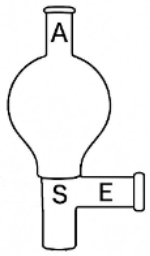
General instructions

- **Safety rules:** At all times you must wear a laboratory coat and safety or corrective goggles; eating and drinking in the laboratory are prohibited.
- **Violation of safety rules:** You will receive only one warning; in the event of a repeated violation you will be disqualified.
- **Exam content:** The exam consists of 2 problems, equal of time intervals are allocated for each, but please note that once time runs out you will not have access to certain equipment. At the beginning of the exam, the lab assistant will inform you which task you should start with.
- **Time:** The total duration of the experimental tour is 5 hours (2 hours 10 minutes for each problem and 20 minutes of break after each problem). During the break between the problems you are allowed to write, but it is forbidden to perform the experiment; during this time the lab assistant will change some of your equipment. After the break, you should start doing the next practical problem.
- **Equipment:** Use the devices provided to you strictly according to the instructions and carefully. If something is unclear or does not work, raise your hand to call the lab assistant. Broken devices will not be replaced.
- **Answer recording:** Record answers only on the designated answer sheets; answers written elsewhere will not be graded. Show all calculations where required.
- **Pipetting:** Draw solutions into pipettes only by using the three-way bulb. It is forbidden to use your mouth to aspirate liquid into pipettes.
  Valves of the three-way bulb:



Valve A (Air) – to release air
Valve S (Suction) – to draw in liquid
Valve E (Expel) – to dispense liquid

- **Reagent limits:** The amount of each reagent provided is limited. Any spilled or entirely consumed reagent will be replaced subject to a penalty.
- **Scratch paper:** You may use the back side of the task sheets for rough work.
- **Workspace:** Keep your working area tidy.

If you need help, please call the lab assistant!

Available equipment

Equipment	Quantity
Per two participants	
pH meter with storage solution	1
Thermometer	1
Stopwatch	1
Plastic spatula	1
Per participant	
Graduated pipette (10.0 mL)	6
Three-way pipette bulb	1
Washing bottle	1
Glass stirring rod	1
Pasteur pipette (1.0 mL)	2
Burette (25.0 mL)	1
Mohr pipette (50.0 mL)	1
Funnel	1
Volumetric flask 250.0 mL with bung	1
Erlenmeyer flask 250.0 mL	1
Burette stand with clamp	1
Plastic beakers	50
Liquid waste container	1
Marker	1
Pen	1
Ruler	1
Tissue	1

Problem 1. Chemical Kinetics: Iodine Clock Reaction

You have following reagents for practical problem 1:

Reagent	Volume	Container	Label
KI, 0.0100 M	250 mL	Plastic bottle	KI 0.01 M
$Na_2S_2O_3$, 0.0010 M	250 mL	Plastic bottle	$Na_2S_2O_3$ 0.001 M
$KBrO_3$, 0.0167 M	250 mL	Plastic bottle	$KBrO_3$ 0.0167 M
HCl, 0.1000 M	250 mL	Plastic bottle	HCl 0.1 M
$(NH_4)_2MoO_4$, 0.0005 M	50 mL	Plastic bottle	$(NH_4)_2MoO_4$ 0.0005 M
$(NH_4)_2MoO_4$, "X" M	50 mL	Plastic bottle	Mo^{VI} – X
Starch, 1%	10 mL	Eppendorf tube	Starch, 1%

The "iodine clock reaction" is one of the best ways to demonstrate the chemical kinetics in practice because of its dramatic color change from colorless to blue. Bromate-iodide reaction in acidic medium in the presence of sodium thiosulphate and starch is an example of such clock reaction. Chemical kinetics studies how the rate of a reaction is changed by such factors as concentrations and presence of catalysts, which are substances that lower the activation energy, without affecting the reaction product(s).

