Assessment Schedule – 2012
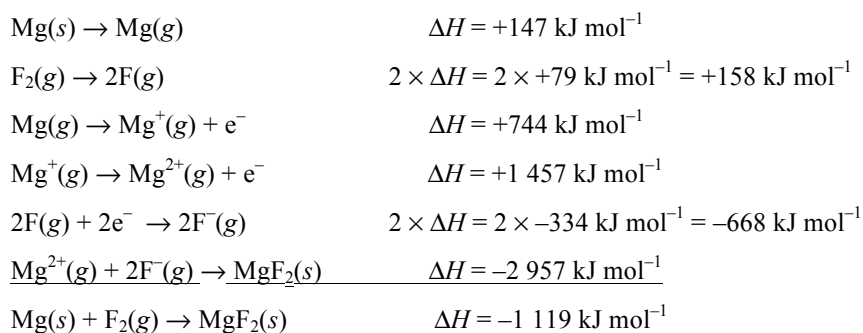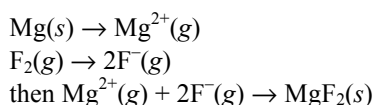
Scholarship Chemistry (93102)

Evidence Statement

Question One

(a)   (i)   A   Atomisation of Mg is endothermic, because energy is required to break the metal–metal bonds and provide the kinetic energy to make the sample gaseous.

              B   Breaking F–F covalent bonds requires energy, hence is an endothermic reaction.

              C   Ionisation of Mg requires energy as the electron has to be pulled away from the nucleus of the atom. Separation of charge requires a large amount of energy.

              D   Removal of a second electron requires even more energy, because the starting ion is smaller than the atom, so that the electron has to be removed from closer to the nucleus (it was closer because the reduced number of electrons in the ion means that there is less electron–electron repulsion, so less shielding effect).

              E   Addition of an electron to a fluorine atom is exothermic. The additional electron can be placed relatively close to the nucleus and the attraction is stronger than the repulsion from the other electrons.

              F   Formation of an ionic solid from gas phase ions is extremely exothermic, as it involves bringing ions with opposite charges together.

    (ii)   Enthalpy is a property of a particular state under a particular set of conditions and does not depend on how you get to that state, so Hess's Law can be used to combine the equations to calculate the enthalpy of formation. Hess's Law assumes the reaction pathway is:

$$Mg(s) \rightarrow Mg^{2+}(g)$$
$$F_2(g) \rightarrow 2F^-(g)$$
$$\text{then } Mg^{2+}(g) + 2F^-(g) \rightarrow MgF_2(s)$$

$Mg(s) \rightarrow Mg(g)$	$\Delta H = +147 \text{ kJ mol}^{-1}$
$F_2(g) \rightarrow 2F(g)$	$2 \times \Delta H = 2 \times +79 \text{ kJ mol}^{-1} = +158 \text{ kJ mol}^{-1}$
$Mg(g) \rightarrow Mg^+(g) + e^-$	$\Delta H = +744 \text{ kJ mol}^{-1}$
$Mg^+(g) \rightarrow Mg^{2+}(g) + e^-$	$\Delta H = +1\,457 \text{ kJ mol}^{-1}$
$2F(g) + 2e^- \rightarrow 2F^-(g)$	$2 \times \Delta H = 2 \times -334 \text{ kJ mol}^{-1} = -668 \text{ kJ mol}^{-1}$
$\underline{Mg^{2+}(g) + 2F^-(g) \rightarrow MgF_2(s)}$	$\underline{\Delta H = -2\,957 \text{ kJ mol}^{-1}}$
$Mg(s) + F_2(g) \rightarrow MgF_2(s)$	$\Delta H = -1\,119 \text{ kJ mol}^{-1}$

(b)   (i)   Xenon is a large atom, low down in the periodic table. It is in Group 18 and has a full valence shell so it is hard to remove or share electrons. Xenon's outer electrons are more easily removed or shared than those of the elements higher in Group 18, because they are much further from the nucleus. Sharing or removal of electrons will only be possible if the electron is placed or shared into a very stable orbital, that is, one on a very electronegative atom OR electron is attracted by a very electronegative atom. Hence fluorine and oxygen are the elements that can best achieve this to form compounds.

