ENTROPY

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(c) (i) Predict the sign of $\Delta S^\ominus$ for this reaction. Explain your answer.

$$2H_2S(g) + CH_4(g) \rightleftharpoons CS_2(g) + 4H_2(g) \qquad \Delta H^\ominus = +241\,kJ\,mol^{-1}$$

....

.... [1]
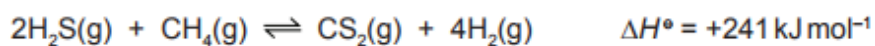
The free energy change, $\Delta G^\ominus$, for this reaction at 1000 K is +51 kJ mol⁻¹.

(ii) Calculate the value of $\Delta S^\ominus$ for this reaction, stating its units.

$\Delta S^\ominus$ = ... units .... [2]

(d) How would the value of $\Delta G^\ominus$, and hence the spontaneity (feasibility) of this reaction change as the temperature increases? Explain your answer.
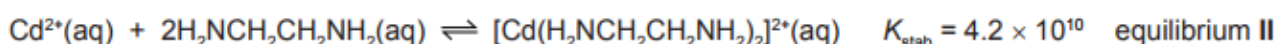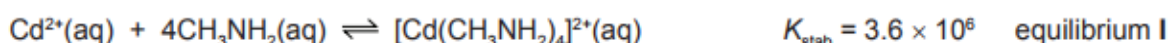
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.... [2]

s/16/qp41

(c)	(i)	$\Delta S^\ominus$ will be positive, because more gas moles on the RHS/products	[1]
	(ii)	$\Delta S^\ominus = (\Delta H^\ominus - \Delta G^\ominus)/T = (241 - 51)/1000 = 0.19$ OR 190 $kJ\,mol^{-1}K^{-1}$ OR $J\,mol^{-1}K^{-1}$	[1] [1]
(d)		$\Delta G^\ominus$ will become less positive/more negative as T increases, ...because $\Delta S^\ominus$ is positive (or $-T\Delta S^\ominus$ is more negative) ...therefore the reaction becomes more feasible/spontaneous as T increases	[2]

5 Cadmium ions form complexes with primary amines and with 1,2-diaminoethane.

$$Cd^{2+}(aq) + 4CH_3NH_2(aq) \rightleftharpoons [Cd(CH_3NH_2)_4]^{2+}(aq) \qquad K_{stab} = 3.6 \times 10^6 \quad \text{equilibrium I}$$

$$Cd^{2+}(aq) + 2H_2NCH_2CH_2NH_2(aq) \rightleftharpoons [Cd(H_2NCH_2CH_2NH_2)_2]^{2+}(aq) \quad K_{stab} = 4.2 \times 10^{10} \quad \text{equilibrium II}$$

(b) Values for ΔH° and ΔG° for equilibria I and II, and the value of ΔS° for equilibrium I, are given in the table below. All values are at a temperature of 298 K.

equilibrium	ΔH° /kJ mol^{-1}	ΔG° /kJ mol^{-1}	ΔS° /J K^{-1} mol^{-1}
I	−57.3	−37.4	−66.8
II	−56.5	−60.7	to be calculated

(i) Suggest a reason why the ΔH° values for the two equilibria are very similar.

....

.... [1]

(ii) Calculate ΔS° for equilibrium II.

ΔS° = ... J K^{-1} mol^{-1} [1]

(iii) Suggest a reason for the difference between the ΔS° you have calculated for equilibrium II and that for equilibrium I given in the table.
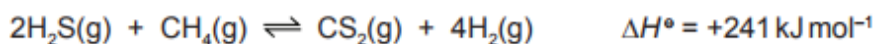
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(iv) Which of the two complexes is the more stable? Give a reason for your answer.

....

.... [1]

S/16/qp42

(b)	(i)	(each complex is formed by) making (4 ×)N-Cd bonds and breaking (6 ×) O-Cd bonds *or* same types of/similar bonds forming/breaking *or* same number of bonds forming/breaking	1
	(ii)	$\Delta S = (\Delta H - \Delta G)/T = (60.7 - 56.5) \times 1000/298 = (+)14/(+)14.1$	1
	(iii)	fewer moles (of solutes) are forming (one mole of) the complex (so less loss of disorder) *or* one en displaces two H_2O whereas one CH_3NH_2 only displaces one H_2O	1
	(iv)	The $[Cd(H_2NCH_2CH_2NH_2)_2]^{2+}$ / equilibrium 2 complex (is more stable) because: *either* K_{stab} is greater *or* ΔG° is more negative.	1

(c) (i) Predict the sign of ΔS° for this reaction. Explain your answer.

$$2H_2S(g) + CH_4(g) \rightleftharpoons CS_2(g) + 4H_2(g) \qquad \Delta H^\circ = +241\,kJ\,mol^{-1}$$

....

