

Chemical Kinetics - 08

Half Life Method

to find order of Reaction

For zero order

$$t_{1/2} = \frac{A_0}{2K}$$

\rightarrow initial concentration
 \rightarrow 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

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

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

\Rightarrow 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 .

Q1) 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

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

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

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

$$n-1 = 1$$

$n=2$ 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)

\nearrow 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

is constant

* $t_{1/2}$ is independent of initial pressure
 \Rightarrow First order $t_{1/2} = \frac{0.693}{k} = \text{constant}$

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

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

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

$$1-n = 0$$

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

Graphical Method to find Order of Reaction

Check the plot of Conc , $\log(\text{Conc})$, $\frac{1}{\text{Conc}}$

$(\text{Conc})^n$ v/s time $\text{Conc} \rightarrow \text{of Reactant}$

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

if Conc v/s t is " " \Rightarrow Zero order

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

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

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

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

Answer is

99% 1st or Zero

else

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 \Rightarrow Second order
(nearly same)

else

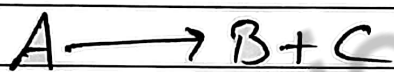
Try on 3rd Order

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

-- else

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

Q1)



following data is obtained experimentally

Vol/L [A]	50	30	18
time (in sec)	0	10	20

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

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

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

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