Iodine Clock –
The Initial Rate Method

Last revised: 2024/10/26

Preparation

Collect the following items

- ❑ Ten 50 mL Erlenmeyer flasks (clean and oven dry)
- ❑ Two cork stoppers
- ❑ Two 5 mL graduated pipets and one pipet filler
- ❑ One stop watch (distributed by TA)

From your personal equipment

- ❑ Two 100 mL beakers (clean and oven dry) – labelled with $K_2S_2O_8$ and K_2SO_4, respectively
- ❑ A scientific calculator

Objective and Principles

- **Objective:** Determine the *rate law* of the chemical reaction between persulfate ($S_2O_8^{2-}$) and iodide (I^-) ions

$$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2 \qquad \text{Rate} = k[S_2O_8^{2-}]^m[I^-]^n$$

- A limiting amount of thiosulfate ion **($S_2O_3^{2-}$)** is added as a measuring tool in order to determine the rate of the above reaction:

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

- **Lab techniques:**
  - Graduated pipet
  - Lab dispenser
  - Measuring initial reaction rate

Determine the Rate of a Reaction

(1) $S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$ ⟸ *Rate and rate law to be determined*

(2) $2S_2O_3^{2-} + I_2 \rightarrow 2I^- + S_4O_6^{2-}$ ⟸ *$S_2O_3^{2-}$ being the limiting reagent*

- The second reaction occurs much faster than the first reaction
  ➔ I_2 formed by the first reaction is consumed immediately by the second reaction
- When the limiting reagent $S_2O_3^{2-}$ is used up, I_2 starts to accumulate and combine with I^- to form I_3^-, which shows purple-blue color in the presence of starch indicator

$$\Delta[S_2O_3^{2-}] = \mathbf{2} \times \Delta[S_2O_8^{2-}]$$

$$\text{rate} = \frac{-\Delta[S_2O_8^{2-}]}{\Delta t} = \frac{-\frac{1}{2}\Delta[S_2O_3^{2-}]}{\Delta t}$$

Initial Rate Method

$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$ Rate = $k[S_2O_8^{2-}]^m[I^-]^n$

Table 1 Volumes of reagents for the initial rate method (total volume of 10.0 mL)

Trial No.	**0.20 *M* NaI (mL)**	0.20 *M* NaCl* (mL)	0.0050 *M* $Na_2S_2O_3$ (mL)	2% Starch (mL)	0.10 *M* K_2SO_4* (mL)	**0.10 *M* $K_2S_2O_8$ (mL)**	Reaction time Δt (s)
1	**2.0**	2.0	1.0	1.0	2.0	**2.0**	109
2	2.0	2.0	1.0	1.0	0	**4.0**	59
3	**4.0**	0	1.0	1.0	2.0	2.0	58

$[I^-]$ ↑
Δt ↓
rate ↑

Limiting reagent
Fixed # of moles

$[S_2O_8^{2-}]$ ↑
Δt ↓
rate ↑

*NaCl and K_2SO_4 are added to maintain the ionic strength of the solution

Reaction Order

$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$ $\qquad$ Rate = $k[S_2O_8^{2-}]^m[I^-]^n$

$$r = \frac{-\Delta[S_2O_8^{2-}]}{\Delta t} = \frac{-\frac{1}{2}\Delta[S_2O_3^{2-}]}{\Delta t} = \frac{-\frac{1}{2}(0 - 0.00050)}{\Delta t} = \frac{0.00025}{\Delta t}$$

Rate is inversely proportional to Δt

$$\frac{\text{rate}_2}{\text{rate}_1} = \frac{0.00025/\Delta t_2}{0.00025/\Delta t_1} = \frac{\Delta t_1}{\Delta t_2} = \frac{109}{59} = \frac{k(2.0[S_2O_8{}^{2-}]_1)^m([I^-]_1)^n}{k([S_2O_8{}^{2-}]_1)^m([I^-]_1)^n} = (2.0)^m$$

$$\frac{\text{rate}_3}{\text{rate}_1} = \frac{0.00025/\Delta t_3}{0.00025/\Delta t_1} = \frac{\Delta t_1}{\Delta t_3} = \frac{109}{58} = \frac{k([S_2O_8{}^{2-}]_1)^m(2.0[I^-]_1)^n}{k([S_2O_8{}^{2-}]_1)^m([I^-]_1)^n} = (2.0)^n$$

