1

Victoria Junior College
2013 H2 Chemistry Prelim Exam 9647/3
Suggested Answers

1 During strenuous exercise, pyruvic acid, $CH_3COCOOH$, is converted to lactic acid, $CH_3CH(OH)COOH$, which builds up in our muscles due to limited oxygen availability.

(a) Such anaerobic respiration is catalysed by the enzyme lactate dehydrogenase, with concomitant conversion of NADH to NAD^+. NADH plays a key role in the production of energy through redox reactions. NADH and NAD^+ are cofactors, substances that act with and are essential to the activity of an enzyme.

(i) Write a balanced equation for anaerobic respiration. Using the data given in the table below, calculate the value of E^{θ}_{cell} for this reaction.

Electrode reaction	E^{θ} /V
$2e^- + H^+ + NAD^+ \rightleftharpoons NADH$	–0.32
$2e^- + 2H^+ + CH_3COCOOH \rightleftharpoons CH_3CH(OH)COOH$	+0.89

C
C
$H_3COCOOH + NADH + H^+ \rightarrow CH_3CH(OH)COOH + NAD^+$
$E^{\ominus}$ = +0.89 – (-0.32) = +1.21V

(ii) It is not possible to use $E^{\ominus}$ values reliably to decide whether a chemical reaction will occur. Suggest a reason for this.

The reaction may be kinetically unfeasible due to high activation energy, even though it is thermodynamically feasible indicated by a positive $E^{\ominus}_{cell}$ value.

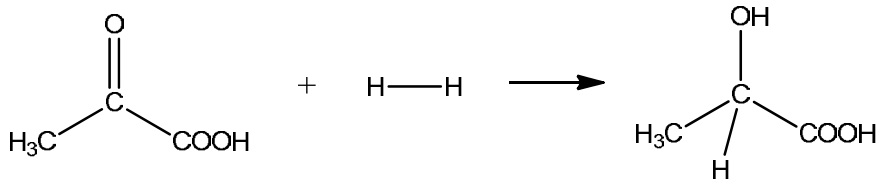
(iii) The activity of lactate dehydrogenase hinges on the active site Fe^{2+} contained in a heme group which can be oxidized to Fe^{3+}. Suggest a mechanism for the catalysis of anaerobic respiration by lactate dehydrogenase. Support your answers with relevant E^{θ} values given above and from the *Data Booklet*.
You may represent the reduced and oxidised forms of the enzyme as LDH–Fe^{2+} and LDH–Fe^{3+}.
Step 1:
$2LDH–Fe^{2+} + CH_3COCOOH + 2H^+ \rightarrow 2LDH–Fe^{3+} + CH_3CH(OH)COOH$
$E^{\ominus}_{cell}$ = +0.89 – (+0.77) = +0.12V (> 0, hence feasible)
Step 2:
$2LDH–Fe^{3+} + NADH \rightarrow 2LDH–Fe^{2+} + NAD^+ + H^+$
$E^{\ominus}_{cell}$ = +0.77 – (-0.32) = +1.09V (> 0, hence feasible)

(iv) After exercising, we do not stop panting immediately because we need to breathe in additional oxygen so that lactic acid can be reconverted back to pyruvic acid. Both breathing and heart rates increase until the excess lactic acid level normalizes.
Write a balanced equation for the conversion of lactic acid back to pyruvic acid. Calculate the value of E^{θ}_{cell} for this reaction, with the help of the *Data Booklet*.
$O_2 + 2CH_3CH(OH)COOH \rightarrow 2H_2O + 2CH_3COCOOH$
$E^{\ominus}$ = +1.23 – (+0.89) = +0.34V

[8]

(b) (i) Using bond energy data obtained from the *Data Booklet*, calculate the enthalpy change of reaction, Δ*H*, for the conversion of pyruvic acid into lactic acid.

$CH_3COCOOH(l) + H_2(g) \rightarrow CH_3CH(OH)COOH(l)$



pyruvic acid lactic acid

Δ*H* = 740 + 436 – 410 – 360 – 460
= –54 kJ mol^{-1}

(ii) Given that the actual enthalpy change of this reaction is –110 kJ mol^{-1}, suggest a reason for the discrepancy between your calculated Δ*H* value in **(b)(i)** and the actual Δ*H* value.

Bond energy is the heat required to break 1 mole of covalent bonds in the gaseous state but pyruvic acid and lactic acid exist as liquid.
OR Bond energy for a polyatomic molecule is an average value.

(iii) Acid-base neutralisation takes place when pyruvic acid reacts with barium hydroxide
Rank barium hydroxide, pyruvic acid, and its salt in increasing melting point. Explain your answer.

Pyruvic acid, barium pyruvate, barium hydroxide.
Pyruvic acid has a simple molecular structure with weak hydrogen bonding between its molecules, hence it has the lowest melting point.
Barium pyruvate and sodium hydroxide, on the other hand, have giant ionic structure with strong ionic bonds between the oppositely charged barium and pyruvate or hydroxide ions. Hence, they have higher melting points as compared to pyruvic acid.
Strength of ionic bond is dependent on lattice energy, which is in turn proportional to $\left|\frac{q^+ \cdot q^-}{r_+ + r_-}\right|$. Since the cation Ba^{2+} is the same and charges of the OH^- and pyruvate anions are the same at -1 for both barium hydroxide and barium pyruvate, lattice energy is only dependent on the size of the anions. And since pyruvate ion is much larger than OH^-, lattice energy for barium pyruvate is less exothermic, hence less energy is required to break the ionic bonds and barium pyruvate has a lower melting point compared to barium hydroxide.

[6]

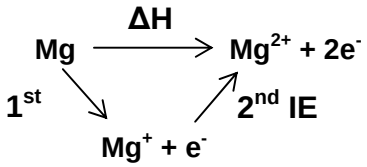
(c) impulse. Calcium causes muscles to contract while magnesium relaxes them. **Y** is another element in Group II.

Element	Mg	Ca	**Y**
E^{θ} /V	–2.37	–2.87	–2.95
Decomposition temperature of carbonates /K	470	1170	1770

(i) Predict the relative melting points of magnesium and calcium.

Magnesium has a higher melting point than calcium, since Mg^{2+} is smaller than Ca^{2+}.

