

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 =
```

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

```
K[t_] = Psat / Ptot;
```

(*BUBBLE POINT CALCULATION*)

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

```
xb1 =  $\xi$ ;
```

```
xb2 = 1 -  $\xi$ ;
```

(*equilibrium expressions to give y_{b1} and y_{b2} from liquid mole fractions*)

```
f1[t_,  $\xi$ _] = xb1 * K[t][1] - yb1 == 0; (* $y_{b1}$  unknown*)
```

```
f2[t_,  $\xi$ _] = xb2 * K[t][2] - yb2 == 0; (* $y_{b2}$  unknown*)
```

```
f3[t_,  $\xi$ _] = yb1 + yb2 == 1; (*sum of mole fractions in vapor*)
```

```
fs[t_,  $\xi$ _] = {f1[t,  $\xi$ ], f2[t,  $\xi$ ], f3[t,  $\xi$ ]};
```

(*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  $y_{b1}$  for FindRoot*)
```

```
yb20 = .5; (*initial guess for  $y_{b2}$  for FindRoot*)
```

```
Tb[ $\xi$ _] :=
```

```
t /. FindRoot[fs[t,  $\xi$ ], {{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.

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

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

superscript "R" refers to "residual"

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

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

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

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

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

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

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

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

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

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

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

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

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

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

- 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.

Problem 6.141 in PS10

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

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

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

(page 497)

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

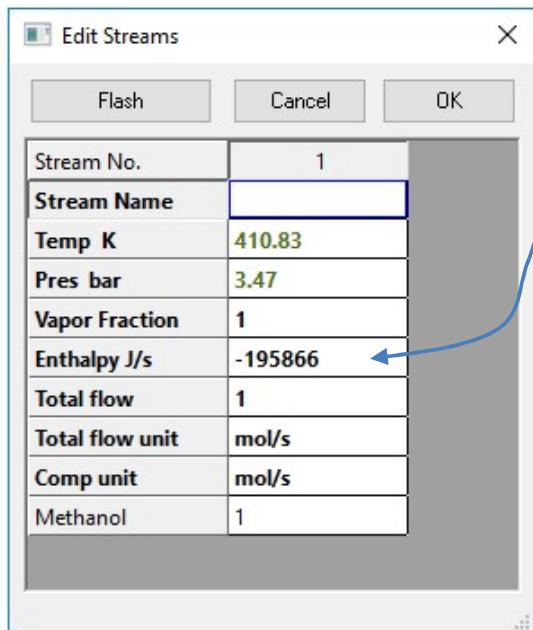
$$I = \frac{1}{\sigma - \varepsilon} \ln \left(\frac{Z + \sigma\beta}{Z + \varepsilon\beta} \right) \quad (13.72)$$

$\varepsilon \neq \sigma$

Connection to Total Properties

Add ideal gas and residual

CHEMCAD



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

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

$H_0^{ig} = \Delta H_f^o_{298}$ = standard formation enthalpy, App C, pp 671-672

Difference between streams:

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

residual property at T_2
residual property at T_1

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

$$S = S_0^{ig} + \int_{T_0}^T C_P^{ig} \frac{dT}{T} - R \ln \frac{P}{P_0} + S^R \quad (\text{Eq. 6.51}) \quad \Delta S = \int_{T_1}^{T_2} C_P^{ig} \frac{dT}{T} - R \ln \frac{P_2}{P_1} + S_2^R - S_1^R \quad (\text{Eq. 6.73})$$

$S_0^{ig} = \Delta S_f^o_{298}$, also from App C, pp 660-662, from $\Delta H_f^o_{298}$ and $\Delta G_f^o_{298}$

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

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

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

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

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

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

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)

$$T_{pc} \equiv \sum_i y_i T_{ci} \quad \begin{matrix} \text{“pseudocritical temperature”} \\ \text{subscript “p”} \end{matrix}$$

(Eq. 6.79)

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

(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

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

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

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

(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?