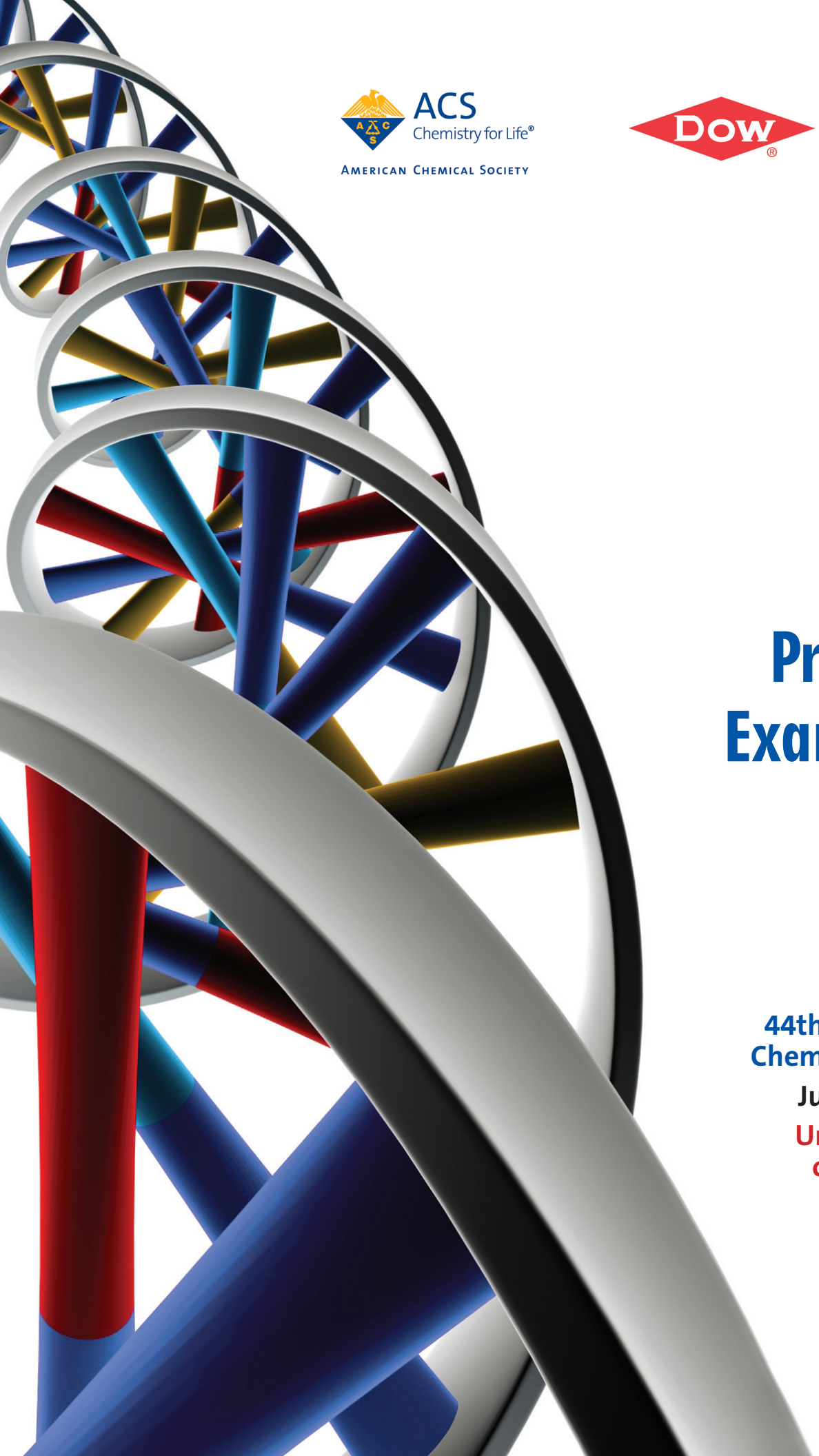

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Washington, D.C. • USA
IChO 44
2012 International Chemistry Olympiad

Practical Examination

44th International Chemistry Olympiad

July 24, 2012

United States of America

Name: Code: USA

Instructions (Task 1)

