

93102



# TOP SCHOLAR



NEW ZEALAND QUALIFICATIONS AUTHORITY  
MANA TOHU MĀTAURANGA O AOTEAROA

## 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 carbon-oxygen 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 <sup>-1</sup>	Bond	Bond dissociation energy for a double bond/kJ mol <sup>-1</sup>
C-C	346	C=C	614
Si-Si	226	Si=Si	315
C-O	358	C=O	804
Si-O	466	Si=O	636
O-O	144	O=O	498

- (i) Discuss the relative reactivity of ethane ( $\text{C}_2\text{H}_6$ ) and disilane ( $\text{Si}_2\text{H}_6$ ) and, based on the data given, suggest a reason why although ethene ( $\text{C}_2\text{H}_4$ ) and ethyne ( $\text{C}_2\text{H}_2$ ) are both well-known compounds, disilene ( $\text{Si}_2\text{H}_4$ ) and disilyne ( $\text{Si}_2\text{H}_2$ ) do not exist.

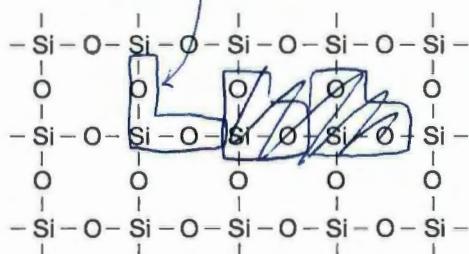
Disilane is possibly more reactive than ethane because the Si-Si bond energy of  $226 \text{ kJ mol}^{-1}$  is less than the C-C bond energy of  $346 \text{ kJ mol}^{-1}$ , possibly due to increased bond length arising from the larger Si atom. We can therefore safely assume that the Si-H bond energy <sup>also</sup> is <sup>high</sup> less than the C-H bond energy. A lower bond energy means a weaker bond because less energy is needed to be absorbed in an endothermic process to break the bond. Disilane is more reactive, therefore. In comparing the C=C bond energy to C-C, the C=C bond is  $\frac{614}{346} = 1.77 \times$  that of C-C, just under double the bond strength. However, Si=Si is only  $\frac{315}{226} = 1.39 \times$  that of Si-Si, not even 50% more strong. In relation to its saturated equivalents, the <sup>high</sup> C=C bond strength of  $614 \text{ kJ mol}^{-1}$  affords ethene a relative stability because greater energy is required to break the bond, while the <sup>low</sup> Si=Si bond strength of ~~315~~  $315 \text{ kJ mol}^{-1}$  means disilene is more reactive and less stable. It may spontaneously undergo reduction into disilane in ~~is~~ a thermodynamically favourable reaction where the creation of 2 new Si-H bonds (bond forming releases energy) more than compensates for the  $89 \text{ kJ mol}^{-1}$  energy difference between Si-Si and Si=Si.

The same can be assumed for disilyne in that multiple bond formation of silicon gives diminishing returns on bond energy and we can expect the ~~Si=Si~~ <sup>weaker</sup> bond to be relatively unstable in relation to both ~~the~~ C≡C (ethyne) and Si-Si.

in a 'unit cell', four Si-O bonds must be broken

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- (ii) The products of the combustion reaction of  $\text{Si}(s)$  and  $\text{C}(s)$  are very different.  $\text{SiO}_2$  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).  $\text{CO}_2$  forms a discrete molecule.

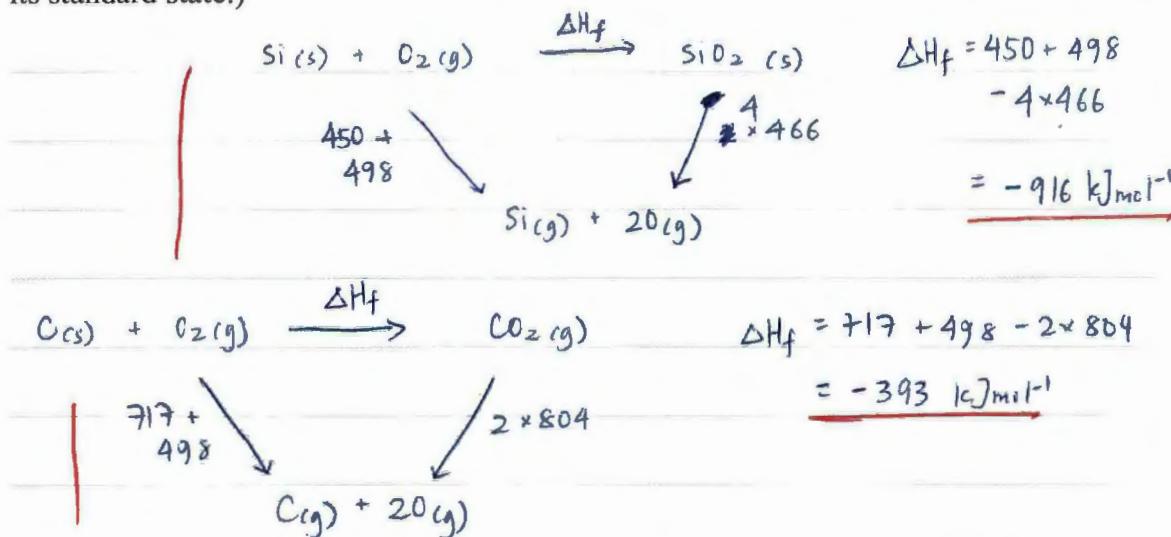


Compare and contrast the enthalpies of formation of  $\text{SiO}_2$  and  $\text{CO}_2$  both as giant lattices and as discrete molecules, using the data given below, and in the table on page 2.

