

Ideal & Real Gases and Thermodynamic Relations

4.1 GAS MIXTURES

Many important thermodynamic applications involve *mixtures* of several pure substances rather than a single pure substance. Therefore, it is important to develop an understanding of mixtures and learn how to handle them.

In this chapter, we deal with nonreacting gas mixtures. A nonreacting gas mixture can be treated as a pure substance since it is usually a homogeneous mixture of different gases. The properties of a gas mixture obviously will depend on the properties of the individual gases (called *components* or *constituents*) as well as on the amount of each gas in the mixture. Therefore, it is possible to prepare tables of properties for mixtures. This has been done for common mixtures such as air. It is not practical to prepare property tables for every conceivable mixture composition, however, since the number of possible compositions is endless. Therefore, we need to develop rules for determining mixture properties from a knowledge of mixture composition and the properties of the individual components.

4.1.1 Composition of a Gas Mixture: Mass and Mole Fractions

To determine the properties of a mixture, we need to know the composition of the mixture as well as the

properties of the individual components. There are two ways to describe the composition of a mixture: either by specifying the number of moles of each component, called **molar analysis**, or by specifying the mass of each component, called **gravimetric analysis**.

Consider a gas mixture composed of k components. The mass of the mixture m_m is the sum of the masses of the individual components, and the mole number of the mixture N_m is the sum of the mole numbers of the individual components (Figs. 4.1 and 4.2). That is,

$$m = \sum_{i=1}^k m_i \quad \text{and} \quad N_m = \sum_{i=1}^k N_i$$

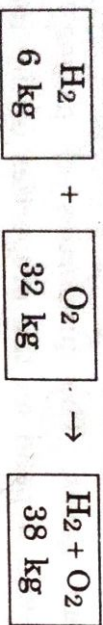


Fig 4.1 The mass of a mixture is equal to the sum of the masses of its components



Fig 4.2 The number of moles of a nonreacting mixture is equal to the sum of the number of moles of its components

4.2 PROPERTIES OF IDEAL AND REAL GASES

A hypothetical gas which obeys the law $P\bar{v} = RT$ (equation of state) is called an **ideal gas**.

But **real gases** do not conform to this equation of state with complete accuracy. Ideal gas do not have intermolecular attractive forces. These ideal gases obeys the equation of state at all ranges of pressure and temperature.

Practically, no ideal gas (perfect gas) exists in nature. However, hydrogen, oxygen, nitrogen and air behave as an ideal gas under normal condition.

4.3 EQUATION OF STATE

The equation which relates the properties P , v and T is known as an **Equation of state**.

$$\text{ie } f(P, v, T) = 0$$

The simplest form of equation of state for the ideal gas is given below.

$$\text{Equation of state: } P\bar{v} = \bar{R}T$$

$$[\bar{R} = \text{universal gas constant in kJ/kg mol.K} \\ \text{and } \bar{v} = \text{molar volume in m}^3/\text{kg mol}]$$

$$\text{Also: } Pv = RT$$

$$[R = \text{characteristic gas constant in kJ/kg K}] \\ v = \text{specific volume in m}^3/\text{kg}$$

The above equation - **Equation of state** is also called **Characteristic gas equation**.

Problem 4.1: Calculate the molecular volume of all gases at 250 kN/m² and 30° C.

Solution:

$$P = 250 \text{ kN/m}^2; \quad T_1 = 30 + 273 = 303 \text{ K.}$$

We know universal gas constant $\bar{R} = 8.3143 \text{ kJ/kg mol K}$

$$\text{Equation of state: } P\bar{v} = \bar{R}T$$

$$\text{molar volume } \bar{v} = \frac{\bar{R}T}{P} = \frac{8.3143 \times 303}{250} = 10.077 \text{ m}^3/\text{kg mole}$$

Problem 4.2: Calculate the molar volume of all gases at N.T.P. condition

Solution:

N.T.P. = Normal Temperature and Pressure

= 0° C and 760 mm of Hg (1.01325 bar ie., 101.325 kN/m²)

We know universal gas constant $\bar{R} = 8.3143 \text{ kJ/kg mol K}$

$$\text{molar volume } \bar{v} = \frac{\bar{R}T}{p} = \frac{8.3143 \times 273}{101.325} = 22.4 \text{ m}^3/\text{kg mole}$$

Problem 4.3: A cylinder of 120 lit capacity contains CO₂ at 100 bar and 20° C. Determine (1) mass of the gas (2) molar volume (3) density of the gas (4) specific volume.

Solution:

$$\bar{R} = 8.3143 \text{ kJ/kg mole K}; \quad V = 120 \times 10^{-3} \text{ m}^3$$

$$P = 100 \times 10^2 \text{ kN/m}^2; \quad T = 20 + 273 = 293 \text{ K}$$

Molecular weight. μ for CO₂ = 44;

Characteristic gas constant R

$$R \text{ for CO}_2 = \frac{\bar{R}}{\mu_{\text{CO}_2}} = \frac{8.3143}{44} = 0.18896 \text{ kJ/kgK}$$

Mass of the gas m

$$PV = mRT$$

$$m = \frac{PV}{RT} = \frac{100 \times 10^2 \times 120 \times 10^{-3}}{0.18896 \times 293} = 21.674 \text{ kg}$$

Molar volume \bar{v}

$$P\bar{v} = \bar{R}T$$

$$\bar{v} = \frac{\bar{R}T}{P} = \frac{8.3143 \times 293}{100 \times 10^2} = \mathbf{0.2436 \text{ m}^3/\text{kg mole}}$$

Density of the gas ρ

Density of the gas

$$\rho = \frac{m}{v} = \frac{21.674}{120 \times 10^{-3}} = \mathbf{180.61 \text{ kg/m}^3}$$

Specific volume v

$$v = \frac{1}{\rho} = \frac{1}{180.61} = \mathbf{5.54 \times 10^{-3} \text{ m}^3/\text{kg}}$$

$$PV = NKT \text{ [where } K = \frac{R}{A} \text{ and}$$

$A = \text{Avogadro number} = 6.023 \times 10^{26} \text{ molecules/kg mol}$

$N = \text{Total number of molecules} = nA$]

4.6 DALTON'S LAW OF PARTIAL PRESSURE

Dalton's law of partial pressures states that the total pressure of a mixture of ideal gases is equal to the sum of the partial pressures.

