Raffles Institution
Year 5 H2 Chemistry 2022

Lecture Notes 5a – Chemical Energetics 1

Content

1. Enthalpy changes: ΔH, of formation, combustion, hydration, solution, neutralisation, atomisation, bond energy, lattice energy, electron affinity
2. Hess' Law, including Born-Haber cycles

Learning Outcomes

Candidates should be able to:

(a) explain that most chemical reactions are accompanied by energy changes, principally in the form of heat usually associated with the breaking and forming of chemical bonds; the reaction can be exothermic (ΔH negative) or endothermic (ΔH positive)

(b) construct and interpret an energy profile diagram, in terms of the enthalpy change of the reaction and of the activation energy (see also Section 8, under Reaction Kinetics)

(c) explain and use the terms:

  (i) *enthalpy change of reaction* and *standard conditions*, with particular reference to: formation; combustion; hydration; solution; neutralisation; atomisation

  (ii) *bond energy* (ΔH positive, i.e. bond breaking) (see also Section 2, Chemical Bonding)

  (iii) *lattice energy* (ΔH negative, i.e. gaseous ions to solid lattice)

(d) calculate enthalpy changes from appropriate experimental results, including the use of the relationship: heat change = $mc\Delta T$

(e) explain, in qualitative terms, the effect of ionic charge and of ionic radius on the numerical magnitude of a lattice energy

(f) apply Hess' Law to construct simple energy cycles, e.g. Born-Haber cycle, and carry out calculations involving such cycles and relevant energy terms (including ionisation energy and electron affinity), with particular reference to:

  (i) determining enthalpy changes that cannot be found by direct experiment, e.g. an enthalpy change of formation from enthalpy changes of combustion

  (ii) the formation of a simple ionic solid and of its aqueous solution

  (iii) average bond energies

References

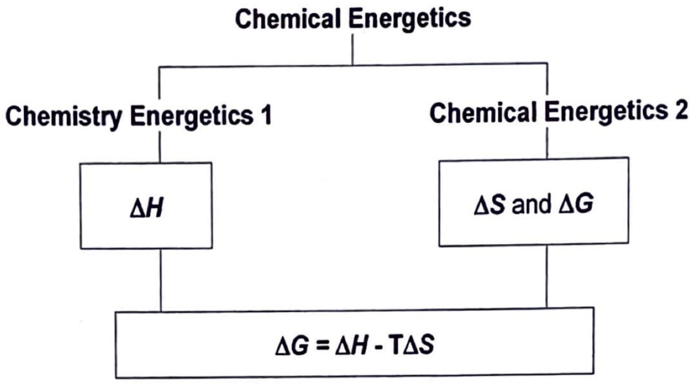
1. Chemistry in Context by Hill and Holman
2. Chemistry: The Molecular Nature of Matter and Change by Martin S. Silberberg
3. A-level Chemistry by EN Ramsden
4. Chemistry in Action by Freemantle

Lecture Outline

1 Introduction

- **Thermodynamics** is the science dealing with the relationship between heat and work and with transformations of energy from one form to another.

- **Thermochemistry** is a branch of thermodynamics dealing with the study of energy changes associated with chemical reactions or physical processes, especially energy changes that appear as heat.



1.1 Enthalpy and Enthalpy Change

- The **enthalpy** of a system is a measure of the **energy content** of the system and has the symbol ***H***. The **higher** the energy content of a system, the more **unstable** it is.

- It is **not** possible to measure the total enthalpy (or absolute enthalpy) of a system. The chemist is interested in the **enthalpy change** that accompanies a physical or chemical process. Enthalpy change is denoted by ΔH (read as "delta H").

- When a system changes, by some physical or chemical process, the new system is likely to have a different energy because new substances may have formed and/or the intermolecular forces/bonding may have changed. This energy change typically appears as **absorption or release of heat**.

Enthalpy, H	**Enthalpy change, ΔH**
• Cannot be measured	• ΔH is the change in energy content (energy absorbed or released) of a process in a system at constant pressure. • $\Delta H = \Sigma H_{products} - \Sigma H_{reactants}$ • Units: kJ mol^{-1}

- The heat absorbed or released in a process **at constant pressure** (which is how most laboratory experiments are carried out) measures the enthalpy change of the system.

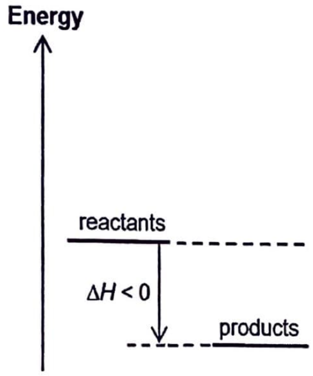
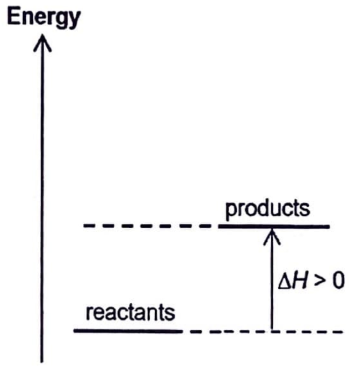
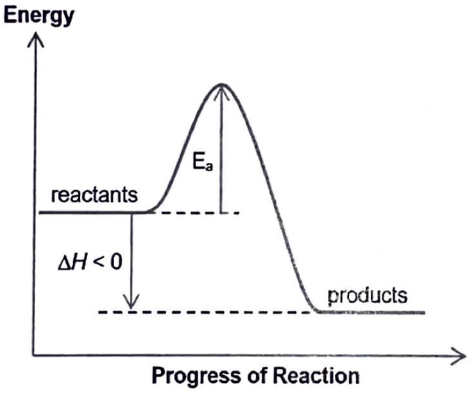
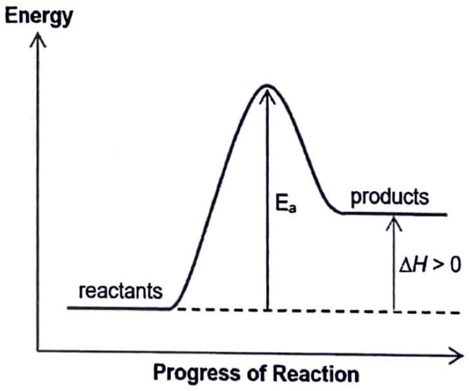
1.2 Endothermic and Exothermic Reactions

- When a chemical reaction take place, bonds are broken and new bonds are formed.

  (a) breaking of bonds **absorbs** energy ⇒ **endothermic** process
  (b) formation of bonds **releases** energy ⇒ **exothermic** process

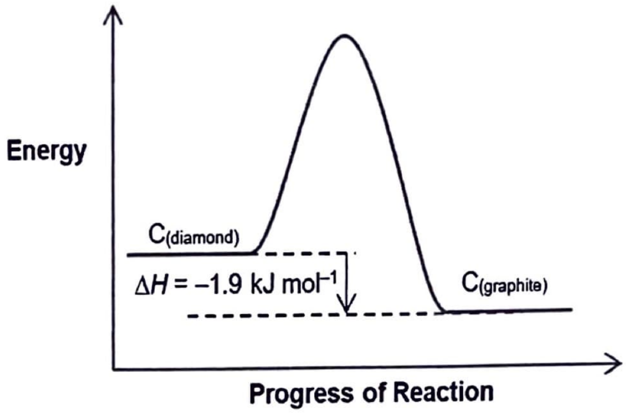
- The **enthalpy change** of a reaction is the difference between the quantity of heat **absorbed to break the bonds** in the reactants and that **released during the formation of new bonds** in the products at constant pressure.

- The table below shows the differences between an exothermic and an endothermic reaction.

	Exothermic reaction	**Endothermic reaction**
Definition	A reaction in which energy is **released** to the surroundings.	A reaction in which energy is **absorbed** from the surroundings.
Temperature change	Temperature of surroundings **increases** in the process.	Temperature of surroundings **decreases** in the process.
Enthalpy change	ΔH is negative. $\Sigma H_{\text{products}} < \Sigma H_{\text{reactants}} \Rightarrow \Delta H < 0$ Products are energetically **more stable** than reactants.	ΔH is positive. $\Sigma H_{\text{products}} > \Sigma H_{\text{reactants}} \Rightarrow \Delta H > 0$ Products are energetically **less stable** than reactants.
Energy level diagram		
Energy profile diagram		
Note	• Exothermic reactions, being more **energetically feasible** than endothermic reactions, are **more likely to occur** once initiated. • The **activation energy, E_a**, of a reaction is the minimum amount of energy that the reactant particles must possess before they can collide successfully to form products. It is related to the *rate* at which the reaction occurs *(to be covered in the next topic on Reaction Kinetics)*.	

- **Question:** Can we predict with certainty whether a reaction will occur by looking at ΔH?

- Consider the following reaction: **C(diamond)** $\longrightarrow$ **C(graphite)**; $\Delta H = -1.9$ kJ mol^{-1}



Note:

- Many reactions are **energetically feasible** ($\Delta H < 0$) but they may occur very slowly.
- The enthalpy change of a reaction is an indication of the energetic stability, **not its kinetic stability, of the products with respect to the reactants.**
- It says nothing of the rate of a reaction (to be covered in the next topic on Reaction Kinetics).

1.3 General notes about enthalpy change, ΔH

1. All ΔH values must be accompanied by "+" or "–".

2. Reversing a chemical equation would also **reverse the sign of ΔH**.

   (a) $A(s) + B(g) \rightarrow C(g) + D(g)$ $\qquad \Delta H_1 = +\mathbf{x}$ kJ mol^{-1}
   (b) $C(g) + D(g) \rightarrow A(s) + B(g)$ $\qquad \Delta H_2 = -\mathbf{x}$ kJ mol^{-1}

3. Multiplying a chemical equation by a factor would also **multiply ΔH by the same factor**.

   (a) $A(s) + B(g) \rightarrow C(g) + D(g)$ $\qquad \Delta H_1 = +\mathbf{x}$ kJ mol^{-1}
   (b) $2A(s) + 2B(g) \rightarrow 2C(g) + 2D(g)$ $\qquad \Delta H_3 = +\mathbf{2x}$ kJ mol^{-1}

4. Always include the **state symbols** of all the chemical species given in a **thermochemical equation**.

   (a) $H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(g)$ $\qquad \Delta H = -214.8$ kJ mol^{-1}
   (b) $H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l)$ $\qquad \Delta H = -258.9$ kJ mol^{-1}

   Some energy is released when gaseous water condenses to liquid water.

$$\underbrace{H_2(g) + \tfrac{1}{2}O_2(g) \xrightarrow{-214.8\text{ kJ mol}^{-1}} H_2O(g) \xrightarrow{-44.1\text{ kJ mol}^{-1}} H_2O(l)}_{-258.9\text{ kJ mol}^{-1}}$$

Note:

- A **thermochemical equation** is a balanced equation that includes ΔH.
- A given ΔH applies only to the amounts of substances in their specified physical states for that given balanced equation (see Section 2.1).

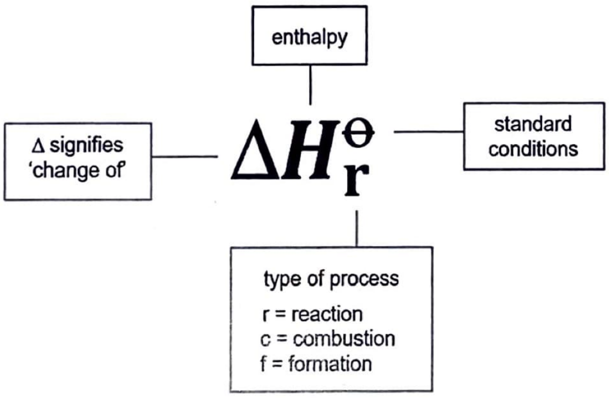
1.4 The standard conditions for thermochemical measurements

- The enthalpy change for a reaction can vary depending on the conditions used. To make a fair comparison of enthalpy changes, chemists determine enthalpy changes under a specific set of conditions termed the **standard conditions**.

- The standard conditions are:

standard conditions	
pressure	1 bar (10^5 Pa)
a stated temperature	usually 298 K (25 °C)
All substances involved are in their **standard states**.	

- The enthalpy changes determined under standard conditions are termed **standard enthalpy changes**.
  - The symbol used to show 'standard conditions' is **$\ominus$**.
  - The standard enthalpy change has the symbol **$\Delta H^\ominus$** (read it as "delta H nought").
  - The units for $\Delta H^\ominus$ are **kJ mol^{-1}**.

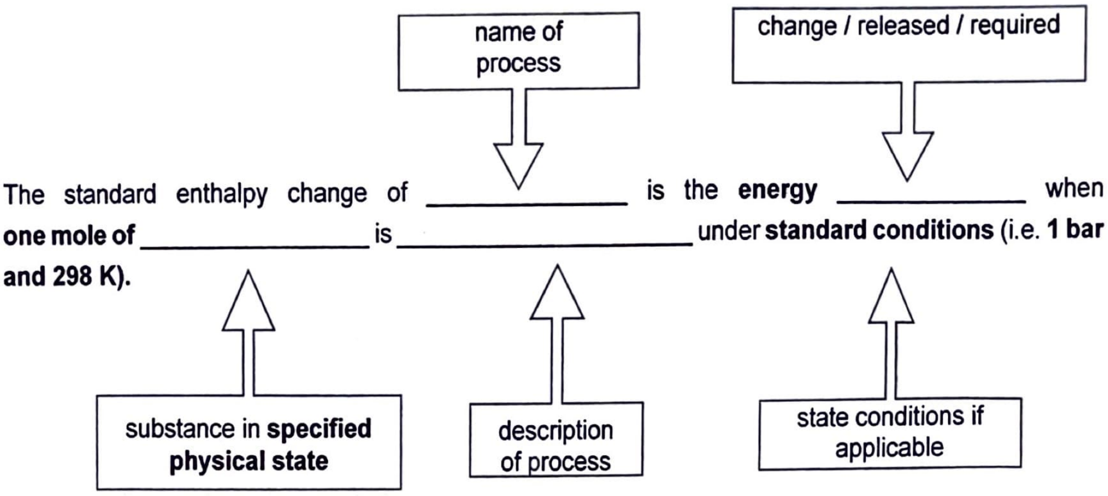


- Under standard conditions, all substances involved are in their **standard states.**
  - The standard state of a substance is its **most stable form** at **1 bar** and **298 K**.
  - When a substance exists as allotropes (i.e. different forms of the substance in the same physical state), it is important to state the allotrope referred to. Usually, it refers to the most stable allotrope.
  - For example, carbon exhibits allotropy and two well-known allotropes are diamond and graphite. Since graphite is energetically more stable than diamond, the standard state of carbon is graphite.
  - In the equation given below, C(s) refers to C(graphite).

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H^\ominus = -393.5 \text{ kJ mol}^{-1}$$

2 Definitions of Enthalpy Changes

- The many definitions given in this section must be remembered and understood well so that they can be used appropriately in calculations.
- A definition for standard enthalpy change/enthalpy change typically has the following form:



The standard enthalpy change of ____________ is the **energy** __________ when **one mole of** ____________ is ______________ under **standard conditions** (i.e. **1 bar and 298 K).**

2.1 Standard enthalpy change of reaction, ΔH_r°

ΔH_r°	The **standard enthalpy change of reaction (ΔH_r°)** is the energy change in a chemical reaction when the molar quantities of reactants stated in the chemical equation react under **standard conditions** (i.e. 1 bar and 298 K).

- Example

$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$ $\Delta H_r^\circ = -100$ kJ mol^{-1}

- **Note:**
  - The 'per mole' in 'kJ mol^{-1}' does not necessarily mean that the enthalpy change is for one mole of product or one mole of reactant.
  - The 'kJ mol^{-1}' is related to the amounts of all the substances given in the balanced equation. In this case 100 kJ of heat is evolved when 1 mole of $N_2(g)$ reacts with 3 moles of $H_2(g)$ to form 2 moles of $NH_3(g)$.
- For a reaction with the same reactants and products but represented by a balanced equation with different stoichiometric coefficients, the ΔH_r° will vary accordingly with the amounts of the substances specified.

$2N_2(g) + 6H_2(g) \longrightarrow 4NH_3(g)$ $\Delta H_r^\circ =$ -200 kJ mol^{-1}

$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g)$ $\Delta H_r^\circ =$ -50 kJ mol^{-1}

2.2 Standard enthalpy change of formation, $\Delta H_f^{\ominus}$

(1) The standard enthalpy change of formation of a substance

$\Delta H_f^{\ominus}$ (substance)	The **standard enthalpy change of formation ($\Delta H_f^{\ominus}$)** of a substance is the energy change when 1 mole of the pure substance in a specified state is formed from its constituent elements in their standard states under **standard conditions** (i.e. 1 bar and 298 K).

- Example 1

  The standard enthalpy change of formation of solid magnesium oxide is the energy change when 1 mole of MgO(s) is formed from Mg(s) and O_2(g) under standard conditions (i.e. 1 bar and 298 K).

$$\underbrace{\mathbf{Mg(s) + \tfrac{1}{2}O_2(g)}}_{\text{contituent elements of MgO}} \longrightarrow \underset{\Uparrow}{\mathbf{MgO(s)}} \qquad \Delta H_f^{\ominus}[\text{MgO(s)}] = -102\ \text{kJ mol}^{-1}$$

$$\boxed{\text{1 mole of MgO(s)}}$$

$$\mathbf{2Mg(s) + O_2(g) \longrightarrow 2MgO(s)} \qquad \Delta H_r^{\ominus} = \boxed{-204\ \text{kJ mol}^{-1}}$$

- Example 2

  The standard enthalpy change of formation of liquid methanol is the energy change when one mole of CH_3OH(l) is formed from C(s), H_2(g) and O_2(g) under standard conditions (i.e. 1 bar and 298 K).

$$\boxed{C(s) + 2H_2(g) + \tfrac{1}{2}O_2(g)} \longrightarrow \mathbf{CH_3OH(l)} \qquad \Delta H_f^{\ominus}[CH_3OH(l)] = -238\ \text{kJ mol}^{-1}$$

- Example 3

  The standard enthalpy change of formation of gaseous nitrogen dioxide is the energy change when one mole of NO_2(g) is formed from N_2(g) and O_2(g) under standard conditions (i.e. 1 bar and 298 K).

$$\boxed{\tfrac{1}{2}N_2(g) + O_2(g)} \longrightarrow \mathbf{NO_2(g)} \qquad \Delta H_f^{\ominus}[NO_2(g)] = +33.2\ \text{kJ mol}^{-1}$$

- **Note:**
  - $\Delta H_f^{\ominus}$ can be **positive** or **negative**.
  - $\Delta H_f^{\ominus}$ is often used to predict the **stability** of a compound relative to its constituent elements.
  - The **more negative** the $\Delta H_f^{\ominus}$ of a compound, the **more stable** the compound is **relative to its constituent elements,** and the less likely the decomposition of the compound back into its constituent elements.

(2) The standard enthalpy change of formation of an element

$\Delta H_f^\ominus$ (element)	Based on the definition of the standard enthalpy change of formation of a substance given, the **standard enthalpy change of formation** of an **element** in its standard state under standard conditions (i.e. 298 K and 1 bar) is **zero.**

- Example: Standard enthalpy change of formation of oxygen gas

$$\boxed{O_2(g) \rightarrow O_2(g)}$$

$\Delta H_f^\ominus[O_2(g)] = 0\ \text{kJ mol}^{-1}$

- More examples:

$\Delta H_f^\ominus[Br_2(l)] = 0\ \text{kJ mol}^{-1}$ $\Delta H_f^\ominus[Na(s)] = 0\ \text{kJ mol}^{-1}$ $\Delta H_f^\ominus[C(\text{graphite})] = 0\ \text{kJ mol}^{-1}$

2.3 Standard enthalpy change of combustion, $\Delta H_c^\ominus$

$\Delta H_c^\ominus$	The **standard enthalpy change of combustion ($\Delta H_c^\ominus$)** of a substance is the energy released when **1 mole of the substance** is completely burnt in excess oxygen under standard conditions (i.e. 1 bar and 298 K).

