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.

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

DOCUMENT 2: The concentrations

Here are the concentrations obtained over time:

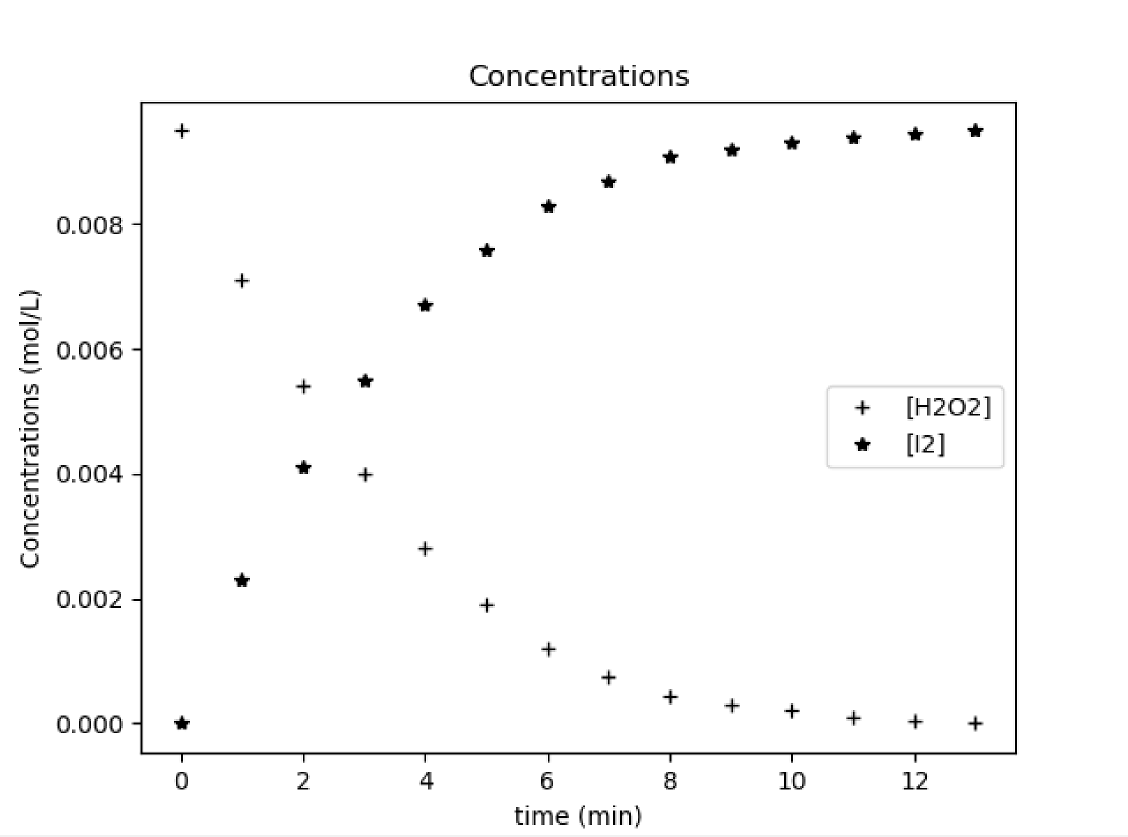
t (min)	$[I_2]$ $(mol \cdot L^{-1})$	$[H_2O_2]$ $(mol \cdot L^{-1})$
0	0,0	$9{,}5 \cdot 10^{-3}$
1	$2{,}3 \cdot 10^{-3}$	$7{,}1 \cdot 10^{-3}$
2	$4{,}1 \cdot 10^{-3}$	$5{,}4 \cdot 10^{-3}$
3	$5{,}5 \cdot 10^{-3}$	$4{,}0 \cdot 10^{-3}$
4	$6{,}7 \cdot 10^{-3}$	$2{,}8 \cdot 10^{-3}$
5	$7{,}6 \cdot 10^{-3}$	$1{,}9 \cdot 10^{-3}$
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 $[A]_0$ to $\frac{1}{2}[A]_0$ 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?

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Are your answers on accordance with document 1?

