

Montogue

QUIZ CE102

Vapor Pressure and Fugacity

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► PROBLEMS

► Problem 1 (Dahm & Visco, 2015, w/ permission)

Estimate the vapor pressure of ethanol at temperatures of 0, 50, 100, and 150°C using the Antoine equation, the Clausius-Clapeyron equation, and the shortcut equation.

Equation	P^{sat} (bar) at 0°C	P^{sat} (bar) at 50°C	P^{sat} (bar) at 100°C	P^{sat} (bar) at 150°C
Antoine				
Clausius-Clapeyron				
Shortcut				

► Problem 2 (Dahm & Visco, 2004, w/ permission)

Estimate the boiling points of 1-propanol at pressures of $P = 0.1, 0.5, 1,$ and 5 bar, using the Antoine equation, the Clausius-Clapeyron equation, and the shortcut equation. Use $\Delta H^{\text{vap}} = 41.44$ kJ/mol.

Equation	T_b (°C) at 0.1 bar	T_b (°C) at 0.5 bar	T_b (°C) at 1 bar	T_b (°C) at 5 bar
Antoine				
Clausius-Clapeyron				
Shortcut				

→ Problem 3.1 (Dahm & Visco, 2004, w/ permission)

For ethanol, make a graph that compares the vapor pressure versus temperature predictions obtained from the Antoine and shortcut equations over the entire region $0.5 < T_r < 1.0$.

→ Problem 3.2

Repeat the previous problem for acetone.

► Problem 4 (Smith et al., 2004, w/ permission)

Determine the fugacity of sulfur dioxide (SO_2) at 600 K and 300 bar. Use equation 4.

- A) $f = 104.5$ bar
- B) $f = 156.3$ bar
- C) $f = 217.3$ bar
- D) $f = 275.2$ bar

→ Problem 5.1 (Smith et al., 2004, w/ permission)

Estimate the fugacity of isobutylene as a gas at 280°C and 20 bar. Use equation 4.

- A) $f = 5.089$ bar
- B) $f = 8.112$ bar
- C) $f = 11.53$ bar
- D) $f = 18.76$ bar

→ Problem 5.2

Estimate the fugacity of isobutylene as a gas at 280°C and 100 bar. Use equation 4.

- A) $f = 38.92$ bar
- B) $f = 51.25$ bar
- C) $f = 73.10$ bar
- D) $f = 91.14$ bar

→ Problem 6.1 (Smith et al., 2004, w/ permission)

Using equation 5, estimate the fugacity of *n*-pentane at its normal-boiling-point temperature and 200 bar. The saturated molar volume can be estimated with equation 6. In addition to the data given in Table 2, use the following information.

Compound	Normal Boiling Point (K)	Critical Molar Volume (cm ³ /mol)	Critical Compressibility Factor
<i>n</i> -Pentane	309.2	313.0	0.270

- A) $f = 1.042$ bar
- B) $f = 2.444$ bar
- C) $f = 3.818$ bar
- D) $f = 5.011$ bar

→ Problem 6.2

Using equation 5, estimate the fugacity of isobutylene at its normal-boiling-point temperature and 200 bar. The saturated molar volume can be estimated with equation 6. In addition to the data given in Table 2, use the following information.

Compound	Normal Boiling Point (K)	Critical Molar Volume (cm ³ /mol)	Critical Compressibility Factor
Isobutylene	266.3	238.9	0.275

- A) $f = 0.6711$ bar
- B) $f = 1.106$ bar
- C) $f = 2.202$ bar
- D) $f = 3.405$ bar

→ Problem 6.3

Using equation 5, estimate the fugacity of 1-butene at its normal-boiling-point temperature and 200 bar. The saturated molar volume can be estimated with equation 6. In addition to the data given in Table 2, use the following information.

Compound	Normal Boiling Point (K)	Critical Molar Volume (cm ³ /mol)	Critical Compressibility Factor
1-Butene	266.9	239.3	0.277

- A) $f = 0.4982$ bar
- B) $f = 1.088$ bar
- C) $f = 2.208$ bar
- D) $f = 3.623$ bar

► Problem 7 (Smith et al., 2004, w/ permission)

Assuming that equation 5 is valid for the vapor phase and that the molar volume of saturated liquid is given by equation 6, prepare plots of fugacity (f) versus pressure and of fugacity coefficient (ϕ) versus pressure for chloroform at 200°C in the pressure range of 0 to 40 bar. In addition to the data given in Table 2, use the following information.

Compound	Normal Boiling Point (K)	Critical Molar Volume (cm ³ /mol)	Critical Compressibility Factor
Chloroform	334.3	239.0	0.293

► **Problem 8** (Dahm & Visco, 2015, w/ permission)

Suppose we have a compound whose vapor phase can be described by the EOS

$$\bar{V} = \frac{RT}{P} + aP^2$$

where $a = 0.01 \text{ L/bar}^2\cdot\text{mol}$. Find a general expression for the fugacity of this compound as a function of T and P . What is the fugacity of this compound at $T = 500 \text{ K}$ and $P = 5 \text{ bar}$?

- A) $f = 5.05 \text{ bar}$
- B) $f = 6.88 \text{ bar}$
- C) $f = 8.21 \text{ bar}$
- D) $f = 9.03 \text{ bar}$

► **Problem 9** (Dahm & Visco, 2015, w/ permission)

This problem involves a compound whose vapor phase can be described by the EOS

$$\bar{V} = \frac{RT}{P} + aTP^2$$

where $a = 0.3 \text{ cm}^3/\text{mol}\cdot\text{bar}^2\cdot\text{K}$. This compound has vapor pressures of $p^{\text{sat}} = 0.5 \text{ bar}$ at $T = 50^\circ\text{C}$ and $P = 5.0 \text{ bar}$ at $T = 100^\circ\text{C}$. Saturated liquid at both $T = 50^\circ\text{C}$ and $T = 100^\circ\text{C}$ has $\bar{V} = 125 \text{ cm}^3/\text{mol}$. True or false?

- 1. () The fugacity in the vapor phase at $T = 50^\circ\text{C}$ and $P = 0.1 \text{ bar}$ is greater than 0.2 bar .
- 2. () The fugacity in the liquid phase at $T = 50^\circ\text{C}$ and $P = 100 \text{ bar}$ is greater than 0.72 bar .
- 3. () The fugacity in the vapor phase at $T = 100^\circ\text{C}$ and $P = 3 \text{ bar}$ is greater than 3.25 bar .
- 4. () The fugacity in the liquid phase at $T = 100^\circ\text{C}$ and $P = 100 \text{ bar}$ is greater than 9 bar .

► **Problem 10** (Dahm & Visco, 2015, w/ permission)

Regarding propylene, are the following statements true or false? Use the Peng-Robinson equation of state.

- 1. () The vapor pressure at $T = 25^\circ\text{C}$ is greater than 10 bar .
- 2. () The fugacity of saturated liquid at $T = 25^\circ\text{C}$ is greater than 8 bar .
- 3. () The normal boiling point is greater than 250 K .

→ **Problem 11.1** (Dahm & Visco, 2015, w/ permission)

Using the shortcut equation, estimate the vapor pressure of benzene at 400 K . Then, using the Peng-Robinson model, estimate the fugacity of benzene in the vapor phase at $T = 400 \text{ K}$ and $P = 100 \text{ bar}$.

- A) $p^{\text{sat}} = 2.23 \text{ bar}$ and $f = 1.98 \text{ bar}$
- B) $p^{\text{sat}} = 2.23 \text{ bar}$ and $f = 3.30 \text{ bar}$
- C) $p^{\text{sat}} = 3.54 \text{ bar}$ and $f = 1.98 \text{ bar}$
- D) $p^{\text{sat}} = 3.54 \text{ bar}$ and $f = 3.30 \text{ bar}$

→ **Problem 11.2**

Using the shortcut equation, estimate the vapor pressure of hexane at 400 K . Then, using the Peng-Robinson model, estimate the fugacity of hexane in the vapor phase at $T = 400 \text{ K}$ and $P = 100 \text{ bar}$.

- A) $p^{\text{sat}} = 2.18 \text{ bar}$ and $f = 1.86 \text{ bar}$
- B) $p^{\text{sat}} = 2.18 \text{ bar}$ and $f = 4.09 \text{ bar}$
- C) $p^{\text{sat}} = 4.63 \text{ bar}$ and $f = 1.86 \text{ bar}$
- D) $p^{\text{sat}} = 4.63 \text{ bar}$ and $f = 4.09 \text{ bar}$

→ **Problem 11.3**

Using the shortcut equation, estimate the vapor pressure of phenol at 400 K . Then, using the Peng-Robinson model, estimate the fugacity of phenol in the vapor phase at $T = 400 \text{ K}$ and $P = 100 \text{ bar}$.

- A) $p^{\text{sat}} = 0.203 \text{ bar}$ and $f = 0.203 \text{ bar}$
- B) $p^{\text{sat}} = 0.203 \text{ bar}$ and $f = 2.08 \text{ bar}$
- C) $p^{\text{sat}} = 2.35 \text{ bar}$ and $f = 0.203 \text{ bar}$
- D) $p^{\text{sat}} = 2.35 \text{ bar}$ and $f = 2.08 \text{ bar}$

► Problem 12

Using equation 10, determine the fugacity coefficients for a chlorine (1)/chloroform (2) mixture at 250 K and 32 bar if the mixture contains 35 mol% Cl₂. Experimental virial coefficients were found to be $B_{11} = -38$, $B_{22} = -100.1$, and $B_{12} = -58.6$ cm³/mol.

- A) $\hat{\phi}_1 = 0.774$ and $\hat{\phi}_2 = 0.861$
 B) $\hat{\phi}_1 = 0.774$ and $\hat{\phi}_2 = 0.994$
 C) $\hat{\phi}_1 = 0.956$ and $\hat{\phi}_2 = 0.861$
 D) $\hat{\phi}_1 = 0.956$ and $\hat{\phi}_2 = 0.994$

► Problem 13 (Smith et al., 2004, w/ permission)

For the system ethylene (1) + propylene (2) as a gas, estimate the fugacity coefficients $\hat{\phi}_1$ and $\hat{\phi}_2$ and the fugacities \hat{f}_1 and \hat{f}_2 for $t = 150^\circ\text{C}$, $P = 30$ bar, and $y_1 = 0.35$. Use the parameters below instead of the data in the Additional Information section. True or false?

Component	Critical Pressure, P_c (bar)	Critical Temperature, T_c (K)	Critical Molar Volume, V_c (cm ³ /mol)	Acentric Factor, ω	Critical Compressibility Factor, Z_c
Ethylene	50.4	282.3	131.0	0.087	0.281
Propylene	46.65	365.6	188.4	0.140	0.289

1. () Fugacity coefficient $\hat{\phi}_1$ is greater than 0.92.
 2. () Fugacity coefficient $\hat{\phi}_2$ is greater than 0.92.
 3. () Fugacity f_1 is greater than 13 bar.
 4. () Fugacity f_2 is greater than 13 bar.

