SEPARATION OPERATIONS 1 (0905451)

03 – SINGLE EQUILIBRIUM STAGES AND FLASH CALCULATIONS

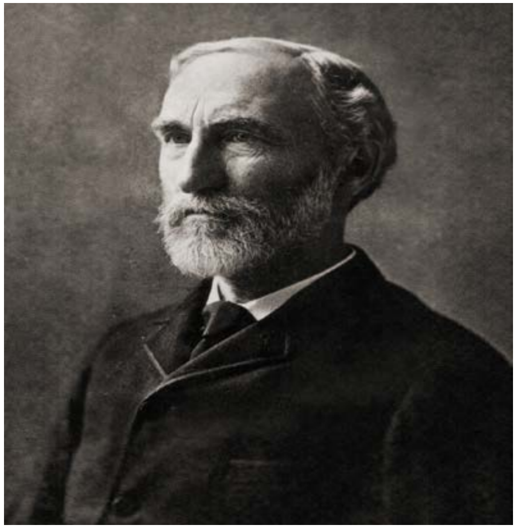
ALI KH. AL-MATAR (aalmatar@ju.edu.jo)

Chemical Engineering Department, University of Jordan
Amman 11942, Jordan

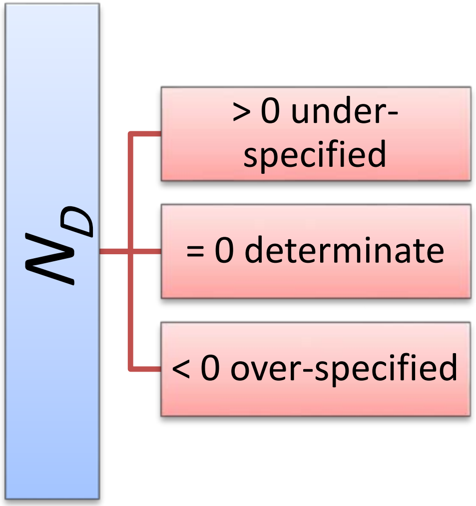
Outline

- Gibbs's Phase Rule and Degrees of Freedom
- What is distillation?
- Single Equilibrium Stage
- Constant-Pressure y–x Diagrams and the q-Line
- Single Equilibrium Stage
- Flash
- Ternary liquid-Liquid (L-L) Systems
- Gas-Liquid Systems
- Vapor –Liquid–Liquid (VLLE) Flash Procedure

Gibbs’s Phase Rule and Degrees of Freedom



- Consider an equilibrium system consisting of one or more phases, N_P, with one or more chemical components, C.
  - In the absence of chemical reactions; and
  - for negligible gravitational, electrical, magnetic, and surface forces,
- Let N_V = the number of variables and N_E = the number of independent equations that relate the intensive variables.
- **intensive thermodynamic variables** (those independent of the mass) are: temperature, T; pressure, P; and composition, e.g., in mole fractions
- Then, the number of **degrees of freedom** ND for the system is $N_D = N_V - N_E$.
- N_D is the number of variables that must be specified so that the remaining variables can be determined from the independent equations.



N_D

> 0 under-specified

= 0 determinate

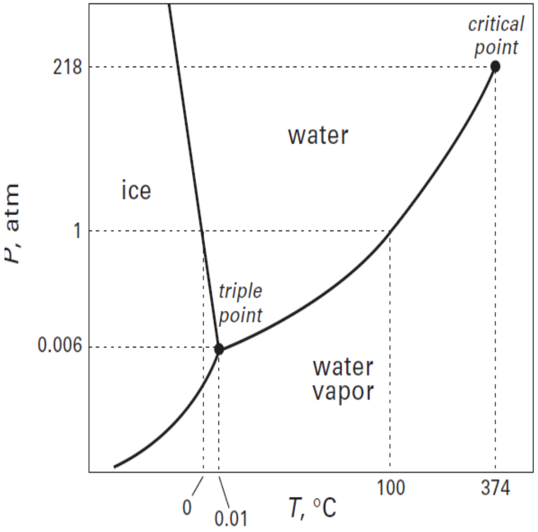
< 0 over-specified

Gibbs’s Phase Rule: Single Component

- The Gibbs’ phase rule:

$$N_D = C - N_P + 2$$

- Consider a one-component system (C = 1) of H_2O. Phase boundaries are shown between vapor (water vapor or steam) and liquid (water), vapor and solid (ice), and liquid (water) and solid (ice).
  - The mole fraction is fixed at 1.0 for a single component.
- If $N_P = 1$, the phase rule gives $N_D = 2$.
  - The only intensive variables remaining are T and P, both of which must be specified to fix the state of the system.
  - Single phases of water vapor, water, and ice exist over ranges of T and P.
- If $N_P = 2$, the phase rule gives $N_D = 1$.
  - We can only specify T or P, each of which is the same for both phases.
  - The remaining intensive variable must lie on a phase boundary, for example on the vapor pressure curve for water in equilibrium with steam.
- If $NP = 3$, the phase rule gives $ND = 0$.
  - Both T and P are fixed for all three phases, resulting in a unique (invariant) triple point!



Gibbs's Phase Rule: Multicomponent Systems

- The number of intensive thermodynamic variables in a multiphase, multicomponent system is:

$$N_V = N_P\left(C+2\right)$$

  - $N_P C$ = number of composition variables.
  - $2N_P$ = T and P of each phase.

- The number of independent equations is:

$$N_E = N_P + \left(C+2\right)\left(N_P-1\right)$$

Mole fractions in each phase sums to unity

$$\sum_{i=1}^{C} x_i = 1, \quad \sum_{i=1}^{C} y_i = 1$$

Phase equilibrium for (C+ 2) conditions: C chemical compositions, T, and P

$$T_1 = T_2 = \cdots = T_{N_P}, \quad P_1 = P_2 = \cdots = P_{N_P}$$

EXAMPLE 4.1 Equilibrium Phase Conditions for a Three-Phase System

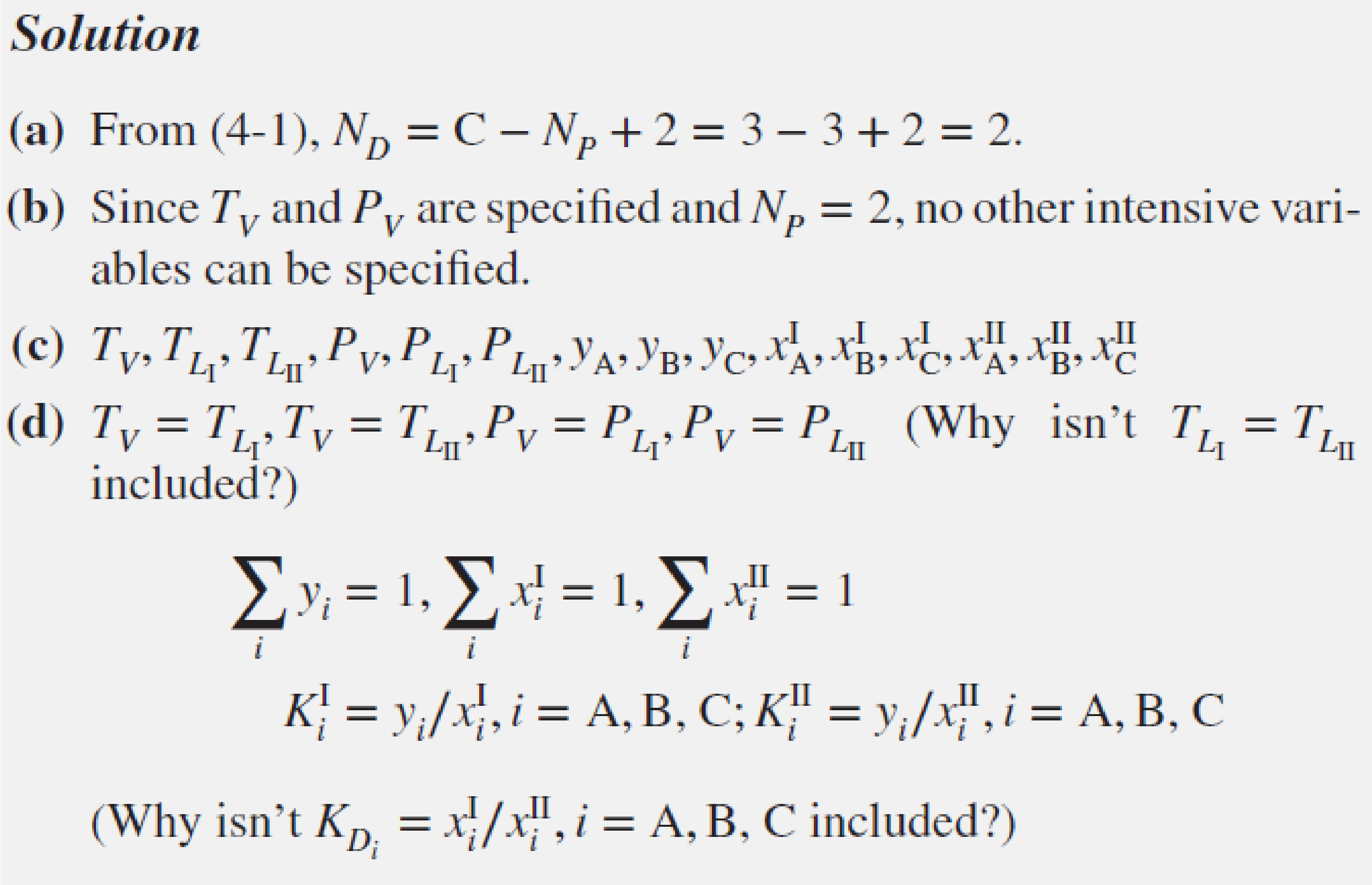
For three components (A, B, and C), a vapor phase (V) and two liquid phases (L_I and L_{II}) with mole fractions, y_I, x_I, and y_{II}, x_{II} are at physical equilibrium.

(a) By Gibbs' phase rule, how many degrees of freedom are there?

(b) If the temperature and pressure of the vapor phase are specified, can any other intensive variables be specified? If so, what would you specify?

(c) What are the $N_P(C + 2) = 3\,(3 + 2) = 15$ intensive variables that apply?

(d) Write the $N_P + (C + 2)\,(N_P - 1) = 3 + (3 + 2)\,(3 - 1) = 13$ independent equations that apply.



Solution

(a) From (4-1), $N_D = C - N_P + 2 = 3 - 3 + 2 = 2$.

(b) Since T_V and P_V are specified and $N_P = 2$, no other intensive variables can be specified.

(c) $T_V, T_{L_I}, T_{L_{II}}, P_V, P_{L_I}, P_{L_{II}}, y_A, y_B, y_C, x_A^I, x_B^I, x_C^I, x_A^{II}, x_B^{II}, x_C^{II}$

(d) $T_V = T_{L_I}, T_V = T_{L_{II}}, P_V = P_{L_I}, P_V = P_{L_{II}}$ (Why isn't $T_{L_I} = T_{L_{II}}$ included?)

$$\sum_i y_i = 1, \sum_i x_i^I = 1, \sum_i x_i^{II} = 1$$

$$K_i^I = y_i/x_i^I, i = A, B, C; K_i^{II} = y_i/x_i^{II}, i = A, B, C$$

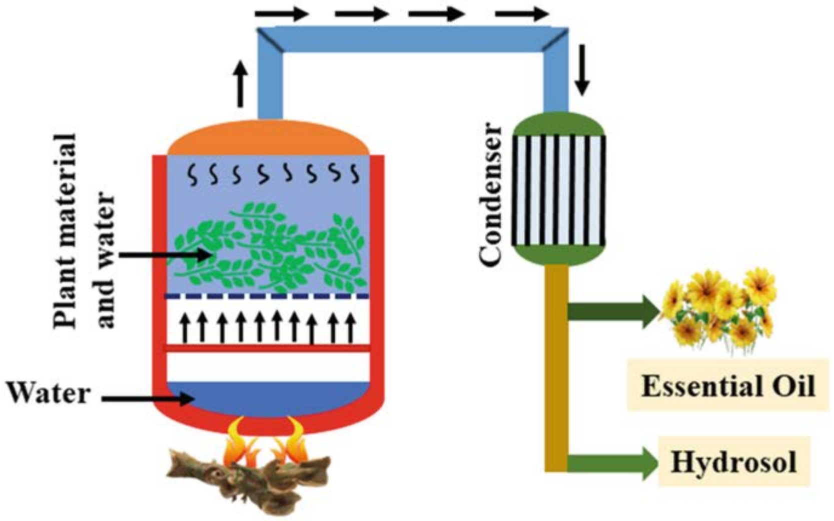
(Why isn't $K_{D_i} = x_i^I/x_i^{II}, i = A, B, C$ included?)

What is distillation?

- Separation between two or more components based on the difference in their boiling points i.e., relative volatility.
- The liquid mixture containing the components to be separated is heated;
  - The component that has low boiling point (B.P.) will evaporate first when the solution temperature approaches its B.P.
  - With the increase in liquid temperature, the next component that has higher B.P. than the previous one will evaporate, and so on.
  - Combining interstage liquid withdrawal coupled with condensation leads to the desired component with “high” purity.

Types of Distillation

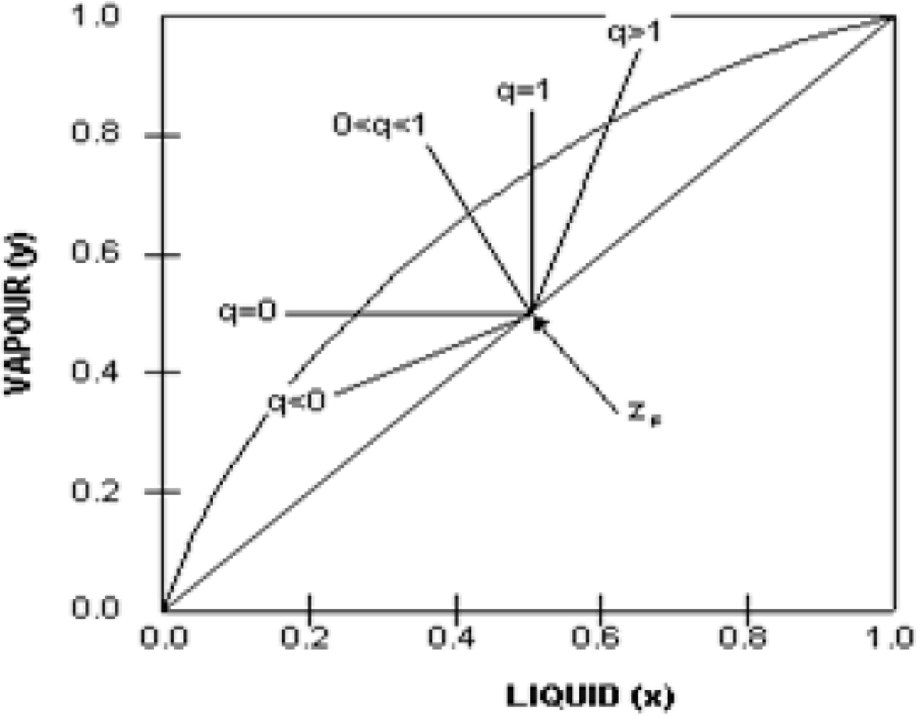
- **Distillation**
  - **Simple (Flash)**
    - Flash (Equilibrium)
      - Concept: Separation of two liquids whose B.P. differ by at least 50^{o}C e.g.,
      - Example: diethyl ether (BP~34^{o}C) and water (BP=100^{o}C)
    - Steam
      - A positive flow is provided by steam from boiling water, rather than by the boiling of the substances of interest
      - Example: Isolation of essential oils for use in perfumes, stripping of light component from heavy ones.
  - Fractional
    - Atmospheric or Pressurized
      - Concept: Separation of two or more liquids having close BPs (< 25^{o}C)
      - Example: Ethanol (BP= 78^{o}C) and water (BP= 100^{o}C)
    - Vacuum
      - Concept: Lowering pressure in the column to a value less than the vapor pressure of the mixture, creating a vacuum, and causing the component with lower vapor pressures to evaporate off.
      - Example: used when the boiling point of the compound (or the solvent) is too high (B.P. > 150oC)



