(1) **(2).** Let the rate of reaction depends on x^{th} power of [A]. Then

$$r_1 = k[A]^x \text{ and } r_2 = k[2A]^x$$

$$\therefore \quad \frac{r_1}{r_2} = \frac{[A]^x}{[2A]^x} = \frac{1}{4} = \left(\frac{1}{2}\right)^2 \quad (\because r_2 = 4r_1)$$

$\therefore$ $x = 2$.

As the reaction rate does not depend upon the concentration of B. Hence, the correct rate law will be

rate $= k[A]^2[B]^o$ or rate $= k[A]^2$

(2) **(3).** The unit of K for zero order reaction

$$= \text{mole litre}^{-1} \text{ sec}^{-1}$$

(3) **(2).** $k = \dfrac{2.303}{t} \log \dfrac{a}{a-x}$

$$\frac{0.693}{T} = \frac{2.303}{t} \log \frac{100}{100-30}$$

$\therefore$ $T = 58.2$ min.

(4) **(2).** Order of reaction $= \dfrac{3}{2} + \dfrac{3}{2} = \dfrac{3+3}{2} = \dfrac{6}{2} = 3$

(5) **(2).** $CH_3COOCH_3 + H_2O$

$$\xrightarrow{H^+} CH_3COOH + CH_3OH$$

It is a pseudo-unimolecular reaction.

(6) **(3).** The relation between half – life period and initial concentration (3) for a nth order reaction is given by

$t_{1/2} \propto \dfrac{1}{C^{n-1}}$ for first order reaction (n=1).

$t_{1/2} \propto \dfrac{1}{C^{1-1}}$ or $t_{1/2} \propto C^0$.

(7) **(2).** The increase in collision frequency brings in an increase in effective collisions and thus rate of reaction increases.

(8) **(1).** $2.303 \log \dfrac{K_2}{K_1} = \dfrac{E_a}{R}\left[\dfrac{T_2 - T_1}{T_1 T_2}\right]$

$$\log \frac{K_2}{K_1} = \frac{9.0 \times 10^3}{2.303 \times 2}\left[\frac{308 - 298}{308 \times 298}\right]$$

$$\frac{K_2}{K_1} = 1.63; \; K_2 = 1.63\, K_1$$

$$\frac{1.63K_1 - K_1}{K_1} \times 100 = 63.0\%$$

(9) **(1).** For zero order, $t_{1/2} = \dfrac{a}{2k}$

In the given curve, slope $= 1 = 1/2k$

i.e. $2k = 1$ $\therefore$ $k = 1/2$

(10) **(3).** $\dfrac{(t_{1/2})_I}{(t_{1/2})_{II}} = \left(\dfrac{a_{II}}{a_I}\right)^{n-1}$

$$\frac{120}{240} = \left(\frac{4 \times 10^{-2}}{8 \times 10^{-2}}\right)^{n-1}$$

$$n - 1 = 1 \Rightarrow n = 2$$

(11) **(1).** $-\dfrac{1}{3}\dfrac{d[A]}{dt} = -\dfrac{d[B]}{dt} = \dfrac{+d[C]}{dt} = \dfrac{+d(D)}{dt}$

(12) **(1).** $p_0 = 500$ atm

$$K = \frac{2.303}{t} \log_{10} \frac{p_0}{p_t}$$

$$3.38 \times 10^{-5} = \frac{2.303}{10 \times 60} \log \frac{500}{p_t}$$

or $0.00880 = \log \dfrac{500}{p_t} \Rightarrow \dfrac{500}{1.02} = 490\,\text{atm}$

(13) **(3).** For following reaction,

$$2NO_{(g)} + O_2(g) \rightarrow 2NO_2(g)$$

When the volume of vessel change into $\dfrac{1}{3}$ then concentration of reactant become three times.

The rate of reaction for first order reaction $\propto$ concentration. So rate of reaction will increases three times.

(14) **(2).** $t_{1/2} = \dfrac{0.693}{k}, \dfrac{0.693}{1.1 \times 10^{-9}} = 6.3 \times 10^8 \text{ sec.}$

(15) **(4).** The rate of this photochemical reaction is independent of the concentration, therefore, it is zero order reaction.

