

# THE SCHOOL FOR EXCELLENCE UNIT 4 CHEMISTRY 2010

## **COMPLIMENTARY WRITTEN EXAMINATION 2 - SOLUTIONS**

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## **SECTION A - MULTIPLE CHOICE QUESTIONS**

1	С	5	А	9	С	13	А	17	С
2	D	6	В	10	А	14	С	18	В
3	В	7	В	11	В	15	D	19	С
4	D	8	В	12	С	16	В	20	D

#### QUESTION 1 Answer is C

The size of the beaker will have no bearing on the initial reaction rate since the concentration of the acid at the surface of the aluminium where the reaction takes place does not change (as long as all of the aluminium is fully submerged in both cases).

A larger volume of acid will also have no bearing on the initial reaction rate since the concentration of the acid at the surface of the aluminium where the reaction takes place does not change. The effect of using a larger volume of acid only becomes apparent as the reaction proceeds.

Cleaning the surface of the aluminium removes the oxide layer exposing more aluminium to the acid and therefore increasing the initial reaction rate.

Neither of the reactants are gases so changing the pressure should have no effect on the initial reaction rate.

## QUESTION 2 Answer is D

If molecules have insufficient energy to overcome the activation energy threshold, they will simply bounce off each other and not react. Reactants also have to collide in the correct orientation (e.g. at the site of a double bond) otherwise the reaction will not proceed.

The concentration will affect the rate of reaction but has no impact on the success of the collision.

Equilibrium is a dynamic state where the forwards and backwards reactions are occurring at the same rate. Therefore successful collisions are still occurring.

#### QUESTION 3 Answer is B

The change in enthalpy ( $\Delta H$ ) value of the given equation is negative indicating that the forward reaction is exothermic. Since the products are lower in enthalpy than the reactants, they are more stable than the reactants. This means they are less likely to react than the reactants and are less able to do work.

#### QUESTION 4 Answer is D

As these Energy profile diagrams are drawn to the same scale, visual comparisons can be made. Note, the activation energy for the forward and back reactions must be considered for both energy profiles.



## QUESTION 5 Answer is A

The reduction in activation energy for the forward and backward reaction is reduced by the same AMOUNT (in the example below 10 kJ/mol), not by the same percentage.



### QUESTION 6 Answer is B

Lead reacts with oxygen to form lead oxide according to the following equation

$$2Pb_{(s)} + O_{2(g)} \rightarrow 2PbO_{(s)}$$

To obtain this equation from the reactions given, multiply reaction (1) by two, cancel common reactants and products and then add the equations together.

Reaction (1)  $2Pb_{(s)} + \frac{2CO_{(g)}}{2} \rightarrow 2PbO_{(s)} + \frac{2C_{(s)}}{2C_{(s)}} \Delta H = -106.8 \, kJ/mol$ Reaction (2)  $2C_{(s)} + O_{2(g)} \rightarrow 2CO_{(g)} \Delta H = -221.0 \, kJ/mol$ 

Hence, repeat this same mathematical manipulation for the  $\Delta H$  (e.g. double  $\Delta H_1$ , and then add  $\Delta H_1$  and  $\Delta H_2$ )

 $\Delta H_{\text{total}} = (2 \text{ x} - 106.8) + -221.0 = -434.6 \text{ kJ/mol}$ 

Next determine the heat released when 250 g of lead is reacted:

$$n(Pb) = \frac{m}{M} = \frac{250}{207.2} = 1.207 \ mol$$

Use ratios or cross multiply to determine the heat released for this amount of lead

2 mol Pb releases 434.6 kJ 1.207 mol Pb releases *x* kJ

1.207 x 434.6 = 2x x = 262.2 kJ

The answer will be positive since the question asks for **HEAT RELEASED**, not for the enthalpy value.

#### QUESTION 7 Answer is B

The pressure is increased by decreasing the volume. This results in a net backwards reaction for the reaction, therefore, the amount of  $N_2$  will decrease. However, the reduction in volume means the concentration of  $N_2$  will still be higher than its original value.

#### QUESTION 8 Answer is B

The change occurring at A is due to the addition of  $N_2O_{4(g)}$ . The addition of  $N_2O_{4(g)}$  will cause a net forward reaction. For every mole of  $N_2O_{4(g)}$  consumed, 2 mole of  $NO_{2(g)}$  will be produced. Therefore, the increase in concentration of  $NO_{2(g)}$  (represented by z) will be double the decrease in concentration of  $N_2O_{4(g)}$  (represented by x) as equilibrium is being re-established.

#### QUESTION 9 Answer is C

The change occurring at *time A* is due to the addition of  $N_2O_{4(g)}$ . Initially, the addition of  $N_2O_{4(g)}$  will dramatically increase the rate of the forward reaction but there will be no change in the back reaction rate. The change also causes a net forward reaction to occur as the system tries to partially oppose the addition of  $N_2O_{4(g)}$ . As equilibrium is re-established, the rate of the forward reaction will decrease as reactants are consumed. The rate of the back reaction will increase as products are produced. When equilibrium is re-established, both the forward and back reaction rates will be higher than their previous values.

QUESTION 10 Answer is A

The equilibrium expression for this reaction is  $K_c = \frac{[SO_2]^2[O_2]}{[SO_2]}$ .

Rearrange this expression to make [SO<sub>2</sub>] the subject results in option (A).

#### QUESTION 11 Answer is B

The equilibrium equation for ethanoic acid is:  $CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$ 

Adding a small amount of  $H_2SO_{4(aq)}$  increases the amount of  $H_{(aq)}^+$  in the system. This results in a net back reaction as the system tries to partially oppose the change. Since the change is only partially opposed, the equilibrium  $c(H^+)$  is higher than before and the pH is lower. The net backwards reaction will also cause the amount of  $CH_3COOH_{(aq)}$  to be higher once equilibrium is re-established. The addition of the acid also has **no effect** on K<sub>w</sub> since equilibrium values are only affected by temperature changes.

