

# ENTROPY

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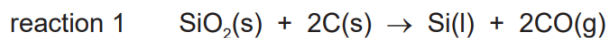
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Question 1

2 Silicon is the second most abundant element by mass in the Earth's crust.

(a) In industry, silicon is extracted from  $\text{SiO}_2$  by reaction with carbon at over  $2000^\circ\text{C}$ .



(i) Explain why the entropy change,  $\Delta S$ , of reaction 1 is positive.

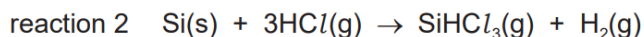
.....  
 ..... [1]

(ii) Reaction 1 is highly endothermic.

Suggest the effect of an increase in temperature on the feasibility of this reaction.  
 Explain your answer.

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

(b) Silicon is purified by first heating it in a stream of  $\text{HCl}(\text{g})$  to form  $\text{SiHCl}_3$ . The  $\text{SiHCl}_3$  formed is then distilled to remove other impurities.



(i) Table 2.1 shows some standard entropy data.

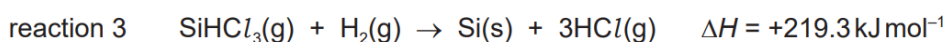
**Table 2.1**

compound	standard entropy, $S^\circ/\text{JK}^{-1}\text{mol}^{-1}$
Si(s)	19
HCl(g)	187
SiHCl <sub>3</sub> (g)	314
H <sub>2</sub> (g)	131

Use the data in Table 2.1 to calculate  $\Delta S^\circ$  for reaction 2.

$\Delta S^\circ = \dots\dots\dots \text{JK}^{-1}\text{mol}^{-1}$  [2]

(ii) Reaction 3 is the reverse of reaction 2 and is used to obtain pure silicon.



Use this information and your answer to (b)(i) to calculate the temperature, in K, at which reaction 3 becomes feasible.  
Show your working.

[If you were unable to answer (b)(i), you should use  $\Delta S^\ominus = -150 \text{ J K}^{-1} \text{ mol}^{-1}$  for reaction 2.  
This is not the correct answer to (b)(i).]

temperature = ..... K [2]

9701/42/F/M/22 (Question 2)

Question	Answer	Marks
2(a)(i)	1 mol liquid and 2 mol gas formed from 3 mol solid <b>OR</b> two solid compounds converted to a liquid and a gas	1
2(a)(ii)	M1: (as $T$ increases) $T\Delta S$ becomes greater (than $\Delta H$ ) <b>OR</b> (as $T$ increases) $T\Delta S$ becomes more positive  M2: (as $T$ increases) feasibility will increase as $\Delta G$ becomes more negative	2
2(b)(i)	M1: = $314 + 131 - (19 + 3 \times 187)$ use of values and correct stoichiometry M2: = <b>-135</b> ( $\text{J K}^{-1} \text{ mol}^{-1}$ )	2
2(b)(ii)	M1: $\Delta G = 0 \therefore T = \Delta H / \Delta S = +219.3 \times 10^3 \div \text{-(b)(i)}$ M2: = <b>1624(.4)</b> (K)	2

Question 2

(c) (i) Explain what is meant by the term *entropy of a system*.

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

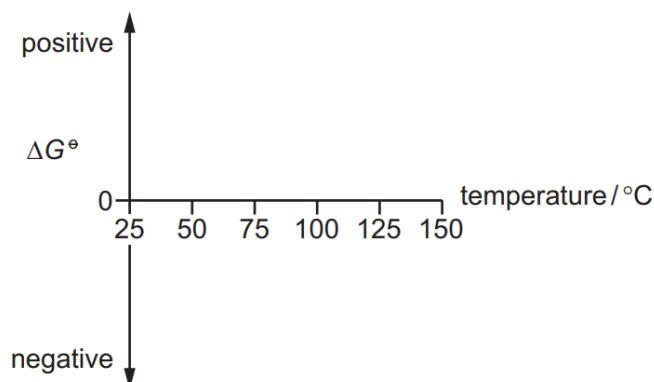
(ii) Place one tick (✓) in each row of the table to show the sign of each entropy change,  $\Delta S$ .

process	$\Delta S$ is negative	$\Delta S$ is zero	$\Delta S$ is positive
NaCl dissolving in water			
water solidifying to ice			

[1]

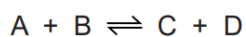
- (iii) The evaporation of one mole of water has a standard Gibbs free energy change,  $\Delta G^\ominus$ , of +8.6 kJ at 25°C.

Sketch a graph on the axes to show how  $\Delta G^\ominus$  changes for this process between 25°C and 150°C at 101 kPa.



[2]

- (d) The reaction between A and B is feasible at low temperatures but is **not** feasible at high temperatures.



Deduce the signs of  $\Delta H$  and  $\Delta S$  for this reaction and explain why the feasibility changes with temperature.

sign of  $\Delta H$  = ..... sign of  $\Delta S$  = .....

.....  
 .....  
 .....  
 .....

[2]

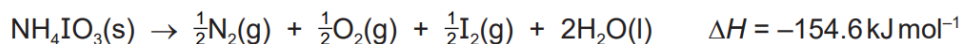
9701/42/M/J/21 (Question 4)

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Question	Answer	Marks												
4(c)(i)	measure / degree of (dis)order / randomness (of a system) OR the number of possible arrangements of the particles and their energy (in a given system)	1												
4(c)(ii)	<table border="1"> <thead> <tr> <th></th> <th><math>\Delta S</math> is negative</th> <th><math>\Delta S</math> is zero</th> <th><math>\Delta S</math> is positive</th> </tr> </thead> <tbody> <tr> <td>solid dissolving in water</td> <td></td> <td></td> <td>✓</td> </tr> <tr> <td>water solidifying to ice</td> <td>✓</td> <td></td> <td></td> </tr> </tbody> </table>		$\Delta S$ is negative	$\Delta S$ is zero	$\Delta S$ is positive	solid dissolving in water			✓	water solidifying to ice	✓			1
	$\Delta S$ is negative	$\Delta S$ is zero	$\Delta S$ is positive											
solid dissolving in water			✓											
water solidifying to ice	✓													
4(c)(iii)	<p>two correct for 1 mark, three correct for two marks:</p> <ul style="list-style-type: none"> <li>starting at +8.6 kJ / in positive region close to the y-axis</li> <li>line passes through x-axis around 100°C</li> <li>negative gradient straight / curve line through the x-axis (no clear positive inflexions)</li> </ul>	2												
4(d)	<p><b>M1:</b> <math>\Delta H</math> negative / - , <math>\Delta S</math> negative / -</p> <p><b>M2:</b> as temperature increase, <math>\Delta G</math> becomes (more) positive / less negative ora OR at low(er) T, (<math>\Delta H</math> more negative than T<math>\Delta S</math>) so <math>\Delta G</math> is negative OR at high(er) T, (<math>\Delta H</math> less negative than T<math>\Delta S</math>) so <math>\Delta G</math> is positive</p>	2												

### Question 3

- (f)  $\text{NH}_4\text{IO}_3$  is an unstable compound that readily decomposes when warmed. The decomposition reaction is shown.



