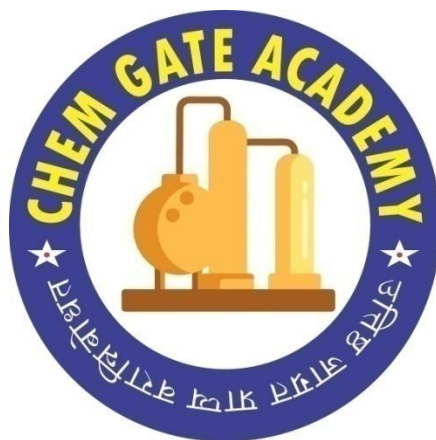# CHEMICAL ENGINEERING (GATE & PSUs)

Postal Correspondence

STUDY MATERIAL (Handwritten Notes)

By Ajay Sir

CHEMICAL REACTION ENGINEERING

To Buy Postal Correspondence Package Call at 8306260631

GATE-2022 Syllabus: Chemical Engineering

Theories of reaction rates; kinetics of homogeneous reactions, interpretation of kinetic data, single and multiple reactions in ideal reactors, <u>kinetics of enzyme reactions (Michaelis-Menten and Monod models),</u> non-ideal reactors; residence time distribution, single parameter model; non-isothermal reactors; kinetics of heterogeneous catalytic reactions; diffusion effects in catalysis; <u>rate and performance equations for catalyst deactivation</u>

CRE COURSE CONTENT

1. **Introduction**
2. **Kinetics of homogeneous reactions**
3. **Ideal Reactor**
   - **Batch, CSTR, PFR**
4. **Non Isothermal Reactor**
5. **Non-Ideal Reactor**
6. **Heterogeneous Catalytic Reaction (CRE-II)**
7. **Kinetics of reactions**
8. **Rate and performance equations for catalyst deactivation**

<u>**Note for Student:**</u>

1. Full GATE Syllabus covers in Notes.

2. Total number of pages in CRE Notes = 240 Pages

3. No. of Questions solved in Notes = 75+ Questions

(GATE PYQs & other good quality question)

CRE

* **Definition:** CRE is that Engineering activity which is concerned with the use of chemical rxn on a commercial scale.

* **Design of chemical Reactor:**

  - calculation of **type** & **size** of the Reactor

  (I) Type of Reactor ⟶ Batch Reactor
                        ⟶ continous (flow Reactor) ⟶ CSTR
                                                    ⟶ PFR

  (II) size of Reactor → volume of Reactor
       (size of Reactor directly related to the cost of Reactor)

SAMPLE

* To calculate size of reactor, we should understand :-

  (I)   kinetics of chemical reaction
  (II) Flow pattern or contacting pattern (Batch or continous)
  (III) mixing (Axial or Radial)

Kinetics of Homogenous chemical Rxn :-

→ kinetics of any given rxn indicates how fast the rxn^n happens.

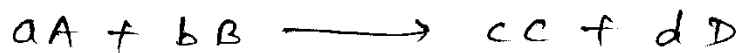* **Homogenous rxn :-** rxn occur in single phase
  (I)   liquid ✓   (molecules easily available)
  (II) GAS ✓   for rxn
  (III) solid ✗
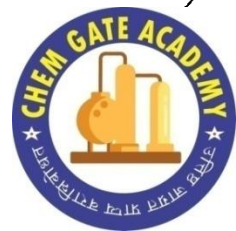
* kinetics of chemical reaction:-
   speed & Rate of a chemical rxn
→ How fast or How slow the rxn take place

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

A, B, C, D → species present in the chemical rxn

a, b, c, d → stoichiometric coefficients.

* stoichiometric coefficients represents :- (I) Moles &
                                            (II) molecules
   (III) volume (In gas'
                                            (IV) pressure   Phase rxn)

$$N_2 + 3H_2 \longrightarrow$$

at $t = 0$	10 mol	10 mol	0 mol	If 1mol N_2 react
at $t = t_1$	9 mol	7 mol	2 mol	t_1-0 or consumed
at $t = t_2$	8 mol	4 mol	4 mol	t_2-t_1 (different time to take place rxn in decreasing order ↓)
at $t = t_3$	7 mol	1 mol	6 mol	t_3-t_2
at $t = t_4$	$\left(7-\frac{1}{3}\right)$	0 mol	$\left(6+\frac{2}{3}\right)$ mol	Rxn is 100% complete

→ stoichiometric coeff^n represent How the rxn's proceeds

* Law of <u>conservation of Mass</u> is valid in chemical Rxn

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

28 grm   6 grm $2 \times 17 = 34$ grm
<u>⌐_____⌐</u>
   34 grm
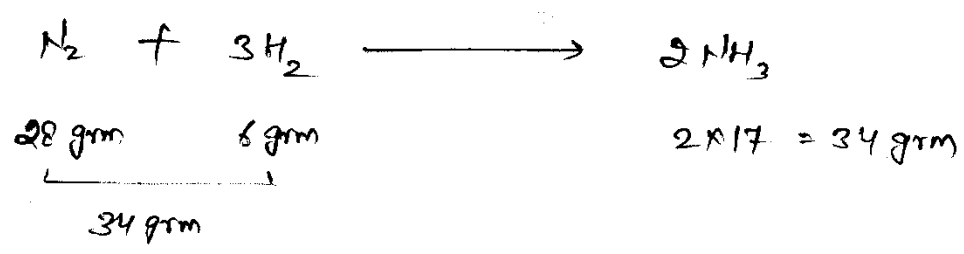
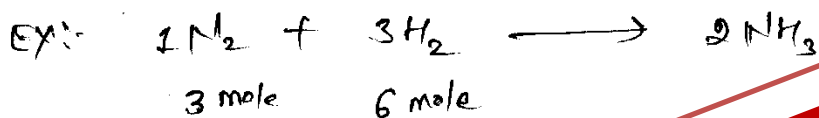→ <u>moles</u> :- conservation of moles is not fixed.

