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CONGRATULATIONS

CHM 305

Chemical Kinetics

Introduction: It is a branch of physical chemistry that the deals with the study of reaction rates and mechanisms of chemical reaction

Rate of reactions are studied to help

Mechanism of rxn deals with step by step processes taken place in a chemical reaction. (such as bond breaking & bond formation)

It invaves an interpretation of ~~chemical laws~~ emperical laws in terms of the reaction mechanism.

Why chemical kinetics is Important

It provide insights into the mechanism of Chemical process which can be used to control rxn and improve processes.



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to the Ogun State Teaching Service Commission

28TH JUNE, 2024

~~Review of Rate Equation Rea~~

Chemical kinetics relates to many aspect of cosmology geology, biology, engineering and even psychology

Assignment

What are the ~~applies~~ Practical applications to the following fields; give at least 3 examples and write chemical equations when necessary

(1) Industrial processing
(2) Pharmacy
(3) Medicine
(4) Psychology
(5) Geology

Review of Rate Equation Reaction Rate

- Instantaneous rate
- Relative rate $\Rightarrow$ $A + B \rightarrow C + D$

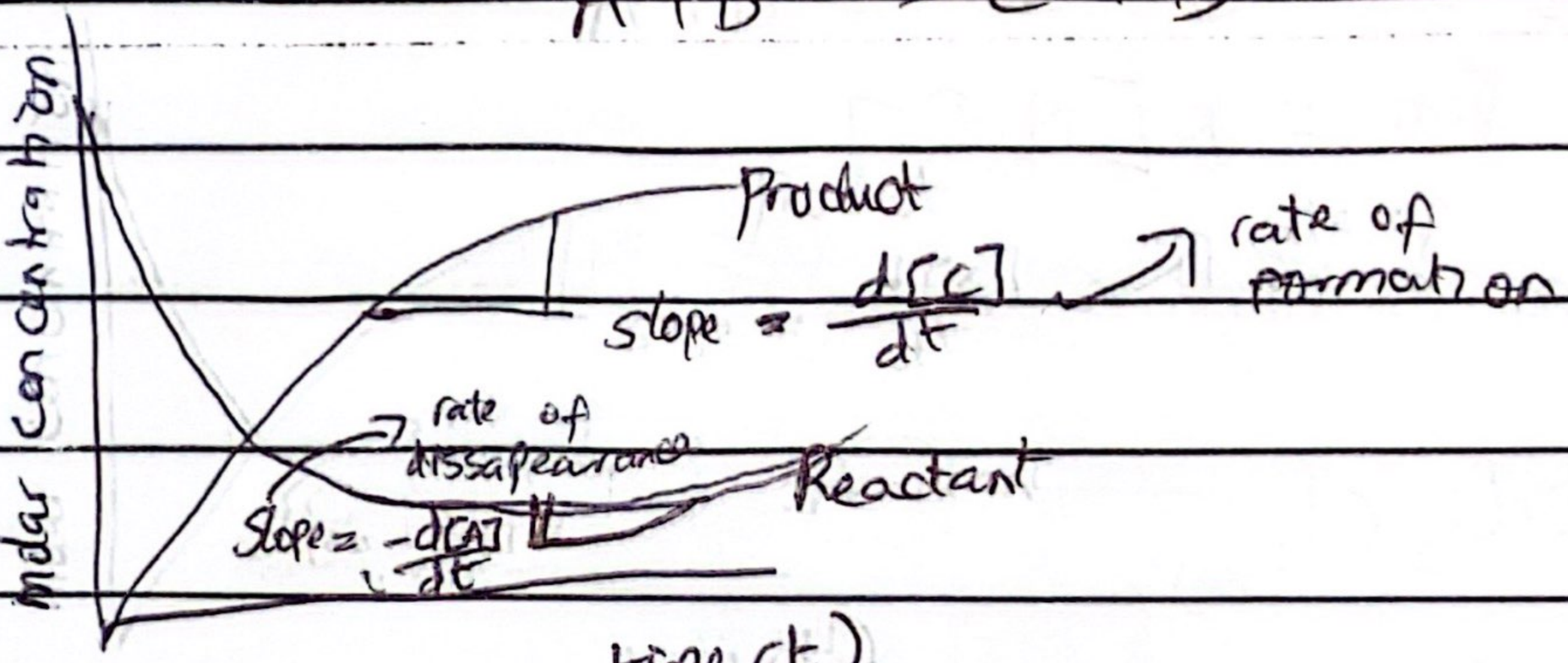
$$-\frac{d[A]}{dt} = \frac{-d[B]}{dt} = \frac{d[C]}{dt} + \frac{d[D]}{dt}$$

Rate of Reaction

It refers to Speed /velocity of the rxn. It can be expressed in terms of concentration of any of the reactant or any of the product

CONGRATULATIONS

$A + B \rightarrow C + D$



Curve showing the concentration of Product and the concentration of reactant as a function of time

Ratio of Reaction

Rate Laws and Rate Constant

Rate $\propto [A]^n$ → concentration

Rate $= k[A]^n$

Order of Reaction

For a reaction $\alpha A + \beta B + \gamma C \rightarrow$ Product

Rate Law: Rate $\propto [A]^\alpha [B]^\beta [C]^\gamma$

Rate $= k[A]^\alpha [B]^\beta [C]^\gamma$

↓

rate constant



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Example

(1) $2N_2O_{5(g)} \longrightarrow 4NO_{2(g)} + O_{2(g)}$

Rate $= K[N_2O_5]$

Rate is first order wrt N_2O_5

(2) $SO_2Cl_{2(g)} \longrightarrow SO_{2(g)} + Cl_{2(g)}$

Rate $= K[SO_2Cl_2]$

Rate is 1st order wrt SO_2Cl_2

Rate constant is independent of conc of reactant but depends on temperature

intermediate

Order and Reaction Stoichiometry

In many cases, this is not necessarily a simple relationship between

You can't examine stoichiometry and conclude the order of reaction.

This is bcos, a rxn occurs by a complex Mechanism, involving a number of steps.

Eg Consider

(1) $CH_3CHO \longrightarrow CH_4 + CO$

$$\text{Rate} = k[CH_3CHO]^{3/2}$$

(2) $Hg_2^{2+} + Tl^{3+} \longrightarrow Hg^{+} + Tl^{+}$

$$\text{Rate} = k\frac{[Hg_2^{2+}][Tl^{3+}]}{[Hg^{2+}]} = k\frac{[Hg_2^{2+}][Tl^{3+}]}{[Hg^{2+}]}$$

$$\Rightarrow k[Hg_2^{2+}][Tl^{2+}][Hg^{2+}]^{-1}$$

Hence, rate laws must be determined experimentally from measurements of reaction rate and cannot be deduced from reaction stoichiometry

Molecularity

It is the sum of the stoichiometry coefficient of Reactant involved in the stoichiometrically balanced equation of reaction.

e.g A → Product molecularity = 1 (unimolecular)

A + B → product 2 (bimolecular)

2A → product 2 (bimolecular)

2A + B → product 3 (Termolecular)

Note: Molecularity is not the same as reaction order

Methods of Determing Reaction Order

(1) The method of integration
(2) Half-life period method
(3) Differential method
(4) Isolation method.

Integrated form of rate expressions is used. Rate equation for reactions can be obtained from the differential form of the rate law.

~~* Conc does not affect the rate of reaction~~

(1) Zero-order reaction

Rate is independent on concentration of such reaction

$$2HI_{(s)} \longrightarrow H_{2(g)} + I_{2(g)}$$

$$Rate = k[HI]^0$$

A → product

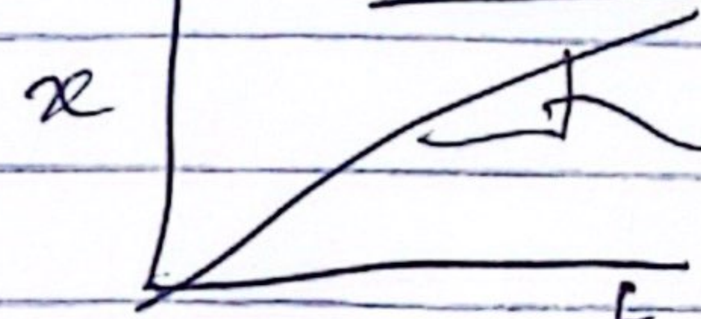
t=0	a	0
t=t	a−x	x

Rate of formation, rate $= \frac{dx}{dt} = K[A]^0$

$\Rightarrow \int dx = \int K$ $\Rightarrow \frac{dx}{dt} = K \Rightarrow \int dx = \int K dt$ ---①

$x = Kt$ // ..... ②
$y = mx$

For zero order;



K is always constant (Pre sand) in Mathematical test

$K = \frac{x}{t}$ $mol\,dm^{-3}s^{-1}$

First Order Reaction

A → product

t=0	a	0
t=t	a−x	x

Rate $= K[A]^1$

Rate of formation of product $= \frac{dx}{dt} = K(a-x)$ ..... ③

$\Rightarrow \int \frac{dx}{(a-x)} = \int K dt$ ..... ④

Integrating;

$\ln \frac{a}{a-x} = Kt$ ⑤

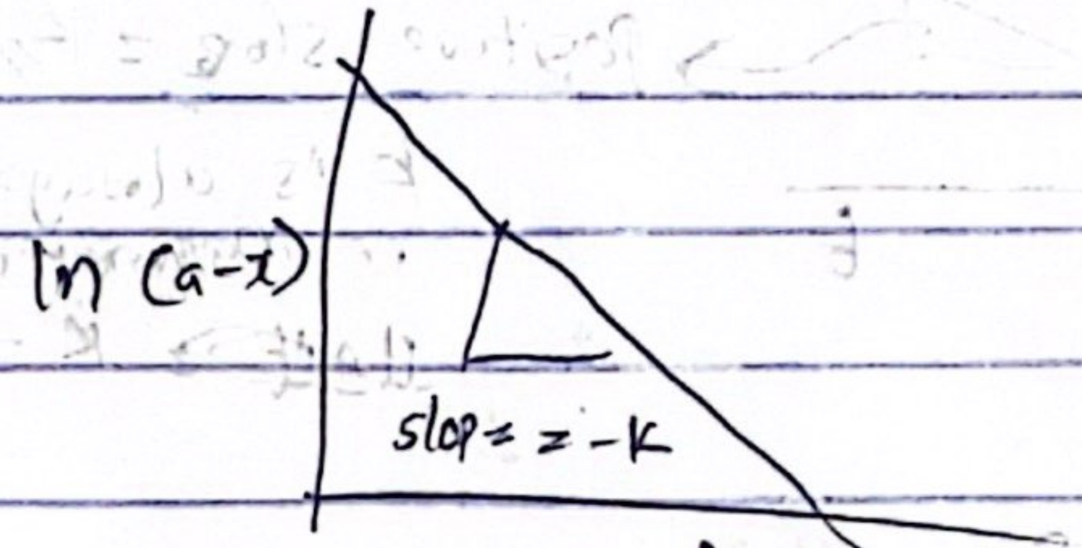
$\Rightarrow \ln a - \ln(a-x) = kt$

In first order, you get a negative slope.

