

Problem No. 1

Problem 4.6, S&H

Given:

Feed composition of benzene/ethyl alcohol binary mixture: 25mol% benzene, 75mol% ethanol

Pressure, $P = 1\text{atm}$

Flash unit is heated from 60°C to 90°C

T-x-y experimental data:

Temperature ($^\circ\text{C}$)											
78.4	77.5	75	72.5	70	68.5	67.7	68.5	72.5	75	77.5	80.1
Mol% benzene in vapor (y_B)											
0	7.5	28	42	54	60	68	73	82	88	95	100
Mol% benzene in liquid (x_B)											
0	1.5	5	12	22	31	68	81	91	95	98	100

Part A:

The bubble point temperature is defined as the temperature at which vaporization begins. First, we graph the experimental T-x-y data provided in the problem statement (see graph). The feed fraction of benzene is 25mol% (point M) and we draw a vertical line and locate the point on the saturated liquid (bubble point) line (point A, see graph) at 25mol% benzene (point N). The temperature at this point is approximately $T=69.4^\circ\text{C}$

Part B:

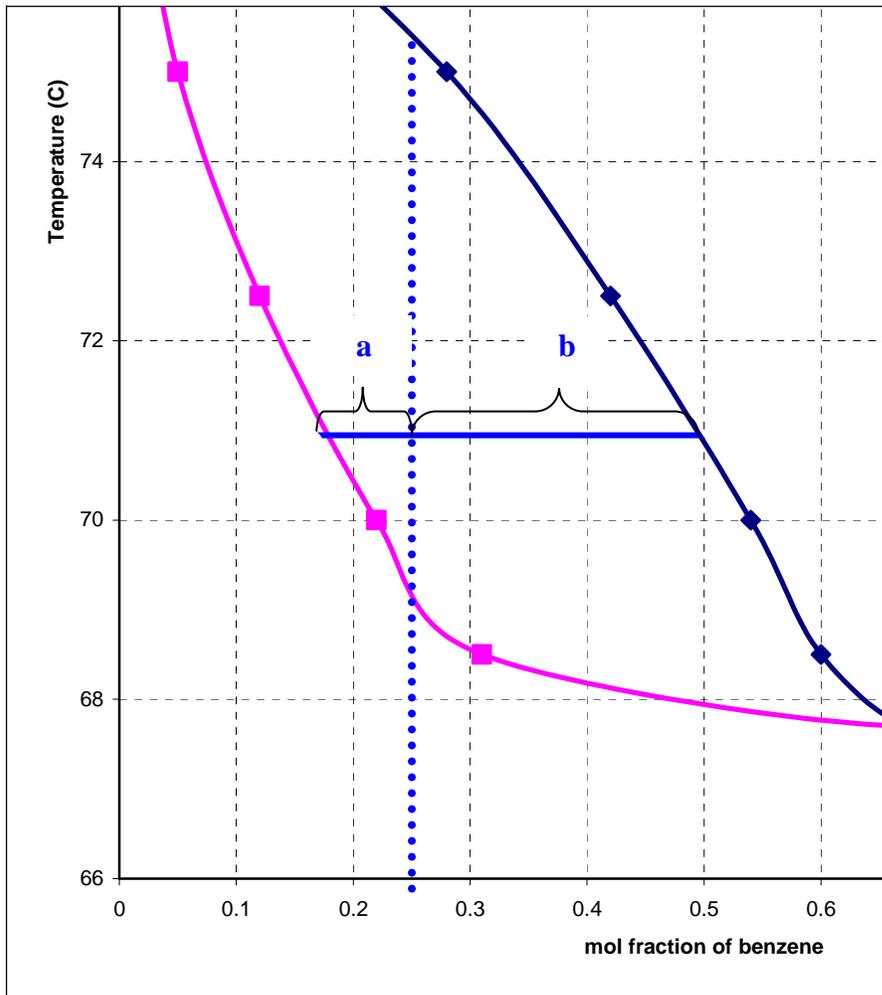
The bubble point temperature was determined graphically in part (a) as $T=69.4^\circ\text{C}$ and we are now asked to find the composition of the vapor at this temperature. First, we draw a horizontal tie line at $T=69.4^\circ\text{C}$ that intersects the saturated vapor line at point P, which represents the composition of the vapor phase in equilibrium with the liquid phase at this temperature and the mole fraction of benzene is 0.56.