Limiting Reactant :- (L·R)

→ Assuming the rxn is going to completion
→ L·R gives which species gets consumed first

* **How to find L·R :-** Divide the initial moles of reactants by their respective stoichiometric coeff.

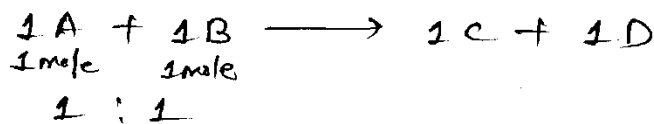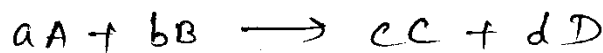→ The reactant for which we are getting lesser value is the L·R

EX:-
$$1N_2 + 3H_2 \longrightarrow 2NH_3$$
3 mole   6 mole
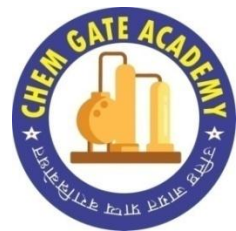
for L·R $\frac{3}{1} = 3$ $\frac{6}{3} = 2$ ~~ H₂ is L·R~~

$$\left[L·R = \frac{\text{no. of moles}}{\text{stoichiometric coeff}^n \text{ corresponding}} \right]$$

→ If the reactants are in stoichiometric proportion

    means
$$aA + bB \longrightarrow cC + dD$$
$$1A + 1B \longrightarrow 1C + 1D$$
1 mole   1 mole
1 : 1

then both reactants will be consumed at the same time & we can consider both as the L·R or we can say that none of them is the L·R.

Rate of Reaction :→ (ROR) Rate of reaction is defined as rate of change of concentrations of reactans or products.

average rate of RXN
$$\text{rate} = -\frac{\Delta[\text{Reactants}]}{\Delta\text{ time}}$$

$$\text{rate} = \frac{\Delta[\text{product}]}{\Delta\text{ time}}$$
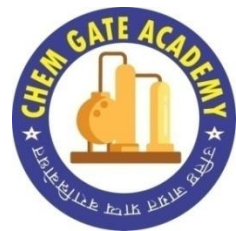
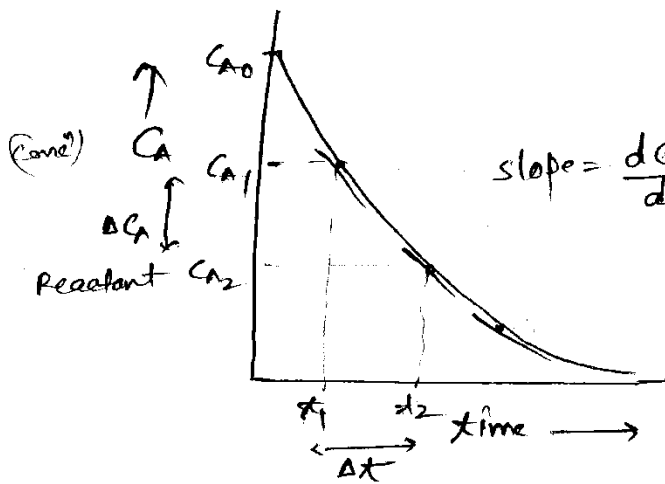$\Delta = \text{final} - \text{initial}$

* Rate of RXN General formula :-

$$\boxed{\text{rate} = \frac{1}{V}\frac{dN_A}{dt}}$$

GATE Que

⊖ for Reactant
⊕ for product.

$$\text{slope} = \frac{dc_A}{dt} = \text{instantanous rate}$$

$$\text{Average value} = \frac{c_{A_1} - c_{A_2}}{t_2 - t_1}$$

* **Instantanous rate of RXN :-** $\left(-r_A = -\frac{dc_A}{dt} \right)$

   is given by the slope of the tangent at that time [only for constant volume]

* **Notation of rate of rxn**

   for a raction $aA + bB \longrightarrow cC + dD$

   Rate of disapperence of A $\boxed{(-r_A) = -\frac{1}{V} \frac{dN_A}{dt}}$ $\left(\begin{array}{c} \text{Applicable everywhere} \\ \text{for CVRs + VVRs} \end{array} \right)$

   Where $\Rightarrow$ V = volume of reactor / mixture

   $\rightarrow (-r_A)$, -ve sign only for Notation, It will not be used for mathematical calculation

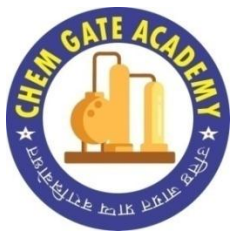 $\rightarrow \frac{-1}{V}$, -ve sign will used in mathematical calculation.

   Rate of Appereance of C $\boxed{r_C = \frac{1}{V} \frac{dN_C}{dt}}$

* **unit of rate of rxn** $\rightarrow \frac{mol}{L-s}$, $\left(\frac{conc^n}{time} \right)$

   or $\left(\frac{mol}{m^3 - s} \right)$

* whatever be order of rxn, unit of rate of rxn is same.

* for a Rxn $\quad aA + bB \longrightarrow cC + dD$

$$\frac{(-r_A)}{a} = \frac{(-r_B)}{b} = \frac{r_C}{c} = \frac{r_D}{d}$$

$-r_A \, \& \, r_B$ = rate of disapperance

$r_C \, \& \, r_D$ = rate of appereance.

Conversion or fraction conversion: (X) :- [Dimensionless no.]

→ The conversion is only defined for reactant and not for product.

→ conversion always increases. It is always gives positive term.