► ADDITIONAL INFORMATION

Equations

Eq. 1 → Antoine equation

$$\log_{10} P^{\text{sat}} = A - \frac{B}{T + C}$$

where P^{sat} is vapor pressure, T is temperature, and A , B , and C are constants that depend on the compound. Normally, the temperature is entered in degrees Celsius and the pressure is returned in millimeters of mercury. Bear in mind that 1 bar = 750.062 mmHg.

Eq. 2 → Clausius-Clapeyron equation

$$\ln\left(\frac{P_2^{\text{sat}}}{P_1^{\text{sat}}}\right) = -\frac{\Delta H^{\text{vap}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where P_i^{sat} is the vapor pressure at state i , T_i is the temperature at state i , and ΔH^{vap} is the change in enthalpy for vaporization.

Eq. 3 → Shortcut equation

$$\log_{10} P_r^{\text{sat}} = \frac{7}{3}(\omega + 1)\left(1 - \frac{1}{T_r}\right)$$

where P_r^{sat} is the reduced vapor pressure, ω is the acentric factor, and T_r is the reduced temperature.

Eq. 4 → Generalized correlation for fugacity coefficient

$$\phi = \phi^0 (\phi^1)^\omega$$

where ϕ^0 and ϕ^1 are fugacity coefficient components in the Lee/Kessler correlation, which can be read from Tables 3 and 4, and ω is the acentric factor.

Eq. 5 → Correlation for fugacity coefficient from the simple virial equation

$$\phi = \exp\left[\frac{P_r}{T_r}(B^0 + \omega B^1)\right]$$

where P_r is the reduced pressure, T_r is the reduced temperature, ω is the acentric factor, and B^0 and B^1 are virial coefficient components given by

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}}$$

and

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}}$$

Eq. 6 → Saturated volume of liquid

$$V^{\text{sat}} = V_c Z_c (1 - T_r)^{2/7}$$

where V_c is the critical molar volume, Z_c is the critical compressibility factor, and T_r is the reduced temperature.

Eq. 7 → Poynting fugacity correction factor

$$\frac{f_2}{f_1} = \exp \left[\frac{\bar{V} (P_2 - P_1)}{RT} \right]$$

where f_i is the fugacity at state i , P_i is the pressure at state i , \bar{V} is molar volume, and T is temperature. Practically speaking, the fugacity is most often known at the vapor pressure, because at the vapor pressure $f^L = f^V$ for vapor-liquid equilibrium and $f^S = f^V$ for solid-vapor equilibrium. Consequently, the Poynting equation is often written as

$$f = f^{\text{sat}} \exp \left[\frac{\bar{V} (P - P^{\text{sat}})}{RT} \right]$$

where P^{sat} is the vapor pressure of the liquid or solid at the temperature of interest T and f^{sat} is the fugacity of saturated vapor at the temperature T and the vapor pressure P^{sat} .

Eq. 8 → General integral for fugacity of a pure species

$$\ln \left(\frac{f}{P} \right) = \int_{P=0}^{P=P} (Z - 1) \frac{dP}{P}$$

where Z is the compressibility factor and P is pressure.

Eq. 9 → Fugacity in the Peng-Robinson model

$$\ln \left(\frac{f}{P} \right) = (Z - 1) - \ln(Z - B) - \frac{A}{2\sqrt{2}B} \ln \left[\frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B} \right]$$

where Z is the compressibility factor and A and B are coefficients given by

$$A = \frac{aP}{R^2 T^2}$$

and

$$B = \frac{bP}{RT}$$

A reminder of the expressions used to determine a and b is provided below.

The Peng-Robinson equation of state is

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

Parameter a is such that $a = a_c \alpha$, where

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

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

with

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

in which ω is the acentric factor. Parameter b , in turn, is given by

$$b = 0.07780 R \frac{T_c}{P_c}$$

Eq. 10 → Fugacity coefficient for a gas mixture, derived from the virial EOS

$$\ln \hat{\phi}_1 = \frac{P}{RT} (B_{11} + y_2^2 \delta_{12})$$

$$\ln \hat{\phi}_2 = \frac{P}{RT} (B_{22} + y_1^2 \delta_{12})$$

where P is pressure, T is temperature, y_i is the liquid phase molar fraction of component i , B_{11} and B_{22} are second virial coefficients for a mixture of two gases, and $\delta_{12} = 2B_{12} - B_{11} - B_{22}$. The equation can be readily extended to a multicomponent gas mixture, in which case we write

$$\ln \hat{\phi}_k = \frac{P}{RT} \left[B_{kk} + \frac{1}{2} \sum_i \sum_j y_i y_j (2\delta_{ik} - \delta_{ij}) \right]$$

where

$$\begin{aligned} \delta_{ik} &= 2B_{ik} - B_{ii} - B_{kk} \\ \delta_{ij} &= 2B_{ij} - B_{ii} - B_{jj} \end{aligned}$$

Problem 13 uses a method in which the fugacity coefficient expression is determined by mean variables, expressed as follows. The mean acentric factor is given by the arithmetic mean

$$\omega_{ij} = \frac{\omega_i + \omega_j}{2}$$

Likewise, the mean critical compressibility factor is given by

$$Z_{ci,j} = \frac{Z_{ci} + Z_{cj}}{2}$$

The mean critical temperature is

$$T_{ci,j} = \sqrt{T_{ci} \times T_{cj}}$$

The mean molar volume is

$$V_{ci,j} = \left(\frac{V_{ci}^{1/3} + V_{cj}^{1/3}}{2} \right)^3$$

The mean critical pressure is

$$P_{ci,j} = \frac{Z_{ci,j} RT_{ci,j}}{V_{ci,j}}$$

The reduced temperature is

$$T_{ri,j} = \frac{T}{T_{ci,j}}$$

Coefficients B^0 and B^1 are given by

$$B_{i,j}^0 = 0.083 - \frac{0.422}{T_{ri,j}^{1.6}} ; B_{i,j}^1 = 0.139 - \frac{0.172}{T_{ri,j}^{4.2}}$$

The second virial coefficients are then

$$B_{i,j} = \frac{RT_{ci,j}}{P_{ci,j}} (B_{i,j}^0 + \omega_{i,j} B_{i,j}^1)$$

Coefficients $\delta_{i,j}$ are given by

$$\delta_{i,j} = 2B_{i,j} - B_{i,i} - B_{j,j}$$

Finally, the fugacity coefficients are determined with the relations

$$\ln \hat{\phi}_1 = \frac{P}{RT} (B_{11} + y_2^2 \delta_{12})$$

$$\ln \hat{\phi}_2 = \frac{P}{RT} (B_{22} + y_1^2 \delta_{12})$$

Table 1 Coefficients for use with the Antoine equation

$$\log_{10} P^{\text{sat}} = A - \frac{B}{T + C}$$

(with T given in °C and P^{sat} expressed in mmHg)

Compound	A	B	C
Acetone	7.11714	1210.595	229.664
Benzene	9.1064	1885.9	244.2
Ethanol	8.32109	1718.10	237.52
<i>n</i> -Hexane	6.87601	1171.17	224.41
1-Propanol	7.84767	1499.21	204.64

Table 2 Physical properties of selected compounds

Compound	Critical Temp. (K)	Critical Pres. (bar)	Acentric Factor
Acetone	508.1	47.0	0.307
Benzene	562.1	48.95	0.121
1-Butene	420.0	40.40	0.191
Chloroform	536.4	54.72	0.222
Ethanol	513.9	61.48	0.649
Ethylene	282.1	50.20	0.085
<i>n</i> -Hexane	507.6	30.25	0.300
Isobutylene	417.9	40.0	0.194
<i>n</i> -Pentane	469.7	33.70	0.252
Phenol	694.3	61.30	0.442
1-Propanol	536.8	51.75	0.629
Propylene	364.9	46.0	0.142
Sulfur dioxide	430.8	78.84	0.245

Table 3 Values of ϕ^0 for use with equation 4

P_r	0.4	0.6	1.2	2.0	3.0	5.0	10.0
$T_r = 1.0$	0.8690	0.8035	0.5781	0.3972	0.3097	0.2483	0.2415
$T_r = 1.10$	0.9016	0.8531	0.7112	0.5408	0.4285	0.3451	0.3296
$T_r = 1.20$	0.9247	0.8892	0.7834	0.6546	0.5420	0.4446	0.4198
$T_r = 1.30$	0.9419	0.9141	0.8318	0.7345	0.6383	0.5383	0.5093
$T_r = 1.40$	0.9550	0.9333	0.8690	0.7925	0.7145	0.6237	0.5943
$T_r = 1.50$	0.9638	0.9462	0.8974	0.8375	0.7745	0.6966	0.6714
$T_r = 2.0$	0.9886	0.9840	0.9683	0.9528	0.9354	0.9183	0.9462
$T_r = 3.0$	1.0023	1.0023	1.0069	1.0116	1.0290	1.0423	1.1298

Table 4 Values of ϕ^1 for use with equation 4

P_r	0.4	0.6	1.2	2.0	3.0	5.0	10.0
$T_r = 1.0$	0.9727	0.9594	0.9204	0.8872	0.8531	0.7962	0.6823
$T_r = 1.10$	1.0023	1.0046	1.0280	1.0990	1.1015	1.0617	0.9572
$T_r = 1.20$	1.0163	1.0280	1.0691	1.1588	1.2388	1.2647	1.2050
$T_r = 1.30$	1.0257	1.0399	1.0914	1.1776	1.2853	1.3868	1.4061
$T_r = 1.40$	1.0304	1.0471	1.0990	1.1858	1.2942	1.4488	1.5524
$T_r = 1.50$	1.0328	1.0496	1.1041	1.1858	1.2942	1.4689	1.6520
$T_r = 2.0$	1.0304	1.0471	1.0965	1.2503	1.2503	1.4191	1.7539
$T_r = 3.0$	1.0233	1.0352	1.0715	1.1803	1.1803	1.3002	1.5813

➤ SOLUTIONS

P.1 ➤ Solution

Per the Antoine equation, eq. 1 in the Additional Information section, the vapor pressure is given by

$$\log_{10} P^{\text{sat}} = A - \frac{B}{T + C}$$

For ethanol, the coefficients are $A = 8.321$, $B = 1718$, and $C = 237.5$, giving

$$\log_{10} P^{\text{sat}} = 8.321 - \frac{1718}{0 + 237.5} = 1.087$$

or

$$P^{\text{sat}} = 10^{1.087} = 12.2 \text{ mmHg}$$

$$\therefore P^{\text{sat}} = 12.2 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} \times \frac{1.013 \text{ bar}}{1 \text{ atm}} = \boxed{0.0163 \text{ bar}}$$

The given data applies to $P = 1 \text{ atm}$, so let this be state 1. Then, the Clausius-Clapeyron equation is written as

$$\ln\left(\frac{P_2^{\text{sat}}}{P_1^{\text{sat}}}\right) = -\frac{\Delta H^{\text{vap}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \rightarrow \ln\left(\frac{P_2^{\text{sat}}}{1.0}\right) = -\frac{42,000}{8.314}\left(\frac{1}{273.15} - \frac{1}{351.5}\right)$$

$$\therefore \ln P_2^{\text{sat}} = -4.122$$

$$\therefore P_2^{\text{sat}} = 0.0162 \text{ atm}$$

$$\therefore P_2^{\text{sat}} = 0.0162 \text{ atm} \times \frac{1.013 \text{ bar}}{1.0 \text{ atm}} = \boxed{0.0164 \text{ bar}}$$