The rate constant *k* can be calculated with *m* and *n* known

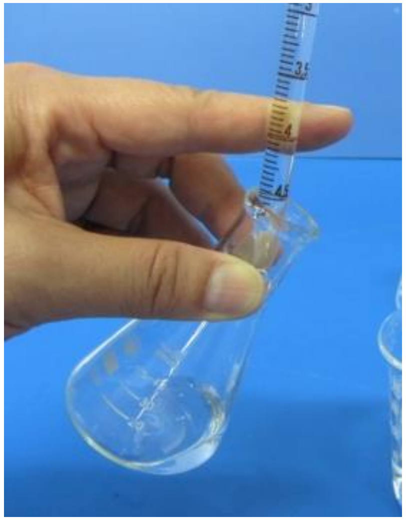
Step 1: Prepare Sample Solutions

- Wash ten 50 mL Erlenmeyer flasks, dry them in oven and **let cool**
- Use 100 mL beakers to take **~30 mL** 0.10 *M* **$K_2S_2O_8$** and 0.10 *M* **K_2SO_4**
- Reference to Table 1, use lab dispensers to measure 0.20 *M* NaI, 0.20 *M* NaCl, 0.0050 *M* $Na_2S_2O_3$, and 2% starch solutions into the first two Erlenmeyer flasks (two copies for each entry)
- Use a 5 mL graduated pipet to measure 0.10 *M* K_2SO_4 accurately, then transfer to Erlenmeyer flasks

- ✓ Use the same set of chemicals through out this lab
- ✓ Rinse graduate pipets twice before use

Step 2: Measure the Reaction Time

- Use a 5 mL graduated pipet to measure the required amount of 0.10 *M* $K_2S_2O_8$, add into the Erlenmeyer flask and start the timer immediately
- Install the cork stopper and swirl the Erlenmeyer flask for 20 s
- Leave the Erlenmeyer flask on the benchtop and record the time it takes for the purple-blue color to appear



✓ Remove the pipet filler to expel the $K_2S_2O_8$ solution from the graduated pipet

Step 3: Calculate Reaction Orders

- Repeat each trial twice (if the reaction times Δt differ for more than 3 s, redo the trial one more time)
- Calculate the average Δt values
- Calculate the values of ***m*** and ***n***, then calculate the rate constant ***k***

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

$$\text{Rate} = k[S_2O_8^{2-}]^m[I^-]^n$$

✓ Keep two significant figures for reaction orders m and n

Example:

Reaction time Δt (s)			
Trial 1	**1'48"**	**1'54"**	**1'49"**
Trail 2	**58**	**59**	
Trail 3	**53**	**57**	**59**

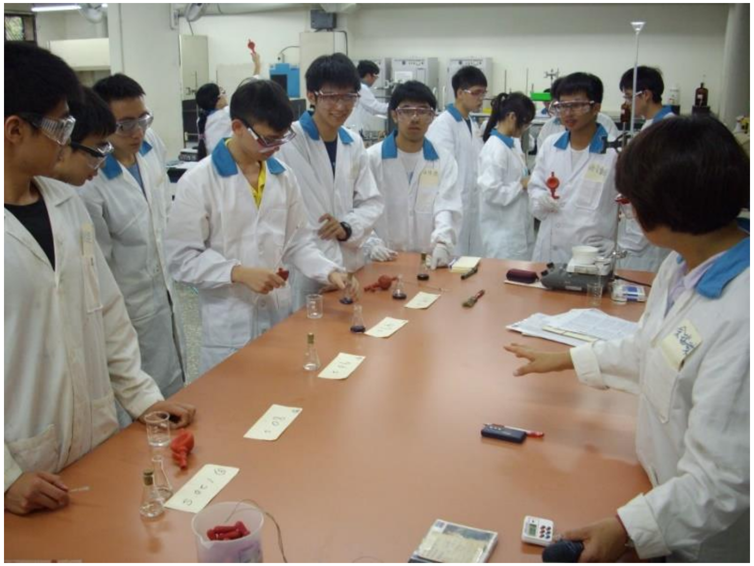
Average Δt_1 = 108.5 = 109 (s)

