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CSIR-NET

Council of Scientific & Industrial Research

CHEMICAL SCIENCE

VOLUME - V

PHYSICAL **CHEMISTRY**

SIERRA INNOVATIONS

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CHEMICAL KINETICS

THERMODYNAMICS

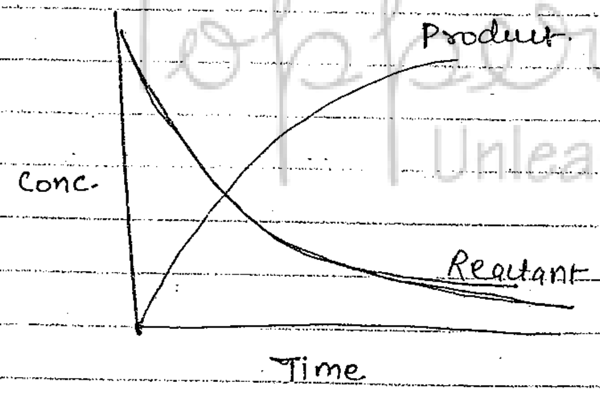
(PHYSICAL CHEM)

CHEMICAL KINETICS

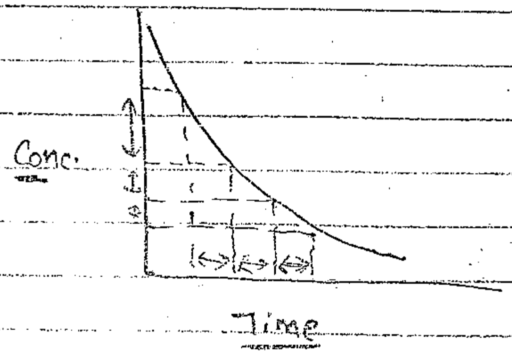
Rate of Reaction →

The Change of concentration of Product or reactant with time is Called Rate of Reaction.

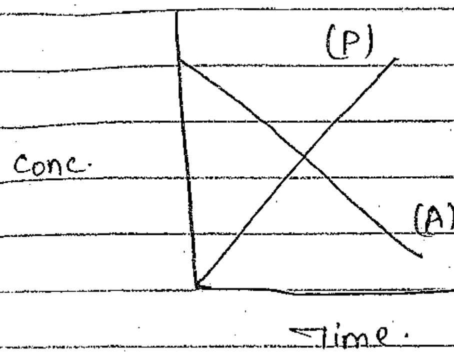
$$Rate = \pm \frac{dx}{dt} = \frac{\text{Change in conc. of Reactant or Product}}{\text{Time taken}}$$

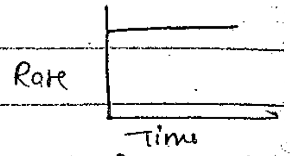


* The magnitude of slope of Concn Change of Reactant decreased with time, so rate of rxn w.r.t Reactant decrease.



(Ex) $A \longrightarrow P$ (zero ~~order~~ Order Rx^n).

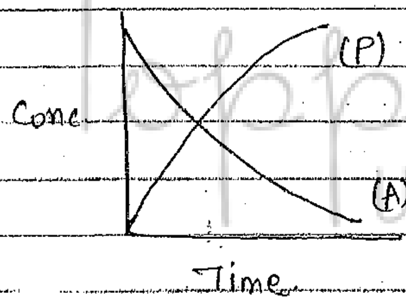




Rate Constant

• Here conc. linearly varies. (but we can say for particular cond^n) (स्व. के द्वारा सिर ने नहीं लिखा।)

