Separation processes I

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Mass Transfer: Separation processes Operations

Introduction

A large number of unit operations are used in the separation of a substance into its component parts. They involve a change in composition of mixtures and solutions. The changes are mostly in nature.

Separations involve a non-spontaneous process because it reverses the process of mixing. Separation decreases the entropy of the system, and a separating agent (energy , mass or membrane) must be used to carry out the process.

Separation of mixtures may be mechanical in nature: filtration, sedimentation, etc.

Separation of solutions involves mass transfer operations characterized by the transfer of a substance through another on a molecular scale. These operations are interphase mass transfer processes involving the creation of a second phase by the addition of an energy-separating agent (ESA) or by a mass separating agent (MSA).

* why the separations process be non-spontaneous ?!

because it reverse the process of mixing.

* Separating agent (عوامل الفصل)

mass separating agent (MSA)

energy agent (ESA)

The main separation techniques are:

- **Phase creation**

  Most common industrial technique. A second phase is created which is immiscible with the feed. This is done by increasing or decreasing the temperature or pressure on the feed

  * تتم عملية الفصل عن طريق خلق طور جديد غير قابل للامتزاج مع الـ mixture feed

- **Phase addition**

  Involves the introduction of a solvent to the system which selectively solvates one component of the feed

  * إضافة مذيب آخر إلى الـ mixture يفصل الخليط عن بعضه عن طريق إذابة أحد مكونات الخليط عن غيره.

- **Barrier separation** ⇒ فصل الحاجز

  Increasingly important. Barrier selectively transports one species relative to another across the membrane

  يتم الانتقال من phase لأخرى عن طريق membrane يفصل بين الـ 2 phases

- **Solid agent separation**

  Solid particles are added to the feed which are either inert and carry substances using separation; or react with the feed to cause separation

  * يتم إضافة مواد صلبة مثل الـ activated carbon يعمل عملية ادمصاص (adsorption) لبعض الغازات العالقة على سطحه ويمرر الغاز النقي

- **Separation by force field**

  Common in laboratory and for specialized separations and involves the use of electric and magnetic fields to preferentially move one species over another

  قوة الطرد المركزي ← تعتمد على الـ density

*ex : phase addition:

mixture ⇒ water + Acetone

يتم فصل الـ Acetone عن طريق إضافة مذيب آخر وهو (Toluene) حيث تكون ذائبية الـ Acetone في الـ Toluene أكبر من ذائبيته في الماء.

* ex : Barrier separation:

غسيل الكلى يتم بطلعوا دم من جسم الانسان ويمرروا في فلاتر، يكون الدم من جهة ومن الجهة الأخرى للفلاتر يوجد سائل آخر (ماء + تركيز معينة من الأملاح)، ينتقل السموم من الدم عبر الفلتر إلى السائل (ماء + أملاح)

* الهدف من إضافة بعض الأملاح مع الماء حتى لا تنتقل أملاح من الدم إلى السائل لأن الهدف تنقية الدم من السموم فقط.

Types of Mass Transfer separation Operations

The type depends on the way different phases are contacted:

I. Direct Contact

-Phases are immiscible or partially miscible

-Most widely used and most important

-Depends on the fact that the contacted phases, consisting of several components, are initially not at equilibrium. The system tends to reach equilibrium as a result of a slow process of diffusion between the two phases.

* phases اللي عملناهم Direct contact في البداية ما بكونوا بحالة اتزان ، بكون تركيز أحد المواد في phase 1 مختلف عن تركيزه في phase 2 وهذا يولّد قوة دافعة لنقل المادة ، وبعد زمن بصل إلى حالة equilibrium .

* كل الـ systems في الطبيعة تميل لتصبح في حالة equilibrium .

- Depending on the state of the phases, the following interfaces may be distinguished:

Gas/Gas: Practically not realized (almost all gases are completely soluble).

حالات نادرة جدا لان الغازات ذائبة ببعضها

Gas/Liquid: - Distillation: all components are present in different proportions in the two phases

- Gas Absorption (or desorption): one or more components distribute between the two phases.

يتم عن طريق غسل الغاز بسائل مناسب لاحدى الغازات تذوب أو تمتص في السائل وبالتالي نوعه إذا التي عن الخليط

- Humidification (or dehumidification): one phase is pure and the other consists of two or more components

Gas/solid: - Fractional sublimation (vaporization of solid solutions (not used practically).

* sublimation ⇒ gas → solid ⇒ تسامي

عن طريق عليه ← انتقال I2 من الحالة الغازية إلى الحالة الصلبة كعمل طبقات حول بعض الأشياء.

* desorption: عملية فيزيائية يتم فيها إطلاق مادة ممتصة سابقاً من سطح تحدث عندما يكتسب الجزيء طاقة كافية للتغلب على حاجز تنشيط الطاقة الحديثة التي تبقيه في السطح

مثال : تجفيف الملابس

- Drying: not all components are present in the two phases.
- Adsorption (or desorption): Diffusion takes place from gas phase to solid phase or vice versa.

مادة صلبة مسامية ماتحت الـ microscope يظهر تجاويف تحتويها السطح تخزن الـ gas بداخلها

Liquid / Liquid: solvent extraction ⇒ exp ⇒ toluene & water + acetone

Liquid/Solid - Crystallization ⇒ بلورة ⇐ مثال : محلول مشبع بالملح حيث بعد عملية التبريد يبدأ الملح يتبلور ويترسب .

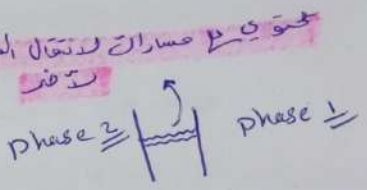
- Leaching ⇒ مثال : اختزال الماء لمادة الـ coffe الموجودة بحبيبات القهوة
" " " الشاي " " الشاي

Solid/Solid: very slow rate of diffusion within solid phases.

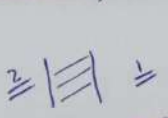
يستخدم في صناعة الرقائق عن طريق عمل شوائب imperfection ، هذه الشوائب بالحالة الصلبة وتعمل diffusion برقائق صلبة .

II) Indirect contact:

* phases are separated by a membrane



* membrane
  - porous (molecular sieves)
  - nonporous



* substances move between phases by diffusion through the membrane
* porous membranes are selective-they permit the diffusion of certain molecules.
* non porous membranes preferentially dissolve the solute or the solute and solvent which then diffuses through the membrane - the process is called permeation or dialysis.

- these operations involve different phases:

- Gas/Gas:
  - effusion-microporous membrane
  - permeation - non—porous membrane.
- Gas/Liquid - permeation processes (non-porous membranes)
- Liquid I Liquid: Dialysis - membrane permeable to solvent and dissolved substance.
- Electro dialysis - electromotive force is used to assist the diffusion process.
- Reverse osmosis (R/O) - desalination of water.

الخاصية الإسموزية هي انتقال المادة من التركيز العالي إلى التركيز المنخفض

وكلمة عكس العلية تكسر الخاصية الإسموزية (reverse) حيث تنتقل المادة

من التركيز المنخفض وهذا يتم عن طريق التأثير بضغط عالي جداً

III) Direct contact of miscible phases:

مثال: نحط محلول ما في cylinder ونبخر الـ cylinder ثم
المزيج، رح يصير اختلاف في الـ density للمحلول، الأقل كثافة
بيرتفع للأعلى والأكثر كثافة للأسفل وهيك بنحصل على الـ separation

- **Thermal diffusion** - concentration difference is created by a temperature gradient
- **Centrifugation** - separation occurs as a result of slightly different forces acting on various molecules of different masses.

الفصل باستخدام الطرد المركزي

IV) Surface Concentration:

الرغوة

Foam separation: some substances when dissolved in a liquid in contact with a gas are found to concentrate on the free surface. By forming foam on the surface of the liquid, the surface area between the gas and the liquid is increased and the solute is concentrated in the foam and can be collected at the surface.

تم العثور على بعض المواد الذائبة في liq معين، عند عمل contact بين الـ solute والـ gas تتركز هذه المواد
على السطح الحر، عن طريق تكوين رغوة على سطح الـ liq، وتزداد مساحة السطح بين الـ liq و الـ gas
وتتركز هذه المواد في الرغوة ويمكن جمعها عن السطح.

2. Phase Equilibrium

توازن ديناميكي ⇒ net transfer = 0

2.1 Review of relations for gaseous mixtures:

Partial Pressure: (P_i)

In a mixture of different gases the molecules of each gas are distributed throughout the available space and their motion contributes to the total pressure of the system.

The partial pressure of a component gas that is present in the mixture is the pressure that would be exerted by that component if it were present alone in the same volume and at the same temperature as the mixture.

* حركة الغاز في الخليط تؤدي إلى تصادم مع جدران الحاوية وهذا يولد pressure force ، الضغط الذي يتسبب فيه كل غاز في الخليط يسمى Partial pressure (كأنه غاز في الحاوية لوحده)

gas A ○ | gas B △

For an ideal gas: $P_i = n_i \frac{RT}{V}$; V : total volume

(P_i ← partial pressure of i)

Pure component volume: V_i

The pure component volume of a component gas that is present in a mixture of gases is the volume that would be occupied by that component if it were present alone at the same temperature and pressure as the mixture.

For an ideal Gas $V_i = n_i \frac{RT}{P}$; P : total pressure

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Relation between Partial pressure, pure component volume and mole fraction:

$$\frac{P_i}{V_i} = \frac{n_i(RT/V)}{n_i(RT/P)} \Rightarrow \frac{P_i}{P} = \frac{V_i}{V}$$

$$\frac{P_i}{P} = \frac{n_i(RT/V)}{n(RT/V)} \Rightarrow \frac{P_i}{P} = \frac{n_i}{n}$$

$$\Rightarrow \frac{P_i}{P} = \frac{V_i}{V} = \frac{n_i}{n} = y_i$$

$$\frac{P_i}{V_i} = \frac{P}{V} \Rightarrow \frac{P_i}{P} = \frac{V_i}{V}$$

Dalton's Law of Partial Pressures:

The total pressure exerted by a gaseous mixture is equal to the sum of the partial pressures of the components present in the mixture:

$$P = \sum P_i$$

Amagats Law:

$$P_{tot} = n_1 \frac{RT}{V} + n_2 \frac{RT}{V} + \cdots = \frac{RT}{V}(n_1 + n_2 + \cdots) = \frac{RT}{V} n_{tot}$$

The total volume occupied by a gaseous mixture is equal to the sum of the pure component volumes.

$$V = \sum V_i$$

Vapor pressure:

A vapor is a gas below its critical point. Vapor pressure is the pressure at which the liquid and vapor phases of a pure substance may exist at equilibrium at a certain temperature.

* Super heated vapor = gas

* vapor ⇒ لازم يكون عند T قريبة من انه يتحول لـ liq
  ↓
  below T_c

Change of vapor pressure with temperature:

Antoine Equation: (predictions of vapor pressures)

* يكون لكل مادة قيم A, B & C ولكن هذه القيم تكون صالحة للاستخدام فقط في range of temperature معين

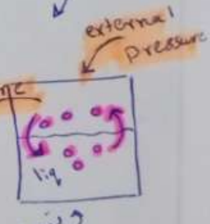
$$\ln(P) = -\frac{A}{T + C} + B$$

(P: absolute P → sat. vap. P; B → من وحدة الـ P; T: absolute temperature)

A, B and C are constants specific for each substance. T is the absolute temperature.

Change of vapor pressure with pressure:

Under normal conditions it is negligible.



يحدث الغليان when: vapor pressure = external pressure

* الجزيئات القريبة من السطح لديها kinetic energy يمكنها انها تفلت من السطح وتتحول لـ vapor

* عند الاتزان (equilibrium) يكون معدل الصعود (التحول لـ vapor) = معدل الهبوط (التحول لـ liquid)، وإذا كان الفراغ يحتوي على vapor لمادة واحدة فقط (يعني الهواء يحتوي على pure vapor) يسمى ضغط الـ vapor في هذه الحالة vapor pressure (saturated vapor)

Boiling point:

It is the temperature at which the vapor pressure of a pure liquid becomes equal to the external pressure.

Saturation:

A gaseous mixture in contact with a pure liquid is said to be saturated when the partial pressure of the liquid vapor in the mixture is equal to the vapor pressure of the liquid at a certain temperature. The vapor and liquid are at equilibrium.

Phase Rule:

For a nonchemically reactive system at heterogeneous equilibrium.

$$F = C - P + 2$$

C = Number of components (chemical species)

P = Number of phases

F = Number of degrees of freedom (variance)

= Number of intensive properties (independent variables) that must be specified to completely fix the state of the system [In this course the intensive properties are T, P and concentration].

Ex:

$F = 1 - 1 + 2$
$= 2$

For a pure gas F = 2 ⇒ T and P can be changed by small amounts without changing the state of the gas [no change in phase].

$F = 1 - 3 + 2$
$-2 + 2$
$= 0$

At Triple Point P = 3 ⇒ F = 0

It is therefore impossible to have solid / liquid / vapor at equilibrium at conditions other than the triple point.

2.2 Vapor Liquid Equilibrium

2.2.1 Binary Vapor Liquid Equilibrium

System: vapor – Liquid mixture of components A and B.

Phase Rule: C = 2 . P = 2 ⇒ F = 2

F = 2 - 2 + 2 = 2

Independent variables: T, P and the concentration of one of the components in the vapor (y) and in the liquid (x).

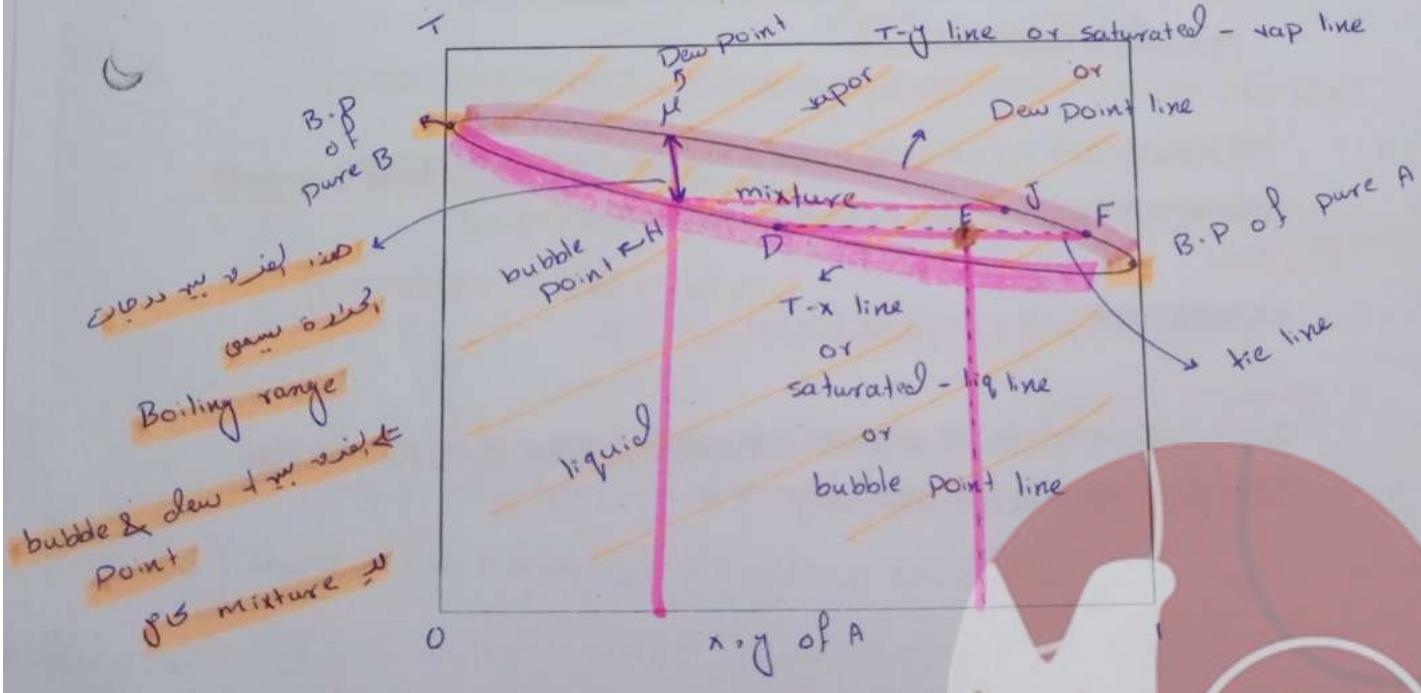
2.2.1.1 Phase equilibrium diagrams:

- Usually pressure is specified (fixed) ⇒ one independent variable remains to be fixed.
- At constant pressure four isobaric phase equilibrium diagrams involving the variables T, x and y can be constructed:

◦ T – x ◦ T – y ◦ T – x – y ◦ x – y

Constant Pressure Equilibrium:

◦ T – x ◦ T – y ◦ T – x - y diagrams:



at cost P (T x-y) diagram

- Liquid and vapor mixtures at equilibrium are at the same temperature and pressure and a horizontal line called a tie line joins their respective compositions.

- A mixture between two equilibrium curves such as E is a two phase mixture consisting of a liquid with composition at D and a vapor with composition at F.

  The relative amounts of equilibrium phases are given by the lever rule

  $$\frac{MolesD}{MolesF} = \frac{\overline{EF}}{\overline{DE}}.$$

- Heating a liquid mixture composition (G):

  Closed system with constant pressure. If the liquid is heated, the first bubble of vapor forms at (H) with vapor composition at (J) richer in the more volatile component (mvc). As more mixture is vaporized more vapor forms at the expense of liquid but the entire mass composition is still the same. The last drop of liquid mixture vaporizes at M and has composition at N. The boiling range of the mixture is HM.

  Open system: If a solution is boiled in an open vessel, the vapor is richer in the more volatile component. As vaporization proceeds the liquid becomes leaner. The temperature and composition of saturated liquid move along HN as vaporization (distillation) proceeds.

x vs. y diagram:

2.2.1.2 Relative volatility

The greater the distance between the equilibrium curve and the diagonal, the greater the difference in VL composition and the easier the separation.

Relative volatility is a measure of the difference between vapor and liquid composition at equilibrium. It is called separation factor.

$$\alpha = \frac{(\text{moles A / moles B}) \text{ in vapor}}{(\text{moles A / moles B}) \text{ in liquid}} = \frac{y_A/(1-y_A)}{x_A/(1-x_A)} = \frac{y_A}{x_A}\frac{(1-x_A)}{(1-y_A)}$$

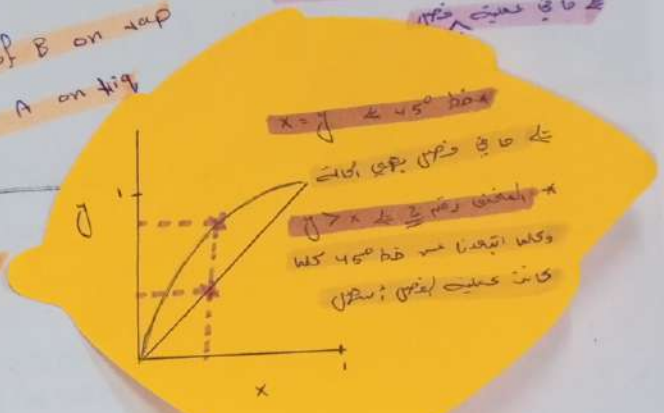
mol fraction of B on vap

mol fraction A on liq

$\alpha = \frac{y_A/y_B}{x_A/x_B}$

$x = y \leftarrow \alpha = 1$ no separation

$\alpha > 1$ separable mixture



2.2.1.3 VLE for ideal solutions:

Characteristics of ideal solutions:

- Average inter molecular forces in the solution are unchanged upon mixing.
- No heat will be absorbed or released upon mixing. $\Delta H = 0$
- Volume of solution varies linearly with composition [i.e. Total solution volume equals the sum of pure component volumes]. $V_{mix} = V_A + V_B$
- The total vapor pressure of solution varies linearly with composition. ⇒ Raoult's Law

Ideal solutions do not exist in reality. However, many solutions approach ideality. For example: adjacent members of homologous series of organic compounds. e.g. benzene in toluene.

Raoult's Law:

When the gas mixture in equilibrium with an ideal liquid solution also follows ideal gas law, the partial pressure of a solute gas is linearly proportional to its

$P_i \propto x_i$

at equilibrium: y_i: A+B, P: vap ⇒ if ideal gas; x_i, P_i: A+B, liq ⇒ if idea solution

Raoult's law

mole fraction in the liquid phase. The constant of proportionality being the vapor pressure of the pure species at the system temperature.

saturated vapor pressure of i

$$P_i = P_i^s \, x_i$$

Equilibrium partial pressure — vapor pressure — mole fraction in liquid

It is seen that the solubility of a certain gas in an ideal solution is independent of the nature of the solvent. $\Rightarrow P_i = P_i^s \, x_i \Rightarrow x_i = \frac{P_i}{P_i^s} \Rightarrow$ ... solvent

For a binary mixture we have:

$$P_A = P_A^S \, x_A \qquad P_B = P_B^S (1 - x_A)$$ (xB)

Dalton's law $\Leftarrow P_t = P_A + P_B$

$$= P_A^S \, x_A + P_B^S (1 - x_A)$$

$$\boxed{P_t = (P_A^S - P_B^S).\, x_A + P_B^S} \Rightarrow \text{straight line equation}$$

slop — intercept

At constant temperature these are linear since P_A^S and P_B^S are constant.

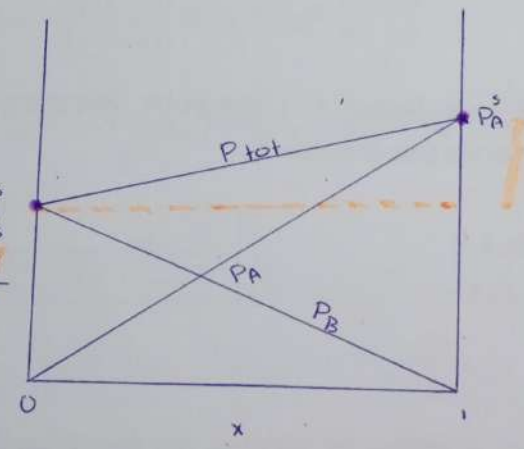
* slop of P_{tot} : $\frac{\Delta y}{\Delta x}$

$\Delta y = P_A^s - P_B^s$

$\Delta x = 1 - 0$

slop of P_{tot} : $\frac{P_A^s - P_B^s}{1}$

*intercept of P_{tot} = P_B^s



P_A is linear proportional with x

at $x_A = 1 \Rightarrow P_A = P_A^s$

P_B is linear proportional with x

at $x_B = 1 \Rightarrow P_B = P_B^s$

$P_{tot} = P_A + P_B$

* P_A^s & $P_B^s \Rightarrow$ constant $\Rightarrow$

... Antoine ...

For ideal solutions it is possible to calculate the vapor liquid equilibria from vapor pressure data of pure substances.

For Binary mixture: At a given temperature: & P

$x_A + x_B = 1.0$; $y_A + y_B = 1.0$

$P_t = (P_A^s - P_B^s)\, x_A + P_B^s$

$x_A = \dfrac{P_t - P_B^s}{P_A^s - P_B^s}$ ⇐

$$x_A = \frac{(P_t - P_B^S)}{(P_A^S - P_B^S)}$$

P_t ⇒ معطى

$$y_A = \frac{P_A}{P_t} \Rightarrow y_A = \left(\frac{P_A^S}{P_t}\right) x_A$$

$P_A = P_A^s\, x_A$ ⇒ Rault's law

$y_A = \dfrac{P_A^s\, x_A}{P_t} = \left(\dfrac{P_A^s}{P_t}\right) x_A$

Relative volatility:

نحسب P_i^s عند T معينة ونحسب x_i

$$\alpha_{AB} = \frac{y_A}{x_A}\frac{(1-x_A)}{(1-y_A)}$$

$$= \frac{P_A^S x_A}{P_t x_A} \frac{(1-x_A)}{\frac{P_B^S}{P_t}(1-x_A)}$$

$$\therefore \quad \alpha_{AB} = \frac{P_A^S}{P_B^S}$$

* range of temperature

ما بين درجة غليان المادة A و B

For Binary mixture: At a given temperature: & P

$x_A + x_B = 1.0$; $y_A + y_B = 1.0$

more volatile than B ← A لـ

$$x_A = \frac{(P_t - P_B^S)}{(P_A^S - P_B^S)}$$

$P_t \Rightarrow$ معطى

$\Rightarrow P_A^S > P_B^S$ لـ A أكبر + لـ B أصغر

$$y_A = \frac{P_A}{P_t} \Rightarrow \boxed{y_A = \left(\frac{P_A^S}{P_t}\right) x_A}$$

$P_t = (P_A^S - P_B^S) x_A + P_B^S$

$x_A = \dfrac{P_t - P_B^S}{P_A^S - P_B^S}$

$P_A = P_A^S x_A \Rightarrow$ Raoult's law

$y_A = \dfrac{P_A^S x_A}{P_t} = \left(\dfrac{P_A^S}{P_t}\right) x_A$

Relative volatility:

x_i معين بحسب P_i^S بحسب

$$\alpha_{AB} = \frac{y_A}{x_A}\frac{(1-x_A)}{(1-y_A)}$$

* range of temperature

يعتمد على نسبة تطاير A و B

* المادة اللي بتكون more volatile

تكون قيمة P_i^S أكبر

$1 - y_A = y_B = \dfrac{P_B^S}{P_{tot}} \cdot x_B = \dfrac{P_A^S x_A}{P_t x_A} \dfrac{(1-x_A)}{\frac{P_B^S}{P_t}(1-x_A)}$

$\alpha_{AB} = \dfrac{y_A / y_B}{x_A / x_B}$ ∴

$$\boxed{\alpha_{AB} = \frac{P_A^S}{P_B^S}}$$

$= \dfrac{(P_A^S x_A / P_t) / (P_B^S x_B / P_t)}{x_A / x_B} = \dfrac{P_A^S}{P_B^S}$

ex. Compute the vapor liquid equilibria at constant pressure of 1 std atm for mixtures of n-heptane and n-octane.

Solution:

We need to establish t-x,y diagram at 1 atm in the temperature range between boiling points of the pure components.

