# Chemical Energetics

**Content**

- Enthalpy changes ($\Delta H$): $\Delta H$ of formation; combustion; hydration; solution; neutralisation; atomisation; bond energy; lattice energy; electron affinity
- 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 ($\Delta H$ negative) or endothermic ($\Delta H$ 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 "Reaction Kinetics" notes)

(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 ($\Delta H$ positive, i.e. bond breaking) (see also "Chemical Bonding" notes)
  (iii) lattice energy ($\Delta H$ 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

## 1 Introduction

**Success Criteria:**

- Explain that most chemical reactions and physical processes are accompanied by changes in heat energy which is a result of the breaking and forming of chemical bonds; $\Delta H = H_{\text{final}} - H_{\text{initial}}$
    - When there is a net release in energy, the reaction is exothermic ($\Delta H$, negative)
    - When there is a net absorption in energy, the reaction is endothermic ($\Delta H$, positive).

- Use the sign in $\Delta H$ to deduce whether the reactant or product is more stable (lower in enthalpy (H)).

- Calculate change in heat energy using the relationship

  *heat change = $\Delta H \times \eta_{\textit{limiting agent}}$ if $\Delta H$ is known*

The study of energy changes which take place during chemical reactions is called chemical energetics or thermochemistry.

### 1.1 Enthalpy Change, Δ*H*

The following are concepts and terms related to understanding of enthalpy change:

**Enthalpy, *H***

- A measure of energy content in any species, given the symbol ***H***.
- Forming stronger bonds (stronger forces of attraction) reduces energy content (smaller value of *H*) => greater stability.

***Note:***
It is not possible to measure the absolute enthalpy of the reactant or product in a system directly. We can only measure changes in enthalpy of the system when it undergoes chemical or physical changes.

**Enthalpy Change, Δ*H***

Enthalpy change refers to the overall energy absorbed or released in a chemical reaction for 1 mole of a particular substance or molar quantities indicated in a written equation. Its units is usually expressed in kJ mol$^{-1}$.

In all chemical reactions, bonds are broken and formed.

**(a)** bond breaking absorbs energy (i.e. endothermic)
**(b)** bond forming releases energy (i.e. exothermic)

$$\Delta H = \begin{array}{c}\text{sum of energy}\\\text{absorbed during}\\\text{bond breaking}\end{array} - \begin{array}{c}\text{sum of energy}\\\text{released during}\\\text{bond forming}\end{array}$$

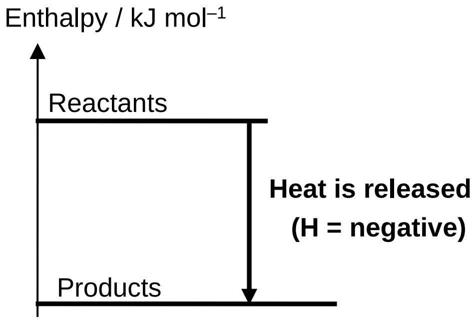
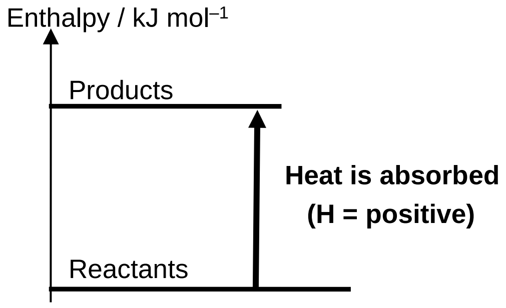
- $\Delta H$ is either determined experimentally by measuring the temperature change or via application of Hess' law.

**Heat Change, *q***

Heat change refers to the overall energy absorbed or released in a chemical reaction. Its units is usually expressed in J or kJ

$$\text{Heat change, } q = \Delta H_r \times \text{no. of moles of limiting reagent}$$

### 1.2 Exothermic / Endothermic reactions

| | **Exothermic reaction** | **Endothermic reaction** |
|---|---|---|
| **Resultant magnitude of energy** | sum of energy absorbed to break chemical bonds < sum of energy **released** from forming chemical bonds. | sum of energy **absorbed** to break chemical bonds > sum of energy released from forming chemical bonds. |
| **$\Delta H$** | $\Delta H < 0$ (−ve)<br>$H_{system}$ decrease | $\Delta H > 0$ (+ve)<br>$H_{system}$ increase |
| **Relative energy levels of reactants and products**<br>**(Energy Level Diagram)** | ● $E_{product} < E_{reactant}$<br>● Products energetically more stable than reactants.<br> | ● $E_{product} > E_{reactant}$<br>● Products energetically less stable than reactants.<br> |
| **Examples** | $NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$<br>$\Delta H = -57.3$ kJ mol$^{-1}$<br>(neutralisation reaction) | $NH_4NO_3(s) + aq \rightarrow NH_4NO_3(aq)$<br>$\Delta H = +26.0$ kJ mol$^{-1}$<br>(dissolving of aqueous ammonium nitrate) |
| **More examples** | Combustion, freezing, condensation, thermite reaction | Photosynthesis, melting, vapourisation |

***Note:***

- An **exothermic** reaction has a higher tendency to take place. i.e. **energetically feasible** ($\Delta G = \Delta H - T\Delta S$, refer to Energetics II).
- Reactions which are energetically feasible **may still not take place** because the reaction is **too slow** i.e. such reactions are kinetically not feasible due to high activation energy (energetically feasible VS kinetically feasible).

### 1.3 Thermochemical Equation

***Note:***
$\Delta H$ is defined differently for different type of reaction.

A thermochemical equation is a balanced chemical equation that shows the state symbols of substances and the associated enthalpy change.

Example:

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$ $\qquad \Delta H = -890.4$ kJ mol$^{-1}$

***Worked Example 1***

**Given the following reaction:**

$Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 3CO_2(g) \qquad \Delta H_r = -27\ \text{kJ mol}^{-1}$

**Calculate the amount of heat released, q, when**

***Note:***
Units of heat energy, q is in J or kJ, as compared to unit of enthalpy change which is in J $mol^{-1}$ or kJ $mol^{-1}$

**(a) 1 mol each of CO(g) and $Fe_2O_3$(s) are added together.**

CO is the limiting agent.

According to the above written equation, when 3 moles of CO react, 37 kJ of heat energy is released.

∴ for 1 mole of CO, heat energy released = 27 ÷ 3 = 9 kJ

**(b) 4 mol of Fe(s) is formed.**

According to the above written equation, when 2 moles of Fe is formed, 37 kJ of heat energy is released.

∴ for 4 mole of Fe, heat energy released = 27 × 2 = 54 kJ

## 1.4 Standard Conditions for Δ*H*

***Note:***
Standard conditions for energetics ≠ standard temperature and pressure for gases (273 K, 1 bar)

- Changes in energy content of a system are most easily compared when there is a set of reference conditions.
- Hence most enthalpy changes are quoted under standard conditions of:
  - **298 K or 25 °C**
  - **$10^5$ Pa or 1 bar**

***Note:***
Enthalpy level of elements in their standard states = zero

***Note:***
C(s) in the form of diamond is not the most stable allotropic form of carbon at standard conditions

- Standard conditions are denoted by the symbol $\ominus$ in superscript. (e.g. $\Delta H_c^{\ominus}$)
- The element in its natural physical state and its most stable allotropic form (when applicable) at 298 K and $10^5$ Pa is said to be in its standard state.
  Example: $S_8$(s) / S(s), C(s) in graphite.
- Similarly, a compound in its natural physical state at 298 K and $10^5$ Pa, is said to be in its standard state.
  Example: $H_2O(l)$, $Br_2(l)$

## 1.5 Magnitude and sign of $\Delta H$

$$\Delta H = \begin{array}{c}\text{sum of energy}\\ \text{absorbed during}\\ \text{bond breaking}\end{array} - \begin{array}{c}\text{sum of energy}\\ \text{released during}\\ \text{bond forming}\end{array}$$

- Types and number of moles of each type of chemical bonds broken and formed can only be deduced from a written thermochemical equation.

Therefore, the following affects the value of $\Delta H$:

### (a) Amount of substance

If we multiply both sides of a thermochemical equation by a factor *n*, then $\Delta H$ (energy change **per molar quantity of a written equation**) must change by the same factor.

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$ $\Delta H_1 = -890.4$ kJ mol$^{-1}$

$2CH_4(g) + 4O_2(g) \longrightarrow 2CO_2(g) + 4H_2O(l)$ $\Delta H_2 = 2 \times (-890.4)$ kJ mol$^{-1}$

### (b) Physical states of reactants and products

$\Delta H$ (energy change **per molar quantity of a written equation**) will change when they physical states of reactants and products change.

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$ $\Delta H_3 = -890.4$ kJ mol$^{-1}$

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$ $\Delta H_4 = -802.4$ kJ mol$^{-1}$

### (c) $\Delta H$ of forward and backward reactions

Same magnitude but opposite in sign. i.e. $\Delta H_{\text{backward}} = -\Delta H_{\text{forward}}$

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$ $\Delta H = -890.4$ kJ mol$^{-1}$

$CO_2(g) + 2H_2O(l) \longrightarrow CH_4(g) + 2O_2(g)$ $\Delta H = +890.4$ kJ mol$^{-1}$

**Checkpoint 1**

Given the equation: $H_2(g) + I_2(s) \longrightarrow 2HI(g)$ $\Delta H = +52.96$ kJ mol$^{-1}$

Calculate **$\Delta H$** for the reaction $HI(g) \longrightarrow \frac{1}{2} H_2(g) + \frac{1}{2} I_2(s)$

## 2 Definitions of Important Standard Enthalpy Changes

**Success Criteria:**

- Explain and use the terms, *enthalpy change of reaction* and *standard conditions* (298 K and 1 bar), with particular reference to: formation; combustion; hydration; solution; neutralisation; atomisation.
- Explain that *bond energy* is endothermic ($\Delta H$ positive) as it is defined as the amount of energy required to break one mole of covalent bonds. (refer to chemical bonding notes)
- Explain that *lattice energy* of an ionic lattice is exothermic ($\Delta H$ negative) as it is a bond forming process where the gaseous ions of opposite charges attract each other electrostatically to form the solid lattice.
- Explain, in qualitative terms, the effects of ionic charge and ionic radius on the numerical magnitude of lattice energy. i.e. $|L.E| \propto |\frac{q_+ \times q_-}{r_+ + r_-}|$.
- Explain, in qualitative terms, the factors affecting the magnitude of
  - standard enthalpy change of neutralisation according to the strength of the acid and alkali used.
  - standard enthalpy change of hydration, according to $|\Delta H^{o}_{hyd}| \propto |\frac{charge\ of\ ion}{ionic\ radius}|$

In order to write the thermochemical equations that represent the different reactions taking place at 298 K and 1 bar, you need to remember the various definitions of standard enthalpy changes.

