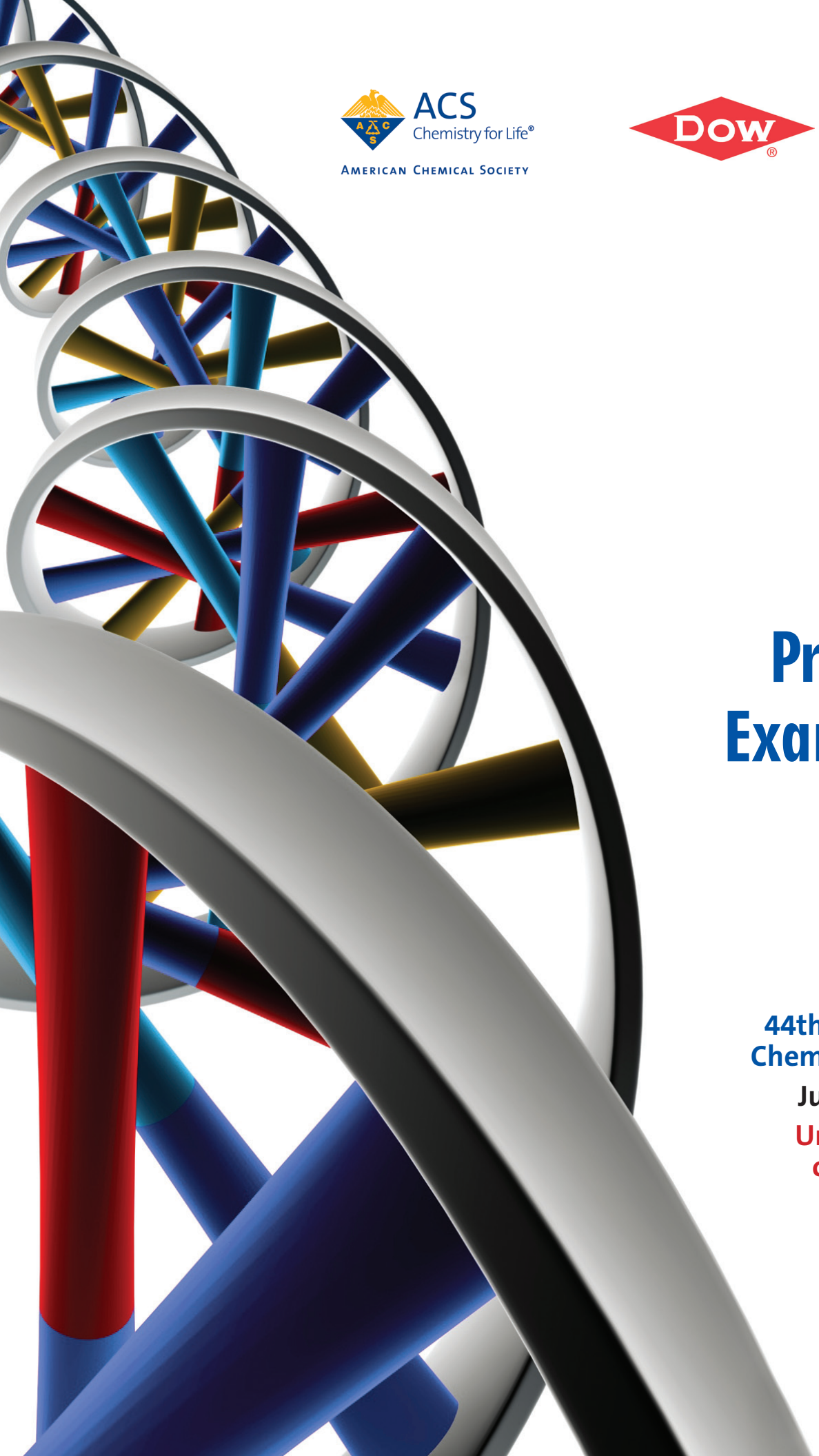

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Washington, D.C. • USA
IChO 44
2012 International Chemistry Olympiad

Practical Examination

44th International Chemistry Olympiad

July 24, 2012

United States of America

Name: Code: MYS

Instructions (Task 1)

- This examination has 10 pages for practical Task 1 as well as the answer sheets.
- You have 15 minutes to read this booklet before starting the experiments.
- You have **2 hours 15 minutes** to complete the practical **Task 1.**
- Begin only when the **START** command is given. You must stop your work immediately when the **STOP** command is announced. **A delay in doing this by 5 minutes will lead to cancellation of your practical exam.** After the **STOP command** has been given, **wait in your lab space**. A supervisor will check your lab space. The following item should be **left on your bench:**
- The problem / answer booklet (this booklet)
- You are expected to follow **safety rules** given in the IChO regulations. While you are in the laboratory, you must wear **safety glasses** or your own prescription safety glasses **if they have been approved.** You may use **gloves** when handling chemicals.
- You will receive only **ONE WARNING** from the laboratory supervisor if you break safety rules. On the second occasion you will be dismissed from the laboratory with a resultant zero score for the entire practical examination.
- Do not hesitate to ask your assistant if you have any questions concerning safety issues or if you need to leave the room.
- You are allowed to work only in the space allocated for you.
- Use only the pen provided, **not a pencil**, for writing the answers.
- Use the calculator provided.
- All results must be written in the appropriate areas on the answer sheets. Anything written elsewhere will not be graded. Use the backside of the sheets if you need scratch papers.
- Use the container labeled "**Used Vials**" to dispose sealed vials with reaction solutions.
- Use the container labeled "**Liquid Waste**" to dispose the waste solutions.
- Use the container labeled "**Broken Glass Disposal**" to dispose the ampule fragments.
- Chemicals and lab ware will be **refilled or replaced** without penalty **only for the first incident**. Each further incident will result in the **loss of 1 point** from your 40 practical exam points.
- The official English version of this examination is available on request only for clarification.

