1 This question looks at two reactions involving sulfur compounds.

(a) Hydrogen reacts with carbon disulfide as shown below.

$$4H_2(g) + CS_2(g) \longrightarrow CH_4(g) + 2H_2S(g)$$

For this reaction, $\Delta H = -234\,kJ\,mol^{-1}$ and $\Delta S = -164\,J\,K^{-1}\,mol^{-1}$.

(i) Why does the reaction have a negative entropy change?

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..... **[1]**

(ii) Standard entropies are shown in the table below.

substance	**$CS_2(g)$**	**$CH_4(g)$**	**$H_2S(g)$**
$S^{\ominus}$ / $J\,K^{-1}\,mol^{-1}$	238	186	206

Calculate the standard entropy for H_2.

$S^{\ominus}$ = ... $J\,K^{-1}\,mol^{-1}$ **[2]**

(iii) Explain, with a calculation, whether this reaction is feasible at 25 °C.

Show your working.

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..... **[3]**

(iv) Explain, with a calculation, the significance of temperatures above 1154 °C for this reaction.

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..... **[2]**

(b) A chemist investigated methods to improve the synthesis of sulfur trioxide from sulfur dioxide and oxygen.

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

The chemist:

- mixed together 1.00 mol SO_2 and 0.500 mol O_2 with a catalyst at room temperature
- compressed the gas mixture to a volume of 250 cm^3
- allowed the mixture to reach equilibrium at constant temperature and without changing the total gas volume.

At equilibrium, 82.0% of the SO_2 had been converted into SO_3.

(i) Determine the concentrations of SO_2, O_2 and SO_3 present at equilibrium and calculate K_c for this reaction.

K_c = ... units ..... **[6]**

(ii) Explain what would happen to the pressure as the system was allowed to reach equilibrium.

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..... **[1]**

(iii) The value of K_c for this equilibrium decreases with increasing temperature.

Predict the sign of the enthalpy change for the forward reaction. State the effect on the equilibrium yield of SO_3 of increasing the temperature at constant pressure.

ΔH: .....

Effect on SO_3 yield: ..... **[1]**

(iv) The chemist repeated the experiment at the same temperature with 1.00 mol SO_2 and an excess of O_2.
The gas mixture was still compressed to a volume of 250 cm^3.

State and explain, in terms of K_c, how the equilibrium yield of SO_3 would be different from the yield in the first experiment.

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..... **[3]**

[Total: 19]

2 This question looks at different aspects of entropy.

(a) Three processes are given below.

For each process, state and explain whether the change would be accompanied by an increase or decrease in entropy.

(i) The freezing of water.

increase or decrease .....

explanation .....

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[1]

(ii) The reaction of calcium carbonate with hydrochloric acid.

increase or decrease .....

explanation .....

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[1]

(iii) The formation of $O_3(g)$ from $O_2(g)$.

increase or decrease .....

explanation .....

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[1]

(b) The enthalpy and entropy changes of a reaction both have a negative sign.

Discuss how the feasibility of this reaction will change as the temperature increases.

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(c) The metal tungsten is obtained on a large scale from its main ore, wolframite. Wolframite contains tungsten(VI) oxide, WO_3.

Tungsten is extracted from wolframite by reduction with hydrogen:

$$WO_3(s) + 3H_2(g) \rightarrow W(s) + 3H_2O(g) \qquad \Delta H = +115\,kJ\,mol^{-1}$$

Standard entropies are given in the table below.

Substance	$WO_3(s)$	$H_2(g)$	$W(s)$	$H_2O(g)$
$\boldsymbol{S^{\ominus}}$ **/ J K^{-1} mol^{-1}**	76	131	33	189

(i) Calculate the free energy change, ΔG, in kJ mol^{-1}, for this reaction at 25 °C.

Show your working.

ΔG at 25 °C = ... kJ mol^{-1} **[2]**

(ii) Calculate the minimum temperature, in K, at which this reaction becomes feasible.

Show your working.

minimum temperature = ... K **[2]**

[Total: 9]

3 The equation for the reaction of CO_2 and H_2O to produce glucose, $C_6H_{12}O_6$, and O_2 is shown below.

$6CO_2(g) + 6H_2O(l) \longrightarrow C_6H_{12}O_6(s) + 6O_2(g)$ $\Delta H = +2879\,kJ\,mol^{-1}$; $\Delta S = -256\,J\,K^{-1}\,mol^{-1}$

Standard entropies are given in the table below.

Substance	$CO_2(g)$	$H_2O(l)$	$O_2(g)$
$S^{\ominus}$ **/ J K^{-1} mol^{-1}**	214	70	205

(a) (i) Calculate the standard entropy of glucose.

$S^{\ominus}$ = ... $J\,K^{-1}\,mol^{-1}$ **[2]**

(ii) Calculate ΔG, in $kJ\,mol^{-1}$, at 25 °C.

Show all your working.

ΔG = ... $kJ\,mol^{-1}$ **[2]**

(iii) Explain why this reaction is **not** feasible at **any** temperature.

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..... **[1]**

(b) Although the reaction between CO_2 and H_2O to form $C_6H_{12}O_6$ and O_2 appears not to be feasible, plants are able to make the reaction take place spontaneously by photosynthesis.

Each year, 3.4×10^{18} kJ of solar energy is taken in by all the plants on the Earth to make photosynthesis take place.

Calculate the mass of carbon dioxide that is removed each year from the atmosphere by photosynthesis on Earth.

mass of CO_2 = ... **[2]**

[Total: 7]

4 Nitrogen dioxide reacts with ozone as shown below.

$$2NO_2(g) + O_3(g) \rightarrow N_2O_5(g) + O_2(g)$$

(a) The kinetics of the reaction between NO_2 and O_3 was investigated and the following experimental results were obtained.

experiment	$[NO_2(g)]$ / mol dm^{-3}	$[O_3(g)]$ / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	0.00150	0.00250	4.80×10^{-8}
2	0.00225	0.00250	7.20×10^{-8}
3	0.00225	0.00500	1.44×10^{-7}

(i) Determine the rate equation and rate constant for the reaction of $NO_2(g)$ and $O_3(g)$.

In your answer you should make clear how your conclusions fit with the experimental results.

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(ii) Suggest a possible two-step mechanism for this reaction.

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(b) The feasibility of the reaction between NO_2 and O_3 is influenced by the enthalpy change and entropy change of the reaction and the temperature.

$$2NO_2(g) + O_3(g) \rightarrow N_2O_5(g) + O_2(g) \qquad \Delta H = -198\,kJ\,mol^{-1}, \quad \Delta S = -168\,J\,K^{-1}\,mol^{-1}$$

(i) Explain why this reaction has a negative entropy change.

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..... **[2]**

(ii) Calculate the value of ΔG, in $kJ\,mol^{-1}$, at 25 °C for the reaction of NO_2 with O_3.

ΔG = ... $kJ\,mol^{-1}$ **[3]**

(iii) State and explain how the feasibility of this reaction will change with increasing temperature.

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..... **[2]**

[Total: 17]