

# **Chapter (2)**

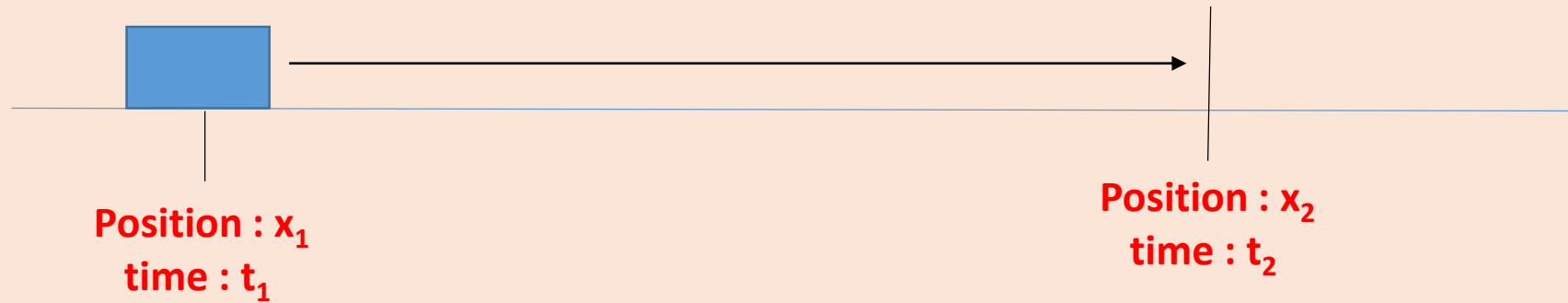
## **Chemical Kinetic**

### **Rate of reaction**

## Kinetic in physics

Kinetic = study of motion = study of variation of distance, velocity or acceleration with respect to time

Variation of distance with respect to time = velocity (v)



The average velocity :

$$\bar{v} = \frac{\Delta x}{\Delta t} = \frac{x_2 - x_1}{t_2 - t_1} = \text{positive value}$$

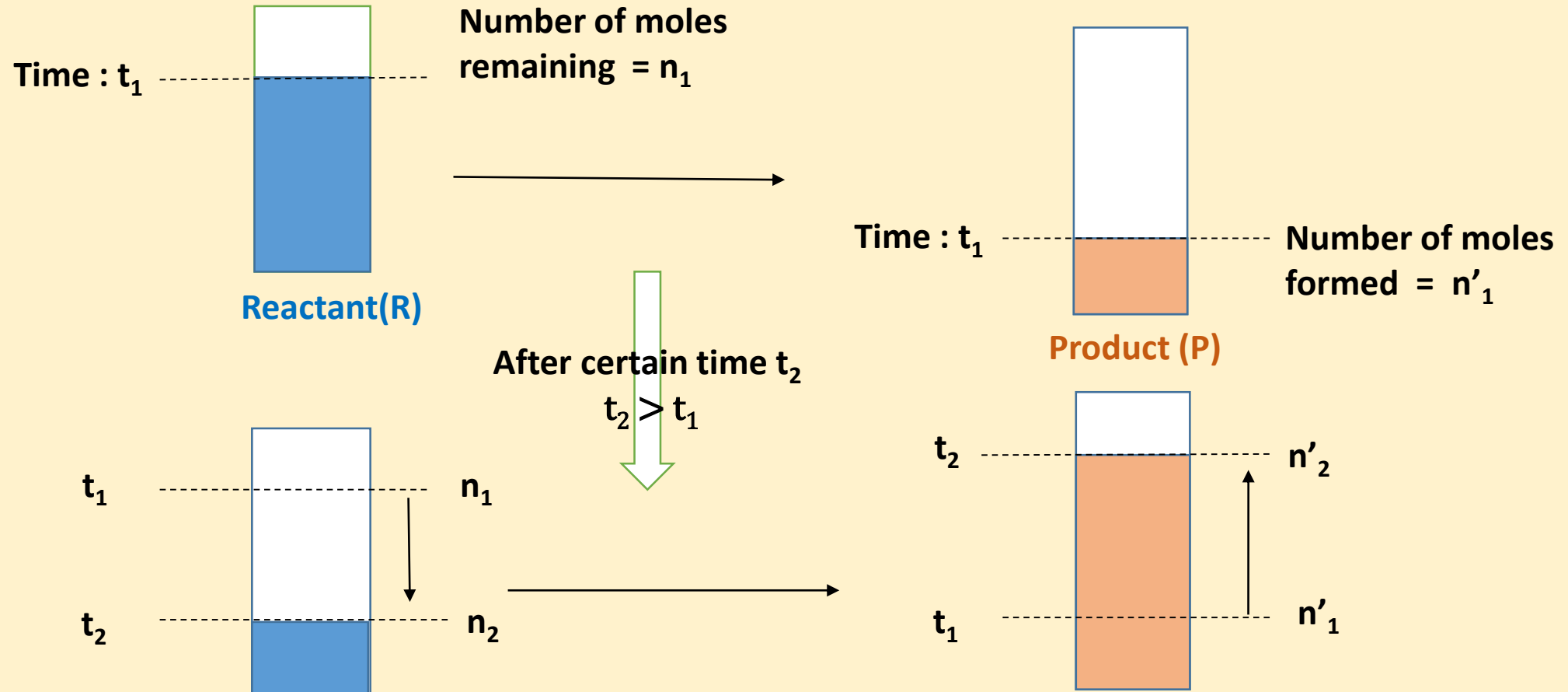
Instantaneous velocity :  $v = \left(\frac{dx}{dt}\right)_t$

# Kinetic in chemistry

Chemical reaction : **reactants**



**products**



$$\text{Average rate} = \frac{\Delta n}{\Delta t} = -\frac{n_2 - n_1}{t_2 - t_1} = \frac{n'_2 - n'_1}{t_2 - t_1} = \text{positive value}$$

## What is chemical kinetic

Chemical kinetic is the study of the progress of a chemical reaction (variation of number of moles or of concentrations) with respect to time

### I- Kinetic curve

The Kinetic curve is the curve representing the variation of **number of moles** or **concentrations** of **reactants** or of **products** as a function of time (sec, min or hours).

In the case of **reactants**, the curve is **decreasing (descending)** and it is called kinetic curve of disappearance.

In the case of **product**, the curve is **increasing (ascending)** and it is called kinetic curve of formation.

