CH365 Chemical Engineering Thermodynamics

Lesson 13
Cubic Equations of State

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Corresponding States

Reduced T: $T_r \equiv \frac{T}{T_C}$ Reduced P: $P_r \equiv \frac{P}{P_C}$

All fluids, when compared at the same reduced temperature and reduced pressure, have approximately the same compressibility factor, and all deviate from ideal-gas behavior to about the same degree.

Two-parameter models in terms of T_C and P_C works for simple fluids (Ar, Kr, Xe)

Three-parameter models are greatly improved: use T_C and P_C, and "ω"

"acentric factor"

$$\omega \equiv -1.0 - \log\left(P_r^{sat}\right)_{T_r=0.7}$$

Eq. 3.52

Tables in App. B.1

- Introduced by Pitzer and coworkers
- Related to molecular structure
- Defined with respect to vapor pressure
- Difference between log of reduced vapor pressure of "simple" fluid and more complex fluids at T_r of 0.7

Example: n-Octane

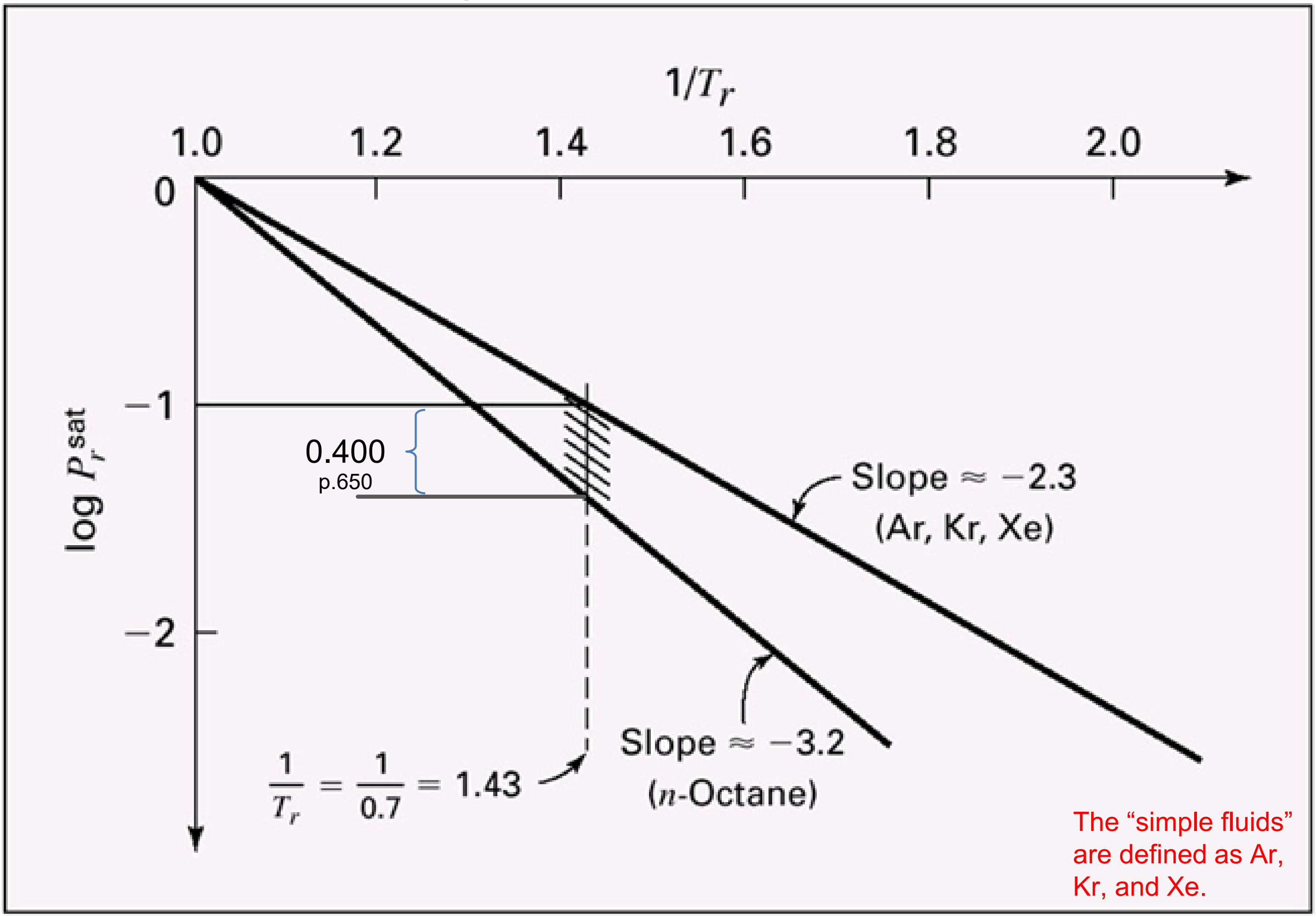


Figure 3.10: Approximate temperature dependence of the reduced vapor pressure.

3-Parameter Theorem of Corresponding States

Characteristic Properties of Pure Species, Table B.1, pages 663-665

	Molar Mass	ω	T_C K	P_C bar	Z_C	V_C cm^3mol^{-1}	T_n K
Methane	16.043	0.012	190.6	45.99	0.286	98.6	111.4
Ethane	30.070	0.100	305.3	48.72	0.279	145.5	184.6
Propane	44.097	0.152	369.8	42.48	0.276	200.0	231.1
n-Butane	58.123	0.200	425.1	37.96	0.274	255.	272.7
⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮
n-Octane	114.231	0.400	568.7	24.90	0.256	486.	398.8
⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮
Nitric Acid	63.013	0.714	520.0	68.90	0.231	145.	356.2
Sulfuric Acid	98.080	…	924.0	64.00	0.147	177.0	610.0

All fluids having the same value of ω, when compared at the same T_r and P_r, have about the same value of Z, and all deviate from ideal-gas behavior to about the same degree.

Pitzer Correlations

For next lesson; needed for Problem 3.44(b)

2nd Virial Coefficient

$$Z = 1 + \frac{BP}{RT} = 1 + \hat{B}\frac{P_r}{T_r} \quad \text{(Eq. 3.57 and 3.36)}$$

where $\hat{B} = \frac{BP_C}{RT_C}$ (Eq. 3.58)

Pitzer and coworkers

$$\hat{B} = B^0 + \omega B^1$$

(Eq. 3.59)

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

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

3rd Virial Coefficient

$$Z = 1 + B\rho + C\rho^2 = 1 + \hat{B}\frac{P_r}{T_r Z} + \hat{C}\left(\frac{P_r}{T_r Z}\right)^2 \quad \text{(Eq. 3.63 and 3.38)}$$

where $\hat{C} \equiv \frac{CP_C^2}{R^2 T_C^2}$ (Eq. 3.64)

$$\hat{C} = C^0 + \omega C^1$$

(Eq. 3.65)

$$C^0 = 0.01407 + \frac{0.02432}{T_r} - \frac{0.00313}{T_r^{10.5}} \quad \text{(Eq. 3.66)}$$

$$C^1 = -0.02676 + \frac{0.05539}{T_r^{2.7}} - \frac{0.00242}{T_r^{10.5}} \quad \text{(Eq. 3.67)}$$

General Cubic Equations of State

$$P = \frac{RT}{V-b} - \frac{a}{(V+\varepsilon b)(V+\sigma b)}$$

(Page 97 Eq. 3.41)

