

CH365 Chemical Engineering Thermodynamics

Lesson 30 Generalized Property Correlations

Today: (1) Admin, (2) Review, (3) Generalized Correlations, (4) Mixtures

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CDP – IPR3

- Friday 18 November by 1630.
- Signed cover sheet and pdf of Mathematica and updated results table.
- MMA, Aspen Plus and CHEMCAD files in SharePoint.
- Corrections to IPR2.
- See published guidance.
 - Include H^R , S^R at (T_1, P_1) and (T_2, P_2) . Enter in table as $H1_{DEP}$, $S1_{DEP}$, $H2_{DEP}$, and $S2_{DEP}$ (“Departure” = Residual; both terms in common usage.)
 - Complete Aspen Plus results pull.
 - CHEMCAD results due at this time.
 - Fugacity coefficients (ϕ) at (T_1, P_1) and (T_2, P_2) are easy to get even though but we have not covered fugacity yet. Not graded but do-able (eq 13.85). Also easily obtained from CHEMCAD and Aspen Plus.
 - Stream properties covered today (eqns. 6.50, 6.51).
- 30 Points (25 tech, 5 writing).

WPR3 WARNO

- WPR 3 is Thursday 17 November
 - 3 problems, 200 points, from Chapter 5 and 6
 - Calculation of ideal enthalpy and entropy changes
 - Calculation of residual enthalpy and entropy
 - Combining ideal and residual properties to get real properties
 - Lost work (as in heat exchangers)
 - Derivations – property relations, Maxwell relations, generating functions
 - 55 minutes, during class hour.
 - Open note, open book, open computer. Calculator, Mathematica authorized.
 - Upload all exam e-work to SharePoint.
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Today's Agenda

- Complete discussion of residual properties
- Discussion of generalized methods
- Continue discussion of homework

Residual Properties

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

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

superscript "R" refers to "residual"
"departure" is used in Aspen Plus.

$$H^{\text{R}} = H - H^{\text{ig}}$$

$$S^{\text{R}} = S - S^{\text{ig}}$$

$$G^{\text{R}} = G - G^{\text{ig}}$$

$$H = H^{\text{ig}} + H^{\text{R}}$$

$$S = S^{\text{ig}} + S^{\text{R}}$$

$$G = G^{\text{ig}} + G^{\text{R}}$$

$$dH^{\text{ig}} = C_P^{\text{ig}} dT \quad (\text{Eq. 6.23})$$

$$dS^{\text{ig}} = \frac{C_P^{\text{ig}}}{T} dT - R \cdot \frac{1}{P} \cdot dP \quad (\text{Eq. 6.24})$$

$$H^{\text{ig}} = H_0^{\text{ig}} + \int_{T_0}^{T_2} C_P^{\text{ig}} dT$$

$$S^{\text{ig}} = S_0^{\text{ig}} + \int_{T_0}^{T_2} \frac{C_P^{\text{ig}}}{T} dT - R \cdot \ln \left(\frac{P}{P_0} \right)$$

$$V^{\text{R}} = V - V^{\text{ig}} \quad \begin{aligned} V &= \frac{ZRT}{P} \\ V^{\text{ig}} &= \frac{RT}{P} \end{aligned}$$

$$V^{\text{R}} = \frac{ZRT}{P} - \frac{RT}{P} = \frac{RT}{P} (Z - 1) \quad (\text{Eq. 6.40})$$

- The true worth of the equations for ideal gases is now evident.
- They are important because they provide a convenient base for the calculation of real gas properties.

Residual Properties from Cubic EOS

Lesson 28, slides 7-9; use the red equations for your calculations

Generic cubic equation of state (WPR2)

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

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

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).

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

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

$$\frac{H^R}{RT} = Z - 1 + T \left(\frac{dq}{dT} \right) \cdot I = Z - 1 + T_r \left(\frac{dq}{dT_r} \right) \cdot I = Z - 1 + \left[\frac{d \ln \alpha(T_r)}{d \ln(T_r)} - 1 \right] \cdot q \cdot I$$

(page 497, not numbered)
(MUCH better for Mathematica!)

