5 Chemical energetics

Enthalpy changes and entropy changes accompany chemical reactions. This topic demonstrates why some reactions and processes are spontaneous and others are not.

5.1 Lattice energy ☐

5.2 ionic solid, its aqueous solution and Born-Haber cycles ☐

ENERGETICS

5 Chemical energetics

Enthalpy changes and entropy changes accompany chemical reactions. This topic demonstrates why some reactions and processes are spontaneous and others are not.

Learning outcomes
Candidates should be able to:

5.1 Enthalpy change, ΔH

a) explain that chemical reactions are accompanied by energy changes, principally in the form of heat energy; the energy changes can be exothermic (ΔH is negative) or endothermic (ΔH is positive)

b) explain and use the terms:
   - (i) *enthalpy change of reaction* and *standard condition*s, with particular reference to: formation, combustion, hydration, solution, neutralisation, atomisation
   - (ii) *bond energy* (ΔH positive, i.e. bond breaking)
   - **(iii) *lattice energy* (ΔH negative, i.e. gaseous ions to solid lattice)**

c) calculate enthalpy changes from appropriate experimental results, including the use of the relationship

$$\text{enthalpy change, } \Delta H = -mc\Delta T$$

d) explain, in qualitative terms, the effect of ionic charge and of ionic radius on the numerical magnitude of a lattice energy

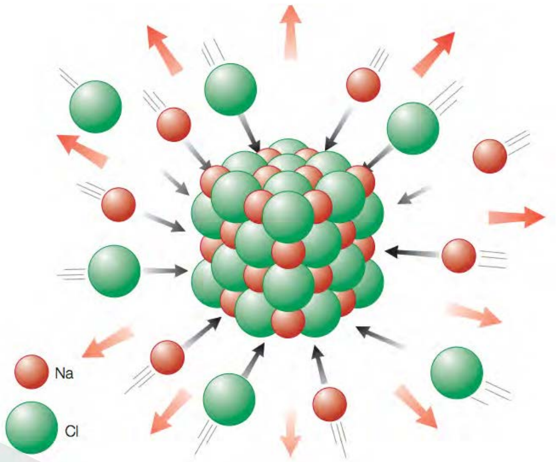
5.2 Hess' Law, including Born-Haber cycles

a) apply Hess' Law to construct simple energy cycles, and carry out calculations involving such cycles and relevant energy terms, with particular reference to:
   - (i) determining enthalpy changes that cannot be found by direct experiment, e.g. an enthalpy change of formation from enthalpy changes of combustion
   - (ii) average bond energies
   - **(iii) the formation of a simple ionic solid and of its aqueous solution**
   - **(iv) Born-Haber cycles (including ionisation energy and electron affinity)**

b) construct and interpret a reaction pathway diagram, in terms of the enthalpy change of the reaction and of the activation energy

LATTICE ENERGY

Lattice enthalpy is the energy that would be given out to the surroundings (red arrows) if one mole of a compound could be formed directly from free gaseous ions coming together (black arrows) and arranging themselves into a crystal lattice.



LATTICE ENERGY EXAMPLE

As gaseous ions form ionic solids, energy is released. This energy is known as the lattice enthalpy.

Gaseous ion → ionic solid

$Ca^{2+}(g) + 2Cl^{-}(g) \rightarrow CaCl_2(s)$ $\Delta H = \Delta L.E$

ionic solid → Gaseous ion

$CaCl_2(s) \rightarrow Ca^{2+}(g) + 2Cl^{-}(g)$ $\Delta H = -\Delta L.E$

Lattice enthalpy is a measure of the strength of the forces between the ions in an ionic solid. The greater the lattice enthalpy, the stronger the forces

LATTICE ENERGY

Lattice energy: the energy change (liberated) when:

1 mole of solid lattice is formed

from its constituent **gaseous** ions

under standard conditions (at 298K and 1 atm).

$M^+(g) + X^-(g) \rightarrow M^+X^-(s)$ $\Delta H = -x\ \text{kJ mol}^{-1}$ (Lattice energy)

this value is always negative

because lattice energy is always exothermic

LATTICE ENERGY

Lattice enthalpies are important because they can be used as a measure of the strength of ionic bonds in different ionic compounds.

The strengths of ionic bonds, measured as lattice enthalpies in kJ mol^{-1}, arise from the energy given out as billions upon billions of positive and negative ions come together to form a crystal lattice.