Problem 3.44

$$a = \Psi \frac{\alpha R^2 T_C^2}{P_C} \quad \text{(Eq. 3.45)}$$

$$\alpha = \alpha(T, T_C, \omega)$$

α, Ψ, ε, σ, and Ω are defined in Table 3.1

$$T_r = \frac{T}{T_C} \quad \text{(reduced temperature)}$$

T_C is the critical temperature, Table B.1

P_C is the critical pressure, Table B.1

R is the gas constant, Table A.2

$$b = \Omega \frac{RT_C}{P_C} \quad \text{(Eq. 3.44)}$$

van der Waals

$\alpha = 1$, $\varepsilon = 0$ and $\sigma = 0$, T3.1

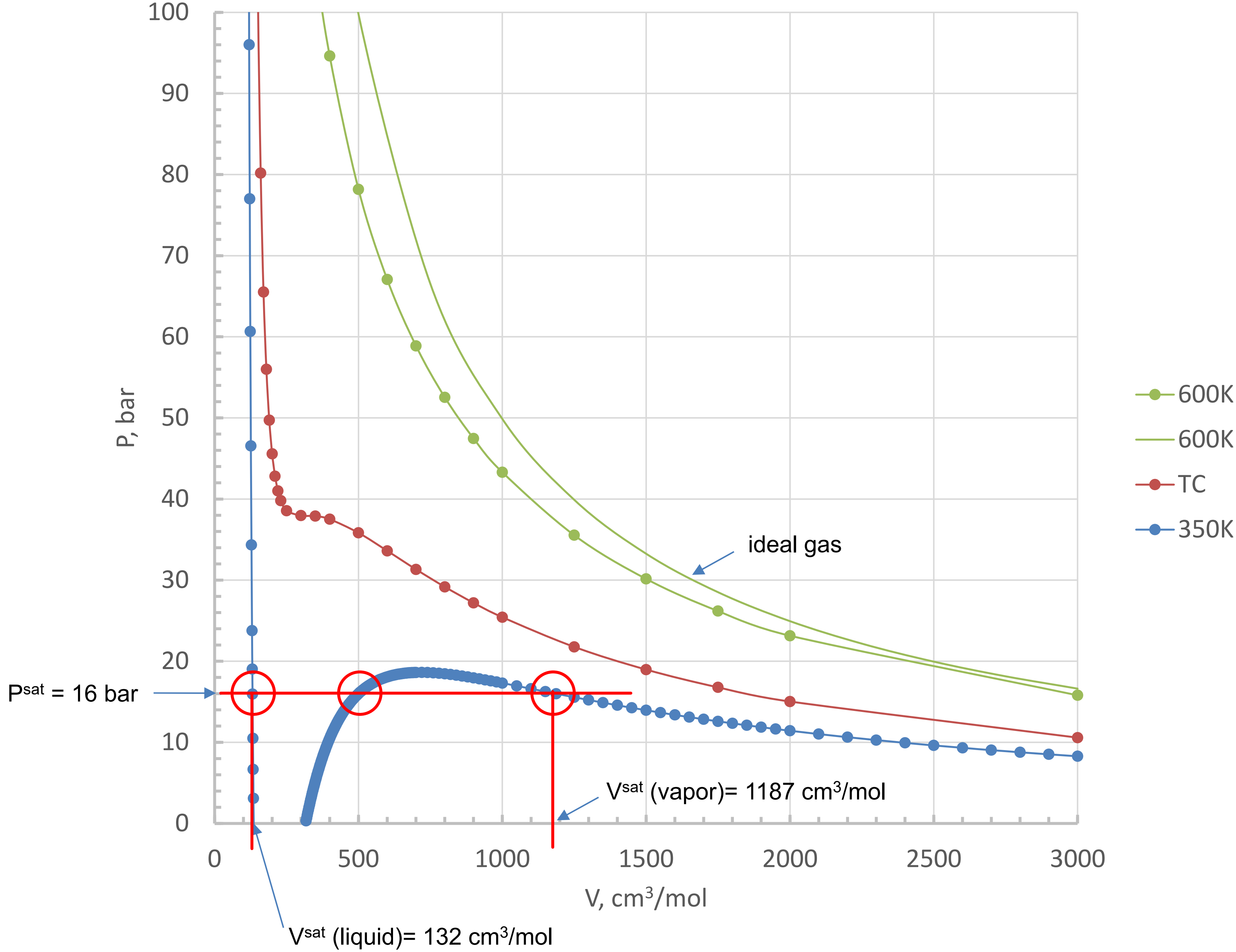
$\Psi = \frac{27}{64}$, $\Omega = \frac{1}{8}$, $\alpha = 1$, T3.1

