

Distillation



Processos de Separação

LEQB

2023/2024

Distillation



Fractionation of the components of a given mixture due to their different partitions between the liquid and vapor phases

All the components present in the mixture should be volatile

That's the difference between DISTILLATION and EVAPORATION (some compounds are volatile, the rest not; example, a saline solution)

Distillation



Fractionation of the components of a given mixture due to their different partitions between the liquid and vapor phases

It differs from Gas Absorption processes

The "second" phase is generated by thermal means (either by vaporization or by condensation) rather than by its direct introduction in the column

Distillation



Fractionation of the components of a given mixture due to their different partitions between the liquid and vapor phases

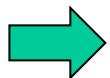
Key advantage: generally, we do not need to add extra components (e.g. a solvent) to the initial mixture to occur separation!

Distillation



Vaporization and condensation

\$\$\$ Energy



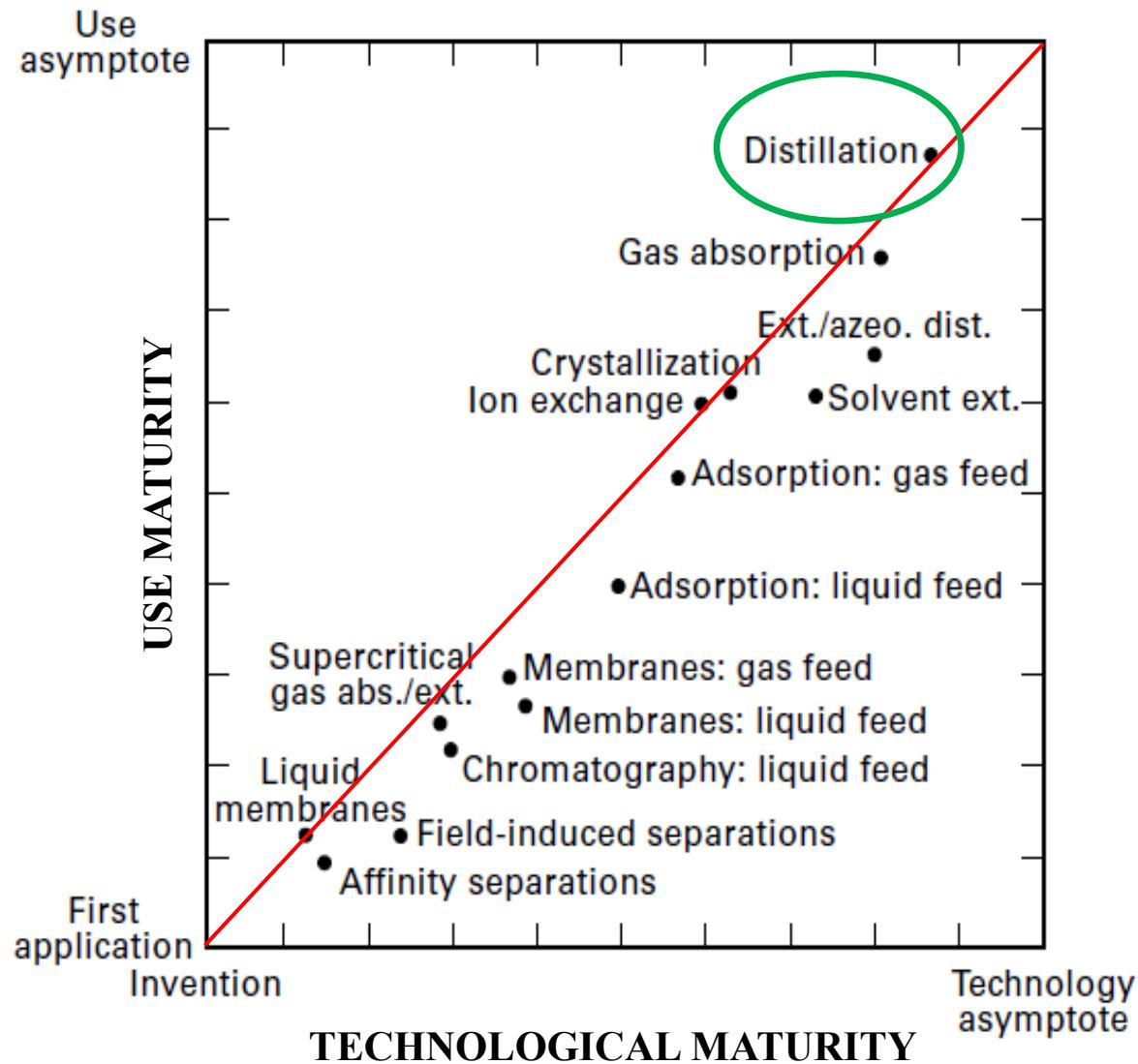
$$[\Delta H_v]$$

Distillation



Main unit operation of Chemical Industry

- To separate crude oil into several fractions
- To recover and purify organic solvents
- To fractionate air into its main components
- To recover and purify small biomolecules (organic alcohols, acids, and ketones) produced from bioreactors



Advantages

- *Simple flowsheet*
- *Investment*
- *Volatile compounds*

Disadvantages

- *Energy consumption*
- *Thermolabile compounds*
- *Azeotropes*
- *Diluted mixtures*

Distillation of the binary mixture Benzene + Toluene

www.youtube.com/watch?v=BaBMXgVBQKk

Feed
bubble-point
liquid

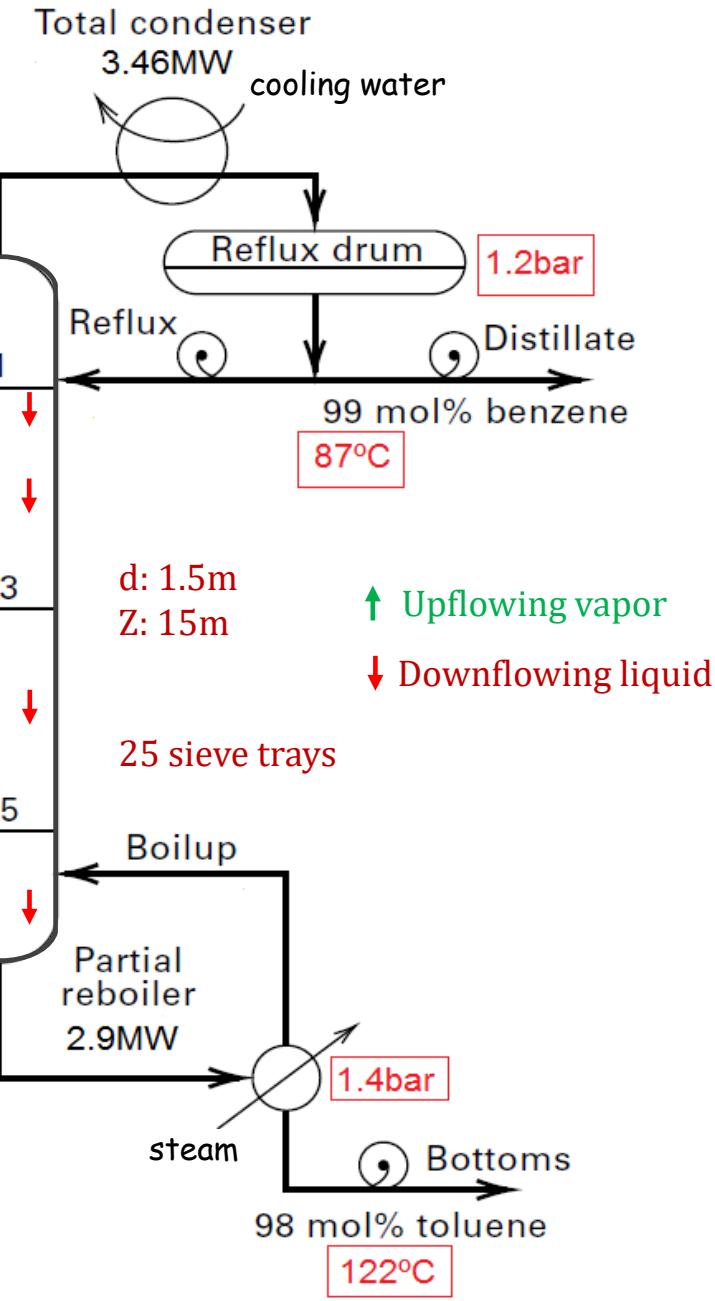
105°C
1.3bar

46 mol% benzene
54 mol% toluene

**T is not
constant!**

$$T_{boiling|_{benzene}} (1.2 \text{ bar}) = 85.7 \text{ }^{\circ}\text{C}$$

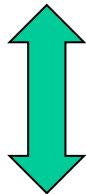
$$T_{boiling|_{toluene}} (1.4 \text{ bar}) = 122.4 \text{ }^{\circ}\text{C}$$



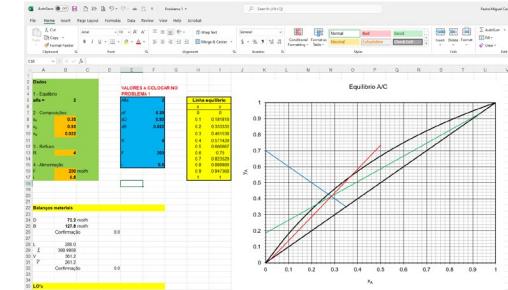
Design

Binary (ternary) mixtures

Graphical resolution methods



(McCabe–Thiele Method)



Multicomponent mixtures

Simulating/computing methods



([ASPEN PLUS](#), [CHEMCAD](#), [PRO/II](#), [SUPERPRO DESIGNER...](#))

Design



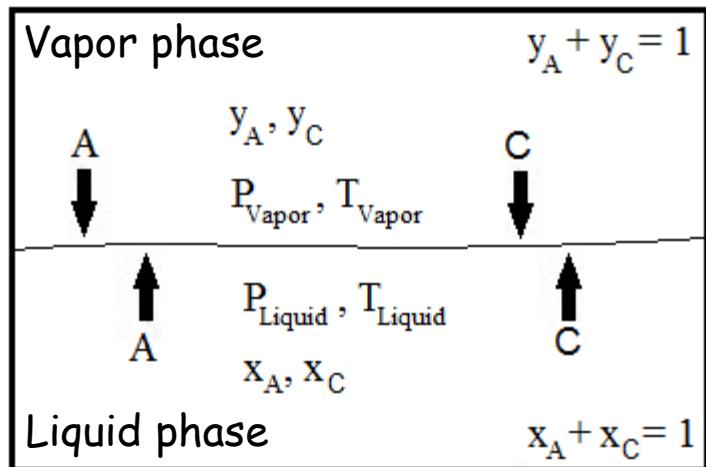
Thermodynamic equilibrium

Its knowledge is upmost essential!