$\Rightarrow -\ln(a-x) = kt - \ln a$

$\ln(a-x) = \ln a - kt$

$\ln(a-x)$: y ; $\ln a$: c ; $-kt$: mx



Note

* unit
* explain Interpretation

Exercise

The Kinetics of reaction was followed by measuring the absorbance due to the reaction at its λ_{max} at 25°C by following

The (log (Abs) vs time (mins) was plotted in a straight line with a negative slope (0.30×10^{-2}) and a positive intercept. Find the half life period of reactant.

Note: Justify your use of integrated first order equation.

$A_z \varepsilon Cl$, $A \propto C$

absorbance

Solution

Because $A \propto C$

and ~~Concentration~~ rate is dependent on concentration in first order reaction

$\therefore$ log(Abs) vs time graph will be linear

It is not zero order because in zero order rate does not depend on concentration $\therefore$ log(Abs) vs time will not be linear.

$\therefore \ln[A]_t = -kt + \ln[A]_0$

Since absorbance $\propto$ concentration, we can substitute Abs for [A]

$\therefore \ln[Abs] = -kt + \ln(Abs)_0$

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Second Order Reaction

Case 1: $A + B \longrightarrow$ Pdt

Case 2: $2A \longrightarrow$ pdt

for case 2: $A \longrightarrow$ product

at $t=0$	a	0
at $t=t$	a-x	x

$$kt = \frac{1}{a-x} - \frac{1}{a}$$

$$kt = \frac{1}{[A]_t} - \frac{1}{[A]_0}$$

Third order

Case 1 $A + B \longrightarrow K[A]^1[A]^2$

case 2 $A \longrightarrow K[A]^3$

Case 3 $A + B + C \longrightarrow K[A][B][C]$

$$Rt = \frac{1}{a-b} \ln \frac{b(a-x)}{a(b-x)}$$

Example

A zero order reaction is 50% complete in 20 mins how much time is will it take to reach 90% completion.

$$k = \frac{x}{t}, \quad x = \frac{a}{2} \text{ @ } 50\%$$

$$K = \frac{a}{2/t_{1/2}} \Rightarrow t_{1/2} = \frac{a}{2K}$$

$$\Rightarrow K = \frac{a}{2 \times 1200\ s} \Rightarrow K = \frac{a}{2400}\ mol.dm^{-3}s^{-1}$$

(c) 90% completion $x = 90\%$ of a

$$K = \frac{x}{t} \qquad t = \frac{x}{K}$$

$$\frac{0.9a}{t} = \frac{a}{2400}$$

$$\Rightarrow t = \frac{0.9a}{a} \times \frac{1}{2400}$$

$$t = 2160\ s //$$

$t =$

Half-Life Period Method

Reaction rate can be expressed in terms of half life period.

$t = t_{1/2}$ when $x = a/2$

$$t_{1/2} = \frac{2^{n-1} - 1}{(n-1)\,K a^{n-1}} \quad \text{for } n \neq 1$$

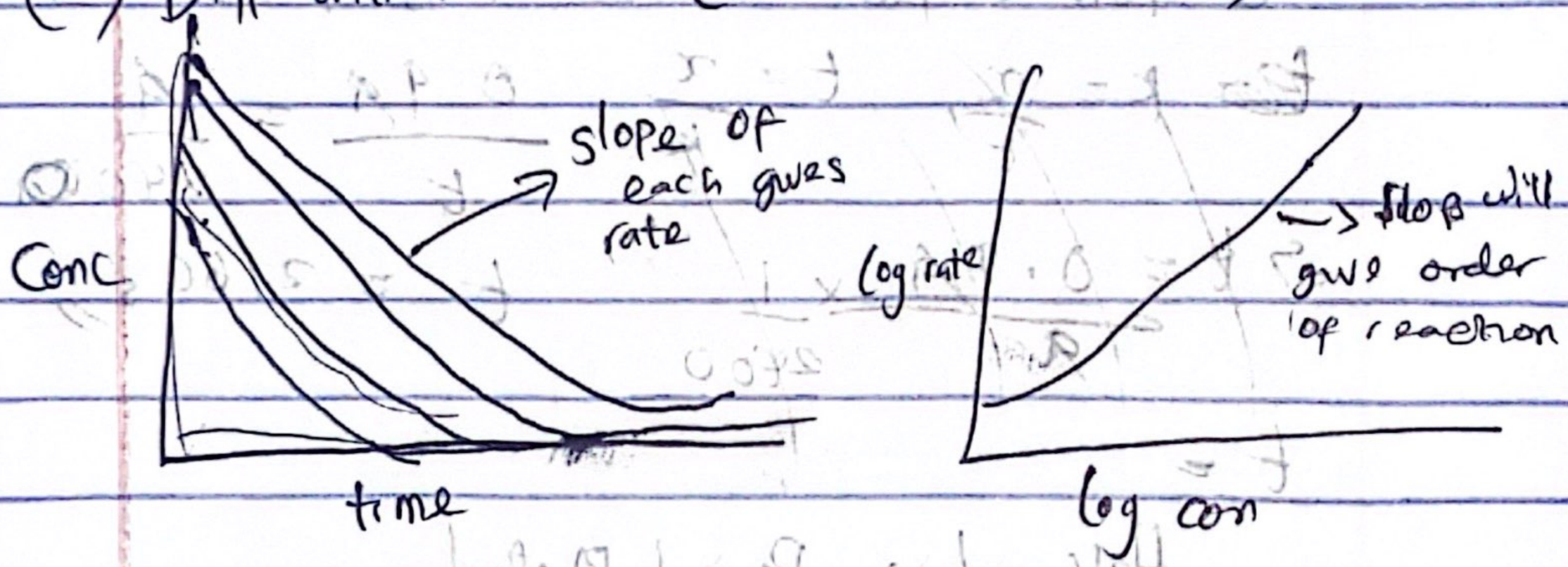
$a_1, a_2 \longrightarrow (t_{1/2})_1, (t_{1/2})_2$

$$(t_{1/2})_1 \propto \frac{1}{(a_1)^{n-1}}$$

$$(t_{1/2})_2 \propto \frac{1}{(a_2)^{n-1}} \Rightarrow \frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{(a_2)}{(a_1)}\right)^{n-1}$$

$$\log \frac{(t_{1/2})_1}{(t_{1/2})_2} = n-1 \log\left(\frac{a_2}{a_1}\right)$$

(iv) Differential Method (initial rate method)



(v) Isolation Method — Without using graph

$$\text{Rate} = k a_1^n$$

$$\text{Rate}_2 = k a_2^n$$

$$n = \log\left(\frac{\text{rate}_1}{\text{rate}_2}\right)$$

Experimental Measurement of Reaction Rate

(a) Carrying Out Reaction Kinetics requires;

(i) Determination of the Concentration of at least one of the reactants or product as a function of time

151 * Amples when it is ages

Physical pr

(2) The method of analysis employed must be faster than the rate of reaction

(3) Accurate measurement and control of temperature/pressure

$RCOOR' + Na^+ + OH^- \rightarrow RCOO^-Na^+ + ROH$

(Conductivity decreases)

for measuring

Dilatometry → Pressure changes, Volume changes

Activity ⇒ Concentration ⇒ potentiometric method

Stopped flow

* Syringe allows to release solution in a little amount
* Mixing is faster
* Readings can be pattern at intervals
* Not affected by rate and pattern of flow
* very small amount of reactant is required.

Continuous flow

* requires large Volume of reactant
* Mixing time is not as faster as stopped flow

Flash photolysis

Suitable for very fast rxn.

Eg

$CH_2COCH_3 + h\nu \rightarrow 2CH_3^{\bullet} + CO$

Needs a rxn of free radicals, (Chemicals that can generate what is needed is called precursors)

In flash, the light radiation period is longer

pulse, short but intense

Purpose of laser is not generate pulse.

* How to Generate Laser Radeation

By mixing Helium with a noble gas and either fluorine or HCl

Relaxation Techniques

* It is also suitable for very fast rxn especially fle reactions with high rate

* Only reactions close to equilibrium can be applied

of sound, temp, conc, temperature)

Types of Relaxation Technique

Change in temperature — T jump

Change in pressure — Pressure jump

Change in sound — Ultrasonic

* Reaction is first allowed to attain equilibrium
* The Perturbed
* Get new equilibrium position
* Then use special techniques

Shock Tubes Techniques

(i) Need high pressure gas (refers to driver gas)

A thin diaphragm is used to partition it

The diaphragm breaks when pressure is high and mixes together.

