TOP SCHOLAR

NZQA

NEW ZEALAND QUALIFICATIONS AUTHORITY
MANA TOHU MĀTAURANGA O AOTEAROA

Scholarship 2009
Chemistry

9.30 am Saturday 28 November 2009
Time allowed: Three hours
Total marks: 48

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.

A periodic table is provided on page 2 of this booklet.

Write all your answers in this booklet.

If you need more space for any answer, use the page(s) provided at the back of this booklet and clearly number the question.

Check that this booklet has pages 2–25 in the correct order and that none of these pages is blank.

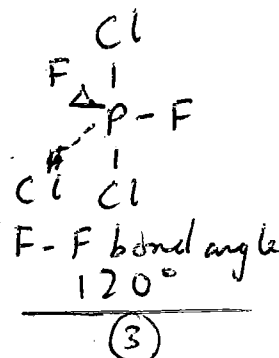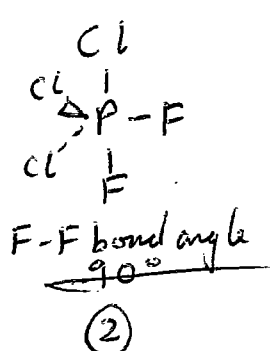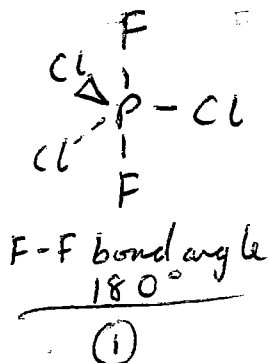You are advised to spend approximately 30 minutes on each question.

YOU MUST HAND THIS BOOKLET TO THE SUPERVISOR AT THE END OF THE EXAMINATION.

You have three hours to complete this examination.

QUESTION ONE (8 marks)

(a) (i) Draw a 3-dimensional structure for each of the possible isomers of the pentahalide PCl_3F_2, indicating the size of the F-P-F bond angle in each isomer.

(ii) In VSEPR theory it is assumed that the bond from the central atom to an atom of lower electronegativity occupies more space than the bond from the central atom to an atom of higher electronegativity.

Comment on the polarity of each of the isomers of PCl_3F_2 and identify the isomer that is most likely to occur.

Fluorine is more electronegative than chlorine, so any polarity would be due to a non-symmetrical arrangement of fluorines around the phosphorous. Due to this, isomer 2 would be the most polar as the fluorine molecules are closest together, while in 3 the bond angle is greater and so the polarity less, and in 1 the molecule is non polar as it is a symmetrical arrangement. 3 would be the most likely isomer as chlorine is less electronegative than chlorine and is larger, so would take up more space. Therefore isomer 1 separates all three chlorine angles from each other the most, as in 2 and 3 there are chlorine-chlorine bond angles which are 90°.

(iii) Upon standing for several days at low temperature, phosphorus pentahalide compounds convert to isomeric ionic solids.

In crystalline PBr_4Cl, only one of the two ions formed contains phosphorus.

Predict the formulae of the ions in solid PBr_4Cl, and justify your answer.

The ions would be PBr_4^+ and Cl^-. This is because the chlorine atom is more electronegative than bromine and phosphorous, and so would be more likely to be able to remove the bond pair of electrons from phosphorous to form an ion. The electronegativities of bromine and phosphorous are too similar to form an ion and No other atom-atom bonds are present so no other ions could be formed, as the molecule consists of bromines and chlorines all bonded to the central phosphorous atom.

(b) Two possible isomers may be formed when H^+ reacts with isocyanate, NCO^-, as the H^+ may bond to either nitrogen or oxygen. A structural study of one of the isomers that is produced shows that it has a bond angle of 105° at the atom to which the H is attached.

- Draw Lewis diagrams for the two possible structures of the product.

- Identify and explain which Lewis diagram better represents the structure of the product with the bond angle of 105° mentioned above.

$$\overset{x}{\underset{x}{N}} \equiv C - \overset{xx}{\underset{xx}{O}}$$
$$|$$
$$H$$

$$H - \overset{xx}{N} = C - O$$
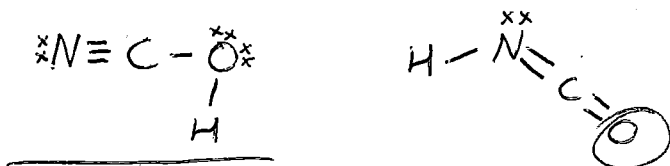
The product with the hydrogen ion attached to the oxygen represents the structure which has a bond angle of 105°. For the other product, HNCO, the nitrogen has one lone pair of electrons and is bonded to two atoms. As, due to VSEPR theory, the electrons in the lone pair and bonds would all repel each other, the most stable arrangement would be in a trigonal planar shape, which has a bond angle of 120°. In NCOH, however, the oxygen has two lone pairs of electrons. These lone pairs repel each other more than the bonded electrons repel, and so the bonds are pushed closer together, resulting in a bond angle of roughly 105°.

