

# Chapter 9:

## Liquid-Liquid Extraction (LLE)

**Extraction** is a process where one or more **solute(s)** are **removed** *from one liquid phase* (technically called a **diluent**) by *transferring* that/those the **solute(s)** *to another liquid phase* (or a **solvent**)

Since this is the operation between the two liquid phases, **no vaporisation** is **needed**; thus, **extraction** can be performed **at low temperatures**

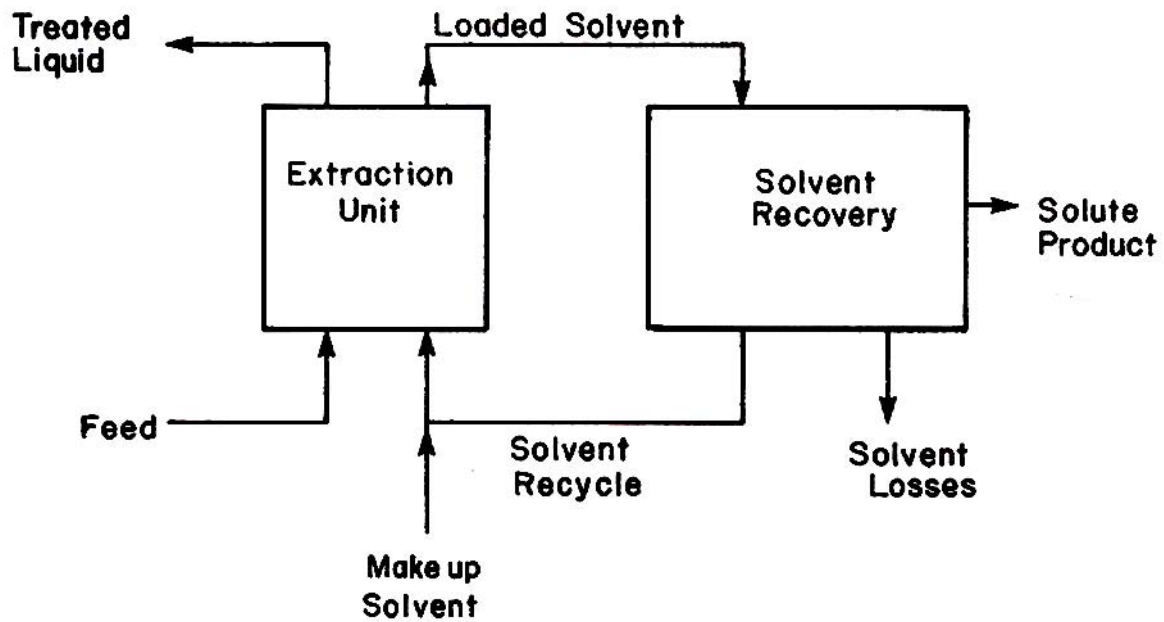
Accordingly, extraction is *suitable* for separating *materials* that may *decompose* or *denature* at *elevated* temperatures

Examples of the uses of extraction are

- The *separation* of *penicillin* from the broth (the liquid phase obtained from biological processes)
- The *separation* of *aromatic-ring hydrocarbons* (*e.g.*, *benzene*, *toluene*) from paraffins using sulpholane

It is important to note that, in many applications, the downstream process that separates solvent from the solute(s) is usually more expensive than the extraction operation itself

A complete extraction process is illustrated in Figure 9.1



**Figure 9.1: A schematic diagram of a complete liquid-liquid extraction process**

(from “Separation Process Engineering” by Wankat, 2007)

In the extraction process, the *feed*, which contains the *first solvent* (or the *diluent*) and the *solute* is sent to the extraction unit (or the extractor)

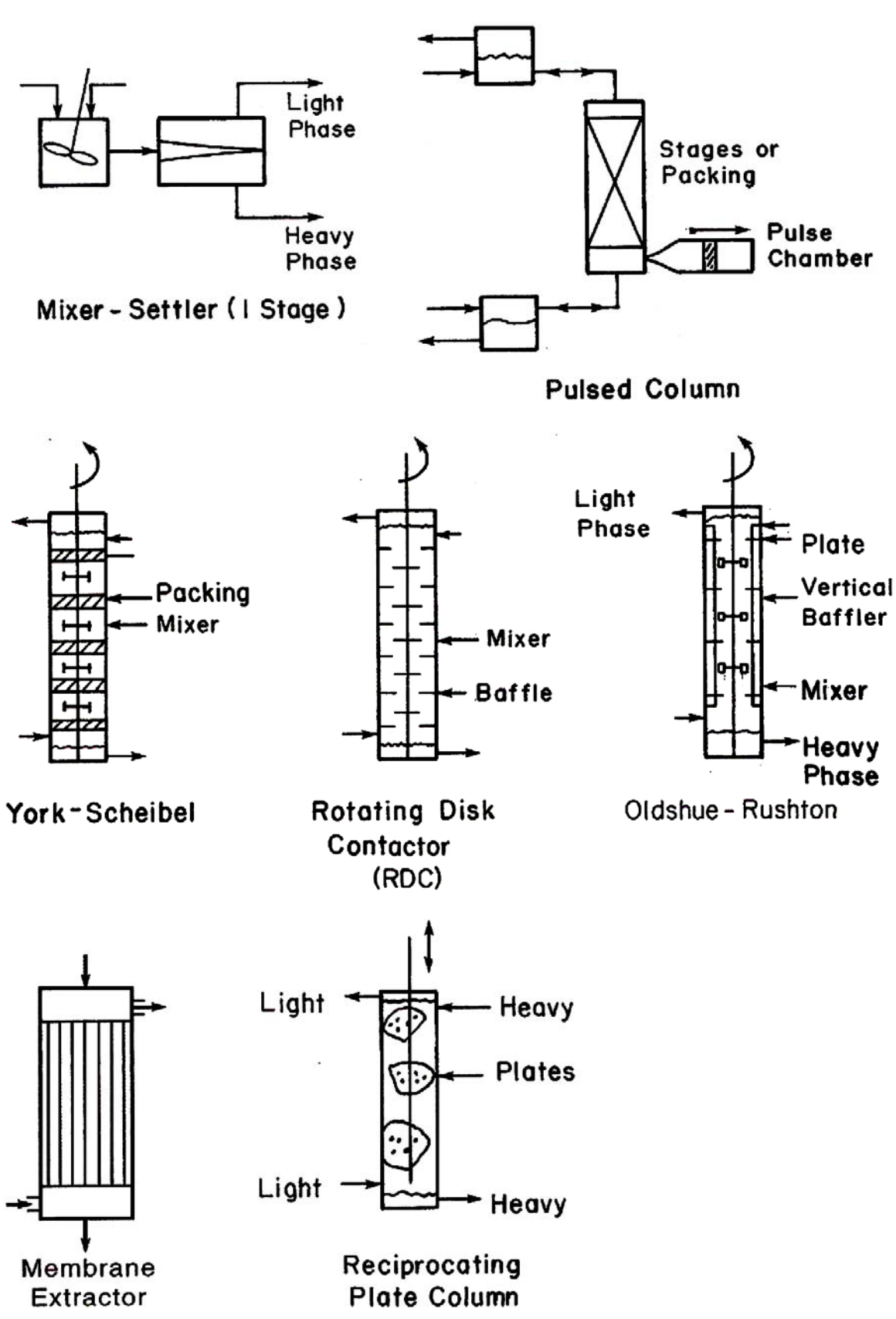
Another solvent (commonly called the *solvent*) is also fed into the extractor, with the *purpose* to *remove* the *solute* from the *diluent*

Normally, the **diluent + the remaining solute** is called the *raffinate phase*, while the *second solvent + the solute* is called the *extract phase*

The *extract phase* (or the *loaded solvent*) is then sent to the *solvent recovery unit*, to

- *separate the desired solute* from the extract phase
- *recover the second solvent*, which can be reused or recycled to be used again as the solvent

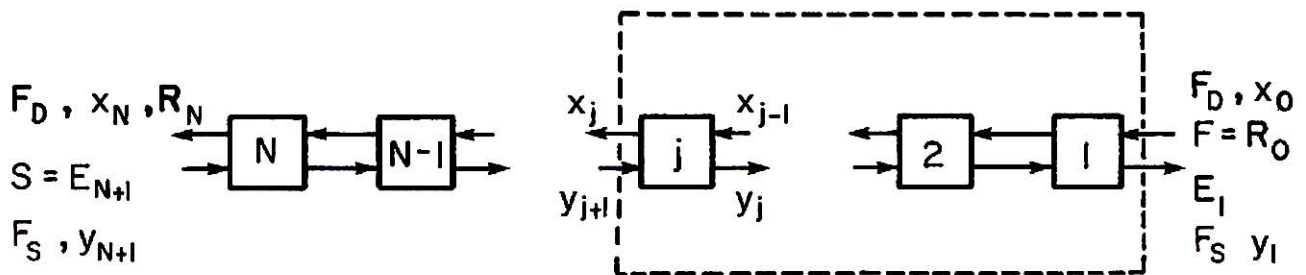
Several types of extraction equipment are employed in various industries; examples are illustrated in Figure 9.2



**Figure 9.2: Examples of extraction equipment**

(from "Separation Process Engineering" by Wankat, 2007)

One of the most common types of extraction is the *counter-current system*, depicted schematically in Figure 9.3



**Figure 9.3: A schematic flow chart of the counter-current extraction process**

(from “Separation Process Engineering” by Wankat, 2007)

In this counter-current extraction system, the raffinate and extract phases are fed into the system in the opposite directions

In Figure 9.3, the **raffinate phase** consisting of the **solute A** and the **diluent D** is fed into the system from the right hand side (RHS), with the total flow rate of  $R_o$  (or  $R$ ) and the concentration (in *mole* or *mass fraction* of the *solute*) of  $x_o$ ; note that the flow rate of just the diluent is  $F_D$

The **extract phase** consisting of **pure solvent S** or the **solvent S** with **some amount of solute A**, with the total flow rate of  $E_{N+1}$  (or  $E$ ) and the concentration (in *mole* or *mass fraction* of the *solute*) of  $y_{N+1}$  is fed into the system from the left hand side (LHS); note that the flow rate of just the second solvent is  $F_s$

The raffinate phase exits the extraction system with the concentration of the solute of  $x_N$ , while the extract phase leaves the system with the concentration of  $y_1$

## 9.1 McCabe-Thiele Diagram for Dilute Extraction Systems

Strictly speaking, from Figure 9.3

- $R \neq F_D$ , as  $R$  is the combined flow rates of the diluent D and the solute A
- $E \neq F_S$ , as  $R$  is the combined flow rates of the solvent S and the solute A



However, for the *dilute* extraction system (*i.e.* the extraction system in which the concentration of the solute is low), we can assume that

- $R \approx F_D$
- $E \approx F_S$

Note that

- $R = \text{raffinate flow rate}$
- $E = \text{extract flow rate}$
- $F_D = \text{diluent flow rate}$
- $F_S = \text{solvent flow rate}$

Additionally, if the *solvent* and *diluent* are *immiscible* (ไม่ละลาย) in each other,  $F_D$  and  $F_S$  can be assumed to be *constant* throughout the system

In order to be able to use the *McCabe-Thiele approach* for the extraction operation, the following **assumptions** must be satisfied:

- The system is *isothermal*
- The system is *isobaric*
- The *heat of mixing* is *negligible*
- The *diluent* and the *solvent* are *immiscible*

Hence, for the dilute extraction system with the above assumptions, the species balance (for the solute A) equation for the envelope shown in the Figure 9.3 can be formulated as follows

$$Ey_{j+1} + Rx_o = Ey_1 + Rx_j \quad (9.1)$$

Re-arranging Eq. 9.1 to obtain the *operating equation* for the extraction process yields

$$y_{j+1} = \frac{R}{E} x_j + \left( y_1 - \frac{R}{E} x_o \right) \quad (9.2)$$

Since  $R$  and  $E$  is assumed to be constant, the slope for the operating line  $\left( i.e. \frac{R}{E} \right)$  is constant

The *operating line* can be plotted on the McCabe-Thiele diagram, in which

- $x$  represents the concentration in the *raffinate* phase
- $y$  represents the concentration in the *extract* phase

The *equilibrium* equation for the extraction can be expressed as

$$K_d = \frac{y_A}{x_A}$$

or

$$y_A = K_d x_A \quad (9.3)$$

where  $K_d$  is the “**distribution ratio**”

Note that, for *dilute systems*,  $K_d$  can be assumed *constant* throughout the operation of the extraction system

The *selection* of the (second) *solvent* is very *crucial* for the *extraction* system

Generally, the *solvent* should

- be able to *dissolve* the *solute* more than the diluent
- be *immiscible* to the *diluent*
- be *highly selective* for the *desired solute*
- not be selective for contaminants
- have a high value of  $\alpha = \frac{K_{d_{\text{desired}}}}{K_{d_{\text{undesired}}}}$  and

$$K_{d_{\text{desired}}}$$

Additionally, the solvent should also be

- non-toxic
- non-reactive or chemically stable
- non-corrosive
- non-flammable or non-explosive
- readily available
- inexpensive
- environmentally friendly (*i.e.* “green”)

**Example** A feed of 100 kg/min of 1.2 wt% mixture of acetic acid in water is to be extracted with 1-butanol at 1 atm and 26.7 °C

The desired outlet concentration in the exiting stream is 0.1 wt% of acetic acid

The solvent of *pure* 1-butanol is fed counter-currently to the feed with the flow rate of 75 kg/min

Determine the composition of the exiting 1-butanol phase (*i.e.* the extract phase)