- Example 1

  The standard enthalpy change of combustion of methane is the energy released when 1 mole of $CH_4(g)$ is completely burnt in excess $O_2(g)$ under standard conditions (i.e. 1 bar and 298 K).

$$\mathbf{CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)} \qquad \Delta H_c^\ominus[CH_4(g)] = -890\ \text{kJ mol}^{-1}$$

1 mole of $CH_4(g)$ is completely burnt

H_2O is a liquid at 1 bar and 298 K.

- Example 2

  The standard enthalpy change of combustion of ethanol is the energy released when 1 mole of $CH_3CH_2OH(l)$ is completely burnt in excess $O_2(g)$ under standard conditions (i.e. 1 bar and 298 K).

$$\mathbf{CH_3CH_2OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)} \qquad \Delta H_c^\ominus[CH_3CH_2OH(l)] = -1363\ \text{kJ mol}^{-1}$$

- **Note:**
  - For a compound containing carbon and hydrogen undergoing combustion, the carbon will be converted to $CO_2(g)$ and the hydrogen will be converted to $H_2O(l)$.

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H_r^\ominus = \Delta H_c^\ominus[CH_4(g)]$$

$$CH_4(g) + \frac{3}{2}O_2(g) \longrightarrow CO(g) + 2H_2O(l) \qquad \Delta H_r^\ominus \neq \Delta H_c^\ominus[CH_4(g)]$$

  - $\Delta H_c^\ominus$ values are used as an indication of the energy values of fuels. The more heat being liberated upon complete combustion, the better the fuel is.

2.4 Standard enthalpy change of neutralisation, $\Delta H^{\ominus}_{\mathrm{neut}}$

$\Delta H^{\ominus}_{\mathrm{neut}}$	**The standard enthalpy change of neutralisation ($\Delta H^{\ominus}_{\mathrm{neut}}$)** between an acid and a base is the energy change when the acid and the base react to form 1 **mole of water** under standard conditions (i.e. 1 bar and 298 K).

- The table below show the values of $\Delta H^{\ominus}_{\mathrm{neut}}$ for different pairs of acids and bases.

Acid	base	$\Delta H^{\ominus}_{\mathrm{neut}}$ / kJ mol^{-1}	Type of acid & base
$\mathrm{HNO_3(aq)}$	$\mathrm{NaOH(aq)}$	–57.3	strong acid – strong base
$\mathrm{HC}l\mathrm{(aq)}$	$\mathrm{NaOH(aq)}$	–57.3	
$\mathrm{CH_3COOH(aq)}$	$\mathrm{NaOH(aq)}$	–55.4	weak acid – strong base
$\mathrm{HCN(aq)}$	$\mathrm{NaOH(aq)}$	–12.0	
$\mathrm{HC}l\mathrm{(aq)}$	$\mathrm{NH_3(aq)}$	–51.7	strong acid – weak base
$\mathrm{CH_3COOH(aq)}$	$\mathrm{NH_3(aq)}$	–50.4	weak acid – weak base

- Example 1

  The standard enthalpy change of neutralisation between $\mathrm{HC}l\mathrm{(aq)}$ and $\mathrm{NaOH(aq)}$ is the energy change when $\mathrm{HC}l\mathrm{(aq)}$ and $\mathrm{NaOH(aq)}$ react to form 1 mole of water under standard conditions (i.e. 1 bar and 298 K).

$$\mathbf{HC}l\mathbf{(aq) + NaOH(aq) \longrightarrow NaC}l\mathbf{(aq) + H_2O(l)} \qquad \Delta H^{\ominus}_{\mathrm{neut}} = -57.3\ \mathrm{kJ\ mol^{-1}}$$

1 mole of $\mathrm{H_2O(l)}$ is produced

- $\mathrm{HC}l$ is a **strong acid**. It undergoes **complete dissociation** in aqueous solution.

$$\mathbf{HC}l\mathbf{(aq) \longrightarrow H^+(aq) + C}l\mathbf{^-(aq)}$$

- NaOH is a **strong base**. It undergoes **complete ionisation** in aqueous solution.

$$\mathbf{NaOH(aq) \longrightarrow Na^+(aq) + OH^-(aq)}$$

- The reaction between $\mathrm{HC}l\mathrm{(aq)}$ and $\mathrm{NaOH(aq)}$ to produce **1 mole of $\mathbf{H_2O}$** is found experimentally to release 57.3 kJ of heat.

- This reaction between a strong acid and a strong base in aqueous solution is essentially the reaction between $\mathrm{H^+(aq)}$ and $\mathrm{OH^-(aq)}$ to produce 1 mole of $\mathrm{H_2O}$.

strong acid-strong base neutralisation	$\mathbf{H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)}$ $\Delta H^{\ominus}_{\mathrm{neut}} = -57.3\ \mathrm{kJ\ mol^{-1}}$

- Note:

$$\mathbf{2HC}l\mathbf{(aq) + 2NaOH(aq) \longrightarrow 2NaC}l\mathbf{(aq) + 2H_2O(l)} \qquad \Delta H^{\ominus}_{\mathrm{r}} = 2\Delta H^{\ominus}_{\mathrm{neut}} = -114.6\ \mathrm{kJ\ mol^{-1}}$$

$$\mathbf{H_2SO_4(aq) + 2NaOH(aq) \longrightarrow Na_2SO_4(aq) + 2H_2O(l)} \qquad \Delta H^{\ominus}_{\mathrm{r}} = 2\Delta H^{\ominus}_{\mathrm{neut}}$$

- Example 2

The standard enthalpy change of neutralisation between $CH_3COOH(aq)$ and $NaOH(aq)$ is the energy change when $CH_3COOH(aq)$ and $NaOH(aq)$ react to form 1 mole of water under standard conditions (i.e. 1 bar and 298 K).

$$\mathbf{CH_3COOH(aq) + NaOH(aq) \longrightarrow CH_3COO^-Na^+(aq) + H_2O(l)} \qquad \Delta H^{\ominus}_{\text{neut}} = -55.4 \text{ kJ mol}^{-1}$$

1 mole of $H_2O(l)$ is produced

- CH_3COOH is a **weak acid**. It undergoes **partial dissociation** in aqueous solution.

$$\mathbf{CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)}$$

- NaOH is a **strong base**. It undergoes **complete ionisation** in aqueous solution.

$$\mathbf{NaOH(aq) \longrightarrow Na^+(aq) + OH^-(aq)}$$

- The reaction between $CH_3COOH(aq)$ and $NaOH(aq)$ to produce 1 mole of H_2O is found experimentally to release 55.4 kJ of heat.

weak acid-strong base neutralisation	$\mathbf{CH_3COOH(aq) + NaOH(aq) \longrightarrow CH_3COO^-Na^+(aq) + H_2O(l)}$ $\Delta H^{\ominus}_{\text{neut}} = -55.4 \text{ kJ mol}^{-1}$
Note: • In this case, the neutralisation reaction is **less exothermic** than that of the strong acid-strong base neutralisation reaction. • In this case, $\Delta H^{\ominus}_{\text{neut}}$ is **less negative** than –57.3 kJ mol^{-1}.	

- Why is this neutralisation reaction **less exothermic** than that of the strong acid-strong base neutralisation reaction?

This is because during the neutralisation reaction, the CH_3COOH molecules have to undergo further dissociation to produce H^+ ions for reaction with the OH^- ions.

$$\mathbf{CH_3COOH(aq) \longrightarrow CH_3COO^-(aq) + H^+(aq)}$$

This dissociation of CH_3COOH involves the

- breaking of the O–H bond (endothermic process) and
- hydration of the CH_3COO^- and H^+ ions (exothermic processes),

and the overall dissociation reaction is endothermic.

Since some energy is consumed to bring about further dissociation of the CH_3COOH molecules during the neutralisation reaction, the energy released from the reaction will be less. Hence the reaction is less exothermic than that of the strong acid-strong base neutralisation reaction.

2.5 Standard enthalpy change of atomisation, $\Delta H^{\ominus}_{atom}$

(1) The standard enthalpy change of atomisation of an element

$\Delta H^{\ominus}_{atom}$ (element)	**The standard enthalpy change of atomisation ($\Delta H^{\ominus}_{atom}$)** of an element is the energy absorbed when **1 mole of gaseous atoms** is formed from the element under standard conditions (i.e. 1 bar and 298 K).

- Example 1

  The standard enthalpy change of atomisation of sodium is the energy absorbed when 1 mole of gaseous Na atoms is formed from Na(s) under standard conditions (i.e. 1 bar) and 298 K).

  $$Na(s) \longrightarrow Na(g) \qquad \Delta H^{\ominus}_{atom}[Na(s)] = +108\ kJ\ mol^{-1}$$

  1 mole of gaseous Na atoms

- Example 2

  The standard enthalpy change of atomisation of chlorine is the energy absorbed when 1 mole of gaseous Cl atoms is formed from $Cl_2(g)$ under standard conditions (i.e. 1 bar and 298 K).

  $$\boxed{\frac{1}{2}Cl_2(g) \rightarrow Cl(g)} \qquad \Delta H^{\ominus}_{atom}[Cl_2(g)] = +122\ kJ\ mol^{-1}$$

  $$Cl_2(g) \longrightarrow 2Cl(g) \qquad \Delta H^{\ominus}_{r} = 2\Delta H^{\ominus}_{atom}[Cl_2(g)] = +244\ kJ\ mol^{-1}$$

(2) The standard enthalpy change of atomisation of a compound

$\Delta H^{\ominus}_{atom}$ (compound)	**The standard enthalpy change of atomisation ($\Delta H^{\ominus}_{atom}$)** of a compound is the energy absorbed when 1 **mole of the compound** is converted to **gaseous atoms** under standard conditions (i.e. 1 bar and 298 K).

- Example 1

  The standard enthalpy change of atomisation of methane is the energy absorbed when 1 mole of methane gas is converted to gaseous atoms under standard conditions (i.e. 1 bar and 298 K).

  $$CH_4(g) \longrightarrow C(g) + 4H(g) \qquad \Delta H^{\ominus}_{atom}[CH_4(g)] = +1664\ kJ\ mol^{-1}$$

  1 mole of $CH_4(g)$

- Example 2

  The standard enthalpy change of atomisation of ethanol is the energy absorbed when 1 mole of ethanol is converted to gaseous atoms under standard conditions (i.e. 1 bar and 298 K).

  $$CH_3CH_2OH(l) \longrightarrow 2C(g) + 6H(g) + O(g) \qquad \Delta H^{\ominus}_{r} = \Delta H^{\ominus}_{atom}[CH_3CH_2OH(l)]$$

- **Note:**

  The $\Delta H^{\ominus}_{atom}$ **of an element or a compound is always positive** because energy must be absorbed to break all the bonds between the atoms in the element / compound during the atomisation reaction.

2.6 Bond Dissociation Energy (BDE) and Bond Energy (BE)

(1) Bond dissociation energy (BDE) of a bond

BDE	The **bond dissociation energy** of a X–Y bond is the energy required to break **1 mole** of that **particular X–Y bond** in a **particular compound in gaseous state**.

- Example 1: Consider the H–H bond in H_2, a diatomic molecule.

  The bond dissociation energy (BDE) of the H–H bond is the energy required to break 1 mole of H–H bonds in H_2 in gaseous state.

  $$\text{H–H(g)} \longrightarrow \text{2H(g)} \qquad \Delta H = \text{BDE(H–H)} = +436 \text{ kJ mol}^{-1}$$

  1 mole of H–H bonds in H_2(g)

  What about ΔH for the reverse reaction? The ΔH for the reverse reaction is –436 kJ mol^{-1} since the reverse reaction involves the formation of 1 mol of H–H bonds.

  $$\text{2H(g)} \longrightarrow \text{H}_2\text{(g)} \qquad \Delta H = -\text{BDE(H–H)} = -436 \text{ kJ mol}^{-1}$$

- **Note:**

  - Bond breaking **absorbs energy**. A reaction which involves *only* bond breakage is endothermic.

    $\text{X–Y(g)} \longrightarrow \text{X(g)} + \text{Y(g)} \qquad \Delta H > 0$

  - Bond formation **releases energy**. A reaction which involves *only* bond formation is exothermic.

    $\text{X(g)} + \text{Y(g)} \longrightarrow \text{X–Y(g)} \qquad \Delta H < 0$

- The bond energy data for bonds in diatomic molecules given in the *Data Booklet* are actually bond dissociation energies.

3 Bond energies

3(a) Bond energies in diatomic molecules (these are exact values)

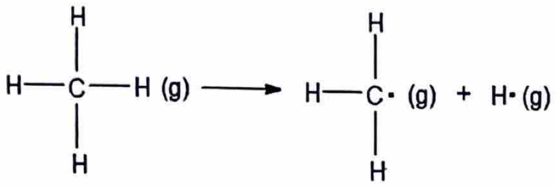
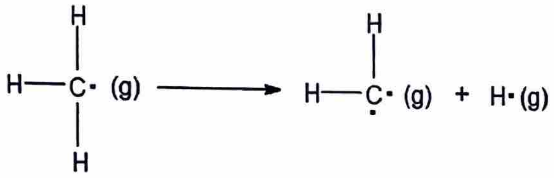
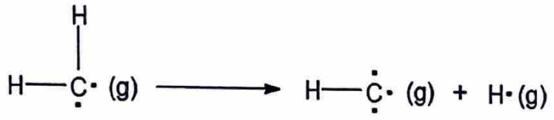
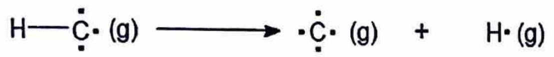
Homonuclear

Bond	Energy/kJ mol^{-1}
H—H	436
D—D	442
N≡N	944
O=O	496
F—F	158
Cl—Cl	244
Br—Br	193
I—I	151

Heteronuclear

Bond	Energy/kJ mol^{-1}
H—F	562
H—Cl	431
H—Br	366
H—I	299
C≡O	1077

- Example 2: Consider the 4 C–H bonds in CH_4, a polyatomic molecule.
  The energy required to break each C–H bond is different.
  In this case, there are **4 different C–H bond dissociation energies**.

	BDE_1(C–H) = +427 kJ mol^{-1}
	BDE_2(C–H) = +418 kJ mol^{-1}
	BDE_3(C–H) = +460 kJ mol^{-1}
	BDE_4(C–H) = +343 kJ mol^{-1}

(2) Bond energy (BE) of a bond

BE	The **bond energy** of a X–Y bond is the average energy required to break **1 mole of the X–Y bonds** in the **gaseous state**.

- Example 1: The bond energy of the C–N bond is the average energy required to break 1 mole of the C–N bonds are broken in the gaseous state.

  From the *Data Booklet*, BE(C–N) = +305 kJ mol^{-1}

- **Note:** The bond energy of the C–N bond given in the *Data Booklet* is an average value of the different C–N bond energies obtained from different compounds containing the C–N bond.

- The bond energy data for bonds in polyatomic molecules given in the *Data Booklet* are average values.

3(b) Bond energies in polyatomic molecules (these are average values)

Homonuclear

Bond	Energy/kJ mol^{-1}
C—C	350
C=C	610
C≡C	840
C⚌C (benzene)	520
N—N	160
N=N	410

Heteronuclear

Bond	Energy/kJ mol^{-1}
C—H	410
C—F	485
C—Cl	340
C—Br	280
C—I	240
C—N	305

- Example 2: The bond energy of the C–H bond in CH_4 is the average energy absorbed when 1 mole of the C–H bonds in CH_4 are broken in the gaseous state.

$$CH_4(g) \longrightarrow C(g) + 4H(g) \qquad \Delta H = 427 + 418 + 460 + 343 = +1648 \text{ kJ mol}^{-1}$$

$$\Delta H = 4\ \mathrm{BE(C–H)} = +1648$$

$$\mathrm{BE(C–H)} = \frac{+1648}{4} = +412 \text{ kJ mol}^{-1}$$

(3) Relationship between bond energy and enthalpy change of atomisation of diatomic gases

- Consider the bond energy of the $Cl–Cl$ bond and the enthalpy change of atomisation of Cl_2 gas

$$Cl–Cl(g) \longrightarrow 2Cl(g) \qquad \Delta H_1 = \mathrm{BE}(Cl–Cl) = 2\Delta H^{\circ}_{\text{atom}}[Cl_2(g)] = +244 \text{ kJ mol}^{-1}$$

1 mole of $Cl–Cl$ bonds

$$\tfrac{1}{2}Cl_2(g) \longrightarrow Cl(g) \qquad \Delta H_2 = \Delta H^{\circ}_{\text{atom}}[Cl_2(g)] = \tfrac{1}{2}\mathrm{BE}(Cl–Cl) = +122 \text{ kJ mol}^{-1}$$

1 mole of $Cl(g)$ atoms

- **Note:**

For a diatomic gas X_2, **bond energy of the X–X bond = 2 $\Delta H^{\circ}_{\text{atom}}[X_2(g)]$**

2.7 Ionisation Energy, IE

1st IE	The **first ionisation energy of an element** is the energy required to remove **1 mole** of electrons from 1 mole of gaseous atoms to form 1 mole of singly positively charged gaseous ions.

- Example: The first ionisation energy (1st IE) of calcium is the energy required to remove 1 mole of electrons from 1 mole of gaseous Ca atoms to form 1 mole of gaseous Ca^+ ions.

$$Ca(g) \longrightarrow Ca^+(g) + e^- \qquad \Delta H = 1^{st}\ \mathrm{IE(Ca)} = +590 \text{ kJ mol}^{-1}$$

2nd IE	The **second ionisation energy of an element** is the energy required to remove **1 mole** of electrons from 1 mole of singly positively charged gaseous ions to form 1 mole of doubly positively charged gaseous ions.

- Example: The second ionisation energy (2nd IE) of calcium is the energy required to remove 1 mole of electrons from 1 mole of gaseous Ca^+ ions to form 1 mole of gaseous Ca^{2+} ions.

$$Ca^+(g) \longrightarrow Ca^{2+}(g) + e^- \qquad \Delta H = 2^{nd}\ \mathrm{IE(Ca)} = +1100 \text{ kJ mol}^{-1}$$

2.8 Electron affinity, EA

1st EA	The **first electron affinity** (1st EA) of an element is the energy change when 1 mole of **gaseous atoms** acquires 1 mole of electrons to form 1 mole of **singly negatively charged gaseous ions**.

- Example: The first electron affinity (1st EA) of O is the energy released when 1 mole of gaseous O atoms acquires 1 mole of electrons to form 1 mole of gaseous O^- ions.

$$O(g) + e^- \longrightarrow O^-(g) \qquad \Delta H = 1^{st}\ EA(O) = -141\ kJ\ mol^{-1}$$

- **Note**:

The 1st electron affinity is usually **negative**. In this case for O, the energy released when the nucleus attracts the additional electron is usually larger than the energy taken in to overcome inter-electronic repulsion.

2nd EA	The **second electron affinity** (2nd EA) of an element is the energy absorbed when 1 mole of **singly negatively charged gaseous ions** acquires 1 mole of electrons to form 1 mole of **doubly negatively charged gaseous ions.**

- Example: The second electron affinity (2nd EA) of O is the energy absorbed when 1 mole of gaseous O^- ions acquires 1 mole of electrons to form 1 mole of gaseous O^{2-} ions.

$$O^-(g) + e^- \longrightarrow O^{2-}(g) \qquad \Delta H = 2^{nd}\ EA(O) = +790\ kJ\ mol^{-1}$$

- **Note**:

The 2nd electron affinity of an element is always **positive** because energy is required to overcome the repulsion between the two negatively charged species.

2.9 Lattice energy, LE

LE or $\Delta H^{\ominus}_{latt}$	The **lattice energy** (LE) of an ionic compound is the energy released when **1 mole** of the **solid ionic compound** is formed from **its constituent gaseous ions** under standard conditions (i.e. 1 bar and 298 K).

- Example 1: The lattice energy (LE) of sodium chloride is the energy released when 1 mole of $NaCl(s)$ is formed from $Na^+(g)$ and $Cl^-(g)$ ions under standard conditions (i.e. 1 bar and 298 K).

$$Na^+(g) + Cl^-(g) \longrightarrow NaCl(s) \qquad \Delta H^{\ominus}_{latt} = LE(NaCl) = -776\ kJ\ mol^{-1}$$

- Example 2: The lattice energy (LE) of calcium fluoride is the energy released when 1 mole of $CaF_2(s)$ is formed from $Ca^{2+}(g)$ and $F^-(g)$ ions under standard conditions (i.e. 1 bar and 298 K).

$$\boxed{Ca^{2+}(g) + 2F^-(g)} \longrightarrow CaF_2(s) \qquad \Delta H^{\ominus}_{latt} = LE(CaF_2) = -2805\ kJ\ mol^{-1}$$

1 mole of $CaF_2(s)$

- Refer to **Section 5** for more details.

