

MAINS+ADVANCED

TOPIC

CHEMICAL
KINETICS

SOLUTIONS

CHEMICAL KINETICS

Exercise-I

1. (B)
 $B + 3D = 2C + 4A$
2. (D)
 $A(g) \rightleftharpoons 2B(g)$
 $K_f = 1.5 \times 10^{-3} \text{ s}^{-1}$
At eq.^m, $R_f = R_b$
 $K_f [A] = K_b [B]^2$
On solving : $K_b = 1.5 \times 10^{-11}$
3. (B)
 $A + B \rightarrow C + D$
 $k = 2.303 \times 10^{-3} \text{ sec}^{-1}$
 $t = \frac{2.303}{k} \log \frac{1}{0.25}$
 $= \frac{2.303}{2.303 \times 10^{-3}} \log \frac{100}{25}$
 $= 10^3 \times (0.605)$
 $= 600 \text{ sec}$
4. (D)
 $k_1 = \frac{2.303}{t} \log \frac{100}{50} = \frac{2.303}{t} \log 2 = \frac{0.6955}{t}$
 $k_2 = \frac{2.303}{t} 2 \log 5 = \frac{2.303}{t} \times 2 \times 0.69 = \frac{3.22}{t}$
 $\frac{k_2}{k_1} = 4.65$
5. (A)
 $\text{sec}^{-1}, \text{Msec}^{-1}$
6. (B)
From the above data, it is clear that on doubling the concentration of B, the rate is doubled hence order w.r.t. B is 1
Similarly, Order w.r.t. A = 2
 $\Rightarrow \text{rate} = K[A]^2[B]$
7. (C)
 $pA + qB \rightarrow \text{Products}$
 $r = k[A]^l[B]^m$
(p + q) may or may not be equal to (l + m)
(order may or may not be equal to stoichiometric coefficient for a complex reaction.)
8. (D)
 $A + 2B \rightarrow 3C + D$
 $-\frac{d[A]}{dt} = -\frac{1}{2} \frac{d[B]}{dt} = \frac{1}{3} \frac{d[C]}{dt} = \frac{d[D]}{dt}$
9. (B)
 $2NO + 2H_2 \rightarrow N_2 + 2H_2O$
 $-\frac{1}{2} \frac{d[NO]}{dt} = -\frac{1}{2} \frac{d[H_2]}{dt} = \frac{d[N_2]}{dt} = \frac{1}{2} \frac{d[H_2O]}{dt}$
.....(1)
Multiplying eqⁿ (1) by 2 gives
 $-\frac{d[NO]}{dt} = -\frac{d[H_2]}{dt} = \frac{2d[N_2]}{dt} = \frac{d[H_2O]}{dt}$
Putting the value of in the given questions
 $K_1' [NO][H_2] = K_1'' [NO][H_2] = 2K_1 [NO][H_2]$
 $= K [NO][H_2]$
 $\Rightarrow K_1' = K_1'' = 2K_1 = K$
10. (D)
 $t_{1/2} \propto \left(\frac{1}{a}\right)^{n-1}$
 $\Rightarrow t_{1/2} \propto (a)^{1-n}$
 $\Rightarrow \frac{(t_{1/2})_1}{(t_{1/2})_2} = \frac{a_1}{a_2}$
 $\Rightarrow \frac{235}{950} = \left(\frac{500}{250}\right)^{1-n}$
 $\Rightarrow \log 23.5 - \log 95 = (1-n) \log 2$
 $\Rightarrow n = 3$

11. (B)

$$t_{1/2} = 20 \text{ min at } 300 \text{ K}$$

$$t'_{1/2} = 5 \text{ min at } 320 \text{ K}$$

$$t_{1/2} = \frac{0.693}{\frac{-E_a}{A \cdot e^{300R}}} = 20$$

$$t'_{1/2} = \frac{0.693}{\frac{-E_a}{A \cdot e^{320R}}} = 5$$

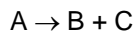
$$\frac{t_{1/2}}{t'_{1/2}} = 4 = \frac{e^{320R}}{e^{300R}}$$

$$4 = e^{\frac{E_a}{R} \left(\frac{1}{300} - \frac{1}{320} \right)}$$

$$\ln 4 = \frac{E_a}{R} \left(\frac{20}{300 \times 320} \right)$$

On solving, $E_a = 55303.12 \text{ J}$
 $= 55.3 \text{ KJ}$

12. (C)



$$\frac{-E_a}{RT} = \frac{3.8 \times 10^{-16}}{100}$$

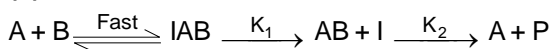
$$\frac{-E_a}{RT} = 2.303 \log(3.8 \times 10^{-18})$$

$$E_a = 100 \text{ KJ/mol}$$

13. (D)

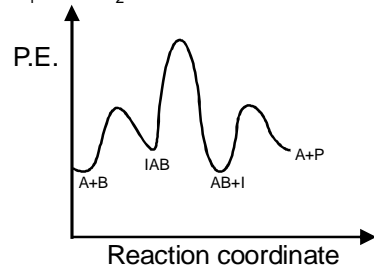
At temperature = ∞
 Rate constant = Arrhenius constant.

14. (A)

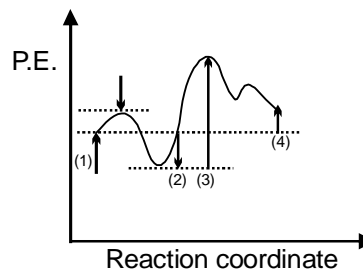


Since

$K_1 \lll K_2$ = most Imp. peak will be higher

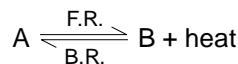


15. (B)



As ΔE overall = 4
 So, first option is correct.

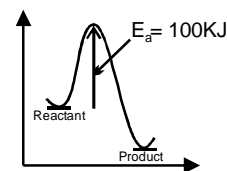
16. (D)



$$E_{af} = 100 \text{ KJ/mol}$$

$$E_{ab} = ?$$

heat of reaction = ?



Only one option because
 $E_b = E_a + \Delta H.O.$ reaction

17. (A)

In a reaction, the threshold energy is equal to :
 Activation energy + Normal energy of reactants.

18. (A)

$$\log K = 15 - \frac{10^6}{T}$$

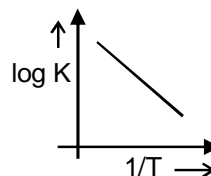
$$\log A = 15$$

$$\Rightarrow A = 10^{15}$$

$$\text{Also, } \frac{E_a}{2.303R} = 10^6$$

$$E_a = 1.9 \times 10^4 \text{ KJ}$$

19. (B)



When line cuts y axis

$$\frac{1}{T} = 0 \Rightarrow T = \infty$$

When it cut X-axis
 $\log K = 0$

$$\Rightarrow \log A = \frac{E_a}{2.303RT}$$

$$\Rightarrow \boxed{T = \frac{E_a}{R \ln A}}$$

20. (B)

$$K = 3 \times 10^{-2} \text{ s}^{-1}$$

$$E_a = 104.4 \text{ KJ/mol}$$

$$A = 6 \times 10^{14}$$

Value of rate constant at $T = \infty$ will be equal to frequency factor i.e. $A = 6 \times 10^{14} \text{ s}^{-1}$

21. (B)

$$\text{Rate} \propto \frac{1}{\text{time}}$$

Since,

Rate becomes four times by doubling the concentration of A

\Rightarrow Order w.r.t A is 2

Also,

by doubling the concentration of B, the rate becomes double

\Rightarrow Order w.r.t B is 1.

22. (B)

$$-\frac{1}{3} \frac{d[\text{H}_2]}{dt} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt}$$

$$\Rightarrow -\frac{d[\text{H}_2]}{dt} = \frac{3}{2} \frac{d[\text{NH}_3]}{dt}$$

$$= \frac{3}{2} \times 3.4$$

$$= 5.1 \text{ Kgmin}^{-1}$$

23. (B)

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

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

Also,

$$K = \frac{2.303}{t} \log \frac{0.60}{0.36}$$

Since, Rate constant will be equal

$$\frac{2.303}{20} \log \frac{1}{0.6} = \frac{2.303}{t} \log \frac{0.60}{0.36}$$

On solving, $t = 20 \text{ min}$

24. (C)

For a first order reaction, the concentration of the reactant varies exponentially with time

$$(A = A_0 e^{-kt})$$

25. (C)

Reaction is or zero order hence, Option C will be correct.

26. (C)

$t_{1/4}$ = time taken for $\frac{1}{4}$ decomposition.

$\Rightarrow \frac{3}{4}$ will be left

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

$$= \frac{2.303}{K} \log \frac{4}{3}$$

27. (C)

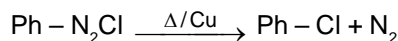
If we calculate K, it comes constant every time

i.e. reaction is of first order.

$$\text{Also, } K = \frac{2.303}{t} \log \frac{C_0}{aC_0}$$

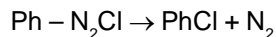
$$= \frac{1}{t} \ln \left(\frac{1}{a} \right)$$

28. (B)



Half life is independent of concentration

\Rightarrow reaction is of first order



$t = 0$

$$A_0 \quad 0 \quad 0$$

$t = 30$

$$A_0 - x \quad x \quad x$$

$t = \infty$

$$0 \quad A_0 \quad A_0$$

$$x \propto 10$$

$$A_0 \propto 50$$

$$\Rightarrow A_0 - x \propto 40$$

$$K = \frac{2.303}{t} \log \frac{A_0}{A_0 - x}$$

$$= \frac{2.303}{10} \log \frac{50}{40}$$

$$= \frac{2.303}{10} \log (1.25) \text{ min}^{-1}$$

29. (D)



$t = 0$

$$C_0 \quad 2C_0 \quad 0 \quad 0$$

$t = 30$

$$C_0 - 2x \quad 2C_0 - x \quad x \quad x$$

$$\text{given, } x = \frac{C_0}{4}$$

$$\text{After 30 min, } [A] = C_0 - 2 \times \frac{C_0}{4} = \frac{C_0}{2}$$

$$[B] = 2C_0 - \frac{C_0}{4} = \frac{7C_0}{4}$$

$$r = K \left[\frac{C_0}{2} \right] \left[\frac{7C_0}{4} \right]$$

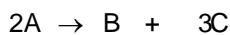
$$\Rightarrow R = \frac{49k C_0^3}{32}$$

30. (D)

$$-\frac{d[\text{BrO}_3]}{dt} = k[\text{BrO}_3][\text{Br}^-][\text{H}^+]^2$$

D option is correct.

