Q13.

In the Contact Process sulfur dioxide reacts with oxygen to form sulfur trioxide as shown in the equation.

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

The table shows some thermodynamic data.

	$\Delta H_f^\ominus$/kJ mol^{-1}	$S^\ominus$/J K^{-1} mol^{-1}
$SO_2(g)$	–297	248
$O_2(g)$	0	205
$SO_3(g)$	–395	256

(a) Use data from the table to calculate the standard enthalpy change for this reaction.

(2)

(b) Use data from the table to calculate the standard entropy change for this reaction.

(2)

(c) State what the sign of the entropy change in your answer to part **(b)** indicates about the product of this reaction relative to the reactants.

(1)

(d) Use your answers to parts **(a)** and **(b)** to calculate a value for the free–energy change for this reaction at 50°C.

(If you were unable to calculate ΔH in part **(a)** assume a value of –250 kJ mol^{-1}.
If you were unable to calculate ΔS in part **(b)** assume a value of –250 J K^{-1} mol^{-1}.
These are not the correct values.)

(3)

(e) Use your answer to part **(d)** to explain whether the reaction is feasible at 50°C.

(1)

(f) Vanadium(V) oxide acts as a heterogeneous catalyst in the Contact Process.

(i) State what is meant by the term heterogeneous.

(1)

(ii) Write **two** equations that show how this catalyst is involved in the Contact Process.

(2)

(iii) Suggest why the vanadium(V) oxide is used in small pellet form rather than as large lumps.

(1)

(iv) State why the reactants should be purified before they come into contact with the vanadium(V) oxide.

(1)

(Total 14 marks)

Q14.

Hydrogen can be manufactured from the reaction of steam with methane.

$$CH_4(g) + H_2O(g) \longrightarrow CO(g) + 3H_2(g)$$

(a) The table contains some enthalpy of formation and entropy data.

Substance	**$\Delta H^\ominus_f$ / kJ mol^{-1}**	**$S^\ominus$ / J K^{-1} mol^{-1}**
$CH_4(g)$	−75	186
$H_2O(g)$	−242	189
$CO(g)$	−111	198
$H_2(g)$	0	131
$CO_2(g)$	−394	214

(i) Use data from the table to calculate the enthalpy change, Δ*H*, for the reaction of steam with methane.

(3)

(ii) Use data from the table to calculate the entropy change, Δ*S*, for the reaction of steam with methane.

(2)

(b) Use your values of Δ*H* and Δ*S* from parts (a)(i) and (a)(ii) to calculate the temperature above which this reaction is feasible.

(4)

(c) The temperature used for this manufacture of hydrogen is usually about 1300 K.

Suggest **one** reason, other than changing the position of equilibrium, why this temperature is used rather than the value that you calculated in part (b).

(1)

(d) Hydrogen can also be obtained by reaction of carbon monoxide with steam.

$CO(g) + H_2O(g) \longrightarrow CO_2(g) + H_2(g)$ $\Delta H = -41$ kJ mol^{-1}, $\Delta S = -42$ J K^{-1} mol^{-1}

(i) Explain, using a calculation, why this reaction should **not** occur at 1300 K.

(3)

(ii) Explain how the conditions for the reaction could be changed to allow this reaction to take place.

(2)

(Total 15 marks)

Q15.

The following table shows some enthalpy change and entropy change data.

	ΔH / kJ mol^{-1}	**ΔS / J K^{-1} mol^{-1}**
$AgCl(s) \longrightarrow Ag^+(g) + Cl^-(g)$	+905	
$AgCl(s) \longrightarrow Ag^+(aq) + Cl^-(aq)$	+77	+33
$AgF(s) \longrightarrow Ag^+(aq) + F^-(aq)$	–15	to be calculated
$Ag^+(g) \longrightarrow Ag^+(aq)$	–464	

(a) Define the term **enthalpy of hydration** of an ion.

(2)

(b) Use data from the table to calculate a value for the enthalpy of hydration of the chloride ion.