From Table 2, $T_c = 513.92 \text{ K}$, $P_c = 61.48 \text{ bar}$, and $\omega = 0.649$. The reduced temperature is

$$T_r = \frac{T}{T_c} = \frac{0 + 273.15}{513.92} = 0.5315$$

so that

$$\log_{10} P_r^{\text{sat}} = \frac{7}{3}(\omega + 1)\left(1 - \frac{1}{T_r}\right) = \frac{7}{3} \times (0.649 + 1) \times \left(1 - \frac{1}{0.5315}\right) = -3.392$$

Resolving the logarithm, we have

$$P_r^{\text{sat}} = 10^{-3.392} = 4.055 \times 10^{-4}$$

Since P_r^{sat} is given by the ratio

$$P_r^{\text{sat}} = \frac{P^{\text{sat}}}{P_c}$$

we ultimately have

$$P_r^{\text{sat}} = \frac{P^{\text{sat}}}{P_c} \rightarrow P^{\text{sat}} = P_r^{\text{sat}} P_c$$

$$\therefore P^{\text{sat}} = 4.055 \times 10^{-4} \times 61.48 = \boxed{0.0249 \text{ bar}}$$

As a second illustration, we will perform the calculations for a temperature of 100°C . Appealing to the Antoine equation, we have

$$\log_{10} P^{\text{sat}} = 8.321 - \frac{1718}{100 + 237.5} = 3.231$$

so that

$$P^{\text{sat}} = 10^{3.231} = 1702 \text{ mmHg}$$

$$\therefore P^{\text{sat}} = 1702 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} \times \frac{1.013 \text{ bar}}{1 \text{ atm}} = \boxed{2.269 \text{ bar}}$$

Next, using the Clausius-Clapeyron equation gives

$$\ln\left(\frac{P_2^{\text{sat}}}{P_1^{\text{sat}}}\right) = -\frac{\Delta H^{\text{vap}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \rightarrow \ln\left(\frac{P_2^{\text{sat}}}{1.0}\right) = -\frac{42,000}{8.314}\left[\frac{1}{(100 + 273.15)} - \frac{1}{351.5}\right]$$

$$\therefore \ln P_2^{\text{sat}} = 0.8339$$

$$\therefore P_2^{\text{sat}} = 2.302 \text{ atm}$$

$$\therefore P_2^{\text{sat}} = 2.302 \text{ atm} \times \frac{1.013 \text{ bar}}{1.0 \text{ atm}} = \boxed{2.332 \text{ bar}}$$

Next, we resort to the shortcut equation, noting that $T_r = T/T_c = (100 + 273.15)/513.92 = 0.7261$, or

$$\log_{10} P_r^{\text{sat}} = \frac{7}{3}(\omega + 1)\left(1 - \frac{1}{T_r}\right) = \frac{7}{3} \times (0.649 + 1) \times \left(1 - \frac{1}{0.7261}\right) = -1.451$$

$$\therefore P_r^{\text{sat}} = 10^{-1.451} = 0.0354 \text{ atm}$$

Lastly,

$$P^{\text{sat}} = P_r^{\text{sat}} P_c = 0.0354 \times 61.48 = \boxed{2.176 \text{ bar}}$$

The values obtained above and those for the other three temperatures are listed below.

Equation	P^{sat} (bar) at 0°C	P^{sat} (bar) at 50°C	P^{sat} (bar) at 100°C	P^{sat} (bar) at 150°C
Antoine	0.0163	0.2953	2.269	10.29
Clausius-Clapeyron	0.0164	0.2871	2.332	11.55
Shortcut	0.0249	0.3291	2.176	9.190

P.2 → Solution

Consider first the boiling point at a pressure of 0.1 bar. From Table 1, the constants for use with the Antoine equation are $A = 7.848$, $B = 1499$, and $C = 204.6$. Referring to the Antoine equation gives

$$\begin{aligned} \log_{10} P^{\text{sat}} &= A - \frac{B}{T + C} \rightarrow \log_{10} \left(0.1 \text{ bar} \times \frac{760 \text{ mmHg}}{1.013 \text{ bar}} \right) = 7.848 - \frac{1499}{T + 204.6} \\ \therefore 1.875 &= 7.848 - \frac{1499}{T + 204.6} \\ \therefore \boxed{T_b = 46.37^\circ \text{C}} \end{aligned}$$

We proceed to apply the Clausius-Clapeyron equation. Since we have $\Delta H^{\text{vap}} = 41.44 \text{ kJ/mol}$ but not a corresponding boiling point, we estimate a normal boiling point using the Antoine equation,

$$\log_{10} 760 = 7.848 - \frac{1499}{T_b} \rightarrow T_b \approx 97.2^\circ \text{C}$$

We can use this relation as a basis for estimating the boiling temperature at other pressures. Accordingly,

$$\begin{aligned} \ln \left(\frac{P_2^{\text{sat}}}{P_1^{\text{sat}}} \right) - \frac{\Delta H^{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) &\rightarrow \ln \left(\frac{0.1 \text{ bar}}{1.013 \text{ bar}} \right) = -\frac{41,440}{8.314} \times \left(\frac{1}{T_b} - \frac{1}{273.15 + 97.2} \right) \\ \therefore -2.316 &= -4984 \times \left(\frac{1}{T_b} - 0.00270 \right) \\ \therefore T_b &= 316.0 \text{ K} = \boxed{42.85^\circ \text{C}} \end{aligned}$$

The boiling point as obtained with the shortcut equation is considered next. From Table 2, we have, for 1-propanol, $T_c = 536.8 \text{ K}$, $P_c = 51.75 \text{ bar}$, and $\omega = 0.629$. Solving for T , we write

$$\begin{aligned} \log_{10} P_r^{\text{sat}} &= \frac{7}{3}(\omega + 1) \left(1 - \frac{1}{T_r} \right) \rightarrow \log_{10} \left(\frac{P^{\text{sat}}}{P_c} \right) = \frac{7}{3}(\omega + 1) \left(1 - \frac{T_c}{T} \right) \\ \therefore \frac{3}{7} \frac{\log_{10} \left(\frac{P^{\text{sat}}}{P_c} \right)}{(\omega + 1)} &= \left(1 - \frac{T_c}{T} \right) \\ \therefore \frac{T_c}{T} &= 1 - \frac{3}{7} \frac{\log_{10} \left(\frac{P^{\text{sat}}}{P_c} \right)}{(\omega + 1)} \\ \therefore \frac{1}{T} &= \frac{1}{T_c} - \frac{3}{7} \frac{\log_{10} \left(\frac{P^{\text{sat}}}{P_c} \right)}{(\omega + 1) T_c} \\ \therefore T &= \left[\frac{1}{T_c} - \frac{3}{7} \frac{\log_{10} \left(\frac{P^{\text{sat}}}{P_c} \right)}{(\omega + 1) T_c} \right]^{-1} \end{aligned}$$

Substituting the numerical values, we obtain

$$T_b = \left[\frac{1}{536.8} - \frac{3}{7} \frac{\log_{10} \left(\frac{0.1}{51.75} \right)}{(0.629+1) \times 536.8} \right]^{-1} = 313.2 \text{ K} = \boxed{40.05^\circ \text{C}}$$

Values obtained for other pressures are summarized below.

Equation	T_b (°C) at 0.1 bar	T_b (°C) at 0.5 bar	T_b (°C) at 1 bar	T_b (°C) at 5 bar
Antoine	46.37	79.63	96.84	146.1
Clausius-Clapeyron	42.85	78.75	96.85	147.1
Shortcut	40.05	77.65	96.85	150.6

P.3 → Solution

Part 1: The Antoine coefficients for ethanol are $A = 8.32109$, $B = 1718.1$, and $C = 237.52$ (Table 1), so that

$$\log_{10} P^{\text{sat}} = A - \frac{B}{T + C} = 8.32109 - \frac{1718.1}{T + 237.52}$$

$$\therefore P^{\text{sat}} = 10^{\frac{8.32109 - \frac{1718.1}{T + 237.52}}{1}} \quad (\text{I})$$

Note that the Antoine equation takes the temperature in °C, not K, and expresses the vapor pressure in mmHg, not bar; accordingly, we shall make conversions as needed. The shortcut equation, in turn, is written as

$$\log_{10} P_r^{\text{sat}} = \frac{7}{3} (\omega + 1) \left(1 - \frac{1}{T_r} \right)$$

$$\log_{10} P_r^{\text{sat}} = \frac{7}{3} \times (0.649 + 1) \times \left(1 - \frac{1}{T_r} \right) = 3.848 \left(1 - \frac{1}{T_r} \right)$$

or, equivalently,

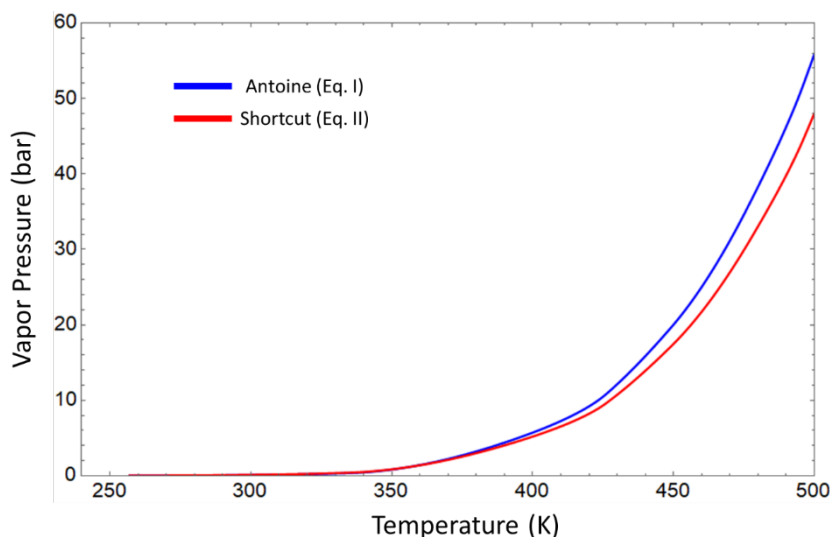
$$P_r^{\text{sat}} = \frac{P}{P_c} \rightarrow P = P_c P_r^{\text{sat}}$$

$$\therefore P = 61.48 \times 10^{3.848(1-1/T_r)} \quad (\text{II})$$

The data are processed in the following table.

T (K)	T (°C)	T_r	P^{sat} (mmHg) (Eq. I)	P^{sat} (bar) (Eq. I)	P^{sat} (bar) (Eq. II)
257	-16	0.5	3.67	0.00490	0.00875
308.4	35.4	0.6	106.1	0.141	0.168
359.7	86.7	0.7	1052	1.402	1.377
411.1	138.1	0.8	5585	7.447	6.704
436.8	163.8	0.85	10964	14.62	12.86
462.5	189.5	0.9	19844	26.46	22.96
488.2	215.2	0.95	33576	44.76	38.55
501.1	228.1	0.975	42773	57.03	49.01

We are looking for plots of vapor pressure (the blue column for the Antoine equation, the red column for the shortcut equation) versus temperature (the yellow column). Both are shown below.



