



Kinetic Chemistry

(222 C)

By
Prof. Dr. Lobna Abdel-Mohsen Ebaid Nassr

23/3/2020

Determination of the Reaction Order (n)

The **order of reaction** with respect to a **reactant** is the power to which the concentration of the reactant is raised into the rate law.

The **overall order of reaction** is the sum of the powers of the concentrations involved in the rate law

$$\text{Rate} = k [\text{A}]^{\alpha} [\text{B}]^{\beta} \dots$$

The reaction would be said to be α^{th} order with respect to **A**, β^{th} order with respect to **B**,

The **overall order of reaction** would be $\alpha + \beta + \dots$

It is very important to identify the role of each component in the reaction (to determine the **order of reaction** with respect to each **component participate in the reaction**).

Method to Determination the reaction Order (n)

There are **various methods**, which can be used to **determine** the order of reaction (n) with respect to a reactant.

Every method requires essentially the measurement of concentration of the reactant or product at various time intervals.

(1) Integration Method

(2) Half-life Period Method

(3) Differential Method

(4) Graphical Method

(5) Ostwald Isolation Method

****All the mentioned methods are practical methods and required the measurement of concentration of the reactant or product at various time intervals.****



(1) Integration Method

To apply this method you should determine experimentally the values of:

- a** (initial concentration of the reactant)
- a – x** (reactant concentration at different time)
- x** (product concentration at different time)

From the obtained values (a, a-x and x) Calculate the values of **rate constant k** for the different rate equations:

- k_1** for first-order
- k_2** for second-order
- k_3** for third-order
- k_0** for zero-order

(1) Integration Method

Remember that

$$\mathbf{k}_1 = \dots\dots\dots$$

$$\mathbf{k}_2 = \dots\dots\dots$$

$$\mathbf{k}_3 = \dots\dots\dots$$

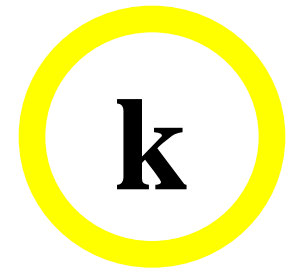
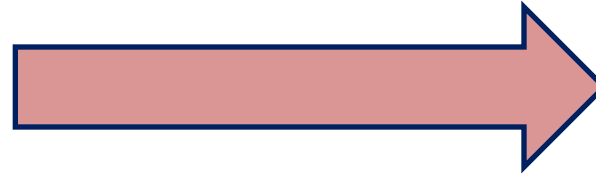
$$\mathbf{k}_0 = \dots\dots\dots$$

Reaction	Order	Differential equation	Integral equation
$\underset{(a)}{A} \xrightarrow{k} \text{Product}$	0	$\frac{dx}{dt} = k$	$k = \frac{x}{t}$
$\underset{(a)}{A} \xrightarrow{k} \text{Product}$	1/2	$\frac{dx}{dt} = k(a-x)^{1/2}$	$k = \frac{2}{t}$ $[a^{1/2} - (a-x)^{1/2}]$
$\underset{(a)}{A} \xrightarrow{k} \text{Product}$	1	$\frac{dx}{dt} = k(a-x)$	$k = \frac{2.303}{t}$ $\log \frac{a}{(a-x)}$
$\underset{(a)}{A} \xrightarrow{k} \text{Product}$	3/2	$\frac{dx}{dt} = k(a-x)^{3/2}$	$k = \frac{2}{t}$ $\left(\frac{1}{(a-x)^{1/2}} - \frac{1}{a^{1/2}} \right)$
$\underset{(a)}{A} + \underset{(a)}{B} \xrightarrow{k} \text{Product}$	2	$\frac{dx}{dt} = k(a-x)^2$	$k = \frac{1}{t}$ $\left(\frac{1}{(a-x)} - \frac{1}{a} \right)$

