Exercise 1 (7 points)

Kinetics study of the synthesis of hydrogen iodide (HI)

It is required to carry out a kinetic study of the synthesis of hydrogen iodide HI. The equation of the slow reaction, assumed to be complete, is:

$$H_{2(g)} + I_{2(g)} \longrightarrow 2HI_{(g)} \quad \text{(Reaction 1)}$$

For this purpose, eight round bottom flasks (1L each) are placed at a constant temperature of 350°C; each contains 0.5 mmol of iodine gas and 5 mmol of hydrogen gas.

At time (t), one of the round bottom flasks is cooled suddenly and the remaining iodine is dissolved, using an appropriate method, so as to obtain 200 mL solution. By adding few drops of starch, the solution turns blue. The solution is then titrated with an aqueous sodium thiosulfate solution ($2Na^{+}_{(aq)} + S_2O_3^{2-}{}_{(aq)}$) having a concentration of $5x10^{-2}$ mol L^{-1}. The volume of sodium thiosulfate solution added to reach the equivalence point is denoted by V. The same procedure is repeated at different time (t) for the contents of the other flasks.

The following table (document -1) shows the results of the different titrations carried out:

Round bottom flask	A	B	C	D	E	F	G	H
Time t (in min)	50	100	150	200	250	300	350	400
V(in mL)	16.6	13.6	11.4	9.0	7.4	5.6	4.0	3.0
n(HI) in mmol	0.17	0.32	0.43	0.55	0.63	0.72	0.80	

Document-1

1. <u>Preliminary Study:</u>

1.1. Determine the number of moles of HI formed at the end of the reaction (1).

1.2. Justify the importance of each of the following steps performed before the titration:

- The sudden cooling of the round bottom flask.
- The addition of starch to the iodine solution.

2. <u>Kinetic study of the synthesis of hydrogen iodide</u>

The net ionic equation of the titration reaction of iodine with thiosulfate ions is:

$$I_{2\,(aq)} + 2S_2O_3^{2-}{}_{(aq)} \rightarrow 2I^{-}_{(aq)} + S_4O_6^{2-}{}_{(aq)} \quad \text{(Reaction 2)}$$

2.1. Show that, at each time (t), the number of moles of HI formed is related to the volume V of thiosulfate solution, poured at time (t) and expressed in mL, by the following relation:

$n(HI)_{(t)\text{ in mmol}} = 1 - 5.10^{-2}\,V$

2.2. Referring to document -1, calculate n (HI) at t= 400 min. Deduce whether the synthesis of HI has gone to completion at this instant of time.

2.3. Plot, on a graph paper, the kinetic curve n(HI) = f (t). Take the following scale:

Abscissa: 1cm for 50 min Ordinate: 1cm for 0.1 mmol.

2.4. The rate of formation of HI is determined at two instants: t_1=150 min and t_2 =250min. The following values were found: $r = 2.24x10^{-4}$ mmol.min^{-1} and $r' = 1.74x10^{-5}$ mmol.min^{-1}.

2.4.1. Assign each value of the rate to the corresponding time.

2.4.2. Specify the kinetic factor that explains this evolution.

2.5. Determine, based on the graph, the half life $t_{1/2}$ of this reaction.

3. Study the effect of some kinetic factors:

In order to study the effect of certain kinetic factors on the rate of reaction (1), two other experiments (2 and 3) are performed. The following table (document-2) summarizes the results of the three experiments (1, 2 and 3). The volume is kept constant for the 3 experiments.

	$n(H_2)_{initial}$ in mmol	$n(I_2)_{initial}$ in mmol	Temperature (°C)	The rate of formation of HI at t= 150min in $mmol.min^{-1}$
Experiment (1)	5	0.5	350	2.24×10^{-4}
Experiment (2)	8	0.5	350	
Experiment (3)	5	0.5	T	3.0×10^{-4}

Document -2

3.1 Specify, based on document -2, whether each of the following statements is true or false.

- The half life of experiment (2) is greater than that of experiment (1).
- At the end of reaction (1), the number of moles of HI in the three experiment reaches the same value.
- The temperature T of the reaction medium in experiment (3) should be greater than 350°C.

Exercise 2 (7points) Sodium Thiosulfate and Hydrochloric Acid

In acidic medium, thiosulfate ions ($S_2O_3^{2-}$) react slowly and completely with the hydronium ions (H_3O^+), according to the following equation:

$$S_2O_{3\,(aq)}^{2-} + 2\,H_3O^+_{(aq)} \rightarrow S_{(S)} + SO_{2(aq)} + 3H_2O_{(\ell)}$$

In order to study the kinetic of the above reaction, the following experiment is carried out, At the instant $t = 0$, a volume $V_1 = 10.0$ ml of a hydrochloric acid solution ($H_3O^+ + C\ell^-$) of concentration $C_1 = 5.0$ mol.L^{-1} is poured into a beaker containing a volume $V_2 = 40.0$ ml of a sodium thiosulfate solution ($2Na^+ + S_2O_3^{2-}$) of a concentration $C_2 = 0.5$ mol.L^{-1}.

