الجامعة التكنولوجية

قسم الهندسة الكيمياوية

المرحلة الثالثة

انتقال كتلة

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Distillation

① Introduction:-

Distillation is the technique of separation of the more volatile component from the less volatile ones in a feed solution by partial vaporization of the feed followed by condensation.

The vapor produced is richer in the more volatile component. The distribution of the components in the phases is governed by the vapor-liquid equilibrium relation ship.

The more volatile components move from the liquid to the vapor phase, and the less volatile move from the vapor to the liquid phase

The function of distillation may be:-

- Separation of products from a mixture, separation of aniline and netrobenzene.
- Recovery of products, recovery of ethanol from its solution in water.
- Increasing the purity of a product, drying of benzene to remove any trace of water.

Because of its importance and wide use in separation of mixtures, distillation is called "The work horse" of chemical engineering, or chemical industries.

- The main difference between distillation and evaporation is that in evaporation a solution containing a volatile solvent and a non volatile solute or a solute having a very low volatility (sugar (non votalite solute) , Water (volatile solvent)) .

Schematic of a typical distillation column is shown in Figure below :-

There are two main types of mixtures :-

1- Binary mixture, consist of two components only.
2- Multi-component mixture, for more than two components

- Bubble point :- temp. cause first bubble on the liquid surface to appear. It is a characteristic for mixture and compounds.

- Boiling point :- temp. at which vap. press. equal to atm. press. It is a characteristic for pure substance like $\rho, \mu, \ldots$

Separation of a mixture by distillation is based on equilibrium distribution of the components between the liquid and vapor phases. Therefore vap.-liq. equilibria is essential in distillation.
Distillation always used when there is difference in boiling points and volatility.

$$\text{Volatility } (\alpha_A) = \frac{P_A}{x_A} = \frac{y_A \cdot P_T}{x_A}$$

for two components (A, B) to be seperated

$$\alpha_A \neq \alpha_B .$$

$$\text{Relative Volatility } (\alpha_{AB}) = \alpha = \frac{\alpha_A}{\alpha_B} = \frac{y_A \cdot x_B}{y_B \cdot x_A}$$

for high (α_{AB}), distillation become easier.

when $\alpha_A = \alpha_B$, Special treatment is used, that is called " extractive-distillation".

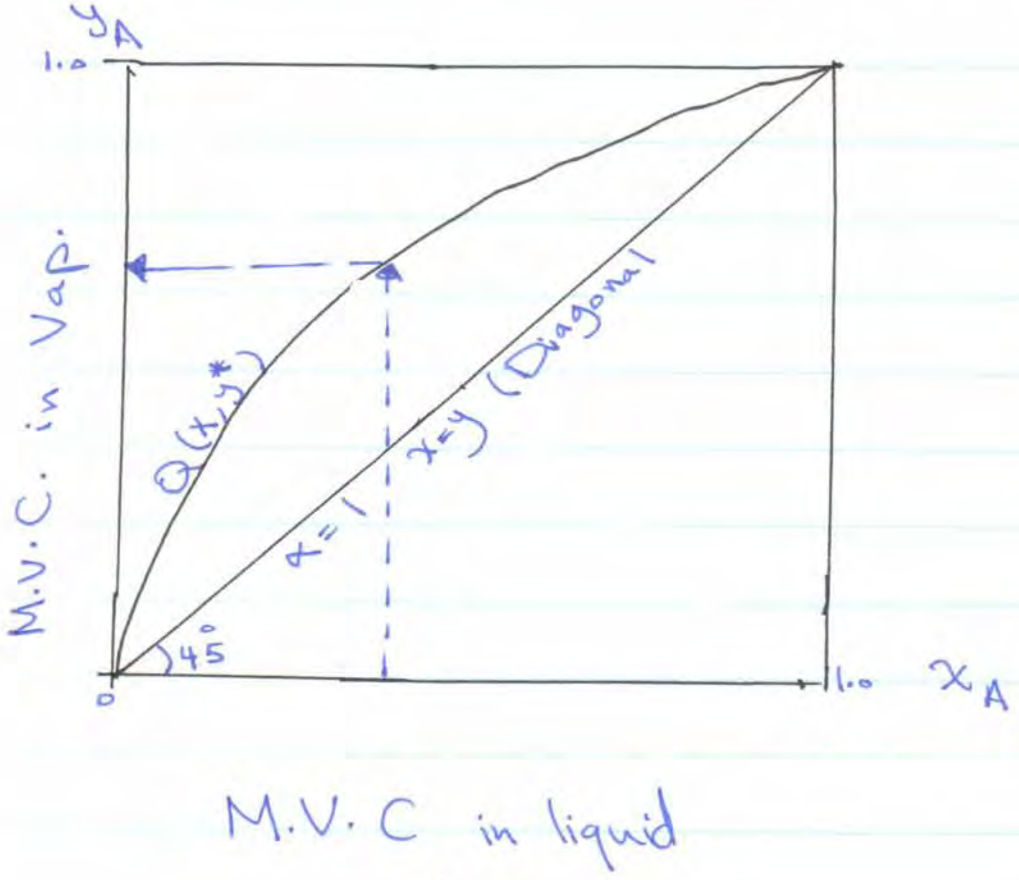
* if $\alpha_{AB} > 1.0$ then (A) is the M.V.C

if $\alpha_{AB} < 1.0$ then (A) is the L.V. C

② Vapour - liquid Equilibria (VLE) :-

هي دالة تعطينا تركيز البخار الذي هو في حالة توازن مع كل تركيز
من تراكيز السائل المتكون من المادتين (A , B).
دائماً تؤخذ عند ضغط ثابت . وهي التي تحدد نوع عملية التقطير
الذي سيتم استخدامها بالإضافة الى عامل (α_{AB}).
الرسم البياني ادناه هو (Vap. Liq. Equil^m) مشتق من
رسم بياني ثاني يدعى (Boiling point diagram)

M.V.C : more volatile Comp. (Less boiling point)
L.V.C : Less volatile comp. (higher boiling point)



