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

$\ln 2=\frac{\varepsilon_0}{8.314}(0.000107526) \quad \Rightarrow \quad \varepsilon_0=53.47\,kJ/mol$

ε_0 for reaction B = 106.941 kJ/mol

For reaction B

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

$\ln 2=\frac{106941}{8.314}\left(\frac{1}{300}-\frac{1}{T_2}\right) \quad \Rightarrow \quad \frac{0.693\times 8.314}{106941}=\left(\frac{1}{300}-\frac{1}{T_2}\right)$

$\frac{1}{T_2}=\frac{1}{300}-\frac{0.6938.314}{106941} \quad \Rightarrow \quad T_2=\frac{1}{0.003279}=304.9$

So, temperature should increased by 4.9 k.

32.(A) From Arrhenius equation $k = Ae^{-E_a/RT}$

Since $\ln\left(\frac{k_2}{k_1}\right)=\frac{1}{RT}\left[\left(E_a\right)_1-\left(E_a\right)_2\right]=\frac{1\times 10\times 10^3}{8.314\times 300}=4$

33.(C) $r = k\left[A\right]^n$

$1=k\left(363\times 0.95\right)^n \quad$ ....(i)

$0.5=k\left(363\times 0.67\right)^n \quad$ ....(ii)

From (i) and (ii)

$n = 2$

34.(D) On changing the concentration of B, there is no effect on the initial rate of the reaction. However, on doubling the conc. of A, the reaction rate doubled.

$\therefore$ The reaction must be first order w.r.t. A.

$R = k[A]^x[B]^y$

$6.93\times 10^{-3}=k[0.10]^x[0.1]^y$

$6.93\times 10^{-3}=k[0.10]^x[0.25]^y$

$1.380\times 10^{-2}=k[0.20]^x[0.30]^y \quad \therefore \; x = 1, y = 0$

Also, $k=\frac{6.93\times 10^{-3}}{0.1}=6.93\times 10^{-2}$

$t_{0.5}=\frac{0.693}{2k}=\frac{0.693}{2\times 6.93\times 10^{-2}}=5$

35.(C) rate $= k[A]^m[B]^n$

So, $r_1 = k[A]^m[B]^n$

$r_2 = k[2A]^m[2B]^n \quad \Rightarrow r_3 = k[2A]^m[B]^n \quad \Rightarrow \quad \frac{r_2}{r_1}=8=2^{m+n}$, so $m + n = 3$

$\frac{r_3}{r_1}=2=2^m \quad$ so, $m = 1$, Hence $n = 2$

36.(C) $A_2 \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} 2A$

$A_2 \xrightarrow{K_1} 2A \qquad 2A \xrightarrow{K_{-1}} A_2$

$\frac{1}{2}\frac{d[A]}{dt} = K_1[A_2] \qquad -\frac{1}{2}\frac{d[A]}{dt} = K_{-1}[A]^2$

$\left.\frac{d[A]}{dt}\right|_{overall} = 2K_1[A_2] - 2K_{-1}[A]^2$

37.(A) $\Delta_r G^\circ = 120^\circ - \frac{3}{8}T \Rightarrow$ For $\Delta_r G^\circ = 0$, $T = 320\,K$

Above 320K, $\Delta_r G^\circ$ is $-ve$, major component would be Y. While below 320K, $\Delta_r G^\circ$ is $+ve$ and major component would be X.

38.(C) $k = Ae^{-Ea/RT}$

$\ln k = \ln A - E_a/RT$

$Slope = -E_a$

$-E_a = -y \qquad \therefore \qquad E_a = y\,unit$

39.(C) According to the unit of rate constant (0.05 μg /year), it is a zero order reaction.

$\Rightarrow \qquad t_{1/2} = \frac{a_o}{2k_o} = \frac{5}{2\times 0.05} = 50\,years$

40.(A) $\ln k = \ln A - \frac{E_a}{RT}$

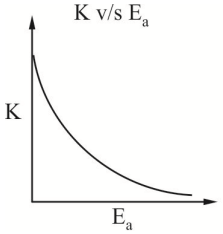
$y = mx + c$

$|Slope| = m = \frac{Ea}{R} = 4606$

$\ln\left(\frac{k_2}{10^{-5}}\right) = +4606 \times \frac{(500-400)}{500\times 400} \qquad \Rightarrow \ln\left(\frac{k_2}{10^{-5}}\right) = 2.303 \qquad \Rightarrow \qquad \ln\left(\frac{k_2}{10^{-5}}\right) = \ln 10$