Average Δt_2 = 58.5 = 59 (s)

Average Δt_3 = 58 (s)

Step 4: Participate in Iodine-Clock Symphony Competition

- Obtain an assigned reaction time Δt from the TA, and design a set of reaction conditions to achieve it (the assigned times will allow the color change of solution to match the beats in the 'Habanera' aria of opera 'Carmen')
- Verify the reaction conditions on your own, and make adjustment as needed
- At the scheduled competition time, bring your Erlenmeyer flask (containing all reactants except for $K_2S_2O_8$) and graduated pipet (containing $K_2S_2O_8$) to the podium
- On TA's mark, add $K_2S_2O_8$ into the Erlenmeyer flask, swirl for 20 s, then place the Erlenmeyer flask in the designated area



- ✓ The total volume of solution should be fixed at 10 mL
- ✓ Balance the ionic strength with NaCl and K_2SO_4

How to Design Reaction Conditions

Example 1: Target time is 90 s (if *m* has been determined to be **0.90**)

Trial No.	**0.20 *M* NaI (mL)**	0.20 *M* NaCl (mL)	0.0050 *M* $Na_2S_2O_3$ (mL)	2% Starch (mL)	0.10 *M* K_2SO_4 (mL)	**0.10 *M* $K_2S_2O_8$ (mL)**	Reaction time Δt (s)
1	**2.0**	2.0	1.0	1.0	2.0	**2.0**	109
$Rate_{90}$	**2.0**	2.0	1.0	1.0	**4.0 – *x***	***x***	**90**

By dispenser (do not adjust the pre-set volume !)

By graduated pipet

$$\frac{rate_1}{rate_{90}} = \frac{\Delta t_{90}}{\Delta t_1} = \frac{90}{109} = \frac{k[S_2O_8^{2-}]^{0.90}[I^-]^{0.90}}{k[S_2O_8^{2-}]'^{0.90}[I^-]^{0.90}} = \left(\frac{2.0}{x}\right)^{0.90}$$

$$\log({}^{90}/_{109}) = 0.90\log({}^{2.0}/_{x})$$

***x* = 2.47 = 2.5 mL (*x* < 4.0 mL)**

How to Design Reaction Conditions

Example 2: Target time is 40 s (if *m* has been determined to be **0.90**)

Trial No.	**0.20 *M* NaI (mL)**	0.20 *M* NaCl (mL)	0.0050 *M* $Na_2S_2O_3$ (mL)	2% Starch (mL)	0.10 *M* K_2SO_4 (mL)	**0.10 *M* $K_2S_2O_8$ (mL)**	Reaction time Δt (s)
3	**4.0**	0	1.0	1.0	2.0	**2.0**	58
$Rate_{40}$	**4.0**	0	1.0	1.0	**4.0 – *y***	***y***	**40**

By dispenser (do not adjust the pre-set volume !)

By graduated pipet

$$\frac{rate_3}{rate_{40}} = \frac{\Delta t_{40}}{\Delta t_3} = \frac{40}{58} = \frac{k[S_2O_8^{2-}]^{0.90}[I^-]^{0.90}}{k[S_2O_8^{2-}]'^{0.90}[I^-]^{0.90}} = \left(\frac{2.0}{y}\right)^{0.90}$$

$$\log(40/58) = 0.90\log(2.0/y)$$

y = 3.02 = 3.0 mL (y < 4.0 mL)

Clean-Up and Check-Out

- Wash all 50 mL Erlenmeyer flasks and place them in the oven
- Waste solution containing iodine should be disposed into the designated container
- Clean up the lab bench and check personal equipment inventory (have an associate TA sign the check list)

