Student Code AAA-1

Practical Problems

"Bonding the World with Chemistry"

49th INTERNATIONAL CHEMISTRY OLYMPIAD

Nakhon Pathom, THAILAND

General Instructions.

- ☐ **<u>Pages:</u>** This exam contains 36 pages for practical exam tasks (including the answer sheets). There are a total of 3 Tasks—Task 1A, Task 1B, and Task 2.

- ☐ **<u>Exam Reading:</u>** Students will have 15 minutes to read this exam booklet before starting the experiments. The official English version of this examination is available on request only for clarification.

- ☐ **<u>Exam Time:</u>** Students will have a <u>total of 5 hours</u> to complete all practical tasks. When planning your work, note that several steps require 20-30 minutes.

- ☐ **<u>Start/Stop:</u>** Students must begin as soon as the **"Start Command"** is given and must stop your work immediately when the **"Stop Command"** is announced.

    - The supervisor will announce 30 minute notification before the stop command.
    - Delaying in stopping the task after the **"Stop Command"** has already announced by **<u>1 minute</u>** will lead to cancellation of your practical exam.
    - After the **"Stop Command"** has been given, place your exam papers in your exam envelope and wait at your lab space. The lab supervisor will come pick up your exam paper and your submitted items as well as check your lab space.

- ☐ **<u>Safety:</u>** You must follow the safety rules given in the IChO regulations. While you are in the laboratory, you must wear laboratory goggle. The prescription safety glasses may be used if the supervisor approves. You may use gloves provided when handling chemicals.

    - If you break the safety rules given in the IChO regulations, you will receive only **ONE WARNING** from the laboratory supervisor. Any breaking safety rules after one warning will result in being dismissed from the laboratory and zero marks for the entire practical examination.
    - No eating or drinking allowed in the laboratory.
    - **Safety issue: Pipetting by mouth is strictly forbidden.**
    - Do not hesitate to ask your assistant or lab supervisor if you have any questions concerning safety issues. Inform your lab supervisor when need to leave the laboratory for a restroom break or having snacks.

- ☐ **<u>Working space:</u>** You are allowed to work only in the space assigned for you. Shared space and shared equipment must be clean after use.

- ☐ **<u>Chemical Refills/Replaced:</u>** Chemicals and labwares, unless noted, are not supposed to be refilled or replaced. Chemical and labwares will be refilled or replaced without penalty only for the first incident. Each further incident will result in the deduction of 1 point from your 40 practical exam points.

- ☐ **<u>Disposal:</u>** Leave all chemicals and labwares on your working space. Chemical waste must be disposed in the designated waste bottle for each task.

- ☐ **<u>Answer sheets:</u>** All results and answers must be clearly written in the appropriate area on the answer sheets for grading. Only answers written with pen will be graded.
  - Write down student code on every page.
  - Use only the pens provided for you.
  - Anything written outside the appropriate area on the answer sheets will not be graded. You may use the backside of the sheets as scratch papers.
  - For any calculation, use only the calculator provided.

- ☐ **<u>Stay hydrated throughout the practical exam</u>**. Drinks and snacks are provided outside the laboratory.

- ☐ **<u>UV spectrophotometer is to be shared between you and another student</u>**.

During the first 2 hours, use it when it is free. You need to wait until the other student finishes. You cannot use the spectrophotometer for more than 1 hour. (Longer than that you will be asked to stop to allow the another student to use.)
You can come back to the spectrophotometer if it is free. Organize your work so that you do not waste your time waiting.

Time	0900-1000	1000-1100	1100-1200	1200-1300	1300-1400
Slot	Free	Free	L	R	Free

L = student on the left side of the spectrophotometer

R = student on the right side of the spectrophotometer

You have the right to work on the tasks <u>in any order</u>.

Practical Exam

Task 1A

Chemicals and Equipment (Task 1A).

I. Chemical and materials (the actual labeling for each is given in bold font)

	Hazard Statements[a]
Instrument check solution, 80 cm^3 in a plastic bottle	
2.00×10^{-4} mol dm^{-3} **Methyl orange indicator solution,** 30 cm^3 in a wide mouth glass bottle	H301
1.00×10^{-3} mol dm^{-3} **Bromothymol blue indicator solution,** 30 cm^3 in a wide mouth glass bottle	
Methyl red indicator solution, 10 cm^3 in a wide mouth glass bottle	H225-H319-H371
1 mol dm^{-3} **HCl**, 30 cm^3 in a plastic bottle	H290-H314-H335
1 mol dm^{-3} **NaOH**, 30 cm^3 in a plastic bottle	H290-H314
buffer **solution A,** 110 cm^3 in a plastic bottle	
Unknown solution X, 50 cm^3 in a plastic bottle	
Unknown solution Y, 50 cm^3 in a plastic bottle	
Unknown solution Z, 50 cm^3 in a plastic bottle	

[a]**See page** 34 **for definition of Health Statements**

II. Equipment and labwares

Shared Equipment	Quantity
UV-Visible spectrophotometer	1 per 2 students
Personal Labwares	**Quantity**
Beaker, 25 cm^3	2
Volumetric flask, 25.00 cm^3	9
Measuring pipette, 2.00 cm^3	2
Measuring cylinder, 10.0 cm^3	3
Pasteur pipette	6
Rubber bulb for Pasteur pipette	6
Pipette filler bulb (3-way)	1
Pipette tray	1
Test tube (13 x 100 mm)	6
Test tube rack	1
Plastic cuvette, optical path length = 1.00 cm	1
Waste bottle, 1 dm^3	1
Sticker label set in a zipped bag	1