The various definitions of standard enthalpy change has the following format:

The standard enthalpy change of **(name of process)** is the energy **(released/ absorbed/ change)** when one mole of **(specific substance with state symbols)** is **(describe process)** at 298 K and 1 bar.

## 2.1 Standard enthalpy change of reaction, $\Delta H^{o}_{r}$

The standard enthalpy change of reaction is the energy change when molar quantities of reactants as stated in the balanced stoichiometric equation react together at 298 K and 1 bar.

E.g. $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$ $\Delta H^{o}_{r} = -92$ kJ mol$^{-1}$

92 kJ of energy is released when 1 mole of nitrogen gas reacts with 3 moles of hydrogen gas to produce 2 moles of ammonia gas at 298 K and 1 bar.

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

The standard enthalpy change of formation is the energy change when one mole of a substance is formed from its constituent elements in their standard states at 298 K and 1 bar.

E.g. $Mg(s) + \frac{1}{2}O_2(g) \rightarrow MgO(s)$ $\Delta H_f^{o} = -602$ kJ mol$^{-1}$

602 kJ of energy is released when 1 mole of magnesium oxide is formed from oxygen gas and magnesium in their standard states at 298 K and 1 bar.

***Worked Example 2***

Given that the equation that represents the standard enthalpy change of formation of solid copper: $Cu(s) \rightarrow Cu(s)$

Explain why the value of $\Delta H_f^{o}$ solid copper is 0 kJ mol$^{-1}$

The initial and final states are the **same**, hence **no change** in energy level.

**More about $\Delta H_f^{o}$:**

- $\Delta H_f^{o}$ of all elements in standard states = 0 kJ mol$^{-1}$
- Enthalpy changes of formation are often theoretical. Such reactions may not take place in practice. E.g. $C_2H_5OH$ cannot be formed by just mixing C, $H_2$ and $O_2$.
- For elements that can exist in several allotropic forms, only the most stable form under standard conditions is given zero standard enthalpy change of formation.

***Note:***
Graphite is the most stable allotrope of graphite.

E.g. C (graphite) → C (graphite) $\Delta H_f^{o}$ (graphite) = 0 kJ mol$^{-1}$

C (graphite) → C (diamond) $\Delta H_f^{o}$ (diamond) = +2 kJ mol$^{-1}$

### 2.3 Standard enthalpy change of combustion, $\Delta H_c^{o}$

The standard enthalpy change of combustion is the energy released when one mole of a substance is completely burnt in excess oxygen at 298 K and 1 bar.

E.g. $C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H_c^{o} = -393$ kJ mol$^{-1}$

393 kJ of energy is released when 1 mole of carbon (graphite) is burnt in excess oxygen under standard conditions of 298 K and 1 bar.

- Even though substantial amount of energy is absorbed to overcome the C−C bonds in graphite, energy absorbed to overcome O=O is significantly less than energy released from formation of C=O bonds in carbon dioxide. Hence there is a net release of heat energy. $\Delta H_c^{o}$ is always negative.

***Worked Example 3***

Write thermochemical equation that represents the following standard enthalpy changes, given that both are exothermic reactions.

**Note:**
$\Delta H_c^o$ is per mole of fuel burnt in excess $O_2$ while $\Delta H_f^o$ is per mole of product from elements in standard states.

(a) standard enthalpy change of combustion of $CH_4(g)$

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ $\Delta H_c^o$ $(CH_4(g)) < 0$

(b) standard enthalpy change of formation of $CH_4(g)$

$C(s) + 2H_2(g) \rightarrow CH_4(g)$ $\Delta H_f^o$ $(CH_4(g)) < 0$

## 2.4 Standard enthalpy change of neutralisation, $\Delta H_n^o$

The standard enthalpy change of neutralisation is the energy released when one mole of water is formed from the reaction between an acid and an alkali at 298 K and 1 bar.

E.g. $NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$ $\Delta H_n^o = -57.3 \text{ kJ mol}^{-1}$

57.3 kJ of energy is released when 1 mole of water is formed as a result of the reaction between NaOH and HC*l* under standard conditions of 298 K and 1 bar.

- Strong acids and strong bases completely ionise (or dissociate) in aqueous solution. Hence the reaction is essentially:

  $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$ $\Delta H_n^o = -57.3 \text{ kJ mol}^{-1}$

- Weak acids and weak bases are only partially dissociated in aqueous solution.

  For example, for a weak acid HA,
  $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$ $\Delta H_1$

  $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$ $\Delta H_2 = -57.3 \text{ kJ mol}^{-1}$

Part of the energy released from $H^+(aq)$ reacting with $OH^-(aq)$, $\Delta H_2$, is used to provide the energy to complete the dissociation of the weak acid or weak base, $\Delta H_1$. Hence the enthalpy change is less exothermic than that of a strong acid−strong base neutralisation.

**Note:**
Ethanoic acid, $CH_3COOH$, commonly found in vinegar is a weak acid.

Strong acid−strong base neutralisation:
$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$ $\Delta H_n^o = -57.3 \text{ kJ mol}^{-1}$

Weak acid−strong base neutralisation:
$NaOH(aq) + CH_3COOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$ $\Delta H_n^o = -55.2 \text{ kJ mol}^{-1}$
**(less exothermic)**

### 2.5 Standard Enthalpy Change of atomisation, $\Delta H^o_{at}$

**For elements:**

The standard enthalpy change of atomisation is the energy absorbed when one mole of gaseous atoms is formed from its element in its standard state at 298 K and 1 bar.

E.g. $\frac{1}{2}F_2(g) \longrightarrow F(g)$ $\Delta H^o_{at} = +79 \text{ kJ mol}^{-1}$

79 kJ of energy is absorbed when one mole of gaseous fluorine atoms are formed from fluorine gas under standard conditions of 298 K and 1 bar.

### 2.6 Bond Energy (*BE*)

***Note:***
*BE* are always positive values (i.e. endothermic) since breaking of bonds always require energy.

Bond energy is the energy absorbed to break one mole of covalent bonds between two atoms in gaseous molecules to form gaseous atoms.

For diatomic molecules:
Bond energy of diatomic molecule is always exactly equals to the values given in page 45 of the *Data Booklet*.

***Note:***
The magnitude of *BE* is directly proportional to the bond strength. The stronger the bond, the larger the magnitude of BE.

E.g. $N{\equiv}N(g) \rightarrow 2N(g)$ *BE* ($N{\equiv}N$) = +944 kJ mol$^{-1}$

$H{-}F(g) \rightarrow H(g) + F(g)$ *BE* ($H{-}F$) = +562 kJ mol$^{-1}$

**Important Concept!**
For diatomic gases, $X_2$: ***BE*(X−X) = 2 × $\Delta H^o_{at}$ $X_2(g)$**

E.g. $F{-}F(g) \longrightarrow 2F(g)$ *BE*(F−F) = +158 kJ mol$^{-1}$

$\frac{1}{2}F_2(g) \longrightarrow F(g)$ $\Delta H^o_{at} = +79 \text{ kJ mol}^{-1}$

For polyatomic molecules:
Unlike diatomic molecules, the bond energy values of polyatomic molecules found in page 46 of the *Data Booklet* are **average values**. This is because, a same type of covalent bonds in different polyatomic molecules can have different bond energy values due to the different types of chemical environment the bond may be in.

Hence, the bond energy given in the *Data Booklet* is an average value, taking into account all the different types of chemical environment the bond is in. This can result in discrepancies between enthalpy change calculated using bond energy data and their actual values (see tutorial questions).

E.g. $H{-}CCl_3 \longrightarrow H(g) + CCl_3$ *BE*(C−H) = +400 kJ mol$^{-1}$

$H{-}CHCl_2 \longrightarrow H(g) + CHCl_2$ *BE*(C−H) = +414 kJ mol$^{-1}$

$H{-}CH_2Cl \longrightarrow H(g) + CH_2Cl$ *BE*(C−H) = +422 kJ mol$^{-1}$

Factors which can affect the chemical environment that the bonds are in included:
1. Presence of electron−withdrawing or electron−donating groups
2. Type of hybridisation
3. Ring strain in cyclic compounds
4. Intermediate bond order due to resonance

Some of these factors had been discussed in the Chemical Bonding chapter. Others will be discussed in greater details in the Organic Chemistry chapters.

## 2.7 Ionisation Energy, *I.E.*

First ionisation energy (1st *I.E.*) of an element is the energy absorbed to remove one mole of most loosely held electrons from one mole of gaseous atoms to form one mole of gaseous single positively charged cations.

E.g. $Mg(g) \longrightarrow Mg^{+}(g) + e^{-}$ 1st *I.E.* of Mg = +736 kJ $mol^{-1}$

Second ionisation energy (2nd *I.E.*) of an element is the energy absorbed to remove one mole of most loosely held electrons from one mole of gaseous single positively charged cations to form one mole of gaseous double positively charged cations.

E.g. $Mg^{+}(g) \longrightarrow Mg^{2+}(g) + e^{-}$ 2nd *I.E.* of Mg = +1450 kJ $mol^{-}$

## 2.8 Electron Affinity, *E.A.*

First electron affinity (1st *E.A.*) of an element is the energy released when one mole of gaseous atoms gain one mole of electrons to form one mole of gaseous single negatively charged anions.

