NATIONAL HIGH SCHOOL CHEMISTRY EXAMINATION 2003 PART A - MULTIPLE CHOICE QUESTIONS (60 minutes)

1. The following WHMIS symbol indicates that a substance is



- A. Acidic B. Alkaline C. Corrosive D. Oxidizing E. Flammable
- 2. The correct formula for tin(IV) sulfate is:
 - A. $SnSO_4$ B. Sn_4SO_4 C. $Sn(SO_4)_2$ D. $Sn_2(SO_4)_3$ E. $Sn(SO_4)_4$
- 3. A student heats some Epsom salts (MgSO₄•7H₂O, M_r = 246.48) in a crucible to constant mass at 100° C. She writes the following readings in her lab book:

Mass of crucible	= 20.465 g
Mass of crucible + Epsom salts	= 25.395 g
Final mass of crucible + residue after heating	= 23.593 g

The formula of the substance **in the residue** is:

A. MgSO ₄	B. $MgSO_4$ ·2 H_2O	C. $MgSO_4 \cdot 4H_2O$
D. MgSO ₄ •5H ₂ O	E. MgSO ₄ •6H ₂ O	

4. Nitrogen exists in two different oxidation states in the compound NH₄NO₃. These oxidation states are:

A. +1, -1 B. -1, +3 C. -3, +3 D. -3, +5 E. -4, +6

5. Which one of the following is **NOT** a **decreasing** order of size of atomic and/or ionic radius?

- 6. When mixed in the proportions shown, which of the following pairs of solutions would give an endpoint mixture with the **lowest conductivity** when titrated together? (Each of the solutions has a concentration of 0.1 mol·L⁻¹ at the beginning of the titration.)
 - A. HCl + NaOH
 - B. AgNO₃ + NaCl
 - $C. \quad Na_2CO_3+2HCl$
 - D. $H_2SO_4 + Ba(OH)_2$
 - E. CH₃COOH + NaOH
- 7. Consider the following reaction:

 $HPO_{4}^{2-}(aq) + CH_{3}COOH(aq) \leftrightarrows H_{2}PO_{4}^{-}(aq) + CH_{3}COO^{-}(aq)$

If $K_c = 290$ for this reaction, then the **strongest base** in the equilibrium mixture is:

A. H₂O B. HPO₄²⁻ C. CH₃COOH D. H₂PO₄⁻ E. CH₃COO⁻

8. In the electrolysis of molten sodium chloride, the **anode** reaction is:

A. Na
$$\rightarrow$$
 Na⁺ + e⁻

B.
$$Na^+ + e^- \rightarrow Na$$

$$C. \quad 2Cl^{+} + 2e^{-} \rightarrow Cl_2$$

D.
$$2Cl^{-} \rightarrow Cl_2 + 2e^{-}$$

E.
$$Cl_2 + 2e^- \rightarrow 2Cl^-$$

9. The table below shows the results of an experiment to test the solubility of some pure solids. Which one of them could be copper (II) oxide?

	Substance	Appearance	Solubility in water	Solubility in 2M HNO ₃
Ī	А.	White powder	Insoluble	Insoluble
	B.	Black powder	Insoluble	Dissolves to give a blue solution
	C.	Orange-brown pellets	Insoluble	Dissolves to give a blue solution and a brown gas
	D.	Green powder	Insoluble	Dissolves to give a blue solution and a colourless gas
	E.	Blue crystals	Dissolves to give a blue solution	Dissolves to give a blue solution

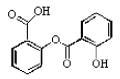
10. The first stage in the production of nitric acid involves the reaction of ammonia and air over a platinum gauze catalyst at 900°C. Only the oxygen in the air reacts with the ammonia, and it does so according to the following equation:

 $4NH_3(g) + 5O_2(g) \leftrightarrows 4NO(g) + 6H_2O(g); \Delta H = -950 \text{ kJ} \cdot \text{mol}^{-1}$

Which one of the following would increase the yield of nitrogen oxide (NO)?

