**Q15.**

Ethanol is an important fuel.

(a) A dilute aqueous solution of ethanol can be produced by the fermentation of an aqueous solution of glucose.
It is claimed that the ethanol obtained from this solution is a carbon-neutral biofuel.

Write an equation for this fermentation reaction.

Give **two** other essential conditions for this reaction to produce a good yield of ethanol.

Name a process used to produce a much more concentrated solution of ethanol from a dilute aqueous solution.

State the meaning of the term **carbon-neutral** in the context of this biofuel.

_____

_____

_____

_____

_____

_____

_____

_____

_____

**(5)**

(b) A student carried out a laboratory experiment to determine the enthalpy change when a sample of ethanol was burned. The heat produced was used to warm some water in a copper calorimeter. The student found that the temperature of 75.0 g of water increased by 5.50 °C when $2.40 \times 10^{-3}$ mol of pure ethanol was burned in air.

Use the student's results to calculate a value, in kJ $mol^{-1}$, for the enthalpy change when one mole of ethanol is burned.
(The specific heat capacity of water is 4.18 J $K^{-1}$ $g^{-1}$)

Deduce **two** reasons why the student's value for the standard enthalpy of combustion of ethanol is different from a Data Book value of –1279 kJ $mol^{-1}$.

**(5)**

(c) Mean bond enthalpies can be used to calculate enthalpies of reaction.

(i) Give the meaning of the term **mean bond enthalpy**.

**(2)**

(ii) Consider the mean bond enthalpy data in the following table.

| | C—H | C—C | C—O | O=O | C=O | O—H |
|---|---|---|---|---|---|---|
| **Mean bond enthalpy / kJ mol$^{-1}$** | 412 | 348 | 360 | to be calculated | 805 | 463 |

Use the data in the table above and the equation shown to calculate a value for the bond enthalpy for the O=O double bond in an oxygen molecule.

$CH_3CH_2OH(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(g)$ $\Delta H = -1279$ kJ mol$^{-1}$

**(3)**

**(Total 15 marks)**

## Q16.

Ethanol is an important industrial compound.

(a) Ethanol can be produced by the hydration of ethene.
The equation for the equilibrium that is established is

$$H_2C{=}CH_2(g) + H_2O(g) \rightleftharpoons CH_3CH_2OH(g) \quad \Delta H = -42 \text{ kJ mol}^{-1}$$

The operating conditions for the process are a temperature of 300 $^{o}$C and a pressure of 7 MPa.
Under these conditions, the conversion of ethene into ethanol is 5%.

(i) Identify the catalyst used in this process.
Deduce how an overall yield of 95% is achieved in this process without changing the operating conditions.

**(2)**

(ii) Use your knowledge of equilibrium reactions to explain why a manufacturer might consider using an excess of steam in this process, under the same operating conditions.

**(3)**

(iii) At pressures higher than 7 MPa, some of the ethene reacts to form a solid with a relative molecular mass greater than 5000.

Deduce the identity of this solid.

Give **one** other reason for **not** operating this process at pressures higher than 7 MPa.
Do **not** include safety reasons.

**(2)**

(b) Write an equation for the reaction that has an enthalpy change that is the standard enthalpy of formation of ethanol.

**(2)**

(c) When ethanol is used as a fuel, it undergoes combustion.

(i) Define the term *standard enthalpy of combustion*.

**(3)**

(ii) Consider these bond enthalpy data.

| | C–H | C–C | C–O | O=O | C=O | O–H |
|---|---|---|---|---|---|---|
| **Bond enthalpy / kJ mol$^{-1}$** | 412 | 348 | 360 | 496 | 805 | 463 |

Use these data and the equation to calculate a value for the enthalpy of combustion of gaseous ethanol.

$$CH_3CH_2OH(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(g)$$

**(3)**

(d) Gaseous ethanol can be used to convert hot copper(II) oxide into copper.

(i) Deduce the role of ethanol in this reaction.

**(1)**

(ii) Draw the structure of the organic compound with $M_r$ = 60 that is produced in this reaction.

**(1)**

**(Total 17 marks)**

## Q17.

Hydrazine ($N_2H_4$) decomposes in an exothermic reaction. Hydrazine also reacts exothermically with hydrogen peroxide when used as a rocket fuel.

(a) Write an equation for the decomposition of hydrazine into ammonia and nitrogen only.

