Suggested Answers

VCE Chemistry 2017 Year 12 Trial Exam Unit 3/4

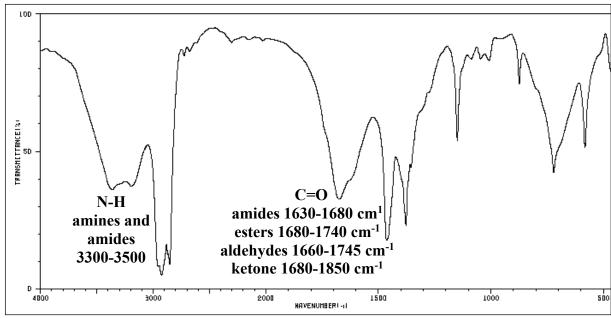
SECTION A – Multiple Choice Answers

Q1. B Need to use the data to calculate the reaction quotient (concentration fraction), Q, (CF).

$$Q = [NO]^{2} / [N_{2}][O_{2}]$$
= $(4.2 \times 10^{-3})^{2} / \{0.50 \times 0.25\}$
= 1.41×10^{-4}

 $Q < K (1.7 \times 10^{-3})$, so system is not at equilibrium and moves to increase Q to get there. The **forward reaction is favoured and proceeds faster than the reverse reaction** as the position of equilibrium shifts to the right.





The two significant peaks on the spectrum are at about 1680 cm⁻¹ and 3300 cm⁻¹. The carbonyl group at **1680 cm⁻¹**, could be part of an amide, an ester or an aldehyde (ketone is less likely according to its absorption band). At **3300 cm⁻¹** the lack of a broad band overlapping C-H (2850-3900 cm⁻¹) rules out O-H acid (2500-3300 cm⁻¹).

- Q3. D Some 'garbage' in landfill that provides a source of methane is from food waste and garden waste. On this basis, the methane can be classified as biogas and renewable. The methane in coal seam gas is not renewable because of its relationship with fossil-fuels. So, depending on the source, methane may be classified as **both renewable and non-renewable**.
- Q4. B Since only spirit burners containing methanol, not the required ethanol, were supplied, a systematic error has occurred. This was not a random selection of the incorrect fuel by the student.
 Because methanol (22.7 kJ g⁻¹) has a lower heat of combustion than ethanol (29.6 kJ g⁻¹), more ethanol will need to react to provide the energy needed to increase the temperature of the water by 20°C.
- Q5. C Chiral molecules have enantiomers, optical isomers which are non-superimposable images. To be chiral a molecule must have a chiral centre, indicated with an asterisk * on the structures below, which has a C atom attached to four different atoms or groups of atoms.

Glycerol is not chiral because none of the C atoms is attached to four different atoms / groups of atoms.

Cysteine
$$CH_2$$
—SH
$$H_2N$$
—CH—COOH

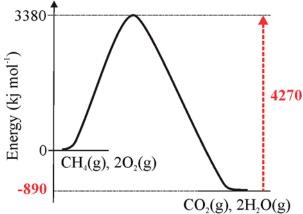
$$\begin{array}{c} \text{CH}_3 \\ \downarrow \\ \text{H}_2\text{N} \longrightarrow \text{CH} \longrightarrow \text{COOH} \end{array}$$

Q6. C Since
$$d = m / V$$

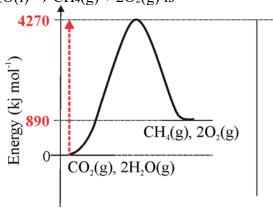
$$m(C_{16}H_{34}) = d \times V$$

 $= 0.775 \text{ g mL}^{-1} \times 20.0 \times 10^{3} \text{ mL}$
 $= 1.55 \times 10^{4} \text{ g}$
 $n(C_{16}H_{34}) \text{ reacting} = 1.55 \times 10^{4} / 226.0$
 $= 68.6 \text{ mol}$
 $n(CO_{2}) \text{ produced} = 16 \times n(C_{16}H_{34})$
 $= 16 \times 68.6$
 $= 1.10 \times 10^{3} \text{ mol}$
 $V(CO_{2}) = 1.10 \times 10^{3} \text{ mol} \times 24.8 \text{ L mol}^{-1}$
 $= 2.72 \times 10^{4} \text{ L}$
 $= 27.2 \text{ ML}$

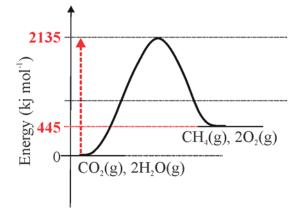
Q7. B $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(1); \Delta H = -889 \text{ kJ mol}^{-1}.$ (*Data Book, Table 10*).



The energy profile for the reverse reaction $CO_2(g) + 2H_2O(1) \rightarrow CH_4(g) + 2O_2(g)$ is



The energy profile for the reverse reaction $\frac{1}{2}CO_2(g) + H_2O(l) \rightarrow \frac{1}{2}CH_4(g) + O_2(g)$ is



This shows the activation energy to be 2135 kJ mol⁻¹.

Q8. B The $c(CH_3COOH)$ values, as calculated from the five investigations are quite consistent and so reflect low random error effect.

However, all the values are **below the true value**, suggesting a **significant systematic error**, such as the use of an incorrectly calibrated pipette, incorrectly calibrated burette or even incorrect indicator

In combination, the results show low random error and high systematic error.

Q9. A Br₂(aq) + 2OH⁻(aq) \rightleftharpoons Br⁻(aq) + OBr⁻(aq) + H₂O(l), $\Delta H = 15 \text{ kJ mol}^{-1}$ Assigning oxidation numbers, as per standard rules.

Since the forward reaction is endothermic, when temperature of the equilibrium solution is decreased, the **reverse** exothermic **reaction is favoured**. Therefore

- the **number of atoms with oxidation number +1 decreases**; there are three atoms on the right (Br in BrO⁻ and 2H in H₂O) but only two 2H atoms on the left (in the 2OH⁻).
- the number of atoms with oxidation number -2 does not change; there are two atoms on the right and two atoms on the left (in the 2OH⁻).
- the number of atoms with oxidation number -1 decreases from one (Br) to zero.
- the number of atoms with oxidation number zero increases from zero to one (Br₂).
- **Q10.** A From the electrochemical series E° (Fe²⁺(aq)/Fe(s)) = -0.44 V.