- This examination has **10** pages for practical Task 1, including 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 paper.
- Use the container labeled as "**Used Vials**" to dispose sealed vials with reaction solutions.
- Use the container labeled as "**Liquid Waste**" to dispose the waste solutions.
- Use the container labeled as "**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: USA

Chemicals and Equipment (Task 1)

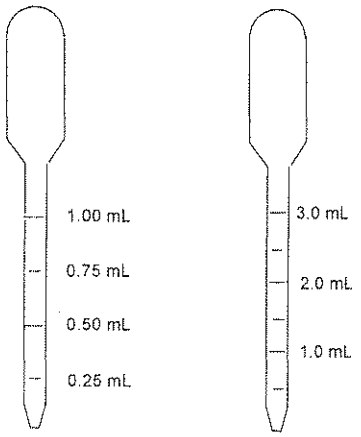
Chemicals (the actual labeling for each package is given in bold font)

	Risk Phrase[+]	Safety Phrase[+]
~2 M HCl,[*] solution in water, 50 mL in a bottle	R34, R37	S26, S45
~0.01 M KI_3,[*] solution in water, 10 mL in a bottle, labeled as "**I_2**".		
Acetone, **$(CH_3)_2CO$**, FW = 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, $(CD_3)_2CO$, FW = 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 molarity 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 pipets graduated in 0.25 mL increments (see drawing in the right).
- Ten 3-mL polyethylene transfer pipets graduated in 0.50 mL increments (see drawing in 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 Vapors 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: USA

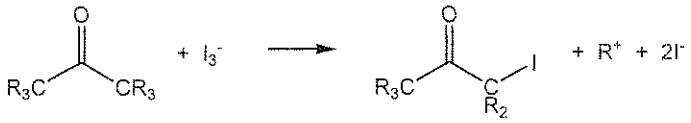
Task 1 — 18% of the total

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 impart similar types of chemical 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 the rate constant k and the integer reaction orders m, n, and p are for you to determine. 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 <u>whole</u> description of this task and PLAN your work before you begin.

Procedure

Reaction rates are dependent on temperature. **RECORD** the temperature in the room you are working in (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

Measure the volumes of hydrochloric acid, distilled water, and potassium triiodide solution (labeled as "I_2") that you choose into the reaction vessel. 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

To initiate the reaction, add the chosen volume of acetone to the solution containing the other reagents, quickly **cap** the reaction vessel, **start** the timer, **shake** the vial vigorously one time, then **put it aside** on a white background. **REPORT** the volumes of reagents that you use in the table provided in (a). When setting up and running a reaction, **do not** hold or touch the vial below the level of liquid in it. The progress of the reaction can be monitored visually by watching the disappearance of the yellow-brown color of the triiodide ion. **RECORD** the time required for the color to disappear. When the reaction is complete, **set aside** the vessel and leave it sealed so that you do not expose yourself to iodoacetone vapors.

Repeat as often as desired with different concentrations of reagents. **REPORT** the concentrations of the reagents that you use in the tables in (c) below. *Hint: change one concentration at a time.*

Once you have studied the rate of reaction of acetone, you should examine 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 of the greater expense of the isotopically labeled material. Therefore, any refilling of acetone-d_6 will be accompanied by 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 are 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 pipets and sealed used vials in designated containers in the hoods;

c) Use a 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.

Name: Code: USA

a. RECORD your data and 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 to disappearance of I_3^-, s
1					
2					
3					
4					
5					
6					
7					
8					

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 to disappearance of I_3^-, s
1d					
2d					
3d					
4d					

c. Use the following tables to **CALCULATE** concentrations and average rates for the reactions you studied. 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* (parts e and f), but you must INDICATE which run or runs you used in your calculation by checking the appropriate box in the right-hand column.**

$(CH_3)_2CO$:

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

$(CD_3)_2CO$:

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

d. GIVE the integer reaction order in acetone, triiodide, and hydrogen ion.

