Suggested Answers

VCE Chemistry 2016 Year 12 Trial Exam Units 3/4

SECTION A – Multiple Choice Answers

Q1. C IR absorptions bands *(Data Book Table 7)* can be used to identify species causing key peaks.

> The presence of the peaks at the around 3400 cm⁻¹ rules out methylpropane. The lack of a significant peak in the absorption band $1670-1750$ cm⁻¹ (C=O) rules out butanoic acid.

 Peaks around 3400 cm-1 might be considered to be evidence of the presence of N-H or O-H(alcohols). However, the presence of **two similar but slightly different peaks is more consistent with the –NH2 of 1-butanamine than the – OH of 1-butanol**.

 Further evidence in support of the amine rather than the alcohol is the lack of a significant peak for C-O in the 1000-1300 cm⁻¹ absorption band.

The ¹H NMR spectrum shows 3 hydrogen environments – a singlet, a quartet and a triplet.

> The quartet and triplet is indicative of the presence of CH3CH2- in the molecule. Consider the alternatives

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- A. Butanoic acid CH₃CH₂CH₂COOH 4 hydrogen environments
- B. Ethyl ethanoate $CH₃COOCH₂CH₃ 3$ hydrogen environments, singlet, quarter, triplet
- C. Methyl propanoate $CH_3CH_2COOCH_3 3$ hydrogen environments, triplet, quartet, singlet

D. 1-propyl methanoate – $HCOOCH_2CH_2CH_3 - 4$ hydrogen environments To decide between CH3COOCH2CH3 and CH3CH2COOCH3 it is necessary to consider chemical shifts.

In *Table 5 of the Data Book*, two hydrogen chemical shifts which relate to esters are

2.0 for C**H**3COOR and 4.1 for RCOOC**H**2R.

On the spectrum, the chemical shift for H atoms causing the **singlet peak** is **around 3.7** which suggests those H atoms are on a **C atom bonded to an O atom (RCOOCH3) of the ester group** rather than a C atom bonded to the C atom of the ester group (CH3COOR).

- The spectrum is that of **methyl propanoate**, CH3CH2COOCH3.
- **Q3. B** Concordant titres should be used in calculating the average titre volume in a titration. Concordant titres are generally accepted as those within 0.1 mL of each other.

There are three concordant titres in the data provided. **19.39 mL**, 19.19 mL, **19.43 mL**, 19.64 mL, **19.51 mL**.

 There are three species in the equilibrium system and the initial concentration changes, and changes following the system changes imposed at the 5, 15 and 25 minute marks, show that **all three have the same mole ratio in the reaction equation**.

Hence the equilibrium reaction must be along the lines of $X + Y \rightleftharpoons Z$ Hence the equation for the reverse reaction **is** $Z(g) \rightleftharpoons X(g) + Y(g)$

- **Q5. D** The concentration-time graphs are consistent with
	- **‐** a **pressure decrease**. This is most obvious at 5 minutes where all concentrations decrease, probably due to a system volume increase.

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‐ a temperature decrease.
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Since the forward reaction is $X + Y \rightarrow Z$, any change that favours the forward reaction will cause two concentrations to decrease and one to decrease. Similarly, any change that favours the reverse reaction $Z \rightarrow X + Y$ will cause two concentrations to increase and one to decrease

A temperature change causes a gradual change in concentrations until the system reaches equilibrium at the new temperature. The temperature change was imposed at 25 minutes.

Since the forward reaction $X + Y \rightarrow Z$ is endothermic, the fact that the **reverse** exothermic reaction $Z \rightarrow X + Y$ was clearly favoured by the temperature **change** suggests the temperature was **decreased**.

‐ Addition of a reactant at equilibrium. The system responds by partially opposing the addition and favouring the forward reaction $X + Y \rightarrow Z$

Addition of a catalyst 16 minutes would cause **an immediate increase** in the rates of both the forward and reverse reaction and so **rates of change of the concentrations of reactants and products**. This is **not evident** on the concentration-time graphs.

- **Q6. A** Consider the alternatives
	- **A.** The forward reaction is $X + Y \rightarrow Z$ so $K_c = [Z]/[X][Y]$ The **lowest equilibrium concentration of Z** and the **highest equilibrium concentrations of X and Y** are at 30 minutes, so the lowest value of K_c is at 30 minutes.
	- B. The system reaches equilibrium **three times**, around 10, 20 and 30 minutes.
	- C. The pressure is decreasing between 0 and 5, 5 and 10, 15 and 20, i.e. a total of **15 minutes,** all the time the reaction $X + Y \rightarrow Z$ was favoured so the total number of particles decreased. Between 25 and 30 minutes, the pressure increases as the reaction $Z \rightarrow X + Y$ is favoured. Whilst the **pressure changes for 20 minutes**, it **decreases for 15** of those **minutes**.
	- D. $CF = [Z]/([X][Y])$. Since the concentration of one of the reactants increases, the **concentration fraction decreases**.
- **Q7. C** Energy required to heat 0.225 kg of water from 20°C to steam at 100° is the **sum of** the energy required to heat
	- **i.** 0.225 kg of water from 25° C to 100° C
		- $E = 4.18$ J g⁻¹ °C⁻¹ x *m*(H₂O) x ΔT $= 4.18$ J g⁻¹ °C⁻¹ x 225 g x 75°C⁻¹
- $= 7.05 \times 10^4$ J
	- $= 70.5$ kJ

and the energy required to

ii. convert 0.225 kg of water to steam at 100°C.

