

# CHEMICAL KINETICS

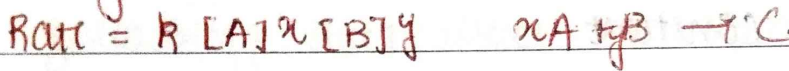
## Different types of numerical problems

### 1. Formulae



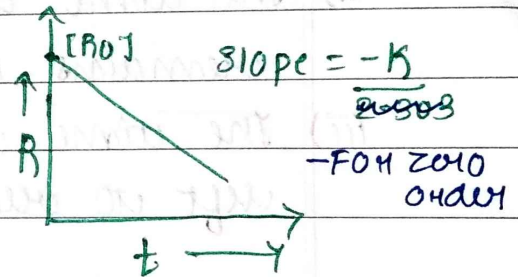
$$1. \text{ Rate} = -\frac{d[R]}{2dt} = \frac{d[P]}{dt}$$

2. According to rate law



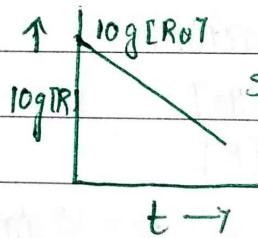
### 3. Integrated rate law for zero order

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

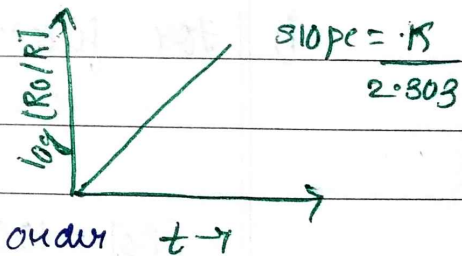


FOR 1st order

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



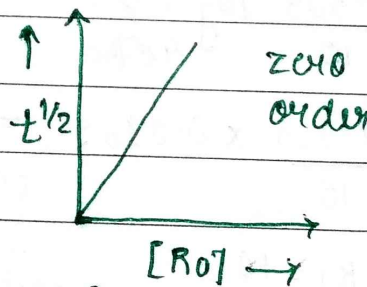
$$\text{SLOPE} = \frac{-k}{2.303}$$



$$\text{SLOPE} = \frac{k}{2.303}$$

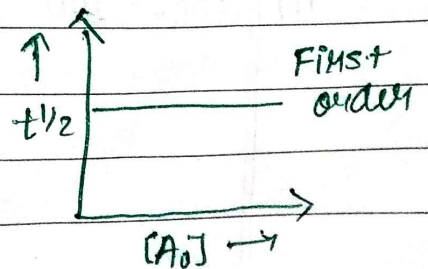
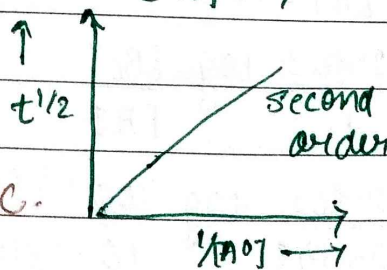
### 4. Half life for zero order

$$t^{1/2} = \frac{[R_0]}{2k}$$



FOR first order

$$t^{1/2} = \frac{0.693}{k}$$



Independent of initial conc.

$$5. k = A e^{-E_a/RT}$$

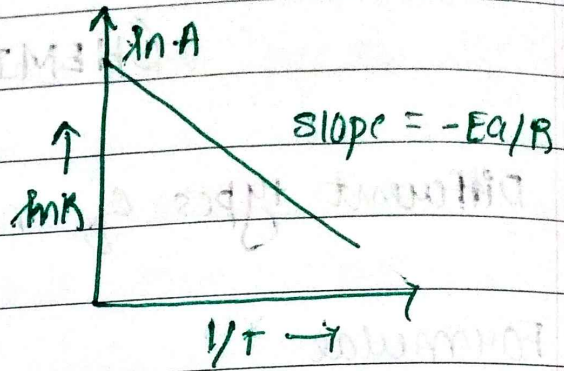
R - Gas constant

$E_a$  - Activation energy

T - Temperature in K

A - Arrhenius factor

$$6. \log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right]$$



1. The decomposition of a compound is found to follow first order rate law. If it 15 minutes for 20% of original material to react, calculate
- Specific rate constant.
  - The time at which 10% of the original material remains unreacted.
  - The time it takes for the next 20% of the reactant left to react after first 15 minutes.