.... [1]

The free energy change, ΔG°, for this reaction at 1000 K is +51 kJ mol^{-1}.

(ii) Calculate the value of ΔS° for this reaction, stating its units.

$\Delta S^\circ =$ .... units .... [2]

(d) How would the value of ΔG°, and hence the spontaneity (feasibility) of this reaction change as the temperature increases? Explain your answer.

....

....

.... [2]

S/16/qp43

(c) (i)	ΔS° will be positive, because more gas moles on the RHS/products	[1]
(ii)	$\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T = (241 - 51)/1000 = 0.19$ OR 190 $kJ\,mol^{-1}K^{-1}$ OR $J\,mol^{-1}K^{-1}$	[1] [1]
(d)	ΔG° will become less positive/more negative as T increases, ...because ΔS° is positive (or $-T\Delta S^\circ$ is more negative) ...therefore the reaction becomes more feasible/spontaneous as T increases	[2]

(d) The equation for the formation of magnesium oxide from its elements is shown.

$$Mg(s) + \tfrac{1}{2}O_2(g) \rightarrow MgO(s) \qquad \Delta H^\circ = -602\,kJ\,mol^{-1}$$

substance	$S^\circ/J\,K^{-1}\,mol^{-1}$
Mg(s)	32.7
O_2(g)	205
MgO(s)	26.9

Use the equation and the data given in the table to calculate ΔG° for the reaction at 25 °C.

ΔG° = ... units ....

[4]

m/17/qp42

M1 correct use of $\Delta G = \Delta H - T\Delta S$	1
M2 $\Delta S = 26.9 - (32.7 + 102.5) = -108.3\,J\,K^{-1}\,mol^{-1}$ **OR** $-0.1083\,kJ\,K^{-1}\,mol^{-1}$	1
M3 $\Delta G = -602 - (298 \times (-0.1083)) = -570$	1
M4 units: $kJ\,mol^{-1}$	1

(c) Iron(III) oxide can be reduced to iron metal using carbon monoxide at a temperature of 1000 °C.

$$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g) \qquad \Delta H^{\ominus} = -43.6\,kJ\,mol^{-1}$$
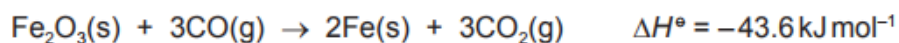
Some relevant standard entropies are given in the table.

substance	$Fe_2O_3(s)$	$CO(g)$	$Fe(s)$	$CO_2(g)$
$S^{\ominus}/J\,K^{-1}\,mol^{-1}$	+90	+198	+27	+214

(i) What is meant by the term *entropy*?

....

.... [1]

(ii) Calculate the standard entropy change, $\Delta S^{\ominus}$, for this reaction.

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

(iii) Calculate the standard Gibbs free energy change, $\Delta G^{\ominus}$, for this reaction at 25 °C.

$\Delta G^{\ominus} = $ .... $kJ\,mol^{-1}$ [2]

(iv) Suggest why a temperature of 1000 °C is usually used for this reaction, even though the reaction is spontaneous (feasible) at 25 °C. Explain your answer.

....

....

.... [1]

3(c)(i)	(entropy is a measure/degree of the) disorder of a **system/substance**	1	
			1
3(c)(ii)	$\Delta S^{\ominus} = (2 \times 27) + (3 \times 214) - (90) - (3 \times 198)$ **OR** $696 - 684$	1	
	$\Delta S^{\ominus} = (+)12 \ (J \ K^{-1} \ mol^{-1})$	1	
			2
3(c)(iii)	$\Delta G^{\ominus} = -43.6 - (298 \times 12 / 1000)$	1	
	$\Delta G^{\ominus} = -47.2 \ (kJ \ mol^{-1})$	1	
			2
3(c)(iv)	high E_a **and** to speed up the rate	1	
			1

The spontaneity (feasibility) of a chemical reaction depends on the standard Gibbs free energy change, $\Delta G^{\ominus}$. This is related to the standard enthalpy and entropy changes by the equation shown.

$$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$$

(a) State and explain whether the following processes will lead to an increase or decrease in entropy.

   (i) the reaction of magnesium with hydrochloric acid

   entropy change ....

   explanation ....