31. (D)



$$t = 0 \quad P_0 \quad 0 \quad 0$$

$$t = 10 \quad P_0 - 2p^1 \quad p^1 \quad 3p^1$$

$$p_0 - 2p^1 = 200 \quad \dots\dots(1)$$

$$p_0 - 2p^1 + p^1 + 3p^1 = 300$$

$$p_0 + 2p^1 = 300 \quad \dots\dots(2)$$

$$(I) + (II) \quad 2p_0 = 500 \Rightarrow p_0 = 250$$

Pressure of A After 10 min

$$= p_0 - p^1 = 200$$

$$K = \frac{1}{2 \times 10} \ln \frac{250}{200}$$

$$K = \frac{1}{2 \times 10} \ln 1.25$$

\(\Rightarrow\) None is correct

32. (D)

$$t_{1/2} = \left(\frac{2 - \sqrt{2}}{K} \right) \times C_0^{1/2}$$

$$\Rightarrow t_{1/2} \propto C_0^{1/2}$$

Also, $t_{1/2} \propto C_0^{1-n}$ (where n is the order of reaction)

$$\Rightarrow 1 - n = 1/2 \Rightarrow n = 0.5$$

33. (A)

$$t_1 = \frac{2.303}{3K} \log \frac{100}{75}$$

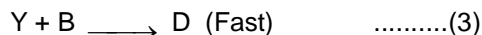
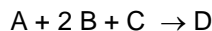
$$t_2 = \frac{2.303}{2K} \log \frac{100}{25}$$

$$\Rightarrow \frac{t_1}{t_2} = \frac{0.311}{1} = 0.311 : 1$$

34. (B)

Slowest step is rate determining step.

35. (C)



$$\text{Rate} = K[X][C] \quad \dots\dots\dots(4)$$

Since X is not in the original reaction, hence it has to be eliminated.

$$\text{from eq}^n (1), K_1 = \frac{[X]}{[A][B]} \Rightarrow [X] = K_1[A][B]$$

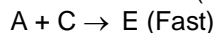
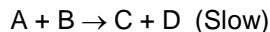
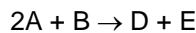
Putting this value in eqⁿ (4)

$$\text{Rate} = KK_1[A][B][C]$$

$$\text{Rate} = K' [A][B][C]$$

$$\Rightarrow \text{Order} = 3$$

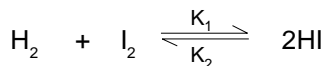
36. (D)



$$\Rightarrow \text{Rate} = K[A][B]$$

[As slowest step is rate determining step].

37. (C)



$$\frac{1}{2} \frac{d[HI]}{dt} = k_1[H_2][I_2] - k_2[HI]^2$$

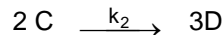
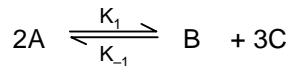
38. (B)

$$k_1 = 1.26 \times 10^{-4} \quad k_2 = 3.8 \times 10^{-5}$$

$$B = \frac{k_1}{k_1 + k_2} \times 100$$

$$C = \frac{k_1}{k_1 + k_2} \times 100$$

39. (A)



$$\frac{1}{3} \frac{d[C]}{dt} = k_1[A]^2 - k_{-1}[B][C]^3$$

$$\Rightarrow \frac{d[C]}{dt} = 3K_1[A]^2 - 3K_{-1}[B][C]^3 \quad \dots\dots\dots(I)$$

from 2nd reaction

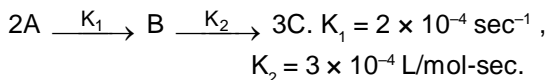
$$-\frac{1}{2} \frac{dC}{dt} = K_2[C]^2$$

$$\Rightarrow \frac{dC}{dt} = -2K_2[C]^2 \quad \dots\dots\dots(II)$$

From (I) & (II)

$$\frac{d[C]}{dt} = 3K_1[A]^2 - 3K_{-1}[B][C]^3 - 2K_2[C]^2$$

40. (C)



From the unit of rate constant for the given sequential reactions, it is clear that first reaction is of first order & the second reaction is of second order.

Hence, rate law is given as

$$\text{Rate} = K_1[A] - K_2[B]^2$$

41. (C)

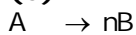
$$\text{m/L-sec} = [K_1][M/L]^3$$

$$[K_1] = \text{L}^2\text{M}^{-2}\text{sec}^{-1}$$

$$\text{ML}^{-1}\text{sec}^{-1} = [K_2][M/L]$$

$$[K_2] = \text{sec}^{-1}$$

42. (C)



$$A_0 \quad 0$$

$$A_0 - x \quad nx$$

$$nx = A_0 - x$$

$$x = \frac{A_0}{n+1}$$

$$\therefore [B] = nx = \frac{nA_0}{n+1}$$

43. (D)

Complex reaction order of reaction depends on rate determining step (RDS) x & y are not related to a & b.

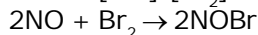
44. (C)

All the reactins

$$r = k[\text{No}][\text{NOBr}_2]$$

Rate of reaction expression do not contain chtermediate

$$\therefore r = k[\text{NO}]^2[\text{Br}_2]$$



45. (B)

$$\frac{dc}{dt} = \left(\frac{dn}{dt}\right) \times \frac{1}{V}$$

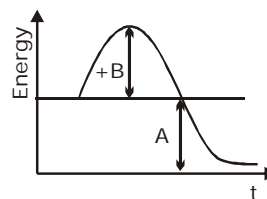
$$c = \frac{n}{V} = \frac{P}{RT}$$

46. (B)

$$\text{At low } C_A = \frac{-dC_A}{dt} = K_1 C_A$$

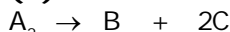
\therefore 1st order & K_1

47. (B)



$$E_a (\text{Backward}) = A + B$$

48. (C)



$$A_0 - x \quad x \quad 2x$$

$$A = A_0 e^{-kt}$$

$$A_0 - = \frac{A_0}{Z} \quad V_1 = 2l$$

$$nx = \frac{A_0}{Z} \quad V_2 = 4l$$

$$[a] = \frac{0.05}{4} = 0.0125$$

49. (D)

$$R_{T+10}^I = 2R_T^I$$

$$R_{T+10}^{II} = 2R_T^{II}$$

$$\frac{K_2}{K_1} = \left(\frac{3}{2a}\right)^5 = 7.6$$

50. (A)

Exercise-II

1. (A)

$$1 - \frac{1}{100} = e^{-\frac{k}{2}}$$

$$K = 2 \ln$$

$$= 0.02 \text{ min}^{-1}$$

2. (A)

$$\text{molarity} = \frac{16.8}{11.2} = \frac{3}{2}$$

Let new lolarity = x

$$\frac{20x}{1000} \times \frac{2}{4} = \frac{37.5 \times 0.02 \times 5}{1000}$$

$$x = 0.375$$

3. (A)

$$0.1 = e^{-\frac{k}{2}}$$

$$\ln 10 = \frac{K}{2}$$

$$K = 4.606$$

4. (C)

$$K = \frac{\ln 2}{10}$$

$$K_2 = \frac{\ln 2}{K^3}$$

10 min

5. (C)

$$A_0 - 2x + 4x + x = 0.15$$

$$A_0 = 0.1$$

$$x = \frac{0.05}{3}$$

$$\frac{2}{6} = e^{-7.5 \times 10^{-3} t}$$

$$\ln(1.5) \times \frac{10^3}{7.5} = t$$

$$t = 53.4 \text{ sec}$$

6. (D)

$$t_{3/4} = \frac{3[A_0]}{4K}$$

7. (C)

$$\frac{dB}{dt} = \frac{-dA}{dt} = A_0 K e^{-kt}$$

8. (C)

$$\log(a_0 - x) = \log a_0 - kt \log e$$

$$k \log e = \frac{2}{10}$$

$$K = \frac{\ln 10}{5} = \frac{2.303}{5} = 0.46$$

9. (A)

$$\frac{0.8}{1.5} = e^{-K \times 20}$$

$$K = \frac{\ln(15/8)}{20}$$

$$= 0.03$$

10. (A, B, D)

$$t_{1/2} = 100 \text{ days}$$

$$a = \text{entry} = \frac{6.93 \times 10^{-6}}{80} \text{ mol/L/day}$$

$$\frac{dx}{dt} = at - kx$$

$$\frac{0.643 \times 10^{-6}}{8} = t = \frac{643}{100} \times x$$

$$x = t \times \frac{10.4}{8}$$

12. (D)

$$(2 - x_B - x_C) 60^\circ - (x_B) + 42^\circ (x_C)$$

$$= 120^\circ - 132^\circ x_B - 18x_C$$

$$\frac{x_B}{x_C} = \frac{1}{2}$$

$$= 120^\circ - 168^\circ x_B$$

$$t \rightarrow \infty \quad x_B \rightarrow 2/3$$

$$A = 0.5$$

$$B = 0.5$$

$$\theta = 36^\circ$$

13. (C)

Order = reaction complex reaction.

14. (C)

eg. Zero order reaction completion time can be determined for order > 1 time can be determined

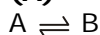
15. (D)

$$E_a > 0$$

If order

$$K_c = \frac{K}{[A]^n}$$

16. (A)



$$\frac{-dA}{dt} = K_1[A] - K_2[B]$$

$$T \uparrow = K_1 \uparrow + K_2 \uparrow$$

17. (A)

$$E_{act_f} > E_{act_b}$$

$$\therefore \Delta H > 0$$

18. (A)

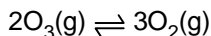
19. (B)

20. (A)

21. (B)

Catalyst forms an alternative path for reactant to convert into product thus decreasing activation energy.