The force of attraction between the ions is stronger, and this results in a more exothermic lattice enthalpy, if:

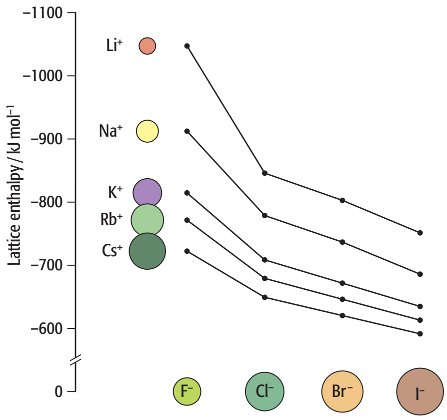
- the charges on the ions are large
- the ionic radii are small, allowing the ions to get closer to each other.

LATTICE ENERGY

The magnitude of Lattice energy depends on the the electrostatic attraction between the ions. It

increases as the charges on the ions increases

decreases as the size of the ions increases.



THE DISTANCE BETWEEN THE IONS

The smaller the distance between the ions, the greater the attraction between them, and the greater will be the lattice enthalpy.

For example, the sizes of the halide ions increase in the order:
$F^- < Cl^- < Br^- < I^-$

Lattice enthalpies for the sodium halides decreases in the same order (Note that each substance has the same ionic charges).

As the size of an anion increases, attraction between ions decreases and so does the lattice enthalpy.

NaF ΔH lat = – 926 kJ mol^{-1}
NaCl ΔH lat = – 787 kJ mol^{-1}
NaBr ΔH lat = – 752 kJ mol^{-1}

LATTICE ENERGY AND CHARGE ON IONS

The greater the charges on the ions, the greater the attraction between them, and the greater will be the lattice enthalpy.

E.g., sodium fluoride(Na^+F^-) and magnesium oxide($Mg^{2+}O^{2-}$) have similar structures.

The sizes of the cations are similar as both Na and Mg are in period 3, and the sizes of the anions are also similar as O and F are in Period 2.

The lattice enthalpy of the oxide is expected to be four times that of the fluoride.

NaF ΔH (lattice) = – 926 kJ mol^{-1} **MgO ΔH (lattice) = – 3800 kJ mol^{-1}**

QUESTIONS

1. Explain the term lattice energy. [2]

2. Write a balanced equation including state symbols to represent the lattice energy of magnesium chloride. [2]

QUESTIONS

3. Describe how, and explain why, the lattice enthalpy of magnesium fluoride differs from that of calcium chloride.

4. How would you expect the magnitude of lattice energy of magnesium oxide to compare with that of sodium oxide? Explain your reasoning.

BORN–HABER CYCLE

Born–Haber cycles are an application of Hess's law. They provide a model for the determination of lattice enthalpies which cannot be measured experimentally. They also enable chemists to test the ionic model of bonding in different substances.

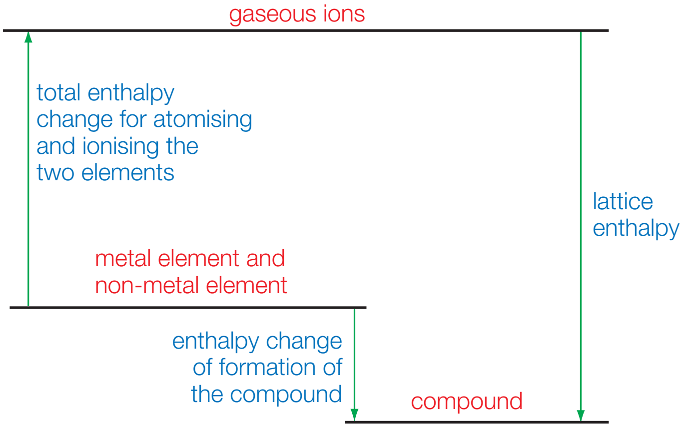
A Born–Haber cycle identifies all the enthalpy changes that contribute to the standard enthalpy change of formation of a compound. These changes involve:

- the energy (enthalpy changes) required to create free gaseous ions by atomising and then ionising the elements
- the energy given out (the lattice enthalpy) when the ions come together to form a crystal lattice.

BORN–HABER CYCLE

A Born–Haber cycle is usually set out like an enthalpy profile diagram, with enthalpy changes one after another.

All the processes in the cycle can be measured experimentally except the lattice enthalpy. So, by using Hess's law it is possible to calculate the lattice enthalpy.



gaseous ions

total enthalpy change for atomising and ionising the two elements

lattice enthalpy

metal element and non-metal element

enthalpy change of formation of the compound

compound

BORN–HABER CYCLE

A method for analysis of thermochemical processes and based on Hess' law.