As can be seen, the two models yield essentially the same values at low temperatures, but the shortcut equation underestimates the vapor pressure somewhat at higher temperatures (assuming, of course, that the Antoine equation is more representative of the actual vapor pressures than the shortcut equation).

Part 2: The Antoine coefficients for acetone are $A = 7.11714$, $B = 1210.595$, and $C = 229.664$, so that the Antoine equation has the form

$$\log_{10} P^{\text{sat}} = 7.11714 - \frac{1210.595}{T + 229.664}$$

$$\therefore P^{\text{sat}} = 10^{7.11714 - \frac{1210.595}{T + 229.664}} \quad (\text{III})$$

As before, bear in mind that the Antoine equation as given above takes temperatures in degrees Celsius and returns vapor pressures in mmHg. We proceed to write the shortcut equation,

$$\log_{10} P_r^{\text{sat}} = \frac{7}{3}(\omega + 1) \left(1 - \frac{1}{T_r}\right)$$

$$\log_{10} P_r^{\text{sat}} = \frac{7}{3} \times (0.307 + 1) \times \left(1 - \frac{1}{T_r}\right) = 3.05 \left(1 - \frac{1}{T_r}\right)$$

or, equivalently,

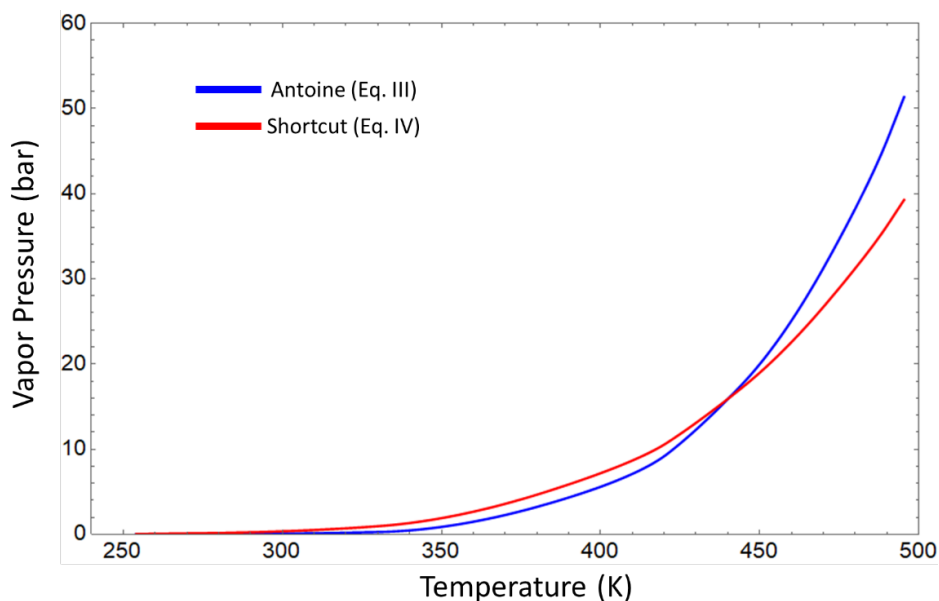
$$P_r^{\text{sat}} = \frac{P}{P_c} \rightarrow P = P_c P_r^{\text{sat}}$$

$$\therefore P = 47.0 \times 10^{3.05(1 - 1/T_r)} \quad (\text{IV})$$

The data are processed below.

T (K)	T ($^{\circ}\text{C}$)	T_r	P^{sat} (mmHg) (Eq. III)	P^{sat} (bar) (Eq. III)	P^{sat} (bar) (Eq. IV)
254.1	-18.9	0.5	23.62	0.03149	0.0420
304.9	31.9	0.6	87.9	0.117	0.436
355.7	82.7	0.7	903	1.204	2.319
406.5	133.5	0.8	4902	6.535	8.124
431.9	158.9	0.85	9706	12.94	13.61
457.3	184.3	0.90	17702	23.60	21.54
482.7	209.7	0.95	30155	40.20	32.48
495.4	222.4	0.975	38498	51.33	39.26

As before, we are looking for plots of vapor pressure (the blue column for the Antoine equation, the red column for the shortcut equation) versus temperature (the yellow column), as follows.



At low temperatures, the shortcut equation seems to overestimate the vapor pressure somewhat. This is followed by a small region of good agreement between the two models and, at higher temperatures, by a region in which the shortcut equation underestimates P^{sat} by a considerable margin.

P.4 → Solution

The reduced properties are $T_r = 600/430.8 = 1.393$ and $P_r = 300/78.84 = 3.805$. Values of ϕ^0 and ϕ^1 for $P_r = 3.0$, read from Tables 3 and 4, respectively, are listed below.

	ϕ^0	ϕ^1
$T_r = 1.30$	0.6383	1.2853
$T_r = 1.40$	0.7145	1.2942

The value of ϕ^0 for $T_r = 1.393$ can be obtained by interpolation,

$$\frac{T_r - T_{r,1}}{T_{r,2} - T_{r,1}} = \frac{\phi^0 - \phi_1^0}{\phi_2^0 - \phi_1^0} \rightarrow \frac{1.393 - 1.30}{1.40 - 1.30} = \frac{\phi^0 - 0.6383}{0.7145 - 0.6383}$$

$$\therefore \phi^0 = 0.7092$$

Likewise, ϕ^1 is given by

$$\frac{T_r - T_{r,1}}{T_{r,2} - T_{r,1}} = \frac{\phi^1 - \phi_1^1}{\phi_2^1 - \phi_1^1} \rightarrow \frac{1.393 - 1.30}{1.40 - 1.30} = \frac{\phi^1 - 1.2853}{1.2942 - 1.2853}$$

$$\therefore \phi^1 = 1.2936$$

In a similar manner, values of ϕ^0 and ϕ^1 for $P_r = 5.0$, also read from Tables 3 and 4, are listed below.

	ϕ^0	ϕ^1
$T_r = 1.30$	0.5383	1.3868
$T_r = 1.40$	0.6237	1.4488

The value of ϕ^0 for $T_r = 1.393$ can be obtained by interpolation,

$$\frac{1.393 - 1.30}{1.40 - 1.30} = \frac{\phi^0 - 0.5383}{0.6237 - 0.5383}$$

$$\therefore \phi^0 = 0.6177$$

Similarly, ϕ^1 is given by

$$\frac{1.393 - 1.30}{1.40 - 1.30} = \frac{\phi^1 - 1.3868}{1.4488 - 1.3868}$$

$$\therefore \phi^1 = 1.4445$$

The results are summarized below.

	ϕ^0	ϕ^1
$P_r = 3.0$	0.7092	1.2936
$P_r = 5.0$	0.6177	1.4445

We can interpolate to determine ϕ^0 at $P_r = 3.805$,

$$\frac{P_r - P_{r,1}}{P_{r,2} - P_{r,1}} = \frac{\phi^0 - \phi_1^0}{\phi_2^0 - \phi_1^0} \rightarrow \frac{3.805 - 3.0}{5.0 - 3.0} = \frac{\phi^0 - 0.7092}{0.6177 - 0.7092}$$

$$\therefore \phi^0 = 0.6724$$

As for ϕ^1 ,

$$\frac{3.805 - 3.0}{5.0 - 3.0} = \frac{\phi^1 - 1.2936}{1.4445 - 1.2936}$$

$$\therefore \phi^1 = 1.3543$$

Given the acentric factor $\omega = 0.245$, the value of ϕ follows from equation 4,

$$\phi = \phi^0 (\phi^1)^\omega = 0.6724 \times 1.3543^{0.245} = 0.7243$$

The fugacity of SO_2 under these conditions is determined to be

$$f = \phi P = 0.7243 \times 300 = \boxed{217.3 \text{ bar}}$$

♦ The correct answer is **C**.

P.5 → Solution

Part 1: The reduced properties are $T_r = 553/417.9 = 1.323$ and $P_r = 20/40 = 0.5$. Values of ϕ^0 and ϕ^1 for $P_r = 0.40$, read from Tables 3 and 4, respectively, are listed below.

	ϕ^0	ϕ^1
$T_r = 1.30$	0.9419	1.0257
$T_r = 1.40$	0.9550	1.0304

The value of ϕ^0 for $T_r = 1.323$ can be obtained by interpolation,

$$\frac{T_r - T_{r,1}}{T_{r,2} - T_{r,1}} = \frac{\phi^0 - \phi_1^0}{\phi_2^0 - \phi_1^0} \rightarrow \frac{1.323 - 1.30}{1.40 - 1.30} = \frac{\phi^0 - 0.9419}{0.9550 - 0.9419}$$

$$\therefore \phi^0 = 0.9449$$

Likewise, ϕ^1 is given by

$$\frac{T_r - T_{r,1}}{T_{r,2} - T_{r,1}} = \frac{\phi^1 - \phi_1^1}{\phi_2^1 - \phi_1^1} \rightarrow \frac{1.323 - 1.30}{1.40 - 1.30} = \frac{\phi^1 - 1.0257}{1.0304 - 1.0257}$$

$$\therefore \phi^1 = 1.0268$$

In a similar manner, values of ϕ^0 and ϕ^1 for $P_r = 0.60$, also read from Tables 3 and 4, are listed below.

	ϕ^0	ϕ^1
$T_r = 1.30$	0.9141	1.0399
$T_r = 1.40$	0.9333	1.0471

The value of ϕ^0 for $T_r = 1.323$ can be obtained by interpolation,

$$\frac{1.323 - 1.30}{1.40 - 1.30} = \frac{\phi^0 - 0.9141}{0.9333 - 0.9141}$$

$$\therefore \phi^0 = 0.9184$$

Similarly, ϕ^1 is given by

$$\frac{1.323 - 1.30}{1.40 - 1.30} = \frac{\phi^1 - 1.0399}{1.0471 - 1.0399}$$

$$\therefore \phi^1 = 1.0416$$

The results are summarized below.

	ϕ^0	ϕ^1
$P_r = 0.40$	0.9449	1.0268
$P_r = 0.60$	0.9184	1.0416

Once again, we utilize interpolation to calculate ϕ^0 for $P_r = 0.50$,

$$\frac{P_r - P_{r1}}{P_{r2} - P_{r1}} = \frac{\phi^0 - \phi_1^0}{\phi_2^0 - \phi_1^0} \rightarrow \frac{0.5 - 0.4}{0.6 - 0.4} = \frac{\phi^0 - 0.9449}{0.9184 - 0.9449}$$

$$\therefore \phi^0 = 0.9317$$

As for ϕ^1 ,

$$\frac{0.5 - 0.4}{0.6 - 0.4} = \frac{\phi^1 - 1.0268}{1.0416 - 1.0268}$$

$$\therefore \phi^1 = 1.0342$$

Given the acentric factor $\omega = 0.194$, the value of ϕ follows as

$$\phi = \phi^0 (\phi^1)^\omega = 0.9317 \times 1.0342^{0.194} = 0.9378$$

The fugacity of isobutylene under these conditions is calculated to be

$$f = \phi P = 0.9378 \times 20 = \boxed{18.76 \text{ bar}}$$

◆ The correct answer is **D**.

Part 2: The reduced properties are $T_r = 553/417.9 = 1.323$ and $P_r = 100/40 = 2.5$. Values of ϕ^0 and ϕ^1 for $P_r = 2.0$, read from Tables 3 and 4, respectively, are listed below.