2.10 Standard enthalpy change of hydration, $\Delta H^{\ominus}_{hyd}$

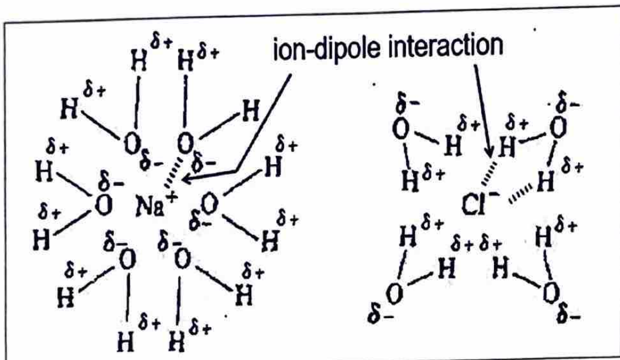
$\Delta H^{\ominus}_{hyd}$	The **standard enthalpy change of hydration** ($\Delta H^{\ominus}_{hyd}$) of an ion is the energy released when 1 **mole** of the **gaseous ion** is hydrated under standard conditions (i.e. 1 bar and 298 K).

- Example 1: The standard enthalpy change of hydration of sodium ion is the energy released when 1 mole of $Na^+(g)$ ions is hydrated under standard conditions (i.e. 1 bar and 298 K).

  $Na^+(g) + aq. \longrightarrow Na^+(aq)$ $\qquad \Delta H^{\ominus}_{hyd}[Na^+(g)] = -405\ kJ\ mol^{-1}$

- Example 2: The standard enthalpy change of hydration of chloride ion is the energy released when 1 mole of $Cl^-(g)$ ions is hydrated under standard conditions (i.e. 1 bar and 298 K).

  $Cl^-(g) + aq. \longrightarrow Cl^-(aq)$ $\qquad \Delta H^{\ominus}_{hyd}[Cl^-(g)] = -364\ kJ\ mol^{-1}$



$$M^+(g) + aq. \xrightarrow{\Delta H^{\ominus}_{hyd}[M^+(g)]} M^+(aq)$$

$$\left|\Delta H^{\ominus}_{hyd}[M^+(g)]\right| \propto \left|\frac{q+}{r_+}\right|$$

$$X^-(g) + aq. \xrightarrow{\Delta H^{\ominus}_{hyd}[X^-(g)]} X^-(aq)$$

$$\left|\Delta H^{\ominus}_{hyd}[X^-(g)]\right| \propto \left|\frac{q-}{r_-}\right|$$

- Refer to **Section 6** for more details.

2.11 Standard enthalpy change of solution, $\Delta H^{\ominus}_{soln}$

$\Delta H^{\ominus}_{soln}$	The **standard enthalpy change of solution** ($\Delta H^{\ominus}_{soln}$) of a substance is the energy change when 1 **mole** of the **substance** is **completely dissolved** in a solvent to form an infinitely dilute solution under standard conditions (i.e. 1 bar and 298 K).

- **Note:** An **infinitely dilute solution** is one that does not produce any further enthalpy change when more solvent is added.

- Example 1: The standard enthalpy change of solution of sodium chloride is the energy absorbed when 1 mole of $NaCl(s)$ is completely dissolved in water to form an infinitely dilute solution under standard conditions (i.e. 1 bar and 298 K).

  $NaCl(s) + aq. \longrightarrow Na^+(aq) + Cl^-(aq)$ $\qquad \Delta H^{\ominus}_{soln}[NaCl(s)] = +5\ kJ\ mol^{-1}$

  Example 2: The standard enthalpy change of solution of magnesium sulfate is the energy released when 1 mole of $MgSO_4(s)$ is completely dissolved in water to form an infinitely dilute solution under standard conditions (i.e. 1 bar and 298 K).

  $MgSO_4(s) + aq. \longrightarrow Mg^{2+}(aq) + SO_4^{2-}(aq)$ $\qquad \Delta H^{\ominus}_{soln}[MgSO_4(s)] = -91.2\ kJ\ mol^{-1}$

- Refer to **Section 6** for more details.

2.12 MCQ Exercises – Definitions

Q1

Which equation defines the enthalpy change of formation of carbon monoxide?

A $C(g) + O(g) \longrightarrow CO(g)$

B $C(g) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$

C $C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$

D $C(s) + CO_2(g) \longrightarrow 2CO(g)$

Q2

For which of the following reactions does the value of $\Delta H^{\ominus}$ represent **both** a standard enthalpy change of combustion and a standard enthalpy change of formation?

1 $C(s) + O_2(g) \rightarrow CO_2(g)$

2 $2C(s) + O_2(g) \rightarrow 2CO(g)$

3 $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$

A 1, 2 and 3 **B** 1 and 2 only

C 2 and 3 only **D** 1 only

Q3

Which equation defines the enthalpy change of atomisation of white phosphorus?

A $P(s) \longrightarrow P(g)$ **C** $\frac{1}{4}P_4(s) \longrightarrow P(g)$

B $P_4(s) \longrightarrow P_4(g)$ **D** $P_4(s) \longrightarrow 4P(g)$

Q4

Which equation represents the change corresponding to the enthalpy change of atomisation of iodine?

A $\frac{1}{2}I_2(s) \rightarrow I(g)$

B $I_2(s) \rightarrow 2I(g)$

C $I_2(l) \rightarrow 2I(g)$

D $I_2(g) \rightarrow 2I(g)$

Q5

Which equation defines the lattice energy of the ionic compound *XY*?

A $X(s) + Y(s) \rightarrow XY(s)$

B $X(g) + Y(g) \rightarrow XY(s)$

C $X^+(s) + Y^-(s) \rightarrow XY(s)$

D $X^+(g) + Y^-(g) \rightarrow XY(s)$

Q6

Which equation corresponds to the enthalpy change stated?

A $2Al^{3+}(g) + 3O^{2-}(g) \rightarrow Al_2O_3(s)$
$2\Delta H^{\ominus}_{\text{lattice energy}}(Al_2O_3(s))$

B $H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$
$\Delta H^{\ominus}_{\text{neutralisation}}$

C $CaCl_2(s) + aq \rightarrow Ca^{2+}(aq) + 2Cl^-(aq)$
$\Delta H^{\ominus}_{\text{solution}}(CaCl_2(s))$

D $S_8(s) + 8O_2(g) \rightarrow 8SO_2(g)$
$\Delta H^{\ominus}_{\text{formation}}(SO_2(g))$

Q7

The value of the enthalpy change for the process represented by the equation

$$Na(s) \longrightarrow Na^+(g) + e^-$$

is equal to

A the first ionisation energy of sodium.

B the enthalpy change of vaporisation of sodium.

C the sum of the first ionisation energy and the electron affinity of sodium.

D the sum of the enthalpy change of atomisation and the first ionisation energy of sodium.

Q8

Which class of reaction always has an endothermic enthalpy change?

A atomisation **B** combustion

C formation **D** solution

Q9

Which reactions represent standard enthalpy changes at 298 K?

1 $NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$

2 $C(g) + 6H(g) \longrightarrow C_2H_6(g)$

3 $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$

A 1, 2 and 3 **B** 1 and 2 only

C 2 and 3 only **D** 1 only

Q10

Which one of the following has the same value as the standard enthalpy change of formation of carbon monoxide?

[$\Delta H^{\ominus}_{C}$ (*X*) is the standard enthalpy change of combustion of *X*;

$\Delta H^{\ominus}_{f}$ (*X*) is the standard enthalpy change of formation of *X*.]

A $\frac{1}{2}\Delta H^{\ominus}_{C}$ (graphite)

B $\Delta H^{\ominus}_{f}(CO_2) - \Delta H^{\ominus}_{C}$ (graphite)

C $\Delta H^{\ominus}_{f}(CO_2) - \frac{1}{2}\Delta H^{\ominus}_{C}$ (graphite)

D $\Delta H^{\ominus}_{C}$ (graphite) $- \Delta H^{\ominus}_{C}$ (CO)

Learn these definitions well.

- standard enthalpy change of reaction
- standard enthalpy change of formation
- standard enthalpy change of combustion
- standard enthalpy change of neutralisation
- standard enthalpy change of atomisation
- bond dissociation energy and bond energy
- ionisation energy
- electron affinity
- lattice energy
- standard enthalpy change of hydration
- standard enthalpy change of solution

3 Experimental Determination of Enthalpy Changes

3.1 Calorimetry

- During a chemical reaction, the enthalpy change in the reaction causes a change in the temperature of the surroundings. For many reactions, this **temperature change, ΔT**, can be measured using a thermometer or a temperature probe.

- The experimental technique used to measure the enthalpy change of a reaction by measuring the change in temperature is generally called **calorimetry**.

- The apparatus used is called a **calorimeter**. A simple calorimeter can be a Styrofoam cup (i.e. a polystyrene cup), a vacuum flask or a metal can.

3.2 Relationship between temperature change (ΔT) and heat change (q)

- Temperature change (ΔT) is related to heat change (q) by the following expressions:

$$\boxed{q = mc\Delta T} \quad \text{or} \quad \boxed{q = C\Delta T}$$

where	q =	heat change	J
	m =	mass of the substance (usually water or solution) to which the temperature change occurs	g
	c =	specific heat capacity of the substance to which the temperature change occurs	$J\ g^{-1}\ {}^{o}C^{-1}$ or $J\ g^{-1}\ K^{-1}$
	ΔT = =	temperature change highest / lowest temperature reached – initial temperature	°C or K
	C =	heat capacity of the substance to which the temperature change occurs	$J\ {}^{o}C^{-1}$ or $J\ K^{-1}$

- Definitions of specific heat capacity and heat capacity

c	The **specific heat capacity** of a substance is the quantity of heat required to raise the temperature of 1 g of the substance by 1 °C (or 1 K).	$J\ g^{-1}\ {}^{o}C^{-1}$ or $J\ g^{-1}\ K^{-1}$
C	The **heat capacity** of a substance is the quantity of heat required to raise the temperature of the substance by 1 °C (or 1 K).	$J\ {}^{o}C^{-1}$ or $J\ K^{-1}$

- Relationship between heat capacity and specific heat capacity of a substance

> Heat capacity of a substance = (mass of the substance) x (specific heat capacity of the substance)
>
> $C = mc$

3.3 Relationship between heat change (q) and enthalpy change (ΔH)

- Heat change (q) is related to enthalpy change (ΔH) by the following expressions:

$$\boxed{\Delta H = -\frac{q}{n}}$$

where ΔH =	enthalpy change of reaction	$kJ\ mol^{-1}$ or $J\ mol^{-1}$
n =	amount of the limiting reagent which reacts and causes the temperature change	mol

- **Note:**
  - If $\Delta H = \Delta H_c$, then n = amount of the fuel which undergoes complete combustion.
  - If $\Delta H = \Delta H_{neut}$, then n = amount of water produced in the neutralisation reaction

3.4 Experimental method to determine enthalpy change

- In general, for the experimental determination of an enthalpy change, the following equations will be used.

$q = mc\Delta T$	$\Delta H = -\frac{q}{n}$

- Hence the experimental data needed to be obtained are:
  - m
  - c
  - ΔT
  - n

- **Assumptions** commonly made in such experiments:
  1. Negligible heat loss to the surrounding air due to insulation. (i.e. all the chemical energy involved in the reaction is transformed into heat which is used to change the temperature of the solution)
  2. The density of the solution, unless otherwise stated, is approximately that of water ($1.00\ g\ cm^{-3}$).
  3. The specific heat capacity of the solution, unless otherwise stated, is approximately that of water ($4.18\ J\ g^{-1}\ K^{-1}$ as in *Data Booklet*).

- **Summary**

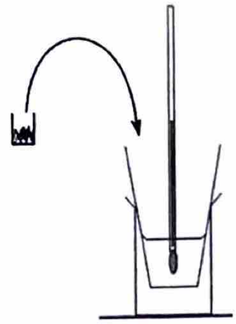
reaction	ΔT	$q = mc\Delta T$	$\Delta H = -\frac{q}{n}$	Remarks
exothermic reaction	+	+	–	Heat is produced by reaction.
endothermic reaction	–	–	+	Heat is absorbed by reaction.

3.5 Experimental determination of enthalpy change of a reaction

- Consider the following reaction: **$Mg(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + H_2(g)$**

Aim To find the enthalpy change for the reaction between magnesium and hydrochloric acid

Method
1. Place a Styrofoam cup in a 250 cm^3 beaker for support.
2. Use a 50 cm^3 measuring cylinder to transfer 40.0 cm^3 of 1.00 mol dm^{-3} hydrochloric acid into the Styrofoam cup.
3. Tear a piece of magnesium ribbon provided into small pieces. Weigh accurately about 0.24 g of the magnesium ribbon in a clean, dry weighing bottle.
4. Place a thermometer into the Styrofoam cup containing the hydrochloric acid. Record the temperature of the solution at 0.5-minute intervals for 2 minutes.
5. At 2.5 minutes, add the magnesium ribbon from the weighing bottle to the Styrofoam cup. Stir the mixture gently with the thermometer to dissolve the magnesium ribbon, and continue to record the temperature at 0.5-minute intervals from 3.0 to 7.5 minutes.

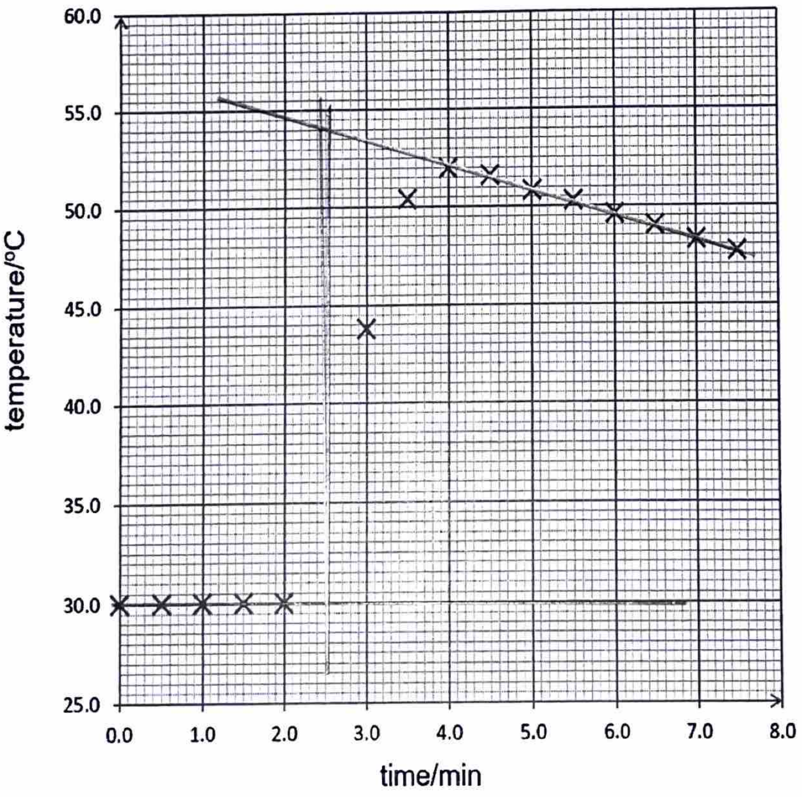


Results Mass of Mg ribbon used = 0.240 g

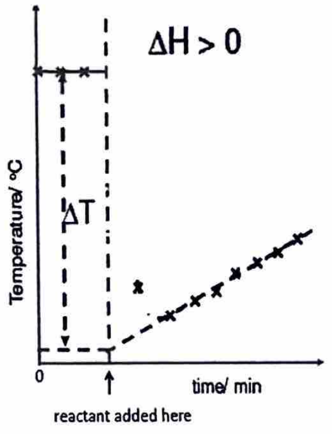
time/min	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5
temperature/°C	30.0	30.0	30.0	30.0	30.0		43.8	50.4

time/min	4.0	4.5	5.0	5.5	6.0	6.5	7.0	7.5
temperature/°C	52.0	51.6	50.8	50.3	49.6	49.0	48.3	47.7

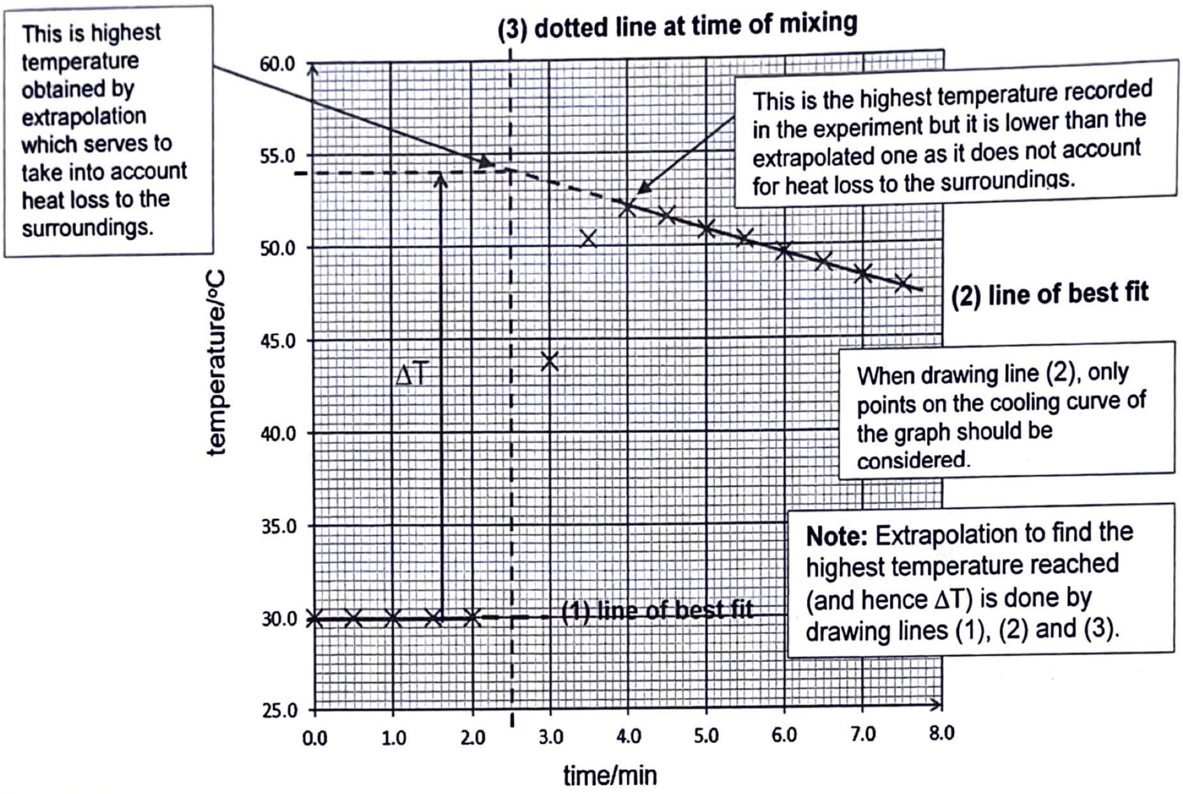
Graph of temperature/°C against time/min



Note: Below shows the corresponding graph obtained for an endothermic reaction.



Graph of temperature/°C against time/min



This is highest temperature obtained by extrapolation which serves to take into account heat loss to the surroundings.

(3) dotted line at time of mixing

This is the highest temperature recorded in the experiment but it is lower than the extrapolated one as it does not account for heat loss to the surroundings.

(2) line of best fit

When drawing line (2), only points on the cooling curve of the graph should be considered.

(1) line of best fit

Note: Extrapolation to find the highest temperature reached (and hence ΔT) is done by drawing lines (1), (2) and (3).

Treatment of results

From the graph, temperature change, **ΔT**= 54.0 – 30.0 = +24.0 °C (or +24.0 K but not 273 + 24.0 K)

Assumption: density of solution = density of water = 1.0 g cm^{-3}

Volume of solution = 40.0 cm^3
Mass of solution, **m** = (40.0)(1.0) = 40.0 g

Assumption: specific heat capacity of solution, **c** = specific heat capacity of water = 4.18 J g^{-1} °C^{-1}

Heat change, **q = mcΔT** = (40.0)(4.18)(24.0) = +4013 J

- **Note:** Do not include the mass of solid in **m**.

