CHEMICAL REACTION ENGINEERING I

BY.
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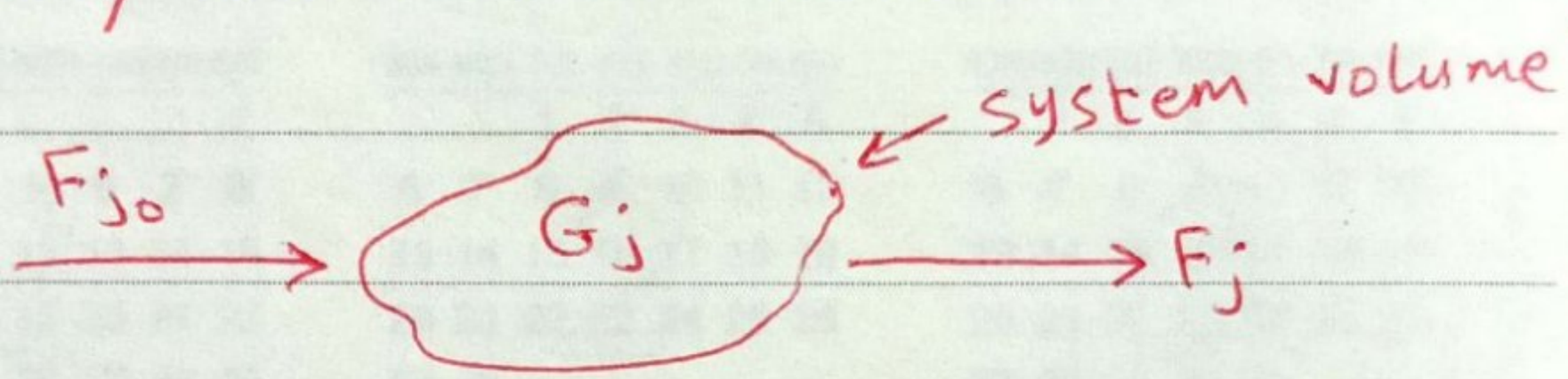
Memo No. _____

Date 18 / 10 / 2021

* Ch 1 :- Mole balance.

* Lec 1.1 :- (General mole balance equation) and Batch reactor.



$$\left[\begin{array}{l}\text{molar Flow}\\ \text{rate of}\\ \text{species j in}\end{array}\right] - \left[\begin{array}{l}\text{molar Flow}\\ \text{rate of}\\ \text{species j}\\ \text{out}\end{array}\right] + \left[\begin{array}{l}\text{molar rate}\\ \text{generation}\\ \text{of species}\\ \text{j}\end{array}\right] = \left[\begin{array}{l}\text{molar rate}\\ \text{accumulation}\\ \text{of species}\\ \text{j}\end{array}\right]$$

generation (+ve) ⟷ (-ve) consumption

$$F_{jo} - F_j + G_j = \frac{dN_j}{dt}$$

$\frac{mole}{time}$ كل هم وحدتهم

$\frac{dN_j}{dt}$ → التغير مع الزمن للشي الموجود جوا ال system.

N_j → number of moles inside the system.

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* If the system is uniform throughout its entire volume (spatially uniform), then
يعني اي نقطة جوا الـ system بصير فيها نفس الاشي

generation of → rate of reaction → $f(C,T)$ التركيز

$G_j = r_j V$ → volume.

+ve → generation

-ve → consumption.

rate of reaction (r) → $\frac{\text{mole}}{\text{time} * \text{volume}}$

r_j → reactant → consumption

product → generation/ Formation.

r_j → product → +ve

reactant → -ve

↳ rate of Formation (generation) of species j.

- If NoT spatially uniform:-

بنقسّم الـ volume الكلي لـ system إلى عدد كبير من الـ small volume (ΔV) بحيث تكون الـ rate ثابتة

*Rate of reaction (r_A):- tell us how fast a number of moles of one chemical species are being consumed to Form another chemical species.

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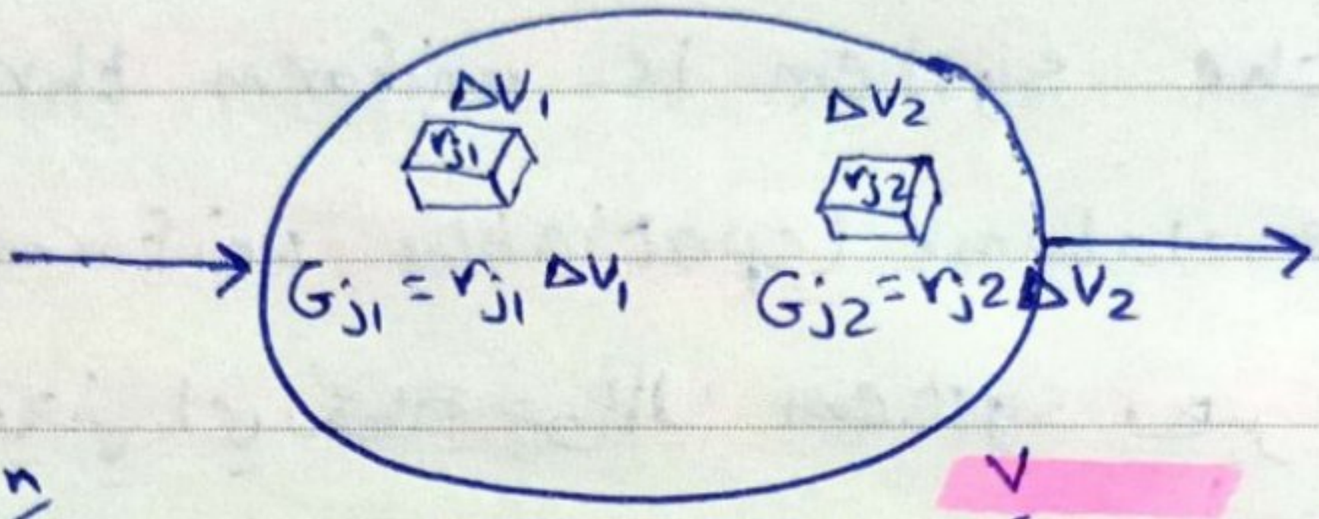

$$G_j = \sum_{i=1}^{n} r_{ji}\,\Delta V_i = \int r_j\,dV$$

$$\lim \Delta V \to 0,\ n \to \infty$$

-general mole balance on system volume V :-

(المعادلة A بدلالة)

In - out + generation = Accumulation

$$F_{A0} - F_A + \int r_A\,dV = \frac{dN_A}{dt}$$

وعلى حسب نوع الreactor بنغير فيها

1 Batch Reactors properties.

بندخل المواد بعدين بنشغل الـ reactor لوقت محدد وبس نخلص بنفل out للمواد.

* Reactants are placed in the reactor, and the reaction is allowed to proceed For some amount of time.

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* closed system: no addition of reactants or removal of products during the reaction.

مسكر

- لأنه في عنا تغير في ال system ← في عنا condition

unsteady state.

steady state, unsteady state ← التغير مرتبطة في

مع ال time اللي جوا ال reactor.

لأنه في reaction ، كمية ال reactant بتقل مع الوقت وكمية ال product بتزيد مع الوقت.

- unsteady state conditions :- the composition changes with time.

* Ideal batch reactor :- (حنتعامل معه في المادة)

- هو نه عنا assumption مبسطة.

- في نفس اللحظة / الوقت ← بكون التركيز والحرارة ثابتة عبر نقاط مختلفة جوا ال reactor.

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- vessel is perfectly mixed.
- Concentration and Temperature are spatially costant, but NoT constant in time.

$$F_{j0}^{0} - F_{j}^{0} + \check{S} r_j dv = dN_j/dt$$

$$\boxed{\check{S} r_j dv = \frac{dN_j}{dt}}$$ Batch Reactor Design Equation.

* well-Mixed:-

If the reactor is perfectly mixed, the T, concentration, and therefore the reaction rate are spatially constant:

$$\boxed{\frac{dN_A}{dt} = r_A V}$$ → Ideal Batch Reactor Design Equation.

- احنا بنحتاج نحدد الوقت اللازم لتغير عدد مولات المواد المتفاعلة حتى تعطينا المواد الناتجة

لـ من N_{A_0} إلى N_A

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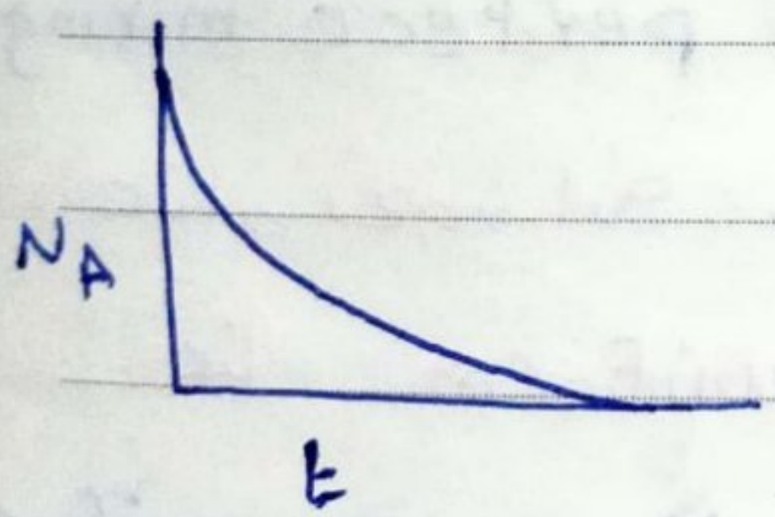
$$dt = \frac{dN_A}{r_{AV}} \longrightarrow \int_{t=0}^{t=t} dt = \int_{N_{A0}}^{N_A} \frac{dN_A}{r_{AV}}$$

$t = 0 \qquad N_A = N_{A0}$

$t = t \qquad N_A = N_A$

$$t = \int_{N_{A0}}^{N_A} \frac{dN_A}{r_{AV}}$$

Time necessary to reduce the number of moles of A From N_{A0} to N_A.



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2 Continuous-Flow Reactors (CSTR)

* Continuous stirred Tank Reactor (CSTR)

properties:-

→ continuously add reactant and remove products (open system).

→ Inlet stream instantaneously mixes with bulk of reactor volume.

main assumption

→ Ideal CSTR: assume perfect mixing occurs in vessel. → عشان نعتبرها

. spatially uniform i.e

• T and concentration are uniform throughout space.

• Composition of the exit stream is the same as that inside reactor.

($C_{A,outlet} = C_{A,tank}$).

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• Steady-state conditions :-

reaction rate is the same at every point and doesn't change with time.

(بالنسبة للي جوا الـ Reactor).

- baffle → mixing (بشاعرفي ال perfect mixing) (بشاعرهاي في ال mixing)

- Impeller → mixing بتعمل بالنص و

- sparger → (Inlet gas stream اذا كانه في).

- Jacket → heating or cooling اذا احتجنا

In - Out + generation = Accumulation.

$$F_{j0} - F_j + \int_v r_j dv = \frac{dN_j}{dt}$$

0

CSTR is at steady state, so no change in moles j with time.

steady state CSTR Design Equation:

$$F_{j0} - F_j + \int_v r_j dv = 0$$

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A perfectly mixed CSTR has no spatial variations in reaction rate.

$$F_{j0} - F_j + r_j V = 0$$

rearrange to put in terms of V.

$$\frac{F_{j0} - F_j}{-r_j} = V$$

(Ideal) steady state (CSTR) Design Equation.

Ideal CSTR ≡ back mix reactor.

r_j is measured at the outlet

because $C_{j,exit} = C_{j,tank}$

*V :- Reactor volume required to reduce the entering flow rate of species j from F_{j0} to F_j at the outlet (and in the tank).

-How we determine the molar flow rate, F_j (units = mol / time)?

$$F_j = (C_j)(V)$$

$$\frac{\text{moles } j}{\text{time}} = \frac{\text{moles}}{\text{volume}} \times \frac{\text{volume}}{\text{time}}$$

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C_j : concentration of j.

V : volumetric Flow rate.

*Ideal SS CSTR design equation in terms of concentration :

$$V = \frac{C_{jo} V_o - C_j V}{-r_j}$$

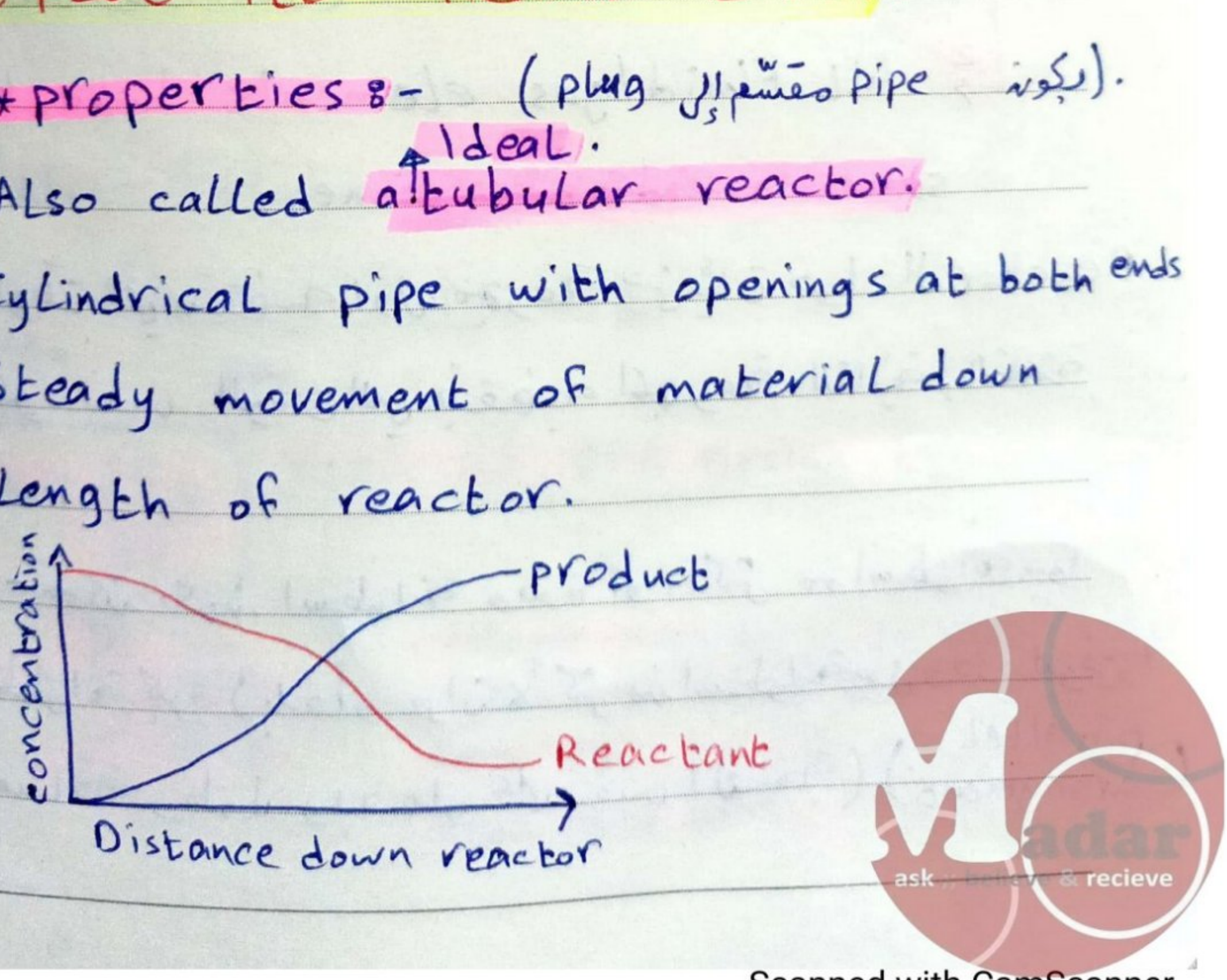
3 PLUG Flow Reactor (PFR).

