NATIONAL HIGH SCHOOL CHEMISTRY EXAMINATION 2006 PART A - MULTIPLE CHOICE QUESTIONS (60 minutes)

All contestants should attempt this part of the examination before proceeding to Part B (the CIC Exam) and/or Part C (the CCO Exam). A CIC/CCO Periodic Table is required, but no other data may be given. Answers should be marked on the Answer Grid provided.

1. A certain substance has the following WHMIS symbol on the label of its bottle.



Which one of the following instructions is best indicated by this symbol?

- A. Keep the material away from heat
- B. Keep the material away from combustible materials
- C. Wear protective clothing and/or respiratory equipment
- D. Keep the material away from heat, shock, air and/or moisture
- E. Handle the material only in areas designed to prevent biological contamination.
- 2. What is the percentage by mass of manganese in the mineral braunite, which has the formula MnSiO₃*3Mn₂O₃ ($M_r = 604.7$)?
 - A. 9.1 %
- B. 18.2 %
- C. 27.3 %
- D. 54.5 %
- E. 63.6 %
- Refined uranium oxide ores are used to make the fuel for CANDU nuclear reactors. A sample of one of these ores contains 11.902 g of uranium and 2.136 g of oxygen. Which one of the following could it be?
 - $A. UO_2$
- B. U₄O₉
- C. U₃O₈
- D. UO₃•H₂O
- E. UO₄•2H₂O
- 4. The following acids all play a role in human metabolism:
 - A. OHCCOOH (glyoxylic acid), $M_r = 74.1$
 - B. HOCH₂COOH (glycolic acid), $M_r = 76.1$
 - C. CH₃CH=CHCOOH (trans-2-butenoic acid), $M_r = 86.1$
 - D. CH₃CH(OH)COOH (lactic acid), $M_r = 90.1$
 - E. $CH_3CH(OH)CH_2COOH$ (beta-hydroxybutyric acid), $M_r = 104.1$

If titration of a solution containing a 0.200–g sample of one of the acids requires 23.25 mL of 0.1 M NaOH solution to reach the endpoint, which one of the above compounds might it be? Assume that all the options will behave as monoprotic acids under these conditions.

- 5. A box of washing soda leaves the factory containing 1.50 kg of $\text{Na}_2\text{CO}_3 \cdot 10 \text{ H}_2\text{O}$ ($M_r = 286.1$). A customer complains because he finds that the box appears partly empty and weighs only 1.34 kg. An independent analyst says that the box contains the correct mass of sodium carbonate, but that it has lost water of crystallisation. What is the composition of the customer's soda?
 - A. Na₂CO₃•1.3 H₂O
- B. Na₂CO₃=1.7 H₂O
- C. Na₂CO₃=5.2 H₂O

- D. Na₂CO₃•8.3 H₂O
- E. Na₂CO₃•8.9 H₂O
- 6. A certain brand of gluestick is pink in the tube, but becomes colourless after it has been applied to a surface. It contains the indicator phenolphthalein and a small amount of alkali, the combination of which gives the glue its pink colour. At lower pH values the indicator turns colourless. Which one of the following substances in air is most likely to be the one that reacts to turn the glue colourless?
 - A. Nitrogen B. Oxygen C. Water vapour D. Argon E. Carbon dioxide
- 7. Which one of the species listed below has the ground state electronic configuration:

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$$
?

- A. As^{3-}
- B. Ge²⁺
- C. Kr
- D. Ni
- E. Zn^{2+}
- 8. Borax (sodium borate) reacts with hydrochloric acid according to the following equation:

$$Na_2B_4O_7(aq) + 2HCl(aq) + 5H_2O(1) \rightarrow 4H_3BO_3(aq) + 2NaCl(aq)$$

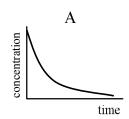
By how much does the oxidation number of each boron atom CHANGE in this reaction?

