

UNIT-IV: REAL GAS MODELS AND PERFECT GAS MIXTURES

1. Real Gas Models

Definition

A **real gas** is a gas whose behavior deviates from the Ideal Gas Law because molecules occupy space and experience intermolecular forces.

Ideal Gas Equation

$$PV = mRT \quad PV = mRT$$

Ideal gas assumptions:

- Molecules have negligible volume.
- No intermolecular forces.
- Elastic collisions.
- Valid at low pressure and high temperature.

Real Gas Behavior

Real gases deviate from ideal behavior:

- High pressure
- Low temperature
- Near liquefaction

Examples:

- Steam
- CO₂
- NH₃
- Refrigerants

2. Van der Waals Equation of State

Equation

For one mole,

$$(P + \frac{a}{V^2})(V - b) = RT$$

For n moles,

$$(P + \frac{an^2}{V^2})(V - nb) = nRT$$

Where

- P = Pressure
- V = Volume
- T = Temperature
- R = Gas constant
- a = Attraction constant
- b = Volume correction constant

Significance of Constants

a (Pressure Correction)

Represents intermolecular attractive force.

Larger value of a

- Strong attraction
- Gas easily liquefies

b (Volume Correction)

Represents actual molecular volume.

Larger molecules have larger b.

Assumptions

- Molecules attract each other.
- Molecules occupy finite volume.
- Corrects Ideal Gas Law.

Limitations

Not accurate near critical point.

3. Compressibility Charts

Compressibility Factor (Z)

$$Z = \frac{PV}{RT} \quad Z = \frac{RT}{Pv}$$

For Ideal Gas

$$Z = 1$$

For Real Gas

$$Z \neq 1$$

Interpretation

- $Z = 1 \rightarrow$ Ideal Gas
 - $Z > 1 \rightarrow$ Repulsive forces dominate
 - $Z < 1 \rightarrow$ Attractive forces dominate
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Reduced Properties

Reduced Pressure

$$P_r = \frac{P}{P_c}$$

Reduced Temperature

$$T_r = \frac{T}{T_c}$$

Where

- P_c = Critical pressure
 - T_c = Critical temperature
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Compressibility Chart

Plots:

- Z vs Reduced Pressure
- Different Reduced Temperatures

Uses

- Determine Z
 - Calculate real gas volume
 - Thermodynamic property estimation
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4. Variable Specific Heats

Specific heat changes with temperature.

At Constant Pressure

$$C_p = f(T) \quad C_{p,p} = f(T) \quad C_p = f(T)$$

At Constant Volume

$$C_v = f(T) \quad C_{v,v} = f(T) \quad C_v = f(T)$$

Relationship

$$C_p - C_v = R \quad C_{p,p} - C_{v,v} = R \quad C_p - C_v = R$$

Importance

Accurate calculations in

- Gas turbines
 - Compressors
 - Internal combustion engines
 - High-temperature gases
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5. Gas Tables

Gas tables provide:

- Enthalpy
- Internal Energy
- Entropy
- Specific Heat
- Pressure
- Temperature

Applications

- Thermodynamic analysis
 - Power cycles
 - Refrigeration
 - Heat transfer
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6. Mixtures of Perfect Gases

Definition

A mixture containing two or more ideal gases.

Examples:

- Air
 - Natural gas
 - Combustion products
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7. Mass Fraction

Mass fraction of component i

$$w_i = \frac{m_i}{m_{\text{total}}} \quad w_i = \frac{m_i}{m_{\text{total}}}$$

Properties

$$\sum w_i = 1 \quad \sum w_i = 1$$

Example

$$\text{O}_2 = 8 \text{ kg}$$

$$\text{N}_2 = 32 \text{ kg}$$

$$\text{Total} = 40 \text{ kg}$$

Mass fraction

$$\text{O}_2$$

$$w = \frac{8}{40} = 0.2$$

$$\text{N}_2$$

$$w = \frac{32}{40} = 0.8$$

8. Mole Fraction

$$x_i = \frac{n_i}{n_{\text{total}}}$$

Where

n = number of moles

Properties

$$\sum x_i = 1$$

Example

$$\text{O}_2 = 2 \text{ kmol}$$

$$\text{N}_2 = 8 \text{ kmol}$$

$$\text{Total} = 10 \text{ kmol}$$

$$\text{O}_2$$

$$x = \frac{2}{10} = 0.2 \quad x = \frac{8}{10} = 0.8$$

N_2

$$x = \frac{8}{10} = 0.8 \quad x = \frac{2}{10} = 0.2$$

9. Gravimetric Analysis

Analysis based on **mass**.

