Solutions

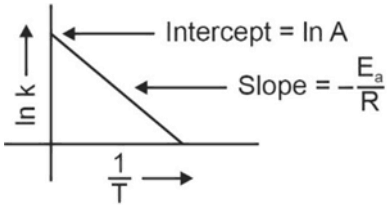
S1. Ans.(c)

The Arrhenius equation is given as

$k = Ae^{-\frac{E_a}{RT}}$

$\therefore \ln k = \ln A - \frac{E_a}{RT}$

ln k v/s 1/T gives a straight-line graph with slope = $-\frac{E_a}{R}$ and intercept = ln A



S2. Ans.(c)

To calculate value of E_a

Equation used is

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

Hence E_a can be calculated if value of rate constant k is known at two different temperatures T_1 and T_2.

S3. Ans.(d)

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

$\log\left(\frac{4}{1}\right) = \frac{E_a}{2.303\ R}\left(\frac{1}{300} - \frac{1}{330}\right)$

$E_a = \frac{(\log(4))\times 2.303\times 8.314\times 300\times 330}{30}$

$= 3.804 \times 10^4$ J/mol

= 38.04 kJ/mol

S4. Ans.(c)

$3A \longrightarrow 2B$

$r = \frac{1}{3}\frac{\Delta[A]}{\Delta t} = +\frac{1}{2}\frac{\Delta[B]}{\Delta t}$

$+\frac{\Delta[B]}{\Delta t} = -\frac{2}{3}\frac{\Delta[A]}{\Delta t}$

S5. Ans.(d)

$r = k[A]^{-1/2}[B]^{3/2}$

$\text{order} = -\frac{1}{2} + \frac{3}{2}$

$= 2/2$

$= 1$

S6. Ans.(b)

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

If [A] is tripled and [B] is kept constant.

$r^1 = k[3A]^2[B]$

$r^1 = 9k[A]^2[B]$

$r^1 = 9r$

Increased by a factor of nine

S7. Ans.(c)

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.

S8. Ans.(b)

$4A + 3B \longrightarrow 6C + 9D$

Rate of reaction $= \frac{-d[A]}{dt}\times\frac{1}{4} = \frac{-d[B]}{dt}\times\frac{1}{3} = \frac{+d[C]}{dt}\times\frac{1}{6} = \frac{+d[D]}{dt}\times\frac{1}{9}$

Rate of reaction $= \frac{+d[C]}{dt}\times\frac{1}{6} = \frac{6\times10^{-2}}{6} = 10^{-2}$ mol L^{-1} s^{-1}

Rate of reaction $= \frac{-1}{3}\frac{d[B]}{dt}$

$\frac{-d[B]}{dt}$ = 3 × rate of reaction = 3×10^{-2} mol L^{-1} s^{-1}

After interval of 10 sec. = $3 \times 10^{-2} \times 10$

= 30×10^{-2} mol L^{-1}

S9. Ans.(c)

For zero order reaction:

$r = k[A]^0$

r = k(constant)

Hence, 'y' as 'rate' & 'x' as concentration will give desired graph.

For first order reaction:

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

Hence, 'y' as '$t_{1/2}$' and 'x' as concentration will give desired graph.

S10. Ans.(b)

For first order reaction,

K = $\frac{2.303}{t}$ log $\frac{[A_0]}{[A]}$; where A_0 is the initial concentration of reactant A.

A_0 = 0.1 M

A = 0.001 M

t = 5 minutes

K = $\frac{2.303}{5}$ log $\frac{0.1}{0.001}$ = $\frac{2.303}{5}$ log 10^2 = $\frac{2.303}{5} \times 2$

K = 0.9212 min^{-1}

S11. Ans.(a)

For a given ΔH is negative. Hence potential energy profile is an exothermic reaction.

S12. Ans.(d)

$lnk = lnA - \frac{Ea}{R}\left(\frac{1}{T}\right)$

In lnk v/s 1/T graph

Slope = –Ea/R

$-5 \times 10^3 = -Ea/8.313$

$Ea = 5 \times 10^3 \times 8.314$

= 41500 J mol^{-1}

= 41.5 KJ/mol

S13. Ans.(c)

When the concentrations of the reactants are raised, the reaction proceeds more quickly. This is due to an increase in the number of molecules that have the minimum required energy.

Collision frequency ∝ no. of reacting molecules or atoms.

Higher the concentration of reactant molecules higher is the probability of collision and so the collision frequency.

