CHEMICAL ENGINEERING THERMODYNAMICS II (0905323)

04. BINARY PHASE DIAGRAMS

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Outline

- K Values & Relative Volatility
- Representation of VLE Data
- Bubble Point
- Dew Point
- *K* Values and Relative Volatility
- *Txy* for *n*-Heptane (1) – *n*-Decane (2)
- The Lever-Rule
- *Pxy* Phase Diagram
- Distillation
- Azeotropes
- The *xy* Diagram
- VLE at High *P* and *T*
- Partially Miscible Liquids
- Ternary Systems for LLE

Prelude

Pure

Any property is a function of *T*, and *P* only.

Molecules are always surrounded by similar species (self-interactions).

Possible phase equilibria: VL, VS, LS, or VLS.

Phase behavior simple and not frequently encountered.

Mixture

Any property is a function of *T*, *P* and *x* where x is the composition.

Molecules are surrounded by both like (self-interactions) and unlike species. (cross-interactions).

Balance of self- and cross-interactions creates phase behavior that is not seen in pure fluids.

Phase equilibria: VL, LL, VLL, VS, LS, …etc.

Phase behavior basis for separations

Cross-Interactions

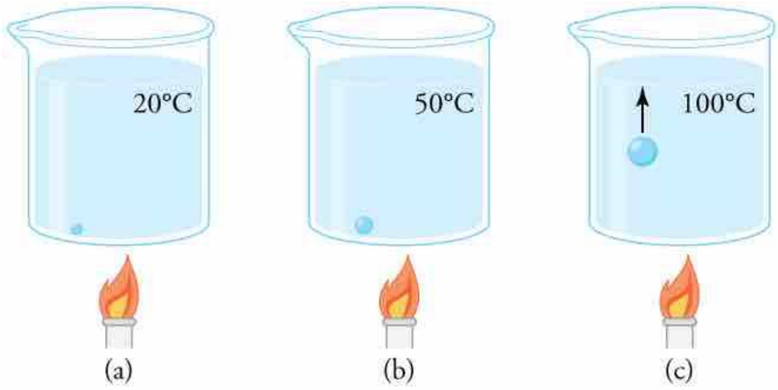
- The balance of self- and cross-interactions creates phase behavior that is not seen in pure fluids.
  - If cross-interactions are favorable, components form strong mixtures that are more difficult to separate.
  - If cross-interactions are unfavorable, the mixture is weaker and separation is easier.
  - If cross-interactions are strongly unfavorable, then components may exhibit partial miscibility.

Representing VLE

- There are three equivalent ways of representing the VLE data:
  - *Pxy*,
  - *Txy* (a liquid *mixture* boils over a *range* of temperatures).
  - *xy*.
- The information contained in any of the methods of representing the data is the same.
- Some representations are more useful in certain situations e.g., *Pxy* is more practical for petroleum refineries' atmospheric distillation.

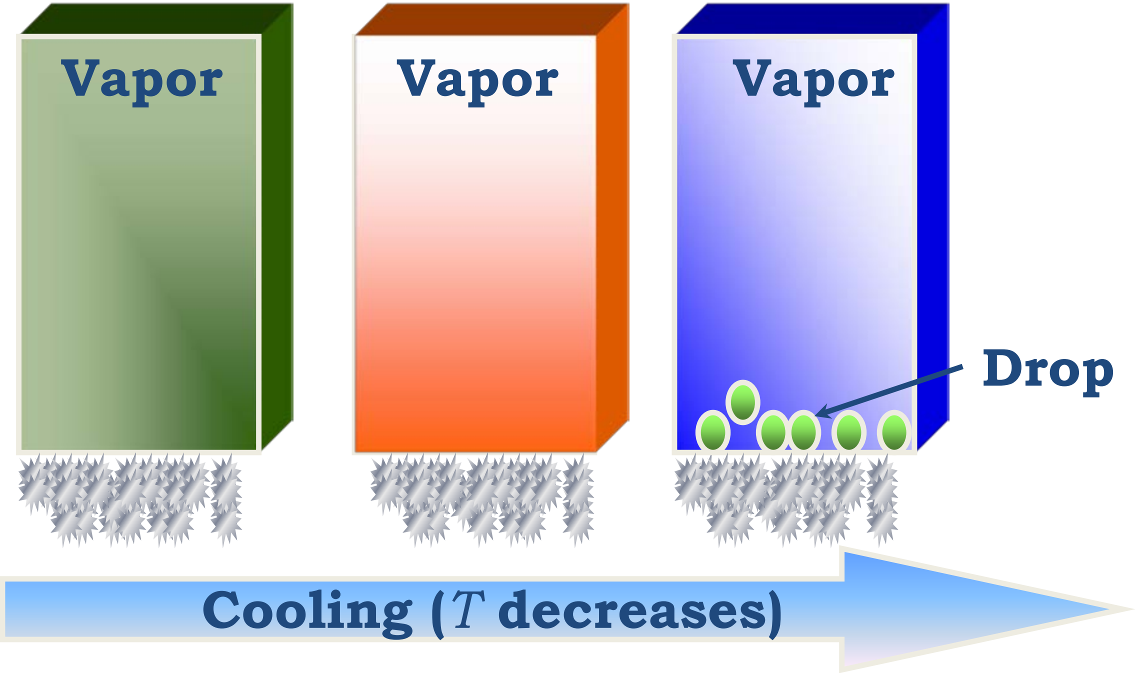
Bubble Point

- The temperature at which the first bubble of vapor forms (at a given pressure).
- Related to vaporization (from liquid phase to vapor phase).



Dew Point

- The temperature at which the first drop of liquid forms (at a given pressure).
- Related to condensation (from vapor phase to liquid phase).



Vapor

Vapor

Vapor

Drop

Cooling (T decreases)

K Values and Relative Volatility

- The *K* value is a **distribution coefficient** between two different phases for a certain component defined as:

$$K_i = \frac{y_i}{x_i}$$

  - Measure of tendency of a component to concentrate in a certain phase.

- The **relative volatility** is a measure of the **selectivity** of getting one species in a certain phase preferentially;

$$\alpha_{1,2} = \frac{K_1}{K_2} = \frac{\left(y_1 / x_1\right)}{\left(y_2 / x_2\right)}$$

  - Measure of the selectivity of separation of two components.

Relative Volatility

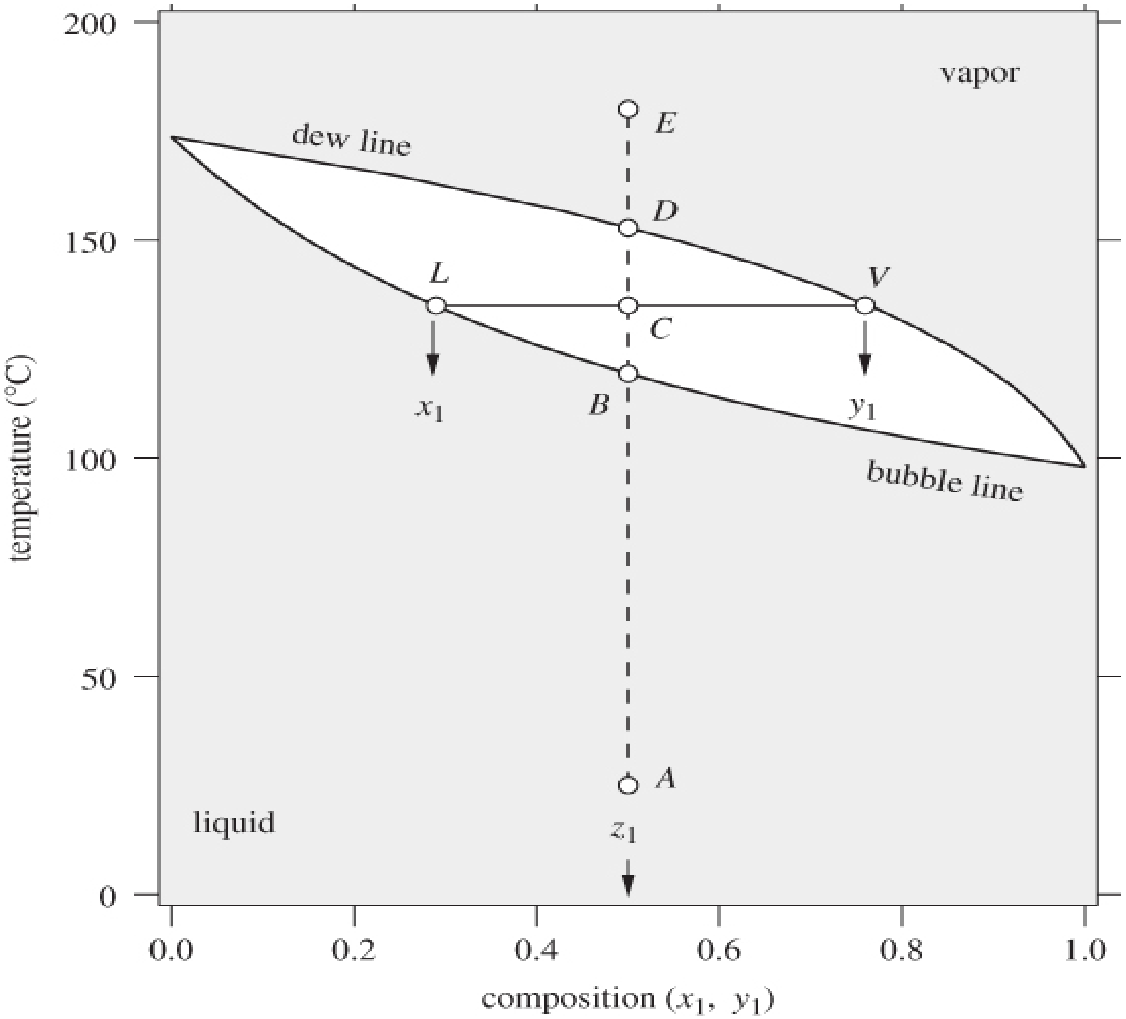
- Relative volatility is a criterion to determine whether normal distillation is a viable choice to separate the more volatile species from the less volatile species in a mixture.
- **Exclude using** ordinary distillation if:

$$0.95 \le \alpha_{1,2} \le 1.05$$

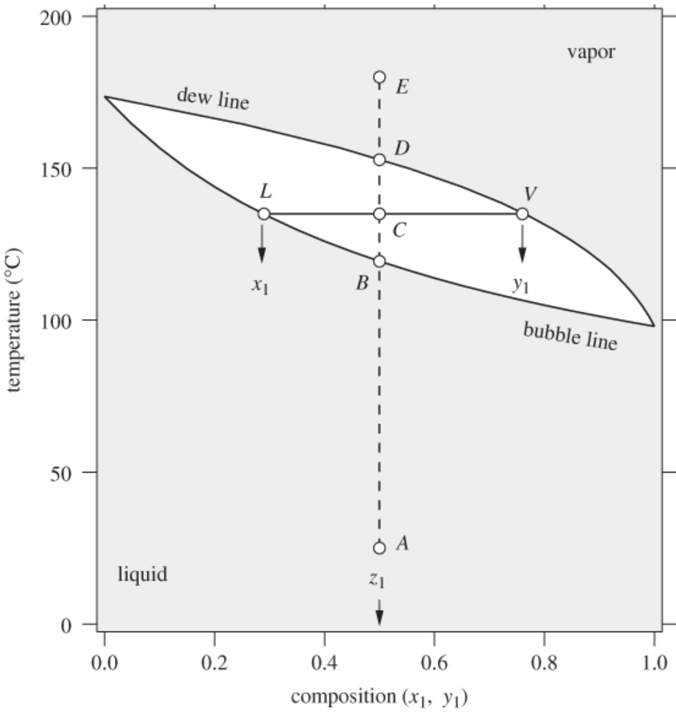
  - Due to the large number of trays required when α is in this range.
  - Does not exclude the use of "**super-fractionators**".

Txy for *n*-Heptane (1) – *n*-Decane (2)

- Plotted as T vs x_1 and T vs y_1 at constant pressure.



The Lever-Rule



- Tie line: the line that connects the compositions of the vapor and the compositions of the liquid (LV).
- It is a horizontal line and passes through C (mixture point) since all three points, L, C, and V are at the same temperature.
- If liquid contains a fraction L of the total number of moles and the vapor contains the remaining fraction $V = 1 - L$.
- The concentration of heptane in the liquid is x_1, in the vapor y_1, and the overall concentration of heptane is z_1 (that would be the concentration of heptane in point C, 50% in our example).
- The mole balance on heptane and the total mole balance give the following two equations:

$$L + V = 1 \quad \text{and} \quad Lx_1 + Vy_1 = z_1$$

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

$$L = \frac{y_1 - z_1}{y_1 - x_1}$$

Example 8.1: Using the Lever Rule

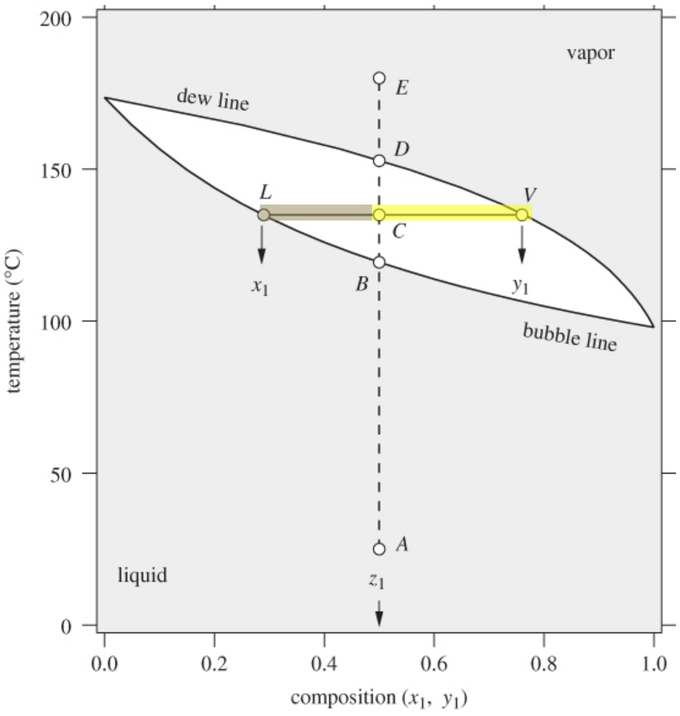
A 50% by mole solution of heptane and decane is heated to 135°C at 1 atm. Determine the state of the system (vapor, liquid, or vapor, liquid mixture). If this is a two-phase system, calculate the amount and composition of two phases.