**(1)**

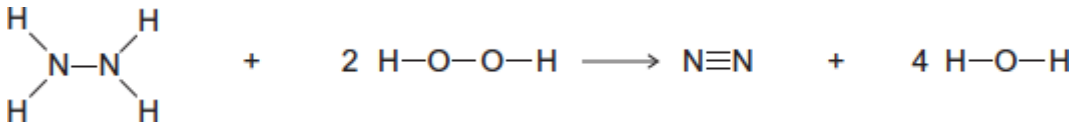
(b) State the meaning of the term *mean bond enthalpy*.

**(2)**

(c) Some mean bond enthalpies are given in the table.

| | N–H | N–N | N≡N | O–H | O–O |
|---|---|---|---|---|---|
| Mean bond enthalpy / kJ $mol^{-1}$ | 388 | 163 | 944 | 463 | 146 |

Use these data to calculate the enthalpy change for the gas-phase reaction between hydrazine and hydrogen peroxide.




**(3)**

**(Total 6 marks)**

## Q18.

This question is about bond dissociation enthalpies and their use in the calculation of enthalpy changes.

(a) Define *bond dissociation enthalpy* as applied to chlorine.

**(2)**

(b) Explain why the enthalpy of atomisation of chlorine is exactly half the bond dissociation enthalpy of chlorine.

**(1)**

(c) The bond dissociation enthalpy for chlorine is +242 kJ $mol^{-1}$ and that for fluorine is +158 kJ $mol^{-1}$. The standard enthalpy of formation of ClF(g) is −56 kJ $mol^{-1}$.

(i) Write an equation, including state symbols, for the reaction that has an enthalpy change equal to the standard enthalpy of formation of gaseous ClF

**(1)**

(ii) Calculate a value for the bond enthalpy of the Cl – F bond.

**(2)**

(iii) Calculate the enthalpy of formation of gaseous chlorine trifluoride, $ClF_3(g)$. Use the bond enthalpy value that you obtained in part (c)(ii).

(If you have been unable to obtain an answer to part (c)(ii), you may assume that the Cl – F bond enthalpy is +223 kJ $mol^{-1}$. This is **not** the correct value.)

**(3)**

(iv) Explain why the enthalpy of formation of $ClF_3(g)$ that you calculated in part (c)(iii) is likely to be different from a data book value.

_____

_____

**(1)**

(d) Suggest why a value for the Na – Cl bond enthalpy is **not** found in any data book.

_____

_____

**(1)**

**(Total 11 marks)**

## Q19.

Ammonia can be manufactured by the Haber Process.

The equation for the reaction that occurs is shown below.

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

(a) The table below contains some bond enthalpy data.

| | N ≡ N | H–H | N–H |
|---|---|---|---|
| Mean bond enthalpy / kJ $mol^{-1}$ | 944 | 436 | 388 |

(i) Use data from the table to calculate a value for the enthalpy of formation for one mole of ammonia.

_____

_____

_____

_____

_____

**(3)**

(ii) A more accurate value for the enthalpy of formation of ammonia is –46 kJ $mol^{-1}$.
Suggest why your answer to part (a) (i) is different from this value.

_____

_____

**(1)**

(b) The table below contains some entropy data.

| | $H_2(g)$ | $N_2(g)$ | $NH_3(g)$ |
|---|---|---|---|
| $S\ominus$ / J $K^{-1}$ $mol^{-1}$ | 131 | 192 | 193 |

Use these data to calculate a value for the entropy change, with units, for the formation of one mole of ammonia from its elements.

**(3)**

(c) The synthesis of ammonia is usually carried out at about 800 K.

(i) Use the $\Delta H$ value of –46 kJ $mol^{-1}$ and your answer from part (b) to calculate a value for $\Delta G$, with units, for the synthesis at this temperature.
(If you have been unable to obtain an answer to part (b), you may assume that the entropy change is –112 J $K^{-1}$ $mol^{-1}$. This is not the correct answer.)

**(3)**

(ii) Use the value of $\Delta G$ that you have obtained to comment on the feasibility of the reaction at 800 K.

**(1)**

**(Total 11 marks)**

## Mark Scheme

## Q15.

(a)

**M1** $C_6H_{12}O_6 \longrightarrow$ **2**$CH_3CH_2OH$ (**2**$C_2H_5OH$) + **2**$CO_2$

*Penalise $C_2H_6O$ for ethanol in **M1**.*

**M2** and **M3**

*Mark **M2** and **M3** independently.*

Any **two** conditions **in any order** for **M2** and **M3** from

- (enzymes from) yeast or zymase
- 25 °C ≤ T ≤ 42 °C OR 298 K ≤ T ≤ 315 K
- anaerobic / no oxygen / no air OR neutral pH

  *A lack of oxygen can mean either without oxygen or not having enough oxygen and does not ensure no oxygen, therefore only credit "lack of oxygen" if it is qualified.*

