NATIONAL HIGH SCHOOL CHEMISTRY EXAMINATION 2002
PART A - MULTIPLE CHOICE QUESTIONS (60 minutes)

1. Someone has accidentally spilled battery acid on his or her skin. The first aid treatment for this is to apply plenty of:
   A. Salt B. Water C. Vinegar D. Baking soda E. Washing soda

2. Which one of the following substances, when dissolved in water, gives a solution with the lowest pH?
   A. Li_2O B. Na_2O_2 C. KO_2 D. H_2S E. HI

3. What is the oxidation state of vanadium in the compound NH_4VO_3 (commonly known as ammonium metavanadate)?
   A. –1 B. +1 C. +3 D. +5 E. +6

4. A technician dissolves 62.425 g of $CuSO_4 \cdot 5H_2O$ (M_f = 249.7) in water and dilutes the solution to 250.00 mL in a standard flask. He then measures out a 25.00 mL aliquot of the solution. What amount (in moles) of $CuSO_4$ does this aliquot contain?
   A. 0.00100 B. 0.01600 C. 0.02500 D. 0.2500 E. 1.000

5. Which of the following statements is correct?
   A. In an electrolytic cell oxidation takes place at a positive anode.
   B. In an electrolytic cell oxidation takes place at a negative anode.
   C. In an electrochemical cell reduction takes place at a positive anode.
   D. In an electrolytic cell oxidation takes place at a positive anode.
   E. In an electrochemical cell reduction takes place at a negative anode.

6. Which one of the following molecular formulae represents an alcohol?
   A. CH_3CHO B. C_2H_5COOH C. $(CH_3)_2O$ D. $(CH_3)_2CO$ E. $(CH_3)_3COH$

7. Monocalcium phosphate ($CaHPO_4$) is used as an acid in baking powders. Solutions of $CaHPO_4$ in water may contain a variety of species. Which of the following is the conjugate base of the HPO_4^{2-} ion?
   A. Ca^{2+} B. OH^- C. H_2O D. PO_4^{3-} E. $H_2PO_4^-$

8. In which one of the following compounds do **all** of the constituent atoms (or ions) obey the octet rule?
   A. NaH B. BF_3 C. PbI_2 D. $TiCl_4$ E. XeO_3

9. The following reaction is used as the basis of the contact process (a step in the production of sulfuric acid).

$2\ SO_2(g) + O_2(g) \rightarrow 2\ SO_3(g); \qquad \Delta H = -197\ kJ \cdot mol^{-1}$

Which one of the changes listed below could be used to **increase the rate** of production of SO_3 but would actually **reduce the amount** of SO_3 in the system if it were allowed to reach equilibrium?

A. Heat the mixture.
B. Use V_2O_5 as a catalyst.
C. Increase the pressure of the mixture.
D. Increase the amount of oxygen fed into the reactor.
E. Increase the amount of sulfur dioxide fed into the reactor.

10. Which of the following substances will conduct electricity in the liquid state but not in the solid state, and will not dissolve in water?

A. Ca B. Cu C. CuI D. Cl_3CCOOH E. $C_6H_{12}O_6$

11. Some students have been measuring the rate of reaction between 5.0 g of zinc granules and 100 mL of 1.0 M hydrochloric acid at room temperature. The equation for the reaction is:

$Zn(s) + 2\ HCl(g) \rightarrow ZnCl_2(aq) + H_2(g)$

Which of the following changes to the procedure would probably **NOT** increase the rate of reaction?

A. Warming the HCl before adding the zinc.
B. Using zinc powder instead of zinc granules.
C. Using 50 mL of 2.0 M HCl.
D. Using 200 mL of 1.0 M HCl.
E. Using 100 mL of 1.0 M H_2SO_4.