Solution The conditions given in this example correspond to point *C* in Figure 8-1 which lies in the vapor-liquid range. The compositions of the two phases are read directly from the graph (normally a more accurate graph will be needed for this type of calculations).

We find $x_1 = 0.3$, $y_1 = 0.8$. The fractions of the liquid and vapor are calculated from the lever rule:

$$L = \frac{0.8 - 0.5}{0.8 - 0.3} = 0.6,$$
$$V = 1 - L = 0.4.$$

Therefore, 60% is in the liquid and the rest is vapor. Since point *C* is near the middle of the line *VL* but closer to the liquid side, we should have guessed that the liquid fraction is somewhat larger than 50%.



Example 8.2: Working with Phase Diagrams

What is the maximum concentration of heptane in the vapor that we can obtain by heating the solution of the previous example at 1 atm?

Solution The maximum concentration in the vapor is when the system is at the bubble point, point *B* in Figure 8-2. Then the vapor has the concentration of point *V*. From the graph we read $y_1 \approx 0.9$. The composition of the liquid at this point is $x_1 = 0.5$, the same as the initial solution. The lever rule then gives $L = 1$ and $V = 0$. Although the purity of the vapor is highest at that is point, the *amount* collected is zero.

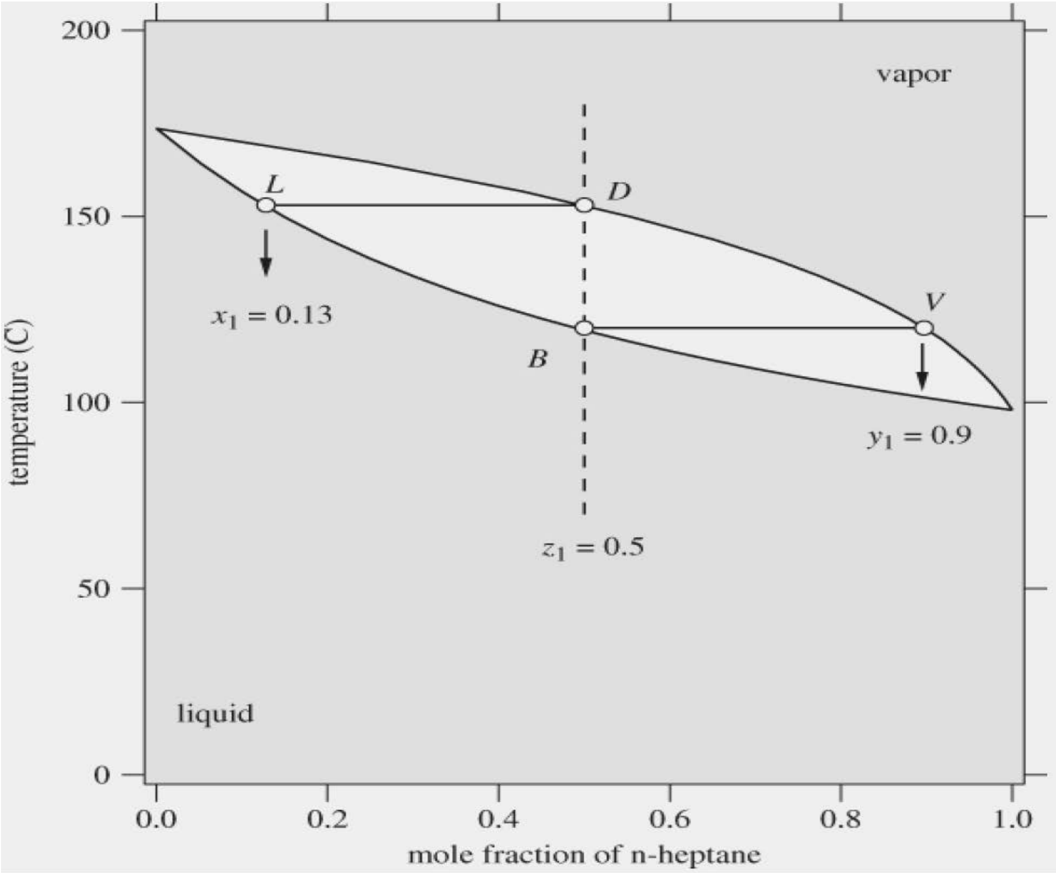


Figure 8-2: Compositions at the bubble and dew point.

Example 8.3: Working with Phase Diagrams–2

A vapor mixture of heptane(1)-decane(2) with $y_1 = 0.5$ is condensed by cooling under constant pressure of 1 atm. What is the composition of the first drop to appear? What is the composition of the last bubble to condense?

Solution When the first drop condenses the system is at the dew point, *D*. If we draw the tie line at *D*, the composition of the first drop is read at the intersection of the tie line with the bubble line. We find $x_1 \approx 0.125$ at $y_1 \approx 0.9$.

Example 8.3Ali: Working with Phase Diagrams–2

Determine the distribution coefficient of both components and their relative volatility at point D.

Solution

At point D: $x_1 \approx 0.125$ and $y_1 = 0.5$.

$$K_1 = \frac{y_1}{x_1} = \frac{0.5}{0.125} = 4$$

$$K_2 = \frac{y_2}{x_2} = \frac{0.5}{0.875} = 0.571$$

$$\alpha_{1,2} = \frac{K_1}{K_2} = \frac{(y_1 / x_1)}{(y_2 / x_2)} = \frac{4}{0.571} = 7$$

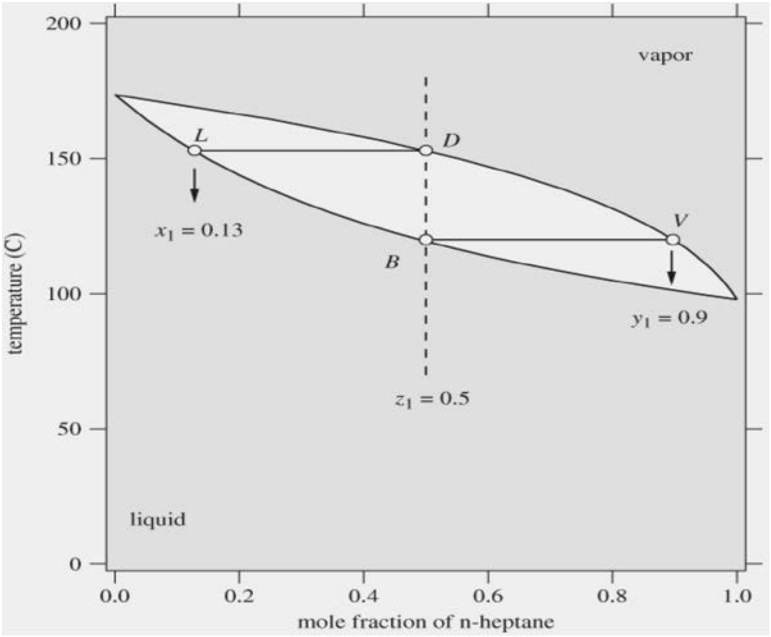


Figure 8-2: Compositions at the bubble and dew point.

Pxy Phase Diagram

- Plotted as *P* vs x_1 and *P* vs y_1 at constant temperature.

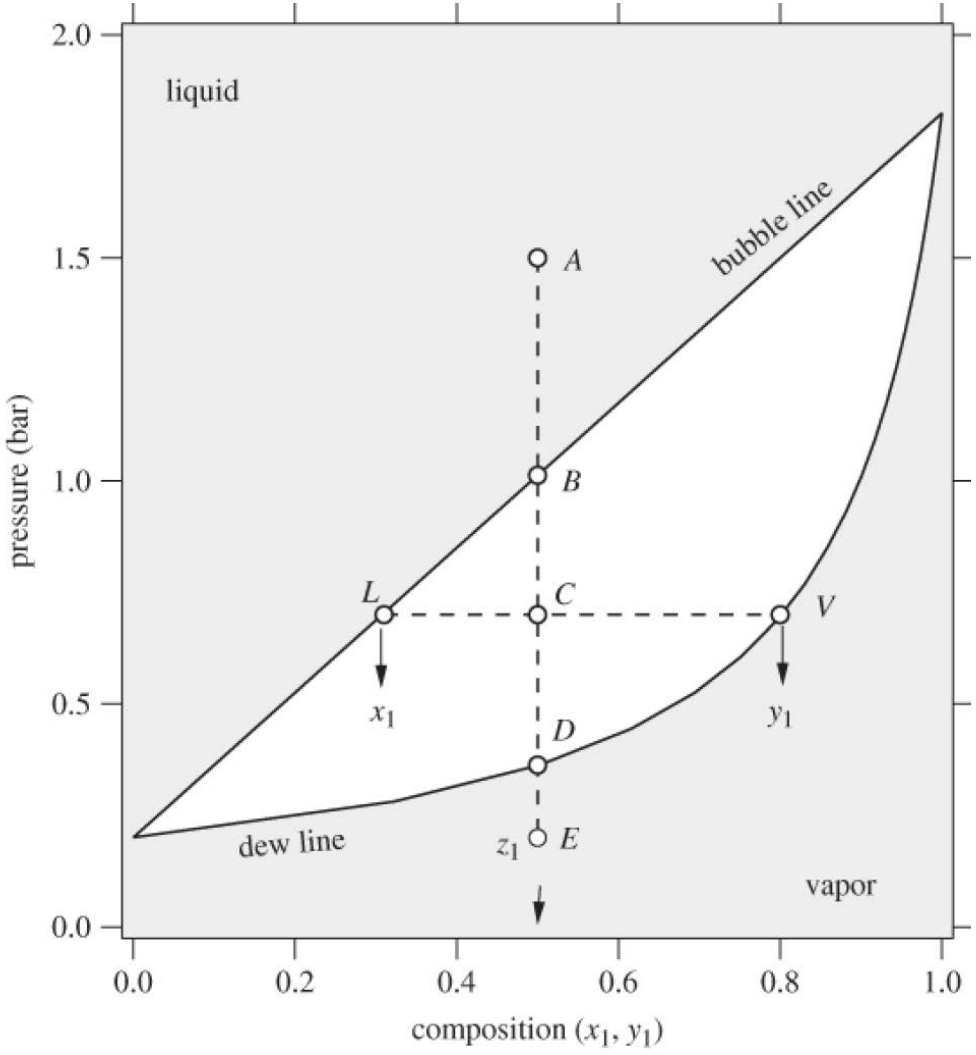


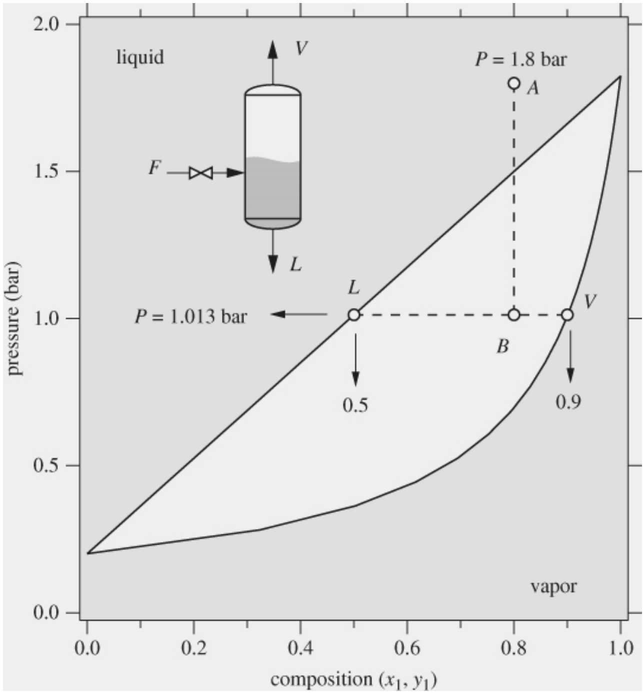
Figure 8-3: *Pxy* graph of heptane (1) decane (2) at 120 °C.

Example 8.4: Flash Separator

When the pressure of a compressed liquid is brought between the bubble point and the dew point, the liquid “flashes,” that is, it partially evaporates, creating a vapor that is enriched in the more volatile components and a liquid that is enriched in the heavier components. This simple process provides partial separation of the components.

