Concept of Fugacity

The concept of **fugacity** is one of the most important concepts in chemical thermodynamics. It was introduced by **Gilbert Newton Lewis** in 1901 to explain the behavior of **real gases**. In thermodynamics, many equations such as those for chemical potential, equilibrium constant, and phase equilibrium are derived assuming that gases behave ideally. However, under practical conditions, especially at high pressures and low temperatures, gases deviate from ideal behavior. Therefore, pressure alone is not sufficient to describe the thermodynamic state of a real gas. To overcome this limitation, Lewis introduced the concept of fugacity, which replaces pressure in thermodynamic equations for real gases.

Why is Fugacity Needed?

According to the kinetic theory of gases, an ideal gas satisfies the following assumptions:

- Gas molecules have negligible volume.
- No intermolecular attractive or repulsive forces exist.
- Collisions between molecules are perfectly elastic.
- The gas obeys the ideal gas equation under all conditions.

Hence, an ideal gas obeys

$$PV = nRT$$

where

- P = Pressure
- V = Volume
- n = Number of moles
- R = Universal gas constant
- T = Absolute temperature

However, no gas is perfectly ideal. At high pressure, gas molecules come closer together and their finite size as well as intermolecular forces become important. Consequently, the observed pressure is no longer a true measure of the tendency of gas molecules to escape from the system. This deviation from ideal behavior necessitates the introduction of a

corrected pressure known as **fugacity**.

Origin of the Word Fugacity

The word *fugacity* is derived from the Latin word **fugere**, meaning **“to flee”** or **“to escape”**. Therefore, fugacity represents the tendency of molecules to escape from one phase into another.

For example, molecules of a compressed gas have a greater tendency to escape than molecules of a gas at low pressure. Thus, higher fugacity indicates a greater escaping tendency.

Definition of Fugacity

Fugacity is defined as the effective pressure or corrected pressure of a real gas that replaces the actual pressure in thermodynamic equations so that the equations become applicable to real gases.

In simple words, fugacity is the pressure that a real gas would have if it behaved ideally while possessing the same chemical potential.

It is denoted by the symbol

$$f$$

The SI unit of fugacity is Pascal (Pa), although bar and atmosphere are also commonly used.

Physical Meaning of Fugacity

Pressure measures the mechanical force exerted by gas molecules on the walls of a container. Fugacity, on the other hand, measures the **escaping tendency** of molecules from a phase.

If the escaping tendency increases, fugacity also increases. Therefore, fugacity is a thermodynamic quantity rather than merely a mechanical quantity.

For example:

- At low pressure, intermolecular forces are negligible, and the escaping tendency is almost equal to the actual pressure.

- At high pressure, intermolecular interactions become significant, causing the escaping tendency to differ from the measured pressure.

Relation Between Pressure and Fugacity

For an ideal gas,

$$\boxed{f = P}$$

Thus, pressure itself represents the escaping tendency of an ideal gas.

For a real gas,

$$\boxed{f \neq P}$$

because intermolecular attractive and repulsive forces alter the effective escaping tendency of gas molecules.

At extremely low pressure,

$$\boxed{\lim_{P \to 0} \frac{f}{P} = 1}$$

This shows that every real gas approaches ideal behavior as the pressure approaches zero.

Characteristics of Fugacity

- Fugacity has the same unit and dimensions as pressure.
- It is an intensive thermodynamic property.
- It depends on temperature and pressure.
- It represents the effective pressure of a real gas.
- It is equal to pressure only for an ideal gas.
- It cannot be measured directly but can be calculated experimentally.
- It is widely used in chemical equilibrium and phase equilibrium calculations.

Importance of Fugacity

- Corrects the deviation of real gases from ideal behavior.
- Provides the true thermodynamic measure of escaping tendency.

- Used in the calculation of chemical potential.
- Essential for studying phase equilibria.
- Used in high-pressure chemical engineering processes.
- Important in petroleum and natural gas industries.
- Required for accurate equilibrium constant calculations involving gases.

Summary

Fugacity is an effective or corrected pressure introduced by G. N. Lewis to describe the behavior of real gases. It represents the escaping tendency of gas molecules and replaces pressure in thermodynamic equations whenever real gases deviate from ideal behavior. At low pressure, fugacity becomes equal to pressure, whereas at high pressure it differs because of intermolecular interactions. Thus, fugacity provides a more accurate thermodynamic description of real gases than pressure alone.