Montogue

QUIZ CE103
Vapor-Liquid Equilibrium and Raoult's Law
Lucas Montogue

▶▶ PROBLEMS

▶ Problem 1

Which of the following systems can be adequately modeled with Raoult's law?

A) n-hexane/n-heptane at 25 bar.

B) Hydrogen/propane at 200 K.

C) Isooctane/n-octane at 100°C.

D) Water/n-decane at 1 bar.

➔ Problem 2.1 (Smith et al., 2004, w/ permission)

Assuming the validity of Raoult's law, do the following calculations for the benzene/toluene system. First, given $x_1 = 0.33$ and $T = 100$°C, find y_1 and P.

A) $y_1 = 0.191$ and $P = 109.3$ kPa

B) $y_1 = 0.191$ and $P = 205.1$ kPa

C) $y_1 = 0.545$ and $P = 109.3$ kPa

D) $y_1 = 0.545$ and $P = 205.1$ kPa

➔ Problem 2.2

Given $y_1 = 0.33$ and $T = 100$°C, find x_1 and P.

A) $x_1 = 0.168$ and $P = 92.11$ kPa

B) $x_1 = 0.168$ and $P = 144.2$ kPa

C) $x_1 = 0.401$ and $P = 92.11$ kPa

D) $x_1 = 0.401$ and $P = 144.2$ kPa

➔ Problem 2.3

Given $x_1 = 0.33$ and $P = 120$ kPa, find y_1 and T.

A) $y_1 = 0.195$ and $T = 56.7$°C

B) $y_1 = 0.195$ and $T = 103.4$°C

C) $y_1 = 0.542$ and $T = 56.7$°C

D) $y_1 = 0.542$ and $T = 103.4$°C

➔ Problem 2.4

Given $y_1 = 0.33$ and $P = 120$ kPa, find x_1 and T.

A) $x_1 = 0.173$ and $T = 109.2$°C

B) $x_1 = 0.173$ and $T = 155.0$°C

C) $x_1 = 0.498$ and $T = 109.2$°C

D) $x_1 = 0.498$ and $T = 155.0$°C

➔ Problem 2.5

Given $T = 105$°C and $P = 120$ kPa, find x_1 and y_1.

A) $x_1 = 0.283$ and $y_1 = 0.485$

B) $x_1 = 0.283$ and $y_1 = 0.723$

C) $x_1 = 0.601$ and $y_1 = 0.485$

D) $x_1 = 0.601$ and $y_1 = 0.723$

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

Consider the 1-hexene (1) + n-hexane (2) system at 328.15 K. Using Raoult's law, predict the system pressure and vapor-phase composition of this mixture and provide a Pxy plot for this mixture. Compare the results of your modeling with the set of experimental data provided for this system. Plot the data on the same plot as your model. Is the system properly modeled by Raoult's law? Why or why not?

Pressure (kPa)	x_1	y_1
64.435	0.0	0.0
65.955	0.102	0.122
67.368	0.200	0.233
68.741	0.300	0.341
70.061	0.400	0.445
71.287	0.500	0.543
72.434	0.600	0.639
73.581	0.700	0.732
74.701	0.799	0.823
75.780	0.900	0.912
76.780	1.0	1.0

▶ Problem 4 (Dahm & Visco, 2015, w/ permission)

Consider the tetrahydrofuran (1) + n-hexane (2) system at 313.15 K. Using Raoult's law, predict the system pressure and vapor-phase composition for this mixture and provide a Pxy plot for this mixture. Compare your results with the set of experimental data provided for this system. Plot the data (as points) on the same plot as your model. Is this system properly modeled by Raoult's law? Why or why not?

Pressure (kPa)	x_1	y_1
37.69	0.0	0.0
39.943	0.098	0.145
42.077	0.185	0.251
43.623	0.275	0.346
44.943	0.385	0.439
45.463	0.448	0.488
45.543	0.488	0.515
45.783	0.52	0.539
45.676	0.535	0.549
45.730	0.573	0.575
45.756	0.620	0.610
45.663	0.665	0.645
45.570	0.713	0.682
45.316	0.738	0.695
44.810	0.803	0.755
44.063	0.843	0.790
43.543	0.883	0.826
42.663	0.925	0.885
41.477	0.975	0.955
40.410	1	1

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

Consider the n-hexane (1)/ethanol (2) system at 1 bar. Using Raoult's law, predict the system temperature and vapor-phase composition for this mixture and provide a Txy plot for this mixture. Compare the results of your modeling with the set of experimental data provided below. Plot the data (as points) on the same plot as your model. Is this system properly modeled by Raoult's law? Why or why not?

T (K)	x_1	y_1
351.45	0	0
349.15	0.010	0.095
346.35	0.020	0.193
340.55	0.060	0.365
339.05	0.080	0.420
334.95	0.152	0.532
332.55	0.245	0.605
331.85	0.330	0.539

2

331.50	0.452	0.640
331.25	0.588	0.650
331.15	0.670	0.660
331.40	0.725	0.670
331.60	0.765	0.675
332.30	0.898	0.710
333.35	0.955	0.745
336.65	0.990	0.840
339.85	0.994	0.935
341.85	1.0	1.0

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

Assuming Raoult's law applies to the n-pentane (1)/n-heptane (2) system, what are the values of x_1 and y_1 at $t = 55°C$ and $P = (1/2)(P_1^{sat} + P_2^{sat})$?

A) $x_1 = 0.50$ and $y_1 = 0.455$

B) $x_1 = 0.50$ and $y_1 = 0.889$

C) $x_1 = 0.751$ and $y_1 = 0.455$

D) $x_1 = 0.751$ and $y_1 = 0.889$

→ Problem 6.2

For the conditions introduced in the previous problem, plot the fraction of the system that is vapor, V, versus the overall composition z_1.

→ Problem 6.3

For $T = 55°C$ and $z_1 = 0.5$, plot P, x_1 and y_1 versus V.

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

A single-stage liquid/vapor separation for the benzene (1)/ethylbenzene (2) system must produce phases with equilibrium compositions $x_1 = 0.35$ and $y_1 = 0.70$. Determine the temperature T and total pressure P in the separator.

A) $T = 135.6°C$ and $P = 107.2$ kPa

B) $T = 135.6°C$ and $P = 214.4$ kPa

C) $T = 190.3°C$ and $P = 107.2$ kPa

D) $T = 190.3°C$ and $P = 214.4$ kPa

→ Problem 8.1 (Smith et al., 2004, w/ permission)

A mixture containing equimolar amounts of benzene (1), toluene (2) and ethylbenzene (3) is flashed to conditions T and P. If $T = 110°C$ and the total pressure is $P = 90$ kPa, determine the equilibrium mole fractions (x_i and y_i) of the liquid and vapor phases formed and the molar fraction $\mathcal{V}$ of the vapor formed. Write down your results in the following table. Assume that Raoult's law applies.

	Benzene (1)	Toluene (2)	Ethyl benzene (3)
Liquid phase molar fraction x_i			
Vapor phase molar fraction y_i			

→ Problem 8.2

Repeat your calculations if the temperature is maintained at 110°C but the pressure is raised to 120 kPa. Write down your results in the following table.

	Benzene (1)	Toluene (2)	Ethyl benzene (3)
Liquid phase molar fraction x_i			
Vapor phase molar fraction y_i			

3

▶ Problem 9 (Smith et al., 2004, w/ permission)

A binary mixture of mole fraction z_1 is flashed to conditions T and P. For the following mixtures, determine the equilibrium mole fractions x_1 and y_1 of the liquid and vapor phases formed and the fractional recovery R of species 1 in the vapor phase (defined as the ratio for species 1 of moles in the vapor to moles in the feed). Assume that Raoult's law applies. True or false?

Mixture 1: Acetone (1)/acetonitrile (2), $z_1 = 0.75$, $T = 340$ K, $P = 115$ kPa

1.( ) The mole fraction of acetone in the liquid phase, x_1, is greater than 0.55.

2.( ) The mole fraction of acetone in the vapor phase, y_1, is greater than 0.85.

3.( ) The fractional recovery of acetone is greater than 0.6.

Mixture 2: Ethanol (1)/propanol (2), $z_1 = 0.25$, $T = 360$ K, $P = 0.80$ atm

4.( ) The mole fraction of ethanol in the liquid phase, x_1, is greater than 0.25.

5.( ) The mole fraction of ethanol in the vapor phase, y_1, is greater than 0.28.

6.( ) The fractional recovery of ethanol is greater than 0.7.

▶ Problem 10 (Smith et al., 2004, w/ permission)

A process stream contains light species 1 and heavy species 2. A relatively pure liquid stream containing mostly 2 is desired, obtained by a single-stage liquid/vapor separation. Specifications on the vapor composition are: $x_1 = 0.002$ and $y_1 = 0.950$. Use the data given below to determine T (K) and P (bar) for the separator. Assume that Raoult's law applies. Use the data provided below.

