BSK1133 PHYSICAL CHEMISTRY

CHAPTER 4
REACTION MECHANISM (PART A)

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CHAPTER 4 REACTION MECHANISM (PART A)
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http://ocw.ump.edu.my/course/view.php?id=470

Description

Aims

- To understand the mechanism of a chemical reaction.

Description

Expected Outcomes

- ❖ Able to understand the mechanism of a chemical reaction.

References

- ✓ Atkins, P & Julio, D. P. (2006).Physical Chemistry (8th ed.). New York: Oxford.
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- ✓ Silbey, R. J., Alberty, A. A., & Bawendi, M. G. (2005). Physical Chemistry. New York: John Wiley & Sons.
- ✓ Mortimer R. G. (2008) Physical Chemistry, Third Edition , Elsevier Academic press, USA.

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- 4.2 Reaction Rate
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- 4.4 Integrated Rate Law
- 4.5 Half-life
- Conclusion

4.1 Theory of Chemical Kinetic

Chemical Kinetics

- Chemical kinetics is concern about the ***speeds*** or ***rates*** of a chemical reactions to be occurred .

- Theories of Chemical Kinetics:
  1. Collision Theory
  2. Transition State Theory

4.1.1 Collision Theory

Collision frequency is the rate of reaction of a chemical process is directly proportional to the number of molecular collisions per unit time.

- When the reacting molecules colliding with one another, only a fraction of the collisions will lead to chemical reaction.

- There are two types of collision:
  1) Effective collision (reaction occur)
  2) Ineffective collision (no reaction will occur)

Effective Collision:

- **The molecular collision can be effective when:**

1. The reactant molecules have sufficient energy (moving energetically).

- ***Activation Energy (E_a)-*** lowest energy that the molecules must bring to their collisions for a chemical reaction to occur.

2. The collision between molecules are oriented correctly (to allow collision)

- ***Proper Orientation of Molecules***

4.1.2 Transition State Theory

Transition state theory explaining the temporary state that species occur after a reaction of substance and before forming a product.

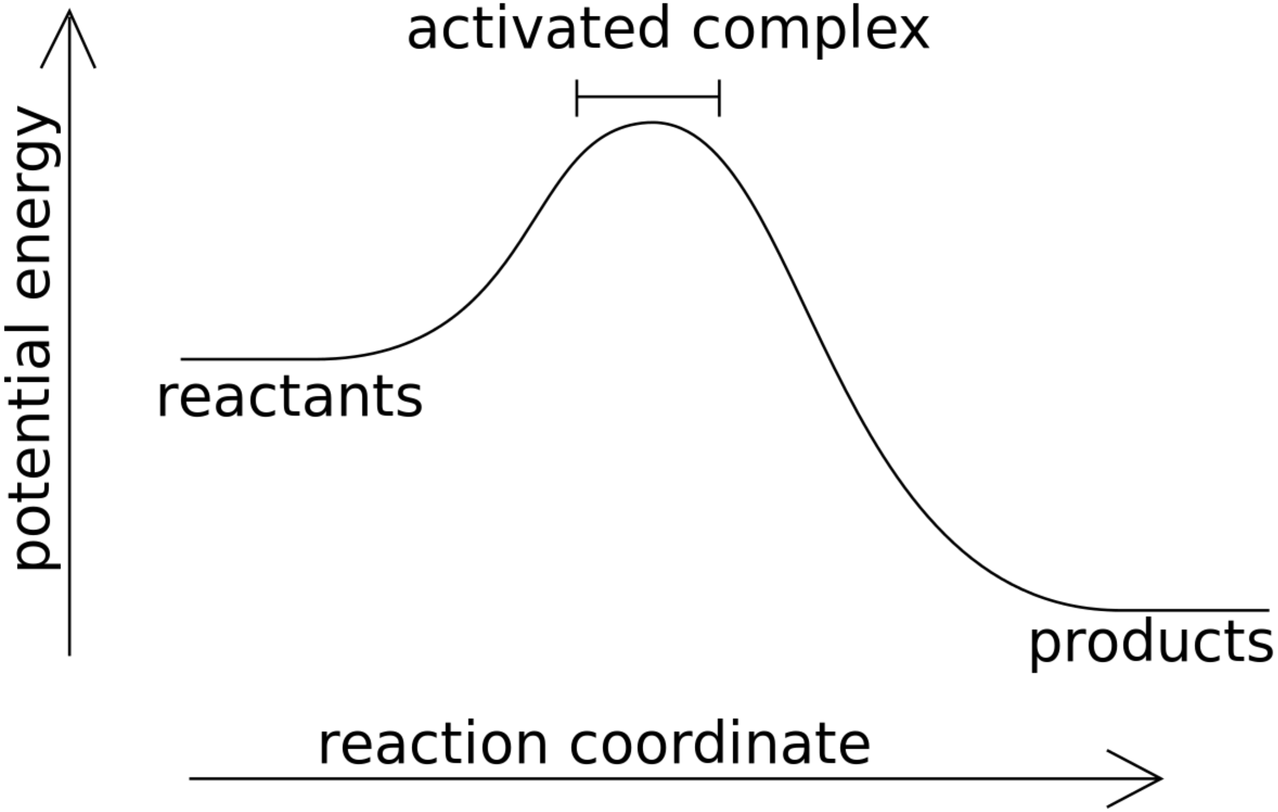
It called an ***activated complex***.

Activated Complex

- Activated complex is a ***transition state*** that appears between the reactants and the products.

