# Problem Set 5 - Solutions

## 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:

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

(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.

## Solution to Part (a) - Truncated virial equation (Eq. 3.38)

*In[ ]:=* **R = 83.14 (\* $\frac{cm^3*bar}{mol*K}$ \*);**

**P = 12. (\*bar\*);**

**T = 298.15 (\*K\*);**

**B = -140. (\* $\frac{cm^3}{mol}$ \*);**

**C = 7 200. (\* $\frac{cm^6}{mol^2}$ \*);**

**$\frac{P*V}{R*T}$ == 1 + $\frac{B}{V}$ + $\frac{C}{V^2}$ // Solve // Quiet (\*Eq 3.38\*)**

*Out[ ]=*

$\{\{V \to 73.33041 - 48.71252\ i\}, \{V \to 73.33041 + 48.71252\ i\}, \{V \to 1919.022\}\}$

**$\frac{P*1919.022}{R*T}$ (\*=Z\*)**

*Out[ ]=*

**0.929 001 4**

**(\*V=1919.022 $\frac{cm^3}{mol}$ and Z=0.9290 //ANS Part (a)\*)**

## Solution to Part (b) - Truncated virial equation (Eq. 3.36) with B from Eqns. 3.58-3.62.

```
(*Table B.1*)
Tc = 282.3; (*K*)
Pc = 50.4 ; (*bar*)
ω = 0.087;


Tr = T / Tc;
```

$$B0 = 0.083 - \frac{.422}{T_r^{1.6}}; (*Eq. \ 3.61*)$$

$$B1 = 0.139 - \frac{0.172}{T_r^{4.2}}; (*Eq. \ 3.62*)$$

$$\hat{B} = B0 + ω * B1 ; (*Eq. \ 3.59*)$$

$$B = \frac{\hat{B} * R * Tc}{Pc}; (*Eq. \ 3.58*)$$

$$\frac{P * V}{R * T} == 1 + \frac{B * P}{R * T} \ // \ Solve \ // \ Quiet (*Eq. \ 3.36*)$$

*Out[●]=*

$$\{\{V \rightarrow 1\,924.355\}\}$$

$$\frac{P * 1\,924.355}{R * T}$$

*Out[●]=*

0.931 583 1

$$(*V=1924.355 \ \tfrac{cm^3}{mol} \ and \ Z=0.9316 \ \ //ANS \ Part \ (b)*)$$

## Solution to Part (c) - Redlich/Kwong equation

*In[●]:=* `(*Table 3.1 for RK equation*)`
`Ω = 0.08664;`
`Ψ = 0.42748;`
$\alpha = (T_r)^{-1/2};$
`σ = 1;`
`ε = 0;`

$a = \Psi \dfrac{\alpha * R^2 * Tc^2}{Pc}; (*Eq\ 3.45*)$

$b = \Omega * \dfrac{R * Tc}{Pc}; (*Eq\ 3.44*)$

$P == \dfrac{R * T}{V - b} - \dfrac{a}{(V + \epsilon * b) * (V + \sigma * b)} // Solve // Quiet (*Eq\ 3.41*)$

*Out[●]=*
$\{\{V \to 74.59371 - 49.10982\ \mathbb{i}\}, \{V \to 74.59371 + 49.10982\ \mathbb{i}\}, \{V \to 1\,916.495\}\}$

$\dfrac{P * 1\,916.495}{R * T} \quad (*=Z*)$

*Out[●]=*
`0.927 778 1`

$(*V=1916.495\ \frac{cm^3}{mol}\ and\ Z=0.9278\ //ANS\ Part\ (c)*)$

## Solution to Part (d) - Soave/Redlich/Kwong equation

*In[●]:=* `(*Table 3.1, SRK - NEW stuff only*)`
$\alpha = \left(1 + \left(0.480 + 1.574 * \omega - 0.176 * \omega^2\right) * \left(1 - \sqrt{T_r}\right)\right)^2;$

$a = \Psi \dfrac{\alpha * R^2 * Tc^2}{Pc}; (*Eq\ 3.45,\ do\ not\ need\ to\ recalculate\ b*)$

$P == \dfrac{R * T}{V - b} - \dfrac{a}{(V + \epsilon * b) * (V + \sigma * b)} // Solve // Quiet (*Eq\ 3.41*)$