270 kJ to convert 110.0 g H₂O(l) to H₂O(g) at 100° C (270/110) kJ to convert one gram $H_2O(1)$ to $H_2O(g)$ at 100° C *E* for 0.225 kg H₂O = 225 g x (270/110) kJ g⁻¹ $= 552$ kJ

Total energy required to heat 100 g of water from 25°C to steam at 100° $= 70.5$ kJ + 552 kJ $= 623$ kJ

Q8. B The self-ionisation of water $2H_2O(1) \rightleftharpoons H_3O^+(aq) + OH$, is the reverse reaction of the exothermic equilibrium shown in the question. Hence it must be endothermic, $\Delta H = +56$ kJ mol⁻¹. **Heating water** will **increase** the $[H_3O^+]$ and $[OH^-]$ equally so water will remain **neutral.**

Since the **[H3O+] increases**, the **pH decreases**.

Q9. A Since $Ca(OH_2)_2(aq) \rightarrow Ca^{2+}(aq) + 2OH(aq)$, [OH⁻] in 0.0500 M Ca(OH)₂(aq) is $2 \times 0.0500 = 0.100$ M 50.0 mL of 0.100 M NaOH and 50.0 mL of 0.0500 M Ca(OH)2(aq) is effectively 100 mL of 0.100 M OH (aq) pH 12.7 \rightarrow [H₃O⁺] = 10^{-12.7} $= 2.00x10^{-13}$ M At 25°C $[OH^-] = 10^{-14} / [H_3O^+] = 10^{-14} / 2.00 \times 10^{-13}$ $= 0.0500 M$ Since the [OH⁻] has halved from 0.100 M to 0.0500 M, the total solution volume must have doubled from 100 mL to 200 mL.

The $V(H_2O)$ in the container was $200 - 100 = 100$ mL or **0.100 L**

- **Q10. C** Limestone is a form of calcium carbonate. The reaction is described by the equation $CaCO₃(s) + 2HCl(aq) \rightarrow CaCl₂(aq) + CO₂(g) + H₂O(l)$ The **decrease in mass during the reaction** is the same as the $m(CO_2)$ produced and the rate of CO2 production will be **highest** for the higher concentration and greater surface area, i.e. **for 2.0 M HCl(aq) and powdered limestone**. Mathematically In the reaction conditions given in the alternatives, $n(CaCO₃) = 20.0 / 100.1 = 0.198$ mol $n(HCl) = 2.00 \times 25.0 \times 10^{-3} = 0.0500 \text{ mol}$ (2 M HCl) *or* $n(HCl) = 1.00 \text{ x } 25.0 \text{x} 10^{-3} = 0.0250 \text{ mol } (1 \text{ M } HCl)$ In all cases $HCl(aq)$ is the limiting reactant, i.e. $(CaCO₃)$ is in excess). Maximum possible mass loss, i.e. maximum *m*(CO2) produced depends on amount of HCl(aq) $n(CO_2) = \frac{1}{2} x n(HCl)$ 2 M HCl(aq); $n(CO_2) = \frac{1}{2} \times 0.0500 = 0.250$ mol $m(CO_2) = 0.0250 \text{ x } 44.0 = 1.10 \text{ g}$ 1 M HCl(aq); $n(CO_2) = \frac{1}{2} \times 0.0250 = 0.125$ mol $m(CO_2) = 0.0125$ x 44.0 = 0.550 g This indicates that investigations 1 and 2 involve 2.00 M HCl(aq) and Investigation 3 involves 1.0 M HCl(aq). Because investigation 2 has a faster rate of mass loss than investigation 1, it **involves powdered CaCO3, i.e. the greater surface area.**
- **Q11. D X** reacts with sodium carbonate to produce $CO_2(g)$, hence **X** is an **acid Y** is converted to X by acidified $Cr_2O_7^2$ (aq), hence **Y** is a primary **alcohol Z** breaks down (hydrolyses) into an acid and an alcohol, hence **Z** is an ester **X** and **Y** must have the same number of carbon atoms in their molecules Whilst all the alternatives are ester, only $CH_3CH_2COOCH_2CH_2CH_3$, i.e. 1-propyl propanoate is consistent with the reaction information supplied.

Q12. A Since
$$
d = m / V
$$

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

= 0.775 g mL⁻¹ x 20.0x10³ mL
= 1.55x10⁴ g

$$
n(C_{16}H_{34}) \text{ reacting} = 1.55x10^{4} / 226.0
$$

$$
= 68.6 \text{ mol}
$$

$$
n(CO_2) \text{ produced } = 16 \times n(C_{16}H_{34})
$$

$$
= 16 \times 68.6
$$

$$
= 1.10x10^{3} \text{ mol}
$$

$$
m(CO_2) = 1.10x10^{3} \times 44.0
$$

$$
= 4.83x10^{4} g
$$

$$
= 48.3 \text{ kg}
$$

Q13. B In all electrochemical cells, electrons flow from the site of oxidation to the site of reduction, i.e. from the anode to the cathode. Hence **electrode 2 is the anode** and electrode 1 is the cathode. In a fuel cell, the **fuel is oxidised** so is supplied to the anode and the oxidant is reduced at the cathode. Hence **Y is the fuel** and X is the oxidant.