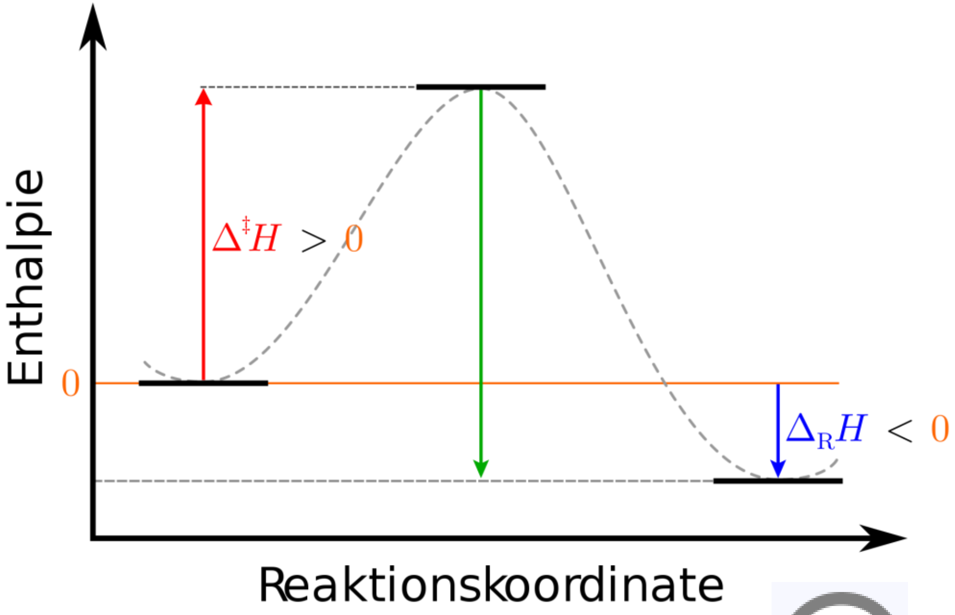
- At this transition state, breaking of chemical bonds of the reactant is in the progress before forming the product.

- At this transition state, the molecule species are very unstable and have high potential energy.



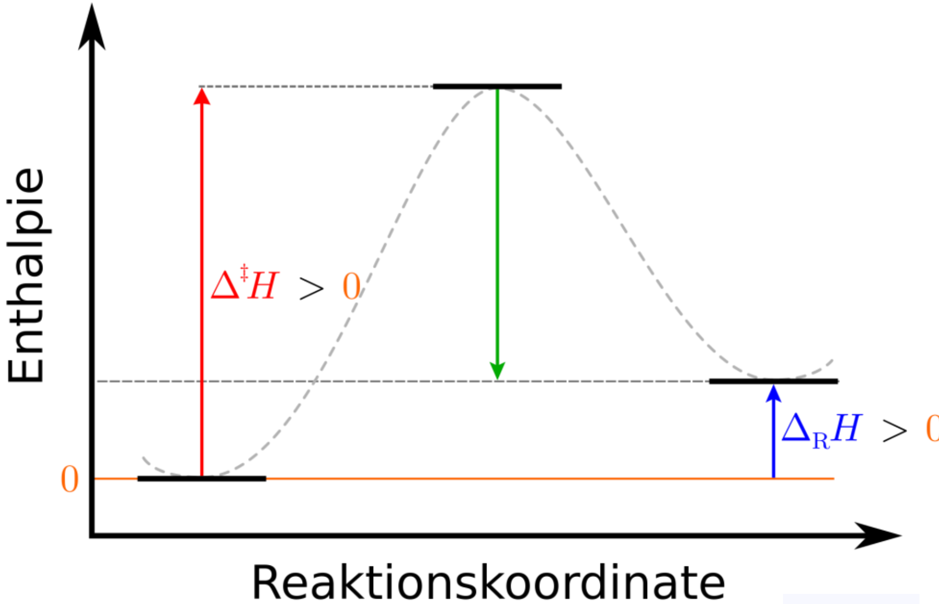
Source: Slashme
https://en.wikipedia.org/wiki/File:Ac_com.svg

Exothermic Reaction



Source: Sponk (talk) https://commons.wikimedia.org/wiki/File:Enthalpy_profile_exothermic_reaction-IT.svg

Endothermic Reaction



Source: Sponk (talk) https://de.wikipedia.org/wiki/Datei:Enthalpy_profile_endothermic_reaction-DE.svg

4.2 Reaction Rate

- ✓ Reaction rate is the speed of the reaction process.
- ✓ it can be indicates through the decreasing in the reactant concentration or the increasing in the product formation with time

Reaction rate is **concentration change** divided by **time change**

$$\text{Reaction rate} = \frac{\Delta[X]}{\Delta t}$$

Changes!
Final minus initial

$$\Delta[X] = [X]_{final} - [X]_{initial}$$

$$\Delta t = t_{final} - t_{initial}$$

Concentration normally in molality ($mol{\cdot}L^{-1}$)

This means that reaction rate has units $mol{\cdot}L^{-1}{\cdot}s^{-1}$

The reaction rate can be indicate by:

- increase in the concentration of a product over time, or
- decrease in the concentration of a reactant over time.

A + B → C + D

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = -\frac{\Delta[B]}{\Delta t} = +\frac{\Delta[C]}{\Delta t} = +\frac{\Delta[D]}{\Delta t}$$

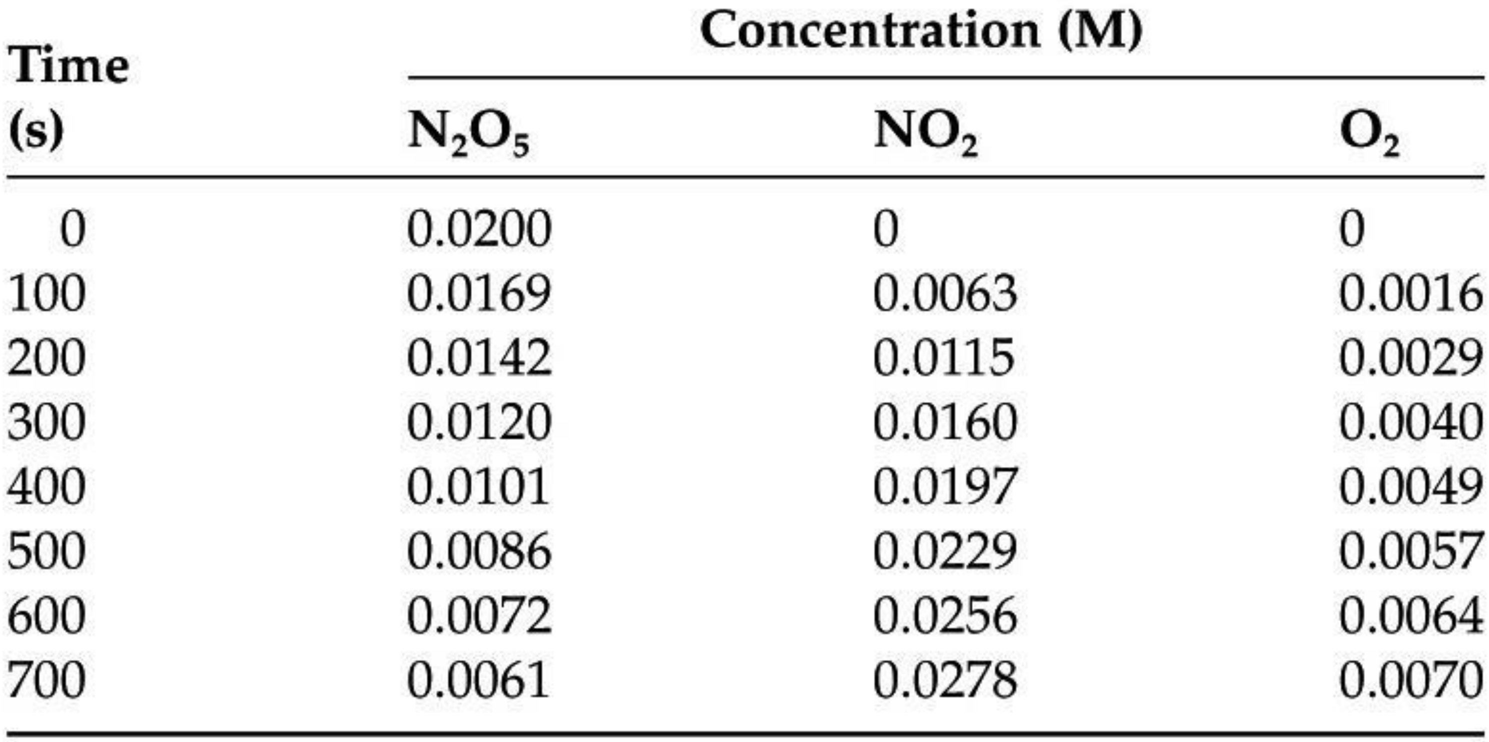
Reaction rate is always a positive value