12. Consider the following reaction, which is allowed to attain equilibrium in an enclosed system:

$CaCO_3(s) \rightarrow CaO(s) + CO_2(g); \qquad \Delta H = +178.3\ kJ \cdot mol^{-1}$

In addition to the temperature, the equilibrium constant for this reaction depends on:

A. The initial amount of $CO_2(g)$
B. The initial amount of $CaCO_3(s)$
C. The equilibrium amount of $CO_2(g)$
D. The equilibrium amount of $CaCO_3(s)$
E. The equilibrium amounts of $CaCO_3(s)$, $CaO(s)$ and $CO_2(g)$

13. Which one of the following molecular formulae can represent a pair of mirror image isomers?

A. H_2NCH_2COOH B. $H_2NCH(CH_3)COOH$ C. $H_2NCH_2CH_2COOH$
D. $H_2NCH_2COOCH_3$ E. $(CH_3)_2CHCOOH$

14. Which one of the following molecules has the **largest bond angle**?
A. CH_4 B. NH_3 C. H_2O D. SO_2 E. CO_2

15. Which one of the following molecules has the **greatest dipole moment**?
A. H_2 B. HF C. HCl D. HBr E. HI

16. Which one of the following molecules has the **highest boiling point**?
A. CH_4 B. CH_3Cl C. CH_2Cl_2 D. $CHCl_3$ E. CCl_4

17. When 0.1 M aqueous solutions of the following pairs of reagents are mixed at room temperature, which pair will **NOT** give a precipitate?
A. $HCl + AgNO_3$
B. $NaOH + CuSO_4$
C. $CaCl_2 + Na_2CO_3$
D. $H_2SO_4 + Ba(OH)_2$
E. $NH_4NO_3 + K_2CrO_4$

18. Benzoic acid (M_f = 122.2) is used for preserving fruit juices. What is the approximate pH of a saturated solution of benzoic acid in water, given that its solubility is 3.4 g/L, $K_a = 6.40 \times 10^{-5}$ (all measurements being made at 298 K)?
A. 1.8 B. 2.9 C. 3.4 D. 4.2 E. 5.7

19. Which one of the following indicators would be best to show the first endpoint of a titration involving an approximately 0.1 M solution of Na_2CO_3 (in the flask) with an approximately 0.1 M solution of HCl (run into the flask from a burette)?

	Indicator	pK_{In}	pH range Acid ←→ alkaline
A.	Methyl violet	0.8	Yellow 0.0 to 1.6 Blue
B.	Bromophenol blue	4.0	Yellow 2.8 to 4.6 Blue
C.	Azolitmin (litmus)	–	Red 5.0 to 8.0 Blue
D.	Thymol blue (base)	8.9	Yellow 8.0 to 9.6 Blue
E.	Alizarin yellow R	12.5	Yellow 10.1 to 13.0 Orange

Questions 20 and 21 concern plaster of Paris, which is used for setting broken limbs. Its formula is $CaSO_4 \cdot 0.5H_2O$ (M_f = 145.1). When water is added it sets to give gypsum, $CaSO_4 \cdot 2H_2O$ (M_f = 172.2)

20. What is the minimum mass of water needed to set 0.500 kg of plaster of Paris?
A. 62.0 g B. 93.1 g C. 0.124 kg D. 2.90 kg E. 3.45 kg

21. What is the heat energy evolved (in kJ) when 0.500 kg of plaster of Paris sets? (Given that $\Delta H_f\{H_2O(l)\} = -285.8$ kJ·mol^{-1}, $\Delta H_f\{CaSO_4\} = -1434$ kJ·mol^{-1}, $\Delta H_f\{CaSO_4 \cdot 0.5H_2O\} = -1577$ kJ·mol^{-1}, and $\Delta H_f\{CaSO_4 \cdot 2H_2O\} = -2023$ kJ·mol^{-1})
A. 17.3 B. 59.6 C. 589 D. 1540 E. 2030