Part C.

The 25mol% evaporation refers to the fraction of the feed stream, F , which is vaporized, or $V/F=0.25$. The total mole fraction of benzene in the reactor is $z_B=0.25$ and both liquid and vapor phases are present. We apply the reverse lever-arm rule, which gives the relative amounts of vapor and liquid present at a given temperature and feed mole fraction. Along the tie line connecting the vapor and liquid saturation lines, we attempt to locate a temperature at which the tie line bisected by $z_B=0.25$ is approximately 3 times longer between $z_B=0.25$ and the vapor line (segment b in graph) than between $z_B=0.25$ and the liquid line. The following example graph illustrates this: $length_a / length_b = 25 / 75 = V / L$.

We employ a trial-and-error approach by sliding along $z_B=0.25$ within the phase diagram to locate a tie line with this geometric requirement. This occurs at approximately $T=71.2^\circ\text{C}$ and the liquid composition is given by the saturated liquid line (point A, large graph) and $x_B=0.175$.

Illustration of Reverse Lever Arm Rule:



Part D:

The approach is similar to (c) and again a trial and error approach is used to find the temperature at which the mole fraction of benzene, $z_B=0.25$, bisects a tie line that is 9 times longer in the segment between the liquid line and $z_B=0.25$ than the vapor line and $z_B=0.25$. This occurs at approximately $T=75.1^\circ\text{C}$ and the saturated liquid phase has a mole fraction of benzene $x_B=0.045$ (point D).

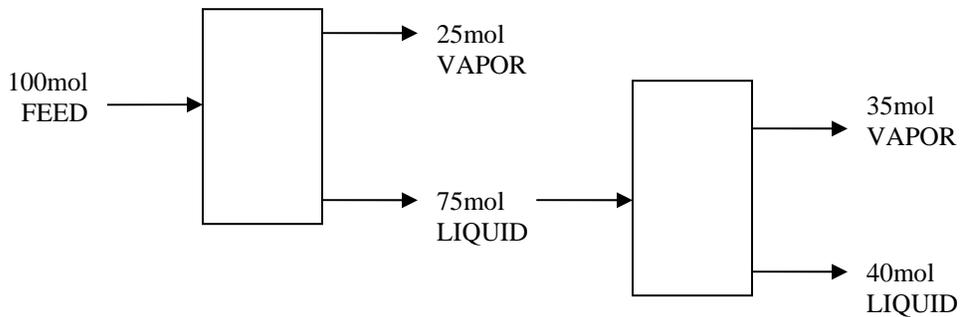
Part E:

We are asked to determine the liquid composition if the liquid product of a 25mol% evaporation is fed to an additional flash drum.

A mass balance simplifies this two-staged separation problem, as illustrated below.

There are a couple of confusing items:

- The problem statement is not clear about whether 35mol% of the FEED or the LIQUID that has been just condensed is vaporized. They are referring to the FEED.
- The problem asks you to repeat part (d), in which 90mol% of the feed has been vaporized; however, they have already specified that 35mol% has been vaporized, so the reference to part (d) is only to repeat the approach (reverse lever-arm rule with known V/F).