Reaction	Order	Differential equation	Integral equation
$\text{A} + \text{B} \xrightarrow{k}$ Autocatalytic Product	2	$\frac{dx}{dt} = k(a-x)(c+x)$	$k = \frac{2.303}{t(a+c)} \log \frac{a(c+x)}{c(a-x)}$
$\underset{(a)}{\text{A}} + \underset{(a)}{\text{B}} + \underset{(a)}{\text{C}} \xrightarrow{k}$ Product	3	$\frac{dx}{dt} = k(a-x)^3$	$k = \frac{1}{2t} \left(\frac{1}{(a-x)^2} - \frac{1}{a^2} \right)$
$\underset{(a)}{\text{A}} + \underset{(b)}{\text{B}} + \underset{(c)}{\text{C}} \xrightarrow{k}$ Product	3	$\frac{dx}{dt} = k(a-x)(b-x)(c-x)$	$k = \frac{2.303}{t(a-b)(b-c)(c-a)} \left(\begin{aligned} & (b-c) \log \frac{a}{(a-x)} \\ & + (c-a) \log \frac{b}{(b-x)} \\ & + (a-b) \log \frac{c}{(c-x)} \end{aligned} \right)$

(1) Integration Method

From the values of
 a , $a - x$, x



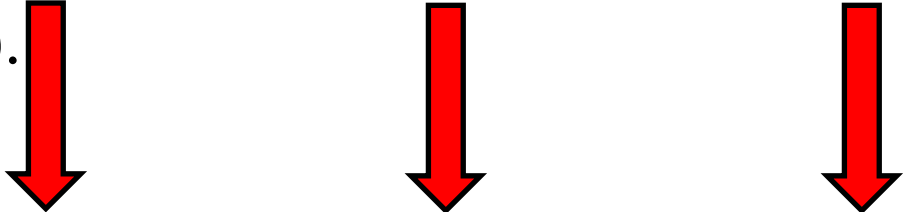
Calculate and complete the following table

time	$a-x$	x	$k_1 = \dots\dots$	$k_2 = \dots\dots$	$k_3 = \dots\dots$
t_1	$(a-X)_1$	X_1	k_1 at t_1	k_2 at t_1	k_3 at t_1
t_2	$(a-X)_2$	X_2	k_1 at t_2	k_2 at t_2	k_3 at t_2
t_3	$(a-X)_3$	X_3
t_4	$(a-X)_4$	X_4	k_3 at t_4
t_5	$(a-X)_5$	X_5
t_6	$(a-X)_6$	X_6	k_2 at t_6
t_7	$(a-X)_7$	X_7
t_8	$(a-X)_8$	X_8	k_3 at t_8
t_9	$(a-X)_9$	X_9	k_1 at t_9
t_{10}	$(a-X)_{10}$	X_{10}	k_1 at t_{10}	k_2 at t_{10}

(1) Integration Method

* Compare **vertically** between the columns of different **k** values.

* The column which has **similar** or **constant** values of **k** **indicates** that, the used equation is the correct one and this is the order of reaction (n).



time	a-x	x	$k_1 = \dots\dots$	$k_2 = \dots\dots$	$k_3 = \dots\dots$
t_1	$(a-X)_1$	X_1	k_1 at t_1	k_2 at t_1	k_3 at t_1
t_2	$(a-X)_2$	X_2	k_1 at t_2	k_2 at t_2	k_3 at t_2
...
...
...
...
t_{10}	$(a-X)_{10}$	X_{10}	k_1 at t_{10}	k_2 at t_{10}	k_3 at t_{10}

(1) Integration Method

* Example

On applying the integration method, the following values are obtained:

time	a-x	x	$k_1 = \dots\dots$	$k_2 = \dots\dots$	$k_3 = \dots\dots$
t_1	$(a-X)_1$	X_1	0.001	0.01	0.02
t_2	$(a-X)_2$	X_2	0.02	0.01	0.002
t_3	$(a-X)_3$	X_3	0.04	0.011	0.015
t_4	$(a-X)_4$	X_4	0.005	0.0099	0.03
t_5	$(a-X)_5$	X_5	0.035	0.01	0.025
t_6	$(a-X)_6$	X_6	0.06	0.01	0.05

What is the reaction order (n)?