Also find the number of equilibrium contacts (stages) needed

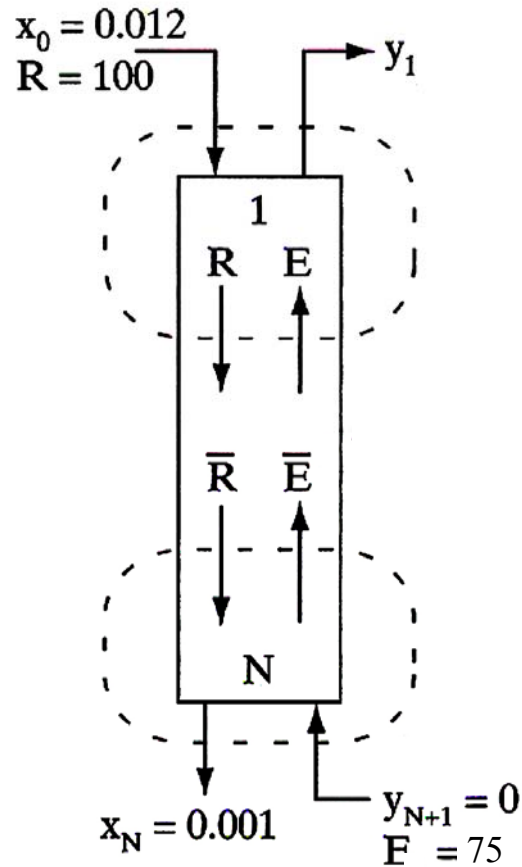
In this case,

- the inlet concentration of the feed (raffinate phase) is given as 1.2 wt% of acetic acid (or  $x_o = 0.012$ )
- the outlet concentration of the raffinate phase is given as 0.1 wt% of acetic acid (or  $x_N = 0.001$ )

The solvent is *pure* butanol; thus,  $y_{N+1} = 0$

The flow chart for this operation is as follows





The concentration of the exiting *extract-phase* stream can be computed using operating-line equation (Eq. 9.2) as follows

$$y_{j+1} = \frac{R}{E} x_j + \left( y_1 - \frac{R}{E} x_o \right)$$

$$y_{N+1} = \frac{R}{E} x_N + \left( y_1 - \frac{R}{E} x_o \right)$$

$$0 = \frac{100}{75}(0.001) + \left[ y_1 - \left( \frac{100}{75} \right) (0.012) \right]$$

$$y_1 = 0.015$$

Thus, the co-ordinates for the operating line are

- $(x_N, y_{N+1}) = (0.001, 0)$
- $(x_o, y_1) = (0.012, 0.015)$

The next thing to do is to establish the equilibrium relationship between acetic acid in water ( $x$ ) and acetic acid in 1-butanol ( $y$ )

From literature [*e.g.*, Table 13-3 (Page 506) in Separation Process Engineering (3<sup>nd</sup> ed.) by P.C. Wankat],  $K_d$  for acetic-water-1-butanol at 26.7 °C is 1.613

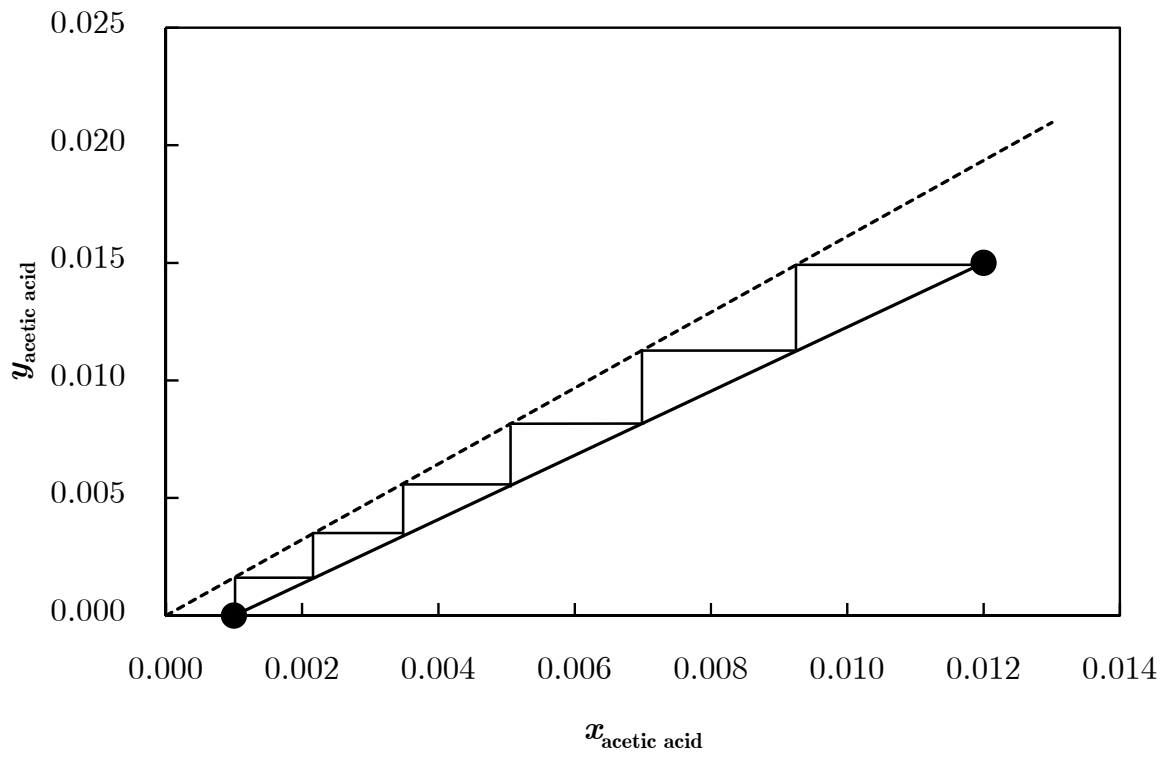
Thus, the equilibrium equation is

$$y = 1.613x \quad (9.4)$$

Drawing operating and equilibrium lines

(*i.e.* McCabe-Thiele diagram on the next Page)

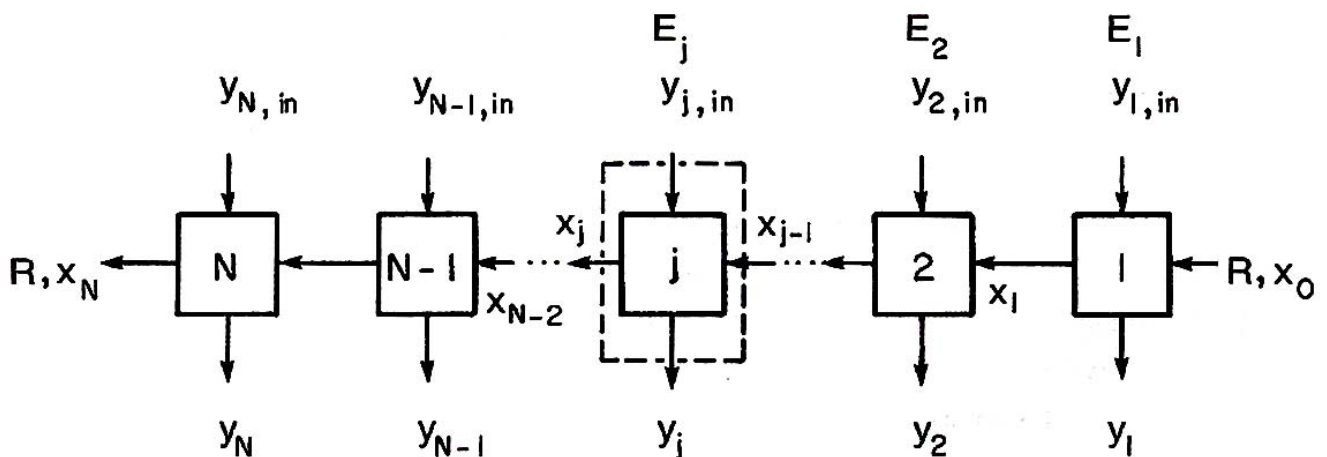
and stepping off stages yields 6 equilibrium stages



## 9.2 Immiscible Single-stage and Cross-flow Extraction

In addition to counter-current cascades or counter-current extraction, which is the most common extraction scheme, there are some other types of extraction cascades

One type of such other cascades is a cross-flow cascade illustrated in Figure 9.4



**Figure 9.4: Cross-flow extraction cascade**

(from “Separation Process Engineering” by Wankat, 2007)

In this type of cascade, a fresh solvent (or an extract stream) is fed to each stage

Note that, for the cross-flow cascade, all assumptions are identical to that of the counter-current flow

To obtain the operating equation for each stage (*i.e.* stage  $j$ ), a material balance is performed as follows

$$Rx_{j-1} + E_j y_{j,\text{in}} = Rx_j + E_j y_j \quad (9.5)$$

Re-arranging Eq. 9.5 gives

$$y_j = -\frac{R}{E_j} x_j + \left( \frac{R}{E_j} x_{j-1} + y_{j,\text{in}} \right) \quad (9.6)$$

which is the operating line for stage  $j$  of the cross-flow extraction, with the slope of  $-\frac{R}{E_j}$

Since each stage is (assumed to be) an equilibrium stage,  $x_j$  and  $y_j$  are in equilibrium with each other

Accordingly, the intersection of the operating line and the equilibrium line is at the point  $(x_j, y_j)$

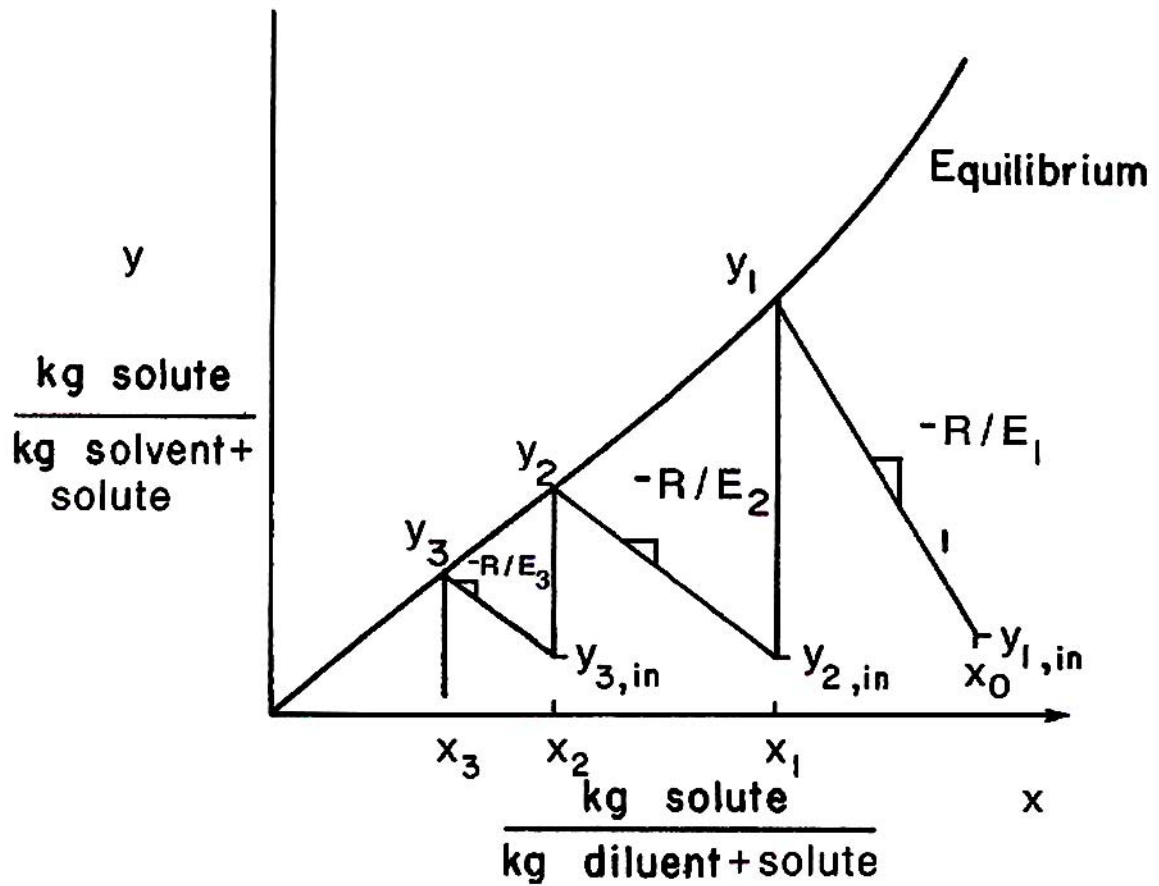
For the raffinate phase, the input of stage  $j$  has the concentration of  $x_{j-1}$  or the input of the stage  $j + 1$  has the concentration of  $x_j$

Thus, one co-ordinate of the operating line is the point  $\left(x_{j-1}, y_{j,\text{in}}\right)$  or  $\left(x_j, y_{j+1,\text{in}}\right)$

The McCabe-Thiele diagram for the cross-flow extraction can be depicted as Figure 9.5

Note that the slopes of equilibrium lines may not be equal to one another, as the value of the flow rate of the extract phase  $\left(E_j\right)$  at each stage may vary





**Figure 9.5: The McCabe-Thiele diagram for the cross-flow extraction**

(from "Separation Process Engineering" by Wankat, 2007)

**Example** We want to extract a dilute solution of the protein (or enzyme) alcohol *dehydrogenase* from an aqueous solution of 5 wt% polyethylene glycol (PEG) with an aqueous solution of 10 wt% dextran

The entering dextran solution contains no protein, and the PEG solution has a flow rate of 20 kg/h

Assume that the two aqueous phases are immiscible; note that the dextran solution is denser than the PEG solution

Determine the following:

- a) If 10 kg/h of dextran is added to a single-stage extractor, find the ***total recovery fraction*** of alcohol dehydrogenase in the dextran-solvent phase

b) If 10 kg/h is dextran is added to each stage of a cross-flow cascade with 2 stages, find the *total recovery fraction* of alcohol dehydrogenase in the dextran solvent

Given the protein distribution coefficient as

$$K = \frac{\left(\text{wt. fraction of protein in PEG, } x\right)}{\left(\text{wt. fraction of protein in dextran, } y\right)} = 0.12$$

What is the *total recovery fraction*?

