



Cambridge International AS & A Level Chemistry

Candidate Name		College Name	
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CHAPTER 23

9701/4

Chemical Energetics (A Level)

2025 – 2027 syllabus

Prerequisites: Atomic Structure
Electrochemistry (AS Level)
Chemical Energetics (AS Level)

BOOKLET SUMMARY

- Lattice energy and Born-Haber cycles
- Enthalpies of solution and hydration
- Entropy change, ΔS
- Gibbs free energy change, ΔG
- Tutorial questions

INFORMATION

- This booklet (version 01) is designed by Vince Hoor © 2024.
- The PDF format of this booklet is password protected.
- The electronic copy of this booklet is available in the Google Classroom.

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Learning Outcomes

23.1 Lattice energy and Born-Haber cycles

- 1 define and use the terms:
 - (a) enthalpy change of atomisation, ΔH_{at}
 - (b) lattice energy, ΔH_{latt} (the change from gas phase ions to solid lattice)
- 2 (a) define and use the term first electron affinity, EA
 (b) explain the factors affecting the electron affinities of elements
 (c) describe and explain the trends in the electron affinities of the Group 16 and Group 17 elements
- 3 construct and use Born–Haber cycles for ionic solids (limited to +1 and +2 cations, –1 and –2 anions)
- 4 carry out calculations involving Born–Haber cycles
- 5 explain, in qualitative terms, the effect of ionic charge and of ionic radius on the numerical magnitude of a lattice energy

23.2 Enthalpies of solution and hydration

- 1 define and use the term enthalpy change with reference to hydration, ΔH_{hyd} , and solution, ΔH_{sol}
- 2 construct and use an energy cycle involving enthalpy change of solution, lattice energy and enthalpy change of hydration
- 3 carry out calculations involving the energy cycles in 23.2.2
- 4 explain, in qualitative terms, the effect of ionic charge and of ionic radius on the numerical magnitude of an enthalpy change of hydration

23.3 Entropy change, ΔS

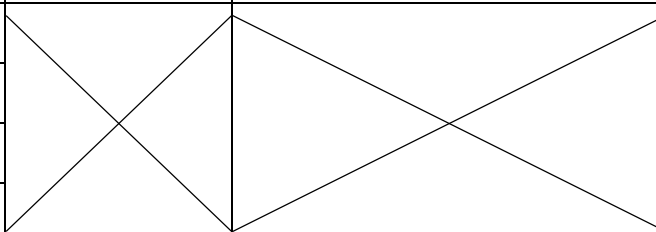
- 1 define the term entropy, S , as the number of possible arrangements of the particles and their energy in a given system
- 2 predict and explain the sign of the entropy changes that occur:
 - (a) during a change in state, e.g. melting, boiling and dissolving (and their reverse)
 - (b) during a temperature change
 - (c) during a reaction in which there is a change in the number of gaseous molecules
- 3 calculate the entropy change for a reaction, ΔS , given the standard entropies, $S^\ominus$, of the reactants and products, $\Delta S^\ominus = \sum S^\ominus(\text{products}) - \sum S^\ominus(\text{reactants})$ (use of $\Delta S^\ominus = \Delta S_{\text{surr}}^\ominus + \Delta S_{\text{sys}}^\ominus$ is not required)

23.4 Gibbs free energy change, ΔG

- 1 state and use the Gibbs equation $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$
- 2 perform calculations using the equation $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$
- 3 state whether a reaction or process will be feasible by using the sign of ΔG
- 4 predict the effect of temperature change on the feasibility of a reaction, given standard enthalpy and entropy changes

Comprehensive Notes

1 Lattice energy and Born-Haber cycles

Standard enthalpy change of atomisation, $\Delta H^\ominus_{\text{at}}$				
definition	enthalpy change when one mole of gaseous atoms is formed from its elements under standard states.			
guideline	elements under standard states (298 K, 101 kPa) $\rightarrow$ 1 mole gaseous atoms			
sign of $\Delta H^\ominus_{\text{at}}$	always endothermic (+)			
reasonings	- energy is absorbed to break covalent bonds between atoms - energy is absorbed to vaporise substance from solid / liquid to gas			
enthalpy change of atomisation of several elements				
element	equation for $\Delta H^\ominus_{\text{at}}$	$\Delta H^\ominus_{\text{at}}$ / kJ mol ⁻¹	bond energy / kJ mol ⁻¹	description
sodium	Na(s) $\rightarrow$ Na(g)	+107		
magnesium	Mg(s) $\rightarrow$ Mg(g)	+148		
zinc	Zn(s) $\rightarrow$ Zn(g)	+131		
calcium	Ca(s) $\rightarrow$ Ca(g)	+193		
oxygen	$\frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{O}(\text{g})$	+248	+496	$\frac{1}{2} \times E(\text{O}=\text{O})$
fluorine	$\frac{1}{2}\text{F}_2(\text{g}) \rightarrow \text{F}(\text{g})$	+79	+158	$\frac{1}{2} \times E(\text{F}-\text{F})$
chlorine	$\frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{Cl}(\text{g})$	+121	+242	$\frac{1}{2} \times E(\text{Cl}-\text{Cl})$
bromine	$\frac{1}{2}\text{Br}_2(\text{l}) \rightarrow \text{Br}(\text{g})$	+112	+193	$\frac{1}{2} \times \Delta H^\ominus_{\text{vap}}(\text{Br}_2) + \frac{1}{2} \times E(\text{Br}-\text{Br})$
iodine	$\frac{1}{2}\text{I}_2(\text{s}) \rightarrow \text{I}(\text{g})$	+107	+151	$\frac{1}{2} \times \Delta H^\ominus_{\text{vap}}(\text{I}_2) + \frac{1}{2} \times E(\text{I}-\text{I})$
remark	$E(\text{X}-\text{X})$: bond energy of X-X(g) (O ₂ , F ₂ , Cl ₂) : enthalpy change of atomisation is half of the bond energy (Br ₂ , I ₂) : enthalpy change of atomisation is more than half of the bond energy			

Case Study	Determine the enthalpy change of atomisation of Br		
description	chemical equation	ΔH° / kJ mol ⁻¹	
$\frac{1}{2} \times$ enthalpy change of vaporisation of $\text{Br}_2(\text{l})$	$\frac{1}{2}\text{Br}_2(\text{l}) \rightarrow \frac{1}{2}\text{Br}_2(\text{g})$	$\frac{1}{2} \times (+31.0) = +15.5$	
$\frac{1}{2} \times$ bond energy of $\text{Br}-\text{Br}(\text{g})$	$\frac{1}{2}\text{Br}_2(\text{g}) \rightarrow \text{Br(g)}$	$\frac{1}{2} \times (+193.0) = +96.5$	
enthalpy change of atomisation of Br	$\frac{1}{2}\text{Br}_2(\text{l}) \rightarrow \text{Br(g)}$	$+15.5 + (+96.5) = +112$	

Lattice energy, $\Delta H_{\text{latt}}^{\ominus}$			
definition	energy released when one mole of ionic compound is formed from its free gaseous ions (under standard conditions).		
guideline	gaseous ions $\rightarrow$ 1 mole of ionic solid		
sign of $\Delta H_{\text{latt}}^{\ominus}$ and explanation	• always exothermic (–) / negative (–), • energy is released to form electrostatic attraction between oppositely charged ions / ionic bonds.		
factors affecting $\Delta H_{\text{latt}}^{\ominus}$	• ionic radius • ionic charge (combined with the ionic radius)		
chemical equations representing $\Delta H_{\text{latt}}^{\ominus}$ and their corresponding values			
category of ions	expected range for $\Delta H_{\text{latt}}^{\ominus}$	chemical equations	$\Delta H_{\text{latt}}^{\ominus}$ / kJ mol ^{–1}
M ⁺ and X [–]	below –1000 kJ mol ^{–1}	K ⁺ (g) + Br [–] (g) $\rightarrow$ KBr(s)	–679
		Na ⁺ (g) + Cl [–] (g) $\rightarrow$ NaCl(s)	–787
M ²⁺ and X [–] M ⁺ and X ^{2–}	–2000 ~ –3000 kJ mol ^{–1}	Zn ²⁺ (g) + 2Br [–] (g) $\rightarrow$ ZnBr ₂ (s)	–2678
		2K ⁺ (g) + O ^{2–} (g) $\rightarrow$ K ₂ O(s)	–2280
M ²⁺ and X ^{2–}	–3000 ~ –4000 kJ mol ^{–1}	Fe ²⁺ (g) + O ^{2–} (g) $\rightarrow$ FeO(s)	–3915
		Zn ²⁺ (g) + O ^{2–} (g) $\rightarrow$ ZnO(s)	–3971
M ³⁺ and X [–]	–5000 ~ –7000 kJ mol ^{–1}	Al ³⁺ (g) + 3F [–] (g) $\rightarrow$ AlF ₃ (s)	–6220
M ²⁺ and X ^{3–} M ³⁺ and X ^{2–}	above –10 000 kJ mol ^{–1}	3Mg ²⁺ (g) + 2N ^{3–} (g) $\rightarrow$ Mg ₃ N ₂ (s)	–12 703
		2Al ³⁺ (g) + 3O ^{2–} (g) $\rightarrow$ Al ₂ O ₃ (s)	–15 916
factors affecting the magnitude of $\Delta H_{\text{latt}}^{\ominus}$			
factor 1	ionic radius (if two different ions have the same ionic charge)		
example	• The lattice energy of MgO is more exothermic than CaO. • Mg²⁺ has smaller ionic radius than Ca²⁺ and Mg²⁺ forms stronger ionic bond to O^{2–}.		
factor 2	ionic radius and ionic charge (if two different ions have different ionic charges)		
example	• The lattice energy of MgO is more exothermic than Na₂O. • Mg²⁺ has smaller ionic radius than Na⁺, Mg²⁺ has greater charge than Na⁺. • Mg²⁺ forms stronger ionic bond to O^{2–}.		
alternative	• The lattice energy of MgO is more exothermic than Na₂O. • The charge density of Mg²⁺ is greater than Na⁺. • Mg²⁺ forms stronger ionic bond to O^{2–}.		

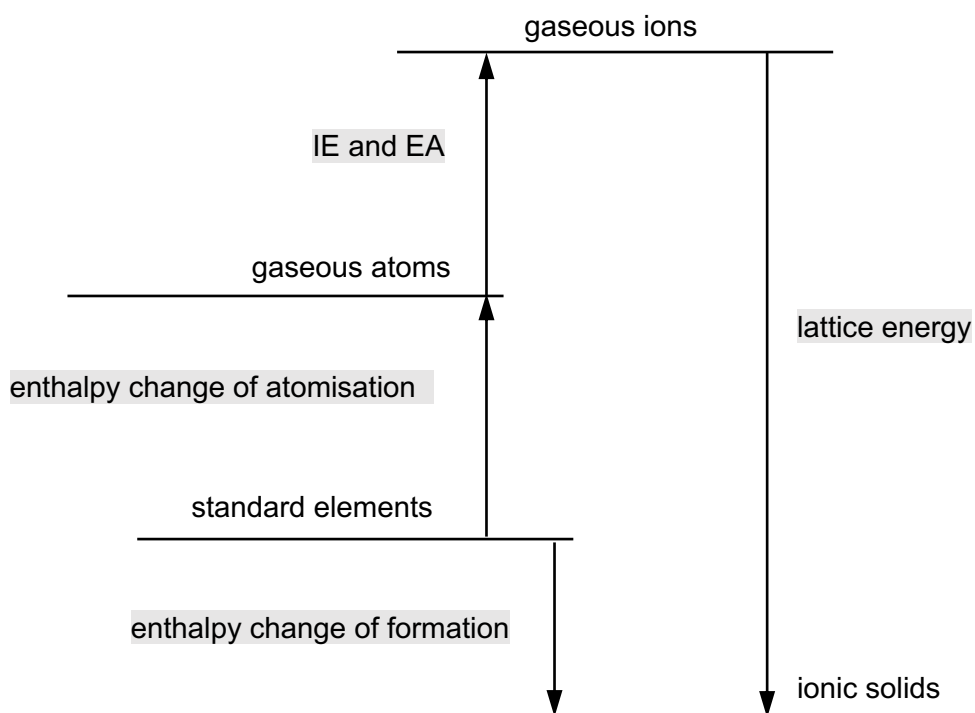
First electron affinity, EA1		
definition	energy released when an electron is added to each atom in one mole of gaseous atoms	
guideline	1 mole gaseous atoms → 1 mole gaseous anions	
sign of EA1 and explanation	• always exothermic (–) / negative (–), • energy is released to form electrostatic attraction between the nucleus and electron	
factors affecting EA1	• nuclear charge (number of protons in the nucleus) • shielding effect (due to increasing number of filled electron shells)	
chemical equations representing EA1 and their corresponding values		
element	chemical equations for EA1	first electron affinity, EA1 / kJ mol ^{–1}
oxygen	$\text{O(g)} + \text{e}^- \rightarrow \text{O}^-\text{(g)}$	–141
iodine	$\text{I(g)} + \text{e}^- \rightarrow \text{I}^-\text{(g)}$	–293
chlorine	$\text{Cl(g)} + \text{e}^- \rightarrow \text{Cl}^-\text{(g)}$	–349
factors affecting EA1 values		
trend 1	EA1 (C → F) becomes more exothermic across the Period	
reason	• there is an increasing nuclear charge across the Period • (the shielding effect remains almost constant). • there is a stronger electrostatic attraction between the nucleus and electron.	
trend 2	EA1 (Cl → I) becomes less exothermic down the Group	
reason	• there is an increasing atomic radius and increasing number of filled electron shells • leading to greater shielding effect - the electrostatic attraction between the nucleus and electron becomes weaker.	

