

Chemical Kinetics

- For a chemical reaction, $2X + Y \longrightarrow Z$, the rate of appearance of Z is $0.05 \text{ mol L}^{-1} \text{ per min}$. Find the rate of disappearance of x in $\text{mol L}^{-1} \text{ min}^{-1}$.
- For the reaction at 273 K
 $\text{NO}(\text{g}) + \text{O}_3(\text{g}) \longrightarrow \text{NO}_2(\text{g}) + \text{O}_2(\text{g})$
 It is observed that the pressure of $\text{NO}(\text{g})$ falls from 700 mm Hg to 500 mm Hg in 250 s. Calculate the average rate of reaction in $10^{-3} \text{ atm s}^{-1}$
- 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.
- 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

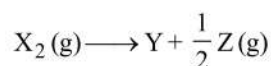
What is order of reaction?

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

$$\text{given by } k = \frac{k_2}{k_3} \left(\frac{k_1}{k_5} \right)^{1/2}$$

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

- 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.
- A gaseous reaction



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} .

- 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} .
- 2 g of a radioactive sample having half-life of 15 days was synthesised on 1st Jan. 2009. What is the amount of the sample left behind on 1st March, 2009 (including both the days) in g?
- Half-lives of decomposition of NH_3 on the surface of a catalyst for different initial pressures are given as:

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

Find the order of the reaction

- 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.
- In a chemical reaction A is converted into B. The rates of reaction, starting with initial concentrations of A as $2 \times 10^{-3} \text{ M}$ and $1 \times 10^{-3} \text{ M}$, are equal to $2.40 \times 10^{-4} \text{ Ms}^{-1}$ and $0.60 \times 10^{-4} \text{ Ms}^{-1}$ respectively. Find the order of reaction with respect to reactant A.
- The instantaneous rate of disappearance of MnO_4^- ion in the following reaction is $4.56 \times 10^{-3} \text{ Ms}^{-1}$.
 $2\text{MnO}_4^- + 10\text{I}^- + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 5\text{I}_2 + 8\text{H}_2\text{O}$
 Find the rate of appearance I_2 in Ms^{-1} .

SOLUTIONS

1. (0.1) Rate of reaction

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

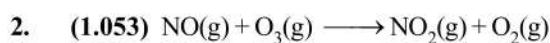
∴ Rate of appearance of

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

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

From equation (i), we get

$$\begin{aligned} -\frac{1}{2} \frac{d[X]}{dt} &= \frac{d[Z]}{dt} \quad \therefore -\frac{d[X]}{dt} = 2 \times \frac{d[Z]}{dt} \\ &= 2 \times \frac{d[Z]}{dt} = 2 \times 0.05 = 0.1 \text{ mol L}^{-1} \text{ min}^{-1} \end{aligned}$$



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

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

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

3. (2) $t_{1/2} = \frac{0.69}{k}$, $t_{3/4} = t_{75\%}$

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

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

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

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

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

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

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

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

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

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

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

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

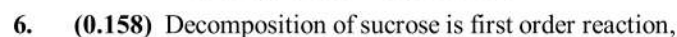
$T_1 = 20 + 273 = 293 \text{ K}$ and $T_2 = 50 + 273 = 323 \text{ K}$

Substituting the given values in the Arrhenius equation,

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

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

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



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

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

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

Substituting $k = 0.231 \text{ hr}^{-1}$ 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) $k = A \cdot e^{-E_a/(RT)}$

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

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

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

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

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

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

$$N_o = 2 \text{ g}$$

From 1st Jan. 2009 to 1st March 2009

no. of day = 60

$$\therefore \text{no. of half lives} = 4$$

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

$$\text{or } \frac{N}{2} = \frac{1}{16}$$

$$N = 0.125 \text{ g}$$

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

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

13. (180) For a zero order reaction,

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

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

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

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

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

14. (2) $A \longrightarrow B$

Initial concentration Rate of reaction

$2 \times 10^{-3} \text{ M}$ $2.40 \times 10^{-4} \text{ Ms}^{-1}$

$1 \times 10^{-3} \text{ M}$ $0.60 \times 10^{-4} \text{ Ms}^{-1}$

rate of reaction

$$r = k[A]^x$$

where $x =$ order of reaction

hence

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

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

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

$$4 = (2)^x$$

$$\therefore x = 2$$

i.e. order of reaction = 2

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

From the reaction given,

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

$$-\frac{1}{2} \frac{d\text{MnO}_4^-}{dt} = \frac{1}{5} \frac{dI_2}{dt}$$

$$\therefore -\frac{5}{2} \frac{d\text{MnO}_4^-}{dt} = \frac{dI_2}{dt}$$

On substituting the given value

$$\therefore \frac{dI_2}{dt} = \frac{4.56 \times 10^{-3} \times 5}{2} = 1.14 \times 10^{-2} \text{ M/s}$$

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