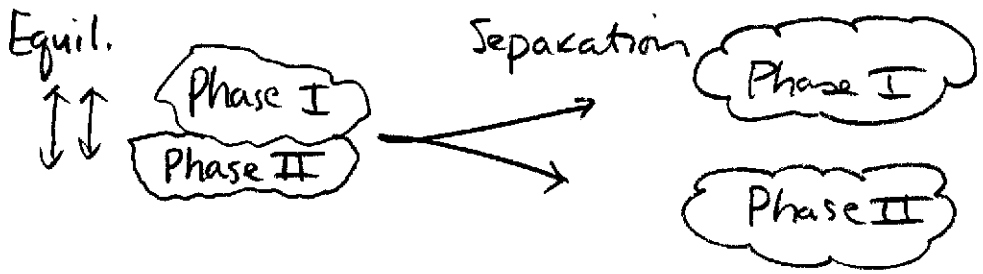
Chapter 4 - Single Stage Equilibrium Stages and Flash Calculations



This type of separation is suitable for systems with SF large.

4.1 Gibbs Phase Rule and Degrees of Freedom

Gibbs Phase Rule → Considers only intensive variables (T, P, h, s, x_i, y_i, etc)

Degrees of Freedom → Considers intensive and extensive variables (esp. Flowrates, Q, W, etc)

See Figure 4.1 (p165)

Note that the Gibbs Phase Rule (GPR) cannot account for feed stream conditions, heat effects, etc.

GPR: $F = C - P + 2$ { applies only at equilibrium }

- F: intensive variables to be specified
- C: components
- P: phases.

3-2

For example, consider a 2 phase equilibrium mixture of n-hexane and n-octane.

$$F = 2-2+2 = 2$$

∴ If we fix 2 intensive variables (any two) the system is fixed (that is, all other intensive variables are determined).

For example, subject this system to $P = 1$ atm and $T = 200°F$, everything else is determined (fixed).

See Figure 3.26 (Supplement) [3-2a]

what is $x_{C6} = ?$

$y_{C6} = ?$

$h_L = ?$

$h_V = ?$

$c_{pV} = ?$

$K_{C6} = ?$

Suppose instead $P = 1$ atm, $T = 140°F$

3-3

DOF Analysis

$$F = V - E$$

Additional Equations Relating IV and EV (MB's, EB, etc)

Intensive and extensive variables
(IV) (EV)

Here if we have V variables and E = V
then F = 0 (Determined)

Notice that DOF analysis does not require specification of P (phases)

In general we will be concerned with DOF

Binary Vapor-Liquid Systems.

Much equilibrium data exists for 2 component systems at either constant pressure or constant temperature

See Table 4.1 (p167) [3,3a] [3,3b]

Three different systems are shown

$\alpha_{AB} \simeq 500$

$\alpha_{AB} \simeq 5$

$\alpha_{AB} \simeq 1.01$

Notice difference in ΔT

3-4

One should "imagine" the difficulty in measuring compositions to such accuracy, as well as temperature, pressure, etc. In addition other properties can be found in these data tabulations.

Some of Table 4.2 is plotted in Figure 4.2 (p170). [3-4a]

The upper diagram is called a Txy diagram whereas the second is a x-y diagram. Generally a 45° reference line is placed on x-y diagrams to allow for visualization of volatity as well as to aid in constructions. Figure 4.4 (p171) shows this line. [3.4-b]

A Txy diagram has no such line (see Figure 4.3 (p171) [3-4 c]

Txy diagrams show considerably more information including:

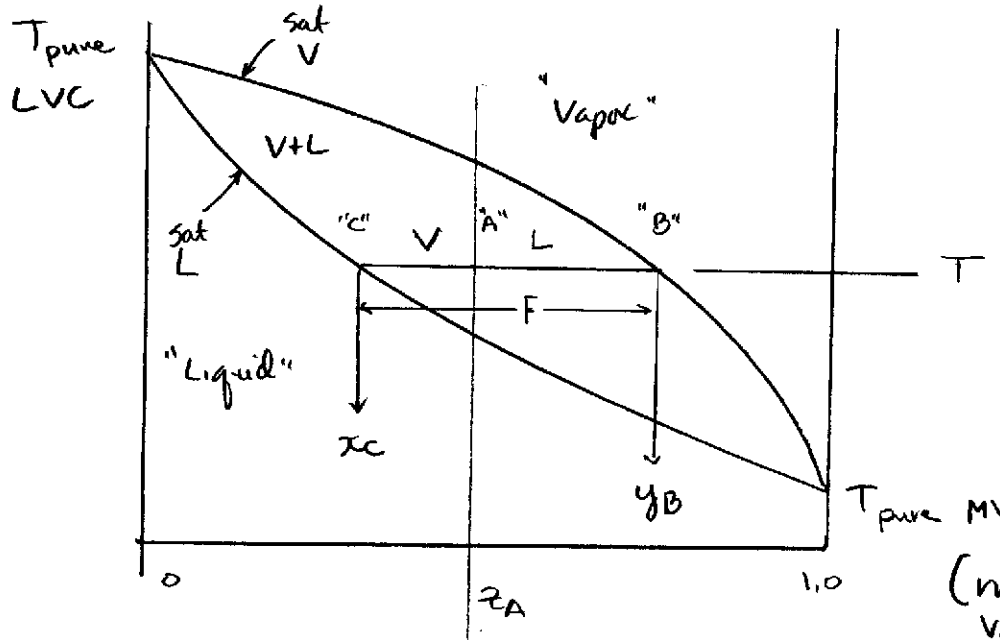
a) pure component boiling points
(b) mixture dew point & bubble point
(c) " phase compositions
(d) " phase amounts

