NATIONAL HIGH SCHOOL CHEMISTRY EXAMINATION 2000
PART A – MULTIPLE CHOICE QUESTIONS (60 minutes)

1. When the unstable nuclide $^{227}_{89}Ac$ undergoes β decay, the resulting nuclide is:
   A. $^{223}_{87}Fr$ B. $^{227}_{89}Ac$ C. $^{227}_{88}Ra$ D. $^{227}_{90}Th$ E. $^{231}_{91}Pa$

2. A sample of H_2 (2.0 g) was burnt in Cl_2 (75.0 g) containing a naturally occurring mixture of isotopes. The resulting gas mixture was analyzed by mass spectrometry. The biggest peak was found at which of the following mass numbers?
   A. 36 B. 38 C. 70 D. 72 E. 74

3. Which of the following species has the greatest number of parallel spin electrons in the ground state?
   A. Cr B. Mn C. Fe^{3+} D. Co^{2+} E. Cu^{+}

4. Which of the following species contains an element in an oxidation state that is not a whole number?
   A. VO_4^{3-} B. Mn_2O_3 C. $S_4O_6^{2-}$ D. Cl_2O_7 E. $Cr_2O_7^{2-}$

5. A certain substance contains 54.50% carbon and 9.09% hydrogen by mass. It molecular formula could be:
   A. CH_2 B. C_2H_4 C. C_2H_5OH D. C_3H_7CHO E.$C_3H_7CO_2H$

6. Which one of the following species has the largest radius?
   A. Cl^- B. Ar C. K D. Ca E. Cu^{+}

7. Which of the following molecules has the smallest bond angle between its atoms?
   A. H_2O B. NH_3 C. SO_3 D. CH_4 E. XeF_4

8. The following sequence of reactions may be used to extract zinc from its sulfide ore:

   $$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

   $$ZnO + C \rightarrow Zn + CO$$

   How many tonnes of zinc can be obtained from 20 tonnes of zinc sulphide, assuming that the yield is 75%?
   A. 5 B. 10 C. 12 D. 15 E. 20

9. Which one of the following substances in their standard state are held together by covalent bonds ONLY?¤
   A. C B. AgBr C. SiO_2 D. NaOH E. $C_6H_{12}O_6$

10. Which one of the following substances has the highest boiling point?
    A. CH_3COCH_3 B. $CH_3CO_2CH_3$ C. $CH_3(CH_2)_2OH$
    D. $CH_3(CH_2)_2CH_3$ E. $CH_3CHOHCH_3$

11. A solution of iodine was prepared by dissolving 12.70g of I2 and 20g of KI in water, and making the volume up to 1 L. A 10.00 mL aliquot of this solution was titrated with standard 0.0500 M sodium thiosulphate solution, according to the following equation;

$$I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI$$

The volume of sodium thiosulphate used was 18.34mL. The molarity of the I_2 solution in mol/L was therefore:

A. 0.04585 B. 0.05004 C. 0.05453 D. 0.1001 E. 0.1205

12. Which one of the following compounds gives the highest pH when dissolved in water?

A. CH_3NH_2 B. CH_3CO_2H C. CH_3CONH_2

D. $CH_3CO_2NH_4$ E. $CH_3NH_2CO_2H$

13. A concentrated aqueous solution of H_2SO_4 is 86% by mass and has a density of 1.78 g/mL. 50 mL of this solution is diluted to 1 L with water. What is the H+ ion concentration of the dilute solution in mol/L? (All measurements are made at 25°C.)

A. 0.15 B. 0.51 C. 0.78 D. 1.01 E. 1.56

14. A container of 250 mL capacity contains 0.374 g of a particular gas at a temperature of 22.5°C and pressure of 1.006 bar. The gas could be:

A. H_2 B. He C. HCl D. H_2S E. CH_4

15. One Spring day the atmospheric temperature and pressure are 15.0°C and 101.23 kPa respectively, and the air contains 2% by volume of water vapour. The next day the temperature is still 15.0°C, but the pressure has dropped to 100.47 kPa. Given that the average relative molecular weight of the gases in dry air is 28.94, the water vapour content of the air is now:

A. 0% B. 1% C. 3% D. 4% E. 5%

16. All of the following reactions occur in the Earth's stratosphere. Which one protects us most from U-V radiation?

A. $O_2 \rightarrow O + O$ B. $O_3 \rightarrow O_2 + O$ C. $O + O \rightarrow O_2$

D. $O + O_2 \rightarrow O_3$ E. $O + O_3 \rightarrow 2O_2$

17. Which of the following combustion reactions would give the maximum energy output per unit mass of **fuel plus oxidant** when used to propel a rocket?

