SUBJECTIVE SOLVED EXAMPLES

Example - 1 *The vapour pressure of two miscible liquids 'A' and 'B' are 300 and 500 mm of Hg respectively. In a flask, 10 mol of 'A' is mixed with 12 mol of 'B'. However, as soon as 'B' is added, 'A' starts polymerising into a completely insoluble solid. This polymerisation follows first-order kinetics. After 100 minutes, 0.525 mol of a solute is dissolved which arrests the polymerisation completely. The final vapour pressure of the solution is 400 mm of Hg. Estimate the rate constant of the polymerisation reaction. Assume negligible volume change on mixing and polymerisation, and ideal behaviour for the final solution.* [*Given,* $\log_{10} 11 = 1.04$]

SOLUTION :

We have :

$P_A^0 = 300\text{ mm Hg}$ and $P_B^0 = 500\text{ mm Hg}$

$n_{A0} = 10\text{ mol}$ and $n_{B0} = 12\text{ mol}$

Let the amount of A after 100 min is reduced to n_A.

At this stage :

$$n_{Total} = n_A + n_B + n_{Solute} = n_A + 12 + 0.525$$

Mole fractions of A and B in the solution will be

$$\chi_A = \frac{n_A}{n_A + 12.525} \text{ and } \chi_B = \frac{12}{n_A + 12.525}$$

Since $P_{Total} = P_A^0 \chi_A + P_B^0 \chi_B$, we get :

$$400 = 300 \times \frac{n_A}{n_A + 12.525} + 500 \times \frac{12}{n_A + 12.525}$$

Solving for n_A, we get :

$$n_A = 9.90\text{ mol}$$

$$nA \longrightarrow A_n$$

For the first-order kinetics, we have :

$$kt = 2.303 \log_{10} \frac{[A]_0}{[A]_t}$$

or $$k(100\text{ min}) = 2.303 \log_{10} \frac{10}{9.9}$$

$$\Rightarrow \quad k = 1.00 \times 10^{-4}\text{ min}^{-1} = 1.67 \times 10^{-6}\text{ s}^{-1}$$

Example - 2 *A first order reaction :* $A \longrightarrow B$ *requires activation energy of 89 kJ/mol. When 20% solution of A was kept at 27°C for 40 minutes, 25% decomposition took place. What will be the percent decomposition in the same time in a 30% solution maintained at 37°C ? Assume that the activation energy remains constant in this range of temperature.*

SOLUTION :

> ***Note :*** It does not matter whether you take 20%, 30%, 40% or 70% of 'A' because first order reaction is independent of the initial concentration of reactant.

At 27°C, 20% of A decomposes 25%

$$\Rightarrow \quad kt = 2.303 \log_{10} \frac{C_0}{C_t}$$

$$= 2.303 \log_{10} \frac{1}{1-\alpha} = \ell n \frac{1}{1-\alpha} \quad [\alpha = 0.25]$$

$$\Rightarrow \quad k(40) = \ell n \frac{100}{75}$$

$$\Rightarrow \quad k\text{ (at 300 K)} = \frac{1}{40} \ell n \frac{4}{3} \text{ min}^{-1}$$

Using Arrhenius equation find k at 310K.

$$\log_{10} \frac{k_{310}}{k_{300}} = \frac{E_a}{2.303\text{ R}} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\log_{10} \frac{k_{310}}{k_{300}} = \frac{89 \times 10^3}{2.303 \times 8.31} \left(\frac{310 - 300}{300 \times 310} \right) = 0.5$$

$$\Rightarrow \quad k(\text{at 310 K}) = k(\text{at 300K}) \times \sqrt{10}$$

Now calculate % decomposition at 310K using first order kinetics.

$$kt = 2.303 \log_{10}\frac{C_0}{C_t}$$

$$\Rightarrow \quad k \times 40 = \ell n\frac{1}{1-\alpha}$$

$$\Rightarrow \quad \ell n\frac{1}{1-\alpha} = \left[\left(\frac{1}{40}\,\ell n\frac{4}{3}\right)\times\sqrt{10}\right]\times 40 = 0.91$$

$$\Rightarrow \quad \log_{10}\frac{1}{1-\alpha} = \frac{0.91}{2.303} = 0.40$$

$$\frac{1}{1-\alpha} \approx 2.5 \quad \Rightarrow \quad \alpha = 0.6$$

⇒ $\alpha = 0.6 \equiv 60.0\,\%$ decomposition of A at 310 K.