#### QUESTION 12 Answer is C

E<sub>released in calorimeter</sub> = 9.06 x 2780 = 25187 J = 25.2 kJ

Use the heat of combustion values from the supplied data book for each fuel to determine which one would release this amount of energy upon combustion of 0.5 g.

Methane:

Ethane:

Propane:	Butane:
E <sub>released</sub> = 0.0313 x 889 = 27.8 kJ	E <sub>released</sub> = 0.0167 x 1557 = 26.0 kJ
= 0.0313 mol	= 0.0167 mol
$n(CH_4) = \frac{0.5}{16}$	$n(C_2H_6) = \frac{0.5}{30}$
$n(CH_4) = \frac{0.5}{2}$	$n(C_{2}H_{c}) = \frac{0.5}{2}$

$$n(C_{3}H_{8}) = \frac{0.5}{44} \qquad n(C_{4}H_{10}) = \frac{0.5}{58}$$
  
= 0.0114 mol = 0.00862 mol  
$$E_{released} = 0.0114 \times 2217 \qquad E_{released} = 0.00862 \times 2874$$
  
= 25.2 kJ = 24.8 kJ

#### QUESTION 13 Answer is A

$$Cr_2 O_{7(aq)}^{2-} + 14H_{(aq)}^+ + 6e^- \rightarrow 2Cr_{(aq)}^{3+} + 7H_2 O_{(l)}$$
 1.33 V

$$Cu_{(aq)}^{2+} + 2e^- \to Cu_{(s)}$$
 0.34 V

$$Cr^{3+}_{(aq)} + e^- \to Cr^{2+}_{(aq)}$$
 -0.41 V

$$Fe_{(aq)}^{2+} + 2e^- \to Fe_{(s)}$$
 -0.44 V

$$Cr^{3+}_{(aq)} + 3e^- \to Cr_{(s)}$$
 -0.76 V

$$Cr^{2+}_{(aq)} + 2e^- \rightarrow Cr_{(s)}$$
 -0.91 V

$$Mn_{(aq)}^{2+} + 2e^- \to Mn_{(s)}$$
 -1.03 V

$$Al_{(aq)}^{3+} + 3e^- \rightarrow Al_{(s)}$$
 -1.67 V

 $Cr_2 O_{7(aq)}^{2-}$  will spontaneously reduce to  $Cr_{(aq)}^{3+}$  when it reacts with anything lower than it on the right hand side of the electrochemical series ( $Cu_{(s)}$ ,  $Cr_{(aq)}^{2+}$ ,  $Fe_{(s)}$ ,  $Cr_{(s)}$ ,  $Mn_{(s)}$  and  $Al_{(s)}$ ). However, only  $Cu_{(s)}$  will reduce it to  $2Cr_{(aq)}^{3+}$  without any further reduction. This is because all of the other substances lie below  $Cr_{(aq)}^{3+}$  on the electrochemical series and will therefore cause the further reduction of  $Cr_{(aq)}^{3+}$  to  $Cr_{(aq)}^{2+}$  or even  $Cr_{(s)}$ .

#### QUESTION 14 Answer is C

The equations in the electrochemical series that need to be considered are:

$H_2O_{2(aq)} + 2H^+_{(aq)} + 2e^- \rightarrow 2H_2O_{(l)}$	+ 1.77 V
$Au_{(aq)}^{+} + e^{-} \rightarrow Au_{(s)}$	+ 1.68 V
$O_{2(g)} + 2H_{(aq)}^{+} + 2e^{-} \rightarrow H_2O_{2(aq)}$	+ 0.68 V
$Fe^{3+}_{(aq)} + e^- \rightarrow Fe^{2+}_{(aq)}$	+ 0.77 V

There are two combinations that would result in an overall cell potential of 1.00 V. They are:

$$\begin{array}{ll} H_2 O_{2(aq)} + 2H^+_{(aq)} + 2e^- \to 2H_2 O_{(l)} & Au^+_{(aq)} + e^- \to Au_{(s)} \\ Fe^{2+}_{(aq)} \to Fe^{3+}_{(aq)} + e^- & H_2 O_{2(aq)} \to O_{2(g)} + 2H^+_{(aq)} + 2e^- \\ E^0 = 1.77 - 0.77 = 1.00V & E^0 = 1.68 - 0.68 = 1.00V \end{array}$$

Since inert electrodes are used in the galvanic cell, the half cells must be  $H_2O_{2(aq)}$ ,  $H^{+}_{(aq)}$  and  $Fe^{3+}_{(aq)}$ ,  $Fe^{2+}_{(aq)}$ .

#### **QUESTION 15**

Answer is D



#### **Reactions occurring are:**

Anode:  $Pb_{(s)} \to Pb_{(aq)}^{2+} + 2e^{-}$ Cathode:  $H_2O_{2(aq)} + 2H_{(aq)}^{+} + 2e^{-} \to 2H_2O_{(l)}$ 

#### When the cell is connected:

- Lead will erode away at the ANODE.
- The pH at the +ve electrode (cathode) will INCREASE as H<sup>+</sup> is consumed.
- Electrons will move from ANODE to CATHODE.
- Anions from the salt bridge WILL move towards the  $Pb_{(s)}/Pb^{2+}_{(aq)}$  half cell (anode) to neutralise the increase in charge that occurs due to the production of  $Pb^{2+}_{(aq)}$ .

#### QUESTION 16 Answer is B

The reactions occurring in the cell are:

Anode:  $Zn_{(s)} \to Zn_{(aq)}^{2+} + 2e^{-}$ Cathode:  $H_2O_{(l)} \to O_{2(g)} + 4H_{(aq)}^{+} + 4e^{-}$ 

Water is acting as an oxidant and a solvent.

