Chemical Kinetics

SOLUTIONS

Exercise-I (Conceptual Questions)

1. Ans. (1)

$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

$$\text{rate} = \frac{\text{rod}}{\text{S.C. of reactent}} = \frac{\text{roa}}{\text{S.C. of product}}$$

$$\text{rate} = \frac{\frac{-d(N_2)}{dt}}{1} = \frac{\frac{-d(H_2)}{dt}}{3} = \frac{+\frac{d(NH_3)}{dt}}{2}$$

$$\text{rate} = \frac{-d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2}{dt} = +\frac{1}{2}\frac{d[NH_3]}{dt}$$

2. Ans. (1)

$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$

$$\text{ror} = \frac{\text{rod of } SO_2}{2} = \frac{\text{rod of } O_2}{1} = \frac{\text{roa of } SO_3}{2}$$

Given ror =

$$\text{rod of } O_2 = \frac{-d[O_2]}{dt} = 2.5\times10^{-4}\ \frac{\text{mol}}{\text{L sec}}$$

$$2.5\times10^{-4} = \frac{\text{rod of } SO_2}{2}$$

$$\text{rod of } SO_2 = 5\times10^{-4}\ \frac{\text{mol}}{\text{L sec}}$$

3. Ans. (3)

$N_2 + 3H_2 \longrightarrow 2NH_3$

$$\text{ror} = \frac{\text{rod of } N_2}{1} = \frac{\text{rod of } H_2}{3} = \frac{\text{roa of } NH_3}{2}$$

$$\text{Given roa of } NH_3 = 2.5\times10^{-4}\ \frac{\text{mol}}{\text{L sec}}$$

$$\frac{\text{rod of } H_2}{3} = \frac{2.5\times10^{-4}}{2}$$

$$\text{rod of } H_2 = 3.75\times10^{-4}\ \frac{\text{mol}}{\text{L sec}}$$

4. Ans. (3)

$X + 2y \longrightarrow P$

$$\frac{\text{rod of x}}{1} = \frac{\text{rod of y}}{2} = \frac{\text{rod of P}}{1}$$

5. Ans. (1)

$N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$

$$\frac{\frac{-d(N_2O_5)}{dt}}{1} = \frac{\frac{-d(NO_2)}{dt}}{2} = \frac{\frac{-d(O_2)}{dt}}{1/2}$$

$$K_1[N_2O_5] = \frac{1}{2}\times K_2[N_2O_5] = 2K_3[N_2O_5]$$

$$K_1 = \frac{K_2}{2} = 2K_3$$

$2K_1 = K_2 = 4K_3$

6. Ans. (4)

$2SO_2 + O_2 \longrightarrow 2SO_3$

$$\text{rof of } SO_3 = 1.6\times10^{-3}\ \frac{\text{kg}}{\text{L min}}$$

M_w → SO_2=64, SO_3=80

$$\frac{\text{rod of } SO_2}{M_w(SO_2)\times2} = \frac{\text{roa of } SO_3}{M_w/(SO_3)\times2}$$

$$\text{rod of } SO_2 = \text{roa of } SO_3 \times \frac{M_w(SO_2)}{M_w(SO_3)}$$

$$= 1.6\times10^{-3}\times\frac{64}{80} = 1.28\times10^{-3}\ \frac{\text{Kg}}{\text{L min}}$$

7. Ans. (1)

$2A + 3B \longrightarrow$ product

$$\frac{\text{rod of A}}{2} = \frac{\text{rod of B}}{3}$$

Given rod of A = r_1 ; rod of B = r_2

$$\frac{r_1}{2} = \frac{r_2}{3}$$

$3r_1 = 2r_2$

8. Ans. (1)

$2A + B \longrightarrow 3C + D$

ror =

$$\frac{\text{rod of A}}{2} = -\frac{\text{rod of B}}{1} = \frac{\text{roa of C}}{3} = \frac{\text{roa of D}}{1}$$

$$\text{ror} = \frac{1}{2}\left[\frac{-d(A)}{dt}\right] = \frac{-d[B]}{dt} = \frac{1}{3}\left[+\frac{d(C)}{dt}\right] = +\frac{d[D]}{dt}$$

9. Ans. (2)

$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

$$\frac{\text{roa of } NH_3}{2} = \frac{\text{rod of } H_2}{3}$$

$$\text{roa of } NH_3 = \frac{2}{3} \text{ rod of } H_2$$

$$+\frac{d[NH_3]}{dt} = \frac{2}{3}\left\{-\frac{d[H_2]}{dt}\right\}$$

10. Ans. (4)

$r = K(A)\ (B)$

$$C \propto \frac{1}{V}$$

If volume decreases $\frac{1}{4}$ then concentration increases 4 times

Old rate = K(A)[(B] ...(1)

New rate = K{4(A)} {4[B]} ...(2)

$$\frac{\text{New rate}}{\text{Old rate}} = 16$$

New rate = 16 × old rate

11. Ans. (2)

2(A)g + B(g) ⟶ product (Elementary reaction)

Old $r_f = KP_A^2P_B$ ...(1)

New $r_f = K(3P_A)^2(3P_B) = 27KP_A^2P_B$ ...(2)

$$\frac{\text{New } r_f}{\text{Old } r_f} = 27$$

New r_f = 27 × (old r_f) ...(2)

12. Ans. (4)

$A + B + C \longrightarrow$ product

$$r = \frac{-d[A]}{dt} = K[A]^{\frac{1}{2}}[B]^{\frac{1}{3}}[C]^{\frac{1}{4}}$$

order = SUM of S.C. in rate law

$$\text{Order} = \frac{1}{2}+\frac{1}{3}+\frac{1}{4} = \frac{13}{12}$$

13. Ans. (3)

Overall order

Option 1 = 1 + 1 + 1 = 3

Option 2 = 0.5 + 0.5 + 0.5 = 1.5

Option 3 = 1.5 – 1 + 0 = 0.5

Option 4 = 1 + 0 – 2 = –1

14. Ans. (1)

Let reaction has two reactant A & B.

$$r \propto \frac{[A]^2}{[B]}$$

$$r \propto [A]^2[B]^{-1}$$

Order = 2–1 = 1

15. Ans. (2)

$H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$

Rate = $K[H_2][Br_2]^{1/2}$

$$\text{Order } 1 + \frac{1}{2} = 1\frac{1}{2}$$

16. Ans. (3)

$A + B \longrightarrow C$

Let Intial rate (r) = $K[A]^x\ [B]^y$

Exp.1 $0.1 = K[0.012]^x\ [0.035]^y$ ...(1)

Exp.2 $1.6 = K[0.024]^x\ [0.07]^y$ ...(2)

$0.2 = K[0.024]^x\ [0.035]^y$ ...(3)

$0.8 = K[0.012]^x\ [0.07]^y$ ...(4)

$$\frac{(3)}{(1)}\ \frac{0.2}{0.1} = 2 = \left(\frac{0.024}{0.012}\right)^x = 2^x \Rightarrow x = 1$$

$$\frac{(4)}{(1)}\ \frac{0.8}{0.1} = 8 = \left(\frac{0.07}{0.035}\right)^y = 2^y$$

$2^3 = 2^y \Rightarrow y = 3$

$R = K[A]^1\ [B]^3$

17. Ans. (2)

$2A + B \longrightarrow C + D$

Let Initial rate (r) = $K[A]^x\ [B]^y$

Exp(1) $7.5\times10^{-3} = K(0.1)^x(0.1)^y$ ...(1)

$9\times10^{-2} = K(0.3)^x(0.2)^y$ ...(2)

$3.6\times10^{-1} = K(0.3)^x(0.4)^y$ ...(3)