A mixture of heptane/decane at 1.8 bar, 120°C contains 80% by mol heptane. At what pressure should it be flashed to obtain a stream that is 90% rich in heptane? What are the composition of the liquid and the amounts of the two phases?

Solution The solution is shown graphically in Figure 8-4. The initial state is *A*. The final state is *B* and is located such that the tie line intersects the dew line at $y_1 = 0.9$. The corresponding pressure is read off the graph and is found to be $P_B = 1.01$ bar. The final system consists of two phases, a vapor that contains the desired 90% in heptane and a liquid that contains 50% heptane. The amounts of the two phases are calculated from the lever rule:

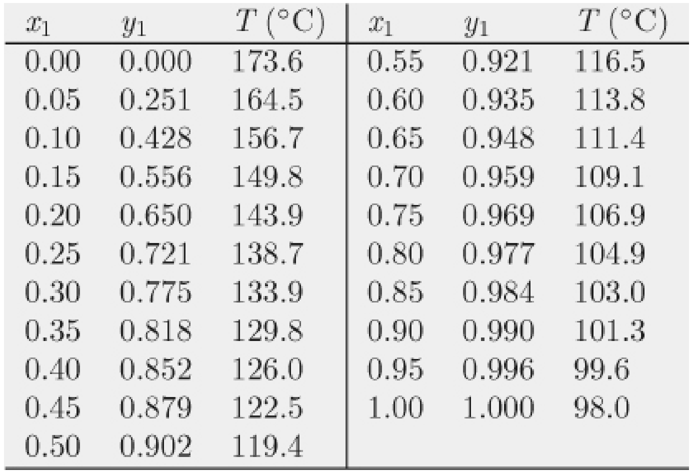


$$L = \frac{0.9 - 0.8}{0.9 - 0.5} = 0.25,$$
$$V = 1 - L = 0.75.$$

Comments By choosing the pressure in the flash drum we can achieve different levels of separation. If the pressure is closer to the bubble line, we obtain a vapor that is highly enriched in heptane but the amount that is collected is small.

Example 8.5:Multiple Flash Units

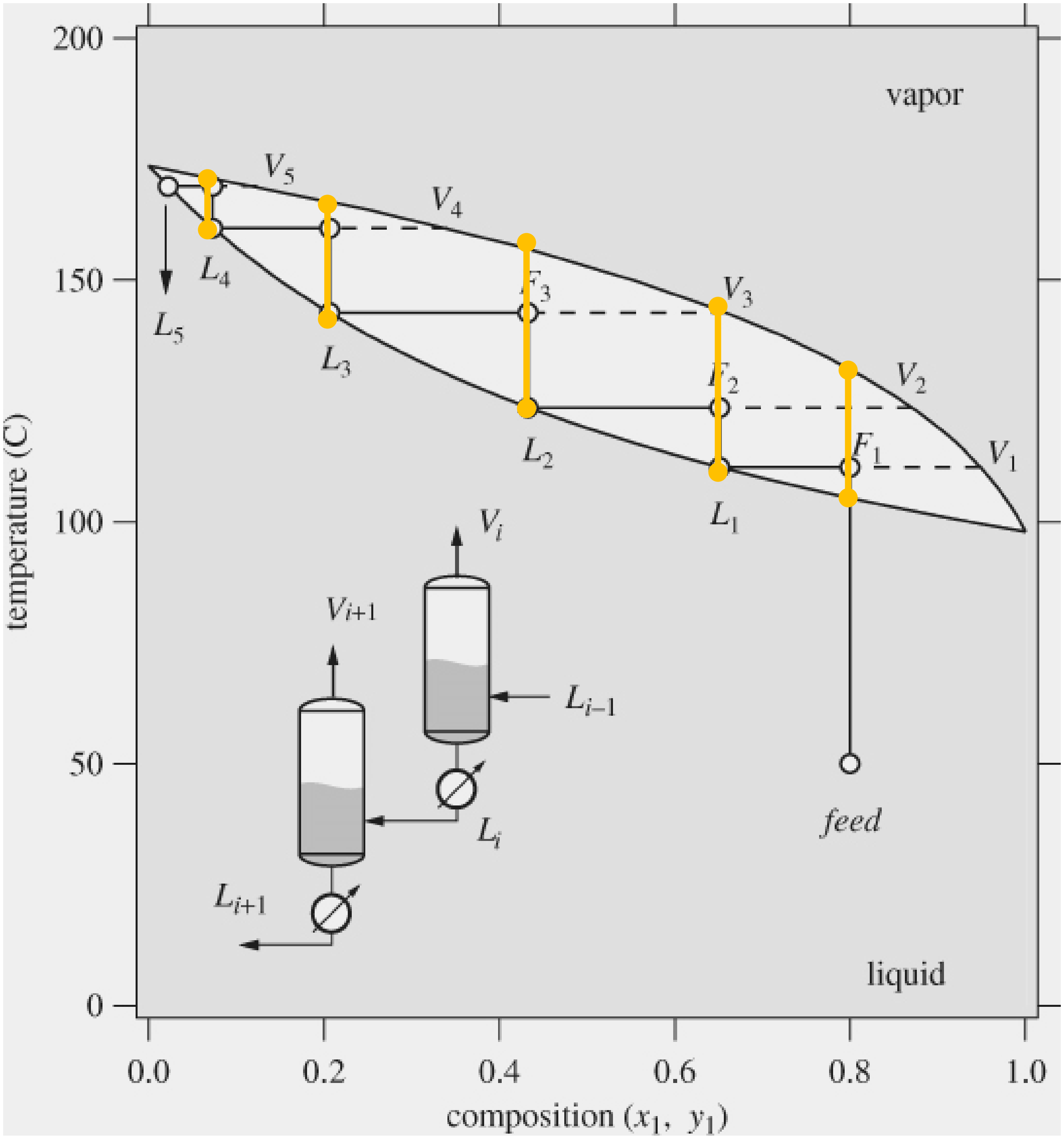
A solution of heptane (1)/decane (2) containing 80% by mol heptane at 1 bar is heated under constant pressure until half of the system is vapor. The liquid is separated from the vapor and is heated again until half of it vaporizes. This procedure, that is, creation of a 50-50 liquid/vapor mixture and separation of the liquid, is repeated for a total of five times. Calculate the amount, composition, and temperature of the remaining liquid. Additional data *Txy* data for this system at 1 bar are shown below:



x_1	y_1	T (°C)	x_1	y_1	T (°C)
0.00	0.000	173.6	0.55	0.921	116.5
0.05	0.251	164.5	0.60	0.935	113.8
0.10	0.428	156.7	0.65	0.948	111.4
0.15	0.556	149.8	0.70	0.959	109.1
0.20	0.650	143.9	0.75	0.969	106.9
0.25	0.721	138.7	0.80	0.977	104.9
0.30	0.775	133.9	0.85	0.984	103.0
0.35	0.818	129.8	0.90	0.990	101.3
0.40	0.852	126.0	0.95	0.996	99.6
0.45	0.879	122.5	1.00	1.000	98.0
0.50	0.902	119.4			

Graphical Solution The solution is easy to construct graphically. Since the process is at constant pressure, the relevant phase diagram is the *Txy* graph. With the data given we construct the graph shown in Figure 8-5.

The feed is at x_1 = 0.8 and is brought to the two-phase region (point F_1) such that half of the liquid boils, that is, $L = V$ = 1/2. Graphically, point F_1 is found by drawing a tie line so that the feed composition lies exactly in the middle. This requires some trial and error, but it can be done. The composition of the liquid fraction (L_1) is read from the graph, and it is about 0.6. This liquid becomes the new feed for the next step. We must now locate a point F_2 with the same composition as L_1 that also lies at equal distance from the dew and bubble lines (since $V = L$ = 1/2 throughout this process). By repeating the process five times, we obtain point L_5. The composition and temperature are read off the graph. We find $x_1 \approx 0.02$ and $T \approx 170$°C. Since each time we collect 50% of the original sample, after 5 steps we are left with L_5 = 0.55 = 0.0313 or 3.13% of the original feed. While this amount is small, it is almost pure decane ($x_2 = 1 - x_1 = 0.98$).


200
150
100
50
0
temperature (C)
0.0
0.2
0.4
0.6
0.8
1.0
composition (x_1, y_1)
vapor
liquid
V_5
V_4
V_3
V_2
V_1
F_3
F_2
F_1
L_5
L_4
L_3
L_2
L_1
feed
V_i
V_{i+1}
L_{i-1}
L_i
L_{i+1}

Numerical Solution The graphical solution is quite simple and fast, but reading numbers off the graph can only be done approximately. For more accurate answers, we must perform a numerical solution. This is done more easily once the graphical solution has been obtained. First, application of the lever rule gives:

$$z = Lx + Vy \quad \Rightarrow \quad Lx + (1 - L)y = z, \qquad \text{[A]}$$

where *z* is the composition of the feed (we drop the subscript “1” from the mole fractions with the understanding that all mole fractions are for heptane), *x* is the composition of the liquid fraction, (point L_1), and *y* that of the vapor (point V_1) and L = 0.5 is the liquid fraction. Point F_1 is at a temperature T_1 such that the bubble and dew compositions satisfy eq. [A]. Temperatures and mole fractions are given in tabular form, so we just have to find the right temperature by looking up the table. To facilitate the solution and avoid interpolations, we fit the tabular data to a polynomial function using a least-squares procedure:

$$\begin{aligned} x &= 14.425 - 0.31757T + 2.7789 \times 10^{-3}T^2 - 1.1277 \times 10^{-5}T^3 + 1.757 \times 10^{-8}T^4 \\ y &= 0.90716 + 5.5548 \times 10^{-3}T - 9.1222 \times 10^{-5}T^2 + 8.1846 \times 10^{-7}T^3 \\ &\quad -3.7472 \times 10^{-9}T^4. \end{aligned}$$

We now repeat the steps of the graphical solution. In the first step we solve for a temperature such that $Lx + (1-L)y = 0.8$. By trial and error, we find $T = 111.32$°C, $x = 0.651$ (this is the composition at L_1), and $y = 0.949$ (this is the composition at V_1). In the next step, the liquid composition $x = 0.651$ becomes the new feed composition. The same procedure is repeated with $z = 0.651$. The results of this calculation are summarized in the table below:

Step	T	z	x	y
1	111.32	0.8000	0.6513	0.9487
2	123.69	0.6513	0.4321	0.8704
3	143.32	0.4321	0.2062	0.6581
4	160.79	0.2062	0.0726	0.3397
5	169.41	0.0726	0.0221	0.1231

The final composition is given by x_1 at the fifth step. This solution contains 2.2% heptane and 97.8% decane.

Distillation

- By partially boiling the solution, we enrich the vapor in the more volatile component and the liquid in the heavier component.
- Repeating this process as many times as necessary, we can achieve as high of a purity as desired.
    - This is equivalent to a series of flash separators.
    - The liquid from each separator is partially boiled at higher temperature and the vapor from each stage is partially condensed at lower temperature.
    - In this manner, the liquid is continuously enriched in the less-volatile component, and the vapor in the more volatile one.
- In reality, distillation columns accomplish this task through:
    - A series of perforated trays, stacked vertically: the liquid drips down to hotter stages and the vapor bubbles up to cooler stages. The entire column is heated at the bottom.
    - In packed columns: the column is filled with a packing material such as beads, rings, or other small objects. As the liquid trickles down and the vapor rises, the packing material forces the two phases into contact and helps them reach equilibrium with each other.

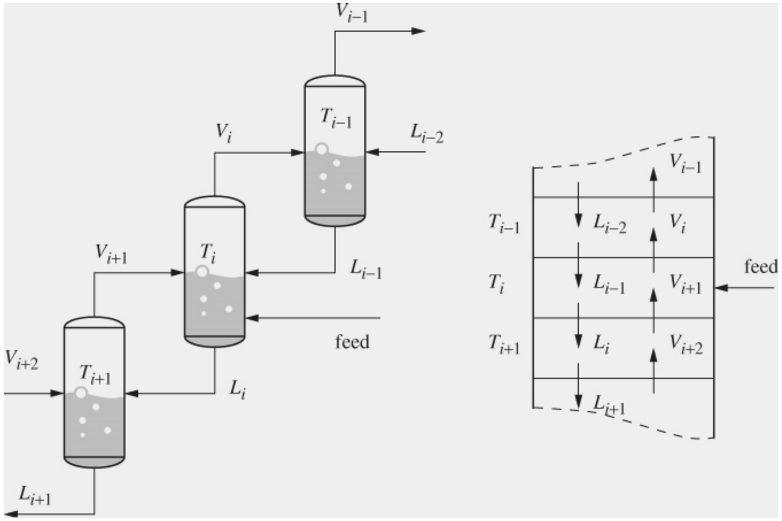
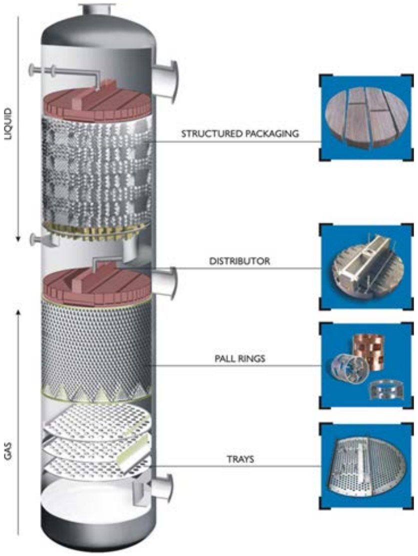


Figure 8-6: Staged separation (distillation). The column is heated at the bottom and cooled at the top ($T_i > T_{i-1}$).