It is the *fraction* of alcohol dehydrogenase (*i.e.* a *solute*) that *is extracted from* the *raffinate phase* into the dextran solvent phase (*i.e.* the extract phase)

The initial (inlet) amount of solute in the raffinate phase is  $Rx_o$

The final (outlet) amount of solute in the raffinate phase is  $Rx_N$

Thus, the *amount* of solute ***extracted from*** the *raffinate phase* is  $Rx_o - Rx_N$

The *fraction* of solute ***extracted from*** the *raffinate phase* or the **total recovery fraction** is

$$\frac{Rx_o - Rx_N}{Rx_o}$$

or

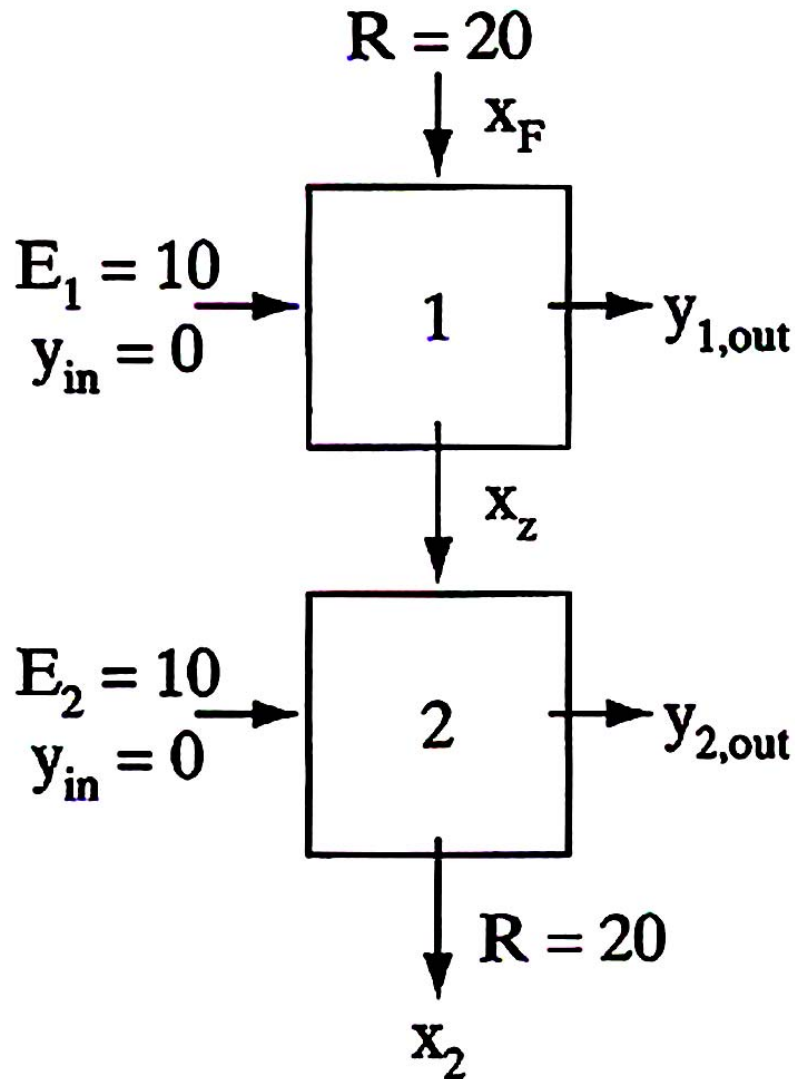
$$1 - \frac{Rx_N}{Rx_o}$$

Since the flow rate of the raffinate phase is assumed to be constant (for the *dilute immiscible* extraction), the **total recovery fraction** can be reduced to

$$1 - \frac{x_N}{x_o}$$

The schematic diagram for this Example is as follows

Note that, in the Figure,  $x_o \equiv x_F$  and  $x_N \equiv x_2$  (when for 2-stage operation)



The equilibrium relationship is given as

$$K = \frac{x}{y} = 0.12 \quad (9.7)$$

and an equilibrium equation can be written as follows (by re-arranging Eq. 9.7)

$$y = \frac{x}{0.12} = 8.33x \quad (9.8)$$

It is given that, the *solvent* (*i.e.* dextran) entering each stage with **no** protein (*i.e.* **no solute**)

Thus,  $y_{in} = 0$  for both stages 1 and 2

(a) Only stage 1 is operated

Given data:

- $R = 20$  kg/h
- $E_1 = 10$  kg/h
- $y_{in} = 0$

Unknowns:

- $x_F$
- $x_z$
- $y_{1,\text{out}}$

However, what the problem wants to know is the *fraction* of protein (alcohol dehydrogenase) extracted into the dextran solvent phase; *i.e.*

$$1 - \frac{x_z}{x_F}$$

Eq. 9.6:

$$y_j = -\frac{R}{E_j} x_j + \left( \frac{R}{E_j} x_{j-1} + y_{j,\text{in}} \right) \quad (9.6)$$

can be modified to be the operating equation for stage 1 as follows



$$y_{1,\text{out}} = -\frac{R}{E_1} x_z + \left( \frac{R}{E_1} x_F + y_{\text{in}} \right) \quad (9.9)$$

Substituting corresponding numerical values into Eq. 9.9 gives

$$y_{1,\text{out}} = -\frac{20}{10} x_z + \left( \frac{20}{10} x_F + 0 \right)$$

$$y_{1,\text{out}} = -2x_z + 2x_F$$

or

$$y = -2x + 2x_F \quad (9.10)$$

From Eq. 9.10, when

- $y = 0, x = x_F$
- $x = 0, y = 2x_F$

Drawing a straight line between the point  $(x_F, 0)$  and the point  $(0, 2x_F)$

This operating line intersects with the equilibrium line at the point  $(x_j, y_j)$ , which is  $(x_z, y_{1,\text{out}})$  in this Example

The intersection point can be calculated as follows

Equating Eq. 9.8 with Eq. 9.10 gives

$$8.33x = -2x + 2x_F \quad (9.11)$$

Solving Eq. 9.11 for  $x$  yields

$$8.33x + 2x = 2x_F$$

$$10.33x = 2x_F$$

$$x = x_z = 0.194x_F$$

Substituting  $x = 0.194x_F$  into Eq. 9.10:

$$y = -2x + 2x_F \quad (9.10)$$

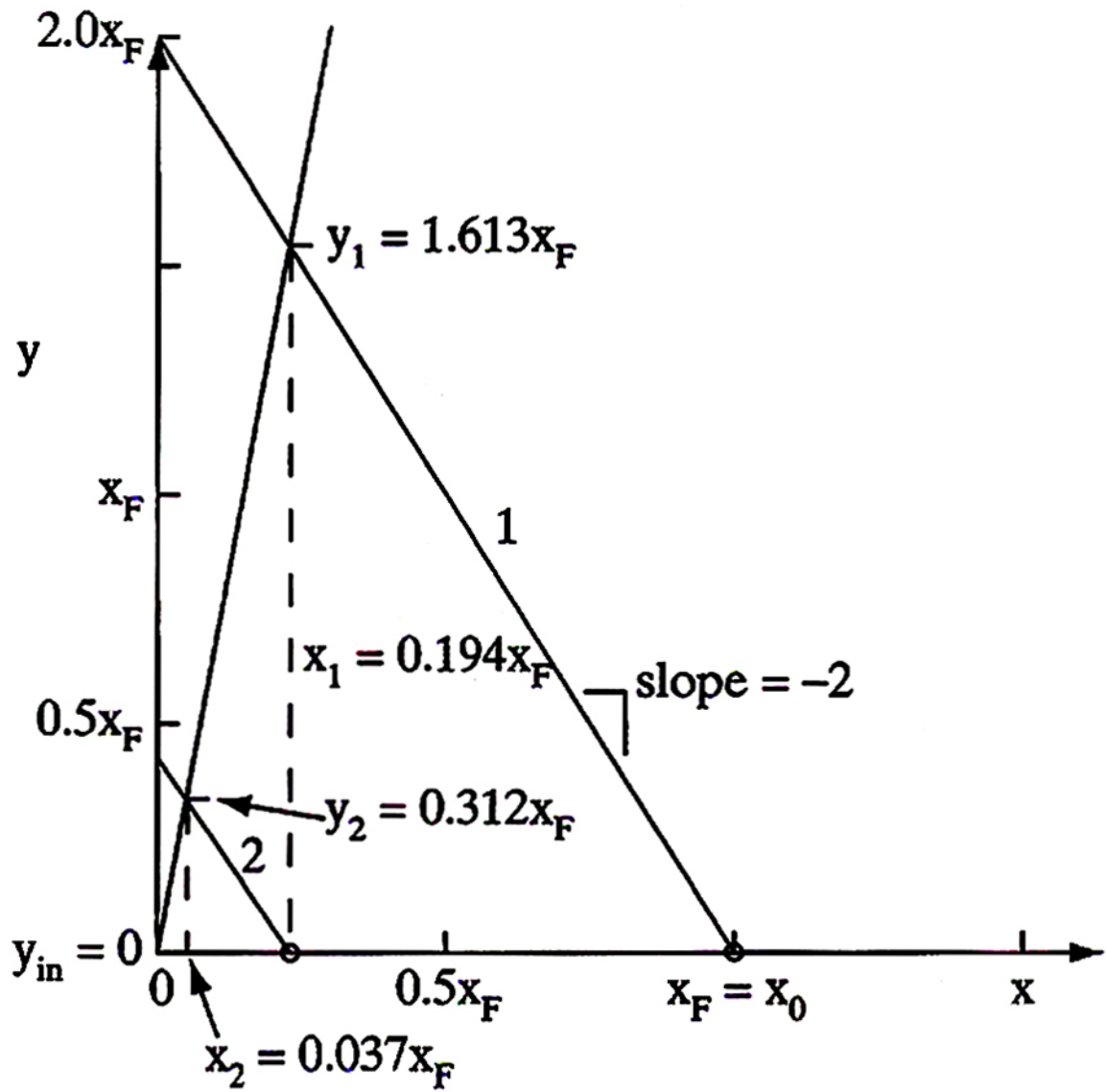
and solving for  $y$  yields

$$y = y_{1,\text{out}} = 1.613x_F$$

All the calculations above can be illustrated using the Figure on the next Page

In this case,  $x_z = 0.194x_F$ ; thus, the total recovery fraction of alcohol dehydrogenase in the dextran solvent phase is

$$1 - \frac{x_z}{x_F} = 1 - \frac{0.194x_F}{x_F} = 0.806$$



(b) When both stages 1 and 2 are operated

The calculations for stage 1 has already been carried out in Question (a)

The operating equation for stage 2 can be written as follows

$$y_{2,\text{out}} = -\frac{R}{E_2} x_2 + \left( \frac{R}{E_2} x_z + y_{\text{in}} \right) \quad (9.12)$$

When substituting corresponding numerical values into Eq. 9.12, it results in

$$y_{2,\text{out}} = -\frac{20}{10} x_2 + \left( \frac{20}{10} x_z + 0 \right)$$

$$y_{2,\text{out}} = -2x_2 + 2x_z \quad (9.13)$$

but, from Question (a),  $x_z = 0.194x_F$

Hence, Eq. 9.13 becomes

$$y_{2,\text{out}} = -2x_2 + 2(0.194x_F)$$

$$y = -2x + 0.388x_F \quad (9.14)$$

which is the operating equation for stage 2

From Eq. 9.14, when

- $y = 0, x = 0.194x_F$
- $x = 0, y = 0.388x_F$

Hence, to obtain the operating line for stage 2, we draw the line between the points  $(0.194x_F, 0)$  [the origin point for stage 2] and  $(0, 0.388x_F)$

The intersection of the operating line of stage 2 with the equilibrium line can be calculated as follows

Equating Eq. 9.8 (the *equilibrium-line* equation) with Eq. 9.14 results in

$$8.33x = -2x + 0.388x_F \quad (9.15)$$

Solving for  $x$  yields

$$8.33x + 2x = 0.388x_F$$

$$10.33x = 0.388x_F$$

$$x = x_2 = 0.0376x_F$$

Substituting  $x = 0.0376x_F$  into Eq. 9.14 and solving for  $y$  yields

$$y = y_{2,\text{out}} = 0.313x_F$$

When both stages 1 and 2 are operated,  $x_2 = 0.0376x_F$

Accordingly, the total recovery fraction of alcohol dehydrogenase in the dextran solvent phase is

$$1 - \frac{x_2}{x_F} = 1 - \frac{0.0376x_F}{x_F} = 0.962$$

## 9.3 Concentrated Immiscible Extraction

When the concentration of a solute in either diluent or the solvent is low (but *still immiscible*), we can assume that

- the flow rate of the raffinate phase is constant or can be replaced by the flow rate of the diluent, or *vice versa* (*i.e.*  $F_D = R$ )
- the flow rate of the solvent can be used for the flow rate of the extract phase, or *vice versa* (*i.e.*  $F_S = E$ ); in other words, the flow rate of the extract phase is constant