   [1]

   (ii) solid potassium chloride dissolving in water

   entropy change ....

   explanation ....

   [1]

   (iii) steam condensing to water

   entropy change ....

   explanation ....

   [1]

(b) Magnesium carbonate can be decomposed.

$$MgCO_3(s) \rightarrow MgO(s) + CO_2(g) \qquad \Delta H^\ominus = +117 \, kJ \, mol^{-1}$$
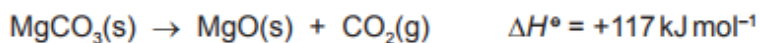
Standard entropies are shown in the table.

substance	$MgCO_3(s)$	$MgO(s)$	$CO_2(g)$
$S^\ominus / J \, mol^{-1} K^{-1}$	+65.7	+26.9	+214

(i) Calculate $\Delta G^\ominus$ for this reaction at 298 K.
Include a relevant sign and give your answer to **three** significant figures.

$\Delta G^\ominus = $ .... $kJ \, mol^{-1}$ [3]

(ii) Explain, with reference to $\Delta G^\ominus$, why this reaction becomes more feasible at higher temperatures.

....

.... [1]

(c) On heating, sodium hydrogencarbonate decomposes into sodium carbonate as shown.

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g) \qquad \Delta H^\ominus = +130 \, kJ \, mol^{-1}$$
$$\Delta S^\ominus = +316 \, J \, mol^{-1} K^{-1}$$
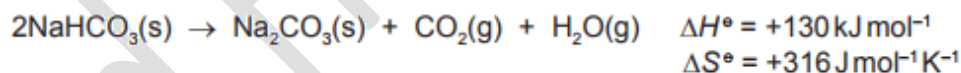
Calculate the **minimum** temperature at which this reaction becomes spontaneous (feasible). Show your working.

temperature = ... K [2]

w/16/qp43

3(a)(i)	(entropy) increases / is positive **and** H_2 / gas is formed	1	
			1
3(a)(ii)	(entropy) increases / is positive **and** (KCl (aq)) solution has (free) moving / mobile ions / aqueous ions	1	
			1
3(a)(iii)	(entropy) decreases / is negative **and** decrease in **gas**	1	
			1
3(b)(i)	$\Delta S^{\ominus} = 26.9 + 214 - 65.7 = (+) 175.2 (J K^{-1} mol^{-1})$	1	
	$\Delta G^{\ominus} = 117 - (298 \times 175.2 / 1000)$ **OR** $\Delta G^{\ominus} = 117\,000 - (298 \times 175.2)$	1	
	$\Delta G^{\ominus} = +64.8 (kJ\,mol^{-1})$	1	
			3
3(b)(ii)	$T\Delta S$ is more positive than ΔH / $T\Delta S$ increases / $-T\Delta S$ more negative		
	and ΔG is negative / decrease / less positive	1	
			1
3(c)	use of $\Delta G = 0$ or $\dfrac{T\Delta S}{\Delta H} = 1$	1	
	$T = 130 / (316 / 1000) = $ **410 / 411 / 412 / 411.4** (K)	1	
			2

2016 Specimen Paper Question on Entropy

7 **(a)** The table lists the equations for five processes.

For each process, predict the sign of ΔS.

process	sign of ΔS
NaBr(s) + (aq) → NaBr(aq)	
$H_2O(l) \rightarrow H_2O(g)$	
$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$	
$CoCl_2(s) + 6H_2O(l) \rightarrow CoCl_2.6H_2O(s)$	

[2]

(b) Ethanol can be combusted as shown in the equation.

$$CH_3CH_2OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$$
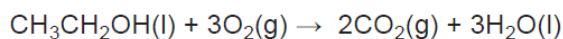
Standard entropies are shown in the table.

substance	$CH_3CH_2OH(l)$	$O_2(g)$	$CO_2(g)$	$H_2O(l)$
$S^\ominus$, J K^{-1} mol^{-1}	161	205	214	70

Calculate the standard entropy change, $\Delta S^\ominus$, for this reaction.

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

(c) The combustion of ethanol is an exothermic reaction.

This reaction occurs spontaneously at low temperatures but does **not** occur at very high temperatures. Explain why.

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....

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.... [2]

(d) The decomposition of calcium carbonate is an endothermic reaction.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$
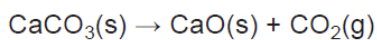
$\Delta H = +178 \text{ kJ mol}^{-1}$ and $\Delta S = +159 \text{ J K}^{-1} \text{mol}^{-1}$

Calculate the **minimum** temperature at which this reaction becomes feasible.
Show all your working.

