Sequence 5: chemical kinetics

Fiches de synthèse mobilisées (collection en français) :

- Fiche 5 : cinétique chimique

Sommaire des activités ETLV :

ACTIVITY 1: Following a reaction using Python

Objective: analyzing a lab experiment in order to acquire vocabulary and determine a half-life

DOCUMENT 1: The reaction

In this activity we study the titration of a hydrogen peroxide solution using iodine ions at pH<7. The iodine ions are in large excess compared to hydrogen peroxide. Hydronium ions, H_3O^+, are also in large excess.

$$\mathrm{H_2O_{2(aq)}} + 2\,\mathrm{I^-_{(aq)}} + 2\,\mathrm{H_3O^+_{(aq)}} \longrightarrow 4\,\mathrm{H_2O_{(liq)}} + \mathrm{I_{2(aq)}}\,.$$

DOCUMENT 2: The concentrations

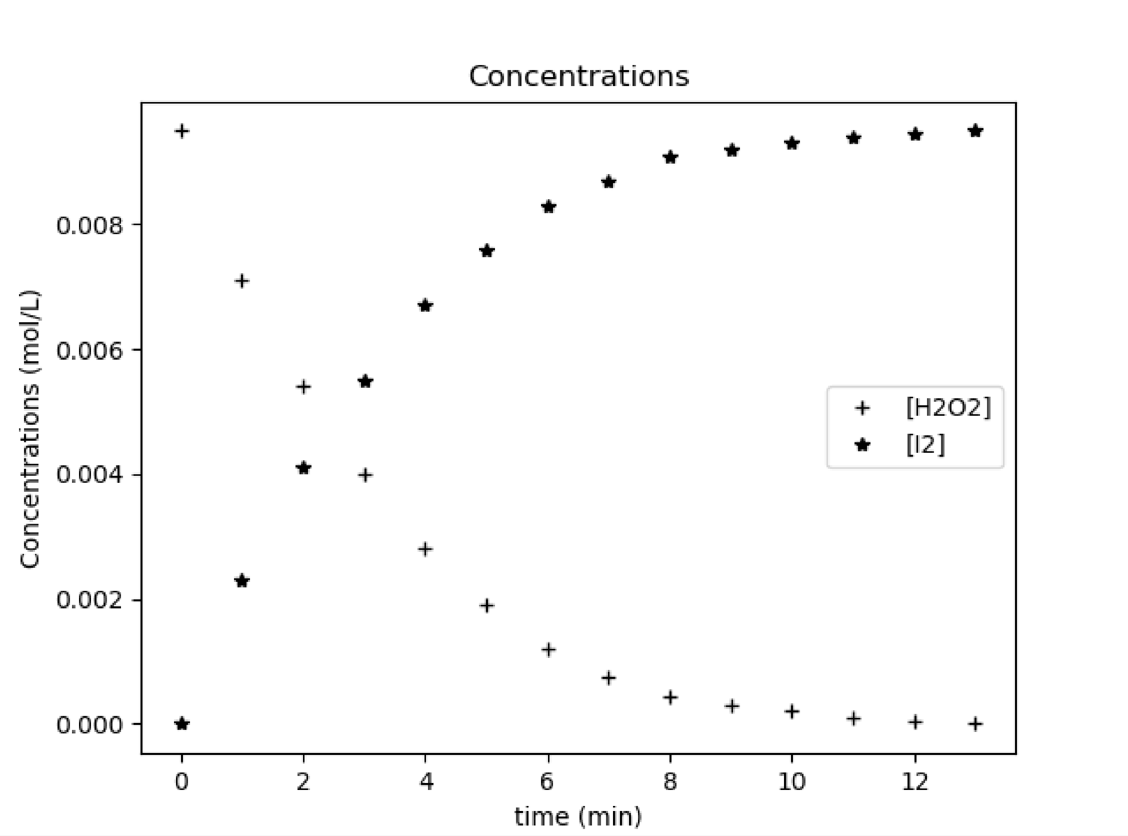
Here are the concentrations obtained over time:

t (min)	$[I_2]$ $(mol \cdot L^{-1})$	$[H_2O_2]$ $(mol \cdot L^{-1})$
0	0,0	$9{,}5 \cdot 10^{-3}$
1	$2{,}3 \cdot 10^{-3}$	$7{,}1 \cdot 10^{-3}$
2	$4{,}1 \cdot 10^{-3}$	$5{,}4 \cdot 10^{-3}$
3	$5{,}5 \cdot 10^{-3}$	$4{,}0 \cdot 10^{-3}$
4	$6{,}7 \cdot 10^{-3}$	$2{,}8 \cdot 10^{-3}$
5	$7{,}6 \cdot 10^{-3}$	$1{,}9 \cdot 10^{-3}$
6	$8{,}3 \cdot 10^{-3}$	$1{,}2 \cdot 10^{-3}$
7	$8{,}7 \cdot 10^{-3}$	$7{,}6 \cdot 10^{-4}$
8	$9{,}1 \cdot 10^{-3}$	$4{,}3 \cdot 10^{-4}$
9	$9{,}2 \cdot 10^{-3}$	$2{,}9 \cdot 10^{-4}$
10	$9{,}3 \cdot 10^{-3}$	$2{,}0 \cdot 10^{-4}$
11	$9{,}4 \cdot 10^{-3}$	$1{,}0 \cdot 10^{-4}$
12	$9{,}45 \cdot 10^{-3}$	$5{,}0 \cdot 10^{-5}$
13	$9{,}5 \cdot 10^{-3}$	$2{,}0 \cdot 10^{-5}$

DOCUMENT 3: The results

One can plot these results using Python:

```
t = [i for i in range(14)]#min
I2 =
[0,2.3E-3,4.1E-3,5.5E-3,6.7E-3,7.6E-3,8.3E-3,8.7E-3,9.1E-3,9.2E-3,9
.3E-3,9.4E-3,9.45E-3,9.5E-3]
H2O2 =
[9.5E-3,7.1E-3,5.4E-3,4.0E-3,2.8E-3,1.9E-3,1.2E-3,7.6E-4,4.3E-4,2.9
E-4,2.0E-4,1.0E-4,5.0E-5,2.0E-5]


plt.figure(1)
plt.plot(t,H2O2,'k+',label="[H2O2]")
plt.plot(t,I2,'k*',label="[I2]")
plt.title ("Concentrations")
plt.xlabel("time (min)")
plt.ylabel("Concentrations (mol/L)")
plt.legend()
plt.savefig("Concentrations")
plt.show()
```



DOCUMENT 4: First order kinetics half-life

In first order reactions, the concentration of the reactant will decrease exponentially

$$[\mathrm{A}] = [\mathrm{A}]_0 exp(-kt)$$

as time progresses until it reaches zero, and the half-life will be constant, independent of concentration.

The time $t_{1/2}$ for [A] to decrease from $[\mathrm{A}]_0$ to $\frac{1}{2}[\mathrm{A}]_0$ in a first-order reaction is given by the following equation:

$$[\mathrm{A}]_0/2 = [\mathrm{A}]_0 exp(-kt_{1/2})$$

It can be solved for

$$kt_{1/2} = -\ln\left(\frac{[\mathrm{A}]_0/2}{[\mathrm{A}]_0}\right) = -\ln\frac{1}{2} = \ln 2$$

For a first-order reaction, the half-life of a reactant is independent of its initial concentration. Therefore, if the concentration of A at some arbitrary stage of the reaction is [A], then it will have fallen to $\frac{1}{2}$[A] after a further interval of (ln 2)/*k*. Hence, the half-life of a first order reaction is given as the following:

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

The half-life of a first order reaction is independent of its initial concentration and depends solely on the reaction rate constant, *k*.

Source: wikipedia

Analyzing and acquiring vocabulary:

In your opinion and using document 3, which is the reactant, which is the product?

____

Are your answers on accordance with document 1?