- In general for

$$aA + bB \rightarrow cC + dD$$

$$\text{Rate} = -\frac{1}{a}\frac{\Delta[\text{A}]}{\Delta t} = -\frac{1}{b}\frac{\Delta[\text{B}]}{\Delta t} = \frac{1}{c}\frac{\Delta[\text{C}]}{\Delta t} = \frac{1}{d}\frac{\Delta[\text{D}]}{\Delta t}$$

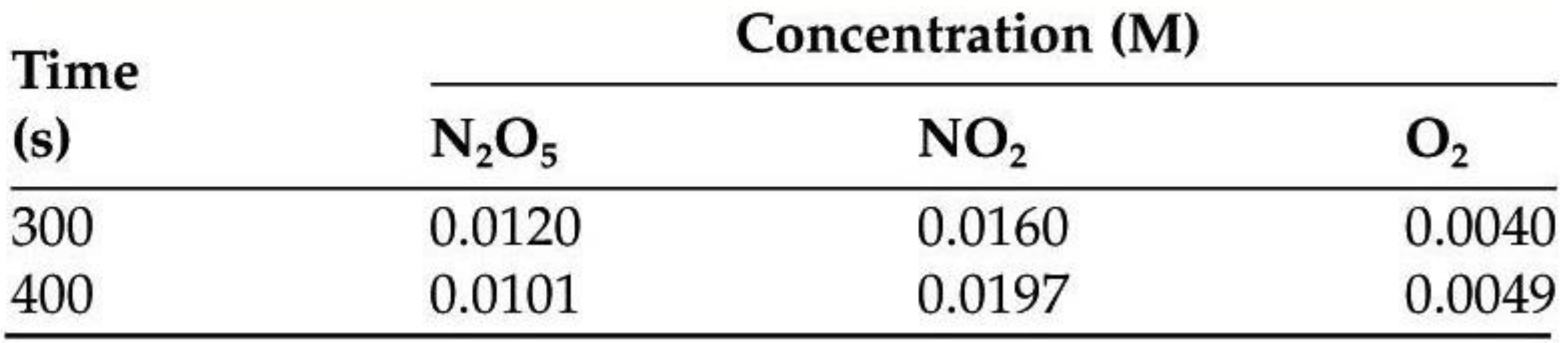
$2\ N_2O_5\ (g) \rightarrow 4\ NO_2\ (g) + O_2\ (g)$



Time (s)	Concentration (M)		
	N_2O_5	NO_2	O_2
0	0.0200	0	0
100	0.0169	0.0063	0.0016
200	0.0142	0.0115	0.0029
300	0.0120	0.0160	0.0040
400	0.0101	0.0197	0.0049
500	0.0086	0.0229	0.0057
600	0.0072	0.0256	0.0064
700	0.0061	0.0278	0.0070

$2\ N_2O_5\ (g) \rightarrow 4\ NO_2\ (g) + O_2\ (g)$

Between 300 and 400 seconds (at 55 °C):



Time (s)	Concentration (M)		
	N_2O_5	NO_2	O_2
300	0.0120	0.0160	0.0040
400	0.0101	0.0197	0.0049

Be Careful!

Rate of decomposition of N_2O_5 =

$$\boxed{-}\,\Delta[N_2O_5]\ /\ \Delta t =$$

$$\boxed{-}\ (0.0101\ \text{mol}\cdot\text{L}^{-1} - 0.0120\ \text{mol}\cdot\text{L}^{-1})\ /\ (400\ \text{s} - 300\ \text{s})$$

$$= 1.9 \times 10^{-5}\ \text{mol}\cdot(\text{L}\cdot\text{s})^{-1}$$

$2\ N_2O_5\ (g) \rightarrow 4\ NO_2\ (g) + O_2\ (g)$

Between 300 and 400 seconds (at 55 °C):

Time (s)	Concentration (M)		
	N_2O_5	NO_2	O_2
300	0.0120	0.0160	0.0040
400	0.0101	0.0197	0.0049

Be Careful!

Rate of formation of NO_2 =

$$\boxed{+}\ \Delta[NO_2] / \Delta t =$$

$$\boxed{+}\ (0.0197\ \mathrm{mol{\cdot}L^{-1}} - 0.0160\ \mathrm{mol{\cdot}L^{-1}}) / (400\ \mathrm{s} - 300\ \mathrm{s})$$

$$= 3.7 \times 10^{-5}\ \mathrm{mol{\cdot}(L{\cdot}s)^{-1}}$$

$2\ N_2O_5\ (g) \rightarrow 4\ NO_2\ (g) + O_2\ (g)$

Between 300 and 400 seconds (at 55 °C):

Time (s)	Concentration (M)		
	N_2O_5	NO_2	O_2
300	0.0120	0.0160	0.0040
400	0.0101	0.0197	0.0049

Be Careful!