Vapour-Liquid equilibrium

Binary system ($A+C$), biphasic ($L+V$)

$P; T$



y_A, y_C : molar fractions of A and C in vapour phase

x_A, x_C : molar fractions of A and C in liquid phase

At equilibrium:

$$P_{Vapor} = P_{Liquid}$$

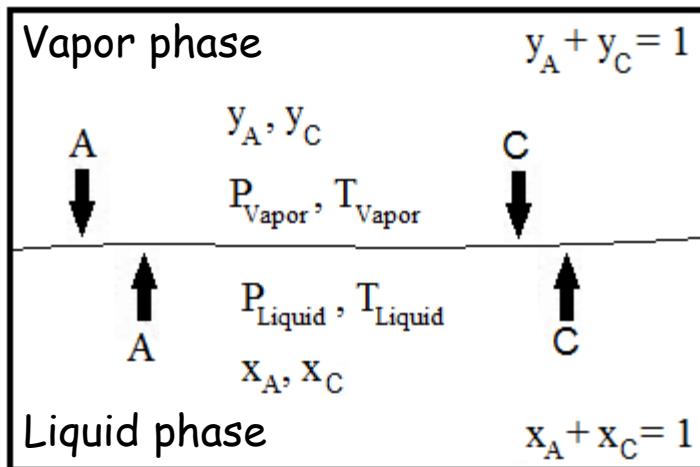
$$T_{Vapor} = T_{Liquid}$$

According to the phase rule, a binary, biphasic, system will have **two degrees of freedom**

Vapour-Liquid equilibrium

Binary system ($A+C$), biphasic ($L+V$)

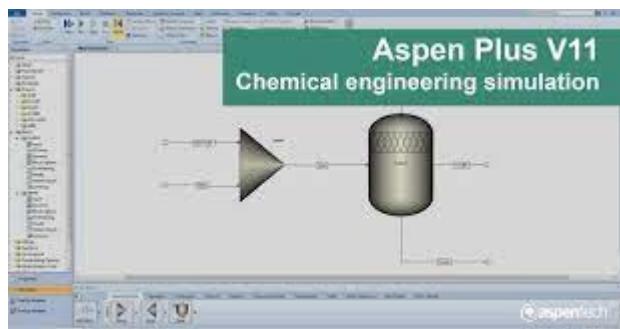
$P; T$



Real mixtures

- Thermodynamic models

Example: cubic equations of state (Peng-Robinson,

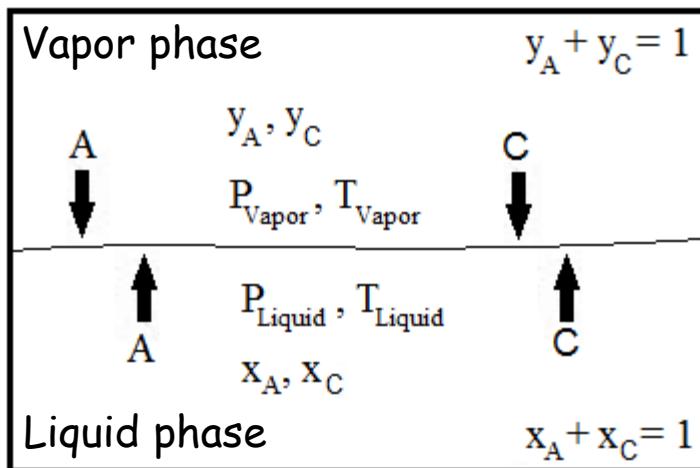


Redlich-Kwong,...)

Vapour-Liquid equilibrium

Binary system ($A+C$), biphasic ($L+V$)

P; T



Ideal mixtures

Raoult's Law

$$p_A^L = P_A^*(T) x_A$$

Dalton's Law

$$p_A^V = y_A P$$

$$y_A = \frac{P_A^*(T)}{P} x_A$$

$$y_C = \frac{P_C^*(T)}{P} x_C$$

Equilibrium

$$p_A^L = p_A^V$$

P_A^* : Vapor pressure of pure A at operating temperature

Vapour-Liquid equilibrium

- Graphical representation

$$y_A = \frac{P_A^*(T)}{P} x_A$$

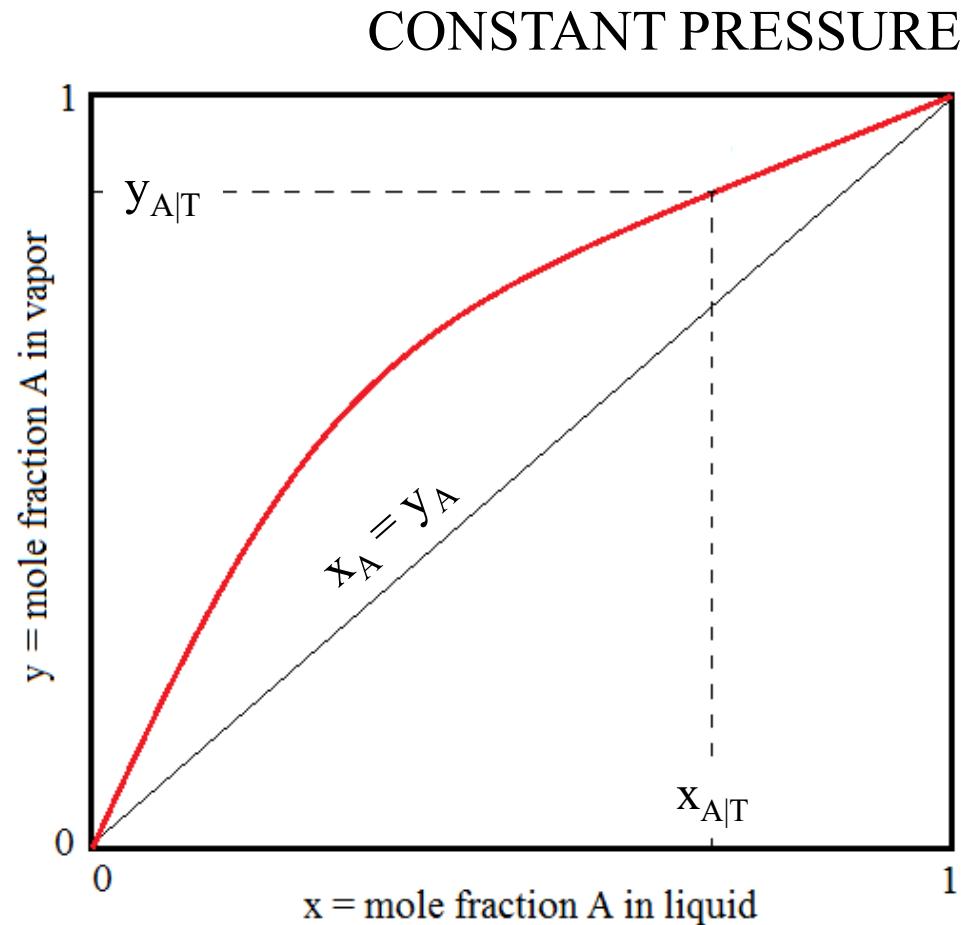
Distribution coefficient, K_A

$$K_A = \frac{y_A}{x_A} = \frac{P_A^*(T)}{P}$$

$K_A > 1 \Rightarrow A$ is volatile



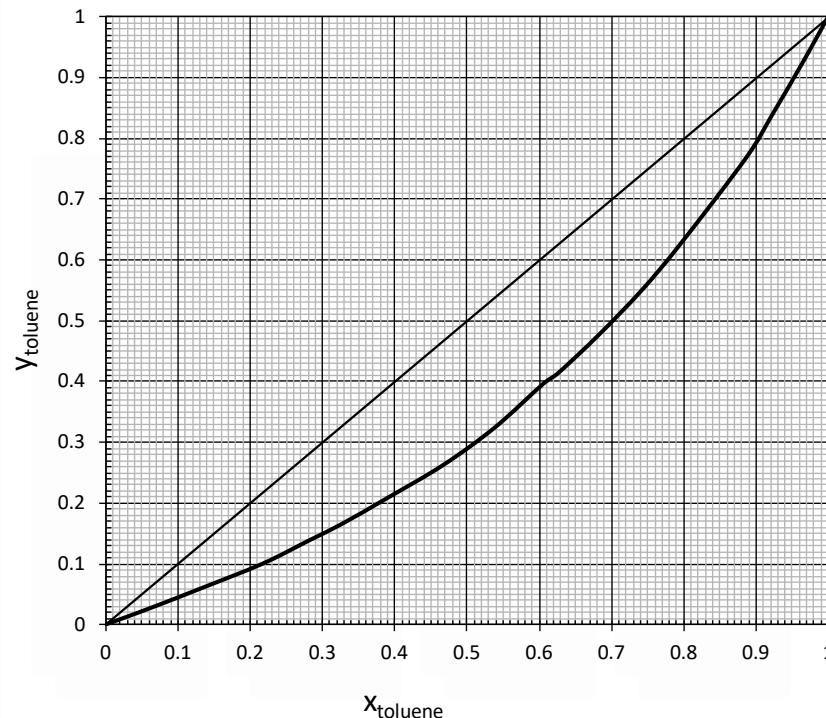
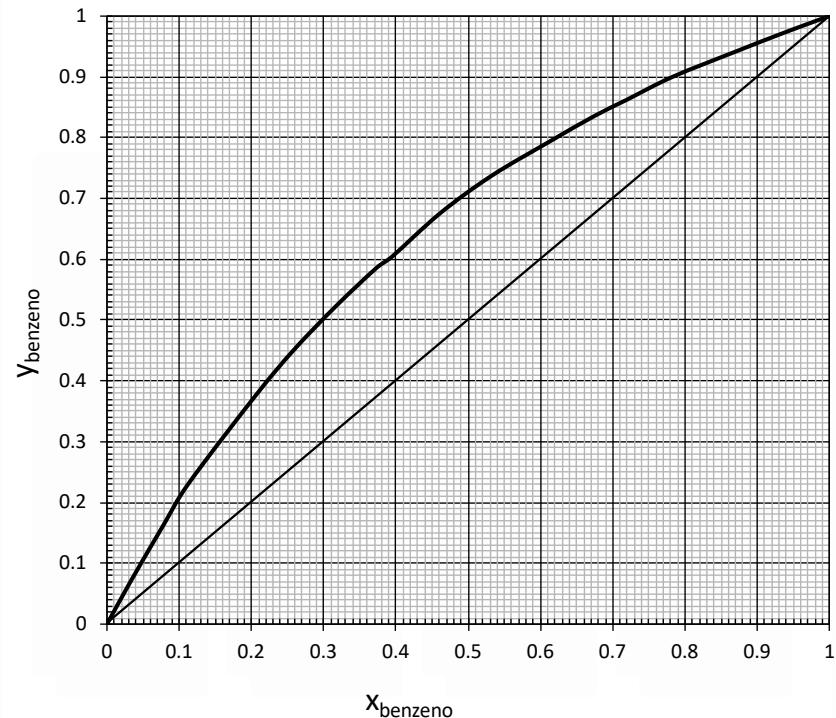
tends to the vapor phase