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

m =	n =	p =

e. CALCULATE the rate constant k_H for the reaction of acetone, $(CH_3)_2CO$, and **INDICATE** the units.

k_H =

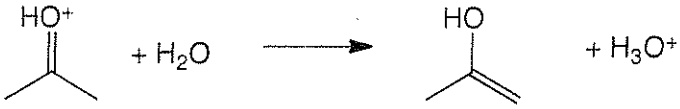
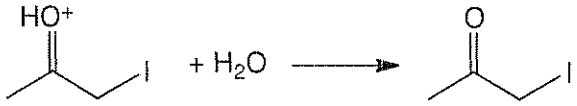
f. CALCULATE the rate constant k_D for the reaction of acetone-d_6, $(CD_3)_2CO$, and **CALCULATE** the value of k_H/k_D (the isotope effect of the reaction).

k_D =

k_H/k_D =

g. From the kinetic and isotope effect data, you may draw certain conclusions about the reaction mechanism. Shown below is a reasonable mechanism for the iodination of acetone. One reaction is the rate-determining step (R.D.S.), with all previous steps rapidly achieving an equilibrium that strongly favors the reactants.

In the box in the first column on the right next to each step, place a check mark (✔) if your *experimentally measured rate law* (part **d**) is **consistent** with that step being rate-determining and an **X** if your measured rate law is **inconsistent** with that step being rate-determining. In the box in the second column on the right next to each step, place a check mark (✔) if your *experimentally measured isotope effect* (part **f**) is **consistent** with that step being rate-determining and an **X** if your measured isotope effect is **inconsistent** with that step being rate-determining.

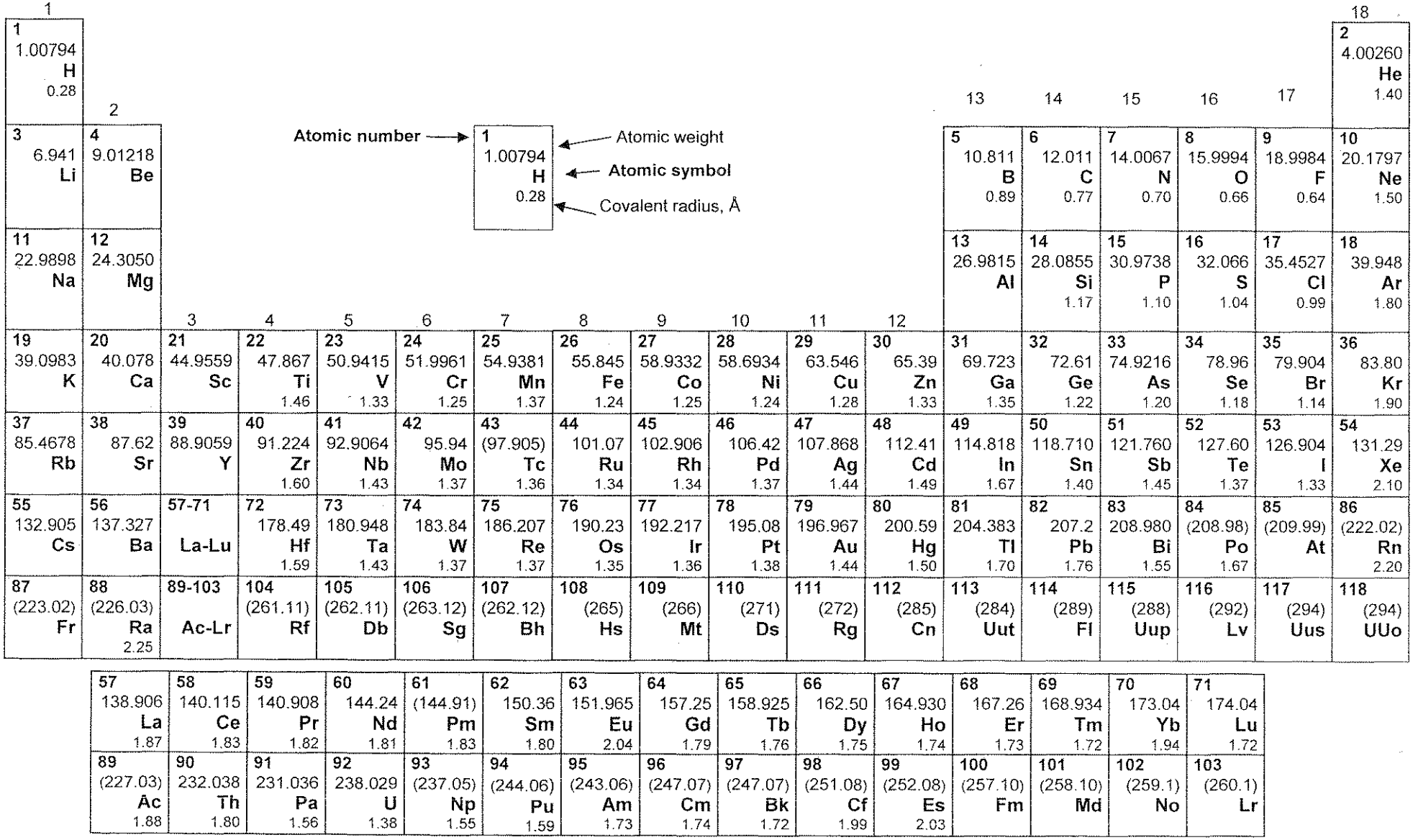
	R.D.S. consistent with rate law?	R.D.S. consistent with isotope effect?
		
