T. D. n° 2 (reaction kinetics and chemical equilibria)
Model answer

Exercise n°1 :

Reaction order :

- We have a monomolecular reaction, so the reaction order can be **0 or 1.**
- To determine the reaction order, we graph **[A] = f(t).**
- The graph obtained is a straight line with a negative slope, so the reaction is of **order 0**.

The rate constant k :

Since the reaction is of order 0, we can write : **$[A] = - kt + [A_0]$** so : **the slope = - k**

Graphically :

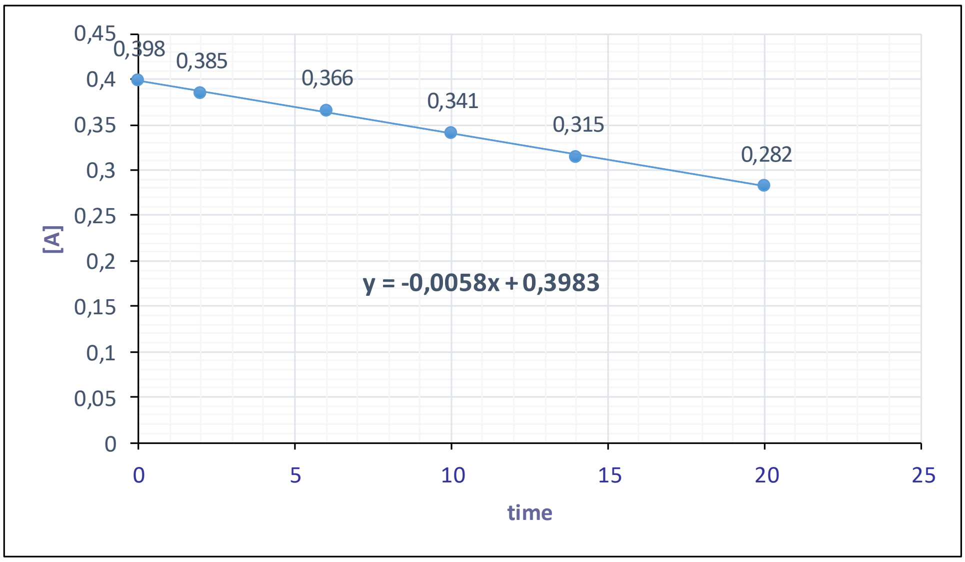
The slope = $- 5{,}75 \times 10^{-3}$ M/S therefore **$k = 5{,}75 \times 10^{-3}\ M.S^{-1}$**

The period (half-reaction time $t_{1/2}$) :

During an order 0 reaction, the half-reaction time is given by the following formula :

$$t_{1/2} = [A_0]/2k$$

Therefore $t_{1/2} = 0{,}398/2 \times 5{,}75 \times 10^{-3}$ from which : **$t_{1/2} = 34{,}6$ S**



Exercise n°2 :

- **Reaction order of each phase :**

The reaction is bimolecular ; therefore, its order can be **1 or 2**. To determine the order of the isocitrate dehydrogenase inactivation reaction for each phase, the Ln(%) activity curve is plotted as a function of time (**Ln(A) = f(t)**) :

Time (min)	0	6	12	18	24	30	36	42	48	54
Ln(A)	4,61	4,53	4,46	4,41	4,35	4,30	4,28	4,22	4,18	4,15
Time (h)	1	1,5	2	3	4	5	6	7	8	9
Ln(A)	4,12	3,99	3,90	3,74	3,60	3,45	3,31	3,16	3,02	2,88

The curves obtained are straight lines with a negative slope ; therefore, the reaction is ***first-order in both phases.***