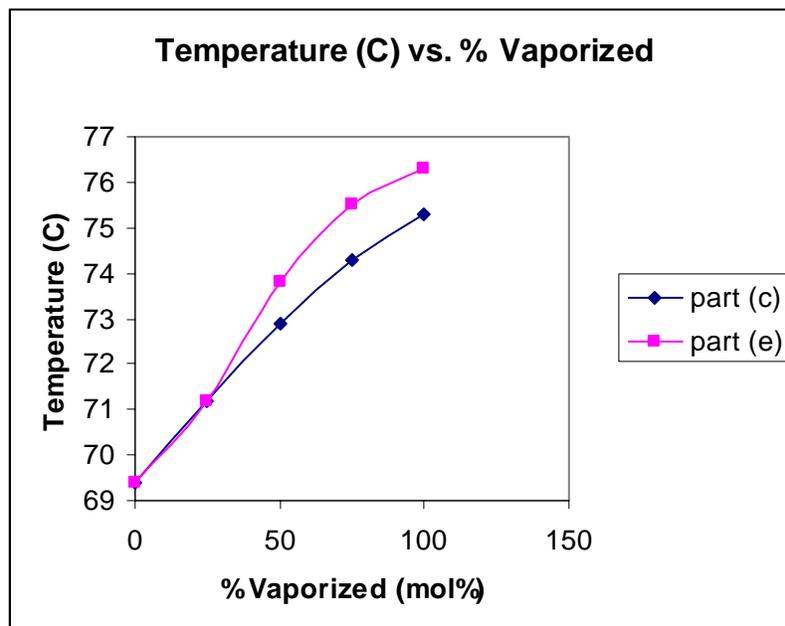
We are asked in a very roundabout way to find the final liquid composition coming out of the second flash unit. From part (c), we know that the composition of the liquid product of the first unit has $x_B=0.175$. This is now the feed to our second drum, so now $z_B=0.175$. Again, we apply the reverse lever-arm rule to find the temperature at which $V/L = 35/40 = 0.467$. Graphically, this corresponds to $length_c / length_d = 0.467$. This occurs at approximately $T=74.9^\circ\text{C}$ and $x_B=0.05$ (point G on graph)

Part F:

We are asked to plot the temperature vs. percent vaporized for parts (c) and (e). If we plot only the temperature, %vapor that we were asked to report, we only have 2 data points. *From the wording of the problem statement, this seems to be what they are asking.* However, if we repeat the reverse lever-arm rule over a range of temperatures to find the relative vapor and liquid fractions at $z_B=0.25$ and $z_B=0.175$ (part e), we can produce a more representative graph.

These data are tabulated and graphed below:

<u>% Vaporization (mol%)</u>	<u>T, part c ($z_B=0.25$)</u>	<u>T, part e ($z_B=0.175$)</u>
0	69.4	69.4
25	71.2	71.2
50	72.9	73.8
75	74.3	75.5
100	75.3	76.3



This graph illustrates how higher temperatures are required to achieve separation when a lower mass fraction of the more volatile component, benzene, is fed to the flash unit.

Part G:

We are given experimental vapor pressure data, or $T = f(P_i^{vap})$. We are asked to construct a T-x-y diagram using Raoult's Law and Dalton's Law to compare with the experimental T-x-y data provided at the beginning of the problem statement. Note that x_B is the mole fraction of benzene and x_E is the mole fraction of ethanol.

$$\text{Raoult's Law: } y_B = \frac{p_B}{P_{tot}} = \frac{x_B P_B^{vap}}{P_{tot}}; \quad y_E = \frac{x_E P_E^{vap}}{P_{tot}} \quad (1)$$

$$\text{Dalton's Law: } \sum_i p = P = \sum_i y_i P = P \therefore y_B + y_E = 1 \quad (2)$$

$$x_B + x_E = 1 \quad (3)$$

These equations can be reduced in terms of K values:

$$K_B = \frac{y_B}{x_B}, \quad K_E = \frac{y_E}{x_E} \quad (4)$$

Equations (2-4) can be further reduced:

$$y_B + y_E = K_B x_B + K_E x_E = x_B + x_E$$

$$K_B x_B + K_E (1 - x_B) = 1$$

$$x_B = \frac{1 - K_E}{K_B - K_E}$$

We must fit our experimental P=f(T) data to equations in order to find the K-values to find the mole fractions of benzene and ethanol. We can fit the experimental data to a form of the Antoine equation,