With the calculation of lattice enthalpies the data required are

atomisation energies for the elements,

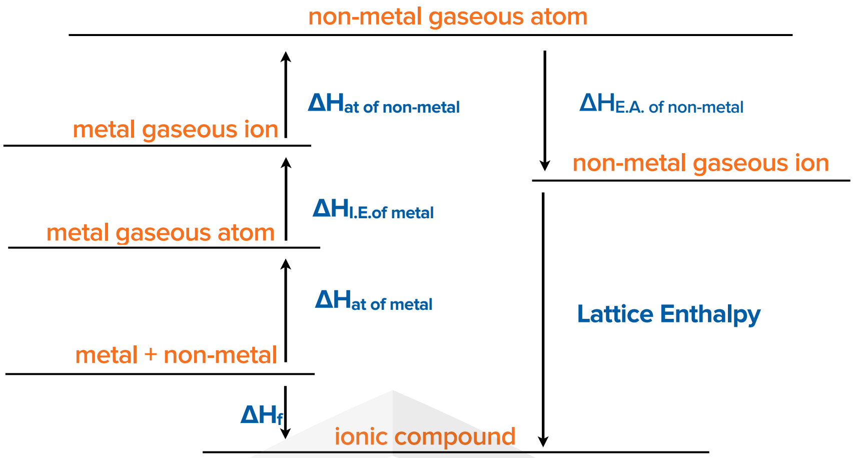
ionisation energies for the metal component, ΔH_{ie},

electron affinities for the non-metal component, ΔH_{ea}, and

the enthalpy change of formation, ΔH_f, for the compound.

ΔH formation = Atomisation energy of metal + Ionisation Energy of Metal
+ Atomisation of non-metal + electron affinity of non-metal + Lattice energy

GENERAL BORN-HABER CYCLE



1ST ELECTRON AFFINITY

Electron affinity of an element is the energy change that occurs when one mole of its gaseous atoms gains a mole of electrons under standard conditions.

$$O(g) + e \rightarrow O^{-}(g) \qquad \Delta H = -141 \text{ kJ mol}^{-1}$$

The first electron affinity 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.

Most first electron affinities are exothermic. This is because energy is released when the electron comes under the attraction of the nucleus

Element	**Si**	**P**	**S**	**Cl**
E.A/ kJ mol^{-1}	**–135**	**–60**	**–200**	**–364**

SUBSEQUENT ELECTRON AFFINITIES

The subsequent electron affinities are always endothermic since the initial repulsion between the negatively charged ion and the incoming electron outweighs the energy released when the electron comes under the attraction of the nucleus.

$O^{-}(g) + e \rightarrow O^{2-}(g) \qquad \Delta H = +791\ \text{kJ mol}^{-1}$

The second electron affinity 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.

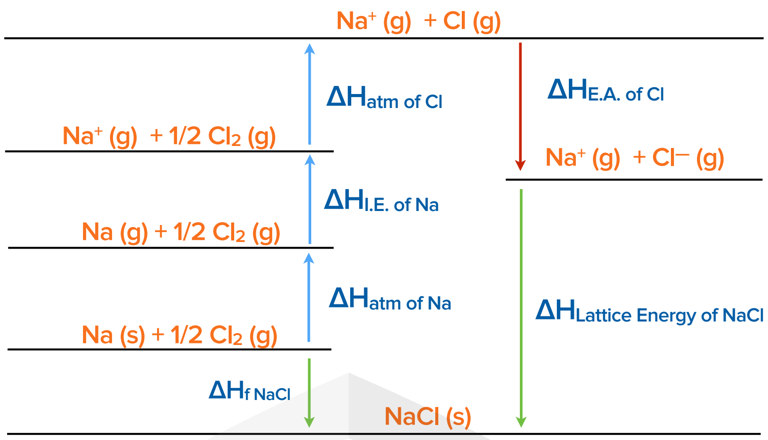
The overall enthalpy change in forming an oxide ion, O^{2-}, from an oxygen atom is found by adding together the 1st and 2nd electron affinities.

EXAMPLE

Calculate the lattice energy of sodium chloride from the following data:

Enthalpy of atomisation of sodium	= 108 kJ mol^{-1}
Bond Enthalpy of chlorine	= 244 kJ mol^{-1}
First ionisation energy of sodium	= 500 kJ mol^{-1}
Electron affinity of chlorine	= – 364 kJ mol^{-1}
Enthalpy of formation of sodium chloride	= – 411 kJ mol^{-1}