③ Boiling Point Diagram

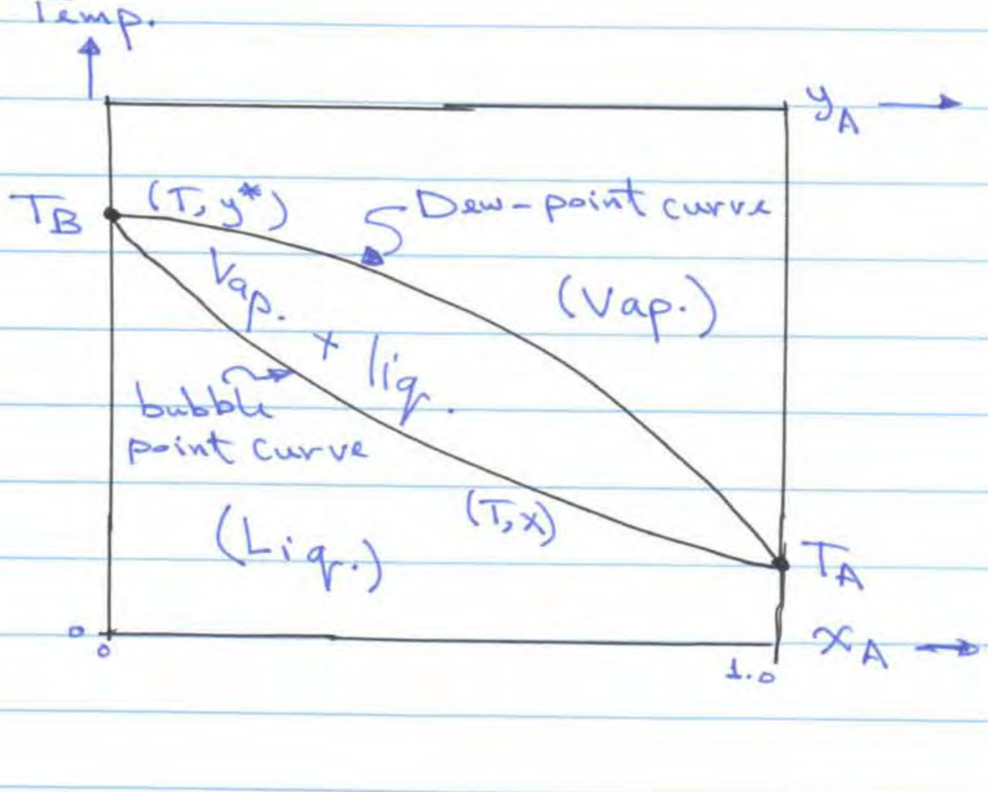
① عند ثبوت الضغط :-

المنحنى الأسفل يوضح لنا درجات الغليان لتراكيز مختلفة من السائل. أي اختلاف في التركيز سيغير درجة الغليان.

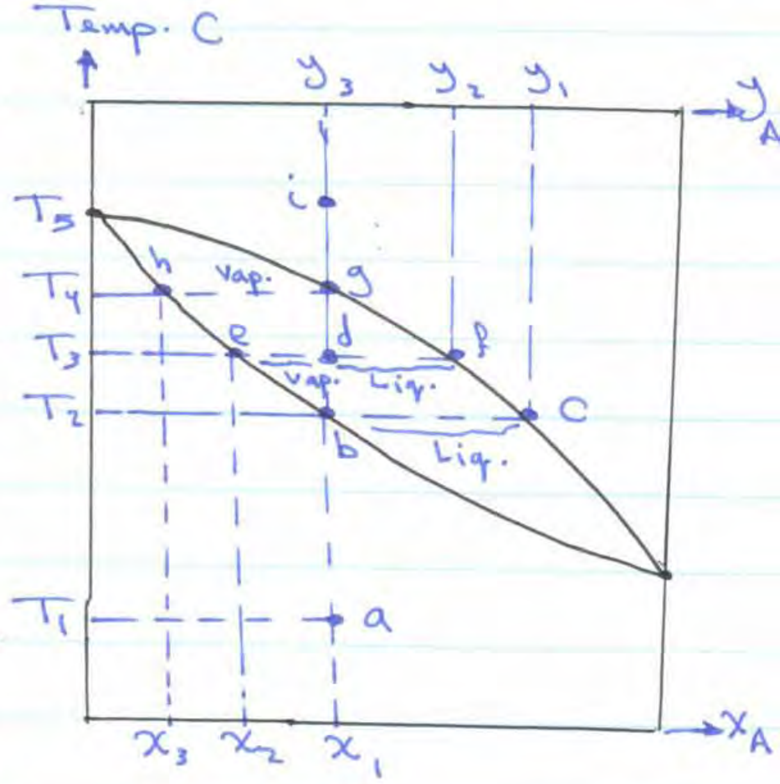
(T_A) درجة غليان المادة (A) النقية.

(T_B) درجة غليان المادة (B) النقية.

المنحنى العلوي يعطي درجة الحرارة التي يبدأ بها الغاز بالتكثف.
كلا من المنحنيات يلتقيان في (T_a)، (T_B) لأن المادة النقية لها درجة غليان تساوي درجة التكثف.
كل نقطة أسفل المنحنى الأسفل تكون في طور سائل.
كل نقطة أعلى المنحنى الأعلى تكون في طور بخار.
بين المنحنيين هناك مزيج من البخار والسائل.



لو عندنا سائل معين بدرجة حرارة معينة ونبدأ بتغيير درجة الحرارة تدريجيا.



- الآن لو نفرض عندنا سائل بدرجة حرارة (T_1) وتركيز (X_1) النقطة ⓐ.
- الآن لو رفعنا درجة الحرارة من (T_1) الى (T_2) فهو يبقى في الحالة السائلة حتى نصل الى نقطة (B). حيث تظهر اول فقاعة بالظهور على سطح السائل وتركيزها في الطور البخاري (y_1). النقطة ⓒ تركيز اول فقاعة من البخار.
- الآن نرفع الحرارة حتى نقطة ⓓ بدرجة حرارة (T_3)، حيث تزداد كمية البخار ويصبح لدينا مزيج من السائل والبخار، تركيز السائل نحدده في النقطة ⓔ بتركيز (x_2)، وتركيز البخار بالنقطة ⓕ ويكونا (y_2).

أول فقاعة ظهرت في (b . c) وتقل كلما ارتفعنا الى الاعلى.

$$\frac{liq.}{vap.} = \frac{dF}{de}$$ where F = vapor (sat.), e = liq. (sat.)

