

# Chemical energetics

A2

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## What you need to know

By the end of this topic you should be able to:

1. **Define and use the enthalpy change of atomisation,  $\Delta H_{\text{at}}$ , and the lattice energy,  $\Delta H_{\text{latt}}$ .** Lattice energy is the change when gaseous ions come together to make the solid lattice, so it is always negative.
2. **Define and use the first electron affinity,  $EA_1$ ,** explain what affects the size of electron affinities, and describe and explain how electron affinity changes down Group 16 and Group 17.
3. **Build and use Born–Haber cycles** for ionic solids with +1 or +2 cations and –1 or –2 anions.
4. **Do calculations with Born–Haber cycles**, finding any one unknown step.
5. **Explain, without numbers, how ionic charge and ionic radius change the size of a lattice energy.**
6. **Define and use the enthalpy changes of hydration,  $\Delta H_{\text{hyd}}$ , and solution,  $\Delta H_{\text{sol}}$ .**
7. **Build and use the energy cycle** that links  $\Delta H_{\text{sol}}$ ,  $\Delta H_{\text{latt}}$  and  $\Delta H_{\text{hyd}}$ , and do calculations with it.
8. **Explain, without numbers, how ionic charge and ionic radius change the size of an enthalpy change of hydration.**
9. **Define entropy,  $S$ ,** as the number of possible arrangements of the particles and their energy in a system.
10. **Predict and explain the sign of an entropy change** for a change of state (melting, boiling, dissolving and their reverses), a change of temperature, and a reaction in which the number of gas molecules changes.
11. **Calculate  $\Delta S^\ominus$  for a reaction** from standard entropies:  $\Delta S^\ominus = \Sigma S^\ominus(\text{products}) - \Sigma S^\ominus(\text{reactants})$ .  
You don't need the entropy change of the surroundings.
12. **State and use the Gibbs equation,  $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$ ,** and do calculations with it.
13. **Say whether a reaction or process is feasible from the sign of  $\Delta G$ ,** and predict how raising or lowering the temperature changes its feasibility from  $\Delta H^\ominus$  and  $\Delta S^\ominus$ .

This builds on the AS topic (standard enthalpy changes, Hess's law, bond energies). Using  $\Delta G^\ominus = -nE_{\text{cell}}^\ominus F$  belongs to electrochemistry.

## Understand it

### Atomisation and lattice energy

The **standard enthalpy change of atomisation**,  $\Delta H_{\text{at}}$ , is the enthalpy change when **one mole of gaseous atoms** forms from the element in its standard state, under standard conditions. It is always positive, because bonds (or metallic bonding, or intermolecular forces) have to be broken.

- $\text{Li(s)} \rightarrow \text{Li(g)}$ ,  $\Delta H_{\text{at}} = +159 \text{ kJ mol}^{-1}$
- $\frac{1}{2}\text{H}_2(\text{g}) \rightarrow \text{H(g)}$ ,  $\Delta H_{\text{at}} = +218 \text{ kJ mol}^{-1}$ : the equation makes **one mole of atoms**, so it has half a mole of  $\text{H}_2$ .

For a gaseous diatomic element,  $\Delta H_{\text{at}}$  is **half the bond energy**: the H–H bond energy is  $436 \text{ kJ mol}^{-1}$ , and breaking half a mole of H–H bonds gives one mole of H atoms,  $+218 \text{ kJ mol}^{-1}$ . For iodine or bromine, which are not gases at 298 K,  $\Delta H_{\text{at}}$  also includes the energy to turn the solid or liquid into gas, so it is **not** half the bond energy.

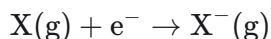
The **lattice energy**,  $\Delta H_{\text{latt}}$ , is the enthalpy change when **one mole of an ionic solid is formed from its gaseous ions**, under standard conditions:



Ions of opposite charge attract, so bringing them together releases energy: lattice energy is **always negative**. It measures the strength of the ionic bonding. It can't be measured directly (you can't collect a mole of gaseous ions), so it is found from an energy cycle.

### Electron affinity

The **first electron affinity**,  $EA_1$ , is the enthalpy change when **one mole of gaseous atoms each gain one electron** to form one mole of gaseous  $1-$  ions. For an element X:



- $EA_1$  is **negative** (exothermic) for Group 16 and 17 elements: the incoming electron is attracted by the nucleus, so energy is released.
- **The second electron affinity,  $EA_2$ , is positive** (endothermic):  $\text{X}^-(\text{g}) + \text{e}^- \rightarrow \text{X}^{2-}(\text{g})$ . The electron is being added to an ion that is already **negative**, so it is **repelled**, and energy has to be put in to force it on.

**What affects the size of  $EA_1$** : the attraction between the nucleus and the incoming electron. That attraction is stronger when

- the **nuclear charge** is larger (across a period);
- the electron goes into a shell **closer to the nucleus** (smaller atomic radius);
- there is **less shielding** by inner electrons.

**Trend down Group 16 (S to Te) and Group 17 (Cl to I):**  $EA_1$  becomes **less exothermic** (less negative). The atoms get bigger and have more inner shells, so the added electron is further from the nucleus and more shielded, and is attracted less strongly. The extra protons are cancelled by the extra shielding. The first members, O and F, break the pattern: their outer shells are so small and crowded that the added electron is repelled by the electrons already there, so  $EA_1$  of F is less exothermic than that of Cl, and O less than S.

Write "becomes less exothermic" or "less negative", never "decreases": for a negative number, "decreases" is ambiguous.

## Born–Haber cycles

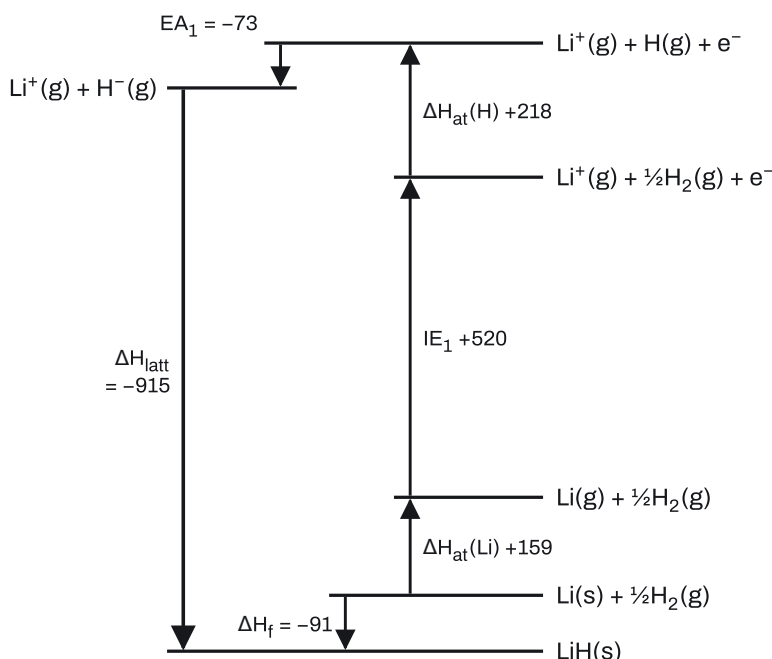
A **Born–Haber cycle** is a Hess's law cycle for making an ionic solid from its elements. There are two routes from the elements to the solid:

- **directly**: the enthalpy change of formation,  $\Delta H_f$ ;
- **the long way round**: turn the elements into gaseous atoms, then into gaseous ions, then let the ions form the lattice.