E.g. $O(g) + e^{-} \longrightarrow O^{-}(g)$ 1st *E.A.* of O = −141 kJ $mol^{-1}$

Second electron affinity (2nd *E.A.*) of an element is the energy change when one mole of gaseous single negatively charged anions gain one mole of electrons to form one mole of gaseous double negatively charged anions.

E.g. $O^{-}(g) + e^{-} \longrightarrow O^{2-}(g)$ 2nd *E.A.* of O = +790 kJ $mol^{-1}$

## 2.9 Lattice Energy, *L.E.*

Lattice energy (*L.E.*) of an ionic compound is the energy released when one mole of ionic solid is formed from its constituent gaseous ions.

E.g. $Na^{+}(g) + Cl^{-}(g) \longrightarrow NaCl(s)$ *L.E.* (NaC*l*) = −776 kJ $mol^{-1}$

**Recall:** $|L.E| \propto \left|\frac{q_{+} \times q_{-}}{r_{+} + r_{-}}\right|$

The larger the charge of the cation and anion, the more exothermic the lattice energy. The smaller the ionic radii of the cation and anion, the more exothermic the lattice energy

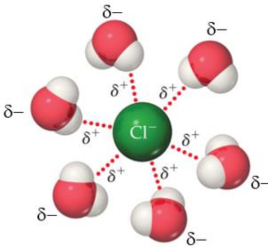
## 2.10 Standard Enthalpy Change of hydration, $\Delta H^{o}_{hyd}$

The standard enthalpy change of hydration is the energy released when one mole of gaseous ions is hydrated to form an infinitely dilute solution at 298 K and 1 bar.

***Note:***

Hydration process is always exothermic because it is a bond forming process.

Ion−dipole interactions are attractive forces formed between the isolated gaseous ions and the permanent dipole of the water molecules.



E.g. $Na^{+}(g) + aq \longrightarrow Na^{+}(aq)$ $\Delta H^{o}_{hyd}(Na^{+}) = -390\ kJ\ mol^{-1}$

$Cl^{-}(g) + aq \longrightarrow Cl^{-}(aq)$ $\Delta H^{o}_{hyd}(Cl^{-}) = -381\ kJ\ mol^{-1}$

Assuming that the number of water molecules interacting with an ion is the same,

$$\boxed{|\Delta H^{o}_{hyd}| \propto \left|\frac{\text{charge of ion}}{\text{ionic radius}}\right|}$$

The higher the $\left|\frac{\text{charge of ion}}{\text{ionic radius}}\right|$ ratio or charge density,

⇒ stronger the ion−dipole interactions between the ions and water molecules,

⇒ larger the magnitude of $\Delta H^{o}_{hyd}$ value,

⇒ more exothermic the $\Delta H^{o}_{hyd}$.

## 2.11 Standard Enthalpy Change of solution, $\Delta H^{o}_{sol}$

The standard enthalpy change of solution is the energy change when one mole of substance is completely dissolved in a solvent to form an indefinitely dilute solution at 298 K and 1 bar.

E.g. $NaCl(s) + aq \longrightarrow Na^{+}(aq) + Cl^{-}(aq)$ $\Delta H^{o}_{sol}(NaCl) = +5\ kJ\ mol^{-1}$

E.g. $LiCl(s) + aq \longrightarrow Li^{+}(aq) + Cl^{-}(aq)$ $\Delta H^{o}_{sol}(LiCl) = -32\ kJ\ mol^{-1}$

**Checkpoint 2**

Write thermochemical equations that represents the following standard enthalpy changes.

State whether $\Delta H$ is < 0, > 0 or depends on considering the energy absorbed to overcome chemical bonds and energy released from forming chemical bonds.

(a) standard enthalpy change of combustion of CO

(b) standard enthalpy change of formation of $C_2H_5OH(l)$

(c) standard enthalpy change of neutralisation between HCl and NaOH.

(d) standard enthalpy change of reaction for 1 mole of $H_2SO_4$ when it reacts with excess NaOH.

## 3 Determination of Enthalpy Change

**Success Criteria:**

- Carry out an experiment to calculate enthalpy changes, $\Delta H$ (J mol$^{-1}$ or kJ mol$^{-1}$) and heat change (J or kJ) by measuring the change in temperature ($\Delta T$) of the surroundings, using relationships such as:

$$\text{heat change} = mc\Delta T \quad \text{and} \quad \Delta H = -\frac{mc\Delta T}{n}$$

or

$$\text{heat change} = C\Delta T\text{, where } \Delta T = T_f - T_i \quad \text{and} \quad \Delta H = -\frac{C\Delta T}{n}$$

1) For reactions involving solid added to solutions
2) For reactions involving two solutions
3) For combustion reactions
4) For experiments involving cooling curve
5) For experiments with given percentage efficiency

- Explain why the magnitude of enthalpy change calculated using direct calorimetry method may deviate from that using indirect method due to
  - heat loss to surroundings or container
  - mass of substance burnt is lesser than expected (for $\Delta H_c^\theta$)

### 3.1 Direct method using Calorimetry

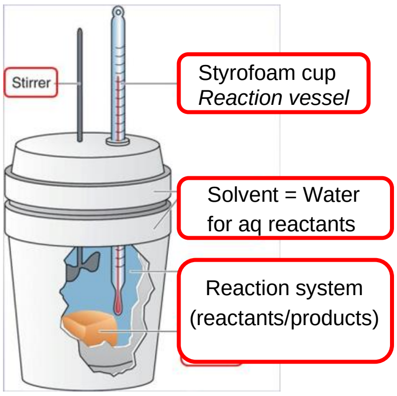
In order to determine the change in energy content of the reaction system experimentally, the principle of law of conservation of energy is used to derive a **relationship** between the heat energy change of the system and the surrounding.

**System**

- A portion of the universe under study.
- Refers to the reactants and products in the chemical reaction.

**Surrounding**

- The rest of the universe that interacts with the system.
- Examples: the reaction vessel, the air around the reaction vessel, the liquid in a thermometer, the solvent (where the reactants and products are in aqueous states)



***Note:***
Energy can neither be created nor destroyed; rather, it can only be transformed or transferred from one form to another.

**energy of reactants** + **initial energy of surrounding** = **energy of products** + **final energy of surrounding**

By rearranging the equation:

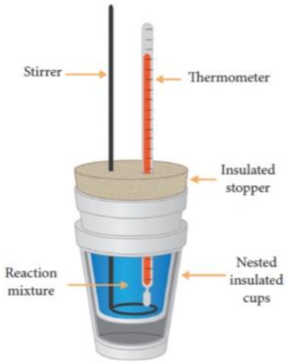
**final energy of surrounding** − **initial energy of surrounding** = **energy of products** - **energy of reactants**

Therefore change in energy of surrounding system = — change in energy of reaction

which can be expressed as heat change, $q$ ----------(1)

- units: J or kJ

Calorimetry is thus the measurement of $\Delta T$ so that heat change can be deduced.



A calorimeter is a well−insulated vessel in which a chemical reaction is carried out.
It is insulated to minimise heat exchange between the reaction system and the surrounding air so that the heat change for the reaction can be measured accurately.

**<u>General steps to determine enthalpy change of a reaction by calorimetry:</u>**

For reaction between reactants **A** and **B**,

1. Known quantities of **A** and **B** are added into a polystyrene cup and stirred.
2. Temperature change, $\Delta T$, of the reaction mixture is measured.
3. When the reaction is exothermic:

$\Delta H = -\text{ve}$ ≡ heat is released by the reaction ≡ Surrounding temp Δ ($\Delta T = +\text{ve}$)

When the reaction is endothermic:

$\Delta H = +\text{ve}$ ≡ heat is absorbed by the reaction ≡ Surrounding temp Δ ($\Delta T = -\text{ve}$)

The enthalpy change can then be determined using the following equations:

**Note:**
1 °C change = 1 K change

$$\boxed{\Delta H\ (\text{J mol}^{-1}) = -\frac{mc\Delta T}{n}}$$

where,

| | | |
|---|---|---|
| $m$ | − | mass of solution in g (ignore mass of any solid added) |
| $\Delta T$ | − | temperature change (highest/lowest temp recorded – initial temp) |
| $n$ | − | amount of specific substance (as per definition in Section 2)<br>(e.g. For $\Delta H_c$, n is the amount of substance burnt.)<br>(e.g. For $\Delta H_n$, n is the amount of water formed.)<br>(e.g. For $\Delta H_{sol}$, n is the amount of ionic compound dissolved.) |
| $c$ | − | specific heat capacity of solution, defined as the amount of heat required to raise the temperature of 1 g of solution by 1 K. Unit is J $g^{-1}$ $K^{-1}$ or J $g^{-1}$ °$C^{-1}$. |

**Note:**
Specific heat capacity of water = 4.18 J $g^{-1}$ $K^{-1}$ is given in the *Data Booklet*

The enthalpy change of reaction, which is dependent on the stoichiometry of the balanced equation, is determined using the following equations:

$$\boxed{\Delta H_r = -\frac{mc\Delta T}{n_{limiting\ reagent}} \times coefficient\ of\ limiting\ reagent}$$

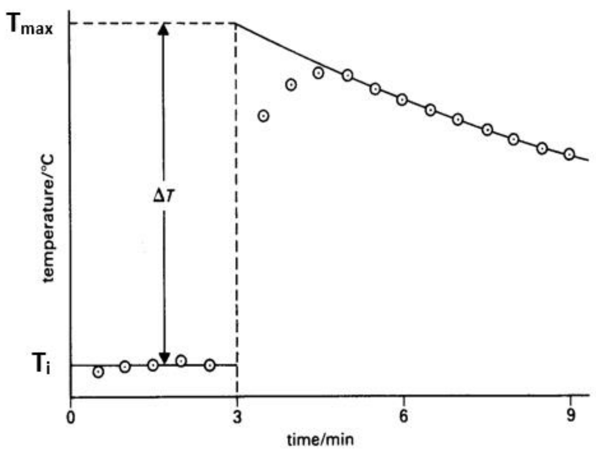
- Enthalpy changes that cannot be measured by calorimetry can be obtained indirectly by applying Hess' Law (See Section 3.2).