Q14. D Consider the alternatives

- A. Correct! Uranium has a much higher energy density than coal.
- B. Correct! Thermal energy released in the nuclear fission of uranium (nuclear power station) and combustion of coal (coal-fired power station) is used to convert water into steam to drive the turbine.
- C. Correct! Mass is conserved in chemical reactions but not in nuclear reactions where a small proportion of the mass of reactants is converted into energy.

D. INCORRECT!

Combustion of coal: $C(s) + O_2(g) \rightarrow CO_2(g)$ Fission of uranium: $235 - 1$ $92 - 141 - 1$ $U + n \rightarrow \mathbb{R}$ Kr + $n \rightarrow \mathbb{R}$ Ba + 3 n 92 0 36 56 0 \rightarrow

In nuclear fission reactions larger nuclei are broken down into smaller nuclei.

Q15. A Equation for respiration is $C_6H_{12}O_6(aq) + 6O_2(q) \rightarrow 6CO_2(q) + 6H_2O(l)$ According to *Data Book Table 13*, $\Delta H_c(C_6H_{12}O_6) = -2816 \text{ kJ} \text{ mol}^{-1}$ $n(O_2)$ reacting = 9.60 g / 32.0 g mol⁻¹ $= 0.300$ mol $n(C_6H_{12}O_6)$ reacting = $n(O_2) / 6$ = 0.300 / 6 $= 0.0500$ mol Energy released = 0.0500 mol x 2816 kJ mol⁻¹ $= 141$ kJ

Q16. B Structural isomers are compounds with the same molecular formulae but different structural arrangements.

> In all four options, the compounds in each pair have the same molecular formula. A. C4H8O2, B. C2H4O2, C. C7H12O3, D. C6H11OCl

> However, in each of the alternatives A, B and D, both structures given are for the same compound.

Whereas, for compound B, C₂H₄O₂, the full structural formulae show that there are two different compounds represented.

HCOOCH3 CH3COOH

Methyl methanoate Ethanoic acid So **HCOOCH3 and CH3COOH are structural isomers**

- **Q17. C** The immediately useful piece of information on the cell diagram is the direction of movement of the $NO₃(aq)$, i.e. anions, from the salt bridge. In electrochemical cells, under standard conditions, anions move towards the anode, and electrons move from the anode (site of oxidation) to the cathode (site of reduction). Also the overall reaction is between the strongest oxidant and the strongest reductant. Oxidation occurs in the Yⁿ⁺(aq) / Y(s) half-cell according to Y(s) \rightarrow Yⁿ⁺(aq) + ne⁻ Reduction occurs in the $X^{n+}(aq) / X(s)$ half-cell according to $X^{n+}(aq) + ne^- \rightarrow X(s)$ Hence, the strongest oxidant in the cell is $Xⁿ⁺(aq)$, and the **strongest reductant is Y(s).**
- **Q18. D** Under standard conditions the cell voltage is the difference between the E° values of the oxidant half-cell and the reductant half-cell. According to the electrochemical series, *Data Book, Table 2*, the only half-cell combination that would produce 1.03 V is $\text{Ag}^{\text{+}}(\text{aq}) + \text{e}^{\text{-}} \rightarrow \text{Ag(s)}$ +0.80 V $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$ -0.23 V $E[Ag^+(aq)/Ag(s)/Ni^2+(aq)/Ni(s)] = 0.80 - (-0.23)$ $= 1.03 V$
- **Q19. B** Applying the accepted rules for applying oxidation states UF₆ – since the oxidation state of F is -1 and the sum of the oxidation states zero, U = $+6$ U_3O_8 – oxygen has oxidation state of -2 in its compounds. Let 'x' = oxidation state of U $3'x' + 8(-2) = 0$

$$
3^{3}x^{3} = 16
$$

$$
x^{3} = 16/3
$$

$$
= 5^{1}/3
$$

 Since **oxidation states are whole numbers** this suggests a **mixture of +5 and +6** for U in U3O8

Li₂U₂O₇ – oxygen has oxidation state of -2, lithium has oxidation state +1

 Let 'x' = oxidation state of U 2(+1) + 2'x' + 8(-2) = 0 2'x' = 14 'x' = 7

 UO_3 – since the oxidation state of O is -2 and the sum of the oxidation states zero, $U = +6$

- **Q20. A** Consider the alternatives.
	- A. INCORRECT, sometimes light of more than one wavelength is absorbed by a particular species and the one which is absorbed most strongly without absorbance by any other species is used.
	- B. Correct, the amount of light absorbed by the species is proportional to the amount of active ingredient present.
	- C. Correct, the energy provided by the light is absorbed by electrons which move to higher energy levels. The wavelength matches an exact energy gap.
	- D. Correct, aqueous solutions of Cu^{2+} are blue because they absorb light with wavelengths in the orange-red region of the spectrum.
- **Q21. C** Analysis of ethanol content by gas chromatogram requires
	- **‐** Knowledge of the retention time of ethanol for the stationary phase, mobile phase, and column temperature used
	- **‐** Preparation of a set of standards of known ethanol content which are then fed through the chromatograph and the peak area of each standard measured
	- **‐** A plot of peak area v ethanol content to be established
	- The sample being tested to be passed through the chromatograph, its peak area measured and compared to the calibration curve to establish ethanol content The number of peaks on the chromatogram is not significant once the retention time of ethanol is known.
- **Q22. A** The absorbance of the treated steel solution was 0.350.