22. A well is sunk in a bed of rock containing fluorspar (CaF_2). Given that $K_{sp}(CaF_2) = 4.0 \times 10^{-11}$ at 298 K, and assuming that the water in the well is saturated with CaF_2, and that the fluorspar is the only source of Ca^{2+} and F^- ions, then the fluoride ion content of the water (in mol·L^{-1} at 298 K) is:
A. 1.3×10^{-5} B. 2.2×10^{-4} C. 4.3×10^{-4} D. 6.3×10^{-6} E. 6.8×10^{-4}

23. Which expression could be used to calculate an approximate enthalpy change of combustion of methoxymethane (CH_3-O-CH_3) from standard bond enthalpy terms (E values)?
A. 6 × E(C-H) + 2 × E(C-O) – 6 × E(O-H) – 4 × E(C=O)
B. 3 × E(O-H) + 4 × E(C=O) – 6 × E(C-H) – 2 × E(C-O) – 3 × E(O=O)
C. 6 × E(C-H) + 2 × E(C-O) + 3 × E(O=O) – 6 × E(C-H) – 4 × E(C=O)
D. 3 × E(O-H) + 4 × E(C=O) – 6 × E(C-H) – 2 × E(C-O) – $3\frac{1}{2}$ × E(O=O)
E. 6 × E(C-H) + 2 × E(C-O) + $3\frac{1}{2}$ × E(O=O) – 3 × E(O-H) – 4 × E(C=O)

24. Which one of the following formulae represents a condensation polymer?
A. –(–CH(C_6H_5)–CH_2–)$_n$–
B. –(–CH_2–CH=CCl–CH_2–)$_n$–
C. –(–C(CH_3)($COOCH_3$)–CH_2–)$_n$–
D. –(–CH_2–C(CN)H–CH_2–CH(CN)–)$_n$–
E. –(–NH–(C_6H_4)NH–CO–(C_6H_4)CO–)$_n$–

25. The two liquids, methyl ethanoate (CH_3COOCH_3) and trichloromethane ($CHCl_3$) combine in such a way that they form a single hydrogen bond between each pair of molecules. In an experiment to determine the approximate strength of this bond, samples of the two liquids were mixed in an insulated glass beaker, and the temperature was found to rise by 0.75°C. Other data are given in the table below:

	Mass, g	Amount of substance, mol	Specific heat capacity, J·g^{-1}·K^{-1}
CH_3COOCH_3	3.71	0.05	1.97
$CHCl_3$	1.19	0.01	0.96
Beaker	60.00	–	0.6

The approximate strength of the hydrogen bond obtained by this experiment is (in kJ·mol^{-1}):
A. 0.73 B. 3.6 C. 4.9 D. 36 E. 49

THIS IS THE END OF PART A OF THE EXAMINATION

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 2002

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. Oil (Petroleum)

In 1872 Mendeleev visited North America. When he reported on this visit to his government he said, *"Oil is too valuable a material to be burned, and should be reserved as a source of chemicals."* Discuss this statement in the light of modern day knowledge of petroleum and its uses. In your essay you might like to consider (I) the chemical composition of petroleum, (ii) the uses of petroleum fractions as fuels, (iii) other products derived from petroleum and their uses, and (iv) alternatives to fuels and other products derived from petroleum. Illustrate your arguments with specific examples wherever possible.

2. The Extraction of Metals

In this essay you should discuss how the process used to extract a metal depends on the reactivity of that metal, and you should summarize the specific processes used to extract several metals with different reactivities. You may like to consider some of the following examples: gold, copper, iron, aluminum and sodium. It is particularly important in this question to provide equations for the reactions you describe.

3. Bonding

In this essay you should describe the three main types of bonds (metallic, covalent and ionic), and discuss how the type of bonding that holds a solid together can affect the physical properties of that solid. Give examples of specific substances wherever you can.