**Assumptions made in calorimetry experiments:**

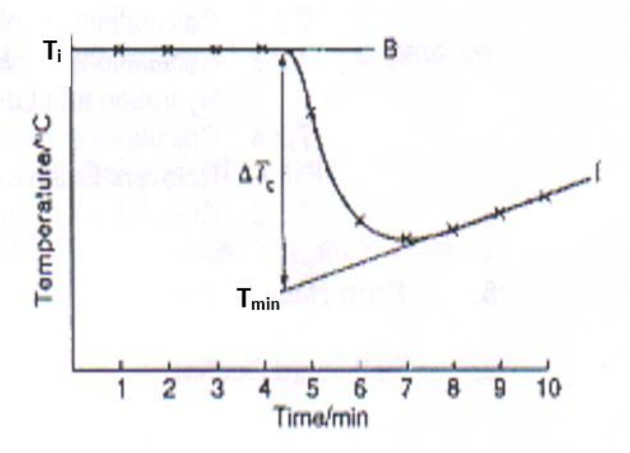
1. There is negligible heat loss to the surrounding as the calorimeter is well−insulated.
2. The density of the solution, unless otherwise stated, is the same as that of water, at 1.00 g $cm^{-3}$. This is a reasonable assumption when the solution is dilute.
3. The specific heat capacity of the solution, unless otherwise stated, is the same as that of water, at 4.18 J $g^{-1}$ $K^{-1}$ or 4.18 J $g^{-1}$ $°C^{-1}$.

**Method to account for heat exchange with the surrounding in calorimetry experiments:**

**Exothermic Reaction**



**Endothermic Reaction**



| | |
|---|---|
| 1. Mixing of reactants occurs at 3 minutes. | 1. Mixing of reactants occurs at 4.5 minutes. |
| 2. Temperature rises due to heat released from reaction. | 2. Temperature drops due to heat absorbed by reaction. |
| 3. When reaction ends, cooling occurs as no more heat is released by the reaction, but heat is slowly lost to the surrounding air. | 3. When reaction ends, temperature starts to rise as no more heat is absorbed by the reaction, but heat is gained slowly from the surrounding air. |
| 4. Extrapolation of graph after maxima to the time of mixing gives $T_{max}$. | 4. Extrapolation of graph after minima to the time of mixing gives $T_{min.}$ |
| 5. Calculate ΔT where $\Delta T = T_{max} - T_i$ | 5. Calculate ΔT where $\Delta T = T_{min} - T_i$ |
| 6. Use the $\Delta T$ to calculate heat change and $\Delta H$. | 6. Use the $\Delta T$ to calculate heat change and $\Delta H$. |

### 3.1.1 Calculations of enthalpy changes using calorimetry

***Worked Example 4a: Determine enthalpy change of reaction,* $\Delta H_r$, for acid−metal reaction)**

0.560 g of zinc powder was added to 30.0 $cm^3$ of 0.500 mol $dm^{-3}$ hydrochloric acid in a polystyrene cup. The initial temperature of the acid was 25.0 °C and the highest temperature reached was 35.5 °C.

Assume that the density of the solution is 1.00 g $cm^{-3}$ and its specific heat capacity is 4.18 J $g^{-1}$ $K^{-1}$.

Calculate the enthalpy change of reaction represented by the following equation:

$$Zn(s) + 2HCl(aq) \longrightarrow ZnCl_2(aq) + H_2(g)$$

***Approach:***

**Step 1:**
Construct balanced chemical equation (check $\Delta H$ definition)

**Step 2:**
Determining limiting reagent, and hence the required n for the respective $\Delta H$

**Step 3:**
Determine the unknown $\Delta H$ using $\Delta H = -\frac{mc\Delta T}{n}$

***Note:***
m = mass of solution in g (ignore mass of any solid added)

**Step 1:** (Already given in the question)

**Step 2:**

Amount of Zn present = $\frac{0.560}{65.4}$ = $8.563 \times 10^{-3}$ mol

Amount of HC*l* present = $0.500 \times \frac{30}{1000}$ = $1.500 \times 10^{-2}$ mol

Since 1 mol Zn ≡ 2 mol HC*l*,
Therefore $8.563 \times 10^{-3}$ mol Zn ≡ $1.713 \times 10^{-2}$ mol HC*l*,

Hence, HC*l* is the limiting reagent.

**Step 3:**

$$\Delta H_r = -\frac{mc\Delta T}{n_{limiting\ reagent}} \times \boldsymbol{coefficient\ of\ limiting\ reagent}$$

$$= -\frac{(30)(4.18)(35.5-25.0)}{1.50 \times 10^{-2}} \times 2 = -\frac{1316.7}{1.50 \times 10^{-2}} \times 2 = -175\ 560\ J\ mol^{-1}$$

$= -176$ kJ $mol^{-1}$ (3 s.f)

### *Worked Example 4b: (Determine enthalpy change of solution, $\Delta H_{sol}$)*

5.6 g of solid ammonium chloride was dissolved in 100 cm$^3$ of water. The initial temperature of the water was 29.0 °C and the lowest temperature reached was 25.9 °C. Calculate the enthalpy change of solution for ammonium chloride, given that enthalpy change of solution is the energy change when one mole of ionic solid is completely dissolved in excess solvent.

***Approach:***

**Step 1:**
Construct balanced chemical equation (check $\Delta H$ definition)

**Step 2:**
Determining limiting reagent, and hence the required n for the respective $\Delta H$

**Step 3:**
Determine the unknown $\Delta H$ using $\Delta H = -\frac{mc\Delta T}{n}$

***Note:***
m = mass of solution in g (ignore mass of any solid added)

**Step 1:** $NH_4Cl(s) + aq \longrightarrow NH_4^+(aq) + Cl^-(aq)$

**Step 2:**

Amount of $NH_4Cl(s) = \frac{5.6}{14.0 + 4(1.0) + 35.5} = 0.1047$ mol

**Step 3:**

$$\Delta H_{sol} = -\frac{mc\Delta T}{n_{NH_4Cl}} = -\frac{(100)(4.18)(25.9-29.0)}{0.1047} = -\frac{(-1295.8)}{0.1047}$$

= +12376.3 J mol$^{-1}$ ≈ +12.4 kJ mol$^{-1}$ (3 s.f)

### *Worked Example 4c: (Determine enthalpy change of neutralisation, $\Delta H_n$)*

When 50 cm$^3$ of 1.00 mol dm$^{-3}$ sodium hydroxide is added to 100 cm$^3$ of 1.00 mol dm$^{-3}$ hydrochloric acid in a polystyrene cup, the temperature of the mixture was found to increase from 25.0 °C to 29.5 °C.

Assuming the specific heat capacity and density of the reaction mixture is 4.18 J g$^{-1}$ K$^{-1}$ and 1 g cm$^{-3}$ respectively, calculate the enthalpy change of neutralisation.

***Approach:***

**Step 1:**
Construct balanced chemical equation (check $\Delta H$ definition)

**Step 2:**
Determining limiting reagent, and hence the required n for the respective $\Delta H$

**Step 3:**
Determine the unknown $\Delta H$ using $\Delta H = -\frac{mc\Delta T}{n}$

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

amount of NaOH = 1.00 × $\frac{50}{1000}$ = 0.0500 mol

amount of HC*l* = 1.00 × $\frac{100}{1000}$ = 0.100 mol

Hence, NaOH is the limiting reagent.

amount of $H_2O$ formed = amount of NaOH = 0.0500 mol

Since density of reaction mixture = 1 g cm$^{-3}$,
mass of reaction mixture = 50 + 100 = 150 g

$$\Delta H_n = -\frac{mc\Delta T}{n_{H_2O}} = -\frac{(150)(4.18)(29.5-25.0)}{0.0500} = -\frac{2821.5}{0.0500} = -56430 \text{ J mol}^{-1}$$

= −56.4 kJ mol$^{-1}$ (exothermic)

***Note:***
The enthalpy change of neutralisation is the heat released **when one mole of water is formed** from the reaction between an acid and an alkali.

### Checkpoint 3a

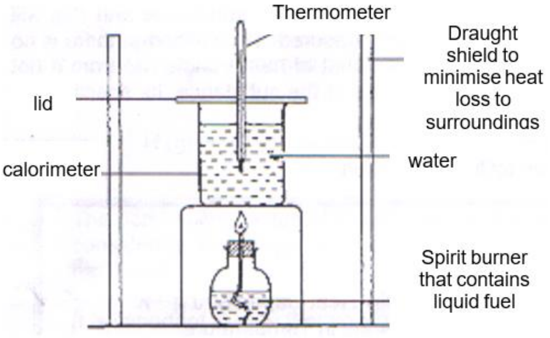
Zinc metal reacts with silver nitrate to give zinc nitrate and silver metal. 1.40 g of zinc powder was added to 50.0 $cm^3$ of 0.100 mol $dm^{-3}$ $AgNO_3$ in a polystyrene cup. Initially the temperature was 21.1 °C and subsequently rose to 25.4 °C. Determine the enthalpy change of reaction for one mole of Zn.

Assume that the density of the solution is 1.00g $cm^{-3}$ and its specific heat capacity is 4.18 J $g^{-1}$ $K^{-1}$.

**[−359 kJ $mol^{-1}$]**

***Note:***
How is the above experiment being set−up?
Watch https://www.youtube.com/watch?v=_99−qeNNozU to find out.

### 3.1.2 Determination of enthalpy change of combustion of liquid fuel using calorimetry



- A spirit burner containing liquid fuel is used. Weighing the spirit burner before and after burning gives the mass of fuel used for combustion.
- A known volume of water is placed in a copper calorimeter and its temperature taken.
- The wick is lighted and the water in the calorimeter is stirred with the thermometer. When the temperature has risen by about 10 °C, the flame is put out and the spirit burner is reweighed immediately.

