# **ENTROPY**

## Fahad H. Ahmad

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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 SiO<sub>2</sub> by reaction with carbon at over 2000 °C.

reaction 1 
$$SiO_2(s) + 2C(s) \rightarrow Si(I) + 2CO(g)$$

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

(ii) Reaction 1 is highly endothermic.

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

**(b)** Silicon is purified by first heating it in a stream of HCl(g) to form  $SiHCl_3$ . The  $SiHCl_3$  formed is then distilled to remove other impurities.

reaction 2 Si(s) + 
$$3HCl(g) \rightarrow SiHCl_3(g) + H_2(g)$$

(i) Table 2.1 shows some standard entropy data.

Table 2.1

compound	standard entropy, S°/JK <sup>-1</sup> mol <sup>-1</sup>
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.

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

	(	(ii)	Reaction	3	is	the	reverse	of	reaction	2	and	is	used	to	obtain	pure	silicor
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reaction 3 SiHC
$$l_3(g)$$
 +  $H_2(g) \rightarrow Si(s)$  + 3HC $l(g)$   $\Delta H = +219.3 \text{ kJ mol}^{-1}$ 

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  $\Delta S^{\circ} = -150 \,\mathrm{J \, K^{-1} \, mol^{-1}}$  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 $\Delta H$ )  OR (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	2
	M2: = $-135$ (J K <sup>-1</sup> mol <sup>-1</sup> )	
2(b)(ii)	M1: $\Delta G = 0 : T = \Delta H / \Delta S = +219.3 \times 10^3 + -(b)(i)$	2
	M2: = <b>1624</b> (.4) (K)	

#### Question 2

(c)	(i)	Explain what is meant by the term entropy of a system.							
		[1	1]						

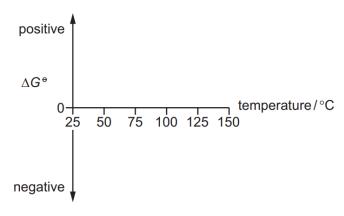
(ii) Place one tick ( $\checkmark$ ) in each row of the table to show the sign of each entropy change,  $\triangle S$ .

process	$\Delta S$ is negative	$\Delta S$ is zero	ΔS is positive
NaC <i>l</i> dissolving in water			
water solidifying to ice			

[1]

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

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



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

$$A + B \rightleftharpoons C + D$$

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

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

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

[2]

Question	Answer Mari								
4(c)(i)	(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)								
4(c)(ii)		$\Delta S$ is negative	ΔS is zero	$\Delta S$ is positive		1			
	solid dissolving in water			✓					
	water solidifying to ice	✓							
4(c)(iii)	positive  AG  O  D  D  D  D  D  D  D  D  D  D  D  D								
4(d)	<ul> <li>negative gradient straight / curve line through the <i>x</i>-axis (no clear positive inflexions)</li> <li>M1: ΔH negative / - , ΔS negative / -</li> <li>M2: as temperature increase, ΔG becomes (more) positive / less negative ora</li> <li>OR at low(er) T, (ΔH more negative than TΔS) so ΔG is negative</li> <li>OR at high(er) T, (ΔH less negative than TΔS) so ΔG is positive</li> </ul>								

#### Question 3

(f)  $NH_4IO_3$  is an unstable compound that readily decomposes when warmed. The decomposition reaction is shown.

$${\rm NH_4IO_3(s)} \ \to \ \tfrac{1}{2}{\rm N_2(g)} \ + \ \tfrac{1}{2}{\rm O_2(g)} \ + \ \tfrac{1}{2}{\rm I_2(g)} \ + \ 2{\rm H_2O(I)} \qquad \Delta H = -154.6\,{\rm kJ\,mol^{-1}}$$

(i) Use the data in the table to calculate the entropy change of reaction,  $\Delta S$ , of the decomposition of NH<sub>4</sub>IO<sub>3</sub>(s).

compound	S/JK <sup>-1</sup> mol <sup>-1</sup>
NH <sub>4</sub> IO <sub>3</sub> (s)	42
N <sub>2</sub> (g)	192
O <sub>2</sub> (g)	205
$I_2(g)$	261
H <sub>2</sub> O(I)	70

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

(ii)	Т	his reaction	n is feasible at all	temperature	es.			
	Ε	xplain why	, using the data in	( <b>f)</b> and you	r answer to (	(f)(i).		
								[1]
9701/4	 2/F	/M/21 (Qu	uestion 3)				_	[1]
3(f)(i)	)	<b>M1</b> : $\Delta S = \frac{1}{2}(19)$ <b>M2</b> : (+)427 (J kg	2) + ½(205) + ½(261) + 2(7 K <sup>-1</sup> mol <sup>-1</sup> ) ecf	0) – 42				2
3(f)(ii)	)	• $\Delta H < 0 / \text{ne}$	egative because egative <b>OR</b> exothermic <b>AND</b> sitive <b>OR</b> $-T\Delta S < 0$ for all $T$					1
Questio	on	4					10	
		er chloride, tion is show	AgC <i>l</i> , is sparingly	y soluble in	water. The e	equation for	the enthalpy ch	ange of
			AgC1(	s) → Ag⁺(a	q) + C <i>l</i> <sup>-</sup> (aq	) ∆H <sub>s</sub>	ol = +65.5 kJ mol	-1
S	tan	dard entro	pies are shown in	the table.				
			species	AgCl(s)	Ag⁺(aq)	C <i>l</i> ⁻(aq)		
			S*/JK <sup>-1</sup> mol <sup>-1</sup>	+96.2	+72.7	+56.5		
(i)	)	Calculate t	the standard entro	py change o	of solution, $\Delta S$	S°.		
					ΔS <sup>e</sup>	· =	JK <sup>-1</sup> m	nol <sup>-1</sup> [1]
(ii)	)	Explain, wi	ith the aid of a cal	culation, why	/ AgC <i>l</i> is inso	oluble in wat	er at 25°C.	
, ,		-	d use data from thi					
				·	•	( // /		
								[31
								. [-]

