

### Topic :- Chemical Kinetics

- 1 (c)  
For a zero order reaction,  
 $R \rightarrow \text{product}$   
Rate =  $-\frac{d[R]}{dt} = k[R]^0 = k$   
 $-d[R] = k \cdot dt$

Integrating the above equation.

$$-\int d[R] = k \int dt$$
$$-[R] = kt + I \quad \dots(i)$$

Where, I is integration constant

$$\text{At } t = 0, R = [R]_0$$

$$-[R]_0 = k \times 0 + I$$

$$I = -[R]_0$$

Put this value in Eq. (i)

$$-[R] = kt - [R]_0$$

$$\text{or } [R] = -kt + [R]_0$$

- 2 (a)  
For first order reaction,  
Half-life period ( $t_{1/2}$ ) =  $\frac{0.693}{k}$   
Where, k=rate constant  
 $t_{1/2} = \frac{0.693}{69.3} \text{ s}^{-1}$   
 $= 0.01 \text{ s}^{-1}$

- 3 (b)  
For  $n$ th order reaction :

$$t_{1/2} \propto \frac{1}{a^{n-1}}$$

For second order reaction

$$t_{1/2} = \frac{1}{ka} = \frac{1}{0.5 \times 0.2} = \frac{100}{10} = 10 \text{ min}$$

- 4 (d)

$$r = K[\text{CH}_3\text{COCH}_3]^a[\text{Br}_2]^b[\text{H}^+]^c$$

$$\therefore 5.7 \times 10^{-5} = K[0.30]^a[0.05]^b[0.05]^c \quad \dots(1)$$

$$5.7 \times 10^{-5} = K[0.30]^a[0.10]^b[0.5]^c \quad \dots(2)$$

$$1.2 \times 10^{-4} = K[0.30]^a[0.10]^b[0.10]^c \quad \dots(3)$$

$$3.1 \times 10^{-4} = K[0.40]^a[0.05]^b[0.20]^c \quad \dots(4)$$

By (1) and (2)  $a = 1$

By (2) and (3)  $b = 0$

By (3) and (4)  $c = 1$

$$\therefore r = K[\text{CH}_3\text{COCH}_3]^1[\text{Br}_2]^0[\text{H}^+]^1$$

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**(c)**

Unit of rate constant

$$= \frac{\text{time}^{-1}}{\text{conc}^{(n-1)}}$$

Where,  $n$  = order of reaction

Given, unit of rate constant =  $L \text{ mol}^{-1} \text{ s}^{-1}$

$$\therefore L \text{ mol}^{-1} \text{ s}^{-1} = \frac{(\text{s})^{-1}}{(L \text{ mol}^{-1})^{n-1}}$$

$$= \frac{(\text{s})^{-1}}{(L \text{ mol}^{-1})^{n-1}}$$

$$= \text{s}^{-1} (L \text{ mol}^{-1})^{n-1}$$

$$\text{Or } 1 = n - 1$$

$$\text{Or } n = 2$$

$$\therefore \text{order of reaction} = 2$$

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**(c)**

Activation energy of a chemical reaction can be determined by evaluating rate constants at two different temperatures

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

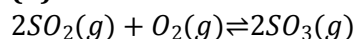
7

**(c)**

Molecularity can never be fractional.

9

**(d)**



For this reaction, rate

$$(r_1) = k[\text{SO}_2]_1^2[\text{O}_2]_1 \quad \dots(i)$$

On doubling the volume of vessel, concentration would be half. Hence,

$$\text{Rate}(r_2) = k \left( \frac{[\text{SO}_2]_1}{2} \right)^2 \left( \frac{[\text{O}_2]_1}{2} \right) = \frac{r_1}{8}$$

$$\frac{r_1}{r_2} = 8:1$$

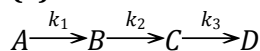
10

**(c)**

$$r = k[\text{RCl}]$$

11 If  $[RCl] = \frac{1}{2}$ , then  $\text{rate} = \frac{r}{2}$

**(a)**



$$\therefore k_3 > k_2 > k_1$$

As  $k_1$  is slowest hence  $A \rightarrow B$  is the rate determining step of the reaction