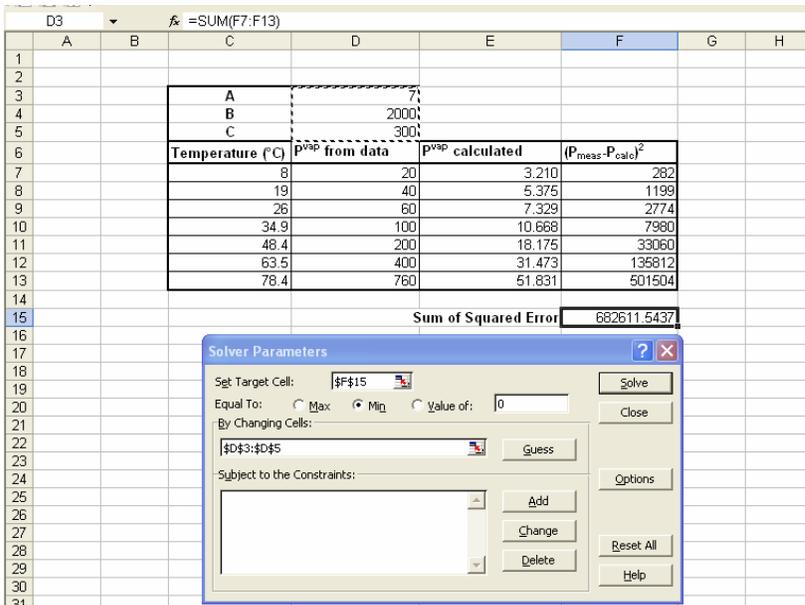
where $P_B^{vp} = 10^{\left(A - \frac{B}{T+C}\right)}$. This can be done using the Excel solver and a least-squares regression.

There are 3 unknown constants: A, B and C; therefore it is helpful to make an educated guess for the constants. If we consult tabulated Antoine constants for various compounds (e.g. *Elementary Principles of Chemical Processes* by Felder and Rousseau), we find the following approximate ranges for A, B and C:

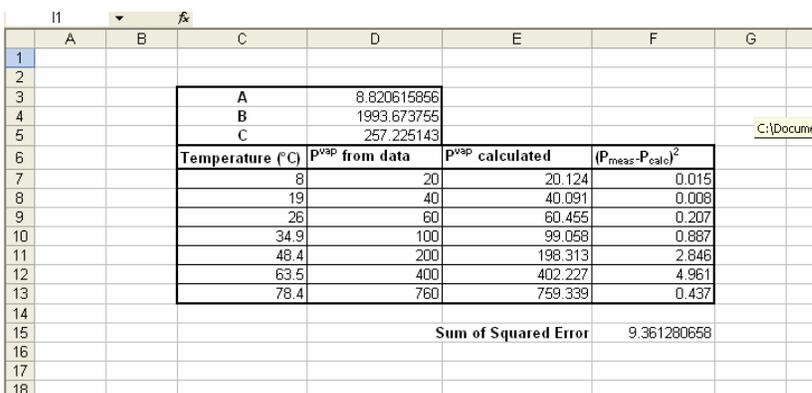
Constant, $\log P = A - B/(T+C)$	Approximate value
A	6-9
B	900-2100
C	100-300

A spreadsheet can be constructed to perform least-squared regression analysis to find values of A, B and C to fit our data.

First, calculate the vapor pressure using the Antoine equation referencing fields with the constants A, B and C. Find the sum of the squared error to assess the accuracy of the constants. Use the solver to determine the values for A, B and C that minimize the sum of the squared error. This is demonstrated below for the ethanol data:



The solver determines the values of A, B and C:



We repeat this approach for the benzene data and we have the following Antoine equations fit to our data:

$$P_B^{vp} = 10^{\left(8.099 - \frac{1954}{T + 294.6}\right)}, \quad P_E^{vp} = 10^{\left(8.821 - \frac{1993}{T + 257.2}\right)}$$