— Liquid Vapor Equilibrium line of system A+C at pressure P

$$K_A = \frac{y_A}{x_A} = \frac{P_A^*(T)}{P}$$

Liquid-Vapour equilibrium of binary mixture benzene (B) + toluene (T) at 1 bar



T °C	x_B	y_B
	mol/mol	
80.1	1	1
80.52	0.9767	0.99
81.53	0.9315	0.97
82.82	0.8732	0.943
84.85	0.7832	0.9002
86.5	0.7193	0.8622
87.47	0.6742	0.8353
89.13	0.6125	0.7935
91.25	0.5326	0.7375
93.49	0.4616	0.6761
95.73	0.3952	0.6049
96.44	0.3731	0.5858
98.19	0.3179	0.524
100.2	0.2588	0.4511
102.1	0.2056	0.3757
105.9	0.1136	0.2323
107.43	0.078	0.1625
109.5	0.0333	0.0714
110.61	0	0

$K_B > 1 \Rightarrow B$ tends to the vapor phase

$K_T < 1 \Rightarrow T$ tends to the liquid phase

Vapour-Liquid equilibrium

- Graphical representation

$$K_A = \frac{y_A}{x_A} = \frac{P_A^*(T)}{P} \quad K_C = \frac{y_C}{x_C} = \frac{P_C^*(T)}{P}$$

Relative volatility, α

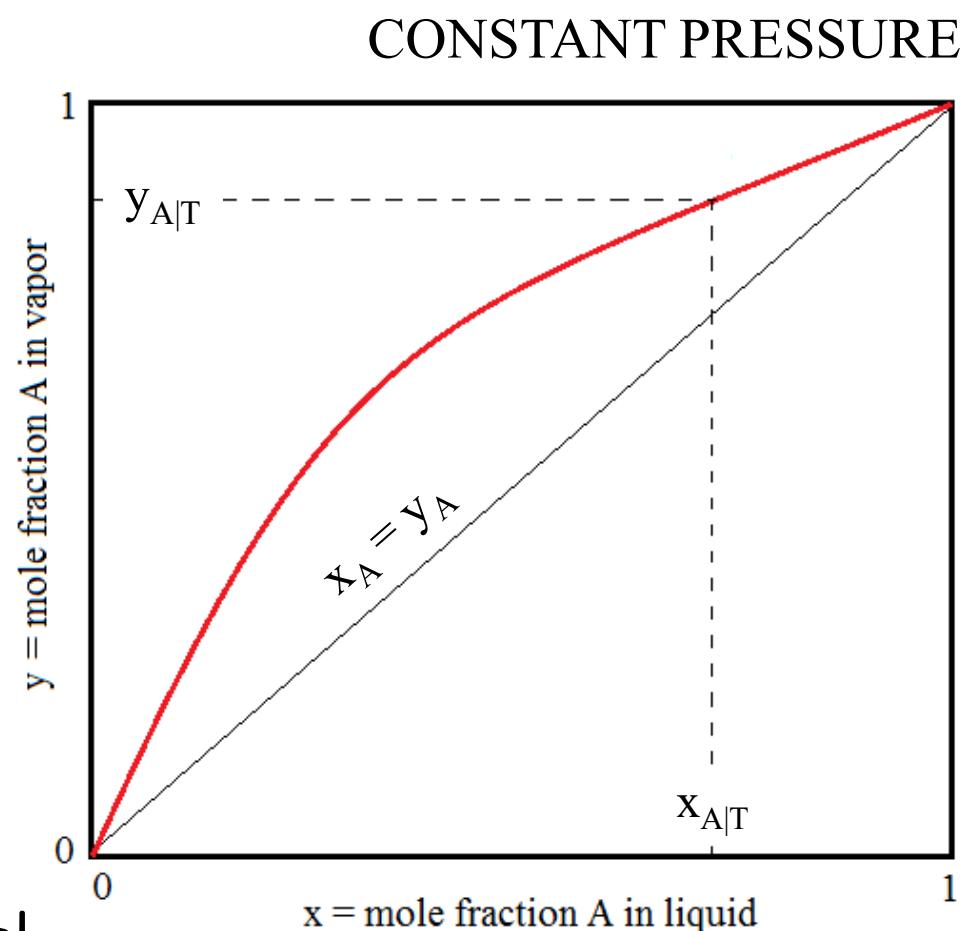
$$\alpha = K_A / K_C$$

$$\alpha = \left(\frac{y_A}{x_A} \right) / \left(\frac{y_C}{x_C} \right) = \frac{P_A^*(T)}{P_C^*(T)}$$

It is a measure of how easy or difficult is a distillation

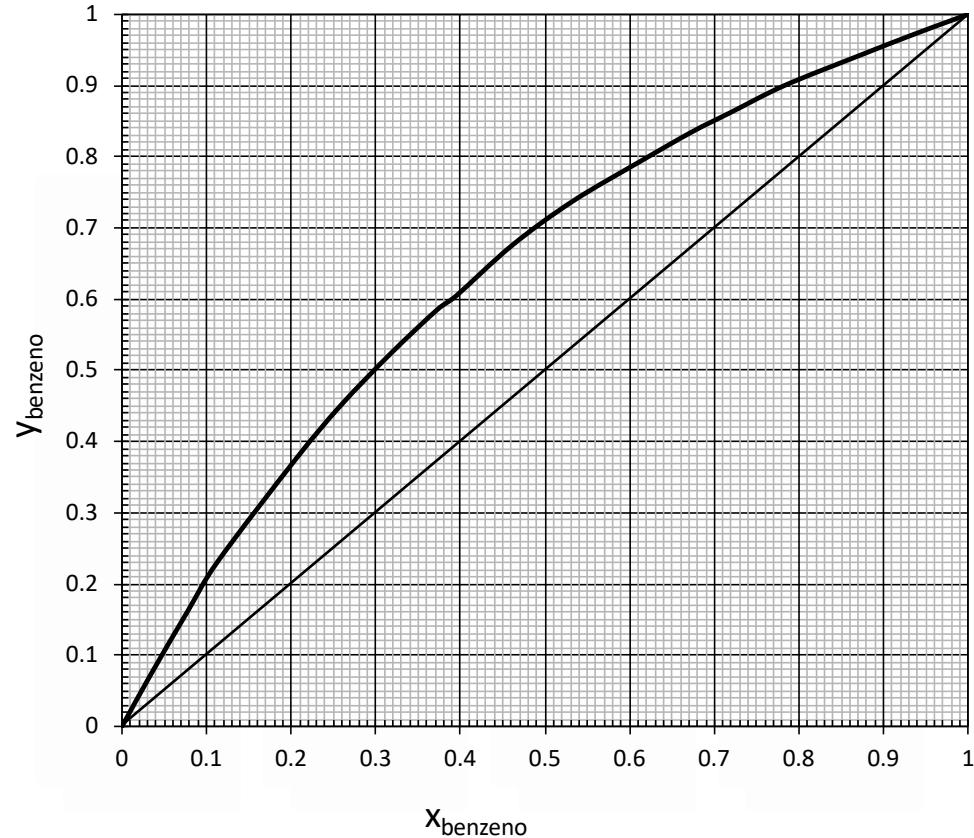


α depends on the temperature!



$$\alpha(T) = \left(\frac{y_A}{x_A}\right) / \left(\frac{y_C}{x_C}\right) = \frac{P_A^*}{P_C^*}$$

Liquid-Vapour equilibrium of binary mixture benzene (B) + toluene (T) at 1 bar



TEMPERATURE	
°C	α
80.1	-
80.52	2.36
81.53	2.38
82.82	2.40
84.85	2.50
86.5	2.44
87.47	2.45
89.13	2.43
91.25	2.47
93.49	2.43
95.73	2.34
96.44	2.38
98.19	2.36
100.2	2.35
102.1	2.33
105.9	2.36
107.43	2.29
109.5	2.23
110.61	-
Média =	
2.38	

Vapour-Liquid equilibrium

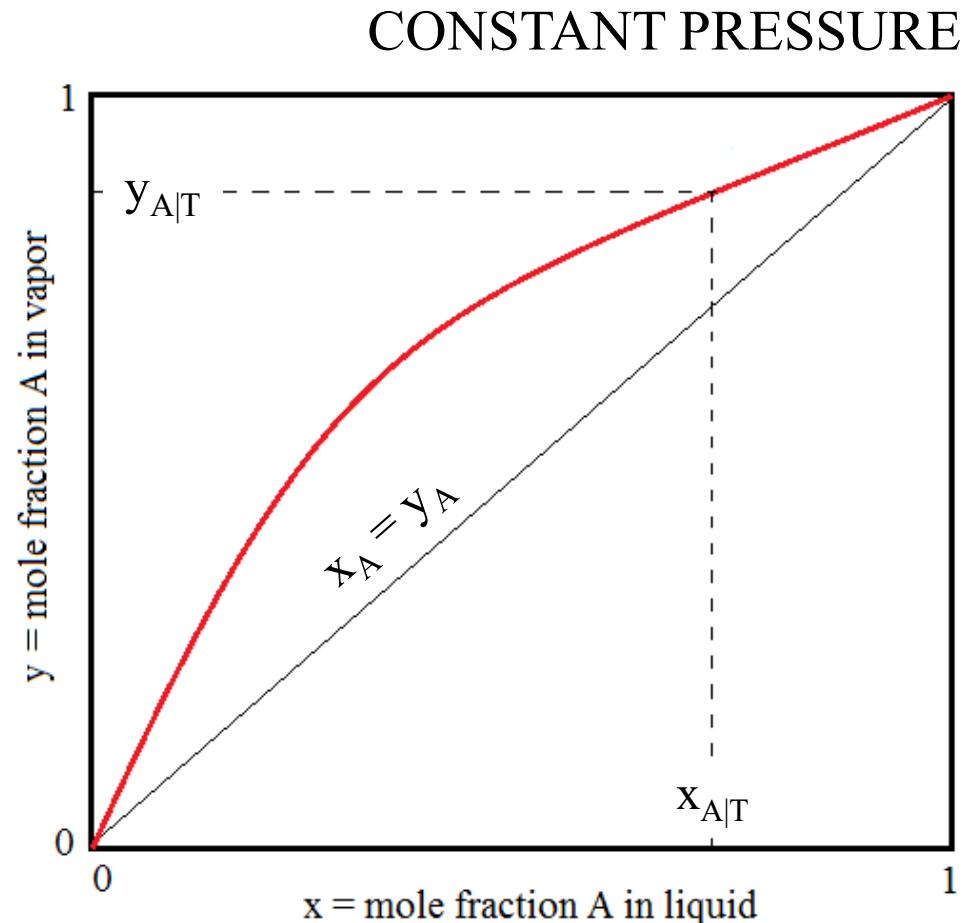
- Graphical representation

Relative volatility, α

$$\alpha = K_A / K_C$$

$$\alpha = \left(\frac{y_A}{x_A} \right) / \left(\frac{y_C}{x_C} \right) = \frac{P_A^*(T)}{P_C^*(T)}$$

If $\alpha = 1$?



