

Methods for Determination the Order of Reaction

1-by using the unite of rate constant (k)

كما بينا مسبقا ان وحدة ثابت سرعة التفاعل تتغير بتغير مرتبة التفاعل ويمكن ايجادها من العلاقة الاتية:

$$\text{Unite of } k = (\text{M})^{1-n} * \text{s}^{-1}$$

2- Initial Rate Method or isolation methods

In this method initial rate of reaction is determined by varying the concentration of one of the reactants while others are kept constant

$$R = k[A]^x[B]^y[C]^z$$

if [B] & [C] = Constant then for two different initial concentrations of A we have

$$R_{0_1} = k[A_0]_1^a \quad \text{and} \quad R_{0_2} = k[A_0]_2^a$$
$$\Rightarrow \frac{R_{0_1}}{R_{0_2}} = \left(\frac{[A_0]_1}{[A_0]_2} \right)^n$$

2- Graphical Method

This method can be used when there is only one reactant. If the plot of $\log [A]$ vs t is a straight line, the reaction follows first-order. If the plot of $1/[A]$ vs t is a straight line, the reaction follows second order. If the plot of $1/[A]^2$ is a straight line, the reaction follows third order. Generally, for a reaction of n th order, a graph of $1/[A]^{n-1}$ vs t must be a straight line.

Here $[A]$ is the concentration of reactant at any given time of the reaction (other $t=0$). $[A] = (a-x)$ where a is the initial concentration and x is the extent of reaction at time t .

3- Half life method

- This method is used only when the rate law involved by only one concentration term.

$$t_{(1/2)} \propto a^{1-n}$$
$$t_{(1/2)} = k \cdot 1/a^{n-1}$$
$$\log t_{(1/2)} = \log k + (1-n)a$$

- Graph of $\log t_{1/2}$ vs $\log a$, gives a straight line with slope $(1-n)$, where 'n' is the order of the reaction.

- Determining the slope we can find the order n.
- If half life at different concentrations is given then.

$$(t_{1/2})_1 \propto \frac{1}{a_1^{n-1}}$$

and

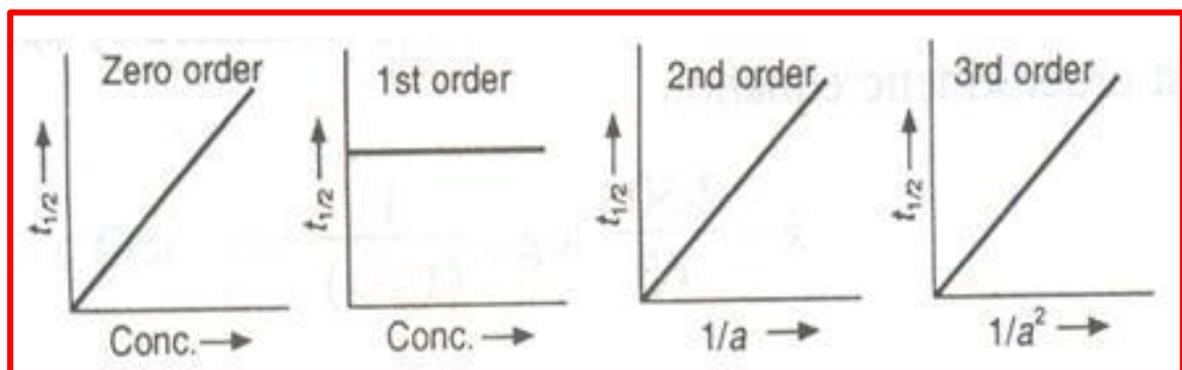
$$(t_{1/2})_2 \propto \frac{1}{a_2^{n-1}}$$

$$\therefore \frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$$

Taking logarithm and rearranging

$$n = 1 + \frac{\log(t_{1/2})_1 - \log(t_{1/2})_2}{\log a_2 - \log a_1}$$

- Plots of half-lives concentration ($t_{1/2} \propto a^{1-n}$):



This relation can be used to determine order of reaction 'n'

Question:

From the following data show that the decomposition of hydrogen peroxide in aqueous solution is a first - order reaction. What is the value of the rate constant?

Time in minutes	0	10	20	30	40
Volume V in ml	25.0	20.0	15.7	12.5	9.6

where V is the number of ml of potassium permanganate required to decompose a definite volume of hydrogen peroxide solution.

Solution:

The equation for a first order reaction is the volume of KMnO_4 used, evidently corresponds to the undecomposed hydrogen peroxide. Hence the volume of KMnO_4 used, at zero time corresponds to the initial concentration **a** and the volume used after time t, corresponds to (a - x) at that time. Inserting these values in the above equation, we get

when t = 10 min.

$$k_1 = 2.23/10 \log (25/20) = 0.022318 \text{ min}^{-1} = 0.000372 \text{ s}^{-1}$$

when t = 20 min.

$$k_1 = 2.23/20 \log (25/12) = 0.023265 \text{ min}^{-1} = 0.0003871 \text{ s}^{-1}$$

when t = 30 min.

$$k_1 = 2.23/30 \log (25/12.5) = 0.02311 \text{ min}^{-1} = 0.000385 \text{ s}^{-1}$$

when t = 40 min.

$$k_1 = 2.23/40 \log (25/19.6) = 0.023932 \text{ min}^{-1} = 0.0003983 \text{ s}^{-1}$$

The constancy of k, shows that the decomposition of H_2O_2 in aqueous solution is a **first order** reaction.

