CHEMICAL EQUILIBRIUM MCQ PART 1

1 In aqueous solution, an equilibrium is established between chromate, CrO_4^{2-} (yellow) and dichromate ions, $Cr_2O_7^{2-}$ (orange).

$$2CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$$

Which statement regarding the ions and the equilibrium is correct?

A The oxidation number of chromium in both chromium-containing ions is different.

B The difference in colour between CrO_4^{2-} and $Cr_2O_7^{2-}$ is due to a difference in energy gap between the 3d orbitals.

C The K_c expression for the equilibrium is $K_c = \dfrac{[Cr_2O_7^{2-}][H_2O]}{[CrO_4^{2-}]^2[H^+]^2}$.

D Increasing the pH turns the solution yellow.

2 Nitrogen dioxide dimerises in a closed system and establishes the following equilibrium:

$$2NO_2\,(g) \rightleftharpoons N_2O_4(g)$$

When 46.0 g of NO_2 was introduced into an evacuated rigid vessel with an initial pressure 2 atm at constant temperature, the apparent M_r value of the equilibrium mixture is 64.4.

What is the K_p value of this equilibrium?

A 0.281
B 0.556
C 0.778
D 1.11

3 The rates of the reversible reaction to produce ammonia in a closed vessel can be affected by changing the pressure of reactants or adding a catalyst.

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

Which of the following statements about the system are correct?

1 Increasing partial pressure of nitrogen increases the rate of the forward reaction.
2 Decreasing the partial pressure of nitrogen increases the rate of the reverse reaction.
3 Adding a catalyst does not affect the value of the rate constant, *k*.
4 Adding a catalyst reduces the activation energies for both the forward and reverse reaction.

A 1, 2 and 4
B 2, 3 and 4
C 2 and 3
D 1 and 4 only

4 Nitrogen dioxide can decompose to form nitrogen monoxide and oxygen.

$$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$$

When 2.50 mol of nitrogen dioxide was allowed to undergo decomposition in a 0.8 dm^3 container, 0.528 mol of oxygen was present at equilibrium.

What is the numerical value of the equilibrium constant, K_c, for this reaction?

A 0.282 **B** 0.353

C 2.83 **D** 3.54

5 The formation of sulfur trioxide from sulfur dioxide and oxygen is a reversible reaction.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H = -197 \text{ kJ mol}^{-1}$$

Which statements about this equilibrium are correct?

1 The K_c value will be halved if the stoichiometric coefficients in the equation are halved.

2 At dynamic equilibrium, the rates of the forward and backward reactions are equal to zero.

3 An increase in pressure of the system will result in a greater yield of SO_3 at equilibrium.

4 When temperature is reduced, the rate constant of the forward reaction, k_f, decreases to a smaller extent than that of the backward reaction, k_b.

A 3 and 4 only **B** 1 and 2 only

C 2, 3 and 4 only **D** 1 and 3 only

6 Which statement is correct to describe the spontaneity of reaction **I**?

reaction **I** $T(aq) + U(s) \rightarrow V(aq) + W(g)$

A Reaction **I** is only spontaneous at low temperatures if the reaction is endothermic.

B Reaction **I** is only spontaneous at low temperatures if the reaction is exothermic.

C Reaction **I** is spontaneous at all temperatures if the reaction is endothermic.

D Reaction **I** is spontaneous at all temperatures if the reaction is exothermic.

7 Known amount of hydrogen and iodine are allowed to come to equilibrium at 500 °C in a vessel of known volume.

$$H_2 + I_2 \rightleftharpoons 2HI$$

From which experimental method can K_c be found?

A Measuring the total pressure in the vessel.

B Slow cooling to 20 °C, breaking open the vessel under aqueous potassium iodide, and titrating the iodine present with aqueous sodium thiosulfate.

C Rapid cooling to 20 °C, breaking open the vessel under aqueous potassium iodide, and titrating the iodine present with aqueous sodium thiosulfate.

D Withdrawal of a measured sample of the equilibrium mixture, followed by complete decomposition of the hydrogen iodide present, and then titrating the total amount of iodine with aqueous sodium thiosulfate.

8 Consider the following equilibrium for the adsorption of gas **G** on the active sites of a metal catalyst, **M**:

$$\mathbf{G}\,(g) + \mathbf{M}\,(s) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathbf{GM}(s) \qquad \Delta H < 0$$

where k_1 is the rate constant for the adsorption, and
k_2 is the rate constant for the desorption.

The percentage occupancy, θ, of metal surface by gas **G** can be represented as:

$$\theta = \frac{\frac{k_1}{k_2} p_G}{1 + \frac{k_1}{k_2} p_G}$$

where p_G is the partial pressure of gas **G**.

Which of the following statements is correct regarding the above system?

A K_p of the system increases with increasing temperature.

B K_p of the system is equal to its K_c.

C The greater the total surface area of the metal catalyst, the greater the percentage occupancy, θ, of the metal surface by gas **G**.

D At high pressures of gas **G**, increasing the temperature does not increase the percentage occupancy, θ, of the metal surface by gas **G**.

9 Silver ions can be used as an alternative disinfecting agent for public swimming pools. The Ag^+ concentration needs to be between 1.0×10^{-7} mol dm^{-3} and 1.0×10^{-6} mol dm^{-3} for effective disinfection.

Saturated solutions of four different compounds were prepared by stirring an excess of each compound in pure water. Which of the following compounds would provide the necessary silver ion concentration required for disinfection?

	compound	K_{sp}
A	Ag_2CO_3	8.1×10^{-12}
B	$AgCl$	1.8×10^{-10}
C	$AgBr$	5.4×10^{-13}
D	$AgIO_3$	3.2×10^{-8}

10 Which statement about the Haber process for the manufacture of ammonia is correct?

A At higher temperatures, the yield decreases but the rate of production of ammonia is faster.

B At lower temperatures, the value of K_p decreases.

C At higher pressures, the yield decreases but the rate of production of ammonia is faster.

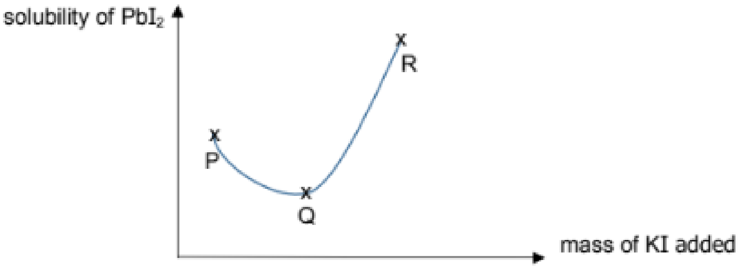
D In the presence of a catalyst, the yield decreases but the rate of production of ammonia is faster.

11 0.50 moles of CH_3CO_2H and 0.50 moles of CH_3CH_2OH were mixed and an esterification reaction took place. The equilibrium constant for this reaction is 4.0.

What is the amount of CH_3CO_2H (in moles) in the mixture at equilibrium?

A 0.17 **B** 0.25 **C** 0.33 **D** 0.67

12 The following graph represents how the solubility of a sparingly soluble salt lead(II) iodide, PbI_2, changes upon addition of solid potassium iodide at a fixed temperature.



Which statement about the above graph is **not** correct?

A The change in solubility along PQ is due to common ion effect.

B The change in solubility along QR is due to the formation of a complex between Pb^{2+} and I^-.

C At Q, the molar concentration of I^- ions is twice that of Pb^{2+} ions.

D K_{sp} remains constant along PR.

13 Gas **A** decomposes to two other gases, **B** and **C**, according to the equation:

$$2\mathbf{A}(g) \rightleftharpoons 3\mathbf{B}(g) + \mathbf{C}(g) \qquad \Delta H = +x\ \text{kJ mol}^{-1}$$

Which of the following correctly describes what will happen if a proposed change is made to this system at equilibrium?

	proposed change	value of K_c	position of equilibrium
A	add inert solid	no change	shift left
B	increase pressure	no change	shift right
C	increase temperature	increase	shift right
D	add catalyst	increase	no change

14 The solubility product of a substance is ***S***. If the concentration of the cation in a saturated solution is found to be $\binom{9S}{4}\frac{1}{5}$, what could be the substance?

- **A** $CaCl_2$
- **B** $Ca_3(PO_4)_2$
- **C** $Al(OH)_3$
- **D** $Al_2(SO_4)_3$

15 Nitrogen and hydrogen form ammonia in an exothermic reaction. The rate and yield of the reaction can be altered by changing the experimental conditions.

Which row correctly describes the effect of the changes in condition?

	change in condition	effects		
		equilibrium yield	rate of forward reaction	rate of backward reaction
1	increasing temperature	decreases	increases	increases
2	increasing temperature	increases	decreases	increases
3	addition of catalyst	increases	increases	no effect
4	addition of catalyst	no effect	increases	increases

A 1 and 4 only **B** 2 and 4 only **C** 2 and 3 only **D** 1 and 3 only

16 Solid calcium hypochlorite pellets, $Ca(ClO)_2(s)$, are added to swimming pools to form $HClO(aq)$ which kills disease-causing bacteria and algae.

$$Ca(ClO)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2ClO^-(aq)$$

$$ClO^-(aq) + H_2O(l) \rightleftharpoons HClO(aq) + OH^-(aq)$$

What is the effect on the solubility of calcium hypochlorite and bacterial growth when pH increases?

	effect on solubility of calcium hypochlorite	effect on bacterial growth
A	decreases	increases
B	decreases	decreases
C	increases	increases
D	increases	decreases

17 In the Haber process, nitrogen and hydrogen is passed over a hot catalyst to produce ammonia.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H < 0$$

Which row correctly describes the operating condition and the possible reason? [POE – position of equilibrium]

	operating condition	reason
A	500 atm	high pressure to shift POE to the right
B	500 °C	high temperature to increase rate of reaction
C	60 atm	low pressure to shift POE to the right
D	60 °C	low temperature to shift POE to the right

18 Ammonium carbamate, NH_2COONH_4, undergoes thermal decomposition.

$$NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g) \qquad \Delta H > 0$$

A vessel containing only NH_2COONH_4 is heated to 250 °C. The reaction reached equilibrium at time t_1. Subsequently both the temperature and volume of the vessel are decreased, and the reaction established a new equilibrium at time t_2.

Which statements are correct?

1 At t_2, $P_{NH_3} : P_{CO_2}$ is 2 : 1.
2 The rate of the forward reaction at t_1 is the same as that at t_2.
3 The degree of decomposition of NH_2COONH_4 at t_1 is smaller than that at t_2.
4 Decreasing the volume of the vessel at constant temperature has no effect on the equilibrium partial pressures of NH_3 and CO_2.

A 2 only
B 1 and 3
C 1 and 4
D 2 and 3

19 When a sample of iron(II) sulfate, $FeSO_4$, is heated to 920 K, reactions 1 and 2 occurred.

reaction 1 $2FeSO_4(s) \rightleftharpoons Fe_2O_3(s) + SO_3(g) + SO_2(g)$ K_1

reaction 2 $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ K_2

At equilibrium, the total pressure is 0.836 atm and the partial pressure of oxygen is 0.0275 atm.

What is the value of K_2 at 920 K?

A 0.000147
B 0.0362
C 0.0476
D 0.160

20 Some equilibria, and the value of their equilibrium constants at 298 K, are given below.

$Cu^+(aq) + Cl^-(aq) \rightleftharpoons CuCl(s)$ $K_1 = 8.33 \times 10^5$

$CuCl(s) + Cl^-(aq) \rightleftharpoons CuCl_2^-(aq)$ $K_2 = 0.104$

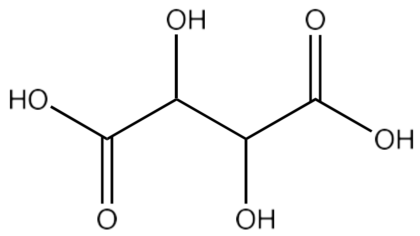
$Cu^+(aq) + 2Cl^-(aq) \rightleftharpoons CuCl_3^-(aq)$ $K_3 = z$

Which row is correct?

	z	value of solubility product of CuCl(s) at 298 K
A	8.66×10^4	1.10×10^{-3}
B	8.66×10^4	1.20×10^{-6}
C	8.01×10^6	1.10×10^{-3}
D	8.01×10^6	1.20×10^{-6}

CHEMICAL EQUILIBRIUM STRUCTURED QUESTIONS PART 1

1 **(a)** Tartaric acid is a white crystalline diprotic organic acid. It can be synthesised from ethene in four steps.



Tartaric acid

$$\text{ethene} \xrightarrow{\text{Step 1}} \textbf{A} \xrightarrow{\text{Step 2}} \underset{(C_2H_2O_2)}{\textbf{B}} \xrightarrow{\text{Step 3}} \textbf{C} \xrightarrow{\text{Step 4}} \text{Tartaric Acid}$$

Draw the structures of the intermediates, **A**, **B** and **C**, and give the required reagents and conditions for each step of the conversion. [7]

2 **(b)** Salts of tartaric acid are known as tartrates or hydrogen tartrates. One of these salts, potassium hydrogen tartrate, $KC_4H_5O_6$, is a weak monobasic acid and is sparingly soluble in water.

An experiment was conducted to determine the K_{sp} of the salt, $KC_4H_5O_6$. 1.00 g of the salt, $KC_4H_5O_6$ was dissolved in a beaker containing 100 cm^3 of water and was stirred constantly for 15 minutes at constant temperature, until a saturated solution was produced.