A. $C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H = -393.5$ kJ/mol

B. $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$ $\Delta H = -285.8$ kJ/mol

C. $\frac{1}{2}H_2(g) + \frac{1}{2}F_2(g) \rightarrow HF(g)$ $\Delta H = -271.1$ kJ/mol

D. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$ $\Delta H = -890.3$ kJ/mol

E. $C_2H_5OH(g) + 3O_2(g) \rightarrow 2CO(g) + 3H_2O(g)$ $\Delta H = -1367.3$ kJ/mol

18. Hydrogen is obtained industrially by the reaction of natural gas (methane) with steam in a continuous flow system. The equation for the reaction is:

$$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g) \qquad \Delta H = +206.1 \text{ kJ/mol}$$

Which of the following would NOT increase the yield of hydrogen?

A. Increasing the pressure
B. Increasing the temperature
C. Removing the hydrogen as it is produced
D. Increasing the proportion of methane in the mixture
E. Increasing the proportion of water vapour in the mixture

19. What is the equilibrium law expression in terms of partial pressure for the following reaction?

$$C(s) + 2H_2O(g) \rightarrow CO_2(g) + 2H_2(g) \qquad \Delta H = +90.0 \text{ kJ/mol}$$

A. $\dfrac{(p_{CO_2})^{\frac{1}{2}} \bullet p_{H_2}}{p_{H_2O}}$ B.. $\dfrac{p_{CO_2} \bullet (p_{H_2})^2}{(p_{H_2O})^2}$ C. $\dfrac{p_{CO_2} \bullet (p_{H_2})^2}{p_C \bullet (p_{H_2O})^2}$

D. $\dfrac{p_{CO_2} \bullet (2p_{H_2})^2}{p_C \bullet (2p_{H_2O})^2}$ E. $\dfrac{p_C \bullet (p_{H_2O})^2}{p_{CO_2} \bullet (p_{H_2})^2}$

20. Ethyl ethanoate (0.20 mol) and water (0.6 mol) are mixed and left for several days to equilibrate in the presence of an acid catalyst. At the end of this time 0.11 mol of ethanoic acid is found to be present in the mixture. The equation for the reaction is:

$$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$$

The equilibrium constant, K_c for the reaction is therefore:

A. 0.10 B. 0.27 C. 3.6 D. 4.0 E. 9.9

21. A group of students left a mixture of calcium hydroxide and water to equilibrate at 20°C. They titrated the resulting saturated solution and found that it contained 0.040 mol/L of OH^- ions. The solubility product constant, $K_{sp}\{Ca(OH)_2\}$ at this temperature is therefore:

A. 8.0×10^{-6} B. 1.6×10^{-5} C. 3.2×10^{-5} D. 6.4×10^{-5} E. 1.3×10^{-4}

22. Hydrogen carbonate ions act as a buffer in blood. When acid comes in contact with hydrogen carbonate ions, which of the following species is formed as the **conjugate acid**?

A. H_2O B. H_3O^+ C. CO_3^{2-} D. HCO_3^- E. H_2CO_3

23. The base dissociation constant, K_b, of NH_3 is 1.8×10^{-5} at 25°C. The pH of a 0.1M solution of NH_3 at this temperature is therefore:

A. 2.9 B. 4.8 C. 9.3 D. 11.1 E. 11.6

24. Two students performed a series of experiments to investigate the rate of the reaction between magnesium and hydrochloric acid at room temperature. In each experiment they used the same mass of magnesium but with different concentrations of acid (the acid always being in excess). They measured the time taken for all the magnesium to react. Here are their results:

Expt #	Concentration of HCl, mol/L	Time taken for all the Mg to react, s
1	2.00	25
2	1.50	30
3	1.00	100
4	0.50	400

The rate expression for this reaction is:

A. $k[H^+]$ B. $k[H^+]^2$ C. k[Mg][HCl] D. $k[H^+]^{-1}$ E. $k[H^+]^{-2}$

25. All of the following metals are used as protective coatings for iron and steel. Which one is most likely to **promote** the rusting process? ($E°(Fe^{2+}/Fe) = –0.44$ V)¤

A. Cadmium ($E°(Cd^{2+}/Cd) = –0.40$ V)
B. Chromium ($E°(Cr^{3+}/Cr) = –0.74$ V)
C. Nickel ($E°(Ni^{2+}/Ni) = –0.25$ V)
D. Tin ($E°(Sn^{2+}/Sn) = –0.14$ V)
E. Zinc ($E°(Zn^{2+}/Zn) = –0.76$ V)

THE CHEMICAL INSTITUTE OF CANADA
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"Chemists, engineers and technologists working together."
"Les chimistes, les ingénieurs et les technologistes travaillant ensemble."