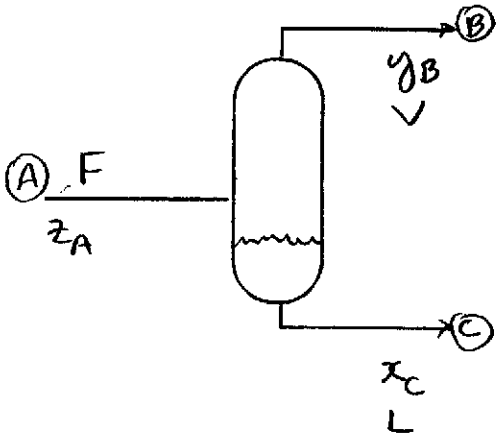
3-5

The technique to determine the phase amounts involves a graphical representation of a material balance.

This method is called the ILAR (inverse lever arm rule).

Although it will be demonstrated for a Txy diagram, similar constructions apply to other composition diagrams as well.





Total MB: $F = L + V$ (A)

MVC MB: $Fz_a = Lx_c + Vy_B$ (B)

Note the graphical representation of L, V, & F

Eliminating "F" from (B) using (A)

$$L z_a + V z_a = L x_c + V y_B$$

$$\therefore \frac{L}{V} = \frac{y_B - z_A}{z_A - x_c} = \frac{\overline{AB}}{\overline{CA}} \qquad (C)$$

Also $$\frac{L}{F} = \frac{\overline{AB}}{\overline{BC}} = \frac{y_B - z_A}{y_B - x_c} \qquad (D)$$

Figure 4.4 also shows the "q" line where q lines are "operating lines" (that is, all possible material balances) for the system with feed composition z_A.

Note $q = \frac{L}{F}$ (liquid fraction)

$f = \frac{V}{F}$ (vapor fraction)

To derive this line ($y = f(x)$) note

Total MB: $F = V + L$ (A)

MVC MB: $Fz = Vy + Lx$ (B)

$$\therefore y = -\frac{L}{V} x + \frac{F}{V} z \qquad (E)$$

Note $\frac{L}{V} = \frac{1-f}{f} = \frac{q}{1-q}$

∴ we can also write

$$y = -\left(\frac{1-f}{F}\right)x + \frac{z}{f} \qquad (F)$$

and $$y = -\left(\frac{q}{1-q}\right)x - \left(\frac{1}{1-q}\right)z \qquad (G)$$

Equations (E), (F) and (G) are equivalent.

Note the q-line can be drawn from the knowlege of any two of the following four conditions:

(1) Slope For example $-\frac{L}{V}$

(2) y-int " " $\frac{F}{V}z$ (set $x=0$)

(3) x-int " " $\frac{F}{L}z$ (set $y=0$)

(4) $x=y=z$ (point on diagonal).

Notice the q-line says where any system can exist with given L, V etc and the equilibrium data says how phase compositions must exist at equilibrium.

∴ The intersection represents the behavior of a particular system under particular conditions.

3-8

Another important relationship which concerns x-y diagrams is for systems with constant relative volatility.

That is $\alpha_{AB} = \frac{K_A}{K_B} \neq f(T) = \text{const}$

since K_A & K_B <u>are</u> strong functions of temperature only systems with similar temperature dependency will "cancel"

This is true generally for relatively close (narrow boiling point difference) binary mixtures with similar structure.

For example: C4 with C5

Under these circumstances we can show

$$y_A = \frac{\alpha_{AB}\, x_A}{1 + x_A(\alpha_{AB} - 1)} \qquad (4\text{-}8)$$

Hence by assuming values for x_A, y_A can be directly determined.

The shape of these curves is shown in Figure 4.5 [3-8a] (p 173).

3-9

One particular type of non-ideality is where the relative volatility of the pair of components "flips". That is,

MVC $\leftrightarrow$ LVC.

This is true for several important systems (i.e., EtOH - water)

At the point of "exchanging roles" both phases have the same chemical potential (equal volatility) and are hence inseparable at these conditions.

Such systems at these conditions are called homogeneous azeotrope (1L) or heterogeneous azeotrope (2L) with V.

Figure 4.6 (p174) [3-9a] shows the isopropyl ether - isopropyl alcohol system which has a minimum boiling point azeotrope (ie, a composition exists with boiling point less than either pure component.