$3.6\times10^{-2} = K(0.4)^x(0.1)^y$ ...(4)

$$\frac{(4)}{(1)}\quad \frac{3.0\times10^{-2}}{7.5\times10^{-3}} = 4 = 4^x \Rightarrow \boxed{x = 1}$$

$$\frac{(3)}{(2)}\quad \frac{3.6\times10^{-1}}{9\times10^{-2}} = 4 = 2^y \Rightarrow \boxed{y = 2}$$

$r = K(A)^1\ (B)^2$

18. Ans. (2)

$A + B \longrightarrow C$

Let rate of reaction (r) = $K[A]^x[B]^y$

$1\times10^{-4} = K(0.01)^x (0.01)^y$ ...(1)

$9\times10^{-4} = K(0.01)^x (0.03)^y$ ...(2)

$2.7\times10^{-3} = K(0.03)^x (0.03)^y$ ... (3)

$\frac{(2)}{(1)}$ $9 = 3^y \Rightarrow \boxed{y = 2}$

$\frac{(3)}{(2)}$ $\frac{2.7\times10^{-3}}{9\times10^{-4}} = 3 = 3^x \Rightarrow \boxed{x = 1}$

$r = K[A]^1 [B]^2$

19. Ans. (1)

Let rate (r) = $K[A]^x [B]^y$

$1.2 \times 10^{-3} = K(0.05)^x (0.05)^y$ ...(1)

$2.4 \times 10^{-3} = K(0.1)^x (0.05)^y$ ...(2)

$1.2 \times 10^{-3} = K(0.05)^x (0.1)^y$ ...(3)

$\frac{(2)}{(1)}$ $2 = 2^x \Rightarrow x = 1$

$\frac{(3)}{(1)}$ $1 = 2^y \Rightarrow y = 0$

Order of reaction wrt A and B are 1 and 0

20. Ans. (3)

Order wrt A & B each is 1

Rate = $K[A]^1[B]^1$

$0.1 = K(0.2)\ (0.05)$ ...(1)

$0.4 = K(x)\ (0.05)$ ...(2)

$0.8 = K(0.4)\ (y)$ ...(3)

$\frac{(2)}{(1)}$ $\frac{0.4}{0.1} = \frac{x}{0.2}$

$\boxed{x = 0.8}$

$\frac{(3)}{(1)}$ $\frac{0.8}{0.1} = \frac{(0.4)(y)}{(0.2)(0.05)}$

$\boxed{0.2 = y}$

21. Ans. (2)

$2A + B \longrightarrow 2C$

Single step reaction is also called elementary

Order of reaction wrt A = 2

Order of reaction wrt B = 1

Rate = $K[A]^2 [B]^1$

22. Ans. (2)

Reaction rate depends on [A] and [B]

Rate (r) = $K[A]^x [B]^y$ ...(1)

$4r = K\{2[A]\}^x [B]^y$ ...(2)

$r = K [A]^x \{2[B]\}^y$ ...(3)

$\frac{(2)}{(1)} = 2^2 = 4 = 2^x$

$\boxed{x = 2}$

$\frac{(3)}{(1)} = 2^\circ = 1 = 2^y$

Rate (r) = $K[A]^2 [B]^0$

Rate = $K[A]^2$

23. Ans. (4)

Rate law is experimental concept whereas Law of mass action is theoretical concept.

Experimental concept is always more realistic and more informative.

In Elementary reaction, rate law and law of Mass action give same rate expression.

24. Ans. (3)

For an elementary reaction molecularity is sum of stoichiometry coefficient of reactant.

So molecularity of given reaction is 3.

25. Ans. (3)

Reaction rate depends on concentration of A & B.

Let rate of reaction,(r) = $K[A]^x[B]^y$ ...(1)

$2r = K\{2[A]\}^x[B]^y$ ...(2)

$2r = K\{2(A)^x\}\{2(B)^y\}$ ...(3)

$\frac{(2)}{(1)}$ $2 = 2^x$

$\boxed{x = 1}$

$\frac{(3)}{(2)}$ $2^\circ = 1 = 2^y$

$\boxed{y = 0}$

Order of reaction wrt A = x = 1

Order of reaction wrt B_0 = y = 0

26. Ans. (2)

Old rate r = $K[A]^1[B]^{1/2}$ ...(1)

New rate $r^1 = K\{4[A]\}^1 \{4(B)\}^{1/2}$ ...(2)

$$\frac{r^1}{r} = 4\times(4)^{\frac{1}{2}} = 8$$

$r^1 = 8r$

New rate = 8 × old rate

27. Ans. (2)

Given old rate (r) = $K[A]^1[B]^2$ ...(1)

Option (1)

New rate (r^1) = $K\{2(A)\}(B)^2$ ...(2)

$$\frac{(2)}{(1)} \quad \frac{r^1}{r} = 2 \Rightarrow \boxed{r^1 = 2r}$$

Option (2)

$$\text{New rate } (r^1) = K[A]\left\{\frac{(B)}{4}\right\}^2 = \frac{K(A)(B)^2}{16}$$

...(3)

$$\frac{(3)}{(1)} \quad \frac{r^1}{r} = \frac{1}{16} \Rightarrow \boxed{r^1 = \frac{1}{16}r}$$

Option (3) New rate (r^1)

$= \{2(A)\}\{2(B)\}^2 = 8K(A)(B)^2$ ...(4)

$$\frac{(4)}{(1)} \quad \frac{r^1}{r} = 8 \Rightarrow \boxed{r^1 = 8r}$$

Option (4) order of reaction = 1+ 2 = 3

28. Ans. (3)

Let rate of reaction (r) = $K(A)^x$ ...(1)

$= 2r = K\{8(A)\}^x$ ...(2)

$$\frac{(2)}{(1)} \quad 2 = 8^x = (2^3)^x = 2^{3x}$$

$3x = 1$

$x = \frac{1}{3}$

Order of reaction wrt A = $x = \frac{1}{3}$

29. Ans. (4)

$K = A\, e^{-Ea/RT}$

rate constant depends on activation energy and temperature.

30. Ans. (2)

If the given reaction is elementary then its order and molecularity will be 10 but usually maximum molecularity of elementary reaction is 3. So given reaction cant be elementary reaction it is a complex reaction.

31. Ans. (2)

We write the rate law from slow step by considering it elementary reaction.

So rate (r) = $K[A]^1[B]^1$

32. Ans. (2)

$$O_3 \underset{}{\overset{K_{Eq}}{\rightleftharpoons}} O_2 + O \text{ (Fast)} \quad ...(1)$$

$$O + O_3 \xrightarrow{K^1} 2O_2 \text{ (slow)} \quad ...(2)$$

* We write rate from slow step by considering it elementary reaction.

$r = K^1[O]\ [O_3]$ ...(3)

Intermediate

* We write equilibrium expression for reversible reaction and eliminate intermediat with the help of this expression.

$$K_C = \frac{[O_2][O]}{[O_3]}$$

$[O] = K_C[O_3][O_2]^{-1}$ ...(4)

Place [O] in equation (3)

$r = K^1\{K_C[O_3][O_2]^{-1}\}\ [O_3]$

$r = K[O_3]^2[O_2]^{-1}$

$\boxed{K^1K_C = K}$

33. Ans. (3)

$$A_2 \underset{}{\overset{K_C}{\rightleftharpoons}} A + A ----\text{(Fast)} \quad ...(1)$$

$$A + B_2 \xrightarrow{K'} AB + B ----\text{(Slow)} \quad ...(2)$$

$$A + B \underset{}{\overset{K''}{\rightleftharpoons}} AB ----\text{(Fast)} \quad ...(3)$$

$r = K'\ [A]\ [B_2]$ ...(4)

↑

Intermediate

$$K_C = \frac{[A][A]}{[A_2]} = \frac{[A]^2}{[A_2]}$$

$[A]^2 = K_C[A_2]$

$[A] = K_C^{\frac{1}{2}}[A_2]^{\frac{1}{2}}$ ...(5)

Place [A] in equation (4)

$$r = K'\left\{K_C^{\frac{1}{2}}[A_2]^{\frac{1}{2}}\right\}[B_2]$$

$r = K[A_2]^{\frac{1}{2}}[B_2]$ $\quad K = K'K_C^{\frac{1}{2}}$

$$\text{order} = \frac{1}{2} + 1 = 1\frac{1}{2}$$

34. Ans. (2)

$r = K_1[RCl]$

On increasing temperature, rate of reaction increases because effective collision between molecules increases.

