Assessment Schedule 2007 Scholarship Chemistry (93102)

Evidence Statement

Question	Evidence	Mark Allocation
1(a) (i)	“*Chemical reactions occur to enable atoms to obtain full outer electron shells or octets”.* eg hydrogen and chlorine gases react spontaneously to form hydrogen chloride. Discussion should include recognition that: • ‘Full outer shells’ are not always octets. The term ‘outer shell’ refers to a property of an atom. As such the number of electrons needed to ‘fill’ the ‘outer shell’ of an atom depends on the period of the Periodic Table in which the atom is found. Only those in the second period have a ‘full outer shell’ of 8 electrons, eg if a hydrogen atom has 2 electrons its ‘outer shell’ is filled. Using the same argument chlorine would need 18 electrons to fill its outer shell. • ‘Obtaining full outer shells’ is not the reason why chemical reactions occur. In the example given the outer shell arrangement of the H and Cl atoms are the same whether they are found in reactants or products, ie H has 2 e^-s in H_2 and in HCl and chlorine has 8 e^-s in Cl_2 and HCl. Chemical reactions are better explained by considering the energy changes that occur during reactions. Many spontaneous chemical reactions (at room temperature) occur because the energy of the products is lower than the energy of the reactants and the activation energy of the reaction is small. As a consequence the products will have stronger bonds than the reactants.	**7–8 marks** Shows understanding of principles of chemistry by (a) recognising misconceptions and providing correct explanations for the observations given AND (b) carrying out thermochemical calculations and linking the answers to the observations. **5–6 marks** Shows understanding of principles of chemistry by (a) identifying misconceptions and providing a reasonable explanation for the observations given AND (b) using the correct procedure for the thermochemical calculations. **1–4 marks** Answers include: • identification of a misconception (s) with limited explanation • correct method for themochemcal calculation.
(ii)	“*Successive ionisation energies for any atom increase because when an electron is removed from an atom or ion, the remaining electrons receive an extra share of the attraction from the nucleus*.” Eg: the first three ionisation energies for sodium are: $Na(g) \rightarrow Na^+(g) + e^- \quad \Delta H = 502\ kJ\ mol^{-1}$ $Na^+(g) \rightarrow Na^{2+}(g) + e^- \quad \Delta H = 4569\ kJ\ mol^{-1}$ $Na^{2+}(g) \rightarrow Na^{3+}(g) + e^- \quad \Delta H = 6919\ kJ\ mol^{-1}$ Discussion should include recognition that: The attraction of the nucleus for an electron is dependant on the distance of the electron from the nucleus and the size of the nuclear charge. The energy needed to remove the outermost electron from a gaseous atom (ionization energy) will be greater for electrons in energy levels closest to the nucleus. When electrons are removed from a filled or partially filled energy level the number of electron–electron repulsions are reduced which allows the electrons to move in closer to the nucleus. This accounts for the increase in energy needed to remove successive electrons from the same energy level. For Na, the electron arrangement is 2, 8, 1. The first electron to be removed is from the energy level furthest from the nucleus. The second electron is removed from a closer energy level so is held more strongly hence ionization energy is higher. The third ionization energy is similar to second because the electron is removed from the same energy level but there is one less electron meaning that there will be fewer electron–electron repulsions. This allows the electrons to be closer to the nucleus so they are more strongly held than in Na^+.	

