

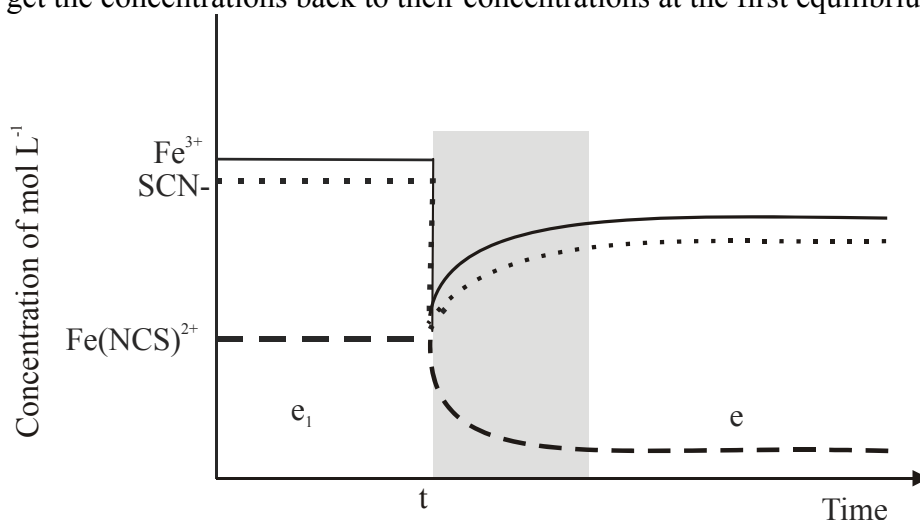
Suggested Answers

VCE Chemistry 2011 Year 12 Trial Exam Unit 4

SECTION A – Multiple Choice Answers

- Q1 A** In the Data Book the specific heat capacity of water is given as $4.18 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1}$. Since the accepted density of water at 25°C is 1 g mL^{-1} , then 100 mL of water is 100 g of water.
The amount of energy required to raise the 100 mL of water in the calorimeter by 1°C (or 1 K) is 418 J.
However **the components in calorimeter, such as the steel container, the electric heater, the thermometer and the stirrer also absorb energy during calibration.** However since their heat capacities are lower than water's, and there is less mass to heat, not a large quantity of extra energy will be required, and so $560 \text{ J }^{\circ}\text{C}^{-1}$ or 560 J K^{-1} **would be a reasonable value of the calorimeter constant for a well insulated calorimeter.**
Since the calorimeter constant is calculated as Electrical Energy / ΔT , a higher temperature change would lead to a significantly smaller calorimeter constant. If the calorimeter contained only 80 mL of water, the temperature change would be larger and the calculated calibration constant would be smaller.
Temperature changes are exactly the same in K as in $^{\circ}\text{C}$, e.g. 25°C (298 K) to 27°C (300 K) is a two degree change in both units.

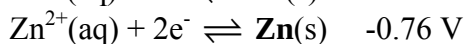
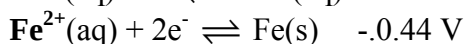
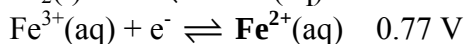
- Q2 C** Adding water to the equilibrium $\text{Fe}^{3+}(\text{aq}) + \text{SCN}^{-}(\text{aq}) \rightleftharpoons \text{Fe}(\text{NCS})^{2+}(\text{aq})$ causes all concentrations to decrease and the reaction quotient (concentration fraction) $[\text{Fe}(\text{NCS})^{2+}] / \{[\text{Fe}^{3+}][\text{SCN}^{-}]\}$ to become $> K$.
So to get back to equilibrium, the position of equilibrium moves to the left, producing more $\text{Fe}^{3+}(\text{aq})$ and $\text{SCN}^{-}(\text{aq})$. However, as the concentration-time graph below shows, the increase in amounts of $\text{Fe}^{3+}(\text{aq})$ and $\text{SCN}^{-}(\text{aq})$ is not enough to get the concentrations back to their concentrations at the first equilibrium.



This is also consistent with Le Chatelier's principle, with the system moving to produce more particles in the larger volume caused by the addition of water. At the new equilibrium $[\text{Fe}(\text{NCS})^{2+}]$ is lower, $n(\text{Fe}(\text{NCS})^{2+})$ is lower; $[\text{SCN}^{-}]$ is lower, $n(\text{SCN}^{-})$ is higher; $[\text{Fe}^{3+}]$ is lower, $n(\text{Fe}^{3+})$ is higher.