Both routes give the same total, so

$$\Delta H_f = \Delta H_{at}(\text{metal}) + \Sigma IE(\text{metal}) + \Delta H_{at}(\text{non-metal}) + \Sigma EA(\text{non-metal}) + \Delta H_{latt}.$$

Lithium hydride, LiH, is an ionic solid made of  $\text{Li}^+$  and hydride ions,  $\text{H}^-$ . Each step happens once: one lithium atom loses one electron and one hydrogen atom gains it.



Reading the diagram: arrows up are endothermic (atomisation, ionisation, a second electron affinity), arrows down are exothermic (a first electron affinity, the lattice energy, and here the formation). Every level shows **all** the species, with state symbols, and keeps track of the electrons: after ionisation the level is  $\text{Li}^+(\text{g}) +$

$\frac{1}{2}\text{H}_2(\text{g}) + \text{e}^-$ , and the electron disappears only when the hydrogen atom takes it.

Going round the cycle for LiH:

$$-91 = 159 + 520 + 218 + (-73) + \Delta H_{\text{latt}}$$

so  $\Delta H_{\text{latt}} = -91 - 824 = -915 \text{ kJ mol}^{-1}$ . Any one of the steps can be the unknown; put it in as  $x$  and solve.

When an ion appears more than once, or has a charge of 2, multiply or add the steps:

- $\text{MX}_2$  (a  $2+$  cation): the metal needs  $IE_1 + IE_2$ , and the non-metal needs  $2 \times \Delta H_{\text{at}}$  and  $2 \times EA_1$  (two atoms, each gaining one electron).
- $\text{M}_2\text{X}$  (a  $2-$  anion): the metal needs  $2 \times \Delta H_{\text{at}}$  and  $2 \times IE_1$ , but no second ionisation energy; the non-metal needs  $EA_1$  (negative) **and**  $EA_2$  (positive).

## What makes a lattice energy large

The attraction between two ions depends on their charges and on the distance between their centres (the sum of their radii). So a lattice energy is **more exothermic** when:

- **the ions have a higher charge:**  $\text{Mg}^{2+}$  and  $\text{O}^{2-}$  attract far more strongly than  $\text{Na}^+$  and  $\text{F}^-$ ;
- **the ions are smaller:** their centres can get closer, so they attract more strongly.  $\text{LiCl}$  has a more exothermic lattice energy than  $\text{RbCl}$ .

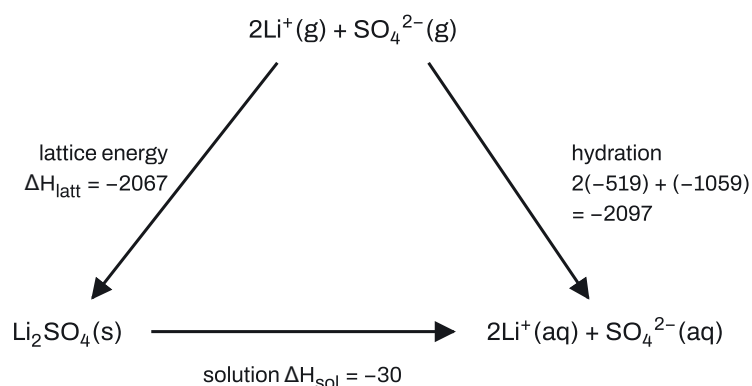
When the charges differ, charge usually wins: doubling the charge on **both** ions makes the attraction about four times as strong, far more than any realistic difference in size. Say "**more exothermic**" or "**more negative**", not "bigger", and give the direction for **both** factors.

## Hydration and solution

When an ionic solid dissolves, its lattice breaks up and the ions become surrounded by water molecules. Two new enthalpy changes describe this.

- **Enthalpy change of hydration,  $\Delta H_{\text{hyd}}$ :** the enthalpy change when **one mole of gaseous ions** dissolves in water to form an aqueous solution:  $\text{Li}^+(\text{g}) \rightarrow \text{Li}^+(\text{aq})$ . It is **always negative**: the ion attracts the polar water molecules (the  $\delta-$  oxygen towards a cation, the  $\delta+$  hydrogens towards an anion), and these **ion-dipole** attractions release energy.
- **Enthalpy change of solution,  $\Delta H_{\text{sol}}$ :** the enthalpy change when **one mole of an ionic solid** dissolves in water to form a very dilute solution:  $\text{Li}_2\text{SO}_4(\text{s}) \rightarrow 2\text{Li}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$ . It can be **positive or negative**.

The two are linked through the gaseous ions. Going from the solid to the solution directly ( $\Delta H_{\text{sol}}$ ) must equal breaking the lattice into gaseous ions ( $-\Delta H_{\text{latt}}$ ) and then hydrating them:



$$\Delta H_{\text{sol}} = \Sigma \Delta H_{\text{hyd}}(\text{ions}) - \Delta H_{\text{latt}}$$

For lithium sulfate,  $\Delta H_{\text{sol}} = 2(-519) + (-1059) - (-2067) = -30 \text{ kJ mol}^{-1}$ . Count each ion as many times as it appears in the formula.

**What makes a hydration enthalpy large:** the same two factors as lattice energy, now for one ion and the water around it. A **smaller** ion and a **higher charge** (together, a higher **charge density**) attract water molecules more strongly, so  $\Delta H_{\text{hyd}}$  is more exothermic.

- Down a group it becomes **less exothermic**:  $\text{F}^- \rightarrow \text{I}^-$ , or  $\text{Li}^+ \rightarrow \text{Rb}^+$ , as the ions get larger.
- Across a period the cations get **smaller and more highly charged**, so  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$  become much more exothermic in turn.
- A large polyatomic ion spreads its charge over a bigger volume than a small single-atom ion with the same charge, so it is hydrated less exothermically.

## Group 2 solubility and energy

The solubility of a Group 2 compound depends on the balance in  $\Delta H_{\text{sol}} = \Sigma \Delta H_{\text{hyd}} - \Delta H_{\text{latt}}$ . Down the group the cation gets larger, so **both**  $\Delta H_{\text{latt}}$  and  $\Delta H_{\text{hyd}}$  become less exothermic. What matters is **which changes more**.

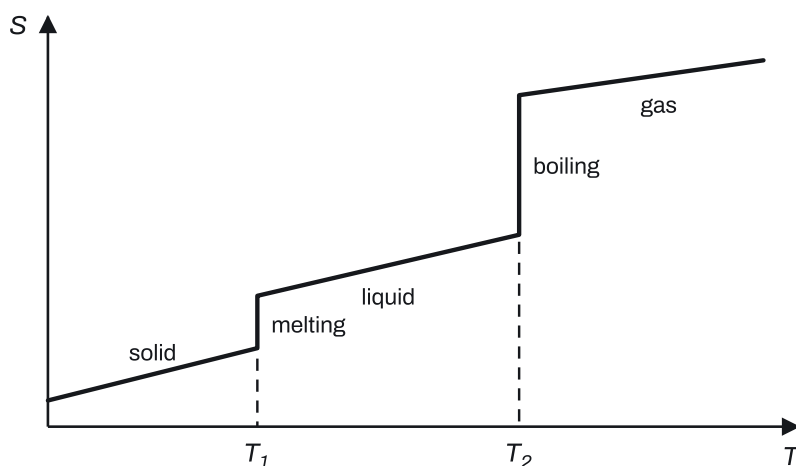
- **Large anion (sulfates, chromates):** the anion is so big that a larger cation hardly changes the distance between ion centres, so the lattice energy changes only a little. The cation's hydration enthalpy depends on the cation alone and falls a lot. Hydration changes more, so  $\Delta H_{\text{sol}}$  becomes **less exothermic (more endothermic)** and the salts become **less soluble** down the group.
- **Small anion (hydroxides, fluorides):** the distance between ion centres grows a lot as the cation grows, so the lattice energy changes **more** than the hydration enthalpy.  $\Delta H_{\text{sol}}$  becomes more exothermic and the compounds become **more soluble** down the group.