Rate of formation of O_2 =

$+\ \Delta[O_2]\ /\ \Delta t =$

$+\ \mathbf{(0.0049\ mol{\cdot}L^{-1} - 0.0040\ mol{\cdot}L^{-1})\ /\ (400\ s - 300\ s)}$

$= \mathbf{9 \times 10^{-6}\ mol{\cdot}(L{\cdot}s)^{-1}}$

$2\ N_2O_5\ (g) \rightarrow 4\ NO_2\ (g) + O_2\ (g)$

The three values for rate that we calculated are not the same!

Why?

We have <u>different molar amounts</u>.

But the <u>**relative rates**</u> **ARE THE SAME!**

$$\begin{pmatrix}\text{Rate of formation}\\ \text{of } O_2\end{pmatrix} = \frac{1}{4}\begin{pmatrix}\text{Rate of formation}\\ \text{of } NO_2\end{pmatrix} = \frac{1}{2}\begin{pmatrix}\text{Rate of decomposition}\\ \text{of } N_2O_5\end{pmatrix}$$

or

$$\frac{\Delta[O_2]}{\Delta t} = \frac{1}{4}\left(\frac{\Delta[NO_2]}{\Delta t}\right) = -\frac{1}{2}\left(\frac{\Delta[N_2O_5]}{\Delta t}\right)$$

$2\ N_2O_5\ (g) \rightarrow 4\ NO_2\ (g) + O_2\ (g)$

The **relative rate of formation** of **O_2** is

(1/1) 9×10^{-6} mol·(L·s)$^{-1}$ = **9×10^{-6} mol·(L·s)$^{-1}$**

The **relative rate of formation** of **NO_2** is

(1/4) 3.7×10^{-5} mol·(L·s)$^{-1}$ = **9.25×10^{-6} mol·(L·s)$^{-1}$**

The **relative rate of decomposition** of **N_2O_5** is

(1/2) 1.9×10^{-5} mol·(L·s)$^{-1}$ = **9.5×10^{-6} mol·(L·s)$^{-1}$**

4.3 Rate Law and Reaction Order

Rate Laws:

Rate law is the equation that showing the relationship of reaction rate and concentrations of the reactants.

$aA + bB \rightarrow$ products

$$\text{Rate} = k\,[A]^m[B]^n$$

k is the rate constant

m and n is the reaction order

remember, it is not stoichiometry coefficient.

The overall reaction order is **m + n**

Reaction order example

$$\text{rate} = k\,[C]^2[D]$$

The **reaction order with respect to C** is **2**
or the reaction is **second order in C**

The **reaction order with respect to D** is **1**
or the reaction is **first order in D**

The **overall reaction order** is **3** (2 + 1 = 3)
or the reaction is **third order overall**

4.3.1 Experimental Determination of a Rate Law

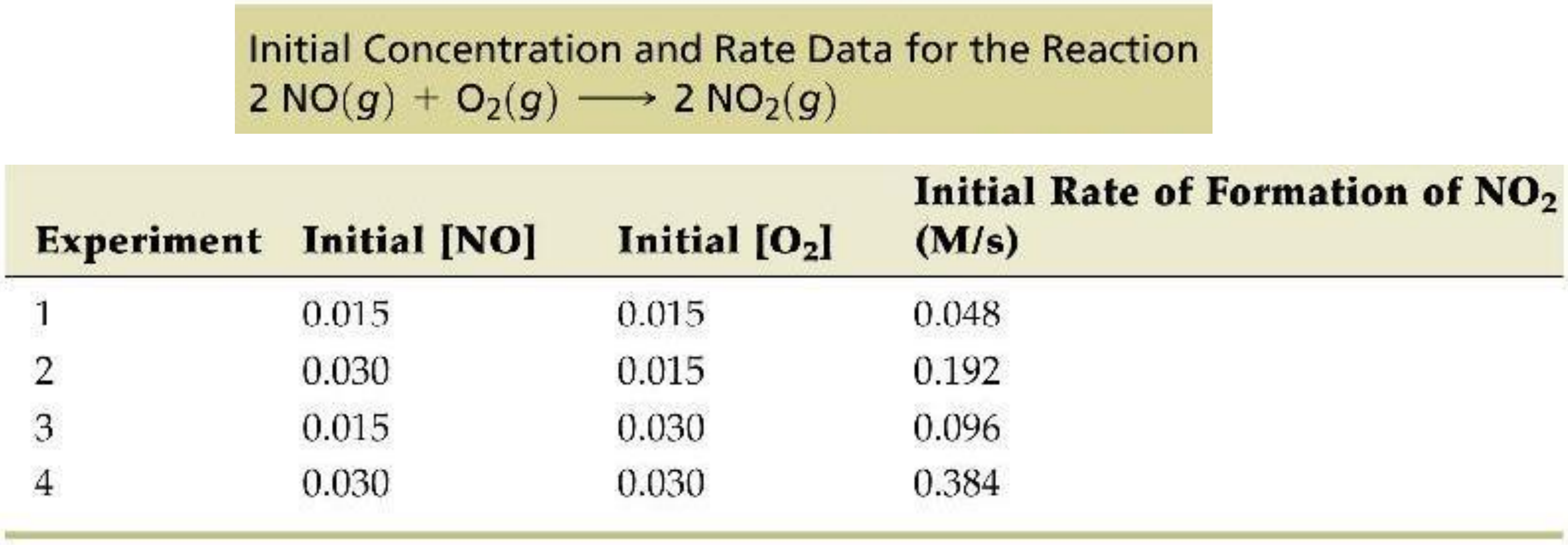
- **Reaction rate laws** can **only** be determined experimentally!