### 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)	<b>M1</b> $\Delta G = \Delta H^{0} - T\Delta S^{0}$	3
	<b>M2</b> $\triangle G = (65.5)-(298\times0.033) = +55.7 \text{ kJ mol}^{-1} \text{ min 3sf}$	
	M3 $\Delta G$ = positive so not feasible/spontaneous	

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3	(a)	Explain what is meant by the term entropy of a system.		
	(b)	State and explain whether the entropy change of each of the following processes is positive or		
		<ul> <li>negative. Do not consider the entropy change of the surroundings.</li> <li>liquid water at 80 °C is cooled to 60 °C</li> </ul>		
		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, $\Delta H_{\rm latt}$ CaC $l_2$ (s), takes place		
		The entropy change is because		
		[3]		

(ii) Describe how the temperature at which the reaction becomes spontaneous can be calculated. Include an equation in your answer.  equation  [2]  [7otal: 7]  9701/43/O/N/19 (Question 3)  [3(a) a measure / degree of disorder / randomness of a system  M2: positive – solid being converted into an aqueous solution  M3: negative – molecules have less energy in the system  M2: positive – solid being converted into an aqueous solution  M3: negative – solid being converted into a solid  [3(c)(i)] (standard) Clibbs free energy change  1 and 1: (A)G → AH − TAS  [2]  Question 6  (f) Copper can form complexes with the ligands ammonia and en, H₂NCH₂CH₂NH₂, as shown.  [Cu(H₂O)₀]²²(aq) + en(aq) ⇌ [Cu(H₂O)₄(en)]²²(aq) + 2H₂O(i)	(c) Th	ne reaction $ZnCO_3(s) \rightarrow ZnO(s) + CO_2(g)$ is not spontaneous at room temperature.				
(ii) Describe how the temperature at which the reaction becomes spontaneous can be calculated. Include an equation in your answer.  equation  [2]  [7otal: 7]  9701/43/O/N/19 (Question 3)  3(a) a measure / degree of disorder / randomness of a system  41  3(b) M1: negative – molecules have less energy in the system  32(c)(i) (standard) Gibbs free energy change  3(c)(i) (standard) Gibbs free energy change  1 (standard) Gibbs free energy change  2 (standard) Gibbs free energy change  3 (standard) Gibbs free energy change  4 (standard) Gibbs free energy change  5 (standard) Gibbs free energy change  6 (f) Copper can form complexes with the ligands ammonia and en, H₂NCH₂CH₂NH₂, as shown.  [Cu(H₂O)₀]²²(aq) + en(aq) ⇌ [Cu(H₂O)₄(en))²²(aq) + 2H₂O(l)	(i)	Give the full name for the term $\Delta G^{\circ}$ .				
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M3: negative – gaseous ions being converted into a solid $3(c)(i)$ (standard) Gibbs free energy change  1 $3(c)(i)$ M1: $(A)G = \Delta H - T\Delta S$ M2: description of calculating the minimum value of T for which $\Delta G$ is zero / becomes negative $\mathbf{OR}$ T = $\Delta H / \Delta S$ [1]  Question 6  (f) Copper can form complexes with the ligands ammonia and $en$ , $H_2NCH_2CH_2NH_2$ , as shown. $[Cu(H_2O)_6]^{2^+}(aq) + en(aq) \rightleftharpoons [Cu(H_2O)_4(en)]^{2^+}(aq) + 2H_2O(l)$ $K_{stab} = 3.98 \times 10^{10}$ equilibrium $4$ [Cu(H_2O)_6]^{2^+}(aq) + 2NH_3(aq) $\rightleftharpoons [Cu(H_2O)_4(NH_3)_2]^{2^+}(aq) + 2H_2O(l)$ $K_{stab} = 5.01 \times 10^7$ equilibrium $4$ (ii) The standard entropy change, $\Delta S^o$ , for equilibrium $4$ is +23 J K <sup>-1</sup> mol <sup>-1</sup> and for equilibrium $5$ is $-8.4$ J K <sup>-1</sup> mol <sup>-1</sup> .  Suggest an explanation for this difference by reference to both equilibria.	3(b)		3			
3(c)(i) (standard) Gibbs free energy change 1  3(c)(ii) M1: ( $\Delta$ )G = $\Delta$ H - T $\Delta$ S 2  M2: description of calculating the minimum value of T for which $\Delta$ G is zero / becomes negative OR T = $\Delta$ H / $\Delta$ S [1]  Question 6  (f) Copper can form complexes with the ligands ammonia and en, H <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> , as shown. [Cu(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup> (aq) + en(aq) $\Longrightarrow$ [Cu(H <sub>2</sub> O) <sub>4</sub> (en)] <sup>2+</sup> (aq) + 2H <sub>2</sub> O(l) $K_{\text{stab}} = 3.98 \times 10^{10}$ equilibrium $\frac{1}{2}$ [Cu(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup> (aq) + 2NH <sub>3</sub> (aq) $\Longrightarrow$ [Cu(H <sub>2</sub> O) <sub>4</sub> (NH <sub>3</sub> ) <sub>2</sub> ] <sup>2+</sup> (aq) + 2H <sub>2</sub> O(l) $K_{\text{stab}} = 5.01 \times 10^{7}$ equilibrium $\frac{1}{2}$ (ii) The standard entropy change, $\Delta$ S°, for equilibrium $\frac{1}{2}$ is -8.4 J K <sup>-1</sup> mol <sup>-1</sup> . Suggest an explanation for this difference by reference to both equilibria. [1] 9701/42/M/J/19 (Question 3)						