Azeotropes

- Derived from Greek: ζέειν (boil) and τρόπος (turning) combined with the prefix α- (no) to give the overall meaning, "no change on boiling“.
- The presence of a maximum or minimum in the bubble and dew lines.
- An azeotrope is a mixture for which $x_i = y_i$ i.e., the dew-point and bubble-point curves are tangent to the same horizontal line.
  - At low pressure, the liquid phase activity coefficient may be obtained from azeotropic composition from:

$$\gamma_i(\mathbf{x}^{AZ}) = \frac{P}{P_i^{vap}}$$

  - The relative volatility for an azeotropic mixture is unity

$$\alpha^{AZ} = 1$$

  - No separation can be achieved of a constant-boiling solution by ordinary distillation.

Azeotrope Types

- Azeotropes
  - Minimum boiling
    - A minimum in *Txy* plane, or a maximum in *Pxy* plane, or is approaching $x = y$ line from above in an *xy* plane.
    - Positive deviations from Raoult's law i.e., when the activity coefficients of at least one species in the mixture is greater than unity.
    - Common: Water (1)– 2-propanol (2)/ Methanol(1)-CCl_4 (2)
  - Maximum boiling
    - A maximum in *Txy* plane, or a minimum in *Pxy* plane, or approaching $x = y$ line from below in an *xy* plane.
    - Negative deviations from Raoult's law i.e., when the activity coefficients of one or more species is less than unity.
    - Not common: acetone (1)– chloroform (2)
  - Complex
    - Double
      - Rare binary systems
      - Water(1) and *N*-methylethylenediamine(2)
    - Saddle
      - Ternary systems and higher.
      - 30% acetone(1), 47% chloroform(2), and 23% methanol(3)

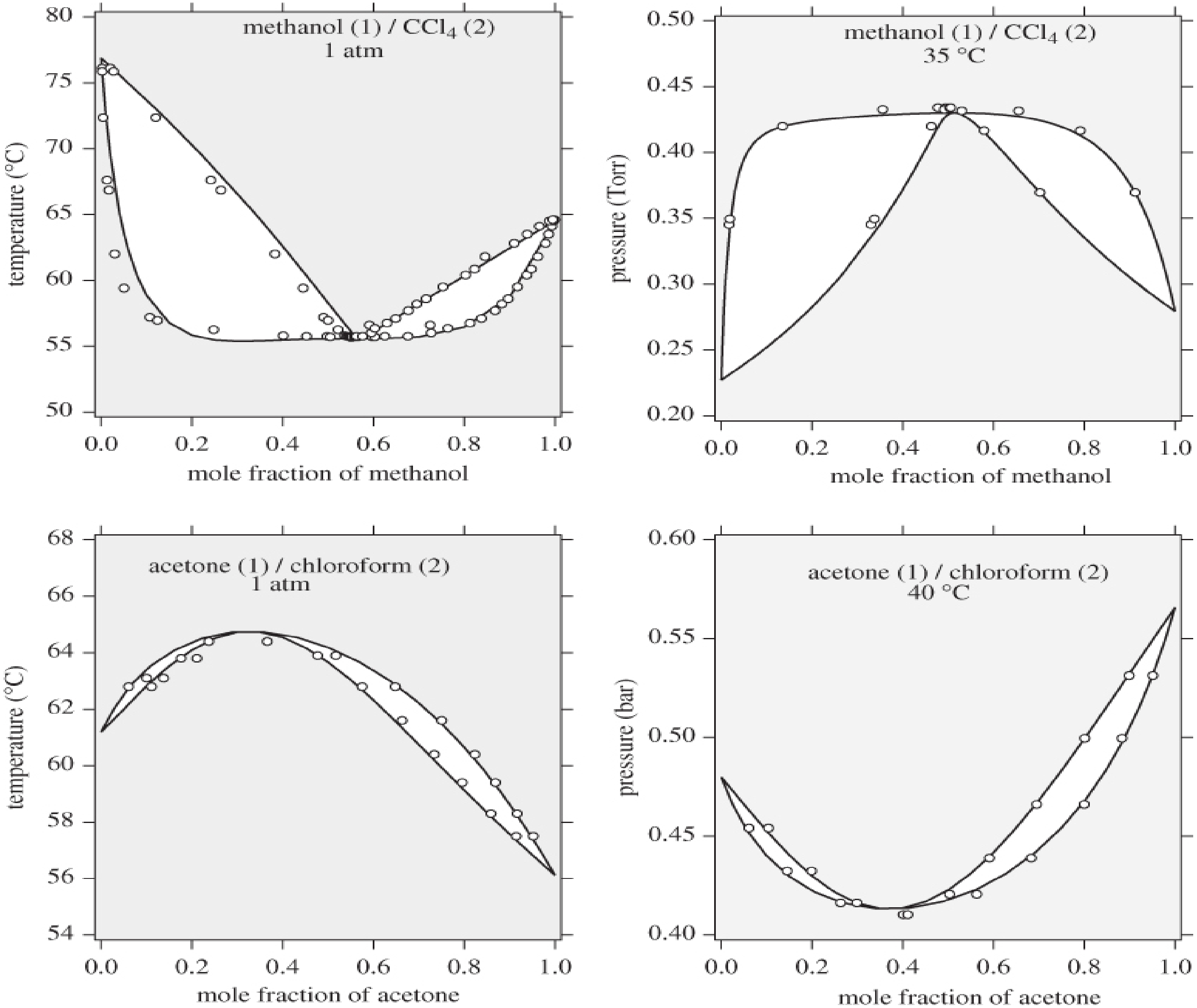
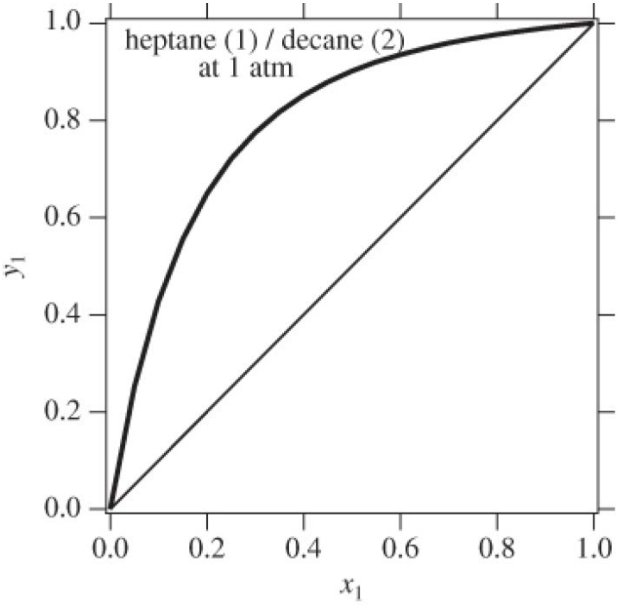
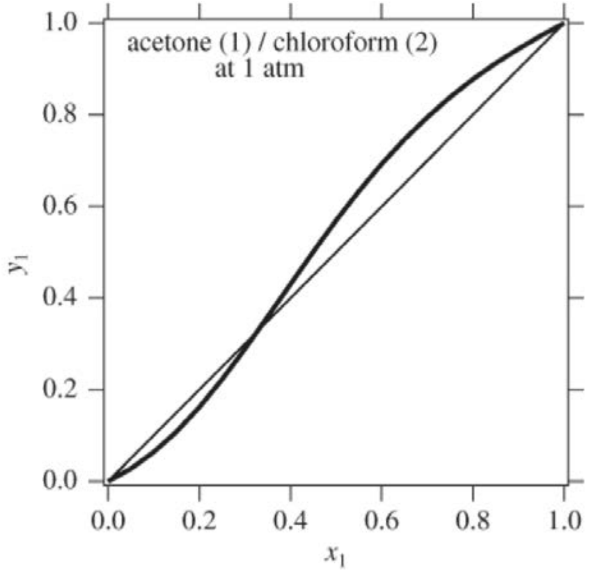


Figure 8-7: Minimum boiling azeotrope (top), and maximum boiling azeotrope (bottom). Data from Vapor-Liquid Equilibrium Data Collection, J. Gmehling, U. Onken, and W. Arlt, DECHEMA.

The *xy* Diagram

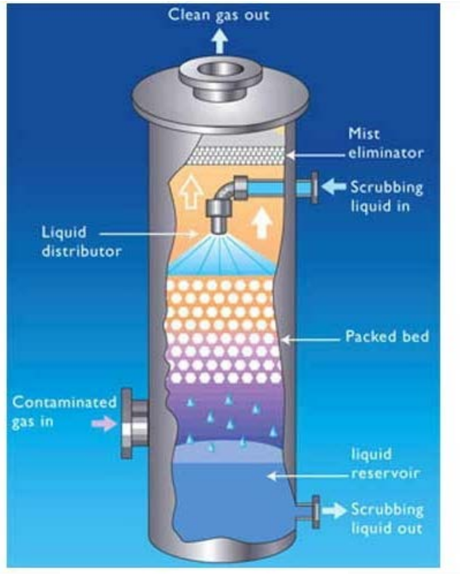
- Plotted as composition of the tie line: vapor mole fraction against the liquid mole fraction.
- Both axes run from 0 to 1 and the diagonal represents points where the vapor composition is equal to that of the liquid.
- Convention: the more volatile component is chosen as component 1.
  - by this convention the *xy* graph generally lies above the diagonal.
- Azeotropes are easily identified on this graph because the *xy* line crosses the diagonal.





VLE at High *P* and *T*

- Typical phase diagrams extend over the entire range of composition i.e., from $x_1 = 0$ (pure saturated component 2) to $x_1 = 1$ (pure saturated component 1).
    - Observed when both components are below their respective critical points.
- If one of both components are above their critical point, the VLE region shrinks and does not cover the entire range of compositions.
    - Dew and bubble lines meet at some intermediate point.
    - Where the bubble and dew lines meet we have a critical point, which is characterized by its own temperature, pressure, and composition.
    - Identified as the point where the tie line is tangent to the VLE curve.
- Such incomplete phase diagrams occur commonly in systems involving typical gases/solutes (e.g., oxygen, nitrogen) in equilibrium with liquids/solvents (e.g., water) at room temperature.
    - The liquid/solvent is below its critical temperature but the gas is above its own.



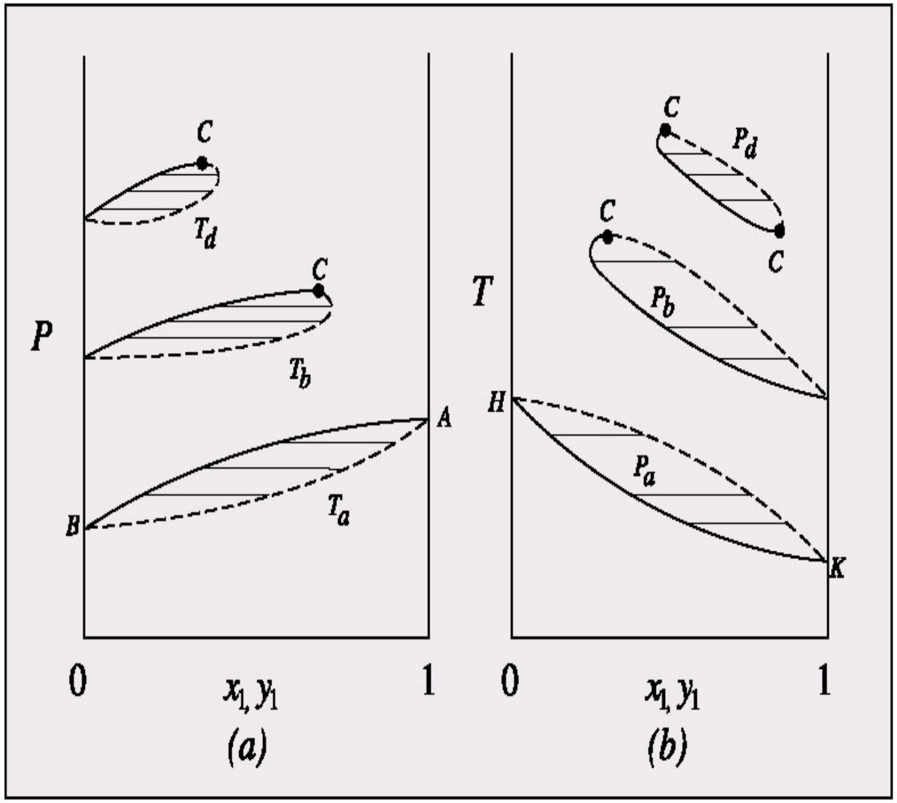


Figure 10.2: (*a*) Pxy diagram for three temperatures. (*b*) Txy diagram for three pressures.
— Saturated liquid (bubble line); - - - Saturated vapor (dew line)

