Assessment Schedule - 2014

Scholarship Chemistry (93102)

Evidence Statement

Question	Evidence	
ONE (a)(i)	Na(s) to Na(g) will require less energy than vaporisation / atomisation of Mg since the metallic bond for Mg stronger. The force of attraction between the delocalised valence e ⁻ and the cations is proportional to the char on the particles involved and the distance between them (radii of the atoms / cations). Hence Mg cations have greater attraction for the shared electrons.	
	Na(g) to Na ⁺ (g) requires less energy. Two electrons will have to be removed from Mg compared with only one to form Na ⁺ . For Mg, the first ionisation energy will be higher than for Na because of the higher charge of the Mg nucleus (given that the shielding is similar for two atoms since the valence e ⁻ s are in the same energy level), and the second ionisation will be much higher because an electron is being taken from something that is already positive / there is reduced electron-electron repulsion once the first electron is removed.	
	Cl ₂ to ½ Cl ⁻ , overall less energy is requ	nired since only ½ mol of anions is needed.
	combined with the Cl ⁻ ions. This will i	of the solid MgCl ₂ will be more favourable since 2+ cations are being result in a stronger forces of attraction (ionic bonds) than for NaCl so solid MgCl ₂ is formed from the gaseous ions.
	The net force, $\Delta_f H$, for NaCl is less sin	ce overall less energy is needed and less energy is released.
(ii)	Steps in the cycle:	
	$Mg(s) \to Mg(g)$	$\Delta_{\rm r}H = 147 \text{ kJ mol}^{-1}$
	$Mg(g) \to Mg^+(g)$	$\Delta_{\rm r} H = 744 \text{ kJ mol}^{-1}$
	$\frac{1}{2}\operatorname{Cl}_2(g) \to \operatorname{Cl}(g)$	$\Delta_{\rm r}H = -121 \text{ kJ mol}^{-1}$
	$Cl(g) + e^- \rightarrow Cl^-(g)$	$\Delta_{\rm r} H = -355 \rm kJ \ mol^{-1}$
	$Mg^+(g) + Cl^-(g)$	$\Delta_{\rm r}H = -753 \text{ kJ mol}^{-1}$
	$\Delta_{\rm f} H({\rm MgCl}) = -96 \ {\rm kJ \ mol}^{-1}$	
	Since the enthalpy change is negative (formation of MgCl ₂ , the reaction will be	(exothermic) but is much less negative than the enthalpy change for the less favorable.

(b) Photosynthesis: $6CO_2 + 6H_2O + \text{energy} \rightarrow C_6H_{12}O_6 + 6O_2$

Enthalpy change: $\Delta_r H = -1\ 271 - [6 \times (-394) + 6 \times (-286)] = 2\ 809\ kJ\ mol^{-1}$

Since $\Delta_r H > 0$ the reaction is endothermic and an input of energy is needed. Energy from the sun is used to break the strong bonds in CO_2 and H_2O molecules (and to separate the H_2O molecules in the liquid), and energy is then released on the formation of the bonds in glucose and oxygen. More energy is needed to break the bonds than that being released in bond formation so the net energy for the reaction is positive. Respiration is the reverse of this. The net energy for respiration is negative since more energy is released in bond formation than is needed in breaking the bonds of the reactants.

Entropy of the photosynthesis reaction does not favour the products. Spontaneous processes tend to be those that increase the amount of disorder and the more molecules there are the more disorder there is. Gases are more disordered than liquids, which are, in turn more disordered than solids. In the photosynthetic reaction, the total number of molecules decreases, the number of gas molecules stays the same, and the first product is a solid while the second reactant is a liquid. This means that overall the products of photosynthesis are much more ordered than the reactants. Hence energy will be required to make this non-spontaneous process happen. There is no 'storage' of energy during / after the photosynthesis process since the energy from the sun is being used to break bonds to allow for the rearrangement of the atoms / the reaction to occur. In a sense; the energy from the sun is 'used up' in the reaction. During respiration, energy is released since there is a net gain of energy as the bonds broken during the reaction require less energy than that released during the formation of the bonds in the products.

Marker Allocation

7 and 8: Comprehensive discussion that includes:

- (a) an accurate identification of all the differences with correct chemical ideas, calculations and connections between ideas
- (b) an accurate account of enthalpy and entropy for 1 reaction + links to the other + the misconception is identified and a correct explanation given.

5 and 6: Logical well organised discussion that includes most of:

- (a) an accurate identification of all the differences with correct chemical ideas, calculations and connections between ideas
- (b) an accurate account of enthalpy and entropy for 1 reaction + links to the other + the misconception is identified and a correct explanation given.