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QUESTION TWO (8 marks)

(a) Titanium is a Group 4 transition metal. There are three different chlorides of titanium: $TiCl_2$, $TiCl_3$ and $TiCl_4$. One of these chlorides, **A**, is a solid that dissolves in water to produce a mildly acidic purple solution. On standing in the presence of air, the colour of this solution fades, and a white solid, TiO_2, is formed. The chlorides **B** and **C** are very reactive toward water. **B** is a liquid and reacts to produce a strongly acidic solution and TiO_2. **C** reacts with acidified water to produce a purple solution and hydrogen gas.
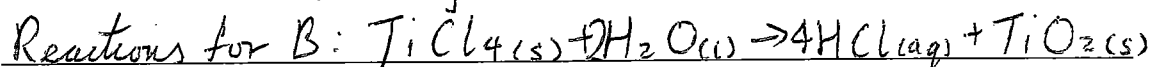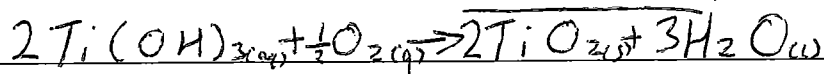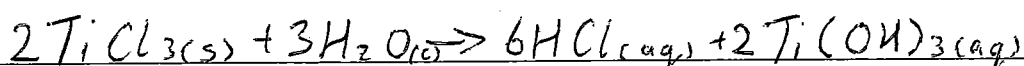
(i) Identify which of the chlorides of titanium is **A**, which is **B** and which is **C**.

Justify your answers using the properties of transition metals, including the colours and reactions outlined above, and/or by analogy with the chemistry of other transition metals. Include balanced equations for the reactions described.
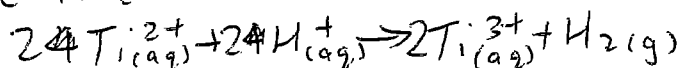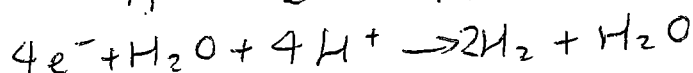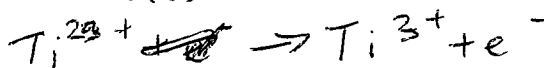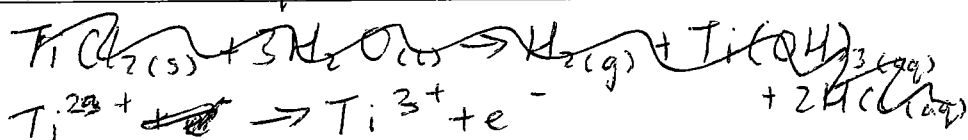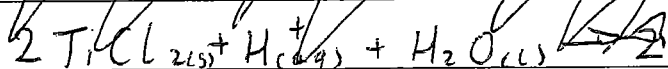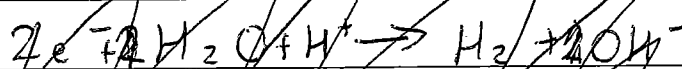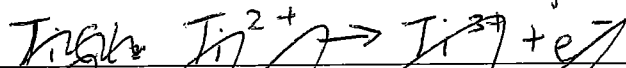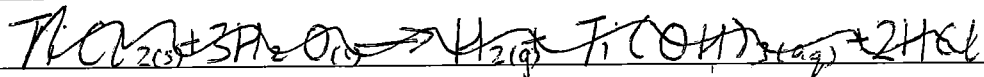
Transition metals ~~form~~ form colored compounds when their ions have ~~unfilled~~ half filled d-orbitals, so in $TiCl_4$, where there ~~is no color~~ are no d-orbital electrons, there is no color, so B is $TiCl_4$.

When C reacts with water, it reduces the hydrogen in the water and forms a colored compound, so it must be oxidised. C therefore is $TiCl_2$ as if $TiCl_3$ ~~were~~ were oxidised it would form Ti^{4+} which ~~has no co~~ does not form colored compounds. Therefore A is $TiCl_3$.

Reactions for A: ~~$TiCl_3 + H_2O \rightarrow 3HCl$~~

$$2TiCl_{3(s)} + 3H_2O_{(l)} \rightarrow 6HCl_{(aq)} + 2Ti(OH)_{3(aq)}$$

$$2Ti(OH)_{3(aq)} + \tfrac{1}{2}O_{2(g)} \rightarrow 2TiO_{2(s)} + 3H_2O_{(l)}$$

Reactions for B: $TiCl_{4(s)} + 2H_2O_{(l)} \rightarrow 4HCl_{(aq)} + TiO_{2(s)}$

Reactions for C:

~~$TiCl_{2(s)} + 3H_2O \rightarrow H_{2(g)} + Ti(OH)_{3(aq)} + 2HCl$~~

~~$Ti^{2+} \rightarrow Ti^{3+} + e^-$~~

~~$2e^- + 2H_2O + H^+ \rightarrow H_2 + 2OH^-$~~

~~$2TiCl_{2(s)} + H_{(aq)}^+ + H_2O_{(l)} \rightarrow$~~

~~$TiCl_{2(s)} + 3H_2O \rightarrow H_{2(g)} + Ti(OH)_{3(aq)} + 2HCl_{(aq)}$~~

$$Ti^{2+} + \rightarrow Ti^{3+} + e^-$$

$$4e^- + H_2O + 4H^+ \rightarrow 2H_2 + H_2O$$

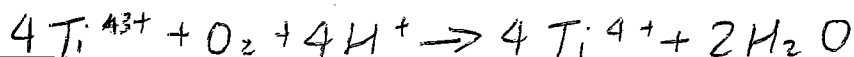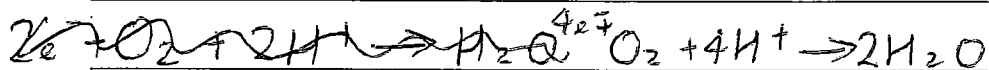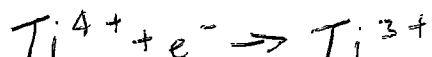$$24Ti_{(aq)}^{2+} + 24H_{(aq)}^+ \rightarrow 2Ti_{(aq)}^{3+} + H_{2(g)}$$

