

CHEMICAL KINETICS

SOLVED SUBJECTIVE EXERCISE

Very Short Answer Type Questions (1 mark)

1. What will be the effect of temperature on rate constant?

Ans. The rate constant of a reaction is nearly doubled with rise in temperature by 10° . The exact dependence of the rate constant on temperature is given by Arrhenius equation, $k = Ae^{-E_a/RT}$ where A is called frequency factor and E_a is the activation energy of the reaction.

2. What do you understand by 'Rate of reaction'?

Ans. The change in the concentration of any one of the reactants or products per unit time is termed as the rate of reaction.

3. For the reaction $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$, how are the reaction expressions $-\frac{d[H_2]}{dt}$ and $\frac{d[NH_3]}{dt}$ interrelated?

Ans. $-\frac{1}{3} \frac{d[H_2]}{dt} = +\frac{1}{2} \frac{d[NH_3]}{dt}$

4. When does the average rate of reaction become equal to instantaneous rate?

Ans. Average rate becomes equal to instantaneous rate when the interval, Δt , approaches zero, i.e., it becomes infinitesimally

small. Thus, r_{inst} , i.e., $\left(\frac{dx}{dt}\right) = \lim_{\Delta t \rightarrow 0} \frac{\Delta x}{\Delta t}$

5. For the reaction $A \rightarrow B$, the rate of reaction becomes twenty seven times when the concentration of A is increased three times. What is the order of the reaction?

Ans. $r = k[A]^n = ka^n$

When concentration is increased three times, $[A] = 3a$.

Hence, $27r = k(3a)^n$

$\therefore \frac{27r}{r} = \frac{k(3a)^n}{ka^n}$

or $27 = 3^n$

or $3^3 = 3^n$

$\therefore n = 3$.

6. When could order and molecularity of a reaction (i) be the same and (ii) be different?

Ans. (i) If the rate determining step involves all the reactants taking part in the reaction, i.e., it is a one-step reaction, then order and molecularity of the reaction is same.

(ii) If reaction involves more than one step, then order and molecularity are different.

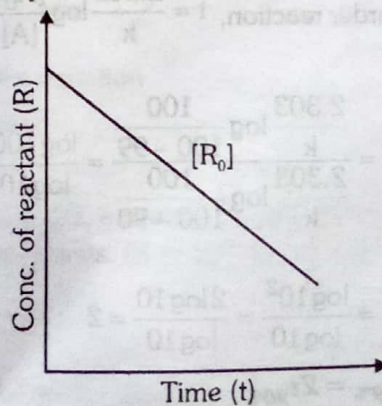
7. A reaction: Reactant \rightarrow Product is represented by

(i) the order of the reaction in this case,

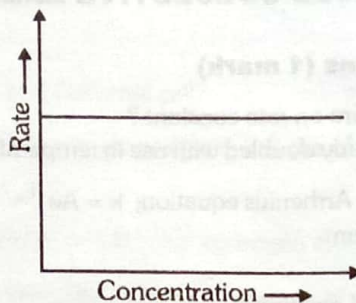
(ii) What does the slope of the graph represent?

Ans. (i) The reaction is of the zero order.

(ii) Slope of the straight line graph $= -k = \frac{d[R]}{dt}$.



8. Following graph is a plot of the rate of a reaction vs concentration of the reactant. What is the order of the reaction?



Ans. Zero order reaction.

9. Define threshold energy of a reaction.

Ans. Threshold energy is the minimum energy which must be possessed by reacting molecules in order to undergo effective collision which leads to formation of product molecule.

10. A reaction is 50% complete in 2 hours and 75% complete in 4 hours. What is the order of the reaction?

Ans. As $t_{75\%} = 2t_{50\%}$
Therefore it is a first order reaction.

Short Answer Type Questions (2 mark)

11. A reactant has a half-life of 10 min.

- (i) Calculate the rate constant for the first order reaction.
- (ii) What fraction of the reactant will be left after an hour of the reaction has occurred?

Ans. (i) $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{10} = 0.0693 \text{ min}^{-1}$

(ii) $N = N_0 \left(\frac{1}{2}\right)^y$

where, $y = \frac{\text{Total time}}{t_{1/2}} = \frac{60}{10} = 6$

$N = 1 \times \left(\frac{1}{2}\right)^6 = 1/64$

(where, N_0 = initial amount of reactant and N = amount of reactant left after time, t)

12. Show that the time required for 99% completion of a first order reaction is twice the time required for the completion of 90%.

Ans. For first order reaction, $t = \frac{2.303}{k} \log \frac{[A_0]}{[A]}$

$$\therefore \frac{t_{99\%}}{t_{90\%}} = \frac{\frac{2.303}{k} \log \frac{100}{100-99}}{\frac{2.303}{k} \log \frac{100}{100-90}} = \frac{\log 100}{\log 10}$$

$$= \frac{\log 10^2}{\log 10} = \frac{2 \log 10}{\log 10} = 2$$

$\therefore t_{99\%} = 2t_{90\%}$

10

13. A first order reaction takes 40 min for 30% decomposition. Calculate $t_{1/2}$.

Ans. For a first order reaction $K = \frac{2.303}{t} \log \frac{[R_0]}{[R]}$

When $t = 40$ minutes, $\frac{[R_0]}{[R]} = \frac{100}{100 - 30} = \frac{10}{7}$

$$K = \frac{2.303}{40} \log \frac{10}{7} = \frac{2.303}{40} \log 1.428 = \frac{2.303}{40} \times 0.1548$$

$$K = 8.91 \times 10^{-3} \text{ min}^{-1}$$

$$t_{1/2} = \frac{0.693}{K} = \frac{0.693}{8.91 \times 10^{-3}}$$

$$t_{1/2} = 77.78 \text{ min.}$$

$$t_{1/2} = \frac{0.693}{K}$$

14. The rate of a reaction quadruples when the temperature changes from 293 K to 313 K. Calculate the energy of activation of the reaction assuming that it does not change with temperature.

