NATIONAL HIGH SCHOOL CHEMISTRY EXAMINATION 2001

PART A - MULTIPLE CHOICE QUESTIONS (60 minutes)

1. A solution of ethanol in water contains 20.0% by mass of ethanol ($M_r = 46.1$) and has a density of 0.96864 g mL^{-1}. A lab technician measures out a 4.80 mL aliquot of this solution. What amount (in moles) of ethanol does the aliquot contain?

A. 0.02 B. 0.020 C. 0.0201 D. 0.0202 E. 0.02017

2. In the titration of HCl (0.1 mol L^{-1}) with Na_2CO_3 (0.1 mol L^{-1}) which of the following species is the major component of the solution at the methyl orange endpoint? The pK_{In} (298 K) of methyl orange is 3.7.

A. CO_2 B. H_2O C. NaCl D. $NaHCO_3$ E. Na_2CO_3

3. A mass of 4.021 g of NaOH is dissolved and made up to 1 litre of solution with water. 10.00 mL of this solution is pipetted into a flask and titrated with 0.050 M HCl solution from a burette. A volume of 19.75 mL of acid had been used at the endpoint. This discrepant result could be due to:

A. The NaOH having absorbed CO_2 from the air after its mass was measured
B. The NaOH having absorbed H_2O from the air after its mass was measured
C. The pipette having been rinsed with water instead of NaOH
D. The flask having been rinsed with NaOH instead of water
E The burette having been rinsed with water instead of HCl

4. A 20.0 g sample of an organic compound was found to give 27.50 g of carbon dioxide on combustion. The compound could be:

A. CH_3OH B. CH_3CHO C. CH_3OCH_3 D. CH_3CO_2H E. CH_3COCH_3

5. Which of the following formulae can represent a pair of geometric (*cis-trans*) isomers?

A. Cl_2CCH_2 B. $HClCCH_2$ C. $HClCCHCl$ D. HCl_2CCH_2Cl E. HCl_2CCHCl_2

6. Each of the following pairs of compounds can be reacted together to form a polymer. Which pair gives Nylon?

A. $H_2N\text{-}CO\text{-}NH_2$ and CH_2O
B. $CH_2\text{=}CH\text{-}CN$ and $CH_2\text{=}CH\text{-}CH\text{=}CH_2$
C. $CH_2\text{=}CH\text{-}CN$ and $CH_2\text{=}CH\text{-}O\text{-}CO\text{-}CH_3$
D. $H_2N\text{-}(CH_2)_6\text{-}NH_2$ and $HO_2C\text{-}(CH_2)_4\text{-}COOH$
E. $CH_3\text{-}O\text{-}CO\text{-}C_6H_4\text{-}CO\text{-}O\text{-}CH_3$ and $HO\text{-}CH_2\text{-}CH_2\text{-}OH$

7. The following numbers represent the first four ionization energies of an element in kJ mol^{-1}: 578; 1817; 2745; 11,578. Which of the following elements could it be?

A. Sodium B. Magnesium C. Aluminium D. Silicon E. Phosphorus

8. Which one of the following species contains a partially filled d orbital?

A. Ag^+ B. Cu^{2+} C. Pb^{2+} D. Sc^{3+} E. Zn^{2+}

9. Which one of the following pairs of elements can combine to give the strongest bond?

A. C, O B. F, F C. Na, Cl D. Na, K E. O, O

10. Hydrogen can form a number of different kinds of bonds. Which of the following are **never** found in pure substances?

