**Born Haber Cycle**: is similar to an extended Hess' Law cycle, in which experimental data for reactions are used to obtain the 'Enthalpy of Lattice Formation'.

Definitions

Enthalpy of Formation: is the enthalpy change when **one mole of a substance** is completely formed from its **constituent elements** under **standard conditions** (298K and 1atm), with all reactants and products in their **standard states**:

$$Mg_{(s)} + \tfrac{1}{2}O_{2(g)} \longrightarrow MgO_{(s)} \qquad \Delta H = exo$$
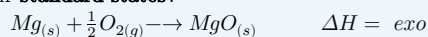
Enthalpy of Atomisation: is the enthalpy change **when one mole of a gaseous atom** is formed from elements in their **standard state**:

$$Mg_{(s)} \longrightarrow Mg_{(g)} \qquad\qquad \Delta H = endo$$
$$\tfrac{1}{2}O_{2((g))} \longrightarrow O_{(g)} \qquad\qquad \Delta H = endo$$

Note: for gaseous diatomic molecules, the bond enthalpy is twice the enthalpy of atomisation. Bond enthalpy equation produces 2 moles of gaseous atoms.

**1ˢᵗ Enthalpy of Ionisation:** is the energy required to **remove one mol of electrons** from **one mole of gaseous atoms** to form **one mole of gaseous unipositive ions**:

$$Mg_{(g)} \longrightarrow Mg^+_{(g)} + e^- \qquad\qquad \Delta H = endo$$
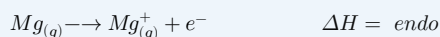
2ⁿᵈ Enthalpy of Ionisation: is the energy required to **remove one mol of electrons** from **one mole of gaseous unipositive ions** to form **one mole of gaseous +2 ions**:

$$Mg^+_{(g)} \longrightarrow Mg^{2+}_{(g)} + e^- \qquad\qquad \Delta H = endo$$

1ˢᵗ Electron Affinity: enthalpy change when **one mole of gaseous atoms**, gain one mole of electrons to form **one mole of gaseous uni-negative (-1) ions**:
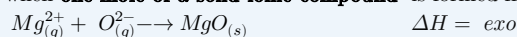
$$O_{(g)} + e^- \longrightarrow O^-_{(g)} \qquad\qquad \Delta H = exo$$
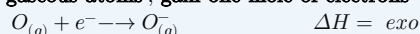
2ⁿᵈ Electron Affinity: enthalpy change when **one mole of gaseous uni-negative ions**, gain one mole of electrons to form **one mole of gaseous 2- ions**:
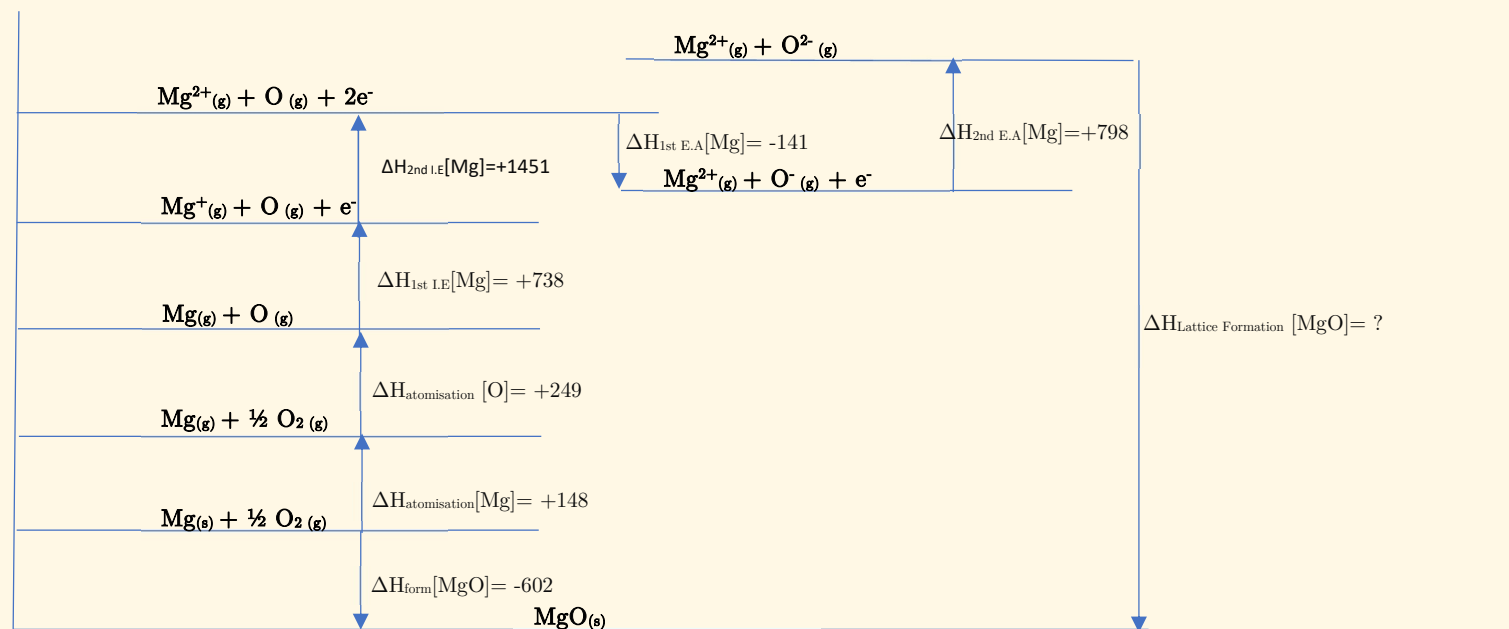
$$O^-_{(g)} + e^- \longrightarrow O^{2-}_{(g)} \qquad\qquad \Delta H = endo$$
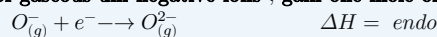
Note: 2ⁿᵈ Electron Affinity and successive E.As are **endothermic**, as energy is required to overcome the **repulsion between the negative ion & electron.**