  *Penalise 'bacteria', 'phosphoric acid', 'high pressure' using the list principle.*

**M4** (fractional) distillation or GLC

*Ignore reference to 'aqueous' or 'water' (ie not part of the list principle).*

**M5** Carbon-neutral **in this context** means

There is no net / overall (annual) carbon dioxide / $CO_2$ emission to the atmosphere

**OR**

There is no change in the total amount / level of carbon dioxide / $CO_2$ present in the atmosphere

*For **M5** – must be about $CO_2$ and the atmosphere.*

*The idea that the carbon dioxide / $CO_2$ given out equals the carbon dioxide / $CO_2$ that was taken in from the atmosphere.*

5

(b) **M1** q = m c ΔT (this mark for correct mathematical formula)

*Full marks for **M1**, **M2** and **M3** for the correct answer.*

*In **M1**, do not penalise incorrect cases in the formula.*

**M2** = (75 × 4.18 × 5.5)

1724 (J) **OR** 1.724 (kJ) **OR** 1.72 (kJ) **OR** 1.7 (kJ)

(also scores **M1**)

*Ignore incorrect units in **M2**.*

**M3** Using 0.0024 mol

therefore $\Delta H$ = **− 718** (kJ $mol^{-1}$)

(Accept a range from −708 to −719 but do not penalise more than 3 significant figures)

*Penalise **M3** ONLY if correct numerical answer but sign is incorrect. Therefore **+718 gains two marks**.*

*If units are quoted in **M3** they must be correct.*

*If $\Delta T$ = 278.5, CE for the calculation and penalise **M2** and **M3**.*

**M4** and **M5** in any order

Any **two** from

- incomplete combustion
- heat loss
- heat capacity of Cu not included
- some ethanol lost by evaporation
- not all of the ($2.40 \times 10^{-3}$ mol) ethanol is burned / reaction is incomplete

*If c = 4.81 (leads to 1984) penalise **M2** ONLY and mark on for **M3** = − 827*

**5**

(c) (i) **M1** enthalpy / heat / energy change (at constant pressure) or enthalpy / heat / energy needed in breaking / dissociating (a) covalent bond(s)

*Ignore bond making.*

**M2** averaged for that type of bond over different / a range of molecules / compounds

*Ignore reference to moles.*

**2**

(ii) **M1**

$\sum$ B(**reactants**) − $\sum$ B(**products**) = $\Delta H$

**OR**

Sum of bonds broken − Sum of bonds formed = $\Delta H$

**OR**

B(C-C) + B(C-O) + B(O-H) + 5B(C-H) + 3B(O=O) – 4B(C=O) – 6B(O–H) = $\Delta H$ = −1279

*Correct answer gains full marks.*

*Credit **1 mark for − 496** (kJ $mol^{-1}$)*

*For other incorrect or incomplete answers, proceed as follows*

- *check for an arithmetic error (AE), which is either*

*a transposition error or an incorrect multiplication;*

*this would score 2 marks (**M1** and **M2**).*

*If no AE, check for a correct method; this requires either a correct cycle with $2CO_2$ and $3H_2O$ OR a clear statement of **M1** which could be in words and scores **only M1**.*

**M2** (also scores **M1**)
348+360+463+5(412)+ 3B(O=O)

(**3231**) (or **2768** if O–H cancelled)
− 4(805) − 6(463) = $\Delta H$ = − 1279

(**5998**) (or **5535** if O–H cancelled)

3B(O=O) = **1488** (kJ $mol^{-1}$)

*Credit a maximum of one mark if the only scoring point is bonds formed adds up to **5998 (or 5535) OR** bonds broken includes the calculated value of **3231 (or 2768)**.*

**M3**

B(O=O) = **496** (kJ $mol^{-1}$)

Award 1 mark for −496

**Students may use a cycle and gain full marks**

**3**

**[15]**

## Q16.

(a) (i) M1 c(oncentrated) phosphoric acid / c(onc.) $H_3PO_4$
***OR*** c(oncentrated) sulfuric acid / c(onc.) $H_2SO_4$

*In **M1**, the acid must be concentrated.*
*Ignore an incorrect attempt at the correct formula that is written in addition to the correct name.*

M2 Re-circulate / re-cycle the (unreacted) ethene (and steam) / the reactants
***OR*** pass the gases over the catalyst several / many times

*In **M2**, ignore "remove the ethanol".*
*Credit "re-use".*

**2**

(ii) M1
(By Le Chatelier's principle) the equilibrium is driven / shifts / moves to the right / L to R / forwards / in the forward direction