NATIONAL HIGH SCHOOL CHEMISTRY EXAMINATION 2000

PART B – ESSAY QUESTIONS (90 minutes)

Answer **TWO** questions only in the form of scientific essays, including any appropriate equations, formulae and diagrams. Each question is of equal value. The judging of the essays will be based on both factual accuracy and presentation. A clear, concise and well-organized essay will be rated more highly than a long rambling one that contains the same information.

1. The Periodic Table and Periodicity

In this essay you might like to consider: (a) the history of the classification of the elements and the development of the periodic table, especially the contribution of Mendeleev, (b) the periodicity of physical properties on the macro scale, such as the "atomic volume", density, melting and boiling points, and structure and bonding of the elements, (c) the periodicity of atomic scale properties, such as atomic and ionic radii, ionisation energies and electron affinities, electronegativity, and oxidation number, and (d) the periodicity of the chemical properties of the elements and their hydrides, oxides and chlorides. Note that you are not expected to have memorized the values of the physical properties but you should discuss the trends across the periods, and the reasons for these trends.

2. Water

In this essay you might like to consider: (a) the bonding and structure of water, (b) the phase diagram of water, (c) the anomalous properties of water, and (d) its solvent properties. In each case you should relate the properties of water with its importance in nature, eg. in the water cycle and the weathering of rocks, and in living organisms and their habitats.

3. Petroleum

In this essay you might like to consider: (a) the way in which petroleum (crude oil) was formed, (b) the chemical composition of petroleum, (c) the way in which petroleum is processed industrially, (d) the uses of petroleum fractions, (e) the environmental problems of burning petroleum products and how to limit these problems, and (f) the likelihood of all the petroleum reserves being used up in the near future, and how we can replace petroleum as a raw material.

CHEMICAL INSTITUTE OF CANADA
and
CANADIAN CHEMISTRY OLYMPIAD

Final Selection Examination 2000

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, is to be returned promptly to your Canadian Chemistry Olympiad Coordinator.

— PLEASE READ —

1. BE SURE TO COMPLETE THE INFORMATION REQUESTED AT THE BOTTOM OF THIS PAGE BEFORE BEGINNING PART C OF THE EXAMINATION.
2. STUDENTS ARE EXPECTED TO ATTEMPT ALL QUESTIONS OF **PART A** AND **PART C**. CREDITABLE WORK ON A LIMITED NUMBER OF THE QUESTIONS MAY BE SUFFICIENT TO EARN AN INVITATION TO THE NEXT LEVEL OF THE SELECTION PROCESS.
3. IN QUESTIONS WHICH REQUIRE NUMERICAL CALCULATIONS, BE SURE TO SHOW YOUR REASONING AND YOUR WORK.
4. ONLY NON-PROGRAMMABLE CALCULATORS MAY BE USED ON THIS EXAMINATION.
5. NOTE THAT A PERIODIC TABLE AND A LIST OF SOME PHYSICAL CONSTANTS WHICH MAY BE USEFUL CAN BE FOUND ON THE DATA SHEET PROVIDED WITH THIS EXAMINATION.

PART A ( )
correct numbers

25 x 1.6 = ... /040

PART C

1. ..... /012
2. ..... /012
3. ..... /012
4. ..... /012
5. ..... /012

TOTAL ..... /100

NAME _____ SCHOOL _____
(Print Clearly)

