

Assessment Schedule – 2013

Scholarship Chemistry (93102)

Evidence Statement

Question	Evidence
<p>ONE (a)(i)</p> <p>(ii)</p>	<p>The Si–Si bond is weaker than the C–C bond, so Si₂H₆ would be expected to be more reactive, since the bond is more easily broken.</p> <p>For Si=Si, the second bond is considerably weaker than the first bond, so forming single bonds would be more favourable than forming a second double bond (more E released). However, for C=C, the second bond, while weaker than the first, is still considerably large, making the formation of the double bond relatively favourable. It would be expected that the triple bond would be even weaker for Si–Si, making the possibility of a Si₂H₂ molecule highly unlikely.</p> <p>For Si forming SiO₂ network solid: $\text{Si}(s) + \text{O}_2(g) \rightarrow \text{SiO}_2(s)$ $\Delta_f H = 450 + 498 - 4 \times 466 = -916 \text{ kJ mol}^{-1}$</p> <p>For Si forming SiO₂ molecule: $\Delta_f H = 450 + 498 - 2 \times 636 = -324 \text{ kJ mol}^{-1}$ Suggests that network lattice is more energetically favourable.</p> <p>For C forming CO₂ molecule: $\text{C}(s) + \text{O}_2(g) \rightarrow \text{CO}_2(s)$ $\Delta_f H = 717 + 498 - 2 \times 804 = -393 \text{ kJ mol}^{-1}$</p> <p>For C forming CO₂ network lattice: $\Delta_f H = 717 + 498 - 4 \times 358 = -217 \text{ kJ mol}^{-1}$ Suggests that CO₂ molecule is more energetically favourable.</p> <p>Since the carbon-oxygen, second bond is stronger than the single bond, it means that double bonds are energetically more favourable than forming another C–O single bond. However since Si–O bond is much stronger than Si=O, it is more likely to form single bonds than double bonds. Therefore, carbon forms discrete molecules with (strong / favourable) double bonds, whereas Si–O forms a 3D lattice of more favourable Si–O single bonds. Since CO₂ forms discrete molecules, which are non-polar, they have weak intermolecular forces of attraction, which are easily broken, and CO₂ is a gas at room temperature. SiO₂ only forms strong covalent bonds in the solid state, and hence it takes a large amount of energy to separate the atoms, giving SiO₂ a very high melting point.</p>
(b)	<p>A = In₂S, so In⁺ electron configuration is [Kr] 4d¹⁰ 5s² B = InS, so In²⁺ electron configuration is [Kr] 4d¹⁰ 5s¹ C = In₂S₃, so In³⁺ electron configuration is [Kr] 4d¹⁰</p> <p>Since these are ionic compounds, the melting point is dependent on both the charge and the size of the ions. It will increase with increasing charge and with smaller ions.</p> <p>Hence, it would be expected that In²⁺ ions would form a stronger bond than In⁺. However, there is not a big difference in the size of these two ions since the electron lost in going from In⁺ to In²⁺ is from the same shell / orbital so, although there is a reduction in the electron-electron repulsions, the change in size is only small. Hence, the major reason for the difference in melting point is the higher charge on the ion.</p> <p>Going from In²⁺ to In³⁺, the ion has one less energy level so will be significantly smaller. The combination of the higher charge and the much smaller ion has a big effect on the strength of the ionic bond, and hence the melting point is much higher.</p>

Marker Allocation

Question One

7-8 marks

Discussion is fully integrated, well planned, fluent and coherent, uses appropriate chemical symbols and terms, and includes:

- (a) reactivity of the given compounds related to the stability of the single and double bonds (given) and the triple bonds (implied by the trend)
structures of CO_2 and SiO_2 are justified from enthalpy of formation values for all 4 proposed structures (calculated) and may include discussion of double and single bonds, and structure related to physical properties of the compounds
- (b) comparison of ionic charge and size identified from electron configurations and used to account for variation in melting points.