22. (C,D)



Slowest step is rate determining step

$$\text{rate} = k[\text{O}_3][\text{O}] \dots\dots\dots(1)$$

Since, [O] is not in the original reaction hence it has to be eliminated.

From first step

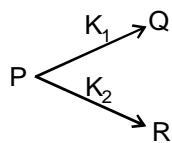
$$K_1 = \frac{[\text{O}_2][\text{O}]}{[\text{O}_3]} \Rightarrow [\text{O}] = \frac{K_1[\text{O}_3]}{[\text{O}_2]} \dots\dots\dots(2)$$

Putting the value of [O] in the eq. (1)

$$\text{rate} = K_1 k [\text{O}_3] \frac{[\text{O}_3]}{[\text{O}_2]}$$

$$\text{Rate} = k[\text{O}_3]^2[\text{O}_2]^{-1}$$

23. (A,B)



Since [Q] = [R] all the times,

$$[\text{P}] = P_0 e^{-(K_1+K_2)t}$$

$$P_0 \left(\frac{K_1}{K_1+K_2} \right) \left(1 - e^{-(K_1+K_2)t} \right)$$

As $K_1 = K_2$

$$\Rightarrow e^{-2K_1 t} = \frac{1}{2} - \frac{1}{2} e^{-2K_1 t}$$

$$\Rightarrow \frac{3}{2} e^{-2K_1 t} = \frac{1}{2}$$

$$\Rightarrow e^{-2K_1 t} = \frac{1}{3}$$

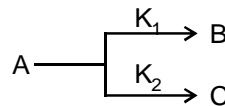
Taking ln of both side

$$-2K_1 t = -\ln 3$$

$$t = \frac{\ln 3}{2K_1} = \frac{2.303}{2K_1} \log_{10} 3$$

As $K_1 = K_2$

24. (A,B)



$$K_1 = 1.26 \times 10^{-4} \text{ sec}^{-1}$$

$$K_2 = 3.8 \times 10^{-5} \text{ sec}^{-1}$$

$$\% \text{ B} = \frac{K_1}{K_1 + K_2} \times 100 = 76.83 \%$$

$$\% \text{ C} = \frac{K_2}{K_1 + K_2} \times 100 = 23.17 \%$$

25. (A,B,C)

Energy of activation can never be negative

Option (D) is incorrect.

26. (B,C,D)

Only ans will be given

27. (A,B,C,D)

(A) For zero order reaction

$$t_{1/2} = \frac{a_0}{2K}$$

$\Rightarrow t_{1/2} \propto a_0$ (initial concentration)

(B) For first order reaction

Average life = 1.44 \times half life

(C) For IInd order reaction

$$t_{1/2} = \frac{1}{KC_0} \quad (\text{Co} = \text{initial concentration})$$

$$\text{Also } Kt = \frac{1}{C} - \frac{1}{C_0}$$

$$t_{3/4} = \frac{1}{t} \left[\frac{1}{C_0/4} - \frac{1}{C_0} \right]$$

$$= \frac{1}{K} \times \frac{3}{C_0} = \frac{3}{KC_0} = 3 \times t_{1/2}$$

$$\Rightarrow t_{3/4} = 3 \times t_{1/2}$$

$${}^{(D)} t_{99.9} = \frac{2.303}{0.0693} \log \frac{100}{0.1}$$

$$t_{99.9} = 100 \text{ min}$$

28. (A,B,C)

$$\text{Rate} = K[A]^2[B]$$

$$\Rightarrow \text{rate w.r.t B} = 1$$

$$\text{Overall order of the reaction} = 2 + 1 = 3$$

for a complex reaction the rate determining step is determined experimentally.

29. (B,D)

In SN^1 reaction, formation of carbocation takes place which is planar.

\Rightarrow equimolar mixture of (I) and (II) will be formed in case of SN^1 . In SN^2 reaction Nucleophile will attack from the opposite to leaving group

\Rightarrow Product (II) will be formed in case of SN^2 reaction.

30. (A,C)

$$\log_{10} K(\text{min}^{-1}) = 5 - \frac{2000}{T}$$

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

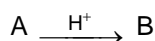
$$\log A = 5 \Rightarrow A = 10^5$$

$$\frac{E_a}{2.303 RT} = \frac{2000}{T}$$

$$E_a = 2000 \times 2.303 \times 8.314 \text{ cal}$$

$$E_a = 9.212 \text{ Kcal}$$

31. (B,C)



$$\text{Rate} = K[H^+][A]$$

$$\text{Rate} = K'[A]$$

If K' has greater value for HA

$\Rightarrow [H^+]$ has to be large

\Rightarrow for that acid has be stronger

$\Rightarrow [HA]$ is strongers that HB

Also Relative strength = 2

32. (A,B,D)

From figure it is clear that $E_a(\text{forward}) = y$

$$E_a(\text{backward}) = Z$$

$$\Delta H_r = + x$$

33. (A,B,C)

From the given data, it is clear that

(A) keeping $[B]$ constant, After doubling the concentration of $[A]$ makes the rate of reaction four times.

\Rightarrow reaction is of order two w.r.t. A.

(B) Similarly order w.r.t. B = 1

$$(C) \text{Rate} = K[A]^2[B]$$

$$5 \times 10^{-4} = K \times (2.5 \times 10^{-4})^2 \times 3.0 \times 10^{-5}$$

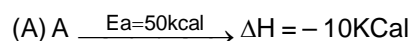
$$\Rightarrow K = 2.67 \times 10^8 \text{ L}^2\text{mol}^{-2} \text{ s}^{-1}$$

$$(D) \text{order} = 2 + 1 = 3$$

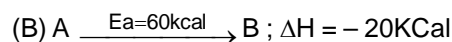
34. (A,C,D)

$t_{1/2}$ of (A) zero (C) second (D) third order varies with concentration.

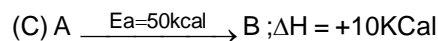
35. (A,B)



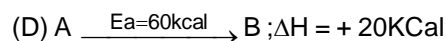
$$E_a(\text{backward}) = 60 \text{ KCal}$$



$$E_a(\text{backward}) = 80 \text{ KCal}$$



$$E_a(\text{backward}) = 40 \text{ KCal}$$



36. (B)

$$\frac{df}{dt} = K(1-f)$$

$$K = \frac{1}{t} \ln \frac{1}{1-f}$$

$$K = \frac{1}{200} [\ln 1 - \ln(1-f)]$$

$$\Rightarrow K = \frac{3}{200}$$

$$t_{1/2} = \frac{0.693}{K} = \frac{0.693}{3/200}$$

$$t_{1/2} = 46.2 \text{ hrs}$$

37. (A)

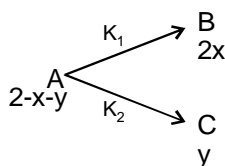
$$1 - f = e^{-kt}$$

$$\Rightarrow f = 1 - e^{-kt}$$

Putting the value of k in from eqⁿ(1)

$$f = 1 - e^{-3t/200}$$

38. (D)



$$2 - x - y = 1$$

$$\Rightarrow x + y = 1 \dots\dots\dots(1)$$

$$\frac{1}{2} \frac{d[B]}{dt} = K_1[A]$$

$$\frac{d[B]}{dt} = 2K_1[A]$$

Also, $\frac{d[C]}{dt} = K_2[A]$

$$\Rightarrow \frac{[B]}{[C]} = \frac{2K_1}{K_2} = 2 \times \frac{1}{2} \text{ (Given } K_1 : K_2 = 1 : 2 \text{)}$$

$$\Rightarrow [B] = [C]$$

$$\Rightarrow 2x = y \dots\dots\dots(2)$$

Solving (1) and (2)

$$x = \frac{1}{3}, y = \frac{2}{3}$$

Total moles after 50% of the reaction
 $= 2 - x - y + 2x + y$
 $= 2 + x = 7/3$

39. (C)

No. of Moles of B = 2x
 $= 2/3$
 $= 0.666$

40. (A)

$$\log k = \log_{10} A - \frac{E_a}{2.303RT}$$

When $E_a = 0$, $k = 3.2 \times 10^5$ & it does not depend on T

41. (B)

When E_a is max,

$\frac{k_{310}}{k_{300}}$ would be max

42. (C)

$$\log \left(\frac{K_1}{K'_1} \right) = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \dots(1)$$

$$\text{Also } \log \left(\frac{K_2}{K'_2} \right) = \frac{E'_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \dots(2)$$

eq. (1)/(2)

$$\frac{\log \left(\frac{K_1}{K'_1} \right)}{\log \left(\frac{K_2}{K'_2} \right)} = \frac{E_a}{E'_a}$$

$$\Rightarrow \frac{\log \left(\frac{K_1}{K'_1} \right)}{\log \left(\frac{K_2}{K'_2} \right)} > 1 \quad (E_a < E'_a)$$

$$\Rightarrow \frac{K_1}{K'_1} > \frac{K_2}{K'_2}$$

43. (A)

$$10^{15} e^{-\frac{2000}{T}} = 10^{15} e^{-\frac{2000}{T}} = 10^{14} e^{-\frac{1000}{T}}$$

$$10 = e^{-\frac{1000}{T} + \frac{2000}{T}}$$

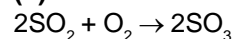
$$10 = e^{\frac{1000}{T}}$$

$$\ln 10 = \frac{1000}{T}$$

$$T = \frac{1000}{2.303}$$

$$T = 434.22 \text{ K}$$

44. (D)



$$\frac{d[\text{SO}_3]}{dt} = 10 \text{ g/sec}^{-1}$$

$$\frac{d[\text{SO}_3]}{dt} = \frac{1}{8} \text{ mol/sec}$$

$$\text{As } \frac{-1}{2} \frac{d[\text{SO}_2]}{dt} = -\frac{d[\text{O}_2]}{dt} = \frac{1}{2} \frac{d[\text{SO}_3]}{dt}$$

$$\Rightarrow -\frac{d[\text{O}_2]}{dt} = \frac{1}{16} \text{ mol/sec}$$

$$\Rightarrow \frac{d[\text{O}_2]}{dt} = 2g \text{ sec}^{-1}$$

45. (A)