CITY _____ PROVINCE _____

Date of birth: _____ Exam Supervisor _____

Home Telephone number: ( ) - _____ Years at a Canadian high school _____

Male ❒ Canadian Citizen ❒ Landed Immigrant ❒ Visa Student ❒

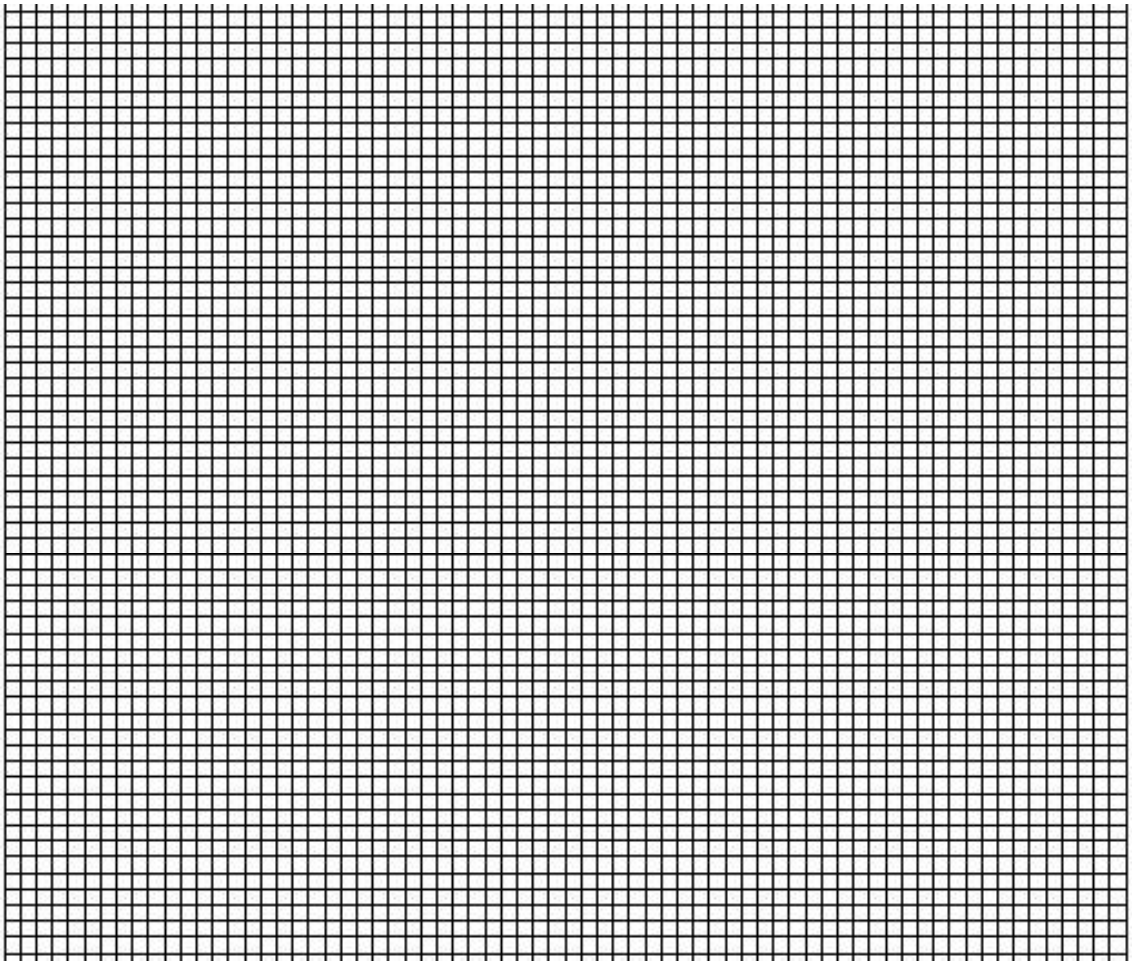
Female ❒

1. a) In 1828 Friedrich Wöhler found that the organic compound urea could be made by evaporating an aqueous solution containing the inorganic compound ammonium cyanate, thus repudiating the concept of "vitalism" which had held that organic compounds could only be formed by living systems. The rate of this reaction has now been examined in an aqueous solution containing 22.9 g of ammonium cyanate in 1.00 L of solution.

$$NH_4CNO \rightarrow CO(NH_2)_2$$

Given the following data, what is the order of the reaction and the mass of ammonium cyanate left after 200 min?

T/min	0	20	50	65	150
NH_4CNO /g	22.9	15.9	10.8	9.1	5.2



1. b) A typical urine sample contains 2.3% by mass of the base urea, $CO(NH_2)_2$. Urea is a monoprotic base with a base dissociation constant, K_b , equal to 1.5×10^{-14} mol L^{-1} at 25°C. If, at 25°C, the density of a urine sample is 1.06 g cm^{-3} and the pH of the sample is 6.35, calculate the concentration of $CO(NH_2)_2$ and of its conjugate acid $CO(NH_2)NH_3^+$ in the sample.