Conversion of A = X_A = $\dfrac{\text{moles of A reacted}}{\text{moles of A feed}}$

* for Batch Reactor :-

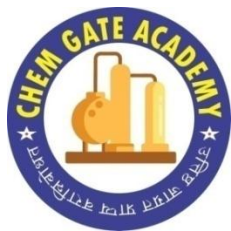$$X_A = \frac{N_{A0} - N_A}{N_{A0}} \quad \Rightarrow \quad \boxed{X_A = 1 - \frac{N_A}{N_{A0}}} \left(\begin{array}{c}\text{valid}\\ \text{everywhere}\end{array}\right)$$

% percentage conversion = $\dfrac{\text{fractional}}{\text{conversion}} \times 100$

* for flow Reactor :- $\quad f_{A0}$ = molar flow rate of A

$$\left(f_{A0} = \frac{N_{A0}}{t} \right) \text{ or } \left(f_A = \frac{N_A}{t} \right)$$

$$\boxed{X_A = \frac{N_{A0} - N_A}{N_{A0}} = 1 - \frac{N_A}{N_{A0}} = 1 - \frac{F_A}{F_{A0}}}$$

$$X_A = 1 - \frac{N_A}{N_{Ao}} \implies \frac{N_A}{N_{Ao}} = 1 - X_A$$

similarly

$$\boxed{\begin{array}{c} N_A = N_{Ao}(1-X_A) \\ F_A = F_{Ao}(1-X_A) \end{array}}$$ $\left(\begin{array}{c}\text{valid everywhere} \\ \text{CVRS \& VVRS}\end{array}\right)$
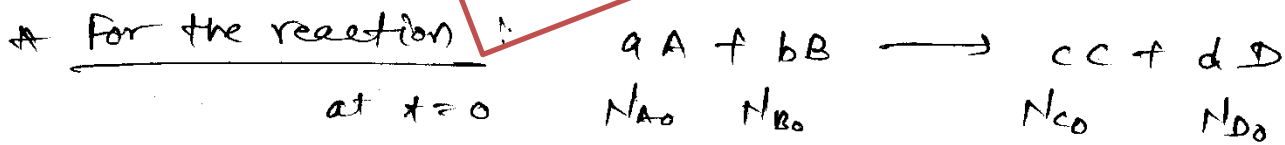
X_A = fraction conversion or fraction reacted

$(1-X_A)$ or $\frac{N_A}{N_{Ao}}$ = fraction left

→ conversion is always defined for L.R. (limiting reactant)

→ The value of conversion always lies b/w

$$\boxed{0 \leq X_A \leq 1}$$

→ for calculation use always fractional value of conversion,

A **for the reaction** : $\quad aA + bB \longrightarrow cC + dD$

at $t=0$ $\quad N_{Ao} \quad N_{Bo} \quad\quad N_{Co} \quad N_{Do}$

given that conversion of A is X_A

moles of A reacted = $N_{Ao} X_A$

moles of A left ⟹ ⎧ $M_A = N_{Ao}(1-X_A) = N_{Ao} - \boxed{N_{Ao}X_A}$ ⟵ amt of A reacted

moles of B left ⟹ ⎪ $M_B = N_{Bo} - \boxed{\frac{b}{a} N_{Ao} X_A}$ amt. of B reacted

moles of C left ⟹ ⎨ $N_C = N_{Co} + \boxed{\frac{c}{a} N_{Ao} X_A}$ amt of C produce

moles of D left ⟹ ⎩ $N_D = N_{Do} + \frac{d}{a} N_{Ao} X_A$

→ ~~valuid~~ valid for both CVRS & VVRS

⎰ CVRS = variable volume Rxn Reactor system ⎱
⎱ VVRS = constant volume Rxn system ⎰
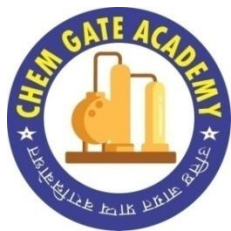
In Rxn engineering we have two type of system :-

① CVRS (constant volume Rxn (Reactor) system)

② VVRS (variable volume Rxn system)
   Reactor

① **CVRS**

$$V = V_0$$
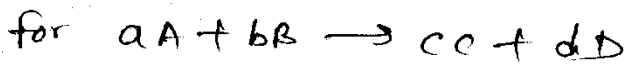
V = volume at any instant

V_0 = Initial volume

$$V \neq f(t, X_A)$$

as $t \uparrow$, $X_A \uparrow$ (always)

(I) All liquid phase and aqueous phase rxn are considered as CVRS system
(irrespective of the stoichiometric
(coefficient

(4) In gas phase rxns if sum of stoichiometric co-efficients of reactants and product are equal then the system is CVRS.

for $aA + bB \longrightarrow cC + dD$

if $\underline{a+b = c+d}$ (CVRS)

② **VVRS**

→ volume of the rxn mixture varies w.r.t time or conversion.

at **constant** T & P :

$$\boxed{V = V_0 (1 + \epsilon_A X_A)}$$

at T & P are changing :

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

by using Ideal gas law $PV = nRT$

$\left(N \propto \dfrac{T}{P} \right)$ $V = f(X_A)$

ϵ_A = volume expansion factor
          or
fractional volume change

ϵ_A can be positive, negative, or zero

* **VVRS** .

$X_A \uparrow V \uparrow$
if $\epsilon_A > 0$; $V > V_0$ expansion

$X_A \uparrow V \downarrow$
$\epsilon_A < 0$; $V < V_0$ contraction

$\epsilon_A = 0$ $V = V_0$ system is CVRS

* If given gas phase rxn then first check system is CVRS or VVRS.

* volume expansion factor (ϵ_A)

$$\boxed{\epsilon_A = \frac{N_T|_{X_A=1} - N_T|_{X_A=0}}{N_T|_{X_A=0}}} = \frac{\text{total moles}|_{X_A=1} - \text{total moles}|_{X_A=0}}{\text{total moles}|_{X_A=0}}$$

Where

N_T = total no. of moles present at any instant

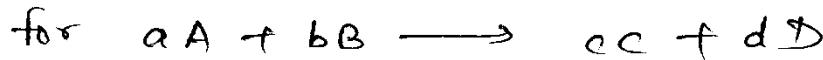$N_T|_{X_A=1}$ = total no. of moles present @ 100% conversion.