GENERAL BORN-HABER CYCLE



$Na^+ (g) + Cl (g)$

$\Delta H_{\text{atm of Cl}}$

$\Delta H_{\text{E.A. of Cl}}$

$Na^+ (g) + 1/2\ Cl_2 (g)$

$Na^+ (g) + Cl^- (g)$

$\Delta H_{\text{I.E. of Na}}$

$Na (g) + 1/2\ Cl_2 (g)$

$\Delta H_{\text{atm of Na}}$

$\Delta H_{\text{Lattice Energy of NaCl}}$

$Na (s) + 1/2\ Cl_2 (g)$

$\Delta H_{\text{f NaCl}}$

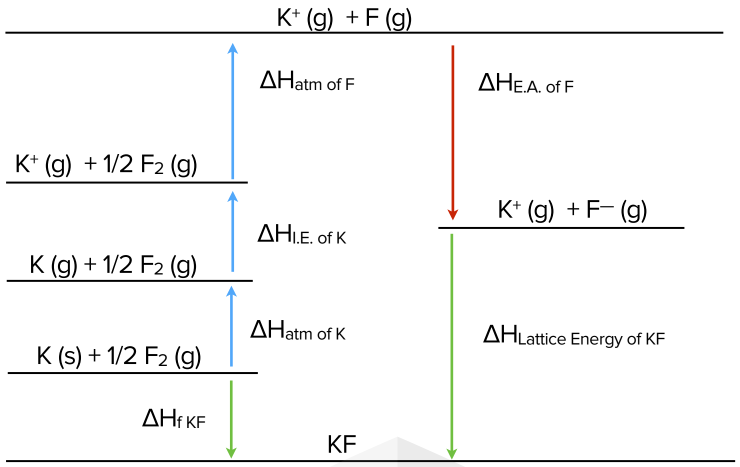
$NaCl (s)$

QUESTION 1

Calculate the enthalpy change of formation of potassium fluoride

Enthalpy of atomisation of K	= 90 kJ mol^{-1}
Bond energy of fluorine	= 158 kJ mol^{-1}
First ionisation energy of K	= 420 kJ mol^{-1}
Electron affinity of fluorine	= – 333 kJ mol^{-1}
Lattice energy of KF	= – 813 kJ mol^{-1}

QUESTION 1



$K^+ (g) + F (g)$

$\Delta H_{\text{atm of F}}$

$\Delta H_{\text{E.A. of F}}$

$K^+ (g) + 1/2\ F_2 (g)$

$K^+ (g) + F^- (g)$

$\Delta H_{\text{I.E. of K}}$

$K (g) + 1/2\ F_2 (g)$

$\Delta H_{\text{atm of K}}$

$\Delta H_{\text{Lattice Energy of KF}}$

$K (s) + 1/2\ F_2 (g)$

$\Delta H_{\text{f KF}}$

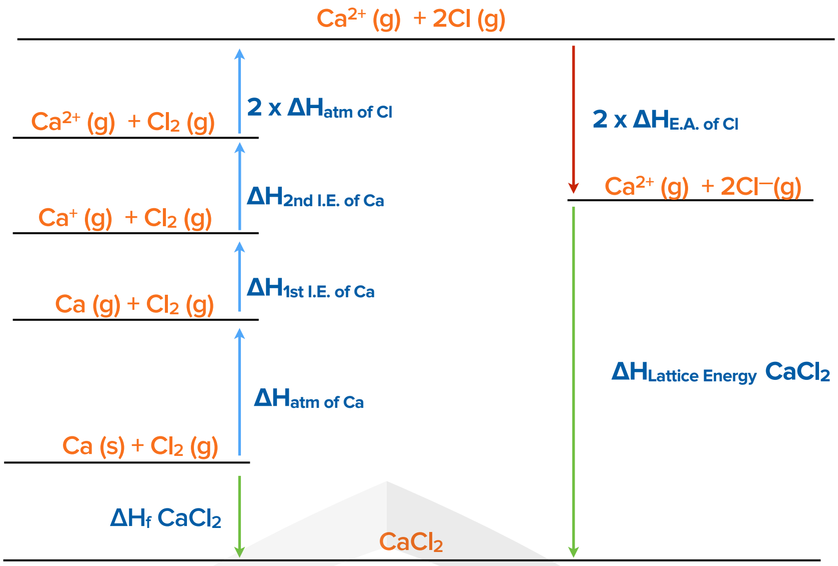
KF

$$\Delta H_{\text{f NaCl}} = \Delta H_{\text{atm of K}} + \Delta H_{\text{I.E. of K}} + \Delta H_{\text{atm of F}} + \Delta H_{\text{E.A. of F}} + \Delta H_{\text{Lattice Energy of KF}}$$

QUESTION 2

Calculate the enthalpy change of formation of calcium chloride

Enthalpy of atomisation of Ca	176 kJ mol^{-1}
Enthalpy of atomisation of chlorine	122 kJ mol^{-1}
First ionisation energy of Ca	590 kJ mol^{-1}
Second energy of ionisation of Ca	1100 kJ mol^{-1}
Electron affinity of chlorine	- 364 kJ mol^{-1}
Lattice energy of $CaCl_2$	- 2197 kJ mol^{-1}