Direct Steam distillation

Constant-Pressure *y*–*x* Diagrams and the *q*-Line

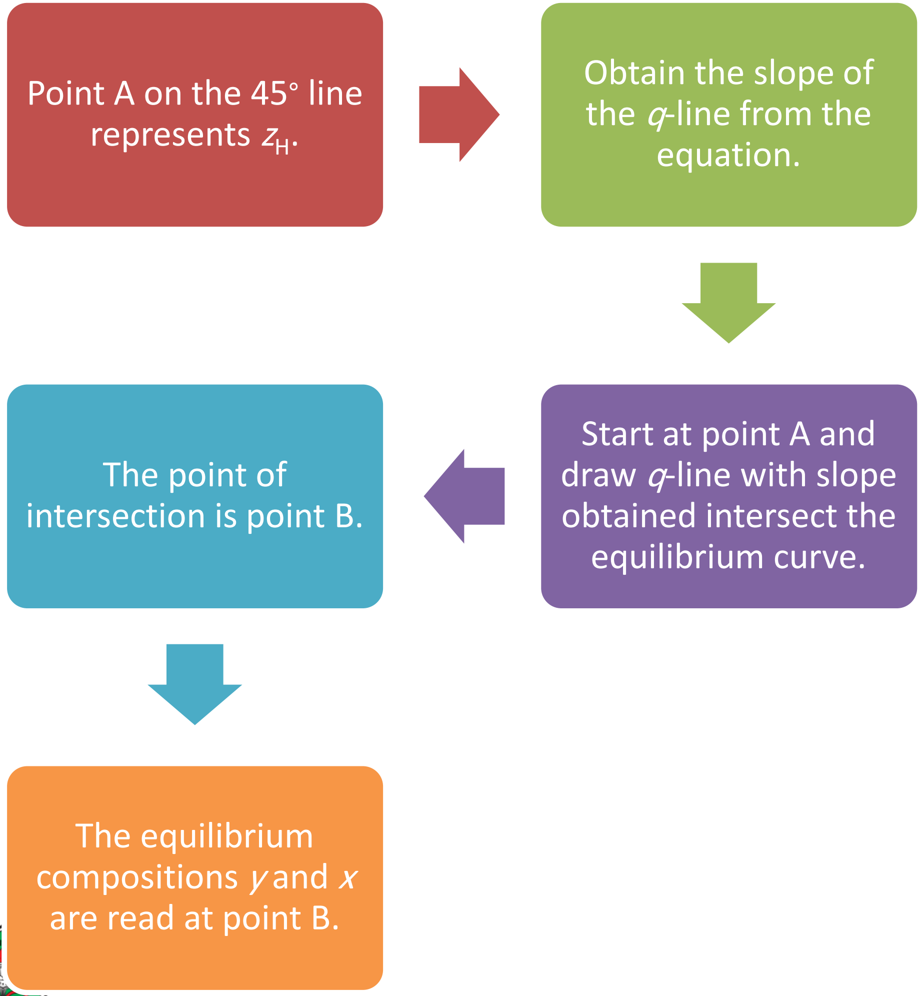
- Useful because the vapor-and-liquid compositions are points on the equilibrium curve.
- Convenient for determining compositions as a function of mole-percent vaporization by geometric constructions.
- Percentage of liquid in the feed is termed *q*.



$q = 0$ (saturated vapour)
$q = 1$ (saturated liquid)
$0 < q < 1$ (mix of liquid and vapour)
$q > 1$ (subcooled liquid)
$q < 0$ (superheated vapour)

Determining the *q*-Line

$$\text{slope} = \frac{\psi - 1}{\psi}, \quad \psi = V/F$$



Point A on the 45° line represents z_H.

Obtain the slope of the *q*-line from the equation.

Start at point A and draw *q*-line with slope obtained intersect the equilibrium curve.

The point of intersection is point B.

The equilibrium compositions *y* and *x* are read at point B.

The equation of the q-line is obtained by combining component mass balance and overall mass balance

Component balance e.g., Hexane

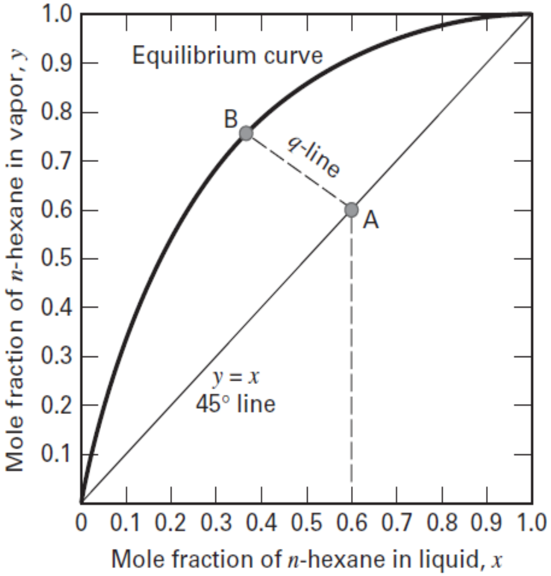
$$Fz_F = Vy + Lx$$

$$F = L + V \Rightarrow L = F - V$$

$$y = \frac{\psi - 1}{\psi} x + \frac{1}{\psi} z_F$$

$$y = \frac{q}{q-1} x - \frac{1}{q-1} z_F$$

EXAMPLE Consider a feed mixture of *F* moles, of overall composition z_H = 0.6. Determine the phase compositions of the equilibrium vapor (*V*) and liquid (*L*) if 60 mol% of the feed is vaporized.

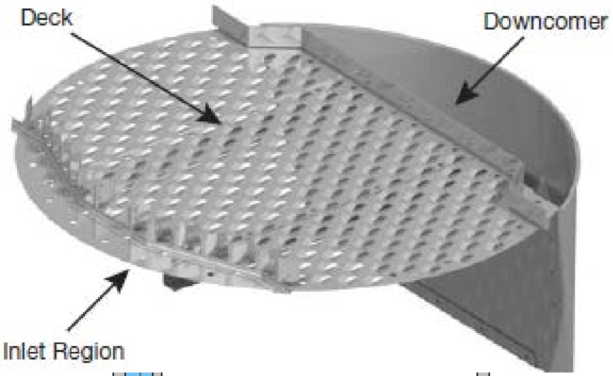


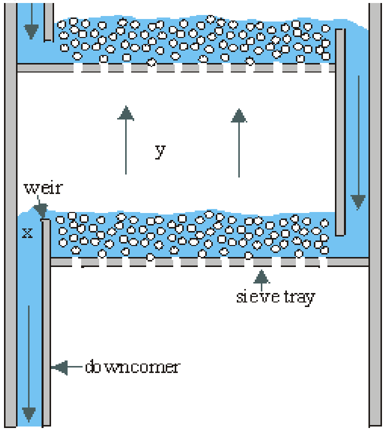
y–*x* phase-equilibrium diagram for the *n*-hexane–*n*-octane system at 1 atm.

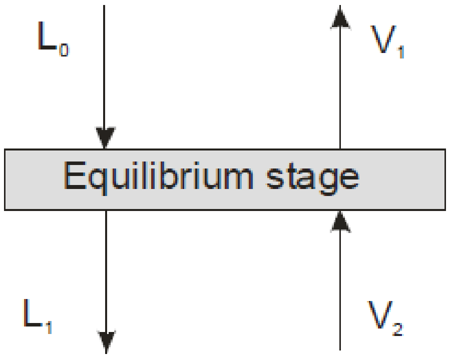
Point A on the 45° line represents z_H. Point B is reached on the phase equilibrium curve by extending the dashed line, called the ***q*-line**, upward and to the left toward the equilibrium curve at a slope equal to $[(V/F) - 1]/(V/F)$. Thus, for 60 mol% vaporization, the slope $= (0.6 - 1)/0.6 = -2/3$. Point B at the intersection of line AB with the equilibrium curve is the equilibrium composition $y_H = 0.76$ and $x_H = 0.37$. The

Single Equilibrium Stage

- Two different phases are brought into intimate contact with each other and then get separated.
- During the time of contact, mixing occurs, and the various components diffuse and redistribute themselves between the two phases.
- If mixing time is long enough, equilibrium in the two phases commences.
- If a vapor stream V_2 is in contact with a liquid stream L_0 then the two streams V_1 and L_1 leaving the equilibrium stage are at equilibrium.
- Composition of the two streams leaving the process (y_{Ai} and x_{Ai}) are related by the equilibrium relation $y_{Ai} = f(x_{Ai})$.
- For a binary mixture of A and B, if sensible heat effects are small and the latent heats of both compounds are the same then we have Constant Molar Overflow (CMO).

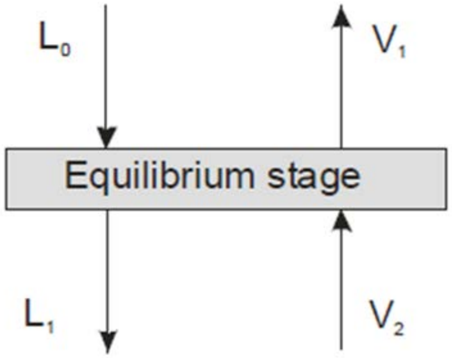






Constant Molar Overflow (CMO)

- When 1 mole of A condenses, then 1 mole of B must vaporize. Hence:
    - The total molar flow V_1 will equal the total molar flow V_2.
    - The total molar flow L_1 will equal the total molar flow L_0.
- When CMO is valid, the compositions in streams V_1 and L_1 can be solved from only the combination of material balance and the equilibrium relations.
- The energy balance is not required since it is satisfied when the material balance is satisfied.



Material Balances

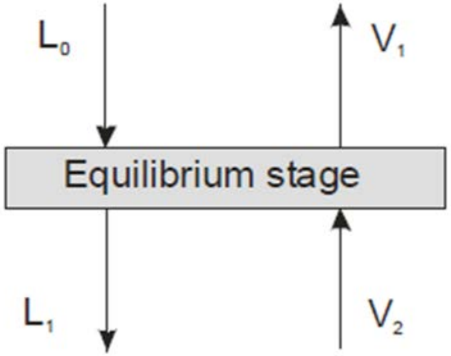
- The overall material (or mole) balance for the system:

$$V_2 + L_0 = V_1 + L_1$$

- Component balance:

$$V_2\, y_{A2} + x_{A0} L_0 = y_{A1} V_1 + x_{A1} L_1$$

- Composition of the two streams leaving the process (y_{Ai} and x_{Ai}) are related by the equilibrium relation $y_{Ai} = f(x_{Ai})$.



Example: Binary mixture at equilibrium

A vapor at the dew point and 200 kPa containing a mole fraction of 0.40 benzene (1) and 0.60 toluene (2) and 100 kmol total is brought into contact with 110 kmol of a liquid at the boiling point containing a mole fraction of 0.30 benzene and 0.70 toluene. The two streams are contacted in a single stage, and the outlet streams leave in equilibrium with each other. Assume constant molar overflow, calculate the amounts and compositions of the exit streams.

Solution

Data: Vapor pressure, P^{sat}, data: $\ln P^{sat} = A - B/(T + C)$, where P^{sat} is in kPa and T is in K.

Compound	A	B	C
Benzene (1)	14.1603	2948.78	– 44.5633
Toluene (2)	14.2515	3242.38	– 47.1806

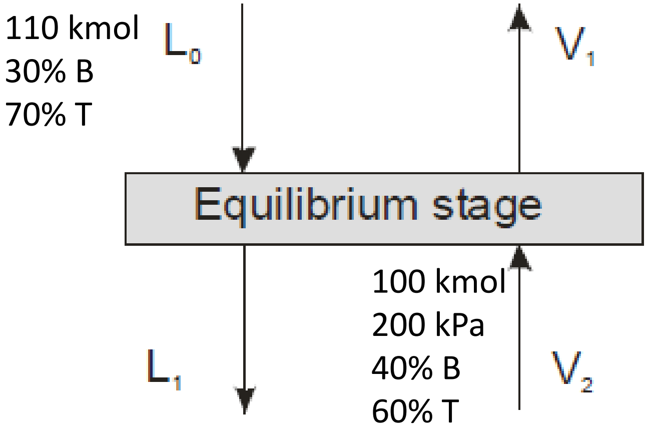
- Component balance for Benzene (B)

$$V_2\,y_{A2} + x_{A0}L_0 = y_{A1}V_1 \;+ x_{A1}L_1$$

$$100 \times 0.4 + 110 \;\times 0.3 = 100\,y_1 + 110\,x_1$$

Divide by 10 the above equation yields

$$11x_1 + 10y_1 = 7.3 \Rightarrow y_1 = 0.73 - 1.1x_1$$



110 kmol
30% B
70% T

L_0

V_1

Equilibrium stage

L_1

100 kmol
200 kPa
40% B
60% T

V_2

Since the two streams V_1 and L_1 are in equilibrium,

Applying Raoult's Law for component 1 (B)

$$\frac{y_1}{x_1} = \frac{P_1^{sat}}{200} \Rightarrow 200y_1 = x_1\exp(14.1603 - 2948.78/(T - 44.5633))$$

For component 2 (T)

$$\frac{1-y_1}{1-x_1} = \frac{P_2^{sat}}{200} \Rightarrow 200(1-y_1) = (1-x_1)\exp(14.2515 - 3242.38/(T - 47.1806))$$

The three equations can be solved for T, x1, and y1 either by graphical or numerical method.

$$x_1 = 0.2164 \qquad y_1 = 0.4425$$

The Equilibrium temperature is also obtained (MATHEMATICA)

$$\mathrm{Solve}[200 * 0.4425 == 0.2164 * \mathrm{Exp}[14.1603 - 2948.78/(T - 44.5633)], T]$$

$$T \to 406.5\ \mathrm{K} = 133.35^{\mathrm{o}}\mathrm{C}$$

Flash

- Flash is a single-equilibrium-stage distillation in which a liquid feed is partially vaporized to give a vapor richer than the feed in the more volatile components.
  - A pressurized liquid feed is heated and flashed adiabatically across a valve to a lower pressure, resulting in creation of a vapor phase that is separated from the remaining liquid in a flash drum.
  - Alternatively, the valve can be omitted and a liquid can be partially vaporized in a heater and then separated into two phases.
  - A vapor feed can be cooled and partially condensed to give, after phase separation, a liquid richer in the less volatile components.