The same argument explains why Group 2 **carbonates** need more heat to decompose down the group ( $\text{MCO}_3 \rightarrow \text{MO} + \text{CO}_2$ ). The small oxide ion makes the lattice energy of MO fall **faster** down the group than that of  $\text{MCO}_3$ , so less energy is released forming the oxide, and the decomposition becomes **more endothermic**.

## Entropy

**Entropy**,  $S$ , is the number of possible arrangements of the particles **and their energy** in a system. More ways to arrange things means higher entropy. Standard entropies,  $S^\ominus$ , are measured in  $\text{J K}^{-1} \text{mol}^{-1}$  (joules, not kilojoules), and every substance, including an element, has a positive  $S^\ominus$ .

- **Gases** have much higher entropy than liquids, and liquids higher than solids: gas particles move freely through the whole volume and can be arranged in far more ways.
- **Heating** a substance raises its entropy: the particles have more energy, which can be shared out among them in more ways, and they move more.



The two vertical jumps are the changes of state. The jump at **boiling** is much larger than at melting, because going from liquid to gas makes a far bigger change in how freely the particles move and how far apart they are.

### Predicting the sign of $\Delta S$ :

| Change                                    | Sign of $\Delta S$ | Why                                                            |
|-------------------------------------------|--------------------|----------------------------------------------------------------|
| Melting, boiling, subliming               | +                  | particles become freer to move                                 |
| Freezing, condensing                      | –                  | particles become more ordered                                  |
| An ionic solid dissolving in water        | usually +          | ions leave the ordered lattice and spread through the solution |
| Heating a substance                       | +                  | more energy to share out, more motion                          |
| Reaction making <b>more</b> moles of gas  | +                  | gases have much the highest entropy                            |
| Reaction making <b>fewer</b> moles of gas | –                  |                                                                |

For a reaction, count the **moles of gas** on each side first:  $\text{N}_2\text{O}_4(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$  goes from 1 to 2 mol of gas, so  $\Delta S$  is positive.

To calculate the entropy change of a reaction, use the standard entropies with the coefficients from the equation:

$$\Delta S^\ominus = \Sigma S^\ominus(\text{products}) - \Sigma S^\ominus(\text{reactants})$$

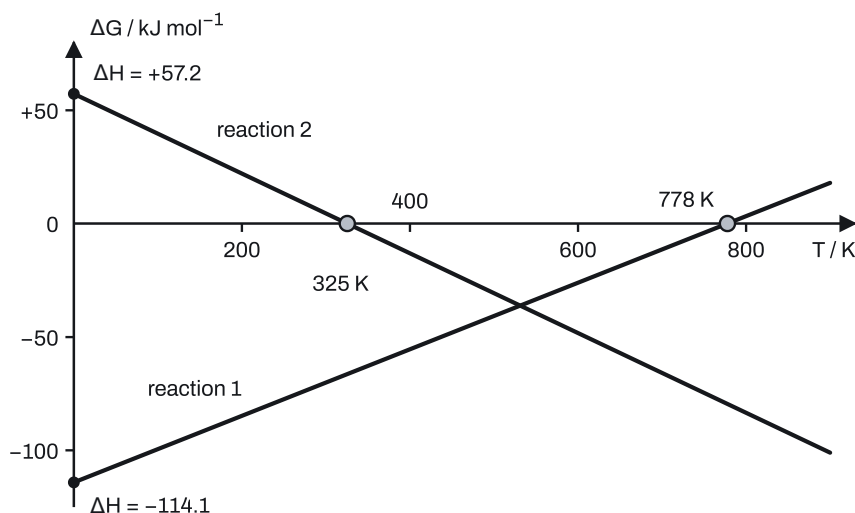
## Gibbs free energy and feasibility

A reaction is **feasible** (it can happen by itself, even if slowly) when the **Gibbs free energy change**,  $\Delta G$ , is **negative**:

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

with  $T$  in **kelvin**.  $\Delta H$  is in  $\text{kJ mol}^{-1}$  but  $\Delta S$  is in  $\text{J K}^{-1} \text{mol}^{-1}$ , so **divide  $\Delta S$  by 1000** first (or multiply  $\Delta H$  by 1000). A feasible reaction may still not be seen if its activation energy is high.

$\Delta H$  and  $\Delta S$  hardly change with temperature, so  $\Delta G$  plotted against  $T$  is a **straight line**: its intercept on the  $\Delta G$  axis (at  $T = 0$ ) is  $\Delta H$ , and its gradient is  $-\Delta S$ .



The two lines in the diagram show the two cases where temperature matters. Reaction 1 has a negative  $\Delta S$ , so its line slopes **up** and it stops being feasible when it crosses zero. Reaction 2 has a positive  $\Delta S$ , so its line slopes **down** and it becomes feasible when it crosses zero. The temperature where a line crosses zero is where the reaction **stops or starts** being feasible:

$$\Delta G = 0 \Rightarrow T = \frac{\Delta H}{\Delta S}$$

How temperature matters depends only on the signs, because it is the  $-T\Delta S$  term that grows with  $T$ :

### $\Delta H$ $\Delta S$ Feasible?

|   |   |                                                                                                                                 |
|---|---|---------------------------------------------------------------------------------------------------------------------------------|
| – | + | at <b>every</b> temperature ( $\Delta G$ always negative)                                                                       |
| + | – | at <b>no</b> temperature                                                                                                        |
| – | – | only <b>below</b> $T = \Delta H / \Delta S$ : raising $T$ makes $-T\Delta S$ more positive, so $\Delta G$ becomes less negative |

## $\Delta H$ $\Delta S$ Feasible?

+ + only **above**  $T = \Delta H / \Delta S$ : raising  $T$  makes  $-T\Delta S$  more negative, so  $\Delta G$  becomes more negative

The same idea applies to dissolving. A salt with an endothermic  $\Delta H_{\text{sol}}$  can still dissolve if  $\Delta S$  is positive enough that  $T\Delta S$  outweighs  $\Delta H$  and  $\Delta G$  is negative; and such a salt becomes **more soluble** as the water gets hotter.