S14. Ans.(b)

For first order reaction:

$k = \frac{2.303}{t} log.\frac{[R_0]}{[R_t]}$

$4.606 \times 10^{-3} = \frac{2.303}{t} \log \frac{[2]}{[0.2]}$

$t = \frac{2.303}{4.606 \times 10^{-3}} log10$

$t = \frac{10^3}{2} = 500\ s$

S15. Ans.(a)

Rate of reaction according to collision theory can be expressed as

Rate = $Z_{AB}\ e^{-E_a/RT}$

Where, Z_{AB} represents the collision frequency of the reactants, A & B and $e^{-E_a/RT}$ represents the fraction of molecules with energies equal to or greater than E_a

The number of collisions per second per unit volume of the reaction mixture (A and B) is known as collision frequency Z_{AB}.

S16. Ans.(d)

For zero order reaction

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

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

$k = \frac{0.02}{2 \times 100}$

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

S17. Ans.(c)

First order rate constant is given as,

$k = \frac{2.303}{t} \log \frac{[A_0]}{[A]_t}$

99% completion of reaction,

$k = \frac{2.303}{t} \log \frac{100}{1}$

$k = \frac{2.303}{t} \times 2log10$

$t = \frac{2.303}{k} \times 2$

$t = \frac{4.606}{k}$

S18. Ans.(c)

$N_2 + 3H_2 \rightleftharpoons 2NH_3$

Rate of reaction is given as

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

S19. Ans.(b)

$\left(t_{1/2}\right)_{zero} = \frac{[A]_0}{2K}$

∴ If $[A]_0$ = doubled, $t_{1/2}$ = doubled

S20. Ans.(b)

- For first order reaction, $t_{1/2} = \frac{0.693}{k}$ which is independent of initial concentration of reactant.
- For second order reaction, $t_{1/2} = \frac{1}{k[A_0]}$, which depends on initial concentration of reactant.

S21. Ans.(a)

In the slowest step.

$X + Y_2 \rightleftharpoons XY + Y$

Half molecule of Y_2 reacts with the one molecule of X

$\therefore$ 1 + 0.5 = 1.5

S22. Ans.(c)

K = 10^{-2} s^{-1}, t = ? $[R_0]$ = 20 g

[R] = 5 g

$t = \frac{2.303}{k}\log\frac{[R_0]}{[R]}$

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

$t = 138.6\ sec$

S23. Ans.(d)

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

Hence, order reaction = 1 + 2 = 3

$\therefore$ Order with respect to NO = 2

S24. Ans.(c)

$\frac{-d[A]}{dt} = \frac{-d[B]}{dt} = \frac{1.5d[C]}{dt}$ …(i)

For the reaction

$xA + yB \rightleftharpoons Zc$

$\frac{-d[A]}{Xdt} = \frac{-d[B]}{Ydt} = \frac{d[C]}{Zdt}$ …(ii)

Comparing equation (i) and (ii)

$X:Y:Z = 1:1:\frac{1}{1.5}$

$= 1:1:\frac{2}{3} = 3:3:2$

$X = Y = 3, Z = 2$

S25. Ans.(a)

At Low P, rate is proportional to the surface coverage and is of Ist order while at high P, it follows zero order due to complete coverage of surface area.

S26. Ans.(b)

For a first order reaction, A → products and for concentration of the reactant at two different times.

$k = \frac{2.303}{t_2 - t_1}\log\frac{[A]_1}{[A]_2}$

$k = \frac{2.303}{t_2 - t_1}\log\frac{(rate)_1}{(rate)_2}$ ($\because$ rate $\propto [A]$)

$k = \frac{2.303}{(20-10)}\log\left(\frac{0.04}{0.03}\right) = 0.0287\ \text{sec}^{-1}$

$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0287\ \text{sec}^{-1}} = 24.14\ sec$

S27. Ans.(a)

When we add catalysts to any chemical reaction. It provides an alternative pathway for the reaction and lowers the activation energy. So the reaction becomes fast. As E_f and E_b (activation energy for forward and backward reaction) is reduced to same extent, so there is no change in enthalpy of reaction.

S28. Ans.(a)

Reaction is of zero order as the unit of rate constant is $mol\ L^{-1}\ s^{-1}$.

$\therefore$ Concentration of B = k × t = 0.6 × 10^{-3} × 20 × 60 = 0.72 M

S29. Ans.(a)

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

Ist order reaction is independent of concentration of reactant.

S30. Ans.(b)

According to Arrhenius equation:

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

$\ln k = \ln A - \frac{E_a}{RT}$

Comparing with y = c + mx

Slope will be ln k

S31. Ans.(d)

$k_p > k_p'$ that is the previous pressure constant was higher as the reaction being exothermic $T_2 > T_1$.

S32. Ans.(c)

Enthalpy (ΔH) = E_f activation energy of forward − E_b activation energy of backward reaction

When $E_f = E_b$

$\Delta H = 0$

S33. Ans.(c)

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

$k_2 = 2k_1, T_1 = 20 + 273 = 293\ K$

or $T_2 = 35 + 273 = 308\ K$

$R = 8.314\ J\ mol^{-1}K^{-1}$