

# CH365 Chemical Engineering Thermodynamics

## Lesson 29 Residual Properties II

Agenda  
Review  
Finish PS10  
Capstone

# Block 6 Look-Ahead (CDP)

## Real Gas Properties

- Residual Properties
- $M = V, U, H, S$ , or  $G$

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

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

Ideal gas (ig) follows ideal gas law

## Real Solution Properties (Liquids)

- Excess Properties
- $M^E = V^E, U^E, H^E, S^E$ , or  $G^E$

$$M^E \equiv M - M^{id} \quad (\text{Eq. 6.41})$$

$$M \equiv M^{id} + M^E$$

$$G^E \equiv G - G^{id}$$

$$H^E \equiv H - H^{id}$$

$$S^E \equiv S - S^{id}$$

Ideal solution (id) follows Raoult's law ( $y_i P = x_i P_i^{sat}$ ).

## $G^E$ is related to the activity coefficients

From Gibbs-Duhem:

$$\frac{G^E}{RT} = \sum_i x_i \ln \gamma_i \quad (\text{Eq. 13.10})$$

Margules  
(1-constant)

$$\log \gamma_1 = A x_2^2 \quad \log \gamma_2 = A x_1^2$$

- The constant  $A$  is known from fitting experimental data.
- These are the so-called “binary interaction parameters” in CHEMCAD and in the *capstone design problem*.

# Residual Properties from Cubic EOS

Numerical Recipe from Lesson 28

(WPR3)

**Important:**  $\alpha$  is written as a function of  $x$  where  $x$  replaces the reduced temperature  $T_r$ .

This is a purely computational issue that arises from the order of operations in the algorithm.

The derivative of  $q$  that appears in  $H^R$  and  $S^R$  must be determined before  $T_r$  is assigned a value in the Mathematica kernel.

$$\alpha = \alpha(\omega, x) \quad \text{instead of } \alpha = \alpha(w, T_r) \quad (\alpha \text{ formula is from Table 3.1})$$

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

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

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

Generic cubic equation of state in Z-Form.

$$\text{RK, SRK, PR: } I = \frac{1}{\sigma - \varepsilon} \ln \left( \frac{Z + \sigma\beta}{Z + \varepsilon\beta} \right) \quad \varepsilon \neq \sigma \quad (\text{eq. 13.72})$$

$$\text{vdW: } I = \frac{\beta}{Z} \quad \varepsilon = \sigma$$

$$\frac{H^R}{RT} = Z - 1 + T_r \left( \frac{dq}{dT_r} \right) \cdot I \quad (\text{page 497})$$

$$\frac{S^R}{R} = \ln(Z - \beta) + \left( q + T_r \frac{dq}{dT_r} \right) \cdot I \quad (\text{page 497})$$

# Questions?