The experimental value obtained for the enthalpy change of combustion of methanol using the above setup is **less exothermic** (**smaller** in **magnitude**) than the actual (true) value due to the following reasons:

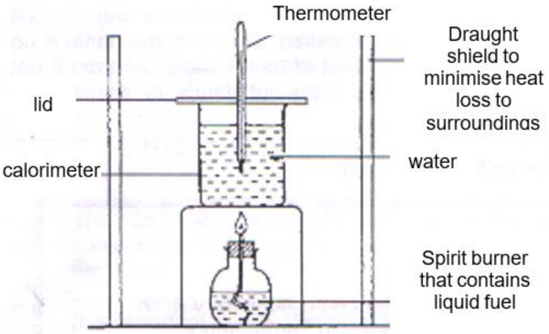
| Reasons | Effect on $\Delta H_c$ $\left(\propto \left\lvert \frac{mc\Delta T}{n_{substance\ burnt}} \right\rvert\right)$ |
|---|---|
| The assumption that methanol undergoes complete combustion to form $CO_2$ and $H_2O$ may not always be true.<br>When inadequate oxygen is supplied, some methanol undergoes incomplete combustion to form carbon monoxide or carbon (soot).<br>Thus, for the same mass of fuel burnt, less energy is released. | $\Delta T$ measured will be smaller than expected and thus the magnitude of $\Delta H_c$ calculated is smaller than actual. |
| The assumption that all the heat released from combustion is absorbed by the water in calorimeter is not true.<br>Significant amount of heat is lost to the surrounding air from the spirit lamp flame.<br>Some heat is also absorbed by the copper calorimeter. | |
| Difference in the mass of methanol and spirit burner before and after combustion ≠ mass of methanol burnt.<br>Evaporation of volatile methanol from the hot spirit burner cause additional loss in mass.<br>Burning of wick can also cause additional mass loss after combustion. | Mass of methanol burnt recorded is larger than the actual mass burnt.<br>Heat change is divided by a larger than expected amount of methanol, resulting in a smaller magnitude of $\Delta H_c$ calculated. |

**Note:**
There is no need to determine the limiting agent in a combustion reaction. By definition, combustion has to be carried out under excess oxygen.

**Note:**
Do not use the mass of the methanol being burnt in *heat change* = *mc*Δ*T*.

Heat released from the combustion is gained by the water. The temperature change recorded is that of the water, not the methanol. Thus mass of the water heated up should be used.

***Worked Example 5***



The above set−up was used to determine the enthalpy change of combustion of methanol, $CH_3OH$. The following results were obtained:

Mass of methanol and burner before combustion = 532.68 g
Mass of methanol and burner after combustion = 531.72 g
Mass of water in the calorimeter = 200 g
Temperature of water at start of experiment = 28.0 °C
Temperature of water at end of experiment = 39.3 °C

Calculate the enthalpy change of combustion of methanol.

$CH_3OH(l) + 3/2\ O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$

amount of methanol burnt = $\frac{\textbf{mass of methanol}}{\boldsymbol{M_r} \textbf{ of methanol}} = \frac{532.68 - 531.72}{12.0 + 4(1.0) + 16.0}$

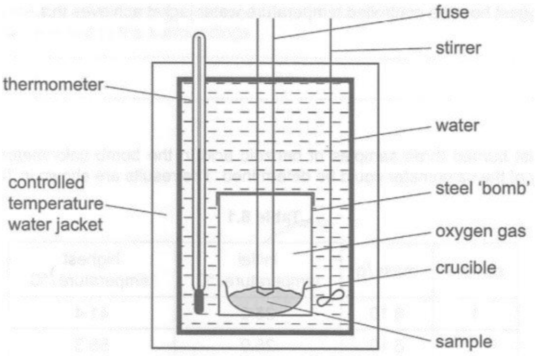
$= 3.00 \times 10^{-2}$ mol

$\Delta H_c = -\frac{mc\Delta T}{n_{methanol}} = -\frac{(200)(4.18)(39.3 - 28.0)}{3.00 \times 10^{-2}} = -\frac{9446.8}{3.00 \times 10^{-2}} = -315\ \text{kJ mol}^{-1}$

***Note:***
The enthalpy change of combustion is the heat released when **one mole of a substance is completely burnt** in excess oxygen.

### 3.1.3 Determination of enthalpy change of combustion using heat capacity of calorimeter

A bomb calorimeter can be used to determine enthalpy change of combustion more accurately.



**a.** The fuel is placed in the crucible and the “bomb” filled with oxygen at a high pressure. High pressure of oxygen is used so that sufficient amount of oxygen is supplied for complete combustion to take place.

**b.** The “bomb” is then placed in an insulated calorimeter containing a known mass of water.

**c.** The fuel is ignited by an electric current and the temperature change of the water heated up by the combustion reaction is measured.

**d.** To eliminate heat losses to the surroundings, the calorimeter is placed in controlled temperature water jacket, whose temperature is raised with an electric heater so that it continuously matches the temperature of the water in the calorimeter.

**e.** $\Delta H = -\frac{C\Delta T}{n}$ , where heat capacity (C) of calorimeter, is defined as the amount of heat required to raise the temperature of **both the water and the reaction vessel** by 1 K. Unit is J $K^{-1}$ or J $°C^{-1}$.

**f.** The heat capacity (C) of the calorimeter is first calibrated by calculating the theoretical amount of heat energy required, from combustion of benzoic acid ($\Delta H_c^{\theta}$ = −3230kJ $mol^{-1}$), to raise the calorimeter by 1K.

**g.** The resulting enthalpy change of combustion values obtained experimentally by this method is found to be highly accurate.

***Note:***
Benzoic acid is used to calibrate bomb calorimeter because it burns completely in oxygen and is readily available in a highly pure form.

***Work Example 6a* [N2017/II/6(b)(iii)−modified]**

A chemist burned a sample of benzoic acid in the bomb calorimeter so that the heat capacity of the calorimeter could be determined. The results are shown in the table below.

| mass of benzoic acid/ g | initial temperature/ °C | highest temperature/ °C |
|---|---|---|
| 6.10 | 25.0 | 54.7 |

The reference value for the energy change of combustion of benzoic acid is −3230 kJ $\text{mol}^{-1}$.

Calculate the heat capacity of the calorimeter from appropriate data in the table above. State its units.

Assume that all the energy released from the combustion process is converted into heat and none is lost to the surroundings.

amount of benzoic acid combusted = $\frac{6.10}{6(12.0)+6(1.0)+16.0}$ = 0.0500 mol

$\Delta H = -\frac{C\Delta T}{n}$

$-3230 = -\frac{C(54.7-25.0)}{0.0500}$

$C$ = 5.38 kJ $°\text{C}^{-1}$

| Limitations of the spirit burner (pg 19) | How does a bomb calorimeter overcome the limitations and accurately determine $\Delta H_c$? |
|---|---|
| The heat loss to surroundings is unaccounted for. | The controlled temperature water jacket ensures that there is no temperature gradient between the water jacket and the water in the steel 'bomb'. As there is no temperature gradient, there is no heat transferred and hence, no heat loss to the surrounding. |
| The heat absorbed by the calorimeter is unaccounted for. | Heat change = $C\Delta T$ is used to calculate heat absorbed by the bomb calorimeter (steel bomb and water). This allows the heat gained by the container holding the reaction mixture to be accounted for.<br>$C$ = theoretical amount of heat energy required to raise the calorimeter (steel bomb and water) by 1 °C.<br>Therefore heat absorbed by the steel bomb is accounted for. |
| Incomplete combustion of substance | The high pressure of oxygen in the 'bomb' ensures sufficient amount of oxygen is supplied for complete combustion of the substance. |

***Worked Example 6b***

An experiment was carried out as follow to determine the standard enthalpy change of combustion of butane ($C_4H_{10}$) contained in the gas cylinder of a camping gas stove.

A large beaker of water was placed on the stove and heated by combusting butane completely in excess oxygen. The temperature rise was recorded. The cylinder was weighed before and after the experiment to determine the mass of gas used. The following results were obtained.

| | |
|---|---|
| mass of butane used/ g | 3.4 |
| mass of water heated/ g | 500 |
| temperature rise/ °C | 44 |

**(i)** Write a thermochemical equation for the combustion of butane.

$$C_4H_{10}(g) + \frac{13}{2}O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(l) \qquad \Delta H_c^{o} < 0$$

**(ii)** Use the data given to calculate the enthalpy change of combustion of butane.

heat change = $mc\Delta T$ = (500)(4.18)(44) = +91960 J

amount of butane burnt = $\frac{mass\ of\ butane}{M_r\ of\ butane} = \frac{3.4}{4(12.0)+10(1.0)}$ = $5.862 \times 10^{-2}$ mol

$$\Delta H_c = -\frac{mc\Delta T}{n_{butane}} = -\frac{91960}{5.862 \times 10^{-2}} = -1570 \text{ kJ mol}^{-1}$$

**(iii)** The true value of $\Delta H_c$ of butane is –2877 kJ mol$^{-1}$.

Suggest a reason for the difference in magnitude between this true value and your calculated value in **(ii)**.

Only a portion of heat released from combustion is absorbed by water. Some heat are lost to the surrounding air and the container.

OR

Incomplete combustion has taken place, hence less heat is released from reaction.

$\Delta T$ measured is lower than actual. $\therefore \Delta H$ calculated is of smaller magnitude. (less exothermic)

**(iv)** State one precaution you should observe when carrying out this experiment in order to get more accurate results.

- Use a windshield to keep draught at bay so that there would be minimal heat loss from the flame.
- Determine the heat capacity of the beaker and 500 g of water so that heat lost to the beaker can be accounted for.

