SOLUTIONS

Module - 4 / JEE-2021

IN-CHAPTER EXERCISES	Chemistry	Chemical Kinetics

EXERCISE-A

1. Rate = k [P] [Q] $\Rightarrow$ Overall order = 1 + 1 = 2

Exp. (i) and (ii), [P] is kept constant and [Q] is doubled, rate is also doubled.

Exp. (i) and (iii), [Q] is kept constant and [P] is doubled, rate is also doubled.

From (i), $0.0012 = k \times 6 \times 10^{-2} \times 10^{-2} \Rightarrow k = 2\ L\ mol^{-1}\ min^{-1}$

2. Rate = k [A] $[B]^0$

Exp. (i) and (ii), [B] is kept constant and [A] is doubled, rate is also doubled.

Exp. (i) and (iii), [A] is kept constant and [B] is doubled, rate remains unchanged.

3.(D) $BrO_3^-(aq.) + 5Br^-(aq) + 6H^+(aq) \longrightarrow 3Br_2(\ell) + 3H_2O(\ell)$ $\quad$ $\text{Rate} = -\frac{1}{5}\frac{d[Br^-]}{dt} = +\frac{1}{3}\frac{d[Br_2]}{dt}$

4.(C) $H_2(g) + I_2(g) \longrightarrow 2HI(g)$ $\quad$ $\text{Rate} = -\frac{1}{1}\frac{d[H_2]}{dt} = -\frac{1}{1}\frac{d[I_2]}{dt} = +\frac{1}{2}\frac{d[HI]}{dt}$

Now, $\frac{d[H_2]}{dt} = -10^{-4}\,Ms^{-1} \Rightarrow \frac{d[I_2]}{dt} = 2\times10^{-4}\,Ms^{-1}$

5.(D) $\text{Rate}_{old} = k[A]^n[B]^m$; $\text{Rate}_{New} = k(2[A])^n\left(\frac{[B]}{2}\right)^m = k.\,2^{n-m}[A]^n[B]^m \Rightarrow \frac{\text{Rate}_{new}}{\text{Rate}_{old}} = 2^{n-m}$

6.(C) $X \longrightarrow Y$ $\quad$ $\text{Rate}_1 = k[X]^m$; $\text{Rate}_2 = 2.25\,\text{Rate}_1 = k(1.5[X])^m \Rightarrow (1.5)^m = 2.25 \Rightarrow m = 2$

7.(CD) $2X + Y \longrightarrow X_2Y$ $\quad$ $\text{Rate} = -\frac{1}{2}\frac{d[X]}{dt} = -\frac{1}{1}\frac{d[Y]}{dt} = +\frac{d[X_2Y]}{dt}$

8.(A) $\text{Rate} = k[A]^m \quad \left(A \xrightarrow{k} B\right)$ $\Rightarrow$ Units of Rate and k are same if m = 0.

EXERCISE-B

1. No. of half lives $= \frac{11540}{5770} = 2 \Rightarrow \frac{N_t}{N_0} = \left(\frac{1}{2}\right)^2 = \frac{1}{4}$ = fraction left

2. $t_{1/2} = 3$ hrs ; t = 15 hrs $\Rightarrow$ No. of half lives $= \frac{15}{3} = 5$

$\Rightarrow \frac{n_t}{n_0} = \left(\frac{1}{2}\right)^5 = \frac{1}{32} \Rightarrow g_{left} = \frac{1}{32}\times100\,gm = 3.125\,gm$

3. $k_{27°C} = \frac{0.693}{5\times10^3}s^{-1}$; $k_{37°C} = \frac{0.693}{10^3}s^{-1}$

$\Rightarrow \frac{k_{37°C}}{k_{27°C}} = 5 \Rightarrow \log_{10}\frac{k_2}{k_1} = \log_{10}5 = \frac{E_a}{2.303\times2}\times\frac{(310-300)}{300\times310}$ $\Rightarrow$ $E_a = 299.85\ kcal\ mol^{-1}$

4. $t_{99.9\%} = \frac{2.303}{k}\log_{10}\frac{C_0}{C_0 - 0.999C_0} = \frac{2.303}{k}\log_{10}1000 = \frac{3\times 2.303}{k}$

$t_{1/2} = \frac{2.303\log_{10}2}{k} \Rightarrow \frac{t_{99.9\%}}{t_{1/2}} = \frac{3}{\log_{10}2} \approx 10$

5. $\left.\begin{array}{l} k\times 8 = \log_e\frac{C_0}{C_0 - 0.4C_0} = \ell n\frac{5}{3} \quad \text{and} \quad k\times t = \log_e\frac{C_0}{C_0 - 0.9C_0} = \ell n 10 \end{array}\right\}$ $t = 36.06\,\text{min}$