Second electron affinity, EA2		
sign of EA2 and explanation	always endothermic (+) / positive (+), - energy is taken in to overcome repulsion between the anion and electron	
element	chemical equations for EA2	second electron affinity, EA2 / kJ mol ^{–1}
oxygen	$\text{O}^-\text{(g)} + \text{e}^- \rightarrow \text{O}^{2-}\text{(g)}$	+798
sulfur	$\text{S}^-\text{(g)} + \text{e}^- \rightarrow \text{S}^{2-}\text{(g)}$	+532
remark	- only ions with ionic charges 2– or more can have EA2. - similar sign applies for subsequent EA.	

(d) Born-Haber cycle

route 1	enthalpy change of formation of ionic solid from its standard elements
route 2	sum of enthalpy changes of atomisations (including bond energies), total ionisation energies (IE1 , IE2 ...), electron affinities (EA1 , EA2 , ...) and lattice energy
Hess' Law	total energy of route 1 = total energy of route 2

General diagram of Born-Haber cycle



Information needed to construct a Born-Haber cycle of LiF

	energy change	corresponding equations
route 1	enthalpy change of formation of LiF(s), $\Delta H_f^\ominus$ of LiF(s)	$\text{Li(s)} + \frac{1}{2}\text{F}_2\text{(g)} \rightarrow \text{LiF(s)}$
route 2	enthalpy change of atomisation of Li, $\Delta H_{\text{at}}^\ominus$ of Li	$\text{Li(s)} \rightarrow \text{Li(g)}$
	enthalpy change of atomisation of F, $\Delta H_{\text{at}}^\ominus$ of F	$\frac{1}{2}\text{F}_2\text{(g)} \rightarrow \text{F(g)}$
	first ionisation energy of Li(g), IE1	$\text{Li(g)} \rightarrow \text{Li}^+\text{(g)} + \text{e}^-$
	electron affinity of F(g), EA	$\text{F(g)} + \text{e}^- \rightarrow \text{F}^-\text{(g)}$
	lattice energy of LiF(s), $\Delta H_{\text{latt}}^\ominus$ of LiF(s)	$\text{Li}^+\text{(g)} + \text{F}^-\text{(g)} \rightarrow \text{LiF(s)}$

Case Study 1	Born-Haber cycle of sodium fluoride, NaF	
enthalpy change		value / kJ mol^{-1}
F–F bond energy (diatomic molecule)		+158
first ionisation energy of sodium		+494
second ionisation energy of sodium		+4560
standard enthalpy change of atomisation, $\Delta H_{\text{at}}^{\circ}$, of sodium		+107
electron affinity of F(g)		–328
standard enthalpy change of formation, $\Delta H_{\text{f}}^{\circ}$, of sodium fluoride		–569
calculation of $\Delta H_{\text{latt}}^{\circ}(\text{NaF})$	$\Delta H_{\text{f}}^{\circ}(\text{NaF}) = \Delta H_{\text{at}}^{\circ}(\text{Na}) + \Delta H_{\text{at}}^{\circ}(\text{F}) + \text{IE1}(\text{Na}) + \text{EA}(\text{F}) + \Delta H_{\text{latt}}^{\circ}(\text{NaF})$ $-569 = (+107) + \frac{1}{2}(+158) + (+494) + (-328) + \Delta H_{\text{latt}}^{\circ}(\text{NaF})$ $\Delta H_{\text{latt}}^{\circ}(\text{NaF}) = -921 \text{ kJ mol}^{-1}$	
remark	- do not include second ionisation energy of sodium - divide bond energy of F_2 by 2 to obtain enthalpy change of atomisation of F	

Case Study 2		Born-Haber cycle of magnesium oxide	
		enthalpy change	value / kJ mol^{-1}
		standard enthalpy change of atomisation of magnesium	+148
		O–O bond energy (polyatomic molecule)	+150
		O=O bond energy (diatomic molecule)	+496
		first ionisation energy of magnesium	+736
		second ionisation energy of magnesium	+1450
		electron affinity of O (g)	–141
		electron affinity of $\text{O}^-(\text{g})$	+798
		standard enthalpy change of formation of magnesium oxide	–602
calculation of $\Delta H_{\text{latt}}^{\circ}(\text{MgO})$	$-602 = (148) + \frac{1}{2}(+496) + (736) + (1450) + (-141) + (798) + \Delta H_{\text{latt}}^{\circ}(\text{MgO})$ $\Delta H_{\text{latt}}^{\circ}(\text{MgO}) = -3841 \text{ kJ mol}^{-1}$		
remark	exclude O–O bond energy (polyatomic molecule)		

2 Enthalpies of solution and hydration

enthalpy change of solution, $\Delta H_{\text{sol}}^{\circ}$			
definition	enthalpy change when one mole of ionic solid dissolves in an excess of water to form a solution of infinite dilution		
sign of $\Delta H_{\text{sol}}^{\circ}$	either endothermic (+) or exothermic (–)		
concept	an ionic solid with highly endothermic $\Delta H_{\text{sol}}^{\circ}$ is less soluble in water at 298 K		
	an ionic solid with highly exothermic $\Delta H_{\text{sol}}^{\circ}$ is more soluble in water at 298 K		
application	- solubility of Group 2 hydroxides increases down the group. - solubility of Group 2 sulfates decreases down the group.		
example of chemical equation and the corresponding enthalpy change of solution, $\Delta H_{\text{sol}}^{\circ}$			
chemical equation	$\Delta H_{\text{sol}}^{\circ}$ / kJ mol ^{–1}	chemical equation	$\Delta H_{\text{sol}}^{\circ}$ / kJ mol ^{–1}
$\text{KI(s)} \rightarrow \text{K}^{+}(\text{aq}) + \text{I}^{-}(\text{aq})$	+11	$\text{Mg(OH)}_2(\text{s}) \rightarrow \text{Mg}^{2+}(\text{aq}) + 2\text{OH}^{-}(\text{aq})$	+3
$\text{AgCl(s)} \rightarrow \text{Ag}^{+}(\text{aq}) + \text{Cl}^{-}(\text{aq})$	+60	$\text{Ca(OH)}_2(\text{s}) \rightarrow \text{Ca}^{2+}(\text{aq}) + 2\text{OH}^{-}(\text{aq})$	–34
$\text{MgCl}_2(\text{s}) \rightarrow \text{Mg}^{2+}(\text{aq}) + 2\text{Cl}^{-}(\text{aq})$	–155	$\text{Sr(OH)}_2(\text{s}) \rightarrow \text{Sr}^{2+}(\text{aq}) + 2\text{OH}^{-}(\text{aq})$	–47
$\text{CaCl}_2(\text{s}) \rightarrow \text{Ca}^{2+}(\text{aq}) + 2\text{Cl}^{-}(\text{aq})$	–85	$\text{Ba(OH)}_2(\text{s}) \rightarrow \text{Ba}^{2+}(\text{aq}) + 2\text{OH}^{-}(\text{aq})$	–89

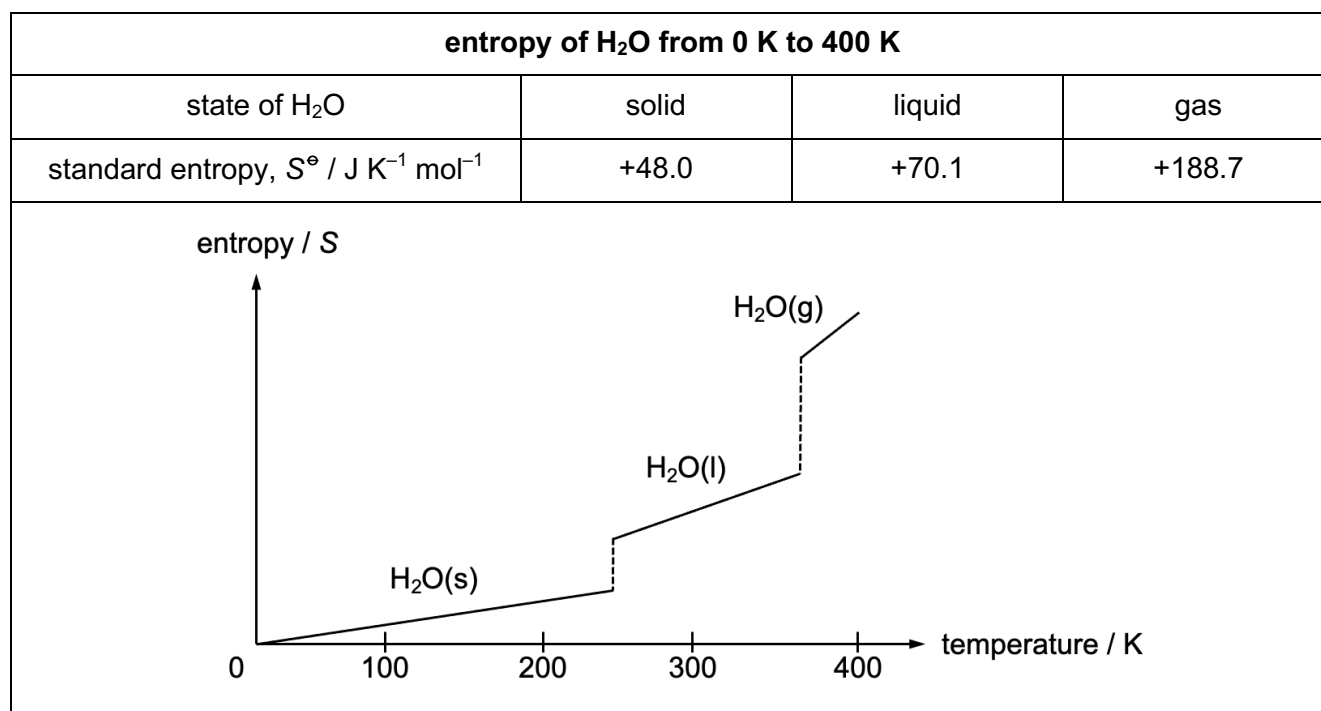
enthalpy change of hydration, $\Delta H_{\text{hyd}}^{\ominus}$			
definition	energy released when one mole of gaseous ions dissolves in an excess of water to form a solution of infinite dilution		
sign of $\Delta H_{\text{hyd}}^{\ominus}$	always exothermic (–)		
concept	a more exothermic $\Delta H_{\text{hyd}}^{\ominus}$ shows stronger ion-dipole attraction with H ₂ O molecules		
factors affecting $\Delta H_{\text{hyd}}^{\ominus}$	• ionic radius (smaller ion has stronger attraction to water molecules) • ionic charge (ion with high charge has stronger attraction to water molecules)		
example of chemical equation and the corresponding enthalpy change of hydration, $\Delta H_{\text{hyd}}^{\ominus}$			
chemical equation	$\Delta H_{\text{hyd}}^{\ominus}$ / kJ mol ^{–1}	chemical equation	$\Delta H_{\text{hyd}}^{\ominus}$ / kJ mol ^{–1}
Na ⁺ (g) → Na ⁺ (aq)	–406	Cl [–] (g) → Cl [–] (aq)	–378
Mg ²⁺ (g) → Mg ²⁺ (aq)	–1926	Br [–] (g) → Br [–] (aq)	–348
Ca ²⁺ (g) → Ca ²⁺ (aq)	–1650	I [–] (g) → I [–] (aq)	–308
explanation	• Mg²⁺ has higher ionic charge and smaller ionic radius than Na⁺, so Mg²⁺ has stronger ion-dipole attraction to water molecules. • Ca²⁺ has larger ionic radius than Mg²⁺ so Ca²⁺ forms weaker ion-dipole attraction to water molecules.		