In this experiment, the reaction between iodide, bromate, and hydrogen ions will be used to study the effects of concentration and a catalyst on the reaction rate. The reaction equation is:

$$6I^-_{(aq)} + BrO_3^-{}_{(aq)} + 6H^+_{(aq)} \rightarrow 3I_{2(aq)} + Br^-_{(aq)} + 3H_2O_{(l)} \qquad (1) \qquad (slow)$$

A controlled volume of thiosulfate is added to the reaction as a "clock" to control the I_2 produced by the main reaction (1). The starch will react with iodine and turn blue as soon as thiosulfate is consumed. Once the thiosulfate is consumed, the specific amount of I_2 will be formed. The above reactions are as followed:

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

$I_{2(aq)}$ + starch → I_2-starch (3) (*fast*)

Using these equations, one would find that:

$$\text{Rate} = \frac{\Delta[BrO_3^-]}{\Delta t} = \frac{1}{6}\frac{[S_2O_3^{2-}]_0}{\Delta t}$$

The overall rate law is:

$$\text{Rate} = k[I^-]^x[BrO_3^-]^y[H^+]^z$$

where ***k*** is rate constant and ***x***, ***y***, ***z*** are the reaction orders of $[I^-]$, $[BrO_3^-]$ and $[H^+]$ respectively. Using the method of initial rates, the reaction orders ***x***, ***y*** and ***z*** can be calculated, which allows us to determine the rate constant (***k***).

Instruction on usage of thermometer

- Thermometer is ready for use.
- **Press ON/OFF** button to turn off/on the thermometer (1, Fig.1.2)
- **HOLD** button (2, Fig.1.2) freezes the current temperature reading on the display, keeping it unchanged until pressed again. **Press HOLD** button again to return to the normal mode.
- Pressing the **MAX/MIN** (3, Fig.1.2) button shows the highest temperature the thermometer has measured (MAX), then the lowest (MIN), and then returns to the current temperature. It helps track temperature changes over time.
- **°C/°F** (4, Fig.1.2) button is used to switch the temperature display between Celsius and Fahrenheit.

Figure 1.1. Overall view of the thermometer

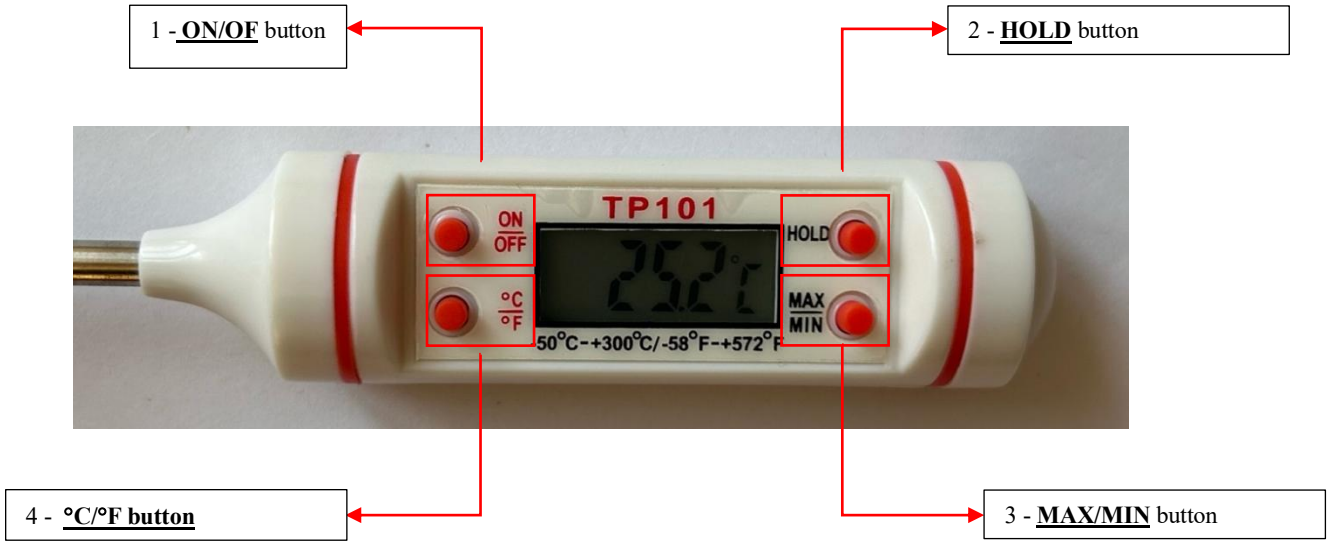


Figure 1.2

Instruction on usage of stopwatch

Figure 1.3

- The stopwatch is ready for use
- **Press START/STOP (**1, Fig.1.3) button to start/stop the stopwatch.
- **Press RESET/SPLIT** (2, Fig.1.3) button to reset the stopwatch.

