IN DEPTH

29. Hydrolysis of sucrose

We dissolve 34.2 g of sucrose in water in order to obtain 100 mL of solution ; we start timing by using the chronometer. Whatever the time chosen as the origin of times, we can deduce that if (n) is the number of mole of sucrose present at this time, it is necessary to wait 200 min to have a remaining number of mole of sucrose in solution equal to ($\frac{n}{2}$) under the conditions of the experiment. The dissolution reaction of sucrose in water is :

$$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6 \text{ (glucose and fructose)}$$

1. Calculate the initial number of moles of sucrose.
   Given : Molar mass of sucrose = 342 $g.mol^{-1}$.

2. Complete the following table **(Document 1)** :

time (min)	0	200	400	600	800	1000
$(n)_{(sucrose)}$ (mol)	0.1					

Document 1

3. Trace the curve $n_{(sucrose)} = f(t)$ in the interval [0 - 1000] min. Use the following scale :
   X-axis : 1 cm = 200 min ; Y-axis : 1 cm = 0.025 mol.
4. By an appropriate method, the determination of the director coefficient of the tangent to the curve $n_{(sucrose)} = f(t)$ at the time t = 300 min gives 1.25×10^{-4}
   4.1. What does this value represent? Give its unit.
   4.2. Deduce the instantaneous rate of formation of glucose at the instant t = 300 min.
   4.3. What is the rate of formation of glucose when t tends to ∞? Justify.

30. Kinetic study of the reaction : $H_2 + I_2 \longrightarrow 2\,HI$

Hydrogen gas reacts with iodine according to the following equation :

$$H_2 + I_2 \rightarrow 2\,HI \quad (1)$$

To study the kinetics of this slow reaction,Four 1 L flasks are brought to 350 °C : A, B, C and D each contains an equimolar mixture of 0.50 mmol of H_2 and 0.50 mmol of I_2. The flasks are kept at that temperature during different instants of time, and then they are suddenly cooled. The remaining iodine in each flask is first dissolved in a solution of potassium iodide (which turns yellow) and is then titrated with a sodium thiosulfate solution of formula $Na_2S_2O_3$ of a molar concentration C = 0.050 mol. L^{-1}. The equation of the titration reaction is as follows :

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-} \quad (2)$$

The end of the titration reaction is indicated by decolorization of the iodine solution. Let V_{eq} be the volume of the sodium thiosulfate solution necessary to obtain the decolorization

1. Show that the number of moles of I_2 remained at time t is related to V_{eq} (in L) by the relation : $n_{(I_2)\text{ remained at t}} = 0.050 \times \frac{V_{eq}}{2}$
2. Complete the following table (**Document 1**) containing the experimental results obtained :

Flask	A	B	C	D
t (min)	50	100	150	200
V_{eq} (mL)	16.6	13.7	11.4	9.4
$n(I_2)_{remaining}$ (mmol)				

Document 1

3. Calculate the number of mole of I_2 which has reacted at 100 min.
4. Deduce the number of mole of H_2 remained at 100 min.
5. Draw the curve $n(I_2) = f(t)$, in the interval [50-200] min, take the following scale X-axis : 1 cm = 50 min ; Y-axis : 1 cm = 0.1 mmol.
6. Deduce graphically how the rate of disappearance of I_2 varies with time.

31. Reaction between iodide ions and peroxodisulfate ions

At 25 °C, a solution containing peroxodisulfate ions $S_2O_8^{-2}$ and iodide ions I^- is slowly transformed according to the following equation :

$$2I^- + S_2O_8^{2-} \rightarrow I_2 + 2SO_4^{2-}$$

The following table (**Document 1**) shows the evolution of a system containing initially 10 mmol of ammonium peroxodisulfate and 50 mmol of potassium iodide.

t (min)	0	2.5	5	10	15	20	25	30
$n_{(S_2O_8^{2-})}$ mmol	10	9	8.3	7	6.15	5.4	4.9	4.4

Document 1

1. Plot the curve $n_{(S_2O_8^{2-})} = f(t)$ in the interval [0-30] min, take the following scale : X-axis : 1 cm = 5 min. ; Y-axis : 1 cm = 1 mmol
2. Is the initial mixture stoichiometric?
3. Calculate the number of moles of iodine at the end of the reaction.
4. Determine the composition of the reaction mixture at t = 7.5 min.

12. Kinetics of the decomposition of iron pentacarbonyl

Carbon monoxide forms, with iron, a compound of formula $Fe(CO)_5$ called iron pentacarbonyl. At a temperature of 200°C and in the dark, the gaseous iron pentacarbonyl undergoes a slow decomposition according to the equation :

$$Fe(CO)_{5(g)} \rightarrow Fe_{(s)} + 5CO_{(g)}$$

We introduce at $t = 0$, $n_0 = 2$ mmol of iron pentacarbonyl in an empty bulb of constant volume $V = 250$ mL, then the bulb is brought to a temperature of 200 °C.

