Rewarding Learning

ADVANCED
General Certificate of Education
2015

Centre Number

Candidate Number

Chemistry

Assessment Unit A2 1
assessing
Periodic Trends and Further Organic Physical and Inorganic Chemistry

MV18

[AC212]

FRIDAY 22 MAY, MORNING

TIME

2 hours, plus your additional time allowance.

INSTRUCTIONS TO CANDIDATES

Write your Centre Number and Candidate Number in the spaces provided at the top of this page.
Answer **all fifteen** questions.
Answer **all ten** questions in **Section A**. Record your answers by marking the appropriate letter on the answer sheet provided. Use only the spaces numbered 1 to 10. Keep in sequence when answering.
Answer **all five** questions in **Section B**. Write your answers in the spaces provided in this question paper.

INFORMATION FOR CANDIDATES

The total mark for this paper is 120.
Quality of written communication will be assessed in Question **14(f)**.
In Section A all questions carry equal marks, i.e. **two** marks for each question.
In Section B the figures in brackets printed at the end of each question indicate the marks awarded to each question or part question.
A Periodic Table of Elements, containing some data, is included in this question paper.

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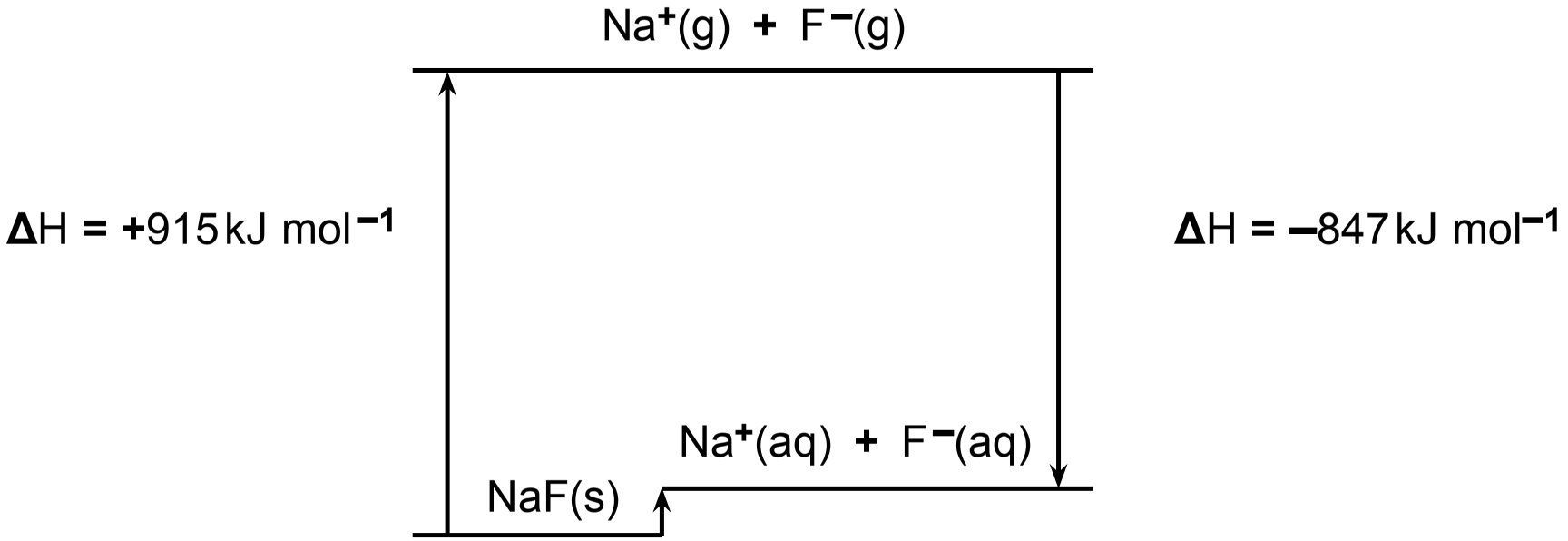
(Questions start overleaf)


Na+(g) + F−(g)
ΔH = +915 kJ mol−1
ΔH = −847 kJ mol−1
Na+(aq) + F−(aq)
NaF(s)

Section A

For each of the questions only **one** of the lettered responses (A–D) is correct.