Task 1A 13%	a		b			c		Total
	a1	a2	b1	b2	b3	c1	c2	
Total	12	2	6	1	1	2	2	26
Score								

Accounted For 13% of Total Score

Task 1A: Acid-base indicator and its application for pH measurement

Acid-base indicators are weak acids (or bases) that exhibit different colors when they are present in solution as their acidic form (HIn, color 1) or as their basic form (In^-, color 2). They undergo the following reaction in dilute aqueous solution.

$$HIn \rightleftharpoons H^+ + In^-$$

As the pH of a solution containing the indicator changes, the equilibrium shown above will be driven either towards reactants (HIn), or products (In^-) causing the solution color to change depending on the concentration of each form present. In strongly acidic solution, most of the indicator will be present in the HIn form (color 1) and in strongly basic solutions, most of the indicator will be in the In^- form (color 2). At intermediate pH values, the solution color will be a mix of color 1 (absorption at wavelength 1) and color 2 (absorption at wavelength 2), depending on the relative amounts of HIn and In^- present.

By monitoring the absorbance values at two wavelengths, the concentrations of HIn and In^- can be calculated by using the following expressions.

$$A^{\lambda 1}_{total} = A^{\lambda 1}_{HIn} + A^{\lambda 1}_{In-}$$

$$= \varepsilon^{\lambda 1}_{HIn}\, b[HIn] + \varepsilon^{\lambda 1}_{In-} b[In^-]$$

$$A^{\lambda 2}_{total} = A^{\lambda 2}_{HIn} + A^{\lambda 2}_{In-}$$

$$= \varepsilon^{\lambda 2}_{HIn}\, b[HIn] + \varepsilon^{\lambda 2}_{In-} b[In^-]$$

where b is pathlength of solution and ε is the molar absorptivity.

At a certain pH value, the relative amounts of HIn and In^- in solution are related to the acid dissociation constant (K_a) of the indicator, as shown in the following equation.

$$K_a = \frac{[H^+][In^-]}{[HIn]}$$

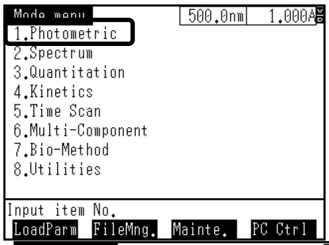
Therefore, for a given pH value, acid dissociation constant (K_a) of the indicator can be calculated when the relative amounts of HIn and In^- in solution are known.

Experimental Set-up

Instructions for using a spectrophotometer

1. Set a spectrophometer to measure the absorbance at the desired wavelength following the procedure shown in the diagram.
2. Wipe the outside of a cuvette containing distilled water and insert the cuvette into the sample compartment.
3. Adjust the zero absorbance using water.
4. Remove the cuvette, replace water in the cuvette by sample solution to be analyzed. Make sure to tap out any bubbles and wipe the outside of the cuvette before placing the cuvette into the sample compartment.
5. Read the absorbance value of the sample.

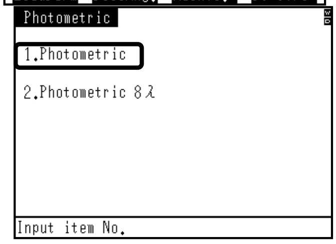
Note: When changing the wavelength, make sure to adjust zero absorbance using "water".



Step 1: Press 1

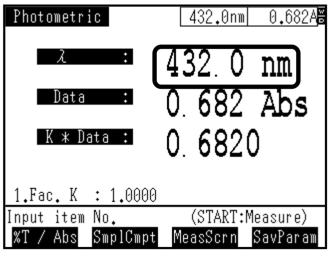
Press 1 icon on the keypad to select Photometric mode

Note: If the main menu as shown in the left picture is not displayed on the screen, press [return] on the keypad.



Step 2: Press 1

Press 1 icon on the keypad to select Photometric mode single wavelength mode



Step 3: Set the wavelength

Press **[GO TO WL]** on the keypad to set the wavelength

Press number on the keypad

Note: For example, if the desired wavelength is 432, press 4 3 2 on the keypad.

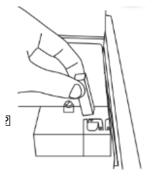
Press **[ENTER]** on the keypad

[GO TO WL] → 4 3 2 → [ENTER]

Note: If the Abs is not displayed on the screen, press [F1] on the keypad to switch between %T and Abs

Rinse with DI water →

Fill the solution around ¾ of the cuvette height and wipe with paper



Step 4: Get the absorbance value

Place cuvette containing water in the sample compartment and press [AUTO ZERO] on the keypad.

Place cuvette containing sample solution in the sample compartment to measure the absorbance

Repeat Step 3-4 to measure the absorbance at another wavelength

General Information

In 0.1 mol dm^{-3} HCl, indicators are in the acidic form (HIn) only.

In 0.1 mol dm^{-3} NaOH, indicators are in the basic form (In^-) only.

There will be no mark for the answer in the dotted line box.

NOTE:

Students are suggested to check the spectrophotometer before use by measuring the absorbance values of the instrument check solution at two different wavelengths, i.e., 430 and 620 nm.

Spectrophotometer No. _________ is used throughout the experiment.

Record the absorbance values of the instrument check solution

	A (at 430 nm)	A (at 620 nm)
Measured value	_________________	_________________
Guided value	0.220 – 0.260	0.450 – 0.510

In case that the measured values are within the guided values, students can proceed with further experiments. If not, students can ask for assistance.

