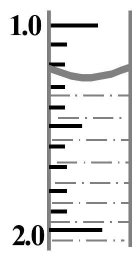
NATIONAL HIGH SCHOOL CHEMISTRY EXAMINATION 2005
PART A: MULTIPLE CHOICE SECTION (60 minutes)

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 provided, but no other data may be given. Answers should be marked on the Answer Sheet provided.

1. Which of the substances given below would normally require the following WHMIS symbol?

A. Ammonia B. Hydrogen C. Octane D. Potassium nitrate E. Sodium nitride

2.



The above diagram shows the cross section of a burette that is partially filled with a solution. What is the burette reading?

A. 1.20 mL B. 1.24 mL C. 1.26 mL D. 2.74 mL E. 2.76 mL

3. Which one of the following bonds is non-polar?

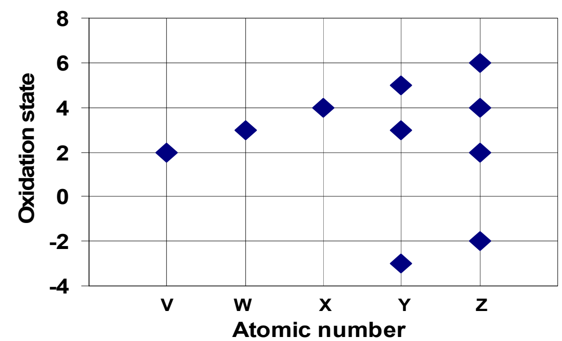
A. Carbon-oxygen bond in CH_3OCH_3
B. Carbon-carbon bond in CH_3CHO
C. Carbon-hydrogen bond in $CHCl_3$
D. Carbon-chlorine bond in CCl_4
E. Carbon-carbon bond in C_2H_4

4. An electron is added to a sodium atom. What is the electronic configuration of the resulting ion?

A. $1s^22s^22p^5$ B. $1s^22s^22p^6$ C. $1s^22s^22p^63s^1$

D. $1s^22s^22p^63s^2$ E. $1s^22s^22p^63s^23p^6$

5. V, W, X, Y and Z are five successive elements in the Periodic Table. (The letters assigned to them do not represent their atomic symbols.) The following chart shows the oxidation states of these elements plotted against their atomic numbers.



The correct atomic number of element Z is:

A. 2 B. 4 C. 6 D. 8 E. 16

6. The pH ranges and colour changes of three indicators are given below.

Indicator	pH range	Colour change
Methyl orange	3.2 – 4.4	Red → yellow
Bromothymol blue	6.0 – 7.6	Yellow → blue
Phenolphthalein	8.2 – 10.0	Colourless → red

Three test tubes containing a buffer solution of pH 7.0 are each tested with one of these indicators. Which one of the following answers shows the colours that would be observed with methyl orange, bromothymol blue and phenolphthalein in that order?

A. Red, yellow, colourless
B. Yellow, blue, red
C. Orange, yellow, colourless
D. Yellow, green, colourless
E. Yellow, green, red

/continued overleaf

Questions 7 and 8 refer to the following reaction sequence, which is used to prepare potash alum crystals from aluminum foil.

$$2Al(s) + 2KOH(aq) + 2H_2O(l) \rightarrow 2KAlO_2(aq) + 3H_2(g) \quad . . . . \quad (1)$$

$$2KAlO_2(aq) + 4H_2SO_4(aq) \rightarrow K_2SO_4(aq) + Al_2(SO_4)_3(aq) + 4H_2O(l) \quad . . . . . \quad (2)$$

7. About 0.6 g of aluminum foil is treated with 10.00 mL of KOH solution (2.00 mol L^{-1}) and the reaction is allowed to proceed until effervescence ceases, at which point the excess aluminum is filtered off. What volume of H_2SO_4 (1.00 mol L^{-1}) needs to be added to the filtrate in order for reaction (2) to take place without any excess reagent remaining in the final solution?