Ans. $k_2 = 4k_1 \Rightarrow \frac{k_2}{k_1} = 4$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\log 4 = \frac{E_a}{2.303 \times 8.34} \left(\frac{313 - 293}{293 \times 313} \right)$$

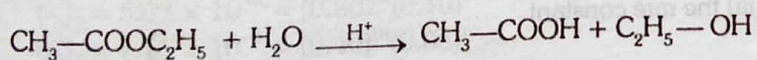
$$2 \times \log 2 = \frac{E_a}{19.147} \left(\frac{20}{91709} \right)$$

$$E_a = \frac{2 \times 0.3010 \times 19.147 \times 91709}{20}$$

$$E_a = 52.85 \text{ kJ/mol.}$$

15. What is meant by a pseudo first order reaction? Give an example of a pseudo first order reaction and write the rate equation for the same.

Ans. A reaction which is of higher order but follows the kinetics of first order under special conditions is called a pseudo first order reaction. Example, Acid hydrolysis of ethyl acetate.



Here, the rate law is given by expression

$$\text{Rate} = K [\text{CH}_3\text{—COOC}_2\text{H}_5]$$

The concentration of H_2O is so large that it hardly undergoes any change during the reaction, therefore, it does not appear in the rate law.

16. Rate constant k of a reaction varies with temperature according to the equation

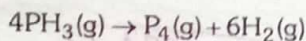
$$\log k = \text{Constant} - \frac{E_a}{2.303 RT}$$

where E_a is the activation energy. When a graph is plotted for $\log k$ vs $1/T$, a straight line with a slope -6670 K is obtained. Calculate the energy of activation for the reaction in proper units. ($R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$)

Ans. Slope = $-\frac{E_a}{2.303 RT} = -6670k$

$$E_a = 6670 \times 2.303 \times 8.314 = 127711.43 \text{ J mol}^{-1} = 127.711 \text{ kJ mol}^{-1}$$

17. The decomposition of phosphine



has the rate law, Rate = $k[\text{PH}_3]$

The rate constant is $6.0 \times 10^{-4} \text{ s}^{-1}$ at 300 K and activation energy is $3.05 \times 10^5 \text{ J mol}^{-1}$.

What is the value of rate constant at 310 K. [$R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$]

Ans. $k_1 = 6.0 \times 10^{-4} \text{ s}^{-1}$ $T_1 = 300 \text{ K}$

$k_2 = ?$ $T_2 = 310 \text{ K}$

$E_a = 3.05 \times 10^5 \text{ J mol}^{-1}$

$$\log \frac{k_2}{k_1} = \frac{3.05 \times 10^5}{2.303 \times 8.314} \left[\frac{310 - 300}{310 \times 300} \right]$$

$$= \frac{3.05 \times 10^5 \times 10}{2.303 \times 8.314 \times 310 \times 300}$$

$$\log \frac{k_2}{k_1} = 1.718$$

$$\frac{k_2}{k_1} = \text{antilog } 1.718 = 51.62$$

$$k_2 = 51.62 \times k_1 = 51.62 \times 6.0 \times 10^{-4} \text{ s}^{-1} = \mathbf{3.1 \times 10^{-2} \text{ s}^{-1}}$$

18. The activation energy for the reaction, $2\text{HI}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{g})$, is $209.5 \text{ kJ mol}^{-1}$ at 581 K. Calculate the fraction of molecules of reactants having energy to or greater than activation energy.

Ans. Fraction of molecules having energy equal to or greater than activation energy = $x = \frac{n}{N} = e^{-E_a/RT}$

$$\therefore \ln x = -\frac{E_a}{RT} \quad \text{or} \quad \log x = -\frac{E_a}{2.303 RT}$$

$$\text{or} \quad \log x = \frac{209.5 \times 10^3 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ JK}^{-1}\text{mol}^{-1} \times 581 \text{ K}} = -18.8323$$

$$\therefore x = \text{Antilog}(-18.8323) = \text{antilog } 19.1677 = \mathbf{1.471 \times 10^{-19}}$$

19. At 373 K, a gaseous reaction $\text{A} \rightarrow 2\text{B} + \text{C}$ is observed to be of first order. On starting with pure A, it was found that at the end of 10 minutes, the total pressure of the system was 176 mm of mercury and after a long time, when dissociation of A was complete, it was 270 mm. From these data, calculate (i) the initial pressure of A (ii) the pressure of A at the end of the 10 minutes. (iii) the rate constant.

Sol. Suppose initial pressure of A = P mm.

Decrease in the pressure of A after time $t = p$ mm.

	A	→	2B	+	C	Total pressure
Initial pressure	P		0		0	P
Pressure after time t	P - p		2p		p	P + 2p
Final pressure	0		2P		P	3P

(i) Final pressure = 270 mm (Given) $\therefore 3P = 270$ or $P = \mathbf{90 \text{ mm}}$

(ii) Pressure after 10 minutes = 176 mm (Given) $\therefore P + 2p = 176$ or $90 + 2p = 176$ or $p = 43 \text{ mm}$

\therefore Pressure of A after 10 min = $P - p = 90 - 43 = \mathbf{47 \text{ mm}}$

(iii) $a \propto P$ and $x \propto p$

$$\therefore k = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{t} \log \frac{P}{P-p}$$

$$\text{or} \quad k = \frac{2.303}{10 \text{ min}} \log \frac{90}{90-43} = \frac{2.303}{10 \text{ min}} \log \frac{90}{47} = \mathbf{6.496 \times 10^{-2} \text{ min}^{-1}}$$

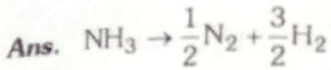
20. The half-life period of a first order reaction is 60 minutes. What percentage will be left after 240 minutes?

Sol. No. of half-lives = $\frac{240}{60} = 4$, i.e., $n = 4$

Amount left after 4 half-lives = $\frac{[A_0]}{2^4} = \frac{[A_0]}{16} = 0.0625$ of $A_0 = 6.25\%$

Short Answer Type Questions (3 mark)

21. The decomposition of NH_3 on platinum surface is zero order. What are the rates of production of N_2 and H_2 if $k = 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$?



Rate = $-\frac{d[NH_3]}{dt} = +\frac{2d[N_2]}{dt} = +\frac{2}{3}\frac{d[H_2]}{dt}$

For zero order reaction, rate = k

$\therefore -\frac{d[NH_3]}{dt} = \frac{2d[N_2]}{dt} = \frac{2}{3}\frac{d[H_2]}{dt}$
 $= 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$

\therefore Rate of production of $N_2 = \frac{d[N_2]}{dt} = \frac{2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}}{2} = 1.25 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$

Rate of production of $H_2 = \frac{d[H_2]}{dt} = \frac{3}{2} \times (2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1})$
 $= 3.75 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$.

