Chemical Kinetics

1. For a chemical reaction, $2X + Y \longrightarrow Z$, the rate of appearance of Z is 0.05 mol L^{-1} per min. Find the rate of disappearance of x in mol $L^{-1} min^{-1}$.

2. For the reaction at 273 K
   $$NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$$
   It is observed that the pressure of $NO(g)$ falls from 700 mm Hg to 500 mm Hg in 250 s. Calculate the average rate of reaction in $10^{-3} atm\ s^{-1}$

3. For a first order reaction, calculate the ratio between the time taken to complete 3/4th of the reaction and time taken to complete half of the reaction.

4. The half-life period and initial concentration for a reaction are as follows.

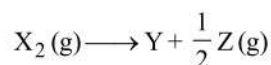 | Initial concentration (M) | 350 | 540 | 158 |
   |---|---|---|---|
   | $t_{1/2}$ (hr) | 425 | 275 | 941 |

   What is order of reaction?

5. The rate of a reaction triples when temperature changes from 20ºC to 50ºC. Calculate energy of activation for the reaction in kJ mol^{-1} (R = 8.314 $JK^{-1} mol^{-1}$).

6. Sucrose decomposes in acid solution into glucose and fructose according to the first order rate law with $t_{1/2} = 3.00$ hours. What fraction of the sample of sucrose remains after 8 hours ?

7. A reaction takes place in various steps. The rate constant for first, second, third and fifth steps are k_1, k_2, k_3 and k_5 respectively. The overall rate constant is given by $k = \dfrac{k_2}{k_3}\left(\dfrac{k_1}{k_5}\right)^{1/2}$.

   If activation energy are 40, 60, 50 and 10 kJ/mol respectively, find the overall energy of activation (kJ/mol).

8. The half life decomposition of gaseous CH_3CHO at constant temperature but at initial pressure of 364 mm and 170 mm of Hg were 410 sec, and 880 sec respectively. Find the order of the reaction.

9. A gaseous reaction
   $$X_2(g) \longrightarrow Y + \frac{1}{2}Z(g)$$
   There is increase in pressure from 100 mm to 120 mm in 5 minutes. Calculate the rate of disappearance of X_2 in mm min^{-1}.

10. The reaction $X \rightarrow Y$ is an exothermic reaction. Activation energy of the reaction for X into Y is 150 kJ mol^{-1}. Enthalpy of reaction is 135 kJ mol^{-1}. Calculate the activation energy for the reverse reaction, $Y \rightarrow X$ in kJ mol^{-1}.

11. 2 g of a radioactive sample having half-life of 15 days was synthesised on Ist Jan. 2009. What is the amount of the sample left behind on Ist March, 2009 (including both the days) in g?

12. Half-lives of decomposition of NH_3 on the surface of a catalyst for different initial pressures are given as:

P(torr)	200	300	500
$t_{1/2}$(min)	10	15	25

    Find the order of the reaction.

13. The decomposition of ammonia on tungsten surface at 500 K follows zero order kinetics. The half-life period of this reaction is 45 minutes when the initial pressure is 4 bar. Find the half-life period (in minutes) of the reaction when the initial pressure is 16 bar at the same temperature.

14. In a chemical reaction A is converted into B. The rates o reaction, starting with initial concentrations of A as 2×10^{-3} M and 1×10^{-3} M, are equal to $2.40 \times 10^{-4} Ms^{-1}$ and $0.60 \times 10^{-4} Ms^{-1}$ respectively. Find the order of reaction with respect to reactant A.

15. The instantaneous rate of disappearance of MnO_4^- ion in the following reaction is $4.56 \times 10^{-3} Ms^{-1}$.
    $$2MnO_4^- + 10I^- + 16H^+ \rightarrow 2Mn^{2+} + 5I_2 + 8H_2O$$
    Find the rate of appearance I_2 in Ms^{-1}.