Discuss the significance of the enthalpy values obtained and relate the physical properties of  $\text{SiO}_2$  and  $\text{CO}_2$  to their actual structure.

$$\Delta H(\text{atomisation}): \text{Si} = 450 \text{ kJ mol}^{-1}, \text{C} = 717 \text{ kJ mol}^{-1}$$

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



The enthalpy of formation of  $\text{SiO}_2$  is ~~heavily~~ more exothermic than that of  $\text{CO}_2$ . This makes it more likely/probable that  $\text{SiO}_2$  is a more stable structure because disregarding entropy changes, the Gibbs free energy change of a more exothermic reaction is more negative and favourable. The formation of a giant lattice in  $\text{SiO}_2$  means ~~more~~ <sup>four</sup> single bonds are formed per mole of Si whereas for C, two ~~be~~ double bonds are formed. It turns out that two Si-O bonds have a total bond energy greater than one C=O bond ( $2 \times 466 = 932$ ,  $932 > 809$ ), affording  $\text{SiO}_2$  greater chemical stability. However, the difference is not too great, and the C=O bond energy is still very strong, explaining the chemical stability of  $\text{CO}_2$ .

There is more space for your answer to this question on the following page.

$\text{CO}_2$  is a discrete molecule that exists as a gas. This is because  $\text{CO}_2$  is non-polar due to the symmetrical, linear nature of the molecule. (Even though  $\text{C}=\text{O}$  bond itself is polar) The electron clouds are also not very large, leading to small temporary-induced dipole forces. The minimal intermolecular forces lead to its low melting boiling point, and ability to sublime. Furthermore, its low solubility in water is also because of its non-polar nature, although some a fraction does react to form carbonic acid. With a Mr of  $44\text{ g mol}^{-1}$   $\text{CO}_2$  is denser than air.

$\text{SiO}_2$  exists as a solid with a very high melting point of several thousand  $^{\circ}\text{C}$ . Its network of strong covalent bonds holding the molecule together is very difficult to break. The tetrahedral arrangement of oxygens around Si ~~lens~~ makes very stable  $109.5^{\circ}$  bond angles.  $\text{SiO}_2$  is also insoluble in water due to its lack of polarity arising from symmetry. It is <sup>a</sup> very hard crystal that finds uses in furnace linings. It is a solid because the bonds extend continuously in all directions to create a macromolecule.

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

Compound	Mass % indium	Melting Point/ °C
A	87.7	653
B	78.2	692
C	70.5	1050

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.

A:	87.7 g In ; M = 115 ; n = 0.763 ; ratio = 2	12.3 g S. ; M = 32.1 ; n = 0.383 ; ratio = 1	B:	78.2 g In ; M = 115 ; n = 0.68 ; ratio = 1	21.8 g S ; M = 32.1 ; n = 0.679 ; ratio = 1	C:	70.5 g ; M = 115 ; n = 0.613 ; ratio = 2	29.5 ; M = 32.1 ; n = 0.919 ; ratio = 3
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Since indium is a metal, it will form a cation. Sulfur must be an anion, and sulfur forms  $S^{2-}$ .

A:  $\text{In}_2\text{S}$ . Indium has charge +1. It will be stabilised by the full s and d subshells / inert pair effect. It has configuration  $[\text{Kr}]5s^24d^10$ .

B:  $\text{InS}$ . Indium has charge +2. It has configuration  $[\text{Kr}]5s^14d^10$ .

C:  $\text{In}_2\text{S}_3$ . Indium has charge +3. It has configuration  $[\text{Kr}]4d^10$ .

From A to C: the anion stays same, but cation changes. Each time, the charge on the cation increases, giving greater attractive force to the  $\text{In}^{+}$  cation/  $\text{S}^{2-}$  anion ionic bond. Furthermore, the cation size decreases because there is less  $e^-$  repulsion and the nuclear charge can pull in the  $e^-$  cloud more closely to itself. In particular the jump from  $\text{In}^{2+}$  to  $\text{In}^{3+}$  is significant ( $692^\circ\text{C}$  to  $1050^\circ\text{C}$ ) possibly due to the removal of a complete electron subshell (5s). Thus ↑ charge, ↓ ionic radii = ↑ charge density. Thus, from  $\text{In}^+$  to  $\text{In}^{3+}$ , ↑ melting point ∵ less distance between cation + anion and greater attractive forces so more difficult to melt.

