

Question Number	Acceptable Answers	Reject	Mark
1 (a)	$\Delta S_{\text{system}} = (3 \times 2 \times 65.3 + 197.6) - (186.2 + 188.7)$ <p>Correct data for CH<sub>4</sub> and CO (186.2 and 197.6) (1)</p> <p>= (+) 214.5 / 215 (J mol<sup>-1</sup> K<sup>-1</sup>) / (+) 0.2145 / 0.215 kJ (mol<sup>-1</sup> K<sup>-1</sup>) (1)</p> <p>Units must be shown if data has been converted to kJ</p> <p>Full marks (2) for correct answer without working Ignore sf except 1</p> <p>Answer of -214.5 scores (1)</p> <p>Answer of +18.6 if entropy of H not doubled scores (1)</p> <p>Answer of -46.7 if entropy of H<sub>2</sub> not tripled scores (1)</p> <p>ALLOW TE in second mark for minor error in data e.g. writing 63.5 instead of 65.3. No TE if data used is not entropy of compounds.</p>	<p>214 0.214</p>	2

Question Number	Acceptable Answers	Reject	Mark
1 (b)	$(\Delta S_{\text{surroundings}}) = \frac{-\Delta H}{T}$ <p>Expression or use of expression, <math>\frac{-206.1 \times (1000)}{298}</math> (1)</p> <p>= -691.6 J (mol<sup>-1</sup> K<sup>-1</sup>) / -0.6916 kJ (mol<sup>-1</sup> K<sup>-1</sup>) (1)</p> <p>Ignore sf except 1</p>		2

Question Number	Acceptable Answers	Reject	Mark
1 (c)	<p><math>\Delta S_{\text{total}} = (214.5 + (-691.6)) = -477.1 \text{ (J mol}^{-1} \text{ K}^{-1}) / -0.4771 \text{ (kJ mol}^{-1} \text{ K}^{-1}) \text{ (1)}</math></p> <p>ALLOW TE for answer to (a) plus answer to (b). If 214.5 is added to -0.69 no TE unless -0.69 is specified to be in joules. Ignore sf except 1</p> <p>Negative / less than zero (so not spontaneous) / would be positive if spontaneous. (1)</p> <p>ALLOW "feasible" for spontaneous.</p> <p>If answer to calculation is positive, accept comment that it would be expected to be negative if not spontaneous</p>	<p>Addition of value in J to specified value in kJ</p> <p>Comments on kinetic stability</p>	2

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*1 (d) (i)	<p><math>K_p = \frac{(p_{H_2})^3 \times (p_{CO})}{(p_{CH_4})(p_{H_2O})}</math> (1)</p> <p>4 Correct partial pressures (3)</p> <table border="1" data-bbox="320 456 786 631"> <tr> <td></td> <td>CH<sub>4</sub></td> <td>H<sub>2</sub>O</td> <td>CO</td> <td>H<sub>2</sub></td> </tr> <tr> <td>pp</td> <td>0.25</td> <td>0.25</td> <td>0.375</td> <td>1.125</td> </tr> </table> <p>ALLOW partial pressures as fractions</p> <p><math>K_p = \frac{(1.125)^3 \times (0.375)}{(0.25)(0.25)} = 8.54 \text{ atm}^2</math></p> <p>value of <math>K_p</math> (1)</p> <p>unit (1) (Stand alone mark)</p> <p>Correct calculation without working scores the 5 calculation marks.</p> <p>TE from <math>K_p</math> expression if inverted Ignore sf except 1</p> <p><b>If any partial pressures are incorrect:</b> Calculating total number of moles (6.4) (1)</p> <p>Calculating mole fractions (0.125, 0.125, 0.1875, 0.5625 if total number of moles is correct) (1)</p> <p>Multiplying mole fractions by total pressure (x 2 atm) (1)</p> <p>value of <math>K_p</math> (1)</p> <p>unit (1) (stand alone mark)</p> <p>ALLOW TE in value of <math>K_p</math> only from incorrect partial pressures, not using values in question as not using equilibrium moles</p> <p>If treated as a <math>K_c</math> calculation following <math>K_p</math> expression : <math>K_p</math> expression (1) units <math>\text{atm}^2</math> (1)</p> <p>Max. mark (2)</p>		CH <sub>4</sub>	H <sub>2</sub> O	CO	H <sub>2</sub>	pp	0.25	0.25	0.375	1.125	<p>Square brackets</p> <p>TE for <math>K_p</math> expression with addition, not multiplication</p>	<p>6</p>
	CH <sub>4</sub>	H <sub>2</sub> O	CO	H <sub>2</sub>									
pp	0.25	0.25	0.375	1.125									

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1 (d) (ii)	$\Delta S_{\text{total}} = (8.31 \ln 8.54) = (+)17.8 \text{ (J mol}^{-1} \text{ K}^{-1}\text{)}$ Accept any value that rounds to 17.8  TE from value in (i)  $K_p$ value of 87.48 (obtained by treating calculation in (i) as $K_c$ ) gives $\Delta S_{\text{total}} = 37.16 / 37.12$		1