Select the correct response in each case and mark its code letter by connecting the dots as illustrated on the answer sheet.

1 The energy cycle for dissolving sodium fluoride in water is shown on page 4.

Which one of the following is the enthalpy change of solution for sodium fluoride?

A $-68\,kJ\,mol^{-1}$

B $+68\,kJ\,mol^{-1}$

C $+847\,kJ\,mol^{-1}$

D $-847\,kJ\,mol^{-1}$

2 Which one of the following molecules has a different empirical formula from that of aldol, $CH_3CHOHCH_2CHO$?

A Ethanal

B Butanoic acid

C Methyl propanoate

D Propanoic acid

3 Which one of the following substances is formed when $CH_3CH{=}CHCH{=}CHCH_2COOH$ is heated with **excess** lithium aluminium hydride?

A $CH_3CH_2CH_2CH_2CH_2CH_2COOH$

B $CH_3CH{=}CHCH{=}CHCH_2CH_2OH$

C $CH_3CH{=}CHCH{=}CHCH_2CHO$

D $CH_3CH_2CH_2CH_2CH_2CH_2CH_2OH$

4 The following data was collected for the reaction:

$$2A + B + 2C \rightarrow D + E + F$$

[A]/mol dm^{-3}	**[B]/mol dm^{-3}**	**[C]/mol dm^{-3}**	**rate of reaction/ mol dm^{-3} s^{-1}**
1.0	0.50	0.40	1.8×10^{-4}
1.0	0.40	0.40	1.8×10^{-4}
1.0	0.30	0.20	9.0×10^{-5}
0.10	0.20	0.40	1.8×10^{-5}

Which one of the following is the rate equation for this reaction?

A Rate = $k[A]^2[B][C]^2$

B Rate = $k[A][B]^2$

C Rate = $k[A][C]$

D Rate = $k[A][C]^2$

5 The reaction of carbon, oxygen, nitrogen and hydrogen to form urea is shown below.

$$C(s) + \tfrac{1}{2}O_2(g) + N_2(g) + 2H_2(g) \rightleftharpoons CO(NH_2)_2(s)$$

When allowed to remain in contact for several years no urea is detected. The thermodynamic values for the reaction are:

$\Delta H_f = -333\,kJ\,mol^{-1}$ and $\Delta G = -205\,kJ\,mol^{-1}$

Which one of the following is the reason for the lack of formation of urea?

A The enthalpy change of formation is greater than the free energy change

B The equilibrium constant for the reaction is very low

C The entropy change for the reaction is positive

D The activation energy for the reaction is very high

6 The compound formed when methanol is added to $CH_2ClCOCl$ is

A CH_2OCH_3COCl

B $CH_2OCH_3COCH_3$

C $CH_2ClCO_2CH_3$

D $CH_2ClCOCH_3$

7 What is the approximate pH of a buffer solution containing 0.20 mol of a weak monobasic acid ($pK_a = 4.8$) and 0.02 mol of the sodium salt of the acid?

A 2.8

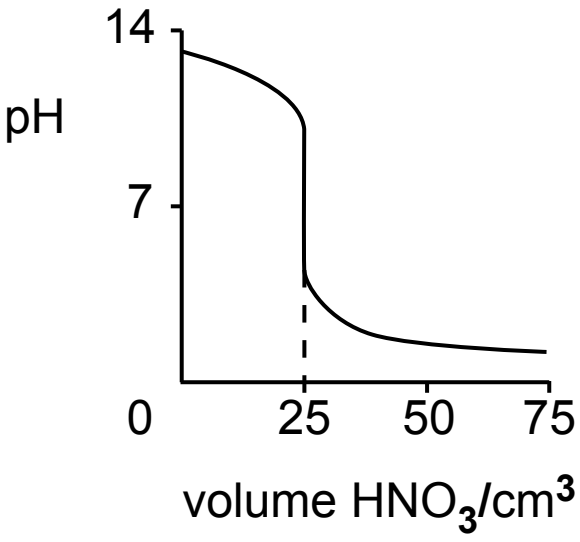
B 3.8

C 4.8

D 5.8

8 Which one of the following curves correctly shows the change in pH during the titration of 25.0 cm^3 of 0.10 mol dm^{-3} sodium carbonate solution with 0.10 mol dm^{-3} nitric acid?