## QUESTION 17 Answer is C

Relevant equations are:

$Cl_{2(g)} + 2e^{-} \rightarrow 2Cl_{(aq)}$	E <sup>0</sup> = + 1.36 V
$O_{\underline{2(g)}} + 4H^+_{(aq)} + 4e^- \rightarrow 2H_2O_{(g)}$	E <sup>0</sup> = +1.23 V
$\underbrace{2H_2O}_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^{(aq)}$	E <sup>0</sup> = -0.83 V
$(Na^+_{(aq)}) + e^- \rightarrow Na_{(s)}$	E <sup>0</sup> = -2.71 V

The circled species are possible reactants for the aqueous solutions. Products of electrolysis are:

Substance to be Electrolysed	Anode Reaction	Cathode Reaction
NaCl <sub>(I)</sub>	$2Cl_{(aq)}^{-} \rightarrow Cl_{2(g)} + 2e^{-}$ Na <sup>+</sup> <sub>(l)</sub> is the only species that can species able to be oxidised sinc	$Na^+_{(aq)} + e^- \rightarrow Na_{(s)}$ n be reduced and $Cl^{(l)}$ is the only e no water is present.
0.05 M NaCl <sub>(aq)</sub>	$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-$ When low concentrations of Native reaction would occur between we strongest reductant and oxidant	$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH_{(aq)}^-$ Cl are electrolysed, the predominant vater molecules since water is the present.
5.0 M NaCl <sub>(aq)</sub>	$2Cl^{-}_{(aq)} \rightarrow Cl_{2(g)} + 2e^{-}$ At high <i>NaCl</i> concentrations ch	$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH_{(aq)}^-$ Norine is produced at the anode.

Both solutions produce  $OH_{(aq)}^{-}$  at the cathode which increases the pH.

## QUESTION 18 Answer is B

When the battery is supplying energy to the headlights, the equations given in the question are reversed.

Anode (-): 
$$Pb_{(s)} + SO_{4(aq)}^{2-} \rightarrow PbSO_{4(s)} + 2e^{-}$$
  
Cathode (+):  $PbO_{2(s)} + SO_{4(aq)}^{2-} + 4H_{(aq)}^{+} + 2e^{-} \rightarrow PbSO_{4(s)} + 2H_2O_{(l)}$ 

At the negative electrode, the oxidation number of Pb **increases** it is oxidised from 0 to +2.  $H^{+}_{(aq)}$  ions are being consumed at the cathode, therefore the pH is **increasing**. The amount  $PbSO_{4(s)}$  is **increasing** as it is being produced at both electrodes. The alternator is not involved when the battery is acting as a galvanic cell and supplying energy.

QUESTION 19 Answer is C

#### QUESTION 20 Answer is D

The first equation shows  $CIO_2$  acting as an oxidant. It oxidises S (0) to  $H_2SO_{4(aq)}$  (+6). A toxic substance is defined as any substance that can cause acute or chronic injury to the human body, or which is suspected of being able to cause diseases or injury under some conditions. Since  $CIO_2$  causes harm to the nose and throat etc, it is considered a toxic substance.

A corrosive substance is defined as one that will destroy or irreversibly damage another substances with which it comes into contact. The second equation shows  $CIO_2$  eroding Zn into a salt.

Since CIO<sub>2</sub> acts as a pesticide it is dangerous to the environment.



## SHORT ANSWER SECTION

a. (i) Initial reaction rate = Gradient of line A.

Gradient Line A =  $\frac{rise}{run}$  =  $\frac{0.002-0.010}{4.8-0}$  = -1.6 x 10<sup>-3</sup> [NOBr] M.s<sup>-1</sup>

(ii) Average reaction rate = Gradient of line B.

Gradient Line B =  $\frac{rise}{run}$  =  $\frac{0.0039 - 0.010}{8 - 0}$  = -7.6 x 10<sup>-4</sup> [NOBr] M.s<sup>-1</sup>

- The rates are -ve since the concentration of NOBr is decreasing with time.
- **b.** The initial rate is greater than the rate over first 8 seconds since the concentration of the reactants is higher at the start of the reaction. As the reaction proceeds, more reactants get used up, the [reactants] decreases, leading to fewer and fewer successful collisions.

#### **QUESTION 1**



For every 2 mole NOBr that reacts, only 1 mole  $Br_2$  is created. Therefore, [ $Br_2$ ] will increase at half the rate that the [NOBr] decreases.

At t = 8 sec, [NOBr] remains stable indicating that the reaction has reached completion. At this stage the  $[Br_2]$  will also remain constant.

[NOBr]	[Br <sub>2</sub> ]
0.01	0
0.0071	0.00145
0.0055	0.00225
0.0045	0.00275
0.0038	0.0031
0.0038	0.0031
0.0038	0.0031
	[NOBr] 0.01 0.0071 0.0055 0.0045 0.0038 0.0038 0.0038

To determine the [Br<sub>2</sub>] at each time interval, find the change in [NOBr] then divide it by 2.

## Sample calculation:

 $[Br_2] \text{ at } 6 \text{ seconds} = \Delta[NOBr]/2$ = (0.01 - 0.0045)/2= 0.00275 M

c.

**d.** (i) Increasing the pressure by decreasing the volume is equivalent to increasing the concentration of reactants. This leads to more successful collisions between two NOBr particles over a particular period of time and so the reaction rate will increase.



#### Note:

Gradients must be steeper and lines need to level out at the same concentrations as before.

(ii) In this case there is only one reactant that decomposes to form the products. Now the number of collisions is irrelevant. What matters is how many of the particles have enough energy to overcome the activation energy and decompose at any one time. So decreasing the pressure in this case has no effect on the reaction rate. Increasing the temperature would increase the reaction rate by providing a greater proportion of the particles with enough energy to overcome the activation energy. Using a catalyst would increase the reaction rate by providing an alternate reaction pathway with a lower activation energy so that a greater proportion of the particles would have enough energy to react.

