Student Code AAA-1

Practical Problems
Revised Grading Scheme

"Bonding the World with Chemistry"

49th INTERNATIONAL CHEMISTRY OLYMPIAD

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General Instructions.

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)	0.318 (SD = 0.009)	0.538 (SD = 0.011)

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)	0.425 (SD = 0.009)	0.141 (SD = 0.004)

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)	0.489 (SD = 0.006)	0.734 (SD = 0.014)

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)

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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										

a1) Balance relevant chemical equations.

…1… $IO_3^-{}_{(aq)}$ + …5… $I^-{}_{(aq)}$ + …6... $H_3O^+{}_{(aq)}$ $\rightarrow$ …3… $I_{2(aq)}$ + …9… $H_2O_{(l)}$ (0.5 points)

…1…$I_2{}_{(aq)}$ + …2… $S_2O_3^{2-}{}_{(aq)}$ $\rightarrow$ …2… $I^-{}_{(aq)}$ + …1… $S_4O_6^{2-}{}_{(aq)}$ (0.5 points)

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 = 12.08 ± 0.20 (5 points)

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

$$\frac{(C_{IO3-} \times V_{IO3-}) \times 6}{V_{S2O32-}} = C_{S2O32-}$$

$$\frac{(0.0100 \times 10.00) \times 6}{12.08} = 0.0497$$

Concentration of $Na_2S_2O_3$, mol dm^{-3}: …0.0497… (answer in 4 digits after decimal point) (1 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 = 13.20 ± 0.20 (6 points)

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

$$\frac{(C_{S2O32-} \times V_{S2O32-}) \times 1}{V_{IO3-} \times 6} = C_{IO3-}$$

$$\frac{(0.0497 \times 13.20) \times 1}{5.00 \times 6} = 0.0219$$

Concentration of IO_3^-, mol dm^{-3}: …0.0219………..(answer in 4 digits after decimal point)

(1 point)

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

$$C_{Ca^{2+}} = \frac{C_{IO_3^-}}{2}$$
$$= \frac{0.0219}{2} = 0.0110$$

Concentration of Ca^{2+}, mol dm^{-3}: ………0.0110……………………

$$Ksp = [Ca^{2+}][IO_3^-]^2$$

$$Ksp = (0.0110) \times (0.0219)^2$$
$$= 5.28 \times 10^{-6}$$

Ksp for $Ca(IO_3)_2$ = ……5.28×10^{-6}……………(answer in 3 significant figures) (2 points)

(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 = 14.43 ± 0.20 (6 points)

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

$$\frac{(C_{S2O32-} \times V_{S2O32-}) \times 1}{V_{IO3-} \times 6} = C_{IO3-}$$

$$\frac{(0.0497 \times 14.43) \times 1}{5.00 \times 6} = 0.0239$$

Concentration of IO_3^-, mol dm^{-3}: …0.0239………(answer in 4 digits after decimal point)

(1 point)

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

$$\frac{Ksp}{[IO_3^-]^2} = \frac{5.28 \times 10^{-6}}{(0.0239)^2} = [Ca^{2+}]$$

$$= 0.00924$$

Concentration of Ca^{2+}, mol dm^{-3}: ………0.00924 ………………………………

$$[KIO_3]_{sample} = [IO_3^-]_{in\ soln.C} - [IO_3^-]_{solubilized\ Ca(IO3)2}$$

$$= 0.0239 - (2 \times [Ca^{2+}])$$

$$= 0.0239 - (2 \times 0.00924)$$

Concentration of IO_3^-, mol dm^{-3}: …0.0542.. (answer in 4 digits after decimal point)

(3 point)

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

Accounted for 14% of Total Score

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 = ______________________________1 point

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

Mass of the empty vial for product:_____________________________

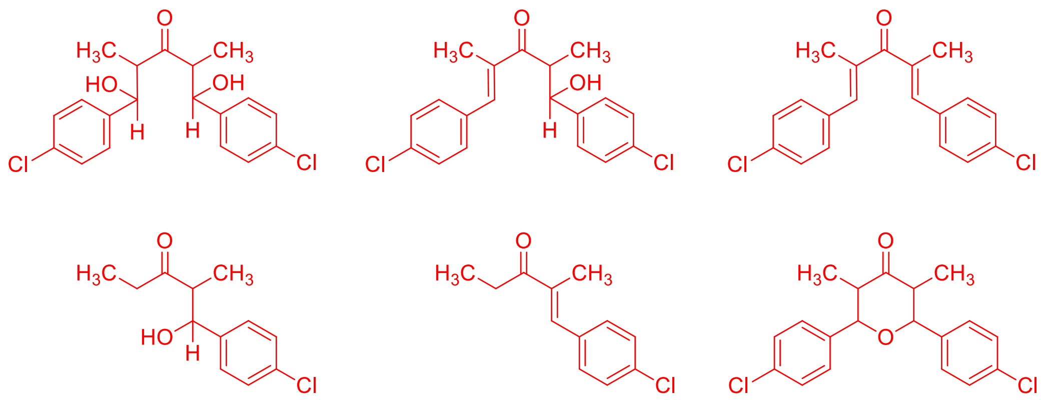
*Signature of the supervisor is required for grading