A



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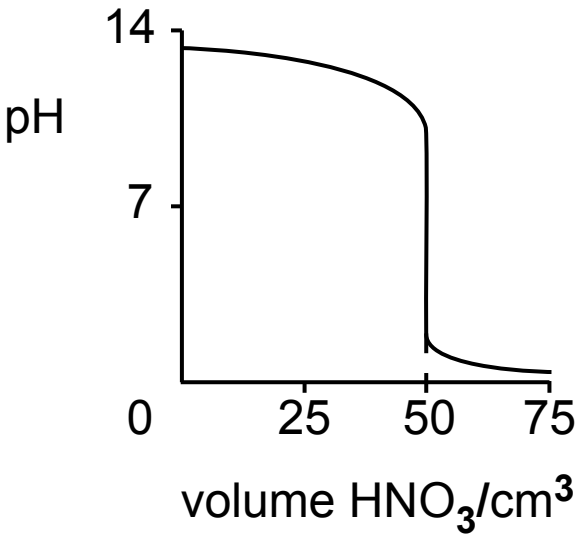

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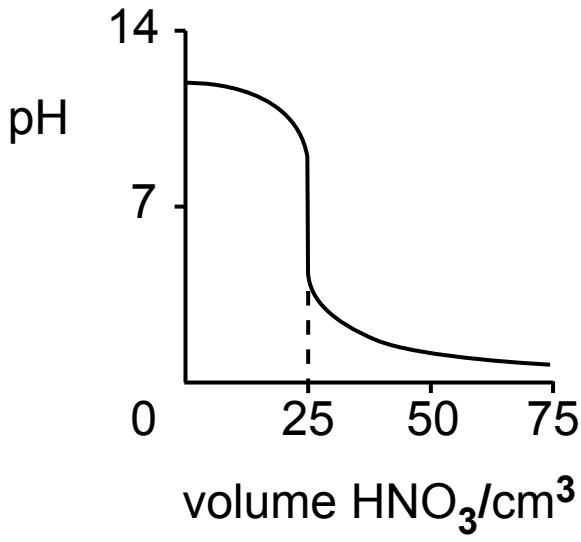

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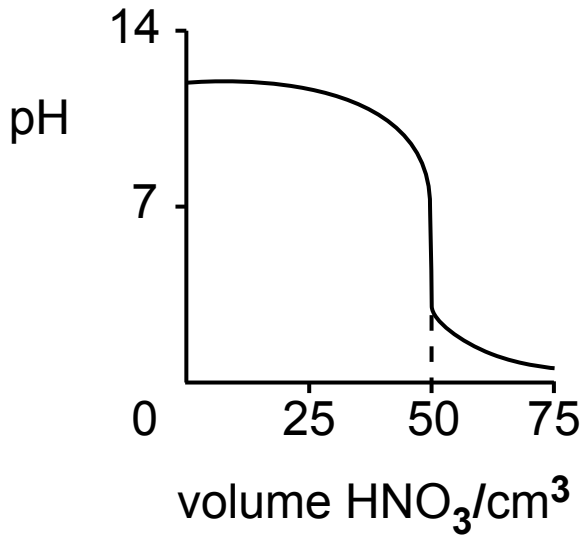


9 The reaction below is for the hydrolysis of an alkyl bromide.

$(CH_3)_3CBr + KOH \rightarrow (CH_3)_3COH + KBr$

Which one of the following is the mechanism for the reaction?

A Electrophilic addition

B Electrophilic substitution

C Nucleophilic addition

D Nucleophilic substitution

10 Bromine reacts with water according to the equation below.

$Br_2 + H_2O \rightleftharpoons HOBr + HBr$

Which one of the following will move the equilibrium to the right?