22. In a reaction between A and B, the initial rate of reaction was measured for different initial concentrations of A and B as given below:

A / mol L ⁻¹	0.20	0.20	0.40
B / mol L ⁻¹	0.30	0.10	0.05
r_0 / mol L ⁻¹ s ⁻¹	5.07×10^{-5}	5.07×10^{-5}	7.16×10^{-5}

What is the order of reaction with respect to A and B?

Ans. The rate law may be expressed as $r_0 = [A]^m[B]^n$

$(r_0)_1 = 5.07 \times 10^{-5} = (0.20)^m(0.30)^n$

$(r_0)_2 = 5.07 \times 10^{-5} = (0.20)^m(0.10)^n$

$(r_0)_3 = 7.16 \times 10^{-5} = (0.40)^m(0.05)^n$

$\frac{(r_0)_1}{(r_0)_2} = 1 = \left(\frac{0.30}{0.10}\right)^n = (3)^n$

$(3)^0 = (3)^n$

$n = 0$

$\frac{(r_0)_3}{(r_0)_2} = \frac{7.16}{5.06} = \left(\frac{0.40}{0.20}\right)^m \left(\frac{0.05}{0.10}\right)^n$

or $1.412 = 2^m \left(\frac{1}{2}\right)^n = (2)^m \quad (\because n = 0)$

or $(2)^{1/2} = 2^m$

$\Rightarrow m = \frac{1}{2} = 0.5$

Thus, order with respect to A = 0.5, order with respect to B = 0.

23. During nuclear explosion, one of the products is ^{90}Sr with half life of 28.1 years. If $1\ \mu\text{g}$ of ^{90}Sr was absorbed in the bones of a newly born baby instead of calcium, how much of it will remain after 10 years and 60 years if it is not lost metabolically?

Ans. As radioactive disintegration follow first order kinetics,

$$\text{Decay constant of } ^{90}\text{Sr}, k = \frac{0.693}{t_{1/2}} = \frac{0.693}{28.1\text{y}} = 2.466 \times 10^{-2} \text{y}^{-1}$$

To calculate the amount left after 10 years,

$$a = 1\ \mu\text{g}, t = 10\ \text{years}, k = 2.466 \times 10^{-2} \text{y}^{-1}, (a - x) = ?$$

$$k = \frac{2.303}{t} \log \frac{a}{(a-x)}$$

$$2.466 \times 10^{-2} = \frac{2.303}{10} \log \frac{1}{(a-x)}$$

$$\text{or } \log(a-x) = -0.1071$$

$$\text{or } (a-x) = \text{Antilog } \bar{1}.8929 = \mathbf{0.7814\ \mu\text{g}}$$

To calculate the amount left after 60 years.

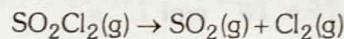
$$2.466 \times 10^{-2} = \frac{2.303}{60} \log \frac{1}{a-x}$$

$$\log(a-x) = 0.6425$$

$$(a-x) = \text{Antilog } \bar{1}.3575 = \mathbf{0.2278\ \mu\text{g}}$$

Calculated

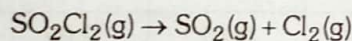
24. The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant value:



Experiment	Time/s	Total Pressure/atm
1	0	0.5
2	100	0.6

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

Ans.



$$\text{Initial pressure } P_0 \quad 0 \quad 0$$

$$\text{After time } t \quad P_0 - P \quad P \quad P$$

$$\text{Total pressure after time } t(P_t) = (P_0 - P) + P + P = P_0 + P$$

$$\text{or } P = P_t - P_0$$

$$a \propto P_0 \text{ and } (a-x) \propto P_0 - P \text{ or substituting the value of } P$$

$$a-x \propto P_0 - (P_t - P_0) \text{ i.e.}$$

$$(a-x) \propto 2P_0 - P_t$$

$$\text{as decomposition of } \text{SO}_2\text{Cl}_2 \text{ is a first order reaction } k = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$k = \frac{2.303}{t} \log \frac{P_0}{2P_0 - P_t}$$

$$\text{When } t = 100\text{s}, k = \frac{2.303}{100\text{s}} \log \frac{0.5}{2 \times 0.5 - 0.6} = \frac{2.303}{100\text{s}} \log(1.25)$$

$$= \frac{2.303}{100\text{s}} (0.0969) = \mathbf{2.2316 \times 10^{-3} \text{ s}^{-1}}$$

$$\text{When } P_t = 0.65 \text{ atm, i.e., } P_0 + p = 0.65 \text{ atm}$$

$$\therefore p = 0.65 - P_0 = 0.50 = 0.15 \text{ atm}$$

$$\therefore \text{Pressure of } \text{SO}_2\text{Cl}_2 \text{ at time } t (P_{\text{SO}_2\text{Cl}_2}) = P_0 - p = 0.50 - 0.15 \text{ atm} = 0.35 \text{ atm}$$

$$\text{Rate at that time} = k \times P_{\text{SO}_2\text{Cl}_2} = (2.2316 \times 10^{-3} \text{ s}^{-1}) (0.35 \text{ atm}) = \mathbf{7.8 \times 10^{-5} \text{ atm s}^{-1}}$$

25. The time required for 10% completion of a first order reaction at 298 K is equal to that required for its 25% completion at 308 K. If the value of A is $4 \times 10^{10} \text{ s}^{-1}$, calculate k at 318 K and E_a .