	ϕ^0	ϕ^1
$T_r = 1.30$	0.7345	1.1776
$T_r = 1.40$	0.7925	1.1858

The value of ϕ^0 for $T_r = 1.323$ follows by interpolation,

$$\frac{T_r - T_{r,1}}{T_{r,2} - T_{r,1}} = \frac{\phi^0 - \phi_1^0}{\phi_2^0 - \phi_1^0} \rightarrow \frac{1.323 - 1.30}{1.40 - 1.30} = \frac{\phi^0 - 0.7345}{0.7925 - 0.7345}$$

$$\therefore \phi^0 = 0.7478$$

Likewise, ϕ^1 is given by

$$\frac{T_r - T_{r,1}}{T_{r,2} - T_{r,1}} = \frac{\phi^1 - \phi_1^1}{\phi_2^1 - \phi_1^1} \rightarrow \frac{1.323 - 1.30}{1.40 - 1.30} = \frac{\phi^1 - 1.1776}{1.1858 - 1.1776}$$

$$\therefore \phi^1 = 1.1795$$

In a similar manner, values of ϕ^0 and ϕ^1 for $P_r = 3.0$, also read from Tables 3 and 4, are listed below.

	ϕ^0	ϕ^1
$T_r = 1.30$	0.6383	1.2853
$T_r = 1.40$	0.7145	1.2942

Proceeding in a similar manner, ϕ^0 for $T_r = 1.323$ is found as

$$\frac{1.323 - 1.30}{1.40 - 1.30} = \frac{\phi^0 - 0.6383}{0.7145 - 0.6383}$$

$$\therefore \phi^0 = 0.6558$$

As for ϕ^1 ,

$$\frac{1.323 - 1.30}{1.40 - 1.30} = \frac{\phi^1 - 1.2853}{1.2942 - 1.2853}$$

$$\therefore \phi^1 = 1.2874$$

The results are summarized below.

	ϕ^0	ϕ^1
$P_r = 2.0$	0.7478	1.1795
$P_r = 3.0$	0.6558	1.2874

We are looking for the ϕ values that apply to $P_r = 2.5$. Since this is midway between $P_r = 2.0$ and $P_r = 3.0$, we can simply take the arithmetic means of the results above instead of using the interpolation formula. Accordingly, we have

$$\phi^0 = \frac{0.7478 + 0.6558}{2} = 0.7018$$

and

$$\phi^1 = \frac{1.1795 + 1.2874}{2} = 1.2335$$

We can then calculate ϕ ,

$$\phi = \phi^0 (\phi^1)^{\omega} = 0.7018 \times (1.2335)^{0.194} = 0.7310$$

Finally, the fugacity of isobutylene under the specified conditions is calculated to be

$$f = \phi P = 0.7310 \times 100 = \boxed{73.10 \text{ bar}}$$

◆ The correct answer is **C**.

P.6 → Solution

Part 1: The reduced temperature is $T_r = 309.2/469.7 = 0.658$, and the reduced pressure is $P_r = 1.01325/33.7 = 0.0301$. The fugacity coefficient ϕ is given by equation 5,

$$\phi = \exp \left[\frac{P_r}{T_r} (B^0 + \omega B^1) \right]$$

Virial coefficients B^0 and B^1 are respectively calculated as

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} = 0.083 - \frac{0.422}{0.658^{1.6}} = -0.741$$

and

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}} = 0.139 - \frac{0.172}{0.658^{4.2}} = -0.859$$

Substituting in the formula for ϕ brings to

$$\phi = \exp \left[\frac{P_r}{T_r} (B^0 + \omega B^1) \right] = \exp \left\{ \frac{0.0301}{0.658} \times [-0.741 + 0.252 \times (-0.859)] \right\} = 0.957$$

The saturated volume of liquid is given by equation 6,

$$V^{\text{sat}} = V_c Z_c^{(1-T_r)^{2/7}} = 313 \times 0.27^{(1-0.658)^{2/7}} = 119.4 \text{ cm}^3/\text{mol}$$

At this point, we invoke the Poynting correction factor (equation 7),

$$f_i = \phi_i P_i^{\text{sat}} \exp \left[\frac{V_i^{\text{sat}} (P - P_i^{\text{sat}})}{RT} \right]$$

so that

$$f_i = 0.957 \times 1.01325 \times \exp \left[\frac{119.4 \times (200 - 1.01325)}{83.14 \times 309.2} \right] = \boxed{2.444 \text{ bar}}$$

♦ The correct answer is **B**.

Part 2: The reduced temperature is $T_r = 266.3/417.9 = 0.637$, and the reduced pressure is $P_r = 1.01325/40 = 0.0253$. The fugacity coefficient ϕ is given by

$$\phi = \exp \left[\frac{P_r}{T_r} (B^0 + \omega B^1) \right]$$

Virial coefficients B^0 and B^1 are respectively computed as

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} = 0.083 - \frac{0.422}{0.637^{1.6}} = -0.785$$

and

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}} = 0.139 - \frac{0.172}{0.637^{4.2}} = -1.0$$

Substituting in the formula for ϕ gives

$$\phi = \exp \left[\frac{P_r}{T_r} (B^0 + \omega B^1) \right] = \exp \left\{ \frac{0.0253}{0.637} \times [-0.785 + 0.194 \times (-1.0)] \right\} = 0.962$$

The saturated volume of liquid is determined as

$$V^{\text{sat}} = V_c Z_c^{(1-T_r)^{2/7}} = 238.9 \times 0.275^{(1-0.637)^{2/7}} = 90.88 \text{ cm}^3/\text{mol}$$

The fugacity of the component at the specified pressure is given by the Poynting equation, namely

$$f_i = \phi_i P_i^{\text{sat}} \exp\left[\frac{V_i^{\text{sat}}(P - P_i^{\text{sat}})}{RT}\right]$$

$$\therefore f = 0.962 \times 1.01325 \times \exp\left[\frac{90.88 \times (200 - 1.01325)}{83.14 \times 266.3}\right] = \boxed{2.202 \text{ bar}}$$

◆ The correct answer is **C**.

Part 3: The reduced temperature is $T_r = 266.9/420.0 = 0.635$, and the reduced pressure is $P_r = 1.01325/40.4 = 0.0251$. The fugacity coefficient ϕ is given by

$$\phi = \exp\left[\frac{P_r}{T_r}(B^0 + \omega B^1)\right]$$

Virial coefficients B^0 and B^1 are respectively calculated as

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} = 0.083 - \frac{0.422}{0.635^{1.6}} = -0.790$$

and

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}} = 0.139 - \frac{0.172}{0.635^{4.2}} = -1.02$$

Substituting in the formula for ϕ gives

$$\phi = \exp\left[\frac{P_r}{T_r}(B^0 + \omega B^1)\right] = \exp\left\{\frac{0.0251}{0.635} \times [-0.790 + 0.191 \times (-1.02)]\right\} = 0.962$$

The saturated volume of liquid is determined as

$$V^{\text{sat}} = V_c Z_c^{(1-T_r)^{2/7}} = 239.3 \times 0.277^{(1-0.635)^{2/7}} = 91.39 \text{ cm}^3/\text{mol}$$

The fugacity of the component at the specified pressure is given by

$$f = 0.962 \times 1.01325 \times \exp\left[\frac{91.39 \times (200 - 1.01325)}{83.14 \times 266.9}\right] = \boxed{2.208 \text{ bar}}$$

◆ The correct answer is **C**.

P.7 → Solution

The reduced temperatures are $T_r = 473.15/536.4 = 0.882$ and, at the boiling point, $T_{rn} = 334.3/536.4 = 0.623$. The saturated volume follows as

$$V_{\text{sat}} = V_c Z_c^{(1-T_{rn})^{2/7}} = 239.0 \times 0.293^{(1-0.623)^{2/7}} = 94.39 \text{ cm}^3$$

Now, the fugacity coefficient is given by equation 5, namely

$$\phi = \exp\left[\frac{P_r}{T_r}(B^0 + \omega B^1)\right]$$

The virial coefficients are given by

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} = 0.083 - \frac{0.422}{0.882^{1.6}} = -0.433$$

and

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}} = 0.139 - \frac{0.172}{0.882^{4.2}} = -0.152$$

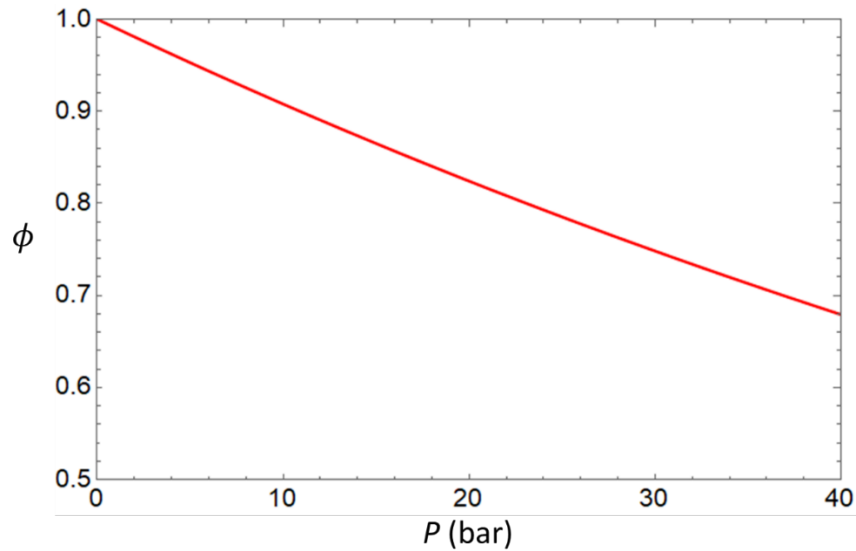
In addition, $P_r = P/P_c$. Substituting in the equation for ϕ yields

$$\phi = \exp\left[\frac{P_r}{T_r}(B^0 + \omega B^1)\right] = \exp\left\{\frac{P}{0.882 P_c} [-0.433 + 0.222 \times (-0.152)]\right\}$$

$$\therefore \phi = \exp\left\{\frac{P}{0.882 \times 54.72} \times [-0.433 + 0.222 \times (-0.152)]\right\}$$

$$\therefore \phi = \exp(-0.00967P)$$

The equation in question is plotted below.