*properties :- (plug مقسّم إلى pipe يكون).

→ Also called a tubular reactor. ← Ideal.

→ Cylindrical pipe with openings at both ends

→ Steady movement of material down Length of reactor.



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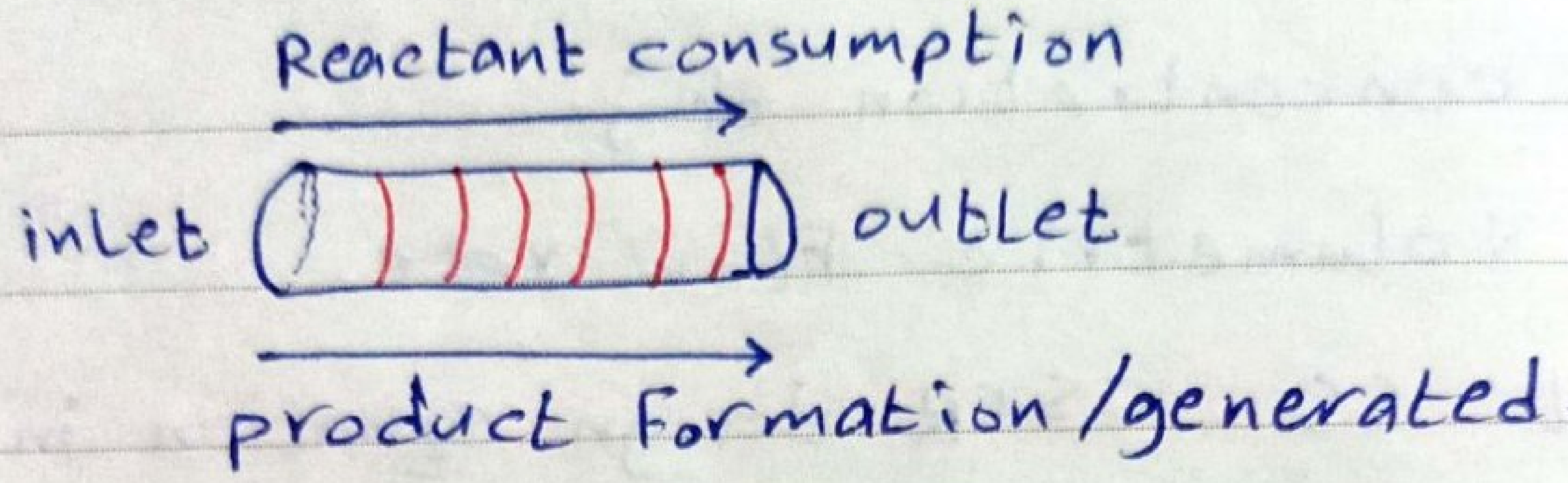

→ Reactants are cosumed as they Flow down the length of the reactor.

→ Operated at steady state

main assumption

① No radial variation in T, concentration, or reaction rate. (عند نفس نصف القطر) وهو المقصود بالعبارة المقطوعة.

② All Fluid/gas elements have the same residance time.

- الوقت اللي بتقضيه اول مجموعة جزيئات جوا الـ Reactor هو نفس الوقت اللي بتقضيه المجموعة الثانية، الثالثة، ....

- ممكن يكون اسطوانة وحدة او اكثر من اسطوانة جوا اسطوانة كبيرة (بلجأو مرات لأكثر من اسطوانة بدل وحدة ليوفروا مساحة وطول وبحصلو على نفس النتيجة) (parallel arangment)

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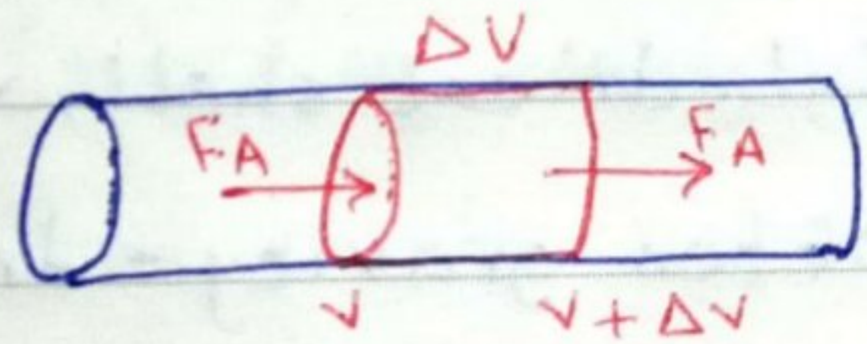
ملاحظة:- اي Flow reactor يكون steady state.

* In a plug Flow reactor the composition of the Fluid varies From point to point along aFlow path.

* material balance For areaction component must be made For adifferential element of volume ΔV.



(In at V) - (out at $V+\Delta V$) + (generation in ΔV) = 0

$$F_A|_V - F_A|_{V+\Delta V} + r_A \Delta V = 0$$

$$\lim_{\Delta V \to 0} \frac{F_A|_{V+\Delta V} - F_A|_V}{\Delta V} = r_A$$

$$r_A = \frac{dF_A}{dV}$$ Ideal SS PFR Design Eqn.

$$V = \int_{F_{A0}}^{F_A} \frac{dF_A}{r_A}$$ ⇝ volume necessary to reduce the entering molar Flow rate (mol/s) From F_{A0} to the exit molar Flow rate of F_A.

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- If we assume the PFR is ideal, the degree of completion isn't affected by PFR shape, only by PFR volume.

4] Packed Bed Reactor (PBR).

- بشبه ال PFR في عمله لكنه هاد عمودي غالباً.

→ Cylindrical shell, vertically oriented.

→ often gravity-driven Flow. (ما في bomb أو driving force)

→ Heterogeneous reaction ? Fixed bed of catalyst inside.

→ Reactants enter top and Flow through the packed bed of catalyst.

→ Concentration gradient of reactant and product down the length of the reactor.

→ Reaction occurs on the surface of the catalyst pellets.

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الفرق الاساسي بينه وبين الـ PFR → Reaction Rate is based on the mass of the solid catalyst (W), not reactor volume (V).

$\frac{dF_j}{dW} = r'_j$

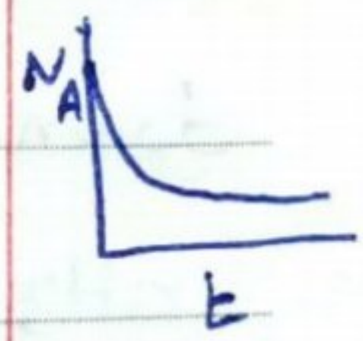
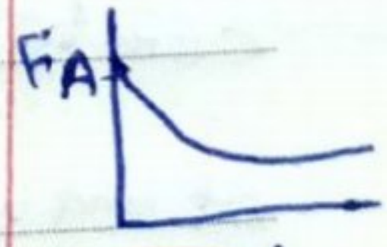
↳ number of moles of j reacting per unit time per unit mass of catalyst.

W → weight of the catalyst.

r'_j → rate of catalytic rxn

↳ (mol / kg catalyst * s)

Summary A → B

Reactor	Differential	ALgebric	Integral	
Batch	$\frac{dN_A}{dt} = r_A V$		$t = \int_{N_{A0}}^{N_A} \frac{dN_A}{r_A V}$	
CSTR		$V = \frac{F_{A0} - F_A}{-r_A}$		
PFR	$\frac{dF_A}{dV} = r_A$		$V = \int_{F_{A0}}^{F_A} \frac{dF_A}{r_A}$	
PBR	$\frac{dF_A}{dW} = r'_A$		$W = \int_{F_{A0}}^{F_A} \frac{dF_A}{r'_A}$	

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$$W = \int_{F_{A0}}^{F_A} \frac{dF_A}{-r'_A}$$

← (PBR) تابع ل

catalyst weight necessary to reduce the entering molar Flow rate of species A (F_{A0}) to aflow rate (F_A).

* There are 3 ways. For a species to Loose its identity:-

يتفكك

① Decomposition → molecule broken down into smaller molecules.

$$CH_3CH_3 \longrightarrow H_2C=CH_2 + H_2$$

يتحد

② combination → molecules combination with another molecule or atom.

$$N_2 + O_2 \longrightarrow 2NO$$

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(3) isomerization → compounds have the same number of atoms of each element, but ~~Kkkkk~~ with different structure oR configuration.

$$H_2C=\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}CH_2CH_3 \longrightarrow CH_3\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}=CHCH_3$$

* Selection of Reactors :-

1. Batch
   - small scale (مثل الادوية).
   - high labour costs per batch.
   - difficult for large-scale production.
   - production of expensive products (e.g pharmacy).

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[2] CSTR : most homogenous Liquid-phase Flow reactors.

- when intense agitation is required.
- relatively easy to maintain good Temperature control.
- the conversion of reactant per volume of reactor is the smallest of the Flow reactors - very large reactors are necessary to obtain high conversions

* كل انواع ال reactor بعبر فيها homogenous reactions
ما عدا ① PBR ② Fluidized bed reactor
التفاعل فيهم heterogeneous.

$W = \frac{F_{A0} - F_A}{-r_A'}$ بس في CSTR بعامل معاملة catalyst.

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3 PFR: most homogenous gas-phase Flow reactors.

- relatively easy to maintain.
- hot spots can occur.
- difficult to control T within the reactor. (rate of reaction يختلف من نقطة لأخرى)
- usually produces the highest conversion per reactor volume (weight of catalyst if it is a packed-bed catalysed gas reaction) of any of the Flow reactors.

* يوجد 3 أوراق عمل.

- أول فيزيوهيته.

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Ch② Conversion and reactor sizing.

(2.1) :- Mole balance in terms of conversion , X.

*Definition of Conversion

- generic equation

$$aA + bB \longrightarrow cC + dD$$

- Choose limiting reactant A as a basis of calculation:-

a, b, c, d → Stoichemtric coeffecient

→ .1 = الـ Stoichemtric coeffecient الـ لازم

$$A + \frac{b}{a}B \longrightarrow \frac{c}{a}C + \frac{d}{a}D$$

- Define Conversion , X_A : the number of moles of A that have reacted per mole of A Fed to the system.

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X_A = moles A reacted / moles A Fed .

- For Batch system : " Moles A Fed " is the amount of A at the start of the reactor (at t=0).

- For Flow system : " Moles A Fed " is the amount of A entering the reactor.

* Example :- $A + 2B \rightarrow 2C$

- start with 1 mole of A and 1 mole of B.

• If A is the basis and at the end we have :-

1 mole A, 1 mole B $\rightarrow$ $X_A = 0/1 = 0$ (no reaction)

$\frac{1}{2}$ mole A, 0 mole B $\rightarrow$ $X_A = 0.5/1 = \frac{1}{2}$

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Not possible !!

0 mole A, -1 mole B → $X_A = 1/1 = 1$ (complete reaction.)

* The correct approach is to take B as the basis because B is the Limiting reagent.

- At the end we have :-

1 mole A, 1 mole B → $X_B = 0/1 = 0$ (no reaction)

$\frac{1}{2}$ mole A, 0 mole B → $X_B = 1/1 = 1$ (complete reaction).

* Expressing other components conversion in Terms of X_A

$$A + \frac{b}{a}B \rightarrow \frac{c}{a}C + \frac{d}{a}D$$

* Batch System :- Longer reactant is in reactor, more reactant is converted to

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product (until reactant is consumed or
the (reaction reaches equilibrium) (in reversible reaction).

∴ conversion (X_j) is a function of time (t)

in the batch reactor.

moles A fed → Moles A consumed.

$$N_A = N_{AO} - (N_{AO})(X_A).$$

↳ Moles A in reactor at time t.

$$N_A = N_{AO}(1 - X_A).$$

$$N_B = N_{BO} \ominus \frac{b}{a}(N_{AO} X_A)$$

⊖ → reactant

⊕ → product

$$N_C = N_{CO} \oplus \frac{c}{a}(N_{AO} X_A)$$

$$N_D = N_{DO} + \frac{d}{a}(N_{AO} X_A).$$

$N_I = N_{IO}$ (inert component).

كل ما يتفاعل .

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* Batch Reactor.

(moles A remaining) = (moles A initially) − (moles A reacted)

$N_A = N_{AO} - N_{AO}X \longrightarrow dN_A = 0 - N_{AO}dX$

↳ const. (0 = ثابت)

$$\frac{dN_A}{dt} = -N_{AO}\frac{dX}{dt} = r_A V.$$

$$\frac{dX}{dt} = \frac{-r_A V}{N_{AO}}$$

$t = 0 \quad X = 0$

$t = t \quad X = X$

Integrating.

$$t = N_{AO}\int_0^X \frac{dX}{-r_A V}$$

The necessary t to achieve conversion X.

CSTR

- generic equation
- choose L.R as basis
- Define conversion, x

} كالسابق

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steady state $\frac{dN_A}{dt} = 0$

well mixed → $\int r_A dV = r_A V$ → $V = \frac{F_{A0} - F_A}{-r_A}$

↓ mol balance (conversion بدلالة)

[moles A leaving] = [moles A entering] - [moles A reacted]

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

$V = \frac{F_{A0} - (F_{A0} - F_{A0}X)}{-r_A}$

$V = \frac{F_{A0}X}{-r_A}$ CSTR volume necessary to achieve conversion X.

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steady state $\frac{dF_A}{dV} = r_A$

$F_A = F_{A0} - F_{A0} X \rightarrow dF_A = 0 - F_{A0} dx$

$$\frac{dx}{dv} = \frac{-r_A}{F_{A0}}$$

$V = 0 \quad X = 0$ Integrating.

$V = V \quad X = X$

$$V = \int_0^X \frac{F_{A0}}{-r_A} dx$$

PFR volume necessary to achieve conversion X.