             (Alternatively, any electron added to xenon would have to be added to a high energy orbital in the next shell, but the small amount of energy gained from doing so would not be sufficient to remove an electron from another atom.)

    (ii) XeO_3: Xe, 8 electrons, plus $3 \times O$, 18 electrons = 26 electrons.
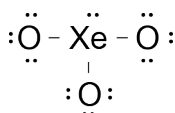
4 electron clouds on the central atom so tetrahedral arrangement of electron pairs in order to minimise repulsion. Molecule takes trigonal pyramidal shape. Expected angle around 109° since basic shape is tetrahedral.

$[XeOF_3]^+$: Xe, 8 electrons, plus 6 for O and 3×7 for F and –1 for charge = 34 electrons.
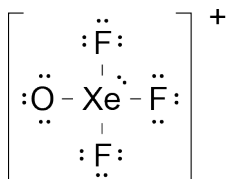
5 electron clouds, so a trigonal bipyramidal base shape. The lone pair O will be equatorial because the greater repulsion (due to the lone pair electron density being held closer to the nucleus OR the extra electrons if a double bond has been drawn) is more easily accommodated in the equatorial plane where the angles are larger. Shape will be see-saw (or distorted tetrahedron), giving bond angles of 180° between Xe and 2 F atoms and an angle of slightly less than 120° for the O–Xe–F in the equatorial position (lone pair takes up more space closer to the central atom, so greater repulsion, leading to smaller angle between atoms).

(iii) Under normal circumstances the reactivity of Group 1 elements involves loss of the valence electron to give a cation and addition of the lost electron to a relatively electronegative element. The resulting ions then combine to form an ionic solid (a process that is very exothermic and can greatly assist in the formation of the products, a major advantage over covalent compounds). This is particularly easily done in the formation of ionic compounds from elements of Group 1 with elements of Group 17. It will be less favourable for Group 18 elements to do this, as the additional electron must go into the next shell of the Group 18 element. The elements low in Group 1 lose their valence most easily, are most easily ionised, while those higher in Group18 will most favourably have an electron added, since they are furthest away from the nucleus. There are very few covalent compounds of Group 1 elements, as they have low electronegativities (and the requirement for covalent compounds is that the electronegativities of the bonded elements should be rather similar). Therefore an ionic compound seems most likely.

Judgement
7 – 8 marks
Shows understanding of chemistry by:
• Accounting for the signs and relative magnitudes of all the enthalpy changes and explaining how Hess's Law is used to calculate $\Delta_f H$ with the correct calculation,

AND

• Discusses the compounds of Group 18 in terms of covalent bonding, molecular shape (with reasons) and the potential to form ionic compounds with Group 1 elements.

5 – 6 marks
Shows understanding of chemistry by:
• Accounting for the signs or relative magnitude of the enthalpy changes and correctly calculating $\Delta_f H$ or explaining how Hess's Law is used,

AND

• Discusses periodic trends related to the formation of compounds of Group 18 elements and correctly predicts the shape of two ions present with a coherent explanation.
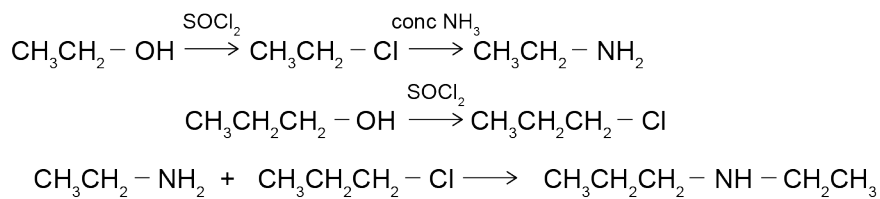
1 – 4 marks
Answers include:
• Reasons for enthalpy changes.

• Calculations of $\Delta_f H$.

