Q1. (a) The gaseous reactants **W** and **X** were sealed in a flask and the mixture left until the following equilibrium had been established.

$$2W(g) + X(g) = 3Y(g) + 2Z(g)$$
 $\Delta H = -200 \text{ kJ mol}^{-1}$

Write an expression for the equilibrium constant, K_{\circ} , for this reaction. State one change in the conditions which would both increase the rate of reaction and decrease the value of K_{\circ} . Explain your answers.

(7)

(b) Ethyl ethanoate can be prepared by the reactions shown below.

Reaction 1

$$CH_{\scriptscriptstyle 3}COOH(I) + C_{\scriptscriptstyle 2}H_{\scriptscriptstyle 5}OH(I) \quad \stackrel{\textstyle \longleftarrow}{\longleftarrow} \quad CH_{\scriptscriptstyle 3}COOC_{\scriptscriptstyle 2}H_{\scriptscriptstyle 5}(I) + H_{\scriptscriptstyle 2}O(I) \qquad \Delta H^{^{\bigodot}} = -2.0 \text{ kJ mol}^{\scriptscriptstyle -1}$$

Reaction 2

CH₃COCl(I) + C₂H₅OH(I)
$$\rightarrow$$
 CH₃COOC₂H₅(I) + HCl(g) $\Delta H^{\bullet} = -21.6 \text{ kJ mol}^{-1}$

- (i) Give one advantage and one disadvantage of preparing ethyl ethanoate by **Reaction 1** rather than by **Reaction 2**.
- (ii) Use the information given above and the data below to calculate values for the standard entropy change, ΔS^{\bullet} , and the standard free-energy change, ΔG^{\bullet} , for **Reaction 2** at 298 K.

	CH ₃ COCI(I)	C ₂ H ₅ OH(I)	CH ₃ COOC ₂ H ₅ (I)	HCI(g)
S [©] /JK¹mol¹	201	161	259	187

(8)

(Total 15 marks)

Q2.The compound lithium tetrahydridoaluminate(III), LiAlH₄, is a useful reducing agent. It behaves in a similar fashion to NaBH₄. Carbonyl compounds and carboxylic acids are reduced to alcohols. However, LiAlH₄ also reduces water in a violent reaction so that it must be used in an organic solvent.

		ich one se?	e of the following concerning the violent reaction between LiAlH₄ and wa	ter is
	Α	A ga	as is produced.	
	В	The	activation energy for the reaction is relatively high.	
	С	The	reaction has a negative free-energy change.	
	D	Aqu	ieous lithium ions are formed.	(Total 1 mark)
Q 3.		(a)	(i) Draw a fully-labelled Born–Haber cycle for the formation of solid chloride, BaCl₂, from its elements. Include state symbols for all specie involved.	
		(ii)	Use your Born–Haber cycle and the standard enthalpy data given bel	ow to
			calculate a value for the electron affinity of chlorine. Enthalpy of atomisation of barium +180 kJ mol ⁻¹ Enthalpy of atomisation of chlorine +122 kJ mol ⁻¹ Enthalpy of formation of barium chloride -859 kJ mol ⁻¹ First ionisation enthalpy of barium +503 kJ mol ⁻¹ Second ionisation enthalpy of barium +965 kJ mol ⁻¹ Lattice formation enthalpy of barium chloride -2056 kJ mol ⁻¹	

(b) Use data from part (a)(ii) and the entropy data given below to calculate the lowest temperature at which the following reaction becomes feasible.

$$BaCl_{{\scriptscriptstyle 2}}\!(s) \ \to \ Ba(s) \ + \ Cl_{{\scriptscriptstyle 2}}\!(g)$$

	BaCl₂(s)	Ba(s)	Cl ₂ (g)
S [♣] / J K⁻¹ mol⁻¹	124	63	223

	(4)

(Total 13 marks)

(9)

Q4.The following information concerns the equilibrium gas-phase synthesis of methanol.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

At equilibrium, when the temperature is 68 °C, the total pressure is 1.70 MPa. The number of moles of CO, H_2 and CH_3OH present are 0.160, 0.320 and 0.180, respectively.

Thermodynamic data are given below.

Substance	ΔH _ℓ / kJ mol⁻¹	S → / J K¹ mol¹
CO(g)	-110	198

H ₂ (g)	0	131	
CH₃OH(g)	-201	240	

The standard entropy change for this reaction is

- **A** -220 J K⁻¹ mol⁻¹
- **B** +220 J K⁻¹ mol⁻¹
- **C** -89 J K⁻¹ mol⁻¹
- **D** +89 J K⁻¹ mol⁻¹

(Total 1 mark)

Q5. Use the data in the table below to answer the questions which follow.

Substance	Fe ₂ O ₃ (s)	Fe(s)	C(s)	CO(g)	CO ₂ (g)
ΔH _f → / kJ mol-1	-824.2	0	0	–110.5	-393.5
S [©] / J K ⁻¹ mol ⁻¹	87.4	27.3	5.7	197.6	213.6

(a) The following equation shows one of the reactions which can occur in the extraction of iron.

$$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$$

(i) Calculate the standard enthalpy change and the standard entropy change for this reaction.

Standard enthalpy change

		Standard entropy change	
	(ii)	Explain why this reaction is feasible at all temperatures.	
			(9)
(b)	The iron.	reaction shown by the following equation can also occur in the extraction of	
		$Fe_2O_3(s) + 3C(s) \rightarrow 2Fe(s) + 3CO(g)$ $\Delta H^{\bullet} = +492.7 \text{ kJ mol}^{-1}$	
	The	standard entropy change, ΔS^{\bullet} , for this reaction is +542.6 J K ⁻¹ mol ⁻¹	
	Use feas	this information to calculate the temperature at which this reaction becomes ible.	
			(3)
(c)	Calc	culate the temperature at which the standard free-energy change, ΔG^{\bullet} has the e value for the reactions in parts (a) and (b).	

(Total 15 marks)

Q6.This question relates to the equilibrium gas-phase synthesis of sulphur trioxide:

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

Thermodynamic data for the components of this equilibrium are:

Substance	ΔH [⇔] / kJ mol⁻¹	S / J K¹ mol¹
SO₃(g)	-396	+257
SO ₂ (g)	-297	+248
O ₂ (g)	0	+204

This equilibrium, at a temperature of 585 K and a total pressure of 540 kPa, occurs in a vessel of volume 1.80 dm 3 . At equilibrium, the vessel contains 0.0500 mol of SO $_2$ (g), 0.0800 mol of O $_2$ (g) and 0.0700 mol of SO $_3$ (g).

The standard entropy change for this reaction is

- **A** −222 J K⁻¹ mol⁻¹
- **B** −195 J K⁻¹ mol⁻¹
- **C** -186 J K⁻¹ mol⁻¹
- **D** +198 J K⁻¹ mol⁻¹

(Total 1 mark)