5-6 marks

Discussion is well organised and coherent, uses appropriate chemical symbols and terms, and includes:

- (a) reactivity of the given compounds related to the stability of the single, and double bonds (given) OR the triple bonds (implied by the trend)
structures of CO_2 and SiO_2 are justified from enthalpy of formation values for at least 2 of the proposed structures (calculated) and structure is related to the physical properties of the compounds
- (b) relates variation in the melting points to different ionic charge and size, determined from electron configurations.

1-4 marks

Answers include:

- relating the reactivity to the relative strength of the bonds given
- calculations of enthalpy of formation for some of the proposed structures
- relating physical properties to the actual structures of the given compounds
- comparison of ionic properties linked to electron configurations
- links between melting point and ionic properties.

Question	Evidence
TWO (a)	<p>At the cathode, reduction will occur.</p> <p>There are 3 possible reduction reactions – involving Ni^{2+}, Cd^{2+} and H_2O. The strongest oxidant is Ni^{2+}, as it has the most positive reduction potential, so Ni metal will form at the cathode.</p> $\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ni}(\text{s})$ <p>At the anode, oxidation will occur.</p> <p>The 3 possible oxidation reactions involve H_2O, Cl^- and SO_4^{2-}.</p> <p>The strongest reductant of these has the lowest reduction potential, so water will be oxidised and bubbles of oxygen gas will be observed at the anode.</p> $2\text{H}_2\text{O}(\ell) \rightarrow \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^-$ <p>Overall reaction equation:</p> $2\text{Ni}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\ell) \rightarrow \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 2\text{Ni}(\text{s})$ <p>E° for this reaction is $-0.25 \text{ V} - (1.23 \text{ V}) = -1.48 \text{ V}$.</p> <p>The negative sign indicates that the reaction as written is not spontaneous, so energy is needed for it to occur.</p> <p>When an Ni electrode is used in place of a Pt electrode as the anode, the Ni has a stronger tendency to oxidise than any of the other species present. This means that the reaction becomes:</p> $\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ni}(\text{s})$ <p>and $\text{Ni}(\text{s}) \rightarrow \text{Ni}^{2+}(\text{aq}) + 2\text{e}^-$</p> <p>The electrode potential will be zero, so very little energy is needed for this reaction to occur.</p> <p>However, the evidence that a reaction is occurring will be the deposition of Ni on the electrode.</p>
(b)(i)	<p>$\text{CH}_3\text{CH}_2\text{OH}$ molecules have a ‘polar’ and a ‘non-polar’ end. This means that they can interact with water molecules (they have the ability to H-bond to water with the $-\text{OH}$ group of the alcohol functional group). The CH_3CH_2- group is non-polar, so can form instantaneous – induced dipole forces with the non-polar petrol molecules.</p> <p>Hence, ethanol can dissolve in either of these substances. However, since the polarity of the water and the petrol molecules are different, the forces of attraction between the two molecules are not sufficient to overcome the forces of attraction between the molecules in each of the pure substances, and hence the water and petrol will not dissolve in each other.</p>
(ii)	<p>Adding ethanol to a water / petrol mixture would lead to a homogeneous mixture, as the ethanol is soluble in both – the non-polar end will interact with the ‘petrol’ molecules and the polar end will H-bond with the water molecules.</p> <p>Small amounts of water will be soluble in an ethanol / petrol mixture, but as the amount of water is increased, a point will be reached where there will be a separation into water and petrol phases, with ethanol being present in both.</p>
(iii)	<p>Salt solubility will increase with the water concentration in the mixture, as energy released by the ion-water interactions is sufficient to overcome the lattice energy of the salt and the H-bonding interactions of the water molecules.</p> <p>This is also the case, to a lesser extent, with the salt-ethanol interactions.</p> <p>However, there is little interaction between the ions and the non-polar petrol molecules, so the salts will not dissolve in the petrol. (Increasing disorder / entropy with mixing and dissolving too).</p>
(c)	<p>The answer to (b) should lead to the idea that mixtures containing significant amounts of ethanol in petrol will support dissolution of water. The presence of water vapour in the atmosphere (and generally in the environment) will lead to water being introduced to the mixture (through dissolution equilibria), with the effect being greater in humid environments.</p> <p>If the amount of water increases, it may get to a point that phase separation could occur. This would make for a much less efficient system. Higher water content will lead to a much higher likelihood of contamination by salts of various kinds, because of the better solubility, and then there will be more corrosion. In short, high fractions of ethanol in fuel might be desirable to replace fossil fuels with sustainable alternatives, but the risks increase with the size of that fraction.</p>