F_{A0} const. → ~~Reactor~~ المفاعل التكامل.

بنقدر نطلعها برا

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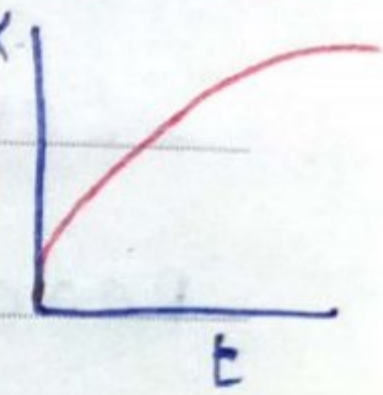
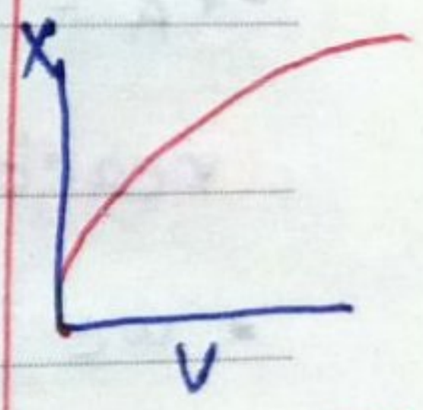
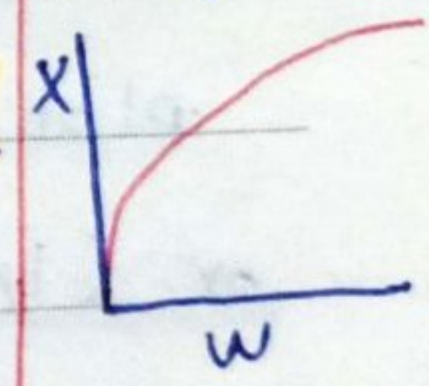
* Reactor Mole Balances Summary in terms of conversion, X.

Reactor	Differential	Algebraic	Integral	
Batch	$N_{A0}\frac{dx}{dt} = -r_A V$		$t = N_{A0}\int_0^x \frac{dx}{-r_A V}$	
CSTR		$V = \frac{F_{A0}X}{-r_A}$		
PFR	$F_{A0}\frac{dx}{dV} = -r_A$		$V = \int_0^x \frac{F_{A0}dx}{-r_A}$	
PBR	$F_{A0}\frac{dx}{dW} = -r_A'$		$W = \int_0^x \frac{F_{A0}dx}{-r_A'}$	

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2.2 :- Reactor sizing using Levenspiel plots.

" Applications of the Design Equations For Continuous-Flow Reactors".

* Levenspiel plots

Reactor Sizing.

- Given $-r_A$ as a function of conversion, $-r_A = F(X)$, one can size any isothermal reaction system.
- we do this by constructing Levenspiel plot. Here we plot either $(F_{AO}/-r_A)$ or $(1/-r_A)$ as a Function of X.

→ For $(F_{AO}/-r_A)$ vs. X, the volume of a CSTR and the volume of a PFR can be represnted as the shaded areas in the Levenspiel plot shown as :-

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$$\frac{F_{A0}}{-r_A} = g(X).$$

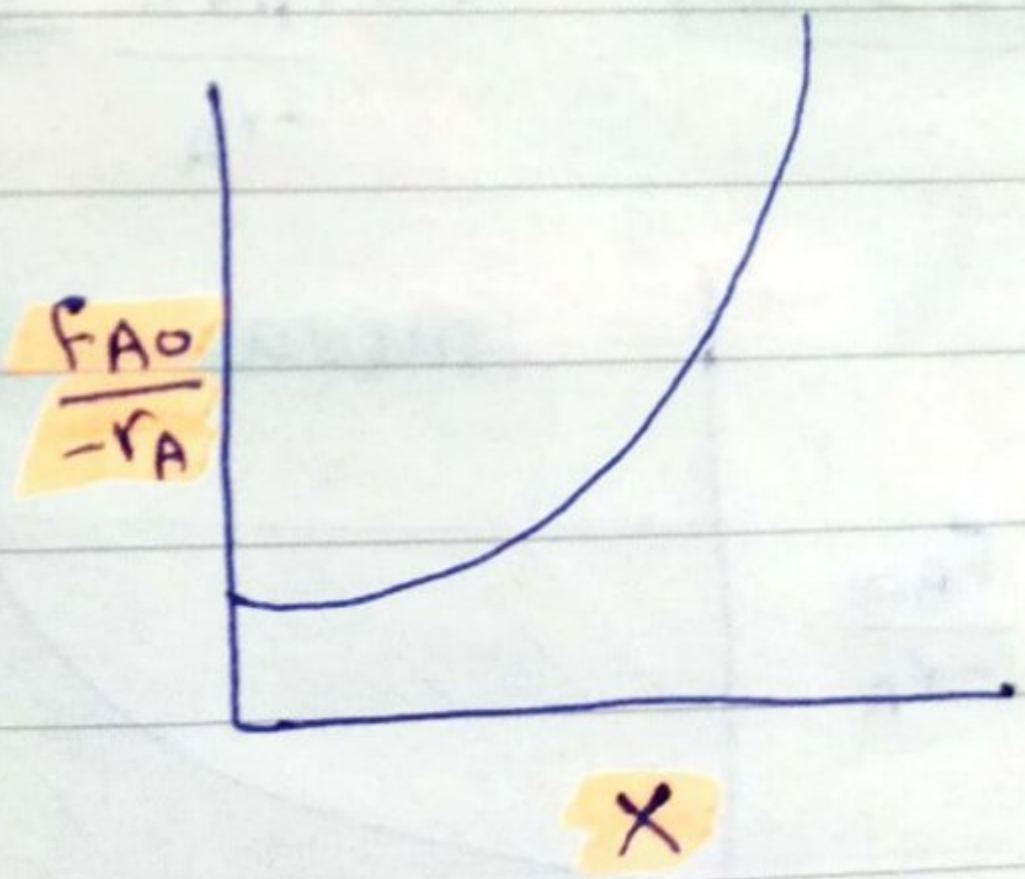
* For all **irreversible reactions** of **order > zero**, as we approach **complete conversion** where **all the limiting reactant is used up**, i.e **X=1**, the reciprocal (مقلوب) rate approaches infinity as does the reactor volume.

⇝ As $X \to 1$,

$-r_A \to 0$, thus

$\frac{1}{-r_A} \to \infty$, therefore

$V \to \infty$.



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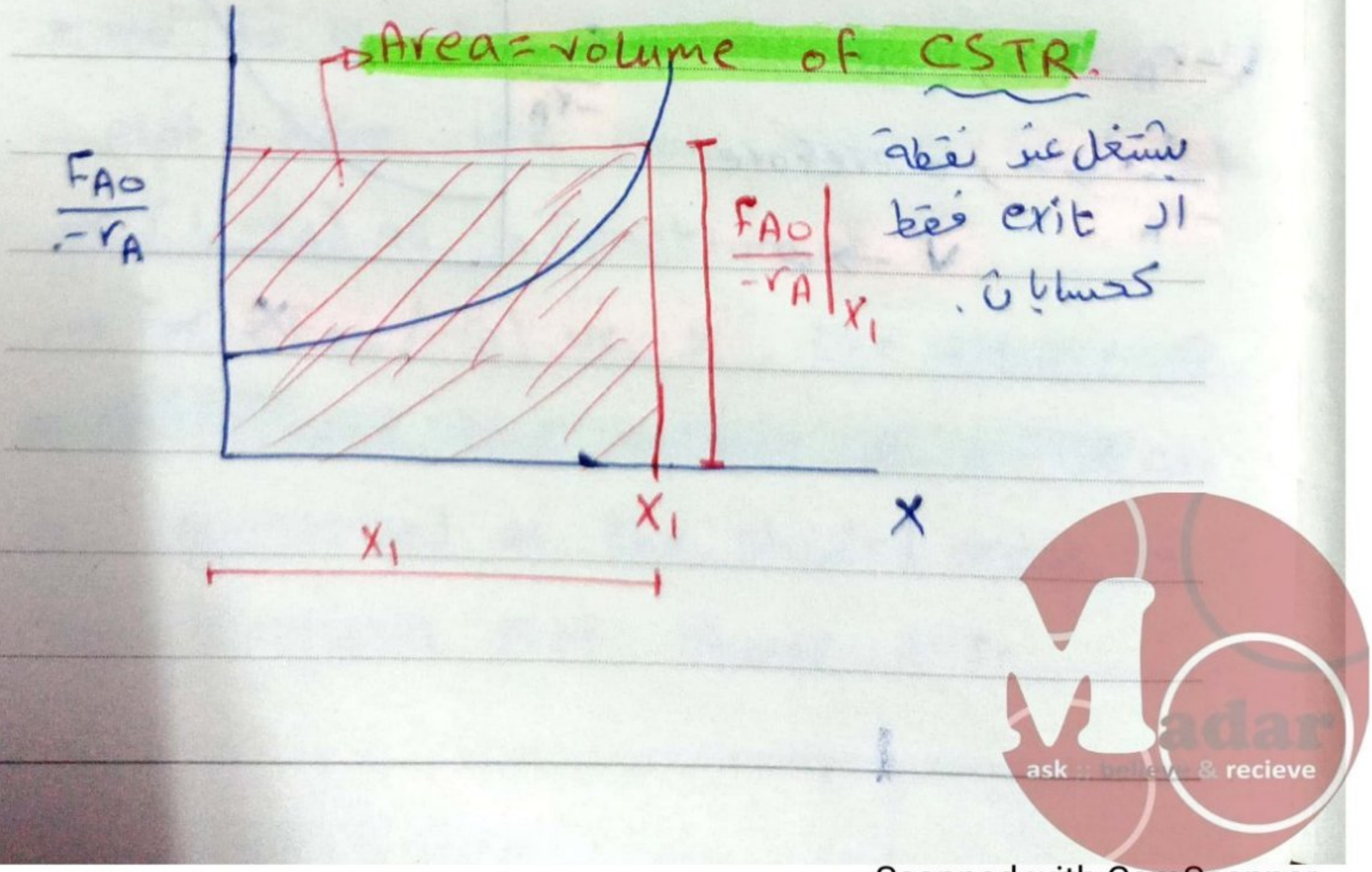
- For reversible reactions, the maximum conversion is the equilibrium conversion Xe
- At equilibrium, the reaction rate is zero ($-r_A = 0$).

Therefore: As $X \to Xe$, $-r_A \to 0$

thus $\frac{1}{-r_A} \to \infty$, and therefore $V \to \infty$

CSTR $V = \frac{F_{A0} X}{-r_A} \rightarrow V = \left(\frac{F_{A0}}{-r_A}\right)_{X_1} X_1$



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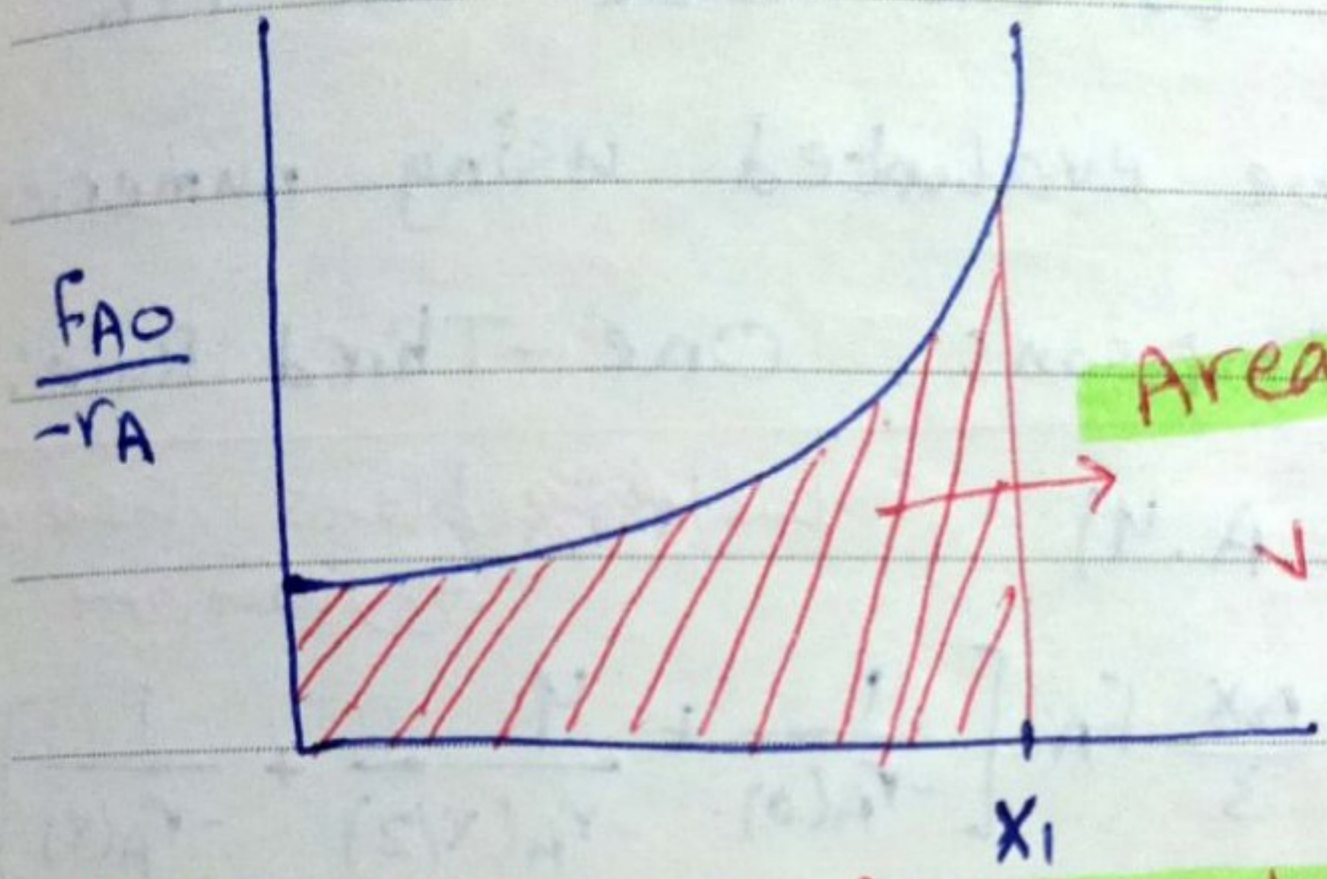
PFR

$$V = \int_0^X \frac{F_{A0}\,dX}{-r_A}$$



Area = volume of PFR

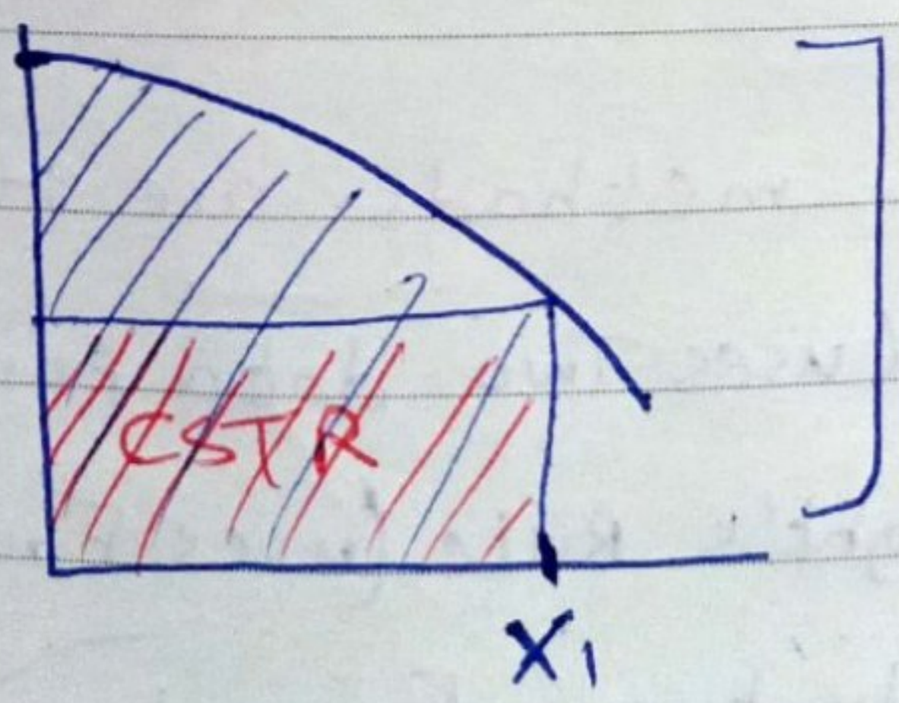
$$V = \int_0^{X_1} \left(\frac{F_{A0}}{-r_A}\right) dX$$

- Integration ⟶ Area under the curve

* order ≥ 1 → $V_{CSTR} > V_{PFR}$.

