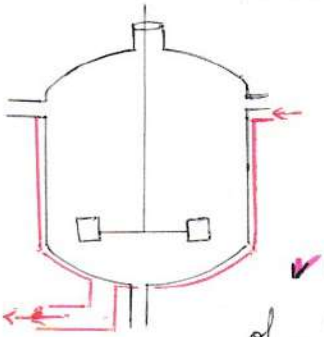
## Stirring Systems:

- ✓ Mobile متحرك
- ✓ Tree شجرة
- ✓ Engine محرك

## II. 1 Heat exchange System: cylindrical reactor

### 01/ Double envelop system:



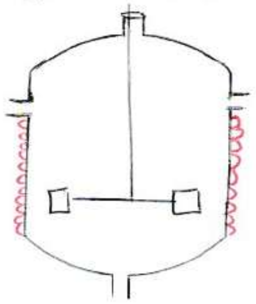
✓ Water bath مبدأ principal حمام مائي

✓ We find a circulation of a heat transfer fluid

✓ If the heat transfert fluid is a vapor, it must be injected from the top of the reactor

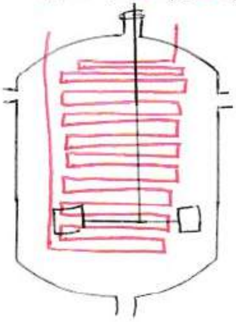
✓ If the heat transfert fluide is a liquid, it introduced from the bottom of the reactor.

### 02/ Outdoor Coil Serpentin extérieur



✓ the exchange coefficient is greater but the problem of lime scale accumulation inside the coil is disadvantageous.

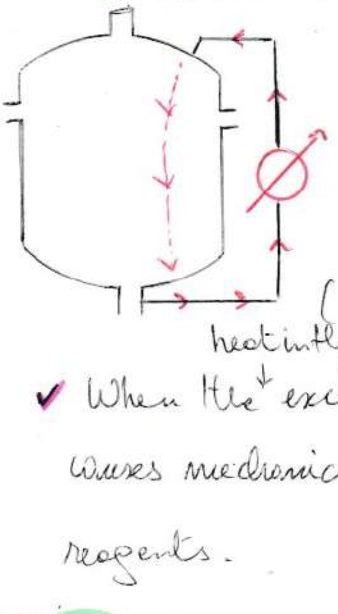
### 03/ Indoor Coil



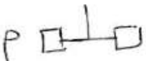
✓ a single heated tube placed inside the system

✓ Here we increase the efficiency of the heat exchange but we will have problems of distribance inside the reactor.
[reagents does'nt well mixed].
[it will hinder the circulation of reagents particules].

### 04/ External exchanger



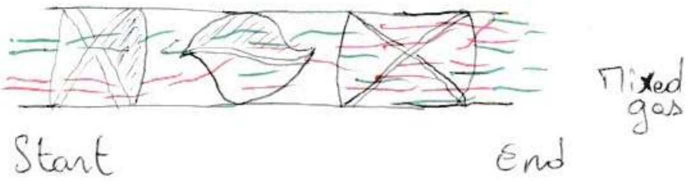
✓ here, there is no need to have the stirring loop



(boucle d'agitation)

✓ When the heat in the exchanger circulates, it causes mechanical agitation of the reagents.

### Special Case



## III.2 Heat Exchange System : Piston reactor

### 0 / Tubular piston reactor

→ lengths : L > 100 Diameter

→ Turbilenflow : $Re > 10^4$

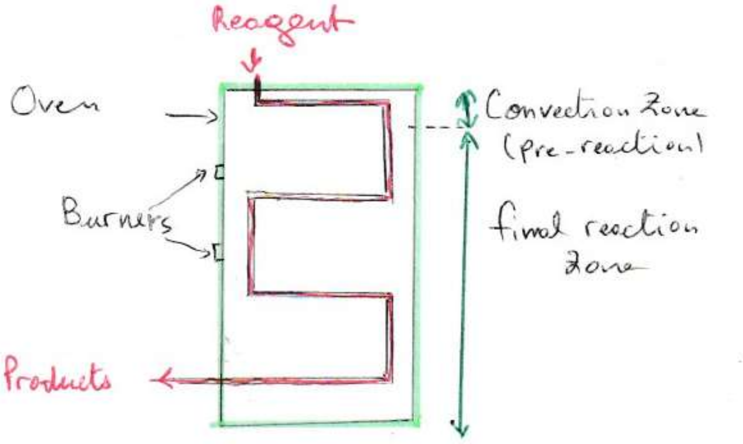
These two criteria are not always sufficients to ensure piston flow but they will allow us to get Closer

Heat Exchange : there are 2 cases :

T < 500°C : Coaxial tube with heat transfer fluid

- this tube will wrapped With heat transfer fluid to maintain the T° at that desired.