 1 mol cobalamin molecules contains 1 mol Co atoms 4.34 % of *M* (cobalamin) = M (Co) 0.0434 X M (cobalamin) = 58.9 g mol⁻¹ M (cobalamin) = 58.9 / 0.0434 $= 1.36 \times 10^3$ g mol⁻¹ M (cobalamin) = 5 x 1.36x10³ $= 6.78x10^{3} g$

Absorbance

- **Q24. B** 1. $4NH_3(g) + 7O_2(g) \rightarrow 4NO_2(g) + 6H_2O(g); \Delta H = -1132 \text{ kJ} \text{ mol}^{-1}$ 2. $6NO_2(g) + 8NH_3(g) \rightarrow 7N_2(g) + 12H_2O(g)$; $\Delta H = -2740 \text{ kJ mol}^{-1}$ Combine the two equations so as to eliminate NO2. This can be done by multiplying 1 by three and 2 by four and then adding the adjusted equations. 1a $12NH_3(g) + 21O_2(g) \rightarrow 12NO_2(g) + 18H_2O(g)$; $\Delta H = -3396 \text{ kJ} \text{ mol}^{-1}$ 2a $12NO_2(g) + 16NH_3(g) \rightarrow 14N_2(g) + 24H_2O(g)$; $\Delta H = -5480 \text{ kJ} \text{ mol}^{-1}$ Adding 1a and 2a will eliminate $NO₂$ giving $28NH_3(g) + 21O_2(g) \rightarrow 14N_2(g) + 42H_2O(g); \ \Delta H = -3396 \text{ kJ} \text{ mol}^{-1} + (-5480 \text{ kJ} \text{ mol}^{-1})$ $= -8876$ kJ mol⁻¹ In the simplest ratio $4NH_3(g) + 3O_2(g) \rightarrow 2N_2(g) + 6H_2O(g);$ $\Delta H = -1268 \text{ kJ mol}^{-1}$ Since the conversion of 4 mol NH3 releases 1268 kJ, conversion of 1 mol NH₃ releases $1268 / 4 = 317$ kJ
- **Q25. D** Primary amines have the general formula RNH₂, and unbranched primary amines with NH₂ on the end follow the sequence CH₃NH₂, CH₃CH₂NH₂, CH3CH2CH2NH2, etc., i.e. form a homologous series, so successive members differ by CH₂.

If a sequence of five of these amines has an average molar mas of 87.0 g mol^{-1} , that must be the molar mass of the middle (third) compound in the sequence. $CH_3CH_2CH_2CH_2CH_2NH_2$, 1-pentanamine – has molar mass 87.0 g mol⁻¹, so the amines in the mixture separated are

CH3CH2CH2NH2, 1-propanamine

CH₃CH₂CH₂CH₂NH₂, 1-butanamine

CH3CH2CH2CH2CH2NH2, 1-pentanamine

CH₃CH₂CH₂CH₂CH₂CH₂NH₂, 1-hexanamine

CH3CH2CH2CH2CH2CH2CH2NH2, 1-heptanamine

Relative attraction to the stationary will increase with molecular mass and so retention times increase from 1-propanamine to 1-heptanamine.

Q26. C 2.06 g Mn + xsHCl \rightarrow 2.32 L of H₂ at 100°C and 752 mm Hg $n(Mn)$ reacting = 2.06 g / 54.9 g mol⁻¹ $= 0.0375$ mol $n(H_2)$ produced = $p(H_2)$ x V / RT = (752/760 x 101.3) x 2.32 / (8.31 x 373) $= 0.0750$ mol $n(\text{H}_2) / n(\text{Mn}) = 0.0750 / 0.0375$ $= 2$ For 2 mol H2 to be produced 1 mol Mn must react with 4 mol HCl The equation for the reaction must be $Mn + 4HCl \rightarrow MnCl₄ + 2H₂$

In MnCl4, manganese has a **+4 oxidation state**

Q27. D Hydrocarbons that become monochlorinated when reacting with $Cl_2(g)$ in the presence of UV light must have molecules with only one hydrogen environment where an H atom can be substituted by a Cl atom.

 ζ H

*

H

H

C

H

H H

*

*

* *

C

H

H

 $c > c$

H

^H ^H

environments hence 3 possible monochlorinated compounds.

B. $\begin{bmatrix} 1 \\ 1 \end{bmatrix}$ $\begin{bmatrix} 1 \\ 1 \end{bmatrix}$ environments, hence 5 possible monochlorinated compounds.

environments hence 2 possible monochlorinated compounds.

D. Only one hydrogen environment, hence 1 monochlorinated compound. **Q28. B** Water reacts across the amide group to produce an amine and a carboxylic acid.

Q29. B The **wavelength** chosen should be one where **Y absorbs strongly with** minimal **absorbance by X**. If X also absorbs at the wavelength selected, the concentration of Y determined will be higher than the true value.