(ionic bond strength proportional to square of ~~distance~~ distance)

## 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
- the anode is nickel metal, and the cathode is platinum.

half reaction	$E^\circ / \text{V}$
$2\text{H}_2\text{O}(l) + 2\text{e}^- \rightarrow \text{H}_2(g) + 2\text{OH}^-(aq)$	-0.83
$\text{Cd}^{2+}(aq) + 2\text{e}^- \rightarrow \text{Cd}(s)$	-0.40
$\text{Ni}^{2+}(aq) + 2\text{e}^- \rightarrow \text{Ni}(s)$	-0.25
$\text{O}_2(g) + 4\text{H}^+(aq) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(l)$	+1.23
$\text{Cl}_2(g) + 2\text{e}^- \rightarrow 2\text{Cl}^-(aq)$	+1.36
$\text{S}_2\text{O}_8^{2-}(aq) + 2\text{e}^- \rightarrow 2\text{SO}_4^{2-}(aq)$	+2.01

When both electrodes are Pt, the strongest oxidant is  $\text{Ni}^{2+}$  because it has the highest  $E^\circ$  of the substances in solution ( $-0.25 > -0.40 \text{ V}$  for example).

The strongest reductant is  $\text{H}_2\text{O}$ , because of  $\text{H}_2\text{O}/\text{Cl}^-/\text{SO}_4^{2-}$  it has the lowest  $E^\circ$  at +1.23 V. Thus the overall cell reaction is



thus this cell needs at least 1.48 V of power to proceed. To produce one mole of Ni we need 2 moles of  $\text{e}^-$ , which is  $2 \times 96500 \text{ C} = 193000 \text{ C}$ .

At 1.48 V this is  $1.48 \text{ J/C} \times 193000 \text{ C} = 286 \text{ kJ}$ . //

When the anode is nickel, nickel is now the strongest reductant at -0.25 V, but  $\text{Ni}^{2+}$  is also the strongest oxidant. So at a cell potential of 0 V, Ni at the anode is being transformed into  $\text{Ni}^{2+}$  while at the cathode,  $\text{Ni}^{2+}$  is being reduced to Ni. no overall reaction occurs, and no energy input is required if the  $\text{Ni}^{2+}$  conc. is  $1 \text{ mol L}^{-1}$ .

~~(B) Electrochemistry~~

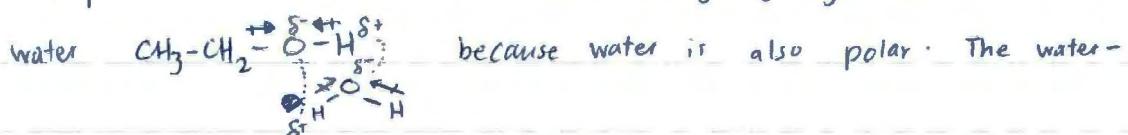
So the cell potential is 0V if the  $\text{Ni}^{2+}$  concentration is  $1\text{ mol L}^{-1}$ . If  $\text{Ni}^{2+}$  conc is  $\uparrow 1\text{ mol L}^{-1}$ , then spontaneous conversion of  $\text{Ni}^{2+}$  to Ni occurs. If  $\text{Ni}^{2+}$  conc is  $\downarrow 1\text{ mol L}^{-1}$ ,  $E^\circ$  of  $\text{Ni}^{2+}/\text{Ni}$  is lower than  $-0.25\text{ V}$  

- (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.

Ethanol is a polar molecule at one end ( $\text{C}-\text{OH}$ ) due to the electronegative O drawing  $e^-$  density towards itself. It can also form hydrogen bonds here. On the other end it is ~~is~~ a non-polar ~~weak~~ alkyl chain ( $\text{CH}_3\text{CH}_2-$ ), only capable of induced dipole forces.

The polar end allows ethanol to form strong hydrogen bonds with water



ethanol bonds are strong enough (release enough energy) for the disruption of  $\text{H}_2\text{O}-\text{H}_2\text{O}$  bonds to be compensated for. Ethanol can also mix well in petrol because of its ~~is~~ non-polar segment which forms induced dipole interactions with the petrol molecules of similar strength to the existing petrol-petrol van der Waals forces. However, water and petrol do not mix because ~~one~~ petrol, as only composed of C and H, is hydrophobic and cannot form strong energy-releasing H-bonds with water. Therefore petrol is not soluble in water, as it would break many  $\text{H}_2\text{O}-\text{H}_2\text{O}$  bonds.

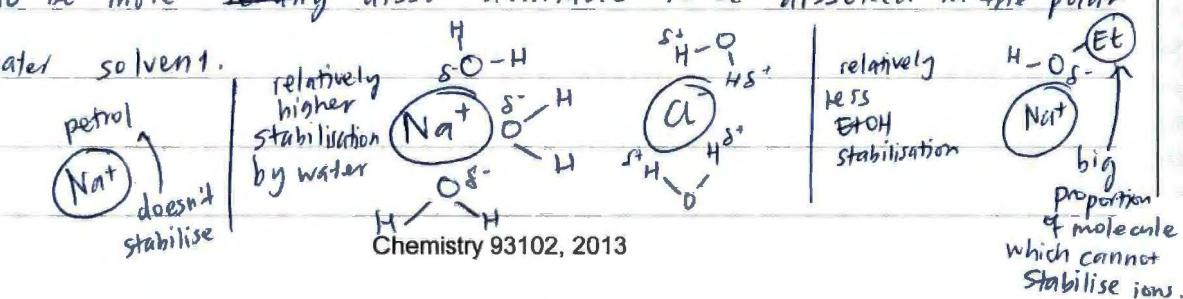
- (ii) Predict, with reasons, what you would observe when ethanol is added to water/petrol mixtures of varying proportions, and when water is added to ethanol/petrol mixtures of varying proportions.