20.0 cm^3 of the filtered solution was titrated against 0.035 mol dm^{-3} NaOH, using phenolphthalein as an indicator. The volume of NaOH needed for the indicator to change colour is 12.50 cm^3.

(i) Calculate the initial concentration of potassium hydrogen tartrate used in the titration. [1]

(ii) Hence, calculate the K_{sp} value of potassium hydrogen tartrate. [1]

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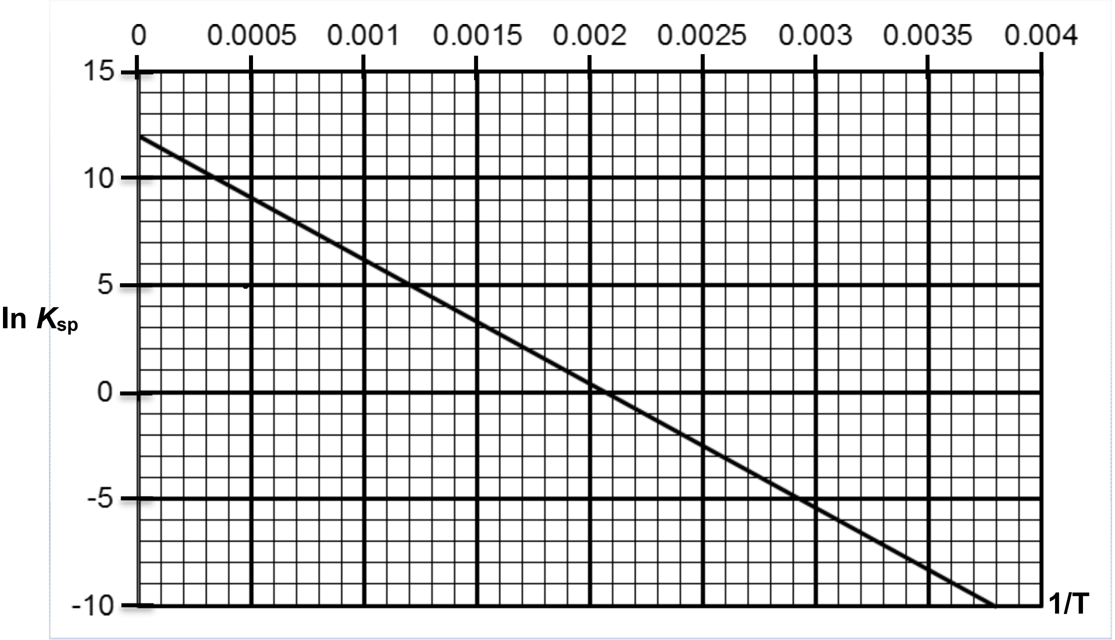
2 **(c)** The van 't Hoff equation relates equilibrium constants to enthalpy (ΔH) and entropy changes (ΔS) as follows:

$$\ln K_{sp} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

where R is the molar gas constant and T is measured is in Kelvin.
The titration in **(b)** was repeated at different temperatures and the following results were obtained.



(i) Using the information provided, calculate ΔH and ΔS for the dissolution of potassium hydrogen tartrate in water. [2]

(ii) Hence, predict the temperature at which potassium hydrogen tartrate becomes soluble in water. [1]

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2 **(d)** At 800 K, nitrogen monoxide reacts with hydrogen as shown below in an enclosed gas tank.

$$2H_2(g) + 2NO(g) \rightarrow 2H_2O(g) + N_2(g)$$
$$\text{rate} = k(P_{H_2})(P_{NO})^2$$

On the same axes, sketch suitable graphs to illustrate clearly how the rate of reaction would vary when partial pressures of

(i) H_2
(ii) and NO

is increased respectively. [1]

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2 **(e)** Nitrogen dioxide, NO_2, is an air pollutant produced from volcanic eruptions and combustion of fossil fuels in automobile engines.

(i) Draw the dot-and-cross diagram for nitrogen dioxide, NO_2, molecule stating its shape and bond angle. [2]

(ii) A 1.00 dm^3 gas cylinder is used to store 35.0 g of NO_2 at 25° C. The gas cylinder is fitted with a safety valve that will rupture when there is a great difference between the internal pressure and the atmospheric pressure.
The gas cylinder fitted with a burst disc can withstand a pressure difference of 2500 kPa.
Calculate the pressure exerted by NO_2 at 25° C in kPa. [1]

(iii) Assuming the atmospheric pressure is 101 kPa, calculate the maximum internal pressure of the gas cylinder. [1]

(iv) Hence, determine the maximum temperature that this gas cylinder can be exposed to before the burst disc ruptures. [1]

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2 **(f)** A gas tank contains a mixture of NO_2 and monoatomic gas **A** in the ratio of 4:1. At 300 K, the total pressure of the gas mixture is 100 kPa.

(i) Given that the density of the gas mixture is 1638 g m^{-3}, calculate the average relative molecular mass of the mixture to 1 decimal place. [1]

(ii) Hence, calculate the A_r of monoatomic gas **A** and suggest its identity. [2]

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[Total: 21]

3 This question is about nitrogen containing compounds.

(a) Nitrogen monoxide reacts with chlorine to form nitrosyl chloride, according to the equation:

$$2NO(g) + C\mathit{l}_2(g) \rightarrow 2NOC\mathit{l}(g)$$

In an experiment, student **A** kept the amount of $C\mathit{l}_2(g)$ in large excess while the initial partial pressure of NO(g) was varied at constant temperature of 550 K.

The table below shows the experimental results obtained.

time / s	P_{NO} / atm	(Rate / P_{NO}) / s^{-1}	(Rate / $(P_{NO})^2$) / (atm $^{-1}$ s^{-1})
0	0.917	1.033×10^{-4}	1.126×10^{-4}
1000	0.827	9.312×10^{-5}	1.126×10^{-4}
2000	0.753	8.486×10^{-5}	1.127×10^{-4}
3000	0.691	7.788×10^{-5}	1.127×10^{-4}
4000	0.638	7.190×10^{-5}	$1.127 \quad 10^{-4}$

(i) Suggest why the amount of $C\mathit{l}_2(g)$ was kept in large excess. [1]

(ii) Define the term *order of reaction*. [1]

(iii) Using the data from the table above, deduce the order of reaction with respect to NO(g). [1]

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3 **(a)** **(iv)** In another experiment, the initial partial pressure of NO(g) was 4.2 atm and it was reacted with Cl_2(g) at a constant temperature of 550 K. The partial pressure of Cl_2(g) was recorded at time intervals of 30 seconds.

The data obtained are tabulated below.

time / s	partial pressure of Cl_2(g)/ atm
0	0.78
30	0.76
60	0.72
90	0.70
120	0.66
150	0.63
180	0.59
210	0.57
240	0.54
270	0.52
300	0.49
330	0.46
360	0.44
390	0.42
420	0.39
450	0.38
480	0.36
510	0.34
540	0.33
570	0.32

Using the data but without plotting of any graph, deduce the order of reaction with respect to Cl_2(g). [1]

(v) Write the rate equation for the overall reaction. Hence, calculate the rate constant, stating its units. [3]

3 **(b)** In another reaction, $2NO_2(g) + 4CO(g) \rightarrow N_2(g) + 4CO_2(g)$, it was found that the rate equation is rate $= k[NO_2]^2$.
A proposed mechanism for this reaction is shown.

Step 1	$NO_2(g) + NO_2(g) \rightarrow 2NO(g) + O_2(g)$	slow
Step 2	$2NO(g) + O_2(g) + 4CO(g) \rightarrow N_2(g) + 4CO_2(g)$	fast

Explain whether it is consistent with the established rate equation. [1]

(c) Tryptophan metabolism plays an important role in the mechanisms associated with the gut-brain axis. At least 90% of human intake of tryptophan is converted to kynurenine for further metabolism via a catalyst.

(i) Explain how the activation energy of a reaction is affected by the presence of a catalyst, and with an appropriate sketch of a Maxwell–Boltzmann distribution curve, explain how a catalyst increases the rate of reaction. [3]

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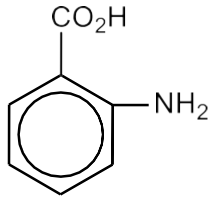
3 **(c) (ii)** Kynurenine has the molecular formula $C_{10}H_{12}N_2O_3$. When dissolved, an aqueous solution of kynurenine is almost neutral and maintains its pH upon addition of small amounts of aqueous sodium hydroxide or hydrochloric acid. Addition of this solution to aqueous 2,4-dinitrophenylhydrazine causes an orange precipitate to form.

Kynurenine reacts with $NaBH_4$ to form compound **L**, $C_{10}H_{14}N_2O_3$. Heating **L** with concentrated H_2SO_4 produces only **M**, $C_{10}H_{12}N_2O_2$. Heating **M** with acidified $KMnO_4$ under reflux results in the formation of compound **N**, $C_3H_5NO_4$ and anthranilic acid.

The molecular structure of anthranilic acid is as shown below.



anthranilic acid

Reaction of **N** with $LiAlH_4$ in dry ether produces compound **O**, $C_3H_9NO_2$. A solution of **O** turns litmus paper blue.

Suggest possible structures for **L, M**, **N**, **O** and kynurenine. For each reaction, state the type of reaction described and explain what the information tells you about the functional groups present in each compound. [13]

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[Total: 24]

4 **(a)** The value of the equilibrium constant is 4.0 for the reaction below:

$$CH_3CO_2H(l) + C_2H_5OH(l) \rightleftharpoons CH_3CO_2C_2H_5(l) + H_2O(l)$$

(i) Write an expression for the equilibrium constant, K_c, of the **reverse** reaction, i.e. the hydrolysis of ethyl ethanoate, stating its numerical value.

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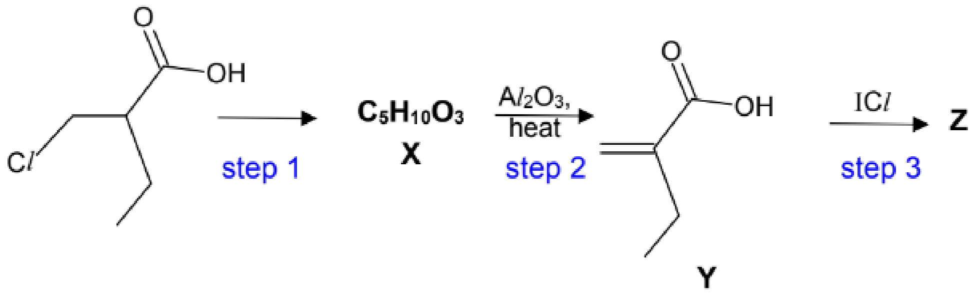
[2]

(ii) In an experiment, 2 mol of ethyl ethanoate and 2 mol of water are mixed.
Calculate the number of moles of each substance present when equilibrium is reached.

[2]

(b) The following shows a flow scheme involving a chlorocarboxylic acid to form compounds **X**,**Y** and **Z**.



(i) Suggest the structure of compound **X**.

[1]

(ii) Give the reagents and conditions for step 1.

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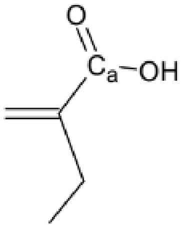
[1]

(iii) State the hybridisation of C_a labelled in the structure of **Y** below.



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[1]

(iv) Give the structure of compound **Z**.

[1]

(v) Give the structure of the product formed when compound **Y** is reacted with hydrogen with nickel, upon heating.

[1]

Aluminium objects that have had the aluminium oxide layer removed may then be oxidised.

(c) **(i)** State why aluminium objects are anodised.

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[1]

(ii) Complete Table 6.1 below to show the type of reaction occurring, with the relevant half-equations, during the anodising of an aluminium object.

	type of reaction	half-equation(s)
anode		
cathode		

Table 6.1

[2]

[Total: 12]

5 Hydrogen cyanide, HCN, is extremely toxic and with sufficient concentrations it leads to rapid death. During the Second World War, a form of hydrogen cyanide known as *Zyklon B* was used in the Nazi gas chambers.

(a) **(i)** Draw a dot–and–cross diagram to illustrate the bonding in HCN. [1]

HCN can be oxidised to cyanogen, C_2N_2.

$$C_2N_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons 2HCN(g) \qquad E^\ominus = +0.37\ V$$

(ii) Suggest a suitable oxidant to oxidise HCN to C_2N_2 in acidic solution, using the *Data Booklet*.

Write an equation for the reaction and calculate the $E^\ominus_{cell.}$ [2]

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(b) The synthesis of HCN was developed in the early 1900s. The most commonly used procedure is the *Andrussow* process. A less common method is the *BMA* process.

Andrussow process:

CH_4 (g) + NH_3 (g) + $\frac{3}{2}$ O_2 (g) $\xrightarrow{\qquad}$ HCN (g) + 3H2O (l) $\Delta H = -506$ kJ mol^{-1}

BMA process:

CH_4 (g) + NH_3 (g)   HCN (g) + $3H_2$ (g)

(i)

Using information from the *Data Booklet*, calculate the enthalpy change of reaction for the *BMA* process given above. [2]

(ii) By considering the spontaneity of reaction, suggest why the *Andrussow* process is the preferred procedure at low temperature. [2]

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(c) The *BMA* process is a reversible reaction at 500 °C. Starting with equal amounts of CH_4 and NH_3, the reaction is allowed to reach equilibrium at 500 °C under a constant pressure of 1 atm.