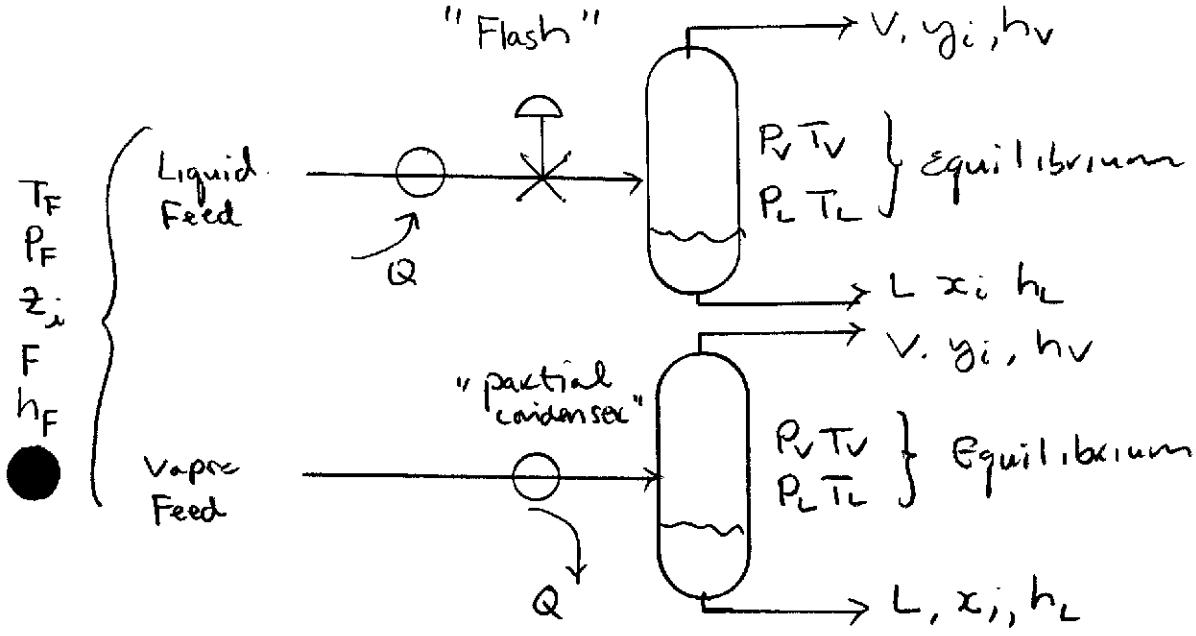
3-10

Figure 4.7 (p175) [3-10a] shows the acetone-chloroform system which has a maximum boiling point azeotrope.

Finally Figure 4.8 (p 176) [3-10b] shows a heterogeneous azeotropic system where 3 phases can coexist. The azeotropic composition is at point "C" in this case (water, n-butanol)

4.4 Bubble point and Dew point calculations.

There a two methods to easily produce the two phases necessary for separation.



3.11

Figure 4.10 shows that (see Table 4.3)

$2C+5$ equations apply

$3C+10$ variables

$(F, V, L, z_i\ y_i\ x_i\ T_F\ T_V\ T_L\ P_F\ P_V\ P_L, Q)$

Assume we are generally given

$F, z_i, T_F, P_F \quad (C+3)$

Then generally the following situations can be studied

variables specified in problem		solution type
T_V, P_V	Isothermal flash	
$V/F=0, P_L$	Bubble point temperature	
$V/F=1, P_V$	Dew " "	
$T_L \quad V/F=0$	Bubble point pressure	
$T_V \quad V/F=1$	Dew " "	
$Q=0 \quad P_V$	Adiabatic Flash	
Q, P_V	Non-adiabatic Flash	
$V/F, P_V$	Percent vaporization Flash	

Many of the methods to be discussed require Trial & Error techniques (TE).

The method of Rachford and Rice (RR) are frequently employed.

3-12

RR assumes $K_i \neq f(x_i)$ only $f(T, P)$

Start w/ $F z_i = L x_i + V y_i$

since $y_i = K_i x_i$

$$\therefore x_i = \frac{F z_i}{L + V K_i} \qquad (H)$$

but $L = F - V$

$$\therefore x_i = \frac{F z_i}{F - V + K_i V} = \frac{z_i}{1 + (K_i - 1) V/F} \qquad (I)$$

$$\therefore y_i = \frac{K_i z_i}{1 + (K_i - 1) V/F} \qquad (J)$$

Apply this to all components $i = 1, \ldots C$

and note $\Sigma x_i = 1 \quad \Sigma y_i = 1 \qquad (K)$

For simplex notation $\psi = V/F$ [psi]

Using (I) (J) (K)

$$1 = \Sigma \frac{z_i}{1 + (K_i - 1)\psi} \qquad (L)$$

$$1 = \Sigma \frac{K z_i}{1 + (K_i - 1)\psi} \qquad (M)$$

Setting up (L)-(K)

$$0 = \sum_{i=1}^{C} \frac{z_i (1 - K_i)}{1 + \psi (K_i - 1)} \qquad (RR)$$