6. $k = Ae^{-Ea/RT}$ Here : $\frac{E_a}{RT} = \frac{187.06\times 10^3}{8.314\times 750} \approx 30 \Rightarrow k = 1.97\times 10^{12}\times e^{-30} = 0.184\,s^{-1}$ and $t_{1/2} = \frac{0.693}{k} = 3.76\,s$

7. Use : $\log_{10}\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$ and $\log_{10}2.5 = 0.4$ and $\log_{10}2 = 0.3$

8. $k\times 10 = \ell n\frac{C_0}{C_0 - 0.2C_0} = \ell n\frac{5}{4} \Rightarrow k = 0.022\ \text{min}^{-1}$; $k\times t = \ell n\frac{C_0}{C_0 - 0.75C_0} = \ell n4 \Rightarrow t = 62.16\ \text{min}$

9.(D) $\log_{10}k = \log_{10}A - \frac{E_a}{2.303RT} \Rightarrow$ Slope of $\log_{10}k$ vs. $\frac{1}{T}$ is : $S = \frac{E_a}{2.303R} \Rightarrow E_a = 2.303\ RS$

10.(A) $(E_a)_b < (E_a)_f$ in case of endothermic reaction. $(E_a)_b > (E_a)_f$ in case of exothermic reaction.

11.(A) $\log_{10}\frac{k_2}{k_1} = \log_{10}2 = \frac{E_a}{2.303\times R}\times\frac{(310-300)}{310\times 300} \Rightarrow E_a = 12.89\,\text{kcal mol}^{-1}$

12.(A) $\left.\begin{array}{l} 0.06M \xrightarrow{10hr} 0.03M \\ 0.12M \xrightarrow{10hr} 0.06M \end{array}\right\}$ Half life is same $\Rightarrow$ First order reaction.

13.(D) Spontaneity doesn't relate to the rate of a chemical reaction.

14.(B) $\log_e\frac{C_0}{C_0 - x}$ vs. t is linear for a first order reaction.

15.(B) $k = Ae^{-Ea/RT} \Rightarrow$ 'A' has same units as 'k'.

16.(C) $\left.\begin{array}{l} C_0 = 0.1M \longrightarrow t_{1/2} = 200\,s \\ C_0 = 0.5M \longrightarrow t_{1/2} = 40\,s \end{array}\right\} \Rightarrow t_{1/2} \propto C_0^{-1} \Rightarrow$ 2^{nd} order reaction.

17.(D) $k = Ae^{-Ea/RT} \Rightarrow$ k will be least when E_a is high and T is low.

18.(C) $A \longrightarrow B \quad \Rightarrow k\times 1 = \ell n\frac{0.8}{0.2} = \ell n4$

	A	B
t = 0 (moles)	0.8	–
t = 1 hr	0.2	0.6

$A \longrightarrow B \quad \Rightarrow k\times 1 = \ell n\frac{0.9}{0.225} = \ell n4$

	A	B
t = 0 (moles)	0.9	–
t = t hr	0.225	0.675

$\Rightarrow t = 1$ hr

EXERCISE-C

1. Radioactive decay follows first order kinetics.

$\therefore \quad t_{1/2} = \dfrac{\ell n}{\lambda}$, where λ = disintegration constant or rate constant.

$\Rightarrow \quad \lambda = \dfrac{\ell n2}{3.8} = 0.18 \text{ day}^{-1}$

Let No. be the initial nuclei at time t = 0

$N_t = \dfrac{1}{20} N_0$ at time t

$\therefore \quad \ell n \dfrac{N_0}{N_t} = \lambda t$

$\Rightarrow \quad \ell n 20 = 0.18\,t \quad \Rightarrow \quad t = 16.63$ days

2. $\ell n \dfrac{N_0}{N_t} = \lambda t$

$\Rightarrow \quad \ell n \dfrac{N_0}{N_0 / 64} = \lambda \times 2 \quad \Rightarrow \quad \lambda = 2.08 \text{ hr}^{-1}$

$t_{1/2} = \dfrac{\ell n2}{2.08} = 0.33$ hr.

3.(C) Mean life $= \dfrac{1}{\lambda}$

$\therefore \quad \dfrac{\ell n2}{\lambda_X} = \dfrac{1}{\lambda_Y} \quad \Rightarrow \quad \lambda_X = \ell n2 \times \lambda_Y$

$\Rightarrow \quad \lambda_X < \lambda_Y \quad \Rightarrow$ Rate of decay of X = λ_X No < Rate of decay of Y = λ_Y No

4.(A) All these particles have same energy – 1/2 mv^2. $\therefore$ Lower the mass, greater wil be the velocity for the same energy $\Rightarrow$ More will be the penetrating power. Here, α has the highest mass whereas γ has the least mass.

