How to draw a graph

http://maths4biosciences.com

Key points to drawing a graph

- Make the best use of the graph paper
- Use a sharp pencil
- Plot your point clearly and add the line
  - Join the points, or use a line of best fit
- Clearly label the axes - don’t forget any units
- Give the graph a title


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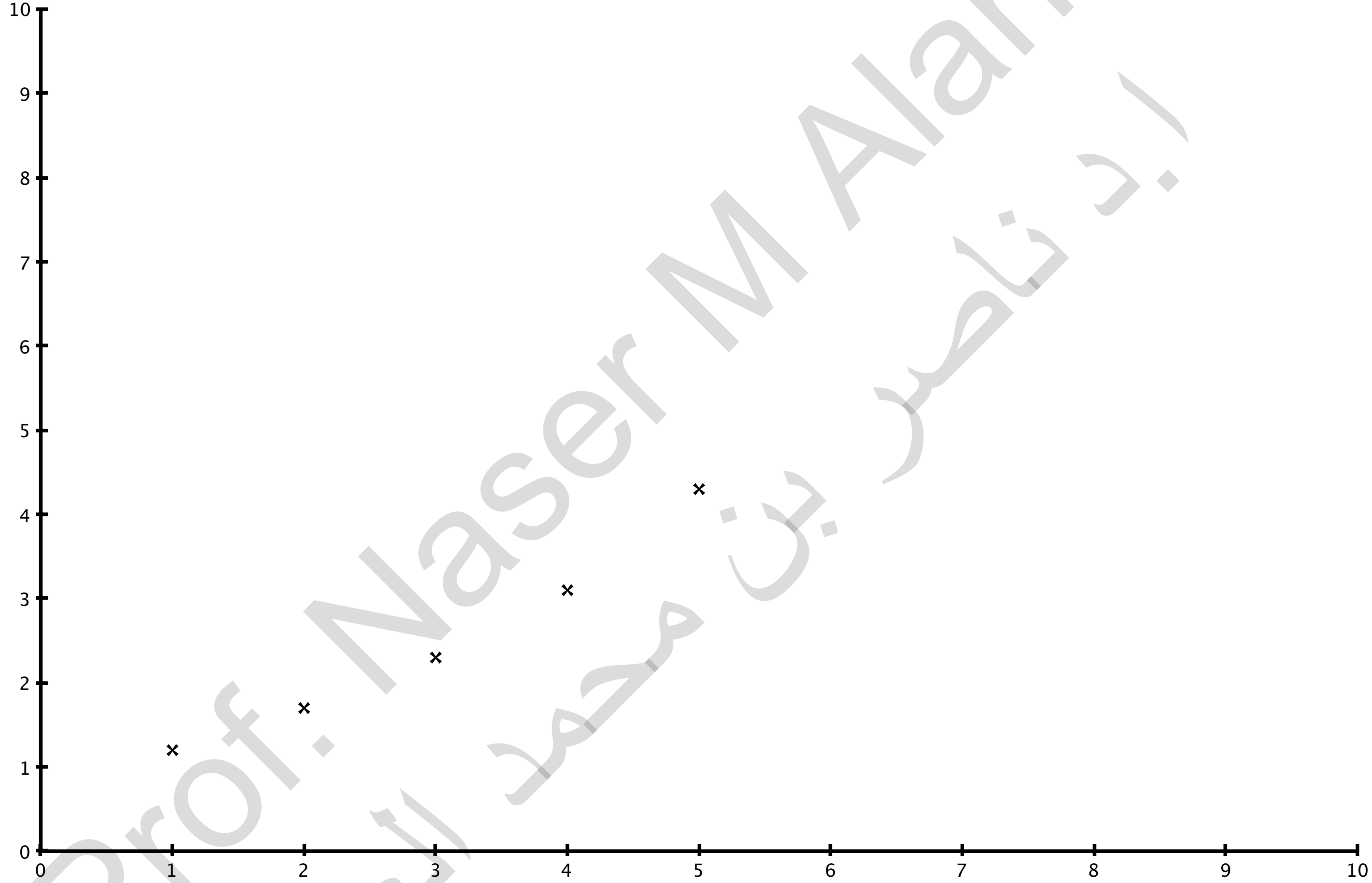
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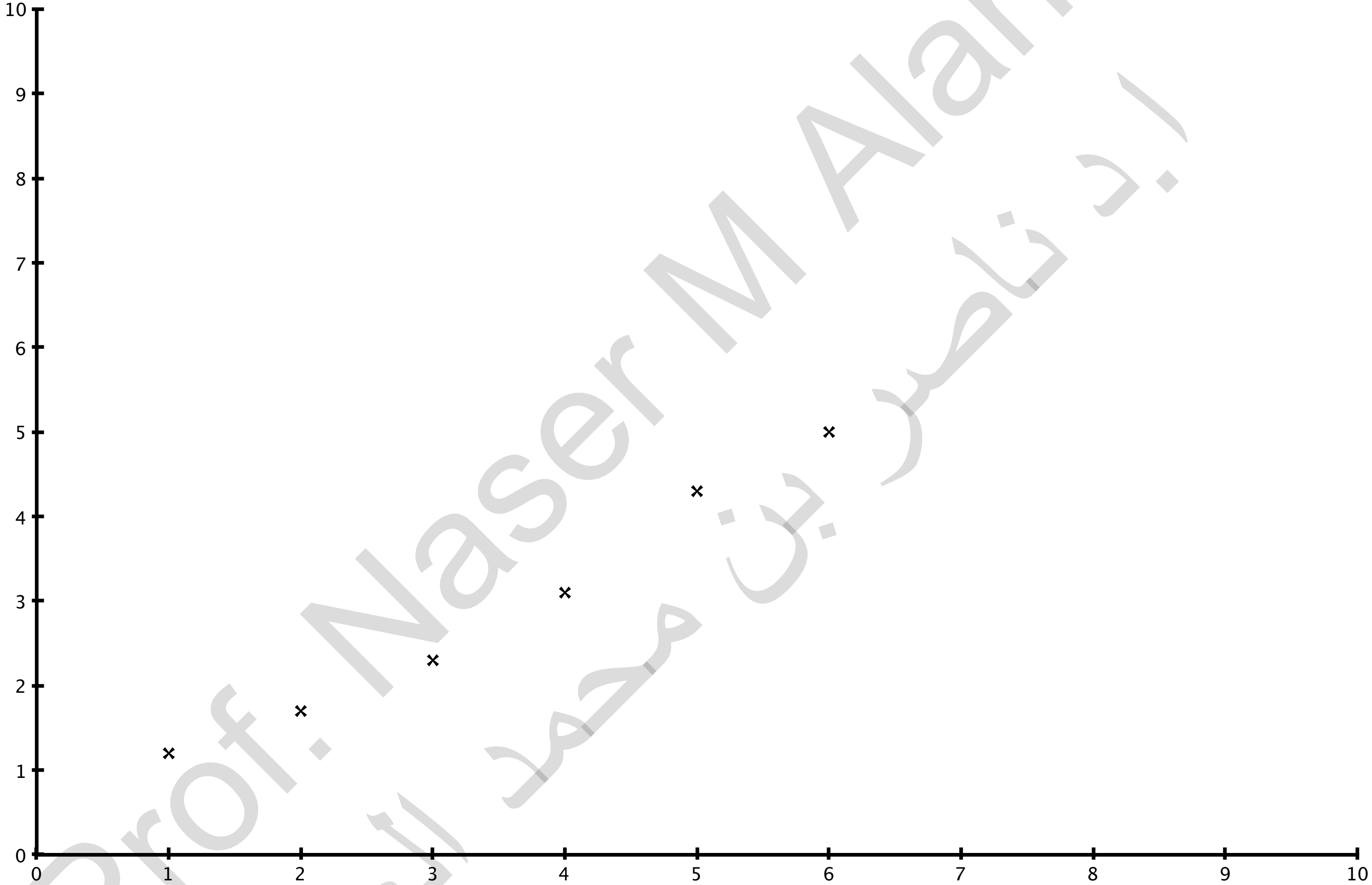
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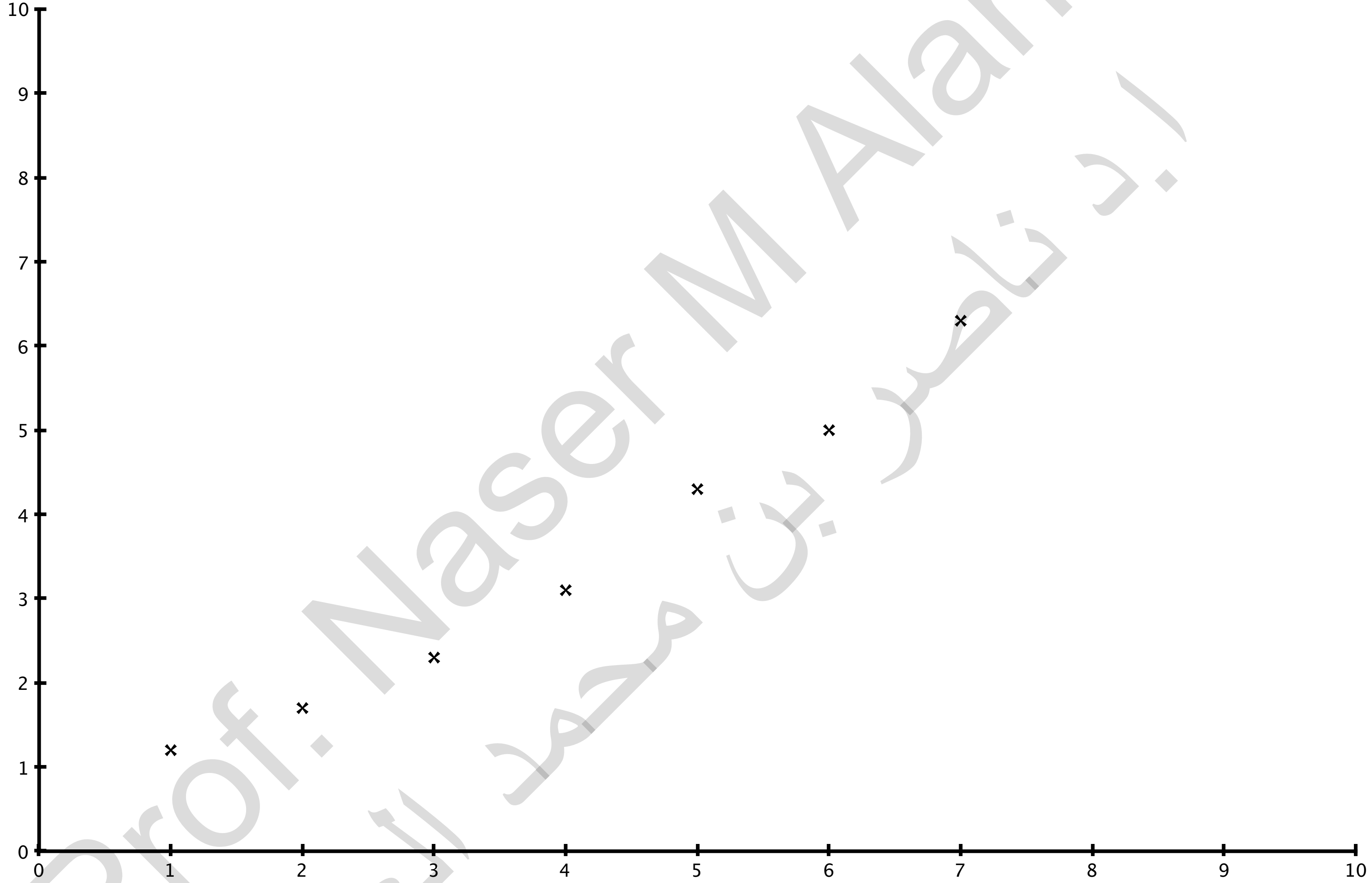
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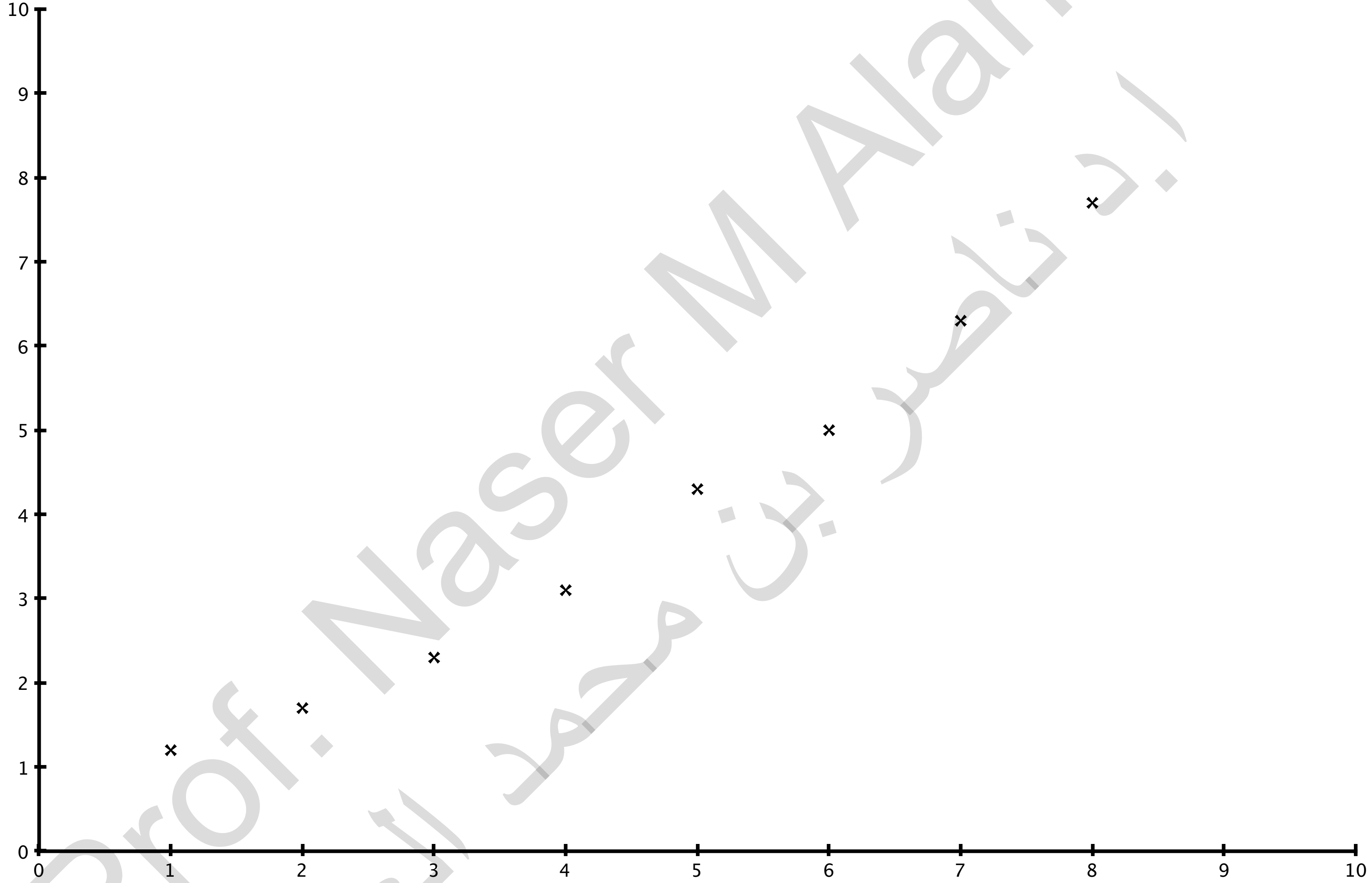
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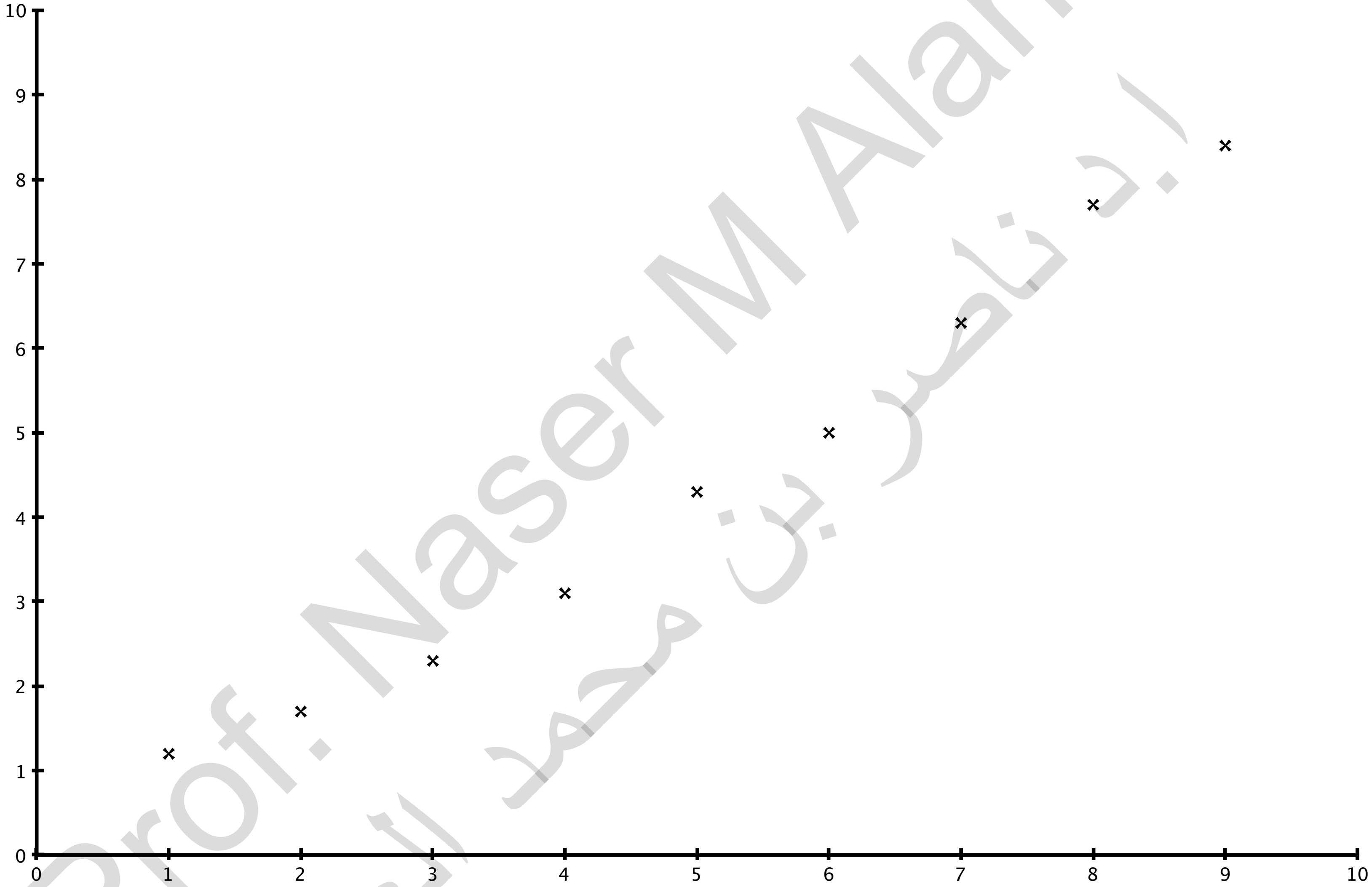
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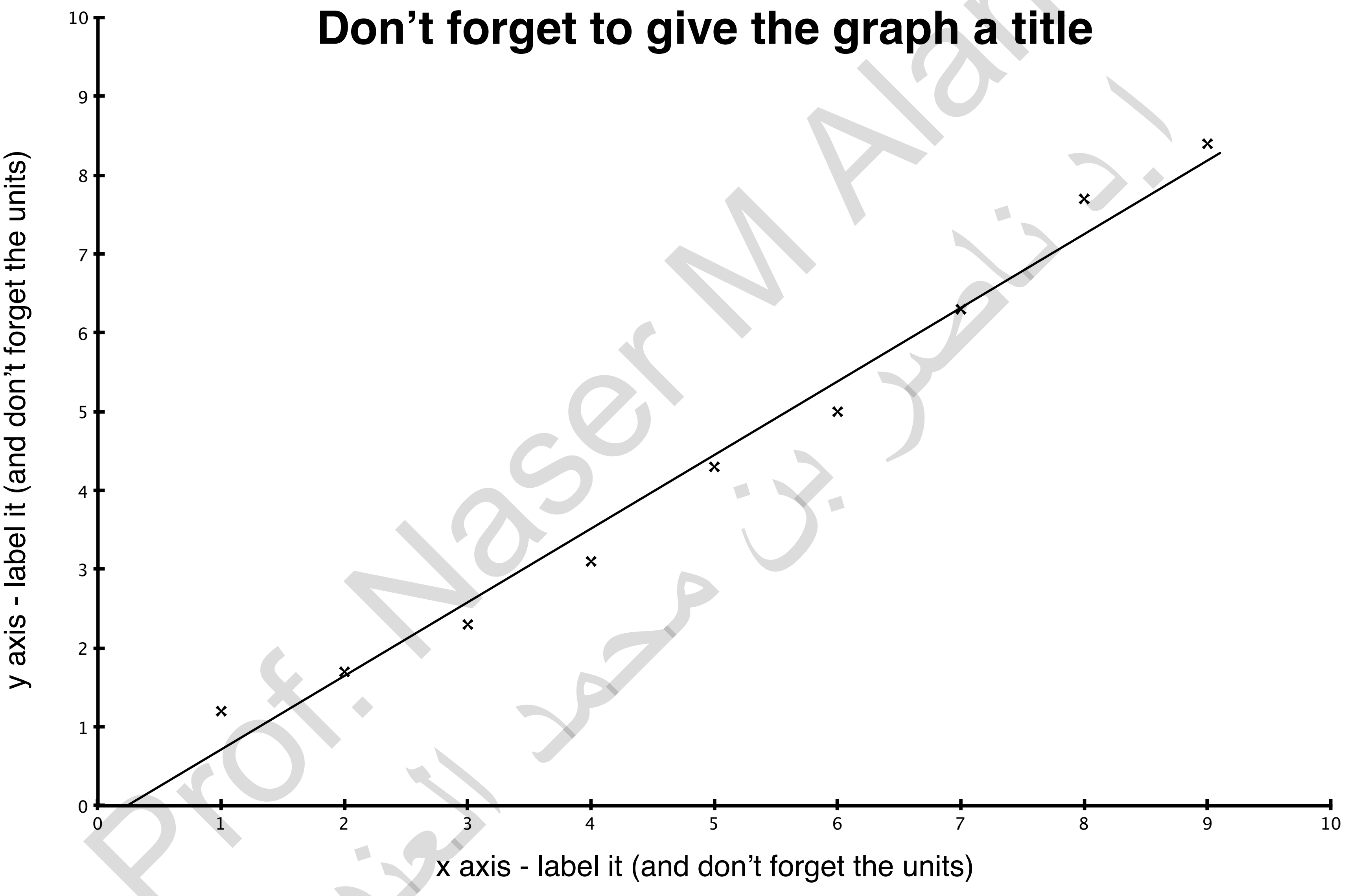
Don’t forget to give the graph a title
y axis - label it (and don’t forget the units)
x axis - label it (and don’t forget the units)
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Key points to drawing a graph

- Make the best use of the graph paper
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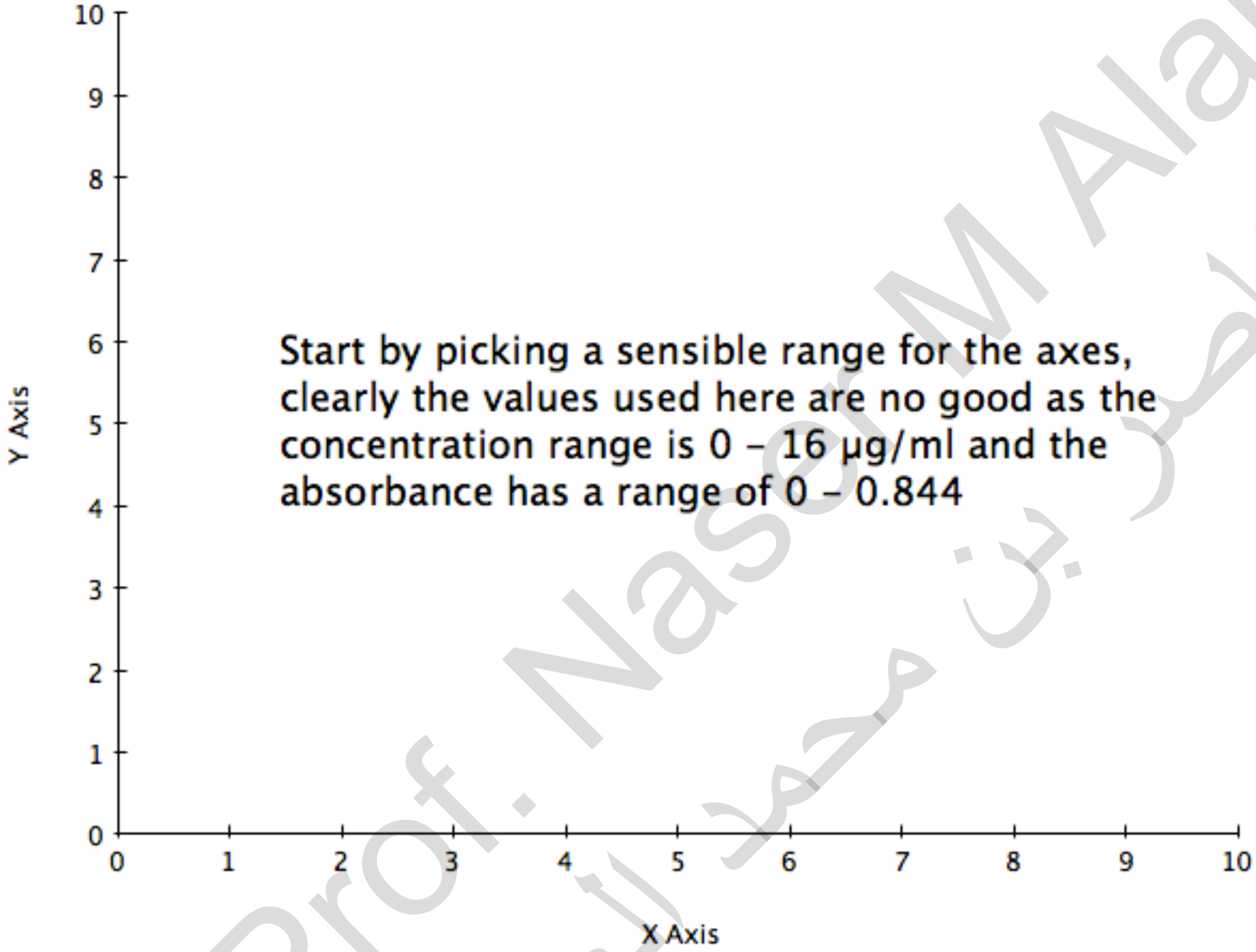
- Clearly label the axes - don’t forget any units
- Give the graph a title

Worked example

You have the data shown in the table

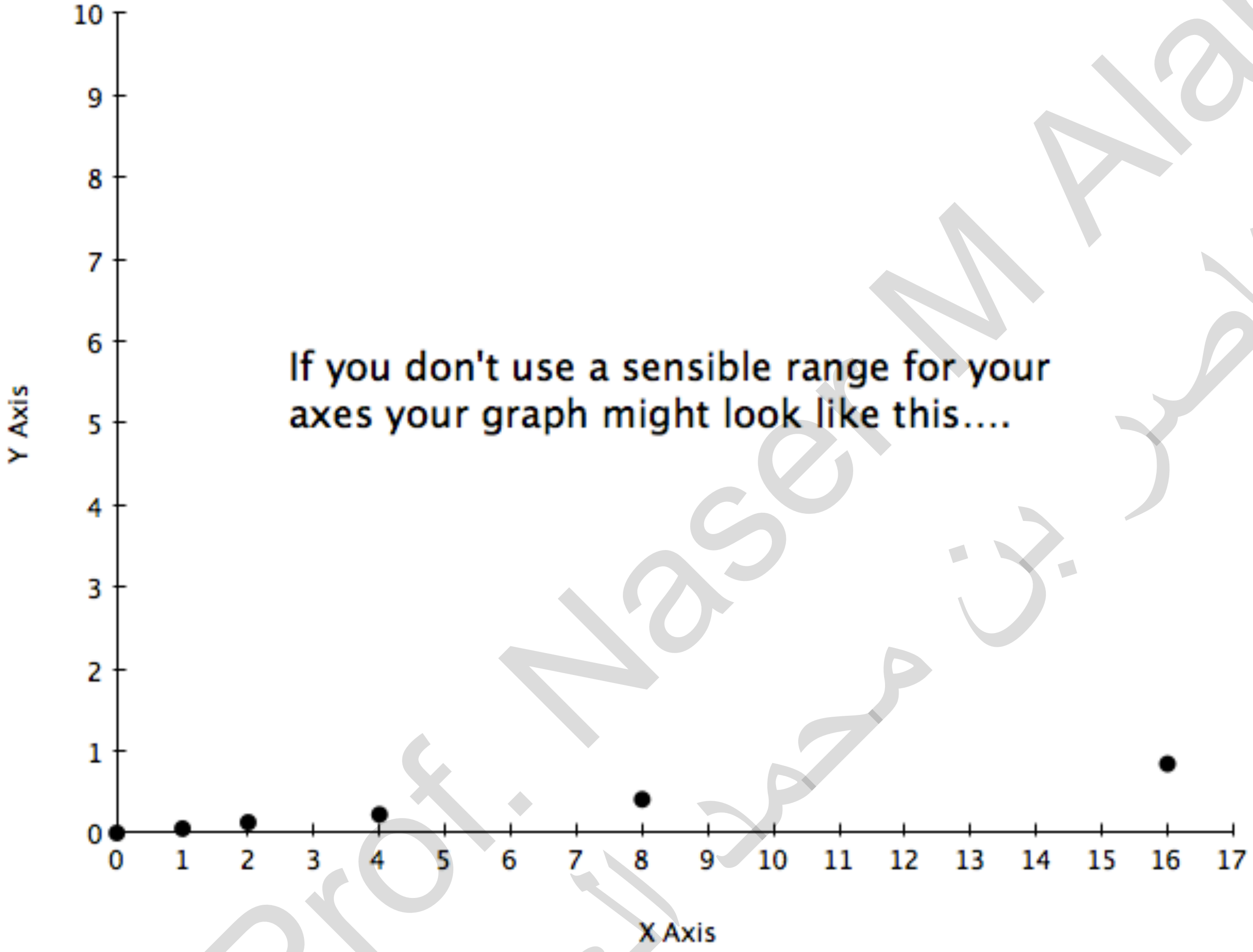
How would you plot it on a graph?

Concentration (μg/ml)	Absorbance (595 nm)
0	0
1	0.054
2	0.130
4	0.225
8	0.410
16	0.844



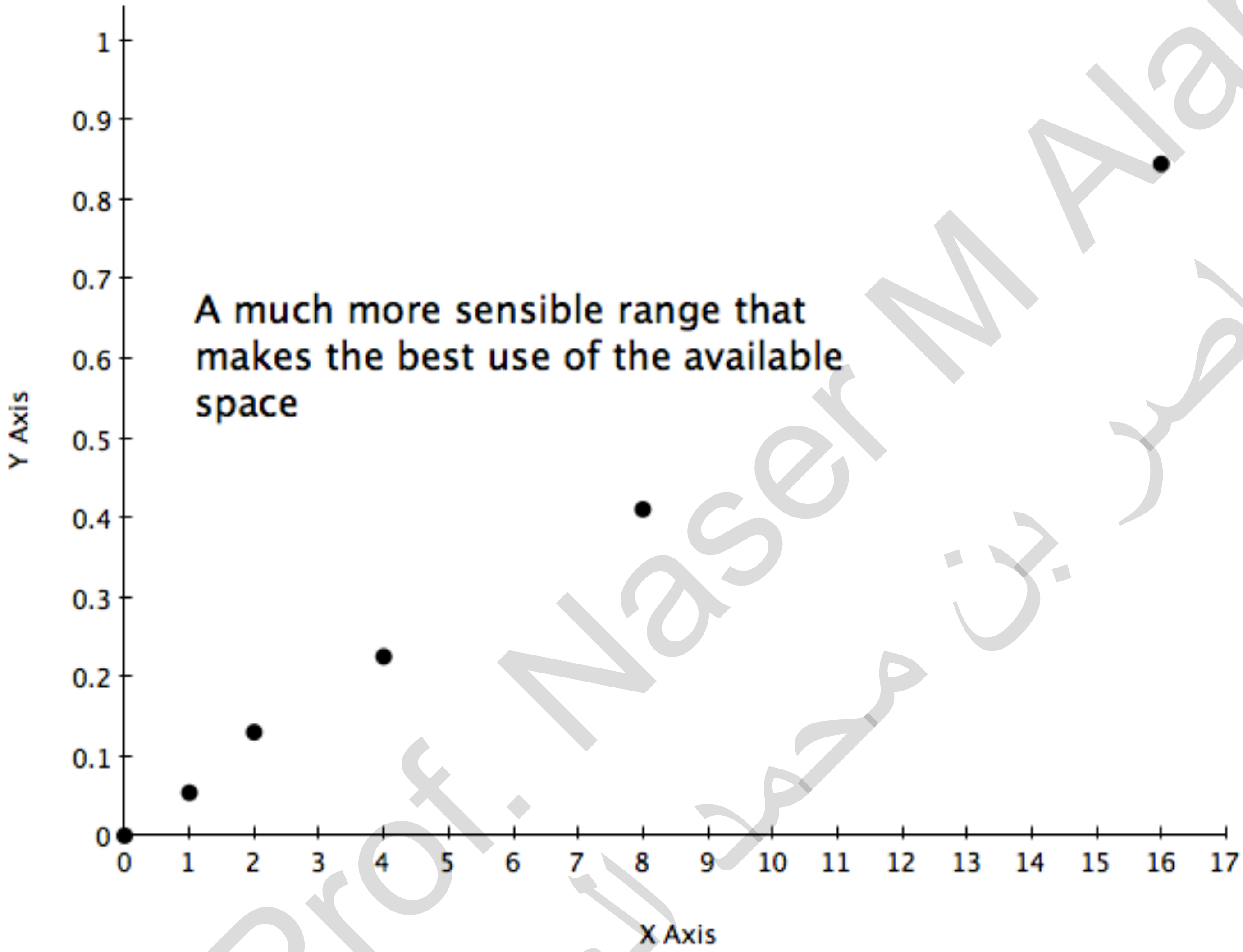
Start by picking a sensible range for the axes, clearly the values used here are no good as the concentration range is 0 – 16 µg/ml and the absorbance has a range of 0 – 0.844

Concentration (µg/ml)	Absorbance (595 nm)
0	0
1	0.054
2	0.130
4	0.225
8	0.410
16	0.844



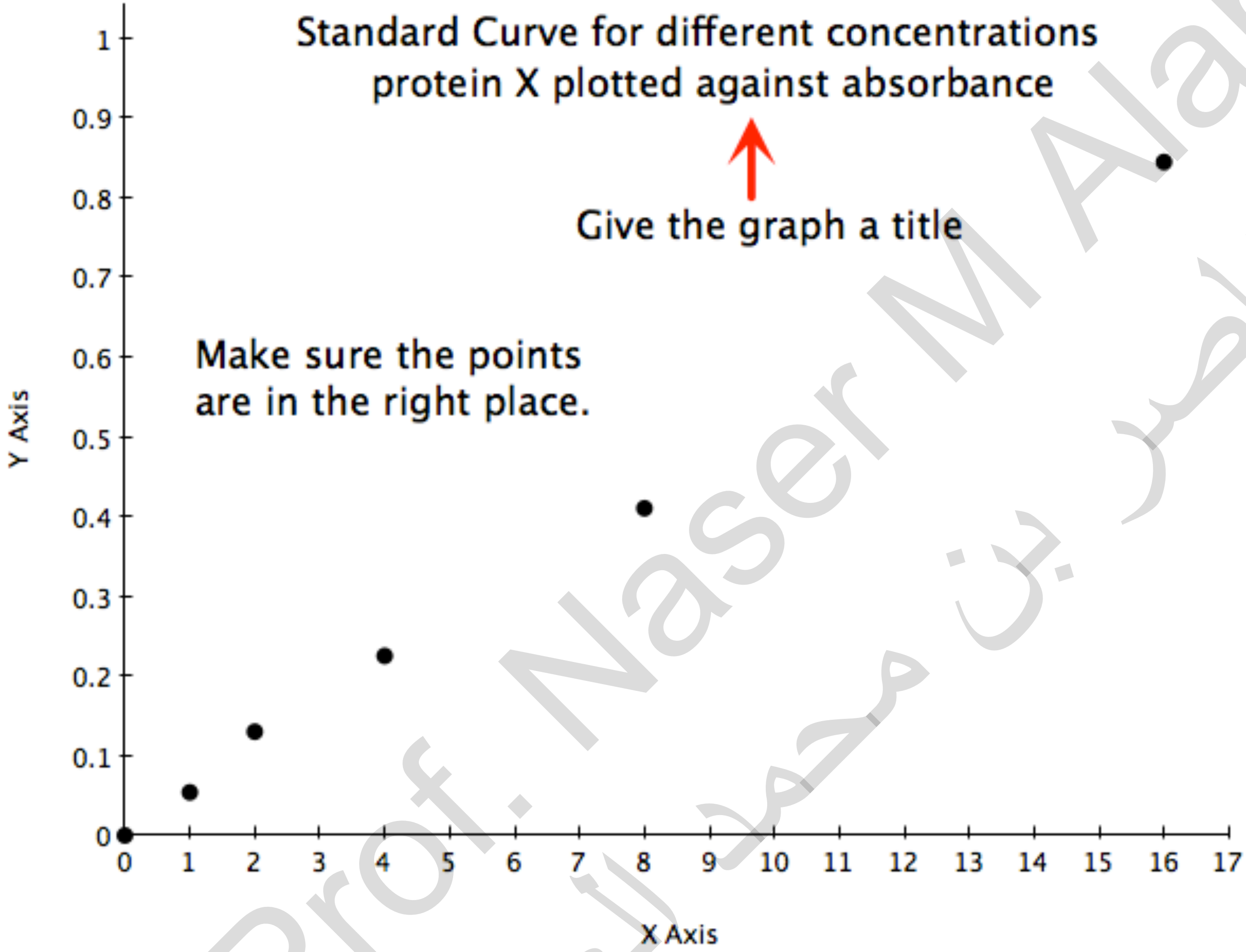
If you don't use a sensible range for your axes your graph might look like this....

