16.(C) $[A_0]$ = initial concentration (amount)

$[A]$ = final concentration (amount)

$\therefore \quad t = \dfrac{2.303 \times 6.93}{0.6932} \log \dfrac{100}{1} = 46.06$ minutes

17.(C) For a zero order reaction $k = \dfrac{x}{t}$ ...... (i)

Where $x =$ amount decomposed

$k =$ zero order rate constant for a zero order reaction

$k = \dfrac{[A]_0}{2t_{1/2}}$ .... (ii)

Since $[A_0] = 2M$, $t_{1/2} = 1\,\text{hr}$; $k = 1$

$\therefore$ from equation (i)

$t = \dfrac{0.25}{1} = 0.25\,\text{hr}$

18.(D) Rate equation is to be derived w.r.t slow step

$\therefore$ from mechanism (A)

$\text{Rate} = k[Cl_2][H_2S]$

19.(B) Temperature coefficient $\mu = 2$;

$\mu^{\frac{\Delta T}{10}} = \dfrac{k_2}{k_1}$; $2^{\frac{50}{10}} = 2^5 = 32 = \dfrac{k_2}{k_1}$ Therefore $32k_1 = k_2$

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

By Arrhenius equation,

$k_1 = A'e^{-E_{a_1}/RT}$

and $k_2 = A'e^{-E_{a_2}/RT}$ [A' is Arrhenius constant]

$\because \ E_{a_2} = 2E_{a_1}$

$\therefore \ k_2 = A'e^{-2E_{a_1}/RT}$ $\quad \therefore \ \dfrac{k_1}{k_2} = \dfrac{A'e^{-E_{a_1}/RT}}{A'e^{-2E_{a_1}/RT}} = e^{E_{a_1}/RT}$ $\quad \therefore \ k_1 = k_2 e^{E_{a_1}/RT}$

21.(B) $k = \dfrac{2.303}{40} \log \dfrac{0.1}{0.025} \quad \Rightarrow \quad k = \dfrac{0.693}{20}$

For a first order reaction, rate $= k[A]$; rate $= \dfrac{0.693}{20} \times 10^{-2} = 3.47 \times 10^{-4}\,\text{M / min}$.

22.(A) First order w.r.t. A and zero order w.r.t. B

$\therefore \quad \dfrac{dc}{dt} = K[A]$

23.(A) Probability of collision of more than three particles simultaneously at certain orientation is very low.

24.(A)

$$\begin{array}{lcc} 2N_2O_5 \longrightarrow & 4NO_2 & +\ O_2 \\ P_0 & - & - \\ P_0 - 2p & 4p & p \end{array}$$

$P_T = p_0 - 2p + 4p + p = po + 3p$

$p = \dfrac{P_T - p_o}{3}$ .....(1)

$$p^0 = p_0 - 2p = P_0 - 2\left(\frac{P_T - P_0}{3}\right)$$

$$P^0 = \frac{3P_0 - 2P_T + 2P_0}{3} = \frac{5P_0 - 2P_T}{3} \quad \Rightarrow \quad K = \frac{2.303}{t}\log\frac{P_0}{P^0} = \frac{2.303}{t}\log\left(\frac{3P_0}{5P_0 - 2P_T}\right)$$

at $t = 30$ min

$$k = \frac{2.303}{30}\log\left(\frac{3 \times 50}{5 \times 50 - 2 \times 87.5}\right)$$

$k = 0.023$ at $t = 60$

$$k = \frac{2.303}{60}\log\left(\frac{3 \times 50}{5 \times 50 - 2P_T}\right)$$

$$0.023 = \frac{2.303}{60}\log\frac{150}{250 - 2P_T} \quad \Rightarrow \quad 4 = \frac{150}{250 - 2P_T} \quad \Rightarrow \quad 1000 - 8P_T = 150 \quad \Rightarrow \quad P_T = 106.25$$

25.(C) $\frac{E_f}{E_b} = \frac{80}{120} = \frac{2}{3}$

26.(C) $\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{k[A][B]}{k[A][2B]} = 2\,\text{Rate}_1 = \text{Rate}_2$

So, rate get doubled

27.(A) Rate constant changes only with change in temperature.

28.(A) In fifty minutes the concentration of H_2O_2 decreases from 0.5 to 0.125 M.

It means two half lives must have passed

$\Rightarrow \quad 2t_{1/2} = 50$ minutes

$t_{1/2} = 25$ minutes $\quad \therefore \quad k = \left(\frac{0.693}{25}\right)\text{min}^{-1}$

Also $\frac{-d[H_2O_2]}{dt} = k[H_2O_2] = \frac{0.693}{25} \times (0.05)\,\text{mol min}^{-1}$

As per reaction

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

$$\frac{d[O_2]}{dt} = -\frac{1}{2}\left(\frac{d[H_2O_2]}{dt}\right) = \frac{1}{2} \times \frac{0.693}{25} \times 0.05\text{ mol min}^{-1} = 6.93 \times 10^{-4}\,\text{mol min}^{-1}$$

29.(A) Slowest step decides the rate constant of overall reaction. So, rate constant of first step is closest to rate constant of overall reaction.

30.(A) $\ln\frac{k_2}{k_1} = \frac{\varepsilon_0}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

$$\ln 4 = \frac{\varepsilon_0}{8.314}\left(\frac{1}{300} - \frac{1}{310}\right) \quad \Rightarrow \quad 1.386 \times 8.314 = \varepsilon_0(0.000107)$$

$$\varepsilon_0 = \frac{1.386 \times 8.314}{0.000107526} \quad \Rightarrow \quad \varepsilon_0 = 107.2\,\text{kJ / mol}$$