[3]

[Total: 9]

Marking Scheme

(a)

process	sign of ΔS
$NaBr(s) + (aq) \rightarrow NaBr(aq)$	+
$H_2O(l) \rightarrow H_2O(g)$	+
$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$	–
$CoCl_2(s) + 6H_2O(l) \rightarrow CoCl_2.6H_2O(s)$	–

2 correct, (1) mark
4 correct, (2) marks   [2]

(b) $\Delta S^\circ = (214 \times 2) + (70 \times 3) - (161 \times 1) - (205 \times 3)$
$= -138 \text{ J K}^{-1} \text{ mol}^{-1}$ [2]

(c) As temperature increases $T\Delta S$ is more negative or $-T\Delta S$ increases (1)
At high temperature $T\Delta S$ is more negative than ΔH (so ΔG is positive) (1)   [2]

(d) the reaction is feasible, ΔG is negative so
$T > \Delta H/T\Delta S$ or use of $T = \Delta H/T\Delta S$ (1)

$T = 178000/159$ (1)
$T = 1119.5 \text{ K}$ units required or $T > 1120 \text{ K}$ (1)   [3]

IB QUESTIONS on ENTROPY

1. Which change leads to an increase in entropy?

    A. $CO_2(g) \rightarrow CO_2(s)$

    B. $SF_6(g) \rightarrow SF_6(l)$

    C. $H_2O(l) \rightarrow H_2O(s)$

    D. $NaCl(s) \rightarrow NaCl(aq)$

    (Total 1 mark)

2. The reaction between but-1-ene and water vapour produces butan-1-ol.

$$C_4H_8(g) + H_2O(g) \rightarrow C_4H_9OH(l)$$
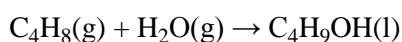
    The standard entropy values ($S^{\ominus}$) for but-1-ene, water vapour and butan-1-ol are 310, 189 and 228 $J\ K^{-1}\ mol^{-1}$ respectively. What is the standard entropy change for this reaction in $J\ K^{-1}\ mol^{-1}$?

    A.   −271

    B.   +271

    C.   −107

    D.   +107

    (Total 1 mark)

3. What are the signs of $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ for a reaction that is non-spontaneous at low temperature but spontaneous at high temperature?

	$\Delta H^{\ominus}$	$\Delta S^{\ominus}$
A.	−	−
B.	+	−
C.	−	+
D.	+	+

    (Total 1 mark)

4. Consider the following reaction:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
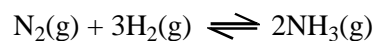
(i)   Suggest why this reaction is important for humanity.

(1)

(ii)   Using the average bond enthalpy values in Table 10 of the Data Booklet, calculate the standard enthalpy change for this reaction.

(4)

(iii)   The absolute entropy values, S, at 238 K for $N_2(g)$, $H_2(g)$ and $NH_3(g)$ are 192, 131 and 193 J K^{-1} mol^{-1} respectively. Calculate $\Delta S^\ominus$ for the reaction and explain the sign of $\Delta S^\ominus$.

(2)

(iv)   Calculate $\Delta G^\ominus$ for the reaction at 238 K. State and explain whether the reaction is spontaneous.

(3)

(v)   If ammonia was produced as a liquid and not as a gas, state and explain the effect this would have on the value of $\Delta H^\ominus$ for the reaction.

(2)
(Total 12 marks)

5. Which reaction causes a decrease in the entropy of the system?

A. $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

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

C. $2C(s) + O_2(g) \rightarrow 2CO(g)$

D. $2SO_3(g) \rightarrow 2SO_2(g) + O_2(g)$

(Total 1 mark)

6. Consider the following reaction.

$$2CH_3OH(g) + H_2(g) \rightarrow C_2H_6(g) + 2H_2O(g)$$
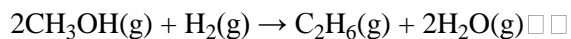
(a) The standard enthalpy change of formation for $CH_3OH(g)$ at 298 K is -201 kJ mol^{-1} and for $H_2O(g)$ is -242 kJ mol^{-1}. Using information from Table 11 of the Data Booklet, determine the enthalpy change for this reaction. (Check the Marking Scheme for Missing Data)

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....

....

(2)

(b) The standard entropy for $CH_3OH(g)$ at 298 K is 238 J K^{-1} mol^{-1}, for $H_2(g)$ is 131 J K^{-1} mol^{-1} and for $H_2O(g)$ is 189 J K^{-1} mol^{-1}. Using information from Table 11 (Check Marking Scheme) of the Data Booklet, determine the entropy change for this reaction.

