G. Anitha, Asst. Prof - Mechanical Department

UNIT-IV

REAL GAS MODELS

Real Gas Models & Perfect Gas Mixtures

Presented By :

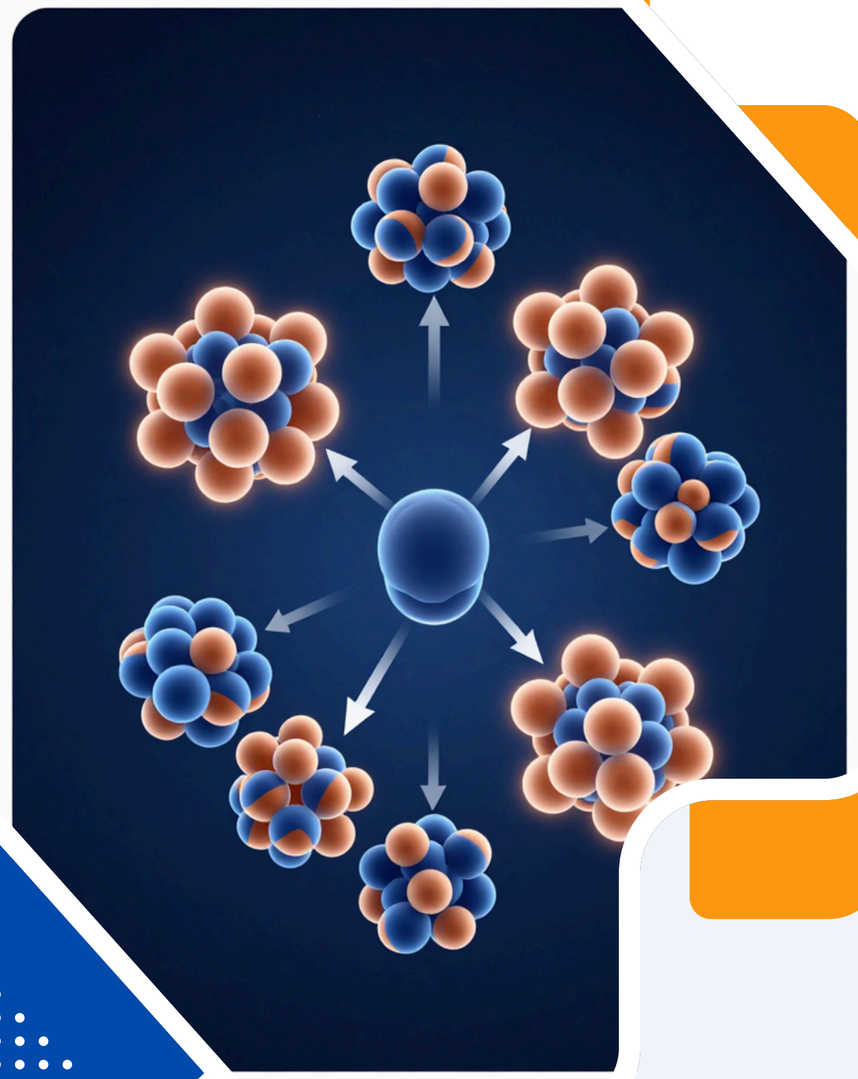
G. Anitha

Subject :

Thermodynamics

G. Anitha, Asst. Prof. Mechanical Dept.

Deviations from Perfect Gas Model

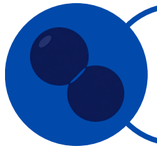


The perfect gas model assumes: (1) negligible molecular volume, and (2) no intermolecular forces. Real gases deviate significantly from this ideal behavior under:

- High Pressure: Molecular volume becomes significant compared to total volume
- Low Temperature: Intermolecular attractive forces dominate
- Near critical point: Both assumptions break down completely

Key deviation indicators: Compressibility Factor $Z = PV/RT$. For ideal gas $Z = 1$. When $Z < 1$, attractive forces dominate. When $Z > 1$, repulsive forces dominate at very high pressures.

Van der Waals Equation of State



Volume Correction (b)

The co-volume 'b' accounts for the finite volume occupied by gas molecules themselves, unlike ideal gas which assumes point masses.

Corrected volume: $(V - nb)$, where n is moles and b is excluded volume per mole of gas molecules.

Van der Waals equation: $(P + a/V^2)(V - b) = RT$ — reduces to ideal gas $PV = RT$ when $a = 0$ and $b = 0$.