BMA process: $CH_4\,(g) + NH_3\,(g) \rightleftharpoons HCN\,(g) + 3H_2\,(g)$

(i) Write an expression for the K_p of *BMA* process, stating its units. [1]

(ii) Given that the equilibrium partial pressure of H_2 is 0.3 atm, calculate the value of K_p at 500 °C.

[2]

(iii) Discuss the effect of increase in total pressure on

- the proportion of HCN,
- K_p value,
- rate of reaction .

[3]

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(d) HCN (aq) has pK_a = 4.79 at 25 °C.

(i) Calculate the concentration of CN^- ion at pH 4, when the concentration of HCN(aq) is 0.06 mol dm^{-3}. [1]

Zinc cyanide, $Zn(CN)_2$, is sparingly soluble in water.
The numerical value of K_{sp} is 8.0 × 10^{-12} at 25°C.

(ii) Write an expression for the K_{sp} of $Zn(CN)_2$, stating its units. [1]

(iii) By considering your answer to **(d)(i)**, determine the minimum concentration of Zn^{2+} required to cause precipitation of $Zn(CN)_2$ at pH 4. [2]

(iv) Describe and explain how the solubility of $Zn(CN)_2$ is affected:

- by adding HC*l*(aq)
- by adding concentrated ZnCl_2(aq)

. [2]

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[Total:19]

6 Glucose comes from the Greek word for "sweet". It is the simplest carbohydrate with molecular formula $C_6H_{12}O_6$ and is the major free sugar circulating in the blood of mammals, serving as the primary source of energy for cell function.

(a) The oxidative breakdown of glucose by our body to produce energy is called respiration. The reaction for the complete combustion of glucose is

$$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l)$$

$$\Delta H^\ominus = -2816 \text{ kJ mol}^{-1}$$
$$\Delta S^\ominus = +181 \text{ J mol}^{-1} \text{ K}^{-1}$$

(i) Write a half-equation to represent the oxidative breakdown of glucose. [1]

(ii) The energy value of food is measured in Calorie. One Calorie is defined as the amount of heat needed to raise the temperature of 1 kg of water by 1 °C. Use the given information, together with data from the *Data Booklet*, to calculate the number of Calories in 1 g of glucose. [2]

(iii) Comment on the sign of $\Delta S^\ominus$ for the combustion of glucose. [1]

(iv) If this combustion reaction could be harnessed as a fuel cell, calculate $\Delta G^\ominus$ and hence the theoretical voltage, $E^\ominus_{\text{cell}}$, that could be produced under standard conditions.

[3]

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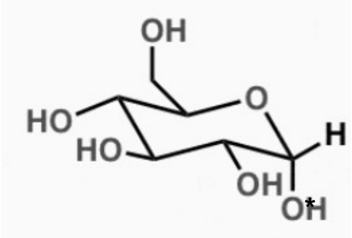
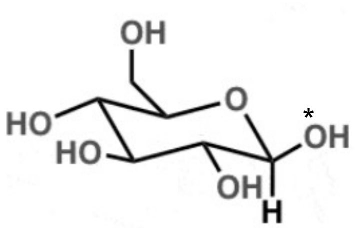
Glucose exists in two forms, α-glucose and β-glucose, with the OH group occupying different spatial arrangement in each form. Some information about the two is given in Table 4.1.

Table 4.1

	α-glucose	**β-glucose**
		
Melting point / °C	146	150
Angle of rotation of plane-polarised light for a 1 mol dm^{-3} sample / °	+20.2	+3.4

(b) **(i)** Suggest a reason for the difference in melting points between α-glucose and β-glucose. [1]

If a solution of α-glucose is left for some time, it will come into dynamic equilibrium with β-glucose.

$$\alpha\text{-glucose} \rightleftharpoons \beta\text{-glucose}$$

(ii) Explain what is meant by *dynamic equilibrium*. [1]

(iii) 1 dm^3 of a freshly prepared solution of 1.0 mol dm^{-3} solution of α-glucose is left to stand at 298 K. At equilibrium, the solution was found to rotate plane-polarised light by +9.45 °. Given angle of rotation of plane-polarised light is directly proportional to concentration of isomer, use information from Table 4.1 to determine [β-glucose] at equilibrium. [1]

(iv) Hence calculate the value of the equilibrium constant, K_c, for the conversion of α-glucose to β-glucose at 298 K. If you were unable to determine [β-glucose] at equilibrium, assume the value is 0.60. Note 0.60 is **not** the correct answer for **(b)(iii)**. [1]

(v) The conversion of α-glucose into β-glucose is catalysed by acids. What will be the effect on the equilibrium position if the conversion is now carried out in the presence of dilute sulfuric acid? Explain your answer. [1]

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(c) Fig. 4.1 shows the mechanism for the conversion of α-glucose into β-glucose.

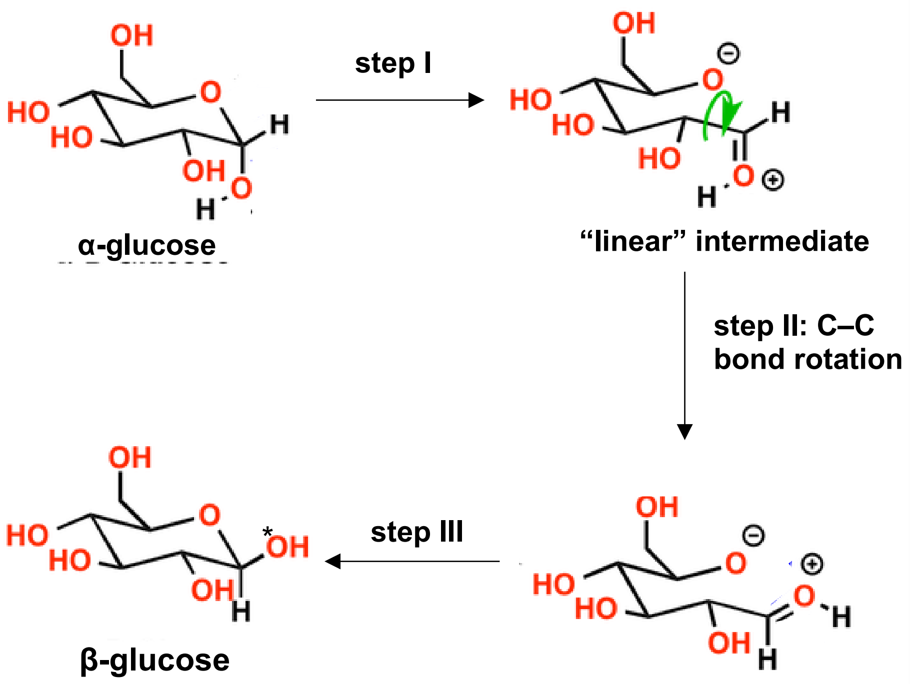

Fig. 4.1

(i) Explain, with reference to the Valence Shell Electron Pair Repulsion theory, why the bond angle around O* increases in step I of the mechanism. [2]

(ii) Complete Fig. 4.1 to suggest the mechanism for steps I and III. Show all relevant lone pairs and show the movement of electron pairs by using curly arrows. [2]

(iii) Suggest the types of reaction taking place in steps I and III. [2]

(iv) A proton transfer can occur between the charged groups in the "linear" intermediate to form another stable electrically neutral intermediate. Identify the new functional group present in this other intermediate and hence suggest a suitable chemical test to confirm its presence during the conversion of glucose. [2]

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[Total: 20]

ANSWERS FOR CHEMICAL EQUILIBRIUM MCQ PART 1

1 In aqueous solution, an equilibrium is established between chromate, CrO_4^{2-} (yellow) and dichromate ions, $Cr_2O_7^{2-}$ (orange).

$$2CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$$

Which statement regarding the ions and the equilibrium is correct?

A The oxidation number of chromium in both chromium-containing ions is different.

B The difference in colour between CrO_4^{2-} and $Cr_2O_7^{2-}$ is due to a difference in energy gap between the 3d orbitals.

C The Kc expression for the equilibrium is $K_c = \frac{[Cr_2O_7^{2-}][H_2O]}{[CrO_4^{2-}]^2[H^+]^2}$.

D Increasing the pH turns the solution yellow.

A: Cr is in the same oxidation number of +6 for both species. Let x be the oxidation number of Cr.
$x + 4(-2) = -2$
$x = +6$ (CrO_4^{2-})

$$K_C = \frac{[Cr_2O_7^{2-}]}{[CrO_4^{2-}]^2[H^+]^2}$$

$x = +6$ ($Cr_2O_7^{2-}$)

B: There are no electrons in the 3d subshell for both chromium-containing species.
Hence the difference in colour is not due to the difference in energy gap between the 3d orbitals.

C: The K_c expression for the equilibrium is $K_C = \frac{[Cr_2O_7^{2-}]}{[CrO_4^{2-}]^2[H^+]^2}$ $[H_2O]$ is not include in the expression as it is a solvent and its concentration remains constant.

D: Increasing the pH results in a decrease in $[H^+]$. Position of equilibrium shifts to the left and the major species in solution is CrO_4^{2-}

2 Nitrogen dioxide dimerises in a closed system and establishes the following equilibrium:

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

When 46.0 g of NO_2 was introduced into an evacuated rigid vessel with an initial pressure 2 atm at constant temperature, the apparent M_r value of the equilibrium mixture is 64.4.

What is the K_p value of this equilibrium?

A 0.281
B 0.556
C 0.778
D 1.11

Amount of $NO_2 = \frac{46}{46}$ = 1 mol

Let x be the mole fraction of NO_2.

$46x + 92(1-x) = 64.4$

$x = 0.6$

	$2NO_2(g)$	$\rightleftharpoons$	$N_2O_4(g)$
I / mol	1		0
C / mol	−2y		+y
E / mol	1−2y		y

$n_T = 1-y$

$$\frac{1-2y}{1-y} = 0.6$$

$y = 0.2857$

$n_T = 1 - 0.2857 = 0.7143$

$$\frac{p_1}{n_1} = \frac{p_2}{n_2}$$

$$\frac{2}{1} = \frac{p_2}{0.7143}$$

$p_2 = 1.429$

$$K_p = \frac{0.4 \times 1.429}{(0.6 \times 1.429)^2} = 0.778$$

3 The rates of the reversible reaction to produce ammonia in a closed vessel can be affected by changing the pressure of reactants or adding a catalyst.

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

Which of the following statements about the system are correct?

1 Increasing partial pressure of nitrogen increases the rate of the forward reaction.
2 Decreasing the partial pressure of nitrogen increases the rate of the reverse reaction.
3 Adding a catalyst does not affect the value of the rate constant, *k*.
4 Adding a catalyst reduces the activation energies for both the forward and reverse reaction.

A 1, 2 and 4
B 2, 3 and 4
C 2 and 3
D 1 and 4 only

Options 2 and 3 are incorrect.
Option 2: Decreasing the partial pressure of nitrogen will decrease the rate of reaction even though the POE will eventually shift to the left.
Option 3: Adding a catalyst should affect the rate constant since it increases the rate of reaction without concentration change.

4 Nitrogen dioxide can decompose to form nitrogen monoxide and oxygen.

$$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$$

When 2.50 mol of nitrogen dioxide was allowed to undergo decomposition in a 0.8 dm^3 container, 0.528 mol of oxygen was present at equilibrium.

What is the numerical value of the equilibrium constant, K_c, for this reaction?

A 0.282 **B** 0.353
C 2.83 **D** 3.54

$$K_C = \frac{[NO]^2[O_2]}{[NO]^2}$$

$$K_C = \frac{\left(\frac{1.056}{0.8}\right)^2\left(\frac{0.528}{0.8}\right)}{\left(\frac{1.444}{0.8}\right)}$$

$= 0.35296$
$= 0.353 \text{ mol dm}^{-3}$

5 The formation of sulfur trioxide from sulfur dioxide and oxygen is a reversible reaction.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H = -197 \text{ kJ mol}^{-1}$$

Which statements about this equilibrium are correct?

1 The K_c value will be halved if the stoichiometric coefficients in the equation are halved.
2 At dynamic equilibrium, the rates of the forward and backward reactions are equal to zero.
3 An increase in pressure of the system will result in a greater yield of SO_3 at equilibrium.
4 When temperature is reduced, the rate constant of the forward reaction, k_f, decreases to a smaller extent than that of the backward reaction, k_b.

A 3 and 4 only **B** 1 and 2 only
C 2, 3 and 4 only **D** 1 and 3 only

✗	1	$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$ If the stoichiometric coefficients are halved, $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$ $K_c' = \frac{[SO_3]}{[SO_2][O_2]^{\frac{1}{2}}} = K_c^{\frac{1}{2}} \neq \frac{1}{2}K_c$
✗	2	At dynamic equilibrium, the rates of the forward and backward reactions are equal but not zero.
✓	3	By Le Chatelier's Principle, when pressure increases, the position of equilibrium shifts to the right to produce less moles of gas, favouring the forward reaction. Hence, more moles of SO3 will be produced.
✓	4	By Le Chatelier's Principle, when temperature is reduced, position of equilibrium shifts to the right to favour the forward exothermic reaction to produce heat. Rates of the forward and backward reaction will decrease but the rate of the forward reaction is decreased to a smaller extent.