There will initially be two layers, one water (at bottom) and one petrol (at top). When EtOH is added, it will dissolve in both solvents at a ratio determined by the partition coefficient constant. Both water + petrol layers will increase in size but possibly not <sup>in</sup> at an equal amount. The more the water originally, the more the water layer will be when EtOH is added, and the more EtOH there will be in the water layer.

Water will only mix with the ethanol and so the <sup>ethanol-</sup>petrol and water-EtOH portions will form two immisicible layers; ~~if the EtOH proportion is 1~~ whereas previously ~~there was~~ there was one ethanol-petrol layer. The greater the petrol proportion initially, the greater the petrol proportion when water is added. (despite some decrease in 'petrol' proportion due to removal of EtOH from petrol into the water layer).

- (iii) Explain how the solubility of a salt, such as sodium chloride, will vary as the composition of a water/petrol/ethanol mixture changes.

NaCl dissolves in water readily but not in petrol and probably ~~only~~ <sup>Slightly</sup> ~~very sparingly~~ in ethanol. Increasing the water proportion increases NaCl solubility. Increasing EtOH proportion might decrease NaCl solubility as it reduces the concentration of H<sub>2</sub>O in the mixture and thus makes it less possible for the Na<sup>+</sup> and Cl<sup>-</sup> ions to be stabilised as hydrated complexes. Increasing the petrol proportion will decrease overall solubility due to NaCl not being able to dissolve in the non-polar compound, but it might increase n(NaCl) dissolved in the water as more ethanol will be dissolved in the petrol instead of the water, leaving NaCl to be more ~~readily~~ <sup>more</sup> available to be dissolved in the polar water solvent.



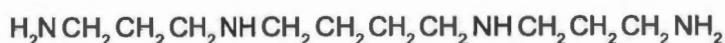
(c) Discuss the implications of introducing ethanol-petrol mixtures as vehicle fuels, given that:

- 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.

The atmosphere contains water ~~and~~ or water vapour and this may dissolve slightly in the fuel system due to the miscibility of ethanol and water, whereas water cannot dissolve /mix in a pure petrol fuel system. The presence of water is detrimental in a combustion reaction due to it acting as a coolant that cannot be combusted (reduces combustion efficiency) and hinders the combustion of ETOH. It can also allow salts to dissolve into the fuel system, which may arise from contamination of the fuel ~~or~~ supply or addition of  $\text{Cl}^-$  ions from the rain. This may increase corrosion of the engine and damage to the vehicle. However, ethanol also has environmental benefits in that it utilises a renewable resource which is sugar cane. It produces proportionally less  $\text{CO}_2$  because of the C-OH alcohol group which contributes relatively some oxygen. It is also <sup>1</sup>carbon neutral because while it releases  $\text{CO}_2$  into the atmosphere, that  $\text{CO}_2$  had been previously fixed by the sugar cane and removed from the atmosphere, although transport ~~of~~ of the fuel ~~will~~ and the fermentation process may still produce some extra  $\text{CO}_2$ . It is a greener alternative to conventional fossil fuels as sugar cane can be continuously grown and excess cane is not wasted. However, ETOH releases less energy per gram than petrol, because less rich in C-H bonds.

### QUESTION THREE

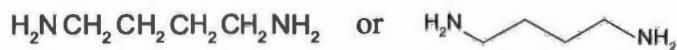
Spermine is a polyamine found in a wide variety of organisms. Its structural formula is:



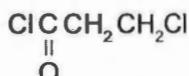
The structure can also be represented in the following way, where each kink in the chain represents a  $\text{CH}_2$  group.



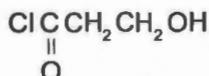
In the laboratory, spermine can be synthesised from putrescine,  $\text{C}_4\text{H}_{12}\text{N}_2$ , a naturally occurring compound, formed during the bacterial decay of animal flesh.



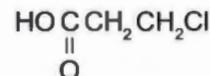
Each of the five compounds given below is a possible reagent for the reaction of putrescine to produce spermine.