*Out[●]=*
$\{\{V \to 73.85654 - 49.58738\ \mathbb{i}\}, \{V \to 73.85654 + 49.58738\ \mathbb{i}\}, \{V \to 1\,917.969\}\}$

$\dfrac{P * 1\,917.969}{R * T} \quad (*=Z*)$

*Out[●]=*
`0.928 491 6`

$(*V=1917.969\ \frac{cm^3}{mol}\ and\ Z=0.9285\ //ANS\ Part\ (d)*)$

## Solution to Part (e) - Peng/Robinson

*In[ ]:=*  ```
(*Table 3.1, PR*)
Ω = 0.0778;
Ψ = 0.45724;
```
$\alpha = \left(1 + \left(0.37464 + 1.54226*\omega - 0.26992*\omega^2\right)*\left(1 - T_r^{1/2}\right)\right)^2;$

$\epsilon = 1 - \sqrt{2}\ ;$

$\sigma = 1 + \sqrt{2}\ ;$

$a = \Psi\ \dfrac{\alpha*R^2*Tc^2}{Pc};\ (*Eq\ 3.45*)$

$b = \Omega*\dfrac{R*Tc}{Pc};\ (*Eq\ 3.44*)$

$P == \dfrac{R*T}{V-b} - \dfrac{a}{(V+\epsilon*b)*(V+\sigma*b)}\ //\ \textbf{Solve}\ //\ \textbf{Quiet}\ (*Eq\ 3.41*)$

*Out[ ]=*

$\{\{V \to 64.44718 - 45.96281\ \dot{\imath}\},\ \{V \to 64.44718 + 45.96281\ \dot{\imath}\},\ \{V \to 1900.558\}\}$

$\dfrac{P*1900.558}{R*T}\ (*=Z*)$

*Out[ ]=*

0.920 062 9

$(*V=1900.558\ \tfrac{cm^3}{mol}\ \text{and Z=0.9201}\ \ //ANS\ Part\ (e)*)$

## Problem 3.58

To a good approximation, what is the molar volume of ethanol vapor at 480 °C and 6,000 kPa?  How does this result compare with the ideal gas value?

### Instructor Comments

The best way to answer this question is to run the calculation for some real models and compare to the ideal model.  To do this, I have divided the problem into three parts to keep things organized:

(a) - Lee-Kesler
(b) - Soave/Redlich/Kwong equation
(c) - Ideal Gas

### Solution to Part (a) - Lee-Kesler

```
R = 83.14 ; (* cm³*bar / mol*K *)
```

```
(*Table B.1 lookups, page 664, for ethanol*)
ω = 0.645;(*dimensionless*)
Tc = 513.9; (*K*)
Pc = 61.48 ;(*bar*)
```

```
P = 60.;(*bar given 6000 kPa with 1 bar = 100 kPa*)
T = 273.15 + 480 ;(*K*)
```

```
Tᵣ = T / Tc
Pᵣ = P / Pc
```

*Out[●]=*

1.465 558

*Out[●]=*

0.975 927 1

```
(*Use these values with Tables D.1 and D.2 and online interpolator to get Z0 and Z1.*)

