

Montogue

QUIZ CE101

Equations of State

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► PROBLEMS

► Problem 1 (Smith et al., 2004)

Reported values for the virial coefficients of an alcohol vapor at 120°C are $B = -400 \text{ cm}^3/\text{mol}$ and $C = -26,000 \text{ cm}^6/\text{mol}^2$. Calculate the molar volume and compressibility factor for alcohol vapor at 120°C and 8 bar with the ideal gas equation. True or false?

1. () The compressibility factor, in this case, is greater than 1.0.
2. () The molar volume, in this case, is greater than $3600 \text{ cm}^3/\text{mol}$.
Repeat your calculations with the simple virial equation (eq. 2).
3. () The molar volume, in this case, is greater than $3800 \text{ cm}^3/\text{mol}$.
4. () The compressibility factor, in this case, is greater than 0.8.
Repeat your calculations with the extended virial equation (eq. 3).
5. () The molar volume, in this case, is greater than $3500 \text{ cm}^3/\text{mol}$.
6. () The compressibility factor, in this case, is greater than 0.8.

► Problem 2 (Moran & Shapiro, 2006)

A cylindrical tank containing 5.0 kg of carbon monoxide gas at -73°C has an inner diameter of 0.25 m and a length of 1.2 m. Determine the pressure, in bar, exerted by the gas using (1) the generalized compressibility chart; (2) the ideal gas equation; (3) the Van der Waals equation; and (4) the Redlich-Kwong equation. List your results in the following table. The critical parameters for carbon monoxide are $T_c = 133 \text{ K}$ and $P_c = 35 \text{ bar}$.

The values of a and b for use with the Van der Waals equation are

$$a = 1.474 \text{ bar} \left(\frac{\text{m}^3}{\text{kmol}} \right)^2 ; b = 0.0395 \frac{\text{m}^3}{\text{kmol}}$$

In the Redlich-Kwong equation, use

$$a = 17.22 \frac{\text{bar} \cdot \text{m}^6 \cdot \text{K}^{1/2}}{\text{kmol}^2} ; b = 0.02737 \frac{\text{m}^3}{\text{kmol}}$$

Method	Pressure (bar)
Compressibility chart	
Ideal gas law	
Van der Waals equation	
Redlich-Kwong equation	

► Problem 3 (Dahm & Visco, 2015, w/ permission)

A compound has a critical temperature of 500 K, a critical pressure of 32 atm, and an acentric factor of $\omega = 0.45$. Estimate the molar volume for this compound in the vapor phase at $T = 450 \text{ K}$ and $P = 7.5 \text{ atm}$ using (1) the ideal gas law; (2) the Van der Waals equation; (3) the Soave equation; (4) the Peng-Robinson equation; and (5) the Lee-Kesler equation. List your results in the following table.

Method	Molar Volume (m^3/kmol)
Ideal gas law	
Van der Waals	
Soave	
Peng-Robinson	
Lee-Kesler	

→ **Problem 4.1** (Dahm & Visco, 2015, w/ permission)

One mole of *n*-butane vapor is compressed at a constant temperature of 400 K from $P = 0.1$ bar to $P = 15$ bar. Using the Peng-Robinson equation of state, estimate the variation in internal energy, ΔU , for the gas in this process. For butane, the critical temperature $T_c = 425$ K, the critical pressure $P_c = 38$ bar, and the acentric factor $\omega = 0.2$.

- A) $\Delta U = -426$ J
- B) $\Delta U = -831$ J
- C) $\Delta U = -1390$ J
- D) $\Delta U = -1880$ J

→ **Problem 4.2**

Calculate the variation in entropy, ΔS , for the gas introduced in the previous problem.

- A) $\Delta S = -19.1$ J/K
- B) $\Delta S = -45.3$ J/K
- C) $\Delta S = -90.2$ J/K
- D) $\Delta S = -133$ J/K

▶ **Problem 5** (Dahm & Visco, 2015, w/ permission)

You are designing a process in which toluene is used as a solvent. In order to size process equipment, you need to know the properties at several conditions. The critical temperature and pressure of toluene are $T_c = 592$ K and $P_c = 41.1$ bar, respectively. The acentric factor $\omega = 0.264$. Using the Peng-Robinson equation, you are asked to do the following:

1. Estimate the molar volume at the critical point.
2. Find the molar volume of the liquid phase at $T = 300$ K and $P = 1$ bar.
3. Find the molar volume in the vapor phase at $T = 500$ K and $P = 3$ bar.
4. Find the change in molar enthalpy when toluene is heated and compressed from $T = 300$ K and $P = 1$ bar to $T = 500$ K and $P = 3$ bar.

True or false?

- 1.() The molar volume obtained in Part 1 is greater than 250 cm³/mol.
- 2.() The molar volume obtained in Part 2 is greater than 180 cm³/mol.
- 3.() The molar volume obtained in Part 3 is greater than 15,000 cm³/mol.
- 4.() The change in molar enthalpy obtained in Part 4 is greater than 50 kJ/mol.

▶ **Problem 6** (Dahm & Visco, 2015, w/ permission)

You are designing a process in which benzene is used as a solvent. In order to size process equipment, you need to know the properties at several conditions. The critical temperature and pressure of toluene are $T_c = 562$ K and $P_c = 49$ bar, respectively. The acentric factor $\omega = 0.216$. Using the Peng-Robinson equation, you are asked to do the following:

1. Estimate the molar volume at the critical point.
2. Find the molar volume of the liquid phase at $T = 500^\circ\text{R}$ and $P = 1$ atm.
3. Find the molar volume in the vapor phase at $T = 800^\circ\text{R}$ and $P = 4$ atm.
4. Find the change in molar enthalpy when benzene is heated and compressed from $T = 500^\circ\text{R}$ and $P = 1$ atm to $T = 800^\circ\text{R}$ and $P = 4$ atm.

True or false?

- 1.() The molar volume obtained in Part 1 is greater than 1.8×10^{-4} m³/mol.
- 2.() The molar volume obtained in Part 2 is greater than 2×10^{-4} m³/mol.
- 3.() The molar volume obtained in Part 3 is greater than 5×10^{-3} m³/mol.
- 4.() The change in molar enthalpy obtained in Part 4 is greater than 60 kJ/mol.

→ Problem 7.1 (Dahm & Visco, 2015, w/ permission)

A compound has critical temperature of 800 K, critical pressure of 45 bar, specific heat $C_p^* = 8R$, and acentric factor $\omega = 0.25$, and is well modeled by the Peng-Robinson equation of state. 10 mol/s of the compound enters a turbine in the vapor state at $T = 600$ K and $P = 10$ bar. It leaves at $T = 450$ K and $P = 0.25$ bar, as a mixture with $q = 0.97$. Determine the rate at which work is produced by the turbine.

- A) $\dot{W}_{s,\text{rev}} = -14.4$ kJ/s
- B) $\dot{W}_{s,\text{rev}} = -80.0$ kJ/s
- C) $\dot{W}_{s,\text{rev}} = -146$ kJ/s
- D) $\dot{W}_{s,\text{rev}} = -212$ kJ/s

→ Problem 7.2

Determine the rate of entropy generation in the turbine.

- A) $\dot{S}_{\text{gen}} = 12.3$ J/(K·s)
- B) $\dot{S}_{\text{gen}} = 34.3$ J/(K·s)
- C) $\dot{S}_{\text{gen}} = 66.7$ J/(K·s)
- D) $\dot{S}_{\text{gen}} = 88.2$ J/(K·s)

→ Problem 7.3

Determine the efficiency of the engine.

- A) $\eta = 0.244$
- B) $\eta = 0.431$
- C) $\eta = 0.611$
- D) $\eta = 0.824$

▶ ADDITIONAL INFORMATION

Equations

Eq. 1 → The ideal gas law

$$P\bar{V} = RT$$

Eq. 2 → Virial equation truncated to two terms

$$Z = \frac{P\bar{V}}{RT} = 1 + \frac{BP}{RT}$$

where B is the second virial coefficient.

Eq. 3 → Virial equation truncated to three terms

$$Z = \frac{P\bar{V}}{RT} = 1 + \frac{B}{\bar{V}} + \frac{C}{\bar{V}^2}$$

where B and C are the second and third virial coefficients, respectively.

Eq. 4 → Van der Waals equation

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

where a and b are coefficients. a is given by

$$a = \frac{27R^2T_c^2}{64P_c}$$

where T_c and P_c are the critical temperature and pressure, respectively. Coefficient b , in turn, is given by

$$b = \frac{RT_c}{8P_c}$$

Eq. 5 → Redlich-Kwong equation

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}(\bar{V} + b)T^{1/2}}$$

where a and b are coefficients.

Eq. 6 → Soave equation

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

where a and b are coefficients. Coefficient b is straightforwardly obtained as

$$b = 0.08664 \frac{RT_c}{P_c}$$

where T_c and P_c are the critical temperature and pressure, respectively. Coefficient a , in turn, is given by the relation $a = a_c \alpha$, with

$$\alpha = \left[1 + m(1 - T_r^{0.5}) \right]^2$$

$$m = 0.48 + 1.547\omega - 0.176\omega^2$$

$$a_c = 0.42747R^2 \frac{T_c^2}{P_c}$$

where $T_r = T/T_c$ is the reduced temperature and ω is the acentric factor.

Eq. 7 → Peng-Robinson equation

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

where a and b are coefficients. Coefficient b is given by

$$b = 0.0778 \frac{RT_c}{P_c}$$

where T_c and P_c are the critical temperature and pressure, respectively. Coefficient a , in turn, is given by the relation $a = a_c \alpha$, with

$$\alpha = \left[1 + \kappa(1 - T_r^{0.5}) \right]^2$$

$$\kappa = 0.37464 + 1.54226\omega - 0.269932\omega^2$$

$$a_c = 0.45724R^2 \frac{T_c^2}{P_c}$$

where $T_r = T/T_c$ is the reduced temperature and ω is the acentric factor.

Eq. 8 → Residual molar internal energy – Peng-Robinson

$$\frac{\bar{U}^R}{RT} = - \left\{ \left[\frac{A}{2\sqrt{2}B} \right] \left[1 + \frac{\kappa\sqrt{T_r}}{\sqrt{\alpha}} \right] \ln \left[\frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B} \right] \right\}$$

where A and B are parameters given by

$$A = \frac{aP}{R^2T^2} ; B = \frac{bP}{RT}$$

Eq. 9 → Residual molar enthalpy – Peng-Robinson

$$\frac{\bar{H}^R}{RT} = (Z - 1) - \left\{ \left[\frac{A}{2\sqrt{2}B} \right] \left[1 + \frac{\kappa\sqrt{T_r}}{\sqrt{\alpha}} \right] \ln \left[\frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B} \right] \right\}$$

where A and B are the same parameters given in eq. 8.

Eq. 10 → Residual molar entropy – Peng-Robinson

$$\frac{\bar{S}^R}{R} = \ln(Z - B) - \left\{ \left[\frac{A}{2\sqrt{2}B} \right] \left[\frac{\kappa\sqrt{T_r}}{\sqrt{\alpha}} \right] \ln \left[\frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B} \right] \right\}$$

where A and B are the same parameters given in eq. 8.