* order of rxn $0 \leq \cdot < 1$

نكونة حجم PFR اكبر من من حجم CSTR



PFR ⟵

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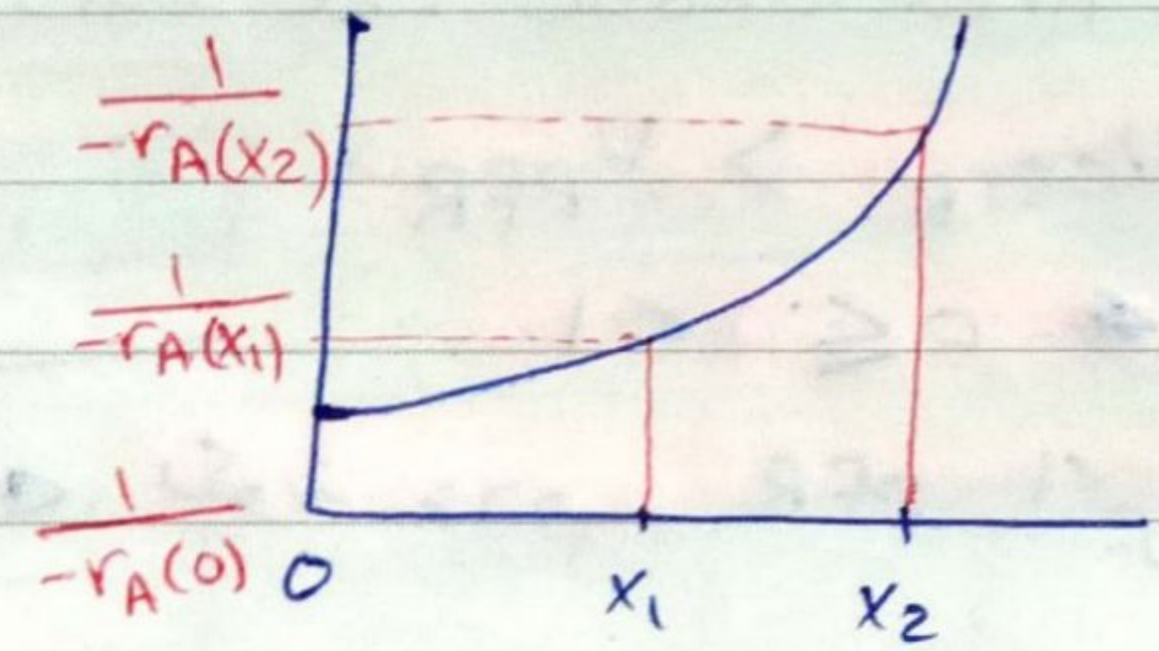
* Numerical Evaluations of Integrals

- The integral to calculate the PFR volume can be evaluated using numerical mebhod as Simpson's One-Third Rule:

(See Appendix A.4)

بنختار 3 نقاط على المسافة بينهم متساوية.

$$V = \int_0^X \frac{F_{A0}}{-r_A} dx = \frac{\Delta x}{3} F_{A0}\left[\frac{1}{-r_{A(0)}} + \frac{4}{-r_{A(x/2)}} + \frac{1}{-r_{A(x)}}\right]$$



- other numerical methods are :-

- Trapezoidal Rule (uses Two data points).
- Simpson's Three-Eight's Rule (uses Four data points)
- Five-point Quadrature Formula.

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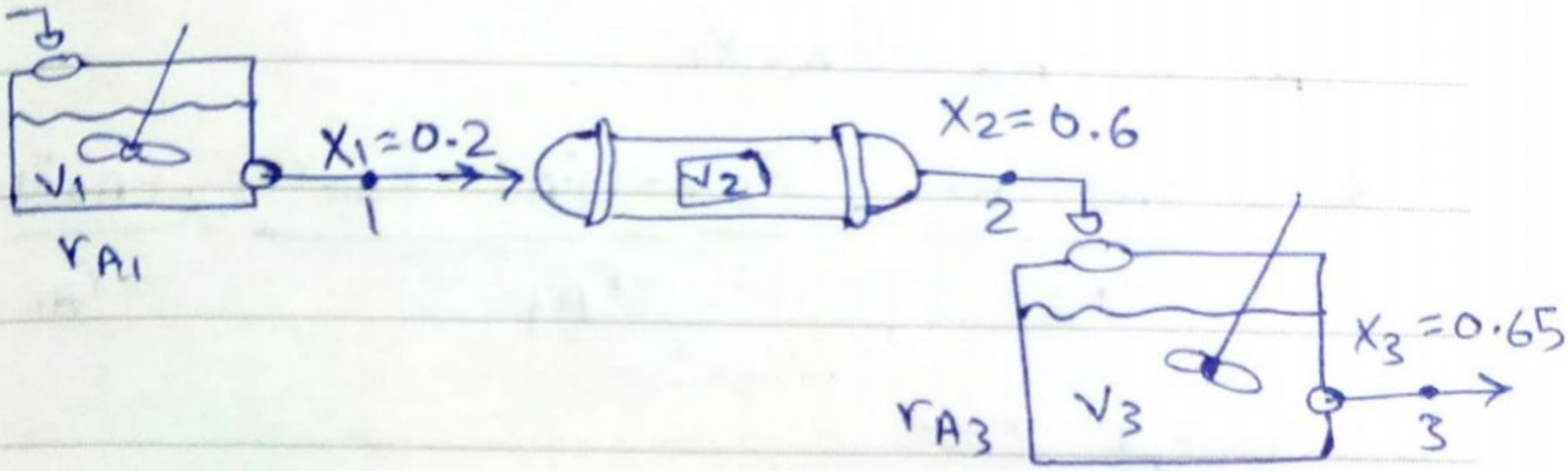
*Reactors in series.



- Given: $-r_A$ as a function of conversion, one can also design any sequence of reactors in series by defining X_i:

X_i = total moles of A reacted up to point i / moles of A fed to First reactor.

↳ Only valid if there are No side streams. Inlet stream (يعني اذا ماني ثانية).

Molar Flow rate of species A at point i:

$$F_{Ai} = F_{A0} - F_{A0} X_i$$

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* Reactor 1 :-

$$F_{A1} = F_{A0} - F_{A0} X_1$$

$$V_1 = \frac{F_{A0} - F_{A1}}{-r_{A1}} = \frac{F_{A0} - (F_{A0} - F_{A0}X_1)}{-r_{A1}} = \frac{F_{A0} X_1}{-r_{A1}}$$

* Reactor 2 :-

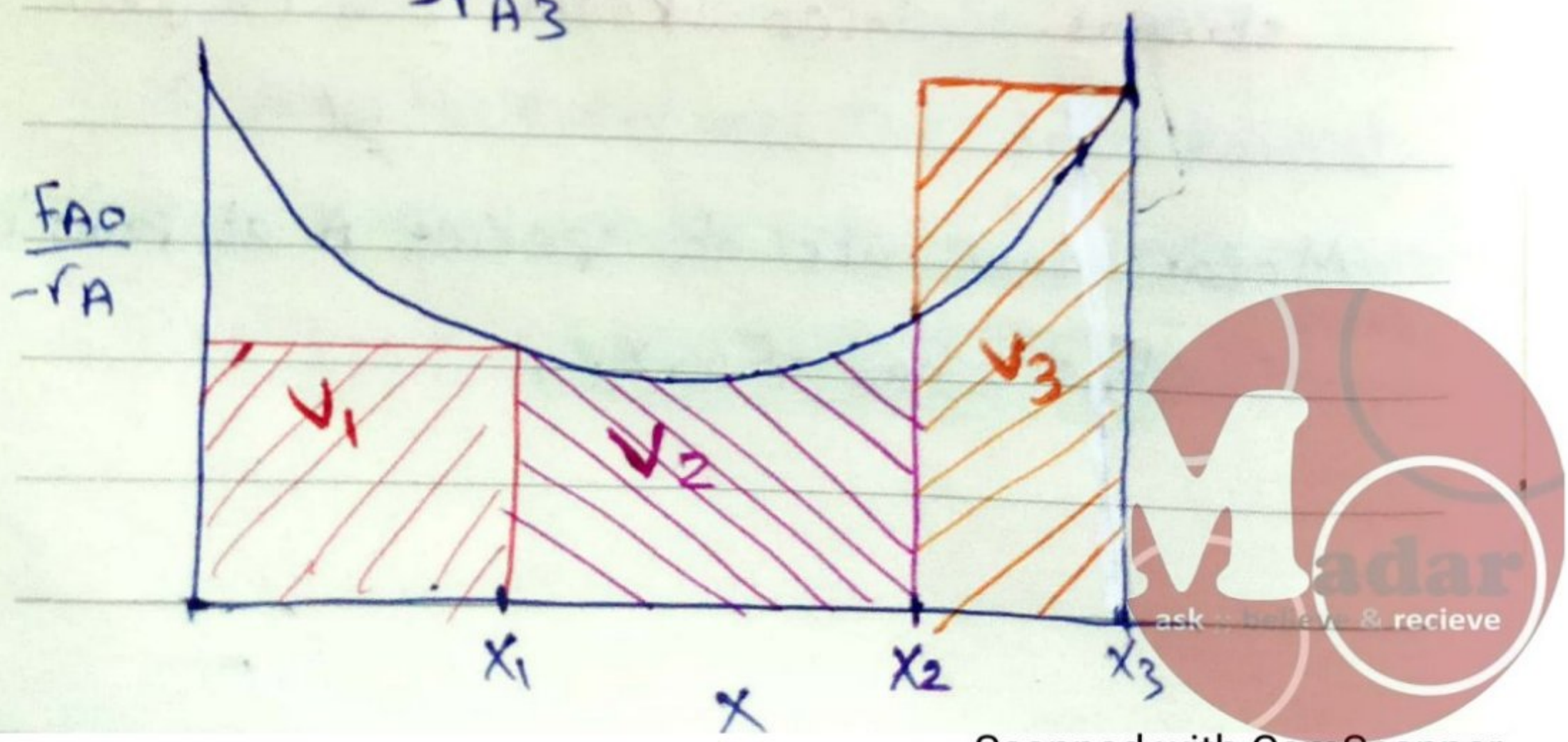
$$V_2 = \int_{X_1}^{X_2} \frac{F_{A0}}{-r_A} dx$$

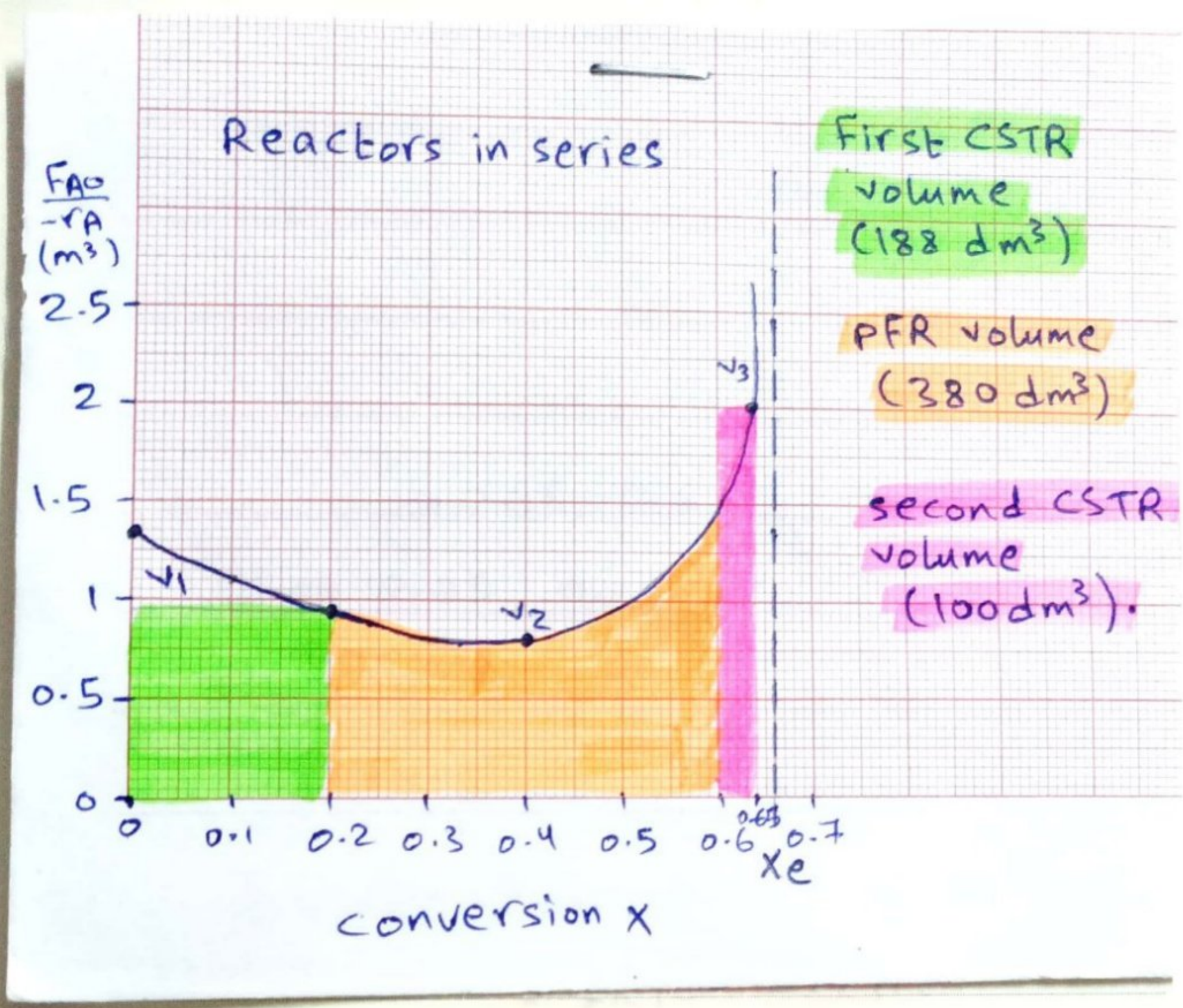
* Reactor 3 :