- A. Increasing the pressure
- B. Drying the reagents used
- C. Increasing the temperature
- D. Adding nitrogen to the reaction mixture
- E. Using a nickel catalyst instead of platinum

11. Salsalate is used as an analgesic and anti-inflammatory drug. Its structural formula is:



The functional groups in this molecule include:

- A. Ester, ketone
- B. Ether, ketone
- C. Carboxylic acid, ether
- D. Carboxylic acid, ester
- E. Carboxylic acid, ketone
- 12. Which of the following molecules is polar?

BF ₃	CBr ₄	CCl ₃ Br	GeBr ₂	NF ₃
	CCl_3Br BF ₃ and NF ₃	B. only NF ₃ E. all of NF)	only GeBr ₂ Id CCl ₃ Br

13. Which of the following substances has the lowest melting point?

C. Al₂O₃ D. SiO₂ E. P₄O₁₀ A. Na₂O B. MgO

- 14. 250.00 mL of a beautiful violet-blue solution is prepared by dissolving $17.912 \text{ g of } Cr_2(SO_4)_3 \cdot 18H_2O (M_r = 716.478) \text{ in water. This solution}$ contains:
 - A. 1.300 g of Cr³⁺
 B. 0.300 mol of SO4²⁻

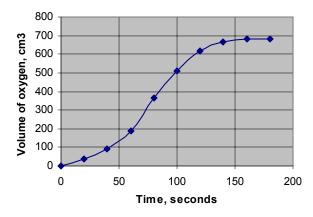
 - C. 8.107 g of H₂O

 - D. $39.219 \text{ g} \cdot \text{L}^{-1} \text{ of } \text{Cr}_2(\text{SO}_4)_3$ E. $0.0250 \text{ mol} \cdot \text{L}^{-1} \text{ of } \text{Cr}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$

15. A student investigated the decomposition of hydrogen peroxide, which takes place according to the following equation:

 $2H_2O_2(\text{aq}) \rightarrow 2H_2O(\text{l}) + O_2(\text{g})$

Using manganese(IV) oxide as catalyst he obtained the following graph:



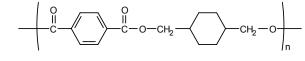
From the graph it can be inferred that the rate _____ during the process. Find the missing term:

A. changes	B. increases	C. decreases
D. is constant	E. is first order	

16. Successive ionization energies, in kJ·mol⁻¹ of 5 elements with sequential atomic numbers are given in the table below. Which element is most likely to form a divalent ion?

Ionization energy # Element key	1	2	3	4
Α.	1681	3374	6051	8408
B.	2081	3952	6122	9370
C.	496	4563	6913	9544
D.	738	1451	7733	10541
E.	578	1817	2745	11578

17. The substance with the formula



is a

- A. rubberB. polyesterC. polyamideD. polysaccharideE. natural oil or fat
- 18. Which of the following formulae could represent a pair of enantiomers?
 - A. CH₃(CH₂)₂NH₂
 - B. CH₃CH(OH)CH₃
 - C. (CH₃)₂CHCONH₂
 - D. CH₃(CH₂)₂COONH₄
 - E. CH₃CH₂CH(NH₂)COOH
- 19. Lead arsenate, $Pb_3(AsO_4)_2$, $K_{SP} = 4.1 \times 10^{-36}$, is used as an insecticide on fruit. A saturated solution contains lead ions at a concentration of:
 - A. $3.3 \times 10^{-8} \text{ mol} \cdot \text{L}^{-1}$ B. $4.8 \times 10^{-8} \text{ mol} \cdot \text{L}^{-1}$ C. $6.6 \times 10^{-8} \text{ mol} \cdot \text{L}^{-1}$ D. $7.4 \times 10^{-8} \text{ mol} \cdot \text{L}^{-1}$ E. $9.8 \times 10^{-8} \text{ mol} \cdot \text{L}^{-1}$
- 20. How much heat can be generated by burning one tonne (1000 kg) of blast furnace gases (containing 46% N₂, 40% CO and 14% CO₂ by mass) given $\Delta H^{\bullet}_{\text{combustion}}(\text{CO}) = -283.0 \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta H^{\bullet}_{\text{formation}}(\text{CO}_2) = -393.5 \text{ kJ} \cdot \text{mol}^{-1}$?

