

## CHEMICAL ENERGETICS (2)

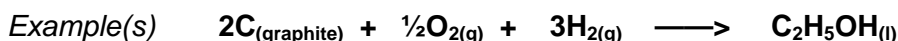
**Introduction** Before starting, make sure you understand the topics studied in the earlier AS modules

*these included ...* Exothermic and endothermic reactions  
 Standard Enthalpy of Formation (  $\Delta H^\circ_{f,298}$  )  
 Standard Enthalpy of Combustion (  $\Delta H^\circ_{c,298}$  )  
 Mean Bond Enthalpy  
 Hess's Law

### Standard Enthalpy 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**



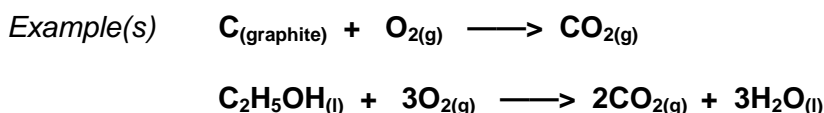
**Notes**

- Elements In their standard states have zero enthalpy of formation.
- Carbon is usually taken as the graphite allotrope.

### Standard Enthalpy of Combustion ( $\Delta H^\circ_c$ )

**Definition** The enthalpy change when ONE MOLE of a substance undergoes complete combustion under standard conditions. All reactants and products are in their standard states.

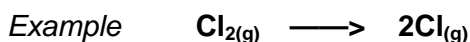
**Values** **Always exothermic**



### Bond Dissociation Energy (Enthalpy)

**Definition** The energy required to break ONE MOLE of gaseous bonds to form gaseous atoms.

**Values** **Endothermic** *Energy must be put in to break any chemical bond*



**Notes**

- the **strength of a bond also depends on its environment**; **MEAN values** are quoted
- making a bond is an exothermic process as it is the opposite of breaking a bond
- for diatomic gases, the bond enthalpy is twice the enthalpy of atomisation
- the smaller the bond enthalpy, the weaker the bond and the easier it is to break

## Standard Enthalpy of Atomisation ( $\Delta H^\circ_{\text{at}, 298}$ )

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

**Notes**

- For elements that are solids, the change is known as ENTHALPY OF SUBLIMATION.
- Do not confuse with Bond (Dissociation) Energy. (see earlier notes)

**Q.1** Write equations representing the standard enthalpies of atomisation / sublimation of

magnesium

carbon

oxygen

hydrogen

## 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** you have to overcome the pull of the nucleus on the electron

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

**Notes**

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

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

**Notes**

- Do not confuse electron affinity with electronegativity.

## Lattice Energy (Enthalpy)

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

### a) Lattice Formation Enthalpy

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

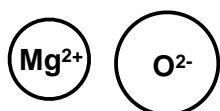
**Values**

- **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.**

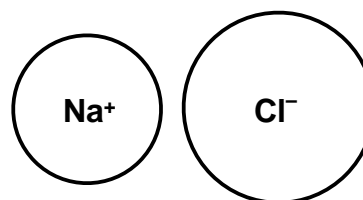
**Example**  $\text{Na}^+_{(g)} + \text{Cl}^-_{(g)} \longrightarrow \text{Na}^+ \text{Cl}^-_{(s)}$

**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**



**HIGH CHARGE DENSITY IONS  
LARGE LATTICE ENTHALPY**



**LOWER CHARGE DENSITY IONS  
SMALLER LATTICE ENTHALPY**

**Q.2** Which substance in the the following pairs has the larger lattice enthalpy?

- $\text{NaCl}$  or  $\text{KCl}$
- $\text{NaF}$  or  $\text{NaCl}$
- $\text{MgCl}_2$  or  $\text{NaCl}$
- $\text{MgO}$  or  $\text{MgCl}_2$

### Consequences

#### 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
- the high lattice enthalpy is due to the attraction between ions of high charge density

	$\text{Mg}^{2+} \text{O}^{2-}$	$\text{Ca}^{2+} \text{O}^{2-}$	$\text{Sr}^{2+} \text{O}^{2-}$	$\text{Ba}^{2+} \text{O}^{2-}$
Lattice Enthalpy ( $\text{kJ mol}^{-1}$ )	<b>-3889</b>	<b>-3513</b>	<b>-3310</b>	<b>-3152</b>
Melting Point ( $^{\circ}\text{C}$ )	<b>2853</b>	— decreasing values —>		

### Thermal stability

- thermal stability of Group II carbonates increases down the group
- $\text{MgCO}_3$  decomposes much easier than  $\text{BaCO}_3$
- BUT the lattice enthalpy of  $\text{MgCO}_3$  is HIGHER!