At 1 atm $BP_t n\text{-}C_7 = 98.4$ °C

$BP_t n\text{-}C_8 = 125.6$ °C

$$x_A = \frac{P_t - P_B^S}{P_A^S - P_B^S} \qquad y_A = \frac{P_A^S}{P_t} x_A$$

Sample calculation

Antoine equation باستخدام

At 110 °C

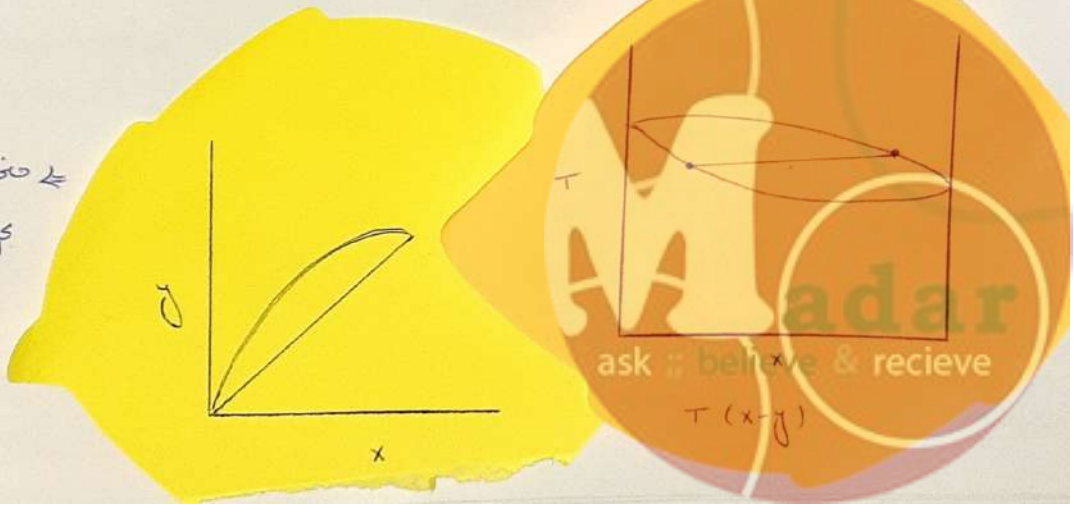
$P_A^S = 1050$ mm Hg $\quad P_B^S = 484$ mm Hg

$P_t = 760$ mm Hg

T(x-y) مشتق من x, y ← مخطط

كل نقطة بمخطط (x,y) تعتبر

T(x-y) مخطط بـ Tie line



$$x = \frac{760-484}{1050-484} = 0.487 \qquad y = \frac{1050}{760} \times 0.487 = 0.674$$

α_{AB}: at 110 °C

$$\alpha_{AB} = \frac{P_A^S}{P_B^S} = \frac{1050}{484} = 2.17$$

Temp. °C	P_A^S mm Hg	P_B^S mm Hg	X_A	Y_A	α_{AB}
98.4					2.28
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110.0	1050	484	.487	.674	2.17
115.0					2.14
120.0					2.08
125.0					2.02

Note: α for ideal solutions does not vary considerably. An average value of α can be calculated and used.

* نفرض نستخدم geometric Average

$$\text{geometric average} = \sqrt[n]{\prod_{i=1}^{n} x_i} = \sqrt[n]{x_1 \cdot x_2 \cdot x_3 \cdots x_n}$$

$$\alpha_{AB} = \frac{y_A}{x_A}\frac{(1-x_A)}{(1-y_A)} \Rightarrow y_A = \alpha_{AB} x_A \frac{(1-y_A)}{(1-x_A)}$$

$$\Downarrow$$

$$y_A[(1-x_A) + \alpha_{AB} x_{AB}] = \alpha_{AB} x_A \Leftarrow y_A(1-x_A) = \alpha_{AB} x_A (1-y_A)$$

$$\Downarrow$$

$$\boxed{y_A = \frac{\alpha_{AB} x_A}{1 + x_A(\alpha_{AB} - 1)}}$$

* إذا بدي احسب y_A & x_A بالاعتماد على قيمة α_{AB} بفرض قيم لـ x ضمن (0 - 1)، وحسب α_{AB} ونعوض بالمعادلة وحسب منها y_A

Notes:

1. Raoult's Law can generally be applied to a component whose mole fraction in the liquid phase approaches unity or to solutions of components quite similar in chemical nature.
2. Equilibrium constant or an equilibrium distribution coefficient is defined.

ideal solution ← بطريقة بسيطة

* Ideal solution :

المكونات لكي تكون solution مثالي :

- Shape
- Size
- Chemical interaction

* at $x_A = 0$

$\Rightarrow y_A = 0$

$$y_A = \frac{\alpha_{AB} x_A^{\to 0}}{1 + x_A(\alpha_{AB} - 1)}$$

* at $x_A = 1$

$$y_A = \frac{\alpha_{AB}}{1 + \alpha_{AB} - 1} = 1$$

$\therefore y_A = 1$

$$P_i = P_i^s . x_i \qquad \text{Raoult's Law}$$

$$P_i = y_i . P_t \qquad \text{Dalton's Law}$$

$$\Downarrow$$

distribution coefficient or equilibrium constant $\Leftarrow$ $K_{i,Raoult} = \frac{y_i}{x_i} = \frac{P_i^s}{P_t}$

- $k > 1$ ⇒ volatile يتبخر أسرع ⇒ $x_i < y_i$
- $k = 1$ ⇒ $x_i = y_i$
- $k < 1$ ⇒ less volatile أسرع ⇒ $x_i > y_i$

In general VLE data may be represented by:

$$y_i = k_i x_i$$

$K_i = f$ (T,P, composition) ⇒ في حالات يتبخر فيها k ثابتة يعني لا يعتمد على شيء

It can be seen that

$$\alpha_{ij} = \frac{K_i}{K_j} = \frac{\frac{y_i}{x_i}}{\frac{y_j}{x_j}} = \frac{y_i}{x_i}.\frac{x_j}{y_j}$$

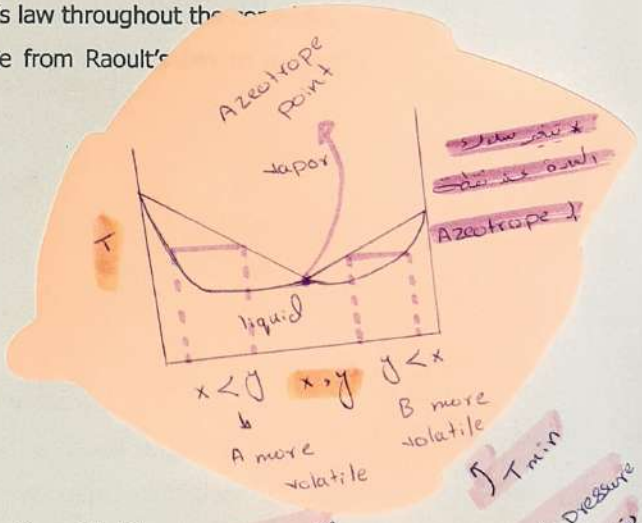
$$= \frac{y_i}{x_i}\frac{(1-x_i)}{(1-y_i)}$$

- $\alpha_{ij} > 1$
- $\alpha_{ij} = 1$ ⇒ لا يوجد separation
- $\alpha_{ij} < 1$

2.2.1.4 Actual solutions:

Miscible binary mixtures: ⇒ 2 phases في ذائبية كاملة ولا يتبخر

Few binary miscible systems obey Raoult's law throughout th... of concentrations. Most systems deviate from Raoult's... lesser extent.



- For real mixtures $P_i \neq P_i^s . x_i$
- but instead $P_i = \gamma_i P_i^s x_i$

γ_i = activity coefficient

$$= \frac{\text{real eqm partial pressure}}{\text{ideal eqm partial pressure}} = \frac{P_i \text{ real}}{P_i^s . x_i}$$

therefore γ is a measure of the deviation from ideality

- $\gamma = 1 \Rightarrow$ ideal solution
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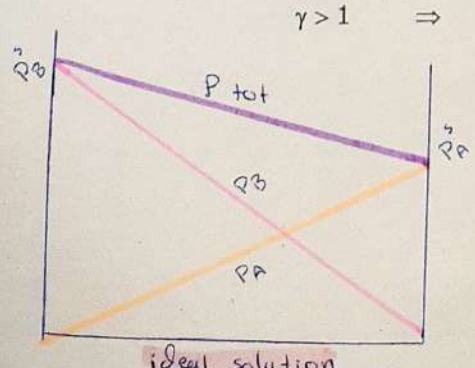
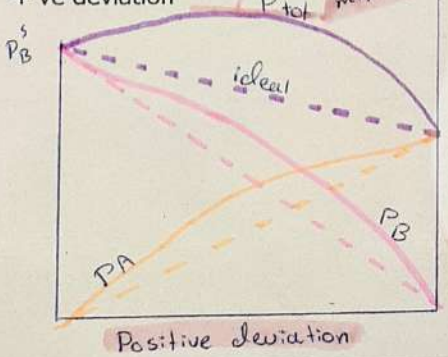




$\gamma < 1 \quad \Rightarrow \quad$ - ve deviation

All miscible pairs can be classified into three general types:

Type I: systems whose total vapor pressure is intermediate between those of pure components.

Ex. CCl_4 – cyclohexane

CCl_4 – benzene

Benzene – toluene

Water – methyl alcohol.

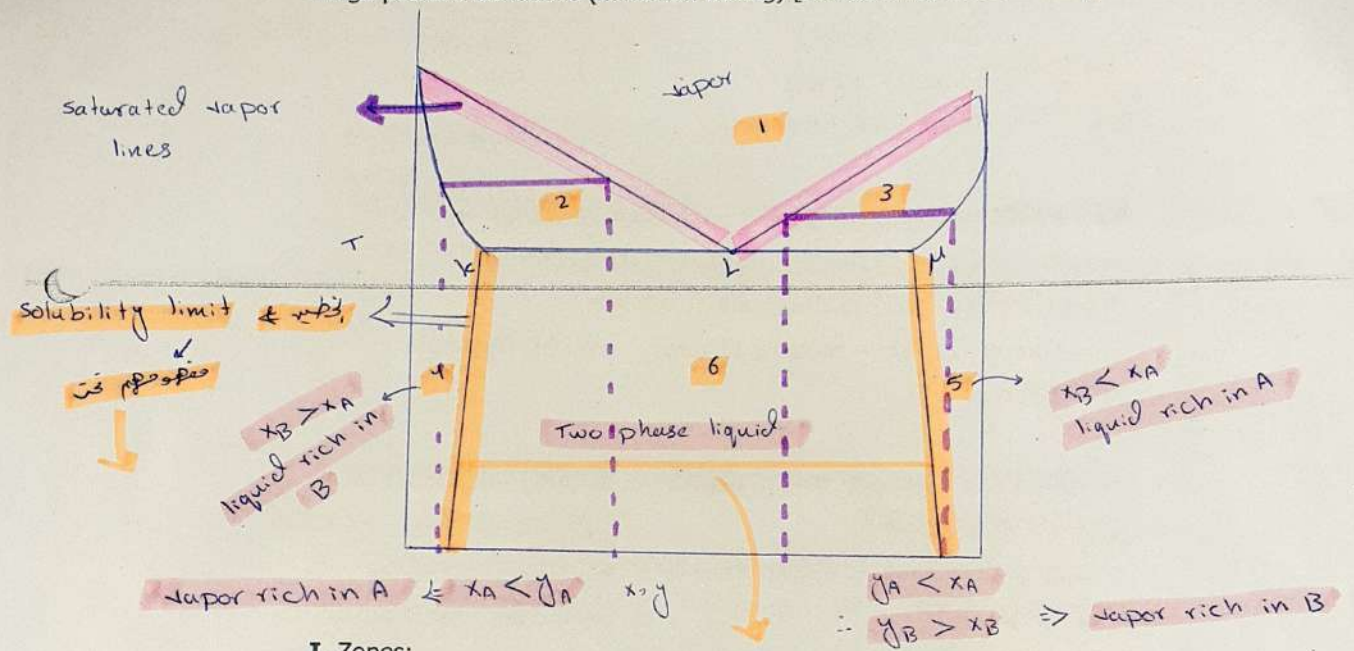
Type II: systems exhibiting a **maximum** in the total vapor pressure curve. They exhibit positive deviation from ideality and they form **minimum boiling point** mixtures.

Ex. Carbon disulfide – acetone, benzene - cyclohexane, water – ethyl alcohol.

Type III: systems exhibiting a minimum in the total vapor pressure curve. They exhibit negative deviation from ideality and they **form maximum boiling point** mixtures.

Partially Miscible Binary Mixtures:

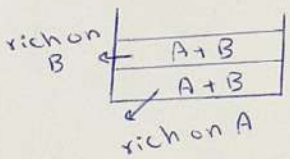
Some systems do not dissolve completely in all proportions. They exhibit large positive deviations (minimum boiling) [Forces of repulsion $\rightarrow 2\phi$]



I. Zones:

1. all vapor
2. vapor and liquid in equilibrium with vapor richer in A
3. vapor and liquid in equilibrium with vapor richer in B
4. Liquid solution richer in B (solution of A in B)
5. Liquid solution richer in A (solution of B in A)
6. Two-phase mixtures. Each phase represents a solution of one component in the other. At constant temperature the composition of each phase is constant; however the proportions of phases are different.

II. For homogeneous liquids (zones 4 and 5), the vapor-liquid equilibrium phenomena are normal.



* solubility limit :

one phase

two phase

soluble A in B

soluble B in A

solvent

rich

بعد الخط ↑ KLM يتحول ل liq إلى (vap - liq) ← وعند هذه درجة الحرارة تكون درجة غليان الـ mixture

III. Two phase mixtures within the range KM will boil at the temperature of line KM, and they all give rise to the same vapor of composition L in equilibrium with two liquids at K and M which are also in equilibrium with each other.

IV. A two-phase mixture of average composition L which produces a vapor of the same composition is sometimes called a **heteroazeotrope.**

V. Phase rule for systems at temperature KM:

C = 2 P = 3 F = C- P+2 ⇒ F = 1

∴ If pressure is set, everything else is specified.

IMMISCIBLE BINARY MIXTURES (heterogeneous solutions)

← ما بذوبوا ببعض ولكن عادة تتصرف بشكل independently

properties of each phase not affect on other phase

متل الزيت والماء

Immiscible liquids are mutually insoluble – addition of one liquid to the other does not affect the properties of either liquid. Each will behave independently and will exert its own vapor pressure corresponding to the pure liquid at a given temperature.

$$P_t = P_A^S + P_B^S$$

The mixture will boil at a certain temperature when the sum of the vapor pressures equals the external pressure. The vapor composition is:

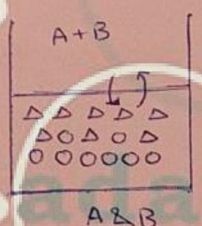
$$y_A = \frac{P_A^S}{P_t}$$

→ partial pressure of A

* boiling point ⇒ when: P_t = P external

Immisciple ← A&B liq ل ab.

(الغازات بالجو ذائبة ببعض) ← misciple ← A&B vap ← ab.



$P_B^s + P_A^s$ ← mixture ← vapor ←

← سرعة التبخر = سرعة التكاثف

Notes:

1. The boiling point of any mixture of two immiscible liquids is less than the boiling point of either of the two liquids.
2. Boiling point of all possible mixtures of two immiscible liquids is the same (no change in vapor pressure with composition).
3. At any boiling point, the vapor composition remains constant and is independent of overall liquid composition.

2.2.2 VLE for multi-component systems:

- Graphical presentation of more than three component systems is extremely complex.
- Many of the multi-component systems of industrial importance can be considered nearly ideal solutions. Raoult's law can be applied and vapor liquid equilibrium data can be calculated from pure component data.
- ... equilibrium data can be calculated from binary

... systems, equilibrium data is represented by means of ...nts.

...nt i

For ideal solutions at moderate pressures, k_i is independent of composition. It depends only on temperature and total pressure.

At equilibrium:

$$k_i = \frac{y_i}{x_i} = \frac{p_i / P_t}{P_i / P_i^s} = \frac{P_i^s}{P_t}$$

It is also customary to choose a convenient reference component (in many cases heaviest component) to which data can be referred:

At equilibrium:

$$\alpha_{ij} = \frac{(y_i / x_i)}{(y_j / x_j)} = \frac{k_i}{k_j}$$ → reference

$$\alpha_{ij} = \frac{P_i^s / P_t}{P_j^s / P_t} = \frac{P_i^S}{P_j^S}$$

VLE For a given vapor-liquid system at equilibrium:

$$\alpha_{ij} = \frac{y_i / y_j}{x_i / x_j}$$

$$\alpha_{ij} = \frac{y_i / x_i}{y_j / x_j}$$

$$y_i = \frac{\alpha_{ij} x_i}{(x_j / y_j)}$$

$$x_i = \frac{y_i / \alpha_{ij}}{(y_j / x_j)}$$

$$\sum_{i=1}^{n} y_i = \sum_{i=1}^{n} \frac{\alpha_{ij} x_i}{(x_j / y_j)} = 1$$

$$\sum x_i = \sum \frac{y_i / \alpha_{ij}}{y_j / x_j} = 1.0$$

$$\left(\frac{x_j}{y_j}\right) = \sum_{i=1}^{n} \alpha_{ij} x_i$$

$$\left(\frac{y_j}{x_j}\right) = \sum y_i / \alpha_{ij}$$

$$\frac{y_j}{x_j} = \frac{1}{\sum \alpha_{ij} x_i}$$

substitute for $\frac{y_j}{x_j} = \frac{y_i}{\alpha_{ij} . x_i}$

$$y_i = \frac{\alpha_{ij} x_i}{\sum \alpha_{ij} x_i}$$

useful for Bubble point calculation

$$x_i = \frac{y_i / \alpha_{ij}}{\sum y_i / \alpha_{ij}}$$

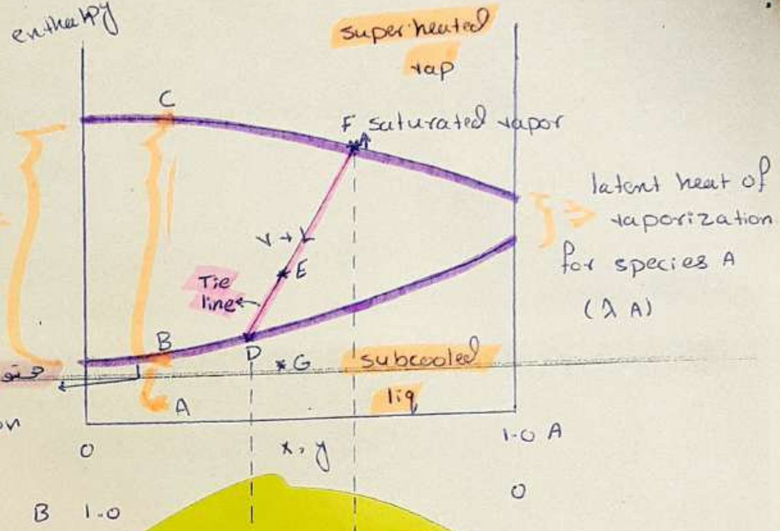
useful for Dew point calculation

2.2.3 Enthalpy concentration diagrams:

Binary VLE data can also be represented by enthalpy concentration diagrams [useful in showing energy changes as well as composition changes].

$\lambda_B > \lambda_A$
more volatile A than B

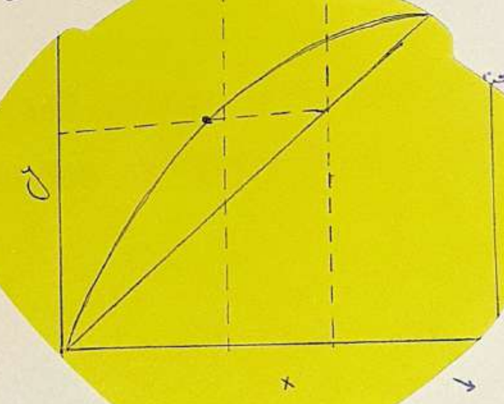
latent heat of vaporization for species B (λ_B)



saturated liquid enthalpy

as function of composition (x & y)

* رفعت درجة حرارة G حتى وصل ل E ← V & L mixture ← يتغير ال
2 phase
vap ↓ F
liq ↓ D
cost T



...ure v...

...ents:

...olution:

كل point على المنحنى يمثل enthalpy - (x-y) من Tie line

H_L = sensible heat and heat of mixing

$H_L = C_L\,(t_L - t_o)\,M_{av} + \Delta H_S$

C_L: heat capacity of solution. For ideal solution it is the weighted average of the pure components heat capacities. (energy / mass. deg.). (average heat capacity of the solution)

M_{av}: average molecular weight.

t_L: liquid temperature (for a saturated liquid it is the bubble point).

T_0: reference temperature.

ΔH_S = heat of solution at to for the given concentration.

$M_{av} = \Sigma$ mol fraction $\cdot M_w$
$M_{av} = x_1 \cdot M_{w_1} + x_2 M_{w_2} \cdots$

enthalpy of heating mixture A to bubble point BPt ← A & B المسافة بين *

latent heat of vaporization of mixture ← B&C المسافة بين *

T refrence ← ليش أخذنا

absolute value of energy ما في ← because the energy is a relative quantity

Saturated vapor:

We can assume pure liquids are heated separately to the dew point t_v, each vaporized at this point and vapors are mixed.

T of vapors — mol fraction of B

H_v = Enthalpy of Vap A + Enthalpy of Vap B.

$H_v = y\,[C_{L,A}\,(t_v - t_o)\,M_a + \lambda_A \cdot M_A] + (1-y)\,[C_{L,B}\,(t_v - t_o)\,M_B + \lambda_B]$ → μ_B

mol fraction of the more volatile compound — $\lambda_B\ \mu_B$

λ: latent heat of vaporization of pure substances at t_v [energy/mass]

C_L: heat capacity of pure liquid energy/mass deg.

⇒ heat of mixing (H_L) ⇒

هو المحتوى الحراري الذي يتم تحريره أو امتصاصه من مادة عند خلطها، عندما يتم مزج مادة مع مواد أخرى، فإن المحتوى الحراري للخليط يكون ناتج من التفاعلات الجديدة بين المواد.

H_L

\+ endothermic — 0 ideal solution — − exothermic

⇒ heat of solution (ΔH_S) ⇒

التغير في المحتوى الحراري الناتج من إذابة وزان داخل حذيب (وتعطى بالوحدة المذابة)

2.3 Gas – Liquid systems, Henry's Law

System: Gaseous mixture A+B

A to be absorbed by liquid S (Solvent)

B carrier gas.

Thermodynamics variables: P, T, x_A, x_B, x_S, y_A, y_B, y_S

Degrees of freedom: C = 3 P = 2 $\Rightarrow$ F = 3 − 2 + 2 = 3

Therefore if three variables are specified, all other variables are determined. If B is insoluble in S, and S has negligible vapor pressure, then the remaining variables are: P, T, x_A and y_A

$x_B = 0$ $y_S = 0$ $y_B = 1 - y_A$ $x_S = 1 - x_A$

* gas absorption تستخدم في حالة إذا كان في خليط غاز وبدي أفرق منه غاز معين قبل م يطلع لـ atmosphere

vap - liq equilb: كل المواد موجودة بـ 2 phase

gas - liq equilb: هو بالضرورة كل المواد تكون موجودة بـ 2 phase ← عشان $x_B = 0$ ← liquid غير ذائب بـ

* The concentration of gas in the liquid phase approach to zero (dilute).

* when $x \leq 0.1$ ← the relation between x & y is linearly.

fraction in the liquid phase approaches zero, a linear equilibrium assumed with reasonable accuracy.

Henry's Law:

$x \leq 0.1$ شرط تكون

$$P_A = k_h \cdot x_A$$

P_A: Partial pressure of A; k_h: Henry's law constant; x_A: mole fraction of A in liquid

almost all liquids will deviate above mole fractions of 0.1.

Equilibrium constant:

$$K_A = \frac{y_A}{x_A} = \frac{k_h}{P_t}$$

For Binary mixture: At a given temperature: & P

$x_A + x_B = 1.0$; $y_A + y_B = 1.0$

more volatile than B ← A لـ

$$x_A = \frac{(P_t - P_B^S)}{(P_A^S - P_B^S)}$$

$P_t \Rightarrow$ معطى

$\Rightarrow P_A^S > P_B^S$ لـ A أكبر + لـ B أصغر

$$y_A = \frac{P_A}{P_t} \Rightarrow \boxed{y_A = \left(\frac{P_A^S}{P_t}\right) x_A}$$

$P_t = (P_A^S - P_B^S) x_A + P_B^S$

$x_A = \dfrac{P_t - P_B^S}{P_A^S - P_B^S}$

$P_A = P_A^S x_A \Rightarrow$ Raoult's law

$y_A = \dfrac{P_A^S x_A}{P_t} = \left(\dfrac{P_A^S}{P_t}\right) x_A$

Relative volatility:

x_i معين بحسب P_i^S بحسب

$$\alpha_{AB} = \frac{y_A}{x_A}\frac{(1-x_A)}{(1-y_A)}$$

* range of temperature

يعتمد على نسبة تطاير A و B

* المادة اللي بتكون more volatile

تكون قيمة P_i^S أكبر

$1 - y_A = y_B = \dfrac{P_B^S}{P_{tot}} \cdot x_B = \dfrac{P_A^S x_A}{P_t x_A} \dfrac{(1-x_A)}{\frac{P_B^S}{P_t}(1-x_A)}$

$\alpha_{AB} = \dfrac{y_A / y_B}{x_A / x_B}$ ∴

$$\boxed{\alpha_{AB} = \frac{P_A^S}{P_B^S}}$$

$= \dfrac{(P_A^S x_A / P_t) / (P_B^S x_B / P_t)}{x_A / x_B} = \dfrac{P_A^S}{P_B^S}$

ex. Compute the vapor liquid equilibria at constant pressure of 1 std atm for mixtures of n-heptane and n-octane.

Solution:

We need to establish t-x,y diagram at 1 atm in the temperature range between boiling points of the pure components.

At 1 atm $BP_t n\text{-}C_7 = 98.4$ °C

$BP_t n\text{-}C_8 = 125.6$ °C

$$x_A = \frac{P_t - P_B^S}{P_A^S - P_B^S} \qquad y_A = \frac{P_A^S}{P_t} x_A$$

Sample calculation

Antoine equation باستخدام

At 110 °C

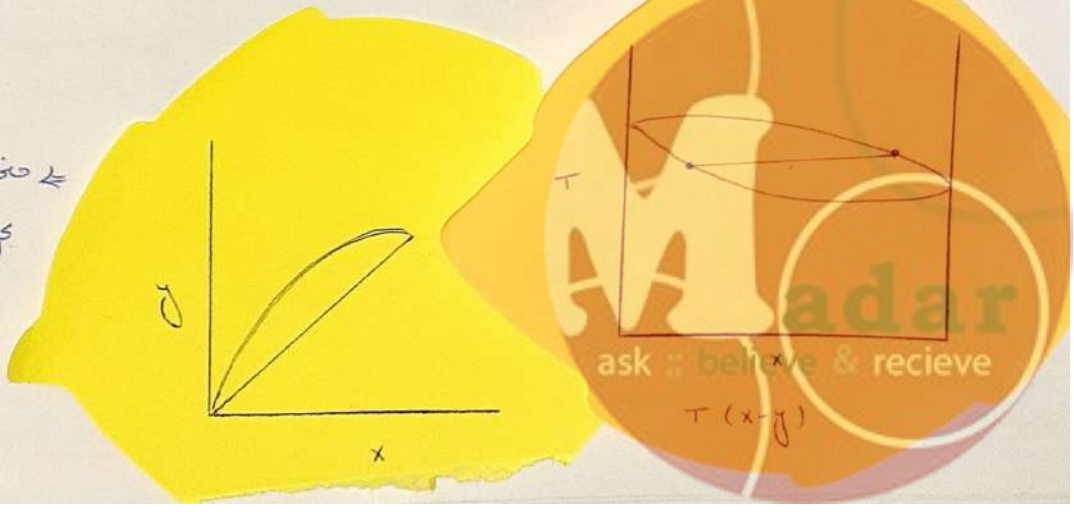
$P_A^S = 1050$ mm Hg $\quad P_B^S = 484$ mm Hg

$P_t = 760$ mm Hg

T(x-y) مشتق من x, y ← مخطط

كل نقطة بمخطط (x,y) تعتبر

T(x-y) مخطط بـ Tie line



$$x = \frac{760-484}{1050-484} = 0.487 \qquad y = \frac{1050}{760} \times 0.487 = 0.674$$

α_{AB}: at 110 °C

$$\alpha_{AB} = \frac{P_A^S}{P_B^S} = \frac{1050}{484} = 2.17$$

Temp. °C	P_A^S mm Hg	P_B^S mm Hg	X_A	Y_A	α_{AB}
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Note: α for ideal solutions does not vary considerably. An average value of α can be calculated and used.