Consider the following chemical equation:



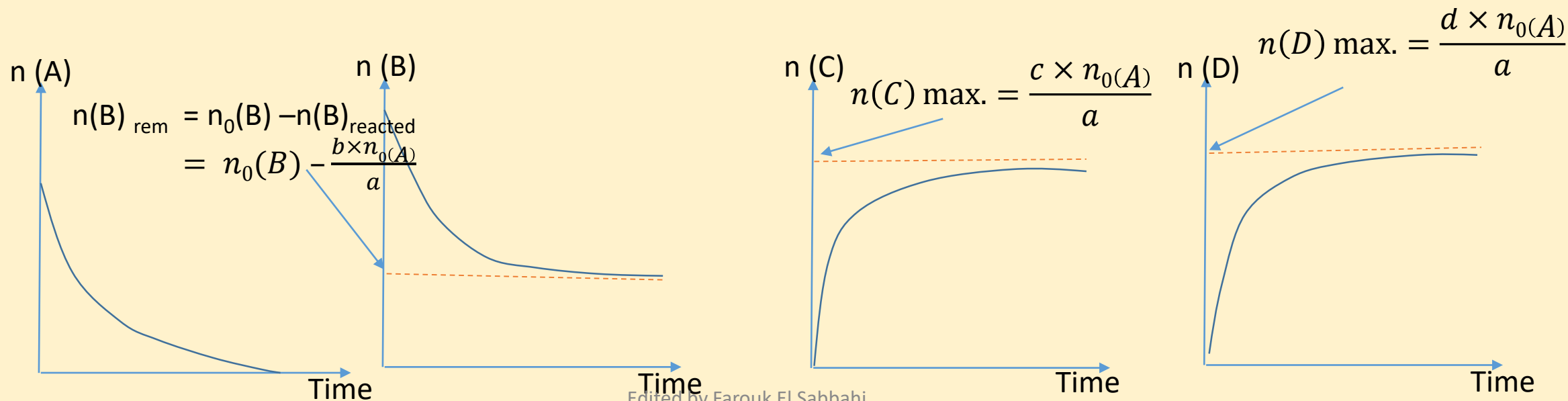
A : is the limiting reactant

B : is the excess reactant

At the end of the reaction, according to S.R :

$$\frac{n_0(A)}{a} = \frac{n(B)_{\text{reacted}}}{b} = \frac{n(C)_{\text{max formed}}}{c} = \frac{n(D)_{\text{max}}}{d}$$

The shapes of kinetic curves of reactants and of products are :



## Application 1

A mass  $m = 32.5 \text{ g}$  of **Zinc** is introduced initially in a solution of **HCl** of concentration  $C = 0.02 \text{ mol/L}$  and of volume  $V = 50 \text{ mL}$ , a reaction took place according to the following equation :



Given :  $M(\text{Zn}) = 65 \text{ g/mol}$

1. Show that the mixture of reactants is not stoichiometric and deduce the limiting reactant.
2. Determine the number of moles of the excess reactant remaining at the end of the reaction.
3. Determine the maximum number of moles of each product at the end of the reaction.
4. Make a progression table representing the initial and the final state of the reaction in mol.
5. Draw the shapes of the kinetic curves of reactants and of products.

## Answer

$$1. \quad n_0(\text{Zn}) = \frac{m_0(\text{Zn})}{M(\text{Zn})} = \frac{32.5}{65} = 0.5 \text{ mol}$$

$$R(\text{Zn}) = \frac{n_0(\text{Zn})}{1} = 0.5$$

$$n_0(\text{HCl}) = C \times V = 0.02 \times 50 \times 10^{-3} = 10^{-3} \text{ mol}$$

$$R(\text{HCl}) = \frac{n_0(\text{HCl})}{2} = \frac{10^{-3}}{2} = 0.0005$$

$R(\text{HCl}) < R(\text{Zn})$  thus **HCl is the limiting** reactant and Zn is in excess.

$$2. \text{ acc. to S.R : } \frac{n(\text{Zn})_{\text{reacted}}}{1} = \frac{n_0(\text{HCl})}{2}$$

$$n(\text{Zn})_{\text{reacted}} = \frac{10^{-3}}{2} = 5 \times 10^{-4} \text{ mol}$$

$$n(\text{Zn})_{\text{remaining}} = n_0(\text{Zn}) - n(\text{Zn})_{\text{reacted}} = 0.5 - 5 \times 10^{-4} = 0.499 \text{ mol}$$

$$3. \text{ acc.to S.R : } \frac{(n(\text{ZnCl}_2)_{\text{max}})}{1} = \frac{n_0(\text{HCl})}{2} = \frac{10^{-3}}{2} = 5 \times 10^{-4} \text{ mol}$$