High temperature is required

Q-11-24

$t_{1/2} = \frac{\ln 2}{\theta}$

Relaxation Technique Contd:-

Consider a simple system

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

$t=0$	a	0
$t=t$	$a-x$	x

The reaction is first order in both direction

Suppose the system is in equilibrium, and a is the initial concentration A and x is the concentration of B at time t.

$$\frac{dx}{dt} = k_1(a-x) - k_{-1}x \quad \cdots \textcircled{1}$$

At equilibrium, $\frac{dx}{dt} = 0$, let $x = x_e$

$$\therefore k_1(a-x_e) - k_{-1}x_e = 0$$

$$k_1(a-x_e) = k_1 x_e \quad \cdots \textcircled{2}$$

As the equilibrium is disturbed, the deviation from equilibrium $\Delta x = x - x_e$

$$\frac{d\Delta x}{dt} = \frac{dx}{dt} = k_1(a-x) - k_{-1}x$$

$$= k_1 a - (k_1 + k_{-1})x$$

$$\frac{d\Delta x}{dt} = k_1 a - (k_1 + k_{-1})(x_e + \Delta x) \quad \cdots \textcircled{3}$$

equilibrium constant = K_c (Capital)
rate constant = k (small)

from eqn (2) and (3) $\frac{d\cdot\Delta x}{dt} = -(K_1 + K_{-1})\Delta x$ ---- (4)

Δx varies with time in the same manner, as does the concentration of a reactant in a first order reaction

Hence $\ln \frac{(\Delta x)_0}{\Delta x} = (K_1 + K_{-1})t$ ---- (5)

Where $\Delta x = (\Delta x)_0$ when $t = 0$ has been taken as boundary conditions. equation 5 gives;

$t^* = \frac{1}{K_1 + K_{-1}}$ when $\ln \frac{(\Delta x)_0}{\Delta x} = 1$

↓

Relaxation time

K_1 K_{-1} can be obtained from the equation

$\frac{k_1}{k_{-1}} = K$ ← equilibrium constant

Questions

(1) The rate constant for the first order decomposition of N_2O_5 has the value of $k = 4.8 \times 10^{-4} s^{-1}$ @ 45°C. (a) What is the half of the reaction. (b) What will be the pressure initially, 500mmHg after (i) 10s and (ii) 10mins after the initiation of the reaction. (p ≡ Concentration)

Answer: At 10 mins $P_t = 374.87 mm Hg$

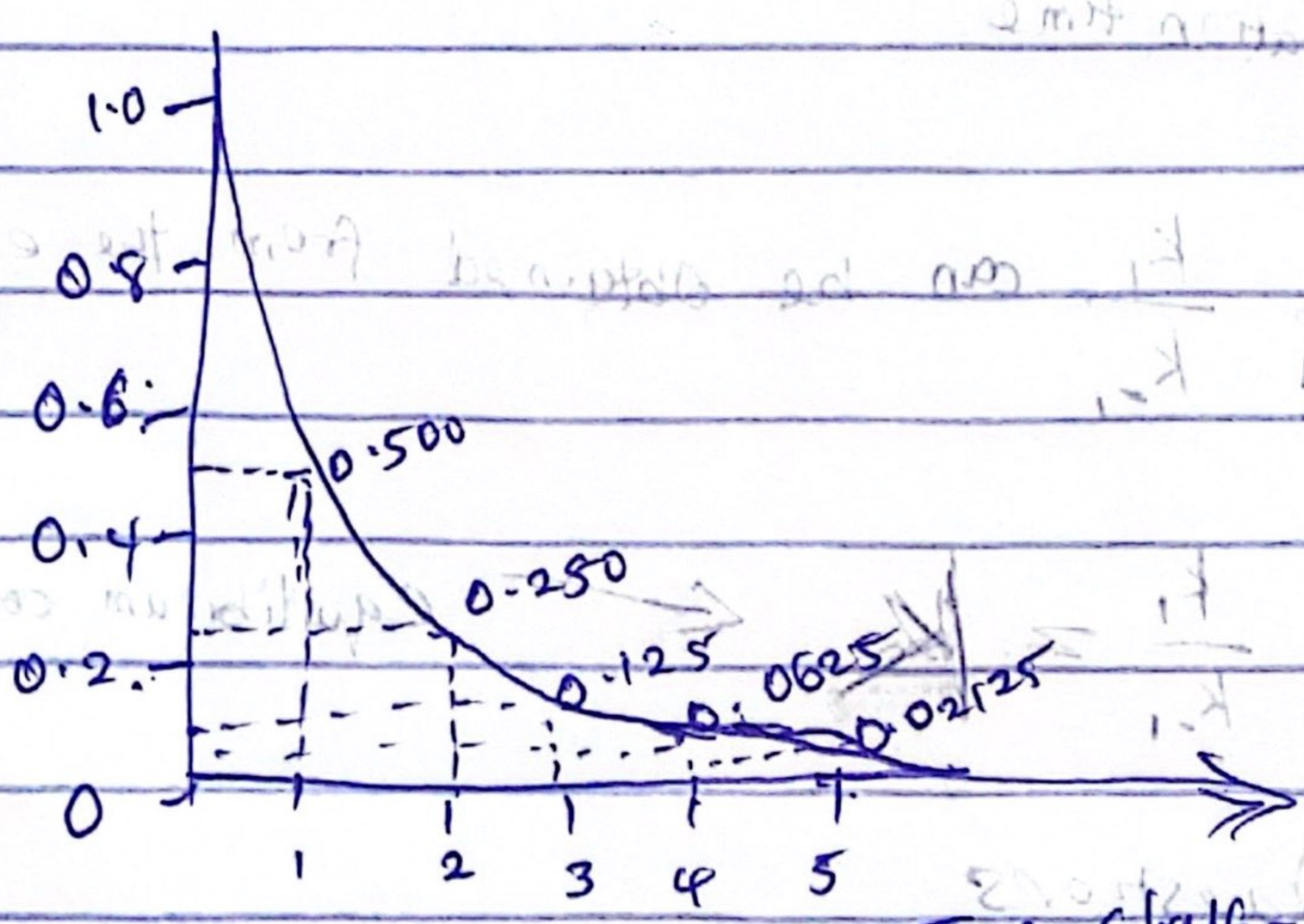
$P_i = C_i - P_t = C_t$

(2) The anti cancer drug cis-platin hydrolyses in water at a rate constant of $1.5 \times 10^{-3} min^{-1}$ at pH 7.0 and 25°C.

(a) Calculate the half life for the hydrolysis under reaction Under these conditions. $(4.6 \times 10^2 mins)$

(b) If a freshly prepared solution of cis-platin has a concentration of 0.053M, what will be the concentration of cis-platin after (i) 5 half lives (38 hrs) (ii) 10 half lives.

(c) What is the percent completion after 5 half lives and after 10 half lives?



Answer

(a) $t_{1/2} = 4.6 \times 10^2 mins$

(b) after 5 half lifes (38 hrs)

$= 0.053 \times \left(\frac{1}{2}\right)^5 = \frac{0.052}{2^5} = 0.0017M$

General Equations

per half lives $\frac{100\%}{2} = 50\%$

And remaining $\frac{1}{2}$ x initial conc $= \frac{1}{2}[A]_0$

$\left(\frac{1}{2}\right)^n \times [A]_0 \Rightarrow \left(\frac{1}{2}\right)^n \%$