Ans. $k_{298\text{K}} = \frac{2.303}{t_1} \log \frac{a}{a - 0.10a} = \frac{2.303}{t_1} \log \frac{10}{9} = \frac{2.303}{t_1} (0.0458) = \frac{0.1055}{t_1}$ or $t_1 = \frac{0.1055}{k_{298\text{K}}}$

$k_{308\text{K}} = \frac{2.303}{t_2} \log \frac{a}{a - 0.25a} = \frac{2.303}{t_2} \log \frac{4}{3} = \frac{2.303}{t_2} (0.125) = \frac{0.2879}{t_2}$ or $t_2 = \frac{0.2879}{k_{308\text{K}}}$

But $t_1 = t_2$. Hence, $\frac{0.1055}{k_{298\text{K}}} = \frac{0.2879}{k_{308\text{K}}}$

or $\frac{k_{308\text{K}}}{k_{298\text{K}}} = \frac{0.2879}{0.1055} = 2.7289$

Now, from Arrhenius equation, $\log \frac{k_{308\text{K}}}{k_{298\text{K}}} = \frac{E_a}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$

$\log(2.7289) = \frac{E_a}{2.303 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1}} \times \frac{(308 - 298)\text{K}}{298\text{K} \times 308\text{K}}$

$0.4360 = \frac{E_a}{2.303 \times 8.314} \times \frac{10}{298 \times 308}$

$E_a = 76.623 \text{ kJ mol}^{-1}$.

Calculation of k at 318 K:

$\log k = \log A - \frac{E_a}{2.303RT} = \log(4 \times 10^{10}) - \frac{76623 \text{ JK}^{-1} \text{ mol}^{-1}}{2.303 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 318\text{K}}$
 $= 10.6021 - 12.5843 = -1.9822$

or $k = \text{Antilog}(-1.9822) = \text{Antilog}(\bar{2}.0178) = 1.042 \times 10^{-2} \text{ s}^{-1}$.

26. (a) List the factors on which the rate of a chemical reaction depends.
(b) The half-life for decay of radioactive ^{14}C is 5730 years. An archaeological artefact containing wood has only 80% of the ^{14}C activity as found in living trees. Calculate the age of the artefact.

Ans. (a) Rate of reaction depends on

- (i) Concentration
- (ii) Temperature
- (iii) Nature of reactant
- (iv) Pressure of the gaseous reactant
- (v) Surface area
- (vi) Catalyst

(b) $t_{1/2} = 5730$ year

$\therefore K = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730} = 1.209 \times 10^{-4} \text{ year}^{-1}$

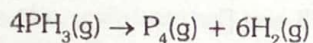
$t = \frac{2.303}{K} \log \frac{[R_0]}{[R]} = \frac{2.303}{1.2 \times 10^{-4}} \log \frac{100}{80}$

$t = \frac{2.303 \times 10^4}{1.2} (\log 10 - \log 8) = \frac{2.303 \times 10^4}{1.2} (1 - 3 \log 2)$

$t = \frac{2.303}{1.2} \times 10^4 (1 - 3 \times 0.3010) = \frac{2.303 \times 0.097 \times 10^4}{1.209}$

$t = 1847.7 \text{ years}$

27. Decomposition of phosphine (PH_3) at 120°C proceeds according to the equation:



It is found that this reaction follows the following rate equation:

$$\text{Rate} = k[\text{PH}_3]$$

The half-life of PH_3 is 37.9 s at 120°C .

- (i) How much time will be required for 3/4 of PH_3 to decompose?
 (ii) What fraction of the original amount of PH_3 will remain undecomposed after 1 minute?

Ans. (i) Given $t_{1/2} = 37.95$

$$t_{1/2} = \frac{0.693}{k}, \quad k = \frac{0.693}{t_{1/2}} = 1.83 \times 10^{-2} \text{ s}^{-1}$$

$$k = \frac{0.693}{37.9} \text{ s}^{-1}, \quad t = \frac{2.303}{k} \log \frac{[\text{A}_0]}{[\text{A}]}$$

$$t_{3/4} = \frac{2.303}{1.83 \times 10^{-2} \text{ s}^{-1}} \log \frac{[\text{A}_0]}{[\text{A}]} = \frac{2.303}{1.83} \times 100 \log 2^2 \text{ s}$$

$$t_{3/4} = \frac{2.303 \times 100 \times 2 \times 0.30105}{1.83} = \frac{138.64}{1.83} \text{ s}$$

$$t_{3/4} = \mathbf{75.76 \text{ s}}$$

(ii) $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{37.9} \text{ s}^{-1} = 1.83 \times 10^{-2} \text{ s}^{-1}$

$$t = 1 \text{ minute} = 60 \text{ s}$$

$$t = \frac{2.303}{k} \log \frac{[\text{A}_0]}{[\text{A}]}$$

$$60 \text{ s} = \frac{2.303}{1.83 \times 10^{-2} \text{ s}^{-1}} \log \frac{[\text{A}_0]}{[\text{A}]}$$

$$\log \frac{[\text{A}_0]}{[\text{A}]} = \frac{60 \times 1.83 \times 10^{-2}}{2.303} = 0.4768$$

$$\log \frac{[\text{A}_0]}{[\text{A}]} = -0.4768 = \bar{1}.5232$$

$$\frac{[\text{A}]}{[\text{A}_0]} = \text{Antilog } \bar{1}.5232 = 0.3336$$

or $\frac{[\text{A}]}{[\text{A}_0]} = \mathbf{0.334}$

28. At 27°C in the presence of a catalyst, the activation energy of a reaction is lowered by 2 kcal. Calculate by how much the rate of reaction will increase?

Sol. In the absence of catalyst, suppose rate constant = k .

$$\text{Then } \log k = \log A - \frac{E_a}{2.303 RT} \dots\dots(i)$$

In the presence of catalyst, suppose rate constant = k' .

Now, activation energy = $E_a - 2$ (if E_a is in kcal mol⁻¹)

$$\therefore \log k' = \log A - \frac{E_a - 2}{2.303RT} \text{ or } \log k' = \log A - \frac{E_a}{2.303RT} + \frac{2 \text{ kcal mol}^{-1}}{2.303RT} \dots\dots(ii)$$

Subtracting equation (i) from equation (ii), we get $\log k' - \log k = \frac{2 \text{ kcal mol}^{-1}}{2.303RT}$

$$\log \frac{k'}{k} = \frac{2 \text{ kcal mol}^{-1}}{2.303(2 \times 10^{-3} \text{ kcal K}^{-1} \text{ mol}^{-1})(300\text{K})} = 1.4474 \quad (\because R = 2 \times 10^{-3} \text{ kcal K}^{-1} \text{ mol}^{-1})$$

$$\text{or } \frac{k'}{k} = \text{antilog } 1.4474 = 28$$

or $k' = 28k$, i.e., the rate of reaction will increase **28 times**.