A Adding bromide ions

B Adding hydrogen ions

C Decreasing the concentration of bromine

D Increasing the concentration of hydroxide ions

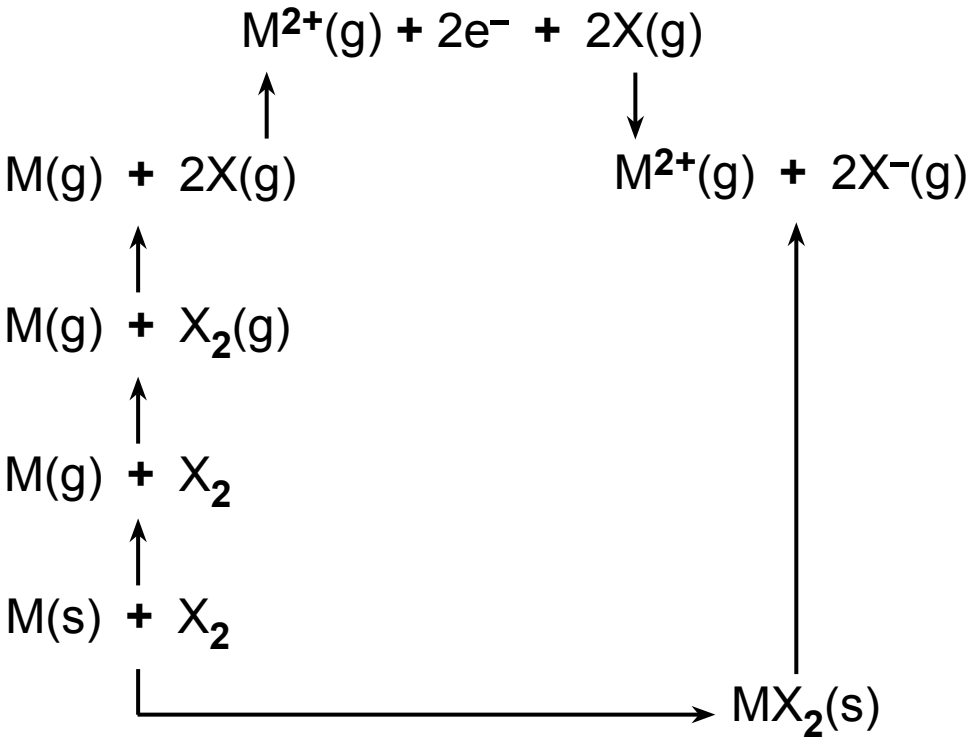
Section B

Answer **all five** questions in this section

11 The Born–Haber cycle below represents the enthalpy changes for the formation of Group II halides from their elements.

M = Be, Mg, Ca or Sr

X_2 = $F_2(g)$, $Cl_2(g)$, $Br_2(l)$, or $I_2(s)$



(a) Explain which element in Group VII has the lowest atomisation enthalpy. [1 mark]

(b) Values for the lattice enthalpies of the calcium halides are shown below.

CaF_2	$CaCl_2$	$CaBr_2$	CaI_2
+2630	**+**2258	**+**2176	**+**2074

(i) Explain why all of these values are positive. [1 mark]

_____

_____

(ii) Suggest why the values of the lattice enthalpies for the calcium halides decrease as Group VII is descended. [1 mark]

_____

_____

(c) Calcium could form the chlorides CaCl and $CaCl_3$. The lattice enthalpies can be calculated using the theoretical sizes of the ions. Values of the calculated lattice enthalpies are:

$CaCl(s) \rightarrow Ca^{+}(g) + Cl^{-}(g)$ $\quad \Delta H_{latt} = +719\,kJ$

$CaCl_2(s) \rightarrow Ca^{2+}(g) + 2Cl^{-}(g)$ $\quad \Delta H_{latt} = +2218\,kJ$

$CaCl_3(s) \rightarrow Ca^{3+}(g) + 3Cl^{-}(g)$ $\quad \Delta H_{latt} = +4650\,kJ$

