VCE CHEMISTRY 2011

YEAR 12 TRIAL EXAM UNIT 4

CONDITION OF SALE:

Time allowed: 90 Minutes
Total marks: 85

Section A
Contains 20 Multiple Choice Questions
20 marks, 21 minutes

Section B
Contains 6 Short Answer Questions
65 marks, 69 minutes

To download the Chemistry Data Book please visit the VCAA website:
http://www.vcaa.vic.edu.au/vce/studies/chemistry/chem1_sample_2008.pdf *Page 20*

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Student Name....………………………...

VCE Chemistry 2011 Year 12 Trial Exam Unit 4

Student Answer Sheet

There are 20 Multiple Choice questions to be answered by circling the correct letter in the table below. Use only a 2B pencil. If you make a mistake, erase and enter the correct answer. Marks will not be deducted for incorrect answers

Question 1	A	B	C	D	*Question 2*	A	B	C	D
Question 3	A	B	C	D	*Question 4*	A	B	C	D
Question 5	A	B	C	D	*Question 6*	A	B	C	D
Question 7	A	B	C	D	*Question 8*	A	B	C	D
Question 9	A	B	C	D	*Question 10*	A	B	C	D
Question 11	A	B	C	D	*Question 12*	A	B	C	D
Question 13	A	B	C	D	*Question 14*	A	B	C	D
Question 15	A	B	C	D	*Question 16*	A	B	C	D
Question 17	A	B	C	D	*Question 18*	A	B	C	D
Question 19	A	B	C	D	*Question 20*	A	B	C	D

VCE Chemistry 2011 Year 12 Trial Exam Unit 4

SECTION A – Multiple Choice Questions

Section A consists of 20 multiple-choice questions.
Section A is worth approximately 24 per cent of the marks available.
Choose the response that is **correct** *or* **best answers** *the question.*
Indicate your choice on the answer sheet provided.

Question 1

A solution calorimeter containing 100 mL of water was calibrated using electrical apparatus. The calorimeter constant was calculated to be 560 J K^{-1}. This calorimeter constant suggests that

A. the calorimeter was well insulated.
B. the temperature change in the calorimeter was too high because the thermometer was in contact with the heating element.
C. the calorimeter actually contained only 80 mL of water.
D. the temperature change was not converted from °C to K prior to calculating the calibration factor.

Question 2

When aqueous solutions of iron(III) nitrate, $Fe(NO_3)_3$, and potassium thiocyanate, KSCN, are mixed together, a deep red colour, characteristic of the thiocyanatoiron(III) ion, $Fe(NCS)^{2+}$(aq), forms, courtesy of the equilibrium $Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons Fe(NCS)^{2+}(aq)$.
If a 10 mL sample of this equilibrium mixture is diluted by the addition of 10 mL of water

A. the $[Fe(NCS)^{2+}]$ will decrease, but the amount present will increase as the system returns to equilibrium.
B. the equilibrium constant is lowered by the addition of water, and more $Fe(NCS)^{2+}$(aq) is produced as the system moves to increase the equilibrium constant.
C. the $[Fe^{3+}]$ will decrease, but the amount present will increase as the system moves back to equilibrium.
D. the $[Fe^{3+}]$ and $[SCN^{-}]$ will both be higher when a new equilibrium is established after the addition of the water.

Question 3

When NO(g) reacts with O_2(g) to produce NO_2(g), equilibrium is established, according to

$$NO(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons NO_2(g); \Delta H = -57.0\,kJ\,mol^{-1}$$

At 200ºC, the equilibrium constant has the value 843 $M^{-1/2}$
Which of the following is correct for the equilibrium
$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$ at 200° C?

A. ΔH = -114 kJ mol^{-1}
B. $K = 1.41 \times 10^{-6}$
C. $\Delta H = 3.25 \times 10^{3}$ kJ mol^{-1}
D. $K = 1.69 \times 10^{3}$

Question 4

In the absence of oxygen, bacteria may derive energy by causing a reaction between nitrate ions and glucose in organic matter, according to the equation

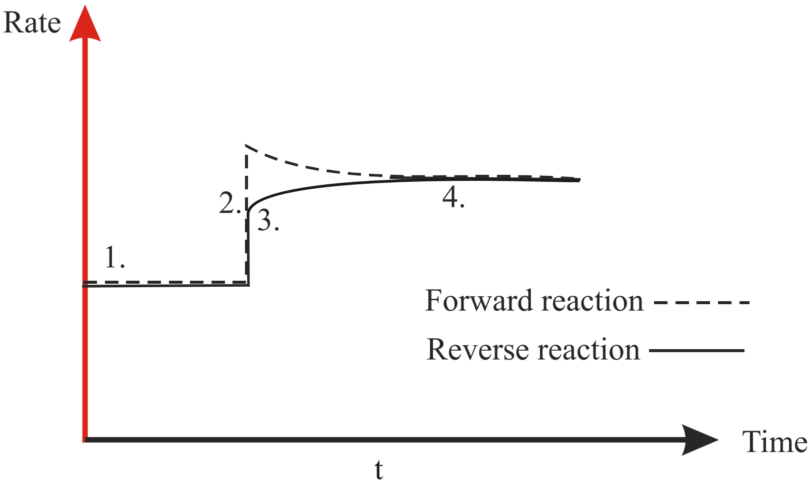
$5C_6H_{12}O_6(s) + 24NO_3^-(aq) \rightarrow 30CO_2(g) + 18H_2O(l) + 24OH^-(aq) + 12N_2(g)$; $\Delta H = -11\,925$ kJ mol^{-1}

The maximum amount of energy available from 1 mole of glucose in this reaction is

A. the same as from the combustion of 1 mole of glucose.
B. greater than from the combustion of 1 mole of glucose.
C. less than from the combustion of 1 mole of glucose.
D. 11 925 kJ.

Questions 5 and 6 refer to the following information.

The diagram below shows rate-time graphs for an equilibrium reaction.



Question 5

The change in the rates at time **t** could be due to

A. the addition of more reactant(s).
B. a temperature decrease.
C. the removal of some product(s).
D. a volume decrease.

Question 6

To which of the following equilibria could the above rate–time graphs apply?

A. $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
B. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
C. $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$
D. $C_4H_{10}(g) \rightleftharpoons C_2H_4(g) + C_2H_6(g)$

Question 7

The iron(II) ion, $Fe^{2+}(aq)$

A. can act as an oxidant but not a reductant.

B. can oxidise solid zinc and reduce liquid bromine.

C. can act as a reductant but not an oxidant.

D. will always be reduced to Fe(s) in redox reactions.

Question 8

Silver oxide – zinc cells have been used as hearing-aid batteries and as sources of constant voltage in scientific equipment. They are characterised by the cell reaction

$$Ag_2O(s) + Zn(s) + H_2O(l) \rightarrow 2Ag(s) + Zn(OH)_2(s)$$

The **change** in oxidation number occurring at the positive electrode when this cell is discharging is

A. -1

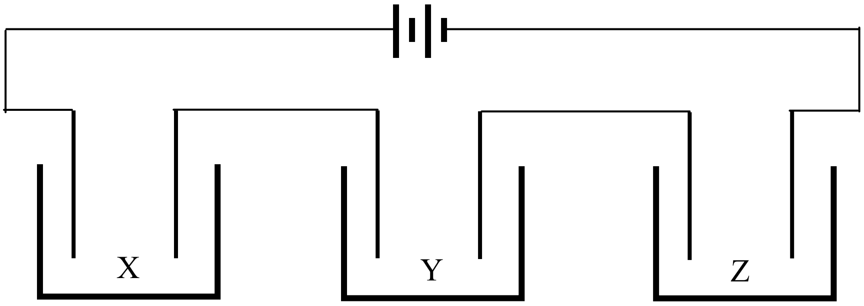
B. +1

C. -2

D. +2

Question 9

A current of 2.5 A is passed for 50 minutes through three cells, X, Y and Z, containing 1 molar solutions of ionic compounds and connected in series.



