### 5.2.2 Enthalpy and Entropy

## Mark scheme - Enthalpy and Entropy



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|  |  |  |  | $\begin{aligned} & \Delta G=\Delta H-T \Delta S \\ &-16.1=-55.8 \\ & 298 \Delta S=-398 \Delta \mathrm{~S} \\ & \Delta S=-0.13322 .14765 \mathrm{kJK}^{-1} \sim 11^{7} \\ &=-133.2214765 \mathrm{Jk} \mathrm{~K}^{-1} \mathrm{nol} \\ & 372.4-(5 \times 69.9)-x=-133.221476 \mathrm{~S} \\ & x=156.121476 \mathrm{~S} \\ &=156 \end{aligned}$ $\qquad$ $\mathrm{JK}^{-1} \mathrm{~mol}^{-1}[4]$ |
| :---: | :---: | :---: | :---: | :---: |
|  |  | Total | 4 |  |
| 3 | i | Equation $\begin{aligned} & \mathrm{Ba}\left(\mathrm{NO}_{3}\right)_{2}(\mathrm{aq})+\mathrm{Na}_{2} \mathrm{SO}_{4}(\mathrm{aq}) \rightarrow \mathrm{BaSO}_{4}(\mathrm{~s}) \\ + & 2 \mathrm{NaNO}_{3}(\mathrm{aq}) \checkmark \end{aligned}$ <br> Entropy change and explanation <br> entropy decreases OR entropy change negative <br> AND <br> ( $\mathrm{BaSO}_{4}$ ) solid / ppt has less disorder / more order / fewer ways of arranging energy / less freedom / less random particles / dispersal of energy $\checkmark$ | 2 | ALLOW multiples <br> M 2 is dependent on $\mathrm{BaSO}_{4}(\mathrm{~s})$ (even if formula is incorrect -eg $\mathrm{Ba}\left(\mathrm{SO}_{4}\right)_{2}(\mathrm{~s})$ ) seen as a product in the attempted equation as long as reactants are not solid. <br> $\mathrm{BaSO}_{4}$ solid / ppt may be assumed from $\mathrm{BaSO}_{4}(\mathrm{~s})$ seen in the attempted equation. <br> Examiner's Comments <br> Candidates who correctly identified barium sulfate as a solid product tended to realise that entropy had decreased, although a significant number failed to state that this decrease in entropy was as a result of less disorder being created. |
|  | ii | Equation $1 / 2 \mathrm{I}_{2}(\mathrm{~s}) \rightarrow \mathrm{I}(\mathrm{~g}) \checkmark$ <br> state symbols required <br> Entropy change and explanation <br> entropy increases OR entropy change positive <br> AND <br> gas has more disorder / less order / more ways of arranging energy / more freedom / more random particles / more dispersal of energy $\checkmark$ | 2 | DO NOT ALLOW $\mathrm{I}_{2}(\mathrm{~s}) \rightarrow 2 \mathrm{I}(\mathrm{g})$ <br> DEPENDENT on $1 / 2 \mathrm{l}_{2}(\mathrm{~s}) \rightarrow \mathrm{l}(\mathrm{g}) \mathrm{OR}_{\mathrm{I}}(\mathrm{s})$ $\rightarrow 21(\mathrm{~g})$ <br> Examiner's Comments <br> Most candidates failed to produce a correct equation for the standard enthalpy change of atomisation of iodine. Of those who were able to produce the correct equation, a significant number failed to state that the increase in entropy was as a result of increased disorder being created. |
|  |  | Total | 4 |  |

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|  |  |  |  | (+)177.875/ Wrong cycle, no  <br> $177.88 / 177.9$ mark   <br> 178 4CO2  <br> -360.5 Used 118.5 2 marks <br> Any other number: CHECK for ECF from 1st marking point for expressions using ALL values with ONE error only e.g. one transcription error:, e.g. 395.3 for 393.5 <br> Examiner's Comments <br> The general method of determining $\Delta_{f} H(C O)$ was known to most candidates, but many examples of avoidable errors were seen. For example, transcription errors in recording $\Delta_{f} H$ values ( -393 for -393.5 and -118.5 for -1118.5). Candidates should be advised to show every step in their calculation. This would allow method marks to be applied in the absence of a correct final answer. |