→ ϵ_A is define by conversion means only define for reactant.

$\underline{\text{or :-}}$ shortcut $\boxed{\epsilon_A = y_{AO}\, \delta_A}$

y_{AO} = Initial mole fraction of A

$$\left(\delta_A = \frac{c+d-a-b}{a}\right):$$

for $aA + bB \longrightarrow cC + dD$

* for any type of rxn $aA + bB \longrightarrow cC + dD$

$$V = V_0(1 + \epsilon_A X_A)$$

$$V = V_0(1 + \epsilon_B X_B)$$

$\boxed{\epsilon_A X_A = \epsilon_B X_B}$

$$N_B = N_{BO} - \frac{b}{a} N_{AO} X_A \Rightarrow$$

$$\epsilon_A X_A = \epsilon_B X_B$$

$$\epsilon_B = \frac{X_A}{X_B}\epsilon_A \Rightarrow$$

$N_B = N_{BO}(1-X_B) \Rightarrow N_{BO} X_B = N_{BO} - N_B$

$$\frac{b}{a} N_{AO} X_A = N_{BO} - N_B = X_B N_{BO}$$

$$\Rightarrow \left(\frac{N_{BO}}{N_{AO}}\right) \cdot \frac{a}{b} = \frac{X_A}{X_B}$$

$$\boxed{\epsilon_B = \epsilon_A \cdot \left(\frac{N_{BO}}{N_{AO}}\right) \cdot \frac{a}{b}}$$
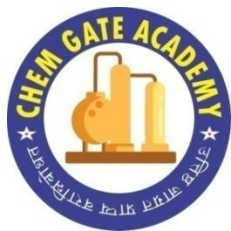
order :- order of a reaction is determined only by experiment so experimental quantity

→ order can be defined as summation of power to which the concn. are raised.

*⟹ order of a reaction is experimental determined quantity, Hence it may { positive, Negative, zero & fraction value

* <u>For Elementary Reaction</u> the order of the rxn is equal to the sum of stoichiometric coefficient of the reaction.

if $aA + bB \longrightarrow$ products
  is a elementary rxn then for elementary rxn

rate $= ... $ |overall order = Molecularity|

then $\alpha = a, \quad \beta = b$

$\alpha + \beta \Rightarrow a + b =$ overall order of rxn

→ Elementary rxn's are those rxn which take place in a single step. & follow "Power law kinetics".

<u>Molecularity</u> :- It is defined as no. of molecules involved in reaction.

→ Molecularity defined only for elementary reaction.

→ Its value may be 1, 2 rarely 3

*⟹ Molecularity of a rxn can never be { negative, zero or fraction
  (always Integer)

→ There is no any known rxn which has molecularity 4 or more than 4.

→ Molecularity is a theoretical value / term.

SAMPLE

CHEM GATE ACADEMY

→ $N_2 + 3H_2 \rightleftharpoons 2NH_3$ rxⁿ shows Molecularity = 4

but no rxn till date which has molecularity = 4

Hence rxn is non-elementary

$$(r_{NH_3}) = \frac{k_1 \, C_{N_2} \, C_{H_2}^{3/2}}{(C_{NH_3})} = \frac{k_2 \, C_{NH_3}}{(C_{H_2})^{3/2}}$$
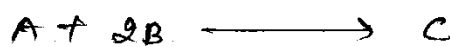
→ The rate Law is independent of the type of reactor.

EX → CSTR, PFR, Batch reactor

→ The multiplication (or) division of any constant quantity throughout the rxⁿ doesnot effect the rate of rxⁿ.

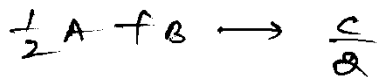→ By multiplying / dividing of any constant quantity in any rxn doesnot change the molecularity as well.

SAMPLE

elementary $A + 2B \longrightarrow C$ $(-r_A) = k_1 \, C_A \, C_B^2$

$2A + 4B \longrightarrow 2C$ $(-r_A) = k_1 \, C_A \, C_B^2$

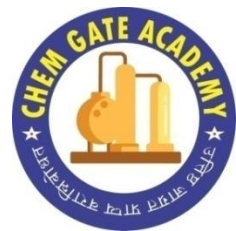$\frac{1}{2}A + B \longrightarrow \frac{C}{2}$ $(-r_A) = k_1 \, C_A \, C_B^2$

✱ Molecularity = 1 (unimolecular) → Radio Active

= 2 (Bi-molecular)

= 3 (Tri-molecular)

Non-elementary rxⁿ's: The rxn in which the rate of rxn doesnot corresponds to stoichiometri coefficient.

→ They are multistep rxn

CHEM GATE ACADEMY

KINETICS OF ELEMENTARY RXN :-

Derivation of integral form of rate equation / kinetic equation

* for __CVRS__ :- (constant volume Reaction system)

$$-r_A = -\frac{1}{V}\frac{dN_A}{dt} = -\frac{dC_A}{dt}$$
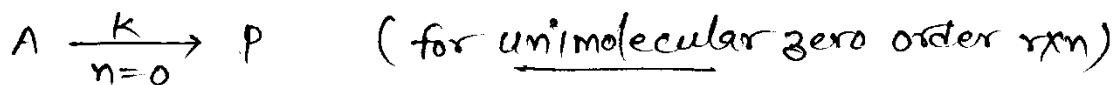
$$N_A = N_{Ao}(1-X_A)$$; $$C_A = C_{Ao}(1-X_A)$$

$$X_A = 1 - \frac{N_A}{N_{Ao}}$$; $$X_A = 1 - \frac{C_A}{C_{Ao}}$$

* $\quad C_A = C_{Ao}(1-X_A)$

$\Rightarrow$ $$\frac{dC_A}{dt} = -C_{Ao}\frac{dX_A}{dt}$$ $\quad\left(C_A = \frac{N_A}{V}\right)$