 400 nm is the best wavelength. Absorbance by X has a significant effect at 300, 500 and 600 nm

Q30. A Half-equations occurring during the electrolysis will be $(-) Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $(+)$ Cu(s) \rightarrow Cu²⁺(aq) + 2e⁻ Ideally the mass decrease at the anode would be equal to the mass increase at the cathode. n (Cu) transferred = 0.298 g / 63.5 g mol⁻¹ $= 4.69x10^{-3}$ mol $n(e^{\cdot})$ transferred = 2 x $n(Cu)$ = 2 x 4.69x10⁻³ $= 9.39x10^{-3}$ mol Charge passed through cell = 915 C Faraday's constant $=$ Charge carried by 1 mol electrons $= 915 \text{ C} / 9.39 \text{x} 10^{-3} \text{ mol}$ $= 9.75 \times 10^5$ C mol⁻¹

SECTION B – Short Answer (Answers)

Question 1 (19 marks)

- **a.** Each sorbitol molecule contains six polar –OH groups \bullet . Water molecules attracted to these groups by hydrogen bonding. \bullet
- **b. i.** m (sorbitol) in 100 g lozenges = 94.5 g *m*(sorbitol) in 1 packet (25 g) lozenges = $(94.5 / 100) \times 25$ $= 23.6 g$ *m*(sorbitol) in one lozenge = $23.6 / 20$ $= 1.18 \times 0$ n (sorbitol) in one lozenge = m (sorbitol) / M (sorbitol) = 1.18 g / 182.0 g mol⁻¹ $= 6.5x10^{-3}$ **O** mol **ii.** According to **Table 13 in Data Book:** ΔH_c (glucose) = -2816 kJ mol⁻¹ $M(C_6H_{12}O_6) = 180.0$ g mol⁻¹ Energy content of one gram of **glucose** $= 2816 / 180$ $= 15.6$ kJ \odot Since 94.5 g sorbitol contains 1395 kJ of energy. Energy content of one gram of sorbitol $= 1395 / 94.5$ $= 14.8$ kJ \odot The energy content of sorbitol is slightly lower than the energy content of glucose. **c. i.** $C_6H_{14}O_6 + 6H_2 \rightarrow C_6H_{14} + 6H_2O$ **0 ii.** *m*(hexane) produced = *d* x $V = 0.659$ g mL⁻¹ x 10.0x10³ mL $= 6.59x10^{3} g$ $n(C_6H_{14}) = 6.59x10^3$ g / 86.0 g mol⁻¹ $= 76.6$ mol \bullet Sorbitol is used in the production of both hydrogen and the production of hexane. $n(H_2)$ used in production of hexane = 6 x $n(C_6H_{14})$ $= 6 \times 76.6$ $= 460$ mol $n(C_6H_14O_6)$ used to produce $H_2 = n(H_2) / 13$ …… APR equation $= 460 / 13$ $= 35.4$ mol \bullet $n(C_6H_{14}O_6)$ used to produce $C_6H_{14} = n(C_6H_{14})$ …… APD/H equation $= 76.6$ mol Total $n(C_6H_14O_6) = 35.4 + 76.6$ $= 112$ mol \bullet $m(\text{soft}$ itol) = 112 mol x 182 g mol⁻¹ $= 2.04 \times 10^4$ g
= 20.4 kg **0 iii.** $19C_6H_{14}O_6 \rightarrow 13C_6H_{14} + 36CO_2 + 42H_2O$ \bullet **d.** \rightarrow CH_{2} ⁻OH **CH OH** CH_2 ⁻OH $CH₂$ CH $\mathsf{CH}_{\bar 2}$ O $\mathsf{O}\text{-}\mathsf{C}\text{--}(\mathsf{CH}_2)_{16}\mathsf{CH}_3$ $\left(\mathsf{CH}_{2}\right)_{12}\!\mathsf{CH}_{3}$ $\left(\text{CH}_2\right)_{12}\text{CH}_3$ + $3CH₃OH$ O $O - C$ O $O - C$ **CH3(CH2)16COOCH3 Methyl stearate 2CH3(CH2)12COOCH3 Methyl laurate** \bullet \bullet \bullet \bullet \bullet

Glycerol

e. *n*(biodiesel) = 500 g / 294.5 g mol⁻¹ $= 1.70$ mol Energy from biodiesel = 1.70 mol x 1.17×10^5 kJ mol⁻¹ $= 1.99x10^{5}$ kJ \bullet ΔH_c (Hexane) = -4158 kJ mol⁻¹ ….. *Data Book Table 13.* $n(C_6H_{14}) = 1.99x10^5$ kJ / 4158 kJ mol⁻¹ $= 47.8$ mol **O**

