Chemistry (A-level)

Lattice energy (Chapter 19 TB)

- **Lattice energy** is the enthalpy change when 1 mole of an ionic compound is formed from its gaseous ions under standard conditions
- The lattice energy is always exothermic; the more exothermic the lattice energy, the stronger the ionic bonding in the lattice

$Na^+(g) + Cl^-(g) \longrightarrow NaCl(s) \quad \Delta H^\ominus_{latt} = -787\ kJ\ mol^{-1}$

$Mg^{2+}(g) + 2Cl^-(g) \longrightarrow MgCl_2(s) \quad \Delta H^\ominus_{latt} = -2526\ kJ\ mol^{-1}$

- The standard **enthalpy change of atomisation**, $\Delta H^\ominus_{at}$, is the enthalpy change when 1 mole of gaseous atoms is formed from its element under standard conditions; is endothermic

$Li(s) \longrightarrow Li(g) \quad \Delta H^\ominus_{at} = +161\ kJ\ mol^{-1}$

$\frac{1}{2}Cl_2(g) \longrightarrow Cl(g) \quad \Delta H^\ominus_{at} = +122\ kJ\ mol^{-1}$

- The **first electron affinity**, $\Delta H^\ominus_{ea1}$, is the enthalpy change when 1 mole of electrons is added to 1 mole of gaseous atoms to form 1 mole of gaseous 1^- ions under standard conditions; is exothermic

$Cl(g) + e^- \longrightarrow Cl^-(g) \quad \Delta H^\ominus_{ea1} = -348\ kJ\ mol^{-1}$

$S(g) + e^- \longrightarrow S^-(g) \quad \Delta H^\ominus_{ea1} = -200\ kJ\ mol^{-1}$

- The **second electron affinity**, $\Delta H^\ominus_{ea2}$, is the enthalpy change when 1 mole of electrons is added to 1 mole of gaseous 1^- ions to form 1 mole of gaseous 2^- ions under standard conditions; is endothermic – so are the 3rd electron affinities

1st electron affinity:

$O(g) + e^- \longrightarrow O^-(g) \quad \Delta H^\ominus_{ea1} = -141\ kJ\ mol^{-1}$

2nd electron affinity:

$O^-(g) + e^- \longrightarrow O^{2-}(g) \quad \Delta H^\ominus_{ea2} = +798\ kJ\ mol^{-1}$

- ➢ The overall enthalpy change in forming an oxide ion from an oxygen atom:

$O(g) + 2e^- \longrightarrow O^{2-}(g)$

$\Delta H^\ominus_{ea1} + \Delta H^\ominus_{ea2} = (-141) + (+798) = +657\ kJ\ mol^{-1}$

- The **1st ionisation energy**, $\Delta H^\ominus_{i}$, of an element is the energy needed to remove one electron from each atom in one mole of atoms of the element in the gaseous state to form one mole of gaseous 1^+ ions

1st ionisation energy: $Ca(g) \longrightarrow Ca^+(g) + e^-$

$\Delta H_{i1} = 590\ kJ\ mol^{-1}$

2nd ionisation energy: $Ca^+(g) \longrightarrow Ca^{2+}(g) + e^-$

$\Delta H_{i2} = 1150\ kJ\ mol^{-1}$

3rd ionisation energy: $Ca^{2+}(g) \longrightarrow Ca^{3+}(g) + e^-$

$\Delta H_{i3} = 4940\ kJ\ mol^{-1}$

- A **Born-Haber cycle** is a particular type of enthalpy cycle used to calculate lattice energy

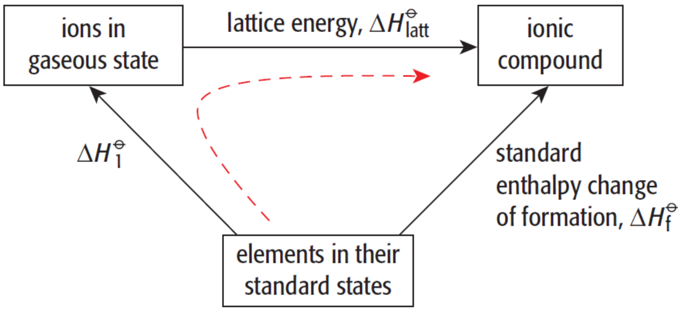


Figure 19.2 A simple enthalpy cycle that can be used to calculate lattice energy. The dashed line shows the two-step route: using Hess's law, $\Delta H^{\ominus}_{1} + \Delta H^{\ominus}_{latt} = \Delta H^{\ominus}_{f}$.