(16) **(1).** Rate consatnt

For first order $\Rightarrow$ time^{-1}

For second order $\Rightarrow$ mole^{-1} litre time^{-1}

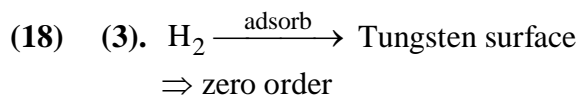**(17)** **(4).** $A \rightarrow$ product $\Rightarrow$ $-\dfrac{d[A]}{dt} = k_1[A]^\circ$

$\Rightarrow$ zero order

$B \rightarrow$ product $\Rightarrow$ $-\dfrac{d[B]}{dt} = k_2[A]$

$\Rightarrow$ 1st order

For zero order $\Rightarrow$ molL^{-1} time^{-1}=Msec^{-1}

For 1st order $\Rightarrow$ time^{-1} or sec^{-1}

(18) **(3).** $H_2 \xrightarrow{\text{adsorb}}$ Tungsten surface

$\Rightarrow$ zero order

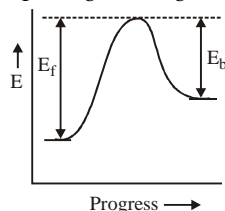**(19)** **(1).** Rate of reaction = k [NO]^2 [O$_2$]

If volume become half concentration of both will become twice.

Then, Rate = k_f {2[NO]}^{2} {[2[O$_2$]]}

$= 8K_f$ [NO]^2.[O$_2$]

(20) **(4).** r = k [A] . [B] $\Rightarrow$ IInd order

The rate equation shows the reaction to be second order. So, the correct statement is (4) because rate constant of a reaction remain constant irrespectively of concentration A or B.

(21) **(2).** $E_f > E_b$ or $E_b < E_f$

(22) **(1).** $k = Ae^{-Ea/RT}$

Ea = The energy below which colliding molecules will not react i.e. activation energy.

(23) **(3).** r = k [NOBr$_2$] [NO]

[NOBr$_2$] = k_{eq} [NO] [Br$_2$]

So, r = k.k$_{eq}$ [NO] [Br$_2$] [NO]

$= k'$ [NO]^2 [Br$_2$]

So, the order with respect to NO = 2

(24) **(3).** For a zero order reaction k = $\dfrac{x}{t}$ .... (1)

Where x = amount decomposed

k = zero order rate constant

For a zero order reaction

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

Since [A$_0$] = 2M , t$_{1/2}$ = 1 hr; k = 1

$\therefore$ From equation (1)

t = 0.25/1 = 0.25hr

(25) **(4).** Rate equation is to be derived wrt slow step $\therefore$ from mechanism (1)

Rate = k [Cl$_2$] [H$_2$S]

(26) **(2).** If one of the reacting species is in excess, a bimolecular reaction becomes first order reaction.

(27) **(2).** The rate of photochemical process varies with the intensity of absorption since greater the intensity of absorbed light more photons will fall at a point, and further each photon causes one molecule to undergo reaction.

(28) **(3).** $K = \dfrac{2.303}{t} \log \dfrac{[A]_0}{[A]_t} = \dfrac{2.303}{2 \times 10^4} \log \dfrac{800}{50}$

$= 1.386 \times 10^{-4}$ s^{-1}

(29) **(4).** Order of reaction is determined experimentally. It may be fractional.

(30) **(1).** For Ist order reaction

For zero order reaction,

$k_1 = \dfrac{\ln 2}{t_{1/2}} = \dfrac{0.693}{40}$ sec^{-1}

$k_0 = \dfrac{C_0}{2t_{1/2}} = \dfrac{1.386}{2 \times 20} \Rightarrow \dfrac{k_1}{k_0} = \dfrac{0.693}{1.386} = 0.5$

(31) **(4).** From Arrhenius equation

$K = Ae^{-Ea/RT}$

$\ln K = \ln A - \dfrac{Ea}{RT}$

$2.303 \log K = 2.303 \log A - \dfrac{Ea}{RT}$

$\log K = \dfrac{-Ea}{2.303R} \times \dfrac{1}{T} + \log A$ .... (1)

$\log K = -(2000)\dfrac{1}{T} + 6$ .... (2)

On comparing eq. (1) and (2),

$\dfrac{-Ea}{2.303R} = -2000$

Ea = $2.303 \times 8.314 \times 2000$ = 38.29 kJ.

and log A = 6 ; A = 10^6

(32) **(1).** $K = \dfrac{C_0 - C}{t} = \dfrac{1 - 0.75}{0.05} = \dfrac{0.25}{0.05} = 5$

$K = \dfrac{0.75 - 0.40}{0.07} = \dfrac{0.35}{0.07} = 5$

So, reaction must be of zero order.