(Enthalpy of liq. & vap.) at equilibrium

- The line (ef) is called "Tie - line"

- section length / section length ed or

$\frac{df}{de}$ is called "Lever - arm rule" (Flash vaporization)

- رفع درجة الحرارة الى النقطة (g)، هنا السائل يتبخر كله ويحدث عندنا تبخر تام، والنقطة (h) تمثل تركيز اخر قطرة من السائل تتبخر.

- رفع درجة الحرارة حتى الوصول الى النقطة (i) يصبح لدينا حالة (Super-heated-vapour) مع ملاحظة ان تركيز البخار فقط يساوي تركيزه في (g).

* الان لو عندنا بخار ونريد ان نكثفه تدريجيا :-

- عندنا بخار في (T_5) وتركيزه (x_1). لو قللنا الحراره الى (T_4) عند نقطة (g) حيث تمثل اول قطره تتكثف الى سائل تركيزها عند (h).

- نقلل الحرارة الى (T_3) عند النقطة (d)، يستمر البخار بالتكثف ونظهر لدينا مزيج من البخار والسائل لان التبريد غير كافي لتكثيف كل البخار.

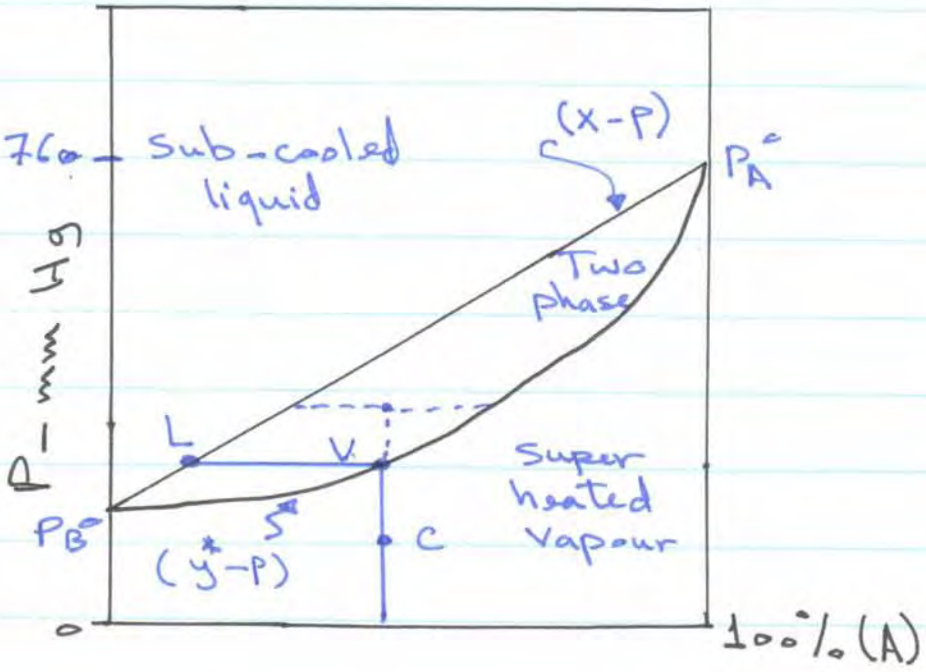
- عند (b) يتحول كل البخار الى سائل ويحدث عندنا فقط سائل :-
(Total condensation)

- الان لو استمرينا لغاية (T_1) نحصل على تركيز ثابت والعملية هي
(sub-cooled liq.)

- من الحالتين المذكورتين السابقتين هنالك خمس حالات للـ feed ظهرت عند استخدامه :-

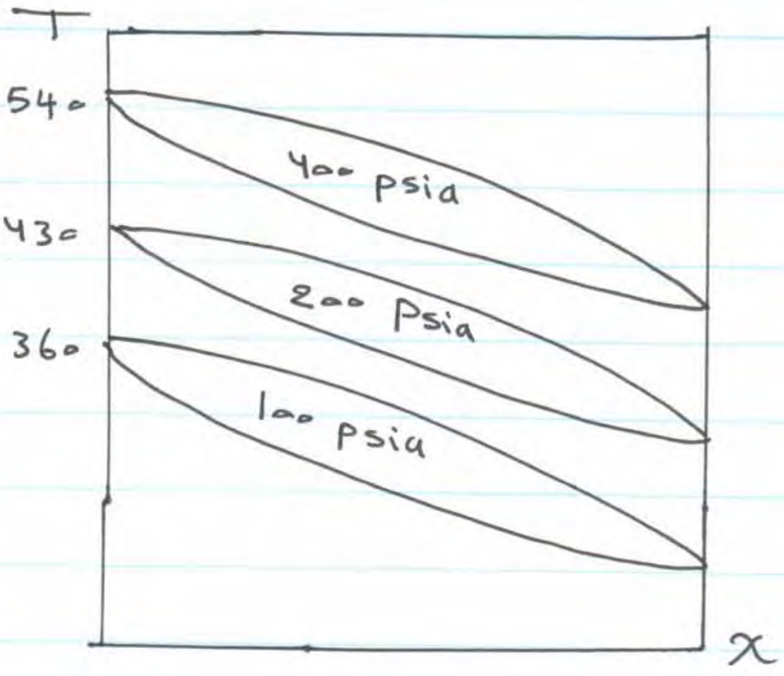
1- sub-cooled, 2- at bubble point
3- partial vaporized, 4- dew point,
5- super heated.

(ج) عند ثبوت درجة الحرارة :-



L: first drop of liquid appear after compression

Effect of pressure on boiling point diagram.



Increasing the pressure will cause the two lines to become closer and closer

How to Find (Vap. – Liq. Equilb^{m}. data) anatylically.

① Raoult's Law (for liq. mixture)

- for component (A) :-

$P_A = P_A^{\circ} \cdot x_A$

where :- P_A° : vap. press

P_A = parti. press

x_A = molefraction in liq. phase

- for component (B) :-

$P_B = P_B^{\circ} \cdot x_B$

- For a binary mixture :-

$$\boxed{x_A = \frac{P_T - P_B^{\circ}}{P_A^{\circ} - P_B^{\circ}}} \text{ ------ (1)}$$

H.W :- Try to find the above relation.