2. HYDROLYSIS OF UREA

Urea, $CO(NH_2)_2$, reacts with water to produce carbon dioxide and ammonia. Thermodynamic data for the possible reactants and products are given below (neglect the solubility of carbon dioxide and ammonia in liquid water).

Compound	ΔH_f^o **(kJ mol^{-1})**	S^o **(J K^{-1} mol^{-1})**
$CO(NH_2)_2$ *(s)*	-333.51	104.60
H_2O *(l)*	-285.83	69.91
H_2O *(g)*	-241.82	188.83
CO_2 *(g)*	-393.51	213.74
NH_3 *(g)*	-46.11	192.45

a) Consider the hydrolysis of urea with H_2O *(l)* (**Reaction A**) and H_2O *(g)* (**Reaction B**) respectively. Calculate ΔH^o, ΔS^o, and ΔG^o at 25°C for each reaction and specify whether or not the reaction is spontaneous.

2. b) Assuming that both ΔH^o and ΔS^o are independent of temperature, find the temperature above which Reaction A shall be spontaneous.

c) What major driving force favors both reactions in the forward direction? Justify your answer.

d) Calculate K_p at 25°C for each reaction and express these values with the proper units.

3. COMPLEX IONS

PART I: Zinc Complex Ion

Zinc hydroxide is not very soluble in water, but in basic solution, it may dissolve as the tetrahydroxozinc complex ion: $Zn(OH)_4^{2-}$.

The solubility product constant of zinc hydroxide is $K_{sp} = 2.1 \times 10^{-16}$.

The formation constant (or stability constant) of $Zn(OH)_4^{2-}$ is $K_f = 2.8 \times 10^{15}$.

a) If 150.0 mg of zinc hydroxide crystals are mixed with 250.0 mL of pure water, what mass of crystals will remain undissolved and what will be the pH of the resulting solution. Justify your answer by showing your calculations.

b) If 150.0 mg of zinc hydroxide crystals are mixed with 250.0 mL of a 0.100 mol/L NaOH solution, what mass of crystals will remain undissolved. Justify your answer by showing your calculations.

3. COMPLEX IONS

PART II: Nickel Complex Ions

Several examples of Ni(II) complex ions appear below. They all possess an octahedral three-dimensional structure.

Complex Ion A: $Ni(NH_3)_3(H_2O)_3^{2+}$
Complex Ion B: $Ni(en)_2(NH_3)_2^{2+}$ where "en" = $H_2N\text{-}CH_2\text{-}CH_2\text{-}NH_2$
Complex Ion C: $Ni(NH_3)_6^{2+}$

a) Draw the possible structural isomers of complex ions **A** and **B**. Specify if any one shows optical isomerism.

b) Complex ion **C** possess a pure octahedral geometry. Using crystal field theory, sketch the energy-level diagram for the "d" orbitals of a metal atom in a pure octahedral field. Then, fill in the d-electrons of the nickel ion using arrows to specify their spin. Label all the orbitals in the diagram with the corresponding "d" notation (*e.g.* d_{xy}).

4. Consider the half reactions shown below

Half reaction	***E*° (V)**
$Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq)$	+1.61
$Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s)$	+0.34
$Sn^{2+}(aq) + 2\ e^- \rightarrow Sn(s)$	–0.14
$Ni^{2+}(aq) + 2\ e^- \rightarrow Ni(s)$	–0.25
$Al^{3+}(aq) + 3\ e^- \rightarrow Al(s)$	–1.66

a) From the list above, identify
   i) the strongest reducing agent

   ii) the strongest oxidizing agent

   iii) which metallic ion(s) can be reduced by Sn?

b) An electrochemical cell with a potential difference of 1.59 V is prepared with aluminum and nickel electrodes in their respective ionic solutions.

   i) Calculate the standard cell potential for the spontaneous reaction.

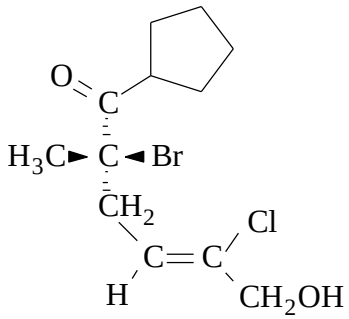
   ii) Given that the observed cell potential is 1.59 V, determine the concentration of the aluminum ion if the concentration of the nickel ion is 2.0 M.

c) A small piece of freshly cleaned aluminum metal is placed in a solution of 1.0 M copper nitrate, $Cu(NO_3)_2$, solution. After some time the blue colour of this solution decreases considerably or disappears.