SOLUTIONS

1. (0.1) Rate of reaction

$$= -\frac{1}{2}\frac{d[X]}{dt} = -\frac{d[Y]}{dt} = +\frac{d[Z]}{dt} \quad \quad \text{.... (i)}$$

∴ Rate of appearance of

$$z = \frac{d[Z]}{dt} = 0.05 \text{ mol L}^{-1} \text{ per min.}$$

∴ Rate of disappearance of $x = -\frac{d[X]}{dt}$

From equation (i), we get

$$-\frac{1}{2}\frac{d[X]}{dt} = \frac{d[Z]}{dt} \quad \therefore \quad -\frac{d[X]}{dt} = 2 \times \frac{d[Z]}{dt}$$

$$= 2 \times \frac{d[Z]}{dt} = 2 \times 0.05 = 0.1 \text{ mol L}^{-1} \text{ min}^{-1}$$

2. (1.053) $NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$

Average rate $= \dfrac{\text{Change of pressure}}{\text{Change of time}} = \dfrac{\Delta P}{\Delta t}$

$$= \frac{700 - 500}{250} = \frac{200}{250}$$

$$= \frac{200}{760 \times 250} \text{ atm s}^{-1} = 1.053 \times 10^{-3} \text{ atm s}^{-1}$$

3. (2) $t_{1/2} = \dfrac{0.69}{k}, \quad t_{3/14} = t_{75\%}$

$$t_{3/4} = \frac{2.303}{k} \log \frac{a}{\left(a - \frac{3a}{4}\right)}$$

$$= \frac{2.303}{k} \log 4 = \frac{2.303}{k} \times 2 \times 0.3010 = \frac{0.69 \times 2}{k}$$

$$\frac{t_{3/4}}{t_{1/2}} = \frac{0.69 \times 2}{k} \times \frac{k}{0.69} \Rightarrow t_{3/4} = 2t_{1/2}$$

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

For I $\quad \Rightarrow \quad 425 \propto (350)^{1-n} \quad$ .... (i)

For II $\quad \Rightarrow \quad 275 \propto (540)^{1-n} \quad$ .... (ii)

For III $\quad \Rightarrow \quad 941 \propto (158)^{1-n} \quad$ .... (iii)

By Eqns. (i) and (ii), $\dfrac{425}{275} = \left(\dfrac{350}{540}\right)^{1-n}$

Taking log $\Rightarrow \log\dfrac{425}{275}$

$$= (1-n)\log\frac{350}{540} \Rightarrow n = 2$$

5. (28.81) $\log\dfrac{k_2}{k_1} = \dfrac{E_a}{R \times 2.303}\left[\dfrac{T_2 - T_1}{T_1 T_2}\right]$

Given $\dfrac{k_2}{k_1} = 3$; R = 8.314 JK^{-1} mol^{-1};

$T_1 = 20 + 273 = 293$ K and $T_2 = 50 + 273 = 323$ K

Substituting the given values in the Arrhenius equation,

$$\log 3 = \frac{E_a}{8.314 \times 2.303}\left[\frac{323 - 293}{323 \times 293}\right]$$

$$E_a = \frac{2.303 \times 8.314 \times 323 \times 293 \times 0.477}{30}$$

$$= 28811.85 \text{ J mol}^{-1} = 28.81 \text{ kJ mol}^{-1}$$

6. (0.158) Decomposition of sucrose is first order reaction,

$$k = \frac{2.303}{t} \log \frac{[A_0]}{[A]} \quad \quad \text{...(i)}$$

For time, $t_{1/2} = 3.0$ hr

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{3 \text{ hr}} = 2.231 \text{ hr}^{-1}$$

Substituting $k = 0.231$ hr^{-1} in (i) we get,

$$2.231 = \frac{2.303}{8} \log \frac{[A_0]}{[A]}$$

$$\log \frac{[A_0]}{[A]} = 0.8024$$

$$\frac{[A_0]}{[A]} = \text{Antilog } 0.8024 = 6.345$$

∴ Fraction of sample remains

$$= \frac{[A]}{[A_0]} = \frac{1}{6.345} = 0.158$$

7. (25) $k = A.e^{-E_a/(RT)}$

∴ Effective overall energy of activation

$$E_a = E_a(2) - E_a(3) + \frac{1}{2}E_a(1) - \frac{1}{2}E_a(5)$$

$$= 60 - 50 + \frac{1}{2} \times 40 - \frac{1}{2} \times 10 = 25 \text{ kJ/mol}$$

8. (2) $\dfrac{t_{1/2}(1)}{t_{1/2}(2)} = \left[\dfrac{p(2)}{p(1)}\right]^{n-1},$

$$\frac{880}{410} = \left[\frac{364}{170}\right]^{n-1},$$

$$[2.14]^1 = [2.14]^{n-1} \; ; \; n - 1 = 1 \; ; \; n = 2$$

9. **(8)** The increase in pressure shows the increase in conc. of Z.