Concentration (µg/ml)	Absorbance (595 nm)
0	0
1	0.054
2	0.130
4	0.225
8	0.410
16	0.844



A much more sensible range that makes the best use of the available space

Concentration (µg/ml)	Absorbance (595 nm)
0	0
1	0.054
2	0.130
4	0.225
8	0.410
16	0.844

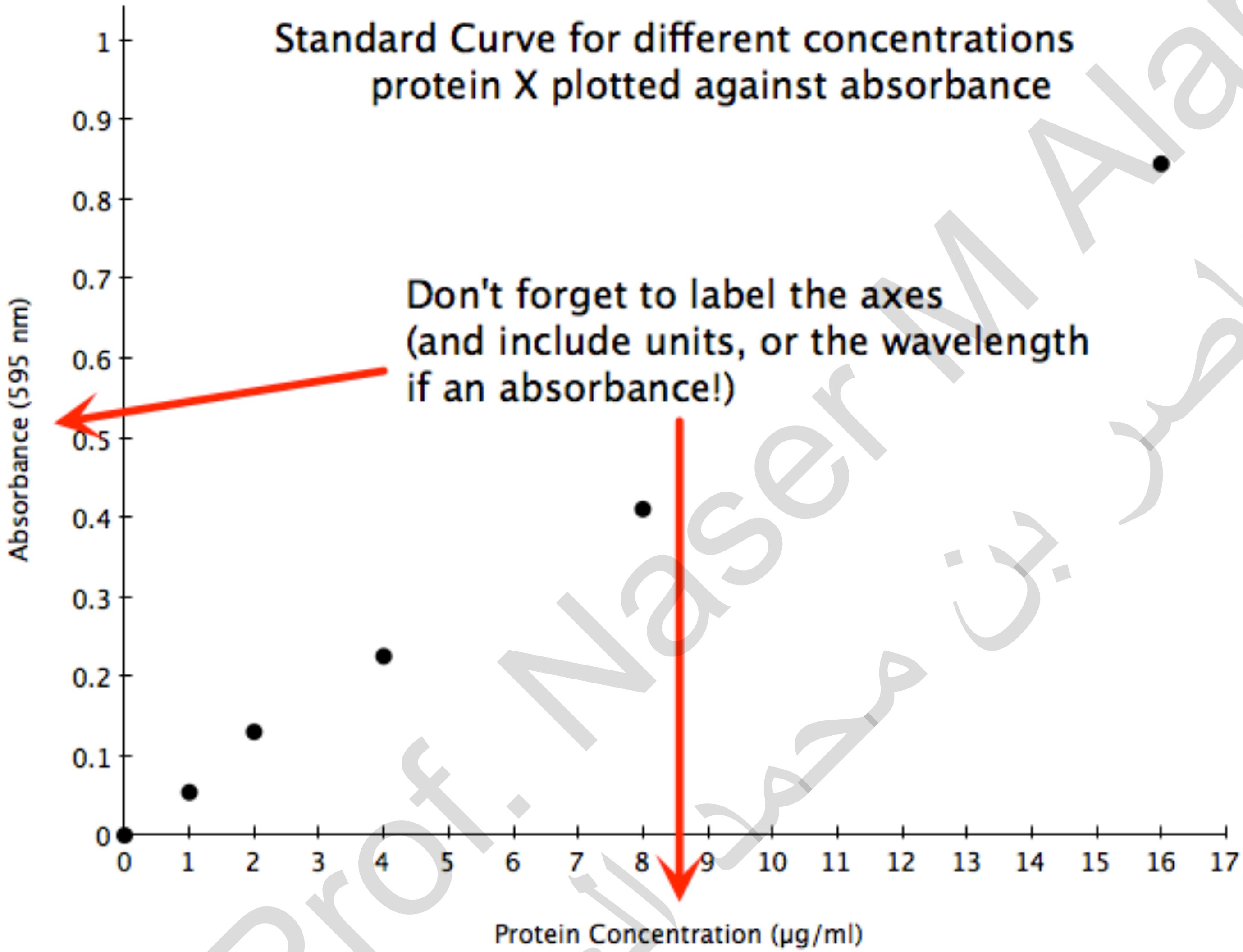


Standard Curve for different concentrations protein X plotted against absorbance

Give the graph a title

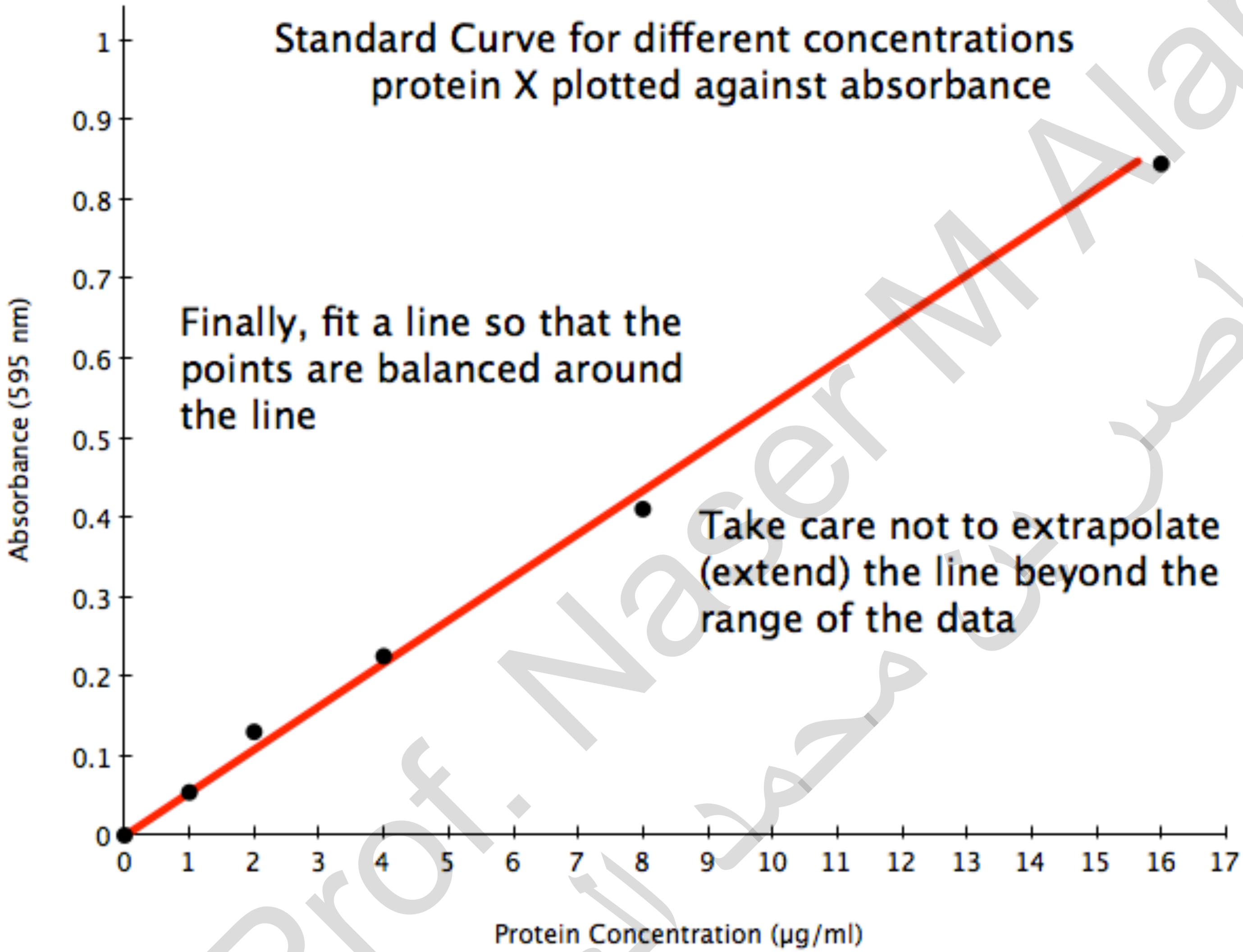
Make sure the points are in the right place.

Concentration (μg/ml)	**Absorbance (595 nm)**
0	0
1	0.054
2	0.130
4	0.225
8	0.410
16	0.844


Standard Curve for different concentrations protein X plotted against absorbance

Don't forget to label the axes (and include units, or the wavelength if an absorbance!)

Concentration (*µ*g/ml)	Absorbance (595 nm)
0	0
1	0.054
2	0.130
4	0.225
8	0.410
16	0.844

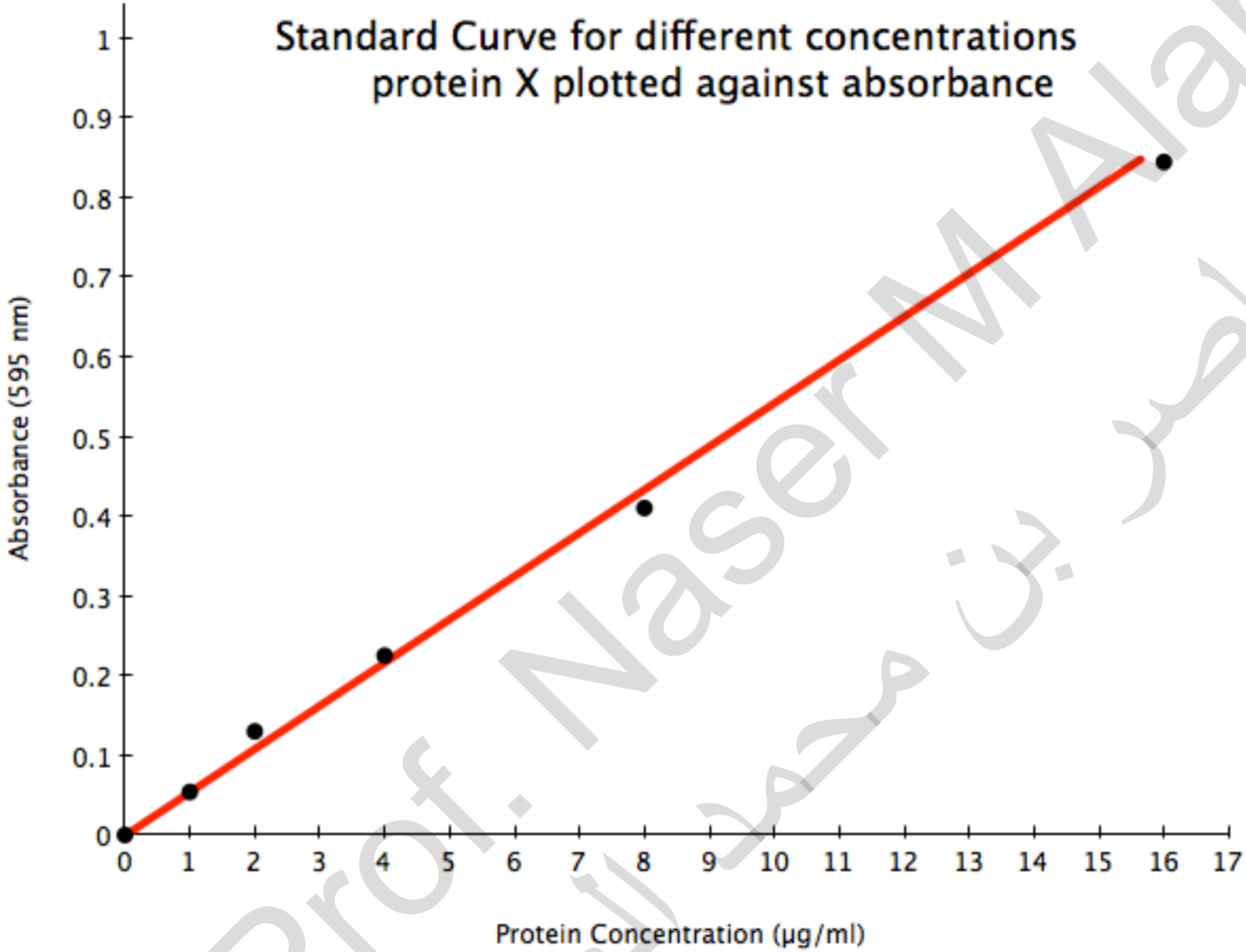


Standard Curve for different concentrations protein X plotted against absorbance

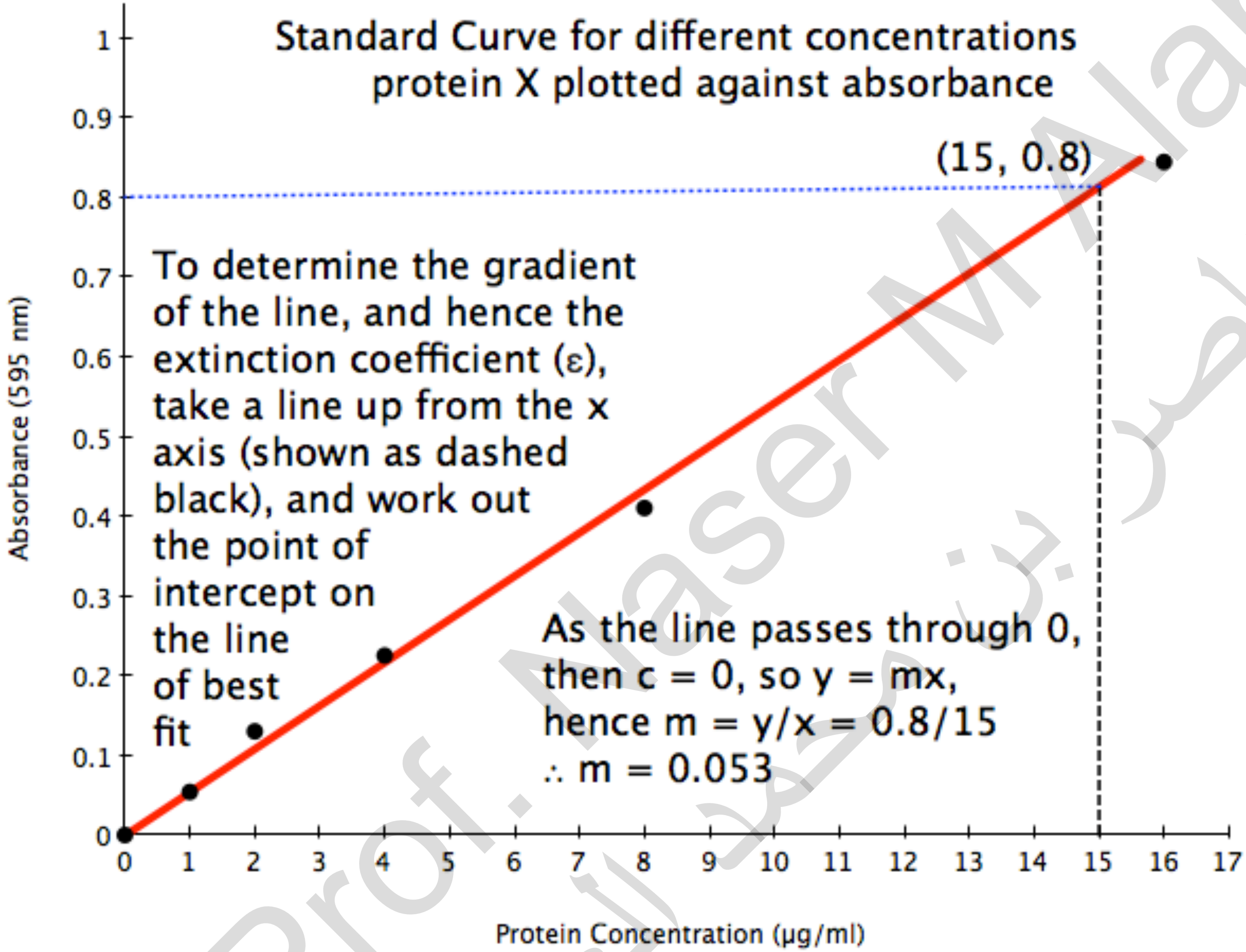
Finally, fit a line so that the points are balanced around the line

Take care not to extrapolate (extend) the line beyond the range of the data

Concentration (μg/ml)	Absorbance (595 nm)
0	0
1	0.054
2	0.130
4	0.225
8	0.410
16	0.844



Concentration ($\mu g/ml$)	Absorbance (595 nm)
0	0
1	0.054
2	0.130
4	0.225
8	0.410
16	0.844



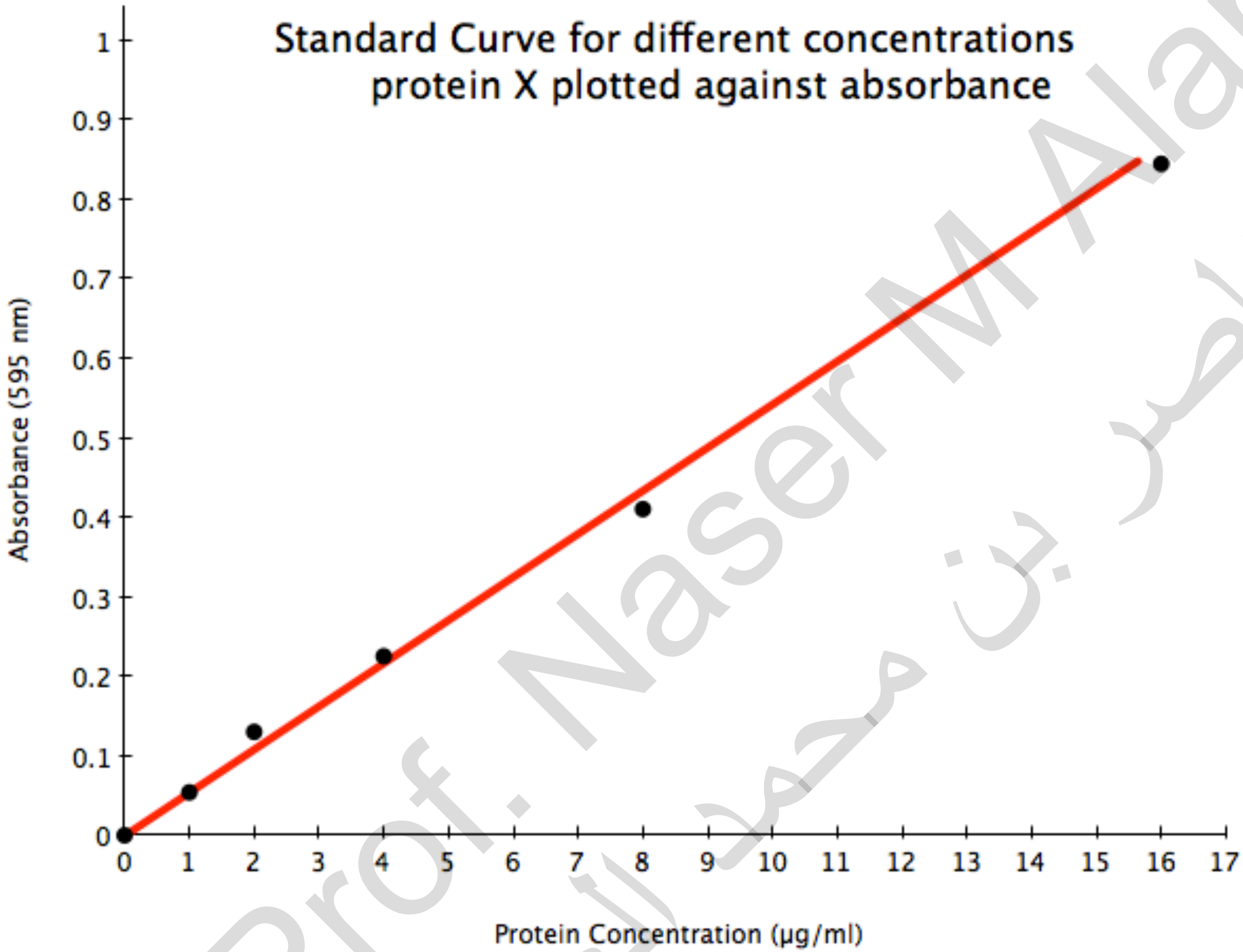
Standard Curve for different concentrations protein X plotted against absorbance

To determine the gradient of the line, and hence the extinction coefficient (ε), take a line up from the x axis (shown as dashed black), and work out the point of intercept on the line of best fit

As the line passes through 0, then c = 0, so y = mx, hence m = y/x = 0.8/15

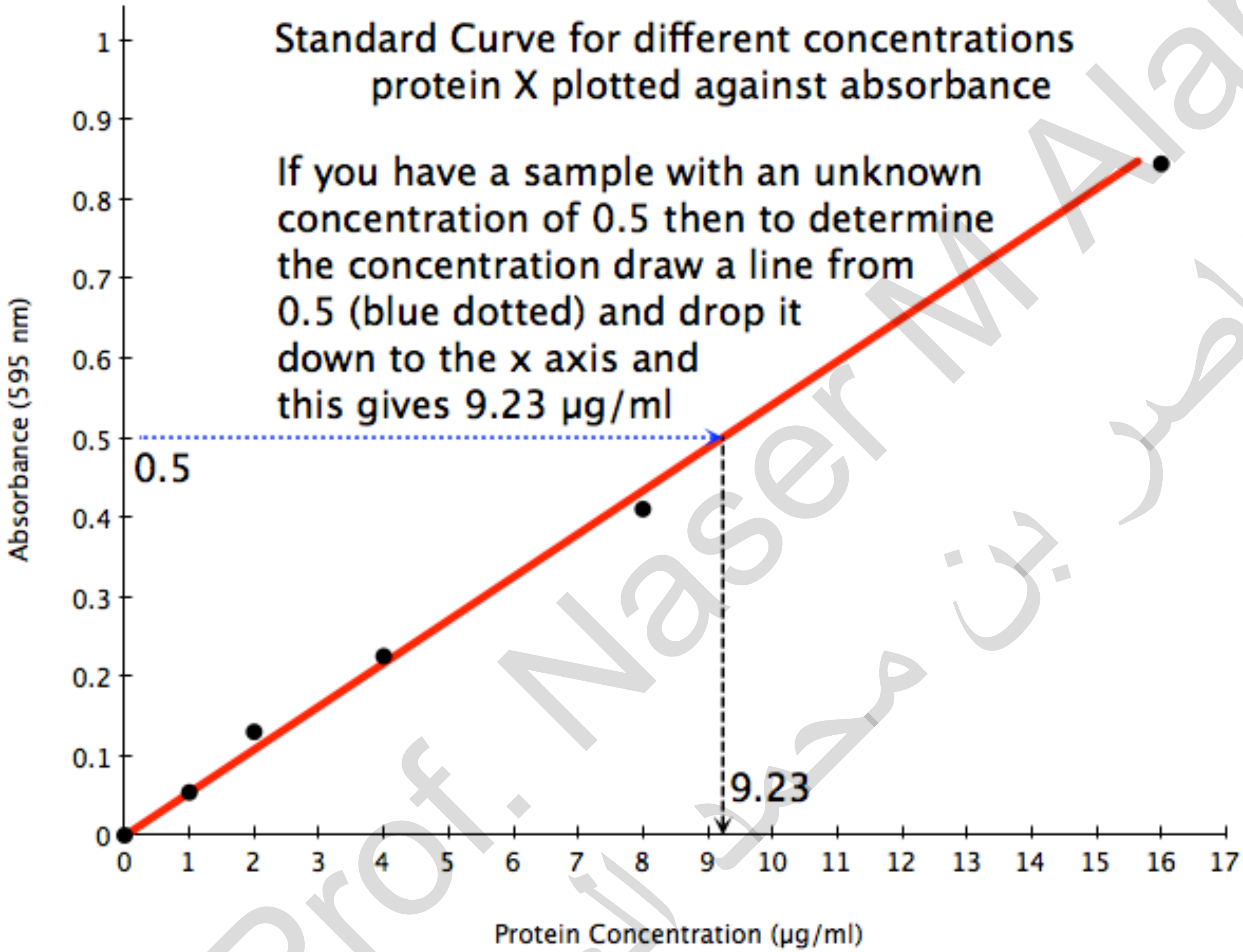
∴ m = 0.053

Concentration (μg/ml)	Absorbance (595 nm)
0	0
1	0.054
2	0.130
4	0.225
8	0.410
16	0.844



Concentration (µg/ml)	Absorbance (595 nm)
0	0
1	0.054
2	0.130
4	0.225
8	0.410
16	0.844

Unknown	Absorbance (595 nm)	Conc. (µg/ml)
1	0.500	

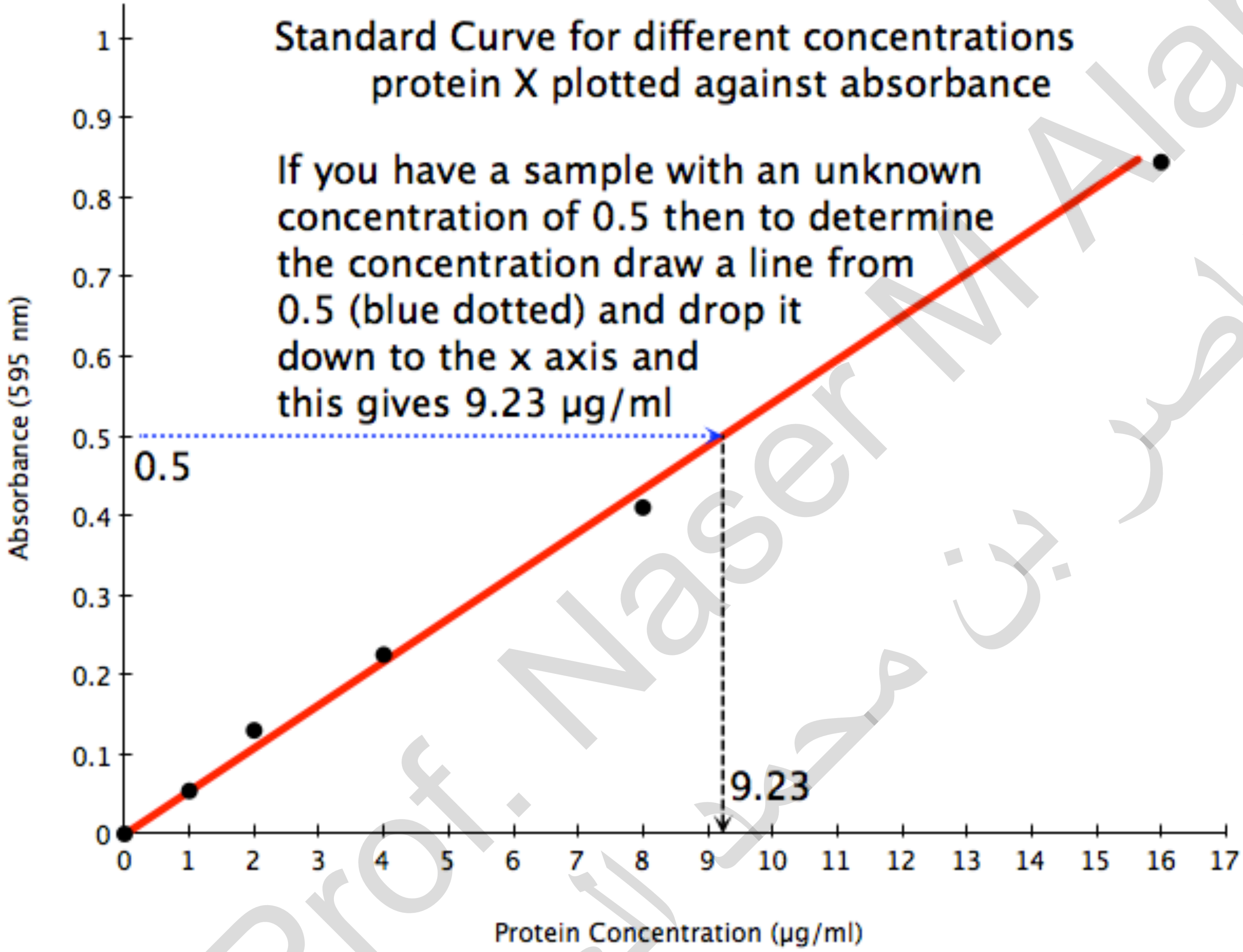


Standard Curve for different concentrations protein X plotted against absorbance

If you have a sample with an unknown concentration of 0.5 then to determine the concentration draw a line from 0.5 (blue dotted) and drop it down to the x axis and this gives 9.23 µg/ml

Concentration (*µ*g/ml)	Absorbance (595 nm)
0	0
1	0.054
2	0.130
4	0.225
8	0.410
16	0.844

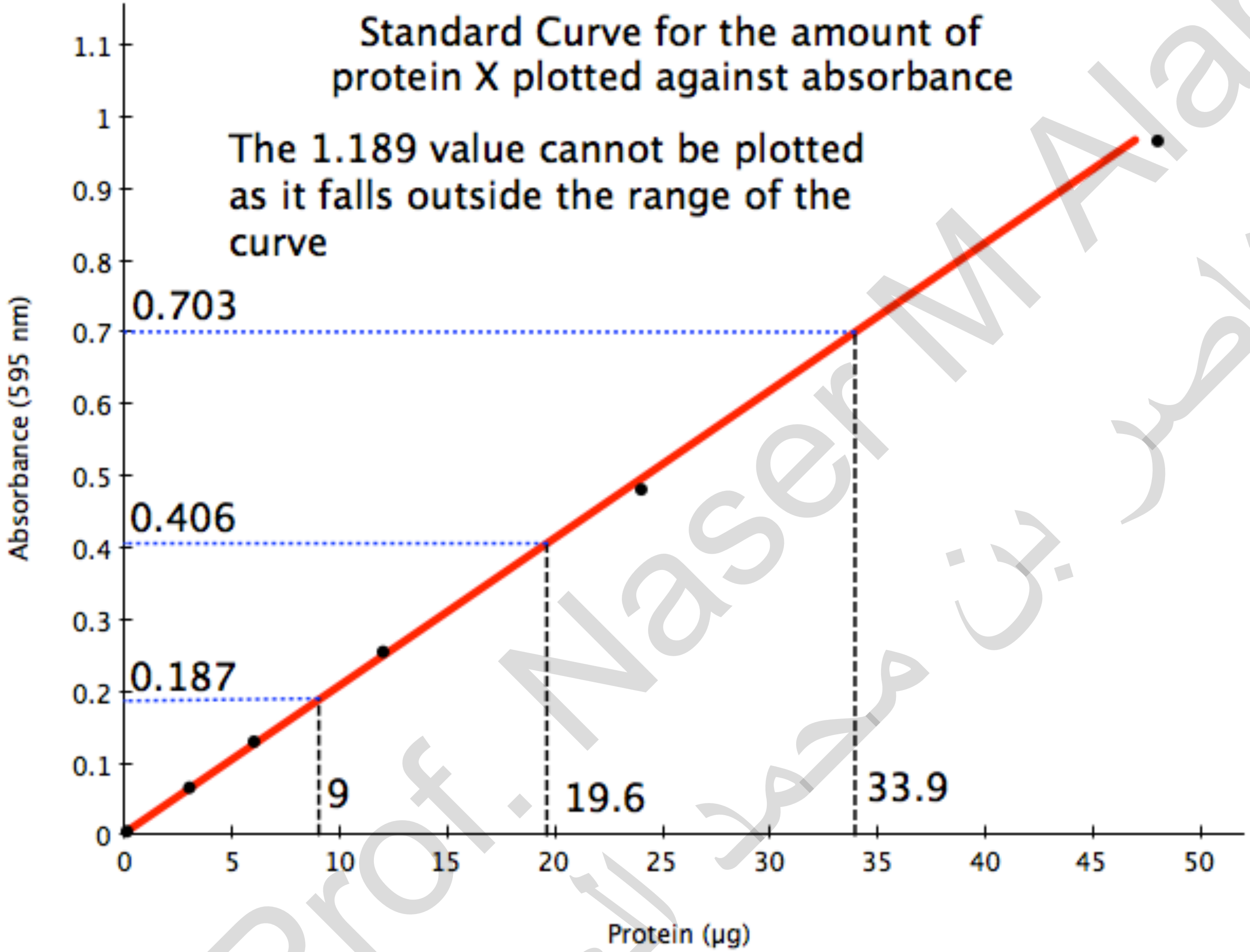
Unknown	Absorbance (595 nm)	Conc. (*µ*g/ml)
1	0.500	


Standard Curve for different concentrations protein X plotted against absorbance

If you have a sample with an unknown concentration of 0.5 then to determine the concentration draw a line from 0.5 (blue dotted) and drop it down to the x axis and this gives 9.23 μg/ml

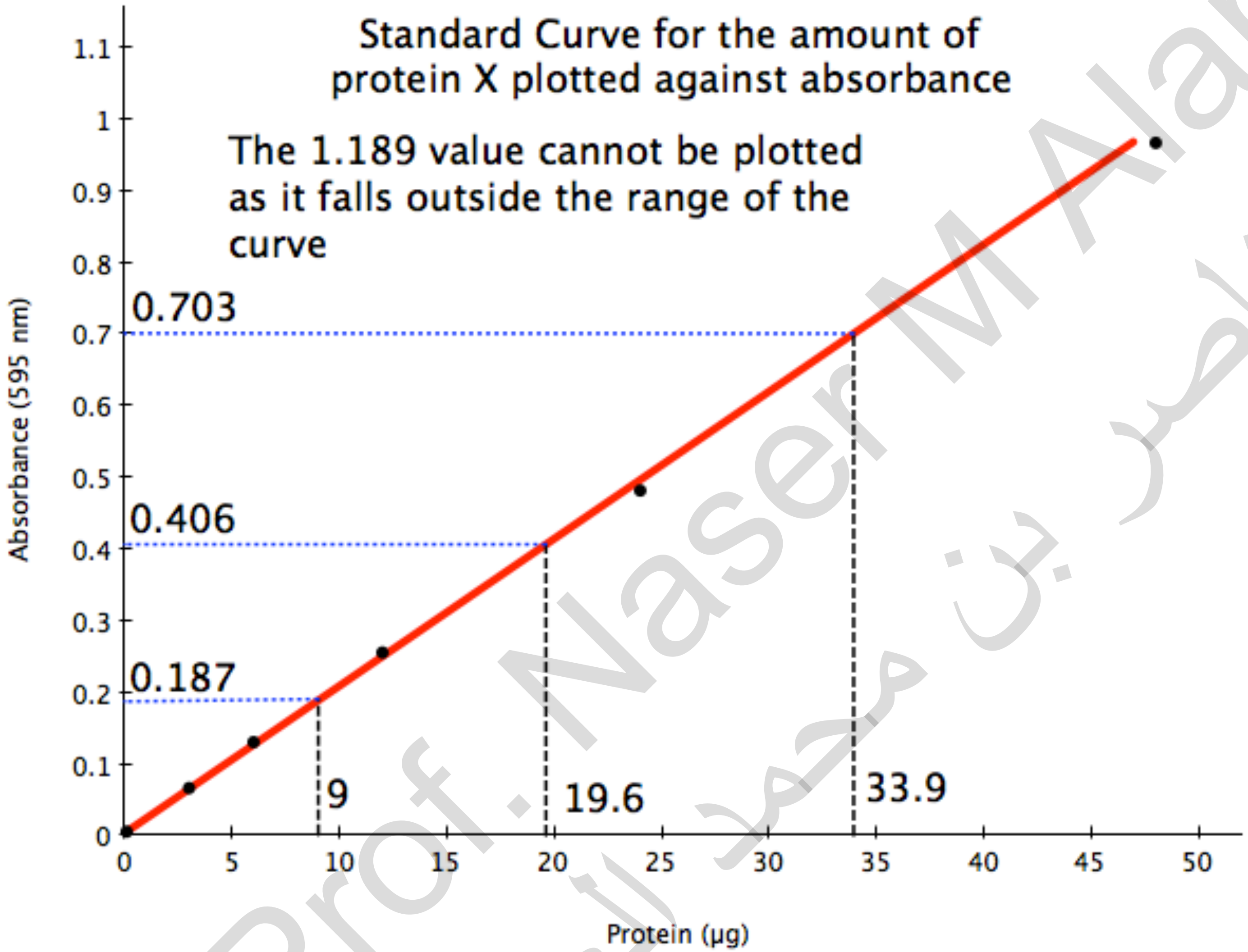
Concentration (µg/ml)	Absorbance (595 nm)
0	0
1	0.054
2	0.130
4	0.225
8	0.410
16	0.844

Unknown	Absorbance (595 nm)	Conc. (µg/ml)
1	0.500	9.23



Amount (μgl)	Absorbance (595 nm)
0	0
3	0.066
6	0.130
12	0.255
24	0.481
48	0.966

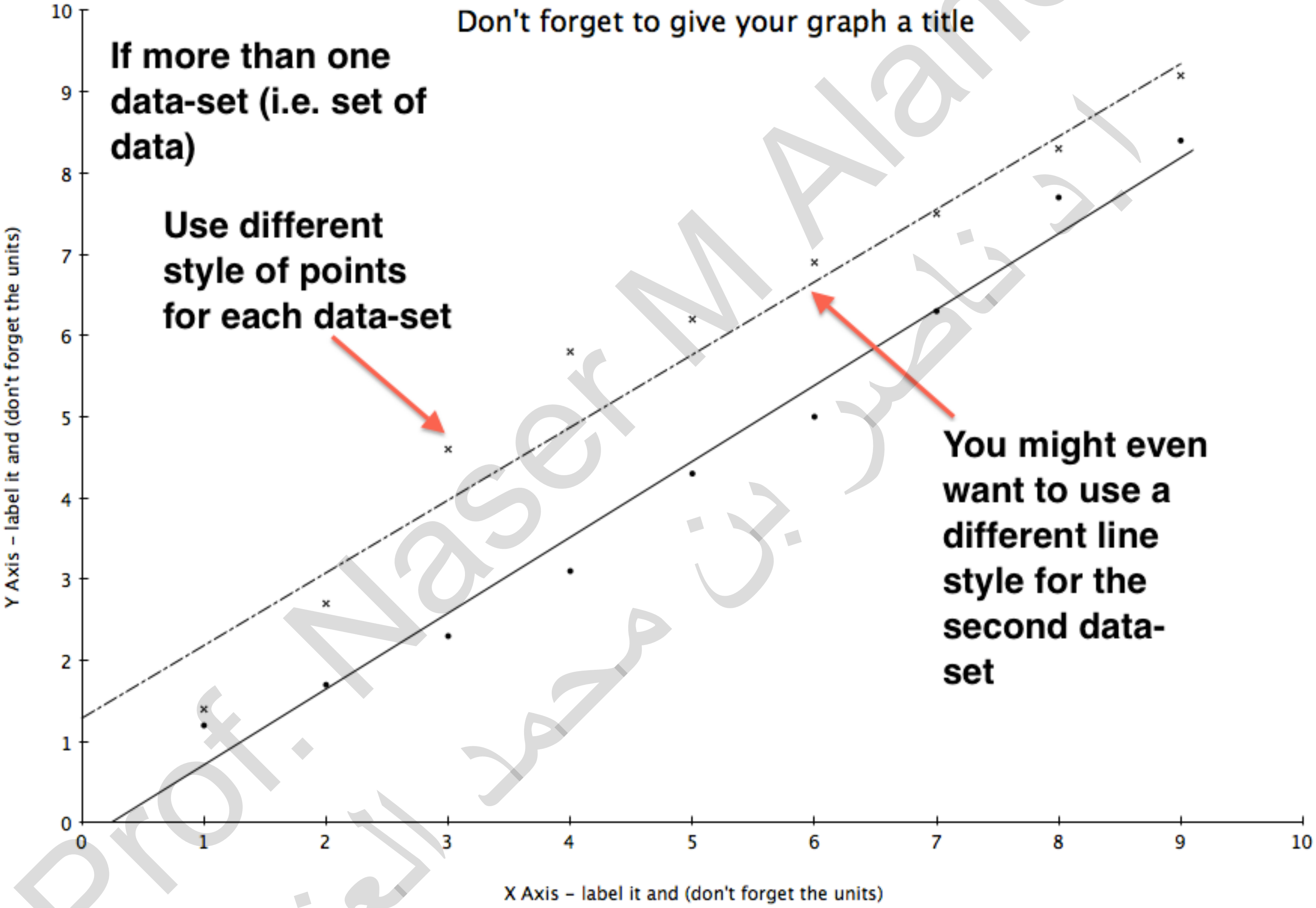
Unknown	Absorbance (595 nm)	Amount (μg)
1	0.187	
2	0.406	
3	0.703	
4	1.189	


Standard Curve for the amount of protein X plotted against absorbance

The 1.189 value cannot be plotted as it falls outside the range of the curve

Concentration (μgl)	Absorbance (595 nm)
0	0
3	0.066
6	0.130
12	0.255
24	0.481
48	0.966

Unknown	Absorbance (595 nm)	Amount (μg)
1	0.187	9.0
2	0.406	19.6
3	0.703	33.9
4	1.189	???