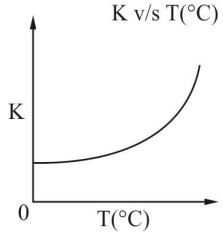
$k = 10^{-4}$

41.(A) $k = Ae^{-\frac{E_a}{RT}}$



If Ea ↑ k ↓

As per Arhenius equation



If T ↑ k ↑

As per Arhenius equation

Hence both graphs are correct

42.(A) $t_{\frac{1}{2}} = \frac{c_0}{2k} \Rightarrow 6 = \frac{0.2}{2k} \Rightarrow k = \frac{1}{60}$

$k = \frac{c_0 - c_t}{t} \Rightarrow \frac{1}{60} = \frac{0.5-0.2}{t} \qquad \therefore \qquad t = 18h$

43.(B) Upto one hour

$N = N_0 e^t$ At $t = 1\,hour$

$N = N_0e$ After one hour $\frac{dN}{dt} = -5N^2$

$$\int_{N_0e}^{N} \frac{dN}{N^2} = -5\int_{1}^{t} dt$$

$$\left[\frac{1}{N}\right]_{N_0e}^{N} = 5\left[t\right]_1^t \quad \Rightarrow \quad \frac{1}{N} - \frac{1}{N_0e} = 5(t-1) \quad \Rightarrow \quad \frac{1}{N} = 5t - 5 + \frac{1}{N_0e}$$

Multiply N_o both side

$$\frac{N_0}{N} = 5N_0t + \left(\frac{1}{e} - 5N_o\right) \quad \Rightarrow \quad y = mx + c$$

44.(A) $R \longrightarrow P$

a o

a – x x

For 1st order reaction

$$+\frac{dx}{dt} = k(a-x)^1$$

$$\int \frac{dx}{a-x} = \int kdt$$

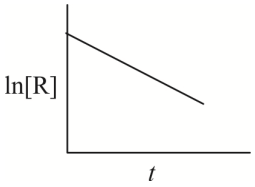
$$-\ln(a-x) = kt + c$$

If $t = 0$

$c = -\ln a \quad \therefore \quad -\ln(a-x) = kt - \ln a$

or $\ln(a-x) = -kt + \ln a$

y m x C



Similarly

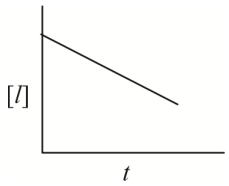
$$\underset{(A_0)}{R} \longrightarrow P$$
$$(A)$$

$$\frac{-d[R]}{dt} = k[R]^0 \quad \text{or} \quad -d(R) = kdt$$

or $\int d[R] = -\int kdt$

$[R] = -kt + c$ or $[A] = -kt + c$

$y = mx + c$



45.(D) From given data

Rate $= k[A]^a[B]^b$

Now, $0.045 = k[0.05]^{a+b}$ ... (i) ; $0.090 = k[0.05]^{a+b}2^a$ ... (ii)

$0.72 = k[0.05]^{a+b} \cdot 2^{2a+b}$ ... (iii)

From equation (i) and (ii) we get,

$$\Rightarrow \quad \frac{1}{2} = \frac{1}{2^a} \Rightarrow a = 1$$

And from equation (i) and (iii) we get

$$\Rightarrow \quad \frac{0.045}{0.72} = \frac{1}{2^{2+b}} \quad \Rightarrow \quad \frac{45}{720} = \frac{1}{2^{2+b}} \quad \Rightarrow \quad \frac{720}{45} = 2^{(2+b)} \quad \Rightarrow \quad 2^4 = 2^{2+b} \quad \Rightarrow \quad b = 2$$

46. (B) Rate of formation of C_4H_8 is equal to twice the rate of dimerisation of C_2H_4

47.(C) Rate of disappearance of $N_2O_5 = \frac{(3-2.75)}{30} = \frac{25}{30} \times 10^{-2}\ M\ min^{-1} = \left(\frac{5}{6}\right) \times 10^{-2}\ M min^{-1}$

Rate of formation of $NO_2 = 2$ (rate of disappearance of N_2O_5) $= \frac{10}{6} \times 10^{-2} = 1.667 \times 10^{-2} M\,min^{-1}$