Relationship between $\Delta H_{\text{hyd}}^{\ominus}$, $\Delta H_{\text{sol}}^{\ominus}$ and $\Delta H_{\text{latt}}^{\ominus}$		
<pre> graph TD GI[gaseous ions] -- "ΔH_latt^⊖" --> IS[ionic solid] GI -- "ΔH_hyd^⊖" --> AI[aqueous ions] IS -- "ΔH_sol^⊖" --> AI </pre>		
expression	$\Delta H_{\text{hyd}}^{\ominus} = \Delta H_{\text{sol}}^{\ominus} + \Delta H_{\text{latt}}^{\ominus}$ $\Delta H_{\text{sol}}^{\ominus} = \Delta H_{\text{hyd}}^{\ominus} - \Delta H_{\text{latt}}^{\ominus}$	
Case Study	determine the enthalpy change of hydration of chloride ion	
description		$\Delta H^{\ominus} / \text{kJ mol}^{-1}$
enthalpy change of solution of magnesium chloride		–155
enthalpy change of hydration of magnesium ion		–1926
lattice energy of magnesium chloride		–2493
<pre> graph TD GI[Mg^2+(g) + 2Cl^-(g)] -- "ΔH_latt^⊖" --> IS[MgCl2(s)] GI -- "ΔH_hyd^⊖" --> AI[Mg^2+(aq) + 2Cl^-(aq)] IS -- "ΔH_sol^⊖" --> AI </pre>		
calculation	$\Delta H_{\text{hyd}}^{\ominus} = \Delta H_{\text{sol}}^{\ominus} + \Delta H_{\text{latt}}^{\ominus}$ $-1926 + 2\Delta H_{\text{hyd}}^{\ominus}(\text{Cl}^-) = (-2493) + (-155)$ $2\Delta H_{\text{hyd}}^{\ominus}(\text{Cl}^-) = -722$ $\Delta H_{\text{hyd}}^{\ominus}(\text{Cl}^-) = -361 \text{ kJ mol}^{-1}$	

3 Standard entropy, S° and entropy change, ΔS°

(a) Definition of entropy, entropies of solid, liquid and gas

definition	entropy is the number of possible arrangements of the particles and their energy in a given system
units of S° and ΔS°	$\text{J K}^{-1} \text{mol}^{-1}$
order of entropy	gas > liquid > solid
sign of ΔS°	positive (+), entropy of the system increases
	negative (–), entropy of the system decreases
factors affect entropy values	- state symbol of substance - relative atomic / molecular / formula mass of substance - temperature of substance



entropy of other selected elements and compounds						
element	C(s)	Si(s)	Zn(l)	Br ₂ (l)	O ₂ (g)	I ₂ (g)
$S^\circ / \text{J K}^{-1} \text{mol}^{-1}$	5.7	19	50.8	152	205	261
compound	ZnO(s)	PbO(s)	H ₂ O(l)	HCl(g)	CO ₂ (g)	SiHCl ₃ (g)
$S^\circ / \text{J K}^{-1} \text{mol}^{-1}$	43.7	69	70	187	213.6	314

(b) Entropy changes of the system, ΔS

qualitative explanation (based on chemical equation)		
	if $\Delta S^\ominus$ is positive / entropy increases	if $\Delta S^\ominus$ is negative / entropy decreases
qualitative reasoning (choose one)	there is an increase in gas molecules	there is a decrease in gas molecules
	there is nett increase in moles of products (same state symbols only)	there is nett decrease moles of products (same state symbols only)
	solid dissolves to form aqueous ions	aqueous ions are used to form a solid
	temperature of the system increases	temperature of the system decreases
	any other relevant reasoning that relates to the state symbols of the substances	

Case Study	Chemical equations, entropy change and explanation		
	chemical equation	$\Delta S^\ominus$	reasoning
	$\text{Zn(s)} + 2\text{HCl(aq)} \rightarrow \text{ZnCl}_2\text{(aq)} + \text{H}_2\text{(g)}$	+	H_2 gas is produced from Zn and HCl.
	$\text{KBr(s)} \rightarrow \text{K}^+\text{(aq)} + \text{Br}^-\text{(aq)}$	+	solid dissolves to form aqueous ions
	$\text{SiO}_2\text{(s)} + 2\text{C(s)} \rightarrow \text{Si(l)} + 2\text{CO(g)}$	+	1 mol liquid, 2 mol gas formed from 3 mol solid.
	$\text{N}_2\text{(g)} + 3\text{H}_2\text{(g)} \rightarrow 2\text{NH}_3\text{(g)}$	–	there is a decrease in gas molecules
	$\text{H}_2\text{O(g)} \rightarrow \text{H}_2\text{O(l)}$	–	there is a decrease in gas molecules
	$\text{Ca(s)} + \text{F}_2\text{(g)} \rightarrow \text{CaF}_2\text{(s)}$	–	there is a decrease in gas molecules

Case Study	Compare the entropy change between two equations	
reaction 1	$\text{Ba(OH)}_2\text{(aq)} + \text{CO}_2\text{(g)} \rightarrow \text{BaCO}_3\text{(s)} + \text{H}_2\text{O(l)}$	ΔS_{r1}
reaction 2	$\text{Ba(OH)}_2\text{(aq)} + 2\text{CO}_2\text{(g)} \rightarrow \text{Ba(HCO}_3)_2\text{(aq)}$	ΔS_{r2}
Suggest with an explanation, whether equation 1 or 2 has a more negative ΔS .		
Reaction 2 will have more negative ΔS value because there are two times more the moles of CO_2 gas being consumed up as compared to reaction 1.		

quantitative calculation of entropy changes, ΔS° (based on entropy, S°)				
calculation	$\Delta S^\circ = (\text{total entropy, } S^\circ, \text{ of products}) - (\text{total entropy, } S^\circ, \text{ of reactants})$			
Case Study 1	$\text{ZnO(s)} + \text{C(s)} \rightarrow \text{Zn(l)} + \text{CO(g)}$			
substance	ZnO(s)	C(s)	Zn(l)	CO(g)
$S^\circ / \text{J K}^{-1} \text{mol}^{-1}$	43.7	5.7	50.8	197.7
calculation for ΔS°	$\Delta S^\circ = 50.8 + 197.7 - 43.7 - 5.7 = +199.1 \text{ J K}^{-1} \text{mol}^{-1}$			
Case Study 2	$\text{Si(s)} + 3\text{HCl(g)} \rightarrow \text{SiHCl}_3\text{(g)} + \text{H}_2\text{(g)}$			
substance	Si(s)	HCl(g)	SiHCl ₃ (g)	H ₂ (g)
$S^\circ / \text{J K}^{-1} \text{mol}^{-1}$	19	187	314	131
calculation for ΔS°	$\Delta S^\circ = 314 + 131 - 19 - 3(187) = -135 \text{ J K}^{-1} \text{mol}^{-1}$			

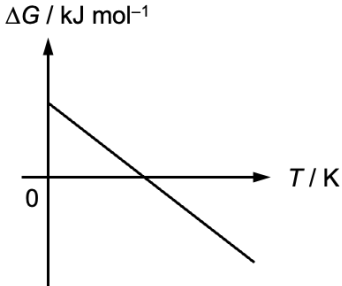
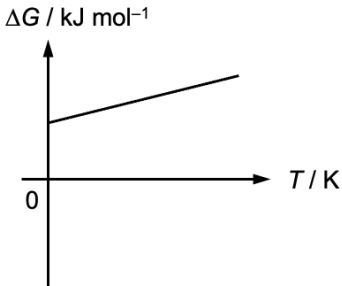
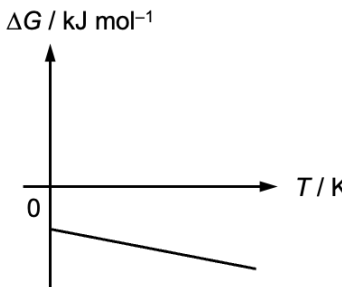
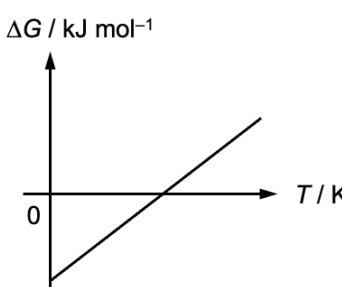
4 Gibbs free energy change, ΔG

expression	$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$		
units of ΔG°	kJ mol^{-1}		
important note	remember to convert the unit of ΔS° from $\text{J K}^{-1} \text{mol}^{-1}$ to $\text{kJ K}^{-1} \text{mol}^{-1}$		
sign of ΔG° and feasibility	- positive (+), the reaction is not feasible - negative (–), the reaction is feasible - zero (0), the reaction is in equilibrium		
example	- AgCl is insoluble in water at 298 K because ΔG is positive at 298 K. - KCl dissolves in water at 298 K because ΔG is negative at 298 K. - H₂O starts to boil at 100 °C as $\Delta G = 0$ at 100 °C		
Case Study	Calculate ΔG° for the thermal decomposition of ZnCO ₃ (s) at 298 K		
equation	$\text{ZnCO}_3\text{(s)} \rightarrow \text{ZnO(s)} + \text{CO}_2\text{(g)}$ $\Delta H_f^\circ = +71.0 \text{ kJ mol}^{-1}$		
chemical	ZnCO ₃ (s)	ZnO(s)	CO ₂ (g)
$S^\circ / \text{J K}^{-1} \text{mol}^{-1}$	82.4	43.6	213.6
$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 71.0 - (298)\left(\frac{+174.8}{1000}\right) = +18.9 \text{ kJ mol}^{-1}$			
conclusion	thermal decomposition of ZnCO ₃ is not feasible at room temperature (298 K) because ΔG° is positive.		

minimum / maximum temperature for a reaction to be feasible		
assumption	$\Delta G = 0$, so $\Delta G = \Delta H - T\Delta S = 0$	
expression	if ΔS is negative, maximum temperature, $T = \frac{\Delta H}{\Delta S}$	if ΔS is positive, minimum temperature, $T = \frac{\Delta H}{\Delta S}$
Case Study	Calculate the minimum temperature, in K, for the thermal decomposition of ZnCO_3 to be feasible.	
	$\text{ZnCO}_3(\text{s}) \rightarrow \text{ZnO}(\text{s}) + \text{CO}_2(\text{g})$ $\Delta H_f^\ominus = +71.0 \text{ kJ mol}^{-1}$, $\Delta S^\ominus = +174.8 \text{ J K}^{-1} \text{ mol}^{-1}$	
calculation	$\begin{aligned} \Delta G &= \Delta H - T\Delta S \\ 0 &= +71.0 - T \times \left(\frac{+174.8}{1000}\right) \\ T &= \frac{+71.0}{+0.1748} = 406 \text{ K} \end{aligned}$	

Case Study 1	The chemical equation for thermal decomposition of $\text{ZnCO}_3(\text{s})$ is given below.
$\text{ZnCO}_3(\text{s}) \rightarrow \text{ZnO}(\text{s}) + \text{CO}_2(\text{g})$ $\Delta H^\ominus = +71.0 \text{ kJ mol}^{-1}$ $\Delta S^\ominus = +174.8 \text{ J K}^{-1} \text{ mol}^{-1}$	
Explain the effect of increasing temperature to the spontaneity of this reaction.	
$T\Delta S^\ominus$ becomes more positive at higher temperature $\Delta G^\ominus$ becomes more negative and feasibility of the reaction increases	

Case Study 2	The chemical equation for combustion of $\text{Ca}(\text{s})$ is given below.
$2\text{Ca}(\text{s}) + \text{O}_2(\text{g}) \rightarrow 2\text{CaO}(\text{s})$ $\Delta H^\ominus = -1144 \text{ kJ mol}^{-1}$ $\Delta S^\ominus = -212 \text{ J K}^{-1} \text{ mol}^{-1}$	
Explain the effect of increasing temperature to the spontaneity of this reaction.	
$T\Delta S^\ominus$ becomes more negative at higher temperature $\Delta G^\ominus$ becomes more positive and feasibility of the reaction decreases	

feasibility of the reaction based on numerical value of ΔH° and ΔS°			
reference	$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$		
ΔH°	ΔS°	graph of ΔG° against T	ΔG° and feasibility
+	+		not feasible at low temperature, feasible at high temperature
+	-		not feasible at all temperatures
-	+		feasible at all temperatures
-	-		feasible at low temperature, not feasible at high temperature
graph information		rearrange $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ into $y = mx + c$ y-axis : Gibbs free energy change, ΔG° (kJ mol ⁻¹) x-axis : temperature, T (K) gradient of the graph, m : $-\Delta S^\circ$ (kJ K ⁻¹ mol ⁻¹)	

Tutorial Questions

Answer **all** the questions in the spaces provided.