- (i) Use the data in the table to calculate the entropy change of reaction,  $\Delta S$ , of the decomposition of  $\text{NH}_4\text{IO}_3(\text{s})$ .

compound	$S/\text{JK}^{-1} \text{ mol}^{-1}$
$\text{NH}_4\text{IO}_3(\text{s})$	42
$\text{N}_2(\text{g})$	192
$\text{O}_2(\text{g})$	205
$\text{I}_2(\text{g})$	261
$\text{H}_2\text{O}(\text{l})$	70

$$\Delta S = \dots\dots\dots \text{JK}^{-1} \text{ mol}^{-1} \quad [2]$$

(ii) This reaction is feasible at all temperatures.

Explain why, using the data in (f) and your answer to (f)(i).

.....

.....

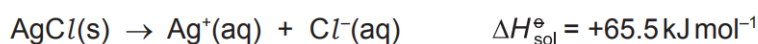
..... [1]

9701/42/F/M/21 (Question 3)

3(f)(i)	<b>M1:</b> $\Delta S = \frac{1}{2}(192) + \frac{1}{2}(205) + \frac{1}{2}(261) + 2(70) - 42$ <b>M2:</b> (+)427 (J K <sup>-1</sup> mol <sup>-1</sup> ) ecf	2
3(f)(ii)	$\Delta G$ (always) negative because <ul style="list-style-type: none"> <li>• <math>\Delta H &lt; 0</math> / negative <b>OR</b> exothermic <b>AND</b></li> <li>• <math>\Delta S &gt; 0</math> / positive <b>OR</b> <math>-T\Delta S &lt; 0</math> for all <math>T</math></li> </ul>	1

Question 4

(b) Silver chloride, AgCl, is sparingly soluble in water. The equation for the enthalpy change of solution is shown.



Standard entropies are shown in the table.

species	AgCl(s)	Ag <sup>+</sup> (aq)	Cl <sup>-</sup> (aq)
S <sup>o</sup> /JK <sup>-1</sup> mol <sup>-1</sup>	+96.2	+72.7	+56.5

(i) Calculate the standard entropy change of solution,  $\Delta S^{\circ}$ .

$$\Delta S^{\circ} = \dots\dots\dots \text{JK}^{-1} \text{mol}^{-1} \quad [1]$$

(ii) Explain, with the aid of a calculation, why AgCl is insoluble in water at 25 °C.

You should use data from this question and your answer to (b)(i).

.....

..... [3]

9701/43/M/J/20 (Question 7)

7(b)(i)	$\Delta S^\circ = 72.7 + 56.5 - 96.2 = +33.0 \text{ J K}^{-1} \text{ mol}^{-1}$	1
7(b)(ii)	<p><b>M1</b> <math>\Delta G = \Delta H^\circ - T\Delta S^\circ</math></p> <p><b>M2</b> <math>\Delta G = (65.5) - (298 \times 0.033) = +55.7 \text{ kJ mol}^{-1}</math> min 3sf</p> <p><b>M3</b> <math>\Delta G = \text{positive so not feasible/spontaneous}</math></p>	3

Question 5

3 (a) Explain what is meant by the term *entropy of a system*.

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

(b) State and explain whether the entropy change of each of the following processes is positive or negative. Do not consider the entropy change of the surroundings.

- liquid water at 80 °C is cooled to 60 °C

The entropy change is ..... because .....

.....

- solid calcium chloride is added to water and the mixture is stirred

The entropy change is ..... because .....

.....

- the change corresponding to the lattice energy of calcium chloride,  $\Delta H_{\text{latt}} \text{ CaCl}_2(\text{s})$ , takes place

The entropy change is ..... because .....

.....

[3]

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(c) The reaction  $\text{ZnCO}_3(\text{s}) \rightarrow \text{ZnO}(\text{s}) + \text{CO}_2(\text{g})$  is not spontaneous at room temperature.

(i) Give the full name for the term  $\Delta G^\circ$ .

..... [1]

(ii) Describe how the temperature at which the reaction becomes spontaneous can be calculated. Include an equation in your answer.

equation .....

.....

.....

.....

[2]

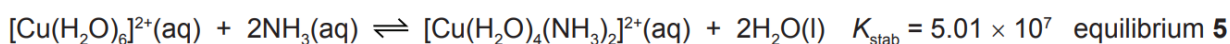
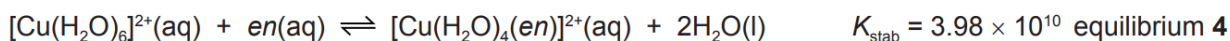
[Total: 7]

9701/43/O/N/19 (Question 3)

3(a)	a <b>measure / degree of disorder / randomness</b> of a system	1
3(b)	<b>M1:</b> negative – molecules have less energy in the system <b>M2:</b> positive – solid being converted into an aqueous solution <b>M3:</b> negative – gaseous ions being converted into a solid	3
3(c)(i)	(standard) Gibbs free energy <u>change</u>	1
3(c)(ii)	<b>M1:</b> $(\Delta)G = \Delta H - T\Delta S$ <b>M2:</b> description of calculating the minimum value of T for which $\Delta G$ is zero / becomes negative <b>OR</b> $T = \Delta H / \Delta S$ [1]	2

Question 6

(f) Copper can form complexes with the ligands ammonia and *en*,  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ , as shown.



(ii) The standard entropy change,  $\Delta S^\circ$ , for equilibrium 4 is  $+23 \text{ JK}^{-1} \text{ mol}^{-1}$  and for equilibrium 5 is  $-8.4 \text{ JK}^{-1} \text{ mol}^{-1}$ .

Suggest an explanation for this difference by reference to both equilibria.

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.....