For the liquid phase, $\ln \gamma_1 = 0.93 x_2^2$ and $\ln \gamma_2 = 0.93 x_1^2$
$\ln P_i^{\text{sat}}(\text{bar}) = A_i + B_i/T(\text{K})$ $A_1 = 10.08$, $B_1 = 2572$, $A_2 = 11.63$, $B_2 = 6254$

A) $T = 376.4$ K and $P = 0.137$ bar
B) $T = 376.4$ K and $P = 0.351$ bar
C) $T = 414.1$ K and $P = 0.137$ bar
D) $T = 414.1$ K and $P = 0.351$ bar

▶ Problem 11 (Smith et al., 2004, w/ permission)

For the acetone (1)/methanol (2) system a vapor mixture for which $z_1 = 0.25$ and $z_2 = 0.75$ is cooled to temperature T in the two-phase region and flows into a separation chamber at a pressure of 1 bar. If the composition of the liquid product is to be $x_1 = 0.175$, what is the required value of T and what is the value of y_1? For liquid mixtures of this system to a good approximation,

$\ln \gamma_1 = 0.64 x_2^2$	$\ln \gamma_2 = 0.64 x_1^2$

A) $T = 31.1°C$ and $y_1 = 0.117$
B) $T = 31.1°C$ and $y_1 = 0.306$
C) $T = 59.5°C$ and $y_1 = 0.117$
D) $T = 59.5°C$ and $y_1 = 0.306$

▶ Problem 12 (Smith et al., 2004, w/ permission)

A liquid mixture of cyclohexanone (1)/phenol (2) for which $x_1 = 0.6$ is in equilibrium with its vapor at 144°C. Determine the equilibrium pressure P and vapor composition y_1 from the following information.

$\ln \gamma_1 = A x_2^2$	$\ln \gamma_2 = A x_1^2$
At 144°C, $P_1^{\text{sat}} = 75.20$ kPa and $P_2^{\text{sat}} = 31.66$ kPa	
The system forms an azeotrope at 144°C for which x_1^{az} and $y_1^{\text{az}} = 0.294$.	

A) $P = 38.10$ kPa and $y_1 = 0.451$
B) $P = 38.10$ kPa and $y_1 = 0.844$
C) $P = 55.92$ kPa and $y_1 = 0.451$
D) $P = 55.92$ kPa and $y_1 = 0.844$

4

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

A binary system of species 1 and 2 consists of vapor and liquid phases in equilibrium at temperature T. The overall mole fraction of species 1 in the system is $z_1 = 0.65$. At temperature T, we have:

$\ln \gamma_1 = 0.67 x_2^2$	$\ln \gamma_2 = 0.67 x_1^2$
$P_1^{sat} = 32.27$ kPa	$P_2^{sat} = 73.14$ kPa

Assuming the validity of modified Raoult's law, true or false?

1.( ) The system exhibits two phases at a pressure of 50 kPa.

2.( ) For a liquid=phase molar fraction $x_1 = 0.75$, the molar of fraction of the system that is vapor is greater than 0.5.

3.( ) This system does not exhibit an azeotrope.

→ Problem 14.1 (Smith et al., 2004, w/ permission)

A binary system of species 1 and 2 consists of vapor and liquid phases in equilibrium at temperature T, for which the following relations apply. For what range of values of the *overall* mole fraction z_1 can this two-phase system exist with a *liquid* mole fraction $x_1 = 0.65$?

$\ln \gamma_1 = 1.8 x_2^2$	$\ln \gamma_2 = 1.8 x_1^2$
$P_1^{sat} = 1.24$ bar	$P_2^{sat} = 0.89$ bar

→ Problem 14.2

What are the pressure and mole fraction x_1 of the azeotrope at temperature T?

A) $P = 0.885$ bar and $x_1 = 0.233$
B) $P = 0.885$ bar and $x_1 = 0.592$
C) $P = 1.673$ bar and $x_1 = 0.233$
D) $P = 1.673$ bar and $x_1 = 0.592$

▶▶ ADDITIONAL INFORMATION

Table 1 Constants of the Antoine equation for vapor pressures of pure species

$$\ln P^{sat} / kPa = A - \frac{B}{t/^{\circ}C + C}$$

	A	B	C
Acetone	14.3145	2756.22	228.06
Acetonitrile	14.895	3413.1	250.523
Benzene	13.7819	2726.81	217.572
Ethanol	16.8958	3795.17	230.337
Ethylbenzene	13.9726	3259.93	212.300
n-Heptane	13.8622	2910.26	216.432
Methanol	16.5785	3638.27	239.500
n-Pentane	13.7667	2451.88	232.014
Propanol	16.1154	3483.67	205.807
Toluene	13.9320	3056.96	217.625

5

P.1 ➡ *Solution*

Although n-hexane/n-heptane are chemically similar, a pressure of 25 bar is much too high for Raoult's law to be applicable. Hydrogen and propane are chemically dissimilar, not to mention that hydrogen at 200 K is supercritical and hence has no specified P^{sat} under these conditions. Water, a polar compound, and n-decane, a nonpolar compound, are immiscible and cannot be adequately modeled by Raoult's law. Lastly, isooctane and n-octane are chemically similar and a temperature of 100°C is close to their normal boiling points (which is 99°C for isooctane and 125.6°C for n-octane), indicating that Raoult's law can be used as a good approximation for this system.

♦ The correct answer is **C**.

P.2 ➡ *Solution*

Part 1: Antoine equation coefficients are taken from Table 1. The vapor pressure of benzene at 100°C is

$$\ln P_1^{sat} = 13.7819 - \frac{2726.81}{100 + 217.572}$$

$$\therefore P_1^{sat} = 180.5 \text{ kPa}$$

Likewise, for toluene,

$$\ln P_2^{sat} = 13.9320 - \frac{3056.96}{100 + 217.625}$$

$$\therefore P_2^{sat} = 74.26 \text{ kPa}$$

The total pressure of the system is calculated as

$$P = x_1 P_1^{sat} + x_2 P_2^{sat} = 0.33 \times 180.5 + 0.67 \times 74.26 = \boxed{109.3 \text{ kPa}}$$

The vapor phase mole fraction is then

$$y_1 = \frac{x_1 P_1^{sat}}{P} = \frac{0.33 \times 180.5}{109.3} = \boxed{0.545}$$

♦ The correct answer is **C**.

Part 2: The vapor pressures remain as calculated in the previous part, namely P_1^{sat} = 180.5 kPa and P_2^{sat} = 74.26 kPa. To calculate the liquid phase mole fraction, we write

$$0.33 \times P = x_1 \times 180.5$$

$$\therefore 0.33 \times \left[x_1 \times 180.5 + (1 - x_1) \times 74.3 \right] = x_1 \times 180.5$$

$$106.2 x_1 + 74.2 = 547.0 x_1$$

$$x_1 = \frac{74.2}{440.8} = \boxed{0.168}$$

The total pressure of the system is then

$$P = x_1 P_1^{sat} + x_2 P_2^{sat} = 0.168 \times 180.5 + (1 - 0.168) \times 74.26 = \boxed{92.11 \text{ kPa}}$$

♦ The correct answer is **A**.

Part 3: From the Antoine equation, the vapor pressures of benzene and toluene are

$$P_1^{sat} = \exp\left(13.7819 - \frac{2727.81}{T + 217.572} \right)$$

$$P_2^{sat} = \exp\left(13.9320 - \frac{3056.96}{T + 217.625} \right)$$

Substituting in the equation for for total pressure P yields

$$P = x_1 P_1^{sat} + x_2 P_2^{sat}$$

6

$$\therefore 120 = 0.33 \exp\left(13.7819 - \frac{2727.81}{T + 217.572}\right) + 0.67 \exp\left(13.9320 - \frac{3056.96}{T + 217.625}\right)$$

The equation above is transcendental and requires trial-and-error to be solved. One way to go is to apply Mathematica's *FindRoot* command,

$$\text{FindRoot}\left[120 - 0.33\text{Exp}\left[13.7819 - \frac{2727.81}{T + 217.572}\right]\right.$$
$$\left. - 0.67\text{Exp}\left[13.932 - \frac{3056.96}{T + 217.625}\right], \{T, 273\}\right]$$

which returns $T = 103.4°C$. Equipped with this quantity, we can determine vapor pressure P_1^{sat},

$$P_1^{\text{sat}} = \exp\left(13.7819 - \frac{2727.81}{103.4 + 217.572}\right) = 197.0 \text{ kPa}$$

Accordingly, the vapor phase mole fraction of benzene is

$$y_1 P = x_1 P_1^{\text{sat}} \rightarrow y_1 = \frac{x_1 P_1^{\text{sat}}}{P}$$

$$\therefore y_1 = \frac{0.33 \times 197.0}{120} = \boxed{0.542}$$

♦ The correct answer is **D**.

