Part II –Thermodynamic properties
Properties of Pure Materials – Chapter 8

Primary objective is to evaluate changes in state in terms of primitive and measurable properties

Secondary objective is to connect molecular properties and interactions to macroscopic properties and processes

Properties of Pure Materials – Chapter 8

- Connections to the Fundamental Equation via *G*
- various forms for equations of state
- reference state condition for $S = S^o$ and the Third Law of Thermodynamics
- Derived property estimation *U* and ΔU, *etc.*
- *Role of* departure or residual functions
- Constitutive *PVTN* volumetric property models
  - Ideal gas law
  - Theorem of Corresponding States
  - Fluid behavior from the Boyle point to the triple point – Zeno condition
  - Pressure and volume explicit semi-empirical EOSs
  - Correlated experimental data
- Ideal gas state heat capacity models
  - translation – kinetic theory - classical
  - rotation – rigid rotator -classical
  - vibration – quantized using the Einstein model
- Property estimation methods
  - Molecular group contributions
  - Corresponding States
  - Conformal fluid theory
  - Molecular simulations

Connections to the Fundamental Equation

$$\underline{U} = T\underline{S} - P\underline{V} + \mu N = f(\underline{S}, \underline{V}, N)$$

$$d\underline{U} = Td\underline{S} - Pd\underline{V} + \mu\, dN$$

$$\underline{G} = \underline{U} + P\underline{V} - T\underline{S} = \underline{H} - T\underline{S} = y^{(2)} = f(T,P,N)$$

$$d\underline{G} = -\underline{S}\, dT + \underline{V}dP + \mu\, dN$$

$$C_p \equiv T\left(\frac{\partial S}{\partial P}\right)_P = \left(\frac{\partial H}{\partial P}\right)_P$$

$$\kappa_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

$$\alpha_P \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

Constitutive PVTN Volumetric Property Models

1. Ideal gas law

   $PV = NRT$ or $P\underline{V} = RT$

   $Z = PV/RT = 1$

2. Theorem of Corresponding States

   $Z = f\,(T_r\ , P_r\,, Z_c\,, \omega, \ldots)$

   scaling to reduced coordinates

   fluids from the Boyle point at low density to the triple point at high density – the Zeno line

3. Cubic type EOS $P = f(T,V)$

   van der Waals $P = RT/(V\text{-}b) - a/V^2$

   Redlich-Kwong (RK)

   Redlich- Kwong-Soave (RKS)

   Peng-Robinson (PR)

4. Virial type EOS $Z = 1 + B/V + C/V^2 + \ldots$

   BWR

   Starling

   Martin-Hou