Guess zero order

(1) __Zero order Reaction__ :- (CVRS)

$$A \xrightarrow[n=0]{k} P \qquad (\text{for unimolecular zero order rxn})$$
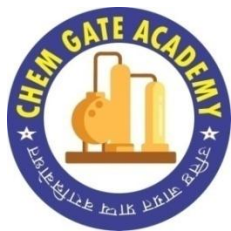
$$(-r_A) = -\frac{dC_A}{dt} = C_{Ao}\frac{dX_A}{dt}$$

$$(-r_A) = kC_A^{0}$$

$$(-r_A) = -\frac{dC_A}{dt} = kC_A^{0} = k$$

$$\int -\frac{dC_A}{dt} = \int k$$

$$-\int_{C_{Ao}}^{C_A} dC_A = k\int_0^t dt$$

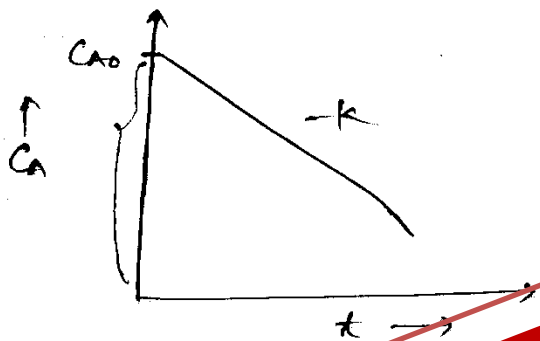$$\int_{C_{A0}}^{C_A} dC_A = -k \int_0^t dt$$

$$\boxed{C_{A0} - C_A = k\,t}$$ Integrated rate equation for zero order rxn

$$C_A = C_{A0} - k\,t$$

$$y = c + mx \qquad \text{slope} = -k$$
$$\text{Intercept} = C_{A0}$$

* $\quad C_{A0} - C_A = kt$

$$C_{A0}\left(1 - \frac{C_A}{C_A}\right) = kt \qquad\qquad \text{for CVRS}$$
$$\because X_A = 1 - \frac{C_A}{C_{A0}}$$

$$\boxed{C_{A0}\, X_A = k\,t}$$

$$X_A = \frac{k}{C_{A0}}\, t \qquad\qquad \text{slope} = k/C_{A0}$$
$$y = mx + c \qquad\qquad \text{Intercept} = 0$$
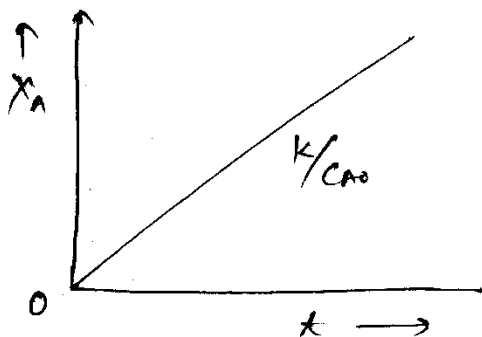
* $\quad -r_A = k\, C_A^{\,0} = k$

$$-r_A = k$$
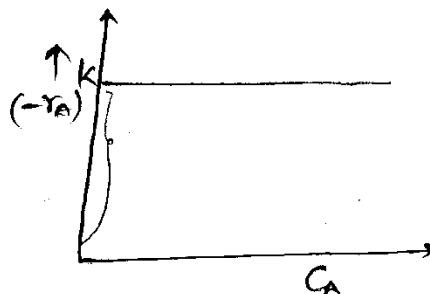
* Zero order rxn can complete :- (for 100 % conversion)

Put $X_A = 1$ in $\quad C_{Ao} X_A = kt$

$$C_{Ao} = kt$$

$$t = \frac{C_{Ao}}{k}$$

Put $C_A = 0$ in $\quad C_{Ao} - C_A = kt$

$$C_{Ao} = kt$$

$$\boxed{t = \frac{C_{Ao}}{k}}$$ → A zero order rxn can go to completion in finite time.

* <u>Note</u> :- Any rxn of <u>order less than 1</u> goes to completion in finite time.

* $\quad C_{Ao} X_A = kt \quad \Rightarrow \quad \boxed{X_A = k...}$

(SAMPLE watermark)

$$\left(\frac{}{C_{Ao}} \right)$$

* <u>Note</u> :- For zero order rxn conversion is inversely proportional to inition concentration. (keeping k & t same)

⟨2⟩ <u>First order Reaction</u> :- (CVRS)

$$A \xrightarrow[n=1]{k} P \qquad (unimolecular)$$

$$(-r_A) = -\frac{dC_A}{dt} = C_{Ao}\frac{dX_A}{dt} = k C_A^1$$
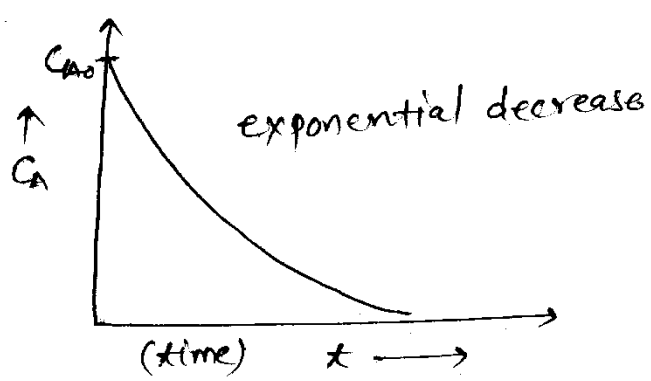
$$-\frac{dC_A}{dt} = k C_A$$

$$\int_{C_{Ao}}^{C_A} \frac{dC_A}{C_A} = -k\int_0^t dt \quad \Rightarrow \quad \ln C_A \Big|_{C_{Ao}}^{C_A} = -kt$$

$$\Rightarrow \ln\left(\frac{C_A}{C_{Ao}}\right) = -kt$$

$$\Rightarrow \boxed{C_A = C_{Ao}\, e^{-kt}}$$ Integrated rate equation for first order rxn.