Name: Code: MYS

Chemicals and Equipment (Task 1)

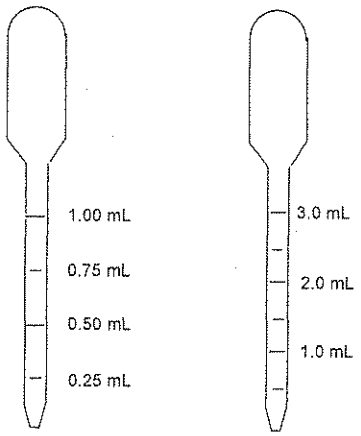
Chemicals (the actual labeling for each package is given in bold font)

	Risk Phrase[+]	Safety Phrase[+]
HCl, ~2 mol L^{-1}* solution in water, 50 mL in a bottle	R34, R37	S26, S45
KI_3, ~0.01 mol L^{-1}* solution in water, 10 mL in a bottle, labeled "**I_2**".		
Acetone, **$(CH_3)_2CO$**, M = 58.08 g mol^{-1}, density = 0.791 g mL^{-1}, 10.0 mL in a vial	R11, R36, R66, R67	S9, S16, S26
Acetone-d_6, $(CD_3)_2CO$, M = 64.12 g mol^{-1}, density = 0.872 g mL^{-1}, 3.0 mL in a pre-scored ampule	R11, R36, R66, R67	S9, S16, S26

[+] See page 3 for definition of Risk and Safety Phrases.
* The exact concentration is indicated on the label, with the concentration given before the name of the substance.

Equipment - Kit #1

- One glass bottle filled with distilled water.
- Fifteen 20 mL screw-cap glass vials with Teflon-lined screw-caps.
- Ten 1 mL polyethylene transfer pipettes graduated in 0.25 mL increments (see drawing on the right).
- Ten 3 mL polyethylene transfer pipettes graduated in 0.50 mL increments (see drawing on the right).
- One digital timer (stopwatch).



Risk and Safety Phrases (Task 1)

R11 Highly flammable

R34 Causes burns

R36 Irritating to eyes

R37 Irritating to respiratory system

R66 Repeated exposure may cause skin dryness or cracking

R67 Vapours may cause drowsiness and dizziness

S9 Keep container in a well-ventilated place

S16 Keep away from sources of ignition

S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice

S45 In case of accident or if you feel unwell, seek medical advice immediately

Name:

Code: MYS

Task 1

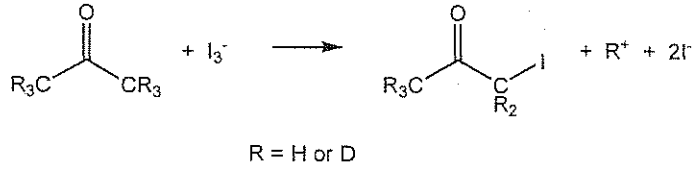
18% of the total

a	b	c	d	e	f	g	Task 1	18%
10	2	10	12	16	12	8	70	

Kinetics, Isotope Effect, and Mechanism of Iodination of Acetone

Discoveries about the mechanisms of chemical reactions underlie advances in catalysis and synthesis. One of the most powerful tools for probing reaction mechanisms is the study of kinetics because the ways in which reaction rates vary with reaction conditions follow directly from the mechanism of reaction. A second powerful tool is the study of isotopically substituted molecules. While isotopes have similar reactivity, there are slight differences in reaction rates as a function of nuclear mass.

In this task you will use both kinetics and isotope effects to provide information about the iodination of acetone in acidic aqueous solution:



R = H or D

The reaction takes place with a rate law

$$\text{Rate} = k[\text{acetone}]^m[I_3^-]^n[H^+]^p$$

where you will determine the rate constant k and the integer reaction orders m, n, and p.

You will also compare the reactivity of acetone with that of acetone-d_6, where the six atoms of protium (^{1}H) have been replaced by deuterium (^{2}H, D), to determine the isotope effect (k_H/k_D) of the reaction. From these data you will make inferences about the mechanism of this reaction.

Please read the whole description of this task and plan your work before you begin.

Procedure

Reaction rates are dependent on temperature. Record the temperature of the room in which you are working (ask the room assistant):

°C

Instructions for using the digital timer (stopwatch)

(1) Press the **[MODE]** button until the **COUNT UP** icon is displayed.

(2) To begin timing, press the **[START/STOP]** button.

(3) To stop timing, press the **[START/STOP]** button again.

(4) To clear the display, press the **[CLEAR]** button.

General Procedure

For each run, decide on the volumes of hydrochloric acid, distilled water, and potassium triiodide solution (labeled as "I_2") that you will use. The initial concentrations of the reagents in the reaction mixtures should be in the ranges given below (you need not explore the full ranges given, but your values should not be significantly outside these ranges):

$[H^+]$: Between 0.2 and 1.0 M

$[I_3^-]$: Between 0.0005 and 0.002 M

[acetone]: Between 0.5 and 1.5 M

For each run, record the volumes of reagents that you use in the table in Section (**a**) of the answer sheet. Place the measured volumes of hydrochloric acid, distilled water, and potassium triiodide solution in the reaction vessel (vial). To initiate the reaction, add your chosen volume of acetone to this mixture, quickly cap the vial, start the timer, shake the vial vigorously once, then place the vial on a white background. When setting up and running each reaction do not hold or touch the vial below the level of liquid. The progress of the reaction can be monitored visually by watching the disappearance of the yellow-brown colour of the triiodide ion. Record the time required for the colour to disappear. When the reaction has completed, set aside the vessel and leave it sealed so that you do not expose yourself to the iodoacetone vapours.

