

LATTICE ENTHALPY

WARNING

*There can be two definitions - one is the opposite of the other!
Make sure you know which one is being used.*

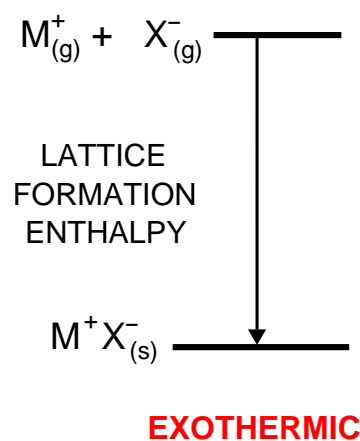
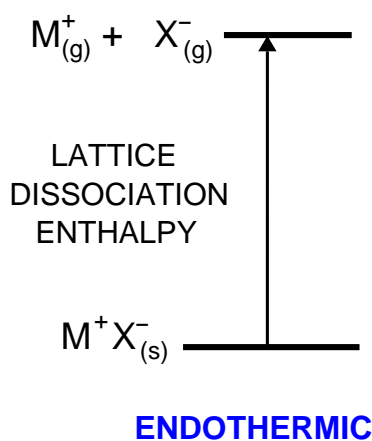
Lattice Dissociation Enthalpy

Definition The enthalpy change when ONE MOLE of an ionic lattice dissociates into isolated gaseous ions.

Values

- **highly endothermic** - there is a strong electrostatic attraction between ions of opposite charge
- a lot of energy must be put in to overcome the attraction

Example $\text{Na}^+ \text{Cl}^- (\text{s}) \longrightarrow \text{Na}^+ (\text{g}) + \text{Cl}^- (\text{g})$



Lattice Formation Enthalpy

Definition The enthalpy change when ONE MOLE of an ionic crystal lattice is formed from its isolated gaseous ions.

Values

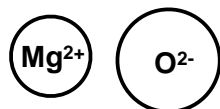
- **highly exothermic** - strong electrostatic attraction between ions of opposite charge
- a lot of energy is released as the bond is formed
- relative values are governed by the charge density of the ions.

Example $\text{Na}^+ (\text{g}) + \text{Cl}^- (\text{g}) \longrightarrow \text{Na}^+ \text{Cl}^- (\text{s})$

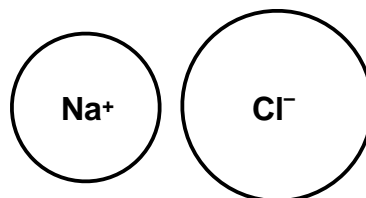
Notes

- one **cannot measure this value directly**; it is found using a Born-Haber cycle
- the greater the charge densities of the ions, the more they attract each other and the larger the lattice enthalpy.
- **the more exothermic the lattice enthalpy, the higher the melting point**

Consequences



HIGH CHARGE DENSITY IONS
GREATER ATTRACTION
LARGE LATTICE ENTHALPY



LOWER CHARGE DENSITY IONS
LESS ATTRACTION
SMALLER LATTICE ENTHALPY

Q.1 Which substance in the the following pairs has the larger lattice enthalpy?

a) NaCl or KCl

b) NaF or NaCl

c) MgCl₂ or NaCl

d) MgO or MgCl₂

Thermal stability and Lattice Enthalpy

Oxides

- **thermal stability of Group II oxides decreases down the group**

	Mg ²⁺ O ²⁻	Ca ²⁺ O ²⁻	Sr ²⁺ O ²⁻	Ba ²⁺ O ²⁻
Lattice Enthalpy (kJ mol ⁻¹)	-3889	-3513	-3310	-3152
Melting Point (°C)	2853	— decreasing values —>		

MgO

- magnesium oxide is used to line furnaces - REFRACTORY LINING
- this is because of its high melting point (2853°C)
- the high melting point is a result of the large (highly exothermic) lattice enthalpy
- high lattice enthalpy due to the attraction between ions of high charge density

Carbonates

- **thermal stability of Group II carbonates increases down the group**
- MgCO₃ decomposes much easier than BaCO₃
- BUT the lattice enthalpy of MgCO₃ is HIGHER!

	MgCO ₃	CaCO ₃	SrCO ₃	BaCO ₃
Decomposes at	350°C	832°C	1340°C	1450°C
Lattice Enthalpy (kJ mol ⁻¹)	-3123	—————>		-2556

- Mg²⁺ ions are **SMALLER** and have a **HIGHER CHARGE DENSITY**
- this makes them **MORE HIGHLY POLARISING**
- they **DISTORT THE CO₃²⁻** ion
- this **WEAKENS THE ATTRACTION BETWEEN IONS**
- the **LATTICE IS NOT AS STRONG**

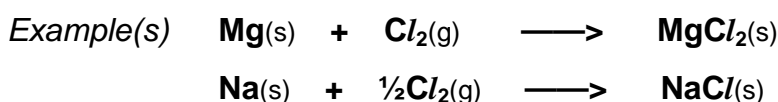
Calculating Lattice Enthalpy

- Introduction**
- you **cannot measure lattice enthalpy directly**
 - values are found using a **Born-Haber cycle**
 - Born-Haber cycles use Hess's Law
 - The following enthalpy changes are part of a Born-Haber cycle.