Consider now the fugacity of the system, which is given by the Poynting equation (equation 7),

$$f = \phi_{\text{sat}} P_{\text{sat}} \exp\left[\frac{V^l(P - P_{\text{sat}})}{RT}\right]$$

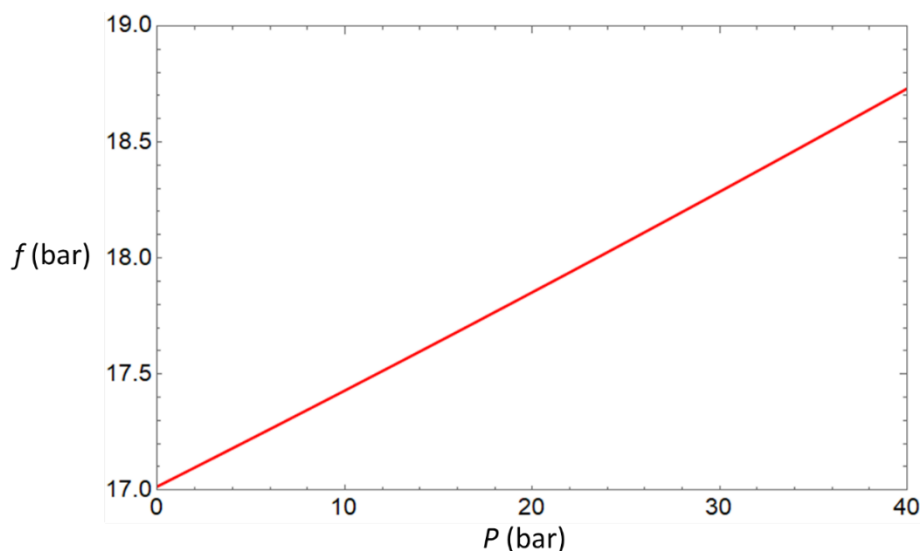
Given the vapor pressure of chloroform at 200°C, we have

$$\phi_{\text{sat}} = \exp(-0.00967 \times 22.27) = 0.806$$

so that

$$f = 0.806 \times 22.27 \times \exp\left[\frac{94.39 \times (P - 22.27)}{83.14 \times 473}\right] = 17.95 \exp[0.0024(P - 22.27)]$$

The fugacity is plotted against pressure in the following figure.



P.8 → Solution

The fugacity is given by equation 8,

$$\ln \frac{f}{P} = \int_{P=0}^{P=P} \frac{Z-1}{P} dP$$

Before proceeding, we need an expression for $(Z - 1)/P$. Manipulating the EOS given, we have

$$\begin{aligned} \bar{V} &= \frac{RT}{P} + aP^2 \\ \therefore \frac{P}{RT} \bar{V} &= \frac{P}{RT} \left(\frac{RT}{P} + aP^2 \right) \\ \therefore Z &= 1 + \frac{aP^3}{RT} \end{aligned}$$

Then, we substitute into the integral to obtain

$$\ln \frac{f}{P} = \int_{P=0}^{P=P} \frac{\left(1 + \frac{aP^3}{RT}\right) - 1}{P} dP$$

or

$$f = \exp\left(\frac{aP^3}{3RT}\right)$$

Substituting the numerical data, we get

$$f = 5.0 \times \exp\left(\frac{0.01 \times 5^3 \times 1000}{3 \times 83.14 \times 500}\right) = \boxed{5.05 \text{ bar}}$$

Factor 1000 was included because coefficient a expresses volume in liters, not cm^3 .

♦ The correct answer is **A**.

P.9 → Solution

1. False. The fugacity is given by

$$\ln \frac{f}{P} = \int_{P=0}^{P=P} \frac{Z-1}{P} dP$$

Before proceeding, we need an expression for $(Z-1)/P$. Manipulating the EOS provided, we get

$$\begin{aligned} \bar{V} &= \frac{RT}{P} + aTP^2 \\ \therefore \frac{\bar{V}P}{RT} &= 1 + \frac{aP^3}{R} \\ \therefore Z-1 &= \frac{aP^3}{R} \\ \therefore \frac{Z-1}{P} &= \frac{aP^2}{R} \end{aligned}$$

Then, we substitute into the integral to obtain

$$\ln \frac{f}{P} = \int_{P=0}^{P=P} \frac{aP^2}{R} dP = \frac{aP^3}{3R}$$

or

$$f = P \exp\left(\frac{aP^3}{3R}\right)$$

Note that the only difference between this expression for fugacity and that of the previous problem is the absence of temperature in the exponent's denominator. Substituting the numerical data, we get

$$f = 0.1 \times \exp\left(\frac{0.3 \times 0.1^3}{3 \times 83.14}\right) = \boxed{0.1 \text{ bar}}$$

2. True. The fugacity of the vapor phase at 0.5 bar and 50°C is

$$f^V = 0.5 \times \exp\left(\frac{0.3 \times 0.5^3}{3 \times 83.14}\right) = 0.5 \text{ bar}$$

Using the Poynting equation (equation 7), it follows that

$$f_2 = f^{\text{sat}} \exp\left[\frac{\bar{V}(P_2 - P_1)}{RT}\right] = 0.5 \times \exp\left[\frac{125 \times (100 - 0.5)}{83.14 \times 323}\right] = \boxed{0.795 \text{ bar}}$$

3. False. We appeal to the equation obtained in part 1, giving

$$f = P \exp\left(\frac{aP^3}{3R}\right) = 3 \times \exp\left(\frac{0.3 \times 3^3}{3 \times 83.14}\right) = \boxed{3.099 \text{ bar}}$$

4.False. We know the vapor pressure of water vapor at $T = 100^\circ\text{C}$ to be 5.0 bar. From the fugacity equation derived in part 1, we have

$$f = P \exp\left(\frac{aP^3}{3R}\right) = 5.0 \times \exp\left(\frac{0.3 \times 5^3}{3 \times 83.14}\right) = 5.811 \text{ bar}$$

From the Poynting equation, the fugacity in the liquid phase is calculated to be

$$f_2 = f^{\text{sat}} \exp\left[\frac{\bar{V}(P_2 - P_1)}{RT}\right] = 5.811 \times \exp\left[\frac{125 \times (100 - 5)}{83.14 \times 373}\right] = \boxed{8.522 \text{ bar}}$$

P.10 → Solution

1. True. The Peng-Robinson equation is

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

We proceed to compute parameters a and b ,

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

$$\therefore \kappa = 0.37464 + 1.54226 \times 0.142 - 0.269932 \times 0.142^2 = 0.588$$

$$T_r = (25 + 273)/364.9 = 0.817$$

$$\alpha = [1 + \kappa(1 - T_r^{0.5})]^2 = [1 + 0.588 \times (1 - 0.817^{0.5})]^2 = 1.12$$

$$a_c = 0.45724R^2 \frac{T_c^2}{P_c} = 0.45724 \times 83.14^2 \times \frac{364.9^2}{46.0} = 9.15 \times 10^6 \frac{\text{bar} \cdot \text{cm}^6}{\text{mol}^2}$$

$$a = a_c \alpha = (9.15 \times 10^6) \times 1.12 = 1.02 \times 10^7 \frac{\text{bar} \cdot \text{cm}^6}{\text{mol}^2}$$

$$b = 0.0778R \frac{T_c}{P_c} = 0.0778 \times 83.14 \times \frac{364.9}{46.0} = 51.3 \frac{\text{cm}^3}{\text{mol}}$$

Parameter b represents the lowest value the molar volume can have, or $51.3 \text{ cm}^3/\text{mol}$. For example, if $\bar{V} = 60 \text{ cm}^3/\text{mol}$, we have

$$P = \frac{83.14 \times 298.15}{60 - 51.3} - \frac{1.02 \times 10^7}{60 \times (60 + 51.3) + 51.3 \times (60 - 51.3)} = 1418 \text{ bar}$$

From the definition of Z , we calculate

$$Z = \frac{P\bar{V}}{RT} = \frac{1418 \times 60}{83.14 \times 298} = 3.43$$

We also need parameters A and B , namely

$$A = \frac{aP}{R^2 T^2} = \frac{(1.02 \times 10^7) \times 1418}{83.14^2 \times 298^2} = 23.6$$

$$B = \frac{bP}{RT} = \frac{51.3 \times 1418}{83.14 \times 298} = 2.94$$

The fugacity is determined next,

$$\ln\left(\frac{f}{P}\right) = (Z - 1) - \ln(Z - B) - \frac{A}{2\sqrt{2}B} \ln\left[\frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B}\right]$$

$$\therefore \ln\left(\frac{f}{P}\right) = (3.43 - 1) - \ln(3.43 - 2.94) - \frac{23.6}{2\sqrt{2} \times 2.94} \ln\left[\frac{3.43 + (1 + \sqrt{2}) \times 2.94}{3.43 + (1 - \sqrt{2}) \times 2.94}\right] = -1.28$$

$$\therefore f = 394 \text{ bar}$$

The vapor pressure is the pressure for which the liquid-phase fugacity f^L equals the vapor-phase fugacity f^V . Substituting $P = 1418$ bar in the Peng-Robinson equation, we have

$$1418 = \frac{83.14 \times 298}{\bar{V} - 51.3} - \frac{1.02 \times 10^7}{\bar{V}(\bar{V} + 51.3) + 51.3(\bar{V} - 51.3)}$$

Solving the equation above, we get two imaginary solutions and $\bar{V} = 60$ cm³/mol. Since there is no corresponding molar volume for a liquid state, we surmise that $P = 1418$ bar is not the vapor pressure of propylene at 100°C. Calculations for other molar volumes are tabulated below.

Liquid Molar Volume (cm ³ /mol)	Pressure (bar)	Z (Liquid)	A	B	ln(f/P) (Liquid)	f (Liquid) (bar)	Vapor Molar Volume (cm ³ /mol)	Z (Vapor)	ln(f/P) (Vapor)	f (Vapor) (bar)
60	1416	3.43	23.5	2.93	-1.29	390	-	-	-	-
65	574	1.51	9.5	1.19	-2.50	47	-	-	-	-
70	246	0.69	4.1	0.51	-2.54	19	-	-	-	-
75	91	0.28	1.5	0.19	-2.00	12	-	-	-	-
80	12	0.04	0.2	0.02	-0.18	9.6626	1644	0.04	-0.2	9.6626

Clearly, the fugacities become equal when the molar volume is 80 cm³/mol. This corresponds to a pressure of 12 bar; thus, we surmise that the vapor pressure of propylene at the temperature in question is about 12 bar.

2. True. From the data tabulated in the analysis of the previous statement, we see that the fugacity of saturated vapor at 25°C is 9.66 bar.

3. False. The calculations summarized in the analysis of the first statement can be adapted to any temperature. The normal boiling point is the temperature at which the vapor pressure is 1 atm, or 1.01325 bar. Since statement 1 showed that the vapor pressure at 25°C is about 12 bar, the normal boiling point must be at a significantly lower temperature. At 225 K, or -48.2°C, the results that correspond to $P = 1.01325$ bar are as shown below.

	V (cm ³ /mol)	Z	f (bar)
Liquid	64.39	0.00348	0.972
Vapor	18,000	0.971	0.976

Since $f^L \approx f^V$, we surmise that -48.2°C is a good estimate of the normal boiling temperature.