Question 6  (f) Copper can form complexes with the ligands ammonia and $en$ , $H_2NCH_2CH_2NH_2$ , as shown.  [ $Cu(H_2O)_6$ ] <sup>2+</sup> (aq) + $en$ (aq) $\rightleftharpoons$ [ $Cu(H_2O)_4(en)$ ] <sup>2+</sup> (aq) + $2H_2O(I)$ $K_{stab} = 3.98 \times 10^{10}$ equilibrium 4 [ $Cu(H_2O)_6$ ] <sup>2+</sup> (aq) + $2NH_3$ (aq) $\rightleftharpoons$ [ $Cu(H_2O)_4$ ( $NH_3$ ) <sub>2</sub> ] <sup>2+</sup> (aq) + $2H_2O(I)$ $K_{stab} = 5.01 \times 10^7$ equilibrium 5 is $-8.4JK^{-1}mol^{-1}$ .  Suggest an explanation for this difference by reference to both equilibria.  [1] 9701/42/M/J/19 (Question 3)	3(c)(i)		1			
Question 6  (f) Copper can form complexes with the ligands ammonia and $en$ , $H_2NCH_2CH_2NH_2$ , as shown. $[Cu(H_2O)_6]^{2^+}(aq) + en(aq) \rightleftharpoons [Cu(H_2O)_4(en)]^{2^+}(aq) + 2H_2O(I) \qquad K_{stab} = 3.98 \times 10^{10} \text{ equilibrium 4}$ $[Cu(H_2O)_6]^{2^+}(aq) + 2NH_3(aq) \rightleftharpoons [Cu(H_2O)_4(NH_3)_2]^{2^+}(aq) + 2H_2O(I) \qquad K_{stab} = 5.01 \times 10^7 \text{ equilibrium 4}$ (ii) The standard entropy change, $\Delta S^\circ$ , for equilibrium 4 is $+23 \text{ J K}^{-1} \text{ mol}^{-1}$ and for equilibrium 5 is $-8.4 \text{ J K}^{-1} \text{ mol}^{-1}$ .  Suggest an explanation for this difference by reference to both equilibria.  [1] 9701/42/M/J/19 (Question 3)  3(f)(iii) equilibrium 4 has a (net) increase in moles of product/2 moles goes to 3 moles whereas equilibrium 5 has same number of	3(c)(ii)	M1: $(\Delta)G = \Delta H - T\Delta S$	2			
(f) Copper can form complexes with the ligands ammonia and $en$ , $H_2NCH_2CH_2NH_2$ , as shown. $ [Cu(H_2O)_6]^{2^+}(aq) + en(aq) \iff [Cu(H_2O)_4(en)]^{2^+}(aq) + 2H_2O(l) \qquad K_{stab} = 3.98 \times 10^{10} \text{ equilibrium 4} $ $ [Cu(H_2O)_6]^{2^+}(aq) + 2NH_3(aq) \iff [Cu(H_2O)_4(NH_3)_2]^{2^+}(aq) + 2H_2O(l) \qquad K_{stab} = 5.01 \times 10^7 \text{ equilibrium 5} $ $ (ii)  \text{The standard entropy change, } \Delta S^e, \text{ for equilibrium 4 is } +23\text{J K}^{-1}\text{mol}^{-1} \text{ and for equilibrium 5} $ $ \text{is } -8.4\text{J K}^{-1}\text{mol}^{-1}. $ Suggest an explanation for this difference by reference to both equilibria. } $ [1] $ $ 9701/42/M/J/19  \text{(Question 3)} $ $ \boxed{ 3(f)(ii) }                                 $		<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]				
(f) Copper can form complexes with the ligands ammonia and $en$ , $H_2NCH_2CH_2NH_2$ , as shown. $ [Cu(H_2O)_6]^{2^+}(aq) + en(aq) \iff [Cu(H_2O)_4(en)]^{2^+}(aq) + 2H_2O(l) \qquad K_{stab} = 3.98 \times 10^{10} \text{ equilibrium 4} $ $ [Cu(H_2O)_6]^{2^+}(aq) + 2NH_3(aq) \iff [Cu(H_2O)_4(NH_3)_2]^{2^+}(aq) + 2H_2O(l) \qquad K_{stab} = 5.01 \times 10^7 \text{ equilibrium 5} $ $ (ii)  \text{The standard entropy change, } \Delta S^e, \text{ for equilibrium 4 is } +23\text{J K}^{-1}\text{mol}^{-1} \text{ and for equilibrium 5} $ $ \text{is } -8.4\text{J K}^{-1}\text{mol}^{-1}. $ Suggest an explanation for this difference by reference to both equilibria. } $ [1] $ $ 9701/42/M/J/19  \text{(Question 3)} $ $ \boxed{ 3(f)(ii) }                                 $	Question	n 6				
$ [Cu(H_2O)_6]^{2^+}(aq) + 2NH_3(aq)                                    $	(f)	Copper can form complexes with the ligands ammonia and <i>en</i> , H <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> , as sh	own.			
<ul> <li>(ii) The standard entropy change, ΔS°, for equilibrium 4 is +23 J K⁻¹ mol⁻¹ and for equilibrium 5 is –8.4 J K⁻¹ mol⁻¹.</li> <li>Suggest an explanation for this difference by reference to both equilibria.</li> <li>[1] 9701/42/M/J/19 (Question 3)</li> <li>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</li> </ul>	[Cu(H <sub>2</sub> (	$(S_{6})^{2+}(aq) + en(aq) \rightleftharpoons [Cu(H_{2}O)_{4}(en)]^{2+}(aq) + 2H_{2}O(I)$ $K_{stab} = 3.98 \times 10^{10} \text{ equilibrium}$	rium 4			
is -8.4 J K <sup>-1</sup> mol <sup>-1</sup> .  Suggest an explanation for this difference by reference to both equilibria.  [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	[Cu(H <sub>2</sub> (	$(O)_{6}^{2+}(aq) + 2NH_{3}(aq) \rightleftharpoons [Cu(H_{2}O)_{4}(NH_{3})_{2}]^{2+}(aq) + 2H_{2}O(I)$ $K_{stab} = 5.01 \times 10^{7}$ equilibrium	rium <b>5</b>			
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	(ii		ium <b>5</b>			
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		Suggest an explanation for this difference by reference to both equilibria.				
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						
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						
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	0704/40		[1]			
	3(f)(ii)		1			