Critical constants: $T_c = 8a/27Rb$, $P_c = a/27b^2$, $V_c = 3b$ — derived from Van der Waals equation at critical point.

Pressure Correction (a)

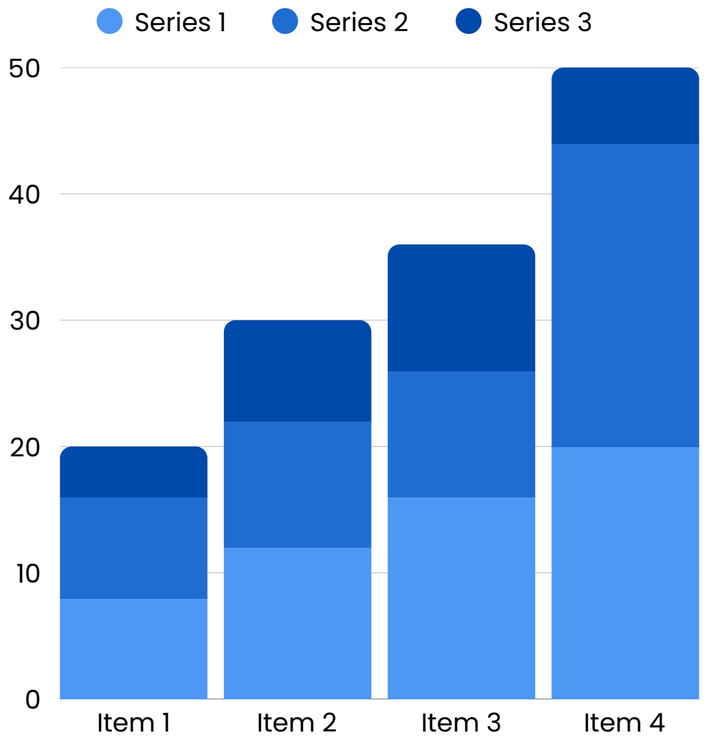
The constant 'a' corrects for intermolecular attractive forces that reduce the pressure exerted by real gas molecules on container walls.

Corrected pressure: $(P + a/V^2)$, where a/V^2 represents internal pressure due to molecular attractions.

Values of 'a' are large for polar or easily liquefied gases (e.g., CO_2, NH_3) and small for noble gases like He and Ar.

Reduced equation of state: $(Pr + 3/Vr^2)(3Vr - 1) = 8Tr$ — basis for generalized compressibility charts for all real gases.

Compressibility Charts



The Compressibility Factor (Z) measures deviation of a real gas from ideal behavior. Z = PV/nRT. For a perfect gas, Z = 1. When Z < 1, intermolecular attraction dominates; when Z > 1, repulsion dominates. Reduced properties: Tr = T/Tc and Pr = P/Pc are used to generalize the chart across all gases.

Z-Factor Analysis

The Generalized Compressibility Chart plots Z vs. Pr at constant Tr for all gases. At low Pr, Z ≈ 1 (ideal behavior). At high Pr or low Tr, significant deviations occur. The chart enables real gas property estimation without specific equations of state. Van der Waals corrections account for molecular volume (b) and intermolecular forces (a): $(P + a/V^2)(V - b) = RT$.

Variable Specific Heats

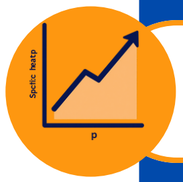
Specific heats Cp and Cv of gases are not constant but vary with temperature. This temperature dependence must be accounted for in accurate thermodynamic analysis of gas processes and cycles.

Key Concepts

Cp and Cv increase with rising temperature for real gases.

Ratio γ = Cp/Cv varies with temperature, not constant.

Polynomial relations: $C_p = a + bT + cT^2 + dT^3$ used.



Gas Tables

Gas tables provide pre-computed thermodynamic properties (h, u, s°, Pr, vr) as functions of temperature, eliminating need for complex integration.

Enthalpy h(T) and internal energy u(T) tabulated at standard pressure.

Relative pressure Pr and relative volume vr used for isentropic processes.

Entropy function s°(T) accounts for temperature-dependent Cp variation.

G. Anitha, Asst Prof -
Mechanical Department

Mixtures of Perfect Gases

Mole & Mass Fraction

A mixture of perfect gases behaves as a perfect gas. Each component retains its individual properties.

Mole Fraction: $x_i = n_i / n$, where n = total moles of mixture.