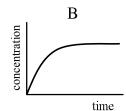
- A. +3
- B. +1
- C. 0
- D. 1
- E. -3

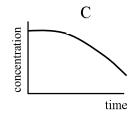
- 9. For which one of the following pairs is the ratio of ionic radius to atomic radius the GREATEST?
 - A. Na⁺:Na
- B. B³⁺:B
- C. $Al^{3+}:Al$
- D. N³⁻:N
- E. F-:F
- 10. Marble (calcium carbonate) reacts with hydrochloric acid according to the following equation:

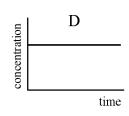
$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(1) + CO_2(g)$$

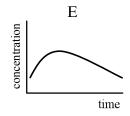
Assuming that the marble is in the form of chips of roughly the same size and shape, which one of the following graphs best shows the change in concentration of hydrochloric acid during the course of the reaction?











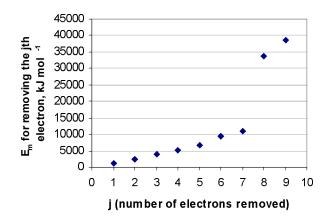
- 11. Some important industrial chemicals can be made by the electrolysis of brine, which is essentially aqueous sodium chloride solution. Which one of the following products is formed at the **anode** in this process?
 - A. Na
- B. H₂
- C. NaOH
- D. HCl
- $E. \ Cl_2$
- 12. Which one of the following species has only two lone pairs of electrons (in addition to bonding pairs) around the central atom?
 - A. BF₄
- B. NF₃
- C. SF₃⁺
- D. ClF₃
- E. XeF₂

13. A group of students did a series of experiments to see how some reactive metals release less reactive metals from solutions of their salts. The following table shows the results they have obtained by the end of the lesson:

Metal	Ni	Ca	Cr	Ag
Solutions				
AgNO ₃	Silver formed	Silver formed	Silver formed	No reaction
CaCl ₂	No reaction	No reaction	No reaction	No reaction
NiCl ₂	No reaction	No data	Nickel formed	No reaction
CrCl ₃	No reaction	Chromium formed	No reaction	No data

Even with incomplete data, the students can still work out the probable order of reactivity of the metals. Putting the most reactive metal first, which one of the following is likely to be the correct order of reactivity?

- A. Ag, Ni, Cr, Ca
- B. Ca, Cr, Ni, Ag
- C. Ca, Ni, Cr, Ag
- D. Cr, Ca, Ni, Ag
- E. Ni, Ca, Ag, Cr
- 14. The following graph shows the molar ionization energies $(E_{\rm m})$ for removing the first nine electrons in succession from atoms of a particular element, Z:

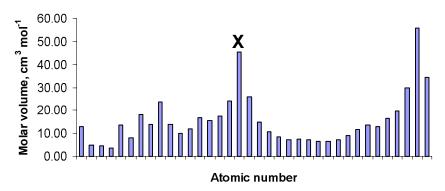


Which one of the following elements could be **Z**?

- A. Sulfur
- B. Chlorine
- C. Argon
- D. Calcium
- E. Scandium

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- 15. Consider the molecules SCl₂, SO₃, SOCl₂. What are the shapes of these molecules, in the order given?
 - A. Linear, trigonal planar, trigonal pyramidal
 - B. Linear, trigonal pyramidal, trigonal planar
 - C. Angular, trigonal planar, linear
 - D. Angular, trigonal planar, trigonal pyramidal
 - E. Angular, trigonal pyramidal, trigonal planar
- 16. Periodicity may be demonstrated by plotting various physical properties of the elements against their atomic numbers. The chart given below shows how the molar atomic volume of the elements varies with atomic number for successive elements (not starting at element 1). Note that the volume given for each element refers to its **solid** state, which may be at a very low temperature if it is normally a gas at room temperature.



In which group of the periodic table does element **X** belong?

- A. the noble gases
- B. the alkali metals
- C. the boron group
- D. the carbon group
- E. the halogens
- 17. Citric acid is a triprotic acid found in many fruits and vegetables. Its acid dissociation constants at 25° C are pKa₁ = 3.13, pKa₂ = 4.76 and pKa₃ = 6.4. Which one of the following is the approximate pH at 25° C of a solution formed by mixing equal volumes of equimolar (0.2 mol L⁻¹) solutions of citric acid and potassium hydroxide?
 - A. 2.2
- B. 3.8
- C. 5.1
- D. 6.4
- E. 8.5

18. A test for alkanes is to add a certain reagent (X) in the presence of ultraviolet light. If an alkane is present reagent X is decolorized and a colourless gas (Y) is formed: Y reacts with ammonia gas to give a white "smoke". Which one of the following responses gives the correct identity for both X and Y?