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

$$\left(-\frac{d[A]}{dt}\right) / \left(\frac{d[B]}{dt}\right) = \frac{a}{b}$$

$$\log\left(-\frac{d[A]}{dt}\right) = \log\left(\frac{d[B]}{dt}\right) + \log\left(\frac{a}{b}\right)$$

$$\Rightarrow \log\left(\frac{a}{b}\right) = 0.6$$

$$\Rightarrow \frac{a}{b} = 3.98$$

46. (B)



$$\frac{-d[\text{ND}_3]}{2 dt} = \frac{d\text{N}_2}{dt} = \frac{1}{3} \frac{d[\text{D}_2]}{dt}$$

$$\frac{-1}{2} K_1[\text{ND}_3] = K_2[\text{N}_2] = \frac{1}{3} \times K_3[\text{D}_2]$$

$$\frac{k_1}{2} = k_2 = \frac{k_3}{3}$$

$$3 k_1 = 6 k_2 = 2 k_3 \text{ (by multiplying with 6)}$$

47. (A)



$$\log_{10} K = 14 - \frac{1.25 \times 10^4}{T} \dots\dots\dots(1)$$

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

Comparing

$$\log A = 14 \Rightarrow A = 10^{14} \text{sec}^{-1}$$

Also

$$\frac{E_a}{2.303RT} = \frac{1.25 \times 10^4}{T}$$

$$\Rightarrow E_a = 2.39.34 \text{ KJ}$$

48. (D)

Exponential factor = 0

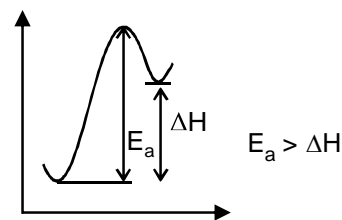
when $T = \infty$

Free radical combination

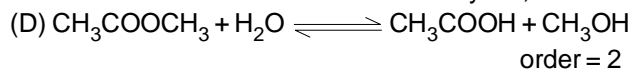
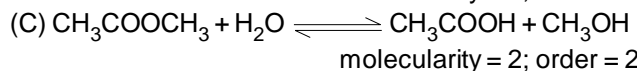
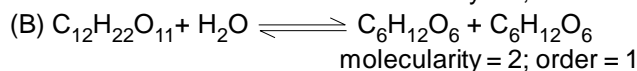
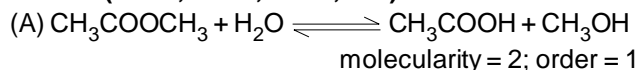
Energy of activation + Threshold energy

49. (A)

For an endothermic reaction

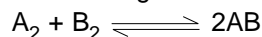


50. (A-QR, B-QR, C-QS, D-S)



51. (A-R, B-Q, C-P, D-S)

From the figure it is clear that.



(A) $E_{at} = 40 \text{ KJ/mol}$

(B) $E_{ab} = 50 \text{ KJ/mol}$

(C) $\Delta H_r = -10 \text{ KJ/mol}$

54.

The reaction is of first order as can be seen from the given data

Also, Rate = $K[\text{H}^+][\text{Complex}]^a$

We have $a = 1$

and $t_{1/2} \propto K[\text{H}^+]^b$

from give data

$$(t_{1/2})_1 \propto \frac{1}{K[\text{H}^+]_1^b}$$

$$\Rightarrow 1 \propto K \frac{1}{K(0.01)^b} \dots\dots\dots(1)$$

$$(t_{1/2})_2 \propto \frac{1}{K[\text{H}^+]_2^b}$$

$$\Rightarrow 0.5 \propto \frac{1}{K(0.02)^b} \dots\dots\dots(2)$$

$$\text{eq}^n(1) / \text{eq. (2)}$$

$$2 = \left(\frac{0.02}{0.01}\right)^b$$

$$b = 1$$

55.

	A →	B +	C
t = 0			
no. of moles	a	0	0
t = 20 min	a - x	x	x
t = ∞	0	a	a

Optical rotation reaction no. of moles

At t = ∞

$$40a - 40a = -20$$

$$\Rightarrow -40a = -20$$

$$a = \frac{1}{2}$$

At, t = 20 min

$$60(a - x) + 40x - 80x = 5$$

$$60a - 100x = 5$$

$$30 - 100x = 5$$

$$x = \frac{25}{100} = \frac{1}{4}$$

No. of moles of A is becoming half after 20 min

$$\therefore t_{1/2} = 20 \text{ min}$$

56.

$$\frac{K_{293}}{K_{276}} = 3, T_2 = 293 \text{ K}, T_1 = 276 \text{ K}$$

$$(a) 2.303 \log \frac{K_2}{K_1} = \frac{E_a}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right] \quad (R = 2 \text{ cal})$$

$$\therefore 2.303 \log 3 = \frac{E_a}{2} \left(\frac{293 - 276}{293 \times 276} \right)$$

$$E_a = 10453.95 \text{ cal} = 10.454 \text{ Kcal}$$

$$(b) \text{ Also, } 2.303 \log \frac{K_3}{K_2} = \frac{E_a}{R} \left[\frac{T_3 - T_2}{T_3 T_2} \right]$$

This time, $E_a = 10.454 \text{ K cal}$, $T_3 = 313 \text{ K}$, $T_2 = 293 \text{ K}$

$$\therefore 2.303 \log \frac{K_3}{K_2} = \frac{10.454 \times 10^3}{2} \frac{313 - 293}{313 \times 293}$$

$$\Rightarrow \frac{K_3}{K_2} = 3.12$$

$$\text{Now, } \frac{K_3}{K_2} = \frac{t_2}{t_3}$$

$$\therefore K \propto \frac{1}{\text{time}}$$

Also, if juice is not spoiled upto 64 hr at 20°C it will not spoil upto 192 hr at 30°C.

Similarly, we can have

$$t_3 = t_2 \times \frac{K_2}{K_3} = 64 \times \frac{1}{3.12} = 20.5 \text{ hr}$$

Sol.57For the change, $A \rightarrow B$

20 % solution of A decomposes 25% in 20 minutes at 25°C.

Let amount of solute undergoing decay = a = 20

∴ amt of solute left (a - x) after 20 minutes

$$= 20 \times \left(\frac{75}{100} \right) = 15$$

$$\therefore K_{25} = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{20} \log \frac{20}{15}$$

$$= 1.44 \times 10^{-2} \text{ min}^{-1}$$

$$\therefore 2.303 \log \frac{K_{40}}{K_{25}} = \frac{E_a}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\therefore 2.303 \log \frac{K_{40}}{0.0144} = \frac{70 \times 1000}{8.314} \left[\frac{313 - 298}{313 \times 298} \right]$$

$$\therefore K_{40} = 5.58 \times 10^{-2} \text{ min}^{-1}$$

The reaction if carried out by 30% solution shows the left amount (a - x) = min 20 min

$$\therefore K_{40} = \frac{2.303}{t} = \log \frac{a}{a-x}$$

$$5.58 \times 10^{-2} = \frac{2.303}{20} \log \frac{30}{m}$$

$$m = 9.83$$

$$\% \text{ decomposition} = [(a - m)/a] \times 100$$

$$= [(30 - 9.83)/30] \times 100$$

$$= 67.2 \%$$

$$\Rightarrow 0.75 = kt = k \times 60$$

$$k = \frac{0.75}{60}$$

when $x = 0.9$

$$t = \frac{0.9}{0.75} \times 60 = \mathbf{1.2 \text{ hour}}$$

14. $t_{1/4} = 72 \text{ min} = 2 \text{ half lives}$
 $t_{1/2} = 36 \text{ min}$
 $t_{1/8} = 3 \text{ half lives} = 3.6 \times 3 = 1.8 \text{ min}$

15. [i] $k = \frac{2.303}{10} \log \frac{100}{80} = \mathbf{0.0223 \text{ min}^{-1}}$

[ii] $t = \left(\frac{2.303}{0.223} \log \frac{100}{25} \right) \text{ min} = 62.11 \text{ sec.}$

16. $t_1 = \frac{2.303}{k} \log \frac{100}{0.1}$

$$t_2 = \frac{2.303}{k} \log \frac{100}{50}$$

$$\frac{t_1}{t_2} = \frac{3}{\log 2} = \mathbf{10}$$

17. $t = \frac{2.303}{1.5 \times 10^{-3}} \log \frac{5}{1.25}$
 $= \mathbf{924.362 \text{ sec}}$

18. $k = \frac{2.303}{20} \log \frac{500}{420}$
 $t_{\text{exp}} = \frac{2.303}{k} \log \frac{100}{70} = \mathbf{41 \text{ months}}$

19. $k = \frac{2.303}{60} \log \frac{100}{98} = \mathbf{3.3 \times 10^{-4} \text{ sec}}$

20. $k = \frac{2.303}{20} \log \frac{1}{0.8}$

$$\Rightarrow t_{1/2} = \frac{0.693}{k} = \mathbf{62.23 \text{ min}}$$

21. $k = \frac{2.303}{90 \times 60} \log \frac{100}{100-x} = 2.2 \times 10^{-5}$

$$\Rightarrow \mathbf{x = 11.2\%}$$

22. [a] keeping concⁿ of H₂ const, when [NO] is doubled, the rate is 4 times.
 keeping [NO] constant, when [H₂] is doubled

the rate is doubled

$$\therefore \text{rate} = k [\text{NO}]^2 [\text{H}_2]$$

$$\therefore \text{order of reaction} = 3$$

[b] $\text{rate} = K [\text{NO}]^2 [\text{H}_2]$

$$\Rightarrow K = \frac{4.4 \times 10^{-4}}{(1.5)^2 \times 10^{-8} \times 4 \times 10^{-3}}$$

[c] $\text{rate} = K [\text{NO}]^2 [\text{H}_2] = \mathbf{8.85 \times 10^{-3} \text{ M sec}^{-1}}$

23. [a] order w.r.t. NO = 2
 order w.r.t. Cl₂ = 1

[b] $\text{rate} = K [\text{NO}]^2 [\text{Cl}_2]$

[c] $k = \frac{1 \times 10^{-3}}{(0.05)^2 (0.05)} = \mathbf{8 \text{ L}^2 \text{ mol}^2 \text{ s}^{-1}}$