29. The decomposition of a compound is found to follow a first order rate law. If it takes 15 min for 20% of original material to react, calculate

(i) the rate constant

(ii) the time at which 10% of the original material remains unreacted.

Ans. (i) 20% decomposition means $[R_0] = 100$,

$$[R] = 100 - 20 = 80$$

$$k = \frac{2.303}{t} \log \frac{[R_0]}{[R]}$$

$$= \frac{2.303}{15} \log \frac{100}{80}$$

$$k = \frac{2.303}{15} \times \log 1.25$$

$$= \frac{2.303}{15} \times 0.0969$$

$$= \mathbf{0.0148 \text{ min}^{-1}}$$

(ii) Time at which 10% of the original material remains unreacted.

$$[R_0] = 100, [R] = 10$$

$$k = \frac{2.303}{t} \log \frac{[R_0]}{[R]}$$

$$= \frac{2.303}{0.0148} \log \frac{100}{10} \quad (\log 10 = 1)$$

$$t = \frac{2.303 \times 1}{0.0148}$$

$$= \mathbf{155.6 \text{ min}}$$

30. The reaction, $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$ contributes to air pollution wherever a fuel is burnt in air at a high temperature. At 1500 K, equilibrium constant K for it is 1.0×10^{-5} . Suppose in a case $[\text{N}_2] = 0.80 \text{ mol L}^{-1}$ and $[\text{O}_2] = 0.20 \text{ mol L}^{-1}$ before any reaction occurs. Calculate the equilibrium concentration of the reactants and the product after the mixture has been heated to 1500 K.

Ans.	$\text{N}_2(\text{g})$	+	$\text{O}_2(\text{g})$	\rightleftharpoons	$2\text{NO}(\text{g})$
Initial conc.	0.8 M		0.20 M		0
At equilibrium	$0.80 - x$		$0.20 - x$		$2x$

$$K_c = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = \frac{(2x)^2}{(0.80 - x)(0.20 - x)} = 1.0 \times 10^{-5} \quad (\text{Given})$$

$$4x^2 = 1.0 \times 10^{-5} (0.16 - 0.80x - 0.20x + x^2)$$

$$\text{or } 4 \times 10^5 x^2 - x^2 + x - 0.16 = 0$$

$$\text{or } 4 \times 10^5 x^2 + x - 0.16 = 0$$

Since, above equation is a quadratic equation, hence $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

Hence, $a = 4 \times 10^5$, $b = 1$ and $c = -0.16$

$$x = \frac{-1 \pm \sqrt{(1)^2 - 4 \times 4 \times 10^5 \times (-0.16)}}{2 \times 4 \times 10^5}$$

$$x = \frac{-1 \pm \sqrt{2.56 \times 10^5}}{8 \times 10^5} = \frac{-1 \pm 506}{8 \times 10^5}$$

$$x = +6.3 \times 10^{-4}, x = 6.3 \times 10^{-4}$$

Since, concentration cannot be negative, hence $x = 6.3 \times 10^{-4}$

$$[\text{NO}] = 2x = 2 \times 6.3 \times 10^{-4} = 1.26 \times 10^{-3} \text{ mol L}^{-1}$$

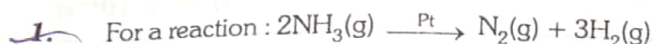
$$[\text{N}_2] = 0.80 - 6.3 \times 10^{-4} = 0.799 \text{ mol L}^{-1}$$

$$[\text{O}_2] = 0.20 - 6.3 \times 10^{-4} = 0.199 \text{ mol L}^{-1}$$

EXERCISE-1

PREVIOUS YEARS BOARD PROBLEMS

CBSE 2016



Rate = k

(i) Write the order and molecularity of this reaction.

(ii) Write the unit of k.

2. The rate constant for the first order decomposition of H_2O_2 is given by the following equation:

$$\log k = 14.2 - \frac{1.0 \times 10^4 \text{ K}}{T}$$

Calculate E_a for this reaction and rate constant k if its half-life period be 200 minutes.

(Given : $R = 8.314 \text{ JK}^{-1} \text{ mole}^{-1}$)

CBSE 2015

1. For the hydrolysis of methyl acetate in aqueous solution, the following results were obtained :

t/s	0	30	60
$[\text{CH}_3\text{COOCH}_3] \text{ mol L}^{-1}$	0.60	0.30	0.15

(i) Show that it follows pseudo first order reaction as the concentration of water remains constant.

(ii) Calculate the average rate of reaction between the time interval 30 to 60 seconds

2. (a) For a reaction $\text{A} + \text{B} \rightarrow \text{P}$, the rate is given by

$$\text{Rate} = k [\text{A}]^2 [\text{B}]$$

(i) How is the rate of reaction affected if the concentration of A is doubled ?

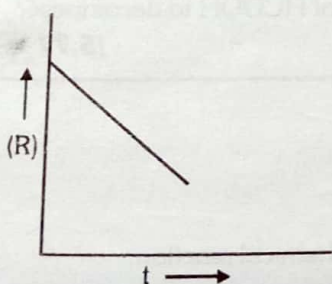
(ii) What is the overall order of reaction if B is present in large excess ?

(b) A first order reaction taken 23.1 minutes for 50% completion. Calculate the time required for 75% completion of this reaction.

(Given : $\log 2 = 0.301$, $\log 3 = 0.4771$, $\log 4 = 0.6021$)

CBSE 2014

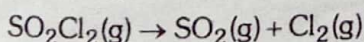
1. For a chemical reaction $\text{R} \rightarrow \text{P}$, the variation in the concentration (R) vs. time (t) plot is given as



(i) Predict the order of the reaction.

(ii) What is the slope of the curve ?

2. The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume:



$[1.38 \times 10^2 \text{ s}^{-1}]$

Experiment	Time/ s^{-1}	Total pressure/atm
1	0	0.4
2	100	0.7

Calculate the rate constant.