Question 2 (20 marks)

a. Using electrical heating to calibrate a calorimeter. **Electrical** \rightarrow **Thermal** Investigating an endothermic reaction in a calibrated calorimeter. **Thermal** \rightarrow **Chemical** Constructing an operating galvanic cell from $Cu^{2+}(aq)/Cu(s)$ and $Zn^{2+}(aq)/Zn$ half-cells. **Chemical** \rightarrow **Electrical** A hydrogen-oxygen fuel cell. **Chemical Electrical** Electrolysis of 1 M NaCl(aq). **Electrical** \rightarrow **Chemical** The reactor in a nuclear power station. **Nuclear** \rightarrow **Thermal** \bullet \bullet **b. i.** Chemical reaction for the reaction between $Mg(s)$ and $HCl(aq)$ is $Mg(s) + 2HCl(aq) \rightarrow MgCl₂(aq) + H₂(g).$ $n(Mg) = 0.235$ g / 24.3 g mol⁻¹ $= 9.67x10^{-3}$ mol $n(HCl) = 0.500$ mol L^{-1} x $100x10^{-3}$ L $= 0.0500 \text{ mol}$ **O** *n*(HCl) required for 9.67×10^{-3} mol Mg = $2 \times 9.67 \times 10^{-3}$ $= 0.0193$ mol. Hence HCl is in excess and all the Mg reacts. \bullet Energy released = 475 J K⁻¹ x 8.35 K ………. NB For ΔT , $^{\circ}C = K$ $= 3.97 \times 10^3$ J Energy released per mol Mg = $3.97x10^3 / 9.67x10^3$ $= 4.01x10⁵$ J $= 401$ kJ \odot Thermochemical equation is $Mg(s) + 2HCl(aq) \rightarrow MgCl₂(aq) + H₂(g); \Delta H = -401 \text{ kJ mol}^{-1}$ **O ii.** 1. The reaction between Mg(s) and HCl(aq) proceeds to completion. \bullet 2. The calorimeter constant for 100 mL of water is valid for 100 ml of HCl(aq). \bullet **c.** (-) electrode: $CH_3OH(g) + H_2O(l) \rightarrow CO_2(g) + 6H^+(aq) + 6e^- \bullet$ $(+)$ electrode: $O_2(1) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(1)$ **O** Equation for the combustion of methanol is $2CH_3OH(g) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(1)$. CH₃OH is oxidised to CO₂ at the anode (-), O₂ is reduced to H₂O at the cathode (+) **d.** Reductants present are Q ^(aq), $X(s)$, $Y(s)$ and $Z(s)$. In an electrochemical cell, electrons move from the anode (where the strongest reductant is oxidised) to the cathode (where the strongest oxidant is reduced). \bullet In a galvanic cell this is from the $(-)$ electrode to the $(+)$ electrode. So the stronger reductant will be reacting at the $(-)$ electrode. \bullet According to the information given Cell 1. $- X(s)$ is a stronger reductant than Q (aq) Cell 2. – $Y(s)$ is a stronger reductant than $Z(s)$ Cell 3. – $Z(s)$ is a stronger reductant than $X(s)$ Cell 4. – $Y(s)$ is a stronger reductant than $X(s)$ **O** The order of increasing reductant strength is $Q'(aq) < X(s) < Z(s) < Y(s)$, i.e. the **strongest reductant is Y(s)**

e. According to the electrochemical series, relevant half-equations are

i. Since the electrolyte is $SnCl₂(aq)$, the metal deposited at the cathode must be $Sn(s)$. The gas will be from the oxidation of the strongest reductant, H2O(l). The half-equations for the initial reaction are

(+) 2H2O(l) O2(g) + 4H+(aq) + 4e-

$$
(\text{-}) \text{ Sn}^{2+}(aq) + 2e^{\text{-}} \rightarrow \text{Sn}(s) \quad \bullet
$$

ii. In order for the electrolyte concentration of $\text{Sn}^{2+}(\text{aq})$ to remain constant with one of the electrodes being consumed, **Sn(s)** must be **oxidised at the anode** and **Sn²⁺(aq) reduced at the cathode**.

$$
(+) \text{ Sn}(s) \rightarrow \text{Sn}^{2+}(aq) + 2e^{-}
$$

 $(-)$ Sn²⁺(aq) + 2e⁻ \rightarrow Sn(s) \bullet

 Initially the **(+) electrode was inert** – C(graphite) or Pt, and the **(-) electrode was Sn(s).**

 Oxidation occurs at the (+) electrode and since this was not Sn, it was not oxidised.

 When **connections** were **swapped**, **(+) electrode was Sn(s)**, **(-) electrode was inert.** Since **Sn(s)** is now the **positive electrode** and it is the **strongest reductant**, it is now **oxidised**.

 In electrochemical cells the strongest reductant is oxidised at the anode and the strongest oxidant is reduced at the cathode.

Question 3 (11 marks)

- **a.** $C_6H_{12}O_6(aq)$ $\xrightarrow{\text{Enzymes}}$ **2CH₃CH₂OH(aq) + 2CO₂(g) 0**
- **b.** 20C the **rate of reaction is increasing** as the **molecules have more energy at higher temperatures** and the **speed of interaction with the active site on the enzyme increases**.
	- 40C the **rate of reaction is maximised** since **enzymes are most effective around 38C** (body temperature).
	- 50C the **rate of reaction has decreased** because the **tertiary structure of the enzyme, critical to the shape and function of the active side, has been** disrupted as the enzyme denatures at temperatures above 38°C. \bullet
- **c.** $CH_2=CH_2(g) + H_2O(g)$ $\xrightarrow{H_3PO_4} CH_3CH_2OH(g)$; Addition reaction \bullet
- **d. i.** Absorption band at 1670-1750 cm⁻¹ suggests presence of C=O.