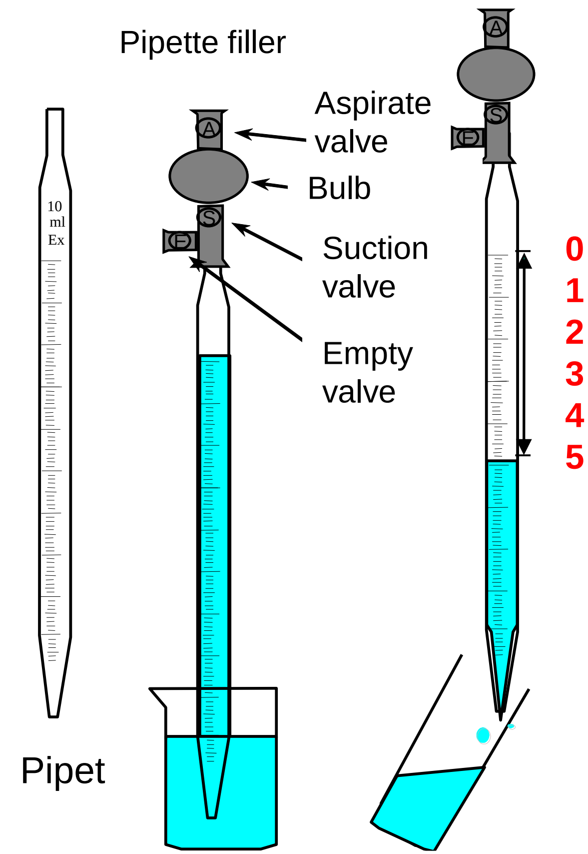
- This is a **Full Report** experiment:
  - Member A: **Have the lab notes and results checked by the TA, and hand in the report next week**
  - Member B: **Hand in prelab to the TA**

- Groups on duty shall stay and help clean up the lab

T12.2 – Measuring (Graduated) Pipet

Deliver 5.00 mL solution – Method 1

- Clean a 10 mL pipet and rinse it twice with small amount of the liquid to be transferred
- Press valve **A** of the pipet filler and simultaneously squeeze the bulb to expel air from it, then insert the top of pipet <u>gently</u> into the pipet filler
- Bring the pipet tip below the liquid surface, press valve **S** to draw liquid to the 0.00 mL marking
- Wipe off any excess liquid near the pipet tip
- Use the other hand to hold the new container. Maintain the pipet in a vertical position and let its tip touch the inner wall of the container. Press valve **E** to drain the liquid to the 5.00 mL marking
- <u>Do not force out any liquid remaining at the tip</u>
- Wash the pipet thoroughly after use

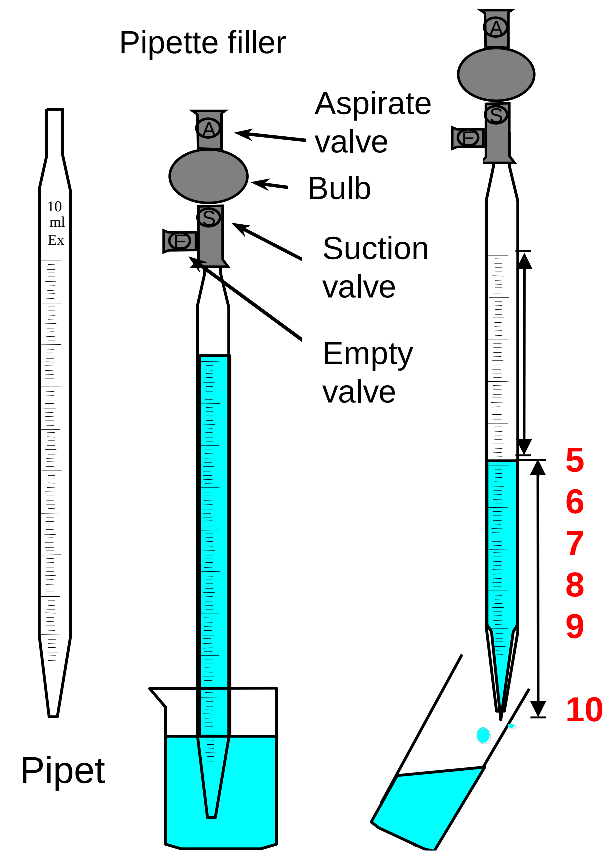


T12 Video (YouTube link)