| :---: | :---: | :---: | :---: | :---: |
|  |  | Total | 12 |  |
| 5 | a i | $2 \mathrm{H}_{2} \mathrm{~S}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{~S}(\mathrm{~s})+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{g}) \checkmark$ | 1 | ALLOW multiples, $\text { e.g. } 6 \mathrm{H}_{2} \mathrm{~S}(\mathrm{~g})+3 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow 6 \mathrm{~S}(\mathrm{~s})+6 \mathrm{H}_{2} \mathrm{O}(\mathrm{~g})$ |
|  | ii | FIRST, CHECK THE ANSWER ON ANSWER LINE IF answer $=3.05 \times 10^{7}(\mathrm{~g})$ award 3 marks $\qquad$ <br> volume of $\mathrm{H}_{2} \mathrm{~S}$ $\begin{aligned} & =1.50 \times 10^{8} \times 16(0) / 100=2.4(0) \times 10^{7} \mathrm{dm}^{3} \text { of } \mathrm{H}_{2} \mathrm{~S} V \\ & n\left(\mathrm{H}_{2} \mathrm{~S}\right)(=n(\mathrm{~S})) \\ & \quad 2.4(0) \times 10^{7} / 24.0 \mathrm{~mol}=1(.00) \times 10^{6} \mathrm{~mol} \checkmark \\ & \text { Mass } \mathrm{S}=1(.00) \times 10^{6} \times 95(.0) / 100 \times 32.1 \\ & =3.05 \times 10^{7}(\mathrm{~g}) \checkmark \end{aligned}$ | 3 | ALLOW ECF from incorrect volume of $\mathrm{H}_{2} \mathrm{~S}$ <br> 3 SF AND standard form required |
|  | i | FIRST, CHECK FOR A VALUE OF $\Delta$ G. <br> IF answer $=-89.96(34)\left(\mathrm{kJ} \mathrm{mol}^{-1}\right)$ <br> award 3 marks $\qquad$ <br> $\Delta S$ calculation ( 2 marks) $\Delta S=(3 \times 31.8)+(2 \times 188.7)-[(2 \times 205.7)+(248.1)]$ <br> OR $\begin{aligned} & \Delta S=472.8-659.5 \checkmark \\ & \Delta S=-186.7 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1} \mathrm{OR}-0.1867 \mathrm{~kJ} \mathrm{~mol}^{-1} \mathrm{~K}^{-1} \checkmark \end{aligned}$ | 5 |  |

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|  |  | $\Delta G$ calculation (1 mark) $\begin{aligned} & \Delta G=\Delta H-T \Delta S=-145.6-(298 \times-0.1867) \\ & =-89.96(34)\left(\mathrm{kJ} \mathrm{~mol}^{-1}\right) \checkmark \end{aligned}$ <br> Comment (1 mark)- sign shows the (forward) reaction is feasible $\sqrt{ }$ <br> Temperature at which feasibility changes (1 mark) $T=\frac{\Delta H}{\Delta S}=\frac{-145.6}{-0.1867}=780 \mathrm{k}$ <br> AND comment that $\Delta G$ OR $\Delta H-T \Delta S=0 \checkmark$ |  | ALLOW (-) 187 OR 0.187 <br> ALLOW ECF from incorrect $\Delta H$ <br> ALLOW -90 up to calculator value of -89.9634 correctly rounded ORA for comment about - sign required for feasibility |
| :---: | :---: | :---: | :---: | :---: |
|  | ii | FIRST, CHECK THE ANSWER ON ANSWER LINE <br> IF answer $=-296.8\left(\mathrm{~kJ} \mathrm{~mol}^{-1}\right)$ award 2 marks $\qquad$ $\begin{aligned} & \text { Correct expression-145.6 }=(2 \times-241.8)-(2 \times-20.6 \\ & \left.+\Delta_{\mathrm{f}} \mathrm{H}(\mathrm{SO} 2)\right) \checkmark \end{aligned}$ <br> Calculation of $\Delta_{\mathrm{f}} \mathrm{H}\left(\mathrm{SO}_{2}\right)$ formation $\begin{aligned} & \Delta_{\mathrm{f}} \mathrm{H}\left(\mathrm{SO}_{2}\right)=(2 \times-241.8)-(2 \times-20.6)+145.6 \\ & =-296.8\left(\mathrm{~kJ} \mathrm{~mol}^{-1}\right) \checkmark \end{aligned}$ | 2 | ALLOW ECF <br> ALLOW 1 mark for (+)296.8 <br> Subtraction the wrong way around |