(2) Half-life Period Method

The general relation between the **initial concentration** and $t_{1/2}$:

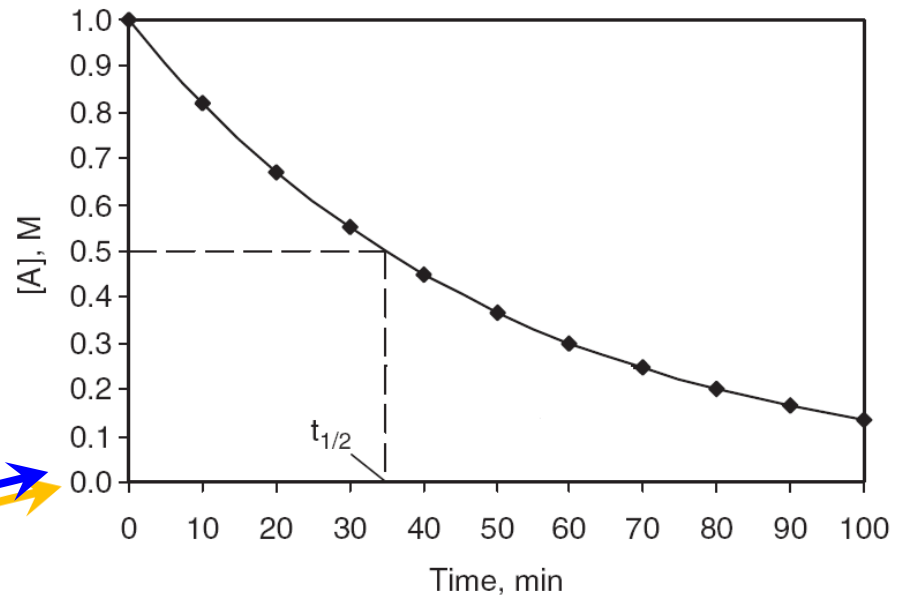
$$t_{1/2} \propto 1/(a^{n-1})$$

To apply this method:

- 1) The kinetic experimental is repeated **twice** with **2 different initial concentrations a_1 and a_2** .
- 2) The relations between the **reactant concentration** and **time** are plotted in case of both **a_1 and a_2** .

3) The values of $t_{1/2}$ are determined from the two obtained plots.

How??



(2) Half-life Period Method

Now you have the values of $\{a_1 \text{ and } a_2\}$ and their corresponding $\{(t_{1/2})_1 \text{ and } (t_{1/2})_2\}$.

And as:

$$(t_{1/2})_1 \propto \frac{1}{(a_1)^{n-1}} \quad \text{and} \quad (t_{1/2})_2 \propto \frac{1}{(a_2)^{n-1}}$$

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

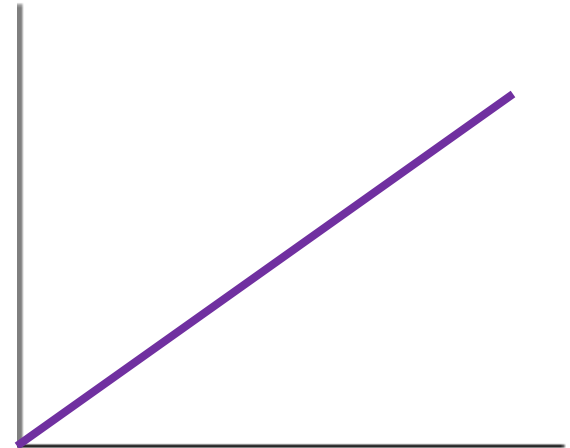
$$\log \left(\frac{(t_{1/2})_1}{(t_{1/2})_2} \right) = (n - 1) \log \left(\frac{a_2}{a_1} \right)$$

The reaction order (n) can be calculated according to the above equation.

(2) Half-life Period Method

The **plot** of **logarithms of ratio of half-life periods** versus **ratio of initial concentrations** will be **linear** passing through the origin with a **slope** equal to $(n - 1)$ and thus **the order** can be determined from its slope.

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



To plot the above relation, how many times do you need to repeat your experimental???