Assumption: Heat loss to the surrounding air is corrected for via extrapolation to find the highest temperature reached from the graph.

Heat released from reaction = Heat absorbed by solution = 4013 J

Reaction: $\mathbf{Mg(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + H_2(g)}$

Amount of HCl used = (40.0/1000)(1.00) = 0.0400 mol
Amount of Mg used = 0.24/24.3 = 9.877 x 10^{-3} mol

In this reaction, 9.877 x 10^{-3} mol of Mg reacted with 0.01975 mol of HCl.
Hence HCl was in excess and the **limiting reagent** was Mg.

Amount of Mg reacted, n = 9.877 x 10^{-3} mol

Enthalpy change for the reaction, $\Delta H_r = -\frac{q}{n} = -\frac{4013}{0.009877} = -4.063 \times 10^5 \text{ J mol}^{-1}$
$= \mathbf{-406\ kJ\ mol^{-1}}$

General steps
1. find **ΔT**
2. find **m** (with assumption made about the density of solution)
3. assume **c** to be that of water if **c** is not given
4. find **q** from q = mcΔT
5. write reaction equation
6. find **n**
7. find **Δ*H***

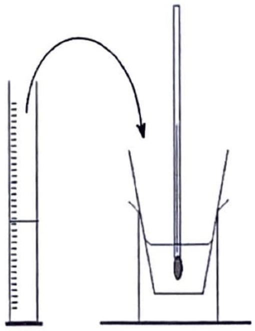
3.6 Experimental determination of enthalpy change of neutralisation

- **Example:** When 40 cm^3 of 1.00 mol dm^{-3} hydrochloric acid was added to 30 cm^3 of 1.00 mol dm^{-3} sodium hydroxide in a Styrofoam cup, there was a temperature rise of 5.8 °C. Calculate the enthalpy change of neutralisation for this reaction between hydrochloric acid and sodium hydroxide solution.

Aim: To find the enthalpy change of neutralisation for the reaction between hydrochloric acid and sodium hydroxide

Method:

1. Use a 50 cm^3 measuring cylinder to measure 40.0 cm^3 of 1.00 mol dm^{-3} hydrochloric acid. Measure and record the temperature of this hydrochloric acid using a thermometer.
2. Place a Styrofoam cup in a 250 cm^3 beaker for support.
3. Use another 50 cm^3 measuring cylinder to transfer 30.0 cm^3 of 1.00 mol dm^{-3} sodium hydroxide into the Styrofoam cup. Measure and record the temperature of this sodium hydroxide solution using the thermometer.
4. Add the hydrochloric acid from the measuring cylinder into the Styrofoam cup containing the sodium hydroxide solution. Stir the reaction mixture gently using the thermometer and record the highest temperature reached.



Results:

Temperature of hydrochloric acid /°C	29.8
Temperature of sodium hydroxide solution /°C	29.6
Highest temperature reached after mixing the solutions /°C	35.5

Treatment of results

Weighted average initial temperature = $(\frac{40.0}{40.0+30.0})(29.8) + (\frac{30.0}{40.0+30.0})(29.6) = 29.7$ °C

Temperature change, $\Delta T = 35.5 - 29.7 = +5.8$ °C

Total volume of solution = 70.0 cm^3

Assumption: density of solution = density of water = 1.0 g cm^{-3}

Mass of solution, **m** = (70.0)(1.0) = 70.0 g

Assumption: specific heat capacity of solution, **c** = specific heat capacity of water = 4.18 J g^{-1} °C^{-1}

Heat change, $q = mc\Delta T$ = (70.0)(4.18)(5.8) = +1697 J

Assumption: There is no heat loss to the surroundings.
There is 100% efficiency in the transfer of heat from the reaction to the solution.

Heat released from reaction = Heat absorbed by solution = 1697 J

Reaction: $NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l)$

Amount of HCl used = (40.0/1000)(1.00) = 0.0400 mol
Amount of NaOH used = (30.0/1000)(1.00) = 0.0300 mol

In this reaction, 0.0300 mol of NaOH reacted with 0.0300 mol of HCl.
Hence HCl was in excess and the **limiting reagent** was NaOH.

Amount of H_2O produced, **n** = Amount of NaOH reacted = 0.0300 mol

Enthalpy change of neutralisation, $\Delta H_{neut} = -\frac{q}{n} = -\frac{1697}{0.0300} = -5.656 \times 10^4$ J mol^{-1}

$= \mathbf{-56.6\ kJ\ mol^{-1}}$

General steps

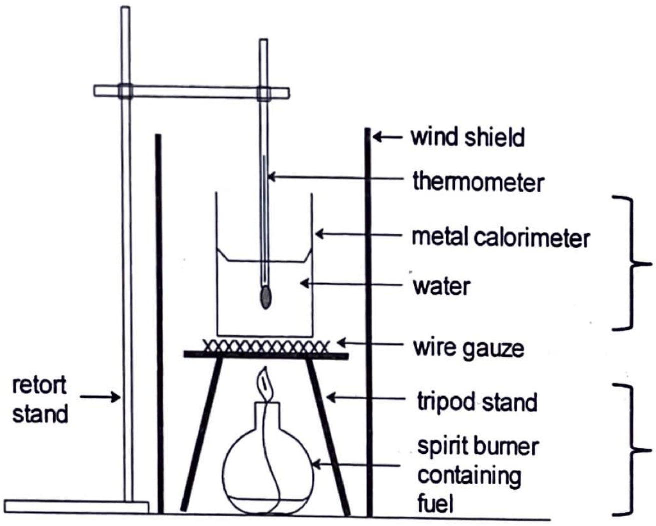
1. find ΔT
2. find **m** (with assumption made about the density of solution)
3. assume **c** to be that of water if **c** is not given
4. find **q** from $q = mc\Delta T$
5. write reaction equation
6. find **n**
7. find ΔH

3.7 Experimental determination of enthalpy change of combustion

- The diagram below shows a simple method to determine an approximate value for the enthalpy change of combustion of a fuel.

$$\text{fuel}(l) + O_2(g) \longrightarrow CO_2(g) + H_2O(l) \qquad \text{(unbalanced equation)}$$

- The fuel could be any organic compound such as ethanol, propanol, octane etc.



Note:

If the heat transfer is 100% efficient (i.e. no heat loss to the surroundings),

heat released from combustion of fuel = heat absorbed by water

Heat absorbed by water
= mcΔT

Heat released by combustion of fuel
= $(n)(-\Delta H_c)$

where n = amount of fuel burnt

Note:

- The spirit burner contains the fuel. Weighing the spirit burner before and after burning gives the mass of fuel burnt.
- The metal calorimeter contains a known mass of water.
- The wind shield reduces heat loss to the surroundings.
- The heat absorbed by the metal calorimeter is ignored unless the specific heat capacity (or heat capacity) of the metal is given or the heat capacity of the calorimeter set-up (metal calorimeter and water) is given.

- **Example:** An experiment was conducted to determine the enthalpy change of combustion of ethanol. When **1.00 g of ethanol** was burned under a container of water, it was found that **100 g of water** was heated from 15.0 °C to 85.0 °C. Assuming the process was 80% efficient, calculate the enthalpy change of combustion of ethanol.

Note: The '**m**' in '**mcΔT**' refers to the mass **of water** and not the mass of ethanol burnt.

It means only 80% of the heat released by reaction was transferred to the water; 20% of the heat released was lost to surroundings.

Heat change, $\mathbf{q_1} = mc\Delta T = (100)(4.18)(85.0 - 15.0) = +29260$ J

This is the **heat absorbed by the water.**

If the process were to be **100% efficient** (i.e. no heat loss to the surroundings),
heat change, $\mathbf{q_2} = (\frac{100}{80})(29260) = +36575$ J

This is the **heat released from the combustion reaction.**

Heat released from combustion of CH_3CH_2OH = 36575 J

M_r of CH_3CH_2OH = 46.0
Amount of CH_3CH_2OH burnt, $\mathbf{n} = \frac{1.00}{46.0} = 0.02174$ mol

Reaction: $\mathbf{CH_3CH_2OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)}$

Enthalpy change of combustion of ethanol, $\Delta H_c[CH_3CH_2OH(l)] = -\frac{q_2}{n} = -\frac{36575}{0.02174} = -1.682 \times 10^6 \text{ J mol}^{-1}$
$= -1680 \text{ kJ mol}^{-1}$

4 Calculation of Enthalpy Changes Using Hess' Law

4.1 Hess' Law

- The enthalpy change of some reactions cannot be determined directly by experiment. Such reactions may be difficult or even impossible to be carried out in the laboratory.
- **Hess' Law** allows us to determine the enthalpy change of these reactions indirectly by calculating them from the known enthalpy change data available.

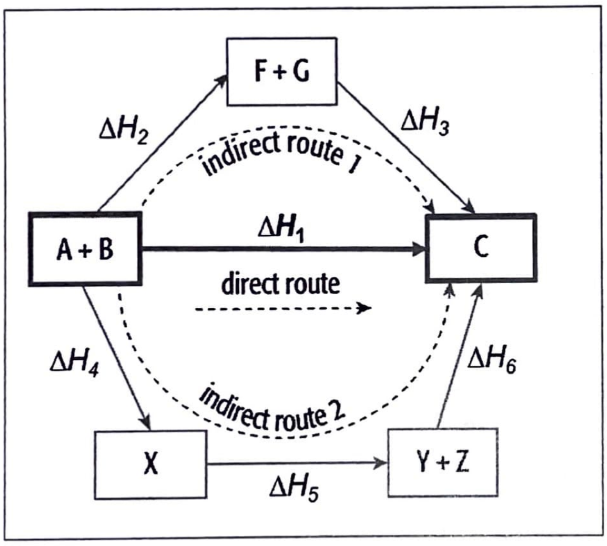
Hess' Law	**Hess' Law** states that the enthalpy change of a reaction is determined by the initial and final states of the system and is independent of the pathways taken.
	Hess' Law states that the enthalpy change of a chemical reaction is the same regardless of whether the reaction takes place in one step or several steps, provided the initial and final states of the reactants and products are the same.

Note:

The Law of Conservation of Energy states that 'energy cannot be created or destroyed'. This is called the First Law of Thermodynamics. This law also applies to chemical reactions.

In 1840 Germain Hess applied the Law of Conservation of Energy to enthalpy changes. He published his law of constant heat summation, which we refer to today as '**Hess' Law**'.

- We can illustrate Hess' law by drawing energy cycles as shown below.



- Consider the following reaction:

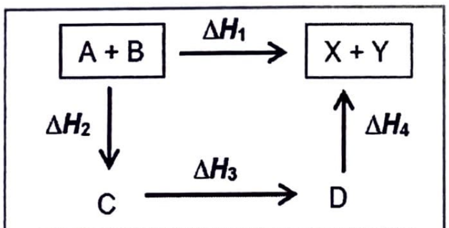
  $A(s) + B(g) \longrightarrow C(s)$

- Hess' law tells us that the enthalpy change of the above reaction for the direct route is the same as for the indirect route. It does not matter how many steps there are in the indirect route.
- By Hess' law,

$\Delta H_1 = \Delta H_2 + \Delta H_3$

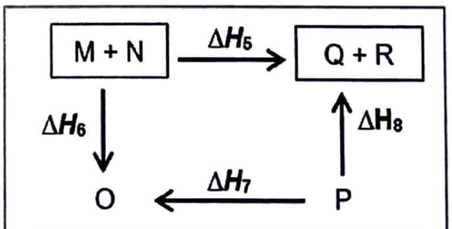
$\Delta H_1 = \Delta H_4 + \Delta H_5 + \Delta H_6$

- More energy cycles to illustrate Hess' law.



By Hess' Law,

$\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4$



By Hess' Law,

$\Delta H_5 = \Delta H_6 - \Delta H_7 + \Delta H_8$

- **A useful rule of thumb:** sum of enthalpy changes in clockwise direction = sum of enthalpy changes in anti-clockwise direction

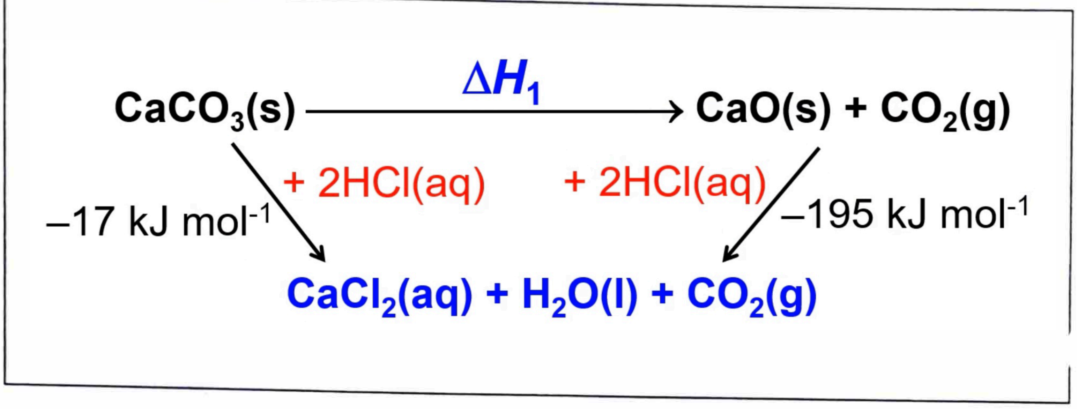
Worked Example 1

The decomposition of calcium carbonate to carbon dioxide only takes place at very high temperatures, making the direct measurement of the enthalpy change for this reaction difficult.

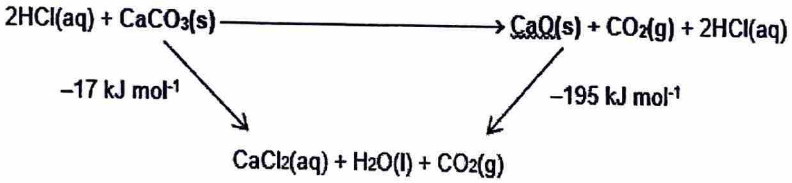
Using the data given below, calculate the enthalpy change for the decomposition of calcium carbonate.

Reaction	ΔH / kJ mol^{-1}
$CaCO_3(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$	–17
$CaO(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + H_2O(l)$	–195

Method 1: Construct an energy cycle and apply Hess' law



- Note that the energy cycle can also be presented as shown below.



- **Note**

General steps in problem solving using energy cycle and Hess' Law:

1. Write a balanced chemical equation at the top of the cycle. This equation is usually for the reaction you need to solve in the question.
2. Inspect the other **given** enthalpy changes of reactions and write down the chemical equations for these reactions.
3. Form an energy cycle involving the reactions and label each arrow with the appropriate enthalpy change, taking into account the number of moles of each reactant and product.
4. Apply Hess' law and calculate the enthalpy change.

Method 2: Algebraic Method (by adding or substracting equation)

(1) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$ $\qquad \Delta H_1 = ?$
(2) $CaCO_3(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$ $\qquad \Delta H_2 = -17$ kJ mol^{-1}
(3) $CaO(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + H_2O(l)$ $\qquad \Delta H_3 = -195$ kJ mol^{-1}

Reverse (3) to get (4):

(4) $CaCl_2(aq) + H_2O(l) \longrightarrow CaO(s) + 2HCl(aq)$ $\qquad \Delta H_4 = -(-195) = +195$ kJ mol^{-1}

Add (2) and (4) to get (1):

(1) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$ $\qquad \Delta H_1 = -17 + 195 = $ **+178 kJ mol^{-1}**

4.2 Calculating enthalpy change from enthalpy changes of combustion data

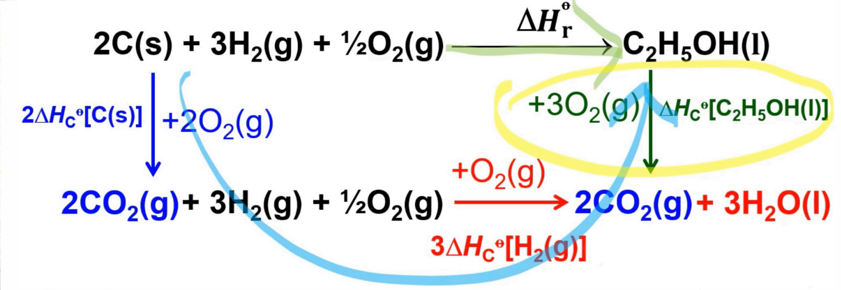
■■ Worked Example 2

Using the given data, construct an energy cycle and use it to calculate the standard enthalpy change of reaction of the following reaction:

$$2C(s) + 3H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow C_2H_5OH(l)$$

$\Delta H_c^{\ominus}[C(s)] = -393\ \text{kJ mol}^{-1}$	$C(s) + O_2(g) \longrightarrow CO_2(g)$
$\Delta H_c^{\ominus}[H_2(g)] = -286\ \text{kJ mol}^{-1}$	$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l)$
$\Delta H_c^{\ominus}[C_2H_5OH(l)] = -1368\ \text{kJ mol}^{-1}$	$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$

Solution



By Hess' Law,

$$\begin{aligned}\Delta H_r^{\ominus} &= 2\Delta H_c^{\ominus}[C(s)] + 3\Delta H_c^{\ominus}[H_2(g)] - \Delta H_c^{\ominus}[C_2H_5OH(l)] \\ &= (2)(-393) + (3)(-286) - (-1368) \\ &= \mathbf{-276\ kJ\ mol^{-1}}\end{aligned}$$

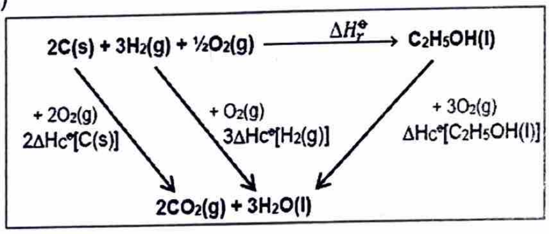
Note :

a. There must be a state symbol written for every species in the cycle.
b. Each arrow in the energy cycle should be labelled with the appropriate enthalpy change or the value of the enthalpy change.
c. Every equation must be balanced in the cycle.

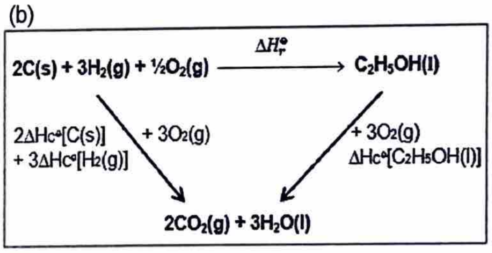
Alternative representations of energy cycle

- You may show the processes involving the enthalpy changes of combustion of C(s) and H₂(g) together as illustrated in (a) or combine them as illustrated in (b).