Part 4: The sum of mole fractions of benzene and toluene must equal 1. Mathematically,

$$x_1 + x_2 = 1$$

$$\therefore \frac{y_1 P}{P_1^{\text{sat}}} + \frac{y_2 P}{P_2^{\text{sat}}} = 1$$

Pressures P_1^{sat} and P_2^{sat} follow from the Antoine equation. Substituting these and other variables brings to

$$\frac{y_1 P}{P_1^{\text{sat}}} + \frac{y_2 P}{P_2^{\text{sat}}} = 1$$

$$\therefore \frac{0.33 \times 120}{\exp\left(13.7819 - \frac{2727.81}{T + 217.572}\right)} + \frac{0.67 \times 120}{\exp\left(13.9320 - \frac{3056.96}{T + 217.625}\right)} = 1.0$$

Once again, we have obtained a transcendental equation. Appealing to Mathematica's *FindRoot* command, we apply the code

$$\text{FindRoot}\left[\frac{0.33 * 120}{\text{Exp}\left[13.7819 - \frac{2727.81}{T + 217.572}\right]} + \frac{0.67 * 120}{\text{Exp}\left[13.932 - \frac{3056.96}{T + 217.625}\right]} - 1., \{T, 273\}\right]$$

which returns $T = 109.2°C$. The corresponding value of P_1^{sat} is then

$$P_1^{\text{sat}} = \exp\left(13.7819 - \frac{2727.81}{109.2 + 217.572}\right) = 229.1 \text{ kPa}$$

The liquid phase mole fraction of benzene is determined as

$$y_1 P = x_1 P_1^{\text{sat}} \rightarrow x_1 = \frac{y_1 P}{P_1^{\text{sat}}}$$

$$\therefore x_1 = \frac{0.33 \times 120}{229.1} = \boxed{0.173}$$

♦ The correct answer is **A**.

Part 5: We first compute the vapor pressures of benzene and toluene at 105°C by dint of the Antoine equation,

$$P_1^{\text{sat}} = \exp\left(13.7819 - \frac{2727.81}{105 + 217.572}\right) = 205.5 \text{ kPa}$$

7

$$P_2^{\text{sat}} = \exp\left(13.932 - \frac{3056.96}{105 + 217.625}\right) = 86.20 \text{ kPa}$$

Given the total pressure P = 120 kPa, we write

$$P = x_1 P_1^{\text{sat}} + x_2 P_2^{\text{sat}} \rightarrow 120 = x_1 \times 205.5 + (1 - x_1) \times 86.20$$

$$\therefore \boxed{x_1 = 0.283}$$

Lastly, we determine y_1 with Raoult's law,

$$y_1 P = x_1 P_1^{\text{sat}} \rightarrow y_1 = \frac{x_1 P_1^{\text{sat}}}{P}$$

$$\therefore y_1 = \frac{0.283 \times 205.5}{120} = \boxed{0.485}$$

◆ The correct answer is **A**.

P.3 ➡ *Solution*

According to the data, the vapor pressures at this temperature are 64.435 kPa for n-hexane (2) and 76.780 kPa for 1-hexene (1). To model the system using Raoult's law, we use

$$P = x_1 P_1^{\text{sat}} + x_2 P_2^{\text{sat}} = x_1 \times 76.78 + (1 - x_1) \times 64.44$$

$$\therefore P = 76.78 x_1 + 64.44 - 64.44 x_1$$

$$\therefore P = 12.34 x_1 + 64.44 \text{ (I)}$$

and

$$y_1 = \frac{x_1 P_1^{\text{sat}}}{P} = \frac{76.78 x_1}{12.34 x_1 + 64.44} \text{ (II)}$$

The data are tabulated below.

P (kPa) (Eq. I)	x_1	x_2	y_1 (Eq.II)
64.44	0	1	0.0000
65.674	0.1	0.9	0.1169
66.908	0.2	0.8	0.2295
68.142	0.3	0.7	0.3380
69.376	0.4	0.6	0.4427
70.61	0.5	0.5	0.5437
71.844	0.6	0.4	0.6412
73.078	0.7	0.3	0.7355
74.312	0.8	0.2	0.8266
75.546	0.9	0.1	0.9147
76.78	1	0	1.0000

We are looking for plots of P (the yellow column) versus x_1 (the blue column), and P versus y_1 (the red column). Both curves, plotted along with the experimental data, are shown below.
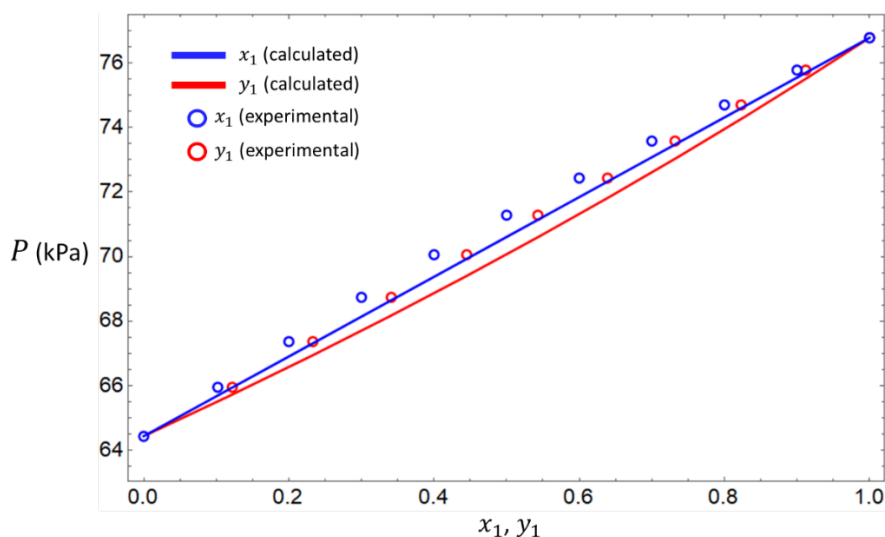
The two components, 1-hexene and n-hexane, are very similar. Their sizes are almost exactly the same and their interactions are similar (i.e., they are both

8

hydrocarbons). 1-hexene does have a dipole moment owing to the double bond, but the structures and interactions are similar enough to make ideal solution a good model in this case. Combined with the fact that the system is at low pressure, Raoult's law provides a very reasonable estimate of the phase behavior.

P.4 ➡ Solution

According to the data, the vapor pressures at this temperature are 37.69 kPa for n-hexane (2) and 40.41 kPa for tetrahydrofuran (1). To model the system using Raoult's law, we use

$$P = x_1 P_1^{sat} + x_2 P_2^{sat} = x_1 \times 40.41 + (1 - x_1) \times 37.69$$

$$\therefore P = 40.41 x_1 + 37.60 - 37.69 x_1$$

$$\therefore P = 2.72 x_1 + 37.60 \text{ (I)}$$

and

$$y_1 = \frac{x_1 P_1^{sat}}{P} = \frac{40.41 x_1}{2.72 x_1 + 37.60} \text{ (II)}$$

The data are tabulated below.

P (kPa) (Eq. I)	x_1	x_2	y_1 (Eq.II)
37.6	0	1	0.0000
37.872	0.1	0.9	0.1067
38.144	0.2	0.8	0.2119
38.416	0.3	0.7	0.3156
38.688	0.4	0.6	0.4178
38.96	0.5	0.5	0.5186
39.232	0.6	0.4	0.6180
39.504	0.7	0.3	0.7161
39.776	0.8	0.2	0.8128
40.048	0.9	0.1	0.9081
40.32	1	0	1.00

We are looking for plots of P (the yellow column) versus x_1 (the blue column), and P versus y_1 (the red column). Both graphs, plotted along with the experimental data, are shown below.
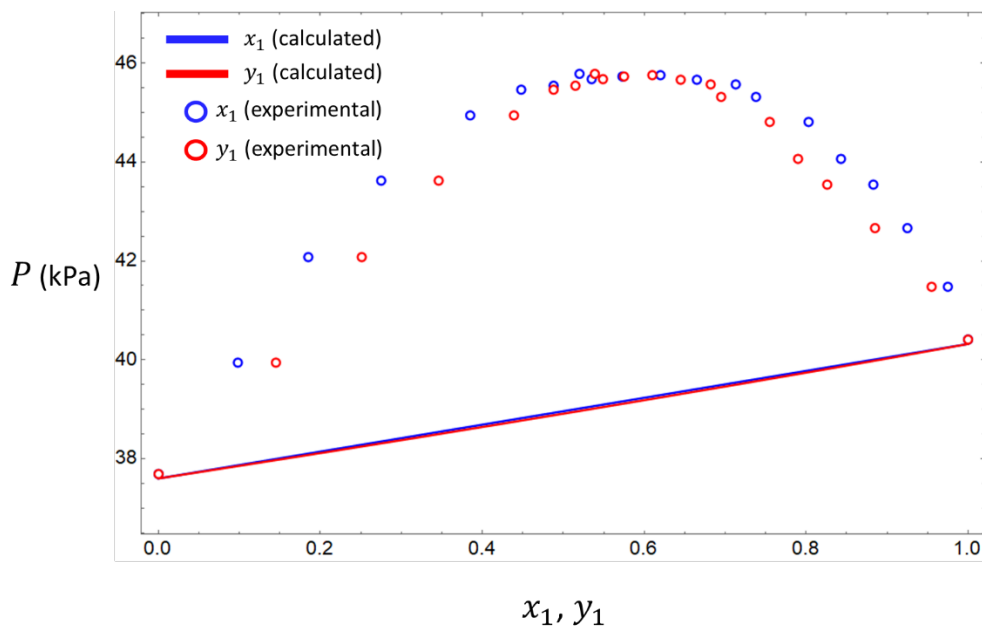
The components of this system, though they have a similar vapor pressure at this temperature, do not behave as an ideal solution. This is because n-hexane is a straight, nonpolar alkane, while tetrahydrofuran is a ringed structure with a large dipole moment. This system, as evidenced by the figure above, is not modeled well by Raoult's law. Note that both the bubble and dew point predictions from Raoult's law virtually overlap on the graph, owing to the similarity in vapor pressures.