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(ii) Determine the upper limit for the reduction potential for each of the Ti(IV)/Ti(III) couple and the Ti(III)/Ti(II) couple.

$$E^\circ(H_2O/H_2) = -0.42 \text{ V} \qquad E^\circ(O_2/H_2O) = 0.82 \text{ V}$$

$$Ti^{4+} + e^- \rightarrow Ti^{3+}$$

$$\cancel{2e^- + O_2 + 2H^+ \rightarrow H_2O} \quad 4e^- \; O_2 + 4H^+ \rightarrow 2H_2O$$

$$4Ti^{3+} + O_2 + 4H^+ \rightarrow 4Ti^{4+} + 2H_2O$$

$$E^\circ_r = E^\circ(O_2/H_2O) - E^\circ(Ti(IV)/Ti(III))$$

$$= 0.82 - E^\circ(Ti(IV)/Ti(III))$$

In order for reaction to be spontaneous, E°_r has to be positive, so upper limit for Ti(IV)/Ti(III) couple is +0.82 V

$$Ti^{3+} + e^- \rightarrow Ti^{2+}$$

$$4e^- + H_2O + 4H^+ \rightarrow 2H_2 + H_2O$$

$$2Ti^{2+} + 2H^+ \rightarrow 2Ti^{3+} + H_2$$
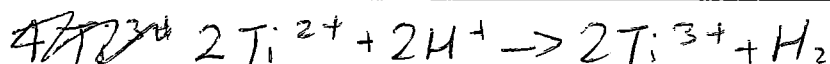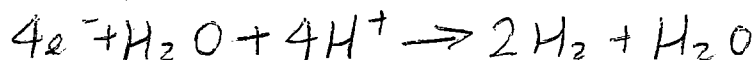
$$E^\circ_r = E^\circ(H_2O/H_2) - E^\circ(Ti(III)/Ti(II))$$

$$= -0.42 - E^\circ(Ti(III)/Ti(II))$$

In order for reaction to be spontaneous, E°_r must be positive, so upper limit for Ti(III)/Ti(II) couple is -0.42 V

(b) Titanium occurs naturally both as ilmenite ($FeTiO_3$) and TiO_2. The isolation of titanium metal from ilmenite involves heating ilmenite, chlorine and carbon to form $TiCl_4$. This is then converted into titanium metal by treatment with magnesium.

$$2FeTiO_3 + 7Cl_2 + 6C \rightarrow 2TiCl_4 + 2FeCl_3 + 6CO$$
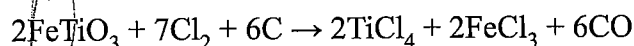
Discuss the possible oxidation number changes and electron transfers that occur in the conversion of ilmenite to $TiCl_4$, taking into consideration the variety of oxidation numbers that are possible for the metals.

In ilmenite, the oxidation number of titanium is

There are 3 possible oxidation states for titanium: +2, +3, +4. In $TiCl_4$, the oxidation state of Ti is +4. In this reaction the chlorine has been reduced, going from +0 in Cl_2 to -1 in Cl^-, while carbon has been oxidised, going from +0 in C to +4 in CO. The oxidation states for oxygen remain the same so it is likely that the oxidation state for iron remained the same as otherwise the oxidation state for Ti would be the same.

First, the Ti (III) oxidised the carbon

$$TiO_{3(s)} + 3C_{(s)} \rightarrow Ti^{2+} + 3CO_2$$
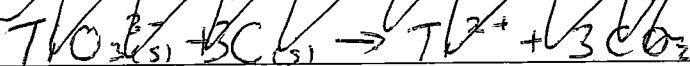
Overall, the Ti oxidised the carbon, and so was reduced to the +2 oxidation state, and the reduced the chlorine, and so it was the Ti was oxidised to +4 in $TiCl_4$.

$$2TiO_3^{3-} + 3C \rightarrow 2Ti^{2+} + 3CO_2 \quad 3CO_2 + Ti^-$$
$$2Ti^{2+} + Cl_2 \rightarrow 2Cl^- + 2Ti^{3+}$$
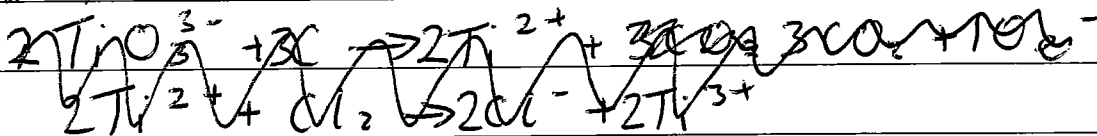
So the Ti removed oxygen + etc

So overall, electrons were transferred from carbon and titanium to chlorine.

QUESTION THREE (8 marks)

(a) (i) The structural formula of the amino acid glycine can sometimes be written as $H_3\overset{+}{N}CH_2COO^-$ (a zwitterion) and sometimes as H_2NCH_2COOH.

Explain which structure is more appropriate, taking into account functional group chemistry and the fact that glycine is a crystalline solid that has a melting point of 233°C.