- 1 (a) Complete Table 1.1 by placing one tick (✓) in each row to indicate the sign of each type of energy change under standard conditions.

Table 1.1

energy change	always positive	always negative	can be either negative or positive
ionisation energy			
enthalpy change of atomisation			
electron affinity			
lattice energy			
enthalpy change of hydration			
enthalpy change of solution			

[2]

- (b) (i) Define enthalpy change of atomisation.

.....

..... [1]

- (ii) Complete Table 1.2 by writing equations, including state symbols that represent the enthalpy change of atomisation.

Table 1.2

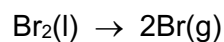
element	chemical equation representing ΔH_{at}
oxygen	
barium	
bromine	
iodine	

[2]

- (iii) Fluorine and chlorine gas have $\Delta H_{\text{at}}^{\circ}$ which are half of their bond energies. Explain why bromine and iodine usually have $\Delta H_{\text{at}}^{\circ}$ value more than half of their bond energies.

.....
 [1]

- (iv) The overall reaction for the atomization of liquid bromine molecules, $\text{Br}_2(\text{l})$, is shown.



This happens via a two-step process.

- Construct a **labelled** energy cycle to represent this atomisation process, including state symbols.
- Use your cycle and bond energy of Br–Br bond (193 kJ mol^{-1}) to calculate the enthalpy change of vaporisation of bromine, $\text{Br}_2(\text{l})$.
 The enthalpy change of atomisation of bromine, $\Delta H_{\text{at}} = +112 \text{ kJ mol}^{-1}$.

$$\Delta H_{\text{vap}} = \dots\dots\dots \text{ kJ mol}^{-1} \text{ [3]}$$

- (c) (i) Define first electron affinity, **EA1**.

.....

 [2]

- (ii) Suggest why the first electron affinity of oxygen is negative.

.....
 [1]

- (iii) Suggest why the second electron affinity of oxygen is positive.

.....
 [1]

- (iv) Write an equation for the following to represent electron affinities.
 Include state symbols.

Table 1.3

description	chemical equation representing EA
first electron affinity of chlorine	
second electron affinity of sulfur	

[1]

- (v) Describe the trend in the first electron affinity of the Group 16 elements S to Te.

Explain your answer.

.....

 [2]

- 2 (a) (i) Define lattice energy.

.....

 [2]

- (ii) Write an equation describing the lattice energy for the compounds listed in Table 2.1. Include state symbols.

Table 2.1

compound	chemical equation
magnesium oxide, MgO	
calcium iodide, CaI ₂	
potassium sulfide, K ₂ S	
sodium azide, NaN ₃	

[2]

- (b) (i) State the **two** major factors that affect the numerical magnitude of a lattice energy.

.....
 [2]

- (ii) For **each** factor you have identified in (b)(i), state whether it tends to make the lattice energy of radium sulfide more or less exothermic than that of sodium chloride.

Explain your answer.

.....

 [2]

- (iii) The lattice energies of sodium chloride, NaCl, and radium sulfide, RaS are -771 kJ mol^{-1} and $-2612 \text{ kJ mol}^{-1}$, respectively.

Identify the **dominant** factor in determining the relative numerical magnitudes of the lattice energies of radium sulfide and sodium chloride.

Explain your answer.

.....
 [1]

- (c) (i) Explain why the lattice energy of MgBr_2 is much **more** exothermic than that of SrBr_2 .

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

- (ii) Explain why the lattice energy of MgBr_2 is much **more** exothermic than that of NaBr .

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

- (iii) The lattice energy of lithium fluoride, LiF(s) , is $-1022 \text{ kJ mol}^{-1}$.

Identify the factor that causes the lattice energy of calcium oxide to be more exothermic than that of lithium fluoride. Explain why this factor causes the difference in lattice energies.

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

- (iv) Explain why the lattice energy, ΔH_{latt} , of ZnO is more exothermic than that of ZnS .

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

- (v) Suggest the trend in the magnitude of the lattice energies of the Group 1 iodides, LiI , NaI , KI .

Explain your answer.

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

- (d) Suggest the trend in the magnitude of the lattice energies of the metal nitrates, $\text{NaNO}_3(\text{s})$, $\text{Mg}(\text{NO}_3)_2(\text{s})$ and $\text{RbNO}_3(\text{s})$.

Explain your answer.

.....

most exothermic least exothermic

.....

.....

.....

.....

..... [3]

- (e) Suggest the trend in the magnitude of the lattice energies of silver compounds Ag_2S , Ag_2O and Ag_2Se .

Explain your answer.

.....

least exothermic most exothermic

.....

.....

.....

..... [2]

3 (a) The most common zinc mineral contains zinc(II) sulfate, ZnS .

(i) Complete the electrons in the boxes diagram in Fig. 3.1 to show the electronic configuration of a zinc(II) ion.



Fig. 3.1

[1]

(ii) Complete Fig. 3.2 to show the Born–Haber diagram for the ionic solid ZnS . Include state symbols of relevant species.

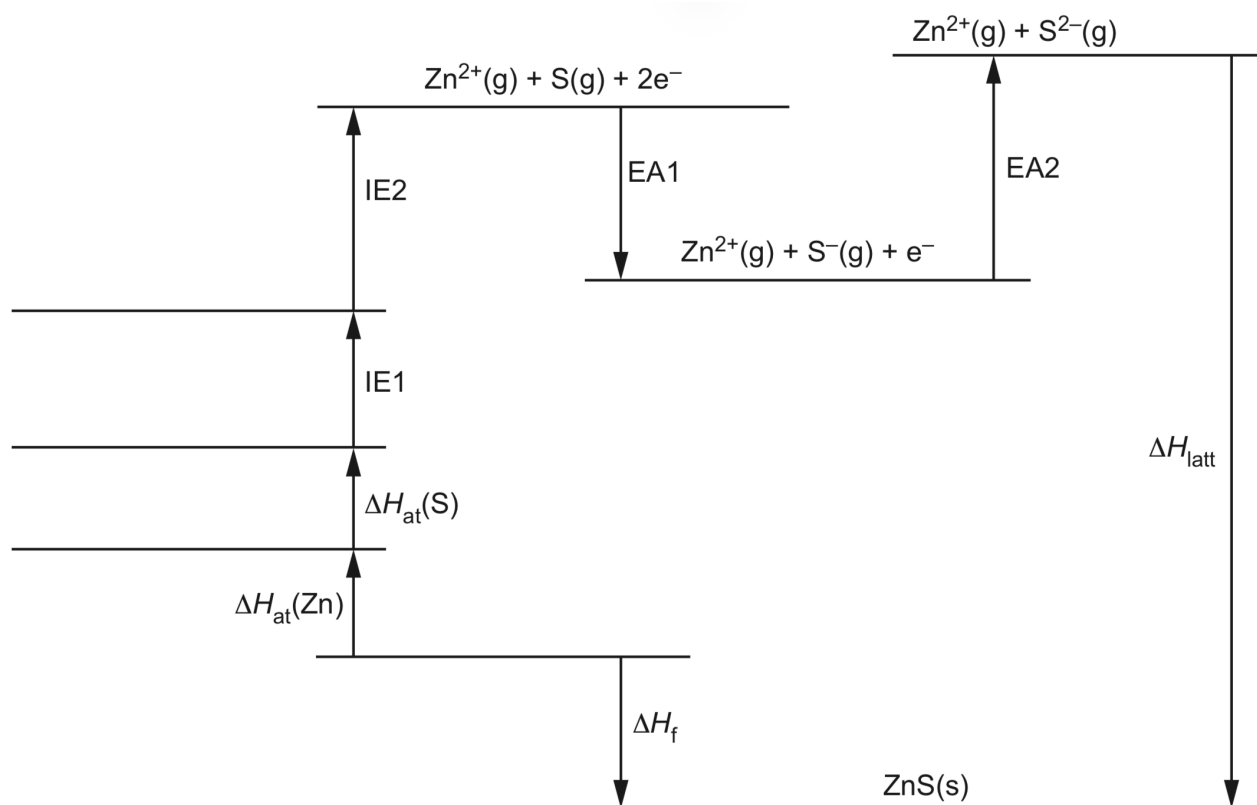


Fig. 3.2

[3]

(b) Table 3.1 shows some energy changes.

Table 3.1

energy change	value / kJ mol^{-1}
standard enthalpy change of atomisation of potassium	+89
first ionisation energy of potassium	+419
second ionisation energy of potassium	+3070
standard enthalpy change of atomisation of sulfur	+279
S–S bond energy	+265
first ionisation energy of sulfur	+1000
second ionisation energy of sulfur	+2260
first electron affinity of sulfur	–200
second electron affinity of sulfur	+640
standard enthalpy change of formation of potassium sulfide, $\text{K}_2\text{S}(\text{s})$	–381

- (i) Born-Haber cycles can be used to determine the lattice energies of ionic compounds. Complete the Born-Haber cycle in Fig. 3.3 for potassium sulfide, $\text{K}_2\text{S}(\text{s})$. Include state symbols for all of the species.

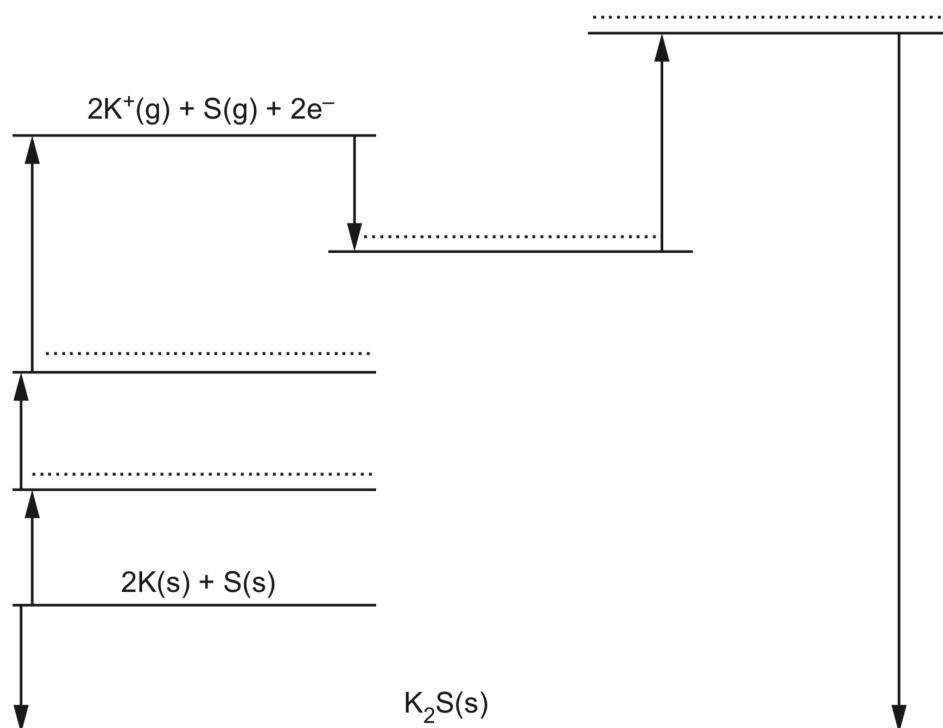


Fig. 3.3

[3]

(ii) Calculate the lattice energy, $\Delta H_{\text{latt}}^{\circ}$, of $\text{K}_2\text{S}(\text{s})$ using relevant data from Table 3.1.

Show your working.

$\Delta H_{\text{latt}}^{\circ}$ of $\text{K}_2\text{S}(\text{s}) = \dots\dots\dots \text{kJ mol}^{-1}$ [2]

(c) Use the following data in Table 3.2 calculate a value for the lattice energy of zinc chloride.