(ii) With the help of the *Data Booklet*, calculate the enthalpy change, Δ*H* when Mg and Ca ionise to Mg^{2+} and Ca^{2+} respectively.



By Hess's law, $\Delta H = 1^{st}$ IE + 2^{nd} IE
ΔH ($Mg \rightarrow Mg^{2+}$) = +736 + 1450 = +2186 kJ mol^{-1}
ΔH ($Ca \rightarrow Ca^{2+}$) = +590 + 1150 = +1740 kJ mol^{-1}

(iii) How does the trend in Δ*H* calculated in **(c)(ii)** relate to the $E^{\ominus}$ values? Hence, predict the relative reducing powers of magnesium and calcium.

The less endothermic the ΔH, the more negative the $E^{\ominus}$ values, the stronger is the reducing agent. Hence, calcium has a greater reducing power than magnesium.

(iv) Account for the difference between the decomposition temperature of $CaCO_3$ and **Y**CO_3.

Ca^{2+} has a higher charge density than Y^{2+}, hence it is more polarising and causes greater distortion to the electron cloud and $CaCO_3$ is thus less stable to heat.

[6]

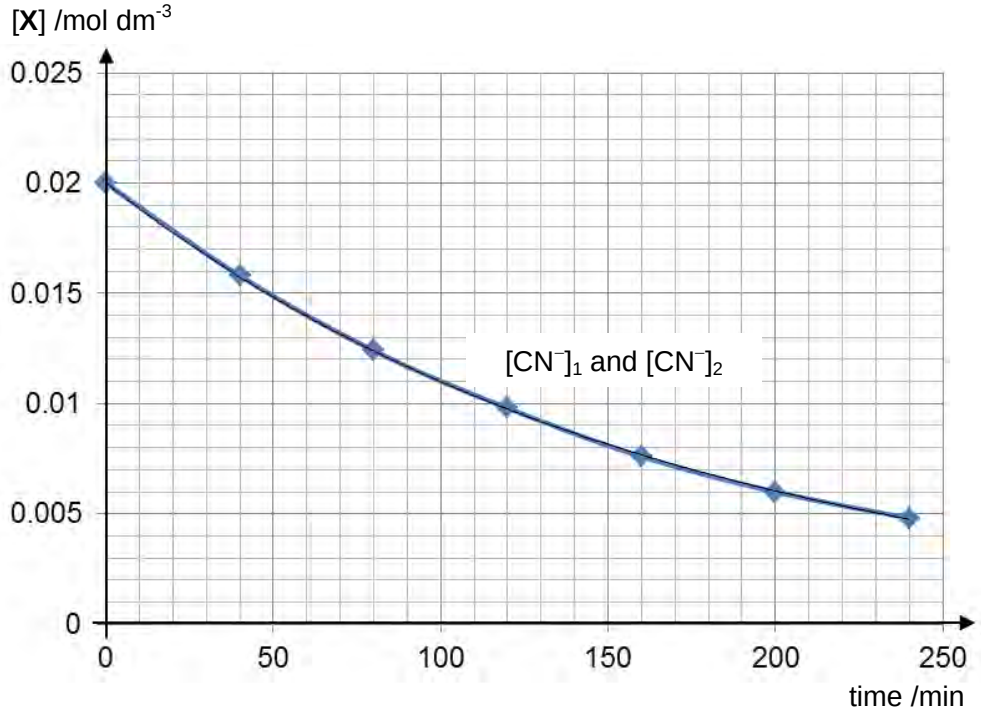
[Total: 20]

2 **(a)** Compound **X**, $CH_3CH=CHCHCl CH_3$, reacts with alcoholic KCN according to the following equation:

$$CH_3CH=CHCHCl CH_3 + CN^- \rightarrow CH_3CH=CHCH(CN)CH_3 + Cl^-$$

To investigate the above reaction, two separate experiments were performed using different initial concentrations of CN^-. In each experiment, the concentration of **X** in the reaction mixture was determined at different times as the reaction progresses. The same graph was obtained in both experiments, as shown below:

The following results were obtained:



(i) Explain why the reaction requires an alcoholic instead of an aqueous medium to take place.

Halogenoalkane X is not soluble in water as it cannot form hydrogen bond with water.

[1]

(ii) Referring to the graphs above, deduce the order of reaction with respect to each of the reactants, CN^- and **X**.

For [X]-time graph, it shows two constant half-lives of 115 min.
Hence, reaction is first order w.r.t. X.

Gradient of the tangent at time=0 remains the same for two different initial [CN^-], the reaction rate is independent of [CN^-]. Hence, reaction is zero order w.r.t. CN^-.

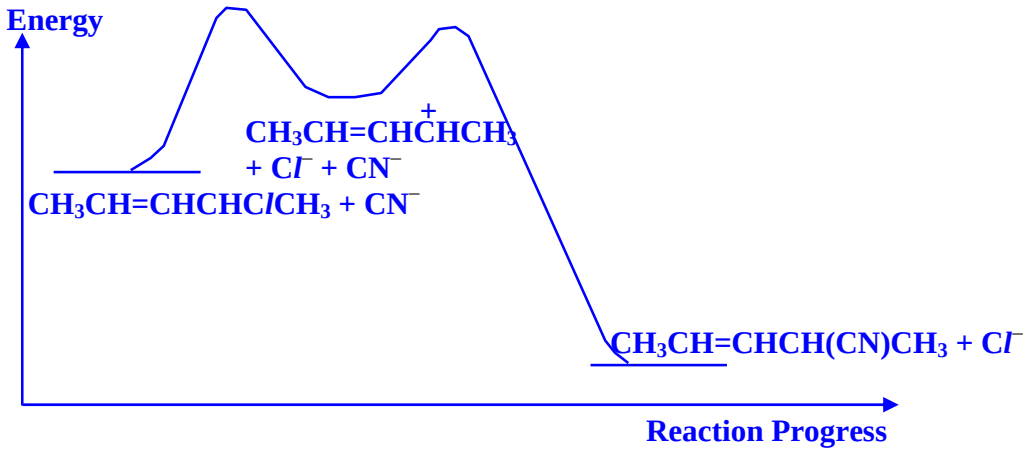
[2]

(iii) State, with a reason, whether the reaction proceeds by the S_N1 or S_N2 mechanism.

