L3 - Chemical kinetics - Practical teaching session

The Effect of Ionic Strength on the Oxidation of Iodide by Iron(III)

This practical teaching includes personal preparatory work to be given to the teacher at the beginning of the session. <u>Access to the practical work room is subject to the delivery of this work</u>.

Preliminary work and experimental report are expected in french.

I. Introduction

The oxidation of iodide by iron(III) (1) has been transformed into a clock reaction using thiosulfate as a limiting reagent and starch as a colorimetric indicator for I_3^- ions.

$$2 \operatorname{Fe}^{3+}_{(aq)} + 3 \operatorname{I}^{-}_{(aq)} \to 2 \operatorname{Fe}^{2+}_{(aq)} + \operatorname{I}^{-}_{3(aq)}$$
(1)

The principle of the clock reaction, based on the extremely fast reaction (2), is to delay the appearance of the characteristic blue colour of the triiodide-starch complex. This allows for the experimental determination of a time corresponding to a known progression of the reaction (1).

$$2 S_2 O_3^{2^-}{}_{(aq)} + I_3^{-}{}_{(aq)} \rightarrow S_4 O_6^{2^-}{}_{(aq)} + 3 I^{-}{}_{(aq)}$$
(2)

It was previously demonstrated that reaction (1) is first order with respect to iron(III) and second order with respect to iodide ions under high ionic strength conditions (l > 1 M). This is expressed by equation (3) where Δt is the time elapsed from the mixing of the two reagents to the sudden colour change and k is the reaction rate coefficient.

$$v_0 = \frac{1}{2} \frac{[S_2 O_3^{2^-}]_0}{\Delta t} = k [Fe^{3^+}]_0 [I^-]_0^2$$
(3)

Based on the above rate law, the following mechanism (4) has been proposed for reaction (1):

step 1	$Fe^{3+}_{(aq)} + I^{-}_{(aq)} \leftrightarrows FeI^{2+}_{(aq)}$	fast, K ₁	
step 2	$Fel^{2+}_{(aq)} + I^{-}_{(aq)} \to Fe^{2+}_{(aq)} + I^{-}_{2^{-}_{}(aq)}$	k ₂	- (4)
step 3	$2 \mid_{2^{-}(aq)} \rightarrow \mid_{3^{-}(aq)} + \mid_{(aq)}$	k ₃ >> k ₂	

The purpose of this experimental session is to investigate and rationalize the influence of the ionic strength on the rate constant of reaction (1). In the following, activity coefficients will be estimated by the extended Debye-Hückel law (5), holding as long as the ionic strength $I \sim 0.1 \text{ mol}\cdot\text{L}^{-1}$.

$$\log \gamma_i = -A_{DH} z_A^2 \frac{\sqrt{I}}{1+\sqrt{I}} \tag{5}$$

where A_{DH} is a constant from the Debye-Hückel law (A_{DH} = 0.511 for aqueous solutions at 25 °C), whereas z_A is the charge number of the reacting ion.

II. <u>Experimental setup</u>

The experiments are conducted in a thermostated cell placed on a magnetic stirrer. A total of 50 mL of solution A (containing $Na_2S_2O_3$, KI and starch) is placed in a 100 mL becher, thermostated at 25°C

and stirred. Then 5 mL of solution B (containing $Fe(NO_3)_3$ and HNO_3) is taken by an automatic pipette and rapidly injected into solution A while simultaneously starting the stop watch.

Warning : see with teacher or technician for the use of automatic pipette.

Time, Δt , is recorded at the moment the solution suddenly turns dark blue. The experiment is conducted three times for each ionic strength, which is adjusted with HNO₃.

Stock solutions :

	$Na_2S_2O_3$	KI	amidon	Fe(NO₃)₃	HNO₃
c (mol·L⁻¹)	1,1×10 ⁻²	1,1	2 %	3,3×10 ⁻¹	3

HAZARDS : Concentrated nitric acid HNO₃ is both a strong acid and a powerful oxidizing agent. Contact with the skin can result in severe burns. The vapor irritates the respiratory system, eyes, and other mucous membranes. Pay particular attention to the handling of this chemical reagent.