3 and 4: Look for evidence of:

- (a) differences that are identified and discussions that are mostly correct + a correct method for the calculation
- (b) correct consideration of entropy and enthalpy factors.

1 and 2: Look for any evidence of:

- (a) identified differences OR the MgCl calculation uses the correct method
- (b) entropy or enthalpy factors considered.

Question	Evidence
TWO	$OCI^- + 2S_2O_3^{2-} + H^+ \rightarrow CI^- + OH^- + S_4O_6^{2-}$
(a)(i)	Average titre = 16.69 mL (titre number 3 is not concordant so cannot use)
	$n(S_2O_3^{2-}) = 0.04562 \times 0.016687 = 7.612 \times 10^{-4} \text{ mol}$
	$n(OCl^{-}) = 3.8062 \times 10^{-4} \text{ mol}$
	$n(OCl^{-}) = \frac{3.806 \times 10^{-4}}{0.01000} = 0.03806 \text{ mol } L^{-1}$
	For undiluted $c(OCl^{-}) = \frac{250}{20} \times 0.03806 = 0.4758 \text{ mol } L^{-1}$
	$c(\text{NaOCl}) = 0.4758 \text{ mol } \text{L}^{-1} \times 74.5 \text{ g mol}^{-1} = 35.45 \text{ g L}^{-1}$
	% available chlorine: 42 g L ⁻¹ $\equiv 4.0\%$ so $\frac{35.45}{42} \times 4.0 = 3.38\%$
	This value suggests that some of the bleach has decomposed but it is still above the value that should be available by the use by date.
	% still available = $3.38 / 4.0 \times 100 = 84.4\%$ so 15.6% dissociated.
(ii)	$ClO^{-} + 2H_{2}O \rightarrow ClO_{3}^{-} + 4H^{+} + 4e^{-}$
	$ClO^- + 2H^+ + 2e^- \rightarrow Cl^- + H_2O$
	$3\text{ClO}^- \to \text{ClO}_3^- + 2\text{Cl}^-$
	$E^{\circ}_{\text{cell}} = 0.89 \text{ V} - 0.50 \text{ V} = +0.39 \text{ V}$
	Since $E^{\circ}_{cell} > 0$, the reaction as written is spontaneous, so the disproportionation reaction can occur.
(b)	An electrolysis reaction is required as the overall reaction is not spontaneous so requires energy input if it is to occur. The overall reaction is:
	$2Cl^{-} + 2H_2O \rightarrow Cl_2 + H_2 + 2OH^{-}$
	$E_{\text{reaction}} = E_{\text{reduction}} - E_{\text{oxidation}} = -0.83 - 1.36 = -2.19 \text{ V}$
	Since this value is < 0 this reaction is not spontaneous.
	During the electrolysis process the strongest oxidant in the solution is H_2O (highest reduction potential) so this is more likely to be reduced than the other oxidant (Na).
	The strongest reductant under these condition is Cl^- (would otherwise have expected OH^- to be oxidised to O_2).
	Cl^- ions are attracted to the anode where they release their electrons and are hence oxidised and combine to form Cl_2 molecules – hence chlorine gas is released.
	$2Cl^- \to Cl_2 + 2e^-$
	The released electrons are transferred to the water molecules at the cathode:
	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$
	Hence the water molecules are reduced and hydrogen gas will be produced. The resulting solution will be basic since OH ⁻ ions are formed.
	In the absence of the half cells being separated, the Cl ₂ molecules disproportionate in the basic conditions (both oxidised and reduced).

$$Cl_2 + 2e^- \rightarrow 2Cl^- (reduction)$$
 $Cl_2 + 2OH^- \rightarrow 2HOCl + 2e^- (oxidation)$
Overall $Cl_2 + OH^- \rightarrow OCl^- + Cl^- + H^+$
 $E_{reaction} = E_{reduction} - E_{oxidation} = 1.36 - 0.42 = 0.94 \text{ V i.e.} > 0$, so reaction is spontaneous.

Marker Allocation

7 and 8: Look for evidence of:

- (a) calculations that are all correct and linked to the data / used to answer the questions
- (b) comprehensive convincing discussion (using correct chemistry language and equations where appropriate) including anode and cathode reactions, reasons for non-spontaneity, reasons for disproportionation of Cl₂.

