

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 1st and 2nd 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.
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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

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

ΔH_f^0 = standard formation enthalpy at 298.15 K, App C, pp 660-662

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

ΔS_f^0 , also from App C, pp 660-662, from ΔH_f^0 and ΔG_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^{ig} are at the same T and P

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

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

- 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.

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

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

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

(Eq. 6.42)

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

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

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

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

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

(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)

$$J = \left(\frac{G^R}{RT} \right)_{P=0}$$



$$\frac{G^R}{RT} = J + \int_0^P \frac{V^R}{RT} dP$$

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)

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



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

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

(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

$$G = H - TS$$

$G^{ig} = H^{ig} - TS^{ig}$

$G^R = H^R - TS^R$

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

Combine pieces from slide 6

Set J=0 (3rd 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)

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

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

For this derivation,

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

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

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

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

(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).

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

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

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

(MUCH better for Mathematica!) (not as useful for Mathematica)

I-terms are on the next slide

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

(MUCH better for Mathematica!) (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 (ω) 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 σ , ε , Ω , and Ψ from Table 3.1 on p.100 for desired equation of state.
3. Determine the correct expression for α from Table 3.1 on p.100. Even though α is a function of reduced temperature, make sure you write α as a function of x , where x is a dummy variable for reduced temperature **[See note below]**.
4. Calculate β 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?