Vapour-Liquid equilibrium

- Graphical representation

Relative volatility, α

$$\alpha = K_A / K_C$$

$$\alpha = \left(\frac{y_A}{x_A} \right) / \left(\frac{y_C}{x_C} \right) = \frac{P_A^*(T)}{P_C^*(T)}$$

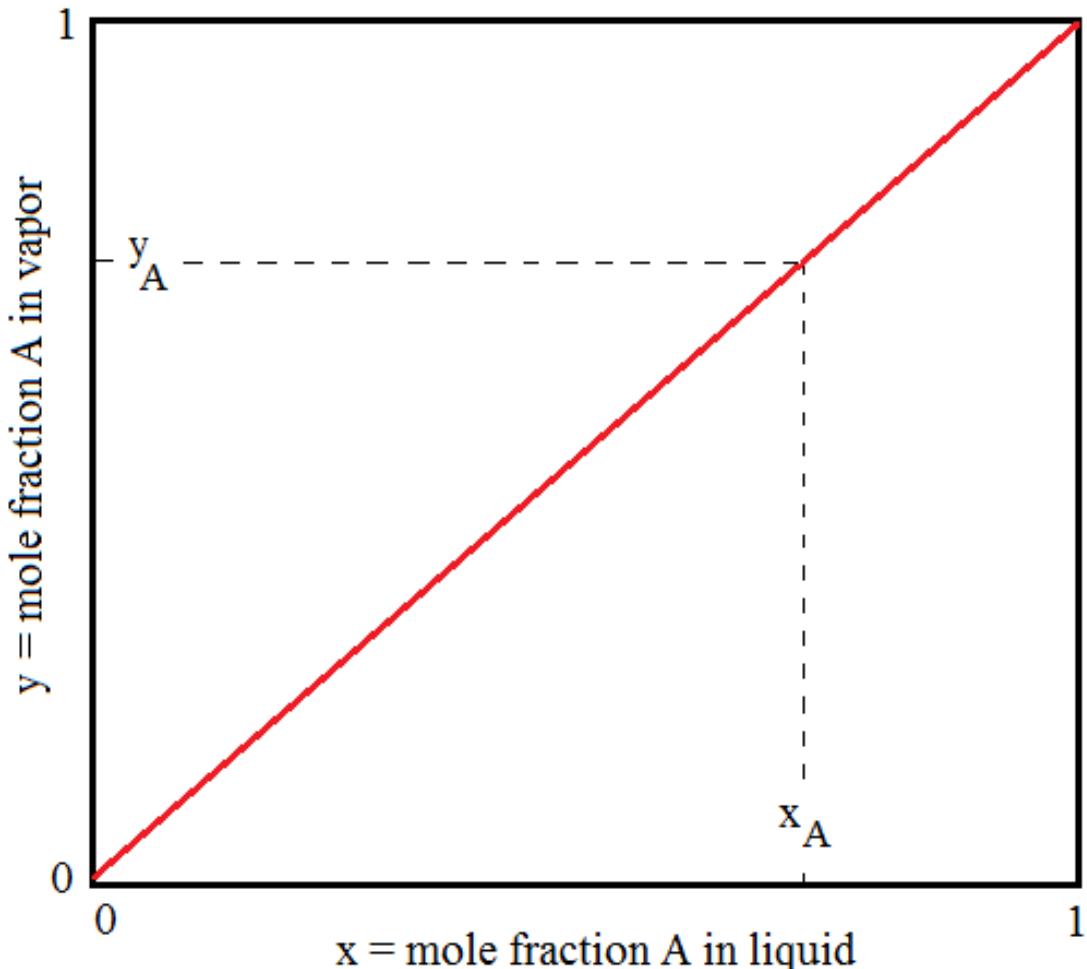
If $\alpha = 1 \Rightarrow y_A = x_A!$

$$\Leftrightarrow K_A = K_C$$

and $y_C = x_C!$

=> NO SEPARATION!

$$(P_A^* = P_C^*)$$



Vapour-Liquid equilibrium

- Graphical representation

Relative volatility, α

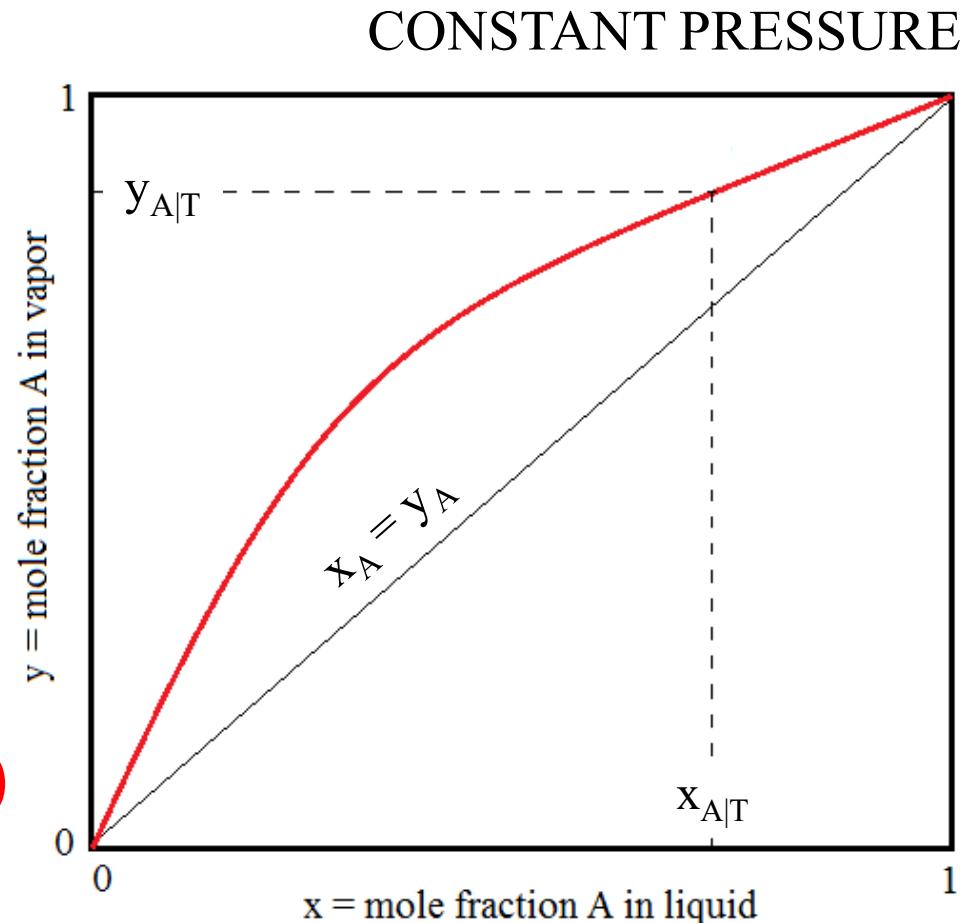
$$\alpha = K_A / K_C$$

$$\alpha = \left(\frac{y_A}{x_A} \right) / \left(\frac{y_C}{x_C} \right) = \frac{P_A^*(T)}{P_C^*(T)}$$

If $\alpha > 1 \Rightarrow y_A \gg x_A!$ $\Leftrightarrow K_A > K_C$

=> $A \rightarrow$ vapor phase
 $C \rightarrow$ liquid phase

$$(P_A^* > P_C^*)$$



Vapour-Liquid equilibrium

- Graphical representation

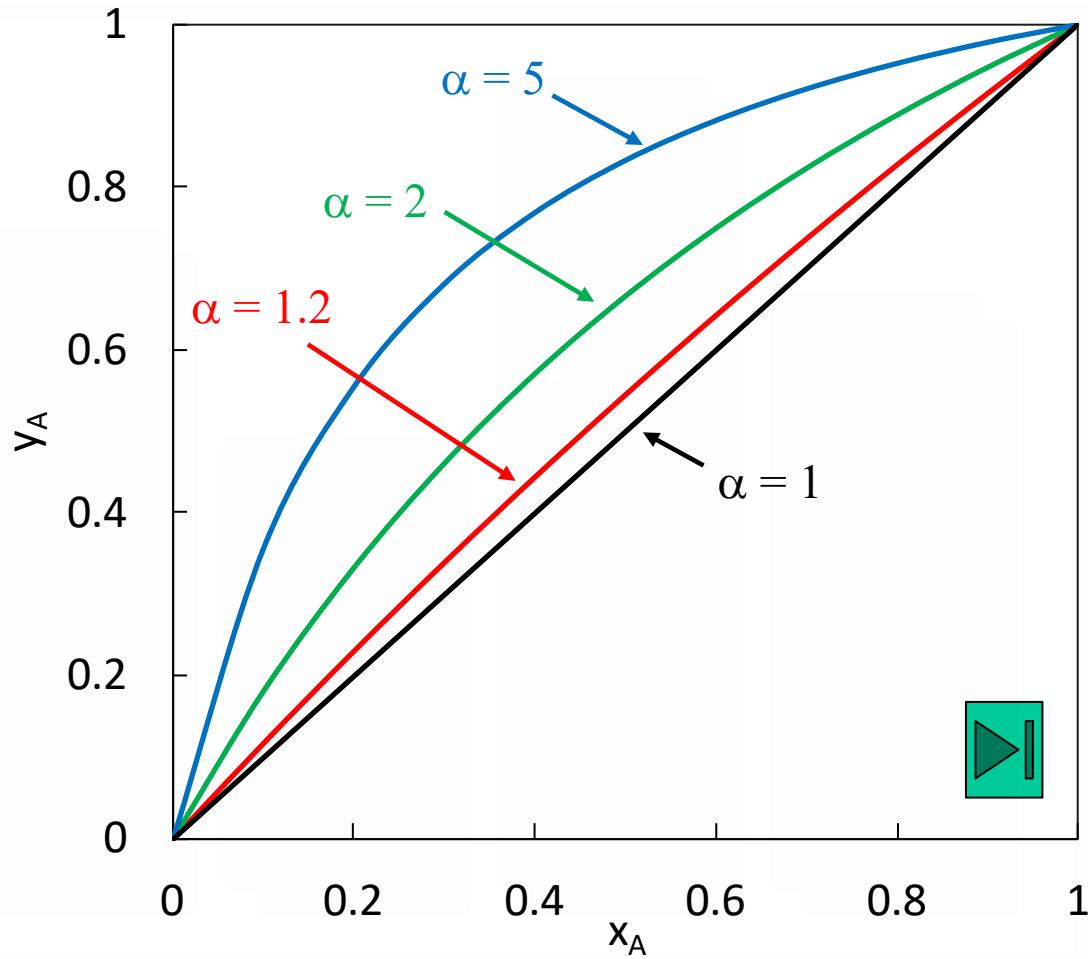
Relative volatility, α

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If $\alpha > 1 \Rightarrow y_A \gg x_A!$ $\Leftrightarrow K_A > K_C$