- Lattice energy of lithium fluoride:

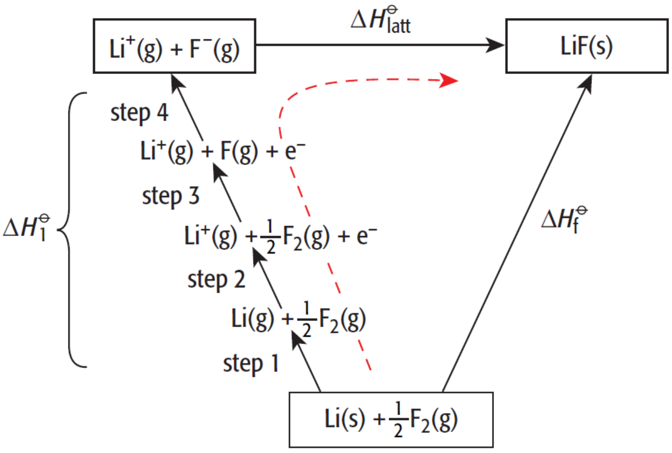


Figure 19.3 An enthalpy cycle that can be used to calculate the lattice energy of lithium fluoride. The dashed line shows the two-step route.

- <u>$\Delta H^{\ominus}_{1}$ obtained by:</u>
  - Step 1: convert solid lithium into gaseous lithium ($\Delta H^{\ominus}_{at}$)

$Li(s) \longrightarrow Li(g)$ $\Delta H^{\ominus}_{at} = +161\ kJ\ mol^{-1}$

  - Step 2: convert gaseous lithium atoms into gaseous lithium ions ($\Delta H^{\ominus}_{i}$)

$Li(g) \longrightarrow Li+(g) + e^-$ $\Delta H^{\ominus}_{i1} = +520\ kJ\ mol^{-1}$

  - Step 3: convert fluorine molecules into fluorine atoms ($\Delta H^{\ominus}_{at}$)

$\frac{1}{2}F_2(g) \longrightarrow F(g)$ $\Delta H^{\ominus}_{at} = +79\ kJ\ mol^{-1}$

  - Step 4: convert gaseous fluorine atoms into gaseous fluoride ions ($\Delta H^{\ominus}_{ea1}$)

$F(g) + e^- \longrightarrow F^-(g)$ $\Delta H^{\ominus}_{ea1} = -328\ kJ\ mol^{-1}$

  - <u>Applying Hess's law:</u>

$$\Delta H^{\ominus}_{latt} = \Delta H^{\ominus}_{f} - \{\Delta H^{\ominus}_{at}[Li] + \Delta H^{\ominus}_{i1}[Li] + \Delta H^{\ominus}_{at}[F] + \Delta H^{\ominus}_{ea1}[F]\}$$

$$\Delta H^{\ominus}_{latt} = (-617) - \{\underbrace{(+161) + (+520) + (+79) + (-328)}_{= +432}\}$$

$$\Delta H^{\ominus}_{latt} = (-617) - (+432) = -1049\ kJ\ mol^{-1}$$

- The **Born-Haber cycle** as an energy level diagram:

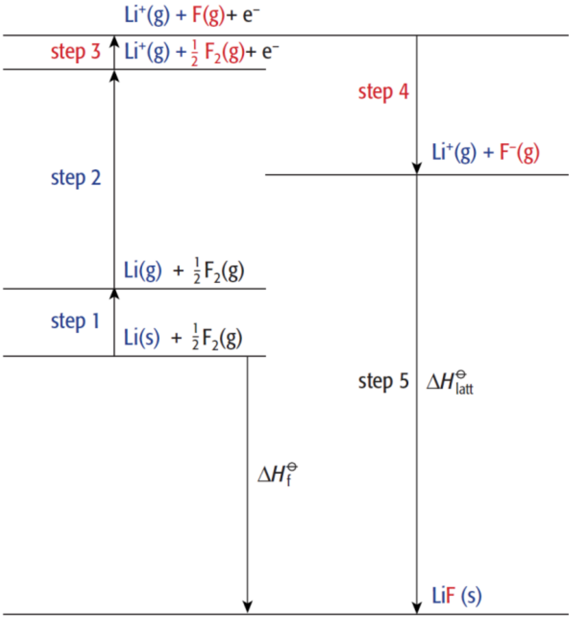


Figure 19.4 Born–Haber cycle for lithium fluoride.

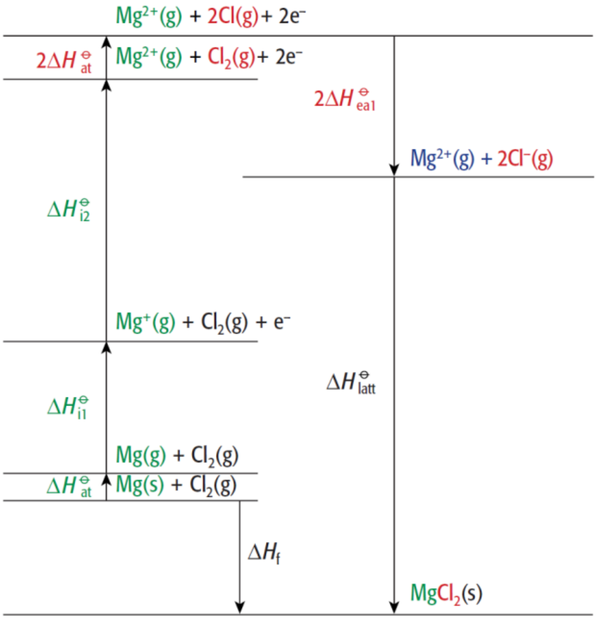


Figure 19.5 Born–Haber cycle for magnesium chloride.