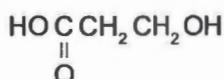
Compound A



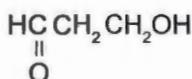
Compound B



Compound C



Compound D

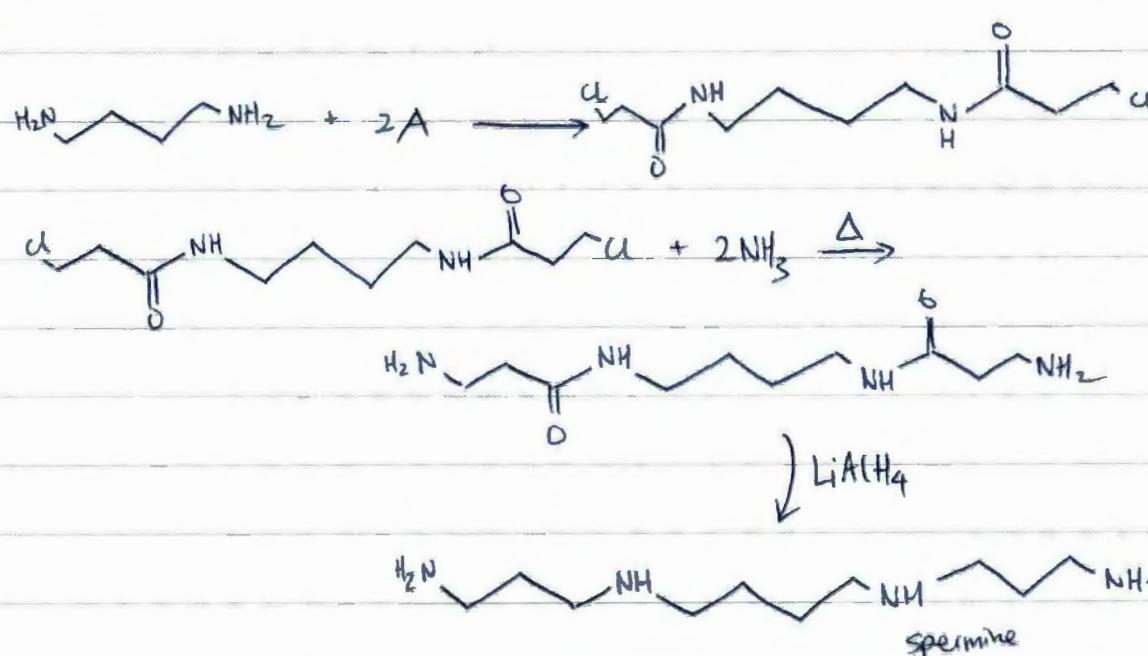


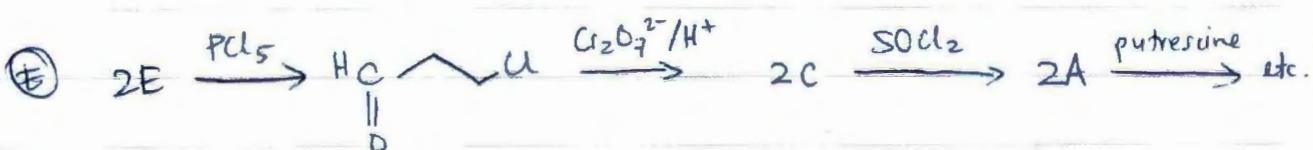
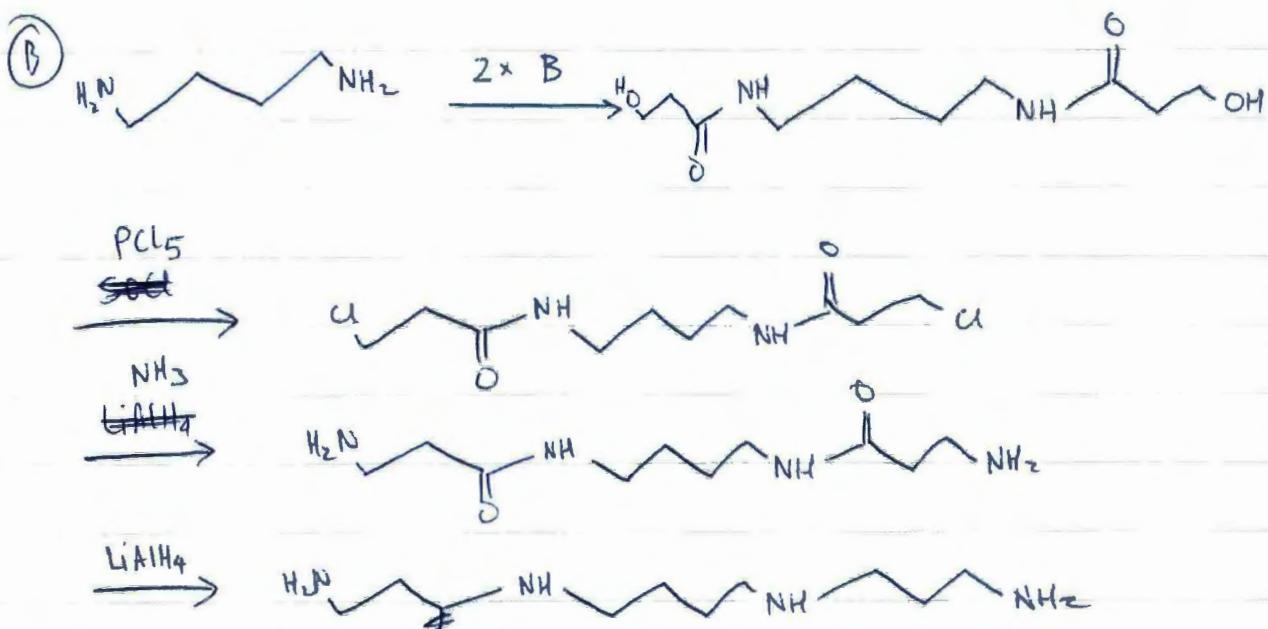
Compound E

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,  $\text{LiAlH}_4$ , reducing an amide to an amine.

