# SEPARATION SCIENCE


1 Role of separation science in industry (1h 1->10)

2 Physico-chemical processus involved in separation (1h 11->17, 2h 17->28, 2h 29->31)

3 Engineering of separation processes

4 Elements for process selection – case studies

# 1- Role of separation science in industry

**Why ?**

**The fonctions of separation processes**

**Where ?**

**The place of separation in processes**

**What ?**

**The nature of species to separate**

**How ?**

**The physico-chemical agents used to separate**

**With what ?**

**The panel of techniques used to separate**

**A problem ?**

**The limitations and the needs**

## 1.1 - Role of separation science in industry : why ?

Separation : a more and more important need in industries (**chemistry, petroleum, pharmaceutical production, food engineering, water and waste water, paper production, electronics …)**

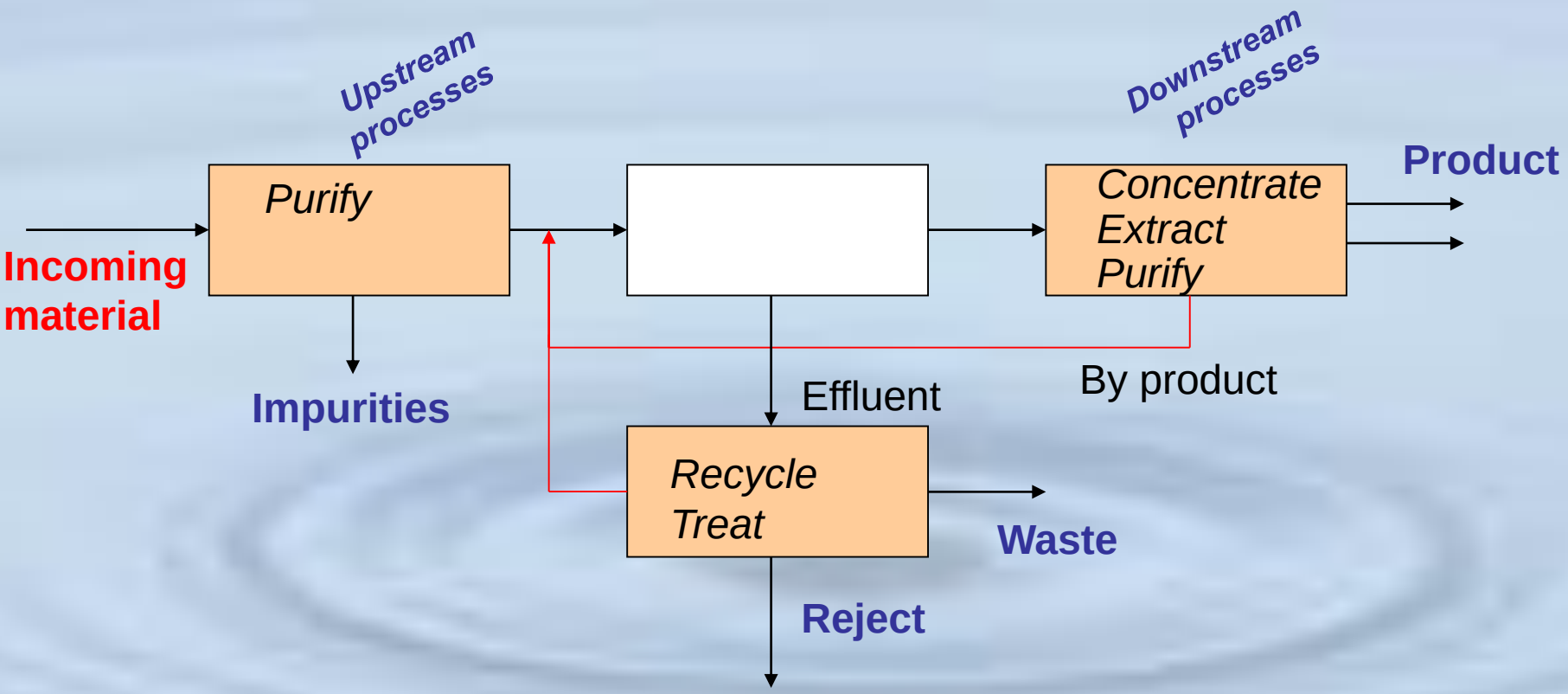
A need to limit the negative impact of processes on the environnement

- **Treat** fluids (to eliminate or to degrade pollutant in air or in water)
- **Capture** a pollutant (ex $CO_2$ capture)
- **Concentrate** products (to reduce the cost of transportation ex : orange juice)
- **Recycle** process fluid (ex rinsing water)
- **Purify** process fluid (to use this fluid for a longer period and avoid a frequent replacement ex : cataphoresis painting bath)
- **Valorize** residue by recovering valuable compounds in waste streams (anti-oxidant from olive waste streams …)

A need to elaborate products of better quality

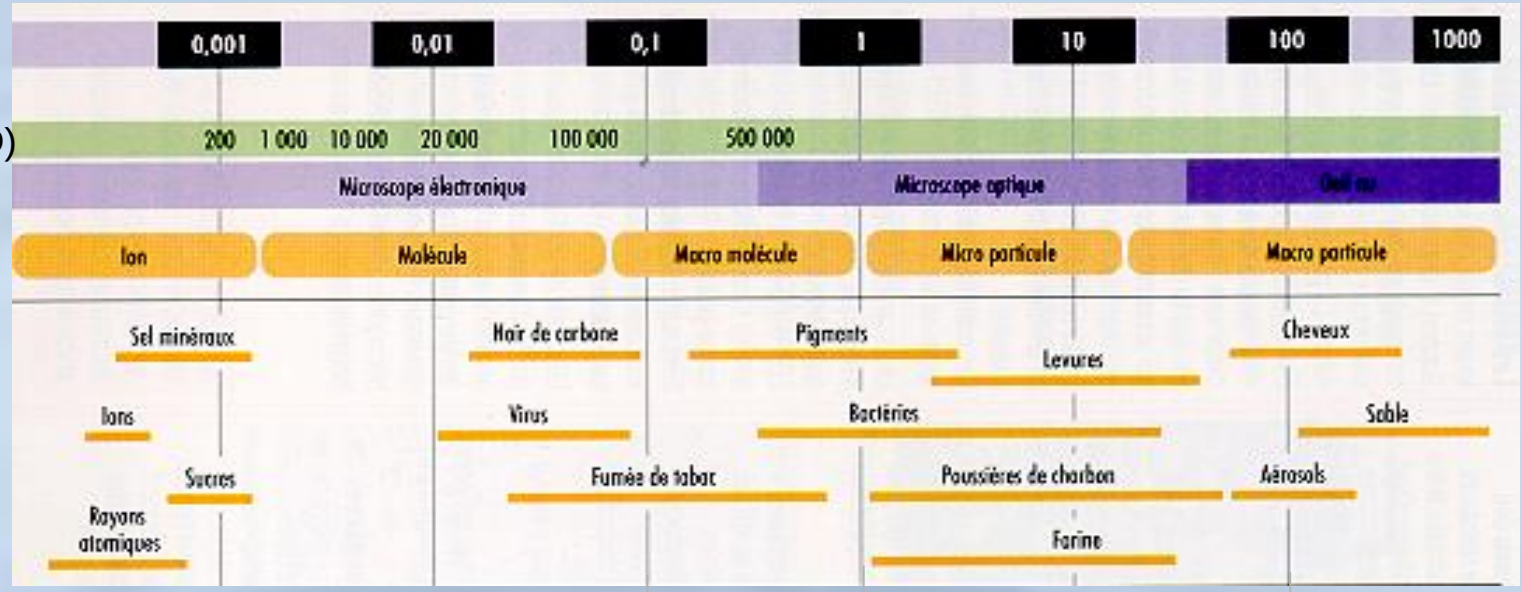
- **Extract** a product from complex medium (ex : extraction of a drug from a fermentation broth or from a plant, extraction of molecule in blood)
- **Purify** (eliminate impurities from end product or incoming material)
- **Fractionnate** (to separate a product in different fractions)
- **Concentrate** recoverable components from dilute solution

## 1.2 - Role of separation science in industry : where ?




The different step in a process where separation occurs

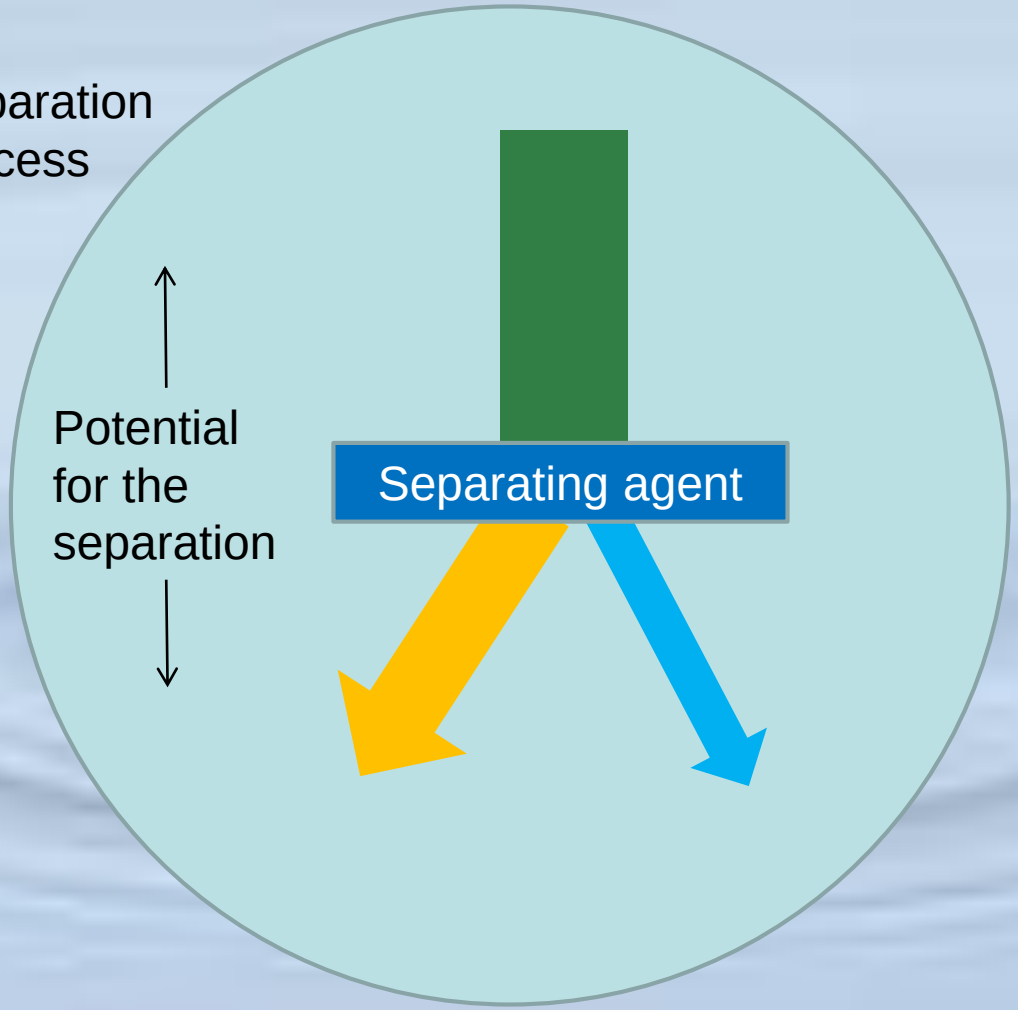
# 1.3 - Role of separation science in industry : What ?




Separation Process

Reverse osmosis
nanofiltration
ultrafiltration
microfiltration
filtration
electrodialysis
Ionic exchange
adsorption -chromato
ultracentrif.
centrifugation
settling
absorption / distillation / extraction
cristallisation / precipitation / coagulation

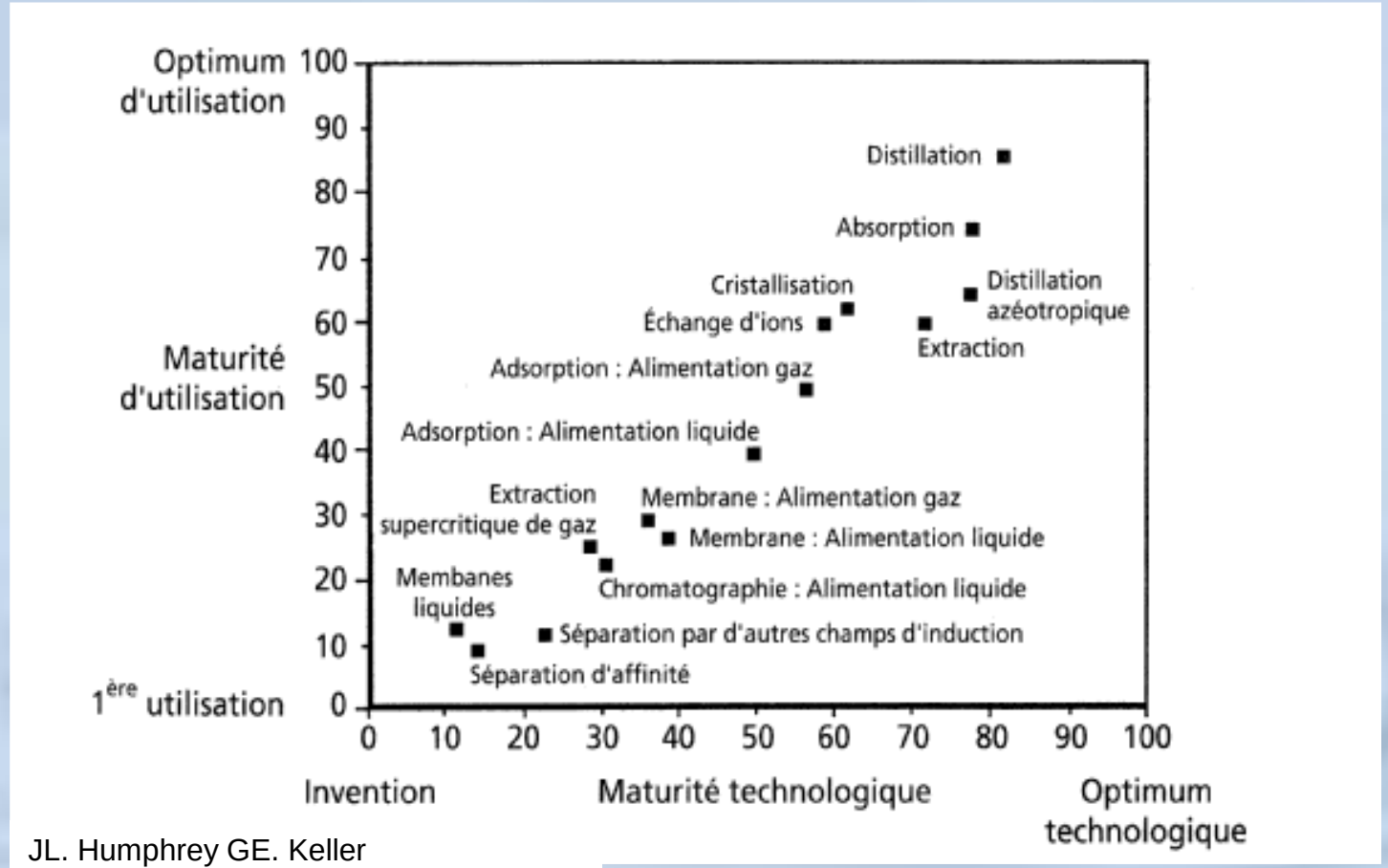
# 1.4 - Role of separation science in industry : How ?



