

# CH365 Chemical Engineering Thermodynamics

## Lesson 28 Residual Properties I

# Lesson 27 Recap

- Mathematical structure of thermodynamics.
  - Developed property relations and Maxwell relations.
  - These along with 1<sup>st</sup> and 2<sup>nd</sup> Laws were used to derive H, S, and G as functions of T and P.
  - Gibbs Energy “generating function.”
- Lesson 27 is very important.  
Go back and review the slides.
- 

## Today's Agenda

- Review generating function.
- Introduce residual properties.
- Residual properties from Gibbs generating function.
  - Functions of T and P using EOS (Z-form).
- Numerical Recipes.
- Homework problems.

# Gibbs Energy Gen. Function - Recap Slide 3

(VDB)

$$d\left(\frac{G}{RT}\right) = \frac{V}{RT}dP - \frac{H}{T^2}dT \quad (\text{Eq. 6.37})$$

L27 Slides 21-22; Gibbs generating function derived by combining the total differential of  $G/RT$  and the property relation eq. 6.11 from L25 slide 8 and the definition of  $G(=H-TS)$ .

$$\frac{G}{RT} = f(T, P) \quad \Rightarrow \quad df \equiv \left( \frac{\partial(G/RT)}{\partial P} \right)_T dP + \left( \frac{\partial(G/RT)}{\partial T} \right)_P dT$$

$$\frac{V}{RT} = \left( \frac{\partial(G/RT)}{\partial P} \right)_T \quad (\text{Eq. 6.38})$$

$$\frac{H}{RT} = -T \cdot \left( \frac{\partial(G/RT)}{\partial T} \right)_P \quad (\text{Eq. 6.39})$$

$G/RT$  allows calculation of other properties – “generating function”

Ex 1 – Entropy

$$G \equiv H - TS$$

$$TS = H - G$$

$$\div RT \quad \frac{S}{R} = \frac{H}{RT} - \frac{G}{RT}$$

$$\frac{S}{R} = -T \cdot \left( \frac{\partial(G/RT)}{\partial T} \right)_P - \frac{G}{RT}$$

Ex 2 – Internal Energy

$$H \equiv U + PV$$

$$U = H - PV$$

$$\frac{U}{RT} = \frac{H}{RT} - \frac{PV}{RT}$$

$$\frac{U}{RT} = -T \cdot \left( \frac{\partial(G/RT)}{\partial T} \right)_P - \frac{PV}{RT}$$

Ex 3 – Helmholtz Energy

$$A \equiv U - TS$$

$$\frac{A}{RT} = \frac{U}{RT} - \frac{S}{R}$$

$$\frac{A}{RT} = \frac{G}{RT} - \frac{PV}{RT}$$

# Lesson 30 Look-Ahead

$$H = \Delta H_f^0 + R \int_{298}^T C_P^{ig} dT + H^R \quad \begin{array}{l} \text{today} \\ \text{(matches CC)} \end{array}$$

$\Delta H_f^0$  = standard formation enthalpy at 298.15 K, App C, pp 660-662

$$S = \Delta S_f^0 + R \int_{T_0}^T C_P^{ig} \frac{dT}{T} - R \ln \frac{P}{P_0} + S^R \quad \begin{array}{l} \text{today} \\ \text{(matches CC)} \end{array}$$

$\Delta S_f^0$ , also from App C, pp 660-662, from  $\Delta H_f^0$  and  $\Delta G_f^0$ , both at 298.15 K

$$\Delta S_f^{ig} = \frac{\Delta H_f^{ig} - \Delta G_f^{ig}}{298.15}$$

(WPR 3)

# Residual Properties

The practical value of ideal-gas properties are that they are the base for calculation of real-gas properties.