	Reagent X	Gas Y
A.	Br ₂ (1)	H ₂
B.	Br ₂ (aq)	HBr
C.	Br ₂ dissolved in 1,1,1–trichloroethane	HBr
D.	HBr(aq)	H ₂
Е	HBr dissolved in 1,1,1–trichloroethane	H ₂

19. Part of a molecule of a plastic used for food wrapping is shown below:

Which one of the following pairs of alkenes could be the monomers used for making this plastic, which is an addition copolymer?

- A. Ethene and propene
- B. Ethene and 1–butene
- C. Ethene and 2-butene
- D. Propene and 1-butene
- E. Propene and 2-butene
- 20. Ethyl 3-methylbutanoate is used to give an apple flavour to candy. Which one of the following is the correct structural formula for this compound?
 - A. CH₃CH₂COOCH₂CH₂CH(CH₃)CH₃
 - B. CH₃CH₂COOCH₂CH(CH₃)CH₂CH₃
 - C. CH₃CH₂CH(CH₃)COOCH₂CH₃
 - D. (CH₃)₂CHCH₂COOCH₂CH₃
 - E. (CH₃)₃CCH₂COOCH₂CH₃

21. In olden times calomel (mercury(I) chloride, Hg₂Cl₂) was used as a laxative, despite the fact that mercury compounds are highly poisonous. If you drank 100 mL of a saturated solution of calomel dissolved in water, what mass of dissolved mercury would you swallow? $(K_{SP} = [Hg_2^{2+}][C\Gamma]^2) = 1.60 \times 10^{-18})$

A.
$$7.4 \times 10^{-7}$$
 g B. 1.5×10^{-5} g C. 3.0×10^{-5} g D. 1.5×10^{-4} g E. 3.0×10^{-4} g

22. When a car battery is discharging the overall reaction that takes place in each cell is:

$$Pb(s) + PbO_2(s) + 4H^+(aq) + 2SO_4^{2-}(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$$

Given the following standard reduction potentials:

$$\begin{split} PbSO_4(s) + 2e^- &\to Pb(s) + SO_4^{2-}(aq); \ E^\Theta = -0.36 \ V \\ PbO_2(s) + 4H^+(aq) + 2e^- &\to Pb^{2+}(aq) + 2H_2O(l) \ ; \ E^\Theta = +1.46 \ V \\ PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- &\to PbSO_4(s) + 2H_2O(l) \ ; \ E^\Theta = +1.69 \ V \end{split}$$

What is the overall cell potential, assuming standard conditions?

23. The neutralisation reaction is usually taken as referring to the ionic equation:

$$H^{+}(aq) + OH^{-}(aq) \rightarrow H_2O(1)$$

(where the anion of the acid and the cation of the base are passive spectator ions). The standard enthalpy change for this reaction, ΔH^{Θ} , is $-57.9 \text{ kJ mol}^{-1}$. My data book, however, gives a value of $\Delta H^{\Theta} = -56.1 \text{ kJ mol}^{-1}$ for the neutralisation of ethanoic acid with sodium hydroxide solution, according to the following equation:

$$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$$

Which one of the following statements best explains the difference in enthalpy changes? (Both values are for the same standard conditions.)

- A. Energy is lost to the surroundings
- B. Energy is used in dissociating the ethanoic acid
- C. Energy is used in dissociating the sodium hydroxide
- D. Energy is used in heating up the acid and the base as well as the water
- E. The two values are essentially the same within the limits of experiment error

24. The enthalpy change of solution often varies with dilution. When doing a series of experiments to test this effect, some students measured out 180.0 mL of water instead of 90.0 mL of water to dissolve 4.76 g of anhydrous magnesium chloride, MgCl₂ (M_r = 95.2 g moΓ¹). This meant that they observed a temperature increase of 10.1°C instead of 20.1°C. What is the percentage error of their result if they base their calculation on 180.0 mL? You may assume that heat losses are negligible and that the solutions have the same specific heat capacity and density as water (4.18 J g K⁻¹ and 1.00 g mL⁻¹ respectively).