* In rate law expression, NaOH is not present so no effect on rate by doubling the concentration of NaOH.

* rate of reaction is directly proportional to [RCl].

As concentration of RCl become half, rate of reaction become half.

35. Ans. (1)

$NO_2 + CO \longrightarrow CO_2 + NO$, Rate $= K(NO_2)^2$

It is not elementary reaction. It is complex reaction

Rate expression Rate $= K(NO_2)^2$ is derived from slowest step.

As there is no CO term in rate expression so CO molecules would not be involved in slowest step.

36. Ans. (2)

$$\text{rate} = \frac{dp}{dt} = K[A]^2[B]$$

If 'A' is taken in large excess then during the reaction its concentration almost remains constant and rate become independent of it.

rate $= \{K[A]^2\}[B]$ $K' = K(A)^2$

(Effective) rate $= K'[B]\uparrow$

Order = 1 New constant

37. Ans. (1)

$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$

Rate $= K[CH_3COO_2H_5]$

and hydrolysis of ester is 1st order reaction

38. Ans. (2)

$2A \underset{}{\overset{K_C}{\rightleftharpoons}} A_2$ (Fast) ...(1)

$A_2 + B \xrightarrow{K'} P$ (slow) ...(2)

Rate $= K'[A_2][B]$

$\uparrow$

Intermediate

$$K_C = \frac{[A_2]}{[A]^2} \Rightarrow [A_2] = K_C[A]^2 \quad \text{... (4)}$$

Place $[A_2]$ in equation (3)

rate $= K'\{K_C[A]^2\}[B] = K'K_C[A]^2[B]$

order $= 2 + 1 = 3$

39. Ans. (1)

$NO + Cl_2 \underset{}{\overset{K_C}{\rightleftharpoons}} NOCl_2$ (Fast) ...(1)

$NOCl_2 + NO \xrightarrow{K'} 2NOCl$ (Slow) ...(2)

Rate $= K'[NOCl_2][NO]$

$\uparrow$

Intermediate

$$K_C = \frac{[NOCl_2]}{[NO][Cl_2]}$$

$[NOCl_2] = K_C[NO][Cl_2]$ ...(4)

Place $(NOCl_2)$ in equation (3)

rate $= K'K_C[NO][Cl_2][NO]$

rate $= K[NO]^2[Cl_2]$

$K = K'K_C$

40. Ans. (3)

reaction 1, 1st order

$r_1 = K[A]$

reaction 2, 2nd order

$r_2 = K[A]^2$

reaction 3, 3rd order

$r_3 = K[A]^3$

when $[A] > 1M$

$r_1 < r_2 < r_3$

41. Ans. (4)

Given 0 order, $K = 2\times10^{-2}\ \frac{\text{mol}}{\text{L sec}}$

$t = 25$ sec, $(A)_t = 0.5M$, $[A]_0 = ?$

$[A]_t = [A]_0 - Kt$

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

$[A]_0 = 1M$

42. Ans. (3)

$2N_2O_5 \longrightarrow 4NO_2 + O_2$, 1st order

This reaction is complex reaction and molecularity is not define for complex reaction. In 1st order reaction half lite $\propto$ (Initial concentration)^0

43. Ans. (1)

	x	$\longrightarrow$	y
Initially	aM		0
At time 't'	a–x		x

Let at time 't' both carve intersect so there concentration will be same.

$a - x = x$

$$x = \frac{a}{2}$$

At point of intersection, half of the reactant converted into product so it is half life so point of intersection of two curve represent $t_{\frac{1}{2}}$.

44. Ans. (3)

$A(g) \longrightarrow$ Product

$\text{Rate} = -\frac{dP_A}{dt}$

$\text{Unit} = \frac{atm}{sec}$

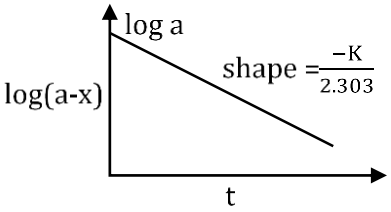
45. Ans. (2)

In 1st order

$$2.303\log\left(\frac{a-x}{a}\right) = -Kt$$

$$\log(a-x) - \log a = \frac{-K}{2.303}t$$

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



log (a-x) Vs time 't' plot is straight line for 1st order.

46. Ans. (1)

Given 1st order, $K = 4\times10^{-3}$ sec^{-1}, [A] = 0.02M

For 1st order reaction

r = K[A]

$r = 4\times10^{-3}\times0.02 = 8\times10^{-5}\frac{M}{S}$

47. Ans. (4)

Given 1st Order

$[A]_0$ = 1M, $[A]_t$ = 0.25 M, t = 20 Min, K ?

$$K = \frac{2.303}{t}\log\frac{[A]_0}{[A]_t}$$

$$= \frac{2.303}{20}\log\frac{1}{0.25}$$

$$= \frac{2.303}{20}\log 4$$

$$K = \frac{2.303\times2\log2}{20} = \frac{0.6931}{10} = 0.06931\,\text{Min}^{-1}$$

48. Ans. (1)

Given 1st order, $\frac{a}{a-x} = 8$, t = 10 Min K ?

$$K = \frac{2.303}{t}\log\left(\frac{a}{a-x}\right)$$

$$K = \frac{2.303}{10}\log 8 = \frac{2.303}{10}\times\log 2^3$$

$$K = \frac{(2.303\times3\log2)}{10}$$

49. Ans. (2)

Given 1st order

$t_{75\%}$ = 32 Min, $t_{50\%}$?

we know that $t_{75\%} = 2t_{50\%}$ = 32 Min

$t_{50\%}$ = 16 Min

50. Ans. (2)

Given 1st order, $t_{1/2}$ = 69.3 sec, [A] = 0.1 $\frac{Mol}{L}$

r ?

$$K = \frac{0.693}{t_{\frac{1}{2}}} = \frac{0.693}{69.3} = 10^{-2}\,\text{sec}^{-1}$$

$r = K[A] = 10^{-2}\times0.1 = 10^{-3}\,M\,S^{-1}$

51. Ans. (4)

1st order, [A] = 0.2M, $r = 1\times10^{-2}\frac{mol}{L\,Min}$, $t_{1/2}$?

r = K[A]

$$K = \frac{r}{(A)} = \frac{10^{-2}}{0.2} = 5\times10^{-2}\,\text{Min}^{-1}$$

$$t_{\frac{1}{2}} = \frac{0.693}{K} = \frac{0.693}{5\times10^{-2}} = 13.86\,\text{min} \simeq 14\text{Min}$$

52. Ans. (4)

Given 1st order, $t_{99\%}$ = 32 Min, $t_{99.9\%}$?

$$Kt = 2.303\log\left(\frac{100}{100-P}\right)$$

P=% of reactant reacted

$$K\times32 = 2.303\log\frac{100}{100-99}$$

$$= 2.303\log 100 = 2.303\times2\log10$$

$$Kt_{99\%} = 2.303\log\left(\frac{100}{100-99.9}\right)$$

$$= 2.303\log 1000 = 2.303\times3\log10$$

$$\frac{(2)}{(1)} \quad \frac{t_{99.9\%}}{32} = \frac{3}{2}$$

$t_{99.9\%}$ = 48 Min

53. Ans. (3)

Given radioactive reaction, $t_{87.5\%} = 40$ Min, $t_{50\%}$?

