

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:

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

(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

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.

Part (a) - Using the truncated virial equation (Eq. 3.38).

Quit [] ;

```
In[ ]:= R = 83.14 (* cm^3*bar / mol*K *) ;
P = 12. (*bar*) ;
T = 298.15 (*K*) ;
B = -140. (* cm^3 / mol *) ;
c = 7200. (* cm^6 / mol^2 *) ;
eqa = (P * V) / (R * T) == 1 + (B / V) + (c / V^2) ; (*Eq 3.38*)
Quiet[sola = Solve[eqa, V, Reals]]

Out[ ]:= { {V -> 1919.02176456} }

In[ ]:= (P * 1919.02) / (R * T) (*=Z*)
Out[ ]:= 0.92900042605

(*V=1919.02 cm^3 / mol and Z=0.929*)
(*//ANS Part (a)*)
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Part (b) - The truncated virial equation (Eq. 3.36) with B from (Eqs. 3.58-3.62).

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In[ ]:= Quit[];

In[ ]:= R = 83.14 (*  $\frac{\text{cm}^3 \cdot \text{bar}}{\text{mol} \cdot \text{K}}$  page 662*);
Tc = 282.3; (*K*) (*Table B.1, page 664*)
Pc = 50.4; (*bar*) (*Table B.1, page 664*)
 $\omega$  = 0.087; (*Table B.1, page 663*)

P = 12. (*bar*);
T = 298.15 (*K*);
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*)

B̂ = B0 +  $\omega$  * B1; (*Eq. 3.59*)
B =  $\frac{\hat{B} * R * Tc}{Pc}$ ; (*Eq. 3.58*)
eqb =  $\frac{P * V}{R * T} == 1 + \frac{B * P}{R * T}$ ; (*Eq. 3.36*)
Quiet[solb = Solve[eqb, V]]

Out[ ]:= { {V → 1924.35462397} }

In[ ]:=  $\frac{P * 1924.35}{R * T}$ 

Out[ ]:= 0.931580686949

(*V=1924.35  $\frac{\text{cm}^3}{\text{mol}}$  and Z=0.931581*)
(*//ANS Part (b)*)

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Part (c) - Using the Redlich/Kwong equation.

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In[ ]:= Quit[];

R = 83.14 (*  $\frac{\text{cm}^3 \cdot \text{bar}}{\text{mol} \cdot \text{K}}$  page 662*);
Tc = 282.3; (*K*) (*Table B.1, page 664*)
Pc = 50.4; (*bar*) (*Table B.1, page 664*)

P = 12. (*bar*);
T = 298.15 (*K*);
Tr = T / Tc;

Ω = 0.08664; (*Table 3.1, RK*)
Ψ = 0.42748; (*Table 3.1, RK*)
α = (Tr)-1/2; (*Table 3.1, RK*)

a = Ψ  $\frac{\alpha * R^2 * Tc^2}{Pc}$ ; (*Eq 3.45*)
b = Ω *  $\frac{R * Tc}{Pc}$ ; (*Eq 3.44*)
σ = 1; (*Table 3.1, RK*)
ε = 0; (*Table 3.1, RK*)
eqc = P ==  $\frac{R * T}{V - b} - \frac{a}{(V + ε * b) * (V + σ * b)}$ ; (*Eq 3.41*)
Quiet[solc = Solve[eqc, V, Reals]]

Out[ ]:= { {V → 1916.4951696} }

In[ ]:=  $\frac{P * 1916.495}{R * T}$  (*=Z*)

Out[ ]:= 0.927778069808

(*V=1916.5  $\frac{\text{cm}^3}{\text{mol}}$  and Z=0.927778*)
(*//ANS Part (c)*)

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Part (d) - Using the Soave/Redlich/Kwong equation.

In[]:= Quit[];

$$R = 83.14 ; (* \frac{\text{cm}^3 \cdot \text{bar}}{\text{mol} \cdot \text{K}} \text{ page 662} *)$$

$$T_c = 282.3 ; (* \text{K} *) (* \text{Table B.1, page 664} *)$$

$$P_c = 50.4 ; (* \text{bar} *) (* \text{Table B.1, page 664} *)$$

$$\omega = 0.087 ; (* \text{Table B.1, page 664} *)$$

$$P = 12. ; (* \text{bar} *)$$