(2)

(c) Suggest why hydration of the chloride ion is an exothermic process.

(2)

(d) Silver chloride is insoluble in water at room temperature.

Use data from the table to calculate the temperature at which the dissolving of silver chloride in water becomes feasible.
Comment on the significance of this temperature value.

Calculation of temperature

Significance of temperature value

(4)

(e) When silver fluoride dissolves in water at 25 °C, the free-energy change is –9 kJ mol^{-1}.

Use this information and data from the table to calculate a value, with units, for the entropy change when silver fluoride dissolves in water at 25 °C.

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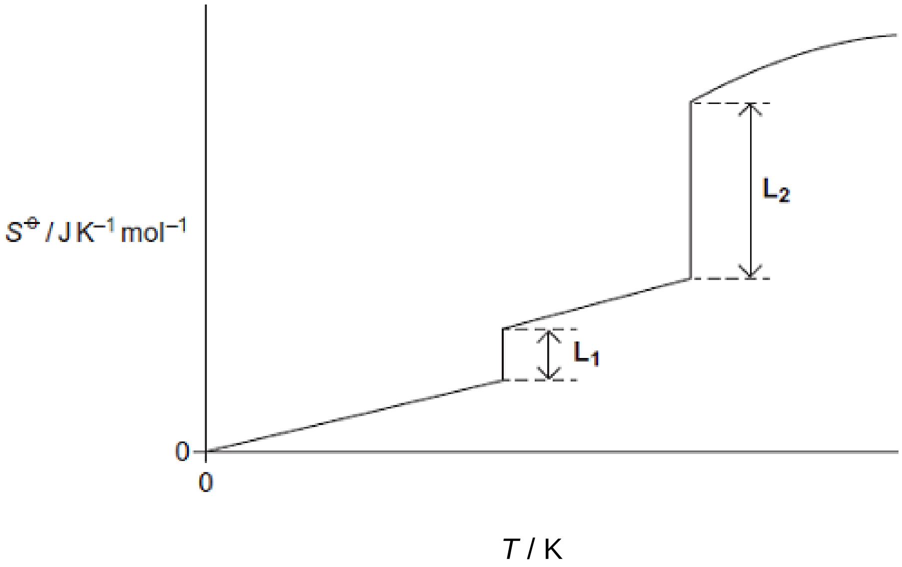
(3)

(Total 13 marks)

Q16.

(a) **Figure 1** shows how the entropy of a molecular substance **X** varies with temperature.

Figure 1



(i) Explain, in terms of molecules, why the entropy is zero when the temperature is zero Kelvin.

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(2)

(ii) Explain, in terms of molecules, why the first part of the graph in **Figure 1** is a line that slopes up from the origin.

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(2)

(iii) On **Figure 1**, mark on the appropriate axis the boiling point (*T_b*) of substance **X**.

(1)

(iv) In terms of the behaviour of molecules, explain why **L_2** is longer than **L_1** in **Figure 1**.