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(2)

(c)   Calculate the standard change in free energy, at 298 K, for the reaction and deduce whether the reaction is spontaneous or non-spontaneous.
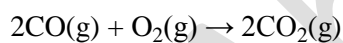
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(3)
(Total 7 marks)

7.   What is the standard entropy change, $\Delta S^{\ominus}$, for the following reaction?

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$$

	CO(g)	**O₂(g)**	**CO₂(g)**
$S^{\ominus}/\text{J K}^{-1} \text{ mol}^{-1}$	198	205	214

A.   −189

B.   −173

C.   +173

D.   +189

(Total 1 mark)

8. A reaction has a standard enthalpy change, $\Delta H^{\ominus}$, of +10.00 kJ mol^{-1} at 298 K. The standard entropy change, $\Delta S^{\ominus}$, for the same reaction is +10.00 J K^{-1} mol^{-1}. What is the value of $\Delta G^{\ominus}$ for the reaction in kJ mol^{-1}?

   A.   +9.75

   B.   +7.02

   C.   −240

   D.   −2970

   (Total 1 mark)

9. Which reaction has the greatest increase in entropy?

   A. $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$

   B. $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$

   C. $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

   D. $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$

   (Total 1 mark)

10. Which reaction has the largest increase in entropy?

   A. $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$

   B. $Al(OH)_3(s) + NaOH(aq) \rightarrow Al(OH)_4^-(aq) + Na^+(aq)$

   C. $Na_2CO_3(s) + 2HCl(aq) \rightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)$

   D. $BaCl_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2NaCl(aq)$

   (Total 1 mark)

11. When hydrogen peroxide decomposes, the temperature of the reaction mixture increases.

$$2H_2O_2(aq) \rightarrow O_2(g) + 2H_2O(l)$$
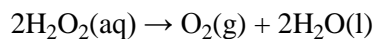
What are the signs of ΔH, ΔS and ΔG for this reaction?

	ΔH	ΔS	ΔG
A.	–	–	–
B.	–	+	–
C.	+	+	–
D.	–	+	+

(**Total 1 mark**)

12. Which reaction has the greatest increase in entropy?

   A. $SO_2(g) + 2H_2S(g) \rightarrow 2H_2O(l) + 3S(s)$

   B. $CaO(s) + CO_2(g) \rightarrow CaCO_3(s)$

   C. $CaC_2(s) + 2H_2O(l) \rightarrow Ca(OH)_2(s) + C_2H_2(g)$

   D. $N_2(g) + O_2(g) \rightarrow 2NO(g)$

(**Total 1 mark**)

13. $\Delta G^{\ominus}$ calculations predict that a reaction is always spontaneous for which of the following combinations of $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$?

   A. $+\Delta H^{\ominus}$ and $+\Delta S^{\ominus}$

   B. $+\Delta H^{\ominus}$ and $-\Delta S^{\ominus}$

   C. $-\Delta H^{\ominus}$ and $-\Delta S^{\ominus}$

   D. $-\Delta H^{\ominus}$ and $+\Delta S^{\ominus}$

(**Total 1 mark**)

14. Some words used in chemistry can have a specific meaning which is different to their meaning in everyday English.

State what the term *spontaneous* means when used in a chemistry context.

....

....

(Total 1 mark)

15. Propene can be hydrogenated in the presence of a nickel catalyst to form propane.
Use the data below to answer the questions that follow.

Compound	Formula	$\Delta H^{\ominus}_f$ / kJ mol^{-1}	$S^{\ominus}$/ J K^{-1} mol^{-1}
hydrogen	$H_2(g)$	0	+ 131
propane	$C_3H_8(g)$	− 104	+ 270
propene	$C_3H_6(g)$	+ 20.4	+ 267

(i) Outline why the value for the standard enthalpy change of formation of hydrogen is zero.

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(1)

(ii) Calculate the standard enthalpy change for the hydrogenation of propene.

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(2)

(iii)   Calculate the standard entropy change for the hydrogenation of propene.

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(2)

(iv)   Determine the value of $\Delta G^{\ominus}$ for the hydrogenation of propene at 298 K.

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(2)

(v)   At 298 K the hydrogenation of propene is a spontaneous process. Determine the temperature above which propane will spontaneously decompose into propene and hydrogen.