9

Recall that 1 bar = 750.1 mmHg. Applying Raoult's law, we have

$$P = x_1 P_1^{sat} + x_2 P_2^{sat} = x_1 P_1^{sat} + (1 - x_1) P_2^{sat} = 750.1$$

Appealing to the Antoine equations provided in the problem statement, we write

$$x_1 10^{6.876 - \frac{1171.1}{[T(K)-273.15]+224.41}} + (1 - x_1) 10^{8.321 - \frac{1718.1}{[T(K)-273.15]+237.52}} = 750.1 \ \ (\text{I})$$

The vapor pressure P_1^{sat}, per the Antoine equation, is given by

$$P_1^{sat} = 10^{6.876 - \frac{1171.1}{224.41+[T(K)-273.15]}} \ \ (\text{II})$$

The vapor phase mole fraction y_1 is expressed as

$$y_1 = \frac{x_1 P_1^{sat}}{P} = \frac{x_1 P_1^{sat}}{750.1} \ \ (\text{III})$$

For each value of x_1, the corresponding temperature can be obtained by solving equation (I) numerically. Then, the value of T can be entered into equation (II) to give the vapor pressure P_1^{sat}. Lastly, the vapor pressure and x_1 are substituted into equation (III) to yield y_1. The calculations are tabulated below.

x_1	x_2	T (K) (Eq. I)	$P1^{sat}$ (mmHg) (Eq. II)	y_1 (Eq. III)
0	1	351.1	1006.47	0.000
0.1	0.9	350.3	982.94	0.131
0.2	0.8	349.3	954.13	0.254
0.3	0.7	348.4	928.76	0.371
0.4	0.6	347.5	903.92	0.482
0.5	0.5	346.5	876.93	0.585
0.6	0.4	345.5	850.58	0.680
0.7	0.3	344.5	824.84	0.770
0.8	0.2	343.5	799.72	0.853
0.9	0.1	342.5	775.20	0.930
1	0	341.5	751.27	1.0

The plots we aim for are one of T (the yellow column) versus x_1 (the blue column) and one of T versus y_1 (the red column); both, along with experimental data, are shown below.
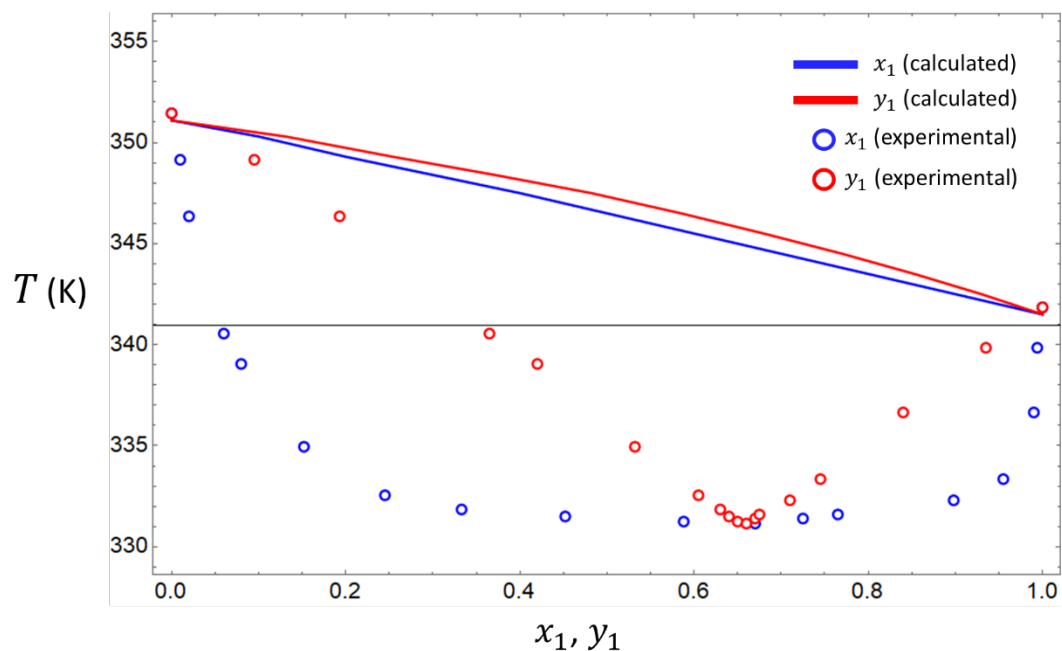
As the plot shows, this mixture deviates from Raoult's law significantly. Physically, this deviation occurs because the ethanol has more beneficial self-interactions (hydrogen bonding) than cross-interactions with the hexane. This system does not form an ideal solution and hence Raoult's law is a poor model to predict the properties of this system.

10

P.6 ➡ *Solution*

Part 1: To begin, we compute vapor pressures for (1) (n-pentane) and (2) (n-heptane) with the Antoine equation; coefficients are taken from Table 1,

$$P_1^{\text{sat}} = \exp\left(13.7667 - \frac{2451.88}{55 + 232.014}\right) = 185.7 \text{ kPa}$$

$$P_2^{\text{sat}} = \exp\left(13.8622 - \frac{2910.26}{55 + 216.432}\right) = 23.11 \text{ kPa}$$

The total pressure is given by the expression we received,

$$P = \frac{1}{2}\left(P_1^{\text{sat}} + P_2^{\text{sat}}\right) = \frac{1}{2} \times (185.7 + 23.11) = 104.4 \text{ kPa}$$

Comparing this with the general relationship $P = x_1 P_1^{\text{sat}} + x_2 P_2^{\text{sat}}$, it is easy to see that $x_1 = 0.5$. The molar fraction of n-heptane in the vapor phase follows from Raoult's law,

$$x_1 P_1^{\text{sat}} = y_1 P \rightarrow y_1 = \frac{x_1 P_1^{\text{sat}}}{P}$$

$$\therefore y_1 = \frac{0.5 \times 185.7}{104.4} = \boxed{0.889}$$

◆ The correct answer is **B.**

Part 2: The overall composition z_1 is given by $z_1 = x_1 L + y_1 V$. Manipulating this relation, we have

$$z_1 = x_1 L + y_1 V \rightarrow z_1 = x_1(1 - V) + y_1 V$$
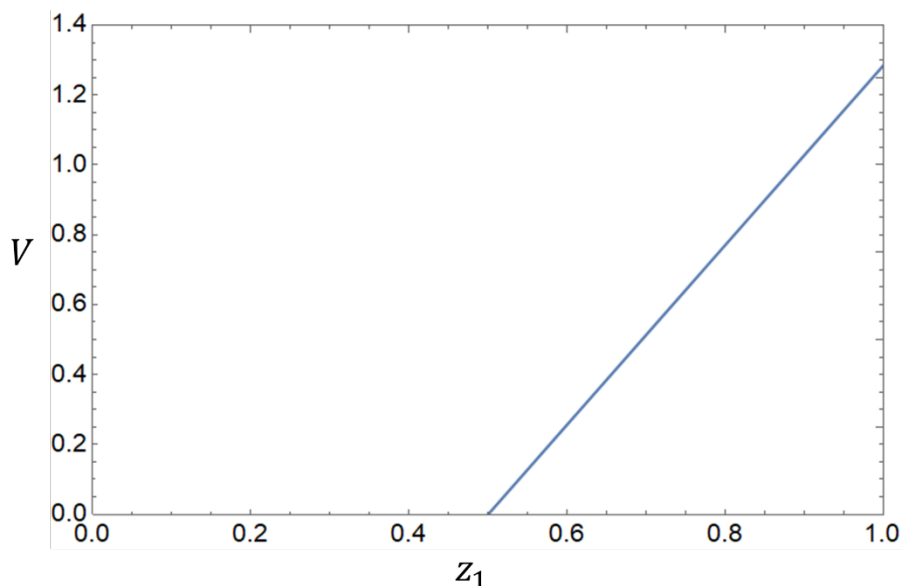
$$\therefore z_1 = x_1 - x_1 V + y_1 V$$

$$\therefore z_1 = x_1 + (y_1 - x_1)V$$

$$\therefore V = \frac{z_1 - x_1}{y_1 - x_1}$$

$$\therefore V = \frac{z_1 - 0.5}{0.889 - 0.5}$$

$$\therefore V = 2.57(z_1 - 0.5)$$

The graph of Z versus z_1 is provided below.