- In defining the rate law, a series of experiments need to carried out by:

Measuring the initial rate of the reaction as function of **different initial concentrations of the reactants**

Method of initial rates

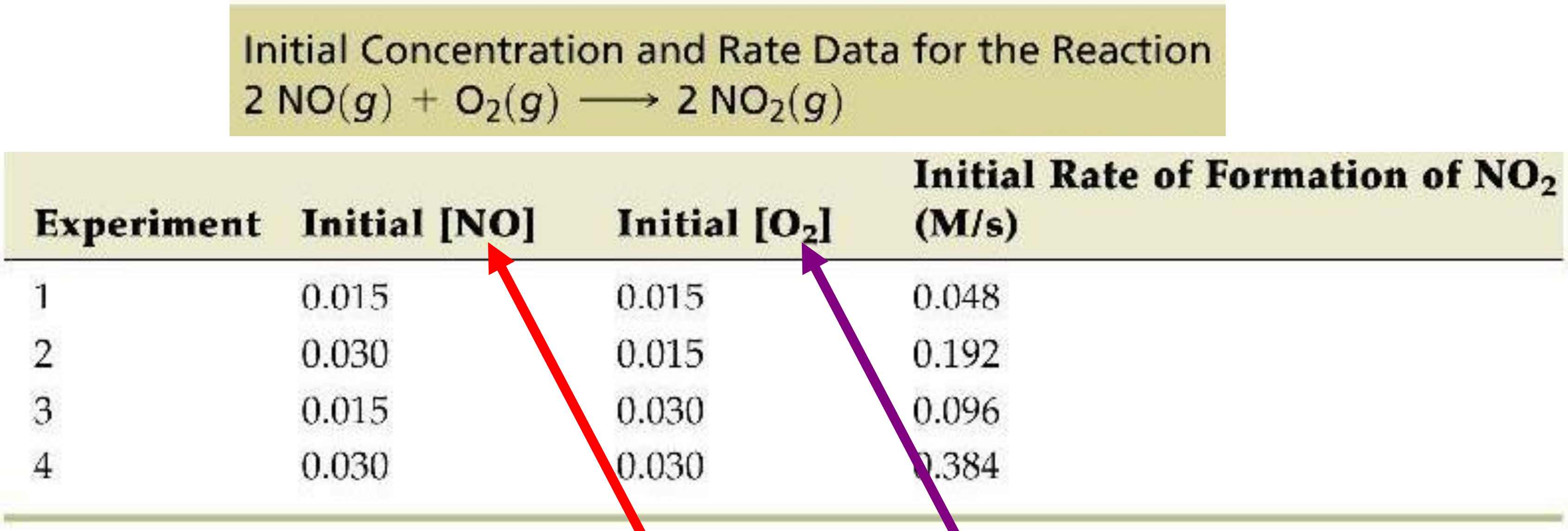
If you see a table like this with **chemical concentrations or pressures** and **rate data**, chances are good the question is a **method of initial rates** problem.



Initial Concentration and Rate Data for the Reaction
$2\,NO(g) + O_2(g) \longrightarrow 2\,NO_2(g)$

Experiment	Initial [NO]	Initial $[O_2]$	Initial Rate of Formation of NO_2 (M/s)
1	0.015	0.015	0.048
2	0.030	0.015	0.192
3	0.015	0.030	0.096
4	0.030	0.030	0.384

$2\,NO\ (g) + O_2\ (g) \rightarrow 2NO_2\ (g)$



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1	0.015	0.015	0.048
2	0.030	0.015	0.192
3	0.015	0.030	0.096
4	0.030	0.030	0.384

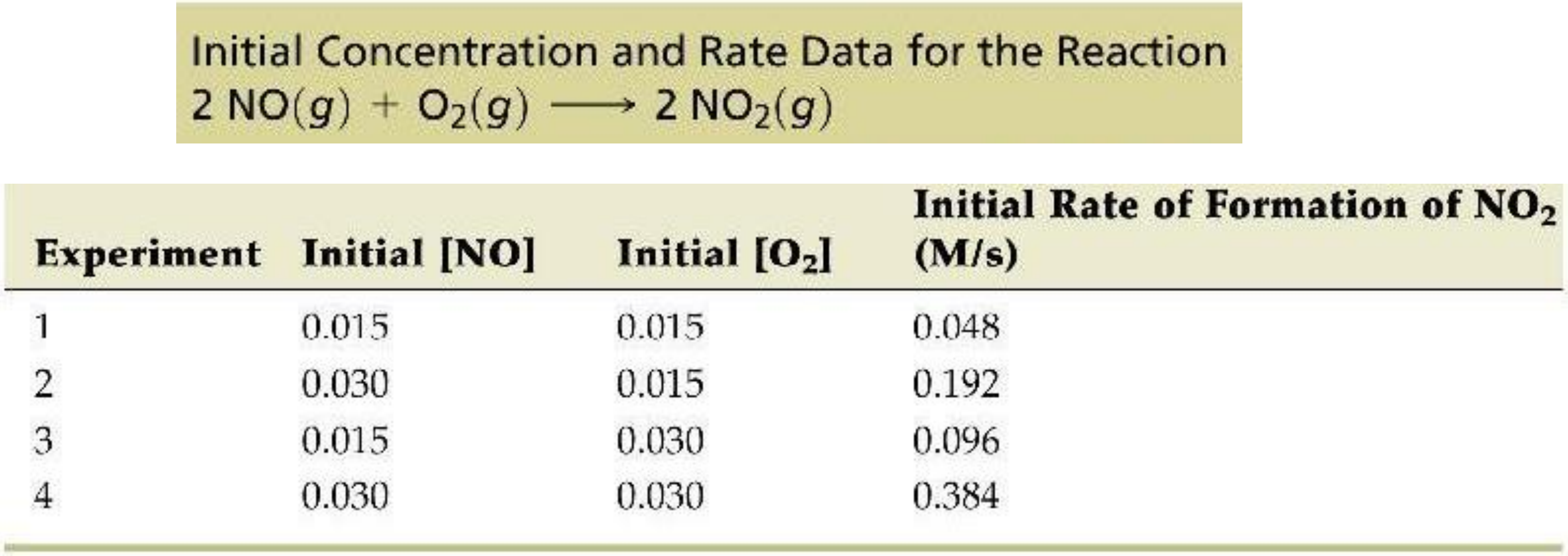
General rate law:

$$\text{rate} = k\,[NO]^m[O_2]^n$$

Method of initial rates

Method to calculate the order of reaction:

1. Choose a pair of reactions where **only one** reactant concentration changes.
2. **In this case, experiments 1 and 2 is being selected.**



Initial Concentration and Rate Data for the Reaction
$2\,NO(g) + O_2(g) \longrightarrow 2\,NO_2(g)$