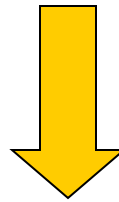


(3) Differential Method (Van't Hoff's differential method)



The rate of reaction at **2** different concentrations **c₁** and **c₂** can be given as

$$\text{Rate}_1 = - \frac{dc_1}{dt} = kc_1^n$$



$$\text{Rate}_2 = - \frac{dc_2}{dt} = kc_2^n$$

1) The reaction is carried out with **2 different initial concentrations** of the reactant.

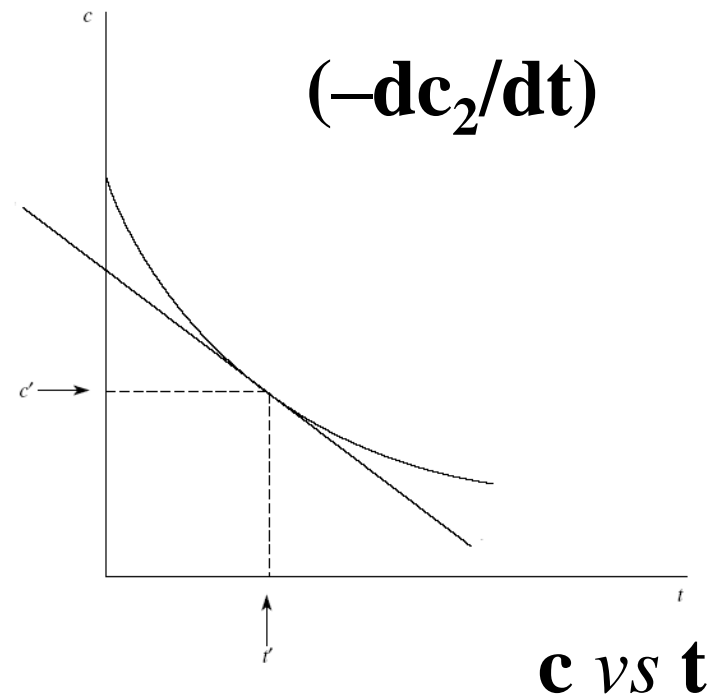
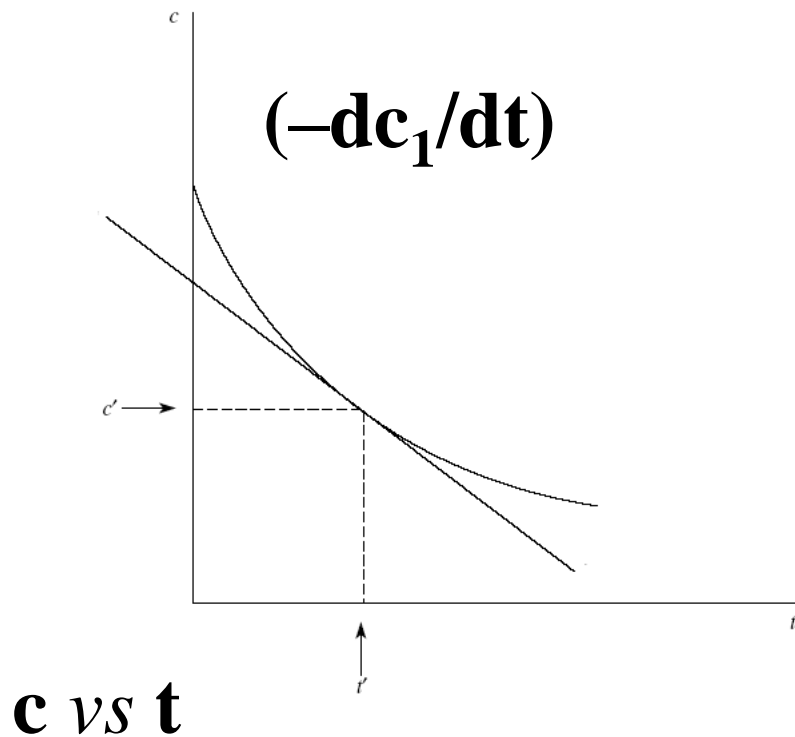
$$[A]_0 = c_1$$

$$[A]_0 = c_2$$

(3) Differential Method (Van't Hoff's differential method)

2) The change in **concentration** versus **time** plots for both the experiments are obtained.