5 and 6: Look for evidence of:

- (a) calculations that are mostly correct with attempts to link to data / used to answer the questions
- (b) logical well organised discussion (using correct chemistry language and equations where appropriate) including most of anode and cathode reactions, reasons for non-spontaneity, reasons for disproportionation of Cl₂.

3 and 4: Look for evidence of:

- (a) calculations that are mostly correct / use the correct method with minor error, use correct chemistry ideas in explanations
- (b) discussion that recognises most of oxidation-reduction processes with some attempt at using correct language/symbols anode and cathode reactions, reasons for non-spontaneity, reasons for disproportionation of Cl₂.

1 and 2: Look for any evidence of:

- (a) (i) the correct method for the calculation, (ii) correct answer, but the explanation is not all complete
- (b) a discussion that recognises oxidation / reduction processes in electrolysis OR disproportionation with some errors / omissions.

QUESTION THREE

Marker Allocation

Processes occurring in the scheme:

- successive substitutions from **A** to **D** to form acid chloride
- substitution of Cl by benzene ring to form **E** from **D**
- hydrolysis to form **F** and **G**,
- substitution of iodine by amine to form **H** from **G**
- G is an amide so Reagent X is acid bromide or chloride reacting with H (amine)
- substitution of bromine for NH₃ to make **J.**
- 8 All answers (A to J + Reagent X) correct OR shows understanding of all steps with a minor error.
- 7 10 of A to J + Reagent X correct OR shows understanding of 5 of the 6 steps.
- 6 2 errors (A to J + Reagent X) correct OR shows understanding of 4 of the 6 steps.
- 5 3 errors (A to J + Reagent X) correct OR shows understanding of 4 of the 6 steps, with a minor error.
- 4 Any 6 correct.
- 3 Any 5 correct.
- 2 Any 4 correct.
- 1 Any 2 correct.

Question **Evidence FOUR** Ar and CO Fundamental particles in Ar are atoms. Forces between atoms can only be induced dipole-induced dipole caused by instantaneous dipoles forming with the random movement of the electrons. CO is a slightly polar molecule but the dipole-dipole attraction does not contribute significantly to the net intermolecular force (not registered on graph). Accounting for the similarity of the induced dipole-dipole forces of CO and Ar: Induced dipole forces depend on the size, shape and polarisability (ease with which electrons can move around the molecule in response to an electric field) of the molecule (or, atom in the case of Ar). The fact that there are more electrons in Ar than in CO $(M(Ar) = 40 \text{ g mol}^{-1} \text{ and } M(CO) = 28 \text{ g mol}^{-1})$ would usually lead to an expectation of stronger induced dipole forces in argon than in carbon monoxide. The similarity in the forces could be attributed to the spreading out of the electron cloud across the two atoms in a CO molecule rather than around the single nucleus as in the Ar atom. Also the linear shape of CO compared to the spherical shape of Ar leads to more points of contact and hence increased forces of attraction. HI, HBr and HCl These are all polar molecules and the polarity (dipole moment) trend can be accounted for by the increase in the electronegativity difference between the halogen and the H atom (electronegativity Cl > Br > I). As the dipole moment increases the dipole-dipole contribution to the total intermolecular force increases (so greater for HCl than for HBr but negligible for HI). As the dipole moment increases there is a relative increase in the effect of the permanent dipole on the electrons in a neighbouring atom and hence the dipole to induced dipole contribution to the total force (dipole-induced dipole effect is not dependent on the dipole being aligned so occurs more frequently than dipole-dipole). The decrease in the induced dipole-induced dipole forces from HI to HBr to HCl is relative to the difference in the number of electrons in the atom / molar mass. HCl has a similar molar mass to Ar but has a considerably larger induced-dipole contribution to the total intermolecular forces. This is because the HCl molecule occupies more space than the Ar atom and the molecule being more polarisable and able to form more points of contact (see discussion for CO). NH₃ and H₂O The molecules of water and ammonia have a much greater dipole-dipole contribution than the others already discussed because they are not only much more polar, but they are also able to hydrogen bond to each other (water to water and ammonia to ammonia). This is possible because of the high electronegativity of the O and N atoms causing the H atoms to which they are bonded to carry a strong δ + charge. This means that the H atoms are strongly attracted to the lone pair of electrons on the N or O atoms of a neighbouring molecule forming a relatively strong H-bond (intermolecular force). This effect is stronger in H₂O than in NH₃ because water molecules are able to form more H-bonds than ammonia molecules and the O-H···O bond is stronger than the N-H···N bond due to O atoms being more electronegative than N atoms. The induced dipole-induced dipole forces in NH₃ are larger than for H₂O because, although the molecules have a similar number of electrons, the electrons in O are closer to the nucleus (O atoms are smaller / the nuclear charge is greater / O is more electronegative) so the electron cloud is less dispersed / the molecule is smaller OR in the water molecules the electrons are held more tightly so the molecule is less polarisable.