### 3.2 Indirect methods of determining enthalpy changes

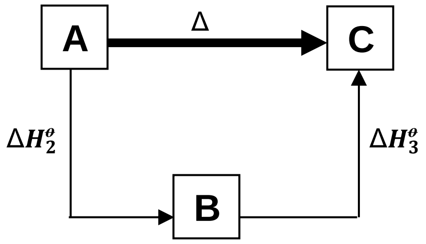
**Success Criteria:**

- Construct an energy cycle and an energy level diagram from a given set of data.
- Calculate the enthalpy change of a reaction by applying Hess' Law with or without an energy cycle/ energy level diagram.
- Calculate enthalpy change of reaction from enthalpy formation data. i.e. $\Delta H_r^{\theta} = \sum n\, \Delta H_f^{\theta}$ (products) – $\sum m\, \Delta H_f^{\theta}$ (reactants)
- Calculate enthalpy change of reaction involving simple covalent molecules using relevant bond energy data from Data Booklet. i.e. $\Delta H_r^{\theta} = \sum$ *BE*(bonds broken) + $\sum$ *BE*(bonds formed)
- Explain why the magnitude of enthalpy change calculated using bond energies data may deviate from the actual value due to:
  - bond energy from *Data Booklet* being average values, and
  - bonds involved in the reactions not in gaseous state.

The standard enthalpy changes of reactions which **cannot be determined by calorimetry** can be **calculated by** applying **Hess' Law**.

#### 3.2.1 Hess' Law

Using the principle of law of conservation of energy, Hess' law is derived. **Regardless of the route** by which the chemical change occurs from initial state A to final state C, the **overall energy change** is always the **same as long as the initial and final states are the same.**



$$\boxed{\Delta H_1^{\theta} = \Delta H_2^{\theta} + \Delta H_3^{\theta}}$$

Two possible approaches when applying Hess' law:

(i) Drawing energy cycles or energy level diagrams.

(ii) Using mathematical formulae

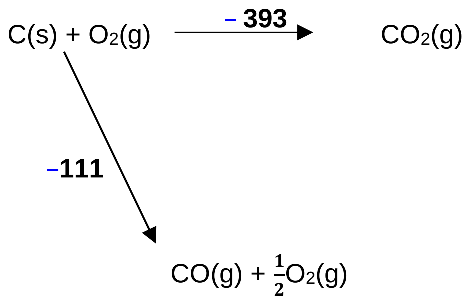
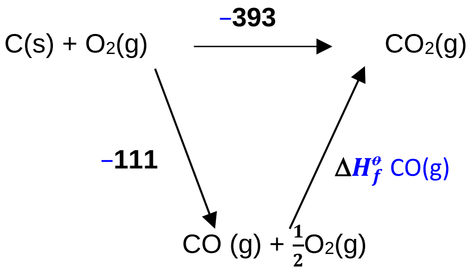
***Worked Example 7***

Find the standard enthalpy change of combustion of carbon monoxide using the following data.

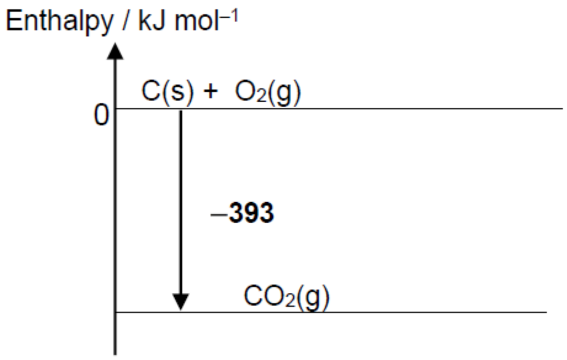
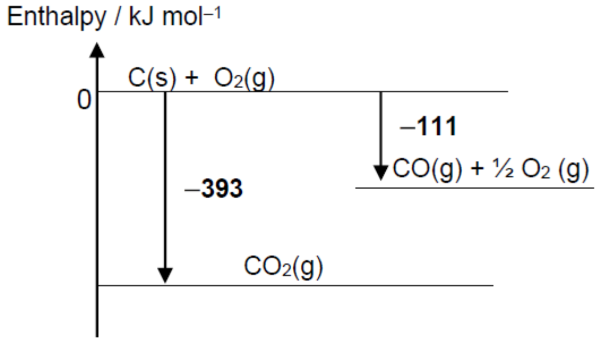
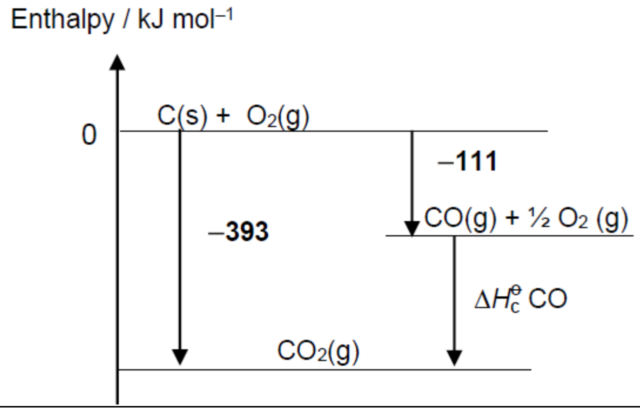
| | |
|---|---|
| standard enthalpy change of formation of carbon dioxide | −393 kJ mol$^{-1}$ |
| standard enthalpy change of formation of carbon monoxide | −111 kJ mol$^{-1}$ |

**Method 1a: By drawing energy cycle**

**Steps to constructing an energy cycle:**

| | |
|---|---|
| 1. Write the balanced chemical equation of the unknown Δ*H* equation. | standard enthalpy change of combustion of carbon monoxide<br>(1) $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$ $\Delta H^{o}_{c}$ CO(g) |
| 2. Write the balanced chemical equations of the other given Δ*H*. | standard enthalpy change of formation of carbon dioxide<br>(2) $C(s) + O_2(g) \longrightarrow CO_2(g)$ Δ $CO_2(g)$ = −393 kJ mol$^{-1}$<br>standard enthalpy change of formation of carbon monoxide<br>(3) $C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$ $\Delta H^{o}_{f}$ CO(g) = −111 kJ mol$^{-1}$ |
| 3. Place the main equation in the energy cycle. (Main equation contains the most number of elements)<br>In this case, equation (1) / (2) / (3) can be the main equation | $C(s) + O_2(g) \xrightarrow{-393} CO_2(g)$ |
| 4. Match remaining equations to either the reactants or products of the main equation.<br>Choosing one equation at a time.<br>Ensuring the conservation of atoms before and after the arrow by adjusting the stoichiometry required. |  |
| 5. Continue to match the other equations, one at a time. Until the cycle is completed.<br>6. Ensure that the arrows are pointing in the right directions in accordance to the equations in step 1 and 2. |  |
| 7. Apply Hess' Law to calculate value for the unknown enthalpy change. | By Hess' law:<br>$-111 + \Delta H^{o}_{c}$ CO(g) = –393<br>∴ $\Delta H^{o}_{c}$ CO(g) = –393 – (–111) = − 282 kJ mol$^{-1}$ |

**Method 1b: By drawing energy level diagram**

| | |
|---|---|
| 1. Write the balanced chemical equation of the unknown Δ*H* equation. | standard enthalpy change of combustion of carbon monoxide<br>(1) $CO(g) + \frac{1}{2} O_2(g) \longrightarrow CO_2(g)$ $\Delta H^{\ominus}_c$ CO(g) |
| 2. Write the balanced chemical equations of the other given Δ*H*. | standard enthalpy change of formation of carbon dioxide<br>(2) $C(s) + O_2(g) \longrightarrow O_2(g)$ $\Delta H^{\ominus}_f$ $CO_2(g) = -393$ kJ mol$^{-1}$<br>standard enthalpy change of formation of carbon monoxide<br>(3) $C(s) + \frac{1}{2} O_2(g) \longrightarrow CO(g)$ $\Delta H^{\ominus}_f$ CO(g) = −111 kJ mol$^{-1}$ |
| 3. Draw the vertical axis and label it enthalpy/ kJ mol$^{-1}$<br>Draw the reactants' and products' energy level for the main equation. In this case, equation (1) / (2) / (3) can be the main equation<br>For exothermic reaction, the reactants should have higher energy level than the products and vice versa for endothermic reaction.<br>**Indicate '0' for the energy level containing elements in their standard states** |  |
| 4. Choose the relevant equations that can relate to the reactants or products of the chosen main equation.<br>Choosing one equation at a time. Ensure the conservation of atoms before and after the arrow. |  |
| 5. Continue to relate the other equations, one at a time. Until the level is completed.<br>Ensure the following upon completion:<br>● arrow pointing upwards = endothermic reaction (Δ*H* > 0)<br>● arrow pointing downwards = exothermic reaction (Δ*H* < 0)<br>● **Length of arrow is proportional to magnitude of given Δ*H*.** |  |
| 6. Apply Hess' Law to calculate value for the unknown enthalpy change. | By Hess' law:<br>$-111 + \Delta H^{\ominus}_c$ CO(g) = –393<br>∴ $\Delta H^{\ominus}_c$ CO(g) = –393 – (–111) = – 282 kJ mol$^{-1}$ |

**Method 2: By using mathematical formulae given enthalpy change of formation data**

When the values of **standard enthalpy change of formation** of the products and reactants are given, the following formula can be used:

$$\boxed{\boldsymbol{H_r^o = \sum n\,\Delta H_f^o \text{ (products)} - \sum m\,\Delta H_f^o \text{ (reactants)}}}$$

where *n* and *m* refer to the stoichiometric coefficients of the products and reactants respectively in the balanced chemical equation.

This formula can be derived and observed from the construction of the energy cycle or the energy level diagram in method **1a** and **1b** respectively.

This mathematical formula can be used if energy cycle is not required as part of working.

standard enthalpy change of combustion of carbon monoxide

$CO(g) + \frac{1}{2} O_2(g) \longrightarrow CO_2(g)$ $\Delta H_c^o$ CO(g) = ?

standard enthalpy change of formation of carbon dioxide

$C(s) + O_2(g) \longrightarrow CO_2(g)$ $\Delta H_f^o$ $CO_2(g)$ = −393 kJ mol$^{-1}$

standard enthalpy change of formation of carbon monoxide

$C(s) + \frac{1}{2} O_2(g) \longrightarrow CO(g)$ $\Delta H_f^o$ CO(g) = −111 kJ mol$^{-1}$

$\boldsymbol{\Delta H_c^o}$ CO(g) **=** $\boldsymbol{\sum n\,\Delta H_f^o}$ **(products) –** $\boldsymbol{\sum m\,\Delta H_f^o}$ **(reactants)**

$\Delta H_c^o$ CO(g) = [1 × $\Delta H_f^o$ $CO_2(g)$] − [1 × $\Delta H_f^o$ CO(g)] = −393 − (−111) = −282 kJ mol$^{-1}$

**Note:** If the question does not specify how the enthalpy is to be calculated, formula like this one or those discussed later can be used without drawing any energy cycle or energy level diagram.