The average value of the rate constant is **0.0003879 s⁻¹**.

4-differeantioal method:

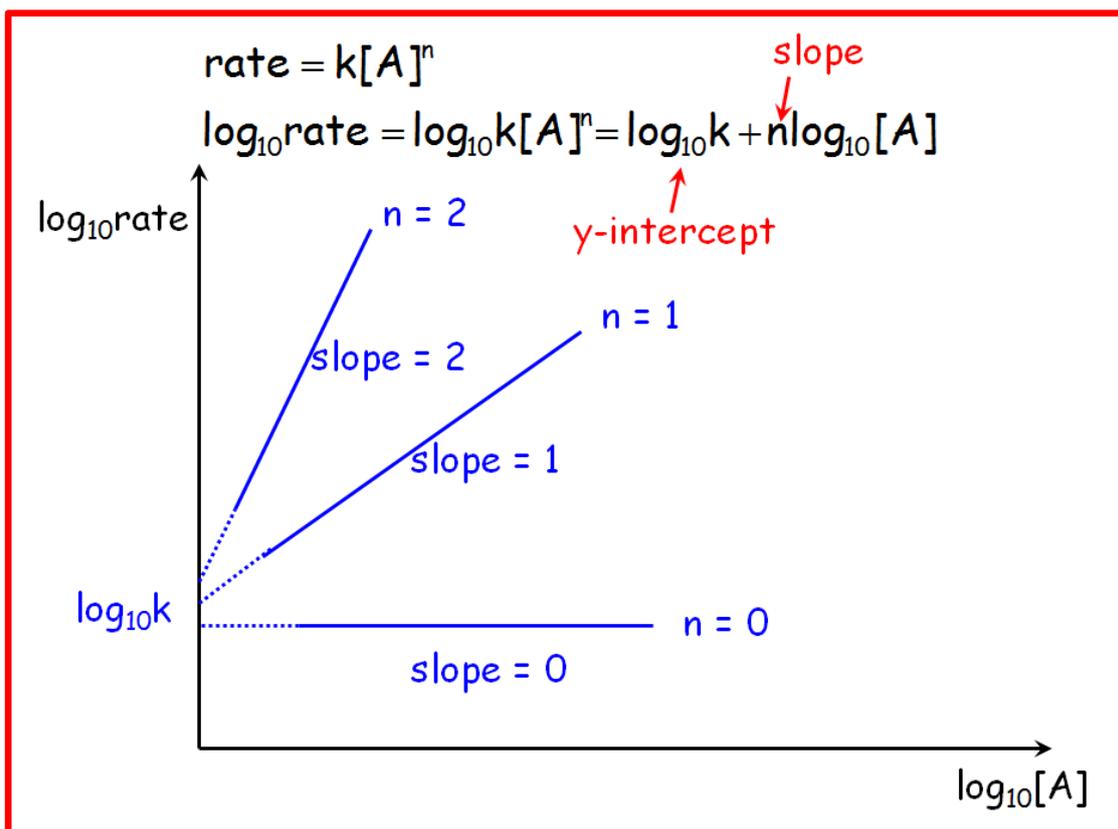
هذه الطريقة يمكن ان تتحقق بشكلين الاول اخذ تركيز واحد من المادة المتفاعلة ونرسم خط برابولي لفترات زمنية مختلفة من خلال رسم مماسات للعلاقة بين التغير في التركيز او التركيز للمتفاعل مع الزمن . الطريقة الثانية تتضمن اخذ تراكيز مختلفة من المادة المتفاعلة ويدرس التغير في تراكيزها مع الزمن وبنفس الترتيب تحسب السرعة وتطبق علاقة السرعة مع التركيز الابتدائي وكما مبين في العلاقات الرياضية الاتية:

$$R = kn [A]^n$$

By take the log for the two sides of equation we can obtained

$$\text{Log } R = \log kn + n \log [A]$$

Than we plot log R vs log [A] the slop from this process give us the value of order n.



The temperature dependence of reaction rates

Question from Atkins

The variation in the partial pressure of azomethane with time was followed at 600 K, with the results given below. Confirm that the decomposition



is first-order in azomethane, and find the rate constant at 600 K.

t/s	0	1000	2000	3000	4000
p/Pa	10.9	7.63	5.32	3.71	2.59

22.1b The rate of the reaction $\text{A} + 3 \text{B} \rightarrow \text{C} + 2 \text{D}$ was reported as $1.0 \text{ mol dm}^{-3} \text{ s}^{-1}$. State the rates of formation and consumption of the participants.

22.10a The second-order rate constant for the reaction
 $\text{CH}_3\text{COOC}_2\text{H}_5(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{CH}_3\text{CO}_2^-(\text{aq}) + \text{CH}_3\text{CH}_2\text{OH}(\text{aq})$
is $0.11 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. What is the concentration of ester after (a) 10 s,
(b) 10 min when ethyl acetate is added to sodium hydroxide so that
the initial concentrations are $[\text{NaOH}] = 0.050 \text{ mol dm}^{-3}$ and
 $[\text{CH}_3\text{COOC}_2\text{H}_5] = 0.100 \text{ mol dm}^{-3}$?

22.1 The data below apply to the formation of urea from ammonium cyanate,



Initially 22.9 g of ammonium cyanate was dissolved in in enough water to prepare 1.00 dm³ of solution. Determine the order of the reaction, the rate constant, and the mass of ammonium cyanate left after 300 min.

t/min	0	20.0	50.0	65.0	150
m(urea)/g	0	7.0	12.1	13.8	17.7