|  |  | Total | 11 |  |
| 6 | a | (enthalpy change for) 1 mole of gaseous ions OR 1 mole of hydrated ions / aqueous ions $\checkmark$ gaseous ions forming aqueous / hydrated ions $\checkmark$ | 2 | one mole can be stated just once EITHER with gaseous ions $\mathbf{O R}$ with aqueous ions, e.g. <br> - 1 mole of gaseous ions forms hydrated ions / aqueous ions <br> - Gaseous ions form 1 mole of hydrated ions / aqueous ions <br> ALLOW 1 mol for 1 mole <br> IGNORE ‘energy released’ OR ‘energy required' <br> For 2nd mark <br> IGNORE gaseous ions are hydrated IGNORE gaseous ions dissolve in water Particles formed not stated <br> ALLOW 1 mark for: 1 mole of gaseous IONS forms aqueous / hydrated atoms / particles / molecules <br> Examiner's Comments <br> This question assessed enthalpy changes in |

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|  |  | ' $2 \times$ ' is NOT required - part of calculation mark |  | - No mark for labels as C and D are combined <br> Therefore 3 max for species on energy levels provided <br> Examiner's Comments <br> This question assessed enthalpy changes in aqueous solutions. <br> Many candidates successfully completed the energy cycle to obtain all marks. Correct species and state symbols are essential in such cycles and marks could not be awarded for species such as $\mathrm{K}^{-}(\mathrm{g})$ or $\mathrm{SO}_{4}^{-}(\mathrm{g})$. Poorlyprepared candidates often scored no marks at all, having shown random species on the energy levels. Candidates are advised to ensure that the state symbols (s) and (g) are clearly distinguished. |
| :---: | :---: | :---: | :---: | :---: |
|  | ii | $\Delta H$ (hydration) $\mathrm{SO}_{4}{ }^{2-}=-1099\left(\mathrm{~kJ} \mathrm{~mol}^{-1}\right) \checkmark$ | 1 | ONLY correct answer <br> Examiner's Comments <br> This question assessed enthalpy changes in aqueous solutions. <br> Although many candidates correctly calculated the lattice enthalpy, errors were common. A common error was use of -320 (instead of $2 \times$ -320 ) giving -1419. <br> Answer $=-1099 \mathrm{~kJ} \mathrm{~mol}^{-1}$ |
| c | i | Aqueous particles are more disordered than solid (particles) <br> OR <br> Solid particles are more ordered than aqueous (particles) $\checkmark$ | 1 | For particles, ALLOW ions <br> DO NOT ALLOW molecules / atoms <br> ALLOW 'When the state changes from solid to aqueous, disorder increases' <br> For more disordered, ALLOW less ordered / more freedom / more ways of arranging energy / more random <br> For aqueous particles, ALLOW particles in solution <br> IGNORE dissolved <br> Examiner's Comments <br> This question assessed enthalpy changes in aqueous solutions. |

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|  |  |  |  | In this part, candidates needed to recognise that solid particles are forming aqueous particles with an increase in disorder. Many candidates incorrectly used 'liquid' instead of aqueous and others started from gaseous particles, perhaps confusing enthalpy change of solution with hydration. |
| :---: | :---: | :---: | :---: | :---: |