Repeat as often as desired using different concentrations of reagents. **Hint: change one concentration at a time.** Note that the concentrations of the reagents that you use will be calculated and recorded in the table in Section (**c**) of the answer sheet.

Once you have studied the rate of reaction of acetone, you should repeat the experiment to investigate the rate of reaction of acetone-d_6. Note that while you have an ample supply of acetone, you will be given only 3.0 mL of acetone-d_6 because isotopically labeled materials are expensive. ***Therefore, any refilling of acetone-d_6 will cost you a one point penalty.*** **When you need to use this reagent, raise your hand and the lab supervisor will open the sealed ampule for you.**

The reactions of deuterium-substituted compounds are generally slower than those of protium-substituted compounds. You would thus be well advised to use reaction conditions that promote faster reactions when working with $(CD_3)_2CO$.

When you have finished working:

a) empty the water bottle and place it along with any unused equipment back to the box labeled Kit #1
b) place used pipettes and sealed used vials in designated containers under the fumehoods;
c) use the container labeled **Broken Glass Disposal** to dispose of all parts of the empty ampule.

You may clean up your area after the STOP command has been given.

Section (**a**).

Record your results for acetone, $(CH_3)_2CO$, in the table below. *You need not fill the entire table.*

Run #	Volume HCl solution, mL	Volume H_2O, mL	Volume I_3^- solution, mL	Volume $(CH_3)_2CO$, mL	Time for disappearance of I_3^-, s
1					
2					
3					
4					
5					
6					
7					
8					

Section (**b**).

Record your results for acetone-d_6, $(CD_3)_2CO$, in the table below. *You need not fill the entire table.*

Run #	Volume HCl solution, mL	Volume H_2O, mL	Volume I_3^- solution, mL	Volume $(CD_3)_2CO$, mL	Time for disappearance of I_3^-, s
1d					
2d					
3d					
4d					

Section (**c**).

Calculate the concentrations and average rates for the reactions you studied. Record the answers in the tables below. In your calculations, assume that the volume of each reaction mixture is equal to the sum of volumes of its constituent solutions.

You need not use all of your runs in your calculation of *k* (Sections (e) and (f)), but you must indicate which run or runs you used by ticking the appropriate box in the right-hand column.

$(CH_3)_2CO$:

Run #	Initial $[H^+]$, mol L^{-1}	Initial $[I_3^-]$, mol L^{-1}	Initial $[(CH_3)_2CO]$, mol L^{-1}	Average rate of disappearance of I_3^-, mol L^{-1} s^{-1}	Run used in calculating k_H **Yes**	**No**
1					☐	☐
2					☐	☐
3					☐	☐
4					☐	☐
5					☐	☐
6					☐	☐
7					☐	☐
8					☐	☐

$(CD_3)_2CO$:

Run #	Initial $[H^+]$, mol L^{-1}	Initial $[I_3^-]$, mol L^{-1}	Initial $[(CD_3)_2CO]$, mol L^{-1}	Average rate of disappearance of I_3^-, mol L^{-1} s^{-1}	Run used in calculating k_D? **Yes**	**No**
1d					☐	☐
2d					☐	☐
3d					☐	☐
4d					☐	☐

Section (**d**).

Give the reaction order (integer) for acetone, triiodide, and hydrogen ion.

rate $= -\frac{d[I_3^-]}{dt} = k[(CH_3)_2CO]^m[I_3^-]^n[H^+]^p$

$m =$	$n =$	$p =$

Section (**e**).

Calculate the rate constant, k_H for the reaction of acetone, $(CH_3)_2CO$, and indicate the units.

$k_H =$

Section (**f**).

Calculate the rate constant, k_D for the reaction of acetone-d_6, $(CD_3)_2CO$, and calculate the value of k_H/k_D (the isotope effect of the reaction).

$k_D =$

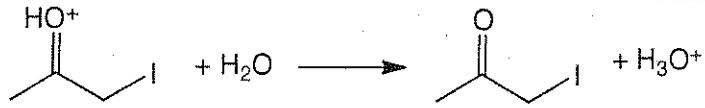
$k_H/k_D =$

Section (**g**).

From the kinetic and isotope effect data you may draw certain conclusions about the reaction mechanism. Shown below are reasonable mechanisms for the iodination of acetone. One of the reactions is the rate-determining step (RDS), with all other steps rapidly achieving an equilibrium that strongly favouring the reactants.

In the appropriate boxes in the first column in the table below, place a check mark (✔) if your *experimentally measured rate law* (Section (**d**)) is **consistent** with that of a rate-determining step and an (**X**) if your measured rate law is **inconsistent** with that of a rate-determining step.

In the appropriate boxes in the second column in the table below, place a check mark (✔) if your *experimentally measured isotope effect* (Section (**f**)) is **consistent** with that of a rate-determining step and an (**X**) if your measured isotope effect is **inconsistent** with that of a rate-determining step.

	RDS consistent with **rate law**?	RDS consistent with **isotope effect**?
		