T12.3 – Measuring (Graduated) Pipet

Deliver 5.00 mL solution – Method 2

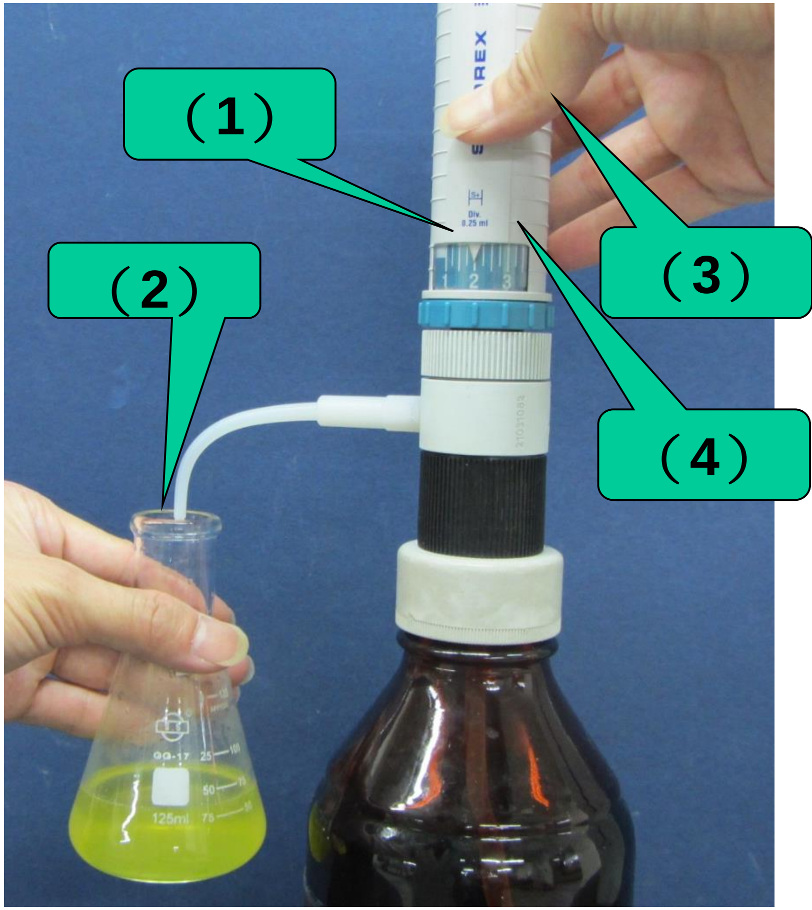
- Clean a 10 mL pipet and rinse it twice with small amount of the liquid to be transferred
- Press valve **A** of the pipet filler and simultaneously squeeze the bulb to expel air from it, then insert the top of pipet gently into the pipet filler
- Bring the pipet tip below the liquid surface, press valve **S** to draw liquid until it rises above the 5.00 mL marking
- Remove the pipet filler and quicky use an index finger to close the top of pipet. Use the finger to adjust the liquid level to the 5.00 mL marking
- Wipe off any excess liquid near the pipet tip
- Use the other hand to hold the new container. Maintain the pipet in a vertical position and let its tip touch the inner wall of the container. Release the index finger so that liquid is transferred
- Do not force out any liquid remaining at the tip
- Wash the pipet thoroughly after use



T12 Video (YouTube link)

Lab Dispenser

1) Check the pre-set volume on the dispenser. Do not change the setting unless instructed to do so
2) Place the receiving flask under the tip of dispenser
3) To remove the air bubbles in the dispenser, lightly pull the piston pump up and down for several times
4) Gently pull the piston pump up until it reaches the end of travel range, then slowly push the piston down to obtain the solution



Final Report (Full Version)

- Four experiments (E5, E8, E10, E12)
- Complete the data analysis and calculation part in the lab manual
- Plot data correctly and discuss potential sources of errors
- Hand in the report in the following week together with the prelab and lab records
- 50 points per report (5 pts deduction for late submission < 1 week)

I. Prelab exercise

- ✓ Objectives
- ✓ Principles
- ✓ Chemicals
- ✓ Procedures

II. Lab Notes

- ✓ Observation
- ✓ Operation
- ✓ Reaction condition
- ✓ Data and results

III. Final report

- ✓ Data analysis
- ✓ Elaborate results
- ✓ **Conclusion**
- ✓ **Error analysis**

15 pts + 10 pts + 25 pts