The structure of the zwitterion $H_3\overset{+}{N}CH_2COO^-$ seems more appropriate, as if it were H_2NCH_2COOH, the strongest intermolecular bonds would be hydrogen bonding between the amine and carboxyl side groups. These bonds are not likely to be strong enough to explain the relatively high melting point and crystalline structure. Instead an ionic structure such as the zwitterion is more appropriate as the ionic lattice formed due to the charged ends would explain both physical features.

(ii) The amino acids serine and asparagine have the zwitterion structures shown below.

$$H_3\overset{+}{N}-CH-COO^-$$
$$|$$
$$CH_2$$
$$|$$
$$OH$$

serine

$$H_3\overset{+}{N}-CH-COO^-$$
$$|$$
$$CH_2$$
$$|$$
$$C=O$$
$$|$$
$$NH_2$$
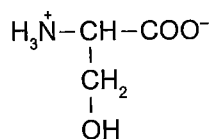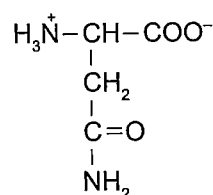
asparagine

These amino acids can be linked to form two different dipeptides.

Discuss how the structures of these dipeptides change as the pH of the aqueous solutions change from highly acidic, through neutral, to highly basic.

Include structural formulae in your answer.

The two structures are: $H_3\overset{+}{N}CH(CH_2OH)\overset{O}{C}O$

$H_3\overset{+}{N}CH(CH_2OH)\overset{O}{C}ONH$

$H_3\overset{+}{N}CH(CH_2OH)\overset{O}{C}-NHCH(CH_2CONH_2)COO^-$

serine - asparagine

$H_3\overset{+}{N}CH(CH_2CONH_2)\overset{O}{C}-NHCH(CH_2OH)COO^-$

asparagine - serine

In highly acidic conditions, the COO^- ends would be protonated to form $-COOH$, while the $-\overset{+}{N}H_3$ end stays the same, due to the high concentration of H^+.

In basic or neutral conditions the $-COOH$ would be deprotonated again as pH rises from acidic conditions to reform the zwitterion.

As the pH increases further the concentration of OH^- ions increases, and in highly basic the $-\overset{+}{N}H_3$ ends would begin to be deprotonated, until they all exist as $-NH_2$ in highly basic solution.

(b)   Esters are hydrolysed by reaction with dilute acid. This reaction and the purification of the organic products involve the use of both reflux and distillation.

Discuss how each of these two processes is involved in preparing and isolating pure samples of the organic products.

Reflux is the process of vaporizing the reactants, and then cooling them as they pass through a condensing tube so that they condense and return to the mixture. This process is used to speed up a reaction as well as ensure thorough mixing of the reactants such that they react fully.

Distillation is used to isolate a substance with a unique boiling point from a mixture. In the hydrolysis of esters, it is used to extract and separate the acid and alcohol formed. The solution is heated to the known boiling point of the substance with the lower boiling point, and is allowed to boil. The gas given off is then passed down a condensing tube and collected in a flask. This process ensures a relatively pure sample as each substance in the mixture only vaporizes above its boiling point, and temperature does not change when a substance is boiling.

(c) Compound **A** has the formula $C_9H_{18}O_3$.

When compound **A** is refluxed with dilute sulfuric acid, it forms compound **B**, $C_6H_{12}O_3$ and compound **C**, C_3H_8O. Both compounds **B** and **C** react with acidified potassium dichromate to produce compounds **D**, $C_6H_{10}O_3$ and **E**, C_3H_6O respectively. Neither compound **D** nor **E** reacts with Tollens' reagent.

When compound **B** is reacted with concentrated sulfuric acid, it produces THREE structural isomers **F**, **G** and **H**, of molecular formula $C_6H_{10}O_2$, all of which are optically active. **F** exists as geometrical isomers, but **G** does not. Both **F** and **G** decolourise a solution of bromine, **H** does not.