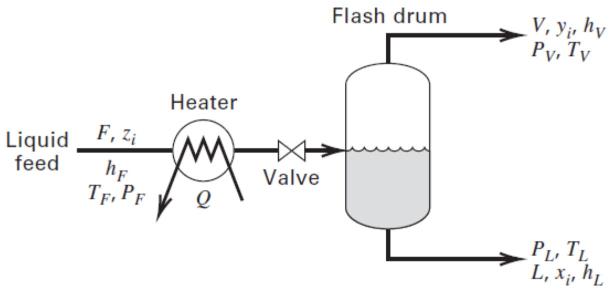


Figure 4.8 Continuous flash vaporization

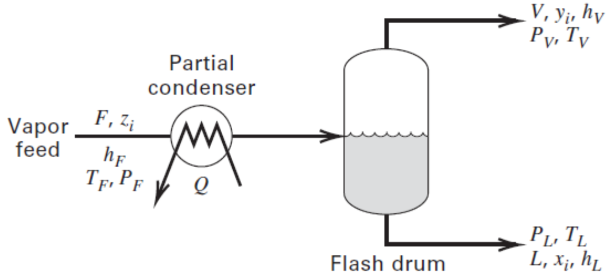
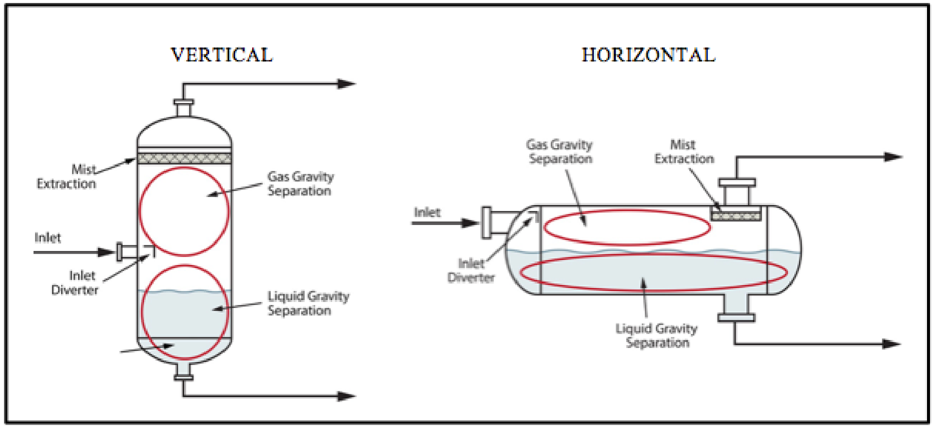
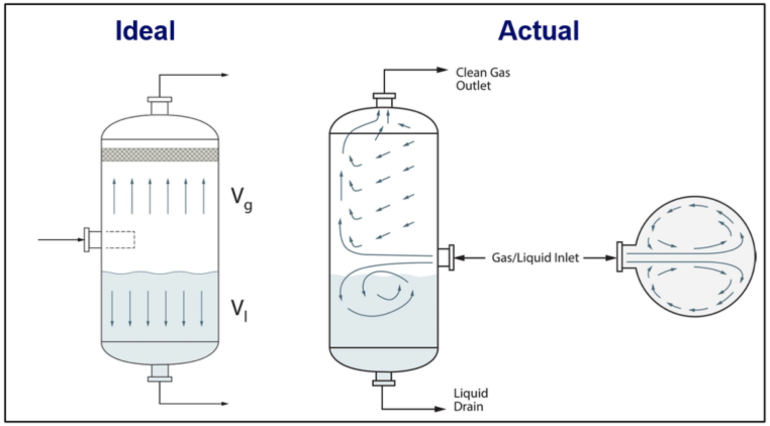
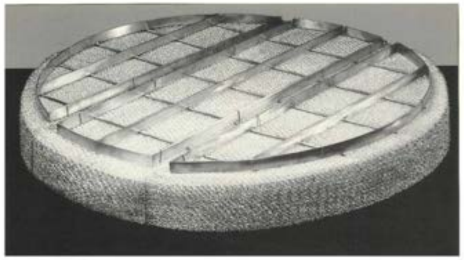


Figure 4.9 Continuous partial condensation.






Courtesy of Koch-Otto York


Courtesy of ACS

http://www.jmcampbell.com/tip-of-the-month/2014/12/troubleshooting-gas-liquid-separators-removal-of-liquids-from-the-gas/

Flash Calculations: Derivation

- Consider a continuous, single-stage partial condensation or flash vaporization process. The feed is a vapor, liquid, or mixture of both.
- The feed can be heated or cooled in a heat exchanger, and its pressure can be decreased by passing the feed through a valve.
- The equilibrium phases separate in the phase separator.
  - The vapor phase is enriched in the more volatile components.
  - The liquid phase is enriched in the less volatile components.

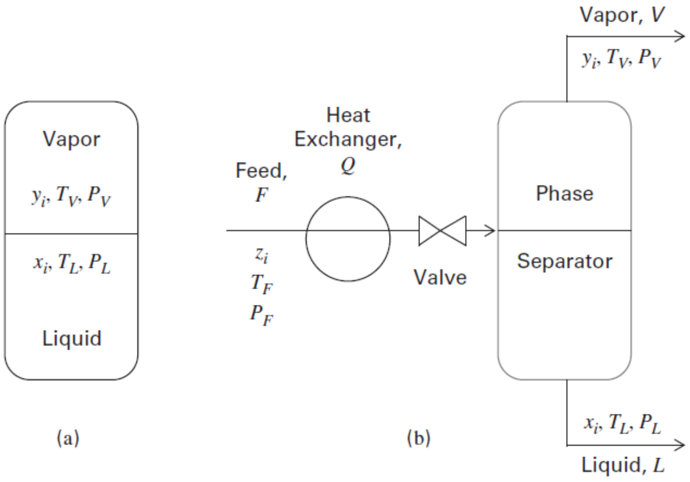


Figure 4.10 Variables for vapor-liquid phase equilibria: (a) Gibbs' Phase Rule for Intensive Variables Only; (b) Extension to Continuous Partial Condensation or Vaporization with both Intensive and Extensive Variables.

Gibbs’s Phase Rule: Extension with Extensive Variables

- The number of degrees of freedom is given by:

$$N_V = N_P\left(C+2\right) + \left(C + N_P + 4\right)$$

$$N_E = N_P + \left(C+2\right)\left(N_P - 1\right) + \left(C+2\right)$$

$$N_D = N_V - N_E = C + 4$$

Comp.MB : $Fz_i = Vy_i + Lx_i, \quad i = 1:\mathrm{C}$

Tot.MB : $F = V + L$

EB : $Fh_F + Q = Vh_V + Lh_L$

Feed : $\sum_{i=1}^{\mathrm{C}} z_i = 1$

- For a two-phase system

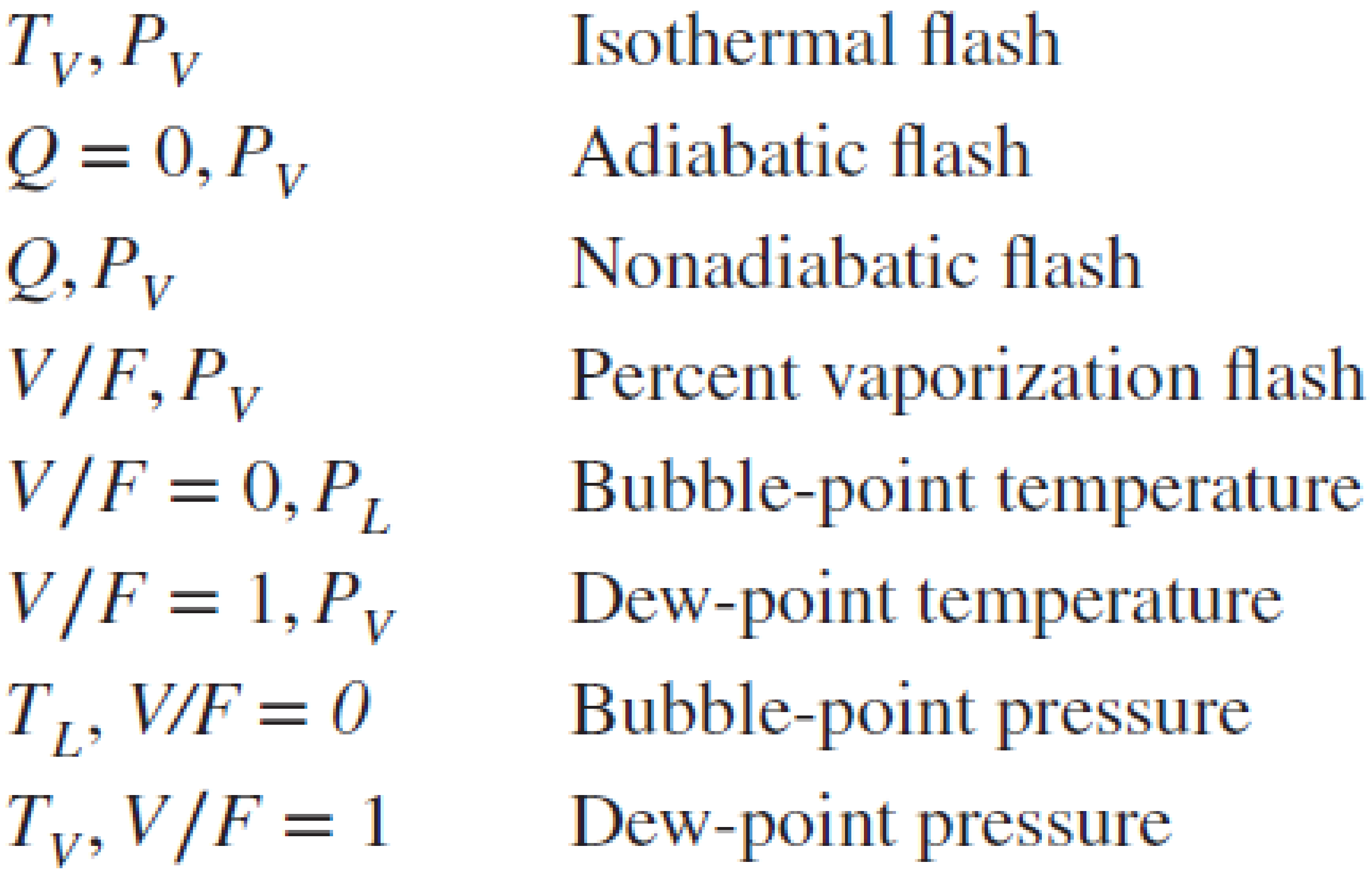
$$N_V = 3C + 10$$

$$N_E = 2C + 6$$

$$N_D = C + 4$$

- Common to specify the feed variables: *F*, T_F, P_F, and (C-1) feed mole fractions.
  - Leaves two more variables to specify!

Flash Types: Which Variables to Specify?



T_V, P_V	Isothermal flash
$Q = 0, P_V$	Adiabatic flash
Q, P_V	Nonadiabatic flash
$V/F, P_V$	Percent vaporization flash
$V/F = 0, P_L$	Bubble-point temperature
$V/F = 1, P_V$	Dew-point temperature
$T_L, V/F = 0$	Bubble-point pressure
$T_V, V/F = 1$	Dew-point pressure

Isothermal Flash Calculation: Rachford and Rice (RR)

- Widely used algorithm for making two-phase flash calculations is the procedure of **Rachford and Rice (RR)** published in 1952 for the case of an **isothermal flash.**
- The (2C + 6) equations constituted a nonlinear system of algebraic equations that could not be solved directly. RR developed a procedure that reduces the number of nonlinear equations that need to be solved to just one.
- **Please review your thermodynamics (2) lecture notes for the derivation of their final equation.**

Rachford, H.H., Jr. and J.D. Rice, J. Pet. Tech., 4(10), Section 1, p. 19, and Section 2, p. 3 (Oct. 1952).

Derivation of the Rachford and Rice (RR) Equation

$$\sum_{i=1}^{C} z_i = 1$$

Use sp (-1) feed mole fractions to calculate the remaining feed mole fraction.

Set $T_V = T_L$ and $P_V = P_L$

$$Fz_i = Vy_i + Lx_i, \quad i = 1:C$$
$$F = V + L$$
$$z_i = \Psi y_i + (1-\Psi)x_i$$

Combine overall and component MB to eliminate L.

$$x_i = \frac{z_i}{1+\Psi(K_i - 1)}$$
$$y_i = \frac{z_i K_i}{1+\Psi(K_i - 1)}$$

Substitute $K_i x_i = y_i$ and eliminate x_i and $x_i = y_i / K_i$ to eliminate y_i

Subtract sum of x and y (unity for each).

$$\sum_{i=1}^{C} x_i - \sum_{i=1}^{C} y_i = 0$$

$$f(\Psi) = \sum_{i=1}^{C} \frac{z_i(1-K_i)}{1+\Psi(K_i - 1)} = 0$$

Obtain the RR equation

Solve the single nonlinear equation for the vapor fraction Ψ

With a converged value of Ψ, calculate V from V = ΨF

Calculate L from L=F –V

Calculate C values of x_i and C values of y_i

If a heat exchanger precedes the phase separator, calculate Q

Checks for Applying the Rachford-Rice Equation

- These checks are only valid for ideal mixtures where Raoult’s law applies, such that K-values do not depend on the compositions of the liquid and vapor phases.
  - Determine whether the mixture is between the bubble and dew points at the specified conditions i.e., $P_d < P_V < P_b$.
  - At T_V and P_V, if all $K_i > 1$, only a superheated vapor is present.
  - At T_V and P_V, if all $K_i < 1$, only a subcooled liquid is present.
  - If one or more K_i are greater than 1 and one or more K_i are less than 1:
    - Calculate $f\{\Psi\}$ from RR with $\Psi = 0$. If $f\{0\} > 0$, the mixture is below the bubble-point temperature.
    - Alternatively, if Ψ is set to 1 and $f\{1\} < 0$, the mixture is above the dew-point temperature.

Solving the Rachford-Equation

- The RR is a single nonlinear equation and is most commonly solved by using Newton's iterative numerical method.

$$\Psi^{(k+1)} = \Psi^{(k)} - \frac{f(\Psi^{(k)})}{f'(\Psi^{(k)})} = \Psi^{(k)} - \frac{\displaystyle\sum_{i=1}^{C} \frac{z_i (1-K_i)}{1+\Psi^{(k)}(K_i-1)}}{\displaystyle\sum_{i=1}^{C} \frac{z_i (1-K_i)^2}{\left[1+\Psi^{(k)}(K_i-1)\right]^2}}$$

- You need an initial guess for which Ψ = 0 is a good starting point.
- A reasonable criterion for stopping iterations (convergence):

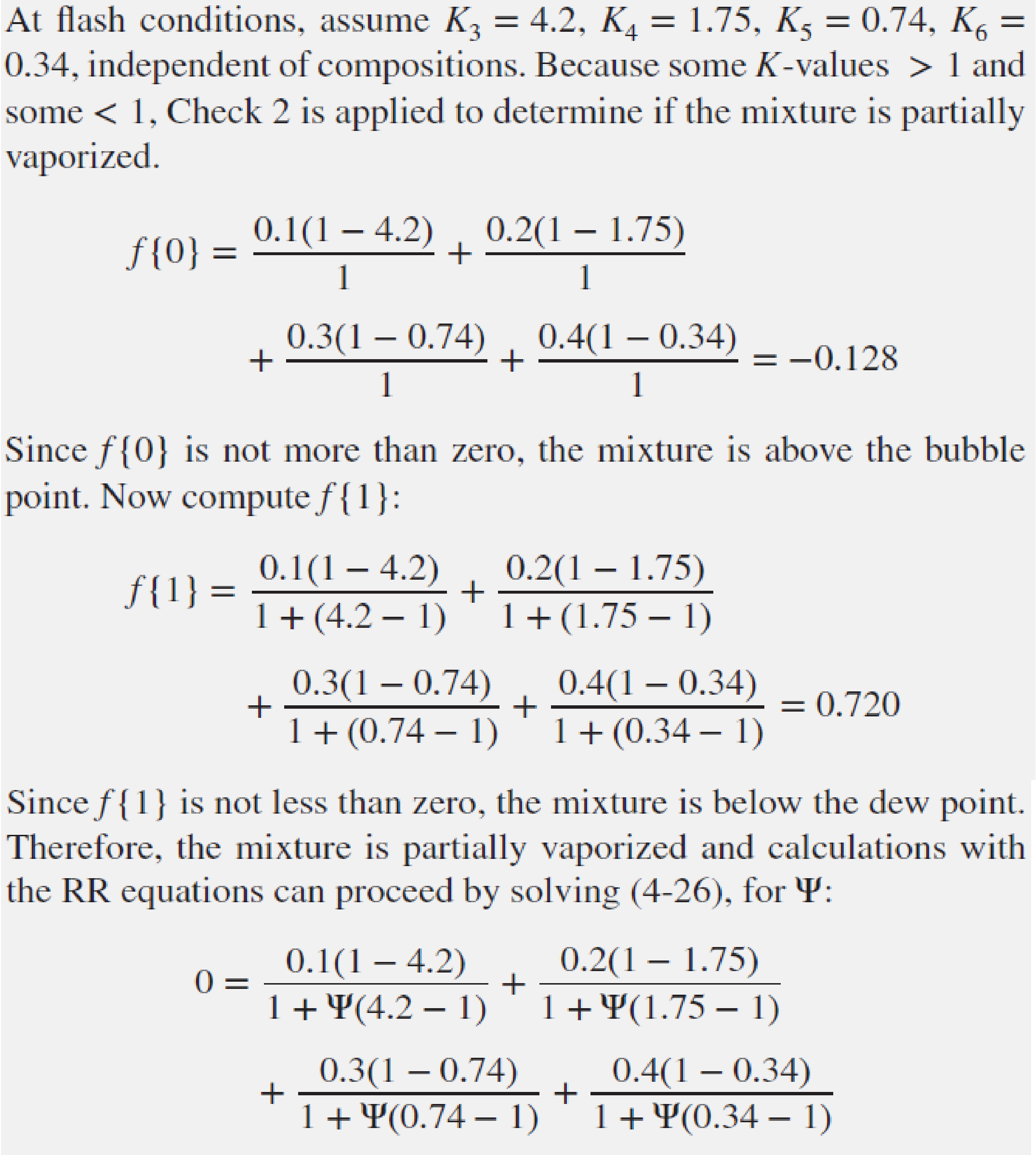
$$\varepsilon^{(k+1)} = \frac{\left|\Psi^{(k+1)} - \Psi^{(k)}\right|}{\Psi^{(k)}} < 0.0001$$

Please visit the Thermodynamics II lectures on flash calculations
https://www.youtube.com/watch?v=NQ4D16fyZpk&t=6s and https://www.youtube.com/watch?v=9mazqmx7ilI&t=20s

EXAMPLE 4.3 Phase Conditions of a Process Stream.