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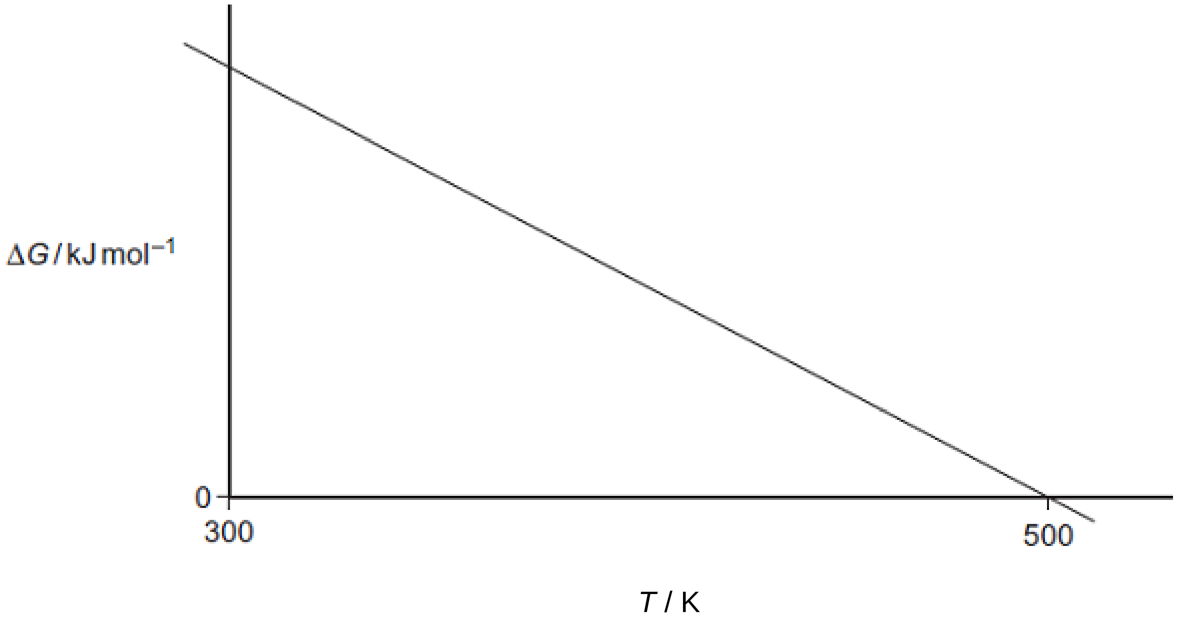
____

____

(2)

(b) **Figure 2** shows how the free-energy change for a particular gas-phase reaction varies with temperature.

Figure 2



(i) Explain, with the aid of a thermodynamic equation, why this line obeys the mathematical equation for a straight line, $y = mx + c$.

(2)

(ii) Explain why the magnitude of ΔG decreases as T increases in this reaction.

(1)

(iii) State what you can deduce about the feasibility of this reaction at temperatures lower than 500 K.

(1)

(c) The following reaction becomes feasible at temperatures above 5440 K.

$$H_2O(g) \longrightarrow H_2(g) + \frac{1}{2}O_2(g)$$

The entropies of the species involved are shown in the following table.

	$H_2O(g)$	$H_2(g)$	$O_2(g)$
S / J K^{-1} mol^{-1}	189	131	205

(i) Calculate the entropy change ΔS for this reaction.

(1)

(ii) Calculate a value, with units, for the enthalpy change for this reaction at 5440 K.

(If you have been unable to answer part (c)(i), you may assume that the value of the entropy change is +98 J K^{-1} mol^{-1}. This is **not** the correct value.)

(3)

(Total 15 marks)

Q17.

The feasibility of a physical or a chemical change depends on the balance between the thermodynamic quantities of enthalpy change (ΔH), entropy change (ΔS) and temperature (T).

(a) Suggest how these quantities can be used to predict whether a change is feasible.

(2)

(b) Explain why the evaporation of water is spontaneous even though this change is endothermic.
In your answer, refer to the change in the arrangement of water molecules and the entropy change.

(4)

(c) This table contains some thermodynamic data for hydrogen, oxygen and water.

	$S^\ominus$ / J K^{-1} mol^{-1}	$\Delta H_f^\ominus$/ kJ mol^{-1}
$H_2(g)$	131	0
$O_2(g)$	205	0
$H_2O(g)$	189	−242
$H_2O(l)$	70	

(i) Calculate the temperature above which the reaction between hydrogen and oxygen to form gaseous water is **not** feasible.

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____

____

____

____

____

____

(4)

(ii) State what would happen to a sample of gaseous water that was heated to a temperature higher than that of your answer to part (c)(i).
Give a reason for your answer.

What would happen to gaseous water ______________________________

____

Reason ____

____

____

(2)

(d) When hydrogen is used as a fuel, more heat energy can be obtained if the gaseous water formed is condensed into liquid water.

