# LATTICE ENTHALPY

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

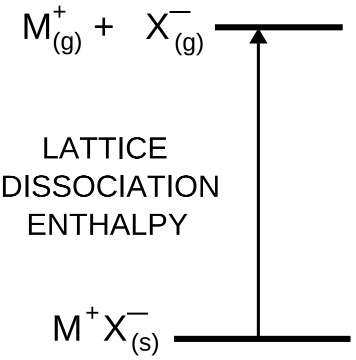
## Lattice Dissociation Enthalpy

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

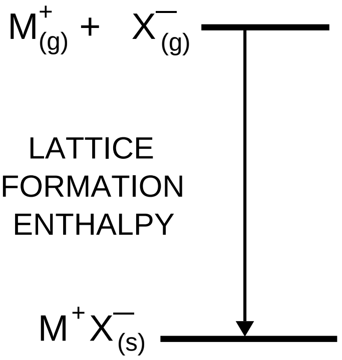
*Values*

- **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* $\mathbf{Na^+\,Cl^-}_{(g)} \longrightarrow \mathbf{Na^+}_{(g)} + \mathbf{Cl^-}_{(g)}$



**ENDOTHERMIC**



**EXOTHERMIC**

## Lattice Formation Enthalpy

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

*Values*

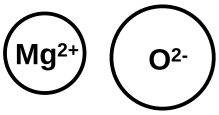
- **highly exothermic** - strong electrostatic attraction between ions of opposite charge
- a lot of energy is released as the bond is formed
- relative **values are governed by the charge density of the ions**.

*Example* $\mathbf{Na^+}_{(g)} + \mathbf{Cl^-}_{(g)} \longrightarrow \mathbf{Na^+\,Cl^-}_{(s)}$

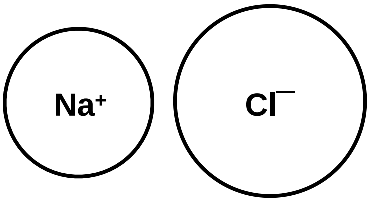
*Notes*

- 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) $MgCl_2$ or NaCl*

*d) MgO or $MgCl_2$*

## 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**
- $MgCO_3$ decomposes much easier than $BaCO_3$
- BUT the lattice enthalpy of $MgCO_3$ 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** |

- $Mg^{2+}$ ions are **SMALLER** and have a **HIGHER CHARGE DENSITY**
- this makes them **MORE HIGHLY POLARISING**
- they **DISTORT THE $CO_3^{2-}$** 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 ( $\Delta H°_f$ )

*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**

*Example(s)* $Mg(s) + Cl_2(g) \longrightarrow MgCl_2(s)$

$Na(s) + \frac{1}{2}Cl_2(g) \longrightarrow NaCl(s)$

*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 ( $\Delta H°_{at\,,\,298}$ )

*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

*Example(s)* $\frac{1}{2}Cl_2(g) \longrightarrow Cl(g)$ and $Na(s) \longrightarrow Na(g)$ *(see note)*

*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)* $\mathbf{Na}(g) \longrightarrow \mathbf{Na^+}(g) + \mathbf{e^-}$ and $\mathbf{Mg}(g) \longrightarrow \mathbf{Mg^+}(g) + \mathbf{e^-}$

*Notes*

- There is an ionisation energy for each successive electron removed.

  *e.g.* SECOND IONISATION ENERGY $\mathbf{Mg^+}(g) \longrightarrow \mathbf{Mg^{2+}}(g) + \mathbf{e^-}$

- 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 calcium*

*2nd IE of calcium*

*1st IE of lithium*

*1st IE of aluminium*

## 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* $\mathbf{Cl}(g) + \mathbf{e^-} \longrightarrow \mathbf{Cl^-}(g)$

*Notes*

- Do not confuse electron affinity with electronegativity.

