NATIONAL HIGH SCHOOL CHEMISTRY EXAMINATION 2004
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 required, but no other data may be given. Answers should be marked on the Answer Grid provided.

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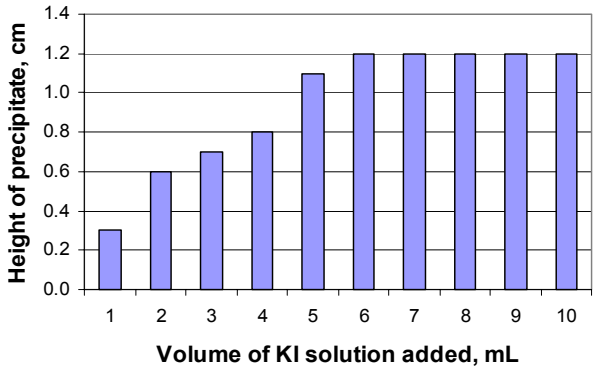
1. Which of the substances given below would normally require the following TWO WHMIS symbols?

A. Alcohol B. Hydrogen C. Oil D. Oxygen E. Sodium

2. The following chart shows the height of a secret metal iodide precipitate that was formed in a series of 10 test tubes. Each test tube contained 3.0 mL of a metal nitrate solution (1.0 mol•L^{-1} with respect to the metal ions). Measured volumes of 1.0 mol•L^{-1} potassium iodide (KI) solution were added to each tube in turn to form the precipitate.



What is the formula of the metal iodide according to this chart?

A. M_2I B. MI C. MI_2 D. MI_3 E. MI_4

3. Magnetite is a naturally occurring oxide of iron that has a formula of Fe_3O_4. It contains two different valencies of iron, with two atoms of one valency for every atom of the other. The two valencies are:

A. 1 and 2 B. 2 and 3 C. 1 and 3 D. 3 and 4 E. 1 and 4

4. Some definitions of the chemical term "mole", taken from old textbooks, are given below. Which one comes closest to the correct modern (IUPAC) definition of the term?

A mole is:

A. 6.02×10^{23} molecules
B. The Avogadro number of any particle of definite composition
C. The quantity of a substance that has a mass in grams numerically equal to its molecular mass
D. A mass unit defined as that mass of material containing 6.02×10^{23} molecules, atoms or other units
E. The amount of substance that contains the same number of specified entities as there are atoms in exactly 12 g of carbon-12.

5. A lemon-flavoured drink contains citric acid as the only acidic component. 10.00 mL of the drink is diluted with 15.00 mL of distilled water and titrated with NaOH solution using phenolphthalein as indicator. Under these conditions citric acid behaves as a diprotic (or dibasic) acid. If 25.00 mL of 0.100 mol•L^{-1} sodium hydroxide solution is used to the endpoint of the titration then the concentration of the citric acid in the drink is:

A. 0.100 mol•L^{-1} B. 0.125 mol•L^{-1} C. 0.200 mol•L^{-1}
D. 0.250 mol•L^{-1} E. 0.500 mol•L^{-1}

6. Many people take zinc pills to boost their immune systems. Zinc can, however, impair the absorption of other minerals, so copper is added to maintain a balance. If a pill contains 49.37 mg of $ZnSO_4$ (M_r = 161.4), what mass of CuO (M_r = 79.5) should be added to give the correct Zn:Cu ratio of 10:1 **by mass**?

A. 2.00 mg B. 2.43 mg C. 2.50 mg D. 4.94 mg E. 7.95 mg

7. Highly charged ions, combined in simple 1:1 ratios, tend to make the strongest crystal lattices. Which of the following pairs of elements are therefore likely to form crystals with the highest melting (or decomposition) temperature?