In two of the cells, a gas is evolved at the (-) electrode, whereas in the other cell a solid collects on the (-) electrode.

The solutions in the cells X, Y and Z may have been

A. $Al(NO_3)_3(aq)$, $KBr(aq)$, $LiNO_3(aq)$

B. $CoCl_2(aq)$, $CuCl_2(aq)$, $CaCl_2(aq)$

C. $MgCl_2(aq)$, $NiCl_2(aq)$, $KCl(aq)$

D. $AgNO_3(aq)$, $SnCl_2(aq)$, $LiCl_2(aq)$

Question 10

Calcium hydroxide, $Ca(OH)_2$, is sparingly soluble in water. An aqueous solution of calcium hydroxide has a pH of 10.0 at 25°C.

The concentration, in mol L^{-1}, of $Ca(OH)_2$, in the solution is

A. 0.00005

B. 0.0001

C. $2x10^{-10}$

D. $1x10^{-10}$

Question 11

The weak acid HA(aq) ionises according to the equilibrium

$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$

The ratio [HA] / [A$^-$] in a specific weak acid was measured as a function of the pH at equilibrium at 25°C. The following data were recorded.

[HA] / [A$^-$]	**pH**
1.32×10^4	4.5

The weak acid was

A. ethanoic acid.
B. methanoic acid.
C. hypochlorous acid.
D. hypobromous acid.

Question 12

One kilojoule of energy

A. is the energy needed to raise the temperature of one kg of water by one degree.
B. is associated with the flow of a current of one ampere for 1000 seconds at a potential difference of one volt.
C. is produced when 2 g H_2 burns in oxygen.
D. is required for the production of 1 mol of H_2 by electrolysis of water.

Question 13

Ammonia is a weak base, which ionises in water according to the equation

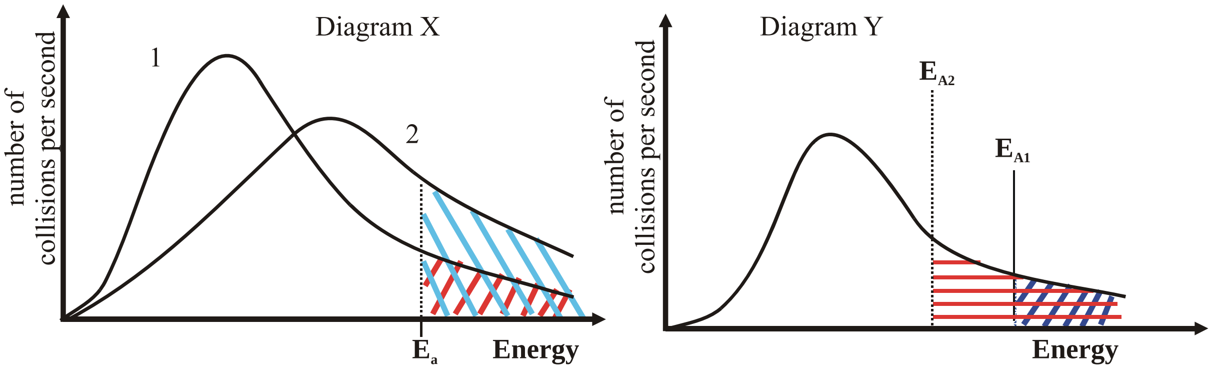
$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq).$$

If 50 mL of water is added to 50 mL of 0.20 M $NH_3(aq)$, which of the following correctly describes the expected change in pH of the solution, and percentage ionisation of NH_3, due to the dilution.

A. pH increases, percentage ionisation increases.
B. pH decreases, percentage ionisation increases.
C. pH increases, percentage ionisation decreases.
D. pH decreases, percentage ionisation decreases.

Question 14

Diagrams X and Y below show, in graphical form, the number of molecular collisions per second against collision energy, for two different factors that influence reaction rate.



The factors represented in each diagram are

A. X – concentration, Y – use of a catalyst.
B. X – use of a catalyst, Y – temperature.
C. X – temperature, Y – pressure.
D. X – temperature, Y – use of a catalyst.

Question 15

Consider the equilibrium: $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g);\ \Delta H = -113\,\text{kJ mol}^{-1}$

A piston contains an equilibrium mixture of NO(g), O_2(g) and NO_2(g) at 300°C.
Which one of the following changes would **not** increase the amount of NO_2 in the equilibrium mixture when equilibrium is re-established after the change?

A. Decreasing the temperature to 200°C.
B. Decreasing the volume of the system at constant temperature.
C. Adding nitrogen gas at constant volume.
D. Adding air at constant volume.

Question 16

Ammonia and chlorine gas react according to the equilibrium equation

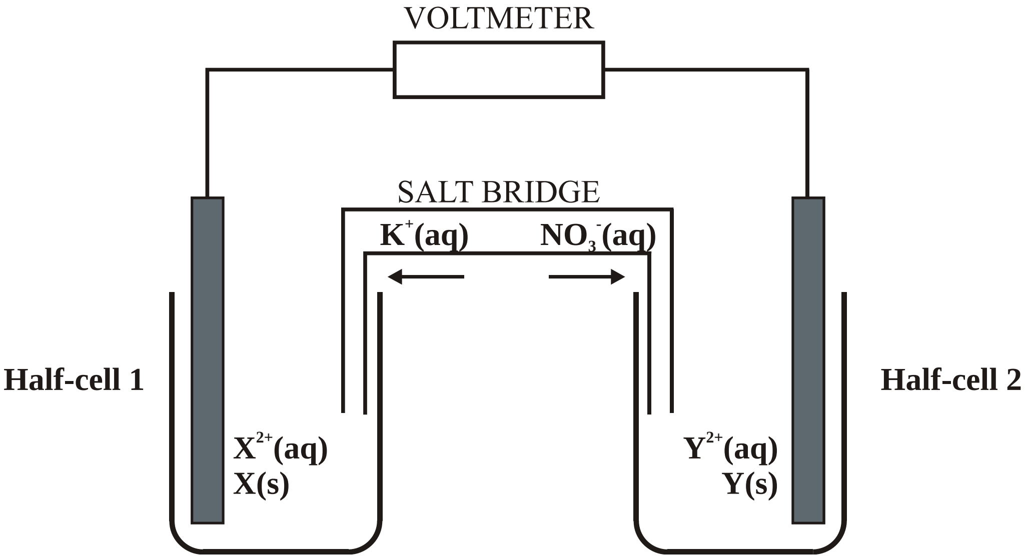
$$NH_3(g) + 3Cl_2(g) \rightleftharpoons NCl_3(g) + 3HCl(g)$$

In an experimental investigation, a mixture of 3 mol NH_3 and 10 mol Cl_2 is allowed to reach equilibrium. The amount of NCl_3 present in the equilibrium mixture is **most likely** to be

A. 2 mol
B. 3 mol
C. 10 mol
D. 13 mol

Question 17

Consider the galvanic cell represented below.