For a homogeneous mixture of ideal gases at temperature T , pressure P , and volume V , the equation of state can be written as

$$PV = (n_1 + n_2 + \dots + n_c) \bar{R}T$$

where $n_1 = \text{no. of moles of gas 1}$

$n_2 = \text{no. of moles of gas 2}$

$$\bar{R} = 8.3143 \text{ kJ/kg mol K}$$

$$P = \frac{n_1 \bar{R}T}{V} + \frac{n_2 \bar{R}T}{V} + \dots + \frac{n_k \bar{R}T}{V}$$

$$P = P_1 + P_2 + \dots + P_k$$

The above equation is known as Dalton's law of partial pressures.

1. To find x - mole fraction of the gas

$$\Sigma n_k = n_1 + n_2 + \dots + n_k$$

= Total no. of moles of gas.

The ratio $\frac{n_1}{\Sigma n_k} = x_1 = \text{mole fraction of the gas 1.}$

$$\text{Similarly, } x_2 = \frac{n_2}{\Sigma n_k}$$

2. To find R_m - Gas constant for the gas

For the gas mixture,

$$PV = (m_1 + m_2 + \dots + m_k) R_m T$$

where $R_m = \text{gas constant for mixture}$

$m_1 = \text{mass of gas 1, } m_2 = \text{mass of gas 2...}$

$$\text{So } R_m = \frac{m_1 R_1 + m_2 R_2 + \dots + m_k R_k}{m_1 + m_2 + \dots + m_k}$$

3. To find equivalent molecular weight of the mixture

$$\mu = x_1 \mu_1 + x_2 \mu_2 + \dots + x_k \mu_k$$

4. To find specific volume and density of the mixture

The partial volume of a component of a mixture is the volume that the component alone will occupy at the pressure and temperature of the mixture.

$$P_1 V_1 = m_1 R_1 T, \quad P V_2 = m_2 R_2 T$$

$$\text{or } P (V_1 + V_2 + \dots + V_k) = (m_1 R_1 + m_2 R_2 + \dots + m_k R_k) T$$

where V_1, V_2 are the partial volume of the component of the mixture.

Total volume is equal to the sum of partial volumes

$$V = V_1 + V_2 + \dots + V_k$$

Specific volume of the mixture

$$= v = \frac{V}{m} = \frac{V}{m_1 + m_2 + \dots + m_k}$$

(or) Density $= \rho = \frac{1}{v} = \frac{m_1 + m_2 + \dots + m_k}{V}$

$$= \frac{m_1}{V} + \frac{m_2}{V} + \dots + \frac{m_k}{V}$$

$$\frac{1}{v} = \frac{1}{v_1} + \frac{1}{v_2} + \dots + \frac{1}{v_k}$$

$$\rho = \rho_1 + \rho_2 + \dots + \rho_k$$

5. To find average specific internal energy, enthalpy and specific heats of the mixture:

$$m u_m = m_1 u_1 + m_2 u_2 + \dots + m_k u_k$$

$$u_m = \frac{m_1 u_1 + m_2 u_2 + \dots + m_k u_k}{m_1 + m_2 + \dots + m_k}$$

Similarly, $h_m = \frac{m_1 h_1 + m_2 h_2 + \dots + m_k h_k}{m_1 + m_2 + \dots + m_k}$

$$C_{um} = \frac{m_1 C_{v1} + m_2 C_{v2} + \dots + m_k C_{vk}}{m_1 + m_2 + \dots + m_k}$$

$$C_{pm} = \frac{m_1 C_{p1} + m_2 C_{p2} + \dots + m_k C_{pk}}{m_1 + m_2 + \dots + m_k}$$

6. To find entropy of the gas mixtures

$$S_f - S_i = -\bar{R} (n_1 \ln x_1 + n_2 \ln x_2 + \dots + n_k \ln x_k)$$

where $x_1 = \frac{P_1}{P}$; $x_2 = \frac{P_2}{P}$; Also, $m_1 R_1 = n_1 \bar{R}$
 $m_2 R_2 = n_2 \bar{R}$

So

$$S_f - S_i = - \left[m_1 R_1 \ln \frac{P_1}{P} + m_2 R_2 \ln \frac{P_2}{P} + \dots + m_k R_k \ln \frac{P_k}{P} \right]$$

Problem 4.4: A closed vessel of 0.5 m³ capacity contained air at 100 kN/m² and 27° C. After hydrogen is added, the pressure become 102 kN/m² at the same temperature.

Find the final masses of oxygen, nitrogen and hydrogen in the vessel and their respective partial pressures. Air contains 77% of nitrogen and 23% of oxygen on mass basis. Take R for air as 0.287 kJ/kg K, R for H₂ is 4.124 kJ/kg K and R for O₂ is 0.2598 kJ/kg K

Solution:

$$V = 0.5 \text{ m}^3; P = 100 \text{ kN/m}^2; T = 273 + 27 = 300 \text{ K}$$

The mass of 0.5 m³ of air at 100 kN/m² and 27° C

$$m_{air} = \frac{PV}{RT} = \frac{100 \times 0.5}{0.287 \times 300} = 0.58072 \text{ kg}$$

$$\therefore \text{The mass of } O_2 = 0.58072 \times 0.23 = 0.134 \text{ kg}$$

i.e., $m_{O_2} = 0.134 \text{ kg}$

Also, the mass of N₂ = 0.58072 × 0.77 = 0.4472 kg

i.e., $m_{N_2} = 0.4472 \text{ kg}$

Partial pressure of Hydrogen = 102 - 100 = 2 kN/m²

The mass of Hydrogen H_2

$$m_{H_2} = \frac{PV}{RT} = \frac{2 \times 0.5}{4.124 \times 300} = 8.083 \times 10^{-4} \text{ kg}$$

Partial pressure of

$$O_2 = \frac{m_{O_2} RT}{V} = \frac{0.134 \times 0.2598 \times 300}{0.5} = 20.89 \text{ kN/m}^2$$

Partial pressure of

$$N_2 = 100 - 20.89 = 79.11 \text{ kN/m}^2$$

Problem 4.5: Calculate the equivalent molecular weight of the gaseous fuel for which the volumetric composition is given below.

$CH_4 = 20\%$; $H_2 = 52\%$; $CO = 16\%$; $C_2H_4 = 2\%$ $CO_2 = 4\%$

and the remaining is Nitrogen.

Also calculate the characteristic gas constant and the density of the mixtures of N.T.P. Find the partial pressures of the constituent gases, if the pressure of the mixture is 100 kN/m^2 .

Solution:

We know

Equivalent molecular weight $\mu_{mix} = x_1\mu_1 + x_2\mu_2 + \dots$

By using the table, we can find μ_{mix} .