6 Which statement is correct to describe the spontaneity of reaction **I**?

reaction **I** $T(aq) + U(s) \rightarrow V(aq) + W(g)$

A Reaction **I** is only spontaneous at low temperatures if the reaction is endothermic.

B Reaction **I** is only spontaneous at low temperatures if the reaction is exothermic.

C Reaction **I** is spontaneous at all temperatures if the reaction is endothermic.

D Reaction **I** is spontaneous at all temperatures if the reaction is exothermic.

		ΔH	ΔS	ΔG
✗	A	+	+	- when temperature is high enough such that ITΔSI > IΔHI
✗	B	-	+	- at all temperatures not just at low T
✗	C	+	+	when temperature is high enough such that ITΔSI > |ΔHI
✓	D	-	+	- at all temperatures

7 Known amount of hydrogen and iodine are allowed to come to equilibrium at 500 °C in a vessel of known volume.

$$H_2 + I_2 \rightleftharpoons 2HI$$

From which experimental method can K_c be found?

A Measuring the total pressure in the vessel.

B Slow cooling to 20 °C, breaking open the vessel under aqueous potassium iodide, and titrating the iodine present with aqueous sodium thiosulfate.

C Rapid cooling to 20 °C, breaking open the vessel under aqueous potassium iodide, and titrating the iodine present with aqueous sodium thiosulfate.

D Withdrawal of a measured sample of the equilibrium mixture, followed by complete decomposition of the hydrogen iodide present, and then titrating the total amount of iodine with aqueous sodium thiosulfate.

A ×: Since there is no change in the number of gaseous particles upon reaction, the total pressure in the vessel remains constant. Hence the amount of reactants and products cannot be determined.

B ×: Slow cooling allows the equilibrium to readjust to the new temperature. Hence, the Ke determined will be that at 20 C and not 500 °C.

C ✓: Rapid cooling will slow down the reaction, allowing the amount of I2 in the equilibrium mixture at 500 C and hence Kc, to be determined.

D ×: If the HI present is decomposed back to H2 and 12, the amount of reactants and product in the equilibrium mixture cannot be determined.

8 Consider the following equilibrium for the adsorption of gas **G** on the active sites of a metal catalyst, **M**:

$$\mathbf{G}\,(g) + \mathbf{M}\,(s) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathbf{GM}(s) \qquad \Delta H < 0$$

where k_1 is the rate constant for the adsorption, and
k_2 is the rate constant for the desorption.
The percentage occupancy, θ, of metal surface by gas **G** can be represented as:

$$\theta = \frac{\frac{k_1}{k_2} p_G}{1 + \frac{k_1}{k_2} p_G}$$

where p_G is the partial pressure of gas **G**.

Which of the following statements is correct regarding the above system?

A K_p of the system increases with increasing temperature.

B K_p of the system is equal to its K_c.

C The greater the total surface area of the metal catalyst, the greater the percentage occupancy, θ, of the metal surface by gas **G**.

D At high pressures of gas **G**, increasing the temperature does not increase the percentage occupancy, θ, of the metal surface by gas **G**.

A ×: Since AH < 0, position of equilibrium lies more to the left with increasing T.

Hence K_p - $\frac{1}{P_{G(g)}}$ ↓es with ↑ing T.

B×: pV=nRT ⇒ p=$\frac{n}{V}$ RT =CRT

$$K_p = \frac{1}{P_{G(g)}} = \frac{1}{[G(g)]RT} = \frac{K_c}{RT}$$

C ×: θ depends only on k_1, k_2 and P_G. It is independent of the total surface area of the catalyst.

D ✓: At high P_G, 1+ P_G Hence, 0 ≈ 1, which is independent of *T*.

9 Silver ions can be used as an alternative disinfecting agent for public swimming pools. The Ag^+ concentration needs to be between 1.0×10^{-7} mol dm^{-3} and 1.0×10^{-6} mol dm^{-3} for effective disinfection.

Saturated solutions of four different compounds were prepared by stirring an excess of each compound in pure water. Which of the following compounds would provide the necessary silver ion concentration required for disinfection?

	compound	K_{sp}
A	Ag_2CO_3	8.1×10^{-12}
B	AgC*l*	1.8×10^{-10}
C	AgBr	5.4×10^{-13}
D	$AgIO_3$	3.2×10^{-8}

A × : $[Ag^+] = 2\sqrt[3]{\frac{K_{sp}(Ag_2CO_3)}{4}} = 2.53 \text{ x} 10^{-4}$

B × : $[Ag^+] = \sqrt{K_{sp}(AgCl)} = 1.34 \text{ x } 10^{-5}$

C ✓ : $[Ag^+] = \sqrt{K_{sp}(AgBr)} = 7.35 \text{ x } 10^{-7}$

D × : $[Ag^+] = \sqrt{K_{sp}(AgIO_3)} = 1.79 \text{ x } 10^{-4}$

10 Which statement about the Haber process for the manufacture of ammonia is correct?

A At higher temperatures, the yield decreases but the rate of production of ammonia is faster.

B At lower temperatures, the value of K_p decreases.

C At higher pressures, the yield decreases but the rate of production of ammonia is faster.

D In the presence of a catalyst, the yield decreases but the rate of production of ammonia is faster.

Recall Haber process: N2(g) + 3H2 ⇌ 2NH3(g) The forward reaction is exothermic.

Option	Explanation
A	High temperature will favour the endothermic backward reaction. Hence the yield will decrease but the rate of the reaction will increase.
B	At lower temperature, Kp increases. There will be more NH3 formed and less N2 and H2 present.
C	Higher pressure will favour the forward reaction to produce less number of gaseous molecules. Hence the yield will increase.
D	The presence of catalyst does not affect the yield.

11 0.50 moles of CH_3CO_2H and 0.50 moles of CH_3CH_2OH were mixed and an esterification reaction took place. The equilibrium constant for this reaction is 4.0.

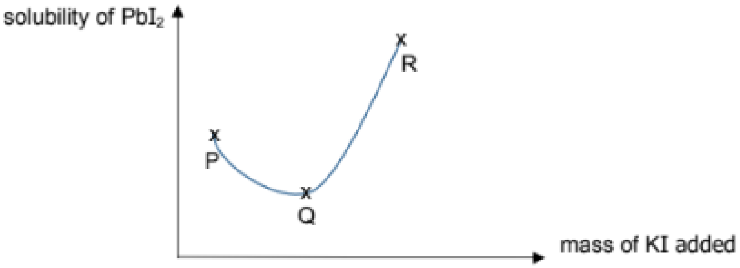
What is the amount of CH_3CO_2H (in moles) in the mixture at equilibrium?

A 0.17 **B** 0.25 **C** 0.33 **D** 0.67

	CH_3CO_2H +	CH_3CH_2OH	$\rightleftharpoons$	$CH_3CO_2CH_2CH_3$	+ H_2O
initial amt/ mol	0.50	0.50		–	–
change/ mol	−x	−x		+x	+x
eqm amt/ mol	0.50 − x	0.50 − x		x	x

$K_c = (x/V)^2 / ((0.50 - x)/V)^2 = 4.0$
Taking square root on both sides, x = 0.33 Hence
amount of CH_3CO_2H = 0.50 – 0.33 = 0.17

12 The following graph represents how the solubility of a sparingly soluble salt lead(II) iodide, PbI_2, changes upon addition of solid potassium iodide at a fixed temperature.



Which statement about the above graph is **not** correct?

A The change in solubility along PQ is due to common ion effect.

B The change in solubility along QR is due to the formation of a complex between Pb^{2+} and I^-.

C At Q, the molar concentration of I^- ions is twice that of Pb^{2+} ions.

D K_{sp} remains constant along PR.

$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$

Option	Explanation
A	As more I^- is added, the above equilibrium will shift to the left, causing the solubility of PbI_2 to decrease. This is the common ion effect.
B	When even more I^- is added, a soluble complex $[PbI_4]^{2-}$ is formed. The formation of this complex decreases the $[Pb^{2+}]$, causing the above equilibrium to shift to the right. This increases the solubility of PbI_2.
C	At Q, the concentration of I^- is not necessarily twice that of Pb^{2+} as I^- is also contributed by the addition of KI.
D	K_{sp} is only dependent on temperature.

13 Gas **A** decomposes to two other gases, **B** and **C**, according to the equation:

$$2\mathbf{A}(g) \rightleftharpoons 3\mathbf{B}(g) + \mathbf{C}(g) \qquad \Delta H = +x \text{ kJ mol}^{-1}$$

Which of the following correctly describes what will happen if a proposed change is made to this system at equilibrium?

	proposed change	value of K_c	position of equilibrium
A	add inert solid	no change	shift left
B	increase pressure	no change	shift right
C	increase temperature	increase	shift right
D	add catalyst	increase	no change

14 The solubility product of a substance is ***S***. If the concentration of the cation in a saturated solution is found to be $\left(\frac{9S}{4}\right)^{\frac{1}{5}}$, what could be the substance?

A $CaCl_2$
B $Ca_3(PO_4)_2$
C $Al(OH)_3$
D $Al_2(SO_4)_3$

15 Nitrogen and hydrogen form ammonia in an exothermic reaction. The rate and yield of the reaction can be altered by changing the experimental conditions.

Which row correctly describes the effect of the changes in condition?

	change in condition	effects		
		equilibrium yield	rate of forward reaction	rate of backward reaction
1	increasing temperature	decreases	increases	increases

2	increasing temperature	increases	decreases	increases
3	addition of catalyst	increases	increases	no effect
4	addition of catalyst	no effect	increases	increases

A 1 and 4 only **B** 2 and 4 only **C** 2 and 3 only **D** 1 and 3 only

The operating conditions of Haber process is 500 °C and 60 atm in the presence of Fe catalyst. A mid-high temperature is used to increase rate of reaction. Very high temperatures shift POE to the left, favouring backward endothermic reaction to absorb heat energy and resulting in poor yield. Low temperatures cause the equilibrium to be established too slowly. A relatively high pressure of 60 atm is used to shift POE to the right to reduce total amount of gas particles. 500 atm is too high resulting in the need for very thick steel containers and high costs.

16 Solid calcium hypochlorite pellets, $Ca(ClO)_2(s)$, are added to swimming pools to form $HClO(aq)$ which kills disease-causing bacteria and algae.

$$Ca(ClO)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2ClO^-(aq)$$

$$ClO^-(aq) + H_2O(l) \rightleftharpoons HClO(aq) + OH^-(aq)$$

What is the effect on the solubility of calcium hypochlorite and bacterial growth when pH increases?

	effect on solubility of calcium hypochlorite	effect on bacterial growth
A	decreases	increases
B	decreases	decreases
C	increases	increases
D	increases	decreases

17 In the Haber process, nitrogen and hydrogen is passed over a hot catalyst to produce ammonia.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H < 0$$

Which row correctly describes the operating condition and the possible reason? [POE – position of equilibrium]

	operating condition	reason
A	500 atm	high pressure to shift POE to the right
B	500 °C	high temperature to increase rate of reaction
C	60 atm	low pressure to shift POE to the right
D	60 °C	low temperature to shift POE to the right

18 Ammonium carbamate, NH_2COONH_4, undergoes thermal decomposition.

$$NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g) \qquad \Delta H > 0$$

A vessel containing only NH_2COONH_4 is heated to 250 °C. The reaction reached equilibrium at time t_1. Subsequently both the temperature and volume of the vessel are decreased, and the reaction established a new equilibrium at time t_2.

Which statements are correct?

1 At t_2, $P_{NH_3} : P_{CO_2}$ is 2 : 1.
2 The rate of the forward reaction at t_1 is the same as that at t_2.
3 The degree of decomposition of NH_2COONH_4 at t_1 is smaller than that at t_2.
4 Decreasing the volume of the vessel at constant temperature has no effect on the equilibrium partial pressures of NH_3 and CO_2.

A 2 only
B 1 and 3
C 1 and 4
D 2 and 3

Statement 1	Correct. As there are no addition of any reactant or product to the system, the mole ratio of $NH_3 : CO_2$ should always stay the same at 2 : 1 (following the stoichiometric ratio of the balanced equation). Since $p \alpha n$, $P_{NH_3} : P_{CO_2}$ is also 2 : 1 at t_2.
Statement 2	Incorrect. Since the temperature at t_1 is higher than that at t_2, the rate of the forward (and backward) reaction at t_1 is greater than that at t_2. (Recall that at higher temperatures, a greater proportion of the reactant molecules have energy greater than or equal to the activation energy for reaction. Hence, the frequency of effective collisions increases resulting in an increase in rate of reaction.)

Statement 3	Incorrect. By Le Chatelier's Principle, a decrease in temperature will favour the backward exothermic reaction and a decrease in volume (or increase in total pressure) will favour the backward reaction which reduces the number of gas particles. Hence at t_2, the degree of decomposition of NH_2COONH_4 is smaller than that at t_1.
Statement 4	Correct. Decreasing the volume of the vessel will cause the total pressure (and partial pressures of NH_3 and CO_2) to increase. By Le Chatelier's Principle, the equilibrium position will shift left to reduce the number of gas particles and the partial pressures of NH_3 and CO_2 will decrease. Since the equilibrium constant (K_p = $(P_{NH_3})^2(P_{CO_2})$) remains unchanged (as temperature is constant) and the $P_{NH_3} : P_{CO_2}$ stays the same at 2 : 1, the equilibrium partial pressures of NH_3 and CO_2 at t_2 will be the same as that at t_1.