P.11 → Solution

Part 1: The reduced temperature is $T_r = 400/562.1 = 0.712$. The vapor pressure can be easily estimated with the shortcut equation (equation 3),

$$\begin{aligned} \log_{10} P_r^{\text{sat}} &= \frac{7}{3}(\omega + 1) \left(1 - \frac{1}{T_r} \right) \\ \therefore \log_{10} P_r^{\text{sat}} &= \frac{7}{3} \times (0.121 + 1) \times \left(1 - \frac{1}{0.712} \right) = -1.14 \\ \therefore P_r^{\text{sat}} &= 10^{-1.14} = 0.0724 \\ \therefore P^{\text{sat}} &= 0.0724 \times 48.95 = \boxed{3.54 \text{ bar}} \end{aligned}$$

To establish the fugacity of benzene at the conditions at hand, we can appeal to the Peng-Robinson model and use equation 9,

$$\ln \left(\frac{f}{P} \right) = (Z - 1) - \ln(Z - B) - \frac{A}{2\sqrt{2}B} \ln \left[\frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B} \right]$$

We first compute parameters a and b as follows,

$$\begin{aligned} \kappa &= 0.37464 + 1.54226\omega - 0.269932\omega^2 \\ \therefore \kappa &= 0.37464 + 1.54226 \times 0.121 - 0.269932 \times 0.121^2 = 0.557 \end{aligned}$$

$$\alpha = [1 + \kappa(1 - T_r^{0.5})]^2 = [1 + 0.557 \times (1 - 0.712^{0.5})]^2 = 1.18$$

$$a_c = 0.45724R^2 \frac{T_c^2}{P_c} = 0.45724 \times 83.14^2 \times \frac{562.1^2}{48.95} = 2.04 \times 10^7 \frac{\text{bar} \cdot \text{cm}^6}{\text{mol}^2}$$

$$a = a_c \alpha = (2.04 \times 10^7) \times 1.18 = 2.41 \times 10^7 \frac{\text{bar} \cdot \text{cm}^6}{\text{mol}^2}$$

$$b = 0.0778R \frac{T_c}{P_c} = 0.0778 \times 83.14 \times \frac{562.1}{48.95} = 74.3 \frac{\text{cm}^3}{\text{mol}}$$

Referring to the Peng-Robinson equation, we have

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}(\bar{V} + b) + b(\bar{V} - b)} = 3.54 \text{ bar}$$

$$\therefore \frac{83.14 \times 400}{\bar{V} - 74.3} - \frac{2.41 \times 10^7}{\bar{V}(\bar{V} + 74.3) + 74.3(\bar{V} - 74.3)} = 3.54$$

Solving the equation above gives $\bar{V} = 102 \text{ cm}^3/\text{mol}$, $\bar{V} = 512 \text{ cm}^3/\text{mol}$, and $\bar{V} = 8710 \text{ cm}^3/\text{mol}$. The largest result represents the saturated vapor. The compressibility factor is then

$$Z = \frac{P\bar{V}}{RT} = \frac{3.54 \times 8710}{83.14 \times 400} = 0.927$$

We also need parameters A and B , namely

$$A = \frac{aP}{R^2T^2} = \frac{(2.41 \times 10^7) \times 3.54}{83.14^2 \times 400^2} = 0.0771$$

$$B = \frac{bP}{RT} = \frac{74.3 \times 3.54}{83.14 \times 400} = 0.00791$$

We now have all the information needed to compute the fugacity. Indeed,

$$\ln\left(\frac{f}{P}\right) = (0.927 - 1) - \ln(0.927 - 0.00791) + (\dots)$$

$$(\dots) - \frac{0.0771}{2\sqrt{2} \times 0.00791} \ln\left[\frac{0.927 + (1 + \sqrt{2}) \times 0.00791}{0.927 + (1 - \sqrt{2}) \times 0.00791}\right] = -0.0711$$

$$\therefore f = 3.54 \times \exp(-0.0711) = \boxed{3.30 \text{ bar}}$$

◆ The correct answer is **D**.

Part 2: The reduced temperature is $T_r = 400/507.6 = 0.788$. The vapor pressure can be readily estimated with the shortcut equation,

$$\log_{10} P_r^{\text{sat}} = \frac{7}{3}(\omega + 1) \left(1 - \frac{1}{T_r}\right)$$

$$\therefore \log_{10} P_r^{\text{sat}} = \frac{7}{3} \times (0.30 + 1) \times \left(1 - \frac{1}{0.788}\right) = -0.816$$

$$\therefore P_r^{\text{sat}} = 10^{-0.816} = 0.153$$

$$\therefore P^{\text{sat}} = 0.153 \times 30.25 = \boxed{4.63 \text{ bar}}$$

To establish the fugacity of this compound, we once again use equation 9,

$$\ln\left(\frac{f}{P}\right) = (Z - 1) - \ln(Z - B) - \frac{A}{2\sqrt{2}B} \ln\left[\frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B}\right]$$

We first compute parameters a and b as follows,

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

$$\therefore \kappa = 0.37464 + 1.54226 \times 0.30 - 0.269932 \times 0.30^2 = 0.813$$

$$\alpha = \left[1 + \kappa (1 - T_r^{0.5}) \right]^2 = \left[1 + 0.813 \times (1 - 0.788^{0.5}) \right]^2 = 1.19$$

$$a_c = 0.45724 R^2 \frac{T_c^2}{P_c} = 0.45724 \times 83.14^2 \times \frac{507.6^2}{30.25} = 2.69 \times 10^7 \frac{\text{bar} \cdot \text{cm}^6}{\text{mol}^2}$$

$$a = a_c \alpha = (2.69 \times 10^7) \times 1.19 = 3.20 \times 10^7 \frac{\text{bar} \cdot \text{cm}^6}{\text{mol}^2}$$

$$b = 0.0778 R \frac{T_c}{P_c} = 0.0778 \times 83.14 \times \frac{507.6}{30.25} = 108.5 \frac{\text{cm}^3}{\text{mol}}$$

Referring to the Peng-Robinson equation, we have

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}(\bar{V} + b) + b(\bar{V} - b)} = 4.63 \text{ bar}$$

$$\therefore \frac{83.14 \times 400}{\bar{V} - 109} - \frac{2.41 \times 10^7}{\bar{V}(\bar{V} + 109) + 109(\bar{V} - 109)} = 4.63$$

Solving the equation above gives $\bar{V} = 268 \text{ cm}^3/\text{mol}$, $\bar{V} = 273 \text{ cm}^3/\text{mol}$, and $\bar{V} = 6550 \text{ cm}^3/\text{mol}$. The largest result represents the saturated vapor. The compressibility factor follows as

$$Z = \frac{P\bar{V}}{RT} = \frac{4.63 \times 6550}{83.14 \times 400} = 0.912$$

We also need parameters A and B , namely

$$A = \frac{aP}{R^2 T^2} = \frac{(3.20 \times 10^7) \times 4.63}{83.14^2 \times 400^2} = 0.134$$

$$B = \frac{bP}{RT} = \frac{108.5 \times 4.63}{83.14 \times 400} = 0.0151$$

Lastly, the fugacity f is computed as

$$\begin{aligned} \ln\left(\frac{f}{P}\right) &= (0.912 - 1) - \ln(0.912 - 0.0151) + (\dots) \\ (\dots) &= \frac{0.134}{2\sqrt{2} \times 0.0151} \ln\left[\frac{0.912 + (1 + \sqrt{2}) \times 0.0151}{0.912 + (1 - \sqrt{2}) \times 0.0151}\right] = -0.124 \\ \therefore f &= 4.63 \times \exp(-0.124) = \boxed{4.09 \text{ bar}} \end{aligned}$$

◆ The correct answer is **D**.

Part 3: The reduced temperature is $T_r = 400/694.3 = 0.576$. Substituting the pertinent data in the shortcut equation yields

$$\begin{aligned} \log_{10} P_r^{\text{sat}} &= \frac{7}{3}(\omega + 1) \left(1 - \frac{1}{T_r} \right) \\ \therefore \log_{10} P_r^{\text{sat}} &= \frac{7}{3} \times (0.442 + 1) \times \left(1 - \frac{1}{0.576} \right) = -2.48 \\ \therefore P_r^{\text{sat}} &= 10^{-2.48} = 0.00331 \\ \therefore P^{\text{sat}} &= 0.00331 \times 61.30 = \boxed{0.203 \text{ bar}} \end{aligned}$$

The vapor pressure seems low enough for us to assume phenol to be an ideal gas, with the result that $f^{\text{sat}} = P^{\text{sat}} = 0.203 \text{ bar}$. Nevertheless, let us carry out the pertaining calculations and verify this hypothesis.

$$\begin{aligned} \kappa &= 0.37464 + 1.54226\omega - 0.269932\omega^2 \\ \therefore \kappa &= 0.37464 + 1.54226 \times 0.442 - 0.269932 \times 0.442^2 = 1.0 \\ \alpha &= \left[1 + \kappa (1 - T_r^{0.5}) \right]^2 = \left[1 + 1.0 \times (1 - 0.576^{0.5}) \right]^2 = 1.54 \end{aligned}$$

$$a_c = 0.45724R^2 \frac{T_c^2}{P_c} = 0.45724 \times 83.14^2 \times \frac{694.3^2}{61.30} = 2.49 \times 10^7 \frac{\text{bar} \cdot \text{cm}^6}{\text{mol}^2}$$

$$a = a_c \alpha = (2.49 \times 10^7) \times 1.54 = 3.83 \times 10^7 \frac{\text{bar} \cdot \text{cm}^6}{\text{mol}^2}$$

$$b = 0.0778R \frac{T_c}{P_c} = 0.0778 \times 83.14 \times \frac{694.3}{61.30} = 73.3 \frac{\text{cm}^3}{\text{mol}}$$

Substituting in the Peng-Robinson equation, we have

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}(\bar{V} + b) + b(\bar{V} - b)} = 0.203 \text{ bar}$$

$$\therefore \frac{83.14 \times 400}{\bar{V} - 73.3} - \frac{2.41 \times 10^7}{\bar{V}(\bar{V} + 73.3) + 73.3(\bar{V} - 73.3)} = 0.203$$

Solving this equation yields $\bar{V} = 86 \text{ cm}^3/\text{mol}$, $\bar{V} = 925 \text{ cm}^3/\text{mol}$, and $\bar{V} = 162,700 \text{ cm}^3/\text{mol}$. The vapor is described by the latter result (which, yes, is very large). The compressibility factor is then

$$Z = \frac{P\bar{V}}{RT} = \frac{0.203 \times 162,700}{83.14 \times 400} = 0.993$$

Parameters A and B , in turn, are given by

$$A = \frac{aP}{R^2T^2} = \frac{(3.83 \times 10^7) \times 0.203}{83.14^2 \times 400^2} = 0.00703$$

$$B = \frac{bP}{RT} = \frac{73.3 \times 0.203}{83.14 \times 400} = 4.47 \times 10^{-4}$$

Finally, the fugacity f is calculated to be

$$\ln\left(\frac{f}{P}\right) = (0.993 - 1) - \ln(0.993 - 4.47 \times 10^{-4}) + (\dots)$$

$$(\dots) - \frac{0.00703}{2\sqrt{2} \times (4.47 \times 10^{-4})} \ln\left[\frac{0.993 + (1 + \sqrt{2}) \times (4.47 \times 10^{-4})}{0.993 + (1 - \sqrt{2}) \times (4.47 \times 10^{-4})}\right] = -0.00660$$

$$\therefore f = 0.203 \times \exp(-0.0066) = \boxed{0.202 \text{ bar}}$$

As expected, $f^{\text{sat}} \approx P^{\text{sat}}$.

◆ The correct answer is **A**.