By an appropriate method the evolution of this reaction is followed and the concentration of the thiosulfate ions is determined at different instants.

The results are grouped in the table of document-1.

t (s)	15	30	60	90	150	210	300
$[S_2O_3^{2-}]$ mol. L^{-1}	0.32	0.26	0.18	0.12	0.06	0.032	0.012

Document-1

1. Preliminary Study

1.1. Show that the initial concentration of the thiosulfate ions is $[S_2O_3^{2-}]_o = 0.40$ mol.L^{-1} and that of hydronium ions is $[H_3O^+]_o = 1.0$ mol.L^{-1} in the reactional mixture.

1.2. Identify the limiting reactant.

2. Kinetic Follow-up

2.1. Plot the curve representing the variation of the concentration of thiosulfate ions as a function of time $[S_2O_3^{2-}] = f(t)$ within the time interval: [0 - 300s]. Take the following scales:

abscissa: 1 cm for 30 s ordinate: 1 cm for 0.04 mol.L^{-1}.

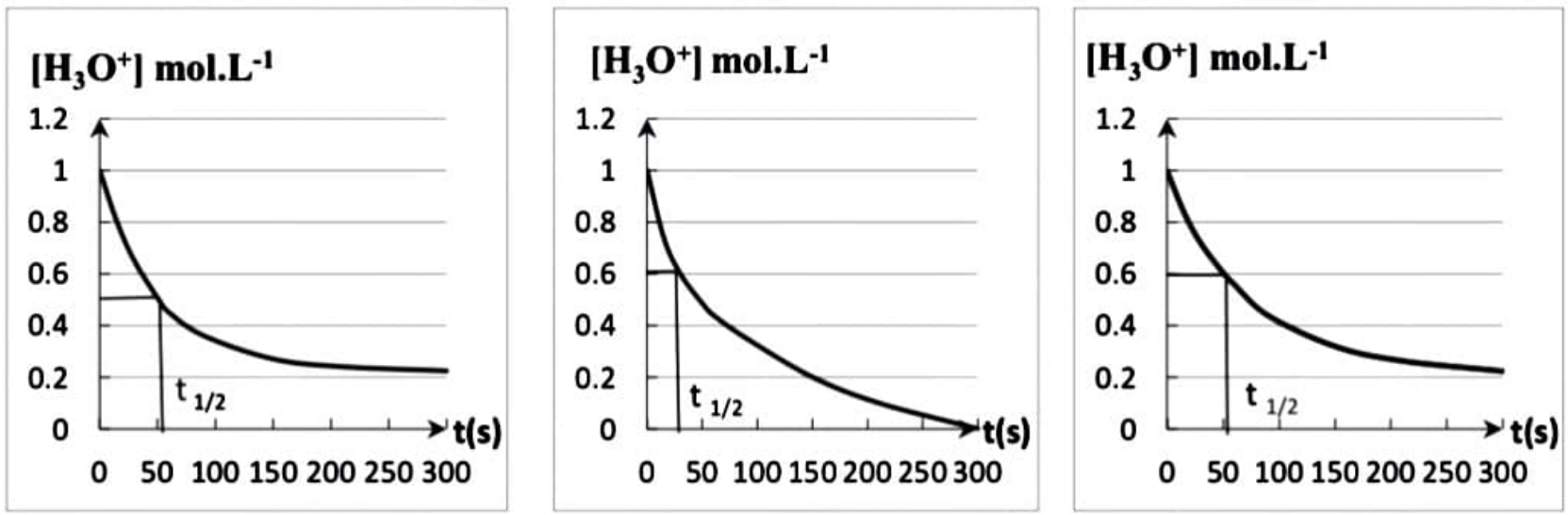
2.2. Determine, graphically, the half-life time $t_{1/2}$.

2.3. Show that at instant $t = t_{1/2}$ the concentration of hydronium ions, $[H_3O^+]_{t_{1/2}}$, is given by the following relation:

$$[H_3O^+]_{t_{1/2}} = [H_3O^+]_o - [S_2O_3^{2-}]_o$$

2.4. Deduce the value of $[H_3O^+]_{t_{1/2}}$.

2.5. Choose among the three graphs of document-2 the one that corresponds to the shape of the curve that represents the variation of the concentration of H_3O^+ ions as a function of time. Justify.



Graph a **Graph b** **Graph c**

Document-2

3. Kinetic Factors

To highlight the effects of the kinetic factors on the duration of this reaction.The three experiments represented in document-3 are carried out, where Δt represents the end time of the reaction in each experiment.

	$[S_2O_3^{2-}]_o$	$[H_3O^+]_o$	Temperature (°C)	Time (t)
Experiment 1	0.4 mol.L^{-1}	1 mol.L^{-1}	40	Δt_1
Experiment 2	0.4 mol.L^{-1}	1 mol.L^{-1}	20	Δt_2
Experiment 3	0.2 mol.L^{-1}	1 mol.L^{-1}	40	Δt_3

Document-3

Compare Δt_2 and Δt_1 as well as Δt_3 and Δt_1 .Justify.