Accordingly, mole or mass fractions in both raffinate ( $x_i$ ) and extract ( $y_i$ ) phases can be used for species balance, as described and illustrated in the previous sections

However, when the concentration of the solute is large (*i.e.* cannot be ignored), the flow rates of the raffinate and extract phases are no longer constant, as

- the *solute* is *removed* from the *raffinate* phase, which makes the flow rate of the *raffinate* phase *decrease*
- the *solute* of *extracted into* the *extract* phase, which results in an *increase* in the flow rate of the *extract* phase

To enable the mass or mole balance,

- the flow rate of the raffinate phase ( $R$ ) must be replaced by the flow rate of the diluent ( $F_D$ )
- the flow rate of the solvent ( $F_S$ ) must be used in *lieu* of the flow rate of the extract phase

Additionally, the mole or mass ratio must be employed to describe the concentrations of the solute in the raffinate and extract phases

As per the *absorption* or *stripping* operation, the mole or mass ratios in the raffinate ( $X_i$ ) and extract ( $Y_i$ ) phases can be calculated from the mole and mass fractions ( $x_i$  and  $y_i$ ) as follows

$$X_i = \frac{x_i}{1 - x_i} \quad (9.16)$$

$$Y_i = \frac{y_i}{1 - y_i} \quad (9.17)$$

and the species balance (*e.g.*, Eqs. 9.1 and 9.5) and the operating-line equations (*e.g.*, Eqs. 9.2 and 9.6) can be written as follows

$$F_S Y_{j+1} + F_D X_o = F_S Y_1 + F_D X_j \quad (9.18)$$

$$F_D X_{j-1} + F_{S_j} Y_{j,\text{in}} = F_D X_j + F_{S_j} Y_j \quad (9.19)$$

and

$$Y_{j+1} = \frac{F_D}{F_S} X_j + \left( Y_1 - \frac{F_D}{F_S} X_o \right) \quad (9.20)$$

(note that the slope for the operating line is  $\frac{F_D}{F_S}$ )

$$Y_j = -\frac{F_D}{F_{S_j}} X_j + \left( \frac{F_D}{F_{S_j}} X_{j-1} + Y_{j,\text{in}} \right) \quad (9.21)$$

(note that the slope for the operating line is  $-\frac{F_D}{F_{S_j}}$ )

The details of the calculations are still the same

## 9.4 Extraction for Partially Miscible Ternary Systems

In the preceding sections, the extraction is based on fact that the diluent and the solvent are immiscible to each other

However, all extraction systems are, in fact, partially miscible to some degree, and when the *miscibility* is **not negligible**, the analysis using the McCabe-Thiele approach is no longer appropriate (if we try to do so, it would not yield an answer with an acceptable accuracy)

To solve the problem of such system, a stage-by-stage analysis is to be employed

At this level of study, ternary systems (*i.e.* the system with 3 components: a diluent, a solute, and a solvent) are to be analysed

When a system consists of **3 components** (or species), mass (or mole) fraction of each component/species can be shown as a **three-component diagram**, which can be presented in the form of

- equilateral triangle, or
- right triangle

demonstrated in the following Example

**Example** A *liquid* mixture of A, B, and C has the *mass* fraction of A and B (at equilibrium) at 25 °C as follows:

$$y_A = 0.40$$

$$y_B = 0.30$$

Locate the exact point of this mixture in a three-component diagram

In the *3-component* diagram, the summit or the tip (ยอด) of each corner represents a 1.0 mass (or mole) fraction (or 100%) of each substance or species

The edge or side (ด้าน) opposite to the tip represents a 0 mass (or mole) fraction (0%) of the substance

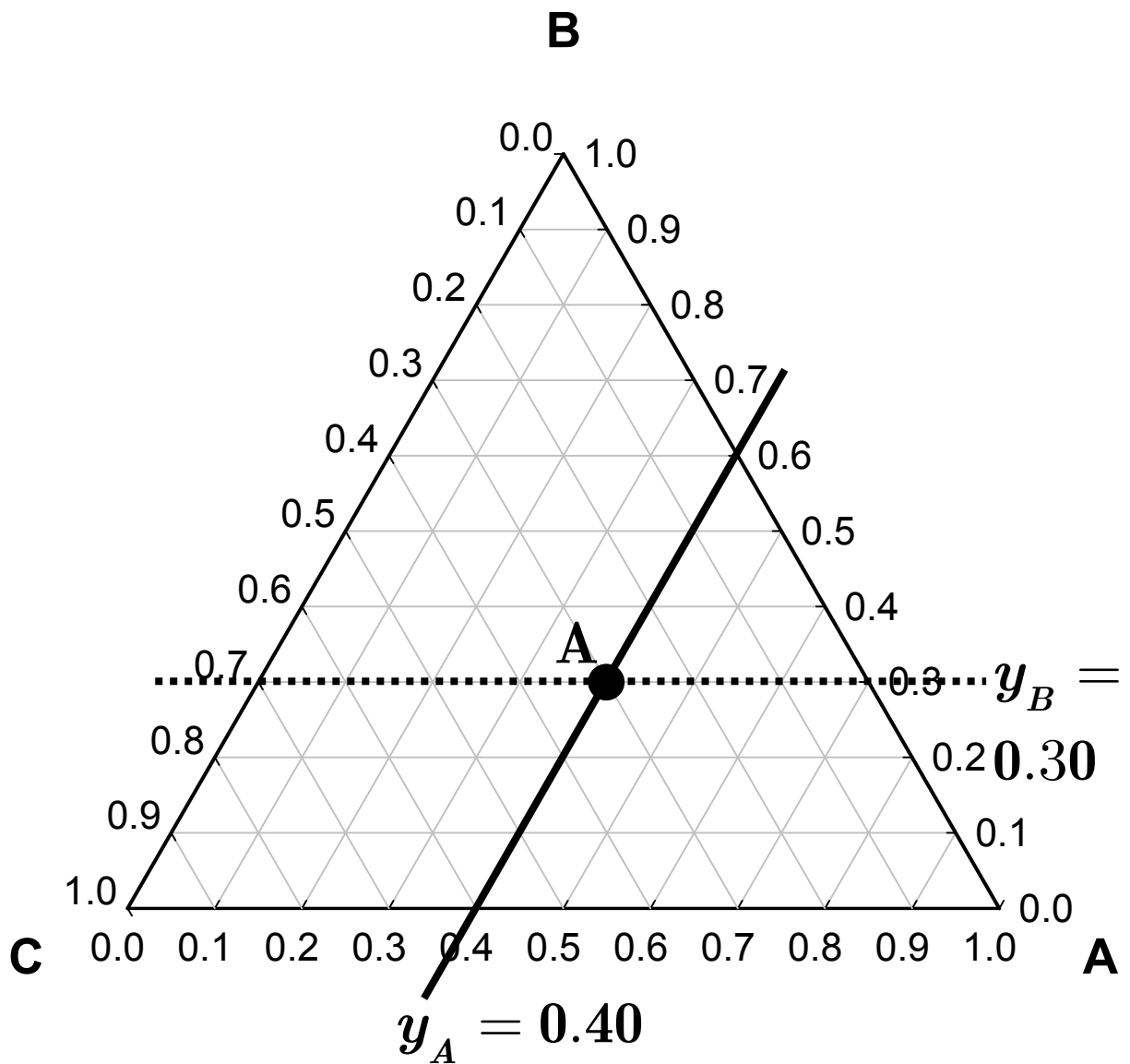
Since this is a *3-component* diagram, **only 2** specified component is sufficient to locate the exact point on the diagram

In this example, species A has a mass fraction of 0.40 and species B has a mass fraction of 0.30, which can be depicted by the solid and dotted lines, respectively, in the *equilateral 3-component* diagram on the next Page

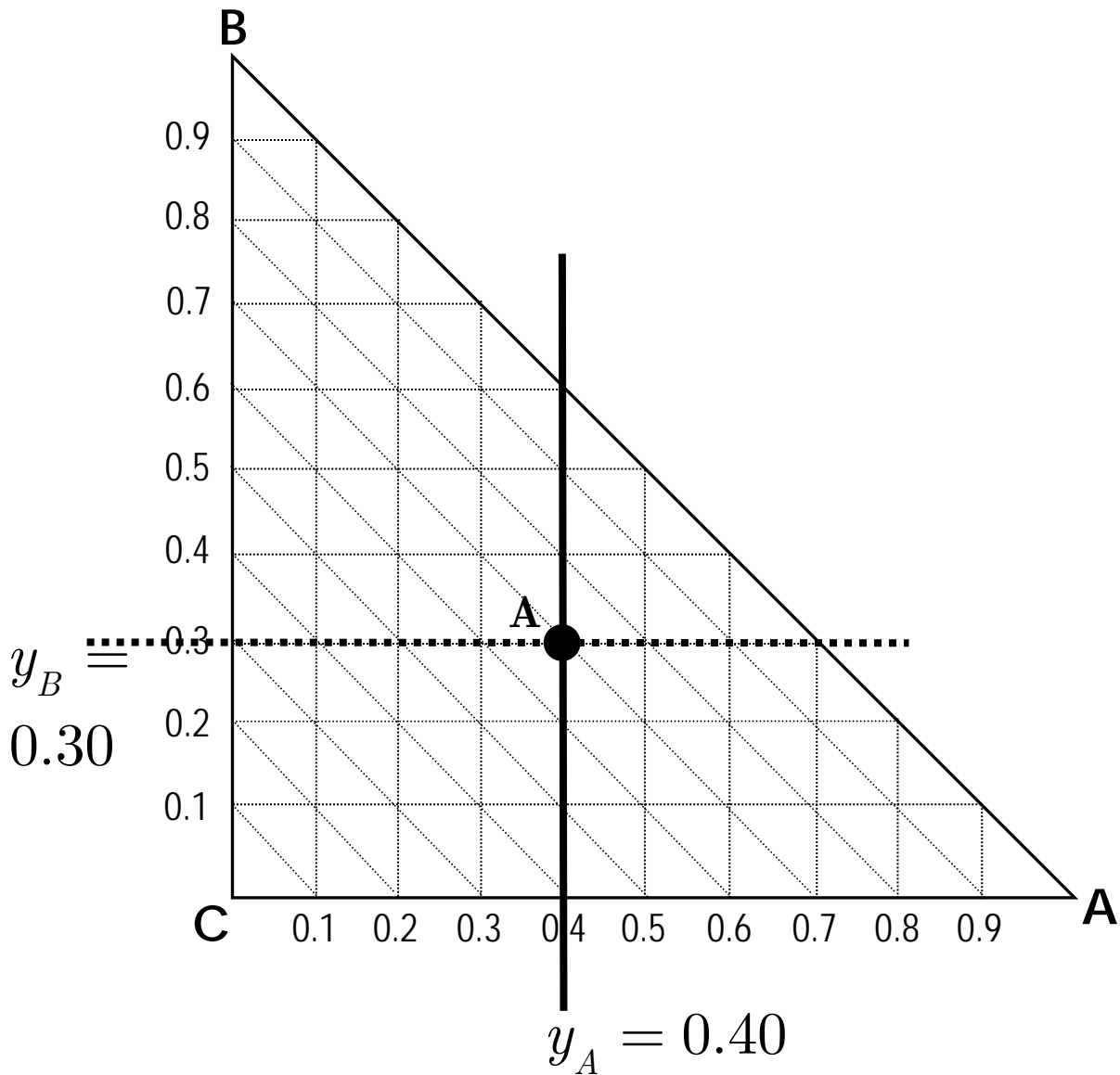
Point A is the intersection of the  $y_A = 0.40$  line and the  $y_B = 0.30$  line; note that, at this point,  $y_C$  is read as 0.30, which corresponds to the fact that

$$y_C = 1 - y_A - y_B = 1 - 0.40 - 0.30 = \mathbf{0.30}$$





The *right-triangle* 3-component diagram can also be used to locate Point A as shown on the next Page



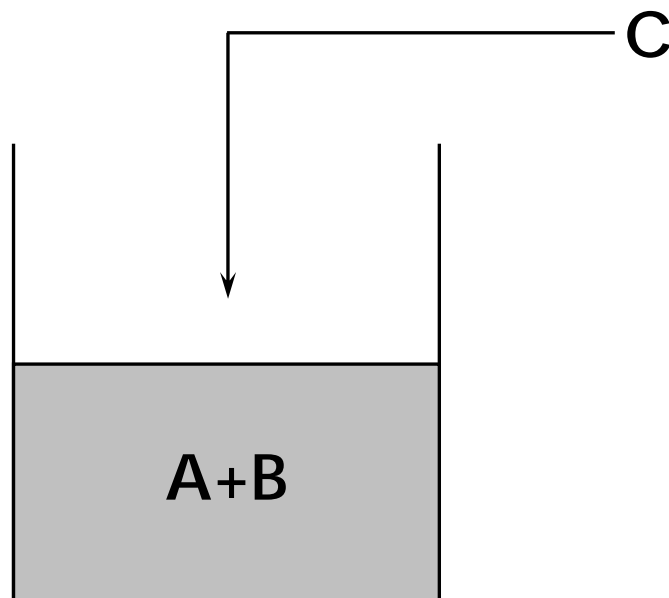
## Exercises

Try locating the following points yourself

- 1)  $y_A = 0.40, y_C = 0.60 \rightarrow$  Point **P**
- 2)  $y_A = 0.20, y_B = 0.50 \rightarrow$  Point **Q**
- 3)  $y_B = 0.25, y_C = 0.35 \rightarrow$  Point **R**