- $M = V, U, H, S, \text{ or } G$
- $M$  and  $M^{\text{ig}}$  are at the same  $T$  and  $P$

$$M^{\text{R}} \equiv M - M^{\text{ig}} \quad (\text{Eq. 6.41})$$

$$M \equiv M^{\text{ig}} + M^{\text{R}}$$

- Residual properties can be calculated from direct comparison with experimental measurement, page 227.
- $Z$  can be calculated from experimental  $P$ - $V$ - $T$  data.
- $Z = PV/RT$  and can be calculated from equations of state.

$$\begin{aligned} G^{\text{R}} &= G - G^{\text{ig}} \\ V^{\text{R}} &= V - V^{\text{ig}} \\ V^{\text{R}} &= \frac{RT}{P}(Z - 1) \end{aligned} \quad \begin{aligned} V &= \frac{ZRT}{P} \\ V^{\text{ig}} &= \frac{RT}{P} \end{aligned} \quad (\text{Eq. 6.40})$$

$$d\left(\frac{G}{RT}\right) = \frac{V}{RT}dP - \frac{H}{T^2}dT \quad \text{---} \quad d\left(\frac{G^{\text{ig}}}{RT}\right) = \frac{V^{\text{ig}}}{RT}dP - \frac{H^{\text{ig}}}{T^2}dT \quad \text{=} \quad d\left(\frac{G^{\text{R}}}{RT}\right) = \frac{V^{\text{R}}}{RT}dP - \frac{H^{\text{R}}}{T^2}dT$$

(Eq 6.37; from total differential + property relation eq 6.11; L27 Slide 21)

(Eq. 6.42)

$$\frac{G^{\text{R}}}{RT} = \frac{G^{\text{R}}}{RT}(P, T) \quad d\left(\frac{G^{\text{R}}}{RT}\right) = \left(\frac{\partial}{\partial P}\left(\frac{G^{\text{R}}}{RT}\right)\right)_T dP + \left(\frac{\partial}{\partial T}\left(\frac{G^{\text{R}}}{RT}\right)\right)_P dT$$

- Lesson 27, Slide 22
- Generating functions for residual properties

$$\frac{V^{\text{R}}}{RT} = \left(\frac{\partial(G^{\text{R}}/RT)}{\partial P}\right)_T \quad (\text{Eq. 6.43})$$

$$\frac{H^{\text{R}}}{RT} = -T \left(\frac{\partial(G^{\text{R}}/RT)}{\partial T}\right)_P \quad (\text{Eq. 6.44})$$

$$\frac{V^R}{RT} = \left( \frac{\partial (G^R/RT)}{\partial P} \right)_T \quad (\text{Eq. 6.43})$$

(integrating at constant T)

$$\int d \left( \frac{G^R}{RT} \right) = \Delta \left( \frac{G^R}{RT} \right) = \left( \frac{G^R}{RT} \right) - \left( \frac{G^R}{RT} \right)_{P=0}$$

$$d \left( \frac{G^R}{RT} \right) = \frac{V^R}{RT} dP \quad (\text{Constant T})$$

$$\frac{G^R}{RT} = \left( \frac{G^R}{RT} \right)_{P=0} + \int_0^P \frac{V^R}{RT} dP \quad (\text{Constant T})$$

(for convenience)

$$J = \left( \frac{G^R}{RT} \right)_{P=0} \Rightarrow \frac{G^R}{RT} = J + \int_0^P \frac{V^R}{RT} dP$$

J is a constant, independent of T  
(J=0 since no residual at P=0)

Z is from equation of state (chapter 3; slide 8)

(Eq. 6.40, slide 5)

$$V^R = \frac{RT}{P} (Z - 1) \Rightarrow \frac{V^R}{RT} = \frac{Z - 1}{P}$$

$$\frac{G^R}{RT} = J + \int_0^P (Z - 1) \frac{dP}{P} \quad (\text{Eq. 6.45})$$

$$\begin{aligned} \frac{\partial}{\partial T} \left( \frac{G^R}{RT} \right)_P &= \frac{\partial}{\partial T} \left( J + \int_0^P Z \frac{dP}{P} - \int_0^P \frac{dP}{P} \right)_P \\ &= \int_0^P \left( \frac{\partial Z}{\partial T} \right)_P \frac{dP}{P} \end{aligned}$$