A. 10.0 mL B. 20.0 mL C. 30.0 mL D. 40.0 mL E. 50.0 mL

8. When the final solution from the reactions described in Question 7 is allowed to evaporate slowly, crystals of potash alum, $K_2SO_4{\bullet}Al_2(SO_4)_3{\bullet}24H_2O$ (M_r = 948.8), are formed. What is the maximum mass of crystals that can be obtained?

A. 9.49 g B. 18.98 g C. 28.46 g D. 37.95 g E. 47.44 g

9. Glauberite is a mineral containing sodium sulfate (M_r = 142.0) and calcium sulfate (M_r = 136.1) only. It is the chief source of sodium sulfate, which is used in making glass. If a 20.00 g sample of glauberite contains 2.88 g of calcium, what mass of sodium sulfate can be extracted from 1 tonne (1000 kg) of glauberite?

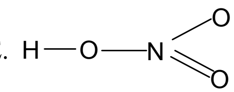
A. 102 kg B. 511 kg C. 719 kg D. 855 kg E. 978 kg

10. The chief constituent of pineapple flavouring is a compound containing 62.04% carbon and 10.41% hydrogen by mass, and with relative molar mass, M_r, = 110 ± 10. What is a possible molecular formula for this compound?

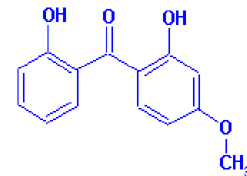
A. C_8H_{16} B. CH_3CH_2CHO C. $CH_3CH{=}CHCH_2CH_3$

D. $CH_3(CH_2)_5CH_2OH$ E. $CH_3(CH_2)_2COOCH_2CH_3$

11. Which one of the following substances has an unpaired electron in its Lewis structure?

A. NH_3 B. $N\equiv N$ C. $N{=}O$ D. $H{-}C\equiv N$ E. 

12. Spectra-Sorb UV 24 is used as a sunscreen. The structural formula of its active ingredient is given below:



Three of the functional groups in this molecule are:

A. Alcohol, ether and ketone
B. Alcohol, ester and ketone
C. Ester, ketone and phenol
D. Ether, ketone and phenol
E. Ester, ether and phenol

13. A substance has the following formula

$$-\!\!\left(CH_2CH_2O_2CC_6H_4CO_2CH_2CH_2O_2CC_6H_4CO_2\right)\!\!-_n$$

This substance is a:

A. Detergent B. Natural oil or fat C. Polyester D. Protein E. Rubber

14. Which one of the following is the main process for the industrial production of chlorine?

A. treating sea water with bromine

B. electrolysis of brine (sodium chloride solution)

C. electrolysis of molten sodium chloride

D. electrolysis of sodium hypochlorite solution

E. electrolysis of aqueous hydrochloric acid

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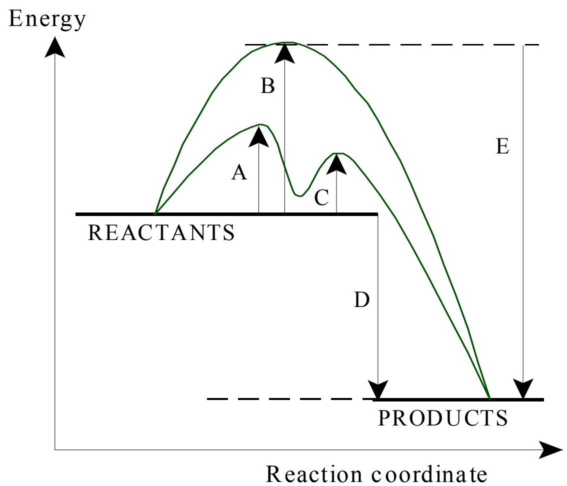
15. Which of the arrows on the following energy diagram refer to the activation energy of the catalysed reaction?