..... [1]

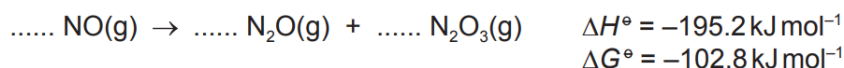
9701/42/M/J/19 (Question 3)

3(f)(ii)	equilibrium 4 has a (net) increase in moles of product / 2 moles goes to 3 moles whereas equilibrium 5 has same number of moles of reactants and products / 3 moles vs 3 moles [1]	1
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Question 7

- (b) Under conditions of high pressure and a catalyst, nitrogen monoxide, NO, forms two other oxides of nitrogen, dinitrogen monoxide, N<sub>2</sub>O, and dinitrogen trioxide, N<sub>2</sub>O<sub>3</sub>.



- (i) Balance the equation above for the formation of N<sub>2</sub>O and N<sub>2</sub>O<sub>3</sub> from NO. [1]

- (ii) State how the oxidation number of nitrogen changes during this reaction.

NO → N<sub>2</sub>O      from ..... to .....

NO → N<sub>2</sub>O<sub>3</sub>      from ..... to .....

[1]

- (iii) Calculate the entropy change for the reaction at 298 K. Include the units in your answer.

$\Delta S^\circ = \dots\dots\dots$

units = .....

[2]

- (iv) State whether the sign of  $\Delta S^\circ$  calculated in (iii) agrees with that predicted from your balanced equation in (i). Explain your answer.

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

9701/42/F/M/19 (Question 1)

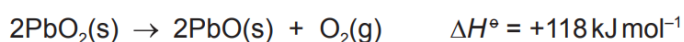
1(b)(i)	$4\text{NO} \longrightarrow \text{N}_2\text{O} + \text{N}_2\text{O}_3$	1
1(b)(ii)	+2 to +1 <b>AND</b> +2 to +3	1
1(b)(iii)	$\begin{aligned} \Delta S &= (\Delta H - \Delta G) / T \\ &= (-195.2 + 102.8) / 298 \\ &= -0.310 \text{ kJ mol}^{-1} \text{ K}^{-1} \end{aligned}$ <p><b>M1</b> numerical answer  <b>M2</b> units</p>	2

Question 8

4 The table shows some standard entropy data.

substance	standard entropy, $S^\ominus$ / JK <sup>-1</sup> mol <sup>-1</sup>
PbO <sub>2</sub> (s)	77
PbO(s)	69
O <sub>2</sub> (g)	205

Lead(IV) oxide, PbO<sub>2</sub>, decomposes to lead(II) oxide, PbO, and oxygen when heated.



(a) Use the data to calculate the value of  $\Delta S^\ominus$  for this reaction.

$$\Delta S^\ominus = \dots\dots\dots \text{ JK}^{-1} \text{ mol}^{-1} \quad [2]$$

(b) Use the value of  $\Delta H^\ominus$  and your answer to (a) to calculate the temperature at which this reaction becomes feasible.

$$T = \dots\dots\dots \text{ K} \quad [3]$$

(c) Solid lead(II) oxide can be made by heating lead metal in air.

Predict the **sign** of the standard entropy change of this reaction. Explain your answer.

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

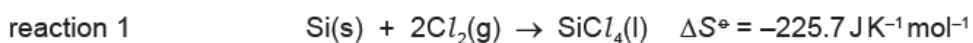
[Total: 6]

9701/42/O/N/19

4(a)	<p><b>M1:</b> correct use of stoichiometry</p> <p><b>M2:</b> answer + 189</p>	2
4(b)	<p><b>M1:</b> States or uses correct form of Gibbs equation <math>\Delta G = \Delta H - T\Delta S</math></p> <p><b>M2:</b> appreciates / includes <math>\Delta G = 0</math> at temperature required</p> <p><b>M3:</b> uses 1000 correctly and answer +624(.339)</p> <p>Award 3 marks for correct answer</p>	3
4(c)	negative <b>and</b> decrease in number / amount of gas molecules	1

Question 9

(c) (i) Silicon tetrachloride can be prepared according to reaction 1.



standard entropy of silicon, $S^\circ \text{ Si(s)}$	$18.7 \text{ JK}^{-1} \text{ mol}^{-1}$
standard entropy of silicon tetrachloride, $S^\circ \text{ SiCl}_4(\text{l})$	$239.0 \text{ JK}^{-1} \text{ mol}^{-1}$

Calculate the standard entropy of chlorine,  $S^\circ \text{ Cl}_2(\text{g})$ . Show all your working.

$S^\circ \text{ Cl}_2(\text{g}) = \dots\dots\dots \text{ JK}^{-1} \text{ mol}^{-1}$  [2]

(ii) Explain why the entropy change for reaction 1 is negative.

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

(d) The standard enthalpy change of formation of silicon tetrachloride,  $\Delta H_f^\circ \text{SiCl}_4(\text{l})$ , is  $-640 \text{ kJ mol}^{-1}$ .

Reaction 1 is spontaneous at lower temperatures, but it is not spontaneous at very high temperatures.

Calculate the temperature above which reaction 1 is **not** spontaneous.

temperature = ..... K [2]

9701/42/M/J/18

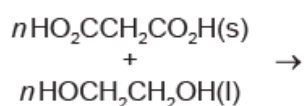
Question 10

7 (a) (i) Complete the equations to show the **two** types of polymerisation. Draw **one** repeat unit for each polymer. Include any other products.

- addition polymerisation



- condensation polymerisation





- (iii) Use bond energy values from the *Data Booklet* to calculate the enthalpy change,  $\Delta H^\circ$ , when **one** mole of amide bonds is formed in the reaction in (i).

$$\Delta H^\circ = \dots\dots\dots \text{kJ} \quad [2]$$

- (c) Amide bonds can also be formed by reacting acyl chlorides with amines.

The enthalpy change for this process,  $\Delta H^\circ$ , is  $-6.00 \text{ kJ mol}^{-1}$ .

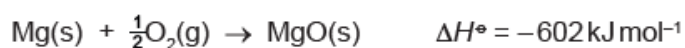
Calculate the minimum entropy change,  $\Delta S^\circ$ , for this reaction to be spontaneous (feasible) at 298 K.

$$\Delta S^\circ = \dots\dots\dots \text{JK}^{-1} \text{mol}^{-1} \quad [2]$$

9701/42/F/M/18

Question 11

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



substance	$S^\circ/\text{JK}^{-1} \text{mol}^{-1}$
Mg(s)	32.7
O <sub>2</sub> (g)	205
MgO(s)	26.9

Use the equation and the data given in the table to calculate  $\Delta G^\circ$  for the reaction at 25 °C.

$$\Delta G^\circ = \dots\dots\dots \text{units} \dots\dots\dots [4]$$

9701/42/F/M/17

Question 12

(b) Entropy is a measure of the disorder of a system.