Attention!

Call lab assistant if stopwatch is not working.

Part 1.1. Investigation of the reaction rate law

Part 1.1 of the experiment is designed to determine the rate orders on iodide, bromate and hydrogen ions. To do this, two plastic beakers (**A** and **B**) of solutions should be prepared, then combined and timed until the mixture turns blue. Record the times of the color change and temperature of the solutions. The volumes (mL) to prepare solutions **A** and **B** are given in Table 1:

Table 1

Experiment #	**Plastic beaker A**			**Plastic beaker B**		
	0.0100 M, mL KI	**0.0010 M, mL $Na_2S_2O_3$**	**mL H_2O**	**0.0167 M, mL $KBrO_3$**	**0.1000 M, mL HCl**	**Starch**
1	10	10	10	10	10	2-3 drops
2	20	10	0	10	10	2-3 drops
3	10	10	0	20	10	2-3 drops
4	10	10	0	10	20	2-3 drops

1. **Transfer** the solutions of "Initial Reagents" into the reaction plastic beakers **A** and **B** (you can mark the plastic beakers with a marker for convenience) for the experiment 1 as shown in Table 1using the graduated pipettes.
2. **Measure** the temperature of solution in the plastic beaker **A** and **record** this temperature on the answer sheets.
3. **Add** the solution in the plastic beaker **B** to the solution in the plastic beaker **A** and **immediately start** the timer. Mix the mixture in the plastic beaker **A** with the glass rod.
4. **Stop** the timer when solution turns blue.
5. **Record the time** it took for the solution to turn from colorless to blue.
6. **Repeat** steps 1-5 for experiments 2-4. You can repeat each particular experiment several times.

1.1.1. **Record** your accepted results (t_1-t_4, seconds) from experiments #1-4 on the answer sheets.

1.1.2. Using your results in experiments #1-4, **determine** values ***x***, ***y***, ***z*** and ***k*** (rate constant).

Part 1.2. Determination of the catalysts effect

Part 1.2 of the experiment is designed to reveal the catalytic effect on a reaction rate. Plastic beaker **A** from the previous concentration chart is used again, but this time certain volume of ammonium molybdate $(NH_4)_2MoO_4$ will be added to plastic beaker **B*** prior to mixing it with plastic beaker **A** (see Table 2).

Table 2

Experiment #	Plastic beaker A			Plastic beaker B*			
	0.0100 M, mL KI	**0.0010 M, mL $Na_2S_2O_3$**	**mL H_2O**	**0.0400M, mL $KBrO_3$**	**0.1000 M, mL HCl**	**0.0005 M, mL $(NH_4)_2MoO_4$**	**Starch**
5	10	10	9.0	10	10	1.0	2-3 drops
6	10	10	8.0	10	10	2.0	2-3 drops
7	10	10	7.0	10	10	3.0	2-3 drops
8	10	10	6.0	10	10	4.0	2-3 drops

7. **Transfer** the solutions of "Initial Reagents" into plastic beakers **A** and **B*** (you can mark the plastic beakers with a marker for convenience) for the experiment 5 as shown in Table 2 using the graduated pipettes.
8. **Measure** the temperature of the solution in the plastic beaker **A** and **record** it on the answer sheet.
9. **Add** the solution in the plastic beaker **B*** to the solution in the plastic beaker **A** and **immediately start** the timer. Mix the mixture in the plastic beaker **A** with the gloss rod.
10. **Stop** the timer when the solution becomes blue.
11. **Record the time** it took for the solution to turn from colorless to blue.
12. **Repeat steps** 7-11 for experiments 6-8. You can repeat each particular experiment several times.

1.2.1. **Record** your results (t_5-t_8, seconds) from experiments #5-8 on the answer sheets.