Dipole-induced dipole forces increase with the increasing size of the dipole moment. The permanent dipole in these molecules will cause further polarisation of the electron cloud of a neighbouring molecule and hence

increasing the force of attraction between the molecules.

Marker Allocation

Possible points for 7 and 8: (allow 1 - 2 errors / omissions for 7)

- Similarities / differences between Ar and CO linked to data
- · Comparison of HI, HBr, HCl induced dipole and dipole forces linked to data
- Comparison of NH₃ and H₂O induced dipole and dipole forces linked to data
- · Discussion of dipole-induced dipoles OR compares induced dipoles across all substances
- Concise, comprehensive discussion.

Possible points for 5 and 6: (allow 1 - 2 errors / omissions for 5)

- Similarities / differences between Ar and CO linked to the data
- · Comparison of HI, HBr, HCl induced dipole and dipole forces linked to data
- Comparison of NH₃ and H₂O induced dipole and dipole forces linked to data
- · Logical, organised discussion.

3 or 4 marks - discussion shows understanding of:

- induced dipole forces linked to at least 4 of the substances
- dipole forces linked to at least 4 of the substances
- hydrogen bonding in NH₃ and H₂O

OR All the forces for at least 3 of the substances are correctly described. Only minor errors in discussion.

1 or 2 marks – discussion shows understanding of any of:

- induced dipole forces linked to at least 2 of the substances
- dipole forces linked to at least 2 of the substances
- hydrogen bonding linked to NH₃ or H₂O

OR All the forces for at least 2 of the substances are mostly correctly described.

Question	Evidence	
FIVE	Hydroxyapatite dissolves as follows according to the following equation:	
(a) (i)	$Ca_5(PO_4)_3OH \Rightarrow 5Ca^{2+} + 3PO_4^{3-} + OH^-$	
,,	A decrease in pH means that H ⁺ concentration increases and H ⁺ can react with OH ⁻ and PO ₄ ³⁻ to remove them from solution.	
	$OH^- + H^+ \rightarrow H_2O \qquad PO_4^{3-} + H^+ \rightarrow HPO_4^{2-}$	
	This causes the equilibrium to move to the right and the hydroxyapatite dissolves.	
	Since the hydroxyapatite is no longer soluble at pH of 5.5 the concentrations of OH ⁻ and PO ₄ ³⁻ must have decreased such that $Q = [Ca^{2+}]^5[PO_4^{3-}]^3[OH^-] < K_s$	
	Fluorapatite dissolves according to:	
	$Ca_5(PO_4)_3F \Rightarrow 5Ca^{2+} + 3PO_4^{3-} + F^{-}$	
	At pH of 5.5, this equilibrium still lies to the left as there are sufficient ions present for the value of Q to exceed K_s . $Q = [Ca^{2+}]^5[PO_4^{3-}]^3[F^-] < K_s$. This is different from the hydroxyapatite at this pH as the F^- ion concentration is not reduced as much as the OH $^-$ ions by the presence of H $^+$ ions and also because the fluorapatite is less soluble than the hydroxyapatite so the solid forms at a lower concentration of the ions.	
	(At a pH lower than 4.5 it might be expected that fluorapatite can no longer be deposited due to the very small concentration of PO ₄ ³⁻).	
	Increasing the pH (removing sugars or plaque) means there will be more OH ⁻ and PO ₄ ³⁻ ions present in the solution so the hydroxyapatite can reform.	
(ii)	$2H_2O = H_3O^+ + OH^-$	
	$K = K_{\rm w} = [{\rm H_3O^+}] \times [{\rm OH^-}] = 10^{-14}$	
	$K_{\rm a} = K / [{\rm H_2O}]$	
	1 L of water has a mass of 1000 g, $M_{\rm r}({\rm H_2O}) = 18 \ {\rm g \ mol}^{-1}$,	
	So $[H_2O] = 55 \text{ mol } L^{-1} \text{ and } pK_a = 15.74$	
	HF is a much stronger acid than H_2O , based on the very big difference in the pK_a values. Therefore F^- is a much weaker base than OH^- . This means that F^- will be much less reactive towards the acids that are produced by bacterial digestion.	
(b)	Steps 3 and 4: H ₂ PO ₄ ⁻ is added and reacted with OH ⁻ to produce HPO ₄ ²⁻ required for precipitation.	
(b) (i)	Steps 3 and 4. $H_2PO_4^-$ is added and reacted with OH to produce HPO_4^- required for precipitation. $OH^- + H_2PO_4^- \rightarrow HPO_4^{2-} + H_2O$	
,,		
	Indicator is used to ensure that sufficient OH ⁻ has been added to produce enough HPO ₄ ²⁻ for the complete precipitation of Sr^{2+} . Precipitation of $SrHPO_4$ will occur: $Sr^{2+} + HPO_4^{2-} = SrHPO_4$, and any unreacted HPO_4^{2-} in solution alongside $H_2PO_4^-$ will create a buffer solution. Indicator is chosen to ensure sufficient HPO_4^{2-} is available for precipitation.	
(ii)	$H_2PO_4^-(aq) + OH^-(aq) \Rightarrow H_2O(l) + HPO_4^{2-}(aq)$	
	$\operatorname{Sr}^{2+}(aq) + \operatorname{HPO_4}^{2-}(aq) = \operatorname{SrHPO_4}(s)$	
	Initial moles $H_2PO_4^- = 0.500 \times 0.0200 = 1.00 \times 10^{-2} \text{ mol}$	
	$n(\mathrm{Sr}^{2+}) = 5.00 \times 10^{-4} \mathrm{mol}$	