[d] $\text{rate} = K [\text{Cl}_2] [\text{NO}]^2 = \mathbf{0.256}$

24. $k_1 = \frac{0.693}{53} = 0.013$

$$k_2 = \frac{2.303}{100} \log \frac{100}{27} = 0.013$$

(i) As $k_1 = k_2$, the reaction is of the first order

(ii) $k = \mathbf{0.013 \text{ min}^{-1}}$

(iii) $\mathbf{73\%}$

25. $\text{Rate} = k [\text{A}]^m [\text{B}]^n$
 $4 \times 10^{-4} = k [0.1]^m [0.1]^n \quad \dots (1)$
 $2 \times 10^{-3} = k (0.5)^m (0.1)^n \quad \dots (2)$

Equation (2)/(1)

$$5 = (5)^m$$

$$\Rightarrow m = 1$$

Also, $2 \times 10^{-3} = k (0.5)^m (0.1)^n \quad \dots (3)$

$$1 \times 10^{-2} = k (0.5)^m (0.5)^n \quad \dots (4)$$

Equation (4)/(3)

$$5 = (5)^n$$

$$\Rightarrow n = 1$$

(ii) $\text{Rate} = K [\text{A}] [\text{B}]$

$$K = \frac{4 \times 10^{-4}}{0.1 \times 0.1} = \mathbf{4 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}}$$

(iii) $\text{Rate} = 4 \times 10^{-2} (0.2) \times (0.35)$
 $= \mathbf{2.8 \times 10^{-3} \text{ M s}^{-1}}$

26.

t	0	100	200	300
$\Delta(\text{Pr})$		0.5×10^3	1×10^3	1.5×10^3
$\frac{\Delta(\text{Pr})}{t}$		0.5×10	0.5×10	0.5×10

As $\frac{\Delta(\text{Pr})}{t} = K$ (Constant) = **5 (Pa/s)**

the reaction of zero order

27. for zero order

$t_{1/2} \propto a$
Alternatively

$$n = 1 + \frac{\log(t_{1/2})_2 - \log(t_{1/2})_1}{\log(a_0)_1 - \log(a_0)_2}$$

28.

Rate = $K[A]^n$

Rate $K (6 \times 10^{-3})^n = 5.2 \times 10^{-5}$ (1)

$K (9 \times 10^{-3})^n = 7.8 \times 10^{-5}$ (2)

$$(2)/(1) \left(\frac{9}{6}\right)^n = \left(\frac{7.8}{5.2}\right)$$

(a) $\rightarrow n = 1$

(b) $\rightarrow \text{Rate} = K[A]$

(c) $\rightarrow K = \frac{7.8 \times 10^{-5}}{9 \times 10^{-3}} = 8.67 \times 10^{-3} \text{ s}^{-1}$

(d) $\rightarrow \text{Rate} 8.67 \times 10^{-3} \times 1.8 \times 10^{-3}$
 $= 1.56 \times 10^{-5} \text{ Ms}^{-1}$

29.

$$k = \frac{0.693}{50}$$

$$t = \frac{0.303}{k} \log \frac{100}{10} = \mathbf{166.6 \text{ min}}$$

30.

$$t_{1/2} = \frac{0.693}{k} = 4.62 \times 10^5 \text{ sec}$$

$$k = \frac{2.303}{10 \times 3600} \log \frac{100}{100-x}$$

$\Rightarrow x = \mathbf{5.26\%}$

31.

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

$$t_2 = \frac{2.303}{k} \log \frac{100}{6.25}$$

$$\frac{t_2}{t_{1/2}} = 4$$

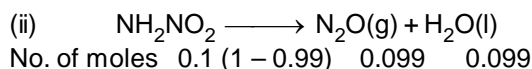
Alternatively fraction left

$$= \frac{1}{2^4} = \frac{1}{16} = 6.25\%$$

\Rightarrow No of half lives = **4**

32. $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{2.1}$

(i) $t = \frac{2.303}{k} \log \frac{100}{1} = 13.96 \text{ hrs}$



$$\text{Volume of H}_2\text{O} = \frac{nRT}{P} = \frac{0.099 \times 0.082 \times 273}{1}$$

$$= \mathbf{2.219 \text{ L}}$$

33.

Time	[A]	[B]
t = 0	a	a

t = 54	$\frac{a}{2}$	$\frac{a}{(2)^3} = \frac{a}{8}$
--------	---------------	---------------------------------

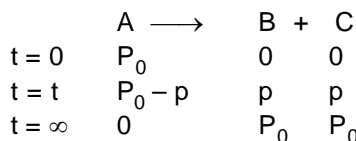
$\therefore t = \mathbf{54 \text{ min}}$

34.

Time	[A]	[B]
0	4a	a
15	$4a \times \frac{1}{(2)^2} = \frac{a}{2}$	$\frac{a}{2}$

\therefore time = **15 min**

35.



Given

and

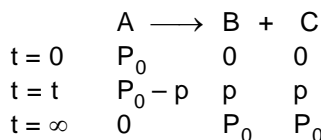
$$2P_0 = p_3$$

$$P_0 + p = p_2$$

We have

$$k = \frac{1}{t} \ln \frac{P_0}{P_0 - p} = \frac{1}{t} \ln \frac{p_3}{2(p_3 - p_2)}$$

36.



Given

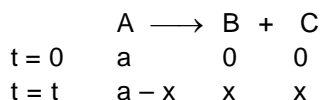
and

$$2P_0 = p_3$$

$$2p = p_2$$

$$k = \frac{1}{t} \ln \frac{P_0}{P_0 - p} = \frac{1}{t} \ln \frac{p_3}{(p_3 - p_2)}$$

37.



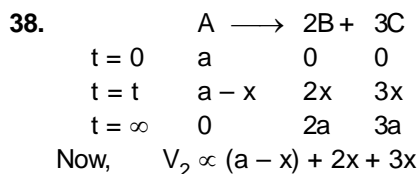
Now,

$$V_1 \propto a$$

$$V_2 \propto (a + x)$$

$\Rightarrow (2V_1 - V_2) \propto (a - x)$

$$\Rightarrow k = \frac{1}{t} \ln \frac{V_1}{(2V_1 - V_2)}$$



Now, $V_2 \propto (a - x) + 2x + 3x$

$$V_2 \propto (a + 4x) \quad \dots (1)$$

Also, $V_3 \propto 5a \quad \dots (2)$

From above equation

$$5V_2 \propto (5a + 20x) \quad \dots (3)$$

From equation (2) and (3)

$$5V_2 - V_3 \propto 20x$$

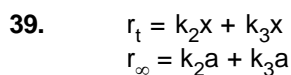
$$x \propto \frac{1}{4} V_2 - \frac{V_3}{20}$$

and, $a \propto \frac{V_3}{5}$,

and $(a - x) \propto \frac{V_3}{5} + \frac{V_3}{20} - \frac{V_2}{4}$

$$\propto \frac{5V_3 - 5V_2}{20}$$

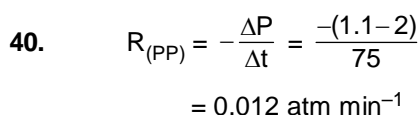
$$\therefore k = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{t} \log \frac{4V_3}{5(V_3 - V_2)}$$



$$a = \frac{r_\infty}{k_2 + k_3}, \quad x = \frac{r_t}{k_2 + k_3}$$

$$\Rightarrow (a - x) = \frac{r_\infty - r_t}{k_2 + k_3}$$

$$\Rightarrow k = \frac{1}{t} \ln \frac{r_\infty}{r_\infty - r_t}$$

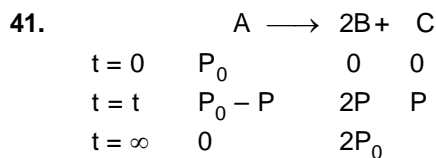


Also, $R_C = \frac{-\Delta C}{\Delta t} = \frac{-\Delta P}{(RT)\Delta t}$

As, $C = \frac{P}{RT}$

$$\therefore R_C = \frac{-(1.1-2)}{0.082 \times 75 \times 60 \times 300}$$

$$= 8.12 \times 10^{-6} \text{ Ms}^{-1}$$



Given $3P_0 = 270 \text{ mm Hg}$

(a) $P_0 = 90 \text{ mm Hg}$

Also, $P_0 + 2P = 176 \text{ mm Hg}$

$$\Rightarrow 2P = 176 - 90$$

$$\Rightarrow P = 43 \text{ mm Hg}$$

[b] $P_0 - P = 90 - 43 = 47 \text{ mm Hg}$

[c] $k = \frac{2.303}{10} \log \frac{90}{47} = 0.0649 \text{ min}^{-1}$

[d] $t_{1/2} = \frac{0.693}{k} = 10.677 \text{ min}$



at 5 $P_0 - x_1 + 3/2 = 827 \rightarrow x_1 = 138$

$$\Rightarrow P_0 - x_1 = 758 - 138 = 620$$

at 10 $P_0 - x_2 + 3/2 = 882 \rightarrow x_2 = 248$

$$P_0 - x_2 = 510$$

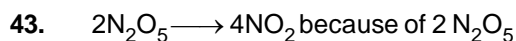
$$\Rightarrow \text{from 0 to 5} = \frac{P_0}{P_0 - x_1} = \frac{758}{620} = 1.2$$

from 5 to 10

$$\frac{P_0 - x_1}{P_0 - x_2} = \frac{620}{510} = 1.2$$

ratio is same

first order



$$K = \frac{1}{2t} \ln \left(\frac{A_0}{A_t} \right)$$

$$P_0 - 2x \quad 4x \quad x \rightarrow P_0 + 3x$$

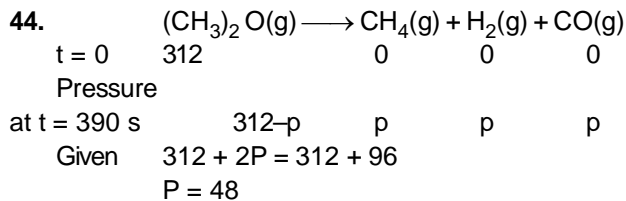
$$\circ 2P_0 P_0/2 \rightarrow \frac{5P_0}{2}$$

$$P_0 + 3x = 284.5 \text{ equation (1)}$$

$$\frac{5P_0}{2} = 584.5 \rightarrow P_0 = 233.8 \rightarrow x = 16.9$$

$$K = \frac{2.303}{2 \times 30} \log \frac{233.8}{200} = 2.60 \times 10^{-3} \text{ min}^{-1}$$

because reactant $2\text{N}_2\text{O}_5$



we have, $k_1 = \frac{2.303}{390} \log \frac{P_0}{P_0 - p}$

$$= \frac{2.303}{390} \log \frac{312}{312 - 48} = 4.28 \times 10^{-4}$$

Similarly, $k_2 = \frac{2.303}{1195} \log \frac{312}{312 - 125}$

$$= 4.28 \times 10^{-4}$$

$$k_3 = \frac{2.303}{3155} \log \frac{312}{312 - 233.5}$$

$$= 4.28 \times 10^{-4}$$

As $k_1 = k_2 = k_3$
the reaction is of 1st order

Rate = $k[(\text{CH}_3)_2\text{O}]$
and $k = 4.28 \times 10^{-4} \text{ sec}^{-1}$