The cell voltage of 1.21 V is the difference between the E° values of the two half cells, so half-cell one must contain a redox pair with E° either 1.21 V higher or 1.21 V lower than $E^{\circ}(\text{Fe}^{2+}(\text{aq})/\text{Fe}(\text{s}))$.

$$E^{\circ}$$
(half-cell 1) = -0.44 + 1.21 = +0.77 V

or

$$E^{\circ}$$
(half-cell 1) = -0.44 - 1.21 = -1.65 V

According to the electrochemical series

$$E^{\circ}$$
 (Fe³⁺(aq)/Fe²⁺(aq)) = +0.77 V

$$E^{\circ} (Al^{3+}(aq)/Al(s)) = -1.66 \text{ V}$$

It is a close call, but $Fe^{3+}(aq)/Fe^{2+}(aq)$ is the more accurate option.

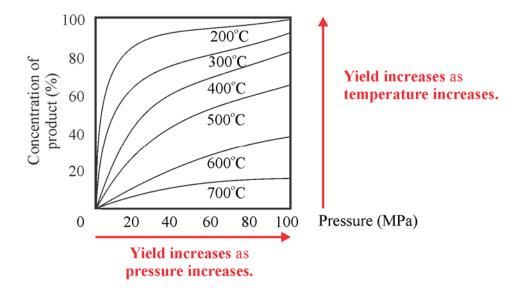
In the Fe³⁺(aq)/Fe²⁺(aq), the electrode must be non-reactive, so it cannot be Fe since it could react with Fe²⁺(aq). So, either a **platinum (Pt) or graphite (C)** electrode would be used.

Half-cell reactions would be

Half-cell 1: Fe(s)
$$\rightarrow$$
 Fe²⁺(aq) + 2e⁻¹

Half-cell 2:
$$Fe^{3+}(aq) + e^{-} \rightarrow Fe^{2+}(aq)$$

Q11. A



Since the yield increases as the temperature decreases, the **forward reaction** is favoured by low temperature, i.e. is **exothermic**.

Since the yield is increasing as the pressure increases, and the equilibrium system responds to partially oppose the pressure increase by moving to **reduce the number of particles** in the system, the **product** must **on the side** of the equilibrium **with fewer particles**.

This behaviour is consistent with the equilibrium involved in ammonia production, i.e.

$$N_2(g) + 3H_2(g) \implies 2NH_3(g), \ \Delta H = -92 \ kJ \ mol^{-1}$$

Q12. D The reactions represented by 1. are all hydrolysis (hydrolytic) reactions which occur during the digestion of the major food groups. Proteins are broken down into amino acids, fats into fatty acids and glycerol, and carbohydrates into monosaccharides.

The reaction represented by **2.** is **respiration** where energy required for the effective functioning of the body is released via the reaction

 $C_6H_{12}O_6(aq) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$

The reactions represented by **3.** are all **condensation** reactions that occur as proteins, fats and glycogen are formed in cells of the body.

- Q13. A To answer this question it is necessary to first deduce that X represents amino acids, Z represents proteins, Q represents glycerol and Y represents glycogen.
 - **Q** formula CH₂OHCHOHCH₂OH or C₃H₈O₃

1 mol (92.0 g) C₃H₈O₃ contains
$$3 \times 16.0 = 48.0$$
 g of O atoms % O = $(48.0 / 92.0) \times 100$ = **52.2** %

X – general amino acid formula is $NH_2CH(Z)COOH$

Consider glycine NH₂CH₂COOH, the amino acid with the lowest molar mass 1 mol (75.0 g) NH₂CH₂COOH contains $2 \times 16.0 = 32.0$ g of O atoms

Aspartic acid NH₂CH(CH₂COOH)COOH, the amino acid with the largest mass of oxygen, has 64.0 g of O atoms in 1 mole (133 g)

- **Z** since proteins are formed from amino acids, and oxygen is released as water in the condensation process, the percentage, by mass, of oxygen in protein is going to be less than 48.1 %.
- Y glycogen is formed from the condensation polymerisation of glucose and can be represented by $nC_6H_{12}O_6 \rightarrow -(C_6H_{10}O_5)_{n^-} + n-1$ H₂O, where n is a very large number.

So, the percentage, by mass, of O in glycogen is effectively the same as the % in $C_6H_{10}O_5$

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1 mol (162 g) C<sub>6</sub>H<sub>10</sub>O<sub>5</sub> contains 5 \times 16.0 = 80.0 g O atoms % O = (80.0 / 162) \times 100 = 49.4 %
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Q14. D Since NiOOH (nickel oxide hydroxide) is reduced, it must be the oxidant. This suggests that H₂ must be the reductant.

As the **reductant**, H₂ causes the reduction of NiOOH to Ni(OH)₂ and is itself **oxidised**.

Since the electrolyte is alkaline, i.e. contains OH⁻(aq), the oxidation half-equation must contain OH⁻(aq) ions and may be obtained from the electrochemical series in the *Data Book*.

$$H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-.$$

- Q15. C Green diesel will exhibit similar properties to petrodiesel and so, compared to FAME biofuel will
 - have <u>higher energy content</u> per gram due to lack of oxygen in the molecules.
 - be less viscous due to weaker intermolecular attraction.
 - <u>have better cold flow properties</u> determined by weaker intermolecular attraction.
 - be <u>less likely to absorb water</u> because it lacks the polar sites present on ester groups in FAME biodiesel.

Q16. B When all gases are measured at the same temperature, the ratios by volume of the reactants and products are the same as the ratio by mole amount as indicated in the balanced equation.

V(methane) reacting = $0.80 \times 2.0 = 1.6 \text{ L}$

The balanced equation for the combustion of methane is

volumes	1.6 L	3.2 L	1.6 L	3.2 L
volume ratio	1 L	2 L	1 L	2L
mole ratio	1 mol	2 mol	1 mol	2 mol
	$CH_4(g) +$	$2O_2(g) \rightarrow$	$CO_2(g) +$	$2H_2O(g)$

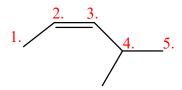
Greenhouse gases

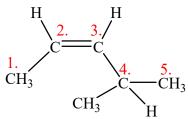
Initially $-1.6 \text{ L CH}_4(g)$

Finally – 1.6 L CO₂(g) and 3.2 L of H₂O(g) = **4.8** L

Change in volume of greenhouse gases = 4.8 - 1.6= 3.2 L

Q17. B The C atoms on the structure are numbered so the alkene C=C double bond starts on the lowest possible numbered C atom.





pent-2-ene five C atoms with C=C between C2 and C3

4-methylpent-2-ene methyl group attached to C4

<u>cis-4-methylpent-2-ene</u> the C atoms attached to the C=C double bond are on the same side of the C=C double bond.