Use entropy data from the table in part (c) to calculate the enthalpy change when one mole of gaseous water is condensed at 373 K.
Assume that the free-energy change for this condensation is zero.

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____

____

(3)

(Total 15 marks)

Mark Scheme

Q13.

(a) $\Delta H^\ominus = \Sigma\Delta H_f^\ominus$ products - $\Sigma\Delta H_f^\ominus$ reactants 1

or $(2 \times -395) - (2 \times -297)$

$= -196$ (kJ mol^{-1})

Penalise incorrect units, ignore missing units 1

(b) $\Delta S^\ominus = \Sigma S^\ominus$ products - $\Sigma S^\ominus$ reactants 1

$= (2 \times 256) - 205 - (2 \times 248)$

$= -189$ JK^{-1} mol^{-1}

Allow -0.189 kJ K^{-1} mol^{-1}

Units must be given and must match value 1

(c) Causes an increase in order / a decrease in disorder

Allow products more ordered / products less disordered

If answer to (b) is +ve, allow products are less ordered / causes an increase in disorder / causes a decrease in order 1

(d) $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$

Do not insist on standard state symbol 1

$= -196 - 323 (-189/1000)$

If conversion of T or ΔS incorrect, then can only score M1 1

$= -134.9$ kJ mol^{-1}

Must have correct units

Allow answers in J mol^{-1}

–135 kJ mol^{-1}

If both alternative values used then -169(.3) kJ mol^{-1}

Allow alternative ΔH and/or alternative ΔS in calculation 1

(e) Feasible because ΔG is negative

Allow mark if a correct deduction from answer to (d)

Both a reference to feasibility and to ΔG needed 1

(f) (i) (The catalyst is in) a different state or phase (from the reactants) 1

(ii) $SO_2 + V_2O_5 \longrightarrow SO_3 + V_2O_4$

Allow 2VO$_2$ *instead of V*$_2$*O*$_4$

Allow multiples

1

$\frac{1}{2}O_2 + V_2O_4 \rightarrow V_2O_5$

Must have equations in this order

1

(iii) Surface area is increased

1

(iv) So that the catalyst is not poisoned

Allow correct reference to the blocking active sites

1

[14]

Q14.

(a) (i) Δ*H* = Σ(enthalpies formation products) − Σ(enthalpies formation reactants)

Or correct cycle with enthalpy changes labelled

1

= −111 −(−75 − 242)

1

= (+)206 (kJ mol^{-1})

−206 scores 1 only

Units not essential if ans in kJ mol^{-1} *but penalise incorrect units*

1

(ii) Δ*S* = Σ(entropies of products) − Σ(entropies reactants)

= 198 + 3 × 131 − (186 + 189)

1

= (+) 216 (J K^{-1} mol^{-1})
OR
0.216 kJ K^{-1} mol^{-1}

Units not essential but penalise incorrect units

1

(b) When Δ*G* = 0 OR Δ*H* = *T*Δ*S*

1

T = Δ*H* / Δ*S*

M2 also scores M1

1

= 206 × 1000 / 216

Allow error carried forward from (a)(i) and (a)(ii)

Ignore unexplained change of sign from − to +

1

= 954 K

Allow 953 − 955, Units of K essential, must be +ve

If values from (a)(i) and (a)(ii) lead to negative value in M3 allow M1 to M3 but do not allow negative temperature for M4

If negative value changed to positive for M4, allow M4

1

(c) To speed up the rate of reaction OR wtte

Allow so that more molecules have energy greater than the activation energy

IF T in (b) > 1300 allow answers such as;

to reduce energy cost

to slow down reaction

do NOT allow to increase rate

1

(d) (i) **Method 1**

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

$\Delta G = -41 - (1300 \times -42 / 1000)$ (M1)

If 42 and not 42 / 1000 used can score M3 only

but allow $\Delta G = -41 \times 1000 - (1300 \times -42)$ *(M1)*

1

= +13.6 kJ mol^{-1}

=13600 J mol^{-1} *(M2)*

Units essential

1

ΔG must be negative for the reaction to be feasible.