Describe and explain what happens to the entropy of a gas when the temperature is increased.

.....

.....

..... [2]

(c) The table shows four reactions.

(i) For each reaction, predict the sign of the entropy change,  $\Delta S^\circ$ . If you predict no entropy change, write 'no change' in the table below. The first one has been done for you.

reaction	sign of $\Delta S^\circ$
$\text{CO(g)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}$	negative
$\text{Mg(s)} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{MgO(s)}$	
$\text{CuSO}_4\text{(s)} + 5\text{H}_2\text{O(l)} \rightarrow \text{CuSO}_4 \cdot 5\text{H}_2\text{O(s)}$	
$\text{NaHCO}_3\text{(s)} + \text{H}^+\text{(aq)} \rightarrow \text{Na}^+\text{(aq)} + \text{CO}_2\text{(g)} + \text{H}_2\text{O(l)}$	

[2]

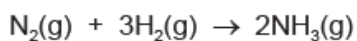
(ii) Explain why the entropy change for the first process is negative.

.....

..... [1]

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(d) Calculate the standard entropy change,  $\Delta S^\circ$ , for this reaction.

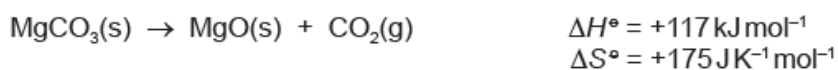


Standard entropies,  $S^\circ$ , in  $\text{JK}^{-1}\text{mol}^{-1}$  are given.

$\text{N}_2(\text{g})$	$\text{H}_2(\text{g})$	$\text{NH}_3(\text{g})$
+192	+131	+193

$\Delta S^\circ$  .....  $\text{JK}^{-1}\text{mol}^{-1}$  [2]

(e) Whether or not a chemical reaction is spontaneous (feasible) can be deduced by calculating the change in free energy,  $\Delta G^\circ$ , at a given temperature.



(i) Calculate the value of  $\Delta G^\circ$  at 298 K for the above reaction.

[2]

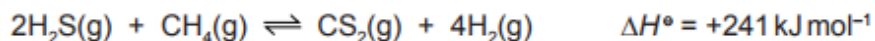
(ii) Use your answer to (i) to explain whether or not this reaction is spontaneous at 298 K.

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



Question 13

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



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

The free energy change,  $\Delta G^\circ$ , for this reaction at 1000K is +51 kJ mol<sup>-1</sup>.

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

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

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

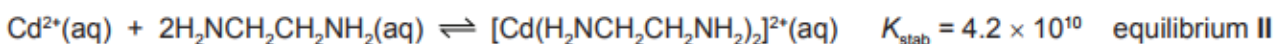
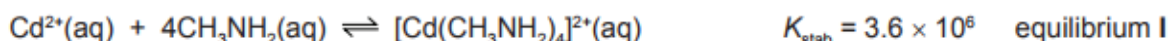
.....  
 .....  
 ..... [2]

s/16/qp41

(c) (i)	$\Delta S^\circ$ 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 <sup>-1</sup> K <sup>-1</sup> OR J mol <sup>-1</sup> K <sup>-1</sup>	[1] [1]
(d)	$\Delta G^\circ$ will become less positive/more negative as $T$ increases, ...because $\Delta S^\circ$ is positive (or $-T\Delta S^\circ$ is more negative) ...therefore the reaction becomes more feasible/spontaneous as $T$ increases	[2]

Question 14

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



- (b) Values for  $\Delta H^\circ$  and  $\Delta G^\circ$  for equilibria I and II, and the value of  $\Delta S^\circ$  for equilibrium I, are given in the table below. All values are at a temperature of 298 K.

equilibrium	$\Delta H^\circ / \text{kJ mol}^{-1}$	$\Delta G^\circ / \text{kJ mol}^{-1}$	$\Delta S^\circ / \text{JK}^{-1} \text{mol}^{-1}$
I	-57.3	-37.4	-66.8
II	-56.5	-60.7	to be calculated

- (i) Suggest a reason why the  $\Delta H^\circ$  values for the two equilibria are very similar.

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

- (ii) Calculate  $\Delta S^\circ$  for equilibrium II.

$\Delta S^\circ = \dots\dots\dots \text{JK}^{-1} \text{mol}^{-1}$  [1]

- (iii) Suggest a reason for the difference between the  $\Delta S^\circ$  you have calculated for equilibrium II and that for equilibrium I given in the table.

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

- (iv) Which of the two complexes is the more stable? Give a reason for your answer.

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

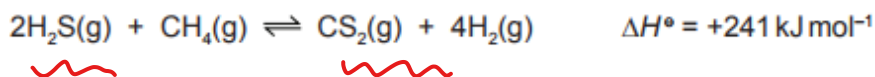
S/16/qp42

(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 <sub>2</sub> O whereas one CH <sub>3</sub> NH <sub>2</sub> only displaces one H <sub>2</sub> O	1
(iv)	The [Cd(H <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> ) <sub>2</sub> ] <sup>2+</sup> / equilibrium 2 complex (is more stable) because: either $K_{\text{stab}}$ is greater or $\Delta G^\circ$ is more negative.	1

Question 15

3 mol                      5 mol

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



$\Delta S = +ve$ , more moles of gas in product

The free energy change,  $\Delta G^\circ$ , for this reaction at 1000K is  $+51 \text{ kJ mol}^{-1}$ .

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

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

$$\frac{-241 + 51}{-1000} = \frac{241 - 1000 \times \Delta S}{-1000}$$

$$\Delta S^\circ = 0.19 \text{ units } \text{kJ mol}^{-1} \text{K}^{-1} \quad [2]$$

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

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

S/16/qp43

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

Question 16

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



substance	$S^\circ/\text{JK}^{-1}\text{mol}^{-1}$
Mg(s)	32.7
O <sub>2</sub> (g)	205 ✓
MgO(s)	26.9 ✓

$$\Delta S = 26.9 - \left( 32.7 + \frac{1 \times 205}{2} \right)$$

$$= -108.3$$

Use the equation and the data given in the table to calculate  $\Delta G^\circ$  for the reaction at 25°C.