Which of the following deductions about this cell is correct?

A. Oxidation is occurring in half-cell 2.
B. The positive electrode is in half-cell 2.
C. Oxidation is occurring in half-cell 1.
D. The negative electrode is in half-cell 1.

Question 18

When a sample of pure octane undergoes complete combustion at 100 % efficiency, 200 MJ of energy is released at SLC. What was the mass of the octane sample?

A. 4.17 g
B. 4.17 kg
C. 36.6 g
D. 36.6 kg

Question 19

The half-equation for the reaction occurring at the (+) electrode in a hydrogen-oxygen fuel which has an alkaline electrolyte would be

A. $H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-$
B. $H_2(g) \rightarrow 2H^+(g) + 2e^-$
C. $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$
D. $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

Question 20

Consider the thermochemical equations

$N_2O_4(g) \rightarrow 2NO_2(g);$ $\Delta H = +57.9$ kJ mol^{-1}

$2NO(g) + O_2(g) \rightarrow 2NO_2(g);$ $\Delta H = -113.1$ kJ mol^{-1}

On the basis of this information ΔH for the reaction

$2NO(g) + O_2(g) \rightarrow N_2O_4(g)$

would be

A. -55.2 kJ mol^{-1}
B. +55.2 kJ mol^{-1}
C. -171 kJ mol^{-1}
D. +171 kJ mol^{-1}

End of Section A

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SECTION B – Short Answer Question

Section B consists of 6 short answer questions.
You should answer all of these questions.
This section is worth approximately 66 per cent of the total marks available.
The marks allotted are shown at the end of each part of each question.
Questions should be answered in the spaces provided.

Question 1

Many chemical reactions do not proceed to completion. Actual product yields lower than those theoretically calculated on the basis of a complete reaction, are quite common. Reactions that do not proceed to completion reach chemical equilibrium.
In Unit 4 you were required to study the industrial production of one of the following chemicals: ammonia, ethene, sulphuric acid or nitric acid.

a. Write the chemical formula of the chemical you studied.

(1 mark)

b. i. Write a balanced equation for an equilibrium reaction associated with the 'industrial production of the selected chemical' which you studied in this unit.

(1 mark)

ii. When the reactants involved in this reaction are added to a reaction vessel, what condition is necessary for reaction to commence?

(1 mark)

iii. Explain **how**, once reaction has commenced, it eventually reaches equilibrium?

(4 marks)

iv. For each of the following changes to the equilibrium reaction, state the effect on the position of equilibrium, i.e. moves left *or* moves right *or* no effect.

Increasing pressure ________________________________

Decreasing temperature ______________________________

(2 marks)

c. Write a balanced equation for the reaction that occurs between your selected chemical and water.

(1 mark)

Total 10 marks

Question 2

A key chemical characteristic of fuel cells is that the overall reaction is the same as the combustion reaction of the fuel which is used in the cell.

a. Write a balanced equation for the combustion of methane.

(1 mark)

b. What is the main energy transformation occurring in an operating fuel cell?

(1 mark)

c. Why are fuel cells more efficient than conventional chemical fuel fired power stations?

(1 mark)

Types of fuel cell are usually characterised by their electrolyte, temperature of operation, transported ion and fuel. In the March 2011 edition of 'Technology Review' published by MIT the following description was given of Solid Oxide Fuel Cells (SOFC).

Solid-oxide fuel cells, which can run a variety of fuels including diesel or natural gas, bring in oxygen from the air to be reduced at the cathode, and then pass the oxygen [oxide] ions through a solid-oxide electrolyte membrane to the anode, where the fuel is oxidized to produce electrons that are drawn out of the device. Their high operating temperatures are dictated by the fact that the ions move more quickly through the electrolyte at higher temperatures (500-1000 °C).

d. Assuming the fuel used in an SOFC is methane, write balanced half-equations for the reactions at

   i. the (-) electrode

(1 mark)

   ii. the (+) electrode

(1 mark)

e. Why could the operating voltage of a SOFC not be accurately predicted from a standard electrochemical series?

(1 mark)

Another type of fuel cell is the Polymer Electrolyte Membrane Fuel Cell (PEMFC). This fuel cell uses hydrogen as its fuel, operates between 20°C and 80°C, and the membrane only allows the conduction of cations.

f. Write half-equations for the reactions occurring at

   i. the anode

(1 mark)

   ii. the cathode

(1 mark)

g. Write a balanced equation for the overall PEMFC reaction.

(1 mark)

Total 9 marks

Question 3

Methanoic acid, HCOOH, is a weak acid. An 18.5 mL sample of an aqueous solution of methanoic acid required 17.25 mL of 0.155 M NaOH to reach the endpoint in a titration.

a. Calculate the amount, in mole, of methanoic acid in the sample.

(1 mark)

b. i. Write the equilibrium law associated with an aqueous solution of methanoic acid.

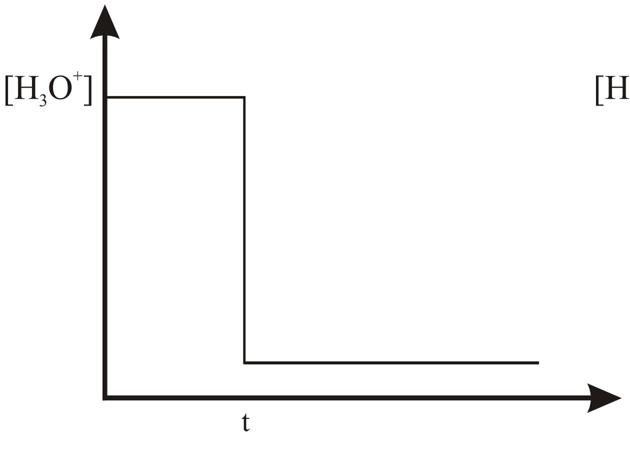
(1 mark)

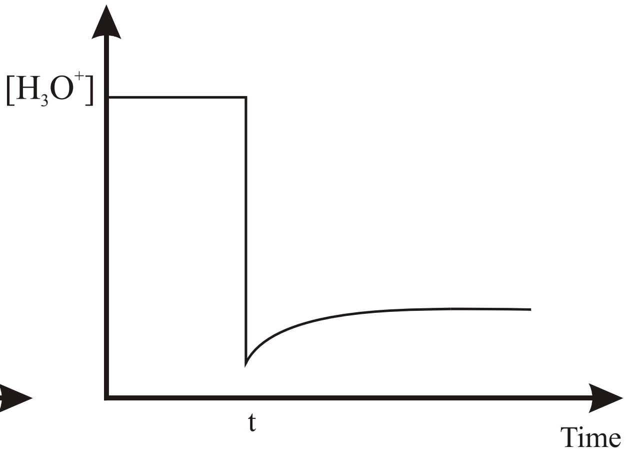
ii. Calculate the pH of the methanoic acid solution.

(4 marks)

c. A 10 mL sample of this methanoic acid solution was diluted to 100 mL with water.

i. Which of the graphs shown below best represents the change in $[H_3O^+]$ as a result of this dilution? Circle your chosen graph.





Explain the shape of your chosen graph.

(2 marks)

ii. What does the graph chosen in (i) indicate about the effect of dilution on the pH of an aqueous solution of methanoic acid?