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(2)
(Total 9 marks)

16. (Not in Syllabus) What is the standard free energy change, $\Delta G^{\ominus}$, in kJ, for the following reaction?

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$$
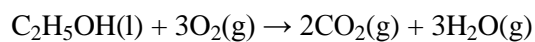
Compound	$\Delta G_f^{\ominus}$ / kJ mol^{-1}
$C_2H_5OH(l)$	−175
$CO_2(g)$	−394
$H_2O(g)$	−229
$O_2(g)$	0

A.   −1650

B.   −1300

C.   − 448

D.   +1300

(Total 1 mark)

17. Which reaction has the most negative change in entropy?

A. $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$

B. $NH_4Cl(s) \rightarrow NH_3(g) + HCl(g)$

C. $PbCl_2(s) \rightarrow Pb^{2+}(aq) + 2Cl^-(aq)$

D. $C(s) + O_2(g) \rightarrow CO_2(g)$

(Total 1 mark)

MARKING SCHEME

1.   D

[1]

2.   A

[1]

3.   D

[1]

4. (i)   fertilizers / increasing crop yields;
       production of explosives for mining;   1 max

     (ii) ΔH = (sum of energies of bonds broken) – (sum of energies of bonds formed);

                Can be implied by working.

        correct substitution of values and numbers of bonds broken;
        correct substitution of values and numbers of bonds made;
        $(\Delta H = (N{\equiv}N) + 3(H{-}H) - 6(N{-}H) = 944 + 3(436) - 6(388) =) -76.0$ (kJ);   4

                Allow ECF.
                Do not penalize for sig. fig. or units.
                Award [4] for correct final answer.

     (iii) $(\Delta S^{\ominus}[2{\times}193] - [192 + 3{\times}131]) = -199$ (J K^{-1} mol^{-1});   2

                Allow ECF.
                four <u>gaseous</u> molecules generating two <u>gaseous</u> molecules /
                fewer molecules of <u>gas</u>;

     (iv) $(\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus} = -76.0 - 298(-0.199)) = -16.7$ (kJ);
        Spontaneous;
        ΔG is negative;   3

                Do not penalize for SF.

     (v)   heat released when gas → liquid;
        $\Delta H^{\ominus}$ becomes more negative;   2

                                                 [12]

5.   B

                                                          [1]

6. (a) $\Delta H^{\ominus}_{\text{reaction}} = \Sigma\Delta H_{f}^{\ominus}(\text{products}) - \Sigma\Delta H_{f}^{\ominus}(\text{reactants})$
            $= [(1)(-85) + (2)(-242)] - [(2)(-201)]$;
            $= -167$ (kJ/kJ mol^{-1});
            Award [1] for (+) 167.   2

     (b) $\Delta S^{\ominus}_{\text{reaction}} = \Sigma S^{\ominus}(\text{products}) - \Sigma S^{\ominus}(\text{reactants})$
            $= [(1)(230) + (2)(189)] - [(2)(238) + (1)(131)]$;

$= 1$ (J K^{-1}/J K^{-1} mol^{-1});   2

(c) $\Delta G^{\ominus}_{reaction} = (\Delta H^{\ominus} - T\Delta S^{\ominus}) = (-167) - (298)(0.001)$;
Award [1] for correct substitution of values.

$= -167$ kJ/-167000 J;
Units needed for mark in (c) only.
Accept -167 kJ mol^{-1} or -167000 J mol^{-1}.

spontaneous;

Award marks for final correct answers throughout in each of (a), (b) and (c).   3

[7]

7.   B

[1]

8.   B

[1]

9.   A

[1]

10.   C

[1]

11.   B

[1]

12.   C

[1]

13.   D

[1]

14.   the reaction gives out (Gibbs Free) energy that can do work;
ΔG for the reaction has a negative value;
a reaction that occurs without adding energy (beyond that required to
overcome energy barrier);   1 max

[1]

15.   (i)   by definition $\Delta H_\text{h}^{\ominus}$ of elements (in their standard states) is zero / no
reaction involved / *OWTTE*;   1

(ii) $\Delta H = -104 - (+20.4)$;
$= -124.4$ (kJ mol^{-1});   2
Award [1 max] for 124.4 (kJ mol^{-1}).
Award [2] for correct final answer.

(iii) $\Delta S = 270 - (267 + 131)$;
$= -128$ (J K mol^{-1});   2
Award [1 max] for +128 (J K^{-1} mol^{-1}).
Award [2] for correct final answer.