(Eq. 13.75)
(not as useful for Mathematica)

I-terms:

$$I = \frac{1}{\sigma - \varepsilon} \ln \left(\frac{Z + \sigma\beta}{Z + \varepsilon\beta} \right)$$

$$\frac{S^R}{R} = \ln(Z - \beta) + \left(q + T_r \frac{dq}{dT_r} \right) \cdot I = \ln(Z - \beta) - \frac{d \ln \alpha(T_r)}{d \ln(T_r)} \cdot q \cdot I$$

(page 497, not numbered)
(MUCH better for Mathematica!)

(Eq. 13.76)
(not as useful for Mathematica)

Connection to Total Properties

Add ideal gas and residual

$$H = H_0^{\text{ig}} + R \int_{T_0}^T C_P^{\text{ig}} dT + H^R \quad (\text{Eq. 6.50})$$

$$H_1 = H_0^{\text{ig}} + R \int_{T_0}^{T_1} C_P^{\text{ig}} dT + H_1^R \quad H_2 = H_0^{\text{ig}} + R \int_{T_0}^{T_2} C_P^{\text{ig}} dT + H_2^R$$

$H_0^{\text{ig}} = \Delta H_{f298}^{\circ}$ = standard formation enthalpy, App C, pp 673-675
(also found in DIPPr, Aspen+, and CHEMCAD)

Difference between streams:

$$\Delta H = H_2 - H_1 = R \int_{T_1}^{T_2} C_P^{\text{ig}} dT + H_2^R - H_1^R \quad (\text{Eq. 6.72})$$

residual property at T_2
residual property at T_1

CHEMCAD

Stream No.	1
Stream Name	
Temp K	410.83
Pres bar	3.47
Vapor Fraction	1
Enthalpy J/s	-195866
Total flow	1
Total flow unit	mol/s
Comp unit	mol/s
Methanol	1

For CHEMCAD entropy, use Report -> Stream Reports -> Customize Property Sets -> Overall

$$S = S_0^{\text{ig}} + \int_{T_0}^T C_P^{\text{ig}} \frac{dT}{T} - R \ln \frac{P}{P_0} + S^R \quad (\text{Eq. 6.51})$$

$$\Delta S = \int_{T_1}^{T_2} C_P^{\text{ig}} \frac{dT}{T} - R \ln \frac{P_2}{P_1} + S_2^R - S_1^R \quad (\text{Eq. 6.73})$$

$S_0^{\text{ig}} = \Delta S_{f298}^{\circ}$, also from App C, pp 673-675, from ΔH_{f298}° and ΔG_{f298}°
(also found in DIPPr, Aspen+, and CHEMCAD)

**CHEMCAD standard enthalpy and Gibbs energy
are in Component Data -> Basic Data**

$$\Delta S_{f298}^{\text{ig}} = \frac{\Delta H_{f298}^{\text{ig}} - \Delta G_{f298}^{\text{ig}}}{298.15}$$

Two Generalized Property Methods

- Lee-Kesler

New for today

- Virial Equation

- Cubic equations of state – Section 13.6

Last two classes

All methods give residual properties.

Lee-Kesler Table Method

Valid for liquids, vapors and gases

$$Z = Z^0 + \omega Z^1 \quad (\text{Pitzer correlation, Eq. 3.53})$$

$$\frac{H^R}{RT_c} = \frac{(H^R)^0}{RT_c} + \omega \frac{(H^R)^1}{RT_c} \quad (\text{Eq. 6.66})$$

$$\frac{S^R}{R} = \frac{(S^R)^0}{R} + \omega \frac{(S^R)^1}{R} \quad (\text{Eq. 6.67})$$

$$Z^0, Z^1, \frac{(H^R)^0}{RT_c}, \frac{(H^R)^1}{RT_c}, \frac{(S^R)^0}{R}, \frac{(S^R)^1}{R}, \phi^0, \text{ and } \phi^1$$