Enthalpy of Lattice Formation: is the enthalpy change when **one mole of a solid ionic compound** is formed from its **gaseous ions**:

$$Mg^{2+}_{(g)} + O^{2-}_{(g)} \longrightarrow MgO_{(s)} \qquad\qquad \Delta H = exo$$

Born Haber Cycle for MgO

      ↑ = endothermic   ↓ = exothermic

General Formula is as follows:

$$\Delta H_{form} = \Delta H_{atm} + \Delta H_{ionisation} + \Delta H_{electronaffinity} + \Delta H_{LatticeFormation}$$

For above cycle:

$$\Delta H_{form} = \Delta H_{atm}[Mg] + H_{atm}[O] + \Delta H_{ionisation}[Mg] + \Delta H_{ionisation}[Mg^+] + \Delta H_{electronaffinity}[O] + \Delta H_{electronaffinity}[O-] + \Delta H_{LatticeFormation}[MgO]$$

Substituting in the numbers:

$$-602 = 148 + 249 + 738 + 1451 + (-141) + 798 + \Delta H_{LatticeFormation}[MgO]$$

$$\Delta H_{LatticeFormation}[MgO] = -3{,}845 KJ/mol$$

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Factors affecting Lattice Enthalpy:

The below two factors affect the electrostatic attraction within the ionic compound, thus affecting lattice enthalpy:

➢ **Size of the ion:** Smaller the ionic radius, the **greater the electrostatic attraction** b/w ions as ions are closer together.
➢ **Charge of the ion:** The **greater the ionic charge**, the **greater the electrostatic attraction** b/w ions.
  o Thus, resulting in a greater **charge density** (charge/size).

	Increasing Radius ------------------------------>			
	F^-	Cl^-	Br^-	I^-
Li^+	-1030	-846	-802	-758
Na^+	-917	-786	-743	-703
K^+	-819	-712	-678	-650
Rb^+	-785	-684	-655	-629
Cs^+	-749	-660	-652	-612

(Increasing Radius — vertical axis)

LiF will has a greater lattice enthalpy of formation compared to any other ionic compound in the left table, since:
➢ Li^+ and F^- have the smallest ionic radius with respect to cation (+ ion) and anion (- ion).
➢ The ionic charge as you go down Group 1 and Group 7 remain constant.
➢ Therefore, Li^+ and F^- have the greatest charge density, which results in the highest lattice formation enthalpy.