Q18. D The species Cu²⁺(aq) and H₂O(l) appear on the electrochemical series (*Data Book*) according to

$$O_2(g) + 4H^+(aq) + 4e^- \qquad \rightleftharpoons \qquad 2\underline{\mathbf{H}_2\mathbf{O}}(1) \qquad +1.77 \text{ V}$$

 $\underline{\mathbf{C}\mathbf{u}^{2+}}(aq) + 2e^- \qquad \rightleftharpoons \qquad Cu(s) \qquad +0.34 \text{ V}$
 $2\underline{\mathbf{H}_2\mathbf{O}}(1) + 2e^- \qquad \rightleftharpoons \qquad H_2(g) + 2OH^-(aq) \quad -0.83 \text{ V}$

The electrolysis involves the strongest oxidant, $Cu^{2+}(aq)$, and strongest reductant, $H_2O(1)$. The half-equations for the reactions at the electrodes are

Anode (+)
$$2H_2O(1) \rightarrow O_2 + 4H^+(aq) + 4e^-$$

Cathode (-)
$$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$$

Consider the four statements

- 1. Incorrect, the **ions are present in solution** prior to the passing of the electric current.
- 2. Incorrect, Cu is deposited on the cathode, which is the (-) electrode in electrolysis.
- 3. Incorrect, whilst H⁺(aq) ions are produced at the anode, **no O²(aq) ions** are formed
- 4. Correct, $O_2(g)$ is produced in the oxidation of $H_2O(l)$ at the anode.
- Q19. D The rate of a chemical reaction is determined by the proportion of reactant molecule collisions that have energy greater than the activation energy for the reaction.

This proportion is reflected, on a Maxwell-Boltzmann kinetic energy distribution curve, as the area under the curve to the right of the activation energy.

This area, and hence the rate of reaction, increases in order of

Reaction 3 < Reaction 1 < Reaction 2 < Reaction 4

Q20. A The two main models of enzyme function are the lock-and-key model and the induced fit model.

In the lock and key model, the shape of the enzyme active site (the lock) is such that only a specifically shaped substrate (the key) fits.

In the **induced fit model**, the shape of the **active site** is **temporarily modified** as it interacts with the substrate molecules to provide a better fit for the substrate.

The active site resumes its normal shape as the product of the reaction leaves.

The shape of the active site is unique to each enzyme.

Coenzymes are not enzymes, rather they are a cofactor (metal ion or non-protein organic compound) which enable some enzymes to catalyse reactions; without the coenzyme, the catalysis would not occur. However, a **coenzyme in isolation does not have catalytic properties** and, in isolation, does not affect reaction rate.

Enzyme activity occurs in a narrow pH range and is significantly decreased by any change to a pH outside that range. Some enzymes are active in alkaline solutions – higher pH, whilst others are active in acidic solutions – lower pH.

- Q21. C Ascorbic acid, also known as Vitamin C, is an **antioxidant**, thus it reduces the impact of free radicals by donating electrons in its role as a water soluble free radical scavenger. A key chemical property of antioxidants is they act as **reductants**. Reductants are oxidised (donate electrons) in chemical reactions.
- Q22. C In conjunction with the information supplied in Tables 14, 15 and 16 of the *VCE Chemistry Data Book*:

The <u>IR spectrum</u> provides evidence of the **presence of** the carbonyl (**C=O**) functional group.

C=O (aldehydes); absorption band 1670-1745 cm⁻¹, or C=O (ketones); absorption band 1680-1850 cm⁻¹

lack of O-H acids, no broad absorption band in absorption band 2500-3500 cm⁻¹ **lack of O-H** alcohols no characteristic absorption in absorption band 3200-3600 cm⁻¹

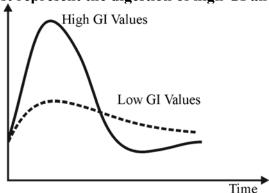
The ¹H NMR spectrum provides evidence of

H attached to a carbonyl group as in RCHO, peak at **9.8 ppm** (in the range 9.4-10.0 ppm),

H in a CH₃ attached to a carbonyl group as in RCOCH₃, peak at 2.2 ppm (in the range 2.1-2.7).

This evidence suggests the **most likely compound** was the **aldehyde CH₃CHO** (ethanal). This is further supported by the ¹³C NMR spectrum which provides evidence of **H** attached to a carbonyl group as in RCHO, peak at **200 ppm** (in the range 205-220 ppm).

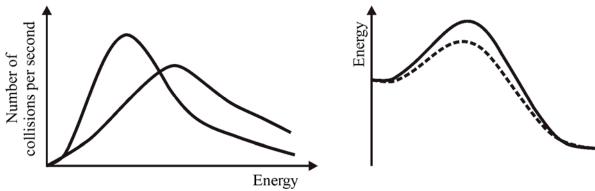
Q23. B The graphs best represent the digestion of high GI and low GI carbohydrates.



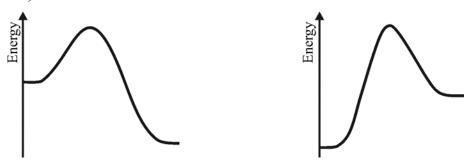
High GI carbohydrates contain a greater proportion of amylopectin, the more easily digestible branched component of starch, and so release glucose more rapidly than low GI carbohydrates, which contain a greater proportion of amylose, the less branched component. The graphs represent the change in blood glucose levels after digestion.

The "0" hour on the horizontal axis represents the time at which one eats. The unbroken curve shows the rise in blood sugar following a high glycaemic index meal. Rapid blood glucose rise in the first hour causes a high insulin output to lower blood glucose. Since cell requirements are not this great in the first hour, much of that glucose is sent to the liver and, if not converted to glycogen, may be converted to triglyceride for fat storage. This happens aggressively in the presence of high insulin, resulting in the blood glucose dropping rapidly by about 2 hours after digestion. This can stimulate hunger and further intake of food. The dashed curve represents the digestion of a low GI index meal and reflects the slower digestion of amylose relative to amylopectin.