* نفرض نستخدم geometric Average

$$\text{geometric average} = \sqrt[n]{\prod_{i=1}^{n} x_i} = \sqrt[n]{x_1 \cdot x_2 \cdot x_3 \cdots x_n}$$

$$\alpha_{AB} = \frac{y_A}{x_A}\frac{(1-x_A)}{(1-y_A)} \Rightarrow y_A = \alpha_{AB} x_A \frac{(1-y_A)}{(1-x_A)}$$

$$\Downarrow$$

$$y_A[(1-x_A) + \alpha_{AB} x_{AB}] = \alpha_{AB} x_A \Leftarrow y_A(1-x_A) = \alpha_{AB} x_A (1-y_A)$$

$$\Downarrow$$

$$\boxed{y_A = \frac{\alpha_{AB} x_A}{1 + x_A(\alpha_{AB} - 1)}}$$

* إذا بدي احسب y_A & x_A بالاعتماد على قيمة α_{AB} بفرض قيم لـ x ضمن (0 - 1)، وحسب α_{AB} ونعوض بالمعادلة وحسب منها y_A

Notes:

1. Raoult's Law can generally be applied to a component whose mole fraction in the liquid phase approaches unity or to solutions of components quite similar in chemical nature.
2. Equilibrium constant or an equilibrium distribution coefficient is defined.

ideal solution ← بطريقة بسيطة

* Ideal solution :

المكونات لكي تكون solution مثالي :

- Shape
- Size
- Chemical interaction

* at $x_A = 0$

$\Rightarrow y_A = 0$

$$y_A = \frac{\alpha_{AB} x_A^{\to 0}}{1 + x_A(\alpha_{AB} - 1)}$$

* at $x_A = 1$

$$y_A = \frac{\alpha_{AB}}{1 + \alpha_{AB} - 1} = 1$$

$\therefore y_A = 1$

$$P_i = P_i^s . x_i \qquad \text{Raoult's Law}$$

$$P_i = y_i . P_t \qquad \text{Dalton's Law}$$

$$\Downarrow$$

distribution coefficient or equilibrium constant $\Leftarrow$ $K_{i,Raoult} = \frac{y_i}{x_i} = \frac{P_i^s}{P_t}$

- $k > 1$ ⇒ volatile يتبخر أسرع ⇒ $x_i < y_i$
- $k = 1$ ⇒ $x_i = y_i$
- $k < 1$ ⇒ less volatile أسرع ⇒ $x_i > y_i$

In general VLE data may be represented by:

$$y_i = k_i x_i$$

$K_i = f$ (T,P, composition) ⇒ في حالات يتبخر فيها k ثابتة يعني لا يعتمد على شيء

It can be seen that

$$\alpha_{ij} = \frac{K_i}{K_j} = \frac{\frac{y_i}{x_i}}{\frac{y_j}{x_j}} = \frac{y_i}{x_i}.\frac{x_j}{y_j}$$

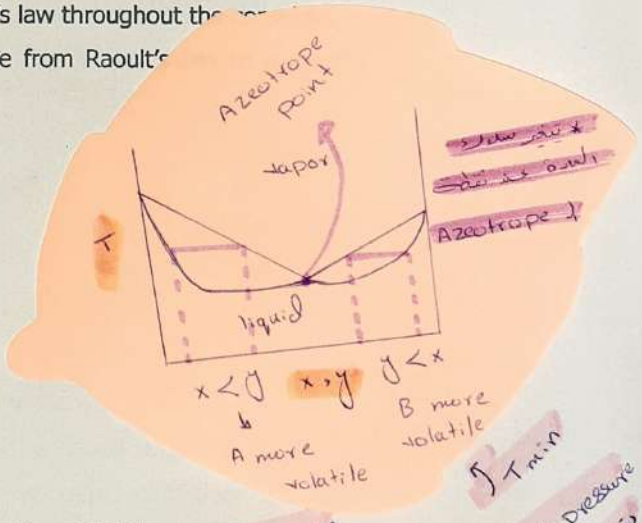
$$= \frac{y_i}{x_i}\frac{(1-x_i)}{(1-y_i)}$$

- $\alpha_{ij} > 1$
- $\alpha_{ij} = 1$ ⇒ لا يوجد separation
- $\alpha_{ij} < 1$

2.2.1.4 Actual solutions:

Miscible binary mixtures: ⇒ 2 phases في ذائبية كاملة ولا يتبخر

Few binary miscible systems obey Raoult's law throughout th... of concentrations. Most systems deviate from Raoult's... lesser extent.



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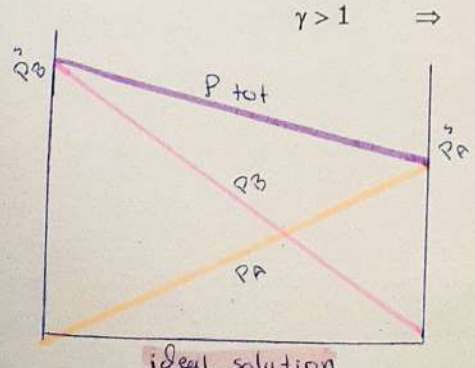
- but instead $P_i = \gamma_i P_i^s x_i$

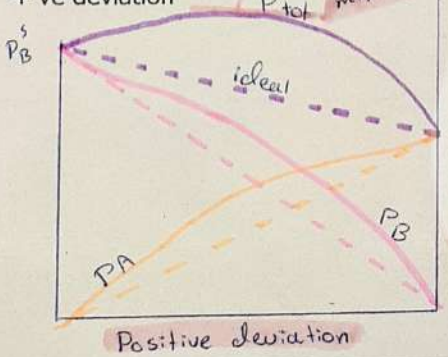
γ_i = activity coefficient

$$= \frac{\text{real eqm partial pressure}}{\text{ideal eqm partial pressure}} = \frac{P_i \text{ real}}{P_i^s . x_i}$$

therefore γ is a measure of the deviation from ideality

- $\gamma = 1 \Rightarrow$ ideal solution
- $\gamma > 1 \Rightarrow$ + ve deviation





$\gamma < 1 \quad \Rightarrow \quad$ - ve deviation

All miscible pairs can be classified into three general types:

Type I: systems whose total vapor pressure is intermediate between those of pure components.

Ex. CCl_4 – cyclohexane

CCl_4 – benzene

Benzene – toluene

Water – methyl alcohol.

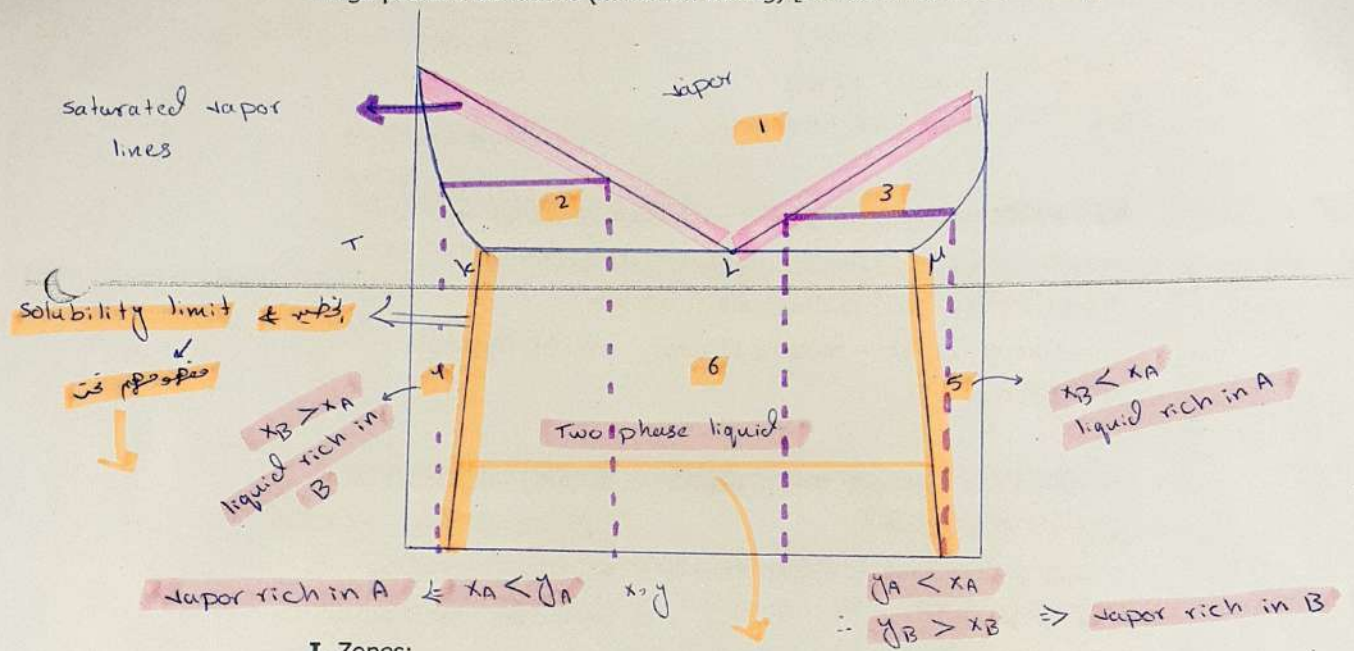
Type II: systems exhibiting a **maximum** in the total vapor pressure curve. They exhibit positive deviation from ideality and they form **minimum boiling point** mixtures.

Ex. Carbon disulfide – acetone, benzene - cyclohexane, water – ethyl alcohol.

Type III: systems exhibiting a minimum in the total vapor pressure curve. They exhibit negative deviation from ideality and they **form maximum boiling point** mixtures.

Partially Miscible Binary Mixtures:

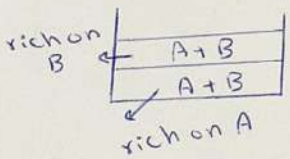
Some systems do not dissolve completely in all proportions. They exhibit large positive deviations (minimum boiling) [Forces of repulsion $\rightarrow 2\phi$]



I. Zones:

1. all vapor
2. vapor and liquid in equilibrium with vapor richer in A
3. vapor and liquid in equilibrium with vapor richer in B
4. Liquid solution richer in B (solution of A in B)
5. Liquid solution richer in A (solution of B in A)
6. Two-phase mixtures. Each phase represents a solution of one component in the other. At constant temperature the composition of each phase is constant; however the proportions of phases are different.

II. For homogeneous liquids (zones 4 and 5), the vapor-liquid equilibrium phenomena are normal.



* solubility limit :

one phase

two phase

soluble A in B

soluble B in A

solvent

rich

بعد الخط KLM يتحول إلى liq إلى (vap - liq) ← وعند هذه درجة الحرارة تكون درجة غليان الـ mixture

III. Two phase mixtures within the range KM will boil at the temperature of line KM, and they all give rise to the same vapor of composition L in equilibrium with two liquids at K and M which are also in equilibrium with each other.

IV. A two-phase mixture of average composition L which produces a vapor of the same composition is sometimes called a **heteroazeotrope.**

V. Phase rule for systems at temperature KM:

C = 2　　　P = 3　　　F = C- P+2　⇒　F = 1

∴　If pressure is set, everything else is specified.

IMMISCIBLE BINARY MIXTURES (heterogeneous solutions)

ما بذوبوا ببعض ولكن عادة تتصرف بشكل independently

properties of each phase not affect on other phase

مثل الزيت والماء

Immiscible liquids are mutually insoluble – addition of one liquid to the other does not affect the properties of either liquid. Each will behave independently and will exert its own vapor pressure corresponding to the pure liquid at a given temperature.

$$P_t = P_A^S + P_B^S$$

The mixture will boil at a certain temperature when the sum of the vapor pressures equals the external pressure. The vapor composition is:

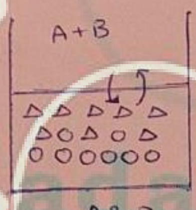
$$y_A = \frac{P_A^S}{P_t}$$

P_A^S → partial pressure of A

* boiling point ⇒ when: P_t = P external

Immisciple ← A&B liq ال ...

(الغازات بالعموم ذائبة ببعض) ← misciple ← A&B vap ال ...



$P_B^S + P_A^S$ ... mixture ... vapor

← سرعة التبخر = سرعة التكاثف

Notes:

1. The boiling point of any mixture of two immiscible liquids is less than the boiling point of either of the two liquids.
2. Boiling point of all possible mixtures of two immiscible liquids is the same (no change in vapor pressure with composition).
3. At any boiling point, the vapor composition remains constant and is independent of overall liquid composition.

2.2.2 VLE for multi-component systems:

- Graphical presentation of more than three component systems is extremely complex.
- Many of the multi-component systems of industrial importance can be considered nearly ideal solutions. Raoult's law can be applied and vapor liquid equilibrium data can be calculated from pure component data.

...s equilibrium data can be calculated from binary

... systems, equilibrium data is represented by means of ...nts.

...nt i

For ideal solutions at moderate pressures, k_i is independent of composition. It depends only on temperature and total pressure.

At equilibrium:

$$k_i = \frac{y_i}{x_i} = \frac{p_i / p_t}{P_i / P_i^s} = \frac{P_i^s}{P_t}$$

It is also customary to choose a convenient reference component (in many cases heaviest component) to which data can be referred:

At equilibrium:

$$\alpha_{ij} = \frac{(y_i / x_i)}{(y_j / x_j)} = \frac{k_i}{k_j}$$ → reference

$$\alpha_{ij} = \frac{P_i^s / P_t}{P_j^s / P_t} = \frac{P_i^S}{P_j^S}$$

VLE For a given vapor-liquid system at equilibrium:

$$\alpha_{ij} = \frac{y_i / y_j}{x_i / x_j}$$

$$\alpha_{ij} = \frac{y_i / x_i}{y_j / x_j}$$

$$y_i = \frac{\alpha_{ij} x_i}{(x_j / y_j)}$$

$$x_i = \frac{y_i / \alpha_{ij}}{(y_j / x_j)}$$

$$\sum_{i=1}^{n} y_i = \sum_{i=1}^{n} \frac{\alpha_{ij} x_i}{(x_j / y_j)} = 1$$

$$\sum x_i = \sum \frac{y_i / \alpha_{ij}}{y_j / x_j} = 1.0$$

$$\left(\frac{x_j}{y_j}\right) = \sum_{i=1}^{n} \alpha_{ij} x_i$$

$$\left(\frac{y_j}{x_j}\right) = \sum y_i / \alpha_{ij}$$

$$\frac{y_j}{x_j} = \frac{1}{\sum \alpha_{ij} x_i}$$

substitute for $\frac{y_j}{x_j} = \frac{y_i}{\alpha_{ij} . x_i}$

$$y_i = \frac{\alpha_{ij} x_i}{\sum \alpha_{ij} x_i}$$

useful for Bubble point calculation

$$x_i = \frac{y_i / \alpha_{ij}}{\sum y_i / \alpha_{ij}}$$

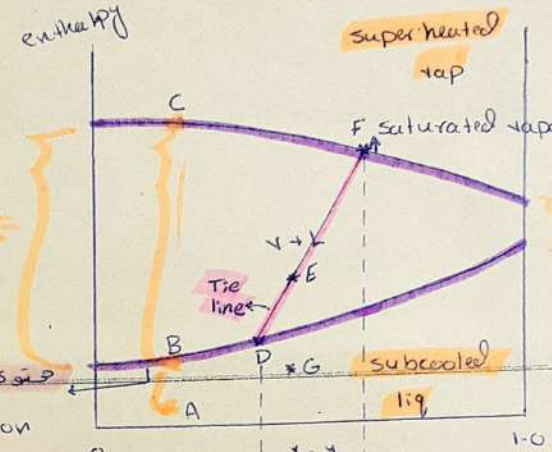
useful for Dew point calculation

2.2.3 Enthalpy concentration diagrams:

Binary VLE data can also be represented by enthalpy concentration diagrams [useful in showing energy changes as well as composition changes].

$\lambda_B > \lambda_A$

more volatile A than B



saturated liquid enthalpy

as function of composition (x & y)

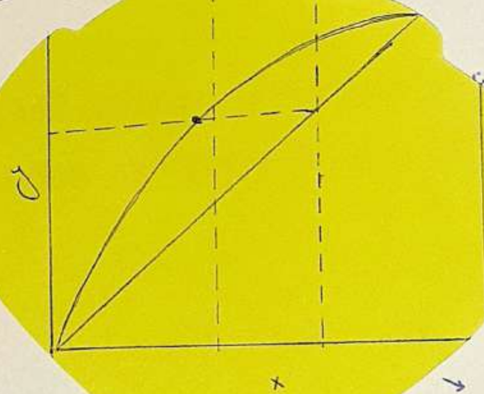
E → V & L mixture

2 phase

vap → F

liq → D

cost T



...ure ...

...ents:

...olution:

enthalpy - (x-y) Tie line

H_L = sensible heat and heat of mixing

$H_L = C_L\,(t_L - t_o)\,M_{av} + \Delta H_S$

C_L: heat capacity of solution. For ideal solution it is the weighted average of the pure components heat capacities. (energy / mass. deg.). (average heat capacity of the solution)

M_{av}: average molecular weight.

t_L: liquid temperature (for a saturated liquid it is the bubble point).

T_0: reference temperature.

ΔH_S = heat of solution at to for the given concentration.

$M_{av} = \Sigma$ mol fraction $\cdot M_w$

$M_{av} = x_1 M_{w1} + x_2 M_{w2} \cdots$

enthalpy of heating mixture A to bubble point BPt ← A & B

latent heat of vaporization of mixture ← B & C

T refrence

absolute value of energy ← because the energy is a relative quantity

Saturated vapor:

We can assume pure liquids are heated separately to the dew point t_v, each vaporized at this point and vapors are mixed.

T of vapors — mol fraction of B

H_v = Enthalpy of Vap A + Enthalpy of Vap B.

$H_v = y\,[C_{L,A}\,(t_v - t_o)\,M_a + \lambda_A \cdot M_A] + (1-y)\,[C_{L,B}\,(t_v - t_o)\,M_B + \lambda_B]$ → μ_B

mol fraction of the more volatile compound — $\lambda_B\ \mu_B$

λ: latent heat of vaporization of pure substances at t_v [energy/mass]

C_L: heat capacity of pure liquid energy/mass deg.

⇒ heat of mixing (H_L) ⇒

هو المحتوى الحراري الذي يتم تحريره أو امتصاصه من مادة عند خلطها، عندما يتم مزج مادة مع مواد أخرى، فإن المحتوى الحراري للخليط يكون ناتج من التفاعلات الجديدة بين المواد.

H_L

\+ endothermic — 0 ideal solution — − exothermic

⇒ heat of solution (ΔH_S) ⇒

التغير في المحتوى الحراري الناتج من إذابة وزان داخل حذيب (وتعطى بالوحدة المذابة)

2.3 Gas – Liquid systems, Henry's Law

صد صعوبة بعض الحسابات في equil وذكر gas وليس vap

System: Gaseous mixture A+B

A to be absorbed by liquid S (solvent) ← بذوّب تفضيلياً واحد من مكونات الـ gas

B carrier gas. → ناقل

Thermodynamics variables: P, T, x_A, x_B, x_S, y_A, y_B, y_S

نتعامل مع الغاز A من الـ gas mixture إلى الـ solvent (S) لحد ما يوصل للاتزان

Degrees of freedom: C = 3   P = 2   ⇒ F = 3 − 2 + 2 = 3

← الفرق بين الـ vap & gas:
vap ⇒ is a gas below T_c
→ we deal with dilute soln
mol fraction in liq phase < 10%.

Therefore if three variables are specified, all other variables are determined. If B is insoluble in S, and S has negligible vapor pressure, then the remaining variables are: P, T, x_A and y_A → $y_B = 1 - y_A$

$x_B = 0$ $y_S = 0$ $x_S = 1 - x_A$

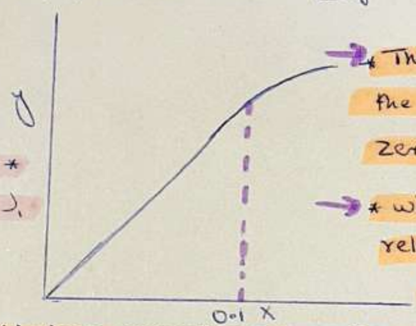
* تستخدم في عمليات الـ gas absorption ← إذا كان في خليط غاز وبدي أنزع منه غاز معين قبل ما يطلع لـ atmosphere

بدرس الـ gas mixture مع solvent معين يقوم بامتصاص الغاز من الخليط ويذوّبه

→ vap - liq equilb:
كل المواد موجودة بـ 2 phase

→ gas - liq equilb:
مو بالضرورة كل المواد تكون موجودة بـ 2 phase
مثلاً ←
غير ذائب بـ liquid
$x_B = 0$ →

* اللي بهمني صعوبة الـ solute



→ * The concentration of gas in the liquid phase approach to zero (dilute).

→ * when x ≤ 0.1 → the relation between x & y is linearly.

fraction in the liquid phase approaches zero, a linear equilibrium
assumed with reasonable accuracy.

Henry's Law:

x ≤ 0.1 نظرية صحيحة إذا تركيز ← $P_A = k_h \cdot x_A$

Partial pressure of A   Henry's law constant   mole fraction of A in liquid

almost all liquids will deviate above mole fractions of 0.1.

Equilibrium constant:

$$K_A = \frac{y_A}{x_A} = \frac{k_h}{P_t}$$

y_1 → mol fraction of solute in phase E

$y_1 = \frac{S_1}{E_s + S} = \frac{S_1}{E_1}$

x_1 → mol fraction of solute in phase R

$x_1 = \frac{S_1}{R_s + S_1^R} = \frac{S_1^R}{R_1}$

mole fraction

$E_1 = E_s + S$ → flow rate of solute; flow rate of solvent

If E_1 is pure → $S = 0$

E and R and single solute transferring from phase R to Phase E

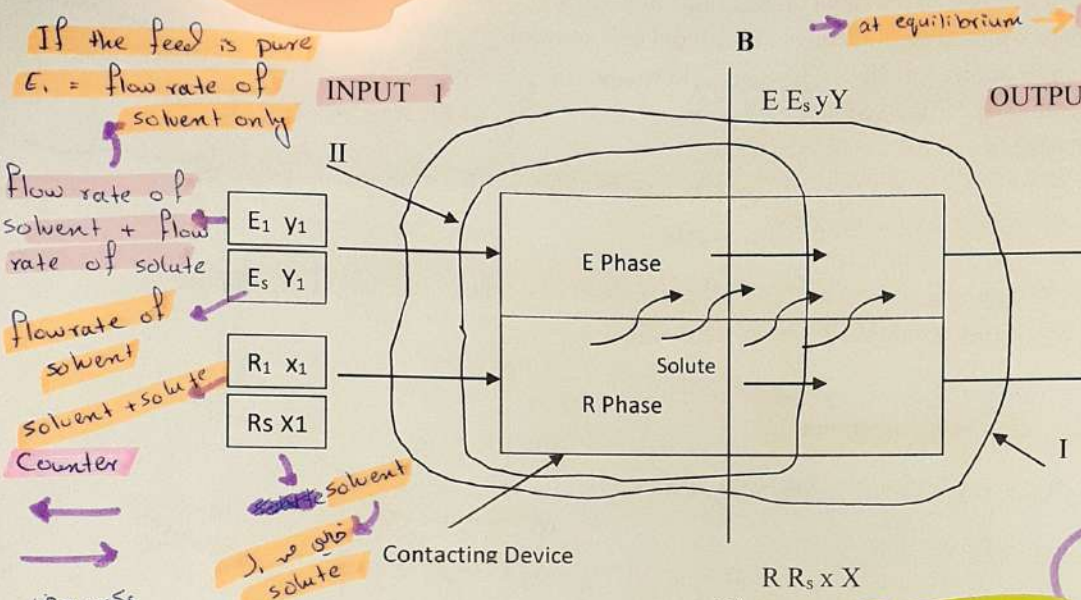
...cting Processes

→ the rate of transfer depend on equilibrium

equilibrium ← ... equilibrium

→ at equilibrium → net transfer = 0

...ess:



If the feed is pure E_1 = flow rate of solvent only

Flow rate of solvent + flow rate of solute

flowrate of solvent

solvent + solute

Counter ← →

عكس بعض

solvent

... solute

Co current ← ... 2 phase ... بنفس الاتجاه

Solvent + solute

$E_1 < E_2$ ... solute ... phase ... E ...

$R_1 > R_2$ ...

... phase → phase ...

@ equilibrium → force driving = 0

R_i, E_i : moles total material/time ; R_s, E_s : ...

x_i, y_i : mole fractions of solute in strea... i

i : stream number

X & Y → mole Ratio ... stant)

... solute ... solvent ... phase

$Y = \frac{S}{E_s} = \frac{y E_1}{(1-y) E_1} = \frac{y}{1-y}$

$X = \frac{S_1^R}{R_s} = \frac{x R_1}{(1-x) R_1} = \frac{x}{1-x}$

Solute Material Balance

Envelope I (overall)

moles of solute in R phase

$$\overbrace{R_1 x_1 + E_1 y_1}^{\text{IN}} = \overbrace{R_2 x_2 + E_2 y_2}^{\text{OUT}}$$

moles of solute in E phase

OR

$$R_1 x_1 - R_2 x_2 = E_2 y_2 - E_1 y_1$$

$y_2 > y_1$ ...

... solute ... ...

$$R_i x_i = R_s \frac{x_i}{1 - x_i} = R_s X_i$$

$x_2 < x_1$ ...

