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BSK1133 PHYSICAL CHEMISTRY

CHAPTER 2
COLLISIONS OF GASES MOLECULES

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Description

Aims

- To understand the collision molecules theory of gases.
- To understand the different types of molecules speed.
- To understand the different between ideal gas and real gas.

Description

Expected Outcomes

- ❖ Able to understand the collision of gas molecule theory
- ❖ Able to understand the diffusion and effusion of gases
- ❖ Able to understand mean free path
- ❖ Able to understand the different between ideal gas and real gas

References

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Contents

2.1 Average Speed of Molecules in A Gas

As discussed previously in Chapter 1:

$$\overline{v^2} = \frac{3RT}{M}; M = m.N_A$$

Root mean square (rms) speed :

$$v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3RT}{M}};$$

often, its more useful to calculate the mean speed :

$$\bar{v} = \int v dP$$

Maxwell – Boltzman distribution :

$$\bar{v} = \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{8RT}{\pi m}}$$

2.2 Diffusion and Effusion

Type of gas movement:

- **Diffusion :**

  A process which spreading of molecules from higher concentration to low concentration.

- **Effusion :**

  A process of molecules escape from a compartment to a vacuum compartment through a small hole.

- ✓ According to the equation of molecular speed, number of molecule hitting the wall of container is proportional to their speed.
- ✓ Thus, the rate of effusion also considered as proportional to its molecular speed (Vrms).

2.3 Graham's Law

- ✓ Stated that the speed (on average) is inversely proportional to the square root of the molecular mass.

- ✓ At the same temperature, the ratio of the gas movement rates is:

$$\frac{Rate_{gas\ A}}{Rate_{gas\ B}} = \sqrt{\frac{Molar\ Mass_{gas\ B}}{Molar\ Mass_{gas\ A}}}$$

Expansion of gases

The pressure difference between the two sides of orifice (small hole) and the orifice diameter determine whether the gas expands **supersonically** or **effusively**:

Effusion :

- ✓ the diameter of orifice is smaller than the average distance a molecule travels between its collision with another molecule (mean free path).
- ✓ No collisions occur between the gas molecules as they move through the orifice and the flow is **‘molecular’**

Supersonic :

- ✓ Diameter of hole is larger than the average distance between collisions.
- ✓ Many collisions between the gas molecule can occur during the expansion through the hole.
- ✓ The collision act to transfer energy from the random atomic and molecular motions of the gas into the directed flow of the gas molecules along the expansion direction.
- ✓ The gas moves as a whole; most of the molecules have the same speed in direction of the flow
- ✓ The speed of the gas molecules relative to each other becomes very small, and the temperature also becomes very low.

2.4 Mean Free Path

- ✓ A gas molecule travels in a straight line and collide with other molecule or wall of the container.
- ✓ **Mean free path is** the average distance a molecule travels between collisions**.**
- ✓ The mean free path of molecule will depend on its **speed** and the **density** of molecules surrounding it.
- ✓ As the pressure increases, the mean free path decreases.

How to calculate mean free path?

1. Imagine that the molecules of gases are evenly distributed in a cube of length L.

$$L^3 = N\,a^3$$

where N is total number of molecules in a cube and a is the average distance of two nearest neighbors.

$$a = \sqrt[3]{\frac{L^3}{N}} = \sqrt[3]{\frac{V}{N}} = \sqrt[3]{\frac{kT}{P}}$$

- Using the ideal gas law equality at P=1 bar and T=273.16 K, the average distance is a=3.3 nm.
- The **free path** (λ) (the distance a molecule traverses between collisions) is much longer than the average distance a because the molecule passes between many neighboring molecules.
- **Assumptions to determine the mean free path (a or $\bar{\lambda}$):**

  1. approximate the molecules as hard sphere

- **Assumptions to determine the free path (λ)** :

  1. Consider a particle of type 1 moving among many particles of type 2 that are so massive that they can be considered nearly stationary.
  2. A collision occurs each time a type 1 particle with radius (r1) touches a type 2 particle with radius (r2).
  3. As type 1 molecule moves through space it sweeps out a cylindrical volume (V_{cyl}).

- Since collision only occurs at correct orientation, thus the diameter of the collided molecules is 2(r1 + r2).

$$V_{cyl} = \pi(r_1 + r_2)^{2}\,\lambda$$

- If there are N type of particle in the total volume V of the gas, then the average volume element for a type 2 particle is V/N and the average cylinder volume ($\overline{V_{cyl}}$) *is*

$$\overline{V_{cyl}} = \frac{V}{N} = \pi(r_1 + r_2)^{2}\bar{\lambda}$$

$$\bar{\lambda} = \frac{V}{N\pi(r_1 + r_2)^{2}}$$

- This equation can be simplify to:

$$\bar{\lambda} = \frac{V}{\sigma N}\ ;\ \ \sigma\ is\ collision\ cross\ section$$

this equation is significant for one light particle among N heavy particles

2.5 Ficks's First Law

Although it is interesting to calculate the average behavior of a molecule, experimentally we most often deal with collections of molecules.

Normally being asked like:

"What amount of bromine vapor emerges through the opening of the cylinder in time, t, if a cylinder has a cross-sectional area A and height H?"

Thus, the Fick's first law equation:

$$\frac{\Delta n}{\Delta t} = -A\ D\ \frac{C_H}{H}$$

dn/dt is considered for sufficiently small time changes, dc/dh concentration gradient in general cases

Where :

Δn *is the concentration of collections molecules vapor, A is the cross-sectional area, D is diffusion coeffision,* C_H *is concentration of liquid, H is the height of cylinder/distance*

2.6 Real Gas

- ✓ A gas is considered as non-ideal when it is not fulfil an ideal gas behavior.
- ✓ Ideal gas assumptions:
  - ○ absent of attractions between gas molecules
  - ○ Gas molecules do not take up space as it elastically collide (based on the kinetic molecular theory).
- ✓ At high pressure and low temperature, this assumptions are not valid for real gases
- ✓ At high pressure, the molar volume of a real gas is larger than predicted by the ideal gas law

Behavior of Real Gases:

1. At low pressure and high temperature:

   The volume of the gas particles is negligible compared to the total volume.

2. At higher pressure and low temperature:

   The volume of the gas particles is more significant compared to the total volume.

Thus, the volume of a real gas is larger than the ideal gas.

Conclusion

- There are some parameters such as mean path, need need to be considered in molecular collisions of gases.

- In specifically, it will relates to some other laws explaining the theories.

- The specific parameter will differentiate the gases properties either as an ideal or non-ideal gas.

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