A 100-kmol/h feed consisting of 10, 20, 30, and 40 mol% of propane (3), *n*-butane (4), *n*-pentane (5), and *n*-hexane (6), respectively, enters a distillation column at 690 kPa and 93◦C. Assuming the feed stream is at phase equilibrium, what molar fraction of the feed enters as liquid, and what are the equilibrium liquid and vapor compositions in mole fractions?

Solution



At flash conditions, assume $K_3 = 4.2$, $K_4 = 1.75$, $K_5 = 0.74$, $K_6 = 0.34$, independent of compositions. Because some K-values > 1 and some < 1, Check 2 is applied to determine if the mixture is partially vaporized.

$$f\{0\} = \frac{0.1(1-4.2)}{1} + \frac{0.2(1-1.75)}{1} + \frac{0.3(1-0.74)}{1} + \frac{0.4(1-0.34)}{1} = -0.128$$

Since $f\{0\}$ is not more than zero, the mixture is above the bubble point. Now compute $f\{1\}$:

$$f\{1\} = \frac{0.1(1-4.2)}{1+(4.2-1)} + \frac{0.2(1-1.75)}{1+(1.75-1)} + \frac{0.3(1-0.74)}{1+(0.74-1)} + \frac{0.4(1-0.34)}{1+(0.34-1)} = 0.720$$

Since $f\{1\}$ is not less than zero, the mixture is below the dew point. Therefore, the mixture is partially vaporized and calculations with the RR equations can proceed by solving (4-26), for Ψ:

$$0 = \frac{0.1(1-4.2)}{1+\Psi(4.2-1)} + \frac{0.2(1-1.75)}{1+\Psi(1.75-1)} + \frac{0.3(1-0.74)}{1+\Psi(0.74-1)} + \frac{0.4(1-0.34)}{1+\Psi(0.34-1)}$$

k	$\Psi^{(k)}$	$f\{\Psi^{(k)}\}$	$f'\{\Psi^{(k)}\}$	$\Psi^{(k+1)}$	$\left\lvert\dfrac{\Psi^{(k+1)}-\Psi^{(k)}}{\Psi^{(k)}}\right\rvert$
1	0.5000	0.2515	0.6259	0.0982	0.8037
2	0.0982	–0.0209	0.9111	0.1211	0.2335
3	0.1211	–0.0007	0.8539	0.1219	0.0065
4	0.1219	0.0000	0.8521	0.1219	0.0000

Convergence is rapid, giving $\Psi = V/F = 0.1219$. The vapor flow rate is 0.1219(100) = 12.19 kmol/h, and the liquid flow rate is (100 – 12.19) = 87.81 kmol/h. Liquid and vapor compositions from (4-23) and (4-24) are:

	x	y
Propane	0.0719	0.3021
n-Butane	0.1833	0.3207
n-Pentane	0.3098	0.2293
n-Hexane	0.4350	0.1479
Total	1.0000	1.0000

A plot of $f\{\Psi\}$ as a function of Ψ is shown in Figure 4.11.

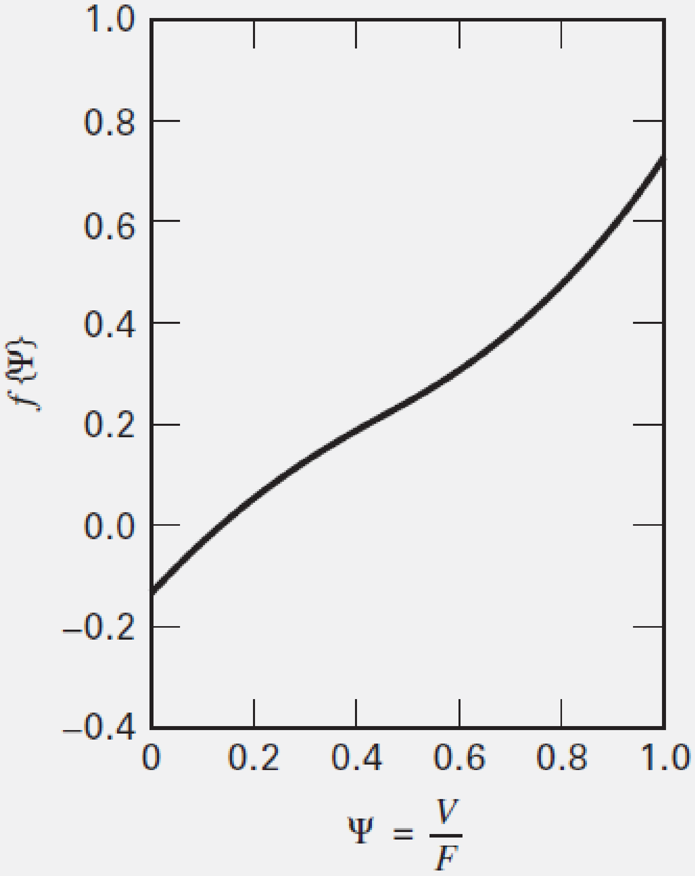


Figure 4.11 Rachford–Rice function for Example 4.3.

This equation can be solved with fzero in MATLAB by defining $f\{\Psi\}$ as the function and using any initial value of Ψ between 0 and 1. Alternatively, it is solved by Newton's method. For an initial guess of $\Psi = 0.50$, the following iteration history is computed

Adiabatic Flash Calculations

- When the pressure of a liquid stream is reduced adiabatically across a valve an **adiabatic-flash** (Q = 0) calculation determines the resulting phases, temperature, compositions, and flow rates for a specified downstream pressure.
- The calculation can be made by applying the isothermal-flash calculation in an iterative manner.
  - First a guess is made of the flash temperature, T_V.
  - Then Ψ, V, x, y, and L are determined by the RR procedure.
  - The guessed value of T_V (equal to T_L) is then checked by an energy balance to determine Q.
  - If Q is not zero to an acceptable degree of accuracy, a new value of T_V is assumed and the RR procedure is repeated.
  - After the first two guesses, a plot of the calculated Q versus the assumed T_V can be made with interpolation or extrapolation used to provide the next guess of T_V.
- This method is tedious because it involves an inner-loop iteration on Ψ and an outer-loop iteration on TV.
- The method is successful for wide-boiling mixtures, but may fail for close-boiling mixtures (e.g., mixtures of isomers). In that case, it is preferable to switch T_V to the inner loop and Ψ to the outer loop.
- For either case, the method is too tedious for hand calculations and is best made with a process simulator.

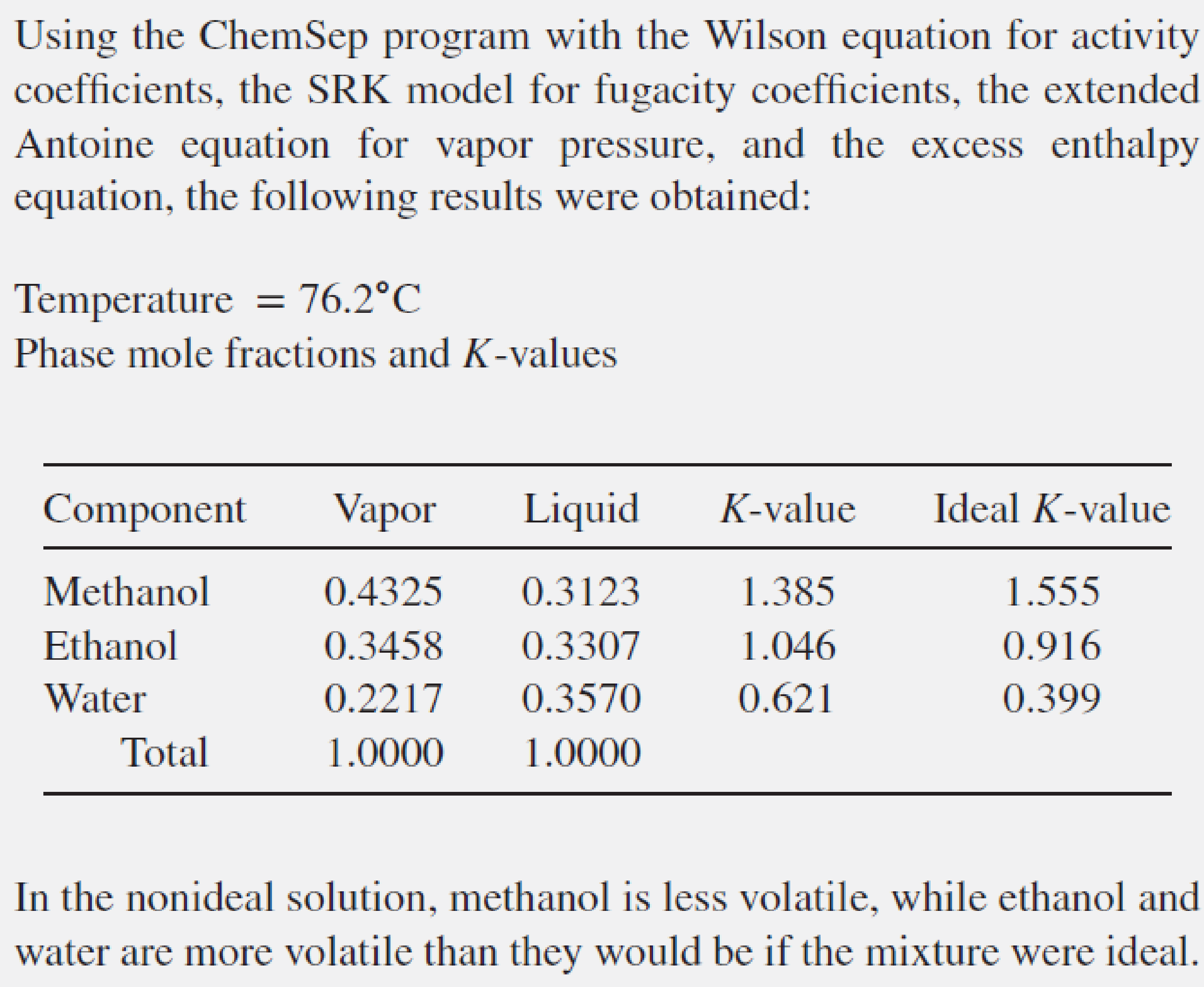
Nonadiabatic, and Percent Vaporization (Ψ) Flash Calculations

- The **nonadiabatic flash** ($Q \neq 0$) calculation is identical to the adiabatic-flash calculation except for a non-zero specification of Q.
- The **percent vaporization flash** can also utilize the RR procedure in the following manner:
  - From two guesses for T_V, two values of Ψ are calculated.
  - From a plot of the calculated values of Ψ versus the assumed values of T_V, interpolation or extrapolation is used to provide the next guess of T_V.

EXAMPLE 4.4 Adiabatic Flash of a Nonideal Mixture.

An equimolar mixture of methanol, ethanol, and water at 5 atm (5.066 bar) and 127∘C is flashed adiabatically to 1 atm. Select an appropriate thermodynamic property set and use a process simulator to compute the equilibrium temperature and phase compositions. Compare the *K*-values to the ideal *K*-values obtained from vapor pressures at equilibrium conditions.

Solution



Using the ChemSep program with the Wilson equation for activity coefficients, the SRK model for fugacity coefficients, the extended Antoine equation for vapor pressure, and the excess enthalpy equation, the following results were obtained:

Temperature = 76.2°C

Phase mole fractions and *K*-values

Component	Vapor	Liquid	*K*-value	Ideal *K*-value
Methanol	0.4325	0.3123	1.385	1.555
Ethanol	0.3458	0.3307	1.046	0.916
Water	0.2217	0.3570	0.621	0.399
Total	1.0000	1.0000		

In the nonideal solution, methanol is less volatile, while ethanol and water are more volatile than they would be if the mixture were ideal.

http://www.chemsep.org/downloads/index.html

Bubble- and Dew-Point Calculations

- At the bubble point, Ψ = 0 and RR equation becomes:

$$f\,(0) = \sum_{i=1}^{C} z_i\left(1-K_i\right) = \sum_{i=1}^{C} z_i - \sum_{i=1}^{C} z_i K_i = 0$$

$$\Rightarrow \sum_{i=1}^{C} z_i K_i = 1$$

- At the dew point, Ψ = 1 and RR equation becomes:

$$f\,(1) = \sum_{i=1}^{C} \frac{z_i\left(1-K_i\right)}{K_i} = \sum_{i=1}^{C} z_i / K_i - \sum_{i=1}^{C} z_i = 0$$

$$\Rightarrow \sum_{i=1}^{C} \frac{z_i}{K_i} = 1$$

- For a specified feed composition z_i, these equations are used to determine P for a given T, or T for a given P.

EXAMPLE 4.5 Bubble- and Dew-Point Calculations for a Nonideal Mixture.

For an equimolar mixture of methanol and water at 1 atm, use a process simulator with the Wilson equation for activity coefficients in the modified Raoult's law K-value to calculate the bubble- and dew-point temperatures and compare the results with Table 4.1b and Figure 4.3a.

Solution

Using the Aspen Plus process simulator with the Wilson property option, the bubble point is 73.1°C and the dew point is 85.0°C. The mole fraction of methanol in the first bubble of vapor is 0.790, while for the first droplet of liquid it is 0.141. These values are in reasonable agreement with Table 4.1b and Figure 4.3a.

Ternary liquid-Liquid (L-L) Systems

- The simplest case is the single equilibrium stage shown in Figure 4.12a,
  - Only component B, called the **solute**, has any appreciable solubility in either component A, the **carrier**, or component C, the **solvent**.
  - The solute enters the equilibrium stage in the feed, F, with the carrier, but is not present in the fresh solvent, S.
  - In the stage, B is extracted by the solvent C to produce the **extract**, E.
  - The unextracted B leaves the stage with carrier A in the **raffinate**, R.
  - Therefore, the flow rate, F_A, of carrier A is the same in the feed and in the raffinate, R; and the flow rate, S, of fresh solvent C is the same in the solvent and in the extract.
  - By convention, the extract is shown leaving from the top of the stage even though it may not have the lower density.