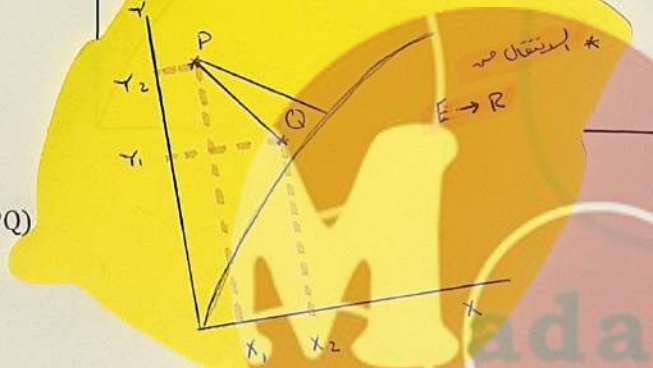
$$E_i y_i = E_s \frac{y_i}{1 - y_i} = E_s Y_i$$

$$R_s (X_1 - X_2) = E_s (Y_2 - Y_1)$$

$\frac{Y_2 - Y_1}{X_1 - X_2} = \frac{-R_s}{E_s}$

Straight line with slope $= -\frac{R_s}{E_s}$ (line PQ)

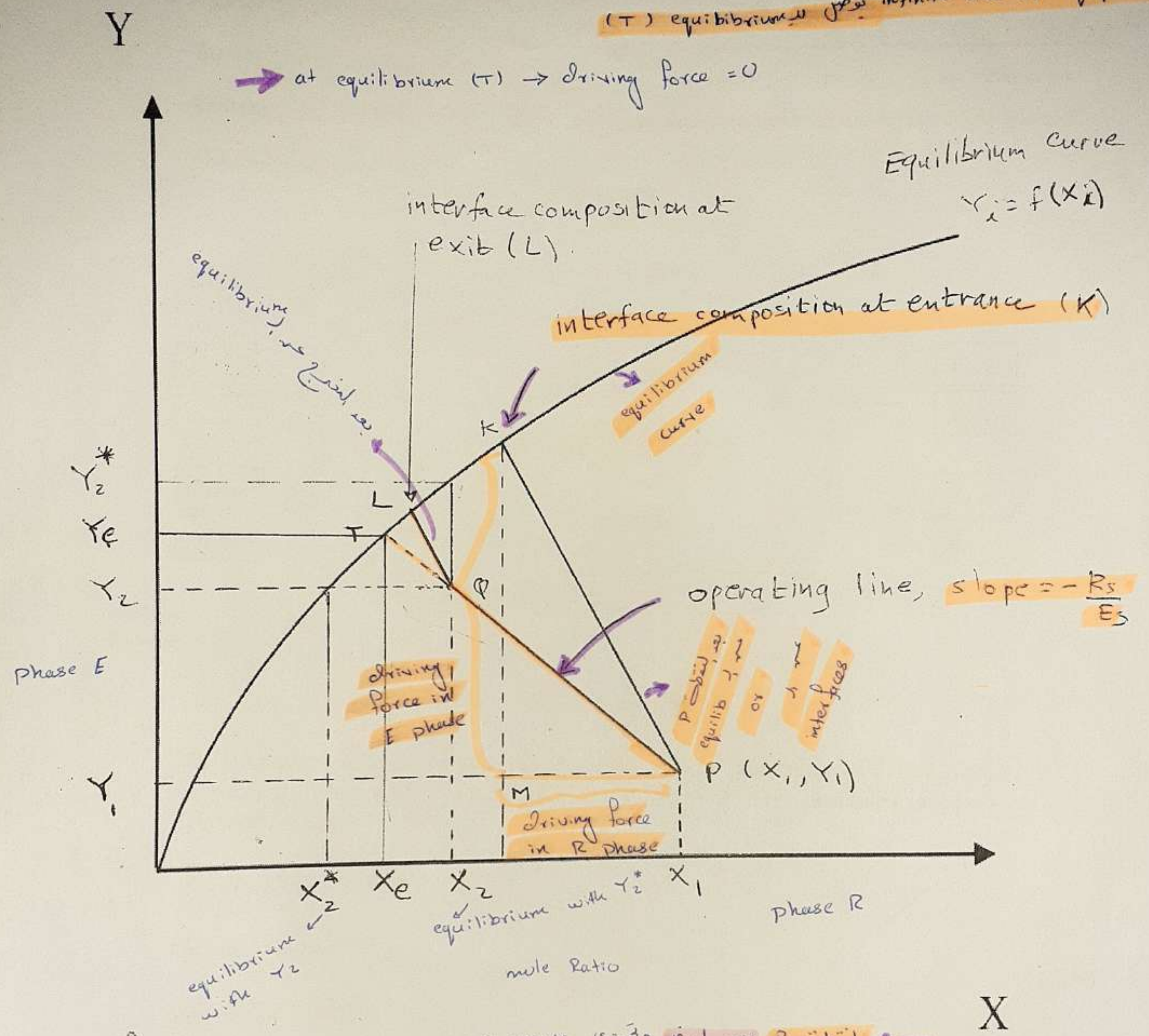
$\rightarrow Y_2 - Y_1 = \frac{-R_s}{E_s} (X_1 - X_2)$



* ... E → R

* تمثل النقطة T امتداد للخط PQ ← لو استمرينا بعملية النقل لـ infinite time وكان عندي infinite size of equipment بنوصل للـ equilibrium (T)

→ at equilibrium (T) → driving force = 0



← النقطة P هي المدخل وتحتوي على 2 phases

S → محور y

R → محور x

← صار في انتقال للـ solute من R → E (صار في نقصان بتركيز الـ solute في الـ R phase من النقطة $X_1 \leftarrow X_2$) بينما الـ E phase ازداد تركيز الـ solute من $Y_1 \leftarrow Y_2$).

← النقطة Q تمثل المخرج وتحتوي على 2 phases $Y < Y_2$ وكمان $X_1 > X_2$ بسبب الانتقال

* اختلاف قيم X_2 & X_1 تمثل driving force في R phase

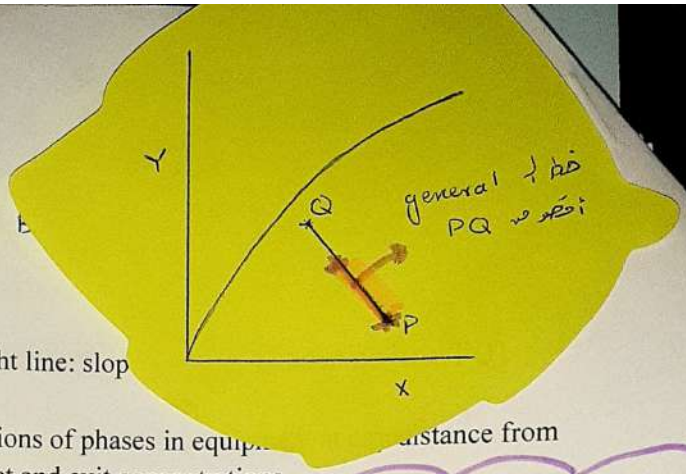
Y_1 & Y_2 " " E phase

BB' بين المذيب والمكثف :

Envelope II (General Balance) →

On solute free basis

$(Y - Y_1)$ Straight line: slop



general خط
PQ معادلة

$R_s(X_1 - X) = E_s(Y - Y_1)$

خط مستقيم ميله slope
يمر بالنقطة (X_1, Y_1) و PQ

ng compositions of phases in equip... istance from

Q represent inlet and exit concentrations

called Operating line → PQ

Operating Line → material balance represented by graph

e at entrance

osition at interface

g forces in E-phase (KM) and R-phase (MP) at entrance conditions

force line at exit

rface composition

Γ represents equilibrium compositions (Xe, Ye) if the equipment were longue enough. At this point the driving force is zero.

PQ →

Representation using other units

curve تظهر

R & E لـ

not constant

mole Ratio في

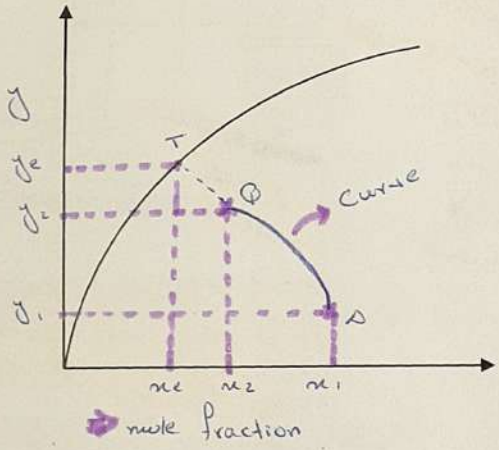
R & E → تتغيرا تبعًا للموقع

$R_1 x_1 - R x = E y - E_1 y_1$ Operating curve

$E y = R_1 x_1 + E_1 y_1 - R x$

$y = \frac{R_1 x_1 + E_1 y_1}{E} - \frac{R}{E} x$ Operating Curve

متغيرة

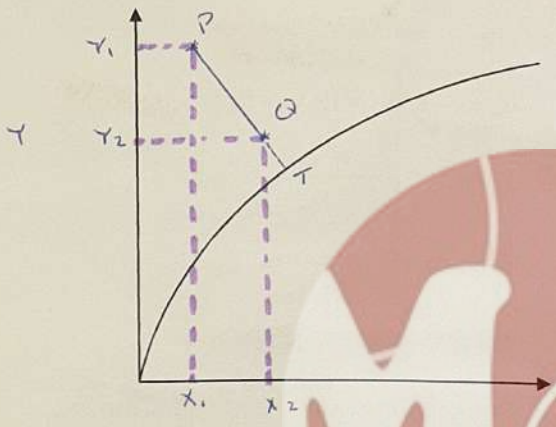


mole fraction

mol Ratio في

Note: If $E_1 = E_2 = E$ and $R_1 = R_2 = R$ ⟹ Straight line operating line in terms of mole fractions

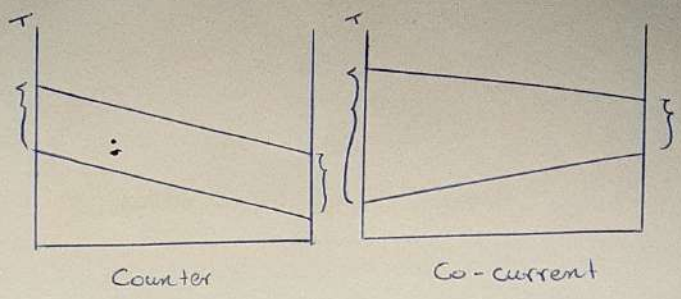
Solute transferring from E → R



heat transfer معلومات عن

driving force في (co-current)

driving force في counter تقريبا ثابتة

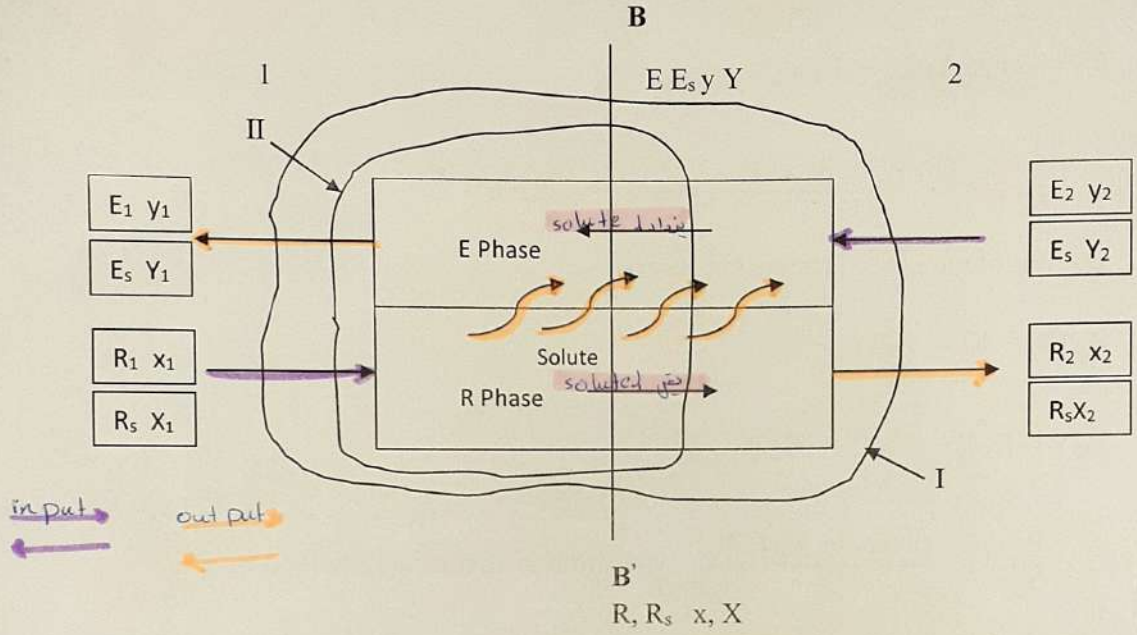


Material Balances:

Steady State Contacting Processes

System: two insoluble phases E and R and single solute transferring from phase R to Phase E

Counter Current Process:



Ri, Ei : moles total material/time ; **Rs, Es** : moles non diffusing material/time (constant)
xi, yi : mole fractions of solute in stream **i** ; **Xi, Yi** : mole ratios of solute in stream i
i : stream number

Solute diffusing from R → E

Solute Material balance

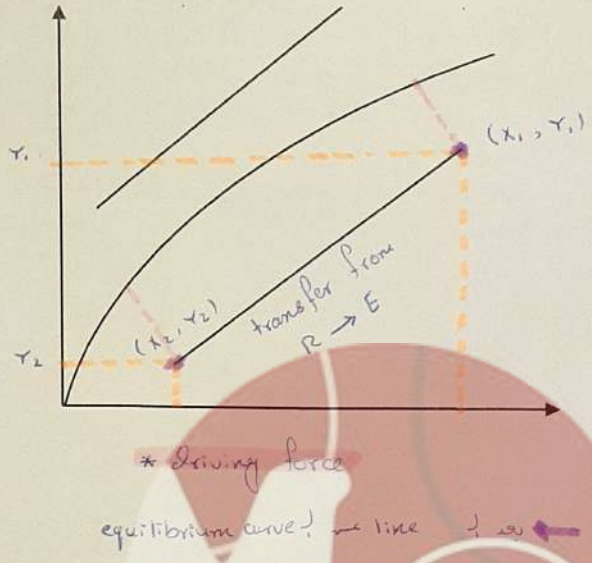
Envelop I (overall)

$$\overbrace{R_1 x_1 + E_2 y_2}^{\text{Input}} = \overbrace{R_2 x_2 + E_1 y_1}^{\text{Output}} \quad \text{mole fractions}$$

$$R_i x_i = R_S X_i \qquad E_i y_i = E_S Y_i$$

$$R_S(X_1 - X_2) = E_S(Y_1 - Y_2) \quad \text{mole ratios}$$

This is a straight line equation with slope $+\frac{R_S}{E_S}$



Envelop II (General) operating lines

In terms of mole fractions:

$$\underbrace{R_1 x_1 + E y}_{\text{Input}} = \underbrace{R x + E_1 y_1}_{\text{Output}} \quad \text{mole fractions}$$

E & R ⇒ Input أو متغيرات حسب البعد عن
or out put

$$E y = R x + E_1 y_1 - R_1 x_1$$

$$y = \frac{R}{E} x + \frac{(E_1 y_1 - R_1 x_1)}{E} \quad \text{operating curve}$$

R/E not cost ⇒ بدها الـ slope متغير

In terms of mole ratios (solute free basis)

$$R_S (X_1 - X) = E_S (Y_1 - Y)$$

$$E_S Y = R_S X - R_S X_1 + E_S Y_1$$

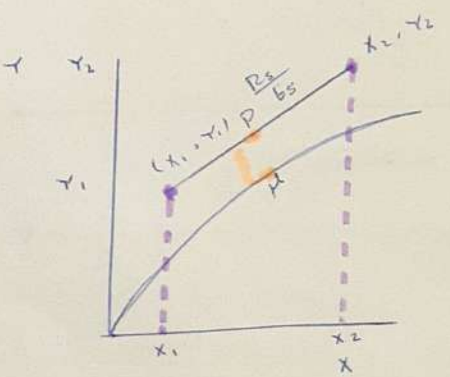
يشترك مع الـ overall line بـ point & slope
نيطبق على الـ overall line, وكمان طوله يعتمد على عدد الـ stages

\# $$Y = \frac{R_S}{E_S} X - \frac{(R_S X_1 - E_S Y_1)}{E_S}$$ straight line operating line slope $= +\frac{R_S}{E_S}$

In the case where the solute is passing from E → R, the operating line will be above the equilibrium curve.

- The operating line represents the material balance passing from point at one end to the point at the other end.
- A point on the operating line represents bulk concentrations of passing streams
- Lines such as PM indicate driving force

From solute material balance ⇒ *net flow ⇒ الفرق بين الـ flowrate in & out ⇒ $Ey - Rx = E_1 y_1 - R_1 x_1 = E_2 y_2 - R_2 x_2 = \text{constant}$



transfer from E → R

PM → driving force → تقريباً ثابتة

Equilibrium Stages ⇒ long time لـ two phase يتلامسوا لـ حتى

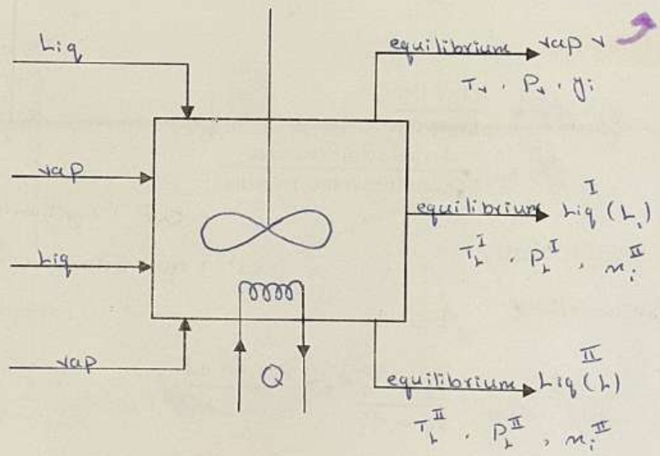
حتى يصير لـ net transfer = 0

- It is a theoretical concept representing the contact of two phases for sufficient time until they reach equilibrium
- The number of equilibrium stages represents the theoretical number of contacts required for a desired separation
- The use of stage efficiencies (based on mass transfer rates) and the number of equilibrium stages can be used to determine the number of the actual stages required for the separation.

$x_A = 0.5$ لـ v_1 , v_2 مثلاً
في $phase_1$ لـ ← ندرس
مع fresh solvent
صار التركيز ٠.٧ وأنا بدي
أوصل لتركيز معين
يعني أوصل لـ product
الي مع fresh solvent
الـ driving force

vapors لـ one stream لـ طلعوا
→ mescible مع بعض

Incoming streams
Not in equilibrium with each other



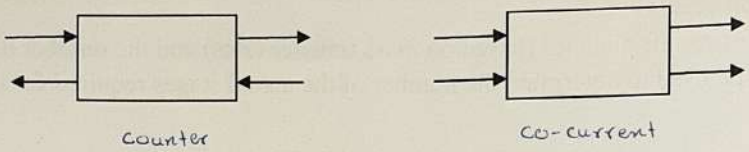
⇒ immescible liq with each other

- T/P equilibrium ⇒
- T & P ⇒ $T_v = T_L^{I} = T_L^{II}$ $P_v = P_v^{I} = P_v^{II}$
- VLE ⇒ $k_i^{I} = \frac{y_i}{x_i^{I}}$ $k_i^{II} = \frac{y_i}{x_i^{II}}$
- LLE ⇒ $k_{D_i} = \frac{x_i^{I}}{x_i^{II}}$ ⇒ Distribution coefficient

* بوحدة العمل إذا ما وصلت لـ equilibrium بوصلها بوحدة فصل ثانية ..... وهكذا !
حتى نوصل لـ equilibrium

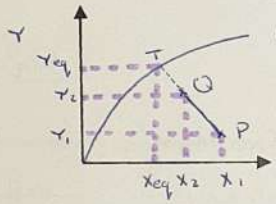
Single Stage

Effectively it is a concurrent operation. If the stage were ideal, the exit streams would be at equilibrium.



Stage efficiency

It is an expression of the fractional approach to equilibrium which a real stage produces.



Possible definitions:

- $\frac{\text{Line Qp}}{\text{Line Tp}}$
- $\frac{\text{Actual solute transfer}}{\text{Equilibrium solute transfer}}$

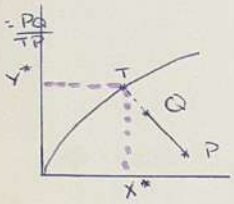
Murphree stage efficiency

E-phase

$$E_{ME} = \frac{Y_2 - Y_1}{Y_2^* - Y_1}$$

R-phase

$$E_{MR} = \frac{X_1 - X_2}{X_1 - X_2^*}$$



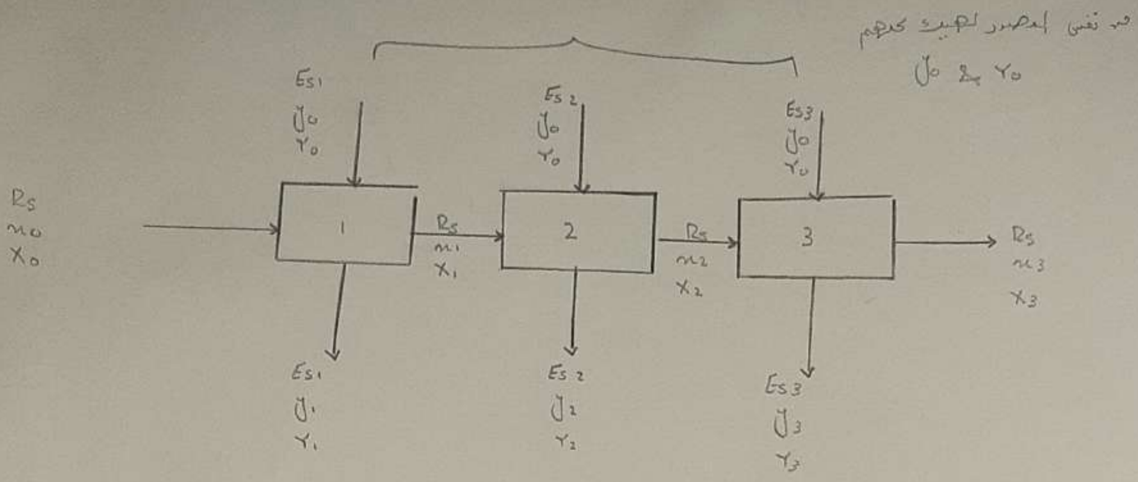
Y_2^* : in equilibrium with X_2

X_2^* : in equilibrium with Y_2

- This is an arbitrary definition since Y_2 will never be greater than Y_e and X_2 will never be lower than X_e
- $E_{ME} \neq E_{MR}$

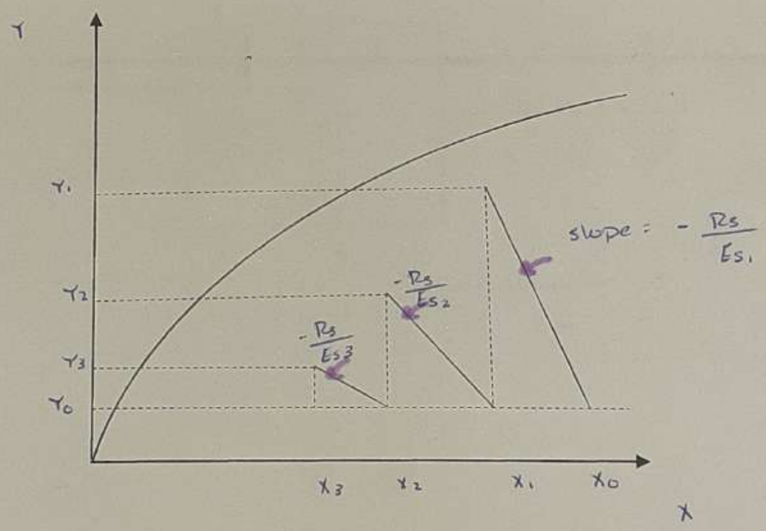
$Y^* > Y_2$

$X^* < X_2$

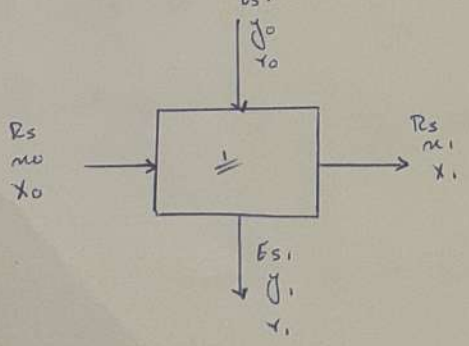


* في كل stage بجيني E_s من نفس المصدر، يعني تركيز ال solute ثابت، ولكن كمية E_s تختلف لهيك y_0، Y_0 ثابتة مع كل E_s

Material balances for each stage are the same as for a single stage.