A. Covalent bonds B. Coordinate bonds C. Hydrogen bonds
D. Ionic bonds involving H^+ ions E. Ionic bonds involving H^- ions

11. Which one of the following substances has the lowest boiling point at one atmosphere pressure?

A. C_6H_6 B. $(CH_2)_6$ C. $C(CH_3)_4$ D. $CH_3(CH_2)_3CH_3$ E. $CH_3CH_2CH(CH_3)_2$

12. Which one of the following molecules has the greatest dipole moment?
(Electronegativity values for the elements concerned are: B = 2.0, Cl = 3.0, F = 4.0, H = 2.1, N = 3.0, O = 3.5, P = 2.1, S = 2.5)

A. BF_3 B. NH_3 C. PH_3 D. PCl_3 E. SO_3

13. Which one of the following molecular formulae could **NOT** represent a compound containing a hydroxyl (-OH) group?

A. H_2O B. CH_4O C. CH_2O D. H_2SO_4 E. C_6H_6O

14. Which one of the following compounds gives the lowest pH when dissolved in water?

A. NH_3 B. N_2O C. NO D. NO_2 E. N_2O_3

15. The pH of an aqueous solution is 6.0 at 50ºC. What is its hydroxide ion concentration in mol L^{-1}?
($K_w = 5.5 \times 10^{-14}$ at this temperature.)

A. 1.0×10^{-6} B. 2.3×10^{-7} C. 1.0×10^{-8} D. 5.5×10^{-8} E. 7.8×10^{-8}

16. What is the conjugate acid of glycine (aminoethanoic acid)?

A. H_3O^+ B. $H_2N\text{-}CH_2\text{-}COOH$ C. $H_3N^+\text{-}CH_2\text{-}COOH$
D. $H_2N\text{-}CH_2\text{-}CO_2^-$ E. $H_3N^+\text{-}CH_2\text{-}CO_2^-$

17. What is the **approximate** dissolved phosphate ion concentration in mol L^{-1} of a slurry of calcium phosphate that is applied to a field as fertilizer, given K_{SP} ($Ca_3(PO_4)_2$) = 1.0×10^{-26} at 25ºC. (Assume that the slurry is at 25ºC and is in equilibrium.)

A. 2.5×10^{-6} B. 3.5×10^{-6} C. 4.0×10^{-6} D. 5.0×10^{-6} E. 7.0×10^{-6}

18. Consider the following equilibrium reaction:

$$CO(g) + 2H_2(g) \Leftrightarrow CH_3OH(l) \quad ; \quad \Delta H = -615.5 \text{ kJ mol}^{-1}$$

Which of the following changes in conditions would **DECREASE** the amount of methanol produced:

A. Increasing the proportion of carbon monoxide
B. Increasing the proportion of hydrogen
C. Increasing the pressure
D. Increasing the temperature
E. Removing the methanol as it is produced

19. Which one of the following pairs of reactants will give a neutral solution when mixed together in equimolar amounts?

A. HCl (aq) + $Pb(NO_3)_2$ (aq) B. H_2SO_4 (aq) + $NaOH$ (aq) C. H_2SO_4 (aq) + K_2O (s)
D. CH_3COOH (aq) + $NaOH$ (aq) E. CH_3COOH (l) + CH_3OH (l)

20. The following reaction takes place in a lime kiln:

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

Given that ΔH_f ($CaCO_3$(s)) = -1207 kJ mol^{-1}; ΔH_f (CaO(s)) = -635.1 kJ mol^{-1}; and ΔH_f (CO_2(g)) = -393.5 kJ mol^{-1}, the energy change involved in producing one tonne (1000 kg) of quicklime (CaO) is:

A. 1.78×10^3 kJ required B. 1.78×10^6 kJ required C. 3.18×10^6 kJ required
D. 1.00×10^6 kJ produced E. 3.18×10^6 kJ produced

21. What is the entropy change (in J mol^{-1} K^{-1}) for the evaporation of water at standard ambient temperature and pressure? Given:

$\Delta H^\circ_{f,298}(H_2O(l))$ = -285.8 kJ mol^{-1} $\Delta G^\circ_{f,298}(H_2O(l))$ = -237.2 kJ mol^{-1}
$\Delta H^\circ_{f,298}(H_2O(g))$ = -241.8 kJ mol^{-1} $\Delta G^\circ_{f,298}(H_2O(g))$ = -228.6 kJ mol^{-1}

A. -120 B. -0.12 C. 0.00 D. +0.12 E. +120

22. Chlorofluorocarbons were widely used as refrigerants until it was discovered that they were destroying the ozone layer. One of these, Freon 12, undergoes a series of reactions as shown below (not in sequence). Which of these is the chain initiation reaction?