## Key facts and formulas

"Given" means the value is in the 9701 Data Booklet. "Learn it" means you must remember it. Questions usually print the energy values they want you to use.

| Formula                                                                                                                                              | Status   |
|------------------------------------------------------------------------------------------------------------------------------------------------------|----------|
| $\Delta H_{\text{latt}}$ : gaseous ions $\rightarrow$ 1 mol of ionic solid (always negative)                                                         | Learn it |
| $\Delta H_{\text{at}}$ : element in standard state $\rightarrow$ 1 mol of gaseous atoms (always positive)                                            | Learn it |
| $EA_1$ : 1 mol of gaseous atoms + 1 mol of electrons $\rightarrow$ 1 mol of gaseous 1- ions                                                          | Learn it |
| $\Delta H_{\text{hyd}}$ : 1 mol of gaseous ions $\rightarrow$ aqueous ions (always negative)                                                         | Learn it |
| $\Delta H_{\text{sol}}$ : 1 mol of solute $\rightarrow$ very dilute solution (either sign)                                                           | Learn it |
| $\Delta H_{\text{f}} = \Delta H_{\text{at}}(\text{metal}) + \Sigma IE + \Delta H_{\text{at}}(\text{non-metal}) + \Sigma EA + \Delta H_{\text{latt}}$ | Learn it |
| $\Delta H_{\text{at}}$ of a gaseous diatomic element = $\frac{1}{2} \times$ its bond energy                                                          | Learn it |
| $\Delta H_{\text{sol}} = \Sigma \Delta H_{\text{hyd}} - \Delta H_{\text{latt}}$                                                                      | Learn it |
| Ionisation energies of the elements                                                                                                                  | Given    |
| Ionic radii                                                                                                                                          | Given    |
| Entropy: the number of possible arrangements of the particles and their energy in a system                                                           | Learn it |
| $\Delta S^{\ominus} = \Sigma S^{\ominus}(\text{products}) - \Sigma S^{\ominus}(\text{reactants})$                                                    | Learn it |
| $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$ ( $T$ in K; $\Delta S$ in $\text{kJ K}^{-1} \text{mol}^{-1}$ )                       | Learn it |
| Feasible when $\Delta G < 0$                                                                                                                         | Learn it |
| Temperature where feasibility changes: $T = \Delta H / \Delta S$                                                                                     | Learn it |
| $\Delta S = \frac{\Delta H - \Delta G}{T}$                                                                                                           | Learn it |
| $0^{\circ}\text{C} = 273 \text{ K}$ , so $25^{\circ}\text{C} = 298 \text{ K}$                                                                        | Learn it |

## How to do it

54 questions tagged for this topic, 2021–2025, all Paper 4. Twelve are Paper 41 copies of Paper 43 questions, which leaves 42 different questions, and the table counts those. 37 of them mix more than one type, so the counts add up to more than 42. Two (**9701/42/M/J/23 Q9** and **9701/42/F/M/22 Q3**) only use  $\Delta G^\ominus = -nE_{\text{cell}}^\ominus F$ , which belongs to electrochemistry.

| Question type                                                                                                  | Questions |
|----------------------------------------------------------------------------------------------------------------|-----------|
| Define an energetics term or write its equation                                                                | 21        |
| Calculate an unknown in a solution–hydration–lattice cycle                                                     | 14        |
| Explain or order lattice energy magnitudes                                                                     | 14        |
| Judge feasibility or solubility, and how it changes with temperature                                           | 14        |
| Calculate an unknown from a Born–Haber cycle                                                                   | 13        |
| Calculate $\Delta S^\ominus$ from standard entropies                                                           | 12        |
| Calculate $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$ and state feasibility                      | 11        |
| Predict and explain the sign of $\Delta S$                                                                     | 9         |
| Define entropy                                                                                                 | 9         |
| Explain hydration enthalpy magnitudes or trends                                                                | 8         |
| Explain Group 2 solubility (or decomposition) trends with $\Delta H_{\text{latt}}$ and $\Delta H_{\text{hyd}}$ | 8         |
| Complete or label a Born–Haber or solution cycle                                                               | 8         |
| Rearrange the Gibbs equation (a temperature, $\Delta S$ or one $S^\ominus$ )                                   | 8         |
| Explain electron affinity signs and trends                                                                     | 7         |
| Use a $\Delta G$ – $T$ graph                                                                                   | 3         |

### 1. Define an energetics term or write its equation (21 questions)

Each definition is **one mole of what, from what state, to what state**. Lattice energy is usually worth 2 marks: "one mole of ionic solid is formed" and "from its gaseous ions".

| Term                    | Key words                                                                    | Example equation                                                                |
|-------------------------|------------------------------------------------------------------------------|---------------------------------------------------------------------------------|
| Lattice energy          | 1 mol of ionic solid formed from its gaseous ions                            | $\text{Li}^+(\text{g}) + \text{H}^-(\text{g}) \rightarrow \text{LiH}(\text{s})$ |
| Atomisation             | 1 mol of gaseous atoms formed from the element in its standard state         | $\frac{1}{2}\text{Br}_2(\text{l}) \rightarrow \text{Br}(\text{g})$              |
| First electron affinity | 1 mol of gaseous atoms each gain 1 electron to form 1 mol of gaseous 1– ions | $\text{X}(\text{g}) + \text{e}^- \rightarrow \text{X}^-(\text{g})$              |

| Term                     | Key words                                                      | Example equation                        |
|--------------------------|----------------------------------------------------------------|-----------------------------------------|
| Second electron affinity | 1 mol of gaseous 1- ions each gain 1 electron                  | $X^-(g) + e^- \rightarrow X^{2-}(g)$    |
| Hydration                | 1 mol of gaseous ions dissolve in water                        | $Li^+(g) \rightarrow Li^+(aq)$          |
| Solution                 | 1 mol of solute dissolves in water (to a very dilute solution) | $CsF(s) \rightarrow Cs^+(aq) + F^-(aq)$ |

#### Variations you will meet:

- **Write the equation** with state symbols: gaseous (g) for every atom and ion in lattice energy, atomisation and electron affinity; the element in its real state at 298 K on the left of an atomisation.
- **A tick table of signs:** lattice energy, hydration, atomisation and bond energy always have **one** sign (–, –, +, +);  $\Delta H_{sol}$  and  $\Delta H_f$  **can be either**.
- **Second ionisation energy equation**, for a metal M:  $M^+(g) \rightarrow M^{2+}(g) + e^-$ .

## 2. Calculate an unknown in a solution–hydration–lattice cycle (14 questions)

1. **Sketch the triangle:** gaseous ions at the top, the solid and the aqueous solution below.
2. **Write the equation**  $\Delta H_{sol} = \Sigma \Delta H_{hyd} - \Delta H_{latt}$ , multiplying each ion's  $\Delta H_{hyd}$  by how many there are (×2 for  $F^-$  in  $BaF_2$ , ×3 for  $Cl^-$  in  $ScCl_3$ ).
3. **Put in the values with their signs**, in brackets, and solve for the unknown.
4. **Give the sign** with the answer, in  $kJ\ mol^{-1}$ .

#### Variations you will meet:

- **The unknown is  $\Delta H_{latt}$  or one ion's  $\Delta H_{hyd}$ :** rearrange the same equation (Example 2).
- **A long table:** pick only the lattice energy, the hydration enthalpies and  $\Delta H_{sol}$ ; ionisation energies and electron affinities are distractors.
- **"Write the expression"** only: for a salt MX,  $\Delta H_{sol}(MX) = \Delta H_{hyd}(M^+) + \Delta H_{hyd}(X^-) - \Delta H_{latt}(MX)$ .
- **Combined with  $\Delta H_f$ :** a cycle from the elements through the gaseous ions to the aqueous ions. Go round it the same way: every route between the same two levels has the same total.
- **Is it soluble?** A negative  $\Delta H_{sol}$  suggests it dissolves; a strongly positive one suggests not (unless entropy wins, type 4).