25. The shift reaction is used to manufacture hydrogen at high temperature. The process involves the following equilibrium reaction:

$$CO(g) + H_2O(g) \longrightarrow CO_2(g) + H_2(g)$$

A chemical engineer is investigating this reaction. She finds that if she begins by mixing 1.45 mol of carbon monoxide and 1.45 mol of water vapour (with no carbon dioxide or hydrogen) in a closed container, she obtains a yield of 1.00 mol of hydrogen at equilibrium. How many **extra** moles of water vapour does she need to add to the materials already in the container to obtain a yield of 1.42 mol of hydrogen in a new equilibrium mixture at the same temperature?

A. 0.03 mol B. 2.89 mol C. 4.94 mol D. 13.6 mol E. 15.0 mol

THIS IS THE END OF PART A OF THE EXAMINATION. NOW GO BACK AND CHECK YOUR WORK.

Solutions to this examination will be published on the website www.chemistry.ca/NHSCE in October 2006.



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NATIONAL HIGH SCHOOL CHEMISTRY EXAMINATION 2006

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. Soaps and detergents

In this essay you should discuss what is meant by the terms "soap" and "detergent". You might like to consider how soaps are related to naturally occurring compounds, and to compare soaps to synthetic detergents. You should explain how soaps and detergents work in reducing the surface tension of water and how they function as cleaning agents. You should give specific examples wherever possible, showing the molecular formulae of the substances you discuss, and indicating how different parts of the molecules behave when they are being used. You could also discuss the issue of pollution by cleaning agents and by the other substances that are added to them in proprietary products, and consider the question of biodegradability of these substances.

2. Plastics

Nowadays many articles made of plastic are marked with recycling codes. These codes identify different types of plastics (polymers) as follows: (1) Polyethylene terephthalate (polyester); (2) High density polyethylene (polyethene); (3) Polyvinyl chloride (polychloroethene); (4) Low density polyethylene (polyethene); (5) Polypropylene (polypropene); (6) Polystyrene (polyphenylethene); (7) Other – these are polymers other than those specified above, or products made out of more than one polymer.

Choose one or more of these plastics and write a magazine article in which you discuss what the names of the polymers mean and give their molecular formulae. You may also like to describe how the polymers are manufactured. You should discuss the properties of the polymers and how these relate to their uses. You might also consider the problems of separating articles made of different plastics, and the uses that are appropriate for the recycled products (which are often different from the the original uses of these materials).

/continued overleaf

3. Transition elements

In this essay you should define what is meant by the term "transition elements", and discuss some of characteristics that these elements have in common. Some of the factors that you might like to consider are the physical properties of the elements themselves, for example their density, melting point, electrical and thermal conductivity, mechanical properties (such as ductility and hardness) and lustre. You should also consider chemical properties such as the existence of multiple oxidation (valency) states, coloured ions, catalytic activity and paramagnetic effects. You should explain these properties as far as you can in terms of the electronic configurations of the elements and their ions, giving specific examples wherever possible. You might also like to consider how the properties of these elements relate to their uses, again giving examples.

4. Experiment Design

Experiments to determine enthalpy changes of combustion (heats of combustion) are important because they enable us to assess the efficiency of fuels.

In answering this question you are required to design an experiment to determine the enthalpy change of combustion of a fuel, "Wizzo", which is a liquid at room temperature, and is known to have a molecular formula of C_7H_6O . For comparison purposes you are provided with a sample of 1–heptanol ($C_7H_{16}O$), which is also a liquid and has an enthalpy change of combustion of -4637.6 kJ mol⁻¹.

In your response you should outline your preferred procedure, giving details of the apparatus and materials you would need for performing the experiment in a high school laboratory. It is important to specify any safety precautions that might be required. You should indicate what readings you would take and how you could use these readings to calculate a result. You should consider any problems that you might encounter when performing your experiment, and how these might give rise to errors in the final value obtained. You might also like to discuss how your experiment might be improved in order to overcome these problems. Note that your suggestions for improvements need not be restricted to equipment available in your school laboratory.

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Final Selection Examination 2006

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

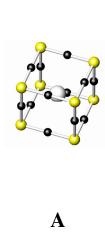
This segment has five (5) questions. While students are expected to attempt **all** questions for a complete examination in 1.5 hours, it is recognized that backgrounds will vary and students will not be eliminated from further competition because they have missed parts of the paper.