Table 1 Coefficients for use with the ideal gas heat capacity equation

$$\frac{C_p^*}{R} = A + BT + CT^2 + DT^3 + ET^4$$

	Formula	A	B × 10 ³	C × 10 ⁵	D × 10 ⁸	E × 10 ¹¹	Range (K)
Benzene	C ₆ H ₆	3.551	-6.184	14.365	-19.807	8.234	50 – 1000
Toluene	C ₇ H ₈	3.866	3.558	13.356	-18.659	7.690	50 – 1000

Figure 1 Generalized compressibility chart for $P_R \leq 1.0$.

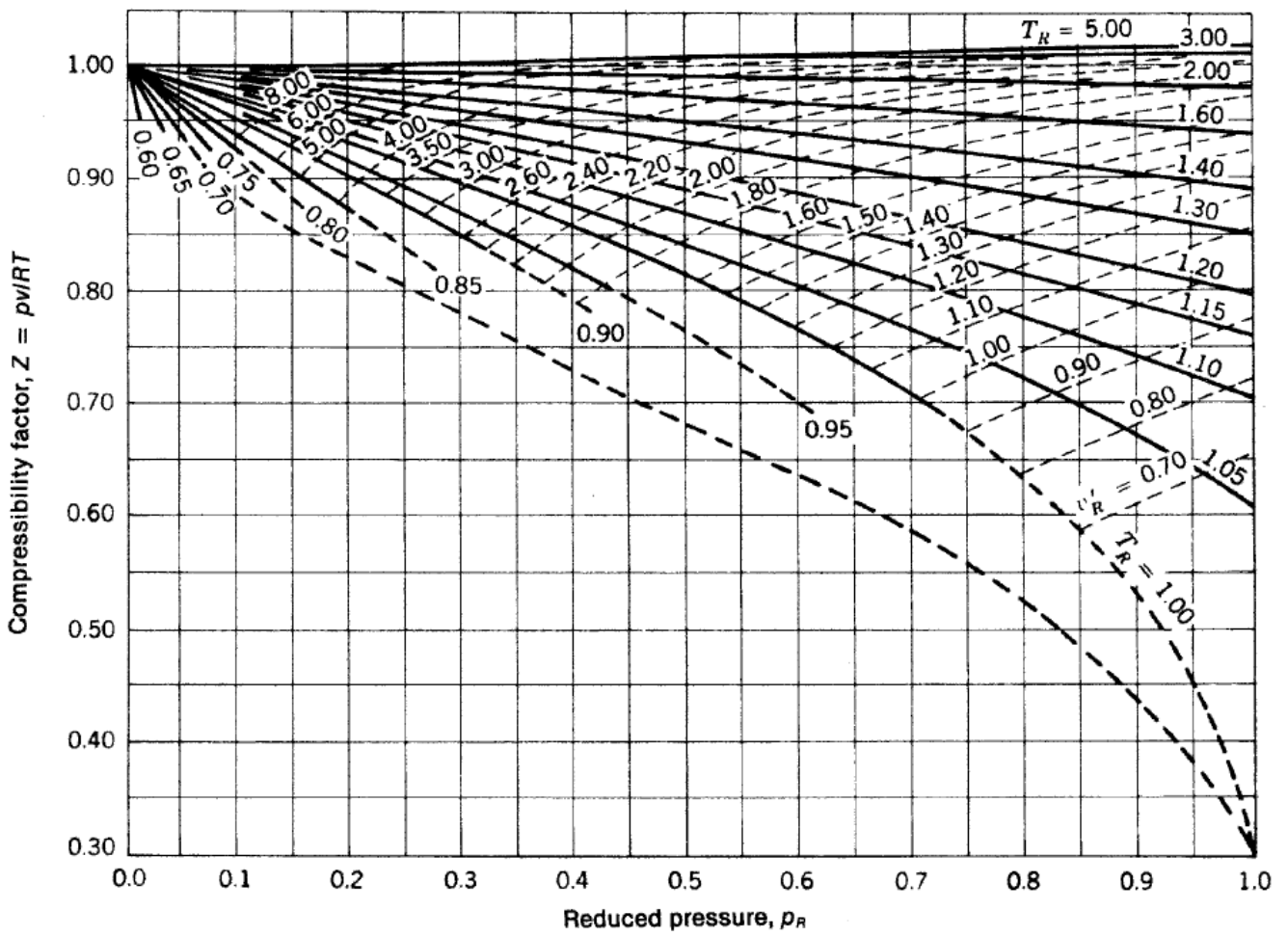


Figure 2 Generalized compressibility chart for $P_R \leq 10.0$.

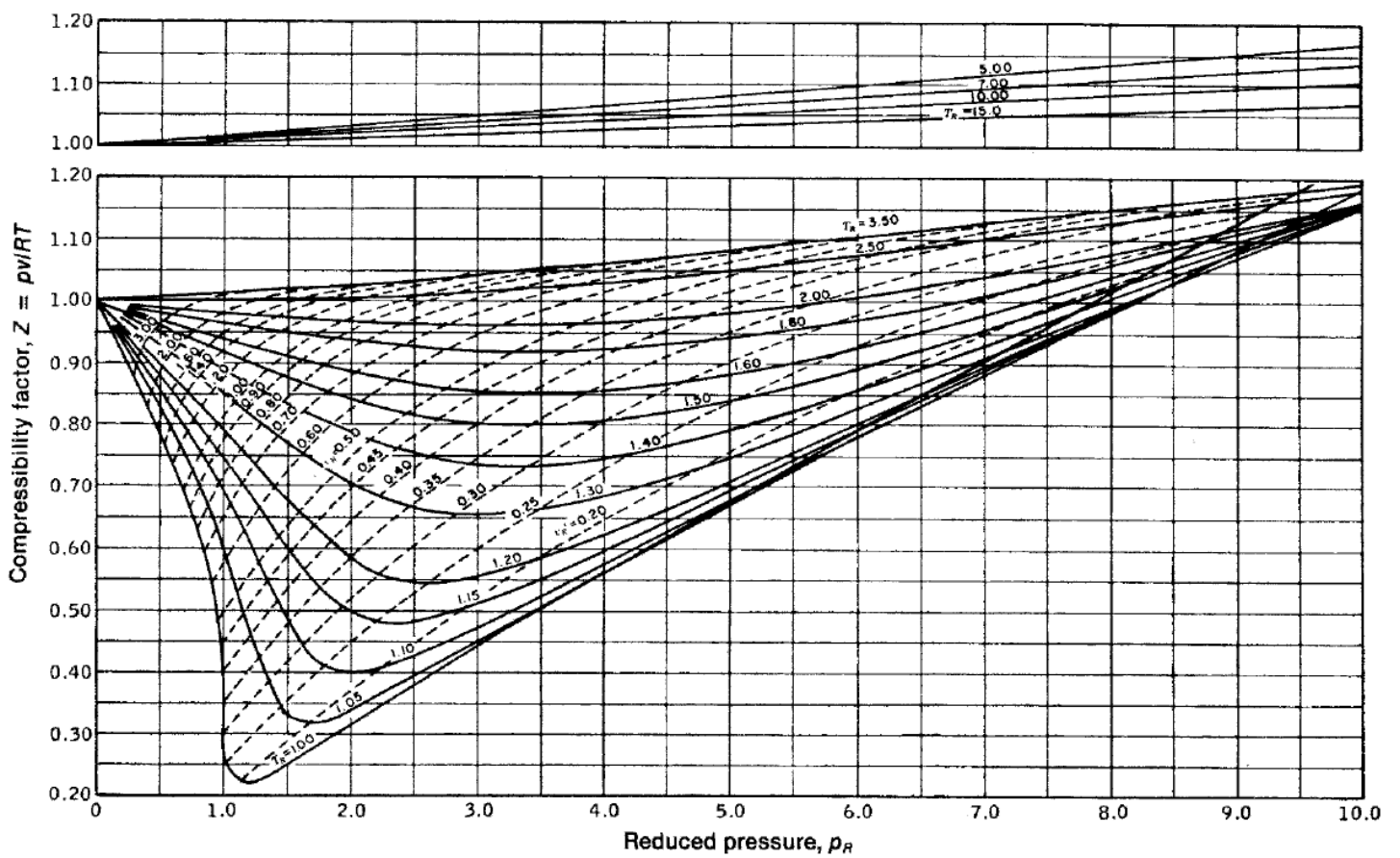


Figure 3 Generalized compressibility chart, $10 \leq P_R \leq 40$.

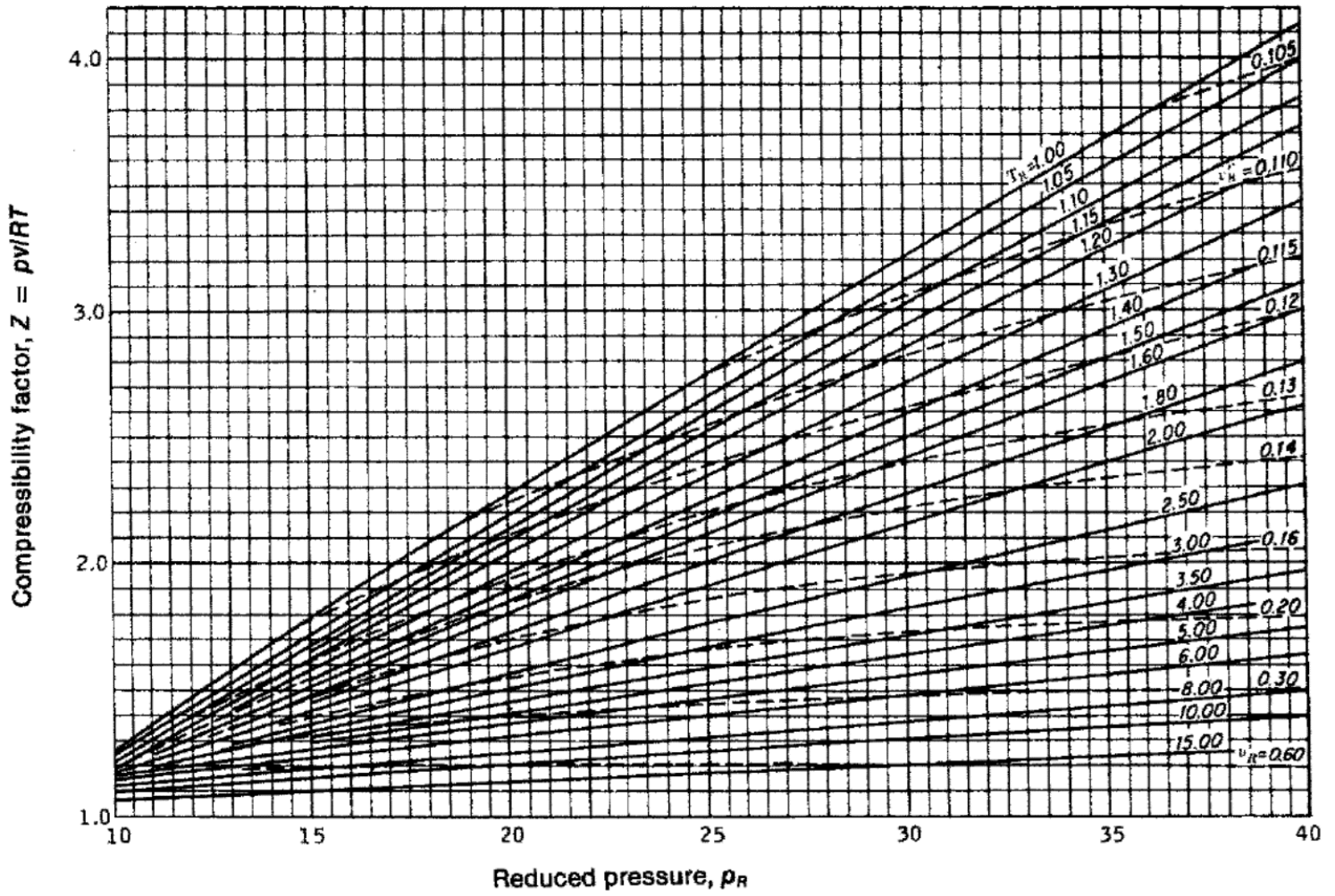


Figure 4 Compressibility factor for a compound with $\omega = 0$ for use with the Lee-Kesler equation.