Experiment	Initial [NO]	Initial $[O_2]$	Initial Rate of Formation of NO_2 (M/s)
1	0.015	0.015	0.048
2	0.030	0.015	0.192
3	0.015	0.030	0.096
4	0.030	0.030	0.384

$$\text{rate} = k\,[\text{NO}]^m[\text{O}_2]^n$$

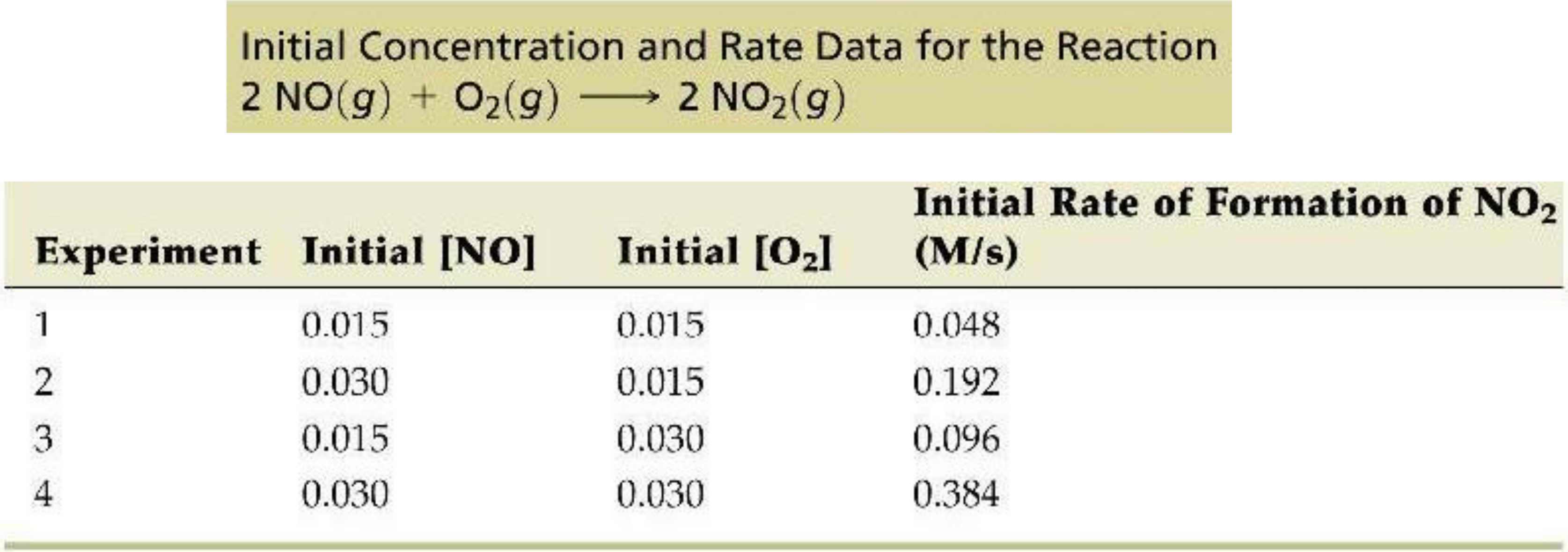
k is the rate constant. Thus, the value is constant through out the reaction

(k for experiment 1 = k for experiment 2)

$$k = \text{rate} / [\text{NO}]^m[\text{O}_2]^n$$

$$\frac{\text{rate}_1}{[\text{NO}]_1^m[\text{O}_2]_1^n} = \frac{\text{rate}_2}{[\text{NO}]_2^m[\text{O}_2]_2^n} \quad \text{so} \quad \frac{\text{rate}_1}{\text{rate}_2} = \frac{[\text{NO}]_1^m[\text{O}_2]_1^n}{[\text{NO}]_2^m[\text{O}_2]_2^n}$$

Reaction order w.r.t. NO



Initial Concentration and Rate Data for the Reaction $2\,NO(g) + O_2(g) \longrightarrow 2\,NO_2(g)$

Experiment	Initial [NO]	Initial [O_2]	Initial Rate of Formation of NO_2 (M/s)
1	0.015	0.015	0.048
2	0.030	0.015	0.192
3	0.015	0.030	0.096
4	0.030	0.030	0.384