48.(C) $k_1 = 2.5 \times 10^{-4}\,dm^3\,mol^{-1}\,s^{-1}$ $T_1 = 327°C \Rightarrow 600K$

$k_2 = 1.0\,dm^3\,mol^{-1}\,s^{-1}$ $T_2 = 527°C \Rightarrow 800K$

$E_A \Rightarrow$ in kJ / mole

Given $R = 8.314\,J$ / k-mole

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

$\log\frac{1}{2.5\times10^{-4}} = \frac{Ea}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \Rightarrow \log\frac{1}{2.5\times10^{-4}} = \frac{Ea}{2.303\times8.314}\left(\frac{1}{600} - \frac{1}{800}\right)$

$E_a = 165.54\,kJ$

49.(B) According to given graph, activation enthalpy to form C is greater than that to form D.

50.(D) $\frac{d[B]}{dt} = k_1[A] - k_2[B] \Rightarrow \frac{d[B]}{dt} = 0$

$\Rightarrow [B] = \frac{k_1}{k_2}[A]$

51.(A) $2H_2(g) + 2NO(g) \longrightarrow N_2(g) + 2H_2O(g)$

rate $= k_f[NO]^2[H_2]^2 \Rightarrow K_{eq} = \frac{k_f}{k_b} = \frac{[N_2][H_2O]^2}{[NO]^2[H_2]^2}$

At equilibrium, $r_f = r_b$

$k_f[H_2][NO]^2 = \frac{k_b[N_2][H_2O]^2}{[H_2]}$

Hence rate expression for reverse rxn

rate $= k_b\frac{[N_2][H_2O]^2}{[H_2]}$

52.(D) $k = Ae^{-Ea/RT}$

$\log k = \log A - \frac{E_a}{2.303RT}$; slope $= \frac{-E_a}{2.303R}$

$\therefore$ In the given graph, greater the slope, more is the E_a

$\therefore$ Order $= E_c > E_a > E_d > E_b$

53.(C) $r_1 = Ae^{-\frac{Ea_1}{RT_1}}$; $r_2 = Ae^{-\frac{Ea_2}{RT_2}}$

$r_1 = r_2$ [Given]

$\therefore$ $Ae^{\left(\frac{-Ea_1}{RT_1}\right)} = Ae^{\left(\frac{-Ea_2}{RT_2}\right)}$ or $\frac{Ea_1}{T_1} = \frac{Ea_2}{T_2}$

Also, $Ea_2 = Ea_1 - 30$, $T_1 = 700\,K$, $T_2 = 500\,K$ (Given)

$\therefore$ $\frac{Ea_1}{700} = \frac{Ea_1 - 30}{500}$

or $5Ea_1 = 7Ea_1 - 210$

$2Ea_1 = 210 \Rightarrow Ea_1 = 105\,kJ/mol \Rightarrow Ea_2 = 105 - 30 \Rightarrow Ea_2 = 75\,kJ/mol$

54.(D) $\therefore \quad k = Ae^{-Ea/RT}$ ...(1)

$\therefore \quad 10^6 \times k = Ae^{(-E_a)_{cat}/RT}$ ...(2)

Dividing equation (2) by (1),

$$10^6 = e^{E_a-(E_a)_{cat}/RT} \quad \Rightarrow \quad 6 \times \ln 10 = \frac{E_a-(E_a)_{cat}}{RT}$$

$$\Rightarrow \quad \Delta E_a = E_a-(E_a)_{cat} = 6 \times \ln 10 \times RT \quad \Rightarrow \quad (E_a)_{cat} - E_a = -6 \times 2.303 \times RT$$

55.(23.03)

$t_{1/2} = 6.93$years

$$t = \frac{2.303}{k}\log\frac{100}{10} \Rightarrow k = \frac{0.693}{6.93} = 0.1 \Rightarrow t = \frac{2.303}{.1} \times 1 = 23.03 \text{ years}$$

56.(3.98)

$$\ln\frac{k_2}{k_1} = \frac{Ea}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\ln\left(\frac{40}{60}\right) = \frac{Ea}{8.3}\left[\frac{1}{300} - \frac{1}{400}\right] = \frac{Ea}{8.3} \times \frac{100}{300 \times 400}$$

$$Ea = \ln\left(\frac{2}{3}\right) \times 8.3 \times 1200 = 3984 \text{ J/mol} = 3.984 \text{ kJ/mol}$$