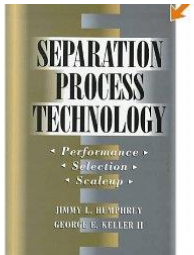
# 1.4 - Role of separation science in industry : How ?

| Processes | Separating agent | Separation potential |
|---|---|---|
| Absorption | Solvant | Chemical activity |
| Extraction | | |
| Ionic exchange | Adsorbant / Resin | Chemical activity |
| Adsorption | | |
| Chromatography | | |
| Cristallisation | Cooling | Temperature |
| Distillation | Heat | Chemical activity |
| Evaporation | | |
| Drying | | |
| Centrifugation/ Settling | Mechanical energy | Gravity / Centrifugal force |
| Conventional filtration | Filter/ Membrane | Pressure |
| Membrane processes | | Pressure, … |
| Electrodialysis | | Electric potential |
| Dialysis | | Concentration |

# 1.5 - Role of separation science in industry : with what ?

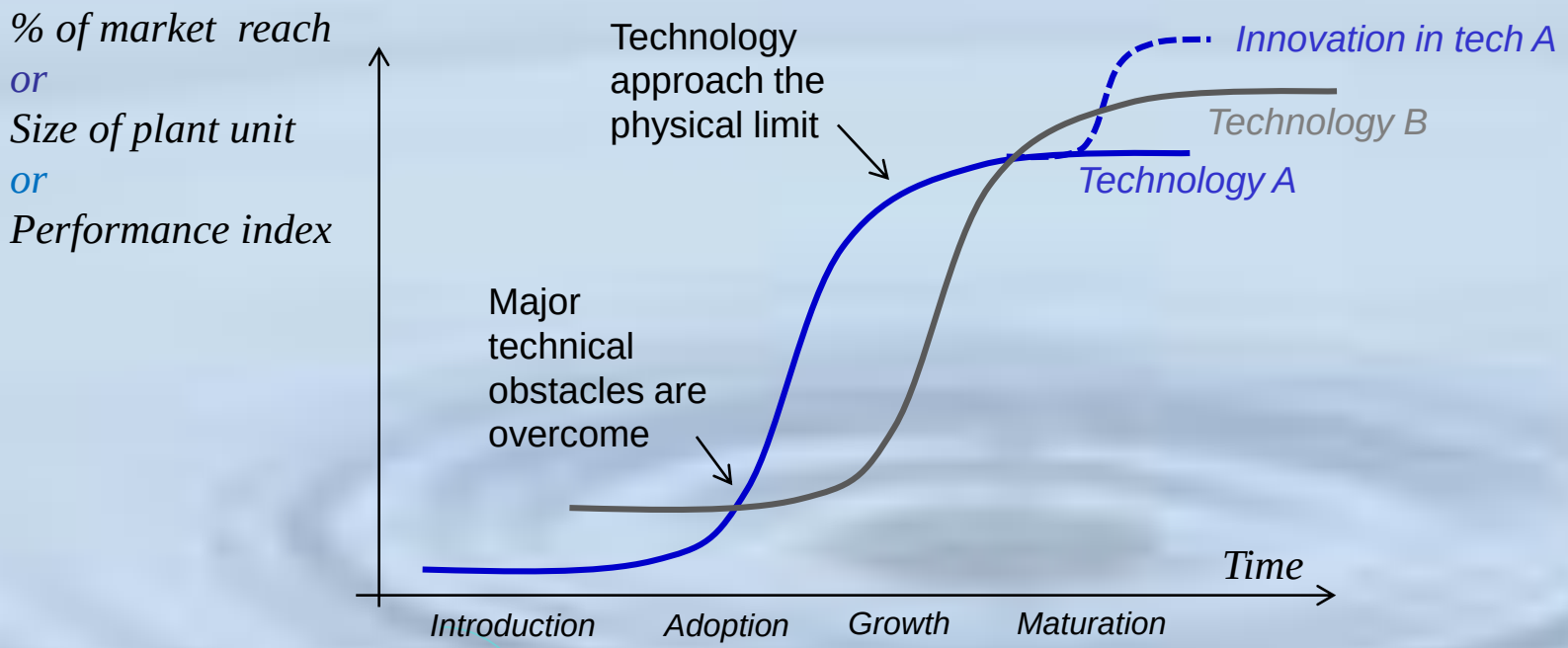



JL. Humphrey GE. Keller
Separation Process Technology 1997



# 1.5 - Role of separation science in industry : how rapid ?

***The development of a process follows the universal S-shaped curve (particularly useful for analyzing technological cycles)***




*Development kinetics of the ultrafiltration process for potable water in industry*

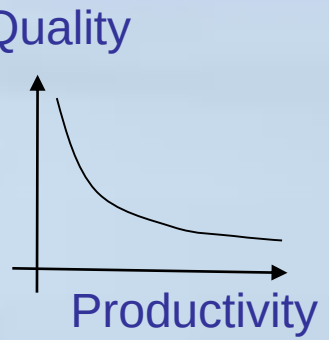
| | | |
|---|---|---|
| Amoncourt | 1989 | 240 $m^3/d$ (first in the world) |
| Fillière | 1994 | 2 000 $m^3/d$ |
| Rouen | 2000 | 24 000 $m^3/d$ |
| Moscou | 2005 | 275 000 $m^3/d$ |

## 1.6 - Role of separation science in industry : Needs

**The use of a separation process is complex and needs good knowledges**

**Production level** — **To control the running of a process**

**Development level** — **To find the optimal working point**
**a compromise between quality / Productivity**
**link to mass transfer consideration !**




**Research level** — **To choose or optimize the process adapted to a separation problem**

**To conceive new separation processes**

**Need of specialists**

- **To reduce economic cost**
- **To increase the quality**
- **To increase the productivity**
- **To reduce the impact on environnment**

# 2 - Physico-chemical processus involved in separation

- **2.1 – States of matter**
  - **The different phase and state of the matter**
  - **The multiphasic aspect of « real life » fluid**

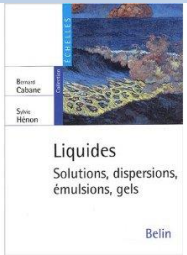
*A fluid to separate …*

- **2.2 – Potential for separation**
  - **Difference of affinity**
  - **Difference of size**
  - **Difference of charge**

*… thank to differences in molecules properties*

- **2.3 – Transfert in separation processes**
  - **Transfert at interfaces : the film model**
  - **Double film model**

*… and with more or less time*




B. Cabane S. Henon
Liquides : solutions, dispersions, gels 2003

# 2.1 – States of matter : the different phase

| | Liquid | Gas | Solid | Supercritical |
|---|---|---|---|---|
| Density kg/m3 | 1000 | 1 | >1000 | Close to liquid density |
| Diffusion m2/s | $10^{-10}$-$10^{-9}$ | $10^{-5}$-$10^{-3}$ | $10^{-15}$-$10^{-13}$ | Close to gaz |
| Viscosity Po | $10^{-4}$-10 | $10^{-5}$-$10^{-6}$ | infinite | Close to gaz |

Condensed phase controled by intermolecular interactions

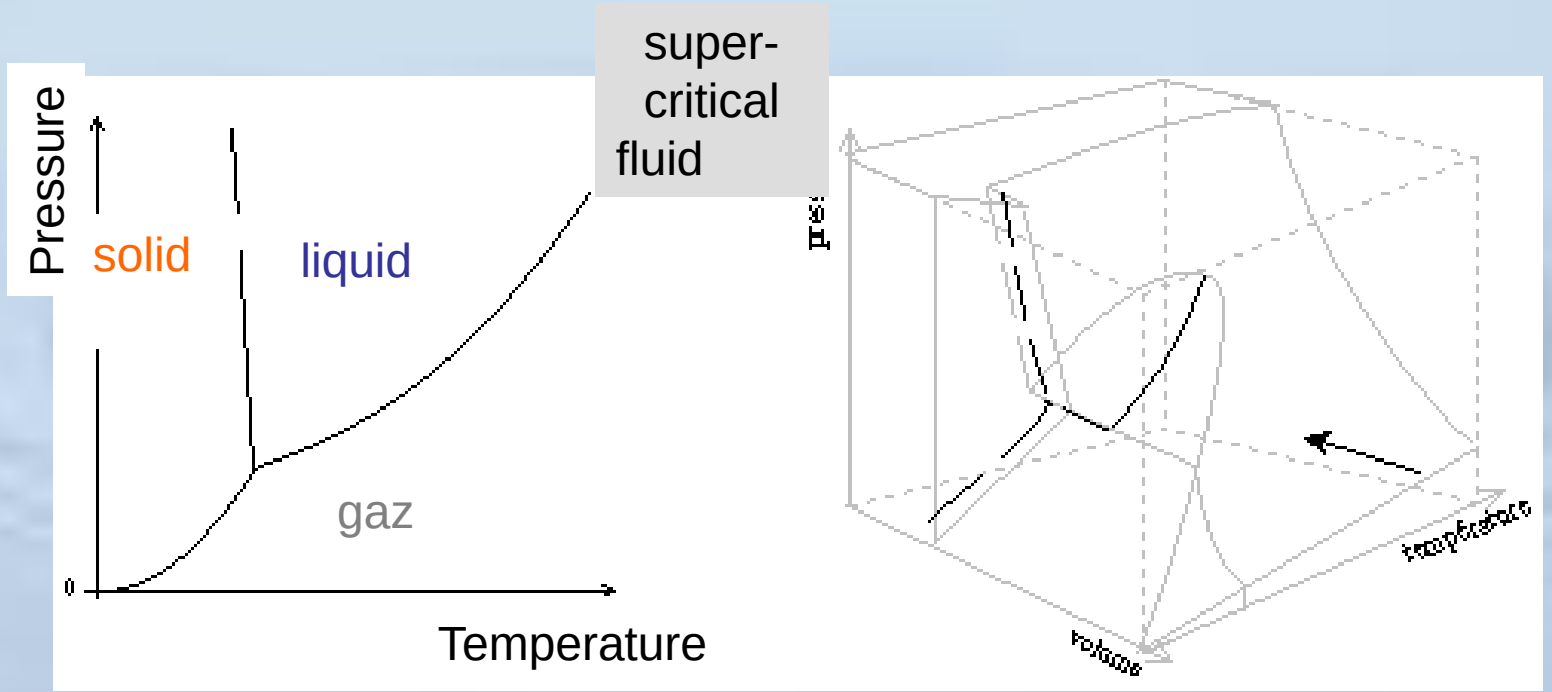
Good solubility and solvatation

Expanded phase controled by molecule mobility and collisions

Large diffusion

# 2.1 – States of matter : the different phase

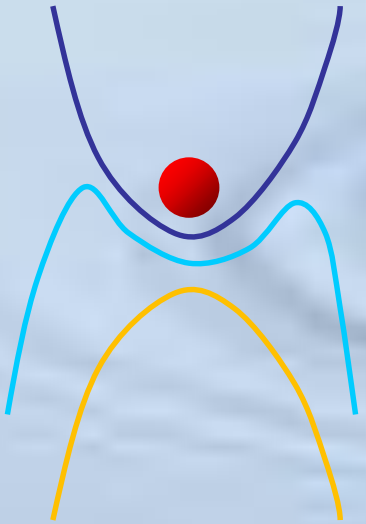
solid
gas
liquid
Supercritical fluid } fluid



## 2.1 – States of matter : liquid states

**Stable state** (at equilibrium)

Pure liquid
Solution of hydrophilic or ionic molecules
Solution of hydrophobic molecules
Solution and association of amphiphilic molecule



**Metastable state** (colloidal state)
(the evolution towards the equilibrium is blocked)

Solid/liquid dispersion
emulsion
gel

**Instable state**
Immiscible solvant

## 2.1 – States of matter : liquid states / pure liquid

### The water : pure but not simple !

→ **Cohesive liquid**: important superfical tension
high boiling temperature

↓ Because of strong hydrogen bonding

→ **Low density**

↓ Porosity between molecules of 0,5 (close packing is 0,3)
-> cavities

→ **Good solvatation properties**
- of small molecules and macromolecules
- of dissolved gaz

## 2.1 – States of matter : liquid states / solutions

### Solutions

solute - organic (protein …) or inorganic (salts…) « solid »
- organic liquid (oil…)

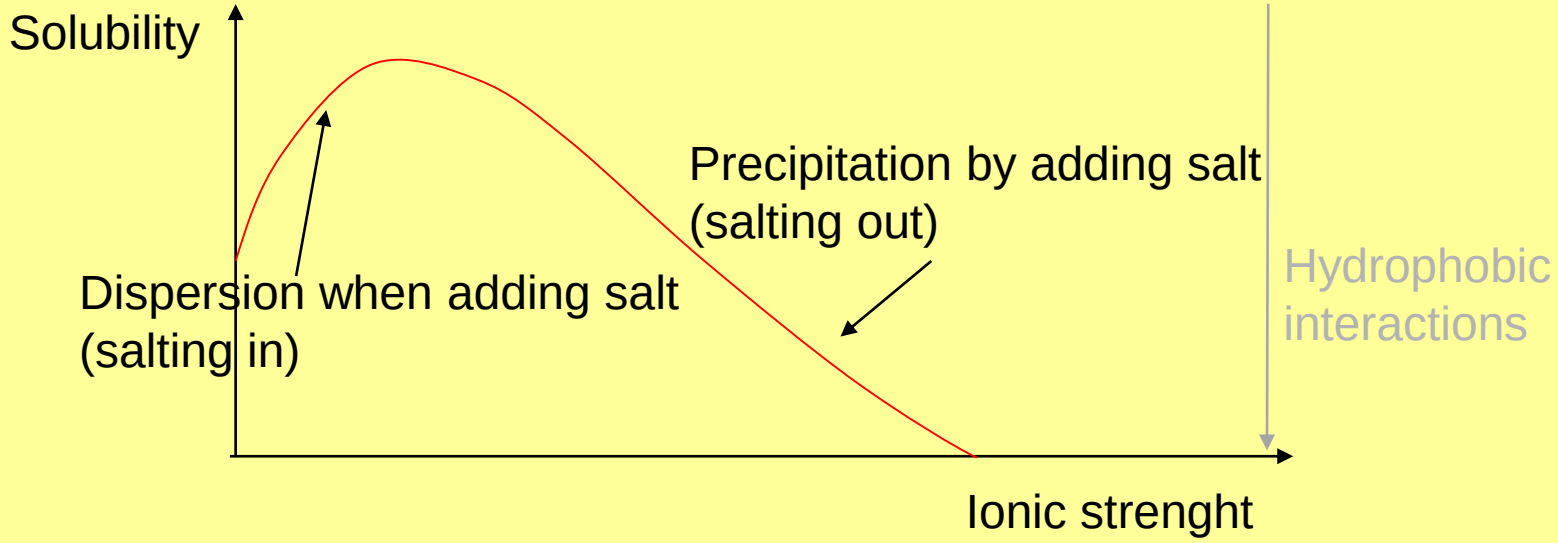
solvent - chosen for the solvatation capacity -hydratation-
,its toxicity, its possible removal…)