NHSCE 2003 Part A Page 4 of 4

21. In a sewage plant the pH of waste water is adjusted to reduce biological activity. If 0.37 g of solid Ca(OH)₂ ($M_r = 74.1$) are added to each litre of water (at pH 7.0) coming into the plant, then, assuming that the temperature remains at 25°C throughout, the pH of the water will become approximately:

A. 2.0 B. 2.3 C. 8.0 D. 11.7 E. 12.0

22. Rhodonite is a decorative stone that consists mainly of pink $MnSiO_3$ ($M_r = 131.022$). Less valuable variants of the stone have black streaks of MnO_2 ($M_r = 86.937$) in them. Analysis of a particular sample of rhodonite indicates that it contains a total of 49.16% of Mn by mass. The percentage of MnO_2 in the sample is therefore approximately:

A. 34 B. 44 C. 55 D. 63 E. 66

23. A student did an experiment to determine the enthalpy change, ΔH , of a chemical reaction. She added excess solid zinc to 25.00 mL of copper sulfate solution (1.00 mol·L⁻¹) in a coffee cup calorimeter, stirred the mixture and measured the rise in temperature, which was 49.8°C. It took about 90 seconds for this temperature to be reached.

She calculated the result using the expression:

$$\Delta H = - \frac{\{(25.00 \text{ ml x } 1.00 \text{ g} \cdot \text{ml}^{-1}) \text{ x } 4.18 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1} \text{ x } 49.8 \text{ K}\}}{(1.00 \text{ mol} \cdot \text{L}^{-1} \text{ x } 0.02500 \text{ L x } 1000 \text{ J} \cdot \text{kJ}^{-1})}$$

= - 208 kJ \cdot mol^{-1}

The literature value is $-217 \text{ kJ} \cdot \text{mol}^{-1}$. Which one of the following could **NOT** have contributed to the error in the student's result?

- A. The density of the solution is less than that of water
- B. The heat capacity of the solution is greater than that of water
- C. The time taken for the temperature to rise has not been considered
- D. The heat capacity of the excess zinc has not been included in the calculation
- E. The heat capacity of the thermometer has not been included in the calculation

24. Some standard bond enthalpy terms (in $kJ \cdot mol^{-1}$) are:

$$(C-H) = 413, (C-O) = 358, (C=O) = 805, (O=O) = 498, and (O-H) = 464.$$

Using these values the standard molar enthalpy change of combustion of methanol, $\Delta H^{\Theta}_{\text{combustion}}$ (CH₃OH), can be estimated to be:

	B. $-409 \text{ kJ} \cdot \text{mol}^{-1}$	$C_{\cdot} - 658 \text{ kJ} \cdot \text{mol}^{-1}$
D. – 689 kJ•mol ⁻¹	E. $-726 \text{ kJ} \cdot \text{mol}^{-1}$	

25. This question needs you to use the following standard reduction potential data for different oxidation states of vanadium:

$$V^{2^{+}} + 2e^{-} \leftrightarrow V \qquad E^{\Theta} = -1.175 \text{ Volts}$$

$$V^{3^{+}} + e^{-} \leftrightarrow V^{2^{+}} \qquad E^{\Theta} = -0.255 \text{ Volts}$$

$$VO^{2^{+}} + 2H^{+} + e^{-} \leftrightarrow V^{3^{+}} + H_2O \qquad E^{\Theta} = +0.337 \text{ Volts}$$

$$VO_2^{+} + 2H^{+} + e^{-} \leftrightarrow VO^{2^{+}} + H_2O \qquad E^{\Theta} = +0.991 \text{ Volts}$$

A technician needs to oxidize a solution of V(II) to V(III) without continuing the oxidation to V(IV). He needs to look in a data table for a substance that has a standard reduction potential (in acid solution) of between:

A. - 1.175 and - 0.255 Volts B. - 0.255 and + 0.337 Volts C. + 0.337 and + 0.991 Volts D. + 0.225 and - 0.337 Volts E. + 0.255 and + 1.175 Volts