A. $O\bullet + O_3 \rightarrow 2O_2$

B. $ClO\bullet + O\bullet \rightarrow Cl\bullet + O_2$

C. $Cl\bullet + O_3 \rightarrow ClO\bullet + O_2$

D. $CF_2Cl_2 \rightarrow \bullet CF_2Cl + Cl\bullet$

E. $\bullet CF_2Cl + \bullet CF_2Cl \rightarrow C_2F_4Cl_2$

23. Which one of the following reactions is **NOT** redox?

A. $Br_2 + H_2O \Leftrightarrow HBr + HBrO$

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

C. $Na_3AsO_3 + H_2O_2 \rightarrow H_2O + Na_3AsO_4$

D. $I_2 + 6NaOH \Leftrightarrow NaIO_3 + 5NaI + 3H_2O$

E. $2K_2CrO_4 + H_2SO_4 \Leftrightarrow K_2Cr_2O_7 + K_2SO_4 + H_2O$

24. The reaction between mercury(II) chloride and ethanedioate (oxalate) ions may be represented by the following equation:

$$2HgCl_2(aq) + C_2O_4^{2-}(aq) \rightarrow 2Cl^-(aq) + 2CO_2(g) + Hg_2Cl_2(s)$$

If the rate of reaction at a particular stage of the reaction is 5.00×10^{-5} mol L^{-1} min^{-1} for $HgCl_2$, which is the correct rate of reaction at that time in terms of another component of the mixture?

A. 5.00×10^{-5} mol L^{-1} min^{-1} for $C_2O_4^{2-}$
B. 5.00×10^{-5} mol L^{-1} min^{-1} for Cl^-
C. 1.14×10^{-6} g min^{-1} for CO_2
D. 2.40×10^{-3} L min^{-1} for CO_2
E. 1.05×10^{-7} g L^{-1} for Hg_2Cl_2

25. Two students set up a simple cell at room temperature and pressure with zinc as the anode and nickel as the cathode. The relevant standard reduction potentials are:

$$Zn^{2+}(aq) + 2e^- \Leftrightarrow Zn(s)\ ; \quad E^o = -0.76V$$
$$Ni^{2+}(aq) + 2e^- \Leftrightarrow Ni(s)\ ; \quad E^o = -0.25V$$

If the concentration of the solution in the nickel half-cell is increased to 2.0 mol L^{-1} with respect to Ni^{2+} ions and the concentration of the solution in the zinc half-cell is kept at 1.0 mol L^{-1} with respect to Zn^{2+} ions, then the overall cell potential will be:

A. more positive than + 0.51 V B. equal to + 0.51 V C. between + 0.51 V and - 0.51 V
D. equal to - 0.51 V E. more negative than - 0.51 V

THIS IS THE END OF PART A OF THE EXAM

THE CHEMICAL INSTITUTE OF CANADA
L'INSTITUT DE CHIMIE DU CANADA

Chemists, engineers and technologists working together
Les chimistes, les ingénieurs et les technologistes travaillant ensemble

NATIONAL HIGH SCHOOL CHEMISTRY EXAMINATION 2001

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. Air Pollution

In this essay you should consider different sources of atmospheric pollution, the reactions taking place in various parts of the Earth's atmosphere, and the effects of pollution on plants, animals, and buildings. You could also discuss how chemists and chemical engineers can help to improve air quality.

2. Catalysts

In this essay consider how catalysts can be used to alter the rate of chemical reactions, giving examples of catalysts that are used in the laboratory, on an industrial scale, and in biological systems. You could also discuss how a catalyst alters the energy profile of a reaction, and how it changes the reaction mechanism.

3. Polymers

In this essay consider some examples of polymers and the reactions that are used to produce them, and discuss how polymers can be designed to have specific properties that enable them to be used for different purposes. You could also compare some man-made polymers with similar compounds that occur in nature.

