

SOLUTIONS

Module - 4 / JEE-2021

IN-CHAPTER EXERCISES Chemical Kinetics Chemistry

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),
$$0.0012 = k \times 6 \times 10^{-2} \times 10^{-2} \implies k = 2 \text{ L mol}^{-1} \text{ min}^{-1}$$

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)
$$\operatorname{BrO}_{3}^{-}(\operatorname{aq.}) + 5\operatorname{Br}^{-}(\operatorname{aq}) + 6\operatorname{H}^{+}(\operatorname{aq}) \longrightarrow 3\operatorname{Br}_{2}(\ell) + 3\operatorname{H}_{2}\operatorname{O}(\ell)$$
 $\operatorname{Rate} = -\frac{1}{5}\frac{\operatorname{d}\left[\operatorname{Br}^{-}\right]}{\operatorname{dt}} = +\frac{1}{3}\frac{\operatorname{d}\left[\operatorname{Br}_{2}\right]}{\operatorname{dt}}$

4.(C)
$$H_2(g) + I_2(g) \longrightarrow 2HI(g)$$
 $Rate = -\frac{1}{1} \frac{d[H_2]}{dt} = -\frac{1}{1} \frac{d[I_2]}{dt} = +\frac{1}{2} \frac{d[HI]}{dt}$
Now, $\frac{d[H_2]}{dt} = -10^{-4} \text{Ms}^{-1} \implies \frac{d[I_2]}{dt} = 2 \times 10^{-4} \text{Ms}^{-1}$

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

6.(C)
$$X \longrightarrow Y$$
 $Rate_1 = k[X]^m; Rate_2 = 2.25 Rate_1 = k(1.5[X])^m \Rightarrow (1.5)^m = 2.25 \Rightarrow m=2$

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

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

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

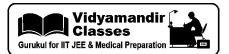
2.
$$t_{1/2} = 3 \text{ hrs}$$
; $t = 15 \text{ hrs} \implies \text{No. of half lives} = \frac{15}{3} = 5$

$$\Rightarrow \frac{n_t}{n_0} = \left(\frac{1}{2}\right)^5 = \frac{1}{32} \Rightarrow g_{left} = \frac{1}{32} \times 100 \,gm = 3.125 \,gm$$

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

$$\Rightarrow \frac{k_{37^{\circ}C}}{k_{27^{\circ}C}} = 5 \Rightarrow \log_{10} \frac{k_{2}}{k_{1}} = \log_{10} 5 = \frac{E_{a}}{2.303 \times 2} \times \frac{(310 - 300)}{300 \times 310} \Rightarrow E_{a} = 299.85 \text{ kcal mol}^{-1}$$

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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.
$$k \times 8 = \log_e \frac{C_0}{C_0 - 0.4 C_0} = \ell n \frac{5}{3}$$
 and $k \times t = \log_e \frac{C_0}{C_0 - 0.9 C_0} = \ell n 10$ $t = 36.06 \, \text{min}$

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

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

$$8. \hspace{1cm} k \times 10 = \ell n \, \frac{C_0}{C_0 - 0.2 \, C_0} = \ell n \frac{5}{4} \hspace{1cm} \Rightarrow \hspace{1cm} k = 0.022 \, \, min^{-1} \hspace{1cm} ; \hspace{1cm} k \times t = \ell n \, \frac{C_0}{C_0 - 0.75 \, C_0} = \ell n 4 \hspace{1cm} \Rightarrow \hspace{1cm} t = 62.16 \, \, min = 0.022 \, \, k + 1.0 \, \, k + 1.0$$

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

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

12.(A)
$$\begin{array}{c}
0.06 \,\mathrm{M} \xrightarrow{10 \,\mathrm{hr}} 0.03 \,\mathrm{M} \\
0.12 \,\mathrm{M} \xrightarrow{10 \,\mathrm{hr}} 0.06 \,\mathrm{M}
\end{array}$$
 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)
$$k = Ae^{-Ea/RT} \implies 'A'$$
 has same units as 'k'.