(2 marks)

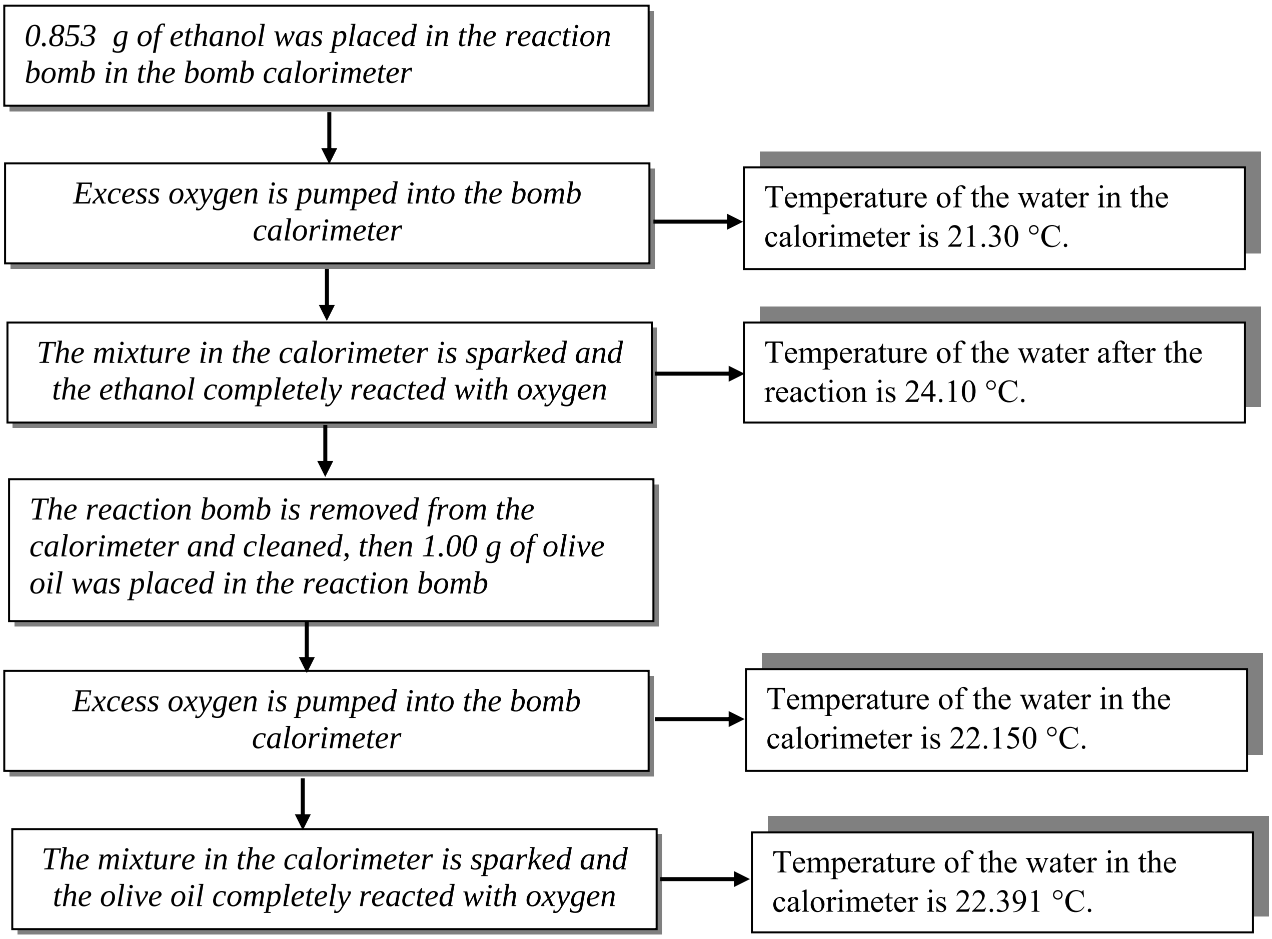
iii. In terms of the dilution of an acid, what does the other graph represent?

(1 mark)

Total 11 marks

Question 4

The energy content of olive oil was determined by bomb calorimetry. The procedure followed is described in the flowchart below.



0.853 g of ethanol was placed in the reaction bomb in the bomb calorimeter

Excess oxygen is pumped into the bomb calorimeter

Temperature of the water in the calorimeter is 21.30 °C.

The mixture in the calorimeter is sparked and the ethanol completely reacted with oxygen

Temperature of the water after the reaction is 24.10 °C.

The reaction bomb is removed from the calorimeter and cleaned, then 1.00 g of olive oil was placed in the reaction bomb

Excess oxygen is pumped into the bomb calorimeter

Temperature of the water in the calorimeter is 22.150 °C.

The mixture in the calorimeter is sparked and the olive oil completely reacted with oxygen

Temperature of the water in the calorimeter is 22.391 °C.

a. Calculate the calorimeter constant of the calorimeter in kJ K^{-1}.

(2 marks)

b. Calculate the energy released, in kJ, by the combustion of the olive oil in the calorimeter.

(1 mark)

c. Assuming that the olive oil is pure glyceryl trioleate, $C_{57}H_{104}O_6$, calculate the heat of combustion of olive oil, in kJ mol^{-1}.

(2 marks)

d. Write a balanced thermochemical equation for the combustion of glyceryl trioleate.

(3 marks)

e. If all the energy released by 1.00 g olive oil was transferred with 100 % efficiency to water, what mass of water would experience a temperature rise of 1.49°C?

(2 marks)

Total 10 marks

Question 5

At 460°C, the equilibrium reaction

$$SO_2(g) + NO_2(g) \rightleftharpoons NO(g) + SO_3(g)$$

has $K_c = 80.6$

A reaction flask, at 460°C, contains all four gases at the following concentrations:
$[SO_2] = 0.00250$ M, $[NO_2] = 0.00350$ M, $[NO] = 0.0250$ M, $[SO_3] = 0.0400$ M.

a. Calculate the pressure, in atm, in the reaction vessel when these concentrations were measured.

(3 marks)

b. i. Show that the reaction mixture is not at equilibrium and indicate the direction in which the reaction must shift to get to equilibrium.

(2 marks)

ii. How is it possible to tell, from pressure measurements, when the system has reached equilibrium?

(1 mark)

c. Subsequent testing shows that when equilibrium is established, all concentrations have changed, i.e. increased or decreased, by 0.00050 mol L^{-1}.
Calculate the pressure, in kPa, in the reaction vessel at equilibrium.

(1 mark)

d. The equilibrium between the weak acid carbonic acid and its conjugate base will resist changes in pH and is known as a buffer system. This equilibrium is described by the equation

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$$

This acts as a buffer system in blood.
Buffers are vital in almost all biological systems where a change in pH can affect the functioning of a cell. To prevent this happening, many pharmaceuticals, e.g. eye drops, are buffered. Buffered systems respond to change in such a way as to keep the pH constant.
The behaviour of a buffer system can be predicted or described by use of Le Chatelier's principle.

i. State Le Chatelier's principle.