A. Li, O B. Mg, O C. Ag, O D. Li, F E. Mg, F

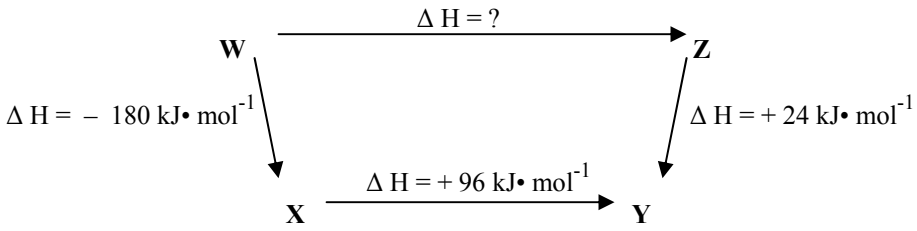
8. The table below shows the results of testing a number of colourless or white solids with hydrochloric acid solution. Which of the following substances could be sodium carbonate?

Substance	Observations
A.	Solid does not dissolve
B.	Solid dissolves, but does not give off a gas
C.	Solid dissolves, giving off a vinegary smell
D.	Solid dissolves, giving off a gas that turns limewater milky
E.	Solid dissolves, giving off a gas that relights a glowing splint

9. Which kind of attractive forces are likely to be holding particles together in a substance that melts at 681^{o}C and that conducts electricity when molten but not when solid?

A. Ionic bonding
B. Metallic bonding
C. Dipole-dipole interactions
D. Network covalent bonding
E. Covalent molecular bonding

10. The enthalpy change for the reaction W → Z cannot be measured directly, so it is determined using the following reaction pathway:

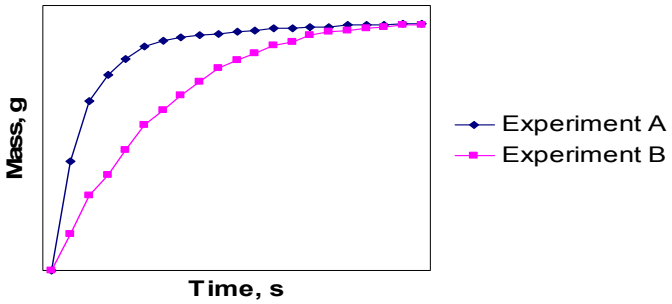


Which of the following is the correct value of ΔH in kJ• mol^{-1} for the reaction W → Z?

A. – 252 kJ• mol^{-1} B. – 108 kJ• mol^{-1} C. – 60 kJ• mol^{-1}

D. + 60 kJ• mol^{-1} E. +108 kJ• mol^{-1}

11. The following graph was plotted by a student using the data from two trials in which he studied the rate of a particular reaction, changing just one of the reaction conditions.



Unfortunately the student lost some of his notes, and when he tried to reconstruct them, he got one thing wrong. Only one of the following statements must be INCORRECT regardless of what the student did. Which one of the following must be the INCORRECT statement?

A. Exactly the same amounts of reactants were used in the two experiments
B. The final rate of reaction was greater in experiment A than in Experiment B
C. The reaction temperature was higher in Experiment A than in Experiment B
D. The mass of one of the products was being measured in the two experiments
E. The initial rate of reaction was greater in Experiment A than in Experiment B

12. Ammonia is manufactured from nitrogen and hydrogen in the Haber process, which is governed by the following equilibrium reaction:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)\ ;\ \Delta H = -92\ kJ{\bullet}mol^{-1}$$

Which of the following will NOT help to increase the amount of ammonia produced from a given amount of hydrogen?

A. Increasing the temperature
B. Increasing the pressure
C. Recycling the reactants
D. Removing ammonia as it is formed
E. Increasing the amount of nitrogen relative to the hydrogen used

13. Which of the following pairs represent isoelectronic species with identical Lewis structures?

A. CO, N_2 B. CO_2, SO_2 C. CS_2, $BeCl_2$ D. CO_2, NO_2^- E. CN^-, NO

14. A group of students is given 100 g of small crystals of $CuSO_4 \bullet 5H_2O$ (M_r = 249.7), which they dissolve in water. What is the approximate mass of the largest single crystal that they can possibly produce from their solution, assuming that 100 mL of solution remains at the end of the experiment along with their crystal? (The solubility of $CuSO_4 \bullet 5H_2O$ is 1.39 mol$\bullet$L^{-1} at the temperature of their experiment.)