____

Using document 4, give an estimation of the reaction half-life:

____

ACTIVITY 2: Obtaining an integrated rate law

Objective: to obtain an integrated rate law

DOCUMENT 1: A integrated rate law

The integrated rate law for a first-order reaction is:

$$\ln[\mathrm{A}] = -kt + \ln[\mathrm{A}]_0,$$

Where $[\mathrm{A}]_0$ is the initial concentration at zero time and [A] is the concentration of A at time t. The first-order rate law is confirmed if ln[A] is in fact a linear function of time. In this case the rate constant k is equal to the slope with sign reversed.

Source: wikipedia

DOCUMENT 2: power law

A common form for the rate equation is a power law:

$$v_0 = k[\mathrm{A}]^x[\mathrm{B}]^y \cdots$$

Source: Wikipedia

For the reaction studied in activity 1, we can consider the iodine ions in large excess, thus their concentration will not vary over time, so we can write:

$$v = k[H_2O_2]^p[I^{\neq}]_0^q = k_{app}[H_2O_2]^p \quad \text{with} \quad k_{app} = k[I^{\neq}]_0^q$$

We can relate the rate, v, to the derivative of the hydrogen peroxide concentration which finally yields the rate law of a first order reaction:

$$v = \frac{1}{-1}\frac{\mathrm{d}[\mathrm{H_2O_2}]}{\mathrm{d}t} = k_{\mathrm{app}}[\mathrm{H_2O_2}]$$

Acquiring vocabulary:

Fill in the blanks:

English	French
a rate law	
in large excess	
half-life	
a first order reaction	
a power law	

Reinvesting:

Using document 1 and the last expression in document 2, compute the integrated rate law for the reaction of hydrogen peroxide on iodine ions:

$$\mathrm{H_2O_{2(aq)}} + 2\,\mathrm{I^-_{(aq)}} + 2\,\mathrm{H_3O^+_{(aq)}} \longrightarrow 4\,\mathrm{H_2O_{(liq)}} + \mathrm{I_{2(aq)}}\,.$$

ACTIVITY 3: Determining a reaction order

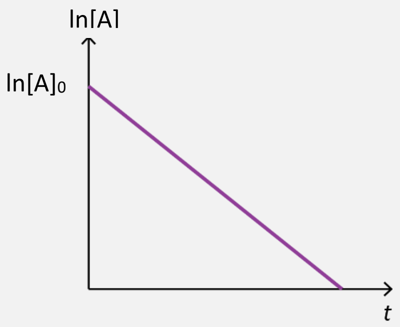
Objective: to determine a reaction order using Python

DOCUMENT 1: Using the integrated rate law

The integrated rate law for a first-order reaction is:

$$\ln[\mathrm{A}] = -kt + \ln[\mathrm{A}]_0,$$

Where $[A]_0$ is the initial concentration at zero time and [A] is the concentration of A at time t. The first-order rate law is confirmed if ln[A] is in fact a linear function of time. In this case the rate constant k is equal to the slope with sign reversed.