• Periodic trends for compounds of Group 18 elements.
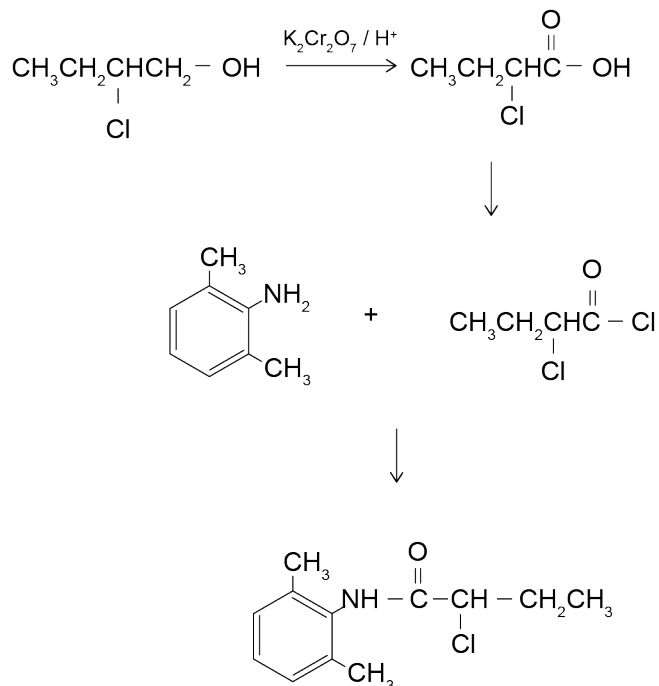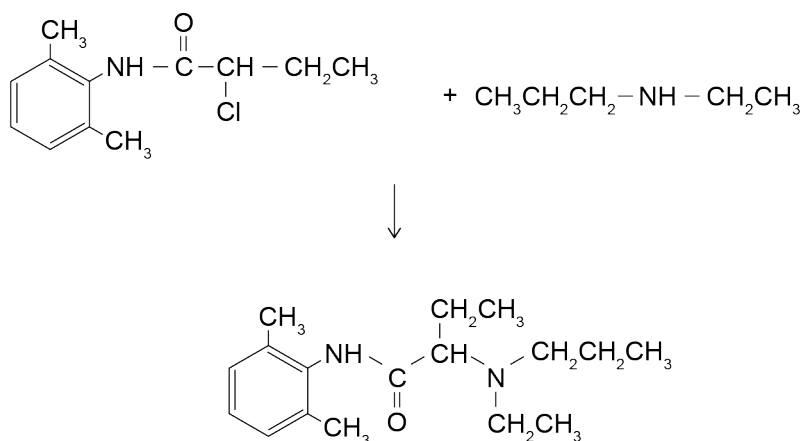
• Shapes and angles of XeO_3 and $[XeOF_3]^+$ with reasons.

Question Two

(a)

1. To make a secondary amine:

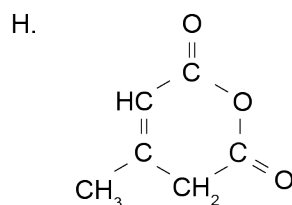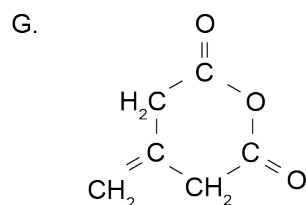$$CH_3CH_2-OH \xrightarrow{SOCl_2} CH_3CH_2-Cl \xrightarrow{conc\ NH_3} CH_3CH_2-NH_2$$

$$CH_3CH_2CH_2-OH \xrightarrow{SOCl_2} CH_3CH_2CH_2-Cl$$

$$CH_3CH_2-NH_2\ +\ CH_3CH_2CH_2-Cl \longrightarrow CH_3CH_2CH_2-NH-CH_2CH_3$$

2. To make an amide:
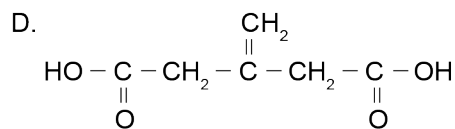

3. To replace the Cl with the amine:

(b)

A.

$$CH-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-CH_2-CH$$

with $\overset{||}{O}$ on the first CH and $\overset{||}{O}$ on the last CH.