Give the structural formulae for compounds **A** to **H** that are consistent with the information above.
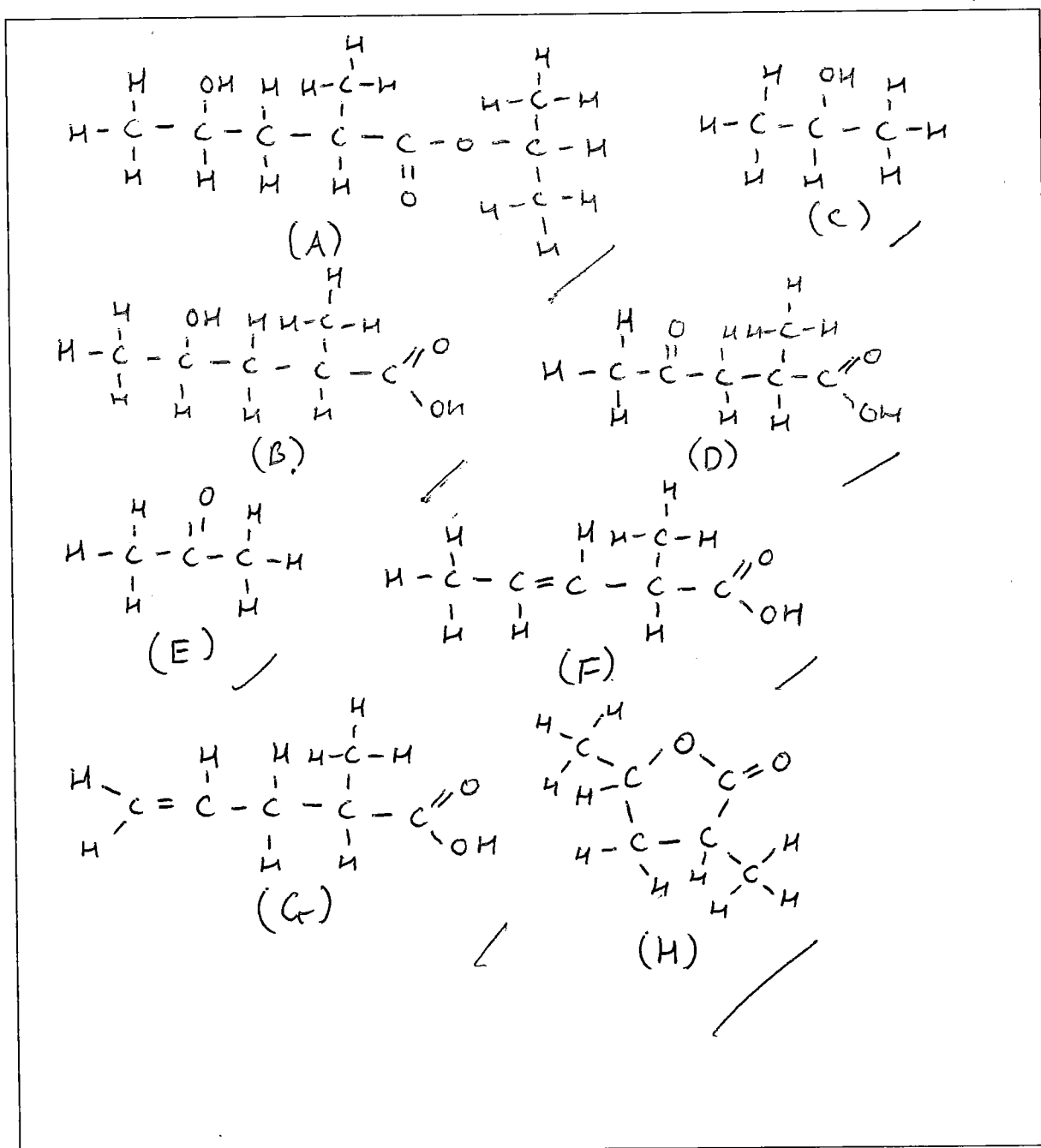
A - ester 6 - 3
B, C - secondary alcohol

Space for working.

QUESTION FOUR (8 marks)

(a) Models are representations used to explain observed phenomena.

A model useful for describing the physical properties of Group 18 elements views the particles of these elements as individual atoms.

In contrast, various properties of metals, both in solid and liquid form, can be explained by a model that views the structure of the metal as cations submerged in a "sea of electrons". In this model, the "electron sea" consists of valence electrons moving freely throughout the metal structure.

The table below shows the melting points (mp) and boiling points (bp) for selected elements in Groups 1 and 18 of the periodic table.

1	2		13	14	15	16	17	18
Li mp: 180°C bp: 1342°C	Be							**Ne** mp: −249°C bp: −246°C
Na mp: 98°C bp: 883°C	Mg							**Ar** mp: −189°C bp: −186°C
K mp: 63°C bp: 760°C	Ca							**Kr** mp: −157°C bp: −152°C
Rb mp: 39°C bp: 686°C	Sr							**Xe** mp: −112°C bp: −108°C

(i) Explain the trend in boiling points of the Group 18 elements.

(ii) Discuss how each of the statements below is evidence for the different models described above.

- *The boiling point of a Group 18 element is significantly lower than the boiling point of the Group 1 element with the next higher atomic number.*

- *The **difference** between the boiling point and the melting point of a Group 1 metal, such as sodium, is much larger than the **difference** between the boiling point and melting point of a Group 18 element, such as argon.*

(iii) Predict, using the "electron sea" model described above, how the boiling points for the Group 1 metals would compare with those for the Group 2 metals.

i) As you go down group 18, the boiling points of the elements show a gradual increase. This is because, with the noble elements, the only intermolecular forces in liquid state are temporary induced dipole dipole interactions, as essentially the particles are individual atoms. As you

go down the group, the size of the electron cloud around each nucleus increases, and so the ~~size of~~ magnitude of the temporary induced dipoles increases, resulting in a higher boiling point as more energy is required to break the stronger bonds.

ii) The first statement provides evidence for this model as the large difference in boiling points ~~when the two elements have the same~~ suggests stronger intermolecular attractions in the metal. This cannot be explained by temporary induced dipole dipole interactions as the atoms have relatively similar atomic masses, and so there must be another type of bonding present - such as that between the nuclei and the sea of electrons.