Let's consider a simple liquid-liquid extraction (LLE) system below

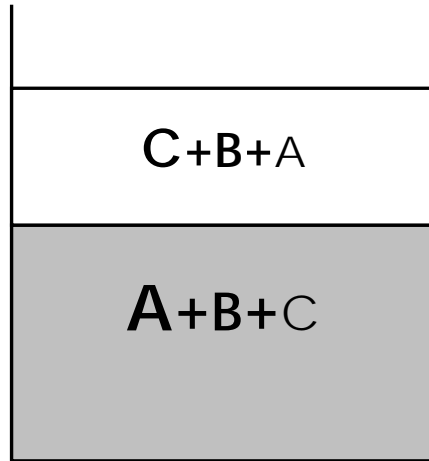
The solvent C is added into the mixture of the diluent A and the solute B



When the system reaches the equilibrium, it

- could be *homogeneous* (*i.e.* all species are mixed together into a single phase)

- could be divided into 2 phases as shown below



One phase (*e.g.*, the lower phase) contains the diluent A; the solute B, with less amount than the starting point; and some amount of the solvent C (this phase is, in fact, the *raffinate* phase)

Another phase (*e.g.*, the upper phase) comprises the solvent C, the incoming solute B, and some amount of the diluent A (this phase is the *extract* phase)

The equilibrium data for the situation that the system is divided into 2 phases are illustrated in Table 9.1, which is the ternary system of water (the diluent), acetone (the solute), and chloroform (the solvent)

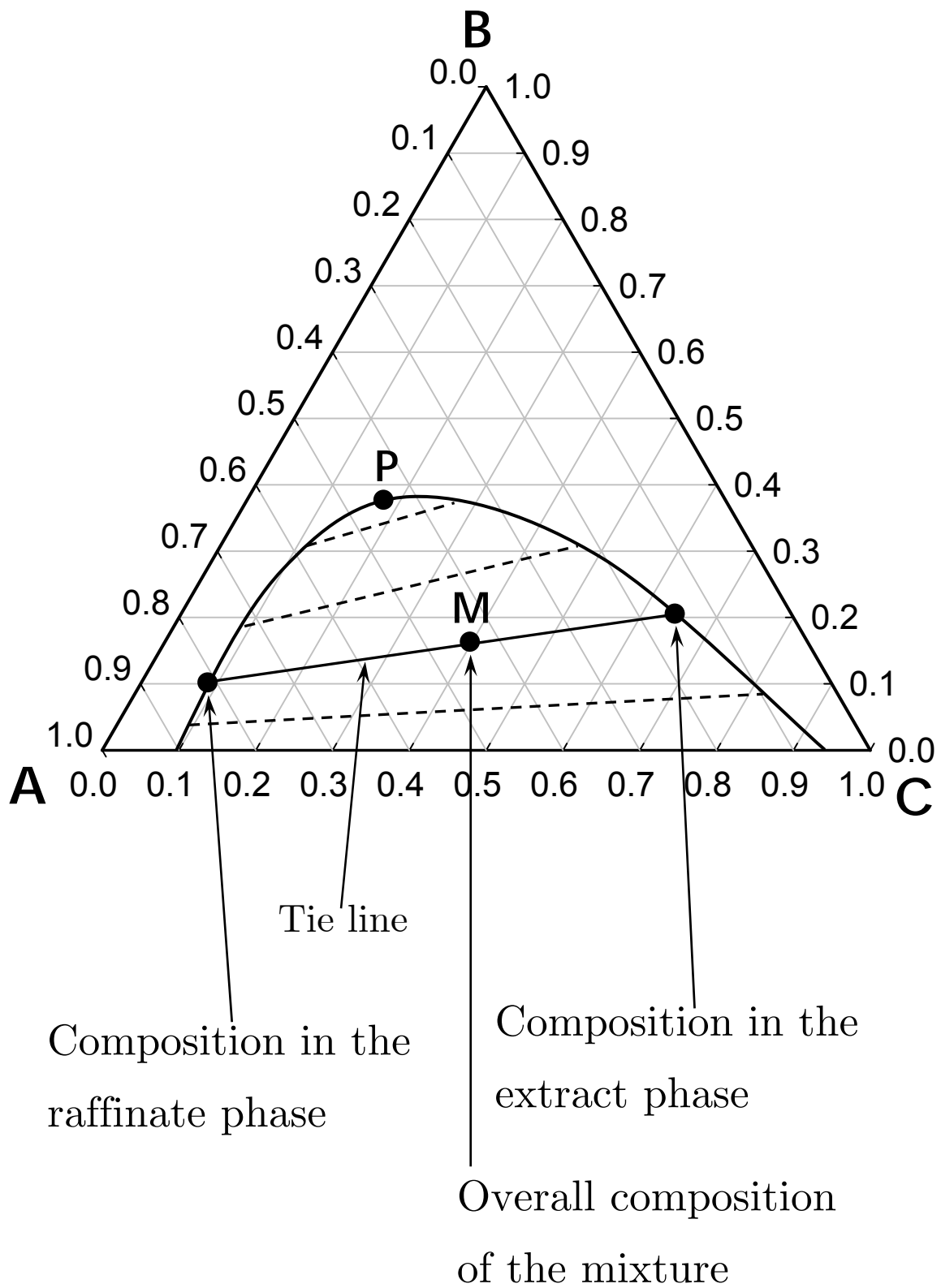
Each pair of data [*e.g.*, between the water (raffinate) phase and the chloroform (extract) phase] are connected together by a **tie-line**, as illustrated in Figure 9.6

**Table 9.1: Equilibrium data for the water-chloroform-acetone system**

Water phase (Raffinate phase)			Chloroform phase (Extract phase)		
$x_D$	$x_S$	$x_A$	$y_D$	$y_S$	$y_A$
Water	Chloroform	acetone	Water	Chloroform	acetone
99.2	0.8	0	0.5	99.5	0
83.0	1.2	15.8	1.3	70.0	28.7
73.1	1.3	25.6	2.2	55.7	42.1
62.3	1.7	36.0	4.4	42.9	52.7
45.6	5.1	49.3	10.3	28.4	61.3
34.5	9.8	55.7	18.6	20.4	61.0

Note that, in Figure 9.6

- A is the diluent
- B is the solute
- C is the solvent



**Figure 9.6: A ternary extraction system**

Note that Point M is the composition of the mixture of the raffinate phase and the extract phase for a given tie-line (will be discussed in detail later)

When all pairs of data in the raffinate and extract phases are plotted (a tie-line of each pair is depicted, in Figure 9.6, as dashed lines), a solubility curve is established

Within the *solubility-curve* envelope, the mixture (*e.g.*, Point M) will always be divided into 2 phases (*i.e.* the raffinate phase and the extract phase)



The composition in each phase for a given point M is dictated by a tie-line

For example, if the mixture has the composition of  $z_A = 0.42$ ,  $z_B = 0.18$ , and  $z_C = 0.40$  (*i.e.* Point M), which is within the *solubility-curve* envelope, it will be divided into 2 phases:

- The *raffinate* phase with the composition of  $x_A = 0.80$ ,  $x_B = 0.10$ , and  $x_C = 0.10$
- The *extract* phase with the composition of  $y_A = 0.15$ ,  $y_B = 0.21$ , and  $y_C = 0.64$

Point P in Figure 9.6 is the “**plait point**”, which is the point where the composition in the raffinate phase is equal to that of the extract phase (note that the plait point is NOT necessary to be the highest point of the solubility curve)

If the composition is NOT within the *solubility-curve* envelope (*i.e.* outside the *solubility-curve* envelope), the system will be a single phase

Consider the solid tie-line in Figure 9.6 once again, by letting

- $R$  as the point on the raffinate phase and the mass of the raffinate phase
- $E$  as the point on the extract phase and the mass of the extract phase
- $M$  as the composition of the mixture and the mass of the mixture

Since  $M$  is divided into 2 phases, the raffinate phase ( $R$ ) and the extract phase ( $E$ )

Thus,

$$R + E = M \quad (9.22)$$

The species balances for the solute (B) and the diluent (A) can be performed as follows

$$x_B R + y_B E = z_B M \quad (9.23)$$

$$x_A R + y_A E = z_A M \quad (9.24)$$

which can be re-arranged to

$$z_B = \frac{x_B R + y_B E}{M} = \frac{x_B R + y_B E}{R + E} \quad (9.25)$$

$$z_A = \frac{x_A R + y_A E}{M} = \frac{x_A R + y_A E}{R + E} \quad (9.26)$$

Eqs. 9.25 and 9.26 are used to compute the composition of any species at Point M when the compositions of the raffinate and the extract phase are known/given

Eqs. 9.23 and 9.24 can be re-written as follows

$$x_B R + y_B E = z_B (R + E) \quad (9.27)$$

$$x_A R + y_A E = z_A (R + E) \quad (9.28)$$

which can be re-arranged to

$$\frac{R}{E} = \frac{(y_B - z_B)}{(z_B - x_B)} \quad (9.29)$$

$$\frac{R}{E} = \frac{(y_A - z_A)}{(z_A - x_A)} \quad (9.30)$$

Since

- $y_A - z_A$  or  $y_B - z_B$  is the distance between Point M and Point E (*i.e.* the distance ME)
- $z_A - x_A$  or  $z_B - x_B$  is the distance between Point R and Point M (*i.e.* the distance RM)

Eqs 9.29 and 9.30 can be written as follows

$$\frac{R}{E} = \frac{\overline{ME}}{\overline{RM}} \quad (9.31)$$

Eq. 9.31 is the **lever-arm rule**

By performing the similar derivation, we obtain the another 2 lever-arm-rule equation as follows

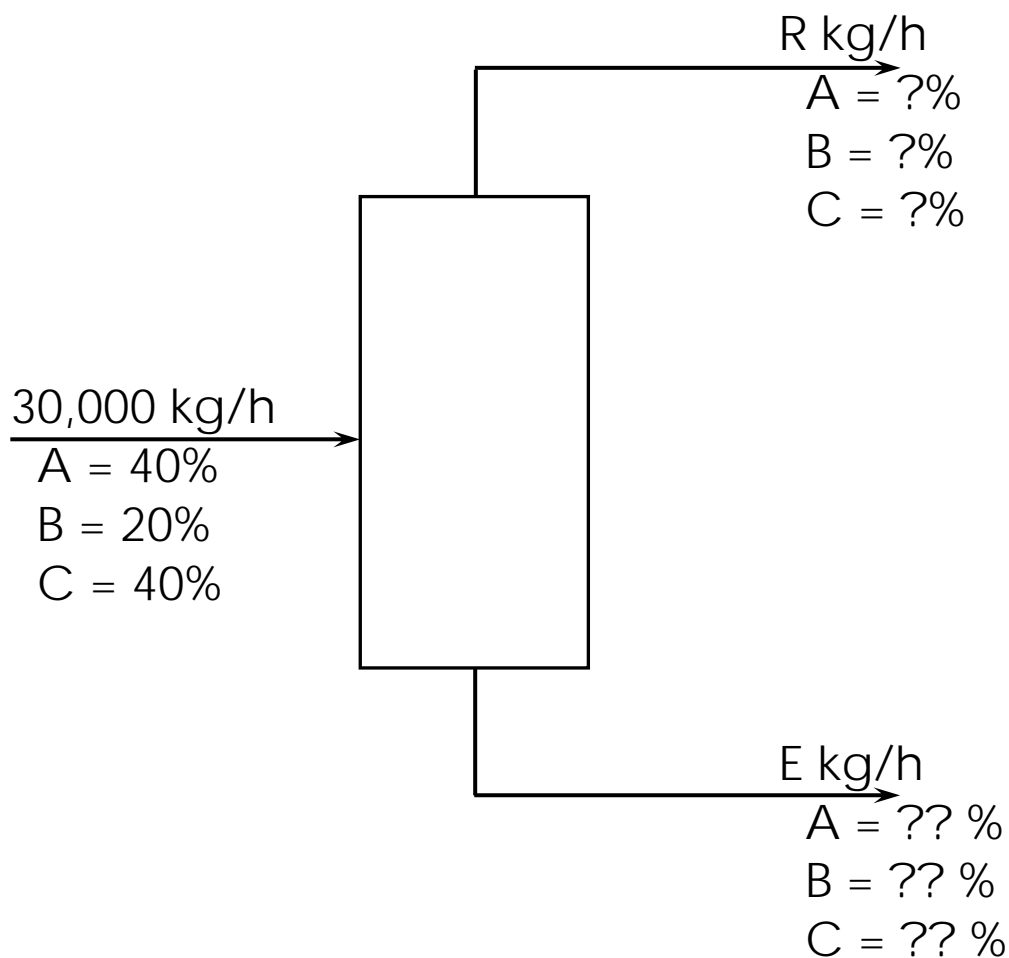
$$\frac{R}{M} = \frac{\overline{ME}}{\overline{RE}} \quad (9.32)$$