		
		
		

Name: Code: MYS

Instructions (Task 2)

- This examination has **13** pages for Task 2, a periodic table and answer sheets.
- You have 15 minutes to read this booklet before starting the experiments.
- You have **2 hours 45 minutes** to complete the practical Task 2. **When planning your work, please note that one of the steps requires 30 minutes.**
- Begin only when the **START** command is given. You must stop your work immediately when the **STOP** command is announced. **A delay in doing this by 5 minutes will lead to cancellation of your practical exam.** After the **STOP command** has been given, **wait in your lab space**. A supervisor will check your lab space. The following items should be **left on your bench:**

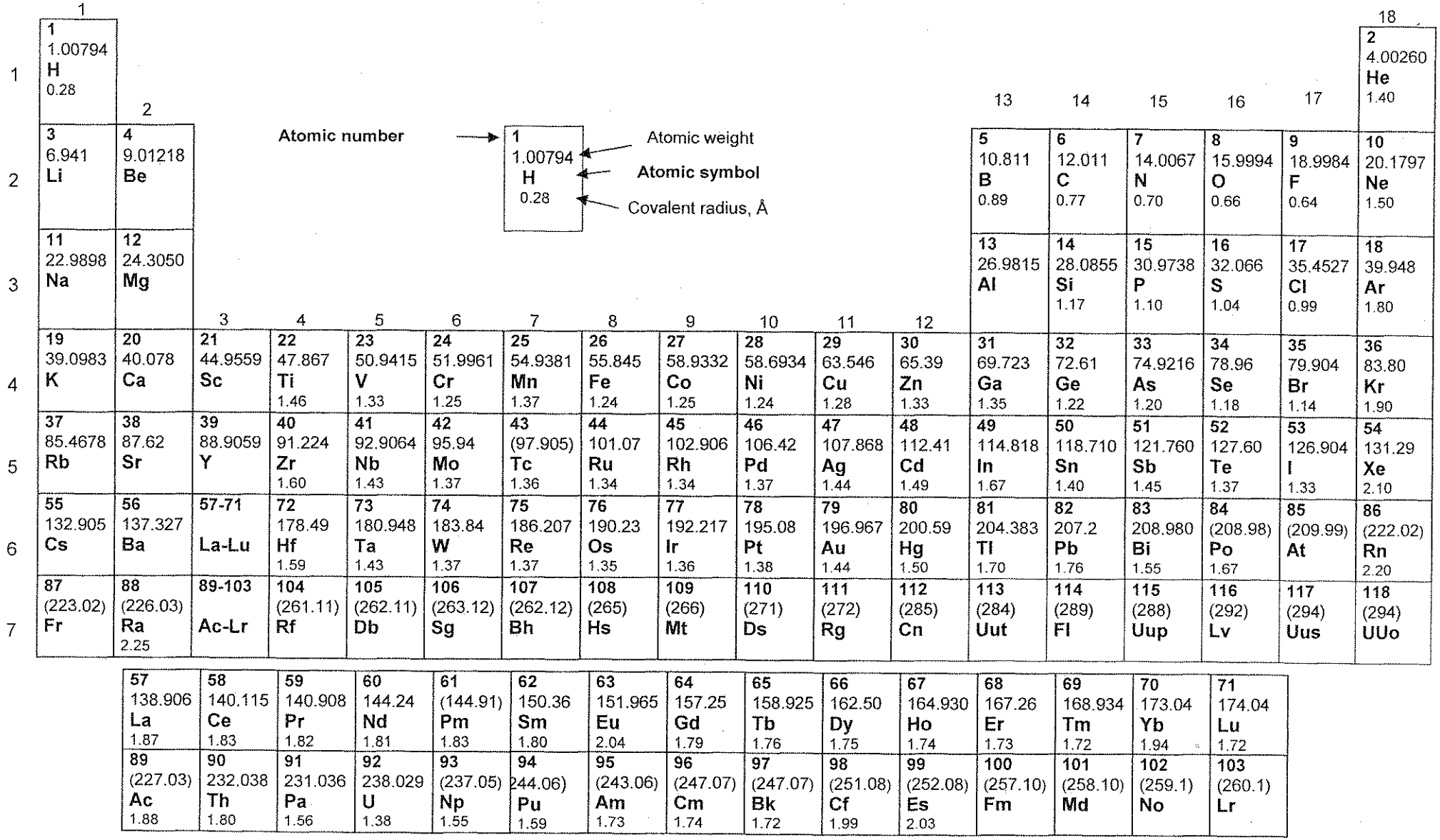
  The problem / answer booklet (this booklet)

  One TLC plate in zipper storage bag with student code

  The vial labeled "Product"

- You are expected to follow **safety rules** given in the IChO regulations. While you are in the laboratory, you must wear **safety glasses** or your own prescription safety glasses **if they have been approved.** Use the **pipette filler bulb** provided. You may use **gloves** when handling chemicals.
- You will receive only **ONE WARNING** from the laboratory supervisor if you break safety rules. On the second occasion you will be dismissed from the laboratory with a resultant zero score for the entire practical examination.
- Do not hesitate to ask your assistant if you have any questions concerning safety issues or if you need to leave the room.
- You are allowed to work only in the space allocated for you.
- Use only the pen provided, **not a pencil**, for writing the answers.
- Use the calculator provided.
- **All results must be written in the appropriate areas on the answer sheets. Anything written elsewhere will not be graded.** Use the backside of the sheets if you need scratch paper.
- Use the container labeled as "**Broken Glass Disposal**" to dispose used vials.
- Use the **container** labeled as "**Liquid Waste**" to dispose all waste solutions.
- Chemicals and lab ware will be **refilled or replaced** without penalty **only for the first incident**. Each further incident will result in the **loss of 1 point** from your 40 practical exam points.
- The official English version of this examination is available on request only for clarification.