#### **QUESTION 2**

**a.** 
$$K_c = \frac{[NH_{3(g)}]^2 [CO_{2(g)}]}{[NH_2 COONH_{4(s)}]} M^3$$

**b.** Equation:  $NH_2COONH_{4(s)} \leftrightarrow 2NH_{3(g)} + CO_{2(g)}$ 

	$NH_2COONH_{4(s)}$	$NH_{3(g)}$	$CO_{2(g)}$
Initial mol	$\frac{30}{78} = 0.385 \ mol$	0	0
Change in mole	$\downarrow x$	<i>↑2x</i>	$\uparrow x$
Equilibrium mole	0.385 - x	2x	x
Equilibrium concentration	_	$\frac{2x}{2} = x$	$\frac{x}{2}$

To find the final pressure, the mole of all the gases present  $(2NH_{3(g)} \text{ and } CO_{2(g)})$  at equilibrium must first be determined. This can be done using the equilibrium constant to solve for *x*.

$$K_{c} = [NH_{3(g)}]^{2}[CO_{2(g)}]$$

(The  $[NH_2COONH_{4(s)}]$  is replaced by the value 1)

1.58 x 10<sup>-8</sup> = x<sup>2</sup> x  $\frac{x}{2} = \frac{x^3}{2}$ 

 $x = \sqrt[3]{1.58 \times 10^{-8} \times 2} = 0.00316 \text{ M}$ 

Therefore at equilibrium:

 $n(NH_3) = 2x$ = 2 x 0.00316 = 0.00632 mol

n(CO<sub>2</sub>) = x = 0.00316 mol

n(gas)<sub>total</sub> = 0.00632 + 0.00316 = 0.00948 mol

$$P = \frac{nRT}{V} = \frac{0.00948 \times 8.32 \times (273+250)}{2.00}$$
$$= 20.6 \text{ kPa}$$

c. % [
$$NH_2COONH_{4(s)}$$
] decomposed =  $\frac{mole \ of \ NH_2COONH_{4(s)} \ reacted}{initial \ mole \ NH_2COONH_{4(s)}} \times 100$   
=  $\frac{0.00316}{0.385} \times 100 = 0.821\%$ 

#### **QUESTION 3**

**a.** 
$$K_c = \frac{[isobutane]}{[butane]}$$

Choose any point on the line and substitute in the concentrations of butane and isobutane.

When [butane] = 1.2 M [isobutane] = 3.0 M

Therefore,  $K_c = \frac{3.0}{1.2} = 2.5$ 

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b. (i) & (ii)
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- (iii) Q would be less than K. This is because more butane has been added to the system making the value of the fraction [isobutane] [butane]↑ smaller. Also, adding a reactant will cause a net forward reaction in order to partially oppose the change. A forward reaction means that the value of [isobutane]↑ [butane]↑ must increase so at the point B, Q<K.</li>
  Note: Q<K at any point below the line on the graph.</li>
- **c.** The line from  $B \rightarrow C$  has a gradient of -1 because, as equilibrium is being re-established, each mole of butane consumed produces one mole of isobutane.



Information from the graph given in the question is:

- When [butane] = 2.4 M, the [isobutane] = 6 M  $\rightarrow$  initial equilibrium amounts.
- When [butane] = 3.2 M, the [isobutane] =  $8 \text{ M} \rightarrow$  final equilibrium amounts.

Since a reactant has been added to the system, a net forward reaction will occur to partially oppose this change. Therefore, while equilibrium is being re-established, the [isobutane] will increase and the [butane] will decrease.

Once equilibrium is re-established, the change in [isobutane] is 2 M. This means that once the butane has been added, its concentration must go down by the same amount. Therefore, the [butane] must increase to 5.2 M when it is initially added to the system.

d.

#### **QUESTION 4**

a. The equation for the dissociation of phenylacetic acid is

 $C_6H_5CH_2COOH_{(aq)} + H_2O_{(l)} \leftrightarrow C_6H_5CH_2COO_{(aq)}^- + H_3O_{(aq)}^+$ 

$$\mathsf{K}_{\mathsf{a}} = \frac{[C_6 H_5 C H_2 C O O^-][H_3 O^+]}{[C_6 H_5 C H_2 C O O H^-]}$$

**b.**  $[H_3O^+] = 10^{-pH} = 10^{-2.6}$ 

At equilibrium,  $[C_6H_5CH_2COO^-] = [H_3O^+] = 10^{-2.6}$  $[C_6H_5CH_2COOH]_{eq} = [C_6H_5CH_2COOH]_{initial}$ 

Therefore,  $K_a = \frac{[C_6H_5CH_2COO^-][H_3O^+]}{[C_6H_5CH_2COOH]} = \frac{[H_3O^+]^2}{[C_6H_5CH_2COOH]} = \frac{(10^{-2.6})^2}{0.12} = 5.23 \times 10^{-5} \text{ M}$ 

- **c.**  $[H_3 O^+]_{\text{total}} = 10^{-2.6}$ 
  - $[H_{3}O^{+}]_{\text{due self ionisation of water}} = 10^{-7} \text{ M}$ %  $[H_{3}O^{+}]_{\text{due self ionisation of water}} = \frac{10^{-7}}{10^{-2.6}} \times 100$  $= 10^{-4.4} \times 100$  $= 3.98 \times 10^{-3} \%$

Therefore the amount of  $[H_30^+]$  due to the self ionisation of water is minimal

**d.** Since phenylacetic acid is a weak acid, the pH will not increase by 1 for every 10 fold dilution as it does for strong acids. Use the K<sub>a</sub> value to determine the new pH.

$$\mathsf{K}_{\mathsf{a}} = \frac{[C_6H_5CH_2COO^-][H_3O^+]}{[C_6H_5CH_2COOH]} = \frac{[H_3O^+]^2}{[C_6H_5CH_2COOH]}$$

$$[H_3O^+] = \sqrt{K_a \times [C_6H_5CH_2COOH]}$$
  
=  $\sqrt{5.23 \times 10^{-5} \times 0.012}$   
= 7.90 x 10<sup>-4</sup> M

 $pH = -log 7.90 \times 10^{-4} = 3.10$ 

- e. (i) As the temperature increases, the value of K<sub>a</sub> decreases. This means that the amount of products is decreasing and the amount of reactants is increasing (<sup>[P]↓</sup><sub>[R]↑</sub>). This indicates that there is a net backward reaction. The back reaction must be endothermic to oppose the temperature increase and therefore the forward reaction is exothermic.
  - Since a net backward reaction occurs as the temperature increases, the [H<sub>3</sub>O<sup>+</sup>] will decrease leading to an increase in pH.

a.