All radioactive reaction are 1st order.

$$Kt = 2.303\log\left(\frac{100}{100-P}\right)$$

$$Kt = 2.303\log\left(\frac{100}{100-87.5}\right)$$

P = % of reactant reacted

$$K \times 40 = 2.303 \log\left(\frac{100}{100-87.5}\right) = 2.303$$

$\log 8 = 2.303 \times 3\log 2$ ...(1)

$$K \times t_{50\%} = 2.303\log\left(\frac{100}{100-50}\right) = 2.303 \log 2$$ ...(2)

$$\frac{(2)}{(1)} \quad \frac{t_{50\%}}{40} = \frac{1}{3}$$

$$t_{50\%} = \frac{40}{3} \text{ Min} = 13 \text{ Min } 20 \text{ sec}$$

54. Ans. (3)

1st Order $(t_2\text{-}t_1) = 20$min,

$(A)_{t_1} = 1M$, $(A)_{t_2} = 0.6M$

$(t_2-t_1)' = ?$ $(A)'_{t_1} = 0.6M$, $(A)'_{t_2} = 0.36M$

$$K(t_2-t_1) = 2.303 \log \frac{[A]_{t_1}}{[A]_{t_2}}$$

$$K \times 20 = 2.303\log\frac{1}{0.6}$$

$$K(t_2-t_1)' = 2.303\log\frac{0.6}{0.36} = 2.303\log\frac{1}{0.6}$$

$$\frac{(2)}{(1)} \quad \frac{(t_2-t_1)'}{20} = 1$$

$(t_2-t_1)^1 = 20$ Min

55. Ans. (2)

In first order reaction in same time interval equal percentage of reactant convert into product and it is independent of the initial concentration of reactant.

P = 80

Alternate method

$$Kt = 2.303 \log \frac{100}{100-P}$$

P = % of reactant converted into product

Case II P=80

56. Ans. (3)

Given $t = 0$ $a = 10g/L$

$t_1 = 30min$ $a_{t_1} = 5g/L$

$t_2 = 90min$ $a_{t_2} = 1.25\ g/L$

$$10 \xrightarrow[t_{1/2}=30min]{} 5g/L \xrightarrow[t_{1/2}=30min]{} 2.5g/L \xrightarrow[t_{1/2}=30min]{} 1.25g/L$$

90 min

1st order

57. Ans. (4)

$t_{1/2} \propto (\text{Initial concentration})^{1-n}$

$t_{1/2} \propto (\text{Initial concentration})^{1-n}$

$t_{\frac{1}{2}} \propto a^{1-n}$ ...(1)

$2t_{1/2} \propto (2a)^{1-n}$ ...(2)

$\frac{(2)}{(1)}$ $2^1 = 2 = 2^{1-n}$

$1-n = 1$

(order) $n = 0$

58. Ans. (3)

$t_{\frac{1}{2}} \propto (\text{Initial Pressure})^{1-n}$

$4 \propto (50)^{1-n}$ ...(1)

$2 \propto (100)^{1-n}$ ...(2)

$$\frac{(2)}{(1)} \quad \frac{2}{4} = \left(\frac{100}{50}\right)^{1-n}$$

$2^{-1} = 2^{1-n}$

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

59. Ans. (2)

Given: $K = 10.8\times10^{-5}$ mol $L^{-1}S^{-1}$, order (n) = ?

General unit of K = $mol^{1-n}\ L^{n-1}\ time^{-1}$

On comparing power of mole

$1-n = 1$

(order) $n = 0$

60. Ans. (3)

Given : A decompose by 1st order

Flask I (1L)	Flask II(100 ml)
$[A]_0 = 1M$	$[A]_0 = 0.6M$
$T = 8hr$, $[A]_t = 0.25M$	t ? $[A]_t = 0.3M$

$$1M \xrightarrow[t_{1/2}]{} 0.5M \xrightarrow[t_{1/2}]{} 0.25M \quad 0.6M \xrightarrow[t_{1/2}]{} 0.3M$$

8 hr

$2t_{1/2} = 8hr$ $t = t_{1/2} = 4hr$

$T_{1/2} = 4hr$

61. Ans. (1)

$2A + B \longrightarrow$ product

t	k
15 sec	2.57×10^{-5} L $mol^{-1}s^{-1}$
30 sec	2.60×10^{-5} L $mol^{-1}s^{-1}$
50 sec	2.55×10^{-5} L $mol^{-1}s^{-1}$

General unit of $K = L^{n-1} mol^{1-n} time^{-1}$

On comparing power of mol : $1-n = -1$

$n = 2$

62. Ans. (3)

Given, 2^{nd} order, $K = 8 \times 10^{-5}\ M^{-1}min^{-1}$

$[A]_0 = 1M$, $[A]_t = 0.5M$, t ?

$$Kt = \frac{1}{[A]_t} - \frac{1}{[A]_0}$$

$$8\times10^{-5} \times t = \frac{1}{[A]_t} - \frac{1}{[A]_0} = 1$$

$$t = \frac{1}{8\times10^{-5}} = 1.25 \times 10^4 \text{ min}$$

63. Ans. (2)

Given $t_{50\%} = t_{1/2} = 10$ min, $[A]_0 = 2$ mol L^{-1}

$t'_{50\%} = t'_{1/2} = t$ min, $[A]_0 = 2$ mol L^{-1}

From the graph it is clear that half life is independent of concentration, So it is 1^{st} order and half-life also remains same, it doesn't depend on initial concentration.

$t'_{1/2} = t_{1/2} = 10\,\text{min}$

n = 1, $t'_{1/2} = 10\,\text{min}$

64. Ans. (3)

Given 1^{st} order, $\frac{t_{99.9\%}}{t_{50\%}} = ?$

$$Kt = 2.303 \log\frac{100}{100-P}$$

P = % of reactant reacted

$$Kt_{99.9\%} = 2.303 \times \log\frac{100}{100-99.9}$$

$= 2.303 \log 1000 = 2.303 \times 3$ ...(1)

$$Kt_{50\%} = 2.303 \times \log\frac{100}{100-50} = 2.303 \log 2$$

...(2)

$$\frac{(2)}{(1)} \quad \frac{t_{99.9\%}}{t_{50\%}} = \frac{3}{\log 2} = \frac{3}{0.3} = 10$$

65. Ans. (3)

Given $t_{1/2} \times a$ = constant

$t_{1/2} \propto a^{-1}$ ...(1), n ?

In General $t_{1/2} \propto a^{1-n}$ ...(2)

Compare power of 'a'

$1-n = -1$

$n = 2$

66. Ans. (2)

Given $r = K$

$r = K[A]^0$

It is zero order reaction

* It is independent of concentration of reactant.

* $t_{1/2} = \frac{[A]_0}{2K}$, $t_{1/2}$ depends on initial concentration of reactant.