Part 3: From the composition balance, we write

$$z_1 = x_1 L + y_1 V \rightarrow z_1 = x_1(1 - V) + y_1 V$$

$$\therefore z_1 - y_1 V = x_1(1 - V)$$

$$\therefore x_1 = \frac{z_1 - y_1 V}{1 - V}$$

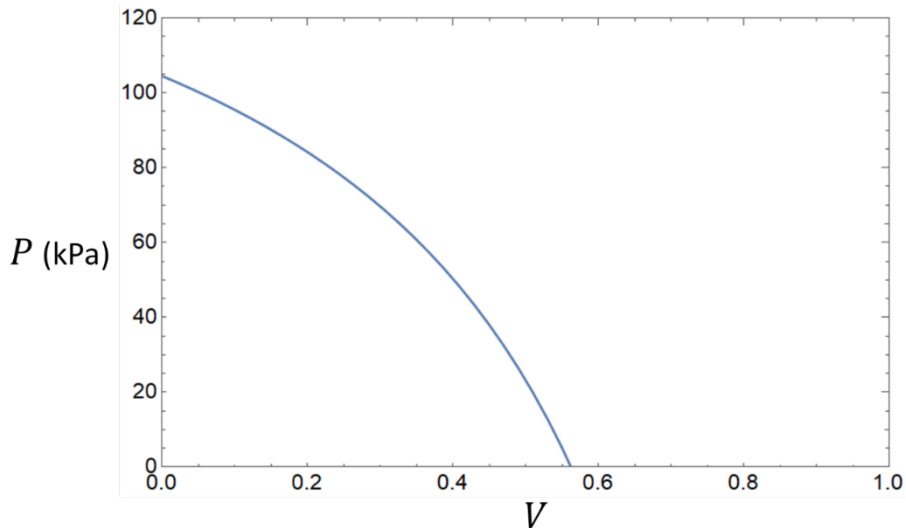From Raoult's law, $x_1 = y_1 P / P_1^{\text{sat}}$, so that

11

$$x_1 = \frac{z_1 - y_1 V}{1 - V} \rightarrow \frac{y_1 P}{P_1^{sat}} = \frac{z_1 - y_1 V}{1 - V}$$

$$\therefore P = \frac{P_1^{sat}}{y_1}\left(\frac{z_1 - y_1 V}{1 - V}\right)$$

$$\therefore P = \frac{185.7}{0.889} \times \left(\frac{0.5 - 0.889 V}{1 - V}\right)$$

$$\therefore P = 208.9\left(\frac{0.5 - 0.889 V}{1 - V}\right)$$

This expression is plotted below.

Returning to the composition balance, we write

$$z_1 = x_1 L + y_1 V \rightarrow z_1 = x_1(1 - V) + \frac{x_1 P_1^{sat}}{P} V$$

$$\therefore 0.5 = x_1(1 - V) + \frac{x_1 \times 185.7}{104.4} V$$

$$\therefore 0.5 = x_1 - x_1 V + 1.78 x_1 V$$
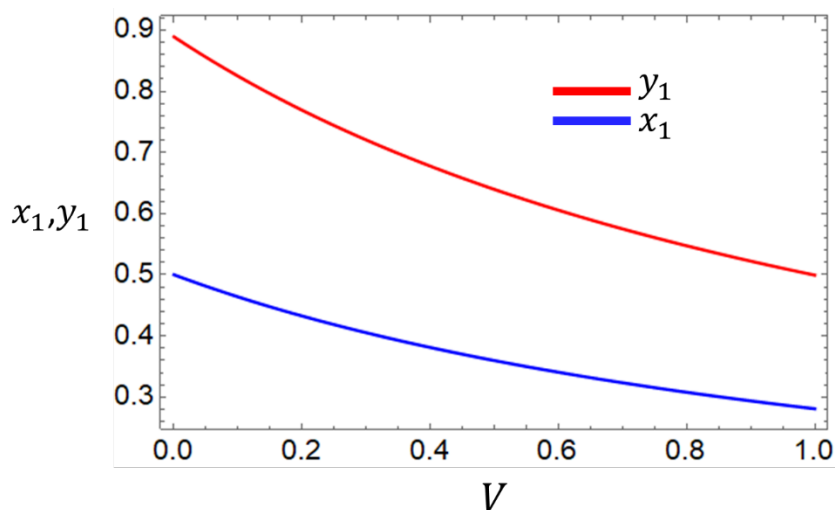
$$\therefore 0.5 = x_1 + 0.78 x_1 V$$

$$\therefore 0.5 = (1 + 0.78 V) x_1$$

$$\therefore x_1 = \frac{0.5}{1 + 0.78 V}$$

In addition,

$$y_1 = \frac{x_1 P_1^{sat}}{P} = \frac{185.7}{104.4} \times \left(\frac{0.5}{1 + 0.78 V}\right) = \frac{0.889}{1 + 0.78 V}$$

The two equations are plotted below.

P.7 ➡ Solution

Given the coefficients in Table 1, the Antoine equations for vapor pressures of pure benzene (1) and ethylbenzene (2) are, respectively,

12

$$\ln P_1^{\text{sat}} = 13.7819 - \frac{2726.81}{T + 217.572}$$

$$\ln P_2^{\text{sat}} = 13.9726 - \frac{3259.93}{T + 212.300}$$

The mole fractions of benzene in liquid (x_1) and vapor (y_1) phases are 0.35 and 0.70, respectively. The sum of pressures from the two components should be such that

$$P = x_1 P_1^{\text{sat}} + x_2 P_2^{\text{sat}}$$

$$\therefore P = 0.35\exp\left(13.7819 - \frac{2726.81}{T + 217.572}\right) + (1 - 0.35)\exp\left(13.9726 - \frac{3259.92}{T + 212.300}\right) \ \ (\text{I})$$

Applying Raoult's law to benzene, we write

$$y_1 P = x_1 P_1^{\text{sat}} \rightarrow 0.70 P = 0.35\exp\left(13.7819 - \frac{2726.81}{T + 217.572}\right)$$

$$\therefore P = 0.5\exp\left(13.7819 - \frac{2726.81}{T + 217.572}\right) \ \ (\text{II})$$

Substituting into equation (I) gives

$$0.5\exp\left(13.7819 - \frac{2726.81}{T + 217.572}\right) = 0.35\exp\left(13.7819 - \frac{2726.81}{T + 217.572}\right) + 0.65\exp\left(13.9726 - \frac{3259.92}{T + 212.300}\right)$$

$$\therefore 0.15\exp\left(13.7819 - \frac{2726.81}{T + 217.572}\right) = 0.65\exp\left(13.9726 - \frac{3259.92}{T + 212.300}\right)$$

$$\therefore 0.231\exp\left(13.7819 - \frac{2726.81}{T + 217.572}\right) = \exp\left(13.9726 - \frac{3259.92}{T + 212.300}\right)$$

Taking logarithms on both sides, it follows that

$$\ln\left[0.231\exp\left(13.7819 - \frac{2726.81}{T + 217.572}\right)\right] = \ln\left[\exp\left(13.9726 - \frac{3259.92}{T + 212.300}\right)\right]$$

$$\therefore \ln 0.231 + 13.7819 - \frac{2726.81}{T + 217.572} = 13.9726 - \frac{3259.92}{T + 212.300}$$

$$\therefore -1.465 + 13.7819 - \frac{2726.81}{T + 217.572} = 13.9726 - \frac{3259.92}{T + 212.3}$$

$$\therefore 12.32 - \frac{2727}{T + 217.6} = 13.97 - \frac{3260}{T + 212.3}$$

$$\therefore \frac{12.32(T + 217.6) - 2727}{T + 217.6} = \frac{13.97(T + 212.3) - 3260}{T + 212.3}$$

$$\therefore \frac{12.32T + 2681 - 2727}{T + 217.6} = \frac{13.97T + 2966 - 3260}{T + 212.3}$$

$$\therefore \frac{12.32T - 46}{T + 217.6} = \frac{13.97T - 294}{T + 212.3}$$

Cross-multiplying,

$$(12.32T - 46)(T + 212.3) = (13.97T - 294)(T + 217.6)$$

$$\therefore 12.32T^2 + 2570T - 9766 = 13.97T^2 + 2746T - 63,970$$

$$\therefore -1.65T^2 - 176T + 54,200 = 0$$

Solving the quadratic equation above yields $T = -242.3°C$, which is unfeasible, and $T = 135.6°C$, which is a viable solution. The temperature in the separator is 135.6°C. Substituting T in equation (II) gives the pressure in the separator,

$$P = 0.5\exp\left(13.7819 - \frac{2726.81}{135.6 + 217.572}\right) = \boxed{214.4 \text{ kPa}}$$

♦ The correct answer is **B**.