No of half lives $(n) = t/t_{1/2}$

$n = \frac{t}{t_{1/2}}$

Effect of Temperature on Reaction Rates

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2}$$

$$k = Ae^{-\frac{E_a}{RT}}$$

$$\ln k = \ln A - \frac{E_a}{RT}$$

Transition State Theory

also known as absolute rate theory

$$A + B \rightleftharpoons [A \cdots B]^{\neq} \longrightarrow \text{Product}$$

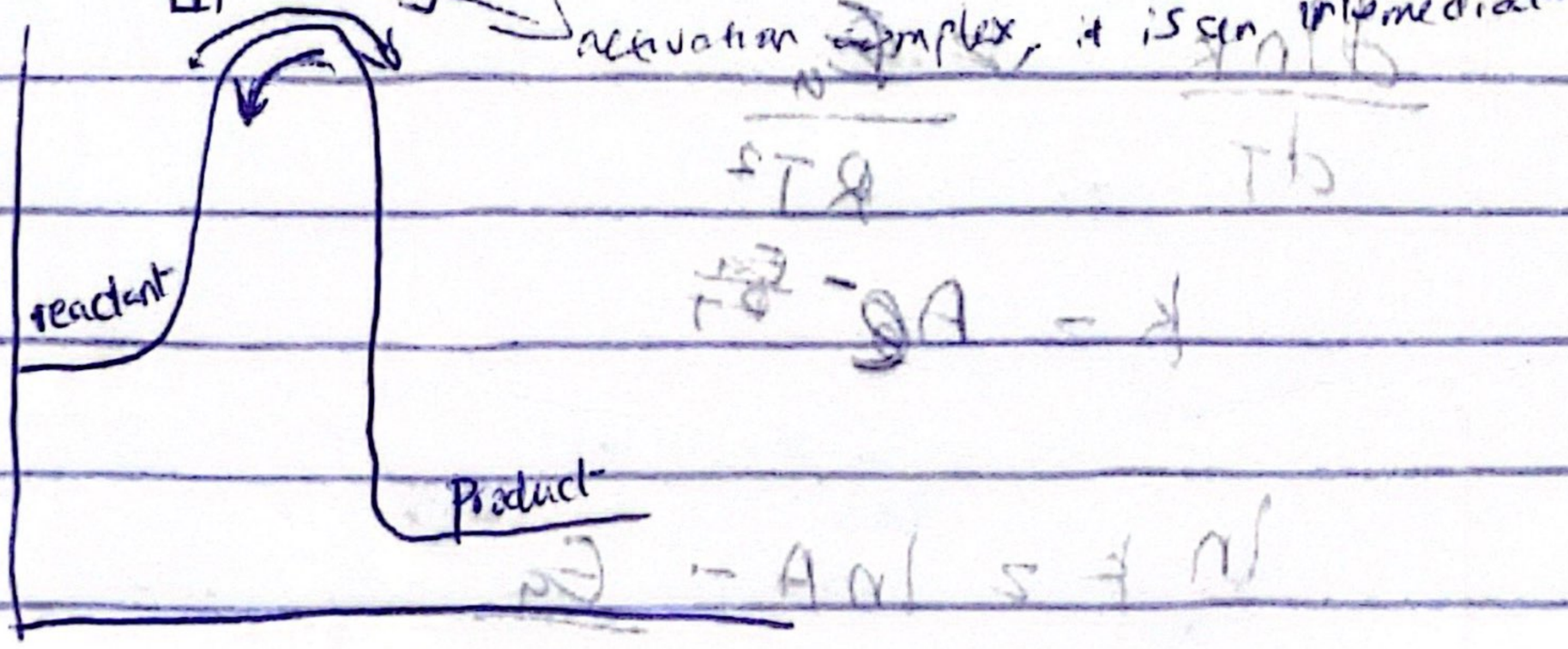
Activated complex

It is assumed that when molecules come together, there is a form of association that occurs. This association forms activation complex.

Assumption

(1) $AB + C \rightleftharpoons [A \cdots B \cdots C]^{\neq} \rightarrow A + BC$

For reaction to occur, the molecules or reactant must close together to form an activated complex.



(2) An equilibrium is set up between the reactant and the product, at every stage of the reaction.

$$A\text{-}B + C \rightleftharpoons A \cdots B \text{------} C$$

$$\rightleftharpoons A \cdots\cdots B \text{------} C$$

$$\rightleftharpoons [A \cdots B \cdots C] \longrightarrow A + BC$$

(3) The activated complex has been considered as a seperate entity

$$A + B \underset{}{\overset{K^{\neq}}{\rightleftharpoons}} X^{\neq} \longrightarrow (+1)$$

(activated complex)

$$[X^{\neq}] = K^{\neq}[A][B] \quad \cdots (1)$$

(4) One Vibrational degree of freedom of a complex is quite unstable and responsible for disrupting the activated complex in the product

$$\therefore E_{vib} = K_b T = h\nu$$

$$\therefore \nu \text{ (frequency)} = \frac{K_b T}{h}$$

The rate at which activated complex breaks into the product is

$$\text{Rate of reaction} = [X^{\neq}]\nu$$

$$\text{Rate} = \frac{K_b T K^{\neq}[A][B]}{h}$$

If $K \equiv$ rate constant

$$A + B \xrightarrow{K} \text{product}$$

Experimentally,

$$\text{Rate} = k[A][B]$$

Then,

$$k[A][B] = \frac{k_b T}{h} K^{\neq}[A][B]$$

$$\therefore \boxed{k = \frac{k_b T}{h} K^{\neq}}$$

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Theories of Bimolecular Reaction Rates

$$K = \frac{K_b T}{h} k^{\neq} \quad \text{---- (6)}$$

(1) Thermodynamic of Reaction rate in TST

$$RT \ln K = -\Delta G$$

$$K = e^{-\frac{\Delta G}{RT}}$$

$$\Delta G = \Delta H - T\Delta S^{\circ}$$

$$\Rightarrow K = e^{-\frac{(\Delta H^{\circ} - T\Delta S^{\circ})}{RT}}$$

$$\Rightarrow K = e^{-\frac{\Delta H^{\circ}}{RT}} \cdot e^{\frac{\Delta S}{R}}$$

$$K^{\neq} = e^{-\frac{\Delta G}{RT}} \cdot e^{-\frac{\Delta H^{*}}{RT}} \quad \text{---- **}$$

Substituting eqn (**) into eqn (6)

$$K = \frac{K_b T}{h} e^{\frac{\Delta S^{\neq}}{R}} \cdot e^{-\frac{\Delta H^{\neq}}{RT}}$$

$$\ln K = \ln \frac{K_b T}{h} + \ln(T) + \ln(K^{\neq})$$

OR

$$\frac{d(\ln K)}{dT} = \frac{1}{T} + \frac{d \ln k}{dT}$$

$$K = A e^{-E_a/RT}$$

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2} \quad \text{---(15)}$$

$$\frac{E_a}{RT^2} = \frac{1}{T} + \frac{d \ln k^{\neq}}{dT} \quad (E_a = E_{exp})$$

$$\frac{d \ln k^{\neq}}{dT} = \frac{E_{exp}}{RT^2} \quad \text{---(16)}$$

$$\frac{d \ln k^{\neq}}{dT} = \frac{\Delta E^{\neq}}{RT^2} \quad \text{---(17)}$$

From eqn (13)

$$\frac{d \ln k}{dT} = \frac{1}{T} + \frac{d \ln k}{dT} \quad \text{---(18)}$$

$$\frac{d \ln k}{dT} = RT + \frac{\Delta E^{\neq}}{RT^2} \quad \text{---(19)}$$

$$E_{exp} = RT + \Delta E^{\neq} \quad \text{---(20)}$$

$$\Delta E^{\neq} = \Delta H^{\neq} - p \Delta V^{\neq}$$

$$E = H - PV$$

$\Delta V^{\neq}$ = Change in volume from initial state to activated state

$$E_{exp} = \Delta H^{\neq} - p \Delta V^{\neq} + RT.$$

$$E_{exp} = \Delta H^{\neq} + RT - \Delta n^{\neq} RT$$

$$\Delta H = E_{exp} - RT(1 - \Delta n^{\neq})$$

$$K = \frac{K_b T}{h} e^{+\frac{\Delta S}{R}} \cdot e^{-\frac{E_{exp}}{RT}} \cdot e^{(1-\Delta n^{\neq})}$$

For Unimolecular $\Delta n = 0$

$$\therefore K = \frac{K_b T}{h} e^{\frac{+\Delta S}{R}} \cdot e^{-\frac{E_{exp}}{RT}} \cdot e$$

for Bimolecular $\Delta n = 1$,

$$K = \frac{K_b T}{h} e^{\frac{+\Delta S}{R}} \cdot e^{-\frac{E_{exp}}{RT}} \cdot e^2$$

$$K = A Q^{-E_a/RT}$$

(11) / Partition function Approach

$$aA + bB \rightleftharpoons cC + dD$$

$$K_c = \frac{Q_C^c \, Q_D^d}{Q_A^a \, Q_B^b} e^{-E_0/RT}$$

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X^{\neq}$$

$$K^{\neq} = \frac{k_1}{k_{-1}} = \frac{[X^{\neq}]}{[A][B]}$$

$$k^{\neq} = \frac{Q^{\neq}}{Q_A Q_B} e^{-\frac{E_0}{RT}}$$

$$\frac{k_b T}{h\nu}$$

$$\therefore K^{\neq} = \frac{[X^{\neq}]}{[A][B]} = \frac{k_b T}{h\nu} \frac{Q^{\neq}}{Q_A Q_B} e^{-\frac{E_0}{RT}}$$

$$[X^{\neq}] = \frac{k_b T}{h\nu} \frac{Q^{\neq}}{Q_A Q_B} e^{-\frac{E_0}{RT}} \cdot [A][B]$$

Transition state expression for the rate constant of an ideal gas;

Rate of reaction $\Rightarrow K = \frac{k_b T}{h} \frac{Q^{\neq}}{Q_A Q_B} e^{-\frac{E_0}{RT}}$

$$k = A e^{-E_a/RT}$$

Recommended Texts

(1) Physical chemistry Textbook by Sharma &
(2) Chemical Kinetics by K.J Laidler
(3) Reaction Kinetic and Dynamics by Santosh Upadhyah

$\Delta \rightarrow CH_3CH=CH_2$

$RX \rightarrow$ Olefinic $+ HX$

$CH_3N_2CH_3 \longrightarrow C_2H_6 + N_2$

Lindemann Laagmuir Principle

(i) Energy is transferred by collision

* There is a time delay Δt between collision and reaction

(ii) Molecules may be deactivated by another during collisions

Equations

Step 1 : $A + A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + A$ ..... (1)

Step 2 : $A^* \xrightarrow{k_2}$ product ------ (2) (time lag)

* The rate determining step is the slow step

$\therefore$ Rate $= k_2[A^*]$

Overall rate => (Rate of formation of A^* − Rate of consumption of A^*)

$$\frac{d[A^*]}{dt} = k_1[A]^2 - [k_{-1}[A^*][A] + k_2[A^*]] \quad \text{---- (3)}$$

Steady state approximation

Rate of formation of A^* − Rate of formation of A^* = 0

∴ From eqn (3)

$$[A^*] = \frac{K_1[A]^2}{K_2 + K_{-1}[A]} \quad \text{---(4)}$$

And Rate = $K_2[A^*]$

$$\Rightarrow \text{Rate} = \frac{K_2 K_1 [A]^2}{K_2 + K_{-1}[A]}$$

$$\Rightarrow \text{Rate} = \frac{K_1 K_2 [A]^2}{K_2 + K_{-1}[A]}$$

To minimize the complexity $\xrightarrow{\text{under high pressure}}$ if K_{-1} is very large, it makes K_2 negligible

$$\Rightarrow \text{Rate} = \frac{K_1 K_2 [A]^2}{K_{-1}[A]}$$

$$r = \frac{K_1 K_2 [A]}{K_{-1}} \quad \text{~~first order~~}$$

$$r = K_\infty [A] \longrightarrow \text{first order}$$

At low pressure $K_{-1} << K_2$

So we have Rate = $\frac{K_1 K_2 [A]^2}{K_2}$

∴ Rate = $k_1[A]^2$ → 2nd order

Outline Dr. Onida

(1) Complex reaction types

— Opposing/reversible reaction

(2) Consecutive reactions

(3) Parallel reactions

(2) Chain reactions

- Main step in chain reactions

- Application of steady state approximation to treatment of rates

- Chain length

- Activation energies

(3) Reactions in solution

- Cage and diffusion effect

- Importance of solvent properties, particularly dielectric constant

- Reaction between ions and Bronsted-Bjerrum equations

Reaction Rates

Importance concepts

The rate of reaction is expressed as the change in reactant concentration with time

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

$$\text{Rate} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$$

Reaction Order

Order of reaction is not determined by stoichiometry, it is determined experimentally.