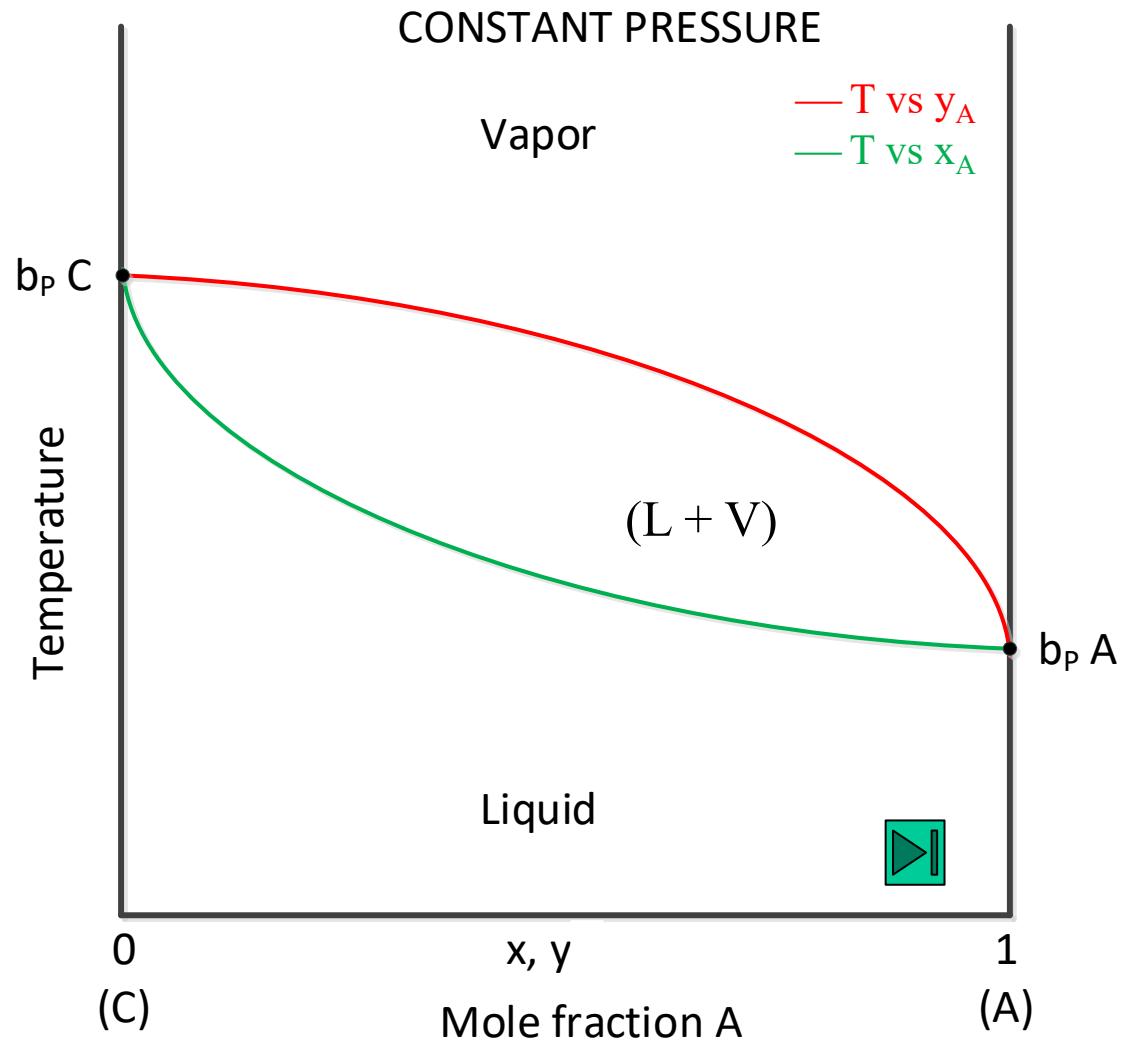
The higher the $\alpha \Rightarrow$ the BETTER the separation



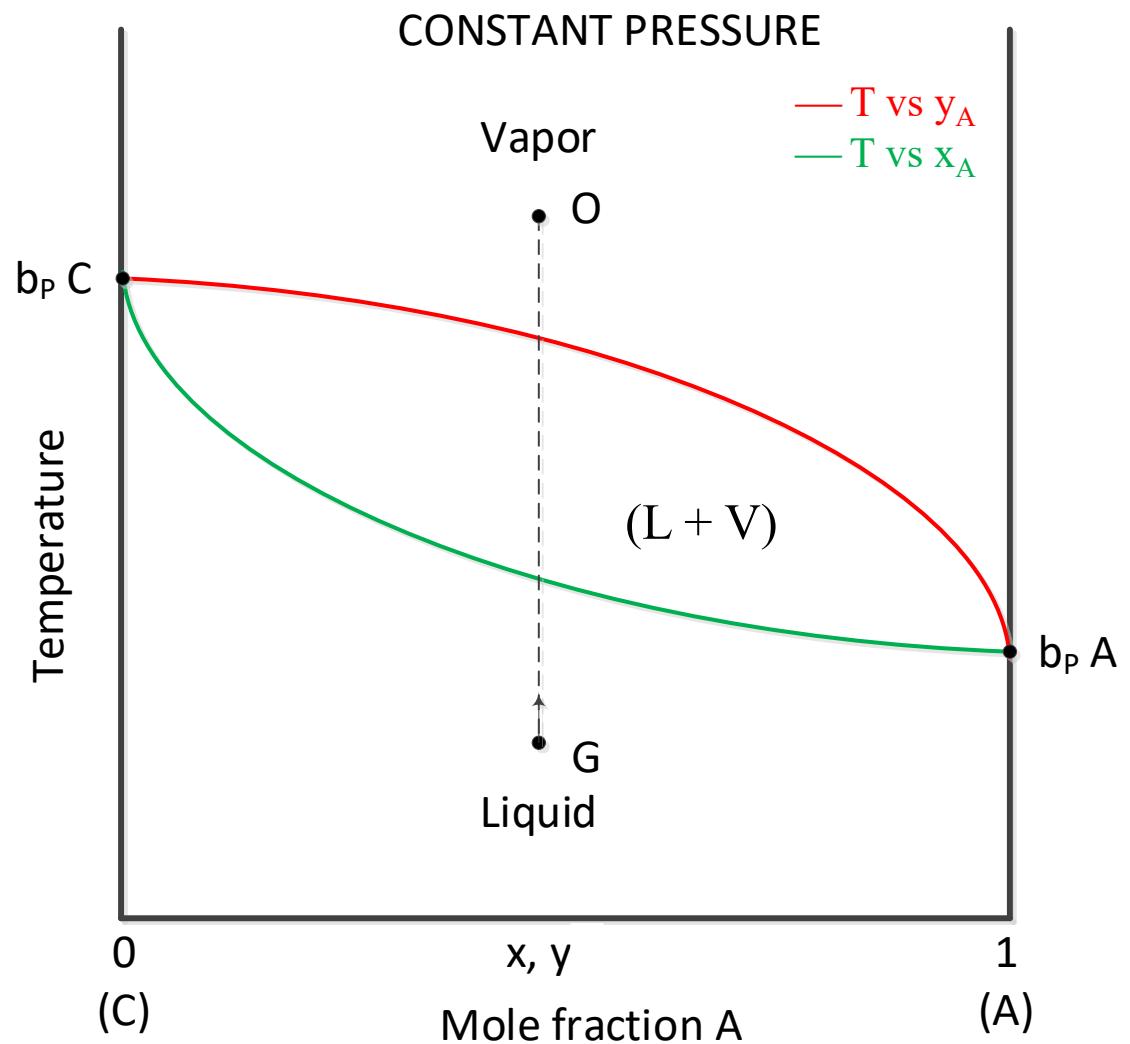
Temperature - composition Diagram

Questions...

- Why is the vapor zone above the liquid zone?
- Which one of A and C is the more volatile?



Heating $G \rightarrow D \rightarrow Q \rightarrow M \rightarrow O$

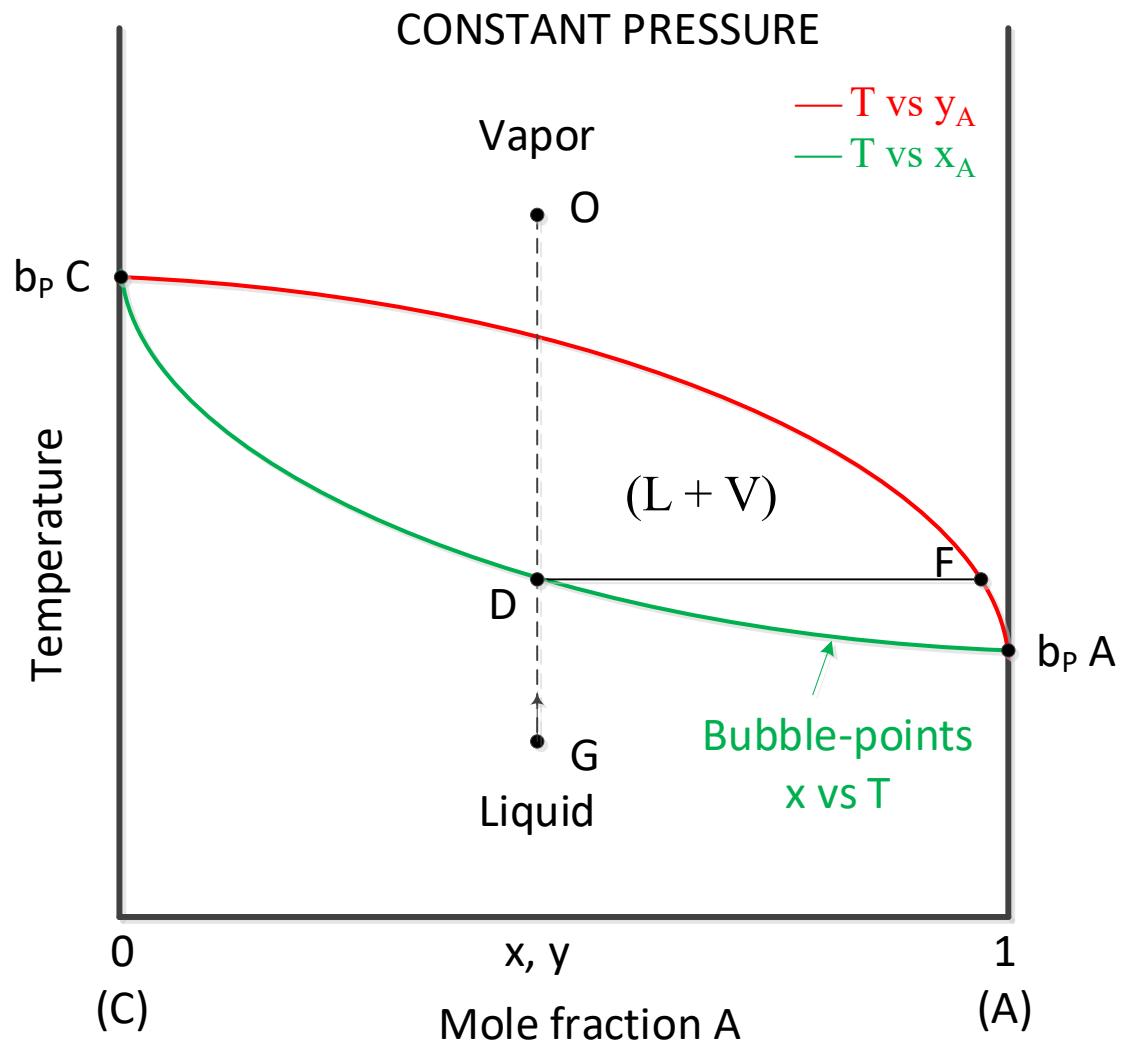


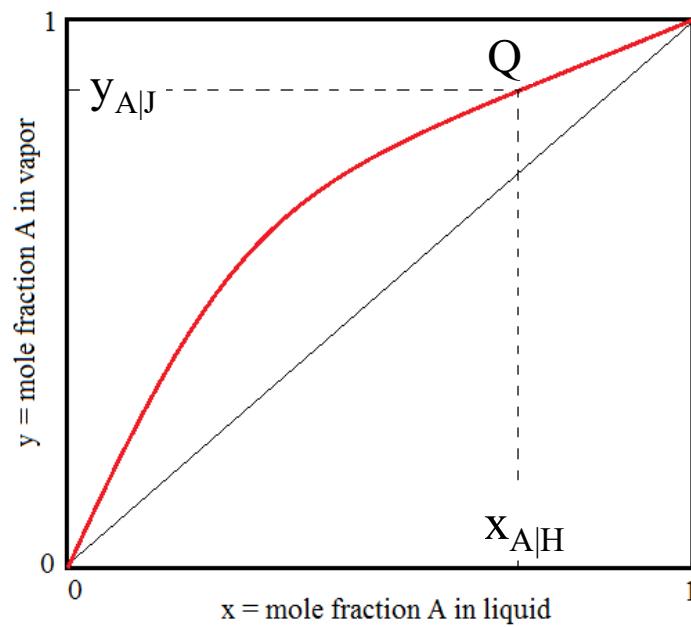
Heating $G \rightarrow D \rightarrow Q \rightarrow M \rightarrow O$

