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 \[
\text{Na}^+ \text{Cl}^- (g) \rightarrow \text{Na}^+(g) + \text{Cl}^-(g)
\]

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 \[
\text{Na}^+(g) + \text{Cl}^-(g) \rightarrow \text{Na}^+ \text{Cl}^-(s)
\]

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

<table>
<thead>
<tr>
<th>Consequences</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(^{2+})</td>
</tr>
<tr>
<td>HIGH CHARGE DENSITY IONS</td>
</tr>
<tr>
<td>Na(^+)</td>
</tr>
<tr>
<td>LOWER CHARGE DENSITY IONS</td>
</tr>
</tbody>
</table>

Thermal stability and Lattice Enthalpy

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

<table>
<thead>
<tr>
<th></th>
<th>Mg(^{2+}) O(^{2-})</th>
<th>Ca(^{2+}) O(^{2-})</th>
<th>Sr(^{2+}) O(^{2-})</th>
<th>Ba(^{2+}) O(^{2-})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice Enthalpy (kJ mol(^{-1}))</td>
<td>-3889</td>
<td>-3513</td>
<td>-3310</td>
<td>-3152</td>
</tr>
<tr>
<td>Melting Point (°C)</td>
<td>2853</td>
<td>——— decreasing values ———</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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!

<table>
<thead>
<tr>
<th></th>
<th>MgCO(_3)</th>
<th>CaCO(_3)</th>
<th>SrCO(_3)</th>
<th>BaCO(_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decomposes at</td>
<td>350°C</td>
<td>832°C</td>
<td>1340°C</td>
<td>1450°C</td>
</tr>
<tr>
<td>Lattice Enthalpy (kJ mol(^{-1}))</td>
<td>-3123</td>
<td>——— decreasing values ———</td>
<td>-2556</td>
<td></td>
</tr>
</tbody>
</table>

- 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

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\(_2\)
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 (\( \Delta H^\circ_f \))

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)

\[
\text{Mg(s)} + \text{Cl}_2(g) \rightarrow \text{MgCl}_2(s)
\]

\[
\text{Na(s)} + \frac{1}{2}\text{Cl}_2(g) \rightarrow \text{NaCl}(s)
\]

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 (\( \Delta H^\circ_{at}, 298 \))

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)

\[
\frac{1}{2}\text{Cl}_2(g) \rightarrow \text{Cl}(g)
\]

and

\[
\text{Na(s)} \rightarrow \text{Na}(g)
\] (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)**

\[
\text{Na}(g) \rightarrow \text{Na}^+(g) + e^- \quad \text{and} \quad \text{Mg}(g) \rightarrow \text{Mg}^+(g) + e^-
\]

**Notes**
- There is an ionisation energy for each successive electron removed.
  
  *e.g.* FIRST IONISATION ENERGY

\[
\text{Mg}(g) \rightarrow \text{Mg}^+(g) + e^-
\]

- 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**

\[
\text{Cl}(g) + e^- \rightarrow \text{Cl}^-(g)
\]

**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**

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

\[
\text{STEP 6} = - (\text{STEP 5}) - (\text{STEP 4}) - (\text{STEP 3}) - (\text{STEP 2}) + (\text{STEP 1})
\]
\[
- (-364) - (+500) - (+121) - (+108) + (-411) = -776 \text{ kJ mol}^{-1}
\]

**Q.6** Construct a similar Born-Haber cycle for NaCl₂.

If the Lattice Enthalpy of NaCl₂ is -3360 kJ mol⁻¹, what is its enthalpy of formation? What does this tell you about the stability of NaCl₂?
**BORN-HABER CYCLE FOR MAGNESIUM CHLORIDE**

**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-Habers 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) \rightarrow Na^+\,(aq) \hspace{1cm} Cl^-\,(g) \rightarrow 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$^+$ \hspace{0.5cm} -390 \hspace{1cm} Mg^{2+} \hspace{0.5cm} -1891 \hspace{1cm} Cl^- \hspace{0.5cm} -384 \hspace{1cm} (all\,in\,kJ\,mol^{-1})

K$^+$ \hspace{0.5cm} -305 \hspace{1cm} Ca^{2+} \hspace{0.5cm} -1561 \hspace{1cm} Br^- \hspace{0.5cm} -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) \rightarrow NaCl\,(aq) \hspace{1cm} [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

<table>
<thead>
<tr>
<th></th>
<th>Cl⁻</th>
<th>Br⁻</th>
<th>I⁻</th>
<th>O²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>-411</td>
<td>-381</td>
<td>-288</td>
<td>-414</td>
</tr>
<tr>
<td>K⁺</td>
<td>-437</td>
<td>-398</td>
<td>-328</td>
<td>-361</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>-641</td>
<td>-524</td>
<td>-364</td>
<td>-602</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>-796</td>
<td>-683</td>
<td>-534</td>
<td>-635</td>
</tr>
</tbody>
</table>

### Enthalpy of atomisation

<table>
<thead>
<tr>
<th></th>
<th>H</th>
<th>Na</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl⁻</td>
<td>+218</td>
<td>+108</td>
<td>+79</td>
</tr>
<tr>
<td>Br⁻</td>
<td>+716</td>
<td>+89</td>
<td>+122</td>
</tr>
<tr>
<td>I⁻</td>
<td>+472</td>
<td>+148</td>
<td>+112</td>
</tr>
<tr>
<td>O²⁻</td>
<td>+249</td>
<td>+178</td>
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### Ionisation Energy

<table>
<thead>
<tr>
<th></th>
<th>1st I.E.</th>
<th>2nd I.E.</th>
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</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>+496</td>
<td>+4563</td>
</tr>
<tr>
<td>Mg⁺</td>
<td>+738</td>
<td>+1451</td>
</tr>
<tr>
<td>Ca⁺</td>
<td>+590</td>
<td>+1145</td>
</tr>
<tr>
<td>K⁺</td>
<td>+419</td>
<td>+3051</td>
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</table>

### Electron Affinity

<table>
<thead>
<tr>
<th></th>
<th>F</th>
<th>Cl</th>
<th>Br</th>
<th>I⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>O²⁻</td>
<td>-348</td>
<td>-349</td>
<td>-342</td>
<td>-314</td>
</tr>
</tbody>
</table>

### 2nd Electron Affinity

<table>
<thead>
<tr>
<th></th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>O²⁻</td>
<td>+798</td>
</tr>
</tbody>
</table>

### Lattice Enthalpy

<table>
<thead>
<tr>
<th></th>
<th>Cl⁻</th>
<th>Br⁻</th>
<th>F⁻</th>
<th>O²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>-780</td>
<td>-742</td>
<td>-918</td>
<td>-2478</td>
</tr>
<tr>
<td>K⁺</td>
<td>-711</td>
<td>-679</td>
<td>-817</td>
<td>-2232</td>
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<tr>
<td>Rb⁺</td>
<td>-685</td>
<td>-656</td>
<td>-783</td>
<td></td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>-2256</td>
<td></td>
<td></td>
<td>-3791</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>-2259</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

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

### Hydration Enthalpy

<table>
<thead>
<tr>
<th></th>
<th>Li⁺</th>
<th>Be²⁺</th>
<th>F⁻</th>
<th>Cl⁻</th>
<th>Br⁻</th>
<th>I⁻</th>
<th>Al³⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>-499</td>
<td>-2385</td>
<td>-457</td>
<td>-384</td>
<td>-351</td>
<td>-307</td>
<td>-460</td>
</tr>
</tbody>
</table>