(A)





Compound A utilises only 3 steps, whereas B, C, D use 4, and E uses 6. Steps in organic chemistry reduce yield, and so compound A can give the highest yield. Furthermore, more steps = more time and more reagents used = more costly. In fact C, D, E rely on conversion of starting compound to A in order to proceed. //

**QUESTION FOUR**

- (a) A buffer solution contains  $0.25 \text{ mol L}^{-1} \text{ NH}_3(aq)$  and  $0.20 \text{ mol L}^{-1} \text{ NH}_4\text{Cl}(aq)$ .

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

$$\text{p}K_a(\text{NH}_4^+) = 9.24$$

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

$$K_a = 10^{-9.24} = 5.754 \times 10^{-10} = \frac{[\text{H}^+][\text{NH}_3]}{[\text{NH}_4^+]} = \frac{[\text{H}^+] \times 0.25}{0.20}$$

$$[\text{H}^+] = 5.754 \times 10^{-10} \times 0.20 \div 0.25$$

$$= 4.6035 \times 10^{-10} \text{ M} \quad (\rightarrow A)$$

$$\text{pH} = -\log [\text{H}^+] = -\log 4.6035 \times 10^{-10}$$

$$= 9.34$$

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

$$60 \times 1.8 \times 10^{-6} \text{ mol} = 1.08 \times 10^{-4} \text{ mol}. \quad 1.08 \times 10^{-4} \div \frac{2.5}{1000} = 0.0432 \text{ mol L}^{-1}$$

$$0.0432 > 4.60 \times 10^{-10} \text{ so just take } [\text{H}^+]_{\text{initial}} = 0.0432 \text{ M.}$$

	$\text{H}^+$	$\text{NH}_3$	$\text{NH}_4^+$	$\text{H}^+ + \text{NH}_3 \rightarrow \text{NH}_4^+$
I	0.0432	0.25	0.20	
C	$-x$	$-x$	$+x$	
E	$0.0432-x$	$0.25-x$	$0.20+x$	<del><math>\text{H}^+ + \text{NH}_3 \rightarrow \text{NH}_4^+</math></del>

$$5.754 \times 10^{-10} = \frac{(0.0432-x)(0.25-x)}{(0.20+x)}$$

$$1.1508 \times 10^{-10} + 5.754 \times 10^{-10}x =$$

$$0.0108 - 0.2932x + x^2$$

$$x^2 - 0.2932x + 0.0108 = 0,$$

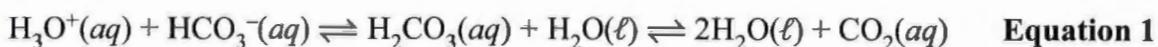
$$x = \frac{1}{2} \approx 0.0432$$

$$x = 0.043199999932$$

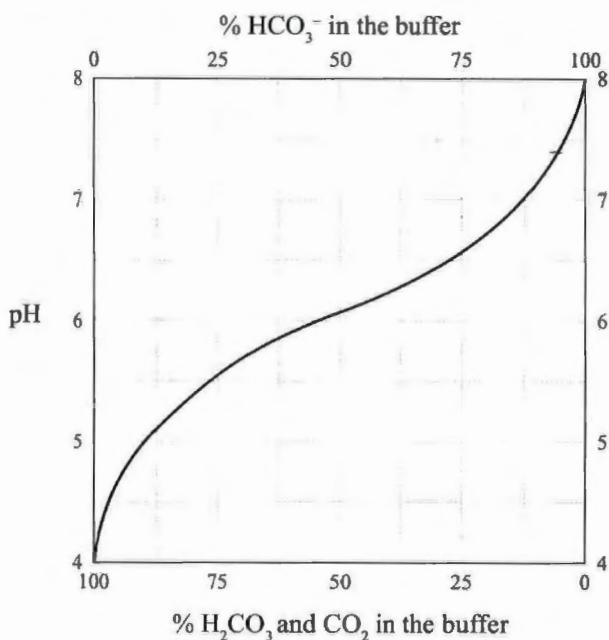
$$[\text{H}^+] = 0.0432 - 0.043199999932 = 6.8 \times 10^{-10}$$

$$\text{pH} = -\log [\text{H}^+] = 9.17$$

- (b) The carbonic acid-hydrogencarbonate buffer helps maintain the acid-base balance in the blood. The equilibrium reactions of interest are:



A partial titration curve for the conversion of  $\text{H}_2\text{CO}_3$  to  $\text{HCO}_3^-$  at body temperature is given below.