Used to determine:

- Mass fraction
 - Total mass
 - Component mass
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10. Volumetric Analysis

Analysis based on **volume**.

For ideal gases,

Volume fraction = Mole fraction

11. Dalton's Law of Partial Pressure

Statement

The total pressure of a gas mixture equals the sum of the partial pressures of individual gases.

$$P = P_1 + P_2 + P_3 + \dots \quad P = P_1 + P_2 + P_3 + \dots$$

Partial pressure

$$P_i = x_i P \quad P_i = x_i P$$

Applications

- Atmospheric air
- Combustion
- HVAC
- Gas turbines

12. Amagat's Law of Partial Volume

Statement

The total volume equals the sum of individual partial volumes.

$$V = V_1 + V_2 + V_3 \quad V = V_1 + V_2 + V_3$$

Partial volume

$$V_i = x_i V \quad V_i = x_i V$$

Difference Between Dalton and Amagat

Dalton's Law	Amagat's Law
Based on Pressure	Based on Volume
Constant Volume	Constant Pressure
Total Pressure = Sum of Partial Pressures	Total Volume = Sum of Partial Volumes

13. Equivalent Gas Constant

Gas constant of mixture

$$R_m = \sum x_i R_i \quad R_m = \sum x_i R_i$$

or

$$R = \frac{R_u}{M} \quad R = \frac{R_u}{M}$$

Where

- R_u = Universal gas constant
- M = Molecular weight

14. Molecular Internal Energy

For gas mixture

$$u = \sum x_i u_i = \sum x_i u_i$$

Where

- u_i = Internal energy of each gas

15. Enthalpy of Gas Mixture

$$h = \sum x_i h_i = \sum x_i h_i$$

16. Specific Heat of Gas Mixture

At Constant Pressure

$$C_{pm} = \sum x_i C_{pi} = \sum x_i C_{pi}$$

At Constant Volume

$$C_{vm} = \sum x_i C_{vi} = \sum x_i C_{vi}$$

17. Entropy of Gas Mixture

Entropy depends on:

- Temperature
- Pressure
- Mixing process

General expression:

$$S = \sum x_i S_i = \sum x_i S_i$$

Entropy increases after mixing.

18. Gases and Vapour

Gas

A substance that cannot be liquefied by pressure alone at ordinary temperature.

Examples:

- Oxygen
- Nitrogen
- Hydrogen

Vapour

A gaseous substance below its critical temperature that can be liquefied by compression.

Examples:

- Steam
 - Refrigerants
 - Alcohol vapour
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Difference Between Gas and Vapour

Gas	Vapour
Above critical temperature	Below critical temperature
Difficult to liquefy	Easily liquefied
Permanent gas	Temporary gaseous phase

Important Formula Sheet

Ideal Gas

$$PV = nRT$$

Van der Waals Equation

$$(P + \frac{a}{V^2})(V - b) = RT \quad \left(P + \frac{a}{V^2} \right) (V - b) = RT \quad (P + \frac{a}{V^2})(V - b) = RT$$

Compressibility Factor

$$Z = \frac{PV}{RT} \quad Z = \frac{PV}{RT} \quad Z = \frac{PV}{RT}$$

Mass Fraction

$$w_i = \frac{m_i}{m} \quad w_i = \frac{m_i}{m} \quad w_i = \frac{m_i}{m}$$

Mole Fraction

$$x_i = \frac{n_i}{n} \quad x_i = \frac{n_i}{n} \quad x_i = \frac{n_i}{n}$$

Dalton's Law

$$P = \sum P_i \quad P = \sum P_i \quad P_i = x_i P \quad P_i = x_i P \quad P_i = x_i P$$

Amagat's Law

$$V = \sum V_i \quad V = \sum V_i \quad V = \sum V_i$$

Equivalent Gas Constant

$$R_m = \sum x_i R_i \quad R_m = \sum x_i R_i \quad R_m = \sum x_i R_i$$

Mixture Enthalpy

$$h = \sum x_i h_i \quad h = \sum x_i h_i \quad h = \sum x_i h_i$$

Mixture Internal Energy

$$u = \sum x_i u_i \quad u = \sum x_i u_i \quad u = \sum x_i u_i$$

Specific Heat

$$C_{pm} = \sum x_i C_{pi} \quad C_{pm} = \sum x_i C_{pi} \quad C_{vm} = \sum x_i C_{vi} \quad C_{vm} = \sum x_i C_{vi}$$