Marker Allocation

Question Two

7-8 marks

Discussion is fully integrated, well planned, fluent and coherent, uses appropriate chemical symbols and terms, and includes:

- (a) comparison of cell reactions and energy requirements, including equations
- (b) polarity of molecules and consequences for miscibility of compounds, and observations of mixtures of varying proportions and solubility of salts
- (c) implications related to dissolution of water and salt in ethanol.

5-6 marks

Discussion is well organised and coherent, uses appropriate chemical symbols and terms, and includes:

- (a) identification of cell reactions and energy requirements, including equations
- (b)&(c) polarity of molecules and consequences for miscibility of compounds, AND attempts to describe observations of mixtures of varying proportions and solubility of salts OR gives implications related to dissolution of water or salt.

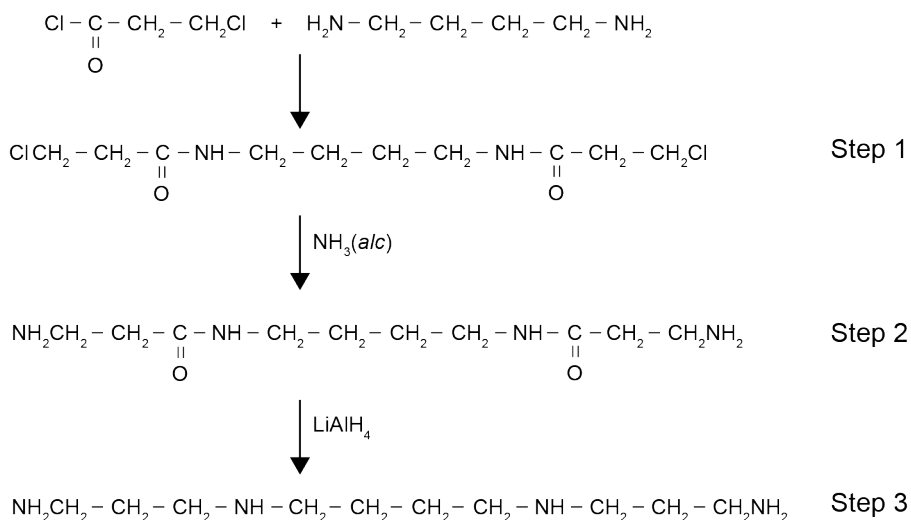
1-4 marks

Answers include:

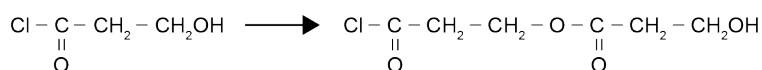
- identification of cell reactions and energy requirements, including equations
- polarity of molecules related to miscibility
- description of mixtures of varying proportions
- discussion of solubility of salts in different solvents.

QUESTION THREE

Compound A

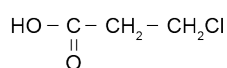


Compound B



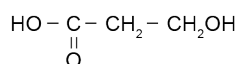
This compound would not exist in solution as it has the ability to self polymerise. The acid chloride and the alcohol can form an ester functional group. A dimer is shown, but this has the potential to polymerise further.