THIS IS THE END OF PART A OF THE EXAMINATION



NATIONAL HIGH SCHOOL CHEMISTRY EXAMINATION 2003

PART B – EXTENDED RESPONSE SECTION (90 minutes)

In this section you should respond to **TWO** topics only, writing in the form of scientific essays (or, for Question 4, an experiment description) including any appropriate equations, formulae and diagrams. Some suggestions are made about the direction(s) you could take, but these are not exclusive. Each essay/experiment is of equal value, and the quality of **both** responses will be considered in the final competition: you should therefore allocate approximately equal time to each of the subjects you choose. The judging of the responses will be based on both factual accuracy and presentation. A clear, concise and well-organized piece of written work will be rated more highly than a long rambling one that contains the same information.

1. The Periodic Table

One of the first things you learn about in chemistry is the Periodic Table, but just why is it so important? There are various ways in which you could approach this topic. You might like to describe the historical development of ways of classifying the elements. Alternatively, you could discuss what the Table can tell us about the trends in physical and chemical properties of elements, both across the periods and down the various groups. Although you do not have numerical data to work with, you should be as specific as possible about the trends you discuss, and the theoretical explanations for them.

2. The Octet Rule

The Octet Rule is often used in elementary chemistry classes as a means of explaining how bonding occurs. In your essay you should state the rule, and give examples of how it works for a simple ionic compound and a simple covalent molecule. You should also consider some examples of compounds in which the rule is broken, either because there are not enough electrons for an octet to be formed, or because there are too many. Some compounds that you might like to consider could include: NaCl, Cl₂, HCl, BCl₃, SF₆, ZnCl₂, PbI₂, and noble gas compounds, but you could equally well discuss other examples. Diagrams, however, are extremely important in all cases.

3. The Kyoto Protocol

The Kyoto protocol, agreed in December 1997, sets legally-binding greenhouse gas emission objectives for industrialized countries. These countries are required to achieve a 5% reduction in emissions from 1990 levels over the 2008 to 2012 period – a significant departure from current trends. The main greenhouse gases covered by the Protocol are CO_2 , CH_4 and N_2O . In your essay you should describe the various ways in which these gases are formed, and suggest how you think that Canada should set about reducing its emissions in accordance with the requirements of the Protocol. You should bear in mind that most people in Canada do not feel that it is acceptable to consider a solution in which large numbers of

people lose their jobs, or in which our general standard of living is significantly reduced.

NHSCE 2003 Part B Page 2

4. Experiment Design

Indigestion tablets are used as a means of neutralizing stomach acid, and sometimes also as a source of calcium in the prevention of osteoporosis. A particular brand of tablets contains approximately equal masses of $Mg(OH)_2$, $Al(OH)_3$ and $CaCO_3$, mixed with an inert binding substance. Design an experiment to determine (1) the "acid neutralizing capacity" in terms of milligrams of HCl that reacts with each one gram tablet, and (2) the mass of calcium present in each tablet. In your response you should give an outline of the procedure you intend to use, including equations for any chemical reactions involved. You should also give details of the apparatus and materials you would need for performing the experiment, and consider any safety precautions that might be required. You should also indicate what readings you would take, and how you would calculate the values required from your readings.

CHEMICAL INSTITUTE OF CANADA and CANADIAN CHEMISTRY OLYMPIAD Final Selection Examination 2003

PART C: Free Response Development Problems 60% Time: 1.5 hours

This segment has five (5) questions. While students are expected to attempt **all** questions for a complete examination in 1.5 hours, it is recognized that backgrounds will vary and students will not be eliminated from further competition because they have missed parts of the paper.

Your answers are to be written in the spaces provided on this paper. All of the paper, including this cover page, along with a photocopy of Part A of the examination, is to be returned <u>promptly</u> to your Canadian Chemistry Olympiad Coordinator.