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(b)	$\Delta_c H°(CH_4) = -812$ kJ mol^{-1} $\Delta_c H°(SiH_4) = -1428$ kJ mol^{-1} $\Delta_c H°$ for both reactions is negative so both are thermochemically favorable. However, only the SiH_4 reaction is spontaneous which suggests that the activation energy for this reaction is lower than that for reaction of CH_4, ie a smaller energy input is needed to get the reaction started.	
2(a)	70% Fe is 0.140 g n(Fe) = 0.140 g / 55.9 g mol^{-1} = 0.00250 mol $[Fe^{3+}]$ = 0.00250mol / 0.200 L = 0.0125 mol L^{-1} 10% Ni is 0.0200 g n(Ni) = 0.020 g / 58.7 g mol^{-1} = 3.41×10^{-4} mol $[Ni^{2+}] = 3.41 \times 10^{-4}$ mol / 0.200 L = 0.00170 mol L^{-1} For $Fe(OH)_3$ to precipitate when the concentration of Fe^{3+} is reduced to 0.1% of original conc then $[Fe^{3+}] = 0.001 \times 0.0125$ mol L^{-1} = 1.25×10^{-5} mol L^{-1} $K_s(Fe(OH)_3)) = 2.79 \times 10^{-39} = [Fe^{3+}] \times [OH^-]^3$ $= 1.25 \times 10^{-5} \times [OH^-]^3$ $[OH^-]^3 = 2.79 \times 10^{-39} / 1.25 \times 10^{-5} = 2.23 \times 10^{-34}$ $[OH^-] = 6.07 \times 10^{-12}$ and $[H_3O^+] = 0.00165$ mol L^{-1} and pH = 2.78 To determine the pH at which $Ni(OH)_2$ will precipitate: $K_s(Ni(OH)_2)) = 5.48 \times 10^{-16} = [Ni^{2+}] \times [OH^-]^2$ $= .00170 \times [OH^-]^2$ $[OH^-]^2 = 5.48 \times 10^{-16} / 0.00170 = 3.22 \times 10^{-13}$ $[OH^-] = 5.68 \times 10^{-7}$ mol L^{-1} and $[H_3O^+] = 1.76 \times 10^{-8}$ mol L^{-1} and pH = 7.75 So precipitation of $Fe(OH)_3$ will occur between pH 2.78 and 7.75	**7–8 marks** Shows understanding of principles of chemistry by (a) using the information given to carry out a calculation to correctly determine the pH range AND (b) using the graph to determine the stresses applied to the equilibrium system and linking the stresses to the changes in the concentrations of the species present **5–6 marks** Shows understanding of principles of chemistry by (a) using the correct procedure for the calculation (allowing a minor error) AND (b) being able to identify most of the stresses applied to the equilibrium but some detail omitted from the discussion **1–4 marks** Answers include: • correct procedure for parts of the calculation • identification of some of the stresses applied with reasons.

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2(b)	At position **W** there is a sudden sharp increase in the concentration of H_2 consistent with the addition of H_2 to the system. Since H_2 is a product of the reaction the equilibrium then shifts to the left, decreasing CO and H_2 concentrations while at the same time increasing the concentration of CH_4 and H_2O. At position **Y** there is a sudden sharp increase in the concentration of all 4 gases. Following this the concentrations of CO and H_2 decrease while the concentrations of the CH_4 and H_2O increase. This is consistent with an increase in pressure causing a shift towards the reactants where there are fewer gas particles than in the products. At point **Z** the stress applied results in an increase in concentrations of CO_2 and H_2 and a decrease in the concentrations of CH_4 and H_2O. This is consistent with a shift towards the products. Since this reaction is endothermic the increase would have been caused by heating the equilibrium system. At position **X** there is no change to the concentration of any of the species. This means any change to the system is something which has no effect on the equilibrium – in other words it is the addition of an inert gas such as nitrogen or the addition of a catalyst.	