#### 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> .

..... NO(g) 
$$\rightarrow$$
 ..... N<sub>2</sub>O(g) + ..... N<sub>2</sub>O<sub>3</sub>(g)  $\Delta H^{\circ} = -195.2 \,\mathrm{kJ} \,\mathrm{mol}^{-1}$   $\Delta G^{\circ} = -102.8 \,\mathrm{kJ} \,\mathrm{mol}^{-1}$ 

/i)	Palance the equation above for the formation of N O and N O from NO	[11
(י)	Balance the equation above for the formation of $N_2O$ and $N_2O_3$ from NO.	נין

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

$$NO \rightarrow N_2O$$
 from ...... to ...... 
$$NO \rightarrow N_2O_3$$
 from ..... to ...... [1]

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

units =	∆S <sup>e</sup> =	
	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.

[11]

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

1(b)(i)	$4NO \longrightarrow N_2O + N_2O_3$	1
1(b)(ii)	+2 to +1 <b>AND</b> +2 to +3	1
1(b)(iii)	$\Delta S = (\Delta H - \Delta G)/T$ = (-195.2+102.8)/298 = -0.310 kJ mol <sup>-1</sup> K <sup>-1</sup> <b>M1</b> numerical answer <b>M2</b> units	2
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#### Question 8

4 The table shows some standard entropy data.

substance	standard entropy, S <sup>e</sup> /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,  $PbO_2$ , decomposes to lead(II) oxide, PbO, and oxygen when heated.

$$2PbO_2(s) \rightarrow 2PbO(s) + O_2(g)$$
  $\Delta H^{\circ} = +118 \text{ kJ mol}^{-1}$ 

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

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

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

$$T = \dots K [3]$$

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

#### Question 9

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

reaction 1

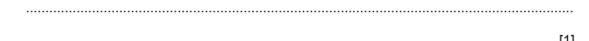
$$Si(s) + 2Cl_2(g) \rightarrow SiCl_4(I)$$
  $\Delta S^{\circ} = -225.7 \,\mathrm{J} \,\mathrm{K}^{-1} \,\mathrm{mol}^{-1}$ 

standard entropy of silicon, S° Si(s)	18.7 J K <sup>-1</sup> mol <sup>-1</sup>
standard entropy of silicon tetrachloride, S° SiC $l_4(I)$	239.0 J K <sup>-1</sup> mol <sup>-1</sup>

Calculate the standard entropy of chlorine,  $S^{\circ} Cl_2(g)$ . Show all your working.

$$S \circ Cl_2(g) = ..... J K^{-1} mol^{-1}$$
 [2]

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



(d) The standard enthalpy change of formation of silicon tetrachloride,  $\Delta H_{\mathrm{f}}^{\bullet} \operatorname{SiC} l_{4}(I)$ , is  $-640 \, \mathrm{kJ} \, \mathrm{mol}^{\text{-}1}$ .