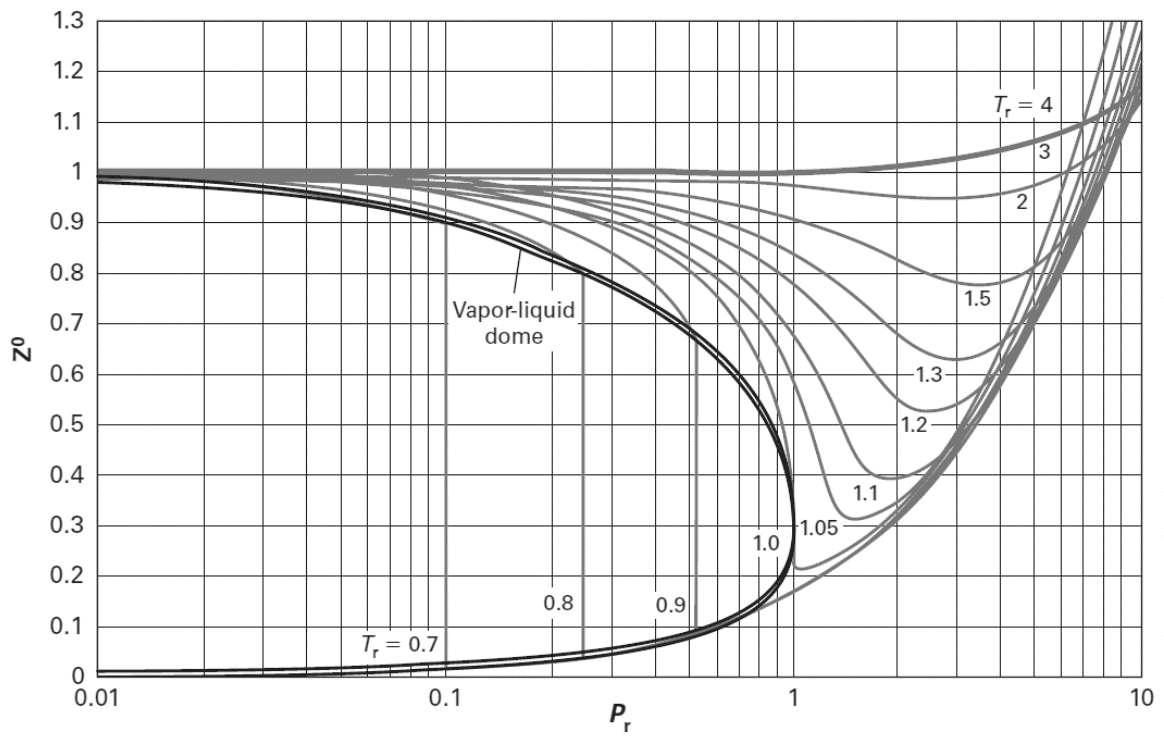


Figure 5 Compressibility factor for a compound with $\omega = 1.0$ for use with the Lee-Kesler equation.

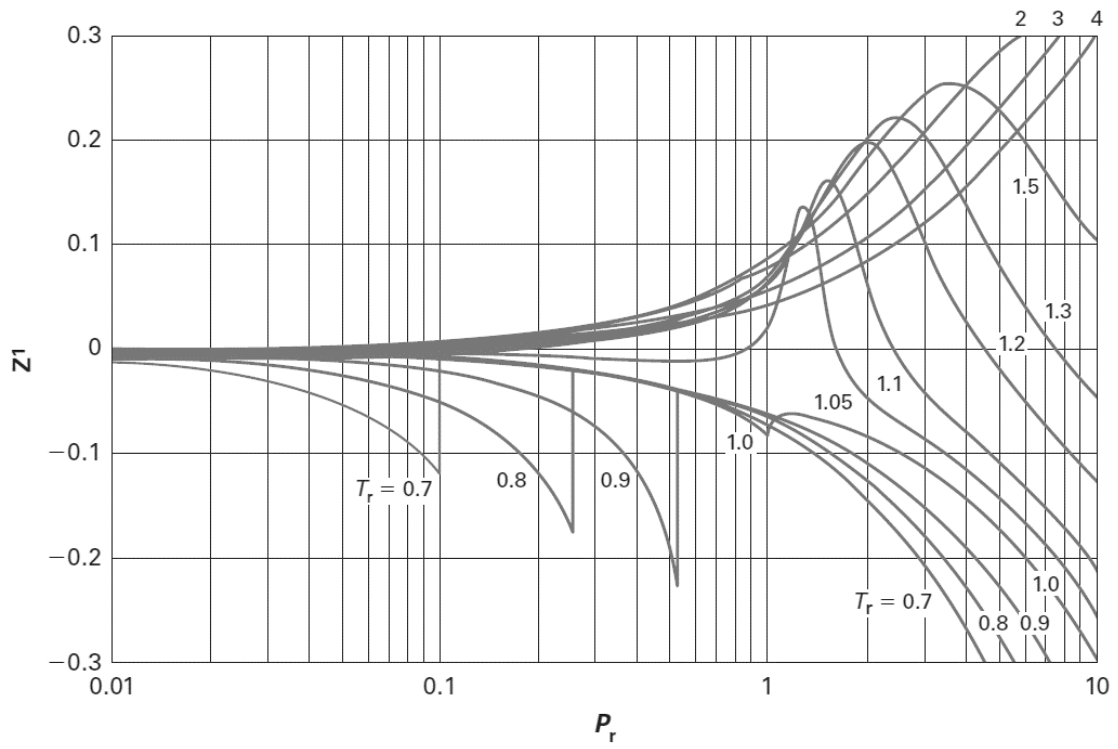


Figure 6 Molar enthalpy residual function for a compound with $\omega = 0$, as determined with the Lee-Kesler equation.

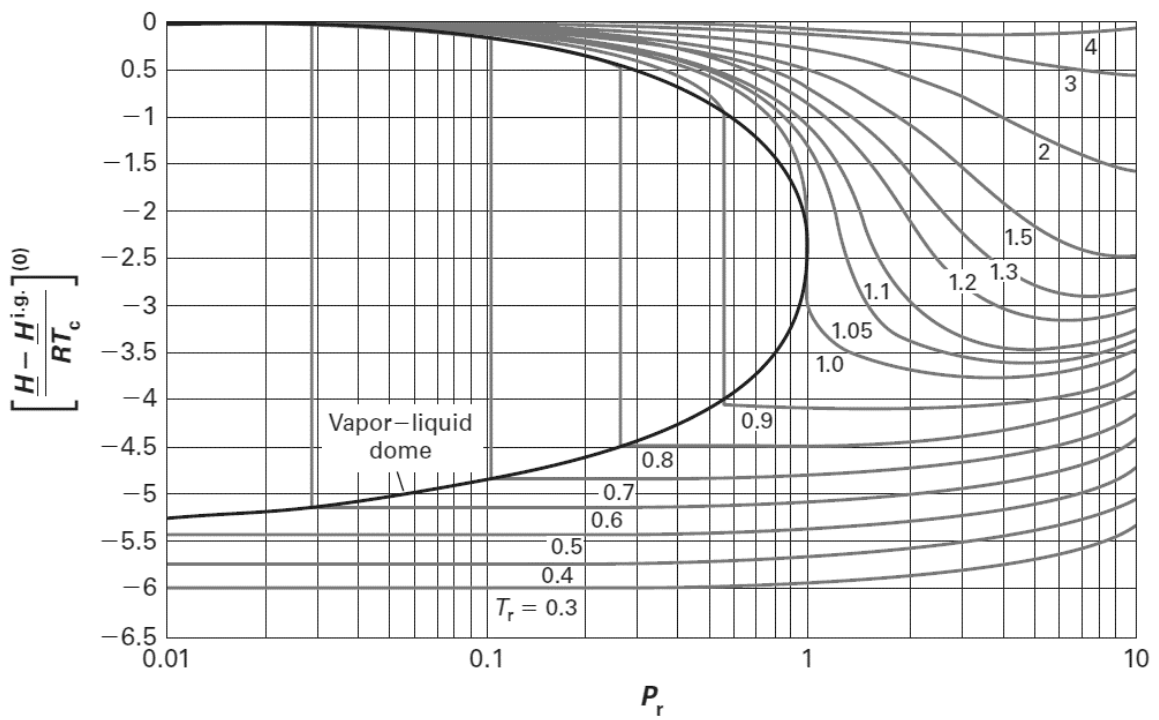
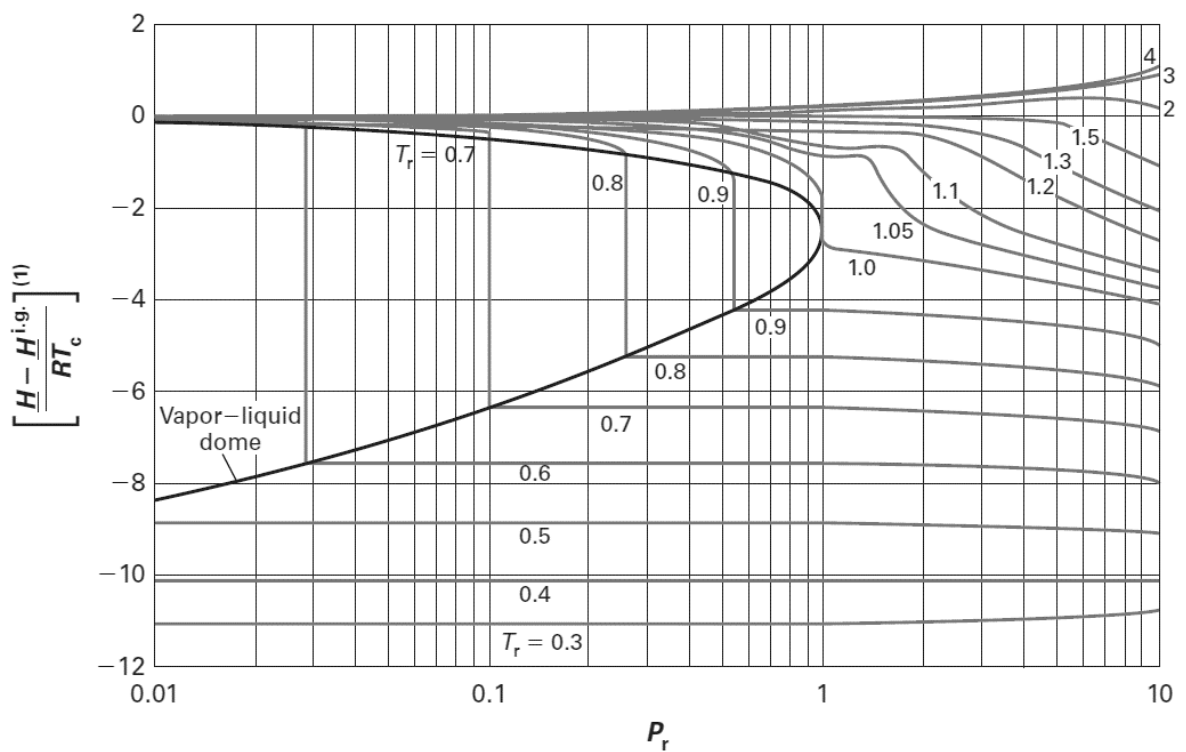


Figure 7 Molar enthalpy residual function for a compound with $\omega = 1$, as determined with the Lee-Kesler equation.