 Possible reactants in Cell 1: Fe<sup>3+</sup>, Cl<sup>-</sup> and water Possible reactants in Cell 2: Zn<sup>2+</sup>, Br<sup>-</sup> and water

### Cell 1:

Electrode A	Anode: $2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-$
Electrode B	Cathode: $Fe^{3+}_{(aq)} + e^- \rightarrow Fe^{2+}_{(aq)}$

## Cell 2:

Electrode C	Anode: $2Br_{(aq)} \rightarrow Br_{2(l)} + 2e^{-1}$
Electrode D	Cathode: $Zn_{(aq)}^{2+} + 2e^- \rightarrow Zn_{(s)}$

- (ii)  $2H_2O_{(l)} + 4Fe_{(aq)}^{3+} \rightarrow O_{2(g)} + 4H_{(aq)}^+ + 4Fe_{(aq)}^{2+}$
- (iii) Voltage for Cell 1 = 0.77 1.23 = -0.46 V

Therefore approx 0.49 V needed

Voltage for Cell 2 = -0.76 - 1.09 = -1.85 V

Therefore approx 1.88 V needed

A greater voltage is needed for Cell 2 than for Cell 1. If 1.88 V is applied to the two cells, there is the potential for other reactions to occur in cell 1 other than those predicted by the electrochemical series.

The relevant equations with the possible reactants highlighted for Cell 1 are:

$H_2O_{2(aq)} + 2H^+_{(aq)} + 2e^- \rightarrow \frac{2H_2O_{(l)}}{2H_2O_{(l)}}$	+ 1.77
$Cl_{2(g)} + 2e^- \rightarrow \frac{2Cl_{(aq)}}{2}$	+ 1.36
$O_{2(g)} + 4H^+_{(aq)} + 4e^- \rightarrow \frac{H_2O_{(l)}}{H_2O_{(l)}}$	+ 1.23
$\frac{Fe^{3+}_{(aq)}}{Fe^{-}_{(aq)}} + e^{-} \rightarrow Fe^{2+}_{(aq)}$	+ 0.77
$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH_{(aq)}^-$	- 0.83

The voltages needed if Fe<sup>3+</sup> reacts with any of the other possible reductants are:

$$\begin{array}{ll} Cl_{2(g)} + 2e^{-} \rightarrow \frac{2Cl_{(aq)}^{-}}{Pe_{(aq)}^{3+}} + e^{-} \rightarrow Fe_{(aq)}^{2+} & +1.36 & \text{Diff} = 0.77 - 1.32 = -0.55 \text{ V} \\ +0.77 & +0.77 & +0.77 & +1.77 & \text{Diff} = 0.77 - 1.77 = -1.00 \text{ V} \\ Fe_{(aq)}^{3+} + e^{-} \rightarrow Fe_{(aq)}^{2+} & +0.77 & +0.77 \end{array}$$

If a voltage of 1.88 V was applied, it is possible that  $Fe^{3+}$  could react with both of these reductants.

The voltages needed if water reacts with any of the other possible reductants are:

 $\begin{array}{l} O_{2(g)} + 4H^+_{(aq)} + 4e^- \rightarrow H_2 O_{(l)} & \pm 1.23 \\ \hline 2H_2 O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)} & -0.83 \end{array}$  Diff = -0.83 - 1.23 = -2.06

The voltage needed for this combination is larger than 1.88 V so water will not react with any of the other reductants at this voltage.

#### **Conclusion:**

If the required voltage to electrolyse Cell 2 was applied to both cells, the reactions predicted for Cell 1 would be expected occur along with other reactions between weaker oxidants and reductants present in the cell. This is because Cell 1 needs much less voltage for the reaction of the strongest oxidant and strongest reductant to occur. A voltage of 1.88 V would also enable the following reactions to proceed:

 $\begin{aligned} Fe_{(aq)}^{3+} + e^{-} &\rightarrow Fe_{(aq)}^{2+} \\ 2Cl_{(aq)}^{-} &\rightarrow Cl_{2(g)} + 2e^{-} \\ Fe_{(aq)}^{3+} + e^{-} &\rightarrow Fe_{(aq)}^{2+} \\ 2H_2O_{(l)} &\rightarrow H_2O_{2(aq)} + 2H_{(aq)}^{+} + 2e^{-} \end{aligned}$ 

**b.** (i)  $Zn^{2+}_{(aq)} + 2e^- \rightarrow Zn_{(s)}$ 

 $n(Zn) = \frac{1.02}{65.4} = 0.0156 \text{ mol}$  $n(e^{-}) = 2 \times n(Zn) = 2 \times 0.0156 = 0.0312 \text{ mol}$ 

(ii)  $Fe_{(aq)}^{3+} + e^- \rightarrow Fe_{(aq)}^{2+}$   $n(Fe_{(aq)}^{3+})_{reacted} = n(e^-)$   $n(Fe_{(aq)}^{3+})_{reacted} = 0.0312 \text{ mol}$   $n(Fe_{(aq)}^{3+})_{left over} = (Fe_{(aq)}^{3+})_{initial} - (Fe_{(aq)}^{3+})_{reacted}$  $= (1.00 \times 0.0500) - 0.0312 = 0.0188 \text{ mol}$ 

$$c(Fe_{(aq)}^{3+})_{\text{left over}} = \frac{0.0188}{0.05} = 0.376 \text{ M}$$

$$t = \frac{Q}{I} = \frac{3010}{2.50} = 1204 \text{ s} = 20.1 \text{ min}$$

- **c.** There would be no difference. The extent of the reaction occurring in Cell 1 is determined by the amount current that runs through the cell, not by the chemical species in Cell 2.
- **d.** The rate of the reaction would increase if the surface area of the electrodes increases. If the electrodes are placed closer together, the overall cell resistance goes down allowing for a faster reaction rate.