D: the first bubble appears

(the composition in A of that bubble is given by point F, y_{AF})

"ponto de bolha"



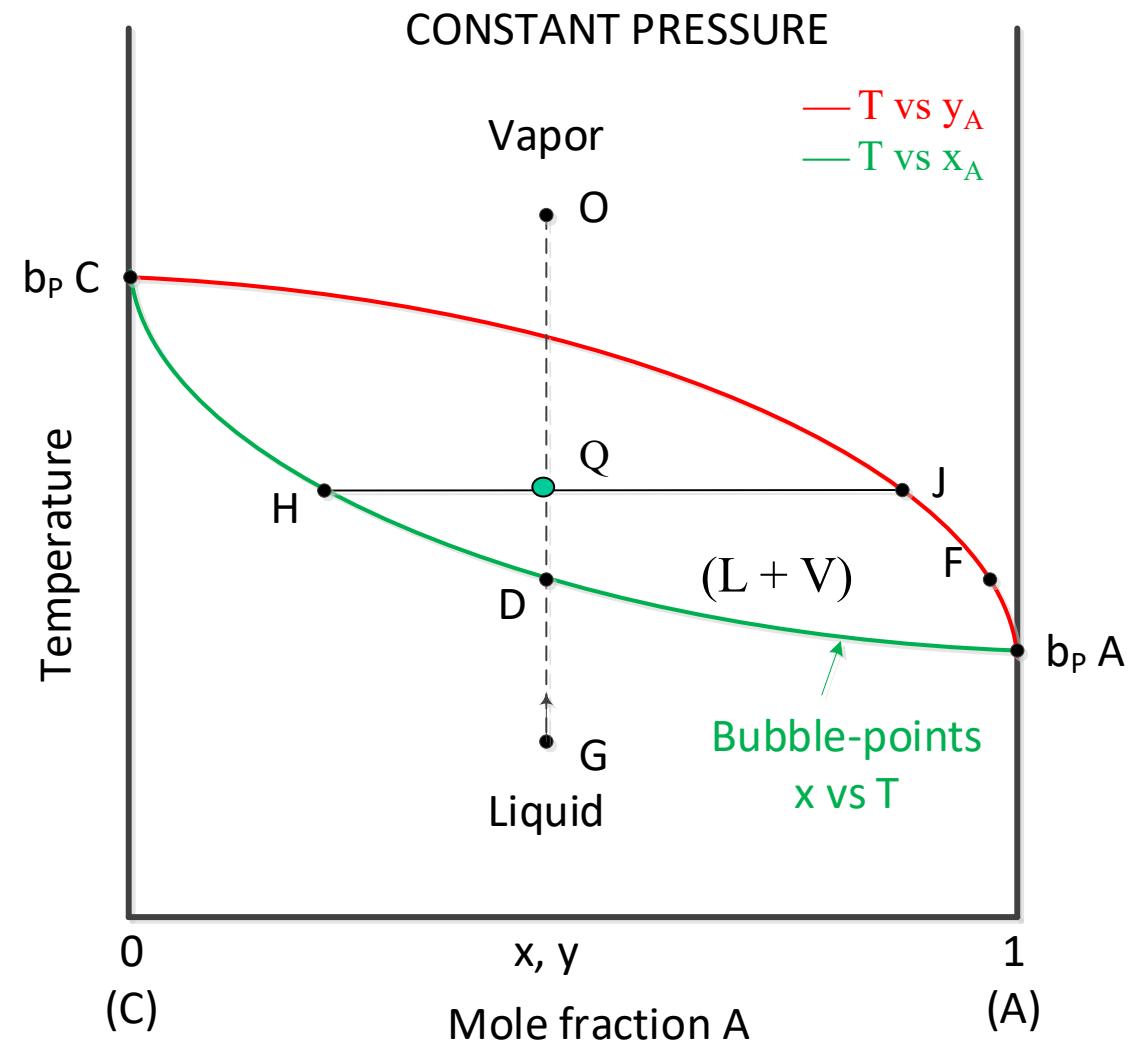


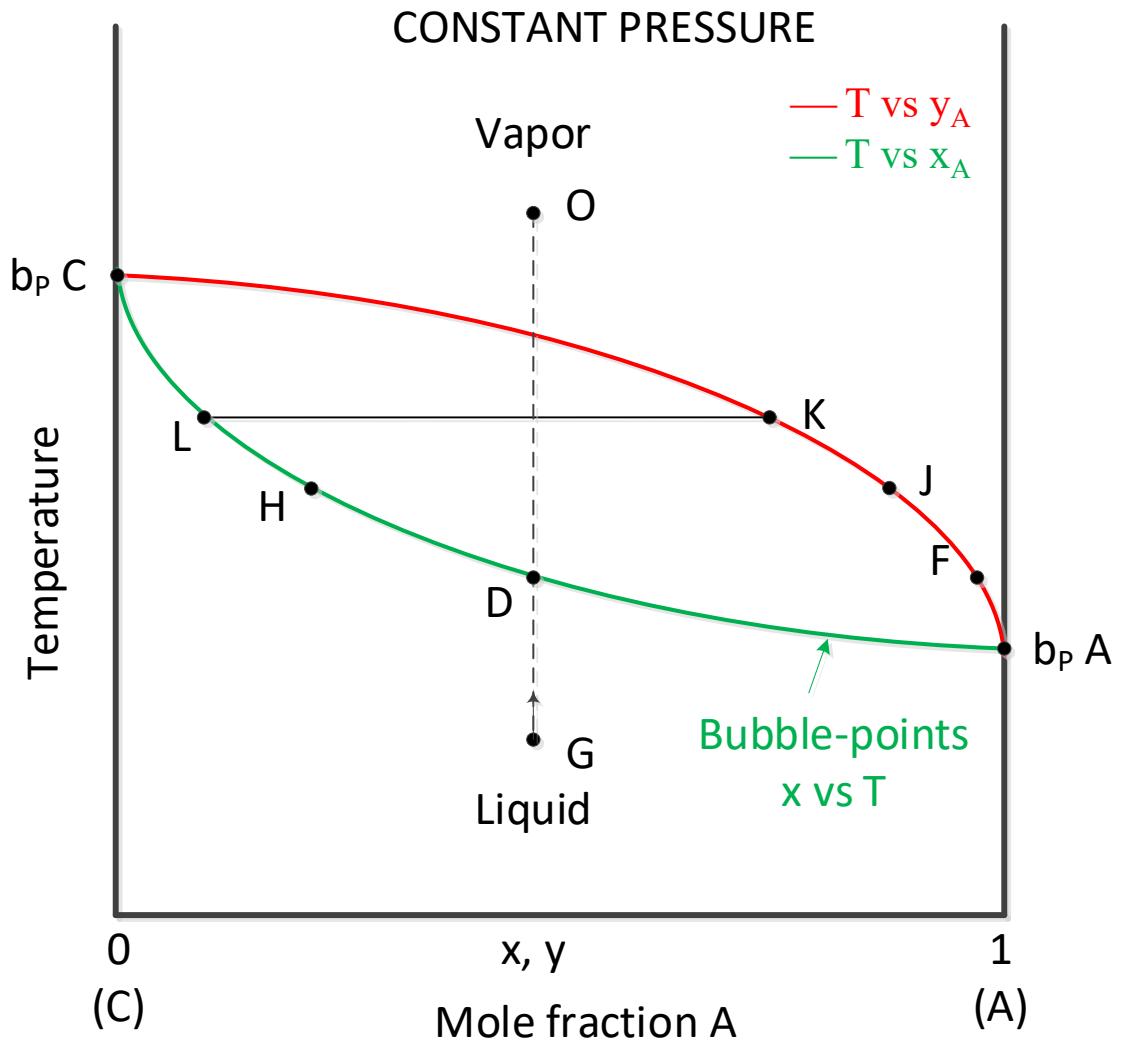
HJ - Isotherm (tie-line)

H- saturated liquid
J- saturated vapor

$$y_{A|J} > x_{A|H}$$

(A is more volatile!)