67. Ans. (4)

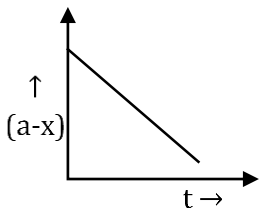
Given : 1^{st} order

$$\log(a-x) = \frac{-K}{2.303}t + \log a$$

$y = mx + C$

$$m(\text{slope}) = \frac{-K}{2.303}$$

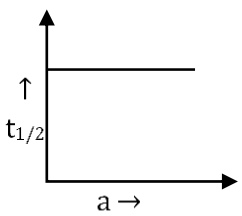
C (Intercept) = log a



$$t_{1/2} = \frac{0.693}{K}$$

$y = C$

$$\text{constant (C)} = \frac{0.693}{K}$$



68. Ans. (3)

$t_{1/2} \propto (\text{Initial pressure})^{1-n}$

$3.64 \propto (50)^{1-n}$ ...(1)

$1.82 \propto (100)^{1-n}$ ...(2)

$\frac{(2)}{(1)} \quad \frac{1.82}{3.64} = \left(\frac{100}{50}\right)^{1-n}$

$\frac{1}{2} = 2^{-1} = 2^{1-n}$

$1-n = -1$

$n = 2$

69. Ans. (1)

Given $K = xs^{-1}$

Rate constant, s^{-1} unit is the unit of 1st order reaction

(Old rate) $r = K[A]^1$ ...(1)

(New rate) $r' = K\{3[A]\}^1$ ...(2)

$\frac{(2)}{(1)} \quad \frac{\text{New rate}}{\text{Old rate}} = \frac{3}{1}$

New rate = 3×old rate

70. Ans. (2)

Zero order : $t_{1/2} = \frac{[A]_0}{2K}$

1st order $t_{1/2} = \frac{0.693}{K}$, $r = K[A]$

General unit of K = $mol^{1-n}\ L^{n-1}\ s^{-1}$

For 2nd order, unit of K = $mol^{-1}\ L^1 s^{-1}$

71. Ans. (2)

Hydrolysis of ester in alkaline medium

$RCOOR' + NaOH \longrightarrow RCOONa + R'OH$

Rate = K[RCOOR'] [NaOH]

Order = 2, Molecularity = 2

72. Ans. (4)

Given : 1st order, $t_{1/4} = t_{25\%}$?

$Kt = 2.303 \log \frac{100}{100-P}$

P = % of reactant reacted

$Kt_{1/4} = 2.303 \log \frac{100}{100-25}$

$t_{1/4} = \frac{2.303}{K} \log \frac{4}{3}$

73. Ans. (2)

Given : 0 order, K = 0.2 mol $dm^{-3}hr^{-1}$

t = 30 min = 0.5 hr, $[A]_t$ = 0.05 mol dm^{-3}, $[A]_0$?

$[A]_t = [A]_0 - Kt$

$0.05 = [A]_0 - 0.2 \times 0.5$

$[A]_0 = 0.05 + 0.1 = 0.15$ mol dm^{-3}

74. Ans. (1)

Given : 1st order,

Case-I $[A]_0$ = 100g,

x = 75g

t = 100 min

% of reactant decompose = $\frac{75}{100} \times 100 = 75\%$

Case II $[A]_0$ = 200g, x = 150g, t' ?

% of reactant decompose in case II

$= \frac{150}{200} \times 100 = 75\%$

In first order equal % of reactant decompose in same time period and it is independent of initial amount.

So in above both cases as 75% reactant is decomposing so time taken will be same, t' = 100min

75. Ans. (2)

For zero order r = K

Unit of rate = unit of rate constant

76. Ans. (4)

Given : 1st order, $t_{1/2}$ = 20 min,

$[A]_0$ = 0.2 mol^{-1}, K ?

$K = \frac{0.693}{t_{1/2}} = \frac{0.693}{20} = 0.034\ min^{-1}$

77. Ans. (4)

Given : 1st order

$t_{100\%} = t_{completion}$ = infinite

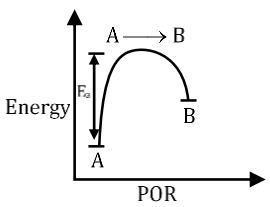
$t_{1/2} = \frac{0.693}{K}$

Unit of K = $time^{-1}$

$t_{1/2} \times K = 0.693$ (constant)

78. Ans. (3)

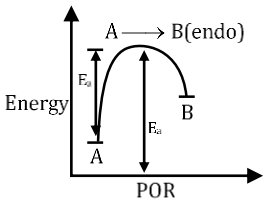
Activation energy is minimum extra energy required to overcome the potential barrier of reaction.



79. Ans. (3)

Activation energy is extra energy required by reactant molecules to enter into chemical reaction.

Threshold energy is minimum total energy required by reactant molecule to enter into chemical reaction.



80. Ans. (2)

$K_1 = 2K_2$ $\quad\downarrow K = Ae^{-\frac{E}{RT}}$

$K_1 > K_2$ $\quad$ if E↑ K↓

$E_1 < E_2$

81. Ans. (3)

$2NO + O_2 \xrightarrow{K_1, E_1} 2NO_2$ (Fast) ...(1)

$2CO + O_2 \xrightarrow{K_2, E_2} 2CO_2$ (Slow) ...(2)

$\downarrow K = Ae^{-\frac{E}{RT}}$

As E↑ K↓ reaction become slow.

Reaction (1)	Fast	$K_1\uparrow$ $E_1\downarrow$
Reaction (2)	Slow	$K_2\downarrow$ $E_2\uparrow$
	$K_1 > K_2$,	$E_1 < E_2$

82. Ans. (3)

Effective collisions are those collision which have energy enough to overcome energy barrier and have proper collision orientation. As Effective collisions increases, rate of reaction increases.

83. Ans. (3)

Given $A \longrightarrow B$, Endothermic,

$\Delta H = +5$ Kcal/ mol

$E_{af} = 15$ Kcal/mol

$B \longrightarrow A$, E_{af} ?

$E_{af}(B \longrightarrow A) = E_{ab}(A \longrightarrow B)$

For the reaction $A \longrightarrow B$

$\Delta H = E_{af} - E_{ab}$

$5 = 15 - E_{ab}$

$E_{ab} = 10$ Kcal/mol

84. Ans. (2)

As temperature increases, number of collisions increases, number of activated molecular doing effective collisions increases and rate of reaction increases.

85. Ans. (1)

As temperature increases, number of collisions increases for all reaction whether it is endothermic or exothermic, number of activated molecules doing effective collisions increases and rate of reaction increases.

86. Ans. (3)

Given : $\mu = 2$, $\Delta T = 60°C$

$r_{T_2} = r_{T_1} M^n$, $n = \frac{\Delta T}{10} = \frac{60}{10} = 6$

$r_{T_2} = r_{T_1} \times 2^6$

$r_{T_2} = 64 r_{T_1}$

So if temperature is increased by 60°C then rate of reaction increases by 64 times.

87. Ans. (3)

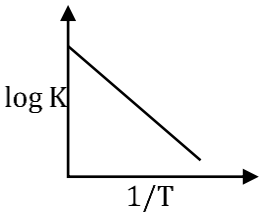
Arrhenius equation logarithm form is

$$\log K = \frac{-Ea}{2.303R}\left(\frac{1}{T}\right) + \log A$$

Y = mx + c

Slope (m) = $\frac{-E_a}{2.303R}$

Intercept (c) = log A



log K vs $\frac{1}{T}$ graph is straight line

88. Ans. (4)

When lnK vs $\frac{1}{T}$ = graph is plotted, it is straight line with slope $\frac{-E_a}{R}$. By measuring this slope we can get value of activation energy.

89. Ans. (4)

$$\log K = \log A - \frac{E_a}{2.303RT}$$

When $T \to \infty$, $\frac{1}{T} \to 0$, $\log K \to \log A$

90. Ans. (2)

Given T = 25°C, K = $3\times10^{-4}s^{-1}$, E_a=104.4Kj, A=$6\times10^{14}s^{-1}$, $T\to\infty$, K ?