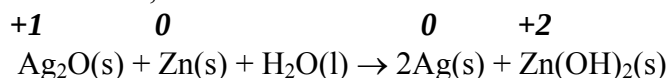
- Q3 B** Original equilibrium equation
 $\text{NO(g)} + \frac{1}{2}\text{O}_2\text{(g)} \rightleftharpoons \text{NO}_2\text{(g)}; \quad \Delta H = -57.0 \text{ kJ mol}^{-1}; K = 843$
 To get to the required equilibrium equation, the original equilibrium equation needs to be doubled and then reversed
- Original equation doubled.
 ΔH value doubled, K value raised to power 2
 $2\text{NO(g)} + \text{O}_2\text{(g)} \rightleftharpoons 2\text{NO}_2\text{(g)}; \quad \Delta H = -57.0 \times 2 \text{ kJ mol}^{-1}; (K = 843^2)$
 $\Delta H = -114 \text{ kJ mol}^{-1}; K = 7.11 \times 10^5$
 - Equation from 1. is reversed
 Sign of previous ΔH value is swapped, reciprocal of previous K value taken.
 $2\text{NO}_2\text{(g)} \rightleftharpoons 2\text{NO(g)} + \text{O}_2\text{(g)}; \quad \Delta H = +114 \text{ kJ mol}^{-1}; K = 1 / (7.11 \times 10^5)$
 $\Delta H = +114 \text{ kJ mol}^{-1}; K = 1.41 \times 10^{-6}$
- Q4 C** According to the equation, 5 mol $\text{C}_6\text{H}_{12}\text{O}_6$ releases 11925 kJ of energy.
 So **1 mol $\text{C}_6\text{H}_{12}\text{O}_6 \rightarrow 11\,925 / 5 = 2385 \text{ kJ}$**
 According to information in Table 13 of the Data Book,
 the **combustion of 1 mol $\text{C}_6\text{H}_{12}\text{O}_6$ releases 2816 kJ**
 The maximum amount of energy available from 1 mol $\text{C}_6\text{H}_{12}\text{O}_6$ in the bacteria driven reaction is **less** than that available from the combustion of 1 mol $\text{C}_6\text{H}_{12}\text{O}_6$.
- Q5 D** The rate-time graphs show:
- Q6 C**
- The rates of the forward and reverse reactions are initially equal – the system is at equilibrium.
 - At time **t** the rates of both the forward and reverse reactions increase suddenly, with the rate of the forward reaction increasing more than the rate of the reverse reaction.
 - The rate of the forward reaction decreases and the rate of reverse reaction increases as the system returns to equilibrium.
- Consider the alternatives for **Question 5**.
- Adding more reactant would cause a sudden increase in the rate of the forward reaction only.
 - A temperature decrease would cause a decrease in reaction rates.
 - Removing some product would cause a sudden decrease in the rate of the reverse reaction only.
 - A **volume decrease would immediately increase the concentrations of both reactants and products** and, since reaction rates increase with increased concentration, **increase the rates of both the forward and reverse reactions**.
- Consider **Question 6**.
 The greater increase in the rate of the forward reaction at time **t** indicates there are **more particles on the reactant side** of the associated equilibrium. Also for a **decrease in volume** on an equilibrium system, the **system will respond by shifting in the direction of the side with fewer particles**.
 Since the rate of the forward reaction decreases and reverse increases as the system responds to the imposed change, the **forward reaction is favoured**. Hence there will be **fewer particles on the product side of the equilibrium**.
 Only alternative C shows fewer particles on the product side.

Q7 B According to the relevant equations from the electrochemical series



These half-equations show that, depending on the species with which it is reacting, **Fe²⁺(aq) can act as an oxidant** (oxidising Zn to Zn²⁺) **and a reductant** (reducing Br₂ to Br⁻). In these roles Fe²⁺(aq) will be converted to Fe(s) and Fe³⁺(aq) respectively.

Q8 A When the cell is discharging electrons flow from the (-) electrode to the (+) electrode. Since electrons always move from the site of oxidation to the site of reduction, the oxidation number will decrease at the (+) electrode.



Change in oxidation number = final value – initial value.

Oxidation number of Zn increases from 0 to +2 at the (-) electrode, i.e. a change of +2

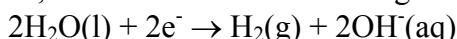
Oxidation number of Ag decreases from +1 to 0 at the (+) **electrode**, i.e. a **change of -1**

Q9 C Since electrolysis is occurring, electrons are being forced from the (+) electrode to the (-) electrode.

Hence reduction is occurring at the (-) electrode.

In each solution there are **two possible oxidants – the metal cation and H₂O – which may be reduced.**

If water is the stronger oxidant, i.e. above the cation on the electrochemical series, it will be reduced according to



and **H₂(g) will be evolved at the negative electrode.**

If the metal cation is the stronger oxidant, i.e. above H₂O on the electrochemical series, **it will be reduced to the solid metal.**

Consider the alternatives.

A. Oxidants Al³⁺(aq), K⁺(aq), Li⁺(aq) and H₂O.

H₂O is the stronger oxidant in all three solutions, so H₂ gas is produced at the (-) electrode in all three.

B. Oxidants Co²⁺(aq), Cu²⁺(aq), Ca²⁺(aq) and H₂O.

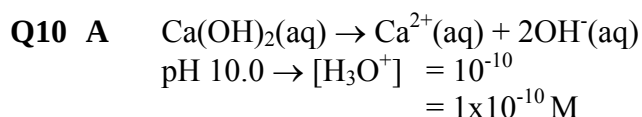
Both Cu²⁺(aq) and Co²⁺(aq) are stronger oxidants than H₂O, so Cu(s) and Co(s) will be produced with H₂(g) evolved in only one cell.

C. Oxidants Mg²⁺(aq), Ni²⁺(aq), K⁺(aq) and H₂O.

H₂O is a stronger oxidant than Mg²⁺(aq) and K⁺(aq), so H₂ gas is produced at the (-) electrode in two of the cells, Ni(s) will be produced at the (-) electrode in the other cell.