Solubility limit ⟶ Salt or protein precipitation
Non miscibility of solvent

To separate solutions, it is possible to change the equilibium data :

- Change the composition by adding a non solvent -> precipitation
- Lower the temperature -> crystallization, precipitation
- Put in contact with a solid -> adsorption
- Permeate through a membrane having a solute/solvent selectivity
- Distillation (difference in volatility)
- Extraction with a non miscible liquid solvant

## Example : Protein precipitation in presence of salt




**Principle of the hydrophobic chromatography**

1- protein immobilisation at high ionic strenght (hydrophobic interaction)

2- protein elution by lowering the concentration of salt (decrease of hydrophobic interaction)

↓

purification of proteins

# 2.1 – States of matter : liquid states / solutions

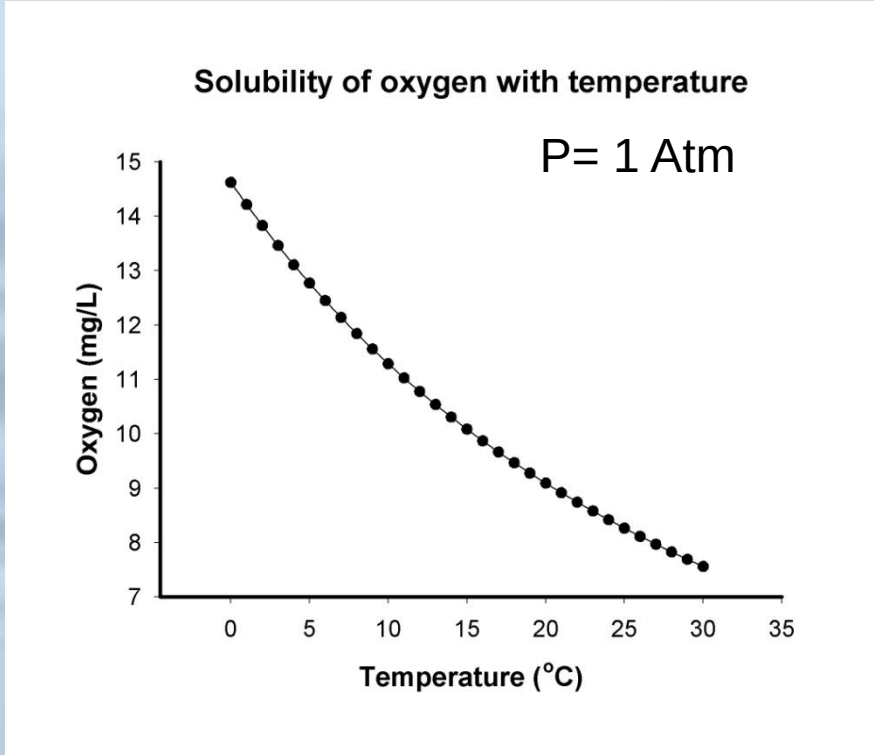
## Solutions of hydrophobic molecules

when the contact solute/water is not favorable (ex : oil , dissolved gaz …)

absorption

- Solubility increases when the temperature decreases

(at the opposite of regular solution – preceding slides)

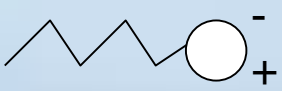


# 2.1 – States of matter : liquid states / solutions

## Solutions of amphiphilic molecules

Molecules having affinities for two incompatible solvant
(ex : water and oil)

→ adsorption at L/L interface : anionic (-), cationic (+) or neutral surfactant,




→ formation of micelles (beyond the c.m.c)
(in order to reduce hydrophobic/water contact)

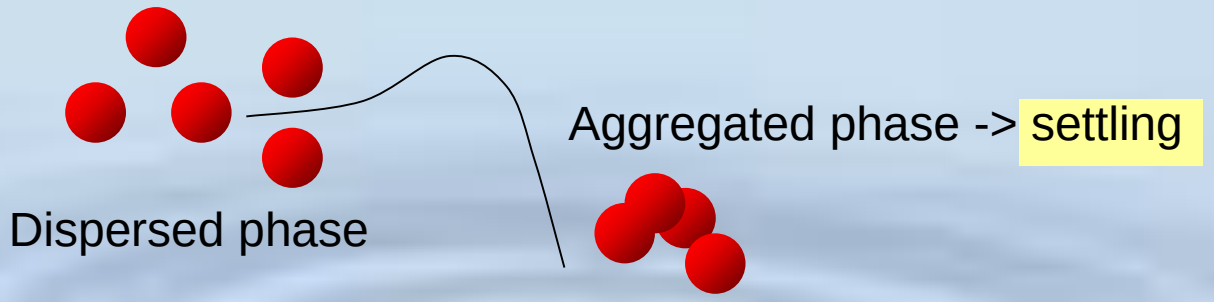
**Applications :**
- detergency
- Emulsion fabrication (to avoid coalescence)
- Dispersion of particles
- flotation (adsorption of surfactant onto hydrophilic particle in order to have hydrophobic particles that can be removed by a stream of buubles))

# 2.1 – States of matter : liquid states / dispersions

## Solid/liquid dispersion (ex : river water…)

- Presence of important interfacial area (more or less hydrated and charged) that control properties : osmotic pressure, swelling, viscosity, aggregation

‘




During water treatment, aggregation is realised by adding a coagulant (as in natural estuary)

- The composition of the dispersion (salt, pH, adsorbed molecule) determine the easiness to aggregate the dispersion

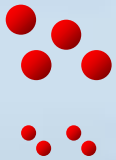
# 2.1 – States of matter : liquid states / emulsions

## Emulsions

Dispersion of small droplets of a liquid in another liquid

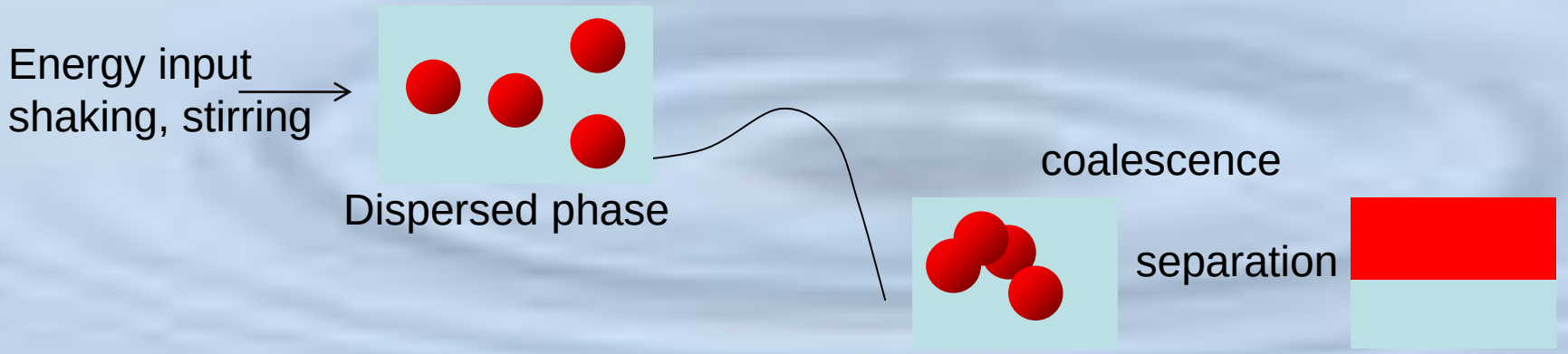
oil in water or water in oil emulsion

→ often with surfactant at the interface



Macroemulsions -> settling or creaming

Miniemulsions -> no settling

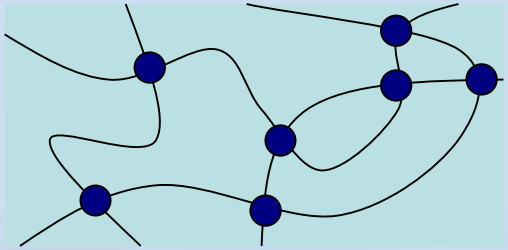



**Applications** : food (milk, vinaigrette …),
Cutting fluid in metal working, cosmetics…

# 2.1 – States of matter : « liquid » states / gels

## Gels

Material constituted of liquid that do not flow in steady state



Cross linked system of macromolecules or particles

Typical properties : swelling, flowing resistance

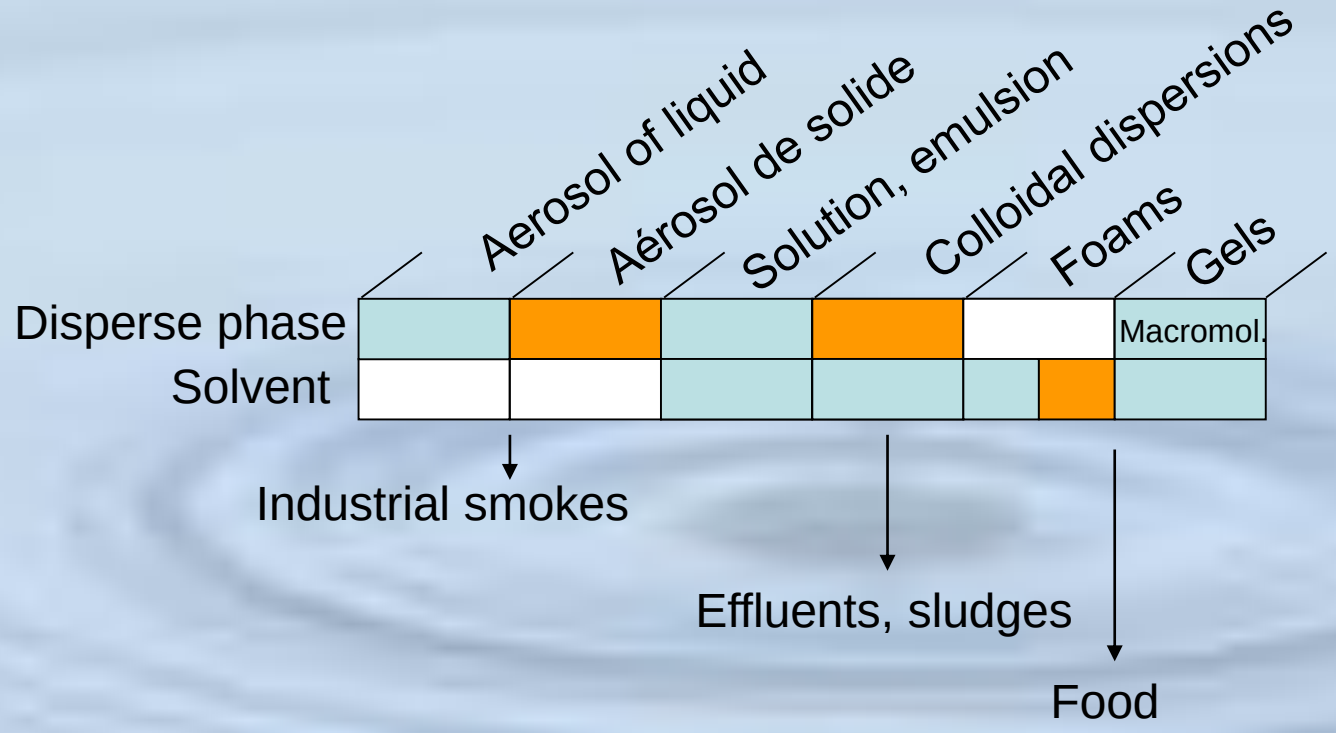
→ difficulties ot extract water — drying, compression

→ possibility to play with the properties of a sludge (pH, …)

**Application** : - sludge in waste water treatment (bacteria +exopolymeric substance)
- membrane fouling

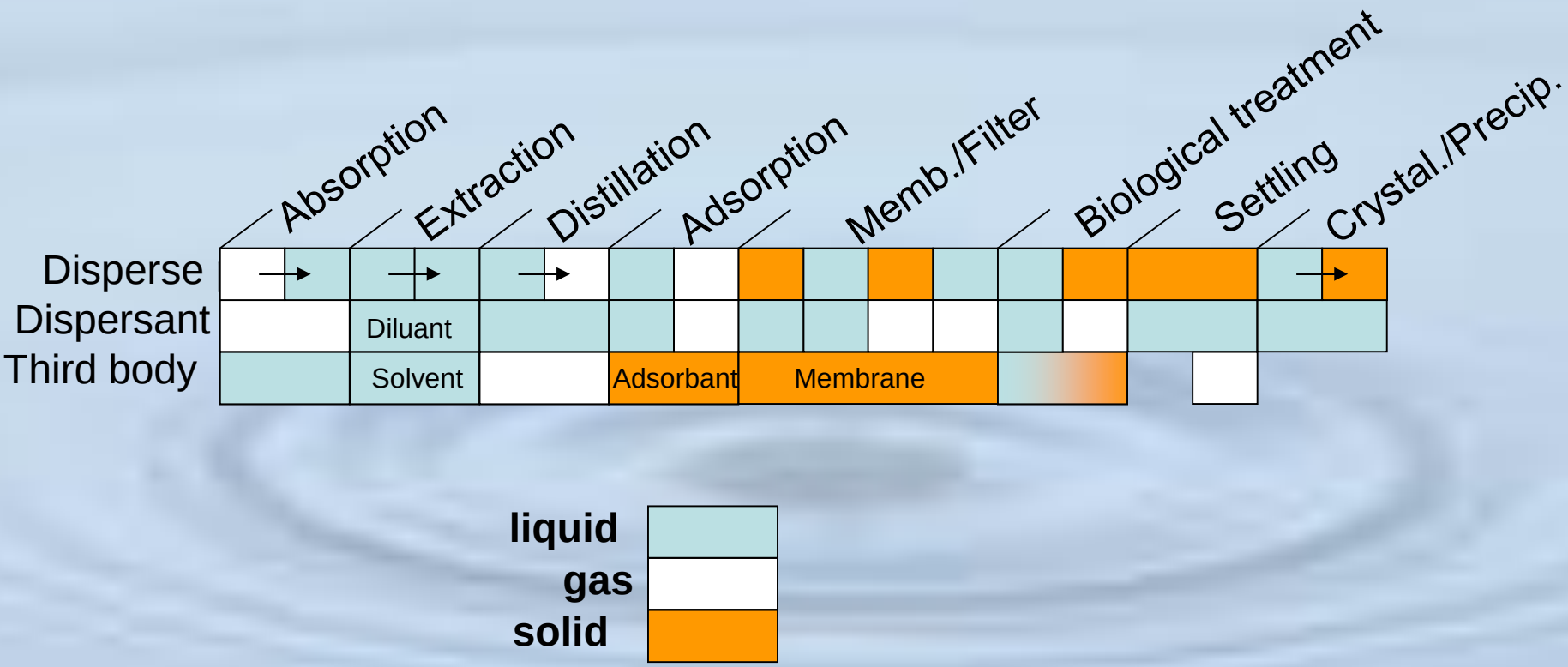
## 2.2 Multiphasic aspects of « real life» process