$$F_{A2} - F_{A3} + r_{A3} V_3 = 0$$

$$(F_{A0} - F_{A0} X_2) - (F_{A0} - F_{A0} X_3) + r_{A3} V_3 = 0$$

$$V_3 = \frac{F_{A0} (X_3 - X_2)}{-r_{A3}} .$$



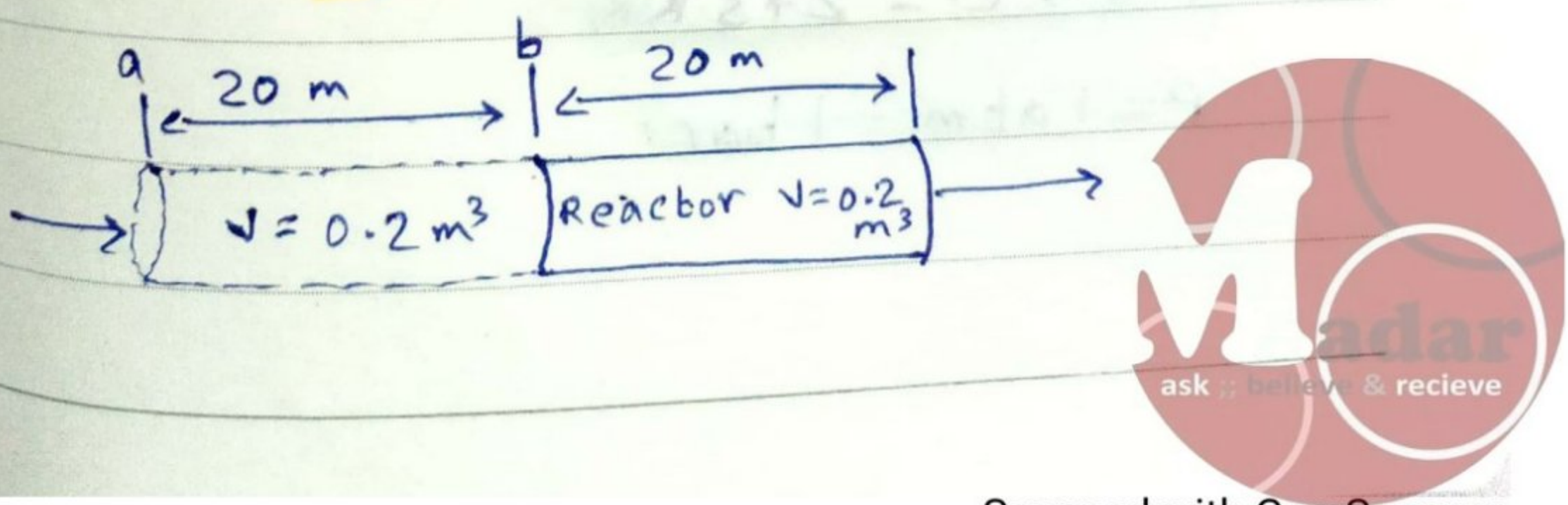


* Space Time (τ) "residance time".

→ is the time necessary to process one reactor volume of fluid at entrance conditions.

$\tau = \frac{V}{\nu_0}$, $V \rightarrow$ volume of the reactor.

$\nu_0 \rightarrow$ volumetric Flow rate.



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* Space velocity :-

$$SV \equiv \frac{\nu_o}{V} \quad , \quad SV = \frac{1}{\tau}$$

- Two space velocities commonly used in industry are :-

- liquid-hourly space velocity, LHSV

$$LHSV = \frac{\nu_{o\,liquid}}{V}$$

- gas-hourly space velocity, GHSV.

$$GHSV = \frac{\nu_{o\,STP}}{V}$$

* STP → standard T and p.

$T = 0^\circ C = 273\ K$

$P = 1\ atm = 1\ bar.$

$V_m = \frac{V}{n} = 22.41\ L/mol$

$dm^3/mol.$

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ch(3) Rate Laws and Stoichiometry.

* Types of Reactions :-

- Homogeneous reaction :- involves only one phase.
- Heterogeneous reaction :- involves more than one phase, and the reaction usually occurs at the interface between the phases.

- irreversible reaction :- proceeds in only one direction and continues in that direction until the reactants are exhasted.
- reversible reaction :- can proceed in either direction, depending on the concentrations of reactants and products relative to the corresponding equilibrium concentrations.

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rate of reaction = 0 (نقطة النهاية) ⟶ reactants are exhausted.

⟶ reach to equilibrium concentration.

* حتى يحصل التفاعل يصير colloide between molecules.

* Molecularity of Reaction

- The molecularity of areaction is the number of atoms, ions, or molecule involved (colliding) in areaction step.
- The terms unimolecular, bimolecular and termolecular refer to reactions involving, respectively, one, two, or three atoms (or molecules) interacting or colliding in any one reaction step.

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- Most common unimolecular reaction example:

$_{92}U^{238} \longrightarrow {}_{90}Th^{234} + {}_{2}He^{4}$ $\quad -r_U = K C_U$

- The True bimolecular reactions that exist are reactions involving Free radical, such as

$Br\bullet + C_2H_6 \rightarrow HBr + C_2H_5\bullet$

$-r_{Br.} = K C_{Br.} C_{C_2H_6}$

- probability of a termolecular reaction occurring is almost nonexistent, and In most instance the reaction pathway follows a series of bimolecular reactions as in the case of the reaction.

$2NO + O_2 \rightarrow 2NO_2$.

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- تفاعلات الـ termolecular تقريبا مش موجودة لأنه شبه مستحيل انه الـ 3molecules يتصادموا مع بعض في نفس اللحظة لتكوين الـ product .

Rate Laws

* Rate Law (Kinetic expression) :-

→ the algebraic equation that ~~relates~~ relates $-r_A$ to the species concentrations (is)

- power Law model :-

$$-r_A = K C_A^{\alpha} C_B^{\beta}$$

α order in A

β s s B

overall Reaction order : $n = \alpha + \beta$

$2A + B \longrightarrow 3C$

- A reaction Follows an elementary rate Law if the reaction orders just

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happens to agree with the stoichiometric coefficients for the reaction as written.

- e.g. If the above reaction follows an elementary rate law

$-r_A = k_A C_A^2 C_B$ → 2nd order in A, 1st order in B, overall 3rd order.

- Rate Laws are determined by experimental observation.

~

* Elementary → occures in one step. (order = stoichiometry) وبقدر اكتب قانون الrate

* Follows Elementary → doesn't occure in one step. (not Elementary).

لكنه بالمعرفة (بالتجربة كما اوجدنا قانون ال (Rate طلعلة ال (order = stoichiometry).

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$2A + B \rightarrow 3C$

- Rate Laws could be non-elementary.

- For example, reaction could be :-

- second order in A $-r_A = k_A C_A^2$
- zero order in B $-r_B = k_B C_A^2$
- overall second order $r_C = k_C C_A^2$

K → اذا ماجود هي غلبة.

① اذا كل stoi. = 1 فهي بتكونة للكل.

② ي ار stoi. مختلفية بتكونة (L.R)

↳ Limiting reactant.

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4.1 stoichiometry (constant volume Batch and Flow systems):-

* How to find $-r_A = f(X)$

step 1 :- Rate Law $-r_A = g(C_i)$

step 2 :- stoichiometry $(C_i) = h(X)$

step 3 :- combine to get $-r_A = f(X)$

* stoichiometry :-

- We shall set up stoichiometry Tables using species A as our basis of calculation in the following reaction.
- We will use the stoichiometric tables to express the concentration as a function of conversion.
- We will combine $C_i = f(X)$ with the appropriate rate law to obtain $-r_A = f(X)$.

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$$A + \frac{b}{a}B \rightarrow \frac{c}{a}C + \frac{d}{a}D$$

A → limiting reactant.

$$N_A = N_{A0} - N_{A0}X = N_{A0}(1 - X)$$

For every mole of A that reacts, (b/a) moles of B react. Therefore moles of B remaining:-

$$N_B = N_{B0} - \frac{b}{a}N_{A0}X = N_{A0}\left(\frac{N_{B0}}{N_{A0}} - \frac{b}{a}X\right)$$

Let $\Theta_B = \frac{N_{B0}}{N_{A0}}$

Then:

$$N_B = N_{A0}(\Theta_B - \frac{b}{a}X)$$

$$N_C = N_{C0} + \frac{c}{a}N_{A0}X = N_{A0}(\Theta_C + \frac{c}{a}X)$$

$$\Theta_C = \frac{N_{C0}}{N_{A0}}$$

في الـ P. 101 ← page. a- Table (3-3) ل - العودة

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For liquid.

$$\Theta_i = \frac{N_{i0}}{N_{A0}} = \frac{C_{i0}V_0}{C_{A0}V_0} = \frac{C_{i0}}{C_{A0}} = \frac{y_{i0}}{y_{A0}}$$

*Stoichiometry Constant volume

Batch System

- Note: (1) If the reaction occurs in the liquid phase.

(2) If a gas phase reaction occurs in a rigid (e.g. steel) batch reactor. (const. volume)

Then $V = V_0$ ← contraction or expansion يصير (2, b)

$$C_A = \frac{N_A}{V} = \frac{N_{A0}(1-X)}{V_0} = C_{A0}(1-X)$$

$$C_B = \frac{N_B}{V} = \frac{N_{A0}}{V_0}\left(\Theta_B - \frac{b}{a}X\right) = C_{A0}\left(\Theta_B - \frac{b}{a}X\right)$$

ويطبق على كل الـ species في الـ reaction.

→

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$$A + \frac{b}{a}B \rightarrow \frac{c}{a}C + \frac{d}{a}D$$

suppose $-r_A = k_A C_A^2 C_B$

Batch: $V = V_0$

$$-r_A = k_A C_{A0}^2 (1-X)^2 C_{A0}\left(\Theta_B - \frac{b}{a}X\right)$$

$$-r_A = k_A C_{A0}^3 (1-X)^2 \left(\Theta_B - \frac{b}{a}X\right)$$

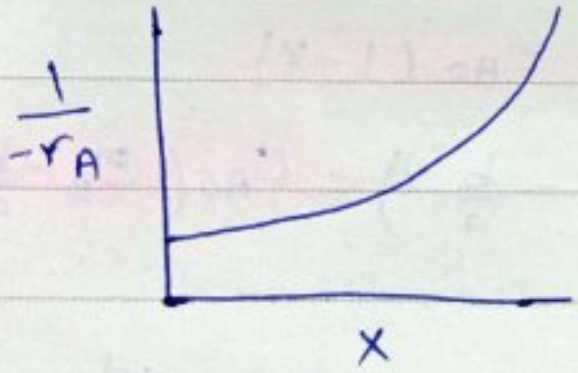
* Equimolar Feed $\rightarrow$ $\Theta_B = 1$

* stoichiometric Feed $\rightarrow$ $\Theta_B = \frac{b}{a}$

$\rightarrow$ constant volume batch.

and we have $-r_A = f(X)$

$X\uparrow$, $-r_A\downarrow$, $\frac{1}{-r_A}\uparrow$



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*Batch Reactor - Equilibrium conversion - Example

Calculate the equilibrium conversion for gas phase reaction, X_e

- consider the Following elementary reaction with $K_c = 20\ dm^3/mol$ and $C_{A0} = 0.2\ mol/dm^3$. Find X_e for a constant volume batch reactor.

$$2A \rightleftharpoons B$$

$$-r_A = k_A\left[C_A^2 - \frac{C_B}{K_c}\right]$$

Solution:- step 1 :- "mole balance"

$$\frac{dX}{dt} = \frac{-r_A V}{N_{A0}}$$

step 2 : rate law $-r_A = k_A C_A^2 - k_B C_B$

$$-r_A = k_A\left[C_A^2 - \frac{C_B}{K_c}\right]$$

rate const. of Forward — $K_c = \frac{k_A}{k_B}$

" " " backward

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Initial + change = Remaining

symbol	Initial	change	Remaining
A	N_{A0}	$-N_{A0}X$	$N_{A0}(1-X)$
B	0	$\frac{1}{2}N_{A0}X$	$N_{A0}\frac{X}{2}$

Totals: $N_{T0} = N_{A0}$, $N_T = N_{A0} - N_{A0}\frac{X}{2}$

Σ remaining

@ equilibrium:- $-r_A = 0$ $\quad 0 = C_{Ae}^2 - \frac{C_{Be}}{K_c}$ (equi.)

stoichiometry: $A \rightarrow B/2$

constant volume: $V = V_0$

$$C_{Ae} = \frac{N_{Ae}}{V} = C_{A0}(1 - X_e) \quad , C_{Be} = C_{A0}\frac{X_e}{2}$$

$$K_e = \frac{C_{Be}}{C_{Ae}^2} = \frac{C_{A0}\,X_e/2}{[C_{A0}(1-X_e)]^2} = \frac{X_e}{2C_{A0}(1-X_e)^2}$$

$$2K_eC_{A0} = \frac{X_e}{(1-X_e)^2} = (2)(20)(0.2) = 8$$

$\boxed{X_{eb} = 0.703}$ → max. conversion under these conditions.

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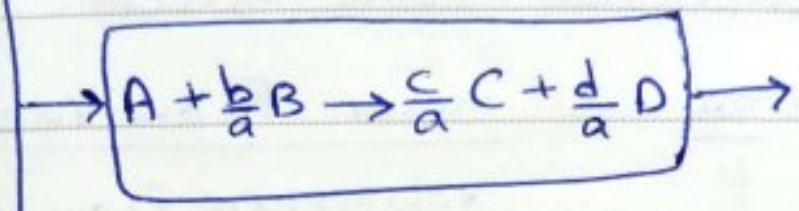
*Flow system stoichiometry Table.

