



UNIT - IV.

(1)

IDEAL AND REAL GASES, THERMODYNAMIC RELATIONS

Gas Mixture :-

Pure substance is defined as a substance which is homogeneous and unchanging in chemical composition. In many important thermodynamics applications, it requires homogeneous mixture of several pure substances rather than a single pure substance.

Composition of a Gas mixture :-

It is very important to know the composition of the mixture as well as the properties of the individual components to determine the properties of mixture. The following two ways are generally used to describe the composition of mixture.

1) Mass Fraction :-

If a gas mixture consists of gases 1, 2, 3 and so on, the mass of the mixture is the sum of masses of the individual component gases.

$$m_m = m_1 + m_2 + m_3 + \dots + m_i$$

$$m_m = \sum_{i=1}^K m_i. \quad \text{--- (1)}$$

The mean fraction or mass fraction of any component is defined as the ratio of mass of a component to the mass of the mixture mathematically.

$$x_i = \frac{m_i}{m_m}$$

2. Molar fraction :-

It is the ratio of the mole number of a component to the mole number of the mixture. The total number of moles of a mixture is the sum of the number of its components.

$$N_m = N_1 + N_2 + N_3 + \dots + N_i$$

$$N_m = \sum_{i=1}^K N_i$$



Then, the mole fraction is given by .

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$$y_i = \frac{N_i}{N_m}$$

In molar analysis, moles of each component are specified. The number of moles N , the mass m , and the molar mass M of a component and the mixture are related by .

$$m_i = N_i M_i \quad \text{--- (2)}$$

$$m_m = N_m M_m \quad \text{--- (3)}$$

From equation (1), (2) & (3).

$$m_m = \sum m_i = \sum N_i M_i$$

$$M_m = \frac{m_m}{N_m} = \frac{\sum N_i M_i}{N_m}$$

$$M_m = \sum y_i M_i$$

$$y_i = \frac{m_i}{m_m} = \frac{N_i M_i}{\sum N_i M_i}$$

2. Partial pressure and Partial volume :-

The sum of partial pressures of the components of a gas mixture is equal to the mixture pressure. The partial pressure P_i of a component i in a gas mixture is given by

$$P_i = y_i P_m$$

where,

y_i = mole fraction

P_m = mixture pressure.

$$\sum P_i = \sum y_i P_m$$

$$= P_m \sum y_i$$

$$\sum P_i = P_m$$

This relation applies to any gas mixtures, whether it is an ideal gas or not. The sum of partial volumes of the components of a gas mixture is equal to the volume of the mixture. The partial volume V_i



of a component in a gas mixture is given by.

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$$V_i = Y_i V_m$$

where,
 V_m = mixture volume.

$$\sum V_i = \sum Y_i V_m \\ = V_m \sum Y_i$$

$$\sum V_i = V_m$$

Dalton's law of Partial Pressure :-

According to Dalton's law of partial pressure, the pressure of a gas mixture is equal to the sum of pressure of all each components if each component is exerted alone at the temperature and volume of the mixture. This law is also called as Dalton's law of additive pressure.



$$P_m = P_1 + P_2 + \dots + P_k.$$

$$P_m = \sum_{i=1}^k P_i.$$

where,
 P_m = Mixture pressure.

P_1, P_2, \dots, P_i = each component pressure.

If there are N_A moles of gas A, N_B moles of gas B and N_C moles of gas C in the mixture, the gas equation is given by.

$$P_m V_m = (N_A + N_B + N_C) \bar{R} T_m.$$

where, $\bar{R} = 8.3143 \text{ kg}/\text{kg mole K}$,

$$P_m = \frac{N_A \bar{R} T_m}{V_m} + \frac{N_B \bar{R} T_m}{V_m} + \frac{N_C \bar{R} T_m}{V_m}.$$



$$= P_m (N_A T_m, V_m) + P_m (N_B T_m, V_m) + P_m (N_C T_m, V_m) \quad (1)$$

where, $P_m (N_A T_m, V_m)$ is the pressure of the mixture of component A at the temperature T_m and volume V_m .

For ideal gas, P_i and N_i can be replaced by N_i , V_i using the ideal gas relation for both the component and gas mixture.

$$\frac{P_m (T_m, V_m)}{P_m} = \frac{N_A R T_m / V_m}{N_m R T_m / V_m} = \frac{N_A}{N_m} = \bar{y}_A$$

for real gas,

$$P_m V_m = Z_m N_m R T_m$$

where,

Z_m = compressibility factor for the mixture.

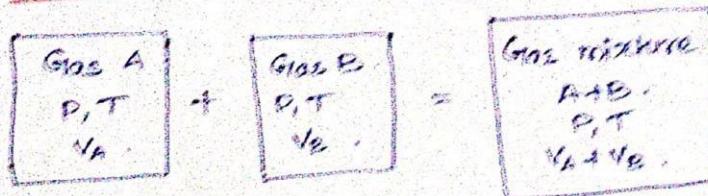
Z_m can be expressed by terms of compressibility factors \bar{y}_i of individual gases i ,

$$Z_m = \sum_{i=1}^k y_i z_i$$

where,

z_i is determined at T_m and V_m .

Amagat's Law of Partial volumes :-



According to Amagat's law of partial volumes, the volume of a gas mixture is equal to the sum of the volumes of each gas if existed alone at the temperature and pressure of the mixture.

$$V_m = V_1 + V_2 + V_3 + \dots + V_k$$

$$V_m = \sum_{i=1}^k V_i$$

where,

V_m = Volume of mixture.

V_1, V_2, \dots, V_k = Volume of each component in mixture.



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If there are N_A , N_B and N_C moles of gases A, B and C respectively in the mixture, the gas equation is given by,

$$P_m V_m = (N_A + N_B + N_C) \cdot \bar{R} T_m$$

$$P_m V_m = \frac{N_A \bar{R} T_m}{P_m} + \frac{N_B \bar{R} T_m}{P_m} + \frac{N_C \bar{R} T_m}{P_m}$$

$$\therefore V_m = \frac{N_A \bar{R} T_m}{P_m} + \frac{N_B \bar{R} T_m}{P_m} + \frac{N_C \bar{R} T_m}{P_m}$$

$$= V_A(N_A, T_m, P_m) + V_B(N_B, T_m, P_m) + V_C(N_C, T_m, P_m)$$

where, $V_A(N_A, T_m, P_m)$ is the volume of N_A moles of component A as the temperature T_m and pressure P_m .