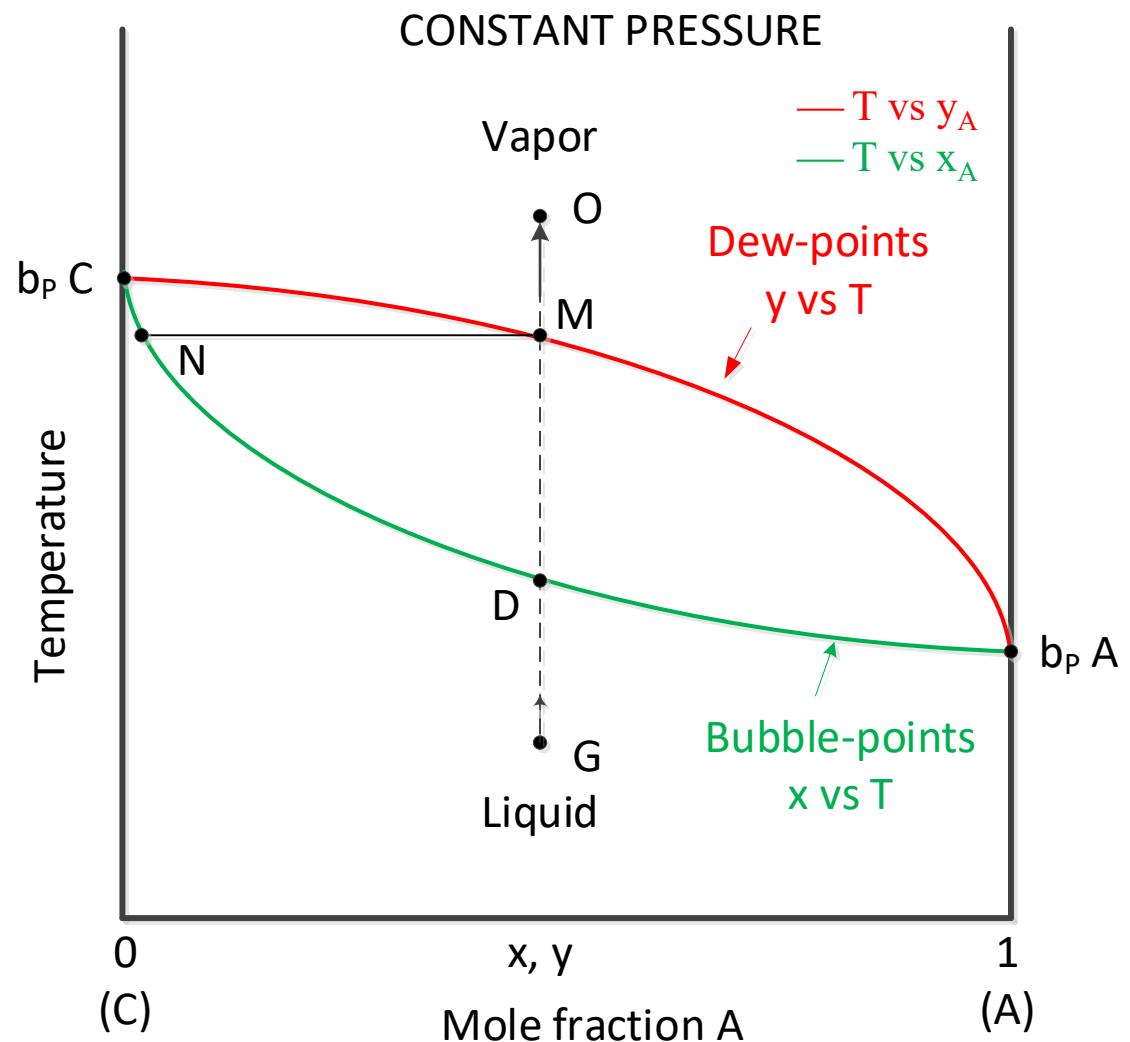




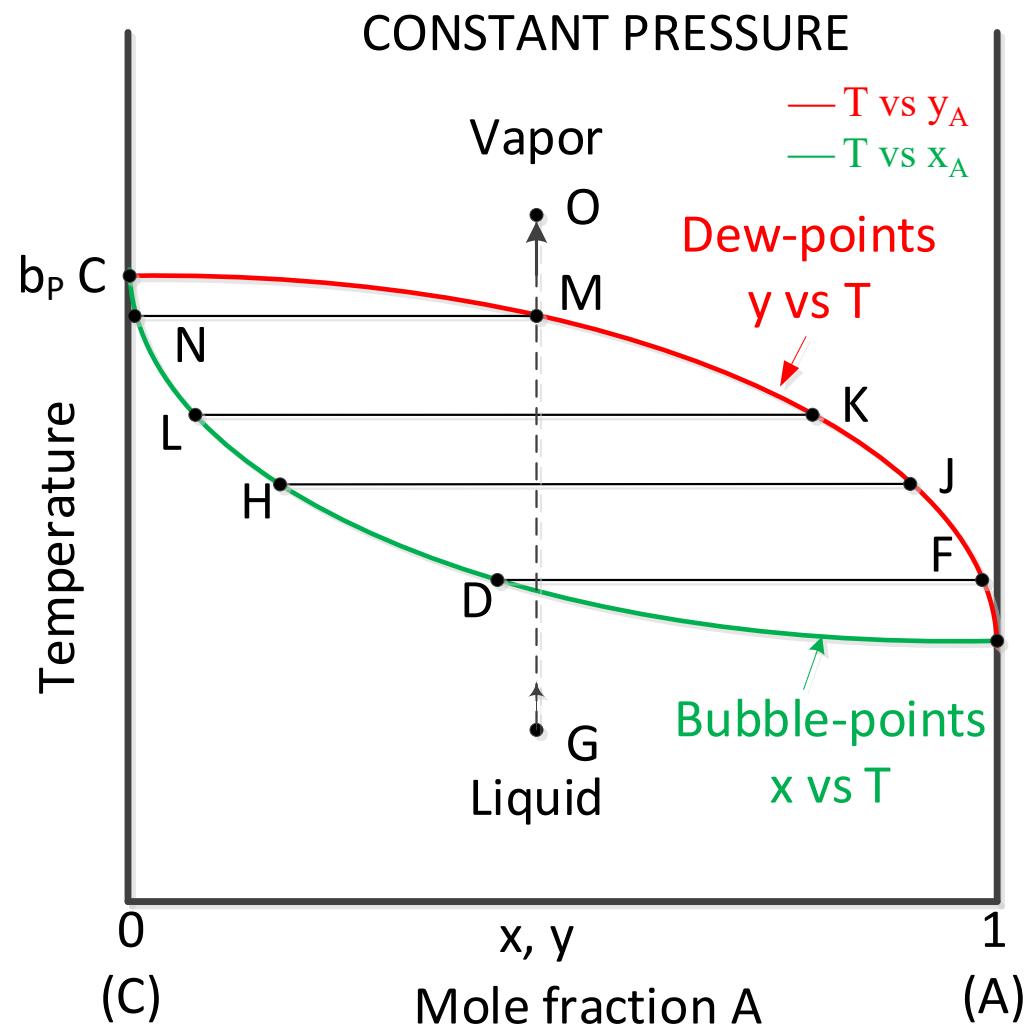
M: the last bubble disappears

Or conversely, the moment
when the first drop of
liquid appears

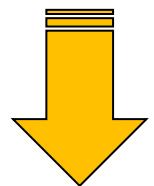
"ponto de orvalho"



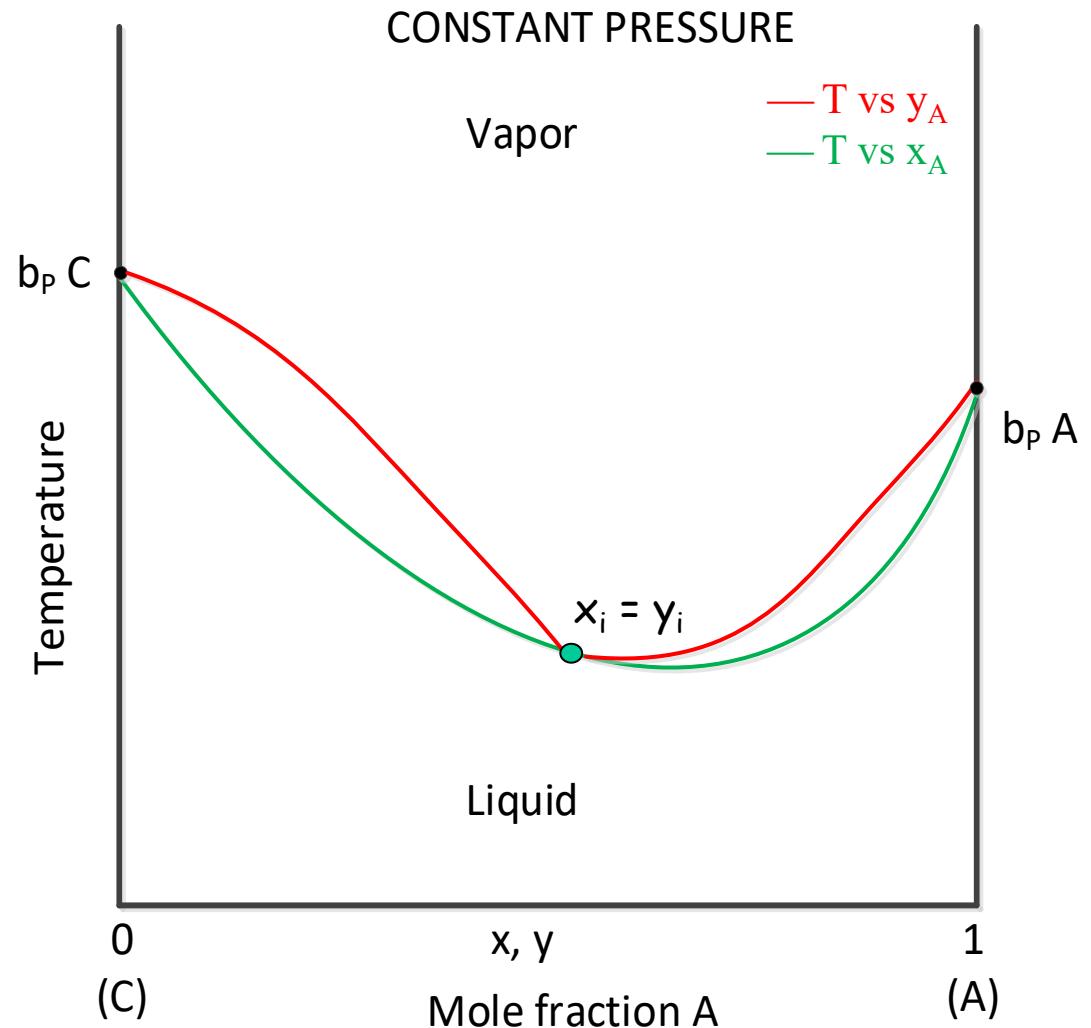
IDEAL
SYSTEM!



NON IDEAL SYSTEMS!



Azeotropes!

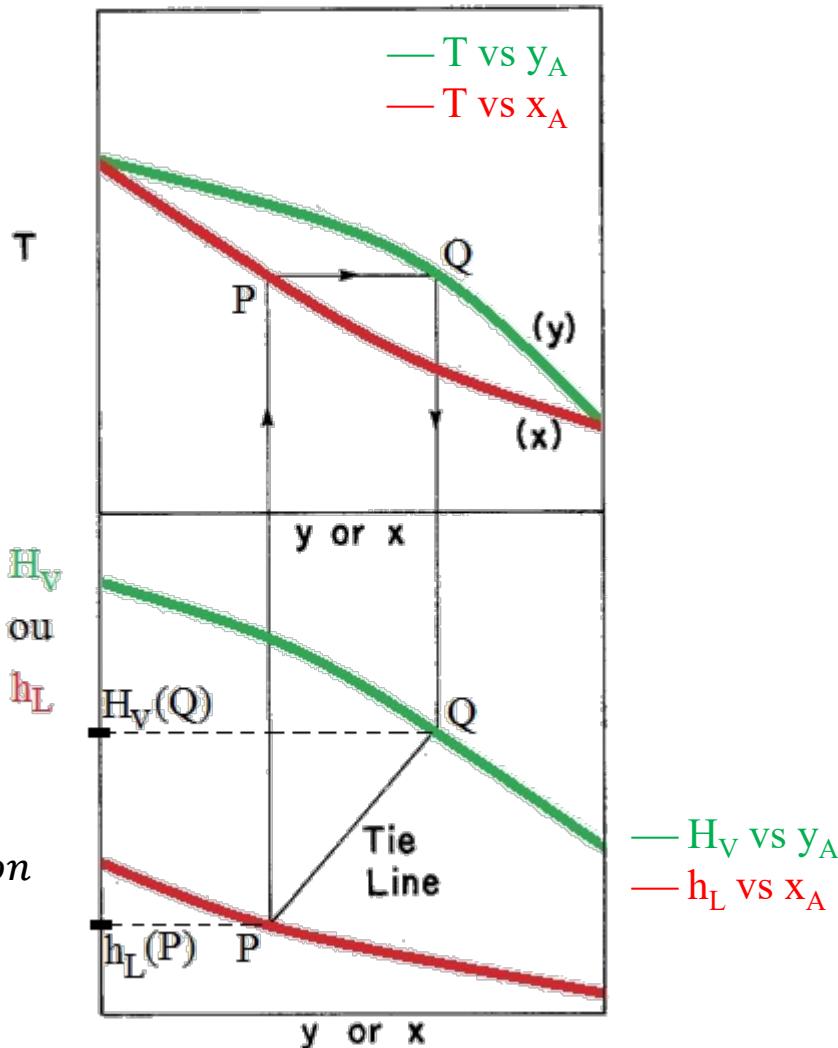


Composition (x, y) - Enthalpy (h, H) Diagram

H_V : Enthalpy of vapor phase

h_L : Enthalpy of liquid phase

$$H_V(Q) - h_L(P) = \Delta H_{vaporization}$$



$$H_V > h_L !$$

$H_V - h_L$
depends on
the composition!