Part a

Absorbance measurement of an acid-base indicator (methyl orange) in strong acid and strong base

1. Pipette 1.50 cm^3 of 2.00×10^{-4} mol dm^{-3} **methyl orange indicator** solution into a 25.00-cm^3 volumetric flask, add 2.5 cm^3 of 1 mol dm^{-3} HCl into the flask and make up to the volume using distilled water. Record the absorbance at 470 and 520 nm.

2. Pipette 2.00 cm^3 of 2.00×10^{-4} mol dm^{-3} **methyl orange indicator** solution into a 25.00-cm^3 volumetric flask, add 2.5 cm^3 of 1 mol dm^{-3} NaOH into the flask and make up to the volume using distilled water. Record the absorbance at 470 and 520 nm.

3. Calculate the molar absorptivities at 470 and 520 nm of acidic and basic forms of **methyl orange**.

a1) Record the absorbance values of methyl orange in acid and basic solutions

(You do not need to fill the entire table.)

methyl orange in acidic form	A (at 470 nm)	A (at 520 nm)
Replicate 1		
Replicate 2		
Replicate 3		
Accepted value (3 digits after decimal point)	________	________

methyl orange in basic form	A (at 470 nm)	A (at 520 nm)
Replicate 1		
Replicate 2		
Replicate 3		
Accepted value (3 digits after decimal point)	________	________

a2) Calculate the molar absorptivities of the acidic form and basic form of methyl orange (unit, $dm^3\ mol^{-1}\ cm^{-1}$)

Blank area for calculation

The molar absorptivities of methyl orange are as follows: (unit, $dm^3\ mol^{-1}\ cm^{-1}$)

	acidic form (HIn)		basic form (In^-)	
methyl orange	ε^{470}_{HIn}	ε^{520}_{HIn}	ε^{470}_{In-}	ε^{520}_{In-}
	________	________	________	________

Part b

Absorbance measurement of an acid-base indicator (bromothymol blue) in buffer solution

Bromothymol blue is an acid-base indicator which shows yellow color when it is present as an acidic form (HIn) and it shows blue color when it is present as a basic form (In^-). The absorption maximum of the bromothymol blue in the acidic form is at 430 nm and that in the basic form is at 620 nm. The molar absorptivities of bromothymol blue in the acidic form are 16,600 $dm^3 mol^{-1} cm^{-1}$ at 430 nm and 0 $dm^3\ mol^{-1}\ cm^{-1}$ at 620 nm. The molar absorptivities of bromothymol blue in the basic form are 3,460 $dm^3\ mol^{-1}\ cm^{-1}$ at 430 nm and 38,000 $dm^3\ mol^{-1}\ cm^{-1}$ at 620 nm.

1. Pipette 1.00 cm^3 of 1.00×10^{-3} mol dm^{-3} **bromothymol blue indicator** solution into a 25.00-cm^3 volumetric flask, and make up to the volume using solution A. (Note: solution A is a buffer solution pH = 7.00)
2. Record the absorbance at 430 and 620 nm.
3. Calculate the concentrations of the acidic form and basic form of **bromothymol blue indicator** solution in the volumetric flask.
4. Calculate the acid dissociation constant of **bromothymol blue**.

b1) Record the absorbance values of bromothymol blue in buffer solution

(You do not need to fill the entire table.)

bromothymol blue in buffer solution	A (at 430 nm)	A (at 620 nm)
Replicate 1		
Replicate 2		
Replicate 3		
Accepted value (3 digits after decimal point)	________	________

b2) Calculate the concentrations of the acidic form and basic form of bromothymol blue indicator in the resulting solution

Blank area for calculation

The concentrations of the acidic form and basic form of bromothymol blue in the resulting solution are as follows:

[HIn], mol dm^{-3}	[In$^-$], mol dm^{-3}
____________ (3 significant figures)	____________ (3 significant figures)

b3) Calculate the acid dissociation constant of bromothymol blue from this experiment.

Blank area for calculation

The acid dissociation constant of bromothymol blue from this experiment is as follows:

The acid dissociation constant = ____________________ (3 significant figures)

Part c

Determination of solution pH by using acid-base indicator (methyl red)

Methyl red is an acid-base indicator which shows reddish-pink color when it is present as an acidic form (HIn) and it shows yellow color when it is present as a basic form (In^-). The molar absorptivities of methyl red in the acidic form are 9,810 $dm^3\ mol^{-1}\ cm^{-1}$ at 470 nm and 21,500 $dm^3\ mol^{-1}\ cm^{-1}$ at 520 nm. The molar absorptivities of methyl red in the basic form are 12,500 $dm^3\ mol^{-1}\ cm^{-1}$ at 470 nm and 1,330 $dm^3\ mol^{-1}\ cm^{-1}$ at 520 nm. The pKa of methyl red is 4.95.

Note: There is no need to accurately measure the volumes used in this part, as it does not affect the accuracy of the results obtained.

1. Fill a test tube to one quarter with solution of unknown pH X. Add three drops of **methyl red** into the solution and mix thoroughly. Record the color.
2. Fill a test tube to one quarter with solution of unknown pH Y. Add three drops of **methyl red** into the solution and mix thoroughly. Record the color.
3. Fill a test tube to one quarter with solution of unknown pH Z. Add three drops of **methyl red** into the solution and mix thoroughly. Record the color.

Record the color change of indicator in sample solutions (no mark)

indicator	Color observed		
	in sample X	in sample Y	in sample Z
Methyl red			

c1) Select one solution from the three sample solutions, of which the pH can be determined spectrophotometrically by using methyl red as an indicator.

☐ Sample X ☐ Sample Y ☐ Sample Z

4. Use a measuring cylinder to transfer 10 cm^3 of the selected unknown solution into a beaker. Add three drops of **methyl red** indicator into the solution and mix thoroughly. Record the absorbance at 470 and 520 nm.
5. Calculate the concentration ratio of basic form and acidic form of **methyl red** in the solution.
6. Calculate the pH of the selected unknown solution.