② Dalton's Law (ideal gas)

$P_T = \sum P_i$

for a binary mixture :-

$P_T = P_A + P_B$

$\because P_A = y_A \cdot P_T$

$P_A = P_A^{\circ} \cdot x_A$

$$\boxed{\therefore y_A = \frac{P_A^{\circ} \cdot x_A}{P_T}} \text{ ------ (2)}$$

③ Using relative - volatility (α_{AB}) or (α)

$$\therefore \alpha_{AB} = \frac{y_A \cdot x_B}{y_B \cdot x_A} = \frac{y_A(1-x_A)}{(1-y_A)\cdot x_A}$$

$$\therefore \boxed{y_A = \frac{\alpha \cdot x_A}{1+x_A(\alpha-1)}} \text{ --- } ③$$

$$\boxed{x_A = \frac{y_A}{\alpha-(\alpha-1)\,y_A}} \text{ --- } ④$$

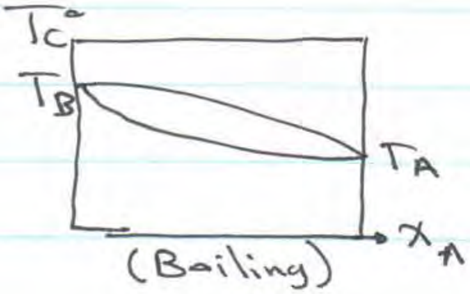
④ Using equilib^m constant (k_i) (Henry's Law) or (equilib^m vaporiz^n ratio) or (distill^n. coeff.)

$$P_A = H\,x_A \Longrightarrow y_A = \frac{H}{P_T}\,x_A$$ (for hydrocarbon mixture)

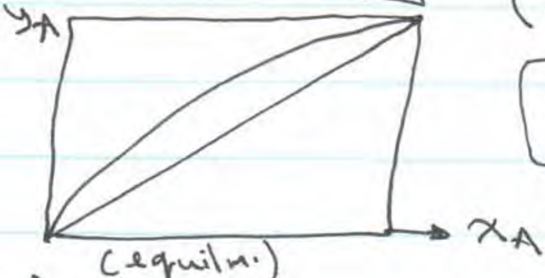
$$\boxed{y_A = k_A \cdot x_A}$$ where then $$\boxed{k_A = \frac{y_A}{x_A}}$$ (for multi-component mixture).

k = called (k) value, it is function of (T) and (P).

for ideal system $$\boxed{\alpha_{AB} = \frac{k_A}{k_B}}$$



(Boiling)



(equiln.)

(Typical system)

$$\boxed{x_A = \frac{1-k_B}{k_A-k_B}}$$

$$\boxed{y_A = \frac{k_A - k_A k_B}{k_A - k_B}}$$

Notes For multicomponent system :-

① if $\sum P_i < P_T$ liq. is sub cooled, below B.Pt
if $\sum P_i > P_T$ " " super heated, above B.Pt

② $y_i = k_i x_i$
③ if $\sum y_i = 1.0$ liq. at bubble Pt.

④ if $\sum y_i < 1.0$ liq. is sub cooled.
⑤ if $\sum y_i > 1.0$ liq. is super heated

⑥ if $\sum y_i / k_i = 1.0$ at dew-point-vap.

⑦ if $\sum y_i / k_i < 1.0$ vap. is super heated
⑧ if $\sum y_i / k_i > 1.0$ sub cooled

⑨ Some times, it is required to calculate (P_i°) if it is not given.

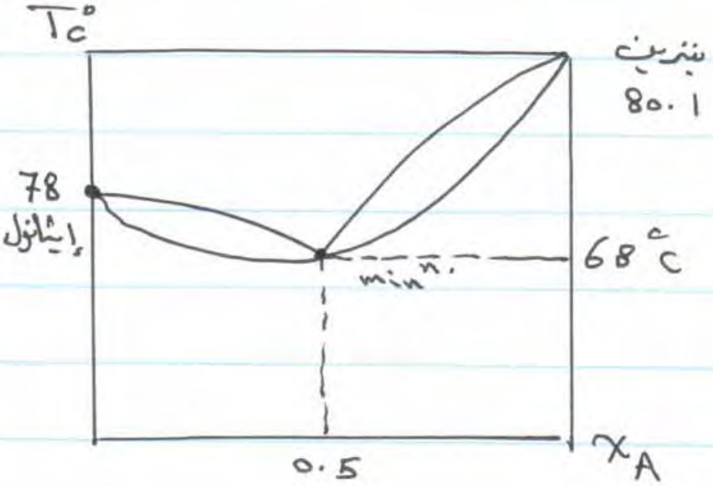
$$\boxed{\ln P_A^\circ = A - \frac{B}{C+T}}$$ Antoine-equation

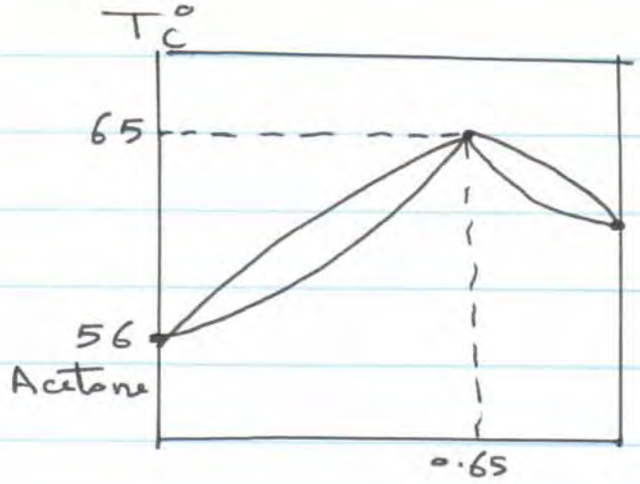
where :- P_A° in mmHg.
T in °C.
(A, B, c) are constants.