1. **Study of the reaction mixture :**
   x represents the number of moles (in mmol) of solid iron formed at time t.
   Copy the table given in the **document 1** on the answer sheet, and complete it in terms of n_0 and x.

Time	$Fe(CO)_{5(g)}$ →	$Fe_{(s)}$ +	$5CO_{(g)}$
0	n_0	0	0
t			
End of reaction			

Document 1

2. **Kinetics of this reaction :**
   By means of a suitable device, the total volume of the gaseous mixture is recorded with time. Then, the total number of moles of the gaseous mixture noted n_t as a function of time is deduced and the results given in **document 2** are obtained :

t (min)	0	5	10	15	20	25	30
n_t (mmol)	2	4.7	6.1	7.3	8.1	8.7	9.1
[CO] ($mmol.L^{-1}$)							

Document 2

2.1. Explain the rise in the total number of moles during time.
2.2. Verify if the time t = 30 min corresponds to the end of the reaction.
2.3. Show that the concentration of carbon monoxide, at any instant t, is given by the relation :

$$[CO]_t = \frac{5}{4}\left(\frac{n_t - n_0}{V.10^{-3}}\right)$$

V is the volume of the bulb in mL.
2.4. Complete the table of **document 2** and draw the curve $[CO]_t = f(t)$.
Take for scales : X : 1 cm→ 2.5 min. Y : 1 cm→ 5 $mmol.L^{-1}$
2.5. Define the instantaneous rate of formation of CO at a given instant t.

2.6. We determine the instantaneous rate of formation of CO at t = 0 and at t = 10 min, we obtain the 2 following values : r = 1.3 mmol. L^{-1}.min^{-1} and r' = 11 mmol. L^{-1}.min^{-1}

2.6.1. Match each rate obtained to the corresponding instant of time.

2.6.2. Explain this result, while indicating the factor responsible for this variation.

33. Kinetic study of the attack of an acid on calcium carbonate $CaCO_3$

Given :

- Molar masses in g.mol^{-1} : C = 12 ; O = 16 ; Ca = 40.
- V_m = 24 L.mol^{-1}.

Solid calcium carbonate $CaCO_3$, is attacked by an acid in a slow and complete reaction given by the equation :

$$CaCO_{3(s)} + 2\,H_3O^+_{(aq)} \rightarrow Ca^{2+}_{(aq)} + CO_{2(g)} + 3\,H_2O_{(l)}$$

For this, all substances containing $CaCO_3$ must not be in direct contact with the acid solutions for a long time.

1. Preparation of a hydrochloric acid solution

100 mL of a hydrochloric acid solution (S) of concentration C = 0.1 mol. L^{-1}, is prepared from a commercial solution (S_0) of concentration C_0 = 2 mol. L^{-1}.

1.1. Determine the volume of (S_0) needed to be taken, to achieve this preparation.

1.2. Choose from the list given below, the convenient glassware for the most precise preparation of (S) :

- volumetric pipettes : 5, 10 and 20 mL - graduated cylinders : 50 and 100 mL
- beakers : 250 and 500 mL - volumetric flasks : 100, 250, and 500 mL

2. Kinetic study

A student poured into a flask a volume Vs = 100 mL of the hydrochloric acid solution (S) of concentration 0.1 mol.L^{-1}. At instant t = 0, he quickly introduced into the flask 2 g of solid calcium carbonate $CaCO_3$, while a fellow triggers the chronometer. The students record the volumes of CO_2 released during time by using a suitable device. The obtained results are grouped in **document 1 :**

t(s)	0	20	40	60	80	120	160	200	240	280	320	360	400
V_{CO_2} (mL)	0	29	49	63	72	84	93	100	106	111	115	118	120
n_{CO_2}($\times 10^{-3}$ mol)													

Document 1

2.1. Determine the initial number of moles (in mol) for each reactant.

2.2. Verify if $CaCO_3$ will disappear completely at the end of the reaction.

2.3. Show that the number of mole of formed CO_2 at an instant t is related to the volume V_{CO_2}, by the relation : $n_{CO_2(t)} = 0.042\times10^{-3}.\ V_{CO_2(t)}$. ($V_{CO_2}$ in mL)

2.4. Complete the table of **document 1** and trace the curve $n_{CO_2} = f(t)$ in this case.
(Use the scale : 1 cm → 20 s ; 1 cm → 0.5×10^{-3} mol.)