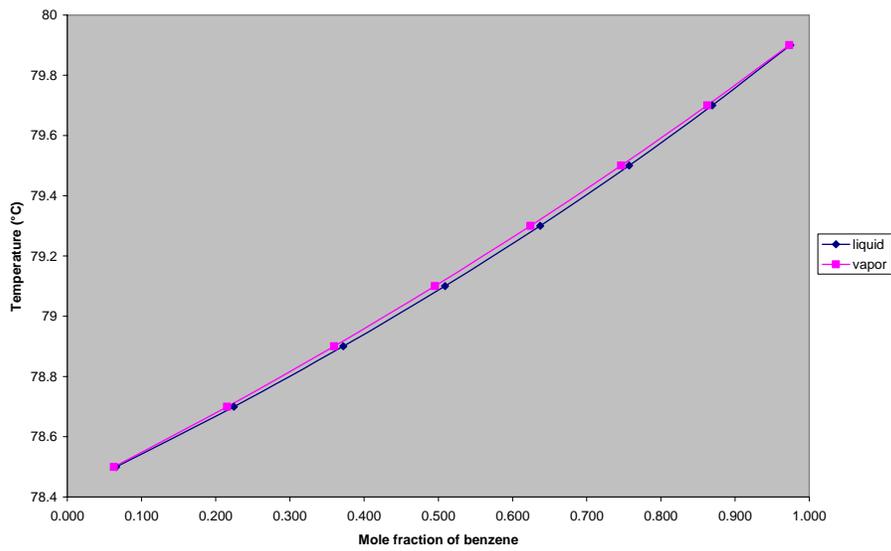
This can be similarly done with a natural logarithmic form of the Antoine equation:

$$P_B^{vp} = \exp\left(15.5645 - \frac{2602.34}{T + 211.271}\right), \quad P_E^{vp} = \exp\left(21.0192 - \frac{5051.06}{T + 272.702}\right)$$

Now, values of the liquid and vapor mole fractions over a range of temperatures can be calculated at a T-x-y plot can be produced. The vapor pressures are calculated using the fitted Antoine equations and are used to calculate K values and x and y (equations 1-5 from earlier). Note that there is vapor/liquid coexistence only between the boiling points of benzene and ethanol.

T	$p^{\text{vap, B}}$	$p^{\text{vap, E}}$	K_B	K_E	x_B	y_B
78.5	725.3	762.4	0.954	1.003	0.066	0.063
78.7	730.0	768.7	0.961	1.011	0.224	0.216
78.9	734.7	774.9	0.967	1.020	0.372	0.359
79.1	739.5	781.3	0.973	1.028	0.509	0.495
79.3	744.3	787.6	0.979	1.036	0.637	0.624
79.5	749.1	794.0	0.986	1.045	0.757	0.746
79.7	753.9	800.5	0.992	1.053	0.869	0.862
79.9	758.8	807.0	0.998	1.062	0.975	0.973

Raoult's and Dalton's Laws Prediction of T-x-y



This T-x-y plot is dramatically different than the experimental data used earlier in the problem and indicates the limitations of Raoult's law. We conclude that Raoult's law does not apply to this binary system.

Point Allocation:

- | | |
|--|---------|
| (a) correct $T=69.4^{\circ}\text{C}$ | 1 point |
| (b) correct $y_B=0.56$ | 1 point |
| (c) correct $x_B=0.175$ (approximate) | 1 point |
| use of reverse lever arm rule or q-line | 1 point |
| (d) correct $x_B=0.045$ (approximate) | 1 point |
| use of reverse lever arm rule or q-line | 1 point |
| (e) correct $x_B=0.05$ (approximate) | 1 point |
| use of reverse lever arm rule or q-line | 1 point |
| (f) graph of T vs. % vaporized | 1 point |
| (g) recognition that Raoult's Law does not apply | 1 point |

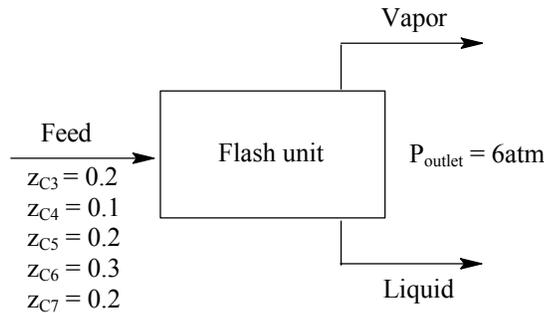
1 point was deducted for not including a T-x-y graph showing work on parts (a-e) if these parts were solved graphically.