 PLEASE READ — 1. BE SURE TO COMPLETE THE INFORMATION REQ 	PART A () Correct Answers
THE BOTTOM OF THIS PAGE BEFORE BEGINNING THE EXAMINATION.	
2. STUDENTS ARE EXPECTED TO ATTEMPT ALL QU PART A AND PART C . CREDITABLE WORK ON A NUMBER OF THE QUESTIONS MAY BE SUFFICIEN	LIMITED
AN INVITATION TO THE NEXT LEVEL OF THE SEL PROCESS.	LECTION 1/012
3. IN QUESTIONS WHICH REQUIRE NUMERICAL CA BE SURE TO SHOW YOUR REASONING AND YOUR	
4. ONLY NON-PROGRAMMABLE CALCULATORS MA ON THIS EXAMINATION.	
5. NOTE THAT A PERIODIC TABLE AND A LIST OF S PHYSICAL CONSTANTS WHICH MAY BE USEFUL FOUND ON THE DATA SHEET PROVIDED WITH TH EXAMINATION.	CAN BE
	TOTAL/100
Name	School
(Print Clearly)	Province
Date of birth	E-Mail
Home Telephone ()	Years at a Canadian high school
Male 🗖 Canadian Citizen 🗖	Landed Immigrant 🗇 Visa Student 🗇
Female D Passport val	id until October 2003 🗖
	Nationality of Passport

1. (12 marks)

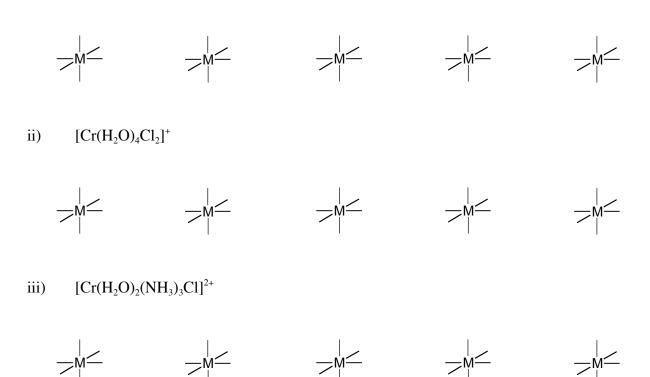
a) Isomerism of Octahedral Complexes:

Using the templates shown below as skeleton structures, draw all possible isomers of each of the following Cr^{3+} octahedral complexes (the quantity of templates shown may be more than is actually necessary for each species).

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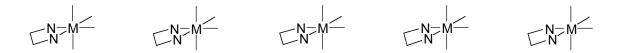
$$M = Cr^{3+}$$
 and "en" = $H_2NCH_2CH_2NH_2 = H_2N$

i) $Cr(H_2O)_3Cl_3$



 $[Cr(en)(NH_3)_2Cl_2]^+$ iv)

(The "en" ligand connects on the metal as shown below; hydrogen atoms are omitted in order to simplify the structures.)



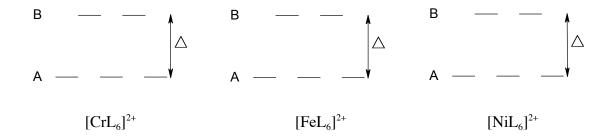
b) Electronic Structures of Octahedral Complexes:

In free transition metal atoms or ions in the gas phase, all five "d" orbitals are degenerate, *i.e.* they possess the same energy. When a transition metal atom (M) or ion (M^{n+}) forms an octahedral complex with six neutral ligands (L) as in ML_6^{n+} , the five "d" orbitals of the metal are divided in two different energy-level groups. In the present problem, the latter are labeled "A" and "B" for the low- and high-level groups, respectively. The "energy splitting" between these two groups (labeled as " Δ ") depends on the electric field strength of the ligands; a strong field ligand creates a large energy splitting (*i.e.* a large Δ value) resulting in pairing of electrons before promotion to the higher energy level.



Consider the following octahedral complexes of transition metals in the +2 oxidation state, $[ML_6]^{2+}$.

i) Using vertical arrows (\uparrow and/or \downarrow) to represent the spin of the electrons in the energy diagrams below, sketch the electron configuration of the "*d*" electrons within each complex, assuming that "L" is a strong electric field ligand.



ii) Which complex(es) is paramagnetic? Explain

2. (12 marks)

A solution is prepared by dissolving sodium acetate (CH₃COONa; 10.00 g), acetic acid (CH₃COOH; 30.02 g) and iron (II) chloride (0.0500 g) in 1.000 L of distilled water. To this solution is bubbled hydrogen sulfide up to the point of saturation, which for this gas corresponds to 0.100 mol L^{-1} .