This was the only alternative for which 'Time' was a valid axis. The Boltzmann distribution curve showing the effect of temperature on particle collision has 'Energy' as the horizontal axis. Energy profiles do not need horizontal axes. The diagrams below represent $\bf A$ (the effect of temperature on particle collision) and $\bf C$ (the effect of a catalyst on activation energy).



The diagrams below represent \mathbf{D} (energy profiles for exothermic and endothermic reactions).



10

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Energy released = 1600 \times 1000 \text{ kJ s}^{-1} \times (60 \times 60) \text{ s}
O24. C
                                                     = 5.76 \times 10^9 \,\text{kJ}
                                = 5.76 \times 10^9 \text{ kJ} / 890 \text{ kJ mol}^{-1}
                 n(CH_4)
                                = 6.48 \times 10^6 \text{ mol}
                               = nRT/PV
                 V(CH_4)
                                =6.48\times10^6\times8.31\times303/150
                                = 1.08 \times 10^8 \, \text{L}
                 However, since the energy conversion is only 60 per cent efficient,
                 1.08 \times 10^8 L = 0.60 \times V(CH_4) needed
                 V(CH_4) needed = 1.08 \times 10^8 / 0.60
                                        = 1.81 \times 10^8 L
                                        = 1.81 \times 10^5 \text{ kL}
                                        = 1.81 \times 10^2 \,\mathrm{ML}
                 Alternatively:
                 E = 1600 \times 1000 \times 3600
                     = 5.76 \times 10^9 \text{ kJ}
                 60 % efficiency
                 E required = 5.76 \times 10^9 / (60/100)
                                 = 9.6 \times 10^9 \text{ kJ}
                 \Delta H_{\rm c}({\rm CH_4}) = -890 \text{ kJ mol}^{-1}
                 n(CH_4) = 9.6 \times 10^9 / 890 = 1.08 \times 10^7 \text{ mol}
                 V = nRT/P
                   = 1.08 \times 10^7 \times 8.31 \times 303 / 150
                   = 1.81 \times 108 L
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 $= 1.81 \times 10^{2} \text{ ML}$

Q25. D Proteins, enzymes and polypeptides must retain secondary, tertiary and, in many cases quaternary structures to maintain their activity. So, anything that will disrupt the structure of these species in the toxin will reduce the impact of the jellyfish sting.

Inorganic ions, acid and **hot water** can all **denature protein structures**. Solution of **inorganic ions will disrupt ion-ion interactions** in the tertiary structure.

Treating with acidic solution will decrease the pH and so disrupt tertiary structure.

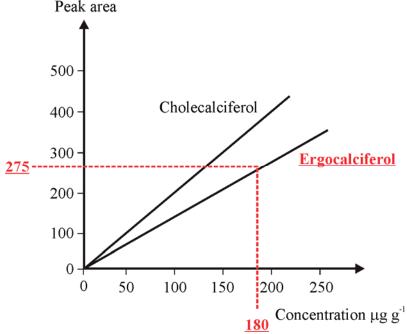
The higher temperature of hot water will disrupt secondary, tertiary and quaternary structures.

The treatment least likely to impact on protein structure is cold water.

Q26. C Vitamin D₃ (cholecalciferol) has the higher retention time.

So the peak area of vitamin D₂ (ergocalciferol) was 275.

Use the calibration graph for ergocalciferol, i.e. the one unlabelled on the diagram in the question, to calculate the answer.



c(ergocalciferol) = 180
$$\mu$$
g g⁻¹
So, m(vitamin D₂) in 50 g sample = 50 × 180
= 9000 μ g
= **9 mg**

Q27. B The semi-structural formula of Levulinic acid is CH₃COCH₂CH₂COOH, so its molecular formula is C₅H₈O₃.

Fructose is structural isomer of glucose and so its molecular formula is C₆H₁₂O₆

Atom economy = (mass of desired product / mass of reactants) \times 100

=
$$[M(C_5H_8O_3) / M(C_6H_{12}O_6)] \times 100$$

= $(116 / 180) \times 100$
= **64** %

Alternatively:

A simple atom balance indicates compound X must be CH₂O₂ (actually methanoic acid – HCOOH)

Equation: $C_6H_{12}O_6 \rightarrow C_5H_8O_3 + HCOOH + 2H_2O$

Atom economy = (mass of desired product / total mass of products) × 100
=
$$[M(C_5H_8O_3) / [M(C_6H_{12}O_6) + M(HCOOH) + M(H_2O)]] \times 100$$

= $(116 / [116 + 46 + 18]) \times 100$
= 64%

O28. B Since lactic acid, C₃H₆O₃, is a carbohydrate, the energy released during the combustion of the lactic acid may be estimated.

Energy from 5.865 g lactic acid = 5.865×15

$$= 88.0 \text{ kJ}$$

Lactic acid combustion:
$$\Delta T = 39.2 - 28.7$$

= 10.5°C

Energy released = Calorimeter constant $\times \Delta T$

Calorimeter constant = $88.0 \text{ kJ} / 10.5^{\circ}\text{C}$

$$= 8.38 \text{ kJ}^{\circ}\text{C}^{-1}$$

Ethanol combustion:
$$\Delta T = 35.4 - 23.1$$

$$= 12.3$$
°C

Energy released during ethanol combustion = 8.38 kJ °C⁻¹ × 12.3°C

$$= 103 \text{ kJ}.$$

Heat of combustion of ethanol = 29.6 kJ g⁻¹ – *Data Book Table 11*.

$$m(\text{ethanol}) \text{ used} = 103 \text{ kJ} / 29.6 \text{ kJ g}^{-1}$$

$$= 3.5 g$$

Alternatively:

The ratio of the energies released by ethanol and lactic acid is equal to the ratio of the temperature changes.

Energy from $CH_3CH_2OH / 88.0 = 12.3 / 10.5$

$$= (12.3 / 10.5) \times 88.0$$

$$= 103 \text{ kJ}$$

$$m(CH_3CH_2OH) = 103 / 29.6$$

$$= 3.5 g$$

Q29. A In discharging reactions, which convert chemical energy to electrical energy, electrons move from the (-) electrode to the (+) electrode. Electrons always move from the site of oxidation (anode) to the site of reduction (cathode).

$$Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^{-}$$

$$PbO_2(s) + SO_4^{2-}(aq) + 4H^{+}$$

$$PbO_2(s) + SO_4^{2-}(aq) + 4H^{+}(aq) + 2e^{-} \rightarrow PbSO_4(s) + 2H_2O(1)$$

So, recharging reactions occurring at these electrodes are the reverse of the discharging reactions.

$$PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2-}(aq)$$

$$PbSO_4(s) + 2H_2O(1) \rightarrow PbO_2(s) + SO_4^{2-}(aq) + 4H^{+}(aq) + 2e^{-}$$

Checking the four alternatives

- A. Pb is produced at the (-) electrode.
- **B.** pH will decrease as H⁺ ions are produced at (+) electrode.
- C. PbSO₄ is consumed NOT produced.
- D. Oxidation numbers of Pb change from +2 to +4 at the anode, and +2 to 0 at the cathode.