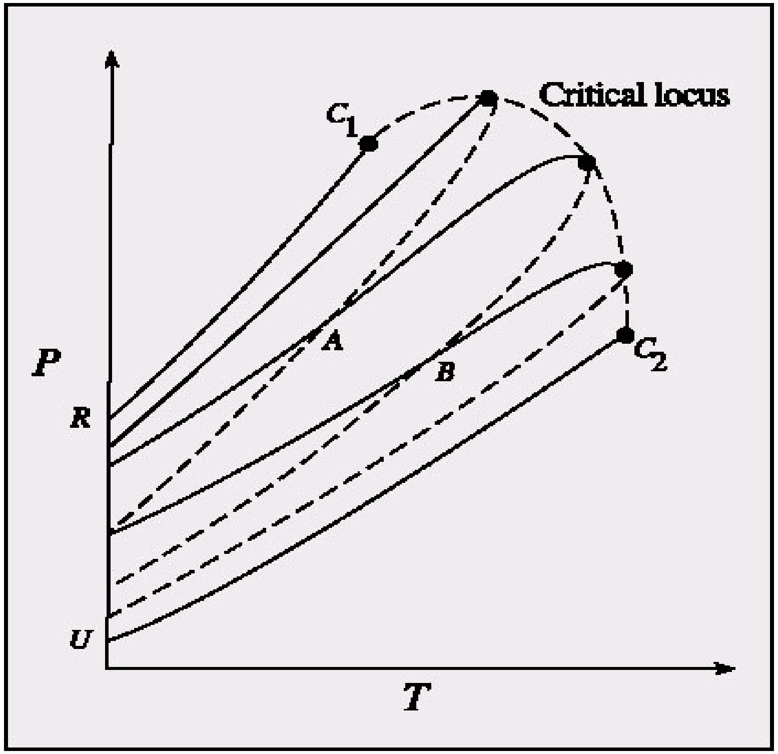


Figure 10.3: PT diagram for several compositions.
— Saturated liquid (bubble line)
- - - Saturated vapor (dew line)

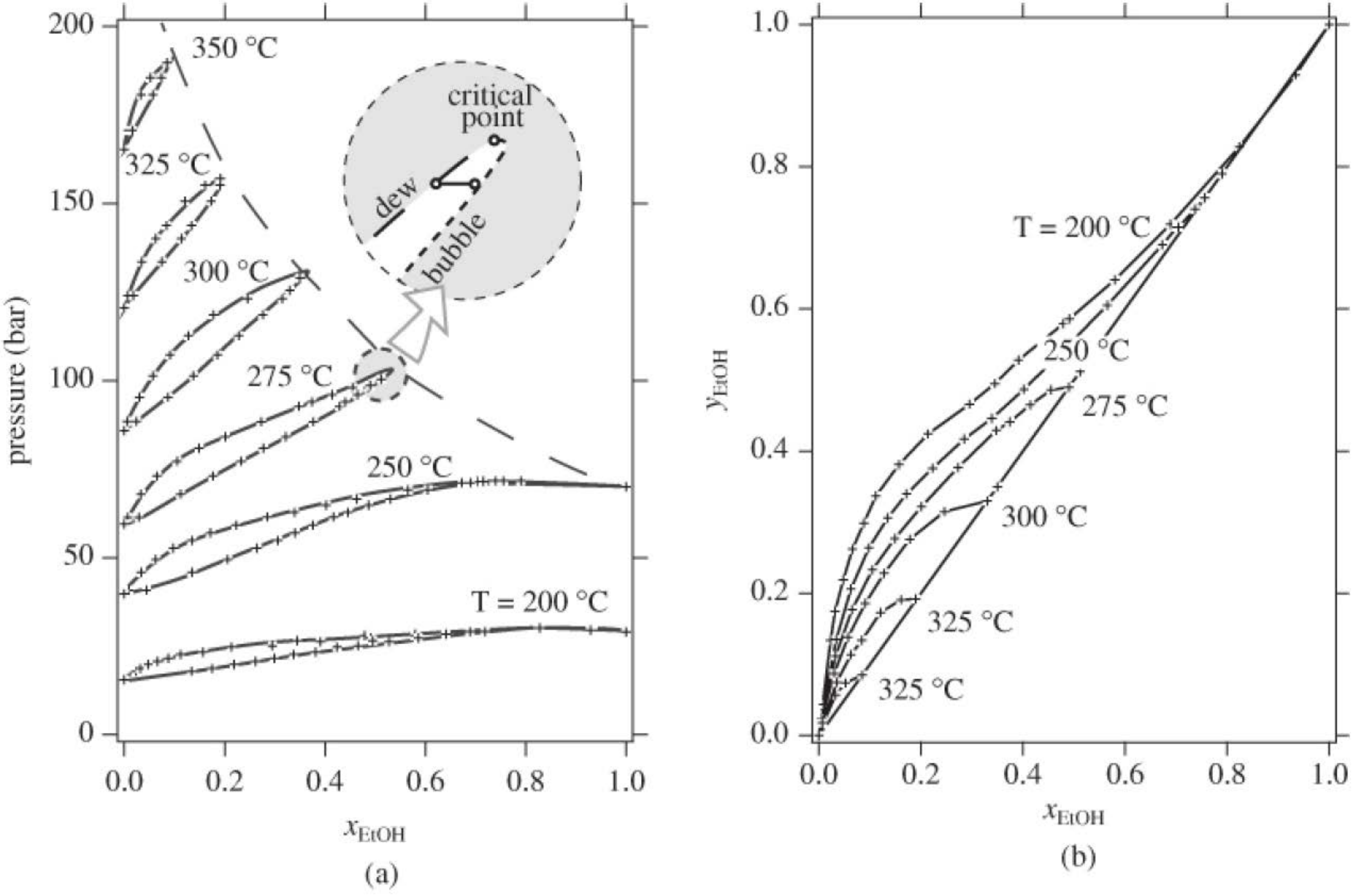
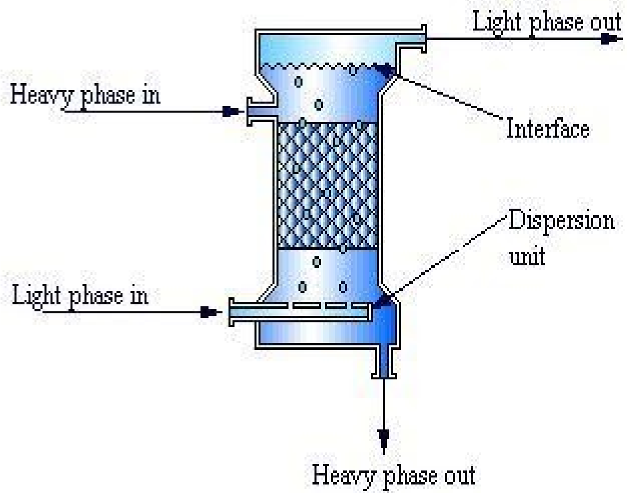
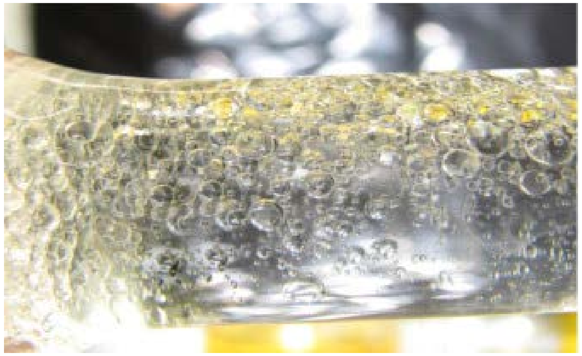


Figure 8-9: Pxy and xy phase diagrams of ethanol/water at elevated temperatures (data from Frank Barr-David and B. F. Dodge, Journal of Chemical & Engineering Data, 4 (2):107-121, 1959).

Partially Miscible Liquids

- Some liquids are only partially miscible in each other.
    - Arises when the constituent molecules contain groups that have low affinity for each other: the system n-hexane/ethanol.
    - Both molecules contain CH_2 and CH_3 groups which are very similar. Ethanol also contains a polar hydroxyl group, –OH, which has little affinity for the alkyl groups.
    - A limited amount of hexane can be accommodated in ethanol and, similarly, small amounts of ethanol can be dissolved in hexane.
    - At certain compositions, however, the system splits into two separate liquid phases due to the lack of affinity between hydroxyls and hydrocarbons.
    - If such a system is brought to boiling it becomes a three-phase system: two liquids and a vapor.
- Solvent (liquid-liquid) extraction is based on this.





Txy of Partially Miscible n-hexane(1)/Ethanol(2) System: Mixing Isothermally

- Start with pure ethanol at 60°C and 1.96 bar.
- Add n-hexane slowly to ethanol.
- Move across isothermally.
- The ethanol-rich phase (L_2) has the composition of point C_1.
- The n-hexane-rich phase (L_1) the composition of point C_2.
- The two-phase system (mixture) is represented by a single point, C, which lies inside the two-phase region at the overall composition of the two-phase system.
- This composition is calculated by the lever rule:

$$z_i = L_1 x_i^{(1)} + L_2 x_i^{(2)}$$

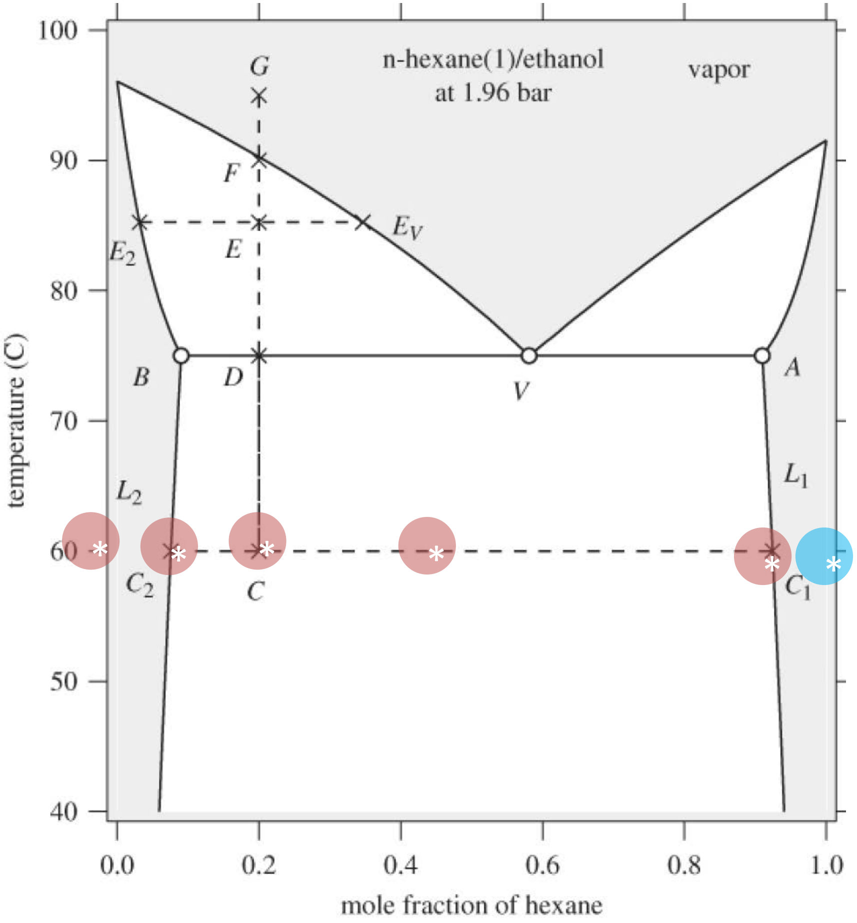


Figure 8-10: *Txy* graph of partially miscible liquids: hexane(1)/ ethanol(2) at 1.96 bar.

Txy of Partially Miscible n-hexane(1)/Ethanol(2) System: Heating under constant composition

- Start at point C and increase *T*.
- The onset of boiling (bubble point) is shown by point D. Three phases present, two liquids and the vapor. As long as two liquids are present in boiling, the state of the system remains pegged at point D: the boiling temperature is constant, and the composition of all phases is also constant given by points A, V, and B. In other words, the system forms an azeotrope. The only change observed during this stage is the continuous decrease of the amounts of the liquids, and the increase in the amount of the vapor.
- Once any of the liquid phases is completely depleted, the state moves up. Which phase is depleted first depends on the overall composition of the starting mixture. For example, state E consists of vapor in equilibrium with the ethanol-rich phase, as indicated by the phases at the end points of the tie line that passes through E; the hexane-rich phase has completely evaporated.
- At point F the system reaches its dew point. Further heating moves the state into the region of superheated vapor.
- **The line CG on the *Txy* graph represents a path of heating under constant overall composition.**