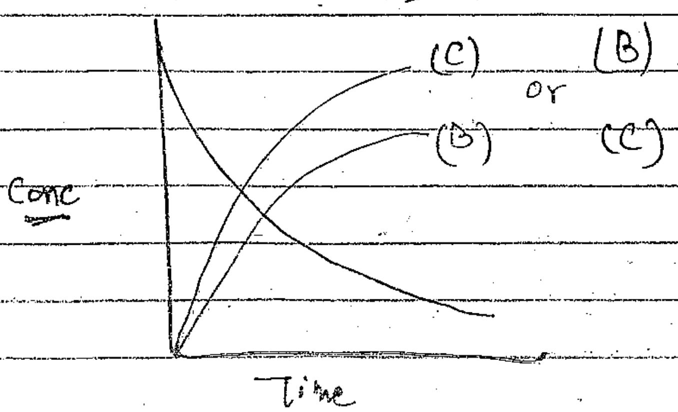
(Ex) $A \longrightarrow P$ (n^{th} order $n > 0$)

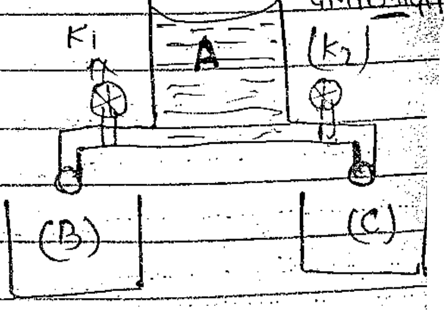


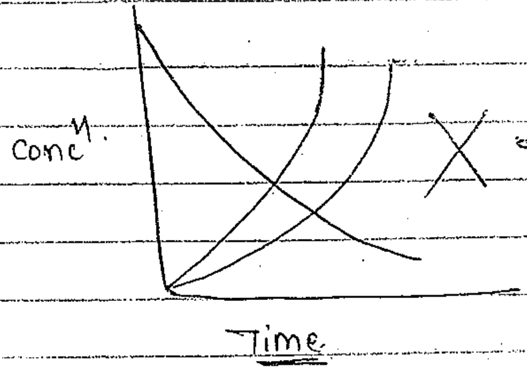
(Ex) $A \xrightarrow{k_1} B$, $A \xrightarrow{k_2} C$ || [al] React^n

समझने की Trick
पानी की टंकी, जिसका नल ज्यादा खुला (i.e. k_1 | k_2) उस Bucket में पानी ज्यादा

$k_2 > k_1$ $k_1 > k_2$



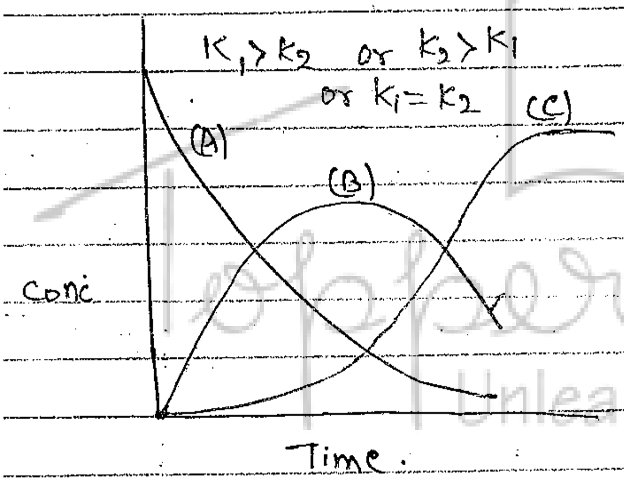


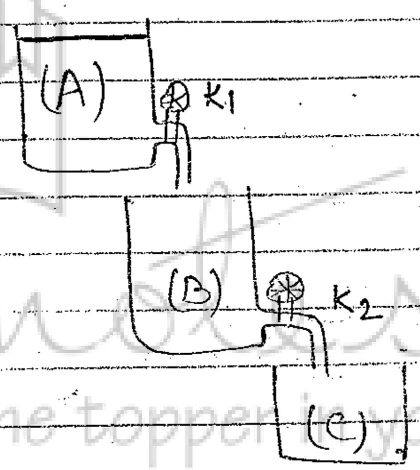


X ऐसा graph नहीं होगा

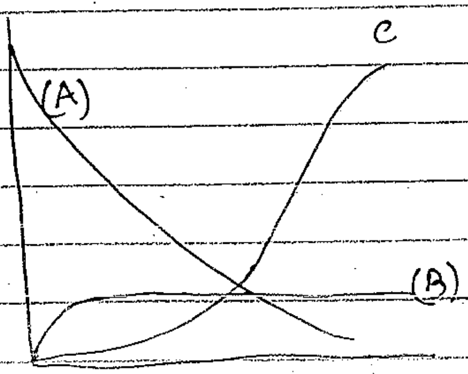
सोचो पानी की टंकी में जब पानी कम हो तो क्या कभी Rate High हो सकता है (शर्त कम पानी में)