Assume essentially all Sr^{2+} is precipitated and that sufficient KOH must be added to provide the $HPO_4^{2-}(aq)$ required for precipitation.

Final moles $H_2PO_4^-(aq) + HPO_4^{2-}(aq)$ in solution = 1.00×10^{-2} mol -5.00×10^{-3} mol

$$= 9.50 \times 10^{-3}$$
 moles.

$$pH = pK_a - log HA / A$$

$$6.0 = 7.21 - \log HA / A$$

therefore $\log HA / A = 1.21$ and

$$HA / A = H_2PO_4^{-}(aq) / HPO_4^{2-}(aq) = 16.22 = (9.5 \times 10^{-3} - x) / x$$

$$x = 9.5 \times 10^{-3} / 17.22 = 5.517 \times 10^{-4} \text{ mol HPO}_4^{2-}(aq)$$

Therefore KOH added must have been $5.517 \times 10^{-4} + 5.00 \times 10^{-4}$ mol or 1.05 mL

Final volume = 60 mL + 20 mL + 1.05 mL = 81.05 mL

$$[HPO_4^{2-}(aq)] = 5.517 \times 10^{-4} / 0.08105 = 6.807 \times 10^{-3} \text{ mol L}^{-1}$$

 $[Sr^{2+}(aq)] = 1.2 \times 10^{-7} / 6.807 \times 10^{-3} = 1.75 \times 10^{-5} \text{ mol L}^{-1}$, which is OK with the assumption (equivalent to 1.76×10^{-5} mol or 0.3% of the strontium).

(iii) Indicator changes colour at a pH that is too low for it to be useful for the reaction (colour change expected to be around 3). Answer could compare the ratio of $H_2PO_4^-(aq) / HPO_4^{-2}$ at this pH and note that very little H_2PO_4 has reacted or calculate the pH of the H_2PO_4 solution (3.45) and recognise that the indicator will not be useful for this reaction.

Marker Allocation

7 and 8: Evidence of:

- (a) (i) Comprehensive discussion of observations using equilibrium principles
 - (ii) calculation (working) for pK_a + uses this to compare acidity of OH⁻ and F⁻ linked to the observations
- (b) calculation correct + linked to the effectiveness of the process OR calculation method is correct with minor error and one of (i) or (ii) is correct.

5 and 6: Evidence of:

- (a) (i) logical discussion of most of the observations using equilibrium principles
 - (ii) some aspects of the calculation for p K_a and / or compares acidity of OH⁻ and F⁻
- (b) some understanding of the process through the answers for (i), (ii) or (iii).

3 and 4: Some evidence of:

- (a) (i) discussion of most of the observations using equilibrium principles
 - (ii) some aspects of the calculation for p K_a OR compares acidity of OH⁻ and F⁻
- (b) an understanding of the process through the answers for (i), (ii) or (iii).

1 and 2: Evidence of:

- (a) (i) discussion of most of the observations using equilibrium principles
 - (ii) aspects of the calculation method correct for p K_a OR comparison of acidity of OH– and F
- (b) some understanding of the process through the answers for (i), (ii) or (iii).