Note: Lattice formation enthalpy highlights strength of the ionic bond. **More exothermic the lattice enthalpy**, the **stronger the ionic bond**.

### Theoretical vs Experimental Lattice Enthalpies

Experimental Lattice Enthalpy: calculated via the use of Born Haber cycle. Recall: the enthalpy values used in Born Haber cycle are from experiments.
Theoretical Lattice Enthalpy: use of computational models which assumes **perfect ionic model.**
Perfect ionic model: assumes **spherical ions**, with **100% ionic interactions** and **no degree of covalency** (covalent character).

Polarising ability of Cation:

The **ability of a cation to distort the electron cloud in an anion** is called its **polarising ability**. Similar to previously, the **greater the ionic charge**, and the **smaller the ionic radius**; the **greater the polarising ability**.


Na⁺   Cl⁻   Al³⁺   Cl⁻

Nearly perfectly ionic   Ionic with covalent
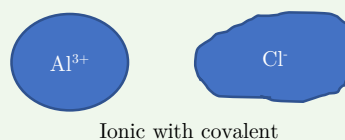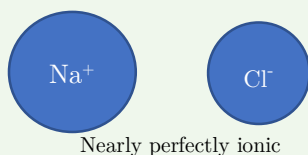
Compound	Experimental $\Delta H_{Lattice\ Formation}$	Theoretical $\Delta H_{Lattice\ Formation}$	Difference (KJ/mol)
Sodium Chloride (NaCl)	-771	-766	-5
Aluminium Chloride (AlCl₃)	-5,492	-5,300	-192

Note: The experimental lattice enthalpies will always be more exothermic than theoretical lattice enthalpies, as they capture both ionic and covalent interactions. Theoretical, assumes perfectly ionic, hence does not account for degree of covalency. As Aluminium Chloride has a greater degree of covalency/covalent character, the difference between experimental and theoretical lattice enthalpies are greater compared to those of Sodium Chloride.

Calculating Enthalpy of Solutions

Enthalpy of Solution: is the enthalpy change when **one mole of a solute is dissolved completely in a solvent**, in which the molecules and ions are far enough apart to not interact with each other:
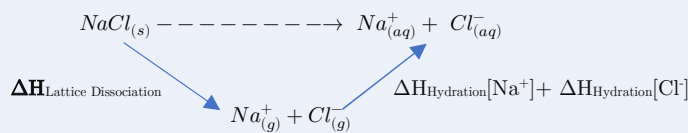
$$NaCl_{(s)} ----\rightarrow Na^+_{(aq)} + Cl^-_{(aq)}$$
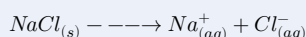
ΔH_{soln} can be either exothermic or endothermic. Generally, when exothermic the substance is more likely be soluble. However, Sodium Chloride for example has a positive enthalpy of solution, but still soluble.

Enthalpy of Hydration: is the enthalpy change when **one water molecules surround one mole of gaseous ions** to form **one mole of aqueous ions**:

$$Na^+_{(g)} ----\rightarrow Na^+_{(aq)} \qquad \Delta H = exo$$

$$Cl^-_{(g)} ----\rightarrow Cl^-_{(aq)} \qquad \Delta H = exo$$
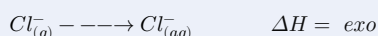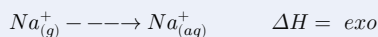
Note: Hydration enthalpies are exothermic, as ions form bonds with the water molecules. Positive ions bond with $O^{\delta-}$ in H_2O and negative ions form bonds with $H^{\delta+}$ in H_2O. Therefore, hydration enthalpies are also affected by charge & size of ion. For e.g. Mg^{2+} has a greater hydration enthalpy than Na^+, as Mg^{2+} has a greater ionic charge, and a smaller ionic radius, thus greater charge density and hydration enthalpy.