Ex $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ समझने के लिए





But if $k_1 << k_2$ i.e B टंकी का नल ही निकाल दिया



यह जब पानी (A) से B में आएगा, तब शुरू में हल्का सा B में level बढ़ेगा लेकिन, नल नहीं होने के वजह से C में तो पानी बढ़ेगा लेकिन (B) Constant हो जाएगा

Ques. करने का तरीका

① stoichiometry Relationship हमेशा Rate of Rx^n से dealing करते समय व यदि किसी एक R/P की conc. दी हो और दूसरे की पूछी है तब use करेंगे

② और यदि किसी P/R की conc. दे रखी है और उसी की formation/dissapn. पूछा है तो stoichiometry use नहीं करते।

For a Reaction

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

$$\text{Rate of } Rx^n = -\frac{1}{2}\frac{d(A)}{dt} = -\frac{d(B)}{dt} = \frac{1}{3}\frac{d(C)}{dt}$$

Avg RoR

~~UAR with reactant~~ stoichiometry

- Reactant → (−)
- Product → (+ve)

(Q) For a Reaction $2A + B \longrightarrow 3C$, the Concentration of A decreases from 3.0 M to 1.0 M in 20 minutes.

(i) The rate of rx^n will be.

(a) ·1 M/minute (b) ·01 M/minute (c) 0.5 M/min. (d) 0.05 M/min

(ii) The rate of dissappearance of 'A' will

(a) ·1 M/minute (b) ·01 M/minute (c) 0.5 M/min. (d) 0.05 M/min

Soln. (i) Rate of Rx^n $= \frac{1}{2}\frac{d(A)}{dt}$

$$= \frac{1}{2} \times \frac{3-1}{20} = \frac{1}{2} \times \frac{2}{20} = 0.05 \text{ M min}$$

(ii) Rate of disappearance of A $= \frac{d(A)}{dt} = \frac{3-1}{20} = \frac{2}{20}$

$= 0.1$

$$* \quad \text{Rate of } Rx^n = \frac{1}{\nu}\frac{dn}{dt}$$

ν = Stoichiometric coefficient

(iii) The rate of disappearance of 'B' will be

$$\frac{1}{2}\frac{dA}{dt} = \frac{dB}{dt} \Rightarrow \frac{0.1}{2} = \frac{dB}{dt} \Rightarrow 0.05 \text{ M min}.$$

(iv) The rate of formatⁿ of C will be

* देखो भाषा मे $2A + B \rightarrow 3C$
C कहता है की B का मे 3 गुना हूँ
आ फिर A का मे 1½ गुना हूँ.

(OR) Rate of $Rx^n = \frac{1}{3}\frac{d(C)}{dt}$ → Rate of formatⁿ

∴ $3 \times \text{Rate of } R^{xn} = \frac{dC}{dt}$

$\frac{1}{2}\frac{dA}{dt} = \frac{1}{3}\left(\frac{dC}{dt}\right)$

$0.05 = \frac{1}{3}\left(\frac{dC}{dt}\right) \Rightarrow \frac{dC}{dt} = 0.05 \times 3 = 0.15$

(Q) consider a Rxⁿ.