Constituent gas	Volumetric composition %	Mole fraction	Molecular Weight μ	Gas constant $R = \frac{8.3143}{\mu}$	Equivalent $\mu = \sum x_i \mu_i$ (or) $\mu_{mix} = \sum x_i \mu_i$
CH_4	20	0.2	16	$R_{CH_4} = \frac{8.3143}{16} = 0.5196$	3.2
H_2	52	0.52	2	4.1571	1.04
CO	16	0.16	28	0.2969	4.48
C_2H_4	2	0.02	28	0.2969	0.56
CO_2	4	0.04	44	0.1889	1.76
N_2	6	0.06	28	0.2969	1.68
					$\mu_{mix} = \sum x_i \mu_i = 12.72 \text{ kg/kg mol}$

Equivalent molecular weight $\mu_{mix} = 12.72 \text{ kg/kg mol}$

To find density of mixture

We know N.T.P. = 0° C & 101.325 kN/m^2

$$P\bar{v} = \bar{R}T$$

$$Pv = RT$$

$$\rho = \frac{1}{v} = \frac{P}{RT} = \frac{101.325}{\left(\frac{8.3143}{12.72}\right) \times 273} = 0.56783 \text{ kg/m}^3$$

To find R_{mix}

$$R_{mix} = \frac{\bar{R}}{\mu_{mix}} = \frac{8.3143}{12.72} = 0.65364 \frac{\text{kJ}}{\text{kg K}}$$

To find partial pressures of constituent gases

The partial pressures of the constituent gases are proportional to mole fraction. The numerical value of the partial pressure of the constituent gases will be equal to value of mole fraction.

So partial pressure of methane $\text{CH}_4 = 20 \text{ kN/m}^2$

Partial pressure of hydrogen $\text{H}_2 = 52 \text{ kN/m}^2$

Partial pressure of $\text{CO} = 16 \text{ kN/m}^2$

Partial pressure of $\text{C}_2\text{H}_4 = 2 \text{ kN/m}^2$

Partial pressure of $\text{CO}_2 = 4 \text{ kN/m}^2$

and Partial pressure of $\text{N}_2 = 6 \text{ kN/m}^2$

Problem 4.6: A mixture of Ideal gases consists of 2.5 kg of N_2 and 4.5 kg of CO_2 at a pressure of 4 bar and a temperature of 25°C . Determine:

1. Mole fraction of each constituent
2. Equivalent molecular weight of the mixture,
3. Equivalent gas constant of the mixture,
4. The partial pressure and partial volumes,
5. The volume and density of the mixture

(Nov/Dec 2009 - Anna University)

Solution

$$m_{\text{N}_2} = 2.4 \text{ kg}; m_{\text{CO}_2} = 4.5 \text{ kg}; P = 4 \text{ bar} = 400 \text{ KPa}$$

$$T = 25 + 273 = 298 \text{ K}$$

1. Mole Fraction

$$\text{Mole fraction } x_i = \frac{n_i}{\sum n_i}$$

$$\therefore x_{\text{N}_2} = \frac{\frac{2.5}{28}}{\frac{2.5}{28} + \frac{4.5}{44}} = \frac{0.08928}{0.19155} = 0.46608$$

$$x_{\text{CO}_2} = \frac{\frac{4.5}{44}}{\frac{2.5}{28} + \frac{4.5}{44}} = \frac{0.10227}{0.19155} = 0.53389$$

2. Equivalent Molecular Weight: μ

$$\mu = x_1 \mu_1 + x_2 \mu_2$$

$$= x_{\text{N}_2} \mu_{\text{N}_2} + x_{\text{CO}_2} \mu_{\text{CO}_2}$$

$$= (0.46608) \times 28 + (0.53389) \times 44$$

$$= 36.5414 \text{ kJ/kg mol}$$

3. The Equivalent gas constant: R

We know, Total mass

$$m = m_{\text{N}_2} + m_{\text{CO}_2} = 2.5 + 4.5$$

$$= 7 \text{ kg}$$

$$R = \frac{m_{\text{N}_2} \times R_{\text{N}_2} + m_{\text{CO}_2} \times R_{\text{CO}_2}}{m}$$

But

$$R_{\text{N}_2} = \left(\frac{\bar{R}}{\mu_{\text{N}_2}} \right) = \frac{8.3143}{28} = 0.29694$$

$$R_{\text{CO}_2} = \left(\frac{\bar{R}}{\mu_{\text{CO}_2}} \right) = \frac{8.3143}{44} = 0.18896$$

$$\therefore R = \frac{2.5 \times 0.29694 + 4.5 \times 0.18896}{7} = 0.22752 \text{ kJ/kgK}$$

4. Partial Pressures and Partial Volumes

$$P_{N_2} = x_{N_2} \times P = 0.46608 \times 400 = 186.452 \text{ kPa}$$

$$P_{CO_2} = x_{CO_2} \times P = 0.53389 \times 400 = 213.556 \text{ kPa}$$

To find V, we can use

$$PV = mRT$$

$$V_{N_2} = \frac{m_{N_2} \times R_{N_2} \times T}{P}$$

$$= \frac{2.5 \times 0.29694 \times 298}{400}$$

$$= 0.553 \text{ m}^3$$

$$V_{CO_2} = \frac{m_{CO_2} \times R_{CO_2} \times T}{P}$$

$$= \frac{4.5 \times 0.18896 \times 298}{400} = 0.633 \text{ m}^3$$

5. Volume and density of the mixture

$$\text{Total volume, } V = V_{N_2} + V_{CO_2} = 0.553 + 0.633 = 1.186 \text{ m}^3$$

and

$$PV = mRT$$

$$\Rightarrow V = \frac{mRT}{P} = \frac{7 \times 0.22752 \times 298}{400} = 1.1865 \text{ m}^3$$

$$\text{Density of mixture } \rho = m/v = \frac{7}{1.1865} = 5.899 \text{ kg/m}^3$$

Problem 4.7: A tank contains 0.2 m³ of gas mixture composed of 4 kg of nitrogen, 1 kg of oxygen and 0.5 kg of carbon-di-oxide. If the temperature is 20°C, determine the total pressure, gas constant and molar mass of the mixture. (May/June-2007-Anna University)