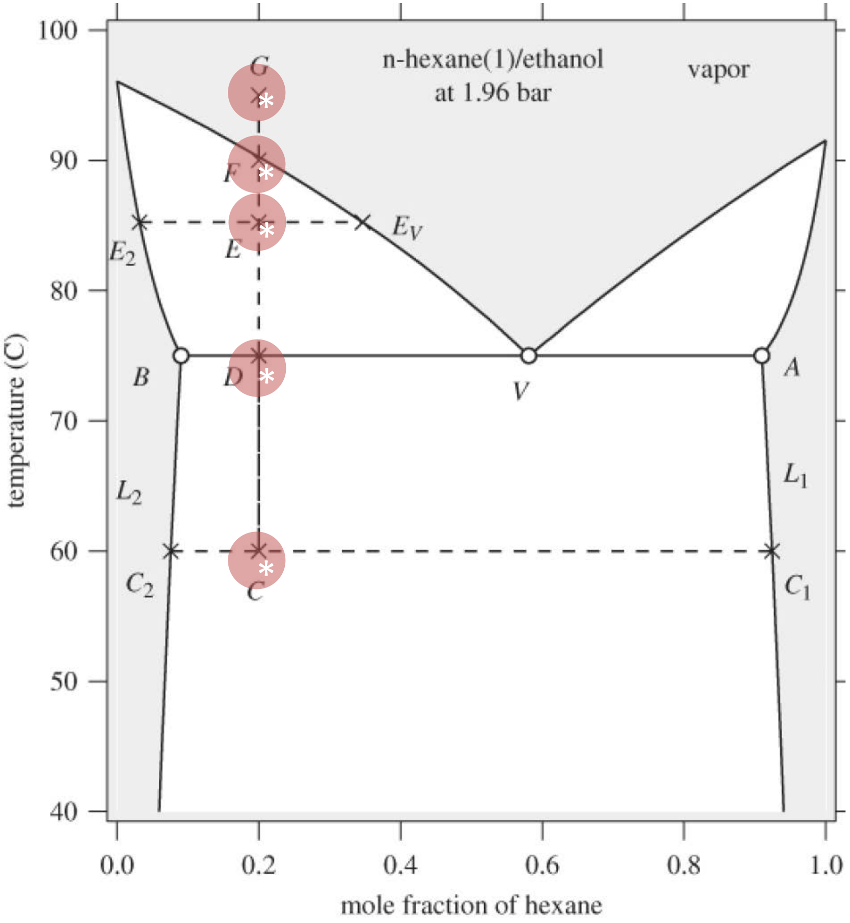
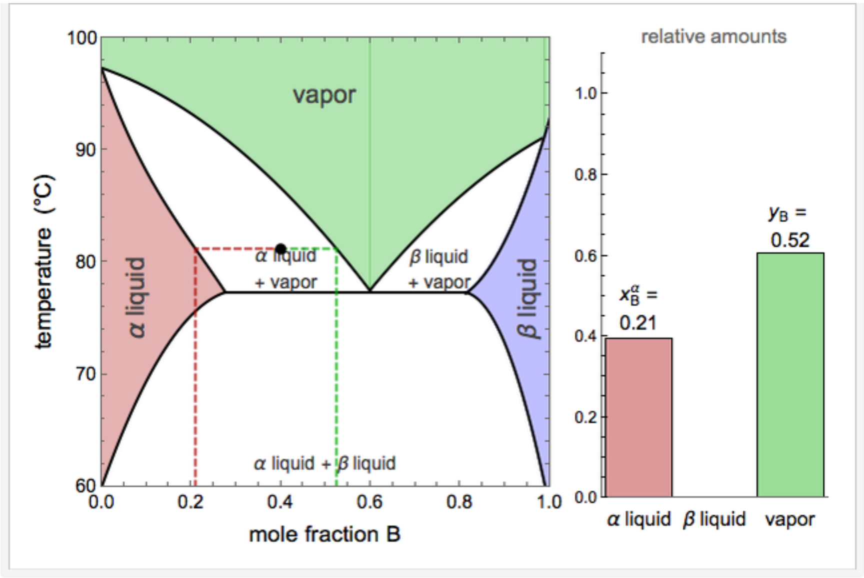
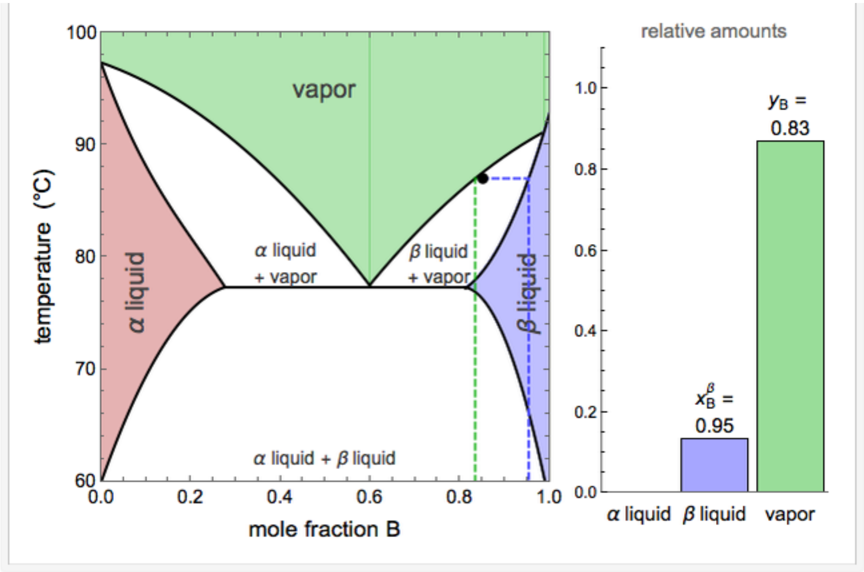
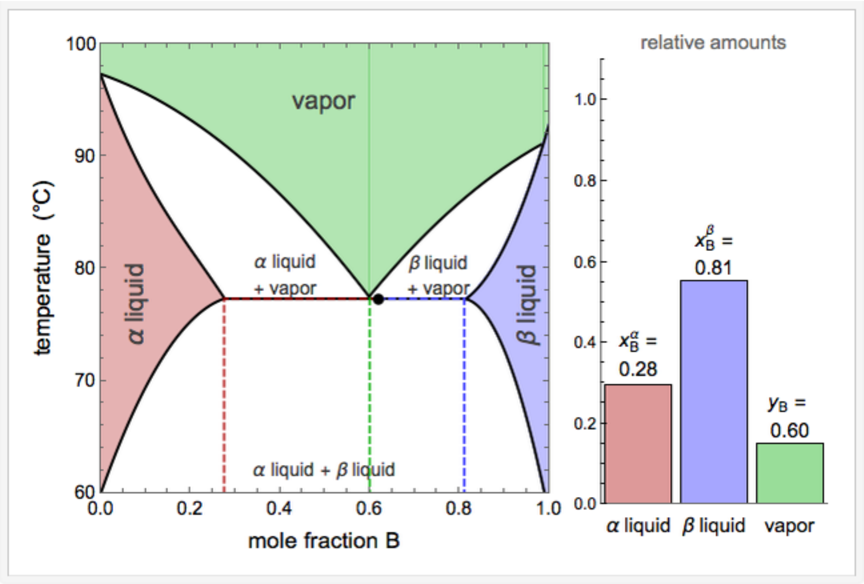


Figure 8-10: *Txy* graph of partially miscible liquids: hexane(1)/ ethanol(2) at 1.96 bar.







Megan Maguire and Neil C. Hendren "Vapor-Liquid-Liquid Equilibrium (VLLE)"
http://demonstrations.wolfram.com/VaporLiquidLiquidEquilibriumVLLE/
Wolfram Demonstrations Project

Pxy of Partially Miscible n-hexane(1)/Ethanol(2) System

- Qualitatively resembles a *Txy* graph turned upside down.
- Since pressure has little effect on the mutual solubility of liquids, the boundaries between the two liquid phases, lines AA′ and BB′, are essentially vertical.
- To read this graph follow same principles as with the *Txy* graph. First we label the single phases (hexane-rich liquid, ethanol-rich liquid, vapor).
- All other regions are areas where two or three phases are present. These phases are identified by drawing tie lines until they intersect a phase boundary.

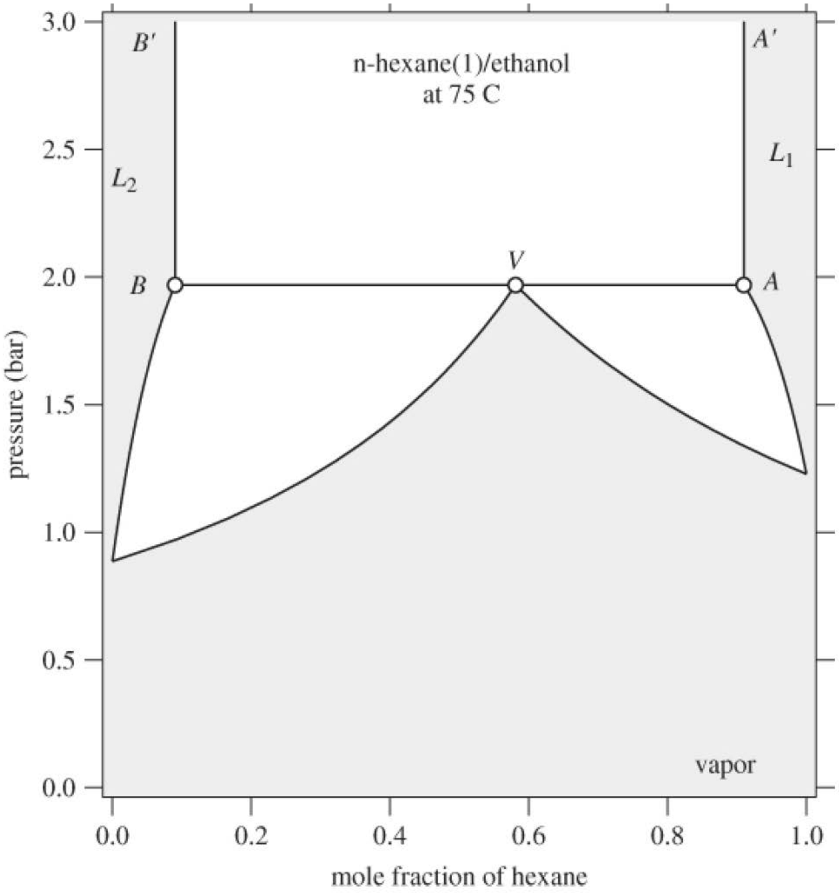
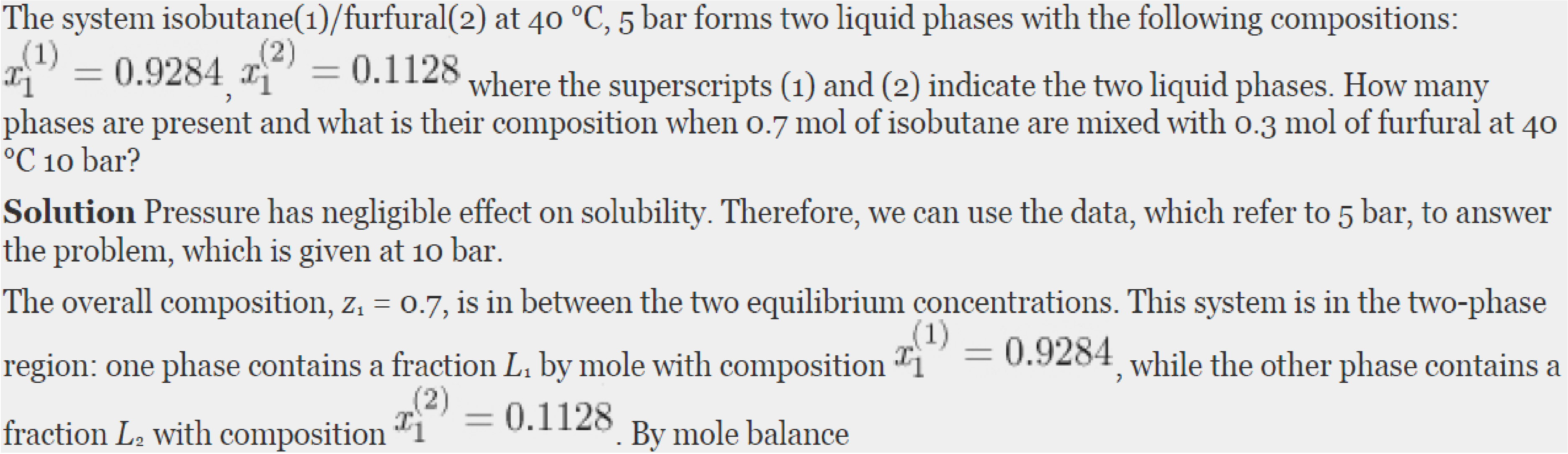


Figure 8-11: *Pxy* graph of partially miscible liquids – hexane(1)/ethanol(2).

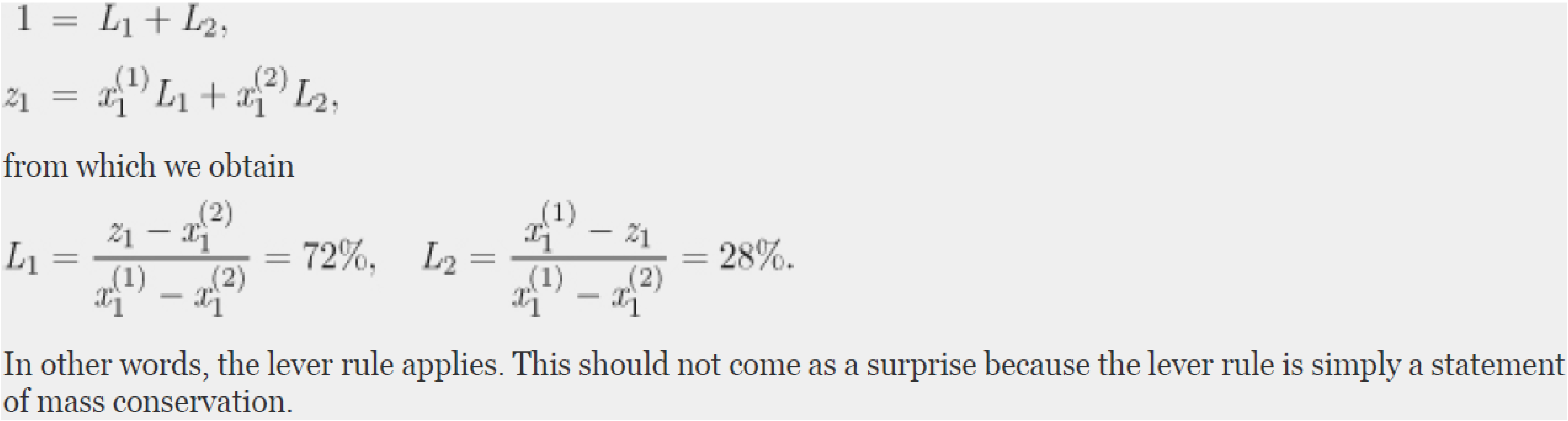
Example 8.6: Partially Miscible Liquids and the Lever Rule



The system isobutane(1)/furfural(2) at 40 °C, 5 bar forms two liquid phases with the following compositions: $x_1^{(1)} = 0.9284$, $x_1^{(2)} = 0.1128$ where the superscripts (1) and (2) indicate the two liquid phases. How many phases are present and what is their composition when 0.7 mol of isobutane are mixed with 0.3 mol of furfural at 40 °C 10 bar?