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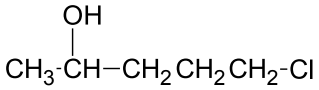
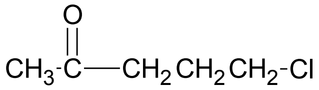
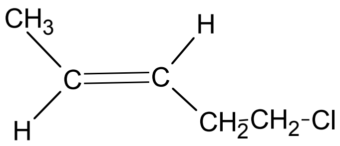
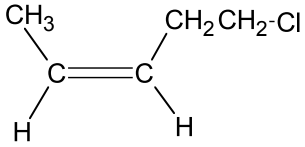
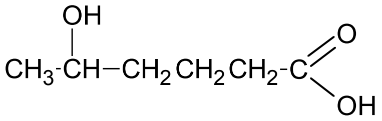
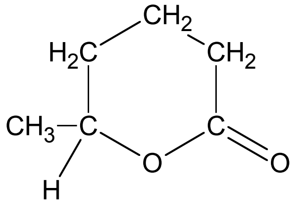
3(a)	Compound A  $CH_3\text{-}\overset{OH}{CH}-CH_2CH_2CH_2\text{-}Cl$ 5–chloropentan–2–ol Compound B  $CH_3\text{-}\overset{O}{\overset{\Vert}{C}}-CH_2CH_2CH_2\text{-}Cl$ 5–chloropentan–2–one Compound C $H_2C{=}CH-CH_2CH_2CH_2-Cl$ 5–chloropent–1–ene Compound D and E  *trans*–5–chloropent–2–ene  *cis*–5–chloropent–2–ene Compound F  5–hydroxyhexanoic acid Compound G  Justification: **B** = ketone (no reaction with Tollens') **A** = 2° alcohol (**B** is a ketone) **C** has double bond on C1 (no geometric isomers) **D, E** double bond on C2 (they are geometric isomers –OH on C2 **F** = acid (–CN substitutes for –Cl then converted to acid with H_2SO_4) **G** = ester (smell and conditions for condensation reaction, acid and alcohol in same molecule so cyclic)	**7–8 marks** Shows understanding of principles of chemistry by (a) determining the formulae of the Compounds **A–F** with justification AND (b) identifying the unknown liquids with justification using ALL the data given **5–6 marks** Shows understanding of principles of chemistry by (a) identifying at least 4 of the Compounds **A – F** with justification AND (b) identifying at least 3 of the unknown liquids with justification **1–4 marks** Answers include: • correct identification of at least 2 of Compounds **A–F** • identification of at least 2 of the unknown liquids with reasons linked to some of the data given.
(b)	**A** 2-propanol **B** water **C** methanol **D** hexane **E** propanone Justification: **B**– dissolves the most glucose (can form the most H bonds with glucose), and has highest evaporation time (has strongest intermolecular forces because of the number of H–bonds that form between molecules) **D** – immiscible with water and doesn't dissolve glucose (it is a non–polar molecule), short evaporation time (weak instantaneous dipole interactions between molecules) **A** and **C** – miscible with water and dissolve larger quantities of glucose than **E** (alcohols can H–bond with water and glucose) **A** is less volatile than **C** (2-propanol has higher molar mass, more electrons in the molecule makes it more polarisable so stronger temporary dipole attractive forces) **E** less evaporation time than hexane (molecule is smaller so weaker	

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	temporary dipoles), dissolves some glucose and mixes with **A, B** and **C** (molecule is polar)	
4(a) (i)	The pH of initial solution of HOBr: $K_a\,(\text{HOBr}) = \frac{[\text{OBr}^-][\text{H}_3\text{O}^+]}{[\text{HOBr}]} = 10^{-8.69} = 2.04 \times 10^{-9}$ $[\text{H}_3\text{O}^+] = \sqrt{[OBr^-]K_a} = \sqrt{0.2 \times 2.04 \times 10^{-9}}$ $= 2.021 \times 10^{-5}$ pH = 4.69 At equivalence point: $n(\text{OBr}^-) = 0.0100 \text{ L} \times 0.200 \text{ mol L}^{-1} = 0.00200 \text{ mol}$ and $V = 0.030$ L $[\text{OBr}^-] = 0.00200 \text{ mol} \ / \ 0.030 \text{ L} = 0.06667 \text{ mol L}^{-1}$ $K_a\,(\text{HOBr}) = \frac{[\text{OBr}^-][\text{H}_3\text{O}^+]}{[\text{HOBr}]} = \frac{[\text{H}_3\text{O}^+]^2}{[\text{HOBr}]} =$ $[\text{H}_3\text{O}^+] = \sqrt{\frac{1\times10^{-14} \times 2.041\times10^{-9}}{0.06667}} = 1.750 \times 10^{-11}$ and pH= 10.76 Note: significant figures in pH values are those after the decimal point. Answers should be given to 2 decimal places to match the significant figures in the pK_a	**7–8 marks** Shows understanding of principles of chemistry by (a) calculating the pHs AND (b) plotting the HOBr$^-$ graph and relating the differences between the curves to the species present AND recognising the reasons for the basics/acidic pH in the buffer regions of the two graphs OR correctly calculating the pH of the given mixture **5–6 marks** Shows understanding of principles of chemistry by (a) calculating the pHs AND (b) recognising similarities and differences in the graphs related to the species present OR recognizes reasons for the basic/acidic nature of the buffer region **1–4 marks** Answers include: • at least one correct calculation • graph drawn correctly and discussion of similarities or differences between the graphs • recognition of the reasons for the difference in pH at the buffer regions.
(b) (i)	Curve begins at 4.7, at 10 mL pH = 8.7, mid-point of vertical region has pH = 10.8, after 20 mL graphs are the same.	
(ii)	Similarities • Shape – both weak acid with strong base • Turning point – same acid concentration • After 20 mL graphs are the same – pH determined by the varying concentration of the same strong base Differences • The initial pH for the HOBr is higher than for the ethanoic acid – (higher pK_a) since HOBr is a weaker acid so has a smaller degree of dissociation and therefore a lower concentration of H_3O^+ • The pH of the buffer region for HOBr is higher – pK_a is larger • The pH at the equivalence point is higher for the HOBr titration – the conjugate base $[\text{OBr}^-]$ is stronger than $[\text{CH}_3\text{COO}^-]$. • For each titration, the pH at the half-equivalence point is equal to the pK_a. At this point the concentration of the weak acid and the conjugate base are equal: ie $[\text{CH}_3\text{COOH}] = [\text{CH}_3\text{COO}^-]$ and $[\text{HOBr}]=[\text{OBr}^-]$	
(iii)	• The pH of the titration solution at this point depends on the relative strength of the weak acid and the weak base species present. In the case of the ethanoic acid titration, the ethanoic acid, CH_3COOH is a stronger acid compared to the conjugate base CH_3COO^- and the solution is overall acidic. For the HOBr titration, the weak base OBr^- is stronger than the weak acid HOBr, and the solution is basic.	
(iv)	$\text{n(NaOH)} = 0.0050 \times 0.100 = 5.0 \times 10^{-4} \text{ mol} = \text{n}(\text{CH}_3\text{COO}^-)$ $\text{n}(\text{CH}_3\text{COOH}) \text{ left} = 2.0 \times 10^{-3} - 5.0 \times 10^{-4} = 1.5 \times 10^{-3} \text{ mol}$ $[\text{H}_3\text{O}^+] = \frac{K_a[CH_3COOH]}{[CH_3COO^-]} = \frac{1.58\times10^{-5} \times 1.5\times10^{-3}}{5.0\times10^{-4}} = 4.74\times 10^{-5}$ pH = 4.28	