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

Given $-\frac{d(A)}{dt} = K_1 (A)(B)$

$-\frac{d(B)}{dt} = K_2 (A)(B)$

$-\frac{d(C)}{dt} = K_3 (A)(B)$

Solⁿ
$-\frac{d(A)}{dt}$, $-\frac{d(B)}{t}$ है, $-\frac{d(C)}{t}$ equal नहीं है.
तो पहले इन्हे equal करो

(A) $K_1 = 2K_2 = 3K_3$
(B) $2K_1 = K_2 = 3K_3$
(C) $3K_1 = K_2 = 2K_3$
(d) $\frac{K_1}{2} = K_2 = \frac{K_3}{K_3}$

∴ $\frac{1}{2}\frac{-d(A)}{dt} = \frac{K_1}{2}(A)(B)$ —(1)

$\frac{d(B)}{dt} = K_1 (A)(B)$ —(2)

$\frac{1}{3}\frac{d(C)}{dt} = \frac{K_3}{3}(A)(B)$ —(3)

NOW L.H.S and R.H.S are equal

∴ साथ मे (A) & (B) in R.H.S भी same है

∴ $\boxed{\frac{K_1}{2} = K_2 = \frac{K_3}{3}}$

(Q) For a Rx^n. $2A + B \longrightarrow 3C$

Given

$$-\frac{1}{2}\frac{d(A)}{dt} = K_1 (A)(B)$$

$$-\frac{d(B)}{dt} = K_2 (A)(B)$$

$$\frac{1}{3}\frac{d(C)}{dt} = K_3 (A)(B)$$

Here Rate of Rx^n same → यह भी same

∴ $\boxed{K_1 = K_2 = K_3}$

(Q) for a Rx^n. $2A + B \longrightarrow 3C$

$$-\frac{d(A)}{dt} = K_1 (A)(B)$$

$$-\frac{1}{3}\frac{d(B)}{dt} = K_2 (A)(B)$$

$$\frac{1}{2}\frac{d(C)}{dt} = K_3 (A)(B)$$

यह Rate equal नहीं है, So पहले Rate equal करो

∴ $\frac{1}{2}\left(-\frac{d(A)}{dt}\right) = \frac{1}{2} K_1 (A)(B)$

$3 \times \left(-\frac{1}{3}\frac{d(B)}{dt}\right) = 3 K_2 (A)(B)$

$\frac{2}{3} \times \left(\frac{1}{2}\frac{d(C)}{dt}\right) = \frac{2}{3} K_3 (A)(B)$

i.e. $-\frac{1}{2}\frac{d(A)}{dt} = \frac{k_1 (A)(B)}{2}$

$-\frac{d(B)}{dt} = 3k_1 (A)(B)$

$\frac{1}{3}\frac{d(C)}{dt} = \frac{2}{3}k_3 (A)(B)$

Now Rate equal so LHS = R.H.S

i.e. $\frac{k_1}{2} = 3k_2 = \frac{2}{3}k_3$

↓ अब इसके Acc^n to opp^n Match करके देखो

(Q) $2A + B \longrightarrow 3C$

Given
$-\frac{1}{3}\frac{d(A)}{dt} = k_1 (A)(B)$

$\frac{d(B)}{dt} = k_2 (A)(B)$

$+\frac{1}{2}\frac{d(C)}{dt} = k_3 (A)(B)$

LHS अभी equal नहीं है तो equal करो
i.e

$\frac{3}{2} \times -\frac{1}{3}\frac{d(A)}{dt} = \frac{3}{2}k_1 (A)(B)$

$\frac{d(B)}{dt} = k_2 (A)(B)$

$\frac{2}{3} \times \frac{1}{2}\frac{d(C)}{dt} = \frac{2}{3}k_3 (A)(B)$

$$-\frac{1}{2}\frac{d(A)}{dt} = \frac{3}{2}k_1(A)(B)$$

$$\frac{d(B)}{dt} = k_2(A)(B)$$

$$\frac{1}{3}\frac{d(C)}{dt} = \frac{2}{3}k_3(A)(B)$$ (NOW L.H.S = R.H.S)

TYPES OF REACTION.

ELEMENTARY REACTION.