Since the reaction is 1st order w.r.t. X and zero order w.r.t. CN^-, the rate-determining / slow step involves 1 molecule of X and no CN^-.
Mechanism is therefore S_N1.

[1]

(iv) Hence, sketch a well labelled reaction pathway diagram for the reaction, given that the reaction is exothermic.



[2]

(v) The reaction of the compound, $CH_3CH_2CH_2CHClCH_3$ with alcoholic KCN occurs via a mixture of S_N1 and S_N2 mechanisms. Propose a rate equation for the reaction.

Rate = $k_1[CH_3CH_2CH_2CHClCH_3] + k_2[CH_3CH_2CH_2CHClCH_3][CN^-]$

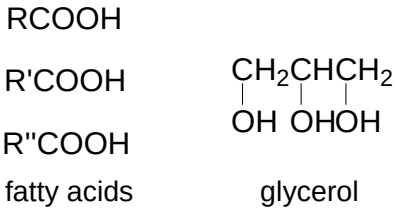
[1]

(vi) Suggest why the reaction of **X** is more likely than that of $CH_3CH_2CH_2CHClCH_3$ to exhibit the mechanism stated in **(ii)**.

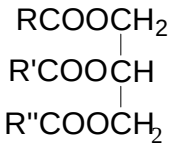
The carbocation formed with X is $CH_3CH=CH\overset{+}{C}HCH_3$. As the p-orbital of the positively charged carbon overlaps with the p-orbitals of the alkene carbons, the positive charge is further dispersed. Hence, the carbocation is stabilized and hence its formation is more favoured.

[2]

(b) The enzymatic hydrolysis of glycerides in oils is recently attempted industrially as an energy-saving method due to mild reaction conditions required. An enzyme such as lipase, is commonly used to speed up the rate of the hydrolysis of glycerides for the production of three fatty acids and glycerol, as shown by the structures below:



(i) Draw the structural formula of glyceride and identify the functional group in the glyceride.



Ester

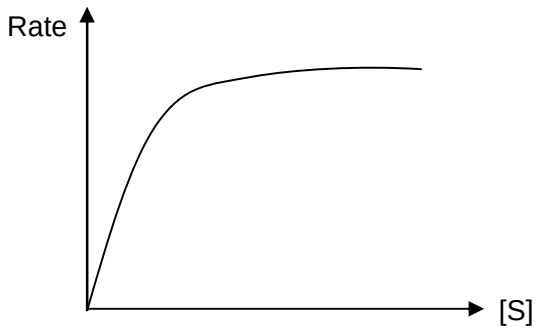
[1]

(ii) State the number of sigma and pi bonds surrounding the carbon atom in the functional group stated in **(i)**. Hence, identify the type of hybridisation of the carbon atom in the functional group.

3 sigma bonds and 1 pi bond surrounding carbon in ester linkage.
sp^2 hybridisation

[1]

(iii) The following graph shows how the rate of enzymatic hydrolysis of glyceride varies with increasing substrate concentration, [S] with a fixed amount of lipase used under fixed temperature. Suggest an explanation for the shape of the curve.



Under fixed temp and constant enzyme concentration, the initial rates of an enzyme catalyzed reaction increases with increase in substrate concentration. The rate increases till max rate when further increase in [S] will have no effect on the rate as the enzyme molecules are all saturated with substrate (working at top speed).

[2]

(iv) Besides using catalyst, the rate of reaction can also be increased by increasing the temperature. The rate of hydrolysis of glyceride is doubled when temperature increased by 10^{o}C. If the rate of reaction at T ^{o}C is r, determine the new temperature if the rate is increased to 16r. Explain your answer.

Rate is doubled when temperature increased by 10^{o}C. Since the rate is increased to 16r, rate is increased by 2^4 times. Hence, the temperature has been increased by 4 x 10^{o}C = 40^{o}C and the new temperature is (T + 40)^{o}C.

[2]

(c) In an experiment involving the decomposition of ammonia, nickel is used as a catalyst to speed up the rate of decomposition of ammonia at 500^{o}C in a reactor of volume 10 dm^3.

(i) State the type of catalysis which nickel exhibits and explain how its presence speeds up the rate of decomposition of ammonia.

Heterogeneous catalysis.

The catalyst provides the surface area allowing the adsorption of the reactants. The formation of the weak interaction between the reactants and catalyst help to weaken the bonds in the reactants molecules. Nickel therefore provides an alternative pathway and reduces the activation energy of the reaction which increases the rate of reaction.

[3]

(ii) It was found that at equilibrium of decomposition for the experiment, 90% of the 6.80 g ammonia has decomposed. Calculate the total pressure of the gas mixture after reaction.

	$2NH_3(g)$	**$N_2(g)$**	**$3H_2(g)$**
Initial no. of mol /mol	**6.80 / 17 = 0.400**	**0**	**0**
Change in no. of mol /mol	**–0.9(0.004) = 0.360**	**+1/2(0.360) = 0.180**	**+3/2(0.360) = 0.540**
Final no. of mol /mol	**0.0400**	**0.180**	**0.540**

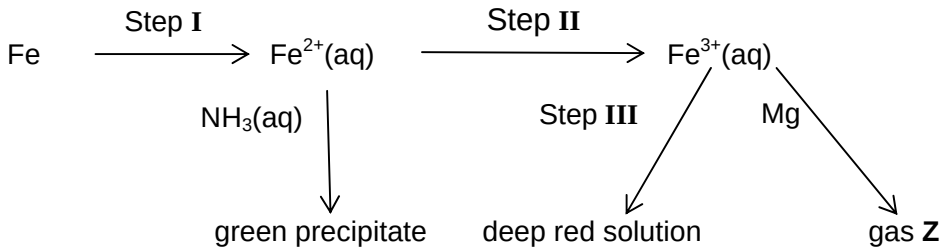
Total no. of moles of gas after reaction
= 0.0400 + 0.180 + 0.540
= 0.760 mol
By PV = nRT
P = (0.760/10 x 10^{-3})(8.31)(500 + 273)
= 488 kPa
Hence, total pressure of the gas mixture after reaction is 488 kPa.