Mass Fraction: $mf_i = m_i / m$; sum of all mass fractions = 1.

$\sum x_i = 1$ (mole fractions); $\sum mf_i = 1$ (mass fractions) for any mixture.

Gravimetric & Volumetric Analysis

Gravimetric analysis expresses composition by mass; volumetric analysis expresses it by volume or moles.

Gravimetric (Mass) Analysis: m_i = mass of component i; total mass $m = \sum m_i$.

Volume Fraction: equals mole fraction for ideal gas mixtures at same T & P.

Molecular weight of mixture: $M = \sum(x_i \times M_i)$; links mole & mass fractions.

G. Anitha, Asst Prof - Mechanical Department

Dalton's Law & Avogadro's Law

Avogadro's Law states that equal volumes of all gases at the same temperature and pressure contain equal numbers of molecules. The volume of a gas mixture equals the sum of partial volumes of its components.

Avogadro's Law of Additive Volumes

V_total = V1 + V2 + V3 + ... + Vn (at same T and P)

Volume fraction equals mole fraction: Vi/V = Ni/N = xi

Partial pressure Pi = xi × P; Volume fraction = Mole fraction

Dalton's Law of Partial Pressure

The total pressure of a gas mixture equals the sum of partial pressures of each component gas, each occupying the same volume at the same temperature.

P_total = P1 + P2 + P3 + ... + Pn

Partial pressure of gas i: Pi = xi × P_total

xi = mole fraction of component i in the mixture.

G. Anitha, Asst Prof - Mechanical

Mole Fraction, Volume Fraction & Partial Pressure

For a mixture of perfect gases, mole fraction (xi), volume fraction (φi), and partial pressure (pi) are interrelated. The mole fraction xi = ni/n, where ni is moles of component i and n is total moles.

Key Relationships

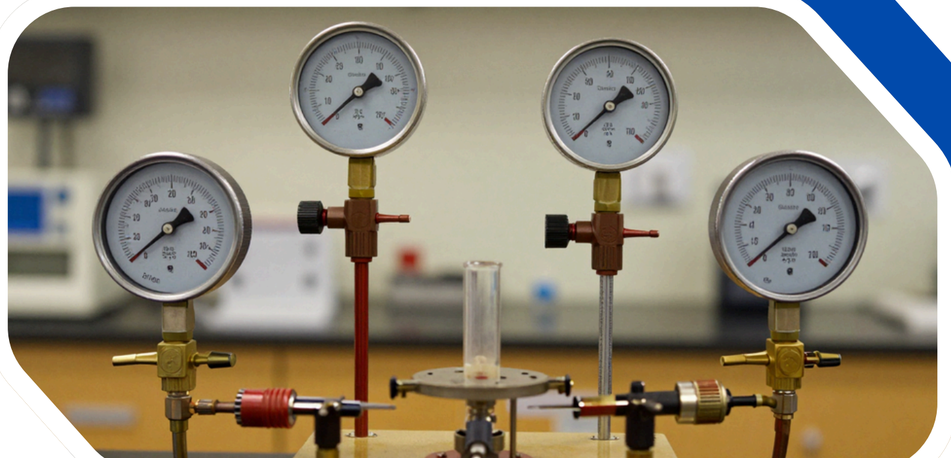
- Mole Fraction = Volume Fraction: xi = Vi/V (Avogadro's Law)
- Partial Pressure: pi = xi × P (Dalton's Law of Partial Pressures)
- Sum of all mole/volume fractions = 1: ∑xi = ∑φi = 1

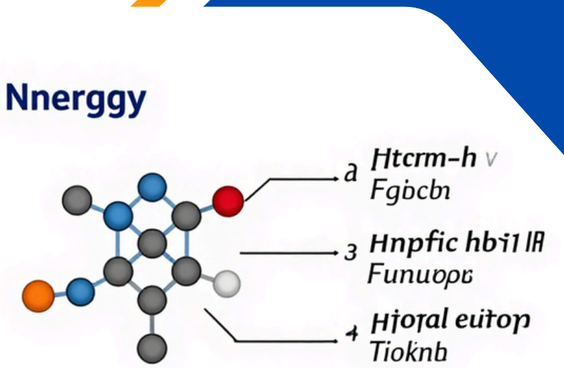
G. Anitha, Asst Prof - Mechanical Department