A. 1.39 g B. 22.0 g C. 34.7 g D. 65.3 g E. 100.0 g

15. A solution of sulfuric acid used in a car battery has a concentration of 4.0 mol$\bullet$L^{-1}. What is its **theoretical** pH (assuming that it is fully dissociated)?

A. – 0.9 B. – 0.6 C. 0.0 D. + 0.4 E. + 0.6

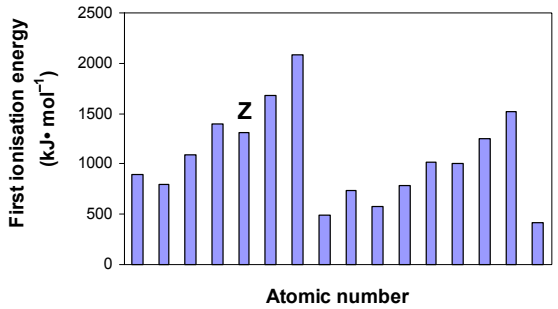
16. Which of the following aqueous solutions (1.0 mol$\bullet$L^{-1}) would react with magnesium ribbon to form hydrogen gas (H_2)?

A. LiCl B. NaBr C. KI D. NH_4Cl E. NH_3 (aq)

17. Which one of the following describes the effect of a catalyst on a chemical reaction?

	Activation energy	Enthalpy change of reaction
A	Decreased	Decreased
B	Decreased	No change
C	Decreased	Increased
D	No change	Decreased
E	Increased	No change

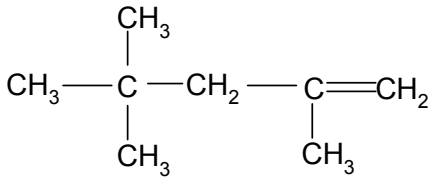
18. The following graph shows the variation in the first ionisation energy with atomic number for a consecutive series of elements in the Periodic Table. The element at which the graph starts is not specified.



In which group of the Periodic Table is the element Z?

A. 1 B. 3 C. 5 (IUPAC 15) D. 6 (IUPAC 16) E. 7 (IUPAC 17)

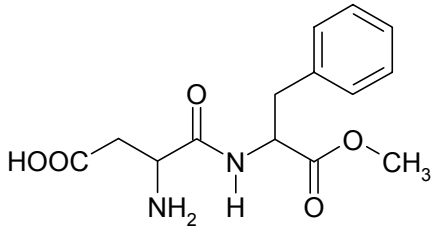
19. The following compound is used as an additive in gasoline to improve its octane value:



Which of the following is a correct IUPAC name for this compound:

A. 2,2,4-trimethyl-1-pentene
B. 2,2,4-trimethyl-2-pentene
C. 2,2,4-trimethyl-5-pentene
D. 2,4,4-trimethyl-1-pentene
E. 2,4,4-trimethyl-2-pentene

Questions 20 and 21 refer to aspartame, which is used as a sweetener in diet drinks. Its structural formula is:



20. The number of carbon atoms in one molecule of aspartame is

A. 12 B. 13 C. 14 D. 15 E. 16

21. The functional groups in aspartame include

A. Amine, ester and ketone
B. Amine, alcohol and ketone
C. Amine, ester and carboxylic acid
D. Alcohol, amine and carboxylic acid
E. Alcohol, ketone and carboxylic acid

22. Iodine dissolves in hot concentrated solutions of sodium hydroxide according to the equation:

$$aI_2(s) + bNaOH(aq) \rightarrow \mathbf{p}NaIO_3(aq) + \mathbf{q}NaI(aq) + aH_2O(l)$$

Where a, b, p and q are the stoichiometric coefficients in the correctly balanced equation.