$$\log 0.25 = \log\left[(0.50)^m\right]$$

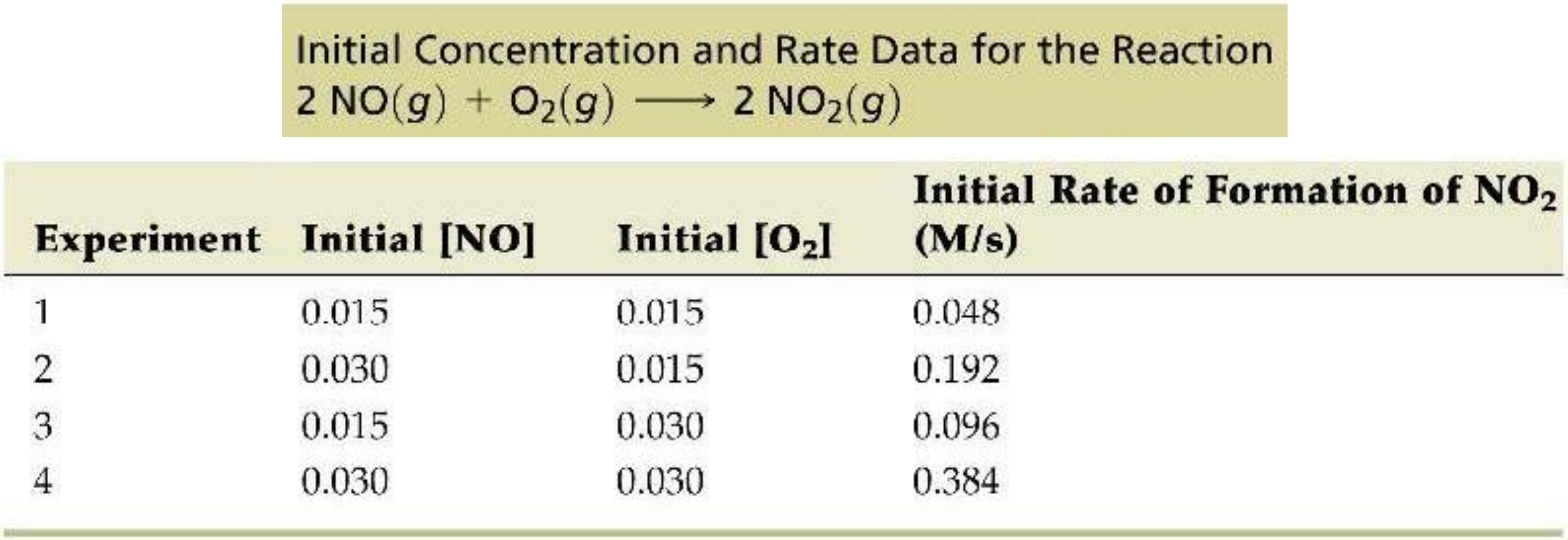
$$\log 0.25 = m \log 0.50$$

$$m = \frac{\log 0.25}{\log 0.50}$$

$$m = \frac{-0.602}{-0.301}$$

$$m = 2$$

Reaction order w.r.t. O_2



Initial Concentration and Rate Data for the Reaction
$2\,NO(g) + O_2(g) \longrightarrow 2\,NO_2(g)$

Experiment	Initial [NO]	Initial $[O_2]$	Initial Rate of Formation of NO_2 (M/s)
1	0.015	0.015	0.048
2	0.030	0.015	0.192
3	0.015	0.030	0.096
4	0.030	0.030	0.384

$$\frac{0.048\,M\cdot s^{-1}}{0.096\,M\cdot s^{-1}} = \frac{\cancel{(0.015M)^2}(0.015M)^n}{\cancel{(0.015M)^2}(0.030M)^n}$$

$$0.50 = (0.50)^n$$

$$\log 0.50 = \log\left[(0.50)^n\right]$$

$$\log 0.50 = n\log 0.50$$

$$n = \frac{\log 0.50}{\log 0.50}$$

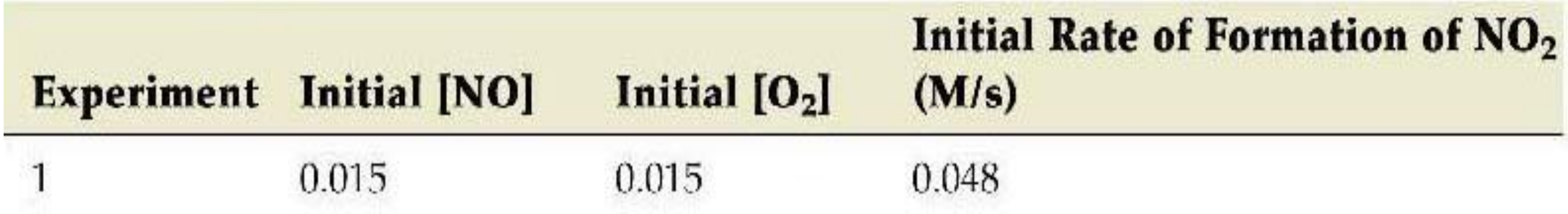
$$n = \frac{-0.301}{-0.301}$$

$$n = 1$$

Our rate law

$$\text{rate} = k\,[NO]^2[O_2]^1$$

Using data from experiment 1, the rate constant calculated as follows:



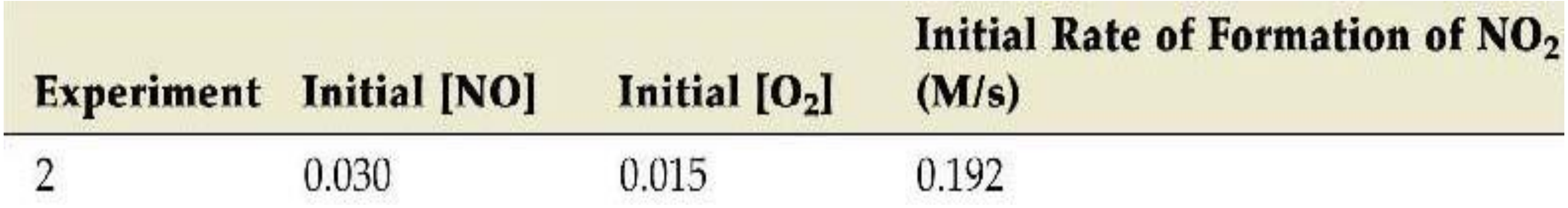
Experiment	Initial [NO]	Initial $[O_2]$	Initial Rate of Formation of NO_2 (M/s)
1	0.015	0.015	0.048

k = rate / $[NO]^2[O_2]^1$

$$k = \frac{\text{rate}}{[NO]^2[O_2]} = \frac{0.048\,M\cdot s^{-1}}{(0.015\,M)^2(0.015\,M)} = \frac{0.048\,M\cdot s^{-1}}{3.38\,x\,10^{-6}\ M^3}$$

$$k = 1.42\,x\,10^4\ M^{-2}\cdot s^{-1}$$

Using data from experiment 2, the rate constant calculated as follows:



Experiment	Initial [NO]	Initial $[O_2]$	Initial Rate of Formation of NO_2 (M/s)
2	0.030	0.015	0.192

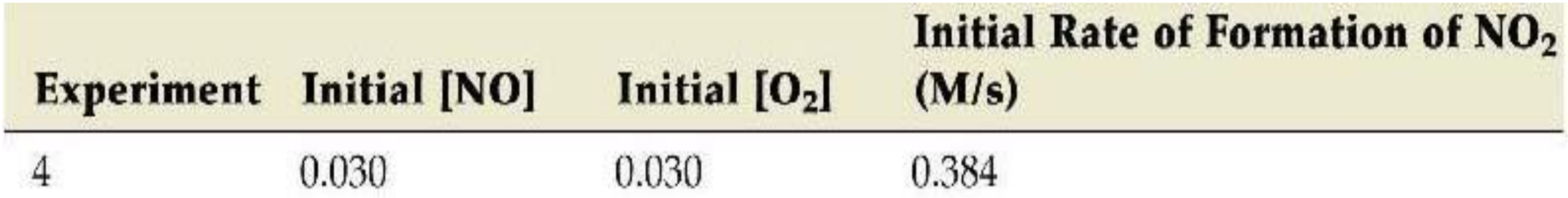
k = rate / $[NO]^2[O_2]^1$

$$k = \frac{\text{rate}}{[NO]^2[O_2]} = \frac{0.192\,M\cdot s^{-1}}{(0.030\,M)^2(0.015\,M)} = \frac{0.192\,M\cdot s^{-1}}{1.35\,x\,10^{-5}\,M^3}$$

$$k = 1.42\,x\,10^4\,M^{-2}\cdot s^{-1}$$

The rate constant is the same, as it should be!