Solution Pressure has negligible effect on solubility. Therefore, we can use the data, which refer to 5 bar, to answer the problem, which is given at 10 bar.

The overall composition, $z_1 = 0.7$, is in between the two equilibrium concentrations. This system is in the two-phase region: one phase contains a fraction L_1 by mole with composition $x_1^{(1)} = 0.9284$, while the other phase contains a fraction L_2 with composition $x_1^{(2)} = 0.1128$. By mole balance



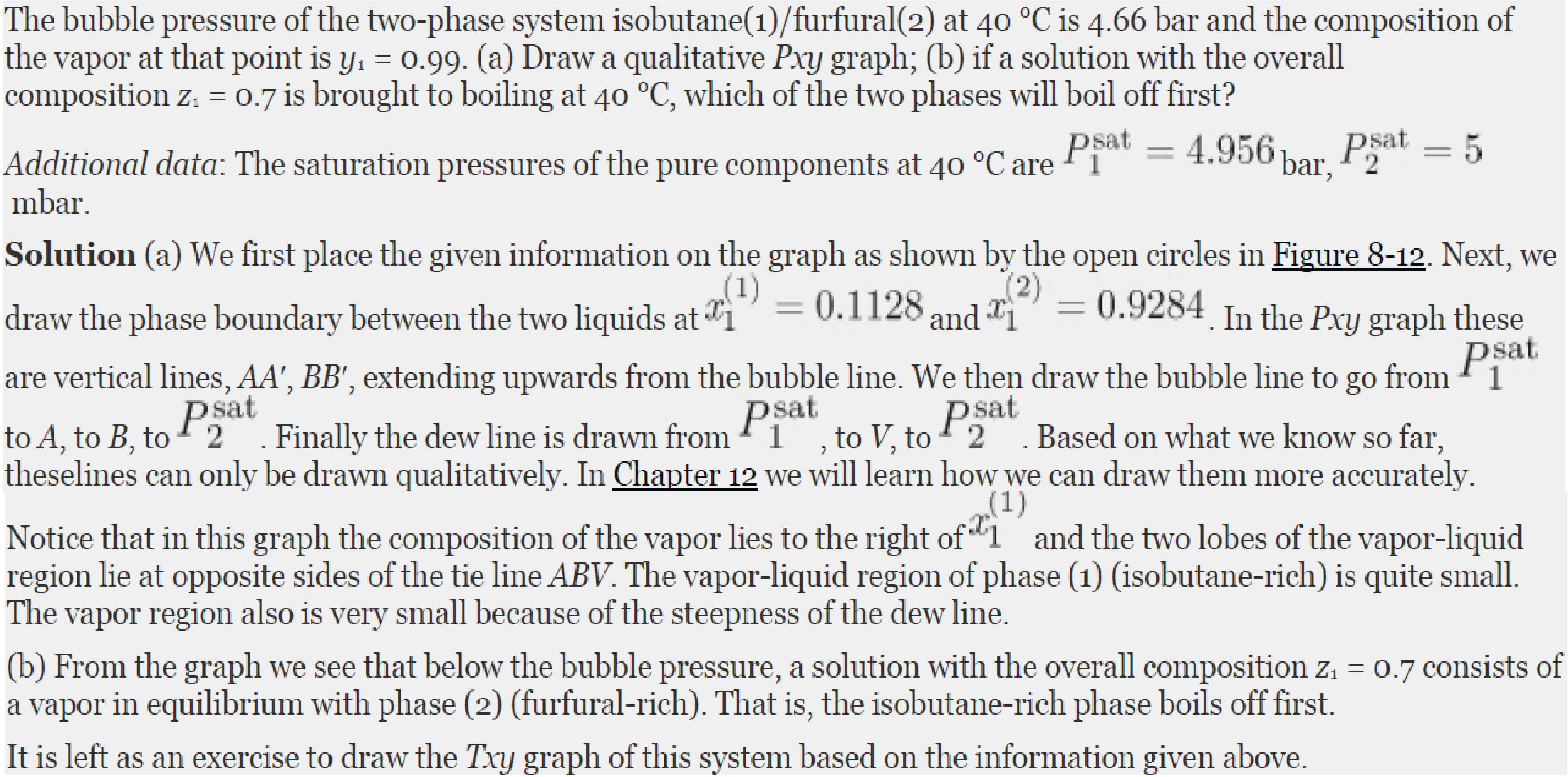
$$
\begin{aligned}
1 &= L_1 + L_2, \\
z_1 &= x_1^{(1)} L_1 + x_1^{(2)} L_2,
\end{aligned}
$$

from which we obtain

$$
L_1 = \frac{z_1 - x_1^{(2)}}{x_1^{(1)} - x_1^{(2)}} = 72\%, \quad L_2 = \frac{x_1^{(1)} - z_1}{x_1^{(1)} - x_1^{(2)}} = 28\%.
$$

In other words, the lever rule applies. This should not come as a surprise because the lever rule is simply a statement of mass conservation.

xm: Qualitative-Phase Diagram



The bubble pressure of the two-phase system isobutane(1)/furfural(2) at 40 °C is 4.66 bar and the composition of the vapor at that point is $y_1 = 0.99$. (a) Draw a qualitative *Pxy* graph; (b) if a solution with the overall composition $z_1 = 0.7$ is brought to boiling at 40 °C, which of the two phases will boil off first?

Additional data: The saturation pressures of the pure components at 40 °C are $P_1^{\mathrm{sat}} = 4.956$ bar, $P_2^{\mathrm{sat}} = 5$ mbar.

Solution (a) We first place the given information on the graph as shown by the open circles in Figure 8-12. Next, we draw the phase boundary between the two liquids at $x_1^{(1)} = 0.1128$ and $x_1^{(2)} = 0.9284$. In the *Pxy* graph these are vertical lines, *AA*′, *BB*′, extending upwards from the bubble line. We then draw the bubble line to go from P_1^{sat} to *A*, to *B*, to P_2^{sat}. Finally the dew line is drawn from P_1^{sat}, to *V*, to P_2^{sat}. Based on what we know so far, theselines can only be drawn qualitatively. In Chapter 12 we will learn how we can draw them more accurately.

Notice that in this graph the composition of the vapor lies to the right of $x_1^{(1)}$ and the two lobes of the vapor-liquid region lie at opposite sides of the tie line *ABV*. The vapor-liquid region of phase (1) (isobutane-rich) is quite small. The vapor region also is very small because of the steepness of the dew line.

(b) From the graph we see that below the bubble pressure, a solution with the overall composition $z_1 = 0.7$ consists of a vapor in equilibrium with phase (2) (furfural-rich). That is, the isobutane-rich phase boils off first.

It is left as an exercise to draw the *Txy* graph of this system based on the information given above.

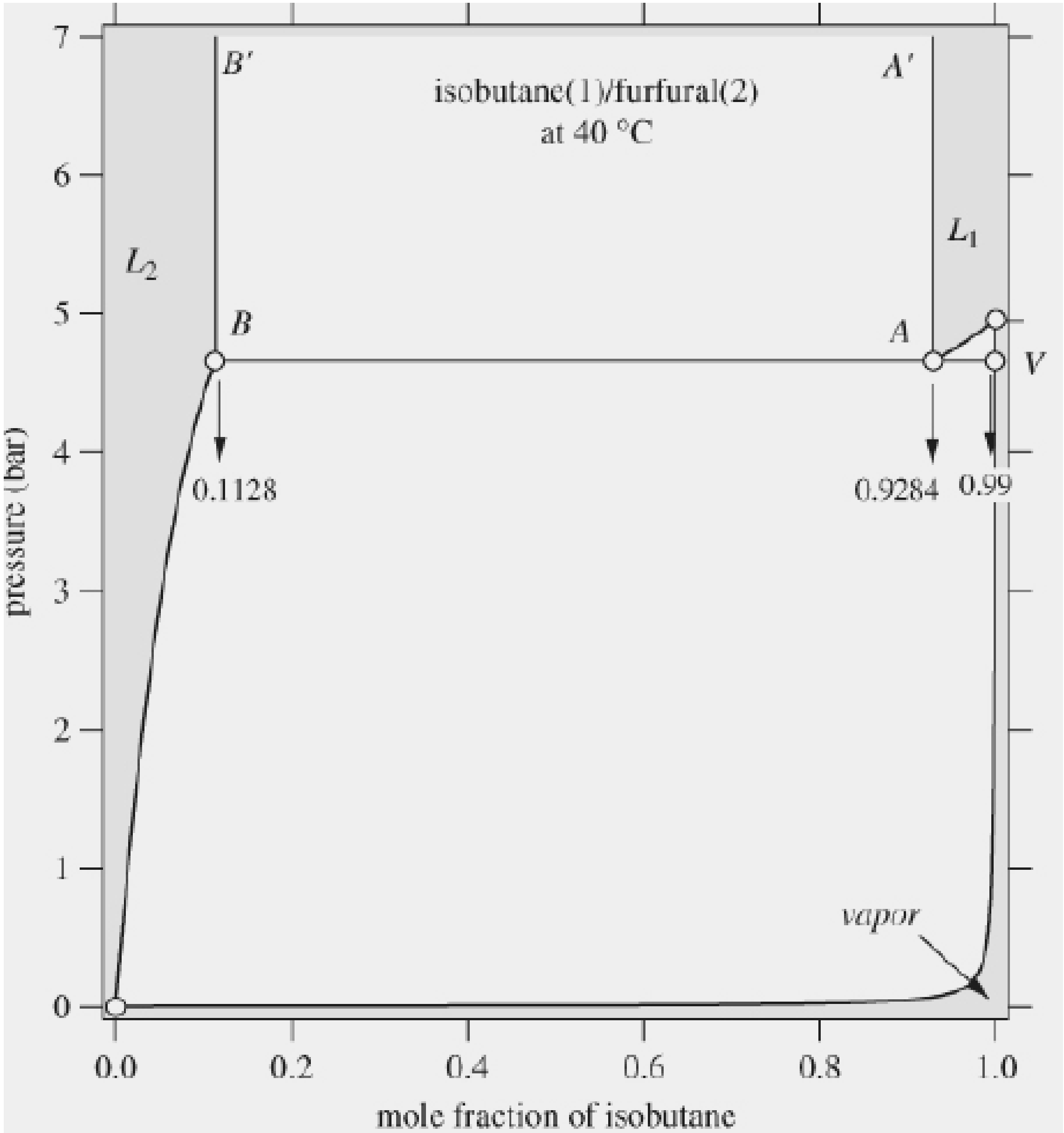


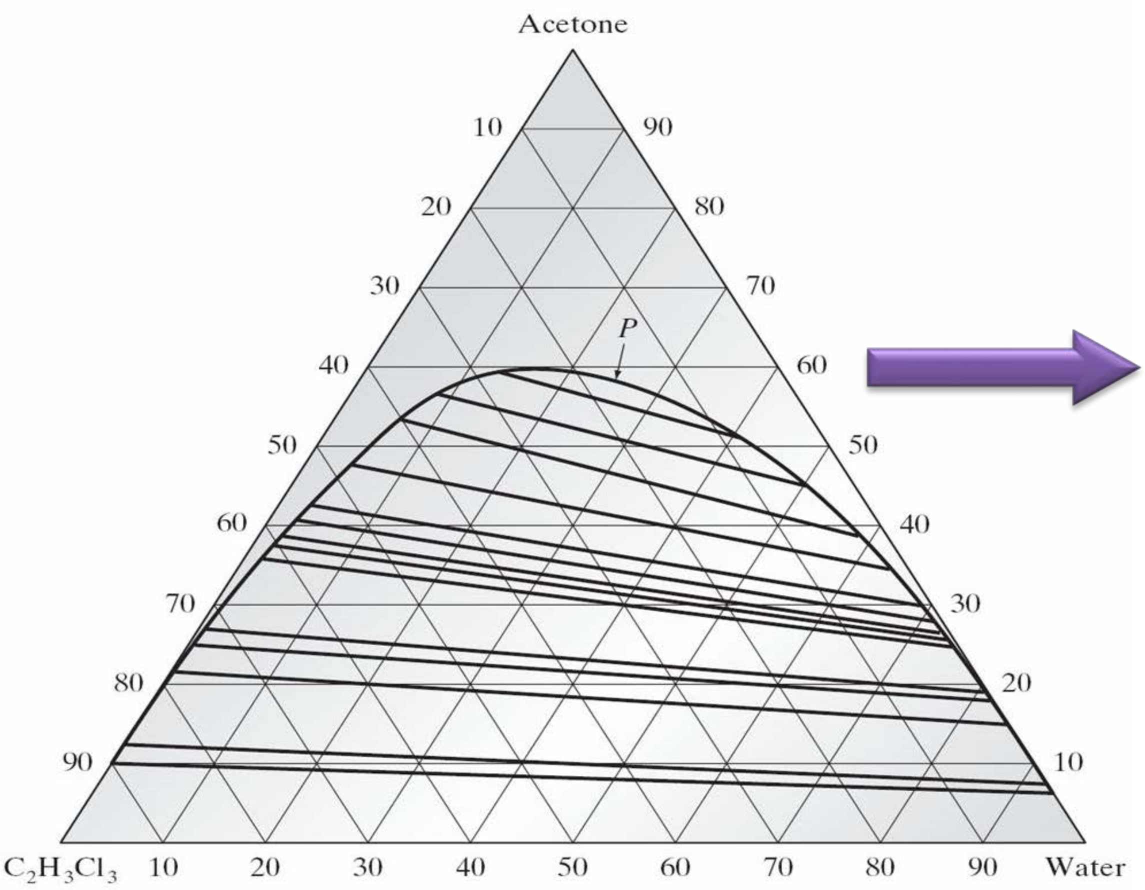
Figure 8-12: *Pxy* graph for the system isobutane(1)/furfural(2) at 40°C. The composition of the two liquids and the vapor at the point of liquid-liquid-vapor equilibrium are shown on the graph.

