

CH365 Chemical Engineering Thermodynamics

Lesson 30 Generalized Property Correlations

CDP – IPR

- Monday 17 November by 2359, pass/fail. Failing grades will remain until repaired.
- Keep it short and simple. Answer Questions 1-2. Show progress toward one other problem.
- Signed cover sheet, PDF of Mathematica combined into single signed PDF (with signed cover sheet).
- Question 1 – Txy plot in CHEMCAD using NRTL. Suggest you place a screen shot of CHEMCAD plot into Mathematica before bundling pdf.
- Question 2 – Txy plot in MMA for ideal case. Suggestion: Txy plot in CHEMCAD using ideal, with screenshot into Mathematica, to show what “right looks like.”
- Ideal Txy plot was covered in CH362 and CH363. Problem 13.1 in CH365 is a guide.

Bubble Point:

x_i is known

$$y_i = K_i \cdot x_i$$

$$\sum_i y_i = 1$$

Dew Point:


y_i is known

$$x_i = y_i \div K_i$$

$$\sum_i x_i = 1$$

$$K_i = f(T, P) = \frac{P_i^{\text{sat}}}{P}$$

Antoine Eq.
CC Eq. 107



Bubble Point Calculation

- At the bubble point an infinitesimal amount of liquid evaporates.
- Let V be the amount of vapor phase and F the total amount of fluid.
- Let x be the liquid mole fraction and z the total (bulk) mole fraction.
- At the bubble point, almost all of the fluid is in the liquid phase.
- This means V/F is very close to zero and the liquid-phase mole fraction x is almost z .
- So we let the bubble point V/F equal 0 and the liquid-phase mole fraction x equal z .
- That is, at $V/F=0$, $x=z$, and $\sum x=1$.
- Meanwhile, in the vapor phase, $y=Kx$ and $\sum y=1$.
- V/F is sometimes referred to as Ψ , so $\Psi=V/F=0$ at the bubble point.
- So at the bubble point, the conditions are: $\Psi=V/F=0$, $x=z$, $y=Kx$, and $\sum y=1$.
- Since K is a function of temperature, we solve for the temperature that satisfies this condition.

Psat =

$$.001 * \text{Exp} \left[a + \frac{b}{t + 273.15} + c * \text{Log}[t + 273.15] + d * (t + 273.15)^e \right];$$

K[t_] = Psat / Ptot;

(*BUBBLE POINT CALCULATION*)

(*ξ is the specified feed mole fraction so z=ξ and x=z=ξ*)

xb1 = ξ;

xb2 = 1 - ξ;

(*equilibrium expressions to give yb1 and yb2 from liquid mole fractions*)

f1[t_, ξ_] = xb1 * K[t][[1]] - yb1 == 0; (*yb1 unknown*)

f2[t_, ξ_] = xb2 * K[t][[2]] - yb2 == 0; (*yb2 unknown*)

f3[t_, ξ_] = yb1 + yb2 == 1; (*sum of mole fractions in vapor*)

fs[t_, ξ_] = {f1[t, ξ], f2[t, ξ], f3[t, ξ]};

(*system of 3 eqns and 3 unks for FindRoot*)

(*solve system of equations*)

t0 = 100.; (*initial guess for t for FindRoot*)

yb10 = .5; (*initial guess for yb1 for FindRoot*)

yb20 = .5; (*initial guess for yb2 for FindRoot*)

Tb[ξ_] :=

t /. FindRoot[fs[t, ξ], {{t, t0}, {yb1, yb10}, {yb2, yb20}}];

Dew Point Calculation

- At the dew point an infinitesimal amount of vapor condenses.
- Let V be the amount of vapor phase and F the total amount of fluid.
- Let y be the vapor mole fraction and z the total (bulk) mole fraction.
- At the dew point, almost all of the fluid is in the vapor phase.
- This means V/F is very close to one, and the vapor-phase mole fraction y is almost z .
- So, we let the dew point V/F equal 1 and the vapor-phase mole fraction y equal z .
- That is, at $V/F=1$ ($\Psi=1$), $y=z$ and $\sum y=1$.
- Meanwhile, in the liquid phase, $x=y/K$ and $\sum x=1$.
- So at the dew point, the conditions are: $\Psi=V/F=1$, $y=z$, $x=K/y$, and $\sum x=1$.
- Since K is a function of temperature, we solve for the temperature that satisfies this condition.

WPR3 WARNO

- WPR3 is Monday 24 November
 - 3 problems, 200 points, from Chapter 5 and 6
 - Calculation of ideal enthalpy and entropy changes
 - Calculation of residual enthalpy and entropy
 - Combining formation, 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

- Continue 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"

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

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

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

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

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

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

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

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

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

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

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

$$V = \frac{ZRT}{P}$$

$$V^{\text{ig}} = \frac{RT}{P}$$

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

- 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

Generic cubic equation of state (in Z-Form)

(WPR3)

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

$$\alpha = \alpha(x)$$

(α is found in Table 3.1)

These are the red equations from L28 slide 8 (cleanup).

Important: α is written as a function of x where x replaces T_r .

q derivatives must be evaluated before process conditions (T_r , P_r) are entered.

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

$$Z = 1 + \beta - q\beta \frac{Z - \beta}{(Z + \varepsilon\beta)(Z + \sigma\beta)} \quad (3.48)$$

$$\frac{H^R}{RT} = Z - 1 + T_r \left(\frac{dq}{dT_r} \right) \cdot I$$

(page 497)

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

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

$$\varepsilon \neq \sigma$$

Problem 6.141 in PS10

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 671-672

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 660-662, from ΔH_{f298}° and ΔG_{f298}°

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

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

Three Methods for Residual Properties

Cubic Equations of States (L28 & L29):

- RK, SRK, PR EOS from Table 3.1

Generalized Methods (New for Today):

- Lee-Kesler Tables
- Virial Equation of State

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 $Z = 1 + \frac{BP}{RT} = 1 + \hat{B} \frac{P_r}{T_r}$ (Eq.3.57) $\hat{B} = \frac{BP_c}{RT_c}$ (Eq.3.58)

Second virial coefficient $\hat{B} = B^0 + \omega B^1$ (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 13

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

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

(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 - Best

Slide 14

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

“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)

Questions?