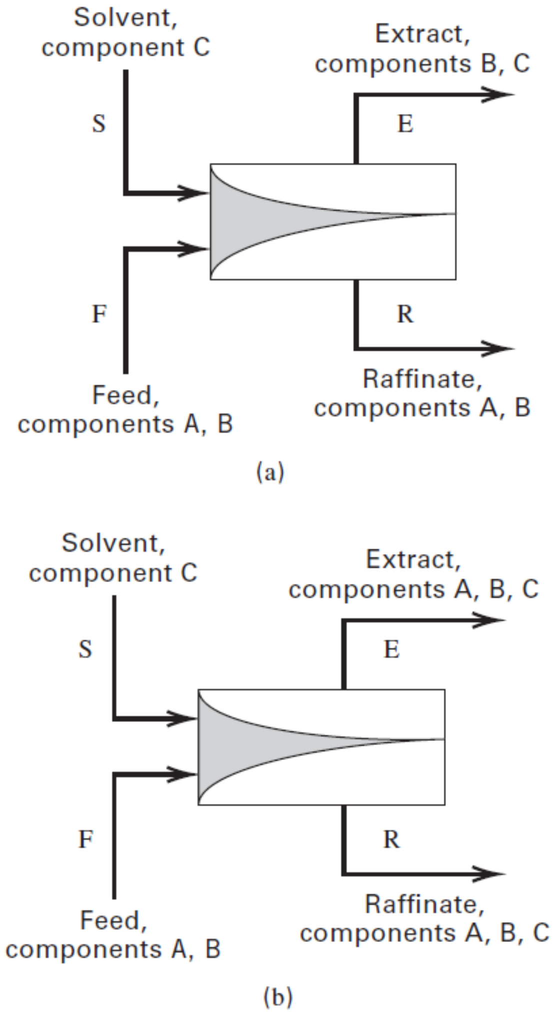


Figure 4.12 Liquid–liquid extraction with ternary mixtures: (a) components A and C are mutually insoluble; (b) components A and C are partially soluble.

Mass Balance on Solute in L-L Stage

- Compositions are in mass ratios, X_i, instead of mass fractions.
  - X_B be the ratio of the mass of solute B to the mass of carrier A in the feed (or raffinate)
  - Y_B be the ratio of the mass of solute B to the mass of solvent C in the extract.

(Solute flow rate in the feed = (solute flow rate in the extract) + (solute flow rate in the raffinate)

$$X_B^{(F)} F_A = Y_B^{(E)} S + X_B^{(R)} F_A$$

  - The phase equilibrium ratio is expressed as:

$$Y_B^{(E)} = K'_{D_B} X_B^{(R)}$$

  - Obtain concentration ratio in raffinate as

$$X_B^{(R)} = \frac{X_B^{(F)} F_A}{F_A + K'_{D_B} S}$$

Extraction Factors

- The extraction factor for the solute Ɛ:

$$\epsilon = \frac{K'_{D_B} S}{F_A} = K'_{D_B} \times \frac{S}{F_A}$$

- Yielding the fraction of B unextracted:

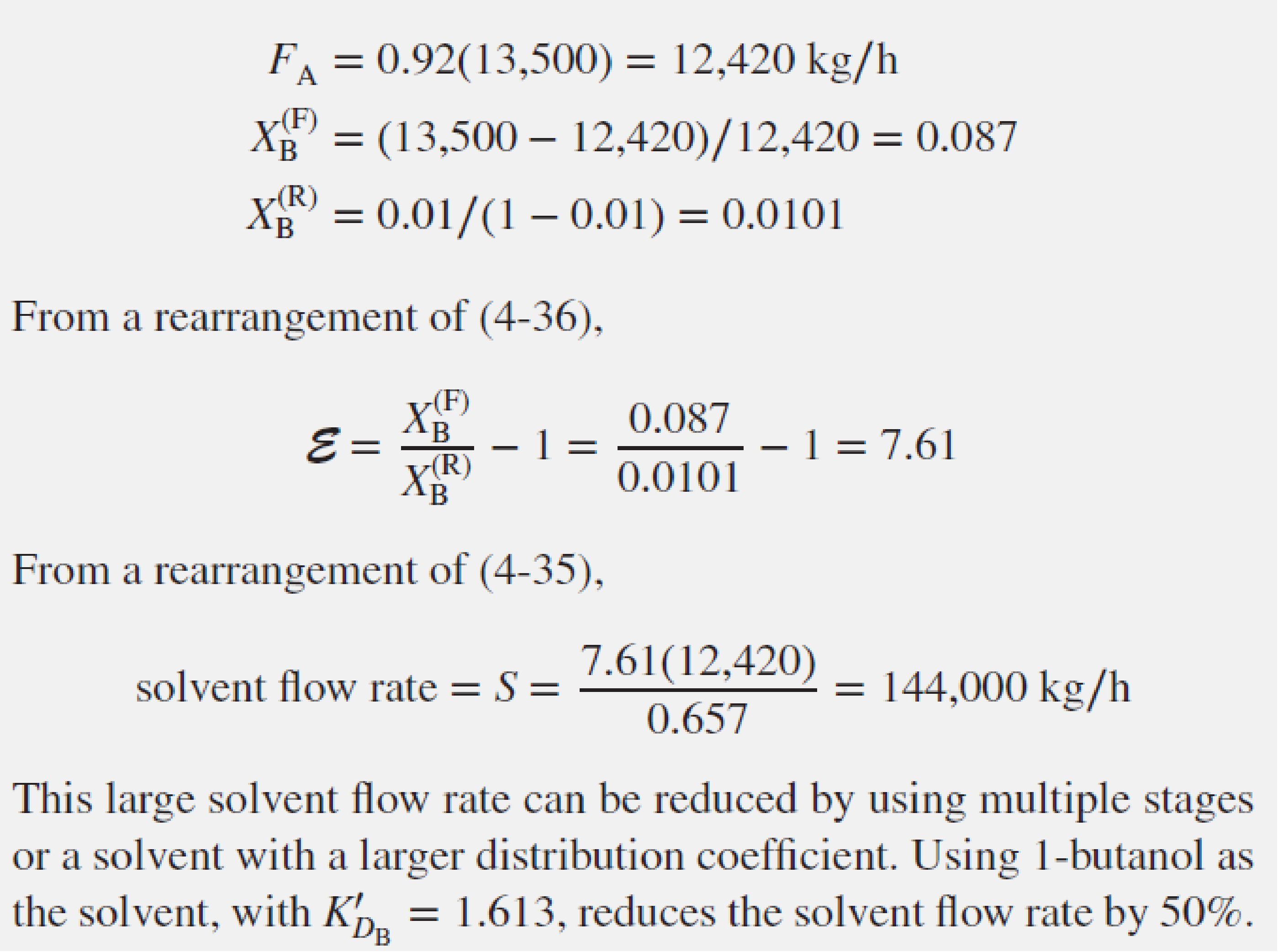
$$\text{Fraction of B unextracted} = \frac{X_B^{(R)}}{X_B^{(F)}} = \frac{1}{1+\epsilon}$$

- To obtain large degrees of extraction you have to have large values of Ɛ :
    - Large distribution coefficients, or
    - large solvent-to-carrier ratio S/F_A

EXAMPLE 4.6 Single-Stage Extraction of Acetic Acid.

Methyl isobutyl ketone (C) is used as a solvent to remove acetic acid (B) from a 13,500 kg/h feed of 8 wt% acetic acid in water (A), because distillation requires vaporization of large amounts of water. If the raffinate is to contain 1 wt% acetic acid, estimate the kg/h of solvent needed for a single equilibrium stage if C and A are assumed to be insoluble in each other. From experimental data in the literature, the distribution coefficient K'_{D_B} = 0.657.

Solution



$$F_A = 0.92(13{,}500) = 12{,}420 \text{ kg/h}$$

$$X_B^{(F)} = (13{,}500 - 12{,}420)/12{,}420 = 0.087$$

$$X_B^{(R)} = 0.01/(1 - 0.01) = 0.0101$$

From a rearrangement of (4-36),

$$\mathcal{E} = \frac{X_B^{(F)}}{X_B^{(R)}} - 1 = \frac{0.087}{0.0101} - 1 = 7.61$$

From a rearrangement of (4-35),

$$\text{solvent flow rate} = S = \frac{7.61(12{,}420)}{0.657} = 144{,}000 \text{ kg/h}$$

This large solvent flow rate can be reduced by using multiple stages or a solvent with a larger distribution coefficient. Using 1-butanol as the solvent, with $K'_{D_B} = 1.613$, reduces the solvent flow rate by 50%.

Equilibrium Calculations with a Triangular Diagram

- The most commonly encountered case: components A and C are partially soluble in each other, and component B distributes between the extract and raffinate phases.
- Different types of phase diagrams, constructed from experimental liquid–liquid phase equilibrium data, have been devised for using material balances to calculate equilibrium compositions and phase amounts.
- The ternary system water (A)–ethylene glycol (B)–furfural (C) at 25°C and 101 kPa:
  - Well above the bubble-point pressure.
  - Water–ethylene glycol and furfural–ethylene glycol are completely miscible binary pairs.
  - Furfural–water is a partially miscible binary pair.
  - The solute is ethylene glycol, and furfural is the solvent that removes ethylene glycol from a binary mixture with water.
  - The furfural-rich phase is the extract, and the water-rich phase is the raffinate.

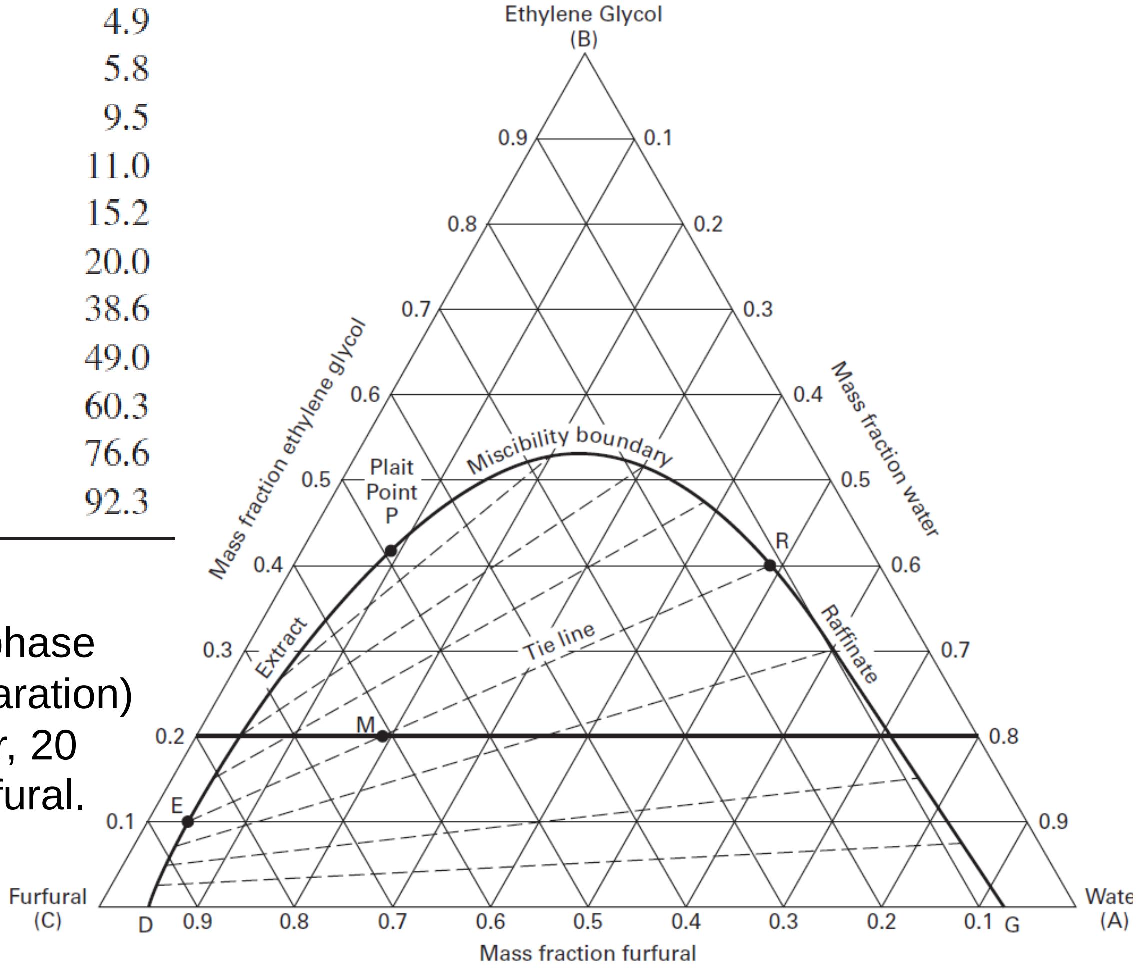
Table 4.2 Equilibrium Miscibility Data in Weight Percent for the Furfural–Ethylene Glycol–Water System at 25°C and 101 kPa

Furfural	Ethylene Glycol	Water
95.0	0.0	5.0
90.3	5.2	4.5
86.1	10.0	3.9
75.1	20.0	4.9
66.7	27.5	5.8
49.0	41.5	9.5
44.5	44.5	11.0
34.3	50.5	15.2
27.5	52.5	20.0
13.9	47.5	38.6
11.0	40.0	49.0
9.7	30.0	60.3
8.4	15.0	76.6
7.7	0.0	92.3

Water Solubility

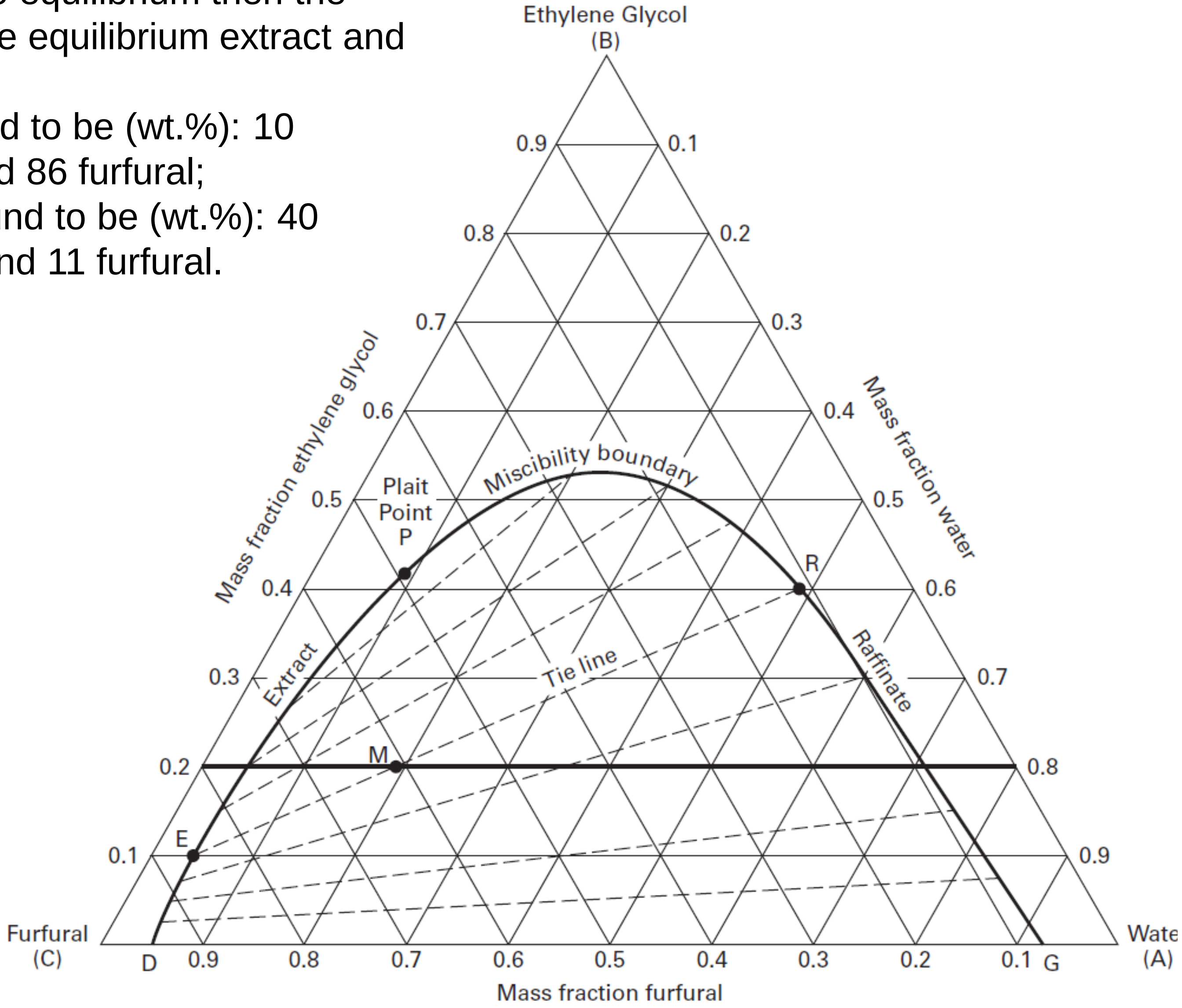
Furfural Solubility

Point M represents a two-phase mixture (before phase separation) containing (wt.%): 19 water, 20 ethylene glycol, and 61 furfural.