$$T = 298.15 ; (* \text{K} *)$$

$$T_r = T / T_c ;$$

$$\Omega = 0.08664 ; (* \text{Table 3.1, SRK} *)$$

$$\Psi = 0.42748 ; (* \text{Table 3.1, SRK} *)$$

$$\alpha = \left(1 + (0.480 + 1.574 * \omega - 0.176 * \omega^2) * (1 - \sqrt{T_r}) \right)^2 ; (* \text{Table 3.1, SRK} *)$$

$$a = \Psi \frac{\alpha * R^2 * T_c^2}{P_c} ; (* \text{Eq 3.45} *)$$

$$b = \Omega * \frac{R * T_c}{P_c} ; (* \text{Eq 3.44} *)$$

$$\sigma = 1 ; (* \text{Table 3.1, SRK} *)$$

$$\epsilon = 0 ; (* \text{Table 3.1, SRK} *)$$

$$\text{eqd} = P == \frac{R * T}{V - b} - \frac{a}{(V + \epsilon * b) * (V + \sigma * b)} ; (* \text{Eq 3.41} *)$$

Quiet[sold = Solve[eqd, V, Reals]]

Out[]:=

$$\{ \{ V \rightarrow 1917.96949739 \} \}$$

$$\text{In[]:= } \frac{P * 1917.97}{R * T} (* = Z *)$$

Out[]:=

$$0.928492119494$$

$$(* V = 1917.97 \frac{\text{cm}^3}{\text{mol}} \text{ and } Z = 0.928492 *)$$

(* //ANS Part (d) *)

Part (e) - Using the Peng/Robinson equation.

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In[ ]:= Quit[];

In[ ]:= R = 83.14 ; (*  $\frac{\text{cm}^3 \cdot \text{bar}}{\text{mol} \cdot \text{K}}$  page 662*)
Tc = 282.3; (*K*) (*Table B.1, page 664*)
Pc = 50.4 ; (*bar*) (*Table B.1, page 664*)
 $\omega$  = 0.087; (*Table B.1, page 651*)

P = 12.; (*bar*)
T = 298.15; (*K*)
Tr = T / Tc;

 $\Omega$  = 0.0778; (*Table 3.1, PR*)
 $\Psi$  = 0.45724; (*Table 3.1, PR*)
 $\alpha = \left(1 + \left(0.37464 + 1.54226 * \omega - 0.26992 * \omega^2\right) * \left(1 - Tr^{1/2}\right)\right)^2$ ; (*Table 3.1, PR*)

a =  $\Psi \frac{\alpha * R^2 * Tc^2}{Pc}$ ; (*Eq 3.45*)
b =  $\Omega * \frac{R * Tc}{Pc}$ ; (*Eq 3.44*)
 $\epsilon = 1 - \sqrt{2}$ ; (*Table 3.1, PR*)
 $\sigma = 1 + \sqrt{2}$ ; (*Table 3.1, PR*)
eqe = P ==  $\frac{R * T}{V - b} - \frac{a}{(V + \epsilon * b) * (V + \sigma * b)}$ ; (*Eq 3.41*)
Quiet[sole = Solve[eqe, V, Reals]]

Out[ ]:= { {V → 1900.55808112} }

In[ ]:=  $\frac{P * 1900.56}{R * T}$  (*=Z*)

Out[ ]:= 0.920063912691

(*V=1900.56  $\frac{\text{cm}^3}{\text{mol}}$  and Z=0.920064*)
(*//ANS Part (e)*)

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Problem 3.58

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

The best way to answer this question is to run the calculation for several different methods and compare. So the problem is answered in parts:

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

Solution

Part (a) - Lee-Kesler.

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

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

(*Table B.1 lookups, page 664, for ethanol*)
 $\omega$  = 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[ ]:= 1.46555750146

Out[ ]:= 0.975927130774

(*Use Table D.1 with online interpolator Z0=.903149*)
(*Use Table D.2 with online interpolator Z1=.083871*)

In[ ]:= Z0 = .903149;
Z1 = .083871;
Z = Z0 +  $\omega$  * Z1

Out[ ]:= 0.957245795

In[ ]:=  $\frac{Z * R * T}{P}$ 

Out[ ]:= 998.995926762

(*V=999.00  $\frac{\text{cm}^3}{\text{mol}}$  //ANS Part (a) *)
```

Part (b) - Soave/Redlich/Kwong equation.