Don't forget to give your graph a title

If more than one data-set (i.e. set of data)

Use different style of points for each data-set

You might even want to use a different line style for the second data-set

Summary

- Make the best use of the graph paper
- Use a sharp pencil
- Plot your point clearly and add the line
    - Join the points, or use a line of best fit
- Clearly label the axes - don't forget any units
- Give the graph a title
- Use different point styles if showing more than one data set

For more information and a free course please visit:

http://maths4biosciences.com

335 Chem

CHEMICAL KINETICS

3 credits (**2** lectures + **1** lab)

Part 1

Vocabulary

“kinetic” is an adjective of Greek origin “kinetikos”, which means “***moving***”.

“kinetics” in sciences represent the dependence of something on time.

Chemical kinetics is a branch of physical chemistry concerning about the ***rates*** of (the reactants or products) concentration changes in a chemical reaction.

Outline

Reaction Rates	How we measure rates.
Rate Laws	How the rate depends on amounts of reactants.
Integrated Rate Laws	How to calculate amount left or time to reach a given amount.
Half-life	How long it takes to react 50% of reactants.
Arrhenius Equation	How rate constant changes with temporature.
Mechanisms	Link between rate and molecular scale processes.

Thermodynamics vs Kinetics

Thermodynamics shows us

- Reaction direction.
- Feasibility of a chemical reaction occurrence (feasible if **$\Delta G < 0$**, at constant **T** and **P**).

$$\mathbf{C(diamond) + O_2(g) \rightarrow CO_2(g) \quad \Delta G^\circ = -397\ kJ/mol}$$

Kinetics shows us:

- How quickly the occurrence of a chemical reaction.

$$\mathbf{C(diamond) + O_2(g) \rightarrow CO_2(g) \quad \Delta G^\circ = -397\ kJ/mol}$$

- This reaction *will not occur* during your lifetime since it is very slow kinetically.

Chemical Kinetics

A) Macroscopic level

Defining “rate of reaction”, “order of reaction” and “rate law”. Examining how “rates” and “orders” are determined. Macroscopic level measure reaction parameters such as (e.g. **T, P, V**).

B) Microscopic level (molecular)

Predicting plausible “reaction mechanisms” from experimental “rate laws”.

Microscopic level will measure reaction parameters that are hard to be measured directly (e.g. **molecule velocity**)

Importance of Reaction kinetics

- Improve production of reactions.
- Improve drug (medicine) activity duration.
- Increase quality and quantity of reaction products.
- Improve pesticide uses on plant.
- Reduce energy needed for the reaction.
- Minimize pollution.

Defining Reaction Rate

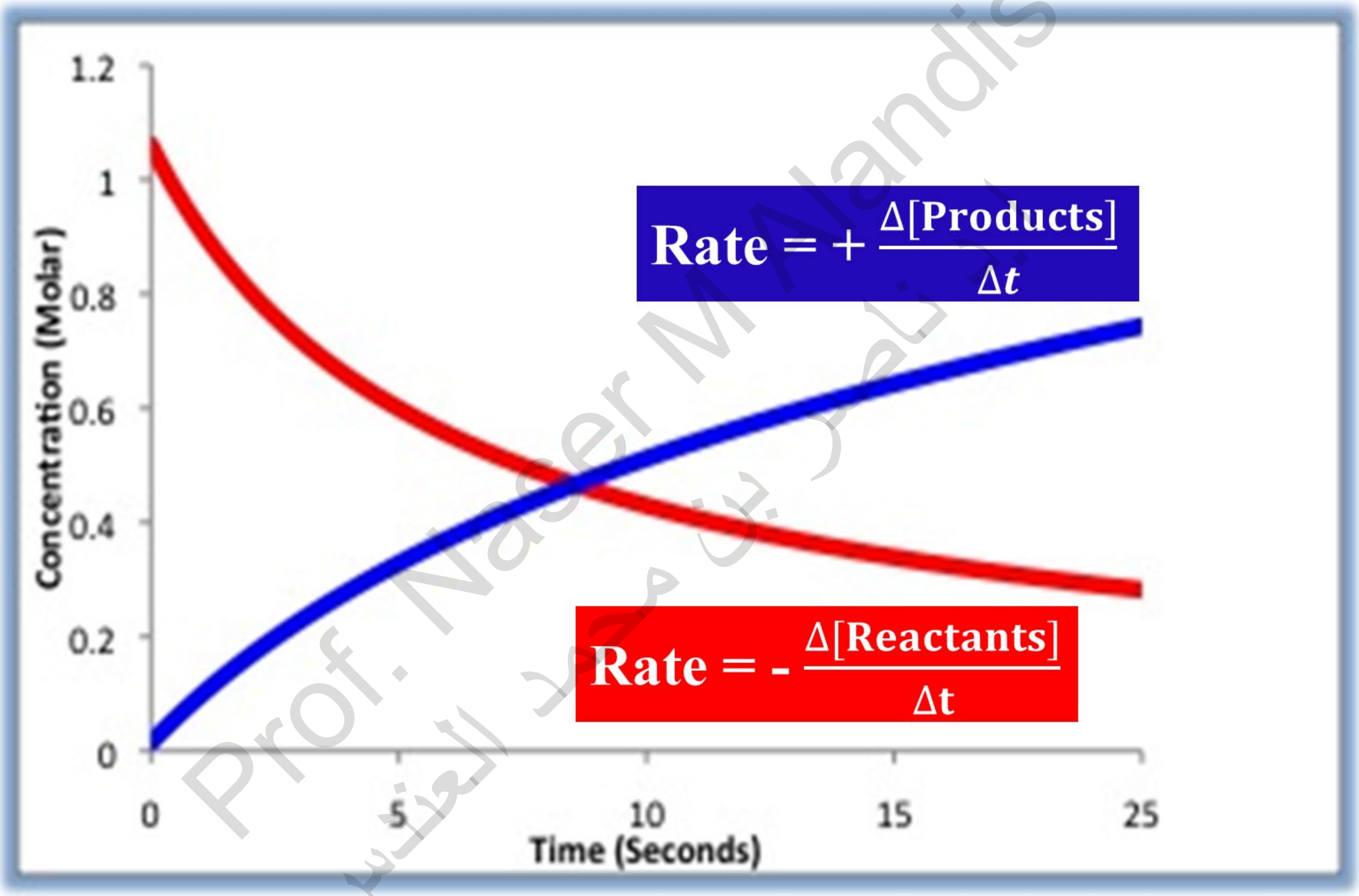
The rate of a chemical reaction is generally measured in terms of how much the **concentration** of a reactant decreases (or a product concentration increases) in a given period of time.

For the general reaction **A → B,** we measure the concentration of **A** and **B** at t_1 and at t_2:

$$\text{Rate} = -\frac{[A_1]-[A_2]}{t_1-t2} = -\frac{\Delta[A]}{\Delta t} \quad \textbf{and} \quad \text{Rate} = \frac{[B_1]-[B_2]}{t_1-t_2} = \frac{\Delta[B]}{\Delta t}$$

Negative sign is used because the concentration of **A** is decreasing.

This gives the rate a positive value. **Units: mol L^{-1} s^{-1}** **(M/s)**



$$\text{Rate} = +\frac{\Delta[\text{Products}]}{\Delta t}$$

$$\text{Rate} = -\frac{\Delta[\text{Reactants}]}{\Delta t}$$

Instantaneous And Average Rates

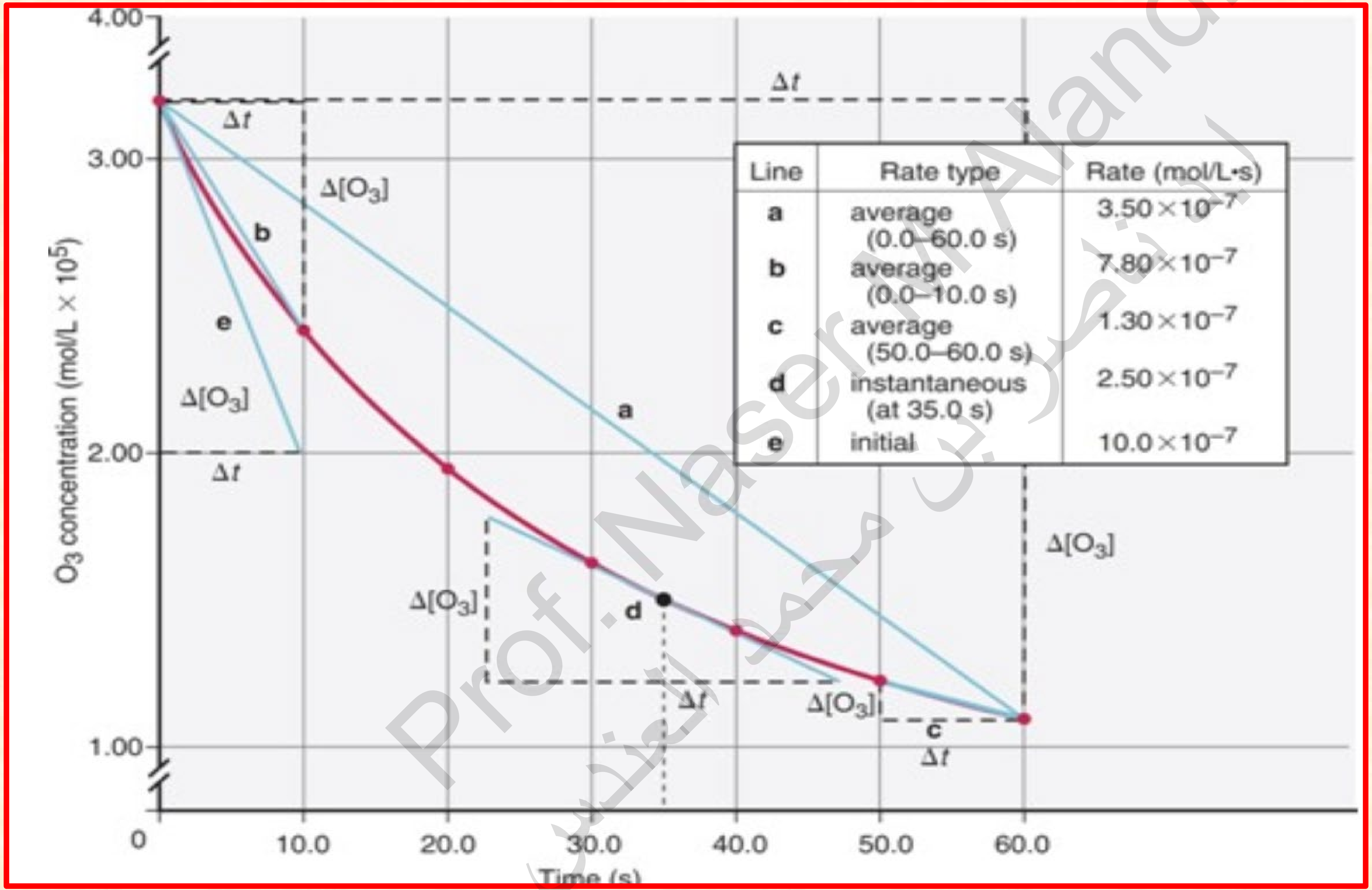
- Rate of reaction is generally not constant. **BUT** In the case of **zero order** reaction the rate is constant
- Rate of reaction generally changes over the course of reaction.
- Concentration of reactants or products are measured at regular time intervals.
- A graph of concentration vs time may be plotted

- **Instantaneous Rate** is a value of the rate at a particular time.
- Can be obtained by computing the slope of a line tangent to the curve at that point.
- Instantaneous rate at a given time is the slope of the tangent to the curve at that time. **Instantaneous rate** $= -\dfrac{d[\text{reactant}]}{dt}$
- Instantaneous rate measured at the beginning of the reaction, which is dependent on the initial concentrations of reactants called ***Initial Rates***
- **Average rate** is measured rate over a time interval.

$$\textbf{Average rate} = -\frac{\Delta[\text{reactant}]}{\Delta t}$$

$$C_2H_4\,(g) + O_3\,(g) \rightleftharpoons C_2H_4O\,(g) + O_2\,(g)$$

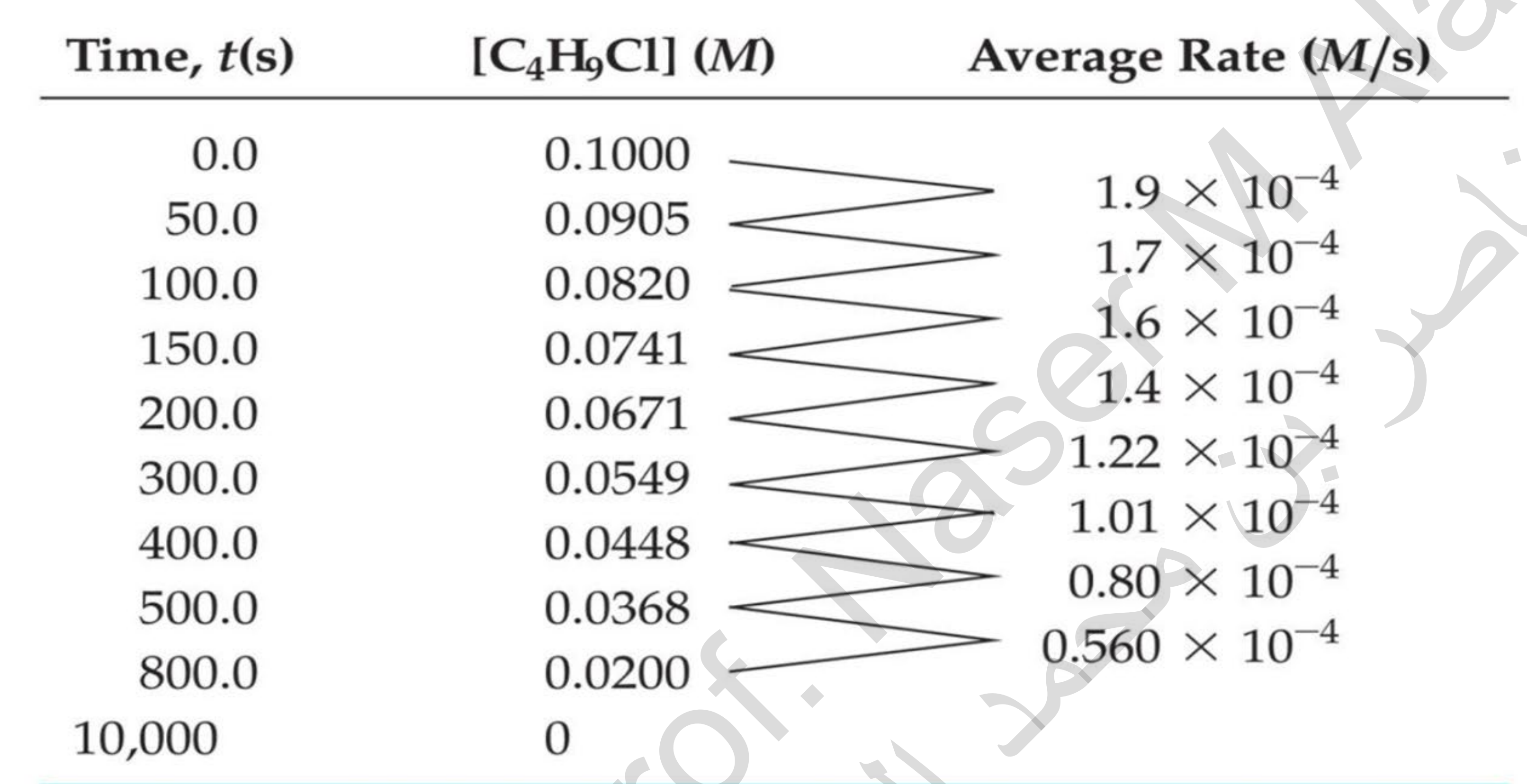
Types of Rates



Line	Rate type	Rate (mol/L•s)
a	average (0.0–60.0 s)	3.50×10^{-7}
b	average (0.0–10.0 s)	7.80×10^{-7}
c	average (50.0–60.0 s)	1.30×10^{-7}
d	instantaneous (at 35.0 s)	2.50×10^{-7}
e	initial	10.0×10^{-7}

Reaction Rate Calculations

$$C_4H_9Cl(aq) + H_2O(\ell) \rightarrow C_4H_9OH(g) + HCl(aq)$$



Time, *t*(s)	$[C_4H_9Cl]$ (*M*)	Average Rate (*M*/s)
0.0	0.1000	1.9×10^{-4}
50.0	0.0905	1.7×10^{-4}
100.0	0.0820	1.6×10^{-4}
150.0	0.0741	1.4×10^{-4}
200.0	0.0671	1.22×10^{-4}
300.0	0.0549	1.01×10^{-4}
400.0	0.0448	0.80×10^{-4}
500.0	0.0368	0.560×10^{-4}
800.0	0.0200	
10,000	0	

The **average rate** of the reaction over each interval is the change in concentration divided by the change in time:

$$\text{Rate} = -\frac{\Delta[C_4H_9Cl]}{\Delta t} = -\frac{[0.1000-0.0905]M}{(50.0-0.0)\ s} = -1.9 \times 10^{-4}\ M\ s^{-1}$$

Reaction Rate and Stoichiometry

Coefficients of most balanced equation are not all the same.

$$H_2\,(g) + I_2\,(g) \rightarrow 2\,HI(g)$$

- So, the change in the number of molecules of (**HI**) substance is twice the change in the number of molecules of (H_2 and I_2).
- For every **1 mole** of H_2 consumed, **1 mole** of I_2 will be consumed and **2 moles** of **HI** will be produced. So the rate of change will be different.
- To be consistent, the change in the concentration of each substance is multiplied by **1/coefficient**.

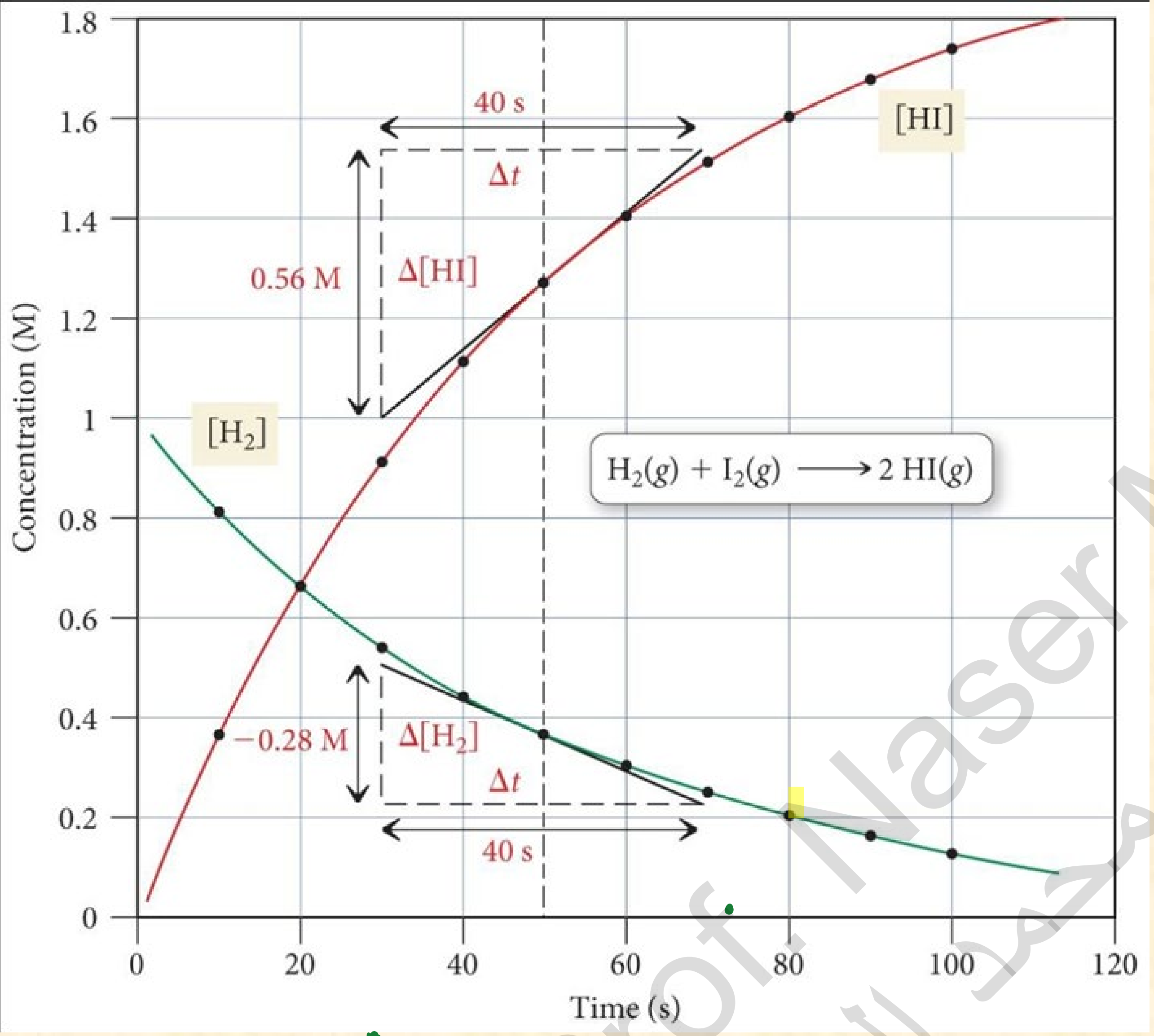
The Rate of Chemical Reactions

$$H_2\,(g) + I_2\,(g) \rightarrow 2\,HI(g)$$

Rate of disappearance of reactants $= -\dfrac{\Delta[H2]}{\Delta t} = -\dfrac{\Delta[I_2]}{\Delta t}$

Rate of appearance of products $= +\dfrac{1}{2}\dfrac{\Delta[HI]}{\Delta t}$

- When the [HI] increases by **2x** the rate of that I_2 or H_2 will decreases by **x**.
- For the overall rate to have the ***same value*** when defined with respect to any reactant the change in HI rate must be multiplied by **1/2**



$H_2\,(g) + I_2\,(g) \longrightarrow 2\,HI(g)$

- ✓2 mole HI produced for every mole of H_2 consumed

$$\text{Rate} = -\frac{\Delta[H2]}{\Delta t} = -\frac{0.28M}{40s} = 0.007Ms^{-1}$$

$$\text{Rate} = +\frac{\Delta[HI]}{\Delta t} = -\frac{0.56M}{40s} = 0.014Ms^{-1}$$

- ✓The rate formation of HI is twice the rate consumption of H_2
- ✓However, the same reaction cannot have 2 different rates…

✓ To compare the rates we divide by the reaction coefficients

General Definition of The Rate of Reaction

$$aA + bB \longrightarrow cC + dD$$

a, b, c and d are the coefficients for the balanced equation

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

- We can predict the rate of change of one reactant or product based on the rate of change of another.
- We cannot predict rate based on the balanced equation alone.

It must be done experimentally

Example For the reaction: $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$

(a) Express the rate for changes in $[H_2]$, $[O_2]$, and $[H_2O]$ with time ?

(b) If $[O_2]$ is decreasing at 0.23 mol/L s, at what rate is $[H_2O]$ increasing?

PLAN:

- We choose O_2 as the reference because its coefficient is 1
- For every molecule of O_2 that disappears, two molecules of H_2 disappear, so the rate of $[O_2]$ decrease is ½ the rate of $[H_2]$ decrease.
- Similarly, the rate at which $[O_2]$ decreases is ½ the rate at which $[H_2O]$ increases.

Solution:

(a) $$\text{Rate} = -\frac{\Delta[O_2]}{\Delta t} = -\frac{1}{2}\frac{\Delta[H_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[H_2O]}{\Delta t}$$

(b) Calculating the rate of change of $[H_2O]$:

$$\frac{1}{2}\frac{\Delta[H_2O]}{\Delta t} = -\frac{\Delta[O_2]}{\Delta t} = -(-0.23)\ \text{mol/L s} = 0.23\ \text{M s}^{-1}$$ **thus** $$\frac{\Delta[H_2O]}{\Delta t} = 2(0.23\ \text{M s}^{-1}) = 0.46\ \text{M s}^{-1}$$

Factors that Affect the Reaction Rate

1. **Temperature**: At higher temperatures, reactant molecules have more kinetic energy, move faster, and collide more often and with greater energy.

- **Collision Theory**: When two chemicals react, their molecules have to collide with each other (in a particular orientation) with sufficient energy for the reaction to take place.
- **Kinetic Theory**: Increasing temperature means the molecules move faster.

2. Concentrations of Reactants

- As the concentration of reactants increases, so does the likelihood that reactant molecules will collide.
- As reaction continue, the rate of a reaction generally slows down because the concentration of the reactants decreases.(In the case of zero order reaction the rate is constant)
- After some time the reaction stops, either because the reactants run out or because the system has reached **equilibrium.**
- After reaching equilibrium the concentration of both reactants and products stay the same although the reaction still going on.

3.Pressure of gaseous reactants or products

Increased number of collisions

4. Surface area of a solid reactant

- More area for reactants to be in contact

5. Reactants Nature Affecting Reaction Rate:

Means both physical condition and reactivity of reactants molecules.

Physical condition of reactants molecules :

- Small molecules tend to react faster than large molecules.

  Diffusion and mobility

- Gases tend to react faster than liquids, which react faster than solids.

  Energy , mobility and contact surfaces

- Powdered solids are more reactive than “blocks.”

  More surface area for contact with other reactants

Extremely small particles may result in very fast reaction rates and may lead to explosion

6. Reactivity of reactants molecules

❑ Reactive molecule is unstable molecule or less stable in comparison with other molecules.

❑ Certain types of chemicals are more reactive than others.

- ✓ **Na** metal is more reactive than **K**
- ✓ **F_2** gas is more reactive than **Cl_2**
- ✓ **CO** gas is more reactive than **CO_2**
- ✓ **H_2O_2** liquid is more reactive than **H_2O**

❑ Ions react faster than molecules.

No bonds need to be broken.

❑ Radical react faster than molecules.

Radical is a result of broken bond

7. Catalysts

- Speed up reactions by lowering activation energy

335 Chem

CHEMICAL KINETICS

3 credits (**2** lectures + **1** lab)

Part 2

The Rate Laws

- The relationship between the rate of the reaction and the concentrations of the reactants expressed in mathematical equation is called *The Rate Law.*

The rate law must be determined experimentally!

- The rate of a reaction is directly proportional to the concentration of each ***reactant*** raised to a power.

$$aA + bB \rightarrow products$$

Rate $\propto [A]^m \times [B]^n$ **becomes** **Rate = k $[A]^m \times [B]^n$**

m and *n* are called the *orders* for each reactants.

- *m* and *n* may take negative or positive or zero value witch determined the influence of the reactant concentration on the rate of the reaction.
- The sum of ($m + n$) = **overall reaction order** , it must be ≥ 0
- **k** is the proportional coefficients witch called *the rate constant .*

k unit changes according to **overall reaction order** *value*

- Rate laws are always determined *experimentally.*
- Reaction order is always defined in terms of reactant (not product) concentrations.
- The **order** of a reactant is not related to the **stoichiometric** coefficient of the reactant in the balanced chemical equation.

$F_2\ (g) + 2ClO_2\ (g) \longrightarrow 2FClO_2\ (g)$

Rate = $k\ [F_2][ClO_2]$

NOTE: DO NOT use number 1 as a power for any reactants.

Order and Rate Constant Units

Reaction order	Reaction order name	k units	
$(m + n)$	Overall order	$mol^{1-(m+n)}\ L^{(m+n)-1}\ s^{-1}$	$M^{1-(m+n)}\ s^{-1}$
0	zero	$mol\ L^{-1}\ s^{-1}$	$M\ s^{-1}$
1	first	s^{-1}	s^{-1}
2	second	$L\ mol^{-1}\ s^{-1}$	$M^{-1}\ s^{-1}$
3	third	$mol^{-2}\ L^{2}\ s^{-1}$	$M^{-2}\ s^{-1}$

Some Reactions and Their Experimental Rate Laws

$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$	$Rate = k[N_2O_5]$
$2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)$	$Rate = k[NO_2][F_2]$
$NO(g) + N_2O_5(g) \rightarrow 3NO_2(g)$	$Rate = k[N_2O_5]$
$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$	$Rate = k[NO]^2[O_2]$
$CH_3CHO(g) \rightarrow CH_4(g) + CO(g)$	$Rate = k[CH_3CHO]^{3/2}$
$CHCl_3\ (g) + Cl_2(g) \rightarrow CCl_4(g) + HCl(g)$	$\text{Rate} = k[CHCl_3]\ [Cl_2]^{1/2}$
$H_2(g) + I_2\ (g) \rightarrow 2HI(g)$	$\text{Rate} = k[H_2][I_2]$

Exercise:

Determine the reaction order with respect to each reactant and the overall reaction order from the given rate law.

(a) $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$; rate $= k[NO]^2[O_2]$

(b) $CH_3CHO(g) \rightarrow CH_4(g) + CO(g)$; rate $= k[CH_3CHO]^{3/2}$

(c) $H_2O_2(aq) + 3I^-(aq) + 2H^+(aq) \rightarrow I^{3-}(aq) + 2H_2O(l)$; rate $= k[H_2O_2][I^-]$

PLAN: Inspect the rate law and not the coefficients in the balanced chemical reaction.

SOLUTION

(a) The reaction is 2nd order in NO, 1st order in O_2, and 3rd order overall.

(b) The reaction is 3/2 order in CH_3CHO and 3/2 order overall.

(c) The reaction is 1st order in H_2O_2, 1st order in I^- and zero order in H^+, and 2nd order overall.

335 Chem

CHEMICAL KINETICS

3 credits (**2** lectures + **1** lab)

Part 3

Determining the Rate Law

Initial Aates Method

- Best for multi-reactant reactions.
- Lower accuracy

Integration Method

- Trial & error approach.
- Not suitable for multi-reactant systems.
- Most accurate.

Flooding or Isolation Method

- Multiple technique
- Uses integration or initial rates methods

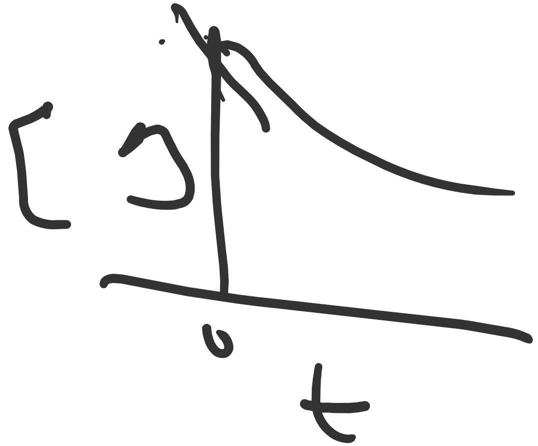
The Initial Rates Method

- The rate law must be determined **experimentally**.
- The rate law shows how the rate of a reaction depends on the **concentration** of the reactants.
- Changing the **initial concentration** of a reactant will therefore affect the **initial rate** of the reaction.

Determining the rate law experimentally:

1. Measure **initial rates** (from concentration measurements).
2. Use initial rates from several experiments to find the reaction **orders .**
3. Calculate the **rate constant .**

Steps of Determination The Kinetic Parameters of a Reaction



Series of plots of concentration vs. time

Determine slope of tangent at t_0 for each plot.

Initial rates

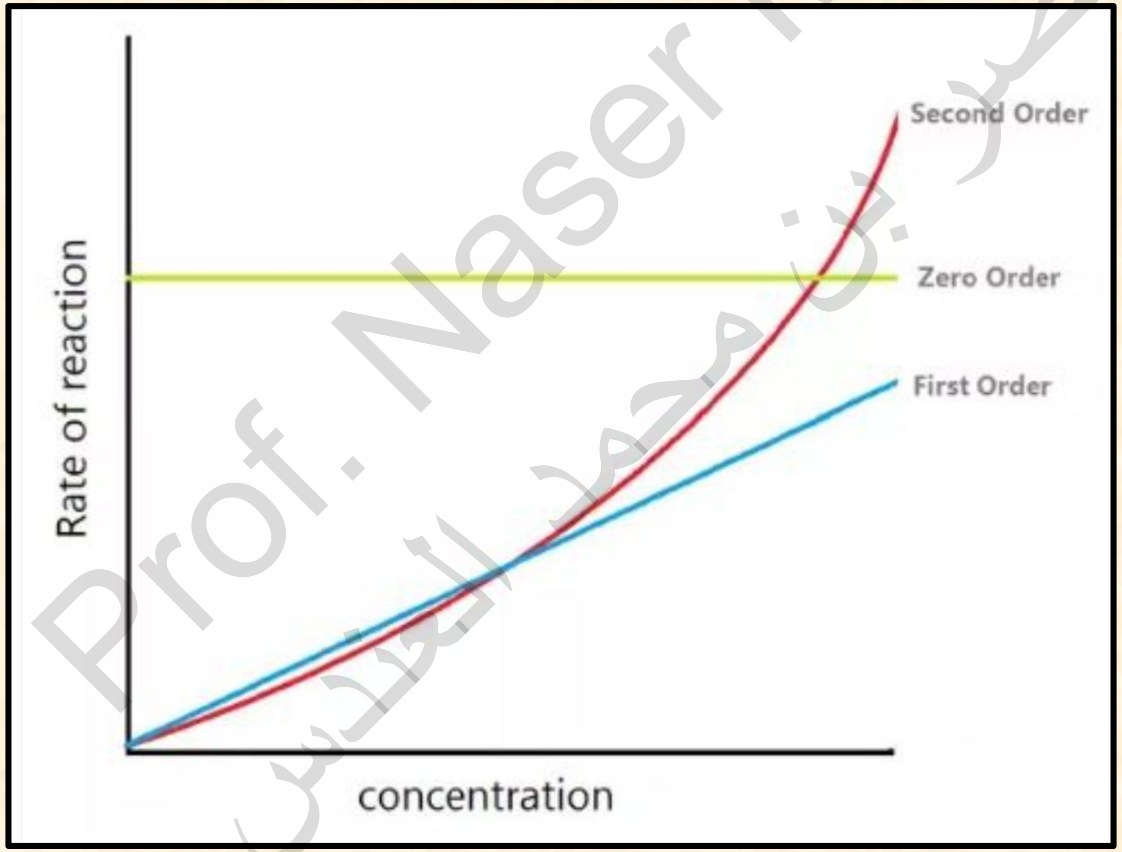
Compare initial rates when [A] *changes and* [B] *is held constant (and vice versa).*

Reaction orders

Substitute initial rates, orders, and concentrations into rate $= k[A]^x[B]^y$, *and solve for k.*

Rate constant (*k*) and actual rate law

- A reaction is **zero order** in a reactant if the change in concentration of that reactant produces ***no effect.***
- A reaction is **1st order** if doubling the concentration causes the rate to double.
- A reaction is **2nd order** if doubling the concentration causes a quadruple(4) increase in rate.
- A reaction is **3rd order** doubling concentration leads to 2^3 (or 8 times) the rate. Extremely rare.



Zero Order ($n = 0$)

[A] (M)	Initial Rate (M/s)
0.10	0.015
0.20	0.015
0.40	0.015

- This set of data shows no effect on rate with increasing [A].
- Rate is independent of [A].
- **Zero order**
- **Rate = k**

First order ($n = 1$)

[A] (M)	Initial Rate (M/s)
0.10	0.015
0.20	0.030
0.40	0.060

- In this set of data when [A] doubles the rate doubles
- Rate is directly proportional to [A]
- It is First order
- **Rate = k [A]**

Second Order ($n = 2$)

[A] (M)	Initial Rate (M/s)
0.10	0.015
0.20	0.060
0.40	0.240

- In this set of data when [A] doubles the rate quadruples.
- Rate is directly proportional to $[A]^2$
- **Second order**
- **Rate = k $[A]^2$**

Example

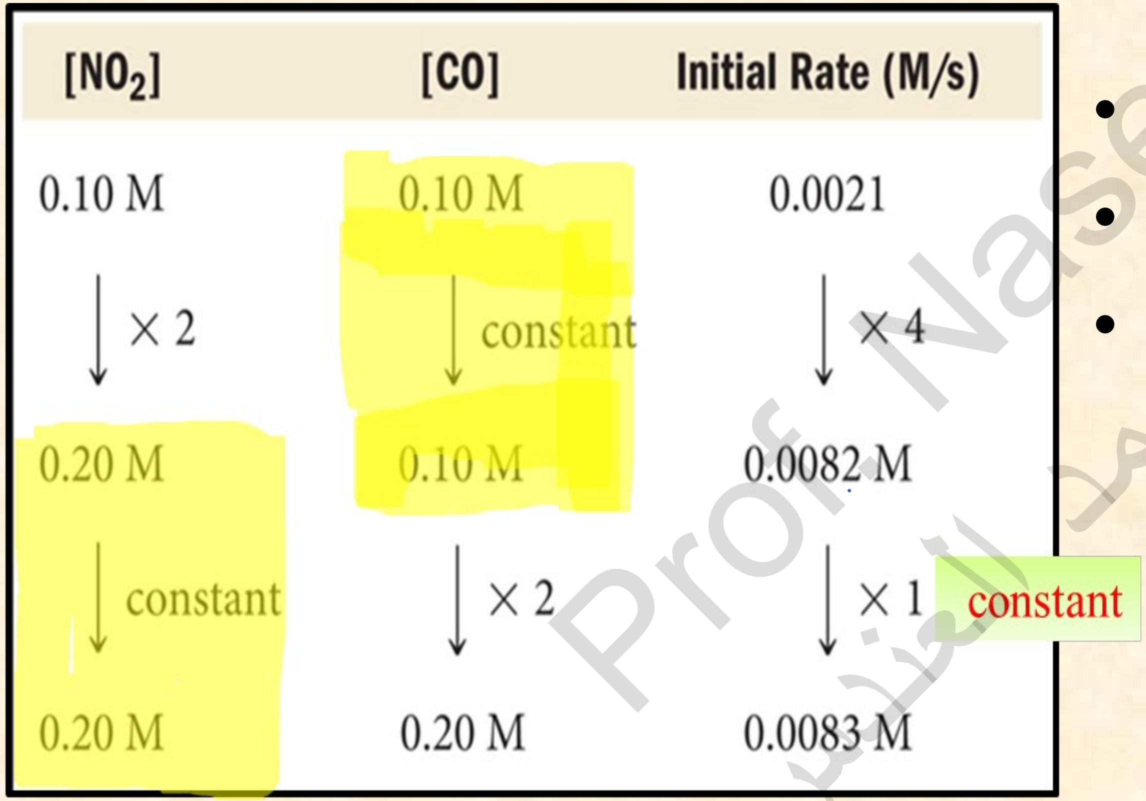
The initial rate of reaction is measured for the reaction

$$NO_2\,(g) + CO\,(g) \rightarrow NO\,(g) + CO_2\,(g)$$

Determine the rate law and rate constant for the reaction.

