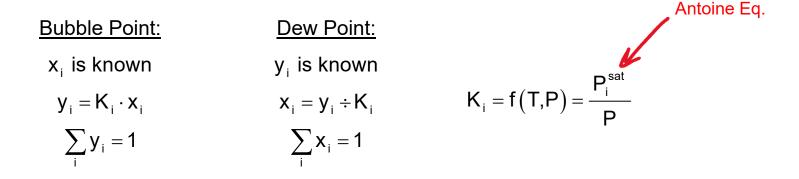# CH365 Chemical Engineering Thermodynamics

Lesson 30
Generalized Property Correlations

CDP – IPR

- Friday 15 November by 2359, pass/fail.

- 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 done in CH362 and CH363. Problem 13.1 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

$x_i = y_i \div K_i$

$\sum_i x_i = 1$

Antoine Eq.

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

WPR3 WARNO

- WPR3 is Wednesday 20 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

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

Residual Properties

superscript "R" refers to "residual"

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

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

$$H^R = H - H^{ig} \qquad\qquad S^R = S - S^{ig} \qquad\qquad G^R = G - G^{ig}$$

$$H = H^{ig} + H^R \qquad\qquad S = S^{ig} + S^R \qquad\qquad G = G^{ig} + G^R$$

$$dH^{ig} = C_P^{ig}\,dT \qquad\qquad dS^{ig} = \frac{C_P^{ig}}{T}\,dT - R \cdot \frac{1}{P} \cdot dP$$

$$\text{(Eq. 6.23)} \qquad\qquad\qquad\qquad \text{(Eq. 6.24)}$$

$$H^{ig} = H_0^{ig} + \int_{T_0}^{T_2} C_P^{ig}\,dT \qquad\qquad S^{ig} = S_0^{ig} + \int_{T_0}^{T_2} \frac{C_P^{ig}}{T}\,dT - R \cdot \ln\!\left(\frac{P}{P_0}\right)$$

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

$$V^{ig} = \frac{RT}{P} \qquad\qquad\qquad\qquad \text{(Eq. 6.40)}$$

- 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)**

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

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

(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

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

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

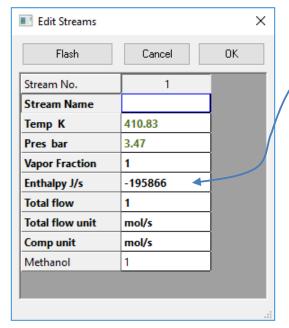$$\frac{H^R}{RT} = Z - 1 + T_r \left(\frac{dq}{dT_r} \right) \cdot I$$

(page 497)

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

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

$$\varepsilon \neq \sigma$$

Connection to Total Properties

Add ideal gas and residual

CHEMCAD

Edit Streams			✕
Flash	Cancel	OK	
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	

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

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

$$H_0^{ig} = \Delta H_{f298}^o = \text{standard formation enthalpy, App C, pp 671-672}$$

Difference between streams:

residual property at T_2

residual property at T_1

$$\Delta H = H_2 - H_1 = R \int_{T_1}^{T_2} C_P^{ig} dT + H_2^R - H_1^R$$

(Eq. 6.72)

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

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

$$S_0^{ig} = \Delta S_{f298}^o, \text{ also from App C, pp 660-662, from } \Delta H_{f298}^o \text{ and } \Delta G_{f298}^o$$

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

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

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

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

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

Appendix D
pages 676-692

Virial Equation

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

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

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

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

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} \qquad \text{(Eq. 3.61)} \qquad\qquad B^1 = 0.139 - \frac{0.172}{T_r^{4.2}} \qquad \text{(Eq. 3.62)}$$

$$\frac{dB^0}{dT_r} = \frac{0.675}{T_r^{2.6}} \qquad \text{(Eq. 6.70)} \qquad\qquad \frac{dB^1}{dT_r} = \frac{0.722}{T_r^{5.2}} \qquad \text{(Eq. 6.71)}$$

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

$$\omega \equiv \sum_i y_i \omega_i$$

(Eq. 6.78)

"pseudocritical acentric factor"

$$T_{pc} \equiv \sum_i y_i T_{ci}$$

(Eq. 6.79)

"pseudocritical temperature"

subscript "p"

$$P_{pc} \equiv \sum_i y_i P_{ci}$$

(Eq. 6.80)

"pseudocritical pressure"

"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.

worked example is in reference, p. 4-25

"pseudocritical" properties

"true critical temperature" of mixture
$$T_{cm} = \sum_{i=1}^{n} \left(\theta_i \cdot T_{ci} \right)$$
(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

$$P_{cm} = P_{pc} + P_{pc} \left[5.808 + 4.93 \cdot \sum_{i=1}^{n} \left(x_i \cdot \omega_i \right) \right] \cdot \left[\frac{T_{cm} - T_{pc}}{T_{pc}} \right]$$
(Eq. 4B2.1-1)

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

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

Questions?