## 3. Explain or order lattice energy magnitudes (14 questions)

1. **Compare the charges** of the ions in the two (or three) compounds.
2. **Compare the radii** (look them up in the Data Booklet if you need to).
3. **Link to attraction:** higher charge and smaller ions → stronger attraction between the ions → **more exothermic** lattice energy.
4. **Order** the compounds, most exothermic first, as the question's labels ask.

**Variations you will meet:**

- **Same charges, different sizes:** only radius matters; the compound with the smaller ions has the more exothermic lattice energy.
- **Different charges and sizes:** give both factors and their directions. If asked which **dominates**, it is usually charge, because doubling both charges roughly quadruples the attraction, far more than a difference in size can do.
- **A tick box** ("more negative / the same / less negative"): tick, then explain with the radius or charge of the ion that differs.

**4. Judge feasibility or solubility, and how it changes with temperature (14 questions)**

1. **Find the signs** of  $\Delta H$  and  $\Delta S$  (given, calculated, or predicted from moles of gas).
2. **Look at  $-T\Delta S$ :** if  $\Delta S > 0$ , raising  $T$  makes  $-T\Delta S$  more negative; if  $\Delta S < 0$ , more positive.
3. **Conclude about  $\Delta G$ :** " $\Delta G$  becomes more negative, so the reaction becomes more feasible" (or less). The mark needs  $\Delta G$  in the sentence.

**Variations you will meet:**

- **Soluble or not:** from the sign of  $\Delta G$  for dissolving; a positive  $\Delta G$  means not soluble at that temperature.
- **"Dissolves even though  $\Delta H_{\text{sol}}$  is endothermic":**  $\Delta S$  is positive, so  $T\Delta S$  outweighs  $\Delta H$  and  $\Delta G$  is negative.
- **Working backwards from the behaviour:** "feasible only at low temperatures" means  $\Delta H < 0$  and  $\Delta S < 0$ ; "only at high temperatures" means both positive; "at all temperatures" means  $\Delta H < 0$  and  $\Delta S > 0$ .
- **More or less soluble when heated:** dissolving usually has  $\Delta S > 0$ , so  $\Delta G$  becomes more negative and solubility rises.

**5. Calculate an unknown from a Born–Haber cycle (13 questions)**

1. **Sketch the cycle** (elements  $\rightarrow$  gaseous atoms  $\rightarrow$  gaseous ions  $\rightarrow$  solid, and elements  $\rightarrow$  solid).
2. **Select only the steps you need**, with a multiplier for each:  $\times 2$  for the metal in  $M_2X$ ,  $\times 2$  for the non-metal in  $MX_2$ ; both  $IE_1$  and  $IE_2$  for a  $2+$  ion; both  $EA_1$  and  $EA_2$  for a  $2-$  ion.
3. **Write one equation:**  $\Delta H_f = \Sigma(\text{all the other steps})$ , every value in brackets with its sign.
4. **Solve** for the unknown and give it with its sign.

**Variations you will meet:**

- **Distractors in the table:** a second ionisation energy for a  $+1$  metal, an ionisation energy of the non-metal, both a bond energy and an atomisation energy. For a gas such as  $Cl_2$  or  $O_2$  use  $\Delta H_{\text{at}}$  or half the bond energy, not both.
- **Any step can be the unknown:**  $\Delta H_f$ ,  $\Delta H_{\text{latt}}$ , an electron affinity, an ionisation energy or an atomisation energy (Example 1).

- **A step given for several electrons at once**, such as  $X_2(g) + 2e^- \rightarrow 2X^-(g)$ : write it as the sum of its parts,  $2\Delta H_{at} + 2EA_1$ , set that equal to the value given, and solve for whichever part is unknown. Watch the factor of 2 on **both** parts.
- **Many-atom elements**: sulfur is  $S_8$ , so  $S_8(s) \rightarrow 8S(g)$  is  $8 \times \Delta H_{at}$ .
- **A gaseous polyatomic ion** (such as  $SO_4^{2-}$ ) treated as one "atom-and-electrons" step: the cycle works the same way.
- **Naming the steps** in words or symbols, instead of calculating.

## 6. Calculate $\Delta S^\ominus$ from standard entropies (12 questions)

1. **Multiply** each  $S^\ominus$  by its coefficient in the equation.
2. **Products minus reactants**. Elements have non-zero entropies:  $O_2$  or  $H_2$  must be included.
3. Give the answer with its **sign** in  $J K^{-1} mol^{-1}$ .
4. **Check the sign** against the change in moles of gas.

**Variations you will meet:**

- **Fractional coefficients** ( $\frac{1}{2}O_2$ ): multiply by  $\frac{1}{2}$ .
- **A value from earlier in the question** or from "other data" in the paper.
- **Straight into  $\Delta G$**  in the next part (type 7).

## 7. Calculate $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$ and state feasibility (11 questions)

1. If needed, **find  $\Delta H^\ominus$**  from enthalpies of formation (products minus reactants) and  $\Delta S^\ominus$  from standard entropies.
2. **Convert**:  $T$  in kelvin ( $25^\circ C = 298 K$ ;  $\theta^\circ C = \theta + 273 K$ ) and  $\Delta S$  into  $kJ K^{-1} mol^{-1}$  (divide by 1000).
3. **Substitute** into  $\Delta G = \Delta H - T\Delta S$ , keeping all signs.
4. **Conclude**: " $\Delta G$  is negative, so the reaction is feasible" (or positive, so not feasible).

**Variations you will meet:** a 3–4 mark version that asks for  $\Delta H$ ,  $\Delta S$  and  $\Delta G$  in one go (Example 3); "show that the reaction is feasible at 298 K" (the calculation plus the sign is the proof).

## 8. Predict and explain the sign of $\Delta S$ (9 questions)

1. **Count the moles of gas** on each side. More gas on the right  $\rightarrow$  positive; fewer  $\rightarrow$  negative. Say this in the answer: "more moles of gas in the products".
2. **No change in gas**: look at other states. A solid dissolving is positive; a liquid freezing is negative.
3. **Changes of state and temperature**: use the table in "Understand it".

**Variations you will meet:** a tick table (positive / negative); an entropy–temperature graph where you name the melting and boiling points and explain why the boiling jump is bigger (gas particles are much more disordered and further apart than liquid particles); why one  $S^\ominus$  is larger than another (a gas is more disordered than a liquid).

## 9. Define entropy (9 questions)

"The number of possible arrangements of the particles **and their energy** in a system." Include both the particles and the energy. "Disorder" alone is not the syllabus definition.

## 10. Explain hydration enthalpy magnitudes or trends (8 questions)

1. **Compare the ions' radii and charges.**
2. **Link:** smaller ion or higher charge (higher charge density) → stronger attraction between the ion and the water molecules (ion–dipole) → **more exothermic**  $\Delta H_{\text{hyd}}$ .
3. **Give the direction:** down Group 17 ( $\text{F}^-$  to  $\text{I}^-$ ) less exothermic;  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$  more exothermic.