Source: wikipedia, collection SPCL PCM terminale

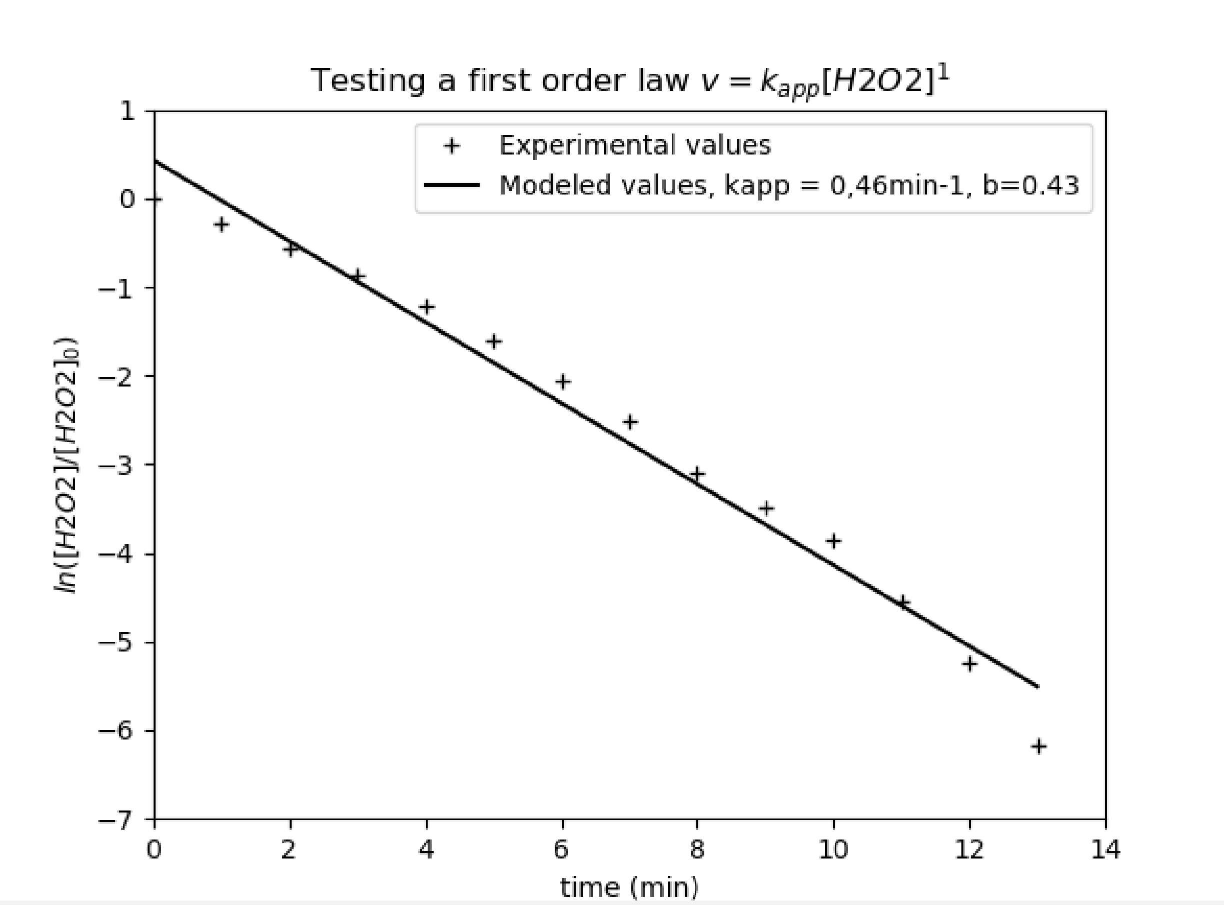
DOCUMENT 2: searching for the reaction order using Python

We decide to test the validity of a first order reaction using Python, therefore we type:

```
from os import chdir
import numpy as np
import matplotlib.pyplot as plt #

t = [i for i in range(14)]
I2 =
[0,2.3E-3,4.1E-3,5.5E-3,6.7E-3,7.6E-3,8.3E-3,8.7E-3,9.1E-3,9.2E-3,9
.3E-3,9.4E-3,9.45E-3,9.5E-3]
H2O2 =
np.array([9.5E-3,7.1E-3,5.4E-3,4.0E-3,2.8E-3,1.9E-3,1.2E-3,7.6E-4,4
.3E-4,2.9E-4,2.0E-4,1.0E-4,5E-5,2.0E-5])

lnH2O2 = np.log(H2O2/H2O2[0])

#model
k,b = np.polyfit(t,lnH2O2,1)
lnH2O2_mod = [k*tps+b for tps in t]

plt.figure(2)
plt.plot(t,lnH2O2,'k+',label='Exprimental values')
plt.plot(t,lnH2O2_mod,'k-',label='Modeled values, kapp = 0,46min-1,
b=0.43')

plt.title ("Testing a first order law $v = k_{app}[H2O2]^1$")
plt.xlabel("time (min)")
plt.ylabel("$ln([H2O2]/[H2O2]_0)$")
plt.xlim(0,14)
plt.ylim(-7,1)
plt.legend()
plt.savefig("Kinetics-order1")
plt.show()
```

DOCUMENT 3: results

The previous code gives:



Analyzing:

Using all documents, document 3 in particular, explain whether a first order was a good hypothesis.