CHEMICAL INSTITUTE OF CANADA
and
CANADIAN CHEMISTRY OLYMPIAD
Final Selection Examination 2002

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 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 _____ E-Mail _____

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

Male ❒ Canadian Citizen ❒ Landed Immigrant ❒ Visa Student ❒

Female ❒ Passport valid until September 2002 ❒

Nationality of Passport _____

1. (12 marks)

When H_2S is dissolved in water it is about saturated at a concentration near 0.1 M. Three species containing sulfur exist in this solution, their proportions depending on the acidity of the solution: H_2S, HS^- and S^{2-}. Given the following equilibrium constants:

$H_2S \rightarrow H^+ + HS^-$ $\qquad K_{a1} = 1.0 \times 10^{-7}$

$HS^- \rightarrow H^+ + S^{2-}$ $\qquad K_{a2} = 1.3 \times 10^{-13}$

a) What is the concentration of the sulfide ion, $[S^{2-}]$, in a saturated 0.100 M solution of H_2S when for the solution the pH = 2.0?

b) A solution contains the cations Mn^{2+}, Co^{2+}, and Ag^+ at an original concentration of 0.010M each. Which of these ions will precipitate when the solution is saturated in H_2S and the pH adjusted to pH = 2.0 by adding HCl? Explain your answer.
Given:

MnS $K_{sp} = 2.5 \times 10^{-10}$ $\qquad$ CoS $K_{sp} = 4.0 \times 10^{-21}$ $\qquad$ Ag_2S $K_{sp} = 6.3 \times 10^{-50}$

c) How many grams of lead(II) sulfide, PbS, will precipitate from 1.00 L of a saturated solution of lead(II) sulfate, $PbSO_4$, if the concentration of sulfide ion, $[S^{2-}]$, is adjusted to give a concentration of 1.00×10^{-17} M?

Given:

Pb SO_4 $K_{sp} = 1.6 \times 10^{-8}$ PbS $K_{sp} = 2.5 \times 10^{-27}$

2. (12 marks)

Consider the following reactions involving the destruction of ozone:

a) For the decomposition of ozone:

$$O_3\,(g) + O\,(g) \rightarrow 2\,O_2\,(g)$$

Draw the structures for the ozone and dioxygen molecules. Use these structural models and your understanding of bond energies to predict whether this reaction is endothermic or exothermic under standard conditions. Explain your answer.

b) Nitrogen monoxide, NO, is an atmospheric pollutant that destroys ozone, O_3, in the stratosphere. Here is the accepted mechanism for the process:

$O_3 + NO \rightarrow NO_2 + O_2$	*slow*
$NO_2 + O \rightarrow NO + O_2$	*fast*
$O_3 + O \rightarrow 2\,O_2$	*net, or overall, reaction*

Draw an energy profile (activation energy diagram, *i.e.*, a graph or diagram of energy *versus* reaction progress or pathway) for this mechanism. Include as many details as possible.

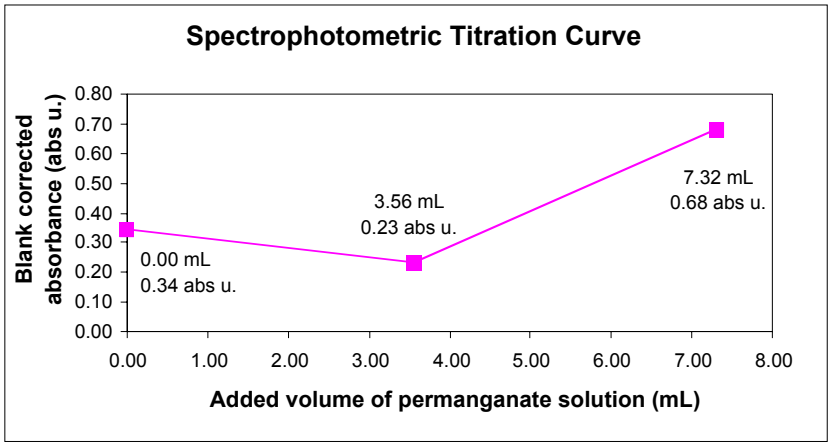
c) Identify any catalyst(s) or intermediate(s) in the mechanism above. Explain your answer.

d) The activation energy for the decomposition of ozone promoted by nitrogen monoxide is 11.9 kJ mol^{-1}. The activation energy for the decomposition of ozone promoted by chlorine atoms is 2.1 kJ mol^{-1}. From the information given, which pollutant is a more serious threat to the ozone layer, chlorine atoms or nitrogen monoxide. Explain your answer, stating all assumptions made.