		
		
		

Name: Code: USA

Instructions (Task 2)

- This examination has **13** pages for Task 2, including 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 **pipet 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: USA



Name: Code: USA

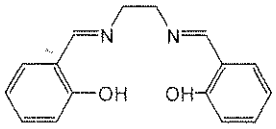
Chemicals and Equipment (Task 2)

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 as "**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		

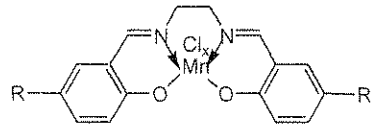
[+] See page 15 for definition of Risk and Safety Phrases.

[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

- Balance (**Common Use**)
- Two **stands** with **clamps** located in the hood labeled with your code
- One **hotplate stirrer**
- One **300 mm ruler**
- One **pencil**

Kit #2:

- Two **250 mL Erlenmeyer 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 paper** circles 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 pipets (see drawing in 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, conditioned and ready to use **25 mL buret**
- One small **plastic funnel**
- Four **125 mL Erlenmeyer flasks**
- One **rubber bulb for pipets**
- One **10 mL volumetric pipet**
- One **5 mL volumetric pipet**

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 Vapors 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

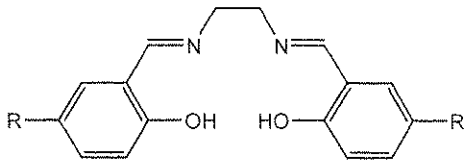
Name: Code: USA

Task 2 — 22% of the Total

Synthesis of a Salen Manganese Complex and Determining 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 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 can prepare a complex of the formula (salen)$MnCl_x$, where x = 0, 1, 2, or 3.

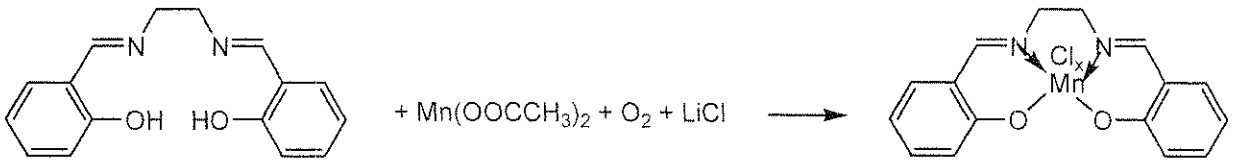
You will need to: i) **determine** the mass of the product, ii) **characterize** the purity of the material prepared using thin-layer chromatography (TLC), and iii) **determine** the metal oxidation state in the complex using an iodometric redox titration. For the redox titration, you will be given a 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 <u>whole</u> 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.