However, if the question specifically requires the use of an energy cycle or energy level diagram, then they must be drawn out.

***Worked Example 8***

Find the standard enthalpy change of reaction of the following reaction using the given data.

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

| | |
|---|---|
| standard enthalpy change of combustion of C(s) | −393 kJ mol$^{-1}$ |
| standard enthalpy change of combustion of $H_2(g)$ | −286 kJ mol$^{-1}$ |
| standard enthalpy change of combustion of $C_2H_5OH(l)$ | −1368 kJ mol$^{-1}$ |

**Try Method 1b by drawing energy level diagram on your own!**

## Method 1a: By drawing energy cycle

**Steps to constructing an energy cycle:**

1. Write the balanced chemical equation of the unknown ΔH equation

   $2C(s) + 3H_2(g) + \tfrac{1}{2}O_2(g)\ C_2H_5OH(l)$ $\qquad \Delta H^{o}_{r} = ?$

2. Write the balanced chemical equations of the other given ΔH.

   $C(s) + O_2(g) \longrightarrow CO_2(g)$ $\qquad \Delta H^{o}_{c}$ C(s) = −393 kJ mol$^{-1}$

   $H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l)$ $\qquad \Delta H^{o}_{c}$ $H_2(g)$ = −286 kJ mol$^{-1}$

   $C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$ $\qquad \Delta H^{o}_{c}$ $C_2H_5OH(l)$ = −1368 kJ mol$^{-1}$

3. Place the main equation in the energy cycle.

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

4. Place the main equation in the energy cycle. (Main equation contains the most number of elements)

   $$C_2H_5OH(l) + 3O_2(g) \xrightarrow{-1368} 2CO_2(g) + 3H_2O(l)$$

5. Match remaining equations to either the reactants or products of the main equation.
6. Choosing one equation at a time. Ensuring the conservation of atoms before and after the arrow by adjusting the stoichiometry required.
7. Continue to match the other equations, one at a time. Until the cycle is completed. Ensure that the arrows are pointing in the right directions in accordance to the equations in step 1 and 2.

$$\begin{tikzcd}
C_2H_5OH(l) + 3O_2(g) \arrow[rr, "-1368"] & & 2CO_2(g) + 3H_2O(l) \\
& & 2CO_2(g) + 3H_2(g) + 1\tfrac{1}{2}O_2(g) \arrow[u, "3\times(-286)"'] \\
2C(s) + 3H_2(g) + 3\tfrac{1}{2}O_2(g) \arrow[uu, "\Delta H^{o}_{r}"] \arrow[urr, "2\times(-393)"'] & &
\end{tikzcd}$$

8. Apply Hess' Law to calculate value for the unknown enthalpy change.

   By Hess' law:

   $H^{o}_{r} + (-1368) = 2(-393) + 3(-286)$

∴ $H^{o}_{r} = 2(-393) + 3(-286) - (-1368) = -276$ kJ mol$^{-1}$

## Method 2: By using mathematical formulae given enthalpy change of formation data

When the values of **standard enthalpy change of combustion** of the products and reactants are given, the following formula can be used:

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

where *n* and *m* refer to the stoichiometric coefficients of the products and reactants respectively in the balanced chemical equation.

This formula can be derived and observed from the construction of the energy cycle or the energy level diagram in method **1a** and **1b** respectively.

This mathematical formula can be used if energy cycle is not required as part of working.

$2C(s) + 3H_2(g) + \frac{1}{2}O_2(g) \longrightarrow C_2H_5OH(l)$ $\Delta H_r^{\ominus} = ?$

$C(s) + O_2(g) \longrightarrow CO_2(g)$ $\Delta H_c^{\ominus}\ C(s) = -393\ \text{kJ mol}^{-1}$

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$ $\Delta H_c^{\ominus}\ H_2(g) = -286\ \text{kJ mol}^{-1}$

$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$ $\Delta H_c^{\ominus}\ C_2H_5OH(l) = -1368\ \text{kJ mol}^{-1}$

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

$H_r^{\ominus} = [2 \times \Delta H_c^{\ominus}\ C(s) + 3 \times \Delta H_c^{\ominus}\ H_2(g)] - [1 \times \Delta H_c^{\ominus}\ (C_2H_5OH(l)]$

$= [2(-393) + 3(-286)] - (-1368)$

$= -276\ \text{kJ mol}^{-1}$

**Note:** There is no need to consider $\Delta H_c^{\ominus}$ $O_2(g)$ in the above calculation since oxygen gas is used in combustion and not combusted.

***Worked Example 9***

Hydrazine is often used as a rocket fuel and reacts with oxygen in an exothermic reaction. Using the bond energy values given below, calculate the enthalpy change of reaction when hydrazine reacts with oxygen.

$$N_2H_4(g) + O_2(g) \longrightarrow N_2(g) + 2H_2O(g) \qquad \Delta H_r = ?$$

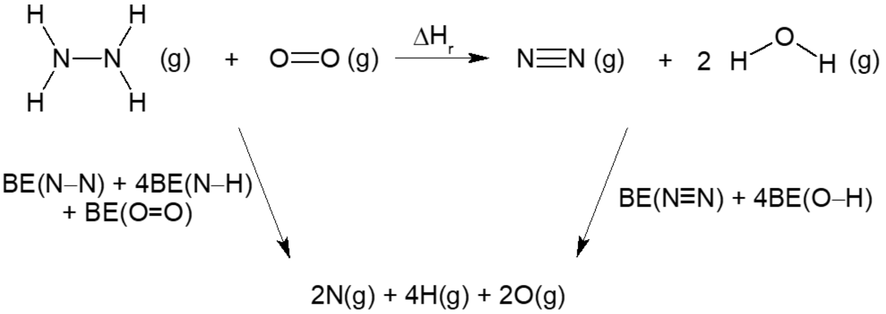
| Bond | Bond energy/ kJ mol$^{-1}$ |
|---|---|
| N−N | +160 |
| N−H | +390 |
| O=O | +496 |

| Bond | Bond energy/ kJ mol$^{-1}$ |
|---|---|
| N≡N | +944 |
| O−H | +460 |

**Note:** If the bond energy is not given in the question, the data can be obtained from the *Data Booklet*.

**Method 1: By drawing energy cycle**

Draw out all the bonds in the reactants and products and break all of them in the energy cycle to get gaseous atoms:



$\Delta H_r$ = *BE*(N−N) + 4 × *BE*(N−H) + *BE*(O=O) – *BE*(N≡N) – 4 × *BE*(O−H)

∴ $\Delta H_r$ = (+160) + 4 × (+390) + (+496) – (+944) – 4 × (+460) = − 568 kJ mol$^{-1}$

**Method 2: By using mathematical formulae given bond energy data**

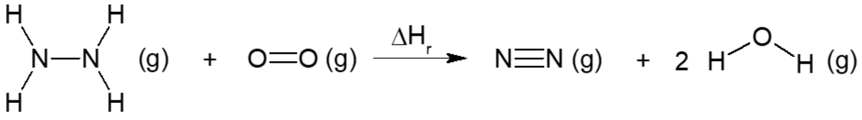
When the values of **bond energies** of all the covalent bonds in the products and reactants are given (either in the question or in the *Data Booklet*), the following formula can be used:

$$\boldsymbol{H_r^{o} = \sum BE \text{ of bonds broken in reactants} - \sum BE \text{ of bonds formed in products}}$$

This formula can be derived and observed from the construction of the energy cycle in method **1**.

This mathematical formula can be used if energy cycle is not required as part of working.

**Note:** For this formula to be used, **all the reactants and products** in the chemical reaction has to be in **gaseous state**. This is because the definition of bond energy is based on covalent bonds broken in gaseous molecules.



$\Delta H_r$ = **∑ BE of bonds broken in reactants – ∑ BE of bonds formed in products**

= *BE*(N−N) + 4 × *BE*(N−H) + *BE*(O=O) – [*BE*(N≡N) + 4 × *BE*(O−H)]

∴ $\Delta H_r$ = (+160) + 4 × (+390) + (+496) – [(+944) – 4 × (+460)] = −568 kJ mol$^{-1}$

***Worked Example 10***

Phosphorus solid can react with chlorine gas to form gaseous phosphorus pentachloride, $PCl_5$. The chemical equation of this reaction is shown below.

$$2P(s) + 5Cl_2(g) \longrightarrow 2PCl_5(g) \qquad \Delta H_r = ?$$

**(a)** By using the data given below and those found in the *Data Booklet*, draw an energy level diagram to determine the enthalpy change of reaction, $\Delta H_r$.

| | |
|---|---|
| Enthalpy change of atomisation of phosphorus solid | +314 kJ $mol^{-1}$ |

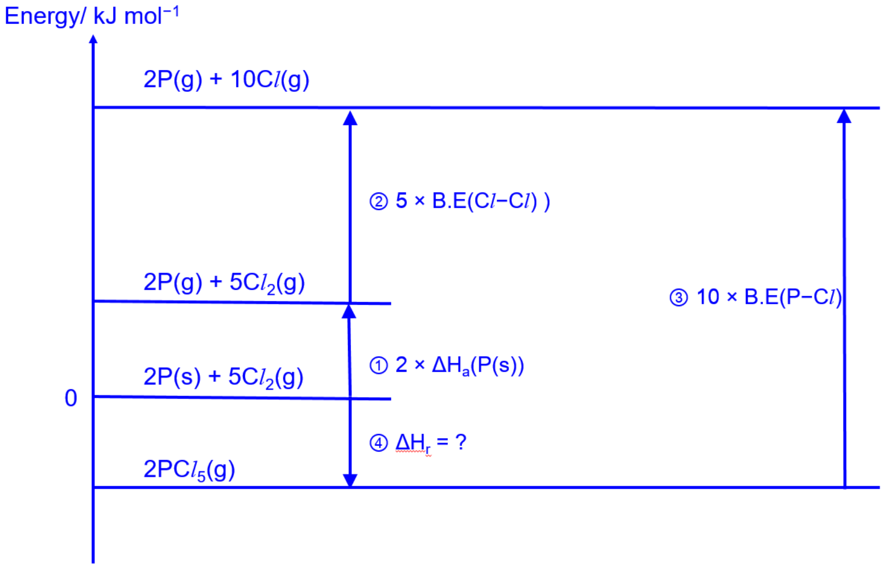
**(b)** Given that the actual enthalpy change of reaction, $\Delta H_r$, is −1350 kJ $mol^{-1}$, suggest a reason for the difference in values of $\Delta H_r$ in **(a)** and **(b)**.