Standard Enthalpy Change of Formation (ΔH_f°)

Definition The enthalpy change when ONE MOLE of a compound is formed in its standard state from its elements in their standard states.

Values Usually, but not exclusively, **exothermic**



Notes

- Elements In their standard states have zero enthalpy of formation.

Q.2 Write equations representing the standard enthalpy changes of formation of
magnesium oxide
sodium oxide
potassium bromide

Standard Enthalpy Change of Atomisation ($\Delta H_{\text{at}}^\circ, 298$)

Definition The enthalpy change when ONE MOLE of gaseous atoms is formed from an element in its standard state.

Values **Always endothermic** - you have to break the bonds holding the atoms together



Note

- for solid elements, the change is known as ENTHALPY OF SUBLIMATION

Q.3 Write equations representing the standard enthalpy changes of atomisation / sublimation of
magnesium
oxygen
potassium

First Ionisation Energy

Definition The energy required to remove one mole of electrons (to infinity) from one mole of gaseous atoms to form one mole of gaseous positive ions.

Values **Always endothermic** need to overcome the pull of the nucleus on the electron

Example(s) $\text{Na(g)} \longrightarrow \text{Na}^{\text{+}}(\text{g}) + \text{e}^{-}$ and $\text{Mg(g)} \longrightarrow \text{Mg}^{\text{+}}(\text{g}) + \text{e}^{-}$

Notes

- There is an ionisation energy for each successive electron removed.
e.g. SECOND IONISATION ENERGY $\text{Mg}^{\text{+}}(\text{g}) \longrightarrow \text{Mg}^{\text{2+}}(\text{g}) + \text{e}^{-}$
- Look back in your notes to refresh your memory about the trends in I.E.'s

Q.4 Write equations representing the following ionisation energy changes;

1st IE of magnesium

2nd IE of magnesium

1st IE of sodium

1st IE of potassium

Electron Affinity

Definition The enthalpy change when ONE MOLE of gaseous atoms acquires ONE MOLE of electrons (from infinity) to form ONE MOLE of gaseous negative ions.

Values **Always exothermic** - a favourable process due to the nucleus attracting the electron

Example $\text{Cl}_{(\text{g})}(\text{g}) + \text{e}^{-} \longrightarrow \text{Cl}^{-}_{(\text{g})}(\text{g})$

Notes

- Do not confuse electron affinity with electronegativity.

Q.5 Write equations representing the following electron affinity (EA) changes;

1st EA of chlorine

1st EA of oxygen

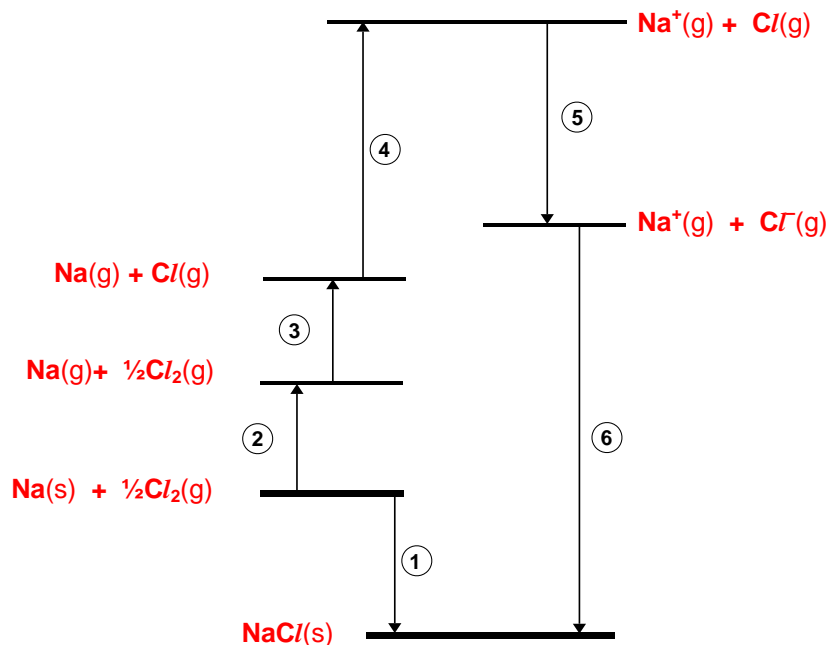
2nd EA of oxygen

BORN-HABER CYCLES

Theory

- involve the application of Hess's Law
- used to outline the thermodynamic changes during the formation of ionic salts
- used to calculate Lattice Enthalpy
- Lattice Enthalpy cannot be determined directly by experiment