Name: Code: MYS



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 1.00794 **H** 0.28																	2 4.00260 **He** 1.40
2	3 6.941 **Li**	4 9.01218 **Be**											5 10.811 **B** 0.89	6 12.011 **C** 0.77	7 14.0067 **N** 0.70	8 15.9994 **O** 0.66	9 18.9984 **F** 0.64	10 20.1797 **Ne** 1.50
3	11 22.9898 **Na**	12 24.3050 **Mg**											13 26.9815 **Al**	14 28.0855 **Si** 1.17	15 30.9738 **P** 1.10	16 32.066 **S** 1.04	17 35.4527 **Cl** 0.99	18 39.948 **Ar** 1.80
4	19 39.0983 **K**	20 40.078 **Ca**	21 44.9559 **Sc**	22 47.867 **Ti** 1.46	23 50.9415 **V** 1.33	24 51.9961 **Cr** 1.25	25 54.9381 **Mn** 1.37	26 55.845 **Fe** 1.24	27 58.9332 **Co** 1.25	28 58.6934 **Ni** 1.24	29 63.546 **Cu** 1.28	30 65.39 **Zn** 1.33	31 69.723 **Ga** 1.35	32 72.61 **Ge** 1.22	33 74.9216 **As** 1.20	34 78.96 **Se** 1.18	35 79.904 **Br** 1.14	36 83.80 **Kr** 1.90
5	37 85.4678 **Rb**	38 87.62 **Sr**	39 88.9059 **Y**	40 91.224 **Zr** 1.60	41 92.9064 **Nb** 1.43	42 95.94 **Mo** 1.37	43 (97.905) **Tc** 1.36	44 101.07 **Ru** 1.34	45 102.906 **Rh** 1.34	46 106.42 **Pd** 1.37	47 107.868 **Ag** 1.44	48 112.41 **Cd** 1.49	49 114.818 **In** 1.67	50 118.710 **Sn** 1.40	51 121.760 **Sb** 1.45	52 127.60 **Te** 1.37	53 126.904 **I** 1.33	54 131.29 **Xe** 2.10
6	55 132.905 **Cs**	56 137.327 **Ba**	57-71 **La-Lu**	72 178.49 **Hf** 1.59	73 180.948 **Ta** 1.43	74 183.84 **W** 1.37	75 186.207 **Re** 1.37	76 190.23 **Os** 1.35	77 192.217 **Ir** 1.36	78 195.08 **Pt** 1.38	79 196.967 **Au** 1.44	80 200.59 **Hg** 1.50	81 204.383 **Tl** 1.70	82 207.2 **Pb** 1.76	83 208.980 **Bi** 1.55	84 (208.98) **Po** 1.67	85 (209.99) **At**	86 (222.02) **Rn** 2.20
7	87 (223.02) **Fr**	88 (226.03) **Ra** 2.25	89-103 **Ac-Lr**	104 (261.11) **Rf**	105 (262.11) **Db**	106 (263.12) **Sg**	107 (262.12) **Bh**	108 (265) **Hs**	109 (266) **Mt**	110 (271) **Ds**	111 (272) **Rg**	112 (285) **Cn**	113 (284) **Uut**	114 (289) **Fl**	115 (288) **Uup**	116 (292) **Lv**	117 (294) **Uus**	118 (294) **UUo**

57 138.906 **La** 1.87	58 140.115 **Ce** 1.83	59 140.908 **Pr** 1.82	60 144.24 **Nd** 1.81	61 (144.91) **Pm** 1.83	62 150.36 **Sm** 1.80	63 151.965 **Eu** 2.04	64 157.25 **Gd** 1.79	65 158.925 **Tb** 1.76	66 162.50 **Dy** 1.75	67 164.930 **Ho** 1.74	68 167.26 **Er** 1.73	69 168.934 **Tm** 1.72	70 173.04 **Yb** 1.94	71 174.04 **Lu** 1.72
89 (227.03) **Ac** 1.88	90 232.038 **Th** 1.80	91 231.036 **Pa** 1.56	92 238.029 **U** 1.38	93 (237.05) **Np** 1.55	94 244.06) **Pu** 1.59	95 (243.06) **Am** 1.73	96 (247.07) **Cm** 1.74	97 (247.07) **Bk** 1.72	98 (251.08) **Cf** 1.99	99 (252.08) **Es** 2.03	100 (257.10) **Fm**	101 (258.10) **Md**	102 (259.1) **No**	103 (260.1) **Lr**

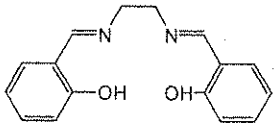
Chemicals and Equipment (Task 2)

Chemicals and materials (the actual labeling for each package in given in bold font)

	Risk Phrase[+]	Safety Phrase[+]
(salen)H_2,[a] ~1.0 g[b] in a vial	R36/37/38	S26 S28A S37 S37/39 S45
$Mn(OOCCH_3)_2$ $4H_2O$, ~1.9 g[b] in a vial	R36/37/38 R62 R63	S26 S37/39
Lithium chloride solution, LiCl, 1M solution in ethanol, 12 mL in a bottle	R11 R36/38	S9 S16 S26
Ethanol, 70 mL in a bottle	R11	S7 S16
Acetone, **$(CH_3)_2CO$**, 100 mL in a bottle	R11 R36 R66 R67	S9 S16 S26
(salen*)$MnCl_x$,[c] ~32 mL of a ~3.5 mg/mL[b] solution in a bottle		
KI_3, ~0.010 M solution in water,[b] 50 mL in a bottle, labeled "**I_2**".		
Ascorbic Acid, ~0.030 M solution in water,[b] 20 mL in a bottle		
1% Starch, solution in water, 2 mL in a bottle		
TLC plate – one 5 cm × 10 cm silica gel strip in a plastic zipper bag		

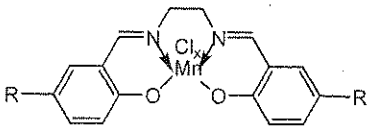
[+] See page 15 for definition of Risk and Safety Phrases.