* Solute material balance in unit 1



* تقل قيمة Y: كلما زاد عدد ال unit ($Y_1 > Y_3$) لانه انتقال المادة يصبح من solvent ليس fresh (مستهلك منه كمية من ال solute)، وبالتالي تقل ال driving force من stage لاخر. وتقل كمية ال solute المنتقل إلى ال phase E (Y)

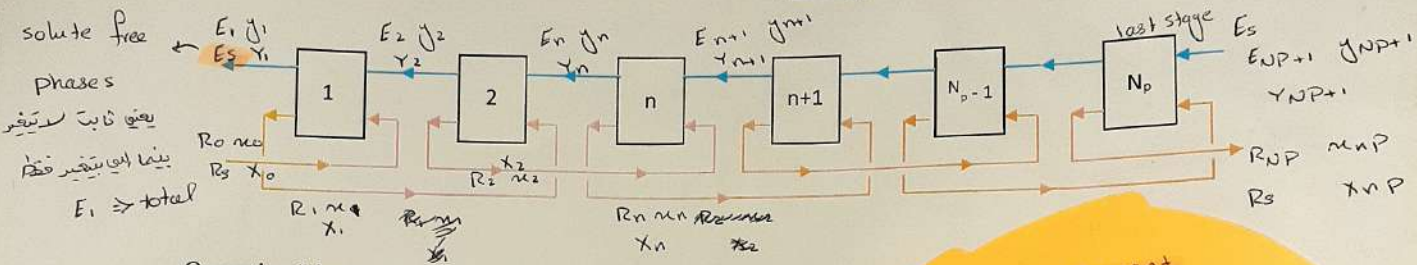
$$E_{s1} Y_1 - E_{s1} Y_0 = -(R_s X_1 - R_s X_0)$$

$$E_{s1}(Y_1 - Y_0) = -R_s (X_1 - X_0)$$

$$\frac{-R_s}{E_{s1}} = \frac{Y_1 - Y_0}{X_1 - X_0}$$

Counter Current Operations

- Most efficient arrangement [least number of stages for a given separation].
- Each stage is identical in its action to a cocurrent process; however, the cascade (battery) has the characteristics of a counter current process.
- Passing streams are not in equilibrium
- Streams leaving a stage are in equilibrium



Operating Lines:

Operating line for any equilibrium stage (n)

INPUT (X_{n-1}, Y_{n+1}) OUTPUT (X_n, Y_n)

Mole fractions: $R_{n-1}.x_{n-1} + E_{n+1}.y_{n+1} = R_n.x_n + E_n.y_n$

Mole ratios: $R_s.X_{n-1} + E_s.Y_{n+1} = R_s.X_n + E_s.Y_n$

$$R_s(X_{n-1} - X_n) = E_s(Y_n - Y_{n+1})$$

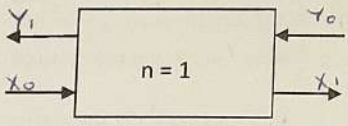
$$E_s Y_n - E_s Y_{n+1} = R_s X_{n-1} - R_s X_n$$

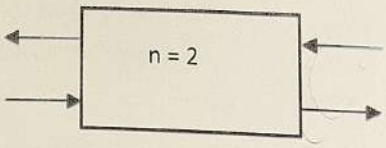
$$Y_{n+1} = \frac{R_s}{E_s} X_n + \frac{E_s Y_n - R_s X_{n-1}}{E_s}$$

$$Y_n = -\frac{R_s}{E_s} X_n + \frac{R_s.X_{n-1} + E_s.Y_{n+1}}{E_s}$$

(slope)

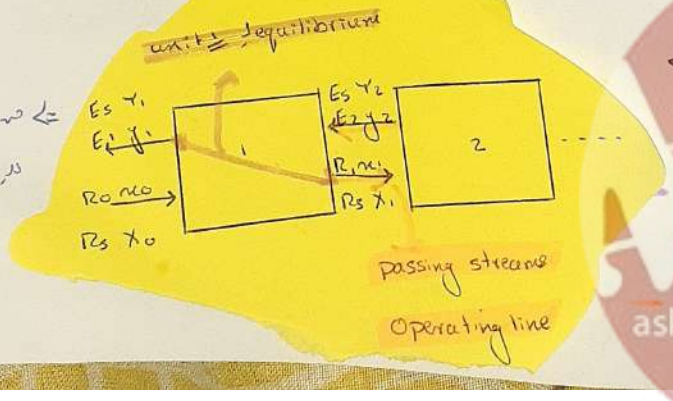
For example, take the first two stages:

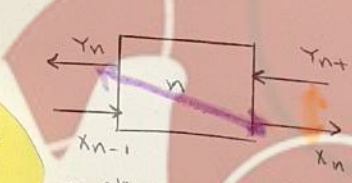




$$Y_2 = + \frac{R_s}{E_s} X_1 + \frac{-R_s X_0 + E_s Y_1}{E_s}$$

$$Y_3 = + \frac{R_s}{E_s} X_2 + \frac{-R_s X_1 + E_s Y_2}{E_s}$$





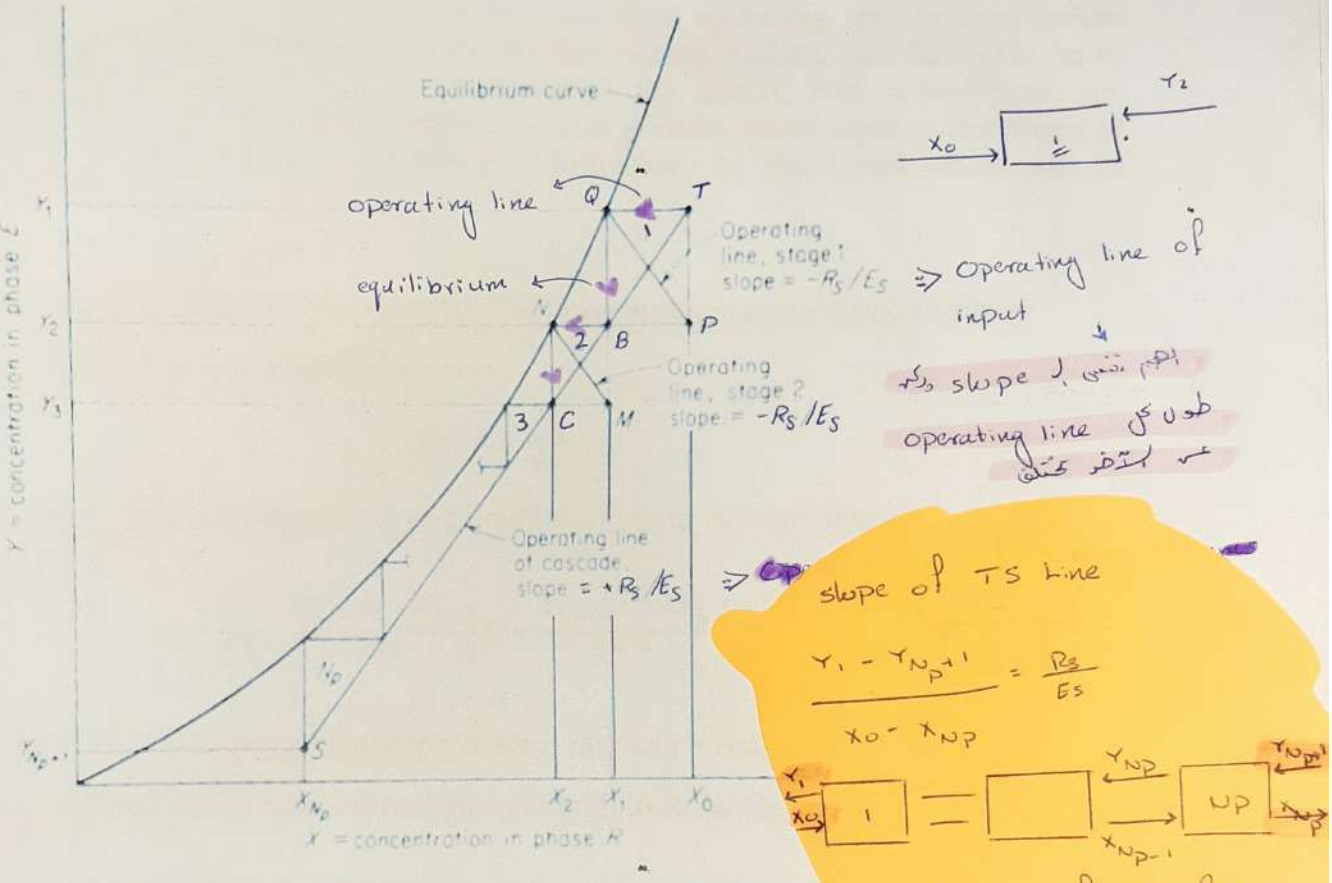


Figure 5.15 Countercurrent multistage cascade, solute transfer from ph

Notes:

- All individual stages have parallel operating lines of slope $= -\frac{R_S}{E_S}$
- Points X_n, Y_n fall on equilibrium curve. They are exit streams from stage n [Q , N]
- Points X_{n-1}, Y_{n-1} these are inlet streams to stage n [P , M]
- Points X_n, Y_{n+1} are compositions of passing streams [T , B , C]. Lines like , have the same slope $= +\frac{R_S}{E_S}$ and they all fall on the same line .

Operating line for the cascade:

Entire cascade: $R_s\left(X_o - X_{N_p}\right) = E_s\left(Y_1 - Y_{N_p+1}\right)$ ⇒ for all units

For any stage n: $R_s(X_o - X_n) = E_s(Y_1 - Y_{n+1})$

$Y_{n+1} = +\frac{R_S}{E_S} X_n + \frac{E_S Y_1 - R_S X_o}{E_S}$, Slope ; This line also coincides with .

Special Case: The equilibrium curve is approximately line

For most cases, because of either a curved operating line or equilibrium curve, the relation between number of stages, compositions, and flow ratio must be determined graphically, as shown. For the *special* case where both are straight, however, with the equilibrium curve continuing straight to the origin of the distribution graph, an analytical solution can be developed which will be most useful.

If the equilibrium-curve slope is $m = \frac{Y_{n+1}}{X_{n+1}}$ (straight line), and if an absorption factor (Extraction factor) A is defined as:

$$A = \frac{R_s}{\dot{m}E_s},$$

then based on material balance and equilibrium data, we can obtain the following equation:

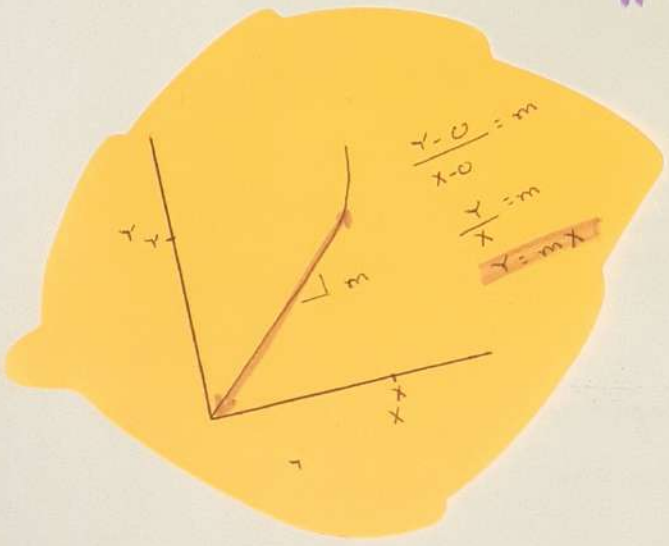
$$X_n = \left(X_0 - \frac{Y_{N_p+1}/m - AX_{N_p}}{1-A}\right)A^n + \frac{Y_{N_p+1}/m - AX_{N_p}}{1-A}$$

التراكيز بطرفين

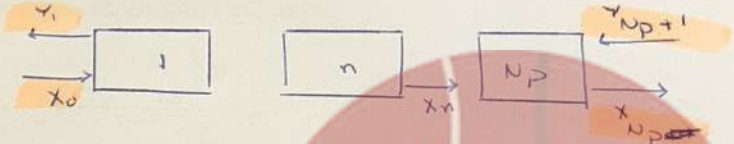
Therefore knowing terminal concentrations, X_n can be calculated.

In the opposite case where the transfer is from E to R, we define a stripping factor S as:

$$S = \frac{1}{A}$$



⇒ Special Case



تعتبر تراكيز طرفية (هم تمثل التراكيز بقد

Terminal Concentration (X_n أعتبر

Kremser Equations: (Kremser-Brown-Souders)

In the case where $n = N_p$, then:

For transfer from R to E (stripping of R)

$A \neq 1$:

$$\frac{X_0 - X_{N_p}}{X_0 - Y_{N_p+1}/m} = \frac{(1/A)^{N_p+1} - 1/A}{(1/A)^{N_p+1} - 1}$$

$$N_p = \frac{\log\left[\dfrac{X_0 - Y_{N_p+1}/m}{X_{N_p} - Y_{N_p+1}/m}(1 - A) + A\right]}{\log 1/A}$$

$A = 1$:

$$\frac{X_0 - X_{N_p}}{X_0 - Y_{N_p+1}/m} = \frac{N_p}{N_p + 1}$$

$$N_p = \frac{X_0 - X_{N_p}}{X_{N_p} - Y_{N_p+1}/m}$$

For transfer from E to R (absorption into R). A similar treatment yields:

$A \neq 1$:

$$\frac{Y_{N_p+1} - Y_1}{Y_{N_p+1} - mX_0} = \frac{A^{N_p+1} - A}{A^{N_p+1} - 1}$$

$$N_p = \frac{\log\left[\dfrac{Y_{N_p+1} - mX_0}{Y_1 - mX_0}\left(1 - \frac{1}{A}\right) + \frac{1}{A}\right]}{\log A}$$

$A = 1$:

$$\frac{Y_{N_p+1} - Y_1}{Y_{N_p+1} - mX_0} = \frac{N_p}{N_p + 1}$$

$$N_p = \frac{Y_{N_p+1} - Y_1}{Y_1 - mX_0}$$

These are called the Kremser-Brown-Souders (or simply Kremser) equations, after those who derived them for gas absorption [7, 14] although apparently Turner [16] had used them earlier for leaching and solids washing. They are plotted in Fig. 5.16, which then becomes very convenient for quick solutions.

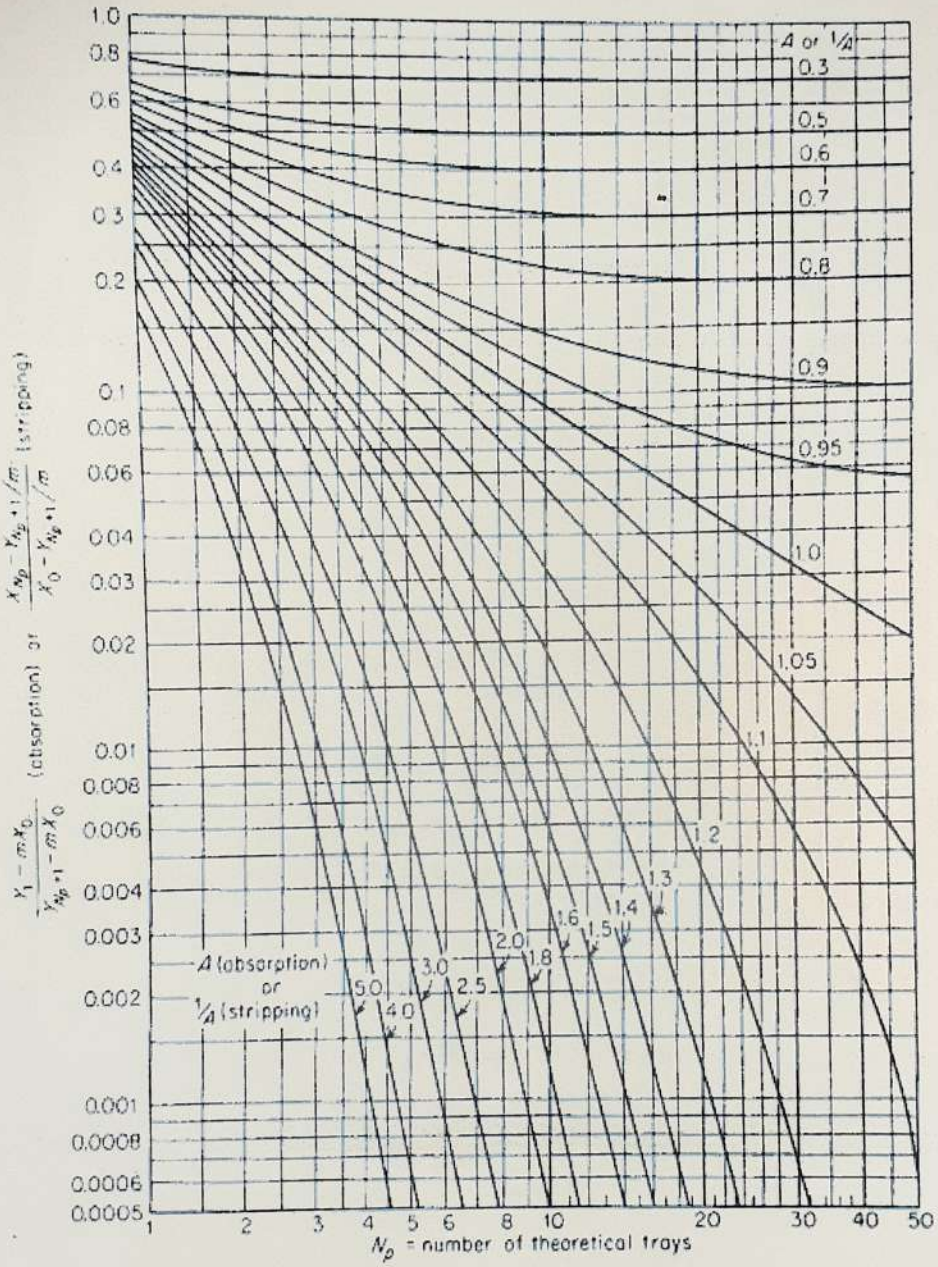


Figure 5.16 Number of theoretical stages for countercurrent cascades, with Henry's law equilibrium and constant absorption or stripping factors. [*After Hachmuth and Vance, Chem. Eng. Prog.*, **48**, *523, 570, 617 (1952).*]

درجات غليانهم متقاربة، يعني نظريًا بنقدر نفصلهم باستخدام distillation لكن عمليًا صعب extraction لأنه.

Mixture of Water and p-dioxane having boiling points of 100°C and 101.1°C respectively at 1 atm which means that they cannot be separated by distillation. However, Benzene can be used to extract p-dioxane form Water at 25°C. It is known that Water and Benzene are mutually insoluble and therefore mass ratios are convenient to use. The equilibrium relationship has the form:

$$Y = K_D X$$

Y: mass ratio of p-dioxane in Benzene (mass p-dioxane/mass Benzene)

X: mass ratio of p-dioxane in Water (mass p-dioxane/mass Water)

From equilibrium data it is known that the distribution coefficient (K_D) varies between 1 to 1.4 over the concentration range of interest. For this problem assume $K_D = 1.2$.

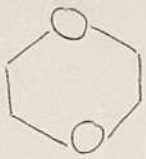
If 10,000 kg/hr of a 25% solution of p-dioxane in Water (R) is to be treated continuously with 15,000 kg/hr of pure Benzene (E), determine the effect of the number and arrangement of stages on the percent extraction of p-dioxane for the following situations:

a- Single equilibrium stage
b- Cocurrent arrangement
c- Cross current arrangement (2 stages)
d- Countercurrent arrangement (2 stages)

⇒ P-dioxane : 1,4 dioxane ⇒ $C_4H_2O_{12}$ it is an ether (R-O-R)

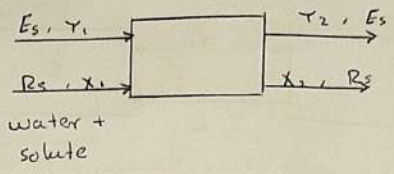
water ذائبة في البنزين أكثر من ذائبيتها في

بشبه structur تبع البنزين



Solute

a) Single equilibrium stage



1) Definition: % extraction of P-dioxane = solute in − solute out / solute in × 100%

$$= \frac{R_s X_1 - R_s X_2}{R_s X_1} \times 100\% = \frac{X_1 - X_2}{X_1} \times 100\%$$

$\Rightarrow R_s X = R_s \frac{S}{R_s} = S \Rightarrow$ solute في

→ Need X_1 & X_2

2) $X_1 = \frac{m_1 R}{(1-m_1)R} = \frac{\text{mass of solute}}{\text{mass of solvent}} = \frac{m_1}{1-m_1} = \frac{0.25}{1-0.25} = \frac{0.25}{0.75} = \frac{1}{3}$

3) X_2: from material balance on - P-dioxane

$$R_s X_1 + E_s Y_1 = R_s X_2 + E_s Y_2 \quad \text{--- 1}$$

in = out → for solute

معطى بالسؤال $Y_2 = k_D X_2$ --- 2

نعوض المعادلة 2 في المعادلة 1

$$R_s X_1 + E_s Y_1 = R_s X_2 + E_s k_D X_2$$

$$X_2 = \left(\frac{R_s X_1 + E_s Y_1}{R_s + E_s K D} \right) \div \frac{R_s}{R_s}$$

$$X_2 = \frac{X_1 + \frac{E_s}{R_s} Y_1}{1 + \frac{E_s}{R_s} k_D}$$ → extraction factor (E)

$Y_1 = 0$ → Pure Benzene

$$E = \frac{E_s}{R_s} k_D = \frac{(Y_1 - Y_2)E}{R_s} k_D = (1 - 0.25) \times 10{,}000$$

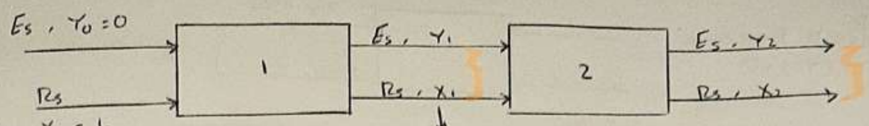
$$E = \frac{E_s}{(1-x)R} k_D = \frac{15{,}000}{(1-0.25) \times 10{,}000} \times 1.2 = 2.4$$

$$X_2 = \frac{X_1 + \frac{E_s}{R_s} Y_1}{1 + E} = \frac{1/3}{1 + 2.4} = 0.0980$$

$$\% \text{ extraction} = \frac{X_1 - X_2}{X_1} \times 100\% = \frac{1/3 - 0.0980}{1/3} \times 100\% = 70.6\%$$

$$Y_2 = X_2 k_D = 0.0980 \times 1.2 = 0.1176$$

b/ Co-current ⇒ consider 2 stages



$X_0 = \frac{1}{3}$ ← من الفرع الأول

⇒ at equilibrium with each other

so $X_1 = X_2$ & $Y_1 = Y_2$

لما two streams (Y_1, X_1)

في حالة اتزان، يعني ما رح يصير

انتقال للمادة في stage 2

$$\% \text{ recovery} = \frac{\overset{\text{in}}{X_0} - \overset{\text{out}}{X_2}}{X_0}$$

- from previous calculation

$$\frac{E_s}{R_s} = \frac{15{,}000}{7500} = 2$$

$$E = \frac{E_s}{R_s} k_D = 2.4$$

} same for both stage

* for stage 1

$X_1 = 0.098$ $\quad Y_1 = 0.1176$

* for stage 2

$$X_2 = \frac{X_1 + \frac{E_s}{R_s} Y_1}{1 + E} = \frac{0.98 + 2 \times 0.1176}{1 + 2.4} = 0.0980 = X_1$$

لما نضع stage 2 في حالة Co-current لا يؤثر وما رح

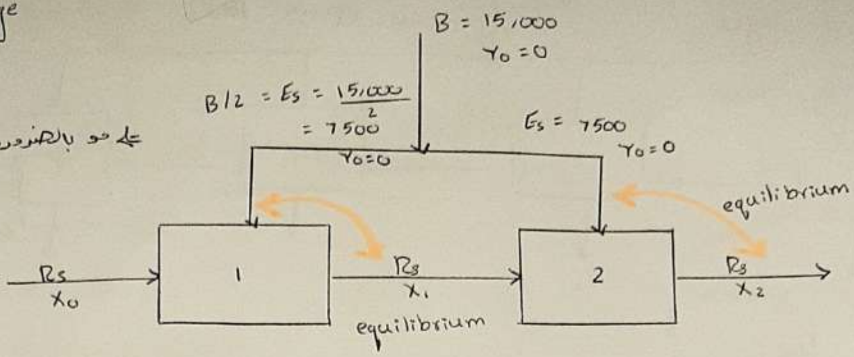
نحصل على شي أفضل من stage 1

$$\% \text{ recovery} = \frac{.333 - .098}{.333} \times 100\% = 70.57\% \simeq \% \text{ recovery for single stage}$$

في الفرع a

c Cross current 2 stage

ع مو بالضرورة ينقسم ال solvent بالتساوي



$$\%\ extraction = \frac{X_0 - X_2}{X_0} \times 100\%$$

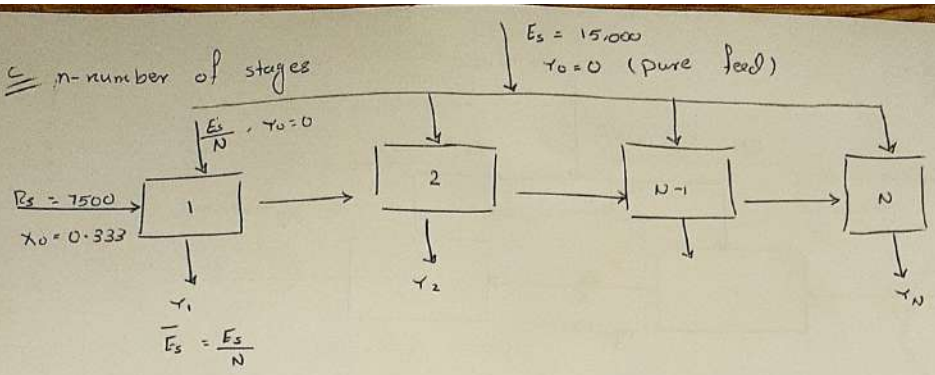
$$E = \frac{E_s}{R_s} k_D = \frac{7500}{7500} k_D = 1.2$$

$$X_1 = \frac{X_0 + 0}{1 + E} = \frac{1/3}{1 + 1.2} = 0.1515$$

$$X_2 = \frac{X_1 + 0}{1 + E} = \frac{0.1515}{1 + 1.2} = 0.0689$$ ⇒ ع ثبت stage 2 ق driving force

$$X_{out} = \frac{X_{in} + \frac{E_s}{R_s} Y_1}{1 + E}$$ → general

$$\%\ extraction = \frac{0.333 - 0.0689}{0.333} = 79.34\%$$



$\Rightarrow \bar{E}_s = \frac{E_s}{N}$ ← flow rate for each stage

$\bar{E} = \frac{(E_s/N)}{R_s} k_D = \frac{E}{N}$ ↓ extraction factor for each stage

$\Rightarrow$ E is effective extraction factor

% Recovery $= \frac{X_0 - X_N}{X_0} \times 100\%$

$\Rightarrow X_1 = \frac{X_0 + \left(\frac{E_s}{N}\right) * Y_0}{R_s} = \frac{X_0}{1 + \bar{E}} = \frac{X_0}{1 + \frac{E}{N}}$

$X_2 = \frac{X_1 + \frac{E_s}{N} \cdot Y_0}{R_s} = \frac{X_1}{1 + \bar{E}}$ ($Y_0 = 0$)

$\Rightarrow X_2 = \frac{X^0}{1 + \frac{E}{N}} * \frac{1}{1 + \frac{E}{N}} = \frac{X^0}{\left(1 + \frac{E}{N}\right)^2}$

$\Rightarrow X_N = \frac{X_0}{\left(1 + \frac{E}{N}\right)^N}$

$\Rightarrow$ % Recovery $= \frac{X_0 - X_N}{X_0} \times 100\%$

$= X_0 - \frac{\frac{X_0}{\left(1 + \frac{E}{N}\right)^N}}{X_0} \times 100\%$

$= 1 - \frac{1}{\left(1 + \frac{E}{N}\right)^N} \times 100\%$

$\% = \frac{\left(1 + \frac{E}{N}\right)^N - 1}{\left(1 + \frac{E}{N}\right)^N} \times 100\%$

From material balance of solute in stage 2

$R_s X_1 + \frac{E_s}{N} Y_0 = \frac{E_s}{N} Y_2 + R_s X_2$

$Y_2 = k_D X_2$

$R_s X_1 + \frac{E_s}{N} Y_0 = \frac{E_s}{N} k_D X_2 + R_s X_2$

$R_s X_1 + \frac{E_s}{N} Y_0 = X_2 \left(\frac{E_s}{N} k_D + R_s\right)$

$X_2 = \left(\frac{R_s X_1 + \frac{E_s}{N} Y_0}{\frac{E_s}{N} k_D + R_s}\right) \div R_s$

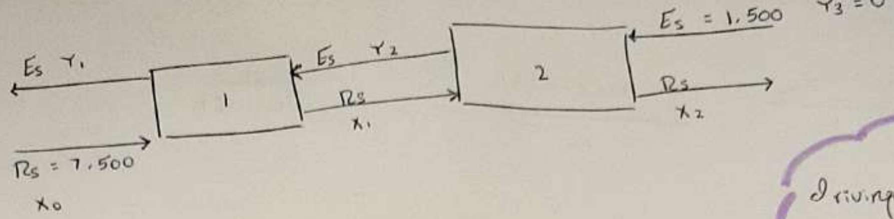
$X_2 = \frac{X_1 + \left(\frac{E_s}{N}\right) / R_s \cdot Y_0}{\bar{E} + 1}$

% Recovery independent on concentration

$\Rightarrow$ % Recovery depend on E ← extraction factor

$E \uparrow$ % Re $\uparrow$

2) Counter current 2 stages



أقوى driving force
وأقوى من ال cross
لانه ال cross بتقل ال driving force
مع الزمن

$E = \frac{E_s}{R_s} k_D = 2.4$ for each stage

$X_0 = 0.333$ $\quad Y_3 = 0$

* Stage 1

$$R_s X_0 + E_s Y_2 = R_s X_1 + E_s Y_1$$

$$Y_1 = k_D X_1$$

$$R_s X_0 + E_s Y_2 = R_s X_1 + E_s k_D X_1$$

$$X_1 = \left(\frac{R_s X_0 + E_s Y_2}{R_s + E_s k_D} \right) \div \frac{R_s}{R_s}$$

$$X_1 = \frac{X_0 + \frac{E_s}{R_s} Y_2}{1 + E}$$

ولكن قبل التعويض،
عوض بدل $Y_2 = k_D X_2$

$$X_2 = \frac{X_1 + \frac{E_s}{R_s} Y_3}{1 + E} = \frac{X_1}{1 + E} \quad (Y_3 \to 0)$$

$$X_2 = \frac{X_0 + \frac{E_s}{R_s} k_D X_2}{(1 + E)^2}$$

$$X_2 = \frac{X_0 + E X_2}{(1 + E)^2} \Rightarrow X_2 = \frac{X_0 + E X_2}{1 + 2E + E^2}$$

$$X_2 = \frac{X_0}{1 + E + E^2} = \frac{0.333}{1 + 2.4 + (2.4)^2} = .036$$

$$\% \text{ Recovery} = \frac{0.333 - 0.036}{0.333} = 89.08\%$$

* $\lim_{N \to \infty} x_N = \dfrac{x_0}{\exp(E)} \Rightarrow x_\infty = \dfrac{x_0}{\exp(E)}$

$$\% \text{ Recovery} = \frac{x_0 - x_\infty}{x_0} = \frac{x_0 - x_0/\exp(E)}{x_0} = 1 - \frac{1}{\exp(E)}$$