This kind of reaction is known as disproportionation because one of the elements is both oxidised and reduced during the course of the reaction.

The values for **p** and **q** are respectively:

A. 1 and 1 B. 1 and 3 C. 3 and 3 D. 5 and 1 E. 1 and 5

23. The average bond enthalpy (or bond energy) of a C—F bond is 485 kJ• mol^{-1}. In which of the following processes is ΔH approximately equal to + 1940 kJ• mol^{-1}?

A. $CF_4(l) \rightarrow C(s) + 2F_2(g)$
B. $CF_4(g) \rightarrow C(s) + 2F_2(g)$
C. $CF_4(g) \rightarrow C(g) + 2F_2(g)$
D. $CF_4(g) \rightarrow C(s) + 4F(g)$
E. $CF_4(g) \rightarrow C(g) + 4F(g)$

24. Some students are trying to make a battery for a model car using a pencil lead (carbon graphite) and cooking foil (aluminium) as electrodes, with sodium chloride solution as electrolyte. Assuming that the carbon electrode is inert, what is the maximum voltage that this cell could produce under standard conditions? The relevant standard reduction potentials are:

$$Na^+(aq) + e^- \rightleftharpoons Na(s)\,;\ E^{\ominus} = -2.71\ V$$
$$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)\,;\ E^{\ominus} = -1.66\ V$$
$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)\,;\ E^{\ominus} = 0.00\ V$$

A. – 1.66 V B. – 1.05 V C. + 1.05 V D. + 1.66 V E. +2.71 V

25. Ammonium thiocyanate is a reagent used to test for iron(III) ions in solution, with which it gives a blood-red colour. The reaction takes place in a series of steps, the first step being:

$$Fe^{3+}(aq) + CNS^-(aq \text{ or } s) \rightleftharpoons [Fe(CNS)]^{2+}(aq)$$

In an experiment to find the equilibrium constant, K_c, for this step, 45.00 mL of a solution containing 0.200 mol•L^{-1} of Fe^{3+} is mixed with 5.00 mL of a solution containing 0.00200 mol•L^{-1} of CNS^-. The equilibrium concentration of $[Fe(CNS)]^{2+}$ in the mixture is found colorimetrically to be 1.99×10^{-4} mol•L^{-1}. Which of the following is the correct value of K_c at the equilibration temperature?

A. 9.0×10^{-4} B. 5.0×10^{-1} C. 5.5×10^{-1} D. 5.5 E. 1.1×10^{3}

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 2004

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. Acids and Bases

Acids and bases are the often the first things you learn about when you begin studying chemistry. Over the years, however, we expand our ideas about them to include a wide range of different compounds and reactions. In this essay you might like to consider the observable properties of acids and bases. You could discuss what is meant by an Arrhenius acid and base, giving examples of the simple reactions that they undergo. You might continue by considering other definitions, such as those for Brønsted-Lowry and Lewis acids and bases, indicating some of the reactions to which these definitions are applied. It is particularly important in this essay to give specific examples of acids and bases, and to write fully balanced symbol equations for the reactions you discuss.

2. Proteins

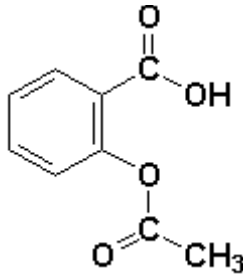
Proteins are important naturally occurring substances some of which are essential to the human diet. In this essay you should discuss what we mean by proteins and describe various possible primary, secondary and tertiary structures, preferably giving some specific examples. You might also like to consider how proteins may be denatured, and also how proteins can be analysed by chromatography and electrophoresis. It is particularly important in this essay to draw neat diagrams to illustrate your work.

