

Instructions (Task 1)

- This examination has 10 pages total for practical Task 1 and 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 organizers' English version of this examination is available on request only for clarification.

Chemicals and Equipment (Task 1)

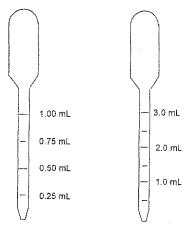
Chemicals (the actual labeling for each package is given in bold font)

	Risk Phrase ⁺	Safety Phrase ⁺
~2 M HCl,* solution in water, 50 mL in a	R34, R37	S26, S45
bottle		
~0.01 M KI ₃ ,* solution in water, 10 mL in a		
bottle, labeled "I2".		
Acetone, $(CH_3)_2CO$, $MW = 58.08 \text{ g mol}^{-1}$,	R11, R36, R66, R67	S9, S16, S26
density = 0.791 g mL^{-1} , 10.0 mL in a vial		
Acetone- d_6 , (CD ₃) ₂ CO, MW = 64.12 g mol ⁻¹ ,	R11, R36, R66, R67	S9, S16, S26
density = 0.872 g mL^{-1} , 3.0 mL in a pre-		
scored ampule		

^{*} See page 3 for definition of Risk and Safety Phrases.

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 in the right).
- Ten 3-mL polyethylene transfer pipettes graduated in 0.50
 mL increments (see drawing in the right).
- One digital timer (stopwatch)



^{*} The exact molarity is indicated on the label, with the concentration given before the name of the substance.

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

Task 1

18% of the total

а	ь	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 manner 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 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:

$$R_3C$$
 CR_3 R_3C R_2 R_3 R_4 R_5 R_5 R_5 R_5 R_6 R_7 R_8 R_8 R_8 R_9 R

The reaction takes place with a rate law

Rate =
$$k[acetone]^m[I_3]^n[H^+]^p$$

where the rate constant k and the reaction orders (integers) 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 or D), to determine the isotope effect ($k_{\rm H}/k_{\rm D}$) 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 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 "I₂") 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):

 $[H^{\dagger}]$: 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 colour of the triiodide ion. Record the time required for the colour to disappear. When the reaction is complete, set aside the vessel, and leave it sealed so that you do not expose yourself to iodoacetone vapours.

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 $(CD_3)_2CO$.

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

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 pipettes and sealed used vials in designated containers under the hoods;
- c) Use a container labeled Broken Glass Disposal to dispose of all parts of the empty ampule.

a. Record your results for acetone, (CH₃)₂CO, in the table below. You need not fill the entire table.

Run#	Volume HCl solution, mL	Volume H ₂ O, mL	Volume I ₃ solution, mL	Volume (CH ₃) ₂ CO, mL	Time to disappearance of I_3 , s
1					0113,3
2					
3					
4	•				
5					
6					
7					
8					

b. Record your results for acetone- d_6 , (CD₃)₂CO, in the table below. You need not fill the entire table.

Run#	Volume HCl solution, mL	Volume H ₂ O, mL	Volume I ₃ ⁻ solution, mL	Volume (CD ₃) ₂ CO, 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.

Code: CAN

$(CH_3)_2CO$:

Run #	Initial [H ⁺], M	Initial [I ₃], M	Initial [(CH ₃) ₂ CO], M	Average rate of disappearance of I ₃ , M s ⁻¹	calcula	used in ting $k_{\rm H}$?
				M s ⁻¹	Yes	No
1						
2						
3						
4						
5			· ·			
6						
7						
8						

$(CD_3)_2CO$:

Run #	Initial [H ⁺], M	Initial [I ₃], M	Initial [(CD ₃) ₂ CO], 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 reaction order (in integers) of acetone, triiodide, and hydrogen ion.

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

$$m =$$

$$n =$$

$$p =$$

e. Calculate the rate constant $k_{\rm H}$ for the reaction of acetone, (CH₃)₂CO, and indicate the units.

$$k_{\rm H} =$$

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

$$k_{\rm D}$$
 =

$$k_{\rm H}/k_{
m D} =$$

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 (\checkmark) 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 (\checkmark) 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	R.D.S. consistent
	with rate law?	with isotope effect?
+ H ₃ O+ + H ₂ O		
HO ⁺ + H ₂ O + H ₃ O ⁺		
HO + 13 + 2 -		
HO+ + H ₂ O + + H ₃ O+		

Instructions (Task 2)

- This examination has 13 pages total for Task 2, 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.
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The 44th IChO – Practical Examination. The Canadian English version