$[NO_2]$ (M)	[CO] (M)	Initial Rate (M/s)
0.10	0.10	0.0021
0.20	0.10	0.0082
0.20	0.20	0.0083
0.40	0.10	0.033

Solution



$[NO_2]$	[CO]	Initial Rate (M/s)
0.10 M	0.10 M	0.0021
↓ × 2	↓ constant	↓ × 4
0.20 M	0.10 M	0.0082 M
↓ constant	↓ × 2	↓ × 1 constant
0.20 M	0.20 M	0.0083 M

- $\text{Rate} = k\ [NO_2]^2\,[CO]^0$
- $\text{Rate} = k\ [NO_2]^2$
- The overall order is **second**

$$k = \frac{\text{rate}}{[NO_2]^2} = \frac{0.0021\ M/s}{[0.01\ M]^2} = 0.21\ M^{-1}\ s^{-1}$$

Example: Many gaseous reactions occur in a car engine and exhaust system. One such reaction is as follows:

$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$ rate = k $[NO_2]^m[CO]^n$

Use the following data to determine the individual and overall reaction orders.

experiment	initial rate (mol/L·s)	initial $[NO_2]$ (mol/L)	initial [CO] (mol/L)
1	0.0050	0.10	0.10
2	0.080	0.40	0.10
3	0.0050	0.10	0.20

PLAN: Solve for each reactant using the general rate law by applying the method described previously.

SOLUTION: rate = k $[NO_2]^m[CO]^n$

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{k\,[NO_2]^m{}_2[CO]^n{}_2}{k\,[NO_2]^m{}_1\,[CO]^n{}_1} = \left(\frac{[NO_2]_2}{[NO_2]_1}\right)^m$$

$$\frac{0.080}{0.0050} = \left(\frac{0.40}{0.10}\right)^m \quad ; \quad 16 = 4^m \quad \text{and} \quad \mathbf{m = 2}$$

The reaction is Second order in NO_2.

$$\frac{\text{Rate 3}}{\text{Rate 1}} = \frac{k\,[NO_2]^m{}_3[CO]^n{}_3}{k\,[NO_2]^m{}_1\,[CO]^n{}_1} = \left(\frac{[CO]_3}{[CO]_1}\right)^n$$

$$\frac{0.0050}{0.0050} = \left(\frac{0.20}{0.10}\right)^n \quad ; \quad 1 = 2^n \quad \text{and} \quad \mathbf{n = 0}$$

The reaction is zero order in CO.

Rate Law: rate $= k\,[NO_2]^2[CO]^0 = k\,[NO_2]^2$

The reaction is second order overall.

Sometimes the exponent is not easy to find by inspection. In those cases, we solve for *order* with an equation of the form

$a = b^{(order)}$

Order = (log a) / (log b)

$$y = x^n$$

$$\log y = n \log x$$

$$\frac{\log y}{\log x} = n$$

Rules of logarithms

$\log(1) = 0$
$\log(10) = 1$
$\log(100) = 2$
$\text{Log}(10^x) = x$

$\ln(1) = 0$
$\ln(e) = 1$
$\ln(e^x) = x$

$\log A^x = x\log A$

$\ln A^x = x\ln A$

$$\log\left(\frac{A^x}{B^x}\right) = \log\left(\frac{A}{B}\right)^x = x\log\left(\frac{A}{B}\right)$$

$$\log(AB) = \log A + \log B$$

$$\log\left(\frac{A}{B}\right) = \log A - \log B$$

The reaction of nitric oxide with hydrogen at 1280 °C is:

$$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$$

From the following data, determine the rate law and rate constant.

1.5

log $\frac{1}{2}$

log 1.5

$\log_{10} \frac{1}{2}$

2

Run	$[NO]_o$ (M)	$[H_2]_o$ (M)	Initial Rate (M/min)
1	0.0100	0.0100	0.00600
2	0.0200	0.0300	0.144
3	0.0100	0.0200	0.0120

$$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$$

The rate law for the reaction is given by:

$$\text{Rate(M/min)} = k\,[NO]^x[H_2]^y$$

Taking the ratio of the rates of runs 3 and 1 one finds:

$$\frac{\text{Rate}(3)}{\text{Rate}(1)} = \frac{k\,[NO]^x_{(3)}[H_2]^y_{(3)}}{k\,[NO]^x_{(1)}[H_2]^y_{(1)}}$$

$$\frac{0.0120\text{M}/\text{min}}{0.00600\text{M}/\text{min}} = 2 = \frac{\cancel{k\,[0.0100]}^x[0.0200]^y}{\cancel{k\,[0.0100]}^x[0.0100]^y} = \frac{[0.0200]^y}{[0.0100]^y}$$

$$\frac{[0.0200]^y}{[0.0100]^y} = \left[\frac{0.0200}{0.0100}\right]^y$$

$$\log\left(\left[\frac{0.0200}{0.0100}\right]^{y} = 2\right)$$

$$\log\left(\frac{0.0200}{0.0100}\right)^{y} = \log 2$$

$$y\log(2) = \log 2$$

$$y = 1$$

Now that "y" is known, we may solve for x in a similar manner:

$$\frac{\text{Rate}(1)}{\text{Rate}(2)} = \frac{k\,[NO]_{(1)}^{x}[H_2]_{(1)}^{y}}{k\,[NO]_{(2)}^{x}[H_2]_{(2)}^{y}}$$

$$\frac{0.00600}{0.144} = \frac{k\,[0.0100]^{x}[0.0100]}{k\,[0.0200]^{x}[0.0300]}$$

$$\frac{1}{24} = \left(\frac{1}{2}\right)^{x} \times \left(\frac{1}{3}\right)$$

$$\left(\frac{1}{2}\right)^{x} = \frac{1}{8}$$

$$x\log\left(\frac{1}{2}\right) = \log\left(\frac{1}{8}\right)$$

$$x = 3$$

The Rate Law is:

$$\text{Rate(M/min)} = k\,[\text{NO}]^3[\text{H}_2]$$

To find the rate constant, choose one set of data and solve:

$$0.0120\,\frac{\text{M}}{\text{min}} = k\,(0.0100\text{M})^3\,(0.0200\text{M})$$

$$k = \frac{0.0120\,\frac{\text{M}}{\text{min}}}{(0.0100\text{M})^3\,(0.0200\text{M})} = \frac{0.0120\,\frac{\text{M}}{\text{min}}}{(0.0100)^3\,(0.0200)\,\text{M}^4}$$

$$k = 6.00 \times 10^5\,\frac{\text{M}^{-3}}{\text{min}}$$

$$2A+B+2C \longrightarrow 3D + 2E$$

Exp.	$[A]_0$(M)	$[B]_0$(M)	$[C]_0$ (M)	Initial rate (M s^{-1})
1	0.2	0.1	0.1	$2.0x10^{-4}$
2	0.2	0.3	0.2	$6.0x10^{-4}$
3	0.2	0.1	0.3	$2.0x10^{-4}$
4	0.6	0.3	0.4	$1.8x10^{-4}$

1) Write the rate law?

2) Calculate k?

Integrated Rate Laws Method

Goal: express concentration as a function of time
Why: experimental data is typically in concentration vs. time
How: integrate the expression of rate law

- Initial Rate Method uses the initial portion of data from multiple experiments graph.
- Integrated Rate Laws Method uses the full time curve data from one experiment graph.
- integrated rate equation relates concentration as a function of time for a given order of reaction [A] = *F*(t). By integrating the differential equation (e.g. $d[A]/dt = -k[A]^m[B]^n$).
- Integrated rate used to calculate the half-life($t_{½}$).
- *$t_{½}$ is the time it takes for half of that reactant concentration to be Consumed.*

- For general reaction ($\boxed{aA \xrightarrow{k} B}$) we can write the differential rate of the order **n** for **A** as:

$$-\frac{1}{a}\frac{d[A]}{dt} = k[A]^n$$

- The integration of this expression for different values of "**n**" gives the "integrated rate laws".

- Note: We can omit the "**a**" term but this approach is more general rate of reaction

Zero-Order Reaction

- The rate of a zero-order reaction does not depend on reactant concentration, as this reaction:

$$A \xrightarrow{k} B$$

- the zero-order rate law for the disappearance of [A] is given by:

$$\text{Rate} = -(d[A]/dt) = k[A]^0 = k = \text{constant}$$

- Integration over the limits **[A]** = $[A]_0$ to $[A]_t$ and t = 0 to t

$$\int_{A_0}^{A_t} d[A] = -\int_{o}^{t} k\,d[t]$$

gives

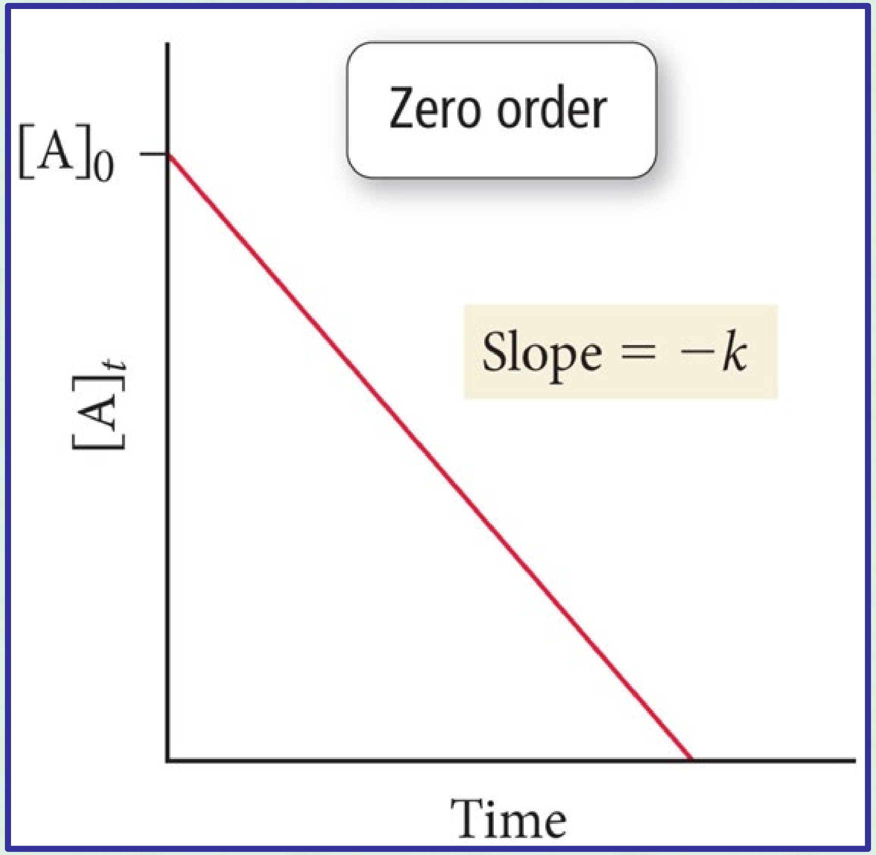
$$[A]_t = [A]_0 - kt$$

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

$$y = a - mx$$

The half-life is : $t_{1/2} = \dfrac{[A]_0}{2k}$

Note that $[A]_0$ has an effect of the value of $t_{1/2}$



Some examples of zero order reaction

$CH_3COCH_3 + I_2 \xrightarrow{H^+} ICH_2COCH_3 + HI$

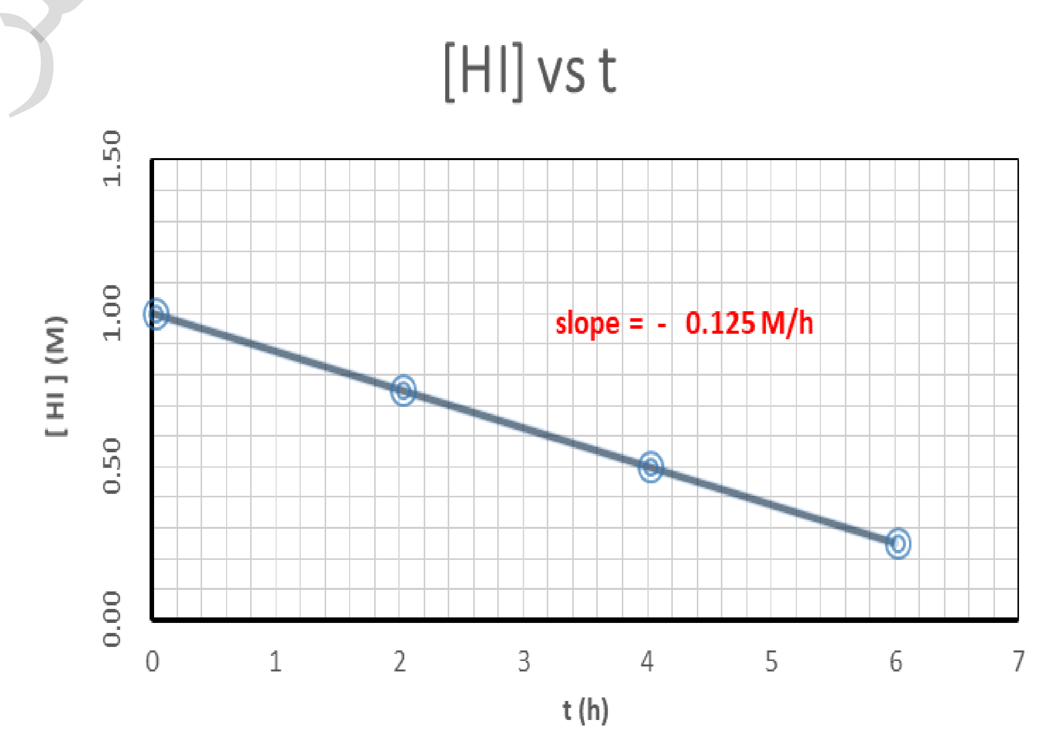
$H_2(g)+Cl_2(g) \xrightarrow{hv} 2HCl(g$

$2N_2O \xrightarrow{Pt(hot)} 2N_2 + O_2$

Example

The following data were obtained for the gas decomposition of hydrogen iodide. If the reaction is **zero order** find its rate constant graphically? What is the concentration after 7.5 hours? What is $\mathbf{t_{1/2}}$ of the reaction ?

Time (hr)	**0**	**2**	**4**	**6**
[HI] M	**1.00**	**0.75**	**0.50**	**0.25**



k = 0.125 M hr^{-1}

$$t_{1/2} = \frac{[A]_0}{2k} = \frac{1.00\ M}{2(0.125\ M\ hr^{-1})} = 4\ hr$$

$$[A]_t = [A]_0 - kt = 1.00\ M - (0.125\ M\ hr^{-1})\ (7.5\ hr) = 0.0625\ M$$

First-Order Reaction

The simplest, irreversible reaction is the first-order, as this reaction: $A \xrightarrow{k} B$

and the rate is: $\text{Rate} = -\dfrac{d[A]}{dt} = \dfrac{d[B]}{dt} = k[A]$

Rearrangement in terms of [A], $\dfrac{d[A]}{[A]} = -k\,dt$

Integration from $t = 0$ $([A]_0)$ to time t $([A]_t)$ gives:

$$\int_{A_0}^{A_t} \frac{1}{[A]} d[A] = -\int_{o}^{t} k d[t]$$

Integrated result: $[A]_t = [A]_0\, e^{-kt}$

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

$y \quad = \quad a \quad - mx$

Or $\ln\left(\dfrac{[A]_t}{[A]_0}\right) = -kt$

$y \quad = -mx$

Or $\ln\left(\dfrac{[A]_0}{[A]_t}\right) = kt$

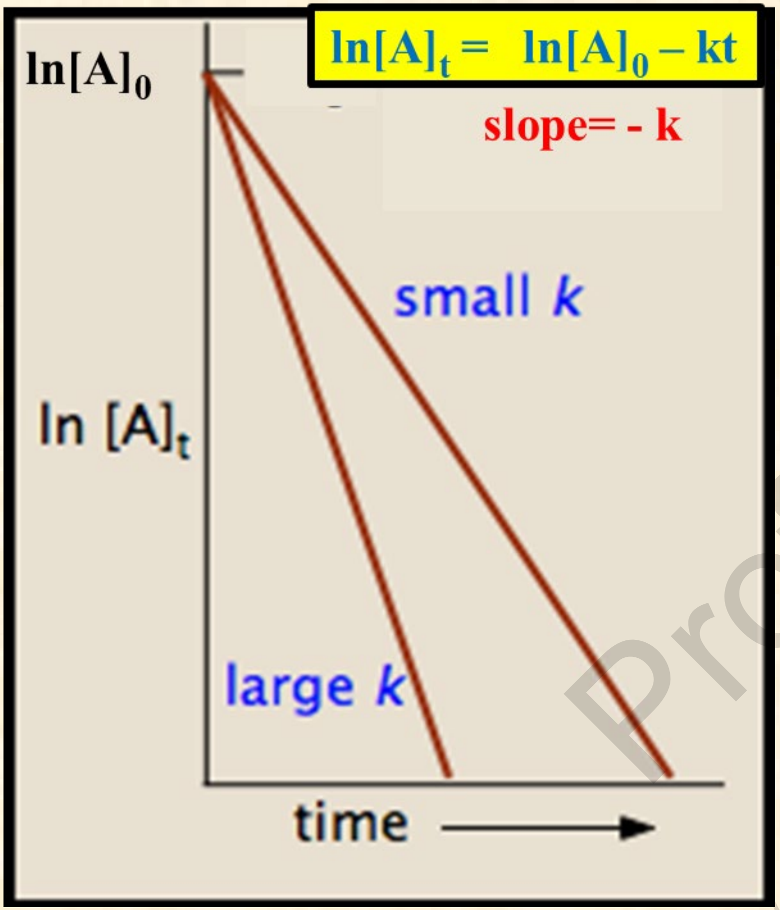
$y \quad = mx$

The rate law in products teamers [B]

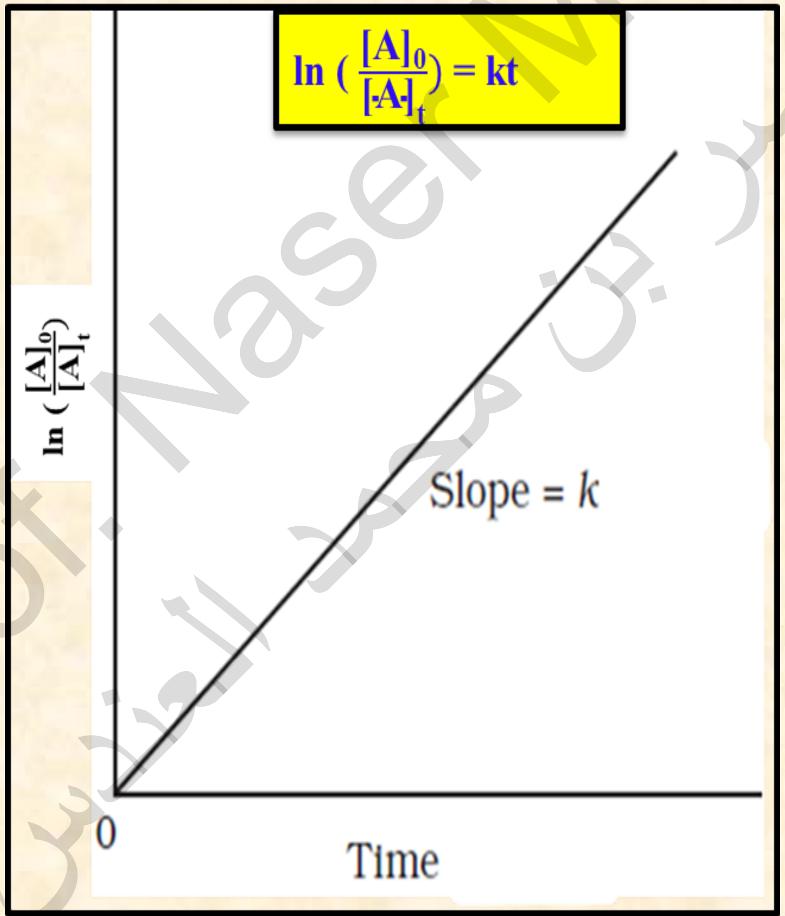
$[A]_t = [A]_0 - [B]_t$ so $[A]_0 = [A]_t + [B]_t$

$[B]_t$, at time **t**, is related to $[A]_0$ by: $[B]_t = [A]_0 - [A]_t$, $[B]_t = [A]_0 - [A]_0\, e^{-kt}$

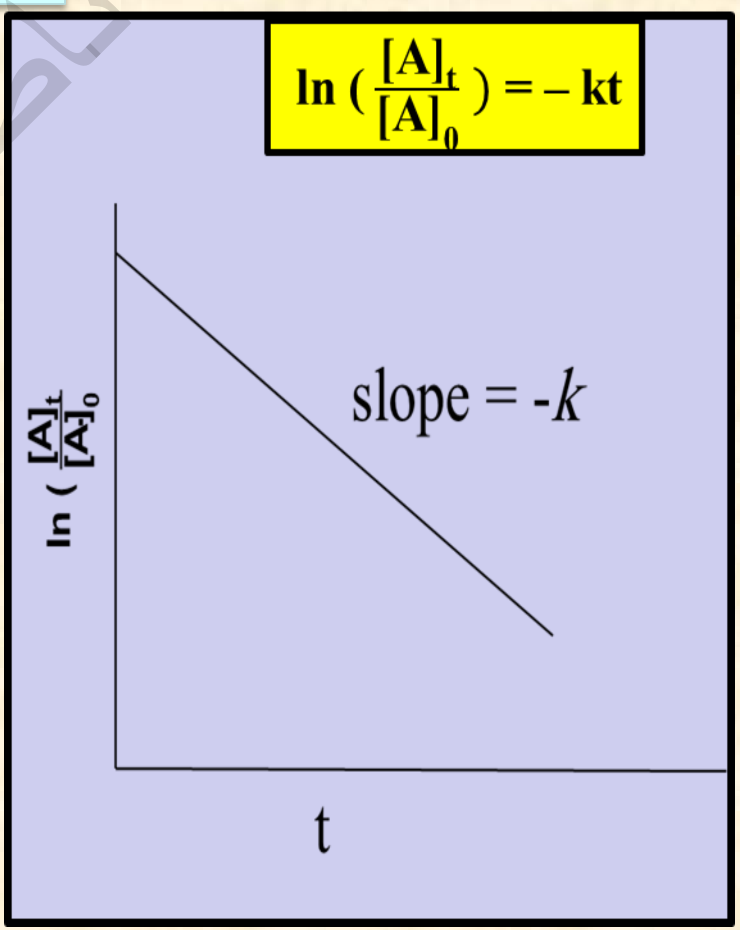
$$[B]_t = [A]_0\,(1 - e^{-kt})$$



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



$$\ln\left(\frac{[A]_0}{[A]_t}\right) = kt$$



$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt$$

First Order half-life, $t_{1/2}$

$t_{1/2}$ is the time that $[A]_t = \frac{1}{2}[A]_0$

$$\ln\left(\frac{[A]_t}{[A]_0}\right) = \quad -kt$$

at $t_{1/2}$

$$\ln\left(\frac{[A]_t}{[A]_0}\right) = \quad -kt$$

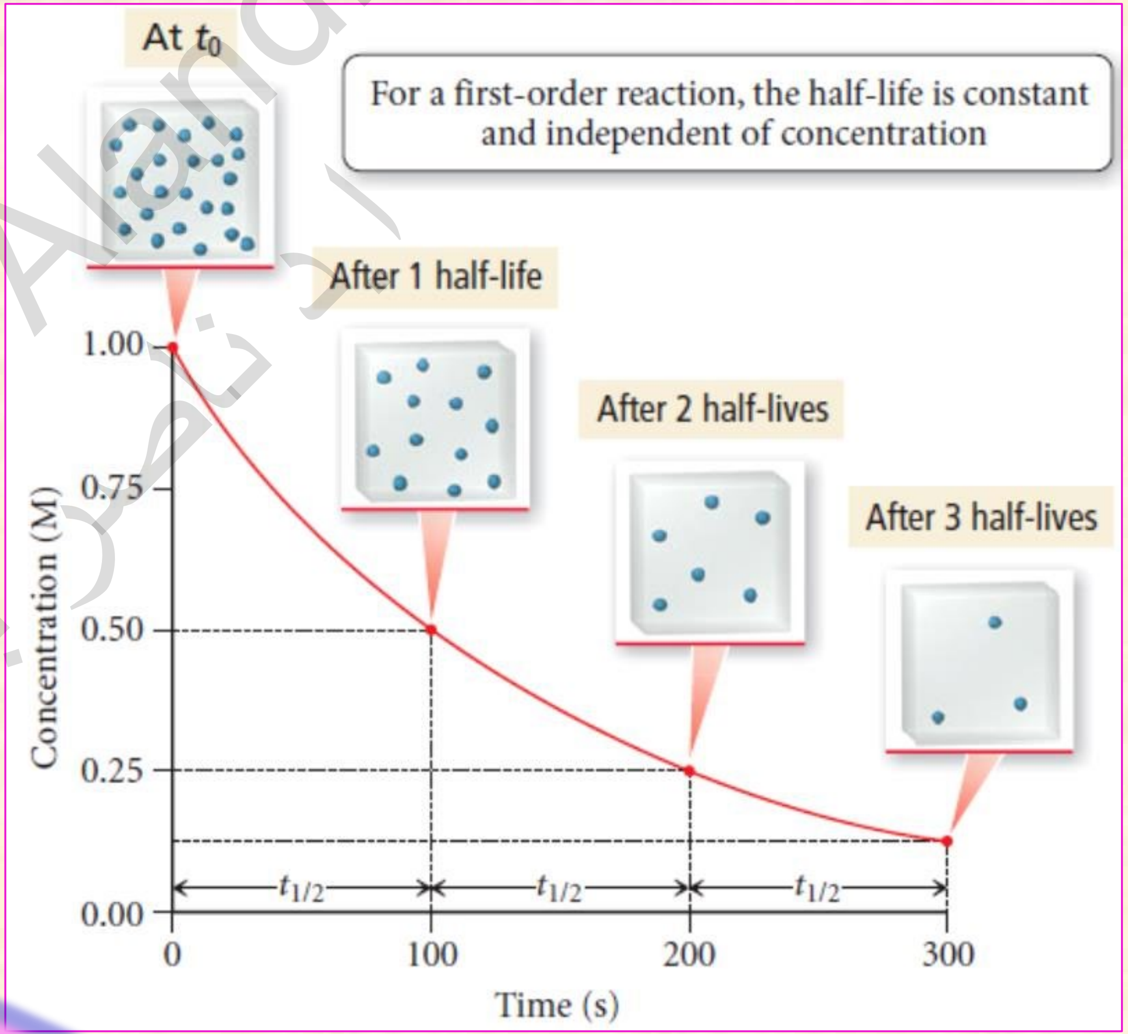
$$\ln\left(\frac{1}{2}\right) = -k\,t_{1/2}$$

$$-\ln\left(\frac{1}{2}\right) = k\,t_{1/2}$$

$$\ln 2 = \quad k\,t_{1/2}$$

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

NO EFFECT of $[A]_0$ on $t_{1/2}$



Example

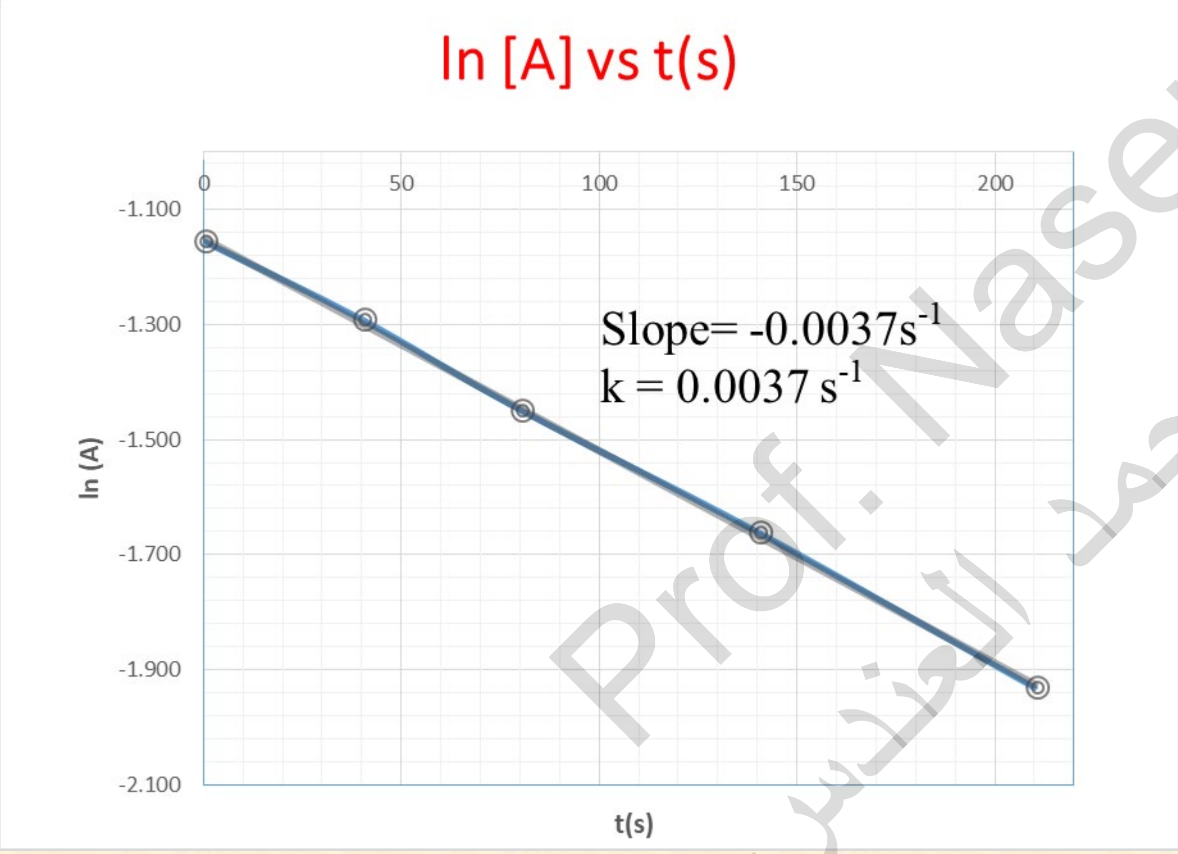
Sucrose (table sugar), $C_{12}H_{22}O_{11}$, will decompose in weakly-acidic according to the reaction :

$$C_{12}H_{22}O_{11\,(aq)} + H_2O_{\,(l)} \rightarrow 2\ C_6H_{12}O_{6\,(aq)}$$

Using the table below, what is the rate law and $t_{½}$?

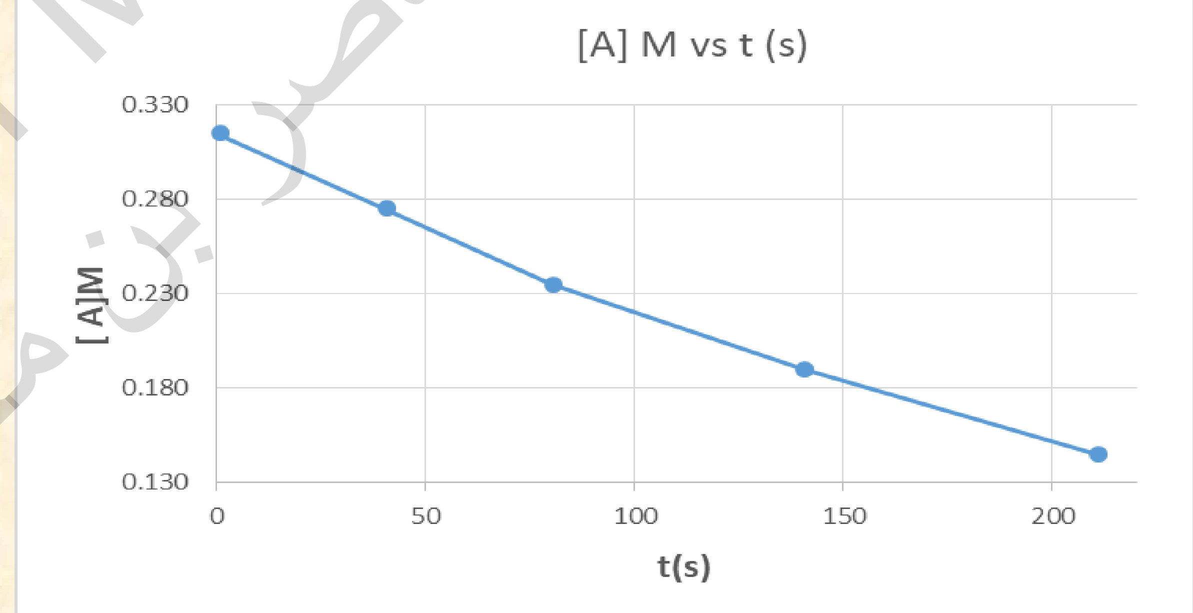
Time(s)	0	40	80	140	210
$[C_{12}H_{22}O_{11}]$ [M]	0.315	0.275	0.235	0.190	0.145

t(s)	ln[A]	[A]
0	-1.155	0.315
40	-1.291	0.275
80	-1.448	0.235
140	-1.661	0.190
210	-1.931	0.145



Slope= $-0.0037\,s^{-1}$

$k = 0.0037\ s^{-1}$



✓ Rate = = $0.0037\ s^{-1}\ [C_{12}H_{22}O_{11}]$

✓ $t_{½} = \frac{0.693}{k} = \frac{0.693}{0.0037\ s^{-1}} = 187.3\ s$

Second-Order Reactions → One Reactant

- The simplest form of a second-order reaction, as this reaction: $A + A \xrightarrow{k} B$

- The reaction rate law is described by:

$$\text{Rate} = -\frac{d[A]}{dt} = k[A]^2 \quad \text{Rearrange to} \quad \frac{d[A]}{[A]^2} = -kdt$$

- Integration from $[A]_0$ at t = 0, to $[A]_t$ at time t, results

$$\int_{A_0}^{A_t} \frac{d[A]}{[A]^2} = -\int_{o}^{t} k\, dt$$

- leads to: $\left(\frac{1}{[A]_t}\right) - \left(\frac{1}{[A]_0}\right) = kt$

- $\left(\frac{1}{[A]_t}\right) = \left(\frac{1}{[A]_0}\right) + kt$

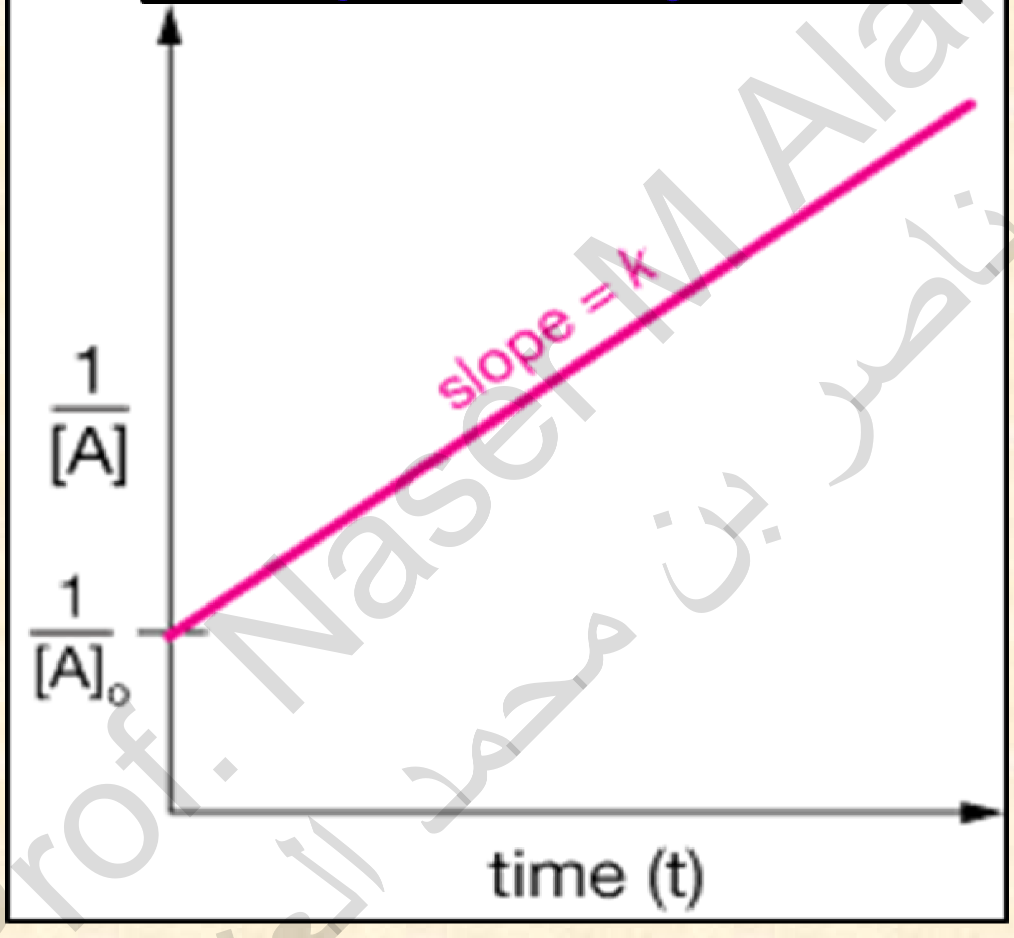
$$y = a + mx$$

- Half-time is defined by: $t_{1/2} = \frac{1}{k[A]_0}$

Note that $[A]_0$ has an effect on the value of $t_{1/2}$

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

$$\left(\frac{1}{[A]_t}\right) = \left(\frac{1}{[A]_0}\right) + kt$$



Two Reactant

$$A + B \xrightarrow{k} C$$

In case $[A]_0 = [B]_0$, the rate law will be:

$$\text{Rate} = k[A]\,[B] = k[A]\,[A] = k[A]^2$$

$$\left(\frac{1}{[A]_t}\right) = \left(\frac{1}{[A]_0}\right) + kt$$

In case $[A]_0 \neq [B]_0$, the rate law will be:

$$\text{Rate} = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k[A]\,[B]$$

Considering that $[A]_0 - [A]_t = [B]_0 - [B]_t$ and $[B]_t = [B]_0 - [A]_0 + [A]_t$