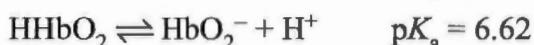
Determine the  $\text{p}K_a$  ( $\text{H}_2\text{CO}_3/\text{HCO}_3^-$ ) at body temperature, and discuss where the normal pH of blood, 7.4, lies in relation to the optimum buffering range of this system.

The  $\text{p}K_a$  is the  $\text{pH}$  when  $\text{H}_2\text{CO}_3 = \text{HCO}_3^-$ , ie at 50%. This can be read off to be at 6.1 - (half-titre point)

The pH of 7.4 relates to a %  $\text{HCO}_3^-$  of about 94% leaving only 6% as  $\text{H}_2\text{CO}_3/\text{CO}_2$ . This means that it is not in the most optimum buffering range of around pH 5.1 to 7.1. It also means that it is relatively easier for addition of acid (and particularly for addition of base) to change the blood pH.

- (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 protonation-deprotonation and oxygenation-deoxygenation. This can be shown simply by representing the haemoglobin molecule as containing only one acidic proton ( $HHb$ ).



**Equation 2**

**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.

When  $H^+$  conc increases, La Chatelier's principle states that the equilibrium will shift towards a direction to minimise that change, i.e. to consume  $H^+$ . Equations 2 and 3 will move backwards, consuming  $Hb^-$  and  $HbO_2^-$  in addition to  $H^+$  to form the protonated versions.

This is after Equation 1 has been shifted from a relatively high  $\frac{HCO_3^-}{H_2CO_3}$  ratio to one in which ~~all~~ the most of the  $HCO_3^-$  has already been used up as the  $HCO_3^- + H^+ \rightleftharpoons H_2CO_3$  equilibrium shifts to the right. As these equilibria shift, the  $H^+$  conc. decreases and so pH rises. As  ~~$H^+$  conc rises~~, when  $H^+$  conc rises, during exercise, the  $HbO_2^-$  shifts to the deoxygenated,  $Hb^-$  state. As the calculations on the next page show, this change increases the uptake of  $H^+$ , reducing  $H^+$  conc and minimising the potential decrease in pH due to exercise.  $Hb$  is intrinsically "wired" to accept more  $H^+$  when pH drops, acting as a negative feedback mechanism. ✓

- (ii) Calculate the percentage dissociation of HHbO<sub>2</sub> and HHb at pH 7.4, and explain how these results show that the deoxygenation of haemoglobin leads to an uptake of protons by the protein.

$$K_a = \frac{[H^+][sAH]}{[acid]}$$

$$[H^+] = K_a \times \frac{[acid]}{[sAH]}$$

$$pH = pK_a + \log \frac{[sAH]}{[acid]}$$

For HHb,  $7.4 = 8.18 + \log \frac{\text{salt}}{\text{acid}}$ ,  $\log \frac{sAH}{\text{acid}} = -0.78$   
 $\frac{sAH}{\text{acid}} = 0.166$ .

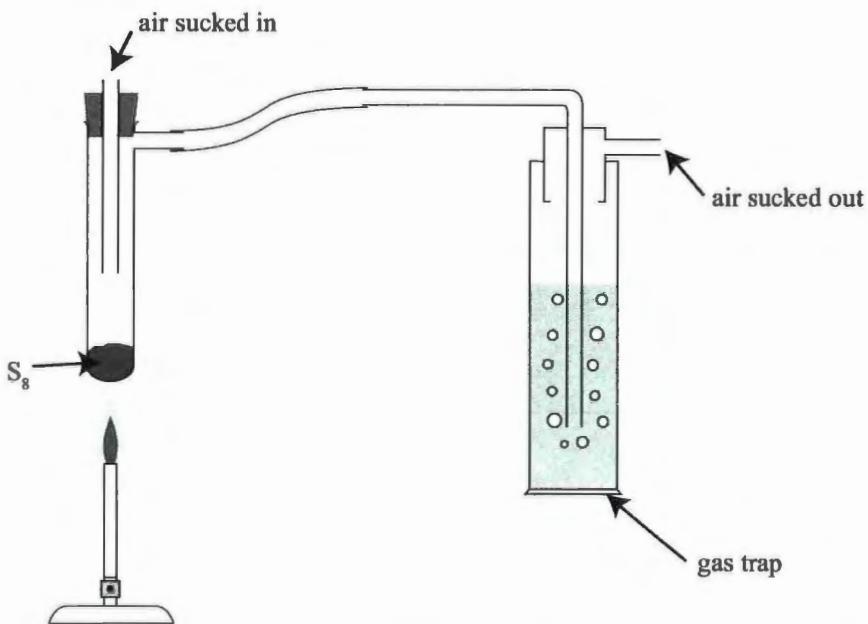
For HHbO<sub>2</sub>,  $7.4 = 6.62 + \log \frac{\text{salt}}{\text{acid}}$   
 $\frac{\text{salt}}{\text{acid}} = 6.026$ .