16. Which of the following statements about a chemical reaction in dynamic equilibrium is TRUE?

A. Reactants form products as fast as they are formed from products
B. The position of equilibrium can be altered using a catalyst
C. Rates of the forward and reverse reactions are both zero
D. Reactants can no longer react together to form products
E. Reactants and products are present in equal amounts

17. What is the approximate pH of a solution containing a 500 mg Vitamin C tablet dissolved in a glass of water (100 mL)? (Vitamin C is ascorbic acid, M_r = 176.13: assume that this behaves as a monoprotic acid with a pK_a value of 4.17.)

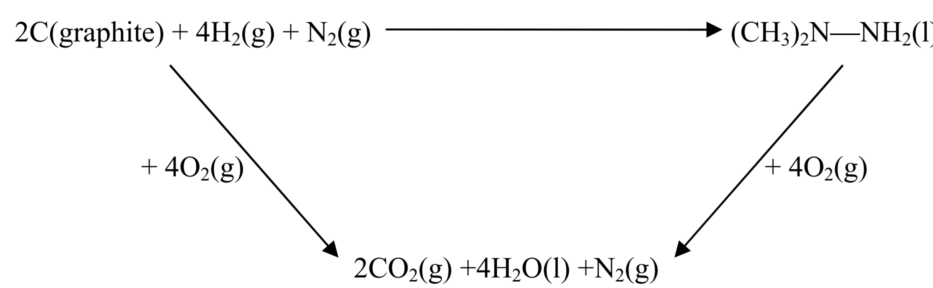
A. 1.9 B. 2.9 C. 3.4 D. 3.9 E. 4.2

18. Calcium phosphate, $Ca_3(PO_4)_2$ (M_r = 310.2, $K_{SP} = 1.0 \times 10^{-26}$ at 25°C) is used in making fertilizers. What is the solubility of $Ca_3(PO_4)_2$ in g L^{-1} at 25°C?

A. 2.5×10^{-6} g L^{-1} B. 7.7×10^{-4} g L^{-1} C. 1.0×10^{-3} g L^{-1}

D. 1.4×10^{-3} g L^{-1} E. 3.1×10^{-3} g L^{-1}

19. UDMH or 1,1–dimethylhydrazine, $(CH_3)_2N—NH_2$, is used as a fuel in spaceships. Use the Hess's law cycle and data given below to calculate the standard enthalpy change of combustion, ΔH^{o}_{c}, of UDMH.



Standard enthalpy change of formation values:
$\Delta H^{o}_{f}\{CO_2(g)\} = -393.5$ kJ mol^{-1}; $\Delta H^{o}_{f}\{H_2O(l)\} = -285.8$ kJ mol^{-1};
$\Delta H^{o}_{f}\{(CH_3)_2N—NH_2\}(l) = +48.3$ kJ mol^{-1}

$\Delta H^{o}_{c}\{(CH_3)_2N—NH_2(l)\}$ from these data is:

A. – 1978.5 kJ mol^{-1} B. – 1930.2 kJ mol^{-1} C. – 1881.9 kJ mol^{-1}

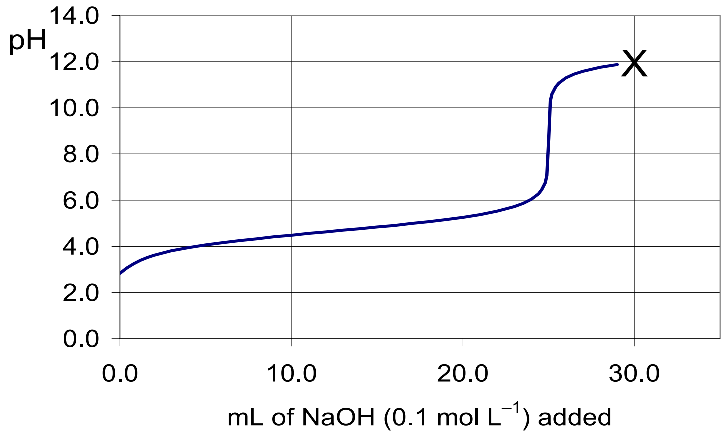
D. – 727.6 kJ mol^{-1} E. – 404.5 kJ mol^{-1}

20. The C ═ O double bond has a bond length of 0.122 nm and a bond energy of around 740 kJ mol^{-1} in some organic compounds. Which of the following pairs of figures is most likely to be correct for a C – O single bond?

