CLASSICAL THERMODYNAMICS

Partial Molar Properties

- Definition: Contribution of a component to an extensive property of the mixture.

$$\bar{X}_i = \left(\frac{\partial X}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$

- Examples: Partial molar volume, enthalpy, Gibbs energy.

Chemical Potential (μ)

- Gibbs energy per mole:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$

Drives diffusion, phase change, chemical reactions.

Gibbs-Duhem Equation

- Relates partial molar quantities:

$$\sum_i n_i d\mu_i = -SdT + VdP$$

At constant T & P,

$\sum_i n_i d\mu_i = 0.$

Determination of Partial Molar Quantities

- Graphical: Tangent method on property vs composition curve.
- Experimental: Using mixtures at varying compositions.

Thermodynamics of Real Gases

- **Fugacity (f)**: Corrected pressure for real gas non-ideality.

$$\mu = \mu^0 + RT \ln f$$

- **Determination:**
  - **Graphical method**: From P–V–T data.
  - **Equation of State method**: Van der Waals, Redlich-Kwong, Peng-Robinson.
- **Dependence**: Function of T, P, and composition.

Thermodynamics of Mixtures

- **Ideal Mixtures**: Properties are mole-fraction weighted.
- **Non-Ideal Mixtures**: Activity (a_i) and activity coefficient (γ_i)

$$\mu_i = \mu_i^0 + RT \ln a_i = \mu_i^0 + RT \ln (\gamma_i x_i)$$

Accounts for deviations from Raoult's law.

STATISTICAL THERMODYNAMICS

Basic Concepts

- Connects microscopic states → macroscopic properties.
- Distinguishable particles: Can be labelled; non-distinguishable: identical quantum particles.

Assemblies & Ensembles

- Assembly: Collection of particles in a state.
- Ensemble: Collection of assemblies under same constraints.
- Canonical ensemble: Fixed N, V, T. Microcanonical Ensemble: Fixed N, V, E (isolated system). Grand Canonical Ensemble: Fixed μ, V, T (open system).

Distribution Laws

- **Boltzmann Distribution**: Probability of energy state E_i:

  $$P_i \propto e^{-(Ei/kT)}$$

- **Bose-Einstein Statistics**: Indistinguishable bosons, multiple occupancy allowed, integer spin.
- **Fermi-Dirac Statistics**: Indistinguishable fermions, Pauli exclusion applies, half integer spin.

Comparison & Application:

Feature	Boltzmann	Bose-Einstein	Fermi-Dirac
Particle type	Classical	Bosons	Fermions
Occupancy	Any	Multiple	0 or 1
Temperature	High T	Low T	Low T
Examples	Ideal gas	Photons, He-4	Electrons, He-3

Kinetic Theory of Gases

- $PV = \frac{1}{3}Nm\bar{c^2}$
- Relates pressure, temperature, molecular speed.

Partition Function (Z)

- Sum over all states:

  $$Z = \sum_i e^{-E_i/kT}$$

- Thermodynamic quantities:

  $$U = -\frac{\partial \ln Z}{\partial \beta}, \quad F = -kT \ln Z, \quad S = k \ln Z + \frac{U}{T}$$