Arrhenius $K = K = Ae^{-E_a/RT}$

as $T\to\infty$, $\frac{E_a}{RT} \to 0$, $e^0 \to 1$

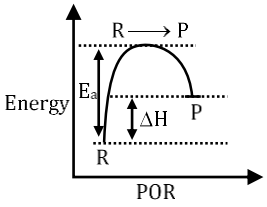
$K \to A$

When $T \to \infty$, $K \to A$

$K = 6\times10^{14}s^{-1}$

91. Ans. (3)

Given : Endothermic reaction



In endothermic reaction activation energy (E_a) is always greater than ΔH

92. Ans. (3)

Given : μ = 2.3, T_1 = 300K, T_2 = 310K

$K_1 = K$, $K_2 = ?$

$K_2 = K_1\mu^n$, $n = \frac{\Delta T}{10} = \frac{310-300}{10} = 1$

$K_2 = K(2.3)^1 = 2.3K$

93. Ans. (3)

Given : 1st order

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

Rate constant depends on activation energy and temperature. It don't depend on concentration. Hence if concentration is reduced by 'n' times then value of rate constant of 1st order or any order remains same of constant.

94. Ans. (4)

In general $R \longrightarrow P$

$Rate(r) = K(R)^n$

(R) is the concentration of reactant

n = order of reaction

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

K = specific rate constant

A → Arrhenius constant

E_a → activation energy

T = Temperature

Reaction rate depends upon reaction temperature, reaction concentration, specific rate constant, activation energy, catalyst.

95. Ans. (4)

Given : 1st order

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

rate constant depends upon activation energy and temperature. It don't depends on concentration of any reactant or product and volume of container.

96. Ans. (4)

Given : $2N_2O_5(g) \to 4NO_2(g) + O_2(g)$, E_a

$N_2O_5(g) \to 2NO_2(g) + \frac{1}{2}O_2(g)$, E_a^1

Activation energy depends on catalyst. It don't depends on stoichiometry coefficient of reaction. So $E_a = E_a^1$

97. Ans. (1)

$\Delta H = E_{af} - E_{ab}$

Of ΔH = 0

$E_{af} - E_{ab} = 0$

$E_{af} = E_{ab}$

98. Ans. (4)

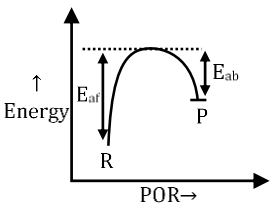
Given : E_{af} = 50 Kcal

There are two types of reaction

(1) Endothermic

(2) Exothermic

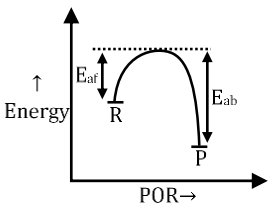
Endothermic



$E_{ab} < E_{af}$

$E_{ab} < 50$kcal

Exothermic



$E_{ab} > E_{af}$

$E_{ab} > 50$ kcal

Hence energy of activation of its backward reaction may be greater than or less than 50 kcal.

99. Ans. (3)

$x \longrightarrow y$, Exothermic, $E_{af} = 30Kj/mol$, $\Delta H = -20KJ$ E_{ab} ?

$\Delta H = E_{af} - E_{ab}$

$-20 = 30 - E_{ab}$

$E_{ab} = 50KJ$

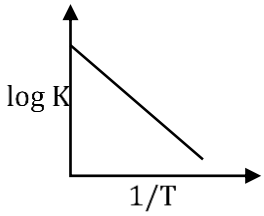
100. Ans. (3)

Arrhenius equation

$$\log K = \log A - \frac{E_a}{2.303R} \times \frac{1}{T}$$

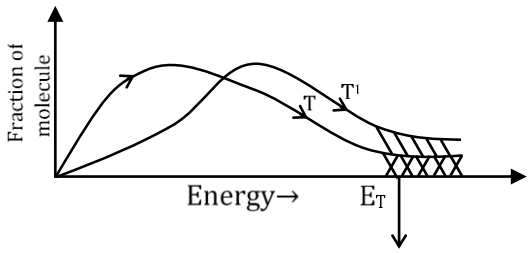
$y = C + mx$

slope (m) $= -\frac{E_a}{2.303R}$, Intercept(C) = logA



101. Ans. (3)

In Maxwell distribution carve



This area represent fraction of molecules possessing energy $\geq E_T$

As T↑, fraction of molecules' possessing energy $\geq E_T$ increases

102. Ans. (4)

Given : $T_1 = 25°C = 298K$, $r_{T_1} = r$

$T_2 = 35°C = 308K$, $r_{T_2} = 2r$

According to Arrhenius equation

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

$$\log \frac{2r}{r} = \frac{E_a}{2.303R}\left(\frac{308 - 298}{298 \times 308}\right)$$

$$0.3010 = \frac{E_a}{2.303R}\left(\frac{10}{298 \times 308}\right)$$

$$E_a = \frac{0.3010 \times 2.303R(298 \times 308)}{10}$$

$$E_a = \frac{0.693R \times 298 \times 308}{10}$$

103. Ans. (4)

According to collision theory,

For effective collisions, the colliding molecules most possess energy equal to or greater than threshold energy as well as proper orientation of collision.

104. Ans. (3)

As temperature increases, No of effective collisions increases, rate of reaction increases, so in lesser time half of the reactant covered into product so half-life decreases.

105. Ans. (2)

Activation energy depends on nature of reacting species, if activation energy is low than rate of reaction is test.

106. Ans. (2)

Activated complex has highest energy in the mechanism, then activated complex decompose, some energy release and stability increases.

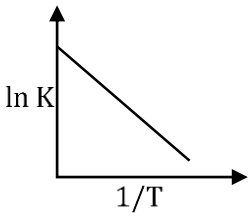
Exercise-II (Previous Year Questions)

1. Ans. (2)

Arrhenius equation :

$$\ln K = \ln A - \frac{E_a}{K}\left(\frac{1}{T}\right) \qquad \text{slope(m)} = \frac{-E_a}{K}$$

$y = C + mx$ Intercept (C) = ln A



ln K Vs $\frac{1}{T}$ graph is straight line by measuring the slope of line we can get the value of activation energy.

2. Ans. (1)

In General $t_{1/2} \propto (\text{Initial concentration})^{1-n}$

When n = 1

$T_{1/2}$ = constant

Hence for 1st order reaction half-life period is not affected by initial concentration.

3. Ans. (2)

Given : $A \longrightarrow B$

$K = 0.6\times10^{-3}$ M sec^{-1}, $[A]_0 = 5M$, $[B]_t = ?$, $t = 20min$

General unit of rate constant (K) = M^{1-n} sec^{-1}

$1-n = 1 \Rightarrow n = 0$

So the given reaction is zero order

$[B]_t = x = Kt$

$[B]_t = x = 0.6\times10^{-3}\times20\times60 = 0.72M$

4. Ans. (1)

Given : 1st order reaction

$t_1 = 10$ s, $r_{t_1} = 0.04\,mol\,L^{-1}s^{-1}$

$t_2 = 20$ s, $r_{t_2} = 0.03\ mol\,L^{-1}s^{-1}$, $t_{1/2} = ?$

$$\frac{r_{t_1}}{r_{t_2}} = \frac{K[A_{t_1}]}{K[A_{t_2}]} \Rightarrow \frac{r_{t_1}}{r_{t_2}} = \frac{[A_{t_1}]}{[A_{t_2}]}$$

Interval formula; $K(t_2 - t_1) = 2.303\log\frac{r_{t_1}}{r_{t_2}}$

$$K(20-10) = 2.303\log\frac{0.04}{0.03}$$

$$K = \frac{2.303}{10}[\log4 - \log3]$$

$$\frac{0.693}{t_{1/2}} = \frac{2.303}{10}[0.6020 - 0.4771]$$

$$t_{1/2} = \frac{0.693\times10}{2.303\times0.1249} \simeq 24.1\ s$$

5. Ans. (4)

When catalyst added to a chemical reaction, its activation energy decreases.

6. Ans. (3)

During decomposition phosphine (PH_3) on tangsten, first PH_3 adsorb on tangsten then it decompose.