CHEMICAL INSTITUTE OF CANADA
and
CANADIAN CHEMISTRY OLYMPIAD

Final Selection Examination 2001

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 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 2.0 = .../050

PART C

1. ..../015
2. ..../015
3. ..../015
4. ..../015
5. ..../015

TOTAL............../125

FINAL ..../100

NAME ______________________________ SCHOOL ____________________________
(Print Clearly)

CITY ____________________________ PROVINCE __________________________

Date of birth: ________________ Exam Supervisor ______________________

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

Male ❐

Female ❐

Canadian Citizen ❐ Landed Immigrant ❐ Visa Student ❐

1. (15 marks)

1 a) A compound of iron and chlorine was readily dissolved in water. An excess of silver nitrate was added to precipitate the chloride ion as silver chloride. If a 0.270 g sample of the compound gave 0.610 g of AgCl, what is the percent (%) chlorine in the compound of iron and chlorine? What is the most probable identity of the compound of iron and chlorine?

1 b) A silver wire and a standard hydrogen electrode (SHE) were placed in a saturated solution of silver oxalate, $Ag_2C_2O_4$, The potential difference between the silver wire and the SHE was measured as 0.589 V. Calculate the solubility product constant, K_{sp}, for silver oxalate.

Given: $2H^+(aq, 1M) + 2\,e^- \rightarrow H_2(g, 1\ atm)$ $\quad \mathcal{E}° = 0.00$ V

$Ag^+(aq) + e^- \rightarrow Ag(s)$ $\quad \mathcal{E}° = +0.80$ V

2. (15 marks)

2 a) Depleted uranium is primarily $^{238}_{92}U$, the remaining material after natural uranium has been refined to remove most of the $^{235}_{92}U$. The present controversy about its use in armor-penetrating shells relates to both its chemical and radioactive properties. Radioactive decay proceeds through a number of individual steps to eventually produce $^{206}_{82}Pb$

A few of the initial reactions are illustrated below and you are expected to fill in the (7) missing species and numbers in the blanks indicated to correctly complete each reaction.

$$^{238}_{92}U \longrightarrow {}^{\_\_}_{\_\_}\alpha + {}^{234}_{\_\_}Th \longrightarrow {}^{0}_{-1}\beta + {}^{\_\_}_{\_\_}Pa \longrightarrow {}^{0}_{-1}\beta + {}^{234}_{\_\_}\_\_$$

2 b) In the February 8, 2001, Letters to Nature, measurement of stellar age from uranium decay was reported by R. CAYREL, et al. They claim their cosmochronometer gives the most direct age determination of the Galaxy.

Radioactive dating of meteoritic material and stars relies on comparing the present abundance ratios of radioactive and stable nuclear species to the theoretically predicted ratios of their production. ^{238}U (half-life 4.5 Gyr) is in principle an age indicator, but even its strongest spectral line, from singly-ionized uranium at a wavelength of 385.957 nm, had previously not been detected in stars. They report a measurement in the very metal-poor star CS31082-001, a star that is strongly overabundant in its heavy elements. If their derived uranium abundance was reported as 0.146, (i.e. the ratio of the radioactive U to that theoretically predicted originally), what is their expected age of the Galaxy?

2 c) The following initial rate data were obtained at 60°C for a reaction between dibromoethane and potassium iodide in methanol. (In methanol, potassium iodide exists mainly as KI molecules.)

$$C_2H_4Br_2 + 3\ KI \rightarrow C_2H_4 + 2\ KBr + KI_3$$

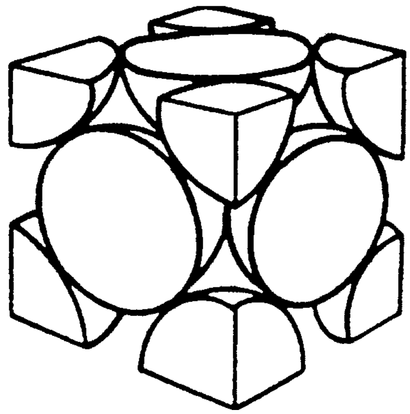
Experiment	Initial conc. $C_2H_4Br_2$ mol L^{-1}	Initial conc. KI mol L^{-1}	Initial rate mol L^{-1} s^{-1}
1	0.50	1.80	0.269
2	0.50	7.20	1.08
3	1.50	1.80	0.807

From these data, what is the rate expression for the reaction? Show your reasoning.