Protocol :

• The initial concentrations at the time of mixing of solutions A and B (i.e. t=0) should be as follows: $[Fe(NO_3)_3]_0 = 3 \text{ mmol}\cdot L^{-1}$, $[KI]_0 = 20 \text{ mmol}\cdot L^{-1}$, $[Na_2S_2O_3]_0 = 0.5 \text{ mmol}\cdot L^{-1}$, w(starch) = 0.02 %. $[HNO_3]_0$ is adjusted to fit initial ionic strength values I_0 ranging from 50 to 200 mM.

• The measurements are conducted at 25 °C.

• Throw away a coin if it falls back on the head side, you will be in charge of the first set of ionic strengthes (50, 100 and 150 mM), if it falls back on the tail side, you'll be in charge of the second set of ionic strength values (i.e. 75, 125, 175 mM).

• Complete the following tables (reproduced in your report) for the preparation of solution A (500 mL) and solution B (25 mL) from the stock solutions.

Solution A	$Na_2S_2O_3$	KI	amidon
V (mL)			

<i>I</i> ⁰ value expected	Solution B	Fe(NO ₃) ₃	HNO₃	HNO₃
just after mixing			Theorical	Experimental
(mol·L⁻¹)			value	value*
	V1 (mL)			
	V ₂ (mL)			
	V₃ (mL)			

* to be completed during the session – For more precision and reproducibility, take both volumes with an automatic pipette.

• Measure the time Δt for each ionic strength <u>three times</u>. Note the results in the following Table (reproduced in your report) and complete also the excel file available in the lab.

<i>I</i> ₀ (mol·L ⁻¹)	Δt_1 (s)	$\Delta t_2(s)$	∆t₃(s)	$\Delta t_{\text{average}}$ (s)

- Clean and store glassware and benchtop before starting the report
- Analyze your experimental data using linear regression on the available computers.

• Are your experimental data in line with the theoretical analysis of the mechanism you have carried out ?

• Can you conclude about the validity of the proposed mechanism ?

Personal preparatory work to be given to the teacher at the beginning of the session.

Preliminary remark : the assumption that activities match concentrations is clearly not valid in the present case.

Part I. Preparation of the experimental session

- 1. Express the ionic strength of the reaction mixture containing $Fe(NO_3)_3$, HNO_3 , $Na_2S_2O_3$ and KI at the very start of the reaction.
- 2. Calculate its value for the following chemical composition : $[Fe(NO_3)_3]_0 = 3 \text{ mmol} \cdot L^{-1}$, $[KI]_0 = 20 \text{ mmol} \cdot L^{-1}$, $[Na_2S_2O_3]_0 = 0.5 \text{ mmol} \cdot L^{-1}$.
- 3. Complete the following table with the amount of HNO₃ from the stock solution added to solution B (25 mL) to reach the following ionic strength values at the mixing time with solution A (50 mL). *Remember that HNO₃ is a strong acid.*

<i>I</i> ₀	50	75	100	125	150	175
(mmol·L⁻¹)						
V _{HNO3} in B						
(mL)						

Part II. Theoretical analysis of mechanism (4)

- 1. Identify the rate-limiting step of mechanism (4) and give the expression of its rate law.
- 2. By applying the transition-state theory to the rate limiting step and using the extended Debye-Hückel law (5), establish the expression of its rate constant k_i as a function of the ionic strength I and k_i^0 , the rate constant value for a ionic strength value equal zero.
- 3. Under experimental conditions where iodide in excess as compared to ferric ions, establish the following expression of [Fel²⁺], valid at short times, as a function of K₁, [Fe³⁺]₀ (which is defined as the total initial amount of ferric ions), [I⁻]₀ and *I*. You will here neglict the amount of products formed at short times by steps 2 and 3.

$$[FeI^{2+}] = \frac{K_1[Fe^{3+}]_0[I^-]_0}{K_1[I^-]_0 + 10^{6A_{DH}\frac{\sqrt{I}}{1+\sqrt{I}}}}$$

- 4. According to this last equation, establish the expression for the initial rate v_0 of reaction (1) as a function of K₁, k₂⁰, [Fe³⁺]₀, [I⁻]₀ and *I*.
- 5. The value reported for K_1 is $3,9 \times 10^3$ at 25°C. Under the ionic strength range investigated in the present study (see Part I.), establish the simplified expression for log(Δt) as a function of ionic strength, *I*.
- 6. Based on your theoretical analysis, which graphical representation will allow you to analyze your experimental results using linear regression to validate (or not) the proposed mechanism?