3. Garbage Disposal and Recycling

In this essay you might like to consider the advantages and disadvantages of different methods of waste disposal, such as landfill sites and incineration. Recycling is often seen as a better alternative than disposal, but there are problems associated with this that you might like to consider. Remember that this is a chemistry essay, so you need to think about how specific substances (in particular pollutants) are dealt with in the disposal system. You might also like to consider some of the chemical engineering aspects of collecting and separating out different materials in the waste for disposal and recycling.

4. Experiment Design

Aspirin tablets are used to relieve pain and reduce fever. The main ingredient of the tablets is acetylsalycylic acid or (2-ethanoyloxy)benzoic acid, $C_9H_8O_4$, which has the following structural formula:



The aspirin is mixed in with a binding substance and other inert materials in the tablets. Each tablet has a mass of about 350 mg. It should be noted that aspirin is only sparingly soluble in water.

Design an experiment to determine the percentage by mass of acetylsalycylic acid in a batch of tablets. In your response you should give an outline of the procedure you intend to use, preferably including equations for any chemical reactions involved. You should give details of the apparatus and materials you would need for performing the experiment, and consider any safety precautions that might be required. You should also indicate what readings you would take, and how you would calculate the value required from your readings.

CHEMICAL INSTITUTE OF CANADA
and
CANADIAN CHEMISTRY OLYMPIAD
Final Selection Examination 2004

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 ____

Male ❒ Canadian Citizen ❒ Landed Immigrant ❒ Visa Student ❒

Female ❒ Passport valid until November 2004 ❒

Nationality of Passport _____

1. (12 marks)

Simplot's Brandon (Manitoba) manufacturing complex is one of the most diverse Nitrogen facilities in North America and ships over one million tonnes of product per year. The initial production is that of ammonia, based on a modification of the Haber–Bosch process. The most economical industrial production is achieved by using Alberta natural gas, air and the good local water supply for the reaction:

$$\underset{\text{methane}}{7CH_4} + \underset{\text{steam}}{10H_2O} + \underset{\text{air}}{8N_2 + 2O_2} \xrightarrow{\text{heat, pressure, catalyst}} \underset{\text{ammonia}}{16NH_3} + \underset{\text{carbon dioxide}}{7CO_2}$$

As with most industrial processes the conditions are a compromise involving not only chemical thermodynamics and kinetics, but also economics and safety. Under the selected conditions, reactions are run at near 500°C, 200–300 atm (~bar), with a porous iron catalyst. Efficiency of conversion of nitrogen and hydrogen to ammonia is about 20%.

The simplified reaction between nitrogen gas and hydrogen gas to produce ammonia gas is exothermic, releasing 92.4kJ/mol of energy at 298K (25°C).

i) Write the reaction of methane and steam to produce dihydrogen

ii) Write the reaction of dinitrogen with dihydrogen to produce ammonia.

iii) Write the equilibrium constant expression for the production of ammonia from dinitrogen and dihydrogen.

iv) Given that at 500°C the equilibrium constant for this ammonia production is about 8.00×10^{-2} $mol^{-2}\ L^2$, what is the concentration of ammonia in the processor when the concentration of H_2 is 2.00 mol L^{-1} and for N_2 is 1.20 mol L^{-1}?

v) Given the table:

Temperature	Mole % NH_3 at pressure (atm)			
(°C)	200 atm	300 atm	400 atm	500 atm
400	38.74	47.85	54.87	60.61
450	27.44	35.93	42.91	48.84
500	18.86	26.00	32.25	37.79
550	12.82	18.40	23.55	28.31
600	8.77	12.93	16.94	20.76

Estimate the pressure at which this plant was operating when producing ammonia at 500°C in part iv) above. For full marks you must show your work.

vi) Account for the data in the table part v) above with 60.6 mol % ammonia being the best yield shown at 400°C and 500 atm and the poorest yield of 8.8 mol % ammonia at 600°C and 200 atm pressure.

vii) Describe BRIEFLY factors other than thermodynamic considerations that determined the operating conditions in the Simplot Canada plant. Be as scientific as possible. Your answer must fit in the box below.