T > 500° : Coaxial tube Will be placed into oven



## Chapter I : Stoichiometry

- Concept of : conversion rate, advancement
- Case of single r° / multi r°

⇒ General notating

$i$ : reaction number

$A + B \to C$ ... ①
$C + d \to E$ ... ②
$A + d \to F$ ... ③

the 1st r° $i = 1$

$j$ : species number (or the name of the chemical specie) ($j = 2$)

$n$ : number of moles [case of Closed reactor]

$F$ : Molar flow [case of open reactor]

Molar titels :
↳ condensed phase
↳ gas phase

$\nu_{ij}$ : Stoichiometric coefficient :

If
reagents $-\nu_{ij}$
products $+\nu_{ij}$

This coefficient is given without dimension

So : $\nu_{ij}$ is the coefficient of the spece $j$ in the reaction number $i$

## Stoichiometric Expansion

$$\Delta\nu_i = \sum_j \nu_{ij}$$

Exp : $A + 2B \to C$ ... ①

$\nu_{1.1} \to -1$
$\nu_{1.2} \to -2$
$\nu_{1.3} \to +1$

So :
$\Delta\nu = -2$

## Conversion rate:

1. ↳ Associated to one species "A" is the limiting reactant

↳ It symbolized by "$X_A$"

⇒ The conversion rate of a chemical reaction is a measurement that indicates the proportion of reactants that convert to products during a chemical reaction.

⇒ the conversion rate depends to the limiting reagent

It given that:

$$n_A = \underbrace{n_{A0}(1 - X_A)}_{n_{A0} - n_{A0}X_A} \quad \text{... Closed reactor}$$

$$F_A = F_{A0}(1 - X_A) \quad \text{... Open reactor}$$

at the begining / entrance of the reactor

"0": indicate the reference state

لـ الحالة المرجعية / الأولى

| Discontinuous operation | Continuous Operation |
|---|---|
| ⇓ | ⇓ |
| 0 → initial moment | 0 → at the entrence of the reactor |

gas:

- Standards state: $P_0 = 1\,bar$
- $T°$ ref.
- initial moment / or / at the intrence

eg: $A + 2B = 4C$ $\quad \Delta\nu = -1 - 2 + 4$

$$\boxed{\Delta\nu = +1}$$

$$F_A = F_{A0}(1 - X_A)$$

$$F_B = F_{B0}(1 - X_B)$$

$$\rightarrow F_A = F_{A0} - F_{A0}X_A$$

$$\rightarrow F_B = F_{B0} - F_{B0}X_B$$

Note that: 1 mol of A needs 2 mols of B so

$$F_{B0}X_B = 2F_{A0}X_A$$

And then:

$$F_B = F_{B0} - 2F_{A0}X_A$$

$$F_C = F_{C0}(1 - X_C)$$

$$\rightarrow F_C = F_{C0} - F_{C0}X_C$$

Note that: 1 mol of A done 4 mols of C so

$$F_{C0}X_C = 4f_{A0}X_A$$

And then:

$$F_C = F_{C0} + 4F_{A0}X_A$$

donc

$$F_A = F_{A0} - F_{A0}X_A$$

$$F_B = F_{B0} - 2F_{A0}X_A$$

$$F_C = F_{C0} + 4F_{A0}X_A$$

---

$$F_{Tot} = F_{A0} + F_{B0} + F_{C0} + \textcircled{1}F_{A0}X_A$$

↓ is the stoichiometric expansion of the reaction

→ So General Conclusion :