► SOLUTIONS

P.1 → Solution

1.False. Needless to say, the value of Z in the ideal gas law is exactly one.

2.True. The molar volume follows from the ideal gas law,

$$\bar{V} = \frac{RT}{P} = \frac{83.14 \times 393}{8} = \boxed{4080 \text{ cm}^3/\text{mol}}$$

3.False. Solving the virial equation (equation 2) for \bar{V} gives

$$\begin{aligned} \frac{P\bar{V}}{RT} &= 1 + \frac{BP}{RT} \rightarrow \bar{V} = \frac{RT}{P} + B \\ \therefore \bar{V} &= \frac{83.14 \times 393}{8} - 400 = \boxed{3680 \text{ cm}^3/\text{mol}} \end{aligned}$$

4.True. The compressibility factor follows as

$$Z = \frac{P\bar{V}}{RT} = \frac{\bar{V}}{RT/P} = \frac{3680}{4080} = \boxed{0.902}$$

5.True. Inserting our data in the equation in question, equation 3, gives

$$\begin{aligned} \frac{P\bar{V}}{RT} &= 1 + \frac{B}{\bar{V}} + \frac{C}{\bar{V}^2} \rightarrow \frac{8 \times \bar{V}}{83.14 \times 393} = 1 - \frac{400}{\bar{V}} - \frac{26,000}{\bar{V}^2} \\ \therefore 2.44 \times 10^{-4} \bar{V} &= 1 - \frac{400}{\bar{V}} - \frac{26,000}{\bar{V}^2} \end{aligned}$$

This is a cubic equation in \bar{V} , and can be easily solved with the Mathematica code

$$\text{Solve}[2.44 * 10^{-4} v == 1 - 400/v - 26000/v^2, v]$$

This returns two invalid solutions and $\bar{V} \approx 3640 \text{ cm}^3/\text{mol}$, which is the one viable solution.

6.True. The compressibility factor follows as

$$Z = \frac{\bar{V}}{RT/P} = \frac{3640}{4080} = \boxed{0.892}$$

In comparison with the result obtained with the extended virial equation – arguably the most accurate of the three calculations – the result from the ideal gas law is about 12% too high, while the result from the short virial equation is about 1.1% too high.

P.2 → Solution

The molar specific volume of the gas is required in each part of the solution. To evaluate it, we first compute the volume of the cylinder,

$$V = \frac{\pi d^2}{4} L = \frac{\pi \times 0.25^2}{4} \times 1.2 = 0.0589 \text{ m}^3$$

The molar specific volume is then

$$\bar{v} = Mv = M \times \frac{V}{m} = 28 \times \frac{0.0589}{5.0} = 0.330 \text{ m}^3/\text{kmol}$$

The critical properties are $T_c = 133 \text{ K}$ and $P_c = 35 \text{ bar}$. The reduced temperature T_r and the pseudoreduced specific volume v'_R are, respectively,

$$T_r = \frac{200}{133} = 1.50$$

$$v'_R = \frac{\bar{v}P_c}{RT_c} = \frac{0.330 \times (35 \times 10^5)}{8314 \times 133} = 1.04$$

Entering these two quantities onto Figure 2, we read a compressibility factor $Z \approx 0.9$. From the definition of Z , we can solve for pressure, giving

$$Z = \frac{P\bar{v}}{RT} \rightarrow P = \frac{ZRT}{\bar{v}}$$

$$\therefore P = \frac{0.9 \times 8314 \times 200}{0.330} = 4.53 \times 10^6 \text{ Pa} = \boxed{45.3 \text{ bar}}$$

Inserting the data in the ideal gas law gives

$$P = \frac{RT}{\bar{v}} = \frac{8314 \times 200}{0.330} = 5.04 \times 10^6 \text{ Pa} = \boxed{50.4 \text{ bar}}$$

Appealing to the Van der Waals equation (equation 4), we have

$$P = \frac{RT}{\bar{v}-b} - \frac{a}{\bar{v}^2} = \frac{8314 \times 200}{0.330 - 0.0395} \times \frac{1}{10^5} - \frac{1.474}{0.330^2} = \boxed{43.7 \text{ bar}}$$

Factor $1/10^5$ in the first term on the right-hand side is used to convert pressure from Pa to bar. Another way to arrive at the same result is to first compute the compressibility factor

$$Z = \frac{v'_R}{v'_R - 1/8} - \frac{27}{64T_r v'_R} = \frac{1.04}{1.04 - 1/8} - \frac{27}{64 \times 1.50 \times 1.04} = 0.866$$

and then solve for P , giving

$$Z = \frac{P\bar{v}}{RT} \rightarrow P = \frac{ZRT}{\bar{v}}$$

$$\therefore P = \frac{0.866 \times 8314 \times 200}{0.330} \times \frac{1}{10^5} = 43.6 \text{ bar}$$

The slight difference is attributed to roundoff.

Substituting the data in the Redlich-Kwong equation (equation 4) brings to

$$P = \frac{RT}{\bar{v}-b} - \frac{a}{\bar{v}(\bar{v}+b)T^{1/2}}$$

$$\therefore P = \frac{8314 \times 200}{0.330 - 0.02737} \times \frac{1}{10^5} - \frac{17.22}{0.330 \times (0.330 + 0.02737) \times 200^{1/2}} = \boxed{44.6 \text{ bar}}$$

Alternatively, we can compute the compressibility factor

$$Z = \frac{v'_R}{v'_R - 0.08664} - \frac{0.42748}{(v'_R + 0.08664)T_r^{3/2}}$$

$$\therefore Z = \frac{1.04}{1.04 - 0.08664} - \frac{0.42748}{(1.04 + 0.08664) \times 1.5^{3/2}} = 0.884$$

and then solve for P ,

$$Z = \frac{P\bar{v}}{RT} \rightarrow P = \frac{ZRT}{\bar{v}}$$

$$\therefore P = \frac{0.884 \times 8314 \times 200}{0.330} \times \frac{1}{10^5} = 44.5 \text{ bar}$$

Again, the slight difference is due to roundoff. In comparison to the value of the first part, the ideal gas equation of state gives a pressure that is 11.3% higher and the Van der Waals equation gives a value that is 3.5% lower. The result from the Redlich-Kwong equation deviates from the first calculation by only 1.5%. The results are summarized in the following table.

Method	Pressure (bar)
Compressibility chart	45.3
Ideal gas law	50.4
Van der Waals equation	43.7
Redlich-Kwong equation	44.6

P.3 → Solution

From the ideal gas law, we have

$$\bar{v} = \frac{RT}{P} = \frac{0.08206 \times 450}{7.5} = \boxed{4.92 \text{ m}^3/\text{kmol}}$$

The Van der Waals equation (equation 4) is

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

Coefficient a is given by

$$a = \frac{27R^2T_C^2}{64P_C} = \frac{27 \times 0.08206^2 \times 500^2}{64 \times 32} = 22.2 \frac{\text{m}^6 \cdot \text{atm}}{\text{kmol}^2}$$

while b is calculated as

$$b = \frac{RT_C}{8P_C} = \frac{0.08206 \times 500}{8 \times 32} = 0.160 \text{ m}^3/\text{kmol}$$

Inserting $P = 7.5$ atm and other data in the Van der Waals equation brings to

$$7.5 = \frac{0.08206 \times 450}{\bar{V} - 0.160} - \frac{22.2}{\bar{V}^2}$$

This equation can be easily solved with the Mathematica code

$$\text{Solve} \left[7.5 == \frac{0.08206 * 450}{v - 0.16} - 22.2/v^2, v \right]$$

which returns two imaginary solutions and $\bar{V} = 4.44$ m³/kmol, which is the viable result.

The Soave equation (equation 6) is

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

The acentric factor $\omega = 0.45$. We first require factor m ,

$$m = 0.48 + 1.547\omega - 0.176\omega^2 = 0.48 + 1.547 \times 0.45 - 0.176 \times 0.45^2 = 1.14$$

In addition, the reduced temperature $T_r = 450/500 = 0.9$, so that

$$\alpha = \left[1 + m(1 - T_r^{0.5}) \right]^2 = \left[1 + 1.14 \times (1 - 0.9^{0.5}) \right]^2 = 1.12$$

Parameter a_c , in turn, is given by

$$a_c = 0.42747R^2 \frac{T_C^2}{P_C} = 0.42747 \times 0.08206^2 \times \frac{500^2}{32} = 22.5 \frac{\text{m}^6 \cdot \text{atm}}{\text{kmol}^2}$$

so that

$$a = a_c \alpha = 22.5 \times 1.12 = 25.2 \frac{\text{m}^6 \cdot \text{atm}}{\text{kmol}^2}$$

It remains to compute factor b ,

$$b = 0.08664R \frac{T_C}{P_C} = 0.08664 \times 0.08206 \times \frac{500}{32} = 0.111 \text{ m}^3/\text{kmol}$$

Inserting $P = 7.5$ atm and other data in the Soave equation gives

$$7.5 = \frac{0.08206 \times 450}{\bar{V} - 0.111} - \frac{25.2}{\bar{V}(\bar{V} + 0.111)}$$

The equation above can be solved with the Mathematica code

$$\text{Solve} \left[7.5 == \frac{0.08206 * 450}{v - 0.111} - \frac{25.2}{v(v + 0.111)}, v \right]$$

This returns two meaningless solutions and $V = 4.29$ m³/kmol, which is the one feasible result.

The Peng-Robinson equation (equation 7) is

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

The acentric factor $\omega = 0.45$. Before anything else, we compute factor κ ,

$$\kappa = 0.3746 + 1.54226\omega - 0.2699\omega^2$$

$$\therefore \kappa = 0.3746 + 1.54226 \times 0.45 - 0.2699 \times 0.45^2 = 1.01$$

The reduced temperature is $T_r = 450/500 = 0.9$. Coefficient α is determined next,

$$\alpha = \left[1 + \kappa(1 - T_r^{0.5})\right]^2 = \left[1 + 1.01 \times (1 - 0.9^{0.5})\right]^2 = 1.11$$

We also require coefficient a_c ,

$$a_c = 0.457274 \frac{R^2 T_c^2}{P_c} = 0.457274 \times \frac{0.08206^2 \times 500^2}{32} = 24.1 \frac{\text{m}^6 \cdot \text{atm}}{\text{kmol}^2}$$

so that

$$a = a_c \alpha = 24.1 \times 1.11 = 26.8 \frac{\text{m}^6 \cdot \text{atm}}{\text{kmol}^2}$$

Parameter b , in turn, is given by

$$b = 0.0778 \frac{RT_c}{P_c} = 0.0778 \times \frac{0.08206 \times 500}{32} = 0.0998 \text{ m}^3/\text{kmol}$$

Substituting $P = 7.5$ atm and other data in the Peng-Robinson equation, we get

$$7.5 = \frac{0.08206 \times 450}{\bar{V} - 0.0998} - \frac{26.8}{\bar{V}(\bar{V} + 0.0998) + 0.0998(\bar{V} - 0.0998)}$$

As recommended in the previous calculation routines, we can easily solve this with the Mathematica code

$$\text{Solve}\left[7.5 == \frac{0.08206 * 450}{v - 0.0998} - \frac{25.2}{v(v + 0.0998) + 0.0998(v - 0.0998)}, v\right]$$

The one meaningful solution, in this case, is $\bar{V} = 4.29 \text{ m}^3/\text{mol}$.