Often the matter is multiphasic …



# 2.2 Multiphasic aspects of « real life» process

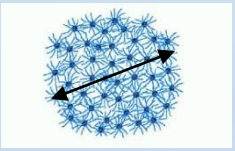
… and the process are also multiphasics



## 2.2. Multiphasic aspects of « real life» process

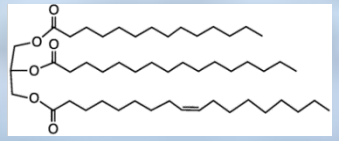
- Example of a complex fluid : the milk

0.1 μm

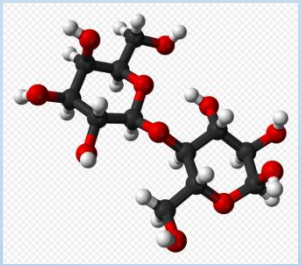


Casein protein micelles: aggregates of several thousand protein molecules, bonded with the help of nanometer-scale particles of calcium phosphate


Fat globules containing butterfat (triglyceride)



surrounded by a membrane made of phospholipids and proteins



342 g/mol

carbohydrate lactose

**Milk = colloids + emulsion + solution**

# 2 - Physico-chemical processus involved in separation

- 2.1 – States of matter
  - The different phase and state of the matter
  - The multiphasic aspect of « real life » fluid

*A fluid to separate …*

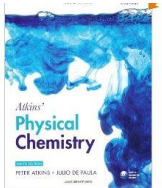
- **2.2 – Potential for separation**
  - **Phase partition**
  - **Difference of size**
  - **Difference of charge**

*… thanks to differences in molecules properties*

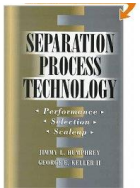
- 2.3 – Transfert in separation processes
  - Transfert at interfaces : the film theory
  - Two film theory

*… and with more or less time*

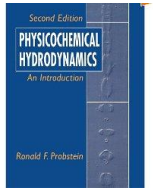
P. Atkins
Physical Chemistry 2009




JL. Humphrey GE. Keller
Sep. Process1997




RF. Probstein
Physico-chemical hydrodynamics 2003



## 2.2 – Potential for separation

### Volatility : partition between a liquid and a vapor phase

| $y_A$ | $y_B$ |
|---|---|
| $x_A$ | $x_B$ |

Volatility of A = $P°_A/P=y_A/x_A$

$\alpha$=relative volatility =$(y_A x_B)/(x_A y_B)$

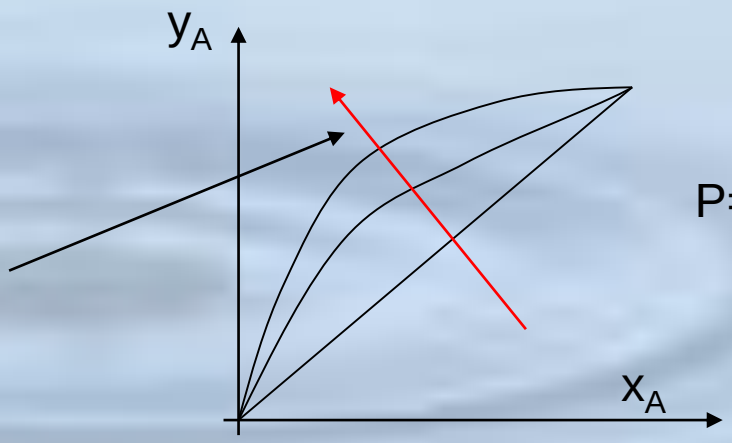
$P_A=y_A P$ Dalton's law

$P_A=x_A P°_A$ Raoult's law (ideal)

↓ Vapour pressure of pure A

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

$\alpha$ ↗ Separation easiness ↗




**Limits**: azeotrope $y_A=x_A$

**Data** : Determination of liquid/vapor **equilibrium** with ebullioscopy

**Application** : distillation, evaporation, drying, pervaporation

## Exercise 1 : Liq/Vap equilibrium

At 373 K, the vapor pressure of n-heptane is 106 kN/m$^2$ and the one of toluene is 73,7 kN/m$^2$
Calculate the different molar fraction in the gas and liquid phase at equilibrium for a total pressure of 101,3 kN/m$^2$

| | |
|---|---|
| $y_A$= | $y_B$ = |
| $x_A$ = | $x_B$ = |

Calculate the relative volatility.

## Exercise 2 : Liq/Vap equilibrium

The vapor pressure of benzene and toluene are given by the following equation

$$\log_{IO} P°(Pa) = (- 0{,}05223\ A / T) + B$$

Where T is the temperature in Kelvin and A et B are constant given below.

| | A (K) | B |
|---|---|---|
| Benzene | 32295 | 9,7795 |
| Toluene | 39198 | 10,45449 |

By considering that the mixture benzene-toluene is ideal, calculate the molar fraction of benzene in :

a) the mixture boiling at 97°C under the normal pressure (101300 Pa)

b) the first condensate obtained

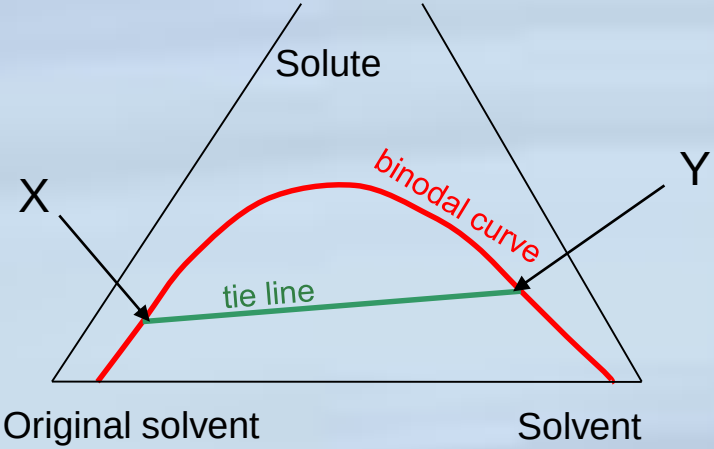
*Additional questions (use a spreadsheet)*

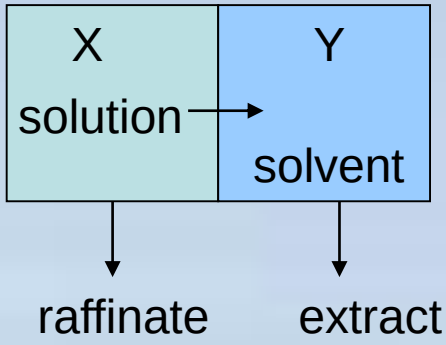
c) Plot the dew point curve and the boiling curve of the mixture at the normal pressure. Determine the boiling temperature of a mixture with a molar fraction of benzene at 0.3 and the vapor composition at equilibrium.

d) Plot the vapor composition as a function of the liquid composition. Compare with the values determined by using the relative volatility.

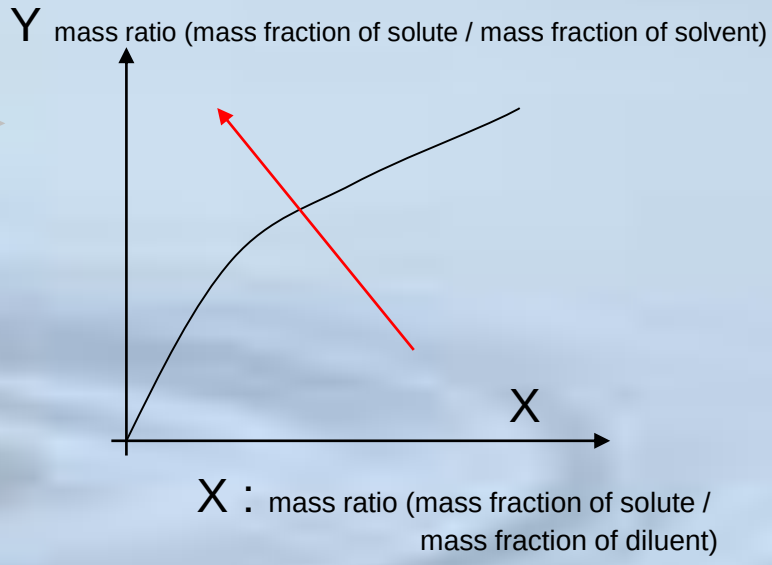
## 2.2 – Potential for separation

### The liquid/liquid partition




If solvent are immiscible




If partition curve is linear

$Y = m X$

Partition coefficient

**Limits**: azeotrope Y=X, solvent miscibility

**Data** : Determination of L/L **equilibrium** with mixer/separator

**Application** : liquid/ liquid or liquid/solid extraction

# Exercise 3 : Liquid/liquid equilibrium

The liquid/liquid equilibrium data water/acetic acid/isopropyl ether (in weight %) is given below.

| Aqueous phase | | | Organic phase | | |
|---|---|---|---|---|---|
| Acid | Water | Ether | Acid | Water | Ether |
| 0,69 | 98,1 | 1,2 | 0,18 | 0,5 | 99,3 |
| 1,41 | 97,1 | 1,5 | 0,37 | 0,7 | 98,9 |
| 2,89 | 95,5 | 1,6 | 0,79 | 0,8 | 98,4 |
| 6,42 | 91,7 | 1,9 | 1,93 | 1 | 97,1 |
| 13,3 | 84,4 | 2,3 | 4,82 | 1,9 | 93,3 |
| 25,5 | 71,1 | 3,4 | 11,4 | 3,9 | 84,7 |
| 36,7 | 58,9 | 4,4 | 21,6 | 6,9 | 71,5 |
| 44,3 | 45,1 | 10,6 | 31,1 | 10,8 | 58,1 |
| 46,4 | 37,1 | 16,5 | 36,2 | 15,1 | 48,7 |

a) Plot the triangular diagram (see spreadsheet)

One realizes 100 g of a mixture water/acid/ether with 29 g in acid and 40 g in ether.

b) How many phases will be observed ?
c) Determine the composition of the phases and their weight.

## 2.2 – Properties differences for separation

### Absorption : liquid/gaz partition

| Y | X |
|---|---|
| Comp A → In the gas | solvant |

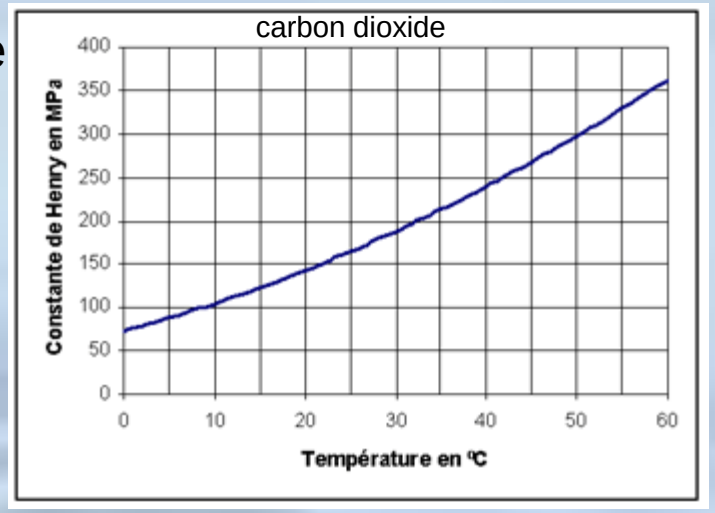
**Equilibrium**

Partial pressure of component A In the gas phase

$x = p_{solute} / He$

Molar fraction of dissolved gaz in the liquid

Henry's constant

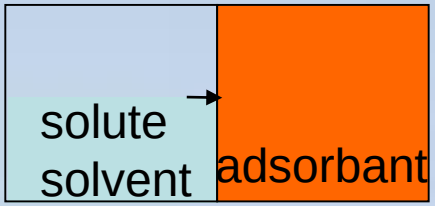


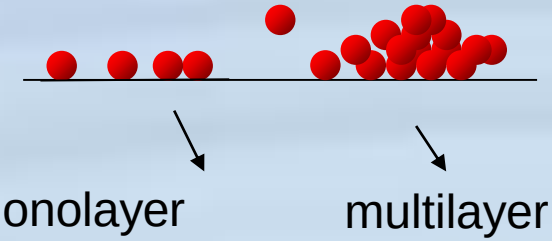

**Application :** absorption and chemical absorption

**Data** : Determination of **equilibrium** (gas -CPG, IR-, liquide –dosage-)

## 2.2 – Properties differences for separation

### Adsorption : affinity with a solid phase



monolayer multilayer

Physisorption when weak interactions (ex : Van der Waals)

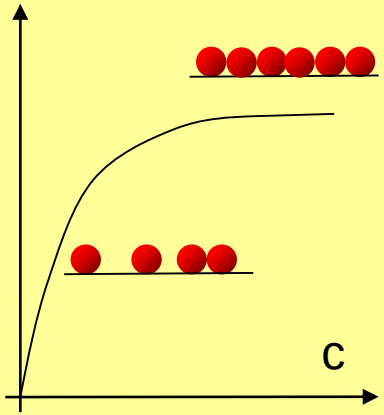
Chimisorption when chemical bonding

Langmuir isotherm for monolayer adsorption

$$Q = \frac{Kc(\text{ou } p)}{Kc(\text{ou } p)+1}$$

Fractional coverage of the surface

Adsorption constant $=K_{ads}/K_{des}$




Selectivity $\alpha_{AB} = \frac{K_A}{K_B}$

(idem than relative volatility)

**Application :**

adsorption and desorption

- By temperature increase $\alpha_{AB} > 5$
- By conc.(or pressure) decrease $\alpha_{AB} > 2$

**Limits :**

complexity – sequential operation - fouling

**Data** : Determination of **equilibrium** (mass balance)

## Exercise 4 : Adsorption (solid/fluid equilibrium)

Aqueous solution with 0.09 kg of phenol per $m^3$ has to be treated by adsorption of phenol on activated carbon. This treatment is realized in a tank by batch of 4 $m^3$ with 100 g of activated carbon.