$$\frac{E}{M} = \frac{\overline{RM}}{\overline{RE}} \quad (9.33)$$

By using Eqs. 9.31-9.33, analytical material balances are not necessary

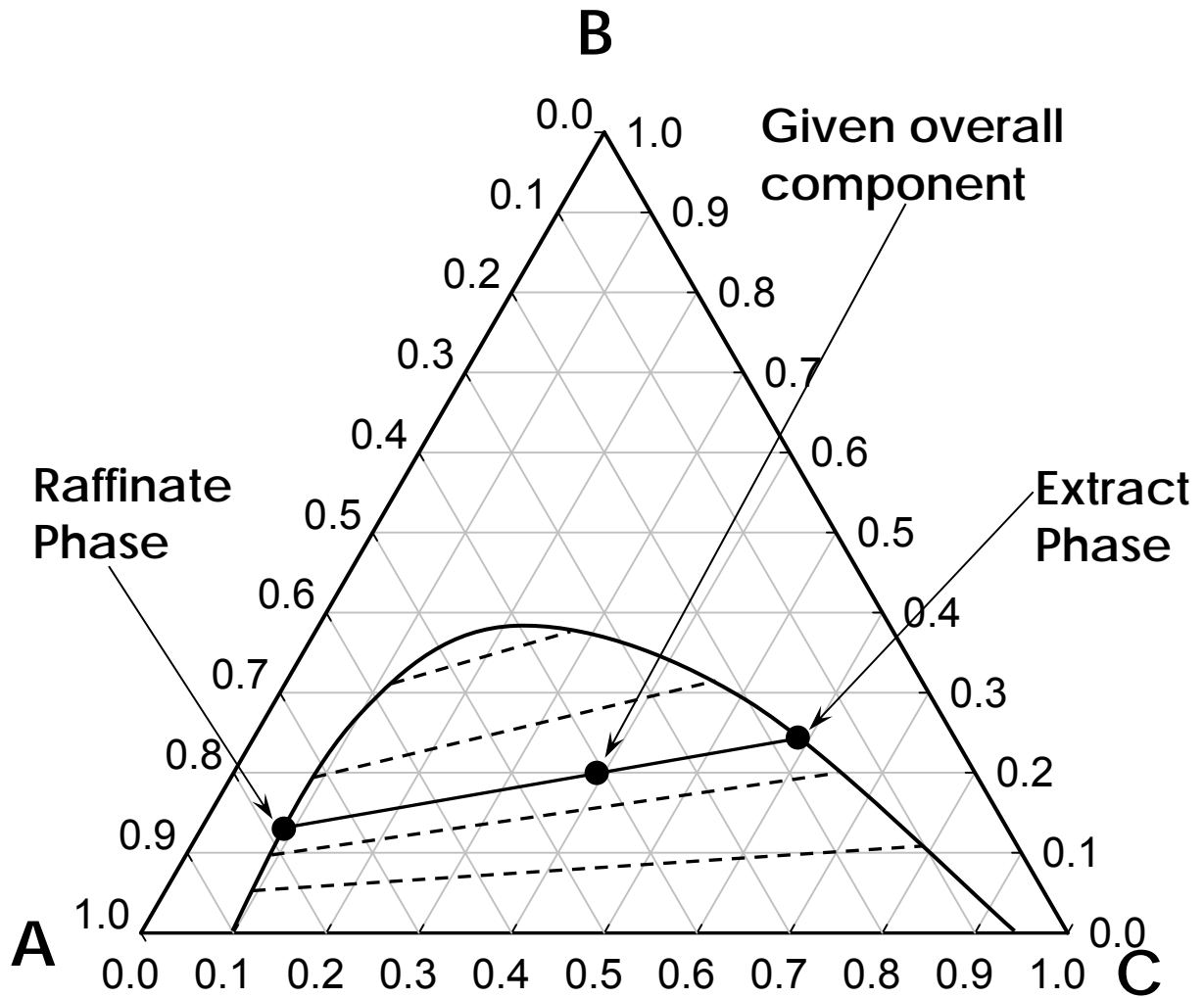
The values of  $R$  (the amount of the raffinate phase) and  $E$  (the amount of the extract phase), and the location of point  $M$  can be obtained by measuring (using a ruler) the distance  $RE$ ,  $RM$ , and/or  $ME$

**Example** Referring to the 3-component diagram in Figure 9.6 on Page 55, if 30,000 kg/h of ternary mixture of 40 wt% of A, 20% of B, and 40% of C was fed into a decanter (a mixer and settler) operating at 25 °C, what would the flow rates of two liquid streams leaving the decanter be?





By employing the diagram, Point M, with the composition of  $z_A = 0.40$ ,  $z_B = 0.20$ , and  $z_C = 0.40$  is located



A tie-line is *arbitrarily* drawn, and the composition in each phase is as follows

## Raffinate Phase

$$A = 78\% \left( x_A = 0.78 \right)$$

$$B = 13\% \left( x_B = 0.13 \right)$$

$$C = 9\% \left( x_C = 0.09 \right)$$

## Extract Phase

$$A = 17\% \left( y_A = 0.17 \right)$$

$$B = 24\% \left( y_B = 0.24 \right)$$

$$C = 59\% \left( y_C = 0.59 \right)$$

**Basis** 1 h of operation

## Overall Balance

$$30,000 = R + E \quad (9.34)$$

## Species “B” balance

$$(30,000)(0.20) = (R)(0.13) + (E)(0.24)$$

$$6,000 = 0.13R + 0.24E \quad (9.35)$$

Solving Eqs. 9.34 and 9.35 simultaneously gives

$$E = 19,091 \text{ kg}$$

$$R = 10,909 \text{ kg}$$

We can verify the above answer by performing species “C” balance as follows:

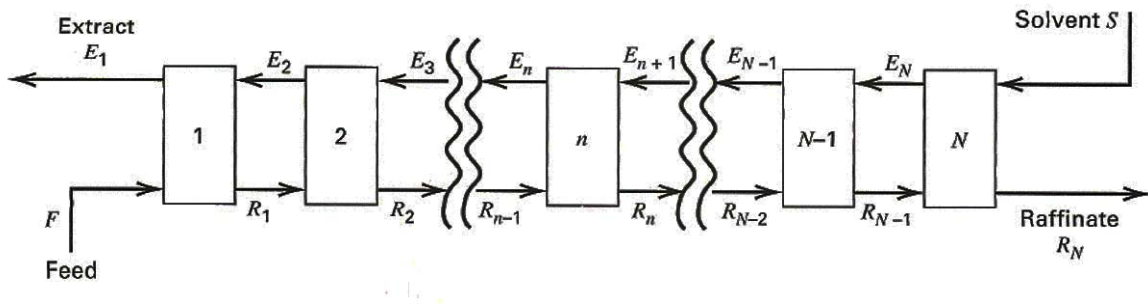
$$\begin{aligned} (30,000)(0.40) &= (10,909)(0.09) + (19,091)(0.59) \\ 12,000 &= 981.8 + 11,263.7 \\ 12,000 &\neq 12,245.5 \end{aligned}$$

Even though the RHS and the LHS are close to each other for species C balance, if we want *higher accurate* answer, a new tie-line has to drawn with a few adjustment (this is, in fact, a trial & error technique)

Note that the trial & error technique is commonly employed to solve an extraction problem, especially for a single-stage extraction

Next, we shall deal with the liquid-liquid extraction problems for the counter-current cascade system (*i.e.* more than one equilibrium stage)

Consider the counter-current liquid-liquid extraction cascade with  $N$  equilibrium stages in Figure 9.7



**Figure 9.7: A counter-current extraction cascade with  $N$  equilibrium stages**

(from “Separation Process Principles” by Henley, Seader, and Roper, 2011)

Feed containing the diluent  $D$  and the solute  $A$  enters the system with the flow rate of  $F$  and the concentration of the solute of  $x_{A_o}$  or  $x_{A_F}$

Solvent  $S$  enters the system with the flow rate of  $S$  and the concentration of the solute of

$$y_{A_{N+1}}$$

The raffinate stream leaves stage  $j$  with the flow rate of  $R_j$  and the solute concentration of  $x_{A_j}$ , and, finally, exits the system with the flow rate of  $R_N$  and the solute concentration of  $x_{A_N}$

The extract phase leaves stage  $j$  with the flow rate of  $E_j$  and the solute concentration of  $y_{A_j}$ ; the extract stream exits the system with the flow rate of  $E_1$  and the concentration of the solute of  $y_{A_1}$

Normally, the *known* variables are

- $F$  or  $R_o$
- $S$  or  $E_{N+1}$
- $x_{A_o}$  or  $x_{A_F}$
- $y_{A_{N+1}}$

- $y_{D_{N+1}}$
- $x_{A_N}$

while the *unknown* variables are

- $R_N$
- $E_1$
- $x_{D_N}$
- $y_{A_1}$
- $y_{D_1}$

Overall and species (A and D) balances can be established as follows

$$S + F = E_1 + R_N \quad (9.36)$$

$$y_{A_{N+1}} S + x_{A_o} F = y_{A_1} E_1 + x_{A_N} R_N \quad (9.37)$$

$$y_{D_{N+1}} S + x_{D_o} F = y_{D_1} E_1 + x_{D_N} R_N \quad (9.38)$$

Since we have 5 unknowns, but we have only 3 independent equations, we need another 2 equations

As  $E_1$  must be related to the *extract-phase* curve (because it is the stream leaving stage 1), this gives a relationship between  $y_{A_1}$  and  $y_{D_1}$

Likewise,  $R_N$  is the stream leaving stage N, it must be related to the *raffinate-phase* curve, which yields a relationship between  $x_{A_N}$  and  $x_{D_N}$

If we can formulate another 2 relationships mentioned above, we shall have 5 equations for 5 unknowns, which will enable us to solve for all unknowns



Alternatively, we can solve such problem **graphically** using a **3-component diagram** with a solubility (or equilibrium) curve

By employing the lever-arm rule, we obtain the following equations:

$$S + F = M = E_1 + R_N \quad (9.39)$$

$$y_{A_{N+1}} S + x_{A_o} F = z_{A_M} M = y_{A_1} E_1 + x_{A_N} R_N \quad (9.40)$$

$$y_{D_{N+1}} S + x_{D_o} F = z_{D_M} M = y_{D_1} E_1 + x_{D_N} R_N \quad (9.41)$$

Note that these are *external* mass balance calculations

Since  $x_{i_o}$  and  $y_{i_{N+1}}$  are known (normally given in the problem statement),  $z_{A_M}$  and  $z_{D_M}$  can be computed as follows

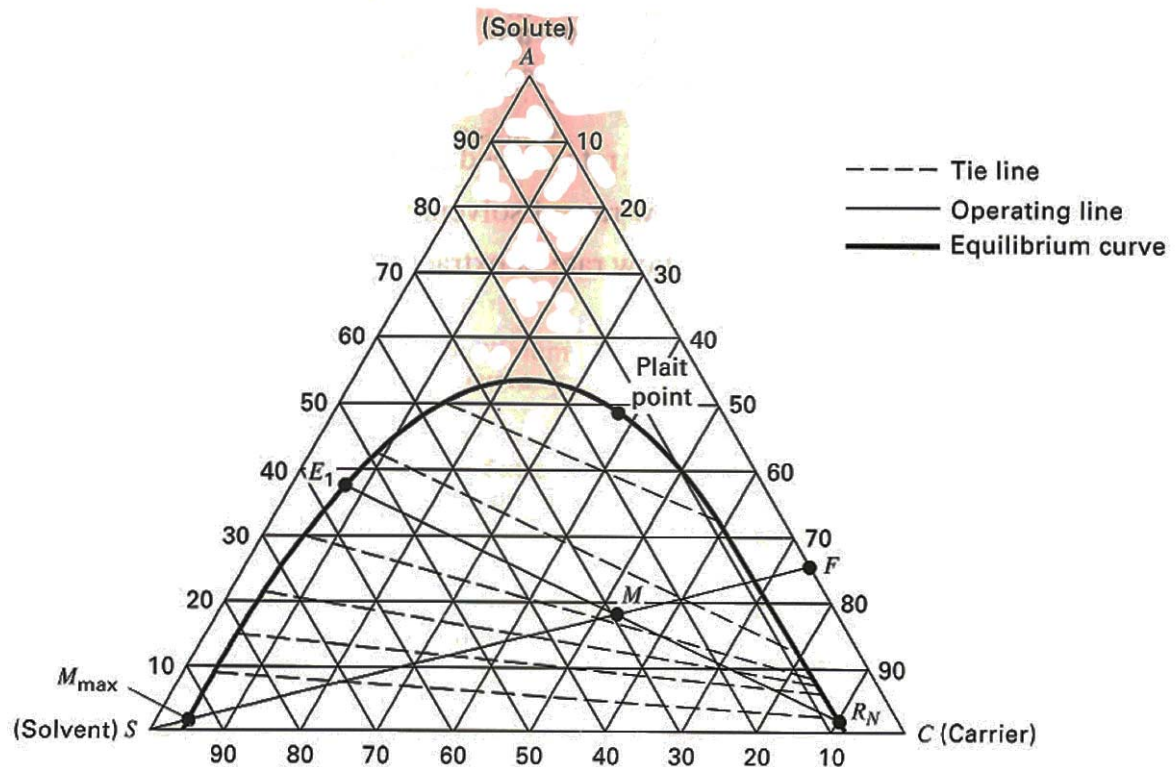
$$z_{A_M} = \frac{y_{A_{N+1}} S + x_{A_o} F}{M} = \frac{y_{A_{N+1}} S + x_{A_o} F}{S + F} \quad (9.42)$$

$$z_{D_M} = \frac{y_{D_{N+1}} S + x_{D_o} F}{M} = \frac{y_{D_{N+1}} S + x_{D_o} F}{S + F} \quad (9.43)$$

Hence,

- the composition of the feed can be specified (**Point F** – see Figure 9.8)
- the composition of the solvent can be specified (**Point S** – see Figure 9.8)

- **Point M** can be located (since  $z_{A_M}$  and  $z_{A_M}$  are known – obtained from Eqs. 9.42 and 9.43)



**Figure 9.8: The inlet, outlet, and product points obtained from the external mass balance calculations**

(from “Separation Process Principles” by Henley, Seader, and Roper, 2011)