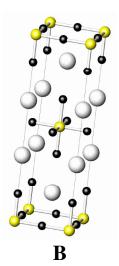
Your answers are to be written in the spaces provided on this paper. All of the paper, including this cover page, along with a photocopy of Part A of the examination, is to be returned <u>promptly</u> to your Canadian Chemistry Olympiad Coordinator.

— PLEASE READ —			PART A () Correct Answer		
	BE SURE TO COMPLETE THE INFORMA' THE BOTTOM OF THIS PAGE BEFORE B THE EXAMINATION.		$25 \times 1.6 = \dots /040$		
	2. STUDENTS ARE EXPECTED TO ATTEMP PART A AND PART C. CREDITABLE WO		PART C		
	NUMBER OF THE QUESTIONS MAY BE S AN INVITATION TO THE NEXT LEVEL O	SUFFICIENT TO EARN	1/012		
	PROCESS. 3. IN QUESTIONS WHICH REQUIRE NUME	RICAL CALCULATIONS	2/012		
	BE SURE TO SHOW YOUR REASONING		3/012		
	4. ONLY NON-PROGRAMMABLE CALCUL ON THIS EXAMINATION.	ATORS MAY BE USED	4/012		
	5. NOTE THAT A PERIODIC TABLE AND A PHYSICAL CONSTANTS WHICH MAY BI		5/012		
	FOUND ON THE DATA SHEET PROVIDE EXAMINATION.		TOTAL/100		
	Name	School			
	(Print Clearly)	Drovingo			
	City	Province			
	Date of birth	E–Mail			
	Home Telephone () – Years at a Canadian high school Number of chemistry courses at a Québec CÉGEP				
	Male Canadian Citize	en 🗖 Landed Immi	grant Visa Student		
	Female Passp	ort valid until November	2006 □		
		Nationality of	Passport		
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(12 marks)

Superconductors are substances in which electrical resistance goes to zero below a certain temperature called "Critical Temperature", T_c . Several metals may behave as superconductors but this happens at very cold temperatures close to 0 K. However, promising salts and oxides of metals may show superconductivity at warmer temperatures. In this problem, we will study the solid state structure of two such compounds made of potassium, nickel, and fluorine ($\bf A$ and $\bf B$), which display good superconducting properties. Their respective unit cells* are shown below.





Where ionic radii are as follows (sphere models are not to scale):

is Potassium (K⁺; ionic radius = ? pm)

 \bigcirc is Nickel (Ni²⁺; ionic radius = 69.6 pm)

• is Fluoride (F⁻; ionic radius = 131 pm)

Equivalence: $1 \text{ pm} = 10^{-10} \text{ cm}$

(* Acta Crystallographica B (39, 1983-) (1993): 39, 557-561 and 49, 806-811)

a) For each compound, find (i) the total number of ions of each element per unit cell and (ii) find the empirical formula of each compound.

a)	The density of compound A is 3.98 g cm ⁻³ . Considering that both potassium and nickel ions are touching fluoride ions, calculate (in pm) the ionic radius of potassium.			
a)	The density of compound B is 3.35 g cm ⁻³ . Considering that its unit cell is square at each end, and that the edge length of this square is 401.30 pm long, calculate (in pm) the length of the long edge of this unit cell.			

2A (G.	ENERAL): Lewis structures, VSEPR, polar bonds, polar molecules (6 marks)
a)	Write the Lewis structure of PF ₂ Br ₃ . Show all lone pairs of electrons.
b)	Draw a 3D representation for each of the geometrical isomers of PF_2Br_3 .
c)	In Part b), underline the NON-POLAR structure and circle the MOST POLAR.
2B (G	ENERAL): Nuclear chemistry (6 MARKS)
a)	Isotopes of 131 I decay by one β ⁻ emission. Write an equation for this process.
b)	Isotopes of $^{26}\mbox{Al}$ can decay by one β^+ emission or by one electron capture. Write an equation for each process.
c)	The skin of a mummified animal contains 7.50% of its original quantity of ¹⁴ C. If the half-life of ¹⁴ C is 5730 years, how long ago did this animal die?