(i) Using the following thermodynamic values, together with the appropriate lattice enthalpy, calculate the enthalpy of formation for $CaCl_3(s)$: [3 marks]

first ionisation energy of calcium $= +590\,kJ\,mol^{-1}$

second ionisation energy of calcium $= +1145\,kJ\,mol^{-1}$

third ionisation energy of calcium $= +4912\,kJ\,mol^{-1}$

standard enthalpy of atomisation of chlorine $= +112\,kJ\,mol^{-1}$

standard enthalpy of atomisation of calcium $= +178\,kJ\,mol^{-1}$

electron affinity of chlorine $= -349\,kJ\,mol^{-1}$

(ii) Using the enthalpy of formation calculated in part **(c)(i)** explain why $CaCl_3(s)$ does not exist. [1 mark]

(iii) Explain why the lattice enthalpies increase from CaCl to $CaCl_2$ to $CaCl_3$. [1 mark]

(iv) The enthalpy of formation for CaCl(s) is **−**178 kJ mol^{-1} whilst that for $CaCl_2(s)$ is **−**796 kJ mol^{-1}. Calculate the enthalpy change for the following reaction: [2 marks]

$$2CaCl(s) \rightarrow CaCl_2(s) + Ca(s)$$

(v) Explain why the term T**Δ**S may be neglected when predicting the feasibility of the reaction shown in part **(c)(iv)**. [1 mark]

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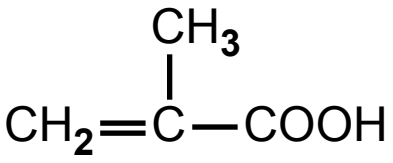
12 Methacrylic acid is an important intermediate in the manufacture of the polymer Perspex, poly(methyl methacrylate). It is a colourless liquid with a disagreeable odour and boils at 161 °C.



methacrylic acid

(a) Suggest a systematic name for methacrylic acid. [2 marks]

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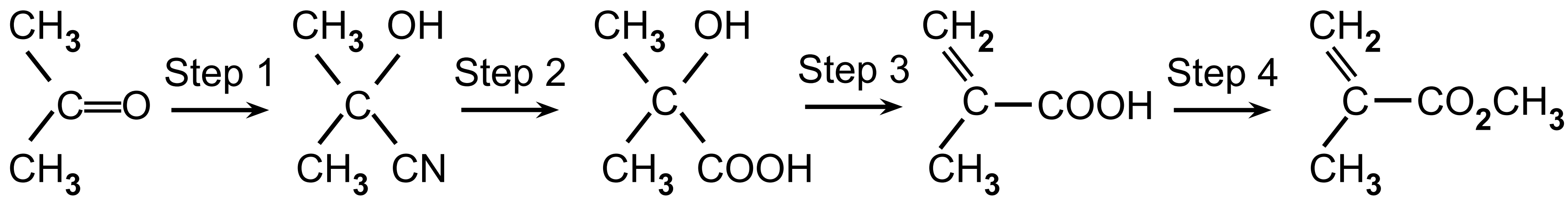
Step 1
Step 2
Step 3
Step 4

(b) The flow scheme on page 18 shows how propanone can be converted into methyl methacrylate.

(i) Draw the mechanism for the reaction of hydrogen cyanide with propanone in Step 1. [3 marks]

(ii) Name **two** catalysts with very different pH values that can be used to hydrolyse the nitrile. [2 marks]

_____

(iii) Name the catalyst and the reactant needed in Step 4 on page 18 to produce methyl methacrylate. [2 marks]

_____

(iv) What is the general name given to the type of reaction occurring in Step 4 on page 18? [1 mark]

_____

(c) The hydrogen cyanide used for the manufacture of methyl methacrylate is produced by the Degussa process which reacts ammonia with methane using a platinum catalyst.

$$NH_3(g) + CH_4(g) \rightarrow HCN(g) + 3H_2(g) \qquad \Delta H_x$$

The reaction is highly endothermic. The only waste product is nitrogen formed by the decomposition of ammonia at 1400 °C, the temperature of the process.

(i) Name the industrial sources of methane and ammonia. [2 marks]

(ii) Deduce the ΔH_x value for the reaction using the following bond energies. [3 marks]

bond	**bond energy/kJ mol^{-1}**
N—H	391
C—H	413
C≡N	887
H—H	436

(iii) The entropy change for the reaction is **+**125 J mol^{-1} K^{-1}. Suggest why the entropy change is positive and calculate the temperature at which the **Δ**G value is zero, using the value from **(c)(ii)**. [3 marks]

(d) Solid domestic and industrial waste contains a high percentage of polymers.