Subsequently, a straight line SMF is drawn

From the explanation above and from Eqs. 9.39-9.41, we obtain the facts that

- Points  $E_1$  and  $R_N$  must be on the extract-phase curve and the raffinate-phase curve, respectively
- A straight line  $E_1R_N$  must pass through Point M

Since  $x_{A_N}$  is known and it must be on the raffinate-phase curve, Point  $R_N$  can be located and the value of  $x_{D_N}$  is known (by reading from the diagram)

Once Point  $R_N$  can be located, and we have already had Point M, Point  $E_1$  can then be specified, as illustrated in Figure 9.8

Performing the overall mass balance around stage 1 gives

$$\begin{aligned}F + E_2 &= E_1 + R_1 \\F - E_1 &= R_1 - E_2\end{aligned}\tag{9.44}$$

Performing the overall mass balance around stage 1 + 2 yields

$$\begin{aligned}F + E_3 &= E_1 + R_2 \\F - E_1 &= R_2 - E_3\end{aligned}\tag{9.45}$$

Performing the overall mass balance from stage 1 to stage N results in

$$\begin{aligned}F + S &= E_1 + R_N \\F - E_1 &= R_N - S\end{aligned}\tag{9.46}$$

In Figure 9.7 (on Page 69),

- streams  $E_2$  and  $R_1$  passes through each other
- streams  $E_3$  and  $R_2$  passes through each other
- streams  $S$  and  $R_N$  passes through each other

These pairs of streams are called the *passing streams*

We have learned from Eqs. 9.44-9.46 that the differences of all pairs of the passing streams are *all* equal to  $F - E_1$  or  $\Delta$

The difference of  $F - E_1$  (or  $\Delta$ ) can be illustrated graphically by drawing a line passing through Points  $E_1$  and  $F$

The difference of  $R_N - S$  ( $= F - E_1 = \Delta$ ) can be also depicted by drawing a line that passes through Points  $S$  and  $R_N$

Since the difference of  $R_N - S$  is equal to that of  $F - E_1$ , these two lines meet at the same point (*i.e.* Point P in Figure 9.9)

Note that, if we let  $\Delta = P$ , it means mathematically that

$$F - E_1 = P$$

which can be re-arranged to

$$F = E_1 + P \quad (9.47)$$

By doing the same for  $R_N - S = \Delta = P$ , we obtain the fact that

$$R_N = S + P \quad (9.48)$$

Comparing Eqs. 9.47 and 9.48 with Eq. 9.22

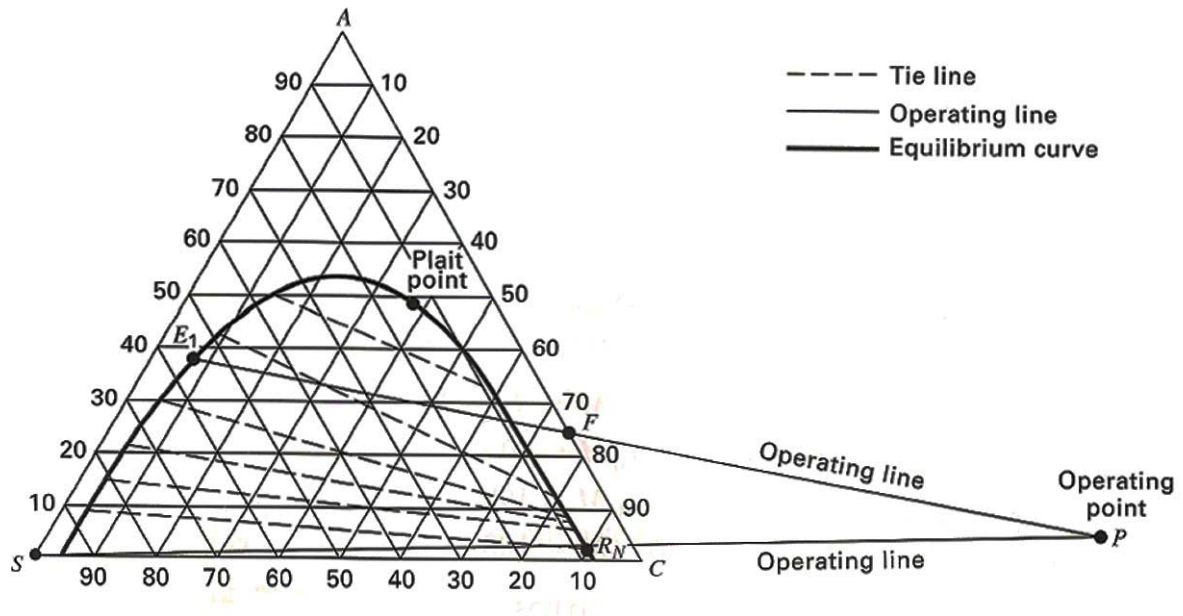
$$R + E = M \quad (9.22)$$

we can deduce the fact that

- $F$ ,  $E_1$ , and  $P$  must be on the same line and that  $F$  is the intermediate point between Point  $E_1$  and Point  $P$
- $R_N$ ,  $S$ , and  $P$  must be on the same line and that  $R_N$  is the middle point between Point  $S$  and Point  $P$



These two lines are the operating lines, and the meeting point (Point P) is called the operating point



**Figure 9.9: The construction of the operating lines and the location of the operating point**

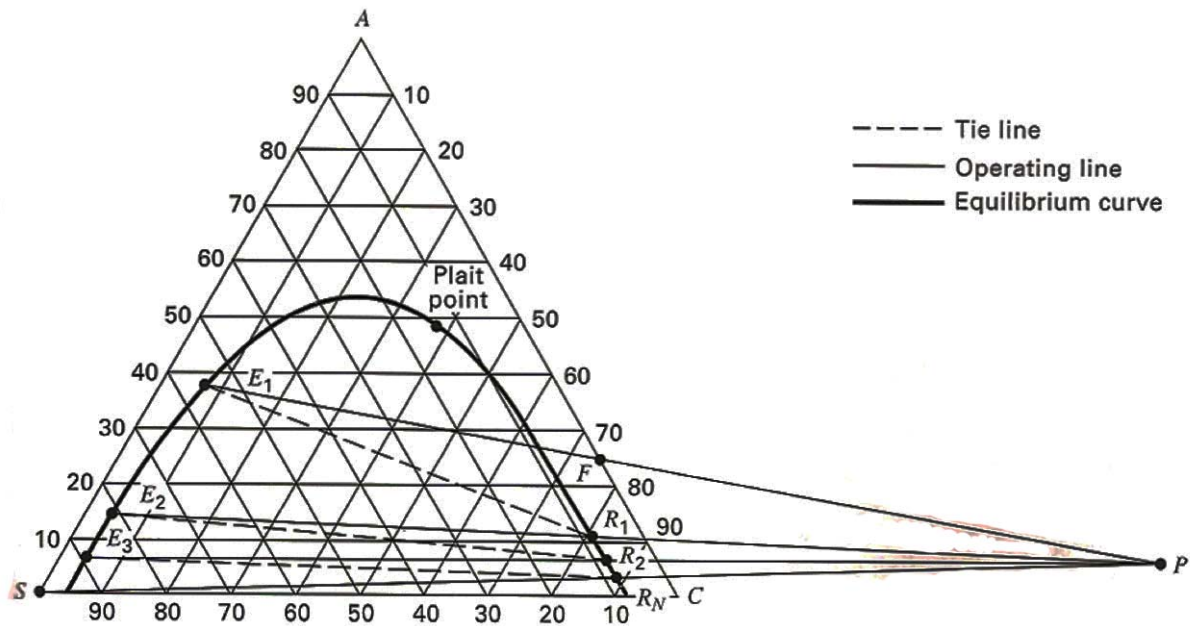
(from “Separation Process Principles” by Henley, Seader, and Roper, 2011)

Since  $E_1$  and  $R_1$  are the streams leaving stage 1, they are *in equilibrium* with each other, which means that there is Point  $R_1$  on the raffinate-phase curve connecting to Point  $E_1$  by a tie-line

In Figure 9.9, Point  $E_1$  is not on a tie-line; however, we can draw the tie-line that passes through Point  $E_1$  by interpolating from the nearest two tie-lines

Drawing a tie-line from Point  $E_1$  to the raffinate-phase curve yields Point  $R_1$ , as illustrated in Figure 9.10

We have just learned that  $R_1$  and  $E_2$  are the passing streams and that the difference of  $R_1 - E_2$  must pass through Point  $R_1$  and Point  $P$



**Figure 9.10: The determination of equilibrium stages for a partially miscible extraction system**

(from “Separation Process Principles” by Henley, Seader, and Roper, 2011)

Thus, when we draw a line starting from Point P and passing through Point  $R_1$  until we reach the *extract-phase* curve, we obtain Point  $E_2$

From Point  $E_2$ , we, once again, draw a tie-line to the raffinate-phase curve and obtain Point  $R_2$

We then use Points P and  $R_2$  to get Point  $E_3$  on the *extract-phase* curve

We do this repeatedly until we reach  $R_N$ , and the number of equilibrium stages is obtained

Figure 9.10 illustrates how the number of equilibrium stages can be determined using a 3-component diagram

Note that the determination of equilibrium stages as illustrated in Figure 9.10 is based on the fact that

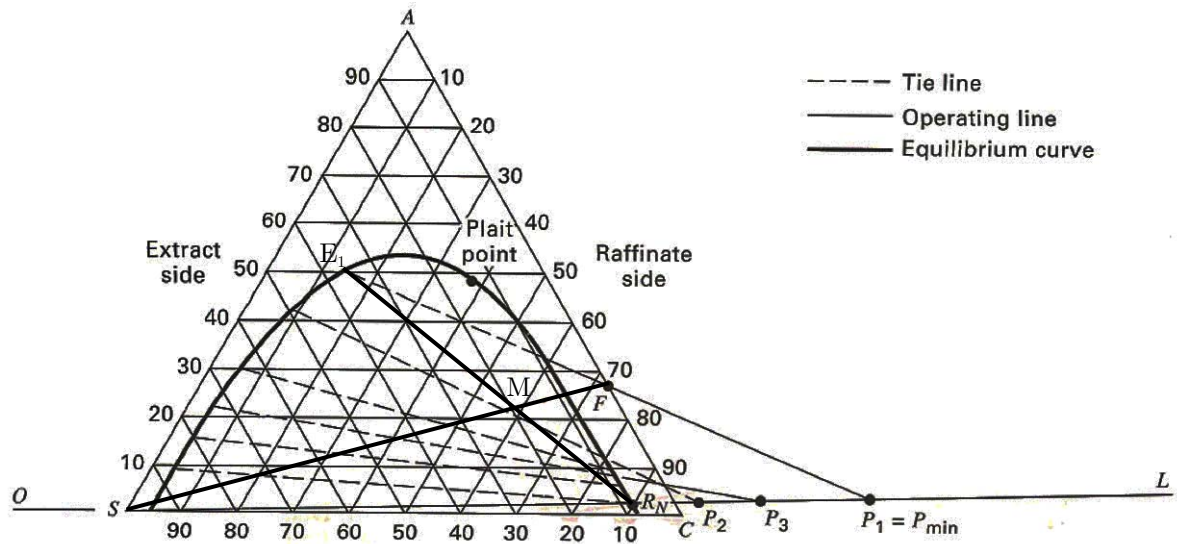
- the solvent-to-feed  $\left(\frac{S}{F}\right)$  ratio is *higher* than the *minimum* ratio
- the  $\frac{S}{F}$  ratio is *lower* than the *maximum* ratio

The *minimum*  $\frac{S}{F}$  ratio leads to the *infinity* ( $\infty$ ) number of stages, while the *maximum*  $\frac{S}{F}$  ratio results in the fact that *no raffinate phase* is *formed* (will be explained in detail later)

In the distillation, gas absorption, and stripping operations, minimum  $\frac{L}{V}$  (or minimum reflux ratio:  $\frac{L}{D}$  in the distillation operation) occurs when the operating line touches or intersects with the equilibrium line

In the liquid-liquid extraction (LLE) operation, minimum  $\frac{S}{F}$  takes place when the operating line coincides (เป็นเส้นเดียวกัน) with the tie-line, which is the equilibrium line for the LLE operation

Figure 9.11 shows the situation when operating lines coincides with tie-lines; note that each operating line gives Point P at various locations



**Figure 9.11: Determination of the minimum  $\frac{S}{F}$  ratio**

(from “Separation Process Principles” by Henley, Seader, and Roper, 2011)

The operating line that gives Point P *farthest away* from Point  $R_N$  is the operating line used to determine the minimum  $\frac{S}{F}$  ratio

In Figure 9.11, Point  $P_1$  is the operating point that is *farthest away* from Point  $R_N$

Accordingly, the line  $P_1F$  is the operating line used for determining the minimum  $\frac{S}{F}$  ratio

The line  $P_1F$  is extended to the *extract-phase* curve and reaches the curve at Point  $E_1$

As *per* Figure 9.8, the intersection of the lines  $E_1R_N$  and  $SF$  is Point M, at which the material balances can be established as follows

$$E_1 + R_N = M = S_{\min} + F \quad (9.49)$$

$$z_{A_M} M = y_{A_S} S_{\min} + x_{A_F} F$$

$$z_{A_M} (S + F) = y_{A_S} S_{\min} + x_{A_F} F \quad (9.50)$$

Eq. 9.50 can be re-arranged to

$$\frac{S_{\min}}{F} = \frac{x_{A_F} - z_{A_M}}{z_{A_M} - y_{A_S}} \quad (9.51)$$



The readings from Figure 9.11 are:

- $x_{A_F} = 0.28$  (28%)
- $y_{A_S} = 0$  (0%)
- $z_{A_M} = 0.22$  (22%)

which yields the  $\frac{S_{\min}}{F}$  ratio of

$$\frac{S_{\min}}{F} = \frac{0.28 - 0.22}{0.22 - 0} = 0.27$$

In the case illustrated by Figure 9.11, the *slope* of the *tie-line* is *downward* toward the raffinate side

If the *slope* of the *tie-line* is *upward* toward the raffinate side (as will be shown in Figure A and B on Pages 93 and 94), the tie-line will be extended to the *left hand side* (LHS) of the 3-component *diagram*

In such case, the point that used to determine the minimum  $\frac{S}{F}$  ratio (or Point  $P_1$ ) is the point that is **closest** to **Point S**

The calculation for the  $\frac{S_{\min}}{F}$  ratio is similar to the case when the slope of the tie-line is downward toward the raffinate side

For the maximum  $\frac{S}{F}$  ratio, consider Figure 9.8 (on Page 75)

According to the lever-arm rule, if the amount of solvent ( $S$ ) increases, the distance  $FM$  becomes longer, which means that Point M moves toward Point S

The maximum  $\frac{S}{F}$  ratio occurs when Point M reaches the *extract-phase* curve, and the  $\frac{S_{\max}}{F}$  ratio can be computed as follows

$$\frac{S_{\max}}{F} = \frac{x_{A_F} - (z_{A_M})_{\max}}{(z_{A_M})_{\max} - y_{A_S}} \quad (9.52)$$

When Point M is on the *extract-phase* curve, no **raffinate phase** is **formed**, and **only a single stage** is **needed**, which is **impractical**

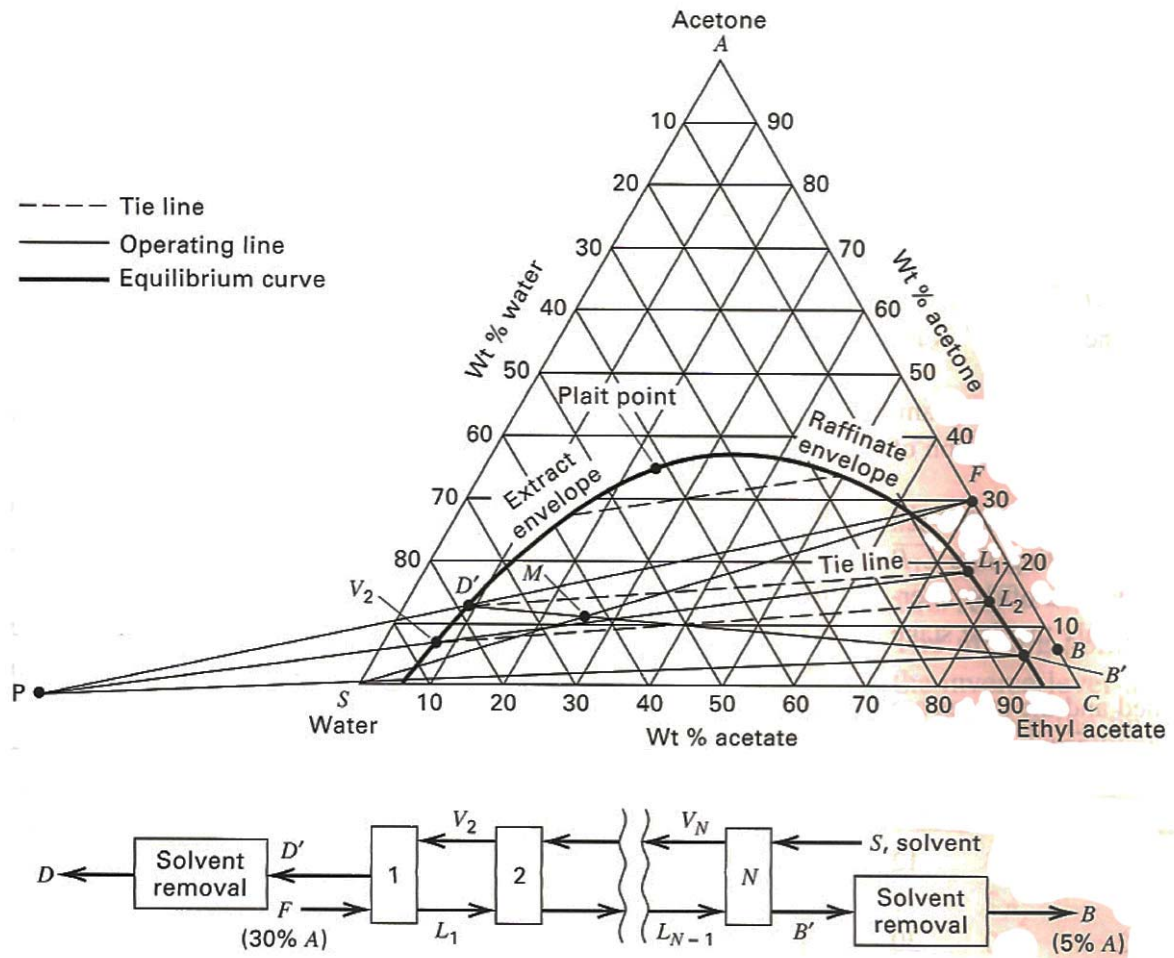
The operating  $\frac{S}{F}$  must be between  $\frac{S_{\min}}{F}$  and  $\frac{S_{\max}}{F}$ ; normally, the optimal  $\frac{S}{F}$  is approximately  $1.5 \left( \frac{S_{\min}}{F} \right)$

**Example** Acetone is to be extracted from a mixture of 30 wt% acetone + 70% ethyl acetate at 30 °C using *pure* water as a solvent

The final raffinate contains no higher than 5% of acetone on the water-free basis

Determine the minimum and maximum  $\frac{S}{F}$  ratios, as well as the number of equilibrium stages required for two *intermediate*  $\frac{S}{F}$  ratios between the minimum and maximum  $\frac{S}{F}$  ratios

The flow chart of this extraction operation and the 3-component diagram for this operation is as shown in the Figure A

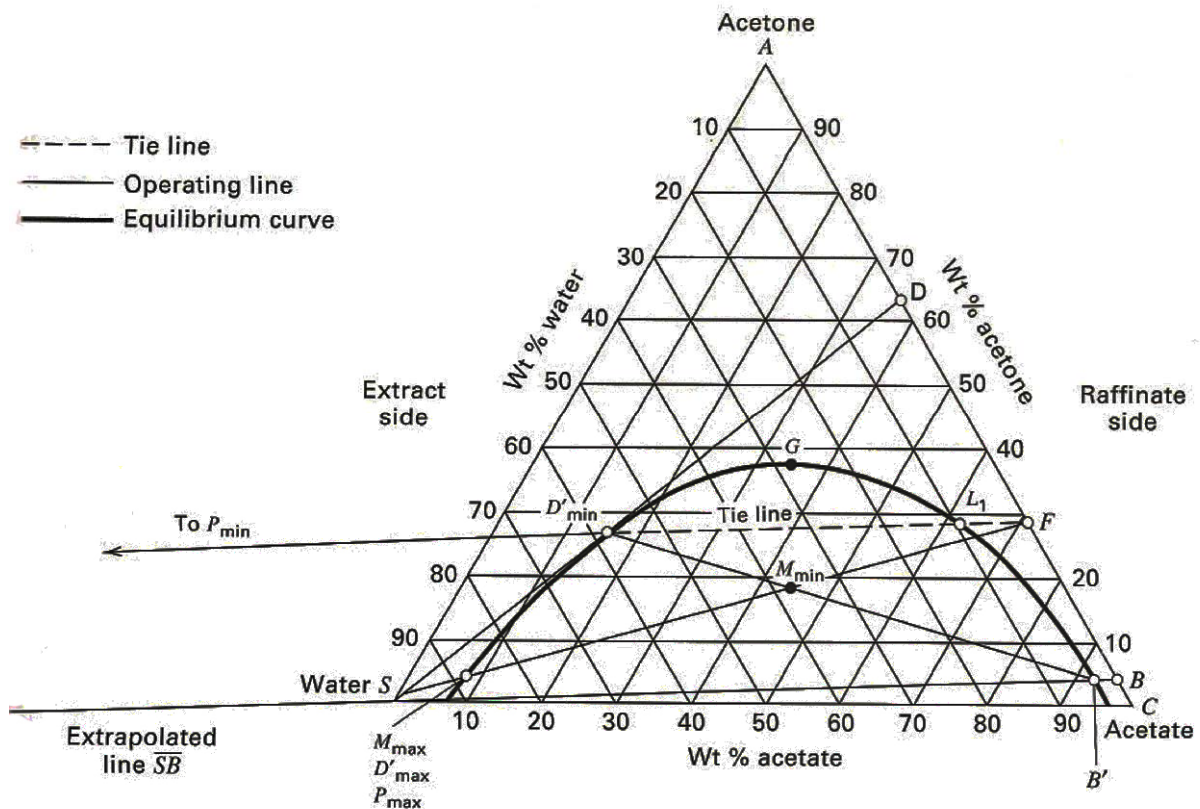


**Figure A**

(from “Separation Process Principles” by Henley, Seader, and Roper, 2011)

The determination of *minimum* and *maximum*

$\frac{S}{F}$  ratios are illustrated in Figure B



**Figure B**

(from “Separation Process Principles” by Henley, Seader, and Roper, 2011)

In this Example, it is given that

- Feed is a mixture of 30% acetone and 70% ethyl acetate, so Point  $F$  can be located
- Solvent is *pure* water; thus, Point  $S$  can be specified

- The **final raffinate** contains **5%** of **acetone** on the *water-free* basis, which is Point B on the line AC (at Point B, the concentration of acetone is 5% and the concentration of water is 0%—water-free ), which corresponds to Point  $R_N$  of 4% (or 0.04 mole fraction) [*i.e.* Point  $B'$  in Figures A and B]

The line  $SR_N$  or  $SB'$  can then be drawn, which can be extended to the left hand side (LHS) of the 3-component diagram

The *minimum*  $\frac{S}{F}$  ratio takes place when the tie-line that starts from Point  $F$  is extended to the point on the extended  $SB'$  line that is closest to Point  $S$ , and Point  $E_1$  on the *extract-phase* curve is then obtained (= Point  $D'_{\min}$  in Figure B)

Subsequently, the lines  $SF$  and  $D'_{\min}B'$  (or  $E_1R_N$ ) can be drawn, and Point  $M_{\min}$  is obtained; at this point,  $z_{A_M}$  is read as 19% (or 0.19 mole fraction)

Accordingly, the *minimum*  $\frac{S}{F}$  ratio can be computed as follows

$$\frac{S_{\min}}{F} = \frac{x_{A_F} - z_{A_M}}{z_{A_M} - y_{A_S}} = \frac{0.30 - 0.19}{0.19 - 0} = 0.58$$

The *maximum*  $\frac{S}{F}$  ratio is obtained when **Point M reaches the extract-phase curve**, which gives the value of  $\left(z_{A_M}\right)_{\max}$  of 4% or 0.04, and the  $\frac{S_{\max}}{F}$  can then be calculated as follows



$$\frac{S_{\max}}{F} = \frac{x_{A_F} - (z_{A_M})_{\max}}{(z_{A_M})_{\max} - y_{A_S}} = \frac{0.3 - 0.03}{0.03 - 0}$$

$$\frac{S_{\max}}{F} = 9.0$$

Hence, the operating  $\frac{S}{F}$  ratio must be between 0.58-9.0

Choose the  $\frac{S}{F}$  ratio of 1.75 (or  $S = 1.75F$ ) as the operating  $\frac{S}{F}$  ratio, which results in Point M with the concentration of acetone (solute) of

$$z_{A_M} = \frac{y_{A_S} S + x_{A_F} F}{S + F} = \frac{(0)(1.75F) + (0.3)(F)}{(1.75F) + (F)} = \frac{0.3F}{2.75F} = 0.11$$

and the concentration of ethyl acetate (diluent) of

$$z_{D_M} = \frac{y_{D_S} S + x_{D_F} F}{M} = \frac{y_{D_S} S + x_{D_F} F}{S + F}$$

$$z_{D_M} = \frac{(0)(1.75F) + (0.7)(F)}{(1.75F) + (F)} = \frac{0.7F}{2.75F} = 0.25$$

Thus, Point M can be specified, as shown in Figure A

When Point M is specified, the line  $SF$  is already drawn (which passes through Point M), and Point  $R_N$  is already located (= Point  $B'$  in Figure A) the line  $R_N M$  can then be drawn and extended to the *extract-phase* curve at Point  $E_1$  (= Point  $D'$  in Figure A)

When Point  $E_1$  (or Point  $D'$  is located) the line  $FE_1$  (or  $FD'$ ) and the line  $SR_N$  (or  $SB'$ ) can then be drawn and extended to the LHS of the diagram; these 2 lines meet at Point P

Drawing a line Point  $E_1$  (or  $D'$ ), using a tie-line, until reaching the *raffinate-phase* curve, Point  $R_1$  (or  $L_1$ ) is specified

Draw the line  $L_1P$  and Point  $E_2$  can be specified on the extract-phase curve, and by using Point  $E_2$  and the corresponding tie-line, Point  $R_2$  is subsequently located

Performing this iteration (ทำซ้ำไป-มาแบบนี้) until we reach Point  $R_N$ , and the number of equilibrium stages is eventually obtained

For the case of the  $\frac{S}{F}$  ratio of 1.75, the number of stages was found to be 4

Try doing it yourself for the  $\frac{S}{F}$  ratio of 3.0 (the number of stages is 2)