2.5. Define the instantaneous rate of formation of CO_2 at a given instant t.

2.6. The students repeat the same experiment but by using a hydrochloric acid solution of concentration $C' = 0.4$ mol.L^{-1} the reactants in this case are in their stoichiometric proportions

2.6.1. Verify if at t = 200s the volume of CO_2 released is lower, equal or higher than 100 mL.

2.6.2. Draw the shape of the curve $n_{CO_2} = g(t)$ in this case.

34. Kinetics of the reduction of iodine

"Lugol solution" is an antiseptic solution based on iodine I_2. When a zinc plate is dipped into this solution, it is possible to observe, after a quite long time, a decolorization and an attack of the zinc. The equation of the occuring slow reaction is given by :

$$Zn_{(s)} + I_{2(aq)} \rightarrow Zn^{2+}_{(aq)} + 2I^-_{(aq)}$$

To study this reaction, we follow the evolution of the remained amount of matter (number of moles) of iodine as a function of time by successive titrations at different instants of time t.

1. Preparation of a solution (S) of iodine

A commercial solution (S_o) of iodine I_2 of concentration 2 mol.L^{-1} was diluted hundred times in order to prepare 1 L of solution (S).

Describe the procedure of preparation by indicating the proper glassware and performing the necessary calculation.

2. Kinetic study

Given : $M_{Zn} = 65$ g.mol^{-1}.

During this experiment, the temperature is maintained at 20°C. The concentration of the iodine is $C_s = 0.020$ mol.L^{-1}. Twelve samples of volume V = 20 mL were made and placed in 12 beakers. At the instant t = 0, in each beaker, zinc granules of respective mass 0.65 g is introduced. At each instant shown in the table below, one of the beakers is rapidly placed in ice bath and then the remaining iodine in it is titrated with a sodium thiosulfate solution of concentration C = 0.020 mol.L^{-1}. The equation of the titration reaction is :

$$2S_2O_3^{2-}{}_{(aq)} + I_{2(aq)} \rightarrow S_4O_6^{2-}{}_{(aq)} + 2I^-_{(aq)}.$$

The results of the titrations are indicated in the table of **document 1**, where V_{eq} represents the volume of sodium thiosulfate added at equivalence.

t(s)	30	60	100	200	300	400	600	800	1000	1200	1400	160
V_{eq} (mL)	31.6	27.4	24.2	19	15.2	12.5	8.4	5.8	4.2	3.2	2.6	2.2
$n_{(I_2)t}$ (mol)												

Document 1

2.1. Calculate the initial number of moles of iodine noted n in each beaker.
2.2. Show that the amount of matter of remaining iodine at the instant t noted $n_{(I_2)t}$ is given by : $n_{(I_2)t} = 5x10^{-4} CxV_{eq}$; (V_{eq} is expressed in mL and $n_{(I_2)t}$ in mol).
2.3. Complete the table of **document 1**.
2.4. Draw the curve $n_{(I_2)t} = f(t)$.
Take for scales : 1 cm → 100s ; 1 cm → $0.4x10^{-4}$ mol
2.5. Explain how the instantaneous rate of disappearance of iodine I_2 graphically evolves.
2.6. Verify if the curve $n_{(I_2)t} = f(t)$ touches the abscissa axis after an infinite time.

35. Kinetics of the Oxidation Reaction of Oxalic Acid

We study, during time, the evolution of a mixture formed of 50 mL of an oxalic acid solution of concentration $C_1 = 6.0x10^{-2}$ mol.L^{-1} and 50 mL of potassium dichromate solution of concentration $C_2 = 0.02$ mol.L^{-1} in presence of an excess of sulfuric acid. We follow the variation of concentration of Cr^{3+} ions formed during the reaction of the following equation :

$$Cr_2O_7^{2-} + 3\,H_2C_2O_4 + 8\,H_3O^+ \longrightarrow 2\,Cr^{3+} + 6\,CO_2 + 15\,H_2O$$

The results obtained are grouped in the following table of **document 1** :

Time t (s)	0	10	20	30	50	70	100	140
$[Cr^{3+}]$ mmol.L^{-1}	0	3.5	6.0	7.6	10.5	12.3	14.2	16

Document 1

1. **Preparation of oxalic acid solution :**
1.1. Calculate the mass of crystallized hydrated oxalic acid of formula ($H_2C_2O_4.2H_2O$) needed to prepare 100 mL of solution of concentration C_1.
($M_H = 1$ g.mol^{-1} ; $M_C = 12$ g.mol^{-1} ; $M_O = 16$ g.mol^{-1}).
1.2. Describe the procedure of preparation.

2. **Kinetic study :**
2.1. Plot the curve $[Cr^{3+}] = f(t)$. Taking the following scales : 1 cm for 10 s in abscissa ; 1 cm for 1 mmol.L^{-1} in ordinate.
2.2. Verify if the instant t = 140 s indicates the end of the reaction.
2.3. Show that at each instant t of the reaction :

$$[Cr_2O_7^{2-}]_t = [Cr_2O_7^{2-}]_{initial} - \frac{[Cr^{3+}]_t}{2}.$$

2.4. Deduce the value of $[Cr_2O_7^{2-}]$ at t 100 s.
2.5. The rate of formation of Cr^{3+} ions decreases with time, although the $[Cr^{3+}]$ increases with time. Explain.