(i) Describe the advantages of landfill and waste incineration to dispose of polymers. [2 marks]

(ii) Describe the disadvantages of landfill and waste incineration. [2 marks]

(iii) Outline strategies to control, reduce and manage the amount of polymer waste. [2 marks]

13 Hydrogen peroxide, H_2O_2, is a liquid which is more acidic than water having a pH of 6.2 when in a pure state and a pH of 4.5 when diluted with water. It ionises in water according to the following equation.

$$H_2O_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HO_2^-(aq)$$

The value of the dissociation constant at 25 °C is 2.5×10^{-12} mol dm^{-3}.

(a) Use the Brønsted–Lowry theory to identify both conjugate acid–base pairs in the hydrogen peroxide solution. [2 marks]

(b) Using the equilibrium equation explain why diluting pure hydrogen peroxide decreases the pH value. [2 marks]

(c) Hydrogen peroxide decomposes to produce water and oxygen. The reaction is catalysed by bromide ions.

$$2H_2O_2(aq) \xrightarrow{Br^-} 2H_2O(l) + O_2(g)$$

(i) Explain how you would use an experimental method to follow this reaction in order to determine the rate of the reaction and hence the order of reaction with respect to hydrogen peroxide. [4 marks]

(ii) The mechanism for the overall reaction is believed to take place in two steps as shown below.

step 1 $H_2O_2 + Br^- \rightarrow H_2O + OBr^-$

step 2 $H_2O_2 + OBr^- \rightarrow H_2O + Br^- + O_2$

The rate equation for the reaction is:

rate = $k[H_2O_2][Br^-]$

Explain how the rate equation is related to the relative speeds of step 1 and step 2. [2 marks]

(iii) Which species in steps 1 and 2 can be regarded as a reactive intermediate? [1 mark]

_____

(iv) What is the overall order for this rate equation? [1 mark]

_____

(v) Using steps 1 and 2 explain why Br^- is a catalyst. [1 mark]

_____

_____

(vi) Outline how you could determine the amount of bromide ion present in the reaction mixture at the end of the reaction. [3 marks]

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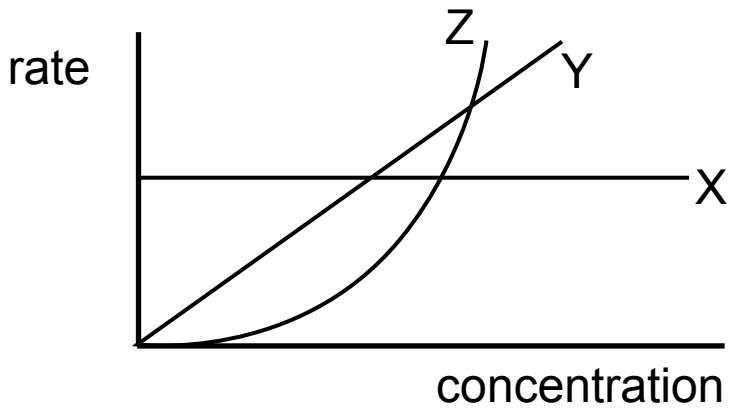
_____

(d) The diagram below shows the relationship between the rate of reaction and the concentration of reactant for different orders of reaction.



State the orders of reaction for X, Y and Z. [2 marks]

14 The percentage composition of three types of oils/fats is shown below.

oil/fat	**source**	**myristic acid**	**palmitic acid**	**stearic acid**	**oleic acid**	**linoleic acid**
animal fat	butter	8–15	25–29	9–12	8–33	2–4
vegetable oil	olive oil	0–1	5–15	1–4	67–84	8–12
marine oil	whale oil	5–10	10–20	2–5	33–40	0

Myristic, palmitic and stearic acids are saturated fatty acid molecules whereas oleic and linoleic acids are unsaturated.

