

93102





Scholarship 2013 Chemistry

2.00 pm Saturday 16 November 2013 Time allowed: Three hours Total marks: 40

Check that the National Student Number (NSN) on your admission slip is the same as the number at the top of this page.

You should answer ALL the questions in this booklet.

Pull out Resource Sheet S-CHEMR from the centre of this booklet.

If you need more room for any answer, use the extra space provided at the back of this booklet.

Check that this booklet has pages 2–24 in the correct order and that none of these pages is blank.

You are advised to spend approximately 35 minutes on each question.

YOU MUST HAND THIS BOOKLET TO THE SUPERVISOR AT THE END OF THE EXAMINATION.



You have three hours to complete this examination.

QUESTION ONE

(a) Multiple bonds, such as the carbon-carbon double bond found in ethene and the carbonoxygen double bond found in carbon dioxide, consist of two bonds that are of unequal bond energy. This can be seen from the data in the table below.

Bond	Bond dissociation energy for a single bond/kJ mol ⁻¹	Bond	Bond dissociation energy for a double bond/kJ mol ⁻¹
C–C	346	C=C	614
Si–Si	226	Si=Si	315
С–О	358	С=О	804
Si–O	466	Si=O	636
0–0	144	O=O	498

(i) Discuss the relative reactivity of ethane (C_2H_6) and disilane (Si_2H_6) and, based on the data given, suggest a reason why although ethene (C_2H_4) and ethyne (C_2H_2) are both well-known compounds, disilene (Si_2H_4) and disilyne (Si_2H_2) do not exist.

(ii) The products of the combustion reaction of Si(s)and C(s) are very different. SiO_2 forms a giant 3-D lattice with each silicon atom bonded to four oxygen atoms, each of which forms a bridge between two silicon atoms (see diagram). CO_2 forms a discrete molecule.



Compare and contrast the enthalpies of formation of SiO_2 and CO_2 both as giant lattices and as discrete molecules, using the data given below, and in the table on page 2.

Discuss the significance of the enthalpy values obtained and relate the physical properties of SiO_2 and CO_2 to their actual structure.

 ΔH (atomisation): Si = 450 kJ mol⁻¹, C = 717 kJ mol⁻¹

 $(\Delta H(\text{atomisation}) = \text{energy needed to form 1 mol of gaseous atoms from an element in its standard state.})$

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(b) Indium, In, forms three different ionic compounds when reacted with sulfur.

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Compound	Mass % indium	Melting Point/ °C
А	87.7	653
В	78.2	692
С	70.5	1 050

Determine the formulae of the three compounds, the electron configuration of indium in each compound and, hence, account for the variation in the melting point.



QUESTION TWO

(a) In electrolysis reactions, an electric current is used to force non-spontaneous reactions to occur. For electrolysis to occur, the voltage supplied must exceed the calculated cell voltage. When electrolysis takes place in aqueous solutions, the strongest oxidant in the solution reacts at one electrode, and the strongest reductant in the solution reacts at the other electrode.

An aqueous solution containing a mixture of nickel sulfate and cadmium chloride is electrolysed.

Compare and contrast the electrode reactions, the overall cell reaction, and the energy requirements of the cell when:

• both electrodes are platinum metal, and

half reaction	<i>E</i> ° /V
$2\mathrm{H}_{2}\mathrm{O}(\ell) + 2\mathrm{e}^{-} \rightarrow \mathrm{H}_{2}(g) + 2\mathrm{OH}^{-}(aq)$	-0.83
$\mathrm{Cd}^{2+}(aq) + 2\mathrm{e}^{-} \rightarrow \mathrm{Cd}(s)$	-0.40
$Ni^{2+}(aq) + 2e^{-} \rightarrow Ni(s)$	-0.25
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(\ell)$	+1.23
$\operatorname{Cl}_2(g) + 2e^- \rightarrow 2\operatorname{Cl}^-(aq)$	+1.36
$S_2O_8^{2-}(aq) + 2e^- \rightarrow 2SO_4^{2-}(aq)$	+2.01

• the anode is nickel metal, and the cathode is platinum.

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- (b) Ethanol is a widely discussed and implemented biofuel additive for petrol. Anhydrous ethanol is infinitely miscible (can mix in any ratio) with petrol or water, but petrol and water are immiscible (do not mix).
 - (i) Explain the observations for miscibility of the three compounds, assuming that petrol is a mixture of mostly C5 to C8 hydrocarbons.

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- (ii) Predict, with reasons, what you would observe when ethanol is added to water/petrol mixtures of varying proportions, and when water is added to ethanol/petrol mixtures of varying proportions.



- (c) Discuss the implications of introducing ethanol-petrol mixtures as vehicle fuels, given that:
 - almost all fuel systems (for storage and use) are open to the atmosphere in some way
 - salts, particularly those containing chloride, can greatly increase corrosion.

QUESTION THREE

Spermine is a polyamine found in a wide variety of organisms. Its structural formula is:

 $\mathrm{H_2N\,CH_2\,CH_2\,CH_2\,NH\,CH_2\,CH_2\,CH_2\,CH_2\,NH\,CH_2\,CH_2\,CH_2\,NH_2}$

The structure can also be represented in the following way, where each kink in the chain represents a CH_2 group.