1.2.2. Using your results in experiments #5-8, **determine** the reaction rates in the presence of the catalyst (r_{cat}, $M \cdot s^{-1}$) for each experiment (#5-8) and **plot** the results as the dependence of r_{cat} ($M\ s^{-1}$) on $[Mo^{VI}]$ (M).

Part 1.3. Determination of the catalyst concentration

You are given a sample of sodium molybdate with unknown concentration (labeled "Mo^{VI} – X"). By measuring the rate of the catalytic reaction as in Part 1.2 and using the graph from i. 1.2.2, determine the concentration of sodium molybdate in your sample.

Table 3

Experiment #	Plastic beaker A			Plastic beaker B*			
	0.0100 M, mL KI	**0.0010 M, mL $Na_2S_2O_3$**	**mL H_2O**	**0.0400M, mL $KBrO_3$**	**0.1000 M, mL HCl**	**X M, mL $(NH_4)_2MoO_4$**	**Starch**
9	10	10	0	10	10	10	2-3 drops

13. **Transfer** the solutions of "Initial Reagents" and $(NH_4)_2MoO_4$ solution with unknown concentration into the plastic beakers **A** and **B*** (you can mark the plastic beakers with a marker) for experiment 9 as shown in Table 3 using the graduated pipettes.
14. **Measure** the temperature of the solution in the plastic beaker **A** and **record** it on the answer sheet.
15. **Add** the solution in the plastic beaker **B*** to the solution in the plastic beaker **A** and **immediately start** the timer. Mix the mixture in the plastic beaker **A** with gloss rod.
16. **Stop** the timer when the solution becomes blue.
17. **Record the time** it took for the solution to turn from colorless to blue.
18. You can repeat the experiment #9 several times.

1.3.1. **Record** your results (t_9, seconds) from experiment #9 to answer sheets.

1.3.2. Using the graph from i. 1.2.2, **determine** the concentration of $(NH_4)_2MoO_4$ ($C_{Mo^{VI}}$, M) in the unknown solution X.

Problem 2. Potentiometry

You have following reagents for practical problem 2:

Reagent	Volume	Container	Label
Solution A	100 mL	Plastic bottle	Solution A
Solution C	250 mL	Plastic bottle	Solution C
NaOH, 0.100 M	250 mL	Plastic bottle	NaOH 0.1 M
Phenophthalein, 1%	10 mL	Eppendorf tube	Phenophthalein, 1%

Acid-base titration is an essential tool for determining the concentration of an unknown acid/base. Titration with an indicator is the most widely used method of acid-base titration.

Part 2.1. Acid-base titration with indicator

1. You are given a solution of a weak acid (HA) prepared by dissolving 1.500 g of the unknown acid in 250.0 ml of distilled water (**solution A**). Consider that the volume of the solution does not change during the dissolution of the acid.
2. **Fill** the burette with the provided 0.100 M NaOH solution using the beaker and funnel.
3. To a 250 mL Erlenmeyer flask, **add:**

- 10.0 mL of **solution A** with a volumetric pipette
- 2-3 drops of the phenolphthalein solution using Pasteur pipette.

4. Titrate the content of the Erlenmeyer flask with constant swirling. **Keep titrating** until the solution becomes pink. Record the titration volume.
5. Repeat the procedure (steps 2-4) as needed.

2.1.1. Report your volumes (V_1, mL) on the answer sheet.

2.1.2. Determine the concentration ($C_{HA,1}$, M) of the unknown acid in **solution A**. Show your calculations.

Part 2.2. Potentiometric titration of a monoprotic acid

Although titration with an indicator is a convenient and fast method for determining concentrations, the results may be subject to error due to the indicator. Therefore, potentiometric titration is used for more accurate determination of concentrations and dissociation constants.

In potentiometric titration there is no need to use an indicator, as a pH meter is applied.