The reduced pressure is $P_r = P/P_c = 7.5/32 = 0.234$. Mapping this quantity and a reduced temperature $T_r = 0.9$ onto Figure 4, we read $Z^0 = 0.9$. Likewise, we read $Z^1 = -0.06$ from Figure 5. The compressibility factor Z is then

$$Z = Z^0 + \omega Z^1 = 0.9 + 0.45 \times (-0.06) = 0.873$$

The molar volume follows as

$$Z = \frac{P\bar{V}}{RT} \rightarrow \bar{V} = \frac{ZRT}{P}$$

$$\therefore \bar{V} = \frac{0.873 \times 0.08206 \times 450}{7.5} = \boxed{4.30 \text{ m}^3/\text{kmol}}$$

The results obtained with each method are summarized in the following table.

Method	Molar Volume (m ³ /kmol)
Ideal gas law	4.92
Van der Waals	4.44
Soave	4.29
Peng-Robinson	4.29
Lee-Kesler	4.30

P.4 → Solution

Part 1: Using residual properties, the change in internal energy for a process is

$$\bar{U}_2 - \bar{U}_1 = (\bar{U}_2 - \bar{U}_2^{\text{ig}}) + (\bar{U}_2^{\text{ig}} - \bar{U}_1^{\text{ig}}) - (\bar{U}_1 - \bar{U}_1^{\text{ig}})$$

In this particular case, there are two simplifications: (1) the initial state is a vapor at 0.1 bar, therefore it can be assumed to be an ideal gas, with the result that $\bar{U}_1 - \bar{U}_1^{\text{ig}} = 0$; and (2) the process is isothermal and, since internal energy is only a

function of temperature for an ideal gas, $\bar{U}_2^{\text{ig}} - \bar{U}_1^{\text{ig}} = 0$. Accordingly, for this process the equation above simplifies to

$$\bar{U}_2 - \bar{U}_1 = (\bar{U}_2 - \bar{U}_2^{\text{ig}}) + (\bar{U}_2^{\text{ig}} - \bar{U}_1^{\text{ig}}) - (\bar{U}_1 - \bar{U}_1^{\text{ig}}) = (\bar{U}_2 - \bar{U}_2^{\text{ig}})$$

We proceed to compute $(\bar{U}_2 - \bar{U}_2^{\text{ig}})$. Before employing the Peng-Robinson equation, we must calculate a few parameters. The reduced temperature is $T_r = 400/425 = 0.941$. Factor κ follows as

$$\kappa = 0.37464 + 1.54226\omega - 0.269932\omega^2$$

$$\therefore \kappa = 0.37464 + 1.54226 \times 0.2 - 0.269932 \times 0.2^2 = 0.672$$

As for α ,

$$\alpha = \left[1 + \kappa(1 - T_r^{0.5})\right]^2 = \left[1 + 0.672 \times (1 - 0.941^{0.5})\right]^2 = 1.04$$

and a_c ,

$$a_c = 0.45724 \frac{R^2 T_C^2}{P_C} = 0.45724 \times \frac{83.14^2 \times 425^2}{38} = 1.50 \times 10^7 \frac{\text{bar} \cdot \text{cm}^6}{\text{mol}}$$

Combining the two previous results,

$$a = a_c \alpha = (1.50 \times 10^7) \times 1.04 = 1.56 \times 10^7 \frac{\text{bar} \cdot \text{cm}^6}{\text{mol}}$$

Lastly, we compute parameter b ,

$$b = 0.07780 \frac{RT_C}{P_C} = 0.07780 \times \frac{83.14 \times 425}{38} = 72.3 \text{ cm}^3/\text{mol}$$

Inserting our results into the Peng-Robinson equation, we write

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

$$\therefore 15 = \frac{83.14 \times 400}{\bar{V} - 72.3} - \frac{1.56 \times 10^7}{\bar{V}(\bar{V} + 72.3) + 72.3(\bar{V} - 72.3)}$$

The equation above can be easily solved with the Mathematica code

$$\text{Solve}\left[15. == \frac{83.14 * 400}{V - 72.3} - \frac{1.56 * 10^7}{V(V + 72.3) + 72.3(V - 72.3)}, V\right]$$

which returns two meaningless imaginary solutions and $\bar{V} = 1770 \text{ cm}^3/\text{mol}$, which is the one viable solution. Entering this value into the definition of the compressibility factor, we get

$$Z = \frac{P\bar{V}}{RT} = \frac{15 \times 1770}{83.14 \times 400} = 0.798$$

The expression for residual molar internal energy to use is equation 8,

$$\frac{\bar{U}^R}{RT} = - \left\{ \left[\frac{A}{2\sqrt{2}B} \right] \left[1 + \frac{\kappa\sqrt{T_r}}{\sqrt{\alpha}} \right] \ln \left[\frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B} \right] \right\}$$

We have all necessary quantities but coefficients A and B , which are given by

$$A = \frac{aP}{R^2 T^2} = \frac{(1.56 \times 10^7) \times 15}{83.14^2 \times 400^2} = 0.212$$

$$B = \frac{bP}{RT} = \frac{72.3 \times 15}{83.14 \times 400} = 0.0326$$

Finally, \bar{U}^R/RT is calculated to be

$$\frac{\bar{U}^R}{RT} = - \left[\left(\frac{0.212}{2\sqrt{2} \times 0.0326} \right) \times \left(1 + \frac{0.672 \times \sqrt{0.941}}{\sqrt{1.04}} \right) \times \ln \left(\frac{0.798 + 2.41 \times 0.0326}{0.798 - 0.414 \times 0.0326} \right) \right] = -0.418$$

and

$$\bar{U}_2 - \bar{U}_2^{\text{ig}} = -0.418 \times 8.314 \times 400 = -1390 \text{ J/mol}$$

Since $n = 1$ mol, we conclude that

$$\boxed{\Delta U = -1390 \text{ J}}$$

◆ The correct answer is **C**.

Part 2: The procedure to calculate ΔS is quite similar to the one used to compute ΔU . We first expand the molar entropy change $\bar{S}_2 - \bar{S}_1$ as

$$\bar{S}_2 - \bar{S}_1 = (\bar{S}_2 - \bar{S}_2^{\text{ig}}) + (\bar{S}_2^{\text{ig}} - \bar{S}_1^{\text{ig}}) - (\bar{S}_1 - \bar{S}_1^{\text{ig}})$$

However, here, the entropy change is not 0 for the ideal gas process; entropy is a function of P and T , even for an ideal gas. It is true, nevertheless, that we can model the butane at the start of the process as an ideal gas, simplifying the relation above to

$$\begin{aligned} \bar{S}_2 - \bar{S}_1 &= (\bar{S}_2 - \bar{S}_2^{\text{ig}}) + (\bar{S}_2^{\text{ig}} - \bar{S}_1^{\text{ig}}) - (\bar{S}_1 - \bar{S}_1^{\text{ig}}) \\ \therefore \bar{S}_2 - \bar{S}_1 &= (\bar{S}_2 - \bar{S}_2^{\text{ig}}) + (\bar{S}_2^{\text{ig}} - \bar{S}_1^{\text{ig}}) \end{aligned}$$

The expression for residual molar entropy, per the Peng-Robinson model, is equation 10,

$$\frac{\bar{S}^R}{R} = \ln(Z - B) - \left\{ \left[\frac{A}{2\sqrt{2}B} \right] \left[\frac{\kappa\sqrt{T_r}}{\sqrt{\alpha}} \right] \ln \left[\frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B} \right] \right\}$$

All necessary quantities were computed in the previous problem. Substituting, we obtain

$$\begin{aligned} \frac{\bar{S}^R}{R} &= \ln(0.798 - 0.0326) \\ &- \left\{ \left[\frac{0.212}{2\sqrt{2} \times 0.0326} \right] \left[\frac{0.672 \times \sqrt{0.941}}{\sqrt{1.04}} \right] \ln \left[\frac{0.798 + 2.41 \times 0.0326}{0.798 - 0.414 \times 0.0326} \right] \right\} = -0.430 \end{aligned}$$

and

$$\bar{S}_2 - \bar{S}_2^{\text{ig}} = -0.430 \times 8.314 = -3.58 \text{ J/mol} \cdot \text{K}$$

The ideal gas component is determined starting with the relation

$$\begin{aligned} d\bar{S} &= \frac{C_V^*}{T} dT + \frac{R}{\bar{V}} d\bar{V} \\ \therefore \bar{S}_2^{\text{ig}} - \bar{S}_1^{\text{ig}} &= \int_{T=400\text{K}}^{T=400\text{K}} \frac{C_V^*}{T} dT + R \ln \left(\frac{\bar{V}_2}{\bar{V}_1} \right) \end{aligned}$$

Since the upper and lower bounds of the integral are the same, the result is zero and we do not need C_V^* . The equation then simplifies to

$$\begin{aligned} \bar{S}_2^{\text{ig}} - \bar{S}_1^{\text{ig}} &= R \ln(\bar{V}_2/\bar{V}_1) = R \ln \left(\frac{RT_2/P_2}{RT_1/P_1} \right) = R \ln \left(\frac{P_1}{P_2} \right) \\ \therefore \bar{S}_2^{\text{ig}} - \bar{S}_1^{\text{ig}} &= 8.314 \times \ln \left(\frac{0.1}{15} \right) = -41.7 \text{ J/mol} \cdot \text{K} \end{aligned}$$

Returning to $\bar{S}_2 - \bar{S}_1$, we obtain

$$\bar{S}_2 - \bar{S}_1 = -3.58 + (-41.7) = -45.3 \text{ J/mol} \cdot \text{K}$$

Since $n = 1$ mol, we conclude that

$$\boxed{\Delta S = -45.3 \text{ J/K}}$$

◆ The correct answer is **B**.

P.5 → Solution

1.True. At the outset, we compute κ ,

$$\kappa = 0.3746 + 1.54226\omega - 0.2699\omega^2$$

$$\therefore \kappa = 0.3746 + 1.54226 \times 0.264 - 0.2699 \times 0.264^2 = 0.763$$

Factor α follows as

$$\alpha = \left[1 + \kappa(1 - T_r^{0.5})\right]^2 = \left[1 + 0.763 \times (1 - 1.0^{0.5})\right]^2 = 1.0$$

This result becomes obvious if we recall that we are dealing with critical conditions; nevertheless, calculating κ was not a waste of time, as we will need it in upcoming calculations. We proceed to compute parameter a_c ,

$$a_c = 0.45724 \frac{R^2 T_c^2}{P_c} = 0.45724 \times \frac{83.14^2 \times 592^2}{41.1} = 2.70 \times 10^7 \frac{\text{bar} \cdot \text{cm}^6}{\text{mol}^2}$$

Gleaning the previous results, parameter a is found as

$$a = a_c \alpha = (2.70 \times 10^7) \times 1.0 = 2.70 \times 10^7 \frac{\text{bar} \cdot \text{cm}^6}{\text{mol}^2}$$

Parameter b is determined next,

$$b = 0.0778 \frac{RT_c}{P_c} = 0.0778 \times \frac{83.14 \times 592}{41.1} = 93.2 \text{ cm}^3/\text{mol}$$

Writing the Peng-Robinson equation and substituting, we have

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

$$\therefore 41.1 = \frac{83.14 \times 592}{\bar{V} - 93.2} - \frac{2.70 \times 10^7}{\bar{V}(\bar{V} + 93.2) + 93.2(\bar{V} - 93.2)}$$

The equation above can be solved with the Mathematica code

$$\text{Solve} \left[41.1 == \frac{83.14 * 592}{V - 93.2} - \frac{2.7 * 10^7}{V(V + 93.2) + 93.2(V - 93.2)}, V \right]$$

which returns two meaningless solutions and $\bar{V} = 308 \text{ cm}^3/\text{mol}$, which is a feasible result.