Table 3.2

energy change	value / kJ mol^{-1}
standard enthalpy change of formation of ZnCl_2	−416
standard enthalpy change of atomisation of $\text{Zn}(\text{s})$	+131
electron affinity of $\text{Cl}(\text{g})$	−349
first ionisation energy of zinc	+905
first ionisation energy of chlorine	+1260
second ionisation energy of zinc	+1730
$\text{Cl}-\text{Cl}$ bond energy (diatomic molecule)	+242

$\Delta H_{\text{latt}}^{\circ}$ of $\text{ZnCl}_2 = \dots\dots\dots \text{kJ mol}^{-1}$ [3]

(d) It is difficult to determine the lattice energy of FeO experimentally.

Use data from Table 3.3 and Born-Haber cycle in Fig. 3.4 to calculate the lattice energy, $\Delta H_{\text{latt}}^{\circ}$ of FeO(s) in kJ mol^{-1} .

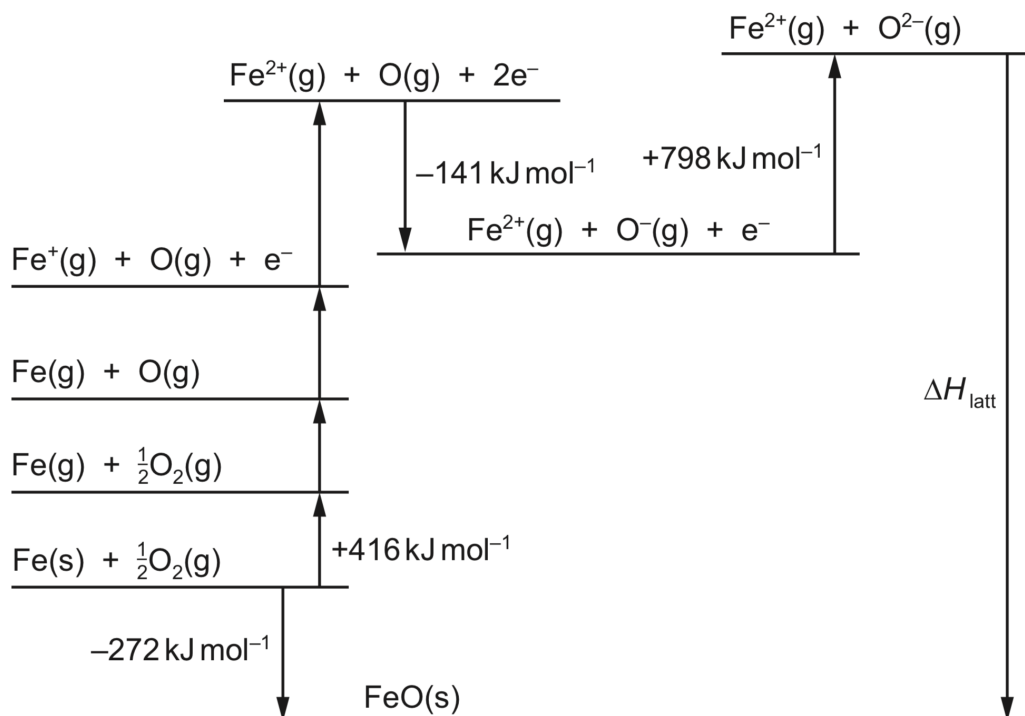


Fig. 3.4

Table 3.3

energy change	value / kJ mol^{-1}
first ionisation energy of iron	+762
second ionisation energy of iron	+1560
third ionisation energy of iron	+2960
O=O bond energy	+496
O–O bond energy	+150

$$\Delta H_{\text{latt}}^{\circ} \text{ FeO(s)} = \dots\dots\dots \text{ kJ mol}^{-1} [2]$$

- (e) (i) Use the data below in Table 3.4 to calculate the lattice energy of sodium oxide, $\Delta H_{\text{latt}}^{\circ} \text{Na}_2\text{O(s)}$.

You might find it helpful to construct an energy cycle.

Table 3.4

energy change	value / kJ mol^{-1}
standard enthalpy change of formation of sodium oxide	−416
electron affinity of O(g)	−142
standard enthalpy change of atomisation of sodium, $\Delta H_{\text{at}}^{\circ} \text{Na(s)}$	+109
electron affinity of $\text{O}^{-}(\text{g})$	+844
first ionisation energy of sodium	+494
$\text{O}=\text{O}$ bond energy (diatomic molecules)	+496
first ionisation energy of oxygen	+1310
second ionisation energy of oxygen	+3390

$$\Delta H_{\text{latt}}^{\circ} \text{Na}_2\text{O(s)} = \dots\dots\dots \text{kJ mol}^{-1} \quad [3]$$

- (iii) State how $\Delta H_{\text{latt}}^{\circ} \text{Na}_2\text{S(s)}$ differs from $\Delta H_{\text{latt}}^{\circ} \text{Na}_2\text{O(s)}$.

Indicate this by placing a tick (✓) in the appropriate box in Table 3.5.

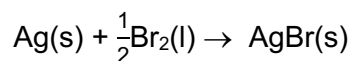
Table 3.5

$\Delta H_{\text{latt}}^{\circ} \text{Na}_2\text{S(s)}$ is more exothermic than $\Delta H_{\text{latt}}^{\circ} \text{Na}_2\text{O(s)}$	$\Delta H_{\text{latt}}^{\circ} \text{Na}_2\text{S(s)}$ is the same as $\Delta H_{\text{latt}}^{\circ} \text{Na}_2\text{O(s)}$	$\Delta H_{\text{latt}}^{\circ} \text{Na}_2\text{S(s)}$ is less exothermic than $\Delta H_{\text{latt}}^{\circ} \text{Na}_2\text{O(s)}$

Explain your answer.

.....
 [2]

- (f) Silver metal reacts with liquid bromine to form silver bromide, AgBr(s).



Use Table 3.6 to calculate a value for the lattice energy of AgBr(s).

Table 3.6

energy change	value / kJ mol ⁻¹
first ionisation energy of silver	+731
electron affinity of bromine	-325
standard enthalpy change of atomisation of silver	+285
standard enthalpy change of atomisation of bromine	+112
standard enthalpy change of formation of silver bromide	-100

$$\Delta H_{\text{latt}}^{\circ} \text{ of AgBr(s)} = \dots\dots\dots \text{ kJ mol}^{-1} \text{ [3]}$$

- (g) Magnesium reacts with excess oxygen to form magnesium oxide.

Use Table 3.7 to calculate a value of $\Delta H_{\text{f}}^{\circ}(\text{MgO})$.

Table 3.7

energy change	value / kJ mol ⁻¹
lattice energy of magnesium oxide	-3791
standard enthalpy change of atomisation of magnesium	+148
electron affinity of O(g)	-141
electron affinity of O ⁻ (g)	+798
first ionisation energy of magnesium	+736
second ionisation energy of magnesium	+1450
O=O bond energy (diatomic molecule)	+496

$$\Delta H_{\text{f}}^{\circ} (\text{MgO}) = \dots\dots\dots \text{ kJ mol}^{-1} \text{ [3]}$$

- 4 (a) Table 4.1 shows some energy changes.

Table 4.1

energy change	value / kJ mol ⁻¹
standard enthalpy change of atomisation of silver	+285
first ionisation energy of silver	+731
second ionisation energy of silver	+2074
bond energy of O=O	+496
bond energy of O—O	+150
first electron affinity of oxygen	−141
second electron affinity of oxygen	+798
first ionisation energy of oxygen	+1314
standard enthalpy change of formation of silver oxide, Ag ₂ O(s)	−31

Calculate the lattice energy, $\Delta H_{\text{latt}}^{\ominus}$, of Ag₂O(s) using relevant data from Table 4.1.

It may be helpful to draw a labelled energy cycle.

Show your working.

$$\Delta H_{\text{latt}}^{\ominus} \text{ of Ag}_2\text{O(s)} = \dots\dots\dots \text{ kJ mol}^{-1} \text{ [3]}$$

(b) Some data relating to calcium and oxygen are listed in Table 4.2.

Table 4.2

process	value / kJ mol^{-1}
first ionisation energy of oxygen	+1310
second ionisation energy of oxygen	+3390
first electron affinity of oxygen	-142
second electron affinity of oxygen	+844
enthalpy change for $\frac{1}{2}\text{O}_2(\text{g}) + 2\text{e}^- \rightarrow \text{O}^{2-}(\text{g})$	+951
enthalpy change for $\text{Ca}(\text{s}) \rightarrow \text{Ca}^{2+}(\text{g}) + 2\text{e}^-$	+1933
lattice energy of $\text{CaO}(\text{s})$	-3517

(i) Oxygen exists as O_2 molecules.

Use the data in this question to calculate a value for the bond energy of the $\text{O}=\text{O}$ bond.
Show all your working.

$\text{O}=\text{O}$ bond energy = kJ mol^{-1} [3]

(ii) Calculate the enthalpy change of formation of calcium oxide, $\text{CaO}(\text{s})$

enthalpy change of formation of $\text{CaO}(\text{s})$ = kJ mol^{-1} [2]

(c) Table 4.3 shows energy changes to be used in this question and in (c).

Table 4.3

energy change	value / kJ mol^{-1}
standard enthalpy change of atomisation of zinc	+131
first ionisation energy of zinc	+906
second ionisation energy of zinc	+1733
standard enthalpy change of formation of $\text{ZnI}_2(\text{s})$	-208
lattice energy, $\Delta H_{\text{latt}}^\circ$, of zinc iodide, $\text{ZnI}_2(\text{s})$	-2605
first ionisation energy of iodine	+1008
second ionisation energy of iodine	+1846
I-I bond energy	+151
enthalpy change of sublimation of iodine, $\text{I}_2(\text{s}) \rightarrow \text{I}_2(\text{g})$	+62

- (i) Calculate the first electron affinity for iodine. Use relevant data from Table 4.3 in your working. It may be helpful to draw a labelled energy cycle.

Show all working.

first electron affinity of iodine = kJ mol^{-1} [3]

- (ii) Predict how $\Delta H_{\text{latt}}^\circ$ of $\text{CdI}_2(\text{s})$ differs from $\Delta H_{\text{latt}}^\circ$ of $\text{ZnI}_2(\text{s})$.
Place a tick (✓) in the appropriate box in Table 4.4.

Table 4.4

$\Delta H_{\text{latt}}^\circ$ of $\text{CdI}_2(\text{s})$ is less negative than $\Delta H_{\text{latt}}^\circ$ of $\text{ZnI}_2(\text{s})$	$\Delta H_{\text{latt}}^\circ$ of $\text{CdI}_2(\text{s})$ is the same as $\Delta H_{\text{latt}}^\circ$ of $\text{ZnI}_2(\text{s})$	$\Delta H_{\text{latt}}^\circ$ of $\text{CdI}_2(\text{s})$ is more negative than $\Delta H_{\text{latt}}^\circ$ of $\text{ZnI}_2(\text{s})$

Explain your answer.

.....
 [1]

- (d) Some data relating to radium and sulfur are listed in Table 4.5. Select relevant data from this list for use in your answers.

Table 4.5

process	value / kJ mol^{-1}
enthalpy change for $\text{Ra(s)} \rightarrow \text{Ra}^{2+}(\text{g}) + 2\text{e}^{-}$	+1619
first ionisation energy of sulfur	+1000
second ionisation energy of sulfur	+2260
first electron affinity of sulfur	−200
second electron affinity of sulfur	+532
enthalpy change for $\frac{1}{8}\text{S}_8(\text{s}) + 2\text{e}^{-} \rightarrow \text{S}^{2-}(\text{g})$	+555
lattice energy of RaS(s)	−2612

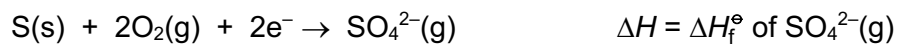
- (i) Sulfur exists as S_8 molecules in the solid state.
Use the data in this question to calculate the enthalpy change for the reaction
 $\text{S}_8(\text{s}) \rightarrow 8\text{S}(\text{g})$.

enthalpy change = kJ mol^{-1} [3]

- (ii) Calculate the standard enthalpy change of formation, $\Delta H_f^\ominus$, of radium sulfide.

standard enthalpy change, $\Delta H_f^\ominus$ = kJ mol^{-1} [2]

- (e) (i) The equation for the formation of a gaseous sulfate ion is shown.



Use relevant data from Table 4.6 in your calculations.

