Practical Session n°8: KINETIC STUDY BY SPECTROPHOTOMETRY

1- INTRODUCTORY PART

Data

Hydrogen peroxide H_2O_2 is an oxidizing agent mainly used as a bleaching agent and disinfectant. In acidic conditions, it reacts with iodide ions to produce diiodine I_2: $H_2O_{2(aq)} + 2\ I^-_{(aq)} + 2\ H^+_{(aq)} \rightarrow 2\ H_2O_{(l)} + I_{2(aq)}$

The colour of an aqueous solution of diiodine goes from yellow to brown depending on its concentration.

The Lambert-Beer law

For one selected wavelength λ, the absorbance A of a chemical species in solution is proportional to the concentration of the solution: $A_\lambda = k.C$ where $k = \varepsilon_\lambda.l$

ε_λ is the molar absorption coefficient. It depends on λ and is usually expressed in $L.mol^{-1}.cm^{-1}$.

l is the thickness of the tank (ie the distance travelled by light through the solution).

OBJECTIVE

We aim at studying the kinetics of this reaction by spectrophotometry. The idea is to draw the graph of the amount of diiodine formed as a function of time and to exploit this curve.

AVAILABLE EQUIPMENT

- a spectrophotometer to measure the absorbance A of a solution for different wavelengths
- 7 identical cuvettes for spectrophotometry
- a data acquisition system, a computer with LatisPro
- 5 calibrated diiodine solutions of concentrations C:
  1.5×10^{-3} mol.L^{-1}, 1.2×10^{-3} mol.L^{-1}, 9.0×10^{-4} mol.L^{-1}, 6.0×10^{-4} mol.L^{-1} and 3.0×10^{-4} mol.L^{-1}
- distilled water
- an aqueous hydrogen peroxide solution of concentration $C_1 = 3.0\times10^{-3}$ mol.L^{-1}
- an aqueous potassium iodide solution ($K^+ + I^-$) of concentration $C_2 = 2.5\times10^{-1}$ mol.L^{-1}
- a concentrated solution of sulphuric acid in a dropping bottle
- a magnetic stirrer + a stir bar
- Glassware : 2 volumetric pipettes of 10.0 mL, beakers
- a propipetter

THE WORK TO BE DONE

Suggest a method to determine the amount of diiodine formed by the reaction as a function of time.

REMINDER

Half-life of a reaction $t_{1/2}$

Time needed by the advancement to reach half its final value.

If the reaction is total, it corresponds to the time needed to decrease by half the initial amount of the limiting reactant.

Concentration for a solution

$$C = \frac{\text{amount of the chemical species that has been dissolved}}{\text{Volume of the solution}} \qquad C = \frac{n}{V}$$

Concentration for a solute X

$$[X] = \frac{\text{amount of the solute X present in solution}}{\text{volume of the solution}} \qquad [X] = \frac{n_X}{V}$$

2- EXPERIMENTAL PROCEDURE

a) Choosing the wavelength λ for the colorimeter

- Open LatisPro.
- Connect the colorimeter to the data acquisition system.
- Setting of the blank (In general, the blank is the solvent): follow the instruction on the computer screen.
  Select the blue radiation (λ = 470 nm) and place a cuvette containing the reference sample (distilled water). Adjust the transmission (TRANS) to 100% by turning the button on the colorimeter.
  - Acquisition parameters:
  Choose **"Pas à pas"**, select **"Abscisse clavier"** then "**Nom: concentration**" and "**unité: mol.L^{-1}**".
- Place a cuvette containing the solution 1 inside the colorimeter.
- Press **F10**. **Caution:** Don't write the value of the concentration and don't click on "Acquérir".
- Record the value of the absorbance A corresponding to the chosen wavelength on your report.
- Measure the absorbance for the other wavelengths (green, yellow and red).

Conclusion: *Which wavelength λ should you choose to carry out your kinetic study?*

b) Plotting the calibration curve

You dispose of 5 calibrated solutions with different concentrations of diiodine.

Solution	1	2	3	4	5
$[I_2]$ in mol.L^{-1}	3.0×10^{-4}	6.0×10^{-4}	9.0×10^{-4}	1.2×10^{-3}	1.5×10^{-3}
A					

- Select the appropriate wavelength. Wait for a minute to stabilize the emitted light.
- Check the blank: place the cuvette containing the reference sample (distilled water). Adjust the transmission (TRANS) to 100% by turning the button on the colorimeter.
- Acquisition
  ☼ Place the cuvette containing the solution 1 in the colorimeter.
  ☼ Write the concentration of the solution and click on "**Acquérir**".
  ☼ Repeat this procedure for each calibrated solution.
  ☼ Press **"Echap"** to stop the acquisition.
- Plot the graph giving the absorbance of the solution as a function of the concentration in diiodine: $A = f([I_2])$.
- Build a model of this curve by a linear function.
- *Record the equation of the model $A = k.[I_2]$ by replacing k with the obtained value.*

c) Following the kinetics of the reaction

- Open a new file: **"Fichier"**, "**Nouveau**".
- Set the blank again.
- Acquisition parameters: choose **"Temporelle"** and **"Durée totale": 20 min**.
- Pour a volume V_1 = 10.0 mL of a solution of hydrogen peroxide in a beaker.
- Add 5 drops of concentrated sulphuric acid. Then add a volume V_2 = 10.0 mL of a solution of potassium iodide.
- **Immediately**: Fill a cuvette with the reaction mixture. Place it in the colorimeter and carry out the acquisition by pressing **F10**. (Press "**Echap**" if you want to stop the acquisition before its end).

d) Exploiting the results

Display the following curves on the computer screen.

a) Concentration of diiodine as a function of time:
Open the calculation sheet in LatisPro to calculate the concentration of diiodine from the equation of the calibration curve.

b) Amount of diiodine which has been formed as a function of time:
On the calculation sheet in LatisPro, calculate the amount of diiodine formed for each measurement.
Display this curve in a new window.

c) Amount of hydrogen peroxide which has not reacted as a function of time:
On the calculation sheet in LatisPro, calculate the amount of hydrogen peroxide remaining for each measurement.
Display this curve in the previous window.

d) ***Determine the half-life of the reaction.***

e) ***Check that hydrogen peroxide is the limiting reactant.***

Report
Write down your report on OpenOffice. Describe the experiments, paste your curves and record your results.