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

$$\text{rate} = k[N_2O_5]$$

Molecularity

An elementary reaction is a one-step reaction that usually only involves the breaking and making of one or two bonds.

It is number of species that are taken part in the reaction

$$NO + O_3 \longrightarrow NO_2 + O_2 \text{ (bimolecular)}$$

It also indicates the number of collision partners involved in the reaction

1 (unimolecular), 2 (bimolecular), 3 (Termolecular)

Composite Reactions

A composite reaction is a reaction that has a mechanism involving two or more elementary steps

In principle, the rate equation of a composite reaction can take any arbitrary form

However, every composite reaction contains a rate-determining Step. A rate determining Step is the elementary Step in the reaction mechanism, that has a great influence on the reaction rate.

Typically, the overall reaction, is the sum of several steps. The sequence of steps by which a reaction occurs is called called the mechanism of the reaction.

There are several features of our reaction System that are a characteristics of composite reaction, including a number of steps, which includes:

(a) multiple bonds being made or broken

(b) The appearance of intermediate

(c) Measuring instantaneous rate that are different from reactant and product.

(d) Rate and rate order that change as a function of time

* rate determining step is the one that has the greatest influence on a reaction

(e) usually dependence on the rate, concentration, pH, temperature or other variable

An intermediate is a specie that is formed in an early elementary step and then consumed in a later elementary step. Although an intermediate appears in the mechanism of a reaction, it does not appear in the overall chemical equation. On the other hand, a catalyst appears as a reactant in a initial elementary step, it invariably forms an intermediate and is regenerated at the end of a reaction

Once we know the mechanism and the rate determing step, we can write the rate law of the reaction which must agree with the experimentally determined rate law

Complex Reaction

The Unimolecular and bimolecular reaction are simple, in the sense that only one reaction is taken place in each case. Unfortunately, this condition is often not satisfied in actual practice.

There are examples of other complex reaction;

Reversible Reaction.

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

$$k = \frac{k_1}{k_{-1}}$$

Most reactions are reversible to a certain extent, and we must consider both the forward and reverse rate. For the reversible reaction that proceeds by two elementary steps

$$\frac{d[A]}{dt} = -k_1[A] + k_{-1}[B]$$

At equilibrium, there is no net change in the concentration of A with time

i.e, $\frac{d[A]}{dt} = 0$

$$\Rightarrow -k_1[A] + k_{-1}[B] = 0$$

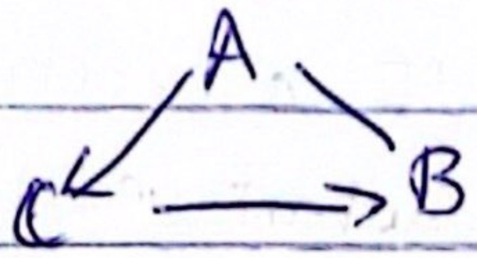
$$\Rightarrow k_1[A] = k_{-1}[B]$$

$$\frac{[A]}{[A]} \quad \frac{[B]}{[A]} = \frac{k_1}{k_{-1}} = K$$

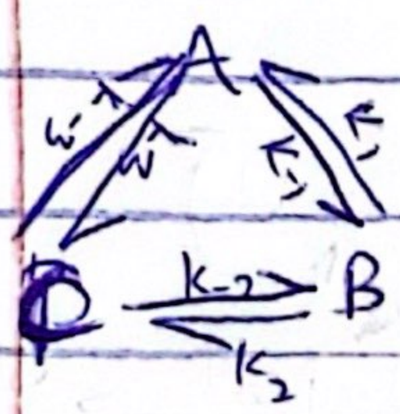
where K is the equilibrium constant

The principle of microscopic reversibility states that the rate of the forward and reverse process are equal, for every elementary reaction occurring

Which means the process A → B is exactly by B → A, so that equilibrium can not be maintained by a cyclic process, in which the forward reaction is A → B and the reverse reaction is B → C → A



Instead for every elementary reaction, we must write a reverse reaction as follow



$$A \rightleftharpoons B$$
$$B \rightleftharpoons C$$
$$C \rightleftharpoons A$$

$$\Rightarrow k_1[A] = k_{-1}[B]$$
$$k_2[B] = k_{-2}[C]$$
$$k_3[C] = k_{-3}[A]$$

The rate constant are not all independent so implemented by simple algebraic manipulation, we can show that

$$k_1 k_2 k_3 = k_{-1} k_{-2} k_{-3}$$

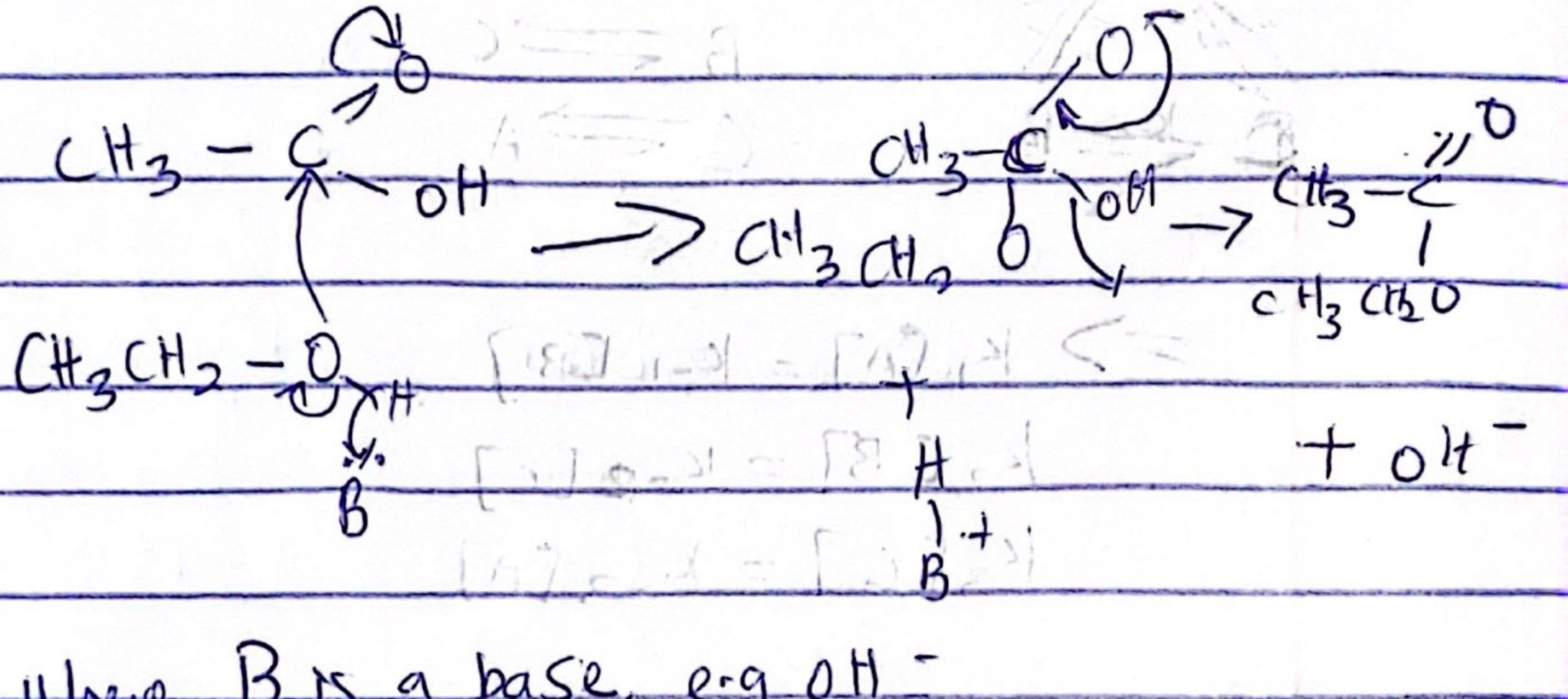
The usefulness of the principle of microscopic reversibity, is that it tell us that the reaction pathway for

the reverse of a reaction at equilibrium is the exact opposite of the pathway of the forward reaction.