Integration gives:

$$\left(\frac{1}{[B]_0 - [A]_0}\right) \ln\left(\frac{[A]_0\,[B]_t}{[A]_t[B]_0}\right) = kt$$

OR

$$\left(\frac{1}{[B]_0 - [A]_0}\right) \ln\left(\frac{[A]_0}{[B]_0}\right) + \left(\frac{1}{[B]_0 - [A]_0}\right) \ln\left(\frac{[B]_t}{[A]_t}\right) = kt$$

ALSO

$$\left(\frac{1}{[B]_0 - [A]_0}\right) \ln\left(\frac{[B]_t}{[A]_t}\right) = kt - \left(\frac{1}{[B]_0 - [A]_0}\right) \ln\left(\frac{[A]_0}{[B]_0}\right)$$

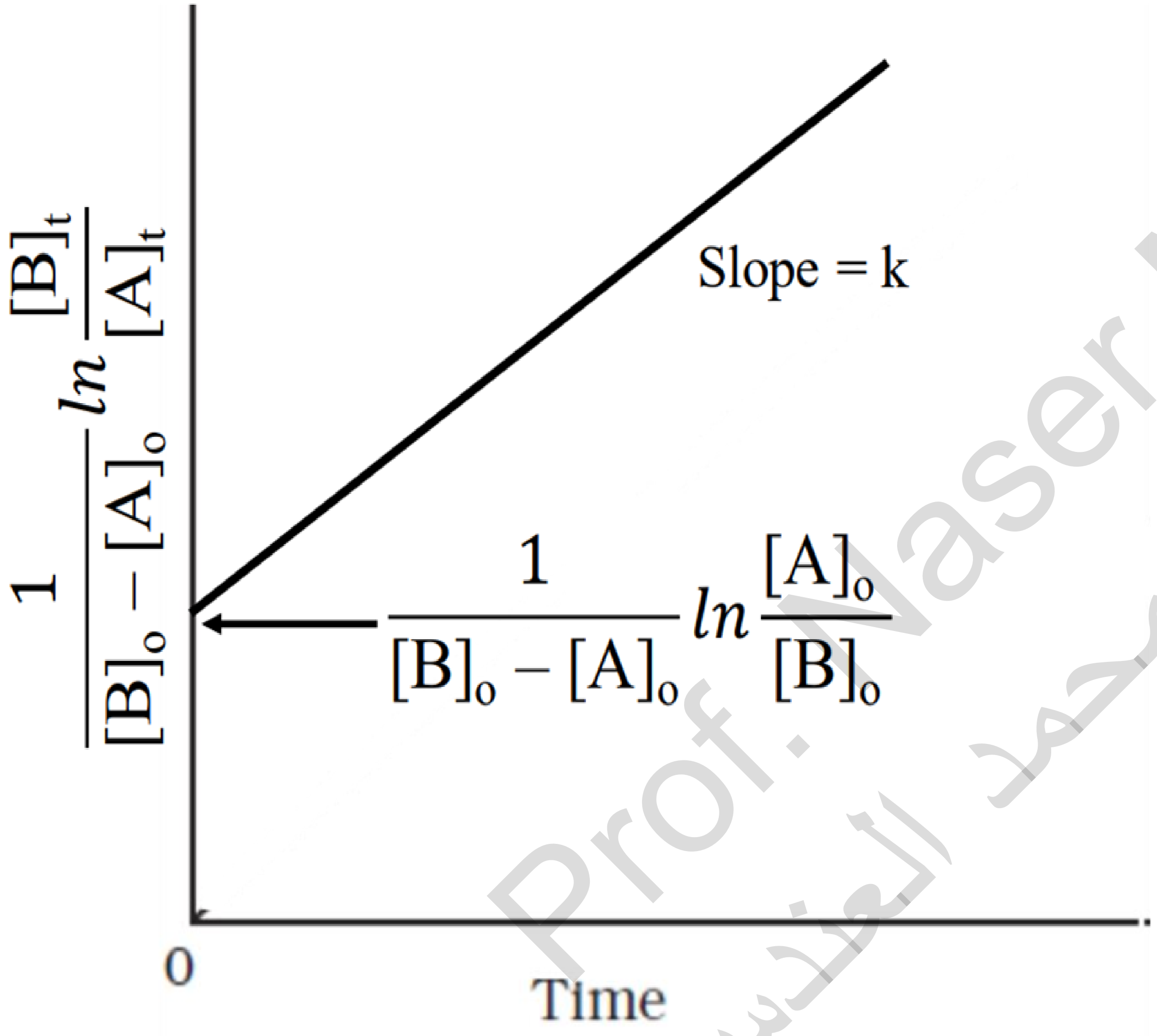
Linear form

$$\ln\left(\frac{[A]_0}{[B]_0}\right) + \ln\left(\frac{[B]_t}{[A]_t}\right) = ([B]_0 - [A]_0)kt$$

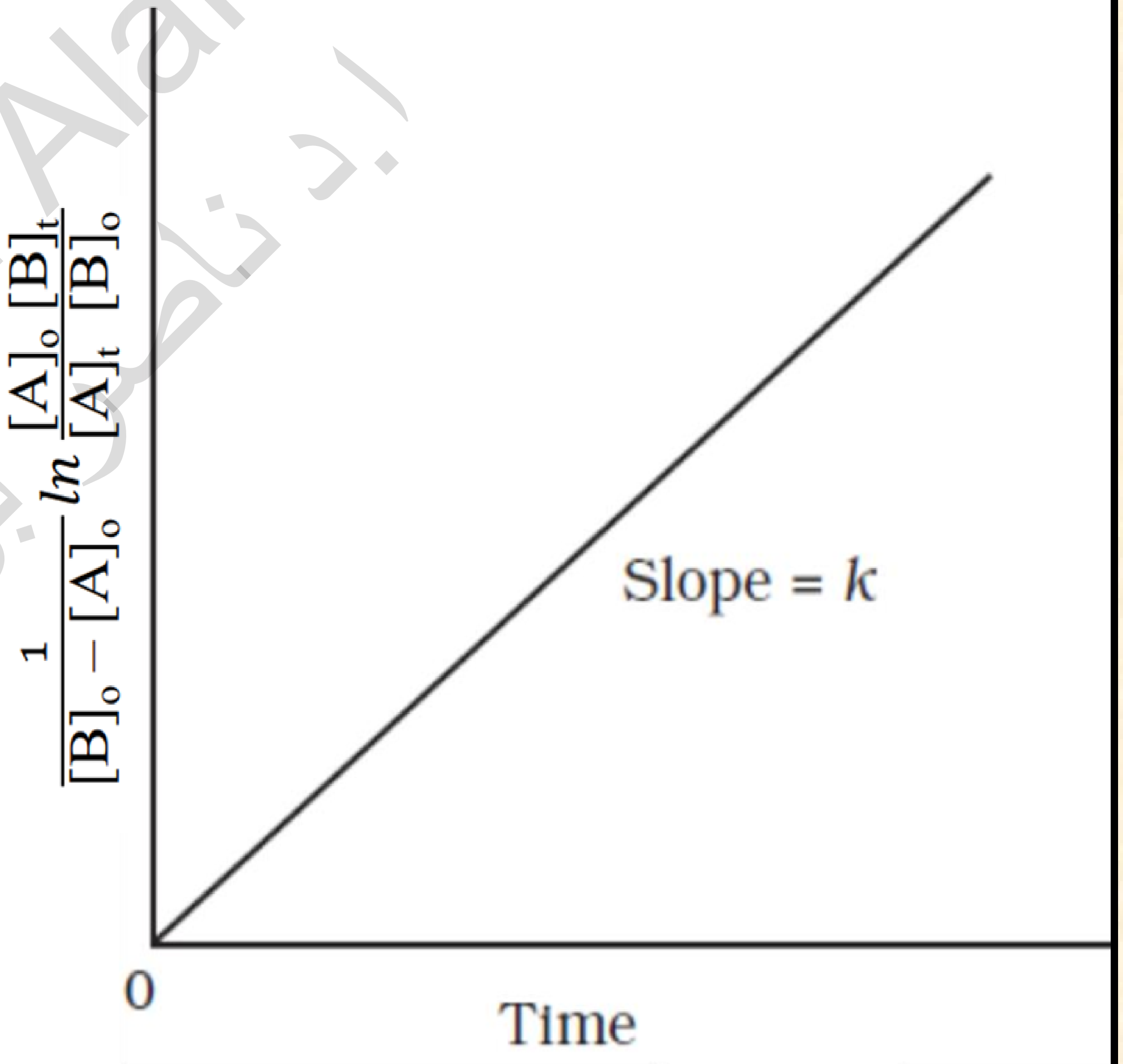
Exponential form

$$\left(\frac{[B]_t}{[A]_t}\right) = \left(\frac{[B]_0}{[A]_0}\right) e^{([B]_0 - [A]_0)\,kt}$$

$$\left(\frac{1}{[B]_0-[A]_0}\right)\ln\left(\frac{[B]_t}{[A]_t}\right) = kt - \left(\frac{1}{[B]_0-[A]_0}\right)\ln\left(\frac{[A]_0}{[B]_0}\right)$$



$$\left(\frac{1}{[B]_0-[A]_0}\right)\ln\left(\frac{[A]_0[B]_t}{[A]_t[B]_0}\right) = kt$$

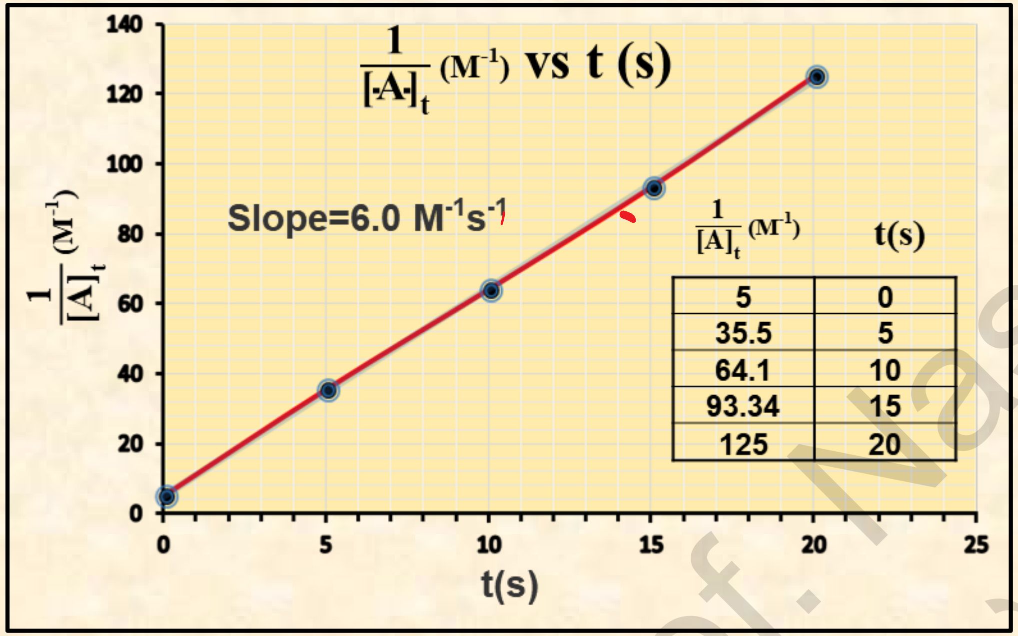


Example

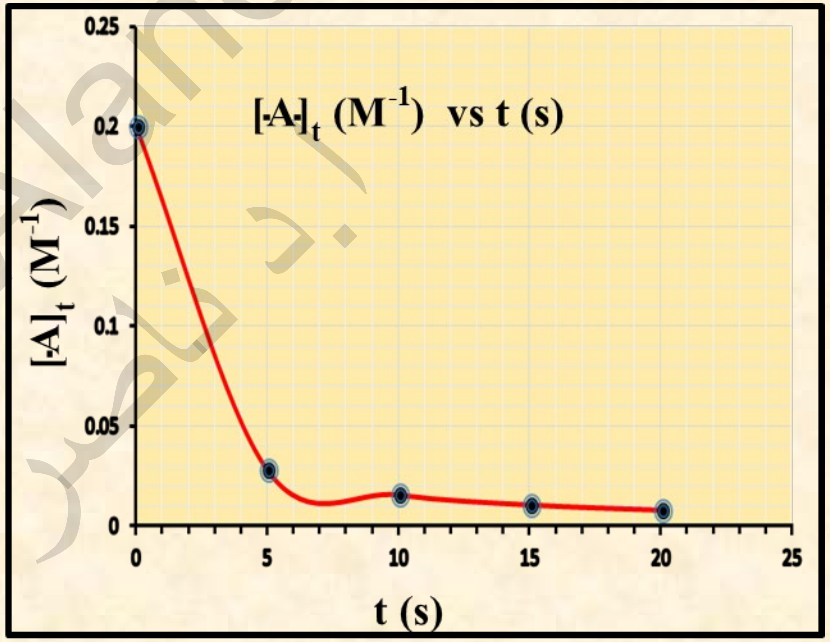
For the reaction below, find the rate law and its $t_{1/2}$ using the following data :

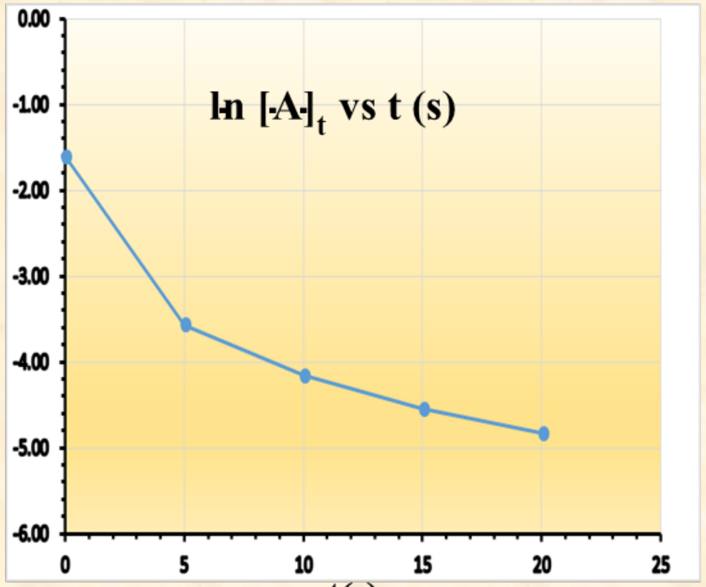
$$3A \rightarrow 2B$$

Time (s)	0	5	10	15	20
[A] M	0.2000	0.0282	0.0156	0.0106	0.008



$\frac{1}{[A]_t}$ (M^{-1})	t(s)
5	0
35.5	5
64.1	10
93.34	15
125	20





✓ $\text{Rate} = 6.0\ M^{-1}s^{-1}[A]^2$

✓ $t_{1/2} = \frac{1}{k[A]_0} = \frac{1}{6.0\ M^{-1}s^{-1}[0.200M]} = 0.8333\ s$

Third-Order Reactions

$$3A \longrightarrow \text{products}$$

$$\text{Rate} = -\frac{d[A]}{dt} = k[A]^3$$

$$\frac{d[A]}{[A]^3} = -kdt$$

Integration from $[A]_0$ at t = 0, to $[A]_t$ at time t

$$\int_{A_0}^{A_t} \frac{d[A]}{[A]^3} = -\int_{o}^{t} k\,dt$$

$$\left(\frac{1}{2[A]_t^2}\right) - \left(\frac{1}{2[A]_0^2}\right) = kt$$

$$\frac{1}{2[A]_t^2} = kt + \frac{1}{2[A]_0^2}$$

$$\frac{1}{[A]_t^2} = 2kt + \frac{1}{[A]_0^2}$$

$$\boxed{y \quad = mx + \quad a}$$

$t_{½}$

$t_{½}$ is the time that $[A]_{t\,½} = \frac{1}{2}[A]_0$

$$\frac{1}{(\frac{1}{2}[A]_0)^2} - \frac{1}{[A]_0^2} = 2kt_{½}$$

$$\frac{4}{[A]_0^2} - \frac{1}{[A]_0^2} = 2kt_{½}$$

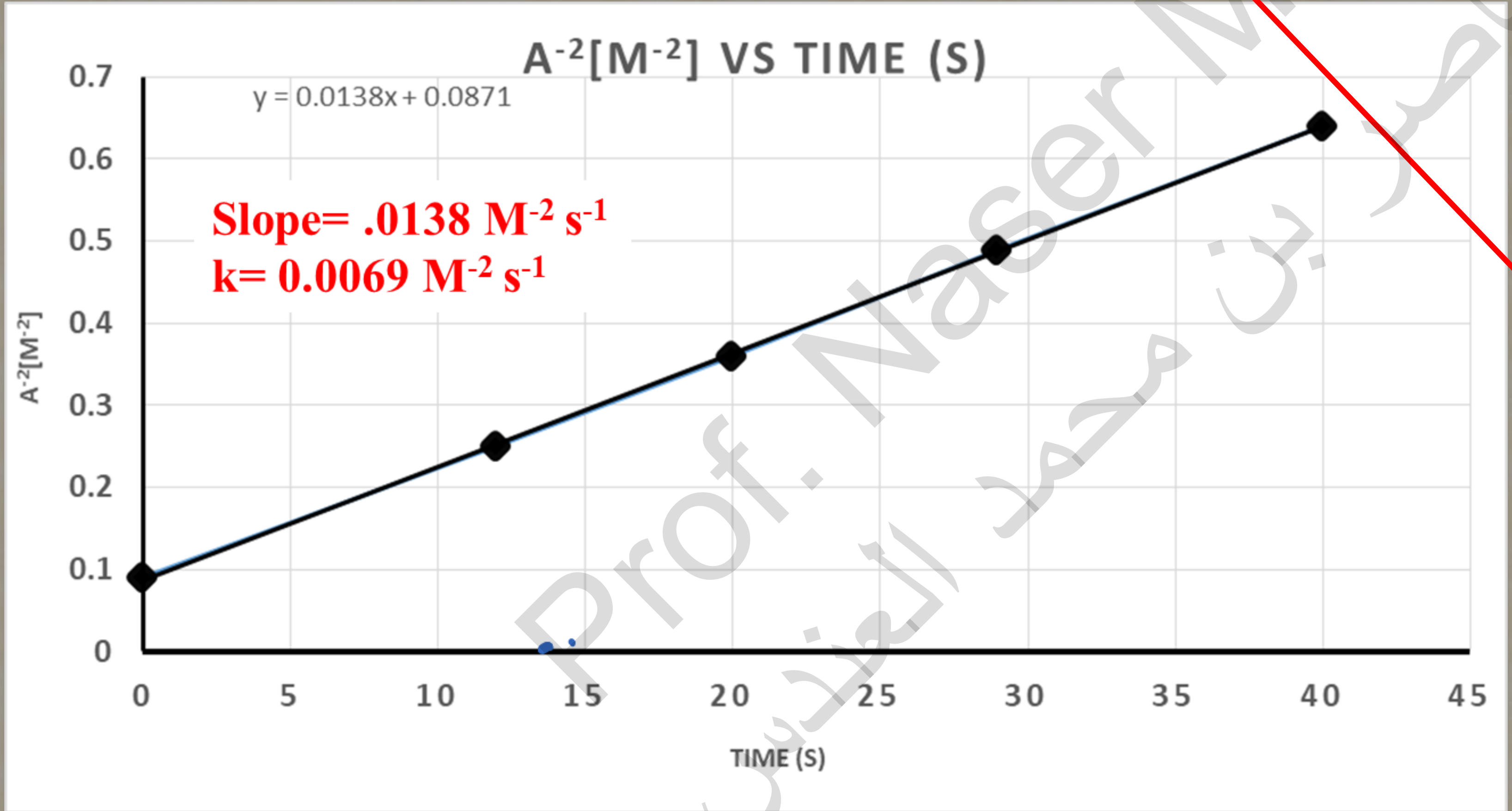
$$\frac{3}{[A]_0^2} = 2kt_{½}$$

$$\boxed{t_{½} = \frac{3}{2\,k[A]_0^2}}$$

The reaction $3A \xrightarrow{} \text{products}$ is a third order reaction. If the concentration changes with time according to the following:

t(s)	0	12	20	29	40
A[M]	**3.33**	**2.00**	**1.67**	**1.43**	**1.25**

Find the half time of the reaction graphically?



Slope= .0138 $M^{-2}\ s^{-1}$

k= 0.0069 $M^{-2}\ s^{-1}$

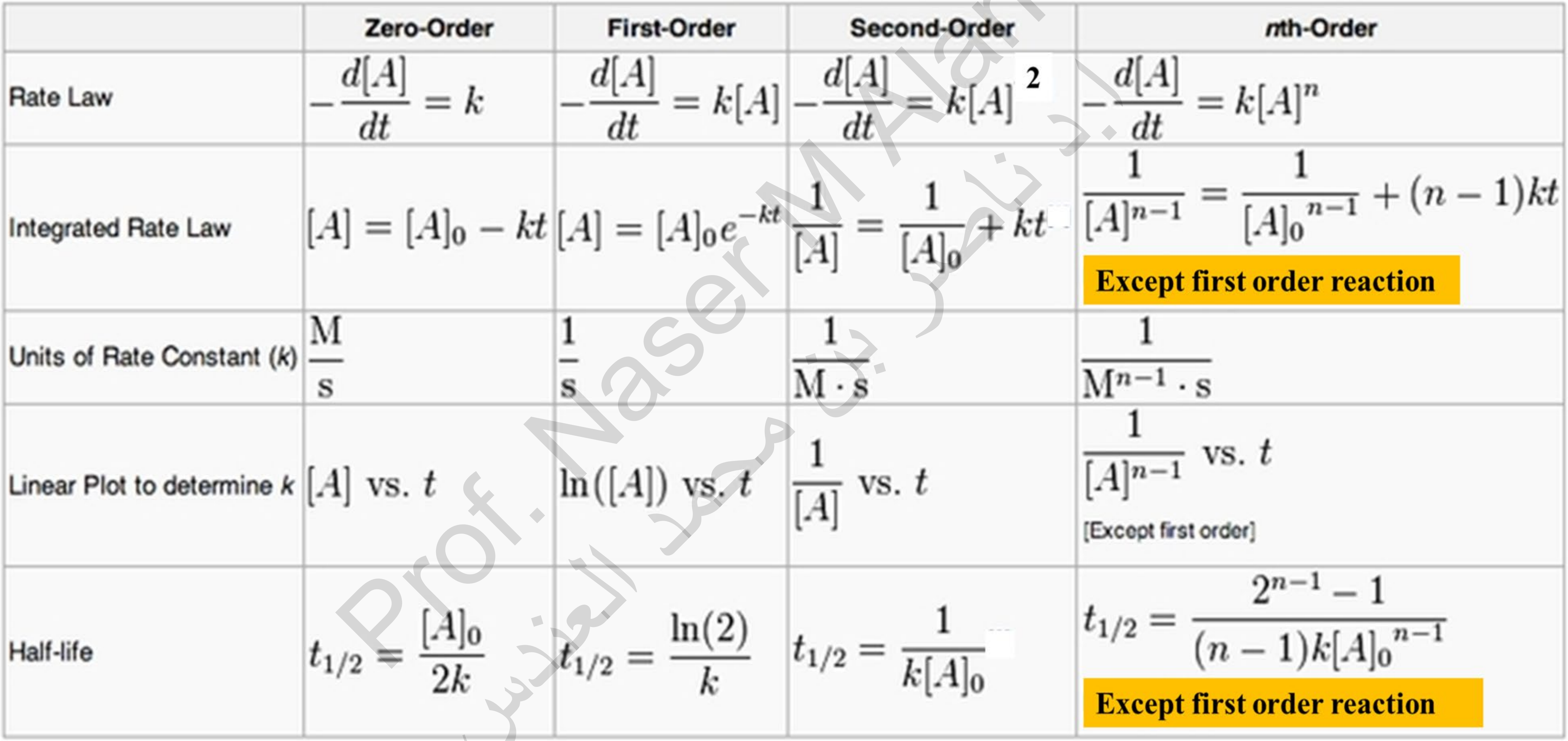
A[M]	$A^{-2}[M^{-2}]$	t(s)
3.33	0.09	0
2	0.25	12
1.67	0.36	20
1.43	0.49	29
1.25	0.64	40

$$t_{½} = \frac{3}{2\,k[A]_0^2}$$

$$= \frac{3}{(2)\ 0.069\ M^{-2}s^{-1}[3.33\ M]^2}$$

$$= 19.6\ s$$

Summary



	Zero-Order	First-Order	Second-Order	*n*th-Order
Rate Law	$-\frac{d[A]}{dt}=k$	$-\frac{d[A]}{dt}=k[A]$	$-\frac{d[A]}{dt}=k[A]^2$	$-\frac{d[A]}{dt}=k[A]^n$
Integrated Rate Law	$[A]=[A]_0-kt$	$[A]=[A]_0e^{-kt}$	$\frac{1}{[A]}=\frac{1}{[A]_0}+kt$	$\frac{1}{[A]^{n-1}}=\frac{1}{{[A]_0}^{n-1}}+(n-1)kt$ **Except first order reaction**
Units of Rate Constant (*k*)	$\frac{\mathrm{M}}{\mathrm{s}}$	$\frac{1}{\mathrm{s}}$	$\frac{1}{\mathrm{M}\cdot\mathrm{s}}$	$\frac{1}{\mathrm{M}^{n-1}\cdot\mathrm{s}}$
Linear Plot to determine *k*	$[A]$ vs. t	$\ln([A])$ vs. t	$\frac{1}{[A]}$ vs. t	$\frac{1}{[A]^{n-1}}$ vs. t [Except first order]
Half-life	$t_{1/2}=\frac{[A]_0}{2k}$	$t_{1/2}=\frac{\ln(2)}{k}$	$t_{1/2}=\frac{1}{k[A]_0}$	$t_{1/2}=\frac{2^{n-1}-1}{(n-1)k{[A]_0}^{n-1}}$ **Except first order reaction**

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CHEMICAL KINETICS

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Part 4

Half Life Method

A) Graphically

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

$$A \longrightarrow B$$

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

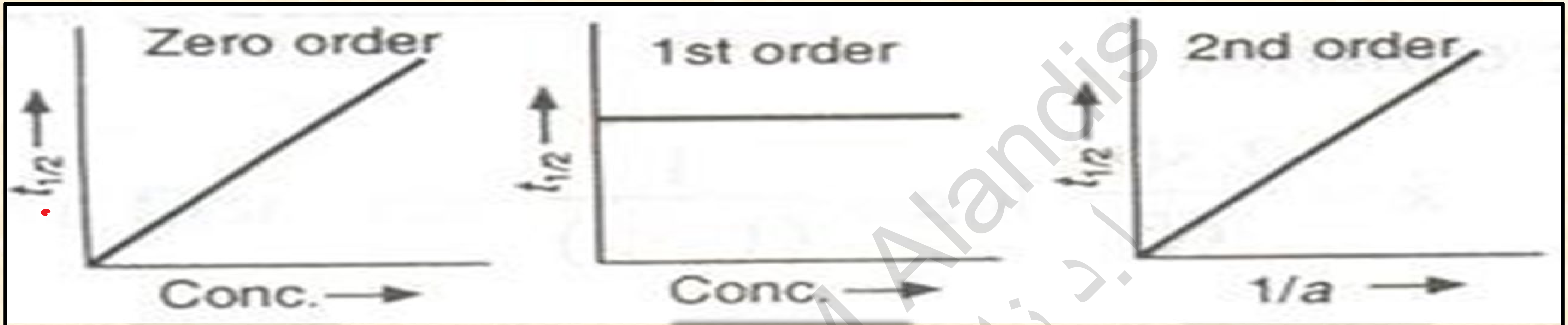
or simply $t_{(1/2)} \propto A_0^{\,1-n}$

$$t_{(1/2)} = k' A_0^{\,1-n} \qquad\qquad t_{(1/2)} = k' \frac{1}{A_0^{\,n-1}}$$

$$\ln t_{(1/2)} = \ln k' + (1-n) \ln A_0$$

[we can use(log)]

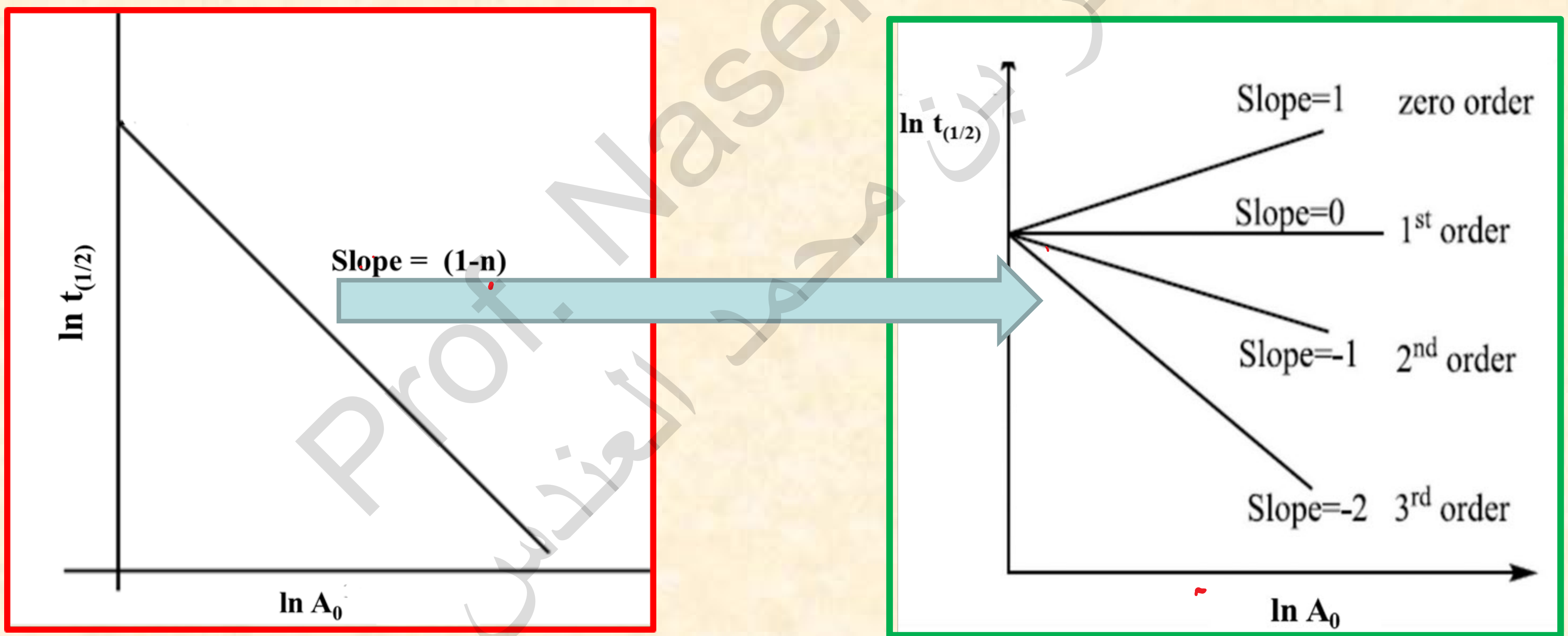
- Graph of **$\ln t_{(1/2)}$** vs **$\ln A_0$** , gives a straight line with slope **(1-n)** , where **'n'** is the order of the reaction.
- It is not valid for **first order (** ***initial concentration*** **($A_0^{\,1-n}$)** ***does not affect*** $t_{(1/2)}$ **)**
- Determining the **slope** we can find the order **n**.



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

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

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



B) Mathematically

$$\frac{(t_{(1/2)})_1}{(t_{(1/2)})_2} = \left(\frac{(A_0)_1}{(A_0)_2}\right)^{1-n}$$

$$\ln\left(\frac{(t_{(1/2)})_1}{(t_{(1/2)})_2}\right) = \ln\left(\frac{(A_0)_1}{(A_0)_2}\right)^{1-n}$$

$$\ln\left(\frac{(t_{(1/2)})_1}{(t_{(1/2)})_2}\right) = (1-n)\ln\left(\frac{(A_0)_1}{(A_0)_2}\right)$$

$$(1-n) = \frac{\ln\left(\frac{(t_{(1/2)})_1}{(t_{(1/2)})_2}\right)}{\ln\left(\frac{(A_0)_1}{(A_0)_2}\right)}$$

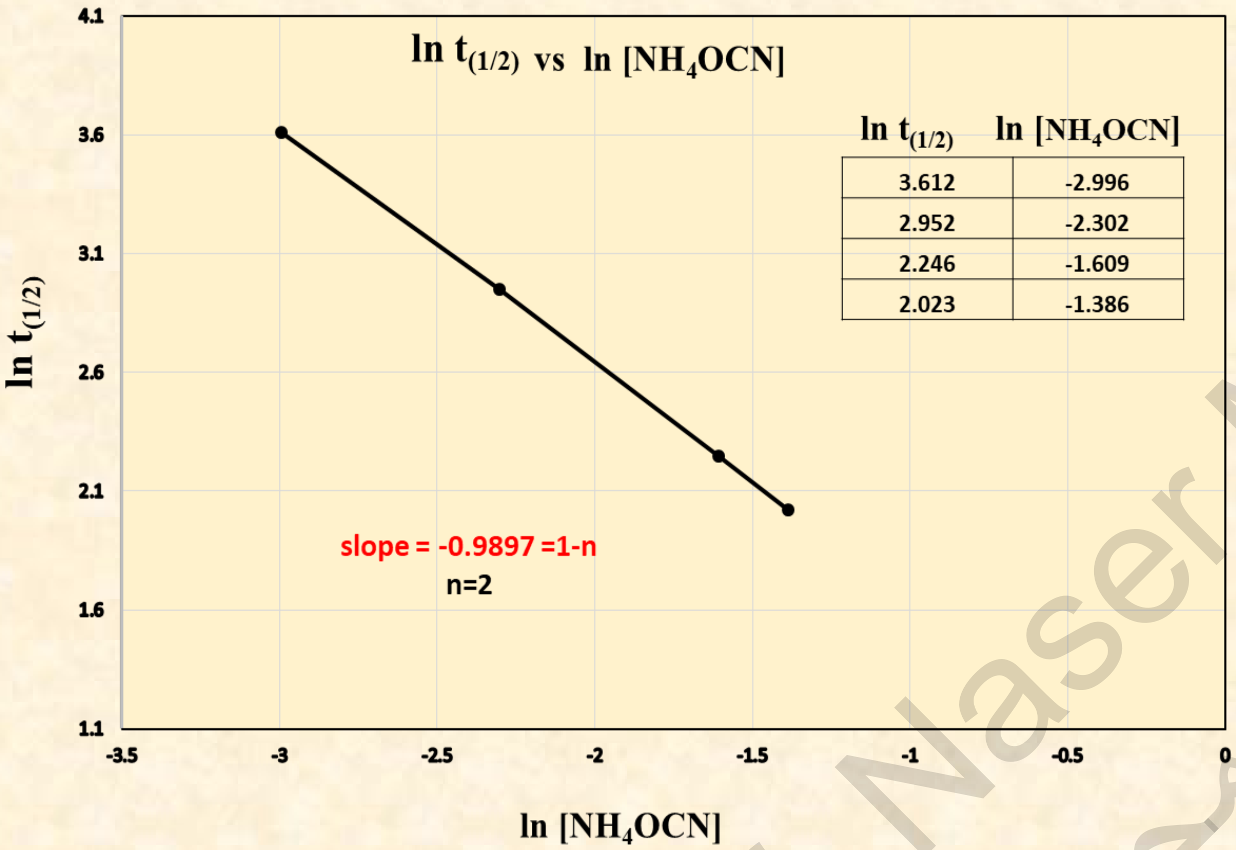
$$n = 1 - \frac{\ln\left(\frac{(t_{(1/2)})_1}{(t_{(1/2)})_2}\right)}{\ln\left(\frac{(A_0)_1}{(A_0)_2}\right)}$$

$(1-n)$ OR $(n-1)$

Example: For the following reaction: $NH_4OCN \longrightarrow CO(NH_4)_2$ the half time changes with the initial concentration of the reactant according to the following table:

$[NH_4OCN]$ (M)	0.05	0.10	0.20	0.25
$t_{(1/2)}$ (h)	37.03	19.15	9.450	7.560

Find the order of the reaction graphically then prove it mathematically and calculate k?



ln $t_{(1/2)}$	ln [NH_4OCN]
3.612	-2.996
2.952	-2.302
2.246	-1.609
2.023	-1.386

- The slope =(1-n) = -0.9897
- n = 2
- **The reaction is a second order**

Mathematically

$$n = 1 - \frac{\ln\left(\frac{t_{(1/2)})_1}{t_{(1/2)})_2}\right)}{\ln\left(\frac{(A_0)_1}{(A_0)_2}\right)}$$

$$= 1 - \frac{\ln\left(\frac{37.03}{9.450}\right)}{\ln\left(\frac{0.05}{0.20}\right)} = 1 - \frac{1.366}{1.386} = 1-(-0.985)=2$$

$$t_{½} = \frac{1}{k[A]_0} =$$

$$k = \frac{1}{t_{½}[A]_0}$$

$$\frac{1}{9.450\ h\ [0.200M]} = 0.5291\ M^{-1}h^{-1}$$

Isolation (Flooding)Method

- In this method all the reactants are taken in very large excess except one.
- the order of the reaction is determined one of the previous methods.
- The concentrations of the substances taken in excess are considered to be constant.
- The experiment is repeated for the other reactants to find their orders.
- The sum of the orders, obtained by the process of isolation of each reactant is the order of the reaction.
- The order is called "*pseudo order*".

Consider this reaction : $A + B \xrightarrow{k} C + D$

$$Rate = k[A]^n[B]^m$$

- To isolate **B** we take **[B] ⪢⪢ [A].** Minimum 20 times but preferably between 50-100 times.
- The Rate becomes **Rate = k' [A]**^{n} where **k' = k** $[B]^m$
- Find n and **k'** by applying the integration method .
- To find **m** we repeat the experiment by flooding the system with **B** using another high concentration of **B**.
- Find the new **k' .**
- To find **m** we compare **k'** in both experiments .Apply $\frac{(k')_1}{(k')_2} = \left(\frac{(B)_1}{(B)_2}\right)^m$ and find the order using logarithms.
- Calculate k using **k' = k** $[B]^m$
- $k = \frac{k'}{[B]^m}$
- Orders found called ***pseudo orders***

The hydrolysis of ester is a first pseudo order reaction on both reactants according to this equation:

$$\textbf{Ester} + \textbf{H}_2\textbf{O} \xrightarrow{\textbf{k}} \textbf{Products}$$

The table below show the change of ester concentration with time.

t (s)	0	30	60	90
[ester]	0.8500	0.8004	0.7538	0.7096

Rate =k [ester] [H_2O] **[H_2O] ⋙[ester]**

at 25 °C [H_2O]= 55 M

The Rate becomes **Rate = k' [A]**

first order equation $\ln \left(\frac{[A]_0}{[A]_t} \right) = kt$

$$k' = \frac{\ln \left(\frac{[A]_0}{[A]_t} \right)}{t} = \frac{\ln \left(\frac{0.8500}{0.8004} \right)}{30\ s} = 2.004\text{x}10^{-3}\ s^{-1}$$

$$k' = k\ [H_2O]$$

$$k = \frac{k'}{[H_2O]} = \frac{2.004\text{x}10{-}3\ s^{-1}}{55\ M} = 3.64\text{x}10^{-5}\ M^{-1}\ s^{-1}$$

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CHEMICAL KINETICS

3 credits (**2** lectures + **1** lab)

Part 5

An agama lizard lies in the sun. As its body warms, the chemical reactions of its metabolism speed up.