The second statement provides evidence for the different models as, if only temporary induced dipole dipole interactions were present, as when the atoms are individual particles, the difference between boiling and melting points would be very small as once the solid lattice is broken very little energy is required to separate the particles and break the weak intermolecular forces. In the metals, however, this difference is much larger, which can be explained by the fact that the sea of electrons is still present in liquid form and much energy is required to separate the nuclei and break the strong intermolecular forces.

iii) The group 2 metals would have higher boiling points than group 1 as each atom has an extra valence electron to donate to the sea of electrons in group 2, as well as each nucleus having an extra unit of positive charge. This results in a stronger metallic bond* and so more energy is required to separate the particles in boiling
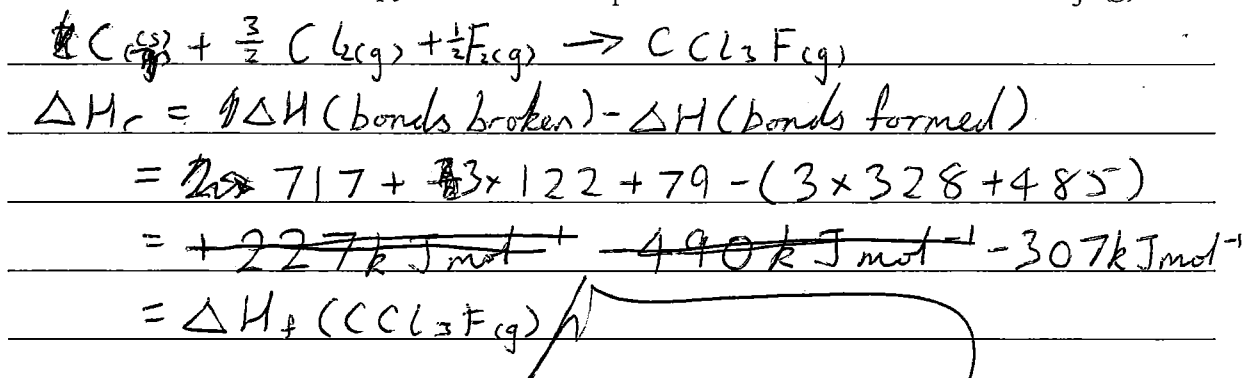
→ * between the sea of electrons and the nuclei as the magnitudes of the charges are greater

(b) The standard enthalpy of atomisation, $\Delta_{at}H°$, is defined as the enthalpy change when 1 mole of atoms, in the gas phase, is formed from the element in its standard state at 25°C.

Element	Standard Enthalpy of Atomisation, $\Delta_{at}H°$ / kJ mol^{-1}
C	717
F	79
Cl	122

	Bond Enthalpy / kJ mol^{-1}
C–F	485
C–Cl	328

Calculate the standard enthalpy of formation, $\Delta_fH°$, of trichlorofluoromethane, $CCl_3F(g)$.

$$C(s) + \frac{3}{2}Cl_2(g) + \frac{1}{2}F_2(g) \rightarrow CCl_3F(g)$$

$$\Delta H_r = \Delta H(bonds\ broken) - \Delta H(bonds\ formed)$$

$$= 717 + 3 \times 122 + 79 - (3 \times 328 + 485)$$

$$= +227\ kJ\ mol^{-1}\ -490\ kJ\ mol^{-1} - 307\ kJ\ mol^{-1}$$

$$= \Delta H_f(CCl_3F(g))$$

Assessor's use only

QUESTION FIVE (8 marks)
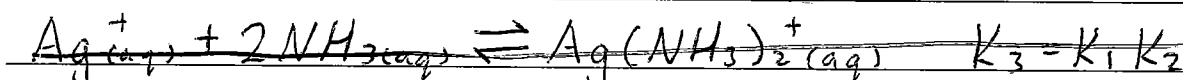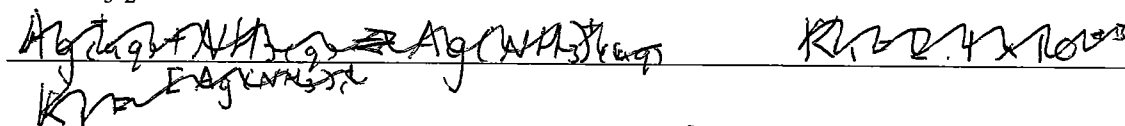
(a) When silver ions are dissolved in an aqueous ammonia solution, complex ions of $Ag(NH_3)_2^+(aq)$ form. The formation of $Ag(NH_3)_2^+(aq)$ occurs in two steps that are represented by the equations below, together with the corresponding equilibrium constant for each reaction.

$$Ag^+(aq) + NH_3(aq) \rightleftharpoons Ag(NH_3)^+(aq) \qquad K_1 = 2.1 \times 10^3$$

$$Ag(NH_3)^+(aq) + NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) \qquad K_2 = 8.2 \times 10^3$$
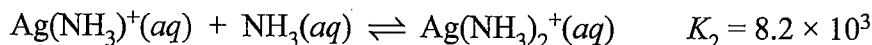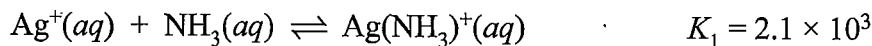
0.15 mol of $AgNO_3(s)$ is dissolved in 1.00 L of a 1.00 mol L^{-1} solution of aqueous ammonia.

Use the values of the equilibrium constants to identify the major species in this solution at equilibrium, and hence calculate the concentrations in mol L^{-1} of the Ag^+, $Ag(NH_3)^+$ and $Ag(NH_3)_2^+$ ions.

$$Ag^+(aq) + NH_3(aq) \rightleftharpoons Ag(NH_3)^+(aq) \qquad K_1 = 2.1 \times 10^3$$

$$K_1 = \frac{[Ag(NH_3)^+]}{}$$

$$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) \qquad K_3 = K_1 K_2$$

Due to the large values of K_1 and especially K_2, the major species in this solution at equilibrium are NH_3, $Ag(NH_3)_2^+$ and $Ag(NH_3)^+$, as all of the silver ions will have been made into complexed.