2 d) The water flea Daphnia seems to have a heart that is capable of a limited number of heartbeats and then it dies. These fleas live twice as long at 15°C as at 25°C. What is the average activation energy for the reaction that controls the rate of the heartbeat of this water flea?

3. (15 marks)

3 a) Spinel structures are found in mineral compounds having the general formula AB_2O_4. These structures can be described as face-centered cubic (fcc) lattices of oxide ions containing A and B metal cations.



Face-centered cubic crystal structure

i) Assume that the oxidation states of A and B metals range from +1 to +6 (no fractional values). What possible AB_2 metal combinations would fit the general AB_2O_4 formula for spinel compounds?

ii) Assume that A and B are both cations from Row 3 (3^{rd} Period).

Which cations of Row 3 allow an acceptable AB_2 metal combination?

Should these cations be of approximately the same size? If not, which cation should be the smallest one and why?

iii) Magnetite, Fe_3O_4, possesses what is called an "inverse spinel" structure still based on fcc lattice of oxide ions. Considering the different types of interstices (tetrahedral and octahedral holes) in such a fcc lattice, calculate the ionic radii of the Fe ions, given that the density of magnetite is 5.18 g cm^{-3} and that the ionic radius of oxide ions is 140 pm (assume that oxide ions are closely packed and that Fe ions are fully occupying the hole in which they are located).

3 b) Let us compare the crystalline structures of sodium iodide and cadmium iodide. Both structures are based on an fcc packing of iodide ions and both cations, Na^+ and Cd^{2+}, are approximately of the same size. Sodium iodide is a brittle solid while cadmium iodide can be used as a graphite-like lubricant. Give an explanation to account for the two very different behaviours of sodium iodide and cadmium iodide.

4. (15 marks)

4 a) Chromium (VI) species are powerful oxidizers, which can oxidize primary alcohols to carboxylic acids. The spectrophotometric determination of potassium dichromate ($K_2Cr_2O_7$), which shows an intense orange colour in solution, was for a long time the basis for the testing of alcohol (ethanol CH_3CH_2OH) in the breath / exhaled air of suspected drunk drivers.

i) Write the balanced equation representing the oxidation of ethanol into acetic acid (CH_3COOH) by an acidified solution of potassium dichromate.

ii) A driver is arrested and asked to pass a "Breathalyser" test. A sample consisting of 56.5 mL of exhaled air is then bubbled into a spectrophotometric cell containing 3.00 mL of a 0.025% (w/v) potassium dichromate solution. The transmittance of the solution, measured at the absorption wavelength of dichromate ion (450 nm), was 41.5% initially, and 43.4% after bubbling the sample though the reaction cell. It is known that the alcohol concentration in the blood stream is 2300 times higher than in the exhaled air, and that the legal limit is 80 mg of alcohol per 100 mL of blood. Determine the concentration of alcohol in the blood and state whether or not the driver should be charged with drunk driving.

4 b) A sample of 0.3657 g of a powder containing only barium nitrate ($Ba(NO_3)_2$) and calcium nitrate ($Ca(NO_3)_2$) are dissolved in about 50 mL of water. Ammonia is added to the solution to raise its pH, then an excess of sodium oxalate ($Na_2C_2O_4$) is added to precipitate the metals. The precipitate is then filtered, washed and transferred to a beaker containing 50.00 mL of water. The solution is acidified to solubilise the precipitate before being titrated with a solution of potassium permanganate ($KMnO_4$) 0.0500 mol L^{-1}. It was found that 13.94 mL of the permanganate solution are required to reach the end point, which is characterised by the pink coloration due to a slight excess of $KMnO_4$.