2.False. The reduced temperature is now $T_r = 300/592 = 0.507$. Factor κ is dependent on the acentric factor only and continues to be $\kappa = 0.763$. The corresponding α is

$$\alpha = \left[1 + 0.763 \times (1 - 0.507^{0.5})\right]^2 = 1.49$$

Parameter a_c is dependent on absolute quantities only and remains unchanged. Thus,

$$a = a_c \alpha = (2.70 \times 10^7) \times 1.49 = 4.02 \times 10^7 \frac{\text{bar} \cdot \text{cm}^6}{\text{mol}^2}$$

Likewise, parameter b continues to be $93.2 \text{ cm}^3/\text{mol}$. Substituting in the Peng-Robinson equation gives

$$1.0 = \frac{83.14 \times 300}{\bar{V} - 93.2} - \frac{4.02 \times 10^7}{\bar{V}(\bar{V} + 93.2) + 93.2(\bar{V} - 93.2)}$$

This equation can be solved with the Mathematica code

$$\text{Solve} \left[1. == 83.14 * 300 / (V - 93.2) - \frac{4.02 * 10^7}{V(V + 93.2) + 93.2(V - 93.2)}, V \right]$$

which returns $\bar{V} = 107 \text{ cm}^3/\text{mol}$, $\bar{V} = 1410 \text{ cm}^3/\text{mol}$, and $\bar{V} = 23,300 \text{ cm}^3/\text{mol}$. The lowest result is the molar volume of the liquid phase.

3.False. The reduced temperature has changed to $T_r = 500/592 = 0.845$, and factor α becomes

$$\alpha = \left[1 + 0.763 \times (1 - 0.845^{0.5}) \right]^2 = 1.13$$

Thus,

$$a = (2.70 \times 10^7) \times 1.13 = 3.05 \times 10^7 \frac{\text{bar} \cdot \text{cm}^6}{\text{mol}^2}$$

Substituting in the Peng-Robinson equation gives

$$3.0 = \frac{83.14 \times 300}{\bar{V} - 93.2} - \frac{3.05 \times 10^7}{\bar{V}(\bar{V} + 93.2) + 93.2(\bar{V} - 93.2)}$$

The solutions to this equation are $\bar{V} = 150 \text{ cm}^3/\text{mol}$, $\bar{V} = 418 \text{ cm}^3/\text{mol}$, and $\bar{V} = 13,200 \text{ cm}^3/\text{mol}$. The largest result is the vapor solution.

4.True. The change in molar enthalpy determined using residual properties is

$$\bar{H}_2 - \bar{H}_1 = (\bar{H}_2 - \bar{H}_2^{\text{ig}}) + (H_2^{\text{ig}} - H_1^{\text{ig}}) - (\bar{H}_1 - \bar{H}_1^{\text{ig}})$$

We know from the problem statement that state (1) is a liquid and state (2) is a vapor, and we will compute the residual molar enthalpy for each. The expression for molar enthalpy is equation 9,

$$\frac{\bar{H}^R}{RT} = (Z - 1) - \left\{ \left[\frac{A}{2\sqrt{2}B} \right] \left[1 + \frac{\kappa\sqrt{T_r}}{\sqrt{\alpha}} \right] \ln \left[\frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B} \right] \right\}$$

where

$$A = \frac{aP}{R^2T^2} ; B = \frac{bP}{RT}$$

To begin, consider vapor (2) at 500 K and 3 bar. We have $a = 3.05 \times 10^7 \text{ bar} \cdot \text{cm}^6/\text{mol}^2$ and $b = 93.2 \text{ cm}^3/\text{mol}$. Coefficients A and B are calculated to be

$$A = \frac{aP}{R^2T^2} = \frac{(3.05 \times 10^7) \times 3.0}{83.14^2 \times 500^2} = 0.0531$$

$$B = \frac{bP}{RT} = \frac{93.2 \times 3.0}{83.14 \times 500} = 6.66 \times 10^{-3}$$

Now, in part 3, we have specified that the molar volume of the vapor phase in question is $13,200 \text{ cm}^3/\text{mol}$. The compressibility factor is then

$$Z = \frac{P\bar{V}}{RT} = \frac{3.0 \times 13,200}{83.14 \times 500} = 0.953$$

We now have all the information necessary to compute \bar{H}^R . Accordingly,

$$\frac{\bar{H}^R}{RT} = (0.953 - 1) - \left\{ \left[\frac{0.0531}{2\sqrt{2} \times (6.66 \times 10^{-3})} \right] \times \left[1 + \frac{0.763 \times \sqrt{0.845}}{\sqrt{1.13}} \right] \times \ln \left[\frac{0.953 + 2.41 \times (6.66 \times 10^{-3})}{0.953 - 0.414 \times (6.66 \times 10^{-3})} \right] \right\}$$

$$\therefore \frac{\bar{H}^R}{RT} = -0.139$$

and

$$\bar{H}_2^R = -0.139 \times 83.14 \times 500 = -5780 \frac{\text{bar} \cdot \text{cm}^3}{\text{mol}} = -578 \text{ J/mol}$$

Let us proceed to the calculations for the initial state (1) at 300 K and 1 bar. As we have established in part 2, for this state, we have $a = 4.02 \times 10^7 \text{ bar} \cdot \text{cm}^6/\text{mol}^2$ and of course $b = 93.2 \text{ cm}^3/\text{mol}$. Parameters A and B are such that

$$A = \frac{aP}{R^2T^2} = \frac{(4.02 \times 10^7) \times 1.0}{83.14^2 \times 300^2} = 0.0646$$

$$B = \frac{bP}{RT} = \frac{92.3 \times 1.0}{83.14 \times 300} = 3.70 \times 10^{-3}$$

In part 2, we established the molar volume of this state to be 107 cm³/mol. Thus,

$$Z = \frac{P\bar{V}}{RT} = \frac{1.0 \times 107}{83.14 \times 300} = 4.29 \times 10^{-3}$$

We can now determine the residual molar enthalpy for this state,

$$\begin{aligned} \frac{\bar{H}^R}{RT} &= (4.29 \times 10^{-3} - 1) \\ - \left\{ \left[\frac{0.0646}{2\sqrt{2} \times (3.70 \times 10^{-3})} \right] \times \left[1 + \frac{0.763 \times \sqrt{0.507}}{\sqrt{1.49}} \right] \times \ln \left[\frac{4.29 \times 10^{-3} + 2.41 \times (3.70 \times 10^{-3})}{4.29 \times 10^{-3} - 0.414 \times (3.70 \times 10^{-3})} \right] \right\} \\ \therefore \frac{\bar{H}^R}{RT} &= -15.0 \end{aligned}$$

so that

$$\bar{H}^R = -15.0 \times 83.14 \times 300 = -374,000 \frac{\text{bar} \cdot \text{cm}^3}{\text{mol}} = -37,400 \text{ J/mol}$$

This leaves the ideal gas enthalpy change

$$\bar{H}_2^{\text{ig}} - \bar{H}_1^{\text{ig}} = \int_{T_1=300 \text{ K}}^{T_2=500 \text{ K}} C_p^* dT$$

Using coefficients from Table 1, the integral above becomes

$$\bar{H}_2^{\text{ig}} - \bar{H}_1^{\text{ig}} = \int_{300}^{500} 8.314 \left(3.866 + 3.558 \times 10^{-3} T + 13.356 \times 10^{-5} T^2 - 18.659 \times 10^{-8} T^3 + 7.690 \times 10^{-11} T^4 \right) dT = 27,700 \text{ J/mol}$$

Finally, returning to the enthalpy equation,

$$\begin{aligned} \bar{H}_2 - \bar{H}_1 &= (\bar{H}_2 - \bar{H}_2^{\text{ig}}) + (\bar{H}_2^{\text{ig}} - \bar{H}_1^{\text{ig}}) - (\bar{H}_1 - \bar{H}_1^{\text{ig}}) \\ \therefore \bar{H}_2 - \bar{H}_1 &= -577 + 27,700 - (-37,400) = \boxed{64.5 \text{ kJ/mol}} \end{aligned}$$

P.6 → Solution

1.True. To begin, we compute factor κ ,

$$\begin{aligned} \kappa &= 0.3746 + 1.54226\omega - 0.2699\omega^2 \\ \therefore \kappa &= 0.3746 + 1.54226 \times 0.216 - 0.2699 \times 0.216^2 = 0.695 \end{aligned}$$

Factor α is, in turn,

$$\alpha = \left[1 + \kappa(1 - T_r^{0.5}) \right]^2 = \left[1 + 0.695 \times (1 - 1.0^{0.5}) \right]^2 = 1.0$$

This result is expected, since we are dealing with a fluid under critical conditions. Next, parameter a_c is given by

$$\begin{aligned} a_c &= 0.45724 \frac{R^2 T_C^2}{P_C} = 0.45724 \times \frac{(8.314 \times 10^{-5})^2 \times 562^2}{41.1} \\ \therefore a_c &= 2.04 \times 10^{-5} \frac{\text{m}^6 \cdot \text{bar}}{\text{mol}^2} \end{aligned}$$

Combining the two previous results, we have

$$a = a_c \alpha = (2.04 \times 10^{-5}) \times 1.0 = 2.04 \times 10^{-5} \frac{\text{m}^6 \cdot \text{bar}}{\text{mol}^2}$$

We also require parameter b ,

$$b = 0.0778 \frac{RT_C}{P_C} = 0.0778 \times \frac{(8.314 \times 10^{-5}) \times 562}{49.0} = 7.42 \times 10^{-5} \text{ m}^3/\text{mol}$$

Substituting these quantities and $P = 49.0$ bar in the Peng-Robinson equation, it follows that

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

$$49.0 = \frac{(8.314 \times 10^{-5}) \times 562}{\bar{V} - 7.42 \times 10^{-5}} - \frac{2.04 \times 10^{-5}}{\bar{V}[\bar{V} + (7.42 \times 10^{-5})] + (7.42 \times 10^{-5})[\bar{V} - (7.42 \times 10^{-5})]}$$

This equation can be solved for the molar volume \bar{V} , for example by using the Mathematica code

$$\text{Solve} \left[49. == \frac{(8.314 * 10^{-5}) * 562}{V - 7.42 * 10^{-5}} - \frac{2.04 * 10^{-5}}{V(V + 7.42 * 10^{-5}) + 7.42 * 10^{-5}(V - 7.42 * 10^{-5})}, V \right]$$

This returns two imaginary solutions and $V = 2.49 \times 10^{-4}$ m³/mol, which is the one feasible result.