Ca^{2+} (g) + 2Cl (g)

2 x $\Delta H_{\text{atm of Cl}}$

Ca^{2+} (g) + Cl_2 (g)

$\Delta H_{\text{2nd I.E. of Ca}}$

Ca^{+} (g) + Cl_2 (g)

$\Delta H_{\text{1st I.E. of Ca}}$

Ca (g) + Cl_2 (g)

$\Delta H_{\text{atm of Ca}}$

Ca (s) + Cl_2 (g)

ΔH_f $CaCl_2$

$CaCl_2$

2 x $\Delta H_{\text{E.A. of Cl}}$

Ca^{2+} (g) + $2Cl^{-}$(g)

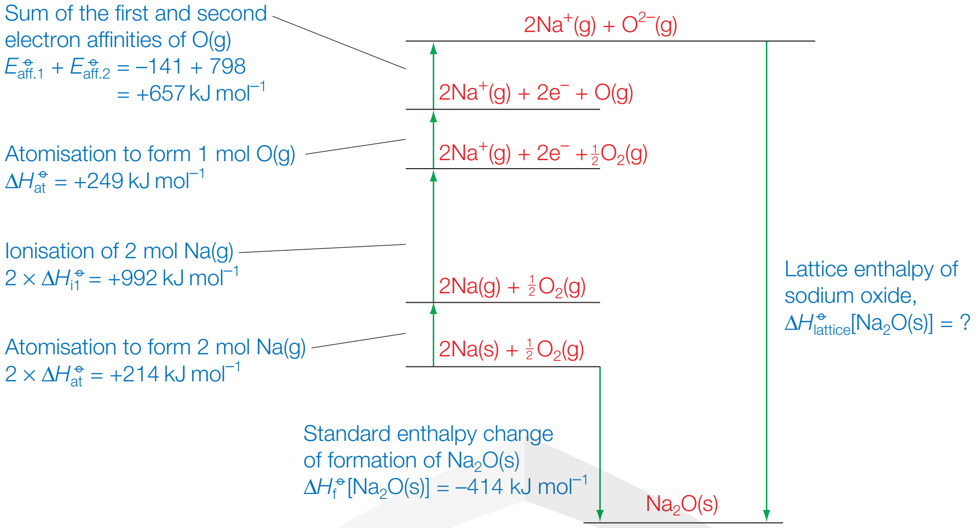
$\Delta H_{\text{Lattice Energy}}$ $CaCl_2$

QUESTION 3

Calculate the lattice energy of sodium chloride from the following data:

Enthalpy of atomisation of Na	107 kJ mol^{-1}
Enthalpy of atomisation of Oxygen	249 kJ mol^{-1}
First ionisation energy of Na	496 kJ mol^{-1}
First Electron affinity of Oxygen	—141 kJ mol^{-1}
First Electron affinity of Oxygen	798 kJ mol^{-1}
Enthalpy of formation of sodium oxide	—414 kJ mol^{-1}

QUESTION 3



$2Na^+(g) + O^{2-}(g)$

$2Na^+(g) + 2e^- + O(g)$

$2Na^+(g) + 2e^- + \frac{1}{2}O_2(g)$

$2Na(g) + \frac{1}{2}O_2(g)$

$2Na(s) + \frac{1}{2}O_2(g)$

$Na_2O(s)$

Sum of the first and second electron affinities of O(g)
$E^{\ominus}_{aff.1} + E^{\ominus}_{aff.2} = -141 + 798$
$= +657\ kJ\ mol^{-1}$

Atomisation to form 1 mol O(g)
$\Delta H^{\ominus}_{at} = +249\ kJ\ mol^{-1}$

Ionisation of 2 mol Na(g)
$2 \times \Delta H^{\ominus}_{i1} = +992\ kJ\ mol^{-1}$

Atomisation to form 2 mol Na(g)
$2 \times \Delta H^{\ominus}_{at} = +214\ kJ\ mol^{-1}$

Standard enthalpy change of formation of $Na_2O(s)$
$\Delta H^{\ominus}_f[Na_2O(s)] = -414\ kJ\ mol^{-1}$