P.8 ➡ *Solution*

Part 1: Given the proper coefficients in the Antoine equation, the vapor pressures of benzene (1), toluene (2) and ethylbenzene (3) are respectively given by

$$P_1^{sat} = \exp\left(13.7819 - \frac{2726.81}{T + 217.572}\right)$$

$$P_2^{sat} = \exp\left(13.9320 - \frac{3056.96}{T + 217.625}\right)$$

$$P_3^{sat} = \exp\left(13.9726 - \frac{3259.93}{T + 212.300}\right)$$

For a temperature of 110°C, the saturation pressures are P_1^{sat} = 234.5 kPa, P_2^{sat} = 99.62 kPa and P_3^{sat} = 47.37 kPa. The k-values for each component are determined next,

$$k_1 = \frac{P_1^{sat}}{P} = \frac{234.5}{90} = 2.606$$

$$k_2 = \frac{P_2^{sat}}{P} = \frac{99.62}{90} = 1.107$$

$$k_3 = \frac{P_3^{sat}}{P} = \frac{47.37}{90} = 0.526$$

The overall composition z_i for each component in an equimolar mixture such as the present one is

$$z_1 + z_2 + z_3 = 1 \rightarrow 3z_i = 1$$

$$\therefore z_i = 0.333$$

Appealing to the flash calculation formula, we write

$$\sum_{i=1}^{3} \frac{z_i k_i}{1 + V(k_i - 1)} = 1 \rightarrow \frac{z_1 k_1}{1 + V(k_1 - 1)} + \frac{z_2 k_2}{1 + V(k_2 - 1)} + \frac{z_3 k_3}{1 + V(k_3 - 1)} = 1$$

$$\therefore \frac{0.333 \times 2.606}{1 + V(2.606 - 1)} + \frac{0.333 \times 1.107}{1 + V(1.107 - 1)} + \frac{0.333 \times 0.526}{1 + V(0.526 - 1)} = 1$$

The equation above is a cubic equation in V, and can be solved with the simple Mathematica code

$$\text{Solve}\left[\frac{0.868}{1 + V(2.606 - 1)} + \frac{0.369}{1 + V(1.107 - 1)} + \frac{0.175}{1 + V(0.526 - 1)} == 1, V\right]$$

This returns V = −6.074, which is preposterous, V = 1.0, which the trivial solution, and V = 0.822, which is a viable solution. The molar fraction of the vapor formed is 0.822. We can then calculate the molar fractions of the vapor phases, namely

$$y_1 = \frac{z_1 k_1}{1 + V(k_1 - 1)} = \frac{0.333 \times 2.606}{1 + 0.822 \times (2.606 - 1)} = 0.374$$

$$y_2 = \frac{z_2 k_2}{1 + V(k_2 - 1)} = \frac{0.333 \times 1.107}{1 + 0.822 \times (1.107 - 1)} = 0.339$$

$$y_3 = \frac{z_3 k_3}{1 + V(k_3 - 1)} = \frac{0.333 \times 0.526}{1 + 0.822 \times (0.526 - 1)} = 0.287$$

Observe that $y_1 + y_2 + y_3$ = 1 as it should be. Next, we can easily determine the molar fractions of the liquid phases,

$$x_1 = \frac{y_1}{k_1} = \frac{0.374}{2.606} = 0.144$$

$$x_2 = \frac{y_2}{k_2} = \frac{0.339}{1.107} = 0.306$$

14

$$x_3 = \frac{y_3}{k_3} = \frac{0.287}{0.526} = 0.546$$

Here, $x_1 + x_2 + x_3 = 0.996 \approx 1$; the small difference is due to roundoff. We have determined the molar fractions of the liquid and vapor phases; the results are summarized below.

Compound	Benzene (1)	Toluene (2)	Ethyl benzene (3)
P_i^{sat} (kPa)	234.5	99.62	47.37
k_i	2.606	1.107	0.526
Liquid phase molar fraction x_i	0.144	0.306	0.546
Vapor phase molar fraction y_i	0.374	0.339	0.287

Part 2: As the temperature is not varied, the saturation pressure values continue to be P_1^{sat} = 234.5 kPa, P_2^{sat} = 99.62 kPa, and P_3^{sat} = 47.37 kPa. The k-values are now

$$k_1 = \frac{P_1^{\text{sat}}}{P} = \frac{234.5}{120} = 1.954$$

$$k_2 = \frac{P_2^{\text{sat}}}{P} = \frac{99.62}{120} = 0.830$$

$$k_3 = \frac{P_3^{\text{sat}}}{P} = \frac{47.37}{120} = 0.395$$

Employing the flash calculation formula as before, we have

$$\sum_{i=1}^{1} \frac{z_i k_i}{1 + V(k_i - 1)} = 1 \rightarrow \frac{z_1 k_1}{1 + V(k_1 - 1)} + \frac{z_2 k_2}{1 + V(k_2 - 1)} + \frac{z_3 k_3}{1 + V(k_3 - 1)} = 1$$

$$\therefore \frac{0.333 \times 1.954}{1 + V(1.954 - 1)} + \frac{0.333 \times 0.830}{1 + V(0.830 - 1)} + \frac{0.333 \times 0.395}{1 + V(0.395 - 1)} = 1$$

Once again, we can appeal to the *Solve* command,

$$\text{Solve}\left[\frac{0.333 * 1.954}{1 + V(1.954 - 1)} + \frac{0.333 * 0.83}{1 + V(0.83 - 1)} + \frac{0.333 * 0.395}{1 + V(0.395 - 1)} == 1, V\right]$$

This returns two impossible solutions and V = 0.143, which is a viable result. The molar fraction of the vapor formed is 0.143. We are now able to calculate the molar fractions of the vapor phases, namely

$$y_1 = \frac{z_1 k_1}{1 + V(k_1 - 1)} = \frac{0.333 \times 1.954}{1 + 0.143 \times (1.954 - 1)} = 0.573$$

$$y_2 = \frac{z_2 k_2}{1 + V(k_2 - 1)} = \frac{0.333 \times 0.830}{1 + 0.143 \times (0.830 - 1)} = 0.283$$

$$y_3 = \frac{z_3 k_3}{1 + V(k_3 - 1)} = \frac{0.333 \times 0.395}{1 + 0.143 \times (0.395 - 1)} = 0.144$$

The molar fractions of the liquid phases follow as

$$x_1 = \frac{y_1}{k_1} = \frac{0.573}{1.954} = 0.293$$

$$x_2 = \frac{y_2}{k_2} = \frac{0.283}{0.830} = 0.341$$

$$x_3 = \frac{y_3}{k_3} = \frac{0.144}{0.395} = 0.365$$

The results are summarized below.

Compound	Benzene (1)	Toluene (2)	Ethyl benzene (3)
P_i^{sat} (kPa)	234.5	99.62	47.37
k_i	2.606	1.107	0.526
Liquid phase molar fraction x_i	0.293	0.341	0.365
Vapor phase molar fraction y_i	0.573	0.283	0.144

P.9 ➡ *Solution*

Using coefficients from Table 1, acetone and acetonitrile are described by the equations

$$\ln P_1^{\text{sat}} = 14.3145 - \frac{2756.22}{T + 228.06}$$

$$\ln P_2^{\text{sat}} = 14.895 - \frac{3413.1}{T + 250.523}$$

The vapor pressures at 340 K = 66.8°C are

$$P_1^{\text{sat}} = \exp\left(14.3145 - \frac{2756.22}{66.8 + 228.06}\right) = 143.6 \text{ kPa}$$

$$P_2^{\text{sat}} = \exp\left(14.895 - \frac{3413.1}{66.8 + 250.523}\right) = 62.74 \text{ kPa}$$

Invoking the flash calculation formula, we have

$$\sum_{i=1}^{n} \frac{z_i k_i}{1 + V(k_i - 1)} = 1 \rightarrow \frac{z_1 P_1^{\text{sat}}/P}{1 + V\left(\dfrac{P_1^{\text{sat}}}{P} - 1\right)} + \frac{(1 - z_2) P_2^{\text{sat}}/P}{1 + V\left(\dfrac{P_2^{\text{sat}}}{P} - 1\right)} = 1$$

$$\therefore \frac{z_1 P_1^{\text{sat}}}{P + V\left(P_1^{\text{sat}} - P\right)} + \frac{(1 - z_1) P_2^{\text{sat}}}{P + V\left(P_2^{\text{sat}} - P\right)} = 1$$

Substituting the numerical values, we get

$$\frac{0.75 \times 143.6}{115 + V(143.6 - 115)} + \frac{(1 - 0.75) \times 62.74}{115 + V(62.74 - 115)} = 1$$

$$\therefore \frac{107.7}{115 + 28.6V} + \frac{15.69}{115 - 52.26V} = 1$$

The equation above is in fact a quadratic equation in V, and can be solved to yield $V = 0.646$. (The other solution is $V = 1$, which is trivial.) The mole fraction of acetone in the vapor phase is then

$$y_1 = \frac{z_1 P_1^{\text{sat}}}{P + V\left(P_1^{\text{sat}} - P\right)} = \frac{0.75 \times 143.6}{115 + 0.646 \times (143.6 - 115)} = \boxed{0.807}$$

The mole fraction of acetone in liquid phase follows from Raoult's law,

$$x_1 P_1^{\text{sat}} = y_1 P \rightarrow x_1 = \frac{y_1 P}{P_1^{\text{sat}}}$$

$$\therefore x_1 = \frac{0.807 \times 115}{143.6} = \boxed{0.646}$$

The recovery is the ratio of acetone moles in the vapor phase to acetone moles in the feed. In the case at hand,

$$R_1 = \frac{V y_1}{z_1} = \frac{0.646 \times 0.807}{0.75} = \boxed{0.695}$$

Consider now mixture 2. The pressure of the system is converted as $P = 101.325 \times 0.80 = 81.06$ kPa. Taking coefficients from Table 1, ethanol and propanol are described by the equations

$$\ln P_1^{\text{sat}} = 16.8958 - \frac{3795.17}{T + 230.337}$$

16

$$\ln P_2^{\text{sat}} = 16.1154 - \frac{3483.67}{T + 205.807}$$

At a temperature of 360 K = 86.85°C, the vapor pressures are

$$P_1^{\text{sat}} = \exp\left(16.8958 - \frac{3795.17}{86.85 + 230.337}\right) = 138.4 \text{ kPa}$$

$$P_2^{\text{sat}} = \exp\left(16.1154 - \frac{3483.67}{86.85 + 205.807}\right) = 67.48 \text{ kPa}$$