$$\boxed{C_A = C_{A0}\, e^{-kt}}$$

C_{A0}

C_A ↑

exponential decrease

(time) $t \longrightarrow$

*
$$C_{A0}\frac{dx_A}{dt} = k\, C_A$$

$$C_{A0}\frac{dx_A}{dt} = k\, C_{A0}(1-x_A)$$
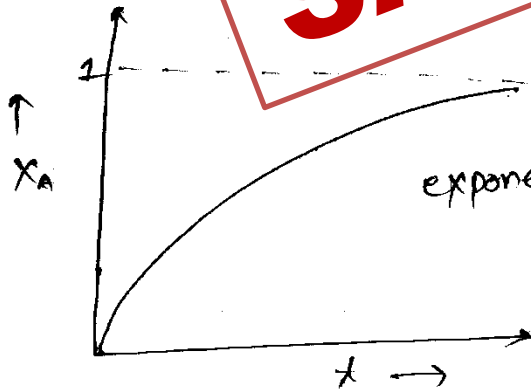
$\left| \; \because C_A = C_{A0}(1-x_A) \right.$

$$\int_0^{x_A} \frac{dx_A}{(1-x_A)} = \int_0^t k\,t$$

$$\boxed{-\ln(1-x_A) = kt}$$ integrated rate eqⁿ in term of conversion.

1

↑
x_A

exponential increase
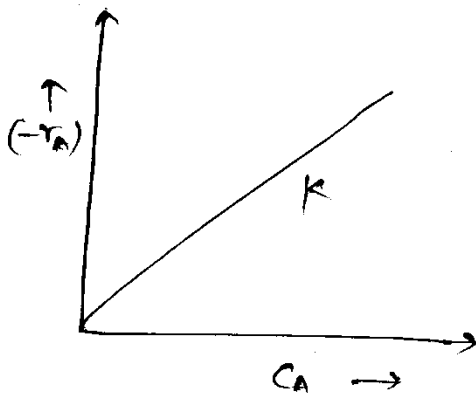
$-\ln(1-x_A) = kt$

$1-x_A = e^{-kt}$

$x_A = 1 - e^{-kt}$

at $t=0$; $x_A = 0$

$t = \infty$; $x_A = 1$

$t \longrightarrow$

* $(-r_A) = k\, C_A$ slope $= k$

↑
$(-r_A)$

k

$C_A \longrightarrow$

SAMPLE

CHEM GATE ACADEMY

unit of Rate constant :- (CVRS)

$$k = \left(\frac{mol}{L}\right)^{1-n} s^{-1}$$

* for zero order $\quad k = \dfrac{mol}{L-s}$

* for first order $\quad k = s^{-1}$

* for second order $\quad k = \left(\dfrac{mol}{L}\right)^{-1} s^{-1} \Rightarrow \dfrac{L}{mol-s}$

Ques 2) consider the rxn (gas phase) $\quad A + 2B \longrightarrow 3C + 4D$
Equimolar amount of A and B the calculated volume
expansion factor (ε_A) ?

Sol→ Method. (I) $\quad$ Basis = mol mixture

equimolar 50 $N_{A0} = 50$ mol , $\quad N_{B0} = 50$ mol

i	$N_i\|_{X_A=0}$	$N_i\|_{X_A=1}$
A	50	0
B	50	−50
C	0	150
D	0	200
N_T	100	300

$N_B = N_{B0} - \dfrac{2}{1}(50)$

$\quad = 50 - 100 = -50$

$N_C = N_{C0} + \dfrac{3}{1}(50)$
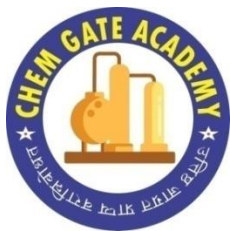
$\quad 0 + 150 = 150$

$N_D = N_{D0} + \dfrac{4}{1}(50)$

$\quad = 0 + 200 = 200$

$$\varepsilon_A = \frac{N_T\|_{X_A=1} - N_T\|_{X_A=0}}{N_T\|_{X_A=0}}$$
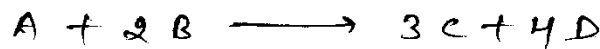
$\varepsilon_A = \dfrac{300 - 100}{100} = 2$

$\boxed{\varepsilon_A = 2}$ Answer

Method - II : shortcut $\boxed{\epsilon_A = y_{A_0}\,\delta_A}$

equimolar A & B in feed; so $y_{A_0} = 0.5$

$$\delta_A = ?$$

$$A + 2B \longrightarrow 3C + 4D$$

$$\delta_A = \frac{3+4-1-2}{1} = 4$$

$$\epsilon_A = y_{A_0}\,\delta_A = 0.5 \times 4 = 2$$

$$\boxed{\epsilon_A = 2} \quad \text{Answer}$$

Que → 3) A feed mixture consisting of 30 mol of A, 50 moles of B, 10 moles of C is undergoing following reaction.

$$2A + 3B \longrightarrow ~~~~ + ~~ D$$

In product mixture leaving the reactor is found to contain 12 moles of A, then calculate composition of product mixtures & final conversion of A & B.