Table 4.6

energy change	value / kJ mol^{-1}
lattice energy of barium sulfate, $\text{BaSO}_4(\text{s})$	−2469
standard enthalpy change of formation of barium sulfate	−1473
standard enthalpy change of atomisation of barium	+180
first ionisation energy of barium	+503
second ionisation energy of barium	+965
standard enthalpy change of atomisation of sulfur	+279
standard enthalpy change for $\text{S}(\text{g}) \rightarrow \text{S}^{2-}(\text{g})$	+440
standard enthalpy change for $\text{O}(\text{g}) \rightarrow \text{O}^{2-}(\text{g})$	+657
O=O bond energy	+496

Calculate the standard enthalpy change of formation, $\Delta H_f^\ominus$, of $\text{SO}_4^{2-}(\text{g})$.
It may be helpful to draw a labelled energy cycle.

$$\Delta H_f^\ominus \text{ of } \text{SO}_4^{2-}(\text{g}) = \dots\dots\dots \text{ kJ mol}^{-1} \quad [3]$$

- (ii) Suggest how the lattice energy of $\text{BaSO}_4(\text{s})$ differs from the lattice energy of $\text{Cs}_2\text{SO}_4(\text{s})$.
Explain your answer.

.....

 [2]

5 (a) (i) Define enthalpy change of solution.

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

(ii) Write an equation that represents $\Delta H_{\text{sol}}^{\circ}$ of the magnesium chloride.
Include state symbols.

..... [1]

(iii) Solubility of Group 2 hydroxides increases down the group.
Suggest why the solubility of $\text{Ba}(\text{OH})_2$ is higher than $\text{Ca}(\text{OH})_2$.

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

(b) (i) Define enthalpy change of hydration.

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

(ii) Write an equation that represents $\Delta H_{\text{hyd}}^{\circ}$ of the F^- ion.
Include state symbols.

..... [1]

(iii) The enthalpy change of hydration of the Br^- ion is more negative than the enthalpy change of hydration of the I^- ion.
Explain why.

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

(iv) Suggest, with a chemical equation, why it is impossible to determine the enthalpy change of hydration of oxide ion, O^{2-} .

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

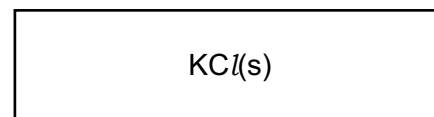
(c) Potassium chloride, KCl , and magnesium chloride, MgCl_2 , are both ionic solids.

Table 5.1

energy change	value / kJ mol^{-1}
standard enthalpy change of solution, $\Delta H_{\text{sol}}^{\ominus}$, of KCl	+15
lattice energy, $\Delta H_{\text{latt}}^{\ominus}$, of KCl(s)	–701
standard enthalpy change of hydration, $\Delta H_{\text{hyd}}^{\ominus}$, of K^+	–322
standard enthalpy change of hydration, $\Delta H_{\text{hyd}}^{\ominus}$, of Cl^-	–364
standard enthalpy change of solution, $\Delta H_{\text{sol}}^{\ominus}$, of MgCl_2	–155
lattice energy, $\Delta H_{\text{latt}}^{\ominus}$, of $\text{MgCl}_2(\text{s})$	–2493

- (i) Complete the energy cycle involving the enthalpy change of solution and the lattice energy of potassium chloride, KCl , and the relevant enthalpy changes of hydration. Label your diagram.

State symbols should be used.



[2]

- (ii) Use the data in Table 5.1 to calculate the enthalpy change of hydration of magnesium ions, Mg^{2+} . Show your working.

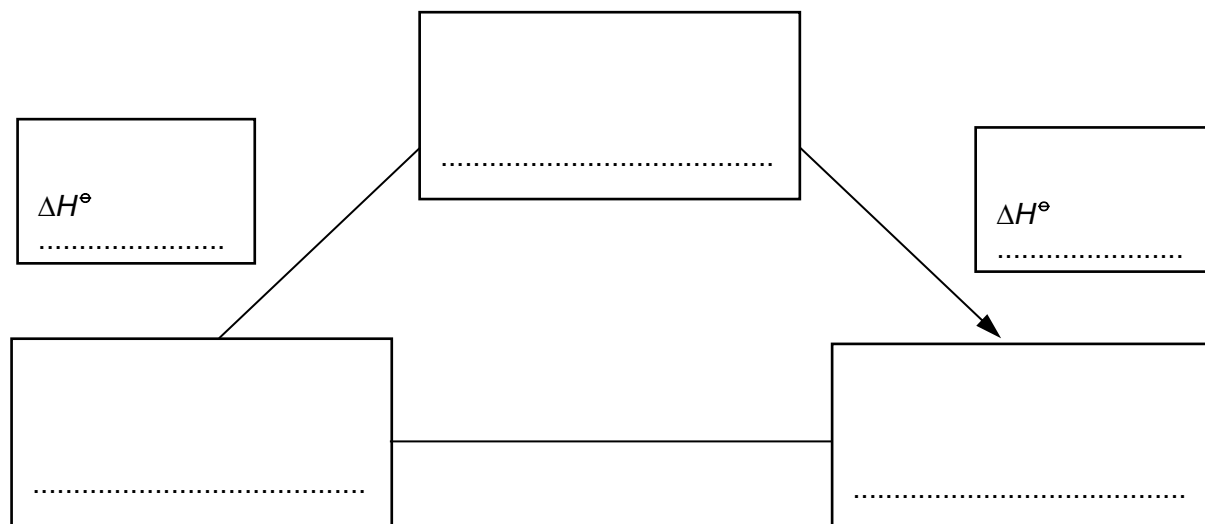
$$\Delta H_{\text{hyd}}^{\ominus}, \text{ of magnesium ions, } \text{Mg}^{2+} = \dots\dots\dots \text{ kJ mol}^{-1} \text{ [2]}$$

(d) Aluminium fluoride, AlF_3 , is an ionic solid.

(i) Complete the and label the energy cycle to show the relationship between:

- the enthalpy change of solution of AlF_3 , $\Delta H_{\text{sol}}^\ominus$
- the lattice energy of AlF_3 , $\Delta H_{\text{latt}}^\ominus$
- the enthalpy change of hydration of Al^{3+} and F^- , $\Delta H_{\text{hyd}}^\ominus$.

Include state symbols for all substances and ions.



[2]

(ii) Relevant data for this question are given.

$$\Delta H_{\text{sol}}^\ominus \text{AlF}_3 = -209 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{hyd}}^\ominus \text{Al}^{3+} = -4690 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{hyd}}^\ominus \text{F}^- = -506 \text{ kJ mol}^{-1}$$

Use these data and your energy cycle in (d)(i) to calculate the $\Delta H_{\text{latt}}^\ominus$ of AlF_3 .

$$\Delta H_{\text{latt}}^\ominus \text{ of } \text{AlF}_3 = \dots\dots\dots \text{ kJ mol}^{-1} \text{ [1]}$$

- (e) (i) Use the data in Table 5.1 to calculate the enthalpy change of solution of potassium iodide, KI.

Table 5.2

process	$\Delta H_f^\circ / \text{kJ mol}^{-1}$
$\text{K}^+(\text{g}) + \text{I}^-(\text{g}) \rightarrow \text{KI}(\text{s})$	-629
$\text{K}^+(\text{g}) \rightarrow \text{K}^+(\text{aq})$	-322
$\text{I}^-(\text{g}) \rightarrow \text{I}^-(\text{aq})$	-293

enthalpy change of solution = kJ mol^{-1} [1]

- (ii) Use the following data to calculate a value for the enthalpy change of solution of copper(II) chloride, $\text{CuCl}_2(\text{s})$. You might find it helpful to construct an energy cycle.

Table 5.3

energy change	value / kJ mol^{-1}
enthalpy change of hydration of Cl^-	-378
enthalpy change of hydration of Cu^{2+}	-2099
lattice energy of $\text{CuCl}_2(\text{s})$	-2824

enthalpy change of solution of $\text{CuCl}_2(\text{s})$ = kJ mol^{-1} [2]

6 Calcium chloride, CaCl_2 , is an ionic solid.

The values of some energy changes are shown in Table 6.1.

Table 6.1

energy change	value / kJ mol^{-1}
lattice energy, $\Delta H_{\text{latt}}^{\ominus}$, of $\text{CaCl}_2(\text{s})$	–2237
standard enthalpy change of atomisation of calcium	+193
first ionisation energy of calcium	+590
second ionisation energy of calcium	+1150
standard enthalpy change of atomisation of chlorine	+121
first electron affinity of chlorine	–364

- (a) Use the data in Table 6.1 to calculate the standard enthalpy change of formation, $\Delta H_{\text{f}}^{\ominus}$, of calcium chloride. It may be helpful to draw an energy cycle. Show all your working.

$$\Delta H_{\text{f}}^{\ominus}(\text{CaCl}_2(\text{s})) = \dots\dots\dots \text{kJ mol}^{-1} \quad [2]$$

- (b) The enthalpy change of hydration of the chloride ion can be calculated using the lattice energy of calcium chloride and the data shown in Table 6.2.

Table 6.2

energy change	value / kJ mol^{-1}
standard enthalpy change of solution of $\text{CaCl}_2(\text{s})$	–83
standard enthalpy change of hydration of $\text{Ca}^{2+}(\text{g})$	–1650
lattice energy, $\Delta H_{\text{latt}}^{\ominus}$, of $\text{CaCl}_2(\text{s})$	–2237

Calculate the standard enthalpy change of hydration of the chloride ion, $\text{Cl}^{-}(\text{g})$. It may be helpful to draw an energy cycle. Show all your working.

$$\Delta H_{\text{hyd}}^{\ominus}(\text{Cl}^{-}(\text{g})) = \dots\dots\dots \text{kJ mol}^{-1} \quad [2]$$

- (c) Three possible values for the first electron affinity of bromine are shown in Table 6.3. One of them is correct.

Place a tick by the correct value. Explain your choice.

Table 6.3

possible values	place one tick (✓) in this column
-342 kJ mol^{-1}	
-364 kJ mol^{-1}	
-386 kJ mol^{-1}	

explanation

..... [1]

- (d) The energy cycle shown in Fig. 6.1 can be used, along with suitable data, to calculate the enthalpy change of hydration of $\text{Ca}^{2+}(\text{g})$.

Each arrow indicates a transformation, **W**, **X**, **Y** and **Z**. Each transformation consists of one or more steps.

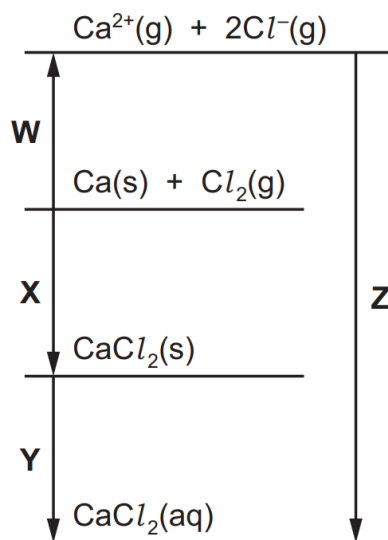


Fig. 6.1

The following data should be used.

electron affinity of $\text{Cl}(\text{g})$	$= -349 \text{ kJ mol}^{-1}$
enthalpy change of atomisation of $\text{Ca}(\text{s})$	$= +193 \text{ kJ mol}^{-1}$
first ionisation energy of $\text{Ca}(\text{g})$	$= +590 \text{ kJ mol}^{-1}$
second ionisation energy of $\text{Ca}(\text{g})$	$= +1150 \text{ kJ mol}^{-1}$
$\text{Cl}-\text{Cl}$ bond energy (diatomic molecule)	$= +242 \text{ kJ mol}^{-1}$
enthalpy change of formation of $\text{CaCl}_2(\text{s})$	$= -795 \text{ kJ mol}^{-1}$
enthalpy change of solution of $\text{CaCl}_2(\text{s})$	$= -83 \text{ kJ mol}^{-1}$
enthalpy change of hydration of $\text{Cl}^-(\text{g})$	$= -364 \text{ kJ mol}^{-1}$

- (i) Calculate the value of the enthalpy change corresponding to transformation W.
Show your working.

enthalpy change **W** = kJ mol^{-1} [2]

- (ii) Use your answer to (d)(i) and other data to calculate the value of the enthalpy change corresponding to transformation Z.

enthalpy change **Z** = kJ mol^{-1} [2]

- (iii) Use your answer to (d)(ii) to calculate the enthalpy change of hydration of $\text{Ca}^{2+}(\text{g})$.

enthalpy change of hydration of $\text{Ca}^{2+}(\text{g})$ = kJ mol^{-1} [2]

- (iv) Write an expression, in terms of **W**, **X**, **Y** and/or **Z**, to show how the enthalpy changes of two of the transformations can be used to calculate the lattice energy of $\text{CaCl}_2(\text{s})$.

lattice energy of $\text{CaCl}_2(\text{s})$ = [1]

(e) Table 6.4 shows various energy changes which can be used in the following questions.

