Chapter 5. Single-Phase Systems

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Introduction

- Physical properties
  - Most important information to construct heat and material balance equations
- How to determine ?
  - Look it up – from literature
    - Perry's Chemical Engineer's Handbook
    - CRC Handbook
    - NBS Databooks
    - Various Databases
  - Estimation
    - "The Properties of Gases and Liquids" (Newest edition)
  - Measurement

5.1 Liquid and Solid Densities

- Liquid and Solids → Incompressible
  - Changes in T or P does not cause significant changes in liquid and solid densities

$$E_k = \frac{mv^2}{2g_c}$$

- See appendix B.1 for solid and liquid densities
- Additivity :
  - Properties of a mixture can be assumed as the following formula (assumption)

$$\overline{M} = \sum_{i=1}^{n} x_i M_i \longrightarrow \frac{1}{\overline{\rho}} = \sum_{i=1}^{n} \frac{x_i}{\rho_i}$$

5.2 Ideal Gases

- Densities of gases → Sensitive to T and P
- P-V-T relation → Equation of State (EOS)
- Ideal Gas Law for Single Component
  - PV = nRT
- Ideal Gas Law for mixtures

$$p_A V = n_A RT$$

$$\frac{p_A}{P} = \frac{n_A}{n} = y_A \qquad \rightarrow p_A = y_A P$$

$$P v_A = n_A RT$$

$$\frac{v_A}{V} = \frac{n_A}{n} = y_A \qquad \rightarrow v_A = y_A V$$

Mole Fraction
= Volume Fraction
= Partial Pressure Fraction

Standard conditions

- Standard conditions can be conveniently used calculate the PVT relations at the other condition.

$$\frac{PV}{P_sV_s} = \frac{nT}{n_sT_s}$$

System	Ts	Ps	Vs	Ns
SI	273 K	1 atm	0.022415 m^3	1 mol
CGS	273 K	1 atm	22.415 liters	1 mol
English	492 ^oR	14.7 psi	359.05 ft^3	1 lb=-mol

5.3 Real Gases

- At low T and high P
  - Ideal gas law → poor description of PVT behavior
- Approaches for real gases
  - Virial EOS – BWR EOS
  - Cubic EOS
    - Van der Waals EOS
    - Redlich-Kwong EOS
    - Soave-Redlich-Kwong EOS
    - Peng-Robinson EOS
  - Compressibility factor EOS – based on CSP (Corresponding State Principles)

Virial Equation of State

- **Virial Equation of State**

$$\frac{P\hat{V}}{RT} = 1 + \frac{B(T)}{\hat{V}} + \frac{C(T)}{\hat{V}^2} + \dots$$

The third Virial coefficient ($C(T)$)

The second Virial coefficient ($B(T)$)

- **Benedict-Webb-Rubin (BWR) EOS**

$$\frac{P\hat{V}}{RT} = 1 + \frac{B(T)}{\hat{V}} + \frac{C(T)}{\hat{V}^2} + \frac{D(T)}{\hat{V}^4} + \frac{E(T)}{\hat{V}^5}$$

* Characteristics

- •High accuracy
- •Cumbersome (Many parameters (8))
- •The meaning is not very clear for mixtures

Cubic Equation of State

- **Soave modification of Redlich-Kwong EOS (SRK – EOS)**

$$p = \frac{RT}{\hat{V} - b} - \frac{\alpha(T)a}{\hat{V}(\hat{V} - b)}$$

$$a = 0.42747 \frac{R^2 T_c^2}{P_c}$$

$$b = 0.08664 \frac{RT_c}{P_c}$$

$$m = 0.48509 + 1.55171\omega - 0.15613\omega^2$$

$$\alpha = \left[1 + m(1 - \sqrt{T / T_c})\right]^2$$

* Molecular parameters

Tc – Critical Temperature

Pc – Critical Pressure

w – Pitzer accentric factor

Cubic Equations of State

- Explicit EOS : V = V (P,T)
- Implicit EOS : P = P (V,T)
  - Numerical methods are required to solve implicit EOS for given P and T.
    - Newton – Raphson Method
    - Secant Method
    - Wegstein Method.
      - See appendix A.2

Estimation of Compressibility Factors - The Law of Corresponding States

- Generalized compressibility chart
  - Z = Z (Tr, Pr)
- Procedure
  - Look up Tc and Pc
  - If helium or Hydrogen (Newton's correction)
    - Tc (adjusted) = Tc + 8K
    - Pc (adjusted) = Pc + 8atm
  - Tr = T/Tc, Pr = P/Pc, Vr = V/Vc
  - Use compressibility chart

Real Gas Mixtures : Kay's Rule

- For mixtures, use SRK using "mixing rules"
- Simple approximation : Kay's Rule

$$PV = z_m nRT$$
$$P\hat{V} = z_m RT$$

- Pseudocritical constants of the mixture

$$T_c' = y_a T_{ca} + y_b T_{cb} + y_b T_{cb} + \ldots$$
$$P_c' = y_a P_{ca} + y_b P_{cb} + y_b P_{cb} + \ldots$$

- Pseudo reduced P and T : T'r = T/T'c , P'r = P / P'c
- Use compressibility chart to get mean compressibility factor for the mixture