Solution

The gas constants of Nitrogen, oxygen, and carbon-dioxide are

$$R_{N_2} = \frac{8314}{28} = 296.9 \text{ J/kgK}$$

$$R_{O_2} = \frac{8314}{32} = 259.8 \text{ J/kgK}$$

$$R_{CO_2} = \frac{8314}{44} = 189 \text{ J/kgK}$$

The partial pressures of each component are

$$P_{N_2} = \frac{m_{N_2} R_{N_2} T}{V_m}$$

$$= \frac{4 \times 296.9 \times 293}{0.2} = 1739834 \text{ N/m}^2 = 17.398 \text{ bar}$$

$$P_{O_2} = \frac{m_{O_2} R_{O_2} T}{V_m}$$

$$= \frac{1 \times 259.8 \times 293}{0.2} = 380607 \text{ N/m}^2 = 3.806 \text{ bar}$$

$$P_{CO_2} = \frac{m_{CO_2} R_{CO_2} T_m}{V_m} = \frac{0.5 \times 189 \times 293}{0.2}$$

$$= 138442.5 \text{ N/m}^2 = 1.384 \text{ bar}$$

$$\therefore \text{Total pressure} = P_{N_2} + P_{O_2} + P_{CO_2}$$

$$= 17.398 + 3.806 + 1.384$$

$$= 22.588 \text{ bar}$$

The molar mass of mixture

$$\mu_m = \frac{m_m}{n_m} = \frac{\text{mass of the mixture}}{\text{mole number of mixture}}$$

$$\text{mass of mixture} = m_{N_2} + m_{O_2} + m_{CO_2}$$

$$= 4 + 1 + 0.5 = 5.5 \text{ kg}$$

The mole number of constituents are

$$n_{N_2} = \frac{m_{N_2}}{\mu_{N_2}} = \frac{4}{28} = 0.1428 \text{ k mol}$$

$$n_{O_2} = \frac{m_{O_2}}{\mu_{O_2}} = \frac{1}{32} = 0.03125 \text{ k mol}$$

$$n_{CO_2} = \frac{m_{CO_2}}{\mu_{CO_2}} = \frac{0.5}{44} = 0.01136 \text{ k mol}$$

The mole number of mixture

$$n_m = \sum n_i = n_{N_2} + n_{O_2} + n_{CO_2}$$

$$= 0.1428 + 0.03125 + 0.01136$$

$$= 0.1854 \text{ kmol}$$

$$\therefore n_m = \frac{5.5}{0.1854} = 29.6 \text{ kg/k mol}$$

Problem 4.8: A mixture of ideal gases consists of 2 kg of nitrogen and 6 kg of carbon dioxide at a pressure of 300 kPa and a temperature of 20° C. Find (1) the mole fraction of each constituent (2) the equivalent molecular weight of the mixture (3) the equivalent gas constant of the mixture (4) the partial pressures and partial volumes (5) the volume and density of the mixture (6) C_p and C_v of the mixture.

Solution:

$$m_{N_2} = 2 \text{ kg}; m_{CO_2} = 6 \text{ kg}; P = 300 \text{ kPa}$$

$$T = 20 + 273 = 293 \text{ K}$$

1. Mole Fraction

$$\text{Mole fraction } x_i = \frac{n_i}{\sum n_i}$$

$$x_{N_2} = \frac{\frac{2}{28}}{\frac{2}{28} + \frac{6}{44}} = 0.34375$$

$$x_{CO_2} = \frac{\frac{6}{44}}{\frac{2}{28} + \frac{6}{44}} = 0.65625$$

2. Equivalent Molecular Weight: μ

$$\mu = x_1 \mu_1 + x_2 \mu_2$$

$$= x_{N_2} \mu_{N_2} + x_{CO_2} \mu_{CO_2}$$

$$= 0.34375 \times 28 + 0.65625 \times 44 = 38.5 \text{ kg/kg mol}$$

3. The equivalent gas constant R

We know total mass

$$m' = m_{N_2} + m_{CO_2} = 2 + 6 = 8 \text{ kg}$$

$$R = \frac{m_{N_2} \times R_{N_2} + m_{CO_2} \times R_{CO_2}}{m}$$

$$R_{N_2} = \left(\frac{\bar{R}}{\mu_{N_2}} \right) = \frac{8.3143}{28} = 0.29694$$

$$R_{CO_2} = \frac{\bar{R}}{\mu_{CO_2}} = \frac{8.3143}{44} = 0.18896$$

$$R = \frac{2 \times 0.29694 + 6 \times 0.18896}{8} = 0.216 \text{ kJ/kg K}$$

4. Partial Pressures and Partial Volumes

$$P_{N_2} = x_{N_2} \times P = 0.34375 \times 300 = 103.125 \text{ kPa}$$

$$P_{CO_2} = x_{CO_2} \times P = 0.65625 \times 300 = 196.875 \text{ kPa}$$

To find V , we can use

$$PV = mRT$$

$$V_{N_2} = \frac{m_{N_2} \times R_{N_2} \times T}{P}$$

$$= \frac{2 \times 0.29694 \times 293}{300} = 0.58 \text{ m}^3$$

$$V_{CO_2} = \frac{m_{CO_2} \times R_{CO_2} \times T}{P} = \frac{6 \times 0.18896 \times 293}{300} = 1.107 \text{ m}^3$$

5. The volume and density of the mixture

$$\text{Total volume } V = V_{N_2} + V_{CO_2} = 0.58 + 1.107$$

$$= 1.687 \text{ m}^3$$

$$\text{(or) } PV = mRT$$

$$V = \frac{mRT}{P} = \frac{8 \times 0.216 \times 293}{300} = 1.687 \text{ m}^3$$

Density of the mixture

$$\rho = \frac{m}{V} = \frac{8}{1.687} = 4.74 \text{ kg/m}^3$$

6. C_p and C_v of the mixture

$$\text{We know } C_p - C_v = R, \quad \frac{C_p}{C_v} = \gamma$$

$$\text{and } C_v = \frac{R}{\gamma - 1} \text{ and } \gamma_{\text{for } N_2} = 1.4$$

$$\text{So } C_{vN_2} = \frac{R_{N_2}}{\gamma - 1} = \frac{0.29694}{(1.4 - 1)} = 0.742 \text{ kJ/kg K}$$

$$C_{pN_2} = 1.4 \times 0.742 = 1.039 \text{ kJ/kg K}$$

$$\gamma_{\text{for } CO_2} = 1.286$$

$$\therefore C_{vCO_2} = \frac{R_{CO_2}}{\gamma - 1} = \frac{0.18896}{1.286 - 1} = 0.6607 \text{ kJ/kg K}$$

$$C_{pCO_2} = 1.286 \times 0.6607 = 0.85032 \text{ kJ/kg K}$$

For the mixture,

$$C_p = \frac{m_{N_2} C_{pN_2} + m_{CO_2} C_{pCO_2}}{m_{N_2} + m_{CO_2}}$$

$$= \frac{2 \times 1.039 + 6 \times 0.85032}{(2 + 6)} = 0.8975 \text{ kJ/kg K}$$

$$C_v = \frac{m_{N_2} C_{vN_2} + m_{CO_2} C_{vCO_2}}{m_{N_2} + m_{CO_2}}$$

$$= \frac{2 \times 0.742 + 6 \times 0.6607}{8} = 0.68103 \text{ kJ/kg K}$$

Problem 4.9: A mixture of ideal gases having same properties as that of the mixture in the previous problem is heated at constant volume to 50° C, find the changes in internal energy, enthalpy and entropy of the mixture. Find the changes in internal energy, enthalpy and entropy of the mixture if the heating is done in constant pressure.