For the following reaction at 25°C and atmospheric pressure and assuming ideal behaviour for the gases and the accompanying thermodynamic values, evaluate the state functions indicated:

$$2~C_6H_6~(1) + 15~O_2(g) \rightarrow 12~CO_2(g) + 6~H_2O(g)$$

(Note: 1 J = 1 kPa L and 1 atm = 101.3 kPa)

Thermodynamic data at 25°C for:	ΔH° (kJ/mol)	$S^{\circ}(J K^{-1} \text{ mol}^{-1})$
$CO_2(g)$	-393.5	213.7
$H_2O(g)$	-241.8	188.8
$C_6H_6(1)$	+49.0	172.8
$O_2(g)$		205.1

a) The enthalpy of reaction, ΔH .

b) The total entropy change of the universe, ΔS° universe.

c)	The free energy of reaction, ΔG .
d)	The internal energy difference of the system, ΔE .

4 (ANALYTICAL): Complexation

(12 marks)

The solubility of transition metal salts is greatly influenced by both the pH of the solution and the presence of complexation agents.

For instance, nickel(II) hydroxide has a very limited solubility in water, with a dissociation constant of $K_{sp} = 6.00 \times 10^{-16}$

$$Ni(OH)_{2(s)} \stackrel{\leftarrow}{\hookrightarrow} Ni^{2+}_{(aq)} + 2 OH_{(aq)}^{-}$$
 $K_{sp} = 6.00 \times 10^{-16}$

a) Calculate the solubility of Ni(OH)₂ in pure water. (The autoprotolytic dissociation of water may be disregarded.)

b) Calculate the solubility of Ni(OH)₂ in a 0.0010 M sodium hydroxide (NaOH) solution.

Nickel(II) hydroxide is dissolved in a solution made up by dissolving 16.05~g of ammonium chloride (NH₄Cl) and 8.68~g of sodium hydroxide (NaOH) in 800~mL of pure water.

Calculate the pH of the resulting buffer solution knowing that the K_b of the ammonia is 1.75 x 10⁻⁵.

$$NH_{3 (aq)} + H_2O \leftrightarrows NH_{3 (aq)}^+ + OH_{(aq)}^-$$

$$K_{\rm b} = 1.75 \times 10^{-5}$$

d) Calculate the solubility of $Ni(OH)_2$ in the buffer solution. (The complexation of nickel(II) by ammonia may be disregarded.)

Interestingly, nickel(II) hydroxide is also slightly soluble under highly basic conditions due to its ability to complex with the hydroxide ion to form the soluble trihydroxonickel(II)ate anion Ni(OH)_{3 (aq)}, according to the complexation equilibria below.

$$Ni^{2+}_{(aq)} + OH^{-}_{(aq)} \hookrightarrow Ni(OH)^{+}_{(aq)}$$
 $K_1 = 1.26 \times 10^4$

$$Ni(OH)^{+}_{(aq)} + OH^{-}_{(aq)} - Ni(OH)_{2 (aq)}$$
 $K_2 = 7.94 \times 10^4$

$$Ni(OH)_{2 \text{ (aq)}} + OH^{-}_{\text{(aq)}} \hookrightarrow Ni(OH)_{3 \text{ (aq)}}$$
 $K_3 = 1.00 \times 10^3$

e) Calculate the solubility of Ni(OH)₂ in a aqueous solution containing 15 mol/L of sodium hydroxide (NaOH). (It may be assumed that Ni(OH)_{3 (aq)} is the only significant nickel species in solution.)

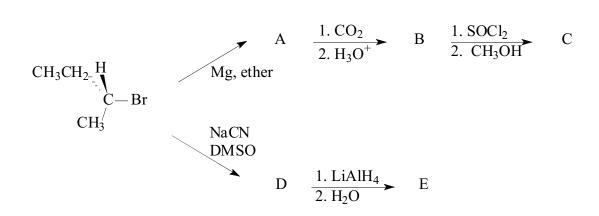
a) Draw two different important resonance structures for the following cation. Do not draw the resonance hybrid.

- H H CH₃
- 1st resonance structure
- 2nd resonance structure
- b) Circle the most important resonance contributor of the three forms above.
- c) Draw the **monomer(s)** that could be used to prepare the following polymer:

Monomer(s)			

d) Complete the structure shown for (2R, 3S)-3-amino-2-methyl-1-butanol:

e) Give the structure of A, B, C, D and E in the following synthetic pathway. Make sure to indicate clearly the stereochemistry of each product.



Structure of A:	Structure of B:	Structure of C:
Structure of D:	Structure of E:	

End of the Examination