[2]

[Total: 20]

3 This question concerns the transition elements iron and chromium, together with their compounds.

(a) Iron is the fourth most common element in the Earth's crust. It is the most common element (by mass) forming much of Earth's outer and inner core.
Some reactions of iron are given below:



(i) State the reagents that could be used for Steps I to III.

Step I: dilute H_2SO_4
Step II: acidified $KMnO_4$ or $K_2Cr_2O_7$
Step III: aqueous KSCN

[2]

(ii) Identify the gas **Z** and write an equation for its formation.

Gas Z is hydrogen.
$Mg + 2H^+ \rightarrow Mg^{2+} + H_2$

[2]

(iii) Describe what you would expect to observe when solid calcium carbonate is added to an aqueous solution of Fe^{3+}.

Effervescence of CO_2 gas observed and a red-brown ppt would be seen.

[2]

(b) The following data are given:

	Iron	Aluminium
Atomic radius / nm	0.116	0.143
Ionic radius / nm	0.076 (Fe^{2+}) 0.064 (Fe^{3+})	0.050

Explain why the atomic radius of iron is smaller than that of aluminium but the ionic radii of iron(II) and iron(III) are larger than that of Al^{3+}.

Atomic radius of Fe < A*l* due to its higher nuclear charge and poor shielding by 3d electrons. Hence higher effective nuclear charge for Fe, resulting in smaller radius.
Fe^{2+} : [Ar]$3d^6$; Fe^{3+}:[Ar]$3d^5$ versus Al^{3+} :[Ne]
The ions of iron have 1 more electron shell compared to Al^{3+} hence a larger ionic radii.

[2]

(c) Chromium is the hardest of all known metal elements in the Periodic Table. It is also odourless and tasteless. The name of the element is derived from the Greek word "chrōma" meaning colour, because many of its compounds are intensely coloured. The metal also reacts with oxygen to form a series of oxides.

One of these oxides, CrO_2, is often used to coat cassette tapes, due to its high conductivity and ferromagnetic properties, which provide a good high audio-frequency response.

When the oxide from a length of tape was dissolved in dilute sulfuric acid, it disproportionates to give Cr^{3+} and $Cr_2O_7^{2-}$. The resulting solution needed 20.0 cm^3 of 0.015 mol dm^{-3} Fe^{2+} solution to reduce the $Cr_2O_7^{2-}$ completely to Cr^{3+}.

(i) Suggest equations for the disproportionation of CrO_2 in acid solution and for the reaction of $Cr_2O_7^{2-}$ with Fe^{2+} in acid solution.

$10H^+ + 6CrO_2 \rightarrow 4Cr^{3+} + Cr_2O_7^{2-} + 5H_2O$
$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$

[2]

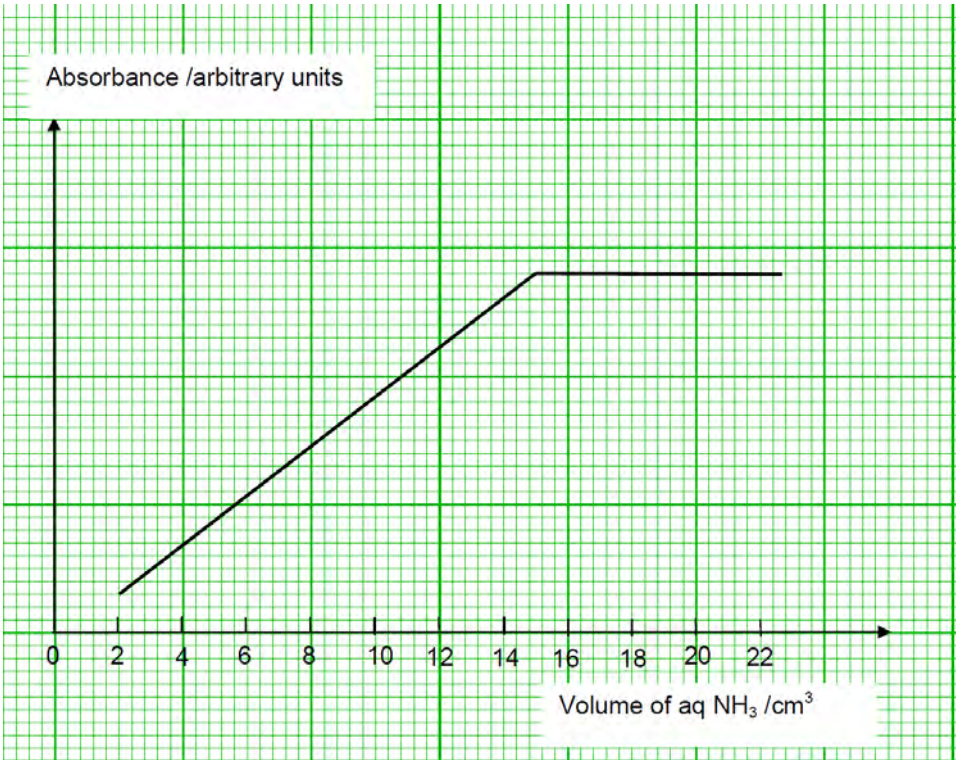
(ii) Use the data to calculate the mass of CrO_2 in the length of cassette tape.

$6CrO_2 \equiv Cr_2O_7^{2-} \equiv 6Fe^{2+}$
Amount of Fe^{2+} used = 0.015 x 0.0200 = 3.00×10^{-4} mol
Hence amount of CrO_2 = 3.00×10^{-4} mol
Mass of CrO_2 = 3.00×10^{-4} x 84.0 = 0.0252 g

[2]

(d) The formula of a complex ion can sometimes be found by using a colorimeter. An aqueous solution of chromium(III) sulfate is green but if aqueous ammonia is added, the solution turns violet.

To eleven containers each containing 20.0 cm^3 of 0.050 mol dm^{-3} of chromium(III) sulfate, different volumes of 0.40 mol dm^{-3} aqueous ammonia was added. The first container had 2 cm^3 of the aqueous ammonia added, the second 4 cm^3 and so on. Distilled water was added to make up the total volume to 50 cm^3. A sample from each container was then placed in a colorimeter and the reading was recorded. The results are shown in the figure below:



(i) Explain the shape of the graph obtained.