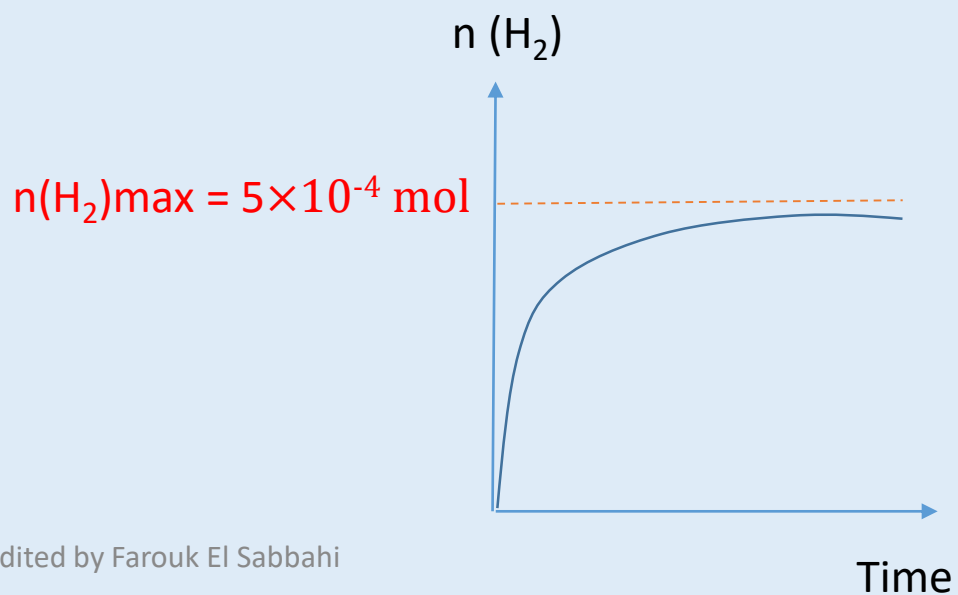
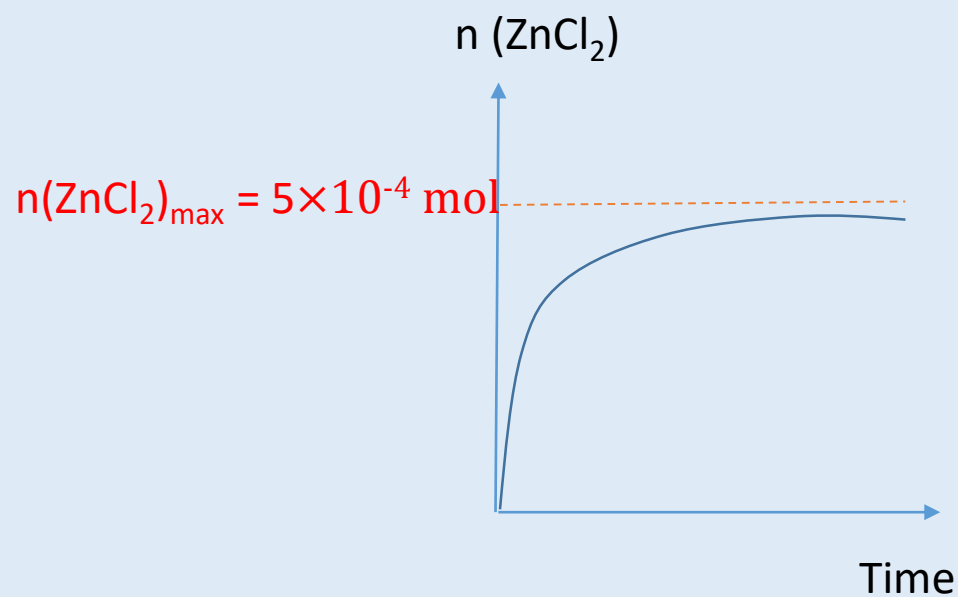
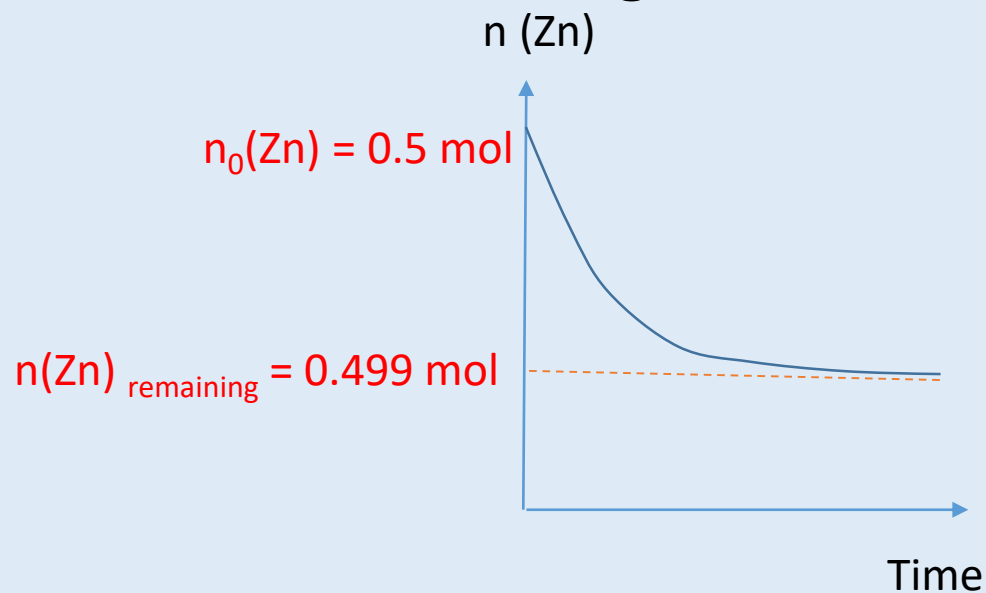
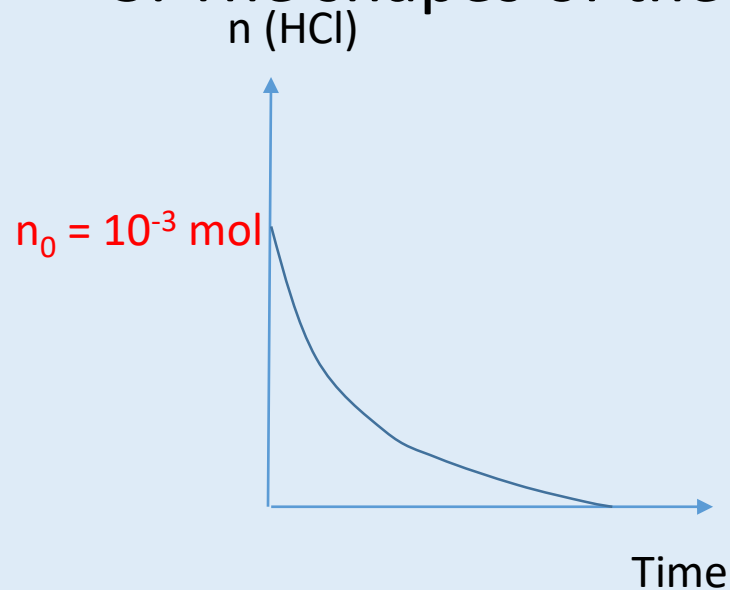
$$n(\text{H}_2)_{\text{max.}} = \frac{n_0(\text{HCl})}{2} = 5 \times 10^{-4} \text{ mol}$$

#### 4. Progression table :

|                     | HCl       | Zn    | ZnCl <sub>2</sub>  | H <sub>2</sub>     |
|---------------------|-----------|-------|--------------------|--------------------|
| Initial state (mol) | $10^{-3}$ | 0.5   | 0                  | 0                  |
| Final state (mol)   | 0         | 0.499 | $5 \times 10^{-4}$ | $5 \times 10^{-4}$ |



## 5. The shapes of the kinetic curves are the following :



## II. Average rate of disappearance of a reactant and average rate of formation of a product

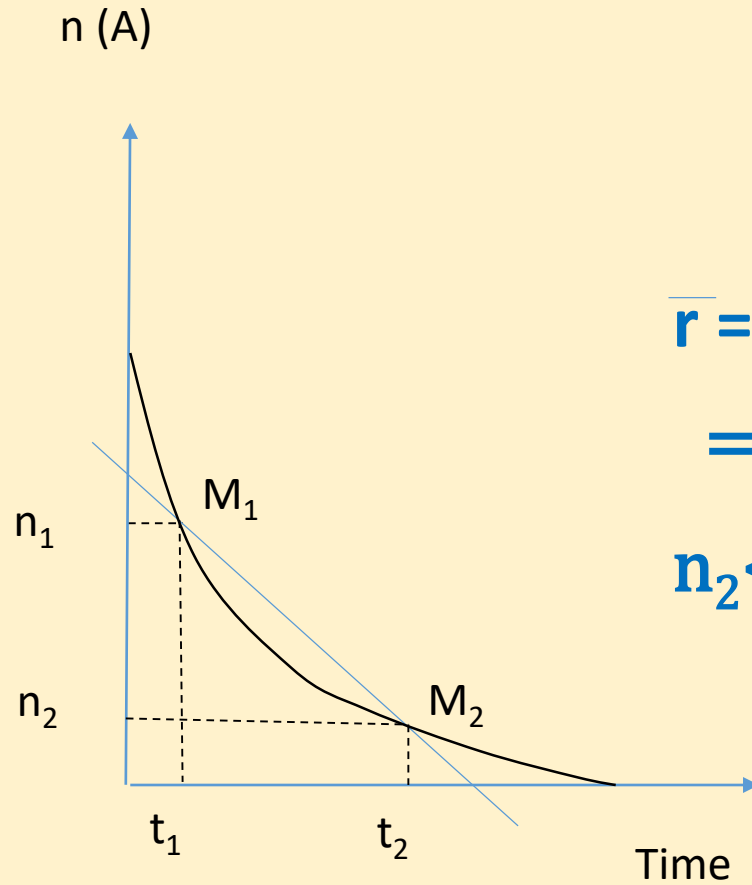
The rate of a reaction can be defined with respect to a reactant (rate of disappearance ) or with respect to a product (rate of formation).

