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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: $A + B \rightarrow C + D$
 $\frac{\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t} = \frac{\Delta[C]}{\Delta t} = \frac{\Delta[D]}{\Delta t}$

INSTANTANEOUS RATE

Consider a reaction: $aA + bB \rightarrow cC + dD$
 $-\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$

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

AFMC 2012

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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

AMU 2010

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RATE LAW

Consider a general reaction,
 $aA + bB \rightarrow \text{product}$
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 Lⁿ⁻¹ s⁻¹

AIMS 2009

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ORDER AND MOLECULARITY

Consider a general reaction,
 $aA + bB \rightarrow \text{product}$
Rate = $k[A]^a [B]^b$
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.

AMU 2006

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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

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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
 $2O_3 \rightleftharpoons 3O_2$
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
 $[O] \propto [O_3]$; From fast step
 $r = k [O_3]^2 [O_2]$

Q Suppose the reaction: $A + 2B \rightarrow AB_2$ occurs by the following mechanism:

Step 1 : $A + B \rightarrow AB$ slow
Step 2 : $AB + B \rightarrow AB_2$ fast
Overall $A + 2B \rightarrow AB_2$
(a) $k[A]$ (b) $k[B]$ (c) $k[A][B]$ (d) $k[B]^2$

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

- Decrease in temperature
- Decreasing concentration of reactants
- Addition of catalyst
- Addition of inhibitor

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INTEGRATED RATE EQUATIONS

Zero order

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

First order

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

Second order

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

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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

$$\begin{aligned} t_{75\%} &= 2t_{\frac{1}{2}} \\ t_{90\%} &= \frac{2.303}{k} \\ t_{99.9\%} &= 10t_{\frac{1}{2}} \end{aligned}$$

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?

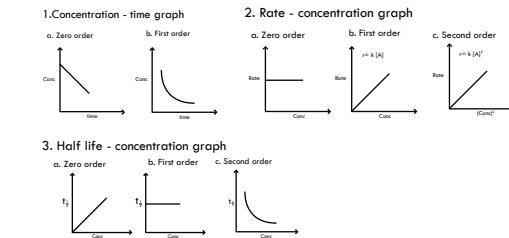
- 138.6 sec (b) 346.5 sec
- (c) 693.0 sec (d) 238.6 sec

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

- zero order
- first order
- second order
- third order

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GRAPHICAL REPRESENTATION



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

- First order
- Second order
- Zero order
- Can't predict

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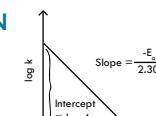
ARRHENIUS EQUATION

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

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

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 $-5 \times 10^3 \text{ K}$. The value of E_a of the reaction is [Given: $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$]
(a) -83 kJ mol^{-1} (b) 41.5 kJ mol^{-1}
(c) 83 kJ mol^{-1} (d) 166 kJ mol^{-1}

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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?

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

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

- Rate constant
- Initial concentration of reactants
- Final concentration of reactants
- Concentration of products

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

- First order
- Second order
- Zero order
- Can't predict

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