2.False. The temperature and pressure are converted as $T = 278$ K and $P = 1.01$ bar, respectively. The reduced temperature is now $T_r = 278/562 = 0.495$. Factor κ is dependent on the acentric factor only and remains $\kappa = 0.695$. We proceed to determine α ,

$$\alpha = \left[1 + \kappa(1 - T_r^{0.5}) \right]^2 = \left[1 + 0.695 \times (1 - 0.495^{0.5}) \right]^2 = 1.45$$

Since a_c is dependent on the ideal gas constant and critical quantities T_c and P_c , we still have $a_c = 2.04 \times 10^{-5}$ m⁶·bar/mol². Coefficient a is determined next,

$$a = a_c \alpha = (2.04 \times 10^{-5}) \times 1.45 = 2.96 \times 10^{-5} \frac{\text{m}^6 \cdot \text{bar}}{\text{mol}^2}$$

Coefficient b is also dependent on unchanged quantities only, so that $b = 7.42 \times 10^{-5}$ m³/mol as before. Inserting our data in the Peng-Robinson equation brings to

$$1.01 = \frac{(8.314 \times 10^{-5}) \times 278}{\bar{V} - 7.42 \times 10^{-5}} - \frac{2.96 \times 10^{-5}}{(\bar{V} + 7.42 \times 10^{-5}) + 7.42 \times 10^{-5}(\bar{V} - 7.42 \times 10^{-5})}$$

The equation can be solved with the Mathematica code

$$\text{Solve} \left[1.01 == \frac{8.314 * 10^{-5} * 278}{V - 7.42 * 10^{-5}} - \frac{2.96 * 10^{-5}}{V(V + 7.42 * 10^{-5}) + 7.42 * 10^{-5}(V - 7.42 * 10^{-5})}, V \right]$$

which returns $\bar{V} = 8.55 \times 10^{-5}$ m³/mol, $\bar{V} = 0.00111$ m³/mol, and $\bar{V} = 0.0216$ m³/mol. Since we are dealing with a compound in the liquid phase, the molar volume is most likely the lowest result, $\bar{V} = 8.55 \times 10^{-5}$ m³/mol.

3.True. The temperature and pressure are converted as $T = 444$ K and $P = 4.05$ bar, respectively. The reduced temperature has changed to $T_r = 444/562 = 0.790$. Factor κ remains unchanged, and α follows as

$$\alpha = \left[1 + \kappa(1 - T_r^{0.5}) \right]^2 = \left[1 + 0.695 \times (1 - 0.790^{0.5}) \right]^2 = 1.16$$

Parameter $a_c = 2.04 \times 10^{-5}$ m⁶·bar/mol² as before. Thus,

$$a = a_c \alpha = (2.04 \times 10^{-5}) \times 1.16 = 2.37 \times 10^{-5} \frac{\text{m}^6 \cdot \text{bar}}{\text{mol}^2}$$

In addition, $b = 7.42 \times 10^{-5}$ m³/mol is unaltered. Inserting our data in the Peng-Robinson equation brings to

$$4.05 = \frac{(8.314 \times 10^{-5}) \times 444}{\bar{V} - 7.42 \times 10^{-5}} - \frac{2.37 \times 10^{-5}}{\bar{V}(\bar{V} + 7.42 \times 10^{-5}) + 7.42 \times 10^{-5}(\bar{V} - 7.42 \times 10^{-5})}$$

The equation can be solved with the Mathematica code

$$\text{Solve } \left[4.05 = \frac{(8.314 * 10^{-5}) * 444}{V - 7.42 * 10^{-5}} - \frac{2.37 * 10^{-5}}{V(V + 7.42 * 10^{-5}) + 7.42 * 10^{-5}(V - 7.42 * 10^{-5})}, V \right]$$

which returns $\bar{V} = 1.09 \times 10^{-4} \text{ m}^3/\text{mol}$, $\bar{V} = 4.11 \times 10^{-4} \text{ m}^3/\text{mol}$, and $\bar{V} = 8.52 \times 10^{-3} \text{ m}^3/\text{mol}$. Since we are dealing with a vapor phase, the correct molar volume is most likely the highest result, $\bar{V} = 8.52 \times 10^{-3} \text{ m}^3/\text{mol}$.

4.False. The difference of molar enthalpies can be expanded as

$$\bar{H}_2 - \bar{H}_1 = (\bar{H}_2 - \bar{H}_2^{\text{ig}}) + (\bar{H}_2^{\text{ig}} - \bar{H}_1^{\text{ig}}) - (\bar{H}_1 - \bar{H}_1^{\text{ig}})$$

Reading enthalpy residuals from Figures 6 and 7, we have, using the Lee-Kesler equation,

$$\frac{(\bar{H}_1 - \bar{H}_1^{\text{ig}})}{RT_C} = \left[\frac{\bar{H} - \bar{H}_{\text{ig}}}{RT_C} \right]^0 + \omega \left[\frac{\bar{H} - \bar{H}_{\text{ig}}}{RT_C} \right]^1 = -5.5 + 0.216 \times (-8.9) = -7.42$$

with the result that

$$\bar{H}_1 - \bar{H}_1^{\text{ig}} = -7.42 \times 8.314 \times 562 = -34,700 \text{ J/mol}$$

Proceeding similarly with $\bar{H}_2 - \bar{H}_2^{\text{ig}}$ gives

$$\frac{(\bar{H}_2 - \bar{H}_2^{\text{ig}})}{RT_C} = \left[\frac{\bar{H} - \bar{H}_{\text{ig}}}{RT_C} \right]^0 + \omega \left[\frac{\bar{H} - \bar{H}_{\text{ig}}}{RT_C} \right]^1 = -0.14 + 0.216 \times (-0.2) = -0.183$$

so that

$$\bar{H}_2 - \bar{H}_2^{\text{ig}} = -0.183 \times 8.314 \times 562 = -855 \text{ J/mol}$$

It remains to compute $\bar{H}_2^{\text{ig}} - \bar{H}_1^{\text{ig}}$, which is given by

$$\bar{H}_2^{\text{ig}} - \bar{H}_1^{\text{ig}} = \int C_p^* dT$$

Using coefficients from Table 1, the integral above becomes

$$\bar{H}_2^{\text{ig}} - \bar{H}_1^{\text{ig}} = \int_{278}^{444} 8.314 \left(3.551 - 6.184 \times 10^{-3} T + 14.365 \times 10^{-5} T^2 - 19.807 \times 10^{-8} T^3 + 8.234 \times 10^{-11} T^4 \right) dT = 16,700 \text{ J/mol}$$

Substituting in the first equation, the change in molar enthalpy is calculated to be

$$\bar{H}_2 - \bar{H}_1 = -855 + 16,700 - (-34,700) = \boxed{50.5 \text{ kJ/mol}}$$

P.7 → Solution

Part 1: The typical energy balance for a turbine is

$$\frac{\dot{W}_{s,rev}}{\eta} = \bar{H}_2 - \bar{H}_1$$

Using residuals, the equation becomes

$$\frac{\dot{W}_{s,rev}}{\eta} = (\bar{H}_2 - \bar{H}_2^{\text{ig}}) + (\bar{H}_2^{\text{ig}} - \bar{H}_1^{\text{ig}}) - (\bar{H}_1 - \bar{H}_1^{\text{ig}})$$

The ideal gas change in enthalpy is straightforwardly obtained as

$$\bar{H}_2^{\text{ig}} - \bar{H}_1^{\text{ig}} = \int_{600}^{450} C_p^* dT = 8R(450 - 600) = -9980 \text{ J/mol}$$

The residual molar enthalpy, per the Peng–Robinson model, is given by equation 9,

$$\frac{\bar{H}^R}{RT} = (Z - 1) - \left\{ \left[\frac{A}{2\sqrt{2}B} \right] \left[1 + \frac{\kappa\sqrt{T_r}}{\sqrt{\alpha}} \right] \ln \left[\frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B} \right] \right\} \quad (\text{I})$$

Before we proceed, we must calculate some of the parameters in the equation above. Consider the initial state of the compound, which enters the turbine at $T = 600$ K and $P = 10$ bar. Given the acentric factor $\omega = 0.25$, we begin by computing factor κ ,

$$\kappa = 0.37464 + 1.54226\omega - 0.269932\omega^2$$

$$\therefore \kappa = 0.37464 + 1.54226 \times 0.25 - 0.269932 \times 0.25^2 = 0.743$$

The reduced temperature is $T_r = 600/800 = 0.75$. Factor α is determined next,

$$\alpha = \left[1 + \kappa(1 - T_r^{0.5})\right]^2 = \left[1 + 0.743 \times (1 - 0.75^{0.5})\right]^2 = 1.21$$

We also need a_c ,

$$a_c = 0.45724 \frac{R^2 T_c^2}{P_c} = 0.45724 \times \frac{83.14^2 \times 800^2}{45} = 4.50 \times 10^7 \frac{\text{bar} \cdot \text{cm}^6}{\text{mol}^2}$$

so that

$$a = a_c \alpha = (4.50 \times 10^7) \times 1.21 = 5.45 \times 10^7 \frac{\text{bar} \cdot \text{cm}^6}{\text{mol}^2}$$

Parameter b is, in turn,

$$b = 0.0778 \frac{RT_c}{P_c} = 0.0778 \times \frac{83.14 \times 800}{45} = 115 \text{ cm}^3/\text{mol}$$

Lastly, we resort to the Peng-Robinson equation,

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

$$\therefore 10 = \frac{83.14 \times 600}{\bar{V} - 115} - \frac{5.45 \times 10^7}{\bar{V}(\bar{V} + 115) + 115(\bar{V} - 115)}$$

The equation above has three solutions: 159, 928, and 3790 cm³/mol. Since the entering fluid is a vapor, the pertinent value is the largest one, $\bar{V} = 3790$ cm³/mol. Having obtained the molar volume, we can establish the compressibility factor,

$$Z_1 = \frac{P_1 \bar{V}_1}{RT_1} = \frac{10 \times 3790}{83.14 \times 600} = 0.760$$

We can also determine parameters A and B ,

$$A = \frac{aP}{R^2 T^2} = \frac{(5.45 \times 10^7) \times 10}{83.14^2 \times 600^2} = 0.219$$

$$B = \frac{bP}{RT} = \frac{115 \times 10}{83.14 \times 600} = 0.0231$$

We now have all the information needed to compute \bar{H}^R using equation (I),

$$\frac{\bar{H}^R}{RT} = (0.760 - 1) - \left\{ \left[\frac{0.219}{2\sqrt{2} \times 0.0231} \right] \left[1 + \frac{0.743 \times \sqrt{0.75}}{\sqrt{1.21}} \right] \ln \left[\frac{0.760 + 2.41 \times 0.0231}{0.760 - 0.414 \times 0.0231} \right] \right\} = -0.683$$

Solving for \bar{H}^R gives

$$\bar{H}_1 - \bar{H}_1^{\text{ig}} = -0.683 \times 8.314 \times 600 = -3410 \text{ J/mol}$$