**To calculate Enthalpy of Solution, the below thermochemical cycle can be drawn:**

$$NaCl_{(s)} ---------\rightarrow Na^+_{(aq)} + Cl^-_{(aq)}$$

$\Delta H_{Lattice\ Dissociation}$ $\Delta H_{Hydration}[Na^+] + \Delta H_{Hydration}[Cl^-]$

$$Na^+_{(g)} + Cl^-_{(g)}$$

$$\Delta H_{Solution} = \Delta H_{Lattice\ Dissociation} + \Delta H_{Hydration}$$

Entropy

Spontaneous/Feasible Reactions : are those which occur on their own accord without any intervention. The definition takes no account into the rate of reaction. E.g. rusting of Iron is a spontaneous reaction, albeit at a very low rate.

Most exothermic reaction are spontaneous as they release energy, hence form products with lower energy thus more thermodynamically stable. Endothermic reactions form products with higher energy than reactants, but these can be spontaneous due to a phenomenon known as entropy.

Entropy (S): is defined a measure of disorder/randomness. As you go from solid to gas, your disorder increases, hence entropy increases. Units: **$JK^{-1}mol^{-1}$**

Solid   Liquid   Gas

Entropy Increases
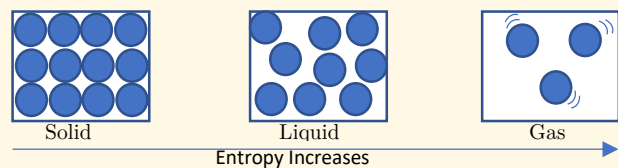
Substance	$S^{\ominus}$ ($JK^{-1}mol^{-1}$)
C (Diamond)$_{(s)}$	2.4
$H_2O_{(l)}$	70.0
$CO_{2(g)}$	213.8

All substances have a **degree of disorder, hence, positive entropy values.**

Note: Entropy of a substance is always positive except at 0K (absolute zero) but **entropy change (ΔS) can be either positive/negative.**
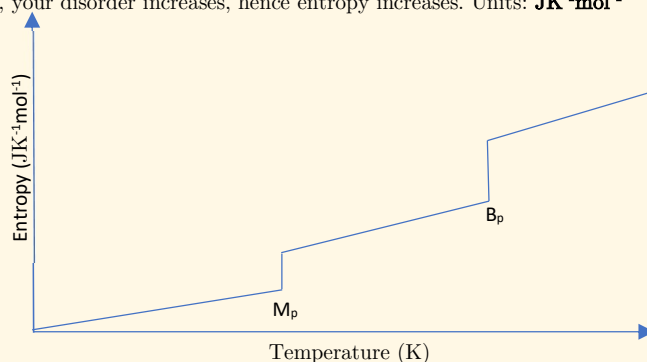

M_p: Sudden increase in entropy reflects increased entropy (disorder) in liquids compared to solids, when melting occurs.

B_p: Sudden increase in entropy reflects increased entropy in gases compared to liquids, when boiling occurs. **Note**: entropy change from liquid to gas, is greater than solid to liquid.

Identifying Entropy Changes in Reactions (Qualitative)

- Reactions can either have a positive or negative entropy change (ΔS). If entropy increases ΔS will be positive and vice versa.
- In general, entropy increases when there is:
  - A change in state from reactants to product that will results in higher entropy E.g. solid reactants to liquid/gaseous products.
  - An increase in the number of moles from reactants to products. E.g. from 2 moles of reactants to 3 moles of products.
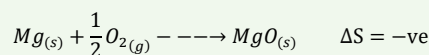
Example 1:

$$CaCO_{3(s)} ----\rightarrow CaO_{(s)} + CO_{2(g)} \qquad \Delta S = +ve$$
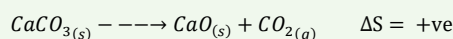
Entropy increases:
- Change from solid reactant to products in solid and gaseous state.
- Increase in no. of moles i.e. 1 reactant mole to 2 moles of product.