- Differences between lithium fluoride's and magnesium chloride's:
    - Mg^{2+} requires 1st and 2nd ionisation energy to be calculated

$$Mg(g) \longrightarrow Mg^{+}(g) + e^{-} \qquad \Delta H^{\ominus}_{i1} = +736\,kJ\,mol^{-1}$$

$$Mg^{+}(g) \longrightarrow Mg^{2+}(g) + e^{-} \qquad \Delta H^{\ominus}_{i2} = +1450\,kJ\,mol^{-1}$$

-
    - Two chloride ions in $MgCl_2$, hence the values of $\Delta H^{\ominus}_{at}$ & $\Delta H^{\ominus}_{ea1}$ should be multiplied by 2

$$Cl_2(g) \longrightarrow 2Cl(g) \quad 2\Delta H^{\ominus}_{at} = 2 \times (+122) = +244\,kJ\,mol^{-1}$$

$$2Cl(g) + 2e^{-} \longrightarrow 2Cl^{-}(g)$$

$$2\Delta H^{\ominus}_{ea1} = 2 \times (-348) = -696\,kJ\,mol^{-1}$$

- Aluminium oxide, Al_2O_3, contains two aluminium ions (Al^{3+}) and three oxide ions (O^{2-})
    - Enthalpy changes for aluminium:

$$Al(s) \xrightarrow[+326\,kJ\,mol^{-1}]{\Delta H^{\ominus}_{at}} Al(g) \xrightarrow[+577\,kJ\,mol^{-1}]{\Delta H^{\ominus}_{i1}} Al^{+}(g) \xrightarrow[+1820\,kJ\,mol^{-1}]{\Delta H^{\ominus}_{i2}} Al^{2+}(g) \xrightarrow[+2470\,kJ\,mol^{-1}]{\Delta H^{\ominus}_{i3}} Al^{3+}(g)$$

-
    - Enthalpy changes for oxygen molecules:

$$O_2(g) \xrightarrow[+249\,kJ\,mol^{-1}]{\Delta H^{\ominus}_{at}} O(g) \xrightarrow[-141\,kJ\,mol^{-1}]{\Delta H^{\ominus}_{ea1}} O^{-}(g) \xrightarrow[+798\,kJ\,mol^{-1}]{\Delta H^{\ominus}_{ea2}} O^{2-}(g)$$

- Lattice energy arises from the electrostatic force of attraction of oppositely charged ions when the crystalline lattice is formed

- As the **size of the ion** increases, the lattice energy becomes less exothermic, e.g. the lattice energy gets less exothermic as the size of the anion increases from F^- to I^-
  - Due to the decrease in charge density with the same ionic charge, as the same charge is spread over a larger volume, resulting in weaker electrostatic forces of attraction in the ionic lattice, e.g. NaF has a less exothermic lattice energy than LiF

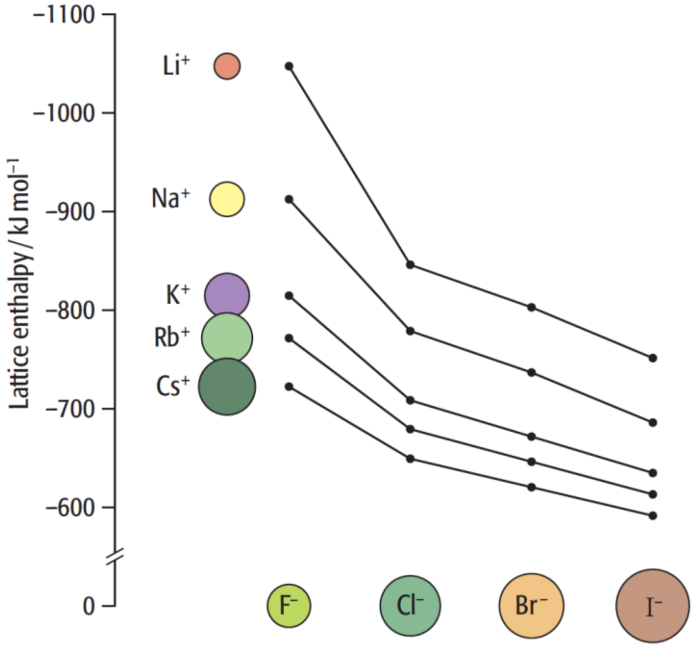


Figure 19.6 Lattice enthalpies of the Group 1 halides.

- The lattice energy becomes more exothermic (stronger ionic bonds formed) as the **ionic charge** increases (higher charge density), e.g. LiF < MgO:

$$\Delta H^{\ominus}_{\text{latt}}[\text{LiF}] = -1049\,\text{kJ mol}^{-1}$$

$$\Delta H^{\ominus}_{\text{latt}}[\text{MgO}] = -3923\,\text{kJ mol}^{-1}$$

Group 2 (Chapter 10)

- The positive charge on the cation in an ionic lattice may attract the electrons in the anion towards it, resulting to distortion of the electron cloud of the anion, causing it to no longer be spherical (**ion polarisation**); the ability of a cation to attract electrons and distort an anion is called the **polarising power** of the cation

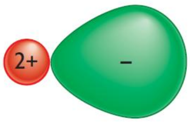


Figure 19.7 Ion polarisation. A small highly charged cation can distort the shape of the anion.