3. (12 marks)

a) Under aqueous acidic conditions, permanganate ions (MnO_4^-) oxidizes oxalate ions ($C_2O_4^{2-}$) to yield carbon dioxide and manganese (II) ions. Give the balanced equations for the two half-reactions.

b) A sample of $K_3[Fe(C_2O_4)_3]\bullet 3H_2O$ is dissolved in 10.00 mL of dilute sulfuric acid, and is titrated spectrophotometrically with 0.0500 M potassium permanganate. Using the titration curve below, calculate the initial mass of the complex present in the sample.

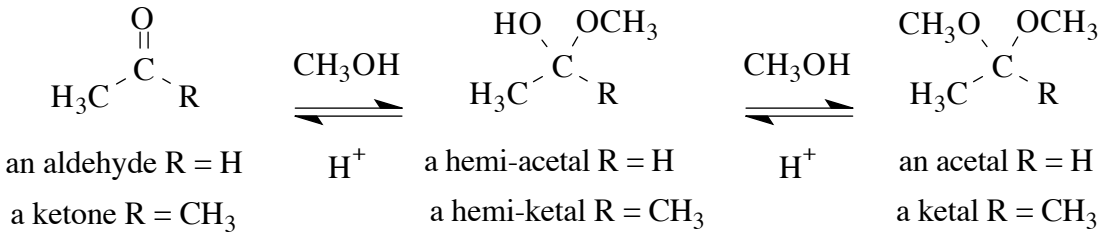


c) The spectrophotometer that was used for the titration cannot properly measure differences in light intensity by less than 1%. Using the above data, calculate the minimal concentration of the complex that can be accurately measured.

d) Another sample weighing exactly 0.101g, and containing only the $K_3[Fe(C_2O_4)_3]\bullet 3H_2O$ complex and $FeCl_3\bullet 6H_2O$ is dissolved in dilute sulfuric acid. The resulting solution is mixed with a zinc amalgam to reduce all iron (III) ions to iron (II) ions. The solution is then titrated against 0.0500 M potassium permanganate, and the equivalence point is detected after the addition of 3.31 mL. Calculate the initial composition of the sample.

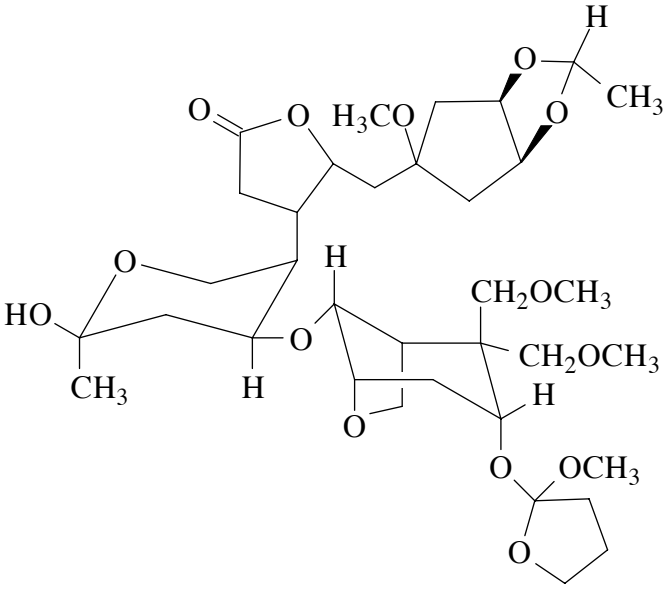
4. (12 marks)

a) Aldehydes and ketones react with alcohols to eventually form acetals and ketals.