(Given : $\log 4 = 0.6021$, $\log 2 = 0.3010$)

CBSE 2013

[5/2]

1. (i) For a reaction $A + B \rightarrow C$, the rate law is given by, $r = k[A]^{1/2} [B]^2$
what is the order of this reaction?
- (ii) A first order reaction is found to have a rate constant $k = 5.5 \times 10^{-14} \text{ s}^{-1}$. Find the half-life of the reaction.
[1.26 × 10¹³ s]

CBSE 2012

1. A reaction is of second order with respect to a reactant. How is rate affected if the concentration of the reactant is
(i) Doubled (ii) Reduced to half?
2. The reaction, $N_2(g) + O_2 \rightleftharpoons 2NO(g)$ contributes to air pollution wherever a fuel is burnt in air at a high temperature. At 1500 K, equilibrium constant K for it is 1.0×10^{-5} . Suppose in a case $[N_2] = 0.80 \text{ mol L}^{-1}$ and $[O_2] = 0.20 \text{ mol L}^{-1}$ before any reaction occurs. Calculate the equilibrium concentrations of the reactants and the product after the mixture has been heated to 1500 K.
[NO] = 1.26 × 10⁻³ mol/L, [N₂] = 0.799 mol/L, [O₂] = 0.199 mol/L

CBSE 2011

1. Define order of a reaction.
2. Identify the reaction order from the following rate constant, $k = 2.3 \times 10^{-5} \text{ L mol}^{-1} \text{ s}^{-1}$.
3. What do you understand by the rate law and rate constant of a reaction? Identify the order of a reaction if the units of its rate constant are (i) $\text{L}^{-1} \text{ mol s}^{-1}$ (ii) $\text{L mol}^{-1} \text{ s}^{-1}$
4. A reaction is of second order with respect to a reactant. How is the rate of reaction affected if the concentration of the reactant is reduced to half? What is the unit of rate constant for such a reaction?
5. Explain the terms
(i) Rate determining step of a reaction (ii) Molecularity of a reaction.
6. What are pseudo first order reactions? Give one example of such reactions.
7. In a first order reaction, the concentration of the reactant is reduced from 0.6 mol L^{-1} to 0.2 mol L^{-1} in 5. Calculate the rate constant of the reaction.
[0.2197 min⁻¹]
8. The thermal decomposition of HCOOH is a first order reaction with a rate constant of $2.4 \times 10^{-3} \text{ s}^{-1}$ certain temperature. Calculate how long will it take for three fourth of initial quantity of HCOOH to decompose?
($\log 0.25 = -0.6021$).
[5.77 × 10² s]

CBSE 2010

1. Define rate of a reaction.
2. Explain the difference between the average rate and instantaneous rate of a chemical reaction.
3. Distinguish between molecularity and order of a reaction.
4. The decomposition of phosphine, PH_3 proceeds according to the following equation.
 $4PH_3(g) \longrightarrow P_4(g) + 6H_2(g)$
It is found that the reaction follows the following rate equation
Rate = $k[PH_3]$
The half-life of PH_3 is 37.9 s at 120°C.
(i) How much time is required for $\frac{3}{4}$ th of PH_3 to decompose?
(ii) What fraction of the original sample of PH_3 remains behind after 1 min?
[75.85%]
[2.997 or 33.3%]

5. In a pseudo first order hydrolysis of ester in water, the following results are obtained:

t (in second)	0	30	60	90
[Ester] M	0.55	0.31	0.17	0.85

(i) Calculate the average rate of reaction between the time interval 30 to 60 s.

$$[4.67 \times 10^{-3} \text{ s}^{-1}]$$

(ii) Calculate the pseudo first order rate constant for the hydrolysis of ester.

$$[1.98 \times 10^{-2} \text{ s}^{-1}]$$

6. The rate of a reaction becomes four times when the temperature changes from 300 K to 320 K. Calculate the energy of activation of the reaction, assuming that it does not change with temperature. ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

$$[55327.58 \text{ J mol}^{-1}]$$

7. The activation energy for the reaction $2\text{HI}(\text{g}) \longrightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{g})$ is $209.5 \text{ kJ mol}^{-1}$ at 581K. Calculate the fraction of molecules having energy equal to or greater than activation energy. ($R = 8.31 \text{ JK}^{-1} \text{ mol}^{-1}$)

$$[X = 1.471 \times 10^{-19}]$$

CBSE 2009

1. Define the following

(i) Elementary step in a reaction (ii) Rate of a reaction.

2. A first order reaction has a rate constant value of 0.00510 min^{-1} . If we begin with 0.10 M concentration of the reactant, how much of the reactant will remain after 3.0 h? $[0.0399\text{M}]$

3. The half-life for a first order reaction is $5 \times 10^4 \text{ s}$. What percentage of the initial reactant will react in 2 hours? Calculate. $[90.497 \text{ \%}]$

4. A first order reaction is 20% complete in 5 min. Calculate the time taken for the reaction to be 60% complete.

$$[20.546 \text{ min.}]$$

5. What is the effect of temperature on the rate constant of a reaction? How can this temperature effect on rate constant be expressed quantitatively?

6. For a decomposition reaction the values of rate constant k at two different temperatures are given below :

$$k_1 = 2.15 \times 10^{-8} \text{ L mol}^{-1} \text{ s}^{-1} \text{ at } 650 \text{ K}$$

$$[E_a = 182201.71 \text{ J mol}^{-1}]$$

$$k_2 = 2.39 \times 10^{-7} \text{ L mol}^{-1} \text{ s}^{-1} \text{ at } 700 \text{ K}$$

Calculate the value of activation energy for this reaction. ($R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$)