16.(C)
$$C_0 = 0.1 \text{M} \longrightarrow t_{1/2} = 200 \text{ s}$$
 $\Rightarrow t_{1/2} \propto C_0^{-1} \Rightarrow 2^{\text{nd}} \text{ order reaction.}$

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

18.(C)
$$A \longrightarrow B \qquad \Rightarrow k \times 1 = \ln \frac{0.8}{0.2} = \ln 4$$

$$t = 0 \text{ (moles)} \qquad 0.8 \qquad -$$

$$t = 1 \text{ hr} \qquad 0.2 \qquad 0.6$$

$$A \longrightarrow B \qquad \Rightarrow k \times 1 = \ln \frac{0.9}{0.225} = \ln 4$$

$$A \longrightarrow B \qquad \Rightarrow k \times 1 = \ell n \frac{6.5}{0.225} = \ell n 4$$

$$0.9 \qquad -$$

$$t = 0 \text{ (moles)}$$
 0.9 -
 $t = t \text{ hr}$ 0.225 0.675 $\Rightarrow t = 1 \text{ hr}$

EXERCISE-C

1. Radioactive decay follows first order kinetics.

 $\therefore \qquad t_{1/2} = \frac{\ell n}{\lambda}, \text{ where } \lambda = \text{disintegration constant or rate constant.}$

$$\Rightarrow \qquad \lambda = \frac{\ln 2}{3.8} = 0.18 \text{ day}^{-1}$$

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

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

$$\therefore \qquad \ell n \frac{N_0}{N_t} = \lambda t$$

$$\Rightarrow$$
 ℓ n20 = 0.18 t \Rightarrow t = 16.63 days

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

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

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

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

$$\therefore \qquad \frac{\ell n2}{\lambda_X} = \frac{1}{\lambda_Y} \qquad \Rightarrow \qquad \lambda_X = \ell n2 \times \lambda_Y$$

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

- 4.(A) All these particles have same energy $1/2 \text{ mv}^2$. \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.

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

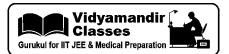
6.(D) For
$$X_1 \Rightarrow N_t^1 = N_0 e^{-10\lambda t}$$

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

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

$$\Rightarrow \qquad e^{-9\lambda t} = e^{-1} \qquad \Rightarrow \qquad t = \frac{1}{9\lambda}$$

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- 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

$$A_t = 6000 \text{ dps}$$

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

$$n=2$$

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

$$\Rightarrow$$
 A₀ = 24000 dps

- **9.(CD)** For ${}_{1}^{1}H$, 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.

$$t_{1/2} = \frac{\ell n2}{\lambda}$$
 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 =
$$1 \times e^{-\frac{\ln 2}{55}} \times 5 \times 60$$

$$=0.023$$
 gms.

Since, decay constant of P_0 is $43.32s^{-1}$, \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.,

- : in five minutes, negligible amount of Pb is decayed
- :. After five minutes,

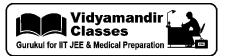
mass of Po left
$$\approx 0 \text{ gm}$$

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

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

14.(B)
$$_{3}\text{Li}^{6} + _{0}\text{n}^{1} \longrightarrow {}_{2}\text{He}^{4} + _{1}\text{H}^{3}$$

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



$$N_0 \equiv x$$

$$N_t \equiv x - y$$

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

Also, given:
$$\frac{x-y}{y} = 3$$

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

$$\Rightarrow \log \frac{N_0}{N_t} = \frac{\ln 2}{k} \times \frac{1}{2.303} \times t$$

$$\Rightarrow \log \frac{4}{3} = \frac{\ln 2}{4.5 \times 10^9} \times \frac{1}{2.303} \times t$$

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

16.(AC) When neutron $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$ is emitted, then atomic no. remains same but mass no. decreases by 1.

So,
$${}^{27}_{13}\text{Al} + {}^{4}_{2}\text{He} \longrightarrow {}^{30}_{15}\text{P} + {}^{1}_{0}\text{n}$$

$${}_{1}^{2}\text{H} + {}_{1}^{3}\text{H} \longrightarrow {}_{2}^{4}\text{He} + {}_{0}^{1}\text{n}$$

17.(B) For stable nucleus, we have

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

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

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

Nucleus decays into proton and emits an electron.

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

Atomic number remains same but mass number Change.

20.(D) According to group displacement law.