#### **QUESTION 6**

- **a.** Calibration Factor =  $\frac{6.00 \times 2.75 \times 90.0}{90.651 90.17}$  = 3087 J.°C<sup>-1</sup>
- **b.** 1 mol  $C_2H_5OH = 46$  g

From the data booklet:

 $\Delta H_{\text{combustion}}$  = -1364 kJ/mol

Energy content =  $\frac{1364}{46}$  = 29.65 kJ/g

 $1 \text{ mol } C_8 H_{18} = 114 \text{ g}$ 

From the data booklet:

 $\Delta H_{\text{combustion}} = -5464 \text{ kJ/mol}$ 

Energy content  $=\frac{5464}{114} = 47.93 \text{ kJ/g}$ 

**c.**  $E_{\text{released from Ethogas}} = 3087 \text{ x} (90.17 - 15.50) = 230506 \text{ J} = 230.5 \text{ kJ}$ 

Mass of ethanol = x Mass of octane = 5-x

29.65x + 47.93(5-x) = 230.5 29.65x - 47.93x + 239.65 = 230.5

% ethanol =  $\frac{0.5}{5.000}$  x 100 = 10.00%

- d. If less voltage was applied, less energy would be released into the calorimeter and the change in temperature would be smaller. The smaller change in temperature would lead to the calculated value for the calibration constant being larger than it should be. The calculated value for energy released by 'Ethogas' would also be larger. This would indicate that the 'Ethogas' is made up of a higher percentage of the higher energy content fuel i.e. a higher percentage of octane and a smaller percentage of ethanol.
- e. Ethanol is made via large scale fermentation of sugars found in sugar cane and corn. The growth of these crops involves the removal of carbon dioxide from the atmosphere and therefore the combustion of ethanol returns the original CO<sub>2</sub> back again rather than adding extra carbon dioxide as the burning of fossil fuels does. This is why it is considered to be eco-friendly.

- f. (i) Overall: Anode:
- II:  $3O_{2(g)} + C_2H_5OH_{(l)} \rightarrow 2CO_{2(g)} + 3H_2O_{(l)}$  $GO_{(in \ ceramic)}^{2-} + C_2H_5OH_{(l)} \rightarrow 2CO_{2(g)} + 3H_2O_{(l)} + 12e^{-1}$

 $C_2H_5OH_{(l)}$ ,  $2CO_{2(g)}$  and  $3H_2O_{(l)}$  in the overall equation come from the reaction occurring at the anode. This leaves oxygen to be reduced at the cathode. Oxide ions will appear as a product at the cathode in order to cancel out those appearing as products at the anode.

Cathode reaction:  $3O_{2(g)} + 12e^- \rightarrow 6O^{2-}_{(in\ ceramic)}$  becomes  $O_{2(g)} + 4e^- \rightarrow 2O^{2-}_{(in\ ceramic)}$ 

(ii) Advantages (any one of):

- Chemical energy from the products is converted directly into electrical energy rather than going through multiple energy transformations as occurs in a coal fired power station. Fuel cells are therefore much more efficient.
- Ethanol is renewable can be derived from plant matter rather than relying solely on that non-renewable resources like coal are not being consumed.
- Ethanol has a lower carbon footprint than coal.

Disadvantages (any one of):

- Fuel Cells are expensive to construct and maintain.
- High temperatures are required which necessitates expensive ancillary systems to run.
- (iii) Electrodes must be able to conduct electricity, separate the reactants, allow contact between reactants and the electrolyte and act as catalysts.

## **QUESTION 7**

**a.** Any conditions that move the equilibrium to the right in order to favour the production of products will maximise atom economy.

Chemical	Temperature Conditions	Pressure Conditions	Other
Sulphuric acid	Low	High	Remove products Add excess reactants
Nitric acid	Low	Low	Remove products Add excess reactants
Ammonia	Low	High	Remove products Add excess reactants
Ethene	High	Low	Remove products Add excess reactants

Chemical	Conflict	Compromise
Ammonia	Low temperatures would result in a reaction rate that is too slow to be commercially viable. High pressures are not	A catalyst is used to increase the rate of reaction in conjunction with lower temperatures.
	commercially viable.	Reactions are performed at moderate pressures as the added costs involved in using high pressures does not justify the improvement in the observed yields.
Ethene	High temperatures are expensive to maintain.	Temperatures are kept as high as viably possible.
	Low pressures can be dangerous. Leaks cause air to be drawn into the reaction mixture which can cause explosions.	Pressure is maintained at less than 1 atmosphere with careful monitoring and safety precautions.
Nitric Acid	Low temperatures would result in a reaction rate for the conversion of $NH_{3(g)}$ to $NO_{(g)}$ that is too slow to be commercially viable.	The process is carried out at high temperatures and, to compensate for the resultant loss in product yield, the gas mixture is passed over a catalyst a number of times to produce a moderate yield of <i>NO</i> .
	The <i>NO</i> formed decomposes to form nitrogen and oxygen. $2NO_{(g)} \leftrightarrow N_{2(g)} + O_{2(g)}$ . To avoid this, the gas mixture is passed across the catalyst very rapidly by using high pressures even though lower pressures result in a higher product yield.	The consequential loss in yield of <i>NO</i> due to the high pressures used is compensated for by the increased reaction rates and the quality of product obtained.
Sulphuric Acid	Low temperatures would result in a reaction rate that is too slow to be commercially viable. High pressures are too expensive to maintain.	A catalyst (vanadium pentoxide) is used to increase the rate of reaction in conjunction with lower temperatures. Reactions are performed at 1 atmosphere of pressure, as the added costs involved in using high pressures does not justify the minimal improvement in the observed yields.
		Excess air (the cheaper reactant) is used to drive the reaction forward.