Name: Code: USA

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 Erlenmeyer flask with a stirring bar. Combine the reagent with 35 mL of 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. Heat the mixture carefully, just below boiling, 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 the pre-weighed ~1.9-g sample of $Mn(OAc)_2 \cdot 4H_2O$. A dark brown color will develop. Return the flask to the hotplate immediately; continue heating and stirring for 15 min. Heat the mixture carefully, just below boiling, so that the neck of the flask remains cool.
5) Remove the flask from the hotplate and add the provided solution of 1M LiCl in ethanol (12 mL, in excess). Return the flask to the hotplate; continue heating and stirring for 10 min. Heat the mixture carefully, just below boiling, 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 10-15 minutes.
7) Use the vacuum line located inside the hood (the corresponding valve is labeled "Vacuum") and suction filter the crystalline solid formed using the small Hirsch funnel and a suction flask. Use a transfer pipet 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", then determine and **RECORD** its mass, m_p, in the box on page 18. Also **RECORD** 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

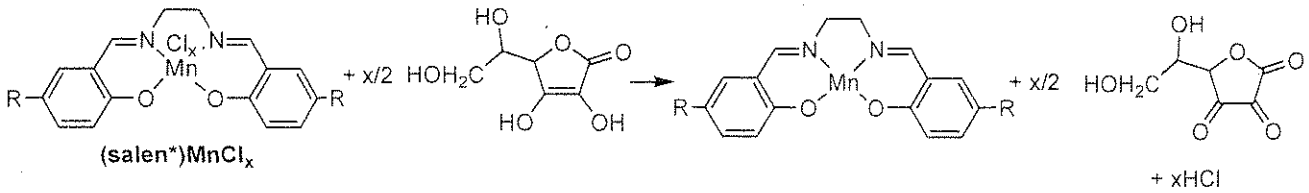
Mass of the product, m_p: _____ g

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

Name: Code: USA

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



R = H, COOH, or SO_3H

Using pipet bulb

- Attach the bulb to a pipet
- Firmly squeeze the rubber bulb
- Squeeze the up arrow button to draw up some solution into the attached pipet
- Squeeze the down arrow button to release the solution from the pipet into a target flask

Note: The pipets and buret are ready to use and do not need to be conditioned.

1) Dispense 10.00 mL of the provided (salen*)$MnCl_x$ solution into a 125 mL Erlenmeyer flask using the volumetric pipet.
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 immediately titrate the solution with the KI_3 solution using 5 drops of a 1% starch solution as an indicator. The blue or blue-green endpoint should persist for at least 30 sec.
4) If time permits, perform 1-2 additional titrations to improve the accuracy of your determination.

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

#	Initial volume reading in buret of KI_3 solution, mL	Final volume reading in buret of KI_3 solution, mL	Volume of KI_3 solution consumed, mL
1			
2			
3			

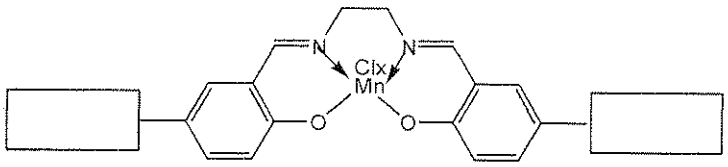
i. RECORD the volume (selected or averaged) of KI_3 solution consumed in mL that you will use for the calculations of the molar mass of (salen*)$MnCl_x$:

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. Using your titration data and 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: _____