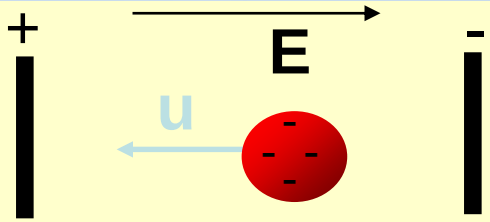
a) What is the phenol concentration in the water when equilibrium is reached ?

*Data :*
Adsorption isotherm of phenol
$m = C/(5.13\ 10^{-3}\ C + 4.06\ 10^{-2})$
with m in kg of adsorbed phenol / kg of activated carbon,
and C in kg of phenol per $m^3$ of solution.

## 2.2 – Properties differences for separation

### The charge

Electrophoretic transport



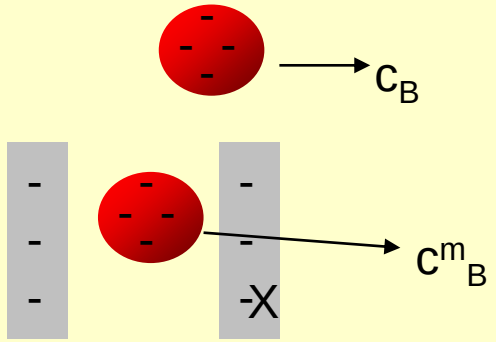

**u : electrophoretic velocity**

**u/E : electrophoretic mobility**

Force balance $u = \dfrac{qE}{6\pi\mu a}$

Partition in a charged porous material

B : co-ion
A : counter-ion
X : membrane




**Donnan exclusion**

based on electroneutrality

Partition (or distribution) coefficient

$$\frac{c_B^m}{c_B} = \left( \frac{|z_B| c_B}{|z_B| c_B^m + |z_X| c_X^m} \right)^{|z_B| / |z_A|}$$

**Process applications :**

Electroseparation (electrophoresis electrodialysis …)

**Analytic applications :** electrophoresis

**Applications :**

Electrostatic retention in membrane (RO, NF, ED), Ion exchange, Chromatography

## Exercise 5 : Donnan equilibrium in a membrane

A negatively charged membrane having a concentration of charge of 10 mol/L ($Z_X$=1) is used to retain salt. The concentration in co-ions in the solution is 1 mol/L.

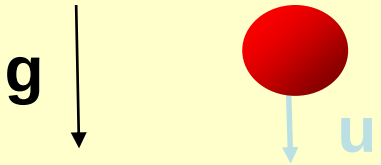
a) Calculate the partition coefficient for $MgCl_2$, $Na_2SO_4$ and NaCl.

b) Sort these electrolytes from the more excluded to the less excluded by the membrane.

## 2.2 – Properties differences for separation

### The size

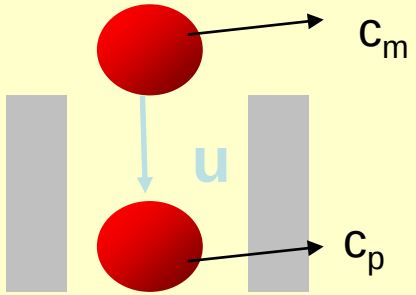
Settling velocity




Force balance

$$u_{\lim} = \frac{2R^2(\rho_s - \rho_l)g}{9\mu}$$ if Re < 1

Transfert through a porous media




Steric retention

Ferry law

$$\frac{c_p}{c_m} = 1-(1-(1-\lambda)^2)^2 \qquad \lambda = \frac{r_s}{r_p}$$

**Applications :**

Gravitational separation : settling, centrifugation

**Applications :**

Filtration (MF, UF, NF …)
Sieving, Size Exclusion chromatography

# Demonstration of Ferry law

## Solvent transport

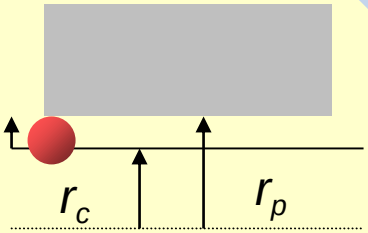
$$Q_s = 2\pi \int_0^{r_p} u_0 (1-(\frac{r}{r_p})^2) r dr = \pi u_0 \frac{r_p^2}{2}$$

## Solvent flow carrying particle

$$Q_p = 2\pi \int_0^{r_c} u_0 (1-(\frac{r}{r_p})^2) r dr$$

$$= \pi u_0 \frac{r_p^2}{2} (2(1-\lambda)^2 - (1-\lambda)^4)$$

Solute radius $r_s$




Carrier radius $r_c = r_p - r_s$

Pore radius

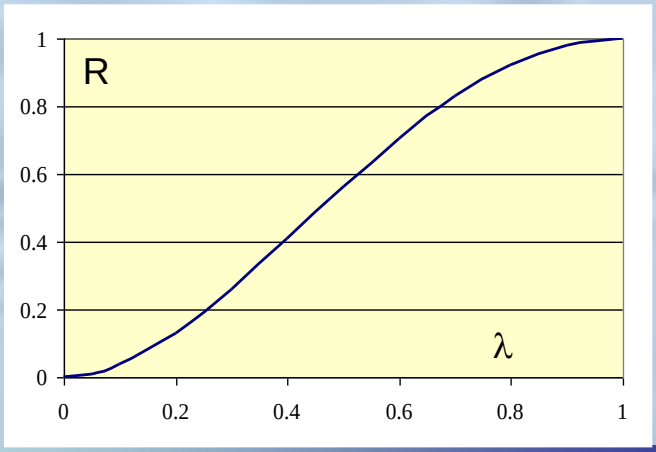
$$\lambda = \frac{r_s}{r_p}$$

$$u = u_0 (1-(\frac{r}{r_p})^2)$$

Solute balance $Q_p c_m = Q_s c_p$

$$c_p = c_m (2(1-\lambda)^2 - (1-\lambda)^4)$$

$$R = 1 - \frac{c_p}{c_m} = (1-(1-\lambda)^2)^2 \qquad \text{(Ferry law)}$$



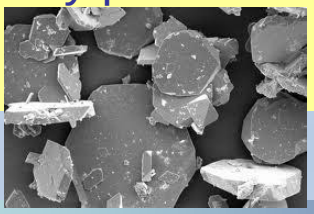
## Exercise 6 : Settling

Clay particles have a density of 1300 kg/m$^3$.

Calculate the sedimentation velocities of clay particles* having a radius of 10nm, 100 nm, 1 μm and 10 μm in water at 20°C.

One want to eliminate by settling these particles from an effluent having a flow rate of 100 m$^3$/h. Estimate the volume of the settling tank (and its radius) needed to settle these particles on a distance of 2 meters.

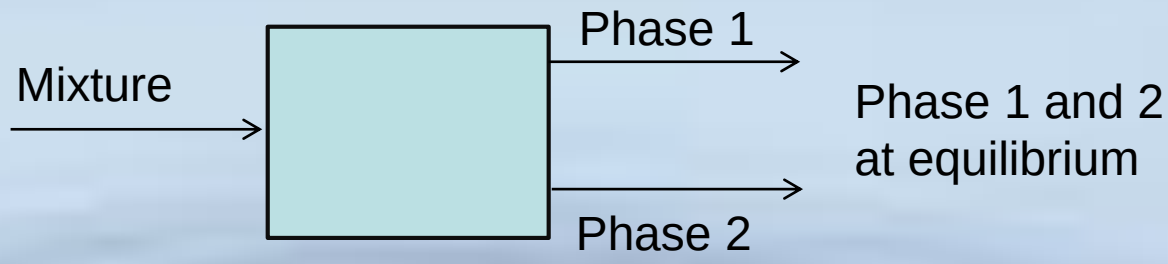
* we will consider in a first approximation that clay platelets are spheres !



## 2.2 – Properties differences for separation

### The concept of theoretical plate (equilibrium stage, ideal stage or a theoretical tray)

An hypothetical zone or stage in which two phases establish an equilibrium with each other.




The performance of separation processes depends on having a series of equilibrium stages and is enhanced by providing more such stages -> having more theoretical plates increases the efficacity of the separation process

**Applications** : distillation, absorption, extraction , chromatographic, adsorption ...

**Chemical engineering concept 1 (based on Thermodynamics)**

# 2 - Physico-chemical processus involved in separation

- 2.1 – States of matter
  - The different phase and state of the matter
  - The multiphasic aspect of « real life » fluid

*A fluid to separate …*

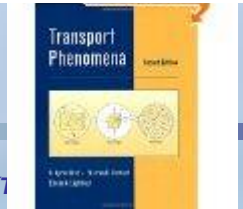
- 2.2 – Potential for separation
  - Difference of volatility
  - Difference of affinity
  - Difference of size
  - Difference of charge

*… thanks to differences in molecules properties*

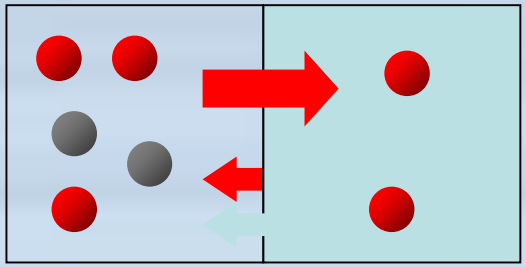
- **2.3 – Transfert in separation processes**
  - **Transfert at interfaces : the film theory**
  - **Two film theory**

*… and with more or less time*

R. Byron Bird, Warren E. Stewart et Edwin N. Lightfoot
Transport phenomena 2007



## 2.3 – Separation : a transfert away the equilibrium by avoiding the mixing



**separation = transfer - mixing**

transfer % : Driving force, Potential difference (gap to the equilibrium), Interfacial area

transfer ↗ hydrodynamic ↗

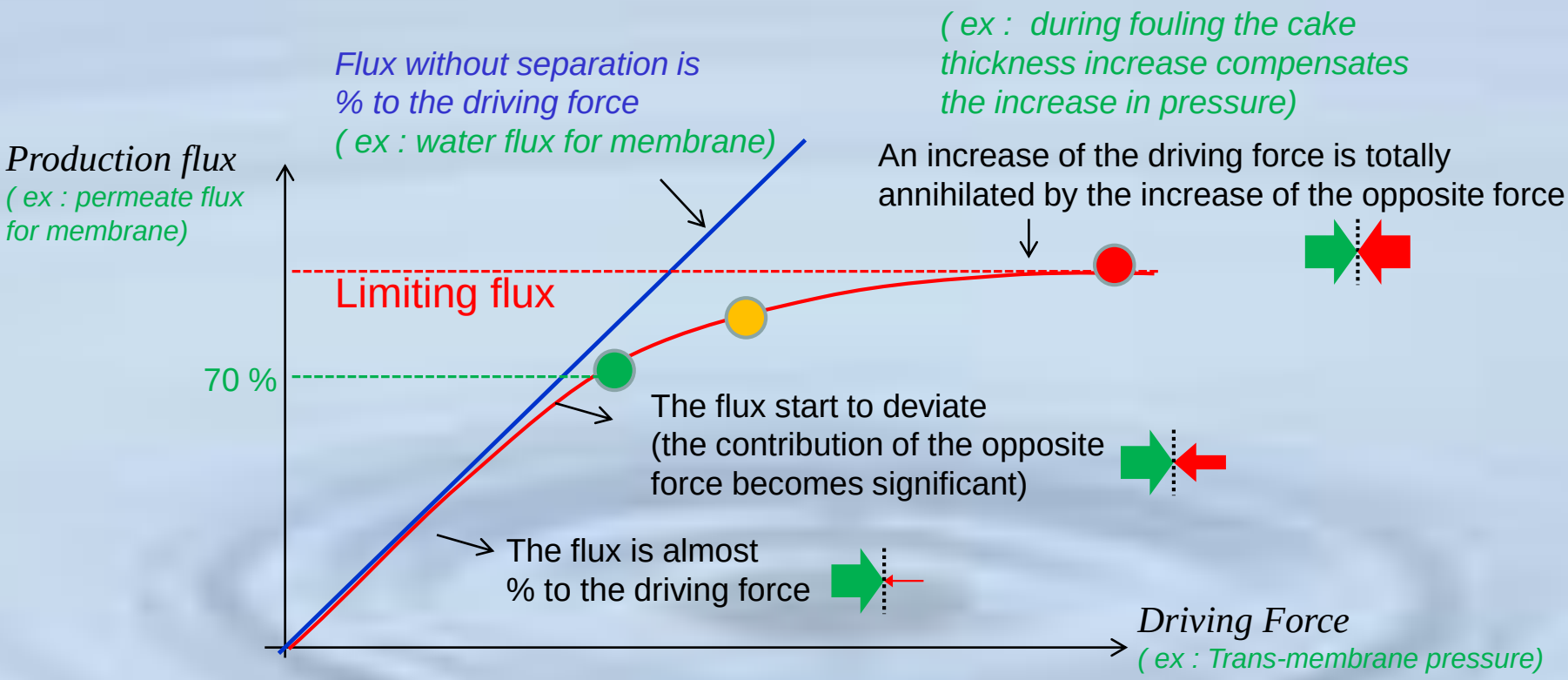
mixing % : Opposite force (back to equilibrium)

mixing ↗ hydrodynamic ↗

**A compromise :**

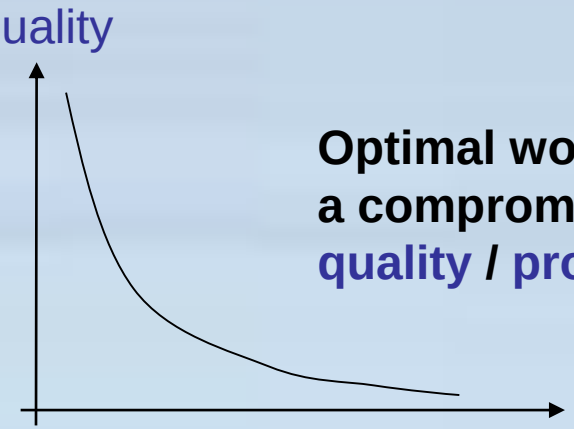
- -Between the driving force and the opposite force
- -Between quantity and quality of separation
- -For the hydrodynamic choice

# Separation : a compromise between driving and opposite forces




A **sustainable way to operate** is to work at 70 % of the limiting flux
(above a significant part of the energy is used to fight against the opposite force)

# Separation : a compromise between quantity and quality




**Optimal working point : a compromise between quality / productivity**

For a given process :