From 2 – 15 cm^3 aq NH_3
As more aqueous ammonia is added, a greater amount of violet complex is formed. Hence more orange / red light is absorbed resulting in an increase in absorbance.
However when 15 cm^3 of aqueous ammonia is added, the maximum amount of complex is formed due to the limited amount of Cr^{3+} present. Subsequently the other tubes with more than 15 cm^3 of Cr^{3+} will form the same amount of complex and give the same absorbance resulting in a constant reading.

[3]

(ii) Determine the formula of the complex.

Amount of Cr^{3+} = 0.020 x 0.050 x 2 = 2.00 x 10^{-3} mol
Amount of NH_3(aq) for maximum amount of complex to be formed
= 0.015 x 0.40 = 6.00 x 10^{-3} mol
Ratio of Cr^{3+} : NH_3 = 2.00 x 10^{-3} : 6.00 x 10^{-3} = 1:3

Hence formula of complex is $[Cr(NH_3)_3(H_2O)_3]^{3+}$

[2]

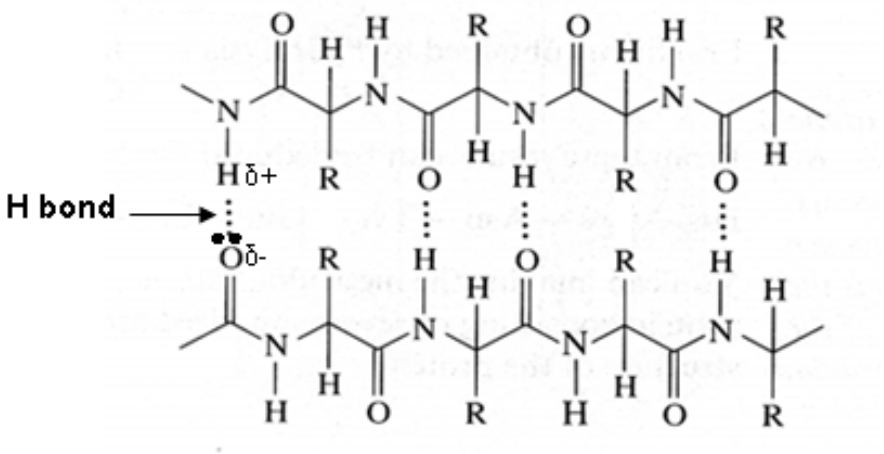
(iii) Account for the difference in colours between the chromium-ammonia complex and the aqueous chromium(III) ion.

The ligands H_2O and NH_3 cause d-d splitting of the 3d orbitals on the Cr^{3+} ion to a different extent. Ligand exchange occurs when aqueous ammonia is added to the aqueous solution. The energy gap in the d-d splitting caused by the NH_3 ligand is smaller than that of the H_2O ligands hence energy required to promote an electron in the lower set to the upper set of orbitals is different for the two complexes, resulting in energy from different parts of the visible light spectrum to be absorbed. The resultant colour observed is the complement of the light absorbed.

[3]

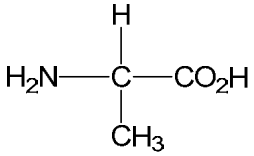
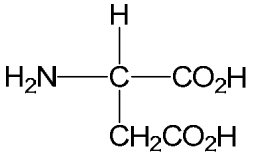
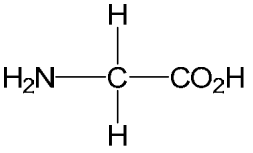
4 **(a)** Ovalbumin is the predominant protein in egg white. Structurally, it consists of 33 % α–helices, 5 % β–pleated sheets and 62 % random coil folded into a globular shape.

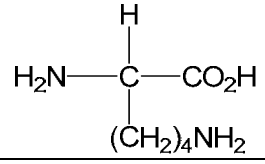
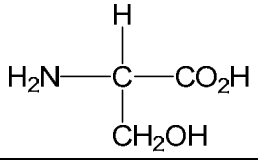
Draw a diagram to show how two strands in ovalbumin can be involved in maintaining a β–pleated sheet structure. Label any bonds established between the strands.



[2]

(b) Some of the amino acids found in ovalbumin are as follows:

alanine	aspartic acid	glycine
		

lysine	serine
	

The various methods of egg preparation are based on the principle of protein denaturation, which is accompanied by a change in the taste and appearance of the egg.

In your answers to this part of the question, reference should be made to the amino acids in the above table where appropriate.

(i) When an egg is boiled, the egg white changes from a transparent and colourless liquid into a white and opaque solid mass. Describe the structural changes that have taken place in the denaturation of ovalbumin which led to the change in appearance.

In globular proteins like ovalbumin, amino acids with hydrophilic R groups like aspartic acid, lysine and serine are located on the surface whereas amino acids with hydrophobic R groups like alanine and glycine are located on the inside away from the aqueous medium. Hence, globular proteins are soluble in water which accounts for the initial appearance of the egg white.
However, heat from the boiling process denatures the protein, which disrupts the tertiary structure. This causes the protein to unfold and exposes amino acids with hydrophobic R groups. This is accompanied by a loss in solubility, hence the final appearance of the egg white.

(ii) The Chinese delicacy known as "century egg" is prepared by coating the eggs with an alkaline clay paste. Through the process, the egg white becomes a dark brown, translucent jelly.
Suggest how the alkaline clay paste might interact with ovalbumin to bring about denaturation.

Alkali reacts with acidic $-NH_3^+$ groups: $-NH_3^+ + OH^- \rightarrow -NH_2 + H_2O$. This will disrupt the ionic bonds initially formed between the $-CH_2CO_2^-$ of aspartic acid and $-(CH_2)_4NH_3^+$ of lysine.

[5]

(c) At low temperatures, 1, 3, 5–trimethylbenzene reacts with HF and BF_3 to form a yellow solid **A**. **A** has the formula $C_9H_{13}BF_4$ and conducts an electric current in the molten state. When heated, **A** evolves BF_3 and regenerates 1, 3, 5–trimethylbenzene.

The formation of **A** provides strong confirmation for the mechanism of aromatic electrophilic substitution.