Record the absorbance values of the resulting solution

selected unknown solution	A (at 470 nm)	A (at 520 nm)

c2) Calculate the concentration ratio of the basic form and acidic form of methyl red indicator in an unknown solution and the pH value of the unknown solution

Blank area for calculation

The concentration ratio of the basic form and acidic form of methyl red indicator in an unknown solution and the pH value of the unknown solution are as follows:

sample	$[In^-] / [HIn]$	pH
	____________ (2 digits after decimal point)	____________ (2 digits after decimal point)

Practical Exam

Task 1B

Chemicals and Equipment (Task 1B)

I. Chemicals and materials (the actual labeling for each is given in bold font)

	Health Statements[a]
Solution A (KIO_3 10.7042 g in 5.00 dm^3), 60 cm^3 in a plastic bottle	H272-H315-H319-H335
Solution B (Saturated $Ca(IO_3)_2$ solution), 50 cm^3 in a plastic bottle	H272-H315-H319-H335
Solution C (Saturated $Ca(IO_3)_2$ in unknown dilute KIO_3 solution)**,** 50 cm^3 in a plastic bottle	H272-H315-H319-H335
Solution of **$Na_2S_2O_3$** 200 cm^3 in a plastic bottle	
KI 10% (w/v), 100 cm^3 in a plastic bottle	H300+H330-H312-H315-H319-H335
HCl 1 mol dm^{-3}, 100 cm^3 in a plastic bottle	H290-H314-H335
Starch solution 0.1% (w/v), 30 cm^3 in a dropping glass bottle	
Distilled water, 500 cm^3 in a **wash bottle**	
Distilled water, 1000 cm^3 in a plastic **gallon**	

[a]See page xx for definition of Risk and Safety Phrases

II. Equipment and labwares

Personal Labwares	**Quantity**
Beaker, 100 cm^3	2
Beaker, 250 cm^3	1
Erlenmeyer flask, 125 cm^3	9
Transfer pipette, 5.00 cm^3	2
Transfer pipette, 10.00 cm^3	1
Measuring cylinder, 10.0 cm^3	1
Measuring cylinder, 25.0 cm^3	2
Pasteur pipette	1
Rubber bulb for Pasteur pipette	1
Glass funnel, 7.5 cm diameter	2
Plastic funnel, 5.5 cm diameter	1
Filter paper in a zipped bag	3
Burette, 50.0 cm^3	1
Burette stand and clamp	1
O-ring with bosshead	2

Task 1B	a			b			c			Total
	a1	a2	a3	b1	b2	b3	c1	c2	c3	
Total	1	5	1	6	1	2	6	1	3	26
Score										

Accounted for 13% of Total Score

<u>Task 1B: Calcium iodate</u>

Calcium iodate is an inorganic salt composed of calcium and iodate ions. $Ca(IO_3)_2$ is sparingly soluble in water. Equilibrium is established between the undissolved salt and saturated solution of the salt.

$$Ca(IO_3)_{2\,(s)} \rightleftharpoons Ca^{2+}_{(aq)} + 2\,IO_3^-{}_{(aq)}$$

Titration data will be used to determine the concentration of iodate ions in a saturated solution of $Ca(IO_3)_2$ and then to determine the value of Ksp for $Ca(IO_3)_2$.

The concentration of iodate ion will be determined by titration with a standard solution of sodium thiosulfate ($Na_2S_2O_3$), in the presence of potassium iodide (KI). Starch will be used as an indicator.

Part a is associated with the standardization of $Na_2S_2O_3$. Part b is the determination of Ksp for $Ca(IO_3)_2$.

In Part C, solid $Ca(IO_3)_2$ is dissolved in an unknown dilute KIO_3 solution. After standing for 3 days, equilibrium is also established between the undissolved salt and saturated solution of the salt. The concentration of iodate ion will be determined using the same titrimetric method, and then used to calculate the concentration of the dilute KIO_3 solution.

Part a

Standardization of $Na_2S_2O_3$

1. Fill the burette with $Na_2S_2O_3$ solution.
2. Pipette 10.00 cm^3 of standard KIO_3 solution (provided as solution A, KIO_3 10.7042 g in 5.00 dm^3) into an Erlenmeyer flask. Add 10 cm^3 of 10%(w/v) KI and 10 cm^3 of 1 mol dm^{-3} HCl into a flask. The solution should turn dark brown as I_2 is formed.
3. Titrate with $Na_2S_2O_3$ solution until the solution has turned pale yellow. Add 2 cm^3 of 0.1%(w/v) starch solution. The solution should turn dark blue. Titrate carefully to the colorless endpoint. Record the volume of $Na_2S_2O_3$ solution.

a1) Balance relevant chemical equations.

…… $IO_3^-{}_{(aq)}$ + …… $I^-{}_{(aq)}$ + …... $H_3O^+{}_{(aq)}$ → …… $I_{2(aq)}$ + …… $H_2O_{(l)}$

……$I_{2\,(aq)}$ + …… $S_2O_3^{2-}{}_{(aq)}$ → …… $I^-{}_{(aq)}$ + …… $S_4O_6^{2-}{}_{(aq)}$

a2) Record volume of $Na_2S_2O_3$ solution.

(You do not need to fill in the entire table)

	Titration no.		
	1	2	3
Initial reading of the burette of $Na_2S_2O_3$ solution, cm^3			
Final reading of the burette of $Na_2S_2O_3$ solution, cm^3			
Consumed volume of $Na_2S_2O_3$ solution, cm^3			

Accepted volume, cm^3; V1 =

a3) Calculate the concentration of the $Na_2S_2O_3$ solution.