[a] (salen)H_2:



[b] The exact value is indicated on the label.

[c] (salen*)$MnCl_x$ (both R groups are equal and can be either H, or COOH or SO_3H):



Equipment

Common Use: Balance

- Two **stands** with **clamps** located under hood labeled with your code
- One **hotplate stirrer**
- One **300 mm ruler**
- One **pencil**

Kit #2:

- Two **250 mL conical flasks** (one for synthesis, one for crystallization)
- One **graduated cylinder**, 50 mL
- One **20 mm long egg-shaped magnetic stirring bar**
- One **Hirsch funnel**
- **Filter papers** for Hirsch funnel and for TLC chamber
- One **125 mL suction flask for vacuum filtration**
- **Rubber adapter** for suction flask
- One 0.5 L **plastic ice bath**
- One **glass rod**
- Two 1 mL plastic transfer pipettes (see drawing on the right)
- One plastic spatula
- One empty **4 mL snap-cap vial** labeled "Product" for reaction product

Kit #3:

- Three empty **small screw-cap vials** (for TLC solutions)
- Ten **short capillary tubes (100 mm)** for TLC spotters
- One **watch glass** (for the TLC chamber)
- One **250 mL beaker** for TLC chamber

Kit #4:

- One assembled and ready to used **25 mL burette**
- One small **plastic funnel**
- Four **125 mL conical flasks**
- One **rubber bulb for pipettes**
- One **10 mL volumetric pipette**
- One **5 mL volumetric pipette**

Risk and Safety Phrases (Task 2)

R11 Highly flammable

R36/37/38 Irritating to eyes, respiratory system and skin

R62 Possible risk of impaired fertility

R63 Possible risk of harm to the unborn child

R66 Repeated exposure may cause skin dryness or cracking

R67 Vapours may cause drowsiness and dizziness

S7 Keep container tightly closed

S9 Keep container in a well-ventilated place

S16 Keep away from sources of ignition

S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.

S28A After contact with skin, wash immediately with plenty of water.

S37 Wear suitable gloves.

S37/39 Wear suitable gloves and eye/face protection.

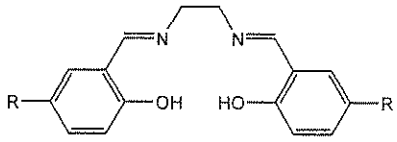
S45 In case of accident or if you feel unwell, seek medical advice immediately

Task 2 22% of the Total

Synthesis of a Salen Manganese Complex and Determining the Formula of the Product

A	B-i	B-ii	C-i	C-ii	Task 2	22%
10	15	4	4	2	35	

Transition metal complexes of the 3*d*-block elements derived from the bis(salicylidene)ethylenediamine (salen) ligand (figure below) have proven to be efficient catalysts of various redox reactions in organic synthesis.



(salen)H_2, R = H
(salen*)H_2, R = H, COOH, or SO_3H

The ability of the salen ligand to stabilize higher oxidation states of 3*d*-block elements is important in this chemistry. In particular, compounds of manganese in oxidation states from +2 to +5 could be generated depending on the reaction conditions when the manganese salen complex is prepared.

In this task you are required to prepare a manganese salen complex by reacting (salen)H_2 with Mn(II) acetate in ethanol, in the air, in the presence of lithium chloride. Under these conditions, you might have obtained a complex of the formula (salen)$MnCl_x$, where x = 0, 1, 2, or 3.

You will need to:

i) determine the mass of the product,

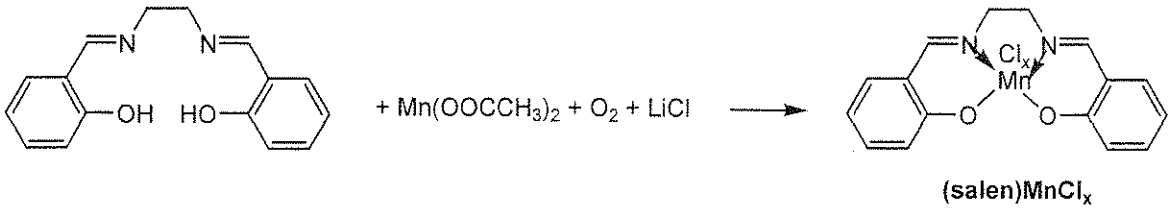
ii) characterize the purity of the material prepared using thin-layer chromatography (TLC), and

iii) determine the metal oxidation state in the complex using an iodometric redox titration. For the redox titration, you will be given a solution of a previously prepared analogue of your compound, (salen*)$MnCl_x$, where manganese has the same oxidation state as in the product and the R-substituent on the benzene ring is either H, COOH, or SO_3H.

Please read the whole description of this task and plan your work before you begin. Some operations have to be performed in parallel in order to complete it in time.

Procedure:

A. Synthesis of (salen)$MnCl_x$



(salen)$MnCl_x$

1) Place 2-3 crystals of (salen)H_2 aside in a small vial to be used for the TLC experiment later.