D. Oxidants Ag⁺(aq), Sn²⁺(aq), Li⁺(aq) and H₂O.

Both Ag⁺(aq) and Sn²⁺(aq) are stronger oxidants than H₂O, so Ag(s) and Sn(s) will be produced and H₂(g) evolved in only one cell.



Since $[\text{H}_3\text{O}^+][\text{OH}^-] = 10^{-14}$ at 25°
 $[\text{OH}^-] = 10^{-14} / 1 \times 10^{-10}$

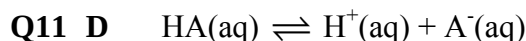
$= 1 \times 10^{-4} \text{ M}$

$= 0.0001 \text{ M}$

$[\text{Ca(OH)}_2] = \frac{1}{2} \times [\text{OH}^-]$

$= \frac{1}{2} \times 0.0001$

$= \mathbf{0.00005 \text{ M}}$



To identify the weak acid, use the data to work out the value of K_a and refer to Table 12 in the Data Book.

$K_a = [\text{H}^+][\text{A}^-] / [\text{HA}]$

$= [\text{H}^+] \times ([\text{A}^-] / [\text{HA}])$

$\text{pH } 4.5 \rightarrow [\text{H}^+] = 10^{-4.5} \text{ M}$

$= \mathbf{3.16 \times 10^{-5} \text{ M}}$

$[\text{HA}] / [\text{A}^-] = 1.32 \times 10^4 \rightarrow ([\text{A}^-] / [\text{HA}]) = 1 / (1.32 \times 10^4)$
 $= \mathbf{7.58 \times 10^{-5}}$

$K_a = 3.16 \times 10^{-5} \times 7.58 \times 10^{-5}$

$= \mathbf{2.4 \times 10^{-9}}$

Hypobromous acid

Q12 B Consider the alternatives:

A. The specific heat capacity of H_2O is $4.18 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$

Energy needed to increase 1 kg H_2O by $1^\circ\text{C} = 4.18 \times 1000 \times 1$

$= 4180 \text{ J}$

$= \mathbf{4.18 \text{ kJ}}$

B. Electrical energy, as in calorimeter calibration, is determined from

$E = VIt$

So for a current of 1 A, at 1 V for 1000 s

$E = 1 \times 1 \times 1000$

$= 1000 \text{ J}$

$= \mathbf{1 \text{ kJ}}$

C. $n(\text{H}_2) = 2 \text{ g} / 2.0 \text{ g mol}^{-1}$

$= 1 \text{ mol}$

According to Table 13 of the Data Book, the combustion of 1 mol H_2 will release 286 kJ of energy.

D. Since the combustion of 1 mol H_2 to form H_2O releases 286 kJ of energy, then the conversion of H_2O to produce 1 mol H_2 will require the input of a similar amount of energy.

Q13 B $\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$.
 Adding 50 mL of water doubles the volume so all concentrations halve.
 Addition of water pushes the equilibrium to the right, causing more NH_3 to ionise, i.e. **increasing the percentage ionisation**.
 The amount of $\text{OH}^-(\text{aq})$ present in the solution also increases.
 Although there is a more **$\text{OH}^-(\text{aq})$** it is in a **larger volume**, the amount of $\text{OH}^-(\text{aq})$ produced in the equilibrium shift only partially compensates for the volume increase by the time equilibrium is regained.
 Overall **$[\text{OH}^-]$ is lower $\rightarrow [\text{H}_3\text{O}^+]$ is higher $\rightarrow$ lower pH.**
 So the **pH decreases and the percentage ionisation increases.**

Q14 D **Diagram X**
 This shows the energy distribution at two different temperatures. Graph 2 represents a higher **temperature** situation.
 In the case of the higher temperature, where the collision energies are higher, the greater shaded area under the curve, for energy greater than E_a , represents a **greater proportion of collisions, with energy greater than the activation energy**, hence **increasing temperature increases the rate of reaction**.
Diagram Y
 This shows the impact of a **catalyst**. Activation energy E_{A2} is **less than** activation energy E_{A1} . This **decrease in the activation energy** is caused by the use of a **catalyst** (the only possibility). Hence **many more collisions will have energy greater than the activation energy at E_{A2}** (as indicated by greater shaded area under graph above E_{A2}) and so the **rate of reaction increases in the presence of a catalyst**.

Q15 C $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g}); \Delta H = -113 \text{ kJ mol}^{-1}$
 Consider the alternatives.
 A. Since the forward reaction is exothermic, decreasing the temperature favours the forward reaction, **increasing the amount of NO_2** .
 B. Decreasing the volume increases the concentration of all species present. This makes the concentration fraction smaller than K . So the forward reaction is favoured as the system returns to equilibrium.
 Also the pressure exerted by species in the equilibrium system increases, since they are occupying a smaller volume. In order to compensate for the pressure increase, the reaction which leads to an overall reduction in the number of particles present is favoured, i.e. the forward reaction, **increasing the amount of NO_2** .
 C. N_2 gas is not part of the equilibrium system, does not react with any of the species in the equilibrium system, and does not change the position of equilibrium. It does not cause a change in the concentration fraction, so the system is not moved from equilibrium. Hence the **amount of NO_2 is not affected**.
 From the pressure perspective, whilst the total pressure in the container will increase, the **pressure exerted by the individual species in the equilibrium mixture does not change**.
 D. Adding air increases the $[\text{O}_2]$ in the system which responds to this change by using up some of the added O_2 . Hence the **forward reaction is favoured and the amount of NO_2 increases**.