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$a = \frac{27}{64} \frac{R^2 T_C^2}{P_C}$$

$$b = \frac{RT_C}{8P_C}$$

n-Butane Isotherms from Redlich-Kwong EOS



Parameters for Cubic Equations

RK, SRK and PR equations of state were specifically developed for vapor-liquid calculations

Equation of State	α	σ	ε	Ω	Ψ	Z_c
vdW	1	0	0	0.12500	0.42188	0.37500
RK	α_{RK}	1	0	0.08664	0.42748	0.33333
SRK	α_{SRK}	1	0	0.08664	0.42748	0.33333
PR	α_{PR}	$1+\sqrt{2}$	$1-\sqrt{2}$	0.07780	0.45724	0.30740

Smith, van Ness, Abbott, and Swihart, **Table 3.1, page 100**

$$\alpha_{RK} = 1/\sqrt{T_r} = T_r^{-1/2}$$

$$\alpha_{SRK} = \left[1 + \left(0.480 + 1.574\ \omega - 0.176\ \omega^2\right)\left(1 - \sqrt{T_r}\right)\right]^2$$

$$\alpha_{PR} = \left[1 + \left(0.37464 + 1.54226\ \omega - 0.26992\ \omega^2\right)\left(1 - \sqrt{T_r}\right)\right]^2$$

vdW – van der Walls – 1873
RK – Redlich-Kwong – 1949
SRK – Soave-Redlich-Kwong – 1972
PR – Peng-Robinson – 1976

Example 3.9

Given that the vapor pressure of n-butane at 350 K is 9.4573 bar, find the molar volumes of (a) saturated vapor and (b) saturated liquid n-butane at these conditions as given by the Redlich-Kwong equation.

Eq. 3.41 gives three roots. Largest is vapor. Smallest is liquid.

$$P = \frac{RT}{V-b} - \frac{a}{(V+\varepsilon b)(V+\sigma b)}$$

(Eq. 3.41)

Claimed to be better for vapor

(Eq. 3.48)

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

$$\beta = \Omega \frac{P_r}{T_r}$$

(Eq. 3.46 combined with 3.44)

$$q = \frac{\Psi \alpha(T_r, \omega)}{\Omega T_r}$$

(Eq. 3.47 with 3.44)

Claimed to be better for liquid

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

(Eq. 3.49)

Easy to demonstrate with “FindRoot” in Mathematica (numerical; requires initial guess)

Example 3.9

Given that the vapor pressure of n-butane at 350 K is 9.4573 bar, find the molar volumes of (a) saturated vapor and (b) saturated liquid n-butane at these conditions as given by the Redlich/Kwong equation.

Solution

The problem is generally straightforward. Apply the equations as stated in the book. You will need to know how to look up and arrange the various terms in the equations.

In[ ]:=
```
Quit[];
```

In[47]:=
```
R = 83.14; (*cm^3*bar/(mol*K)*)
P = 9.4573;(*bar*)
Pc = 37.96 ;(*bar*) (*Table B.1, page 663*)
Pr = P / Pc;

T = 350. ;(*K*)
Tc = 425.1; (*K*) (*Table B.1, page 663*)
Tr = T / Tc;
```

In[24]:=
```
Ω = 0.08664;(*page 100 Table 3.1 for RK; slide 8*)
Ψ = 0.42748;(*page 100 Table 3.1 for RK; slide 8*)
α = 1/Sqrt[Tr];(*page 100 Table 3.1 for RK; slide 8*)
a = Ψ (α * R^2 * Tc^2)/Pc;(*Eq 3.45; slide 8*)
b = Ω * (R * Tc)/Pc;(*Eq 3.44; slide 8*)
σ = 1;(*page 100 Table 3.1 for RK; slide 8*)
ϵ = 0;(*page 100 Table 3.1 for RK; slide 8*)
eq1 = P == (R * T)/(V - b) - a/((V + ϵ * b) * (V + σ * b));(*page 97 Eq 3.41*)


sol1 = Quiet[Solve[eq1, V]]
```