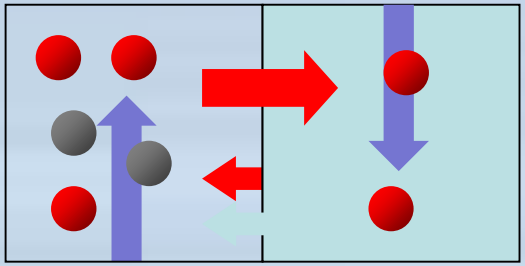
- increasing the productivity (flow rate of production)
- decreases the residence time in the process and then the “time used to reach the equilibrium”

-> leads to a lower quality of the separation (difference of concentration in the separated streams)

**Example** : the increase of the reflux ratio in distillation (lower productivity) increases the quality of the distillate

**Counterexample** : There is some exception for process where the advection (flow rate) allows to overcome the diffusion process (reverse osmosis)
-> productivity and selectivity increase simultaneously

# Separation : a compromise for the choice of the hydrodynamic



Increasing the hydrodynamic increases the mass transfer

↓ Energy losses

↓ Productivity increase

Energy balance to find the sustainable operating conditions

Furthermore, a process can not accept too high hydrodynamic conditions

Exemples 1 : - Maximum pressure drop in reverse osmosis (-> mechanical damages and heterogeneous permeate flux distribution along the membrane)

# A compromise for the choice of the hydrodynamic

## Below the flooding point

## Above the flooding point

| | Below the flooding point | Above the flooding point |
|---|---|---|
| Flows : | well distributed | plug flow |
| Pressure drop : | + | + + + (with fluctuations) |
| Interfacial area : | ++ | - - |
| Mass transfer : | + | ++ |

A rule is to work at 70 % of the critical flow blockage
(to have good mass transfer conditions and good interfacial area)

## Prerequisite : The diffusion …

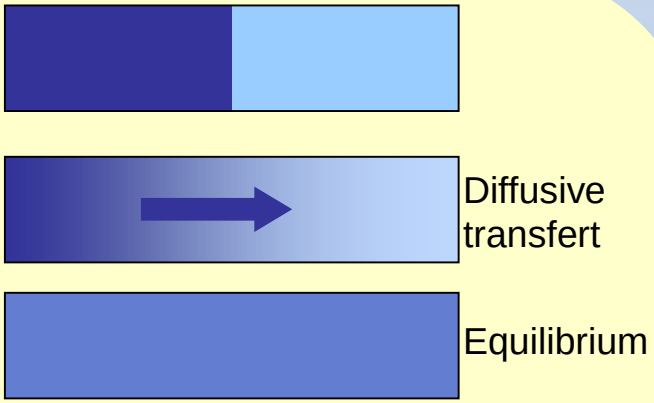
Mass transfert from concentrated to diluted zones :

**A mission** : back to equilibrium
**A way** : the Brownien motion

Diffusion coefficient $m^2/s$

Fick's law: $N = -D \frac{dc}{dx}$

Mass flux density



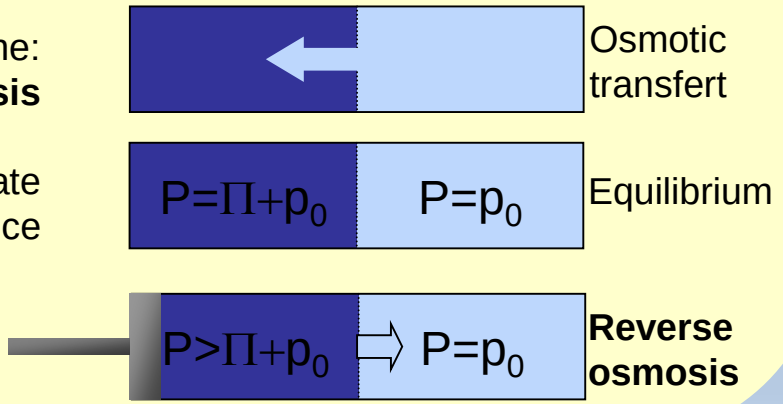

## … and osmotic pressure

Transfert of the solvent toward concentrated zone: **osmosis**

At equilibrium: an osmotic pressure compensate the concentration difference

If a presssure > $\Pi$ Is applied

Semi-permeable membrane :
Solvent permeable
But non permeable for a solute

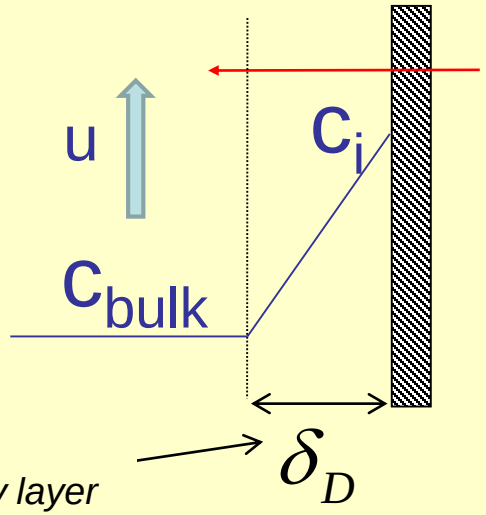


## Prerequisite : Transfer at an interface…

Mass transfert coefficient, k in m/s

$$N = k(c_i - c_b)$$

The potential difference




### The film theory

$$k = \frac{D}{\delta_D}$$

*Mass boundary layer*

*Estimated with adimensionnal correlation Sh=f(Re,Sc)*

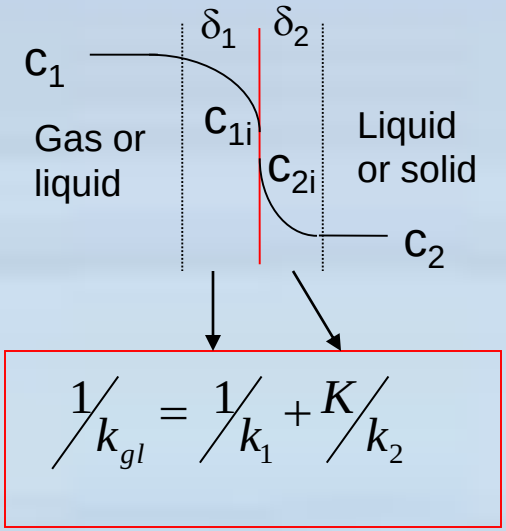
u ↗ $\delta_D$ ↘ k ↗

**Chemical engineering concept 2 (based on transport phenomena)**

# Two film theory

$$N = \frac{c_1 - c_{1i}}{1/k_1} = \frac{c_{2i} - c_2}{1/k_2} = \frac{Kc_{2i} - Kc_2}{K/k_2}$$

$$N = \frac{c_1 - Kc_2}{1/k_1 + K/k_2} = k_{gl}(c_1 - Kc_2)$$




$$\frac{1}{k_{gl}} = \frac{1}{k_1} + \frac{K}{k_2}$$

Interface equilibrium $c_{1i} = Kc_{2i}$

Partition coefficient

## Extreme cases for gas/liquid absorption

- If K is high (low solubility of the gas in the liquid $O_2/H_2O$)

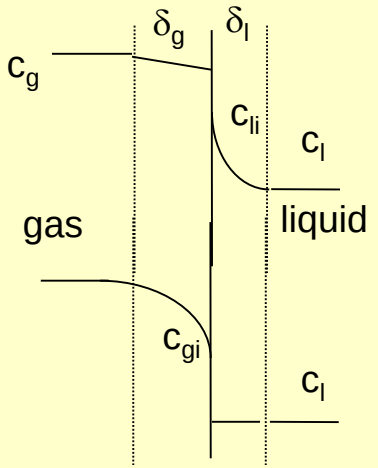
$$\frac{1}{k_{gl}} \approx \frac{K}{k_l} \qquad N \approx k_l(c_{li} - c_l)$$

resistance localised in the liquid film

- If K is low (high solubility of the gaz in the liquid $NH_3/H_2O$)

$$\frac{1}{k_{gl}} \approx \frac{1}{k_g} \qquad N \approx k_g(c_g - c_{gi})$$

resistance localised in the gas film



## Exercise 7 : Gas/liquid transfer (two film theory)

a) Calculate the mass flux density of oxygen through a gas/liquid interface. The partial pressure of dioxygen is 0.2 atm in the gas phase and the concentration in the liquid is zero.
b) In which phase is located the transfer resistance ?
c) Give the concentration in the gas and the liquid at the interface.
d) What will be the concentration in water when the equilibrium will be reached ?
e) Plot the concentration profile.

Data :
$D_{O2}$ = 0.219 $cm^2/s$ in the air
$D_{O2}$ = 0.0000197 $cm^2/s$ in the water
The mass boundary layer thicknesses are $10^{-5}$ m in the two phases

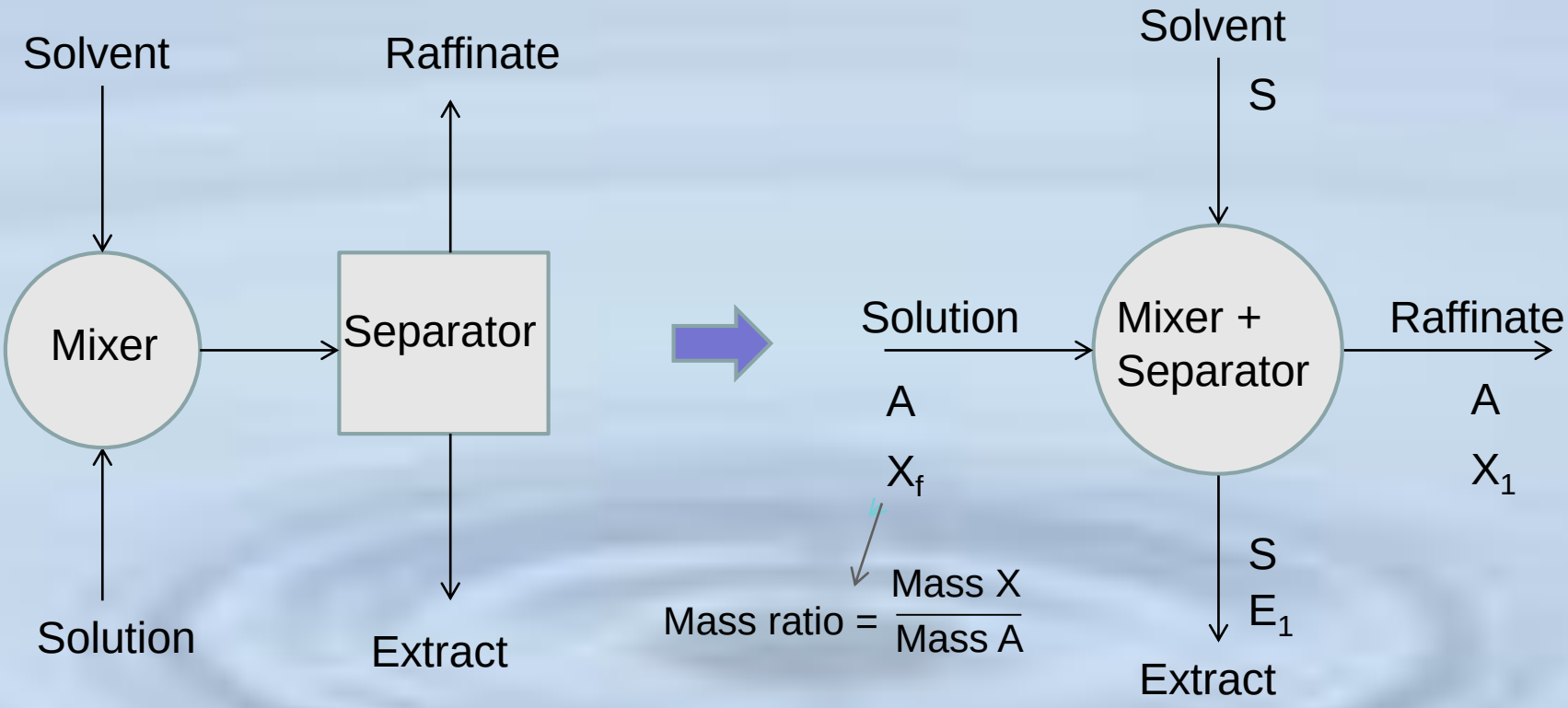
Table 1: Some forms of Henry's law and constants (gases in water at 298.15 K), derived from [4]

| equation: | $k_{H,pc} = \frac{p}{c}$ | $k_{H,cp} = \frac{c}{p}$ | $k_{H,px} = \frac{p}{x}$ | $k_{H,cc} = \frac{c_{aq}}{c_{gas}}$ |
|---|---|---|---|---|
| units: | $\frac{L \cdot atm}{mol}$ | $\frac{mol}{L \cdot atm}$ | atm | *dimensionless* |
| $O_2$ | 769.23 | $1.3 \times 10^{-3}$ | $4.259 \times 10^{4}$ | $3.181 \times 10^{-2}$ |

# 3 – The engineering of the separation process

- 3.1 – The theoretical plate : one stage
  - Equilibrium and material balance on a stage
  - Material balance and operating line : graphical method
- 3.2 – Multi-stage processes
  - Cross-current
  - Co-current
  - Counter-current : the use of an operating line
  - Graphical methods
- 3.3 – Efficiency of a separation process

# 3.1 A theoretical plate

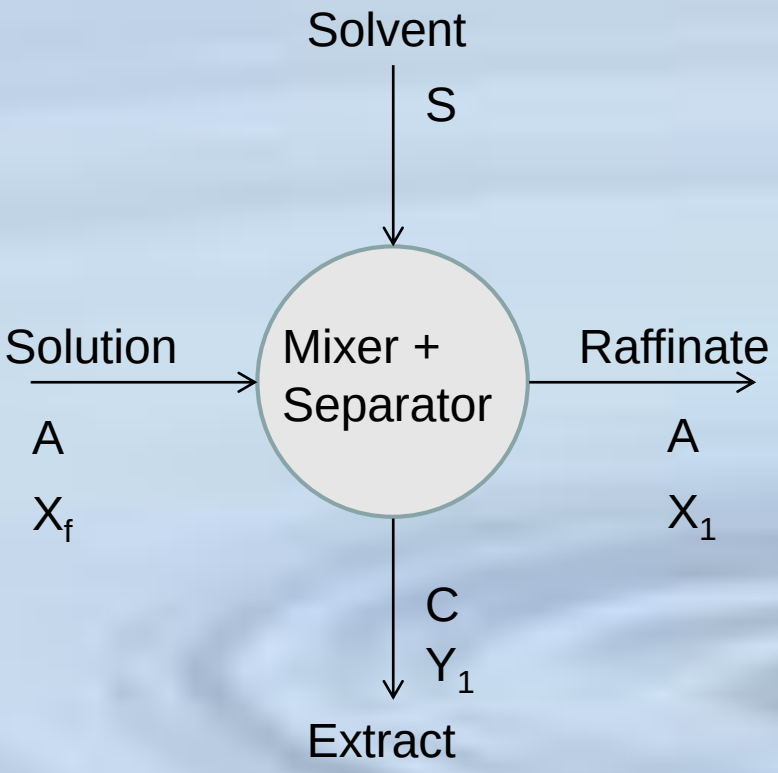



If <u>solvents are immiscible</u> :