Compound C



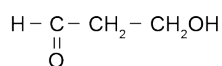
This compound would first need to be reacted with SOCl_2 to form Compound A, and then the reaction would proceed as described above. Reaction of Compound C directly with putrescine would result in a salt. OR with heat, there is the potential of the acid group to react with putrescine to form the amide, then proceed from Step 2 above.

Compound D



Needs to be converted to Compound A using SOCl_2 etc, then react as Compound A. OR with heat there is the potential for the acid group to react with the amine to form an amide, then substitute the alcohol for Cl, then proceed from Step 2 above.

Compound E



React with SOCl_2 to convert $-\text{OH}$ to $-\text{Cl}$, then oxidise the aldehyde to acid, then as for Compound C. Also there is added potential for multiple alkylations.

Compound A is the 'best' choice as it has fewer steps and less possibility of extra alkylations at the amine group.

Marker Allocation

Question Three

7-8 marks

Answer is correct, well planned and not repetitive (ie developed so as to take similarities between synthetic routes into account). Comparisons of efficiency of each synthetic route with that starting with Compound A are fluent, coherent and sensible.

5-6 marks

Answer is mostly correct and shows evidence of planning. Comparisons of efficiency of most synthetic routes, with that starting with Compound A, are coherent and sensible.

1-4 marks

Answers include:

- synthetic routes using the starting materials provided
- identification of difficulties with some of the starting materials or the synthetic routes described.

Question	Evidence
FOUR (a)	(i) pH = 9.34 (ii) pH = 9.16
(b)	<p>$pK_a = 6.1$ At this point the acid and conjugate base concentrations are the same. The buffering capacity is $pH = pK_a \pm 1$. Outside of this range, it can be seen that the pH rise is much more rapid, and so the buffering ability has been lost.</p>
(c)(i)	<p>Increasing the CO_2 causes increase in H^+ because of the equilibrium: $CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$ The increase in H^+ causes a reaction with the conjugate bases of the buffers given: $H^+ + Hb^- \rightleftharpoons HHb$ and $HbO_2^- + H^+ \rightleftharpoons HHbO_2$ The first reaction is more favourable, as HHb can bond H^+ more strongly (size of pK_a). Low pH will trigger the release of O_2, thus producing more HHb, increasing the uptake of H^+. Excess H^+ in the blood (not absorbed by the buffer system) will shift the carbonic acid equilibrium to the left, and removing CO_2 from the lungs during heavy breathing, will reduce the H^+ and increase the pH, so that the required blood pH is maintained.</p> <p>(ii)</p> <p>For oxygenated Hb: $HHbO_2 \rightleftharpoons HbO_2^- + H^+$ $K_a = [HbO_2^-][H^+] / [HHbO_2] = 2.40 \times 10^{-7}$ $[HbO_2^-] / [HHbO_2] = 2.40 \times 10^{-7} / 3.98 \times 10^{-8} = 6.03$ % dissociation = 85.7%</p> <p>For deoxygenated Hb: $HHb \rightleftharpoons Hb^- + H^+$ $K_a = [Hb^-][H^+] / [HHb] = 1.6 \times 10^{-9}$ $[Hb^-] / [HHb] = 1.6 \times 10^{-9} / 3.98 \times 10^{-8} = 0.166$ % dissociation = 14.3%</p> <p>Since the HHb is less dissociated at $pH=7.4$ than $HHbO_2$, it will be more effective in removing H^+ from solution at this pH, as it has a stronger tendency to accept protons than the oxygenated form. So deoxygenating the blood allows more uptake of H^+.</p>

Marker Allocation**Question Four****7-8 marks**

Calculations are correct. Discussion is fully integrated, well planned, fluent and coherent, uses appropriate chemical symbols and terms, and includes:

- (a) recognition of limits for buffering capacity
- (b) recognition of the role of the given equilibria in maintaining the pH of blood and the significance of the size of pK_a in determining the species involved in the uptake of H^+
- (c) links between percentage dissociation and uptake of H^+ .