Out[32]=

{{V → 133.26632425}, {V → 388.296983138}, {V → 2555.31910091}}

```
(*V=2555.32 cm3/mol for saturated vapor //ANS*)

(*V=133.266 cm3/mol for saturated liquid //ANS*)
```

```
(*units of "a"; a=Ψ α*R^2*Tc^2/Pc *)
```

In[ ]:=

$$\frac{\left(\frac{bar*cm^3}{mol*K}\right)^2 * K^2}{bar}$$

Out[ ]=

$$\frac{bar\ cm^6}{mol^2}$$

```
(*units of "b"; b=Ω* R*Tc/Pc *)
```

In[ ]:=

$$\frac{\frac{bar*cm^3}{mol*K} * K}{bar}$$

Out[ ]=

$$\frac{cm^3}{mol}$$

```
(*units of "eq1"; eq1=P== R*T/(V-b) - a/((V+ϵ*b)*(V+σ*b)) *)
```

```
(*Use R*T/(V-b) *)
```

In[ ]:=

$$\frac{\frac{bar*cm^3}{mol*K} * K}{\frac{cm^3}{mol}}$$

Out[ ]=

bar

```
(*SOLUTION USING EQUATION 3.48 - See Slide 9*)
```

In[54]:= $q = \frac{\Psi * \alpha}{\Omega * T_r}$

Out[54]= 6.60437839513

In[55]:= $\beta = \Omega * \frac{P_r}{T_r}$

Out[55]= 0.0262169681354

In[56]:= $eq2 = Z == 1 + \beta - q * \beta * \frac{Z - \beta}{Z * (Z + \beta)};$

In[57]:= `sol2 = Quiet[Solve[eq2, Z]]`

Out[57]= {{Z → 0.0433121278508}, {Z → 0.12619818752}, {Z → 0.83048968463}}

In[58]:= $Vv = \frac{.83049 * R * T}{P}$

Out[58]= 2555.32007127

In[59]:= $Vl = \frac{.0433121 * R * T}{P}$

Out[59]= 133.266238556

```
(*Answers are identical to previous*)
```

```
(*SOLUTION USING EQUATION 3.49 - See Slide 9*)
```

In[60]:= $eq3 = \beta + Z * (Z + \beta) * \left(\frac{1 + \beta - Z}{q * \beta}\right);$

In[61]:= `sol2 = Quiet[Solve[eq2, Z]]`

Out[61]= {{Z → 0.0433121278508}, {Z → 0.12619818752}, {Z → 0.83048968463}}

```
(*Answers are identical to previous*)
```

Homework

Problem 3.44

Calculate Z and V for ethylene at 25 deg C and 12 bar by the following equations:

(a) The truncated virial equation (Eq. 3.38) with the following experimental values of virial coefficients:

$$Z = 1 + \frac{B}{V} + \frac{C}{V^2} \qquad (3.38)$$

$$B = -140.\ \mathrm{cm^3\ mol^{-1}} \quad \text{and} \quad C = 7,200\ \mathrm{cm^6\ mol^{-2}}$$

(b) The truncated virial equation (Eq. 3.36), with a value of B from the generalized Pitzer correlation (Eqs. 3.58-3.62)

(c) The Redlich/Kwong equation.

(d) The Soave/Redlich/Kwong equation

(e) The Peng/Robinson equation.

CHEMCAD Thermodynamics

Which EOS is best?

- Selection of the appropriate thermodynamic method is key to producing accurate simulations
- PR is the most widely used thermodynamic package as it applies to all applications involving hydrocarbons
- Special packages should be used when simulation involves non-hydrocarbon components: TEG, amines, sour water, etc.
- Methanol for hydrate prevention has special fit of BIPs in PR equation of state
- In refinery models, review oil characterization before suspecting thermodynamics

Same comments for Aspen/HYSYS