Q30. D The expanded structure of **glutathione** shown below may be used to show that **three 2-amino acids** may be identified (using *Table 17 in the Data Book*) as contributing to the structure.

Hence alternative **D** is **incorrect**.

As a free radical scavenger, glutathione is an antioxidant.

Glutathione is a tripeptide, because it contains three amino acid residues. The **four functional groups** present are -NH₂ (amino), -COOH (carboxyl), -CONH- (peptide), -SH(thiol).

SECTION B – Short Answer (Answers)

Question 1 (11 marks)

- a. $2\text{CH}_3\text{OH}(1) + 3\text{O}_2(g) \rightarrow 2\text{CO}_2(g) + 4\text{H}_2\text{O}(1); \Delta H = -1452 \text{ kJ mol}^{-1} \bullet \text{ or } \text{CH}_3\text{OH}(1) + 1.5\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(1); \Delta H = -726 \text{ kJ mol}^{-1}$
- **b.** i. Energy added to water $= 4.18 \text{ J g}^{-1} \, ^{\circ}\text{C}^{-1} \times m(\text{H}_2\text{O}) \times \Delta T$ $= 4.18 \times 200 \times (54.7-23.5)$ $= 4.18 \times 200 \times 31.2$ $= 2.61 \times 10^4 \text{ J}$ $= 26.1 \text{ kJ} \, \Phi$

$$m(CH_3OH)$$
 used = $125.62 - 121.56$
= 4.06 g

Energy released by CH₃OH = m(CH₃OH) × Energy released per gram CH₃OH *According to the Data Book*, Heat of combustion = 22.7 kJ g⁻¹

=
$$4.06 \text{ g} \times 22.7 \text{ kJ g}^{-1}$$

= $92.2 \text{ kJ} \bullet$

% energy transferred to water = (energy added to water / energy released by CH₃OH) \times 100 = $(26.1 / 92.2) \times 100$ = 28.3 % •

<u>Alternatively</u> – for the second mark:

$$n(CH_3OH)$$
 used = 4.06 / 32.0
= 0.127 mol

Energy released by CH₃OH = $n(\text{CH}_3\text{OH}) \times \text{Energy}$ released per mole CH₃OH

According to the **Data Book**, 1 mol CH₃OH \rightarrow 726 kJ = 0.127 mol \times 726 kJ mol⁻¹ = **92.1 kJ**

- ii. Possible answers include:
 - 1. Put a lid on the can this reduces heat escaping from the water to the atmosphere.
 - 2. Move the flame closer to the can this reduces heat loss to the surrounding atmosphere.
 - 3. Place a reflective shield around the burner and flame this reduces heat loss to the atmosphere and the impact of air currents on the flame.
 - mark for an appropriate answer.
- c. i. (-) electrode

The fuel, CH₃OH, is oxidised to CO₂

$$CH_3OH(1) \rightarrow CO_2(g)$$

$$CH_3OH(1) + H_2O(1) \rightarrow CO_2(g) + 6H^+(aq) + 6e^-$$

(+) electrode

Oxygen is reduced, since the electrolyte is acid, the reduction half-equation is obtained from the electrochemical series by looking for O_2 – the oxidant – in a half-equation with $H^+(aq)$

$$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$$
 0

ii. Porous electrodes allow for better contact between the fuel and the electrolyte, and with oxygen and the electrolyte thereby increasing the reaction rate. • They can also be impregnated with catalyst.

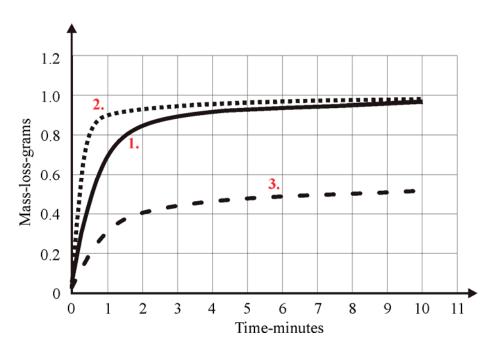
Electrodes in a fuel cell must:

- conduct electricity.
- not react with the fuel, oxygen or electrolyte.
- d. i. Both steps involve equilibria with exothermic reactions. To maximise yield, low temperatures should be used. However, the reaction rate decreases at lower temperatures. Using a catalyst means that both a good yield and a good reaction rate can be achieved.
 - ii. The much smaller bioDME molecules have less intermolecular attraction, so bioDME is less viscous than methyl stearate. The low viscosity means the bioDME is a poor lubricant. •

Question 2 (8 marks)

a.
$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$
 • or $CaCO_3(s) + 2H^+(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$

b.



- i. Since the gradients of all three graphs decrease, reaction rate decreases **0** as the reaction proceeds (time increases).
- ii. As the reaction proceeds, reactant concentration in this case c(HCl(aq)) decreases. This reduces the number of collisions, and the number of successful collisions. \bullet
- c. i. Increase in surface area.

The initial reaction rate is higher. This could be caused by a temperature increase, higher c(HCl), addition of a catalyst, or increased surface area. Since it was clearly stated the starting temperature was the same and no catalyst was used for all three investigations, either the surface area was larger – smaller marble chips used or a higher c(HCl) was used. • However, since the CaCO₃ was in excess (HCl was the limiting reactant), a higher c(HCl) would produce a greater overall mass loss. •

ii. Lower c(HCl)

The initial reaction rate is lower and the overall mass loss in investigation 3 is half of that for investigation 1 both observations are consistent with using a lower c(HCI) – most likely half the c(HCI) used in investigation 1. \bullet

d.