- Q16 A** According to the equation

$$\text{NH}_3(\text{g}) + 3\text{Cl}_2(\text{g}) \rightleftharpoons \text{NCl}_3(\text{g}) + 3\text{HCl}(\text{g})$$
 if the reaction did proceed to completion, then with 3 mol NH_3 and 10 mol Cl_2 present at the start, 3 mol NH_3 would react with 9 mol Cl_2 to produce 3 mol NCl_3 and 9 mol HCl leaving 1 mol Cl_2 in excess.
 However all 3 mol NH_3 cannot react if the mixture reaches equilibrium, since equilibrium requires the presence of all reactants and all products.
 Hence less than 3 mol NH_3 will have reacted and **less than 3 mol NCl_3 will be present** when equilibrium is reached.
- Q17 A** The diagram shows the direction of movement of ions in the salt bridge. Anions, in this case NO_3^- ions, move towards the anode – the site of oxidation – which is (-) in a galvanic cell, and is in half-cell 2.
 So **half-cell 2** contains the (-) electrode and is the **site of oxidation**.
 Half-cell 1 contains the (+) electrode and is the site of reduction.
- Q18 B** Energy released = 200 MJ = 200×10^3 kJ
 Energy available from one mole of C_8H_{18} = 5464 kJ (Data Book Table 13)

$$n(\text{C}_8\text{H}_{18}) = \text{energy released} / \text{energy per mole } \text{C}_8\text{H}_{18}$$

$$= 200 \times 10^3 \text{ kJ} / 5464 \text{ kJ mol}^{-1}$$

$$= 36.6 \text{ mol}$$

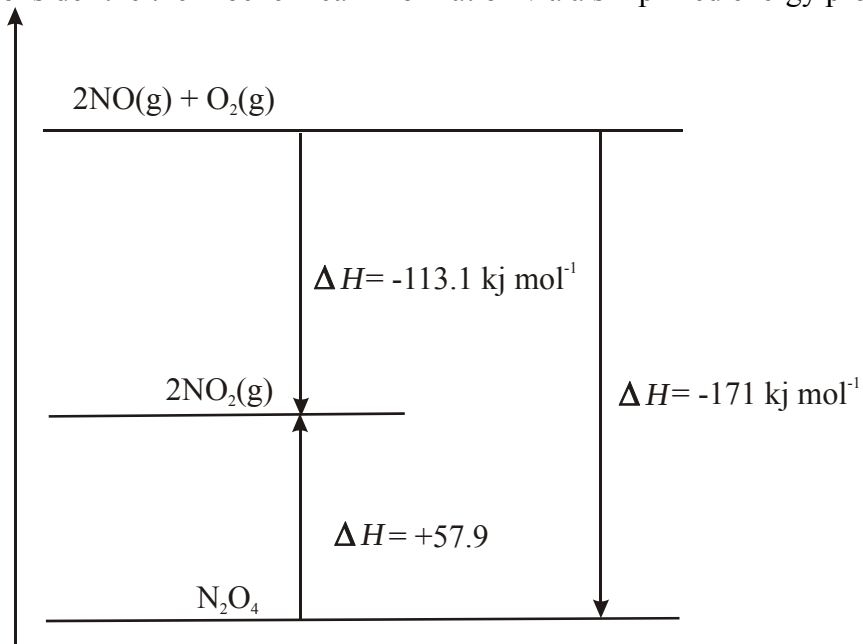
$$m(\text{C}_8\text{H}_{18}) = 36.6 \text{ mol} \times 114 \text{ g mol}^{-1}$$

$$= 4.17 \times 10^3 \text{ g}$$

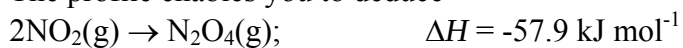
$$= \mathbf{4.17 \text{ kg}}$$
- Q19 D** This question requires recognition that, in a fuel cell, electrons flow from the (-) electrode to the (+) electrode.
 So oxidation occurs at the (-) electrode and **reduction at the (+) electrode**.
 In a fuel cell, the fuel is oxidised at the (-) electrode and **$\text{O}_2(\text{g})$ is reduced at the (+) electrode**. In a H_2 - O_2 fuel cell, H_2 is the fuel.
 An alkaline electrolyte contains **$\text{OH}^-(\text{aq})$ ions**.
 Then it is a case of effective use of the electrochemical series – identifying the half-equation which includes both $\text{O}_2(\text{g})$ and $\text{OH}^-(\text{aq})$, i.e.

$$\mathbf{\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^- \rightarrow 4\text{OH}^-(\text{aq})}$$

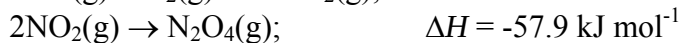
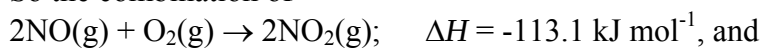
Q20 C Consider the thermochemical information via a simplified energy profile.