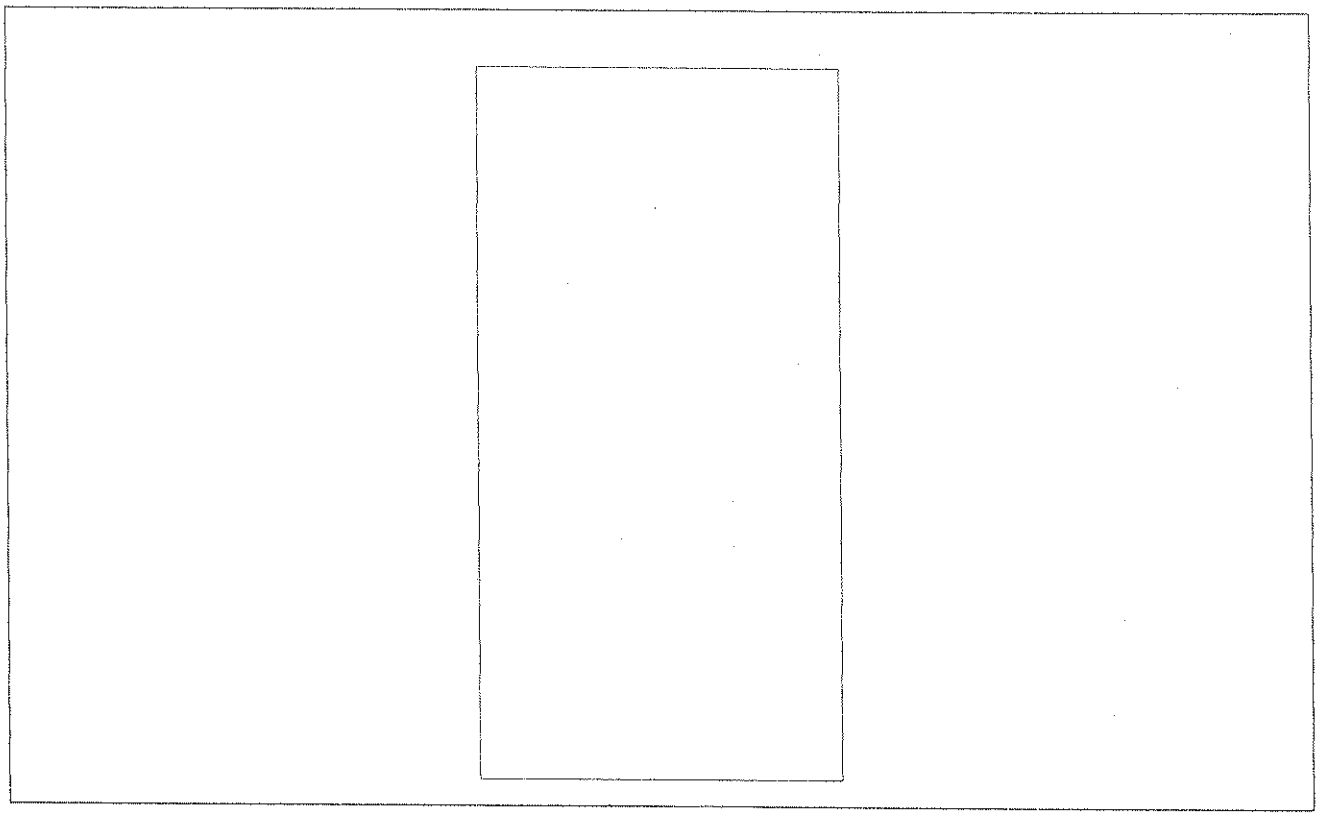
R	x	(Theoretical molar mass)/x, g/mol
H	1	357
H	2	196
H	3	143
COOH	1	445
COOH	2	240
COOH	3	172
SO_3H	1	517
SO_3H	2	276
SO_3H	3	196

C. TLC characterization of (salen)$MnCl_x$

1) Using a small vial and a plastic transfer pipet, dissolve a few crystals of the (salen)$MnCl_x$ that you have prepared in a few drops of ethanol.
2) Using another small vial, dissolve a few crystals of (salen)H_2 in few drops of ethanol.
3) If necessary, use scissors (available upon request from a lab assistant) 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 in the beaker. This is required to saturate the chamber with ethanol vapor. Add ethanol to the beaker to wet the filter paper and cover the bottom with a 3-4 mm thick layer of the solvent. Close the beaker with the watch glass.
5) Mark the start.
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 colored spots on the TLC plate using a pencil.
9) Dry the TLC plate in the air and place it back into the zipper bag.
10) **CALCULATE** the R_f for both the (salen)H_2 and the (salen)$MnCl_x$.

Name: Code: USA

i. SKETCH the TLC plate below.



ii. DETERMINE and **RECORD** the R_f values for the (salen)H_2 and the (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".