Example - 3 *A certain reaction $A + B \longrightarrow$ products ; is first order w.r.t. each reactant with $k = 5.0 \times 10^{-3}\ M^{-1}s^{-1}$. Calculate the concentration of A remaining after 100s if the initial concentration of A was 0.1 M and that of B was 6.0 M. State any approximation made in obtaining your result.*

SOLUTION :

$A + B \longrightarrow$ products

Given : Rate = k [A][B] (2nd Order reaction)

Now, since [B] >> [A], [B] can be assumed to remain constant throughout the reaction. Thus, the rate law for the reaction, becomes :

Rate $\approx k_0$ [A]

where $k_0 = k\,[B] = 5.0 \times 10^{-3} \times 6.0\ s^{-1} = 3.0 \times 10^{-2}\ s^{-1}$

Thus, the reaction is now of first order [Pseudo first order].

Note :

	A	+	B	$\xrightarrow{k}$	products
	0.1M		6.0M		
	$0.1 - x$		$6.0 - x$		

Using, $2.303 \log_{10}\frac{C_{0A}}{C_{tA}} = k_0 t$

$$\Rightarrow \quad 2.303 \log_{10}\frac{0.1}{C_{tA}} = k_0 t = 3$$

$$\Rightarrow \quad \log_e\frac{0.1}{C_{tA}} = 3 \qquad [\because \log_e x = 2.303 \log_{10} x]$$

$$\Rightarrow \quad C_{tA} = 10\,e^{-3} = 5\times10^{-3}\ M$$

Check your approximation :

$$[B]_{change} = x = 0.1 - 5\times10^{-3} = 0.095\ M$$

$$\%\,[B]_{change} = \frac{0.095}{6}\times 100\% = 1.58\%$$

Example - 4 *The gas phase decomposition of N_2O_5 to NO_2 and O_2 is monitored by measurement of total pressure. The following data are obtained.*

P_{total} *(atm)*	0.154	0.215	0.260	0.315	0.346
Time (sec)	1	52	103	205	309

Find the average rate of disappearance of N_2O_5 for the time interval between each interval and for the total time interval. [Hint : Integrated rate law is NOT to be used].

SOLUTION :

	$2N_2O_5(g)$	$\longrightarrow$	$4NO_2(g)$	+	$O_2(g)$
Initial Pressure (at t = 0)	P_0		0		0
At t = t	$P_0 - 2x$		$4x$		x

Now : $P_{Total} = (P_0 - 2x) + 4x + x \qquad \Rightarrow \qquad x = \frac{1}{3}(P_{Total} - P_0)$

$$P_{N_2O_5} = P_0 - 2x = \frac{(5P_0 - 2P_{Total})}{3} = P_t$$

Thus, $\Delta P_{N_2O_5} = \frac{2}{3}(P_{t1} - P_{t2})$ where P_{t2} and P_{t1} are the total pressures at time instants t_2 and t_1 $(t_2 > t_1)$ respectively

P_{total} (atm)	Time (sec)	$\frac{\Delta P_{N_2O_5}}{\Delta t}$ = Avg. Rate of disappearance of N_2O_5 (atm/sec.)
0.154	1	$\frac{2}{3}\frac{(0.154-0.215)}{(52-1)} = -7.97 \times 10^{-4}$
0.215	52	$\frac{2}{3}\frac{(0.215-0.260)}{(103-52)} = -5.88 \times 10^{-4}$
0.260	103	$\frac{2}{3}\frac{(0.260-0.315)}{(205-103)} = -3.59 \times 10^{-4}$
0.315	205	$\frac{2}{3}\frac{(0.315-0.346)}{(309-205)} = -1.99 \times 10^{-4}$
0.346	309	

Example - 5 *In an ore containing Uranium, the ratio of U^{238} to Pb^{206} nuclei is 3. Calculate the age of the ore, assuming that all the lead present in the ore is the final stable product of U^{238}. The half life of U^{238} is 4.5×10^9 years.*

SOLUTION :