We can use the flash calculation formula in the same form obtained for mixture 1, giving

$$\frac{z_1 P_1^{\text{sat}}}{P + V\left(P_1^{\text{sat}} - P\right)} + \frac{\left(1 - z_1\right) P_2^{\text{sat}}}{P + V\left(P_2^{\text{sat}} - P\right)} = 1$$

$$\therefore \frac{0.25 \times 138.4}{81.06 + V\left(138.4 - 81.06\right)} + \frac{\left(1 - 0.25\right) \times 67.48}{81.06 + V\left(67.48 - 81.06\right)} = 1$$

$$\therefore \frac{34.6}{81.06 + 57.34V} + \frac{50.61}{81.06 - 13.58V} = 1$$

As before, the equation above is in fact a quadratic equation in V. Solving it, we obtain $V = 0.432$. The mole fraction of ethanol in the vapor phase is then

$$y_1 = \frac{z_1 P_1^{\text{sat}}}{P + V\left(P_1^{\text{sat}} - P\right)} = \frac{0.25 \times 138.4}{81.06 + 0.432 \times \left(138.4 - 81.06\right)} = \boxed{0.327}$$

The corresponding mole fraction of ethanol in liquid phase follows from Raoult's law,

$$x_1 P_1^{\text{sat}} = y_1 P \rightarrow x_1 = \frac{y_1 P}{P_1^{\text{sat}}}$$

$$\therefore x_1 = \frac{0.327 \times 81.06}{138.4} = \boxed{0.192}$$

Lastly, the recovery of ethanol is

$$R = \frac{V y_1}{z_1} = \frac{0.432 \times 0.327}{0.25} = \boxed{0.565}$$

♦ Statements **1**, **3**, and **5** are true, while statements **2**, **4** and **6** are false.

P.10 ➡ *Solution*

Applying Raoult's law to compound 1, we write

$$y_1 P = x_1 \gamma_1 P_1^{\text{sat}} \rightarrow P_1^{\text{sat}} = \frac{y_1 P}{x_1 \gamma_1}$$

Likewise, for compound 2,

$$P_2^{\text{sat}} = \frac{y_2 P}{x_2 \gamma_2}$$

Dividing one equation by the other, we obtain

$$\frac{P_1^{\text{sat}}}{P_2^{\text{sat}}} = \frac{\dfrac{y_1 \cancel{P}}{x_1 \gamma_1}}{\dfrac{y_2 \cancel{P}}{x_2 \gamma_2}} = \frac{y_1 x_2 \gamma_2}{y_2 x_1 \gamma_1}$$

Substituting the numerical data yields

$$\frac{\exp\left(A_1 - \dfrac{B_1}{T}\right)}{\exp\left(A_2 - \dfrac{B_2}{T}\right)} = \frac{0.950 \times \left(1 - 0.002\right) \times \exp\left(0.93 \times 0.002^2\right)}{\left(1 - 0.950\right) \times 0.002 \times \exp\left(0.93 \times 0.998^2\right)} = 3755$$

17

$$\therefore \exp\left(A_1 - \frac{B_1}{T} - A_2 + \frac{B_2}{T}\right) = 3755$$

$$\therefore \exp\left(10.08 - \frac{2572}{T} - 11.63 + \frac{6254}{T}\right) = 3755$$

$$\therefore \exp\left(-1.55 + \frac{3682}{T}\right) = 3755$$

Applying logarithms to both sides,

$$-1.55 + \frac{3682}{T} = \ln 3755 = 8.231$$

$$\therefore \frac{3682}{T} = 9.781$$

$$\therefore \boxed{T = 376.4 \text{ K}}$$

The temperature of the separator has been established. Lastly, the total pressure is determined as

$$P = \frac{x_1 \gamma_1 P_1^{\text{sat}}}{y_1} = \frac{0.002 \times \exp\left[0.93(1-0.002)^2\right] \times \exp\left(10.08 - \frac{2572}{376.4}\right)}{0.95} = \boxed{0.137 \text{ bar}}$$

The pressure of the separator has been computed.

♦ The correct answer is **A**.

P.11 ➡ *Solution*

Taking coefficients from Table 1, the Antoine equations for acetone and methanol are, respectively,

$$P_1^{\text{sat}} = \exp\left(14.3145 - \frac{2756.22}{T + 228.060}\right)$$

$$P_2^{\text{sat}} = \exp\left(16.5785 - \frac{3638.27}{T + 239.500}\right)$$

The activity coefficients of acetone (1) and methanol (2) are computed next,

$$\gamma_1 = \exp\left(0.64 x_2^2\right) = \exp\left(0.64 \times 0.825^2\right) = 1.546$$

$$\gamma_2 = \exp\left(0.64 x_1^2\right) = \exp\left(0.64 \times 0.175^2\right) = 1.020$$

Applying modified Raoult's law, we have

$$P = x_1 \gamma_1 P_1^{\text{sat}} + x_2 \gamma_2 P_2^{\text{sat}}$$

$$\therefore 100 = 0.175 \times 1.546 \times P_1^{\text{sat}} + 0.825 \times 1.020 P_2^{\text{sat}}$$

$$\therefore 100 = 0.271 P_1^{\text{sat}} + 0.842 P_2^{\text{sat}}$$

Substituting P_1^{sat} and P_2^{sat} from the Antoine equations, we get

$$0.271 \exp\left(14.3145 - \frac{2756.22}{T + 228.060}\right) + 0.842 \exp\left(16.5785 - \frac{3638.27}{T + 239.5}\right) = 100.1$$

This transcendental equation can be easily solved with Mathematica's *FindRoot* command,

$$\text{FindRoot}\left[0.271\text{Exp}\left[14.3145 - \frac{2756.22}{T + 228.06}\right] + 0.842\text{Exp}\left[16.5785 - \frac{3638.27}{T + 239.5}\right]\right.$$
$$\left. - 100.1, \{T, 10\}\right]$$

This returns T = 59.5°C. The boiling point of the acetone/methanol mixture is 59.5°C. The corresponding vapor pressure P_1^{sat} is

$$P_1^{\text{sat}} = \exp\left(14.3145 - \frac{2756.22}{59.5 + 228.060}\right) = 113.3 \text{ kPa}$$

18

It remains to compute the vapor phase mole fraction of acetone, y_1,

$$y_1 P = x_1 \gamma_1 P_1^{\text{sat}} \rightarrow y_1 = \frac{x_1 \gamma_1 P_1^{\text{sat}}}{P}$$

$$\therefore y_1 = \frac{0.175 \times 1.546 \times 113.3}{100.1} = \boxed{0.306}$$

♦ The correct answer is **D**.

P.12 ➡ Solution

Before anything else, we must establish the value of A. To do so, we take the expressions

$$\ln \gamma_1 = A x_2^2$$

$$\ln \gamma_2 = A x_1^2$$

and subtract one from the other, giving

$$\ln \gamma_2 - \ln \gamma_1 = A x_1^2 - A x_2^2$$

$$\therefore \ln\left(\frac{\gamma_2}{\gamma_1}\right) = A\left(x_1^2 - x_2^2\right) \ \text{(I)}$$

At the azeotrope, we have $x_i = y_i$ and, consequently,

$$y_i P = x_i \gamma_i P_i^{\text{sat}} \rightarrow \gamma_i = \frac{P}{P_i^{\text{sat}}}$$

Substituting this result into equation (I) brings to

$$\ln\left(\frac{\gamma_2}{\gamma_1}\right) = A\left(x_1^2 - x_2^2\right) \rightarrow \ln\left(\frac{\cancel{P}/P_2^{\text{sat}}}{\cancel{P}/P_1^{\text{sat}}}\right) = A\left(x_1^2 - x_2^2\right)$$

$$\therefore \ln\left(\frac{P_1^{\text{sat}}}{P_2^{\text{sat}}}\right) = A\left(x_1^2 - x_2^2\right)$$

$$\therefore \ln\left(\frac{75.20}{31.66}\right) = A \times \left(0.294^2 - 0.706^2\right)$$

$$\therefore 0.865 = A \times (-0.412)$$

$$\therefore A = -2.10$$

We have $x_1 = 0.6$ and $x_2 = 0.4$. We proceed to determine the γ activity coefficients, namely

$$\ln \gamma_1 = A x_2^2 = -2.11 \times 0.4^2 = -0.338$$

$$\therefore \gamma_1 = 0.713$$

and

$$\ln \gamma_2 = A x_1^2 = -2.11 \times 0.6^2 = -0.760$$

$$\therefore \gamma_2 = 0.468$$

The total pressure follows from modified Raoult's law,

$$P = x_1 \gamma_1 P_1^{\text{sat}} + x_2 \gamma_2 P_2^{\text{sat}}$$

$$\therefore P = 0.6 \times 0.713 \times 75.2 + 0.4 \times 0.468 \times 31.66 = \boxed{38.10 \text{ kPa}}$$

The mole fraction of cyclohexanone in vapor phase is then

$$y_1 P = x_1 \gamma_1 P_1^{\text{sat}} \rightarrow y_1 = \frac{x_1 \gamma_1 P_1^{\text{sat}}}{P}$$

$$\therefore y_1 = \frac{0.6 \times 0.713 \times 75.20}{38.10} = \boxed{0.844}$$

♦ The correct answer is **B**.