* ex : $N = 5$

$$E = \frac{E_s}{R_s} \times k_D = \frac{15{,}000}{7{,}500} \times 1.2 = 2.4$$

$$\% \text{ recovery} = \left(1 - \frac{1}{\left(1 + \frac{E}{N}\right)^N}\right) \times 100\%$$

$$= \left[1 - \frac{1}{\left(1 + \frac{2.4}{5}\right)^5}\right] \times 100\% = 85.92\%$$

تقريبا نوصل لل ∞ من ال stages

الفرق بين 5 # of stages & 100 # of stages ≃ 5%

* ex : $N = 100$

$$x_{100} = \frac{.333}{\left(1 + \frac{2.4}{100}\right)^{100}} = 0.0311$$

$$\% \text{ Recovery} = \left(1 - \frac{1}{\left(1 + \frac{2.4}{100}\right)^{100}}\right) \times 100\% = 90.67\%$$

* ex : $N = \infty$

$$x_\infty = \frac{0.333}{\exp(2.4)} = 0.0302$$

$$\% \text{ Recovery} = 1 - \frac{1}{\exp(2.4)} = 90.93\%$$

تحسن قيمة % Recovery بزيادة ال (E) extraction factor

وترتفع قيمة E بزيادة ال solvent

$E = \dfrac{E_s}{R_s} \times k_D$

$E_s \uparrow \quad E \uparrow$

ويفضل ان تكون E > 1

n - Number of stage ⇒ Counter

$X_N = \frac{X_0}{\sum_{i=0}^{N} E^i}$

ex: $N = 5$

$$X_5 = \frac{X_0}{1 + E + E^2 + E^3 + E^4 + E^5} = 0.0025$$

$$\%\ \text{Recovery} = \frac{0.333 - 0.0025}{0.333} \times 100\% = 99.26\%$$

Lim $N \to \infty$

⇒ $X_\infty = 0$ $\quad 1 \leq E \leq \infty$ ⇒ % Recovery = 100%

⇒ $X_\infty = (1 - E) X_0$ $\quad E \leq 1$ ⇒ % Recovery $= \frac{X_0 - (1-E)X_0}{X_0} = 1 - (1-E) = E$

* Summery: % Recovery

صوفي البنسبي (.5 : .5)

# of stage	1 eqm stage	Co-current	Cross flow (X)	Counter current
1	70.6	—	—	—
2	70.6	70.6	79.34	89.08
5	70.6	70.6	85.92	99.26
∞	70.6	70.6	90.93	100% $\quad 1 \leq E \leq \infty$ E $\quad$ if $\quad E \leq 1$

في قسم بقيل % Recovery

% recovery في قسم بقصل

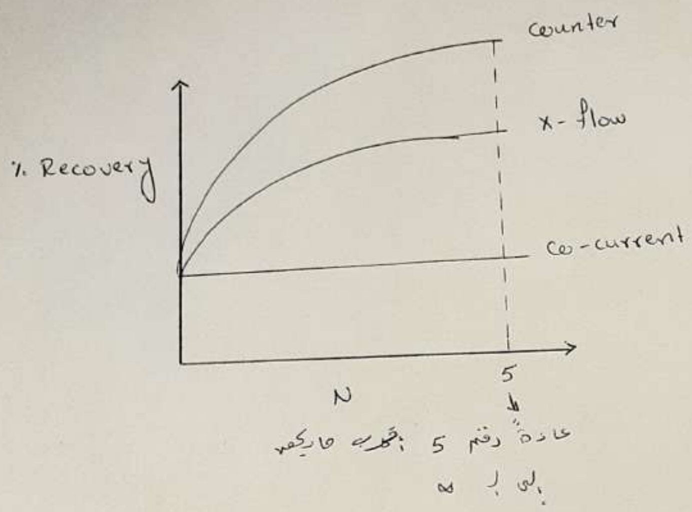
* Note: for very small values of E (0.1 for example)

	Cross flow (X)	Counter-current
X_∞	$\frac{X_0}{\exp(E)} = 0.301$	$(1-E)X_0 = 0.2997$
% Recovery	9.55%	10%

* يفضل استخدام counter - current على cross flow لأنها تكون % Recovery أعلى إذا كان $E \geq 1$

- The difference is small

- Counter current is preferred since it is desirable to operate with E>1



Specification of Design Variables:

Solution of separation problems requires specification of a sufficient number of design variables in order to determine unknown (output) variables by solving an equal number of independent equations. The process will then be uniquely specified if the input variables are correctly specified.

The number of design variables reflects the number of degrees of freedom (N_D) one has in correctly specifying a process. It is suggested that this number can be found as follows:

$$N_D = N_V - N_E$$

-Independent design variables -Degrees of Freedom -Variance	All Pertinent Variables	Independent Equations

Number of Variables N_V:

The variables which can be counted in N_V are:

- ✓ Intensive: Variables T, P, x, ... → concentration (mole fraction, mass fraction, ...)
- ✓ Extensive: Flow rates, Q, ...
- ✓ Equipment Parameters: Number of Stages

Physical properties such as Enthalpy, K are not counted

Number of Independent Equations N_E:

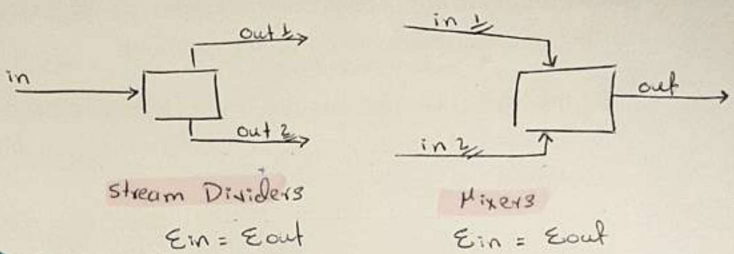
Care must be taken in identification of independent equation

Types of Equations which can be used:

- ✓ Material Balances
- ✓ Energy Balances
- ✓ Phase Equilibrium Restrictions
- ✓ Process Specifications T, P
- ✓ Equipment configurations (counter, ...)

Separation Equipment Consist of:

- ✓ Physically identifiable elements: Equilibrium stages, Condensers, Reboilers
- ✓ Stream Dividers
- ✓ Stream Mixers



Examples:

1- Stream Variables:

For single phase stream containing C components; the phase rule states that the intensive variables are:

$$C-\mathcal{P}+2 = C+1$$

These are C-1 concentrations (mole fractions or others), and to this we add Temperature and Pressure as intensive variables. To this number we add the flow rate (extensive variable).

Nv:

Category	Variable	Number*	
Intensive	mole fractions	C	C-1
	T	1	1
	P	1	1
Extensive	Flow rate	1	1
Nv	=	C+3	C+2

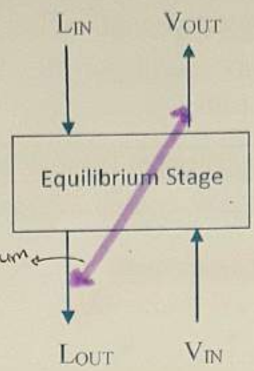
* In counting the number of intensive variables, usually C-1 concentrations specify all compositions since the remaining concentration is obtained by difference. However, we can specify all concentrations (C) in counting the number of intensive variables and include in the list of equations the summation of concentrations constraints, such as the summation of mole fractions:

$$\sum_{i=1}^{C} mole\ fractions = 1$$

Therefor:

Nv = C+3 Or Nv = C+2

2- Adiabatic Equilibrium Stage:



NV:

The only variables are those associated with streams:

$$N_V = 4(C+3) = 4C + 12 \quad \text{Or} \quad N_V = 4(C+2) = 4C + 8$$

NE

Category	Number of Equations	
Equilibrium Restrictions:		
$P_{VOUT} = P_{LOUT}$	1	1
$T_{VOUT} = T_{LOUT}$	1	1
Phase Equilibrium $(y_i)_{VOUT} = k_i (x_i)_{LOUT}$	C	C
Component Balances	C-1	C-1
Total Material Balance	1	1
Adiabatic Enthalpy Balance	1	1
Mole Fraction Constraints (Sum of Mole Fractions)	4	-
NE =	2C+7	2C+3

Component material balance:

$$L_{IN}(x_i)_{L_{IN}} + V_{IN}(y_i)_{V_{IN}} = L_{OUT}(x_i)_{L_{OUT}} + V_{OUT}(y_i)_{V_{OUT}}$$

Total material balance:

$$L_{IN} + V_{IN} = L_{OUT} + V_{OUT}$$

Adiabatic enthalpy balance:

$$H_{L_{IN}} L_{IN} + H_{V_{IN}} V_{IN} = H_{L_{OUT}} L_{OUT} + H_{V_{OUT}} V_{OUT}$$

Mole fraction constraints in any stream:

$$\sum_{i=1}^{C} mole\ fractions = 1$$

Design Variables, N_D:

$N_D = N_V - N_E$	(4C+12) – (2C+7)	(4C +8) – (2C+3)
N_D =	2C + 5	2C + 5

Therefore (2C+5) variables must be specified.

Typical Set of Variables: Complete specification of the two incoming streams as well as stage pressure.

Specified Variable	Number of Variables
Liquid IN mole fractions $(x_i)_{LIN}$	C-1
L_{IN}: Liquid IN flow rate	1
Vapor IN mole fractions $(y_i)_{VIN}$	C-1
V_{IN}: Vapor IN flow rate	1
Temperature and Pressure of L_{IN}	2
Temperature and Pressure of V_{IN}	2
Stage Pressure (P_{VOUT} OR P_{LOUT})	1
ND =	(2C+5)

*إذا ما زبط الفصل بال Distillation بلجأ لطرق أخرى مثل الـ extraction
add mass to creat a phase

Distillation:

add energy to creat a phases ⇒ يستهلك طاقة (مشكلة)

- ✓ Separation is based on volatility difference
- ✓ Heat is supplied to create a vapour phase in equilibrium with a li[…]
- ✓ All components in the feed are present in both phases in differe[…] phase is richer in mvc; while liquid phase is richer in lvc
- ✓ Separation is not isothermal but may be considered to be clos[…]
- ✓ Process may be single stage (Flash vaporization or partial co[…] distillation, or continuous fractionation (packed towers or m[…] tray columns), each offering a varying degree of separation.

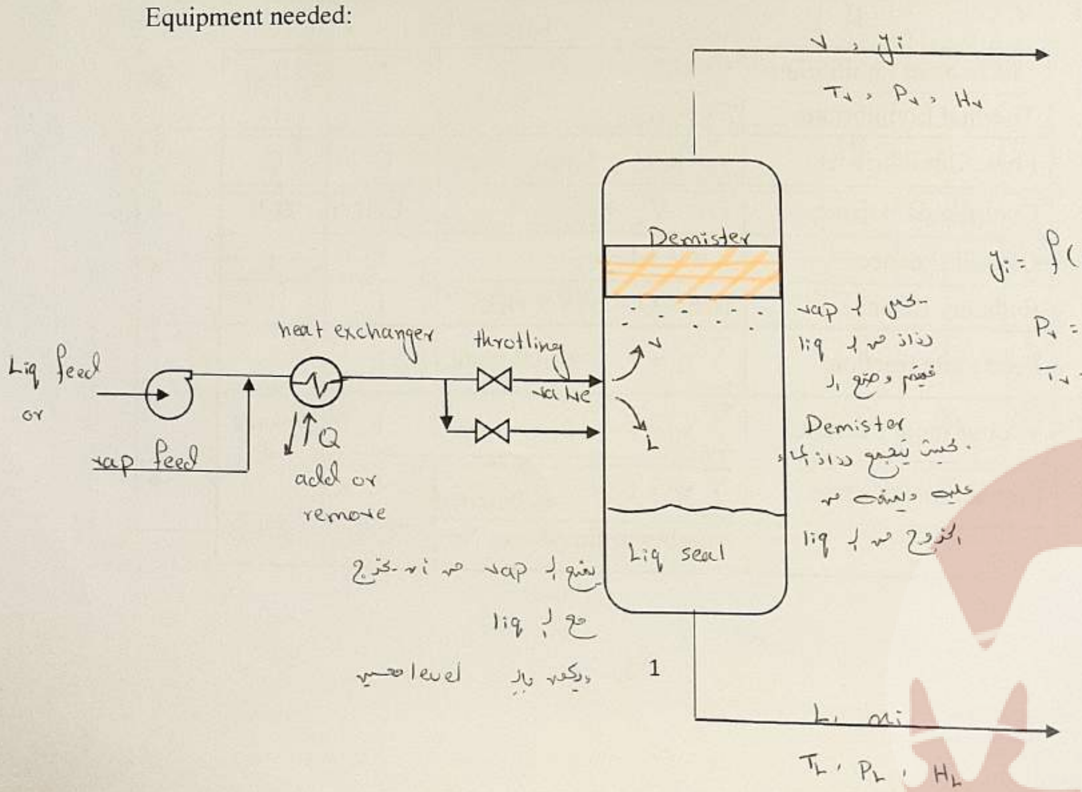
mvc ⇒ more volatile component.
lvc ⇒ less volatile component.
equi. stage

0.95 < α < 1.05 ⇐ يصعب الفصل عن طريق الـ distillation لأن الـ volatility تكون تقريباً متساوية، فنلجأ لطريقة أخرى مثل الـ extraction

Equilibrium Flash Vaporization and Partial condens[…]

- ➢ Single equilibrium stage separation processes
- ➢ Unless relative volatilities are very large, the degree of separation […]
- ➢ Useful for removal of light components from heavy ones (e.g. removal of NH_3, […] from crude oil)
- ➢ Flash vaporization: A liquid feed is partially vaporized to give a vapour richer in mvc in equilibrium with a liquid richer in lvc. The liquid may be flashed:
  - ❖ Adiabatically across a throttling valve (high pressure liquid is throttled into a flash drum).
  - ❖ Isothermally: throttling valve is not used (liquid under low pressure is vaporized in a heater then separated into two phases in a flash drum.
- ➢ Partial condensation: A vapour feed is cooled and partially condensed with phase separation taking place in a flash drum.
- ➢ Vapour and liquid leaving a flash drum are in equilibrium with each other
- ➢ Flash calculations can be used to determine the state of a stream of known composition, Temperature and Pressure.

Equipment needed:



$y_i = f(x_i)$ ⇒ equilibrium
$P_V = P_L$
$T_V = T_L$

1

Operation: (Ex: adiabatic flash)

- Feed is pressurised and heated (if necessary)
- Feed is the passed through a throttling valve or nozzle into a flash drum at a lower pressure
- Due to large drop in pressure, a fraction of the liquid vaporises
- Vapour is taken off overhead, while the liquid drains to the bottom of the drum
- Demister prevents liquid droplet from being entrained in the vapour

Design Considerations

The design of an equipment involves

- → Stream variables calculations (chemical engineering) ⇒ m, T, P, ---
- → Size of equipment (last calculation)

Stream and process variables for flash or partial condensation, N_V:

composition of feed

$$F, V, L, \vec{Z}, \vec{y}, \vec{x}, T_F, T_V, T_L, P_F, P_V, P_L, \text{ and } Q$$

3 stream

∴ $N_V = 3\,(C+3) + 1$ OR $N_V = 3\,(C+2) + 1$

T&P & flow rate   Q (extensive property)   C-1

Number of Equations, N_E:

k is function on T, volatility

k ⇒ cost

Mechanical Equilibrium	$P_V = P_L$	1	1
Thermal Equilibrium	$T_V = T_L$	1	1
Phase Equilibrium	$y_i = k_i\, x_i$	C	C
Component Balance	$Fz_i = V\, y_i + L\, x_i$	C-1	C-1
Overall Balance	$F = V + L$	1	1
Enthalpy Balance	$H_F F + Q = H_V V + H_L L$	1	1
Feed mole fraction	$\sum z_i = 1$	1	Not Counted
Vapour mole fractions	$\sum y_i = 1$	1	
Liquid mole fraction	$\sum x_i = 1$	1	
	Number of Equations, N_E	2C+6	2C+3

Degrees of Freedom, N_D:

$N_D = N_V - N_E$	$[3(C+3)+1] - [2C+6]$	$[3(C+2)+1] - [2C+3]$
N_D	$C + 4$	$C + 4$

Usually the designer has information about:

- Feed flow rate F 1
- Feed Temperature T_F 1
- Feed Pressure P_F 1
- Feed Composition $\vec{z}$ C-1 since $\sum z_i = 1$ is not needed

$C + 2$

$(C+4) - (C+2) = 2$ أغلب الحسابات تكون معطيات موجودة Feed لـ $\therefore N_D = 2$

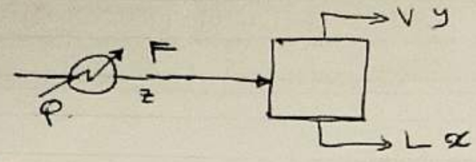
This means that two additional variables can be specified and the rest are calculated.

The choice of the specified variables controls the choice of the computational procedure. The designer may be required to solve material balance equations and equilibrium equation then solve for energy balance (sequential solution procedure) or solve material , equilibrium and energy equation (simultaneous solution).

Examples:

Case	Specified variables	Type of Computational Procedure	Output Variables					
1	T_V, P_V	Isothermal	Q		V	$\vec{y}$	L	$\vec{x}$
2	P_V and $Q = 0$	Adiabatic		T_V	V	$\vec{y}$	L	$\vec{x}$
3	L, P_V	Percent Liquid	Q	T_V	V	$\vec{y}$		$\vec{x}$
4	V, P_V (or T_V)	Percent Vapour	Q	$T_V(P_V)$		$\vec{y}$	L	$\vec{x}$
5	$P_V, Q \neq 0$	Non Adiabatic		T_V	V	$\vec{y}$	L	$\vec{x}$
6	P_V, x_j	Liquid Purity	Q	T_V	V	$\vec{y}$	L	$\vec{x}_{i\neq j}$
7	P_V, y_j	Vapour purity	Q	T_V	V	$\vec{y}_{i\neq j}$	L	$\vec{x}$
8	y_j, x_k	Separation	P_V, Q	T_V	V	$\vec{y}_{i\neq j}$	L	$\vec{x}_{i\neq k}$

Binary Mixtures: Graphical Methods



x-y diagram: material balance with equilibrium

Material Balances for mvc & less volatile component by difference

$zF = yV + Lx$

➡ Component: $y = -\frac{L}{V}x + \frac{F}{V}\cdot z$ $\frac{y-z}{x-z} = -\frac{L}{V}$

Total : $L = F - V$

$\Psi = \frac{V}{F}$ (fraction vaporized).

$y = -\frac{(F-V)}{V}x + \frac{F}{V}z$

$= -\frac{1-V/F}{\frac{V}{F}}x + \frac{1}{\frac{V}{F}}z$

$= -\frac{(1-\Psi)}{\Psi}x + \frac{z}{\Psi}$ — st. line (operating line).

slope, intercept.

*when $\psi = 0$
$y = -\frac{1}{0}x + \frac{z}{\psi}$ ⇒ slope = ∞ ⇒ يعني الخط عامودي

*when $\psi = 1$
$y = -(0)x + z$ ⇒ slope = 0 ⇒ يعني الخط أفقي

... line also passes through the point $z = x = y$

[... $= y \rightarrow z = x$]

(sticky note:)

* $y = -\frac{(1-\psi)}{\psi}x + \frac{z}{\psi}$

$x = y = z$ *خط ال 45°

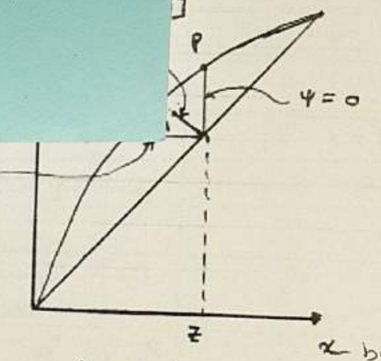
- عوض $x = y$

$x = -\frac{(1-\psi)}{\psi}x + \frac{z}{\psi}$

$\left(x + \frac{(1-\psi)}{\psi}x = \frac{z}{\psi}\right)\psi$

$\psi x + (1-\psi)x = z$

$x(1) = z$ #



⇐ أكبر كمية vap يكون كلها vap

$\psi = 0$ (Bubble point → Saturated liquid.

- M : non eqm Stage product
- N : eqm Stage product
- P : richest point of feed $\Psi = 0$
- T : leanest point of feed $\psi = 1$

x bubble point ⇐ $\Psi = 0 = \frac{V}{F}$ ⇒ $V = 0$ → more rich in feed

(sat liquid ما في vap لسا (الخروج)

(sat vapor) كل السائل vap صار dew point ⇐ $\psi = 1 = \frac{V}{F}$ ⇒ $V = F$ → leanest point of feed

4

energy & material balance with equilibrium

Hyx diagram: (solving material and Energy Balances)

قد يكون + أو - أو 0 إذا لا يوجد تسخين أو تبريد

EB: $H_F \cdot F + Q = H_V \cdot V + H_L \cdot L$

$$F\left(H_F + \frac{Q}{F}\right) = H_V \cdot V + H_L \cdot L$$

material with energy balance $\Rightarrow (V+L)\left(H_F + \frac{Q}{F}\right) = H_V \cdot V + H_L \cdot L$

$$\Rightarrow \left[H_V - \left(H_F + \frac{Q}{F}\right)\right] V = -\left[H_L - \left(H_F + \frac{Q}{F}\right)\right] \cdot L$$

$$\Rightarrow \boxed{-\frac{L}{V} = \frac{H_V - (H_F + Q_F/F)}{H_L - (H_F + Q_F/F)} = \frac{y - z}{x - z}}$$

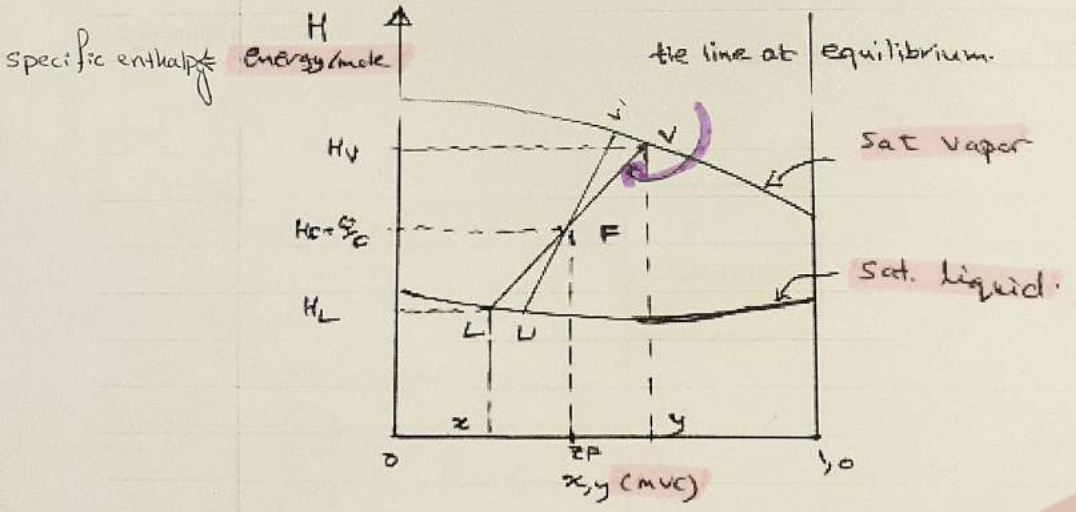
Enthalpy of feed after Heat exchanger.

This is a straight line on the Hyx diagram with the following coordinates:

Point V $\longrightarrow (H_V, y)$

Point L $\longrightarrow (H_L, x)$

Point F $\longrightarrow \left[\left(H_F + \frac{Q}{F}\right), z\right]$



LV is also a tie line for an equilibrium process

L' V' corresponds to a non equilibrium stage.

Multicomponent Isothermal Flash and Partial condensation Calculations:

Given
- ▲ Feed data $(F, T_F, P_F, C-1 \text{ values of } \vec{z})$ — $\vec{z}$: composition of feed
- ▲ T_V (or T_L)
- ▲ P_V (or P_L)

Required: $V, L, Q, \vec{y}, \vec{x}, T_L (\text{or } T_V), P_L (\text{or } P_V), Z_c$ (Remaining)

Remaining unknowns: $2C+6$

Procedure: The solution procedure is sequential.

Step 1:

Solve equations containing one variable.

$$T_L = T_V$$
$$P_L = P_V$$
$$Z_k = 1 - \sum_{\substack{i=1 \\ i \neq k}}^{c} z_i \qquad c: \text{no. of components.}$$

Step 2: Solution of Material Balance and Eqm Relations

- ▲ Material balances are non linear → computational procedure is not straight forward and many solution strategies can be adopted
- ▲ K_i values may be function of composition or independent of composition. This influences the solution strategy.

T is cost ⇐ بنفرض قيم الـ k_i تعتمد عالـ composition

ودائماً الـ case هاي بنعتبر قيم الـ k_i لا تعتمد عالـ x يعني k_i is cost

Case 1: K_i values independent of composition.

component balance $\boxed{Fz_i = Vy_i + Lx_i}$

+

total balance $\boxed{F = V + L}$

$\Rightarrow \boxed{Fz_i = Vy_i + (F-V).x_i}$

x_i & K_i عوض عن y_i بدلالة

y_i & K_i عوض عن x_i بدلالة

Substitute for y_i or x_i $\boxed{y_i = K_i . x_i}$

solve for y_i | solve for x_i

$\boxed{Fz_i = Vy_i + (F-V).\frac{y_i}{K_i}}$ | $\boxed{Fz_i = VK_ix_i + (F-V)x_i}$

$y_i\left[V + \frac{(F-V)}{K_i}\right] = Fz_i$ | $x_i\left[VK_i + (F-V)\right] = Fz_i$

$$y_i = \frac{Fz_i K_i}{VK_i + (F-V)} \qquad x_i = \frac{Fz_i}{VK_i + (F-V)}$$

$$y_i = \frac{z_i \cdot K_i}{\left(\frac{V}{F}\right)K_i + \left(1-\frac{V}{F}\right)} \qquad x_i = \frac{z_i}{\frac{V}{F}K_i + \left(1-\frac{V}{F}\right)}$$

$\psi = \frac{V}{F}$ | $\psi = \frac{V}{F}$

$$\boxed{y_i = \frac{K_i . z_i}{1 + \psi(K_i - 1)}} \xrightarrow{y_i = K_i x_i} \boxed{x_i = \frac{z_i}{1 + \psi(K_i - 1)}}$$

لازم نفترض قيمة لـ ψ حيث $\sum y_i = \sum x_i = 1$

بعدين نغير بقيمة ψ لحد ما نوصل لـ sum = 1

Constraints $\sum y_i = 1$ | $\sum x_i = 1$

In iterative solutions: $\sum < 1$ reduce ψ; $\sum > 1$ increase ψ

One Strategy consists of

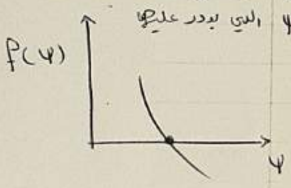
- Finding K_i's at T_v
- Guessing values of ψ until $\sum y_i = 1$ or $\sum x_i = 1$

Another strategy:

The equations for y_i and x_i can be combined to give a non linear equation in ψ only.