- Rx^{ns} which completes in a single step and there is no experimentally detectable intermediate is form, then Rx^n is c/d "ELEMENTARY Rx^n".
- The order and molecularity of elementary Rx^n are same (EXCEPT Pseudo order)

COMPLEX REACTION

- Rx^{ns} which are complete in more than one step and atleast one experimentally detectable intermediate is formed, then Rx^n is c/d "COMPLEX Rx^n"
- There is no significance of molecularity and order of Rx^n determined by S.S.A (steady state approximation). method or equilibrium method.
- Each step of complex Rx^n is elementary Rx^n.
- The steps involved in complex Rx^n are conjugative
  i.e. $A \rightarrow B$
  $B \rightarrow C$
  $C \rightarrow D$

→ The order and molecularity of ~~Com~~ Elementary reaction are (Same) (except pseudo-order)

→ There is no Significance of Molecularity and order of Rx^n determined by (SSA) Steady State Method or equillibrium Method

(each step has its own Arhenius eqⁿ in Complex rxⁿ.) → Each step of Complexation, each is elementary rx^n

→ The steps involve in Complex reaction are Consecutive

* Order and Molecularity :-

Molecularity → The total no of (reactant) molecule participate in an stichiometric equation of elementary reaction.

⇓

$2A + B \rightarrow 3C$

divide
करना
तो fraction
value होगा

2. Moleculority never "zero", never "-ve" & never fractional (Integer Value)

3. The moleculority of the rxn not change with changing the balance equation.

$H_2 + I_2 = 2HI$ — Moleculority = 2

Balance eqn change: $[2H_2 + 2I_2 = 4HI]$ — but moleculority will be [2]

4. The value of moleculority is not very / high bcos of effective collisions.

5.* There is no significance of moleculority in Complex reactions, Each step of Complex reaction has there individuall moleculority, but sometimes Moleculority of Complex reaction expressed by the moleculority of RDS. (slow step).

* ORDER OF REACTION

The no. of reactant molecule effectively participate in the (RDS) step of the reaction, called order of rxn.

* Elementary rx^n whose order and moleculority are diff called pseudoorder rx^n.

In other words, the order of reaction is the Sum of, the powers of Conc^n terms present in the rate law of the rx^n

$$rate = [A]^x [B]^y$$

$[x+y] \Rightarrow$ order

→ Order of reaction may be Zero, fractional or -ve.

→ The order of reaction also not high, bcos of effective Collision factor.

→ Experimentally there is no eg. of overall -ve order.

* Rate Law :- Of the Reaction →

Acc. to rate law rate of rx^n is directly proportional to the effective Concentration of reactants.

$$2A + B \longrightarrow P$$

Acc. to rate Law →

$$Rate \propto [A]^x [B]^y$$

$$Rate = k [A]^x [B]^y$$

k - rate Const

imp

$$\text{Unit of } k = (mol\ lit^{-1})^{1-n}\ time^{-1}$$

$k = [A]^n$

$$k = \frac{rate}{(A)^n} = \frac{(mol\ lit^{-1})\ time^{-1}}{(mol\ lit^{-1})^n}$$

$$\text{Unit of } k = (mol\ lit^{-1})^{1-n}\ time^{-1}$$

- Zero order: $n=0$ → $mol\ lit^{-1}\ time^{-1}$
- 1^{st} order: $n=1$ → $time^{-1}$
- 2^{nd} order: $n=2$ → $lit\ mol^{-1}\ time^{-1}$
- 3^{rd} order: $n=3$ → $lit^2\ mol^{-2}\ time^{-1}$
- 4^{th} order: $n=4$ → $lit^3\ mol^{-3}\ time^{-1}$

Net June 2018

$$Rate = k(A)^n$$

if $[A] = 1M$ (Unity)

then $rate = k$

Specific Rate ⇒ Specific Rate Constant

"The Value of specific rate and specific rate Constant will be Same."

The Unit of specific rate Constant depends on order of rxn i.e

$[(M.\ lit^{-1})^{1-n}\ (time)^{-1}]$