OR ΔG is positive so reaction is not feasible

1

Method 2

For reaction to be feasible ΔG must be negative or zero

1

T when $\Delta G = 0 = \Delta H / \Delta S = 976K$

1

ΔS is −ve so ΔG must be +ve at temperatures above 976K / at 1300 K

1

(ii) If the temperature is lowered

(Ignore reference to catalyst and / or pressure)

Alternative mark scheme (if T is calculated)

Allow T reduced to 976 K or lower M1

1

ΔG will become (more) negative because

the $-T\Delta S$ term will be less positive / $T\Delta S > \Delta H$

At this temperature (the reaction becomes feasible because) ΔG *<*

= 0 M2

1

[15]

Q15.

(a) Enthalpy change / *ΔH* when 1 mol of a gaseous ion

Enthalpy change for $X^{+/-}(g) \rightarrow X^{+/-}(aq)$ scores M1 and M2

1

forms aqueous ions

Allow heat energy change instead of enthalpy change

Allow 1 mol applied to aqueous or gaseous ions

If substance / atoms in M1 CE = 0

If wrong process (eg boiling) CE = 0

1

(b) *ΔH*(solution) = *ΔH*(lattice) + <u>Σ</u>(*ΔH*hydration)

OR +77 = +905 – 464 + *ΔH*(hydration, Cl^-)

OR *ΔH*(hydration, Cl^-) = +77 –905 + 464

Allow any one of these three for M1 even if one is incorrect

1

= –364 (kJ mol^{-1})

Allow no units, penalise incorrect units, allow kJ mol^-

Allow lower case j for J (Joules)

+364 does not score M2 but look back for correct M1

1

(c) Water is polar / water has Hδ+

1

(Chloride ion) attracts (the H in) water molecules

(note chloride ion can be implied from the question stem)

Idea that there is a force of <u>attraction</u> between the chloride ion and water

Do not allow H bonds / dipole–dipole / vdW / intermolecular but ignore loose mention of bonding

Do not allow just chlorine or chlorine atoms / ion

Mark independently

1

(d) $\Delta G = \Delta H - T\Delta S$

Look for this equation in part (d) and / or (e); equation can be stated or implied by correct use. Record the mark in part (d)

1

($\Delta G = 0$ so) $T = \Delta H / \Delta S$

1

T = 77 × 1000 / 33 = 2333 <u>K</u> (allow range 2300 to 2333.3)

Units essential, allow lower case k for K (Kelvin)

Correct answer with units scores M1, M2 and M3

2.3 (K) scores M1 and M2 but not M3

1

Above the boiling point of water (therefore too high to be sensible) / water would evaporate

Can only score this mark if M3 >373 K

1

(e) $\Delta S = (\Delta H - \Delta G) / T$ OR $\Delta S = (\Delta G - \Delta H) / -T$

1

$= ((-15 + 9) \times 1000) / 298$ OR $(-15 + 9) / 298$

1

$= -20$ J K^{-1} mol^{-1} OR -0.020 kJ K^{-1} mol^{-1}

(allow –20 to –20.2) (allow –0.020 to –0.0202)

Answer with units must be linked to correct M2

For M3, units must be correct

Correct answer with appropriate units scores M1, M2 and M3 and possibly M1 in part (d) if not already given

Correct answer without units scores M1 and M2 and possibly M1 in part (d) if not already given

Answer of –240 / –0.24 means temperature of 25 used instead of 298 so scores M1 only

If ans = +20 / +0.020 assume AE and look back to see if M1 and possibly M2 are scored

1

[13]

Q16.

(a) (i) (At 0 K) particles are stationary / not moving / not vibrating

Allow have zero energy.

Ignore atoms / ions.

1

No disorder / perfect order / maximum order

Mark independently.