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

$$= -602 - 298 \times \left( \frac{-108.3}{1000} \right)$$

$$\Delta G^\circ = \underline{-570} \text{ units } \underline{\text{kJ mol}^{-1}}$$

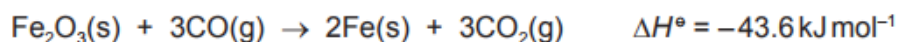
[4]

m/17/qp42

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

## Question 17

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



Some relevant standard entropies are given in the table.

substance	Fe <sub>2</sub> O <sub>3</sub> (s)	CO(g)	Fe(s)	CO <sub>2</sub> (g)
S°/JK <sup>-1</sup> mol <sup>-1</sup>	+90	+198	+27	+214

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

..... *measure of disorder of a system* ..... [1]

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

$$\begin{aligned} \Delta S &= S^\circ(\text{P}) - S^\circ(\text{R}) \\ &= (2 \times 27 + 3 \times 214) - (90 + 198 \times 3) \end{aligned}$$

$$\Delta S^\circ = \dots \dots \dots 12 \checkmark \dots \dots \dots \text{JK}^{-1} \text{mol}^{-1} \quad [2]$$

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

$$\begin{aligned} \Delta G &= \Delta H - T\Delta S \\ &= -43.6 - 298 \times 12 / 1000 \end{aligned}$$

$$\Delta G^\circ = \dots \dots \dots -47.2 \dots \dots \dots \text{kJ mol}^{-1} \quad [2]$$

(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.

.....  

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

$$-ve - T(+ve)$$
..... [1]  

$$-ve \text{ (bigger)}$$

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

## Question 18

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 ..... *+ve* .....

explanation ..... *gas produced* .....

(ii) solid potassium chloride dissolving in water



entropy change ..... *+ve* .....

explanation ..... *ionic crystal dissociates into aqueous ions, no. of particles increase* ..... [1]

(iii) steam condensing to water

entropy change ..... *-ve* .....

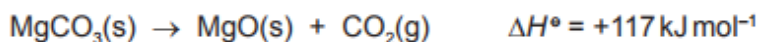
explanation .....  $\text{H}_2\text{O(g)} \rightarrow \text{H}_2\text{O(l)}$  .....

*moles of gas decrease* ..... [1]



Question 19

(b) Magnesium carbonate can be decomposed.



Standard entropies are shown in the table.

substance	MgCO <sub>3</sub> (s)	MgO(s)	CO <sub>2</sub> (g)
S°/J mol <sup>-1</sup> K <sup>-1</sup>	+65.7	+26.9	+214

$$\Delta S = S^\circ(\text{P}) - S^\circ(\text{R}) = (26.9 + 214) - (65.7) = 175.2 \text{ J mol}^{-1} \text{ K}^{-1}$$

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

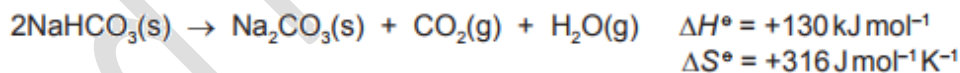
$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = 117 - 298 \times \frac{175.2}{1000} \quad \Delta G^\circ = 64.8 \text{ kJ mol}^{-1} \text{ [3]}$$

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

Increase T then  $\Delta G = \Delta H - T\Delta S$   
 $T\Delta S$  becomes bigger  $(+ve) - T \times (+ve)$   
 hence  $\Delta G$  becomes -ve  $-ve$  (bigger) [1]

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



Calculate the minimum temperature at which this reaction becomes spontaneous (feasible). Show your working.

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

$$\Delta G < 0$$

$$\Delta H - T\Delta S < 0$$

temperature = ..... K [2]

$$130 - T \times \frac{316}{1000} < 0$$

$$+ T \times \frac{316}{1000} > + 130 \times \frac{1000}{316} = 411.4 \text{ K}$$

w/16/qp43

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

## 2016 Specimen Paper Question on Entropy



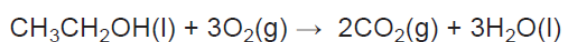
7 (a) The table lists the equations for five processes.

For each process, predict the sign of  $\Delta S$ .

process	sign of $\Delta S$
$\text{NaBr(s)} + (\text{aq}) \rightarrow \text{NaBr(aq)}$	
$\text{H}_2\text{O(l)} \rightarrow \text{H}_2\text{O(g)}$	
$2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g})$	
$\text{CoCl}_2(\text{s}) + 6\text{H}_2\text{O(l)} \rightarrow \text{CoCl}_2 \cdot 6\text{H}_2\text{O(s)}$	

[2]

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



Standard entropies are shown in the table.

substance	$\text{CH}_3\text{CH}_2\text{OH(l)}$	$\text{O}_2(\text{g})$	$\text{CO}_2(\text{g})$	$\text{H}_2\text{O(l)}$
$S^\ominus, \text{J K}^{-1} \text{mol}^{-1}$	161	205	214	70

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

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

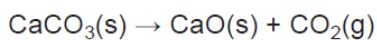
(c) The combustion of ethanol is an exothermic reaction.

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

.....  
 .....  
 .....  
 .....

[2]

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



$$\Delta H = +178 \text{ kJ mol}^{-1} \text{ and } \Delta S = +159 \text{ J K}^{-1} \text{ mol}^{-1}$$

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

[3]

[Total: 9]

Marking Scheme

(a)

process	sign of $\Delta S$
$\text{NaBr}(\text{s}) + (\text{aq}) \rightarrow \text{NaBr}(\text{aq})$	+
$\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$	+
$2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g})$	-
$\text{CoCl}_2(\text{s}) + 6\text{H}_2\text{O}(\text{l}) \rightarrow \text{CoCl}_2 \cdot 6\text{H}_2\text{O}(\text{s})$	-

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  $\Delta H$  (so  $\Delta G$  is positive) (1)

[2]

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

$$T = 178000 / 159 \quad (1)$$

$$T = 1119.5 \text{ K units required or } T > 1120 \text{ K} \quad (1)$$

[3]

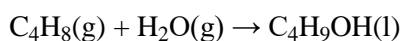
**IB QUESTIONS on ENTROPY**

1. Which change leads to an increase in entropy?

- A.  $\text{CO}_2(\text{g}) \rightarrow \text{CO}_2(\text{s})$
- B.  $\text{SF}_6(\text{g}) \rightarrow \text{SF}_6(\text{l})$
- C.  $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{s})$
- D.  $\text{NaCl}(\text{s}) \rightarrow \text{NaCl}(\text{aq})$

(Total 1 mark)

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



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

- A. -271
- B. +271
- C. -107
- D. +107

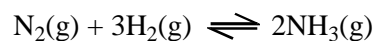
(Total 1 mark)

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:



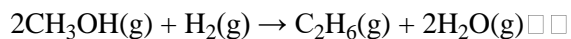
- (i) Suggest why this reaction is important for humanity. (1)
- (ii) Using the average bond enthalpy values in Table 10 of the Data Booklet, calculate the standard enthalpy change for this reaction. (4)
- (iii) The absolute entropy values,  $S$ , at 238 K for  $\text{N}_2(\text{g})$ ,  $\text{H}_2(\text{g})$  and  $\text{NH}_3(\text{g})$  are 192, 131 and  $193 \text{ J K}^{-1} \text{ mol}^{-1}$  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.  $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
- B.  $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l})$
- C.  $2\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow 2\text{CO}(\text{g})$
- D.  $2\text{SO}_3(\text{g}) \rightarrow 2\text{SO}_2(\text{g}) + \text{O}_2(\text{g})$

**(Total 1 mark)**

6. Consider the following reaction.



- (a) The standard enthalpy change of formation for  $\text{CH}_3\text{OH}(\text{g})$  at 298 K is  $-201 \text{ kJ mol}^{-1}$  and for  $\text{H}_2\text{O}(\text{g})$  is  $-242 \text{ kJ mol}^{-1}$ . Using information from Table 11 of the Data Booklet, determine the enthalpy change for this reaction. (Check the Marking Scheme for Missing Data)

.....  
.....  
.....

(2)

- (b) The standard entropy for  $\text{CH}_3\text{OH}(\text{g})$  at 298 K is  $238 \text{ J K}^{-1} \text{ mol}^{-1}$ , for  $\text{H}_2(\text{g})$  is  $131 \text{ J K}^{-1} \text{ mol}^{-1}$  and for  $\text{H}_2\text{O}(\text{g})$  is  $189 \text{ J K}^{-1} \text{ mol}^{-1}$ . Using information from Table 11 (Check Marking Scheme) of the Data Booklet, determine the entropy change for this reaction.

.....  
.....  
.....

(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.

.....

.....

.....

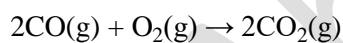
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.....

.....

(3)  
(Total 7 marks)

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



	<b>CO(g)</b>	<b>O<sub>2</sub>(g)</b>	<b>CO<sub>2</sub>(g)</b>
$S^\ominus/\text{J K}^{-1} \text{mol}^{-1}$	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  $+10.00 \text{ kJ mol}^{-1}$  at 298 K. The standard entropy change,  $\Delta S^\ominus$ , for the same reaction is  $+10.00 \text{ J K}^{-1} \text{ mol}^{-1}$ . What is the value of  $\Delta G^\ominus$  for the reaction in  $\text{kJ mol}^{-1}$ ?

- A. +9.75
- B. +7.02
- C. -240
- D. -2970

(Total 1 mark)

9. Which reaction has the greatest increase in entropy?

- A.  $\text{C}_3\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{g})$  □ □
- B.  $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g})$
- C.  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$
- D.  $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g})$

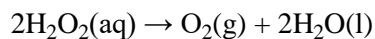
(Total 1 mark)

10. Which reaction has the largest increase in entropy?

- A.  $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g})$
- B.  $\text{Al}(\text{OH})_3(\text{s}) + \text{NaOH}(\text{aq}) \rightarrow \text{Al}(\text{OH})_4^-(\text{aq}) + \text{Na}^+(\text{aq})$
- C.  $\text{Na}_2\text{CO}_3(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow 2\text{NaCl}(\text{aq}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$
- D.  $\text{BaCl}_2(\text{aq}) + \text{Na}_2\text{SO}_4(\text{aq}) \rightarrow \text{BaSO}_4(\text{s}) + 2\text{NaCl}(\text{aq})$

(Total 1 mark)

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



What are the signs of  $\Delta H$ ,  $\Delta S$  and  $\Delta G$  for this reaction?

	$\Delta H$	$\Delta S$	$\Delta G$
A.	-	-	-
B.	-	+	-
C.	+	+	-
D.	-	+	+

(Total 1 mark)

12. Which reaction has the greatest increase in entropy?

- A.  $\text{SO}_2(\text{g}) + 2\text{H}_2\text{S}(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + 3\text{S}(\text{s})$   
B.  $\text{CaO}(\text{s}) + \text{CO}_2(\text{g}) \rightarrow \text{CaCO}_3(\text{s})$   
C.  $\text{CaC}_2(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{Ca}(\text{OH})_2(\text{s}) + \text{C}_2\text{H}_2(\text{g})$   
D.  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$

(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	$\Delta H_f^\ominus / \text{kJ mol}^{-1}$	$S^\ominus / \text{J K}^{-1} \text{mol}^{-1}$
hydrogen	$\text{H}_2(\text{g})$	0	+ 131
propane	$\text{C}_3\text{H}_8(\text{g})$	- 104	+ 270
propene	$\text{C}_3\text{H}_6(\text{g})$	+ 20.4	+ 267

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

.....  
 .....

(1)

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

.....  
 .....  
 .....

(2)

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

.....  
.....  
.....  
.....

(2)

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

.....  
.....  
.....  
.....