Temperature and The Reaction Rate

- Rate of chemical reactions are highly sensitive to temperature
- The order of the reaction usually does not change with temperature
- For many reactions, an increase of 10 °C will double the rate.
- Where does the temperature dependence of kinetics (rate) come from? → Rate $=k[A]^n$

The Answer

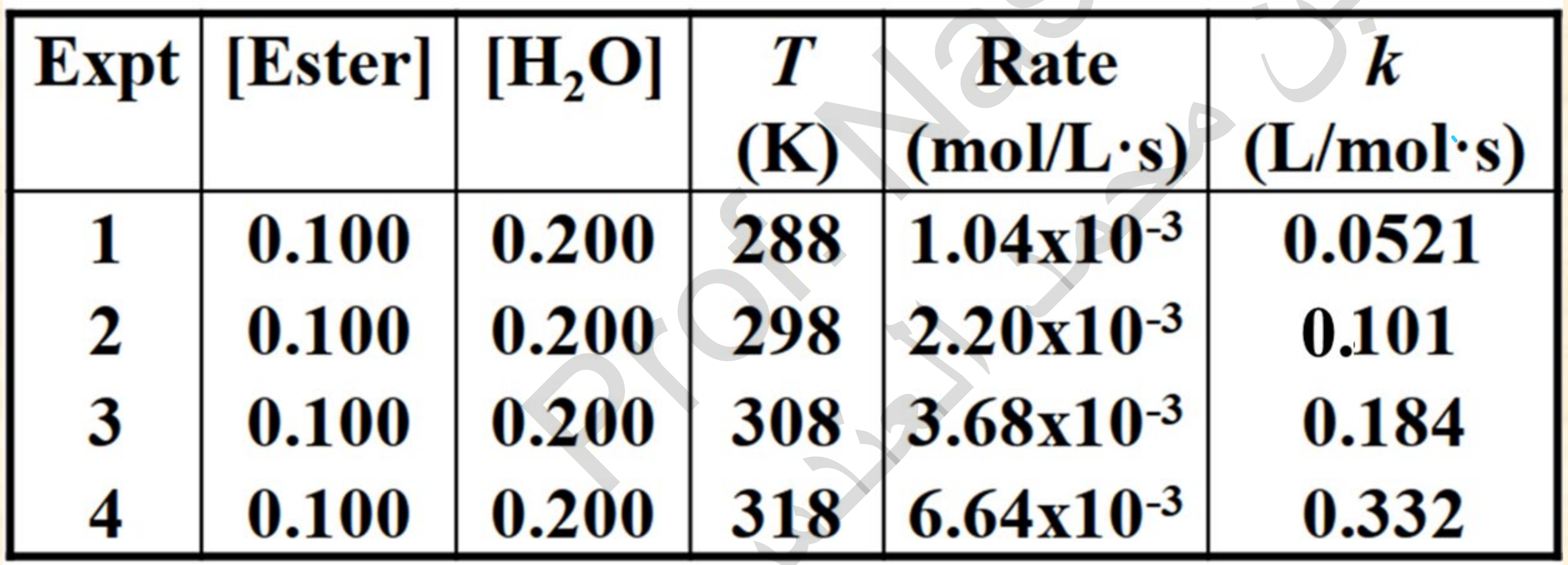
- ❑ Temperature dependence hides in the rate constant **(k)**
- ❑ Actually **k** is ***constant*** only when the **temperature** is ***constant.***

- Experimental data shows that **k** increases exponentially as **T** increases.
- This is expressed in the *Arrhenius equation*:

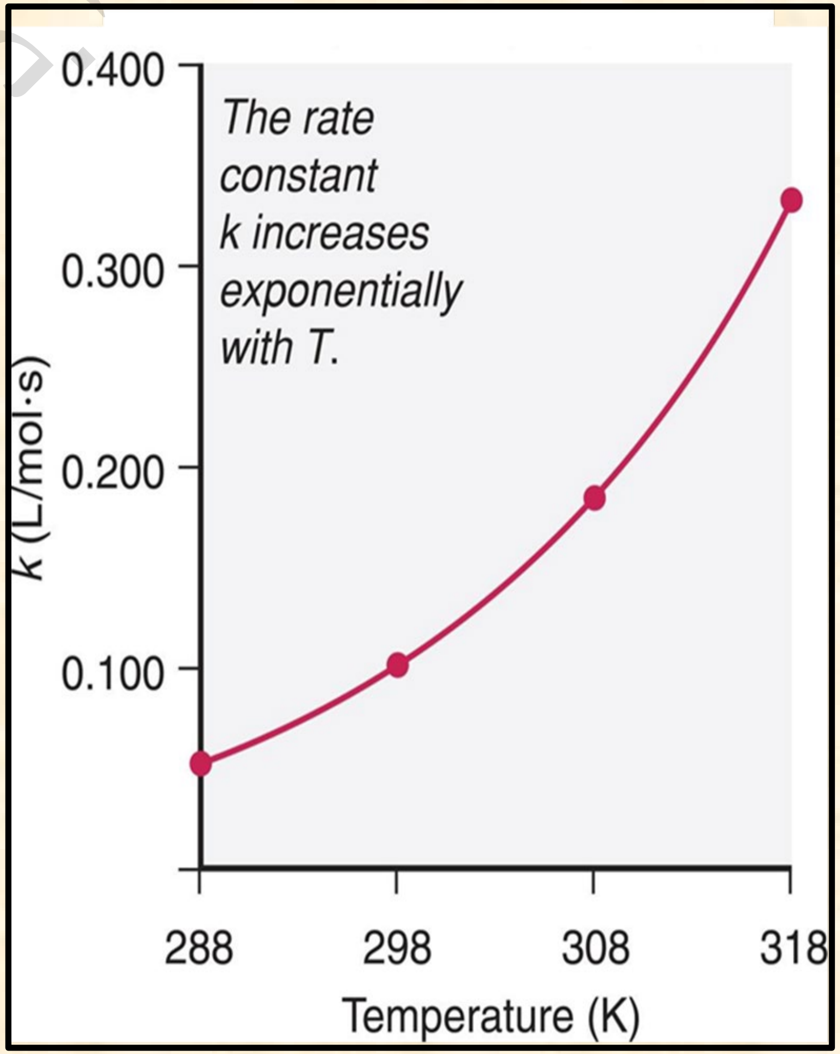
$$k = A\,e^{-Ea/RT}$$

k = rate constant **A** = frequency factor **Ea** = activation energy

Higher T **Leads to** **Larger k** **Leads to** **Increased Rate**



Expt	[Ester]	[H_2O]	*T* (K)	Rate (mol/L·s)	*k* (L/mol·s)
1	0.100	0.200	288	1.04×10^{-3}	0.0521
2	0.100	0.200	298	2.20×10^{-3}	0.101
3	0.100	0.200	308	3.68×10^{-3}	0.184
4	0.100	0.200	318	6.64×10^{-3}	0.332



The rate constant k increases exponentially with T.

Arrhenius equation

$$k = A\, e^{-E_a/RT}$$

- It was first proposed by Dutch chemist, **J.H. van't Hoff** but Swedish chemist, **Arrhenius** provided its physical justification and interpretation.

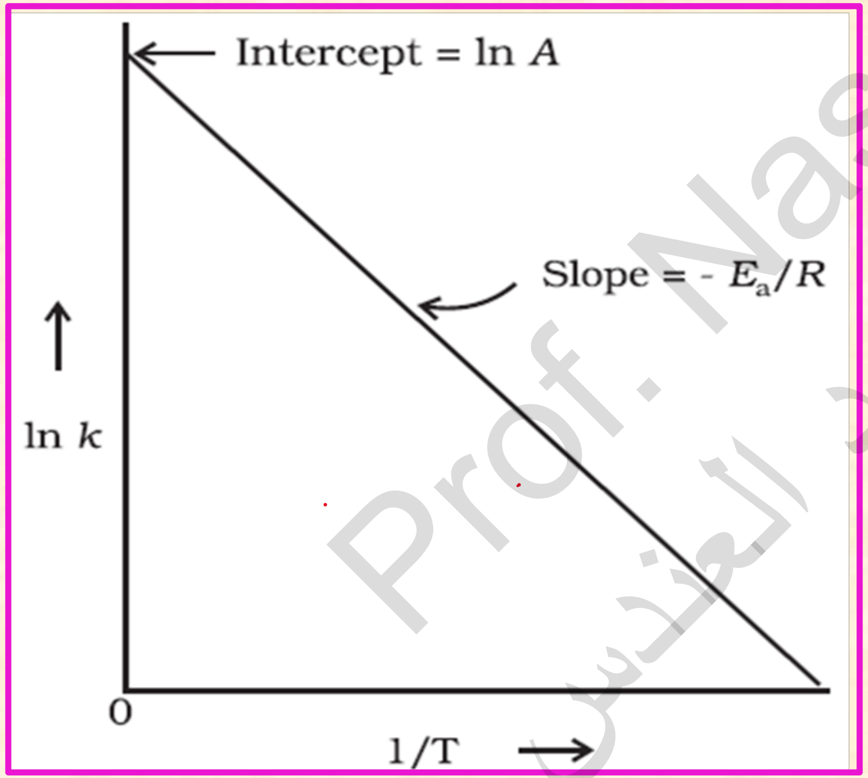
E_a is activation energy measured in $\mathbf{J\ mol^{-1}}$ and $\mathbf{R = 8.314\ J\ K^{-1}\ mol^{-1}}$

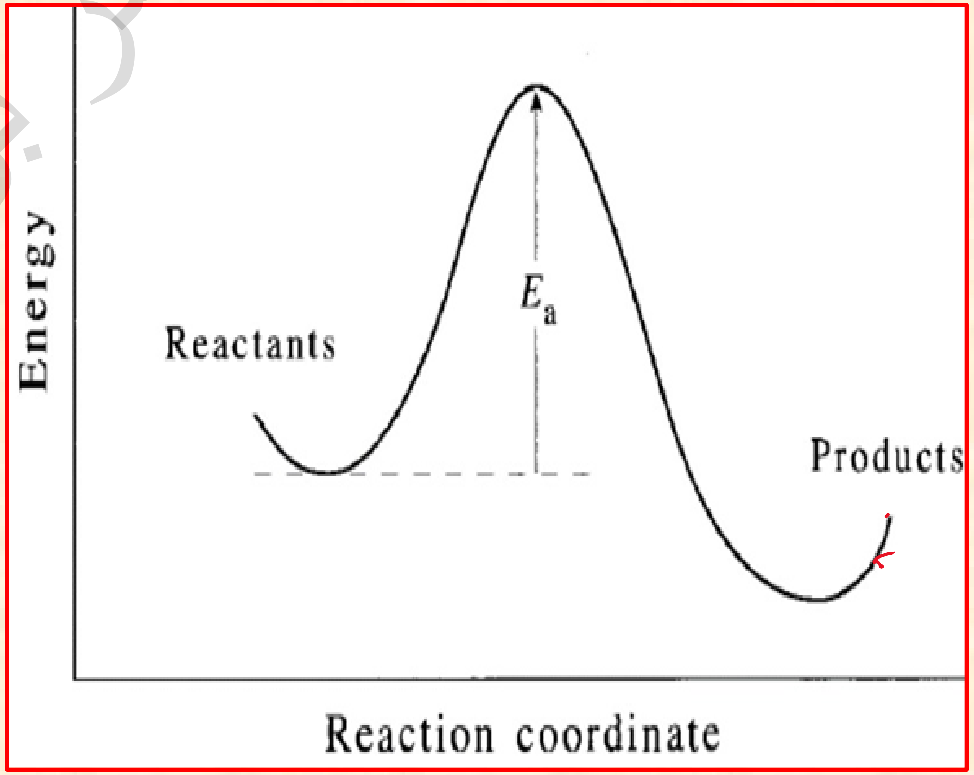
- Plot of **ln k** vs **1/T**

$$\ln k = -\frac{E_a}{R}\,\frac{1}{T} + \ln A$$

Slope = $-E_a/R$

intercept = $\ln A$





At T_2 $\ln k_2 = -\frac{E_a}{R}\frac{1}{T_2} + \ln A$ *and at* T_1 $\ln k_1 = -\frac{E_a}{R}\frac{1}{T_1} + \ln A$

Subtracting the second equation from the first equation

$$\ln k_2 - \ln k_1 = [-\frac{E_a}{R}\frac{1}{T_2} + \ln A] - [-\frac{E_a}{R}\frac{1}{T_1} + \ln A]$$

$$\boxed{\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]}$$

Example : A particular reaction has a rate constant of k= 2.3×10^{-3} at 20 ºC, and 4.3×10^{-2} at 90 ºC. What is the activation energy of the reaction?

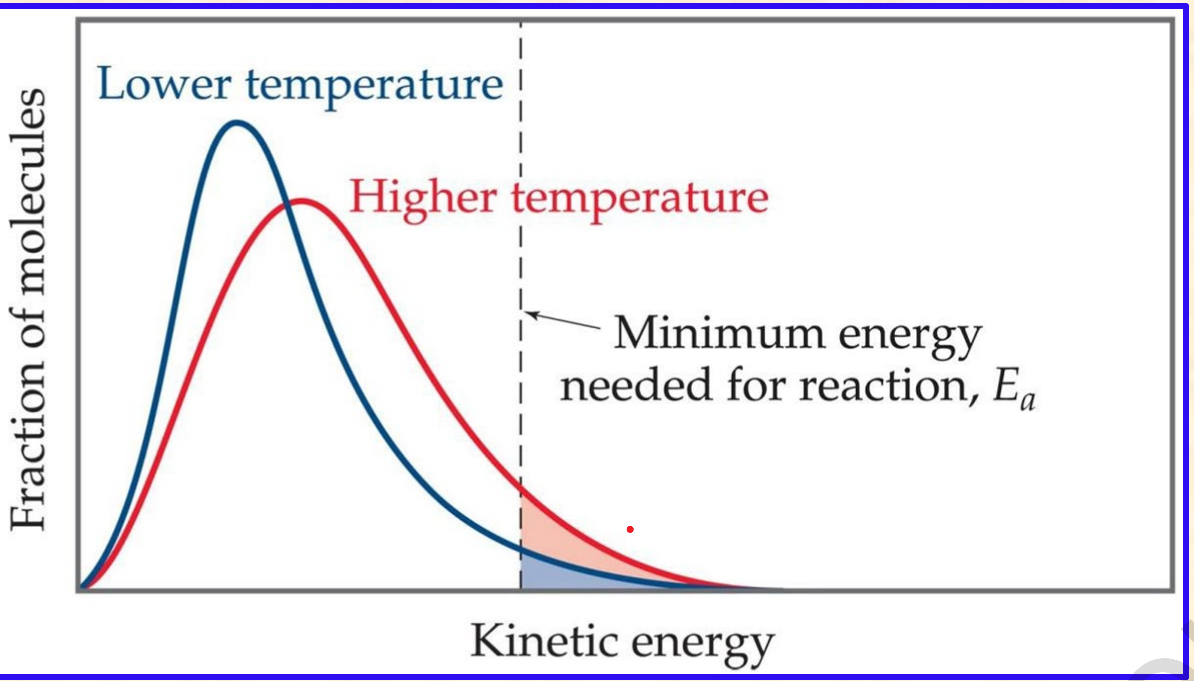
Answer

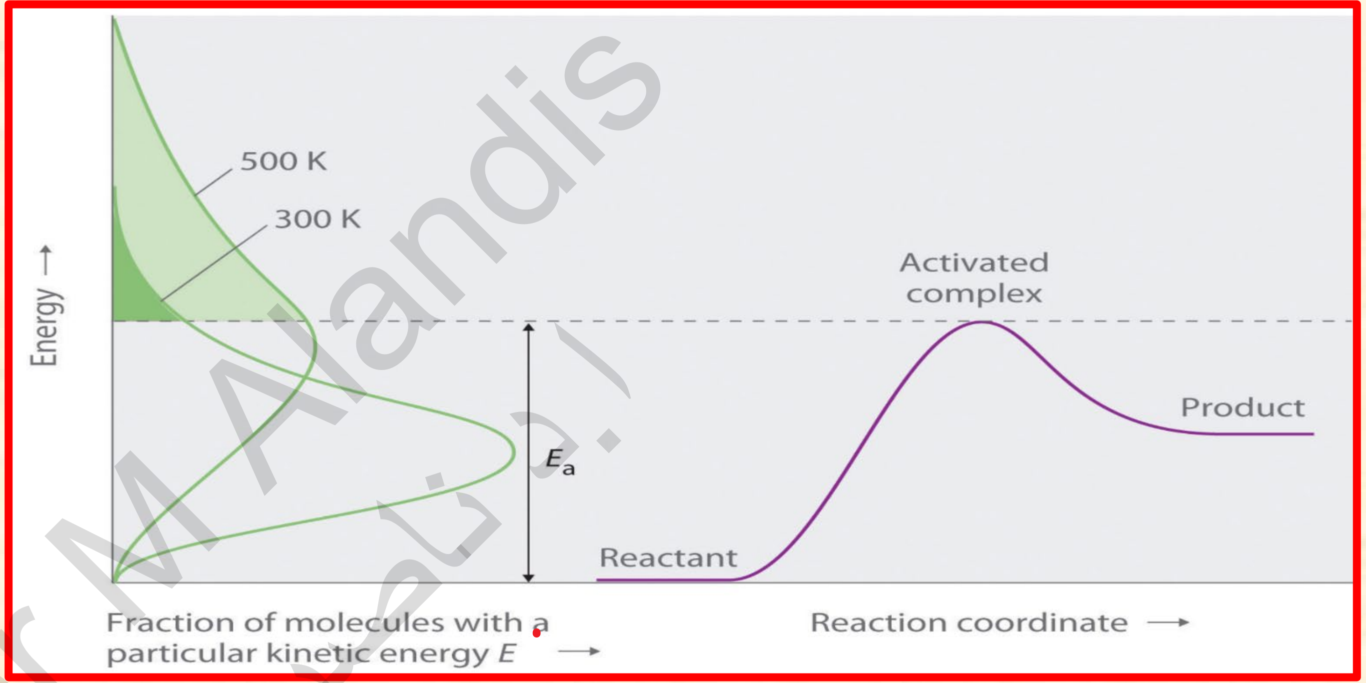
T_1= 293K , T_2= 363K , $k_1 = 2.3 \times 10^{-3}$, $k_2 = 4.3 \times 10^{-2}$

$$\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \Longrightarrow \ln\left(\frac{4.3 \times 10^{-2}}{2.3 \times 10^{-3}}\right) = \frac{E_a}{R}\left[\frac{1}{293\ \text{K}} - \frac{1}{363\ \text{K}}\right]$$

$$2.928 = \frac{E_a}{R}[\,6.581 \times 10^{-4}\ \text{K}^{-1}\,] \Longrightarrow \frac{E_a}{R} = 4.\,449\ \text{x}103\text{K}$$

$$E_a = (\,8.314\ \text{J K}^{-1}\ \text{mol}^{-1}\,)\,(4.\,449\ \text{x}103\ \text{K}\,) = 3.6990 \times 10^{4}\ \text{J mol}^{-1} \qquad = 37\ \text{kJ mol}^{-1}$$





- At any temperature there is a wide distribution of kinetic energies.
- As the temperature increases, the curve flattens and broadens.
- Thus at higher temperatures, a larger population of molecules has higher energy.
- If the dotted line represents the activation energy, as the temperature increases, so does the fraction of molecules that can overcome the activation energy barrier.
- This fraction of molecules can be found through the expression: The **exponential factor**

$$f = e^{-Ea/RT}$$

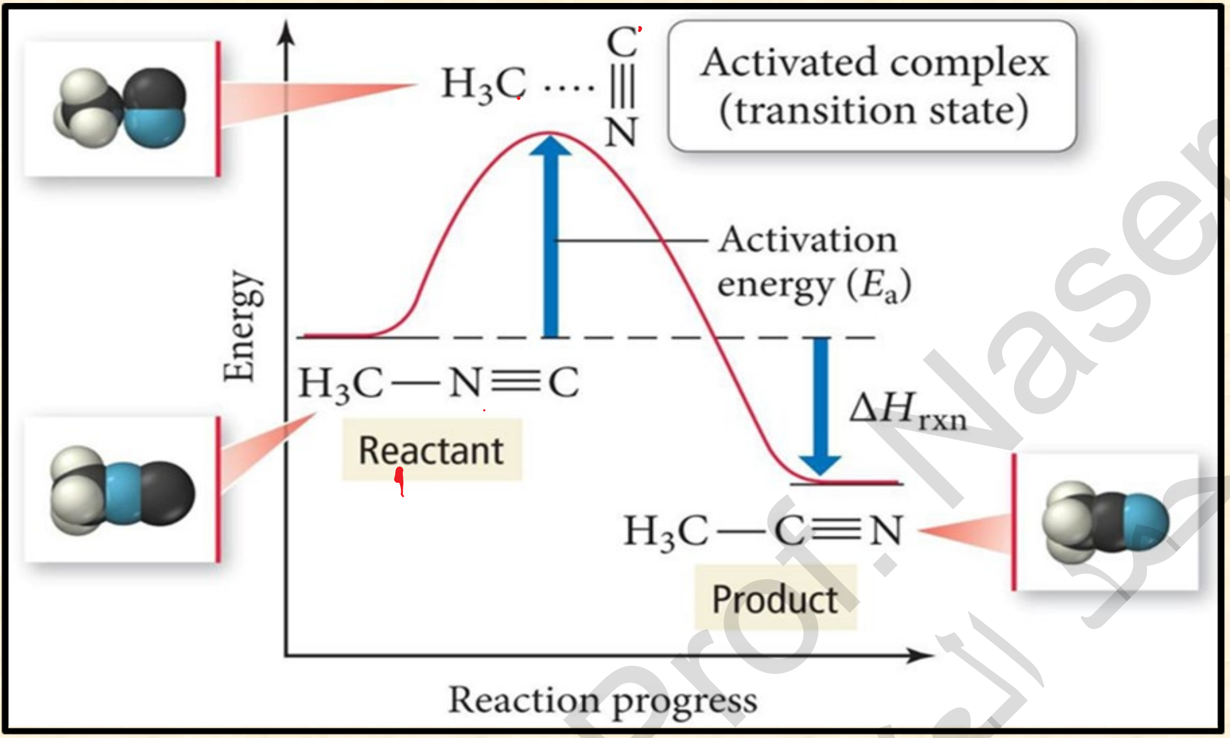
$$k = A\, e^{-E_a/RT}$$

- **A** is the frequency factor or *"pre-exponential factor"*
- $f = e^{-E_a/RT}$ is the "*exponential factor"*
- E_a is the activation energy *"activation barrier"*

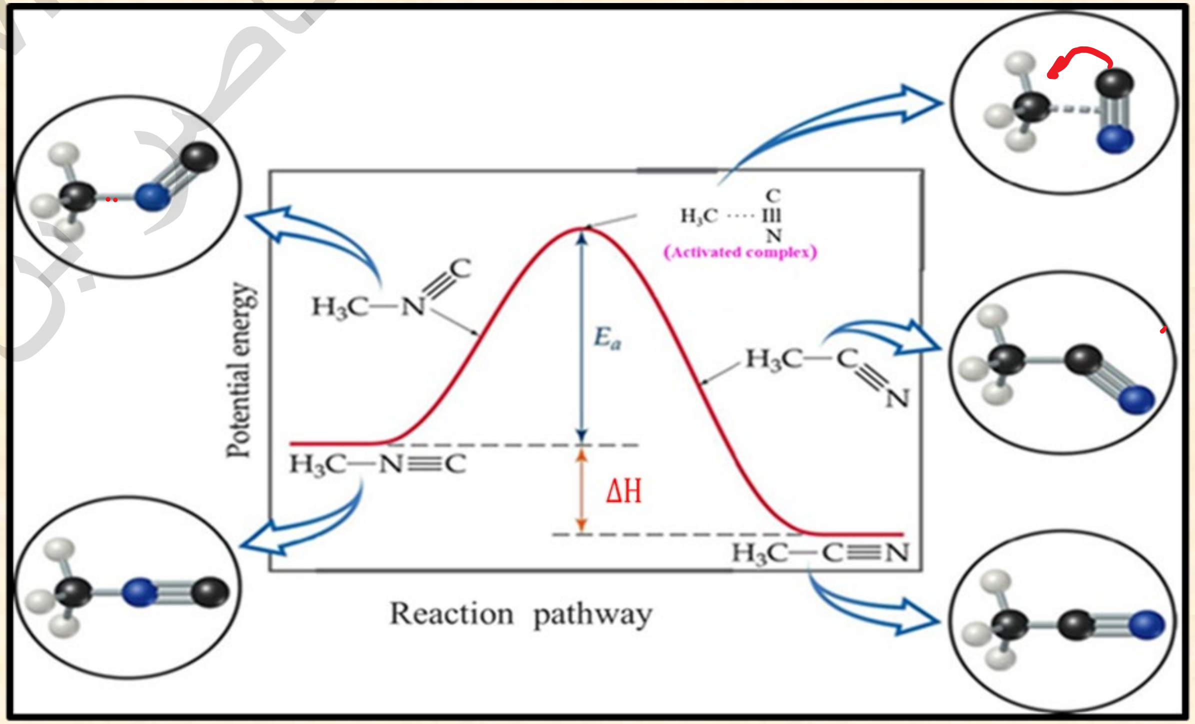
❖ How these three affected k in this reaction

$CH_3{-}N{\equiv}C \longrightarrow CH_3{-}C{\equiv}N$

Methyl isonitrile **acetontrile**

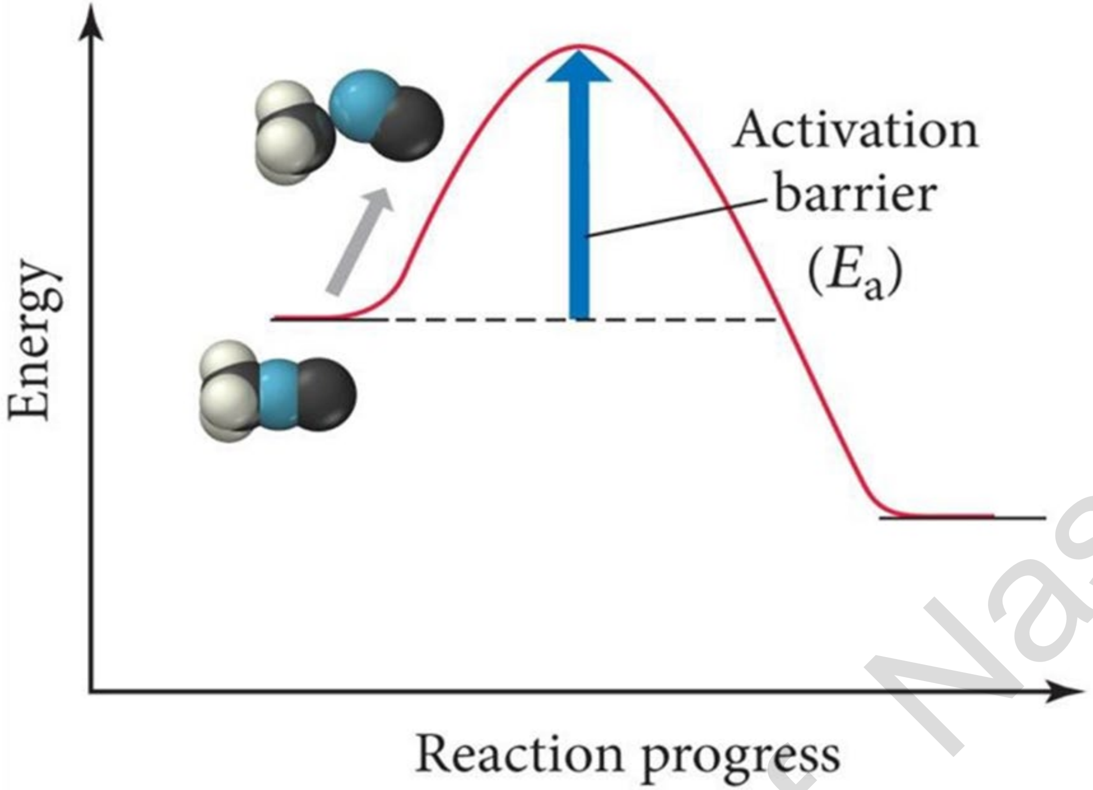


E_a is the energy required to destabilize the reactant (weaken the **C-N bond**) and allow the product to begin to form.



Reaction Coordinate Diagrams

Each wag is an approach to the activation barrier.



Frequency factor **(A)** or pre-exponential factor represents ***the number of approaches to the activation barrier.***

- ❖ The exponential factor depends on both temperature **(T)** an **(E_a).**
- ❖ Is a number between **0 and 1**
- ❖ High **T** and low **E_a** means high exponential factor Which lead to:
  - larger value of **k** = Higher reaction rate
  - More of successful hops over the barrier per approach

Concept Check

- ✓ Two reactions A and B
- ✓ They have identical frequency factors (A)
- ✓ Reaction B has a higher activation energy than reaction A.
- ✓ Which reaction has a higher rate constant and why?

Example: Using the data in the table below, prepare an Arrhenius plot and determine

1) E_a and frequency factor for the reaction.

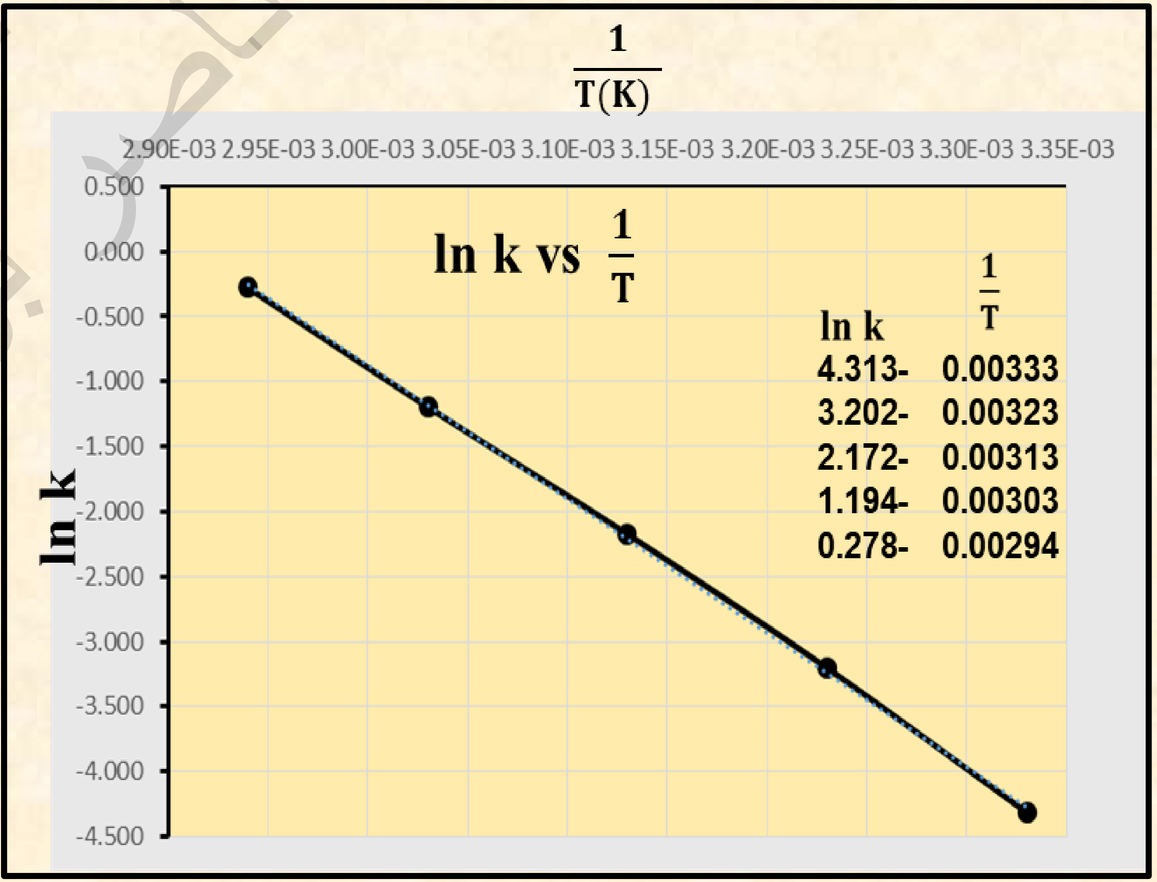
2) What is the value of the rate constant for the previous reaction at 17 °C.

Remember that we can also use a two point form of the Arrhenius equation.

Temperature (K)	k (s^{-1})
300	0.0134
310	0.0407
320	0.114
330	0.303
340	0.757

Slope = -10286 = $-E_a/R$
intercept = 29.98= ln A

$A = e^{29.98} = 1.05 \times 10^{13}\ s^{-1}$



ln k	$\frac{1}{T}$
4.313-	0.00333
3.202-	0.00323
2.172-	0.00313
1.194-	0.00303
0.278-	0.00294

E_a= -(-10286 K)(8.314 J K^{-1} mol^{-1}) = 85518J =85.5 kJ

$$\ln k = -\frac{E_a}{R}\frac{1}{T} + \ln A = -10286\text{ K}\left(\frac{1}{290\text{ K}}\right) + 29.98 = -5.489$$

k= $4.13 \times 10^{-3}\ s^{-1}$

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CHEMICAL KINETICS

3 credits (**2** lectures + **1** lab)

Part 6

Theoretical Models for Chemical Kinetics

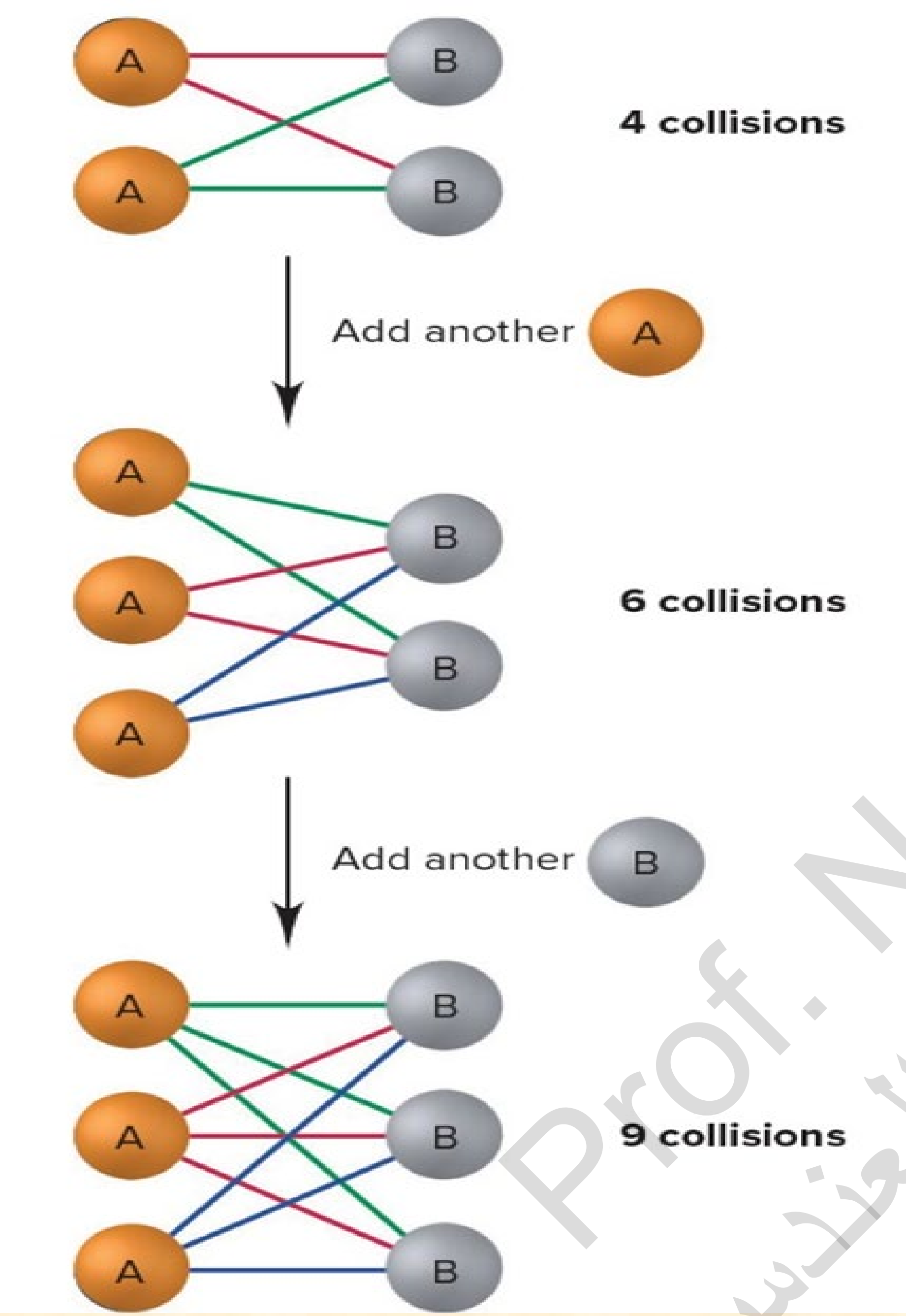
Collision Theory

- In order for two molecules to react, old chemical bonds have to be broken which requires energy!
- Collision theory considers that such energy is provided by kinetic energies of molecules upon their collisions.
- Collision theory can qualitatively explain:

  1) why the reaction rate, **k**, increases with increasing temperature and

  2) why only **1** of $\mathbf{10^{10}}$ collisions results in reaction

- An increase in the concentration of a reactant leads to a larger number of collisions, hence increasing reaction rate.
- The number of collisions depends on the ***product of the numbers*** of reactant particles, not their sum.
- Concentrations are multiplied in the rate law, not added.



The number of collisions depends on the *product of the numbers* of reactant particles, not their sum.

- ❖ Collision theory is simple : for a reaction to occur, particles must collide successfully.
- ❖ A successful collision has two components:
  - ✓ Particles must collide at the right *geometry*
  - ✓ Particles must collide with enough *energy (E_a)*.
- ❖ Factors which influence the geometry or energy of collision will affect the Rate of the reaction.