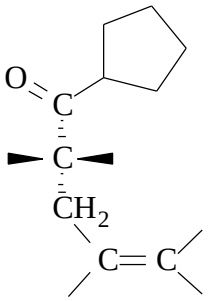
i) Describe what is happening, including any other observations that might be expected.

ii) Determine the free energy change, $\Delta G°$, for this reaction.

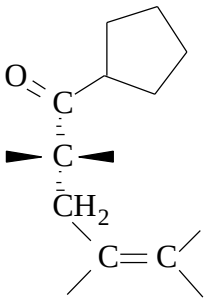
5. A) Complete the structural formulas located to the right of compound **A** in order to illustrate, respectively, a diastereoisomer of **A** and the enantiomer of **A**.



Compound **A**



Diastereoisomer of **A**



Enantiomer of **A**

Circle the most appropriate choices regarding Compound **A**:

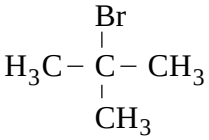
i) The stereochemistry assignments are: R S as well as E Z

ii) The number of lone pairs of electrons is: 2 4 6 8 10 12 14 16

iii) The degree of unsaturation is: 1 2 3 4 5 6 7 8

B)

i) Nuclear magnetic resonance (NMR) spectroscopy is a technique that can probe the structural differences of various hydrogen atoms in a molecule. Assuming that free rotation is occurring about all bonds and thus equivalent hydrogens are able to interconvert, indicate how many different NMR signals you would expect to see in each of the following isomeric compounds.



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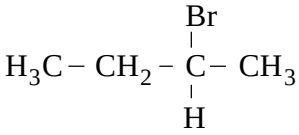

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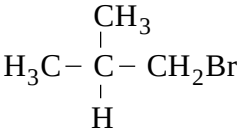

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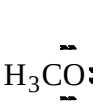
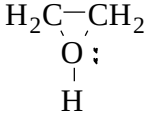
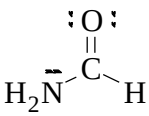
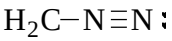
iii) Circle the structure that represents a positively charged species and underline the negatively charged species.

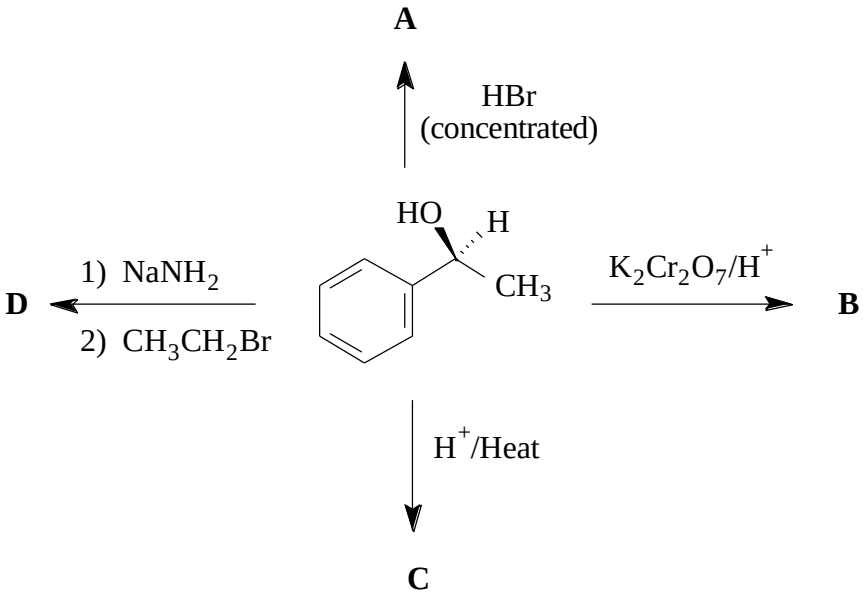








ii) Draw the structures of the major organic products necessary to complete the following reactions. Pay close attention to stereochemistry. Indicate whether the product is achiral, racemic or enantiomerically pure. In cases where a racemic mixture will be formed, draw only one of the two possible enantiomers, but indicate that the product is racemic.



(End of Part C Examination)