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

* فبحصل ψ اللي بتخلي المعادلة = 0 هي ψ اللي بندور عليها



$$\sum^{c} \frac{K_i z_i}{1+\psi(K_i-1)} - \sum \frac{z_i}{1+\psi(K_i-1)} = 0$$

$$\boxed{\sum \frac{z_i (K_i-1)}{1+\psi(K_i-1)} = 0}$$

This equation can be Solved for ψ.

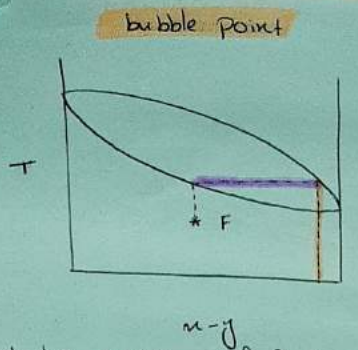
Step 3:

- $V = \psi F \Rightarrow L = F - V$
- $x_i = \dfrac{z_i}{1+\psi(K_i-1)}$
- $y_i = K_i x_i$

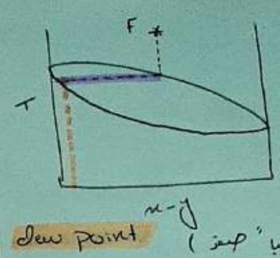
صاروا قيم ψ معروفة فبحسب y_i & x_i

$$Q = H_V \cdot V + H_L \cdot L - H_F \cdot F$$

Note: If T_F or/and P_F are not specified, then Q cannot be calculated. In this case eqm phase conditions are calculated only.



* بتسخين ال feed لحد ما نوصل لل sat. liq
عند هذه النقطة تكون كمية ال vap قليلة جداً (تقريباً صفر)



* تبريد ال feed لحد ما نوصل لل sat. vap
عند هذه النقطة تكون كمية ال liq قليلة جداً (تقريباً صفر)

...oint Calculations: special case from flash calculate

... a two phase equilibrium mixture

... ?

A: • As a first estimate

If all k values > 1 ⇒ exit phase above dew point (superheated vapor)

If all K values < 1 ⇒ exit phase below bubble point (subcooled liquid)

or $k > 1$ أكثر دقة من
$k < 1$

• Use of parameter Ψ (more precise). فقط T معينة نحسب عندها ال k_i

- $\Psi \in [0, 1]$ $\qquad f(\Psi) = \sum \frac{z_i(1-K_i)}{1+\Psi(K_i-1)}$ مجموع x_i & y_i

- Bubble Point. ⇒ $\Psi = 0$ $\quad \frac{V}{F} = 0 \Rightarrow$ ما في vap (sat. liq)

$\Psi = 0 \Longrightarrow f[\Psi=0] = 1 - \sum \underbrace{z_i K_i}_{y_i}$

If $f[\Psi=0] > 0 \Rightarrow$ exit mixture below bubble
$1 - \sum y_i > 0$ vapor is not rich enough $\sum y_i < 1$

If $f[\Psi=0] = 0 \Rightarrow$ exit mixture at bubble point $\quad \sum y_i = 0$

∴ Bubble point criterian is

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

with $x_i = z_i$, $y_i = z_i K_i$ } In first bubble

* when $\Psi = 0$ → bubble point

$\sum z_i (1 - k_i) = f(\Psi)$

$f(\Psi) = \sum z_i - \sum z_i k_i$

⇒ bubble point → this mean the feed is liq. ⇒ $z_i = x_i$

$f(\Psi) = 1 - \sum x_i * \frac{y_i}{x_i}$

$f(\Psi) = 1 - \sum y_i$

Note:

$$y_i = \frac{\alpha_{ij} z_i}{\sum \alpha_{kj} z_k} \Rightarrow \sum \alpha_{kj} z_k = \frac{\alpha_{ij} z_i}{y_i} = \frac{K_i}{K_j} \frac{1}{K_i} = \frac{1}{K_j}$$

$$\therefore \sum \frac{K_k}{K_j} z_k = \frac{1}{K_j}$$

j: reference component ↙ heavy component

$$y_i = \frac{\alpha_{ij} \, z_i}{\sum \alpha_{kj} z_k}$$

$$\sum \alpha_{kj} z_k = \frac{\alpha_{ij} z_i}{y_i} = \frac{k_i}{k_j} \frac{x_i}{y_i} = \frac{k_i}{k_j} \frac{1}{k_i} = \frac{1}{k_j}$$

↙ at bubble $x_i = z_i$

$z_i = x_i$ @ bubble point

Dew point:

$$f(\psi) = \sum \frac{z_i(1-k_i)}{1+\psi(k_i-1)} \longleftarrow \quad \psi = 1 \Rightarrow f[\psi=1] = \sum \frac{z_i}{k_i} - 1 \qquad \sum z_i = 1$$

$$f(\psi) = \sum \frac{z_i(1-k_i)}{k_i}$$

$$f(\psi) = \sum \frac{z_i}{k_i} - z_i$$

$$f(\psi) = \sum \frac{z_i}{k_i} - 1$$

if $f[\psi=1] < 0$ exit stream above its dew point [super heated vapor $K>1$]

if $f[\psi=1] = 0$ exit stream is at its Dew point

at dew point $z_i = y_i$

vapor feed

$\therefore \sum \frac{y_i}{y_i/m_i} = \sum m_i$

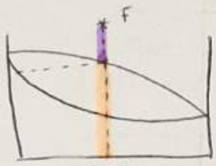
$\therefore$ Dew point criterion is

$$\sum \left(\frac{z_i}{K_i}\right) = 1 \quad \text{with} \quad \left.\begin{matrix} y_i = z_i \\ x_i = \frac{z_i}{K_i} \end{matrix}\right\} \sum x_i = 1$$

Note:

$$x_i = \frac{y_i/\alpha_{ij}}{\sum y_k/\alpha_{kj}} \Rightarrow \sum \frac{y_k}{\alpha_{kj}} = \frac{y_i}{x_i}\frac{1}{\alpha_{ij}} = K_j$$

Assume T find $\frac{y_k}{\alpha_{kj}} \Rightarrow \sum \frac{y_k}{\alpha_{kj}} \overset{?}{=} K_j$



$z_i = y_i$

@ dew point

Note:

Bubble point and Dew point Calculations are used to determine saturatio conditions for liquid and vapor streams respectively.

in VLE
- → Vap is at its dew point (saturated)
- → Liq at its bubble point (saturated).

بيح للتقطير: L, D, V out of column ⇒ مش بالضرورة يكونوا equilibrium with each other

بس إذا كان single stage بس إذا كان single stage بيكونوا في equilib

بعرف إنه بكون V ← sat. vap يعني بحسب عند dew point

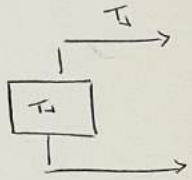
L ← sat. liq " " bubble point

Adiabatic Flash:

Given : ▲ Feed data
▲ P_V
▲ $Q = 0$

Readi: $\overset{1}{V}, \overset{2}{L}, \overset{C}{\vec{y}}, \overset{C}{\vec{x}}, \overset{3}{T_V}, \overset{4}{T_L}, \overset{5}{P_L}, \overset{6}{Z_c}$

Remaining unknowns $2C+6$



Procedure : The solution procedure is simultaneous

- T_V is unknown ∴ K values cannot be obtained
- To find T_V → solve enthalpy balance
- Since EB depends on composition of Ψ
- it cannot be solved alone ← ما يقدر أحل بشكل منفرد
- Net result → Simultaneous soln

comp لـ EB

Simultaneous solve & Ψ مجهولين لازم يحلوا بنفس الوقت

One strategy:

Step 1: solve equations containing one variable

$P_L = P_V$

$Z_c = 1 - \sum_{i=1}^{c-1} Z_i$

Step 2: Estimate T_V ⇒ guess value of T_V ← بين B.P لـ mixture و B.P

Step 3: use isothermal flash procedure at T_V, P_V ← T_V فرضي معروف

- obtain K_i at T_V, P_V
- Solve for Ψ,
- Solve for $\vec{y}, \vec{x}$
- Solve for V, L

Step 4 : Calculate H_L, H_V

step 5: Check T_v للتأكد من صحة T_v المستخدم في enthalpy balance

From Enthalpy balance $Q=0$ and M.B. $L=F-V$

$$Q = H_v V + H_L(F-V) - H_F F$$

$$\Psi H_v + (1-\Psi)\cdot H_L - H_F = 0 = f\{T_v\}$$

$f\{T_v\} = 0$ at equ.

Calculate $\frac{f\{T_v\}}{1000} = \frac{\Psi H_v - (1-\Psi)H_L - H_F}{1000} \stackrel{?}{=} 0$ نقسم على 1000 حتى تصغر H_v & H_L كبيرة جدا، للتعامل مع أرقام أصغر

step 6: if $f\{T_v\} \neq 0$ reestimate T_v and Go back to step 3. إذا $f(T_v) \neq 0$ يرجع يقترح T_v ثانية

step 7: Stop and Print results.

* procedure for doing isothermal flashing

* ex:

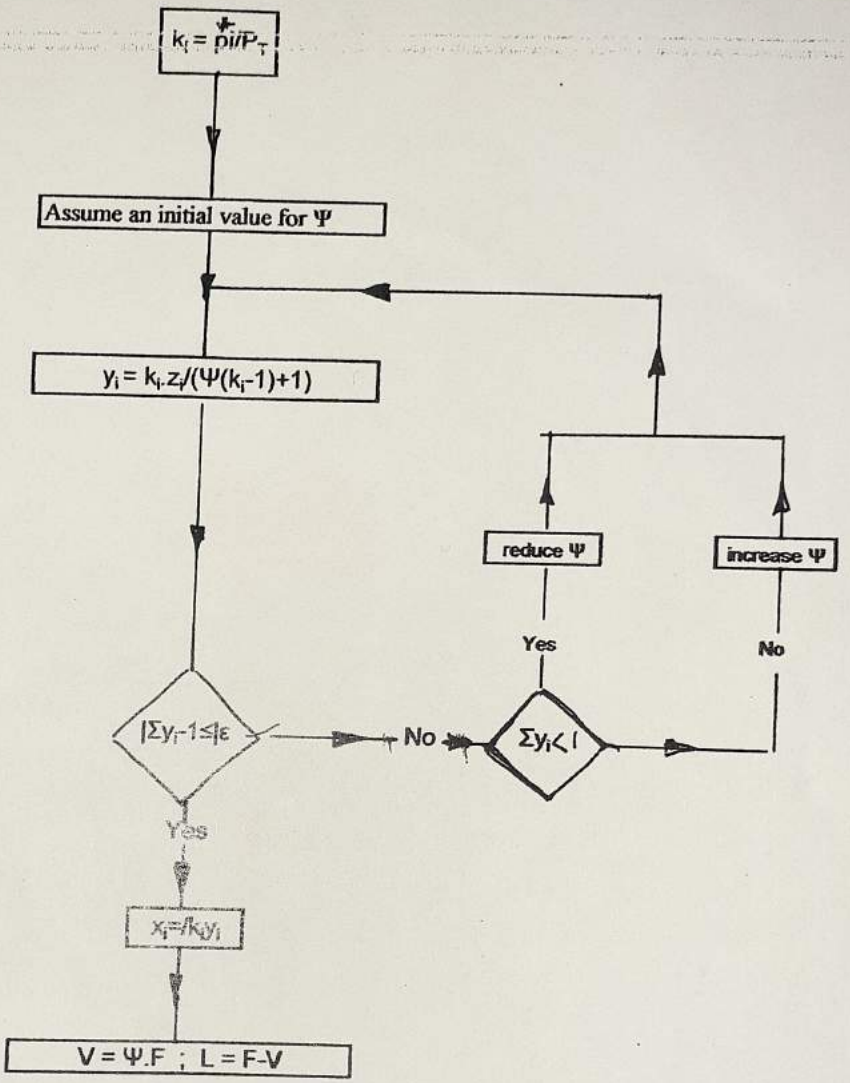
50% mole of Benzene (A)

25% mole of Toluene (B)

25% mole of O-Xylene (C)

P = atm

T = 100°C isothermal



P_i^*/P

Component	p_i mmHg	k_i	z_i	$k_i.z_i$	(k_i-1)	$y_i = k_i.z_i/(\psi(k_i-1)+1)$			$x_i = y_i/k_i$
						$\Psi = .5$	$\Psi =$ [illegible]	$\Psi = .325$	
A	1370	1.803	.5	.901	.803	.643		.715	.397
B	550	.724	.25	.181	-.276	.210		.199	.274
C	200	.263	.25	.066	-.737	.104		.087	.329
	↓		$\Sigma z_i = 1$			$\Sigma y = .957$		$\Sigma y = 1.007$	$\Sigma x = 1.000$

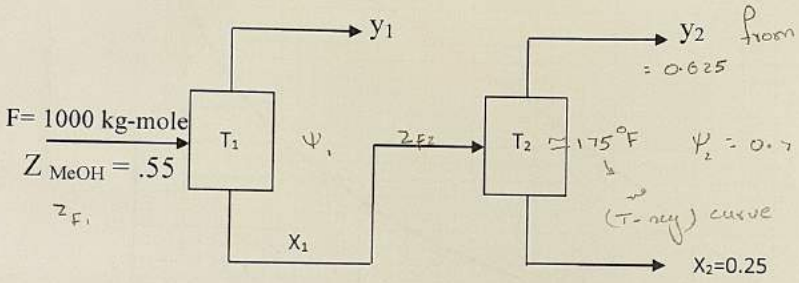
↓

vapor pressure from Antoine equation at T = 100°C

↓

[illegible] Ψ [illegible]

Two flash distillation chambers are connected together as shown in the diagram. Both are at 1 atm pressure. The feed to the first drum is a binary mixture of methanol and water having 55 mole% methanol. Feed flow rate is 1000 kg-moles/hr. The second drum operates with a vapor to feed ratio of 0.7 and the liquid product is 25 mole % methanol. Equilibrium diagrams are given.



a. What are y_1, y_2, x_1, T_1 and T_2?

b. What is the fraction vaporized in the first drum?

* from material balance:

$$F \cdot z_f = L \cdot x + y \cdot V$$

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

equilibrium curve

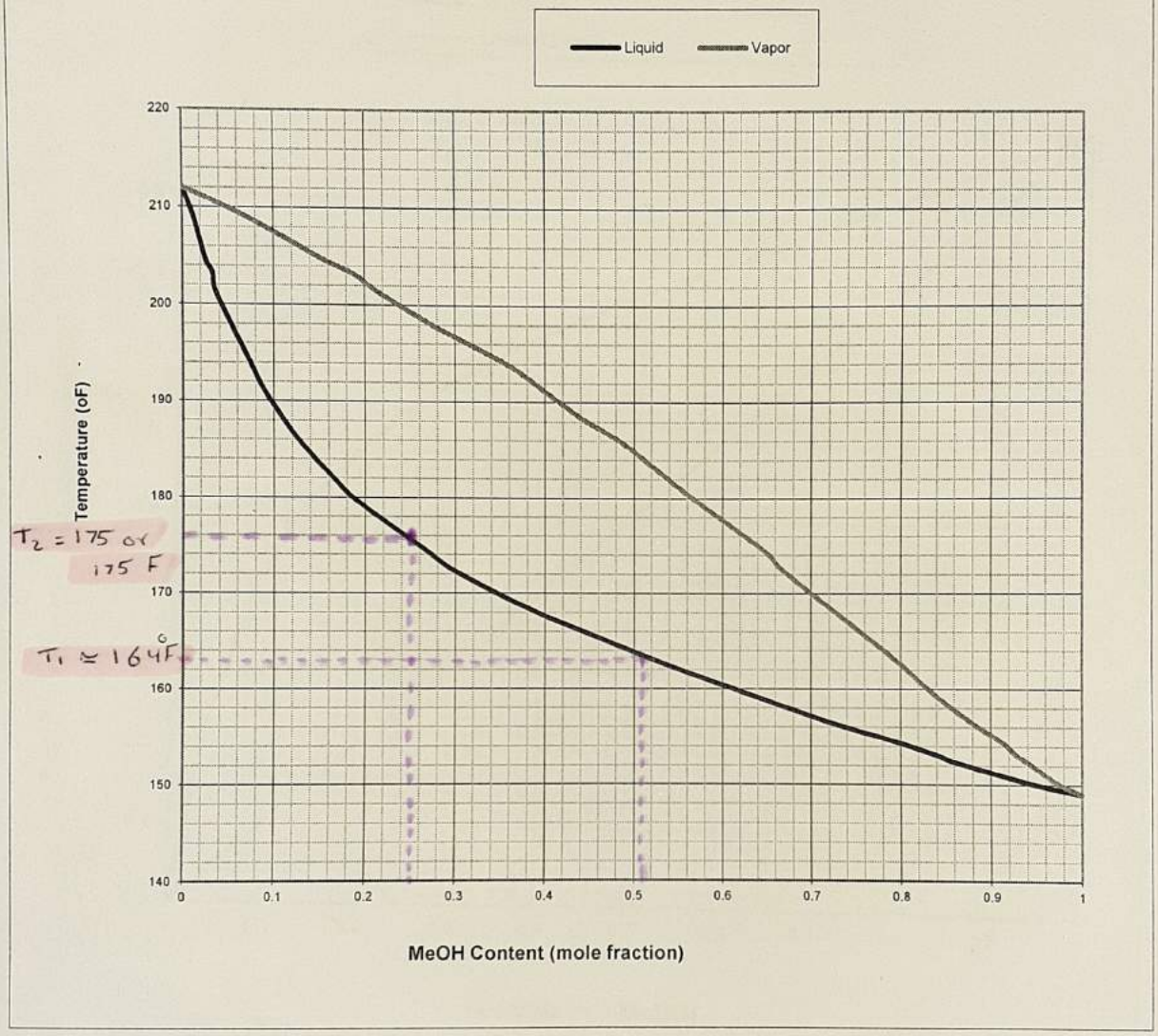
$$y_1 = .732$$

Operating line

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

$$\psi = 1.47$$

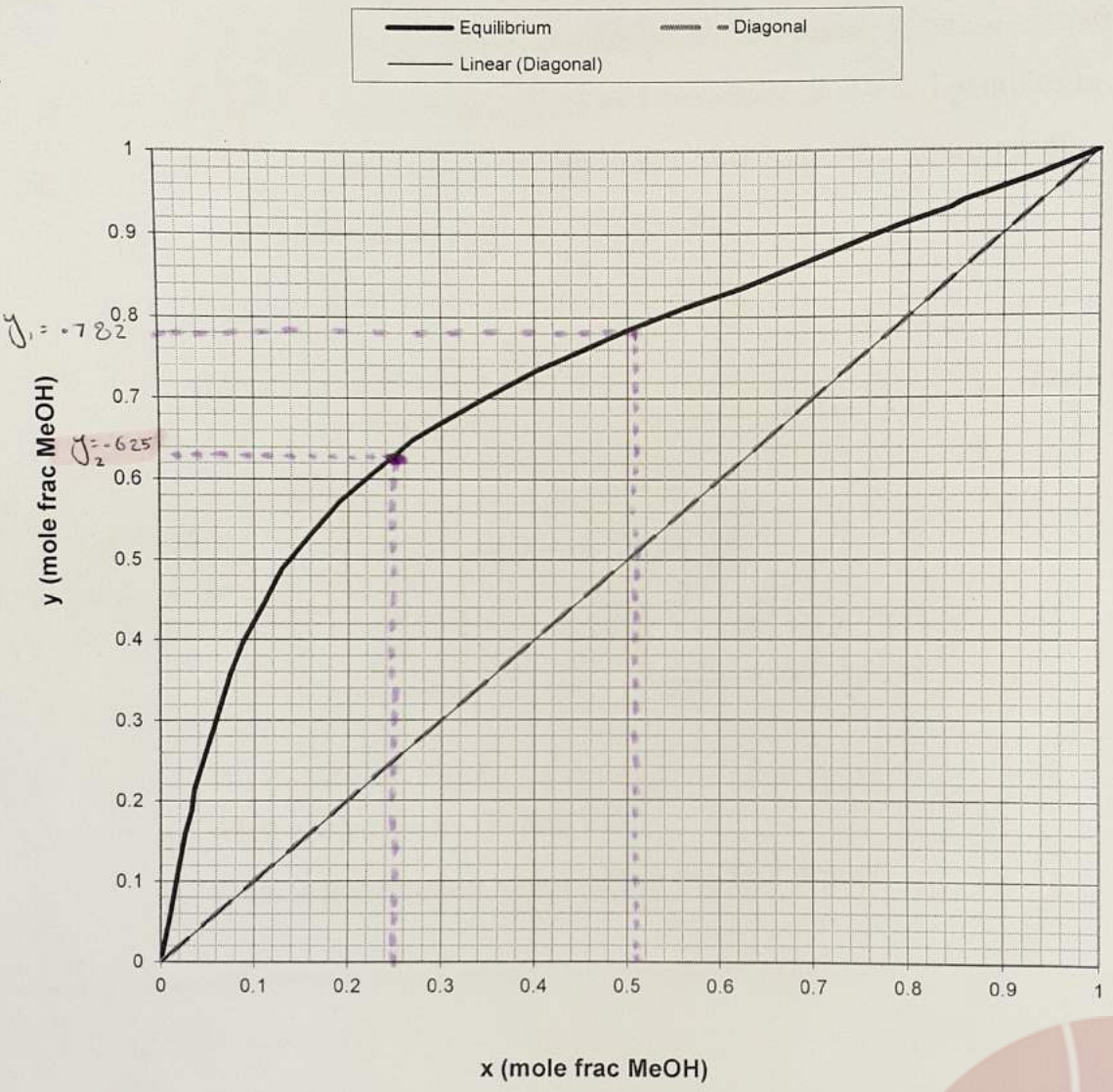
VLE for MeOH/H2O system @ 1 atm



$T_2 = 175$ or 175 F

$T_1 \approx 164$ F

VLE for MeOH/H2O system @ 1 atm



2.9 Size Calculation

Once the vapor and liquid compositions and flow rates have been determined, the flash drum can be sized. This is an empirical procedure. We will discuss the specific procedure first for vertical flash drums (Figure 2-1) and then adjust the procedure for horizontal flash drums.

Step 1. Calculate the permissible vapor velocity, u_{perm},

$$u_{perm} = K_{drum}\sqrt{\frac{\rho_L - \rho_v}{\rho_v}} \qquad \textbf{(2-64)}$$

u_{perm} is the maximum permissible vapor velocity in feet per second at the maximum cross-sectional area. ρ_L and ρ_v are the liquid and vapor densities. K_{drum} is in ft/s.

K_{drum} is an empirical constant that depends on the type of drum. For vertical drums the value has been correlated graphically by Watkins (1967) for 85% of flood with no demister. Approximately 5% liquid will be entrained with the vapor. Use of the same design with a demister will reduce entrainment to less than 1%. The demister traps small liquid droplets on fine wires and prevents them from exiting. The droplets then coalesce into larger droplets, which fall off the wire and through the rising vapor into the liquid pool at the bottom of the flash chamber. Blackwell (1984) fit Watkins' correlation to the equation

$$K_{drum} = (\text{Const.})\exp[A + B\ln F_{lv} + C(\ln F_{lv})^2 + D(\ln F_{lv})^3 + E(\ln F_{lv})^4] \qquad \textbf{(2-65)}$$

where $F_{lv} = \frac{W_L}{W_v}\sqrt{\frac{\rho_v}{\rho_L}}$ and const = 1.0 ft/s,

with W_L and W_v being the liquid and vapor flow rates in weight units per hour (e.g., lb/h). The constants are (Blackwell, 1984):

A = –1.877478097
B = –0.8145804597
C = –0.1870744085
D = –0.0145228667
E = –0.0010148518

The resulting value for K_{drum} typically ranges from 0.1 to 0.35.

Step 2. Using the known vapor rate, V, convert u_{perm} into a horizontal area. The vapor flow rate, V, in lbmol/h is

$$V\left(\frac{\text{lbmol}}{\text{h}}\right) = \frac{u_{perm}\left(\frac{\text{ft}}{\text{s}}\right)\left(\frac{3600\ \text{s}}{\text{h}}\right) A_c\ (\text{ft}^2)\ \rho_v\left(\frac{\text{lbm}}{\text{ft}^3}\right)}{MW_{vapor}\left(\frac{\text{lbm}}{\text{lbmol}}\right)}$$

Solving for the cross-sectional area,

→ Cross sectional area & Diameter

$$A_c = \frac{V(MW_v)}{u_{perm}(3600)\rho_v} \quad \text{(2-66)}$$

For a vertical drum, diameter D is

$$D = \sqrt{\frac{4A_c}{\pi}} \quad \text{(2-67)}$$

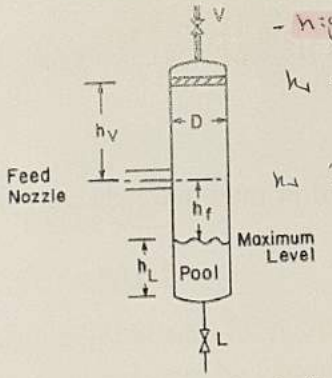
Usually, the diameter is increased to the next largest 6-in. increment.

Step 3. Set the length/diameter ratio either by rule of thumb or by the required liquid surge volume. For vertical flash drums, the rule of thumb is that h_{total}/D ranges from 3.0 to 5.0. The appropriate value of h_{total}/D within this range can be found by minimizing the total vessel weight (which minimizes cost).

Flash drums are often used as liquid surge tanks in addition to separating liquid and vapor. The design procedure for this case is discussed by Watkins (1967) for petrochemical applications. The height of the drum above the centerline of the feed nozzle, h_N, should be 36 in. plus one-half the diameter of the feed line (see Figure 2-14). The minimum of this distance is 48 in.

→ * location of feed Nozzle : h_N

Figure 2-14. Measurements for vertical flash drum



The height of the center of the feed line above the maximum level of the liquid pool, h_f, should be 12 in. plus one-half the diameter of the feed line. The minimum distance for this free space is 18 in. The depth of the liquid pool, h_L, can be determined from the desired surge volume, V_{surge}.

$$h_L = \frac{V_{surge}}{\pi D^2/4} \quad \text{(2-68)}$$

The geometry can now be checked, since

$$\frac{h_{total}}{D} = \frac{h_v + h_f + h_L}{D}$$

should be between 3 and 5. These procedures are illustrated in Example 2-4. If $h_{total}/D < 3$, a larger liquid surge volume should be allowed. If $h_{total}/D > 5$, a horizontal flash drum should be used.