45. $k = \frac{2.303}{t} \log \frac{V_0}{V_t}$

$$k_1 = \frac{2.303}{10} \log \frac{22.8}{13.3} = 0.0539$$

$$k_2 = \frac{2.303}{20} \log \frac{22.8}{8.25} = 0.0508$$

$$k_{\text{avg}} = 0.052$$

As $k_1 = k_2$, the reaction is of **first order**.

46. Same as above question

[a] order = 1

[b] $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.052} = 13.26 \text{ min}$

[c] $k = \frac{2.303}{t} \log \frac{100}{100 - x}$

$$13.26 = \frac{2.303}{25} \log \left(\frac{100}{100 - x} \right)$$

$$\Rightarrow \frac{x}{100} = 0.716$$

47. $k = \frac{2.303}{t} \log \frac{r_0 - r_\infty}{r_t - r_\infty}$

$$k_1 = \frac{2.303}{60} \log \left(\frac{13.1 + 3.8}{11.6 + 3.8} \right)$$

$$k_2 = \frac{2.303}{120} \log \left(\frac{13.1 + 3.8}{10.2 + 3.8} \right)$$

$$k_3 = \frac{2.303}{180} \log \left(\frac{13.1 + 3.8}{9 + 3.8} \right)$$

$$k_4 = \frac{2.303}{360} \log \left(\frac{13.1 + 3.8}{5.87 + 3.8} \right)$$

As, $k \approx k_2 \approx k_3 \approx k_4$, Calculate k_{avg}

The reaction is of 1st order

At zero reading $r_t = 0$

and $k_{\text{avg}} = \frac{2.303}{t} \log \frac{13.1 + 3.8}{(3.8)}$

$$\Rightarrow t = 966 \text{ min}$$

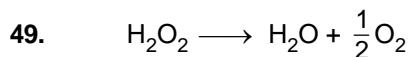
48. $k = \frac{2.303}{t} \log \frac{100}{100 - x}$

$$\Rightarrow k_1 = \frac{2.303}{60} \log \frac{100}{(100 - 18.17)}$$

$$k_2 = \frac{2.303}{350} \log \frac{100}{(100 - 69.12)}$$

$$k_{\text{avg}} = \frac{k_1 + k_2}{2}$$

$$t_{1/2} = \frac{0.693}{k_{\text{avg}}}$$



t = 0 a 0

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

t = ∞ 0 $\frac{a}{2}$

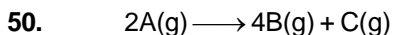
$x \propto$ volume of O_2 liberated at time t

$a \propto$ volume of O_2 liberated at time = ∞

$$\Rightarrow k = \frac{2.303}{5.1} \log \frac{46.34}{(46.34 - 10.31)}$$

$$\Rightarrow t = \frac{2.303}{k} \log \frac{46.34}{(46.34 - 20)}$$

$$= 11.45 \text{ days.}$$



$$t = 0 \quad 0.1 \quad 0 \quad 0$$

PP

$$t = t \quad 0.1 - x \quad 2x \quad \frac{x}{2}$$

$$\text{Given} \quad 0.1 + \frac{3x}{2} = 0.145$$

$$\Rightarrow x = 0.03$$

$$\text{Also,} \quad \frac{-\Delta[A]}{\Delta t} = 7.48 \times 10^{-3} [A]$$

$$\text{We have,} \quad k = \frac{2.303}{t} \log \frac{0.1}{0.1-x}$$

$$7.48 \times 10^{-3} = \frac{2.303}{t} \log \frac{0.1}{0.07}$$

$$t = 47.69 \text{ second}$$

$$\text{Also,} \quad 7.48 \times 10^{-3} = \frac{2.303}{100} \log \frac{0.1}{0.1-x}$$

Calculate x,

$$\text{Total pressure} = 0.1 + \frac{3x}{2} = 0.180 \text{ atm}$$

51.

$$\frac{[x]}{[y] + [z]} = \frac{[x]_0 e^{-(k_1+k_2)t}}{\frac{k_1[x]_0}{k_1+k_2} [1 - e^{-(k_1+k_2)t}] + \frac{k_2[x]_0}{(k_1+k_2)} [1 - e^{-(k_1+k_2)t}]}$$

$$= \frac{e^{-(k_1+k_2)t}}{[1 - e^{-(k_1+k_2)t}]} = \frac{1}{[e^{(k_1+k_2)t} - 1]}$$

52. $\frac{[C]}{[A]} = \frac{k_2[A]_0 [1 - e^{-(k_1+k_2)t}]}{(k_1+k_2)[A]_0 e^{-(k_1+k_2)t}}$

$$= \frac{10}{11} (e^{11x} - 1)$$

53. $\% B = \frac{k_1}{(k_1+k_2)} \times 100 = \frac{1.26}{(1.26+0.36)} \times 100$

$$= 77.77\%$$

$$\% C = 22.22\%$$

54. $t_{\max} = \frac{\ln\left(\frac{k_2}{k_1}\right)}{(k_2 - k_1)} = 4 \text{ min}$

$$\text{where,} \quad k_1 = \frac{0.693}{4}$$

$$k_2 = \frac{0.693}{2}$$

55. $E_{a(f)} - E_{a(b)} = \Delta H$
 $E_{a(b)} = 77 - 72 = 5 \text{ kJ mol}^{-1}$

56. $\log k = \log A - \frac{E_a}{2.303} \times \frac{1}{T}$

$$k = \frac{0.693}{60}, \quad A = 5 \times 10^{13} \text{ sec}^{-1}$$

$$E_a = 104.5 \times 10^3 \text{ J mol}^{-1}$$

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

$$\log 4 = \frac{E_a}{2.303R} \left[\frac{1}{300} - \frac{1}{320} \right]$$

$$E_a = 55.33 \text{ KJmol}^{-1}$$

58. $K_2 = \frac{0.693}{2 \times 3600} \text{ Sec}^{-1}$

$$K_1 = 3.46 \times 10^{-5} \text{ sec}^{-1}$$

$$\text{We have} \log \frac{K_2}{K_1} = \frac{100 \times 10^3}{2.303R} \left[\frac{1}{298} - \frac{1}{T} \right]$$

$$T = 306 \text{ K}$$

59. (a) $K_1 = K_{27^\circ\text{C}} = \frac{0.693}{30}$

$$K_2 = K_{47^\circ\text{C}} = \frac{0.693}{10}$$

(b) $\log \frac{K_2}{K_1} = \frac{E_a}{2.303R} \left[\frac{1}{300} - \frac{1}{320} \right]$

$$\Rightarrow E_a = 43.85 \text{ KJ mol}^{-1}$$

60. $K_1 = A e^{-(E_a)_1/RT}$

$$K_2 = A e^{-(E_a)_2/RT}$$

$$\frac{K_2}{K_1} = e^{-(E_{a2} - E_{a1})/RT} = e^{50000/(4.314 \times 298)}$$

$$= 5.81 \times 10^8$$

61. $\log \frac{K_{35^\circ}}{K_{25^\circ}} = \frac{E_a}{2.303R} \left[\frac{1}{298} - \frac{1}{308} \right]$

$\frac{K_{35^\circ}}{K_{25^\circ}} = 1.75$, $R = 2 \text{ Calorie mol}^{-1} \text{ K}^{-1}$

$\Rightarrow E_a = 10.757 \text{ K cal mol}^{-1}$

62. $\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$

$T_1 = 380 + 273 = 653 \text{ k}$

$T_2 = 723 \text{ k}$

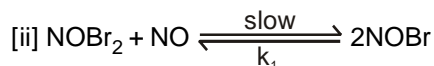
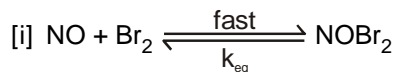
$k_1 = \frac{0.693}{360} \text{ min}^{-1}$

$E_a = 200 \times 10^3 \text{ J mol}^{-1}$

Calculate k_2

& $t = \frac{2.303}{k_2} \log \frac{100}{25}$

$\Rightarrow t = 20.4 \text{ mintues}$

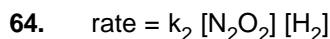


rate = $k_1 [\text{NO}] [\text{NOBr}_2]$

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

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

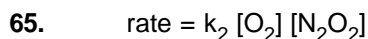
$\therefore \text{rate} = k_1 k_{eq} [\text{NO}]^2 [\text{Br}_2]$
 $= k_{eff} [\text{NO}]^2 [\text{Br}_2]$



$k_{eq} = \frac{[\text{N}_2\text{O}_2]}{[\text{NO}]^2} = k_1$

$\Rightarrow [\text{N}_2\text{O}_2] = k_1 [\text{NO}]^2$

$\therefore \text{rate} = k_1 k_2 [\text{NO}]^2 [\text{H}_2]$



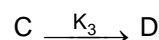
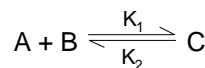
$\frac{k_1}{k_{-1}} = \frac{\text{N}_2\text{O}_2}{[\text{NO}]^2}$

$[\text{N}_2\text{O}_2] = \frac{k_1}{k_{-1}} [\text{NO}]^2$

$\therefore \text{rate} = \frac{k_2 k_1}{k_{-1}} [\text{O}_2] [\text{NO}]^2$

$\Rightarrow \frac{d[\text{NO}_2]}{2dt} = k [\text{NO}]^2 [\text{O}_2]$

66.