(iv) $\Delta G = \Delta H - T\Delta S = -124.4 - \dfrac{(-128 \times 298)}{1000}$;

$= -86.3$ kJ mol^{-1};   2
Units needed for the mark.
Award [2] for correct final answer.
Allow ECF if only one error in first marking point.

(v) $\Delta G = \Delta H - T\Delta S = 0 \, / \, \Delta H = T\Delta S$;

T $= \dfrac{-124.4}{-128/1000} = 972$ K / 699 °C;   2
Only penalize incorrect units for T and inconsistent ΔS value
once in (iv) and (v).

[9]

16. B

[1]

17. A

[1]

SHOEIFFAT QUESTIONS

Basic Questions

BQ 1 Predict the sign of the entropy change, $\Delta S°$, for the following processes:

a. $PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$
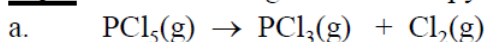
1 mole of a gas is producing 2 moles of gases $\Rightarrow$ disorder increases.
$\Delta S°$ is positive.

b. $2H(g) \rightarrow H_2(g)$
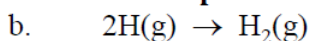
2 moles of gases are producing 1 mole of gas $\Rightarrow$ disorder decreases.
$\Delta S°$ is negative.

(c) Fluorine gas, an oxidizing agent, is bubbled into a solution of potassium bromide at 25°C. The balanced equation for the reaction occurring is: $F_2(g) + 2Br^-(aq) \rightarrow 2F^-(aq) + Br_2(aq)$

Predict the sign of $\Delta S°$ for the reaction at 25°C. Justify your prediction.
The sign of $\Delta S°$ is negative.
One of the reactants, F_2, is a gas at 25°C, but there are no gaseous products. Gases have high entropies, so the entropy of the reactants is greater than the entropy of the products, making $\Delta S°$ negative.

BQ 2 Consider the following process: $Zn(s) + \frac{1}{2}O_2(g) \rightarrow ZnO(s)$

a. Calculate $\Delta S°$ at 298K, given the following S° values, in $J.K^{-1} mol^{-1}$:
ZnO: 44; Zn: 42; O_2: 205.

$$\Delta S° = S°_{ZnO(s)} - S°_{Zn(s)} - \frac{1}{2}S°_{O_2(g)} = (44) - (42) - (\frac{205}{2}) = \textbf{-100.5J/mol K}$$

b. Is the sign of $\Delta S°$ expected?
yes, because 1 mole of solid and 0.5 mole of gas are becoming 1 mole of solid.

BQ 4 Consider the following process: $H_2O(s) \rightarrow H_2O(l)$ $\Delta H° = 6.03 kJ$
Given $\Delta S° = 22.1 J/K.mol$, show that the melting of ice becomes spontaneous at 0°C.
Given $\Delta S° = 22.1 J/K.mol$, $\Delta H° = 6.03 kJ$, T = 0°C + 273 = 273K
RTF: rxn is spontaneous
$$\Delta G° = \Delta H° - T\Delta S° = (6.03) - (273)(22.1 \times 10^{-3}) = -3.3 \times 10^{-3} kJ$$
Since $\Delta G°$ is negative then the process is spontaneous.

BQ 5 Consider the following process: $C_6H_6(l) \rightarrow C_6H_6(g)$
Given for the above process $\Delta H°_{vap} = 30.8 kJ/mol$, and $\Delta S°_{vap} = 87.2 J/K.mol$.
Calculate the boiling point of benzene.
Given: $\Delta H°_{vap} = 30.8 kJ/mol$, $\Delta S°_{vap} = 87.2 J/K.mol$ **RTF: boiling point of benzene**

**A phase change at equilibrium is isothermal, ie occurs at same t, therefore $\Delta G° = 0kJ$**
$$\Delta G° = \Delta H°_{vap} - T\Delta S°_{vap} = (30.8) - T(87.2 \times 10^{-3}) = 0kJ \Rightarrow T = \frac{30.8}{87.2 \times 10^{-3}} = 353K \Rightarrow t = 80°C$$

BQ 7 Answer the following questions about nitrogen, hydrogen, and ammonia.

