, the curves have altogether different appearances. Consider, for example, a typical curve abcd.
- As the pressures increase, the volume of the gas decreases (curve a to b).
- At the point, b liquefaction commences and the volume decreases rapidly as the gas converted to a liquid with much higher density. This conversion takes place at constant pressure P.
- At point C, liquefaction is complete and thus the cd is evidence of the fact that the liquid cannot be easily compressed. Thus, we note that ab represents the gaseous state, bc, liquid, and vapor in equilibrium, and cd shows the liquid state only.

Andrews experiment

Behaviour of gases was devised by **Andrews** in 1863

He used carbon dioxide as the test gas.

- Using the apparatus shown in Figure 1, he plotted a series of isothermals (PV curves) to test the validity of Boyle's law over a wide range of pressures.
- The gases were compressed by tightening the screw and the pressure was estimated using the nitrogen assuming that under the conditions of the experiment it still obeyed Boyle's law.
- The capillary tubes were very strong and Andrews obtained results up to pressures of 10^7 Pa.

The results are shown in the two graphs in Figure 2. Above about $50\text{ }^{\circ}\text{C}$ Boyle's law was fairly closely obeyed. But as you can see the behaviour of the 'gas' is different above and below about $30\text{ }^{\circ}\text{C}$ - in fact Andrews found that the critical temperature for carbon dioxide was $30.9\text{ }^{\circ}\text{C}$.

Above this temperature carbon dioxide could not be liquefied by pressure alone, while below this temperature an increase in pressure would finally result in liquid carbon dioxide. At the critical point the gas and liquid are in equilibrium.

Andrews experiment

A vapour is a gas below its critical temperature

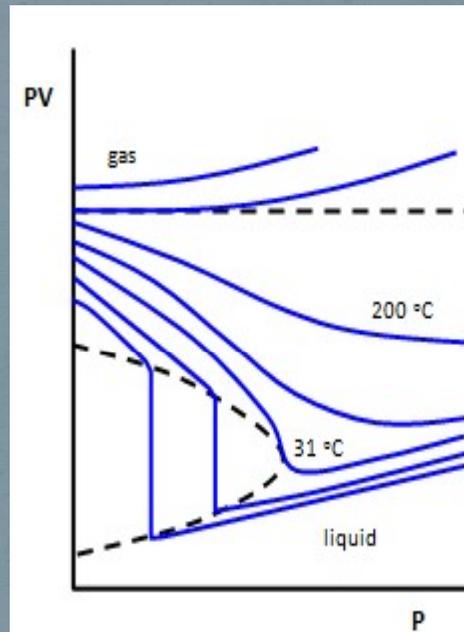
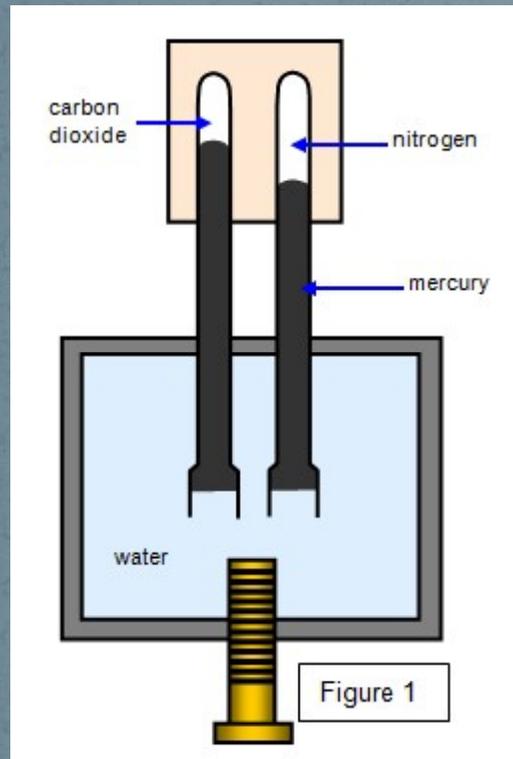
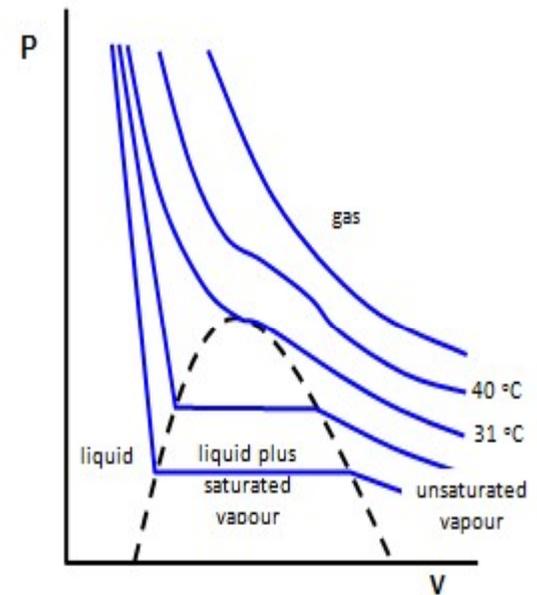


Figure 2



Problem for practice:

1. What is collision number in chemistry?
2. How do you calculate collision number?
3. What do you mean by **Andrews experiment** ?