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
	Parket line and the second sec	S45
$Mn(OOCCH_3)_2 \cdot 4H_2O$, ~1.9 g ^b in a vial	R36/37/38 R62 R63	S26 S37/39
Lithium chloride solution, LiCl, 1M solution	R11 R36/38	S9 S16 S26
in ethanol, 12 mL in a bottle		To compare the state of the sta
Ethanol, 70 mL in a bottle	R11	S7 S16
Acetone, (CH ₃) ₂ CO, 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 "I2".		
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)H₂:

^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 SO₃H):

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 Erlenmeyer flasks (one for synthesis, one for crystallization)
- One 50 mL graduated cylinder
- 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 pipettes (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 and ready to used 25 mL burette
- One small plastic funnel
- Four 125 mL Erlenmeyer 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 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.

R—OH HO—R
$$(salen)H_2, R = H$$

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

The ability of the salen ligand to stabilize higher oxidation states of 3d-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)H₂ with Mn(II)acetate in ethanol in the presence of lithium chloride. Under these conditions, you could obtain 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 SO₃H.

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

$$+ Mn(OOCCH_3)_2 + O_2 + LiCI$$

$$(salen)MnCI_x$$

- 1) Place 2-3 crystals of (salen)H₂ aside in a small vial to be used for the TLC experiment later.
- 2) Transfer the pre-weighed ~1.0-g sample of (salen)H₂ provided into a 250 mL Erlenmeyer flask with a stirring bar. Combine the reagent with 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)₂·4H₂O. 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 min.
- 7) Use 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 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", then determine and record its mass, m_p , in the box below. Record also the mass of the following reagents used in the synthesis: (salen)H₂, m_S , and Mn(OOCCH₃)₂·4H₂O, m_{Mn} .
- 9) Place the labeled vial with product into a zipper bag.

WARNING: You will **NOT be given** extra time for clean up after the STOP command has been given.

Code: CAN

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 (cop	by from the label), m_S :
Mass of (salen) H_2 from label on the vial (cor	by from the label), m_S :
Mass of (salen) H_2 from label on the vial (cop Mass of Mn(OOCCH ₃) ₂ ·4 H_2 O from label on	g

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

Using 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 washed with titrant.
- 1) Dispense 10.00 mL of the provided (salen*)MnCl_x solution into a 125 mL Erlenmeyer 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 min.
- 3) To avoid oxidation of ascorbic acid with O₂ do not delay and titrate the solution <u>immediately</u> with the KI₃ 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) Only if required and 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	Final volume reading in	Volume of KI ₃ solution
	in burette of KI ₃	burette of KI ₃ solution,	consumed, mL
	solution, mL	mL	
1			100 100 100 100 100 100 100 100 100 100
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):

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, SO₃H). Show them in the template below:

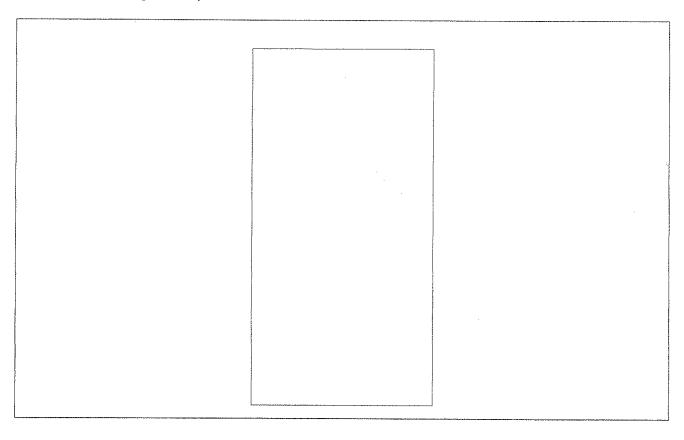
R	x	(Theoretical molar mass)/x, g/mol
Н	1	357
Н	2	196
Н	3	143
СООН	1	445
COOH	2	240
СООН	3	172
SO ₃ H	1	517
SO ₃ H	2	276
SO ₃ H	3	196

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)H₂ 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 in the beaker so that it takes almost the full height of the beaker. This is required to saturate the chamber with ethanol vapour. Add ethanol to the beaker to wet the filter, and cover the bottom with a 3-4 mm thick layer of the solvent. Close the beaker with watch glass.
- 5) Mark the start and label the plate.
- 6) Using the capillary tubes provided spot the TLC plate with both solutions.
- 7) Run a 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 :	4.000.000.000.000	
	4	

WARNING: You will **NOT be given** extra time for clean up after the STOP command has been given.

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".