19 When a sample of iron(II) sulfate, $FeSO_4$, is heated to 920 K, reactions 1 and 2 occurred.

reaction 1 $2FeSO_4(s) \rightleftharpoons Fe_2O_3(s) + SO_3(g) + SO_2(g)$ K_1

reaction 2 $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ K_2

At equilibrium, the total pressure is 0.836 atm and the partial pressure of oxygen is 0.0275 atm.

What is the value of K_2 at 920 K?

A 0.000147
B 0.0362
C 0.0476
D 0.160

SO_3 and SO_2 are found in both reactions 1 and 2. For the forward reaction of reaction 2 to proceed, SO_3 must first be formed from reaction 1.
Since the mole ratio of SO_3 and SO_2 is 1 : 1 in reaction 1, let x atm be the initial partial pressures of SO_3 and SO_2 for reaction 2.

	$2SO_3(g)$	$\rightleftharpoons$	$2SO_2(g)$	+	$O_2(g)$
initial pressure / atm	x		x		0
change in pressure / atm	–2(0.0275)		+2(0.0275)		+0.0275
eqm pressure / atm	x – 2(0.0275)		x + 2(0.0275)		0.0275

Since total pressure at equilibrium is 0.836 atm,

$P_{SO_3} + P_{SO_2} + P_{O_2} = 0.836$ atm

x – 2(0.0275) + x + 2(0.0275) + 0.0275 = 0.836
x = 0.40425

P_{SO_3} = 0.40425 – 2(0.0275) = 0.34925 atm
P_{SO_2} = 0.40425 + 2(0.0275) = 0.45925 atm

$$K_2 = \frac{(P_{SO_2})^2(P_{O_2})}{(P_{SO_3})^2} = \frac{(0.45925)^2(0.0275)}{(0.34925)^2} = \underline{\mathbf{0.0476\ atm}}$$

20 Some equilibria, and the value of their equilibrium constants at 298 K, are given below.

$Cu^+(aq) + Cl^-(aq) \rightleftharpoons CuCl(s)$ $K_1 = 8.33 \times 10^5$

$CuCl(s) + Cl^-(aq) \rightleftharpoons CuCl_2^{\ -}(aq)$ $K_2 = 0.104$

$Cu^+(aq) + 2Cl^-(aq) \rightleftharpoons CuCl_3^{\ -}(aq)$ $K_3 = z$

Which row is correct?

	z	value of solubility product of CuC*l*(s) at 298 K
A	8.66×10^4	1.10×10^{-3}
B	8.66×10^4	1.20×10^{-6}
C	8.01×10^6	1.10×10^{-3}
D	8.01×10^6	1.20×10^{-6}

① $Cu^+(aq) + Cl^-(aq) \rightleftharpoons CuCl(s)$ $K1 = 8.33 \times 10^5$

② $CuCl(s) + Cl^-(aq) \rightleftharpoons CuCl2^-(aq)$ $K2 = 0.104$

③ $Cu^+(aq) + 2Cl^-(aq) \rightleftharpoons CuCl2^-(aq)$ $K3 = z$

③ = ① + ②

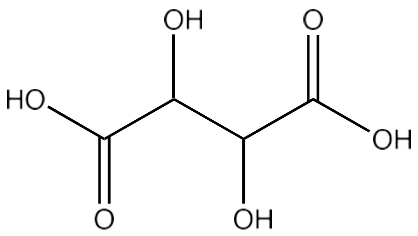
$K_3 = \frac{[CuCl_2-]}{[Cu^+][Cl^-]^2} = \frac{1}{[Cu^+][Cl^-]} \text{ x } \frac{[CuCl_2^-]}{[Cl^-]} = K_1 \text{ x } K_2 = 86632 \text{ mol}^{-2} \text{ dm}^6$

Hence, z = **$8.66 \text{ x } 10^4$**

Solubility product, K_{sp} of CUC*l* (s) = $[Cu^+][Cl^-] = \frac{1}{K_1} = \frac{1}{(8.33 \text{ x } 10^5)} = 1.20 \text{ x } 10^{-6} \text{ mol}^2 \text{ dm}^{-6}$

ANSWERS FOR CHEMICAL EQUILIBRIUM STRUCTURED QUESTIONS PART 1

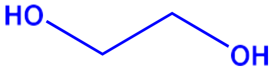
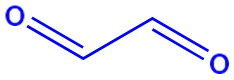
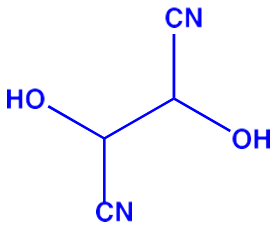
1 **(a)** Tartaric acid is a white crystalline diprotic organic acid. It can be synthesised from ethene in four steps.



Tartaric acid

$$\text{ethene} \xrightarrow{\text{Step 1}} \textbf{A} \xrightarrow{\text{Step 2}} \underset{(C_2H_2O_2)}{\textbf{B}} \xrightarrow{\text{Step 3}} \textbf{C} \xrightarrow{\text{Step 4}} \text{Tartaric Acid}$$

Draw the structures of the intermediates, **A**, **B** and **C**, and give the required reagents and conditions for each step of the conversion. [7]

A	**B**	**C**
		

Step 1:...cold, NaOH(aq), $KMnO_4$..

Step 2:...$K_2Cr_2O_7$ in dilute H_2SO_4, heat with (immediate) distillation..........

Step 3:...HCN(aq), trace amount of NaCN(aq)/NaOH(aq), cold.............................

Step 4:...dilute H_2SO_4, heat...

EXAMINERS' COMMENTS

With the molecular formula of compound B provided, it is pleasing to see that most students can deduce this. However, a fair number used $KMnO_4$ in Step 2 which is not accepted as it will oxidise the resultant molecule, ethanedioic acid to carbon dioxide. In addition, it is important to state the acidifying agent (H_2SO_4) or alkaline agent (NaOH) to remove ambiguity as other agents such as hydrochloric acid would result in the latter being oxidised to chlorine gas.

2 **(b)** Salts of tartaric acid are known as tartrates or hydrogen tartrates. One of these salts, potassium hydrogen tartrate, $KC_4H_5O_6$, is a weak monobasic acid and is sparingly soluble in water.

An experiment was conducted to determine the K_{sp} of the salt, $KC_4H_5O_6$. 1.00 g of the salt, $KC_4H_5O_6$ was dissolved in a beaker containing 100 cm^3 of water and was stirred constantly for 15 minutes at constant temperature, until a saturated solution was produced.

20.0 cm^3 of the filtered solution was titrated against 0.035 mol dm^{-3} NaOH, using phenolphthalein as an indicator. The volume of NaOH needed for the indicator to change colour is 12.50 cm^3.

(i) Calculate the initial concentration of potassium hydrogen tartrate used in the titration. [1]

Amt. of $KC_4H_5O_6 = 0.035 \times \frac{12.50}{1000}$

$= 4.375 \times 10^{-4}$ mol

$[KC_4H_5O_6] = 4.375 \times 10^{-4} \div \frac{20.0}{1000} =$ 0.0219 mol dm^{-3} (3 sf)

(ii) Hence, calculate the K_{sp} value of potassium hydrogen tartrate. [1]

$K_{sp} = [K^+][C_4H_5O_6^-] = (0.0219)^2 = 4.79 \times 10^{-4}$ $mol^2\ dm^{-6}$

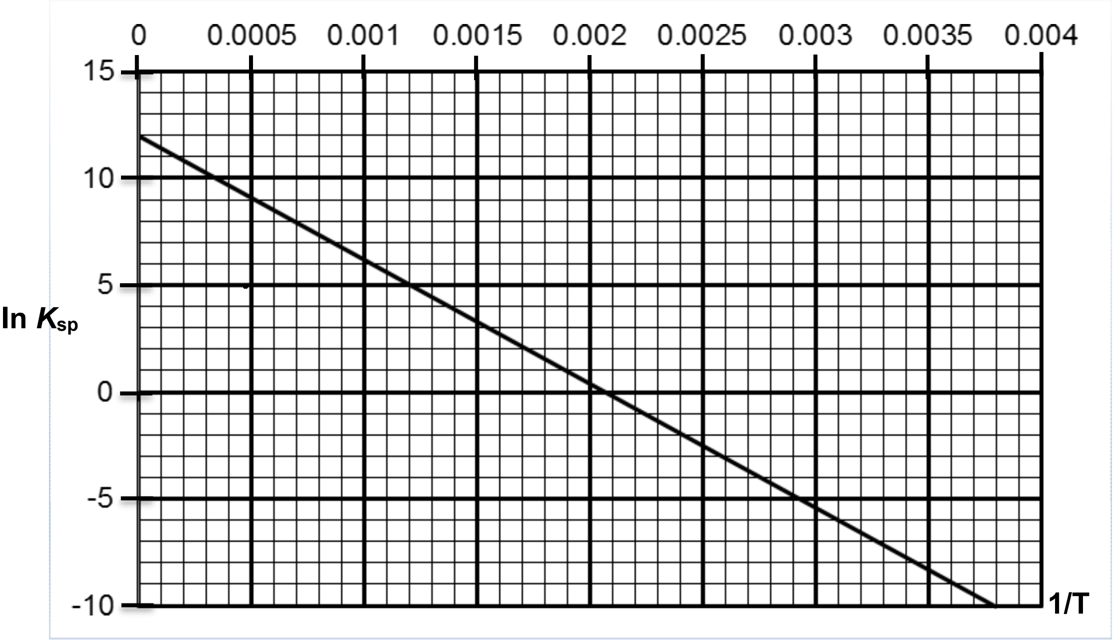
EXAMINER'S COMMENTS

Poorly answered question. It is worrying that most students that obtained an incorrect answer is due to the assumption that all the 1.00 g of potassium salt dissolved in water when is clearly stated it is sparingly soluble in the first paragraph. Hence, back titration with NaOH was required.

2 **(c)** The van 't Hoff equation relates equilibrium constants to enthalpy (ΔH) and entropy changes (ΔS) as follows:

$$\ln K_{sp} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

where R is the molar gas constant and T is measured is in Kelvin.
The titration in **(b)** was repeated at different temperatures and the following results were obtained.



(i) Using the information provided, calculate ΔH and ΔS for the dissolution of potassium hydrogen tartrate in water. [2]

Gradient value = $\frac{\Delta H}{R} = \left| \frac{12+10}{0.0038-0} \right|$

= 5789

ΔH = 5789 x 8.31 = +48110 J mol^{-1}
= +48.1 kJ mol^{-1}

y-intercept value = $\frac{\Delta S}{R}$ = 12

ΔS = 12 x 8.31 = +99.7 J K^{-1} mol^{-1}

(ii) Hence, predict the temperature at which potassium hydrogen tartrate becomes soluble in water. [1]

$$\Delta G = \Delta H - T\Delta S = 0$$

$$T = \Delta H / \Delta S = 48110 / 99.7 = 483 \text{ K}$$

EXAMINER'S COMMENTS
This question demonstrates the poor mathematical interpretation of the expression provided. To solve both thermodynamic constants, some students were busy solving simultaneous questions when a simple conversion using linear law was sufficient to obtain it.

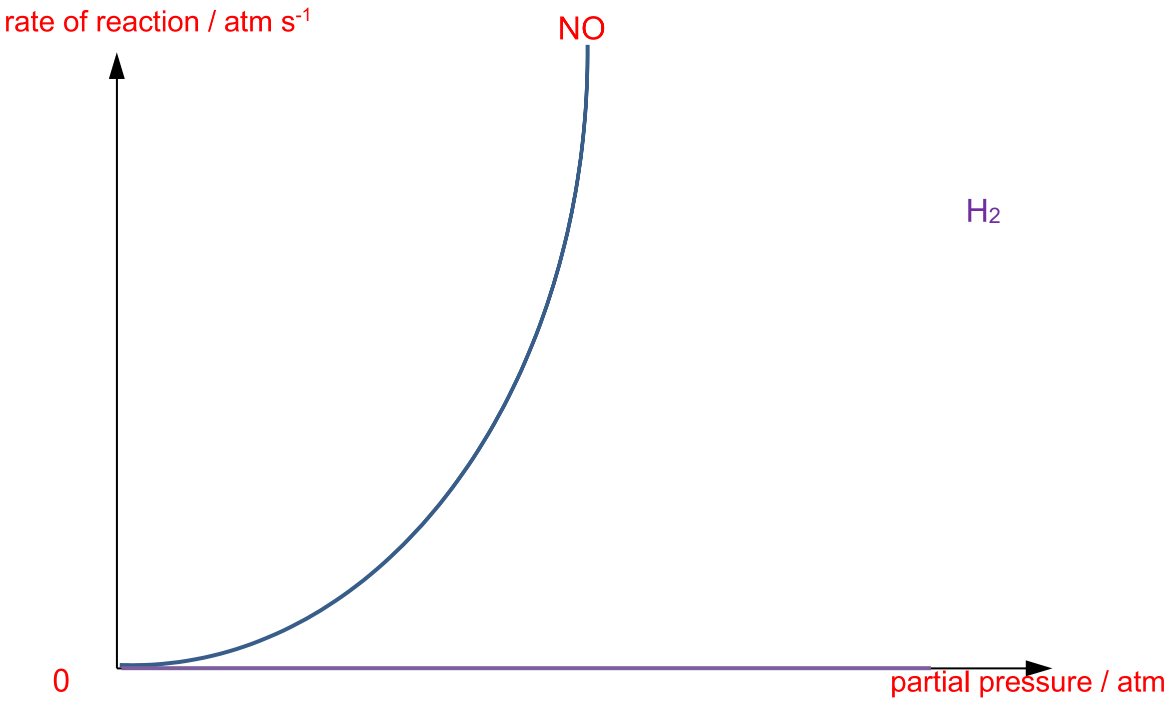
2 **(d)** At 800 K, nitrogen monoxide reacts with hydrogen as shown below in an enclosed gas tank.

$$2H_2(g) + 2NO(g) \rightarrow 2H_2O(g) + N_2(g)$$
$$\text{rate} = k(P_{H_2})(P_{NO})^2$$

On the same axes, sketch suitable graphs to illustrate clearly how the rate of reaction would vary when partial pressures of

(i) H_2
(ii) and NO

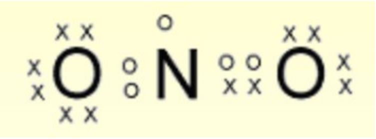
is increased respectively. [1]



EXAMINER'S COMMENTS
This question is poorly attempted due to overthinking on the students' part. Some left the axis blank while others were drawing equilibrium graphs of concentration against time. It is important that candidates realise what is asked in the question before presenting their answers.