Investigations	Independent variables	Dependent variables	Controlled variables
1 and 2	Surface area (particle size) of CaCO3	m(CO2) / mass loss / reaction rate	Temperature V(HCl) c(HCl)
1 and 3	Concentration of HCl(aq)	m(CO2) / mass loss / reaction rate	Temperature V(HCl) Surface area CaCO3

Question 3 (7 marks)

- a. Cathode. There are 4 oxidants present in the cell $Cu^{2+}(aq)$, $Ag^{+}(aq)$, $K^{+}(aq)$ and $H_2O(l)$, but only 1 reductant $H_2O(l)$, so multiple products are only possible at the cathode (where oxidants are reduced). \bullet
- **b.** Referring to the relevant half-reactions on the electrochemical series.

$$O_{2}(g) + 4H^{+}(aq) + 4e^{-} \qquad \rightleftharpoons 2\underline{H_{2}O}(l) \qquad +1.77 \text{ V}$$

$$\underline{Ag^{+}}(aq) + e^{-} \qquad \rightleftharpoons Ag(s) \qquad +0.80 \text{ V}$$

$$\underline{Cu^{2+}}(aq) + 2e^{-} \qquad \rightleftharpoons Cu(s) \qquad +0.34 \text{ V}$$

$$2\underline{H_{2}O}(l) + 2e^{-} \qquad \rightleftharpoons H_{2}(g) + 2OH^{-}(aq) \qquad -0.83 \text{ V}$$

$$K^{+}(aq) + e^{-} \qquad \rightleftharpoons K(s) \qquad -2.93 \text{ V}$$

- i. Ag, silver the strongest oxidant, $Ag^+(aq)$ is the first to be reduced. \bullet
- ii. Cu, copper as the $c(Ag^{2+})$ decreases, a point will be reached where the next strongest oxidant, $Cu^{2+}(aq)$ will be reduced at the cathode. \bullet
- iii. 2H₂O(l) + 2e⁻ → H₂(g) + 2OH⁻(aq) ●
 H₂, hydrogen is the third substance formed as the c(Cu²⁺) decreases, a point will be reached where the next strongest oxidant, H₂O(l) will be reduced at the cathode.
 NB. K(s) will not be produced because H₂O(l) is a much stronger oxidant and is reduced preferentially to K⁺(aq).
- c. The layers of Ag and Cu deposited would be far more irregular and we are assuming that the behaviour predicted by standard conditions, 1 M solutions, 25°C and 100 kPa will be followed. or

There may be areas – depending on concentration - where both Ag(s) and Cu(s) or Cu(s) and $H_2(g)$ are produced simultaneously.

- d. $2H_2O(1) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
- e. Total cation concentration is increased.

Cations consumed as $Ag^+(aq)$ and $Cu^{2+}(aq)$ are reduced and replaced by $H^+(aq)$ ions from the oxidation half-equation $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$.

Each Ag⁺ is replaced by one H⁺,

$$4Ag^{+}(aq) + 2H_{2}O(e) \rightarrow O_{2}(g) + 4H^{+}(aq)$$
.

Each Cu²⁺ is replaced by 2H⁺,

$$2Cu^{2+}(aq) + 2H_2O(1) \rightarrow 2Cu(s) + 4H^{+}(aq) + O_2(q)$$
.

Overall, the number of cations increases.

Question 4 (7 marks)

- a. Incomplete combustion of carbon containing fuels. \bullet Any balanced combustion equation of a fuel showing CO as a product, e.g. \bullet 2CH₄(g) + 3O₂(g) \rightarrow 2CO(g) + 4H₂O(g)
- b. Haemoglobin has a greater affinity for CO(g) than $O_2(g)$, so in the presence of CO the equilibrium

 $Hb(aq) + 4CO(aq) \rightleftharpoons Hb(CO)_4(aq)$ is established. \bullet This impacts on the haemoglobin-oxygen equilibrium as the decrease in [Hb] causes the equilibrium $Hb(aq) + 4O_2(aq) \rightleftharpoons Hb(O_2)_4(aq)$ to shift to the left \bullet to compensate. Consequently, CO is carried round the body rather than O_2 .

c. The presence of CO in the air effectively establishes the equilibrium Hb(O₂)₄(aq) + 4CO(g)
 ⇒ Hb(CO)₄(aq) + 4O₂(g)

 This equilibrium lies far to the right and so treatment of CO poisoning must involve intervention that will push the equilibrium to the left to allow more Hb(O₂)₄ to form

intervention that will push the equilibrium to the left to allow more $Hb(O_2)_4$ to form. Since $O_2(g)$ is a product in this equilibrium, pure oxygen therapy will achieve this goal as the system moves to compensate for the increased oxygen concentration. \bullet

- d. Haemoglobin has a quaternary structure, i.e. contains two or more protein (polypeptide) chains clustered into a specific shape. Haemoglobin has four heme units each containing an Fe²⁺ ion (a cofactor) and each haemoglobin molecule can carry four O₂ molecules.
- e. Low blood pH is due to the $[H_3O^+]$ being too high. The system compensates by using up some of the $H_3O^+(aq)$ thereby pushing all the linked equilibria to the left. \bullet This increases the amount of $CO_2(g)$ released in the lungs to be exhaled.

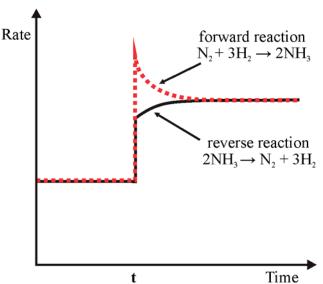
Question 5 (8 marks)

- a. The data show that, at constant temperature, the yield of NH₃ increases as the pressure increases. This is consistent with Le Chatelier's principle which suggests that the system strives to partially oppose a pressure increase by favouring the side of the reaction with fewer particles and so favours the NH₃ producing a forward reaction. •
- **b.** $K_c = [NH_3]^2 / \{[N_2] [H_2]^3\} M^{-2}$
- c. Exothermic.

The data show that at constant pressure $(2.00 \times 10^5 \text{ kPa})$, the yield of NH₃ decreases as the temperature increases. •

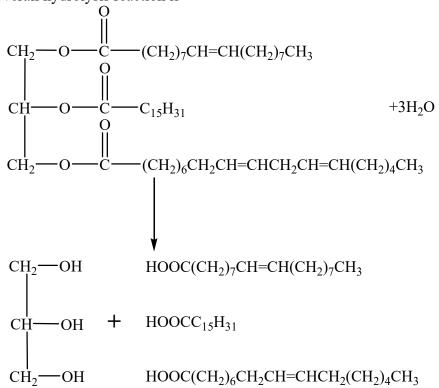
d. No effect. A catalyst would increase the rate of production of NH₃ but since it would not change the position of equilibrium, it would not affect the equilibrium yield. •

e.