Reaction 1 is spontaneous at lower temperatures, but it is not spontaneous at very high temperatures.				
Calculate the temperature above which reaction 1 is <b>not</b> 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 fo each polymer. Include any other products.				
addition polymerisation				
$n  \text{CH}_2 = \text{CHCH}_3(g) \rightarrow$				
condensation polymerisation				
PHO CCH CO H/o)				
$n HO_2CCH_2CO_2H(s)$ + $\rightarrow$ $n HOCH_2CH_2OH(I)$				

(ii)	Suggest the sign of the entropy changes, ΔS*, for each of the two types of polymers. Explain your answers.				
	•	ΔSʻ	for additio	n polymerisation	
	•	ΔS'	or conder	nsation polymerisation	
				[2]	
	(b)	An	amide bond	forms when a carboxylic acid reacts with an amine.	
		(i)	Complete t	he equation by writing the products in the box.	
R-	-CO₂H	+	H₂N−R' →	+	
				[1]	
	(	(ii)		answer to (i) to work out the bonds that are broken and the bonds that are ing the reaction between a carboxylic acid and an amine.	
			• bonds	that are broken	
			• bonds	that are formed	
				[2]	

(iii)	Use bond energy values from the Data Booklet to calculate the enthalpy change, $\Delta H^{\epsilon}$
	when <b>one</b> mole of amide bonds is formed in the reaction in (i).

$$\Delta H^{\bullet} = ..... kJ [2]$$

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

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

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

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

9701/42/F/M/18

#### Question 11

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

$$Mg(s) + \frac{1}{2}O_2(g) \rightarrow MgO(s)$$
  $\Delta H^{o} = -602 \text{ kJ mol}^{-1}$ 

$$\Delta H^{\bullet} = -602 \text{ kJ mol}^{-1}$$

substance	Se/JK-1mol-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.

[4]

9701/42/F/M/17

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(b)	Entrop	y is a	measure of	of the	disorder	of a	system.
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Describe and explain what happens to the entropy of a gas when the temperature is increased

(c) The table shows four reactions.

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

reaction	sign of ∆S•
$CO(g) + O_2(g) \rightarrow CO_2(g)$	negative
$Mg(s) + \frac{1}{2}O_2(g) \rightarrow MgO(s)$	
$CuSO_4(s) + 5H_2O(I) \rightarrow CuSO_4.5H_5O(s)$	
$NaHCO_3(s) + H^+(aq) \rightarrow Na^+(aq) + CO_2(g) + H_2O(l)$	

[2]

(ii)	Explain	why t	he entropy	change	for the	first	process	is nega	itive.

(d)	Calculate t	the	standard	entropy	change,	ΔS <sup>e</sup> ,	for this	reaction.
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$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

Standard entropies, Se, in JK-1 mol-1 are given.

N <sub>2</sub>	(g)	H <sub>2</sub> (g)	NH <sub>3</sub> (g)
+1	92	+131	+193

$$\Delta S^{\bullet}$$
 ...... J K<sup>-1</sup> mol<sup>-1</sup> [2]

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

$$MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$$
  $\Delta H^{\circ} = +117 \text{ kJ mol}^{-1}$   
 $\Delta S^{\circ} = +175 \text{ J K}^{-1} \text{ mol}^{-1}$ 

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

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

9701/42/F/M/16

[2]

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(	C	(i	) [	Predict	the	sian	of	۸S <sup>e</sup>	for	this	reaction.	Explain	vour	answer.
١	•	' ''	, '	Toulot	uic	Sign	OI.	40	101	uno	reaction.	LAPIGIII	you	answer.

 $2H_2S(g) + CH_4(g) \rightleftharpoons CS_2(g) + 4H_2(g)$   $\Delta H^0 = +241 \text{ kJ mol}^{-1}$ 

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

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

(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.

\_\_\_\_\_[i

s/16/qp41

(c) (i)	$\Delta \emph{S}^{f e}$ will be positive, because more gas moles on the RHS/products	[1]
(ii)	$\Delta S^{\circ} = (\Delta H^{\circ} - \Delta G^{\circ})/T = (241 - 51)/1000 = 0.19 \text{ OR } 190 \text{ kJ mol}^{-1} \text{ K}^{-1} \text{ OR J mol}^{-1} \text{ K}^{-1}$	[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 14

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

$$Cd^{2+}(aq) + 4CH_3NH_2(aq) \rightleftharpoons [Cd(CH_3NH_2)_4]^{2+}(aq)$$
  $K_{stab} = 3.6 \times 10^6$  equilibrium I  $Cd^{2+}(aq) + 2H_2NCH_2CH_2NH_2(aq) \rightleftharpoons [Cd(H_2NCH_2CH_2NH_2)_2]^{2+}(aq)$   $K_{stab} = 4.2 \times 10^{10}$  equilibrium II

(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	ΔH° /kJ mol⁻¹	∆G°/kJ mol⁻¹	ΔS°/JK-1mol-1
I	-57.3	-37.4	-66.8
II	-56.5	-60.7	to be calculated