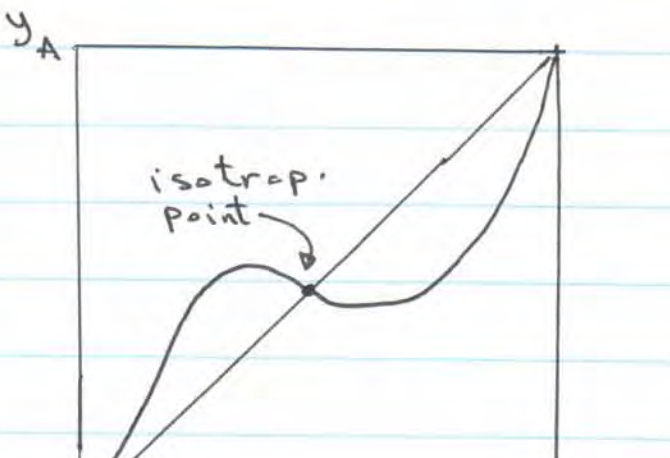
Deviation from ideality and formation of Azeotropes

Deviation from ideality may be of two types :-

- Positive - deviation, causing min$^{m.}$ boiling azeotropes
- Negative - deviation, causing max$^{m.}$ 〃 〃







Case ①:
Benzene - Ethanol
system

Case ②:
Acetone - chloroform
system

Ex.:- Calculate and plot the boiling point and equilib^{m}. diagrams of the system of benzene-toloune at total press. of 1 atm. Assuming all mixtures are ideal mixtures. The vap. press. data of the system as f

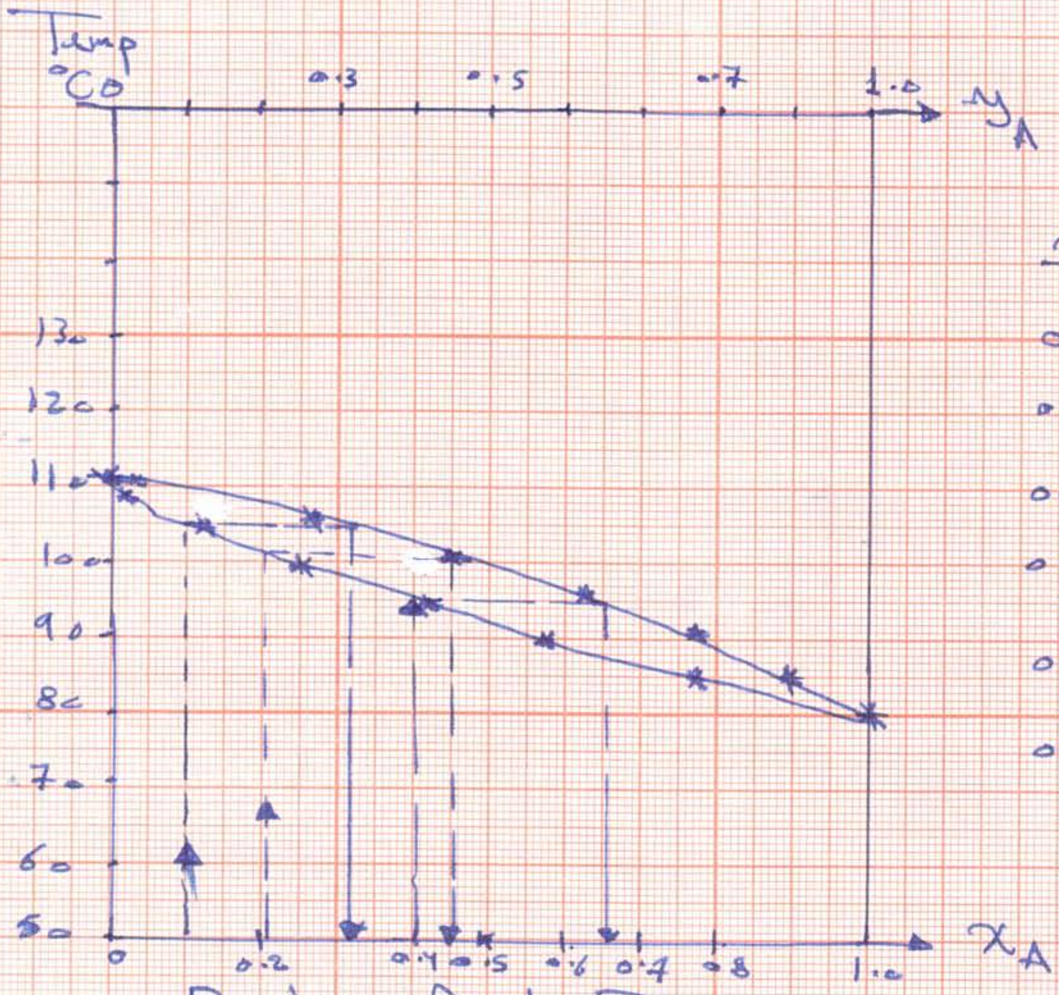
Temp. °C	P_A° (Benzene)	P_B° (Toloune)
80.1	760	300
85.0	877	354
90.0	1016	405
95.0	1168	475
100.0	1344	557
105.0	1532	645
110.0	1748	743
110.6	1800	760

Sol.:- $P_T = 1 \text{ atm} = 760 \text{ mm Hg}$.

$$x_A = \frac{P_T - P_B^\circ}{P_A^\circ - P_B^\circ} \quad , \quad y_A = \frac{P_A^\circ \cdot x_A}{P_T}$$