2. (12 marks)

2a) Medical texts indicate that lithium is used for the treatment of bipolar disorder (manic depression). It is believed it changes the strength of chemicals like serotonin and norepinephrine in the brain. Most often it is administered as lithium carbonate, Li_2CO_3, or lithium citrate. Since it is used in a population at relatively high risk for overdose, and desired blood serum levels of about 1.0 mmol L^{-1} Li^+ cannot be exceeded appreciably without risk, careful monitoring is necessary. Fortunately, it is absorbed only slowly and is excreted efficiently with a biological half–life from 18 to 30 hours, depending on the patient.

i) Assuming a blood volume about 4.7 L for a standard adult, what is the maximum concentration of serum Li^+ that can be attained by rapid absorption of a 300 mg pill of Li_2CO_3 ?

ii) In setting up the treatment protocol a concentration near 1.0 mmol L^{-1} has been maintained by a patient. Then a morning pill is omitted and the physician monitoring the blood finds that Li^+ blood level is 0.75 mmol L^{-1} after 9.0 hours. Assuming the excretion follows first order kinetics, what is the biological half–life of Li^+ for this patient?

2b) Hydrogen peroxide can be used as a disinfectant on small cuts since it goes through a decomposition reaction to form water and dioxygen which can kill germs. This process is quite slow at normal body temperature of 37°C, with an activation energy near 70 kJ/mol, but is much faster in the presence of blood containing an enzyme. The catalyzed mechanism, which is about 15 billion (15×10^9) times as fast, is proposed:

$H_2O_{2(aq)}$ + enzyme → [H_2O_2–enzyme complex] slow process

[H_2O_2–enzyme complex] → $H_2O_{(l)}$ + 0.5 $O_{2(g)}$ + enzyme rapid

i) Write the overall stoichiometric equation for production of one mole of dioxygen and the rate law equation for the catalyzed reaction.

ii) What is the activation energy for the catalyzed reaction (assuming the pre–exponential constant, A, in the Arrhenius relationship is the same for the normal and catalyzed reaction)?

2c) Codeine is a derivative of morphine used as an analgesic. Because it is addictive, codeine is only available by prescription, although formerly it was often used in over–the–counter cough syrups. Codeine is a weak monoprotic base, formula $C_{18}H_{21}NO_3$, in aqueous solution. Ten milligrams (10.0 mg) of codeine were dissolved in enough water to make 20.0 mL of solution. The pH of this solution was measured as 9.67.

What is the value of the base equilibrium constant K_b for codeine?
(For complete marks you must clearly show how you arrived at the correct value.)

3. (12 marks)

3a) In the past, calcium cyanamide ($CaCN_2$) was directly used as a fertilizer. In nature, its reaction with water (hydrolysis) releases fertilizing species in the environment. In this problem, we will look at the steps that are possibly involved in this process. For your information: The skeleton structure of CN_2^{2-} ion has the carbon atom located between the two nitrogen atoms.

A first hydrolysis step, done in a 1:1 molar ratio of $CaCN_2$ and H_2O, forms two intermediate, calcium–containing, ionic compounds: **A** and **B**. This first step can be described as a simple acid–base reaction. Compounds **A** and **B** are not thermally stable and decompose easily upon heating.

If **A** is thermally decomposed, it forms **C** and **D**, which are ionic and covalent compounds respectively. However, if **A** reacts with carbon dioxide, it forms the same covalent compound **D** with a new ionic compound **E**. Thermal decomposition of **E** gives **C** and CO_2.

Compound **B** reacts with carbon dioxide and water to form **E** and a new covalent compound **F**. Simple hydrolysis (in 1:1 molar proportion) of **F** leads to a single covalent compound **G** which is frequently used as a fertilizer. Complete hydrolysis of **G** forms CO_2 and another gas **H**.

i) What compounds are represented by letters **A** through **H**?

ii) Write the balanced chemical equations of all the reactions described in this problem.

iii) Draw the complete Lewis structure of **G**.