P.12 → Solution

By definition, $\delta_{12} = 2B_{12} - B_{11} - B_{22}$. Accordingly,

$$\delta_{12} = 2 \times (-58.6) - (-38) - (-100.1) = 20.9 \text{ cm}^3 \text{ mol}^{-1}$$

Substituting into equation 10, we obtain

$$\ln \hat{\phi}_1 = \frac{P}{RT} (B_{11} + y_2^2 \delta_{12}) = \frac{32}{83.14 \times 250} \times (-38 + 0.65^2 \times 20.9) = -0.0449$$

$$\ln \hat{\phi}_2 = \frac{P}{RT} (B_{22} + y_1^2 \delta_{12}) = \frac{32}{83.14 \times 250} \times (-100.1 + 0.35^2 \times 20.9) = -0.150$$

It follows that

$$\hat{\phi}_1 = \exp(-0.0449) = \boxed{0.956}$$

and

$$\hat{\phi}_2 = \exp(-0.150) = \boxed{0.861}$$

◆ The correct answer is **C**.

P.13 → **Solution**

To begin, we compute the ω terms,

$$\omega_{1,1} = \frac{\omega_1 + \omega_1}{2} = \frac{0.087 + 0.087}{2} = 0.087$$

$$\omega_{1,2} = \frac{\omega_1 + \omega_2}{2} = \frac{0.087 + 0.140}{2} = 0.114$$

$$\omega_{2,1} = \frac{\omega_2 + \omega_1}{2} = \frac{0.140 + 0.087}{2} = 0.114$$

$$\omega_{2,2} = \frac{\omega_2 + \omega_2}{2} = \frac{0.140 + 0.140}{2} = 0.140$$

We proceed to calculate the T_c terms,

$$T_{c1,1} = \sqrt{T_{c,1} \times T_{c,1}} = \sqrt{282.3 \times 282.3} = 282.3 \text{ K}$$

$$T_{c1,2} = \sqrt{T_{c,1} \times T_{c,2}} = \sqrt{282.3 \times 365.6} = 321.3 \text{ K}$$

$$T_{c2,1} = \sqrt{T_{c,2} \times T_{c,1}} = \sqrt{365.6 \times 282.3} = 321.3 \text{ K}$$

$$T_{c2,2} = \sqrt{T_{c,2} \times T_{c,2}} = \sqrt{365.6 \times 365.6} = 365.6 \text{ K}$$

The Z_c terms are computed next,

$$Z_{c1,1} = \frac{Z_{c,1} + Z_{c,1}}{2} = \frac{0.281 + 0.281}{2} = 0.281$$

$$Z_{c1,2} = \frac{Z_{c,1} + Z_{c,2}}{2} = \frac{0.281 + 0.289}{2} = 0.285$$

$$Z_{c2,1} = \frac{Z_{c,2} + Z_{c,1}}{2} = \frac{0.289 + 0.281}{2} = 0.285$$

$$Z_{c2,2} = \frac{Z_{c,2} + Z_{c,2}}{2} = \frac{0.289 + 0.289}{2} = 0.289$$

The V_c terms are computed next,

$$V_{c1,1} = \left(\frac{V_{c,1}^{1/3} + V_{c,1}^{1/3}}{2} \right)^3 = \left(\frac{131.0^{1/3} + 131.0^{1/3}}{2} \right)^3 = 131.0 \text{ cm}^3/\text{mol}$$

$$V_{c1,2} = \left(\frac{V_{c,1}^{1/3} + V_{c,2}^{1/3}}{2} \right)^3 = \left(\frac{131.0^{1/3} + 188.4^{1/3}}{2} \right)^3 = 158.0 \text{ cm}^3/\text{mol}$$

$$V_{c2,1} = \left(\frac{V_{c,2}^{1/3} + V_{c,1}^{1/3}}{2} \right)^3 = \left(\frac{188.4^{1/3} + 131.0^{1/3}}{2} \right)^3 = 158.0 \text{ cm}^3/\text{mol}$$

$$V_{c2,2} = \left(\frac{V_{c,2}^{1/3} + V_{c,2}^{1/3}}{2} \right)^3 = \left(\frac{188.4^{1/3} + 188.4^{1/3}}{2} \right)^3 = 188.4 \text{ cm}^3/\text{mol}$$

The P_c terms are computed next,

$$P_{c1,1} = \frac{Z_{c1,1}RT_{c1,1}}{V_{c1,1}} = \frac{0.281 \times 83.14 \times 282.3}{131.0} = 50.33 \text{ bar}$$

$$P_{c1,2} = \frac{Z_{c1,2}RT_{c1,2}}{V_{c1,2}} = \frac{0.285 \times 83.14 \times 321.3}{158.0} = 48.18 \text{ bar}$$

$$P_{c2,1} = \frac{Z_{c2,1}RT_{c2,1}}{V_{c2,1}} = \frac{0.285 \times 83.14 \times 321.3}{158.0} = 48.18 \text{ bar}$$

$$P_{c2,2} = \frac{Z_{c2,2}RT_{c2,2}}{V_{c2,2}} = \frac{0.289 \times 83.14 \times 365.6}{188.4} = 46.63 \text{ bar}$$

The reduced temperatures are determined in continuation,

$$T_{r1,1} = \frac{T}{T_{c1,1}} = \frac{423.15}{282.3} = 1.499$$

$$T_{r1,2} = \frac{T}{T_{c1,2}} = \frac{423.15}{321.3} = 1.317$$

$$T_{r2,1} = \frac{T}{T_{c2,1}} = \frac{423.15}{321.3} = 1.317$$

$$T_{r2,2} = \frac{T}{T_{c2,2}} = \frac{423.15}{365.6} = 1.157$$

The B^0 coefficients are determined in continuation,

$$B_{1,1}^0 = 0.083 - \frac{0.422}{T_{r1,1}^{1.6}} = 0.083 - \frac{0.422}{1.499^{1.6}} = -0.138$$

$$B_{1,2}^0 = 0.083 - \frac{0.422}{T_{r1,2}^{1.6}} = 0.083 - \frac{0.422}{1.317^{1.6}} = -0.189$$

$$B_{2,1}^0 = 0.083 - \frac{0.422}{T_{r2,1}^{1.6}} = 0.083 - \frac{0.422}{1.317^{1.6}} = -0.189$$

$$B_{2,2}^0 = 0.083 - \frac{0.422}{T_{r2,2}^{1.6}} = 0.083 - \frac{0.422}{1.157^{1.6}} = -0.251$$

The B^1 coefficients are determined in continuation,

$$B_{1,1}^1 = 0.139 - \frac{0.172}{T_{r1,1}^{4.2}} = 0.139 - \frac{0.172}{1.499^{4.2}} = 0.108$$

$$B_{1,2}^1 = 0.139 - \frac{0.172}{T_{r1,2}^{4.2}} = 0.139 - \frac{0.172}{1.317^{4.2}} = 0.0849$$

$$B_{2,1}^1 = 0.139 - \frac{0.172}{T_{r2,1}^{4.2}} = 0.139 - \frac{0.172}{1.317^{4.2}} = 0.0849$$

$$B_{2,2}^1 = 0.139 - \frac{0.172}{T_{r2,2}^{4.2}} = 0.139 - \frac{0.172}{1.157^{4.2}} = 0.0458$$

The results obtained heretofore are shown below.

Numbering	ω	T_c (K)	Z_c	V_c (cm ³ /mol)	P_c (bar)	T_r	B^0	B^1
1,1	0.087	282.3	0.281	131	50.33	1.499	-0.138	0.108
1,2	0.114	321.3	0.285	158	48.18	1.317	-0.189	0.0849
2,1	0.114	321.3	0.285	158	48.18	1.317	-0.189	0.0849
2,2	0.14	365.6	0.289	188.4	46.63	1.157	-0.251	0.0458

Using the tabulated data, we can establish the B coefficients,

$$B_{1,1} = \frac{RT_{c1,1}}{P_{c1,1}} (B_{1,1}^0 + \omega_{1,1} B_{1,1}^1) = \frac{83.14 \times 282.3}{50.33} (-0.138 + 0.087 \times 0.108) = -59.97 \text{ cm}^3/\text{mol}$$

$$B_{1,2} = \frac{RT_{c1,2}}{P_{c1,2}} (B_{1,2}^0 + \omega_{1,2} B_{1,2}^1) = \frac{83.14 \times 321.3}{48.18} (-0.189 + 0.114 \times 0.0849) = -99.42 \text{ cm}^3/\text{mol}$$

$$B_{2,1} = \frac{RT_{c2,1}}{P_{c2,1}} (B_{2,1}^0 + \omega_{2,1} B_{2,1}^1) = \frac{83.14 \times 321.3}{48.18} (-0.189 + 0.114 \times 0.0849) = -99.42 \text{ cm}^3/\text{mol}$$

$$B_{2,2} = \frac{RT_{c2,2}}{P_{c2,2}} (B_{2,2}^0 + \omega_{2,2} B_{2,2}^1) = \frac{83.14 \times 365.6}{46.63} (-0.251 + 0.140 \times 0.0458) = -159.4 \text{ cm}^3/\text{mol}$$

and then the δ_{12} and δ_{21} coefficients,

$$\delta_{12} = 2B_{1,2} - B_{1,1} - B_{2,2} = 2 \times (-99.42) - (-59.97) - (-159.4) = 20.53 \text{ cm}^3/\text{mol}$$

$$\delta_{21} = 2B_{2,1} - B_{2,2} - B_{1,1} = 2 \times (-99.42) - (-159.4) - (-59.97) = 20.53 \text{ cm}^3/\text{mol}$$

The fugacity coefficients are calculated as

$$\ln \hat{\phi}_1 = \frac{P}{RT} (B_{11} + y_2^2 \delta_{12}) = \frac{30}{83.14 \times 423} \times (-59.97 + 0.65^2 \times 20.53) = -0.0438$$

$$\therefore \hat{\phi}_1 = \exp(-0.0438) = \boxed{0.957}$$

and

$$\ln \hat{\phi}_2 = \frac{P}{RT} (B_{22} + y_1^2 \delta_{12}) = \frac{30}{83.14 \times 423} \times (-159.4 + 0.65^2 \times 20.53) = -0.129$$

$$\therefore \hat{\phi}_2 = \exp(-0.129) = \boxed{0.879}$$

Lastly, we can determine the fugacities themselves, namely

$$\hat{f}_1 = \hat{\phi}_1 y_1 P = 0.957 \times 0.35 \times 30 = \boxed{10.05 \text{ bar}}$$

and

$$\hat{f}_2 = \hat{\phi}_2 y_2 P = 0.879 \times 0.65 \times 30 = \boxed{17.14 \text{ bar}}$$

The results are summarized in the following table.

	1	2
Fugacity coeff.	0.957	0.879
Fugacity (bar)	10.05	17.14

◆ Statements **1** and **4** are true, while statements **2** and **3** are false.

➤ ANSWER SUMMARY

Problem 1		Open-ended pb.
Problem 2		Open-ended pb.
Problem 3	3.1	Open-ended pb.
	3.2	Open-ended pb.
Problem 4		C
Problem 5	5.1	D
	5.2	C
Problem 6	6.1	B
	6.2	C
	6.3	C
Problem 7		Open-ended pb.
Problem 8		A
Problem 9		T/F
Problem 10		T/F
Problem 11	11.1	D
	11.2	D
	11.3	A
Problem 12		C
Problem 13		T/F

➤ REFERENCES

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



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