	Bond length, nm	**Bond energy, kJ mol^{-1}**
A.	0.113	335
B.	0.113	1080
C.	0.116	805
D.	0.143	360
E.	0.143	1080

/continued overleaf

21. The graph below shows the changes of pH that occur when sodium hydroxide solution (0.1 mol L^{-1}) is added to 25.00 mL of ethanoic acid solution (0.1 mol L^{-1}).



What is contained in the solution at point X?

A. Acid only B. Acid + salt C. Salt only D. Base + salt E. Base only

22. What is the total number of non-cyclic isomeric alkenes (including geometric isomers) with the formula C_5H_{10}?

A. 4 B. 5 C. 6 D. 8 E. 10

23. Given the following standard reduction potentials:

$$Cu^{+}(aq) + e^{-} \rightarrow Cu(s) \qquad E^{\ominus} = +0.52\ V$$
$$Cu^{2+}(aq) + e^{-} \rightarrow Cu^{+}(aq) \qquad E^{\ominus} = +0.16\ V$$

What is the standard potential for the following disproportionation reaction, which is spontaneous?

$$2Cu^{+}(aq) \rightarrow Cu^{2+}(aq) + Cu(s)$$

A. – 0.68 V B. – 0.36 V C. + 0.36 V D. + 0.68 V E. + 0.88 V

24. Caves are formed in limestone when rainwater containing dissolved carbon dioxide reacts with the rock. Inside the caves the reaction is often reversed causing limestone stalagmites and stalactites to form. The equations governing these processes are:

$$CaCO_3(s) + CO_2(aq) + H_2O(l) \rightleftharpoons Ca(HCO_3)_2(aq)$$

also $CO_2(aq) \rightleftharpoons CO_2(g)$, and $H_2O(l) \rightleftharpoons H_2O(g)$

Which one of the following processes will be most likely to **inhibit** the formation of stalagmites and stalactites?

A. Global warming
B. Low pressure weather systems
C. Increasing the flow of air through the caves
D. Removing stack gases from local coal-fired power plants
E. Increasing humidity from the breath of visitors to the caves

25. Some students are doing an experiment to find the equilibrium constant, K_c for the acid catalysed hydrolysis of ethyl ethanoate according to the equation:

$$CH_3COOC_2H_5(l) + H_2O(l) \overset{H^+}{\rightleftharpoons} CH_3COOH(l) + C_2H_5OH(l)$$

The students are told to begin by mixing 4.40 g (0.05 mol) of ethyl ethanoate with 5.00 g (0.28 mol) of water, which should have given them $K_c = 0.27$ at the temperature of their lab during the equilibration period. Although they did not know this, the ester they used was contaminated with water, so they were effectively adding only 0.045 mol of it to make the mixture. If the students with the contaminated ester found that the chemical amount of CH_3COOH in their equilibrated mixture was 0.03 mol, what was the error in their value of K_c?

A. + 33% B. + 11% C. + 0 % D. –11% E. – 33%

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

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 2005

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. Fire!

In this essay you should consider the chemistry of combustion reactions, in particular the nature of fuels and oxidants. You need to discuss the energetics of combustion reactions and to compare the thermal and kinetic stabilities of reactions. You should indicate how the relative sizes of the activation energy of a reaction and its enthalpy change of combustion affect the burning process. You might also like to show how the "Fire triangle" is used in preventing and fighting unwanted combustion. In this essay it is important to give some examples of combustion reactions, with equations, although you are not expected to cite energy values from memory.