$\frac{d[\text{C}]}{dt} = k_1[\text{A}][\text{B}] - k_2[\text{C}] - k_3[\text{C}]$

At steady state $\frac{d[\text{C}]}{dt} = 0$

$\Rightarrow [\text{C}] = \frac{K_1[\text{A}][\text{B}]}{(K_2 + K_3)}$

Also, $\frac{d[\text{D}]}{dt} = k_3[\text{C}] = \frac{K_1 k_3 [\text{A}][\text{B}]}{(K_2 + K_3)}$

Also, $K_{eff} = \frac{K_1 k_3}{K_2}$ as $(K_2 \gg K_3)$

$\Rightarrow A e^{-E_a/RT} = \frac{A_1 e^{-E_a/RT} \times A_3 e^{-E_{a_3}/RT}}{A_2 e^{-E_{a_2}/RT}}$

$= \frac{A_1 A_3}{A_2} e^{-(E_{a_1} - E_{a_3} + E_{a_2})/RT}$

Comparing LHS & RHS

$A = \frac{A_1 A_3}{A_2}$

and $E_a = E_{a_1} + E_{a_3} - E_{a_2}$

67.

Rate = $K_3 [\text{COCl}][\text{Cl}_2]$ (i)

$\frac{K_1}{K_{-1}} = \frac{[\text{Cl}]^2}{[\text{Cl}_2]}$ (ii)

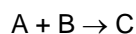
& $\frac{K_2}{K_{-2}} = \frac{\text{COCl}}{[\text{CO}][\text{Cl}]}$; from (i) & (iii)

Rate = $\frac{K_3 K_2}{K_{-2}} \sqrt{\frac{K_1}{K_{-1}}} \sqrt{[\text{Cl}_2]} [\text{CO}][\text{Cl}_2]$

$= \frac{K_3 K_2}{K_{-2}} \left(\frac{K_1}{K_{-1}} \right)^{1/2} [\text{CO}][\text{Cl}_2]^{3/2}$

$= K [\text{CO}][\text{Cl}_2]^{3/2}$

68.



$$(a) \frac{-d[A]}{dt} = K[A][B]^0 = K[A]$$

$$\text{fraction left} = \frac{1}{(2)^2} \text{ in 1 hr}$$

No. of half lives = 2

$$\therefore t_{1/2} = \frac{1}{2} \text{ hr}$$

 \therefore The amt left after 2 hr (no. of $t_{1/2} = 4$)

$$(b) \frac{-d[A]}{dt} = K[A][B] = K[A]^2$$

for 2nd order as $[A]_0 = [B]_0$

$$\therefore \frac{1}{a-x} = \frac{1}{a} + Kt$$

$$\frac{1}{100-75} = \frac{1}{100} + K \times 1$$

$$K = \frac{1}{25} - \frac{1}{100} = \frac{4-1}{100} = \frac{3}{100}$$

When $t = 2$ hr

$$\frac{1}{100-x} = \frac{1}{100} + 2K = \frac{1}{100} + \frac{6}{100} = \frac{7}{100}$$

$$\Rightarrow 700 - 7x = 100$$

$$\Rightarrow x = \frac{600}{7} = 85.7\% \text{ fraction left} = 14.3\%$$

(C) For zero order

$$\frac{-d[A]}{dt} = K$$

for zero order

$$x = Kt$$

$$\therefore 75 = K \times t$$

Also, $x = K \times 2$

$$\Rightarrow x = 150\%$$

Hence the reaction is complete & fraction left = 0%

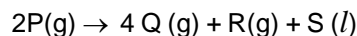
69.

$$-\frac{\Delta}{\Delta t} [\text{PtCl}_4^{2-}] = K_f [\text{PtCl}_4^{2-}] - K_b [\text{Pt}(\text{H}_2\text{O})\text{Cl}_3][\text{Cl}^-]$$

$$K_{\text{eq}} \text{ for given reaction} = \frac{K_f}{K_b}$$

$$K_{\text{eq}} \text{ for reverse reaction} = \frac{K_b}{K_f} = \frac{2.1 \times 10^{-3}}{3.9 \times 10^{-5}} = 53.84$$

70.



$$t = 0 \quad P_0 \quad 0 \quad 0 \quad 32.5$$

PP(mm Hg)

$$t = 30\text{m} \quad P_0 - P \quad 2P \quad \frac{P}{2} \quad 32.5$$

$$t = \infty \quad 0 \quad 2P_0 \quad \frac{P}{2} \quad 32.5$$

$$\text{Given, } 2P_0 + \frac{P_0}{2} + 32.5 = 617 \Rightarrow \frac{5P_0}{2} = 584.5$$

$$\Rightarrow 233.8$$

$$\& P_0 - P + 2P + \frac{P}{2} = P_0 + \frac{3P}{2} = 317 - 32.5$$

$$= 284.5$$

$$\Rightarrow P = 33.8$$

$$P^0 - P = 200$$

$$\therefore K = \frac{2.303}{30} \log \frac{P^0}{P^0 - P}$$

$$= \frac{2.303}{30} \log \frac{233.8}{200}$$

$$= 0.0052$$

Also, When $t = 75$ min

$$K = \frac{2.303}{30} \log \frac{233.8}{233.8 - P'} = 0.0052$$

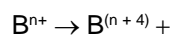
$$\Rightarrow P' = 75.5 \text{ mm Hg}$$

$$\therefore \text{Total pressure} = P_0 + \frac{3P'}{2} + 32.5$$

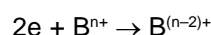
$$= 233.8 + 113.26 + 32.5$$

$$= 379.55 \text{ mm Hg}$$

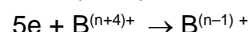
71.



initial a 0



$$t = t(a-x)x$$



Let normality of reducing agent be N

thus at $t = 0$, $a \times 2 = N \times 2S$

$$2a = 25 N$$

at

$$t = t(a - x) \cdot 2 + x \cdot 5 = 32 N$$

$$3x = 7 N$$

$$x = \frac{7}{3} N$$

$$\text{Now } K = \frac{2.303}{10} \log \frac{25/2N}{\left(\frac{25}{2} - \frac{7}{3}\right)N} = 2.07 \times 10^{-2} \text{ min}^{-1}$$

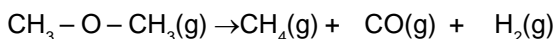
72.

$$K = \frac{2.303}{t} \log \frac{\tau_0}{(\tau_0 - \tau)}$$

$$K = \frac{2.303}{6} \log \frac{3.956}{(3.956 - 1.281)}$$

$t = 15.13$ weeks

73.



$$t = 0 \quad 0.4 \quad 0 \quad 0$$

$$\text{After } x \quad 0.4 - x \quad x \quad x$$

$$\text{time } t \quad K = \frac{2.303}{t} \log \frac{0.4}{(0.4 - x)}$$

$$4.78 \times 10^{-3} = \frac{2.303}{4.5 \times 60} \log \frac{0.4}{A}$$

$$0.4 - x = 0.110$$

$$x = 0.4 - 0.110 = 0.290$$

$$M_m = \frac{0.11 \times 46 + 0.29 + 0.29 \times 28 + 0.29 \times 2}{0.98}$$

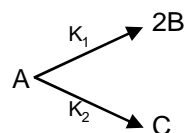
$$= 18.78$$

$$\frac{r_0}{r_m} = \sqrt{\frac{18.78}{46} \times \frac{0.4}{0.98}}$$

$$= 0.261$$

74.

No. of moles \propto pressure of the system (As, T & V constant)



Total pressure at $t = 10$ sec

$$[A]_0 e^{-(K_1+K_2) \times 10} + \frac{2K_1[A]_0}{K_1+K_2} [1 - e^{-(K_1+K_2) \times 10}]$$

$$+ \frac{K_2}{K_1+K_2} [A]_0 [1 - e^{-(K_1+K_2) \times 10}] = 1.4$$

Also, $t = \infty$

$$\left[\frac{2K_1}{K_1+K_2} + \frac{K_2}{K_1+K_2} \right] [A]_0 = 1.5$$

$$\frac{2K_1+K_2}{K_1+K_2} = 1.5 \Rightarrow \frac{K_1}{K_1+K_2} + 1 = 1.5$$

$$\Rightarrow \frac{K_1}{K_1+K_2} = 0.5$$

Also,

$$e^{-(K_1+K_2) \times 10} + \frac{(2K_1+K_2)}{K_1+K_2} [1 - e^{-(K_1+K_2) \times 10}] = 1.4$$

$$\Rightarrow e^{-(K_1+K_2) \times 10} + 1.5 [1 - e^{-(K_1+K_2) \times 10}] = 1.4$$

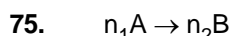
$$\Rightarrow 1.5 - 0.5 e^{-(K_1+K_2) \times 10} = 0.1$$

$$\Rightarrow e^{-(K_1+K_2) \times 10} = \frac{1}{5} = 0.2$$

$$\Rightarrow -(K_1+K_2) \times 10 = \ln(0.2)$$

$$\Rightarrow K_1 + K_2 = \frac{\ln(0.2)}{-10} = 0.16$$

$$\therefore K_1 = 0.5 \times 0.16 = 0.0805$$



$$t = 0 \quad a_0 \quad 0$$

$$t = t \quad a_0 - x \quad \frac{n_2}{n_1} x$$

We have

$$= \frac{-d[A]}{dt} = n_1 K[A]$$

$$[A]_t = [A]_0 e^{-n_1 kt}$$

$$a = a_0 e^{-n_1 kt}$$

$$a_0 - x = a_0 e^{-n_1 kt}$$

$$x = a_0 [1 - e^{-n_1 kt}]$$

$V \propto$ no. of moles

So,

$$\frac{V}{V_0} = \frac{a_0 - x + \frac{n_2}{n_1}x}{a_0} = \frac{V}{V_0} = \frac{a_0 + \left(\frac{n_2}{n_1} - 1\right)x}{a_0}$$

$$= \frac{a_0 + a_0(1 - e^{-n,kt})\left(\frac{n_2}{n_1} - 1\right)}{a_0}$$

$$= V_0 \left[1 + \left(\frac{n_2}{n_1} - 1\right)(1 - e^{-n,kt}) \right]$$

$$= V_0 \left[1 + \frac{n_2}{n_1} - 1 - \left(\frac{n_2}{n_1} - 1\right)e^{-n,kt} \right]$$

$$= V_0 \left[\frac{n_2}{n_1} - \left(\frac{n_2}{n_1} - 1\right)e^{-n,kt} \right]$$