- The degree of polarisation on an anion depends on:
  - The charge density of the cation
  - The anion's polarisability
- And more polarised if:
  - The cation is small

  - The cation has a charge of 2+ or 3+
  - The anion is large
  - The anion has a charge of 2- or 3-
- Many ionic bonding have some covalent character due to ion polarisation
- The Group 2 carbonates decompose to their oxides and carbon dioxide on heating:

$$CaCO_3(s) \xrightarrow{heat} CaO(s) + CO_2(g)$$

- The further down the group, the higher temperature required to decompose the carbonate

Group 2 carbonate	**Decomposition temperature / °C**	**Enthalpy change of reaction / kJ mol^{-1}**
magnesium carbonate	540	+117
calcium carbonate	900	+176
strontium carbonate	1280	+238
barium carbonate	1360	+268

Table 19.1 Enthalpy change of reaction values for the decomposition of some Group 2 carbonates.

  - So their relative stabilities increases down the group:

$$BaCO_3 > SrCO_3 > CaCO_3 > MgCO_3.$$

- Ion polarisation of **carbonates**:
  - The ionic carbonate ion has large ionic radius, hence easily polarised (given a small highly charged cation)
  - Group 2 cations' ionic radius increase down the group:

$$Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$$

  - The smaller the ionic radius of the cation, the better the polarising power, hence degree of polarisation of carbonate ion by Group 2 cation follows:

$$Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$$

  - The greater the polarisation, the easier it is to weaken a C – O bond in the carbonate and form the CO2 and oxide on heating
- Thermal decomposition of Group 2 nitrates has a similar pattern, decompose to form nitrogen dioxide, oxygen and the oxide:

$$2Mg(NO_3)_2(s) \longrightarrow 2MgO(s) + 4NO_2(g) + O_2(g)$$

  - Order of stability:

$$Ba(NO_3)_2 > Sr(NO_3)_2 > Ca(NO_3)_2 > Mg(NO_3)_2.$$

Figure 19.8 Magnesium ions are better polarisers of carbonate ions than calcium ions.

- The **enthalpy change of solution**, $\Delta H^{\ominus}_{sol}$, is the energy when 1 mole of an ionic solid dissolve in sufficient water to form a very dilute solution; can be exothermic and endothermic

$$MgCl_2(s) + aq \longrightarrow Mg^{2+}(aq) + 2Cl^-(aq) \qquad \Delta H^{\ominus}_{sol} = -55\,kJ\,mol^{-1}$$

$$NaCl(s) + aq \longrightarrow Na^+(aq) + Cl^-(aq) \qquad \Delta H^{\ominus}_{sol} = +3.9\,kJ\,mol^{-1}$$

- Ion-dipole bonds are formed when ionic solid dissolves in water:

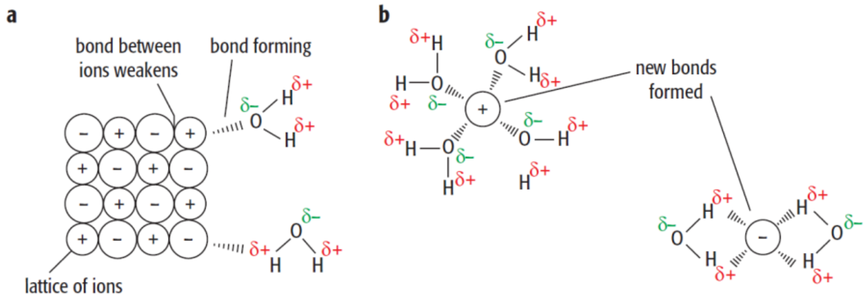


Figure 19.9 **a** Water molecules forming ion–dipole bonds with an ionic compound. **b** Hydrated ions in solution.

- The **enthalpy change of hydration**, $\Delta H^{\ominus}_{hyd}$, is the enthalpy change when 1 mole of a gaseous ion dissolves in sufficient water to form a very dilute solution; is exothermic

$$Ca^{2+}(g) + aq \longrightarrow Ca^{2+}(aq) \qquad \Delta H^{\ominus}_{hyd} = -1650\,kJ\,mol^{-1}$$

$$Cl^-(g) + aq \longrightarrow Cl^-(aq) \qquad \Delta H^{\ominus}_{hyd} = -364\,kJ\,mol^{-1}$$

  - More exothermic for ions with the same charge but smaller ionic radii, e.g. $\Delta H^{\ominus}_{hyd}$ is more exothermic for Li+ than for Na+
  - More exothermic for ions with the same radii but a larger charge, e.g. $\Delta H^{\ominus}_{hyd}$ is more exothermic for Mg2+ than for Li+.
- Enthalpy changes in solution:

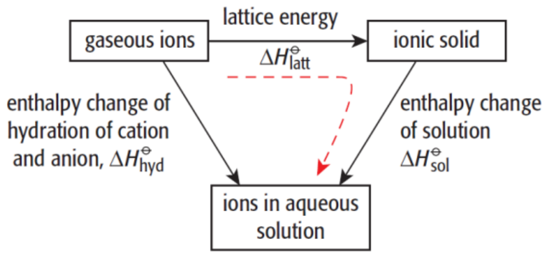


Figure 19.10 An enthalpy cycle involving lattice energy, enthalpy change of hydration and enthalpy change of solution.

$$\Delta H^{\ominus}_{latt} + \Delta H^{\ominus}_{sol} = \Delta H^{\ominus}_{hyd}$$

- The solubility of Group 2 sulfates decreases as the radius of the metal ion increases

Compound	Solubility / mol dm^{-3}
magnesium sulfate	1.83
calcium sulfate	4.66×10^{-2}
strontium sulfate	7.11×10^{-4}
barium sulfate	9.43×10^{-6}

Table 19.2 Solubilities in water of some Group 2 sulfates.

- Change in hydration enthalpy down the group:
  - Smaller ions (with same charge) have greater enthalpy changes of hydration
  - So the enthalpy change of hydration decreases (gets less exothermic) following:

$Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$

  - Decrease is large down the group, depending entirely on the increase in size of the cation, as the anion is unchanged
- Change in lattice energy down the group:
  - Smaller ions form greater lattice energy
  - So the lattice energy decreases following:

$Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$

  - Lattice energy is inversely proportional to the sum of the radii (cation & anion)
  - Sulfate ion much larger than group 2 cations, hence it contributes a greater part to the change in lattice energy down the group
  - Hence decrease in lattice energy is small down the group, determined more by the size of the sulfate ions than the size of the cations
- The lattice energy of the sulfates decreases by relatively smaller values
- The enthalpy change of hydration decreases by relatively larger values down the group
- $\Delta H^{\ominus}_{sol}$ becomes more endothermic down the group (figure 19.14)
- Solubility of Group 2 sulfates decreases down the group

- The higher the positive value of $\Delta H^{\ominus}_{sol}$ the less soluble the salt

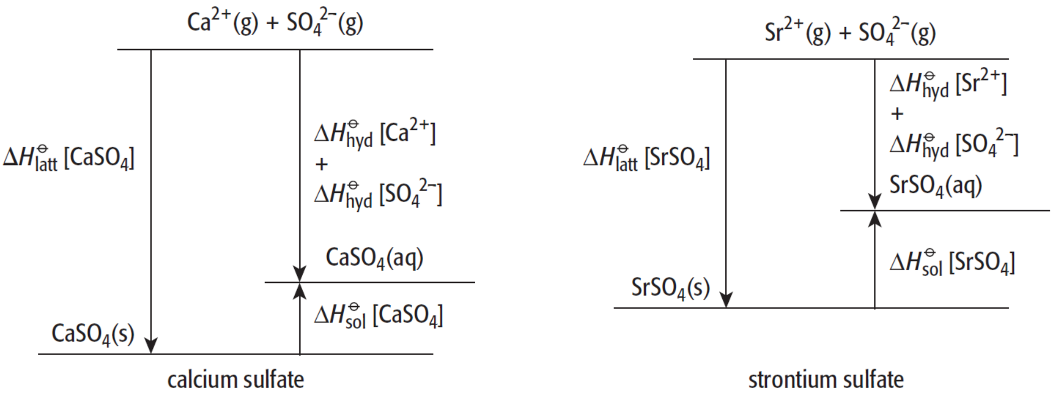


Figure 19.14 Enthalpy cycles comparing the enthalpy change of solution of calcium sulfate and strontium sulfate.

Entropy and Gibbs free energy (Chapter 23 TB):

- **Entropy** is a measure of the 'disorder' of a system, and that a system becomes more stable when its energy is spread out in a more disordered state
- **Standard molar entropy** is the entropy when one mole of substance in its standard state
- The values of all molar entropies are positive
- Gases generally have much higher entropy values than liquids – which have higher entropy values than solids; hence the more gas molecules present, the greater the number of ways of arranging them, hence higher entropy:

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

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

- Increase in entropy of the system due to the greater number of moles of gas molecules in the products (5 molecules) than in the reactants (2 molecules); there are two different product molecules and only one type of reactant molecule, contributing to a greater disorder, increasing the stability (energetically) of the system

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

- Decrease in entropy, hence the reactants are more stable than the product

- Simpler substances with fewer atoms have lower entropy values than more complex substances (more no. of atoms)
- For similar substances, the harder substance has lower entropy value
- Gradual increase in entropy as the temperature of the substance is increased

Substance	$S^\ominus$ / J K^{-1} mol^{-1}	Substance	$S^\ominus$ / J K^{-1} mol^{-1}
diamond (s)	2.4	methanol (l)	239.7
graphite (s)	5.7	water (l)	69.9
calcium (s)	41.4	carbon monoxide (g)	197.6
lead (s)	64.8	hydrogen (g)	130.6
calcium oxide (s)	39.7	helium (g)	126.0
calcium carbonate (s)	92.9	ammonia (g)	192.3
mercury (l)	76.0	oxygen (g)	205.0
bromine (l)	151.6	carbon dioxide (g)	213.6

Table 23.1 Standard molar entropy values of some solids, liquids and gases. The states are shown as state symbols after each substance.