Consider the general equation of a reaction :



The average rate of disappearance of the reactant (A) is equal graphically to the negative slope of the secant  $M_1M_2$  on the curve  $n(A) = f(t)$  , it is defined within an interval of time  $\Delta t = t_2 - t_1$  by :

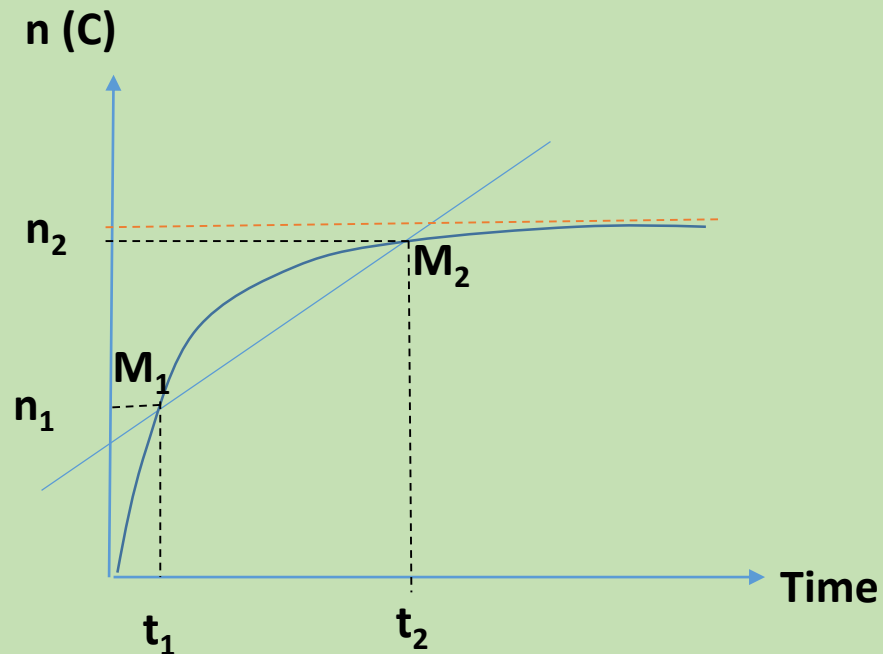
$$\bar{r} = \frac{-\Delta n(A)}{\Delta t} = \frac{-(n_2 - n_1)}{t_2 - t_1}$$



$$\begin{aligned}\bar{r} &= - \text{slope (secant } M_1M_2) \\ &= - \frac{n_2 - n_1}{t_2 - t_1} = \text{positive value} \\ n_2 &< n_1, n_2 - n_1 < 0\end{aligned}$$

The average rate of formation of the product (C) is equal graphically to the slope of the secant  $M_1M_2$  on the curve  $n(C) = f(t)$ , it is defined within an interval of time  $\Delta t = t_2 - t_1$  by:

$$\overline{r} = \frac{\Delta n(C)}{\Delta t} = \frac{n_2 - n_1}{t_2 - t_1}$$



$$\begin{aligned}\overline{r} &= \text{slope (secant } M_1M_2) \\ &= \frac{n_2 - n_1}{t_2 - t_1} = \text{positive value} \\ n_2 &> n_1, n_2 - n_1 > 0\end{aligned}$$

### III. Instantaneous rate of disappearance and instantaneous rate of formation

The instantaneous rate of disappearance of the reactant (A) at a time t is equal to the negative derivative of the function  $n(A) = f(t)$  at the time t:

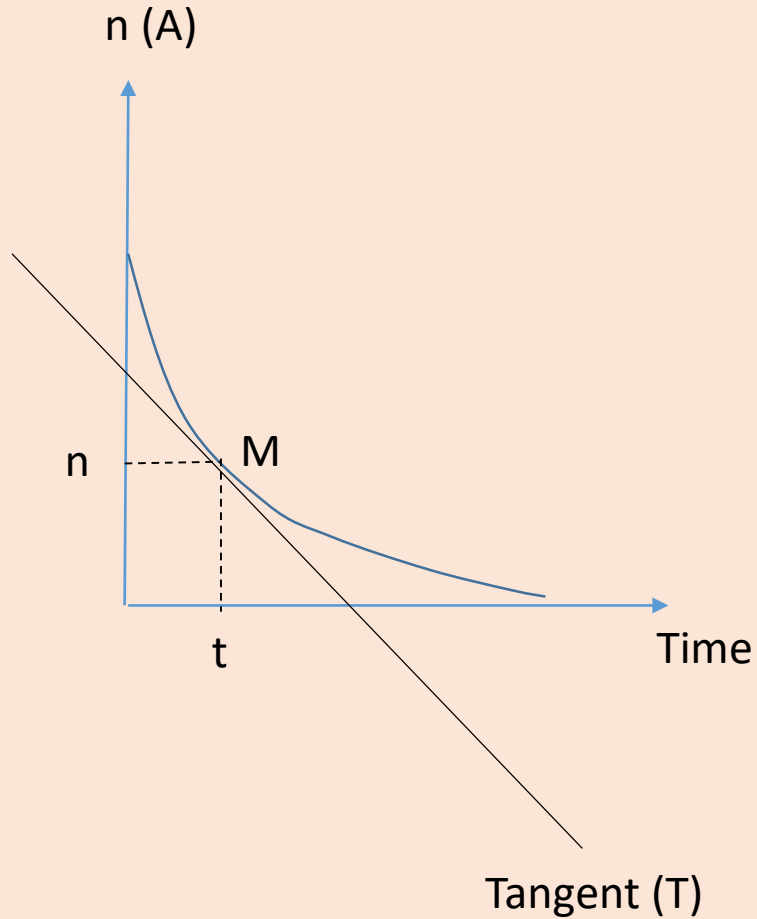
$$r(A)_t = \left( -\frac{dn(A)}{dt} \right)_t$$

Graphically, this rate is equal to the negative slope of the tangent on the curve  $n(A) = f(t)$  at the point M of abscissa t.