BORN-HABER CYCLE FOR SODIUM CHLORIDE



STEPS (values are in kJ mol^{-1})

①	Enthalpy change of formation of NaCl	$\text{Na(s)} + \frac{1}{2}\text{Cl}_2(\text{g}) \longrightarrow \text{NaCl(s)}$	- 411
②	Enthalpy change of sublimation of sodium	$\text{Na(s)} \longrightarrow \text{Na(g)}$	+ 108
③	Enthalpy change of atomisation of chlorine	$\frac{1}{2}\text{Cl}_2(\text{g}) \longrightarrow \text{Cl(g)}$	+ 121
④	1st Ionisation Energy of sodium	$\text{Na(g)} \longrightarrow \text{Na}^+(\text{g}) + \text{e}^-$	+ 500
⑤	Electron Affinity of chlorine	$\text{Cl(g)} + \text{e}^- \longrightarrow \text{Cl}^-(\text{g})$	- 364
⑥	Lattice Enthalpy of NaCl	$\text{Na}^+(\text{g}) + \text{Cl}^-(\text{g}) \longrightarrow \text{NaCl(s)}$	

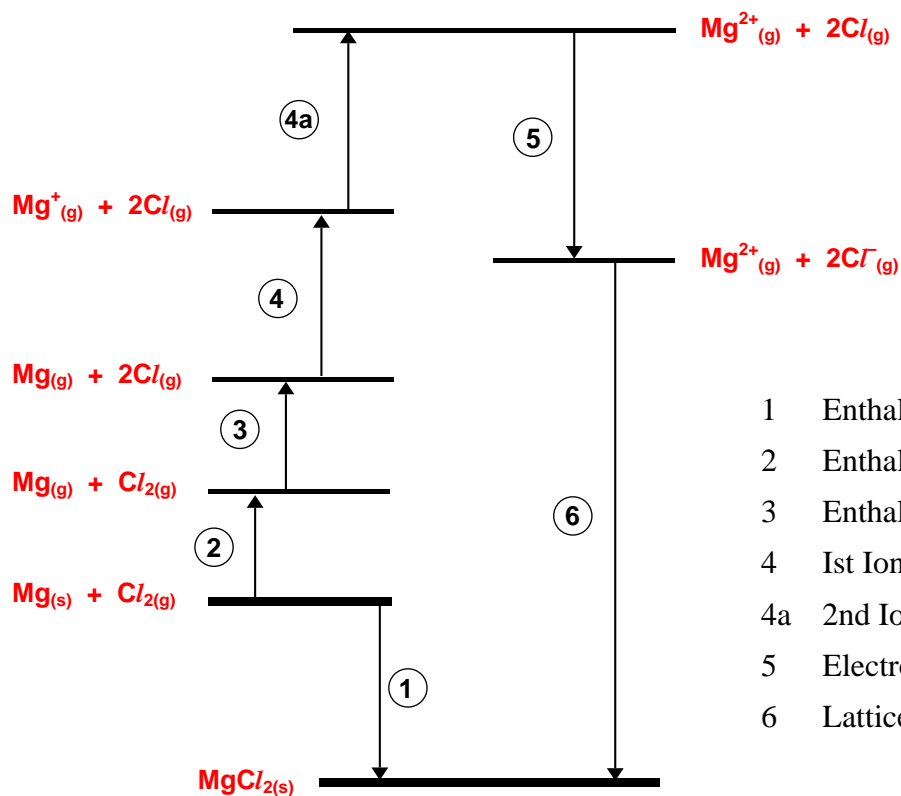
According to **Hess's Law**, the enthalpy change is independent of the path taken. Therefore...

$$\begin{aligned} \text{STEP 6} &= - (\text{STEP 5}) - (\text{STEP 4}) - (\text{STEP 3}) - (\text{STEP 2}) + (\text{STEP 1}) \\ &= - (-364) - (+500) - (+121) - (+108) + (-411) = \mathbf{- 776 \text{ kJ mol}^{-1}} \end{aligned}$$

Q.6 Construct a similar Born-Haber cycle for NaCl_2 .

If the Lattice Enthalpy of NaCl_2 is $-3360 \text{ kJ mol}^{-1}$, what is its enthalpy of formation? What does this tell you about the stability of NaCl_2 ?