Note : The radio active decay follows first order kinetics. Here, we take $N_0 \equiv C_0$ and $N_t \equiv C_t$ and $\lambda \equiv k$

The first order rate equation for radioactive decay is :

$$\lambda t = 2.303 \log \frac{N_0}{N_t} \qquad \text{where } \lambda = \frac{0.693}{t_{\frac{1}{2}}}$$

N_0 = initial nuclei (at $t = 0$)

N_t = final nuclei (at t)

λ = decay constant or disintegration constant

$$U^{238} \longrightarrow Pb^{206}$$

$$\begin{array}{llll} N_0 & \equiv & x & 0 \\ N_t & \equiv & x - y & y \end{array}$$

$$\Rightarrow \quad \frac{N_0}{N_t} = \frac{x}{x-y}$$

Using $\lambda t = 2.303 \log_{10} \frac{x}{x-y}$

Given : $\frac{x-y}{y} = 3 \qquad \Rightarrow \qquad \frac{x}{x-y} = \frac{4}{3}$

$$\Rightarrow \quad t = \frac{2.303}{0.693} \times 4.5 \times 10^9 \log_{10} \frac{4}{3}$$

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

Example - 6 *The nucleidic ratio of $_1H^3$ to $_1H^1$ in a sample of water is* $8.0 \times 10^{-18} : 1$. *Tritium undergoes decay with a half life period of* 12.0 *years. How many tritium atoms would a* 10.0 *gm of such sample contain* 36 *years after the original sample is collected ?*

SOLUTION :

The ratio of tritium atoms to that of H–atoms will be same as the ratio of moles of T-atoms to that of H–atoms, since 1 mole of $T_2O \equiv 2$ mole of T atoms and 1 mole of $H_2O \equiv 2$ mole of H atoms.

Calculate the initial number of tritium atoms.

$$10 \text{ gm} = \text{mass of } T_2O + \text{mass of } H_2O$$

$$= n_{T_2O} \times 22 + n_{H_2O} \times 18$$

$$= \left(8 \times 10^{-18}\, n_{H_2O}\right) \times 22 + n_{H_2O} \times 18$$

$$\approx n_{H_2O} \times 18$$

$$\Rightarrow \quad n_{H_2O} = \frac{10}{18} = \frac{5}{9}$$

$$\Rightarrow \quad n_{T_2O} = \frac{5}{9} \times 8 \times 10^{-18} = \frac{40}{9} \times 10^{-18}$$

$$\Rightarrow \quad (N_T)_O = \left(N_{T_2O}\right) \times 2 = \left(\frac{40}{9} \times 10^{-18} \times 6 \times 10^{23}\right) \times 2$$

$$= 5.33 \times 10^6 \text{ atoms}$$

$$\text{No. of half lives} = \frac{36}{12} = 3$$
(x)

$$\text{Use}: \ N_t = N_0 \left(\frac{1}{2}\right)^x = N_0 \left(\frac{1}{2}\right)^3 = \frac{1}{8} \times 5.33 \times 10^6 \text{ atoms}$$

$$= 6.66 \times 10^5 \text{ atoms}$$

Example - 7 *Dimethyl ether decomposes according to the following reaction :*

$$CH_3 - O - CH_3\,(g) \longrightarrow CH_4\,(g) + CO(g) + H_2\,(g)$$

At a certain temperature, when ether was heated in a closed vessel, the increase in pressure with time was noted down.

Time (min)	0	10	20	30
Pressure (mm Hg)	420	522	602	678

(i) *Show that the reaction is first order.* **(ii)** *Compute the pressure of CO (g) after 109 minutes.*

SOLUTION :

$$CH_3 - O - CH_3\,(g) \longrightarrow CH_4\,(g) + CO\,(g) + H_2\,(g)$$

(all are gases)

time	$CH_3 - O - CH_3$	CH_4	CO	H_2
$t = 0$	$C_0 \equiv P_0$	0	0	0
$t = t$	$C_t \equiv P_0 - x$	x	x	x

$$\Rightarrow \quad P_t = P_0 + 2x$$

$$\Rightarrow \quad x = \frac{1}{2}\left(P_t - P_0\right)$$

$$\Rightarrow \quad \frac{C_0}{C_t} = \frac{P_0}{P_0 - x} = \frac{2P_0}{3P_0 - P_t}$$