Knowing the following constants, provide answers to the questions below.

Acetic acid	$K_a = 1.75 \times 10^{-5}$	
Hydrogen sulfide	$K_a 1 = 9.6 \times 10^{-8}$	$K_{a2} = 1.3 \times 10^{-14}$

Solubility product constants:

iron (II) hydroxide $K_{sp} = 4.1 \times 10^{-15}$ iron (II) sulfide $K_{sp} = 8 \times 10^{-19}$

a) What is the pH of the resulting solution?

b) Using appropriate calculations, show whether a precipitate of iron (II) hydroxide will be present in the resulting solution.

c) Using appropriate calculations, show whether a precipitate of iron (II) sulfide will be present in the resulting solution.

d) What will be the concentration of free iron (II) in the resulting solution?

In a subsequent manipulation, sodium hydroxide (16.58 g) is then added to the above solution, and the mixture is mixed thoroughly.

e) What is the pH of the resulting solution?

f) Using appropriate calculations, show whether a precipitate of iron (II) hydroxide will be present in the resulting solution.

g) Using appropriate calculations, show whether a precipitate of iron (II) sulfide will be present in the resulting solution.

h) What will be the concentration of free iron (II) in the resulting solution?

3. (12 marks)

a) Is the free energy change (ΔG) for the dissolution of a salt in water positive or negative? Explain.

b) A student added 4.00 g of solid ammonium nitrate, NH_4NO_3 , to 100.0 g of water in a polystyrene coffee cup. The temperature of the water dropped from 24.1 to 21.0 °C. Estimate the approximate enthalpy of solution (ΔH_{soln}) of ammonium nitrate.

(Assume that the heat capacity of the coffee cup and thermometer is zero; that the specific heat of the ammonium nitrate solution is, $Cp = 4.027 \text{ J g}^{-1} \text{K}^{-1}$; that the polystyrene coffee cup is a perfect insulator.)

c) Explain the role the lattice energy of the ammonium nitrate solid and the hydration of the ionic species in the dissolution. Which dominates in determining ΔH_{soln} ?

d) Is the entropy change (ΔS) positive or negative for this dissolution process? Explain

e) From the literature, the enthalpy of formation of ammonium nitrate aqueous solution is listed as: of $\Delta H^{\circ}f$ NH₄NO₃(aq) = -339.9 kJ mol⁻¹. What is the enthalpy of formation of solid ammonium nitrate, $\Delta H^{\circ}f$ NH₄NO₃(s)?

- 4. (12 marks)
- a) Ozone is of interest at both the lower and upper atmosphere. In the lower atmosphere this powerful oxidizing agent can react with other substances to pollute the air we breath. At high levels it helps prevent dangerous UV-radiation from reaching us.

Nitric oxide, NO, is involved in both of these processes. At low levels NO is produced by combustion in automobile engines and is involved in the following reaction mechanism:

Sequence i)

 $NO(g) + 0.5 O_2(g) \rightarrow NO_2(g)$ $NO_2(g) + h\nu \rightarrow NO(g) + O(g)$ $O_2(g) + O(g) \rightarrow O_3(g)$

In the upper atmosphere the reaction system is:

Sequence ii)

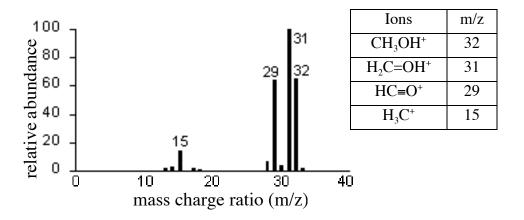
$$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$$

$$O(g) + NO_2(g) \rightarrow NO(g) + O_2(g)$$

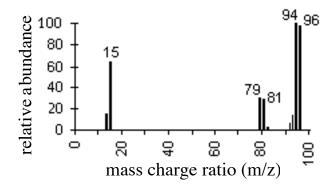
Write the overall (net) equation for each reaction sequence i) and ii) and identify any catalyst or intermediate compounds.