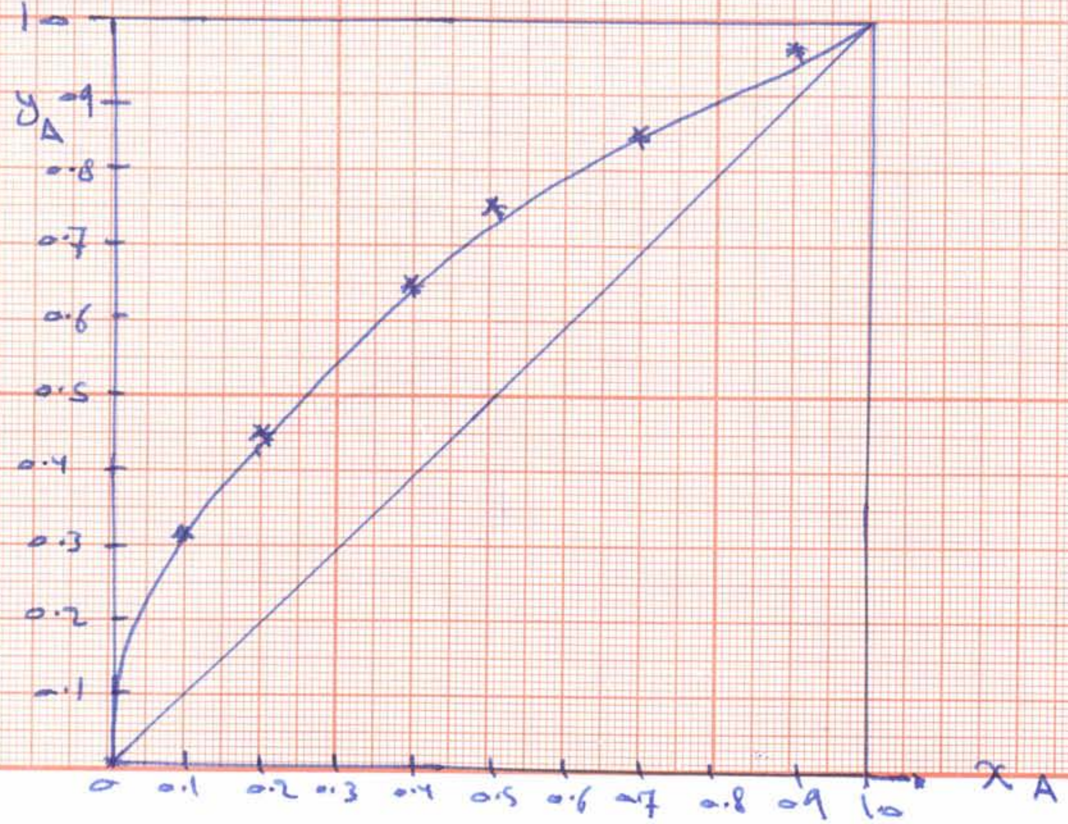
Temp.	x_A	y_A
80.1	1	1
85.0	0.782	0.90
90.0	0.581	0.77
95.0	0.411	0.63
100.0	0.25	0.45

Temp.	x_A	y_A
105.0	0.12	0.24
110.0	0.016	0.038
110.6	0.0	0.0



Boiling Point Diagram

x_A	y_A
0.1	0.31
0.2	0.45
0.4	0.65
0.5	0.75
0.7	0.85
0.9	0.96



V.L.E

Distillation Processes

Distillation processes can be classified according to:-

A- Type of separation method
  1- Differential distillation.
  2- Flash or equilibrium distillation.
  3- Rectification distillation.

B- Number and type of component.
  1- Binary distillation
  2- Multicomponent distillation.
  3- Complex distillation.
  4- Azeotropic and extractive distillation.

C- Operating design and conditions.
  1- Batch distillation.
  2- Continuous distillation.
  3- Vacuum distillation.
  4- Steam distillation.

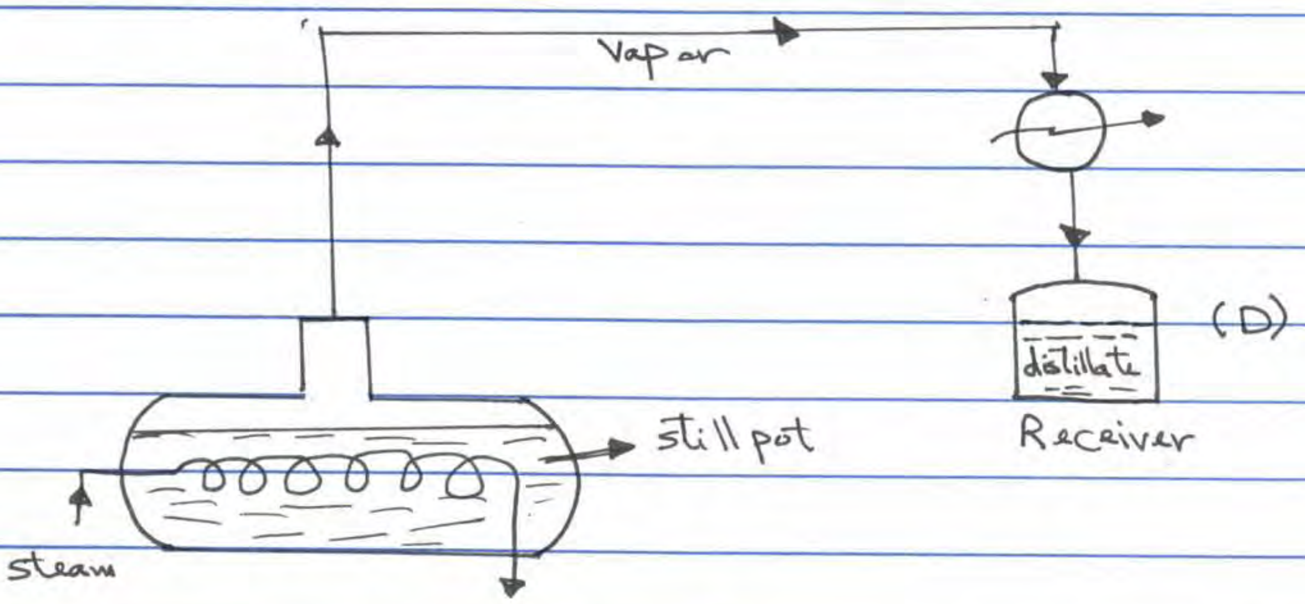
1- Differential Distillation (Batch).

Feed is charged to the still pot to which heat is supplied continously through a steam jacket or a steam coil. As the mixture boils, it generates a vapor richer in the M.V.C. But as boiling contianuse, concentrations of M.V.C in the liquid decrease. It is generally assumed that equilib" vaporization occurs in the still. The vapor is led to a condenser and the condensate or top product is collected in a receiver.

At the beginning, the condensate will be rich in the M.V., but the concentrations of the M.V in it will decrease as the condensate is usually withdrawn intermittently having products or cuts of different Concentrations.

Batch distillation is used when the feed rate is not large enough to justify install" of a continous distillation unit

The schematic of a batch distillation setup is shown belo



Batch or Differential or Rayleigh distill^{n}.