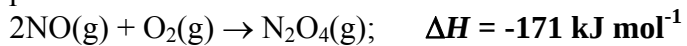
The profile enables you to deduce



So the combination of



produces



SECTION B – Short Answer (Answers)

Question 1

- a. NH_3 or C_2H_4 or H_2SO_4 or HNO_3 ①
- b. i. $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ or
 $\text{C}_3\text{H}_8(\text{g}) \rightleftharpoons \text{C}_2\text{H}_4(\text{g}) + \text{CH}_4(\text{g})$ / other cracking equation with C_2H_4 as a product or
 $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$ or
 $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ / $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$ ①
- ii. For reaction to commence the **reactant particles must have energy equal to or greater than the activation energy.** ①
- iii. When the reactants, e.g. SO_2 and O_2 , are mixed together and start reacting, **the rate of the forward reaction** (e.g. $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$) is at its **maximum.** ①
As the **forward reaction** proceeds, its **rate decreases**, due to the **decreasing concentration of reactants.** ①
Simultaneously the **concentration of the products increases**, and so the **rate of the reverse reaction** (e.g. $2\text{SO}_3 \rightarrow 2\text{SO}_2 + \text{O}_2$) **increases.** ①
Eventually the **rates of the forward and reverse reactions become equal** and the reacting system has reached **chemical equilibrium.** ①
- iv. When the pressure on an equilibrium system is increased, the system responds by favouring the side with fewer particles.
When the temperature in an equilibrium system is decreased, the system responds by favouring the direction of the exothermic reaction.
 NH_3 : Increasing pressure right ①; Decreasing temperature right ①
 $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}); \Delta H < 0$
 C_2H_4 : Increasing pressure left; Decreasing temperature left
 $\text{C}_3\text{H}_8(\text{g}) \rightleftharpoons \text{C}_2\text{H}_4(\text{g}) + \text{CH}_4(\text{g}); \Delta H > 0$
 H_2SO_4 : Increasing pressure right; Decreasing temperature right
 $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g}); \Delta H < 0$
 HNO_3 : Increasing pressure right; Decreasing temperature right
 $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g}); \Delta H < 0$ / $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g}); \Delta H < 0$
- c. $\text{NH}_3(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$ ①
 $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CH}_3\text{CH}_2\text{OH}(\text{l})$
 $\text{H}_2\text{SO}_4(\text{l}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{HSO}_4^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$
 $\text{HNO}_3(\text{l}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{NO}_3^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$

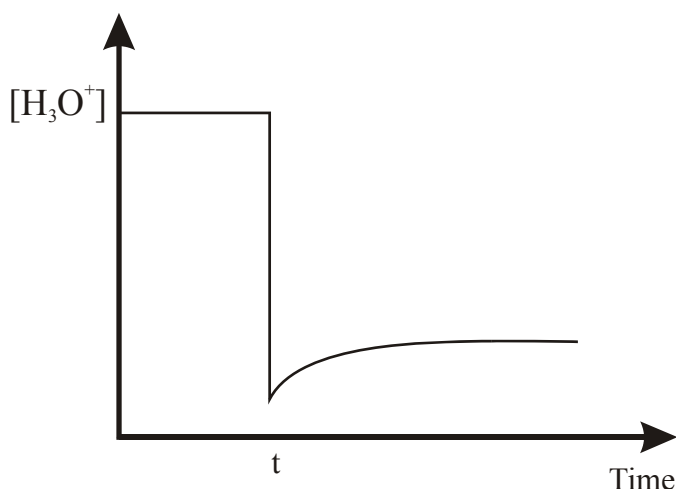
Question 2

- a. $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g or l})$ ①
- b. Chemical $\rightarrow$ Electrical ①
- c. In a **fuel cell the conversion from chemical energy to electrical energy is direct** and hence more efficient than the **multistep conversion (chemical $\rightarrow$ thermal $\rightarrow$ mechanical $\rightarrow$ electrical) of a conventional fuel (gas) fired power station.** ①
- d. i. (-) electrode (anode) $\text{CH}_4(\text{g}) + 4\text{O}^{2-}(\text{l}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g}) + 8\text{e}^-$ ①
ii. (+) electrode (cathode) $\text{O}_2(\text{g}) + 4\text{e}^- \rightarrow 2\text{O}^{2-}(\text{l})$ ①
The description of solid-oxide fuel cells indicated that O_2 was reduced to O^{2-} ions at the cathode - *'bring in oxygen from the air to be reduced at the cathode, and then pass the oxide ions through a solid-oxide membrane to the anode'* – therefore both the CO_2 and H_2O , characteristic products of the use of methane as a fuel, had to be produced at the anode, where the only source of oxygen for the oxidation was $\text{O}^{2-}(\text{l})$ ions.
- e. The **operating temperature of SOFCs (500-1000°C) is well beyond the reference temperature (25°C) of the electrochemical series.** ①
- f. i. $\text{H}_2(\text{g}) \rightarrow 2\text{H}^+(\text{aq}) + 2\text{e}^-$ ①
ii. $\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$ ①
- g. $2\text{H}_2(\text{g}) + \text{O}_2(\text{l}) \rightarrow 2\text{H}_2\text{O}(\text{l})$ ①