A in kg or kg/s of diluent (original solvent) in solution and raffinate

and S in kg or kg/s of solvent in solvent and extract

# 3.1 A theoretical plate




The equilibrium equation

$$Y_1 = K\ X_1$$

(If the equilibrium curve is a straight line)

+

The material balance equation

$$A\,X_f = A\,X_1 + S\,Y_1$$

=

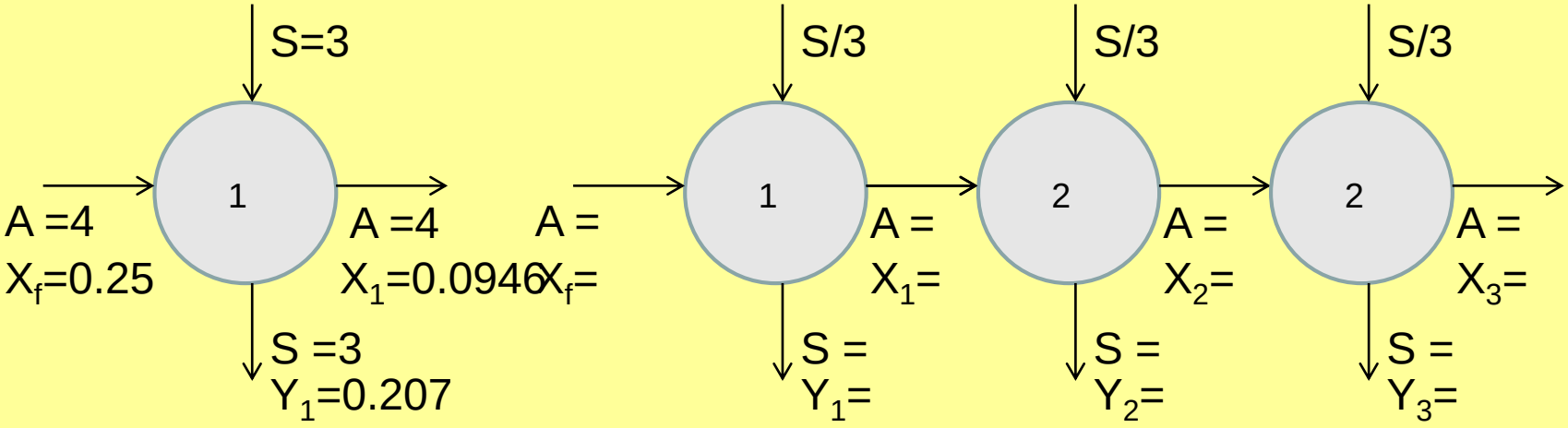
$$X_1 = \left[\frac{A}{A + KS}\right] X_f$$

## Exercise 8 : Liquid/liquid extraction with multi-stage cross-current process

One mix a solution of 4 kg of isopropyl ether and 1 kg of acetic acid with 3 kg of water (equilibrium data seen in exercise 3)
Calculate the composition and the mass of the extract and of the raffinate

a) by considering that solvent are partially miscible with the triangular diagram
b) by considering that solvent are immiscible and a linear distribution law

c) By using the assumptions of immiscible solvent and linear distribution law, complete the following flowsheet. Comment the results by calculating the efficiency of the extraction.



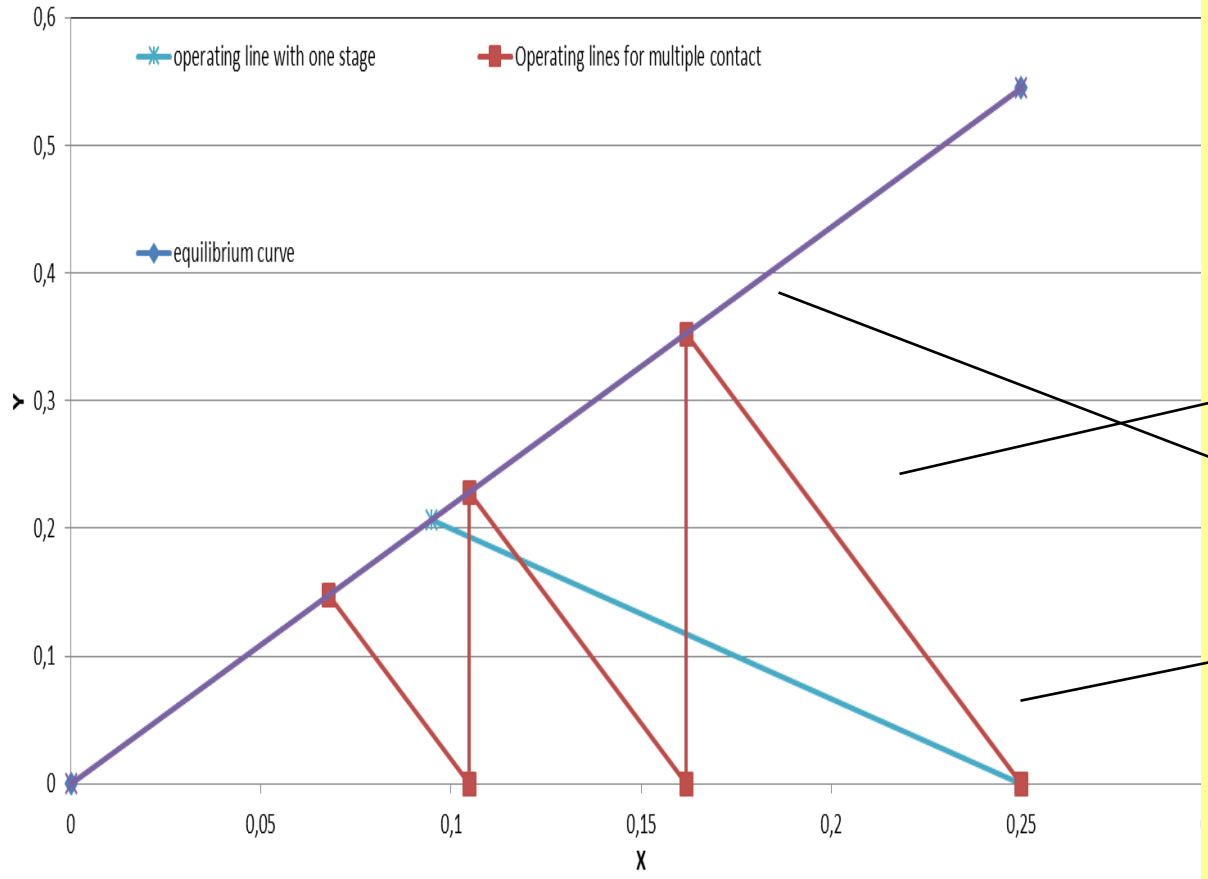
## Exercise 8 : Liquid/liquid extraction with multi-stage cross-current process

d) Demonstrate that for n cross-current stages, one can write :

$$n = \frac{\ln\left(\frac{X_n}{X_f}\right)}{\ln\left(\frac{A}{A+SK}\right)}$$

Additionnal question : redo the calculation of c) without the assumptions i.e. by using the triangular diagram.

# 3.2. Operating line and equilibrium curve (graphical method)




The material balance equation

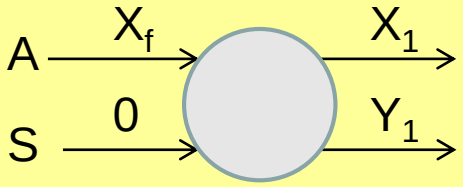
$$A\,X_f = A\,X_1 + S\,Y_1$$

$$\frac{Y_1}{X_1 - X_f} = -\frac{A}{S}$$

slope

Operating line

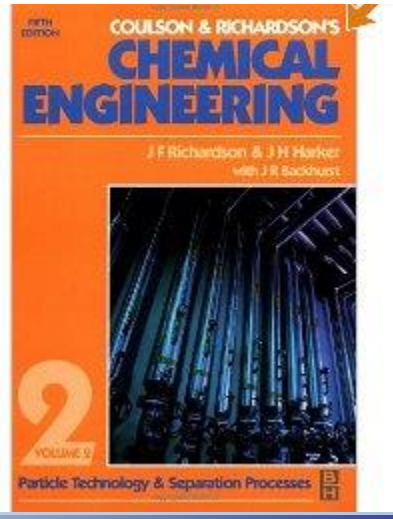
| $X=X_f$ | $X=X_1$ |
|---|---|
| $Y=0$ | $Y=Y_1$ |



# 3 – The engineering of the separation process

- 3.1 – The theoretical plate : one stage
  - Equilibrium and material balance on a stage
  - Material balance and operating line : graphical method
- **3.2 – Multi-stage processes**
  - **Cross-current**
  - **Co-current**
  - **Counter-current**
  - **Graphical method of Mac Cabe and Thiele**
- 3.3 – NUT and HUT
- 3.3 – Efficiency of a separation process
  - Generic case
  - Application to membrane processes

Coulson & Richardsons Chemical Engineering : Particle technology and separation processes 2002



## Interest for multistage processes

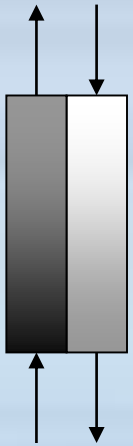
- Why multiple contact leads to more important yield ?

When the separation is more difficult (at the end) the raffinate is in contact with fresh solvent

(or it is better to leave the difficulty of the separation to a few number of plate)

# *multistage and counter-current processes : a simple way to optimize the separation*

**Optimise the transfer between phases**

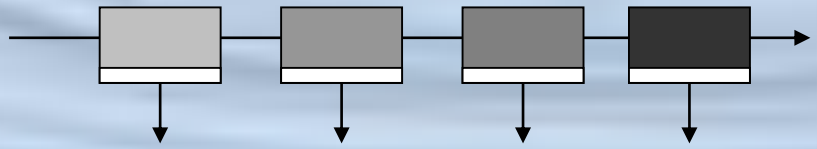


Counter-current processes

(the more difficult separation is realised with the better conditions)

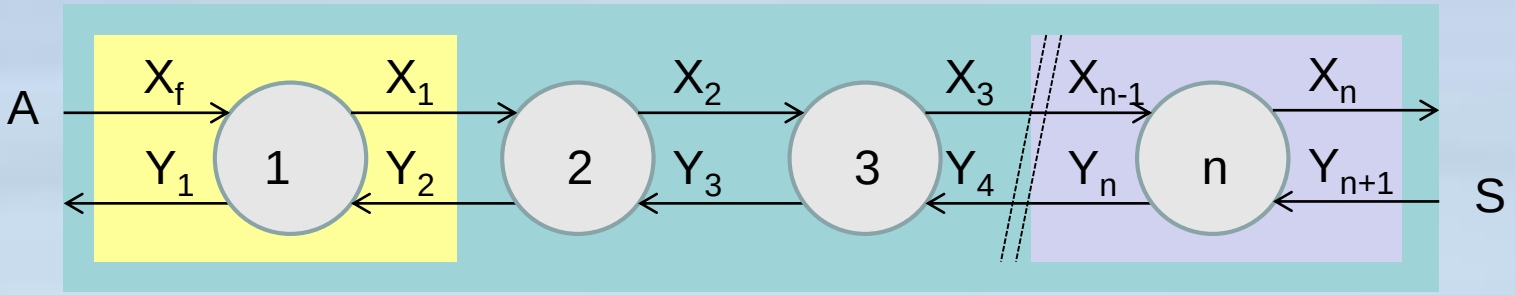
Multistage processes

(the unfavorable conditions are reserved to a smaller part of the process)



**Chemical engineering concept 3** **(based on transfert optimisation)**

# Mass balance in counter-current operation




material balance for 1st stage

$$A\,X_f + S\,Y_2 = A\,X_1 + S\,Y_1$$

material balance for nth stage

$$A\,X_{n-1} + S\,Y_{n+1} = A\,X_n + S\,Y_n$$

material balance for the whole unit

$$A\,X_f + S\,Y_{n+1} = A\,X_n + S\,Y_1$$

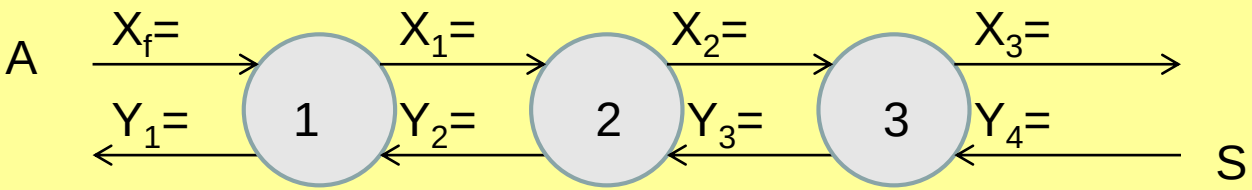
$$Y_{n+1} = \frac{A}{S}\left(X_n - X_f\right) + Y_1$$

Operating line (slope A/S) passing through the points :

| | |
|---|---|
| $X=X_f$ | $X=X_n$ |
| $Y=Y_1$ | $Y=Y_{n+1}$ |

# Exercise 8 : Liquid/liquid extraction with multi-stage cross-current process

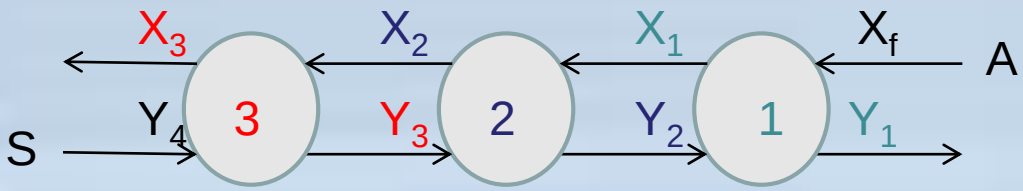
d) Calculate the working points of a counter-current operation with three theoretical plate. Fill the following flowsheet. Calculate the extraction yield. Compare with the result obtained with the abac (slide 58).