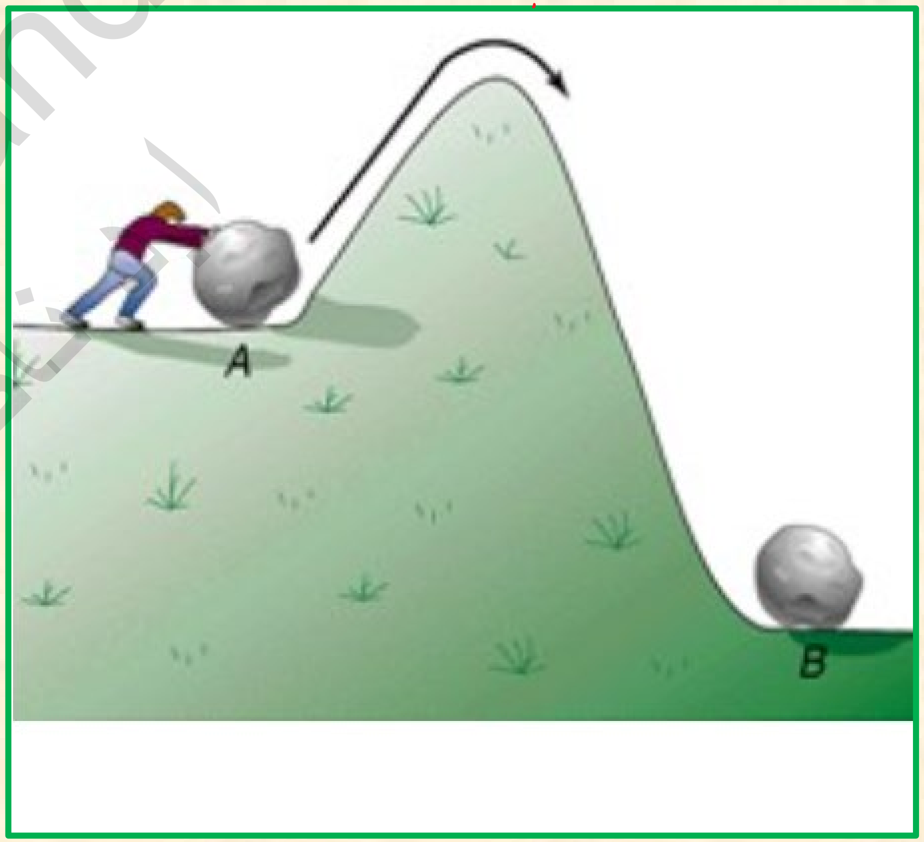
The Collision Model: A Closer look at the Frequency Factor

- ✓ The **frequency factor** is defined as the number of approaches to the activation barrier.
- ✓ What exactly does this mean?
- ✓ The collision model dissects the frequency factor (A) into.
  - ➢ orientation of collision P
  - ➢ frequency of collision Z

$$k = A\, e^{-Ea/RT}$$

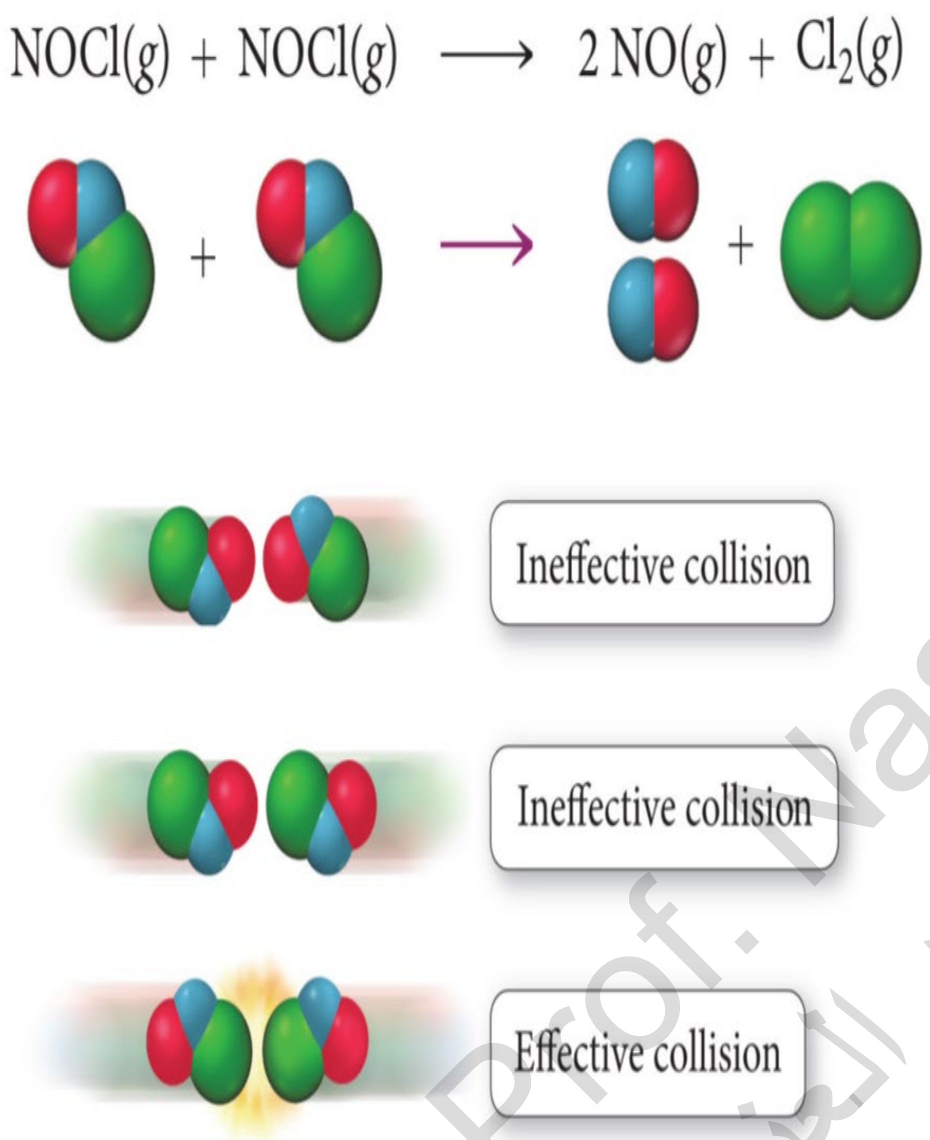
$$\text{If} \quad A = pZ$$

$$k = pZ\, e^{-Ea/RT}$$



P is the orientation factor .Usually between **0** and **1**, which represents ***the fraction of collisions with an orientation that allows the reaction to occur***

Z is the collision frequencies, which represents the number of collisions that occurs per unit time.



- ❖ If every collision had the perfect orientation then every collision would result in reaction.
- ❖ But this is not always the case some collisions are not productive (*ineffective*)
- ❖ For this reaction ***p* = 0.16**

only **16/100** sufficiently energetic collisions are effective

The Effect of E_a and T on the Fraction *(f)* of Collisions with Sufficient Energy to Allow Reaction

T	f (at Ea = 50 (kJ/mol)
25 °C (298K)	1.70×10^{-9}
35 °C (308K)	3.29×10^{-9}
45 °C (318K)	6.12×10^{-9}

Ea (kJ/mol)	*f* (at T = 298 K)
50	1.70×10^{-9}
75	7.03×10^{-14}
100	2.90×10^{-18}

$$f \propto T$$

$$f \propto \frac{1}{Ea}$$

Summary

For most reactions.

1) Most collisions don’t have *sufficient energy* to overcome the activation barrier and the particles just *bounce off* of each other.
2) A fraction of the collisions have the *right energy* but most of these don’t have the correct orientation.
3) Only that *small fraction* of collisions with *sufficient energy and correct orientation* produces reaction.

Collision theory illustrates how reactions occur; it can be used to approximate the rate constants of reactions, and its concepts can be directly applied in the laboratory

But it has limitations

Limitations of collision theory

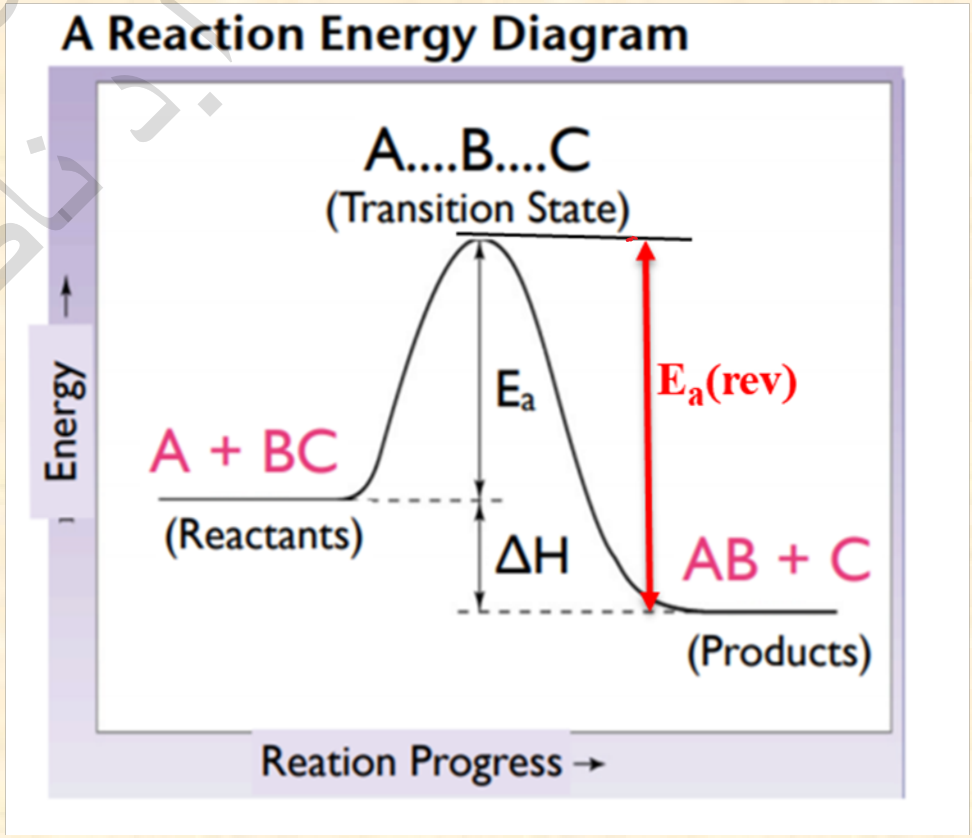
1) The theory only applies to *simple gases* and *sometime for solution* where the reacting species are simple molecules.
2) The expression from the collision theory (Arrhenius equation) only applies to *simple bimolecular* reactions. For *complex reactions* the experimental value does not match with the calculated one.
3) In this theory only **kinetic energy** (*transitional energy*) of reacting molecules are considered, while the *rotational* and *vibrational energy* are ignored.
4) It doesn’t explain the *break* and *formation* of bonds during the reaction.

Transition State Theory

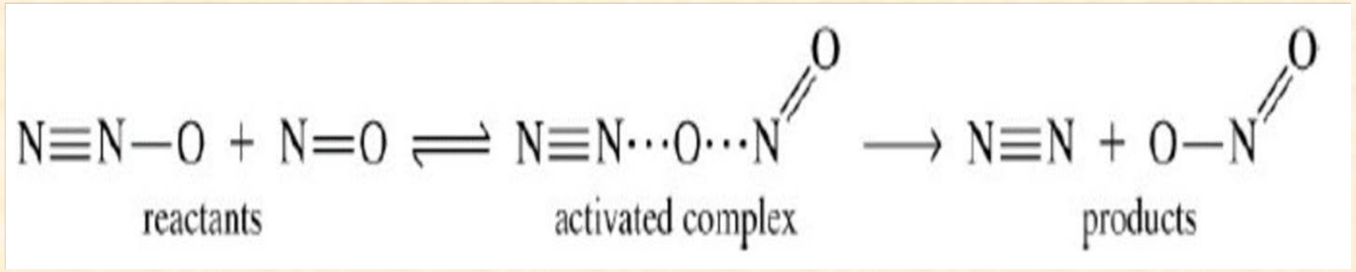
- known as theory of **absolute reaction rates** (ART) and **the theory of activated state** (complex),
- It is essentially a **refined version** of crude collision theory, which treats the reacting molecules as the rigid spheres without any internal degree of freedom.
- The theory explains the rate of chemical reaction assuming a special type of chemical equilibrium (**quasi-equilibrium**) between the reactants and activated state (***transition state complex***).
- This special molecule decomposes to form the products of reaction.
- The **rate** of this reaction is then equal to the rate of decomposition of activated complex.

- **activated complexes** proposed to exist as a transition state between reactants and products.
- The activated complex is short-lived because it is **highly reactive** (may break apart to form products or revert to reactants).
- **Transition states (activated complexes)** cannot be isolated.
- The transition state exists at the point of **maximum potential energy**.
- The energy required to form the transition state is the **activation energy.** It has always positive sign.

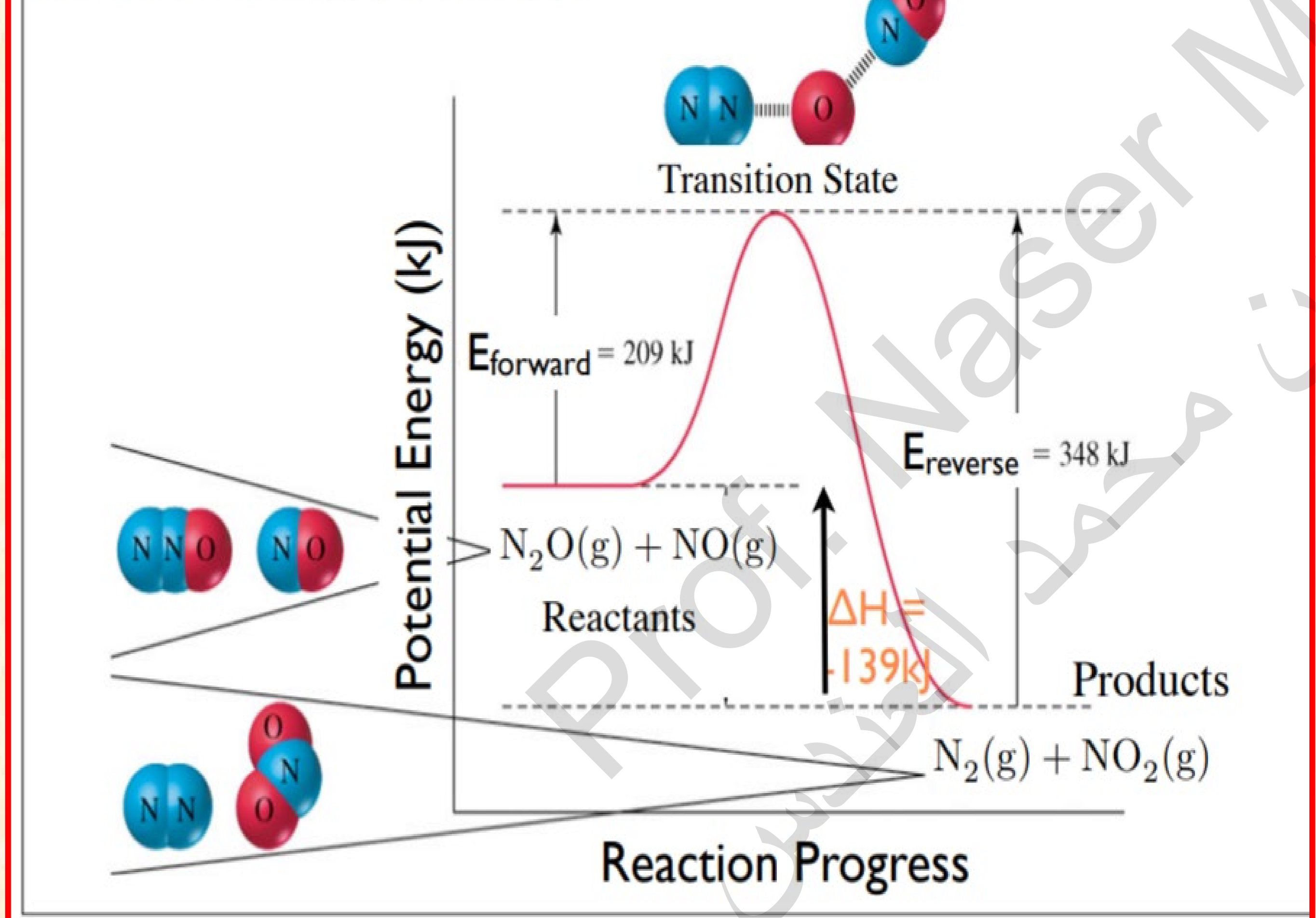
$$A + BC \longrightarrow AB + C$$

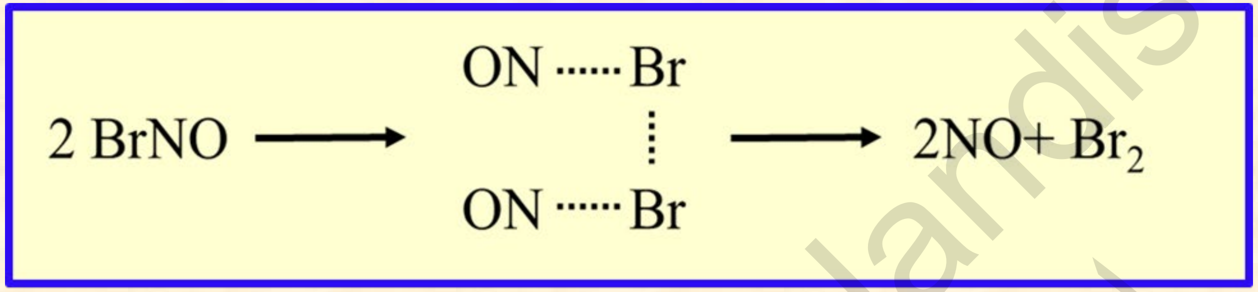


☐ Example: $N_2O(g) + NO(g) \rightarrow N_2(g) + NO_2(g)$

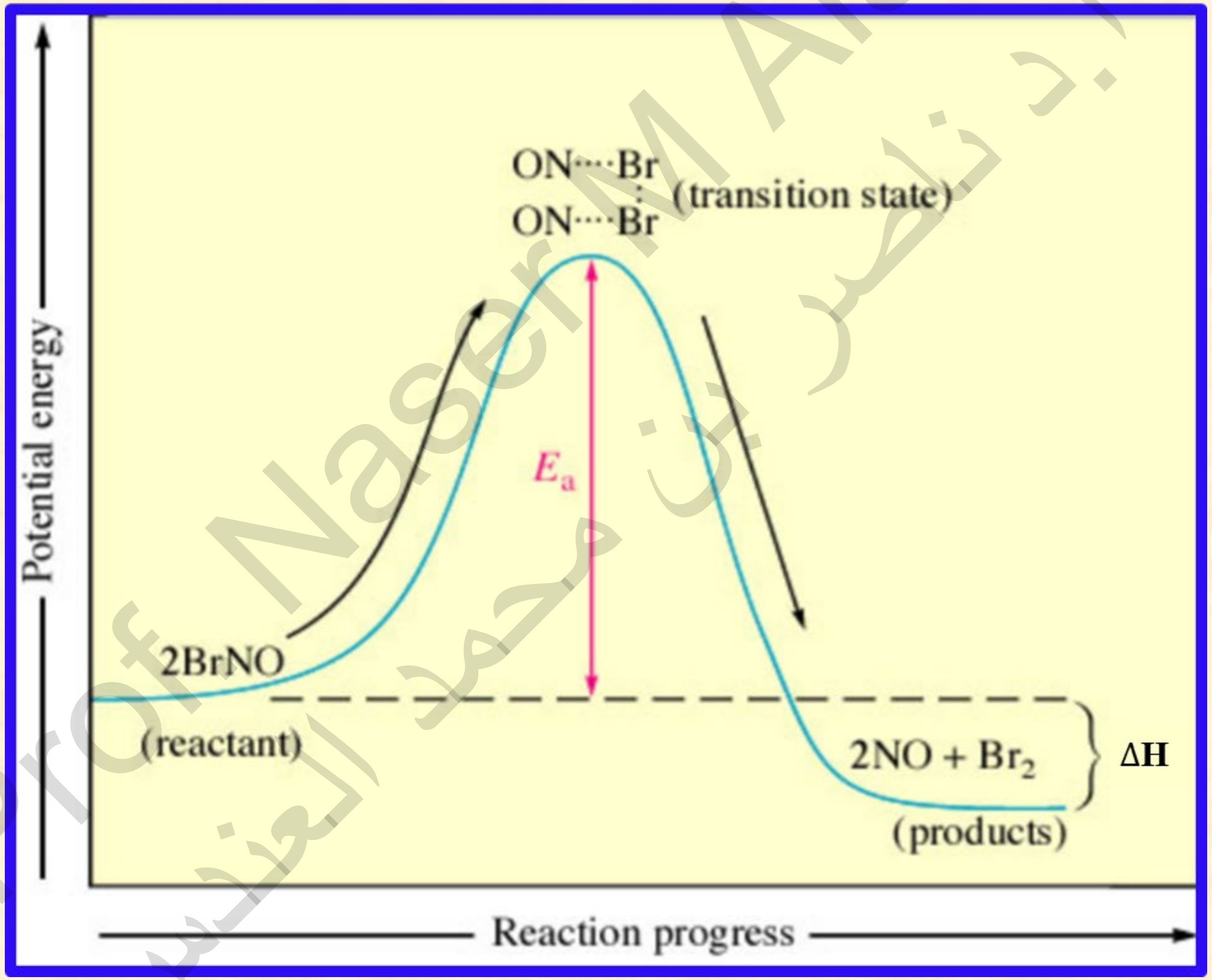


transformed to products.





$$2\,\text{BrNO} \longrightarrow \begin{matrix}\text{ON}\cdots\cdots\text{Br}\\ \vdots \\ \text{ON}\cdots\cdots\text{Br}\end{matrix} \longrightarrow 2\text{NO} + \text{Br}_2$$



General Principles of TS Theory

- *transition states* (**TS**) or *activated complexes* :During the transformation of reactant into product, one or more *very short-lived* chemical species form that *resemble* (but are different from) reactant or product; these transitional species contain ***partial bonds***.
- The activation energy **(E_a)** is used to stretch/deform specific bonds in the reactant(s) in order to reach the transition state.
- Every reaction (and each step in an overall reaction) goes through its own *TS*.
- All reactions are ***reversible***.
- Transition states are *identical* for the individual forward and reverse reactions in an equilibrium reaction.

Example : For the following equation :

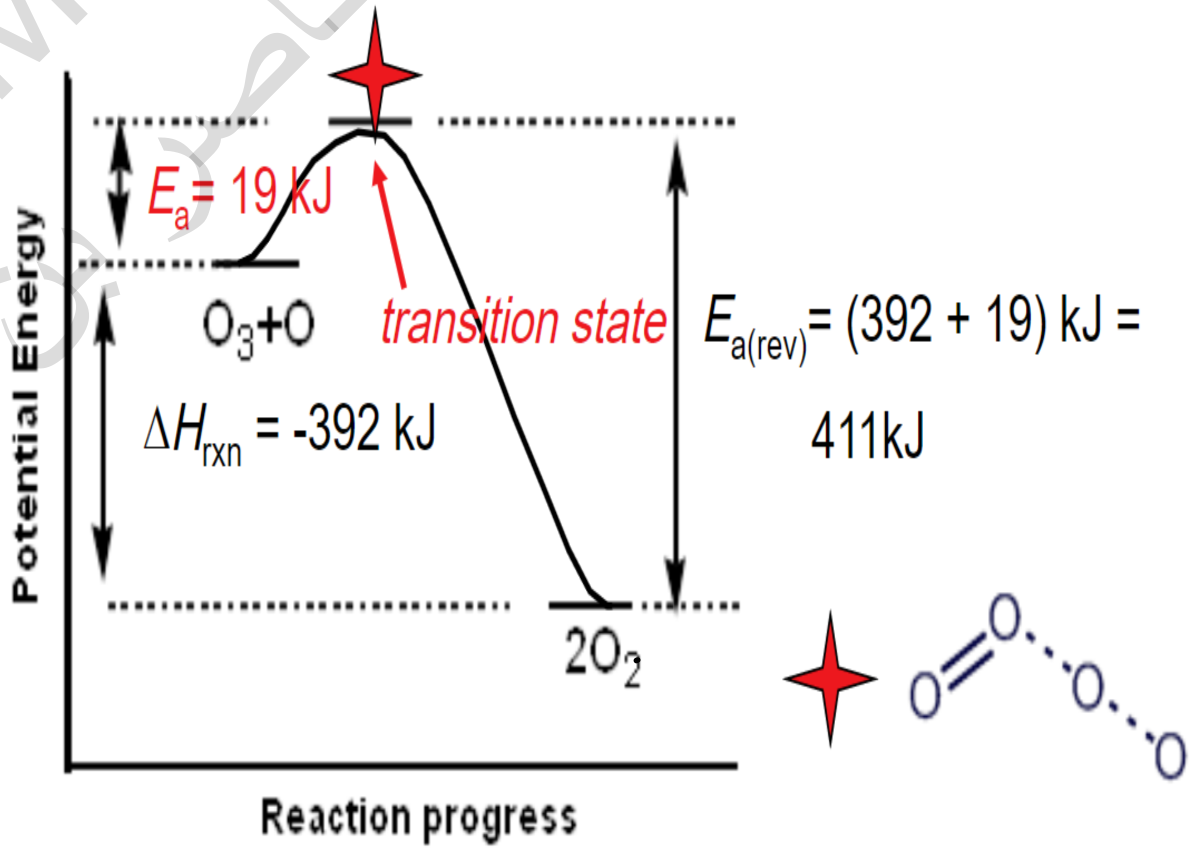
$O_3(g) + O(g) \longrightarrow 2O_2(g)$

The $E_{a\,(fwd)}$ is 19 kJ, and $\Delta H_{(rxn)}$ is -392 kJ. Draw a reaction energy diagram for this reaction, postulate a transition state, and calculate $E_{a\,(rev)}$.

SOLUTION:

$\Delta H_{rxn} = E_{a(fwd)} - E_{a(rev)}$

So $E_{a(rev)} = + E_{a(fwd)} - \Delta H_{rxn} = 19\text{ kJ} - (-392\text{ kJ}) = \mathbf{411\text{ kJ}}$



Collision Theory vs Transition State Theory

- They are very similar.
- They using slightly different approaches.
- Both theories explain:
  1) why **k** depends on **T**
  2) why **k** may be very low
- Both can be used to get a very important formula for the dependence of **k** on **T.**

335 Chem

CHEMICAL KINETICS

3 credits (**2** lectures + **1** lab)

Part 7

Reaction Mechanisms

- Every chemical reaction proceeds according to a reaction mechanism.
- It is a **step-by-step** description of what occurs during a reaction on the molecular level.
- Each step of the mechanism is known as an **elementary process**, which describes a single moment during a reaction in which molecules break and/or form new bonds.
- ***Molecularity***; that is, by how many molecules are involved in the given step.
  1) unimolecular $A \rightarrow \textbf{products}$
  2) bimolecular $A + B \rightarrow \textbf{products}$
  3) termolecular $A + B + C \rightarrow \textbf{products}$
- It is important to keep in mind that every reaction mechanism is simply a proposed version of what might be occurring at the molecular level.

- Even if a mechanism agrees with experimental results, it is impossible to **prove** a reaction mechanism for certain.
- There are two strict requirements that must be fulfilled for a reaction mechanism to be valid. They are:
  1) The sum of each elementary step in a reaction mechanism must yield the overall reaction equation.
  2) The rate law of the ***rate-determining step*** must agree with the experimentally determined rate law.
- The **rate-determining** step is the **slowest step** in a reaction mechanism. Because it is the slowest, it determines the rate of the overall reaction.
- *Orders of reaction* in the rate law for the elementary reaction are **the same as the stoichiometric coefficients** in the balanced equation for the process ,but not true for the **overall rate law** and the overall balanced equation.
- Elementary processes can be reversible reactions.

Difference Between Molecularity And Order Of The Reaction

Molecularity of Reaction	Order of Reaction
1. It is the total number of atoms, molecules or ions present in a single step.	1. It is the sum of all the exponents of the concentration of reactants involved in rate equation.
2. It’s value always in the whole number.	2. Its value can be in whole number or fraction.
3. Its value can be more than three.	3. Its value can never be more than three.
4. It can never be zero.	4. It can be zero

Transition States (TS) or Activated Complexes or Intermediate Species

- They are species that are neither one of the reactants, nor one of the products. It **transiently exists** during the course of the reaction.
- It is a highly reactive species (often free radicals);
- Its production is usually slower than that of its consumption
- Due to its high reactivity an intermediate very rapidly reaches its **“steady-state**” concentration which is much lower than the concentrations of reactants and products during the steady-state period.
- It may be hard to observe intermediates experimentally.
- The last allows us to use so-called **steady-state approximation .**

Steady State Approximation

Consider this reaction : $A \longrightarrow B$

If the reaction proceed according to the following mechanism :

$A \xrightarrow{k_1} I$ First order $\frac{d[A]}{dt} = -k_1\,[A]$ integral $[A] = [A_0]\,e^{-k_1 t}$

$I \xrightarrow{k_2} B$ SS $\frac{d[I]}{dt} = k_1\,[A] - k_2\,[I] = 0$ $\rightarrow$ $[I] = \frac{k_1\,[A]}{k_2}$ $\rightarrow$ $[I] = \frac{k_1}{k_2}\,[A_0]\,e^{-k_1 t}$

$\frac{d[B]}{dt} = \text{Rate} = k_2\,[I]$ $\rightarrow$ $\frac{d[B]}{dt} = k_1\,[A_0]\,e^{-k_1 t}$ $\rightarrow$ $\int d[B] = k_1\,[A_0]\,e^{-k_1 t}\,dt$

$$\int_0^{[B]} d[B] = k_1\,[A]_0 \int_0^t e^{-k_1 t}\,dt$$

$$[B] = \cancel{k_1}\,[A]_0\,(1 - e^{-k_1 t})\,\frac{1}{\cancel{k_1}}$$

Concentration of product

$$\boxed{[B] = [A]_0\,(1 - e^{-k_1 t})}$$

Consider this reaction : $A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I \xrightarrow{k_2} C$

Appling steady state approximation :

$$\left(\frac{d[I]}{dt}\right)_{ss} = 0 = k_1[A]\,[B] - k_{-1}[I] - k_2[I]$$

$$k_1[A]\,[B] = k_{-1}[I] + k_2[I]$$

$$k_1[A]\,[B] = [I]\,(k_{-1} + k_2)$$

$$[I]_{ss} = \frac{k_1[A]\,[B]}{(k_{-1} + k_2)}$$

Intermediate concentration at the steady state

$$\left(\frac{d[C]}{dt}\right) = k_2[I] = k_2\frac{k_1[A]\,[B]}{(k_{-1} + k_2)}$$

$$\left(\frac{d[C]}{dt}\right) = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \text{Rate} = k_2\frac{k_1[A]\,[B]}{(k_{-1} + k_2)}$$

$$\text{Rate} = k_{(\text{observed})}\,[A]\,[B]$$

The reaction 2ed overall order

$$k_{(\text{observed})} = \frac{k_2 k_1}{(k_{-1} + k_2)}$$

Cases

First: $k_{-1} \ll k_2$

$$k_{(obs)} = \frac{k_2k_1}{(k_{-1}+k_2)} = \frac{k_2k_1}{(k_{-1}+k_2)} = \frac{\cancel{k_2}k_1}{\cancel{(k_2)}} = k_1$$

Rate = $k_1[A]\,[B]$

Second: $k_{-1} \gg k_2$

$$k_{(obs)} = \frac{k_2k_1}{(k_{-1}+k_2)} = \frac{k_2k_1}{(k_{-1}+k_2)} = \frac{k_2k_1}{k_{-1}} = k_2\,K$$

Rate = $k_2K[A]\,[B]$

K= equilibrium constant $= \frac{k_1}{k_{-1}}$

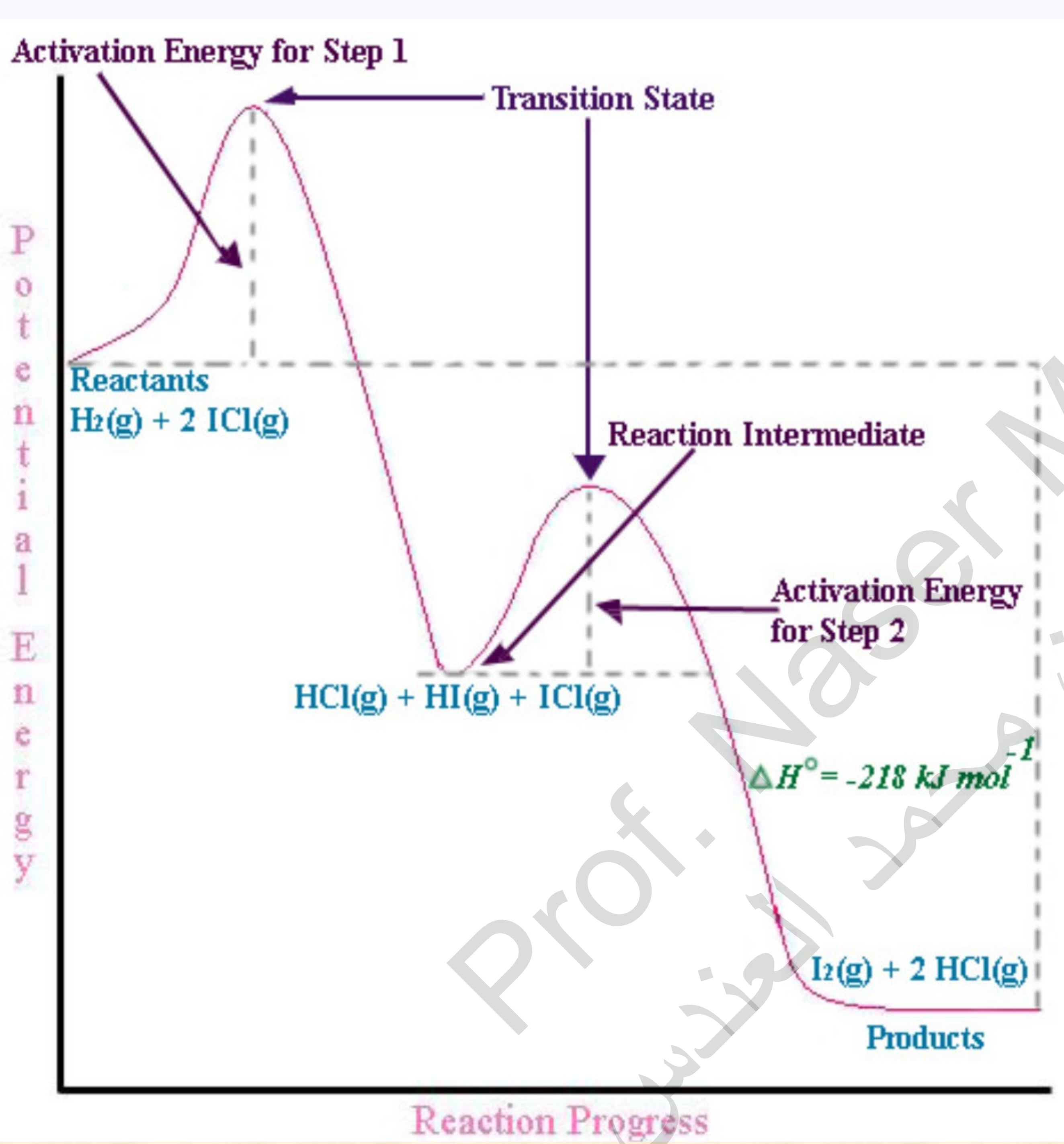
It is called repaid pre-equilibrium

1) Check the proposed mechanism if it adds up to the reaction balanced equation

2) Write the expression for the reaction rate using the **last elementary process** in the reaction mechanism, which ***does not produce intermediates*** at the right-hand side. Determine the steady state concentration of the intermediate using $(d[I]/dt)_{ss} = 0$.

3) Substitute **[I]** in the reaction rate found in in(2) with [I] determined in (3).

4) Compare the theoretical and experimental rates of reaction.