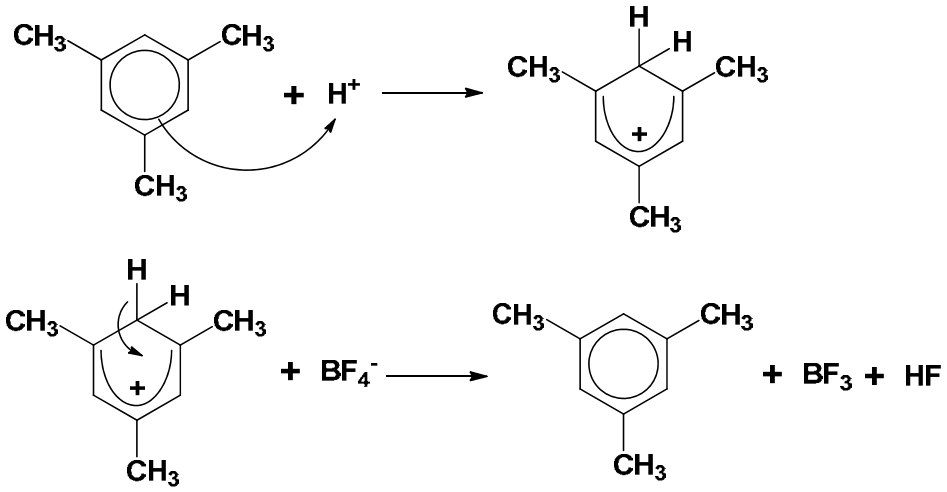
(i) HF and BF_3 react to generate the electrophile. By using the Lewis theory of acids and bases, construct an equation for the reaction between HF and BF_3.

$$\mathbf{HF + BF_3 \rightarrow BF_4^- + H^+}$$

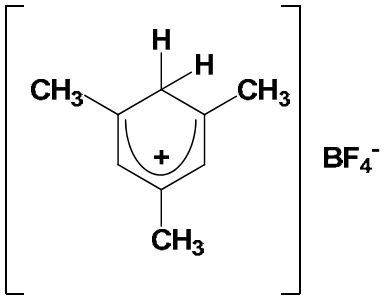
[1]

(ii) Outline the mechanism for this reaction, showing clearly how 1, 3, 5–trimethylbenzene and BF_3 are regenerated when **A** is heated. Hence, suggest a structure for **A**.

Mechanism

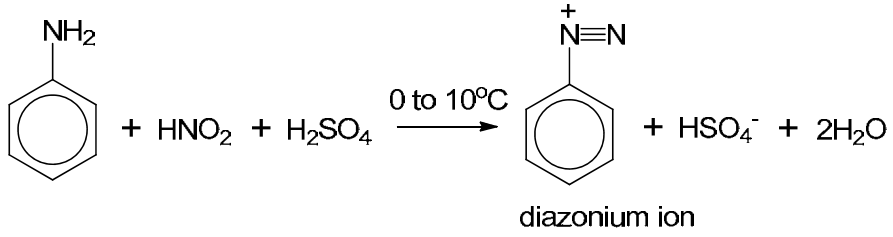


Structure of A



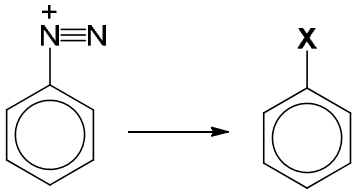
[3]

(d) A fairly stable diazonium salt can be prepared by treating a primary aromatic amine with nitrous acid in a cool solution:



In a process named the Sandmeyer reaction, the $-\overset{+}{N}\equiv N$ group can be replaced by a new group –**X** when the appropriate reagents are used:

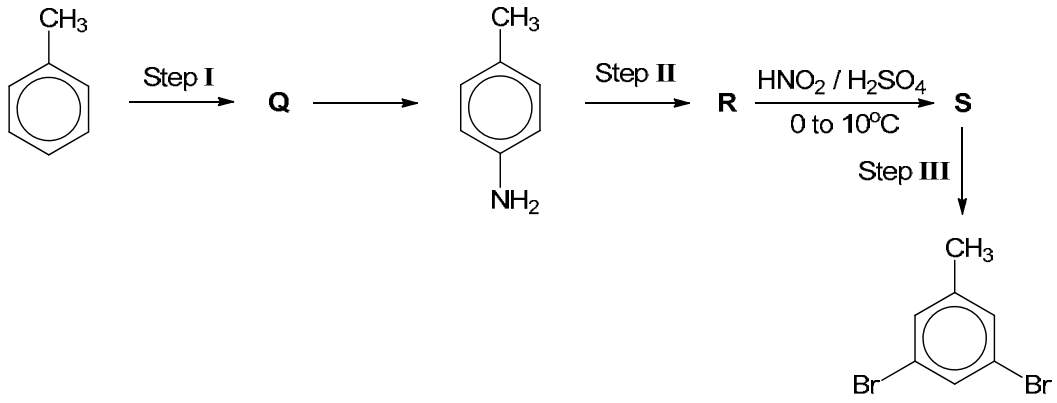
14



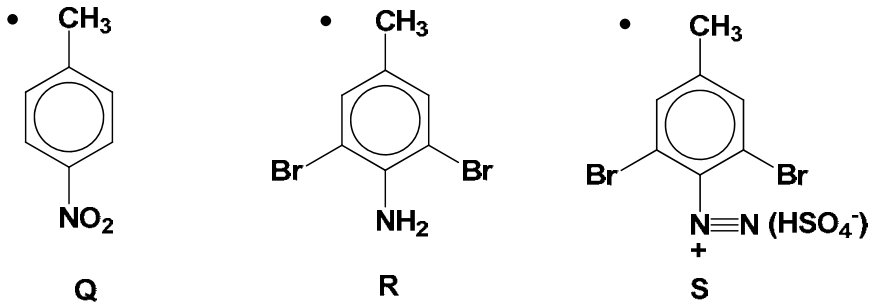
Some possible identities of **X** together with the corresponding reagents are shown below:

Identity of **X**	reagents and conditions
-Br	HBr and CuBr, room temperature
-H	H_3PO_2, room temperature
-OH	$Cu(NO_3)_2$ and Cu_2O, room temperature

This highly versatile reaction is widely used in the synthesis of aromatic compounds. An example is shown below, with methylbenzene as the starting compound:



(i) Deduce the structures of **Q**, **R** and **S**.