Appendix D
pages 676-692

Virial Equation

Truncated
$$Z = 1 + \frac{BP}{RT} = 1 + \hat{B} \frac{P_r}{T_r} \quad (\text{Eq. 3.57})$$

$$\hat{B} = \frac{BP_c}{RT_c} \quad (\text{Eq. 3.58})$$

Second virial coefficient
$$\hat{B} = B^0 + \omega B^1 \quad (\text{Pitzer Correlation, Eq. 3.59})$$

$$\frac{H^R}{RT_c} = P_r \left[B^0 - T_r \frac{dB^0}{dT_r} + \omega \left(B^1 - T_r \frac{dB^1}{dT_r} \right) \right] \quad (\text{Eq. 6.68})$$

$$\frac{S^R}{R} = -P_r \left(\frac{dB^0}{dT_r} + \omega \frac{dB^1}{dT_r} \right) \quad (\text{Eq. 6.69})$$

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} \quad (\text{Eq. 3.61})$$

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}} \quad (\text{Eq. 3.62})$$

$$\frac{dB^0}{dT_r} = \frac{0.675}{T_r^{2.6}} \quad (\text{Eq. 6.70})$$

$$\frac{dB^1}{dT_r} = \frac{0.722}{T_r^{5.2}} \quad (\text{Eq. 6.71})$$

Mixtures of Gases I - Textbook

Slide 10

The critical temperature of a gas is the maximum temperature at which compression can cause liquefaction. The critical pressure of a gas is the minimum pressure at which cooling causes liquefaction. **Mixing of gases results in new critical properties for the mixture, and the mixture behaves as a “pseudocritical” pure component.**

“pseudocritical” properties

(This method is simpler but is not used in process simulators)

$$\omega \equiv \sum_i y_i \omega_i \quad \text{“pseudocritical acentric factor”}$$

(Eq. 6.78)

$$T_{pc} \equiv \sum_i y_i T_{ci} \quad \text{“pseudocritical temperature”}$$

(Eq. 6.79) subscript “p”

$$P_{pc} \equiv \sum_i y_i P_{ci} \quad \text{“pseudocritical pressure”}$$

(Eq. 6.80)

“pseudoreduced temperature”

$$T_{pr} = \frac{T}{T_{pc}}$$

(Eq. 6.81)

“pseudoreduced pressure”

$$P_{pr} = \frac{P}{P_{pc}}$$

(Eq. 6.82)

Mixtures of Gases II - API

Slide 11

API Technical Data Book, T.T. Daubert, ed., 5th Edition, American Petroleum Institute, 1992. Standard method now widely used.

(preferred method but
somewhat harder)

“pseudocritical” properties

worked example is in
reference, p. 4-25

“true critical temperature” of mixture $T_{cm} = \sum_{i=1}^n (\theta_i \cdot T_{ci})$ (Eq. 4B1.1-1)

volume fraction of component i $\theta_i = \frac{x_i \cdot V_{ci}}{V_{pc}}$ (Eq. 4B1.1-2)

molar average critical volume $V_{pc} = \sum_i x_i \cdot V_{ci}$ (Eq. 4B1.1-3.79)

“true critical pressure” of mixture

$$P_{cm} = P_{pc} + P_{pc} \left[5.808 + 4.93 \cdot \sum_{i=1}^n (x_i \cdot \omega_i) \right] \cdot \left[\frac{T_{cm} - T_{pc}}{T_{pc}} \right]$$

worked example is in
reference, pp. 4-28 to 4-29

(Eq. 4B2.1-1)

pseudocritical temperature of mixture $T_{pc} = \sum_i (x_i \cdot T_{ci})$ (Eq. 4B2.1-2)

pseudocritical pressure of mixture $P_{pc} = \sum_{i=1}^n (x_i \cdot P_{ci})$ (Eq. 4B2.1-3)

Homework

Problem 6.84 (e,f)

Calculate VR, HR, and SR for each of the following using the generalized virial method:

(e) Ethylbenzene at 620 K and 20 bar

(f) Methane at 250 K and 90 bar

Problem 6.101

Use the API mixture rules in slide 11 to estimate the critical temperature and pressure of air at 50% relative humidity, 25 C and 1 bar total pressure. Check your answers with CHEMCAD.

To simplify your answer, use the air pseudocomponent in CHEMCAD so that your mixture has two components (air and water).