**M2 depends on a correct statement of M1**
The equilibrium moves / shifts to

- oppose the addition of / increased concentration of / increased moles / increased amount of water / steam
- to decrease the amount of steam / water

**Mark M3 independently**

M3 Yield of product / conversion increase ***OR*** ethanol increases / goes up / gets more

**3**

(iii) M1 Poly(ethene) / polyethene / polythene / HDPE / LDPE

**M2 At higher pressures**
More / higher <u>cost</u> of electrical <u>energy to pump</u> / <u>pumping cost</u>
***OR***
<u>Cost</u> of higher pressure <u>equipment / valves / gaskets / piping etc</u>.
***OR*** <u>expensive equipment</u>

*Credit all converse arguments for **M2***

**2**

(b) M1 for balanced equation

M2 for state symbols in a <u>correctly balanced equation</u>

$$2C(s \text{ / graphite}) + 3H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow CH_3CH_2OH(l) \ (C_2H_5OH)$$

*Not multiples but credit correct state symbols in a correctly balanced equation.*

*Penalise $C_2H_6O$ but credit correct state symbols in a correctly balanced equation.*

**2**

(c) (i) M1 The <u>enthalpy change</u> / <u>heat change at constant pressure</u> when <u>1 mol</u> of a compound / substance / element

*If standard enthalpy of formation **CE=0***

M2 is <u>burned / combusts / reacts completely</u> in <u>oxygen</u>
***OR*** <u>burned / combusted / reacted in excess oxygen</u>

M3 with (all) <u>reactants and products /</u> (all) <u>substances in standard / specified states</u>
***OR*** (all) <u>reactants and products /</u> (all) <u>substances in normal states under standard conditions</u> / 100 kPa / 1 bar <u>and</u> specified T / 298 K

*For **M3***
*Ignore reference to 1 atmosphere*

**3**

(ii) M1

*Correct answer gains full marks*

<u>ΣB(**reactants**) − ΣB(**products**) = *ΔH*</u>

*Credit 1 mark for (+) 1279 (kJ mol$^{-1}$)*

OR
<u>Sum of bonds broken − Sum of bonds formed = ΔH</u>
OR
B(C-C) + B(C-O) + B(O-H) + 5B(C-H) + 3B(O=O) (LHS)
− 4B(C=O) − 6B(O−H) (RHS) = <u>*ΔH*</u>

M2 (also scores **M1**)
348+360+463+5(412)+3(496) [LHS = **4719**]
(2060) (1488)
− 4(805) − 6(463) [RHS = − **5998**] = *ΔH*
(3220) (2778)
OR using only bonds broken and formed (**4256 − 5535**)

*For other incorrect or incomplete answers, proceed as follows*

- *check for an arithmetic error (AE), which is either a transposition error or an incorrect multiplication; this would score 2 marks (**M1** and **M2**)*
- *If no AE, check for a correct method; this requires either a correct cycle with 2C and 6H and 7O OR a clear statement of **M1** which could be in words and scores **only M1***

M3
ΔH= **− 1279** (kJ $mol^{-1}$)

*Allow a maximum of one mark if the only scoring point is LHS = 4719 **OR** RHS = 5998*

Award 1 mark for +1279

**Candidates may use a cycle and gain full marks**

**3**

(d) (i) Reducing agent ***OR*** reductant ***OR*** electron donor ***OR*** to reduce the copper oxide

*Not "reduction".*
*Not "oxidation".*
*Not "electron pair donor".*

**1**

(ii) $CH_3COOH$

**1**

**[17]**

## Q17.

(a) $3N_2H_4 \longrightarrow 4NH_3 + N_2$

*Or multiples*
*Ignore state symbols*

**1**

(b) M1 enthalpy / heat (energy) change / required / needed to break / dissociate a covalent bond (or a specified covalent bond)

*Ignore bond making*
*Ignore standard conditions*
***M2** requires an attempt at **M1***

M2 average / mean over different molecules / compounds / substances

**2**

(c) M1
∑ (bonds broken) − ∑ (bonds formed) = *ΔH*

***M1** could stand alone*

***OR***

Sum of bonds broken − Sum of bonds formed = *ΔH*

*Award full marks for correct answer*

M2 (also scores **M1**)

*Ignore units*

4(+388) + 163 + 2(146) + 4(463) − 944 − 8(463) = *Δ*H
OR broken +3859 (2007) formed − 4648 (2796)

M3

*Δ*H = **− 789** (kJ mol$^{-1}$)

*Two marks can score with an arithmetic error in the working*

Award 1 mark for + 789

*Credit **one mark only** for calculating either the sum of the bonds broken or the sum of the bonds formed provided this is the only mark that is to be awarded*