Entering

F_{A0}
F_{B0}
F_{C0}
F_{D0}
F_{I0}



Leaving

F_A
F_B
F_C
F_D
F_I

species	symbol	Reactor Feed	change	Reactor Effluent
A	A	F_{A0}	$-F_{A0}X$	$F_A = F_{A0}(1-X)$
B	B	$F_{B0} = F_{A0}\Theta_B$	$\frac{-b}{a}F_{A0}X$	$F_B = F_{A0}(\Theta_B - \frac{b}{a}X)$

where $\Theta_i = \frac{F_{i0}}{F_{A0}} = \frac{C_{i0}V_0}{C_{A0}V_0} = \frac{C_{i0}}{C_{A0}} = \frac{y_{i0}}{y_{A0}}$

C	C	$F_{C0} = F_A\Theta_C$	$\frac{c}{a}F_{A0}X$	$F_C = F_{A0}(\Theta_C + \frac{c}{a}X)$
D	D	$F_{D0} = F_{A0}\Theta_D$	$\frac{d}{a}F_{A0}X$	$F_D = F_{A0}(\Theta_D + \frac{d}{a}X)$
Inert	I	$F_{I0} = F_{A0}\Theta_I$	—	$F_I = F_{A0}\Theta_I$
		F_{T0}		$F_T = F_{T0} + \delta F_{A0}X$

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where:

$$\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1$$

↳ Σ stoi. of (product − reactant).

concentration - Flow system

$$C_A = \frac{F_A}{v} \equiv \frac{\text{molar Flow rate}}{\text{volumetric Flow rate}}$$

* stoichiometry

- concentration Flow system: $C_A = \frac{F_A}{v}$.

- Liquid phase Flow system: $v = v_o$

$$C_A = \frac{F_A}{v} = \frac{F_{Ao}(1-X)}{v_o} = C_{Ao}(1-X)$$

$$C_B = \frac{N_B}{V} = \frac{N_{Ao}}{V_o}\left(\Theta_B - \frac{b}{a}X\right) = C_{Ao}\left(\Theta_B - \frac{b}{a}X\right)$$

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*Liquid Systems:-

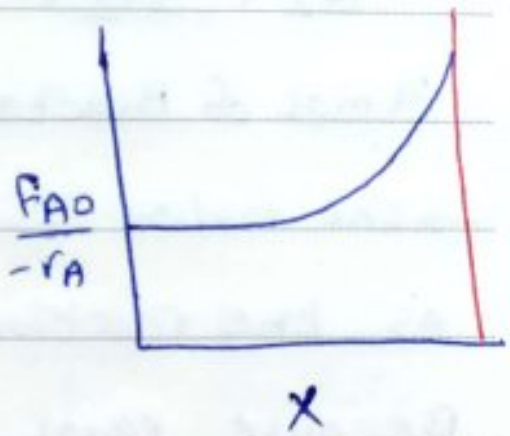
If the rate of reaction were $-r_A = kC_A C_B$

then we would have

$$-r_A = C_{A0}^2 (1-x)\left(\Theta_B - \frac{b}{a}x\right)$$

This gives us

$$-r_A = f(x)$$



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4.2 Stoichiometry (Gas phase flow systems).

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

4 mol of Reactants gives 2 mol of product.

→ the molar flow rate will be changing as the reaction progresses.

Because equal numbers of moles occupy equal volumes in the gas phase at the same T and p.

→ the volumetric flow rate will also change.

- العلاقة بين (n و V) طردية عند P,T ثابتين.

-Combining the compressibility factor equation of state with $Z = Z_0$

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stoichiometry: $C_T = \frac{P}{ZRT}$

$$C_{T_0} = \frac{P_0}{Z_0 R_0 T_0}$$

out → $F_T = C_T V$

in → $F_{T_0} = C_{T_0} V_0$

$$\therefore V = \frac{F_T}{C_T} = \frac{F_T Z R T}{P} = \frac{F_T R T}{P} \frac{P_0}{C_{T_0} R_0 T_0}$$

we obtain

$$\boxed{V = V_0 \frac{F_T}{F_{T_0}} \frac{P_0}{P} \frac{T}{T_0}}$$

$$C_A = \frac{F_A}{V} = \frac{F_A}{V_0 \left(\frac{F_T}{F_0}\right)} \frac{P}{P_0} \frac{T_0}{T} = \frac{F_{T_0}}{V_0} \frac{F_A}{F_T} \frac{P}{P_0} \frac{T_0}{T}$$

since $C_{T_0} = F_{T_0} / V_0$

$$C_A = \frac{F_A}{V} = C_{T_0} \frac{F_A}{F_T} \frac{P}{P_0} \frac{T_0}{T}$$

- using the same method,

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$$C_B = C_{T0} \frac{F_B}{F_T} \frac{P}{P_0} \frac{T_0}{T}$$

* The total molar flow rate is:-

$$F_T = F_{T0} + F_{A0}\delta X$$

substituting F_T gives: $v = v_0 \frac{F_T}{F_{T0}} \frac{P_0}{P} \frac{T_0}{T}$

$$v = v_0 \left(\frac{F_{T0} + F_{A0}\delta X}{F_{T0}} \right) \frac{T}{T_0} \frac{P_0}{P} = v_0 \left(1 + \frac{F_{A0}}{F_{T0}}\delta X\right) \frac{T}{T_0} \frac{P_0}{P}$$

$$v = v_0 (1 + y_{A0}\delta X) \frac{T}{T_0} \frac{P_0}{P} = v_0 (1 + \varepsilon X) \frac{T}{T_0} \frac{P_0}{P}$$

where $\varepsilon = y_{A0}\delta$.

Concentration Flow system: $C_A = \frac{F_A}{v}$

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Gas phase Flow system : $V = V_0(1+\varepsilon X)\frac{T}{T_0}\frac{P_0}{P}$

L.R

$$C_A = \frac{F_A}{V} = \frac{F_{A0}(1-X)}{V_0(1+\varepsilon X)\frac{T}{T_0}\frac{P_0}{P}} = C_{A0}\frac{(1-X)}{(1+\varepsilon X)}\frac{T_0}{T}\frac{P}{P_0}$$

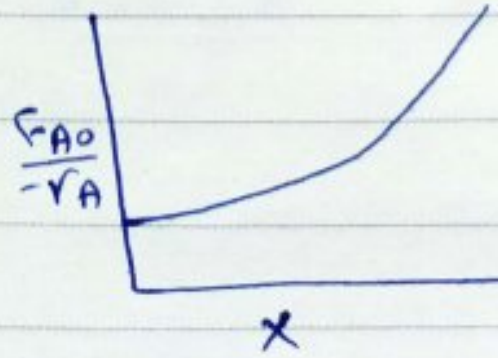
$$C_B = \frac{F_B}{V} = \frac{F_{A0}(\Theta_B - \frac{b}{a}X)}{V_0(1+\varepsilon X)\frac{T}{T_0}\frac{P_0}{P}} = C_{A0}\frac{(\Theta_B - \frac{b}{a}X)}{(1+\varepsilon X)}\frac{T_0}{T}\frac{P}{P_0}$$

For any species.

IF $-r_A = kC_AC_B$

$$-r_A = k_A C_{A0}^2\left[\frac{(1-X)}{(1+\varepsilon X)}\frac{(\Theta_B - \frac{b}{a}X)}{(1+\varepsilon X)}\left(\frac{P}{P_0}\frac{T_0}{T}\right)^2\right]$$

This gives us



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where

$$\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1$$

δ = change in total number of moles / moles of A reacted

$$\varepsilon = \left(\frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1\right) \frac{F_{A0}}{F_{T0}} = y_{A0}\,\delta$$

ε = change in total number of moles For complete conversion / total number of moles fed to the reactor.

δ → -ve, 0, +ve

- في فرق بينه Xe في الـ batch أو Flow.

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*Equilibrium Conversion (X_{ef}) For Gas phase Flow Reaction System.

- Example :- "change in volume" consideration في حالة

Consider the Following elementary reaction where

$$2A \rightleftharpoons B$$

$$-r_A = k_A\left[C_A^2 - \frac{C_B}{K_c}\right]$$

$K_c = 20\ dm^3/mol$ and $C_{A0} = 0.2\ mol/dm^3$.

- calculate Equilibrium Conversion For an isothermal isobaric Flow reactor (X_{ef}) ؟؟

- Solution :-

Rate Law : $-r_A = k_A\left[C_A^2 - \frac{C_B}{K_c}\right]$.

Stoichiometry : $A \rightarrow \frac{1}{2}B$

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species	Feed	change	Effluent
A	F_{A0}	$-F_{A0}X$	$F_A = F_{A0}(1-X)$
B	0	$+F_{A0}X/2$	$F_B = F_{A0}X/2$
Total	$F_{T0}=F_{A0}$		$F_T = F_{A0} - F_{A0}X/2$

Stoichiometry: Gas isothermal $T=T_0$

Gas isobaric $P=P_0$

$$V = V_0(1+\varepsilon X)$$

$$C_A = \frac{F_{A0}(1-X)}{V_0(1+\varepsilon X)} = \frac{C_{A0}(1-X)}{1+\varepsilon X}$$

$$C_B = \frac{F_B}{V} = \frac{F_{A0}X/2}{V_0(1+\varepsilon X)} = \frac{C_{A0}X}{2(1+\varepsilon X)}$$

$$-r_A = k_A\left[\left(\frac{C_{A0}(1-X)}{1+\varepsilon X}\right)^2 - \frac{C_{A0}X}{2(1+\varepsilon X)K_c}\right]$$

pure $A \rightarrow y_{A0} = 1$

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$C_{A0} = y_{A0} P / RT_0 \rightarrow C_{A0} = P_0 / RT_0$

$\varepsilon = y_{A0} \delta = (1)\left(\frac{1}{2} - 1\right) = \frac{-1}{2}$

At equilibrium : $-r_A = 0$

$$2K_c C_{A0} = \frac{X_e (1 + \varepsilon X_e)}{(1 - X_e)^2}, \quad \varepsilon = \frac{-1}{2}$$

$$2K_c C_{A0} = 2 \times \frac{20\, dm^3}{mol} \times \frac{0.2\, mol}{dm^3} = 8$$

$$8 = \frac{X_e - 0.5 X_e^2}{1 - 2X_e + X_e^2} \rightarrow 8.5 X_e^2 - 17 X_e + 8 = 0$$

$X_{ef} = 0.757$

For Batch system:

$X_{eb} = 0.703$

ε → -ve ,
→ 0 .
→ +ve .

N considiration في حالة ε بتختلف عن بعض

change in volume.

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Memo No. part (3)

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* Design of Continuous stirred Tank Reactors (CSTRs)

- typically used For Liquid-phase reactions

$$V = \frac{F_{A_0} X}{(-r_A)_{exit}} \quad , \quad \tau = \frac{V}{v_0} = \frac{C_{A_0} X}{-r_A}$$

* CSTRs in Parallel:-

- For equal sized reactors, and feed distributed equally:

$$V_i = \frac{F_{A_{0i}}}{-r_{A_i}} x_i \quad , \quad V_i = \frac{V}{n}$$

$$F_{A_{0i}} = \frac{F_{A_0}}{n}$$

$x_i = X$ and $-r_{A_i} = -r_A$ (same in all reacts)

$$\rightarrow \boxed{V = \frac{F_{A_0} X}{-r_A}}$$

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* CSTRs in Series :-

$$V_1 = \frac{F_{A0}}{-r_{A1}} X_1 \rightarrow C_{A1} = \frac{C_{A0}}{1 + k_1 \tau_1}$$

$$V_2 = \frac{F_{A0}}{-r_{A2}} (X_2 - X_1)$$

$$C_{A2} = \frac{C_{A1}}{1 + k_2 \tau_2} = \frac{C_{A0}}{(1 + k_1 \tau_1)(1 + k_2 \tau_2)}$$

• For equal sized reactors operating at the same T.

$$C_{An} = \frac{C_{A0}}{(1 + \tau k)^n} = \frac{C_{A0}}{(1 + Da)^n} \quad \text{and}$$

$$X = 1 - \frac{1}{(1 + Da)^n} = 1 - \frac{1}{(1 + \tau k)^n}$$

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* A single CSTR :-

• Damköhler number (Da) is a dimensionless number that can give us a quick estimate of the degree of conversion that can be achieved in continuous flow reactors.

if $Da < 0.1$, then $X < 0.1$

, $Da > 10$, , $X > 0.9$

$$Da = \frac{-r_{A_o} V}{F_{A_o}}$$

- For First order reaction, $Da = \tau k$.

- what is Da For a second order reaction?

• First-order irreversible reaction,

$$-r_A = k C_A$$

$$\tau = \frac{1}{k}\left(\frac{X}{1-X}\right) \rightarrow X = \frac{\tau k}{1+\tau k}$$

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$\tau k = Da$ = Damköhler number

• Dam Köhler number is the ratio of the rate of reaction of A to the rate of convective transport of A at the entrance to the reactor.

$$Da = \frac{-r_{AO} V}{F_{AO}} = \frac{\text{Rate of reaction at entrance}}{\text{Entering Flow rate of A}}$$

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5.1 Isothermal Reactors Design

* Algorithm for Isothermal Reactor Design

1. Mole balances and Design Equation.
2. Rate Laws.
3. Stoichiometry.
4. Combine
5. Evalute
   - → graphically.
   - → Numerically.
   - → Analytically.
   - → Software packages.

- الرجوع لصفحة 147 في الكتاب 4th Edition.

*Example (1):-

Liquid phase Undergraduate Laboratory Experiment

$$(CH_2CO)_2O + H_2O \rightarrow 2CH_3COOH$$

$$A + B \longrightarrow 2C$$

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Feed

- Volumetric Flow rate $V_o = 0.0033\ dm^3/s$
- Acetic Anhydride 7.8% (1M)
- Water 92.2% (51.2M)
- Elementary with k' $1.95 \times 10^{-4}\ dm^3/(mol \cdot s)$

Case 1 CSTR $V = 1\ dm^3$

Case 2 PFR $V = 0.311\ dm^3$

"موجود في الـ e-Learning & pdf و Example ② أيضاً."