Rate of appearance of $Z = \dfrac{120-100}{5} = 4 \text{ mm min}^{-1}$

Rate of disappearance of $X_2 = 2 \times$ rate of appearance of $Z = 2 \times 4 \text{ mm min}^{-1} = 8 \text{ mm min}^{-1}$

10. **(285)** $X \longrightarrow Y$; $\Delta H = -135 \text{ kJ/mol}$,

$E_a = 150 \text{ kJ/mol}$

For an exothermic reaction

$E_a(\text{F.R.}) = \Delta H + E'_a(\text{B.R.})$

$150 = -135 + E'_a(\text{B.R.})$

$E'_a(\text{B.R.}) = 285 \text{ kJ/mol}$

11. **(0.125)** Given, $t_{1/2} = 15$ days

$N_o = 2$ g

From Ist Jan. 2009 to Ist March 2009

no. of day $= 60$

$\therefore$ no. of half lives $= 4$

$\therefore \dfrac{N}{N_o} = \left(\dfrac{1}{2}\right)^4$

or $\dfrac{N}{2} = \dfrac{1}{16}$

$N = 0.125$ g

12. **(0)** $\dfrac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\dfrac{a_2}{a_1}\right)^{n-1}$; $\dfrac{10}{15} = \left(\dfrac{300}{200}\right)^{n-1}$

or, $\left(\dfrac{2}{3}\right)^1 = \left(\dfrac{3}{2}\right)^{n-1} = \left(\dfrac{2}{3}\right)^{1-n}$; $1-n = 1$, $n = 0$

13. **(180)** For a zero order reaction,

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

$(t_{1/2})_1 \propto P_1$

$(t_{1/2})_2 \propto P_2$

$\dfrac{(t_{1/2})_2}{(t_{1/2})_1} = \dfrac{P_2}{P_1}$, $\dfrac{(t_{1/2})_2}{45} = \dfrac{16}{4}$

$(t_{1/2})_2 = \dfrac{16}{4} \times 45 = 180 \text{ min}$

14. **(2)** $A \longrightarrow B$

Initial concentration	Rate of reaction
2×10^{-3} M	2.40×10^{-4} Ms^{-1}
1×10^{-3} M	0.60×10^{-4} Ms^{-1}

rate of reaction

$r = k[A]^x$

where $x = $ order of reaction

hence

$2.40 \times 10^{-4} = k[2 \times 10^{-3}]^x$ ......(i)

$0.60 \times 10^{-4} = k[1 \times 10^{-3}]^x$ ......(ii)

On dividing eqn.(i) from eqn. (ii) we get

$4 = (2)^x$

$\therefore x = 2$

i.e. order of reaction $= 2$

15. **(0.0114)** $\dfrac{d\text{MnO}_4^-}{dt} = 4.56 \times 10^{-3} \text{ Ms}^{-1}$ (Given)

From the reaction given,

$-\dfrac{1}{2}\dfrac{d\text{MnO}_4^-}{dt} = \dfrac{4.56 \times 10^{-3}}{2} \text{ Ms}^{-1}$

$-\dfrac{1}{2}\dfrac{d\text{MnO}_4^-}{dt} = \dfrac{1}{5}\dfrac{d\text{I}_2}{dt}$

$\therefore -\dfrac{5}{2}\dfrac{d\text{MnO}_4^-}{dt} = \dfrac{d\text{I}_2}{dt}$

On substituting the given value

$\therefore \dfrac{d\text{I}_2}{dt} = \dfrac{4.56 \times 10^{-3} \times 5}{2} = 1.14 \times 10^{-2} \text{ M/s}$

$= 0.0114 \text{ Ms}^{-1}$.