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In[ ]:= Quit[];

In[ ]:= R = 83.14 ; (*  $\frac{\text{cm}^3 \cdot \text{bar}}{\text{mol} \cdot \text{K}}$  *) (*Table A.2, page 662*)

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

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

(*Table 3.1 lookups, page 100, for SRK*)
 $\Omega = 0.08664$ ;
 $\Psi = 0.42748$ ;
 $\sigma = 1$ ;
 $\epsilon = 0$ ;
 $\alpha = \left(1 + (0.480 + 1.574 * \omega - 0.176 * \omega^2) * (1 - \sqrt{T_r})\right)^2$ ;

(*Equations 3.41, 3.44, and 3.45*)
eqa = P ==  $\frac{R * T}{V - b} - \frac{a}{(V + \epsilon * b) * (V + \sigma * b)}$ ; (*Eq 3.41*)
b =  $\Omega * \frac{R * T_c}{P_c}$ ; (*Eq 3.44*)
a =  $\Psi * \frac{\alpha * R^2 * T_c^2}{P_c}$ ; (*Eq 3.45*)

Quiet[sola = Solve[eqa, V, Reals]]

Out[ ]:= { {V → 1012.83044364} }

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

```

Part (c) - Ideal Gas

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In[ ]:= Quit[];

In[ ]:= R = 83.14 ; (*  $\frac{\text{cm}^3 \cdot \text{bar}}{\text{mol} \cdot \text{K}}$  *)
P = 60.; (*bar given 6000 kPa with 1 bar per 100 kPa*)
T = 273.15 + 480 ; (*K*)
eqb =  $\frac{P \cdot V}{R \cdot T} == 1$ ;
Quiet[solb = Solve[eqb, V]]

Out[ ]:= { { V  $\rightarrow$  1043.61485 } }

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

```

Comparison

According to the kinetic molecular theory, pressure results from momentum transfer during collisions of gas molecules with the walls of the container. In an ideal gas, these collisions are elastic, so momentum is conserved during the collisions. In a real gas, collisions are inelastic, resulting in deformations of the molecules, and loss of momentum during collisions at the wall. As a result, pressure is lower.

However, in this problem, we are comparing real and ideal gas at the same pressure, 60 bar. In the real gas, molar volume has to be a little less to maintain the constant pressure. This is easy to visualize with a truncated virial equation like equation 3.36 from problem 3-44b:

$$\frac{PV_{\text{ideal}}}{RT} = 1 \Rightarrow \frac{P}{RT} = \frac{1}{V_{\text{ideal}}} \quad (\text{ideal})$$

$$\frac{PV_{\text{real}}}{RT} = 1 + \frac{BP}{RT} \Rightarrow \frac{PV_{\text{real}}}{RT} - \frac{BP}{RT} = 1 \Rightarrow \frac{P}{RT}(V_{\text{real}} - B) = 1 \Rightarrow \frac{P}{RT} = \frac{1}{(V_{\text{real}} - B)} \quad (\text{non-ideal})$$

We see that if P and T are the same, then

$$\frac{1}{V_{\text{ideal}}} = \frac{1}{V_{\text{real}} - B} \quad \text{or} \quad V_{\text{ideal}} = V_{\text{real}} - B$$

If B is negative, which it is (see problem 3.42, 3.44, or equations 3.58-3.61), the only way for this equation to be true is if V_{real} is less than V_{ideal} . In fact, we see that the second virial coefficient B is the deviation in the molar volume: $B = V_{\text{ideal}} - V_{\text{real}}$.