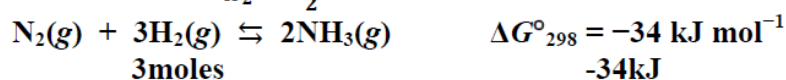a. Draw the complete Lewis electron-dot diagrams for N_2 and NH_3.

$$: \text{N} :: \text{N} : \quad / \quad : \text{N} \equiv \text{N} :$$

$$\text{H} \cdot \cdot \ddot{\text{N}} \cdot \cdot \text{H} \quad / \quad \text{H} - \ddot{\text{N}} - \text{H}$$
$$\text{H} \qquad\qquad \text{H}$$
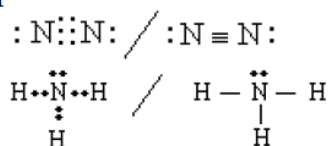
(b) Calculate the standard free-energy change, ΔG, that occurs when 24.0 g of $H_2(g)$ react with excess $N_2(g)$ at 298 K according to the reaction represented below.

$N_2(g) + 3H_2(g) \leftrightarrows 2NH_3(g) \qquad \Delta G^\circ_{298} = -34 \text{ kJ mol}^{-1}$
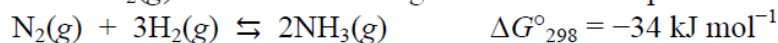
Given: m of H_2 = 24.0 g, $\Delta G^\circ_{298} = -34 \text{ kJ mol}^{-1}$

RTF: ΔG

$$n_{H_2} = \frac{24.0}{2} = 12.0 \text{moles}$$

$N_2(g) + 3H_2(g) \leftrightarrows 2NH_3(g) \qquad \Delta G^\circ_{298} = -34 \text{ kJ mol}^{-1}$

3moles   -34kJ

12.0moles ΔG_{298} $\Delta G_{298} = \frac{12.0\,(-34)}{3} = -136 \text{ kJ}$

Multiple Choice

1. Which of the following is true of a reaction that is spontaneous at <u>higher</u> temperatures?

   [-A-] ΔS° and ΔH° are both negative
   [-B-] ΔS° and ΔH° are both positive
   [-C-] ΔS° is negative and ΔH° is positive
   [-D-] ΔS° is positive and ΔH° is negative
   [-E-] ΔS° and ΔH° are both equal to zero

2. When solid NH_4SCN is mixed with solid $Ba(OH)_2$ in a closed container, the temperature drops and a gas is produced. Which of the following indicates the correct signs for ΔG, ΔH and ΔS for the process?

	ΔG	ΔH	ΔS
[-A-]	-	-	-
[-B-]	-	+	-
[-C-]	-	+	+
[-D-]	+	-	+
[-E-]	+	-	-

   A gas is produced from solids $\Rightarrow$ entropy increased $\Rightarrow \Delta S$ is positive
   Temperature drops $\Rightarrow$ reaction is endothermic $\Rightarrow \Delta H$ is positive

3. When a solid sample of $NaNO_3$ is added to a cup of water, the temperature of the resulting solution decreases. Which of the following must be true?

	ΔG	ΔH	ΔS
[-A-]	-	-	-
[-B-]	-	+	-
[-C-]	-	+	+
[-D-]	+	-	+
[-E-]	+	-	-

   Sodium nitrate dissolves $\Rightarrow$ reaction is spontaneous $\Rightarrow \Delta G$ negative
   Temperature decreases $\Rightarrow$ reaction is endothermic $\Rightarrow$ enthalpy must be positive
   Products are aqueous $\Rightarrow$ entropy increased $\Rightarrow \Delta S$ is positive

5. $X(s) \leftrightarrow X(l)$
        Which of the following is true for any substance undergoing the process represented above at its
        normal melting point?

[-A-] $\Delta S < 0$
[-B-] $\Delta H = 0$
[-C-] $\Delta H = T \Delta G$
[-D-] $T\Delta S = 0$
[-E-] $\Delta H = T\Delta S$

6.   For a certain reaction, the standard free energy is -70.0kJ at 100K and -40.0Kj at 200 K. For this
reaction
        [-A-] $\Delta H > 0 ; \Delta S < 0$
        [-B-] $\Delta H < 0 ; \Delta S < 0$
        [-C-] $\Delta H > 0 ; \Delta S > 0$
        [-D-] $\Delta H < 0 ; \Delta S < 0$

Sample Questions

SQ1   Define a spontaneous process?
A process is said to be spontaneous if it occurs without external or outside interference.
SQ2   What are the driving forces for spontaneous processes?
minimizing energy and maximizing randomness
SQ   Define entropy. **It is a thermodynamic function that measures randomness or disorder.**
SQ4   State the second law of thermodynamics.
**The second law of thermodynamics states that in any spontaneous process there is always an
increase in the entropy of the universe.**
SQ5   When will water have higher entropy, at 25°C or at 80°C?
At 80°C, water will have greater entropy. Entropy increases with an increase in temperature.