Question 3

- a. $\text{NaOH}(\text{aq}) + \text{HCOOH}(\text{aq}) \rightarrow \text{HCOONa}(\text{aq}) + \text{H}_2\text{O}(\text{l})$
 $n(\text{HCOOH}) \text{ reacting} = n(\text{NaOH}) \text{ required}$
 $= 0.155 \text{ mol L}^{-1} \times 17.25 \times 10^{-3} \text{ L}$
 $= 2.67 \times 10^{-3} \text{ mol}$ ①
- b. i. Since the equation for the ionisation of $\text{HCOOH}(\text{aq})$ is
 $\text{HCOOH}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HCOO}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$
the equilibrium law is
 $K_a = [\text{HCOO}^-][\text{H}_3\text{O}^+] / [\text{HCOOH}]$ ①
ii. $K_a(\text{HCOOH}) = 1.8 \times 10^{-4}$ (from Data Book)
Since 18.5 mL of the methanoic acid solution contained $2.67 \times 10^{-3} \text{ mol HCOOH}$
 $c(\text{HCOOH}) = 2.67 \times 10^{-3} \text{ mol} / 18.5 \times 10^{-3} \text{ L}$
 $= 0.144 \text{ M}$ ①
Using the standard weak acid assumptions: $[\text{HCOOH}]_{\text{equilibrium}} = 0.144 \text{ M}$
 $[\text{HCOO}^-] = [\text{H}_3\text{O}^+]$, i.e. negligible H_3O^+ from the self-ionisation of water.
 $1.8 \times 10^{-4} = [\text{H}_3\text{O}^+]^2 / 0.144$ ①
 $[\text{H}_3\text{O}^+] = \sqrt{(0.144 \times 1.8 \times 10^{-4})}$
 $= 5.10 \times 10^{-3} \text{ M}$ ①
 $\text{pH} = -\log_{10}(5.10 \times 10^{-3})$
 $= 2.3$ ①

c. i.



When 10 mL methanoic acid is diluted to 100 mL with water, the $[\text{H}_3\text{O}^+]$ **immediately decreases by a factor of 10**. However because the **dilution decreases all concentrations, the reaction quotient** (concentration fraction), i.e. $[\text{HCOO}^-][\text{H}_3\text{O}^+] / [\text{HCOOH}]$, decreases and **become less than K_a** . **For the system to return to equilibrium, the position of equilibrium moves to the right and the $[\text{H}_3\text{O}^+]$ increases**, i.e. there are more H_3O^+ ions present, but **the concentration is still well below its value prior to dilution when equilibrium is regained**.

- ii. Since the $[\text{H}_3\text{O}^+]$ decreases then increases as the equilibrium moves to the right, the **pH will increase and then decrease**. However the **pH after dilution will be higher than before dilution**.
 [pH of 0.0144 M $\text{HCOOH}(\text{aq}) = 2.8$].
- iii. The **dilution of a strong acid**, e.g. $\text{HCl}(\text{aq})$. When $\text{HCl}(\text{aq})$ ionises, effectively all the HCl molecules have donated $\text{H}^+(\text{aq})$ and so there is no increase in the amount of H_3O^+ present as a result of the dilution.

Question 4

- a. According to the supplied data, the calorimeter was calibrated by the combustion of ethanol in the reaction bomb.

$$n(\text{ethanol}) \text{ used} = 0.853 \text{ g} / 46.0 \text{ g mol}^{-1} \\ = 1.85 \times 10^{-2} \text{ mol}$$

$$\Delta H_c(\text{ethanol}) = -1364 \text{ kJ mol}^{-1} \text{ (Data Book)}$$

$$\text{Energy released} = 1.85 \times 10^{-2} \text{ mol} \times 1364 \text{ kJ mol}^{-1} \\ = 25.3 \text{ kJ}$$

$$\Delta T \text{ calibration} = 24.10 - 21.30 \\ = 2.80 \text{ }^\circ\text{C}$$

$$\text{Calibration Constant} = 25.3 \text{ kJ} / 2.80^\circ\text{C} \\ = 9.03 \text{ kJ }^\circ\text{C}^{-1} \\ = 9.03 \text{ kJ K}^{-1}$$