Point M represents a two-phase mixture (before phase separation) containing (wt.%): 19 water, 20 ethylene glycol, and 61 furfural.

If mixture at M, is brought to equilibrium then the resulting compositions of the equilibrium extract and raffinate phases are:
The extract, point E, is found to be (wt.%): 10 ethylene glycol, 4 water, and 86 furfural;
The raffinate, point R, is found to be (wt.%): 40 ethylene glycol, 49 water, and 11 furfural.

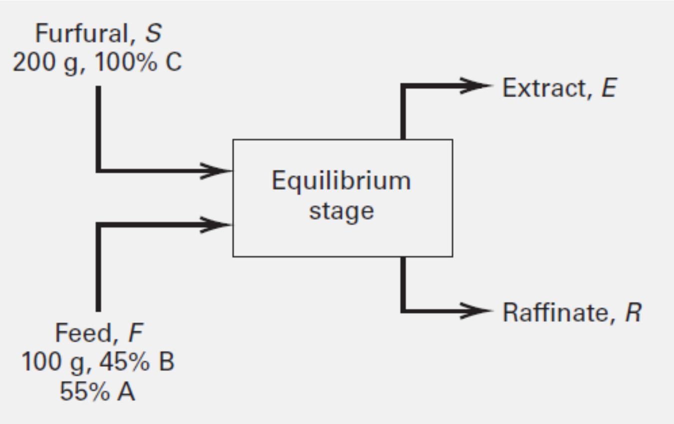


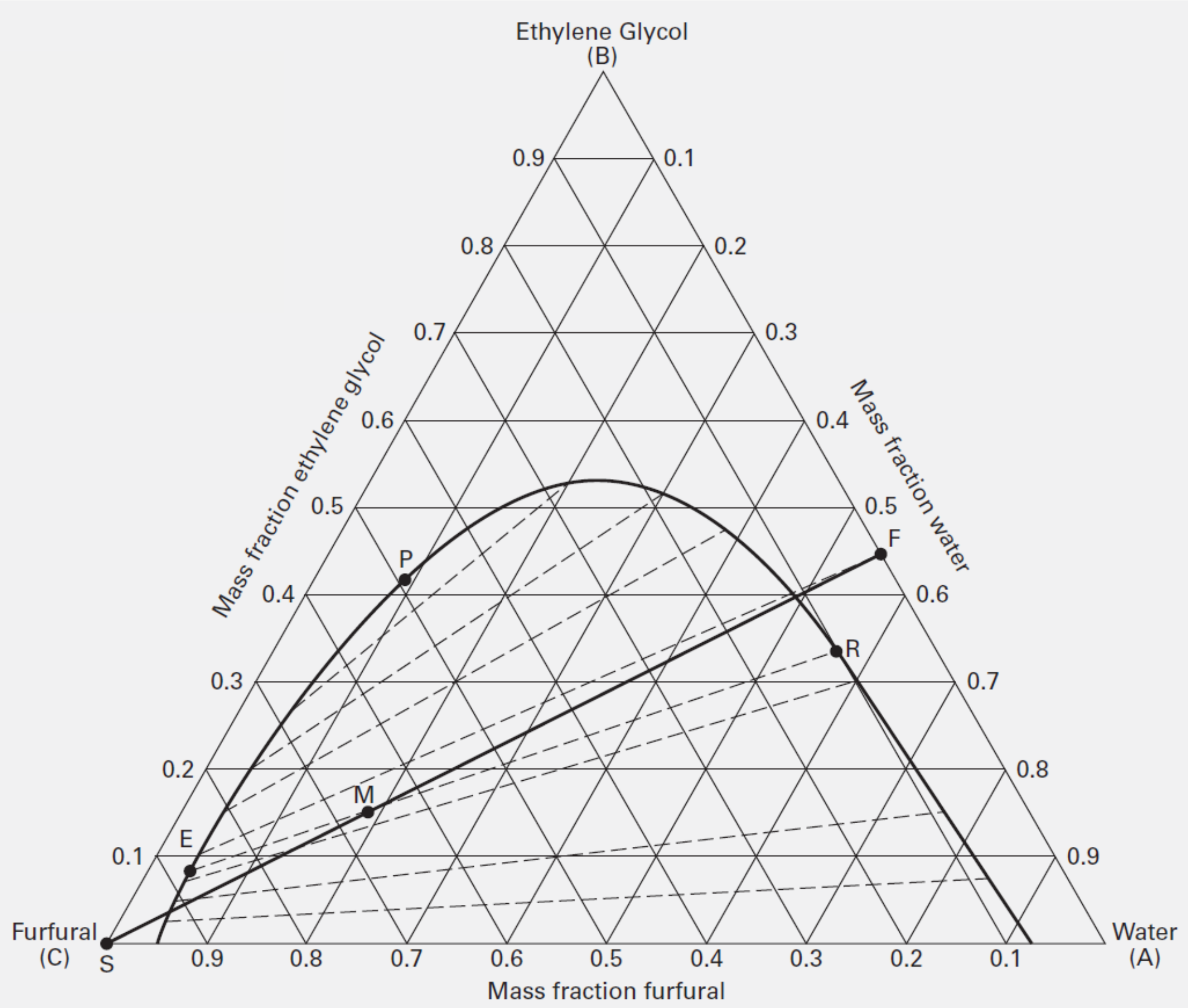
Calculations on a Triangular Diagram

- There are three degrees of freedom for a three-component, two-liquid-phase system,
- With *T* and *P* specified, the concentration of one component in either phase suffices to define the equilibrium system.
- One value for wt.% ethylene glycol on the miscibility boundary curve fixes that liquid-phase composition.
- By means of the corresponding tie line, the composition of the other phase is fixed.
- Ternary diagrams can be used to solve equilibrium-stage problems by using material balances in conjunction with data in the diagram.

EXAMPLE 4.7 Single Equilibrium-Stage Extraction of Ethylene Glycol.

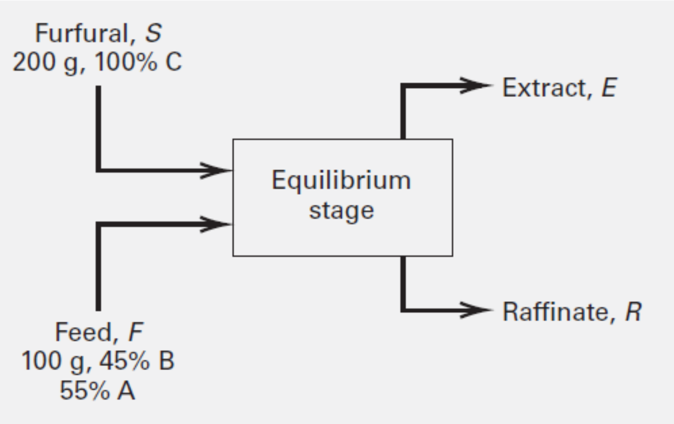
Determine (a) equilibrium compositions and (b) amounts of extract, *E*, and raffinate, *R*, when a feed, *F*, of 100 g of 45 wt.% ethylene glycol (B)–55 wt.% water (A) is contacted with 200 g of solvent, *S*, of pure furfural (C) at 25°C and 101 kPa, using data in the ternary diagram.

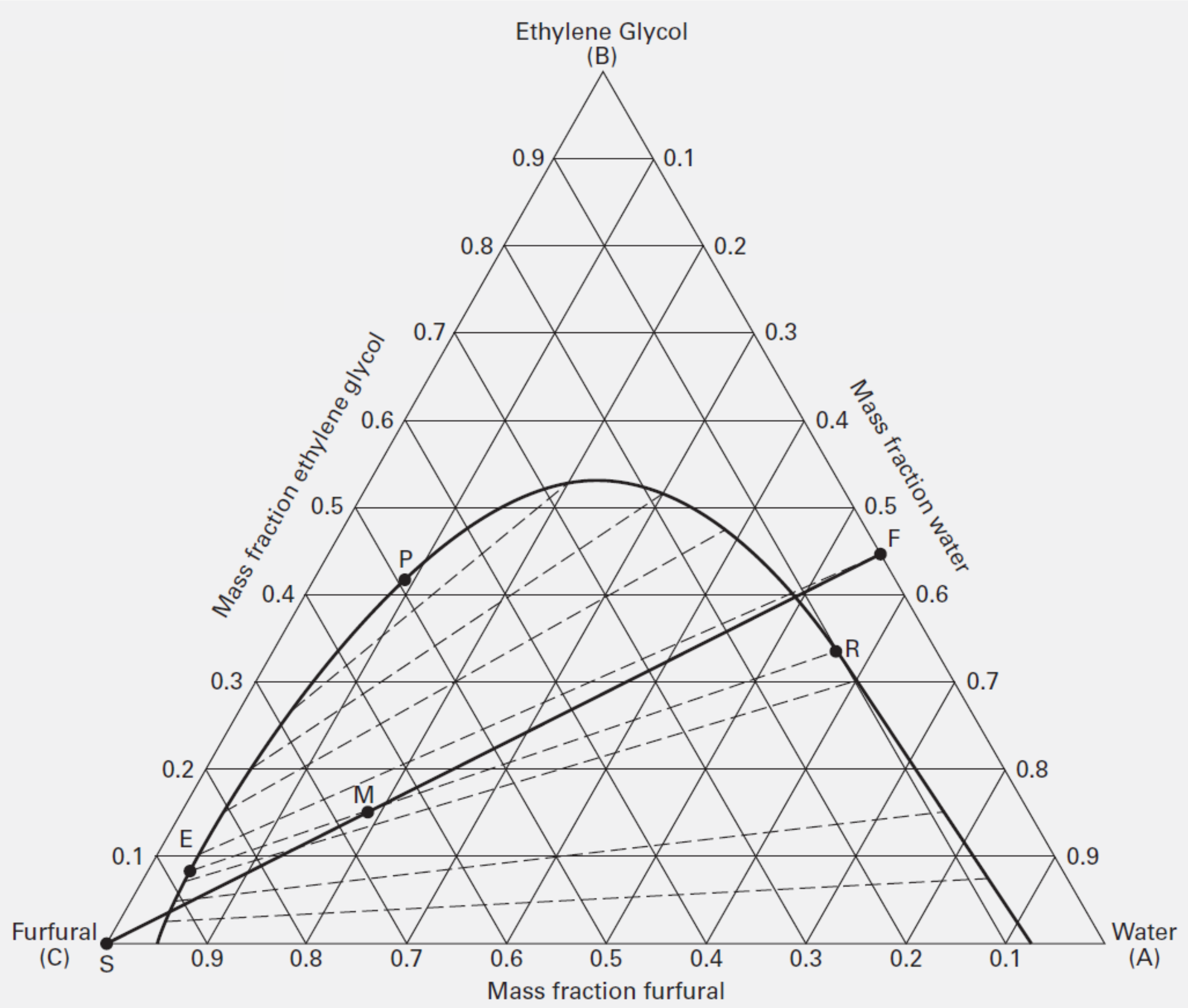




EXAMPLE 4.7 Single Equilibrium-Stage Extraction of Ethylene Glycol.

Determine (a) equilibrium compositions and (b) amounts of extract, *E*, and raffinate, *R*, when a feed, *F*, of 1000 g of 20 wt.% ethylene glycol (B)–80 wt.% water (A) is contacted with 2000 g of solvent, *S*, of pure furfural (C) at 25°C and 101 kPa, using data in the ternary diagram.





Solution

(a) The graphical construct is shown in Figure 4.14, where the compositions of feed, *F*, and solvent, *S*, are plotted as points and connected by a straight line. A **mixing point**, M, is defined as the sum of the amounts of *F* and *S*. The composition of that point corresponds to 45 g of B, 55 g of A, and 200 g of C, which gives 15.0 wt% B, 18.3 wt% A, and 66.7 wt% C.

By material balance, the amount of *M*, is the sum of $E + R = S + F$. Furthermore, as shown, the mixing point is located on an equilibrium tie line. Since it is unlikely that a tie line from experimental data going through point M will already exist, one is drawn by interpolation between the tie lines on either side of point M. An interpolated tie line is included in Figure 4.14 with termination points at the extract, *E*, at a composition of 8.5 wt% B, 4.5 wt% A, and 87.0 wt% C; and at the raffinate, *R*, at 34.0 wt% B, 56.0 wt% A, and 10.0 wt% C.

The inverse-lever-arm rule can be used with the tie line that runs through point M to determine the amounts of E and R. Using a ruler to measure line lengths,

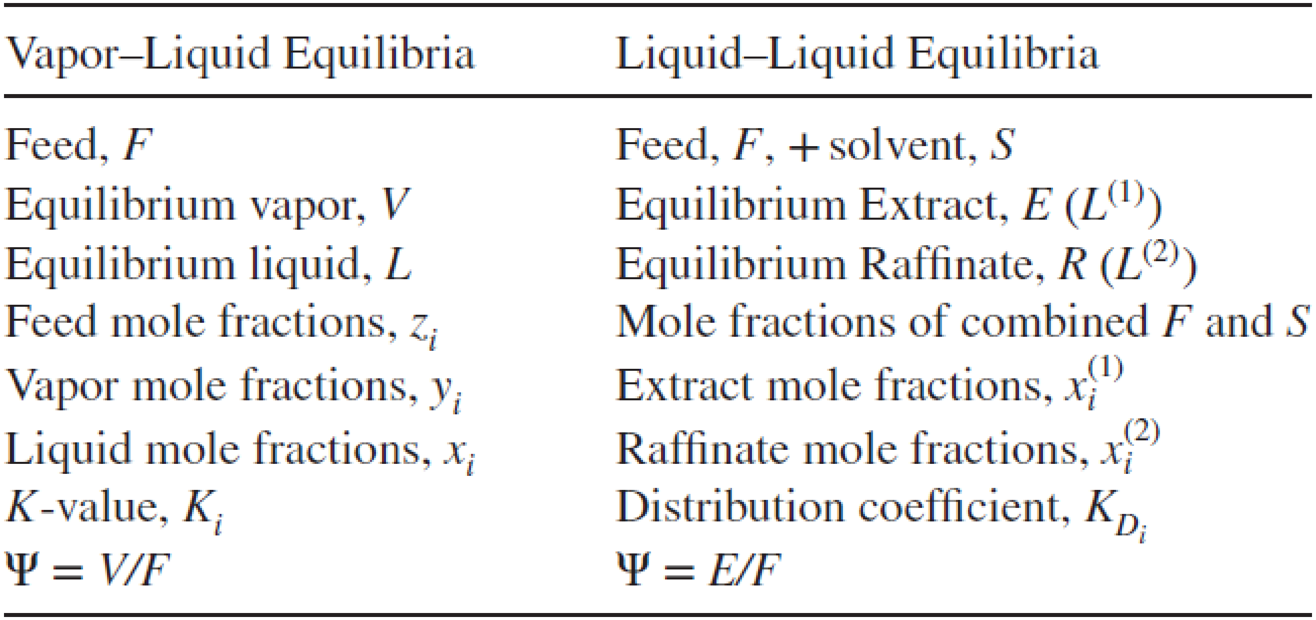
$$\frac{E}{F+S} = \frac{E}{E+R} = \frac{\overline{\mathrm{MR}}}{\overline{\mathrm{ER}}} = 0.733$$

Thus, $E = 0.733(100 + 200) = 220$ g and $R = (100 + 200) - 220 = 80$ g.