$$F_j = F_{j_0} - \frac{\nu_j}{\nu_A} \cdot F_{A_0} \cdot X_A$$

at the entrence

Verification : Exp : B $\nu_B = -2$

$$F_B = F_{B0} - \frac{-2}{-1} F_{A0} X_A$$

$$F_B = F_{B0} - 2 F_{A0} X_A$$

☆ If : in general case : $\nu_A = -1$

So :

$$F_j = F_{j0} \left( - \frac{\nu_j}{-1} \right) \cdot F_{A0} \cdot x_A$$

$$F_j = F_{j_0} + \nu_j \cdot F_{A0} \cdot x_A$$

Result :

$$\boxed{F_{total} = \sum_j F_{j0} + \Delta\nu \cdot F_{A0} \cdot X_A}$$

هو مجموع التدفقات الداخلة في البداية

$F_{A_0}, F_{B_0} \dots$

this rule is applied when we work with Open reactor

* in the case of Closed reactor, $F \to n$

## التقدم الموحد Standardized advancement $X_i$

↳ Used when we have many reactions in the same time or separated in time.

$X$ → advancement

$i$ → number of the r°

$$dF_{ij} = F_0 \cdot \nu_{ij} \cdot dX_i$$

$dF_{ij}$ → the variation of the molar flux of the species "j" due to the reaction number "i"

$\nu_{ij}$ → stoichiometric coefficient of the species "j" in the reaction number "i"

$dX_i$ → advancement variation of the r° number "i"

$F_0$ ↳ is the sum (la somme +) of the incoming molar flux (we do not count the inert reagents).

— $F_0$ : Without - inert

* $F_0$ is correspond to - reagents or products onely → onely species that participate in the reaction.

⇒ So General conclusion :

$$F_j = F_{j0} + \underset{\text{Hors inerts}}{F_0} \cdot \sum_i \nu_{ij} \cdot X_i$$

→ de tous les r°

Exp : $A + B \longrightarrow 2C$ --- ①

$A + D \longrightarrow E$ --- ②

$C + 2E \longrightarrow 3F$ --- ③

① You must write the molar flux of each species :

$$F_A = F_{A0} + F_0 \cdot [(-1 X_1) + (-1 X_2)]$$

$$F_B = F_{B0} + F_0 \cdot [(-1 X_1)]$$

$$F_C = F_{C0} + F_0 \cdot [(+2 X_1) + (-1 X_3)]$$

$$F_D = F_{D0} + F_0 \cdot [(-1 X_2)]$$

$$F_E = F_{E0} + F_0 \cdot [(+1 X_2) + (-X_3)]$$

$$F_F = F_{F_0} + F_0\left[(+3\chi_3)\right]$$

$$F_{tot} = \underbrace{\left(F_{A0} + F_{B0} + F_{C0} + F_{D0} + F_{E0} + F_{F0}\right)}_{=0} +$$

$$F_0\left(1 + (\underset{0}{\cancel{0\chi_1}}) + (-\chi_2) + (\underset{0}{\cancel{0\chi_3}})\right)$$

$$\boxed{F_{tot} = F_0\left(1 - \chi_2\right)}$$

Note (Used to Check -- التحقق)

$$\boxed{\begin{aligned} 0\chi_1 &\longrightarrow \Delta\nu_1 = 0 \;\ldots\; r_1^\alpha \\ -1\chi_2 &\longrightarrow \Delta\nu_2 = -1 \;\ldots\; r_2^\alpha \\ 0\chi_3 &\longrightarrow \Delta\nu_3 = 0 \;\ldots\; r_3^\alpha \end{aligned}}$$

Attention : il we have inerte species We must add his value :

$$F_{tot} = F_0\left(1 - \chi_2\right) + F_I$$

→ Molar flux of the inert

General

$$\boxed{F_{total} = F_I + F_0\left(1 + \sum \Delta\nu_i \cdot \chi_i\right)}$$

## General Rules :

$$a_1 A_1 + a_2 A_2 = a_3 A_3 + a_4 A_4$$

$$a_1 A_1 + a_2 A_2 - a_3 A_3 - a_4 A_4 = 0$$

Number of Substances that participate at the $r^\alpha$ →

$$\sum_{i=1}^{s} \nu_i A_i = 0$$

→ Stoichiometric coefficient of the species $A_i$

★ Advancement of the $r^\alpha$ $\xi$

$$\xi = \frac{n_i - n_{i0}}{\nu_i}$$

★ Conversion of Reagents $\chi_i$

$$\chi_i = \frac{n_{i0} - n_i}{n_{i0}}$$

★ Standarized Advancement

$$n_i = n_{i0} + \nu_i\, n_0\, \chi$$

# Concept of advancement

## Case of single reaction

Equations of mole numbers and
معادلات الأعداد المولية ومعدل التدفق
molar flow rate as a function of
المولي بتغير متغير التقدم كما يلي
progress variable is written as follows:

⇒ Closed system :

$$\boxed{n_j = n_{j_0} + \nu_j \xi}$$

⇒ Open system :

$$\boxed{F_j = F_{j_0} + \nu_j \xi}$$

as: $\xi$ is the advancement variable taken by (mol)

→ the disatvantage of this notion in practice, is that $\xi$ has a dimension (mol) which depends on the initial quantities of reagents.

However, there is a formula that links between the variable of advancement and a number without dimension; it is the

normalized advancement $\chi$

this formula is represented by the following equation :

Closed System : $\boxed{\chi = \dfrac{\xi}{n_0}}$

Open System : $\boxed{\chi = \dfrac{\xi}{F_0}}$

~~ex~~ With:

$n_0$ and $F_0$ are respectively, the total mole number and the total molar flow rate.

Closed System : $\boxed{n_0 = \sum_j n_{j0}}$

Open System : $\boxed{F_0 = \sum_j F_{j0}}$

So General case:

$$\boxed{\begin{gathered} n_j = n_{j0} + \nu_j n_0 \chi \\ f_j = f_{j0} + \nu_j f_0 \chi \end{gathered}}$$

## Case of Multi-reactions:

Equations of number of moles and molar flow rate of species j as a function of the normalized rate of advancement become:

⇒ Closed System : $\boxed{n_j = n_{j0} + n_0 \sum \nu_{ij} \cdot \chi_i}$

⇒ Open System : $\boxed{F_j = f_{j0} + f_0 \sum \nu_{ij} \chi_i}$

Exp: Considering the following reaction mechanism which takes place in a closed reactor:

$A + B \rightarrow 2C$ ... ①

$A + D \rightarrow E$ .. ②

$C + 2E \rightarrow 2F$ .. ③

We Write the mole number equations as a function of the normalized rate of advancement:

$$n_A = n_{A_0} + n_0(-x_1 - x_2)$$

$$n_B = n_{B_0} + n_0(-x_1)$$

$$n_C = n_{C_0} + n_0(2x_1 - x_3)$$

$$n_D = n_{D_0} + n_0(-x_2)$$

$$n_E = n_{E_0} + n_0(x_2 - 2x_3)$$

$$n_F = n_{F_0} + n_0(2x_3)$$

$$\downarrow 0$$

$$\boxed{n_{tot} = n_0(1 - 0x_1 - 1x_2 + 0x_3)}$$

So: $\boxed{n_{tot} = n_0 \sum \nu_{ij} x_i}$

$\boxed{f_{tot} = f_0 \sum \nu_{ij} x_i}$

Note: If ever there was an inert in the system, it will be added into the formula either as "n" or "f"

$$n_{tot} = n_0 \left(1 + \sum \nu_{ij} x_i\right)$$

$$f_{tot} = f_0 \left(1 + \sum \nu_{ij} x_i\right)$$

## Volume and Volume flow

Sizing a reactor generally involves Calculating a volume V or a flow rate volume $\mathcal{Q}$.

they are represented as:

$$V = \beta V_0 \left(1 + \sum_j \alpha_j x_j\right) \leftarrow \text{Closed reactor}$$

$$V = \beta \mathcal{Q}_{V_0} \left(1 + \sum_j \alpha_j x_j\right) \leftarrow \text{Open reactor}$$

Where:

$V_0$: the volume of the reactor at the reference state.

$\mathcal{Q}$: is the volume flow in the reference state.

$\beta$: is the physical expansion factor.