EXERCISE-1**SOLUTIONS OF PREVIOUS YEARS BOARD PROBLEMS****CHEMICAL KINETICS****CBSE 2016**

Sol.1 (i) zero order, bimolecular/ unimolecular

(ii) $\text{mol L}^{-1} \text{s}^{-1}$

Sol.2 $\log k = \log A - E_a/2.303RT$

$$E_a / 2.303 RT = 1 \times 10^4 \text{ k/ T}$$

$$E_a = 1.0 \times 10^4 \times 2.303 \times 8.314$$

$$= 191471.4 \text{ J/mol}$$

$$t_{1/2} = 0.693/k$$

$$k = 0.693/200$$

$$= 0.0034 \text{ min}^{-1} / 3.4 \times 10^{-3} \text{ min}^{-1}$$

CBSE 2015

Sol.1 (i) $A_0 = 0.60$ $A = 0.30$ when $t = 30\text{s}$

$$k = \frac{2.303}{t} \log \frac{[A_0]}{[A]}$$

$$k = \frac{2.303}{30} \log \frac{0.60}{0.30}$$

$$k = \frac{2.303}{30} \log 2 = \frac{2.303}{30} \times 0.3010$$

$$k = \frac{0.693}{30} = 0.231 \text{ s}^{-1}$$

When $A_0 = 0.60$ $A = 0.15$ when $t = 60\text{s}$

$$k = \frac{2.303}{t} \log \frac{0.60}{0.15}$$

$$k = \frac{2.303}{60} \log \frac{0.60}{0.15}$$

$$k = \frac{2.303}{60} \log 4 = \frac{2.303}{60} \times 0.6021$$

$$k = \frac{1.3866}{60} = 0.231 \text{ s}^{-1}$$

As for both cases k is approximately same reaction is of pseudo first order

$$(ii) \text{ Average rate during the interval } 30 - 60 \text{ sec} = \frac{\text{Change in concentration}}{\text{Change in time}}$$

$$= \frac{0.15 - 0.30}{60 - 30}$$

$$= \frac{-0.15}{30} = 0.005 \text{ mol L}^{-1} \text{S}^{-1}$$

Sol.2 (a) (i) Rate increases by 4 times

(ii) 2nd order

(b) Reaction is 50% completed in 23.1 min i.e. Half-life is 23.1 min

$$\therefore k = \frac{0.693}{t_{1/2}}$$

$$= \frac{0.693}{23.1} = 0.03 \text{ min}^{-1}$$

$$k = \frac{2.303}{t} \log \frac{[A_0]}{[A]}$$

$$0.03 \text{ min}^{-1} = \frac{2.303}{t} \log \frac{100}{25}$$

$$0.03 = \frac{2.303}{t} \log 4$$

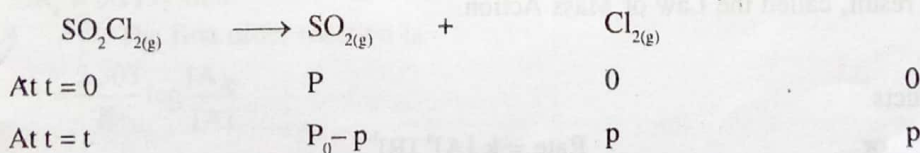
$$t = \frac{2.303}{0.03} \times 0.6021 = \frac{1.3866}{0.03} : - 46.221 \text{ min}$$

CBSE 2014

Sol.1 (i) Zero order

(ii) Slope = -K

Sol.2 The thermal decomposition of SO_2Cl_2 at a constant volume is represented by the following equation.



After time, t , total pressure, $P_t = (P_0 - p) + p + p$

$$\Rightarrow P_t = P_0 + p \Rightarrow p = P_t - P_0$$

$$\text{Therefore, } P_0 - p = P_0 - (P_t - P_0) = 2P_0 - P_t$$

For a first order reaction,

$$k = \frac{2.303}{t} \log \frac{P_0}{P_0 - p} = \frac{2.303}{t} \log \frac{P_0}{2P_0 - P_t}$$

$$\text{When } t = 100 \text{ s, } k = \frac{2.303}{100 \text{ s}} \log \frac{0.4}{2 \times 0.4 - 0.7} = 1.386 \times 10^{-2} \text{ s}^{-1}$$

CBSE 2013

Sol.1 (a) 2.5

$$(b) t_{1/2} = \frac{0.693}{k} = \frac{0.693}{5.5 \times 10^{-14}} = 0.126 \times 10^{14} \text{ sec.}$$

CBSE 2012Sol.1 Rate = $K[A]^2$

(i) 4 times

Sol.2 $N_2 + O_2 \rightleftharpoons 2NO$

(ii) 1/4 times

Since, above equation is a quadratic equation, hence

.8

0.2

2x

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

.8-x

.2-x

2x

Hence, $a = 4 \times 10^5$, $b = 1$ and $c = -0.16$

$$1 \times 10^{-5} = K_c = \frac{(2x)^2}{(0.8x)(.2-x)}$$

$$x = \frac{-1 \pm \sqrt{(1)^2 - 4 \times 4 \times 10^5 \times (-0.16)}}{2 \times 4 \times 10^5}$$

$$= \frac{-1 \pm \sqrt{2.56 \times 10^5}}{8 \times 10^5} = \frac{-1 \pm 506}{8 \times 10^5}$$

$$x = +6.3 \times 10^{-4}, x = -6.3 \times 10^{-4}$$

$$4x^2 = 1 \times 10^{-5} (0.16 - 0.80x - 0.2x + x^2)$$

since, concentration cannot be negative, hence $x = 6.3 \times 10^{-4}$

$$4 \times 10^{-5} x^2 - x^2 + x - 0.16 = 0$$

$$[NO] = 2x = 2 \times 6.3 \times 10^{-4} = 1.26 \times 10^{-3} \text{ mol lit}$$

$$4 \times 10^{-15} x^2 + x - 0.16 = 0$$

$$[N_2] = 0.80 - 6.3 \times 10^{-4} = 0.799 \text{ mol L}^{-1}$$

$$[O_2] = 0.20 - 6.3 \times 10^{-4} = 0.199 \text{ mol L}^{-1}$$

CBSE 2011

Sol.1 Order of reaction : Order of a reaction is the sum of the powers of the concentration terms in the experimentally determined rate equation.

Sol.2 $n = 2$

Sol.3 The effect of concentration on the rate reaction was first studied by Guldberg and Wage in 1867. They put forward the following result, called the Law of Mass Action.

For a general reaction.



Rate $\propto [A]^a [B]^b$

or

Rate = $k [A]^a [B]^b$

It is observed that the rate of this reaction may not depend upon all the 'a' concentration term of A and all the 'b' concentration term of B. Suppose, experimentally the rate of the reaction is found to depend upon ' α ' concentration term of A and ' β ' concentration term of B. Then,

Rate $\propto [A]^\alpha [B]^\beta$

or

Rate = $k [A]^\alpha [B]^\beta$

where A and B are the molar concentrations of A and B respectively and k is a constant called velocity constant or rate constant. The above expression is called Rate Law.