(1 mark)

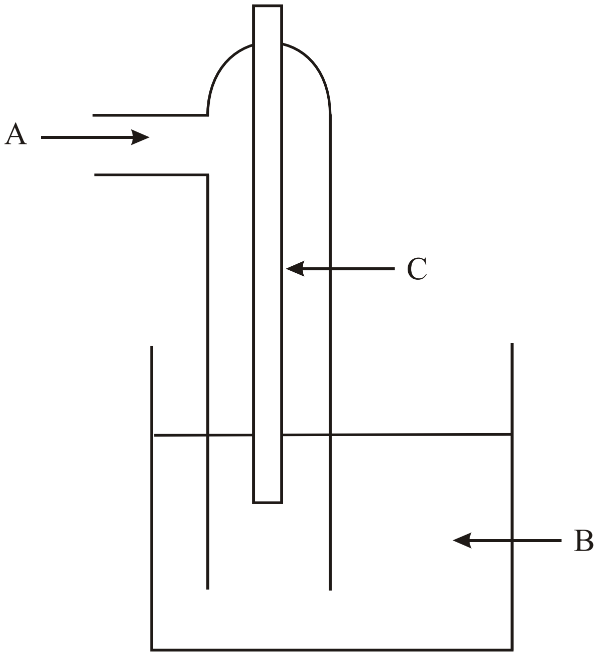
ii. How does Le Chatelier's principle suggest this buffer system will respond to an increase in pH of blood and why is this response consistent with relative reaction rates?

(2 marks)

Total 10 marks

Question 6

a. The diagram shown below represents a half-cell set up for use in a galvanic cell in which one of the components of the redox pair which constitute the half-cell is a gas.



i When this half-cell is connected to a Cu^{2+}(aq)/Cu(s) half-cell under standard conditions, the cell voltage as predicted from the electrochemical series would be 1.02 V.
Write the chemical formulae and states for the species, A, B and C, present in the half-cell.

A.___________

B.___________

C.___________

(3 marks)

ii. In terms of the solutions in the half-cells of a galvanic cell set up in a laboratory, explain why a salt bridge is essential to the operation of the cell and describe how and why it interacts with the half-cell containing the cathode in the half-cell identified in (i).

(3 marks)

iii. Why is silver nitrate, $AgNO_3$, not an appropriate salt to use in the salt bridge in a cell containing the Cl_2(g)/Cl^-(aq) half-cell?

(1 mark)

b. In an extended electrochemical series the following half-equations appear

$O_3(g) + H_2O(l) + 2e^- \rightleftharpoons O_2(g) + 2OH^-(aq)$ $E^0 = +1.24$ V

$In^{3+}(aq) + 3e \rightleftharpoons In(s)$ $E^0 = -0.34$ V

$Y^{3+}(aq) + 3e^- \rightleftharpoons Y(s)$ $E^0 = -2.37$ V

i. In terms of definitions of reduction, what is unusual about the ozone, O_3, half-equation?

(1 mark)

ii. Write half-equations for the electrode reactions occurring during the electrolysis of a 1 M aqueous solution of yttrium(III) chloride, $YCl_3(aq)$.
(-) electrode

(+) electrode

(2 marks)

iii Electrolysis of 1 M aqueous solution of indium(III) nitrate using a consistent current of 2.51 A, produced 0.448 g of non-aqueous product at the (-) electrode. Given that 75 % of the electrical energy was converted to chemical energy, for how long, in minutes, did the electrolysis proceed?

(5 marks)

Total 15 marks

End of Section B

End of Trial Exam

Suggested Answers

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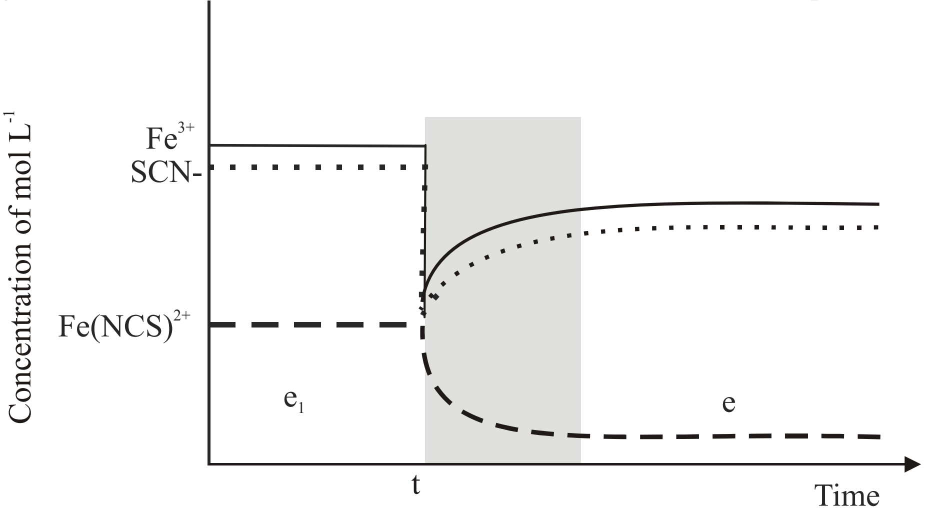
SECTION A – Multiple Choice Answers

Q1 A In the Data Book the specific heat capacity of water is given as 4.18 J g^{-1} $°C^{-1}$. 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 J $°C^{-1}$ 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 °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 $Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons Fe(NCS)^{2+}(aq)$ causes all concentrations to decrease and the reaction quotient (concentration fraction) $[Fe(NCS)^{2+}] / \{[Fe^{3+}][SCN^{-}]\}$ to become > K.
So to get back to equilibrium, the position of equilibrium moves to the left, producing more $Fe^{3+}(aq)$ and $SCN^{-}(aq)$. However, as the concentration-time graph below shows, the increase in amounts of $Fe^{3+}(aq)$ and $SCN^{-}(aq)$ 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 $[Fe(NCS)^{2+}]$ is lower, $n(Fe(NCS)^{2+})$ is lower; $[SCN^{-}]$ is lower, $n(SCN^{-})$ is higher; $[Fe^{3+}]$ is lower, $n(Fe^{3+})$ is higher.

Q3 B Original equilibrium equation

$NO(g) + ½O_2(g) \rightleftharpoons NO_2(g)$; $\Delta H = -57.0\ kJ\ mol^{-1}; K = 843$

To get to the required equilibrium equation, the original equilibrium equation needs to be doubled and then reversed

1. Original equation doubled.
   ΔH value doubled, K value raised to power 2
   $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$; $\Delta H = -57.0x2\ kJ\ mol^{-1}; (K = 843^2)$
   $\Delta H = -114\ kJ\ mol^{-1}; K = 7.11x10^5$
2. Equation from 1. is reversed
   Sign of previous ΔH value is swapped, reciprocal of previous K value taken.
   $\mathbf{2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g);}$ $\Delta H = +114\ kJ\ mol^{-1}; K = 1 / (7.11x10^5)$
   $\mathbf{\Delta H = +114\ kJ\ mol^{-1}; K = 1.41x10^{-6}}$

Q4 C According to the equation, 5 mol $C_6H_{12}O_6$ releases 11925 kJ of energy.

So **1 mol $C_6H_{12}O_6$** → 11 925 / 5 = **2385 kJ**

According to information in Table 13 of the Data Book,

the **combustion of 1 mol $C_6H_{12}O_6$ releases 2816 kJ**

The maximum amount of energy available from 1 mol $C_6H_{12}O_6$ in the bacteria driven reaction is **less** than that available from the combustion of 1 mol $C_6H_{12}O_6$.