$\alpha_i$: is the Chemical expansion factor of the reaction number "i"

| State | $\beta$ | $\alpha_i$ |
|---|---|---|
| Perfect gas | $\frac{P^\circ \times T}{P \times T^\circ}$ | $\frac{\Delta\nu_i}{1+I}$ |
| Indilatable liquid | 1 | 0 |
| Ideal liquid | function $\frac{T}{T_0}$ | $C_0 \sum_j \nu_{ji} v_j^\circ$ |

$v_j^\circ$: is the partial molar volume of the species j

I: is the ratio of inerts

## Advancement $\xi_i$

- The advancement of the reaction "i" is noted "$\xi_i$"
- It represent the variation of the number of moles of the species "j" during the reaction "i"

$$dn_{ij} = \nu_{ij} . d\xi_i$$

$$\xi_i = \frac{n_j - n_{jo}}{\nu_{ij}} \Big|_{\text{reaction } i}$$

=> for a finished transformation, with several reactions taking place simultaneously;

$$n_j = n_{j_o} + \sum_i \nu_{ij} . \xi_i$$ ... Closed reactor

$$f_j = f_{jo} + \sum_i \nu_{ij} \xi_i$$ ... Open reactor

## relation between: Advancement and Standrized advancement:

$$X_i = \frac{\xi_i}{n_o}$$ ... Closed reactor $[\xi_i : \text{mol}]$

$$X_i = \frac{\xi_i'}{f_o}$$ ... Open reactor $[\xi_i : \text{mol/s}]$

**NOTE:**

In the presence of **inert** species, (spacies not involved in any reaction), $n_o$ and $f_o$ are the number of moles and the molar flux at the begining of the r° or at the entrence of the reactor Whith out **inerts**.

So:

$$n_j = n_{jo} + n_o \sum_i \nu_{ij} . X_i$$ ... Closed reactor

$$f_j = f_{jo} + f_o \sum_i \nu_{ij} . X_i$$ ... Open reactor

**NOTE:**

In real life, in real reactor, $\xi_i$ does'nt existe, it does'nt been taken in consideration, we almost use the standarized advancement $X_i$.

## Volume and Volume flow

-> Sizing a reactor generally involves Calculating a volume V or flow rate volume $Q_v$.

-> they are given by:

$$V = \beta . V_o . \left(1 + \sum_i \alpha_i . X_i\right)$$ ... Closed reactor

$$Q_v = \beta . Q_{vo} \left(1 + \sum_i \alpha_i X_i\right)$$ ... Open reactor

$V_o$: the volume of the reaction medium in refrence state.

$Q_{vo}$: the volume flow at the reference state.

→ the coefficient "$\beta$" is called the physical expansion factor of r° "i"

→ the coefficient "$\alpha_i$" is called the Chemical expansion factor of r° "i"

| State | $\beta$ | $\alpha_i$ |
|---|---|---|
| Perfect gas | $\frac{P^\circ}{P} \cdot \frac{T}{T_0}$ | $\frac{\Delta\nu_i}{1+I}$ |
| Indilatable liquide | 1<br>→ Sa masse volumique ne varie pas en | de la T°<br>0 fonction |
| Ideal liquide | function<br>$T/T_0 \simeq 1$ | $C_0 \cdot \sum_j \nu_{ij} v_j^\circ$ |

$v_j^\circ$ : is the partial molar volume of the species j

I : is the ratio of inerta ... rapport d'inertes

$I = \frac{n_I}{n_0}$ ... Closed reactor

$I = \frac{F_I}{F_0}$ ... Open reactor

## Speed of the reaction

Definition:

* We define the speed of a reaction "i" in a closed reactor as follow:

$$\boxed{r_i = \frac{1}{V} \cdot \frac{d\xi_i}{dt}}$$

V : is the reaction volume

* It is represented on the international system of unites by **mol / m³ s**

* the variation in the number of moles of species "j" due to reaction "i" is given:

$$\boxed{\left.\frac{dn_j}{dt}\right|_{\text{reaction "i"}} = \nu_{ij} \cdot r_i \cdot V}$$

* Also, the variation in the number of moles of species "j" due to all reactions is given:

$$\boxed{\left.\frac{dn_j}{dt}\right|_{\text{reactions}} = \left(\sum_i \nu_{ij} \cdot r_i\right) V}$$

Note that V is the reaction Volume and it is "cst"