- For an exothermic reaction, energy released to the surroundings, and causes translation and rotation of molecules in the surroundings – increasing its arrangements – hence there is likely to be an increase in entropy and increase in the chance for chemical change to occur spontaneously
- For an endothermic reaction, energy absorbed from the surroundings, decreasing its arrangements, hence there is likely to be a decrease in entropy and decrease in the chance for a chemical reaction to occur spontaneously
- Total enthalpy change is given by:

$$\Delta S^\ominus_{\text{total}} = \Delta S^\ominus_{\text{system}} + \Delta S^\ominus_{\text{surroundings}}$$

- When the total enthalpy change is positive, the reaction will occur spontaneously, reaction is **feasible**
- When it is negative, the reaction is not likely to occur (not feasible)

- Entropy change of the system is given by:

$$\Delta S^\ominus_{\text{system}} = S^\ominus_{\text{products}} - S^\ominus_{\text{reactants}}$$

Calculate the entropy change of the system for the reaction:

$$2Ca(s) + O_2(g) \longrightarrow 2CaO(s)$$

The standard entropy values are:

$S^\ominus[Ca(s)] = 41.40$ J K^{-1} mol^{-1}

$S^\ominus[O_2(g)] = 205.0$ J K^{-1} mol^{-1}

$S^\ominus[CaO(s)] = 39.70$ J K^{-1} mol^{-1}

$\Delta S^\ominus_{\text{system}} = S^\ominus_{\text{products}} - S^\ominus_{\text{reactants}}$

$= 2 \times S^\ominus[CaO(s)] - \{2 \times S^\ominus[Ca(s)] + S^\ominus[O_2(g)]\}$

$= 2 \times 39.70 - \{(2 \times 41.40) + 205.0\}$

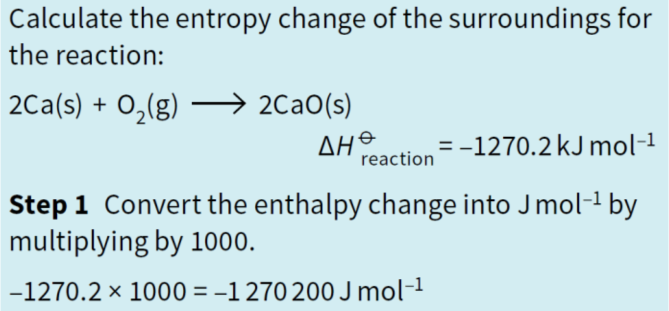
$= 79.40 - 287.8$

$\Delta S^\ominus_{\text{system}} = -208.4$ J K^{-1} mol^{-1}

- Entropy change of the surroundings is given by:

$$\Delta S^{\ominus}_{\text{surroundings}} = \frac{-\Delta H^{\ominus}_{\text{reaction}}}{T}$$

  - $\Delta H^{\ominus}_{\text{reaction}}$ is the standard enthalpy change of the reaction
  - T is the temperature in Kelvin; where at standard temperature: 298 K

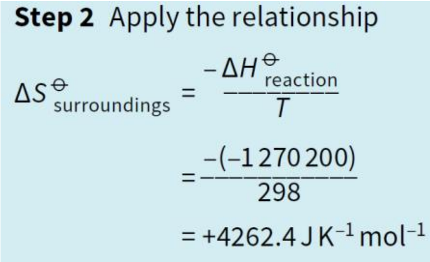

Calculate the entropy change of the surroundings for the reaction:

$$2Ca(s) + O_2(g) \longrightarrow 2CaO(s)$$

$$\Delta H^{\ominus}_{\text{reaction}} = -1270.2\ \text{kJ mol}^{-1}$$

Step 1 Convert the enthalpy change into J mol^{-1} by multiplying by 1000.

$-1270.2 \times 1000 = -1\,270\,200\ \text{J mol}^{-1}$

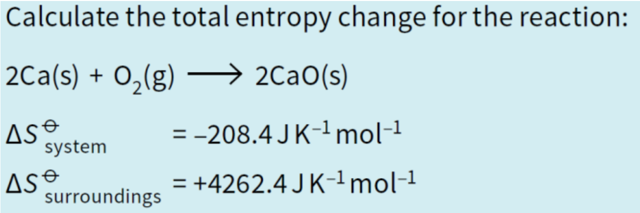

Step 2 Apply the relationship

$$\Delta S^{\ominus}_{\text{surroundings}} = \frac{-\Delta H^{\ominus}_{\text{reaction}}}{T} = \frac{-(-1\,270\,200)}{298} = +4262.4\ \text{J K}^{-1}\text{mol}^{-1}$$

- Total enthalpy change can also be written as:

$$\Delta S^{\ominus}_{\text{total}} = \Delta S^{\ominus}_{\text{system}} - \Delta H^{\ominus}_{\text{reaction}}/T$$