#### c. Waste and Management

#### Ammonia

Any two of the following:

- Sulfur-containing compounds need to be removed from the hydrocarbon feedstock so as to minimise the emissions of damaging sulfur dioxide gases and to prevent the poisoning of catalysts. This process is called desulfurisation.
- Carbon dioxide is the major gaseous waste product resulting from the production of hydrogen gas from methane. As carbon dioxide is a major greenhouse gas, its release into the atmosphere needs to be restricted.
- Carbon dioxide may be collected and sold to soft drink manufacturers, or reacted with ammonia to produce urea, a widely used fertiliser.
- Wastage of raw materials is minimised by recycling un-reacted gases back into the converter for further passes over the catalyst. In this way, almost complete conversion is achieved.
- Heat produced from exothermic processes is recycled and used to maximise energy efficiency. This heat is used to generate steam to drive turbines, compressors and other machines and pre-heat gas mixtures. Similarly, the heat energy released by the ammonia as it is cooled is collected by heat exchangers for use elsewhere in the process.

#### Ethene

Any two of the following:

- Organic compounds can react with nitrogen oxides in the atmosphere in the presence of sunlight to form photochemical smog. Leaks of hydrocarbons are therefore minimised preventing environmental contamination.
- Unconverted feedstock is recycled back to the cracking furnace, so there is very little wastage of hydrocarbons.
- Undesirable products are treated in the following manner:

Ethyne ( $C_2H_2$ ) is converted to additional ethene by reacting it with hydrogen using a transition metal catalyst, such as Pd or an Fe/Ni mixture.

Carbon dioxide and hydrogen sulfide (both which are weak acids) are removed by treatment with dilute sodium hydroxide solution.

Propene is extracted and used for making polypropene.

Butadiene is extracted and is used to make synthetic rubber.

Hydrogen and methane are extracted and used as a fuel gas for furnaces.

The coke that builds up on the walls of the furnace is periodically removed and is used as a fuel.

Waste hydrocarbons are burned (flared) using high-pressure steam to ensure that smoke is not produced.

- Thermal energy from the hot cracked gases is used in heat recovery boilers to generate high-pressure steam. This drives compressors and pumps and heats distillation columns.
- Waste water from cooling and cleaning is treated to remove hydrocarbons, and may be reused in production or used for watering gardens.
- Noise from burners/compressors is minimised.
- To reduce *SO*<sub>2</sub> emissions when fuels are burned, desulfurisation is undertaken to removal of sulfur containing compounds and is carried out before fractions are sent to a refinery for cracking. Desulfurisation is also desirable since sulfur acts as a catalytic poison, impeding or destroying the catalytic activity of many catalysts that are used in the refinery. The sulfur that is removed during the desulfurisation process is used as a raw material for the production of chemicals such as sulfuric acid.

#### **Nitric Acid**

Any two of the following:

- The oxidation of ammonia is highly exothermic, generating sufficient heat energy to meet the energy needs of the rest of the plant.
- The main gaseous emissions from the Ostwald process include NO and  $NO_2$ . Both gases contribute to photochemical smog, and therefore, careful attention must be paid to minimising how much of these gases are emitted into the atmosphere. One approach involves the heating of these gases using a fuel such as natural gas, naphtha or hydrogen, over a catalyst, so that the  $NO_x$  is reduced to  $N_2$ . In addition, the absorption tower may be modified by increasing its size or operating pressure so as to maximise conversion of  $NO_x$  to nitric acid.
- The gas mixture entering the converter is filtered to remove catalytic poisons, which increases the efficiency of the catalysts and hence decreasing the pressure (and energy) required to force the gas through the catalyst bed.
- Heat exchangers are employed to remove heat released by the reaction in the converter and then using it to heat incoming gases or generate electricity.
- At the high temperatures and pressures used in the converter, the catalyst slowly vaporises and is lost. Gases leaving the converter are passed through a filter to recover the metals and minimise the impact of these vapours on the environment.
- Specific catalysts are added to the converter to decompose any  $N_2O$  formed. Note: Nitrogen(I) oxide is a significant greenhouse gas.

## Sulphuric Acid

Any two of the following:

- To minimise  $SO_2$  emissions and hence the formation of acid rain, most plants use a double absorption processes. In this way the percentage of sulfur dioxide converted can be increased from 98% to better than 99.6%.
- The amount of sulfuric acid mist emitted from the process is minimised by controlling the operating temperature of the absorber, gas flow rates, and concentrations.
- Small amounts of caesium are added to the vanadium(V) oxide catalyst to increase its efficiency (and hence maximise yields of *SO*<sub>3</sub>) and allow it to operate at lower temperatures.
- Mildly toxic vanadium from spent catalyst is disposed of in landfill sites.
- Cooling water is usually recycled.
- The heat exchanger removes the heat produced during the exothermic reaction. The heat collected is recycled and is used to heat the incoming gas. This reduces the costs associated with this process and conserves energy.
- The oxidation of sulfur dioxide to sulfur trioxide is highly exothermic, generating sufficient heat energy to meet the energy needs of the rest of the plant.
- Surplus energy is produced and converted to electricity.
- Waste water is treated before being released into the environment.

## d. Health and Safety

#### Ammonia

The occupational health and safety issues associated with ammonia production and storage include:

Fire/explosion injuries Poisoning Suffocation

- Ammonia is a toxic gas that is highly irritating to eyes and lungs. Exposure to high doses can be fatal. Plants must be well ventilated and contain readily available breathing apparatus.
- Ammonia reacts readily and explosively with a wide range of chemicals such as acids.
- Fires and explosions may occur in the parts of the plant where hydrogen is produced, requiring careful design and safety features.
- Ammonia boils at –33°C and hence liquid ammonia can cause frost bite and severe burning.
- As ammonia is highly soluble in water, it is extremely toxic to the environment, both in its gaseous form and when dissolved in water.
- Workers involved in the handling of liquid ammonia storage and transport need to wear impervious gloves, face shields, and rubber boots and aprons.
- The carbon monoxide gas produced during reforming is toxic and exposure to this gas must also be carefully monitored.
- The site used for ammonia production is often connected directly to the sites of plants synthesising other chemicals, such as urea and nitric acid, thus minimising the hazards and costs associated with transport of the chemical.