- **Rate constants :**

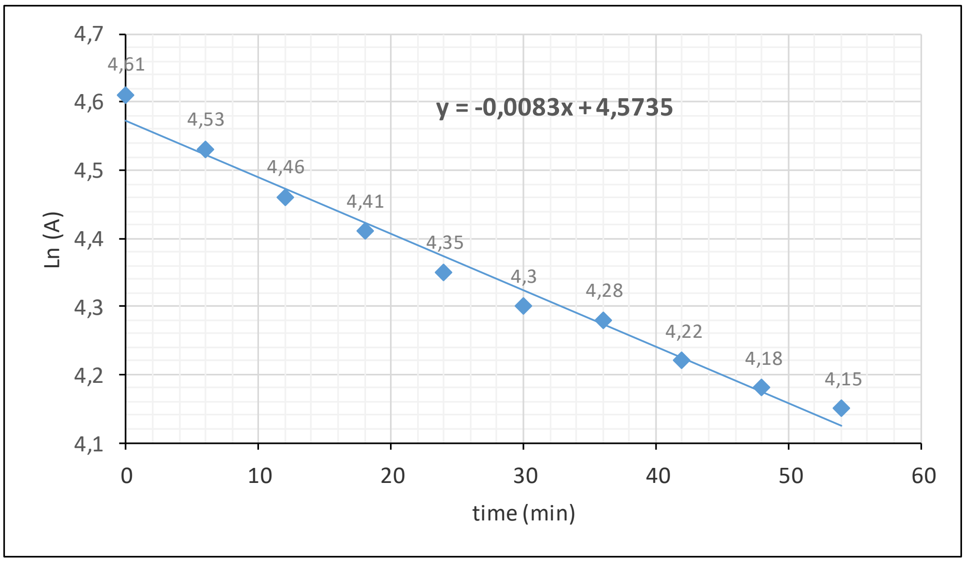
Since the reaction is first order, the activity is given by the following formula :

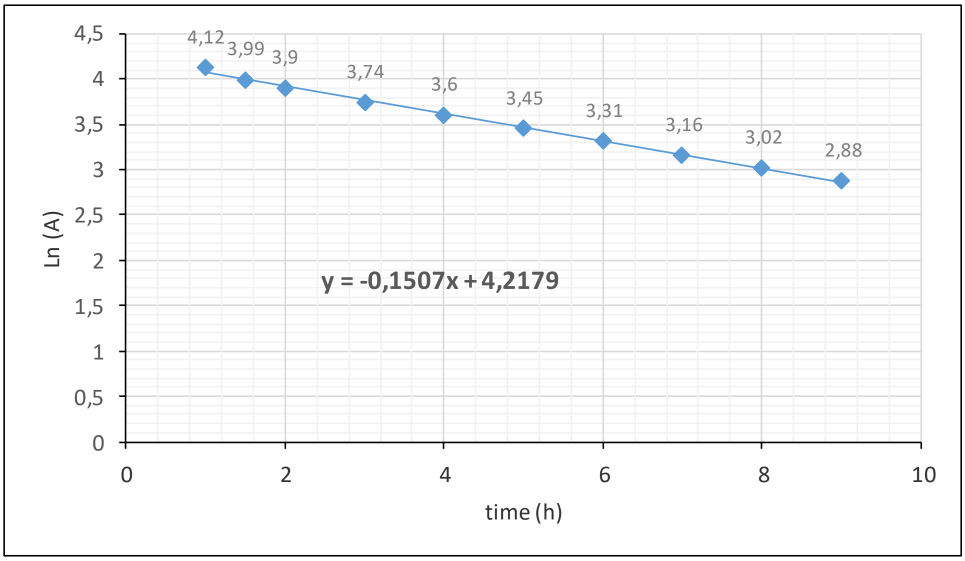
$\ln(A) = -kt + \ln(A)_0$; so the slope of the line obtained is equal to **(-k)**

Graphically :

The rate constant for the fast phase (1) is : **$k = 0{,}0085\ \text{min}^{-1}$**

The rate constant for the slow phase (2) is : **$k = 0{,}0024\ \text{min}^{-1} = 0{,}147\ \text{h}^{-1}$**





Half-reaction time :

The reaction studied is first order, therefore : **$t_{1/2}$ = ln2 / k = 0.69 / k**

The half-reaction time of phase (1) : **$t_{1/2}$ = 81,18 min**

The half-reaction time of phase (2) : **$t_{1/2}$ = 287,5 min**

Exercise n° 3 :

Reaction order :

- The reaction studied is monomolecular, so the reaction order can be **0 or 1**.
- However, the concentration of the remaining native protein **$[P]_n$** reaches a constant value after a certain amount of time.
- This suggests that the reaction tends toward **equilibrium** and is of **order 1**, so we can write:

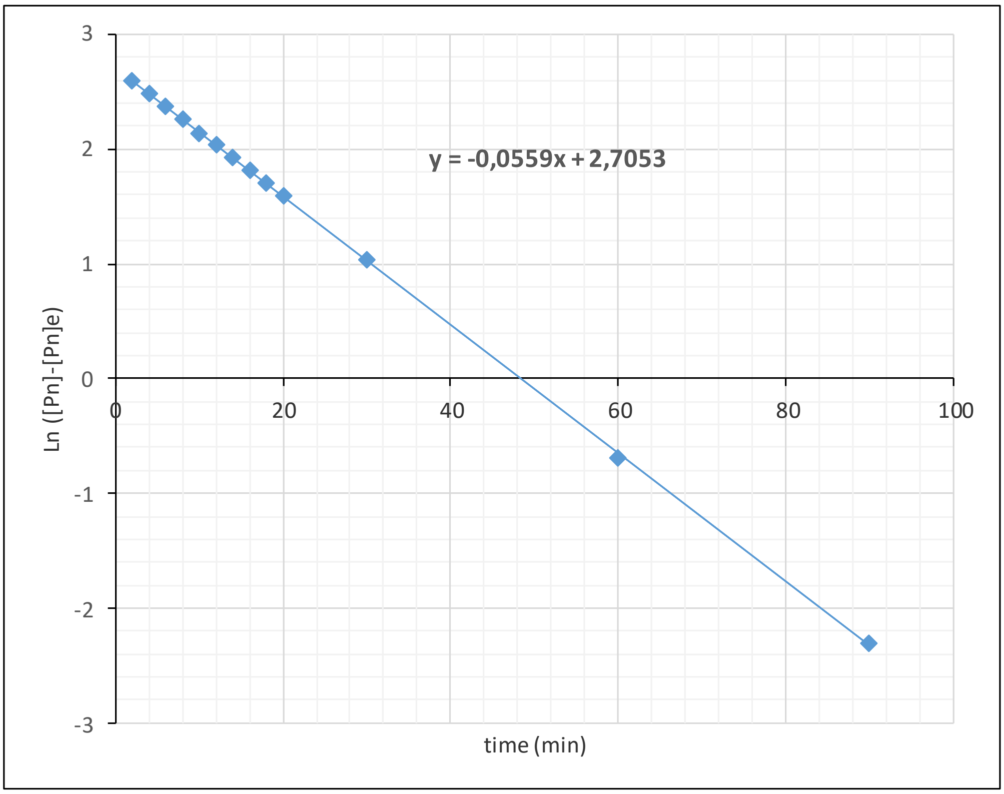
$$P_N \underset{k_{-1}}{\overset{k_1}{\Longleftrightarrow}} P_D$$

With **$k = k_1 + k_{-1}$**

- To confirm the reaction order, the curve is traced : **$Ln([P]_n - [P]_{neq}) = f(t)$** with **$[P]_{neq}$ = 5,2 mg/mL**

T (min)	2	4	6	8	10	12	14	16	18	20	30	60	90
$[P]_n - [P]_{neq}$ (mg/ml)	13,4	12	10,7	9,6	8,5	7,7	6,8	6,2	5,5	4,9	2,8	0,5	0,1
$Ln([P]_n - [P]_{neq})$	2,60	2,48	2,37	2,26	2,14	2,04	1,92	1,82	1,70	1,59	1,03	-0,69	-2,3

The graph obtained is a straight line with a negative slope, so the reaction is ***first-order*** and ***reversible***.



Calculation of the rate constant :

In this case, we can write : $\mathbf{Ln([P]_n - [P]_{neq}) = -kt + Ln([P]_{n0} - [P]_{neq})}$ from which : **the slope = -k**

Graphically :

The slope = - 0,056 therefore : $\mathbf{k = 0{,}056\ min^{-1}}$

Specific constants (k_1 and k_{-1}) :

we have :

$$P_N \overset{k_1}{\underset{k_{-1}}{\longleftrightarrow}} P_D$$

Therefore : $\mathbf{v_1 = k_1 [P]_n}$ and $\mathbf{v_2 = k_{-1}[P]_D}$

in equilibrium : $\mathbf{v_1 = v_2}$ so : $k_1 [P]_{neq} = k_{-1}[P]_{Deq}$ from which : $\mathbf{k_1/k_{-1} = [P]_{Deq} /[P]_{neq}}$