 No broad peak at absorption band 2500-3300 suggests no OH(acid), i.e. **no –COOH** group.

Ester – CH3COOCH2CH3 – **ethyl ethanoate**

ii. Oxidise some ethanol to ethanoic acid with acidified dichromate, $Cr_2O_7^2$ (aq)/H⁺(aq). \bullet

 Separate the ethanoic acid from the other reaction products. React ethanol with ethanoic acid in the presence of **concentrated H2SO4** to **produce ethyl ethanoate**.

e. *V*(ethanol) in 750 mL wine $= (14.5/100) \times 750$ $= 109$ mL *V*(ethanol) in one standard drink $= 109 / 8.5$ $= 12.8$ mL \bullet m (CH₃CH₂OH) in one standard drink = *d* x *V* = 0.785 g mL⁻¹ x 12.8 mL $= 10.0 \text{ g}$ n (CH₃CH₂OH) in one standard drink = 10.0 g / 46.0 g mol⁻¹ $= 0.22$ mol \bullet

Question 4 (15 marks)

a.

First mark for correct representation and attachment of HOOC and OCOCH3 Second mark if the structure is fully correct with benzene ring expanded.

b. Ethanoic anhydride.

 $(Salicylic acid + ethanoic (acetic) anhydride \rightarrow acetylsalicylic acid (aspirin) + ethanoic acid).$

$$
\begin{array}{ccc}\n & O & O & O \\
 & || & || & \n\end{array}
$$
 \n COCC₆H₄OH + CH₃C.O.CCH₃ → HOOCC₆H₄.O.CCH₃ + CH₃COOH

- **c. i.** Since aspirin is a monoprotic acid, it reacts with KOH(aq) in a 1:1 mole ratio. n (aspirin) reacting $= n(KOH)$ used in titre $= 0.0235$ mol L⁻¹ x 28.71x10⁻³ L $= 6.75 \times 10^{-4}$ mol \bullet *m*(aspirin) reacting = $6.75x10^{-4}$ mol x 180.0 g mol⁻¹ $= 0.121$ g \bullet % aspirin in pain killer = $(0.121 / 0.225)$ x 100 $= 54.0 \%$ **O**
- ii. Since the aspirin solution is initially acidic, the **pH will rise** as OH (aq) is added **during the titration**. Using **phenolphthalein** as indicator, the **colour change will start once the pH reaches 8.3** *(8.3–10 Data Book Table 11)*. If **methyl red** is used, the **colour change will start once the pH reaches 6.8** (6.8–8.4). \bullet The endpoint will be reached for a smaller titre, i.e. **less titre (KOH(aq)), with methyl red** and so the calculated **percentage of aspirin** will be calculated to be **lower**.
- **d.** In **alkaline** solution, the **carboxyl group on the aspirin molecules becomes** deprotonated (gives up H⁺) and assumes a **negative charge**. Acetylsalicylic acid molecules are converted to **acetylsalicylate ions, OOCC₆H₄OCOCH₃.** These ions are more soluble in water because the **ion-dipole bonds between the deprotonated carboxyl groups and water molecules are stronger than the hydrogen bonds between by carboxyl groups and water molecules.**

e. i. When the solution is boiled, the **ester group** in aspirin molecules is **hydrolysed into -OH and –COOH groups**.

ii. *n*(NaOH) available for reaction with aspirin = 0.500 mol L⁻¹ x 50.0x10⁻³ $= 0.0250$ mol \bullet Excess NaOH reacts with HCl

 $NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$ $n(NaOH)$ in excess = $n(HCl)$ reacting = 0.275 mol L⁻¹ x 27.35x10⁻³ L $= 0.00752$ mol $n(NaOH)$ **reacting** with aspirin = $0.0250 - 0.00752$ $= 0.0175$ mol \bullet $n(\text{aspirin}) = \frac{1}{2} \times n(\text{NaOH}) = \frac{1}{2} \times 0.0175$ $= 0.00874$ mol $m(C9H8O4) = 0.00874$ mol x 180.0 g mol-1 $= 1.57$ g \bullet % purity = $[m(C9H8O4) / m(extracted)] \times 100$ $= 98.5 \%$ O

Question 5 (8 marks)

- **a.** Because all the acids have the same initial concentration, the initial pH values reflect the extent of their reaction with water, so they have **different degrees of ionisation in aqueous solution** \bullet *or* different K_a values *or* are of different strengths.
- **b.** According to the titration curves, **50 mL aliquots of the acids require 50 mL of 0.10 M NaOH(aq)** \bullet to reach the endpoint. Since the acids are **monoprotic** they react in a 1:1 **ratio with NaOH** $[n(\text{acid}) = n(\text{NaOH})]$, and must be **0.10 M solutions** \bullet
- **c. Acid 'a',** which shows a pH of 1.0 on the titration graph. **HCl(aq) is a strong acid** and ionises completely in aqueous solution. In 0.10 M HCl(aq), $[H_3O^+] = 0.10$ M and so $pH = 1.0$ **O**
- **d.** Weak acids can be identified using *K*a values using *Table 12 in the Data Book*. $K_a(HOBr) = 2.4 \times 10^{-9}$, this allows us to determine the pH of 0.10 M HOBr. $HOBr(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + BrO^-(aq)$ $K_a = [H_3O^+][BrO^-] / [HOBr]$ *Using standard weak acid assumptions – limited ionisation of the acid, and negligible contribution to H3O+ from self-ionisation of H2O.* $2.4 \times 10^{-9} = [H_3O^+]^2 / 0.10$ O $[H₃O⁺]$ ² = 0.10 x 2.4x10⁻⁹ $[H₃O⁺] = \sqrt{(2.4 \times 10^{-10})}$ $= 1.5x10^{-6}$ M $pH = -log_{10}(1.5x10^{-6})$ $= 4.8$ **O Acid 'e'** is hypobromous acid.