Solution:

$$m = 8 \text{ kg}; C_v = 0.68103 \text{ kJ/kg K}; C_p = 0.8975 \text{ kJ/kg K}$$

$$R = 0.216 \text{ kJ/kg K}; T_1 = 20 + 273 = 293 \text{ K}$$

$$T_2 = 50 + 273 = 323 \text{ K};$$

Case (a) When mixture is heated at constant volume

Change in internal energy

$$\begin{aligned} \Delta U &= U_2 - U_1 = m C_v (T_2 - T_1) \\ &= 8 \times 0.68103 (323 - 293) = 163.45 \text{ kJ} \end{aligned}$$

Change in enthalpy

$$\begin{aligned} \Delta H &= H_2 - H_1 = m C_p (T_2 - T_1) \\ &= 8 \times 0.8975 (323 - 293) \\ &= 215.4 \text{ kJ} \end{aligned}$$

Change in entropy

$$\begin{aligned} \Delta S &= S_2 - S_1 = m C_v \ln \frac{T_2}{T_1} + m R \ln \frac{V_2}{V_1} \\ &= 8 \times 0.68103 \times \ln \left[\frac{323}{293} \right] + 0 \\ &= 0.531 \text{ kJ/K} \end{aligned} \quad [\because V_2 = V_1]$$

Case (b) When mixture is heated at constant pressure

The ΔU and ΔH remain same, i.e., $\Delta U = 163.45 \text{ kJ}$

$$\Delta H = 215.4 \text{ kJ}$$

Change in entropy

$$\begin{aligned} S_2 - S_1 &= m C_p \ln \frac{T_2}{T_1} - m R \ln \frac{P_2}{P_1} \\ &= 8 \times 0.8975 \times \ln \left[\frac{323}{293} \right] - 0 \\ &= 0.699 \text{ kJ/K} \end{aligned}$$

Problem 4.10: Find the increase in entropy when 3 kg of oxygen at 70° C are mixed with 5 kg of nitrogen at the same temperature. The initial pressure of each constituent is 103 kPa and is the same as that of the mixture.

4.10 THERMODYNAMIC RELATIONSHIPS

Before applying first law of thermodynamics, we studied the relationships among the properties P , v and T . Then, on the basis of first law of thermodynamics, we studied two more properties u and h (internal energy and enthalpy). Then on the basis of second law of thermodynamics, we studied three more additional properties s , a and g i.e. entropy, Helmholtz function and Gibbs function.

Now, on the basis of both the first and second law of thermodynamics, we can study the relationships among these properties. Such thermodynamic properties relationships are studied by discussing the following.

1. The Maxwell Equations

2. Clapeyron Equation
3. General Equation for Internal Energy, Enthalpy and Entropy in terms of P, v, T and specific heats.
4. Specific heat Relations.
5. Joule-Thomson Coefficient (or) Joule-Kelvin coefficient.
6. General Equations for internal energy, enthalpy and entropy in terms of P, v, T and specific heats

4.11 Tds RELATIONS

Entropy Equations (Tds Equations)

The entropy of a pure substance is a function of T and v

ie $s = f(T, v)$

$$ds = \left(\frac{\partial s}{\partial T} \right)_v dT + \left(\frac{\partial s}{\partial v} \right)_T dv$$

Multiply by T , we get

$$Tds = T \left(\frac{\partial s}{\partial T} \right)_v dT + T \left(\frac{\partial s}{\partial v} \right)_T dv \quad \dots (1)$$

But for a reversible constant volume process,

$$dq = C_v (dT)_v = T (ds)_v$$

$$C_v = T \left(\frac{\partial s}{\partial T} \right)_v \quad \dots (2)$$

By using third Maxwell equation,

$$\text{we get } \left(\frac{\partial s}{\partial v} \right)_T = \left(\frac{\partial p}{\partial T} \right)_v \quad \dots (3)$$

Substitute (2) and (3) in equation (1), we get

$$Tds = C_v dT + T \left(\frac{\partial p}{\partial T} \right)_v dv \quad \dots (4)$$

This equation is known as **first Tds equation (or) the first form of entropy equation.**

Similarly, by starting with $s = f(T, P)$, it can be shown that

$$Tds = T \left[\left(\frac{\partial s}{\partial T} \right)_P dT + \left(\frac{\partial s}{\partial P} \right)_T dP \right] \quad \dots (5)$$

We know for constant pressure process,

$$dq = C_p (dT)_P = T (ds)_P$$

$$C_p = T \left(\frac{\partial s}{\partial T} \right)_P \quad \dots (6)$$

By using fourth maxwell equation,

$$\left(\frac{\partial v}{\partial T} \right)_P = - \left(\frac{\partial s}{\partial P} \right)_T \quad \dots (7)$$

Substitute (6) and (7) in equation (5), we get

$$Tds = C_p dT - T \left(\frac{\partial v}{\partial T} \right)_P dP \quad \dots (8)$$

This is known as **second Tds equation (or) the second form of entropy equation.**

So general equation for entropy (or two equations) are

$$Tds = C_p dT + T \left[\frac{\partial p}{\partial T} \right]_s ds$$

$$Tds = C_p dT - T \left[\frac{\partial v}{\partial T} \right]_p dp$$

4.12 EQUATION FOR INTERNAL ENERGY AND ENTHALPY

For any process between equilibrium states of substance,

$$du = Tds - Pdv$$

Substitute equation (4) in first Tds equation in the above du equation, we get

$$du = C_p dT + T \left[\frac{\partial p}{\partial T} \right]_s ds - Pdv$$

$$(or) du = C_p dT + \left[T \left[\frac{\partial p}{\partial T} \right]_s - P \right] ds$$

This is known as general equation for internal energy. This is also called the energy equation. Similarly,

$$we know dh = Tds + vdp$$

Substitute equation (8) in second Tds equation into the above dh equation, we get

$$dh = C_p dT - T \left[\frac{\partial v}{\partial T} \right]_p dp + vdp$$

$$(or) dh = C_p dT - \left[T \left[\frac{\partial v}{\partial T} \right]_p - v \right] dp \quad \dots (10)$$

This equation is known as general equation for enthalpy.