#### Ethene

- Working with gases at pressures below 1 atmospheric is hazardous as a leak would cause air to be drawn in, which may form an explosive mixture.
- Ethene is an asphyxiant and at moderate to high concentrations can cause nausea and headaches.
- Butadiene gas emissions are carefully monitored because high exposures may cause damage to the nervous system, and other illnesses.
- Ethene is a highly volatile and flammable gas posing a great threat to the environment through explosions. Having industries that use the products of the refining process in close proximity means that the explosive materials do not have to be transported across large distances, reducing the threat of explosions and consequential damage to the surrounding environment. In addition, extensive fire prevention and fire fighting strategies are employed by the industry.

- The biggest risk to workers in the petrochemical industry is usually considered to be explosions and fire. Like other hydrocarbons, ethene can readily form explosive mixtures with air. As a consequence, strict safety procedures are enforced.
- Since both high temperature and low temperature stages are involved in ethene production, special attention is also given to the prevention of burning and freezing injuries.

#### **Nitric Acid**

- Concentrated nitric acid is corrosive and causes severe burns to the skin and eyes. Its fumes evolve nitrogen dioxide gas which at low concentrations may cause lung oedema (fluid in the lungs) and may be fatal with excessive exposure.
- As a strong oxidant, nitric acid reacts readily with a range of organic materials and metals to produce flammable and/or explosive products.
- *NO<sub>x</sub>* gases are significant greenhouse gases and some can react with water to form acid rain.

## Safety Measures Employed:

- There is careful monitoring in nitric acid plants for leaks and spills and all employees are trained to handle such if they do occur.
- Equipment must be carefully maintained to avoid corrosion.
- Acid spills are contained using materials such as earth, clay or sand, and then neutralised with a base such as slaked lime ( $Ca(OH)_2$ ) or sodium carbonate.
- Full protective equipment and breathing apparatus is readily accessible across the plant.
- The ratio of ammonia to air in the gas entering the converter is continuously measured and controlled to ensure it does not reach explosive conditions.
- Unreacted gases are recycled where possible.
- Various methods are employed to limit *NO<sub>x</sub>* emissions, maximise conversion efficiency, and minimise loss of energy.

## **Sulfuric Acid**

Sulfuric acid is highly corrosive and can: Cause severe burns to the skin and eyes. Cause blindness. Damage plants.

- Exposure to sulfuric acid mist can result in a build-up of fluid in the lungs (pulmonary oedema).
- Sulfur dioxide and sulfur trioxide are respiratory irritants, damage plants, and contribute to a major extent to acid rain.
- Oleum is a highly corrosive oily liquid that produces sulfur trioxide fumes. Industries . must therefore engage in strict safety procedures to minimise the escape of gases and trap fumes.
- Work areas must be well ventilated and employees must wear protective clothing.
- Acid spills are contained using materials such as earth, clay or sand, and then slowly diluted with water (sulfuric acid releases large amounts of energy when added to water) before being neutralised with a base such as limestone ( $CaCO_2$ ) or sodium carbonate.
- There are strict protocols in place for the transport and loading/unloading of the acid to • minimise accidents.

Chemical	Equation
Ammonia	$\begin{array}{c} 4 \text{ NH}_{3(g)} + 3 \text{ O}_{2(g)} \rightarrow 2 \text{ N}_{2(g)} + 6 \text{ H}_2\text{O}_{(g)} \\ 2NH_{3(g)} \rightarrow N_{2(g)} + 3H_{2(g)} \end{array}$
Ethene	$C_2H_{4(g)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 2H_2O_{(g)}$
Nitric Acid	$Cu_{(s)} + 4HNO_{3(aq)} \rightarrow Cu(NO_3)_{2(aq)} + 2H_2O_{(l)} + 2NO_{2(g)}$
Sulphuric Acid	$\begin{split} Mg_{(s)} &+ 2H_2 SO_{4(l)} \rightarrow Mg SO_{4(aq)} + 2H_2 O_{(l)} + SO_{2(g)} \\ 3Mg_{(s)} &+ 4H_2 SO_{4(l)} \rightarrow 3Mg SO_{4(aq)} + 4H_2 O_{(l)} + S_{(g)} \\ 4Mg_{(s)} &+ 5H_2 SO_{4(l)} \rightarrow 4Mg SO_{4(aq)} + 4H_{2(l)} + H_2 S_{(g)} \end{split}$

e.

## **BONUS QUESTION**

a. Energy produced from hydro-electric schemes

= 15400 GWh=  $15400 \times 10^6 \text{ kWh}$ =  $15400 \times 10^6 \times 3.6$ =  $5.544 \times 10^{10} \text{ MJ}$ 

Energy produced by the average home in 1 year

= 15 kWh/day = 15 x 365 = 5475 kWh per year = 5475 x 3.6 = 19710 MJ

Number of houses that could be supplied by hydroelectricity for 1 year

$$= \frac{5.544 \times 10^{10}}{19710}$$
$$= 2812785$$
$$= 2.81 \times 10^{6}$$

**b.**  $2C_8H_{18(l)} + 25O_{2(g)} \rightarrow 16CO_{2(g)} + 18H_2O_{(g)}$ 

 $n(CO_2) = \frac{4.57 \times 10^{12}}{44} = 1.04 \times 10^{11} \text{ mol}$ 

n(octane) =  $\frac{1.04 \times 10^{11}}{8}$  = 1.30 x 10<sup>10</sup> mol

m(octane) =  $1.30 \times 10^{10} \times 114 = 1.48 \times 10^{12}$ g

v(octane) = 
$$\frac{1.48 \times 10^{12}}{0.703}$$
 = 2.11 x 10<sup>12</sup> mL = 2.11 x 10<sup>9</sup> L

No. of cars =  $\frac{2.11 \times 10^9}{2500}$  = 8.42 x 10<sup>5</sup>

c. Once hydroelectric schemes are built, the running costs are very low. Water is a renewable energy source so hydroelectric schemes prevent non-renewable resources from getting depleted and there is little or no pollution generated. These ongoing benefits outweigh the initial cost of setting up the scheme in the first place.