(b) Alternatively, E can be calculated by combining an overall mass balance around the extraction unit with an overall ethylene glycol mass balance, using the wt% values of ethylene glycol determined graphically in part (a).

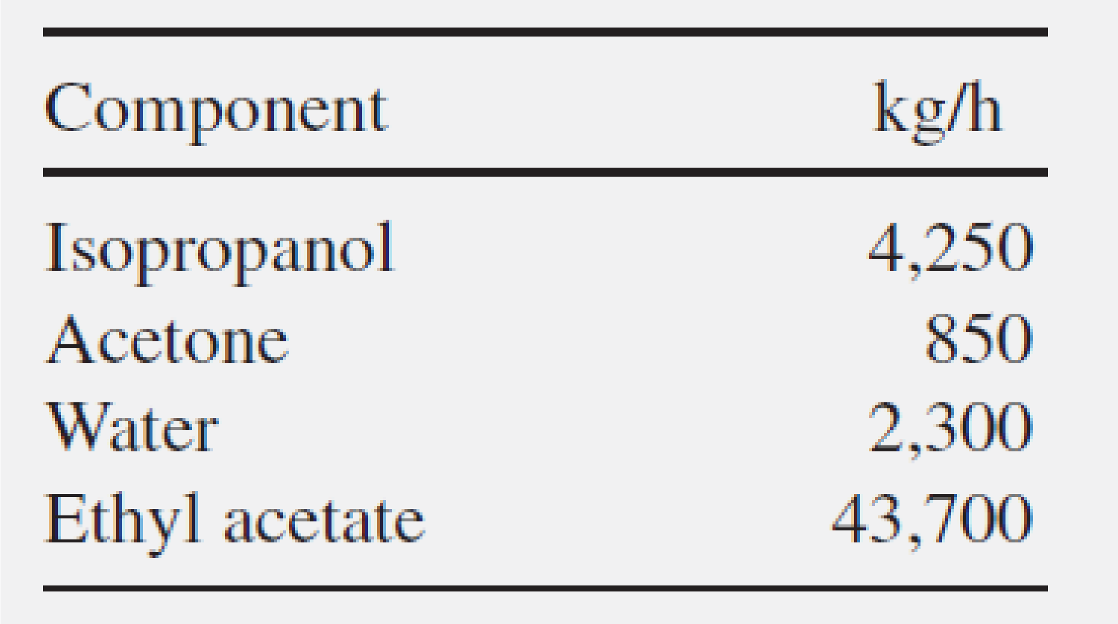
Multicomponent L-L Systems

- When only two liquid phases occur at equilibrium,
  - Use a modification of the Rachford–Rice flash procedure of multicomponent vapor–liquid equilibrium.
  - For single-stage liquid–liquid extraction, the following symbol transformations are made, and extraction calculations are typically made with moles.
  - Computational issues arise due to use of complicated activity coefficient models.

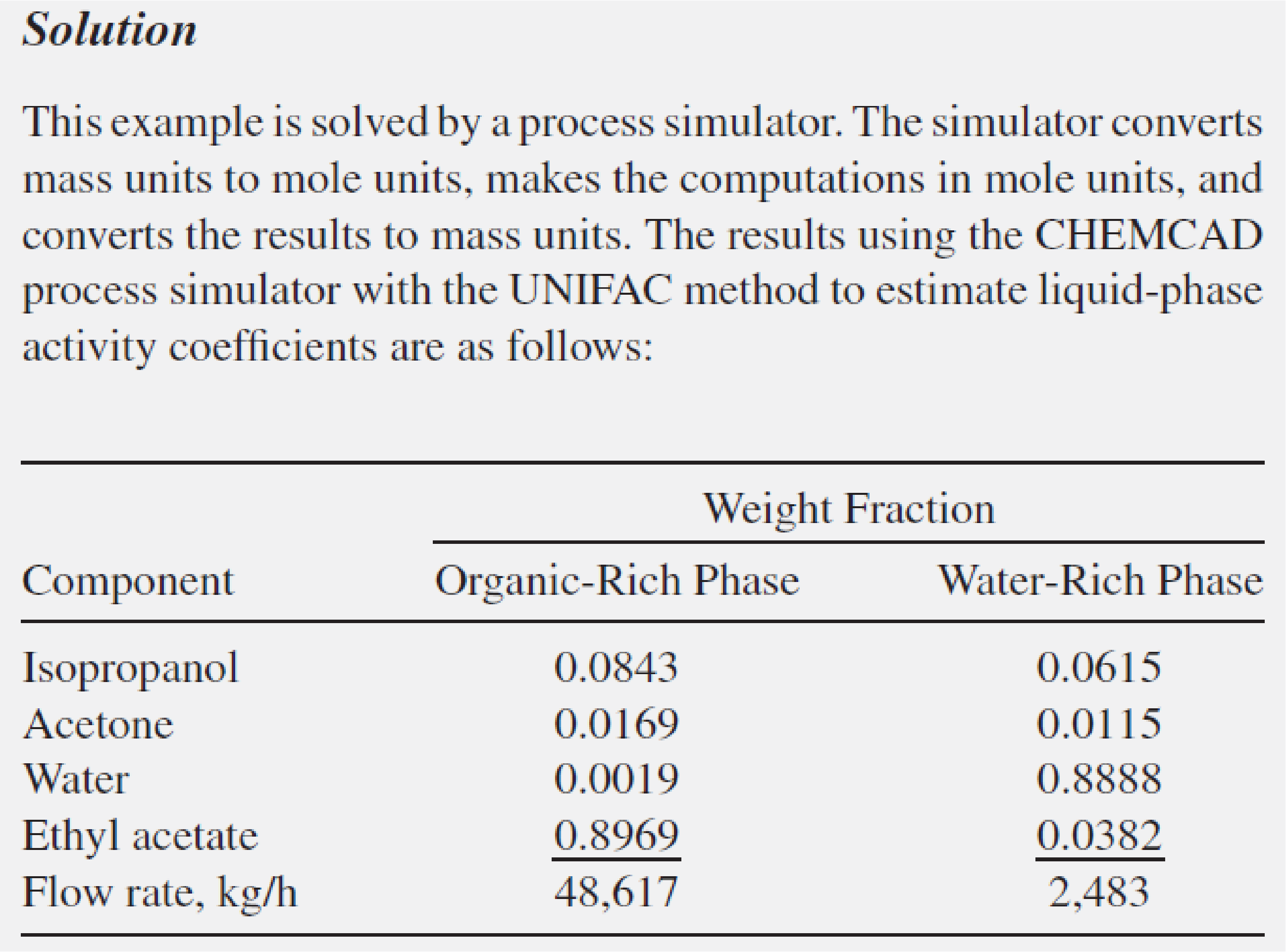


Vapor–Liquid Equilibria	Liquid–Liquid Equilibria
Feed, F	Feed, F, + solvent, S
Equilibrium vapor, V	Equilibrium Extract, E $(L^{(1)})$
Equilibrium liquid, L	Equilibrium Raffinate, R $(L^{(2)})$
Feed mole fractions, z_i	Mole fractions of combined F and S
Vapor mole fractions, y_i	Extract mole fractions, $x_i^{(1)}$
Liquid mole fractions, x_i	Raffinate mole fractions, $x_i^{(2)}$
K-value, K_i	Distribution coefficient, K_{D_i}
$\Psi = V/F$	$\Psi = E/F$

EXAMPLE 4.8 Liquid–Liquid Equilibrium for a Four-Component Mixture. An azeotropic mixture of isopropanol, acetone, and water is dehydrated using ethyl acetate in two distillation columns. Benzene, rather than ethyl acetate was previously used as the dehydrating agent, but legislation has made benzene undesirable because it is carcinogenic. The overhead vapor from the first column, at 20 psia and 80°C with the composition listed below, is condensed and cooled to 35°C, without significant pressure drop, resulting in the formation of two equilibrium liquid phases. Estimate the phase flow rates in kg/h and the equilibrium phase compositions in wt%.



Component	kg/h
Isopropanol	4,250
Acetone	850
Water	2,300
Ethyl acetate	43,700



Solution

This example is solved by a process simulator. The simulator converts mass units to mole units, makes the computations in mole units, and converts the results to mass units. The results using the CHEMCAD process simulator with the UNIFAC method to estimate liquid-phase activity coefficients are as follows:

Component	Weight Fraction	
	Organic-Rich Phase	Water-Rich Phase
Isopropanol	0.0843	0.0615
Acetone	0.0169	0.0115
Water	0.0019	0.8888
Ethyl acetate	0.8969	0.0382
Flow rate, kg/h	48,617	2,483

Your first project

Solve this problem using Excel or Matlab and compare with CHEMCAD solution.

Gas-Liquid Systems

- If a component in the vapor has a critical temperature below the system temperature, it is **non-condensable**, its vapor pressure does not exist and Raoult’s/Modified Raoult’s law can’t be applied.
- Non-condensable components can dissolve, to some extent, into a liquid phase containing other components.
  - Equilibrium *K*-values of non-condensable components can be calculated at near-ambient pressure conditions, by the following version of Henry’s law:

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

- Unfortunately, Henry’s law is not applicable to gases at high pressure or for non-condensable components with a high solubility in the liquid phase, e.g., ammonia in water.
  - Then, experimental data at the system T and P are needed.

EXAMPLE 4.11 Absorption of Ammonia from Air by Water Using an Equilibrium Diagram.

The partial pressure of ammonia (A) in air–ammonia gas mixtures in equilibrium with their aqueous solutions at 20°C is given in Table below. Using these data, and neglecting the vapor pressure of water and the solubility of air in water, construct an equilibrium diagram at 101 kPa using mole ratios Y_A= mol NH_3/mol air in the gas phase and X_A= mol NH_3 /mol H_2O in the liquid phase as coordinates. Henceforth, the subscript A is dropped. If 10 mol of feed gas of $Y = 0.3$ are contacted with 10 mol of aqueous liquid solution of $X = 0.1$, what are the compositions of the resulting equilibrium phases? The process is assumed to be isothermal at 20°C and 1 atm.

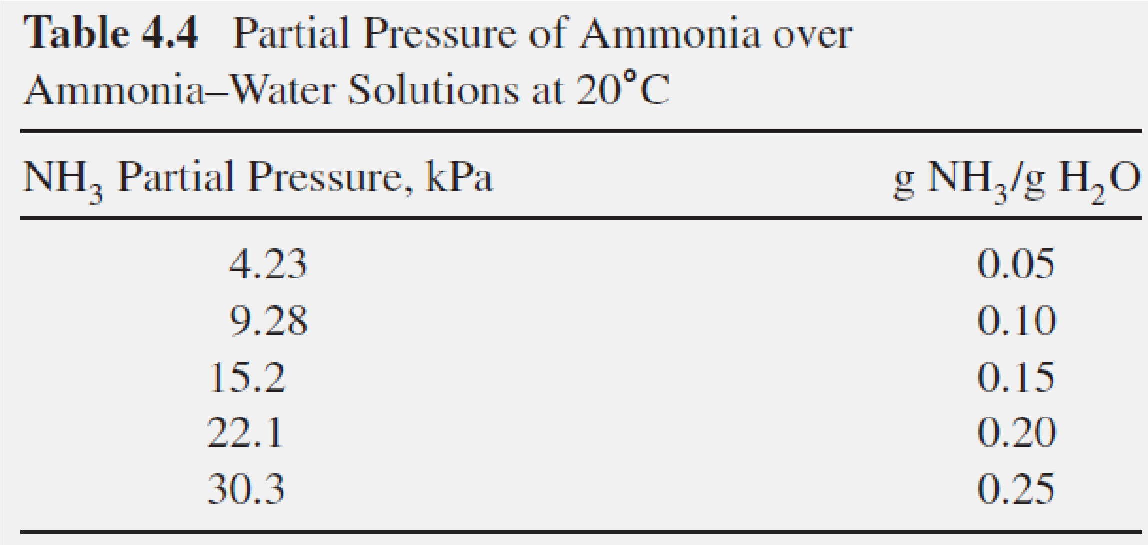
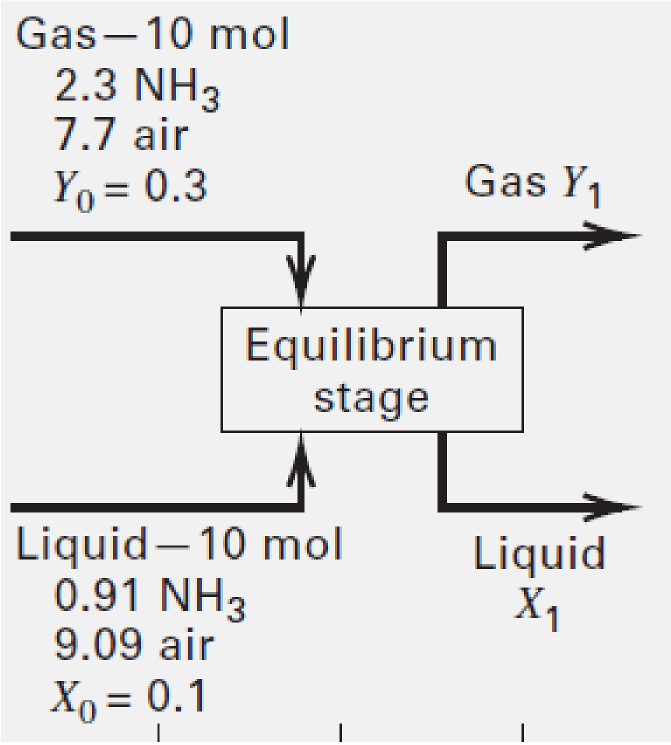


Table 4.4 Partial Pressure of Ammonia over Ammonia–Water Solutions at 20°C

NH_3 Partial Pressure, kPa	g NH_3/g H_2O
4.23	0.05
9.28	0.10
15.2	0.15
22.1	0.20
30.3	0.25



Solution

Equilibrium data in Table 4.4 are recalculated in terms of mole ratios and listed in Table 4.5. The equilibrium curve is plotted in Figure 4.19.