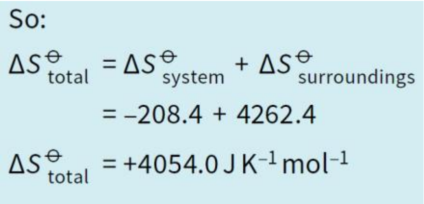
- E.g. of a feasible reaction:


Calculate the total entropy change for the reaction:

$$2Ca(s) + O_2(g) \longrightarrow 2CaO(s)$$

$\Delta S^{\ominus}_{\text{system}} = -208.4\ \text{J K}^{-1}\text{mol}^{-1}$

$\Delta S^{\ominus}_{\text{surroundings}} = +4262.4\ \text{J K}^{-1}\text{mol}^{-1}$


So:

$\Delta S^{\ominus}_{\text{total}} = \Delta S^{\ominus}_{\text{system}} + \Delta S^{\ominus}_{\text{surroundings}}$

$= -208.4 + 4262.4$

$\Delta S^{\ominus}_{\text{total}} = +4054.0\ \text{J K}^{-1}\text{mol}^{-1}$

- E.g. of thermal decomposition of zinc carbonate:

$$ZnCO_3(s) \longrightarrow ZnO(s) + CO_2(g)$$

$$\Delta H^{\ominus}_{\text{reaction}} = +72.3\ \text{kJ mol}^{-1}$$

For this reaction $S^{\ominus}_{\text{system}} = +174.8\ \text{J K}^{-1}\text{mol}^{-1}$ (the same for both temperatures).

Reaction at 298 K

$\Delta S^{\ominus}_{\text{surroundings}} = \frac{-72\,300}{298}$

$= -242.6\ \text{J K}^{-1}\text{mol}^{-1}$

$\Delta S^{\ominus}_{\text{total}} = +174.8 - 242.6\ \text{J K}^{-1}\text{mol}^{-1}$

$\Delta S^{\ominus}_{\text{total}} = -67.8\ \text{J K}^{-1}\text{mol}^{-1}$

Reaction at 550 K

$\Delta S^{\ominus}_{\text{surroundings}} = \frac{-72\,300}{550}$

$= -131.5\ \text{J K}^{-1}\text{mol}^{-1}$

$\Delta S^{\ominus}_{\text{total}} = +174.8 - 131.5\ \text{J K}^{-1}\text{mol}^{-1}$

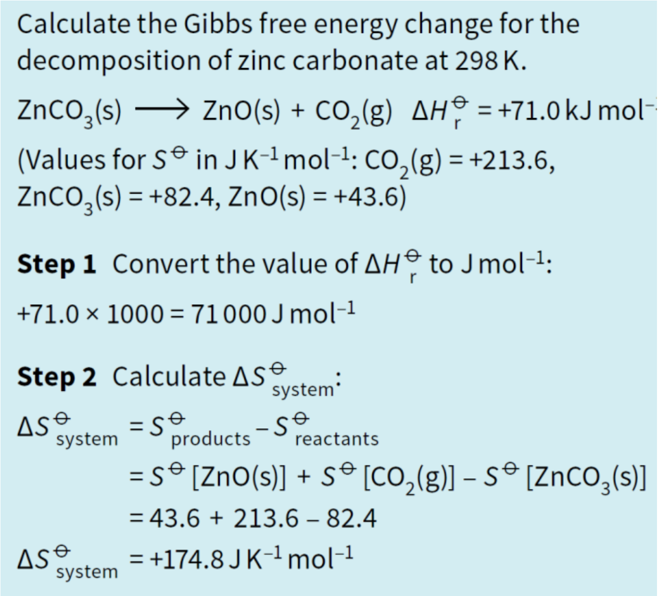
$\Delta S^{\ominus}_{\text{total}} = +43.3\ \text{J K}^{-1}\text{mol}^{-1}$

  - Reaction is spontaneous at 550 K, and does not occur at 298 K
- During exothermic reactions, the enthalpy change plays a bigger role than the entropy change of the system

- The Gibbs free energy change, Δ*G*, is given by:

$$\Delta G = \Delta H_{\text{reaction}} - T\Delta S_{\text{system}}$$

- The value of Δ*G* must be negative for a reaction to be spontaneous, as ΔS_{total} should be positive



Calculate the Gibbs free energy change for the decomposition of zinc carbonate at 298 K.