Find the composition of the initial mixture.

K_{sp}: $BaC_2O_4 = 1.50 \times 10^{-8}$
$CaC_2O_4 = 2.34 \times 10^{-9}$

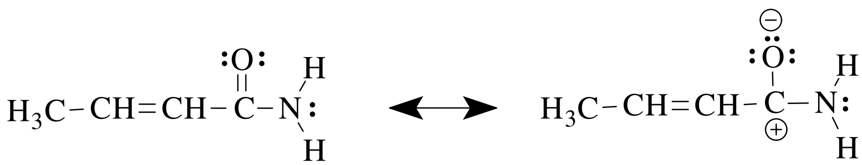
Half-Reactions:

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ $\mathcal{E}° = +1.51$ V

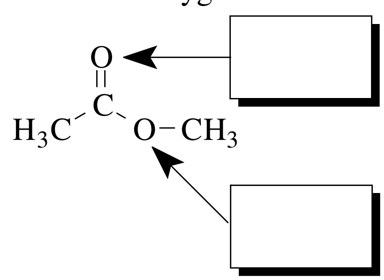
$2CO_2 + 2H^+ + 2e^- \rightarrow H_2C_2O_4$ $\mathcal{E}° = -0.49$ V

5. (15 marks)

5 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 two additional resonance structures of the amide shown below clearly indicating the positions of any lone pairs of electrons and formal charges that may be present.

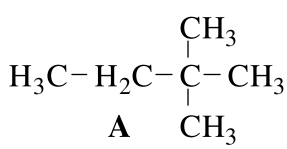


5 b) Write, in the boxes, the hybridizations of the oxygen atoms indicated in the ester below.



5 c) In the ester shown above in part b), _______ is the maximum number of atoms that simultaneously could lie in the same plane.

5 d) Knowledge of symmetry aids in predicting the number of products of a reaction and also in interpreting the spectroscopic features of a molecule. Assume that free rotation is occurring about all bonds in the molecule **A** below, and thus that equivalent atoms cannot be distinguished.



A

i) How many chemically different types of carbon atoms exist in **A**? _______

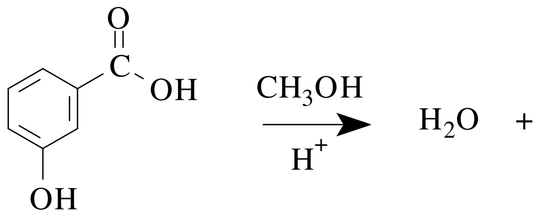
ii) How many chemically different types of hydrogen atoms exist in **A**? _______

iii) How many different dibrominated positional (also called constitutional) isomers of **A** could be formed in the reaction of **A** with bromine? _______

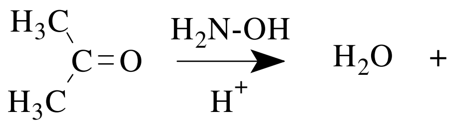
iv) Two of the possible dibrominated positional isomers of **A** can be chiral and thus exist in the form of enantiomers (compounds not superimposable on their mirror images). Draw these two different enantiomers.

5 e) Clearly show the structure of the one major organic product of each of the following reactions that all involve the loss of water (i.e. dehydration).

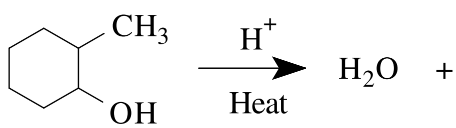
i)



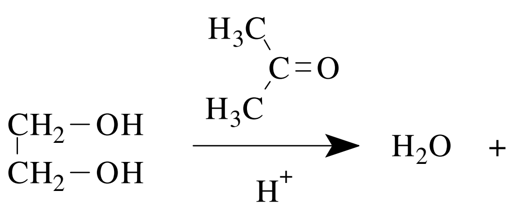
ii)



iii)



iv)



v)

$$HO_2C-CH_2CH_2-CO_2H \xrightarrow{\text{Heat}} H_2O \quad +$$

END OF EXAMINATION