Alternate Answer:

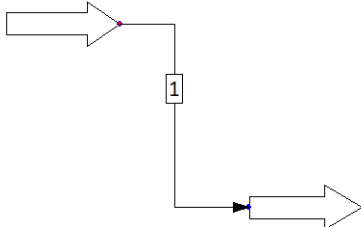
In ideal gases, according to the kinetic molecular theory, there are no intermolecular forces of attraction (IMFs). In a real gas, the IMFs collectively "pull" on the molecules. As a molecule approaches the wall of the container, there is a collective pull from the IMFs of the molecules in the bulk fluid. This average pull inward results in a lower molar volume (at the same pressure). Reference: Khan Academy, "The kinetic molecular theory of gases," in Science AP®/College Chemistry Intermolecular forces and properties Kinetic molecular theory.

Lesson 14 - Bonus

Use CHEMCAD to calculate the molar volume of ethanol vapor at 480 deg C and 6,000 kPa using the SRK equation of state.
How does your answer compare with your Mathematica results?

Solution

CHEMCAD and SRK.



Stream No.	1
Name	
-- Overall --	
Temp K	753.15002441
Pres bar	60.00000000
Enth MJ/hr	-192.83
Vapor mole fraction	1.000
Molar flow kmol/hr	1.00000000
Mass flow kg/hr	46.06900024
Std liq m3/h	0.05785367
Std vap 0 C m3/h	22.41364670
Actual dens kg/m3	45.48284912
Actual vol m3/h	1.01288724

(*Mass density reported from CHEMCAD was 45.4895 kg/m³*)

$$\text{In}[1]:= \left(45.48284912 \cdot \frac{\text{kg}}{\text{m}^3} \cdot \left(\frac{1 \text{ m}}{100 \text{ cm}} \right)^3 \cdot \frac{1000 \text{ g}}{\text{kg}} \cdot \frac{1 \text{ mol}}{46.069 \text{ g}} \right)^{-1}$$

$$\text{Out}[1]= \frac{1012.88729469 \text{ cm}^3}{\text{mol}}$$

$$(*V=1012.89 \frac{\text{cm}^3}{\text{mol}} \quad // \text{ANS Part (c) } *)$$

$$(*V=1012.83 \frac{\text{cm}^3}{\text{mol}} \quad \text{calculated in 3.58b } *)$$

(*Alternate Calculation*)

(*Actual volume reported from CHEMCAD was 1.0127 m³/h*)

(*Flow rate in CHEMCAD was 1.0000 kmol/h*)

$$\text{In}[2]:= \frac{1.01288724 \text{ m}^3 / \text{h}}{1.0000 \text{ kmol} / \text{h}} \cdot \left(\frac{1 \text{ kmol}}{1000 \text{ mol}} \right) \cdot \left(\frac{100 \text{ cm}}{\text{m}} \right)^3$$

$$\text{Out}[2]= \frac{1012.88724 \text{ cm}^3}{\text{mol}}$$

$$(*V=1012.89 \frac{\text{cm}^3}{\text{mol}} \quad // \text{ANS Part (c) } *)$$

Problem 3.78

The *Boyle temperature* is the temperature for which:

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

(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[];

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

$$\text{Limit}[\partial_P Z, P \rightarrow 0]$$

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 $T = T_{\text{Boyle}}$. 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 Part (a)*)

Solution to Part (b)

The acentric factor ω 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 $B^0=0$.

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

This can be solved using *Mathematica* as follows:

In[*]:= Quit[];

$$\text{eq1} = 0 == 0.083 - \frac{0.422}{T_r^{1.6}}; (*Eq. 3.61*)$$

$$T_r = T_r /. \text{Quiet}[\text{Solve}[\{\text{eq1}\}, T_r]] [[1]]$$

Out[2]= 2.76309918093

(*//ANS Part (b)*)

```
(*Actual Boyle temperatures in degrees K*)  
(*Simple fluids are Ar, Kr, Xe*)  
(*Lookup Tc in Table B.1*)  
Tc = {150.9, 209.4, 289.7};
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```
In[4]:= Tr * Tc
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```
Out[4]= {416.951666403, 578.592968487, 800.469832716}
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```
(*//ANS Part (b) in K*)
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