5.(D) Nucleus containing even no. of neutrons and protons is stable. ${}^{64}_{29}Cu$ has odd no. of neutrons and protons and $\therefore$ decays to ${}^{64}_{30}Zn$ which has even no. of neutrons and protons.

$${}^{64}_{29}Cu \longrightarrow {}^{64}_{30}Zn + {}^{0}_{-1}e$$

6.(D) For $\quad X_1 \Rightarrow N_t^1 = N_0 e^{-10\lambda t}$

$X_2 \Rightarrow N_t^2 = N_0 e^{-\lambda t}$

At time t, $\dfrac{N_t^1}{N_t^2} = \dfrac{1}{e}$

$\Rightarrow \quad e^{-9\lambda t} = e^{-1} \quad \Rightarrow \quad t = \dfrac{1}{9\lambda}$

7.(C) Neutrons transform into a proton within the nucleus emitting an e^-.

8.(B) Half life $t_{1/2} = 140$ days

After 280 days, i. e. two half - lives

$A_t = 6000$ dps

As $\frac{A_0}{A_t} = 2^n$

$n = 2$

$\therefore \quad \frac{A_0}{6000} = 2^2 = 4$

$\Rightarrow \quad A_0 = 24000$ dps

9.(CD) For ${}_1^1H$, mass number = atomic number and usually, mass number > atomic number

10.(D) Nuclear fusion process involves combining of two or more light nuclei into heavier nucleus.

11.(B) For a first order kinetics.

$$t_{1/2} = \frac{\ell n 2}{\lambda} \text{ and mean - life } \tau = \frac{1}{\lambda} \left[\tau = \frac{\int_0^{\infty} \lambda t\ N_0 e^{-\lambda t} dt}{N_0} \right]$$

12.(C) Let 1 gm of Rn is allowed to decay.

After five minutes, (i.e. 5×60 seconds)

mass of Rn left $= 1 \times e^{-\frac{\ell n 2}{55} \times 5 \times 60}$

$= 0.023$ gms.

Since, decay constant of P_0 is $43.32 s^{-1}$, $\therefore$ as soon as Po is formed, it decays into Pb . $\therefore$ All of Po is converted to Pb which then decays to Bi.

Also, since $t_{1/2}$ for decay of Pb is 10.6 hrs.,

$\therefore$ in five minutes, negligible amount of Pb is decayed

$\therefore$ After five minutes,

mass of Po left $\simeq$ 0 gm

mass of Pb left $\simeq 1 - 0.023$ gms $\simeq 0.977$ gms.

13.(B) Because of higher n/p ratio ${}_{13}^{29}Al$ disintegrate by β-emission.

14.(B) ${}_3Li^6 + {}_0n^1 \longrightarrow {}_2He^4 + {}_1H^3$

15.(A) $U^{238} \longrightarrow Pb^{206}$

$N_0 \equiv x \qquad 0$

$N_t \equiv x - y \qquad y$

$\Rightarrow \quad \frac{N_0}{N_t} = \frac{x}{x-y}$ Also, given : $\frac{x-y}{y} = 3$

$\therefore \quad \frac{x}{x-y} = \frac{4}{3}$

$\Rightarrow \quad \log\frac{N_0}{N_t} = \frac{\ell n2}{k} \times \frac{1}{2.303} \times t$

$\Rightarrow \quad \log\frac{4}{3} = \frac{\ell n2}{4.5 \times 10^9} \times \frac{1}{2.303} \times t$

$\Rightarrow \quad t = 1.85 \times 10^9$ years

16.(AC) When neutron $\left({}_0^1n\right)$ is emitted, then atomic no. remains same but mass no. decreases by 1.

So, $\quad {}_{13}^{27}Al + {}_2^4He \longrightarrow {}_{15}^{30}P + {}_0^1n$

${}_1^2H + {}_1^3H \longrightarrow {}_2^4He + {}_0^1n$

17.(B) For stable nucleus, we have

$1 \le \frac{n}{p} \le 1.5$

$\Rightarrow \quad \frac{P}{n} \le 1$

$\therefore$ For instability, $\frac{P}{n} \ge 1$ i.e. high proton to neutron ratio.

18.(D) Nucleus decays into proton and emits an electron.

19.(B) ${}_xA^y \longrightarrow {}_xA^{y-4} + {}_2^4\alpha + 2{}_{-1}^{0}\beta$

$\therefore$ Atomic number remains same but mass number Change.

20.(D) According to group displacement law.