B.

$$HO-\overset{\overset{}{}}{\underset{\underset{\displaystyle O}{||}}{C}}-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-CH_2-\overset{}{\underset{\underset{\displaystyle O}{||}}{C}}-OH$$

C.

$$HO-\overset{}{\underset{\underset{\displaystyle O}{||}}{C}}-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}-CH_2-\overset{}{\underset{\underset{\displaystyle O}{||}}{C}}-OH$$

D.

$$HO-\overset{}{\underset{\underset{\displaystyle O}{||}}{C}}-CH_2-\overset{\overset{\displaystyle CH_2}{||}}{C}-CH_2-\overset{}{\underset{\underset{\displaystyle O}{||}}{C}}-OH$$

E.

$$HO-\overset{}{\underset{\underset{\displaystyle O}{||}}{C}}-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{||}}{C}}=C-CH_2-\overset{}{\underset{\underset{\displaystyle O}{||}}{C}}-OH$$

F.

$$HO-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle O}{||}}{C}}-\overset{\overset{\displaystyle CH_3}{|}}{C}=C-CH_2-\overset{}{\underset{\underset{\displaystyle O}{||}}{C}}-OH$$

G.

(cyclic structure: H_2C and C with $=O$, ring with O, CH_2, CH_2, and $C=O$)

H.

(cyclic structure: HC and C with $=O$, ring with O, CH_3, CH_2, and $C=O$)
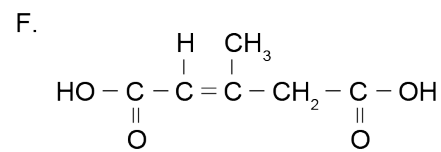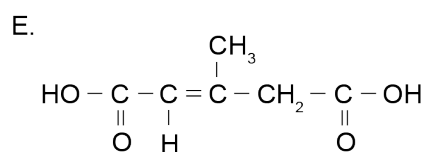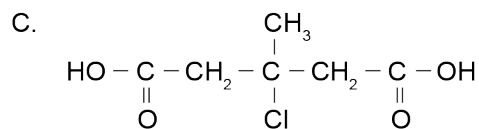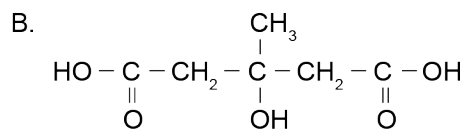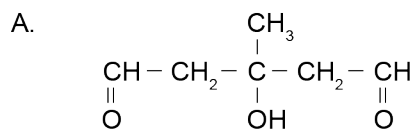
Judgement

7 – 8 marks

Shows understanding of chemistry by:
- Proposing a workable pathway including structures AND
- Correctly identifying structures A to H.

5 – 6 marks

Shows understanding of chemistry by:
- Correctly describes most steps of the synthesis AND
- Correctly identifies at least 5 of structures A to F.

1 – 4 marks

Answers include:
- Identity of some of the steps for the synthesis.
- Valid structures of some of the compounds A to F.
- Recognition of functional groups or isomerism in compounds A to F.

Question Three

(a) (i) V^{2+} is the best reductant – readily oxidised to V^{3+}. VO_2^+ has the highest value for $E°$ so is the best oxidant. It is more readily reduced than VO^{2+}. V^{3+} is the most stable species.

(ii) $n(VO_2^+) = 0.09243 \times 0.025 = 2.311 \times 10^{-3}$ mol

After reduction by SO_2 the vanadium is oxidised back to VO_2^+ by MnO_4^-.

$n(MnO_4^-) = 0.0216 \times 0.02138 = 4.62 \times 10^{-4}$ mol

Ratio MnO_4^- to vanadium = 4.62 : 23.11 = 1 : 5

Half equation for MnO_4^- / H^+ reduction is: $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

i.e. 5 e^- transfer so vanadium oxidation is a 1 e^- transfer reaction VO_2^+

Hence VO_2^+ must have initially lost 1 e^- to form VO^{2+}.

$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$

$2VO_2^+ + SO_2 \rightarrow 2VO^{2+} + SO_4^{2-}$

For the second reaction:

$n(MnO_4^-) = 0.0216 \times 0.06414 = 1.39 \times 10^{-3}$ mol

Ratio MnO_4^- to vanadium = 1.39 : 2.31 = 1 : 1.67 = 3 : 5

So the vanadium oxidation must be a 3 e^- transfer meaning the original VO_2^+ was reduced from +5 to +2,

i.e. VO_2^+ to V^{2+}.