Also,

$$[A]_t = \frac{a_0 - x}{V} = [A]_0 \left[\frac{e^{(-n,kt)}}{\frac{n_2}{n_1} - \left\{ \left(\frac{n_2}{n_1} - 1\right) e^{-n,kt} \right\}} \right]$$

Exercise-IV

Level-I

- | | | | | | |
|-------|-------|-------|-------|-------|-------|
| 1. C | 2. D | 3. A | 4. A | 5. D | 6. C |
| 7. A | 8. A | 9. B | 10. A | 11. D | 12. B |
| 13. B | 14. A | 15. B | 16. A | 17. C | 18. D |
| 19. A | 20. A | 21. B | 22. C | 23. B | 24. D |
| 25. C | | | | | |

Exercise-IV

Level-II

1. **(A,B,D)**
(A) is correct because on plotting a graph between $\log K_p$ vs $\frac{1}{T}$ It is a straight line.
- $$\log K_p = -\frac{\Delta H}{R} \frac{1}{T} + I$$
- (B) For the 1st order reaction, plot a graph between $\log(x)$ vs time, it is a straight line.
 $\log(x) = \log(x_0) + Kt$
 $y = c + mx$
- (D) P vs $\frac{1}{V}$ or $P \propto \frac{1}{V}$ or $PV = \text{constant}$ is Boyle's law.
The plot of P vs $\frac{1}{V}$ is a straight line.
2. **(D)**
Rate constant (K) = $3 \times 10^{-5} \text{ sec}^{-1}$
Rate of reaction = $2.40 \times 10^{-5} \text{ mole litre}^{-1} \text{ sec}^{-1}$
Rate of reaction = $K \times [\text{Molar conc. of } N_2O_5]$
- $$[N_2O_5] = \frac{2.40 \times 10^{-5}}{3 \times 10^{-5}} = 0.8 \text{ mol/litre}$$
3. **(B)**
In photochemical reactions, the rate of reaction is dependent upon intensity of absorbed light i.e., $\text{rate} \propto I$.
4. **(A)**
 $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
Rate = $-\frac{d[N_2]}{dt} = -\frac{1}{3} \frac{d[H_2]}{dt} = \frac{1}{2} \frac{d[NH_3]}{dt}$
- Hence, $A = \text{Rate} = \frac{-d[N_2]}{dt} = \frac{-1}{3} \frac{d[H_2]}{dt} =$
- $$\frac{1}{2} \frac{d[NH_3]}{dt}$$
5. **(C)**
 $a = 800 \text{ mol/dm}^3$ $t = 2 \times 10^4 \text{ sec}$
 $a - x = 50 \text{ mol/dm}^3$
- $$k = \frac{2.303}{t} \log \frac{a}{a-x} \text{ for a first order reaction}$$
- $$= \frac{2.303}{2 \times 10^4} \log \frac{800}{50} = \frac{2.303}{2 \times 10^4} \times 4 \times 0.3010$$
- $$= 1.386 \times 10^{-4} \text{ M/min}$$

6. (C)

The concentration reduces from 0.1 M to 0.025 M in 40 minutes = $2t_{1/2}$

$$0.1 \xrightarrow{t_{1/2}} 0.05 \xrightarrow{t_{1/2}} 0.025$$

$$2t_{1/2} = 40 \therefore t_{1/2} = 20 \text{ min} \quad (40 \text{ min})$$

$$K = \frac{0.693}{t_{1/2}} = \frac{0.693}{20}$$

Rate of reaction $A \rightarrow B$

$$(A) = 0.01 \text{ M}$$

$$= K \times [A] = \frac{0.693}{20} \times 0.01$$

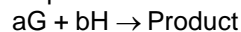
$$= 3.465 \times 10^{-4} \text{ M/min}$$

7. (D)

The order of reaction can have values 0, 1, 2, 3 or even in a fraction. It is always determined experimentally.

8. (D)

Let a moles of G combine with b moles of H forming the product



Rate of reaction $\propto [G]^a \times [H]^b$

$$\text{Rate (r)} = K \times (G)^a \times (H)^b \dots\dots\dots(1)$$

When conc. of both G and H are doubled, the rate becomes 8 times

$$8r = K \times (2G)^a \times (2H)^b$$

$$8r = K \times 2^{a+b} [G]^a \times [H]^b \dots\dots\dots(2)$$

Substitute the value of r in eq. (2)

$$8 \times K \times [G]^a \times [H]^b = K \times 2^{a+b} [G]^a \times [H]^b$$

$$2^{a+b} = 8 = 2^3$$

$$\text{or } a + b = 3$$

The order of reaction = 3

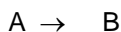
9. (A)

For a first order reaction

$$K_1 = \text{Rate constant}$$

$$K_1 = \frac{0.693}{40} \dots\dots\dots(1)$$

For a zero order reaction



$$1.386 \text{ mol/dm}^3$$

$$\text{Half conc.} = \frac{1.386}{2} = 0.693 \text{ mol dm}^{-3}$$

time = 20 sec

$$K_0 = \frac{dx}{dt} = \frac{0.693}{20} \dots\dots\dots(2)$$

Divide eq. (1) by (2)

$$\frac{K_1}{K_0} = \frac{0.693}{40} \times \frac{20}{0.693} = 0.5 \text{ mol}^{-1} \text{ dm}^3$$

10. (D)

$A \rightarrow P$, a first order reaction equation of first order

$$\log K = \log_{10} A - \frac{E_a}{2.303RT}$$

Given equation is

$$\log K = 6.0 - \frac{2000}{T}$$

Equating eqs. (1) and (2)

$$\log_{10} A = 6 \text{ or } A = 10^6 \text{ or } 1.0 \times 10^6 \text{ S}^{-1}$$

$$\frac{E_a}{2.303R} = 2000$$

$$E_a = 2000 \times 2.303 \times R$$

$$= 2000 \times 2.303 \times 8.314 \times 10^{-3} \text{ kJ mol}^{-1}$$

$$= 38.3 \text{ kJ mol}^{-1}$$

11. (A)

$$12. \quad A = \frac{A_0}{2^8} = \frac{A_0}{256}$$

$$\% \text{ completion} = \frac{255}{256} \times 100$$

$$= 99.6\%$$

SUBJECTIVE

13.

$A \rightarrow B$ rate constant = $4.5 \times 10^{-3} \text{ sec}^{-1}$

$r = 60 \text{ sec}$, $a = 1.0 \text{ M}$, conc. left = $(a - x) = x$

$$4.5 \times 10^{-3} = K = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$\Rightarrow K = \frac{2.303}{60} \log \frac{1}{a-x}$$

$$\log \frac{1}{a-x} = \frac{4.5 \times 10^{-3} \times 60}{2.303}$$

$$\frac{1}{a-x} = 1.310$$

$$a-x = \frac{1}{1.31} = 0.7634 \text{ M}$$

Rate of reaction = Rate constant \times conc. after 1 hr

$$= 4.5 \times 10^{-3} \times 0.7634$$

$$= 3.44 \times 10^{-3} \text{ mol/litre/min}$$

14.

$$K = A e^{-E_a/RT} \dots\dots\dots(1)$$

Arrhenius equation

$$\text{at } 500 \text{ K, } K = A e^{-E_a/500T} \dots\dots\dots(2)$$

at 400 K, the lowering of activation energy = $(E_a - 20)$

$$\text{at } 400 \text{ K } K = A e^{-(E_a-20)/400T} \dots\dots\dots(3)$$

Since the rate is same at 500 K without catalyst and at 400 K with catalyst.

Dividing Eq. (2) by (3)

$$1 = \frac{e^{-E_a/500R}}{e^{-(E_a-20)/400R}}$$

$$e^{\frac{(E_a-20)}{400R}} = e^{-E_a/500R}$$

$$\frac{E_a - 20}{400} = \frac{E_a}{500}$$

$$5E_a - 100 = 4E_a$$

$$E_a = 100 \text{ kJ/mol}$$

15. Rate = $K \times \text{conc. of reactant} = K \times C$

$$r_1 = K \times 0.04$$

$$r_2 = K \times 0.03$$

$$\frac{r_1}{r_2} = \frac{C_1}{C_2} = \frac{0.04}{0.03}$$

$$t = 10 \text{ minutes}$$

$$K = \frac{2.303}{t} \log \frac{C_1}{C_2} = \frac{2.303}{10} \times \log \frac{0.04}{0.03}$$

$$K = \frac{2.303}{10} \times \log \frac{4}{3} = \frac{2.303}{10} [\log 4 - \log 3]$$

=

$$\frac{2.303}{10} \left((0.6021 - 0.4771) = \frac{2.303}{10} \times 0.1250 \right)$$

$$= 0.0287 \text{ min}^{-1}$$

$$t_{1/2} = \frac{0.693}{K} = \frac{0.693}{0.0287} = 24.14 \text{ min}$$

16. (i) The data show that pressure is reduced to half in 100 minutes and to $\frac{1}{4}$ th in 200 minutes showing it to be a 1st order reaction.

(ii) $t_{1/2} = 100 \text{ min}$

$$K = \frac{0.693}{t_{1/2}} = \frac{0.693}{100} = 6.93 \times 10^{-3} \text{ min}^{-1} = \frac{0.693}{100}$$

(iii) $t = \frac{2.303}{K} \log \frac{100}{25}$