Overall M.B.:-

$F = D + W$ ---- ①

No. of moles present in the still = No. of moles in Vapor + No. of moles in residue

$$F * x = dF * y + (F - dF)(x - dx) \quad \text{--- ②}$$

where :- F = No. of moles of a mixture in the still.
x = mole fraction in liq. phase.
y = " " " Vapor phase.
dF = amount of liquid vaporize at any time.
(F-dF) = amount of residue.
(x-dx) = mole fraction of residue.

$$\cancel{F\cdot x} = y\,dF + \cancel{xF} - x\,dF - F\,dx + \cancel{dx\,dF} \rightarrow \text{Small}$$

$$F\,dx = (y-x)\,dF$$

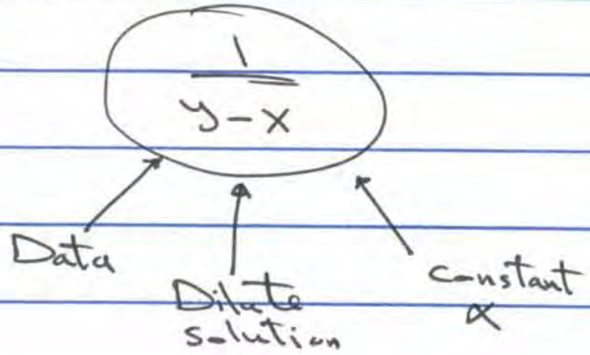
$$\frac{dF}{F} = \frac{dx}{y-x} \Rightarrow \int_{F}^{W} \frac{dF}{F} = \int_{x_f}^{x_w} \frac{dx}{y-x}$$

$$\boxed{\ln \frac{W}{F} = \int_{x_f}^{x_w} \frac{dx}{y-x}} \text{ ——— ③ (Rayleigh Eq.)}$$

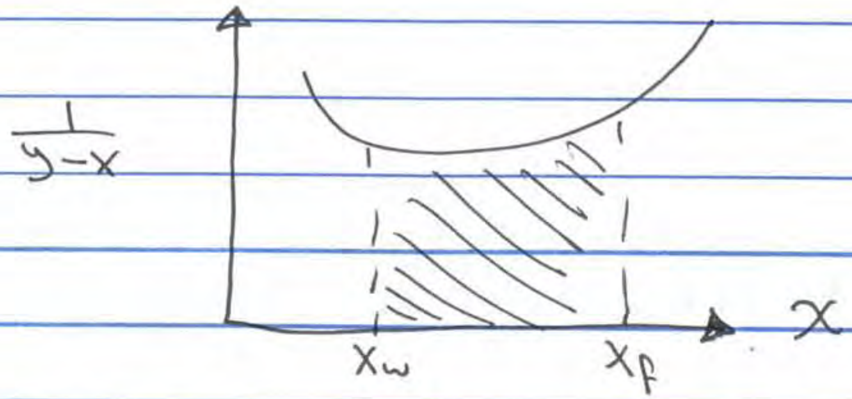
For the R.H.S term :-

the relation between (y) and (x) is an equilibrium relation, So :-

* $y = m.x$
* $y = k.x$
* data (x, y)



① if the equilibrium data are known, then by plotting $\frac{1}{y-x}$ vs. (x) and getting area under curve.



② For dilute solution where

$$y = m x$$

$$\boxed{\left(\frac{W}{F}\right)^{m-1} = \frac{x_w}{x_f}} \quad \text{———} \quad (4)$$

③ For mixture of constant (α)

$$y = \frac{\alpha . x}{1 + (\alpha - 1) x}$$

$$\therefore \int \frac{dx}{y - x} = \int \frac{dx}{\dfrac{\alpha . x}{1 + (\alpha - 1) . x} - x}$$

$$= \int \frac{1 + (\alpha - 1) x}{(\alpha - 1)(x - x^2)} dx$$

$$= \underbrace{\int \frac{dx}{x (\alpha - 1)(1 - x)}}_{\text{Solved by Partial fractions}} + \underbrace{\int \frac{\cancel{(\alpha - 1)} \cancel{x}}{\cancel{x} \cancel{(\alpha - 1)} (1 - x)} dx}_{\nwarrow \ \ln \frac{1}{1 - x}}$$

$$\boxed{\therefore \ln\left(\frac{W}{F}\right) = \frac{1}{\alpha - 1} \ln\left(\frac{x_w (1 - x_f)}{x_f (1 - x_w)}\right) + \ln\left(\frac{1 - x_f}{1 - x_w}\right)}$$

↰ for constant (α) ↑ (5)

Ex.(1) :- 1000 kg of mixture containing 60% wt of ethanol and 40% wt of water, is subjected to batch distill^n. (1 atm) to produce a residue concentration of 5% wt. ethanol. Calculate

1- A mount of distilled and residue (D, W).
2- Composition of total distilled obtained (X_D or y_D)

V.L.E. for (ethanol - H_2O) system at 1 atm is :-

$\bar{x}$:	0.025	0.05	0.1	0.2	0.3	0.4	0.5	0.6	0.7
$\bar{y}$:	0.225	0.36	0.516	0.655	0.71	0.74	0.76	0.78	0.81