Concentration of $Na_2S_2O_3$, mol dm^{-3}: …………… (answer in 4 digits after decimal point)

(If the student cannot find the concentration of $Na_2S_2O_3$, use the concentration of 0.0700 mol dm^{-3} for further calculations.)

Part b

Determination of Ksp of $Ca(IO_3)_2$

1. You are provided with the filtrate of the filtered saturated solution of $Ca(IO_3)_2$. (Solution B)
2. Pipette 5.00 cm^3 of the filtrate into an Erlenmeyer flask. Add 10 cm^3 of 10% (w/v) KI and 10 cm^3 of 1 mol dm^{-3} HCl into a flask.
3. Titrate with $Na_2S_2O_3$ solution until the solution has turned pale yellow. Add 2 cm^3 0.1% (w/v) starch solution. The solution should turn dark blue. Titrate carefully to the colorless endpoint. Record the volume of $Na_2S_2O_3$ solution.

b1) Record volume of $Na_2S_2O_3$ solution.

(You do not need to fill in the entire table)

	Titration no.		
	1	2	3
Initial reading of the burette of $Na_2S_2O_3$ solution, cm^3			
Final reading of the burette of $Na_2S_2O_3$ solution, cm^3			
Consumed volume of $Na_2S_2O_3$ solution, cm^3			

Accepted volume, cm^3; V2 =

b2) Calculate the concentration of the IO_3^- solution.

Concentration of IO_3^-, mol dm^{-3}: …………………(answer in 4 digits after decimal point)

b3) Calculate value of Ksp for **$Ca(IO_3)_2$.**

Ksp for $Ca(IO_3)_2$ = ………………………………….(answer in 3 significant figures)

(If the student cannot find Ksp, use the value of 7×10^{-7} for further calculations.)

Part c

Determination of concentration of unknown dilute KIO_3 solution

1. You are provided with the filtrate of the filtered saturated solution of $Ca(IO_3)_2$ dissolved in the unknown dilute KIO_3 (provided as solution C).
2. Pipette 5.00 cm^3 of the filtrate solution into an erlenmeyer flask. Add 10 cm^3 of 10% (w/v) KI and 10 cm^3 of 1 mol dm^{-3} HCl into a flask.
3. Titrate with $Na_2S_2O_3$ solution until the solution has turned pale yellow. Add 2 cm^3 0.1% (w/v) starch solution. The solution should turn dark blue. Titrate carefully to the colorless endpoint. Record the volume of $Na_2S_2O_3$ solution.

c1) Record volume of $Na_2S_2O_3$ solution

(You do not need to fill in the entire table)

	Titration no.		
	1	2	3
Initial reading of the burette of $Na_2S_2O_3$ solution, cm^3			
Final reading of the burette of $Na_2S_2O_3$ solution, cm^3			
Consumed volume of $Na_2S_2O_3$ solution, cm^3			

Accepted volume, cm^3; V3 =

c2) Calculate the concentration of the IO_3^- in solution C.

Concentration of IO_3^-, mol dm^{-3}: ……………………(answer in 4 digits after decimal point)

c3) Calculate the concentration of the unknown dilute KIO_3 sample.

Concentration of IO_3^- , mol dm^{-3}: ……………… (answer in 4 digits after decimal point)

Practical Exam

Task 2

Chemicals and Equipment (Task 2).

I. Chemicals and materials

Chemicals	Labeled as	Health Statements [a]
3-Pentanone (MW 86.13), ~0.86 g[b] in a vial	**A**	H225-H319-H335-H336
***p*-chlorobenzaldehyde (MW140.57)**, ~3.5 g[c] in a vial	**B**	H302-H315-H319-H335
Ethanol, 200 cm^3 in a wash-bottle	**Ethanol**	H225-H319
2 mol dm^{-3} **NaOH** solution in water (**labelled as 2N NaOH**), 25 cm^3 in a bottle	**2N NaOH**	H290-H314

[a] See **page 34 for definition of Health Statements**
[b] You will need to weigh the vial containing 3-pentanone right before using. The exact value can be calculated based on the information given on the label.
[c] The exact value is indicated on the label.

II. Equipment and labwares

Shared equipment	Quantity
Balance	Shared 12 per room
Water aspirator	Shared 2 per bench
Foam bucket filled with ice	Shared 1 per row (Refill could be requested)
Personal Equipment	**Quantity**
Hotplate stirrer with temperature probe	1
Stand	1
Clamps	2
100-cm^3 Round bottom flask	1
Measuring cylinder, 25 cm^3	1
Measuring cylinder, 50 cm^3	1
Air condenser	1
Crystallizing dish, 250 cm^3	1
125-cm^3 Erlenmeyer flask	2
Suction flask, 250 cm^3	1
Buchner funnel, 25 cm^3	1
Watch glass	1
Pasteur pipettes (droppers)	5
Rubber bulbs	2
Suction rubber	1
Rubber support ring	1
Magnetic bar	1
Filter papers	3 (pack in 1 zipped bag)
Spatula	1
Stirring Rod	1
Forceps	1
Plastic joint clips	1
Wash Bottle (filled with EtOH)	1 (can be refilled)
Nitrile gloves	2 (exchange size if needed)
Towels	2
Paper clip	1
“Waste Task 2”, 500 cm^3-glass bottle	1
Vial labeled “Student code” for submitting product.	1
Goggles	1

Task 2	a			b	Total
	a1	a2	a3	b1	
Total	2	2	2	18	24
Score					

Accounted for 14% of Total Score

Task 2: Elaborating Carbon Framework

The core structure of organic molecules is mostly based on carbon-carbon skeleton. Carbon-carbon bond formations have played a vital role in the construction of complex structures from smaller starting materials. Therefore, the synthetic transformations to efficiently achieve carbon-carbon bond formation has long been of interest. In this experiment, you are required to transform commercially available *p*-chlorobenzaldehyde and 3-pentanone to a more elaborated structure.

