



DPP – 7 [SPECIAL CASES OF FIRST ORDER REACTIONS]

Chapter: Chemical Kinetics

“Tumhare sapne tumse zyada mehnat deserve karte hain... Aur sach yeh hai—abhi tak tumne utni mehnat ki hi nahi.”

TYPE–1 : Pseudo Order Reactions

- The hydrolysis of ethyl acetate**, $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH}$ is a reaction of
 - zero order
 - first order
 - second order
 - third order
- The acid hydrolysis of ester is –**
 - Pseudo Ist order reaction
 - Bimolecular reaction
 - Pseudo unimolecular reaction
 - All
- The value of rate constant of a pseudo first order reaction _____ .**
 - depends on the concentration of reactants present in small amount.
 - depends on the concentration of reactants present in excess.
 - is independent of the concentration of reactants.
 - depends only on temperature.
- In pseudo unimolecular reactions?**
 - both the reactants are present in low concentration
 - both the reactants are present in same concentration
 - one of the reactants is present in excess
 - one of the reactants is non-reactive
- The rate law of the reaction $\text{A} + 2\text{B} \rightarrow \text{product}$ is given by $\frac{d[P]}{dt} = K[A]^2[B]$. If A is taken in large excess, the order of the reaction will be –**
 - Zero
 - 1
 - 2
 - 3
- The rate for the reaction $\text{RCl} + \text{NaOH(aq)} \rightarrow \text{ROH} + \text{NaCl}$ is given by rate = $k_1[\text{RCl}]$. The rate of the reaction is –**
 - Doubled on doubling the concentration of NaOH
 - Halved on reducing the concentration of RCl to half
 - Decreased on increasing the temperature of reaction
 - Unaffected by increasing the temperature of the reaction

TYPE–2 : Pressure Based Problems

- In the given reaction $\text{PCl}_5(\text{g}) \rightarrow \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ initially only $\text{PCl}_5(\text{g})$ is present at 1.5 atm. After 10 minutes the pressure becomes 2.5 atm. The rate constant of the reaction will be (in minute⁻¹)**

- (1) $0.2303 \log \frac{5}{3}$ (2) $0.2303 \log 3$
 (3) $0.2303 \log \frac{3}{5}$ (4) $0.2303 \log \frac{5}{2}$

8. **The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume.** $\text{SO}_2\text{Cl}_2(\text{g}) \longrightarrow \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$

Experiment	Time/ s^{-1}	Total pressure/atm
1	0	0.5
2	100	0.6

Calculate the rate of the reaction when total pressure is 0.65 atm.

9. **For the decomposition of azoisopropane to hexane and nitrogen at 543 K, the following data are obtained.**

t (sec)	P(mm of Hg)
0	35.0
360	54.0
720	63.0

Calculate the rate constant.

10. **Consider a first order gas phase decomposition reaction given below : $\text{A}(\text{g}) \longrightarrow \text{B}(\text{g}) + \text{C}(\text{g})$. The initial pressure of the system before decomposition of A was p_i . After lapse of time 't', total pressure of the system increased by x units and became ' p_t '. The rate constant k for the reaction is given as**

- (i) $k = \frac{2.303}{t} \log \frac{p_i}{p_i - x}$
 (ii) $k = \frac{2.303}{t} \log \frac{p_i}{2p_i - p_t}$
 (iii) $k = \frac{2.303}{t} \log \frac{p_i}{2p_i + p_t}$
 (iv) $k = \frac{2.303}{t} \log \frac{p_i}{p_i + x}$

11. **N_2O_5 decomposes to NO_2 and O_2 and follows first order kinetics. After 50 minutes, the pressure inside the vessel increases from 50 mm Hg to 87.5 mm Hg. The pressure of the gaseous mixture after 100 minute at constant temperature will be :** [JEE(Main) 2018 Online (15-04-18), 4/120]

- (1) 136.25 mm Hg (2) 108.25 mm Hg
 (3) 175.0 mm Hg (4) 116.25 mm Hg

12. **The reaction $2\text{N}_2\text{O}_5(\text{g}) \longrightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$ follows first order kinetics. The pressure of a vessel containing only N_2O_5 was found to increase from 50 mmHg to 87.5 mm Hg in 30 min. The pressure exerted by the gases after 60 min. will be (Assume temperature remains constant) :** [JEE(Main) 2015 Online (10-04-15), 4/120]

- (1) 125 mm Hg (2) 106.25 mm Hg
 (3) 116.25 mm Hg (4) 150 mm Hg

13. **Formation of NO_2F from NO_2 and F_2 as per the reaction $2\text{NO}_2(\text{g}) + \text{F}_2(\text{g}) \longrightarrow 2\text{NO}_2\text{F}(\text{g})$ is a second order reaction, first order with respect to NO_2 and first order with respect to F_2 . If NO_2 and F_2 are present in a closed vessel in ratio 2:1 maintained at a constant temperature with an initial total pressure of 3 atm, what will be the total pressure in the vessel after the reaction is complete?**

- (1) 1 atm (2) 2 atm
 (3) 2.5 atm (4) 3 atm

14. The gas phase decomposition of A as $A(g) \longrightarrow 2B(g) + C(g)$ follows first order kinetics and pressure measured after 15 minute and infinite time are 205 and 450 mm of Hg respectively, in a constant volume container at a constant temperature. Calculate the total pressure inside the flask after 50 minute.
- (1) 122.5 mm (2) 293.26 mm
 (3) 150 mm (4) 50 mm
15. The reaction $2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$ is first order with respect to N_2O_5 . Which of the following graph would yield a straight line :
- (1) $\log(P_{N_2O_5})$ v/s time with negative slope
 (2) $P_{N_2O_5}^{-1}$ v/s time
 (3) $P_{N_2O_5}$ v/s time
 (4) $\log(P_{N_2O_5})$ v/s time with positive slope
16. The following data were obtained at a certain temperature for the decomposition of ammonia

p (mm)	50	100	200
$t_{1/2}$	3.64	1.82	0.91

The order of the reaction is :-

- (1) 0 (2) 1
 (3) 2 (4) 3
- ### TYPE-3 : Rotation Based Problems
17. Inversion of sucrose ($C_{12}H_{22}O_{11}$) is first-order reaction and is studied by measuring angle of rotation at different instant of time
- $$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$
- (Sucrose \rightarrow Glucose + Fructose). If $(r_\infty - r_0) = a$ and $(r_\infty - r_t) = (a - x)$ (where r_0 , r_t and r_∞ are the angle of rotation at the start, at the time t and at the end of the reaction respectively), then there is 50% inversion when :
- (1) $r_0 = 2r_t - r_\infty$ (2) $r_0 = r_t - r_\infty$
 (3) $r_0 = r_t - 2r_\infty$ (4) $r_0 = r_t + r_\infty$
18. The following data were obtained in an experiment on inversion of cane sugar (a first order kinetics)

Time (min)	0	10	After a long time
Total angle of rotation (degree)	+40	+15	-10

The rate constant (in second^{-1}) is [$\ln 2 = 0.693$]

- (1) 0.0693 (2) 1.15×10^{-3}
 (3) 0.693 (4) 1.15×10^{-2}
19. For a reaction $A \longrightarrow B + C$, it was found that at the end of 10 minutes from the start the total optical rotation of the system was 50° and when the reaction is complete, it was 100° . Assuming that only B and C are optically active and dextrorotatory. Calculate the rate constant of this first order reaction.
- (1) 0.693 min^{-1} (2) 0.0693 sec^{-1}
 (3) 0.0693 min^{-1} (4) 0.00693 sec^{-1}