Students may use a cycle and gain full marks

**3**

**[6]**

## Q18.

(a) (Enthalpy change to) break the bond in 1 mol of chlorine (molecules)

*Allow (enthalpy change to) convert 1 mol of chlorine molecules into atoms*
*Do not allow energy or heat instead of enthalpy, allow heat energy*

**1**

To form (2 mol of) gaseous chlorine atoms / free radicals

*Can score 2 marks for 'Enthalpy change for the reaction':*
*$Cl_2(g) \rightarrow 2Cl(g)$*
*Equation alone gains M2 only*
*Can only score M2 if 1 mol of chorine molecules used in M1 (otherwise it would be confused with atomisation enthalpy)*
*Any mention of ions, CE = 0*

**1**

(b) (For atomisation) only 1 mol of chlorine atoms, not 2 mol (as in bond enthalpy) is formed / equation showing ½ mol chlorine giving 1 mol of atoms

*Allow breaking of one bond gives two atoms*
*Allow the idea that atomisation involves formation of 1 mol of atoms not 2 mol*
*Allow the idea that atomisation of chlorine involves half the amount of molecules of chlorine as does dissociation*
*Any mention of ions, CE = 0*

**1**

(c) (i) $\frac{1}{2}F_2(g) + \frac{1}{2}Cl_2(g) \rightarrow ClF(g)$

1

(ii) $\Delta H = \frac{1}{2}E(F–F) + \frac{1}{2} E(Cl–Cl) – E(Cl–F)$

*Allow correct cycle*

1

$E(Cl–F) = \frac{1}{2}E(F–F) + \frac{1}{2}E(Cl–Cl) – \Delta H$

$= 79 + 121 – (–56)$

$= 256$ (kJ mol$^{-1}$)

*–256 scores zero*

*Ignore units even if wrong*

1

(iii) $\frac{1}{2}Cl_2 + 3/2\ F_2 \rightarrow ClF_3$

*If equation is doubled CE=0 unless correcr answer gained by / 2 at end*

*This would score M1*

1

$\Delta H = \frac{1}{2} E(Cl–Cl) + 3/2\ E(F–F) – 3E(Cl–F)$

$= 121 + 237 – 768$ / (or 3 × value from (c)(ii))

*This also scores M1 (note = 358 – 768)*

1

$= –410$ (kJ mol$^{-1}$)

*If given value of 223 used ans = –311*

*Allow 1 / 3 for +410 and +311*

1

(iv) (Bond enthalpy of) Cl–F bond in ClF is different from that in $ClF_3$

*Allow Cl-F bond (enthalpy) is different in different compounds (QoL)*

1

(d) NaCl is ionic / not covalent

1

**[11]**

## Q19.

(a) (i) $\Delta H = \Sigma$ bonds broken $–\Sigma$ bonds formed

1

$= 944/2 + 3/2 \times 436 – 3 \times 388$

1

$= –38$ (kJ mol$^{–1}$)

*ignore units even if incorrect*

*correct answer scores 3*

*–76 scores 2/3*

*+38 scores 1/3*

1

(ii) mean / average bond enthalpies are from a range of compounds
or
mean / average bond enthalpies differ from those in a single compound / ammonia

1

(b) $\Delta S = \Sigma S$ products $- \Sigma S$ reactants

1

$= 193 - (192/2 + 131 \times 3/2)$

1

$= -99.5$ J $K^{-1}$ $mol^{-1}$

*units essential for M3*
*correct answer with units scores 3*
*–199 J $K^{-1}$ $mol^{-1}$ & –99.5 score 2/3*
*–199 and + 99.5 J $K^{-1}$ $mol^{-1}$ score 1/3*

1

(c) (i) $\Delta G = \Delta H - T\Delta S = -46 + 800 \times 99.5/1000$

*mark is for putting in numbers with 1000*
*if factor of 1000 used incorrectly CE = 0*

1

= 33.6 or 33600

*allow 33 to 34 (or 33000 to 34000)*

1

kJ $mol^{-1}$ with J $mol^{-1}$

*correct units for answer essential*
*if answer to part (b) is wrong or if -112 used, mark consequentially e.g.*
- *–199 gives 113 to 114 kJ $mol^{-1}$ (scores 3/3)*
- *–112 gives 43 to 44 kJ $mol^{-1}$ (scores 3/3)*

1

(ii) If answer to (c) (i) is positive: not feasible / not spontaneous

If answer to (c) (i) is negative: feasible / spontaneous

*if no answer to (c) (i) award zero marks*

1

**[11]**