Rate $\propto$ surface area of tangsten covered with PH_3 $\propto$ Partial pressure of $PH_3(g)$

at low pressure as $P_{PH_3(g)}$ $\uparrow$ surface area of tangsten $\uparrow$ rate $\uparrow$ covered with PH_3

at high pressure as $P_{PH_3(g)}$ $\uparrow$ surface area of rate is tangsten covered with constant PH_3 remains constant

rate $\propto$ (Pressure of PH_3)^0

7. Ans. (3)

Rate = K'(X) $[y_2]$ ...(1)

$\uparrow$

Intermediate

$$K_C = \frac{[x]^2}{[x_2]} \Rightarrow [x] = K_C^{1/2}[x_2]^{1/2}$$

Place [x] value in equation (1)

$$\text{Rate} = K^1K_C^{\frac{1}{2}}[x_2]^{\frac{1}{2}}[y_2] = K[x_2]^{0.5}[y_2]^1$$

Overall order = 0.5 + 1 = 1.5

8. Ans. (1)

Given : 1st order, $K = 10^{-2}s^{-1}$, $[A]_0 = 20g$, $[A]_t = 5g$, t ?

$$Kt = 2.303\log\frac{[A]_0}{[A]_t}$$

$$10^{-2}t = 2.303\log\frac{20}{5} = 2.303\log4$$

$$t = \frac{2.303\times0.6020}{10^{-2}} = 138.6\ s$$

9. Ans. (2)

First order reaction : $r = K(A)^1$, $t_{1/2} = \frac{0.693}{K}$

Second order reaction : $r = K(A)^2$, $t_{1/2} = \frac{1}{K(A)_0}$

10. Ans. (2)

Given : zero order

$$t_{1/2} = \frac{[A]_0}{2K}$$

$T_{1/2} \propto$ Initial concentration reactant.

As initial concentration of the reactant is doubled, half-life period of a zero order also doubled.

11. Ans. (3)

Given : first order, rate constant = K,

Time required for 99% completion of reaction ?

$$Kt = 2.303\log\frac{100}{100-P}$$ P = % of reactant converted into product

$$Kt' = 2.303\log\frac{100}{100-99}$$

$$t' = \frac{2.303\times2}{K} = \frac{4.606}{K}$$

12. Ans. (3)

Given : $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

$$\frac{\text{rod of } N_2}{1} = \frac{\text{rod of } H_2}{3} = \frac{\text{roa of } NH_3}{2}$$

$$-\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = +\frac{1}{2}\frac{d[NH_3]}{dt}$$

13. Ans. (4)

Given : 1st order, $K = 2.303\times10^{-3}s^{-1}$, $[A]_0=40g$, $[A]_t = 10\ g$, t ?

$$Kt = 2.303\log\frac{[A]_0}{[A]_t}$$

$$2.303\times10^{-3}t = 2.303\log\frac{40}{10}$$

$$t = \frac{2\log2}{10^{-3}} = \frac{2\times0.3010}{10^{-3}}$$

t = 602 sec.

14. Ans. (2)

$E_a = 0$,

T	K
200K	$1.6\times10^6s^{-1}$
400K	?

$$\log\frac{K_2}{K_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]$$

$$\log\frac{K_2}{K_1} = 0 \Rightarrow K_2 = K_1$$

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

If $E_a = 0$

$K = Ae^0$

$K = A$

When $E_{a.} = 0$ then rate constant don't depend on temperature. At all temperature, its value will be same. So at 200K of rate constant is $1.6\times10^6s^{-1}$ then at 400K also its value will be $1.6\times10^6s^{-1}$.

15. Ans. (4)

Given : 1st order, $K = 4.606\times10^{-3}s^{-1}$, $[A]_0=2g$, $[A]_t=0.2g$, t ?

$$Kt = 2.303\log\frac{[A]_0}{[A]_t}$$

$$4.606\times10^{-3}t = 2.303\log\frac{2}{0.2}$$

$$t = \frac{1}{2\times10^{-3}} = 500s$$

16. Ans. (1)

When Concentration of the reactant of a reaction increase then number of reactant molecule's per unit volume increases and collision frequency increases.

17. Ans. (1)

Given : zero order, $t_{1/2} = 100$ sec, $[A]_0 = 0.02M$, K ?

$$t_{1/2} = \frac{[A]_0}{2K}$$

$$K = \frac{[A]_0}{2t_{1/2}} = \frac{0.02}{2\times100} = 1\times10^{-4}.\text{mol}\,L^{-1}s^{-1}$$

18. Ans. (2)

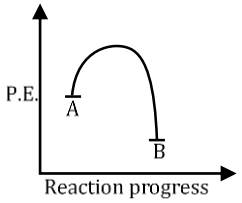
In collision theory Z_{AB} symbol means collision frequency of reactant A and B.

19. Ans. (2)

Given : $A \longrightarrow B$, $\Delta H = -4.2$ KJ/mol

$E_a = 9.6$ KJ/mol

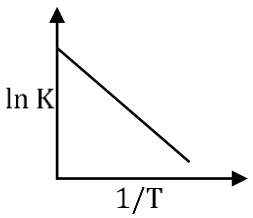
Given reaction is exothermic so potential energy of product will be less than potential energy of reactant.



20. Ans. (1)

$$\ln K = \ln A - \frac{E_a}{A}\times\frac{1}{T} \qquad \text{slope}(m) = \frac{-Ea}{R}$$

y = C + mx Intercept (C) = ln A



Given : $\text{slope} = \frac{-E_a}{R} = -5\times10^3$

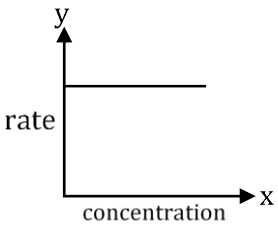
$Ea = 5\times10^3R = 5\times10^3\times8.314$

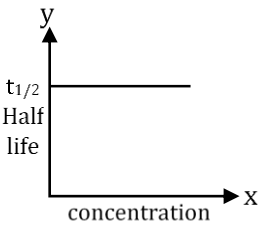
$Ea = 41.5\times10^3$ J ml^{-1}

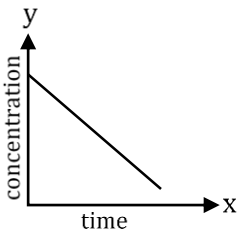
$Ea = 41.5$ KJ mol^{-1}

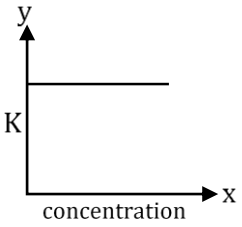
21. Ans. (2)

Zero order	First order
r = K	$t_{1/2} = \frac{0.693}{K}$
T = constant	$t_{1/2}$ = constant, T = constant
$[A]_t = [A]_0 - Kt$	$K = \frac{0.693}{t_{1/2}}$, K = constant







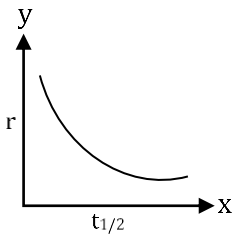


First order

$r = K(A) = \frac{0.693}{t_{1/2}}(A)$

T = constant

(A) = constant



22. Ans. (1)

Given : 1st order

$[A]_0$ = 0.1 M, $[A]_t$ = 0.001 M, t = 5min, K ?

$$Kt = 2.303 \log \frac{[A]_0}{[A]_t}$$

$$K \times 5 = 2.303 \log \frac{0.1}{0.001} = 2.303 \times \log 100$$

$= 2.303 \times 2 \log 10 \Rightarrow K = 0.9212 \text{ min}^{-1}$

23. Ans. (2)

Given : 1st order,

$t_{1/2}$ = 2000 year, t = 8000 years,

$[A]_0$? $[A]_t$ = 0.02 M

$[A_t] = \frac{[A]_0}{2^n}$ n = No. of half life = $\frac{\text{total time}}{t_{1/2}}$