4.13 THE MAXWELL EQUATIONS

The maxwell equation relate entropy to P, v and T

The maxwell equations can be derived from the Tds equation.

$$ie Tds = du + Pdv$$

$$(or) du = Tds - Pdv \quad \dots (1)$$

It is the differential of u with two independent variables (properties) s and v.

Also du is the exact differential. It is the exact differential of the type $du = Mdv + Nds$, then

$$\left[\frac{\partial M}{\partial v} \right]_s = \left[\frac{\partial N}{\partial s} \right]_v. \text{ So we can immediately write}$$

$$du = Tds - Pdv$$

$$\left[\frac{\partial T}{\partial v} \right]_s = - \left[\frac{\partial P}{\partial s} \right]_v \quad \text{First Maxwell equation} \quad \dots (2)$$

Similarly,

We know enthalpy $h = u + Pv$
Differentiating,

equations) are

$$Tds = C_v dT + T \left(\frac{\partial p}{\partial T} \right)_v du \quad \dots (4)$$

$$Tds = C_p dT - T \left(\frac{\partial v}{\partial T} \right)_p dp \quad \dots (8)$$

4.12 EQUATION FOR INTERNAL ENERGY AND ENTHALPY

For any process between equilibrium states of pure substance,

$$du = Tds - Pdu$$

Substitute equation (4) (ie first Tds equation) into the above du equation; we get

$$du = C_v dT + T \left(\frac{\partial p}{\partial T} \right)_v dv - Pdu$$

$$(or) du = C_v dT + \left[T \left(\frac{\partial p}{\partial T} \right)_v - P \right] du \quad \dots (9)$$

This is known as **general equation for internal energy**. This is also called the **energy equation**.

Similarly,

$$we know dh = Tds + vdp$$

Substitute equation (8) (ie second Tds equation) into the above dh equation, we get

$$dh = C_p dT - T \left(\frac{\partial v}{\partial T} \right)_p dP + vdp$$

$$(or) dh = C_p dT - \left[T \left(\frac{\partial v}{\partial T} \right)_p - v \right] dp \quad \dots (10)$$

This equation is known as **general equation for enthalpy**.

4.13 THE MAXWELL EQUATIONS

The maxwell equation relate entropy to P , v and T

The maxwell equations can be derived from the Tds equation.

$$ie Tds = du + Pdv$$

$$(or) du = Tds - Pdv \quad \dots (1)$$

It is the differential of u with two independent variables (properties) s and v .

Also du is the exact differential. It is the exact differential of the type $dz = Mdx + Ndy$, then

$$\left(\frac{\partial M}{\partial y} \right)_x = \left(\frac{\partial N}{\partial x} \right)_y. \text{ So we can immediately write}$$

$$du = Tds - Pdv$$

$$\left(\frac{\partial T}{\partial v} \right)_s = - \left(\frac{\partial P}{\partial s} \right)_v \quad \text{First Maxwell equation} \quad \dots (2)$$

Similarly,

$$We know enthalpy h = u + Pv$$

Differentiating,

$$dh = du + d(Pv)$$

$$= du + Pdv + vdp$$

$$= Tds + vdp \quad (\text{Substitute } du + pdv = Tds)$$

$$\text{So } dh = Tds + vdp$$

... (3)

It is the differential of h with two independent variables (properties) s and p . Also, dh is the exact differential. It is the exact differential of the type $dz = Mdx + Ndy$, then $\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$. So we can immediately write

$$dh = Tds + vdp$$

$$\left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial v}{\partial s}\right)_p \quad \text{Second Maxwell equation}$$

... (4)

Similarly,

We know Helmholtz function a

$$a = u - Ts$$

$$da = du - d(Ts)$$

$$= du - Tds - sdT$$

$$= -pdv - sdT$$

$$da = -Pdv - sdT$$

$$[\dots Tds - du = Pdv]$$

... (5)

It is the differential of a with two independent variable (properties) v and T . Also, da is the exact differential. It is the exact differential of the type

$dz = Mdx + Ndy$, then $\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$. So we can immediately write,

$$da = -pdv - sdT$$

$$\left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T \quad \text{Third Maxwell equation} \quad \dots (6)$$

Similarly,

We know Gibbs function $g = h - Ts$

Differentiating, $dg = dh - d(Ts)$

$$= dh - Tds - sdT$$

$$= d(u + Pv) - Tds - sdT$$

$$= du + Pdv + vdp - Tds - sdT$$

$$= Tds + vdp - Tds - sdT$$

$$[\dots Tds = du + Pdv]$$

$$dg = vdp - sdT \quad \dots (7)$$

It is the differential of g , with two independent variables P and T . Also dg is the exact differential. It is the exact differential of the type $dz = Mdx + Ndy$, then $\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$. So we can immediately write,

$$dg = vdp - sdT$$

$$\left(\frac{\partial v}{\partial T}\right)_P = - \left(\frac{\partial s}{\partial P}\right)_T \quad \text{Fourth Maxwell equation} \quad \dots (8)$$

So the equations 2, 4, 6 and 8 are called Maxwell equations which are given below.

Maxwell equations

First $\rightarrow \left(\frac{\partial T}{\partial v} \right)_s = - \left(\frac{\partial P}{\partial s} \right)_v$

Second $\rightarrow \left(\frac{\partial T}{\partial P} \right)_s = \left(\frac{\partial v}{\partial s} \right)_P$

Third $\rightarrow \left(\frac{\partial P}{\partial T} \right)_v = \left(\frac{\partial s}{\partial v} \right)_T$

Fourth $\rightarrow \left(\frac{\partial v}{\partial T} \right)_P = - \left(\frac{\partial s}{\partial P} \right)_T$

Maxwell Equations

We can note that each equation involves entropy s and other three fundamental properties P, v and T .