____

____

DOCUMENT 4: First order kinetics half-life

In first order reactions, the concentration of the reactant will decrease exponentially

$$[\mathrm{A}] = [\mathrm{A}]_0 exp(-kt)$$

as time progresses until it reaches zero, and the half-life will be constant, independent of concentration.

The time $t_{1/2}$ for [A] to decrease from $[\mathrm{A}]_0$ to $\frac{1}{2}[\mathrm{A}]_0$ in a first-order reaction is given by the following equation:

$$[\mathrm{A}]_0/2 = [\mathrm{A}]_0 exp(-kt_{1/2})$$

It can be solved for

$$kt_{1/2} = -\ln\left(\frac{[\mathrm{A}]_0/2}{[\mathrm{A}]_0}\right) = -\ln\frac{1}{2} = \ln 2$$

For a first-order reaction, the half-life of a reactant is independent of its initial concentration. Therefore, if the concentration of A at some arbitrary stage of the reaction is [A], then it will have fallen to $\frac{1}{2}$[A] after a further interval of (ln 2)/*k*. Hence, the half-life of a first order reaction is given as the following:

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

The half-life of a first order reaction is independent of its initial concentration and depends solely on the reaction rate constant, *k*.

Source: wikipedia

Analyzing:

Using document 4, give an estimation of the reaction half-life:

____

ACTIVITY 4: Where have all the honeybees gone?

DOCUMENT 1: The case of the vanishing honeybees

Sources : http://ed.ted.com/lessons/the-case-of-the-vanishing-honeybees-emma-bryce

According to the Emma Bryce investigation about honeybees, answer the following questions:

1. Which trivial detail enables to understand why honeybees are vanishing?
2. What are the four elements you can find on the crime scene?

1	2	3	4

3. What are the enigmatic names given by beekeepers for occasional bee disappearance?
4. What are the roles of the bees and why is their disappearance a calamity?
5. What are the three reasons that could explain massive bee disappearance?

Exhibits	A	B	C
Names			
Explanations			

ACTIVITY 5: Pheromones and kinetic monitoring

Within a single hive, thousands of individuals can live in a seamless organization. Honeybees have developed many communication ways:

- chemical communication (through pheromones);
- physical communication (through antennal contact);
- symbolic communication (through dance);

We are interested in the structure of pheromones used by bees to search for food, to locate, to defend themselves or to reproduce.

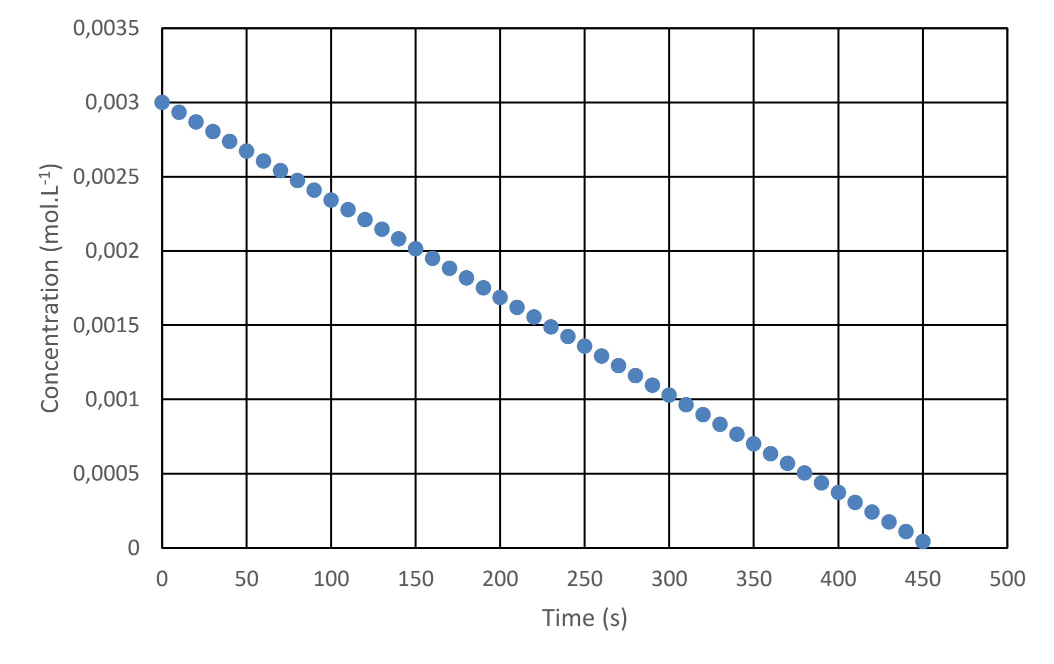
DOCUMENT 1: Pheromones, roles and structure