(a)

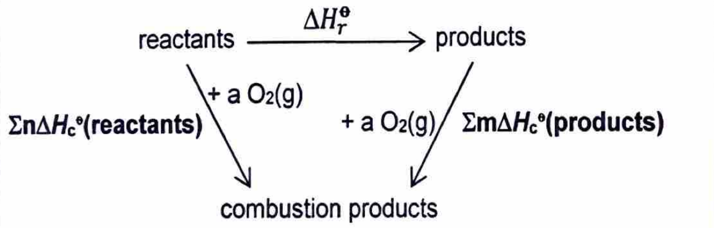


(b)



- **Note**

Since the $\Delta H_r^{\ominus}$ in Worked Example 2 is calculated from $\Delta H_c^{\ominus}$ values, a formula can be derived using Hess' Law to obtain the $\Delta H_r^{\ominus}$ more quickly from the balanced equation alone without having to draw the energy cycle.



$$\boldsymbol{\Delta H_r^{\ominus} = \Sigma n\Delta H_c^{\ominus}\,(\text{reactants}) - \Sigma m\Delta H_c^{\ominus}\,(\text{products})}$$

$\Delta H_r^{\ominus}$
= standard enthalpy change of reaction

$\Sigma n\Delta H_c^{\ominus}$(reactants)
= sum of standard enthalpy changes of **combustion** of reactants multiplied by the respective stoichiometric coefficients

$\Sigma m\Delta H_c^{\ominus}$(products)
= sum of standard enthalpy changes of **combustion** of products multiplied by the respective stoichiometric coefficients

4.3 Calculating enthalpy change from enthalpy changes of formation data

■■ Worked Example 3

Using the given data, construct an energy cycle and use it to calculate the standard enthalpy change of reaction of the following reaction:

$$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$$

$\Delta H_f^\ominus[C_3H_8(g)] = -144.1$ kJ mol^{-1}
$\Delta H_f^\ominus[H_2O(l)] = -295.9$ kJ mol^{-1}
$\Delta H_f^\ominus[CO_2(g)] = -393.5$ kJ mol^{-1}

$3C(s) + 4H_2(g) \longrightarrow C_3H_8(g)$
$H_2(g) + ½O_2(g) \longrightarrow H_2O(l)$
$C(s) + O_2(g) \longrightarrow CO_2(g)$

Solution

$$\begin{tikzcd}
C_3H_8(g) + 5O_2(g) \arrow[r, "\Delta H_r^\ominus"] & 3CO_2(g) + 4H_2O(l) \\
 & 3C(s) + 3O_2(g) + 4H_2O(l) \arrow[u, "3\Delta H_f^\ominus[CO_2(g)]"'] \\
 & 3C(s) + 4H_2(g) + 5O_2(g) \arrow[u, "4\Delta H_f^\ominus[H_2O(l)]"'] \arrow[uul, "\Delta H_f^\ominus[C_3H_8(g)]"]
\end{tikzcd}$$

By Hess' law,

$$\Delta H_r^\ominus = -\Delta H_f^\ominus[C_3H_8(g)] + 4\Delta H_f^\ominus[H_2O(l)] + 3\Delta H_f^\ominus[CO_2(g)]$$
$$= -(-144.1) + (4)(-295.9) + (3)(-393.5)$$
$$= \underline{-2220 \text{ kJ mol}^{-1}}$$

or

$$\begin{tikzcd}
C_3H_8(g) + 5O_2(g) \arrow[rr, "\Delta H_r^\ominus"] & & 3CO_2(g) + 4H_2O(l) \\
 & 3C(s) + 4H_2(g) + 5O_2(g) \arrow[ul, "-144.1 \text{ kJ mol}^{-1}"] \arrow[ur, "(3)(-393.5) + (4)(-295.9) \text{ kJ mol}^{-1}"'] &
\end{tikzcd}$$

By Hess' law,

$$\Delta H_r^\ominus = -(-144.1) + (4)(-295.9) + (3)(-393.5)$$
$$= \underline{-2220 \text{ kJ mol}^{-1}}$$

By Hess' law, $\Delta H_r^\ominus = -(-144.1) + (4)(-295.9) + (3)(-393.5) = \underline{-2220 \text{ kJ mol}^{-1}}$

- **Note**

Since the $\Delta H_r^\ominus$ in Worked Example 3 is calculated from $\Delta H_f^\ominus$ values, a formula can be derived using Hess' Law to obtain the $\Delta H_r^\ominus$ more quickly from the balanced equation alone without having to draw the energy cycle.

$$\begin{tikzcd}
\text{reactants} \arrow[rr, "\Delta H_r^\ominus"] & & \text{products} \\
 & \text{elements} \arrow[ul, "\Sigma n\Delta H_f^\ominus(\text{reactants})"] \arrow[ur, "\Sigma m\Delta H_f^\ominus(\text{products})"'] &
\end{tikzcd}$$

$$\Delta H_r^\ominus = \Sigma n\Delta H_f^\ominus\,(\text{products}) - \Sigma m\Delta H_f^\ominus\,(\text{reactants})$$

$\Delta H_r^\ominus$
= standard enthalpy change of reaction

$\Sigma n\Delta H_f^\ominus$(reactants)
= sum of standard enthalpy changes of **formation** of reactants multiplied by the respective stoichiometric coefficients

$\Sigma m\Delta H_f^\ominus$(products)
= sum of standard enthalpy changes of **formation** of products multiplied by the respective stoichiometric coefficients

4.4 Calculating enthalpy change from bond energy data

■■ Worked Example 4

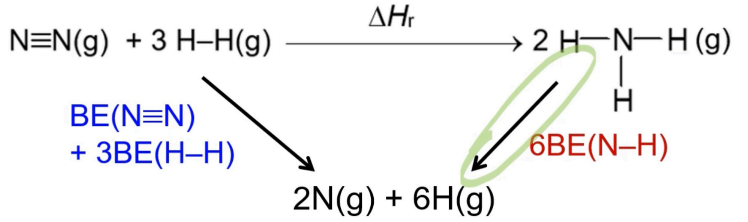
With the aid of relevant data from the *Data Booklet*, calculate the enthalpy change of the following reaction:

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

From the *Data Booklet*:

Bond	Bond energies / kJ mol^{-1}
N≡N	944
H–H	436
N–H	390

Method 1: Draw energy cycle and apply Hess' law



By Hess' law, ΔH_r = BE(N≡N) + 3BE(H–H) – 6BE(N–H)

$= +944 + (3)(436) - (6)(390)$

$= \underline{-88.0 \text{ kJ mol}^{-1}}$

By Hess' law,

ΔH_r = BE(N≡N) + 3BE(H–H) – 6BE(N–H) = +944 + (3)(436) – (6)(390) = $\underline{-88.0 \text{ kJ mol}^{-1}}$

Method 2: Consider all the bonds broken and all the bonds formed and sum up the enthalpy change for bonds broken (positive value) and the enthalpy change for bonds formed (negative value)

$$N_2(g) + 3H_2(g) \xrightarrow{\Delta H_r} 2NH_3(g)$$

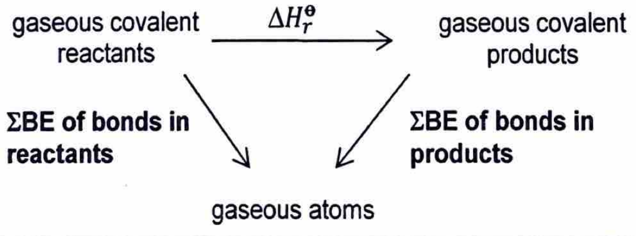
Bonds broken
1N≡N
3H-H

Bonds formed
6N-H

ΔH_r = +BE(N≡N) + 3BE(H–H) – 6BE(N–H) = +944 + (3)(436) – (6)(390) = $\underline{-88.0 \text{ kJ mol}^{-1}}$

- **Note**

- Bond breaking absorbs energy. The bond-breaking process is endothermic.
- Bond formation releases energy. The bond-forming process in exothermic.



ΔH_r° = ΣBE of bonds in reactants – ΣBE of bonds in products

Note:

The bond energy (BE) data given in the *Data Booklet* refers to the breaking of bonds in the **gaseous state**.

4.5 Calculating enthalpy changes from different data

■■ Worked Example 5

Phosphorus can react with chlorine to form phosphorus trichloride, PCl_3.

(a) Write a balanced equation for the enthalpy change of formation of gaseous PCl_3.

(b) By using the data given below, construct an energy cycle to determine the mean P–C*l* bond energy, i.e. BE(P–C*l*).

Enthalpy change of formation of gaseous PCl_3,	$\Delta H_1 = -315$ kJ mol^{-1}
Enthalpy change of atomisation phosphorus,	$\Delta H_2 = +314$ kJ mol^{-1}
Enthalpy change of atomisation chlorine,	$\Delta H_3 = +121$ kJ mol^{-1}

Solution

(a) $P(s) + \frac{3}{2}Cl_2(g) \longrightarrow PCl_3(g)$

(b)

$$\begin{tikzcd}
P(s) + \frac{3}{2}Cl_2(g) \arrow[r, "-315\text{ kJ mol}^{-1}"] \arrow[d, "+314\text{ kJ mol}^{-1}"'] & PCl_3(g) \arrow[d, "3BE(P\text{–}Cl)"] \\
P(g) + \frac{3}{2}Cl_2(g) \arrow[r, "(3)(+121)\text{ kJ mol}^{-1}"'] & P(g) + 3Cl(g)
\end{tikzcd}$$

By Hess' law,
3BE(P–C*l*) = –(–315) + 314 + (3)(121) = 992
BE(P–C*l*) = 992/3 = 330.7
= **<u>+331 kJ mol^{-1}</u>**

By Hess' law,
3BE(P–C*l*) = –(–315) + 314 + (3)(121) = 992
BE(P–C*l*) = 992/3 = 330.7 = **<u>+331 kJ mol^{-1}</u>**

■■ Worked Example 6

Oxy-acetylene torches, which operate at temperatures as high as 3300 °C, are fuelled by the combustion of acetylene, C_2H_2.

$$2C_2H_2(g) + 5O_2(g) \rightarrow 4CO_2(g) + 2H_2O(g)$$

(a) Estimate $\Delta H^\ominus$ for this reaction using bond energies (data from *Data Booklet*).
(b) Calculate $\Delta H^\ominus$ using the enthalpy changes of formation given below.
(c) Comment on the difference in the values of $\Delta H^\ominus$ obtained in **(a)** and **(b)**.

($\Delta H_f^\ominus$ / kJ mol^{-1}: $C_2H_2(g) = +226.7$; $CO_2(g) = -395.5$; $H_2O(g) = -241.8$)

Solution

(a) 2H–C≡C–H(g) + 5O=O(g) → 4O=C=O(g) + 2H–O–H(g)

bonds broken	ΣBE / kJ mol^{-1}	bonds formed	ΣBE/ kJ mol^{-1}
2 C≡C	2 x 840	8 C=O	8 x 805
4 C – H	4 x 410	4 O–H	4 x 460
5 O=O	5 x 496		

ΔH° = ΣBE of bonds broken in reactants – ΣBE of bonds formed in products
= 2(840) + 4(410) + 5(496) – [8(805) + 4(460)]
= –2480 kJ mol^{-1}

(b) ΔH° = $\Sigma n \Delta H_f^\circ$(products) - $\Sigma m \Delta H_f^\circ$(reactants)
= 4(–395.5) + 2(–241.8) – 2(226.7) = –2519 kJ mol^{-1}

- **Note** that the standard enthalpy change of formation of an element in its standard state is zero.
  $\Delta H_f^\circ[O_2(g)] = 0$ kJ mol^{-1}

(c) Difference in value could be due to the fact that bond energies used in **(a)** are average values and not specific for $C_2H_2(g)$ and $H_2O(g)$.

4.6 Calculating enthalpy changes using energy level diagrams

- In addition to energy cycles, **energy level diagrams** are sometimes used. When drawing energy level diagrams, there are additional requirements to take note of.

Note:

- Vertical axis drawn and labelled.
- Usually contains an energy level for 0 kJ mol^{-1}. This corresponds to the elements in their standard states.
- Arrows only point up or down.
  - ↑ for *positive* values of ΔH
  - ↓ for *negative* values of ΔH
- The height of each arrow should roughly reflect the magnitude of the enthalpy change.
- Start and end arrows on the energy levels (not mid-air).

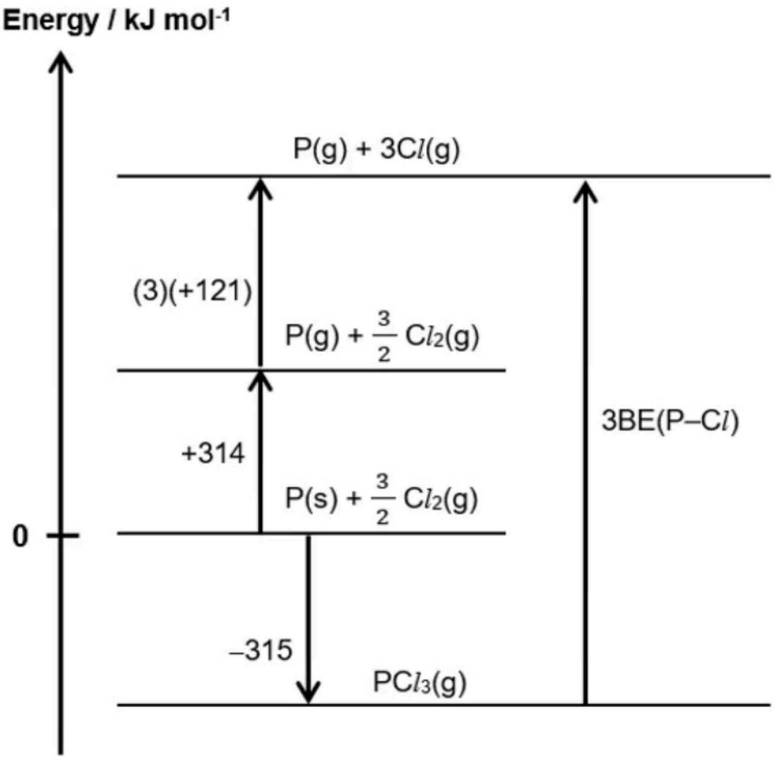
■■ Worked Example 7

Phosphorus can react with chlorine to form phosphorus trichloride, PCl_3.

By using the data given below, construct an **energy level diagram** to determine the mean P–C*l* bond energy, i.e. BE(P–C*l*).

Enthalpy change of formation of gaseous PCl_3,	$\Delta H_1 = -315$ kJ mol^{-1}
Enthalpy change of atomisation phosphorus,	$\Delta H_2 = +314$ kJ mol^{-1}
Enthalpy change of atomisation chlorine,	$\Delta H_3 = +121$ kJ mol^{-1}

Solution



By Hess' Law, 3BE(P–C*l*) = –(–315) + 314 + (3)(121) = +992 kJ mol^{-1}

BE(P–C*l*) = (992 / 3) = 330.7 = **+331 kJ mol^{-1}**

Worked Example 8

Tin(IV) oxide reacts with carbon monoxide according to the following reaction:

$$SnO_2(s) + 2CO(g) \longrightarrow Sn(s) + 2CO_2(g)$$

The enthalpy changes of formation data are as follows:

$\Delta H_f[SnO_2(s)] = -581$ kJ mol^{-1}
$\Delta H_f[CO(g)] = -111$ kJ mol^{-1}
$\Delta H_f[CO_2(g)] = -394$ kJ mol^{-1}

Recall:

$Sn(s) + O_2(g) \rightarrow SnO_2(s)$	$\Delta H_f[SnO_2(s)] = -581$ kJ mol^{-1}
$C(s) + \frac{1}{2} O_2(g) \rightarrow CO(g)$	$\Delta H_f[CO(g)] = -111$ kJ mol^{-1}
$C(s) + O_2(g) \rightarrow CO_2(g)$	$\Delta H_f[CO_2(g)] = -394$ kJ mol^{-1}

(a) Draw an **energy cycle** using the given data and use it to calculate the enthalpy change for the reaction between tin(IV) oxide and carbon monoxide.

(b) Draw **an energy level diagram** using the given data and use it to calculate the enthalpy change for the reaction between tin(IV) oxide and carbon monoxide.

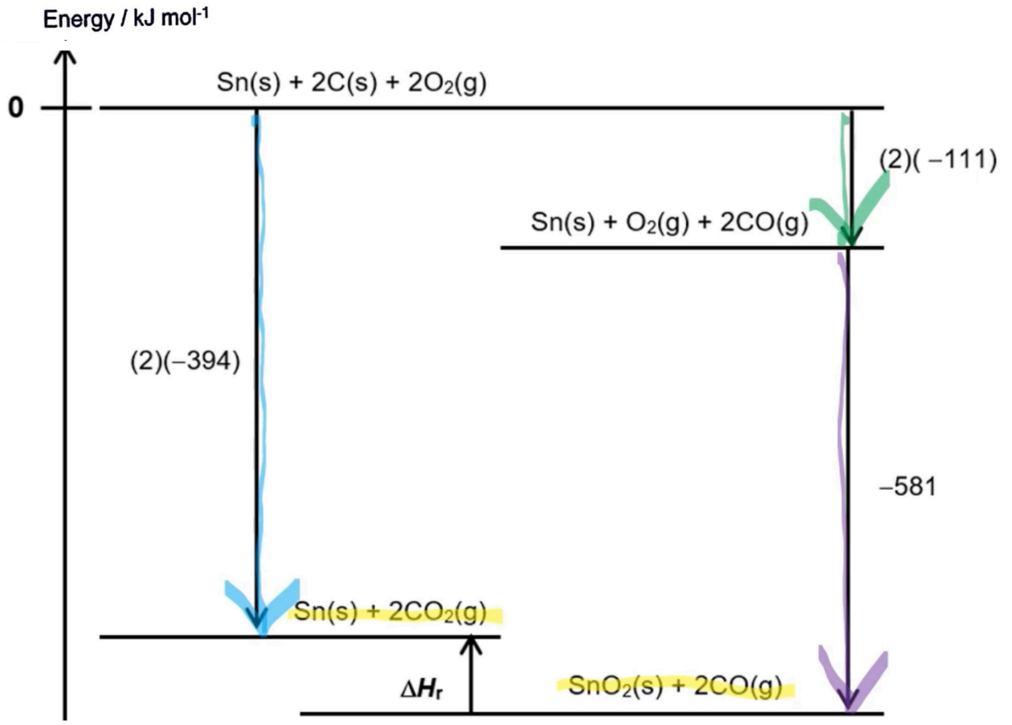
Solution

(a)

$$\begin{tikzcd}
SnO_2(s) + 2CO(g) \arrow[r, "\Delta H_r"] & Sn(s) + 2CO_2(g) \\
Sn(s) + O_2(g) + 2CO(g) \arrow[u, "-581\text{ kJ mol}^{-1}"] & Sn(s) + 2C(s) + 2O_2(g) \arrow[l, "(2)(-111)\text{ kJ mol}^{-1}"'] \arrow[u, "(2)(-394)\text{ kJ mol}^{-1}"']
\end{tikzcd}$$

By Hess' law, $\Delta H_r = -(-581) - (2)(-111) + (2)(-394) =$ **+15 kJ mol^{-1}**

(b)



By Hess' law, $\Delta H_r = -(-581) - (2)(-111) + (2)(-394) =$ **+15 kJ mol^{-1}**

4.7 Calculating enthalpy changes using algebraic method

- **General steps involved in algebraic method:**

1. Construct a **balanced chemical equation** for the reaction in question. Label it as equation (1).
2. Inspect the **given** enthalpy changes of reactions and write down the chemical equations for these reactions in such a way that
   (a) **reactants** appear on the **left-hand side**
   (b) **products** appear on the **right-hand side**
3. **Add** the equations by cancelling out the same substances.
4. Enthalpy change of reaction is equal to the **algebraic sum** of the given enthalpy changes of the reactions that have been added.