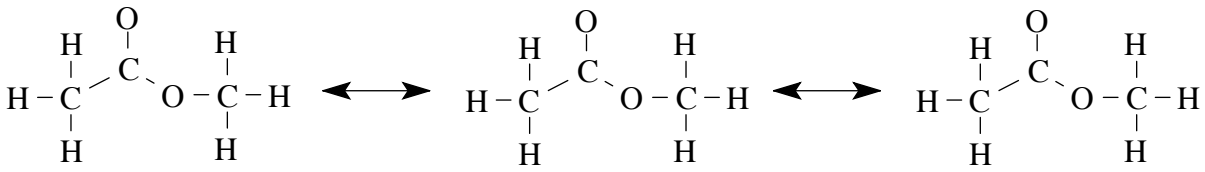


an aldehyde R = H
a ketone R = CH_3

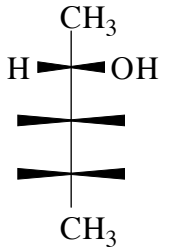
A number of oxygen functions are present in the structure below. Using the example above as a guide, indicate the positions of the TWO aldehyde/ketone derivatives by drawing an arrow to the carbon atoms of the former carbonyl (C=O). Indicate whether the group is a hemi-actetal, hemi-ketal, acetal or ketal.



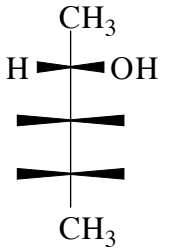
b) A resonance structure is one of several valence-bond structures with localized electrons that approximate the true structure of a compound that has delocalized electrons.
Complete the templates below to show three major resonance structures of the ester shown below by clearly adding any missing bonds, lone pairs of electrons and formal charges that may be present.



c) Optically active compounds are not superimposable upon their mirror images. Three-dimensional awareness is important in predicting optical activity. Complete the structures below by adding an H and an OH group to each unspecified bond to generate an optically active and a non-optically active system. Note the three-dimensional convention used for the bonds.

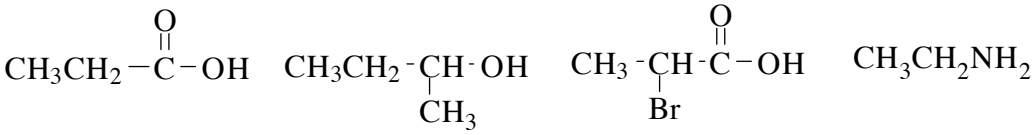


Optically Active



NOT Optically Active

d) Place the following compounds in order of <u>increasing</u> acidity.



A **B** **C** **D**

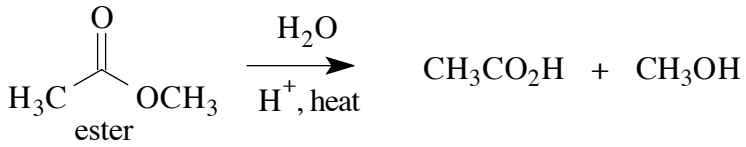
_____ _____ _____ _____

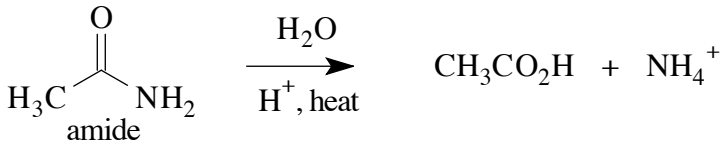
least acidic most acidic

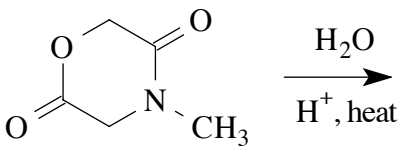
e) A compound that lacks a carbonyl group (C=O) and has the formula $C_{14}H_{24}O$ reacts rapidly with an excess of H_2 in the presence of a catalyst to yield a new compound with the formula $C_{14}H_{28}O$. The general formula of a non-cyclic alkane is $C_nH_{(2n+2)}$.