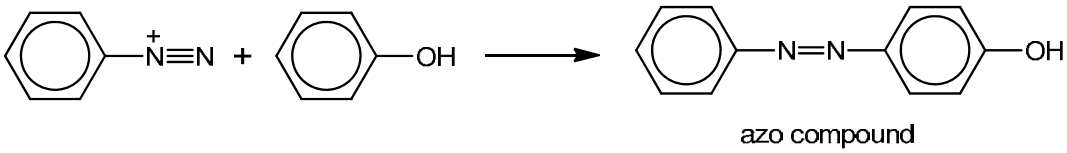
[3]

(ii) Hence, state the reagents and conditions for effecting steps **I**, **II** and **III**.

Step I: concentrated HNO_3 and concentrated H_2SO_4, 30°C
Step II: Br_2(aq), room temperature
Step III: H_3PO_2, room temperature

[3]

(e) Under the proper conditions, diazonium salts undergo a coupling reaction with phenol to obtain a brightly coloured azo compound:



azo compound

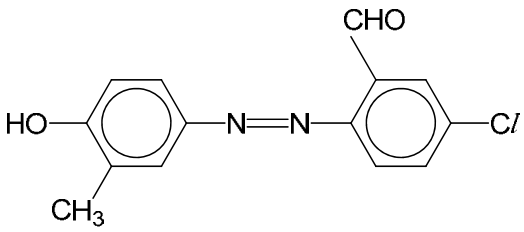
The process is a typical electrophilic substitution reaction in which the positively charged diazonium ion acts as the electrophile that attacks the strongly activated benzene ring in phenol.

(i) As shown above, substitution typically takes place at the para rather than at the ortho position relative to –OH, i.e. position 4 rather than 2. Give a reason why this occurs.

As the diazonium ion is a relatively bulky electrophile, it will experience considerable steric hindrance at the ortho position, hence the preference for the para position.

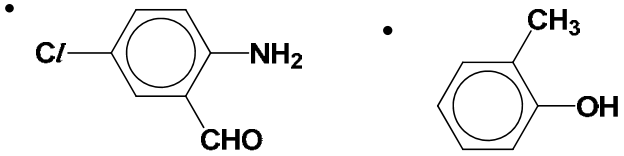
[1]

(ii) The structure of an azo compound, **H**, is given below:



H

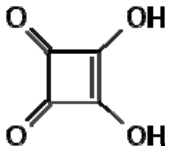
Deduce the structure of the amine and phenol that can be used as starting materials to synthesize **H**.



[2]

[Total: 20]

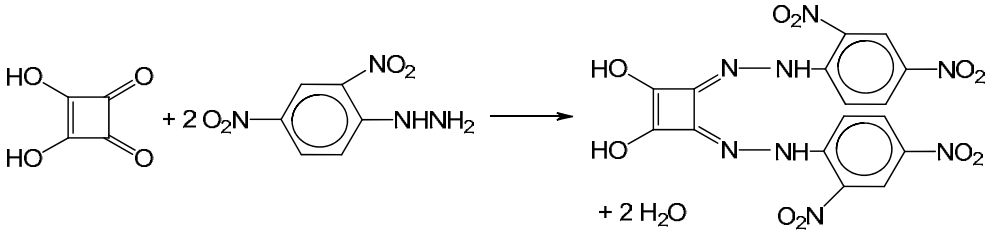
5 **(a)** Quadratic acid, used medically in the treatment of wart, is an unusual organic compound with molecular formula, $C_4H_2O_4$ and has the following structure:



(i) Suggest what you would see when quadratic acid reacts with:

1. 2,4-dinitrophenylhydrazine agent

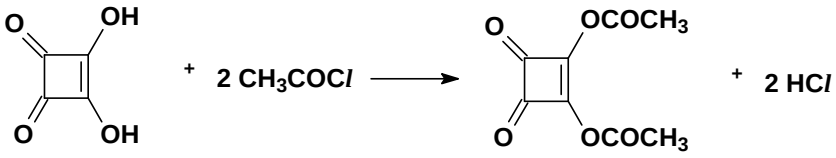
Observation : Orange ppt



2. ethanoyl chloride

Write a balanced equation for each reaction that occurs.

Observation: Steamy fumes



[3]

(ii) Quadratic acid is unusually acidic for an alcohol with a pK_a value of 1.5. Explain why this is so.

The conjugate base of quadratic acid is resonance stabilized such that it very much resembles a carboxylic acid in its behaviour.

[1]

(iii) An aqueous solution of quadratic acid is titrated against aqueous sodium hydroxide.
An acid-base indicator (HIn) has a K_a value of 3.00×10^{-5} mol dm^{-3}.

$$HIn(aq) \rightleftharpoons H^+(aq) + In^-(aq)$$

The acidic form of the indicator (HIn) is red and the basic form (In^-) is blue. Given that the indicator appears red when it contains at least 75% of HIn, and appears blue when it contains at least 75% of In^-.

What is the pH range for colour change of this indicator? Based on your answer, briefly explain if this indicator is suitable for the quadratic acid titration.

$$K_a = \frac{[H^+][In^-]}{[HIn]}$$

$$[H^+] = \frac{K_a \times [HIn]}{[In^-]}$$

$For\ 75\%\ red,$

$$[H^+] = \frac{(3.00\times10^{-5})(75)}{25} = 0.00009\ mol\ dm^{-3}$$

$$\Rightarrow pH = 4.05$$

$For\ 75\%\ blue,$

$$[H^+] = \frac{(3.00\times10^{-5})(25)}{75} = 0.00001\ mol\ dm^{-3}$$

$$\Rightarrow pH = 5$$

The indicator is not suitable as its working range of pH 4–5 is not within the range of rapid pH change of 7 – 10 for a weak acid–strong base titration.

[2]

(b) A large shipment of quadratic acid is contaminated with boracic acid, BH_3O_3, which is widely used as an insecticide.
The standard enthalpy change of combustion of quadratic acid is -1.26×10^3 kJ mol^{-1}. However, boracic acid does not burn as it is in the fully oxidised state.
When a 4.91 g sample of contaminated quadratic acid is burned in a bomb calorimeter, the temperature increases by 3.5 ^oC.

