First order Reaction -

$$A \longrightarrow P$$

	A	P
initial	a	0
after time t	(a-x)	x

$$\boxed{\text{Rate constant } (k) = \frac{2.303}{t} \log \frac{a}{(a-x)}}$$

a – Initial conc. of reactant
x – Product formed after time "t"
(a-x) – Reactant left after time "t"

$$\boxed{\text{Half life time } t_{1/2} = \frac{0.693}{k}}$$

Second order Reaction :-

$$\boxed{k = \frac{1}{t} \frac{x}{a(a-x)}} \qquad \boxed{t_{1/2} = \frac{1}{ka}}$$

Ques 1 :- A first order reaction take 40.5 min for 25% decomposition of the reactant. Calculate the rate constant.

Ans :- Rate constant $k = \frac{2.303}{t} \log \frac{a}{(a-x)}$

Since reactant amount is not given. Assume it is 100.

$a = 100$ then $x = 25$

$$k = \frac{2.303}{40.5} \log \frac{100}{100-25} = 7.1 \times 10^{-3} \text{ min}^{-1}$$

Ques 2 :- A first order reaction is 20% complete in 10 min. Calculate the rate constant and the time taken for the reaction to go to 75% completion.

Ans :- Rate constant $k = \frac{2.303}{10} \log \frac{100}{100-20} = 0.022 \text{ min}^{-1}$

Rate constant will remain fix at a given temperature. It does not depend on time & reactant concentration.

for 75% completion.

$$k = \cancel{0.22}\ 0.022 = \frac{2.303}{t} \log \frac{100}{100-75}$$

$$t = 63.02 \text{ min.}$$

Ques 3 :- The half life time of a first order reaction is 30 min. Calculate the rate constant and the amount of reactant left after 70 min.

Ans :- $t_{1/2} = \frac{0.693}{R} \Rightarrow R = \frac{0.693}{t_{1/2}} = \frac{0.693}{30} = 0.0231 \, min^{-1}$

Amount of reactant left after time t $= (a-x)$

$$R = \frac{2.303}{t} \log \frac{a}{(a-x)} \Rightarrow 0.0231 = \frac{2.303}{70} \log \frac{100}{(a-x)}$$

$$\Rightarrow (a-x) = 19.95$$

Ques 4 :- Show that for a first order reaction, the time required for 99.9% completion of the reaction is 10 times that required for 50 completion.

Ans :- for 90% completion $R = \frac{2.303}{t_1} \log \frac{100}{100-99.9}$

For 50% completion $k = \frac{2.303}{t_2} \log \frac{100}{100-50}$

$$\Rightarrow \frac{2.303}{t_1} \log \frac{100}{100-99.9} = \frac{2.303}{t_2} \log \frac{100}{100-50}$$

$$\Rightarrow \frac{t_1}{t_2} = \frac{\log \frac{100}{100-99.9}}{\log \frac{100}{100-50}} = \frac{\log \frac{100}{0.1}}{\log \frac{100}{50}} = \frac{\log 1000}{\log 2}$$

$$\frac{t_1}{t_2} = \frac{3}{0.3010} \simeq 10$$

$$t_1 \simeq 10 t_2$$

Ques 5 :- A second order reaction is 20% complete in 500 sec. Calculate the rate constant & the time taken for 60% completion.

Ans :- for 2nd order Reaction

$$R = \frac{1}{t} \frac{x}{a(a-x)} = \frac{1}{500} \frac{20}{100 \times (100-20)} = \frac{1}{500} \times \frac{20}{100 \times 80} = \frac{1}{200000}$$

$$R = 5 \times 10^{-6} \, mole^{-1} L \, sec^{-1}$$

For 60% completion $x = 60$

$$5 \times 10^{-6} = \frac{1}{t} \frac{60}{100 \times 40} \Rightarrow t = \frac{6}{400 \times 5 \times 10^{-6}} = \frac{6 \times 10^6}{2000}$$

$$t = 3 \times 10^3 \, sec$$

Ques6 :- Decomposition of a gas is of 2nd order. When the initial conc. of the gas is 5×10^{-4} mole/litre, it is 40% decomposed in 50 min. What is the value of rate or velocity constant.

Ans :-

$a = 5\times10^{-4}$ mol/l

$x = 40\%$ of $a = 5\times10^{-4}\times\frac{40}{100} = 2\times10^{-4}$

$$k = \frac{1}{50}\;\frac{2\times10^{-4}}{5\times10^{-4}(5\times10^{-4} - 2\times10^{-4})}$$

$$= \frac{1}{50}\times\frac{2\times10^{-4}}{5\times10^{-4}\times3\times10^{-4}}$$

$$= 26.67\ mol^{-1}\,L\,min^{-1}$$

Arrhenius eqn —

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

k - Rate constant
A - Arrhenius factor
E_a = Activation energy
R = gas const. = 8.314 $JK^{-1}mole^{-1}$
T - Temperature.

$$2.303\log\frac{k_2}{k_1} = \frac{E_a}{R}\left[\frac{T_2-T_1}{T_1T_2}\right]$$

k_1 - Rate const at T_1 Temp
k_2 - " " " T_2 "

Ques7 :- The rate constant of a 2nd order reaction is $5.70\times10^{-5}\,dm^3\,mol^{-1}\,sec^{-1}$ at 25°C & $1.65\times10^{-4}\,dm^3\,mole^{-1}\,sec^{-1}$ at 40°C. Calculate the activation energy of the reaction.

Ans :

$k_1 = 5.7\times10^{-5}$, $T_1 = 25°C = 25+273 = 298\,K$

$k_2 = 1.65\times10^{-4}$, $T_2 = 40°C = 40+273 = 313\,K$.

$$2.303\log\frac{k_2}{k_1} = \frac{E_a}{R}\left[\frac{T_2-T_1}{T_1T_2}\right]$$

$$2.303\log\frac{1.65\times10^{-4}}{5.7\times10^{-5}} = \frac{E_a}{8.314}\left[\frac{313-298}{313\times298}\right]$$

$$\Rightarrow E_a = 54478\ J\,mole^{-1}$$

$$= 54.48\ kJ\,mole^{-1}.$$

Ques 8 :- The rate of reaction triples when the temperature change from 20°C to 50°C. Calculate the activation energy.

Ans :-
$k_1 = K \quad , \quad T_1 = 20 + 273 = 293\,K$

$k_2 = 3K \quad , \quad T_2 = 50 + 273 = 323\,K$

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

$E_a = 28817.9 \ J\,mole^{-1}$

$= 28.8 \ kJ\,mole^{-1}$.

Ques 9 :- Calculate the activation energy of a reaction whose rate constant is tripled by a 10°C rise in temperature in the vicinity of 27°C.

Ans :- Vicinity means - near by - आस पास

Rise in temp $= 10°C \Rightarrow$ change $- \frac{10}{2} = 5°C$.

$k_1 = K \quad , \quad T_1 = 27 - 5 = 22°C = 22 + 273 = 295\,K$.

$k_2 = 3k, \quad T_2 = 27 + 5 = 32 = 32 + 273 = 305\,K$.

$$2.303 \log \frac{3K}{K} = \frac{E_a}{8.314}\left[\frac{305 - 295}{305 \times 295}\right]$$

$E_a = 82182 \ J\,mole^{-1} = 82.18 \ kJ\,mole^{-1}$.