A temperature change is the same magnitude in both $^\circ\text{C}$ and K

- b. ΔT combustion of olive oil = $22.391 - 22.150$
 $= 0.241\text{ }^{\circ}\text{C}$
 Energy released = $9.03\text{ kJ K}^{-1} \times 0.241\text{ K}$
 $= \mathbf{2.18\text{ kJ}} \text{ ①}$
- c. $M(\text{C}_{57}\text{H}_{104}\text{O}_6) = 57 \times 12.0 + 104 \times 1.0 + 6 \times 16.0$
 $= 884.0\text{ g mol}^{-1}$
 $n(\text{C}_{57}\text{H}_{104}\text{O}_6) = 1.00\text{ g} / 884.0\text{ g mol}^{-1}$
 $= 1.13 \times 10^{-3}\text{ mol} \text{ ①}$
 Heat of combustion olive oil = $2.18\text{ kJ} / 1.13 \times 10^{-3}\text{ mol}$
 $= \mathbf{1.93 \times 10^3\text{ kJ mol}^{-1}} \text{ ①}$
- d. This is simply a matter of effective combustion equation balancing.
- Reactants and products
 $\text{C}_{57}\text{H}_{104}\text{O}_6(\text{l}) + ___\text{O}_2(\text{g}) \rightarrow ___\text{CO}_2(\text{g}) + ___\text{H}_2\text{O}(\text{g})$
 - Balance for 'C'
 $\text{C}_{57}\text{H}_{104}\text{O}_6(\text{l}) + ___\text{O}_2(\text{g}) \rightarrow \mathbf{57}\text{CO}_2(\text{g}) + ___\text{H}_2\text{O}(\text{g})$
 - Balance for 'H'
 $\text{C}_{57}\text{H}_{104}\text{O}_6(\text{l}) + ___\text{O}_2(\text{g}) \rightarrow \mathbf{57}\text{CO}_2(\text{g}) + \mathbf{52}\text{H}_2\text{O}(\text{g})$
 - Balance for 'O'
 On RHS – $2 \times 57 + 52 = 166$ 'O'
 On LHS – 6 'O'
 So 160 'O', i.e. 80 O_2 is required
 $\text{C}_{57}\text{H}_{104}\text{O}_6(\text{l}) + \mathbf{80}\text{O}_2(\text{g}) \rightarrow \mathbf{57}\text{CO}_2(\text{g}) + \mathbf{52}\text{H}_2\text{O}(\text{g})$
 The thermochemical equation, which includes ΔH , is
 $\mathbf{\text{C}_{57}\text{H}_{104}\text{O}_6(\text{l}) + 80\text{O}_2(\text{g}) \rightarrow 57\text{CO}_2(\text{g}) + 52\text{H}_2\text{O}(\text{g}); \Delta H = -1.93 \times 10^3\text{ kJ mol}^{-1}}$
 ① for correct chemical formulae and states
 ① for correct balancing
 ① for ΔH consistent with the equation.
- e. Specific heat capacity of water = $4.18\text{ J g}^{-1}\text{ K}^{-1}$ (Data Book)
 Energy into water = $4.18\text{ J g}^{-1}\text{ K}^{-1} \times m(\text{H}_2\text{O}) \times \Delta T$
 $2.18 \times 10^3\text{ J} = 4.18\text{ J g}^{-1}\text{ K}^{-1} \times m(\text{H}_2\text{O}) \times 1.49\text{ K} \text{ ①}$
 $m(\text{H}_2\text{O}) = 2.18 \times 10^3 / (4.18 \times 1.49)$
 $= \mathbf{350\text{ g}} \text{ ①}$

Question 5

- a. Using $pV = nRT \rightarrow p = nRT / V$
 Since you are given the concentrations of all gases and $c = n/V$
 Then $p = cRT$ and the **total pressure depends on the total concentration.**
 Total concentration = $0.00250 + 0.00350 + 0.0250 + 0.0400$
 $= 0.0710\text{ mol L}^{-1} \text{ ①}$
 $p = 0.0710 \times 8.31 \times (460 + 273)$
 $= 0.0710 \times 8.31 \times 733$
 $= 433\text{ kPa} \text{ ①}$
 According to the data book, $101.3\text{ kPa} = 1\text{ atm}$
 $p = 433 / 101.3\text{ atm}$
 $= \mathbf{4.27\text{ atm}} \text{ ①}$

- b. i. To show the reaction mixture is at equilibrium, calculate the reaction quotient, Q , (concentration fraction) and compare it with the stated equilibrium constant.

$$\begin{aligned} Q &= [\text{NO}][\text{SO}_3] / [\text{SO}_2][\text{NO}_2] \\ &= [0.0250 \times 0.0400 / 0.00250 \times 0.00350] \\ &= \mathbf{114} \text{ ①} \end{aligned}$$

Since $Q > K_c$, the system is not at equilibrium.

To get to equilibrium the value of Q must decrease and so the reverse (backward) reaction will dominate. ①

- ii. When the system is at equilibrium, the pressure will remain constant. ① Forward and reverse reactions are occurring at the same rate.
- c. Since the reverse reaction is favoured as the system shifts to equilibrium, and there is a 1:1 mole ratio through the equation, each reactant concentration must each increase by $0.00050 \text{ mol L}^{-1}$ and each product concentration decrease by $0.0050 \text{ mol L}^{-1}$.
Hence the total concentration, and number of moles, in the reaction vessel does not change and so the pressure at equilibrium will be the same as before equilibrium, i.e. **432 kPa** ①

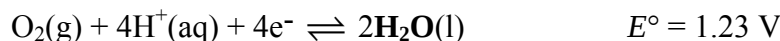
This is also consistent with the equilibrium having the same number of particles on both sides so that the pressure does not change as reaction proceeds in either direction.

- d. i. Le Chatelier's principle states that 'if a system at equilibrium is disturbed by a change in conditions, the reaction moves in the direction that will counteract the effect of the change and, if possible, return the system to equilibrium'. ①
- ii. The equilibrium system $\text{H}_2\text{CO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HCO}_3^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$ will respond to an increase in pH, i.e. a decrease in $[\text{H}_3\text{O}^+]$, by moving to increase the $[\text{H}_3\text{O}^+]$ – and decrease the pH, by favouring the forward reaction and moving the position of equilibrium to the right. ①
This occurs because when the $[\text{H}_3\text{O}^+]$ decreases, the rate of the reverse (backward) reaction drops relative to the rate of the forward reaction. This drives the reaction forward until the rates of forward and reverse reactions are again equal and equilibrium is regained. ①