2. What is the best kind of water to drink?

Nowadays almost everyone drinks water out of bottles, and many people believe that it is better to drink bottled water than tap water. In this essay you should use your knowledge of water sources and purification systems to debate which kind of water is best to drink. You could discuss home water treatment systems, such as filters, as well as municipal water treatment plants and processes used in the commercial production of bottled water. You may also like to consider the effect of storage and transport conditions on water that has been purified.

3. Gasoline

In this essay you should consider the composition of the oil fraction that is used to produce gasoline for cars, and how cracking of heavier oil fractions is used to increase the amount of gasoline produced. You should indicate what is meant by the term "octane number" and how this value can be enhanced using catalytic reforming. You could discuss why additives such as oxygenated compounds and tetraethyl lead are put into gasoline, and why some of these products have now been prohibited in many countries. You might also like to consider alternative fuels such as ethanol, which could be used to reduce our dependence on petroleum products. In this essay it is important to draw out the formulae of some of the substances you are discussing.

/See overleaf for Question 4

4. Experiment Design

Experiments to determine the rate of a reaction are important because they can help chemists to work out the mechanism by which a reaction takes place.

In answering this question you need to devise an experiment to determine the rate of the reaction between potassium permanganate and ethanedioic acid (oxalic acid) under acid conditions. This reaction takes place according to the following equation:

$$2KMnO_4(aq) + 5(COOH)_2(aq) + 3H_2SO_4(aq) \rightarrow K_2SO_4(aq) + 2MnSO_4(aq) + 10CO_2(g) + 8H_2O(l)$$

There are a number of different ways in which this reaction can be studied. You should choose just one of them, and in your response you should outline your preferred procedure, giving details of the apparatus and materials you would need for performing the experiment. It is important to specify any safety precautions that might be required. You should also indicate what readings you would take, how you could use your readings to obtain a graph (if this is appropriate), and how you would calculate a result.

CHEMICAL INSTITUTE OF CANADA
and
CANADIAN CHEMISTRY OLYMPIAD
Final Selection Examination 2005

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 Answers

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 ___

Number of chemistry courses at a Québec CÉGEP ___

Male ❒ Canadian Citizen ❒ Landed Immigrant ❒ Visa Student ❒

Female ❒ Passport valid until November 2005 ❒

Nationality of Passport _________________

1A (INORGANIC): Crystal Packing in Salts **(6 points)**

In the crystal structure of barium chloride, chloride ions are inserted into all the tetrahedral cavities of the cubic close packed array of barium ions. The ionic radii of barium and chloride ions are respectively of 156 pm and 167 pm. Assume that ions are in contact with one another in the crystal.

a) What are the coordination numbers of barium and chloride ions in the crystal?

b) Calculate the edge length of the unit cell in pm.

c) Calculate the density of barium chloride.

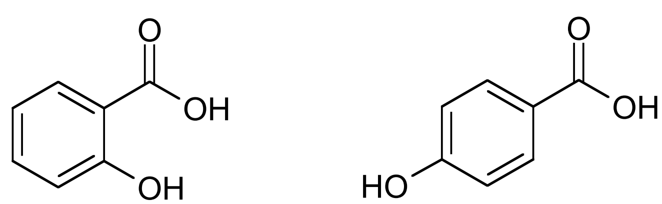
1B (INORGANIC): Radiochemistry **(6 points)**

A thorium radioactive decay series begins with ^{228}Th. It decays to stable ^{208}Pb by emission of several α- and β-particles with a half-life of 1.91 years ($t_{1/2}$ = 1.91 y) for this overall process. What volume of helium at 0 °C at 1 atmosphere (100 bar or 101.3 kPa) is collected when 1.000 gram of ^{228}Th is stored in a container for 2.00 years?

2A (GENERAL) **(4 points)**

a) Briefly account for the fact that the first ionization energy of potassium is less than that of sodium despite sodium having a smaller effective nuclear charge.

b) Salicylic acid, or 2-hydroxybenzoic acid (Structure **A**), has a melting point of 158ºC. An isomer of salicylic acid, 4-hydroxybenzoic acid (Structure **B**), has a melting point of 214ºC. Propose an explanation for the difference in the melting points of these substances.