Check using extra experiment



Experiment	Initial [NO]	Initial [O$_2$]	Initial Rate of Formation of NO$_2$ (M/s)
4	0.030	0.030	0.384

rate = (1.42 x 10^4 M^{-2}·s^{-1}) [NO]^2[O$_2$]^1

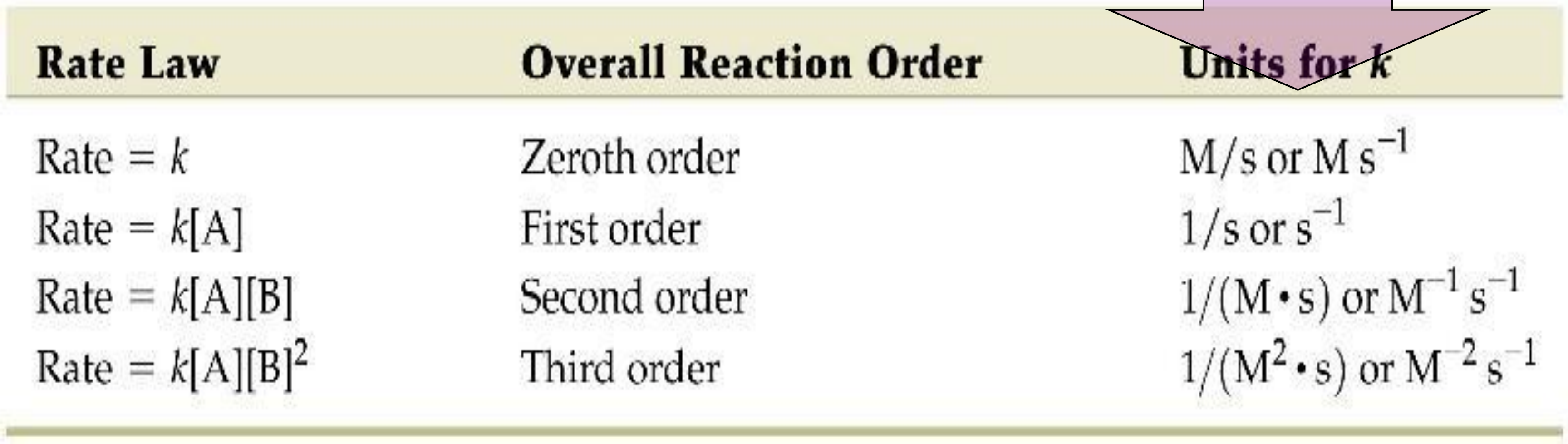
$$\text{rate} = \left(1.42\,\text{x}\,10^4\ \text{M}^{-2}\cdot\text{s}^{-1}\right)[\text{NO}]^2[\text{O}_2]$$
$$\text{rate} = \left(1.42\,\text{x}\,10^4\ \text{M}^{-2}\cdot\text{s}^{-1}\right)(0.030\,\text{M})^2(0.030\,\text{M})$$
$$\text{rate} = \left(1.42\,\text{x}\,10^4\ \text{M}^{-2}\cdot\text{s}^{-1}\right)\left(2.7\,\text{x}\,10^{-5}\ \text{M}^3\right)$$
$$\text{rate} = 3.83\,\text{x}\,10^{-1}\ \text{M}\cdot\text{s}^{-1}$$

The rate value of the rate of reaction using rate law equation should same (within rounding errors) for each experimental concentration data.

Units of rate constants

Unit for rate constant k, is depends on its overall reaction order as follows

Be Careful!



Rate Law	**Overall Reaction Order**	**Units for *k***
Rate = k	Zeroth order	M/s or M s^{-1}
Rate = $k[A]$	First order	1/s or s^{-1}
Rate = $k[A][B]$	Second order	$1/(M \cdot s)$ or $M^{-1} s^{-1}$
Rate = $k[A][B]^2$	Third order	$1/(M^2 \cdot s)$ or $M^{-2} s^{-1}$

4.4 Integrated Rate Law

Integrating the rate law of first order given as:

$$\ln \frac{[A]_t}{[A]_0} = -kt$$

where

$[A]_0$ is the initial concentration of A.
$[A]_t$ is the concentration of A at time, t.
t is the time of reaction process

Integrated Rate Laws

From the integrated rate law (1st order) equation:

$$\ln \frac{[A]_t}{[A]_0} = -kt$$

$$\ln [A]_t - \ln [A]_0 = -kt$$

$$\ln [A]_t = -kt + \ln [A]_0$$

Could be graphically identify the important parameters

$$y = mx + b$$

First-Order Processes

- Concentration can be also being indicated by using pressure according to the theory of properties relationship.
- When a graph of ln *P* vs time is plotted, a straight line results with negative slope.

Second-Order Processes

From the integrated rate law (2st order) equation:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

$$y = mx + b$$

Could be graphically identify the important parameters

Second-Order Processes

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

- When a graph of 1/[A] vs time is plotted, a straight line results with positive slope.

4.5 Half-life

The half life calculations for 1st order reaction as follows:

$$\ln \frac{0.5\,[A]_0}{[A]_0} = -kt_{1/2}$$

$$\ln 0.5 = -kt_{1/2}$$

$$-0.693 = -kt_{1/2}$$

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

NOTE: For a first-order process, the half-life does not depend on initial concentration, $[A]_0$.

For a 2nd order process:

$$\frac{1}{0.5\,[A]_0} = kt_{1/2} + \frac{1}{[A]_0}$$

$$\frac{2}{[A]_0} = kt_{1/2} + \frac{1}{[A]_0}$$

$$\frac{2-1}{[A]_0} = \frac{1}{[A]_0} = kt_{1/2}$$

$$\frac{1}{k[A]_0} = t_{1/2}$$

NOTE: For a 2nd order is depending on initial concentration, $[A]_0$.

Conclusion

- ❖ A chemical reaction goes through its mechanism which depends on its order of reaction.

- ❖ The value of certain parameters such as half life, reaction constant could be calculated using equation or graphic

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