|  |  | Calculation (2 marks) <br> $\Delta G=24-(298 \times 0.225)$ OR 24-67.05 (in kJ) <br> OR 24000-(298×225) OR 24000-67050 (in J) $\checkmark$ <br> Calculation of $\boldsymbol{\Delta G}$ (IGNORE UNITS) <br> $\Delta G=-43\left(\mathrm{~kJ} \mathrm{~mol}^{-1}\right)$ OR -43000 $\left(\mathrm{J} \mathrm{mol}^{-1}\right) \checkmark$ <br> Subsumes 1st calculation mark <br> Reason for solubility <br> Calculated value of $\Delta G$ that is negative <br> AND <br> Statement that: <br> $\Delta G$ is negative $O R \Delta G<0$ OR $-43<0$ <br> OR $\Delta H-T \Delta S<0$ OR $T \Delta S>\Delta H \checkmark$ | 3 | Contact TL if solely entropy approach rather than $\boldsymbol{\Delta G}$ <br> ALLOW-43.1 OR-43.05 (calculator value) <br> ALLOW 1 calculation mark (IGNORE units) for <br> -67.(026) OR -67026 ECF from 225 instead of 0.225 <br> 18.(375) OR +18.375 ECF from 25 instead of 298 <br> ALLOW other ECF from ONE error in 1st step of calc, e.g. incorrect value for $\Delta H$ such as -1099 from 3bii $\rightarrow-1166.05$ <br> TAKE CARE that same units used for $\Delta H$ and $\Delta S$ <br> NO reason mark from a +ve value of $\Delta G$ <br> Examiner's Comments <br> This question assessed enthalpy changes in aqueous solutions. <br> The majority of candidates recognised that the Gibbs' equation was required. Usually the correct enthalpy change of $+24 \mathrm{~kJ} \mathrm{~mol}^{-1}$ was used to obtain a negative value for $\Delta G$. The majority then went on to link the negative value to feasibility for the dissolving process. A significant number of candidates used the wrong enthalpy change (or no enthalpy change at all) or mixed units of $J$ and kJ . <br> Answer: $\Delta G=-43 \mathrm{~kJ} \mathrm{~mol}^{-1}$ |
|  |  | Total | 12 |  |
| 7 |  | $5 \mathrm{~mol} /$ molecules (of gas) forms $3 \mathrm{~mol} /$ molecules (of gas) $\checkmark$ | 1 | ALLOW reaction forms fewer moles / molecules IF stated, numbers of molecules MUST be correct <br> IGNORE comments related to $\Delta G$ <br> OR disorder (even if wrong) |

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|  |  |  |  | 1427 K and therefore $1154^{\circ} \mathrm{C}$ is the temperature at which $\Delta G$ has a value of $0 \mathrm{~kJ} \mathrm{~mol}^{-1}$. Although most candidates were successful here, many weaker candidates seemed unaware of what to do. It was then common to see random numbers being used and ${ }^{\circ} \mathrm{C}$, instead of K , in the $\Delta G$ expression (much more common than in (iii). The best candidates also identified that the reaction becomes unfeasible above $1147^{\circ} \mathrm{C}$. <br> The explanation was marked consequentially of the sign obtained in (iii). |
| :---: | :---: | :---: | :---: | :---: |
|  |  | Total | 8 |  |
| 8 | a i | (entropy) decreases <br> AND <br> (solid / ice has) less disorder / more order / fewer ways of arranging energy / less freedom / less random molecules $\checkmark$ | 1 | ORA decreases and reason required for mark <br> ASSUME change is for freezing of water unless otherwise stated <br> DO NOT ALLOW atoms are more ordered <br> Examiner's Comments <br> This part was usually answered, the best responses linking the state change from liquid to solid with increased order and a decrease in entropy. |