Sol. :- $F = 1000\ kg$, $x_f = 0.6$, $x_w = 0.05$

$$\ln \frac{W}{F} = \int_{x_f}^{x_w} \frac{dx}{y - x}$$

From equilibrium data : $(1/\bar{y} - \bar{x})$ was calculated

$(1/\bar{y} - \bar{x})$:	5.0	3.22	2.4	2.2	2.4	2.9	3.7	5.8	9.1

To plot, we will use simple rule :-

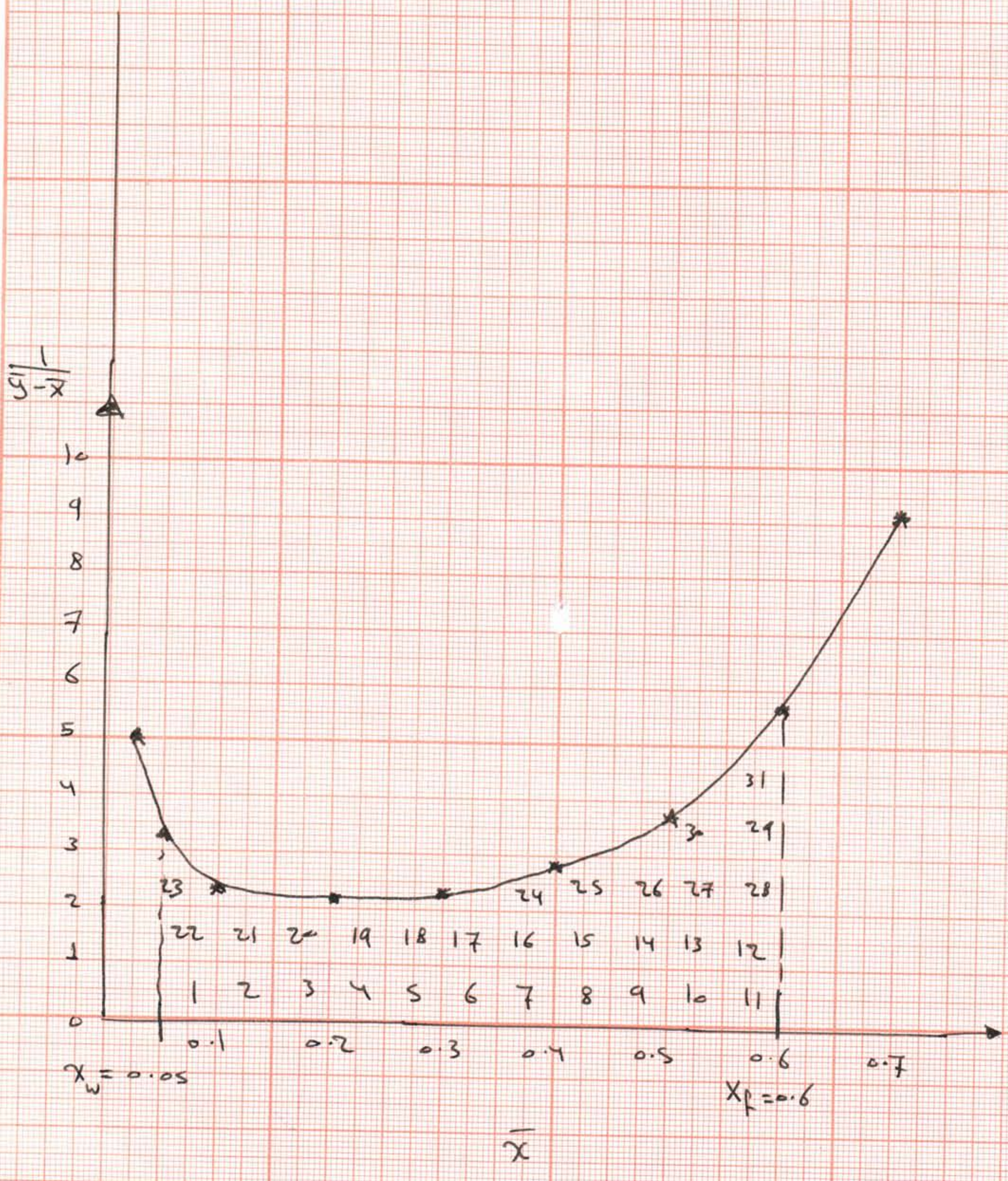
Let $n = 6$, $h = (x_f - x_w)/n \Rightarrow h = \frac{0.6 - 0.05}{6} = 0.09$

Area under - curve from (0.6) to (0.05)

$$Area = (h/3) * \sum y$$

$$A = \frac{0.09}{3} * 31 \Rightarrow \boxed{A = 0.93 = \int \frac{d\bar{x}}{\bar{y} - \bar{x}}}$$

$$\ln \frac{W}{F} = -0.93 \Rightarrow \frac{W}{1000} = 0.394$$


$\frac{1}{\bar{y}-\bar{x}}$
0
1
2
3
4
5
6
7
8
9
10
0.1
0.2
0.3
0.4
0.5
0.6
0.7
$x_w = 0.05$
$X_f = 0.6$
$\bar{x}$
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31

$W = 394$ kg

Distillate $(D) = 1000 - 394 = 606$ kg

2- To find distillate composition :-

$1000 * 0.6 = 606 * x_D + 394 * 0.05$

$600 = 606 * x_D + 19.7$

$606\, x_D = 580.3$

$x_D = 0.957$

Ex.(2) :- A charge of 50 kmol of a mixture of benzene and chlorobenzene, having 55 % of the L.V. is to be batch distillation.

- If 25 moles of the solution is vaporized and condensed as the distillate, Calculate the conc". of accumulated distillate.
- If the concentration of the accumulated product is found to be 72 mol % benzene, calculate its amount.

Take $(\alpha_{Benzene}) = 4.15$

Sol. :- $F = 50$ kmol

$x_f = 1 - 0.55 \Rightarrow x_f = 0.45$

ⓐ 25 Mole to be vaporized $\therefore D = 25$ kmole

$F = D + W \Rightarrow W = 25$ kmole

To find x_D ($y_{av.}$)
using eq. (5) to find x_w

$$\ln\left(\frac{W}{F}\right) = \frac{1}{\alpha - 1} \ln\left(\frac{x_w(1-x_f)}{x_f(1-x_w)}\right) + \ln\left(\frac{1-x_f}{1-x_w}\right)$$

$$\ln\left(\frac{25}{50}\right) = \frac{1}{4.15-1} \ln\left(\frac{x_w(1-0.45)}{0.45(1-x_w)}\right) + \ln\left(\frac{1-0.45}{1-x_w}\right)$$

$$-0.7 = 0.32 \ln\left(\frac{0.55\, x_w}{0.45(1-x_w)}\right) + \ln\left(\frac{0.55}{1-x_w}\right)$$

$$\boxed{\therefore x_w = 0.218}$$

From M.B., x_D can be found.

$F \cdot x_f = D \cdot x_D + W * x_w$

$50 * 0.45 = 25 * x_D + 25 * 0.218$

$\therefore x_D = y_{av.} = 0.682$

ⓑ if $y_{av.} = x_D = 0.72$, find (D)

$F = D + W \Rightarrow 50 = D + W \Rightarrow \boxed{D = 50 - W}$

From M.B. :-

$F * x_f = D * x_D + W * x_w$

$50 * 0.45 = D * 0.72 + W * x_w$

sub. for (D) $22.5 = 0.72(50 - W) + W * x_w$