A **B**

2B (INORGANIC): Metal Carbonyl compounds (8 points)

In metal carbonyl complexes $[M_a(CO)_b]$, the oxidation state (O.S.) of the metal is "0". Their synthesis can be done by Direct Combination (*i.e.* the reaction of metal with carbon monoxide), or by Reductive Carbonylation (*i.e.* the reaction of a metallic salt with carbon monoxide and a reducing agent such as aluminum, dihydrogen gas, or carbon monoxide itself). The formula of a metal-carbonyl complex depends of the number of valence electrons surrounding the metal. A stable structure contains 18 electrons around the metal. Each CO unit contributes for 2 electrons and other electrons come from the metal (*i.e.* from the total of its "ns^x $(n\text{-}1)d^y$" valence electrons). For example, nickel electron configuration is [Ar] $4s^2\ 3d^8$, for a total 10 valence electrons. Since each CO contributes for 2 electrons then the nickel carbonyl compound should have the formula $Ni(CO)_4$, showing a total of 18 valence electrons around the metal.

a) Predict the simplest formula, $[M_a(CO)_b]$, of the respective carbonyl compounds of chromium and iron. Justify your answers with proper electron counts.

If a metal contains a odd number of electrons in its “ns^x (n-1)d^y” configuration, then dinuclear complexes (*i.e.* complexes containing two metallic units) are formed. In these complexes, electrons can be shared between two metal atoms (just like a metal-metal 2-electron covalent bond). This structure adjustment allows an electron count of 18 valence electrons around each metal atom (like covalent bonds respect the octet rule in common covalent compounds).

b) Considering the possibility of forming dinuclear complexes as described above, predict the formula, $[M_a(CO)_b]$, of the carbonyl compound cobalt. Justify your answer with proper electron counts.

“Reductive Carbonylation” method is a simple oxidation-reduction reaction (the reducing agent gets oxidized while the metal is getting reduced). For example, if H_2 (where H atoms are in O.S. “0”) is used as the reducing agent, it is transformed in H_2O (where H atoms are in O.S. +1).

c) Complete and balance the following equations with the proper chemical formulas. Each reaction leads to two products: a metal carbonyl complex and the resulting oxidized substance from the reducing agent.

__ $MoCl_3$ + __ Al + __ CO → _______________ + _______________

__ Re_2O_7 + __ CO → _______________ + _______________

3 (PHYSICAL): Nitrogen Oxides (12 points)

Nitrogen monoxide, NO, is an interesting molecule involved in both essential biological processes and environmental pollution. It is commonly produced in the following reaction:

$$N_2(g) + O_2(g) \rightarrow 2NO(g) \qquad \Delta H = 180 \text{ kJ}$$

Another reaction between nitrogen and oxygen to form nitrogen dioxide has the following enthalpy change:

$$N_2(g) + 2O_2(g) \rightarrow 2NO_2(g) \qquad \Delta H = 68 \text{ kJ}$$

a) What is the enthalpy change for the reaction of nitrogen monoxide, first formed in automobile exhaust, with dioxygen in the air?

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

b) Using the data in the table, for the initial concentration of reactants and initial rate of formation of product $NO_2(g)$:

Exp	**[NO] /mol L^{-1}**	**[O_2] /mol L^{-1}**	**Initial Rate /mol L^{-1} s^{-1}**
1	0.001	0.001	7 x 10^{-6}
2	0.001	0.003	21 x 10^{-6}
3	0.002	0.003	84 x 10^{-6}
4	0.003	0.003	189 x 10^{-6}

i) Write the rate expression for the reaction of nitrogen monoxide and dioxygen.

ii) Calculate the rate of formation of $NO_2(g)$ when $[NO(g)] = [O_2(g)] = 0.005$ mol L^{-1}.