12 **(b)**

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$$

$$= \frac{2.303}{10} \log_{10} \frac{100}{80}$$

$$= \frac{2.303}{10} [\log 10 - 3 \log 2]$$

$$= \frac{2.303}{10} [1 - 3 \times 0.3010]$$

$$k = 0.0223$$

13 **(d)**

$$E_a(A \rightarrow B) = 80 \text{ kJ mol}^{-1}$$

$$\text{Heat of reaction } (A \rightarrow B) = 200 \text{ kJ mol}^{-1}$$

For  $(B \rightarrow A)$  backward reaction,

$$E_a(B \rightarrow A) = E_a(A \rightarrow B) + \text{heat of reaction}$$

$$= 80 + 200 = 280 \text{ kJ mol}^{-1}$$

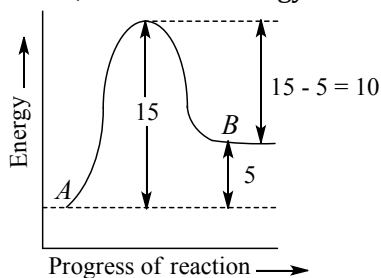
14 **(c)**

For endothermic reaction  $A \rightarrow B$

Activation energy = 15 kcal/mol

Energy of reaction = 5 kcal/mol

Hence, activation energy for the reaction  $B \rightarrow A$  is  $15 - 5 = 10$  kcal/mol



15 **(d)**

$$\text{For zero order } [A]_t = [A]_0 - kt$$

$$0.5 = [A]_0 - 2 \times 10^{-2} \times 25$$

$$\therefore [A]_0 = 1.0 \text{ M}$$

16 **(b)**

$$t = \frac{2.303}{k} \log \frac{a}{a-x}$$

Where,  $k$  = rate constant =  $10^{-3} \text{ s}^{-1}$

$a$  = initial amount = 100

$a - x$  = amount left after time  $t = 25$

$t$  = time to leave 25% reaction

$$\therefore t = \frac{2.303}{10^{-3}} \log \frac{100}{25}$$

$$= \frac{2.303}{10^{-3}} \log 4$$

$$= \frac{2.303 \times 0.6020}{10^{-3}}$$

$$= 1386 \text{ s}$$

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**(d)**

By increasing 10 K temperature the rate of reaction becomes double. When temperature is increased from 303 K to 353 K, the rate increases in steps of  $10^\circ$  and has been made 5 times. Hence, the rate of reaction should increase  $2^5$  times *i.e.*, 32 times.

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**(a)**

Temperature coefficient

$$= \frac{\text{rate of reaction at } 35^\circ\text{C}}{\text{rate of reaction at } 25^\circ\text{C}} = 2$$

Thus, increase in rate is two times, when temperature is increased  $10^\circ\text{C}$ . Hence, by the increase of  $70^\circ\text{C}$  ( $100 - 30 = 70^\circ\text{C}$ ), the increase in rate will be

$$= (2)^7 \quad \because 70^\circ = 7 \times 10^\circ$$

$$= 128 \text{ times}$$

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**(d)**

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left( \frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\log \frac{k_2}{k_1} = \frac{9000}{2.303 \times 2} \left( \frac{5}{295 \times 300} \right)$$

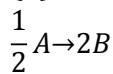
$$\log \frac{k_2}{k_1} = 0.1103$$

$$\frac{k_2}{k_1} = 1.288, k_2 = 1.288 k$$

*ie*, increase by 28.8%

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**(b)**



Remember for  $a A \rightarrow b B$

$$-\frac{1d[A]}{a dt} = \frac{1d[B]}{b dt} = \text{Rate of reaction}$$

For the given reaction

$$-\frac{2d[A]}{dt} = \frac{1d[B]}{2 dt} = \text{rate of reaction}$$

Rate of disappearance of A

$$= -\frac{d[A]}{dt} = \frac{1}{2 \times 2} \frac{d[B]}{dt}$$

$$= \frac{1}{4} \frac{d[B]}{dt}$$

ANSWER-KEY										
<b>Q.</b>	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>	<b>7</b>	<b>8</b>	<b>9</b>	<b>10</b>
<b>A.</b>	<b>C</b>	<b>A</b>	<b>B</b>	<b>D</b>	<b>C</b>	<b>C</b>	<b>C</b>	<b>D</b>	<b>D</b>	<b>C</b>
<b>Q.</b>	<b>11</b>	<b>12</b>	<b>13</b>	<b>14</b>	<b>15</b>	<b>16</b>	<b>17</b>	<b>18</b>	<b>19</b>	<b>20</b>
<b>A.</b>	<b>A</b>	<b>B</b>	<b>D</b>	<b>C</b>	<b>D</b>	<b>B</b>	<b>D</b>	<b>A</b>	<b>D</b>	<b>B</b>