$0.02 = \frac{[A]_0}{2^4}$ $n = \frac{8000}{2000} = 4$

$[A]_0 = 0.02 \times 16 = 0.32$ M

24. Ans. (1)

Given : rof of C = $6\times10^{-2} \frac{\text{mol}}{\text{Ls}}$,

rod of A = $4 \times 10^{-2} \frac{\text{mol}}{\text{Ls}}$

ror ?, $\Delta[B]$ = ?, ΔT = 10sec

$$\text{ror} = \frac{\text{rod of A}}{4} = \frac{\text{rod of B}}{3} = \frac{\text{rof of C}}{6} = \frac{\text{rof of D}}{9}$$

$$\text{ror} = \frac{\text{rod of A}}{4} = \frac{4\times10^{-2}}{4} = 1\times10^{-2} \text{ml L}^{-1}\text{s}^{-1}$$

$$\text{ror} = \frac{\text{rod of B}}{3}$$

$$\text{rod of B} = -\frac{\Delta[B]}{\Delta t} = 3 \times \text{ror}$$

$$-\frac{\Delta[B]}{10} = 3\times10^{-2}$$

$\Delta(B) = -30\times10^{-2}$ mol L^{-1}

Amount of B consumed = 30×10^{-2} mol L^{-1}

25. Ans. (3)

A reaction cannot have zero activation energy.

E_a is minimum extra amount of energy absorbed by reactant molecules so that their energy becomes equal to threshold value.

26. Ans. (4)

$$\log_{10}\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Here k_1 is rate constant at T_1.

k_2 is rate constant at T_2.

27. Ans. (4)

$k = A \cdot e^{-E_a/RT}$

$\ell n\, k = \ell n\, A - \frac{E_a}{RT}$

$\ell nk = \frac{-E_a}{R}\left(\frac{1}{T}\right) + \ell nA$

$y = mx + c$

On comparing $\Rightarrow \ell n\, k \to y\,;\ \frac{1}{T} \to x$

This is a equation of straight line with negative slope.

28. Ans. (1)

$\frac{r_2}{r_1} = 4 = \frac{k_2}{k_1}$

$\log_{10}\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

$\log_{10}(4) = \frac{E_a \times 1000}{2.303 \times 8.314}\left(\frac{1}{300} - \frac{1}{330}\right)$

$E_a = 38.04\ kJ/mol$

29. Ans. (3)

$r = k[A]^x[B]^y$ ...(1)

from experimental data of I & II; order with respect to A is 1

from experimental data of II & III; order with respect to B is 2

30. Ans. (3)

$\ell nk = \ell nA - \frac{E_a}{R} \times \frac{1}{T}$ ....(1)

$y = c + mx$

slope = $-E_a/R$ = (–) Ve

intercept = ℓnA = (+)Ve

So ans is (3)

31. Ans. (3)

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

$\log\left(\frac{0.14}{0.04}\right) = \frac{E_a}{2.303 \times 8.31} \times \left(\frac{200}{500 \times 700}\right)$

E_a = 18219 J

Exercise-III (Analytical Questions)

1. Ans. (4)

For zero order ; r = K

K depends on temperature, so rate (r) also depends on temperature. So statement I is false.

For zero order $t_{1/2} = \frac{[A]_0}{2K}$

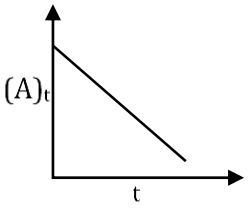
Half-life depends on initial concentration so statement II is also false.

2. Ans. (1)

(a) 'o' order

$[A]t = [A]_0 - kt$

$y = C + mx$

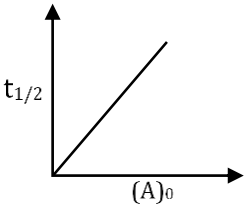


a ⟶ r

(b) 0 order

$t_{1/2} = \frac{1}{2K}(A)_0$

$y = mx$

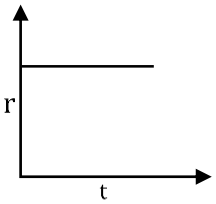


b ⟶ s

(c) '0' order

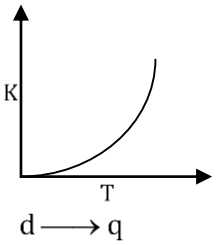
r = K

y = constant



c ⟶ p

(d) $K = A e^{-\frac{E_a}{RT}}$



3. Ans. (2)

$A \longrightarrow P$

rate = $K(A)^n$

when (A) = 1 M

rate (r) = K (rate constant)

Assertion is correct.

$A \longrightarrow P$

For zero order r = K

Reason as a independent statement is correct but it is not a correct explanation of assertion.

4. Ans. (2)

$$K_{eq} = \frac{K_f}{K_b}$$

Catalyst increases K_f and K_b equally and there is no effect on the value of K_{eq} statement I is correct.

Catalyst increases rate of reaction in forward as well as backward direction equally and equilibrium establish rapidly. Statement II is correct but it is not the proper explanation of statement I.

5. Ans. (3)

Order of a reaction is experimental quantity. Order is applicable for elementary as well as complex reaction unit of rate constant for 1st order is s^{-1}.

As temperature increases, rate of reaction increases, half-life period decrease.

Statement (a) and (d) are correct.

6. Ans. (1)

(a) When temperature increase, effective collision increases, rate of reaction increase.

(b) When activation energy decreases, rate constant value increases, more reactant molecule convert into product, rate of reaction increases.

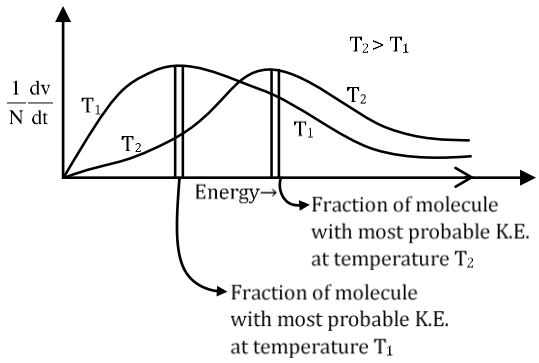
(c) $K = \frac{A}{e^{\frac{E_a}{RT}}}$ as $T \uparrow \frac{E_a}{RT} \downarrow e^{\frac{E_a}{RT}} \downarrow e^{\frac{A}{\frac{E_a}{RT}}} \uparrow K \uparrow$

Rate constant increases exponentially with increase in temperature.

(d) Statement (d) is wrong

Only statement (a) and (b) are correct

7. Ans. (2)



Fraction of molecule with most probable K.E. decreases at higher temperature.

$$V_{mp} = \sqrt{\frac{2RT}{M}}, \qquad (K.E.)_{m.p.} = \frac{1}{2}mv^2$$

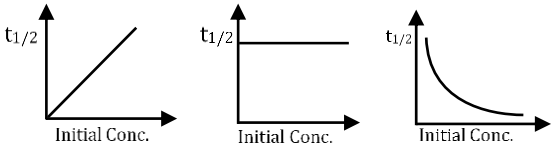
As $T \uparrow$ $V_{mp} \uparrow$ $(K.E.)_{mp} \uparrow$

Statement a and c are correct

8. Ans. (1)

0 order	1st order	2nd order
$t_{1/2} = \frac{[A]_0}{2K}$	$t_{1/2} = \frac{0.693}{K}$	$t_{1/2} = \frac{1}{K[A]_0}$

$$y = \frac{1}{2K}x$$



(ii) → (b) (i) → (a) (iii) → (c)