Let x be the equto $[Ag(NH_3)_2^+]$ at equilibrium

$$K_2 = \frac{x}{(0.15-x)(0.85-x)}$$

$$8.2 \times 10^3 = \frac{x}{(0.15 \times 0.85 - x + x^2)}$$

$$8.2 \times 10^3 x^2 - 8.2 \times 10^3 x - 1045.5 = 0$$

$$x = 0.15 \text{ or } 0.85, \quad x \neq 0.85$$

∴ major species at equilibrium are $NH_3(aq)$ and $Ag(NH_3)_2^+(aq)$, and $[NH_3(aq)] = 0.70$ mols L^{-1}

and $NO_3^-(aq)$ $\quad [Ag(NH_3)_2^+(aq)] = 0.15$ mols L^{-1}

$$[NO_3^-(aq)] = 0.15 \text{ mols } L^{-1}$$

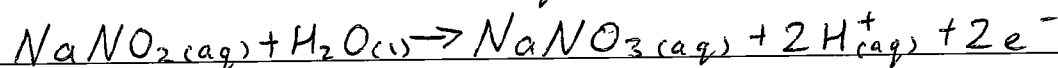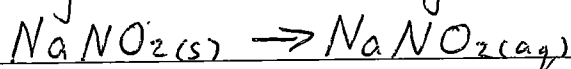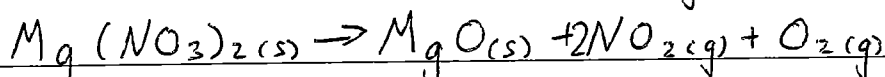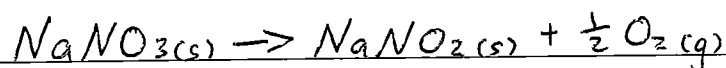Due to the large value of K_1, it can be assumed that all of the silver is complexed. //

(b) 15.35 g of a mixture of sodium nitrate, $NaNO_3$, and magnesium nitrate, $Mg(NO_3)_2$, was heated until no more gases were evolved. The $NaNO_3$ decomposes giving sodium nitrite, $NaNO_2$, and oxygen gas, while the $Mg(NO_3)_2$ decomposes to give the metal oxide, nitrogen dioxide and oxygen. The water-soluble part of the residue produced on heating was used to prepare 1.00 L of solution. 10.00 mL of this solution was reacted with 20.00 mL of 0.0200 mol L^{-1} acidified potassium permanganate (which oxidises nitrite to nitrate). The excess potassium permanganate required 10.25 mL of 0.0500 mol L^{-1} oxalic acid, $H_2C_2O_4$, for complete reaction in which oxalic acid is oxidised to form CO_2.

Write balanced equations for all of the reactions occurring above, and hence calculate the mass, in grams, of each metal nitrate present in the original mixture.

$$NaNO_{3(s)} \rightarrow NaNO_{2(s)} + \tfrac{1}{2}O_{2(g)}$$

$$Mg(NO_3)_{2(s)} \rightarrow MgO_{(s)} + 2NO_{2(g)} + O_{2(g)}$$

$$NaNO_{2(s)} \rightarrow NaNO_{2(aq)}$$

$$NaNO_{2(aq)} + H_2O_{(l)} \rightarrow NaNO_{3(aq)} + 2H^+_{(aq)} + 2e^-$$

$$5e^- + MnO_{4(aq)}^- + 8H^+_{(aq)} \rightarrow Mn^{2+}_{(aq)} + 4H_2O_{(l)}$$

$$5NaNO_{2(aq)} + 2MnO_{4(aq)}^- + 6H^+_{(aq)} \rightarrow 5NaNO_{3(aq)} + 2Mn^{2+}_{(aq)} + 3H_2O_{(l)}$$

$$C_2O_{4(aq)}^{2-} \rightarrow 2CO_{2(g)} + 2e^-$$

$$5C_2O_{4(aq)}^{2-} + 2MnO_{4(aq)}^- + 16H^+_{(aq)} \rightarrow 10CO_{2(g)} + 2Mn^{2+}_{(aq)} + 8H_2O_{(l)}$$
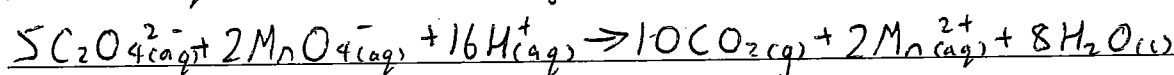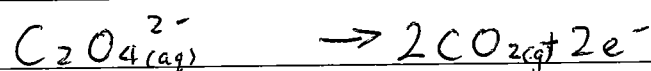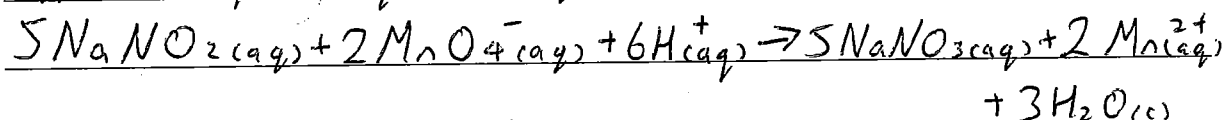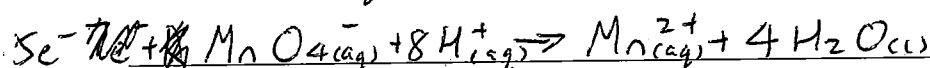
$$n(H_2C_2O_4)_{consumed} = 0.01025 \times 0.05$$
$$= 5.125 \times 10^{-4} \text{ mols}$$