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

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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 $[A]_0$ 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:

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

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ACTIVITY 3: Determining a reaction order

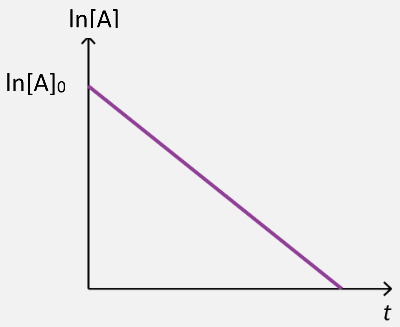
Objective: to determine a reaction order using Python

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

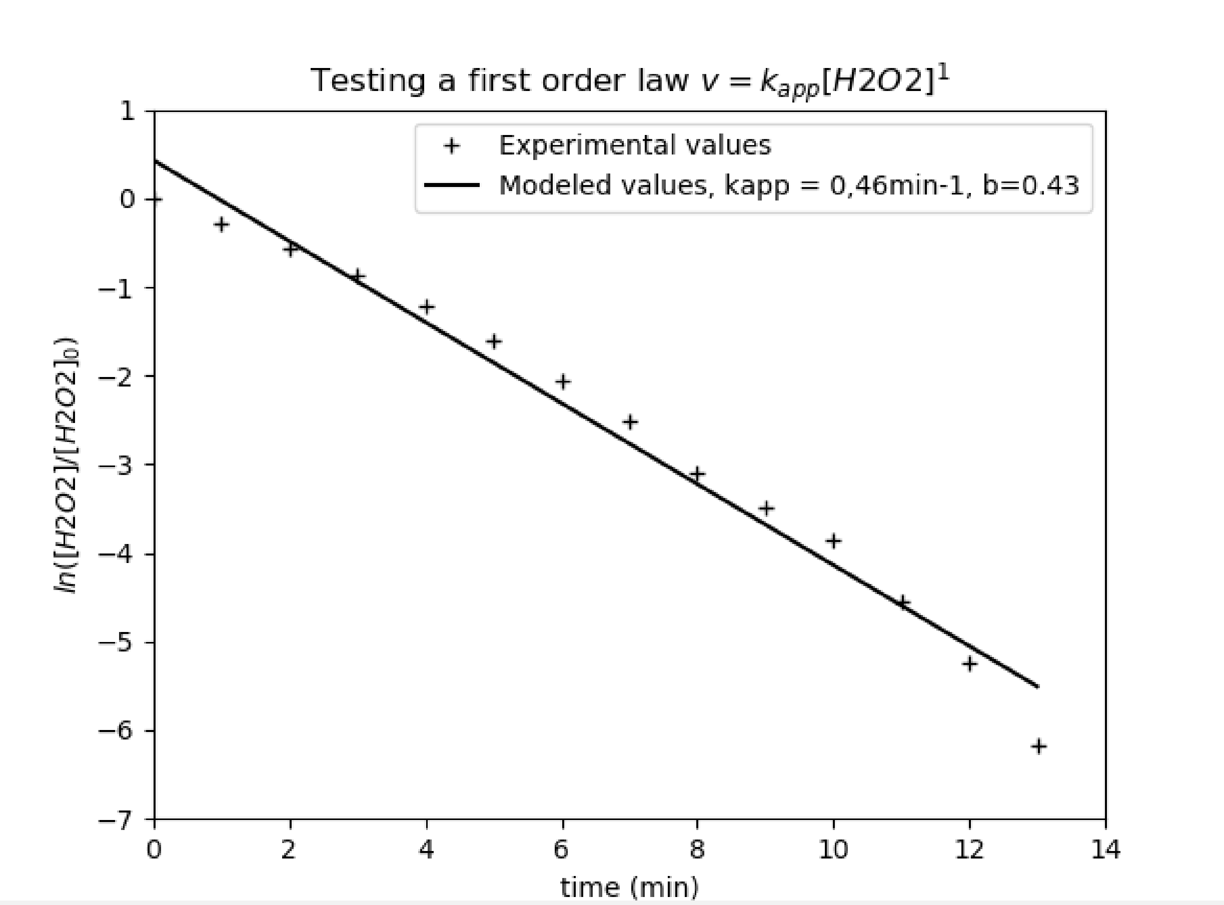
DOCUMENT 2: searching for the reaction order using Python

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.

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DOCUMENT 4: First order kinetics half-life

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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:

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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 et 3
	Lire et comprendre des documents scientifiques	Activités 1, 2 et 3
ANA	Mettre en lien des documents pour émettre des hypothèses en réponse à une question scientifique	Activités 1 et 3
COM	S'exprimer à l'écrit en utilisant le vocabulaire adapté	Activités 1, 2 et 3
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. • Déterminer l'ordre d'une réaction et la constante de vitesse en exploitant des données issues d'un suivi cinétique. • Déterminer le temps de demi-réaction. • Capacités numériques : exploiter un suivi cinétique pour déterminer l'ordre de réaction.	Activité 2 Activité 3 Acticités 1 et 3 Activité 3