$\frac{L}{D_{drum}} < 3$ (تكبير تقصير) ⇒ Means that Surge capacity should be increased

$\frac{L}{D_{drum}} > 5$ (طويل) ⇒ horizontal drum should be used

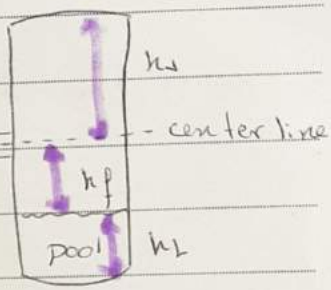
* Surge volume : liquid holding time of approximately 10 minutes should be allowed

⇒ high of center line of feed line above max level of the liquid pool : h_f

h_f : 12 in + $\frac{1}{2}$ diameter of feed line

if $h_f > 18$ in ⇒ [illegible]

if $h_f < 18$ in ⇒ $h_f = 18$ in [illegible]



⇒ Length of liquid pool , h_L

$$h_L = \frac{\forall surge}{\pi \, \delta^2 drum / 4}$$

$$L_{tot} = h_w + h_f + h_L$$

check on ratio $\left(\frac{L}{D}\right)_{Drum}$ $\quad 3 < \frac{L}{D} < 5$

horizontal or vertical [illegible]

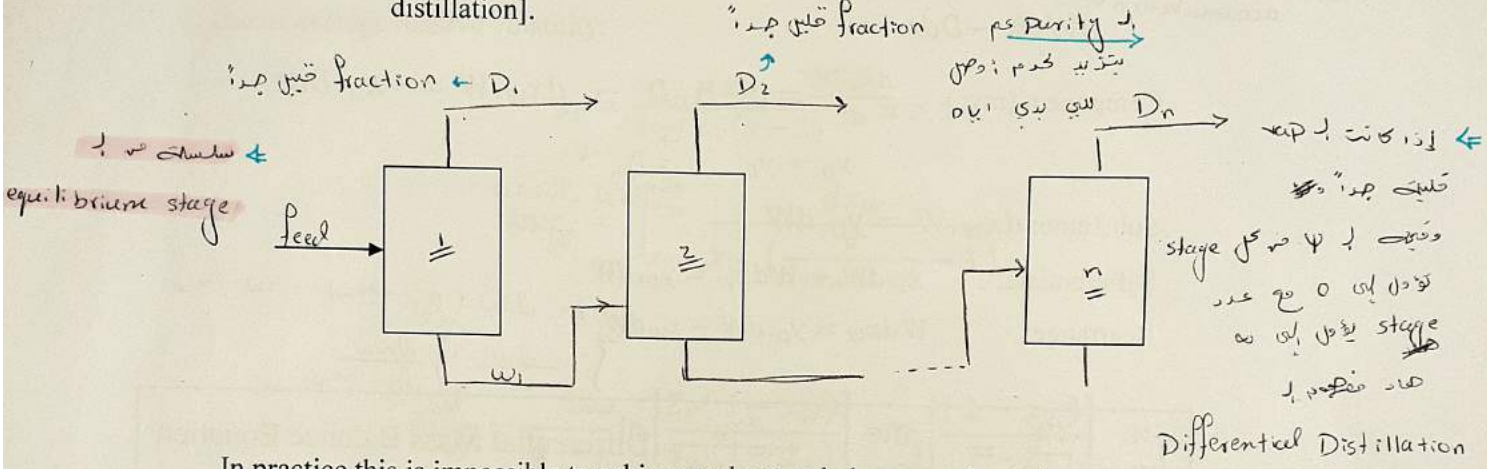
Batch Distillation:

Used when:

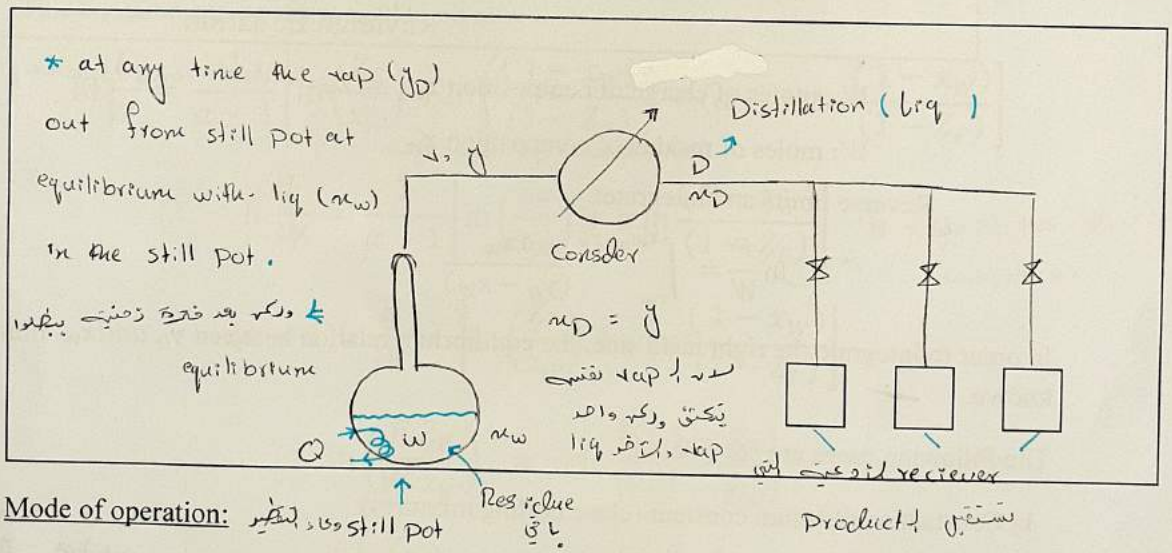
- The required operating capacity is very small
- Batch equipment offer more operating flexibility [feed fluctuations]

Differential distillation [Simple distillation]

Definition: It is the limit of a multistage flash process in which $n \to \infty$ and $\psi \to 0$ [differential distillation].



In practice this is impossible to achieve and can only be approximated:



Mode of operation:

- Still pot is initially charged with feed [Charge]
- Heat is supplied at a constant rate, and the charge is boiled
- Vapors are withdrawn immediately and collected in cuts as required

Features:

- The first cut will be richest in mvc ⇒ more volatile
- Operation is unsteady → product composition changes with time
- At any instant, the vapor leaving the still pot is assumed to be in equilibrium with the liquid in the pot (residue) → y_D *in equilibrium with* x_W.

Material Balances:

Binary Mixtures:

General: Rate of material = Rate of Material - Rate of Material

Accumulation IN OUT

input ⇒ close system (0)

Total: $\frac{dW}{dt} = 0 - D$ D: distillate flow rate mole/hr

accumulation

$$dW = -Ddt$$

Component (mvc): $\frac{dx_W.W}{dt} = 0 - x_D D \rightarrow dx_W.W = -x_D.Ddt$

$x_D = y_D$ = y_N لأنه تغني التركيز بين بيدكتي

Substitute: $dx_W.W = y_D.dW$

Differentiate: $x_W dW + W dx_W = y_D.dW$

Rearrange: $W dx_W = y_D.dW - x_W dW \Rightarrow dW(y_D - x_W) = W dx_W$

$$\int_{W_o}^{W} \frac{dW}{W} = \int_{x_{W_o}}^{x_W} \frac{dx_W}{(y_D - x_W)}$$

Differential Mass Balance Equation

Rayleigh Equation

W_o: moles of charge of composition $x_{W_o} = Z_F$ initial concentration of the charge

W: moles of residue of composition x_W

Reverse limits and integrate:

$$\ln\frac{F}{W} = \int_{x_W}^{x_{W_o}=Z_F} \frac{dx_W}{(y_D - x_W)}$$

In order to integrate the right hand side, the equilibrium relation between y_D and x_W must be known.

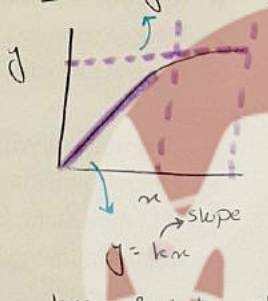
The following cases are considered:

1] Constant equilibrium constant (close boiling mixtures)

- $y = k\,x$; $k > 1$

$$\ln\frac{F}{W} = \frac{1}{k-1}\ln\frac{Z_F}{x_W}$$

≃ straight line $y = kx + c$



linear & intercept = 0

If k varies slightly with composition, an average value can be used in the concentration range.

- Local equilibrium constant: $y = k'x + c$

$$\ln\frac{F}{W} = \frac{1}{k'-1}\ln\left(\frac{Z_F(k'-1)+c}{x_W(k'-1)+c}\right)$$

2] Use of average relative volatility:

$$y_D = \frac{\alpha\, x_W}{1 + x_W(\alpha-1)} \qquad \alpha > 1$$

$$\ln\frac{F}{W} = \int_{x_W}^{Z_F} \frac{dx_W}{x_W\left(\frac{\alpha}{1+x_W(\alpha-1)} - 1\right)}$$

$$\ln\frac{F}{W} = \frac{1}{\alpha-1}\ln\left[\frac{Z_F(1-x_W)}{x_W(1-Z_F)}\right] + \ln\left[\frac{(1-x_W)}{(1-Z_F)}\right]$$

This equation can be rearranged to give:

$$\ln\frac{F}{W} = \frac{1}{\alpha-1}\left[\ln\left(\frac{Z_F}{x_W}\right) + \ln\left(\frac{(1-x_W)}{(1-Z_F)}\right) + (\alpha-1)\ln\frac{(1-x_W)}{(1-Z_F)}\right]$$

more volatile component (A)

$$\ln\frac{F}{W} = \frac{1}{\alpha-1}\left[\ln\left(\frac{Z_F}{x_W}\right) + \alpha\ln\frac{(1-x_W)}{(1-Z_F)}\right]$$

B = (1-A) less volatile component

$$(\alpha-1)\ln\frac{F}{W} = \left[\ln\left(\frac{Z_F}{x_W}\right) + \alpha\ln\frac{(1-x_W)}{(1-Z_F)}\right]$$

$$\ln\left(\frac{F\,Z_F}{W\,x_W}\right) = \alpha\ln\frac{F\,(1-Z_F)}{W(1-x_W)}$$

$$\ln\left(\frac{F\,Z_F}{W\,x_W}\right)_{mvc} = \alpha\ln\left(\frac{F\,Z_F}{W\,x_W}\right)_{lvc}$$

3] Graphical Integration:

Plot $\frac{1}{(y_D - x_W)}$ vs x_W

$\Rightarrow \ln\left(\frac{F}{W}\right)$ = area under the curve between Z_F and x_W

Multicomponent Mixtures (ideal solutions): Reference component

The equations used for binary mixtures can be used for each component in the mixture:

For any component i with reference component j:

$$\ln\left(\frac{F\,Z_{i,F}}{W\,x_{i,W}}\right) = \alpha_{i,j}\ln\left(\frac{F\,Z_{j,F}}{W\,x_{j,W}}\right)$$

$$\sum_{i=1}^{c} x_{i,W} = 1$$

Average composition:

- The total amount of vapor (distillate) is not in equilibrium with the residue
- Overall vapor composition (composited distillate composition, average composition) is obtained from material balance as follows:

$$F\,Z_{i,F} = D\,(y_{i,D})_{Average} + W\,x_{i,W}$$

D = F – W

$$F\,Z_{i,F} = (F-W)(y_{i,D})_{Average} + W\,x_{i,W}$$

$$\boxed{(y_{i,D})_{Average} = \frac{F\,Z_{i,F} - W\,x_{i,W}}{(F-W)}}$$

ABET: Ex. Comparison of Flash distillation and Differential distillation:

A liquid containing 50 mole% Benzene (A), 25 mole % Toluene (B) and 25 mole % O-Xylene.

a) The liquid is flash vaporized at 1 atm and 100°C. What is the fraction vaporized (ψ) ? And what is the vapor composition?
b) Under the same pressure and with the same (ψ), the liquid is to be differentially distilled. Calculate the distillate and residue compositions.

Component	$Z_{i,F}$	P_{mmHg} at 100°C	Flash ψ=0.325		Differential distillation		
			y_{iD}	x_{iW}	α (100°C)	$(y_{i,D})_{Ave}$	$x_{i,W}$
A	0.50	1370	0.715	0.397	2.49		
B	0.25	550	0.198	0.274	1.00		
C	0.25	220	0.087	0.329	0.364		
		∑	1.000	1.000	∑	1.000	1.000

reference comp ←

Basis: F =100 moles → D = 32.5 moles and W = 67.5 moles

For A: $$\ln\left(\frac{100*0.5}{67.5*x_{A,W}}\right) = 2.49 \ln\left(\frac{100*0.25}{67.5*x_{B,W}}\right)$$

For C: $$\ln\left(\frac{100*0.25}{67.5*x_{C,W}}\right) = 0.364 \ln\left(\frac{100*0.25}{67.5*x_{B,W}}\right)$$

$$x_{A,W} + x_{B,W} + x_{C,W} = 1.000$$

Solve Simultaneously.

Continuous Fractionation (Rectification):

Fractionation Process:

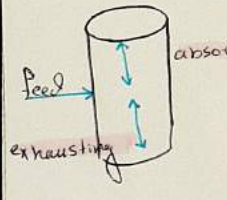
There are three methods used in distillation, each offering a varying degree of separation:

- Flash or equilibrium distillation
- Differential distillation
- Continuous Fractionation

Fractionation is the most important as it offers a greater degree of separation. It is the most widely used unit operation process in the chemical industry. It is a multistage counter-current operation, where the liquid flows counter current to vapor with the feed introduced at some intermediate point. Some of the vapor is condensed (mainly lvc) and some of the liquid is vaporized (mainly mvc). This partial condensation and vaporization continuously enriches the vapor phase with the mvc, with the net result of a better separation.

The operation takes place in a vertical cylindrical pressure vessel (called distillation column or tower, or a fractionator), divided into compartments by a series of perforated plates which permit the upward flow of vapor. The fractionator consists of two main sections:

- Top section above the feed point called absorption, enriching, or rectifying section
- Bottom section below the feed point called exhausting or stripping section.



The feed is introduced continuously into the fractionator where it is eventually split into two products. One removed from the top of the column richer than the feed in the mvc (called distillate, top product, overheads product, or light product); the other product withdrawn from the bottom of the column weaker in the mvc (called bottom product, waste, residue or heavy product). The purities of the products depend on the liquid/gas ratio and the number of stages.

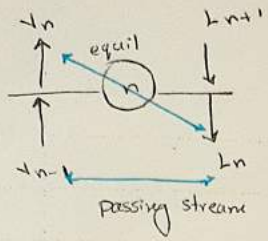
of sections = # of feed + 1

In some cases, multiple feeds and side streams are available. Some distillation columns consist of the top section only and they are called rectification columns.

Vapors rising from the top are totally (or partially) condensed in a condenser and some of the liquid is returned to the top of the column. This liquid is called reflux. The ratio of reflux to distillate is called reflux ratio or sometimes external ratio.

The liquid at the bottom is either heated by a coil placed at the base of the column or by an external reboiler; the more volatile material returns as vapor to the column. Inside the tower liquids and vapors are always at their bubble points and dew points respectively. Their flow rates are not constant along the column.

Material and Energy Balances.



* $\bar{L}$ & $\bar{V}$ ⇒ Bottom section
* L & V ⇒ Top section

Partial condenser : considered as a stage

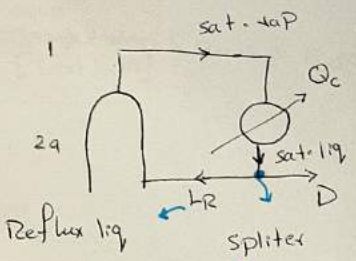
Partial Reboiler : considered as a stage

Bottoms & Distillate are not in equilibrium with each other

Material Balances:

Envelope I : $F = D + B$ over all

Envelope II : $V_{N_p} = L_R + D$ condensor



let $R = \frac{L_R}{D}$: reflux ratio.

$V_{N_D} = L_R + D$ ⟵ $V_{N_p} = RD + D$

$V_{N_p} = D(R+1)$

2b

Envelope III : (Down to stage n)

$$V_{n-1} = L_n + D \quad (3a)$$

$V_{n-1} - L_n = D$ (cost value) [Net Flow: const of vap ↑] (3b)

Envelope IV : (up to stage m)

$$\bar{L}_{m+1} = \bar{V}_m + B \quad (4a)$$

$\bar{L}_{m+1} - \bar{V}_m = B$ (cost value) [net flow: const of liq]

Envelope V : (Feed stage)

$$F + L_{f+1} + \bar{V}_{f-1} = V_f + \bar{L}_f$$

⇒ where :

- n ⇒ Top section
- m ⇒ Bottom section

Component Balances: (For any component)

D&B في comp لـ بعرفت ← Envelope I $\quad z_F \cdot F = x_D \cdot D + x_B \cdot B$

$$x_D = \frac{z_F F - x_B B}{F - B}$$

$$x_B = \frac{z_F F - x_D D}{F - D}$$

Enriching Section (Envelope III)

$$y_{n-1} \cdot V_{n-1} = x_n \cdot L_n + D \cdot x_D \qquad [D x_D : \text{net Flow}]$$

Operating Line for enriching section ⇐

$$y_{n-1} = \frac{L_n}{V_{n-1}} \cdot x_n + \frac{D x_D}{V_{n-1}}$$

op. line for enriching section

if cost ⇒ Operating Line

if variables from stage to another stage ⇒ Operating curve

Stripping Section (Envelope IV)

$$x_{m+1} \cdot \bar{L}_{m+1} = y_m \cdot \bar{V}_m + x_B \cdot B$$

Operating line or curve ⇐

$$y_m = \frac{\bar{L}_{m+1}}{\bar{V}_m} x_{m+1} - \frac{B}{\bar{V}_m} \cdot x_B$$

Enthalpy Balances (Calculation of Q_c, Q_B)

* the separating agent is energy to creat a new phase

Envelope II: (condenser duty)

* مصدر الـ Q :
- عكس تكبير ناقص مع flowrate
- اذا Q بيتم ! ضيقوا لـ system

Specific enthalpy

$$V_{N_P} \cdot h_{V N_P} = Q_c + L_R \cdot h_R + D h_D \qquad (L_R = RD)$$

$$Q_c = V_{NP} \cdot h_{V NP} - D(R \cdot h_R + h_D)$$

إذا تم تبريد الـ steam بواسطة cooling water

$$Q_c = D\left[(R+1) \cdot h_{V,NP} - (R h_R + h_D)\right]$$

$\dot{m} c_p \Delta T$ ← Q_c تيجي

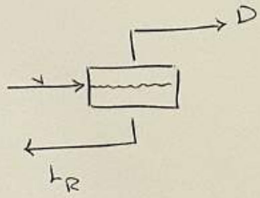
Rate of cooling Water: $\quad \dot{m} = \dfrac{Q_c}{c_p \Delta t}$

$\Delta t = T_{out} - T_{in}$ (T_{out}: T_D or T_{LR})

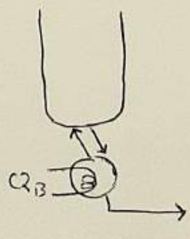
$T_{in} = 20\text{–}25°C$

Total condensor

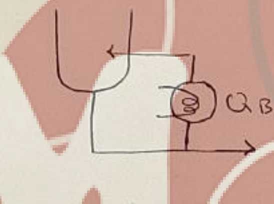
Partial condensor



Total boiler



partial boiler



Envelope I:

losses = ضياعات

$$F \cdot h_F + Q_B = D h_D + B h_B + Q_c + Q_L$$

Q_L: negligible if well insulated [Total losses]

$$Q_B = D\left(h_D + \frac{Q_c}{D}\right) + B \cdot h_B - F \cdot h_F + Q_L$$

Envelope III

$$\frac{Q_c}{D} = q_c$$

$$V_{n+1} \cdot h_{V_{n+1}} - L_n \cdot h_{L_n} = D\left(\frac{Q_c}{D} + h_D\right) = \Delta_D \quad (P')$$

$$= D(q_c + h_D)$$

= net Flow

Envelope IV:

$$\bar{L}_{m+1} \cdot h_{\bar{L},m+1} - \bar{V}_m \cdot h_{\bar{V},m} = B\left(h_B - \frac{Q_B}{B}\right) = \Delta_W \quad (P'')$$

$$= B(h_B - q_B)$$

= net flow.

P' & P'' ⇒ source & sink

The above relations together with equilibrium relations give the necessary equations for the design of distillation columns.

At the end of design calculations, one hopes to have

- Np
- Product flow rates, compositions
- operating conditions (T, P)
- Q_c, Q_B boiler & condensor

Specifications:

Two types of problems may be encountered with any equipment, in this ca distillation column:

- Design Problem
- Simulation Problem

Design Problem: Desired separation is set and column is designed that will achieve this separation

Simulation Problem: Column is already built and the procedure should predict how much separation can be achieved for a given feed.

For both problems we usually specify:

- Column pressure, (sets equilibrium data)
- Feed composition
- Feed flow rate.
- Feed temperature and pressure (or enthalpy or quality – state of the feed L_f and V_f).
- Reflux temperature or enthalpy (usually saturated liquid) (Simulation Problem).

Other variables which must be set for adequate specification.
For a binary system the most usual specifications and the resulting calculated variables are:

Specifications	Calculated variables	
Design: - x_D, x_B (mvc) - R (L_R/D)	D, B, Q_c, Q_B, N_p, feed location. Column Diameter.	
Simulation: - Np, feed location - column diameter - Reboiler size (gives max vapor) and - x_D and x_B or - R, x_D (or x_B) or - x_D (or x_B), V=V_{max}	 R, B, D, Q_c, Q_R x_B (or x_D),B,D,Q_c,Q_R R, x_B (or x_D), B, D, Q_c, Q_R	 Check v<v_{max} Check v<v_{max} Check v<v_{max}

⇒ Two approaches may be used:

- Approximate: simple sequential, (adequate in many cases), graphs, simple algorithms
- Rigorous: requires detailed stage to stage calculations (simulation), handles all situations

Binary Rectification:

Approximate Methods:

⇒ Simplifying assumptions: (constant flowrate & pressure)

First assumption ⇒ 1. Constant molal overflows: valid if (over range of temperature and Pressure):

لصلاحية الافتراض لتجنيد سائل

heat of vaporiz يتكون قيم إذا كان components متقاربة (chemical structure متشابهات

➢ Molar heats of vaporization of both species of the binary system are equal

➢ Heats of mixing, stage heat losses and sensible heat changes of both liquid and vapour are negligible

This assumption indicates that every mole of condensing vapour vaporizes exactly ONE mole of liquid.

ينتج عن assumption السابق أن كل مول تتجدد يقابله مول يتكون

ينتج عنه كميتي 1 & 1 are cost in the column

This means that on molal basis in each section of a column;

$$\Rightarrow \frac{Moles of\ Liquid}{Moles\ of\ Vapor} = constatnt\ ;\ Ln = L\ ,\ Vn = V\ \ and\ \bar{L}_m = \bar{L}\ ,\ \bar{V}_m = \bar{V}$$

ينتج متشابهات 1 & 1 لـ كميتي operating line معادلة في

This results in a straight line operating line for each section.

Second assumption ⇒ 2. Distillation takes place at constant pressure (small variations of pressure inside the column)

ينتج عن ثبات الضغط ثبات في equilibrium relation

Plate to plate calculations: Lewis-Sorel Method

Consider the following case for the distillation of a binary mixture:

⇝ Given Information:

$$F, \overrightarrow{Z}, x_D, x_B, R, P_{Column}$$

bottom

reflux ratio

Feed, Distillate, Bottoms product and reflux are saturated liquids at their bubble points.

* إذا بدي أحسب لـ T في كل stage بستخدم حسابات bubble points لـ كل layer

Required: Np and Feed location.

of theoritical stages

Analysis:

- Operating lines give relations between vapour and liquid compositions of passing streams:

Top Rectifying Section: $\Rightarrow y_{n-1} = \frac{L}{V}.x_n + \frac{D}{V}.x_D$ (net flow (D/V); between passing streams)

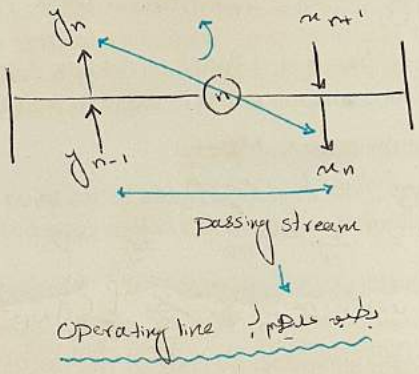
Bottom Stripping Section: $\Rightarrow y_m = \frac{\bar{L}}{\bar{V}}.x_{m+1} - \frac{B}{\bar{V}}.x_B$ (cost; Net flow down (B/$\bar{V}$))

- Equilibrium data give relations between liquid and vapour compositions leaving a stage

relative volatility or curve يعطى هذه العلاقة ك $\Rightarrow x_n = f(y_n)$

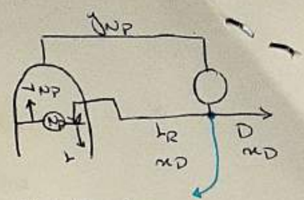
or curve fitting

equilibrium $\Rightarrow (x_n = f(y_n))$



* The Feed is sat. liq

Calculation Procedure:



$V = D + L_R$

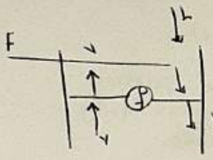
$V = D + R \cdot D$

3 $V = D(1+R)$

4 $L = RD$

5 $\bar{L} = L + F = RD + F$

6 $\bar{V} = V$



- Use column balances to calculate D, B, L and V, $\bar{L}$, $\bar{V}$

* Over all component balance :

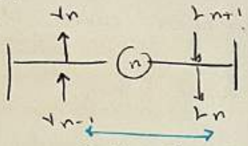
$z_F F = x_D D + x_B B \rightarrow z_F F = x_D D + x_B (F - D)$

1 $\Rightarrow D = \dfrac{F(z_F - x_B)}{x_D - x_B}$ ⇐ كل قيم معطى نحسب منهم D

2 $\Rightarrow B = F - D$ or $B = D \dfrac{(z_F - x_D)}{(x_B - z_F)}$

- Starting with top specification, find ..y_{NP}...... from ...operating line...

$$y_{n+1} = \frac{L}{V} \cdot x_n + \frac{D}{V} x_D \quad , \; n = N_{P+1}$$



passing stream → operating line

اذا liq تركيبه ثابت نعوض عن الرفع ال ... y_{NP} & x_{NP+1}

$\Leftarrow y_{NP} = \frac{L}{V} \cdot x_{NP+1} + \frac{D}{V} x_D$

x_D = condensor جاية من ال

- Find..x_{NP}......from ....equilibrium data

$x_{NP} = f(y_{NP})$

- Repeat for stage ....N_{P-1}

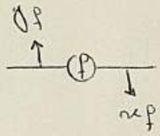
- $n = N_P$ محسوبة من الخطوة السابقة

$\Rightarrow y_{NP-1} = \frac{L}{V} \cdot x_{NP} + \frac{D}{V} x_D$

$\Rightarrow$ equilibrium relation ... $f(y_{NP-1})$

* كل ما نزلنا بال column نقل composition of mvc

- Repeat for stages below until ...x_n.. calculated is nearly the same as ....z_F..



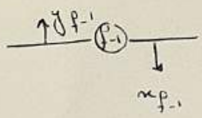
قيمة x_n مستحيل تساوي z_F ولكن بتصير قريبة منها

قيمة x_n لما تصير اقل من z_F بوقف شغل ال top section وندخل ال bottom section

- Change ...operating line..., and starting with ...x_{f-1}..., $x_{m+1} = x_f$ (below the feed stage)

محسوبة فوق

$\Rightarrow y_{f-1} = \frac{L}{V} x_f + \frac{D}{V} x_D$



- Find..x_{f-1}.....from .....equilibrium data

$x_{f-1} = f(y_{f-1})$

- Repeat for stages below until ...x_m... calculated is nearly the same as ...x_B..

- Stop ⇒ بعدد كم مرة غيرنا operating & equilibrium ويساوي عدد stages on ال column