	$\text{MgCO}_3$	$\text{CaCO}_3$	$\text{SrCO}_3$	$\text{BaCO}_3$
Decomposes at	350°C	832°C	1340°C	1450°C
Lattice Enthalpy ( $\text{kJ mol}^{-1}$ )	-3123	—————>		-2556

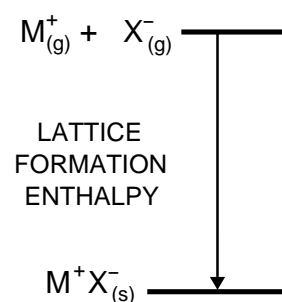
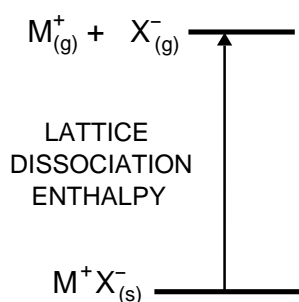
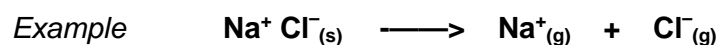
- $\text{Mg}^{2+}$  ions are **SMALLER** and have a **HIGHER CHARGE DENSITY**
- this makes them **MORE HIGHLY POLARISING**
- they **DISTORT THE  $\text{CO}_3^{2-}$**  ion
- this **WEAKENS THE ATTRACTION BETWEEN IONS**
- the **LATTICE IS NOT AS STRONG**

### b) Lattice Dissociation Enthalpy

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

**Values**

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

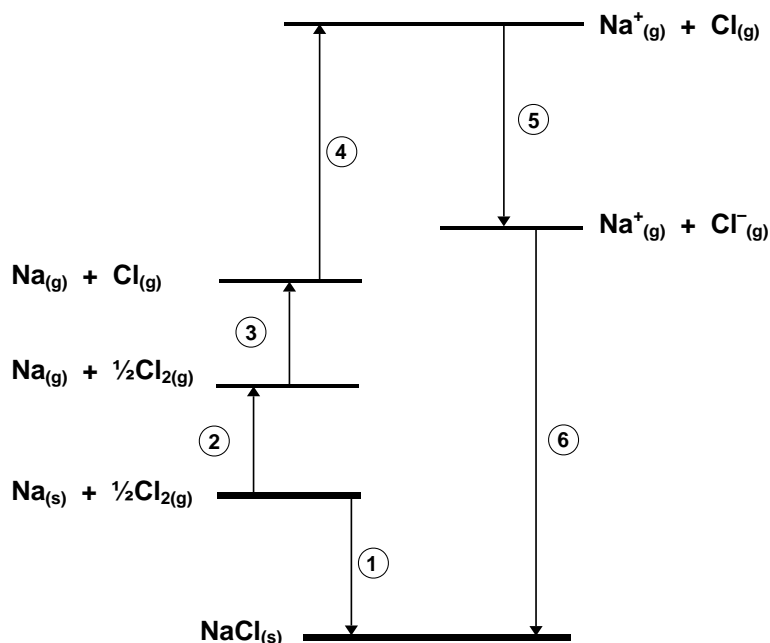


## BORN-HABER CYCLES

### 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 which cannot be determined directly by experiment

### BORN-HABER CYCLE FOR SODIUM CHLORIDE



#### STEPS (values are in $\text{kJ mol}^{-1}$ )

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

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

**Q.3** Construct similar Born-Haber cycles for  $\text{NaCl}_2$  and  $\text{MgCl}_2$  using suitable data.

If the Lattice Enthalpy of  $\text{NaCl}_2$  is  $-3360 \text{ kJ mol}^{-1}$ , what is its enthalpy of formation? What does this tell you about the stability of  $\text{NaCl}_2$ ?