Therefore, for the transition state for the forward and reverse reactions are identical

The transition state of a reaction is the complex formed between the reactant and the product along the reaction coordinates

Consider the base catalyzed esterification between acetic acid and ethanol

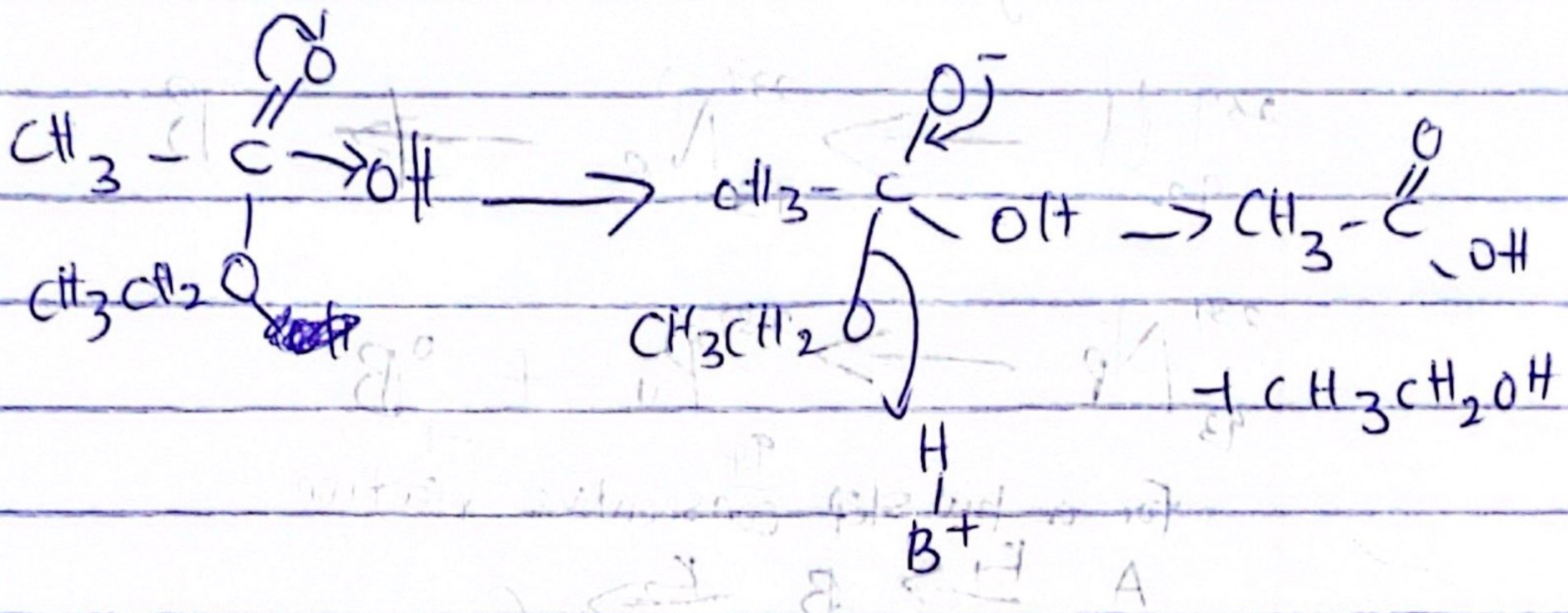


Where B is a base, e.g OH^-

The Specie formed in the first step is a Tetrahedral intermediate.

Now, according to the principle of microscopic reversible reaction, the reverse reaction, i.e the hydrolysis of ethyl acetate must involve the acid catalyzed

expulsion of ethoxide ion from te same tetrahedral intermediate



8th January

Consecutive Reaction

$A \longrightarrow B \longrightarrow C$

A Consecutive reaction is the one in which te product from te first step, becomes the reactant for te second step and so on.

The thermal decomposition of acetone in te gas phase is an example

$$CH_3COCH_3 \longrightarrow CH_2=CO + CH_4$$

$$CH_2=CO \longrightarrow CO + \frac{1}{2}C_2H_6$$

This is a form of consecutive reaction. Many nuclear decays are also consecutive. For

example, upon the capture of a neutron, a ^{238}U isotope is converted to ^{239}U isotope which then decays as follows

$$^{239}_{92}U \longrightarrow {}^{239}_{93}Np + {}^{0}_{-1}\beta$$

$$^{239}_{93}Np \longrightarrow {}^{239}_{94}Pu + {}^{0}_{-1}\beta$$

For a two step consecutive reaction

$$A \xrightarrow{K_1} B \xrightarrow{K_2} C$$

Because each step is first order, the rate law equations are;

$$\frac{d[A]}{dt} = -K_1[A]$$

$$\frac{d[B]}{dt} = K_1[A] - K_2[B]$$

$$\frac{d[C]}{dt} = K_2[B]$$

We assume that initially, only A is present and its concentration is $[A]_0$

The rate equation for A

$$A = [A]_0 e^{-Kt} \quad \text{---- (i)}$$

The rate equation for the intermediate B is Quite Complex, the System can be Simplified by applying the Steady State approximation to B, that is, by assuming that the concentration of B remains Constant over a certain period of time.

That means,

$$K_1[A] - K_2[B] = 0$$

$$K_1[A] = K_2[B]$$

$$[B] = \frac{K_1}{K_2}[A] \quad \ldots\ldots (iii)$$

Incorporating equation (iii) into eqn (i), we have

$$[B] = \frac{K_1}{K_2}[A]_0 e^{-Kt} \quad \ldots\ldots (i)$$

Eqn (iii) holds if $K_2 >> K_1$, under this Condition, B molecules are converted as soon as they are formed.

The concentration of [B] is kept constant and low compared to [A]

To get an expression for C, we note that at any instant, $[A]_0 = [A] + [B] + [C]$

Therefore, from eqn (i) and eqn (ii)

$$[C] = [A]_0 - [A] - [B]$$

Therefore;

$$[C] = [A]_0 - [A]_0 e^{-kt} - \frac{k_1}{k_2}[A]_0 e^{-kt}$$

The $\frac{k_1}{k_2}[A]_0 e^{-kt}$ is eliminated because it is much smaller than 1

$$\Rightarrow [C] = [A]_0 - [A]_0 e^{-kt}$$

$$\Rightarrow [C] = [A]_0 (1 - e^{-kt}) \quad \text{---} (4)$$

Graphically,

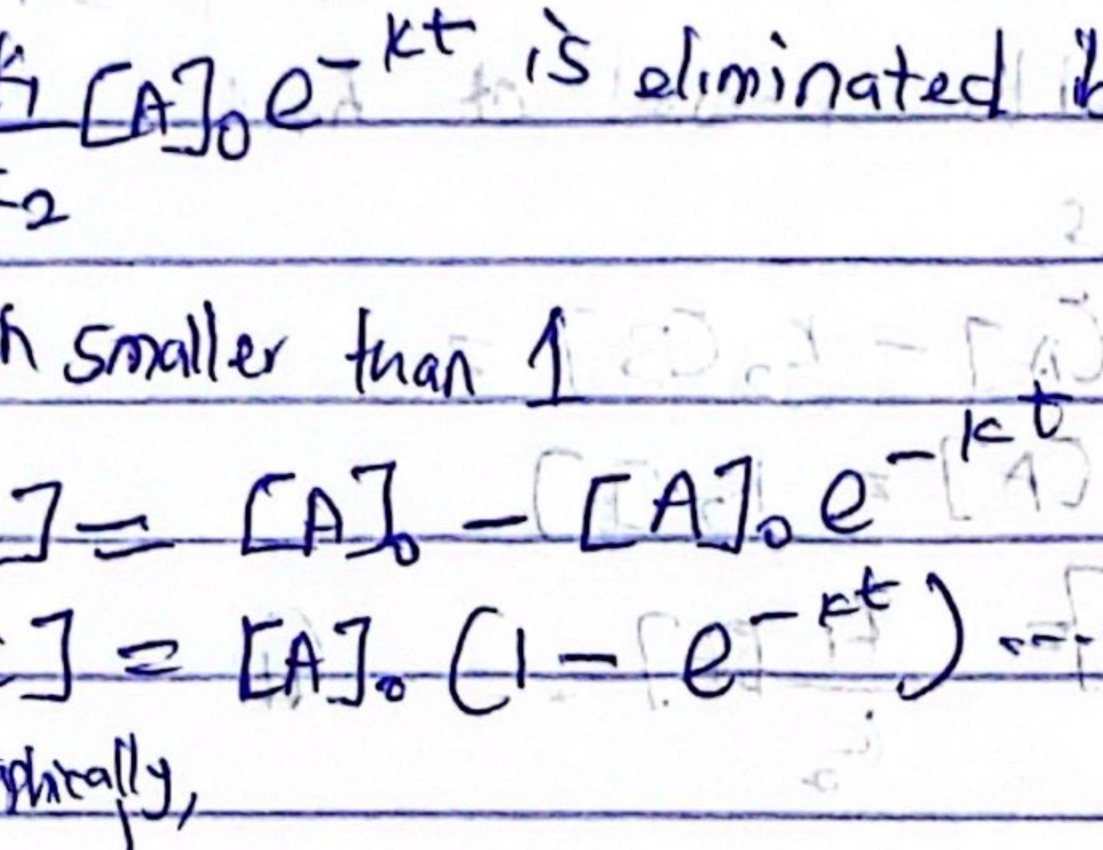


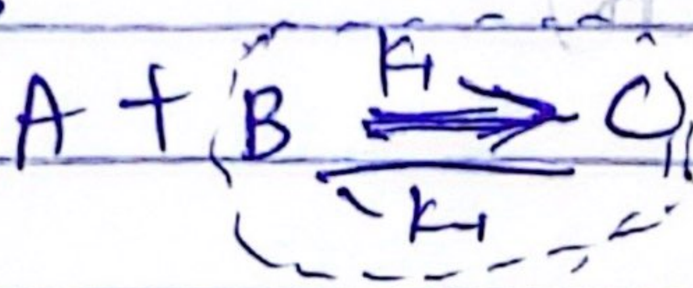
fig 1.

fig 1 shows the plot of [A], [B] and [C] with time. [A] falls steadily from $[A]_0$ to zero while [C] rises from zero to $[A]_0$.