$$n(KMnO_4)_{left\ over} = 5.125 \times 10^{-4} \times \tfrac{2}{5}$$
$$= 2.05 \times 10^{-4} \text{ mols}$$

$$n(KMnO_4)_{consumed\ by\ NO_2^-} = 0.02 \times 0.02 - 2.05 \times 10^{-4}$$
$$= 1.95 \times 10^{-4} \text{ mols}$$

$$n(NaNO_2) = 1.95 \times 10^{-4} \times \tfrac{5}{2}$$
$$= 4.875 \times 10^{-4} \text{ mols}$$

$$n(NaNO_2)_{in\ 1L\ of\ solution} = 4.875 \times 10^{-4} \times \frac{1000}{10}$$
$$= 0.04875 \text{ mols}$$

$$n(NaNO_3) = 0.04875 \text{ mols}$$

$$m(NaNO_3) = 0.04875 \times (23 + 14 + 3 \times 16)$$
$$= 4.14 g$$

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$$m(Mg(NO_3)_2) = 15.35 - 4.14$$
$$= 11.21 g$$

Scholarship Chemistry 93102, 2009

QUESTION SIX (8 marks)
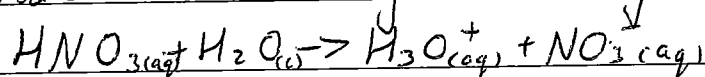
Three flasks contain aqueous solutions of the **same pH**. One of the solutions is 0.0010 mol L^{-1} nitric acid, one is 0.0060 mol L^{-1} methanoic acid (HCOOH) and one is 0.040 mol L^{-1} anilinium hydrochloride ($C_6H_5NH_3Cl$).

(a) Use the information above to calculate the pK_a for HCOOH and for $C_6H_5NH_3^+$.

Explain why the different concentrations of the three acids produce the same pH.

Nitric acid is a strong base and fully dissociates:

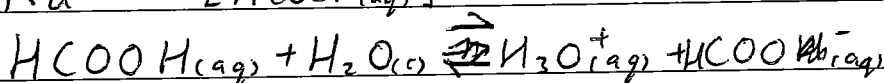$HNO_{3(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + NO^-_{3(aq)}$

so $[H_3O^+_{(aq)}] = 0.0010$ mol L^{-1}

~~pH = ~~ ~~-log(0.001) =~~

In HCOOH solution, pH is the same, so $[H_3O^+] = 0.001$ mol L^{-1}

$K_a = \dfrac{[H_3O^+_{(aq)}][HCOO^-_{(aq)}]}{[HCOOH_{(aq)}]}$

$HCOOH_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + HCOO^-_{(aq)}$

$[H_3O^+_{(aq)}] = [HCOO^-_{(aq)}] = 0.006 - [HCOOH_{(aq)}]$

$K_a(HCOOH) = \dfrac{(0.001)^2}{0.005} = 2 \times 10^{-4}$

$pK_a = ~~-log(2\times10^{-4})~~ = -log(2\times10^{-4}) = 3.70$

For $C_6H_5NH_3Cl$

$C_6H_5NH_3Cl_{(aq)} + H_2O_{(l)} \rightleftharpoons C_6H_5NH_{2(aq)} + H_3O^+_{(aq)} + Cl^-_{(aq)}$

$K_a = \dfrac{[C_6H_5NH_2Cl_{(aq)}][H_3O^+_{(aq)}]}{[C_6H_5NH_3Cl_{(aq)}]} = \dfrac{(0.001)^2}{(0.04-0.001)}$
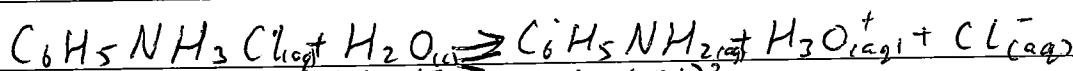
$= 2.56 \times 10^{-5}$

$pK_a = -log(2.56\times10^{-5}) = 4.59$

The different concentrations produce the same pH as both methanoic acid and anilinium hydrochloride are only weak acids, and only partially dissociate in water. Anilinium hydrochloride dissociates to a lesser extent and so a higher concentration is needed to produce the same amount of H_3O^+. Nitric acid dissociates the most as it is a strong acid and fully dissociates, so it needs the lowest concentration for the same pH.

(b) The three acid solutions in part (a) are diluted by a factor of 10.

Discuss the change in both the pH of each of the solutions and the concentrations of the species present.

NO CALCULATIONS ARE REQUIRED.

Nitric acid is a strong acid, so when it is diluted by a factor of 10, the concentration of hydronium ions in solution decreases by a factor of 10, so pH ~~decreases~~ (increases) by 1.

Methanoic acid and anilinium hydrochloride are weak acids, and form an equilibrium between the acid and the basic salt.

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

When this solution is diluted, the ~~concent~~ total concentration on the right hand side decreases more, as $[H_2O]$ is taken to be constant or, in this case would increase slightly. This causes the equilibrium to favor the forward reaction due to Le Chatelier's principle, so the ~~decr~~ increase in pH will be less than 1. It will also be ~~less~~ (more) for ~~aliniun~~ anilinium ~~of~~ hydrochloride than methanoic acid as its Ka is ~~less~~ smaller and so the overall change is ~~smaller~~ more basic towards as less acid will dissociate.

→ * as ~~more a~~ a larger proportion of acid will dissociate//