At equilibrium : $[P]_{neq} = 5{,}2$ mg/ml and $[P]_{Deq} = 20{,}2 - 5{,}2 = 15$ mg/ml

Therefore : $k_1/k_{-1} = [P]_{Deq} /[P]_{neq} = 15/5{,}2 = 2{,}88$

This gives the system of equations : $\mathbf{k_1/k_{-1} = 2{,}88}$ and $\mathbf{k_1 + k_{-1} = 0{,}056}$

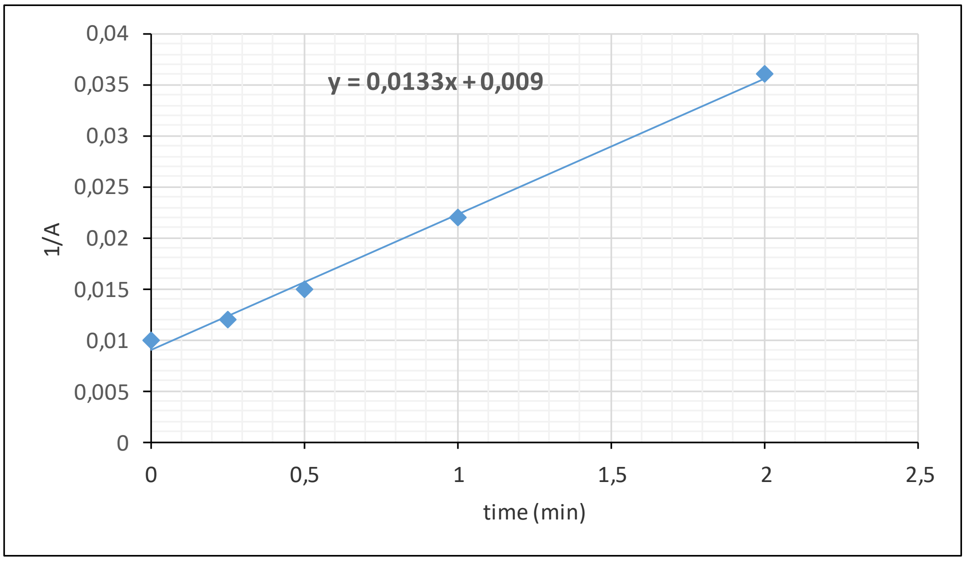
Therefore : $\mathbf{k_1 = 0{,}042\ min^{-1}}$ and $\mathbf{k_{-1} = 0{,}014\ min^{-1}}$

Exercise n° 4 :

Order of reaction :

- The reaction is bimolecular, so the reaction order can be **1 or 2**.
- However, a stoichiometry of **1:1** means that the reaction **order is 2**.
- To confirm order 2, we make a graph : **1/A = f(t)**

Incubation time (min)	0	0,25	0,5	1	2
1/A	0,010	0,012	0,015	0,022	0,036



The graph obtained is a straight line with a positive slope that does not pass through the origin, so the reaction is of **order 2**.

Calculation of the speed constant :

Since the reaction is second order, we can write : **$1/A = kt + 1/A_0$** so : **the slope = k**

Graphically :

The slope = 0,0136 so : **the slope = 0,0136 min^{-1}**

Since this is a percentage of activity and we know that : **$A = v = k\,[E_t]$**

Therefore : k = 0,0136 / 36 x 100

From which : **$k = 3,78 \,.\, 10^{-6}\ nM^{-1}.min^{-1}$**

Exercise n° 5 :

The reaction studied :

pyruvate dehydrogenase + ATP* $\longrightarrow$ pyruvate dehydrogenase - phosphorylated* + ADP

This reaction is catalyzed by protein kinase (PK), so this reaction involves 3 reacting molecules.

Partial order of reaction in relation to protein kinase :

- The partial order is determined by studying the function : **v = f([reagent])**.
- In this reaction, we study the rate of incorporation of **P**^{32} into pyruvate dehydrogenase as a function of protein kinase concentration.

N.B. : *the partial order can be 0 or 1 only.*

- To do this, we make a graphical representation : **v = f([PK])**
- The graph obtained is a straight line with a positive slope that passes through the origin, so the partial order of the reaction with respect to protein kinase is **1.**