|  | ii | (entropy) increases <br> AND <br> $\left(\mathrm{CO}_{2}\right)$ gas is formed $\checkmark$ <br> Could be from equation with $\mathrm{CO}_{2}(\mathrm{~g})$ | 1 | increases and reason required for mark <br> ASSUME gas is $\mathrm{CO}_{2}$ unless otherwise stated BUT DO NOT ALLOW an incorrect gas (e.g. $\mathrm{H}_{2}$ ) <br> ALLOW more gas <br> Examiner's Comments <br> Candidates were expected to predict an increase in entropy from formation of a gas $\left(\mathrm{CO}^{2}\right)$. This was communicated either in text or as an equation with state symbols and both approaches were credited. |
|  | iii | entropy decreases <br> AND <br> $3 \mathrm{~mol} \mathrm{O}_{2}$ form $2 \mathrm{~mol} \mathrm{O}_{3}$ <br> OR $3 \mathrm{O}_{2} \rightarrow 2 \mathrm{O}_{3}$ <br> OR 3 mol gas form 2 mol gas $\checkmark$ | 1 | decreases and reason required for mark <br> For mol, ALLOW molecules <br> ALLOW multiples, e.g. $11 / 2 \mathrm{O}_{2} \rightarrow \mathrm{O}_{3} ; \quad \mathrm{O}_{2}+1 / 2 \mathrm{O}_{2} \rightarrow \mathrm{O}_{3}$ <br> ALLOW $\mathrm{O}_{2}+\mathrm{O} \rightarrow \mathrm{O}_{3}$ <br> Note: DO NOT ALLOW 2 mol gas forms 1 mol gas unless linked to $\mathrm{O}_{2}+\mathrm{O} \rightarrow \mathrm{O}_{3}$ <br> IGNORE reaction forms fewer moles / molecules |

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|  |  | (Minimum temperature when) $\Delta G=0 \mathrm{OR} \Delta H-T \Delta S=0$ OR <br> (For feasibility) $\Delta G=0$ OR $\Delta G<0$ OR $\Delta H-T \Delta S<0$ OR ${ }^{T=\frac{\Delta H}{\Delta S},}$ $T=\frac{115}{0.131}=878 \mathrm{~K}_{\checkmark}$ |  | ALLOW ECF from incorrect calculated value of $\Delta S$ from 2(c)(i) <br> ALLOW 878 up to calculator value of 877.862595 correctly rounded <br> Examiner's Comments <br> This part was answered correctly by almost all candidates, using the provided $\Delta H$ value and the candidate's calculated $\Delta S$ value from (c)(i). Some candidates unexpectedly converted their correct K value into ${ }^{\circ} \mathrm{C}$. The only significant error seen here was with incorrect rounding. <br> Answer: 878 K |
| :---: | :---: | :---: | :---: | :---: |
|  |  | Total | 9 |  |
| 9 |  | $\Delta H$ calculation from experiment $\begin{align*} & q=100 \times 4.18 \times 20.5 \mathrm{OR} 8569 \mathrm{~J} \text { OR } 8.569 \mathrm{~kJ}(1) \\ & \text { Amount of butan-1-ol }=\frac{0.259}{74}=3.5 \times 10^{-3} \mathrm{~mol}  \tag{1}\\ & \Delta H=-2448 \mathrm{~kJ} \mathrm{~mol}^{-1}(1) \end{align*}$ <br> $\Delta S$ calculation $\Delta S=S_{\text {products }}-S_{\text {reactants }}$ $\Delta S=(4 \times 214)+(5 \times 70)-[(228)+(6 \times 205)]$ <br> OR $\Delta S=1206-1458(1)$ $\Delta S=-252 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1} \text { OR }-0.252 \mathrm{~kJ} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}(1)$ <br> $\Delta G$ calculation $\begin{aligned} & \Delta G=\Delta H-T \Delta S \\ & \Delta G=-2448-(298 \times-0.252)(1) \\ & \Delta G=-2373\left(\mathrm{~kJ} \mathrm{~mol}^{-1}\right)(1) \end{aligned}$ | 7 | allow calculator value for $\Delta H=-2448.285714$ correctly rounded to three or more significant figures <br> mark for use of correct expression with $\Delta S$ in kJ $\mathrm{K}^{-1} \mathrm{~mol}^{-1}$ <br> allow three or more sig figs for $\Delta G$ |
|  |  | Total | 7 |  |