Table 6.4

energy change	value / kJ mol ⁻¹
standard enthalpy change of atomisation of calcium	+178.2
first ionisation energy of calcium	+590
second ionisation energy of calcium	+1145
standard enthalpy change of atomisation of bromine	+111.9
Br–Br bond energy	+192.9
standard enthalpy change of solution of calcium bromide, CaBr ₂ (s)	–103.1
standard enthalpy change of formation of calcium bromide, CaBr ₂ (s)	–682.8
standard enthalpy change of hydration of Ca ²⁺	–1579
first electron affinity of bromine	–324.6
first ionisation energy of bromine	+1140

- (i) Select and use relevant data from Table 6.4 to calculate the lattice energy, $\Delta H_{\text{latt}}^{\ominus}$, of CaBr₂(s).

It may be helpful to draw a labelled energy cycle.

Show your working.

$$\Delta H_{\text{latt}}^{\ominus} \text{ of CaBr}_2(\text{s}) = \dots\dots\dots \text{ kJ mol}^{-1} \text{ [3]}$$

- (ii) Select and use relevant data from Table 6.4 and your answer to (d)(i) to calculate the standard enthalpy change of hydration, $\Delta H_{\text{hyd}}^{\ominus}$, of Br[–].

It may be helpful to draw a labelled energy cycle.

If you were not able to answer (d)(i), use –2500 kJ mol^{–1} as your value for $\Delta H_{\text{latt}}^{\ominus}$ of CaBr₂(s). This is **not** the correct value.

Show your working.

$$\Delta H_{\text{hyd}}^{\ominus} \text{ of Br}^{-} = \dots\dots\dots \text{ kJ mol}^{-1} \text{ [2]}$$

7 (a) (i) Define entropy.

.....
 [1]

(ii) Assume the entropy, S , for H_2O is zero at 0 K.

Sketch a graph on the axes in Fig. 7.1 to show how the entropy changes for H_2O between 0 K and 300 K.

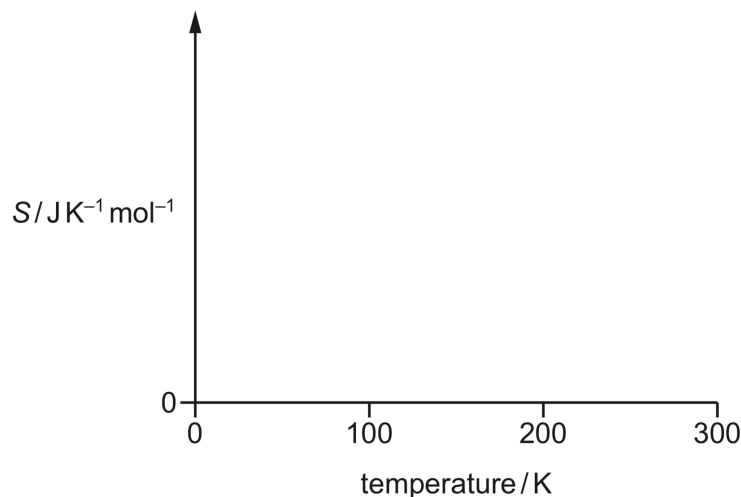


Fig. 7.1

[2]

(b) The three physical states of H_2O have different standard entropies, $S^\ominus$, associated with them. Table 7.1 shows these $S^\ominus$ values.

Table 7.1

state of H_2O	solid	liquid	gas
standard entropy, $S^\ominus / \text{J K}^{-1} \text{mol}^{-1}$	+48.0	+70.1	+188.7

(i) Explain the difference in the $S^\ominus$ values of $\text{H}_2\text{O}(\text{s})$ and $\text{H}_2\text{O}(\text{l})$.

.....
 [1]

(ii) Explain why the increase in $S^\ominus$ is **much** greater when H_2O boils than when it melts.

.....
 [1]

(c) Place one tick (✓) in each row of the table to show the sign of each entropy change, ΔS .

Table 7.2

process	ΔS is negative	ΔS is zero	ΔS is positive
NaCl dissolving in water			
water solidifying to ice			
water boiling to steam			

[2]

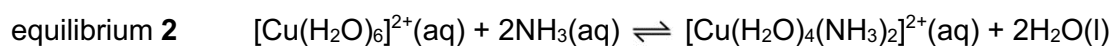
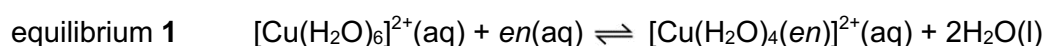
(d) Use Table 7.3 to state and explain whether the following processes will lead to an increase or decrease in entropy.

Table 7.3

description / process	sign of ΔS	reasoning
The reaction of magnesium with hydrochloric acid		
Solid potassium chloride dissolving in water		
Steam condensing to water		
$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$		

[4]

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



The standard entropy change, ΔS° , for equilibrium 1 is $+23 \text{ J K}^{-1} \text{ mol}^{-1}$ and for equilibrium 2 is $-8.4 \text{ J K}^{-1} \text{ mol}^{-1}$.

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

.....

 [1]

- 8 (a) (i) State the full term for ΔG .

..... [1]

- (ii) Give the expression for ΔG in terms of ΔH and ΔS .

..... [1]

- (iii) Use Table 8.1 to state whether ΔG for the selected process is positive, negative or zero.

Table 8.1

description / process	sign of ΔG
thermal decomposition of CaCO_3 does not occur at 298 K	
$\text{Ba}(\text{OH})_2$ is soluble in water at 298 K	
ethanol, $\text{C}_2\text{H}_5\text{OH}$ starts to boil at 351 K	

[1]

- (b) 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.

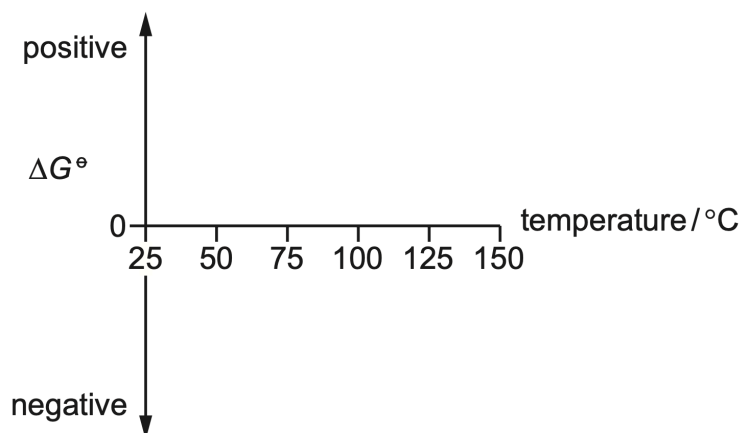
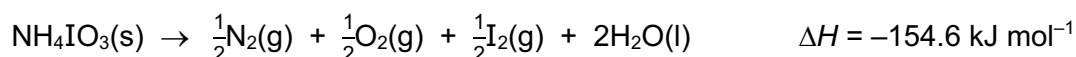


Fig. 8.1

[2]

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



- (i) Use the data in Table 8.2 to calculate the entropy change of reaction, ΔS of the decomposition of $\text{NH}_4\text{IO}_3(\text{s})$.

Table 8.2

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

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

- (ii) The reaction is feasible at all temperatures.

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

.....

 [1]

- (d) The equation for the formation of magnesium oxide from its elements is shown in Table 8.3.



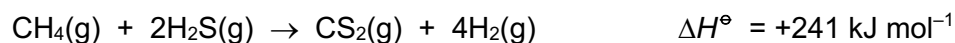
Table 8.3

substance	$\text{Mg}(\text{s})$	$\text{O}_2(\text{g})$	$\text{MgO}(\text{s})$
$S^\ominus / \text{J K}^{-1} \text{mol}^{-1}$	32.7	205	26.9

Use the equation and the data given in Table 8.3 to calculate $\Delta G^\ominus$ for the reaction at 25 °C.

$$\text{standard Gibbs free energy change, } \Delta G^\ominus = \dots\dots\dots \text{kJ mol}^{-1} \quad [3]$$

- (e) At high temperature, hydrogen sulfide, $\text{H}_2\text{S}(\text{g})$ reacts with excess methane, $\text{CH}_4(\text{g})$ to form carbon disulfide, $\text{CS}_2(\text{g})$ and hydrogen gas, $\text{H}_2(\text{g})$.



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

.....
 [2]

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

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

$$\Delta S^\circ = \dots\dots\dots \text{ units} = \dots\dots\dots [2]$$

- (f) Carbon disulfide, CS_2 is flammable and reacts readily with oxygen, as shown in reaction 1.

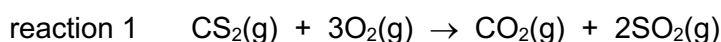


Table 8.4 shows the standard enthalpy of formation, ΔH_f° , and the standard entropy, S° , for some substances.

Table 8.4

	$\text{CS}_2(\text{g})$	$\text{O}_2(\text{g})$	$\text{CO}_2(\text{g})$	$\text{SO}_2(\text{g})$
$\Delta H_f^\circ / \text{kJ mol}^{-1}$	116.7	0.0	-393.5	-296.8
$S^\circ / \text{J K}^{-1} \text{ mol}^{-1}$	237.8	205.2	213.8	248.2

Calculate the standard Gibbs free energy change, ΔG° , in kJ mol^{-1} , for reaction 1 at 25°C .

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

- 9 (a) The energy changes for $\text{H}_2\text{O(s)} \rightarrow \text{H}_2\text{O(l)}$ are shown.

$$\Delta G = 0.00 \text{ kJ mol}^{-1}$$

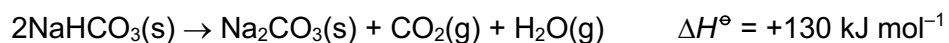
$$\Delta H = +6.03 \text{ kJ mol}^{-1}$$

$$\Delta S = +22.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

Use these data to show that the melting point of $\text{H}_2\text{O(s)}$ is 0°C .

[1]

- (b) On heating, sodium hydrogencarbonate decomposes into sodium carbonate as shown:

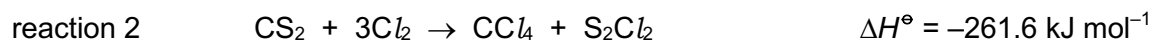


$$\Delta S^\ominus = +316 \text{ J K}^{-1} \text{ mol}^{-1}$$

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

temperature = K [2]

- (c) Carbon disulfide reacts with chlorine to form tetrachloromethane, as shown in reaction 2.



$$\Delta S^\ominus = -365.5 \text{ J K}^{-1} \text{ mol}^{-1}$$

Calculate the maximum temperature, in K, for reaction 2 to be feasible.

temperature = K [2]

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

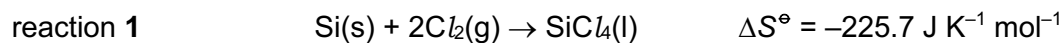


Table 9.1

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

Use relevant data in Table 9.1 to calculate the standard entropy of chlorine, $S^\ominus \text{Cl}_2(\text{g})$.
Show all your working.

standard entropy of chlorine, $S^\ominus \text{Cl}_2(\text{g}) = \dots\dots\dots \text{J K}^{-1} \text{ mol}^{-1}$ [2]

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

.....

..... [1]

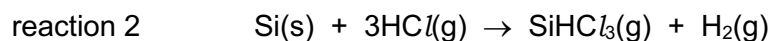
- (iii) The standard enthalpy change of formation of $\text{SiCl}_4(\text{l})$, is -640 kJ mol^{-1} .

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]

- (e) 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.



- (i) Table 9.2 shows some standard entropy data.

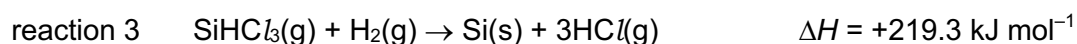
Table 9.2

substance	Si(s)	HCl(g)	SiHCl ₃ (g)	H ₂ (g)
$S^\circ / \text{J K}^{-1} \text{mol}^{-1}$	19	187	314	131

Use the data in Table 9.2 to calculate ΔS° for reaction 2.