#### Note

If the kinetic curve is  $[A] = f(t)$ , the instantaneous rate becomes :

$$r(A)_t = \left( -\frac{d[A]}{dt} \right)_t$$



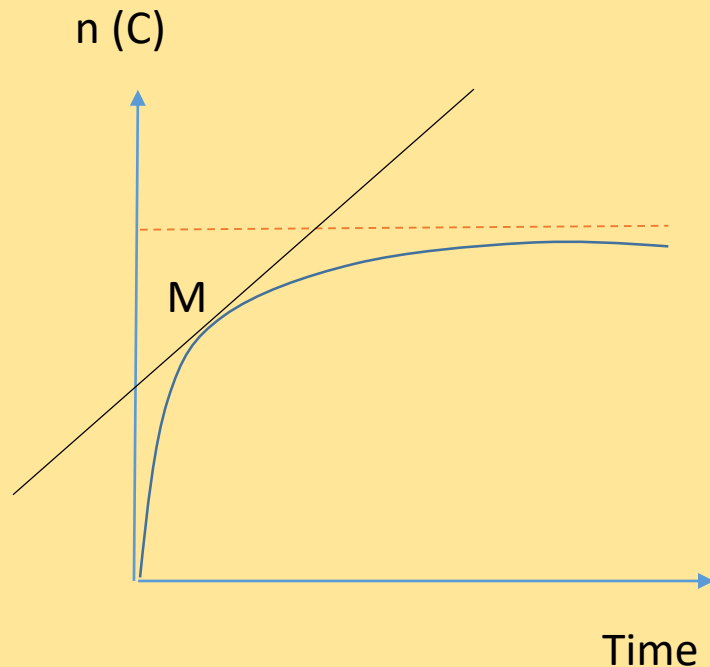
**The value of the slope of the tangent (T) at the point M is negative.**

**The instantaneous rate on the point M is equal to the negative slope of this tangent**

The instantaneous rate of formation of the product (C) at a time  $t$  is equal to the derivative of the function  $n(C) = f(t)$  at the time  $t$ :

$$r(C)_t = \left( \frac{dn(C)}{dt} \right)_t$$

Graphically, this rate is equal to the slope of the tangent on the curve  $n(C) = f(t)$  at the point M of abscissa  $t$ .



**The value of the slope of the tangent at the point M is positive.**

**The instantaneous rate at this point is equal to the slope of the tangent.**

## IV. Unit of rate

The rate (average and instantaneous) has no SI unit.

**The unit of the rate depends on the kinetic curve given.**

- If the curve is  $n(\text{reactant}) = f(t)$  or  $n(\text{product}) = f(t)$ , the rate can be expressed in :

mol/sec ( $\text{mol}.\text{sec}^{-1}$ )

mmol/sec

mol/min( $\text{mol}.\text{min}^{-1}$ )

mmol/min

mol/h( $\text{mol}.\text{h}^{-1}$ )

mmol/h

- If the curve is  $[\text{reactant}] = f(t)$  or  $[\text{product}] = f(t)$ , the rate can be expressed in :

mol/L/sec ( $\text{mol}.\text{L}^{-1}.\text{sec}^{-1}$ )

mmol/L/sec

mol/L/min

mmol/L/min

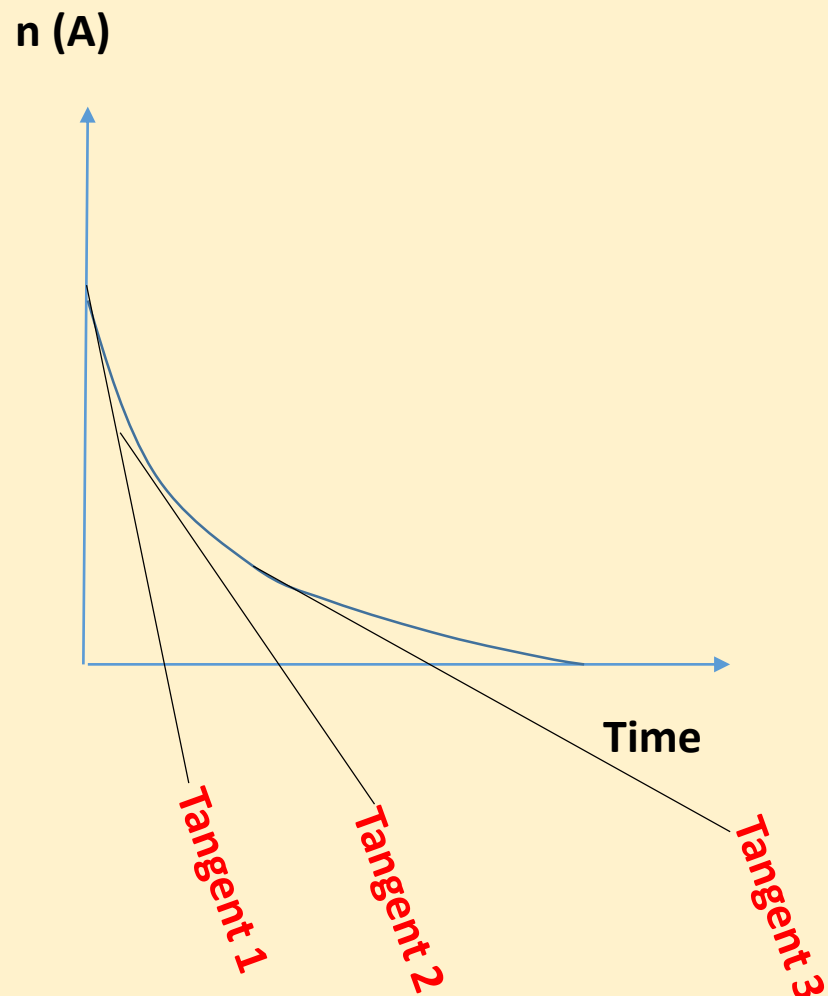
mol/L/h

mmol/L/h



## V. Variation of rate with time

consider the following kinetic curves (reactant and product) :