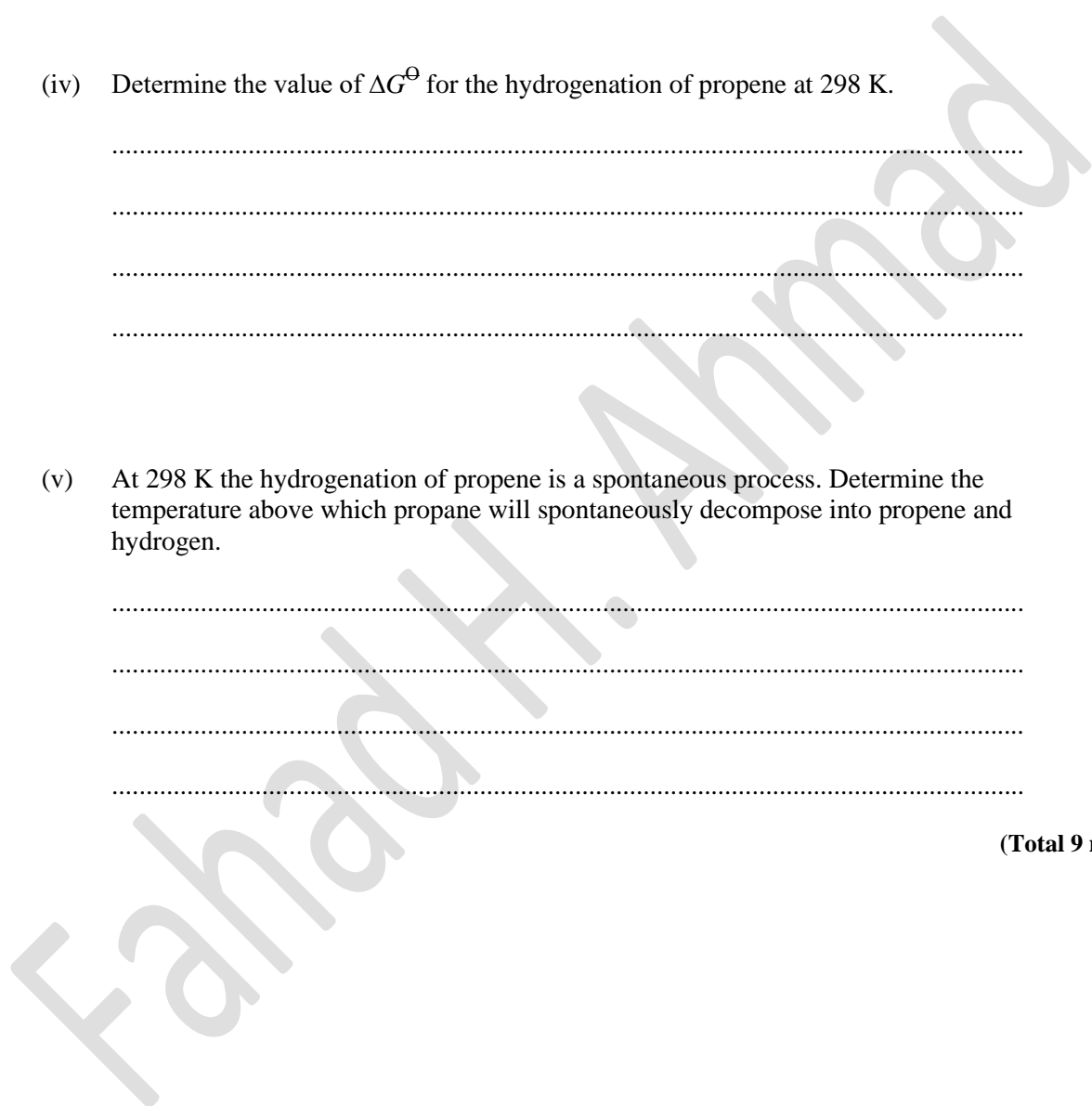
(2)

(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.

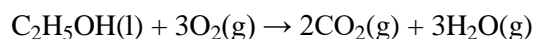
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.....  
.....

(2)

(Total 9 marks)



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



Compound	$\Delta G_f^\ominus / \text{kJ mol}^{-1}$
$\text{C}_2\text{H}_5\text{OH}(\text{l})$	-175
$\text{CO}_2(\text{g})$	-394
$\text{H}_2\text{O}(\text{g})$	-229
$\text{O}_2(\text{g})$	0

- A. -1650  
 B. -1300  
 C. -448  
 D. +1300

(Total 1 mark)

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

- A.  $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$   
 B.  $\text{NH}_4\text{Cl}(\text{s}) \rightarrow \text{NH}_3(\text{g}) + \text{HCl}(\text{g})$   
 C.  $\text{PbCl}_2(\text{s}) \rightarrow \text{Pb}^{2+}(\text{aq}) + 2\text{Cl}^{-}(\text{aq})$   
 D.  $\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$

(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)  $\Delta H = (\text{sum of energies of bonds broken}) - (\text{sum of energies of bonds formed})$ ;  
*Can be implied by working.*  
correct substitution of values and numbers of bonds broken;  
correct substitution of values and numbers of bonds made;  
 $(\Delta H = (\text{N}\equiv\text{N}) + 3(\text{H}-\text{H}) - 6(\text{N}-\text{H}) = 944 + 3(436) - 6(388) = -76.0 \text{ (kJ)})$ ; 4  
*Allow ECF.*  
*Do not penalize for sig. fig. or units.*  
*Award [4] for correct final answer.*
- (iii)  $(\Delta S^\ominus [2 \times 193] - [192 + 3 \times 131]) = -199 \text{ (J K}^{-1} \text{ mol}^{-1})$ ; 2  
*Allow ECF.*  
*four gaseous molecules generating two gaseous molecules / fewer molecules of gas;*
- (iv)  $(\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus = -76.0 - 298(-0.199)) = -16.7 \text{ (kJ)}$ ;  
Spontaneous;  
 $\Delta G$  is negative; 3  
*Do not penalize for SF.*
- (v) heat released when gas  $\rightarrow$  liquid;  
 $\Delta H^\ominus$  becomes more negative; 2 [12]
5. B [1]
6. (a)  $\Delta H^\ominus_{\text{reaction}} = \Sigma \Delta H_f^\ominus(\text{products}) - \Sigma \Delta H_f^\ominus(\text{reactants})$   
 $= [(1)(-85) + (2)(-242)] - [(2)(-201)]$ ;  
 $= -167 \text{ (kJ/kJ mol}^{-1})$ ;  
*Award [1] for (+) 167.* 2
- (b)  $\Delta S^\ominus_{\text{reaction}} = \Sigma S^\ominus(\text{products}) - \Sigma S^\ominus(\text{reactants})$

$$= [(1)(230) + (2)(189)] - [(2)(238) + (1)(131)];$$
$$= 1 \text{ (J K}^{-1}\text{/J K}^{-1} \text{ mol}^{-1}\text{);}$$

2

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

$$= -167 \text{ kJ/-167000 J;}$$

*Units needed for mark in (c) only.*

*Accept  $-167 \text{ kJ mol}^{-1}$  or  $-167000 \text{ J mol}^{-1}$ .*

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;  
 $\Delta G$  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  $\Delta H_h^\ominus$  of elements (in their standard states) is zero / no reaction involved / OWTTE; 1
- (ii)  $\Delta H = -104 - (+20.4)$ ;  
 $= -124.4 \text{ (kJ mol}^{-1}\text{)}$ ; 2  
*Award [1 max] for 124.4 (kJ mol<sup>-1</sup>).*  
*Award [2] for correct final answer.*
- (iii)  $\Delta S = 270 - (267 + 131)$ ;  
 $= -128 \text{ (J K mol}^{-1}\text{)}$ ; 2  
*Award [1 max] for +128 (J K<sup>-1</sup> mol<sup>-1</sup>).*  
*Award [2] for correct final answer.*
- (iv)  $\Delta G = \Delta H - T\Delta S = -124.4 - \frac{(-128 \times 298)}{1000}$ ;  
 $= -86.3 \text{ kJ mol}^{-1}$ ; 2  
*Units needed for the mark.*  
*Award [2] for correct final answer.*  
*Allow ECF if only one error in first marking point.*
- (v)  $\Delta G = \Delta H - T\Delta S = 0 / \Delta H = T\Delta S$ ;  
 $T = \frac{-124.4}{-128/1000} = 972 \text{ K} / 699 \text{ }^\circ\text{C}$ ; 2  
*Only penalize incorrect units for T and inconsistent  $\Delta S$  value once in (iv) and (v).*