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

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



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

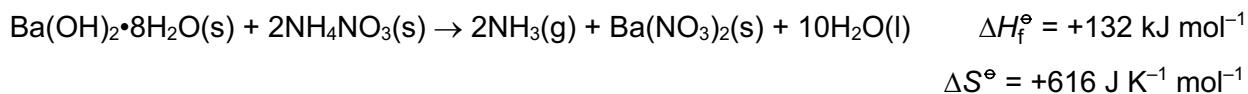
Show your working.

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

$$\text{temperature} = \dots\dots\dots \text{K} [2]$$

(f) The reaction of solid hydrated barium hydroxide, $\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$, with ammonium salts is endothermic.

(i) Calculate the minimum temperature at which the reaction of $\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$ with NH_4NO_3 becomes feasible. Show all your working.



temperature = °C [2]

(ii) Barium hydroxide reacts readily with ammonium chloride on mixing at room temperature.



Some relevant standard entropies are given in Table 9.3.

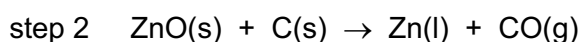
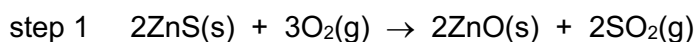
Table 9.3

substance	$\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O(s)}$	$\text{NH}_4\text{Cl(s)}$	$\text{NH}_3\text{(g)}$	$\text{BaCl}_2 \cdot 2\text{H}_2\text{O(s)}$	$\text{H}_2\text{O(l)}$
$\Delta S^\ominus / \text{J K}^{-1} \text{ mol}^{-1}$	427	95	192	203	70

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

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

(g) Zinc metal can be obtained in a two-step process as shown.



The reactions are carried out at 800 °C.

(i) Predict the sign of the entropy change, ΔS° , of the reaction in step 1.

Explain your answer.

.....
 [1]

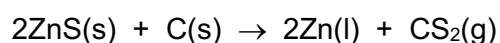
(ii) Use the data in Table 9.4 to calculate ΔS° of the reaction shown in step 2.

Table 9.4

chemical	ZnO(s)	C(s)	Zn(l)	CO(g)
$S^\circ / \text{J K}^{-1} \text{mol}^{-1}$	43.7	5.7	50.8	197.7

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

(iii) An equation for the direct reduction of ZnS by carbon is shown.



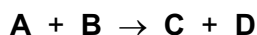
$$\begin{aligned} \Delta H^\circ &= +733 \text{ kJ mol}^{-1} \\ \Delta S^\circ &= +218 \text{ J K}^{-1} \text{mol}^{-1} \end{aligned}$$

This reaction is **not** feasible at 800 °C.

Calculate ΔG° for this reaction at 800 °C.

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

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



Deduce the signs of ΔH and ΔS for this reaction and explain why the feasibility changes with temperature

sign of ΔH = sign of ΔS =

.....

 [2]

- (b) (i) Potassium chloride is very soluble in water at 20 °C.

Explain the solubility of potassium chloride by reference to change in entropy, ΔS .

.....
 [1]

- (ii) Use the Gibbs equation and your answer to (b)(i) to predict whether potassium chloride is more soluble in water at 20 °C or at 80 °C. Explain your answer.

.....

 [1]

- (c) The standard enthalpy change of solution, $\Delta H_{\text{sol}}^{\circ}$, of $\text{AgNO}_3(\text{s})$ in water is +22.6 kJ mol⁻¹.

Suggest how the feasibility of dissolving $\text{AgNO}_3(\text{s})$ in water changes with temperature.

Explain your answer.

.....

 [2]

- (d)** Calcium fluoride, $\text{CaF}_2(\text{s})$, can be synthesised directly from its elements.

The value of $\Delta H_f^\ominus(\text{CaF}_2(\text{s}))$ is $-1214 \text{ kJ mol}^{-1}$.

- (i)** Predict the sign of the entropy change, $\Delta S^\ominus$, for this synthesis. Explain your answer.

The sign of the entropy change is

explanation

.....

[1]

- (ii)** Use the value of $\Delta H_f^\ominus(\text{CaF}_2(\text{s}))$ given in **(d)** and your answer to **(d)(i)** to predict how the feasibility for this synthesis will change with increasing temperature.

.....

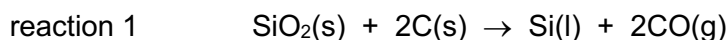
.....

.....

..... [2]

- (e)** Silicon is the second most abundant element by mass in the Earth's crust.

In industry, silicon is extracted from SiO_2 by the reaction with carbon at over 2000°C .



- (i)** Explain why the entropy change, ΔS , 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]

- 11 (a) The standard entropies, S° , of three species are given in the Table 11.1.

Table 11.1

species	$S^\circ / \text{J K}^{-1} \text{mol}^{-1}$
HCl(g)	+187
$\text{H}_2(\text{g})$	+131
$\text{Cl}_2(\text{g})$	+223

- (i) Calculate ΔS° for the reaction $2\text{HCl(g)} \rightarrow \text{H}_2(\text{g}) + \text{Cl}_2(\text{g})$

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

- (ii) ΔH° for the reaction $2\text{HCl(g)} \rightarrow \text{H}_2(\text{g}) + \text{Cl}_2(\text{g})$ is +185 kJ mol⁻¹.

Calculate ΔG° for this reaction at 298 K.

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

- (iii) Predict the effect of increasing temperature on the spontaneity of this reaction.
Explain your answer.

.....

..... [1]

(b) The standard entropies, S° , of three species are given in Table 11.2.

Table 11.2

species	$S^\circ / \text{J K}^{-1} \text{mol}^{-1}$
$\text{H}_2\text{O(l)}$	+70
$\text{H}_2\text{(g)}$	+131
$\text{O}_2\text{(g)}$	+205

(i) Calculate ΔS° for the reaction $2\text{H}_2\text{O(l)} \rightarrow 2\text{H}_2\text{(g)} + \text{O}_2\text{(g)}$

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

(ii) ΔH° for the reaction $2\text{H}_2\text{O(l)} \rightarrow 2\text{H}_2\text{(g)} + \text{O}_2\text{(g)}$ is +572 kJ mol⁻¹.

Calculate ΔG° for this reaction at 298 K.

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

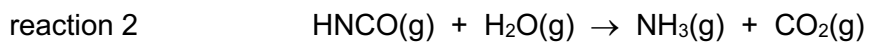
(iii) Predict the effect of increasing temperature on the spontaneity of this reaction.

Explain your answer.

.....

..... [1]

(c) Isocyanic acid reacts with water vapour to form ammonia and carbon dioxide.



Some values for standard enthalpy changes of formation, ΔH_f° , and standard entropies, S° , are given in Table 11.3.

Table 11.3

compound	$\Delta H_f^\circ / \text{kJ mol}^{-1}$	$S^\circ / \text{J K}^{-1} \text{mol}^{-1}$
HNCO(g)	−101.7	+238.2
H ₂ O(g)	−241.8	+188.8
NH ₃ (g)	−45.9	+192.8
CO ₂ (g)	−393.5	+213.8

Use the data in Table 11.3 to calculate ΔG° for **reaction 2** at 25 °C.
Show your working.

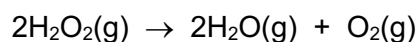
$\Delta G^\circ = \dots\dots\dots \text{kJ mol}^{-1}$ [4]

12 (a) Some bond energy data are shown in Table 12.1.

Table 12.1

type of bond	bond energy / kJ mol ⁻¹
O–O	150
O–H	460
O=O	496

Use the data in Table 12.1 to show that the enthalpy change of the following reaction is –196 kJ mol⁻¹.



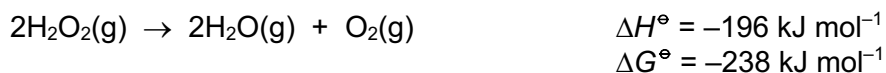
[1]

(b) Some standard entropies, S° , are shown in Table 12.2.

Table 12.2

substance	S° / J K ⁻¹ mol ⁻¹
H ₂ O ₂ (l)	+102
H ₂ O(l)	+70

The enthalpy change and Gibbs free energy change for the following reaction are shown.



Use the data given in Table 12.2 to calculate the standard entropy of oxygen, S° , O₂(g).

S° , O₂(g) = J K⁻¹ mol⁻¹ [3]

- (c) Iron(II) chloride, FeCl_2 , is oxidised by chlorine to form iron(III) chloride, FeCl_3 , under standard conditions.

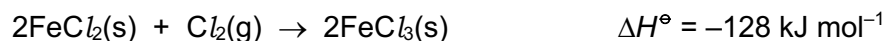


Table 12.3

substance	$S^\circ / \text{J K}^{-1} \text{ mol}^{-1}$
$\text{Cl}_2(\text{g})$	223
$\text{FeCl}_2(\text{s})$	120
$\text{FeCl}_3(\text{s})$	142

- (i) Use Table 12.3 and other data to calculate the Gibbs free energy change, ΔG° , for this reaction.

Show your working.

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

- (ii) Predict whether this reaction becomes more or less feasible at a higher temperature.

Explain your answer.

The reaction becomes feasible.

explanation

.....

[1]

- (d) Calcium carbonate decomposes on heating.



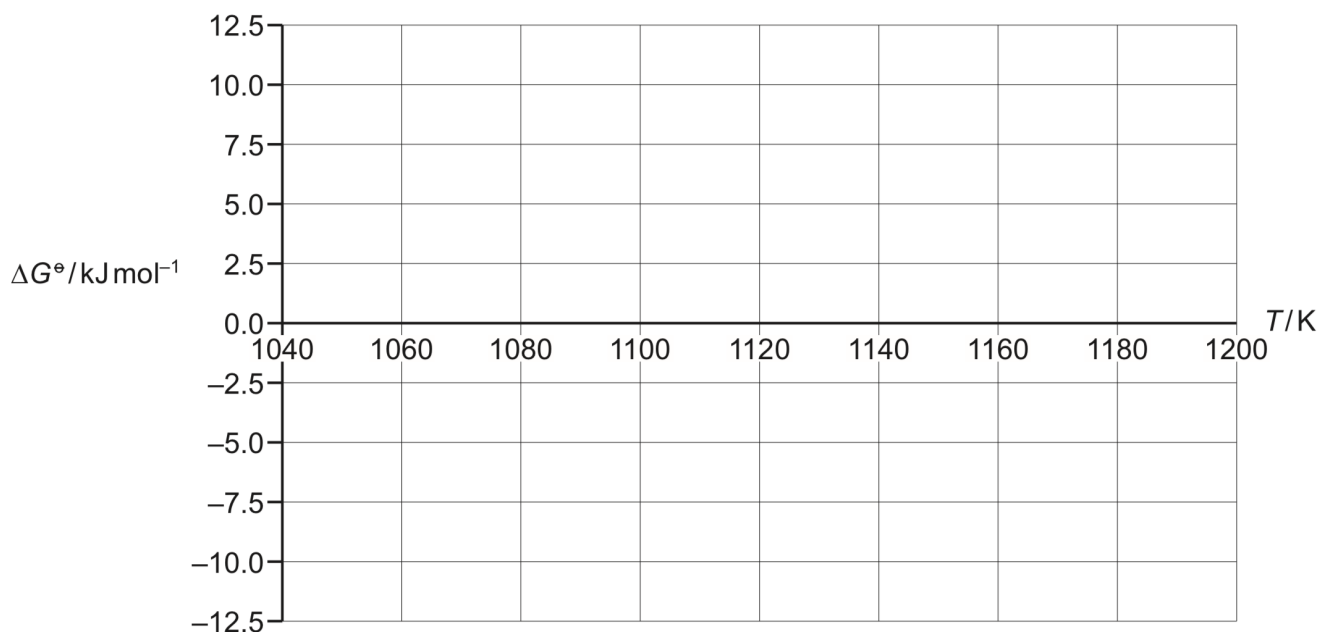
Table 12.4 shows the values of the Gibbs free energy change, ΔG° , for this reaction at various temperatures.

Table 12.4

T / K	$\Delta G^\circ / \text{kJ mol}^{-1}$
1050	9.9
1085	4.3
1120	-1.3
1148	-5.8
1176	-10.3

Assume the standard enthalpy change, ΔH° , and the standard entropy change, ΔS° , for this reaction remain constant over this temperature range.

- (i) Use the data in Table 12.4 to plot a graph of ΔG° against T on the grid.



[2]

- (ii) Calculate the gradient of your graph. Determine the ΔS° in $\text{J K}^{-1} \text{mol}^{-1}$ for this reaction. Show all working.

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