**Variations you will meet:**

- **Two ions of the same charge:** look up their ionic radii in the Data Booklet; the smaller one is hydrated more exothermically.
- **A simple ion against a polyatomic ion:** the polyatomic ion is larger, so its  $\Delta H_{\text{hyd}}$  is less exothermic. (An oxyanion can also hydrogen-bond to water through lone pairs on its oxygen atoms, which mark schemes may accept.)
- **Why  $\Delta H_{\text{sol}}$  hardly changes down a series:**  $\Delta H_{\text{latt}}$  and  $\Sigma \Delta H_{\text{hyd}}$  both become less exothermic by similar amounts, so their difference stays about the same.

## 11. Explain Group 2 solubility (or decomposition) trends with $\Delta H_{\text{latt}}$ and $\Delta H_{\text{hyd}}$ (8 questions)

Four linked points, each usually a mark:

1. **The trend:** sulfates (and chromates) less soluble down the group; hydroxides (and fluorides) more soluble.
2. **Both  $\Delta H_{\text{latt}}$  and  $\Delta H_{\text{hyd}}$**  become **less exothermic** down the group (the cation gets larger).
3. **Which changes more:** for sulfates,  $\Delta H_{\text{hyd}}$  changes more (the large anion means the lattice energy hardly changes); for hydroxides,  $\Delta H_{\text{latt}}$  changes more.
4. **So  $\Delta H_{\text{sol}}$ :** for sulfates it becomes less exothermic (more endothermic) → less soluble; for hydroxides it becomes more exothermic → more soluble.

**Variations you will meet:** "which sample needs the most water (or acid) before a solid appears or disappears" (use the solubility trend, then give the energy reasons); carbonate decomposition down the group, from the different rates at which  $\Delta H_{\text{latt}}(\text{MO})$  and  $\Delta H_{\text{latt}}(\text{MCO}_3)$  change (see "Understand it").

## 12. Complete or label a Born–Haber or solution cycle (8 questions)

1. **Start from the elements** in their standard states at zero.
2. **Each level lists every species** with state symbols, including the electrons still "loose":  $\text{Li}^+(\text{g}) + \frac{1}{2}\text{H}_2(\text{g}) + \text{e}^-$ .

3. **Arrows up** for endothermic steps, **down** for exothermic, each labelled with its name or symbol.
4. For a solution cycle, the bottom right is the aqueous ions,  $2\text{Li}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$ , not the solid.

Marks are given for the species (often "any two, then all four") and separately for **all** state symbols being right.

### 13. Rearrange the Gibbs equation (8 questions)

- **Temperature where feasibility changes:** set  $\Delta G = 0$ , so  $T = \frac{\Delta H}{\Delta S}$  with  $\Delta S$  in  $\text{kJ K}^{-1} \text{mol}^{-1}$ . It is a **minimum** temperature when both are positive, a **maximum** when both are negative. Convert to  $^{\circ}\text{C}$  if asked (subtract 273).
- **A melting or boiling point:** at the melting point  $\Delta G = 0$  for melting, so  $T_{\text{m}} = \frac{\Delta H_{\text{fus}}}{\Delta S_{\text{fus}}}$ .
- **$\Delta S$  from  $\Delta G$  and  $\Delta H$ :**  $\Delta S = \frac{\Delta H - \Delta G}{T}$ , then multiply by 1000 for  $\text{J K}^{-1} \text{mol}^{-1}$ .
- **One unknown standard entropy:** find  $\Delta S$  as above (after finding  $\Delta H$  from  $\Delta H_{\text{f}}$  values if needed), then write  $\Delta S = \Sigma S(\text{products}) - \Sigma S(\text{reactants})$  with the unknown as  $x$  and solve, remembering its coefficient.

### 14. Explain electron affinity signs and trends (7 questions)

- **$EA_1$  negative:** the nucleus attracts the incoming electron, so energy is released.
- **$EA_2$  positive:** the electron is added to a **negative ion**, so it is repelled and energy must be put in.
- **Trend down Group 16 or 17:** larger atomic radius and more shielding  $\rightarrow$  less attraction between the nucleus and the incoming electron  $\rightarrow EA_1$  **less exothermic**.
- **Pick a value** that fits the trend: an element between two others in a group has an  $EA_1$  between theirs.

### 15. Use a $\Delta G$ - $T$ graph (3 questions)

1. **The line is**  $\Delta G = \Delta H - T\Delta S$ , a straight line in  $T$ .
2. **Gradient** =  $-\Delta S$ : take two well-separated points, find the gradient in  $\text{kJ mol}^{-1} \text{K}^{-1}$ , change the sign and multiply by 1000.
3. **Intercept on the  $\Delta G$  axis (at  $T = 0$ )** =  $\Delta H$ .
4. **Where the line crosses  $\Delta G = 0$**  is the temperature where feasibility changes.

**Variations you will meet:** plotting given values of  $\Delta G$  first, then taking the gradient; sketching  $\Delta G$  for a change such as boiling a liquid (positive below the boiling point, zero at it, negative above).

## Worked examples

The bold codes show where marks are earned, as in Cambridge mark schemes. The number is how many marks.

- **M1** method mark: for a correct method, even if the numbers slip.
- **A1** accuracy mark: for a correct answer; it needs the M mark before it.
- **B1** mark for a correct result on its own, with no method needed.

### Example 1

Lithium hydride, LiH, is an ionic solid containing  $\text{Li}^+$  and  $\text{H}^-$  ions. Some energy changes are given.

| Energy change                                   | Value / $\text{kJ mol}^{-1}$ |
|-------------------------------------------------|------------------------------|
| enthalpy change of atomisation of lithium       | +159                         |
| first ionisation energy of lithium              | +520                         |
| second ionisation energy of lithium             | +7298                        |
| H–H bond energy                                 | +436                         |
| enthalpy change of hydration of $\text{Li}^+$   | –519                         |
| enthalpy change of formation of $\text{LiH(s)}$ | –91                          |
| lattice energy of $\text{LiH(s)}$               | –915                         |

(a) Write the equation for the standard enthalpy change of atomisation of hydrogen, and use the table to find its value. **[2]**

(b) Calculate the first electron affinity of hydrogen, using relevant data from the table. **[3]**

(c) Explain why the second ionisation energy of lithium and the enthalpy change of hydration of  $\text{Li}^+$  are not used in (b). **[2]**

**(a)**  $\frac{1}{2}\text{H}_2(\text{g}) \rightarrow \text{H}(\text{g})$  **B1**. It breaks half a mole of H–H bonds:  $\frac{1}{2} \times 436 = +218 \text{ kJ mol}^{-1}$  **B1**.