[9]

16. B

[1]

17. A

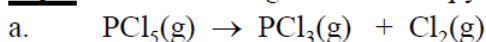
[1]

Fahad H. Ahmad

## SHOEIFFAT QUESTIONS

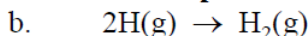
Basic Questions

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



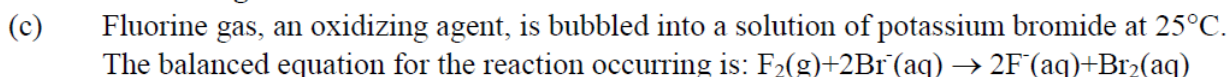
**1 mole of a gas is producing 2 moles of gases  $\Rightarrow$  disorder increases.**

**$\Delta S^\circ$  is positive.**



**2 moles of gases are producing 1 mole of gas  $\Rightarrow$  disorder decreases.**

**$\Delta S^\circ$  is negative.**



Predict the sign of  $\Delta S^\circ$  for the reaction at  $25^\circ\text{C}$ . Justify your prediction.

**The sign of  $\Delta S^\circ$  is negative.**

**One of the reactants,  $\text{F}_2$ , is a gas at  $25^\circ\text{C}$ , 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  $\Delta S^\circ$  negative.**

**BQ 2** Consider the following process:  $\text{Zn}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{ZnO}(\text{s})$

a. Calculate  $\Delta S^\circ$  at 298K, given the following  $S^\circ$  values, in  $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ :  
ZnO: 44; Zn: 42;  $\text{O}_2$ : 205.

$$\Delta S^\circ = S^\circ_{\text{ZnO}(\text{s})} - S^\circ_{\text{Zn}(\text{s})} - \frac{1}{2}S^\circ_{\text{O}_2(\text{g})} = (44) - (42) - \left(\frac{205}{2}\right) = -100.5\text{J/mol K}$$

b. Is the sign of  $\Delta S^\circ$  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:  $\text{H}_2\text{O}(\text{s}) \rightarrow \text{H}_2\text{O}(\text{l})$   $\Delta H^\circ = 6.03\text{ kJ}$

Given  $\Delta S^\circ = 22.1\text{ J/K}\cdot\text{mol}$ , show that the melting of ice becomes spontaneous at  $0^\circ\text{C}$ .

Given  $\Delta S^\circ = 22.1\text{ J/K}\cdot\text{mol}$ ,  $\Delta H^\circ = 6.03\text{ kJ}$ ,  $T = 0^\circ\text{C} + 273 = 273\text{K}$

RTF: rxn is spontaneous

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ = (6.03) - (273)(22.1 \times 10^{-3}) = -3.3 \times 10^{-3}\text{kJ}$$

Since  $\Delta G^\circ$  is negative then the process is spontaneous.

**BQ 5** Consider the following process:  $\text{C}_6\text{H}_6(\text{l}) \rightarrow \text{C}_6\text{H}_6(\text{g})$

Given for the above process  $\Delta H^\circ_{\text{vap}} = 30.8\text{ kJ/mol}$ , and  $\Delta S^\circ_{\text{vap}} = 87.2\text{ J/K}\cdot\text{mol}$ .

Calculate the boiling point of benzene.

Given:  $\Delta H^\circ_{\text{vap}} = 30.8\text{ kJ/mol}$ ,  $\Delta S^\circ_{\text{vap}} = 87.2\text{ J/K}\cdot\text{mol}$  RTF: boiling point of benzene

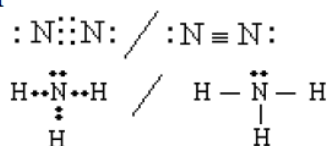
A phase change at equilibrium is isothermal, ie occurs at same t, therefore  $\Delta G^\circ = 0\text{kJ}$

$$\Delta G^\circ = \Delta H^\circ_{\text{vap}} - T \Delta S^\circ_{\text{vap}} = (30.8) - T(87.2 \times 10^{-3}) = 0\text{kJ} \Rightarrow T = \frac{30.8}{87.2 \times 10^{-3}} = 353\text{K} \Rightarrow t = 80^\circ\text{C}$$

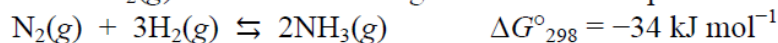


**BQ 7** Answer the following questions about nitrogen, hydrogen, and ammonia.

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



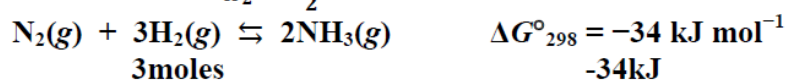
(b) Calculate the standard free-energy change,  $\Delta G$ , that occurs when 24.0 g of  $H_2(g)$  react with excess  $N_2(g)$  at 298 K according to the reaction represented below.



**Given:** m of  $H_2 = 24.0 \text{ g}$ ,  $\Delta G^\circ_{298} = -34 \text{ kJ mol}^{-1}$

**RTF:**  $\Delta G$

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



12.0moles

$\Delta G_{298}$

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

## Multiple Choice

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

- [-A-]  $\Delta S^\circ$  and  $\Delta H^\circ$  are both negative
- [-B-]  $\Delta S^\circ$  and  $\Delta H^\circ$  are both positive**
- [-C-]  $\Delta S^\circ$  is negative and  $\Delta H^\circ$  is positive
- [-D-]  $\Delta S^\circ$  is positive and  $\Delta H^\circ$  is negative
- [-E-]  $\Delta S^\circ$  and  $\Delta H^\circ$  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  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  for the process?

	$\Delta G$	$\Delta H$	$\Delta S$
[-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?

	$\Delta G$	$\Delta H$	$\Delta S$
[-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  $-70.0\text{kJ}$  at  $100\text{K}$  and  $-40.0\text{Kj}$  at  $200\text{K}$ . 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  $25^\circ\text{C}$  or at  $80^\circ\text{C}$ ?

**At  $80^\circ\text{C}$ , water will have greater entropy. Entropy increases with an increase in temperature.**