(1)	Suggest a reason why the $\Delta H^*$ values for the two equilibria are very similar.	
(ii)	Calculate A Se for equilibrium II	[1]
(ii)	Calculate $\Delta S^{\circ}$ for equilibrium II. $\Delta S^{\circ} = \dots $	-1 [1]
		1.1
(iii)	Suggest a reason for the difference between the $\Delta S^{\circ}$ you have calculated for equilibrand that for equilibrium I given in the table.	ium <b>II</b>
		[1]
		[1]
(iv) \	Which of the two complexes is the more stable? Give a reason for your answer.	
		[1]
S/16/qp	42	
(b) (i)	(each complex is formed by) making (4 ×)N-Cd bonds and breaking (6 ×) O-Cd bonds	1
(2) (1)	or same number of bonds forming/breaking  or same number of bonds forming/breaking	
(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 $[Cd(H_2NCH_2CH_2NH_2)_2]^{2+}$ / equilibrium 2 complex (is more stable) because: either $K_{\text{stab}}$ is greater or $\Delta G^{\bullet}$ is more negative.	1
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(c) (i	i) Predict the sign of ΔS° for this reaction. Explain your answer.	
	$2H_2S(g) + CH_4(g) \rightleftharpoons CS_2(g) + 4H_2(g)$ $\Delta H^0 = +241 \text{ kJ mol}$	-1
		[1]
Т	The free energy change, $\Delta G^{\circ}$ , for this reaction at 1000 K is +51 kJ mol <sup>-1</sup> .	
(ii	) Calculate the value of $\Delta S^{\circ}$ for this reaction, stating its units.	>
	$\Delta S^{\circ}$ =	[2] ge as
		[2]
 S/16/qr	043	[-]
(c) (i)	$\Delta S^{\bullet}$ will be positive, because more gas moles on the RHS/products	[1]
(ii)	$\Delta S^{\circ} = (\Delta H^{\circ} - \Delta G^{\circ})/T = (241 - 51)/1000 = 0.19 \text{ OR } 190 \text{ kJ mol}^{-1} \text{K}^{-1} \text{ OR J mol}^{-1} \text{K}^{-1}$	[1] [1]
(d)	$\Delta G^{\rm e}$ will become less positive/more negative as $T$ increases,because $\Delta S^{\rm e}$ is positive (or $-T\Delta S^{\rm e}$ 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.

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

substance	Sº/JK-1 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.

#### m/17/qp42

<b>M1</b> correct use of $\Delta G = \Delta H - T\Delta S$	
<b>M2</b> $\Delta$ S = 26.9 – (32.7 + 102.5) = –108.3 J K <sup>-1</sup> mol <sup>-1</sup> <b>OR</b> –0.1083 kJ K <sup>-1</sup> mol <sup>-1</sup>	
<b>M3</b> $\Delta G = -602 - (298 \times (-0.1083)) = -570$	
M4 units: kJ mol⁻¹	

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( )	ue	STI	OI	n	I /

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

$$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$$
  $\Delta H^{o} = -43.6 \text{ kJ mol}^{-1}$ 

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

	0 7010 11101	. 50	. 100	. 21	.214	
(i)	What is meant by th	e term entrop	by?			
						[1]
(ii)	Calculate the standa	ard entropy ch	nange, ∆S°, fo	or this reaction	1.	
				ΔS° =		J K <sup>-1</sup> mol <sup>-1</sup> [2]
/:::\	Onlawlate the atomst	and Oilebe for a	and the second			
(iii)	Calculate the standa	ard Gibbs free	energy chan	ge, ∆G°, for tr	ils reaction at	25°C.

$$\Delta G^{e} = ..... kJ mol^{-1}$$
 [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.

3(c)(i)	(entropy is a measure/degree of the) disorder of a system/substance	1	
			1
3(c)(ii)	$\Delta S^{\alpha} = (2 \times 27) + (3 \times 214) - (90) - (3 \times 198)$ <b>OR</b> 696 - 684	1	
	$\Delta S^{e} = (+) 12 (J K^{-1} mol^{-1})$	1	2
3(c)(iii)	$\Delta G^{a} = -43.6 - (298 \times 12/1000)$	1	
	$\Delta G^{\bullet} = -47.2 \text{ (kJ mol}^{-1}\text{)}$	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,  $\Delta G^{\circ}$ . This is related to the standard enthalpy and entropy changes by the equation shown.

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

(a)	State and explain whether the following processes will lead to an increase or decrease entropy.		
	(i)	the reaction of magnesium with hydrochloric acid	
		entropy change	
		explanation	
	(ii)	solid potassium chloride dissolving in water	[1]
		entropy change	
		explanation	
(	iii)	steam condensing to water	[1]
		entropy change	

explanation ......

[1]

#### Question 19

(b) Magnesium carbonate can be decomposed.

$$MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$$
  $\Delta H^{\circ} = +117 \text{ kJ mol}^{-1}$ 

Standard entropies are shown in the table.

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

(i) Calculate ΔG<sup>o</sup> for this reaction at 298 K.
 Include a relevant sign and give your answer to three significant figures.

$$\Delta G^{\circ} = \dots kJ \, \text{mol}^{-1} \, [3]$$

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

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

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$$
  $\Delta H^e = +130 \text{ kJ mol}^{-1}$   $\Delta S^e = +316 \text{ J mol}^{-1} \text{ K}^{-1}$ 

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

w/16/qp43

3(a)(i)	(entropy) increases/is positive and H <sub>2</sub> /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)	$\Delta S^{\circ} = 26.9 + 214 - 65.7 = (+) 175.2 (\text{J K}^{-1} \text{ mol}^{-1})$	1	
	$\Delta G^{\circ} = 117 - (298 \times 175.2/1000)$ <b>OR</b> $\Delta G^{\circ} = 117000 - (298 \times 175.2)$	1	
	$\Delta G^{\circ} = +64.8 \text{ (kJ mol}^{-1}\text{)}$	1	3
3(b)(ii)	$T\Delta S$ is more positive than $\Delta H/T\Delta S$ increases/ $-T\Delta S$ more negative		
	and $\Delta G$ is negative/decrease/less positive	1	1
3(c)	use of $\Delta G = 0$ or $\underline{T\Delta S} = 1$	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  $\Delta S$ .