**(b)** Going round the Born–Haber cycle (the first diagram in "Understand it"):

$$\Delta H_{\text{f}} = \Delta H_{\text{at}}(\text{Li}) + IE_1(\text{Li}) + \Delta H_{\text{at}}(\text{H}) + EA_1(\text{H}) + \Delta H_{\text{latt}}$$

**M1** for the right five values only, **M1** for using 218 (half the bond energy), not 436:

$$\begin{aligned} -91 &= 159 + 520 + 218 + EA_1 + (-915) \\ -91 &= EA_1 - 18 \Rightarrow EA_1 = -73 \text{ kJ mol}^{-1} \end{aligned}$$

**A1** (with the – sign: the hydrogen atom releases energy when it gains an electron).

(c) Lithium only loses one electron to form  $\text{Li}^+$ , so no second ionisation happens in the cycle. **B1** Hydration is a step in dissolving (it makes aqueous ions); the Born–Haber cycle forms the solid from its elements and never involves water. **B1**

## Example 2

| Energy change                                                     | Value / $\text{kJ mol}^{-1}$ |
|-------------------------------------------------------------------|------------------------------|
| lattice energy of $\text{Li}_2\text{SO}_4(\text{s})$              | −2067                        |
| enthalpy change of hydration of $\text{Li}^+$                     | −519                         |
| enthalpy change of solution of $\text{Li}_2\text{SO}_4(\text{s})$ | −30                          |

(a) Define enthalpy change of hydration. **[1]**

(b) Draw an energy cycle and calculate the enthalpy change of hydration of the sulfate ion,  $\text{SO}_4^{2-}$ . **[2]**

(c) Suggest whether the enthalpy change of hydration of  $\text{Na}^+$  is more or less exothermic than that of  $\text{Li}^+$ . Explain your answer. **[2]**

(a) The enthalpy change when one mole of gaseous ions dissolves in water to form an aqueous solution. **B1**

(b) The cycle is the second diagram in "Understand it".  $\Delta H_{\text{sol}} = 2\Delta H_{\text{hyd}}(\text{Li}^+) + \Delta H_{\text{hyd}}(\text{SO}_4^{2-}) - \Delta H_{\text{latt}}$ :

$$-30 = 2(-519) + x - (-2067)$$

**M1** for the right values with  $\times 2$  on  $\text{Li}^+$ .

$$x = -30 + 1038 - 2067 = -1059 \text{ kJ mol}^{-1}$$

**A1**

(c) Less exothermic. **B1**  $\text{Na}^+$  has the same charge but a larger ionic radius (lower charge density), so it attracts water molecules less strongly. **B1**

## Example 3

Propene is made industrially by removing hydrogen from propane over a hot catalyst:  $\text{C}_3\text{H}_8(\text{g}) \rightarrow \text{C}_3\text{H}_6(\text{g}) + \text{H}_2(\text{g})$ .

| Substance                        | $\Delta H_f^\ominus / \text{kJ mol}^{-1}$ | $S^\ominus / \text{J K}^{-1} \text{ mol}^{-1}$ |
|----------------------------------|-------------------------------------------|------------------------------------------------|
| $\text{C}_3\text{H}_8(\text{g})$ | −104.7                                    | 270.3                                          |
| $\text{C}_3\text{H}_6(\text{g})$ | +20.0                                     | 267.0                                          |
| $\text{H}_2(\text{g})$           | 0                                         | 130.7                                          |

(a) Predict the sign of  $\Delta S^\ominus$  for this reaction. Explain your answer. **[1]**

(b) Calculate  $\Delta G^\ominus$  at 25 °C, and state whether the reaction is feasible at this temperature. **[4]**

(c) Calculate the minimum temperature, in °C, at which the reaction is feasible. [2]

(a) Positive: one mole of gas becomes two moles of gas. **B1**

(b)  $\Delta H^\ominus = (+20.0) + 0 - (-104.7) = +124.7 \text{ kJ mol}^{-1}$  **M1**

$\Delta S^\ominus = 267.0 + 130.7 - 270.3 = +127.4 \text{ J K}^{-1} \text{ mol}^{-1}$  **M1** (the element hydrogen has a zero  $\Delta H_f$  but **not** a zero entropy).

$$\Delta G^\ominus = 124.7 - 298 \times 0.1274 = +86.7 \text{ kJ mol}^{-1}$$

**M1** for the Gibbs equation with  $T = 298$  and  $\Delta S$  in kJ, **A1** for +86.7 and "positive, so not feasible at 25 °C".

(c) At the minimum temperature  $\Delta G = 0$ , so **M1**

$$T = \frac{\Delta H}{\Delta S} = \frac{124.7}{0.1274} = 979 \text{ K} = 706 \text{ °C}$$

**A1** (subtract 273 to convert to °C). This is why the process runs in a hot furnace, not at room temperature.

### Example 4

The table gives  $\Delta H^\ominus$  and  $\Delta S^\ominus$  for two reactions of nitrogen oxides. Assume they do not change with temperature.

| Reaction                                                                            | $\Delta H^\ominus / \text{kJ mol}^{-1}$ | $\Delta S^\ominus / \text{J K}^{-1} \text{ mol}^{-1}$ |
|-------------------------------------------------------------------------------------|-----------------------------------------|-------------------------------------------------------|
| 1: $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$ | -114.1                                  | -146.7                                                |
| 2: $\text{N}_2\text{O}_4(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$              | +57.2                                   | +175.8                                                |

(a) Explain, without calculating, whether the graph of  $\Delta G^\ominus$  against  $T$  slopes upwards or downwards for each reaction. [2]

(b) Calculate  $\Delta G^\ominus$  for each reaction at 400 K. [2]

(c) Find the range of temperatures over which **both** reactions are feasible. [3]

(a) The gradient of the line is  $-\Delta S$ . Reaction 1 makes fewer moles of gas ( $3 \rightarrow 2$ ), so  $\Delta S$  is negative and the line slopes **upwards**. **B1** Reaction 2 makes more moles of gas ( $1 \rightarrow 2$ ), so  $\Delta S$  is positive and the line slopes **downwards**. **B1** The fourth diagram in "Understand it" shows both lines.

(b) Reaction 1:  $\Delta G = -114.1 - 400 \times (-0.1467) = -55.4 \text{ kJ mol}^{-1}$ . Reaction 2:  $\Delta G = 57.2 - 400 \times 0.1758 = -13.1 \text{ kJ mol}^{-1}$ . **B1 B1**

(c) Reaction 1 is feasible only **below**  $T = \frac{-114.1}{-0.1467} = 778 \text{ K}$ . **M1** Reaction 2 is feasible only **above**  $T = \frac{57.2}{0.1758} = 325 \text{ K}$ . **M1** So both are feasible between 325 K and 778 K. **A1** (Part (b) agrees: 400 K is in this range and both values are negative.)