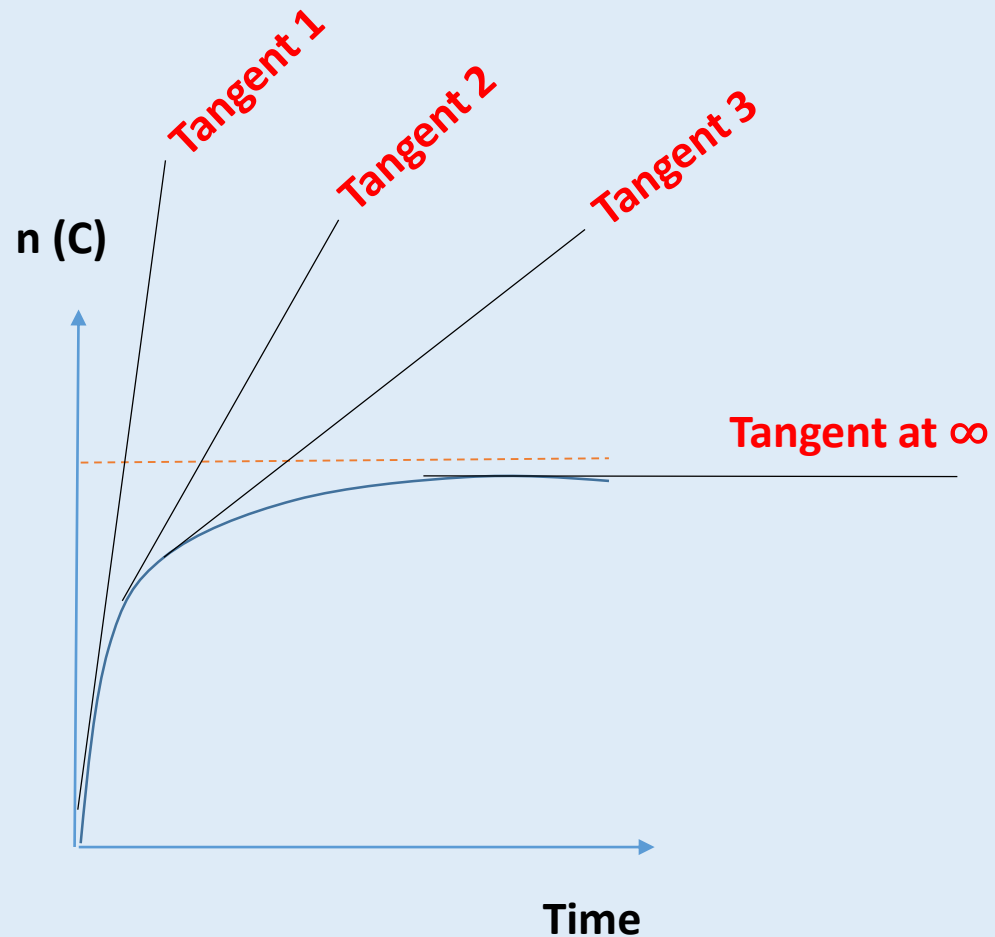


By comparing the negative slopes of the three tangents (1,2 and 3) plotted at three different times ( $t_1 < t_2 < t_3$ ), we remark that :

$$-\text{slope}(1) > -\text{slope}(2) > -\text{slope}(3)$$

Therefore :

$$\text{rate (at } t_1) > \text{rate (at } t_2) > \text{rate (at } t_3)$$



By comparing the slopes of the three tangents (1,2 and 3) plotted at three different times ( $t_1 < t_2 < t_3$ ), we remark that :

$$\text{slope (1)} > \text{slope(2)} > \text{slope(3)}$$

Thus :

$$\text{rate (at } t_1) > \text{rate (at } t_2) > \text{rate (at } t_3)$$

The slope of the tangent plotted at  $\infty$  is equal to zero.

## Conclusion about the variation of rate with time

The rate (disappearance and formation) is maximum at the beginning of the reaction and it decreases as the time elapses to reach zero at the end of the reaction.

## VI. Rate of the whole reaction

Consider the general equation of a reaction :



The rate of the whole reaction and the rates of disappearance of reactants and of formation of products are related by the stoichiometric relation :

$$r(\text{reaction}) = r(A)/a = r(B)/b = r(C)/c = r(D)/d$$

This relation can be applied to the **average** and to the **instantaneous rates**.

## Application 2

At the instant  $t=0$ , a solution of  $\text{H}_2\text{O}_2$  is mixed with a solution of  $\text{KI}$  in the presence of an excess of  $\text{H}_2\text{SO}_4$ .

A reaction took place according to the following equation:



The concentration of  $\text{I}_2$  formed is determined at each instant of time  $t$  and the results obtained are given in the following table:

|                       |   |   |     |     |      |      |      |      |    |    |
|-----------------------|---|---|-----|-----|------|------|------|------|----|----|
| Time (min)            | 0 | 3 | 6   | 9   | 12   | 15   | 18   | 21   | 27 | 30 |
| $[\text{I}_2]$ mmol/L | 0 | 5 | 7.3 | 9.5 | 11.1 | 12.3 | 13.3 | 14.3 | 15 | 15 |

1. Plot the curve  $[\text{I}_2] = f(t)$  in interval of time  $[0 - 30 \text{ min}]$

Scale :  $1\text{cm} = 1\text{mmol/L}$  (y axis)       $1\text{cm} = 2\text{min}$  (x axis)

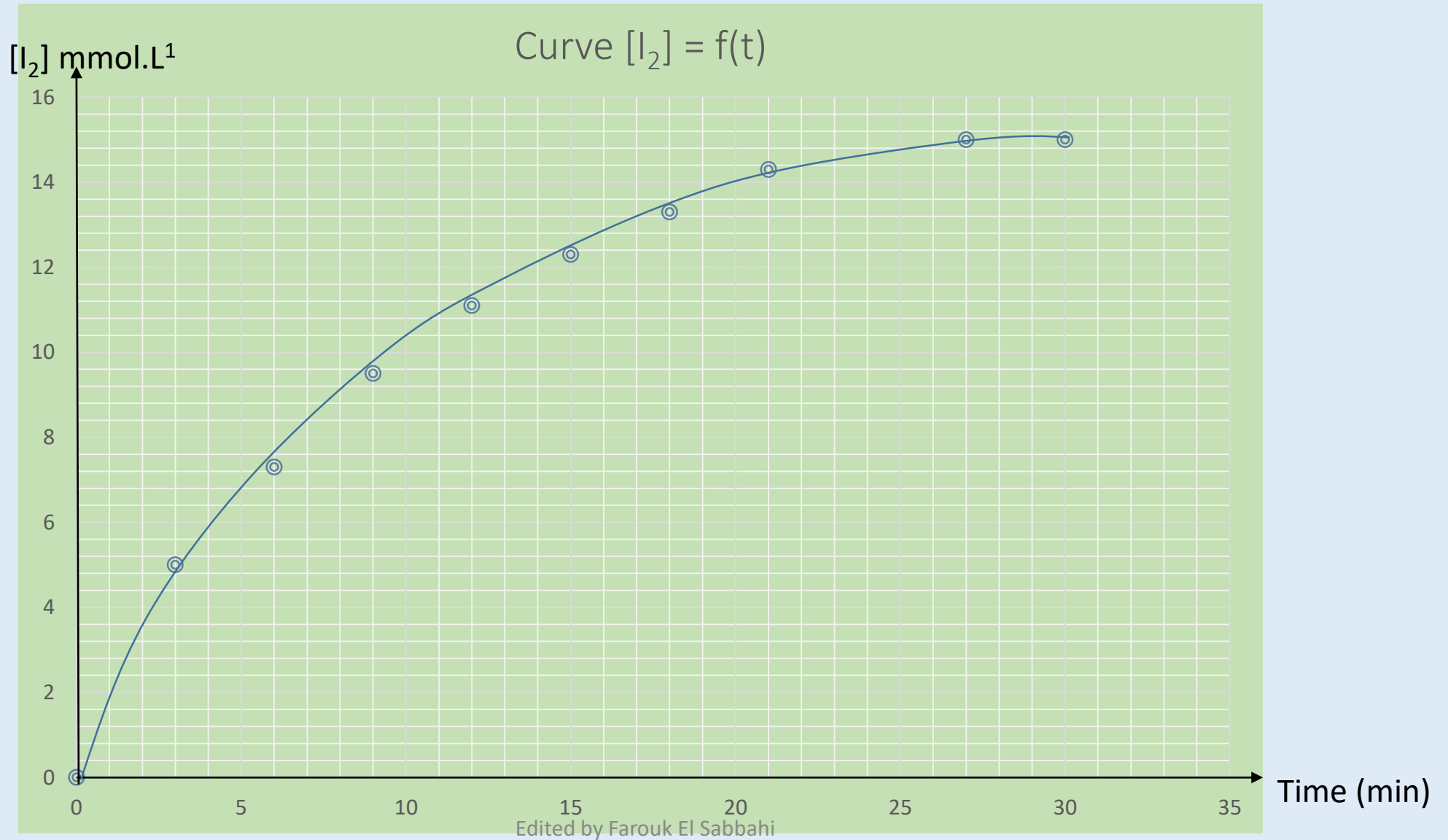
2. Determine the average rate of formation of  $\text{I}_2$  within the interval of time  $[3\text{min}- 15 \text{ min}]$ . Deduce the average rate of disappearance of  $\text{I}^-$  at the same interval.