Important Notes:

- Ethanol can be refilled with no penalty.
- All weighing processes require verification from lab supervisor. The supervisor will need to sign in the student's answer sheet for grading. No mark will be given for unverified values.
- Total of 18 points of this exam score will be based on the quality and quantity of the product submitted. **We could not give any score on this part if the product is not submitted for grading.**
- ^{1}H-NMR and melting point determination techniques will be used by the grader to verify the quality of your product.

Part a

1. Take the vial containing 3-pentanone (**A**) (Code Axxx, For example: A305) and unwrap the parafilm. Weigh the vial with caps. Record the weight in the answer sheet question a1.
2. Setup a water bath by filling water in the 250 cm^3-crystallizing dish and heat to 55±2°C. Add paper clip into the water bath and let it stir so that the heat could be distributed evenly.
3. Ensure a magnetic stirring bar is in the 100-cm^3 round bottom flask. Transfer the pre-weighed 3-pentanone (labeled as **A**) and *p*-chlorobenzaldehyde (labeled as **B**) to the flask. Add 50 cm^3 ethanol to the mixture and swirl to dissolve.

4. Measure 15 cm^3 of 2 mol dm^{-3} NaOH (labeled as 2N NaOH) using a measuring cylinder and add to the reaction mixture. Be careful not to wet the ground joint with NaOH solution.

5. Setup the reaction as shown in **Figure 1**. The reaction flask is placed in the 55±2°C water bath. Attach the air condenser to the reaction flask with plastic joint clip. Heat the reaction mixture while stirring for 30 minutes using the water bath.

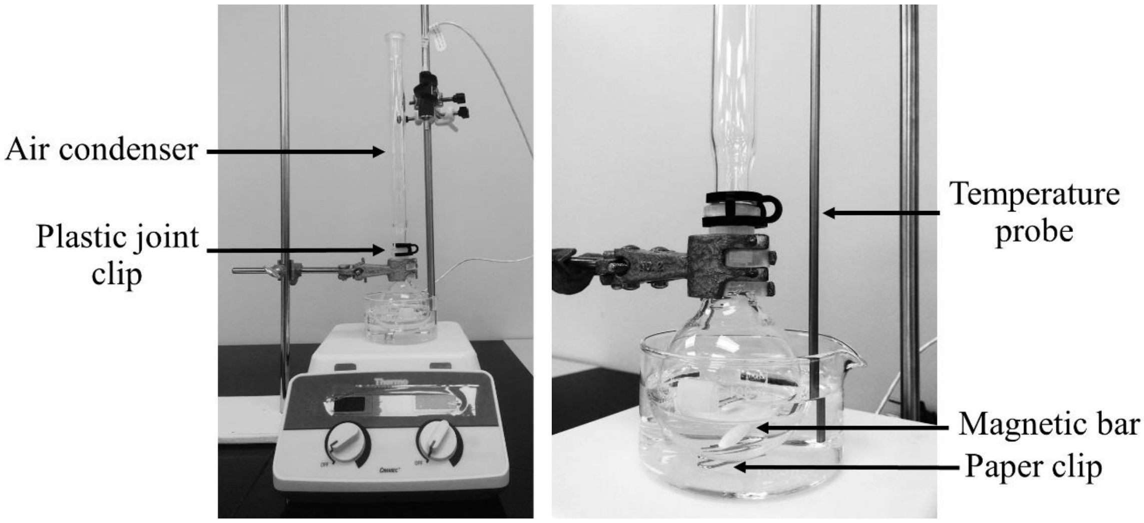


Figure 1: Set up needed for heating the reaction with water bath.

6. Remove the reaction flask from the water bath. **(Be careful! The flask might be hot.)** Place the flask on the rubber supporting ring.

7. **(Important)** Detach the probe from the hotplate/stirrer to avoid over-heating of the hotplate in the recrystallizing steps. After you detach the probe, inform the supervisor to check and submit the probe to the supervisor.

8. Prepare the ice bath by replacing the warm water in the 250 cm^3-crystalizing dish with ice and small amount of water. Place the reaction flask on the ice bath to cool down the reaction. Solid should be observed. (**Suggestion:** If you do not observe any solid within 5 minutes, you may use a stirring rod to scratch the side of the flask. This could induce precipitation.)

9. Keep the mixture cool for approximately 20 minutes to allow complete precipitation.

10. Set up the suction filtration equipment (**Figure 2**). Connect the suction flask to the water aspirator. Place a Buchner funnel fitted with a rubber adapter onto the suction flask. Place a filter paper at the center of the funnel. Filter the precipitate *via* suction filtration and wash the precipitate with small amount of cold ethanol. Let air suck through the precipitates for 2-3 minutes to dry the product.

Figure 2: Set up needed for suction filtration.

11. Disconnect the vacuum (before turning off the water aspirator). Bring your equipment back to your space and keep the common area clean. Collect the crude precipitates from the filter paper and transfer to the Erlenmeyer flask. **Careful not to scrape the paper too hard as you may obtain small pieces of paper as contaminant**. Student may use Ethanol to rinse the Buchner funnel.