5-6 marks

Calculations are mostly correct. Discussion is well organised and coherent, uses appropriate chemical symbols and terms, and includes at least TWO of:

- (a) recognition of limits for buffering capacity
- (b) recognition of the role of the given equilibria in maintaining the pH of blood and the significance of the size of pK_a in determining the species involved in the uptake of H^+
- (c) links between percentage dissociation and uptake of H^+ .

1-4 marks

Answers include:

- correct calculations / correct methods for calculations
- appropriate chemical equations
- recognition of limits for buffering capacity
- recognition of the role of the given equilibria in maintaining the pH of blood
- recognition of the significance of the size of pK_a in determining the position of an equilibrium
- links between percentage dissociation and uptake of H^+ .

Question	Evidence
FIVE (a)	<p>Sulfur burns in air to produce SO₂.</p> $\text{S}(s) + \text{O}_2(g) \rightarrow \text{SO}_2(g)$ <p>In the gas trap – SO₂ is oxidised to SO₃</p> $\text{H}_2\text{O}_2 + \text{SO}_2 \rightarrow \text{H}_2\text{O} + \text{SO}_3$ $\text{SO}_3(g) + \text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{SO}_4(aq)$ <p>The sulfate is precipitated out as BaSO₄.</p> <p>From the mass of the precipitate, we can work out the mass of sulfur present.</p> <p>This leads to the percentage purity of sulfur.</p> <p>Total mass of BaSO₄ = 7.7575 g = 0.033269 mol</p> $\text{Mass of S collected} = 0.033269 \times 32.07 = 1.0669 \text{ g}$ <p>Using the titration data: $n(\text{OH}^-) = 0.01665 \text{ mol}$ $n(\text{SO}_4^{2-}) = 0.03331 \text{ mol}$</p> $m(\text{S collected}) = 0.03331 \text{ mol} \times 32.07 \text{ g mol}^{-1} = 1.06825 \text{ g}$ <p>Implies percentage purity is 95%.</p> <p>This result could either be from the purity of the sulfur or the equipment used in the experiment – need to know that all the product of burning the sulfur was trapped and contained in the experiment.</p>
(b)	<p>Experiment 2: Check to see if all the SO₂ was dissolved in the solution in the gas trap, or if some was in the extracted air. Checks on the equipment will help ascertain if the result was because of the purity of sulfur or experimental technique. Any precipitate formed in the reaction vessel could be added to the answer above.</p> <p>Experiment 3: Would show if there was any SO₃ produced during the combustion reaction, as this would form H₂SO₄ with the water and be precipitated with the added Ba²⁺.</p>
(c)	<p>Implications for the environment are in the acidic nature of the sulfur oxides and the potential to create acid rain.</p>

Marker Allocation

Question Five

7-8 marks

Calculations are correct. Discussion is fully integrated, well planned, fluent and coherent, uses appropriate chemical symbols and terms, and includes:

- an explanation of the chemistry involved in terms of the combustion reaction products and their identification
- recognition of the reasons for the experiments 2 and 3
- implications for the environment when carbon fuels are burned based on the results of the experiment.

5-6 marks

Calculations are mostly correct. Discussion is well organised and coherent, uses appropriate chemical symbols and terms, and includes at least TWO of:

- an explanation of the chemistry involved in terms of the combustion reaction products OR their identification
- &(c) some recognition of the reasons for the experiments 2 and 3 OR the implications for the environment when carbon fuels are burned based on the results of the experiment

1-4 marks

Answers include:

- correct calculations / correct methods for calculations
- appropriate chemical equations
- identification of some of the chemistry involved in the combustion reaction
- identification of some of the chemistry involved in the identification of the products of the combustion reaction
- identification of the reasons for the extra experiments
- identification of the implications for burning carbon fuels based on the experimental results.