2 **(e)** Nitrogen dioxide, NO_2, is an air pollutant produced from volcanic eruptions and combustion of fossil fuels in automobile engines.

(i) Draw the dot-and-cross diagram for nitrogen dioxide, NO_2, molecule stating its shape and bond angle. [2]

Species	Dot-and-cross diagram	Shape and bond angle
NO_2		Shape: bent Bond angle: **x>120°** **range of values** **(121° – 179°**

EXAMINER'S COMMENTS
Most candidates were able to draw a structure of NO_2, albeit the central nitrogen atoms has 9 electrons around it. It is important for candidates to check upon drawing, especially for Period 2 elements, that it does not exceed 8 electrons which on this occasion requires the formation of a dative covalent bond from N to O.

(ii) A 1.00 dm^3 gas cylinder is used to store 35.0 g of NO_2 at 25° C. The gas cylinder is fitted with a safety valve that will rupture when there is a great difference between the internal pressure and the atmospheric pressure.
The gas cylinder fitted with a burst disc can withstand a pressure difference of 2500 kPa.
Calculate the pressure exerted by NO_2 at 25° C in kPa. [1]

$$PV = \frac{m}{M_r} RT$$

$$P = \frac{nRT}{V}$$

$$= \frac{\frac{35.0}{46.0} \times 8.31 \times 298}{1.00 \times 10^{-3}}$$

= 1 884 kPa

(iii) Assuming the atmospheric pressure is 101 kPa, calculate the maximum internal pressure of the gas cylinder. [1]

Maximum pressure difference = Internal pressure – Atmospheric pressure

2500 = Internal pressure – 101

Internal pressure = 2500 + 101

= 2601 kPa

(iv) Hence, determine the maximum temperature that this gas cylinder can be exposed to before the burst disc ruptures. [1]

$$PV = nRT$$

$$T = \frac{PV}{nR}$$

$$= \frac{2601 \times 10^3 \times 1.00 \times 10^{-3}}{8.31 \times \frac{35.0}{46.0}}$$

$$= 411\ K$$

2 **(f)** A gas tank contains a mixture of NO_2 and monoatomic gas **A** in the ratio of 4:1. At 300 K, the total pressure of the gas mixture is 100 kPa.

(i) Given that the density of the gas mixture is 1638 g m^{-3}, calculate the average relative molecular mass of the mixture to 1 decimal place. [1]

$$M_t = \frac{pRT}{P} = \frac{1638\ x\ 8.31\ x\ 300}{100\ 000}$$

= 40.8

(ii) Hence, calculate the A_r of monoatomic gas **A** and suggest its identity. [2]

Given that the mixture of NO_2 and monoatomic gas A is in the ratio of 4:1,

(0.8 x 46.0) + (0.2 x A_r of monoatomic gas A) = 40.8

A_r of A = 20.0

A is neon

EXAMINER'S COMMENTS
Other than the handful of careless mistakes involving the conversion of units, most students are able to solve these questions pretty well.

[Total: 21]

3 This question is about nitrogen containing compounds.

(a) Nitrogen monoxide reacts with chlorine to form nitrosyl chloride, according to the equation:

$$2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$$

In an experiment, student **A** kept the amount of $Cl_2(g)$ in large excess while the initial partial pressure of NO(g) was varied at constant temperature of 550 K.

The table below shows the experimental results obtained.

time / s	P_{NO} / atm	($Rate / P_{NO}$) / s^{-1}	($Rate / (P_{NO})^2$) / ($atm^{-1}\ s^{-1}$)
0	0.917	1.033×10^{-4}	1.126×10^{-4}
1000	0.827	9.312×10^{-5}	1.126×10^{-4}
2000	0.753	8.486×10^{-5}	1.127×10^{-4}
3000	0.691	7.788×10^{-5}	1.127×10^{-4}
4000	0.638	7.190×10^{-5}	$1.128\ \ 10^{-4}$

(i) Suggest why the amount of $Cl_2(g)$ was kept in large excess. [1]

Since the amount of Cl_2 (g) was kept in large excel, the partial pressure of Cl_2 (g) remains relatively constant so that **any change in rate is due to the changes in the partial pressure of (NO(g) only.**

EXAMINER'S COMMENTS
This question requires students to see the reason behind keeping the amount of $Cl_2(g)$ in large excess and hence link to how it affect the determination of the rate of reaction. Many students were not able to be awarded full credit.

(ii) Define the term *order of reaction*. [1]

The order of reaction **with respect to a reactant** is defined as the power to which the **concentration of a reactant** is raised to in the **experimentally – determined rate equation.**

(iii) Using the data from the table above, deduce the order of reaction with respect to NO(g). [1]

Since Rate = $k(P_{NO})^{2,}$

Rate/($(P_{NO})^2$ = k is constant throughout the reaction (and thus rate of reaction is directly proportional to $(P_{NO})^2$), the reaction is second order with respect to NO.

EXAMINER'S COMMENTS
This question required students to see that Rate/$(P_{NO})^2 = k$ is constant throughout the reaction and hence determine the order of reaction. Students were not able to get full credit.

3 (a) (iv) In another experiment, the initial partial pressure of NO(g) was 4.2 atm and it was reacted with Cl_2(g) at a constant temperature of 550 K. The partial pressure of Cl_2(g) was recorded at time intervals of 30 seconds.

The data obtained are tabulated below.

time / s	partial pressure of Cl_2(g)/ atm
0	0.78
30	0.76
60	0.72
90	0.70
120	0.66
150	0.63
180	0.59
210	0.57
240	0.54
270	0.52

time / s	partial pressure of Cl_2(g)/ atm
300	0.49
330	0.46
360	0.44
390	0.42
420	0.39
450	0.38
480	0.36
510	0.34
540	0.33
570	0.32

Using the data but without plotting of any graph, deduce the order of reaction with respect to Cl_2(g). [1]

1st $t_{1/2}$

= time taken for P_{Cl_2} to decrease from 0.78 atm to 0.39 atm
= 420 s

2nd $t_{1/2}$
= time taken for P_{Cl_2} to decrease from 0.76 atm to 0.38 atm (or 0.66 ⟶ 0.33)
= 480 – 60
= 420 s

Since $t_{1/2}$ is constant at 420s, the reaction is first order with respect to Cl_2.

EXAMINER'S COMMENTS
This question required students find the half life which was not well attempted.

(v) Write the rate equation for the overall reaction. Hence, calculate the rate constant, stating its units. [3]

Rate = k $(P_{NO})^2(P_{Cl2})$
Rate = k' (P_{Cl2}) where k' = k $(P_{NO})^2$
$t_{1/2} = 420\ s = \frac{\ln 2}{k(P_{NO})^2} = \frac{\ln 2}{k(4.2)^2}$
$k = 9.36 \times 10^{-5}\ atm^{-2}\ s^{-1}$

EXAMINER'S COMMENTS
This question required students to determine the rate equation from the above parts. And hence calculate with the units stated. Common mistakes includes leaving the rate equation in terms of concentration instead of partial pressures and some thought that the rate is s^{-1} but it should be atm s^{-1}

3 **(b)** In another reaction, $2NO_2(g) + 4CO(g) \rightarrow N_2(g) + 4CO_2(g)$, it was found that the rate equation is rate = $k[NO_2]^2$.
A proposed mechanism for this reaction is shown.

Step 1	$NO_2(g) + NO_2(g) \rightarrow 2NO(g) + O_2(g)$	slow
Step 2	$2NO(g) + O_2(g) + 4CO(g) \rightarrow N_2(g) + 4CO_2(g)$	fast

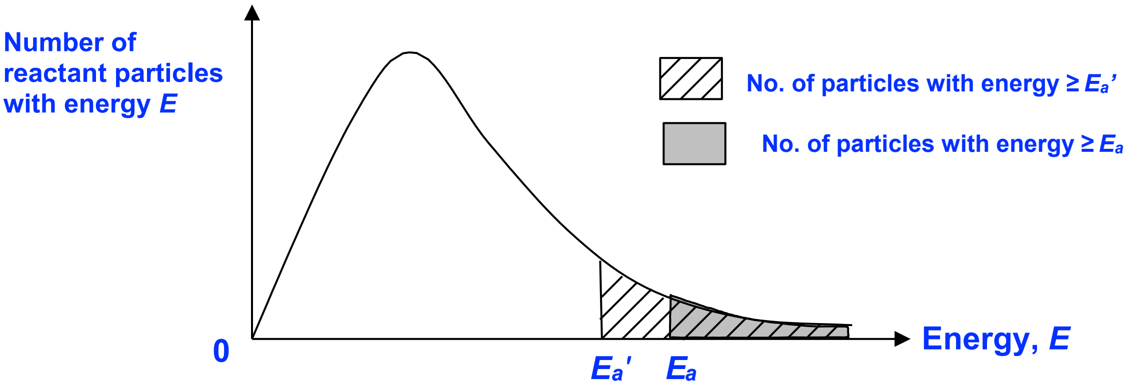
Explain whether it is consistent with the established rate equation. [1]

The mechanism is consistent with the established rate equation. One molecule of NO_2 reacts with one molecules of NO_2 in the slow rate determining step whereas rate equation shows 2 moles of NO_2 reacting in the slow rate determining step.

EXAMINER'S COMMENTS
This question required students to state the correlation of the number of reactants in the slow step with the rate equation. This question is fairly well attempted.

(c) Tryptophan metabolism plays an important role in the mechanisms associated with the gut-brain axis. At least 90% of human intake of tryptophan is converted to kynurenine for further metabolism via a catalyst.

(i) Explain how the activation energy of a reaction is affected by the presence of a catalyst, and with an appropriate sketch of a Maxwell–Boltzmann distribution curve, explain how a catalyst increases the rate of reaction. [3]



The catalyst lowers the activation energy of the reaction by providing an alternative pathway for the reaction to occur.

With a lower activation energy according to the Maxwell – Boltzman distribution, there will be a higher proportion of reactants with energy greater or equal to this lower activation energy, E_a'. Thus, there is higher frequency of effective collisions between reactants since they possess sufficient energy for reaction, Therefore, the rate of reactions increases.

EXAMINER'S COMMENTS

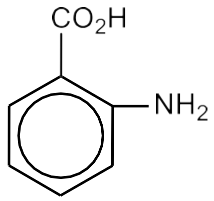
This is recall question on the Maxwell-Boltzmann distribution curve. However, this was not well attempted with many keywords or marking points missed hence not given full credit.

Common mistakes includes the wrong Maxwell-Boltzmann curve, the lack of keywords like "frequency of effective collisions".

3 **(c)** **(ii)** Kynurenine has the molecular formula $C_{10}H_{12}N_2O_3$. When dissolved, an aqueous solution of kynurenine is almost neutral and maintains its pH upon addition of small amounts of aqueous sodium hydroxide or hydrochloric acid. Addition of this solution to aqueous 2,4-dinitrophenylhydrazine causes an orange precipitate to form.

Kynurenine reacts with $NaBH_4$ to form compound **L**, $C_{10}H_{14}N_2O_3$. Heating **L** with concentrated H_2SO_4 produces only **M**, $C_{10}H_{12}N_2O_2$. Heating **M** with acidified $KMnO_4$ under reflux results in the formation of compound **N**, $C_3H_5NO_4$ and anthranilic acid.

The molecular structure of anthranilic acid is as shown below.



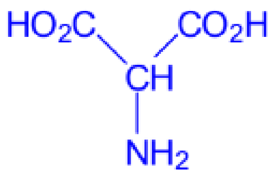
anthranilic acid

Reaction of **N** with $LiAlH_4$ in dry ether produces compound **O**, $C_3H_9NO_2$. A solution of **O** turns litmus paper blue.

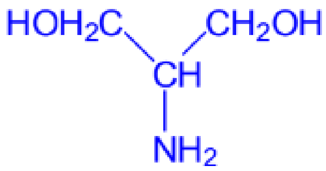
Suggest possible structures for **L, M**, **N**, **O** and kynurenine. For each reaction, state the type of reaction described and explain what the information tells you about the functional groups present in each compound. [13]

INFORMATION	**DEDUCTION**
Kynurenine has the molecular formula $C_{10}H_{12}N_2O_3$	C:H is approximately 1:1. It contains a benzene ring
When dissolved, an aqueous solution of kynurenine is almost neutral	
Kynurenine maintained its pH upon addition of small amounts of aqueous sodium hydroxide or hydrochloric acid	It functions as a buffer.