Lattice enthalpy of sodium oxide,
$\Delta H^{\ominus}_{lattice}[Na_2O(s)] = ?$

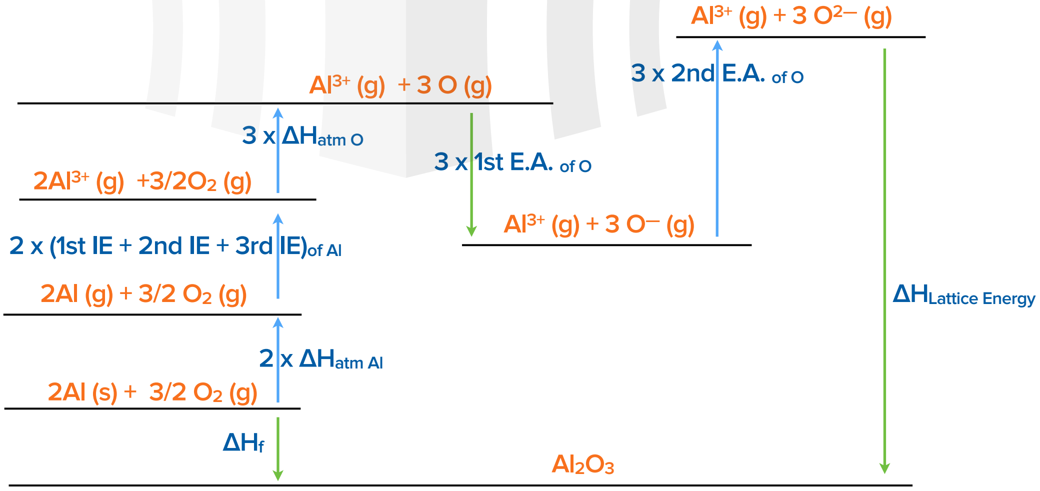
QUESTION 4

Calculate the enthalpy change of formation of magnesium oxide

Enthalpy of atomisation of Mg	146 kJ mol^{-1}
Bond Enthalpy of Oxygen	496 kJ mol^{-1}
First ionisation energy of Mg	736 kJ mol^{-1}
Second ionisation energy of Mg	1446 kJ mol^{-1}
First electron affinity of Oxygen	–141 kJ mol^{-1}
Second electron affinity of Oxygen	+791 kJ mol^{-1}
Enthalpy of formation of MgO	– 602 kJ mol^{-1}

QUESTION 4

BORN HABER CYCLE FOR Al_2O_3



Al^{3+} (g) + 3 O^{2-} (g)

3 x 2nd E.A. of O

Al^{3+} (g) + 3 O (g)

3 x $\Delta H_{atm\ O}$

3 x 1st E.A. of O

$2Al^{3+}$ (g) +3/2O_2 (g)

Al^{3+} (g) + 3 O^{-} (g)

2 x (1st IE + 2nd IE + 3rd IE)$_{of\ Al}$

2Al (g) + 3/2 O_2 (g)

$\Delta H_{Lattice\ Energy}$

2 x $\Delta H_{atm\ Al}$

2Al (s) + 3/2 O_2 (g)

ΔH_f

Al_2O_3

BORN-HABER CYCLES

If the cycles are examined it will be seen that:

the largest single contributions in each cycle are made by lattice energy and ionization energy and these two are always opposite in sign

the magnitude of the enthalpy of formation depends on the relative values of the lattice energy and the ionisation energy

if ionisation energy is too high to be supplied by lattice energy then such a compound will not form ionically

ENTHALPY CHANGES DURING DISSOLVING

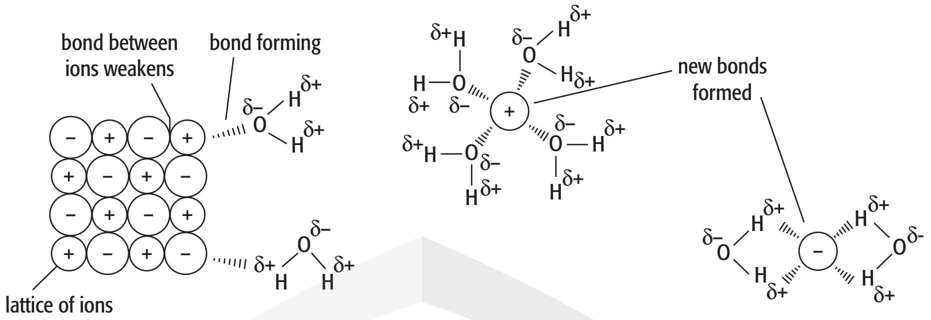
Why do ionic crystals dissolve in water, even though ions in the lattice are strongly attracted to each other?

