PHYSICS WALLAH

CHEMICAL KINETICS

01

RATE OF A CHEMICAL REACTION

$\frac{\text{decrease in conc of reactant}}{\text{Time taken}}$ OR $\frac{\text{Increase in conc of reactant}}{\text{Time taken}}$

AVERAGE RATE

Consider a reaction: A + B ⟶ C + D

$-\frac{\Delta[A]}{\Delta t} = -\frac{\Delta[B]}{\Delta t} = \frac{\Delta[C]}{\Delta t} = \frac{\Delta[D]}{\Delta t}$

INSTANTANEOUS RATE

Consider a reaction: aA + bB ⟶ cC + dD

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

Unit of Rate = mol $litre^{-1}$ s^{-1}

Q During the decomposition of H_2O_2, 48 g O_2 is formed per minute at a certain point of time. The rate of formation of water at this point is

(a) 0.75 mol min^{-1} (b) 1.5 mol min^{-1}
(c) 2.25 mol min^{-1} (d) 3.0 mol min^{-1}

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FACTORS INFLUENCING RATE OF REACTION

Factors	Effect on reaction rate
Increase in concentration	Increases
Increase in temperature	Increases
Presence of catalyst	Increases

Q Which of the following will lead to an increase in the rate of the reaction?

a) Decrease in temperature
b) Decreasing concentration of reactants
c) Addition of catalyst
d) Addition of inhibitor

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RATE LAW

Consider a general reaction,
aA + bB ⟶ product
Rate = $k[A]^a [B]^b$ (law of mass action)
Rate = $k[A]^x [B]^y$ (rate law expression)
x & y are determined experimentally and may or may not be equal to a & b
x & y represents the order of reaction with respect to A & B

RATE CONSTANT

- Larger the value of k, faster is the reaction.
- The value of k changes only with temperature for given reaction.

unit of rate constant = $(mol)^{1-n} L^{n-1} s^{-1}$

Q The rate constant of a zero-order reactions has the unit

(a) s^{-1} (b) mol L^{-1} s^{-1}
(c) L^2 mol^{-2} s^{-1} (d) L mol^{-1} s^{-1}

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ORDER AND MOLECULARITY

Consider a general reaction,
aA + bB ⟶ product
Rate = $k[A]^x [B]^y$
molecularity = a + b
order = x + y

Molecularity	Order
Theoretical concept.	An experimentally determined quantity.
It cannot be zero, fractional, infinite and imaginary.	It can be equal to zero positive, negative and fractional.

Q When the rate of the reaction is equal to the rate constant, the order of the reaction is

(a) zero order
(b) first order
(c) second order
(d) third order

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PSEUDO ORDER REACTIONS

Consider the reaction

$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$

In these reactions, concentration of water (one of the reactants) is in excess and its concentration remains constant throughout the reaction.

Thus, rate $\propto [C_{12}H_{22}O_{11}]$

Therefore, order = 1

Q For a pseudo first-order reaction, what is the unit of the rate of the reaction?

(a) s^{-1}
(b) mol $L^{-1}s^{-1}$
(c) mol^{-1} L s^{-1}
(d) mol^{-2} L^2 s^{-1}

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ELEMENTARY & COMPLEX REACTIONS

- Reactions occurring only in one step are called elementary reactions while that involving a sequence of elementary reactions, are called complex reactions.
- In case of complex reactions, the slowest step is called rate determining step.

Note Consider the reaction
$2O_3 \rightarrow 3O_2$
Step - 1
$O_3 \rightleftharpoons O_2 + O$ (fast)
Step - 2
$O + O_3 \rightarrow 2O_2$ (slow)

From slow step
r = k [O] $[O_3]$
Here
$[O] \propto \frac{[O_3]}{[O_2]}$; From fast step
r = k $[O_3]^2 [O_2]^{-1}$

Q Suppose the reaction: A + 2B ⟶ AB_2 occurs by the following mechanism:

Step 1 : A + B ⟶ AB slow
Step 2 : AB + B ⟶ AB_2 fast
Overall A + 2B ⟶ AB_2

(a) k[A] (b) k[B] (c) k[A][B] (d) $k[B]^2$

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INTEGRATED RATE EQUATIONS

Zero order

$k = \frac{[A]_0 - [A]_t}{t}$

First order

$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]_t}$

Second order

$k = \frac{1}{t}\left[\frac{1}{[A]_t} - \frac{1}{[A]_0}\right]$

Q A first order reaction has a specific reaction rate of 10^{-2} sec^{-1}. How much time will it take for 20 g of the reactant to reduce to 5 g?

(a) 138.6 sec (b) 346.5 sec
(c) 693.0 sec (d) 238.6 sec

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HALF LIFE PERIOD

Zero order

$t_{\frac{1}{2}} = \frac{[A]_0}{2k}$

First order

$t_{\frac{1}{2}} = \frac{0.693}{k}$

Second order

$t_{\frac{1}{2}} = \frac{1}{k[A]_0}$

FIRST ORDER TRICKS

$t_{75\%} = 2t_{\frac{1}{2}}$

$t_{90\%} = \frac{2.303}{k}$

$t_{99.9\%} = 10t_{\frac{1}{2}}$

Q The half-life period of zero order reaction is directly proportional to the ___________

a) Rate constant
b) Initial concentration of reactants
c) Final concentration of reactants
d) Concentration of products

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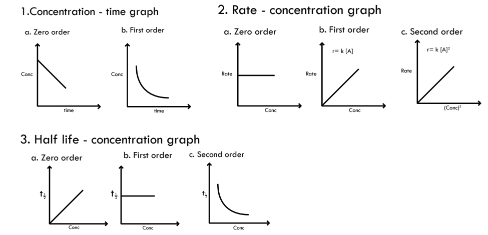
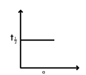
GRAPHICAL REPRESENTATION



Q The graph of $t_{\frac{1}{2}}$ versus initial concentration 'a' is for



a) First order
b) Second order
c) Zero order
d) Can't predict

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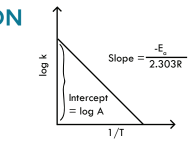
ARRHENIUS EQUATION

$k = Ae^{-Ea/RT}$

$\log k = \log A - \frac{E_a}{2.303R}\left(\frac{1}{T}\right)$



NOTE

- For every 10° rise in temperature, rate becomes double and hence, rate constant becomes double.
- A reaction with higher value of E_a will have smaller value of rate constant.

Q The slope of Arrhenius plot (ln k vs $\frac{1}{T}$) of first order reaction is - 5 x 10^3 K. The value of E_a of the reaction is [Given: R=8.314 J K^{-1} mol^{-1})

(a) -83 kJ mol^{-1} (b) 41.5 kJ mol^{-1}
(c) 83 kJ mol^{-1} (d) 166 kJ mol^{-1}