Composition (x,y) - Enthalpy (h,H) Diagram

H_V : Enthalpy of vapor p

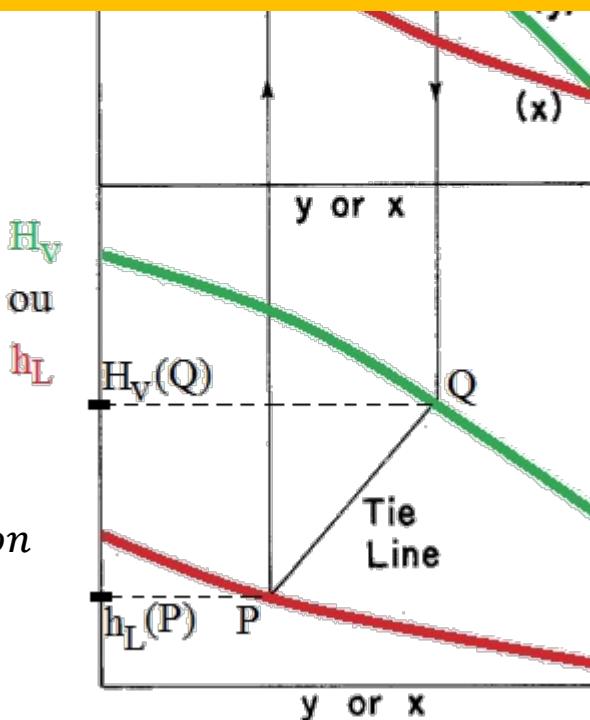
h_L : Enthalpy of liquid p

The enthalpy of vaporization of a mixture depends on its composition!

$$H_V > h_L !$$

$H_V - h_L$
depends on
the composition!

$$H_V(Q) - h_L(P) = \Delta H_{vaporization}$$



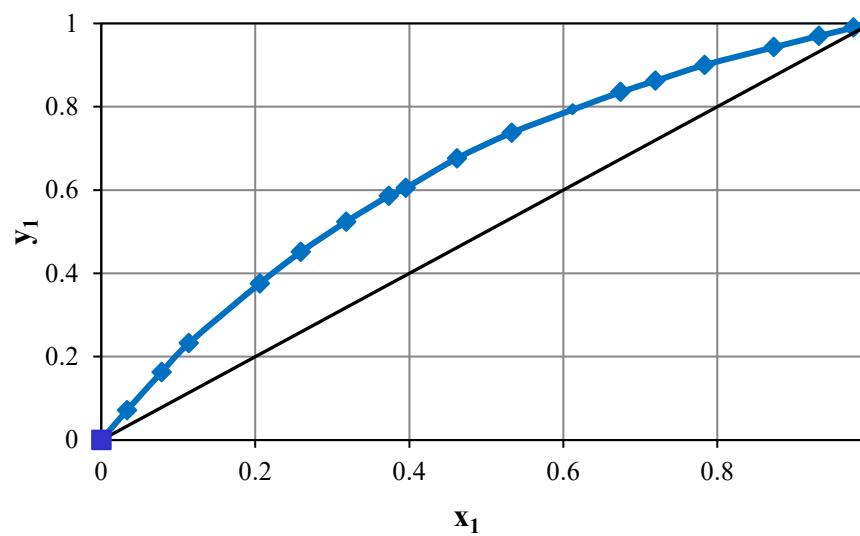
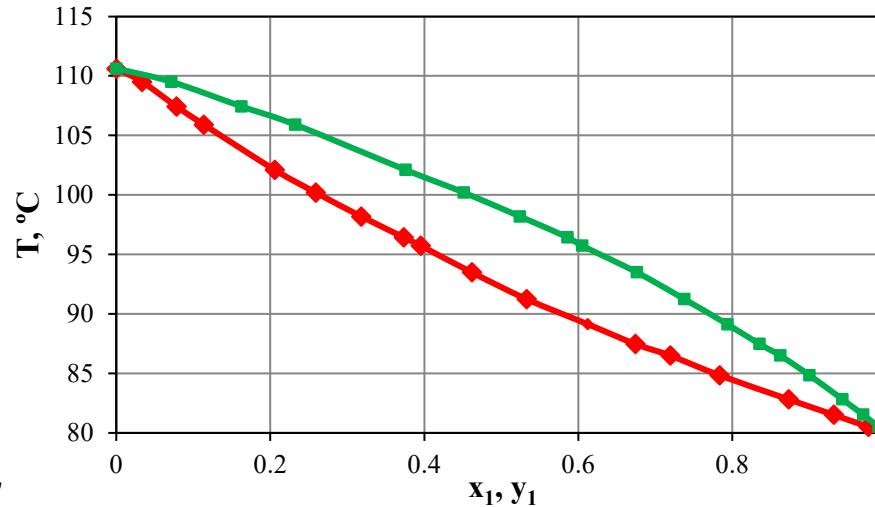
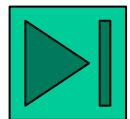
(kJ/kg)	$\Delta\hat{H}_{\text{Fusion}}$	$\Delta\hat{H}_{\text{Vaporization}}$
Acetone	98.0	520.0
Water	333.5	2256.4
Benzene	126.0	393.9
Ethanol	109.0	837.4
Hexane	151.2	334.8
Methanol	98.9	1100.8
Toluene	71.8	406.7





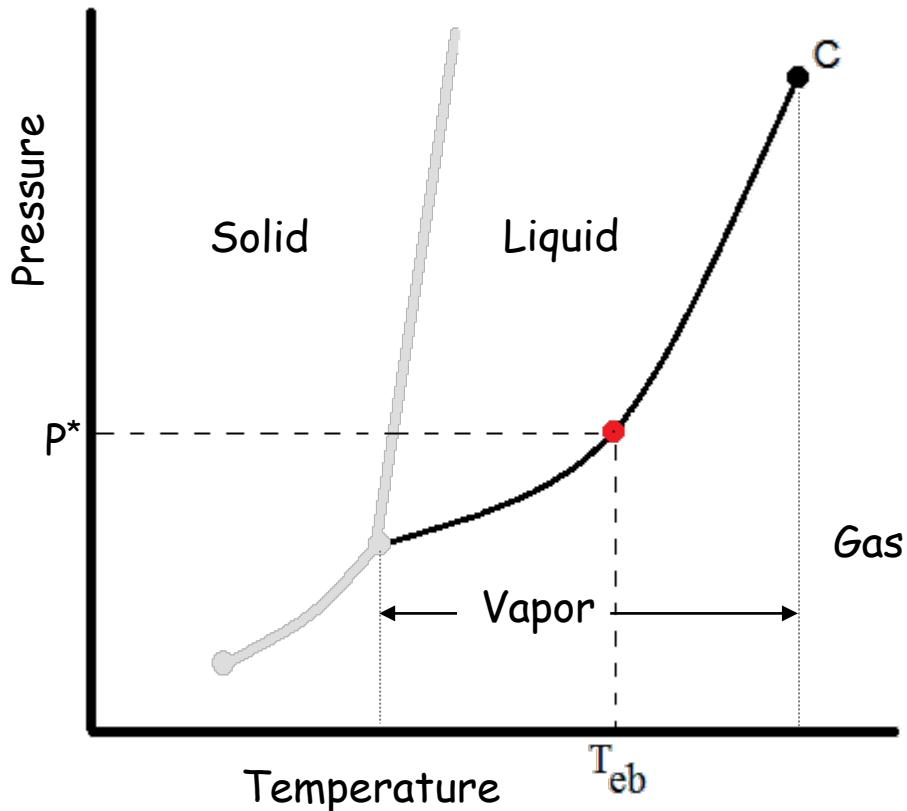
$$T_{boiling}|_{benzene} \text{ (1.2 bar)} = 80.1^\circ\text{C}$$

$$T_{boiling}|_{toluene} \text{ (1.4 bar)} = 110.6^\circ\text{C}$$



Liquid-Vapour equilibrium of binary mixture benzene (1) + toluene (2) at 1 bar

Liquid - Vapour equilibrium of a pure substance A



⇒ T_{eb} : temperature at which A **vaporizes** at constant pressure

⇒ P^* : pressure at which A **condensates** at constant temperature

Example of water:

$$T_{eb} (1 \text{ atm}) = 100^\circ\text{C}$$

$$P^* (100^\circ\text{C}) = 1 \text{ atm}$$

T_{eb} : Boiling Temperature

P^* : Vapor Pressure (depends on T)

Table 7.1 Representative Commercial Binary Distillation Operations

Binary Mixture	Average Relative Volatility (α)	Number of Trays
1,3-Butadiene/vinyl acetylene	1.16	130
Vinyl acetate/ethyl acetate	1.16	90
<i>o</i> -Xylene/ <i>m</i> -xylene	1.17	130
Isopentane/ <i>n</i> -pentane	1.30	120
Isobutane/ <i>n</i> -butane	1.35	100
Ethylbenzene/styrene	1.38	34
Propylene/propane	1.40	138
Methanol/ethanol	1.44	75
Water/acetic acid	1.83	40
Ethylene/ethane	1.87	73
Acetic acid/acetic anhydride	2.02	50
Toluene/ethylbenzene	2.15	28
Propane/1,3-butadiene	2.18	40
Ethanol azeotrope/water	2.21	60
Isopropanol/water	2.23	12
Benzene/toluene	3.09	34
Methanol/water	3.27	60
Cumene/phenol	3.76	38
Benzene/ethylbenzene	6.79	20
HCN/water	11.20	15
Ethylene oxide/water	12.68	50
Formaldehyde/methanol	16.70	23
Water/ethylene glycol	81.20	16

$\alpha \nearrow \Rightarrow N_{\text{trays}} \searrow$



BETTER separation!

Liquid-Vapour equilibrium of binary mixture benzene (B) + toluene (T) at 1 bar