(i) Define standard enthalpy change of combustion of quadratic acid.

The standard enthalpy change of combustion of quadratic acid is the heat change when one mole of quadratic acid is completely burnt in excess oxygen under standard conditions of 298 K and 1 atm.

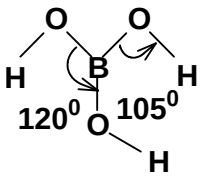
[1]

(ii) Given that the heat capacity of the calorimeter is 13.6 kJ K^{-1}, calculate the percentage by mass of boracic acid in the sample of contaminated quadratic acid.

Heat absorbed by bomb calorimeter = 13.6 x 3.5 = 47.6 kJ
Amount of quadratic acid = 47.6 / (1.26 x 10^3) = 0.0378 mol
Mass of quadratic acid = 0.0378 x 114 = 4.31 g
Mass of boracic acid = 4.91 – 4.31 = 0.60 g
Percentage by mass of boracic acid = 0.60 / 4.91 x 100% = 12.3 %

[2]

(iii) Draw the displayed formula of boracic acid to illustrate its shape with respect to the boron and oxygen atoms. Indicate the bond angles clearly on the diagram.



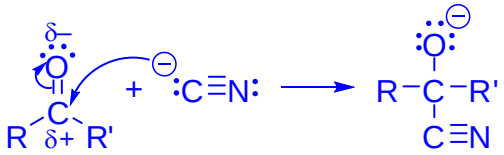
[2]

(c) Hydrogen cyanide has been used in America to execute convicted murderers. A carbonyl–based antidote has been developed.

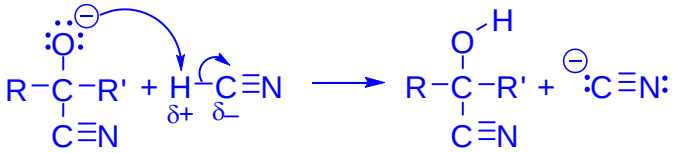
(i) Name and outline the mechanism of the reaction between propanone and hydrogen cyanide.

Nucleophilic addition

CN^- functions as a nucleophile and it attacks the electron deficient carbonyl carbon.



The tetrahedral intermediate is a strong base and quickly captures a proton from HCN, regenerating CN^-.



[2]

(ii) The carbonyl–based antidote **X** has molecular formula $C_4H_6O_2$.

X reacts with hydrogen cyanide to form **Y**, $C_6H_8O_2N_2$. **Y** reacts with excess hot acidified potassium dichromate(VI) solution to produce **Z**, $C_6H_8O_6$. 2.16 g of **Z** (M_r = 176) was dissolved in 250 cm^3 of water. 25.0 cm^3 of the solution required 24.50 cm^3 of 0.100 mol dm^{-3} of sodium hydroxide for complete neutralisation.

Calculate the amount of sodium hydroxide that will be neutralised by one mole of **Z**. Hence suggest possible structural formulae of **X**, **Y** and **Z**.

Amount of NaOH = 0.100 x 24.5/1000 = 0.00245 mol
Amount of Z in 25.0 cm^3 of the solution
= (2.16 x 25/250) / 176
= 0.001227 mol
Amount of NaOH that will neutralise 1 mol of Z = 2 mol
Hence Z is a dibasic acid.
X is CH_3COCH_2CHO
X undergoes nucleophilic addition with HCN to form Y.

Y is $CH_3C(OH)(CN)CH_2CH(OH)CN$
The 2° alcohol in Y undergoes oxidation while both the nitrile groups undergo acid hydrolysis on heating to form dicarboxylic acid Z.
Z = $CH_3C(OH)(CO_2H)CH_2COCO_2H$

[4]

(d) Lead azide, $Pb(N_3)_2$, is used as a shock-sensitive detonator in car airbags. The impact of a collision causes lead azide to be converted into an enormous amount of gas that fills the airbag.

(i) In the determination of solubility product, K_{sp} of lead azide, 25.0 cm^3 of a saturated solution of lead azide was passed through a cation exchange column and the column washed down through with water. The washings required 10.50 cm^3 of 6.00 x 10^{-3} mol dm^{-3} of NaOH(aq) for complete neutralisation. The lead(II) ions in the saturated solution replaced all the H^+ ions from the cation exchange column such that

$$Pb^{2+}(aq) + 2H^+(column) \rightarrow Pb^{2+}(column) + 2H^+(aq)$$

Calculate the solubility product of lead azide, stating its units.

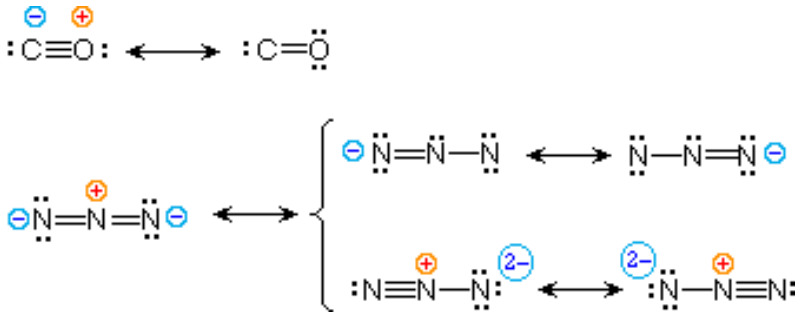
Amount of NaOH = (10.50×10^{-3}) (6.00×10^{-3}) = 6.30×10^{-5} mol
From the equation given:

$$Pb^{2+}(aq) \equiv 2H^+(aq)$$

$[Pb^{2+}] = (6.30 \times 10^{-5} / 2) / 25 \times 10^{-3} = 1.26 \times 10^{-3}$ mol dm^{-3}
$[N_3^-] = 2(1.26 \times 10^{-3}) = 2.52 \times 10^{-3}$ mol dm^{-3}
$K_{sp} = [Pb^{2+}][N_3^-]^2 = (1.26 \times 10^{-3})(2.52 \times 10^{-3})^2 = 8.00 \times 10^{-9}$ mol^3 dm^{-9}

[2]

(ii) Draw the Lewis structure of the azide ion.



[1]

[Total: 20]