Example 2:

$$Mg_{(s)} + \frac{1}{2}O_{2(g)} ----\rightarrow MgO_{(s)} \qquad \Delta S = -ve$$

Entropy decreases:
- Change from solid & gaseous reactant to products in solid state.
- Decrease in no. of moles i.e. 1.5 reactant moles to 1 moles of product.
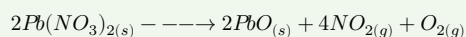
Calculating Entropy Changes (Quantitative)

In order to calculate entropy changes, we apply the below formula. The below simply is the sum of entropy of all products less the sum of entropy of all reactants. Entropy values are quoted on a per mole basis and are temperature dependant, and these will be given to you in the data table.

$$\Delta S = \sum S^{\ominus}_{products} - \sum S^{\ominus}_{reactants}$$

Example 3:

Calculate the Entropy change for the thermal decomposition of Pb(NO$_3$)$_2$ at standard conditions using the entropy values provided in the table to the right?

$$2Pb(NO_3)_{2(s)} ----\rightarrow 2PbO_{(s)} + 4NO_{2(g)} + O_{2(g)}$$

$$\Delta S = \sum S^{\ominus}_{products} - \sum S^{\ominus}_{reactants}$$

$$\Delta S = [(2 \text{ x } 68.8) + (4 \text{ x } 239.0) + (1 \text{ x } 204.9)] - [(2 \text{ x } 214)]$$

$$\Delta S = \mathbf{870.5 \ JK^{-1}mol^{-1}}$$

Substance	$S^{\ominus}$ ($JK^{-1}mol^{-1}$)
Pb(NO$_3$)$_{2(s)}$	214.0
PbO$_{(s)}$	68.8
NO$_{2(g)}$	239.0
O$_{2(g)}$	204.9

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Gibbs Free Energy

Two factors, namely: Entropy change and Enthalpy change affect the feasibility of a reaction. Thus, the Gibbs Free Energy incorporates the aforementioned:

$$\Delta G = \Delta H - T\Delta S$$

If ΔG is negative, then reaction is feasible. If positive, then not feasible.

Where:
$\mathbf{\Delta G}$ = Gibbs Free Energy (KJ/mol)
$\mathbf{\Delta H}$ = Enthalpy Change (KJ/mol)
$\mathbf{\Delta S}$ = Entropy Change in $Jk^{-1}mol^{-1}$
$\mathbf{T}$ = Temperature (K)

Note: Convert entropy units from $JK^{-1}mol^{-1}$ to $KJ\ K^{-1}\ mol^{-1}$ by dividing by 1,000.

Example 4:

Calculate the Gibbs free energy for the below reaction and state if feasible at 25°C (298K)?

$$MgCO_{3(s)} ----\rightarrow MgO_{(s)} + CO_{2(g)} \qquad \Delta H = +118 KJ/mol$$
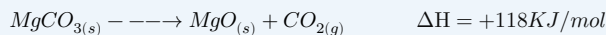
Substance	$S^{\ominus}$ ($JK^{-1}mol^{-1}$)
$MgCO_{3(s)}$	214.0
$MgO_{(s)}$	68.8
$CO_{2(g)}$	239.0

1. Calculate ΔS:

$$\Delta S = \sum S^{\ominus}_{products} - \sum S^{\ominus}_{reactants}$$

$$\Delta S = (68.8 + 239) - (214)$$

$$\mathbf{\Delta S = 93.8\ JK^{-1}mol^{-1}}$$

2. Calculate ΔG:

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = (118) - (298\ \text{x}\ \frac{93.8}{1000})$$

$$\mathbf{\Delta G = 90.1\ KJmol^{-1}},\ \textit{positive hence not feasible.}$$

Calculating minimum temperature at which reaction becomes feasible?

The minimum temperature at which a reaction becomes feasible is when:

$$\Delta G = 0$$

Therefore, we can calculate the temperature as follows:

$$\Delta G = \Delta H - T\Delta S$$

$$0 = \Delta H - T\Delta S$$

$$\textit{Rearranging results in } \mathbf{T = \frac{\Delta H}{\Delta S}}$$

Note: Remember to convert entropy units from $JK^{-1}mol^{-1}$ to $KJ\ K^{-1}\ mol^{-1}$ by dividing by 1,000.

Example 5:

Calculate the minimum temperature, the reaction in Example 4 becomes feasible?

$$T = \frac{\Delta H}{\Delta S}$$

$$T = \frac{118\ KJmol^{-1}}{93.8\ JK^{-1}mol^{-1}/1000} = \mathbf{1,257.9K}$$

The thermal decomposition of Magnesium oxide becomes feasible at 1,257.9K.