Note:

It follows directly from Hess' law that chemical equations can be treated as algebraic equations. They can be added, subtracted or multiplied by a constant value

■■ Worked Example 9

Find the standard enthalpy change of the reaction given below if the standard enthalpy changes of combustion of C and CO are –393 kJ mol^{-1} and –283 kJ mol^{-1} respectively.

$$C(s) + \tfrac{1}{2}O_2(g) \longrightarrow CO(g)$$

Solution

(1)	$C(s) + \tfrac{1}{2}O_2(g) \longrightarrow CO(g)$	$\Delta H^{\ominus}_{r} = ?$
(2)	$C(s) + O_2(g) \longrightarrow CO_2(g)$	$\Delta H^{\ominus}_{c}[C(s)] = -393$ kJ mol^{-1}
(3)	$CO(g) + \tfrac{1}{2}O_2(g) \longrightarrow CO_2(g)$	$\Delta H^{\ominus}_{c}[CO(g)] = -283$ kJ mol^{-1}
Reverse (3) to get (4)	$CO_2(g) \longrightarrow CO(g) + \tfrac{1}{2}O_2(g)$	$\Delta H_4 = +283$ kJ mol^{-1}
Add (2) and (4) to get (1)	$C(s) + \tfrac{1}{2}O_2(g) \longrightarrow CO(g)$	$\Delta H^{\ominus}_{r} = -393 + 283$ = **–110 kJ mol^{-1}**

■■ Worked Example 10

The standard enthalpy changes for two reactions are given by

(2) $2Cr(s) + {}^{3}/_{2}O_2(g) \rightarrow Cr_2O_3(s)$ $\Delta H^{\ominus} = -1130$ kJ mol^{-1}
(3) $C(s) + \tfrac{1}{2}O_2(g) \rightarrow CO(g)$ $\Delta H^{\ominus} = -110$ kJ mol^{-1}

What is the standard enthalpy change for the following reaction?
(1) $3C(s) + Cr_2O_3(s) \rightarrow 2Cr(s) + 3CO(g)$ $\Delta H^{\ominus} = ?$

Solution

(1)	$3C(s) + Cr_2O_3(s) \rightarrow 2Cr(s) + 3CO(g)$	$\Delta H^{\ominus}_{1} = ?$
(2)	$2Cr(s) + {}^{3}/_{2}O_2(g) \rightarrow Cr_2O_3(s)$	$\Delta H^{\ominus}_{2} = -1130$ kJ mol^{-1}
(3)	$C(s) + \tfrac{1}{2}O_2(g) \rightarrow CO(g$	$\Delta H^{\ominus}_{3} = -110$ kJ mol^{-1}
Reverse (2) to get (4)	$Cr_2O_3(s) \rightarrow 2Cr(s) + {}^{3}/_{2}O_2(g)$	$\Delta H^{\ominus}_{4} = +1130$ kJ mol^{-1}
3 x (3) to get (5)	$3C(s) + 3/2O_2(g) \rightarrow 3CO(g)$	$\Delta H^{\ominus}_{5} = -330$ kJ mol^{-1}
Add (4) and (5) to get (1)	$3C(s) + Cr_2O_3(s) \rightarrow 2Cr(s) + 3CO(g)$	$\Delta H^{\ominus}_{1} = +1130 - 330$ = **+800 kJ mol^{-1}**

5 Lattice Energy of an Ionic Compound

5.1 Definition of lattice energy

LE or ΔH°_{latt}	The **lattice energy** (LE) of an ionic compound is the <u>energy released</u> when 1 **mole** of the **solid ionic compound** is formed from **its constituent gaseous ions** under standard conditions (i.e. **1 bar and 298 K).**

- Example: The lattice energy (LE) of calcium fluoride is the energy released when 1 mole of $CaF_2(s)$ is formed from $Ca^{2+}(g)$ and $F^-(g)$ ions under standard conditions (i.e. at 1 bar and 298 K).

  $Ca^{2+}(g) + 2F^-(g) \longrightarrow CaF_2(s)$ $\Delta H^{\circ}_{latt} = LE(CaF_2) = -2805\ kJ\ mol^{-1}$

- The lattice energy of an ionic compound is generally a **large negative value** because forming a solid ionic compound from its constituent gaseous ions is a strongly **exothermic process** as there is strong attraction between the oppositely charged ions.

- The lattice energy of an ionic compound can be used as a measure of the **strength of ionic bonding** in the compound.
  - The **more negative** the lattice energy of an ionic compound, **the stronger is the ionic bonding** present in the compound.
  - The **greater the magnitude** of the lattice energy of an ionic compound, **the stronger is the ionic bonding** present in the compound.

5.2 Factors affecting lattice energy

- The magnitude of the lattice energy of an ionic compound is directly proportional to the product of the cationic charge and anionic charge, and inversely proportional to the inter-ionic distance.

$$|\text{lattice energy}| \propto \left|\frac{q_+ q_-}{r_+ + r_-}\right|$$

where
- q_+ and q_- refer to the ionic charge on the cation and anion respectively
- r_+ and r_- refer to the ionic radius of the cation and anion respectively
- $(r_+ + r_-)$ is the inter-ionic distance

(a) Effect of ionic charge

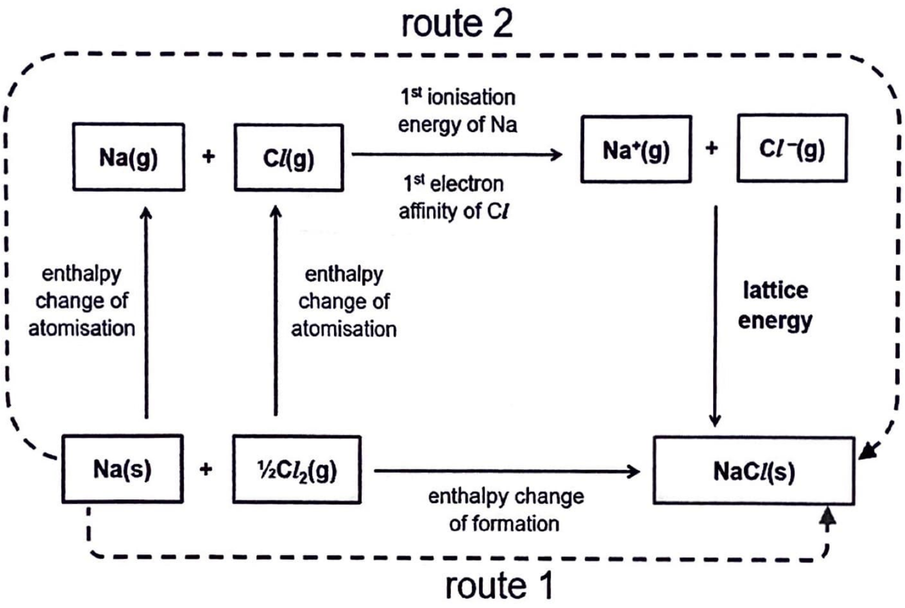
- The **bigger** the **cationic charge (q_+) or anionic charge (q_-)**,
  - the greater the magnitude of the lattice energy
  - or the **more negative** the lattice energy

(b) Effect of ionic size

- The **smaller** the **cationic radius (r_+)** or the anionic radius **(r_-)**,
  - the greater the magnitude of the lattice energy
  - or the **more negative** the lattice energy.

5.3 The Born-Haber Cycle

- The lattice energy of an ionic compound **cannot be measured directly**. It can be calculated from a Born-Haber cycle by applying Hess' law.
- A **Born-Haber cycle**
  - is an energy cycle used commonly to calculate the lattice energy of an ionic compound from other standard enthalpy changes
  - shows the various steps involved in the formation of an ionic compound from its constituent elements
  - can be presented as an energy cycle but is more commonly presented as an energy level diagram
- Consider the formation of NaCl(s) from Na(s) and Cl_2(g) as shown in the Born-Haber cycle below.
  - The reaction can be considered as taking place directly via route 1.
  - The reaction can also be considered as taking place step-wise via route 2.
  - If all the other enthalpy changes are known, the lattice energy can be calculated by applying Hess' law.



- Some of the enthalpy changes considered in the Born-Haber cycle are listed below.

$\Delta H^{\ominus}_{\text{atom}}$ (element)	**The standard enthalpy change of atomisation ($\Delta H^{\ominus}_{\text{atom}}$) of an** element is the energy absorbed to form 1 **mole** of **gaseous atoms** from the **element** under standard conditions (i.e. 1 bar and 298 K).	$Na(s) \longrightarrow Na(g)$ $\frac{1}{2}Cl_2(g) \longrightarrow Cl(g)$

1st IE	The **first ionisation energy of an element** is the energy required to remove **1 mole** of electrons from 1 mole of gaseous atoms to form 1 mole of singly positively charged gaseous ions.	$Na(g) \longrightarrow Na^+(g) + e^-$

1st EA	The **first electron affinity** (1st EA) of an element is the energy change when 1 mole of **gaseous atoms** acquires 1 mole of electrons to form 1 mole of **singly negatively charged gaseous ions**.	$Cl(g) + e^- \longrightarrow Cl^-(g)$

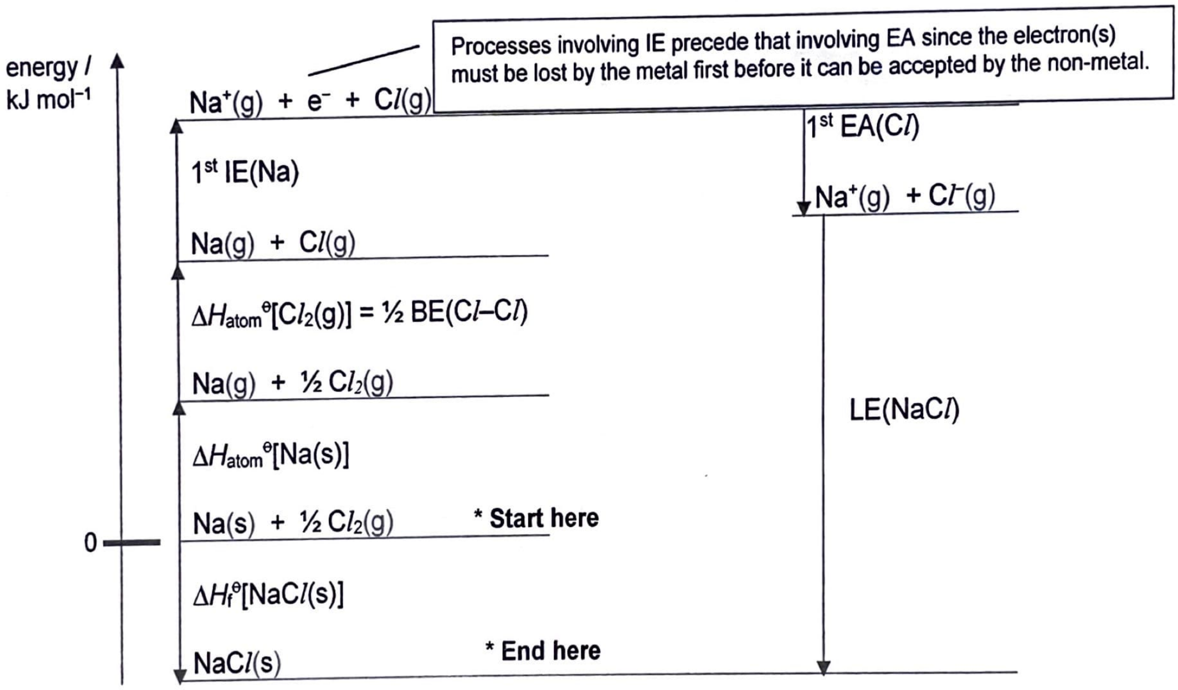
5.4 Calculating lattice energy using a Born-Haber cycle

■■ Worked Example 11

Using the data provided and also relevant data from the *Data Booklet*, draw an energy level diagram to calculate the lattice energy of sodium chloride.

Data given		
standard enthalpy change of formation of sodium chloride =	–411 kJ mol^{-1}	$Na(s) + \frac{1}{2}Cl_2(g) \rightarrow NaCl(s)$
standard enthalpy change of atomisation of sodium =	+108 kJ mol^{-1}	$Na(s) \rightarrow Na(g)$
first electron affinity of chlorine =	–364 kJ mol^{-1}	$Cl(g) + e^- \longrightarrow Cl^-(g)$
Data from *Data Booklet*		
first ionisation energy of sodium =	+494 kJ mol^{-1}	$Na(g) \rightarrow Na^+(g) + e^-$
BE(C*l*–C*l*) =	+244 kJ mol^{-1}	$Cl_2(g) \rightarrow 2Cl(g)$

Solution



Processes involving IE precede that involving EA since the electron(s) must be lost by the metal first before it can be accepted by the non-metal.

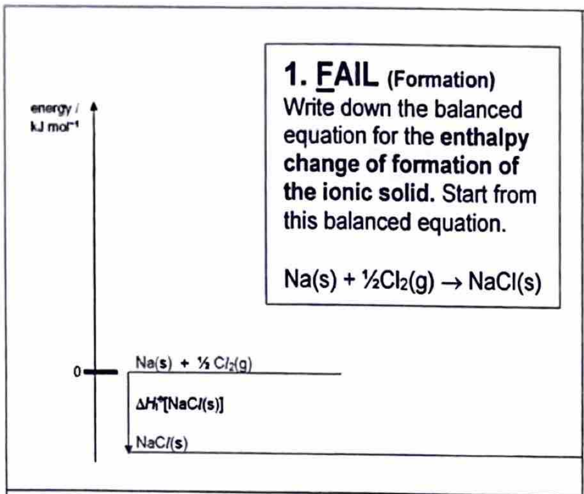
By Hess' law,

$$\Delta H_f^{\ominus}[NaCl(s)] = \Delta H_{atom}^{\ominus}[Na(s)] + \tfrac{1}{2}\,BE(Cl\text{–}Cl) + 1^{st}\,IE(Na) + 1^{st}\,EA(Cl) + LE(NaCl)$$

$-411 = +108 + (\frac{1}{2})(244) + 494 - 364$ + lattice energy of NaCl

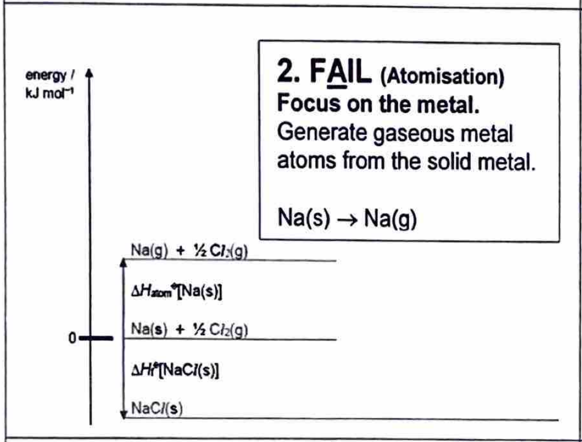
lattice energy of NaCl = **<u>–771 kJ mol^{-1}</u>**

- General steps involved in the **construction of the Born-Haber cycle** presented in the form of an energy level diagram.



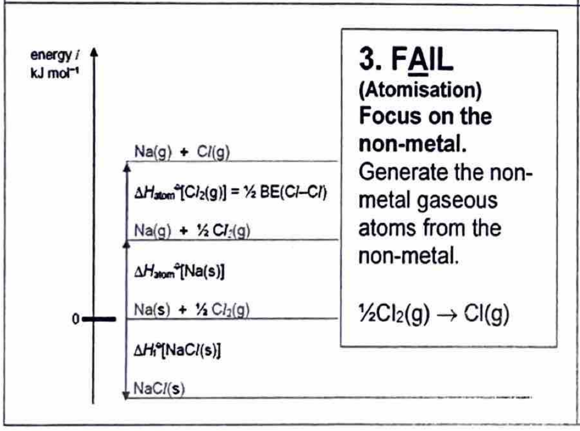
1. FAIL (Formation)
Write down the balanced equation for the **enthalpy change of formation of the ionic solid.** Start from this balanced equation.

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



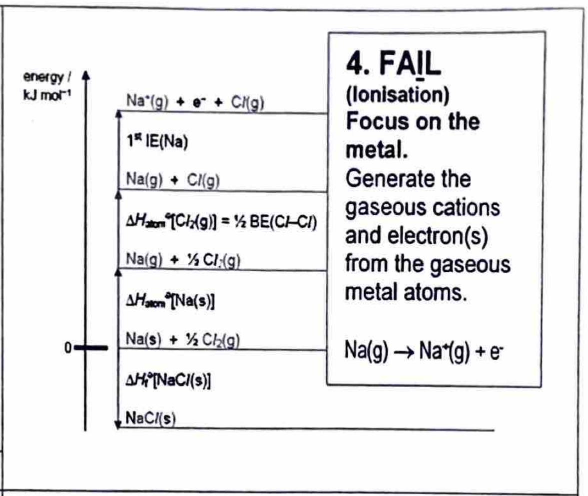
2. FAIL (Atomisation)
Focus on the metal.
Generate gaseous metal atoms from the solid metal.

$Na(s) \rightarrow Na(g)$



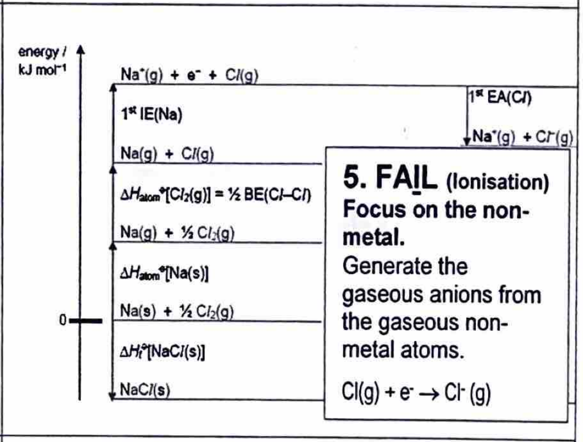
3. FAIL
(Atomisation)
Focus on the non-metal.
Generate the non-metal gaseous atoms from the non-metal.

$\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$



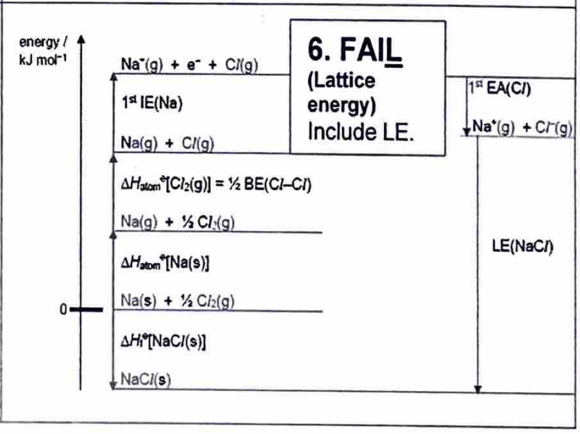
4. FAIL
(Ionisation)
Focus on the metal.
Generate the gaseous cations and electron(s) from the gaseous metal atoms.

$Na(g) \rightarrow Na^+(g) + e^-$



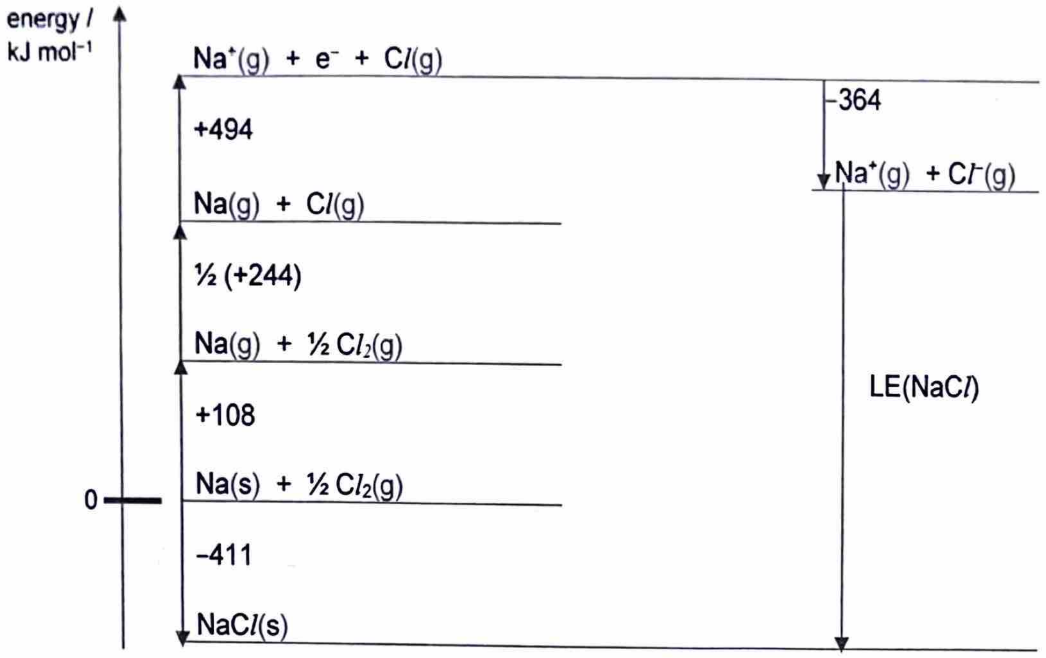
5. FAIL (Ionisation)
Focus on the non-metal.
Generate the gaseous anions from the gaseous non-metal atoms.