19

P.13 ➡ Solution

1. True. The range of pressures for a system to have two phases is from the dew point pressure to the bubble point pressure. At dew point, $y_1 = z_1 = 0.65$ and $y_2 = 1 - y_1 = 0.35$. From the expression for total pressure, we write

$$P = x_1\gamma_1 P_1^{sat} + x_2\gamma_2 P_2^{sat} \to y_1 P = x_1\gamma_1 P_1^{sat}$$

$$\therefore y_1 P = x_1\gamma_1 P_1^{sat}$$

$$\therefore P = \frac{x_1\gamma_1 P_1^{sat}}{y_1}$$

$$\therefore P = \frac{x_1 \exp\left[0.67(1-x_1)^2\right] \times 32.27}{0.65}$$

In a similar manner,

$$y_2 P = x_2\gamma_2 P_2^{sat} \to P = \frac{x_2\gamma_2 P_2^{sat}}{y_2}$$

$$\therefore P = \frac{(1-x_1)\exp(0.67x_1^2) \times 73.14}{0.35}$$

Equating the two previous expressions, we have

$$\frac{x_1 \exp\left[0.67(1-x_1)^2\right] \times 32.27}{0.65} = \frac{(1-x_1)\exp(0.67x_1^2) \times 73.14}{0.35}$$

This is a transcendental equation in x_1, and as such requires a numerical method to be solved. We can apply Mathematica's *FindRoot* function with an initial guess $x_1 = 0.1$,

$$\text{FindRoot}\left[\frac{x * \text{Exp}[0.67(1 - x)^2] * 32.27}{0.65} - \frac{(1 - x) * \text{Exp}[0.67x^2] * 73.14}{0.35}, \{x, 0.1\}\right]$$

This returns $x_1 = 0.874$. We can then determine the dew point pressure,

$$P_{dew} = \frac{0.874 \times \exp\left[0.67 \times (1-0.874)^2\right] \times 32.27}{0.65} = 43.85 \text{ kPa}$$

At the bubble point, we have $x_1 = z_1 = 0.65$ and $x_2 = 1 - x_1 = 0.35$. The bubble point pressure follows as

$$P_{bubble} = x_1\gamma_1 P_1^{sat} + x_2\gamma_2 P_2^{sat}$$

$$\therefore P_{bubble} = 0.65 \times \exp\left[0.67(1-0.65)^2\right] \times 32.27 + 0.35 \times \exp(0.67 \times 0.65^2) \times 73.14 = 56.74 \text{ kPa}$$

The range of pressures for which the system can have two phases spans 43.85 kPa to 56.74 kPa. This of course includes $P = 50$ kPa.

2. False. Resorting to a bubble-point calculation, the pressure is

$$P_{bubble} = x_1\gamma_1 P_1^{sat} + x_2\gamma_2 P_2^{sat}$$

$$\therefore P_{bubble} = 0.75 \times \exp\left[0.67(1-0.75)^2\right] \times 32.27 + 0.25 \times \exp(0.67 \times 0.75^2) \times 73.14 = 51.89 \text{ kPa}$$

The molar fraction of vapor-phase species 1 is then

$$y_1 P = x_1\gamma_1 P_1^{sat} \to y_1 = \frac{x_1\gamma_1 P_1^{sat}}{P}$$

$$\therefore y_1 = \frac{0.75 \times \exp\left[0.67(1-0.75)^2\right] \times 32.27}{51.89} = 0.486$$

Lastly, we can determine the molar fraction of the system that is vapor,

$$V = \frac{z_1 - x_1}{y_1 - x_1} = \frac{0.65 - 0.75}{0.486 - 0.75} = \boxed{0.379}$$

20

3. True. At an azeotrope, $y_1 = x_1$. For component 1, we write

$$y_1 P = x_1 \exp\left[0.67(1-x_1)^2\right] \times 32.27$$

$$\therefore P = 32.27 \exp\left[0.67(1-x_1)^2\right]$$

Similarly, for component 2,

$$y_2 P = x_2 \exp\left(0.67 x_1^2\right) \times 73.14$$

$$\therefore P = 73.14 \exp\left(0.67 x_1^2\right)$$

Equating the two previous expressions brings to

$$32.27 \exp\left[0.67(1-x_1)^2\right] = 73.14 \exp\left(0.67 x_1^2\right)$$

As before, we can use *FindRoot*,

$$\text{FindRoot}[32.27\text{Exp}[0.67(1-x)^2] - 73.14\text{Exp}[0.67x^2], \{x, 0.1\}]$$

This returns $x_1 = -0.111$, which is impossible. As a result, we conclude that the system does not exhibit an azeotrope.

P.14 ➡ Solution

Part 1: Applying modified Raoult's law brings to

$$P = x_1 \gamma_1 P_1^{\text{sat}} + x_2 \gamma_2 P_2^{\text{sat}}$$

$$\therefore P = 0.65 \times \exp\left[1.8 \times (1-0.65)^2\right] \times 1.24 + 0.35 \times \exp\left(1.8 \times 0.65^2\right) \times 0.89 = 1.671 \text{ bar}$$

The vapor phase mole fraction of species 1 is then

$$y_1 P = x_1 \gamma_1 P_1^{\text{sat}} \rightarrow y_1 = \frac{x_1 \gamma_1 P_1^{\text{sat}}}{P}$$

$$\therefore y_1 = \frac{0.65 \times \exp\left(1.8 \times 0.35^2\right) \times 1.24}{1.671} = 0.601$$

Consider a unit mole of the binary system. The sum of the number of moles in the liquid phase, L, and the number of moles in the vapor phase, V, must equal unity; that is,

$$L + V = 1$$

A mole balance for species 1 yields

$$z_1 = L x_1 + V y_1$$

From the previous equation, $L = 1 - V$. Thus,

$$z_1 = (1-V) x_1 + V y_1$$

$$\therefore z_1 = x_1 - x_1 V + V y_1$$

$$\therefore z_1 = x_1 + V(y_1 - x_1) \text{ (I)}$$

In the following, values of z_1 are tabulated for V ranging from zero to unity.

V	z_1
0	0.65
0.1	0.6451
0.2	0.6402
0.3	0.6353
0.4	0.6304
0.5	0.6255
0.6	0.6206
0.7	0.6157
0.8	0.6108
0.9	0.6059
1	0.601

21

Accordingly, this two-phase system can exist with a liquid mole fraction of $x_1 = 0.65$ for overall mole fraction z_1 ranging from 0.601 to 0.65.

Part 2: An azeotropic system has the same composition for both phases and, accordingly, is associated with a relative volatility equal to one. In mathematical terms,

$$\alpha = \frac{\gamma_1 P_1^{sat}}{\gamma_2 P_2^{sat}} = 1.0 \rightarrow \frac{\exp\left[1.8(1-x_1)^2\right] \times P_1^{sat}}{\exp\left(1.8x_1^2\right) \times P_2^{sat}} = 1.0$$

$$\therefore \frac{\exp\left[1.8(1-x_1)^2\right]}{\exp\left(1.8x_1^2\right)} = \frac{0.89}{1.24} = 0.718$$

$$\therefore \exp\left[1.8(1-x_1)^2 - 1.8x_1^2\right] = 0.718$$

$$\therefore \exp\left(1.8 - 3.6x_1 + \cancel{1.8x_1^2} - \cancel{1.8x_1^2}\right) = 0.718$$

$$\therefore \exp\left(1.8 - 3.6x_1\right) = 0.718$$

$$\therefore 1.8 - 3.6x_1 = \ln 0.718 = -0.331$$

$$\therefore x_1 = \frac{-2.131}{-3.6} = \boxed{0.592}$$

Lastly, we can establish the pressure at which the system exhibits azeotropism,

$$y_1 P = x_1 \gamma_1 P_1^{sat} \rightarrow P = \frac{x_1 \gamma_1 P_1^{sat}}{y_1}$$

$$\therefore P = \frac{0.592 \times \exp\left[1.8 \times (1-0.592)^2\right] \times 1.24}{0.592} = \boxed{1.673 \text{ bar}}$$

♦ The correct answer is **D**.

▶ ANSWER SUMMARY

Problem 1		C
	2.1	C
	2.2	A
Problem 2	2.3	D
	2.4	A
	2.5	A
Problem 3		Open-ended pb.
Problem 4		Open-ended pb.
Problem 5		Open-ended pb.
	6.1	B
Problem 6	6.2	Open-ended pb.
	6.3	Open-ended pb.
Problem 7		B
Problem 8	8.1	Open-ended pb.
	8.2	Open-ended pb.
Problem 9		T/F
Problem 10		A
Problem 11		D
Problem 12		B
Problem 13		T/F
Problem 14	14.1	Open-ended pb.
	14.2	D

22

▶ 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.

Got any questions related to this quiz? We can help!
Send a message to contact@montogue.com and we'll
answer your question as soon as possible.