

Topic :- Chemical Kinetics

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(a)

It is the definition of molecularity.

2

(c) $\left(\frac{dx}{dt}\right) = k[NO]^2[o_2]$ $=k\left(\frac{n_{NO}}{V}\right)^2\left(\frac{n_{O_2}}{V}\right)$ $\left(\frac{dx}{dt}\right) = \frac{k}{V^3} (n_{No})^2 (n_{O_2})$ $\left(\frac{dx}{dt}\right) = \frac{k(n_{No})^2(n_{O_2})}{\left(\frac{V}{2}\right)^3}$ $=8\left(\frac{dx}{dt}\right)$ (c)

3

No doubt order cannot be predicted by merely looking chemical reaction but this can be treated as standard example of II order reaction.

4

(a)

(a)

Rate =
$$-\left[\frac{dc}{dt}\right] = \left[-\frac{dn}{dt}\right]\frac{1}{V}$$
 $\left[\because c = \frac{n}{V}\right]$
 $\therefore -\left[\frac{dc}{dt}\right] = -\frac{1}{RT}\left[\frac{dP}{dt}\right]$. $\left[c = \frac{P}{RT}\right]$

5

For zero order reaction Rate = $[A]^0 = k$ $\frac{mol L^{-1}}{s} = k$ K=mol L⁻¹ s⁻¹ (b)

6

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

By Arrhenius equation, $R_1 = A'e^{-E_a 1/RT}$ and $k_2 = A'e^{-E_a 2/RT}$

(A' is Arrhenius constant) (Since,
$$E_{a2} = 2E_{a1}$$
)
 $\therefore k_2 = A'e^{-2E_{a'}|RT}$
 $\frac{k_1}{k_2} = \frac{A'e^{-E_a 1|RT}}{A'e^{-2E_a|RT}} = e^{E_a 1|RT}$
 $\therefore k_1 = k_2 e^{E_a 1/RT}$
(d)
For the reaction, $2A + B \rightarrow A_2 B$
According to rate laws,
Rate \propto concentration of reactants
 $rate = k[A]^2[B]$
Where, k=rate constant
(d)

This is activation state and orientation concept for mechanism of reactions.

9

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Rate depends upon the slowest step. Hence, from equation $0 + 0_3 \rightarrow 20_2$

$$r = k[0_3][0]$$

(b)

And from equation $0_3 \rightleftharpoons 0_2 + 0$

$$K_{eq} = \frac{[O_2][O]}{[O_3]}$$
$$[O] = \frac{K_{eq}[O_3]}{[O_2]}$$
$$\therefore r = k[O_3] \frac{K_{eq}[O_3]}{[O_2]}$$
$$= k'[O_3]^2[O_2]^{-1}$$

10

(a) Amount of *A* left in n_1 halves $=\frac{[A_0]}{2^{n_1}}$ Amount of *B* left in n_2 halves $=\frac{[B_0]}{2^{n_2}}$ Also if $\frac{[A_0]}{2^{n_1}} = \frac{[B_0]}{2^{n_2}}$ when *A* decays to n_1 halves and *B* decays to n_2 halves. $[A_0] = 4[B_0]$ ÷ $4 = \frac{2^{n_1}}{2^{n_2}} = (2)^{n_1 - n_2}$:. $(n_1 - n_2) = 2$ $n_2 = n_1 - 2$ or **:**. ...(i) Now, $T = n_1 \times t_{1/2A}$ and $T = n_2 \times t_{1/2B}$ $\frac{n_1 \times t_{1/2A}}{n_2 \times t_{1/2B}} = 1$:. $\frac{n_1 \times 5}{n_2 \times 15} = 1$ or

 $\frac{n_1}{n_2} = 3$ or ...(ii) : By Eqs. (i) and (ii) $n_1 = 3, n_2 = 1$ Thus. $T = 3 \times 5 = 15$ minute 11 (c) : On doubling the concentration of A, the rate of reaction becomes two times. : The order of reaction w.r.t. A is 1 : On doubling the concentration of B, the rate of reaction does not change. \therefore the order of reaction respect to B is 0 : on doubling the concentration of C, the rate of reaction becomes four times : the order of reaction w.r.t. C is 2 : the overall order of reaction = 1+0+2=312 (c) For *n*th order; unit of rate constant may be derived by rate $K = \frac{1}{[\text{reactant}]^n}$ 13 (c) $r = K[N_2O_5] = 6.2 \times 10^{-4} \times 1.25 = 7.75 \times 10^{-4} M/s$ 14 (c) Α \rightarrow product 0 Initially а After time t (a-x) Х After $t_{1/4}$ $\left(a - \frac{a}{4}\right)$ For the first order kinetics, $k = \frac{2.303}{t} \log\left(\frac{a}{a-x}\right)$ $k = \frac{2.303}{t_{1/4}} \log \frac{a}{\frac{3a}{4}}$ $t_{1/4} = \frac{2.303 \log \frac{4}{3}}{k}$ $=\frac{0.29}{k}$ 15 (a) The order of reaction is zero. Suppose the following reaction take place. $A + B \rightarrow product$ \therefore rate = $[A][B]^{-1}$: order = 1 + (-1) = 016 (d) Pseudo first order reactions are those reactions which are not truly first order but show

Pseudo first order reactions are those reactions which are not truly first order but show first order kinetics under specific conditions. For examples, acidic hydrolysis of an ester and hydrolysis of cane sugar.

17 **(d)**

The differential rate law for the reaction,

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$$
 is
 $Rate = -\frac{1}{4} \frac{d[NH_3]}{dt} = -\frac{1}{5} \frac{d[O_2]}{dt}$
 $= +\frac{1}{4} \frac{d[NO]}{dt} = +\frac{1}{6} \frac{d[H_2O]}{dt}$
(a)
 $_{79}Au^{198} \xrightarrow{-B} _{80}Hg^{198}$
 $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{65}$
After 260 hr,
 $k = \frac{2.303}{260} \log \frac{a}{a-x}$
 $\frac{0.693}{65} = \frac{2.303}{260} \log \frac{a}{a-x}$
 $\frac{a}{a-x} = 16$
 $\frac{1}{1-x} = 16$
 $x = \frac{15}{16} g = 0.9375 g$

18

19

(d) Rate = $k[NO_2Cl]$ Hence ,rate determining step is $NO_2CL \rightarrow NO_2 + CL$

20

(b)

 $RCl + NaOH \rightarrow ROH + NaCl$

Rate = k[RCl]

For this reaction rate of reaction is depends upon the concentration of RCl

It means, the rate of reaction is halved by reducing the concentration of *R*Cl by one half

ANSWER-KEY										
Q .	1	2	3	4	5	6	7	8	9	10
A.	Α	С	С	Α	Α	В	D	D	В	А
Q .	11	12	13	14	15	16	17	18	19	20
A.	С	С	С	С	A	D	D	Α	D	В