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5(a)	$CH_2(OH)CH(OH)CH_2(OH) + 3H_2O \rightarrow 3HCOOH + 8H^+ + 8e^-$ $Ce^{4+} + 2e^- \rightarrow Ce^{2+}$ $Fe^{2+} \rightarrow Fe^{3+} + e^-$ $n(Ce^{4+})_r = .050\text{ L} \times 0.0837\text{ mol L}^{-1} - ½ \times 0.01211 \times 0.0448$ $= 0.004185 - .0002712 = 0.0039138$ $n(\text{glycerol}) = n(Ce^{4+}) /4 = 0.0009784$ $m(\text{glycerol}) = 92.1\text{ g mol}^{-1} \times 0.0009784$ % glycerol = 90.1 mg / 100 mg x100 = 90.1% Titration reactions need to be fast. The reaction between glycerol and cerium (IV) needed heating for 15 minutes so was too slow for a direct titration to be used. The titration between Ce^{4+} and Fe^{2+} is fast and hence suitable for titration OR in a back titration there is an extra error introduced as there are 2 measurements needed each of which has its own uncertainty.	**7–8 marks** Shows understanding of principles of chemistry by (a) calculating the % of glycerol with appropriate significant figures and identifying the need for a back titration AND (b) using data from the graph to determine the correct species for the pH range **5–6 marks** Shows understanding of principles of chemistry by (a) recognising the features of the back titration and the appropriate calculations AND (b) showing some understanding of the data in the graph and how it relates to the question **1–4 marks** Answers include: • the correct procedure for the calculation • a reason for using the back titration • the correct method for determination of the vanadium species or a correct interpretation of graph.
(b)(i)	**For pH = 0 → 1** $V^{3+} + O_2 \rightarrow H_2O + VO^{2+}$ $E°_{cell} = E°_{reduction} - E°_{oxidation} = 1.10 - 0.34\text{ V} > 0$ so spontaneous $VO^{2+} + O_2 \rightarrow VO_2^+ = H_2O$ $E°_{cell} = E°_{reduction} - E°_{oxidation} = 1.10 - 1.00 > 0$ so spontaneous Species present: $\mathbf{VO_2^+}$ **For pH 1 → 14** $V^{3+} + O_2 \rightarrow H_2O + VO^{2+}$ $E°_{cell} = E°_{reduction} - E°_{oxidation} = 1.00 \text{ to } 0.45 - 0.34 > 0$ so spontaneous $VO^{2+} + O_2 \rightarrow VO_2^+ = H_2O$ $E°_{cell} = E°_{reduction} - E°_{oxidation} = 1.00 \text{ to } 0.45 - 1.00 < 0$ so not spontaneous Species present for this pH range: $\mathbf{VO^{2+}}$ No reaction between H_2O and any of the vanadium species.	