TOTAL POINTS = 10

Average homework grade: 7.96/10

Problem No. 2

Summary of Information in Problem Statement



- Mixture contains 5 components, C3, C4, C5, C6, C7
- Mixtures are ideal in both liquid and vapor phases.
- $\ln(P_i^{\text{vap}}) = A_i - \frac{D_i}{T}$
- Flash unit at steady state

Part A:

In order for the flash unit output to contain both the liquid and vapor phases, the mixture must be in the 2-phase region in the T-x-y graph. Therefore, the bubble point temperature would be the lower limit for the temperature range and the dew point temperature would be the higher limit for the temperature range. To find the bubble point and dew point temperatures, we utilize the Rachford-Rice Flash Function (RRFF).

$$\Phi = \sum_i \frac{z_i(K_i - 1)}{1 - \Psi + \Psi K_i} = 0$$

At the **bubble point**, $\Psi = 0$ since there is essentially no vapor outlet stream (only one bubble of vapor). This reduces the RRFF to

$$\Phi = \sum_i z_i(K_i - 1) = 0$$

In order to solve this equation, we need a relationship to calculate the K-value for each component. Since both the vapor and liquid phase mixtures are assumed to be ideal, we can use Raoult's Law. From Raoult's

Law we get the following relationship: $K_i = \frac{P_i^{\text{vap}}}{P_{\text{total}}}$

Given the data in the problem statement we can solve for the vapor pressure of the pure component for each component in the mixture given the relationship provided in the problem statement and then solve for the corresponding K-value. Note that since the vapor pressure has temperature dependence, the K-value will also have temperature dependence. When using Goal Seek or Solver, you will need to make an initial guess for the temperature. Plugging in the K-values and solving for the temperature which will satisfy the simplified RRFF leads to a **bubble point temperature of 337.2K**. At this low-end temperature extreme, the liquid and vapor stream compositions are as follows.

Component	x_i	y_i
C3	0.2000	0.7504
C4	0.1000	0.1145
C5	0.2000	0.0786
C6	0.3000	0.0451
C7	0.2000	0.0114
Total	1.0000	1.0000

At the **dew point**, $\Psi = 1$ since there is essentially no liquid outlet stream (only one drop of liquid). In this case, the RRFF reduces to $\sum_i \frac{z_i}{K_i} = 1$

Using the relationships for K-values derived for the bubble point calculations, we can again solve the simplified RRFF for temperature resulting in a **dew point temperature of 405.3K**. At this high-end temperature extreme, the liquid and vapor stream compositions are as follows.

Component	x_i	y_i
C3	0.0173	0.2000
C4	0.0228	0.1000
C5	0.1064	0.2000
C6	0.3498	0.3000
C7	0.5043	0.2000
Total	1.0006	1.0000

Therefore, the range of outlet temperatures for the flash unit is **337.2K \leq T \leq 405.3K**.

Part B:

Using the results from Part A, the **midway temperature is 371.2K**. The fraction of the outlet flow that is vapor is the ratio of the vapor outlet stream to the feed stream which is also known as Ψ .

$$\frac{V}{L+V} = \frac{V}{F} = \Psi$$

This time, given the temperature of the flash unit, the unknown variable is Ψ and the RRFF must be used to solve for Ψ . The value of Ψ was found to be 0.345. Therefore **34.5% of the outlet flow is vapor**. The liquid and vapor mole fractions were determined using the following relationships.

$$x_i = \frac{z_i}{1 + \Psi(K_i - 1)}, \quad y_i = \frac{z_i K_i}{1 + \Psi(K_i - 1)} \quad (\text{Table 4.4, Eq. 5 and 6})$$

Component	x_i	y_i
C3	0.0656	0.4551
C4	0.0677	0.1613
C5	0.2054	0.1897
C6	0.3802	0.1478
C7	0.2810	0.0462
Total	0.9999	1.0002

Part C:

In order to achieve the desired 90% of C3 in the vapor outlet stream, the ratio of the amount of C3 in the vapor outlet stream with respect to the amount of C3 in the feed stream must be 0.9. The amount of C3 in the vapor outlet stream is Vy_{C3} and the amount of C3 in the feed stream is Fz_{C3} . Therefore,

$$\frac{Vy_{C3}}{Fz_{C3}} = 0.9 \text{ which can be simplified to } \Psi \frac{y_{C3}}{z_{C3}} = 0.9$$

With this constraint, there are two unknowns in this problem, temperature and psi. Solving the problem using Solver, **$\Psi = 0.516$ and $T = 383.5K$** and the liquid and vapor compositions are as follows.