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

[2]

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

$$\text{CH}_3\text{CH}_2\text{OH(I)} + 3\text{O}_2(g) \rightarrow \ 2\text{CO}_2(g) + 3\text{H}_2\text{O(I)}$$

Standard entropies are shown in the table.

substance	CH <sub>3</sub> CH <sub>2</sub> OH(I)	O <sub>2</sub> (g)	CO <sub>2</sub> (g)	H <sub>2</sub> O(I)
S <sup>o</sup> , J K <sup>-1</sup> mol <sup>-1</sup>	161	205	214	70

Calculate the standard entropy change,  $\Delta S^{o}$ , for this reaction.

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

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

This reaction occurs spontaneously at low temperatures but does  ${f not}$  occur at very high temperatures. Explain why.

.....[

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

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

 $\Delta H$  = +178 kJ mol<sup>-1</sup> and  $\Delta S$  = +159 J K<sup>-1</sup> mol<sup>-1</sup>

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

[3]

[Total: 9]

#### Marking Scheme

(a)

process	sign of ∆S
$NaBr(s) + (aq) \rightarrow NaBr(aq)$	+
$H_2O(I) \rightarrow H_2O(g)$	+
$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$	-
$\begin{array}{c} CoCl_2(s) + 6H_2O(l) \rightarrow \\ CoCl_2.6H_2O(s) \end{array}$	-

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 J K<sup>-1</sup> mol<sup>-1</sup> [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)

$$T = 178000/159$$
 (1)  
 $T = 1119.5$  K units required or T>1120 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.  $H_2O(1) \rightarrow H_2O(s)$
  - 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 ( $S^{\Theta}$ ) for but-1-ene, water vapour and butan-1-ol are 310, 189 and 228 J K<sup>-1</sup> mol<sup>-1</sup> respectively. What is the standard entropy change for this reaction in J K<sup>-1</sup> mol<sup>-1</sup>?

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

(Total 1 mark)

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

	$\Delta H^{\Theta}$	$\Delta S^{m{ heta}}$
A.	-	-
B.	+	_
C.	_	+
D.	+	+

**4.** Consider the following reaction:

$$N_2(g) + 3H_2(g) \implies 2NH_3(g)$$

(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<sup>-1</sup> mol<sup>-1</sup> respectively. Calculate  $\Delta S^{\bullet}$  for the reaction and explain the sign of  $\Delta S^{\bullet}$ .

**(2)** 

(iv) Calculate  $\Delta G^{\Theta}$  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  $\Delta H^{\Theta}$  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. 
$$2H_2(g) + O_2(g) \rightarrow 2H_2O(1)$$

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

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

<b>6.</b> Consider the following reaction	6.	Consider	the	follov	wing	reaction
---	----	----------	-----	--------	------	----------

$$2CH_3OH(g) + H_2(g) \rightarrow C_2H_6(g) + 2H_2O(g) \, \square \, \, \square$$

(a)	The standard enthalpy change of formation for CH <sub>3</sub> OH(g) at 298 K is -201 kJ mol <sup>-1</sup> and	
	for $H_2O(g)$ is $-242$ kJ mol <sup>-1</sup> . 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 $CH_3OH(g)$ at 298 K is 238 J $K^{-1}$ mol <sup>-1</sup> , for $H_2(g)$ is	
	131 J K <sup>-1</sup> mol <sup>-1</sup> and for H <sub>2</sub> O(g) is 189 J K <sup>-1</sup> mol <sup>-1</sup> . 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.
	(3)
	(Total 7 marks)

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

$$2\mathrm{CO}(g) + \mathrm{O}_2(g) \to 2\mathrm{CO}_2(g)$$

	CO(g)	$O_2(g)$	CO <sub>2</sub> (g)
$S^{\Theta}/J \text{ K}^{-1} \text{ mol}^{-1}$	198	205	214

- A. –189
- B. -173
- C. +173
- D. +189

- 8. A reaction has a standard enthalpy change,  $\Delta H^{\Theta}$ , of +10.00 kJ mol<sup>-1</sup> at 298 K. The standard entropy change,  $\Delta S^{\Theta}$ , for the same reaction is +10.00 J K<sup>-1</sup> mol<sup>-1</sup>. What is the value of  $\Delta G^{\Theta}$  for the reaction in kJ mol<sup>-1</sup>?
  - A. +9.75
  - B. +7.02
  - C. –240
  - D. -2970

(Total 1 mark)

- **9.** Which reaction has the greatest increase in entropy?
  - A.  $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g) \square \square$
  - 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.  $BaCl_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2NaCl(aq)$

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  $\Delta H$ ,  $\Delta S$  and  $\Delta G$  for this reaction?

	$\Delta H$	$\Delta S$	$\Delta G$
A.	_	_	_
B.	_	+	_
C.	+	+	_
Ъ			

(Total 1 mark)

**12.** Which reaction has the greatest increase in entropy?

A. 
$$SO_2(g) + 2H_2S(g) \rightarrow 2H_2O(1) + 3S(s)$$

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

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

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

(Total 1 mark)

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

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

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

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

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

			Γ)
be hydrogenated in below to answer the		nickel catalyst to form llow.	n propane.
Compound	Formula	$\Delta H^{\Theta}_{f} / \text{kJ mol}^{-1}$	S <sup>O</sup> / J K <sup>-1</sup> mol <sup>-1</sup>
hydrogen	H <sub>2</sub> (g)	0	+ 131
propane	$C_3H_8(g)$	- 104	+ 270
propene	C <sub>3</sub> H <sub>6</sub> (g)	+ 20.4	+ 267
 propene ne why the value for	$C_3H_6(g)$ the standard entha	+ 20.4  alpy change of format  the hydrogenation of p	ion of hydrogen is