[B] rises from zero to a maximum and then falls back to zero

Not that as K_2 becomes larger than K_1, the steady state approximation will remains valid over the time period when [B] remains constant

A more complicated, but common consecutive reaction is



where. P denotes product

This scheme involves a pre equilibrium in which an intermediate is in equilibrium with the reactant.

A pre equilibrium arises when the rate of formation of the intemediate and of its decay back into reactant are much faster than its rate of formation of product

$$K_{-1} >> K_2$$

Because [A], B and C are assumed to be in equilibrium

Then $K = \frac{[C]}{[A][B]} = K_1$, $[C] = \frac{K_1[A][B]}{K_{-1}}$

And the rate of formation of P is given by,

$$\frac{d[P]}{dt} = \frac{d[\quad]}{dt} k_2[C]$$

Rate of formation of product $= k_2[C]$

$$= \frac{k_1}{k_{-1}} k_2 [A][B]$$

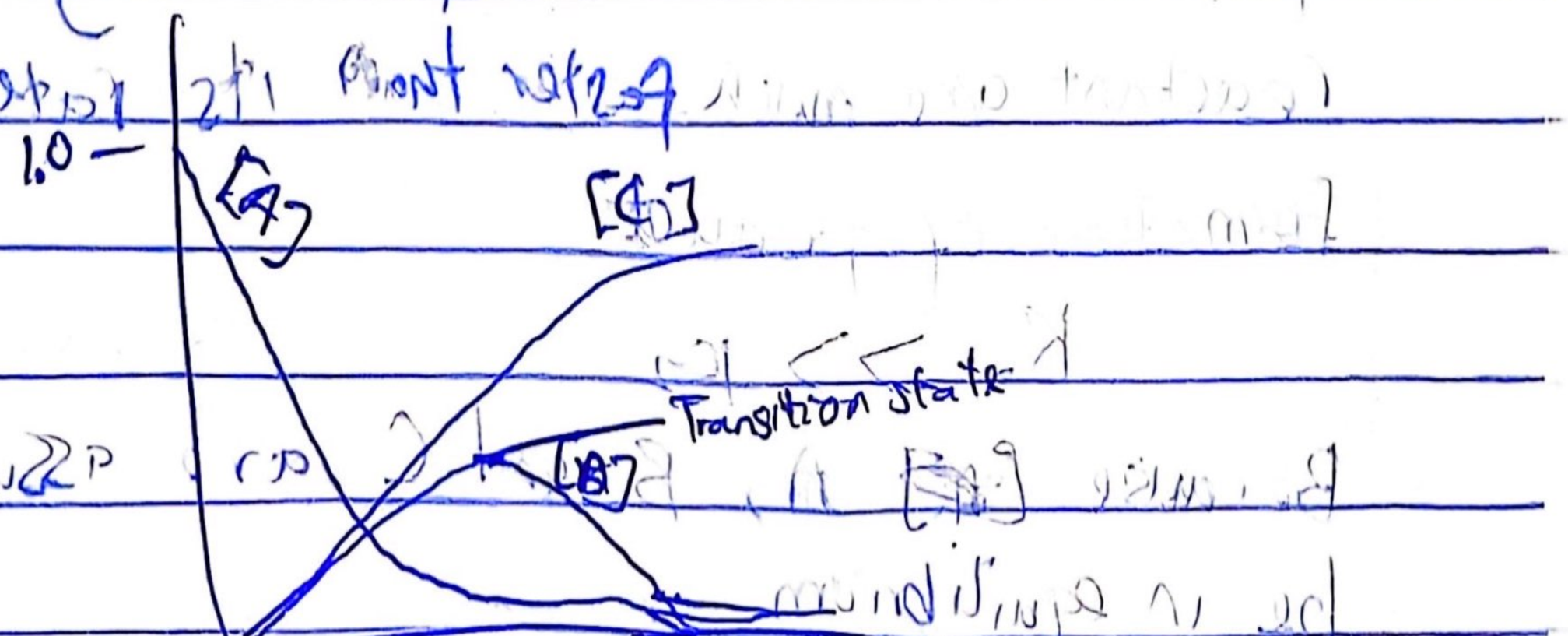
$$\frac{d[P]}{dt} = \frac{k_1 k_2}{[C]} [A][B]$$

15th January, 2024

Chain Reactions

$A \xrightarrow{k_1} B \xrightarrow{k_2} C$

Intermediate



A reaction proceeding in a series of successive steps initiated by a suitable primary process is called a chain reaction.

Chain reactions proceed through a complex sequence of elementary steps. The various steps can be classified as follows;

(1) Chain initiation step
(2) Chain propagation step
(3) Chain termination step

(1) Chain Initiation Step: The first step in which highly reactive species such as atoms and free radicals are produced. is known as the chain initiation step

(2) Chain Propagation Step: In this step, the highly reactive intemediate from the chain initiation step reacts with one of the stable reactant molecule to form a product molecule and another reactive intermediate.. The produced reactive intermediate then reacts with another stable reactant molecule to form a product molecule and other reactive intermediate.

$$A + B \rightarrow P$$

$$A \rightarrow A^{\cdot} \text{ — initiation}$$

$$A + B \rightarrow P + B^{\cdot} \text{ — propagation}$$

$B^{\cdot} + A \longrightarrow P + A^{\cdot}$ — propagation

$A^{\cdot} + B^{\cdot} \longrightarrow$ — termination

(2) Chain Inhibition Step: The reative intermediate combines with a product molecule producing a reactant molecule and other reactive intermediate

Though, a reactive intermediate is generated, the net effect of chain inhibition step is to decrease the rate of overall reaction.

(3) Chain Termination step: The reactive intermediate is destroyed by combining with another reactive intermediate. The process can also be terminated by the addition of certain substances

~~Kinetic~~

Kinetic study of chain reaction is based upon the principle of steady state. It is assumed that in a chain reaction, the intermediate such as atoms and free radicals, which have low concentration acquire. Constant concentration during the course of the reaction, i.e, the concentration of each and every intermediate is constant

i.e, $\frac{d[F]}{dt} = 0$

This allows for significant simplifications of the mathematical treatment of complex reaction

An example is

$$H_{2(g)} + Br_{2(g)} \longrightarrow 2HBr$$

which follows a 5-step mechanism to produce HBr. The reaction is initiated by collisional initiation of Bromine

$Br_2 \xrightarrow{k_1} 2Br^{\cdot}$ — Initiation

$Br^{\cdot} + H_2 \xrightarrow{k_2} HBr + H^{\cdot}$ } propagation

$H^{\cdot} + Br_2 \xrightarrow{k_3} HBr + Br^{\cdot}$ }

$H^{\cdot} + HBr \xrightarrow{k_4} H_2 + Br^{\cdot}$ — inhibition (it slows down the reaction)

$2Br^{\cdot} \xrightarrow{k_5} Br_2$ — termination (puts an end to the reaction)

Evidently, the chain carriers are the $H^{\cdot}$ and $Br^{\cdot}$ are present in low concentration, hence they can be assumed to be steady state concentration during the chain reaction, which means their concentration do not change with time.

$$\frac{d[H^{\cdot}]}{dt} = 0 \quad ; \quad \frac{d[Br^{\cdot}]}{dt} = 0$$

$$-\frac{d[Br^{\cdot}]}{dt} = 0 \quad k_1[Br^{\cdot}] - k_2$$

$$\frac{d[Br^\cdot]}{dt} = 0 = k_1[Br_2] - k_2[Br^\cdot][H_2] + k_3[H^\cdot][Br_2] + k_4[H^\cdot][HBr] - k_5[Br^\cdot]^2 \quad \text{.... (i)}$$

$$\frac{d[H^\cdot]}{dt} = 0 = k_2[Br^\cdot][H_2] - k_3[H^\cdot][Br_2] - k_4[H^\cdot][HBr] \quad \text{(ii)}$$

Adding eqn (i) and eqn (ii)

$$\Rightarrow k_1[Br_2] - k_5[Br^\cdot]^2 = 0$$

$$k_1[Br_2] = k_5[Br^\cdot]^2$$

$$\Rightarrow \frac{k_1}{k_5} = \frac{[Br^\cdot]^2}{[Br_2]}$$

$$\Rightarrow [Br^\cdot]^2 = \frac{k_1}{k_5}[Br_2]$$

$$\boxed{\Rightarrow [Br^\cdot] = \left(\frac{k_1}{k_5}\right)^{1/2}[Br_2]^{1/2}}$$

Substituting $[Br^\cdot]$ into eqn (ii)

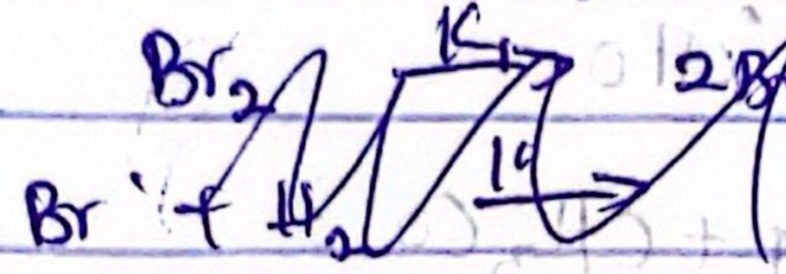
$$k_2\left(\frac{k_1}{k_5}\right)^{1/2}[Br_2]^{1/2}[H_2] - k_3[H^\cdot][Br_2] - k_4[H^\cdot][HBr] = 0$$

$$k_2\left(\frac{k_1}{k_5}\right)^{1/2}[Br_2]^{1/2}[H_2] = k_3[H^\cdot][Br_2] + k_4[H^\cdot][HBr]$$

$$[H^\cdot]\left(k_3[Br_2] + k_4[HBr]\right) = k_2\left(\frac{k_1}{k_5}\right)^{1/2}[Br_2]^{1/2}[H_2]$$

$$\boxed{[H^\cdot] = \frac{k_2\left(\frac{k_1}{k_5}\right)^{1/2}[Br_2]^{1/2}[H_2]}{k_3[Br_2] + k_4[HBr]}}$$