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5.2 pressure Drop in PBR

Concentration Flow system: $C_A = \frac{F_A}{\dot{V}}$

Gas phase Flow system $V = V_o(1+\varepsilon X)\frac{T}{T_o}\frac{P_o}{P}$

$$C_A = \frac{F_A}{\dot{V}} = \frac{F_{Ao}(1-X)}{V_o(1+\varepsilon X)\frac{T}{T_o}\frac{P_o}{P}} = \frac{C_{Ao}(1-X)}{1+\varepsilon X}\frac{T_o}{T}\frac{P}{P_o}$$

$\frac{P}{P_o}$ → تأثر عند تركيز المتفاعلات والنواتج.

$$C_B = \frac{F_B}{\dot{V}} = \frac{F_{Ao}(\theta_B - \frac{b}{a}X)}{V_o(1+\varepsilon X)\frac{T}{T_o}\frac{P_o}{P}} = \frac{C_{Ao}(\theta_B - \frac{b}{a}X)}{1+\varepsilon X}\frac{T_o}{T}\frac{P}{P_o}$$

Note:- press. drop doesn't affect Liquid phase reactions.

* Sample Question:-

Analyze the Following second order gas phase reaction that occurs isothermally in a PBR:

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$A \longrightarrow B$

- Mole balance: Must use the differential Form of the mole balance to seperate variables:

$$F_{A0}\frac{dX}{dw} = -r_A'$$

- Rate Laws: second order in A and irreversible

$$-r_A' = kC_A^2$$

- Stoichiometry

$$C_A = \frac{F_A}{\dot{v}} = \frac{C_{A0}(1-X)}{(1+\varepsilon X)}\frac{P}{P_0}\frac{T_0}{T}$$

$$\xrightarrow[T=T_0]{\text{Isothermal}} C_A = \frac{F_A}{v} = \frac{C_{A0}(1-X)}{(1+\varepsilon X)}\frac{P}{P_0}$$

- Combine:- $$\boxed{\frac{dX}{dw} = \frac{kC_{A0}^2}{F_{A0}}\frac{(1-X)^2}{(1+\varepsilon X)^2}\left(\frac{P}{P_0}\right)^2}$$

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Need to find $\frac{P}{P_0}$ as a function of W (or V if you have a PFR).

$\frac{P}{P_0}$ → (يحصل في الـ PBR و الـ PFR)

* Ergun Equation:

$$\frac{dP}{dz} = \frac{-G}{\rho g_c D_p}\left(\frac{1-\phi}{\phi^3}\right)\left[\frac{150(1-\phi)M}{D_p} + 1.75G\right]$$

(Laminar) (Turbulent)

G → mass Flux , ϕ → void

Constant mass Flow:

$$\dot{m} = \dot{m}_0 \rightarrow \rho = \rho_0 v_0 \rightarrow \rho = \rho_0 \frac{v_0}{v}$$

$$v = v_0 \frac{F_T}{F_{T0}} \frac{P_0}{P} \frac{T}{T_0} = v_0(1+\varepsilon X)\frac{P_0}{P}\frac{T}{T_0}$$

* Variable Density

$$\rho = \rho_0 \frac{P}{P_0}\frac{T_0}{T}\frac{F_{T0}}{F_T}$$

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*in Gases.

*variable density → (change of P → change of density)

* $\rho \rightarrow f(T, P)$

$$\frac{dP}{dz} = \frac{-G}{\rho_0 g_c D_p}\left(\frac{1-\phi}{\phi^3}\right)\left[\frac{150(1-\phi)M}{D_p} + 1.75G\right]\frac{P_0}{P}\frac{T}{T_0}\frac{F_T}{F_{T0}}$$

Let: $$\beta_0 = \frac{G}{\rho_0 g D_p}\left(\frac{1-\phi}{\phi^3}\right)\left[\frac{150(1-\phi)M}{D_p} + 1.75G\right].$$

Catalyst Weight → الارتفاع.

$$W = z A_c \rho_b = z A_c (1-\phi)\rho_c$$

ρ_b = bulk density

ρ_c = solid catalyst density

ϕ = porosity (void fraction)

$(1-\phi)$ = solid fraction.

A_c → cross sectional Area of the bed.

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$$\frac{dP}{dW} = \frac{-\beta_0}{A_c(1-\phi)\rho_c} \frac{P_0}{P} \frac{T}{T_0} \frac{F_T}{F_{T0}}$$

Let $\alpha = \frac{2\beta_0}{A_c(1-\phi)\rho_c} \frac{1}{P_0}$

$$\frac{dy}{dW} = \frac{-\alpha}{2y} \frac{T}{T_0} \frac{F_T}{F_{T0}}, \quad y = \frac{P}{P_0}$$

we will use this form for single reactions :

$$\frac{d(P/P_0)}{dW} = \frac{-\alpha}{2} \frac{1}{(P/P_0)} \frac{T}{T_0} (1+\varepsilon X)$$

$$\boxed{\frac{dy}{dW} = \frac{-\alpha}{2y} \frac{T}{T_0} (1+\varepsilon X)}$$

$$\boxed{\frac{dy}{dW} = \frac{-\alpha}{2y} (1+\varepsilon X)}$$ Isothermal case.

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$$\frac{dX}{dw} = \frac{k C_{A0}^2 (1-X)^2}{F_{A0} (1+\varepsilon X)^2} y^2$$

$\frac{dX}{dw} = f(X,P)$ and $\frac{dP}{dw} = f(X,P)$ or $\frac{dy}{dw} = f(y,X)$

→ For the special case of isothermal operations and epsilon=0 we can obtain an analytical solution.

- Packed bed Reactors

For $\varepsilon = 0$, isothermal

$$\frac{dy}{dw} = \frac{-\alpha}{2y} (1+\varepsilon X)$$

when $W=0 \rightarrow y=1$ $\xrightarrow{\text{or}}$ $(P_0 = P)$

$$dy^2 = -\alpha\, dw \rightarrow y^2 = 1 - \alpha w$$

$$\boxed{y = (1-\alpha w)^{\frac{1}{2}}}$$

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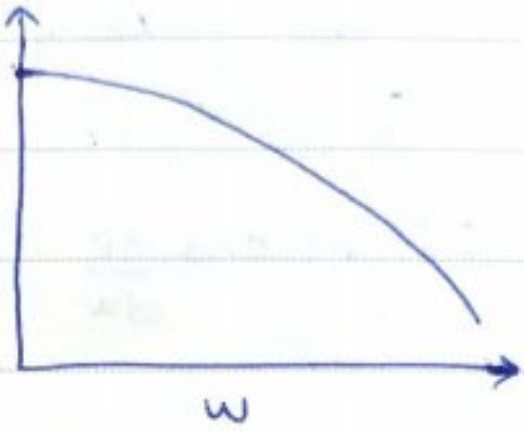
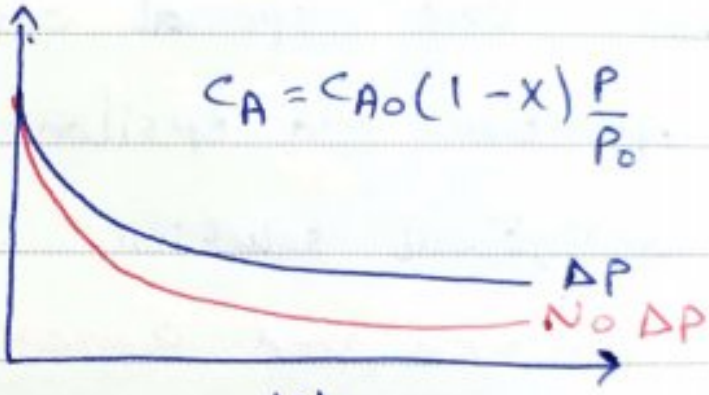
① * pressure drop in a PBR



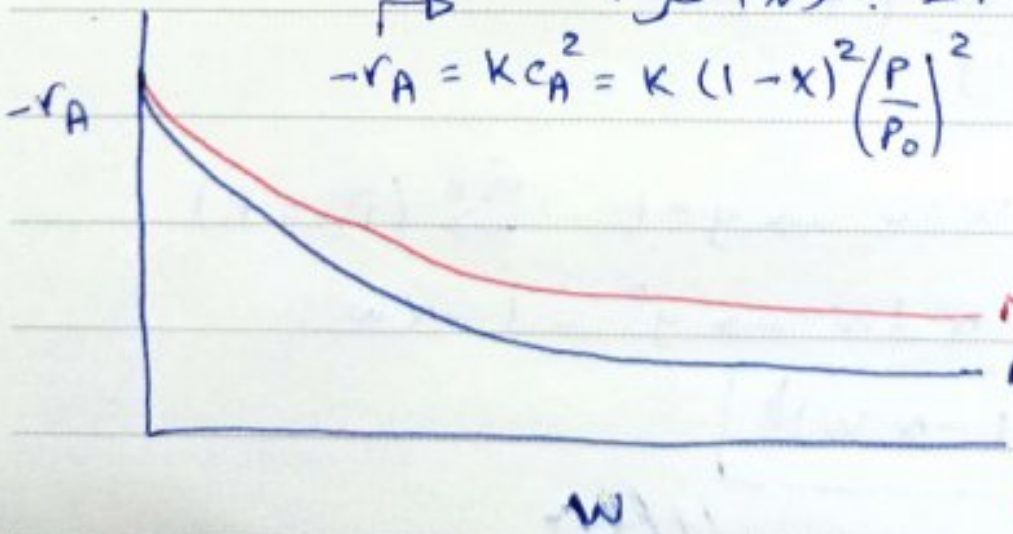
* التركيز بالنهاية بدون ΔP بكون اقل من لو في ΔP .



② Concentration profile in a PBR.

بدون ΔP بتكون اكثر.

$$-r_A = kC_A^2 = k(1-X)^2\left(\frac{P}{P_0}\right)^2$$



③ Reaction Rate in a PBR

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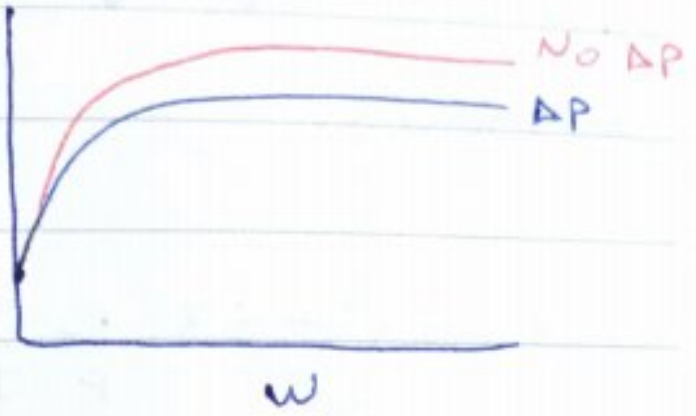
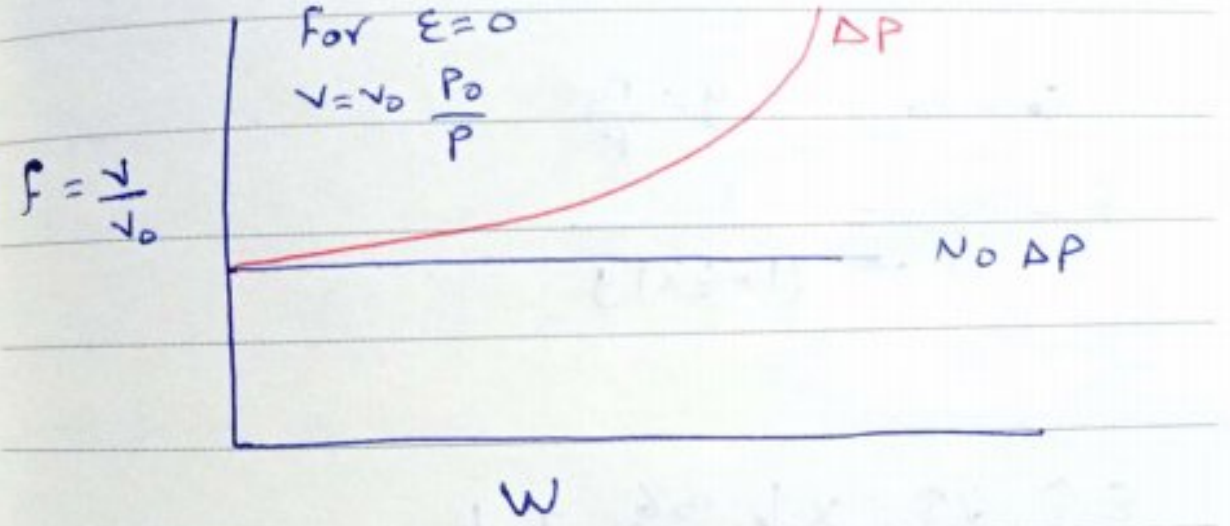
④ Conversion in a PBR.



- بدونه ΔP بكونه أعلى.



⑤ Flow Rate in a PBR.

- No ΔP → ($\frac{V}{V_0}$ → constant).

ΔP → (P ↓ V ↑) "اذا اي شي ثاني ثابت"

- كما يزداد ال volumetric Flow rate بقل ال Residance Time. فبقل ال conversion.

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P↓ $\dot{V}$↑ τ↓ X↓

*summery :-

$$V = V_0 (1 + \varepsilon X) \frac{P_0}{P} \frac{T}{T_0}$$

$$T_0 = T_0 \qquad y = \frac{P_0}{P}$$

$$f = \frac{V_0}{V} = \frac{1}{(1+\varepsilon X)\, y}$$

ε↑ $\dot{V}$↑ X↓ ثابت τ↓

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5.3 Examples on pressure Drop.

- Example 1 :- Gas phase Reaction in PBR For $\delta = 0$

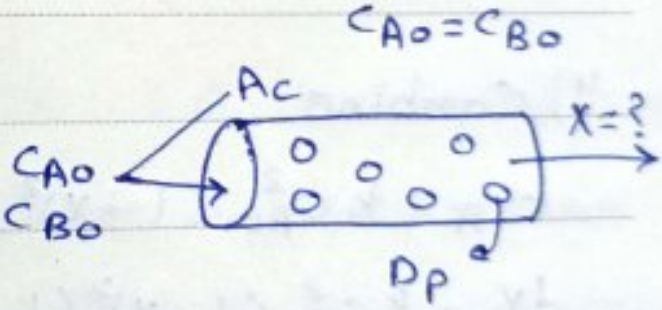
Gas phase reaction in PBR with $\delta = 0$ (Analytical solution) $A + B \rightarrow 2C$

Equimolar Feed of A and B and:

$k_A = 1.5\ dm^3/mol/kg/min$

$\alpha = 0.0099\ kg^{-1}$

Find X at 100 kg



1) mole balance $\frac{dX}{dW} = \frac{-r_A'}{F_{A0}}$

2] Rate Law $-r_A' = kC_A C_B$

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3) stoichiometry $C_A = C_{A0}(1-x)y$

$C_B = C_{A0}(1-x)y$

$$\frac{dy}{dw} = \frac{-\alpha}{2y}, \quad 2y\,dy = -\alpha\,dw$$

$w=0$, $y=1$ $\quad y^2 = 1-\alpha w$

$$\boxed{y = (1-\alpha w)^{\frac{1}{2}}}$$

4) Combine

$$-r_A = k C_{A0}^2 (1-x)^2 y^2 = k C_{A0}^2 (1-x)^2 (1-\alpha w)$$

$$\frac{dx}{dw} = \frac{k C_{A0}^2 (1-x)^2 (1-\alpha w)}{F_{A0}}$$

$$\frac{dx}{(1-x)^2} = \frac{k C_{A0}^2}{F_{A0}} (1-\alpha w)\,dw$$

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$$\frac{X}{1-X} = \frac{k C_{A0}^2}{F_{A0}} \left(W - \frac{\alpha W^2}{2} \right)$$

@ $W=0$, $X=0$ and @ $W=W$, $X=X$

$X=0.6$ (with pressure drop).