i) For first order reaction

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

$$[R_0] = 100, [R] = 80, t = 15 \text{ min}$$

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

$$= \frac{2.303}{15} \times 0.0969 = 0.0149 \text{ min}^{-1}$$

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

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

$$= \frac{2.303}{0.0149} \log \frac{100}{10}$$

$$= 154.6 \text{ min}$$

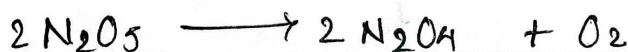
$$(ii) [R_0] = 80, [R] = 80 - \frac{20}{100} \times 80 = 64$$

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

$$= \frac{2.303}{0.0149} \log \frac{80}{64} = \frac{2.303}{0.0149} \log \frac{10}{8}$$

$$= \frac{2.303}{0.0149} \times 0.0969 = 15 \text{ min}$$

2. The following data were obtained during the first order thermal decomposition of  $N_2O_5$  at constant volume,



t.	Time	Total pressure
1.	0	0.5
2.	100	0.512

Calculate rate constant.



t=0	0.5	0	0
t=100	(0.5-2x)	2x	x

$$P_t = 0.5 - 2x + 2x + x = 0.512$$

$$x = 0.512 - 0.5$$

$$= 0.012 \text{ atm}$$

$$P_{100} = 0.5 + 0.024 = 0.524 \text{ atm}$$

For first order

$$k = \frac{2.303}{100} \log \frac{[N_2O_5]_0}{[N_2O_5]_t}$$

$$= \frac{2.303}{100} \log \frac{0.5}{0.476}$$

$$= \frac{2.303}{100} \log 1.0504 = \frac{2.303}{100} \times 0.0214 = 4.93 \times 10^{-4} \text{ s}^{-1}$$

3. A first order reaction is 20% complete in 10 minutes. Calculate the time for 75% completion of the reaction.

For first order reaction

$$[R_0] = 100 \quad [R]_1 = 100 - 20 = 80$$

$$t_1 = 10 \text{ min}$$

$$[R_0] = 100 \quad [R]_2 = 100 - 75 = 25$$

$$t_2 = t$$

$$\frac{2.303}{t_1} \log \frac{[R_0]}{[R]_1} = \frac{2.303}{t_2} \log \frac{[R_0]}{[R]_2}$$

$$\frac{2.303}{10} \log \frac{100}{80} = \frac{2.303}{t} \log \frac{100}{25}$$

$$\frac{2.303}{10} \times 0.0969 = \frac{2.303}{t} \times 0.6021$$

$$t = \frac{0.6021}{0.00969}$$

$$t = 62.18 \text{ min}$$

4. The rate constant for a first order reaction is  $60 \text{ s}^{-1}$ . How much time will it take to reduce the concentration of the reactant to  $1/10$ th of its initial value?

For a first order reaction

$$k = 60 \text{ s}^{-1} \quad [R_0] = [R_0] \quad [R] = \frac{1}{10} [R_0]$$

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

$$t = \frac{2.303}{60} \log \frac{[R_0]}{\frac{1}{10} [R_0]}$$

$$= \frac{2.303}{60} \log 10$$

$$= \frac{2.303}{60} = 0.0384 \text{ s}$$

5. A first order decomposition reaction takes 40 minutes for 30% decomposition. Calculate its  $t_{1/2}$  value.

For first order reaction.

$$t = 40 \text{ min} \quad [R_0] = 100 \quad [R] = 100 - 30 = 70$$

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

$$= \frac{2.303}{40} \log \frac{100}{70}$$

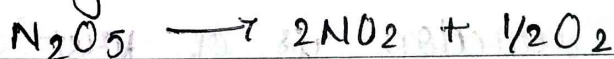
$$= \frac{2.303}{40} \log 1.42$$

$$= \frac{2.303}{40} \times 0.1523$$

$$= 0.035 \text{ min}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.035} = \frac{693}{35} = 19.8 \text{ min}$$

6. Following data are obtained for reaction:



t/s	0	300	600
$[\text{N}_2\text{O}_5] / \text{mol L}^{-1}$	$1.6 \times 10^{-2}$	$0.8 \times 10^{-2}$	$0.4 \times 10^{-2}$

a) Show that it follows first order reaction.

b) Calculate the half-life ( $\log 2 = 0.3010$ ,  $\log 4 = 0.6021$ )