H₂N NH NH₂

In the laboratory, spermine can be synthesised from putrescine, $C_4H_{12}N_2$, a naturally occurring compound, formed during the bacterial decay of animal flesh.

 $H_2 N CH_2 CH_2 CH_2 CH_2 NH_2$ or $H_2 N NH_2$

Each of the five compounds given below is a possible reagent for the reaction of putrescine to produce spermine.

CICCH, CH, CI	CI C CH ₂ CH ₂ OH	HO C CH, CH,CI
0	0	0
Compound A	Compound B	Compound C

HO C CH ₂ CH ₂ OH	HC CH ₂ CH ₂ OH
2 2	2 2
0	0
Compound D	Compound E

Suggest a synthetic route for **each** of these compounds reacting with putrescine to form spermine, and comment on reasons why Compound A is regarded as the 'best' starting material.

Information: Amides are more resistant to reduction than aldehydes and ketones, and thus require a stronger reducing agent than sodium borohydride. The commonest one used is lithium aluminium hydride, LiAlH, reducing an amide to an amine.

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QUESTION FOUR

(a) A buffer solution contains 0.25 mol L⁻¹ NH₃(aq) and 0.20 mol L⁻¹ NH₄Cl(aq).

The activity of an enzyme in 2.50 mL of this buffer solution produces hydrogen ions at the rate of 1.8×10^{-6} mol s⁻¹.

 $pK_{a}(NH_{4}^{+}) = 9.24$

(i) Calculate the pH of the initial buffer solution.

(ii) Calculate the pH after the enzyme has been active for 60 seconds (assuming there was no change to the volume).

$$H_3O^+(aq) + HCO_3^-(aq) \rightleftharpoons H_2CO_3(aq) + H_2O(\ell) \rightleftharpoons 2H_2O(\ell) + CO_2(aq)$$
 Equation 1

A partial titration curve for the conversion of H_2CO_3 to HCO_3^- at body temperature is given below.



Determine the $pK_a(H_2CO_3/HCO_3^-)$ at body temperature, and discuss where the normal pH of blood, 7.4, lies in relation to the optimum buffering range of this system.

(c) When there is an excess of H^+ and CO_2 in the blood as a result of strenuous exercise, the H_2CO_3/HCO_3^- buffer is unable to effectively control the pH of the blood, and the buffering action of haemoglobin becomes important in removing the extra H^+ . When the amount of H^+ exceeds the capacity of the haemoglobin buffer, the pH of the blood is lowered and this triggers deep-breathing responses to remove excess CO_2 from the blood.

Haemoglobin acts as a buffer through a series of equilibria involving protonationdeprotonation and oxygenation-deoxygenation. This can be shown simply by representing the haemoglobin molecule as containing only one acidic proton (HHb).

$\mathrm{HH} b \rightleftharpoons \mathrm{H} b^- + \mathrm{H}^+$	$pK_a = 8.18$	Equation 2
$\mathrm{HHbO}_2 \rightleftharpoons \mathrm{HbO}_2^- + \mathrm{H}^+$	$pK_a = 6.62$	Equation 3

Haemoglobin, HHb, binds oxygen gas, O_2 , more strongly at high pH and less strongly at low pH.

(i) Explain, using equilibrium principles, how the body maintains the pH balance in the blood during strenuous exercise, using the equations 1 to 3 given previously.

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(ii) Calculate the percentage dissociation of HHbO₂ and HHb at pH 7.4, and explain how these results show that the deoxygenation of haemoglobin leads to an uptake of proton by the protein.



QUESTION FIVE

A 1.1258 g sample of sulfur, S_8 , was burnt in the apparatus shown below. The gas trap contained a solution of hydrogen peroxide, $H_2O_2(aq)$. (Sulfur spontaneously ignites at ~250°C, well within the range of a Bunsen burner, and at lower temperatures if finely divided.) Suction was maintained to pull air through the apparatus for some time after combustion was complete.



Subsequently the solution in the gas trap was divided into four equal aliquots (parts). Barium chloride solution, $BaCl_2(aq)$, was added to each aliquot and the resulting white precipitate was collected by filtration under suction, washed with water, and dried to constant weight. The filtrates were also collected and each one titrated with 1.950 mol L⁻¹ sodium hydroxide solution, using a methyl orange indicator (p $K_a = 3.7$). The results are presented in the table below.

Aliquot	Mass of precipitate/g	Titre volume/mL
1	1.9367	8.52
2	1.9386	8.64
3	1.9417	8.54
4	1.9405	8.54

Analysis	results	for	gas	trap	solutio
1 111001 9 515	I COMICO	101	5.00		Solution

(a) Explain the chemistry that is occurring during this experiment, and calculate the apparent % purity of the sulfur sample using both sets of data supplied.



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Question Five continues on the following page.

(b) Two further experiments were performed. In Experiment 2, a second gas trap containing hydrogen peroxide solution was placed after the first one. In Experiment 3, a new gas trap containing only water was inserted between the combustion chamber and the gas trap containing hydrogen peroxide solution. Suction was again maintained to pull air through the apparatus for some time after combustion was complete. The samples in the gas traps were treated as before with BaCl₂ and any precipitate collected, dried, and the filtrates analysed by titration.

Explain how the two further experiments can be used to determine the efficiency of the apparatus and/or the nature of the products of the combustion reaction.

- (c) Discuss briefly the environmental implications of using carbon fuels that have a significant sulfur impurity.

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