$X=0.75$ (without pressure drop, $\alpha=0$).

- نلاحظ انه X اكبر بدون pressure drop.

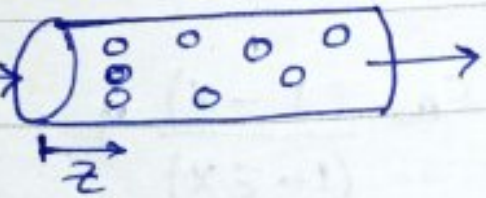
*Example (2) Gas phase Reaction in PBR For $\delta \neq 0$.

The reaction $A+2B \rightarrow C$ is carried out in apacked bed reactor in which there is pressure drop. The Feed is stoichiometric in A and B.

$P_0 = 10 atm$

$C_{A0} = 0.2 \frac{mol}{dm^3}$

$F_{A0} = 2 \frac{mol}{min}$



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Plot the conversion and pressure ratio $y = P/P_o$ as a function of catalyst weight up to 100 kg.

- Additional information

$k_A = 6\ dm^3/mol^2/kg/min$

$\alpha = 0.02\ kg^{-1}$

$A + 2B \rightarrow C$

1) mole balance $\frac{dx}{dw} = \frac{-r_A'}{F_{Ao}}$

2) Rate Law $-r_A' = kC_A C_B^2$

3) Stoichiometry : Gas, Isothermal

$$V = V_o(1 + \varepsilon X)\frac{P_o}{P}$$

$$C_A = C_{Ao}\frac{(1-X)}{(1+\varepsilon X)}y$$

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4) $C_B = C_{A0} \dfrac{(\theta_B - 2X)}{(1+\varepsilon X)} y$

5) $\dfrac{dy}{dw} = \dfrac{-\alpha}{2y} (1+\varepsilon X)$

6) $f = \dfrac{v}{v_0} = \dfrac{1+\varepsilon X}{y}$

7) $\varepsilon = y_{A0}[1-(-2)] = \frac{1}{3}(-2) = -2/3$

$C_{A0}=0.2$, $F_{A0} = 2$, $k = 6$, $\alpha = 0.02$

Initial values $w=0$, $x=0$, $y=1$

Final $w = 100$

Combine with polymath.

If $\delta \neq 0$, polymath must be used to solve.

(في صورة لحل الـ Polymath).

+ رسمة بيانية (بالبرنامج).

Example 2: Gas Phase Reaction in PBR for δ≠0

POLYMATH Results
POLYMATH Report 01-30-2006, Rev5.1.233

Calculated values of the DEQ variables

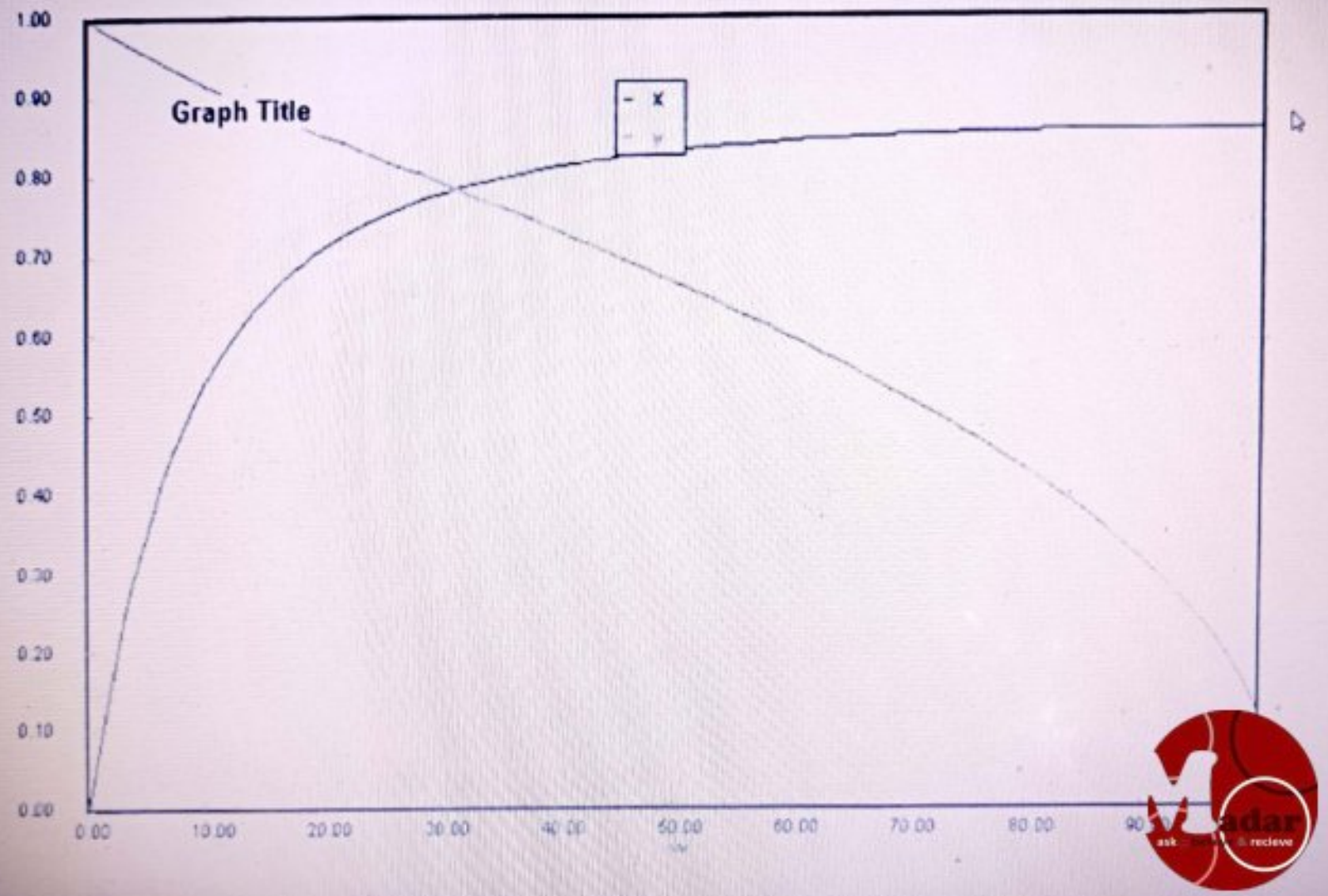
Variable	initial value	minimal value	maximal value	final value
W	0	0	100	100
X	0	0	0.8587763	0.8587763
y	1	0.1148659	1	0.1148659
eps	-0.6666667	-0.6666667	-0.6666667	-0.6666667
Cao	0.2	0.2	0.2	0.2
ThetaB	2	2	2	2
Cb	0.4	0.0151789	0.4	0.0151789
Fao	2	2	2	2
k	6	6	6	6
Ca	0.2	0.0075895	0.2	0.0075895
alpha	0.02	0.02	0.02	0.02
ra	-0.192	-0.192	-1.049E-05	-1.049E-05

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(X)/d(W) = -ra/Fao
[2] d(y)/d(W) = -alpha*(1+eps*X)/2/y

Explicit equations as entered by the user
[1] eps = (1-2-1)/3
[2] Cao = 0.2
[3] ThetaB = 2
[4] Cb = Cao*(ThetaB-2*X)/(1+eps*X)*y
[5] Fao = 2
[6] k = 6
[7] Ca = Cao*(1-X)/(1+eps*X)*y
[8] alpha = 0.02
[9] ra = -k*Ca*Cb^2

Example 2: Gas Phase Reaction in PBR for δ≠0



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- الرسمة البيانية ← بنلاحظ انه الـ X صارت ثابتة تقريباً من عند (W=80) وبعد وبالتالي ما في داعي نستخدم $W_{(catalyst)}$ اكثر من 80 Kg وبقدر نعرف لما W=80, كم الـ pressure ratio في الرسمة.

* Gas phase reaction in PBR with pressure Drop $T = T_o$

mole balance (1) $\frac{dX}{dW} = \frac{-r_A'}{F_{A0}}$

Rate Law (2) $-r_A' = k C_A$

stoichiometry Gas $T = T_o$

(3) $C_A = \frac{C_{A0}(1-X)}{(1+\varepsilon X)} y$

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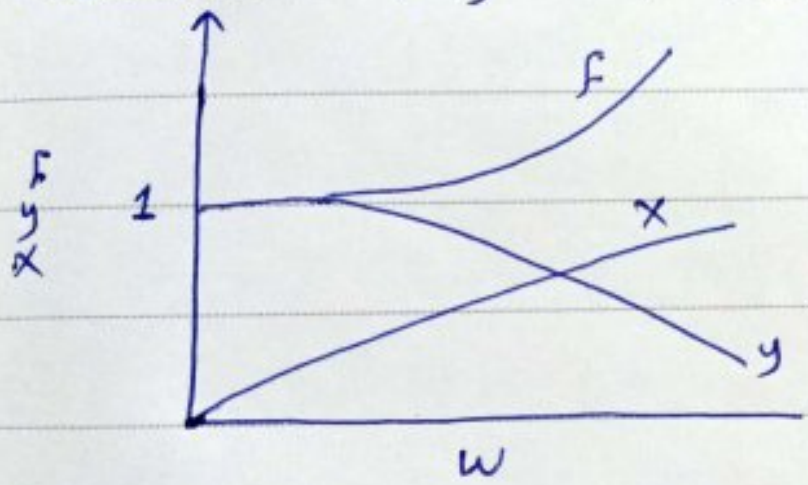
(4) $\frac{dy}{dw} = \frac{-\alpha(1+\varepsilon X)}{2y}$

(5)-(9) parameters, $\varepsilon, \alpha, \cdots$

combine : polymath with combine For you



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* Collection and analysis of Rate Data:-

① power law models for homogeneous reaction $-r_A = kC_A^{\alpha}$, $-r_A = kC_A^{\alpha}C_B^{\beta}$

② Select reactor type and corresponding mole balance.

- batch reactor

$$-r_A = \frac{-dC_A}{dt}$$

- differential PBR (mole balance on product P)

$$-r_A = \frac{F_P}{\Delta W} = \frac{v_o C_P}{\Delta W}$$

③ process your data in terms of measured variable (N_A, C_A or P_A), rewrite your mole balance in terms of the measured variable.

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(4) Simplification :- if one of the reactants is in excess, assume its concentration is constant.

* **Batch reactor**

(A) - Differential analysis

$$-r_A = k C_A^{\alpha} = -dC_A/dt$$

$$\rightarrow \ln\left(\frac{-dC_A}{dt}\right) = \ln k + \alpha \ln C_A$$

↳ slope

(1) Find $\frac{-dC_A}{dt}$ From C_A versus t data by

1) graphical method.

2) Finite differential method.

3) polynomial.

(2) plot $\ln(-dC_A/dt)$ vs $\ln(C_A)$, reaction order (α) → slope.

k → From intercept.

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(B) Integral method :- (trial and error).

→ **Zero order** ($\alpha = 0$)

$$\frac{dC_A}{dt} = r_A = -K$$

at $t = 0$, $C_A = C_{A0}$

$$C_A = C_{A0} - Kt$$

→ **First order** ($\alpha = 1$)

$$\frac{dC_A}{dt} = r_A = -K C_A$$

at $t = 0$, $C_A = C_{A0}$

$$\ln\left(\frac{C_{A0}}{C_A}\right) = Kt \rightarrow \ln C_A = \ln C_{A0} - Kt$$

→ **second order** ($\alpha = 2$)

$$dC_A/dt = r_A = -K C_A^2$$

at $t = 0$, $C_A = C_{A0}$

$$\frac{1}{C_A} = \frac{1}{C_{A0}} + Kt$$

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* Method of Initial Rates

slope = $-r_{A0}$ ← ([C] vs t) عن طريق ①

at C_{A0}

C_{A0}, $-r_{A0}$ بكونه في قيم مختلفة ل

② $-r_{A0} = k C_{A0}^{\alpha}$

$\ln(-r_{A0}) = \ln k + \alpha \ln C_{A0}$

($\ln(-r_{A0})$ vs. $\ln C_{A0}$) → slope = α.

* Method of half Live :-

$$-r_A = k C_A^{\alpha} = \frac{-dC_A}{dt}$$

$$t_{\frac{1}{2}} = \frac{2^{\alpha-1} - 1}{k(\alpha-1)} \left(\frac{1}{C_{A0}^{\alpha-1}} \right)$$

$$t_{\frac{1}{n}} = \frac{n^{\alpha-1} - 1}{k(\alpha-1)} \left(\frac{1}{C_{A0}^{\alpha-1}} \right)$$

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$$\ln t_{\frac{1}{2}} = \ln \frac{2^{\alpha-1}-1}{k(\alpha-1)} + (1-\alpha)\ln C_{A0}$$

$(\ln t_{\frac{1}{2}}$ vs $\ln C_{A0}) \rightarrow$ slope $= 1-\alpha$

~~x~~method of excess:- $A + B \rightarrow P$

$-r_A = k_A C_A^{\alpha} C_B^{\beta}$

- reaction First berun in an excess of B so that C_B remain unchanged ~~during the course~~ $-r_A = k' C_A^{\alpha}$

$k' = k C_B^{\beta} \simeq k_A C_{B0}^{\beta}$

After determining α, the reaction is carried out in an excess of A

$-r_A = k'' C_B^{\beta}$, $k'' = k_A C_A^{\alpha} \simeq k_A C_{A0}^{\alpha}$

Mo Tu We Th Fr Sa Su

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* **Differential Reactors** :-

$$-r_A' = \frac{F_{A0} - F_{Ae}}{\Delta W} = \frac{V_0 C_{A0} - V C_{Ae}}{\Delta W}$$

- in terms of conversion or product Flow rate F_p :-

$$-r_A' = \frac{F_{A0} X}{\Delta W} = \frac{F_p}{\Delta W} = \frac{V_0 C_p}{\Delta W} = \frac{V_0 (C_{A0} - C_{Ae})}{\Delta W}$$

For constant volumetric Flow.