$H_{2\,(g)} + 2ICl_{(g)} \longrightarrow I_{2\,(g)} + 2HCl_{(g)}$

- The experimental rate of reaction = $k_{exp}[H_2][ICl]$
- If the following mechanism is propose:

1 $H_2 + ICl \xrightarrow{k_1} \cancel{HI} + HCl$

2 $\cancel{HI} + ICl \xrightarrow{k_2} I_2 + HCl$

$H_2 + 2ICl \longrightarrow I_2 + 2HCl$

- **The sum of all steps yield the overall reaction thus the proposed mecanisme is possible.**
- Rate of the first step = **k_1 [H_2][ICl]**
- Rate of the second step = **k_2 [HI][ICl]**
- Rate of the first step = the experimental rate so the first step is **the slowest step** and its **the rate determining step**

$$H_{2\,(g)} + 2ICl_{(g)} \longrightarrow I_{2\,(g)} + 2HCl_{(g)}$$

Mechanism

① $H_2 + ICl \xrightarrow{k_1} \cancel{HI} + HCl$

② $\cancel{HI} + ICl \xrightarrow{k_2} I_2 + HCl$

$$-\frac{d[H_2]}{dt} = -\frac{1}{2}\frac{d[ICl]}{dt} = \frac{d[I_2]}{dt} = \frac{1}{2}\frac{d[HCl]}{dt} = \text{Rate}$$

Applying **steady-state approximation** for intermediate **[HI]**

$$\frac{d[HI]}{dt} = 0 = k_1\,[H_2]\,[ICl] - k_2\,[HI]\,[ICl]$$

$$k_1\,[H_2]\,[ICl] = k_2\,[HI]\,[ICl]$$

$$\frac{d[I2]}{dt} = k_2\,[HI]\,[ICl] = k_1\,[H_2]\,[ICl]$$

$$\frac{d[HCl]}{dt} = k_1\,[H_2]\,[ICl] + k_2\,[HI]\,[ICl] = 2k_1\,[H_2]\,[ICl]$$

$$\text{Rate} = \frac{1}{2}\frac{d[HCl]}{dt} = k_1\,[H_2]\,[ICl]$$

The first step is the rate of the reaction SO it is the slow step thus **rate determining step (RDS)**

$$k_{exp} = k_1$$

- Molecularity is bimolecular

$$2NO + Cl_2 \xrightarrow{k_{exp}} 2NOCl$$

The reaction will occur in two steps

Step (1) $2NO \underset{K_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2$ **fast**

Step (2) $N_2O_2 + [Cl_2] \xrightarrow{k_2} 2NOCl$ **slow**

$$\frac{d[N_2O_2]}{dt} = 0 = k_1\,[NO]^2 - k_{-1}\,[N_2O_2] - k_2\,[N_2O_2]\,[Cl_2]$$

$$k_1\,[NO]^2 = k_{-1}\,[N_2O_2] + k_2\,[N_2O_2]\,[Cl_2] = (k_{-1} + k_2[Cl_2]\,)\,[N_2O_2]$$

$$\boxed{[N_2O_2]_{ss} = \frac{k_1[NO]^2}{k_{-1} + k_2[Cl_2]}}$$

$$\frac{1}{2}\left(\frac{d[NOCl]}{dt}\right) = k_2\,[N_2O_2]\,[\,Cl_2] = k_2\,\frac{k_1[NO]^2[\,Cl_2]}{k_{-1} + k_2[\,Cl_2]}$$

step 2 is slow, which means k_2 is small so that $k_{-1} >> k_2\,[Cl_2]$

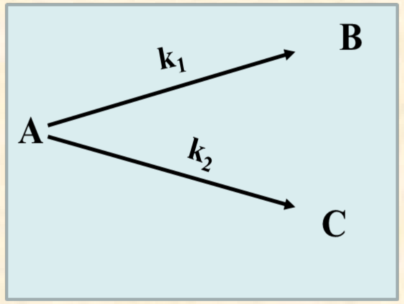
$$k_{exp} = \frac{k_2 k_1}{k_{-1}} = k_2\,K$$

$$\frac{1}{2}\left(\frac{d[NOCl]}{dt}\right) = \frac{d[Cl_2]}{dt} = \text{Rate} = k_2\,K\,[NO]^2\,[\,Cl_2]$$

Kinetics of Complex Systems

(1)Parallel Reactions (Competitive Reactions)

first-order :



$$-\frac{d[A]}{dt} = k_1\,[A] + k_2\,[A]$$

$$-\frac{d[A]}{dt} = (k_1 + k_2\,)\,[A]$$

$$k = (k_1 + k_2\,)$$

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

$$[A] = [A]_0\;e^{-kt}$$

$$[A] = [A]_0\;e^{-(k_1+k_2)t}$$

① $$\frac{d[B]}{dt} = k_1\,[A] = k_1\,[A]_0\;e^{-(k_1+k_2)t}$$

② $$\frac{d[C]}{dt} = k_2\,[A] = k_2\,[A]_0\;e^{-(k_1+k_2)t}$$

Solve for [B]

$$[B] = -\frac{k_1\,[A]_0}{(k_1 + k_2\,)}\;e^{-(k_1+k_2)t} + \text{const.}$$

To find cons. We know that $[B]_0 = 0$

$$0 = -\frac{k_1\,[A]_0}{(k_1 + k_2\,)} + \text{const.}$$

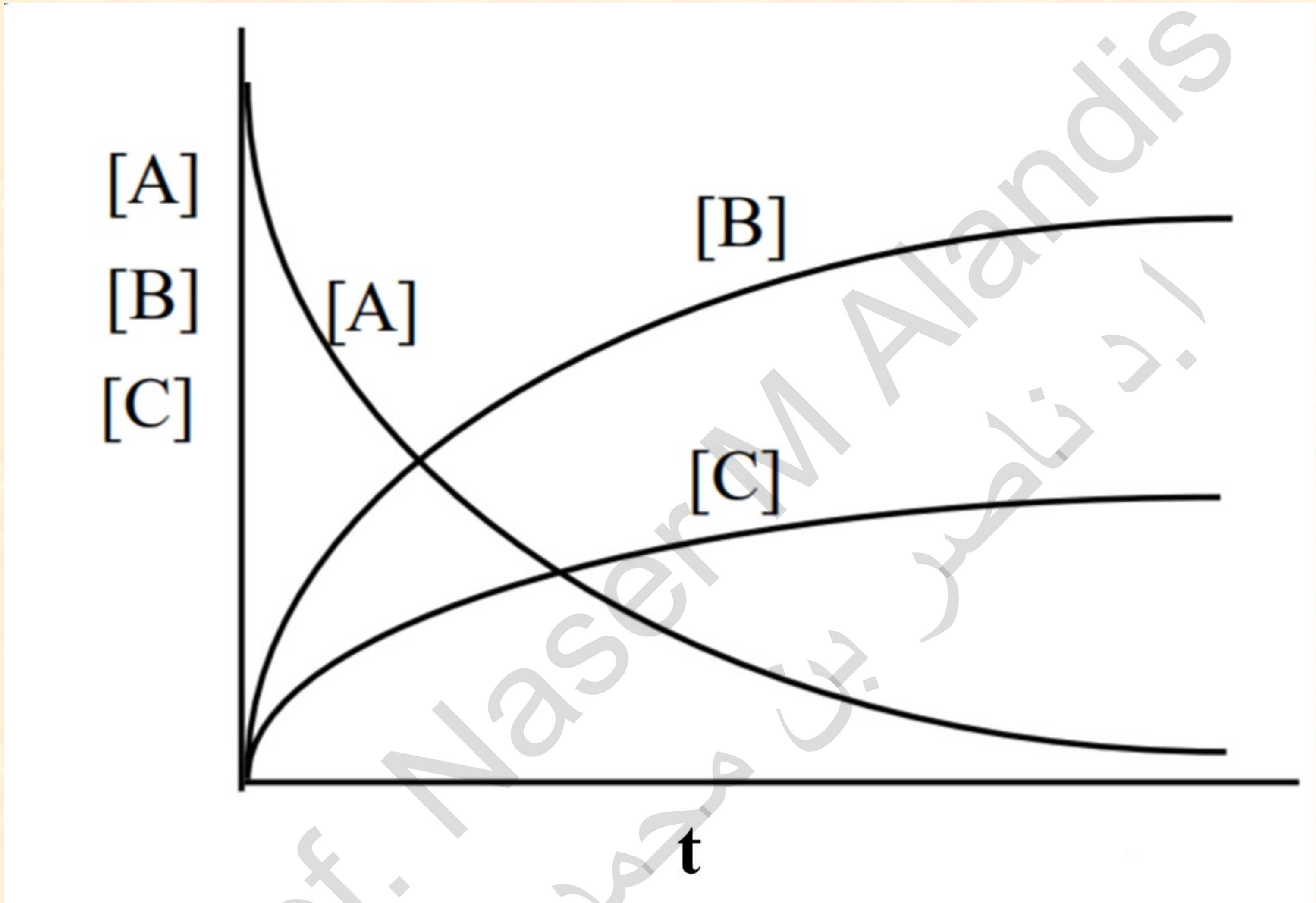
$$\text{const.} = \frac{k_1\,[A]_0}{(k_1 + k_2\,)}$$

$$[B] = \frac{k_1\,[A]_0}{(k_1 + k_2\,)}\,(1-\;e^{-(k_1+k_2)t}\,)$$

The same way for [B]

$$[C] = \frac{k_2\,[A]_0}{(k_1 + k_2\,)}\,(1-\;e^{-(k_1+k_2)t}\,)$$

$$\frac{[B]}{[C]} = \frac{k_1}{k_2}$$


[A]
[B]
[C]
[A]
[B]
[C]
t

(2) Series Reactions (Consecutive Reactions)

FIRST-ORDER

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

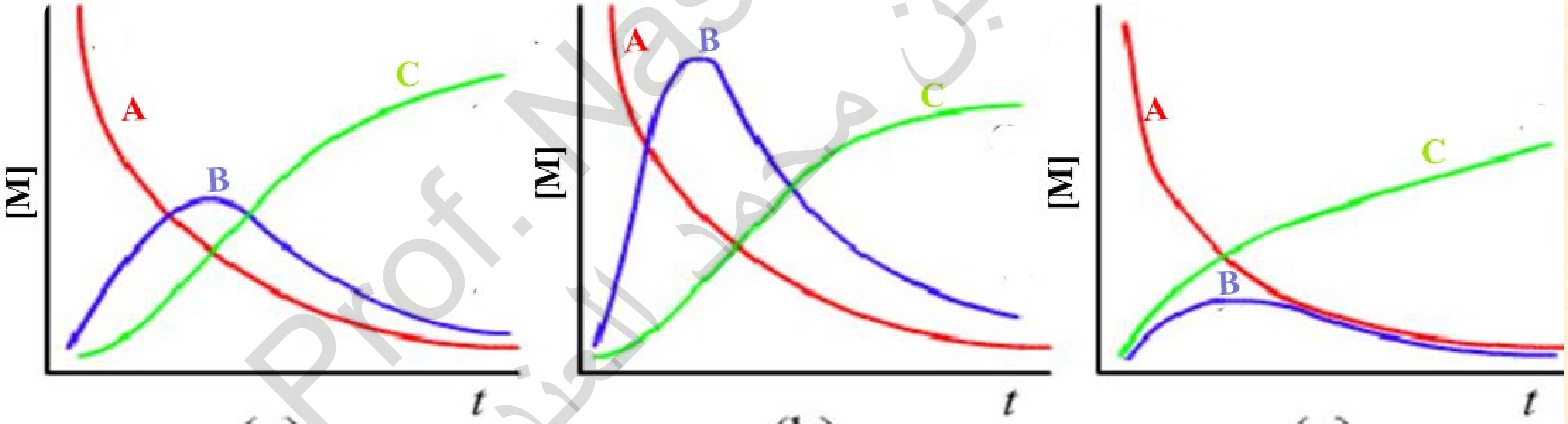
Case $k_1 \gg k_2$

$$[A]_0 = [A]_t + [B]_t + [C]_t$$

$$\frac{d[A]}{dt} = -\,k_1\,[A] \rightarrow [A]_t = [A]_0\ e^{-k_1 t}$$

$$\frac{d[B]}{dt} = k_1\,[A] - k_2\,[B] \rightarrow [B]_t = [A]_0 \left(\frac{k_1}{(k_2 - k_1)}\right)\left(e^{-k_1 t} - e^{-k_2 t}\right)$$

$$\frac{d[C]}{dt} = k_2\,[B] \rightarrow [C]_t = [A]_0 \left(1 + \frac{k_1}{(k_1 - k_2)}\right)\left(k_2 e^{-k_1 t} - k_1\,e^{-k_2 t}\right)$$



(a) $k_1 \approx k_2$ (b) $k_1 >> k_2$ (c) $k_1 << k_2$

[B] reaches it‘s maximum at t_{max} and $\frac{d[B]}{dt} = 0$

$$[B]_{max} = [A]_0 \left(\frac{k_1}{(k_2 - k_1)}\right) \left(e^{-k_1 t_{max}} - e^{-k_2 t_{max}}\right)$$

$$t_{max} = \left(\frac{\ln\frac{k_1}{k_2}}{(k_1 - k_2)}\right)$$

$[B]_{max}$ can be written in terms of constants

$$[B]_{max} = [A]_0 \left(\frac{k_1}{(k_2)}\right)^{\left(\frac{k_2}{(k_1 - k_2)}\right)}$$

3) REVERSIBLE REACTIONS

FIRST-ORDER

$$A \underset{K_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

$$\frac{d[A]}{dt} = -k_1\,[A]_t + k_{-1}\,[B]_t$$

At equilibrium - $\frac{d[A]}{dt} = 0$

$$k_1\,[A]_e = k_{-1}\,[B]_e$$

$$\frac{k_1}{k_{-1}} = K_c = \frac{[B]_e}{[A]_e}$$

To find $[A]_t$

When $[B]_0 = 0$ then

$$[B]_t = [A]_0 - [A]_t$$

$$\frac{d[A]}{dt} = -k_1\,[A]_t + k_{-1}\,([A]_0 - [A]_t)$$

$$= -k_1\,[A]_t + k_{-1}\,[A]_0 - k_{-1}[A]_t$$

$$\frac{d[A]}{dt} = k_{-1}\,[A]_o - (k_1 + k_{-1})[A]_t$$

integrating for A

①

$$\ln \frac{k_1\,[A]_o}{(k_1 + k_{-1})[A]_t - k_{-1}\,[A]_0} = (k_1 + k_{-1})t$$

At equilibrium $\frac{d[A]}{dt} = 0$

$[A]_t$ and $[B]_t$ becomes $[A]_e$ and $[B]_e$

$$k_1\,[A]_e = k_{-1}\,[B]_e = k_{-1}\,([A]_0 - [A]_t) = k_{-1}\,[A]_0 - k_{-1}[A]_t$$

$$k_1\,[A]_e = k_{-1}\,[A]_0 - k_{-1}[A]_e$$

$$k_1\,[A]_e + k_{-1}[A]_e = k_{-1}\,[A]_0$$

$$[A]_o = \frac{(k_1 + k_{-1})\,[A]_e}{k_{-1}}$$ **And** $$[A]_e = \frac{k_{-1}[A]_0}{(k_1 + k_{-1})}$$

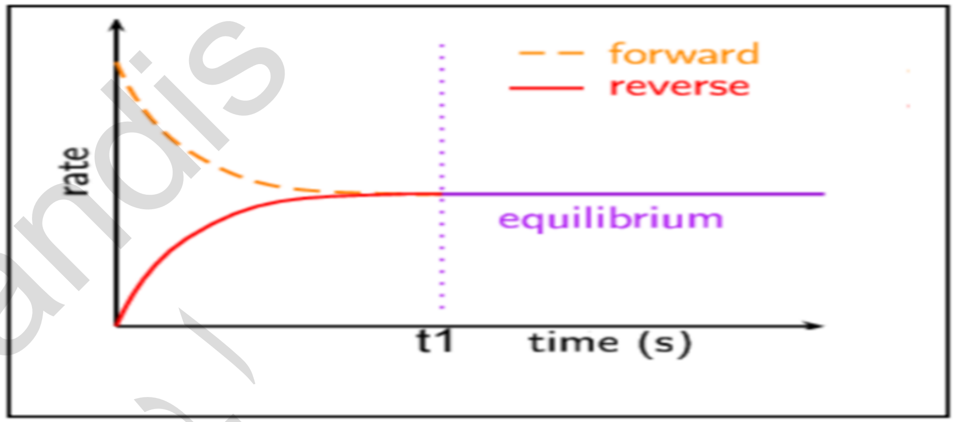
In Equation (1) becomes

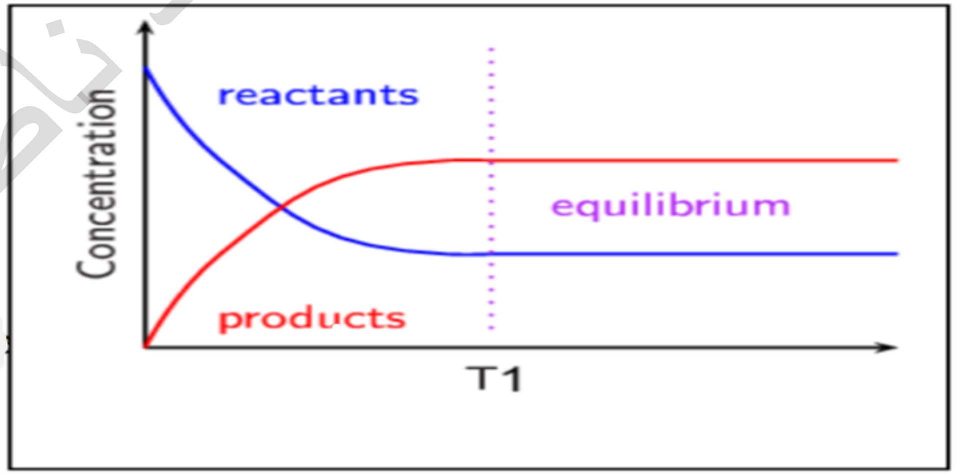
$$\ln \frac{k_1\,[A]_o}{(k_1 + k_{-1})[A]_t\ - k_{-1}\,[A]_0} = (k_1 + k_{-1})t$$ ①

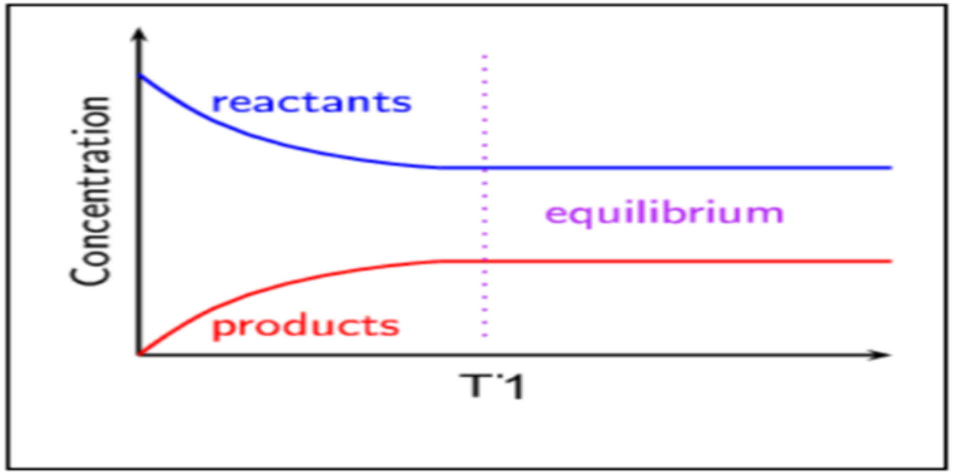
Equation (1) becomes

$$\ln \frac{[A]_o - [A]_e}{[A]_e - [A]_0} = (k_1 + k_{-1})t$$

$$[A]_t = [A]_e + ([A]_o - [A]_e)\, e^{-(k_1 + k_{-1})t}$$







4) Chain Reaction

- usually consist of many repeating elementary steps, each of which has a **chain carrier**.
- Once started, chain reactions continue until the reactants are exhausted.
- Fire and explosions are some of the phenomena associated with chain reactions.
- The **chain carriers** are some intermediates that appear in the repeating elementary steps. It maintains the chain reaction
- **Chain carriers** are usually **free radicals**.
- The chain reaction mechanism is involved in explosions, polymerizations, food spoilage and nuclear reactors.
- The mechanisms of chain reactions can be grouped into 4 steps:

1) initiation step
2) propagation steps
3) inhibition steps
4) termination steps

1) Initiation Step

- It starts usually by the free radical.
- Light ($h\nu$) (**thermolysis (heating)**)can often be used to initiate chain reactions since they can generate intermediates via a photodissociation reaction.
- *Does not affect the rate law.*

2) Propagation steps

- The chain carrier makes another carrier.
- Elementary steps in which the number of free radicals consumed is equal to the number of free radicals generated .
- In each of these steps, a radical is consumed, and another radical is generated.
- Propagation steps generally accomplish bulk of chemical reactions. The sum of steps gives **net stoichiometry**.

3) Inhibition Steps

- Converts active chain-carrying intermediates molecules into stable molecules such as products or inert bi-products.
- *It does not have any influence on mathematical form of rate law.*

4) Termination step

- Elementary steps that consume radicals. When reactants are used up, free radicals combine with one another to give stable molecules

$$\text{Chain length} = \frac{\text{Overall Rate (propagation)}}{\text{Rate (initiation step)}}$$

$$CH_3CHO \xrightarrow{k_{exp}} CH_4 + CO \qquad \text{Rate} = k_{exp}\ [CH_3CHO]^{3/2}$$

$$CH_3CHO \xrightarrow{k_1} {}^{\bullet}CH_3 + {\cdot}CHO$$

Initiation Step

$${}^{\bullet}CH_3 + CH_3CHO \xrightarrow{k_2} CH_4 + CH_3CO{\cdot}$$

$$CH_3CO{\cdot} \xrightarrow{k_3} {}^{\bullet}CH_3 + CO$$

propagation Steps

$$2\,{}^{\bullet}CH_3 \xrightarrow{k_4} CH_3CH_3$$

termination Steps

Applying steady-state approximation for the intermediates [$^{\bullet}CH_3$] and [$CH_3CO^{\bullet}$]

$$\frac{d[\cdot CH_3]}{dt} = 0 = k_1\ [CH_3CHO] - k_2\ [CH_3CHO]\ [{}^{\bullet}CH_3] + k_3\ [CH_3CO\cdot] - 2\ k_4[\cdot CH_3]^2$$

$$\frac{d[CH_3CO\cdot]}{dt} = 0 = k_2\ [CH_3CHO]\ [{}^{\bullet}CH_3] - k_3\ [CH_3CO\cdot]$$

Adding two equations

$$0 = k_1\ [CH_3CHO] - -2\ k_4[\cdot CH_3]^2$$

Concentration at steady-state

$$[{}^{\bullet}CH_3]_{ss} = \sqrt{\frac{k_1\ [CH_3CHO]}{2\ k_4}} = \left(\frac{k_1}{2\ k_4}\right)^{1/2} [CH_3CHO]^{1/2}$$

Find the rate for one of the products of the main reaction in the propagation steps **especially the slow step** if not given the rate wanted.

$$-\frac{d[CH_3CHO]}{dt} = k_1\,[CH_3CHO] + k_2\,[CH_3CHO]\,[\cdot CH_3]_{ss}$$

Substituting for $[\cdot CH_3]_{ss}$

$$-\frac{d[CH_3CHO]}{dt} = k_1\,[CH_3CHO] + k_2\,[CH_3CHO]\,(\frac{k_1}{2\,k_4})^{1/2}[CH_3CHO]^{1/2}$$

Initiation step does not affect the rate law. Thus $k_1\,[CH_3CHO] = 0$

$$-\frac{d[CH_3CHO]}{dt} = k_2\,(\frac{k_1}{2\,k_4})^{1/2}\,[CH_3CHO]^{3/2}$$

$$k_{exp} = k_2\,(\frac{k_1}{2\,k_4})^{1/2}$$

$$\text{Chain length} = \frac{\text{Rate (propagation)}}{\text{Rate (initiation step)}} = \frac{k_2\,(\frac{k_1}{2\,k_4})^{1/2}\,[CH_3CHO]^{3/2}}{k_1\,[CH_3CHO]}$$

$k_{exp} = 5.4 \times 10^{-3}\ s^{-1}$ $k_1 = 1.8 \times 10^{-7}\ s^{-1}$ $[CH_3CHO] = 10^{-4}\ M$

$$\text{Chain length} = 5.4 \times 10^{-3} \times [10^{-4}]^{1/2} = 600$$

$C_2H_6 + H_2 \xrightarrow{k_{exp}} CH_4$ Prove that the rate law is : $\frac{d[CH_4]}{dt} = k_{exp}\ [C_2H_6]^{1/2}[H_2]$

If the reaction's mechanism is :

$C_2H_6 \xrightarrow{k_1} 2CH_3^{\bullet}$ **Initiation Step**

$CH_3^{\bullet} + H_2 \xrightarrow{k_2} CH_4 + H^{\bullet}$

$C_2H_6 + H^{\bullet} \xrightarrow{k_3} CH_4 + CH_3^{\bullet}$

$\Big\}$ **propagation Steps**

$2CH_3^{\bullet} \xrightarrow{k_4} C_2H_6$ **termination Steps**

Applying steady-state approximation for the intermediates $[CH_3^{\bullet}]$ and $[H^{\bullet}]$

$$\frac{d[CH_3^{\bullet}]}{dt} = 0 = 2k_1\ [C_2H_6] - k_2\ [CH_3^{\bullet}]\ [H_2] + k_3\ [H^{\bullet}][C_2H_6] - 2k_4\ [CH_3^{\bullet}]^2 \quad \text{———} \quad 1$$

$$\frac{d[H^{\bullet}]}{dt} = 0 = k_2\ [CH_3^{\bullet}]\ [H_2] - k_3\ [H^{\bullet}][C_2H_6] \quad \text{———} \quad 2$$

$$0 = 2k_1\ [C_2H_6] - 2k_4\ [CH_3^{\bullet}]^2$$

$$[CH_3^{\bullet}]^2_{ss} = \frac{\cancel{2}k_1[C_2H_6]}{\cancel{2}\,k_4} \longrightarrow [CH_3^{\cdot}]_{ss} = \left(\frac{k_1}{k_4}\right)^{1/2}[C_2H_6]^{1/2}$$

Find the rate wanted $\frac{d[CH_4]}{dt}$

$$\frac{d[CH_4]}{dt} = k_2\,[CH_3^{\cdot}]\,[H_2] + k_3\,[H^{\cdot}][C_2H_6] \quad \text{———} \; 3$$

We have to get rid of [H•] using equation 2

$$0 = k_2\,[CH_3^{\bullet}]\,[H_2] + k_3\,[H^{\bullet}][C_2H_6] \longrightarrow k_2\,[CH_3^{\bullet}]\,[H_2] = k_3\,[H^{\bullet}][C_2H_6]$$

Equation 3 becomes :

$$\frac{d[CH_4]}{dt} = 2k_2\,[CH_3^{\cdot}]\,[H_2]$$

Substituting for $[CH_3^{\cdot}]_{ss}$

$$\frac{d[CH_4]}{dt} = 2k_2\left(\frac{k_1}{k_4}\right)^{1/2}[C_2H_6]^{1/2}\,[H_2] \longrightarrow k_{exp} = 2k_2\left(\frac{k_1}{k_4}\right)^{1/2}$$

$$\text{Chain length} = \frac{2k_2\left(\frac{k_1}{k_4}\right)^{1/2}[C_2H_6]^{1/2}\,[H_2]}{2k_1\,[C_2H_6]} = \frac{k_2}{k_1}\sqrt{\frac{k_1}{k_4}}\,\frac{1}{\sqrt{[C_2H_6]}}\,[H_2]$$

$2NO + O_2 \xrightarrow{k_{exp}} 2NO_2$ If the reaction’s mechanism is :

$2NO \quad \overset{k_1}{\underset{k_2}{}} \quad N_2O_2$ —— 1

$N_2O_2 + O_2 \quad \overset{k_3}{} \quad 2NO_2$ (slow step) —— 2

Prove that the rate law is : $- \frac{d[NO]}{dt} = 2k_3\ K\ [NO]^2\ [O_2]$

Solution

RDS is the slow step . Thus **RDS** is the Rate step.

Applying steady-state approximation for the intermediate $[N_2O_3]$.

$$\frac{d[N_2O_2]}{dt} = 0 = 2k_1\ [NO]^2 - 2k_2\ [N_2O_2] - 2k_3\ [N_2O_2]\ [O_2]$$

$$2k_1\ [NO]^2 = 2k_2\ [N_2O_2] + 2k_3\ [N_2O_2]\ [O_2]$$

Taking the common factor $[N_2O_3]$.

$$2k_1\,[NO]^2 = (2k_2 + 2k_3\,[O_2])\,[N_2O_2]$$

$$[N_2O_2]_{ss} = \frac{2k_1\,[NO]^2}{(2k_2 + 2k_3\,[O_2])}$$

The rate constant of the slow step k_3 is small that it can be omitted thus :

$$[N_2O_2]_{ss} = \frac{2k_1\,[NO]^2}{2k_2} = \frac{k_1\,[NO]^2}{k_2}$$

Since $\frac{k_1}{k_2} = K$ (equilibrium constant)

$$[N_2O_2]_{ss} = K\,[NO]^2$$

$$\text{Rate} = \frac{1}{2}\,\frac{d(NO_2)}{d(t)} = k_3\,[N_2O_2]\,[\,O_2\,] = k_3\,K\,[NO]^2\,[\,O_2\,]$$

$$\frac{d(NO_2)}{d(t)} = 2\,k_3\,K\,[NO]^2\,[\,O_2\,]$$

335 Chem

CHEMICAL KINETICS

3 credits (**2** lectures + **1** lab)

Part 8

Catalyst

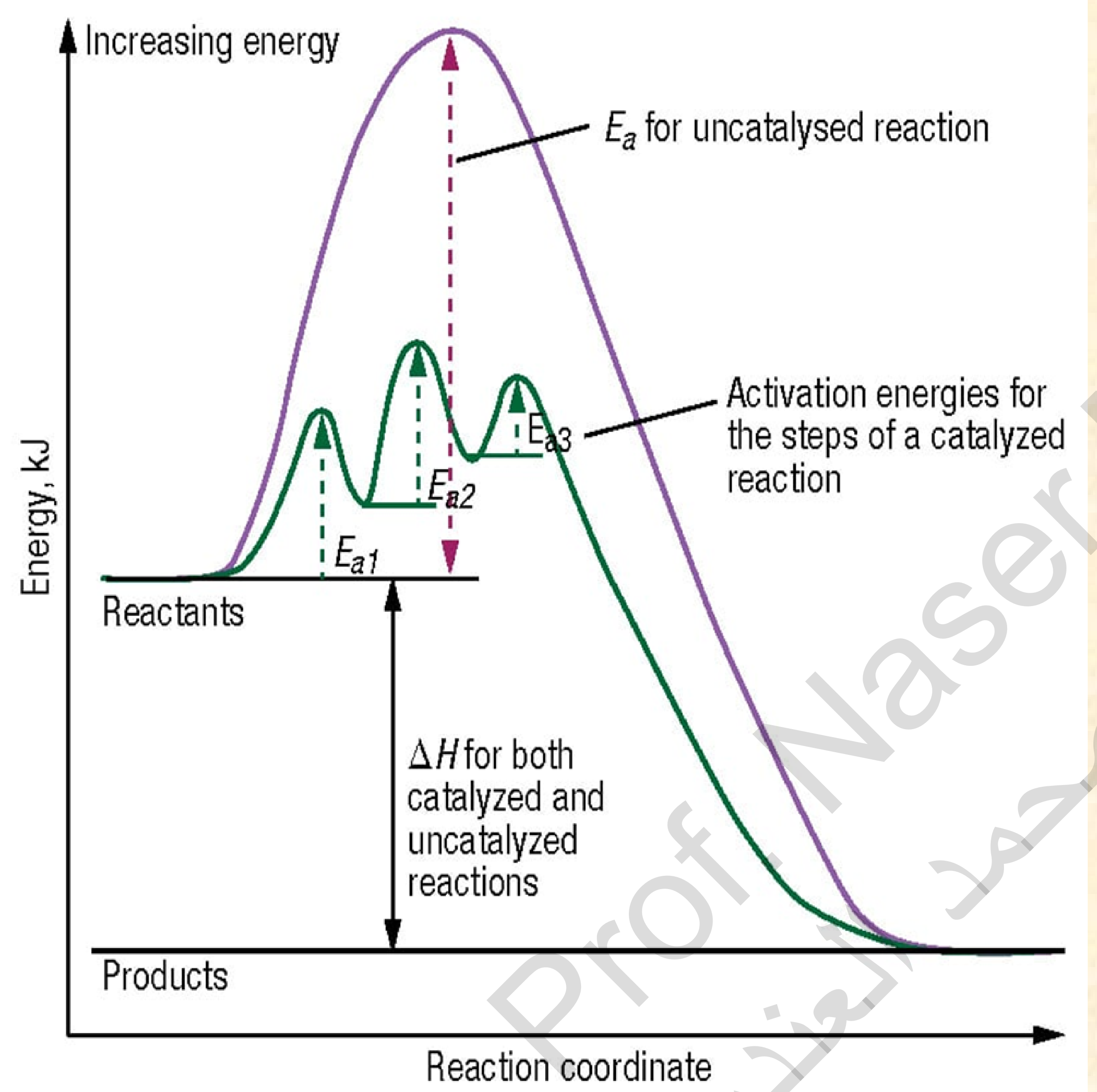
1) Substances that increase the reaction rate of a chemical reaction without being ***consumed*** in the process.
2) It interacts with chemical reactants to increase the reaction rate ***at the same temperature***.
3) It forms intermediate chemical complexes with reactants, allowing the reaction to follow a different mechanistic pathway that requires lower activation energy **(Ea)** than the corresponding uncatalyzed reaction.
4) In the case of ***reversible reactions***, the catalyst acts on both the forward and reverse reactions.
5) The catalyst does not affect the position of the ***equilibrium.***
6) It accelerates the rate at which equilibrium is reached.
7) The presence of catalyst does not affect the potential energy of the reactants or products.
8) It affects only the ***activation energy***.
9) In reactions with multiple feasible mechanisms, catalysts can often exhibit **selectivity** by binding to the transition state in a way that favors one reaction pathway over others.
10) Catalyzed reactions often show a different product distribution than the same uncatalyzed reaction.

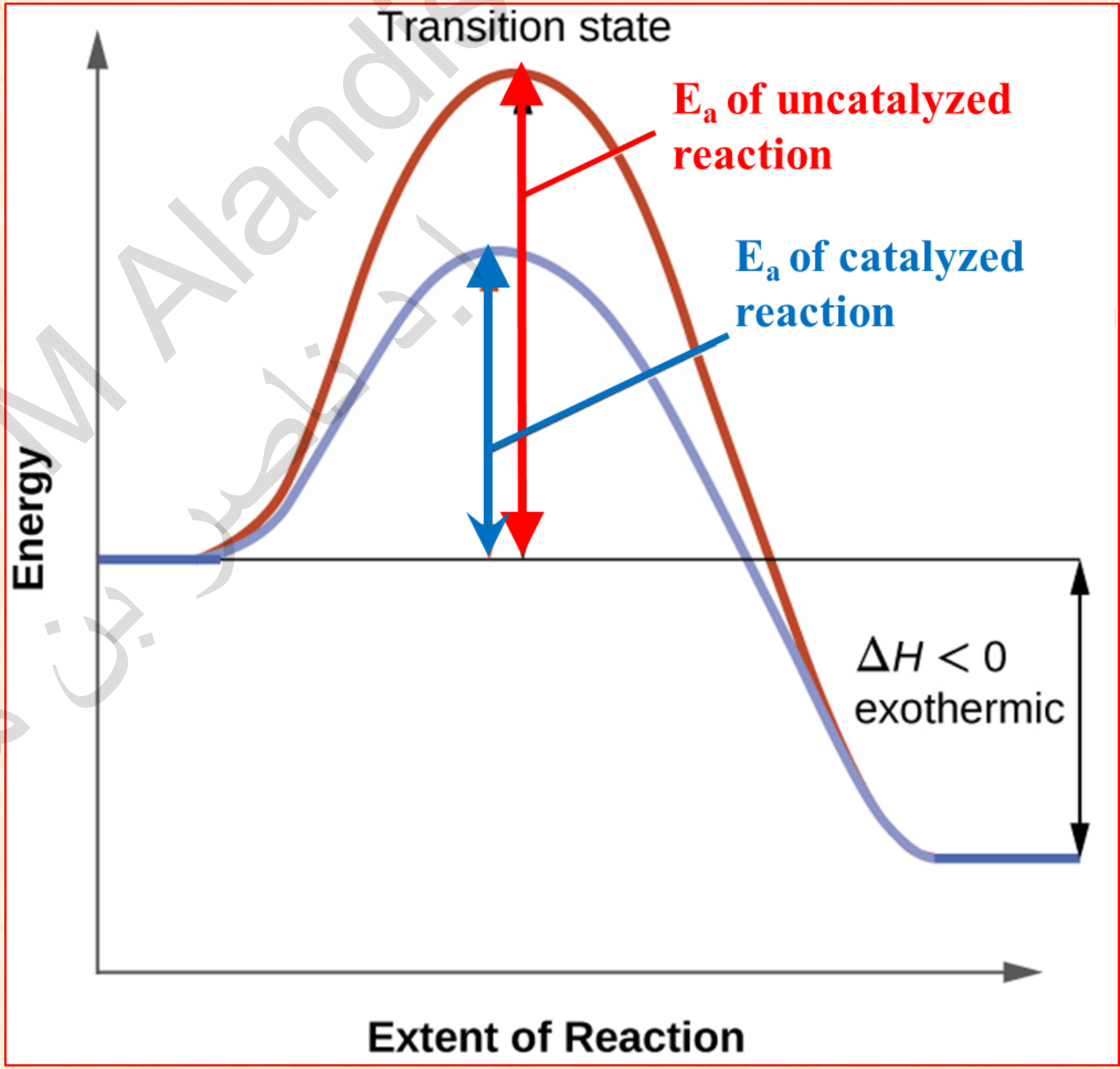
TYPES CATALYST

1. Catalysts are categorized as ***homogeneous*** or ***heterogeneous***.
2. ***Homogeneous*** refers to those catalysts that are dissolved in the reaction medium, forming a single phase with the reactants.
3. The reaction rate is generally proportional to the concentration of the catalyst.
4. ***Heterogeneous catalysts*** exist as a distinct phase from the reaction mixture and are often porous solid particles.
5. The reaction rate is proportional to the surface area of the solid catalyst and the concentration of active centers (catalytic sites).
6. Both categories are important for industrial chemistry.
7. Examples of liquid-phase, acid-base-catalyzed reactions include hydrolysis of esters and amides, enolization of aldehydes and ketones, esterification of alcohols, halogenation of acetone and others.
8. Heterogeneous catalysts play a key role in the production of petrochemicals, including cracking, alkylation, polymerization, isomerization, dehydrogenation and many others.

MECHANISM OF ACTION

1. Most chemical reactions involve simultaneous bond breaking and bond forming.
2. Along the pathway of reactants to products, the molecules form a configuration called the ***transition state*** with potential energy higher than either reactants or products.
3. The transition state is characterized by bonds that are both partially formed and partially broken.
4. Catalysts form an intermediate species with one of the reactants and ***stabilize*** the transition state, allowing the reaction to proceed with a mechanism that requires lower energy.
5. As products form, the catalyst is regenerated.


Increasing energy
Energy, kJ
E_a for uncatalysed reaction
Activation energies for the steps of a catalyzed reaction
E_{a1}
E_{a2}
E_{a3}
Reactants
Products
ΔH for both catalyzed and uncatalyzed reactions
Reaction coordinate


Transition state
E_a of uncatalyzed reaction
E_a of catalyzed reaction
Energy
$\Delta H < 0$
exothermic
Extent of Reaction

SOLID-CATALYZED REACTION STEPS

1. **Diffusion**: Reactants in the fluid phase diffuse to the exterior surface of a catalyst particle and into the catalyst pores
2. **Adsorption:** Reactants adsorb to the active centers in catalyst pores Reaction. The surface-adsorbed reactants form products
3. **Desorption:** The product molecules desorb from the exterior surface of the catalyst pores
4. **Diffusion:** Product molecules diffuse back into the bulk fluid In most cases.
5. One of these steps contributes most significantly to the overall reaction rate, and often the others steps can be ignored or combined when determining reaction rates.
6. The significance of each step depends heavily on the reactants and the reaction conditions.

FACTORS INFLUENCING SOLID CATALYSIS

1. Fluid-dynamic factors
2. Catalyst properties (such as particle size, porosity, pore geometry and surface characteristics)
3. Diffusion characteristics of fluid reactants and products
4. Activation energy requirements for adsorption and desorption of reactants and products to and from solid surfaces
5. Overall **E_a** of the catalyzed reaction
6. Thermal factors (temperature and heat-transport characteristics)

H_2O_2 degrades in the presence of I^-,the reaction takes place in two steps:

$$2H_2O_2 \xrightarrow{k_{exp}} 2H_2O + O_2$$

$$\text{step (1)} \quad H_2O_2 + I^- \xrightarrow{k_1} H_2O + IO^- \quad \text{slow}$$

$$\text{step (2)} \quad H_2O_2 + IO^- \xrightarrow{k_2} H_2O + O_2 + I^- \quad \text{fast}$$

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

I^- is the catalyst

IO^- is the intermediate

step (1) is the slowest step so it’s the rate determining step (**RDS**)

Rate = k_1 [H_2O_2] [I^-]

Molecularity is 1+1 =2 ***(Bimolecular)***

Rate = k_{exp} [H_2O_2] [I^-]