Ternary Systems for LLE

- The majority of LLE data deals with ternary mixtures (solvent I-Solute-Solvent II).
- Usually plotted on a ternary diagram.
- The ternary diagram are “a smart way” to escape from plotting three dimensional graphs.
- LLE data takes many shapes depending on the system under study.
- When a component “the solute” is distributed between two partially miscible liquid phases we define the distribution coefficient as:

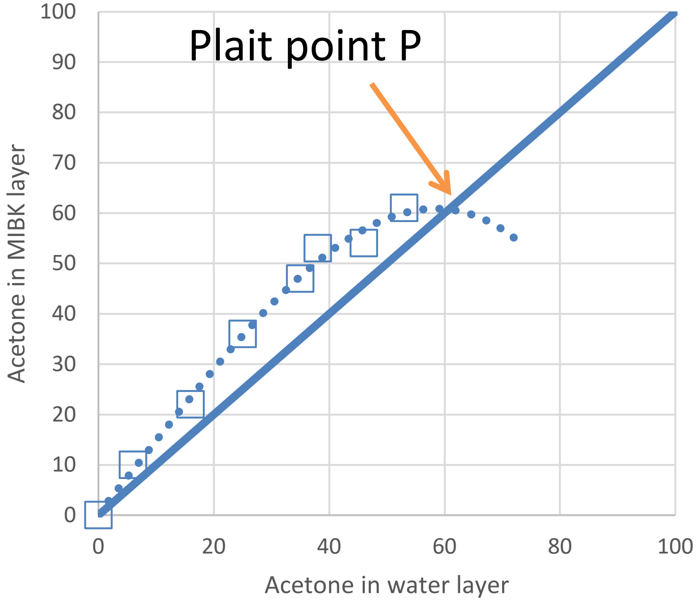
$$K = \frac{\text{Concentration of solute in phase I}}{\text{Concentration of solute in phase II}}$$

A: solute



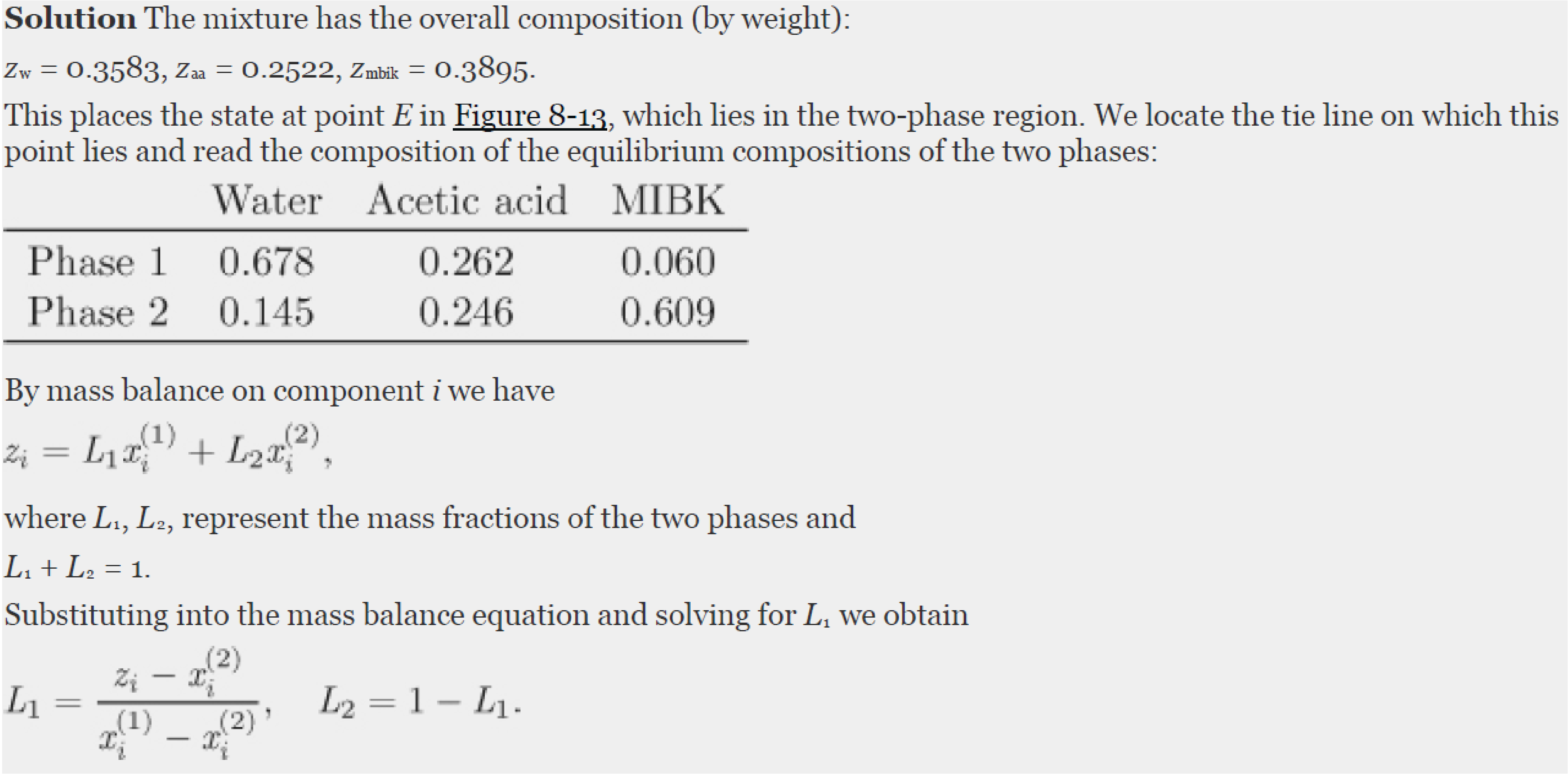
B: solvent I

B: solvent II



Example 8.8: Ternary Systems

Ten kilograms of water are mixed with 10.4 kg acetic acid and 10.87 kg methylisobutyl ketone (MIBK) at 25 °C. Determine the phase of the mixture. If a two-phase system, report the amount and composition of each phase.



Solution The mixture has the overall composition (by weight):

$z_w = 0.3583,\ z_{aa} = 0.2522,\ z_{mbik} = 0.3895.$

This places the state at point *E* in Figure 8-13, which lies in the two-phase region. We locate the tie line on which this point lies and read the composition of the equilibrium compositions of the two phases:

	Water	Acetic acid	MIBK
Phase 1	0.678	0.262	0.060
Phase 2	0.145	0.246	0.609

By mass balance on component *i* we have

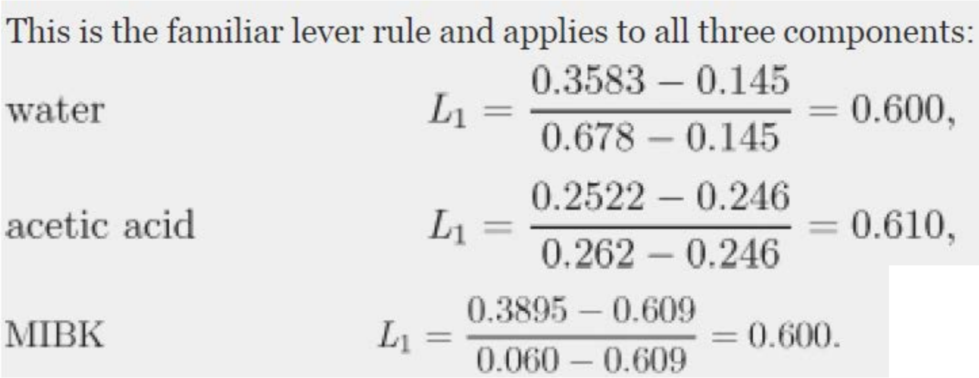
$$z_i = L_1 x_i^{(1)} + L_2 x_i^{(2)},$$

where L_1, L_2, represent the mass fractions of the two phases and

$L_1 + L_2 = 1.$

Substituting into the mass balance equation and solving for L_1 we obtain

$$L_1 = \frac{z_i - x_i^{(2)}}{x_i^{(1)} - x_i^{(2)}}, \quad L_2 = 1 - L_1.$$



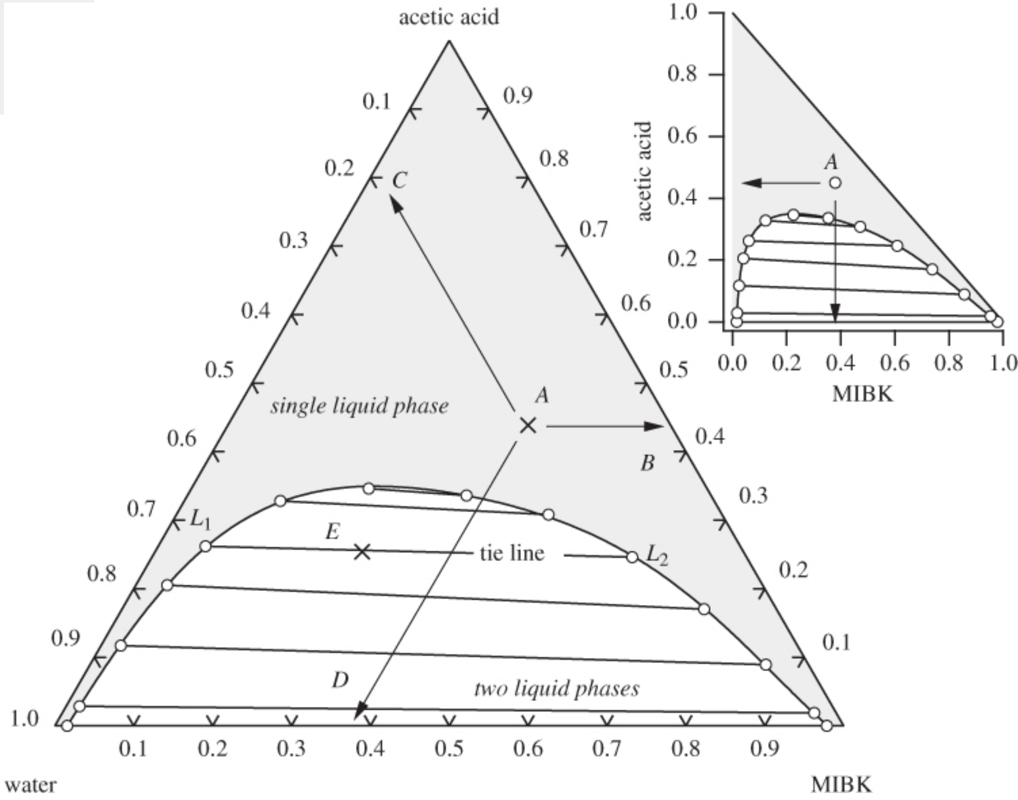
This is the familiar lever rule and applies to all three components:

water $$L_1 = \frac{0.3583 - 0.145}{0.678 - 0.145} = 0.600,$$

acetic acid $$L_1 = \frac{0.2522 - 0.246}{0.262 - 0.246} = 0.610,$$

MIBK $$L_1 = \frac{0.3895 - 0.609}{0.060 - 0.609} = 0.600.$$

The system contains 60% (wt) of liquid phase 1 and 40% of liquid phase 2. Comments The lever rule gives the same answer regardless of which component is used. The small discrepancy between these values arises from inaccuracies in reading the composition of the equilibrium calculation of the tie line that passes through the given state. Often, ternary graphs will show selected tie lines, but if the desired state does not lie on one of them, we must obtain one through interpolation between the existing tie lines.



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- Sandler, Stanley I. *Chemical, biochemical, and engineering thermodynamics*. John Wiley & Sons, 2017.
- Kortesky, Milo D. Engineering and chemical thermodynamics. John Wiley & Sons, 2012.