6. **Transfe**r 10.00 mL of **solution A** to the 250 mL volumetric flask and bring to the mark with deionized water. This solution is further referred to as **solution B.**
7. **Transfer** 50.0 mL of **solution B** into a plastic beaker using Mohr pipette.
8. Your electrode is calibrated, being stored in the KCl solution and ready to measure. **Set up** the equipment (burette, pH meter, plastic beaker) for potentiometric titration as shown in the figure below:

Initial set-up
(electrode in storage KCl solution)

Set-up for measurements (side view)

Set-up for measurements (top view)

Figure 2.1

Instruction on usage of the pH meter

- pH meter is calibrated and is ready for use.
- Electrode of pH meter is inside 3 M KCl solution. **Do not leave** the electrode dry for too long when it is not in use.
- **Either leave** it in the sample solution between measurements, or in 3 M KCl storage solution if not in use for a long period of time.
- **Remove** the electrode from the 3 M KCl solution, **rinse** with deionized water, and **dry** with tissue.
- **Rinse** the electrode with deionized water and **dry** it with tissue between measurements.

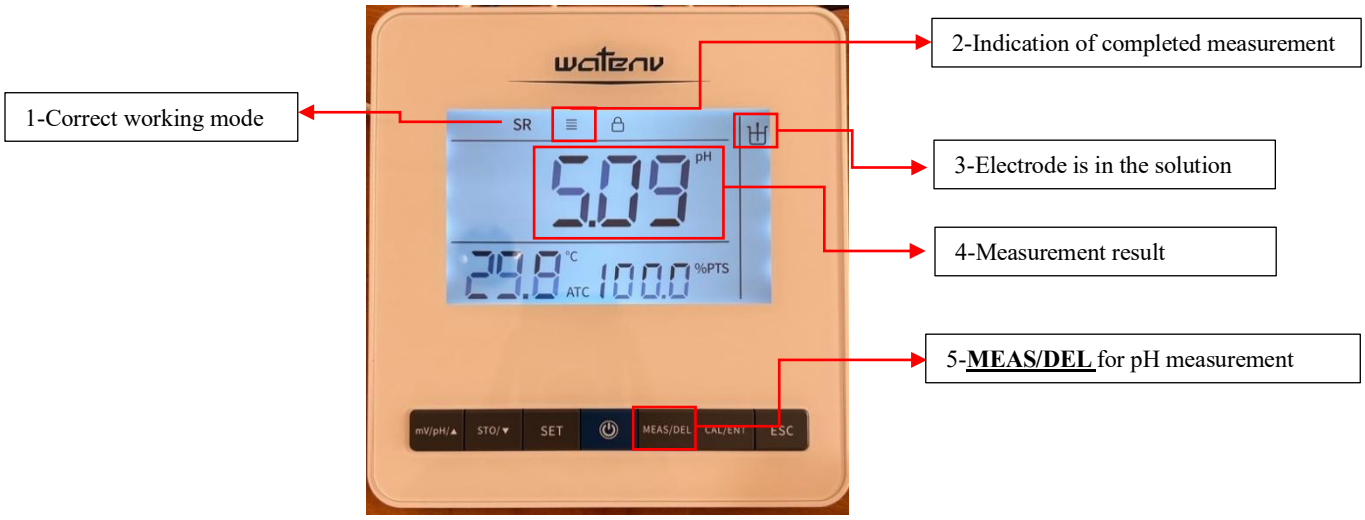


Figure 2.2

- You should **see** **'SR'** – sign (1, Fig.2.2) and sign that electrode is inside solution (3, Fig.2.2) on the display. If you **do not see** **'SR'** sign, **immediately call** the lab assistant.
- **Make sure** that electrode in the solution, is not touching the wall and the bottom of the beaker.
- After you set up your experiment, **press** **MEAS/DEL** button (5, Fig.2.2) to measure the pH of solution. You will hear a short sound and indication (2, Fig.2.2) when measurement is complete.
- **Attention! Do not press any other button, as it may change the settings of the pH meter.**
- After each addition of the solvent, stir with provided plastic spatel for 5 seconds, and **measure** pH of the solution by pressing **MEAS/DEL** button (5, Fig.2.2).

- The result, i.e. the pH of the solution, will appear in the center of the display (4, Fig.2.2).
- **Attention! Do not touch the electrode with the plastic spatel or hand as it may damage the electrode.**
- **When you finish your experiment completely, rinse** the electrode with deionized water, and **dry** with tissue. Then **put** the electrode into 3M KCl solution. If the time ends before you do that, **leave** the electrode inside your solution.