If the Lattice Enthalpy of  $\text{MgCl}_2$  is  $-2493 \text{ kJ mol}^{-1}$ , what is its enthalpy of formation?

## Enthalpy of Hydration

**Definition** The enthalpy change when ONE MOLE of gaseous ions dissolves in (an excess of) water.

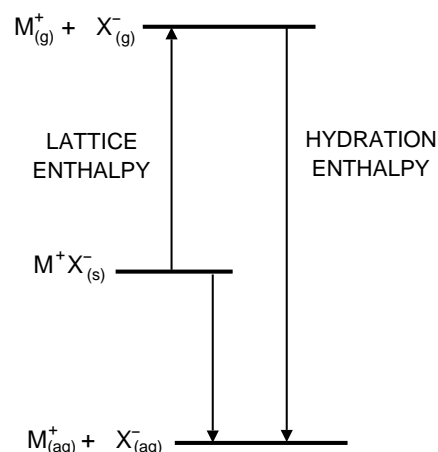
**Values** **Exothermic**

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

**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.

Comparing Lattice Energy (LE) with the Hydration Enthalpy (HE) of the ions gives an idea of the solubility of a substance.



**If  $LE \gg HE$  then the salt will probably be insoluble.**

**Q.4** What name is given to the third step in the above diagram involving the change...  
 $M^+X^-(s) \longrightarrow M^+(\text{aq}) + Cl^-(\text{aq})$

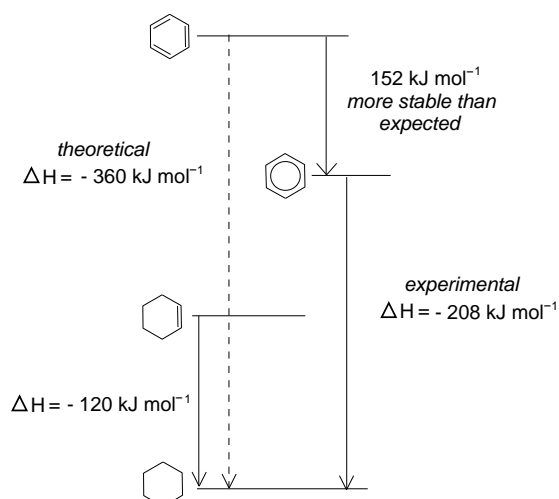
## Enthalpy of Hydrogenation

**Definition** The enthalpy change when ONE MOLE of double bonds is reduced to single bonds by reacting with gaseous hydrogen.

**Values** **Exothermic**

**Example**  $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \longrightarrow \text{C}_2\text{H}_6(\text{g})$

**Notes** See "Thermodynamic stability of benzene" notes for more details.



**Q.5** Why are average bond enthalpies quoted in calculations?

## SOME USEFUL VALUES FOR THERMODYNAMIC CHANGES

Values, which may be slightly different in other books, are in  $\text{kJ mol}^{-1}$

## Enthalpy of formation and combustion

	$\Delta H_f$	$\Delta H_c$
H <sub>2</sub>	0	-286
O <sub>2</sub>	0	0
C	0	-393
CO <sub>2</sub>	-393	0
H <sub>2</sub> O	-242	0
CH <sub>4</sub>	-75	-890
C <sub>2</sub> H <sub>6</sub>	-85	-1560
C <sub>3</sub> H <sub>8</sub>	-104	-2219
C <sub>2</sub> H <sub>4</sub>	+52	-1410
C <sub>6</sub> H <sub>10</sub>	-38	-3752
CH <sub>3</sub> COOH	-484	-874
C <sub>2</sub> H <sub>5</sub> OH	-277	-1367

## 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 <sup>-</sup>	-314
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## Lattice Enthalpy

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

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

## Hydration Enthalpy

Li <sup>+</sup>	-499	Be <sup>2+</sup>	-2385
Na <sup>+</sup>	-390	Mg <sup>2+</sup>	-1891
K <sup>+</sup>	-305	Ca <sup>2+</sup>	-1561

## Bond Enthalpy (average)

C-C	+347	C=C	+612
C-H	+413	C-O	+336
C=O	+805 (CO <sub>2</sub> )	C=O	+740 (ald/ket)
O-H	+464	H-H	+436
O=O	+498		