An ionic compound such as sodium chloride does not dissolve in non-polar solvents like hexane, but it will dissolve in a polar solvent like water. When one mole of sodium chloride dissolves in excess water to produce a very dilute solution under standard conditions, there is an enthalpy change of +3.8 kJ mol^{-1}. This enthalpy change is described as the standard enthalpy change of solution, ΔH solution, of sodium chloride. The process can be summarised by the equation:

$$NaCl(s) + aq \rightarrow Na^+(aq) + Cl^-(aq) \qquad \Delta H_{\text{solution}} = +3.8\ \text{kJ mol}^{-1}$$

ENTHALPY CHANGES DURING DISSOLVING

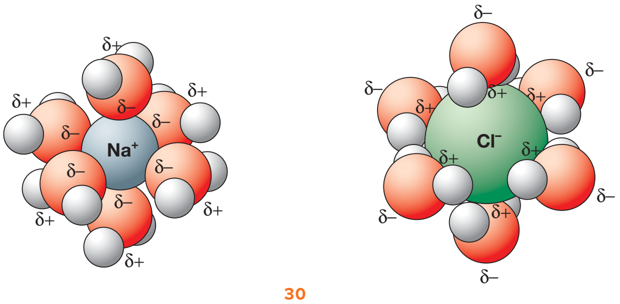
When ionic compounds, like NaCl, dissolve in water the crystal lattice should be broken down and this requires input of energy. This energy is supplied through the energy of hydration.



ENTHALPY CHANGES DURING DISSOLVING

First of all, Na+ and Cl– ions must be separated from the solid NaCl crystals to form well-spaced ions in the gaseous state, $Na^+_{(g)}$ and $Cl^-_{(g)}$. This is the reverse of the lattice enthalpy (+787 kJ mol^{-1})

In the second stage, gaseous $Na^+_{(g)}$ and $Cl^-_{(g)}$ ions are hydrated by polar water molecules forming a solution of sodium chloride, $Na^+_{(aq)}$ and $Cl^-_{(aq)}$. Under standard conditions, this process is the sum of the standard enthalpy changes of hydration of $Na^+_{(g)}$ and $Cl^-_{(g)}$.



ENTHALPY CHANGES DURING DISSOLVING

Enthalpy of Hydration:

The enthalpy change of hydration, ΔH hyd, is the enthalpy change when 1 mole of a specified gaseous ion dissolves in sufficient water to form a very dilute solution.

$$Ca^{2+}(g) \rightarrow Ca^{2+}(aq)$$

gaseous ion → aqueous ion

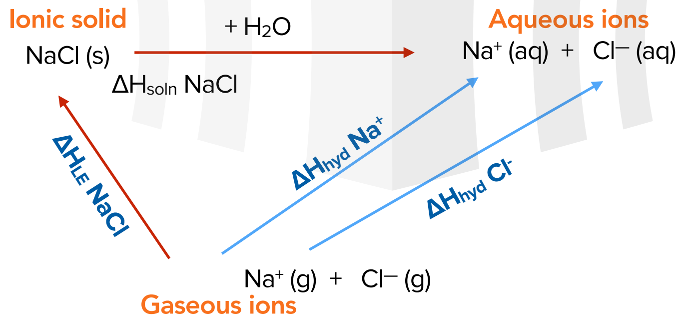
Enthalpy of Solution:

The enthalpy change of solution, ΔH sol, is the energy absorbed or released when 1 mole of an ionic solid dissolves in sufficient water to form a very dilute solution.

$$CaCl_2(s) \rightarrow Ca^{2+}(aq) + 2Cl^{-}(aq)$$

Solid → aqueous ion

ENTHALPY OF SOLUTION



Ionic solid

NaCl (s)

+ H_2O

ΔH_{soln} NaCl

Aqueous ions

$Na^+(aq) + Cl^-(aq)$

ΔH_{LE} NaCl

$\Delta H_{hyd}\ Na^+$

$\Delta H_{hyd}\ Cl^-$

$Na^+(g) + Cl^-(g)$

Gaseous ions

$$\Delta H_{LE}\ NaCl + \Delta H_{soln}\ NaCl = \Delta H_{hyd}\ Na^+ + \Delta H_{hyd}\ Cl^-$$