3. Establish a relation between  $[\text{H}_2\text{O}_2]$  remaining at a time  $t$  and  $[\text{I}_2]$  formed at the same time  $t$ .

4. Show that the time  $t=27 \text{ min}$  is the end time of the reaction.

# Answer

1.



2. The average rate of formation of  $I_2$  within the interval [3-15 min] is equal to the slope of the secant  $M_1M_2$  on the curve  $[I_2] = f(t)$  at the points  $M_1$  and  $M_2$  of abscissa  $t_1 = 3$  and  $t_2 = 15$  min :

$$\begin{aligned} r(I_2) &= \frac{\Delta[I_2]}{\Delta t} = \frac{[I_2]_{t=15} - [I_2]_{t=3}}{15-3} \\ &= \frac{12.3 - 5}{12} = 0.608 \text{ mmol.L}^{-1}.\text{min}^{-1} \end{aligned}$$

Acc. to .SR:  $\frac{r(I^-)}{2} = \frac{r(I_2)}{1}$

$$r(I^-) = 2 \times r(I_2) = 2 \times 0.608 = 1.216 \text{ mmol.L}^{-1}.\text{min}^{-1}$$

3. at any time  $t$  :

$$\text{Acc.to.S.R : } \frac{n(H_2O_2)_{\text{reacted}}}{1} = \frac{n(I_2)_{\text{formed}}}{1}$$

$$\text{And at the same time } t : n(H_2O_2)_{\text{rem}} = n_0(H_2O_2) - n(H_2O_2)_{\text{reacted}}$$

$$\text{Thus : } n(H_2O_2)_{\text{rem}} = n_0(H_2O_2) - n(I_2)_{\text{formed}}$$

Divide the two sides by the total volume of solution, we obtain :

$$[H_2O_2]_t = [H_2O_2]_0 - [I_2]_t$$

4.  $[I_2]_{t=27} = [I_2]_{t=30} = 15 \text{ mmol/L}$

The concentration of  $I_2$  becomes constant at  $t=27$  min, thus the time  $t=27$  min is the end time of the reaction.

### Application 3

The oxidation of  $\text{I}^-$  by  $\text{S}_2\text{O}_8^{2-}$  is a slow reaction that takes place as the following equation :



The measurement of concentration of  $\text{I}_2$  formed at different times are arranged in the following table :

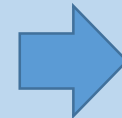
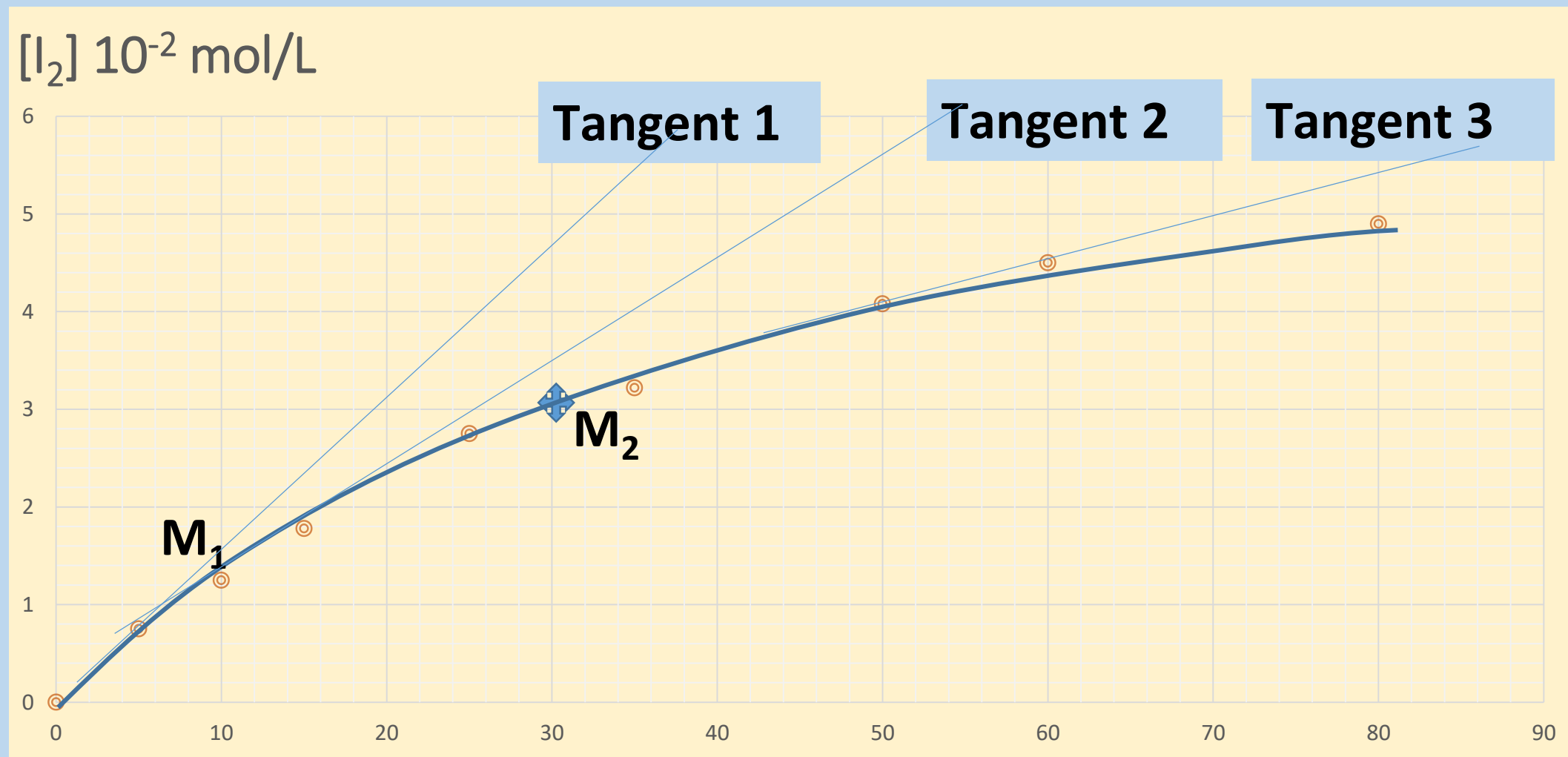
| Time (sec)                                  | 0 | 5    | 10   | 15   | 25   | 35   | 50   | 60   | 80   |
|---|---|------|------|------|------|------|------|------|------|
| $[\text{I}_2] \times 10^{-2} \text{ mol/L}$ | 0 | 0.75 | 1.25 | 1.78 | 2.75 | 3.22 | 4.08 | 4.50 | 4.90 |