Q5 D The rate-time graphs show:

Q6 C

1. The rates of the forward and reverse reactions are initially equal – the system is at equilibrium.
2. 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.
3. 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.**

A. Adding more reactant would cause a sudden increase in the rate of the forward reaction only.
B. A temperature decrease would cause a decrease in reaction rates.
C. Removing some product would cause a sudden decrease in the rate of the reverse reaction only.
D. 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

$Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq)$ 1.09 V

$Fe^{3+}(aq) + e^- \rightleftharpoons \mathbf{Fe^{2+}}(aq)$ 0.77 V

$\mathbf{Fe^{2+}}(aq) + 2e^- \rightleftharpoons Fe(s)$ -.0.44 V

$Zn^{2+}(aq) + 2e^- \rightleftharpoons \mathbf{Zn}(s)$ -0.76 V

These half-equations show that, depending on the species with which it is reacting, **Fe^{2+}(aq) can act as an oxidant** (oxidising Zn to Zn^{2+}) **and a reductant** (reducing Br_2 to Br^-). In these roles Fe^{2+}(aq) will be converted to Fe(s) and Fe^{3+}(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.

$$\overset{+1}{Ag_2}O(s) + \overset{0}{Zn}(s) + H_2O(l) \rightarrow 2\overset{0}{Ag}(s) + \overset{+2}{Zn}(OH)_2(s)$$

<u>Change</u> 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 H_2O – 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

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

and **H_2(g) will be evolved at the negative electrode**.

If the metal cation is the stronger oxidant, i.e. above H_2O on the electrochemical series, **it will be reduced to the solid metal.**

Consider the alternatives.

A. Oxidants Al^{3+}(aq), K^+(aq), Li^+(aq) and H_2O.
   H_2O is the stronger oxidant in all three solutions, so H_2 gas is produced at the (-) electrode in all three.

B. Oxidants Co^{2+}(aq), Cu^{2+}(aq), Ca^{2+}(aq) and H_2O.
   Both Cu^{2+}(aq) and Co^{2+}(aq) are stronger oxidants than H_2O, so Cu(s) and Co(s) will be produced with H_2(g) evolved in only one cell.

C. Oxidants Mg^{2+}(aq), Ni^{2+}(aq), K^+(aq) and H_2O.
   H_2O is a stronger oxidant than Mg^{2+}(aq) and K^+(aq), so **H_2 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), Sn^{2+}(aq), Li^+(aq) and H_2O.
   Both Ag^+(aq) and Sn^{2+}(aq) are stronger oxidants than H_2O, so Ag(s) and Sn(s) will be produced and H_2(g) evolved in only one cell.

Q10 A $Ca(OH)_2(aq) \rightarrow Ca^{2+}(aq) + 2OH^-(aq)$

pH 10.0 → $[H_3O^+] = 10^{-10}$
$= 1x10^{-10}$ M

Since $[H_3O^+][OH^-] = 10^{-14}$ at 25°
$[OH^-] = 10^{-14} / 1x10^{-10}$
$= 1x10^{-4}$ M
$= 0.0001$ M
$[Ca(OH)_2] = ½ \text{ x } [OH^-]$
$= ½$ x 0.0001
= **0.00005** M

Q11 D $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$

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.

$K_a = [H^+][A^-] / [HA]$
$= [H^+] \text{ x } ([A^-]/[HA])$
pH 4.5 → $\mathbf{[H^+]} = 10^{-4.5}$ M
$= \mathbf{3.16x10^{-5}\ M}$
$[HA] / [A^-] = 1.32x10^4 \rightarrow \mathbf{([A^-]/[HA])} = 1 / (1.32x10^4)$
$= \mathbf{7.58x10^{-5}}$
$K_a = 3.16x10^{-5} \text{ x } 7.58x10^{-5}$
$= \mathbf{2.4x10^{-9}}$

Hypobromous acid

Q12 B Consider the alternatives:

A. The specific heat capacity of H_2O is 4.18 J g^{-1} $°C^{-1}$
Energy needed to increase 1 kg H_2O by 1 °C = 4.18 x 1000 x 1
= 4180 J
= 4.18 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 x 1 x 1000
= 1000 J
= **1 kJ**

C. $n(H_2)$ = 2 g / 2.0 g mol^{-1}
= 1 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 $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$.

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 $OH^-(aq)$ present in the solution also increases.

Although there is a more **$OH^-(aq)$** it is in a **larger volume**, the amount of $OH^-(aq)$ produced in the equilibrium shift only partially compensates for the volume increase by the time equilibrium is regained.

Overall **$[OH^-]$** is **lower** → $[H_3O^+]$ is higher → **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 $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$; $\Delta H = -113 \text{ kJ mol}^{-1}$

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 $[O_2]$ 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

$NH_3(g) + 3Cl_2(g) \rightleftharpoons NCl_3(g) + 3HCl(g)$

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)

$n(C_8H_{18})$ = energy released / energy per mole C_8H_{18}
= 200×10^3 kJ / 5464 kJ mol^{-1}
= 36.6 mol

$\boldsymbol{m(C_8H_{18})}$ = 36.6 mol x 114 g mol^{-1}
= 4.17×10^3 g
= **4.17 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**.

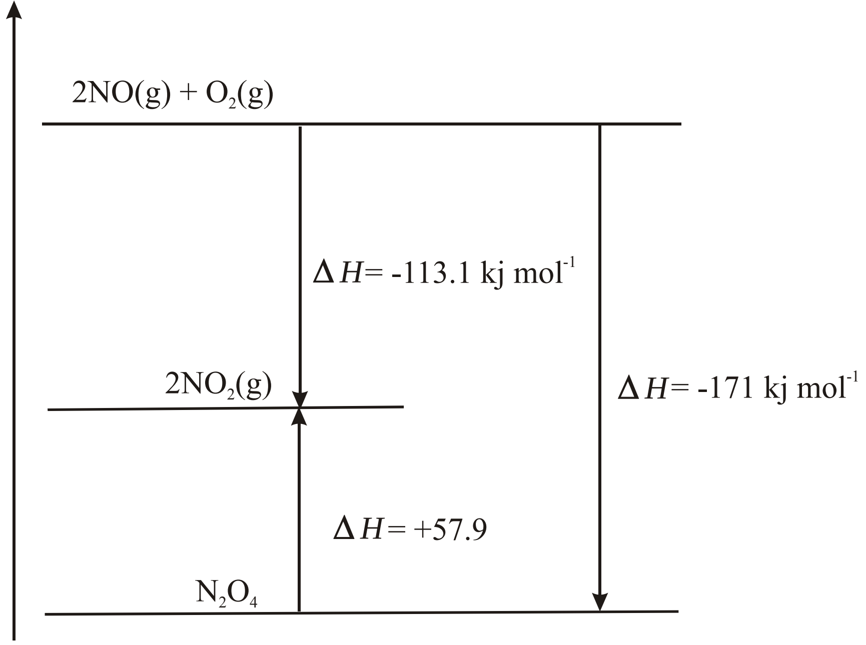
In a fuel cell, the fuel is oxidised at the (-) electrode and **$O_2(g)$ is reduced at the (+) electrode**. In a H_2-O_2 v fuel cell, H_2 is the fuel.

An alkaline electrolyte contains **$OH^-(aq)$ ions**.

Then it is a case of effective use of the electrochemical series – identifying the half-equation which includes both $O_2(g)$ and $OH^-(aq)$, i.e.