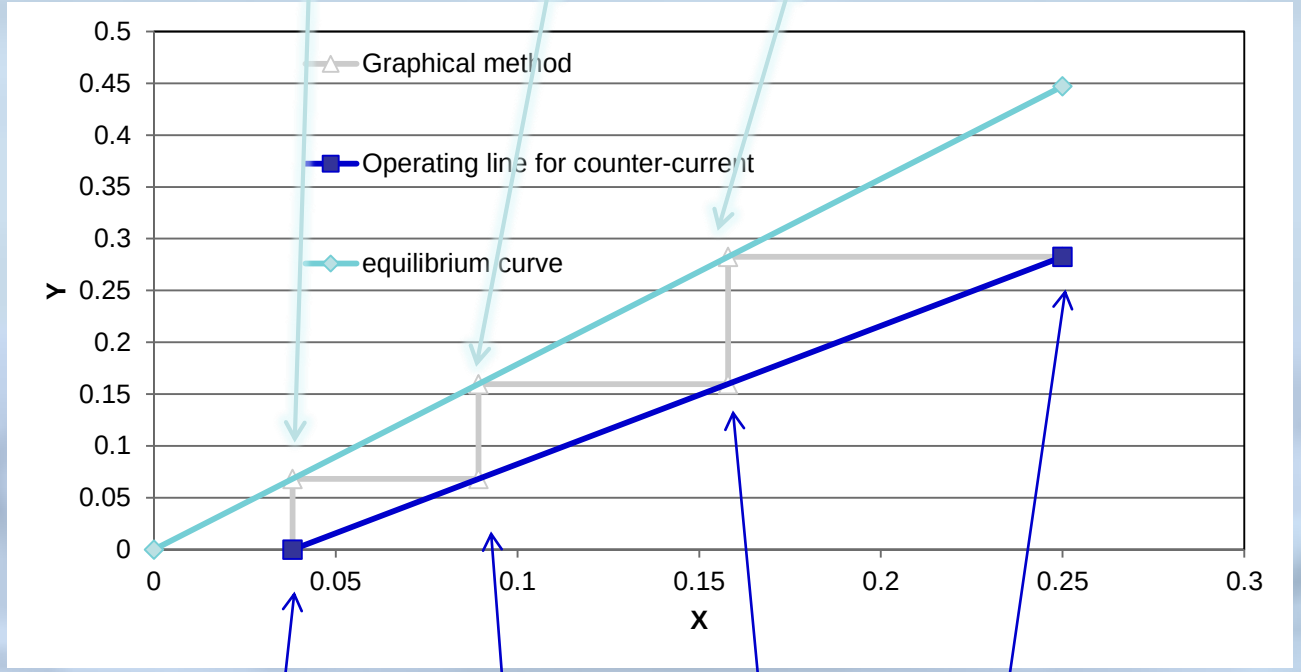



e) Compare the different working mode (one stage, cross-current, co-current, counter current)

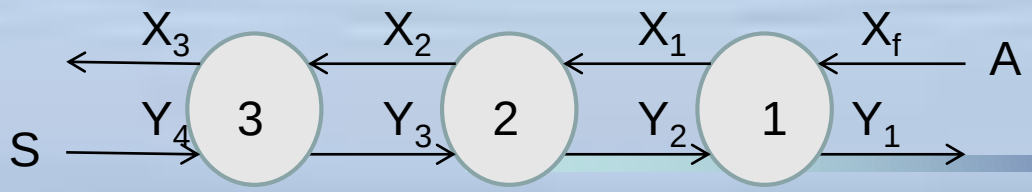
# Graphical methods (Mac Cabe and Thiele)

Equilibrium of the theoretical plate (between plate outlet)




Material balance (between the flow crossing)

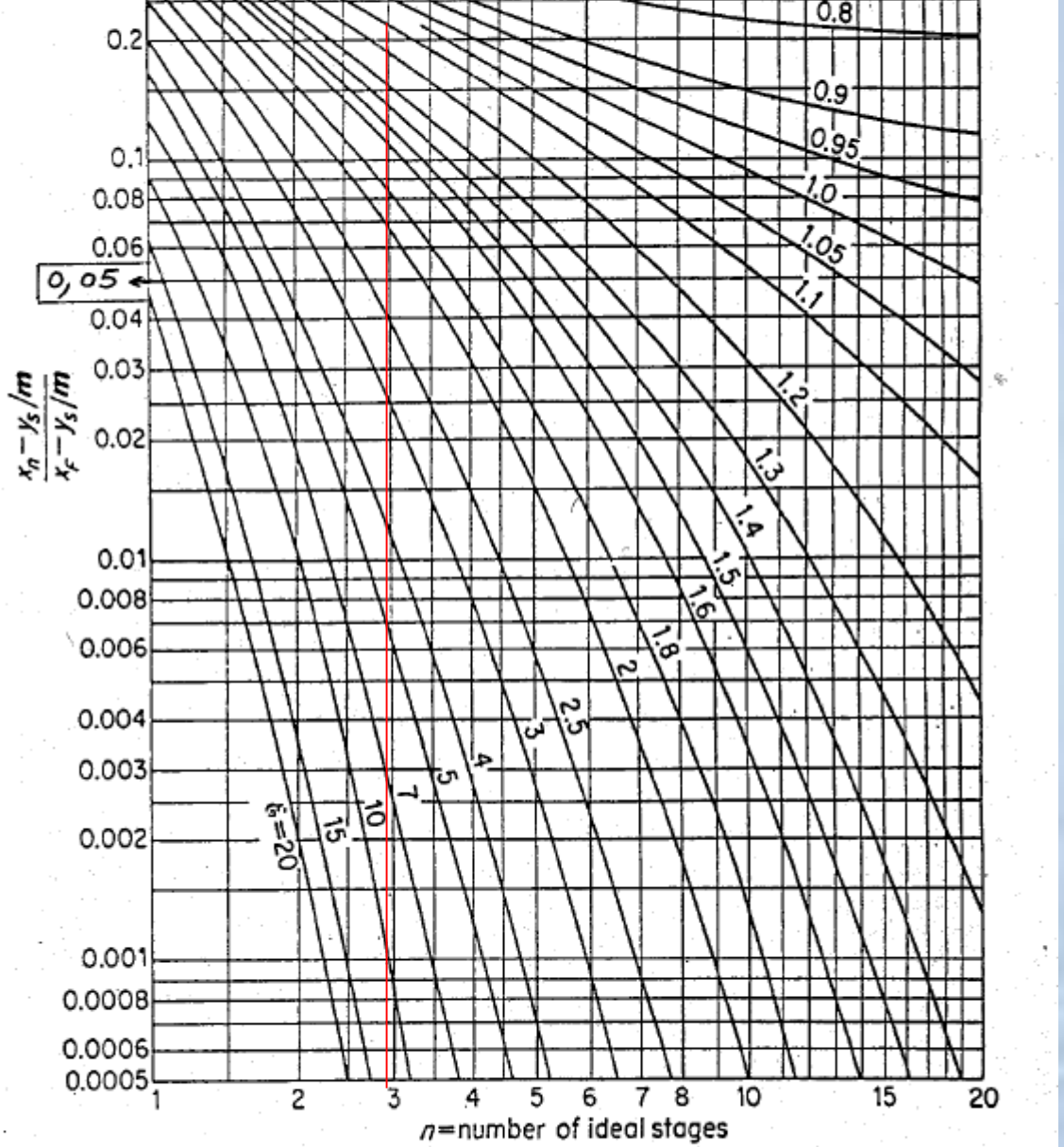


# Abac

$\varepsilon = m.S/A$

↓

Partition ratio




* Countercurrent multistage extraction with immiscible solvents and constant distribution coefficient.

with $\varepsilon = m \times \frac{S}{A}$

# 3 – The engineering of the separation process

- 3.1 – The theoretical plate : one stage
  - Equilibrium and material balance on a stage
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- 3.2 – Multi-stage processes
  - Cross-current
  - Co-current
  - Counter-current
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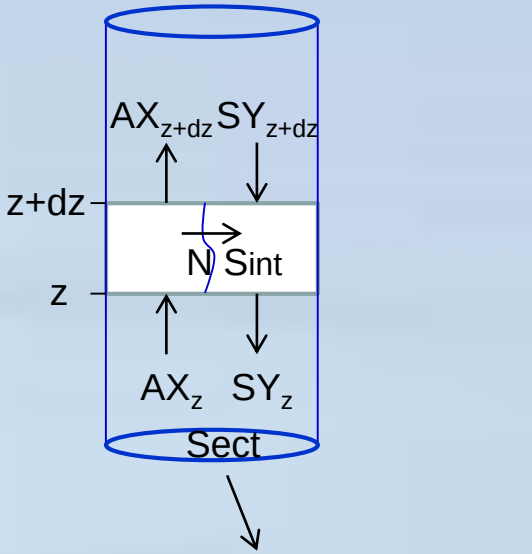
- **3.3 – NUT and HUT**
- 3.3 – Efficiency of a separation process
  - Generic case
  - Application to membrane processes

# Transfer unit : height and number

Differential mass balance

$$-SdY = -AdX = N\,a\,Sect\,dz$$

Sint
Interfacial area




$$N = k_x\left(X - X_e\right) \qquad N = k_y\left(Y_e - Y\right)$$

$$Z = \frac{A}{a\,Sect\,k_x}\int_{X_0}^{X_z}\frac{dX}{X_e - X} \qquad Z = \frac{A}{a\,Sect\,k_y}\int_{Y_0}^{Y_Z}\frac{dY}{Y - Y_e}$$

$Z = H_x \quad N_x$ $\qquad$ $Z = H_Y \quad N_Y$

Height of the raffinate film transfer unit

Number of raffinate film transfert units

# Log mean driving force

For a constant partition coefficient, one can demonstrate

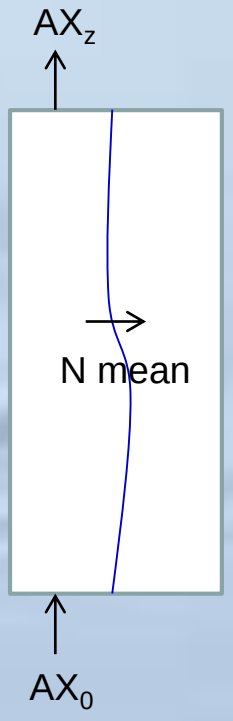
$$N_X = \int_{X_0}^{X_z} \frac{dX}{X_e - X} = \frac{\varepsilon}{\varepsilon - 1} \ln\left(\frac{X_0 - X_0^e}{X_z - X_z^e}\right)$$

$$= \frac{X_0 - X_z}{(X - X^e)_{\ln mean}}$$

$$N_Y = \int_{Y_0}^{Y_z} \frac{dY}{Y - Y_e} = \frac{1}{\varepsilon - 1} \ln\left(\frac{Y_0^e - Y_0}{Y_z^e - Y_z}\right)$$

$$= \frac{Y_0 - Y_z}{\left(Y - Y^e\right)_{\ln mean}}$$

Log mean driving force : $\Delta C_{\ln mean} = \dfrac{\Delta C_0 - \Delta C_Z}{\ln \dfrac{\Delta C_0}{\Delta C_Z}}$




Mass balance over the whole column can be written :

$$A\left(X_0 - X_z\right) = \underbrace{k_x \left(X - X^e\right)_{\ln mean}}_{\text{N mean}} a \; Sect \; Z$$

# Number of transfert unit and number of theoretical plate

Number of theoretical plate

$$NTP = \frac{\ln\left(\frac{X_0 - X_0^e}{X_z - X_z^e}\right)}{\ln \varepsilon} = \frac{\varepsilon - 1}{\varepsilon \ln \varepsilon} N_X = \frac{\varepsilon - 1}{\ln \varepsilon} N_Y$$

*In practical case, $\varepsilon$ varies between 0,2 and 2 : the number of theoretical plate and the number of transfer unit are in the same range*

*NTP : a tool to characterise the working of a process (by comparing to the equilibrium)*

*NX and NY : a tool to scale up the process (by analysing mass transfer)*

## Exercise 8 : Liquid/liquid extraction with multi-stage cross-current process

f) Determine the number of transfer unit in the raffinate and in the extract side.

g) Calculate the height of a transfer unit in the raffinate and in the extract side.

h) Determine the total height of the column required to achieve this separation.

Data : Flowrate of ether : 100 L/h
Mass transfer coefficient in the raffinate : $10^{-4}$ m/s
Mean droplet size : 4.3 mm
Fractional hold up : 10 %
Cross sectional area : 40 $cm^2$

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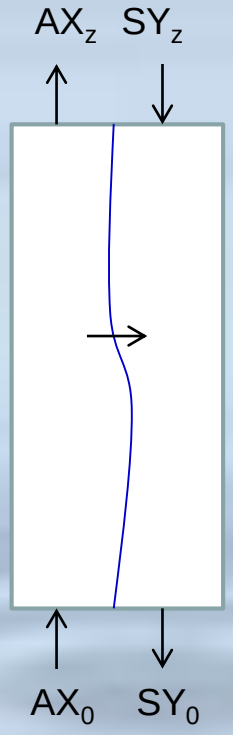
# 3.4. Efficiency of a separation process

## Exchange efficiency

Efficiency in the raffinate film

$$\eta_X = \frac{X_0 - X_z}{X_0 - X_z^{\,e}}$$

$$X_z^{\,e} = \frac{Y_z}{K}$$




Efficiency in the extract film

$$\eta_X = \frac{Y_0 - Y_Z}{Y_0^{\,e} - Y_Z}$$

$$Y_0^{\,e} = KX_0$$

Ratio of the real exchange over the maximum reachable (for a column with an infinite length)

the raffinate outlet could be in equilibrium with the solvent

the extract phase could be in equilibrium with the feed

# Exercise 8 : Liquid/liquid extraction with multi-stage cross-current process

i) Determine the efficiency for the raffinate and the extract phase.

# References

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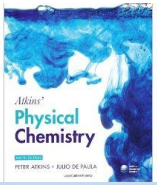
Physical Chemistry 2009




*Thermodynamics*
*Material science*
*Chemistry*

## Physical-chemistry

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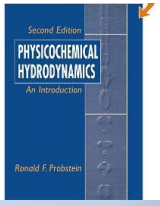


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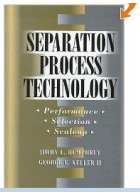


# Process

*Hydrodynamics*
*Mass and heat transfer*

## Transport phenomena

R. Byron Bird, Warren E. Stewart et Edwin N. Lightfoot
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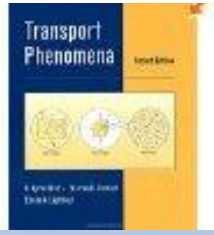


## Engineering

*Material balance*
*Transfer unit*
*Multi-stage processing*

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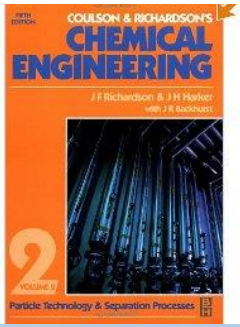

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  - Generic case
  - Application to membrane processes (Pierre Aimar)

# 4 – Elements for process selection – case studies

## 4.1 - Desalting by reverse osmosis -comparison with distillation- 4h (PA)

## 4.2 - Pervaporation -comparison with distillation- 8h (JCRY)