→ If we replace : $\sum_i \nu_{ij} \cdot r_i$ by $R_j$ it will be :

$$\boxed{\left.\frac{dn_j}{dt}\right|_{\text{reactions}} = R_j \cdot V}$$

## NOTE

In the case of a reaction involving a solide catalyst, the $r^{\alpha}_{speed}$ Will generally defined as a mass of reagent consumed per unite of time

## Usual speed Laws

| Type of reaction | Speed of $r^{\alpha}$ | Order of $r^{\alpha}$ |
|---|---|---|
| A ⟶ Products | $r = k \cdot C_A$ | 1st order $r^{\alpha}$ |
| 2A ⟶ Products | $r = k \cdot C_A^2$ | 2nd order $r^{\alpha}$ |
| A+B ⟶ Products | $r = k \cdot C_A \cdot C_B$ | 1 st Order $r^{\alpha}$ for A<br>1st Order $r^{\alpha}$ for B |
| A ⟶ Products | $r = k \cdot C_A^2$ | 2nd Order $r^{\alpha}$ for A |
| A ⟶ Products | $r = k$ | 0 order $r^{\alpha}$ |
| A ⟶ P | $r = k \cdot C_A \cdot C_P$ | Autocatalyzed reaction |
| | ultra speed $r^{\alpha}$ With many P | |

In General:

$$r_i = k_i \cdot \prod_j C_j^{x_{ij}} \quad \text{... liquid phase}$$

Or: $$r_i = k_i \cdot \prod_j P_j^{x_{ij}} \quad \text{... gas phase}$$

Note that: $x_{ij}$: Order of the $r^{\alpha}$ of the species "j" in reaction "i"

$C_j$: Molar Concentration of the species "j".

$P_j$: Partial pressure of the species "j" in a gas.

$k$: Speed constant

$$\boxed{\underbrace{k}_{\text{depends on } T°} = k_0 \cdot \exp\left(\frac{-E_a}{RT}\right)}$$

depends on T°

R: constant of Perfect gas

$E_a$: Activation Energy nécessaire pour le rearrangement des atomes ds la molécule

Case of: reversible reaction:

$$K = \frac{k}{k'}$$

**Arrhenius law**

$Cl_2 + C_3H_6 + 2NaOH \rightarrow C_3H_6O + 2NaCl + H_2O$

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

$-4 + 4 = 0$

# Theorical reminder

## Classification of Chemical reactions

### ① Number of phases عدد الاطوار

1 single phase → homogeneous (gas or liq or solid)

multiphases → heterogenous (gas-liq sol-gas)

### ② Number of chemical reactions عدد التفاعلات

1 single reaction

★ multi reactions → consecutive ↓

(reagent which degrads into other products) التفاعلات في المادة ② هي نواتج المادة ①

★ Competitive → in parallel ↓

(one reagent leads to several products) في الحالة النهائية نجد النواتج و نجد ايضا بعض المتفاعلات .

### ③ Equilibrium of the reaction

↲ Either ↳

total          reversible

كلي          إما          عكسي

### ④ Termicity of the reaction

↲ either ↳

Endothermic $\Delta h$          $\Delta h$          Exothermic

ماصة للحرارة          إما          ناشرة للحرارة

## Classification of reactors

Evolution in time

→ Transitional regime (transitoire) نظام انتقالي

(Discontinuous Operation)

→ Steady state (régime permanent)

(Continuous operation) نظام دائم

✓ Circulation of the reaction mixture

→ Closed reactor مغلق
→ Semi-Closed reactor نصف مغلق
} Transitional regime

→ Open reactor مفتوح } Steady state

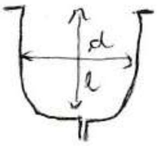
✓ Degree of mixing

→ Perfectly stirred reactor (uniformity of all species inside) ---
→ Piston reactor -----
} Reactor idéaux (ideal reactors)

→ Intermediate case } Real reactors

## Homogeneous reactors with a single phase : liquid or gas

General case:

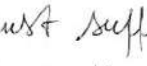


* for a correct agitation it is necessary that:

✓ ↕ $l = d$ ↔ ;

✓ a lid is essential ;

✓ An agitation system is obligatory



✓ We must supply this reactor with heat otherwise remove heat from it