**(33)** **(2).** $\dfrac{r_2}{r_1} = \left(\dfrac{[M]_2}{[M]_1}\right)$

$8 = (2)^a$; a = 3

So, order of reaction is 3.

2

(34) **(1).** Average rate $= -\dfrac{1}{2}\dfrac{\Delta[R]}{\Delta t}$

$= -\dfrac{1}{2}\times\dfrac{0.4-0.5}{10} = \dfrac{1}{2}\times\dfrac{0.1}{10}$

$= 5\times 10^{-3}\ M\ min^{-1}$

(35) **(2).** Apart from energy considerations, the colliding molecules should have proper orientation for effective collisions.

(36) **(2).** First order reaction given a straight line plot of log (a − x) and time.

(37) **(2).** A catalyst does not alter Gibbs energy, ΔG of a reaction.

(38) **(2).** $2N_2O_4 \rightleftharpoons 4NO_2$

$Rate = -\dfrac{1}{2}\dfrac{d[N_2O_4]}{dt} = +\dfrac{1}{4}\dfrac{d[NO_2]}{dt}$

$= \dfrac{1}{2}k = \dfrac{1}{4}k'\ \ or\ \ k' = 2k$

(39) **(3).** Catalyst alters the activation energy of both forward and backward reactions equally hence heat of reaction remains unchanged.

(40) **(4).** The unit of rate of reaction is mol $L^{-1}\ s^{-1}$. It does not change with order.

(41) **(2).** If x atm be the decrease in pressure of A at time t and one mole each of B and C is being formed, the increase in pressure of B and C will also be x atm each.

$$A_{(g)} \rightarrow B_{(g)} + C_{(g)}$$

At t = 0 p_i atm   0 atm   0 atm

At time t (p_i–x) atm   x atm   x atm
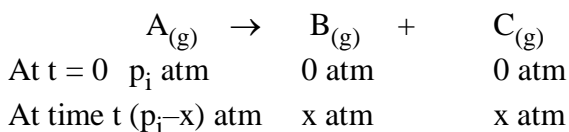
where, p_i is the initial pressure at time t = 0

$p_i = (p_i − x) + x + x = p_i + x$

$x = (p_t − p_i)$

where, $p_A = p_i − x = p_i − (p_t − p_i) = 2p_i − p_t$

$k = \left(\dfrac{2.303}{t}\right)\left(\log\dfrac{p_i}{p_A}\right) = \dfrac{2.303}{t}\log\dfrac{p_i}{(2p_i − p_t)}$

(42) **(4).** Given, [A] 0 = 0.01 M

Rate $= 2.0\times 10^{-5}$ mol $L^{-1}S^{-1}$.

For a first order reaction, Rate = k [A]

$k = \dfrac{2.0\times 10^{-5}}{[0.01]} = 2\times 10^{-3}$

$t_{1/2} = \dfrac{0.693}{2\times 10^{-3}} = 347\ sec$

(43) **(2).** $Rate_I = k\,[A]^x\,[B]^y$ .... (1)

$\dfrac{Rate_I}{4} = k\,[A]^x\,[2B]^y$ .... (2)

or $Rate_I = 4k\,[A]^x\,[2B]^y$

From (1) and (2), we get

$\dfrac{k\,[A]^x[B]^y}{4} = k\,[A]^x[2B]^y$

$\dfrac{[B]^y}{4} = [2B]^y$

$\dfrac{1}{4} = \left(\dfrac{2B}{B}\right)^y \Rightarrow \dfrac{1}{4} = 2^y\ \ or\ 2^{-2} = 2^y$

or $y = −2$

(44) **(4).** In the given options $-\dfrac{d[C]}{3\,dt}$ will not represent the reaction rate. It should not have −ve sign as it is product.

Since $\dfrac{1}{3}\dfrac{dC}{dt}$ show the rate of formation of product C which will be positive.

(45) **(1).** If we write rate of reaction in terms of concentration of NH_3 and H_2, then

Rate of reaction $= \dfrac{1}{2}\dfrac{d[NH_3]}{dt} = -\dfrac{1}{3}\dfrac{d[H_2]}{dt}$

So, $\dfrac{d[NH_3]}{dt} = -\dfrac{2}{3}\dfrac{d[H_2]}{dt}$