9. **Perform** a potentiometric titration of **solution B** with 0.100 M NaOH solution by measuring pH value **only** at the points indicated in the table on the answer sheets, **add** 0.1 mL of titrant.

2.2.1. Record the results in the table provided and **fill in** the blanks.

2.2.2. Write down the equivalent volume (V_2, mL) of NaOH. To accurately determine the equivalent point, use the ratio $\frac{\Delta pH}{\Delta V}$. It can be calculated as shown in Table 4:

Table 4

V_{NaOH}, mL	pH	$\frac{\Delta pH}{\Delta V}$
5.0	11.00	-
5.1	11.05	$\frac{11.05-11.00}{5.1-5.0}=0.5$
5.2	11.08	$\frac{11.08-11.05}{5.2-5.1}=0.3$

Figure 2.3

At the equivalence point the ratio $\frac{\Delta pH}{\Delta V}$ will reach its maximum.

2.2.3. Determine the concentration ($C_{HA,2}$, M) of the unknown acid in **solution A** by potentiometric titration.

10. **Transfer** 50.0 ml aliquots **of solution B** into a plastic beaker. Add ½ V_2 mL of 0.100 M NaOH solution to obtain buffer solution with molar ratio HA:NaA as 1:1. Mix the resulting solution and measure the pH.

2.2.4. Report the pH value of the obtained solution. **Determine** the p*K*a value of the unknown acid.

2.2.5. Determine the molar mass (M_{HA}, g/mol) and **suggest** an acid that corresponds to the weak acid HA.

Part 2.3. Potentiometric titration of a polyprotic acid

11. You are given a solution of a polyprotic acid prepared by dissolving 0.1225 g of the unknown acid (H_nB) in 250.0 ml of distilled water (**solution C**). Consider that the volume of the solution does not change during the dissolution of the acid.
12. **Transfer** 50.0 mL of **solution C** into a plastic beaker using Mohr pipette.
13. **Set up** your equipment as shown on Figure 2.1.
14. **Perform** a raw potentiometric titration of **solution C** with 0.100 M NaOH solution by measuring pH value **only** at the points in the table on the answer sheets, **add** 1.0 mL of titrant.

2.3.1. **Record** the results and **fill in** the table.

2.3.2. **Look** at the number of pH jumps during the titration (you can use the ratio $\frac{\Delta pH}{\Delta V}$) and **determine** the number of acidic protons (N_{H^+}) in this polyprotic acid.

2.3.3. **Determine** the approximate volumes (V_{a3}, V_{a4}, V_{a5} … V_{an}, mL) of sodium hydroxide solution at equivalent points. **You are not required** to fill all cells.

This time you will perform the same potentiometric titration to identify the exact volumes (V_{e3}, V_{e4}, V_{e5} … V_{en}, mL) of sodium hydroxide solution.

15. **Transfer** 50.0 mL of **solution C** into a plastic beaker, using Mohr pipette.
16. **Set up** your experiment as shown on Figure 2.1.
17. **Perform** precise potentiometric titration of **solution C** with 0.100 M NaOH solution in the range of (V_{eq}-1.0…V_{eq}+1.0), **add** 0.1 mL of titrant. For example, if V_{a3} = 10.0 mL, you should perform precise titration in the range of 9.00 to 11.0 mL of 0.100 M NaOH solution.

2.3.4. **Record** the results in the table on the answer sheets. **You are not required** to fill all cells.

2.3.5. **Determine** the exact volumes (V_{e3}, V_{e4}, V_{e5} … V_{en}, mL) of sodium hydroxide solution at equivalent points. **You are not required** to fill all cells.

18. **Transfer** 50.0 ml aliquots **of solution C** into a plastic beaker, using Mohr pipette. Add ½V_{e3} mL of 0.100 M NaOH to obtain buffer solution with molar ratio H_nB: $NaH_{n-1}B$ as 1:1.

Mix the resulting solution and **measure** the pH. **Repeat** the experiment with other possible buffer compositions with molar ratio of conjugated acid-base as 1:1.

2.3.6. **Record** your results in the table. **Determine** the pK_a values for the polyprotic acid.

2.3.7. **Determine** the molar mass (M_{H_nB}, g/mol) and **suggest** acid the composition of the polyprotic acid H_nB.