c) The Arrhenius equation has been proposed to explain the temperature dependence of the rate of reaction, wherein the rate constant, *k*, changes with temperature. In this approach the activation energy, *Ea,* is always a positive quantity. Thus, for every reaction an increase in temperature should increase the rate. But there's always the exception that tests the rule; such as for some enzyme reactions and five reactions involving nitrogen monoxide, NO. You are provided with four possible reaction mechanisms which you must examine and decide whether or not they conform to the rate expression derived in part b) and then decide the one that best conforms to the experimental fact that the reaction decreases in rate with certain increases in temperature. Each mechanism list facts about the elementary steps involved and about the enthalpy change in the first forward reaction. Fill in the boxed space provided with a "yes" or "no" if the mechanism conforms to the experiment and then briefly explain the relative probability of each mechanism in explaining the decrease in rate with increase in temperature.

i)

	Proposed mechanism	Conforms	Explain (why or why not)
1	$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ $\Delta H < 0$		
2	$NO(g) + O_2(g) \rightarrow NO_3(g)$ $\Delta H < 0$ $NO_3(g) + NO(g) \rightarrow 2NO_2(g)$ fast		
3	$2NO(g) \rightleftharpoons N_2O_2(g)$ equil $\Delta H < 0$ $N_2O_2(g) + O_2(g) \rightarrow 2NO_2(g)$ slow		
4	$NO(g) + O_2(g) \rightleftharpoons NO_3(g)$ equil $\Delta H > 0$ $NO_3(g) + NO(g) \rightarrow 2NO_2(g)$ slow		

ii) It was mentioned that the other reactions that may decrease in rate as temperature increases involve enzymes. Briefly explain what enzymes are and why reactions involving them often decrease as temperature increases.

4 (ANALYTICAL) (12 points)

A solid sample containing only sodium hydrogen oxalate ($NaHC_2O_4$) and oxalic acid ($H_2C_2O_4$) is dissolved in 100.00 mL water. In a first experiment, 10.00 mL of this solution is reacted with 10.00 mL of a 0.100 M solution of sodium hydroxide (NaOH). It takes 7.00 mL of a 0.100 M solution of hydrochloric acid (HCl) to titrate the resulting mixture up to the end point indicated by the color change of the thymolphthalein indicator.

In a second experiment, another 10.00 mL of the sample solution is reacted with 10.00 mL of a 5.00 M solution of strontium chloride ($SrCl_2$) solution and enough sodium hydroxide (NaOH) to maintain the pH at 13.0. The resulting precipitates are filtered and redissolved in dilute sulfuric acid. It takes 1.60 mL of a 0.0500 M solution of potassium permanganate ($KMnO_4$) to titrate the redissolved precipitates.

Equilibrium Data:

$H_2C_2O_4 \rightleftharpoons HC_2O_4^- + H^+$	$K_{A1} = 5.60 \times 10^{-2}$
$HC_2O_4^- \rightleftharpoons C_2O_4^{2-} + H^+$	$K_{A2} = 5.42 \times 10^{-5}$
$SrC_2O_4 \rightleftharpoons C_2O_4^{2-} + Sr^{2+}$	$K_{sp} = 5.0 \times 10^{-8}$
$2\ CO_2 + 2\ H^+ + 2\ e^- \rightleftharpoons H_2C_2O_4$	$E_0 = -0.49$ V
$MnO_4^- + 8\ H^+ + 5\ e^- \rightleftharpoons Mn^{2+} + 4\ H_2O$	$E_0 = +1.51$ V

a) Knowing that the tymolphthalein indicator changes color in a pH range of 9.4 to 10.6, the concentration of which of the basic species then present in solution can be determined by the first titration? (circle all valid applicable and justify your answer briefly)