Thus when HHbO<sub>2</sub> is deoxygenated to HHb, the proportion of acid ~~is~~ compared to ~~salt~~ becomes much higher ( $0.166 < 6.026$ ) meaning that the Hb exists ~~is~~ more commonly / preferentially in the protonated state. Only 14% of HHbO<sub>2</sub> is in the protonated form, whereas 86% of HHb exists in the protonated form.

So deoxygenation is accompanied by the Hb taking up more H<sup>+</sup>

**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  $\sim 250^\circ C$ , 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.

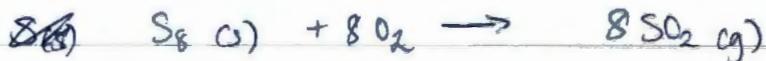


Subsequently the solution in the gas trap was divided into four equal aliquots (parts). Barium chloride solution,  $BaCl_2(aq)$ , was added to each aliquot and the resulting white precipitate was collected by filtration under suction, washed with water, and dried to constant weight. The filtrates were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

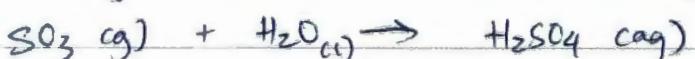
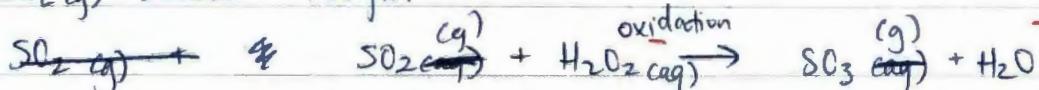
**Analysis results for gas trap solution**

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

- (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.



$SO_2(g)$  sucked through.





filtered out as white ppt.



$$\text{mass of ppt (average)} = \frac{1}{4} (1.9367 + 1.9386 + 1.9917 + 1.9403) \\ = 1.9394 \text{ g}$$

$$n(\text{BaSO}_4) = 1.9394 \text{ g} \div (137 + 32.1 + 16.0 \times 4) \text{ g mol}^{-1} = 8.3199 \times 10^{-3} \text{ mol}$$

$$n(\text{SO}_4^{2-}) \text{ total} = 4 \times 8.3199 \times 10^{-3} \text{ mol} = 0.03328 \text{ mol}$$

~~$$n(s) = n(\text{SO}_4^{2-}), m(s) = 0.03328 \text{ mol} \times 32.1 \text{ g mol}^{-1}$$~~

$$= 1.068 \text{ g}$$

$$\frac{1.068}{1.1258} \times 100\% = \underline{\underline{94.891\%}}$$

$$\text{titre avg} = 8.56 \text{ mL}$$

$$n(\text{NaOH}) = 1.950 \text{ mol L}^{-1} \times \frac{8.56}{1000} \text{ L} = 0.016692 \text{ mol}$$

$$n(\text{HCl}) \text{ total} = 0.016692 \times 4 = 0.066768 \text{ mol}$$

$$n(\text{SO}_4^{2-}) = \frac{1}{2} n(\text{HCl}) = 0.033384 \text{ mol}$$

$$n(s) = n(\text{SO}_4^{2-}), m(s) = 0.033384 \times 32.1 = 1.0716 \text{ g}$$

$$\frac{1.0716 \text{ g}}{1.1258 \text{ g}} \times 100\% = \underline{\underline{95.188\%}}$$



slightly higher because we included  
8.64 as an acceptable titre when  
in fact it was not concordant.

so we could have not used 8.64 ~~(15)~~

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  $\text{BaCl}_2$  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.

In the ~~first one~~ experiment 2, we can use the second gas trap of  $\text{H}_2\text{O}_2$  to test if all the gas had been collected by the first gas trap. If we get a titre value for the 2nd gas trap or it ppt is formed, then we can say not all  $\text{SO}_2/\text{SO}_3$  captured by first gas trap. Our % purity would be an underestimate.

$\text{SO}_3$  readily dissolves in water but  $\text{SO}_2$  doesn't, so by testing the water gas trap and the  $\text{H}_2\text{O}_2$  gas trap we can determine the ratio of  $\text{SO}_2/\text{SO}_3$  produced using ratio of ppt weights or ratio of titre values. The  $\text{SO}_2$  would move past the water gas trap and into the  $\text{H}_2\text{O}_2$  one, being oxidised to  $\text{SO}_3$  as before.

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

In the burning of carbon fuels eg. petrol, ~~etc~~ coal etc, we also burn the sulfur impurities to  $\text{SO}_2(\text{g})$  which is released into the atmosphere, eg in car exhaust. If untreated ~~by~~ by processes such as flue gas desulfurization, the  $\text{SO}_2$  is readily oxidised to  $\text{SO}_3$  by oxygen in the air, and the  $\text{SO}_3(\text{g})$  dissolves in rain / water vapour / clouds to form acid rain. Acid rain damages forests, rivers, soils and carbonate structures by changing the pH / dissolving the limestone. Rivers may be too acidic for fish to live in and forests may be killed off by the strong sulphuric acid (which may be increased in potency by other acids like  $\text{HNO}_3$ ).