(i) Zero order

(ii) Second order

Sol.4 Let the concentration of the reactant be $[A] = a$

$$\begin{aligned} \text{Rate of reaction, } R &= K[A]^2 \\ &= Ka^2 \end{aligned}$$

(i) If the concentration of the reactant is doubled, i.e. $[A] = 2a$ then the rate of the reaction would be

$$\begin{aligned} R' &= K(2a)^2 \\ &= 4Ka^2 \\ &= 4R \end{aligned}$$

Therefore, the rate of the reaction would increase by 4 times.

(ii) If the concentration of the reactant is reduced to half, i.e. $A = \frac{1}{2}a$

then the rate of the reaction would be

$$R'' = K\left(\frac{1}{2}a\right)^2 = \frac{1}{4}Ka = \frac{1}{4}R$$

Therefore the rate of the reaction would be reduced to $\frac{1}{4}$ th.

Sol.5 (a) The rate determining step is the slowest step of a chemical reaction that determines the speed(rate) at which the overall reaction proceeds.

(b) The number of reacting species taking part in an elementary reaction. Which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction.

Sol.6 There are circumstances where a second order reaction might, under an experiment, to be first order. That is when one of the reactants in the rate equation is present in great excess over the other in the reaction mixture.

Sol.7 $K_c = \frac{2.303}{5} \log \frac{6}{2}$

$$K_c = \frac{2.303}{5} \log 3$$

$$K_c = \frac{2.303 \times 4.771}{5}$$

$$K_c = 0.2197 \text{ min}^{-1}$$

Sol.8 The first order reaction is

$$t = \frac{2.303}{K} \log \frac{[A]_0}{[A]}$$

where $[A]_0 = 1$, $[A] = \frac{3}{4}$, $\log 0.25 = -0.6021$, $k = 2.4 \times 10^{-3}$

$$t = \frac{2.303}{2.4 \times 10^{-3}} [\log(A)_0 - \log(A)_2]$$

$$t = \frac{2.303}{2.4 \times 10^{-3}} [\log 1 - \log 25]$$

$$t = \frac{2.303}{2.4 \times 10^{-3}} [10 - (-0.6021)]$$

$$= 578 \text{ s}$$

CBSE 2019

Sol.1 Rate of reaction: The rate of a reaction is the change in the concentration of any one of the reactants or products per unit time.

Sol.2 → Average rate of a reaction is the change in concentration of reactants or products over a particular

interval of time. It is represented as $\left(\frac{\Delta C}{\Delta t}\right)$

→ Instantaneous rate of a reaction is the change in the concentration of reactants or products over an infinitely

small interval of time. It is represented as $t_{\text{lim}} = \lim_{\Delta t \rightarrow 0} \frac{\Delta C}{\Delta t}$

Sol.3

	Molecularity		Order
(1)	The number of reacting species which must collide simultaneously in order to carry out a chemical reaction is called molecularity of a reaction.	(1)	The sum of powers of the concentration of the reactants in the rate law expression is called the order of that chemical reaction.
(2)	Molecularity is always a whole number value only i.e., 1, 2, 3, ...	(2)	Order of reaction may have zero, whole number or fractional values.
(3)	Molecularity is a theoretical concept.	(3)	order of reaction is determined experimentally.
(4)	Molecularity of a reaction can not be zero.	(4)	Order of a reaction can be zero.
(5)	Molecularity is applicable to elementary reactions only for complete reactions & law of massing.	(5)	Order of reaction is applicable to elementary as well as complex reactions.
(6)	For simple reactions, Molecularity can be obtained from the stoichiometry of the equation.	(6)	For a simple reaction, order of a reaction may not be equal to the number of molecules of the reactants as seen from the balanced equation.

Sol.4 (a) (i) Here $t_{1/2} = 17.3 \text{ s}$

Let initial concentration = a

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

Using the formula

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$k = \frac{2.303}{17.3} \log \frac{a}{\frac{a}{2}} \quad \left[-k = \frac{0.693}{t_{1/2}} \right]$$

$$t = 2.303 \times \frac{t_{1/2}}{0.693} \log \frac{a}{\frac{1}{4}a}$$

$$t = \frac{2.303 \times t_{1/2}}{0.693} \times \log 4 = \frac{2.303 \times t_{1/2} \times \log 2}{0.693}$$

$$t = \frac{2.303 \times 37.9 \times 2 \times 0.3010}{0.693} \quad [\because t_{1/2} = 37.9s]$$

$$= \frac{52.544}{0.693} = 75.82 \text{ sec.}$$

(ii) Here $t = 1 \text{ min} = 60s$ and $t_{1/2} = 37.9s$

Using the formula

$$t = \frac{2.303}{k} \log \frac{[A]_0}{[A]_t} \text{ and } k = \frac{0.693}{t_{1/2}}$$

$$\therefore t = \frac{2.303}{\frac{0.693}{t_{1/2}}} \log \frac{[A]_0}{[A]_t}$$

$$t = 2.303 \times \frac{t_{1/2}}{0.693} \times \log \frac{[A]_0}{[A]_t}$$

$$1 = \frac{2.303 \times 37.9}{0.693} \log \frac{[A]_0}{[A]_t}$$

$$\therefore \log \frac{[A]_0}{[A]_t} = \frac{1 \times 0.693}{2.303 \times 37.9} = \frac{0.693}{87.2837} = 0.0079$$

$$\frac{[A]_0}{[A]_t} = \text{anti} - \log (0.0079) = 1.018$$

Sol.5 (i) $\frac{\Delta C}{\Delta t} = \frac{C_2 - C_1}{t_2 - t_1} = \frac{.17 - .31}{60 - 30} = \frac{-14}{30} = 0.0046$
 $= 4.6 \times 10^{-3} s^{-1}$

(ii) $K = \frac{2.303}{30} \log \frac{.55}{.31} = 1.98 \times 10^{-2} s^{-1}$

Sol.6 $\log \frac{K_2}{K_1} = \frac{E_a}{2.303K} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$

$$\log \frac{4K_1}{K_2} = \frac{E_a}{2.303 \times 8.314} \left[\frac{1}{300} - \frac{1}{320} \right]$$

$$\log 4 = \frac{E_a}{2.303 \times 8.314} \times \frac{20}{300 \times 320}$$

$$E_a = 52.8 \text{ kJ/mol}$$