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

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



The profile enables you to deduce
$2NO_2(g) \rightarrow N_2O_4(g)$; ΔH = -57.9 kJ mol^{-1}
So the combination of
$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$; ΔH = -113.1 kJ mol^{-1}, and
$2NO_2(g) \rightarrow N_2O_4(g)$; ΔH = -57.9 kJ mol^{-1}
produces
$2NO(g) + O_2(g) \rightarrow N_2O_4(g)$; **$\Delta H$ = -171 kJ mol^{-1}**

SECTION B – Short Answer (Answers)

Question 1

a. NH_3 *or* C_2H_4 *or* H_2SO_4 *or* HNO_3 ❶

b. i. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ *or*
$C_3H_8(g) \rightleftharpoons C_2H_4(g) + CH_4(g)$ / other cracking equation with C_2H_4 as a product *or*
$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ *or*
$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$ / $2NO_2(g) \rightleftharpoons N_2O_4(g)$ ❶

ii. For reaction to commence the **reactant particles must have energy equal to or greater than the activation energy**. ❶

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. $2SO_2 + O_2 \rightarrow 2SO_3$) is at its **maximum**. ❶
As the **forward reaction** proceeds, its **rate decreases**, due to the **decreasing concentration** of **reactants**. ❶
Simultaneously the **concentration of the products increases**, and so the **rate of the reverse reaction** (e.g. $2SO_3 \rightarrow 2SO_2 + O_2$) **increases**. ❶
Eventually the **rates of the forward and reverse reactions become equal** and the reacting system has reached **chemical equilibrium**. ❶

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** ❶; Decreasing temperature **right** ❶
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g); \Delta H < 0$
C_2H_4: Increasing pressure **left**; Decreasing temperature **left**
$C_3H_8(g) \rightleftharpoons C_2H_4(g) + CH_4(g) ; \Delta H > 0$
H_2SO_4: Increasing pressure **right**; Decreasing temperature **right**
$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g); \Delta H < 0$
HNO_3: Increasing pressure **right**; Decreasing temperature **right**
$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g); \Delta H < 0$ / $2NO_2(g) \rightleftharpoons N_2O_4(g); \Delta H < 0$

c. $NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$ ❶
$C_2H_4(g) + H_2O(g) \rightleftharpoons CH_3CH_2OH(l)$
$H_2SO_4(l) + H_2O(l) \rightarrow HSO_4^-(aq) + H_3O^+(aq)$
$HNO_3(l) + H_2O(l) \rightarrow NO_3^-(aq) + H_2O(l)$

Question 2

a. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g \text{ or } l)$ ❶

b. Chemical → Electrical ❶

c. In a **fuel cell the conversion from chemical energy to electrical energy is direct** and hence more efficient than the **multistep conversion (chemical → thermal → mechanical → electrical) of a conventional fuel (gas) fired power station**. ❶

d. i. (-) electrode (anode) $CH_4(g) + 4O^{2-}(l) \rightarrow CO_2(g) + 2H_2O(g) + 8e^-$ ❶

ii. (+) electrode (cathode) $O_2(g) + 4e^- \rightarrow 2O^{2-}(l)$ ❶

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 $O^{2-}(l)$ ions.

e. The **operating temperature of SOFCs (500-1000°C) is well beyond the reference temperature (25°C) of the electrochemical series.** ❶

f. i. $H_2(g) \rightarrow 2H^+(aq) + 2e^-$ ❶

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

g. $2H_2(g) + O_2(l) \rightarrow 2H_2O(l)$ ❶

Question 3

a. $NaOH(aq) + HCOOH(aq) \rightarrow HCOONa(aq) + H_2O(l)$

$n(HCOOH)$ reacting $= n(NaOH)$ required
$= 0.155 \text{ mol L}^{-1} \times 17.25\times10^{-3} \text{ L}$
$= 2.67\times10^{-3} \text{ mol}$ ❶

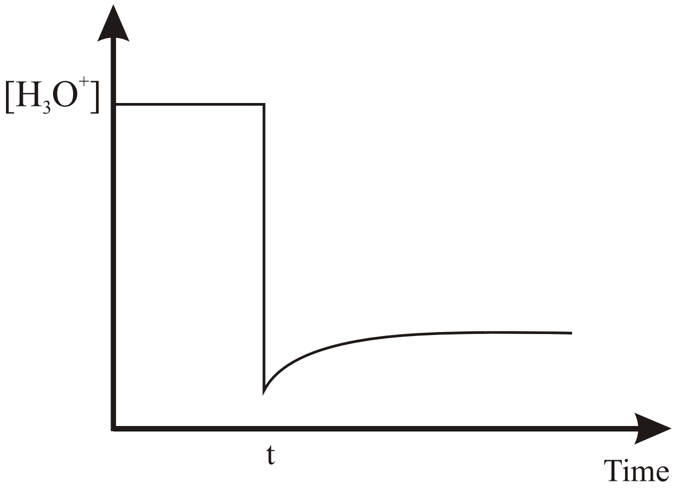
b. i. Since the equation for the ionisation of $HCOOH(aq)$ is
$HCOOH(aq) + H_2O(l) \rightleftharpoons HCOO^-(aq) + H_3O^+(aq)$
the equilibrium law is
$K_a = [HCOO^-][H_3O^+] / [HCOOH]$ ❶

ii. $K_a(HCOOH) = 1.8\times10^{-4}$ (from Data Book)
Since 18.5 mL of the methanoic acid solution contained 2.67×10^{-3} mol HCOOH
$c(HCOOH) = 2.67\times10^{-3} \text{ mol} / 18.5\times10^{-3} \text{ L}$
$= 0.144 \text{ M}$ ❶

Using the standard weak acid assumptions: $[HCOOH]_{equilibrium} = 0.144 \text{ M}$
$[HCOO^-] = [H_3O^+]$, i.e. negligible H_3O^+ from the self-ionisation of water.

$1.8\times10^{-4} = [H_3O^+]^2 / 0.144$ ❶
$[H_3O^+] = \sqrt{(0.144 \times 1.8\times10^{-4})}$
$= 5.10\times10^{-3} \text{ M}$ ❶
$pH = -\log_{10}(5.10\times10^{-3})$
$= 2.3$ ❶

c. i.



When 10 mL methanoic acid is diluted to 100 mL with water, the **$[H_3O^+]$ immediately decreases by a factor of 10**. However because the **dilution decreases all concentrations, the reaction quotient** (concentration fraction), i.e. $[HCOO^-][H_3O^+]$ / [HCOOH], decreases and **become less than K_a**. ❶For the system to return to equilibrium, the **position of equilibrium moves to the right and the $[H_3O^+]$ increases**, ❶ 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 $[H_3O^+]$ decreases then increases as the equilibrium moves to the right, the **pH will increase and then decrease**. ❶ However the **pH after dilution will be higher than before dilution** ❶
[pH of 0.0144 M HCOOH(aq) = 2.8].

iii. The **dilution of a strong acid**, e.g. HCl(aq). ❶ When HCl(aq) ionises, effectively all the HCl molecules have donated H^+(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(ethanol) used = 0.853 g / 46.0 g mol^{-1}
= 1.85x10^{-2} mol
ΔH_c(ethanol) = -1364 kJ mol^{-1} (Data Book)
Energy released = 1.85x10^{-2} mol x 1364 kJ mol^{-1}
= 25.3 kJ ❶
ΔT calibration = 24.10 - 21.30
= 2.80 °C
Calibration Constant = 25.3 kJ / 2.80°C
= 9.03 kJ °C^{-1}
= **9.03 kJ K^{-1}** ❶

*A temperature **change** is the same magnitude in both °C and K*

b. ΔT combustion of olive oil = 22.391 – 22.150
= 0.241 °C
Energy released = 9.03 kJ K^{-1} x 0.241 K
= **2.18 kJ** ❶

c. $M(C_{57}H_{104}O_6)$ = 57x12.0 + 104x1.0 + 6x16.0
= 884.0 g mol^{-1}
$n(C_{57}H_{104}O_6)$ = 1.00 g / 884.0 g mol^{-1}
= 1.13×10^{-3} mol ❶
Heat of combustion olive oil = 2.18 kJ / 1.13×10^{-3} mol
= $\mathbf{1.93 \times 10^{3}}$ **kJ** $\mathbf{mol^{-1}}$ ❶

d. This is simply a matter of effective combustion equation balancing.