12. Place ethanol in a separate Erlenmeyer flask and heat it gently on a hotplate. (Student may set the temperature mark at 100-120°C) **Before heating, please make sure that the temperature probe is detached from the hotplate.**

13. Recrystallize the product from hot ethanol. You can follow the procedure below.

    Add small amount of hot ethanol to the flask containing crude solid while swirling. Continue addition of hot ethanol (swirling after each addition) until the solid is completely dissolved. During the dissolution process, keep the flask hot at all times by resting it on the hotplate. **Be careful that the flask may be hot.** You may use paper towels or towels provided to wrap around the flask while swirling. Once the dissolution is complete, set the flask containing the dissolved compound on a benchtop and let the flask cool down to room temperature without disturbance. The crystalline product should be observed. If not, you may use the stirring rod to scratch the side of the flask to induce crystallization. Place the flask into the ice bath to complete crystallization.

14. Filter the recrystallized product *via* suction filtration (See step 10 for suction filtration protocol) and wash the product with small amount of cold ethanol. Let air suck through the precipitates for 2-3 minutes. Disconnect the vacuum. Let the purified product air-dry on the benchtop for at least 15 minutes.

15. Weigh the vial (without cap) labeled with your student code provided. Record the value in the answer sheet question a1.

16. Transfer the recrystallized product to the pre-weighed vial. Determine and record the mass of the purified product in the answer sheet question a1.

17. Fill the information on the label of the product vial. Place the product-containing vial on the benchtop. The supervisor will pick up your vial and sign on your answer sheet question b after the “Stop command”. The student also must sign the answer sheet question b for grading. Once both supervisor and student sign, place the vial into a zipped bag and submitted for grading.

These following items should be left on your bench:

- The exam/answer booklet (this booklet) placed in an exam envelope
- The vial labeled “Student Code” with filled information

Student Code **AAA-1**

Supervisor will place a label here
when randomly distributed the compounds:

Axxx (For example: A567) =	Code of vial containing 3-pentanone
Tared (w/caps):	Mass of (vial + label + caps) **before** adding 3-pentanone
Bxxx (For example: B567) =	Code of vial containing *p*-chlorobenzaldehyde
Net:	Mass of *p*-chlorobenzaldehyde

a1) Use the information provided in the label above along with your experimental data for your calculation. Write down all the results in this Table.

Mass of 3-pentanone in the vial provided (must weigh with caps) = ________________

*Signature of the supervisor is required for grading

Mass of pentan-3-one = ______________________________

Mass of *p*-chlorobenzaldehyde (copy from the label):__________________________

Mass of the empty vial for product:_____________________________

*Signature of the supervisor is required for grading

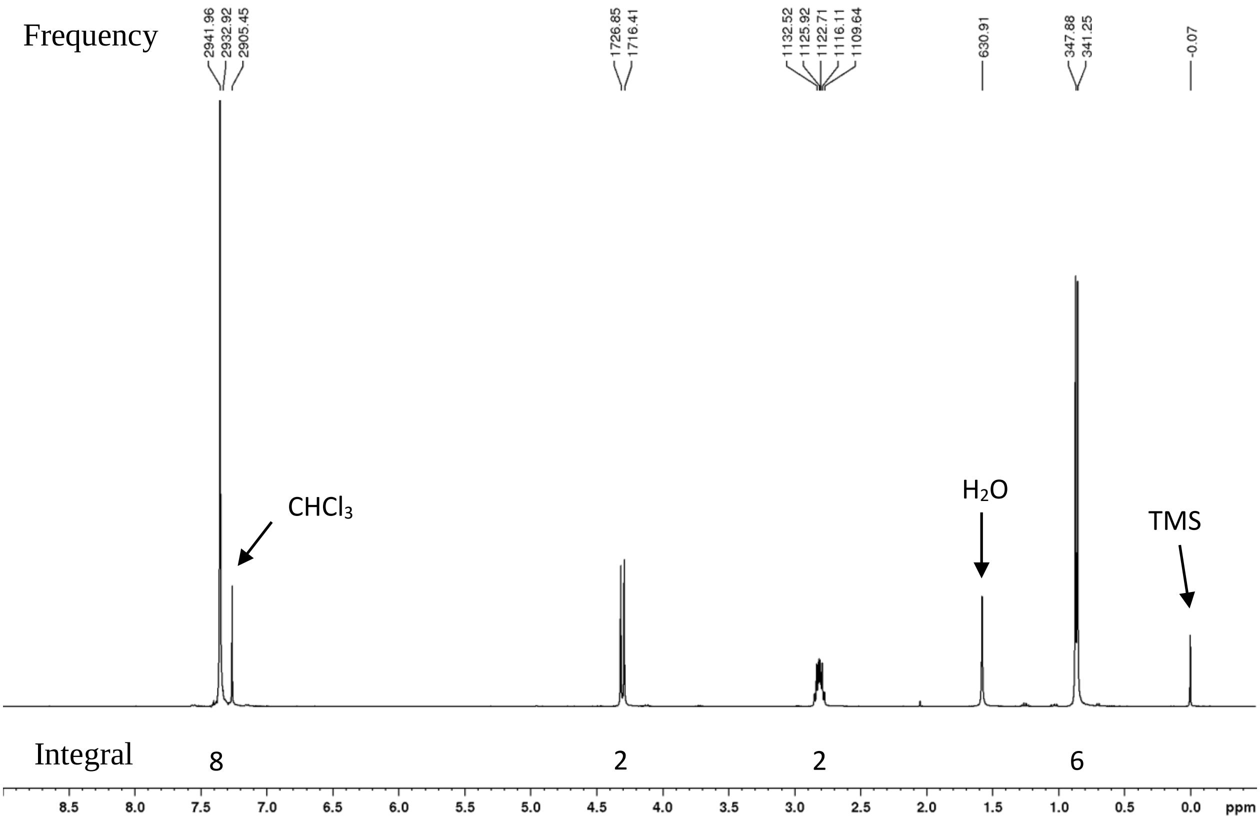
Mass of the vial with the recrystallized product:______________________________

*Signature of the supervisor is required for grading

Mass of the recrystallized product:______________________

a2) Write 4 plausible aromatic compounds that may occur from this reaction. Stereoisomers are excluded.

a3) Given the 400MHz ^{1}H-NMR (in $CDCl_3$) of the product below, write the structure of the product.