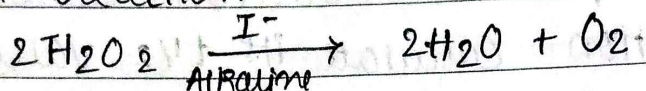
$$k = \frac{2.303}{t} \log \frac{[R_0]}{[R]} = \frac{2.303}{300} \log \frac{1.6 \times 10^{-2}}{0.8} = \frac{2.303 \times \log 2}{300} = 2.31 \times 10^{-3} \text{ s}^{-1}$$

At 600 s

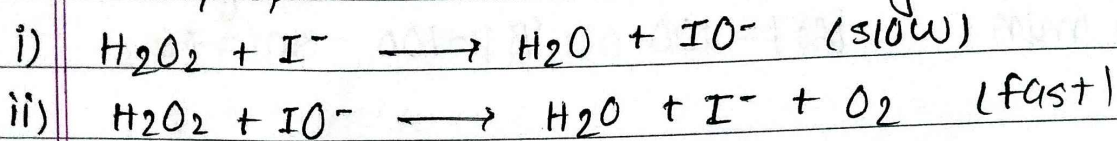
$$k = \frac{2.303}{600} \log \frac{1.6 \times 10^{-2}}{0.4 \times 10^{-2}} = \frac{2.303}{600} \log 4 = \frac{2.303 \times 0.6021}{600} = 2.31 \times 10^{-3} \text{ s}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{2.31 \times 10^{-3}} = 300 \text{ s}$$

7. For a reaction



the proposed mechanism is as given below:



- Write the rate law for the reaction.
- Write the overall order of reaction.
- Out of steps (1) and (2) which one is rate determining step?

a)  $\text{Rate} = k [\text{H}_2\text{O}_2] [\text{I}^-]$

b) According to rate law the <sup>order</sup> rate determining step reaction is

$$\text{Order} = 1 + 1 = 2$$

c) Step (1) is rate determining step.

8. In the Arrhenius equation for a certain reaction, the values of  $A$  and  $E_a$  are  $4 \times 10^{13} \text{ s}^{-1}$  and  $98.6 \text{ kJ mol}^{-1}$  respectively. If the reaction is of first order, at what temperature will its half life period be 10 min?

$$t_{1/2} = 10 \text{ min} = 600 \text{ s}$$

$$A = 4 \times 10^{13} \text{ s}^{-1} \quad E_a = 98600 \text{ J mol}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} \quad k = \frac{0.693}{600} = 1.155 \times 10^{-3}$$

According to Arrhenius eqn

$$k = A e^{-E_a/RT}$$

$$\log \frac{k}{A} = \frac{-E_a}{RT} \quad \frac{2.303}{2.303}$$

$$\log \frac{1.55 \times 10^{-3}}{4 \times 10^{-3}} = \frac{98600}{2.303 \times 8.314 \times T}$$

$$-16.54 = \frac{98600}{2.303 \times 8.314 \times T}$$

$$T = \frac{98600}{2.303 \times 8.314 \times 16.54}$$

$$T = 311.34 \text{ K}$$

9. A certain reaction is 50% complete in 20 minutes at 300K and the same reaction is again 50% complete in 5 minutes at 350K. Calculate the activation energy if it is a first order reaction. [R = 8.314 J K<sup>-1</sup> mol<sup>-1</sup>; log 4 = 0.602]

Let us first calculate  $k_1$  and  $k_2$  at temperatures 300K and 350K. We know that

$$\log \frac{k_2}{k_1} = \frac{E_a}{R \times 2.303} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$t_{1/2} = 20 \text{ min} \quad k_1 = \frac{0.693}{20}$$

$$t_{1/2} = 5 \text{ min} \quad k_2 = \frac{0.693}{5}$$

$$\log \frac{0.693}{\cancel{0.693}} \times \frac{20}{\cancel{20}} = \frac{E_a}{8.314 \times 2.303} \left[ \frac{350 - 300}{350 \times 300} \right]$$

$$0.602 = \frac{E_a}{8.314 \times 2.303} \left[ \frac{50}{105000} \right]$$

$$E_a = \frac{0.602 \times 8.314 \times 2.303 \times 105000}{50}$$

$$= 19.15 \times 0.602 \times 2100$$

$$= 24213 \text{ J mol}^{-1}$$