Chemical Kinetics – 08

Half Life Method to find Order of Reaction

For Zero Order

$t_{1/2} = \frac{A_0}{2K}$ → A_0 → initial concentration, K → rate constant

$t_{1/2} \propto (A_0)^{1-0}$

For First Order

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

$t_{1/2} \propto (A_0)^{1-1}$

For Second Order

$t_{1/2} = \frac{3}{2KA_0}$

$t_{1/2} \propto (A_0)^{1-2}$

⇒ For n^{th} order reaction

$$\boxed{t_{1/2} \propto (A_0)^{1-n}}$$

Now, if we know two initial concentrations & half life for each initial concentration, we can find n.

$\frac{A_0}{A_1}$	$\frac{t_{1/2}}{t_1}$
A_2	t_2

then $t_{1/2} \propto (A_0)^{1-n}$

$$\boxed{\frac{t_1}{t_2} = \left(\frac{A_1}{A_2}\right)^{1-n}}$$

put values of A_1, A_2 t_1 & t_2 find n.

Q) the half-life Period of a Compound is 20 minutes. If the initial concentration is doubled, the half-life period is reduced to 10 minutes. What is the order of the reaction?

A_0	$t_{1/2}$
x	20 min
$2x$	10 min

$$\frac{t_1}{t_2} = \left(\frac{A_1}{A_2}\right)^{1-n}$$

$$\frac{20}{10} = \left(\frac{x}{2x}\right)^{1-n}$$

$$2^1 = 2^{n-1}$$

$$n-1 = 1$$

$$\boxed{n=2}$$ Second order reaction

Q2) At a certain temperature, the half life Periods of a reaction at different initial pressures were as follows :

P (kPa)	$t_{1/2}$ (in mins)
100	105
66.67	235
33.33	950

$$\frac{t_1}{t_2} = \left(\frac{A_1}{A_2}\right)^{1-n}$$

$$\frac{950}{235} = \left(\frac{33.33}{66.67}\right)^{1-n}$$

$$\frac{190}{47} = \left(\frac{1}{2}\right)^{1-n}$$

(data is experimental)

$\approx$ nearly

$$4 = 2^{n-1}$$

$$2^2 = 2^{n-1}$$

$$n-1 = 2$$

$$\boxed{n = 3}$$ Third order reaction

Q3)

initial Pressure (mm of Hg)	$t_{1/2}$ (in mins)
707	84
500	83.8
79	84

Solution

* $t_{1/2}$ is independent of initial Pressure (is constant)

$\Rightarrow$ First order $t_{1/2} = \frac{0.693}{k}$ = Constant

$$\frac{t_1}{t_2} = \left(\frac{A_1}{A_2}\right)^{1-n}$$

$$\frac{84}{84} = \left(\frac{707}{79}\right)^{1-n}$$

$$1 = \left(\frac{707}{79}\right)^{1-n}$$

$$1-n = 0$$

$$\boxed{n=1}$$ First order

Graphical Method to find Order of Reaction

Check the plot of Conc, $\log(\text{Conc})$, $\frac{1}{\text{Conc}}$, $\frac{1}{(\text{Conc})^n}$ v/s time

Conc → of Reactant

if $\log(\text{Conc})$ v/s t is straight line ⇒ First order

if Conc v/s t is " " ⇒ Zero order

if $\frac{1}{\text{Conc}}$ v/s t is " " ⇒ Second order

if $\frac{1}{(\text{Conc})^2}$ v/s t is " " ⇒ Third order

if $\frac{1}{(\text{Conc})^3}$ v/s t is " " ⇒ Fourth order

if $\frac{1}{(\text{Conc})^{n-1}}$ v/s t is " " ⇒ n^{th} order

Integrated Rate Law Method
or
Hit & Trial Method
to find Order of Reaction.

Substitute the given data in Integrated Rate Law of first order & calculate two values of Rate constant (K) from data

$$K = \frac{2.303}{t} \log_{10} \frac{A_0}{A}$$

if two values of K are same ⇒ first order (or nearly same)

else

Repeat the process on Rate Law of ~~second~~ Zero Order

$$A = A_0 - Kt$$

$$K = \frac{A_0 - A}{t}$$

if two values of K are same ⇒ Zero order (nearly same)

else

Answer is 99% 1st or Zero

Repeat on Integrated Rate Law of second order

$$K = \frac{1}{t}\left[\frac{1}{A} - \frac{1}{A_0}\right]$$ ----

if two values of K are same ⇒ second order
(nearly same)

else

Try on 3rd Order

$$K = \frac{1}{2t}\left[\frac{1}{A^2} - \frac{1}{A_0^2}\right]$$

- - -

- - else

4th order $K = \frac{1}{3t}\left[\frac{1}{A^3} - \frac{1}{A_0^3}\right]$

- - - -

Q1) $A \longrightarrow B + C$

following data is obtained experimentally

mol/L [A]	50	30	18
time (in min)	0	10	20

Try First order $K = \frac{2.303}{t}\log_{10}\frac{A_0}{A}$

$50 \to 30$ $\quad K_1 = \frac{2.303}{10}\log_{10}\left(\frac{50}{30}\right)$ — (i)

$50 \to 18$ $\quad K_2 = \frac{2.303}{20}\log_{10}\left(\frac{50}{18}\right) = \frac{2.303}{20}\log_{10}\left(\frac{25}{9}\right)$

$K_1 = K_2 \Rightarrow$ First order $= \frac{2.303}{20}\log_{10}\left(\frac{5}{3}\right)^2 = \frac{2.303}{10}\log_{10}\frac{5}{3}$