$Cl(g) + e^- \rightarrow Cl^-(g)$

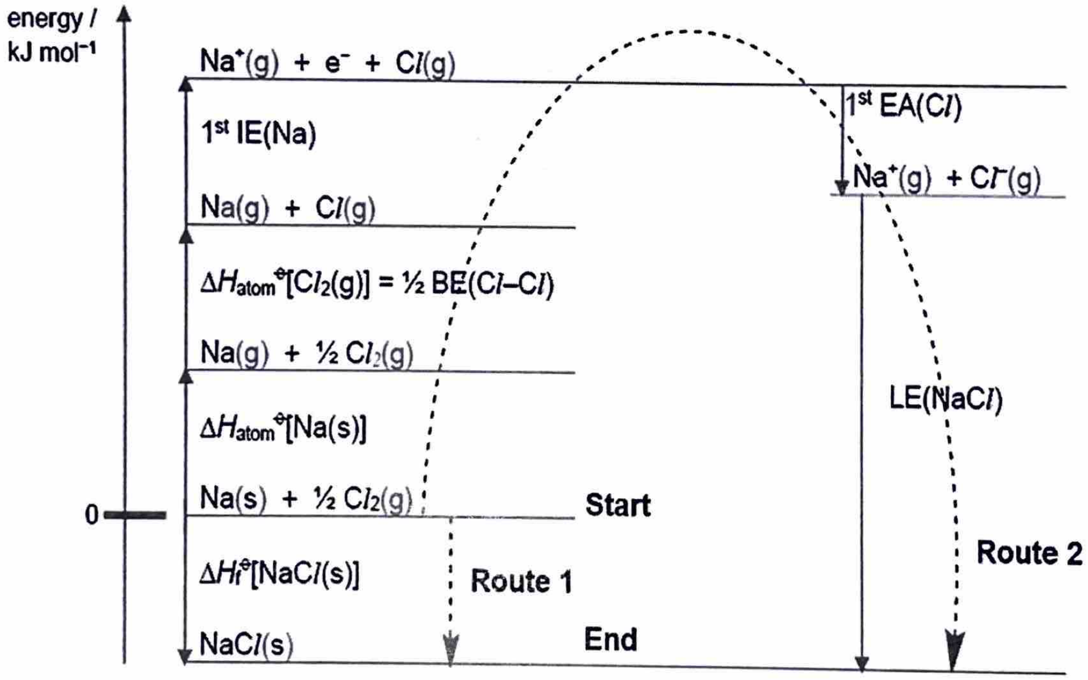


6. FAIL
(Lattice energy)
Include LE.

- **Note**: Each arrow in the Born-Haber cycle should be labelled with the appropriate enthalpy change or the value of the enthalpy change.



- Apply Hess' law by considering routes 1 and 2.

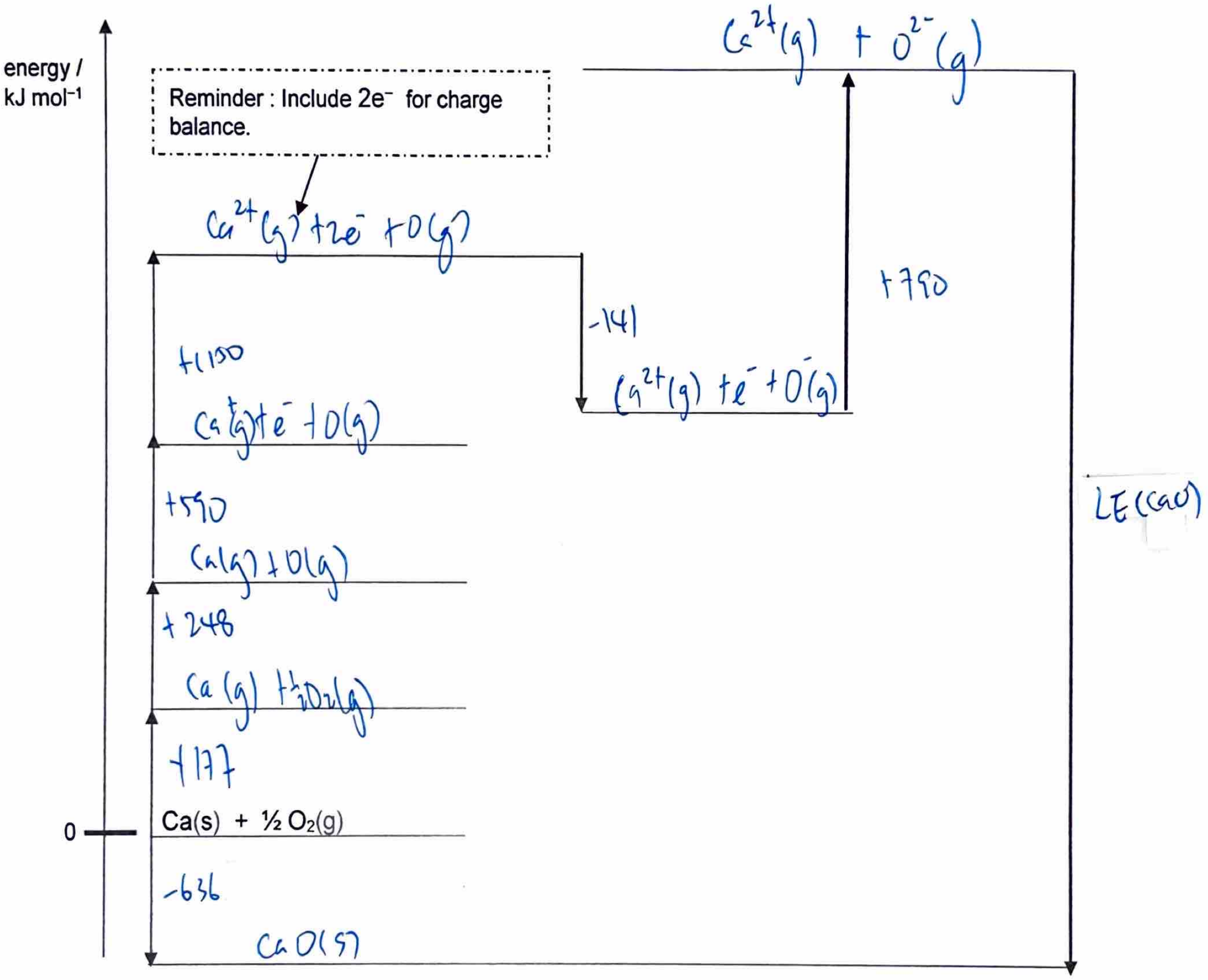


■■ Worked Example 12

Using the data provided and also relevant data from the *Data Booklet*, draw an energy level diagram to calculate the lattice energy of calcium oxide.

Data given		
standard enthalpy change of formation of calcium oxide =	–636 kJ mol^{-1}	$Ca(s) + ½O_2(g) \rightarrow CaO(s)$
standard enthalpy change of atomisation of calcium =	+177 kJ mol^{-1}	$Ca(s) \rightarrow Ca(g)$
first electron affinity of oxygen =	–141 kJ mol^{-1}	$O(g) + e^- \longrightarrow O^-(g)$
second electron affinity of oxygen =	+790 kJ mol^{-1}	$O^-(g) + e^- \longrightarrow O^{2-}(g)$
Data from *Data Booklet*		
first ionisation energy of calcium =	+590 kJ mol^{-1}	$Ca(g) \rightarrow Ca^+(g) + e^-$
second ionisation energy of calcium =	+1150 kJ mol^{-1}	$Ca^+(g) \rightarrow Ca^{2+}(g) + e^-$
BE(O=O) =	+496 kJ mol^{-1}	$O_2(g) \rightarrow 2O(g)$

Solution



Reminder : Include 2e$^-$ for charge balance.

By Hess' law,

$\Delta H_f^\circ[CaO(s)] = \Delta H_{atom}^\circ[Ca(s)] + ½\ BE(O{=}O) + 1^{st}\ IE(Ca) + 2^{nd}\ IE\ Ca) + 1^{st}\ EA\ O) + 2^{nd}\ EA\ O) + \mathbf{LE(CaO)}$

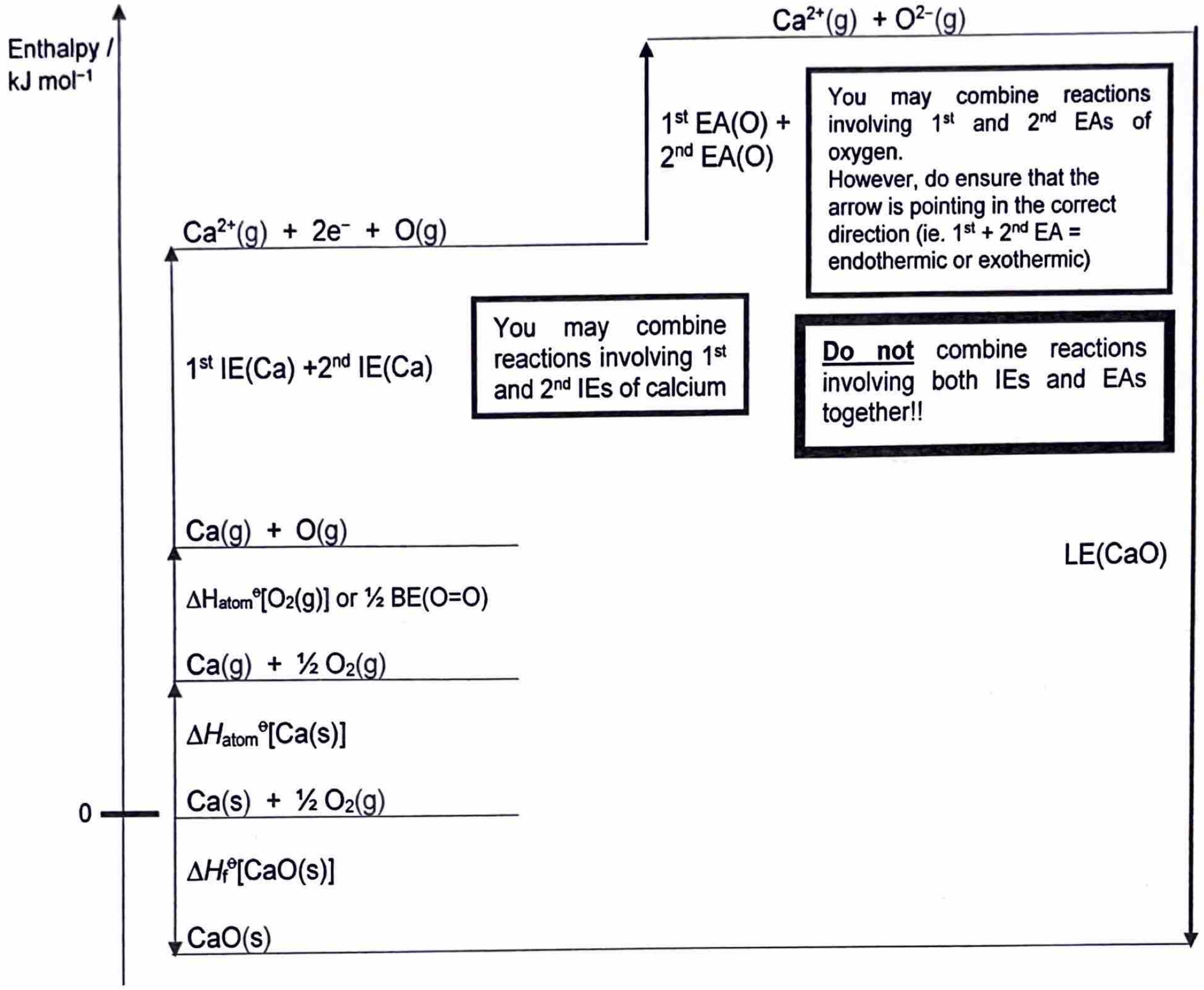
$–636 = +177 + (½)(496) + 590 + 1150 – 141 + 790 + LE(CaO)$

lattice energy of CaO = **<u>–3450 kJ mol^{-1}</u>**

Alternative Solution

1. Simplified Born-Haber Cycle (Energy level diagram)

- **Note:** You can combine similar reactions when drawing Born-Haber cycle.



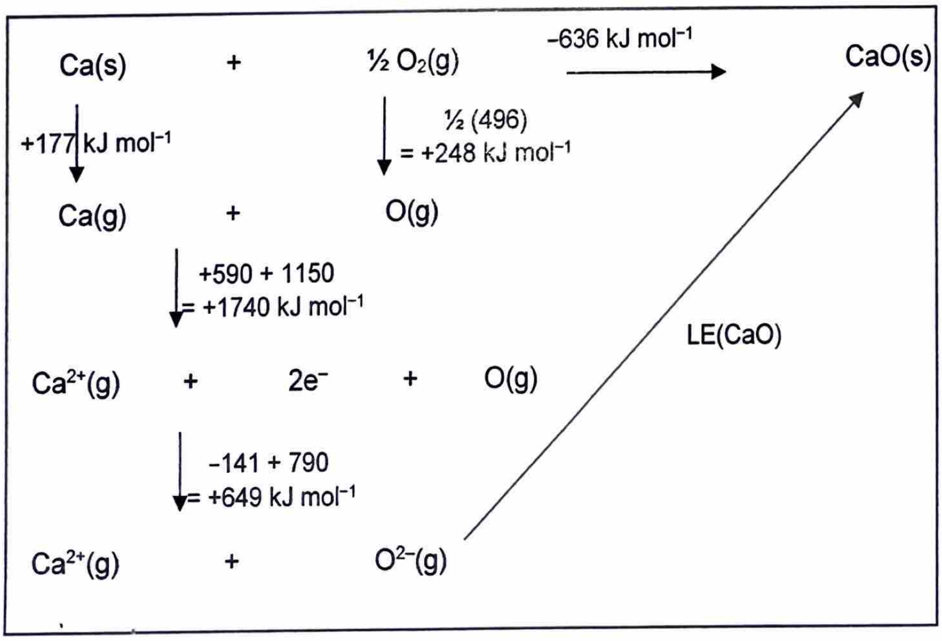
You may combine reactions involving 1st and 2nd EAs of oxygen. However, do ensure that the arrow is pointing in the correct direction (ie. 1st + 2nd EA = endothermic or exothermic)

You may combine reactions involving 1st and 2nd IEs of calcium

Do not combine reactions involving both IEs and EAs together!!

Alternative representation of Born-Haber Cycle (NOT using energy level diagram)

- **Note:** The Born-Haber cycle can be presented in the form of an energy cycle as shown below.



5.5 Theoretical and experimental lattice energy values

- There are two ways to work out the lattice energy of an ionic compound giving rise to two types of lattice energy – experimental lattice energy and theoretical lattice energy.

experimental lattice energy	theoretical lattice energy
• The **experimental lattice energy** is obtained the **experimental** way, using **experimentally obtained enthalpy changes** in a Born-Haber cycle.	• The **theoretical lattice energy** is obtained the **theoretical** way, doing some calculations using an equation based on the **purely ionic model** of a lattice. • The purely ionic model of a lattice assumes that **all the ions are spherical** and **have their charge evenly distributed** around them. The ions exert non-directional electrostatic forces on their neighbouring ions in the crystal lattice.

- For an ionic compound, the comparison between the experimental lattice energy and the theoretical lattice energy indicates how 'ionic' the ionic lattice of the compound is.

(a) Predominantly ionic compounds

ionic compound	**experimental lattice energy** (obtained via Born-Haber cycle) **/ kJ mol^{-1}**	**theoretical lattice energy** (based on a purely ionic lattice model) **/ kJ mol^{-1}**
$NaCl$	–771	–766
NaBr	–733	–732
NaI	–684	–686

- For the three sodium halides shown in the table below, the experimental lattice energy values are in **good agreement** with the theoretical lattice energy values.

- This indicates that the structure of the lattice for these compounds is **quite close to being purely ionic**. These compounds are said to be **predominantly ionic** and they fit the 'purely ionic' model with the lattice consisting of spherical ions with evenly distributed charge.

(b) Ionic compounds with partial covalent character

ionic compound	**experimental lattice energy** (obtained via Born-Haber cycle) **/ kJ mol^{-1}**	**theoretical lattice energy** (based on a purely ionic lattice model) **/ kJ mol^{-1}**
$MgCl_2$	–2526	–2326
$MgBr_2$	–2440	–2097
MgI_2	–2327	–1944
$AgCl$	–890	–768
AgBr	–877	–759
AgI	–867	–736

- For the magnesium halides and silver halides shown in the table below, the experimental lattice energy values differ from the theoretical lattice energy values by a fair bit.

- The **discrepancy** between the experimental and theoretical lattice energies shows that the bonding in the magnesium halides and silver halides is not as close to 'purely ionic' as it is with the sodium halides. These ionic compounds have **some covalent character**. This covalent character arises due to substantial polarisation of the anion by the cation.

- The experimental lattice energy values are **more negative**. This indicates that the bonding in these compounds is, in fact, stronger than that predicted by the purely ionic model.

6 Energetics of Aqueous Solution Formation

6.1 Enthalpy changes involved in dissolving an ionic solid

- When an ionic solid dissolves in water to form an aqueous solution, heat is usually evolved or absorbed.

- The enthalpy changes involved in dissolving an ionic solid in water to form an aqueous solution are given below.

$\Delta H^{\ominus}_{\text{soln}}$	The **standard enthalpy change of solution** ($\Delta H^{\ominus}_{\text{soln}}$) of a substance is the energy change when 1 **mole** of the **substance** is **completely dissolved** in a solvent to form an infinitely dilute solution under standard conditions (i.e. 1 bar and 298 K).

LE	The **lattice energy** (LE) of an ionic compound is the energy released when 1 **mole** of the **solid ionic compound** is formed from **its constituent gaseous ions** under standard conditions (i.e. 1 bar and 298 K).

$\Delta H^{\ominus}_{\text{hyd}}$	The **standard enthalpy change of hydration** ($\Delta H^{\ominus}_{\text{hyd}}$) of an ion is the energy released when 1 **mole** of the **gaseous ion** is hydrated under standard conditions (i.e. 1 bar and 298 K).

6.2 Steps involved in dissolving an ionic solid M^+X^- (e.g. NaCl) in water

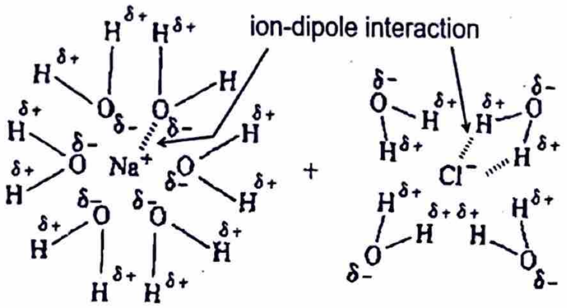
- Consider the dissolution dissolving an ionic solid, M^+X^- (e.g. NaCl) in water to form an aqueous solution. The overall reaction can be represented by the following equation.

$$M^+X^-(s) + aq. \xrightarrow{\Delta H^{\ominus}_{\text{soln}}[M^+X^-(s)]} M^+(aq) + X^-(aq)$$

- The overall process of solution can be divided into two distinct steps.

Step 1 **Separation of the ions in the solid ionic lattice into monatomic gaseous ions** • This step involves the breakdown of the ionic crystal lattice to form isolated gaseous ions. • The process is **endothermic**. • An amount of energy equals to the lattice energy is absorbed to break the ionic bonds and force the ions apart to form gaseous ions.	$M^+X^-(s) \xrightarrow{\text{– lattice energy of } M^+X^-(s)} M^+(g) + X^-(g)$ $\lvert\text{lattice energy}\rvert \propto \left\lvert\frac{q_+ q_-}{r_+ + r_-}\right\rvert$
Step 2 **Hydration of the gaseous ions** • This step involves the formation of **ion-dipole interactions** between the gaseous ions and water molecules to produce hydrated ions in aqueous solution. • This hydration process is **exothermic**. • The energy released is when gaseous ions dissolve in water is the enthalpy change of hydration. It is sometimes termed the hydration energy.	$M^+(g) + aq. \xrightarrow{\Delta H^{\ominus}_{\text{hyd}}[M^+(g)]} M^+(aq)$ $\lvert\Delta H^{\ominus}_{\text{hyd}}[M^+(g)]\rvert \propto \left\lvert\frac{q_+}{r_+}\right\rvert$ $X^-(g) + aq. \xrightarrow{\Delta H^{\ominus}_{\text{hyd}}[X^-(g)]} X^-(aq)$ $\lvert\Delta H^{\ominus}_{\text{hyd}}[X^-(g)]\rvert \propto \left\lvert\frac{q_-}{r_-}\right\rvert$

- **Example:** The dissolution of $NaCl(s)$ in water.