Sol →   In feed A & B $N_{A_0} = 30$ mol   , $N_A = 12$ mol

$N_{B_0} = 50$ mol

$N_{C_0} = 10$ mol

$$\boxed{X_A = 1 - \frac{N_A}{N_{A_0}}} = 1 - \frac{12}{30} = 0.6$$

$$\boxed{X_A = 0.6}$$

$$\boxed{N_B = N_{B_0} - \frac{b}{a}\,C_{A_0} X_A} = 50 - \frac{3}{2} \times 18 = 23 \text{ mole}$$

$$\boxed{X_B = 1 - \frac{N_B}{N_{B_0}}} = 1 - \frac{23}{50} = 0.54$$

$$X_B = 0.54$$

$$N_C = N_{C_0} + \frac{c}{a}\,\underline{C_{A_0} X_A}$$

$$C_{A_0} X_A = C_{A_0} - C_A$$

$$= 0 + \frac{4}{2} \times (18)$$

$$\underline{N_C = 46 \text{ mol}}$$

$$N_D = N_{D_0} + \frac{d}{a}\,C_{A_0} X_A = 0 + \frac{1}{2}(18) = 9 \quad \Rightarrow \quad \underline{N_D = 9 \text{ mol}}$$
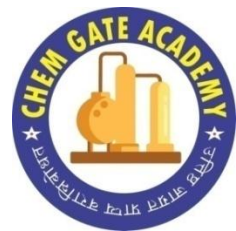
Query7) for 2nd order rxn, $k = 2 \times 10^{-4} \frac{L}{mol\text{-}min}$. If conc^n of A is 10 mol/L after 1hr, find conc^n of A at $t=0$.

Sol→ kinetics for 2nd order rxn $\frac{1}{C_{Ao}} - \frac{1}{C_A} = -kt$

$$\boxed{\frac{1}{C_A} - \frac{1}{C_{Ao}} = kt}$$

1hr = 60 min

$$\Rightarrow \frac{1}{C_A} - \frac{1}{10} = \underset{\frac{L}{mol\text{-}min}}{2 \times 10^{-4} \times 60} \; min$$

$$C_A = \underset{8.928}{\cancel{11.36}} \; mol/L \quad \text{Answer}$$

---

* short Notes :- (kinetics of CNRC problem)

① for zero order rxn :-

$$\boxed{\begin{array}{c} C_{Ao} - C_A = kt \\ \hline C_{Ao} X_A = kt \end{array}}$$

② for first order rxn :

$$\boxed{\begin{array}{c} C_A = C_{Ao}\, e^{-kt} \\ \hline -\ln(1 - X_A) = kt \end{array}}$$

③ for second order rxn :-

$$\boxed{\begin{array}{c} \left(\dfrac{1}{C_A} - \dfrac{1}{C_{Ao}}\right) = kt \\ \hline \dfrac{X_A}{1 - X_A} = k\, C_{Ao}\, t \end{array}}$$
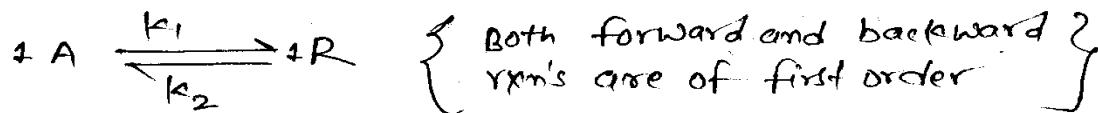
④ for nth order rxn :- ***

$$\boxed{C_A^{1-n} - C_{Ao}^{1-n} = (n-1)kt}$$

not valid for $n = 1$

Kinetics of a first order Reversible rxn (CVRS):→

for the reversible rxn

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R \quad \left\{ \begin{array}{l} \text{Both forward and backward} \\ \text{rxn's are of first order} \end{array} \right\}$$

$$(-r_A) = k_1 C_A - k_2 C_R$$

X_{Ae} = equilibrium conversion, the conversion attained by the rxn when it reaches equilibrium.

$$(-r_A) = k_1 C_A - k_2 C_R$$

At equilibrium net rate = 0

$$k_1 C_{Ae} = k_2 C_{Re}$$

$$k_1 C_{A0}(1-X_{Ae}) = k_2 (C_{R0} + C_{A0} X_{Ae})$$

Assuming $C_{R0} = 0$

$$k_1 C_{A0}(1-X_{Ae}) = k_2 C_{A0} X_{Ae}$$

$$\frac{k_1}{k_2} = \frac{X_{Ae}}{1-X_{Ae}}$$

Assume Rate constant $K_c = \dfrac{k_1}{k_2}$

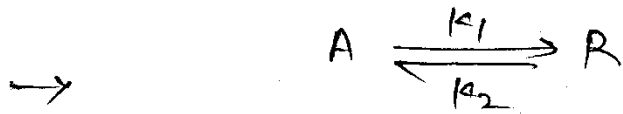$$\boxed{K_c = \frac{X_{Ae}}{1-X_{Ae}}} \quad ; \quad \boxed{X_{Ae} = \frac{K_c}{1+K_c}}$$

$$\text{Imp} \left\{ \begin{array}{l} K_c \uparrow \text{ then } X_{Ae} \uparrow \\ K_c \downarrow \text{ then } X_{Ae} \downarrow \end{array} \right.$$

Note: X_{Ae} is only function of K_c

$$\text{ex:- } X_{Ae} = \frac{9}{1+9} = 0.90$$

$$X_{Ae} = \frac{99}{1+99} = 0.99$$

Derive the relation b/w Actual conversion, equilibrium conversion & time for a first order reversible rxn, Assuming that some amount of R present initially : $\left(\frac{C_{Ro}}{C_{Ao}} = M\right)$