1. Plot the curve  $[\text{I}_2] = f(t)$ . Take the following scale : x axis : 1cm = 10 sec  
y axis : 1 cm =  $0.5 \times 10^{-2} \text{ mol/L}$ .
2. Determine the average rate of formation of  $\text{I}_2$  in the interval of time [10 - 30sec].
3. Compare graphically the instantaneous rates of formation of  $\text{I}_2$  at the instants  $t = 5$ ,  $t = 15$  and  $t = 50$  sec. Conclude.



## Answer

1. Curve :  $[I_2] = f(t)$



2. The average rate of formation of  $I_2$  in interval [10-30 sec] is equal to the slope of the secant  $M_1M_2$  on the curve  $[I_2] = f(t)$  at the points  $M_1$  and  $M_2$  :

$$\text{average rate } r = \frac{(\Delta [I_2])}{\Delta t} = \frac{[I_2]_{t=30} - [I_2]_{t=10}}{30 - 10}$$

$[I_2]_{t=30} = 3 \times 10^{-2} \text{ mol/L}$  (this value is deduced from the graph)

$$r = \frac{(3 - 1.25) \times 10^{-2}}{20} = 0.087 \times 10^{-2} \text{ mol/L/sec}$$

3. The instantaneous rate of formation of  $I_2$  at an instant  $t$  is equal to the slope of tangent plotted on the curve  $[I_2] = f(t)$  at the point of abscissa  $t$ . we plot three tangents 1,2 and 3 on the curve at the points of abscissa  $t = 5$ ,  $t=15$  and  $t = 50$  sec.

By comparing the slopes of these tangents, we find : slope 1 > slope 2 > slope 3, thus (rate at  $t=5$ ) > (rate at  $t= 15$ ) > (rate  $t=50$ )

Conclusion : as the time elapses, the rate of the reaction (formation and disappearance ) decreases till reach zero at the end of the reaction.



### Application 4

Given the reaction :  $3 \text{N}_2\text{O} + \text{C}_2\text{H}_2 \rightarrow 3\text{N}_2 + 2\text{CO} + \text{H}_2\text{O}$

At the instant of time  $t = 5$  sec, the rate of formation of  $\text{H}_2\text{O}$  is  $r(\text{H}_2\text{O})_{t=5} = 0.1 \text{ mol.L}^{-1}.\text{sec}^{-1}$ .

1. Calculate the rate of disappearance of each reactant and the rate of formation of each product at the time  $t = 5$  sec.
2. Deduce the rate of reaction at  $t = 5$  sec.

### Answer

1. acc. to. SR :

$$\frac{r(\text{N}_2\text{O})_{t=5}}{3} = \frac{r(\text{C}_2\text{H}_2)_{t=5}}{1} = \frac{r(\text{N}_2)_{t=5}}{3} = \frac{r(\text{CO})_{t=5}}{2} = \frac{r(\text{H}_2\text{O})_{t=5}}{1} = r(\text{Reaction})_{t=5}$$

By replacing  $r(\text{H}_2\text{O})_{t=5}$  by its value we find:

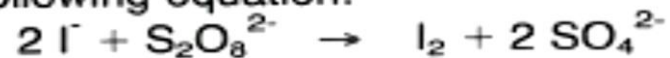
$$r(\text{N}_2\text{O})_{t=5} = 3 r(\text{H}_2\text{O}) = 3(0.1) = 0.3 \text{ mol/L/s}$$

$$r(\text{C}_2\text{H}_2)_{t=5} = r(\text{H}_2\text{O}) = 0.1 \text{ mol/L/s} \quad r(\text{N}_2)_{t=5} = 3 r(\text{H}_2\text{O}) = 0.3 \text{ mol/L/s}$$

$$r(\text{CO})_{t=5} = 2 r(\text{H}_2\text{O}) = 2(0.1) = 0.2 \text{ mol/L/s}$$

2.  $r(\text{reaction})_{t=5} = r(\text{H}_2\text{O}) = 0.1 \text{ mol/L/s}$

- 6 The oxidation of  $I^-$  by  $S_2O_8^{2-}$  is a slow reaction that takes place according to the following equation:



The measurement of the concentrations of  $I_2$  formed at different time intervals are given in the following table:

| Time (s)                                    | 0 | 5    | 10   | 15   | 25   | 35   | 50   | 60   | 80   |
|---|---|------|------|------|------|------|------|------|------|
| $[I_2]$<br>( $10^{-2} \text{ mol.L}^{-1}$ ) | 0 | 0.75 | 1.25 | 1.78 | 2.75 | 3.22 | 4.08 | 4.50 | 4.90 |

- a) Plot the above data on a graph paper and trace the curve  $[I_2] = f(t)$ .

take the following scale :

X axis : 1cm = 5 sec

Y axis : 1 cm =  $0.5 \times 10^{-2} \text{ mol.L}^{-1}$

- b) Determine the average rate of formation of  $I_2$  during the interval of time [10 - 25 sec].

- c) Establish a relation between  $[I^-]$  remained at a time t and  $[I_2]$  formed at the same time t.