$$\Delta H_{LE} + \Delta H_{soln} = \Delta H_{hyd}$$

$$\Delta H_{soln} = -\Delta H_{LE} + \Delta H_{hyd}$$

ENTHALPY OF SOLUTION

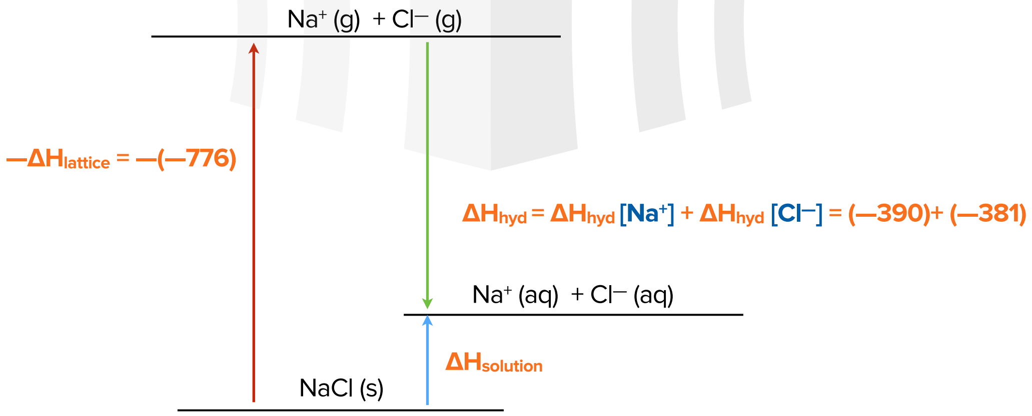
Draw a simple energy cycle & calculate the enthalpy of solution of sodium chloride from the following data

Lattice energy of sodium chloride = -776 kJ mol^{-1}

Hydration energy of $Na^+(g)$ = -390 kJ mol^{-1}

Hydration energy of $Cl^-(g)$ = -381 kJ mol^{-1}

ENTHALPY OF SOLUTION



$Na^+(g) + Cl^-(g)$

$-\Delta H_{lattice} = -(-776)$

$\Delta H_{hyd} = \Delta H_{hyd}[Na^+] + \Delta H_{hyd}[Cl^-] = (-390) + (-381)$

$Na^+(aq) + Cl^-(aq)$

$\Delta H_{solution}$

$NaCl(s)$

QUESTION 1

(a) What is meant by the term enthalpy change of hydration, ΔH_{hyd}?

(b) Write an equation that represents the of the ΔH_{hyd} Mg^{2+} ion.

(c) Suggest a reason why ΔH_{hyd} of the Mg^{2+} ion is greater than of the Ca^{2+} ion.

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

HYDRATION

If the energy of hydration of ions:

outweighs the lattice energy the compound dissolves exothermically

is much lower than the lattice energy of the ions the compound will not dissolve

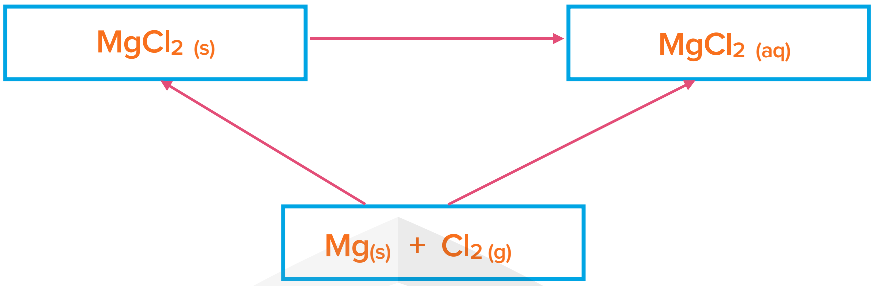
is slightly less than the lattice energy, the little extra energy required for the breakdown of the lattice is obtained from the thermal energy of the solvent. Hence the process would be endothermic resulting in a drop in temperature

Most salts dissolve endothermically. Hence an increase of temperature favors the equilibrium point to shift forwards resulting in an increase in the solubility.

ENTHALPY OF SOLUTION

By constructing relevant thermochemical cycles, use the above data to calculate a value for ΔH_{sol} ($MgCl_2$(s))

enthalpy change	value / kJ mol^{-1}
ΔH_f ($MgCl_2$(s))	—641
ΔH_f ($MgCl_2$(aq))	—801



$—641 + x = —801$ $\qquad$ $x = —160$ kJmol$^{–1}$

QUESTION 2

Iron(III) chloride readily dissolves in water.

$$FeCl_3(s) \rightarrow Fe^{3+}(aq) + 3Cl^{-}(aq)$$

Use the following data to calculate the standard enthalpy change for this process.

species	ΔH_f°/kJ mol^{-1}
$FeCl_3$(s)	–399.5
Fe^{3+}(aq)	–48.5
Cl^{-}(aq)	–167.2

QUESTION 2

By constructing relevant thermochemical cycles, use the above data to calculate a value for ΔH_{sol} ($MgCl_2(s)$)

$$\begin{tikzcd}
FeCl_{3\,(s)} \arrow[rr, "x"] & & Fe^{3+}_{(aq)} + 3Cl^{-}_{(aq)} \\
& Fe_{(s)} + 1.5\,Cl_{2\,(g)} \arrow[ul, "-399.5"] \arrow[ur, "(-48.5) + 3(-167.2)"'] &
\end{tikzcd}$$

$$(-48.5) + 3(-167.2) = -399.5 + x$$

$$x = -150.6$$