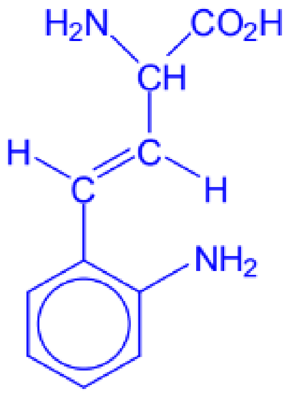
Addition of the kynurenine to aqueous 2,4-DNPH caused an orange precipitate to form.	Presence of carbonyl group Condensation reaction.
Kynurenine reacts with NaBH$_4$ to form compound **L**, $C_{10}H_{14}N_2O_3$	Reduction of ketone group in kynurenine.
Heating **L** with concentrated H_2SO_4 produces only **M**, $C_{10}H_{12}N_2O_2$.	Elimination of H and OH groups from **L** to form alkene in **M**. Indicate the presence of –OH group on **L**.
Heating **M** with acidified KMnO$_4$ under reflux results in the formation of compound **N**, $C_3H_5NO_4$ and anthranilic acid	Oxidative cleavage of C=C bond occurred as 2 molecules were obtained
Reaction of **N** with LiA/H$_4$ in dry ether produces compound **O**, $C_3H_9NO_2$. A solution of **O** turns litmus blue.	Reduction of carboxylic acid group in **N**.



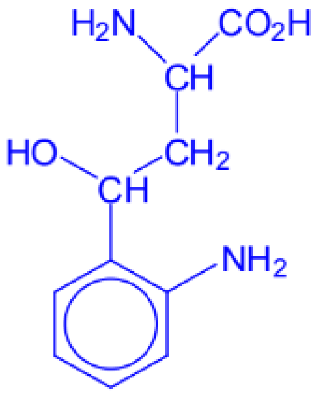
N



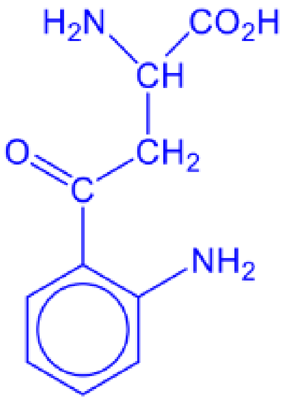
O



M



L



Kynurenine

EXAMINER'S COMMENTS

This is an elucidation question that requires students to use the information to explain the type of reaction and functional group present. And hence deduce the structures.

Many students were only able to achieve partial credits.

Some of the common mistakes includes:

- deduction of amide groups in kynurenine,
- identification of type of reaction when L is reacted with concentrated H_2SO_4 as hydrolysis

[Total: 24]

4 **(a)** The value of the equilibrium constant is 4.0 for the reaction below:

$$CH_3CO_2H(l) + C_2H_5OH(l) \rightleftharpoons CH_3CO_2C_2H_5(l) + H_2O(l)$$

(i) Write an expression for the equilibrium constant, K_c, of the **reverse** reaction, i.e. the hydrolysis of ethyl ethanoate, stating its numerical value.

$$K_c = \frac{[CH_3CO_2H][C_2H_5OH]}{[CH_3CO_2C_2H_5][H_2 0]} = \frac{1}{4} = \underline{0.25}$$

[2]

(ii) In an experiment, 2 mol of ethyl ethanoate and 2 mol of water are mixed.
Calculate the number of moles of each substance present when equilibrium is reached.

	CH_3CO_2H +	C_2H_5OH ⇌	$CH_3CO_2C_2H_5$ +	H_2O
Initial amount/mol	0	0	2	2
Change in amount/ mol	$+x$	$+x$	$-x$	$-x$
Equilibrium amount/ mol	x	x	$2-x$	$2-x$
Equilibrium conc /mol dm^{-3}.	x/v	x/v	$(2-x)/v$	$(2-x)/v$

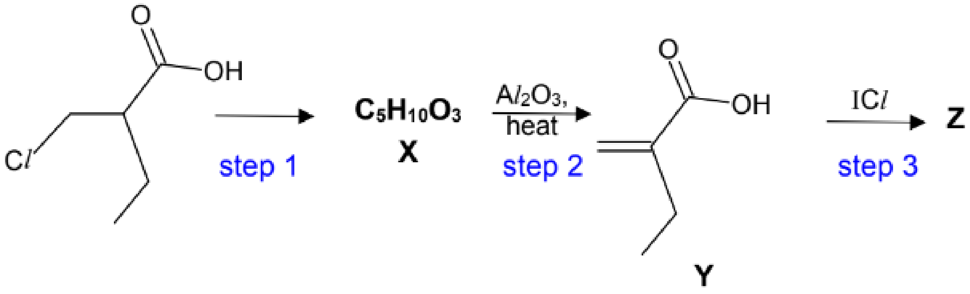
$$K_c = \frac{(x / v)^2}{((2 - x)/ v)^2} = 0.25$$

$\therefore x = 0.667$

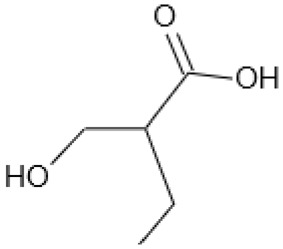
Therefore, amount of acid = amount of alcohol = 0.667 mol
Amount of water = amount of ester = 1.33 mol

[2]

(b) The following shows a flow scheme involving a chlorocarboxylic acid to form compounds **X**,**Y** and **Z**.



(i) Suggest the structure of compound **X**.

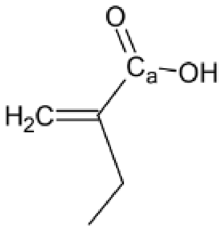


[1]

(ii) Give the reagents and conditions for step 1.

NaOH(aq), heat [1]

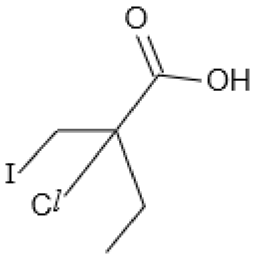
(iii) State the hybridisation of C_a labelled in the structure of **Y** below.



sp^2 hybridised

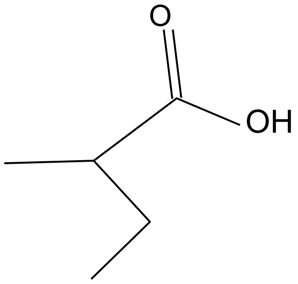
[1]

(iv) Give the structure of compound **Z**.



[1]

(v) Give the structure of the product formed when compound **Y** is reacted with hydrogen with nickel, upon heating.



[1]

Only C=C is reduced by H_2, Ni, heat, -COOH is not reduced

Aluminium objects that have had the aluminium oxide layer removed may then be oxidised.

(c) **(i)** State why aluminium objects are anodised.

To increase the thickness of a protective corrosion–resistant Al_2O_3 layer on the surface of Al object.

[1]

(ii) Complete Table 6.1 below to show the type of reaction occurring, with the relevant half-equations, during the anodising of an aluminium object.

	type of reaction	half-equation(s)
anode	Oxidation	$2Al(s) + 3H_2O(l) \rightarrow Al_2O_3(s) + 6H^+(aq) + 6e^-$
cathode	Reduction	$2H^+(aq) + 2e^- \rightarrow H_2(g)$

Table 6.1

[2]

[Total: 12]

5 Hydrogen cyanide, HCN, is extremely toxic and with sufficient concentrations it leads to rapid death. During the Second World War, a form of hydrogen cyanide known as *Zyklon B* was used in the Nazi gas chambers.

(a) **(i)** Draw a dot–and–cross diagram to illustrate the bonding in HCN. [1]

HCN can be oxidised to cyanogen, C_2N_2.

$$C_2N_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons 2HCN(g) \qquad E^\ominus = +0.37\text{ V}$$

(ii) Suggest a suitable oxidant to oxidise HCN to C_2N_2 in acidic solution, using the *Data Booklet*.

Write an equation for the reaction and calculate the $E^\ominus_{cell}$. [2]

$KMnO_4$ in acidic medium

$E^\circ_{cell} = +1.52 - (+0.37) = +1.15V > 0$ (reaction is spontaneous) 1m

$2MnO_4^- + 6H^+ + 10HCN \rightarrow 5C_2N_2 + 2Mn^{2+} + 8H_2O$ 1m

Note: Can use any oxidizing agent with $E^\ominus > +0.37V$

(b) The synthesis of HCN was developed in the early 1900s. The most commonly used procedure is the *Andrussow* process. A less common method is the *BMA* process.

Andrussow process:

$CH_4\ (g) + NH_3\ (g) + \frac{3}{2}\ O_2\ (g) \longrightarrow HCN\ (g) + 3H2O\ (l)$ $\Delta H = -506$ kJ mol^{-1}

BMA process:

$CH_4\ (g) + NH_3\ (g) \qquad HCN\ (g) + 3H_2\ (g)$

(i) Using information from the *Data Booklet*, calculate the enthalpy change of reaction for the *BMA* process given above. [2]

$\Delta H = 4 \times 410 + 3 \times 390 - [410 + 890 + 3 \times 436]$
$= +202$ kJ mol^{-1}

1m for final answer, 1 m for working (correct number and type of bonds identified- 1m)

(ii) By considering the spontaneity of reaction, suggest why the *Andrussow* process is the preferred procedure at low temperature. [2]

Andrussow process has a negative ΔS since there is decrease in number of gas particles, which causes an decrease in number of ways to arrange the particles in space. 1m
$\Delta G = \Delta H - T\Delta S$, at low temperature, $\Delta H > |T\Delta S|$, it is more likely to have $\Delta G < 0$ at low temperature

(c) The *BMA* process is a reversible reaction at 500 °C. Starting with equal amounts of CH_4 and NH_3, the reaction is allowed to reach equilibrium at 500 °C under a constant pressure of 1 atm.

BMA process: $CH_4\ (g) + NH_3\ (g) \rightleftharpoons HCN\ (g) + 3H_2\ (g)$

(i) Write an expression for the K_p of *BMA* process, stating its units. [1]

$$K_p = \frac{P_{HCN} P_{H2}^{\ 3}}{P_{CH4}\ P_{NH3}} \qquad units: atm^2$$

1/2 each for expression and units (0 if wrong expression)

(ii) Given that the equilibrium partial pressure of H_2 is 0.3 atm, calculate the value of K_p at 500 °C.

[2]

$CH_4 (g) + NH_3 (g) \rightleftharpoons HCN (g) + 3 H_2 (g)$

At equilibrium, $P_{H2} = 3 \times P_{HCN}$

$\therefore P_{HCN} = 0.1$ atm

Since the reaction is carried out at a constant pressure of 1 atm,

$P_{CH4} + P_{NH3} + P_{CH4} + P_{NH3} = 1$ atm

since partial pressure of the gaseous products ($P_{HCN} + P_{H2}$) = 0.4 atm $P_{CH4} + P_{NH3} = 0.6$ atm

1m for partial pressures

Hence $P_{CH4} = 0.3$ atm $= P_{NH3}$

$K_p = \frac{0.1(0.3)^3}{(0.3)(0.3)} = 0.03$ 1m (ecf)

(iii) Discuss the effect of increase in total pressure on

- the proportion of HCN,
- K_p value,
- rate of reaction .

[3]

Increase in pressure will shift the equilibrium to the reactant side as it has smaller number of gas particles ½, this is to partially offset increase in total pressure. Hence proportion of HCN is reduced½.

Changes in pressure has no effect on K_p value½ as K_p values are affected by changes in T only½.

Increase in total pressure increases the concentration of the gaseous particles, increase in collision frequency increases the frequency of effective collision½, hence rate is expected to increase½.

(d) HCN (aq) has pK_a = 4.79 at 25 °C.

(i) Calculate the concentration of CN^- ion at pH 4, when the concentration of HCN(aq) is 0.06 mol dm^{-3}. [1]

Zinc cyanide, $Zn(CN)_2$, is sparingly soluble in water.
The numerical value of K_{sp} is 8.0 × 10^{-12} at 25°C.

(ii) Write an expression for the K_{sp} of $Zn(CN)_2$, stating its units. [1]

(iii) By considering your answer to **(d)(i)**, determine the minimum concentration of Zn^{2+} required to cause precipitation of $Zn(CN)_2$ at pH 4. [2]

(iv) Describe and explain how the solubility of $Zn(CN)_2$ is affected:

- by adding HC*l*(aq)
- by adding concentrated ZnC*l*$_2$(aq)

. [2]

(i)

$$10^{-4.79} = \frac{10^{-4}[CN^-]}{0.06}$$

$$[CN^-] = 9.73 \times 10^{-3} moldm^{-3}$$ 1m

(ii) $K_{sp} = [Zn^{2+}][CN^-]^2$ mol^3dm^{-9} ½ each with correct expression.

(iii) For precipitation to occur, ionic product > K_{sp}

$$[Zn^{2+}](9.73 \times 10^{-3})^2 > 8.0 \times 10^{-12}$$ 1m

$$[Zn^{2+}] = 8.45 \times 10^{-8}$$ moldm^{-3} 1m (ecf)

(iv) Addition of strong acid will suppress the dissociation of weak acid HCN, causing the concentration of CN^- to reduce ½ hence *more $Zn(CN)_2$ solid dissolves* ½ to partially offset the reduction in $[CN^-]$/ *solubility of $Zn(CN)_2$ increases*½.