$VO_2^+ + 4H^+ + 3e^- \rightarrow V^{2+} + 2H_2O$

$3Zn + 2VO_2^+ + 8H^+ \rightarrow 3Zn^{2+} + 2V^{2+} + 4H_2O$

Since SO_2 only reacts with VO_3^- but not with VO^{2+}, it must have a reduction potential that lies between 0.99 V and 0.34 V. (For a reaction to occur $E_{red} - E_{SO_2} > 0$)

However, Zn is able to reduce VO_2^+, VO^{2+} and V^{3+}. So the reduction potential must be less than -0.26 V.

(iii) In the second reaction, the reaction product was added to excess ammonium vanadate because of its instability.

$2V^{2+} + VO_2^+ + 4H^+ \rightarrow 3V^{3+} + 2H_2O$

2 mol of V^{2+} loses $2 \times 3e^- = 6e^-$ when reacted with MnO_4^- to produce VO_2^+ (oxidation number goes up by 3)

3 mol of V^{2+} also loses $3 \times 2e^- = 6e^-$ when reacted with MnO_4^- to produce VO^{2+} (oxidation number goes up by 2)

So the same titre of $KMnO_4$ is needed.

(b) alanine   – non-polar

aspartic acid   – pH > pK_a, so acid group will be in the form CH_2COO^-

glutamic acid – as for aspartic acid

leucine   – non-polar, since a hydrocarbon chain

lysine   – pH < pK_a, so protonated form prevails as written

serine   – polar due to difference in electronegativity making the O–H bond polar.

Hydrogen bonding to water would be expected for polar groups (and the amide backbone of the protein) and charged groups should also have strong attractive interactions with water (and be able to compete with water-water H-bonds). Non-polar groups will essentially be repelled from water, as they cannot make new H-bonds to water. They can, however, have favourable instantaneous induced dipole interactions with each other. Thus proteins should fold up to allow non-polar groups to engage with each other and not be exposed to water, and to have polar / charged groups with stabilising interactions with the solvent water.

Judgement

7 – 8 marks

Shows understanding of chemistry by:

- Comparing the relative oxidising/reducing strength of the ions and correctly accounts for the changes in the oxidation states of the vanadium species including calculations, relative reduction potentials and alternative procedures,

AND

- Discusses the nature of the side chains and their interactions in terms of their charge/polarity and the implications for protein folding.

5 – 6 marks

Shows understanding of chemistry by:

- Comparing the relative oxidising/reducing strength of the ions and correctly calculates the changes in the oxidation states of the vanadium species,

AND

- Identifies the charge/polarity of the side chains and the implications of their interactions (for protein folding).

1 – 4 marks

Answers include:

- Recognition of the strongest/weakest oxidants / reductants.
- Linking of titration data to stoichiometry.
- Identification of charge/polarity of side chains.
- Recognition of interactions between side chains.

Question Four

(a) Separation requires the breaking of hydrogen bonds. Longer fragments have more hydrogen bonds to break, so need a higher temperature. For chains of similar length, GC leads to higher melting than AT as there are more H-bonds between the GC pairs than the AT pairs.

Separating of DNA in water will involve breaking H-bonds between the strands and forming new H-bonds from the bases to water molecules. Each water molecule will only be able to form a single H-bond to a particular base. The functional groups of urea are similar to those in the DNA bases and more than one H-bond is possible in each case. For example:
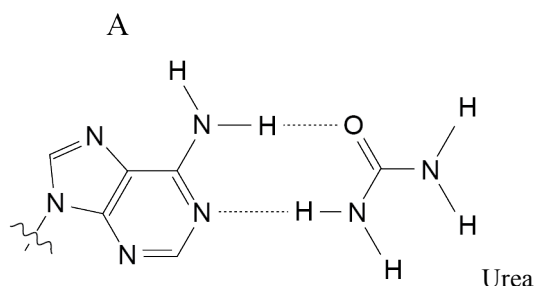
The separated form is more stable with these new H-bonds (as compared to water), so more energy is released and hence a lower temperature is required.