Mass of the vial with the recrystallized product:______________________________

*Signature of the supervisor is required for grading

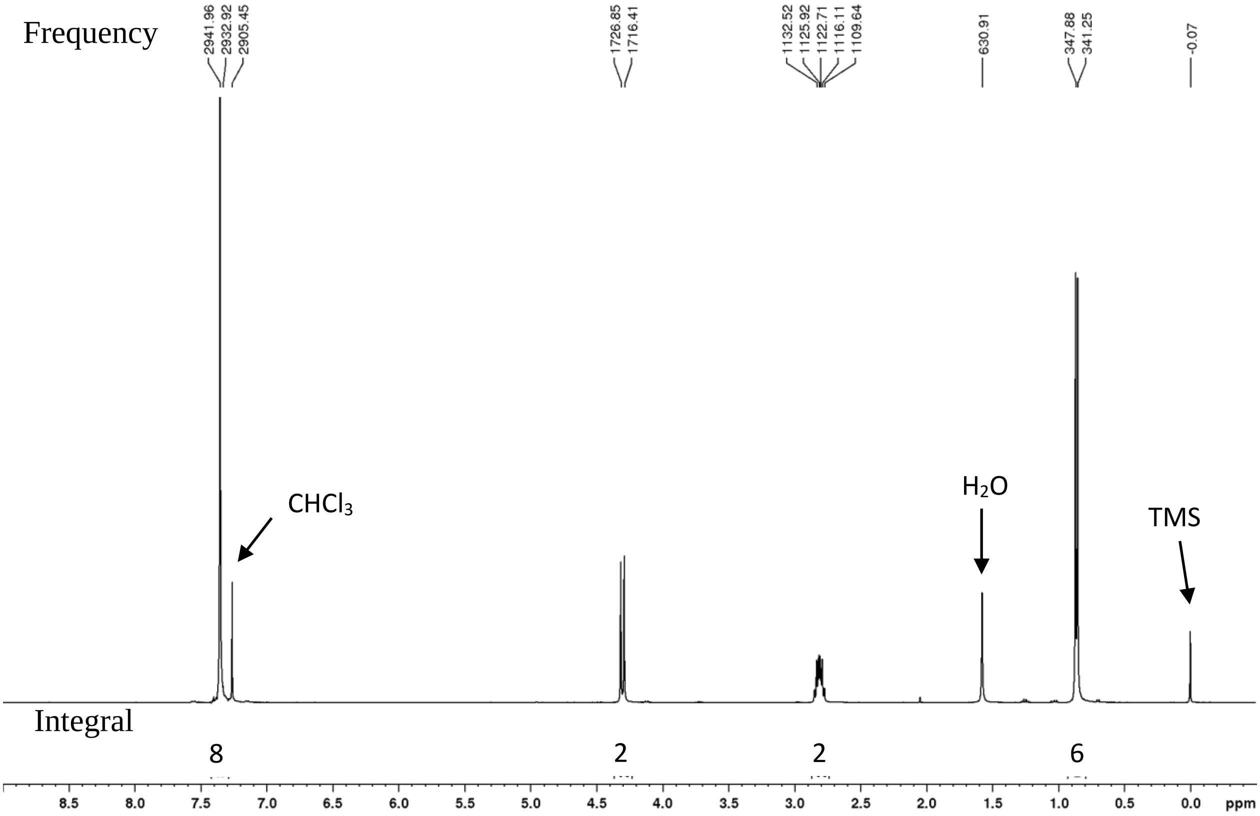
Mass of the recrystallized product:______________________ 1 point

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



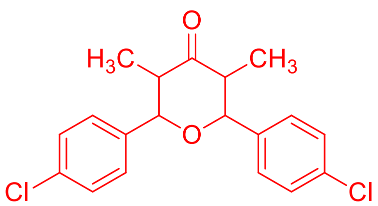
0.5 point each, maximum 2 points

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.

2 points.



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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)