1. Reactants and products
$C_{57}H_{104}O_6(l) + \_\_\_O_2(g) \rightarrow \_\_\_CO_2(g) + \_\_\_H_2O(g)$
2. Balance for ‘C’
$C_{57}H_{104}O_6(l) + \_\_\_O_2(g) \rightarrow \mathbf{57}CO_2(g) + \_\_\_H_2O(g)$
3. Balance for ‘H’
$C_{57}H_{104}O_6(l) + \_\_\_O_2(g) \rightarrow \mathbf{57}CO_2(g) + \mathbf{52}H_2O(g)$
4. Balance for ‘O’
On RHS – 2x57 + 52 = 166 ‘O’
On LHS – 6 ‘O’
So 160 ‘O’, i.e. 80 O_2 is required
$C_{57}H_{104}O_6(l) + \mathbf{80}O_2(g) \rightarrow \mathbf{57}CO_2(g) + \mathbf{52}H_2O(g)$
The thermochemical equation, which includes ΔH, is
$\mathbf{C_{57}H_{104}O_6(l) + 80O_2(g) \rightarrow 57CO_2(g) + 52H_2O(g); \Delta H = -1.93 \times 10^{3}\ kJ\ mol^{-1}}$
❶ *for correct chemical formulae and states*
❶ *for correct balancing*
❶ *for ΔH consistent with the equation.*

e. Specific heat capacity of water = 4.18 J g^{-1} K^{-1} (Data Book)
Energy into water = 4.18 J g^{-1} K^{-1} x $m(H_2O)$ x ΔT
2.18×10^{3} J = 4.18 J g^{-1} K^{-1} x $m(H_2O)$ x 1.49 K ❶
$m(H_2O)$ = 2.18×10^{3} / (4.18 x 1.49)
= **350 g** ❶

Question 5

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

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.

Q = $[NO][SO_3]$ / $[SO_2][NO_2]$
= [0.0250 x 0.0400 / 0.00250 x 0.00350]
= **114** ❶

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.** ❶

ii. When the system is at equilibrium, the **pressure will remain constant.** ❶ 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 mol L^{-1} and each product concentration decrease by 0.0050 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** ❶
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'. ❶

ii. The equilibrium system $H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$ will respond to an increase in pH, i.e. a decrease in $[H_3O^+]$, by moving to increase the $[H_3O^+]$ – and decrease the pH, by **favouring the forward reaction and moving the position of equilibrium to the right**. ❶
This occurs because **when the $[H_3O^+]$ 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. ❶

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 $Cu^{2+}(aq)/Cu(s)$ half-cell and the reductant in the 'unknown' half-cell then

$1.02\ V = E°(Cu^{2+}/Cu) – E°(\text{unknown half-cell})$
$1.02\ V = 0.34 - E°(\text{unknown half-cell})$
$E°(\text{unknown half-cell}) = 0.34 – 1.02$
$= -0.68\ V$

There is no half-cell in the electrochemical series in the Data Book with $E°= - 0.68\ V$

If the reductant was in the $Cu^{2+}(aq)/Cu(s)$ half-cell and the oxidant in the 'unknown' half-cell then

$1.02\ V = E°(\text{unknown half-cell}) – E°(Cu^{2+}/Cu)$
$1.02\ V = E°(\text{unknown half-cell}) – 0.34$
$\boldsymbol{E°}\textbf{(unknown half-cell)} = 1.02 + 0.34$
$= \mathbf{1.36\ V}$

This corresponds to the ***E***° value for the $Cl_2(g)/Cl^-(aq)$ half-cell, and the species are

A $Cl_2(g)$ ❶
B 1 M $Cl^-(aq)$ ❶
C Pt(s) *or* C(s) ❶

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.** ❶

In the $Cl_2(g)/Cl^-(aq)//Cu^{2+}(aq)/Cu(s)$ cell the cathode is in the $Cl_2(g)/Cl^-(aq)$ half-cell.

The reduction half-equation $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$ shows that the **release of Cl^-(aq) ions would increase the (-) charge in the solution around the cathode**. ❶ To counteract that situation and **keep the solution electrically neutral, cations flow through the salt bridge into the half-cell.** ❶

iii. **Ag^+(aq) ions would react with Cl^-(aq) to form insoluble AgCl.** ❶ This would interfere with the effective operation of the cell.

b. i. In the half-equation $O_3(g) + H_2O(l) + 2e^- \rightarrow O_2(g) + 2OH^-(aq)$ there is **no change in oxidation number** of any of the elements. ❶

The fundamental definition of reduction as the 'gain of electrons' applies.

ii. According to the electrochemical series, the relevant species $Y^{3+}(aq)$,$Cl^-(aq)$ and $H_2O(l)$ appear in the electrochemical series data in the half-equations.

$Cl_2(g) + 2e^- \rightleftharpoons 2\mathbf{Cl^-}(aq)$ $E° = 1.36$ V

$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2\mathbf{H_2O}(l)$ $E° = 1.23$ V

$2\mathbf{H_2O}(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$ $E° = -0.83$V

$\mathbf{Y^{3+}}(aq) + 2e^- \rightleftharpoons Y(s)$ $E° = -2.37$ V

The strongest oxidant, $H_2O(l)$, is reduced at the cathode, **the (-) electrode** , according to
$\mathbf{2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)}$ ❶
The strongest reductant, $H_2O(l)$, is oxidised at the anode, **the (+) electrode** , according to
$\mathbf{2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-}$ ❶

iii. According to the electrochemical series data, only $H_2O(aq)$ and $In^{3+}(aq)$ can be reduced at the (-) electrode (cathode).

$\mathbf{In^{3+}}(aq) + 3e^- \rightleftharpoons In(s)$ $E° = -0.34$ V

$2\mathbf{H_2O}(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$ $E° = -0.83$V

Since $In^{3+}(aq)$ is the stronger oxidant, the reductant half-equation will be
$In^{3+}(aq) + 3e^- \rightarrow In(s)$
$n(In)$ produced $= m(In) / M(In)$
$= 0.448 \text{ g} / 114.8 \text{ g mol}^{-1}$
$= 0.00390$ mol ❶
$n(e^-)$ required $= 3 \times n(In)$
$= 3 \times 0.00390$
$= 0.0117$ mol ❶
$Q = n(e^-) \times F$
$= 0.0117 \text{ mol} \times 96500 \text{ C mol}^{-1}$
$= 1.13\times10^3$ C ❶
However the conversion of electrical energy to chemical energy is only 75 % efficient, so
$1.13\times10^3 \text{ C} = 0.75 \times Q_{TOTAL}$
$Q_{TOTAL} = 1.13\times10^3 / 0.75$
$= 1.51\times10^3$ C ❶
Since $Q = It$
$t = 1.51\times10^3 \text{ C} / 2.51 \text{ A}$
$= 600$ s
= **10.0 minutes** ❶

End of Suggested Answers