3b)

Silicon carbide and diamond are covalent solids which crystallize in a cubic structure. In silicon carbide, carbon atoms occupy points of a face–centered cubic lattice (fcc) and silicon atoms occupy half of the tetrahedral holes available. In diamond, the same proportion of tetrahedral holes is occupied by other carbon atoms.

Given that the density of silicon carbide is 3.21 g cm^{-3} and that of diamond is 3.51 g cm^{-3}, calculate the covalent radius of a silicon atom in silicon carbide crystal.

4. (12 marks)

The following half–reactions relate to the speciation of vanadium in aqueous solutions:

$2\ H^+ + 2\ e^-$	$\Leftrightarrow$	H_2	$E^o =$	0.000 V	
$V^{2+} + 2\ e^-$	$\Leftrightarrow$	V	$E^o =$	–1.175 V	(1)
$V^{3+} + e^-$	$\Leftrightarrow$	V^{2+}	$E^o =$	–0.255 V	(2)
$VO^{2+} + 2\ H^+ + e^-$	$\Leftrightarrow$	$V^{3+} + H_2O$	$E^o =$	0.337 V	(3)
$VO_2^+ + 2\ H^+ + e^-$	$\Leftrightarrow$	$VO^{2+} + H_2O$	$E^o =$	0.991 V	(4)
$V_2O_5 + 6\ H^+ + 2\ e^-$	$\Leftrightarrow$	$2\ VO^{2+} + 3\ H_2O$	$E^o =$	0.957 V	(5)
$V_2O_5 + 10\ H^+ + 10\ e^-$	$\Leftrightarrow$	$2\ V + 5\ H_2O$	$E^o =$	–0.242 V	(6)

i) Assign the oxidation states of the vandium found in each of the different vanadium–containing species appearing **on the left-hand side** of the half–reactions (1) through (5) shown above.

ii) By analysis of the above half–reactions, determine the ultimate chemical fate of a small piece of vanadium metal placed in contact with a 1 molar solution of a strong monoprotic acid HX, and in the presence of 1 atm of dihydrogen gas at 25°C. Show your work.

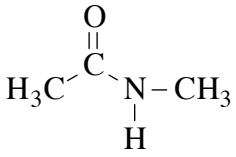
Note: it can be assumed that the conjugate base X^- does not interact, nor react with any of the vanadium species.

iii) What is the most stable vanadium–containing species at pH = 4 (all other conditions being standard)? Show your work.

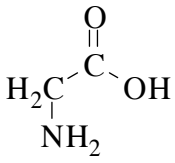
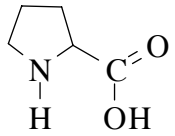
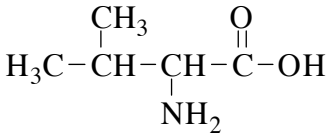
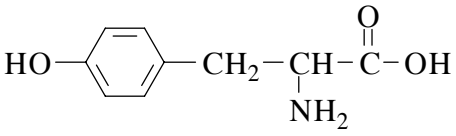
iv) Determine the exact pH range, under which a 1 molar solution of VO_2^+ would be stable if all other conditions are standard. Hint: The range is from acidic to slightly basic. Show your work.

5. (12 marks)

5a) All proteins are made up of many amino acid units linked together by peptide bonds (amide bonds). As an example, the following molecule (N–methylacetamide) contains an amide functional group:


N-methylacetamide

Here is the structure of 4 common amino acids:

Name	**Abbr'n**	**Structure**	**pKa of carboxylic acid**	**pKa of ammonium group**	**pKa of side chain**
Glycine	Gly		2.34	9.60	
Proline	Pro		1.99	10.60	
Valine	Val		2.32	9.62	
Tyrosine	Tyr		2.20	9.11	10.07