(b)

From Henry's Law $\dfrac{[CO_2(aq)]}{P_{CO_2}} = 3.317 \times 10^{-4}$ mol L^{-1} kPa^{-1}

$[CO_2(aq)] = 3.317 \times 10^{-4}$ mol L^{-1} $kPa^{-1} \times 0.0397$ kPa

$= 1.317 \times 10^{-5}$ mol L^{-1}

and $CO_2(aq) + H_2O \rightleftharpoons H_2CO_3$ $\qquad K = 1.70 \times 10^{-3}$

$\dfrac{[H_2CO_3]}{[CO_2(aq)]} = 1.70 \times 10^{-3}$ and $[H_2CO_3] = 1.70 \times 10^{-3} \times 1.317 \times 10^{-5}$
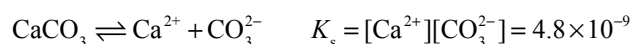
$= 2.239 \times 10^{-8}$

$H_2CO_3 + H_2O \rightleftharpoons HCO_3^- + H_3O^+$
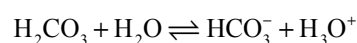
$\dfrac{[HCO_3^-][H_3O^+]}{[H_2CO_3]} = 2.51 \times 10^{-4}$ $\qquad [HCO_3^-] = \dfrac{2.51 \times 10^{-4} \times 2.239 \times 10^{-8}}{10^{-8.10}}$

$= 7.08 \times 10^{-4}$

$HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+$
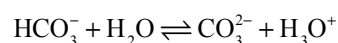
$\dfrac{[CO_3^{2-}][H_3O^+]}{[H_2CO_3]} = 5.62 \times 10^{-11}$ $\qquad [CO_3^{2-}] = \dfrac{5.62 \times 10^{-11} \times 7.08 \times 10^{-4}}{10^{-8.10}}$

$= 5.01 \times 10^{-6}$

$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-}$ $\qquad K_s = [Ca^{2+}][CO_3^{2-}] = 4.8 \times 10^{-9}$

$[Ca^{2+}] = \dfrac{4.8 \times 10^{-9}}{5.01 \times 10^{-6}} = 9.59 \times 10^{-4}$ mol L^{-1}

Ans $= 9.6 \times 10^{-4}$ mol L^{-1}

Judgement

7 – 8 marks

Shows understanding of chemistry by:

• Providing a coherent discussion of hydrogen bonding in the DNA strands and the effect of urea on separation temperature,
AND

• Correctly calculating the concentration of Ca^{2+} in the oceans.

5 – 6 marks

Shows understanding of chemistry by:

• Recognising the influence of hydrogen bonding on separation temperature and the new bonds formed when urea is present,
AND

• Uses the correct method to calculate Ca^{2+}.

1 – 4 marks

Answers include:

• Discussion of hydrogen bonds in DNA.

• Recognition of the link between separation temperature and the breaking of hydrogen bonds in DNA.

• Recognition of hydrogen bonding between urea and DNA.

• Correct use of information to calculate the concentration of $[H_2CO_3]$ and $[CO_2]$.

Question Five

(a)   Only the strongest acid with the largest K_a value will contribute an appreciable $[H_3O^+]$. In the equilibrium constant expression for K_a of ethanoic acid, $[H_3O^+]$ value due to strong hydrochloric acid so that $[CH_3COO^-]/[CH_3COOH]$ term equals 1.75×10^{-5} i.e. $[CH_3COO^-]$ is small.

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

Added CH_3COOH $n = 0.0700\ L \times 0.400\ mol\ L^{-1} = 0.0280\ mol$

$n(H_3O^+) = 0.100\ L \times 0.0200\ mol\ L^{-1} = 0.00200\ mol$

Total volume $= 0.170\ L$

$[CH_3COOH] = 0.0280\ /\ 0.170\ L = 0.165\ mol\ L^{-1}$

$[H_3O^+] = 0.00200\ mol\ /\ 0.170\ L = 0.0118\ mol\ L^{-1}$

$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$
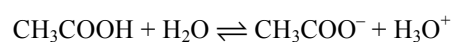
$K_a = 10^{-4.76} = 1.74\ x\ 10^{-5}$