Now find k_1, k_2 and k_3 using the first order kinetics

$$kt = 2.303 \log_{10} \frac{2P_0}{3P_0 - P_t}$$

$$k_1 = \frac{2.303}{10} \log_{10} \frac{2(420)}{3(420) - 522} = 0.0129 \text{ min}^{-1}$$

$$k_2 = \frac{2.303}{20} \log_{10} \frac{2(420)}{3(420) - 602} = 0.0122 \text{ min}^{-1}$$

$$k_3 = \frac{2.303}{30} \log_{10} \frac{2(420)}{3(420) - 678} = 0.0123 \text{ min}^{-1}$$

As $k_1 \sim k_2 \sim k_3$, the reaction is first order.

$$k_{average} = \frac{1}{3}(k_1 + k_2 + k_3) = 0.0127\ \text{min}^{-1}$$

$$\Rightarrow \quad t_{1/2} = \frac{0.693}{k} = 54.56\ \text{min}$$

$$\text{No. of half lives} = \frac{109}{54.56} \approx 2$$

$$\Rightarrow \quad (P_t)_{CH_3OCH_3} = P_0\left(\frac{1}{2}\right)^2 = \frac{420}{4}$$

$$= 105\ \text{mm Hg} = P_0 - x$$

$$\Rightarrow \quad x = P_{CO} = 420 - 105 = 315\ \text{mm Hg}$$

Example - 8 *The decomposition of N_2O_5 according to following reaction is first order reaction :*

$$2N_2O_5(g) \longrightarrow 4\,NO_2(g) + O_2(g)$$

After 30 min. from start of the decomposition in a closed vessel, the total pressure developed is found to be 250 mm of Hg and on complete decomposition, the total pressure is 500 mm of Hg. Calculate the rate constant of the reaction.

SOLUTION : $2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$

$t = 0$	P_0	0	0
$t = t$	$P_0 - 2x$	$4x$	x
$t = \infty$	–	$2P_0$	$P_0/2$

P_0 : initial presure ; Let P_t : pressure at 30 min and P_∞ : pressure at the end of decomposition

$$\Rightarrow \quad P_t = P_0 + 3x \quad \Rightarrow \quad x = \frac{1}{3}(P_t - P_0)$$

$$\text{and} \quad P_\infty = 2P_0 + \frac{1}{2}P_0 = \frac{5}{2}P_0$$

$$\Rightarrow \quad P_0 = \frac{2}{5}P_\infty = \frac{2}{5} \times 500 = 200\ \text{mm Hg}$$

For the first order kinetics

$$kt = 2.303\log_{10}\frac{C_0}{C_t}$$

C_0 : initial concentration ; C_t : final concentration

$$\text{Now} \quad \frac{C_0}{C_t} = \frac{P_0}{P_0 - 2x} \quad \text{and} \quad x = \frac{1}{3}(250 - 200) = \frac{50}{3}$$

$$\Rightarrow \quad \frac{C_0}{C_t} = \frac{200}{200 - 2\times\frac{50}{3}} = \frac{6}{5}$$

$$\Rightarrow \quad k = \frac{1}{30} \times 2.303\log_{10}\frac{6}{5} = 6.08 \times 10^{-3}\ \text{min}^{-1}$$

ANSWERS - IN-CHAPTER EXERCISE

A	**1.** 2, 2 L mol^{-1} min^{-1}		**2.** Rate = 0.5 [A]	**3.** D	**4.** C	**5.** D	
	6. C	**7.** CD	**8.** A				
B	**1.** 0.25	**2.** 3.125 gm	**3.** 299.85 kcal mol^{-1}	**5.** 36.06 min	**6.** 3.76 s	**7.** 2, 2.5	
	8. 0.022 min^{-1}, 62.16 min		**9.** D	**10.** A	**11.** A	**12.** A	
	13. D	**14.** B	**15.** B	**16.** C	**17.** D	**18.** C	
C	**1.** 16.43 days	**2.** 0.33 hr	**3.** C	**4.** A	**5.** D	**6.** D	**7.** C
	8. B	**9.** CD	**10.** D	**11.** B	**12.** C	**13.** B	**14.** B
	15. A	**16.** AC	**17.** B	**18.** D	**19.** B	**20.** D	