Step 1: $NaCl(s) \longrightarrow Na^+(g) + Cl^-(g)$	–lattice energy of $NaCl$
Step 2: $Na^+(g) + Cl^-(g) + aq. \longrightarrow Na^+(aq) + Cl^-(aq)$  	$\Delta H^{\ominus}_{\text{hyd}}[Na^+(g)] + \Delta H^{\ominus}_{\text{hyd}}[X^-(g)]$
Overall: $NaCl(s) + aq. \longrightarrow Na^+(aq) + Cl^-(aq)$	$\Delta H^{\ominus}_{\text{soln}}[NaCl(s)]$
Note: $\Delta H^{\ominus}_{\text{soln}}[NaCl(s)] = -$ lattice energy of $NaCl + \Delta H^{\ominus}_{\text{hyd}}[Na^+(g)] + \Delta H^{\ominus}_{\text{hyd}}[X^-(g)]$	

6.3 Energy cycle for the dissolving of an ionic solid, M^+X^-

$$\begin{tikzcd}
\boxed{M^+X^-(s) + aq} \arrow[rr, "\Delta H^{\ominus}_{\text{soln}}[MX(s)]"] \arrow[dr, "-\text{ lattice energy }[MX(s)]"'] & & \boxed{M^+(aq) + X^-(aq)} \\
& \boxed{M^+(g) + X^-(g)} \arrow[ur, "+\text{ aq.}", "\Delta H^{\ominus}_{\text{hyd}}[M^+(g)] + \Delta H^{\ominus}_{\text{hyd}}[X^-(g)]"'] &
\end{tikzcd}$$

By Hess law,

$$\Delta H^{\ominus}_{\text{soln}}[MX(s)] = -\text{ lattice energy }[MX(s)] + \Delta H^{\ominus}_{\text{hyd}}[M^+(g)] + \Delta H^{\ominus}_{\text{hyd}}[X^-(g)]$$

- In general, for the dissolution of $M_aX_b(s)$ in water,

$$\Delta H^{\ominus}_{\text{soln}}[M_aX_b(s)] = -\text{ lattice energy }[M_aX_b(s)] + a\Delta H^{\ominus}_{\text{hyd}}[M^+(g)] + b\Delta H^{\ominus}_{\text{hyd}}[X^-(g)]$$

- **Example:** The dissolution of $MgCl_2$ in water.

$$\Delta H^{\ominus}_{\text{soln}}[MgCl_2(s)] = -\text{ lattice energy }[MgCl_2(s)] + \Delta H^{\ominus}_{\text{hyd}}[Mg^{2+}(g)] + 2\Delta H^{\ominus}_{\text{hyd}}[Cl^-(g)]$$

- In general, the **more negative** the enthalpy change of solution, the **more soluble** the ionic compound in water.

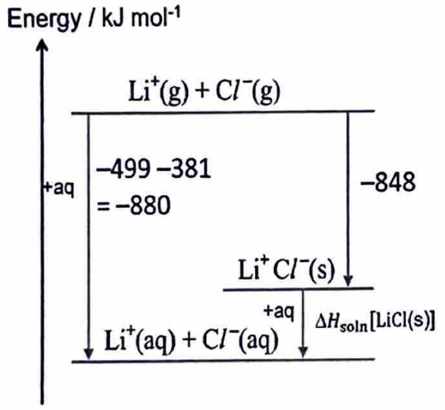
6.4 Energy level diagrams for the dissolving of an ionic solid, M^+X^-

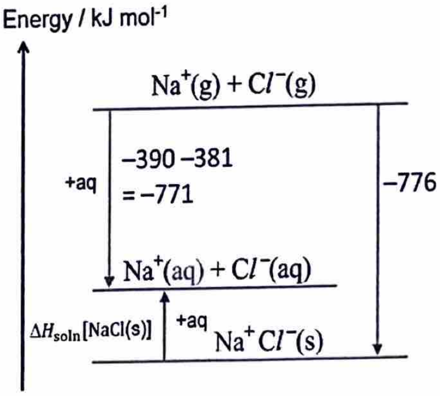
■■ Worked Example 13

Using the data given below, draw energy level diagrams to determine the enthalpy change of solution of LiCl and the enthalpy change of solution of NaCl.

	$LiCl(s)$	$NaCl(s)$	$Li^+(g)$	$Na^+(g)$	$Cl^-(g)$
lattice energy/kJ mol^{-1}	–848	–776			
enthalpy change of hydration/kJ mol^{-1}			–499	–390	–381

Solution





By Hess' law,
$\Delta H_{soln}[LiCl(s)]$ = +848 – 880 = **–32 kJ mol^{-1}**

Note:
- In this case, the enthalpy change of solution is **negative**.
- Dissolving LiC*l*(s) in water is an **exothermic** process.

By Hess' law,
$\Delta H_{soln}[NaCl(s)]$ = +776 – 771 = **+5 kJ mol^{-1}**

Note:
- In this case, the enthalpy change of solution is **positive**.
- Dissolving NaC*l*(s) in water is an **endothermic** process.

6.5 Solubility of ionic compounds

- Ionic compounds may be soluble in water if ΔH_{soln} is negative. They are less soluble if ΔH_{soln} is positive.

$\Delta H_{soln} = \Sigma\Delta H_{hyd} - LE$	$\Sigma\Delta H_{hyd} = a\Delta H_{hyd}(M^{b+}) + b\Delta H_{hyd}(X^{a-})$ LE = lattice energy of M_aX_b

- An ionic salt is more likely to be **soluble** in water if $\Delta H_{soln} < 0$.
  - In the case, LE is **less negative** than $\Sigma\Delta H_{hyd}$
  - Total hydration energy released is **enough** to **compensate** for the energy required to break down the solid ionic crystal lattice.
- An ionic salt is more likely to be **insoluble (or less soluble)** if $\Delta H_{soln} > 0$
  - In this case, LE is more negative than $\Sigma\Delta H_{hyd}$
  - Total hydration energy released is **not enough to compensate** for the energy required to break down the solid ionic crystal lattice.
- **Note:** $\Delta H_{soln} < 0$ does not necessarily imply that the salt is soluble in water and vice versa. Additional factors that can affect the solubility of a salt will be discussed in **Chemical Energetics 2**.

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Tutorial 5a – Chemical Energetics I

Self-Check Questions

1 With the aid of relevant equations, define the following terms.

- **(a)** standard enthalpy change of formation of $CH_3OH(l)$
- **(b)** standard enthalpy change of combustion of $C_3H_8(g)$
- **(c)** standard enthalpy change of neutralisation
- **(d)** standard enthalpy change of atomisation of iodine
- **(e)** standard enthalpy change of solution of $MgCl_2(s)$
- **(f)** standard enthalpy change of hydration of $Ca^{2+}(g)$
- **(g)** bond energy
- **(h)** first ionisation energy of Ca
- **(i)** second ionisation energy of Ca
- **(j)** first electron affinity of O
- **(k)** second electron affinity of O
- **(l)** lattice energy of $Na_2O(s)$

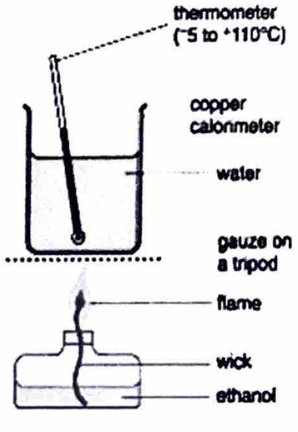
2 The enthalpy change of combustion of butane, C_4H_{10}, is –3000 kJ mol^{-1}. Calculate the mass of water at 20 °C that could be brought to the boiling point by burning 1.2 dm^3 of gaseous butane at room temperature and pressure. Assume that 80 % of the heat from combustion of butane was absorbed by the water.

3 Nitrogen and steam undergo a reaction to form ammonia and oxygen as given.

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2O(g) \rightarrow NH_3(g) + \frac{3}{4}O_2(g)$$

Determine the enthalpy change for the above reaction using appropriate bond energy information from the *Data Booklet*.

4 *(Refer to video 'Combustion of Ethanol' on IVY)*
A student attempted to determine the enthalpy change of combustion of ethanol using the apparatus shown below.



The student's results were as follows:

Mass of empty calorimeter /g	120
Mass of water in calorimeter / g	150
Mass of ethanol, wick and container before experiment /g	43.56
Mass of ethanol, wick and container after experiment /g	41.36
Initial temperature of water in calorimeter / °C	20
Final temperature of water / °C	85
Specific heat capacity of copper / J g^{-1} K^{-1}	0.387
Specific heat capacity of water / J g^{-1} K^{-1}	4.18
Molar mass of ethanol / g mol^{-1}	46.1

Use the above results to calculate a value for the enthalpy change of combustion of ethanol given the process is 75% efficient.

5 Calcium bromide is used primarily in concentrated solution as an industrial drilling fluid.
Use the information given below to construct an energy cycle and calculate the standard enthalpy change of solution of calcium bromide.

Lattice energy of calcium bromide = –2132 kJ mol^{-1}
Standard enthalpy change of hydration of Ca^{2+}(g) = –1591 kJ mol^{-1}
Standard enthalpy change of hydration of Br^-(g) = –284 kJ mol^{-1}

6 **[2001/III/8]**
Which equation defines the enthalpy change of formation of carbon monoxide?

A $C(g) + O(g) \rightarrow CO(g)$

B $C(g) + \frac{1}{2}O_2(g) \rightarrow CO(g)$

C $C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$

D $C(s) + CO_2(g) \rightarrow 2CO(g)$

7 **[2000/III/7]**
In oil refineries, an important process is the recovery of any sulfur from petroleum. Sulfur compounds are converted into the gas hydrogen sulfide, H_2S, by using a catalyst. The H_2S is then oxidised by using a controlled amount of air to give steam, H_2O(g), and sulfur, S(s).

The enthalpy change of formation of H_2S(g) is -20.5 kJ mol^{-1} and that of H_2O(g) is -243.0 kJ mol^{-1}.

What is the enthalpy change of reaction per mole of H_2S?

A -202.5 kJ mol^{-1} **C** -263.5 kJ mol^{-1}

B -222.5 kJ mol^{-1} **D** -445.0 kJ mol^{-1}

8 **[J2003/I/7]**
Gaseous phosphorus pentachloride can be decomposed into gaseous phosphorus trichloride and chlorine by heating. The table below gives the bond energies.

Bond	Bond energy / kJ mol^{-1}
P-C*l* (in both chlorides)	330
C*l* -C*l*	240

What is the enthalpy change in the decomposition of PCl_5 to PCl_3 and Cl_2?

A -420 kJ mol^{-1} **C** +90 kJ mol^{-1}

B -90 kJ mol^{-1} **D** +420 kJ mol^{-1}

9 **[2011/I/6]**
The table shows the charge and radius of each of six ions.

ion	J^+	L^+	M^{2+}	X^-	Y^-	Z^{2-}
radius / nm	0.14	0.18	0.15	0.14	0.18	0.15

The ionic solids JX, LY and MZ are of the same lattice type.
What is the correct order of their lattice energies, placing the most exothermic first?

A JX, MZ, LY **C** MZ, JX, LY

B LY, MZ, JX **D** MZ, LY, JX

10 **[2016/I/9]**

The enthalpy change of formation of potassium chloride can be calculated using a Born-Haber cycle.

The relevant enthalpy changes are shown in the table.

	enthalpy change / kJ mol^{-1}
$K(s) \rightarrow K(g)$	+90
$Cl_2(g) \rightarrow 2Cl(g)$	+242
$K(g) \rightarrow K^+(g) + e^-$	+418
$Cl(g) + e^- \rightarrow Cl^-(g)$	–355
$K^+(g) + Cl^-(g) \rightarrow KCl(s)$	–710

What is the enthalpy change of formation of KC*l*?

A –315 kJ mol^{-1}

B –436 kJ mol^{-1}

C –616 kJ mol^{-1}

D –670 kJ mol^{-1}

Practice Questions

11 **(a)** Define Hess' Law and explain why it plays such an important role in thermochemistry.

(b) Use the information given below to construct an energy cycle and calculate the standard enthalpy change of formation, ΔH_f°, of propane, C_3H_8(g).

(c) 5.60 dm^3 of a mixture of propane and butane (measured at s.t.p) on complete combustion evolved 654 kJ of heat. Calculate the percentage composition of the mixture by volume.

Given :
ΔH_c° [C_3H_8(g)] = –2220 kJ mol^{-1};
ΔH_f° [H_2O(*l*)] = –285.9 kJ mol^{-1};
ΔH_f° [CO_2(g)] = –393.5 kJ mol^{-1};
ΔH_c° [C_4H_{10} (g)] = –2877 kJ mol^{-1}.

12 **(a)** When 2.76 g of potassium carbonate was added to 30.0 cm^3 of *approximately* 2 mol dm^{-3} hydrochloric acid, the temperature rose by 5.20 °C.

(i) Write an equation, including state symbols, for this reaction.
(ii) Calculate the enthalpy change for this reaction per mole of potassium carbonate. Assume that the specific heat capacity and density of all solutions are 4.18 J g^{-1} K^{-1} and 1.00 g cm^{-3} respectively.
(iii) Explain why the hydrochloric acid need only be approximately 2 mol dm^{-3}.

(b) When 2.00 g of potassium hydrogencarbonate was added to 30.0 cm^3 of the same hydrochloric acid, the temperature fell by 3.70 °C.

(i) Write an equation, including state symbols, for this reaction.
(ii) Calculate the enthalpy change for this reaction per mole of potassium hydrogencarbonate.

(c) When potassium hydrogencarbonate is heated, it decomposes into potassium carbonate, carbon dioxide and water. By applying Hess' Law and your results in **(a)** and **(b)**, calculate the enthalpy change for the decomposition of potassium hydrogencarbonate.

13 **(a)** Define the term standard enthalpy change of neutralisation.

(b) The enthalpy change of reaction between $NaHCO_3$ and HC*l* was determined experimentally. 3.50 g of $NaHCO_3$ (M_r = 84.0) and 50 cm^3 of 1.0 mol dm^{-3} HC*l* (aq) were mixed at time = 2 min, and several temperature readings were taken at fixed intervals. Fig. 1 shows the graph of temperature against time.

Using the information from the graph and assuming that the specific heat capacity and density of all solutions are 4.18 J g^{-1} K^{-1} and 1.00 g cm^{-3} respectively, calculate the enthalpy change of the reaction:

$$NaHCO_3\,(s) + HCl\,(aq) \longrightarrow NaCl\,(aq) + H_2O\,(l) + CO_2\,(g)$$

State one assumption used in your calculation.

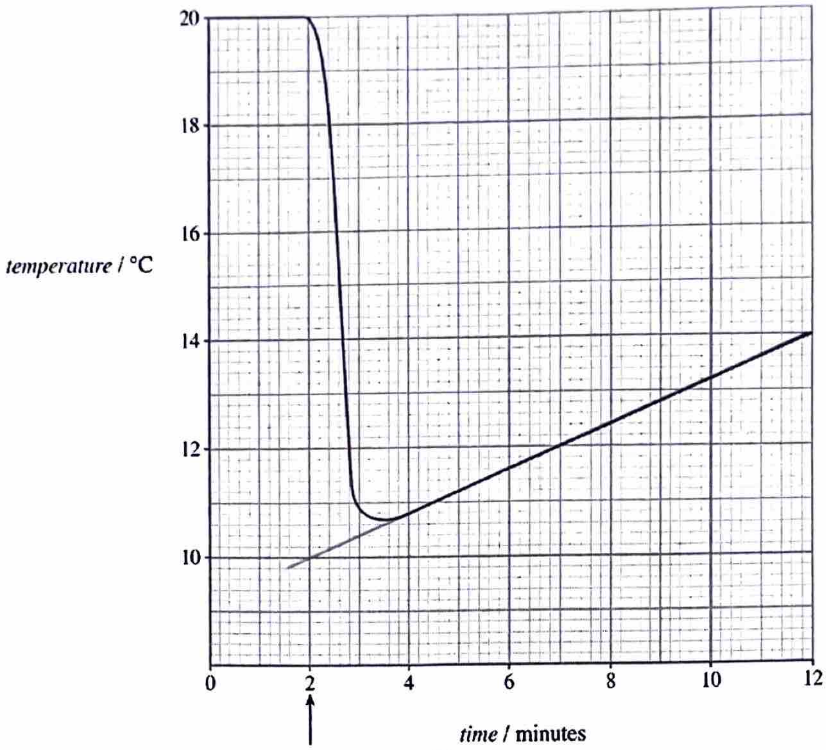


Fig. 1

(c) The enthalpy change of neutralisation of HC*l* with NaOH is given to be –57.3 kJ mol^{-1}.

The enthalpy change of solution for $NaHCO_3(s)$ is given below:

$$NaHCO_3(s) + aq \longrightarrow NaHCO_3(aq);\ \Delta H = +17.6\ kJ\ mol^{-1}$$

By using these information and your answer to **(b)**, construct an energy cycle and calculate Δ*H* for the reaction:

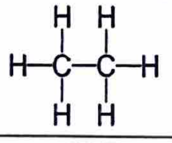
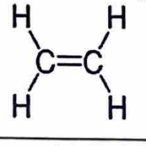
$$CO_2(g) + NaOH(aq) \longrightarrow NaHCO_3(aq)$$

(d) A similar experiment carried out with hydrogen cyanide, HCN(aq), and aqueous ammonia gave a value of –5.4 kJ mol^{-1} for the enthalpy change of neutralisation. The corresponding value for sodium hydroxide with hydrochloric acid was –57.0 kJ mol^{-1}.

Suggest a possible explanation for the difference in these two values.

14 (a) By referring to CH_4, explain what you understand by the term 'bond energy'.

(b) The standard enthalpy change of formation of the following three hydrocarbons are given below:

Hydrocarbon	Ethane, $C_2H_6(g)$ 	Ethene, $C_2H_4(g)$ 	Ethyne, $C_2H_2(g)$ H–C≡C–H
$\Delta H_f^{\ominus}$/ kJ mol^{-1}	–84.7	+52.3	+227

(i) Using bond energy data from the *Data Booklet* and given that the standard enthalpy change of atomisation of graphite = +715 kJ mol^{-1}, calculate the carbon–carbon bond energies of the three hydrocarbons and comment on their values.

(ii) Suggest why the bond energy of the C–C bond in ethane calculated in **(b)(i)** differs from the C–C bond energy found in the Data Booklet.

15 **(a)** Describe, in terms of the enthalpy involved, the process of dissolution of an ionic solid in water.

(b) Given: lattice energy of lithium chloride = –843 kJ mol^{-1} and
hydration energy of lithium chloride = –883 kJ mol^{-1},
draw an **energy level diagram** and use it to calculate the enthalpy change of solution of lithium chloride.

(c) The enthalpy change of solution of potassium chloride was found to be +17.2 kJ mol^{-1}.

By considering your answer in **(a)**, comment on the values of the enthalpy changes of solution of lithium chloride and potassium chloride.

16 (a) Using the information below and the *Data Booklet*, construct a Born–Haber diagram and calculate the lattice energy of copper(I) oxide (Cu_2O).

	Energy change / kJ mol^{-1}
Atomisation energy of Cu	339
First electron affinity of O	– 141
Second electron affinity of O	791
Enthalpy change of formation of copper(I) oxide	– 166

(b) The lattice energies of copper(I) oxide and copper(II) oxide are provided below.

	experimental lattice energy / kJ mol^{-1}	**theoretical lattice energy / kJ mol^{-1}**
copper(I) oxide	from **(a)**	–3190
copper(II) oxide	x	–4050

Predict if the experimental lattice energy of copper (II) oxide, x, will deviate more from its theoretical value, compared to copper(I) oxide. Explain your answer

(c) Using the information in **(a)**, given that the lattice energy of copper(II) oxide is –4143 kJ mol^{-1}, draw an appropriate energy cycle and calculate the enthalpy change of reaction for:

$$Cu_2O(s) \longrightarrow CuO(s) + Cu(s)$$

(d) Consider the following reaction:

$$Cu_2O(s) + H_2SO_4(aq) \longrightarrow CuSO_4(aq) + Cu(s) + H_2O(l)$$

When 2.86 g of solid Cu_2O is added to 60.0 cm^3 of dilute sulfuric acid of approximately 2 mol dm^{-3}, the temperature of the solution was raised by 8.9 K. Calculate the enthalpy change for the above reaction, stating the assumptions made.

(e) Hence, calculate the enthalpy change of neutralisation for the reaction between $H_2SO_4(aq)$ and $CuO(s)$.