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R$$

$$(-r_A) = k_1 C_A - k_2 C_R$$

$$= k_1 C_{Ao}(1-X_A) - k_2 (C_{Ro} + C_{Ao} X_A)$$

$$= k_1 C_{Ao}(1-X_A) - k_2 C_{Ao}\left(\frac{C_{Ro}}{C_{Ao}} + X_A\right) \qquad C_{Ro} \neq 0$$

$$(-r_A) = k_1 C_{Ao}(1-X_A) - k_2 C_{Ao}\left(M + X_A\right)$$

at equilibrium $(-r_A) = 0$
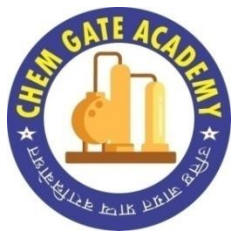
$$k_1 C_{Ae} = k_2 C_{Re}$$

$$k_1 C_{Ao}(1-X_{Ae}) = k_2 \cdot (C_{Ro} + C_{Ao} X_{Ae})$$

$$\left\{ k_c = \boxed{\frac{k_1}{k_2}} = \frac{C_{Ro} + C_{Ao} X_{Ae}}{C_{Ao}(1-X_{Ae})} = \frac{M + X_{Ae}}{1 - X_{Ae}} \right\} \qquad \boxed{k_c = \frac{M + X_{Ae}}{1 - X_{Ae}}}$$

$$(-r_A) = -\frac{dC_A}{dt} = C_{Ao}\frac{dX_A}{dt} = k_1\left[C_{Ao}(1-X_A) - \frac{k_2}{k_1} C_{Ao}(M + X_A)\right]$$

$$\frac{dX_A}{dt} = k_1\left[(1-X_A) - \boxed{\frac{k_2}{k_1}}(M + X_A)\right]$$

$$\int_0^{X_A} \frac{dx}{k_1[(1-X_A) - \frac{M + X_A}{\left(\frac{M + X_{Ae}}{1 - X_{Ae}}\right)}]} = \int_0^t dt$$

$$\int_0^{X_A} \frac{dx}{\frac{k_1(m+1)}{(m+X_{Ae})}(X_{Ae}-X_A)} = \int_0^t dt$$

$$\Rightarrow \qquad (-1)\ln(X_{Ae}-X_A)\Big|_0^{X_A} = \frac{k_1(m+1)}{m+X_{Ae}} \times t$$

$$\Rightarrow \qquad -[\ln(X_{Ae}-X_A)-\ln X_{Ae}] = \frac{k_1(m+1)}{m+X_{Ae}} \cdot t$$

$$\Rightarrow \qquad -\ln\left(1-\frac{X_A}{X_{Ae}}\right) = \frac{k_1(m+1)}{m+X_{Ae}} \cdot t$$

$$\Rightarrow \qquad \boxed{-\ln\left(1-\frac{X_A}{X_{Ae}}\right) = \frac{k_1(m+1)}{(m+X_{Ae})} \cdot t}$$

$\qquad \qquad \hookrightarrow$ for Reversible first order rxn (CVRS)

Que→10) The 1st order reversible liquid phase rxn $A \rightleftharpoons R$ takes place in a batch reactor after 8 min. conversion of A is 33.3%. While the eqb^m conversion is 66.7%. find the rate constant for this rxn. if $C_{Ao} = 0.5$ mol/L and $C_{Ro} = 0$.
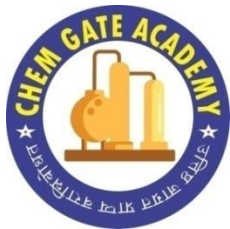
Sol → $\dfrac{k_1}{k_2} = k_c = \dfrac{X_{Ae}}{1-X_{Ae}} = \dfrac{0.667}{1-0.667} = 2.003 \simeq 2$

$$\boxed{-\ln(1-X_A) = kt} \qquad \text{for } 1^{st} \text{ order CVRS}$$

$$\ln\left(\frac{1}{1-X_A}\right) = k_1 t$$

$$\ln\left(\frac{1}{1-0.333}\right) = k_1 \times 8 \implies \boxed{k_1 = 0.057}$$

$\left| \begin{array}{l} k_2 = \dfrac{k_1}{k_c} = \dfrac{0.057}{2} \\[2mm] k_2 = 0.028 \text{ Ans} \end{array} \right.$

II) Method

$$\left[-\ln\left(1 - \frac{X_A}{X_{Ae}}\right) = \frac{k_1\,(\overset{o}{M}+1)}{\overset{o}{M}+X_{Ae}} \times t\right] \qquad \left(M = \frac{\overset{o}{C_{RO}}}{C_{AO}}\right)$$

$$\underline{M = 0}$$

$$-\ln\left(1 - \frac{0.033}{0.667}\right) = \frac{k_1}{0.166} \times 8$$

$$\underline{k_1 = 0.057} \qquad Ans$$

$$\frac{k_1}{k_2} = 2 \implies k_2 = \frac{k_1}{2} = \frac{0.057}{2}$$
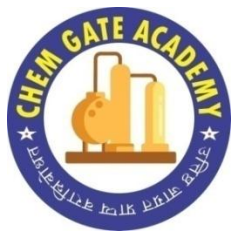
$$\underline{k_2 = 0.028} \qquad Answer$$

* <u>concept :-</u>

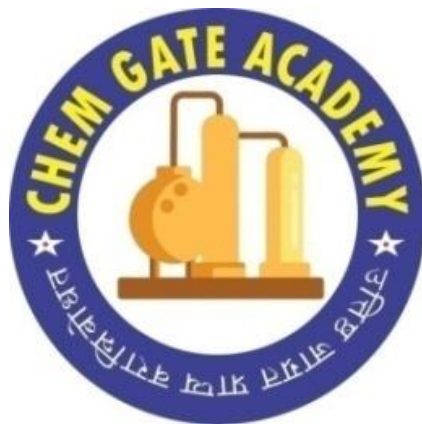Ⓘ for Endothermic rxn $\boxed{T\uparrow \quad k_c\uparrow \quad X_{Ae}\uparrow}$

Ⓘ for Exothermic rxn $\boxed{T\uparrow \quad k_c\downarrow \quad X_{Ae}\downarrow}$

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