Question 6 (9 marks)

a. $K_c = [H I]^2 / ([H_2][I_2])$

Since equal mole amounts of H_2 and I_2 react as the system moves to equilibrium and equal mole amounts of both were added to the reaction vessel, then at equilibrium $[H_2] = [I_2] = 'x', so$

 $45.2 = 1.05^2 /$ 'x² \bullet 45.2 'x² = $1.05^2 \rightarrow$ 'x² = 1.05^2 / 45.2 $x' = \sqrt{(1.05^2 / 45.2)}$ $= 0.156 M$ [H₂] at equilibrium = 0.156 M [I₂] at equilibrium = 0.156 M \bullet As the system moves to equilibrium 1 mol H_2 reacts with 1 mol I_2 to give 2 mol HI The change in [I₂] as the system moves to equilibrium = $\frac{1}{2}$ x [HI] at equilibrium. $= \frac{1}{2} \times 1.05$ $= 0.525 M$

Initial $[I_2] = 0.156 M + 0.525 M$ $= 0.681 M$ **O**

b. If $K_c = 0.0174$, at 800°C for 2HI(g) $\implies H_2(g) + I_2(g)$, then for $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, at $800^{\circ}C$, $K_c = 1/0.0174$ $= 57.5$ 0

Since the equilibrium constant is higher at 800° C (57.5) than at 400° C (45.2), the **forward reaction** is favoured by higher temperatures, i.e. is **endothermic**.

ii. When the **volume is increased, say doubled**, all the **concentrations halve**, as does the pressure, and remain at the lower values. However as there are **equal number of moles on both sides of the equilibrium**, the system cannot adjust to increase the pressure. The system **remains at equilibrium** because, in this situation, the concentration fraction remains equal to the equilibrium constant. Similarly, **the rates of the forward and reverse reactions decrease due to the concentration decreases** but, in this situation**, remain equal**, although lower than prior to the change. \bullet

Question 7 (13 marks)

a. Negative charges on amino acids result from deprotonation of carboxyl, -COOH, groups on the amino acid. A charge of -2 suggests the amino acid must contain two –COOH groups, as in aspartic acid and glutamic acid *(Data Book Table 8)*. Aspartic acid has four different carbon environments.

Glutamic acid \bullet has five different carbon environments.

In the zwitterion the –NH₂ and –COOH groups bonded to the 2-carbon (α -carbon) are respectively protonated to -*NH₃ and deprotonated to COO⁻.

b. i. The molecular from of glutamic acid *(Data Book Table 8)* is

There are **six (6) O** different hydrogen environments.

 ii. In alkaline solution **both –COOH groups are deprotonated** so there will **be two fewer signals, i.e. four (4) signals**.

$$
\begin{array}{c}\n\begin{array}{c}\n\stackrel{\#}{\leftarrow} & \stackrel{\#}{\leftarrow} & \stackrel{\#}{\leftarrow} & \stackrel{\#}{\leftarrow} \\
\downarrow & \downarrow & \downarrow \\
\stackrel{\#}{\leftarrow} & \stackrel{\#}{\leftarrow} & \stackrel{\#}{\leftarrow} & \stackrel{\#}{\leftarrow} \\
\downarrow & \downarrow & \downarrow & \downarrow \\
\end{array}\end{array}
$$

- **iii.** Only **H atoms on adjacent carbon atoms have their signals split** so there will be **three (3) split signals.** \bullet - the hydrogens on CH and on both CH₂ groups.
- **iv**. The relative molecular mass of glutamic acid, $C_5H_9NO_4 = 5x12.0 + 9x1.0 + 14.0 + 4x16.0$ $= 147.0$

Parent molecular ion peak would be expected to appear at a **mass/charge ratio of 147**.

Non-appearance of this peak would be due to **fragmentation of all glutamic acid molecules** in the mass spectrometer.

- **c. i.** The biomolecule is **DNA** (deoxyribonucleic acid).
	- The asterisked **N atoms are covalently bonded to C atoms** on deoxyribose.
	- **ii. Hydrogen bonds between nucleic acids in base pairs** two hydrogen bonds between Thymine and Adenine, three hydrogen bonds between Cytosine and Guanine – **maintain the secondary structure of DNA** molecules.

iii. Hydrogen bonding is associated with the secondary and tertiary structure of proteins.

 Secondary structure – **hydrogen bonding between H atoms on one peptide (CONH) group and the O atom on a different peptide group** in a protein chain. \bullet

 Tertiary structure – **hydrogen bonding between different side (Z-) groups**, e.g. between **–OH group** on serine (-CH2OH side group) and **–OH group** on **threonine** $(CH_3CHOH$ side group). \bullet

End of Suggested Answers