Initially the system is at equilibrium and the rates of forward and reverse reactions are equal. The volume decrease instantaneously increases reactant and product concentrations and so the rates of the forward and reverse reactions increase. The forward rate increases more because of the greater number of reactant particles in the equation. As the system moves to counteract the volume decrease (concentration increase), the reactant that produces fewer particles is favoured, i.e. the forward reaction. As the forward reaction proceeds, its rate drops as [N2] and [H2] (reactants) decrease, and the rate of the reverse reaction increases as the [NH3] (product) increases. Eventually equilibrium is established again and the rates of the forward and reverse reactions are again equal.

Question 6 (17 marks)



ii. Two **00** of the following:

Oleic acid [CH₃(CH₂)₇CH=CH(CH₂)₇COOH] – monounsaturated fatty acid. Palmitic acid [C₁₅H₃₁COOH] – saturated fatty acid. Linoleic acid [CH₃(CH₂)₄CH=CHCH₂CH=CHCH₂(CH₂)₆COOH – polyunsaturated fatty acid.

- iii. An omega-6 unsaturated fatty acid has its first C=C double bond beginning with the sixth carbon from the beginning of the hydrocarbon chain. Linoleic acid, CH₃CH₂CH₂CH₂CH=CHCH₂CH=CHCH₂(CH₂)6COOH, is an omega-6 fatty acid.
- iv. Linolenic acid,

20

CH₃(CH₂)₄CH=CHCH₂CH=CHCH₂CH=CHCH₂(CH₂)₆COOH **●**

- **b.** The molecular formula of the triglyceride is $C_{52}H_{98}O_6$
 - 1. Skeleton equation $C_{55}H_{100}O_6(l) + O_2(g) \rightarrow CO_2(g) + H_2O(g)$
 - 2. Balance C atoms $C_{55}H_{100}O_6(1) + O_2(g) \rightarrow 55CO_2(g) + H_2O(g)$
 - 3. Balance H atoms $C_{55}H_{100}O_6(1) + O_2(g) \rightarrow 55CO_2(g) + 50H_2O(g)$
 - 4. Balance O atoms, 110 + 50 = 160 on right, 6 on left, need 154 O, i.e. 77O₂ on left.

$$C_{55}H_{100}O_6(1) + 77O_2(g) \rightarrow 55CO_2(g) + 50H_2O(g)$$
 00

- c. i. The presence of C=C bonds in unsaturated fatty acids in olive oil are very reactive. Oxidative rancidity is associated with autoxidation of fats from which foul smelling short chain aldehydes and ketones can result. Antioxidants prevent this happening by inhibiting the propagation of free radicals associated with autoxidation.
 - ii.

Ascorbic acid (from *Data Book*)

To have enantiomers, a molecule must be chiral, i.e. have a chiral centre. Carbon atoms making single bonds to four different atoms or groups are chiral centres. •

Hydroxytyrosol has no chiral centre, whereas ascorbic acid has two chiral centres, • indicated by the asterisks (*).

d. Energy released by oil =
$$(517 / 15) \times 7.5$$

$$= 258.5 \text{ kJ}$$

Energy transferred to water = 0.40×258.5

$$= 103.4 \text{ kJ}$$
 0

$$103.4 \times 10^3 \text{ J} = 4.18 \text{ J g}^{-1} \, {}^{\circ}\text{C}^{-1} \times 500 \text{ g} \times \Delta T \, \bullet$$
 assume $d(\text{H}_2\text{O}) = 1 \text{ g mL}^{-1}$
 $\Delta T = 103.4 \times 10^3 \, / \, (4.18 \times 500)$

e. According to *Data Book*, *Table 13*.

Energy content of fats and oils = 37 kJ g^{-1}

15 mL olive oil \rightarrow 517 kJ

$$m$$
(olive oil) for 517 kJ = 517 / 37

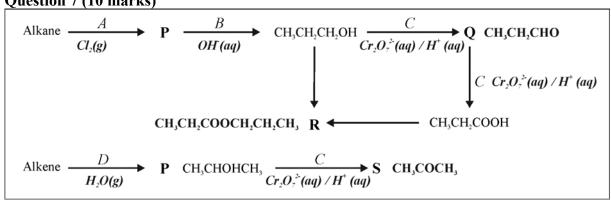
$$= 14 g 0$$

So, 14 g olive oil is equivalent to 15 mL olive oil

$$d(olive oil) = 14 g / 15 mL$$

$$= 0.93 \text{ g mL}^{-1}$$

Question 7 (10 marks)



- a. $Q CH_3CH_2CHO$
 - R CH₃CH₂COOCH₂CH₃ **0**
 - S CH₃COCH₃ **0**
- b. $B OH^{-}(aq) / NaOH(aq)$
 - $C Cr_2O_7^{2-}(aq) / H^{+}(aq)$
 - $D H_2O(g)$ 0
- c. Oxidation: $CH_3CHOHCH_3(aq) \rightarrow CH_3COCH_3(l) + 2H^+(aq) + 2e^-$ Reduction: $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(1)$
- **d.** Compound R is propylpropanoate produced via the equilibrium

 $CH_3CH_2COOH(1) + CH_3CH_2CH_2OH(1) \rightleftharpoons CH_3CH_2COOCH_2CH_2CH_3(1) + H_2O(1)$

Because equal chemical amounts of each reactant were used, the initial amount may be assumed to be, say 0.50 mol, of which 75 %, i.e. 0.375 mol (0.75×0.50) reacts as the system gets to equilibrium

 $CH_3CH_2COOH(1) + CH_3CH_2CH_2OH(1) \rightleftharpoons CH_3CH_2COOCH_2CH_2CH_3(1) + H_2O(1)$

Equilibrium	0.125	0.125	0.375	0.3750
Reacting (mol)	0.375	0.375	0.375	0.375
Initially (mol)	0.50	0.50	-	-

Because there are the same number of mol on both sides of the balanced equation, volume is not a significant issue in the calculation; it may be assumed to be 1 L

$$K_c = [CH_3CH_2COOCH_2CH_2CH_3][H_2O] / [CH_3CH_2COOH][CH_3CH_2CH_2OH]$$

= $(0.375 \times 0.375) / (0.125 \times 0.125)$
= 9.0 ①

Alternatively:

Since 75 % percent of each of the reactants were consumed in getting to equilibrium, and equal mole amounts of reactants were initially present, the ratio of each of the products to each of the reactants at equilibrium will be 3:1.