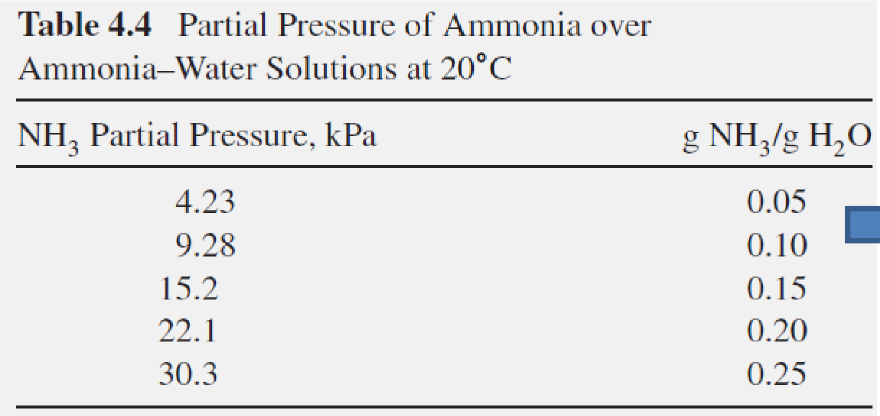


Table 4.4 Partial Pressure of Ammonia over Ammonia–Water Solutions at 20°C

NH_3 Partial Pressure, kPa	g NH_3/g H_2O
4.23	0.05
9.28	0.10
15.2	0.15
22.1	0.20
30.3	0.25

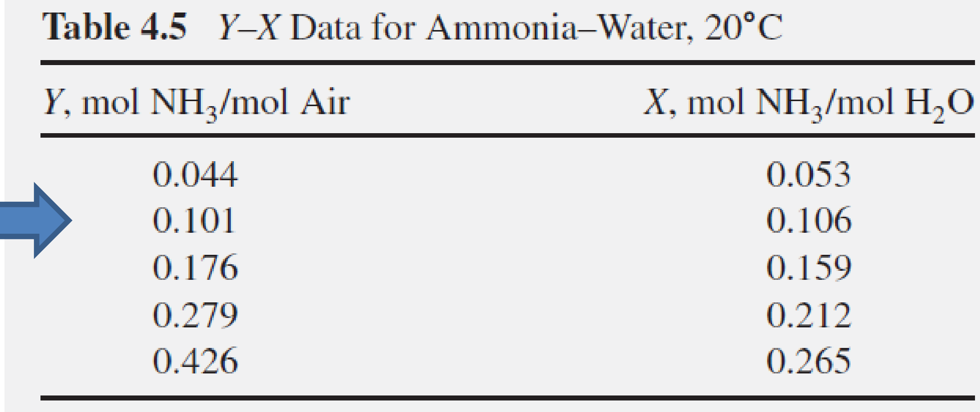
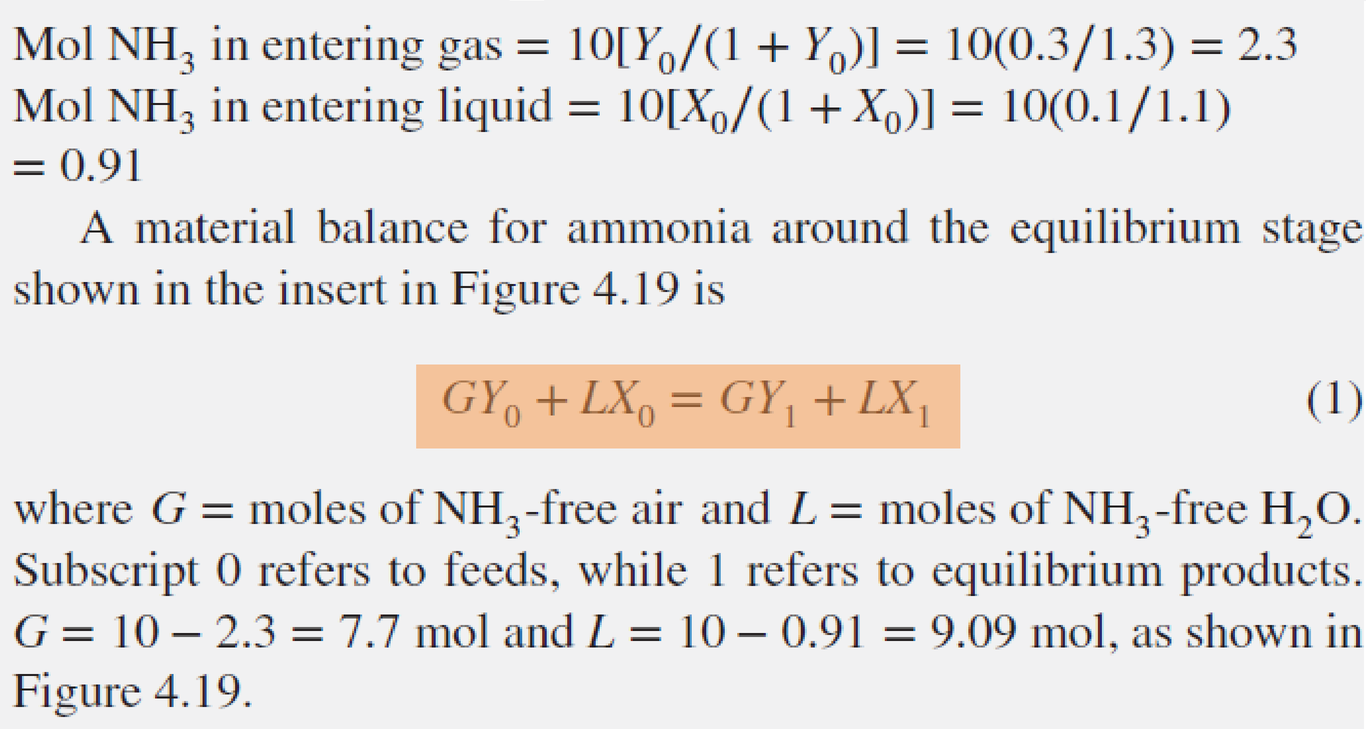


Table 4.5 *Y*–*X* Data for Ammonia–Water, 20°C

Y, mol NH_3/mol Air	*X*, mol NH_3/mol H_2O
0.044	0.053
0.101	0.106
0.176	0.159
0.279	0.212
0.426	0.265



Mol NH_3 in entering gas $= 10[Y_0/(1 + Y_0)] = 10(0.3/1.3) = 2.3$

Mol NH_3 in entering liquid $= 10[X_0/(1 + X_0)] = 10(0.1/1.1) = 0.91$

A material balance for ammonia around the equilibrium stage shown in the insert in Figure 4.19 is

$$GY_0 + LX_0 = GY_1 + LX_1 \tag{1}$$

where G = moles of NH_3-free air and L = moles of NH_3-free H_2O. Subscript 0 refers to feeds, while 1 refers to equilibrium products. $G = 10 - 2.3 = 7.7$ mol and $L = 10 - 0.91 = 9.09$ mol, as shown in Figure 4.19.

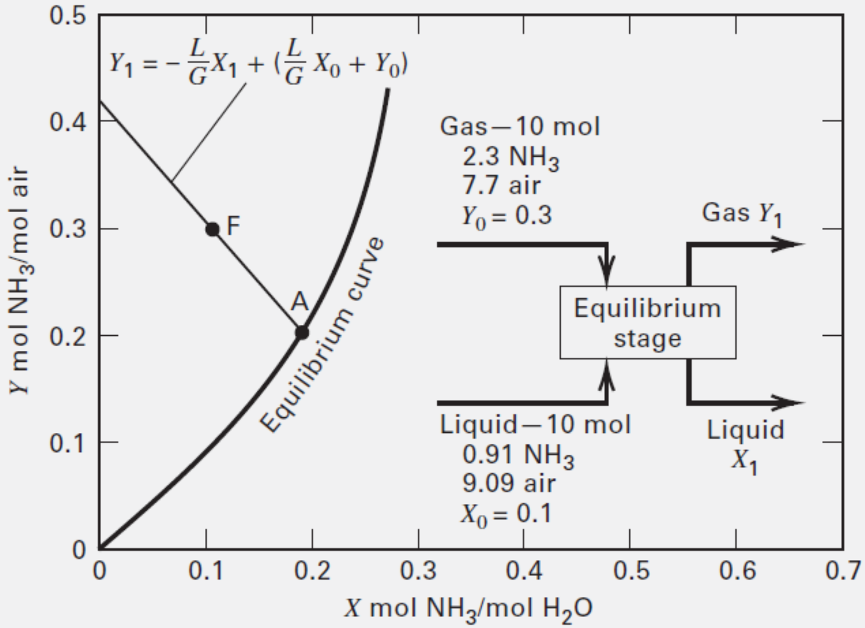


Figure 4.19 Equilibrium for air–NH_3–H_2O at 20°C, 1 atm, in Example 4.11.

Solving for Y_1 from (1),

$$Y_1 = -\frac{L}{G}X_1 + \left(\frac{L}{G}X_0 + Y_0\right) \tag{2}$$

This is an equation of a straight line of slope $(-L/G) = -9.09/7.7 = -1.19$, with an intercept of $(L/G)(X_0) + Y_0 = -(-1.19)(0.1) + 0.3 = 0.42$. The intersection of this material-balance line with the equilibrium curve, as shown in Figure 4.19, gives the ammonia composition of the gas and liquid leaving the stage as $Y_1 = 0.193$ and $X_1 = 0.19$. This result can be checked by an NH_3 balance, since the amount of NH_3 leaving is $(0.193)(7.7) + (0.19)(9.09) = 1.48 + 1.73 = 3.21$, which equals the total moles of NH_3 entering the stage.

Vapor–Liquid–Liquid (VLLE) Flash Procedure

- Rigorous computer methods for treating a vapor–liquid–liquid equilibrium system at a given T and P are called **three-phase isothermal flash** algorithms. As first presented.
  - Analogous to the isothermal two-phase flash algorithm.
- The two liquid phases are labeled with superscripts (1) and (2).
- Combination of material balances and two phase-equilibrium relations apply for each component.

Derivation of the VLLE Equations

- Material Balances and equilibrium relationships:

$$Fz_i = Vy_i + L^{(1)}x_i^{(1)} + L^{(2)}x_i^{(2)}$$

$$K_i^{(1)} = \frac{y_i}{x_i^{(1)}}, \quad K_i^{(2)} = \frac{y_i}{x_i^{(2)}}$$

- A modified Rachford-Rice procedure is developed, but first define:

$$\Psi = V / F \text{ and } \xi = \frac{L^{(1)}}{L^{(1)} + L^{(2)}} \quad \text{where } 0 \le \Psi \le 1, \quad 0 \le \xi \le 1$$

- Combine MB and equilibrium relationships using

$$\sum x_i^{(1)} - \sum y_i = 0, \text{ and } \sum x_i^{(1)} - \sum x_i^{(2)} = 0$$

- This will eliminate all mole fractions and reduce the system to two simultaneous nonlinear equations in the phase split ratios.

The Modified Rachford-Rice Equation for VLLE

- After reducing the system by eliminating the mole fractions in all phases the modified Rachford-Rice equation for VLLE:

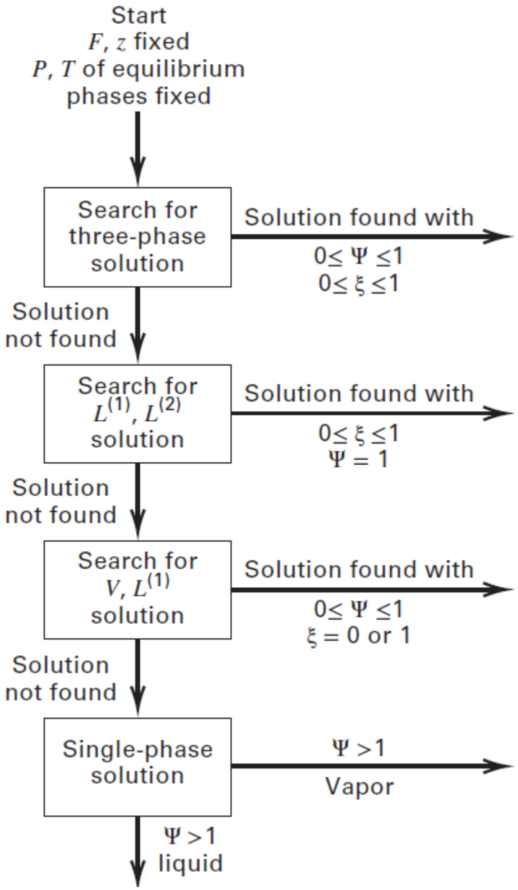
$$\sum_{i=1}^{C} \frac{z_i\left(1-K_i^{(1)}\right)}{\xi\left(1-\Psi\right)+\left(1-\Psi\right)\left(1-\xi\right)\frac{K_i^{(1)}}{K_i^{(2)}}+\Psi K_i^{(1)}}=0$$

$$\sum_{i=1}^{C} \frac{z_i\left(1-\frac{K_i^{(1)}}{K_i^{(2)}}\right)}{\xi\left(1-\Psi\right)+\left(1-\Psi\right)\left(1-\xi\right)\frac{K_i^{(1)}}{K_i^{(2)}}+\Psi K_i^{(1)}}=0$$

- Solve simultaneously for Ψ and ξ.

Solving Modified RR Equation

- Starting guesses are provided for the phase compositions, from which the corresponding *K*-values are estimated.
- Values of Ψ and ξ are then computed by solving nonlinear equations simultaneously using solve in MATLAB or Newton's method.
- The results are used to calculate the phase amounts and compositions.



Start
F, z fixed
P, T of equilibrium phases fixed

Search for three-phase solution
Solution found with $0 \le \Psi \le 1$, $0 \le \xi \le 1$
Solution not found

Search for $L^{(1)}$, $L^{(2)}$ solution
Solution found with $0 \le \xi \le 1$, $\Psi = 1$
Solution not found

Search for V, $L^{(1)}$ solution
Solution found with $0 \le \Psi \le 1$, $\xi = 0$ or 1
Solution not found

Single-phase solution
$\Psi > 1$ Vapor
$\Psi > 1$ liquid

$$\Psi = V/F$$

$$\xi = \frac{L^{(1)}}{L^{(1)} + L^{(2)}}$$

Solving for Unknowns

$$V = \Psi F$$

$$L^{(1)} = \xi\left(F - V\right)$$

$$L^{(2)} = F - V - L^{(1)}$$

$$y_i = \frac{z_i}{\dfrac{\xi\left(1-\Psi\right)}{K_i^{(1)}} + \dfrac{\left(1-\Psi\right)\left(1-\xi\right)}{K_i^{(2)}} + \Psi}$$

$$x_i^{(1)} = \sum_{i=1}^{C} \frac{z_i}{\xi\left(1-\Psi\right) + \left(1-\Psi\right)\left(1-\xi\right)\frac{K_i^{(1)}}{K_i^{(2)}} + \Psi K_i^{(1)}}$$

$$x_i^{(2)} = \sum_{i=1}^{C} \frac{z_i}{\xi\left(1-\Psi\right)\frac{K_i^{(2)}}{K_i^{(1)}} + \left(1-\Psi\right)\left(1-\xi\right) + \Psi K_i^{(2)}}$$

EXAMPLE 4.14 Three-Phase Isothermal Flash.

In a process for producing styrene from toluene and methanol, the gaseous reactor effluent is as follows:

Component	kmol/h
Hydrogen	350
Methanol	107
Water	491
Toluene	107
Ethylbenzene	141
Styrene	350

If this stream is brought to equilibrium at 38°C and 300 kPa, compute the amounts and compositions of the phases present.

Solution

Because water, hydrocarbons, an alcohol, and a light gas are present, the possibility of a vapor and two liquid phases exists, with methanol distributed among all three phases. The isothermal three-phase flash module of the CHEMCAD process simulator was used with Henry's law for H_2 and the UNIFAC method for activity coefficients for the other components. The results were:

	kmol/h		
Component	V	$L^{(1)}$	$L^{(2)}$
Hydrogen	349.96	0.02	0.02
Methanol	9.54	14.28	83.18
Water	7.25	8.12	475.63
Toluene	1.50	105.44	0.06
Ethylbenzene	0.76	140.20	0.04
Styrene	1.22	348.64	0.14
Totals	370.23	616.70	559.07

As expected, little H_2 is dissolved in either liquid. The water-rich liquid phase, $L^{(2)}$, contains little of the hydrocarbons, but a greater fraction of the methanol. The organic-rich phase, $L^{(1)}$, contains most of the hydrocarbons, a small amount of water and a lesser fraction of the methanol. Additional calculations at temperatures higher than 38°C and 300 kPa indicate that the organic phase condenses first, with a dew point of 143°C, while the aqueous phase condenses with a secondary dew point of 106°C.