21st January, 2024



Rate of formation of HBr;

$$\frac{d[HBr]}{dt} = K_2[Br^\cdot][H_2] + K_3[H^\cdot][Br_2] - K_4[H^\cdot][HBr]$$

$$\frac{d[HBr]}{dt} = K_2\left(\frac{K_1}{K_5}\right)^{1/2}[Br_2]^{1/2}[H_2] + \left[\frac{K_2K_3\left(\frac{K_1}{K_5}\right)^{1/2}[Br_2]^{1/2}[H_2][Br_2]}{K_3[Br_2] + K_4[HBr]} - \right]$$

$$\frac{K_2K_4\left(\frac{K_1}{K_5}\right)^{1/2}[Br_2]^{1/2}[H_2]\cdot[HBr]}{K_3[Br_2] + K_4[HBr]}$$

$$\frac{d[HBr]}{dt} = K_2\left(\frac{K_1}{K_5}\right)^{1/2}[Br_2]^{1/2}[H_2] + \frac{}{K_3[Br_2] + K_4[HBr]}$$

$$\Rightarrow \frac{d[HBr]}{dt} = \frac{2K_2\left(\frac{K_1}{K_5}\right)^{1/2}[H_2][Br_2]^{1/2}}{1 + K_4[HBr]/K_3[Br_2]}$$

(1)

$CH_3CHO \xrightarrow{K_1} {}^{\bullet}CH_3 + {}^{\bullet}CHO$

$CH_3CHO + {}^{\bullet}CH_3 \xrightarrow{K_2} CH_4 + CH_3CO$

$CH_3CO \xrightarrow{K_3} {}^{\bullet}CH_3 + CO$

$2\,{}^{\bullet}CH_3 \xrightarrow{K_4} C_2H_6$

The proposed mechanism of decomposition of acetylaldehyde is as above. Show that the rate law for the equation is given by;

Show $\dfrac{d[CH_4]}{dt} = K_2\left(\dfrac{K_1}{K_4}\right)^{1/2}[CH_4CHO]^{3/2}$

Solutions to be submitted

(2) The rate law for the decomposition of ozone molecular oxygen

$2O_3(g) \longrightarrow 3O_2(g)$

$\text{rate} = \dfrac{[O_3]^2}{[O_2]}$

and the proposed mechanism for the process is;

$O_3 \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} O + O_2$

$O + O_3 \xrightarrow{K_2} 2O_2$

(i) Derive the rate law for these elementary steps.

(i) Clearly state the assumptions you used in the derivation.

(ii) Explain why the rate decreases with increasing $[O_2]$

(3) $I_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2I$

$H_2 + 2I \xrightarrow{k_2} 2HI$

The gas phase reaction between H_2 and I_2 to form HI involves a two step mechanism as above

(i) Assume the first step is a rapid equilibrium, derive the rate law for the reaction.

(ii) The rate of formation of HI increases with the intensity of visible light. How does this fact support the two step mechanism given.

22nd January, 2024

Reaction in Solution

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \xrightarrow{k_2} B$$

$$\frac{d[A]}{dt} = -k_1[A] + k_{-1}[B]$$

$$k_1[A] = k_{-1}[B]$$

$$\frac{k_1}{k_{-1}} = \frac{[B]}{[A]}$$

$$I_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2I$$

$$H_2 + 2I \xrightarrow{k_2} 2HI$$

$$\frac{d[HI]}{dt} = k_2[H_2][I]^2$$

$$\frac{k_1}{k_{-1}}[I_2] = [I]^2$$

The rate of formation of HI is

$$k_2 \frac{k_1}{k_{-1}}[I_2][H_2]$$

$$O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O + O_2$$

$$O + O_3 \xrightarrow{k_2} 2O_2$$

$$k_2 \frac{k_1}{k_{-1}} = \frac{[O][O_2]}{[O_3]}$$

$$[O] = \frac{k[O_3]}{[O_2]}$$

$$\text{rate} = \frac{d[O_2]}{dt} = k_2[O][O_3]$$

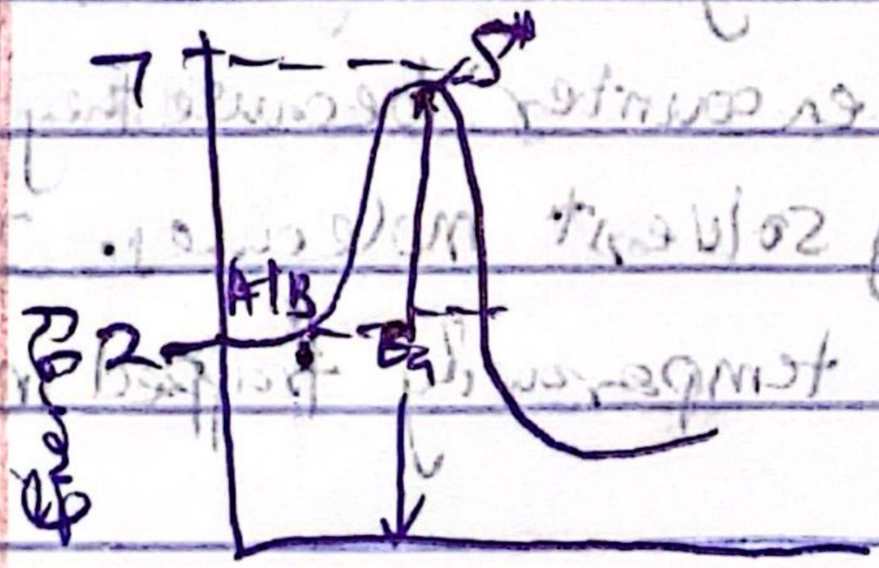
$$\frac{k_1 k_2 [O_3][O_2]}{[O_2]} \Rightarrow \frac{k_1 k_2 [O_3]^2}{k_{-1}[O_2]}$$

Where. $\frac{k_1 k_2}{k_{-1}} = k$

$$\text{rate} = \frac{k[O_3]^2}{[O_2]}$$

Reaction in Solution



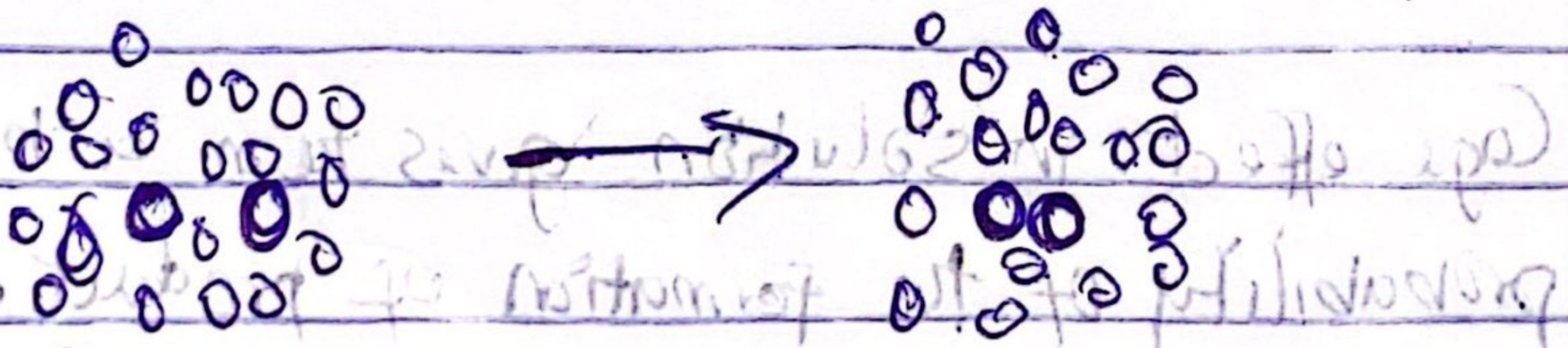


Cage effect in solution gives them a better probability of the formation of product in gaseous form

The major difference between gas phase, and reaction in solutions lies in the roles of the solvent In terms of simple kinetic theory, the frequency of Solution between reacting molecules depends only on the concentration of reactant, it is not affected by the solvent molecule

There is a difference however in the outcome of an encounter between reactants molecules in Solution Compared with the Collision of molecules in the gas phase. If two molecules collide in the gas phase and do not react. they will normally move away from each other. There is very little likelyhood that this same pair will collide again

In constrast, when two solute molecules diffuse together in a solution, they cannot move apart again quickly, after initial encounter because they are surrounded closely by solvent molecules. In this case, the reactant are temporarily trapped in a cage of Solvent



Note: The cage is not rigid as the solvent molecules are constantly in motion and changing positions.

Nevertheless, the cage effect, cause the reactant molecules to remain together for a longer time than they would in the gas phase and they may collide with each other hundreds of times before they drift apart.

Therefore we speak of molecular collision in the gas phase and molecular encounter in the liquid solution.

For reactions that have relatively low activation energies, the cage effect virtually ensures reactions during each encounter. The steric factor no longer place an important role because the reacting molecule will sooner or later become properly oriented for reaction during the collision.

$$K = A e^{-\frac{E_a}{RT}}$$

Under these conditions, the rate of the reaction is limited only by how fast the reactant can diffuse together

Factors Determining Reaction Rate in Solution

The reaction between two molecules in solution can be thought of as occuring in three well defined stages

(A) <---> <c (B) ---(1)

(A)(B) ---(2)

(P) ---> ---(3)

(1) Diffusion of the molecules to each other
(2) Actual chemical transformation
(3) Diffusion of the product away from each other

Diffusion in liquid have activation energy, but the magnitude of this is generally not greater than 5K Cal