4.14 The CLAPEYRON EQUATION (Also called CLAUSIUS - CLAPEYRON EQUATION)

The Clapeyron equation provides the relationship between the saturation pressure, temperature, the enthalpy (latent heat) of evaporation and the specific volume of the two phases involved. This equation will be useful for finding the properties of pure substances existing in two phases in equilibrium. It defines the slope of the curve separating the two phases in the P-T diagram. Refer the Fig. 4.8.

Refer the third Maxwell equation

$$\left(\frac{\partial P}{\partial T} \right)_v = \left(\frac{\partial s}{\partial v} \right)_T$$

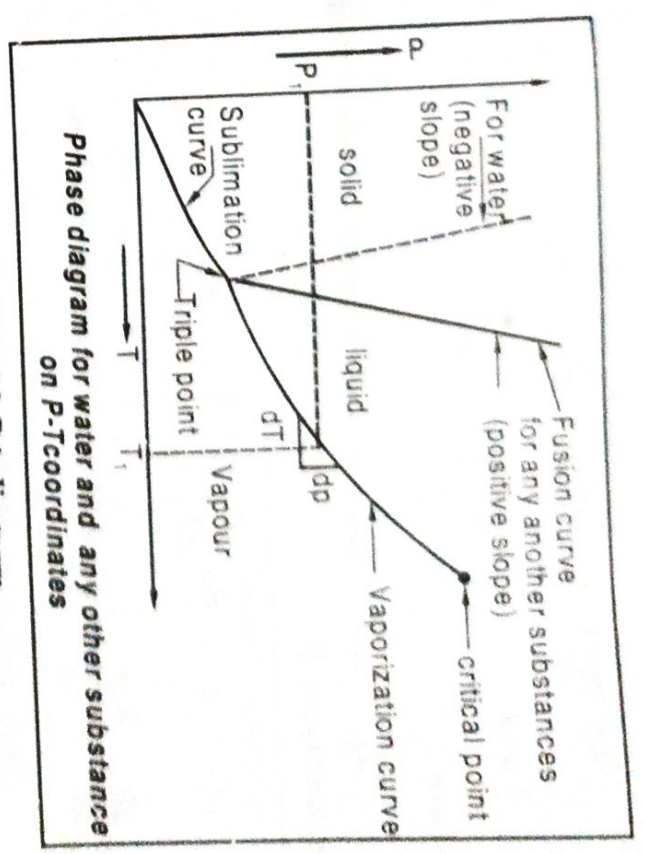


Fig. 4.8 P-T diagram

Consider the vapourisation of saturated liquid to saturated vapour at constant temperature.

During the vapourization, the pressure and temperature are independent of volume.

$$\text{ie } \frac{dP}{dT} = \frac{s_g - s_f}{v_g - v_f}$$

where s_g = specific entropy of saturated vapour

s_f = specific entropy of saturated liquid

v_g = specific volume of saturated vapour

v_f = specific volume of saturated liquid

We know, $s_g - s_f = s_{fg} = \frac{h_{fg}}{T}$

and $v_g - v_f = v_{fg}$

where

h_{fg} = latent heat of vapourization at saturation temperature T

$$\text{So } \frac{dP}{dT} = \frac{s_g - s_f}{v_g - v_f} = \frac{h_{fg}}{T \times v_{fg}}$$

ie $\frac{dP}{dT} = \frac{h_{fg}}{T \cdot v_{fg}}$ This is known as **Clapeyron equation**.

This equation relates readily three measurable properties: the slope of the saturation pressure-temperature line, the latent heat and change in volume during a phase transformation. In other words, knowing the slope of vapour pressure and temperature $\left(\frac{dP}{dT}\right)$ and change in specific volume v_{fg} , we can determine the latent heat of evaporation (h_{fg}) which is very difficult to measure accurately.

4.15 JOULE-THOMSON COEFFICIENT (JOULE-KELVIN COEFFICIENT)

When a fluid is flowing through a restricted passage in a pipe (Throttling process), the pressure is reduced and temperature is changed but the enthalpy remains constant.

The change in temperature with drop in pressure at constant enthalpy is known as **Joule-Kelvin Coefficient**

(μ_J) (or) **Joule-Thomson Coefficient** (μ_J). This throttling process is also called **Joule-Kelvin expansion**.

$$\mu_J = \left(\frac{\partial T}{\partial P} \right)_h$$

4.15.1 Joule Kelvin effect

Assume a fluid is flowing through a restricted passage in a pipe as shown in Fig 4.9 (partly open valve fitted in a pipe). This pipe is well insulated. So there is no heat transfer.

By rotating the valve manually, set a initial temperature and pressure of the gas in the up-stream side.

Let P_1 and T_1 are the initial pressure and temperature before throttling process. Measure P_1 and T_1 i.e., the pressure

and Temperature after throttling process. By opening valve more and more, we get different final pressures and temperatures for different positions of the valve. So we get final pressure & Temperature as $P_2, T_2; P_3, T_3$ and P_n . These values can be plotted in the $T - P$ diagram.