Question Number	Acceptable Answers	Reject	Mark
1 (d) (iii)	$17.8 = 225 - \frac{206.1 \times 1000}{T} \quad (1)$ $T = \frac{(206.1 \times 1000)}{207.2} = 995 / 990 \text{ (K)} \quad (1)$  Correct answer with no working shown scores 2 Correct method with wrong answer or missing $10^3$ scores 1  TE from (ii) $K_p$ value of 87.48 gives $T = 1097$  <b>OR</b>  If $\Delta S_{\text{total}}$ is taken as zero $0 = 225 - \frac{206.1 \times 1000}{T} \quad (1)$ $T = 916\text{K} \quad (1)$  $K_p$ value of 87.48 gives $T = 916$  Ignore sf except 1		2



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2 (a)	$\Delta S^{\circ}_{\text{total}}$ is positive / $\Delta S^{\circ}_{\text{total}} > 0$ with or without superscript  <b>NOTE: This mark may be awarded from answer to Q25(b)(v)</b>  <b>Accept</b> $\Delta G^{\circ}$ is negative	<b>Just</b> “the entropy is positive”	<b>1</b>

Question Number	Acceptable Answers	Reject	Mark
2 (b)(i)	(+ )27.3 and (+ )87.4 (J mol <sup>-1</sup> K <sup>-1</sup> )  <i>IGNORE</i> incorrect units		<b>1</b>

Question Number	Acceptable Answers	Reject	Mark
2 (b)(ii)	$\Delta S^{\circ}_{\text{sys}} = (2 \times 87.4) - \{(4 \times 27.3 + (3 \times 205.0))\}$ (1) = -549.4 / -549 (J mol <sup>-1</sup> K <sup>-1</sup> ) (1) Correct answer with or without correct units (2) <i>IGNORE any wrong units</i>  <b>Accept</b> TE from (b)(i)  <b>NOTE:</b> +549/ +549.4 scores (1)  <b>Check working</b>  <b>NOTE:</b> 1 <sup>st</sup> mark: for x2, x4 and x3 2 <sup>nd</sup> mark: for (products - reactants), with correct arithmetic		<b>2</b>

Question Number	Acceptable Answers	Reject	Mark
2 (b)(iii)	$\Delta S_{\text{surr}} = -\frac{\Delta H}{T}$ $= -(-1648 \times 10^3) \div 298(.15) \text{ (J mol}^{-1} \text{ K}^{-1}\text{)}$ $= (+) 5530 \text{ (J mol}^{-1} \text{ K}^{-1}\text{)}$ OR $= (+) 5.53 \text{ kJ mol}^{-1} \text{ K}^{-1} \quad (1)$ <b>NOTES:</b> <ul style="list-style-type: none"> <li>• Correct answer, with or without working, scores <span style="float: right;">(1)</span></li> <li>• If 5530 (J mol<sup>-1</sup> K<sup>-1</sup>) given, <b>IGNORE</b> any subsequent incorrect attempts to convert it to a value in kJ mol<sup>-1</sup> K<sup>-1</sup></li> </ul> <i>IGNORE</i> s.f. except one s.f.	<b>Just (+)5.53 with no units OR (+)5.53 kJ mol<sup>-1</sup></b>	<b>1</b>

Question Number	Acceptable Answers	Reject	Mark
2 (b)(iv)	$\Delta S_{\text{total}} = (-549.4) + (+5530)$ $= +4980.6 / + 4981 \text{ J mol}^{-1} \text{ K}^{-1}$ OR $+4.981 \text{ kJ mol}^{-1} \text{ K}^{-1}$ <b>(1)</b> for value <b>(1)</b> for correct sign and units <i>IGNORE</i> s.f. except one s.f. <b>Accept TE from (b)(ii) and (b)(iii)</b>	<b>Just the formula:</b> $\Delta S_{\text{total}} = \Delta S_{\text{sys}}^{\circ} + \Delta S_{\text{surr}}$	<b>2</b>

Question Number	Acceptable Answers	Reject	Mark
2 (b)(v)	<p>(<math>\Delta S_{\text{system}}</math> is negative):</p> <p>as loss of disorder as gas <math>\rightarrow</math> solid</p> <p>OR</p> <p>more order as gas <math>\rightarrow</math> solid</p> <p>OR</p> <p>as decrease in entropy as gas <math>\rightarrow</math> solid</p> <p style="text-align: right;">(1)</p> <p>(<math>\Delta S_{\text{surr}}</math> is positive):</p> <p>(heat) energy released (increases kinetic energy and hence movement of the surrounding molecules)</p> <p style="text-align: right;">(1)</p> <p><math>\Delta S_{\text{total}}</math> is positive because <math>\Delta S_{\text{surr}}</math> is (numerically) greater than <math>\Delta S_{\text{sys}}</math></p> <p>OR</p> <p><math>\Delta S_{\text{surr}}</math> “outweighs” <math>\Delta S_{\text{sys}}</math></p> <p>OR</p> <p><math>\Delta S_{\text{surr}}</math> sufficiently large so that <math>\Delta S_{\text{total}}</math> is positive</p> <p style="text-align: right;">(1)</p>	<p><b>Just “reaction is exothermic”</b></p> <p><math>\Delta S_{\text{total}}</math> is negative <b>(0)</b> for third scoring point</p>	3