Component	x_i	y_i
C3	0.0414	0.3486
C4	0.0491	0.1477
C5	0.1803	0.2184
C6	0.3973	0.2089
C7	0.3320	0.0764
Total	1.0000	1.0000

Part D:

Since helium is considered to be non-condensable, this means that it will always exist in the vapor phase and $x_{\text{helium}} = 0$. At the dew point temperature of this system, the output stream from the flash unit will be all vapor. The **lower limit temperature for this system will be 0K**.

In order to solve for the dew point temperature of this system, we again look at the RRF. In this case, the K-value for helium is unknown. Since no data is provided for helium, we must look at other ways to estimate a K-value. Looking back at Raoult's Law, we see that

$$K_i = \frac{P_i^{vap}}{P_{total}} = \frac{y_i}{x_i} . \text{ From this, we see that } K_{\text{helium}} = \infty \text{ since } x_{\text{helium}} = 0 .$$

Performing an order of magnitude analysis on the term in the RRF that corresponds to helium, we see that

$$\frac{z_{\text{helium}}(K_{\text{helium}} - 1)}{1 - \Psi + \Psi K_{\text{helium}}} \sim \frac{z_{\text{helium}}}{\Psi} \text{ since } z_{\text{helium}} K_{\text{helium}} \gg z_{\text{helium}}, \Psi K_{\text{helium}} \gg 1, \text{ and } \Psi K_{\text{helium}} \gg \Psi .$$

Replacing this term in the RRF, we get

$$\Phi = \frac{z_{C3}(K_{C3} - 1)}{1 - \Psi + \Psi K_{C3}} + \frac{z_{C4}(K_{C4} - 1)}{1 - \Psi + \Psi K_{C4}} + \frac{z_{C5}(K_{C5} - 1)}{1 - \Psi + \Psi K_{C5}} + \frac{z_{\text{helium}}}{\Psi}$$

At the dew point, this equation reduces to:

$$\Phi = \frac{z_{C3}(K_{C3} - 1)}{K_{C3}} + \frac{z_{C4}(K_{C4} - 1)}{K_{C4}} + \frac{z_{C5}(K_{C5} - 1)}{K_{C5}} + z_{\text{helium}} = 0$$

Not required for homework: Solving this equation, we get a **dew point temperature of 334.1K** and the liquid and vapor stream compositions are

Component	x_i	y_i
C3	0.0710	0.2500
C4	0.2353	0.2500
C5	0.6937	0.2500
Helium	0.0000	0.2500
Total	1.0000	1.0000

This solution could also be arrived at by performing a mass balance on the helium in the flash unit.

$$Fz_{\text{helium}} = Vy_{\text{helium}} + Lx_{\text{helium}} \text{ which becomes } Fz_{\text{helium}} = Vy_{\text{helium}} \text{ since } x_{\text{helium}} = 0 .$$

This equation can be further simplified to get $\frac{z_{\text{helium}}}{y_{\text{helium}}} = \Psi$ or that $y_{\text{helium}} = \frac{z_{\text{helium}}}{\Psi}$.

In order to use the vapor mole fraction relationship derived in the mass balance, we must look back at how the RRF was derived. The Rachford-Rice Equation comes from

$$\sum_i y_i - \sum_i x_i = 0$$

Using this equation instead, and Eqs. 5 and 6 from Table 4.4. We will arrive at the same conclusion.

Point Breakdown:

Part A:

(1 point): Identifying the correct limits for the temperature range (bubble point and dew point)

(1 point): Correct bubble point and dew point temperatures.

(1 point): Correct compositions for bubble point and dew point.

Part B:

(1 point): Correct T and Ψ

(1 point): Correct compositions

Part C:

(1 point): Performing the mass balance and identifying the constraint.

$$\frac{Vy_{C3}}{Fz_{C3}} = 0.9$$

(1 point): Correct T, Ψ , and compositions

Part D:

(1 point): Correct temperature limits

(1 point): Understanding that $x_{\text{helium}} = 0$ since helium is non-condensable

(1 point): Showing how the He term in the RRFF is changed because helium is non-condensable.