$ZnCO_3(s) \longrightarrow ZnO(s) + CO_2(g) \quad \Delta H^{\ominus}_r = +71.0\ \text{kJ mol}^{-}$

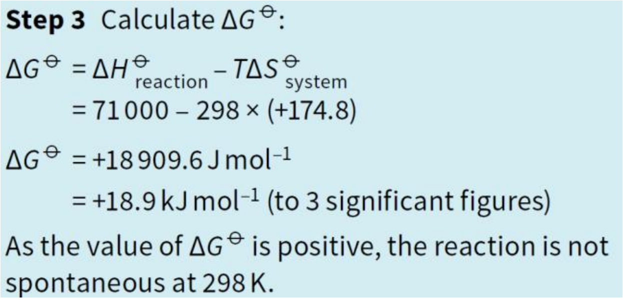
(Values for $S^{\ominus}$ in $\text{J K}^{-1}\text{mol}^{-1}$: $CO_2(g) = +213.6$, $ZnCO_3(s) = +82.4$, $ZnO(s) = +43.6$)

Step 1 Convert the value of $\Delta H^{\ominus}_r$ to J mol^{-1}:

$+71.0 \times 1000 = 71\,000\ \text{J mol}^{-1}$

Step 2 Calculate $\Delta S^{\ominus}_{\text{system}}$:

$$\begin{aligned}\Delta S^{\ominus}_{\text{system}} &= S^{\ominus}_{\text{products}} - S^{\ominus}_{\text{reactants}}\\ &= S^{\ominus}[ZnO(s)] + S^{\ominus}[CO_2(g)] - S^{\ominus}[ZnCO_3(s)]\\ &= 43.6 + 213.6 - 82.4\\ \Delta S^{\ominus}_{\text{system}} &= +174.8\ \text{J K}^{-1}\text{mol}^{-1}\end{aligned}$$

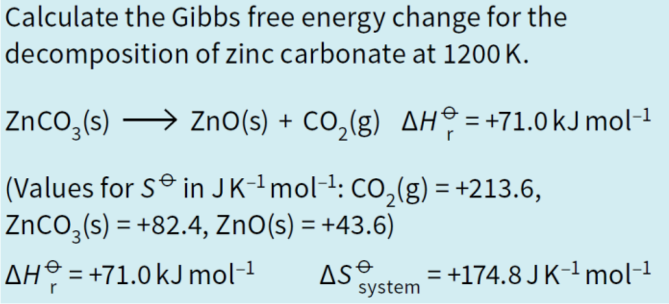


Step 3 Calculate $\Delta G^{\ominus}$:

$$\begin{aligned}\Delta G^{\ominus} &= \Delta H^{\ominus}_{\text{reaction}} - T\Delta S^{\ominus}_{\text{system}}\\ &= 71\,000 - 298 \times (+174.8)\\ \Delta G^{\ominus} &= +18\,909.6\ \text{J mol}^{-1}\\ &= +18.9\ \text{kJ mol}^{-1}\ \text{(to 3 significant figures)}\end{aligned}$$

As the value of $\Delta G^{\ominus}$ is positive, the reaction is not spontaneous at 298 K.

- In Gibbs free energy:
  - An exothermic reaction causes $\Delta H_{\text{reaction}}$ to be negative
    - If the value of ΔS_{system} is positive, the reaction will be spontaneous, Δ*G* is negative
    - If the value of ΔS_{system} is negative in low temperatures, Δ*G* is negative
    - If the value of ΔS_{system} is negative in high, Δ*G* is positive
  - An endothermic reaction causes $\Delta H_{\text{reaction}}$ to be positive
    - If the value of ΔS_{system} is negative, Δ*G* is positive
    - If the value of ΔS_{system} is positive in high temperatures, Δ*G* is negative
    - If the value of ΔS_{system} is positive in low temperatures, Δ*G* is positive

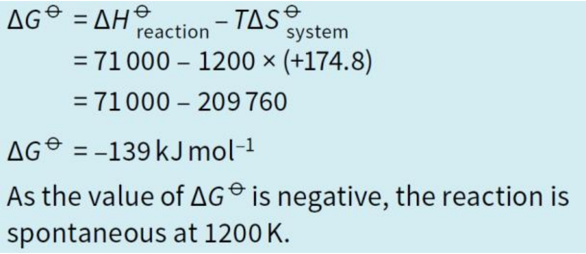


Calculate the Gibbs free energy change for the decomposition of zinc carbonate at 1200 K.

$ZnCO_3(s) \longrightarrow ZnO(s) + CO_2(g) \quad \Delta H^{\ominus}_r = +71.0\ \text{kJ mol}^{-1}$

(Values for $S^{\ominus}$ in $\text{J K}^{-1}\text{mol}^{-1}$: $CO_2(g) = +213.6$, $ZnCO_3(s) = +82.4$, $ZnO(s) = +43.6$)

$\Delta H^{\ominus}_r = +71.0\ \text{kJ mol}^{-1} \qquad \Delta S^{\ominus}_{\text{system}} = +174.8\ \text{J K}^{-1}\text{mol}^{-1}$



$$\begin{aligned}\Delta G^{\ominus} &= \Delta H^{\ominus}_{\text{reaction}} - T\Delta S^{\ominus}_{\text{system}}\\ &= 71\,000 - 1200 \times (+174.8)\\ &= 71\,000 - 209\,760\\ \Delta G^{\ominus} &= -139\ \text{kJ mol}^{-1}\end{aligned}$$

As the value of $\Delta G^{\ominus}$ is negative, the reaction is spontaneous at 1200 K.

- The electron affinity is a measure of the attraction between the incoming electron and the nucleus - **the stronger the attraction, the more energy is released** – hence electron affinity increases upward for the groups and from left to right across periods of a periodic table