Pheromones	trans-9-oxodec-2-enoïc acid **(A)**	trans-9-hydroxydec-2-enoïc acid **(B)**	Ethyl cis-octadec-9-enoate	Heptan-2-one	3-methylbutyl ethanoate
Structures					
Secreting bees	Queen	Queen	Queen	Workers	Workers
Signal	Cohesion of the hive, and command to the workers	Queen fertilization	Foraging and rearing behaviour of young bees	Warning	Danger, attack to defend the colony
Symbol					

DOCUMENT 2: Kinetic monitoring of a pheromone transformation

We focus on the rate of biochemical transformation of pheromone **A** to pheromone **B** in the presence of the oxydaze enzyme.

$$pheromone\ \boldsymbol{A}_{(aq)} \rightarrow pheromone\ \boldsymbol{B}_{(aq)}$$



1. Draw the structure of the pheromones in skeletal formula.
2. Which reaction's conditions could be used to transform pheromone **A** to pheromone **B**?
3. Write the volume rate of the reduction reaction of pheromone **A** to pheromone **B**.
4. Using document 2, deduce the order of the reduction reaction.
5. Write the rate law for this reaction.
6. Give the expression of the evolution of the concentration of pheromone **A**: [A] as a function of time.
7. Determine the value of the rate constant **k** of this reaction and indicate its unit.
8. Give the definition of $t_{1/2}$ the half-reaction time.
9. Graphically and by calculation, determine $t_{1/2}$ the half-reaction time.
10. Without the oxydaze enzyme the half-reaction time $t_{1/2}$ is near 90 hours. What is the role of the enzyme?
11. Why is the study of this reaction potentially interesting to save honeybees?

Activity summary

What you must remember:

- **rate law**
- **half-life**
- **integrated rate law**

Skills linked to the curriculum**:**

Compétences	Capacités à maîtriser	Où dans cette séquence ?
APP	Utiliser du vocabulaire spécifique	Activités 1, 2, 3, 4, 5
	Lire et comprendre des documents scientifiques	Activités 1, 2, 3, 4 et 5
ANA	Mettre en lien des documents pour émettre des hypothèses en réponse à une question scientifique	Activités 1, 3, 5
COM	S'exprimer à l'écrit en utilisant le vocabulaire adapté	Activités 1, 2, 3 et 5
REA	• Etablir la loi d'évolution de la concentration d'une espèce en fonction du temps pour une réaction d'ordre 0 ou d'ordre 1.	Activité 2
	• Déterminer l'ordre d'une réaction et la constante de vitesse en exploitant des données issues d'un suivi cinétique.	Activité 3
	• Déterminer le temps de demi-réaction.	Acticités 1 et 3
	• Capacités numériques : exploiter un suivi cinétique pour déterminer l'ordre de réaction.	Activité 3
	• Effectuer des conversions d'unité	Activité 5