3) The slope ($-\mathbf{dc}/\mathbf{dt}$) at a **given time** interval is measured in **both cases**.



(3) Differential Method (Van't Hoff's differential method)

4) Now you have the values of $\{c_1 \text{ and } c_2\}$ and their corresponding $\{-dc_1/dt \text{ and } -dc_2/dt\}$.

And as:

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{(-dc_1/dt)}{(-dc_2/dt)} = \left(\frac{c_1}{c_2}\right)^n$$

$$n = \frac{\log(\text{Rate}_1) - \log(\text{Rate}_2)}{\log c_1 - \log c_2}$$

So the reaction order (**n**) is determined.

(3) Differential Method (Van't Hoff's differential method)

****The differential rate equation can also be used alternatively as**

$$-\frac{dc}{dt} = kc^n \quad \longrightarrow \quad -\log\left(\frac{dc}{dt}\right) = \log k + n \log c$$

Or

$$dx/dt = k_n (a-x)^n \quad \longrightarrow \quad \log dx/dt = \log k_n + n \log(a-x)$$

***log (rate) versus log [concentration]:**
Intercept = **log k**
Slope = **n**

***log dx/dt against log(a-x):**
Intercept =
Slope = ...

(4) Graphical Method

* The **general rate** law is:

$$-\frac{d[A]}{dt} = k[A]^n$$

* On **integration** of the above equation ($n \neq 1$) the following relation is obtained, **where $[A]_0 = a$ and $[A] = (a - x)$** :

$$\frac{1}{[A]^{n-1}} - \frac{1}{[A]_0^{n-1}} = (n - 1)kt$$

* **Applying** this method required the values of **$(a - x)$** or **$[A]$** at different intervals **time**.

(4) Graphical Method

$$\frac{1}{[A]^{n-1}} - \frac{1}{[A]_0^{n-1}} = (n-1)kt$$

****For 2nd – order (n=2):**

the equation will be: $1/[A] - 1/[A]_0 = kt$

And the plot between $1/[A]$ versus time is linear.

****For 3rd – order (n=3):**

the equation will be: $1/[A]^2 - 1/[A]_0^2 = 2kt$

And the plot between $1/[A]^2$ versus time is linear.

****For zero – order (n=0):**

the equation will be: $[A] - [A]_0 = -kt$

And the plot between $[A]$ versus time is linear.

(4) Graphical Method

To determine n by this method, plot the following:

- (1) $1/[A]$ versus **time**
- (2) $1/[A]^2$ versus **time**
- (3) $[A]$ versus **time**

The **liner plot** will indicate the correct reaction order value

(5) Ostwald Isolation Method

When more than one reactant is involved in the reaction, it is necessary to isolate one of the reactants and its influence on the rate of reaction.

“If any reactant is taken in large excess, its concentration virtually remains constant, and thus it will not affect the rate of reaction”

For a reaction with 3 reactants (A, B and C), and α , β and γ are the order with respect to A, B and C, respectively.

The overall reaction order: $n = \alpha + \beta + \gamma$

If reaction is carried out under the conditions of large excess of B and C, ($[B]$ and $[C] \gg [A]$) the reaction rate will be given by:

$$-\frac{d[A]}{dt} = kC_A^\alpha$$

And the value of α (reaction order related to reactant A) can be determined by any method mentioned previously.

(5) Ostwald Isolation Method

By similar way

* The value of β can similarly be determined by using a large excess of **A** and **C**.

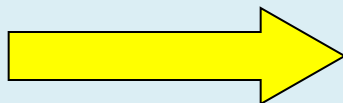
At $[A]$ and $[C] \gg [B]$



The value of β

* For determination of γ , the experiment can be repeated by taking large excess of **A** and **B**.

At $[A]$ and $[B] \gg [C]$



The value of γ

** Thus, order with respect to each reactant can be determined.

$$n = \alpha + \beta + \gamma$$

Method to Determination the reaction Order (n)

(1) Integration Method



(2) Half-life Period Method



(3) Differential Method



(4) Graphical Method



(5) Ostwald Isolation Method



<https://staffsites.sohag-univ.edu.eg/lobna.nassr>