1

(ii) As *T* increases, particles start to move / vibrate

Ignore atoms / ions.

Allow have more energy.

If change in state, CE = 0

1

Disorder / randomness increases / order decreases

1

(iii) Mark on temperature axis vertically below second ‘step’

Must be marked as a line, an 'x' , T_b or 'boiling point' <u>on the temperature axis</u>.

1

(iv) L_2 corresponds to boiling / evaporating / condensing / l → g / g → l

And L1 corresponds to melting / freezing / s → l / l → s

There must be a clear link between L_1, L_2 and the change in state.

1

Bigger change in <u>disorder</u> for L_2 / boiling compared with L_1 / melting

M2 answer must be in terms of changes in state and not absolute states eg must refer to change from liquid to gas not just gas.

Ignore reference to atoms even if incorrect.

1

(b) (i) $\Delta G = \Delta H - T\Delta S$

1

$\Delta H = c$ and $(-)\Delta S = m$ / ΔH and ΔS are constants (approx)

Allow ΔH is the intercept, and (−)ΔS is the slope / gradient.

Can only score M2 if M1 is correct.

1

(ii) Because the entropy change / ΔS is positive / $T\Delta S$ gets bigger

Allow -TΔS gets more negative

1

(iii) <u>Not</u> feasible / <u>un</u>feasible / <u>not</u> spontaneous

1

(c) (i) + 44.5 J K^{-1} mol^{-1}

Allow answer without units but if units given they must be correct (including mol^{-1})

1

(c) (ii) At 5440 $\Delta H = T\Delta S$

= 5440 × 44.5 = 242 080

1

(***OR*** using given value = 5440 × 98 = 533 120)

Mark is for answer to (c)(i) × 5440

1

ΔH = 242 kJ mol^{-1}

(***OR*** using given value ΔH = 533 kJ mol^{-1})

Mark is for correct answer to M2 with correct units (J mol^{-1} or kJ mol^{-1}) linked to answer.

If answer consequentially correct based on (c)(i) except for incorrect sign (eg −242), max 1 / 3 provided units are correct.

1

[15]

Q17.

(a) $\Delta G = \Delta H - T\Delta S$

Or expression $\Delta H - T\Delta S$ must be evaluated

1

If ΔG / expression ≤ 0 reaction is feasible

Or any explanation that this expression <=0

Do not allow just $\Delta G = 0$

1

(b) The molecules become more disordered / random when water changes from a liquid to a gas / evaporates

For M1 must refer to change in state AND increase in disorder

1

Therefore the entropy change is positive / Entropy increases

Only score M2 if M1 awarded

1

$T\Delta S > \Delta H$

Allow M3 for T is large / high (provided M2 is scored)

1

$\Delta G < 0$

Mark M3, M4 independently

1

(c) (i) Condition is $T = \Delta H / \Delta S$

1

$\Delta S = 189 - 205 / 2 - 131 = -44.5$;

1

$\Delta H = -242$ therefore $T = (-242 \times 1000) / -44.5)$

1

= 5438 K (allow 5400 − 5500 K)

Units essential (so 5438 alone scores 3 out of 4)

2719 K allow score of 2

5.4 (K) scores 2 for M1 and M2 only

1646 (K) scores 1 for M1 only

1

(ii) It would decompose into <u>hydrogen and oxygen</u> / its elements

Can score this mark if mentioned in M2

1

Because ΔG for this reaction would be ≤ 0

Allow the reverse reaction / decomposition is feasible

Only score M2 if M1 awarded

1

(d) $\Delta H = T\Delta S$

Allow correct substituted values instead of symbols

1

$\Delta S = 70 - 189 = -119\ JK^{-1}\ mol^{-1}$

1

$\Delta H = (-119 \times 373) / 1000 = -44.4$ kJ (mol^{-1}) (allow −44 to −45)

Allow −44000 to −45000 J (mol^{-1})
Answer must have correct units of kJ or J

1

[15]