Question 6

- a. i. The cell voltage, 1.02 V, is the difference between the E° values of the half-cell containing the oxidant and the half-cell containing the reductant.
If the oxidant was in the $\text{Cu}^{2+}(\text{aq})/\text{Cu}(\text{s})$ half-cell and the reductant in the 'unknown' half-cell then
 $1.02 \text{ V} = E^\circ(\text{Cu}^{2+}/\text{Cu}) - E^\circ(\text{unknown half-cell})$
 $1.02 \text{ V} = 0.34 - E^\circ(\text{unknown half-cell})$
 $E^\circ(\text{unknown half-cell}) = 0.34 - 1.02$
 $= -0.68 \text{ V}$
There is no half-cell in the electrochemical series in the Data Book with $E^\circ = -0.68 \text{ V}$
If the reductant was in the $\text{Cu}^{2+}(\text{aq})/\text{Cu}(\text{s})$ half-cell and the oxidant in the 'unknown' half-cell then
 $1.02 \text{ V} = E^\circ(\text{unknown half-cell}) - E^\circ(\text{Cu}^{2+}/\text{Cu})$
 $1.02 \text{ V} = E^\circ(\text{unknown half-cell}) - 0.34$
 $E^\circ(\text{unknown half-cell}) = 1.02 + 0.34$
 $= 1.36 \text{ V}$
This corresponds to the E° value for the $\text{Cl}_2(\text{g})/\text{Cl}^-(\text{aq})$ half-cell, and the species are
A $\text{Cl}_2(\text{g})$ ①
B $1 \text{ M Cl}^-(\text{aq})$ ①
C $\text{Pt}(\text{s})$ or $\text{C}(\text{s})$ ①
When the half-cell redox pair does not include a conducting solid, an inert electrode, Pt or C, is used.
- ii. A salt-bridge is essential **to allow electrolytic conduction between the electrodes and so complete the circuit. ①**
In the $\text{Cl}_2(\text{g})/\text{Cl}^-(\text{aq})//\text{Cu}^{2+}(\text{aq})/\text{Cu}(\text{s})$ cell the cathode is in the $\text{Cl}_2(\text{g})/\text{Cl}^-(\text{aq})$ half-cell.
The reduction half-equation $\text{Cl}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{Cl}^-(\text{aq})$ shows that the **release of $\text{Cl}^-(\text{aq})$ ions would increase the (-) charge in the solution around the cathode. ①**
To counteract that situation and **keep the solution electrically neutral, cations flow through the salt bridge into the half-cell. ①**
- iii. **$\text{Ag}^+(\text{aq})$ ions would react with $\text{Cl}^-(\text{aq})$ to form insoluble AgCl . ①** This would interfere with the effective operation of the cell.
- b. i. In the half-equation $\text{O}_3(\text{g}) + \text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{O}_2(\text{g}) + 2\text{OH}^-(\text{aq})$ there is **no change in oxidation number** of any of the elements. ①
The fundamental definition of reduction as the 'gain of electrons' applies.

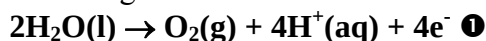
- ii. According to the electrochemical series, the relevant species $\text{Y}^{3+}(\text{aq})$, $\text{Cl}^{-}(\text{aq})$ and $\text{H}_2\text{O}(\text{l})$ appear in the electrochemical series data in the half-equations.



The strongest oxidant, $\text{H}_2\text{O}(\text{l})$, is reduced at the cathode, **the (-) electrode**, according to



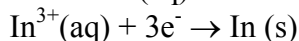
The strongest reductant, $\text{H}_2\text{O}(\text{l})$, is oxidised at the anode, **the (+) electrode**, according to



- iii. According to the electrochemical series data, only $\text{H}_2\text{O}(\text{aq})$ and $\text{In}^{3+}(\text{aq})$ can be reduced at the (-) electrode (cathode).



Since $\text{In}^{3+}(\text{aq})$ is the stronger oxidant, the reductant half-equation will be



$$\begin{aligned} n(\text{In}) \text{ produced} &= m(\text{In}) / M(\text{In}) \\ &= 0.448 \text{ g} / 114.8 \text{ g mol}^{-1} \\ &= 0.00390 \text{ mol} \quad \text{①} \end{aligned}$$

$$\begin{aligned} n(\text{e}^{-}) \text{ required} &= 3 \times n(\text{In}) \\ &= 3 \times 0.00390 \\ &= 0.0117 \text{ mol} \quad \text{①} \end{aligned}$$

$$\begin{aligned} Q &= n(\text{e}^{-}) \times F \\ &= 0.0117 \text{ mol} \times 96500 \text{ C mol}^{-1} \\ &= 1.13 \times 10^3 \text{ C} \quad \text{①} \end{aligned}$$

However the conversion of electrical energy to chemical energy is only 75 % efficient, so

$$\begin{aligned} 1.13 \times 10^3 \text{ C} &= 0.75 \times Q_{\text{TOTAL}} \\ Q_{\text{TOTAL}} &= 1.13 \times 10^3 / 0.75 \\ &= 1.51 \times 10^3 \text{ C} \quad \text{①} \end{aligned}$$

Since $Q = It$

$$\begin{aligned} t &= 1.51 \times 10^3 \text{ C} / 2.51 \text{ A} \\ &= 600 \text{ s} \\ &= \mathbf{10.0 \text{ minutes}} \quad \text{①} \end{aligned}$$

End of Suggested Answers