BORN-HABER CYCLE FOR MAGNESIUM CHLORIDE



STEPS

- 1 Enthalpy of formation of MgCl_2
- 2 Enthalpy of sublimation of Mg
- 3 Enthalpy of atomisation of Cl x 2
- 4 1st Ionisation Energy of Mg
- 4a 2nd Ionisation Energy of Mg
- 5 Electron Affinity of Cl x 2
- 6 Lattice Enthalpy of MgCl_2

Q.7 If the Lattice Enthalpy of MgCl_2 is $-2493 \text{ kJ mol}^{-1}$, what is its enthalpy of formation ?

Q.8 Construct a Born-Haber cycle for magnesium oxide, MgO .

Will an ionic salt dissolve in water?

Introduction If a pair of oppositely charged gaseous ions are placed together, they will attract each other. The energy change (**LATTICE ENTHALPY**) is highly exothermic.

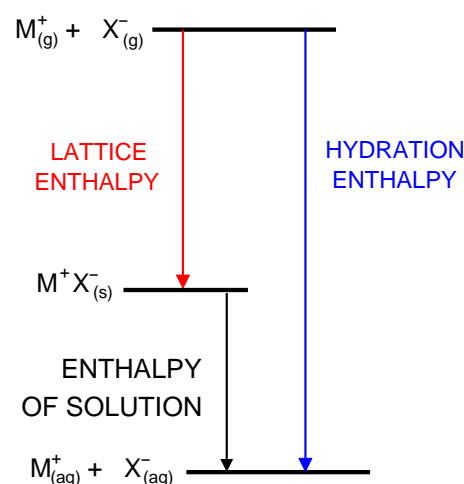
If the ions were put in water, they would be attracted to polar water molecules. the resulting energy change (**HYDRATION ENTHALPY**) is highly exothermic.

In both; the greater charge density of the ions = a more exothermic reaction

The missing stage of the cycle is known as the **ENTHALPY OF SOLUTION**.

The size and value of the enthalpy of solution depends on the **relative values** of the lattice enthalpy and the hydration enthalpy.

If **HE** >> **LE** then the salt will probably be soluble



Enthalpy Change of Hydration

Definition The enthalpy change when ONE MOLE of a gaseous ion dissolves in (an excess of) water to give an infinitely dilute solution.

Values **Exothermic**

Example $\text{Na}^+(\text{g}) \longrightarrow \text{Na}^+(\text{aq})$ $\text{Cl}^-(\text{g}) \longrightarrow \text{Cl}^-(\text{aq})$

Notes The polar nature of water stabilises the ions.

The greater the charge density of the ion, the greater the affinity for water and the more exothermic the process will be.

Na^+	-390	Mg^{2+}	-1891	Cl^-	-384	(all in kJ mol^{-1})
K^+	-305	Ca^{2+}	-1561	Br^-	-351	

Enthalpy Change of Solution

Definition The enthalpy change when ONE MOLE of a substance dissolves in (an excess of) solvent to give an infinitely dilute solution.

Values **Mainly exothermic**

Example $\text{NaCl}(\text{s}) \longrightarrow \text{NaCl}(\text{aq})$ [for ionic compounds, the ions will be dissociated]

SOME USEFUL VALUES FOR THERMODYNAMIC CHANGES

Values, which may be slightly different in other books, are in kJ mol⁻¹

Enthalpy change of formation

	<i>Cl⁻</i>	<i>Br⁻</i>	<i>I⁻</i>	<i>O²⁻</i>
Na ⁺	-411	-381	-288	-414
K ⁺	-437	-398	-328	-361
Mg ²⁺	-641	-524	-364	-602
Ca ²⁺	-796	-683	-534	-635

Enthalpy of atomisation

H	+218	Na	+108	F	+79
C	+716	K	+89	Cl	+122
N	+472	Mg	+148	Br	+112
O	+249	Ca	+178		

Ionisation Energy

	<i>1st I.E.</i>	<i>2nd I.E.</i>
Na	+496	+4563
Mg	+738	+1451
Ca	+590	+1145
K	+419	+3051

Electron Affinity

F	-348	Cl	-349	Br	-342	I ⁻	-314
O	-141						

2nd Electron Affinity

O	+798
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Lattice Enthalpy

Check which definition is being used and use appropriate sign for ΔH

	<i>Cl⁻</i>	<i>Br⁻</i>	<i>F⁻</i>	<i>O²⁻</i>
Na ⁺	-780	-742	-918	-2478
K ⁺	-711	-679	-817	-2232
Rb ⁺	-685	-656	-783	
Mg ²⁺	-2256			-3791
Ca ²⁺	-2259			

Hydration Enthalpy

Li ⁺	-499	Be ²⁺	-2385	F ⁻	-457
Na ⁺	-390	Mg ²⁺	-1891	Cl ⁻	-384
K ⁺	-305	Ca ²⁺	-1561	Br ⁻	-351
		Al ³⁺	-4613	I ⁻	-307
				OH ⁻	-460