b) ^{99m}Tc, which has a half-life of 6.0 hours, is an artificially produced isotope of technetium which decays to the ground state ⁹⁹Tc by emission of a gamma ray. Technegas[™] is comprised of ^{99m}Tc incorporated onto very small carbon particles. It is used in medicine in procedures such as lung scans. The particles are adsorbed onto surfaces in the lungs and the emitted gamma rays can be detected and analyzed. What percentage of the metastable isotope ^{99m}Tc remains in the lungs 1 day (24 hours), after administration, if radioactive decay is the only process leading to its removal?

c) The mass spectrum for methanol is shown with the fragment ions indicated. The parent ion (Ions) and other abundant ions are prominent on the y-axis with their mass/charge (m/z) ratio indicated.



An acid catalyzed reaction of this methanol with a hydrogen halide produced a new compound with the following spectrum:

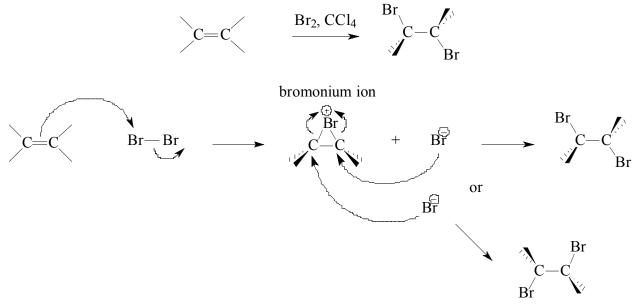


Decide the identity of the hydrogen halide and write the equation for the reaction. Explain the five major (i.e. labeled) peaks.

5. (12 marks)

It is known that the addition of bromine in CCl_4 to a double bond occurs with anti stereochemistry. This specific stereochemistry is due to the formation of a bromonium ion which prevents attack of the bromide ion on the same side of the molecule.

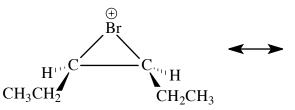
Overall reaction:



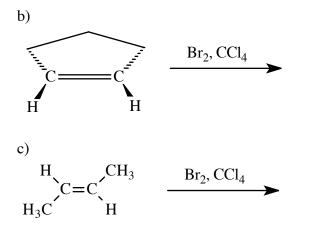
Mechanism

The products obtained may or may not be different - It depends on the initial compound.

a) A resonance structure is one of several valence-bond structures with localized electrons that approximate the true structure of a compound that has delocalized electrons. Draw a major resonance structure of the bromonium ion shown below clearly showing any lone pairs of electrons and the location of any formal charges that may be present.

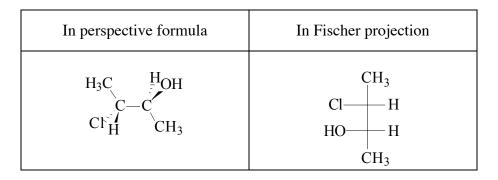


Show, in 3-D, the product(s) obtained from the addition of bromine to the following compounds:



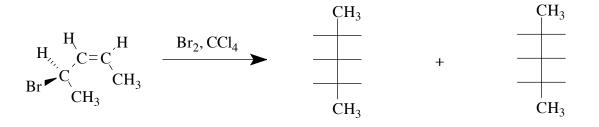
The Fischer projection is a convenient method of representing the arrangement of groups bonded to a chirality center (a carbon bonded to four different groups). To obtain a Fischer projection, place the carbon chain vertically. Vertical lines represent bonds that project back from the plane of the paper away from the viewer while horizontal lines represent bonds that project out of the plane of the paper toward the viewer.

The following example shows two equivalent forms of the same compound.



Complete the templates to show the Fischer projection of the products obtained by the addition of bromine to the following compounds:

d)



e) As in Part d), there are two products of this reaction. Show ONLY the isomer that is NOT formed in d) above