$[CH_3COO^-] = 0.165\ x\ 1.74\ x\ 10^{-5}\ /\ 0.0118$

$[CH_3COO^-] = 2.43\ x\ 10^{-4}\ mol\ L^{-1}$

(b)   (i)

Titration	Initial	Half way to Equivalence Point	Equivalence Point	After Equivalence Point
(1) NH_4^+	5.27	9.24	10.92	12.5
(2) NH_3	10.97	9.24	5.3	1.48
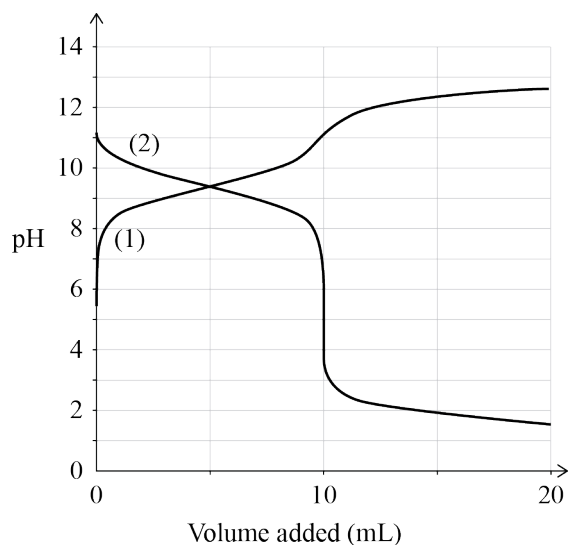
(ii)   Similarities – Half way to equivalence point, pH = pK_a since $[NH_3] = [NH_4^+]$

Buffer region – across similar volume but reversed in shape

For Titration (1) the initial pH 5.27 reflects the acidic nature of NH_4^+

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$
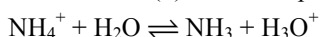
Before half equivalence point pH is less than pK_a since 'buffer' has greater $[NH_4^+]$ and pH depends on $[NH_3] / [NH_4^+]$. This is reversed after 5 mL is added.

Equivalence point has pH of 10.95. This is greater than 7 since the product of the titration is a base.

$$NH_4^+ + OH^- \rightarrow NH_3 + H_2O \text{ and } NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$$
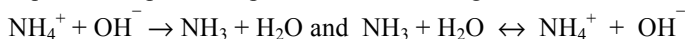
After equivalence point the pH gets close to the pH of the base used, but since it is being diluted on addition to the titration solution it will be less than this.

For Titration (2) the initial pH is 11 because the solution is basic:

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$$
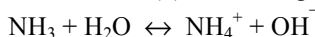
The shape of the buffer region is determined by the gradual addition of acid, which reduces $[NH_3]$.

pH at equivalence point is 5.3. This is less than 7 because the product of the titration is an acidic salt

$$NH_3 + HCl \rightarrow NH_4^+ + Cl^- \text{ and } NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$

After equivalence point, the pH gets close to the pH of the acid used, but since it is being diluted on addition to the titration solution it will be less than this.

(c)   Colour of the indicator depends on the ratio of $[In^-]/[HIn]$ which depends on the pH of the solution.

$$pH = pK_a + \log [In^-]/[HIn]$$

For methyl red the orange colour occurs when there is a similar concentration of the red and the yellow species. This will be close to the point where pH = pK_a.

If more than a few drops of indicator are used, then the added acid from the indicator will also react with the titrant, meaning that the volume used will be higher than the required amount for the titration reaction.

Judgement
7 – 8 marks
Shows understanding of chemistry by:
• Discussing the reason for the small pH change including the correct calculation,
AND
• Sketches both titration curves correctly with coherent discussion of similarities and differences,
AND
• Correct discussion of indicator colour changes.
5 – 6 marks
Shows understanding of chemistry by:
• Correct calculation of pH change,
AND
• Graphs drawn with some discussion,
AND
• Reasons for indicator colour changes given.
1 – 4 marks
Answers include:
• Correct procedure for pH calculation.
• pH calculations for some graph points.
• Reasons for some similarities and differences.
• Link colour change to ratio link of species present.