2) Transfer the pre-weighed ~1.0-g sample of (salen)H_2 provided into a 250 mL conical flask with a stirring bar in it. Then add 35 mL of absolute ethanol.

3) Place the flask on a hot plate/stirrer. Heat the contents with constant stirring until the solid dissolves (usually, dissolution is complete when the ethanol **is about** to boil). Then decrease the temperature setting to maintain the mixture close but below its boiling point. **Do not boil the mixture** so that the neck of the flask remains cool. If the flask is too hot to hold with bare hands, use a folded paper towel.

4) Remove the flask from the hotplate and add to its content a pre-weighed ~1.9-g sample of $Mn(OAc)_2 \cdot 4H_2O$. A dark brown colour will develop. Return the flask to the hotplate immediately; continue heating and stirring for 15 min. **Do not boil the mixture** so that the neck of the flask remains cool.

5) Remove the flask from the hotplate and add to its contents the provided solution of 1M LiCl in ethanol (12 mL, an excess). Return the flask to the hotplate; continue heating and stirring for 10 min. **Do not boil the mixture** so that the neck of the flask remains cool.

6) After this time remove the flask from the hotplate, and place it in an ice bath for crystallization for 30 min. Every 5 min gently scratch the walls of the flask from inside under the liquid level with a glass rod to accelerate crystallization of (salen)$MnCl_x$. The first crystals may appear immediately upon cooling or after a period of only 10-15 minutes.

7) Use the vacuum line located inside the fumehood (the valve labeled "Vacuum") and filter by suction the crystalline solid formed using the small Hirsch funnel and a suction flask. Use a transfer pipette to wash the solid with few drops of acetone without disconnecting the flask from the vacuum line, and leave it on the filter (with the suction on) for 10-15 min to air-dry.

8) Transfer the solid product into a pre-weighed vial labeled "Product", determine and record its mass, m_p, in the box below. Record also the mass of the following reagents used in the synthesis: (salen)H_2, m_S, and $Mn(OOCCH_3)_2 \cdot 4H_2O$, m_{Mn}.

9) Place the labeled vial with product into a zipper bag.

Mass of the empty vial for the product: _____ g

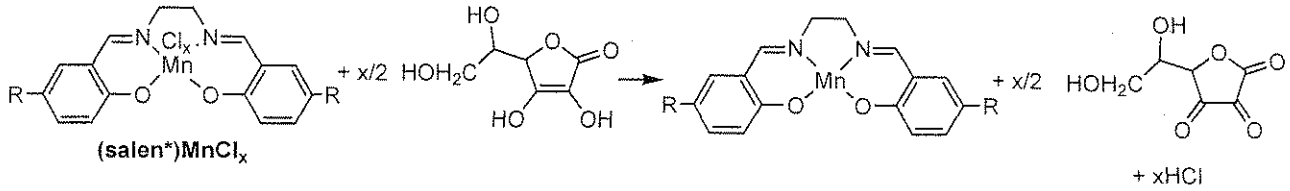
Mass of the vial with the dried product: _____ g

Mass of the product, m_p: _____ g

Mass of (salen)H_2 from label on the vial (copy from the label), m_S:
_____ g

Mass of $Mn(OOCCH_3)_2 \cdot 4H_2O$ from label on the vial (copy from the label), m_{Mn}:
_____ g

B. Volumetric analysis of a sample of (salen*)$MnCl_x$ provided



R = H, COOH, or SO_3H

Using the squeeze bulb

1) Attach the bulb to a pipette
2) Squeeze firmly the rubber bulb
3) Squeeze the up arrow button to suck in some solution into pipette attached
4) Squeeze the down arrow button to release some solution from the pipette into a target flask

Note: The pipettes and burette are ready to use and need not be rinsed.

1) Dispense 10.00 mL of the provided (salen*)$MnCl_x$ solution into a 125 mL conical flask using the volumetric pipette.
2) Add 5.00 mL of the ascorbic acid solution to this solution and mix well. Allow the solution to stand for 3-4 minutes.
3) To avoid oxidation of ascorbic acid with O_2 do not delay and **titrate the solution <u>immediately</u>** with the KI_3 solution using 5 drops of a 1% starch solution as indicator. The blue or blue-green endpoint should persist for at least 30 sec.
4) If time permits, perform 1-2 replicate titrations to improve the accuracy of your determination.

Place results of your titration experiment(s) in the table below:

#	Initial volume reading in burette of KI_3 solution, mL	Final volume reading in burette of KI_3 solution, mL	Volume of KI_3 solution used, mL
1			
2			
3			

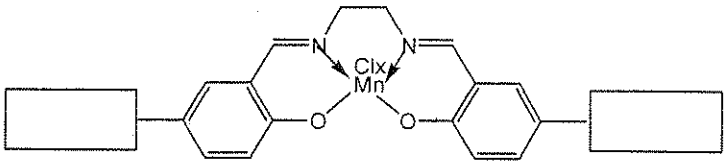
i. Indicate the volume (selected or averaged) of KI_3 solution consumed in mL that you will use for calculations of molar mass of (salen*)$MnCl_x$:

Volume of KI_3 solution used in calculations: _____ mL

Concentration of (salen*)$MnCl_x$ (from label on the bottle): _____ mg/mL

Concentration of ascorbic acid (from label on the bottle): _____ M

ii. From your titration data and referring to the table below **deduce the value of *x*, the oxidation state of manganese** and **the identity of the substituent on the salen ligand** (R = H, COOH, SO_3H). Show them in the template below:



x = _____

Manganese oxidation state: _____

R	x	(Theoretical molar mass)/x, g/mol
H	1	357
H	2	196
H	3	143
COOH	1	445
COOH	2	240
COOH	3	172
SO_3H	1	517
SO_3H	2	276
SO_3H	3	196

C. TLC characterization of (salen)$MnCl_x$

1) Dissolve a few crystals of the (salen)$MnCl_x$ that you have prepared in a few drops of absolute ethanol using a small vial and a plastic transfer pipette for ethanol.