Integrals are for all protons presented in the molecule.

Part b

b1) Your submitted product will be characterized and graded for its %yield and purity. Provide information of the product you submitted.

Status: ☐ Solid ☐ Liquid

Signature of Supervisor: ____________________________(Signed when submitted)

Signature of Student: ______________________________ (Signed when submitted)

Health Statements

H225	Highly flammable liquid and vapor
H272	May intensify fire; oxidizer
H290	Maybe corrosive to metals
H300	Fatal if swallowed
H301	Toxic if swallowed
H302	Harmful if swallowed
H314	Causes severe skin burns and eye damage
H315	Causes skin irritation
H319	Causes serious eye irritation
H330	Fatal if inhaled
H335	May cause respiratory irritation
H336	May cause drowsiness or dizziness
H371	May cause damage to organs

Characteristic ^1H NMR Chemical Shifts

Type of Hydrogen (R=Alkyl, Ar=Aryl)	Chemical Shift (ppm)	Type of Hydrogen (R=Alkyl, Ar=Aryl)	Chemical Shift (ppm)
$(CH_3)_4Si$	0 (by definition)		
$RC\mathbf{H}_3$	0.9	$RC\mathbf{H}{=}O$	9.5-10.1
$RC\mathbf{H}_2R$	1.2-1.4	$RCOO\mathbf{H}'$	10-13
$R_3C\mathbf{H}$	1.4-1.7	$RCOC\mathbf{H}_3$	2.1-2.3
$RC\mathbf{H}_2I$	3.2-3.3	$RCOC\mathbf{H}_2R$	2.2-2.6
$RC\mathbf{H}_2Br$	3.4-3.5	$RCOOC\mathbf{H}_3$	3.7-3.9
$RC\mathbf{H}_2Cl$	3.6-3.8	$RCOOC\mathbf{H}_2R$	4.1-4.7
$RC\mathbf{H}_2F$	4.4-4.5	$R_2C{=}CRC\mathbf{H}R_2$	1.6-2.6
$RC\mathbf{H}_2NH_2$	2.3-2.9	$R2C{=}C\mathbf{H}_2$	4.6-5.0
$RC\mathbf{H}_2OH$	3.4-4.0	$R_2C{=}C\mathbf{H}R$	5.0-5.7
$RC\mathbf{H}_2OR$	3.3-4.0	$RC{\equiv}C\mathbf{H}$	2.0-3.0
$RC\mathbf{H}_2CH_2OR$	1.5-1.6	$ArC\mathbf{H}_3$	2.2-2.5
$R_2N\mathbf{H}$	0.5-5.0	$ArC\mathbf{H}_2R$	2.3-2.8
$RO\mathbf{H}$	0.5-6.0	$Ar\mathbf{H}$	6.5-8.5

Periodic table of elements

1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9 8B	10 8B	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1 **H** 1.008																	2 **He** 4.003
3 **Li** 6.941	4 **Be** 9.012											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.31											13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.07	17 **Cl** 35.45	18 **Ar** 39.95
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.88	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.55	30 **Zn** 65.39	31 **Ga** 69.72	32 **Ge** 72.61	33 **As** 74.92	34 **Se** 78.97	35 **Br** 79.90	36 **Kr** 83.80
37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.95	43 **Tc** (98)	44 **Ru** 101.1	45 **Rh** 102.9	46 **Pd** 106.4	47 **Ag** 107.9	48 **Cd** 112.4	49 **In** 114.8	50 **Sn** 118.7	51 **Sb** 121.8	52 **Te** 127.6	53 **I** 126.9	54 **Xe** 131.3
55 **Cs** 132.9	56 **Ba** 137.3	57 **La** 138.9	72 **Hf** 178.5	73 **Ta** 180.9	74 **W** 183.8	75 **Re** 186.2	76 **Os** 190.2	77 **Ir** 192.2	78 **Pt** 195.1	79 **Au** 197.0	80 **Hg** 200.6	81 **Tl** 204.4	82 **Pb** 207.2	83 **Bi** 209.0	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** (226)	89 **Ac** (227)	104 **Rf** (261)	105 **Db** (262)	106 **Sg** (263)	107 **Bh** (262)	108 **Hs** (265)	109 **Mt** (266)	110 **Ds** (281)	111 **Rg** (272)	112 **Cn** (285)	113 **Nh** (286)	114 **Fl** (289)	115 **Mc** (289)	116 **Lv** (293)	117 **Ts** (294)	118 **Og** (294)

58 **Ce** 140.1	59 **Pr** 140.9	60 **Nd** 144.2	61 **Pm** (145)	62 **Sm** 150.4	63 **Eu** 152.0	64 **Gd** 157.3	65 **Tb** 158.9	66 **Dy** 162.5	67 **Ho** 164.9	68 **Er** 167.3	69 **Tm** 168.9	70 **Yb** 173.0	71 **Lu** 175.0
90 **Th** 232.0	91 **Pa** 231.0	92 **U** 238.0	93 **Np** (237)	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (262)