Z0 = .903 149;
Z1 = .083 871;
Z = Z0 + ω * Z1
```

*Out[●]=*

0.957 245 8

```
Va = Z * R * T / P
```

*Out[●]=*

998.9959

```
(*V=999.00 cm³/mol   //ANS Part (a) *)
```

## Solution to Part (b) - Soave/Redlich/Kwong

*In[ ]:=* `(*Table 3.1 lookups, page 100, for SRK*)`
`Ω = 0.08664;`
`Ψ = 0.42748;`
`σ = 1;`
`ϵ = 0;`
$\alpha = \left(1 + \left(0.480 + 1.574 * \omega - 0.176 * \omega^2\right) * \left(1 - \sqrt{T_r}\right)\right)^2;$

$b = \Omega * \dfrac{R * Tc}{Pc};$ `(*Eq 3.44*)`

$a = \Psi \dfrac{\alpha * R^2 * Tc^2}{Pc};$ `(*Eq 3.45*)`

$P == \dfrac{R * T}{V - b} - \dfrac{a}{(V + \epsilon * b) * (V + \sigma * b)}$ `// Solve // Quiet` `(*Eq 3.41*)`

*Out[ ]=*

$\{\{V \rightarrow 15.3922 - 77.03595\,\mathbb{i}\}, \{V \rightarrow 15.3922 + 77.03595\,\mathbb{i}\}, \{V \rightarrow 1\,012.83\}\}$

`(*V=1012.83` $\frac{cm^3}{mol}$ `//ANS Part (b) *)`

## Solution to Part (c) - Ideal Gas

$eqb = \dfrac{P * V}{R * T} == 1;$

`Quiet[solb = Solve[eqb, V]]`

*Out[ ]=*

$\{\{V \rightarrow 1\,043.615\}\}$

`(*V=1043.61` $\frac{cm^3}{mol}$ `//ANS Part (b) *)`

## Comparison

In an ideal gas, according to the kinetic molecular theory, there are assumed to be no intermolecular forces of attraction (IMFs) and the molecules themselves occupy zero volume. That is, in the ideal gas equation of state, as T→0, V→0. In a real gas, on the other hand, the IMFs collectively "pull" on the molecules and the models are corrected for nonzero molecular volume. As a molecule approaches the wall of the container, there is a collective pull from the IMFs of the molecules in the bulk fluid. This average inward pull results in a lower molar volume (at the same pressure). Also, consider that as T is dropped to the point where condensation is observed, the liquid volume is on the order of 30-50 $cm^3/mol$ (see for example 3.14 in lesson 14 slide 5 for a calculation).

## Problem 3.78

The *Boyle temperature* is the temperature for which:

$$\lim_{P \to 0} \left( \frac{\partial Z}{\partial P} \right)_T = 0$$

(a) Show that the second virial coefficient B is zero at the Boyle temperature.

(b) Use the generalized correlation for B, Eqs. 3.58 to 3.62, to estimate the reduced Boyle temperature for simple fluids.

### Solution to Part (a)

*In[ ]:=* **Quit[];**

*In[ ]:=* **Z = 1 + B' \* P + C' \* P$^2$ + D' \* P$^3$; (\*Eq. 3.33 truncated\*)**

**TraditionalForm[HoldForm[Limit[∂$_P$ Z, P → 0]] == Limit[∂$_P$ Z, P → 0]]**

*Out[ ]//TraditionalForm=*

$$\lim_{P \to 0} \frac{\partial Z}{\partial P} = B'$$

This calculation shows that the limit of $(\partial Z/\partial P)_T$ as P approaches 0 is $B'$. This limit is defined as being equal to zero at the Boyle temperature. That is, $B' = 0$ at $T = T_{Boyle}$. However, equation 3.35a defines $B'$ as $B' = \frac{B}{R*T}$. Since R is a positive constant, for any nonzero value of T including the Boyle temperature, if $B' = 0$, then B must also be zero. //ANS

### Solution to Part (b)

The acentric factor $\omega$ is zero for simple fluids by definition. (Simple fluids include Argon, Krypton, and Xenon.) Equation 3.59 is the Pitzer equation for the reduced second virial coefficient $\hat{B}$, and states that $\hat{B} = B^0 + \omega B^1$. Since $\omega=0$, we have $\hat{B} = B^0$.

Equation 3.58 defines the reduced second virial coefficient $\hat{B}$ in terms of B as $\hat{B} = \frac{BP_c}{RT_c}$. If B=0 (from part (a)), then $\hat{B}=0$ and $B^0=0$.

Equation 3.61 gives $B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} = 0$, which can be solved for $T_r$:

**0 == 0.083 − $\dfrac{\textbf{0.422}}{\textbf{T}_r^{\textbf{1.6}}}$ // Solve // Quiet**

*Out[ ]=*

$\{\{T_r \to 2.763\,099\}\}$

**(\*T$_r$=2.763 for simple fluids at the Boyle temperature. //ANS Part (b)\*)**

**T$_r$ = T$_r$ /. %⟦1⟧**

*Out[ ]=*

2.763 099

```
(*Actual Boyle temperatures in degrees K*)
(*Simple fluids are Ar, Kr, Xe*)
(*Lookup Tc in Table B.1*)
```

$T_c = \{150.9, 209.4, 289.7\};$

$T_r * T_c$

*Out[ ]=*

$\{416.9517, 578.593, 800.4698\}$

```
(*//ANS Part (b) in K*)
```