OH^- $\quad$ $C_2O_4^{2-}$ $\quad$ $HC_2O_4^-$ $\quad$ H_2O $\quad$ Cl^-

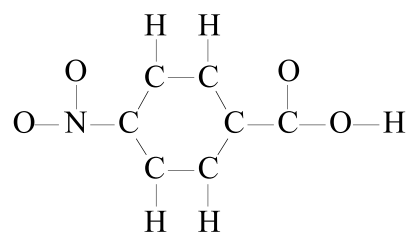
b) Give the balanced chemical equation for the oxidation of oxalic acid by potassium permanganate in aqueous acid solution.

c) What proportion of the total oxalates (oxalic acid & sodium hydrogen oxalate) present in the 10.00 mL aliquot will be precipitated as strontium oxalate after the strontium chloride / sodium hydroxide treatment?

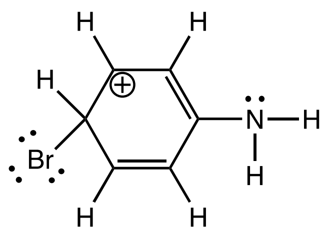
d) Based on the titration data given to you, calculate the initial quantity of each of sodium hydrogen oxalate and of oxalic acid in the initial solid sample.

5 (ORGANIC) **(12 points)**

a) Complete the following Lewis structure of para-nitrobenzoic acid by adding any lone pair(s) or bonded pair(s) and clearly indicate any formal charges.

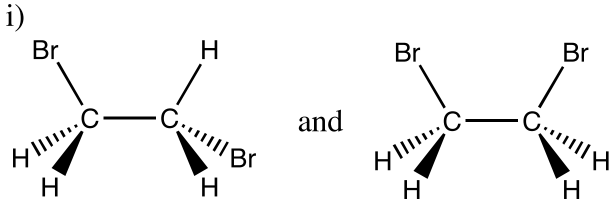


b) Draw two contributing resonance structures for the following intermediate:



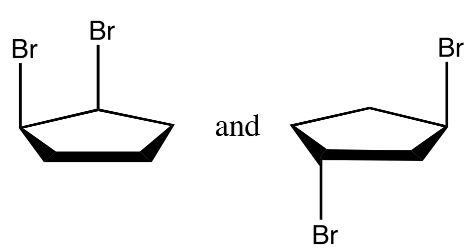
c) Choose which of the following relation best applies to each of the following pairs of molecules. Use the following possible relations: Conformational isomers, Constitutional isomers, Enantiomers, Diastereoisomers, etc.

i)



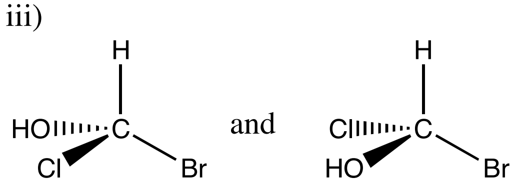
Relation:

ii)



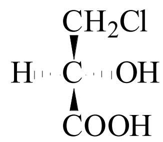
Relation:

iii)

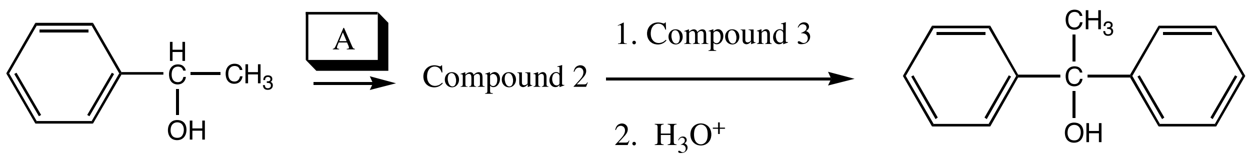


Relation:

d) Is the following compound an R or an S isomer? Clearly indicate how you obtain your answer.



e) Complete the following synthetic pathway. **A** represents the necessary inorganic reagents and solvents to make Compound 2 from Compound 1. Compound 3 is the Grignard reagent needed to complete the synthesis of Compound 4.



Compound 1

Compound 4

A:

Compound 2

Compound 3

End of Examination