(Eq. 6.44, slide 5)

$$\frac{H^R}{RT} = -T \left( \frac{\partial (G^R/RT)}{\partial T} \right)_P$$



$$\frac{H^R}{RT} = -T \int_0^P \left( \frac{\partial Z}{\partial T} \right)_P \frac{dP}{P} \quad (\text{Eq. 6.46})$$

Derivative of Eq. 6.45  
with respect to T,  
multiplied by -T

$$G = H - TS$$

$$\begin{aligned} G^{ig} &= H^{ig} - TS^{ig} \\ \hline G^R &= H^R - TS^R \end{aligned}$$

$$\frac{S^R}{R} = \frac{H^R}{RT} - \frac{G^R}{RT} \quad (\text{Eq. 6.47})$$

Combine pieces from slide 6

Set J=0 (3<sup>rd</sup> Law)

$$\frac{S^R}{R} = \underbrace{\left[ -T \int_0^P \left( \frac{\partial Z}{\partial T} \right)_P \frac{dP}{P} \right]}_{(\text{Eq. 6.46, slide 6})} - \underbrace{\left[ J + \int_0^P (Z - 1) \frac{dP}{P} \right]}_{(\text{Eq. 6.45, slide 6})}$$

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

From equation of state  
(next slide)

$$\frac{S^R}{R} = -T \int_0^P \left( \frac{\partial Z}{\partial T} \right)_P \frac{dP}{P} - \int_0^P (Z - 1) \frac{dP}{P} \quad (\text{Eq. 6.48})$$

$$\frac{G^R}{RT} = \int_0^P (Z - 1) \frac{dP}{P} \quad (\text{Eq. 6.49})$$

$$\frac{H^R}{RT} = -T \int_0^P \left( \frac{\partial Z}{\partial T} \right)_P \frac{dP}{P} \quad (\text{Eq. 6.46})$$

Integrals are evaluated from equations of state and shown on the next slide

# Residual Properties from Cubic EOS

Use the red equations for your calculations

Generic cubic equation of state (WPR2)

$$a = \Psi \frac{R^2 \cdot T_c^2}{P_c} \quad b = \Omega \frac{R \cdot T_c}{P_c} \quad \text{(Eq. 3.45)} \quad \text{(Eq. 3.44)}$$

$$P = \frac{RT}{V - b} - \frac{a(T)}{(V + \epsilon b)(V + \sigma b)} \quad \text{(Eq. 3.41)}$$

For this derivation,

$$q = \frac{\alpha(T)}{bRT} \quad \text{(Eq. 3.47)}$$

Operationally, in Mathematica, use Eq. 3.51 for calculations.

$$q = \frac{\Psi \alpha}{\Omega T_r} \quad \text{(Eq. 3.51)}$$

$$Z = \frac{1}{1 - \rho b} - q \frac{\rho b}{(1 + \epsilon \rho b)(1 + \sigma \rho b)} \quad \text{(p. 487)}$$

(This equation is introduced on page 496 to allow derivations of residual properties. It is derived from Eq. 3.41 by dividing through 3.41 by  $RT/V$ , substituting  $\rho = 1/V$ , and using  $q$  from Eq. 3.51.). **Operationally, in Mathematica, you should use Eq. 3.48 to calculate  $Z$  (not 3.41).**

$$Z = 1 + \beta - q\beta \frac{Z - \beta}{(Z + \epsilon\beta)(Z + \sigma\beta)} \quad \beta = \Omega \frac{P_r}{T_r} \quad \text{(3.48)} \quad \text{(3.50)} \quad \text{(WPR3)}$$

$$\frac{G^R}{RT} = Z - 1 - \ln(Z - \beta) - q \cdot I \quad \text{(Eq. 13.74)}$$

$$\frac{H^R}{RT} = Z - 1 + T \left( \frac{dq}{dT} \right) \cdot I = \underbrace{Z - 1 + T_r \left( \frac{dq}{dT_r} \right) \cdot I}_{\text{(page 497, not numbered) (MUCH better for Mathematica!)}} = \underbrace{Z - 1 + \left[ \frac{d \ln \alpha(T_r)}{d \ln(T_r)} - 1 \right] \cdot q \cdot I}_{\text{(Eq. 13.75) (not as useful for Mathematica)}}$$