2) Dissolve a few crystals of (salen)H_2 in few drops of absolute ethanol using another small vial.

3) If necessary, use scissors (available from lab assistant upon request) to trim the TLC plate so it is an appropriate height for the TLC chamber.

4) Fold or trim a large circle of filter paper, and place it into the beaker so that it is almost the height of the beaker. This is required to saturate the chamber with ethanol vapour. Add ethanol to the beaker to wet the filter, and fill the bottom of the beaker with a 3-4 mm layer of the solvent. Close the beaker with the watch glass.

5) Mark the start on the TLC plate.

6) Using the capillary tubes provided, spot the TLC plate with both solutions.

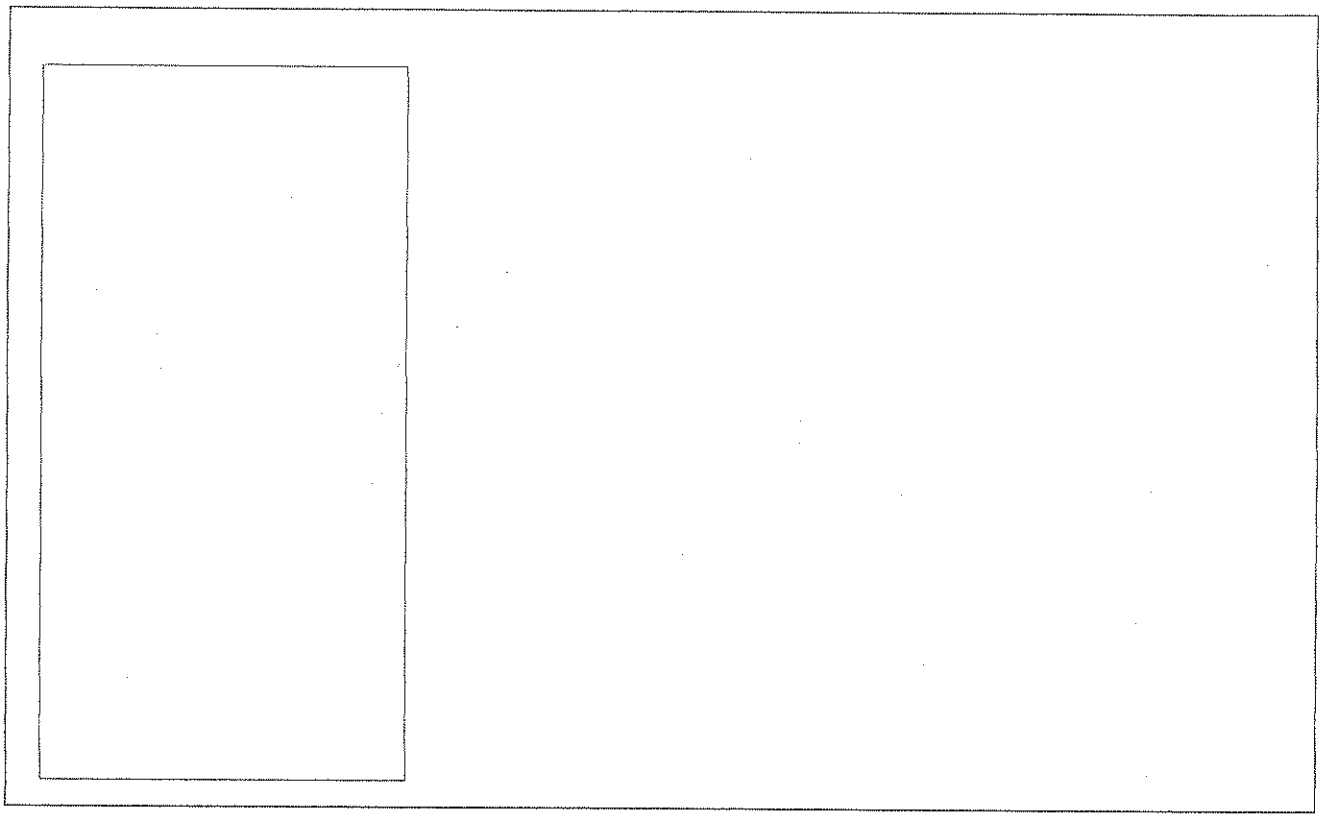
7) Develop the TLC in the beaker covered with a watch glass for 10-15 min.

8) Mark the solvent front as well as the coloured spots on the TLC plate using a pencil.

9) Dry the TLC plate in air and place it back into a zipper bag.

10) Calculate the R_f for both (salen)H_2 and (salen)$MnCl_x$.

i. Sketch the TLC plate on your answer sheet



ii. Determine and record the R_f values for (salen)H_2 and (salen)$MnCl_x$

R_f, (salen)H_2: _____

R_f, (salen)$MnCl_x$: _____

When you are finished working:

a) Place liquid wastes into a container marked **Liquid Waste**.

b) Place used vials into a contained labeled **Broken Glass Disposal**.

c) Place used glassware back to appropriate boxes labeled "Kit #2", "Kit #3" and "Kit #4".