(a) Which one of the oils/fats is likely to be the most unsaturated? [1 mark]

_____

(b) Suggest an experimental test that would **quickly** show that an oil or a fat was unsaturated. [3 marks]

_____

_____

_____

(c) A sample of olive oil was contaminated with petroleum. Explain how it would be possible to determine the approximate amount of petroleum present using hydrochloric acid. [2 marks]

(d) A sample of oil/fat was found to require 0.0025 mol of sodium hydroxide for complete saponification. The sample reacted with 0.84 g of iodine, I_2. Calculate the average number of double bonds per fatty acid molecule. [3 marks]

(e) The hydrolysis of 1 mole of an oil gave 1 mole of oleic acid and 2 moles of stearic acid together with propane-1,2,3-triol. The oil molecule is optically active.

(i) Give the common name for propane-1,2,3-triol. [1 mark]

(ii) Using the following formulae for the acids draw the structure of the oil and label the asymmetric centre with an asterisk (*). [3 marks]

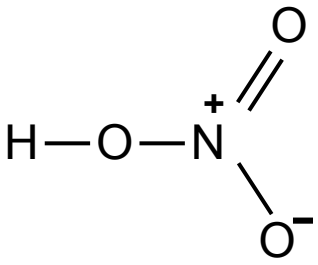
oleic acid R_1COOH stearic acid R_2COOH

(iii) Explain how this oil can be hydrogenated. [3 marks]

(f) The difference between oils and fats is based upon their melting points. Oils are liquid at room temperature and fats are solid. Describe how you would measure the melting point range of a **frozen** oil/fat and then explain how you would determine whether the substance was an oil or a fat at 25°C. [5 marks]

Quality of written communication [2 marks]

15 Nitric acid has the following structure.



When dissolved in water nitric acid establishes the following equilibrium.

$HNO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_3^-(aq)$

Nitric acid is a strong acid with a dissociation constant of $40\,mol\,dm^{-3}$.

(a) Draw a dot and cross diagram for nitric acid using outer shell electrons only. [2 marks]

(b) (i) Calculate the pK_a value for nitric acid. [2 marks]

(ii) Calculate the pH of a 2.0 M solution of fully ionised nitric acid. [2 marks]

(iii) Using the dissociation constant of nitric acid calculate the pH of a 2.0 M solution of nitric acid. [3 marks]

(iv) Explain, using your calculations in parts **(ii)** and **(iii)**, why the pH values are different. [1 mark]

(c) Nitric acid will react with all of the metal oxides in Period 3 of the Periodic Table and will also react with aqueous ammonia.

(i) Write the equation for the reaction of sodium oxide with nitric acid. [1 mark]

(ii) Write the equation for the reaction of aluminium oxide with nitric acid. [1 mark]

(iii) Write the equation for the reaction of ammonia with nitric acid. [1 mark]

(iv) Aluminium oxide is amphoteric. Explain the term **amphoteric**. [1 mark]

(d) The nitrate ion and nitric acid are reduced by aluminium metal in alkali to form ammonia. The aluminium reacts with the alkali to form sodium aluminate and hydrogen which then reduces the nitric acid.

(i) Write the equation for the reaction of aluminium with aqueous sodium hydroxide. [1 mark]

_____

(ii) Write the equation for the reduction of nitric acid by hydrogen to form ammonia. [1 mark]

_____

(iii) Write the equation for the reduction of the nitric acid with sodium hydroxide and aluminium to form ammonia. [1 mark]

_____

(e) Aluminium nitrate, sodium nitrate and ammonium nitrate form solutions with different pH values. Explain which one is acidic, which one is slightly acidic and which one is neutral. [3 marks]

_____

_____

_____

_____

_____

(f) The nitrate ion is present in the artificial fertiliser ammonium nitrate. However, the use of fertilisers in agriculture can be a source of water pollution.

(i) Describe the advantages and disadvantages of using artificial fertilisers. [2 marks]

(ii) Describe the advantages and disadvantages of using natural fertilisers. [2 marks]

THIS IS THE END OF THE QUESTION PAPER

For Examiner's use only	
Question Number	**Marks**
Section A	
1–10	
Section B	
11	
12	
13	
14	
15	
Total Marks	