Hence, for **this** equilibrium, $K = 3 \times 3 / 1 \times 1 = 9.0$

Question 8 (11 marks)

- a. i. $C_2H_2O_4(aq) + 2NaOH(aq) \rightarrow C_2H_2O_4^{2-}(aq) + 2H_2O(l)$ **0** ii. $C_7H_8O_7(aq) + 3NaOH(aq) \rightarrow C_7H_5O_7^{3-}(aq) + 3H_2O(l)$ **0**
- b. The data in the third column (V(NaOH) required to react with citric acid in the fruit juice) should have been presented separately to avoid confusion; these data are not linked to the individual amounts of oxalic used. ●
- c. Oxalic acid is a primary standard. Sodium hydroxide absorbs water from the atmosphere and reacts with atmospheric CO₂, hence the samples used are unlikely to be pure and the accurate concentration of the solution will not be 1.00 M.

By reacting the NaOH(aq) with oxalic acid, the accurate c(NaOH) can be determined.

```
d. Average m(C_2H_4O_4) used = (1.25 + 1.23 + 1.26) / 3

= 1.247 g

Average V(NaOH) used = (27.6 + 27.1 + 27.4) / 3

= 27.37 mL \bullet

n(C_2H_4O_4) reacting = 1.247 / 90

= 0.0139 mol \bullet

n(NaOH) required = 2 \times n(C_2H_4O_4)

= 2 \times 0.0139

= 0.0277 mol

c(NaOH) = 0.0277 mol / 0.0237 L

= 1.012 mol L^{-1} \bullet
```

e. Average V(NaOH) used in titrating citric acid in fruit juice = (33.6 + 33.4 + 33.9)= 33.63 mL

n(NaOH) reacting with citric acid in juice sample = 1.012 mol L⁻¹ × 33.63× 10⁻³ L = 0.0340 mol **①**

$$n(\text{C}_7\text{H}_8\text{O}_7) \text{ reacting } = n(\text{NaOH}) / 3$$

= 0.0340 / 3
= 0.0113 mol \bullet
 $m(\text{C}_7\text{H}_8\text{O}_6) \text{ in 50.0 sample of juice } = 0.0113 \text{ mol} \times 204.0 \text{ g mol}^{-1}$
= 2.32 g

$$m(C_7H_8O_6)$$
 in one L of juice = $(2.32 / 50) \times 1000$
= $46.3 \text{ g L}^{-1} \bullet$

f. The calculated concentration of citric acid will be higher than the true value because the total V(NaOH) added includes some that will have reacted with malic acid. \bullet

Question 9 (11 marks)

a. Parent-ion peak at m/z = 88, indicating that the **relative molecular mass** of the compound is **88**. •

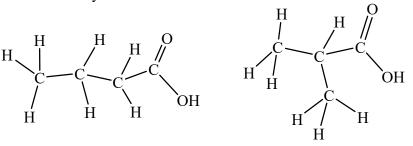
Reference peak at m/z = 43, indicating that the **relative mass of the most abundant** fragment is 43. \bullet

- **b.** The compound has 4 different carbon environments. **0**
- c. The compound has 3 different hydrogen environments. \bullet The presence of a quartet and a triplet indicates the presence of a CH₃CH₂- group. \bullet The singlet at $\delta = 2.0$ ppm is consistent with H on a carbon which is bonded to the carbon of an ester or amide group, i.e. CH₃COOR, or CH₃COONHR. [Data Book, Table 16] \bullet
- d. All the information deduced so far indicates that the compound could be either CH₃COOCH₂CH₃ or CH₃CONHCH₂CH₃. $M_r(\text{CH}_3\text{COOCH}_2\text{CH}_3) = 88.0$

 $M_r(CH_3CONHCH_2CH_3) = 79.0$

Compound is CH₃COOCH₂CH₃ **0** − ethyl ethanoate.

- e. 1720-1840 cm⁻¹ C=O esters and 2850-3090 cm⁻¹ C-H **0**
- **f.** Carboxylic acids are structural isomers of esters with the same number of C atoms. There are two 4 C carboxylic acids.



Butanoic acid

Methylpropanoic acid

Differences in ¹H NMR spectra, from the spectrum for the compound would be

Butanoic acid \bullet -Peak at δ = 9.0-13.0 for H in the carboxyl group -COOH \bullet or Four hydrogen environments rather than three.

or

Methyl propanoic acid - Peak at δ = 9.0-13.0 for H in the carboxyl group -COOH or Singlet, doublet and septet, rather than singlet, triplet and quartet on its high resolution spectrum.

End of Suggested Answers

Question 10 (13 marks) BONUS QUESTION

a. Two. O

The structure of aspartame was supplied in Table 10 in the *Data Book*. This is shown below with the two chiral carbons (those bonded to four different groups) indicated by an asterisk (*).

- b. At pH 10, the carboxyl group (-COOH) is deprotonated to COO⁻, as aspartame acts as an acid in the alkaline solution and the molecules are negatively charged.

 At pH 4, the amino (-NH₂) group is protonated to ⁺NH₃, as aspartame acts as a base in the acidic solution and the molecules are positively charged.

 (Also, NH in the amide group could be protonated to ⁺NH₂).
- c. The fact that we taste L-aspartame but not D-aspartame indicates that only the chiral molecules interact with our taste buds. •
- d. i. Aspartame: peptide (amide) → carboxyl + amino ①
 Sucrose: ether (glycoside) → hydroxyl ①
 - ii. Aspartic acid **0**, phenylalanine **0** (from *Table 17 in the Data Book*)
 - iii. Glucose O, Fructose O
 - iv. The glycaemic index ranks carbohydrate-intense foods based on their effect on blood-sugar (glucose) levels (over a 2-hour period). Glucose is released during the hydrolysis of starch but the rate at which glucose is released into the blood depends on the relative amounts of amylose and amylopectin (polymers of glucose) present in the starch. Straight chain amylose is more difficult to digest than branched chain amylopectin, so a more rapid higher peak in blood glucose levels indicate a greater proportion of amylopectin in the starch. •

End of Suggested Answers (Bonus Question)