I-terms are on the next slide

$$\frac{S^R}{R} = \ln(Z - \beta) + \underbrace{\left( q + T_r \frac{dq}{dT_r} \right) \cdot I}_{\text{(page 497, not numbered) (MUCH better for Mathematica!)}} = \ln(Z - \beta) - \underbrace{\frac{d \ln \alpha(T_r)}{d \ln(T_r)} \cdot q \cdot I}_{\text{(Eq. 13.76) (not as useful for Mathematica)}}$$



# Evaluation of Integral I

for Residual Properties from Cubic EOS

Generic cubic equations of state

Case I:  $\varepsilon \neq \sigma$

$$I = \frac{1}{\sigma - \varepsilon} \ln \left( \frac{1 + \sigma \rho b}{1 + \varepsilon \rho b} \right) \quad (\text{Eq. 13.71})$$

$$b = \Omega \frac{RT_c}{P_c} \quad (\text{Eq. 3.44})$$

$$\rho b = \frac{\beta}{Z} \quad (\text{p. 496})$$

$$I = \frac{1}{\sigma - \varepsilon} \ln \left( \frac{Z + \sigma \beta}{Z + \varepsilon \beta} \right) \quad (\text{Eq. 13.72})$$

(Better for Mathematica)

$$\beta = \Omega \frac{P_r}{T_r} \quad (\text{Eq. 3.50})$$

Case II:  $\varepsilon = \sigma$

$$I = \frac{\rho b}{1 + \varepsilon \rho b} = \frac{\beta}{Z + \varepsilon \beta} \quad (\text{no equation number})$$

(for van der Waals)

$$I = \frac{\beta}{Z}$$

# Computer Procedure for Cubic Equations of State

1. Collect  $T$  and  $P$  as well as the critical temperature ( $T_c$ ), critical pressure ( $P_c$ ), and acentric factor ( $\omega$ ) from Table B.1 on pages 663-65 or from the DIPPr website (or from CC or Aspen+). Note your source. Use given  $T$  and  $P$  to calculate the reduced temperature and pressure ( $T_r$  and  $P_r$ ).
2. Collect  $\sigma$ ,  $\varepsilon$ ,  $\Omega$ , and  $\Psi$  from Table 3.1 on p.100 for desired equation of state.
3. Determine the correct expression for  $\alpha$  from Table 3.1 on p.100. Even though  $\alpha$  is a function of reduced temperature, make sure you write  $\alpha$  as a function of  $x$ , where  $x$  is a dummy variable for reduced temperature **[See note below]**.
4. Calculate  $\beta$  from Eq. 3.50 and  $q$  from Eq. 3.51 on page 99. Make sure you write  $q$  as a function of  $x$ , where  $x$  is a dummy variable for reduced temperature **[See note below]**.
5. Write the implicit equation for compressibility ( $Z$ ) for of the cubic equation of state, Eq. 3.48 on p. 99, solve it for  $Z$ , and select the correct value for  $Z$ .
6. Determine the correct form of the integral ( $I$ ) in Eqns. 13.71 and 13.72 on p. 496 (or slide 8) and calculate the value of  $I$ .
7. Use Eqns. 13.75 and 13.76 on pages 496-97 (or slide 7) to evaluate  $H^R$  and  $S^R$ . Write these equations as functions of the dummy variable  $x$ , where  $x$  represents the reduced temperature. **[See note below]**.

**Note:** At this point in the procedure, reduced temperature  $T_r$  has a numerical value. Therefore, when you try to take the derivative of  $q(T_r)$  with respect to  $T_r$ , you will get a serious error in Mathematica. You MUST write these terms as functions of a dummy variable, such as  $x \cdot q(x)$ . Problem 6.141 illustrates this.

# Questions?