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

*1st EA of bromine*

*1st EA of oxygen*

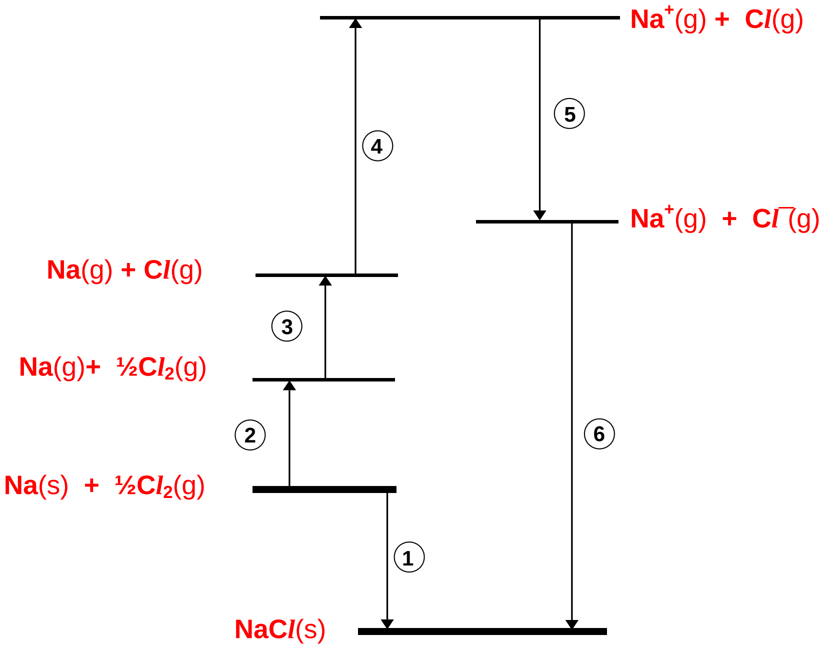
*2nd EA of oxygen*

# 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 | $Na(s) + ½Cl_2(g) \longrightarrow NaCl(s)$ | **– 411** |
| ② | Enthalpy change of sublimation of sodium | $Na(s) \longrightarrow Na(g)$ | **+ 108** |
| ③ | Enthalpy change of atomisation of chlorine | $½Cl_2(g) \longrightarrow Cl(g)$ | **+ 121** |
| ④ | Ist Ionisation Energy of sodium | $Na(g) \longrightarrow Na^+(g) + e^-$ | **+ 500** |
| ⑤ | Electron Affinity of chlorine | $Cl(g) + e^- \longrightarrow Cl^-(g)$ | **– 364** |
| ⑥ | Lattice Enthalpy of NaCl | $Na^+(g) + Cl^-(g) \longrightarrow NaCl(s)$ | |

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

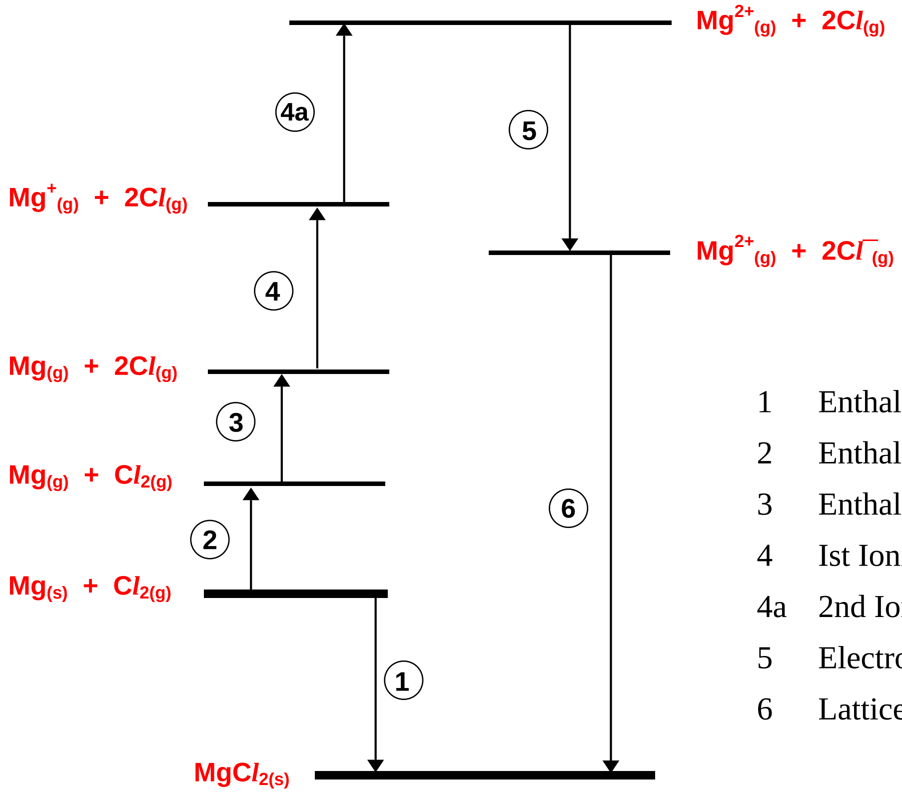
STEP 6 = - (STEP 5) - (STEP 4) - (STEP 3) - (STEP 2) + (STEP 1)

**- (-364) - (+500) - (+121) - (+108) + (-411) = - 776 kJ mol$^{-1}$**

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

*If the Lattice Enthalpy of $NaCl_2$ is -3360 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 Ist 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 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.

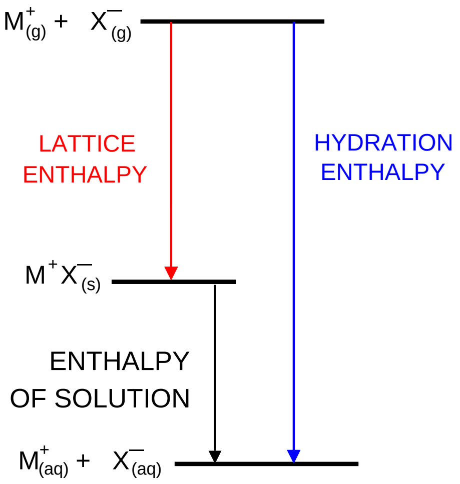
If the ions were put in water, they would be attracted to polar water molecules. the resulting energy change (**HYDRATION ENTHALPY**) is highly exothermic.

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* $Na^+(g) \longrightarrow Na^+(aq)$ $Cl^-(g) \longrightarrow Cl^-(aq)$

*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* $NaCl(s) \longrightarrow NaCl(aq)$ [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**

| | $Cl^-$ | $Br^-$ | $I^-$ | $O^{2-}$ |
|---|---|---|---|---|
| $Na^+$ | -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**

| | *1st I.E.* | *2nd I.E.* |
|---|---|---|
| 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**

**Lattice Enthalpy**

*Check which definition is being used and use appropriate sign for $\Delta H$*

| | $Cl^-$ | $Br^-$ | $F^-$ | $O^{2-}$ |
|---|---|---|---|---|
| $Na^+$ | -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 |