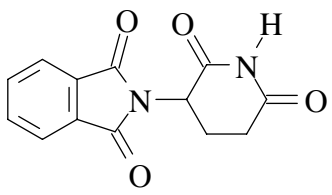
i) Draw the chemical structure of the following tripeptide at pH = 7.0 : Gly – Pro – Val
(Clearly indicate any formal charges)

ii) Give the structure, including any formal charges, of Tyrosine at the following pH:

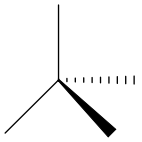
pH = 5.0	pH = 13

5b) Thalidomide was used in the 1950's as a sleeping pill and a treatment for morning sickness during pregnancy. Tragically, pregnant women who took the drug gave birth to severely deformed babies.

i) Circle the stereogenic or chirality center in thalidomide:

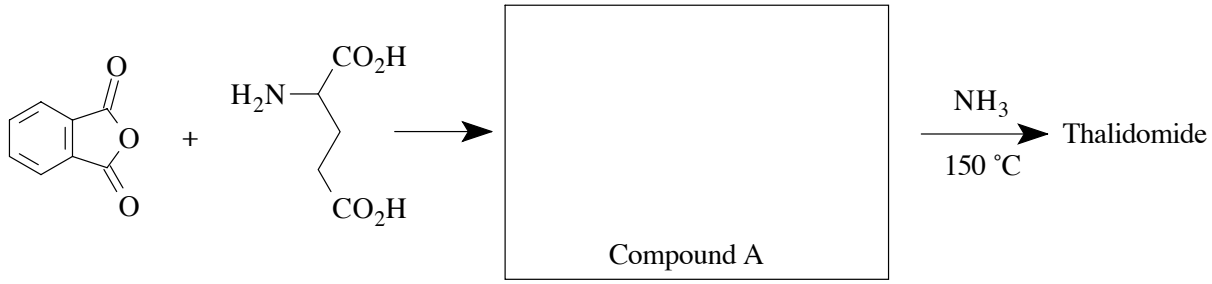


Thalidomide



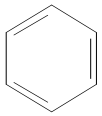
ii) In the above box, complete the partial structure showing the **R–isomer** of thalidomide

iii) Shown below is a simplified synthetic route leading to thalidomide.
Give the structure of A:

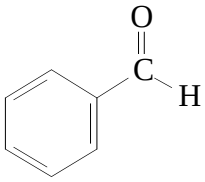


5c) In the early days of organic chemistry, the word aromatic was used to describe such fragrant substances as benzaldehyde (from cherries, peaches, and almonds) and benzene (from coal distillate). It was soon realized, however, that substances grouped as aromatic differed from most other organic compounds in their chemical behavior. They all have some common features. According to Hückel`s rule, an aromatic system must have the following properties:

- cyclic
- fully conjugated (a series of overlapping p orbitals)
- planar
- contain 4n+2 π–electrons (where n is an integer: 0,1,2,3...)

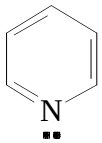


Benzene



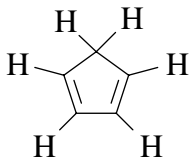
Benzaldehyde

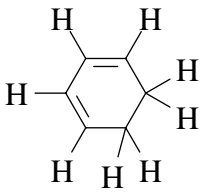
i) For each of the following compounds, indicate if they are aromatic and briefly explain your answer in the cases of any non–aromatic compounds:

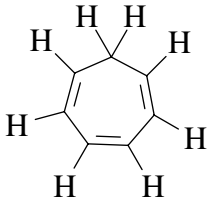
Compound	Aromatic?
	❑ Yes ❑ No. Explain why: _____ _____
	❑ Yes ❑ No. Explain why: _____ _____
	❑ Yes ❑ No. Explain why: _____ _____

ii) **Circle the compound** below which can lose a proton (H^+) to form an aromatic anion and indicate the hydrogen to be lost.

Underline the compound below which can lose a hydride ion (H^-) to form an aromatic cation and indicate the hydrogen to be lost.







END OF EXAMINATION