(iii)	Calculate the standard entropy change for the hydrogenation of propene.	
		(2)
(iv)	Determine the value of $\Delta G^{O}$ 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.	
		••
		(2)
		Total 9 marks)

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

$$C_2H_5OH(1) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$$

Compound	$\Delta G_{ m f}^{\Theta}$ / kJ mol $^{-1}$
C <sub>2</sub> H <sub>5</sub> OH(l)	-175
CO <sub>2</sub> (g)	-394
H <sub>2</sub> O(g)	-229
$O_2(g)$	0

(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

2. A [1]

**3.** D

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

1 max

4

(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;

$$(\Delta H = (N \equiv N) + 3(H - H) - 6(N - H) = 944 + 3(436) - 6(388) =) -76.0 \text{ (kJ)};$$

Allow ECF.

Do not penalize for sig. fig. or units.

Award [4] for correct final answer.

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

Allow ECF.

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

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

Do not penalize for SF.

(v) heat released when gas  $\rightarrow$  liquid;  $\Delta H^{\circ}$  becomes more negative;

2 **[12]** 

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

(b)  $\Delta S^{\Theta}_{\text{reaction}} = \Sigma S^{\Theta}(\text{products}) - \Sigma S^{\Theta}(\text{reactants})$ 

 $\mathbf{C}$ **12.** 

[1]

**13.** D

[1]

[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

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

1

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

2

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

2

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

 $= -86.3 \text{ kJ mol}^{-1}$ ;

2

Units needed for the mark.

Award [2] for correct final answer.

Allow ECF if only one error in first marking point.

 $\Delta G = \Delta H - T\Delta S = 0 / \Delta H = T\Delta S$ ;

$$T = \frac{-124.4}{-128/1000} = 972 \text{ K} / 699 \text{ °C};$$

2

Only penalize incorrect units for T and inconsistent  $\Delta S$  value once in (iv) and (v).

[9]

**16.** B [1]

17. A [1]

#### **SHOEIFFAT QUESTIONS**

### **Basic Questions**

**<u>BO 1</u>** Predict the sign of the entropy change,  $\Delta S^{\circ}$ , 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.  $\Delta S^{\circ}$  is positive.

b.  $2H(g) \rightarrow H_2(g)$ 

2 moles of gases are producing 1 mole of gas  $\Rightarrow$  disorder decreases.  $\Delta S^{\circ}$  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  $\Delta S^{\circ}$  for the reaction at 25°C. Justify your prediction.

The sign of  $\Delta S^{\circ}$  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  $\Delta S^{\circ}$  negative.

- **<u>BO 2</u>** Consider the following process:  $Zn(s) + \frac{1}{2}O_2(g) \rightarrow ZnO(s)$
- a. Calculate  $\Delta S^{\circ}$  at 298K, given the following  $S^{\circ}$  values, in J.K<sup>-1</sup> mol<sup>-1</sup>: ZnO: 44; Zn: 42; O<sub>2</sub>: 205.

$$\Delta S^{\circ} = S_{Zn0(s)}^{\circ} - S_{Zn(s)}^{\circ} - \frac{1}{2} S_{0_{2}(g)}^{\circ} = (44) - (42) - (\frac{205}{2}) = -100.5 \text{J/mol K}$$

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.

**<u>BQ 4</u>** Consider the following process:  $H_2O(s) \rightarrow H_2O(l)$   $\Delta H^{\circ} = 6.03 \text{ kJ}$ 

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

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

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.

**<u>BQ 5</u>** Consider the following process:  $C_6H_6(l) \rightarrow C_6H_6(g)$ 

Given for the above process  $\Delta H^{\circ}_{Vap}$  = 30.8 kJ/mol, and  $\Delta S^{\circ}_{Vap}$  = 87.2 J/K.mol.

Calculate the boiling point of benzene.

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

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

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

- **BQ** 7 Answer the following questions about nitrogen, hydrogen, and ammonia.
- Draw the complete Lewis electron-dot diagrams for N<sub>2</sub> and NH<sub>3</sub>.

H--N--H / H - N - H / H - N - H / H + Calculate the standard free-energy change,  $\Delta G$ , that occurs when 24.0 g of H<sub>2</sub>(g) react with (b) excess  $N_2(g)$  at 298 K according to the reaction represented below.

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

RTF:  $\Delta G$ 

$$n_{H_2} = \frac{24.0}{2} = 12.0 \text{moles}$$
 $N_2(g) + 3H_2(g) \leftrightarrows 2NH_3(g)$ 
 $\Delta G^{\circ}_{298} = -34 \text{ kJ mol}^{-1}$ 
3moles
 $-34 \text{kJ}$ 
12.0 moles
$$\Delta G_{298} = \frac{12.0 (-34)}{3} = -136 \text{ kJ}$$

#### Multiple Choice

- 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
- When solid NH<sub>4</sub>SCN is mixed with solid Ba(OH)<sub>2</sub> 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

When a solid sample of NaNO<sub>3</sub> is added to a cup of water, the temperature of the resulting solution 3. 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 ⇒ reaction is endothermic ⇒ 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-]  $\Delta \mathbf{H} = \mathbf{T} \Delta \mathbf{S}$
- 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-]  $\Delta \mathbf{H} < \mathbf{0}$ ;  $\Delta \mathbf{S} < \mathbf{0}$
  - [-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.
- **SO2** 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.