Addition of ZnC*l*$_2$(aq) causes the concentration of Zn^{2+} to increase ½ , hence the precipitation ½ process is favoured in order to partially offset the increase in $[Zn^{2+}]$/ hence solubility of $Zn(CN)_2$ decreases ½ .

[Total:19]

6 Glucose comes from the Greek word for “sweet”. It is the simplest carbohydrate with molecular formula $C_6H_{12}O_6$ and is the major free sugar circulating in the blood of mammals, serving as the primary source of energy for cell function.

(a) The oxidative breakdown of glucose by our body to produce energy is called respiration. The reaction for the complete combustion of glucose is

$$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l)$$

$$\Delta H^{\ominus} = -2816 \text{ kJ mol}^{-1}$$
$$\Delta S^{\ominus} = +181 \text{ J mol}^{-1} \text{ K}^{-1}$$

(i) Write a half-equation to represent the oxidative breakdown of glucose. [1]

$C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24H^+ + 24e^-$ [1]

(ii) The energy value of food is measured in Calorie. One Calorie is defined as the amount of heat needed to raise the temperature of 1 kg of water by 1 °C. Use the given information, together with data from the *Data Booklet*, to calculate the number of Calories in 1 g of glucose. [2]

- n(glucose) = $\dfrac{1}{12.0(6) + 1.0(12) + 16.0(6)}$ = 0.005555 mol
- q produced by 1 g glucose = 2816 x 0.005555 =15.64 kJ
- One Calorie = q needed to raise temperature of 1 kg of water by 1 °C = (1000) x 4.18 x 1 = 4180 J ⇨ This means that 1 Calorie = 4180 J
- Number of calories in 1 g of glucose = 15.64 x 1000 / 4180 = 3.74

Any 2 points [1] x 2

(iii) Comment on the sign of $\Delta S^{\ominus}$ for the combustion of glucose. [1]

ΔS is positive as there is an increase in number of particles (7 to 12), resulting in more ways to arrange the particles, giving rise to greater disorder. Hence entropy(S) increases and ΔS is positive. [1] OR

ΔS is positive as reaction is exothermic ($\Delta H < 0$) hence temperature increase during reaction. There is an increase in kinetic energy of particles, resulting in more ways to distribute energy amongst the particles, giving rise to greater disorder. Hence entropy(S) increases and ΔS is positive. [1]

Avoid change in state that’s more applicable to X (s) → X (g) or special cases where magnitude of ΔS is small (see 2019 P3 Q5diii).

(iv) If this combustion reaction could be harnessed as a fuel cell, calculate $\Delta G^{\ominus}$ and hence the theoretical voltage, $E_{\text{cell}}{}^{\ominus}$, that could be produced under standard conditions.

[3]

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$
$= -2816 - (298)(+181)/(1000)$
$= -2869 = -2870 \text{ kJ mol}^{-1}$ [1]

$\Delta G^{\ominus} = -nF\,E^{\ominus}_{cell}$

n = 24 (As 24e are transferred in overall eqn given in a(i) where 1 mol of glucose is oxidised. Alternatively, if student was unable to solve a(i), they can also simply check change in O.S. of oxygen: 2 x 12 e^- is gained when 12 oxygen atoms is reduced from 0 in $6O_2$ to -2 in CO_2/H_2O).

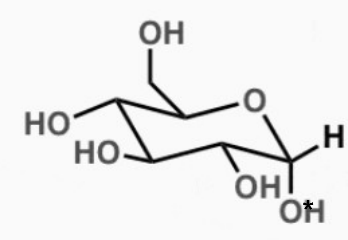
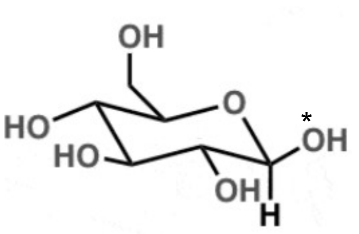
$E_{cell} = \Delta G^{\ominus} / -nF = (-2869 \times 1000) / [-24(96500)] = +1.24 \text{ V}$

- Correct formula and subst F = 96500
- Conversion of kJmol^{-1} to Jmol^{-1}
- Subst n = 24 (ECF ans a(i))
- Ans (ECF ans $\Delta G^{\ominus}$) + sign + units (BOD)

Any 2 points [1] x 2

Glucose exists in two forms, α-glucose and β-glucose, with the OH group occupying different spatial arrangement in each form. Some information about the two is given in Table 4.1.

Table 4.1

	α-glucose	**β-glucose**
		
Melting point / °C	146	150
Angle of rotation of plane-polarised light for a 1 mol dm^{-3} sample / °	+20.2	+3.4

(b) (i) Suggest a reason for the difference in melting points between α-glucose and β-glucose. [1]

As α-glucose contains two adjacent OH groups that are in close proximity, they can form intramolecular hydrogen bonds. Hence less energy is needed to break the less extensive intermolecular hydrogen bonds, giving rise to a lower melting point. [1]

If a solution of α-glucose is left for some time, it will come into dynamic equilibrium with β-glucose.

$$\alpha\text{-glucose} \rightleftharpoons \beta\text{-glucose}$$

(ii) Explain what is meant by *dynamic equilibrium*. [1]

Dynamic equilibrium is established when rate of forward reaction is equal to rate of backward reaction and there is no net change in concentrations of reactants and products. [1]

(iii) 1 dm^3 of a freshly prepared solution of 1.0 mol dm^{-3} solution of α-glucose is left to stand at 298 K. At equilibrium, the solution was found to rotate plane-polarised light by +9.45 °. Given angle of rotation of plane-polarised light is directly proportional to concentration of isomer, use information from Table 4.1 to determine [β-glucose] at equilibrium. [1]

Let concentration of β-glucose at equilibrium be x mol dm^{-3}.

	α-glucose	β-glucose
Initial conc /mol dm^{-3}	1	0
Eqm conc /mol dm^{-3}	1–x	x

x mol dm^{-3} β-glucose should rotate p-p.light by x(+3.4).
(1 – x) mol dm^{-3} α-glucose should rotate p-p.light by (1–x)(+20.2). Net rotation of equilibrium mixture = x(+3.4) + (1 – x)(+20.2) = +9.45

$$3.4x + 20.2 - 20.2x = 9.45$$

$$x = 0.6398 \text{ mol dm}^{-3}$$ [1]

(iv) Hence calculate the value of the equilibrium constant, K_c, for the conversion of α-glucose to β-glucose at 298 K. If you were unable to determine [β-glucose] at equilibrium, assume the value is 0.60. Note 0.60 is **not** the correct answer for **(b)(iii)**. [1]

K_c = [β-glucose] / [α-glucose]
= 0.6398 / (1–0.6398)
= 1.78 [1] or 1.50 if students use [β-glucose] = 0.60 mol dm^{-3}

(v) The conversion of α-glucose into β-glucose is catalysed by acids. What will be the effect on the equilibrium position if the conversion is now carried out in the presence of dilute sulfuric acid? Explain your answer. [1]

No effect on equilibrium position as catalyst increases rate of both forward and backward reaction to the same extent / only increases rate at which equilibrium is established. [1]

(c) Fig. 4.1 shows the mechanism for the conversion of α-glucose into β-glucose.

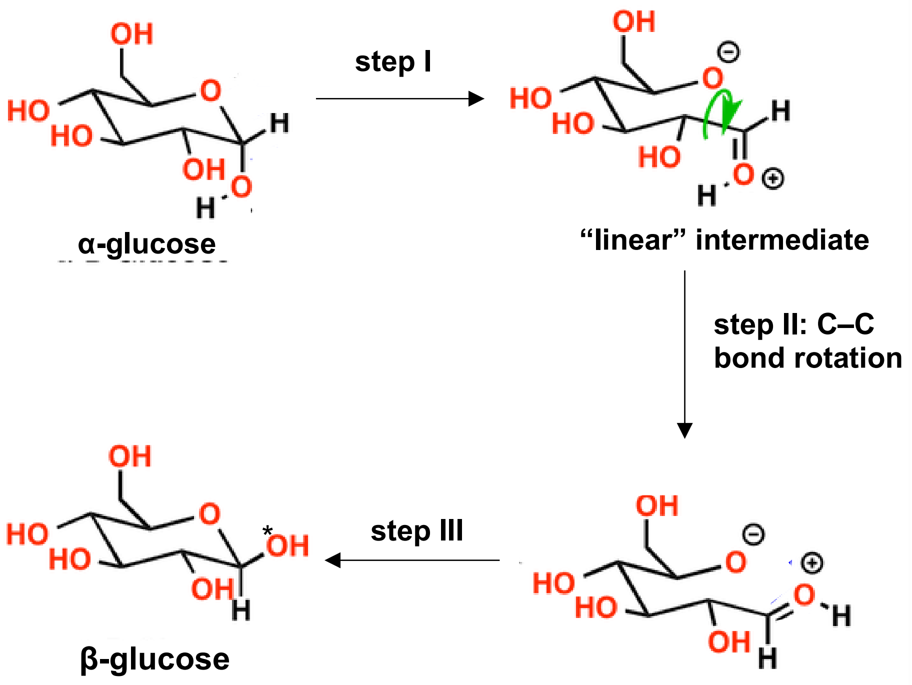


Fig. 4.1

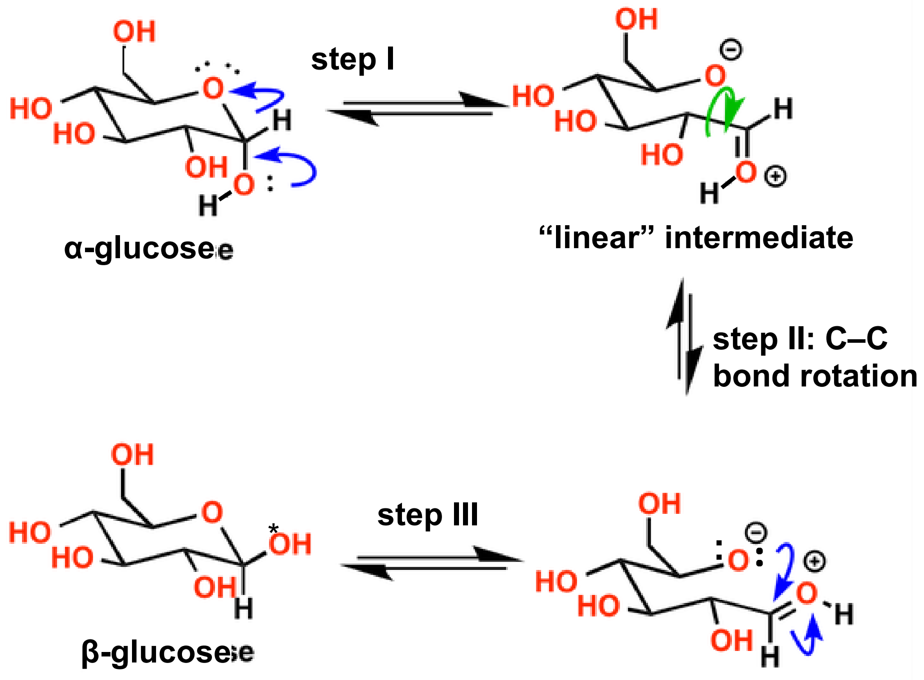
(i) Explain, with reference to the Valence Shell Electron Pair Repulsion theory, why the bond angle around O^* increases in step I of the mechanism. [2]

Initially, it was 105 ° as there are 2bp, 2lp around O^* and it increases to 118/<120 ° as there are 2bp, 1lp around O^* after step I. [1]

Bond angle increases as there are less electron pairs around O^* (4→3) hence the 3 remaining electron pairs spread themselves further to minimize repulsion. [1]

Cannot explain by lp-lp > lp-bp as the number of e are different hence first VSEPR principle is more relevant.

(ii) Complete Fig. 4.1 to suggest the mechanism for steps I and III. Show all relevant lone pairs and show the movement of electron pairs by using curly arrows. [2]

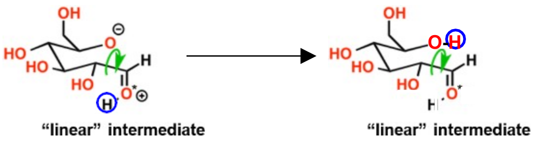


Step I – 1 lp, 2 curly arrows
Step III – 1 lp, 2 curly arrows Any 2 correct [1]x2
No partial charges needed. Do not penalise if students indicate.

(iii) Suggest the types of reaction taking place in steps I and III. [2]

Step I – Elimination [1] Step III – Nucleophilic Addition [1]

(iv) A proton transfer can occur between the charged groups in the "linear" intermediate to form another stable electrically neutral intermediate. Identify the new functional group present in this other intermediate and hence suggest a suitable chemical test to confirm its presence during the conversion of glucose. [2]



As indicated by the circled H, a proton (H$^+$) can be transferred from the C=O$^+$–H group to O$^-$ to form an aldehyde and alcohol (ROH).

An aldehyde functional is formed. [1] Do not accept carbonyl
Test: Add Tollens' Reagent or Fehling's Reagent, Warm [1] Accept 2,4-DNPH (ecf)

[Total: 20]