The ORIGINAL compound contained ____ ring(s) and ____ double bond(s).

f) Esters hydrolyze to form alcohols and carboxylic acids, whereas amides hydrolyze to form amines and carboxylic acids. Write the products of the acidic aqueous hydrolysis of the compound below that incorporates both an ester and an amide functionality.

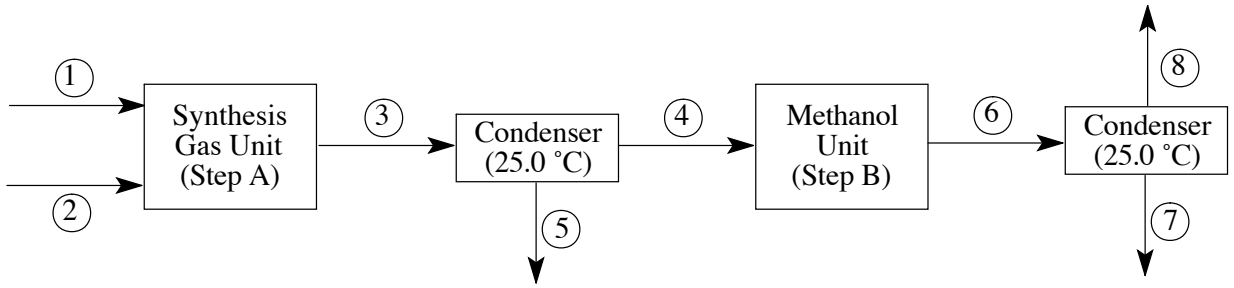






5. (12 marks)

Methanol (CH_3OH) can be produced industrially from Synthesis Gas (CO and H_2). The latter can be obtained from methane (CH_4; a major component of natural gas) and steam (H_2O (g)). The whole continuous process is illustrated in the flow chart below; Step A is the preparation of Synthesis Gas and Step B is the preparation of methanol.



The feedstock of Step A is composed of pure methane gas (1) at a pressure of 250.0 kPa and a temperature of 25.0°C, and steam (2) at a pressure of 200.0 kPa and 100.0°C (assume that steam is pure water vapor). The flow rates of (1) and (2) are 55.0 L/s and 150.0 L/s, respectively. Flowing out of Step A is a mixture (3) of Synthesis Gas and an excess reactant from the first step that is condensed (5) at 25.0°C. Methanol is produced in Step B from the feedstock (4) and the effluent (6) from this reaction contains methanol and another excess reactant. The latter is removed as (8) after condensation of pure methanol at 25.0°C in (7).

Compound	Molar Mass ($g\ mol^{-1}$)	Melting Point (°C)	Boiling Point (°C)	Density at 25.0°C
CH_4 *(g)*	16.04	-183	-161	0.716 $g\ L^{-1}$
H_2O *(l)*	18.02	0	100	1.000 $g\ mL^{-1}$
CO *(g)*	28.01	-205	-191.5	1.250 $g\ L^{-1}$
H_2 *(g)*	2.016	-259.2	-252.8	-----
CH_3OH *(l)*	32.04	-98	64.7	0.791 $g\ mL^{-1}$

Assume ideal gas behavior; complete reactions in Steps A and B; and complete separation from each condenser.

a) Write the balanced chemical equation for the reaction of Step A.

Write the balanced chemical equation for the reaction of Step B.

b) Which reactant is in excess after Step A?

Which reactant is in excess after Step B?

c) Calculate the flow rates (in the proper units) at the following positions:

i) The flow of the excess reactant at position (5) **in L/s** at 25.0˚C and 101.3 kPa:

ii) The flow of the excess reactant at position (8) **in L/s** at 25.0˚C and 101.3 kPa:

iii) The flow of pure liquid methanol at position (7) **in L/s** at 25.0˚C and 101.3 kPa:

END OF EXAMINATION