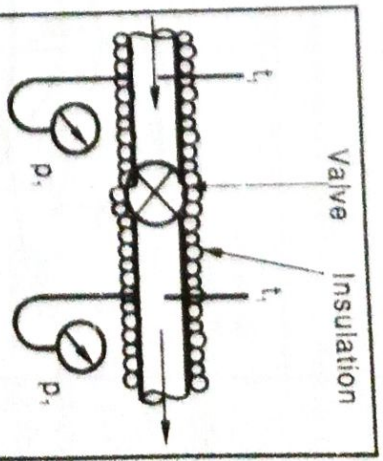


Fig (a) Joule - Thomson expansion

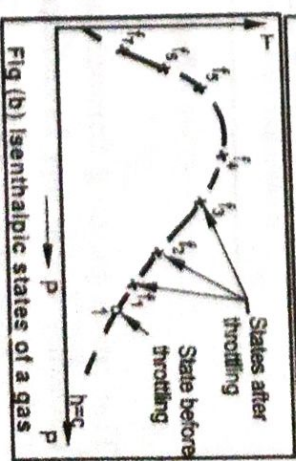


Fig. 4.9

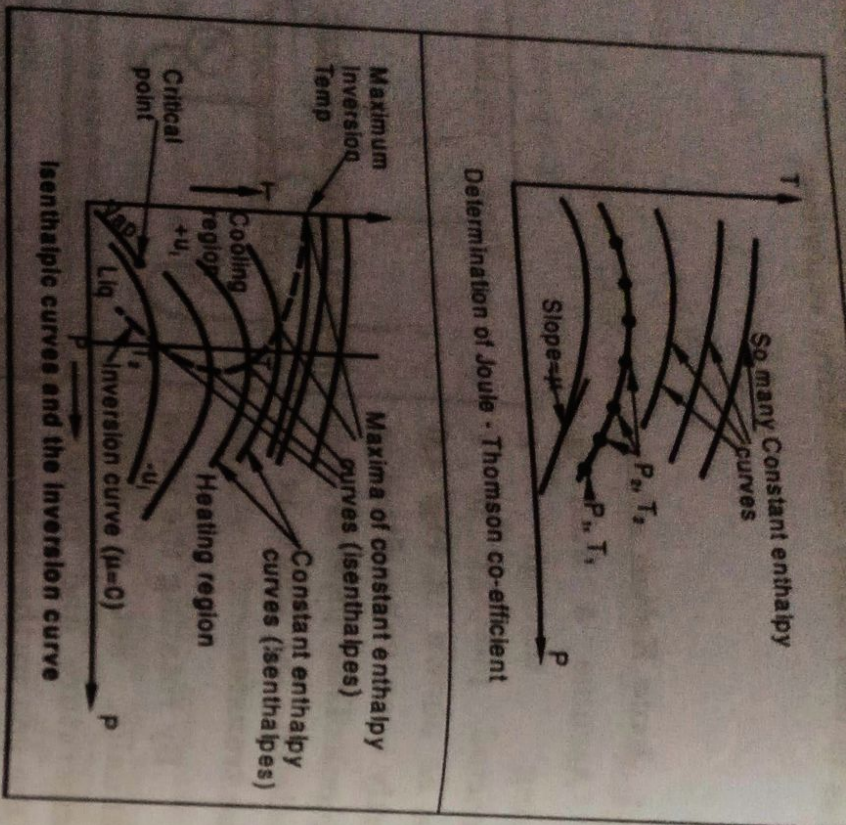


Fig. 4.10

The curve passing through all these points is a **constant enthalpy curve (or) isenthalpe**.

Now the initial pressure and temperature of the fluid is set to new values, and by throttling to different states, so many 'constant enthalpy curves' are obtained.

The slope of the constant enthalpy curve on a $T-P$ diagram at any point is called **Joule-Kelvin Coefficient (μ_J)** Fig. 4.10.

The curve passing through maxima (maximum h_t) of all 'constant enthalpy curves' is known as the inversion curve. The region leftside of the inversion curve is cooling region and the region right side of the inversion curve is heating region. The temperature at the maxima of the constant enthalpy curve is maximum inversion temperature.

To achieve the cooling effect by Joule-Kelvin expansion, the initial temperature of the fluid must be below maximum inversion temperature.

Refer the Fig. 4.11. The initial state of fluid before throttling is at A. If the final pressure lies between A and B, the fluid is heated (heating effect). If the final pressure is at C, there will be no change in temperature. If the final pressure is below C, there will be a cooling effect. It is called **Joule-Kelvin effect**.

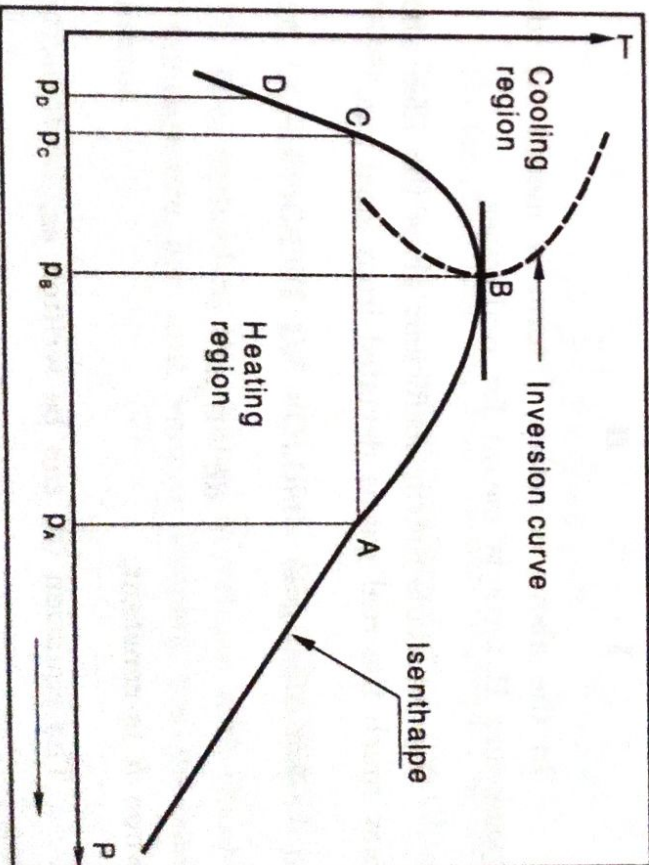


Fig. 4.11 Maximum cooling by Joule-Kelvin expansion

We know,

$$dh = Tds + vdP$$

The second Tds equation is given as

$$Tds = C_p dT - T \left(\frac{\partial v}{\partial T} \right)_p dP$$

Substitute the value of Tds in equation (i), we get

$$dh = \left[C_p dT - T \left(\frac{\partial v}{\partial T} \right)_p dP \right] + v dP$$

$$dh = C_p dT - \left[T \left(\frac{\partial v}{\partial T} \right)_p - v \right] dP$$

I

II

In the above equation, I term is meant for ideal gases and II term is meant for real gases.

So the Joule-Kelvin coefficient gives the idea about how much the real gas is deviated from ideal gas.

For ideal gas

$$dh = C_p dT$$

when h is constant,

The equation (ii) can be written as,

$$C_p dT = \left[T \left(\frac{\partial v}{\partial T} \right)_p - v \right] dP$$

$$\text{or } \left(\frac{\partial T}{\partial P} \right)_h = \frac{1}{C_p} \left[T \left(\frac{\partial v}{\partial T} \right)_p - v \right]$$

$$\text{We know } \mu_J = \left(\frac{\partial T}{\partial P} \right)_h = \frac{1}{C_p} \left[T \left(\frac{\partial v}{\partial T} \right)_p - v \right]$$

For an ideal gas,

$$Pv = RT$$

$$v = \frac{RT}{P}$$

$$\left(\frac{\partial v}{\partial T} \right)_p = \frac{R}{P} = \frac{v}{T}$$

Substitute the above in μ_J equation, we get,

$$\mu_J = \frac{1}{C_p} \left[T \times \frac{v}{T} - v \right] = 0$$

So for ideal gas, the Joule-Kelvin coefficient is zero and there is no change in temperature during throttling process.