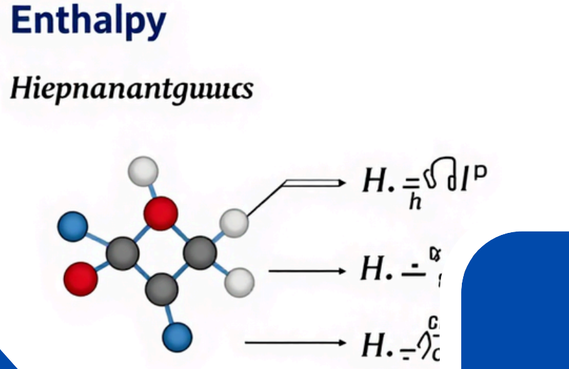
Equivalent Gas Constant & Molecular Properties

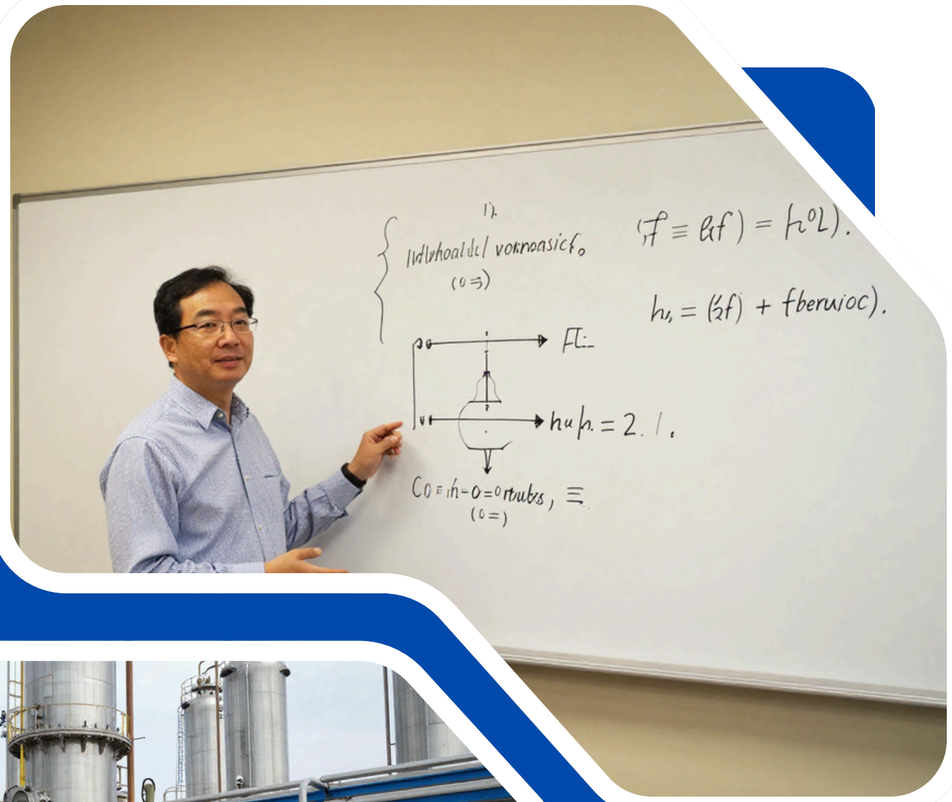
The Equivalent Gas Constant (R_mix) of a perfect gas mixture is determined by the mole fractions and individual gas constants. Internal Energy of a mixture is the sum of internal energies of each component: U_mix = ∑(m_i × u_i). Since internal energy depends only on temperature for perfect gases, each component contributes proportionally to its mass fraction.

Enthalpy of the mixture: H_mix = ∑(m_i × h_i). Specific heats at constant pressure and volume: Cp_mix = ∑(mf_i × Cp_i), Cv_mix = ∑(mf_i × Cv_i). The ratio γ_mix = Cp_mix / Cv_mix governs isentropic processes. These properties enable thermodynamic analysis of real gas mixture behavior.









Entropy of Mixtures

Gibbs' theorem states that the total entropy of a mixture of perfect gases equals the sum of the entropies each gas would have if it occupied the total volume alone at the mixture temperature. Entropy change accounts for both temperature variation and partial pressure effects across all component gases in the mixture.

Key Takeaways

- Entropy of mixture = sum of individual gas entropies at partial pressures.
- Gibbs theorem applies only to perfect (ideal) gas mixtures.
- Entropy increases due to mixing — irreversible process at molecular level.

THANK YOU!

For Your Attention

Presented By :

G. Anitha

Designation :

Asst. Prof, Mechanical Dept.