It remains to compute $\bar{H}_2 - \bar{H}_2^{\text{ig}}$. Since the pressure of the outlet gas is quite low (0.75 bar), we might suggest that it is an ideal gas. But the fluid is a liquid-vapor mixture and only the vapor can be modeled as an ideal gas. Conveniently, the intensive properties of VLE mixtures can be computed as a weighted average of the properties of the individual phases, or

$$\bar{H}_2^R = q\bar{H}^{R,V} + (1 - q)\bar{H}^{R,L}$$

Modeling the vapor as an ideal gas, its residual molar enthalpy (and all residual properties) is 0. This leaves

$$\bar{H}_2 - \bar{H}_2^{\text{ig}} = 0.03\bar{H}^{R,L}$$

At $P = 0.75$ bar and $T = 450$ K, we appeal to the Peng-Robinson model a second time, with the following results,

$$\kappa = 0.743$$

$$T_r = \frac{T}{T_c} = \frac{450}{800} = 0.563$$

$$\alpha = \left[1 + \kappa(1 - T_r^{0.5})\right]^2 = \left[1 + 0.743 \times (1 - 0.563^{0.5})\right]^2 = 1.41$$

$$a_c = 0.45724 \frac{R^2 T_c^2}{P_c} = 0.45724 \times \frac{83.14^2 \times 800^2}{45} = 4.50 \times 10^7 \frac{\text{bar} \cdot \text{cm}^6}{\text{mol}^2}$$

$$a = a_c \alpha = (4.50 \times 10^7) \times 1.41 = 6.35 \times 10^7 \frac{\text{bar} \cdot \text{cm}^6}{\text{mol}^2}$$

$$b = 0.0778 \frac{R T_c}{P_c} = 0.0778 \times \frac{83.14 \times 800}{45} = 115 \text{ cm}^3/\text{mol}$$

Referring to the Peng-Robinson equation, we have

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

$$\therefore 0.75 = \frac{83.14 \times 450}{\bar{V} - 115} - \frac{6.35 \times 10^7}{\bar{V}(\bar{V} + 115) + 115(\bar{V} - 115)}$$

The equation above has solutions $\bar{V} = 137 \text{ cm}^3/\text{mol}$, $\bar{V} = 1380 \text{ cm}^3/\text{mol}$, and $\bar{V} = 48,300 \text{ cm}^3/\text{mol}$. Since we are modeling a liquid, we take the molar volume to be the lowest result, $\bar{V} = 137 \text{ cm}^3/\text{mol}$. We proceed to compute the compressibility factor,

$$Z_2 = \frac{P_2 \bar{V}_2}{RT_2} = \frac{0.75 \times 137}{83.14 \times 450} = 2.75 \times 10^{-3}$$

In sequence, parameters A and B are

$$A = \frac{aP}{R^2 T^2} = \frac{(6.35 \times 10^7) \times 0.75}{83.14^2 \times 450^2} = 0.0340$$

$$B = \frac{bP}{RT} = \frac{115 \times 0.75}{83.14 \times 450} = 2.31 \times 10^{-3}$$

We now have all the information needed to compute $\bar{H}_2^{R,L}$,

$$\frac{\bar{H}^R}{RT} = (2.75 \times 10^{-3} - 1)$$

$$-\left\{ \left[\frac{0.0340}{2\sqrt{2} \times (2.31 \times 10^{-3})} \right] \left[1 + \frac{0.743 \times \sqrt{0.563}}{\sqrt{1.41}} \right] \ln \left[\frac{2.75 \times 10^{-3} + 2.41 \times (2.31 \times 10^{-3})}{2.75 \times 10^{-3} - 0.414 \times (2.31 \times 10^{-3})} \right] \right\} = -12.7$$

so that

$$\bar{H}_2^{R,L} = -12.7 \times 8.314 \times 450 = -47,500 \text{ J/mol}$$

and

$$\bar{H}_2 - \bar{H}_2^{\text{ig}} = 0.03\bar{H}^{R,L} = 0.03 \times (-47,500) = -1430 \text{ J/mol}$$

Returning to the energy balance, we write

$$\frac{\dot{W}_{s,\text{rev}}}{\dot{n}} = (\bar{H}_2 - \bar{H}_2^{\text{ig}}) + (\bar{H}_2^{\text{ig}} - \bar{H}_1^{\text{ig}}) - (\bar{H}_1 - \bar{H}_1^{\text{ig}})$$

$$\therefore \frac{\dot{W}_{s,\text{rev}}}{\dot{n}} = -1430 + (-9980) - (-3410) = -8000 \text{ J/mol}$$

Finally,

$$\dot{W}_{s,\text{rev}} = 10 \times (-8000) = \boxed{-80.0 \text{ kJ/s}}$$

◆ The correct answer is **B**.

Part 2: The typical energy The rate of entropy generation, \dot{S}_{gen} , can be estimated by applying an entropy balance to the turbine,

$$0 = \dot{m}_{in} \hat{S}_{in} - \dot{m}_{out} \hat{S}_{out} + \dot{S}_{gen}$$

On a molar basis,

$$0 = \dot{n}(\bar{S}_1 - \bar{S}_2) + \dot{S}_{gen}$$

$$\therefore \dot{S}_{gen} = \dot{n}(\bar{S}_2 - \bar{S}_1) \quad (\text{II})$$

Introducing residuals, we write

$$\bar{S}_2 - \bar{S}_1 = (\bar{S}_2 - \bar{S}_2^{\text{ig}}) + (\bar{S}_2^{\text{ig}} - \bar{S}_1^{\text{ig}}) - (\bar{S}_1 - \bar{S}_1^{\text{ig}})$$

Since C_p^* is constant, the ideal gas portion can be found with the usual equation

$$\bar{S}_2^{\text{ig}} - \bar{S}_1^{\text{ig}} = C_p^* \ln\left(\frac{T_2}{T_1}\right) - R \ln\left(\frac{P_2}{P_1}\right)$$

$$\therefore \bar{S}_2^{\text{ig}} - \bar{S}_1^{\text{ig}} = (8 \times 8.314) \times \ln\left(\frac{450}{600}\right) - 8.314 \times \ln\left(\frac{0.75}{10}\right) = 2.40 \text{ J/mol}$$

The residual entropy per the Peng-Robinson model is given by equation 10,

$$\frac{\bar{S}^R}{R} = \ln(Z - B) - \left\{ \left[\frac{A}{2\sqrt{2}B} \right] \left[\frac{\kappa\sqrt{T_r}}{\sqrt{\alpha}} \right] \ln \left[\frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B} \right] \right\}$$

All parameters on the right-hand side have been calculated in the previous part. For state 1,

$$\frac{\bar{S}^R}{R} = \ln(0.760 - 0.0231)$$

$$- \left[\left(\frac{0.219}{2\sqrt{2} \times 0.0231} \right) \left(\frac{0.743 \times \sqrt{0.75}}{\sqrt{1.21}} \right) \ln \left(\frac{0.760 + 2.41 \times 0.0231}{0.760 - 0.414 \times 0.0231} \right) \right]$$

$$\therefore \frac{\bar{S}^R}{R} = -0.469$$

with the result that

$$\bar{S}_1 - \bar{S}_1^{\text{ig}} = -0.469 \times 8.314 = -3.90 \text{ J/mol} \cdot \text{K}$$

Proceeding similarly with stage 2, we obtain

$$\frac{\bar{S}^R}{R} = \ln(2.75 \times 10^{-3} - 2.31 \times 10^{-3})$$

$$- \left\{ \left[\frac{0.0340}{2\sqrt{2} \times (2.31 \times 10^{-3})} \right] \left[\frac{0.743 \times \sqrt{0.563}}{\sqrt{1.41}} \right] \ln \left[\frac{2.75 \times 10^{-3} + 2.41 \times (2.31 \times 10^{-3})}{2.75 \times 10^{-3} - 0.414 \times (2.31 \times 10^{-3})} \right] \right\}$$

$$\therefore \frac{\bar{S}^R}{R} = -11.5$$

so that

$$\frac{\bar{S}_2 - \bar{S}_2^{\text{ig}}}{R} = 0.03 \frac{\bar{S}_2^{R,L}}{R} = 0.03 \times (-11.5)$$

$$\therefore \bar{S}_2 - \bar{S}_2^{\text{ig}} = -2.87 \text{ J/mol} \cdot \text{K}$$

Combining the individual terms gives

$$\bar{S}_2 - \bar{S}_1 = (\bar{S}_2 - \bar{S}_2^{\text{ig}}) + (\bar{S}_2^{\text{ig}} - \bar{S}_1^{\text{ig}}) - (\bar{S}_1 - \bar{S}_1^{\text{ig}})$$

$$\therefore \bar{S}_2 - \bar{S}_1 = -2.87 + 2.40 - (-3.90) = 3.43 \text{ J/mol} \cdot \text{K}$$

Finally, substituting into equation (II) gives the rate of entropy generation,

$$\dot{S}_{\text{gen}} = 10 \times 3.43 = \boxed{34.3 \text{ J}/(\text{K} \cdot \text{s})}$$

◆ The correct answer is **B**.

Part 3: A reversible turbine with the same outlet pressure would have zero entropy generation; in mathematical terms,

$$\bar{S}_2 - \bar{S}_1 = (\bar{S}_2 - \bar{S}_2^{\text{ig}}) + (\bar{S}_2^{\text{ig}} - \bar{S}_1^{\text{ig}}) - (\bar{S}_1 - \bar{S}_1^{\text{ig}}) = 0$$

The reversible turbine has the same inlet stream as the actual turbine, so the residual for the inlet stream is as calculated in part 2. Assuming the stream leaving the reversible turbine is a VLE mixture, it will be at 450 K. Consequently, the ideal gas entropy change is also the same as it was in part 2. Thus,

$$(\bar{S}_2 - \bar{S}_2^{\text{ig}}) + 2.40 - (-3.90) = 0$$

$$\therefore (\bar{S}_2 - \bar{S}_2^{\text{ig}}) = -6.30 \text{ J/mol} \cdot \text{K}$$

The residual entropy of the VLE mixture is

$$(\bar{S}_2 - \bar{S}_2^{\text{ig}}) = q\bar{S}^{R,V} + (1-q)\bar{S}^{R,L}$$

We are still modeling the vapor as an ideal gas, so its residual entropy is 0. The residual entropy of the saturated liquid was calculated in part 2. Accordingly,

$$-6.30 = q \times 0 + (1-q) \times (-11.5R)$$

$$\therefore q = 0.934$$

The fluid leaving the reversible turbine is 93.4% vapor. Returning to the enthalpy balance for a turbine,

$$\frac{\dot{W}_{s,\text{rev}}}{\dot{n}} = (\bar{H}_2 - \bar{H}_2^{\text{ig}}) + (\bar{H}_2^{\text{ig}} - \bar{H}_1^{\text{ig}}) - (\bar{H}_1 - \bar{H}_1^{\text{ig}})$$

the only difference between this and the energy balance in part 1 is the quality of stream 2, for which we write

$$\bar{H}_2 - \bar{H}_2^{\text{ig}} = (1-0.934)\bar{H}^{R,L} = (1-0.934) \times (-47,500) = -3140 \text{ J/mol}$$

so that

$$\frac{\dot{W}_{s,\text{rev}}}{\dot{n}} = -3140 + (-9980) - (-3410) = -9710 \text{ J/mol}$$

From part 1, $\dot{W}_{s,\text{rev}}/\dot{n} = 8000 \text{ J/mol}$. The efficiency of the engine is then

$$\eta = \frac{8000}{9710} = \boxed{0.824}$$

◆ The correct answer is **D**.

▶ REFERENCES

- DAHM, K. and VISCO, D. (2015). *Fundamentals of Chemical Engineering Thermodynamics*. Stamford: Cengage Learning.
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- SMITH, J., VAN NESS, H., and ABBOTT, M. (2004). *Introduction to Chemical Engineering Thermodynamics*. 7th edition. New York: McGraw-Hill.



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