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## Common mistakes

- **Saying a lattice energy is "bigger" or "greater".** Examiners can't tell whether you mean more negative or less. Write "more exothermic" or "more negative", and do the same for hydration enthalpies.
- **Giving only one factor.** In lattice energy and hydration questions, candidates often mention only the radius and ignore the higher charge (for example on  $\text{Mg}^{2+}$ ), or give a factor without its direction. State both, each with "so the attraction is stronger/weaker".
- **"Electron affinity decreases down the group."** For a negative quantity this is ambiguous. Say "becomes less exothermic".
- **Confusing electron affinity with ionisation energy:** an electron affinity **gains** an electron; an ionisation energy **removes** one.
- **Using the wrong data in a Born–Haber cycle:** the bond energy instead of the atomisation energy (or both), a second ionisation energy for a +1 metal, an ionisation energy of the non-metal. Tables include these deliberately.
- **Missing multipliers.** Two halide ions in  $\text{MX}_2$  means  $2\Delta H_{\text{at}}$  and  $2EA_1$ ; two metal ions in  $\text{M}_2\text{X}$  means  $2\Delta H_{\text{at}}$  and  $2IE_1$ . The same goes for  $\Delta H_{\text{hyd}}$  in a solution cycle and for coefficients in  $\Delta S^\ominus$ .
- **Mixing J and kJ.** Entropies are in  $\text{J K}^{-1} \text{mol}^{-1}$ ;  $\Delta H$  is in  $\text{kJ mol}^{-1}$ . Divide  $\Delta S$  by 1000 before using the Gibbs equation.
- **Using °C in the Gibbs equation.** 25 °C is 298 K; 450 °C is 723 K. Some candidates don't convert.
- **Explaining feasibility without  $\Delta G$ .** "The reaction is more feasible because  $\Delta S$  is positive" is not enough; say what happens to  $-T\Delta S$  and therefore to  $\Delta G$ .
- **Explaining an entropy sign vaguely.** "It becomes more disordered" without the reason loses the mark; say "more moles of gas are formed" or name the change of state.
- **Drawing a Born–Haber cycle for the wrong reaction,** such as a combustion. A Born–Haber cycle is always for forming an ionic solid from its elements.
- **Not showing working.** Many energy-cycle marks are for the set-up expression; with only a final number, one slip loses everything.

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## How to get the marks

- **Definitions** are marked point by point: one mole, of what, in which state, turning into what. For lattice energy both "one mole of ionic solid formed" and "from gaseous ions" are needed for 2 marks.
- **Equations for energy changes** need the right amount (one mole of the species being defined) and **every** state symbol.
- **Born–Haber and solution calculations** usually have three marks: choosing the right values, the multipliers, then signs and the answer. Write the full expression with every value in brackets before evaluating.
- **"It may be helpful to draw a labelled energy cycle":** do. It shows the examiner your route and protects the method marks.

- **Gibbs calculations:** write  $\Delta G = \Delta H - T\Delta S$ , show  $T$  in kelvin and  $\Delta S$  in kJ, and end with a conclusion about feasibility. Answers are often required to at least 3 significant figures.
- **"Show that" a reaction is feasible:** calculate  $\Delta G$  and say "negative, so feasible".
- **"Explain" for trends:** factor  $\rightarrow$  effect on attraction  $\rightarrow$  effect on the energy change, in that order. For Group 2 solubility, say what happens to **both** energies, **which** changes more, and what that does to  $\Delta H_{\text{sol}}$ .
- **"Suggest"** means you apply the ideas to something unfamiliar (a new compound or ion); a reasoned answer from charge and radius is what is wanted.
- **Error carried forward:** a wrong earlier answer used correctly still earns later marks, so always finish the calculation.
- **Graph questions:** use widely spaced points for the gradient, show the working, and give units ( $\text{J K}^{-1} \text{mol}^{-1}$  for  $\Delta S$ ).

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## Quick check

1. Write equations, with state symbols, for (a) the standard enthalpy change of atomisation of mercury, (b) the lattice energy of magnesium hydroxide, (c) the enthalpy change of solution of ammonium nitrate.
2. Give the sign of  $\Delta S$  for each change and a reason: (a) molten naphthalene solidifying; (b)  $\text{CaC}_2(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{Ca}(\text{OH})_2(\text{s}) + \text{C}_2\text{H}_2(\text{g})$ ; (c) a sample of argon warmed from 300 K to 400 K; (d)  $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$ .
3. For  $\text{C}_2\text{H}_2(\text{g}) + 2\text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g})$ ,  $\Delta H^\ominus = -311.4 \text{ kJ mol}^{-1}$ . The standard entropies, in  $\text{J K}^{-1} \text{mol}^{-1}$ , are  $\text{C}_2\text{H}_2$  200.9,  $\text{H}_2$  130.7 and  $\text{C}_2\text{H}_6$  229.2. Calculate  $\Delta S^\ominus$ , then  $\Delta G^\ominus$  at 298 K and at 1400 K. Find the highest temperature at which the reaction is feasible.
4. Put SrO, SrS and NaBr in order of lattice energy, most exothermic first, and explain the order.
5. For bromine boiling,  $\text{Br}_2(\text{l}) \rightarrow \text{Br}_2(\text{g})$ ,  $\Delta H^\ominus = +30.9 \text{ kJ mol}^{-1}$ . The standard entropies of  $\text{Br}_2(\text{l})$  and  $\text{Br}_2(\text{g})$  are 152.2 and  $245.5 \text{ J K}^{-1} \text{mol}^{-1}$ . Calculate  $\Delta S^\ominus$  and use it to estimate the boiling point of bromine in  $^\circ\text{C}$ .

## Answers

- (a)  $\text{Hg(l)} \rightarrow \text{Hg(g)}$  (mercury is a liquid at 298 K). (b)  $\text{Mg}^{2+}(\text{g}) + 2\text{OH}^{-}(\text{g}) \rightarrow \text{Mg(OH)}_2(\text{s})$ . (c)  $\text{NH}_4\text{NO}_3(\text{s}) \rightarrow \text{NH}_4^{+}(\text{aq}) + \text{NO}_3^{-}(\text{aq})$  (or + aq on the left).
- (a) Negative: a liquid becomes a solid, so the particles are more ordered. (b) Positive: a gas is made from a solid and a liquid (no gas becomes one mole of gas). (c) Positive: the atoms have more energy to share out and move faster. (d) Negative: three moles of gas become two.
- $\Delta S^{\ominus} = 229.2 - 200.9 - 2(130.7) = -233.1 \text{ J K}^{-1} \text{ mol}^{-1}$  (three moles of gas become one). At 298 K,  $\Delta G^{\ominus} = -311.4 - 298 \times (-0.2331) = -241.9 \text{ kJ mol}^{-1}$ : negative, so feasible. At 1400 K,  $\Delta G^{\ominus} = -311.4 - 1400 \times (-0.2331) = +14.9 \text{ kJ mol}^{-1}$ : positive, so not feasible. Both  $\Delta H$  and  $\Delta S$  are negative, so the reaction is feasible only **below**  $T = \frac{-311.4}{-0.2331} = 1336 \text{ K}$ .
- $\text{SrO} > \text{SrS} > \text{NaBr}$ . SrO and SrS both have  $2+$  and  $2-$  ions, so they attract far more strongly than the  $1+$  and  $1-$  ions in NaBr.  $\text{O}^{2-}$  is smaller than  $\text{S}^{2-}$ , so in SrO the ion centres are closer and the attraction is stronger than in SrS.
- $\Delta S^{\ominus} = 245.5 - 152.2 = +93.3 \text{ J K}^{-1} \text{ mol}^{-1}$ . At the boiling point liquid and gas are in balance, so  $\Delta G = 0$ :  $T = \frac{30.9}{0.0933} = 331 \text{ K}$ , which is  $58^{\circ} \text{C}$ .

## Past questions to try

- 9701/42/O/N/24 Q2**: hydration trends across a period, a solution cycle with distractors, and  $\Delta G$  for dissolving.
- 9701/42/M/J/24 Q1**: Group 2 sulfate solubility, lattice energy factors and a Born–Haber cycle for a  $+1/-2$  solid.
- 9701/42/M/J/24 Q3**:  $\Delta G$  from formation and entropy data, then a maximum feasible temperature.
- 9701/42/M/J/22 Q4**: plotting a  $\Delta G-T$  graph and finding  $\Delta S$  from its gradient (part (a)).