**<u>Method 1b: By drawing energy level diagram</u>**

**(a)**

| | |
|---|---|
| 1. Write the balanced chemical equation of the unknown $\Delta H$ equation. | enthalpy change of reaction<br>$2P(s) + 5Cl_2(g) \longrightarrow 2PCl_5(g) \qquad \Delta H_r = ?$ |
| 2. Write the balanced chemical equations of the other given $\Delta H$. | enthalpy change of atomisation of phosphorus solid<br>$P(s) \longrightarrow P(g) \qquad \Delta H_{at}\,P(s) = +314$ kJ $mol^{-1}$<br><br>From *Data Booklet*,<br>$Cl_2(g) \longrightarrow 2Cl(g) \qquad BE(Cl{-}Cl) = +244$ kJ $mol^{-1}$<br>$PCl_5(g) \longrightarrow P(g) + 5Cl(g) \qquad 5 \times BE(P{-}Cl) = 5(+330)$ kJ $mol^{-1}$ |

3. Draw the energy level diagram using the equations constructed above.



**<u>Note:</u>**
Step ① is required because P cannot be in solid state for bond energy to be used in Step ③ .

| | |
|---|---|
| 4. Apply Hess' Law to calculate value for the unknown enthalpy change. | $\Delta H_r = 2(+314) + 5(+244) - 10(+330) = -1452$ kJ $mol^{-1}$ |

**(b)** The bond energy data from the *Data Booklet* used in **(a)** are <u>average values</u> which differs from the actual bond energy of P−Cl bonds in $PCl_5$.

| **Note: 2 limitations of using bond energy to calculate Δ*H*** |
|---|
| Use of bond energy values to calculate Δ*H* is accurate when simple covalent molecules are in **gaseous state**.<br><br>Bond energy in polyatomic molecule from *Data Booklet* is an **average value**. This may **deviate significantly** from true bond energy value in a given molecule. |

## Checkpoint 5

**1** The standard enthalpy change of reaction of $2NO_2(g) \rightarrow N_2O_4(g)$ is *x* kJ $mol^{-1}$.
The standard enthalpy change of formation of $N_2O_4(g)$ is *y* kJ $mol^{-1}$.

What is the standard enthalpy change of formation of $NO_2(g)$?

**A** $y - x$
**B** $x - y$
**C** $\frac{1}{2}(y - x)$
**D** $\frac{1}{2}(x - y)$

**2** Draw an energy cycle diagram and hence, find the standard enthalpy change of reaction of the following reaction using the given data.

$$C_3H_6(g) + H_2(g) \longrightarrow C_3H_8(g)$$

| | |
|---|---|
| standard enthalpy change of combustion of $H_2(g)$ | −286 kJ $mol^{-1}$ |
| standard enthalpy change of combustion of $C_3H_6(g)$ | −2058 kJ $mol^{-1}$ |
| standard enthalpy change of combustion of $C_3H_8(g)$ | −2220 kJ $mol^{-1}$ |

## 4 Energetics of Ionic Compounds

**Success Criteria**

- Construct a Born−Haber cycle (an energy level diagram including ionisation energy and electron affinity). And use it to calculate the enthalpy change of formation or lattice energy of an ionic solid.

- Explain why the magnitude of theoretical lattice energy may deviate from experimental value due to:
  - bond energy from *Data Booklet* being average values, and
  - bonds involved in the reactions not in gaseous state.

- Explain, in qualitative terms, the factors affecting the magnitude of:
  - lattice energy, according to $|L.E.| \propto \left|\frac{q_+ \times q_-}{r_+ + r_-}\right|$
  - standard enthalpy change of hydration, according to $|\Delta H^o_{hyd}| \propto \left|\frac{charge\ of\ ion}{ionic\ radius}\right|$

- Calculate enthalpy processes involved in the dissolution of ionic solid.
  i.e. $\Delta H^o_{sol} = -\,L.E. + \sum (\Delta H^o_{hyd}\text{ (ions)})$

- Predict the solubility of a compound in water using the sign of $\Delta H^o_{sol}$.

### 4.1 Born−Haber Cycle – an energy level diagram showing formation of an ionic compound

A Born−Haber cycle is an energy level diagram that describes the relationship by Hess' Law between:

| | |
|---|---|
| **Route 1:** | ① **F**ormation of an ionic compound, and |
| **Route 2:** | ② **A**tomisation of elements at standard state + ③ **I**onisation of the resultant gaseous atoms + ④ **L**attice energy of the resultant ions to form the ionic compound. |

The acronym for the steps involved in these two routes is **F−A−I−L**.

In general, for an ionic compound **MX**(s):

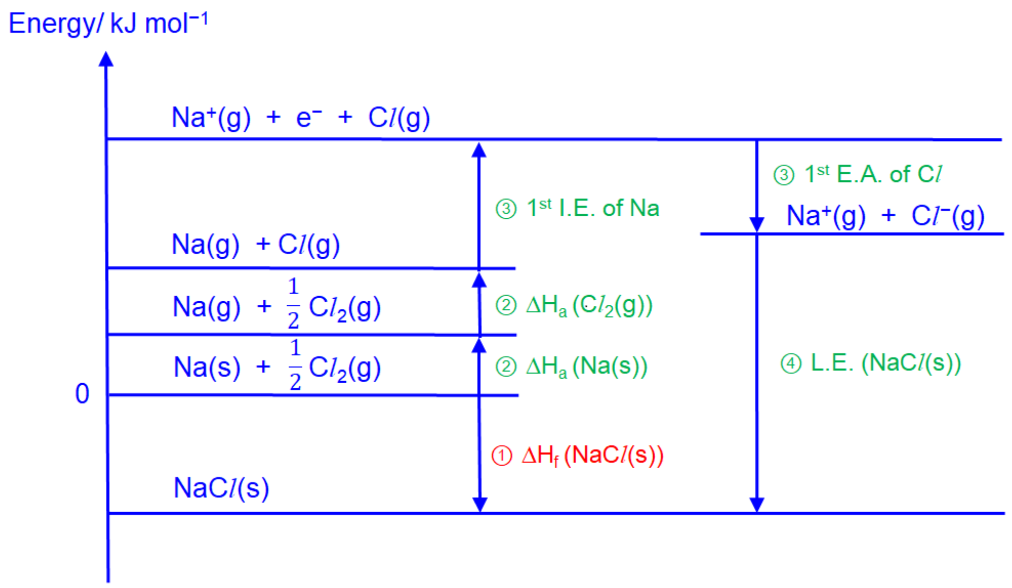
| **Steps in Route 1:** | **Enthalpy change involved** |
|---|---|
| ① **F**ormation | $\Delta H_f$ (ionic compound, **MX**(s)):<br>$M(s) + \frac{1}{2}X_2(g) \longrightarrow MX(s)$ |
| **Steps in Route 2:** | **Enthalpy change involved** |
| ② **A**tomisation | $\Delta H_{at}$ (metal element, **M**(s)):<br>$M(s) \longrightarrow M(g)$<br>$\Delta H_{at}$ (non−metal element, $X_2$(g)):<br>$\frac{1}{2}X_2(g) \longrightarrow X(g)$<br>B.E.(**X−X**) can be used in place of $\Delta H_{at}$ ($X_2$(g)) in this case. Why? |
| ③ **I**onisation (to get both cations and anions) | 1st *I.E.* of metal **M**(g):<br>$M(g) \longrightarrow M^+(g) + e^-$<br>1st *E.A.* of non−metal **X**(g):<br>$X(g) + e^- \longrightarrow X^-(g)$ |
| ④ **L**attice energy | *L.E.* of **MX**(s):<br>$M^+(g) + X^-(g) \longrightarrow MX(s)$ |

### *Worked Example 11*

Use the following data and relevant data from the *Data Booklet*, construct a Born−Haber cycle to determine the lattice energy of NaC*l*(s).

| | |
|---|---|
| enthalpy change of formation of sodium chloride solid | $\Delta H_f = -411$ kJ mol$^{-1}$ |
| enthalpy change of atomisation of sodium | $\Delta H_{at} = +108.4$ kJ mol$^{-1}$ |
| enthalpy change of atomisation of chlorine | $\Delta H_{at} = +121.1$ kJ mol$^{-1}$ |
| ***1st *I.E.* of sodium (from *Data Booklet*)** | 1st *I.E.* = +496 kJ mol$^{-1}$ |
| 1st *E.A.* of chlorine | 1st *E.A.* = −348 kJ mol$^{-1}$ |

Using the F−A−I−L approach,



**Note:** When drawing the steps ③ of the energy level diagram, the *I.E.* of the metal must take place before the *E.A.* of the non−metal. The metal must first lose the electrons before those same electrons can be gained by the non−metal.

By Hess' Law,

$\Delta H_f$ NaC*l*(s) = $\Delta H_{at}$ Na(s) + $\Delta H_{at}$ $Cl_2$(g) + 1st *I.E.* Na + 1st *E.A* C*l* + *L.E.* NaC*l*(s)

−411 = (+108.4) + (+121.1) + (+496) + (−348) + *L.E.* NaC*l*(s)

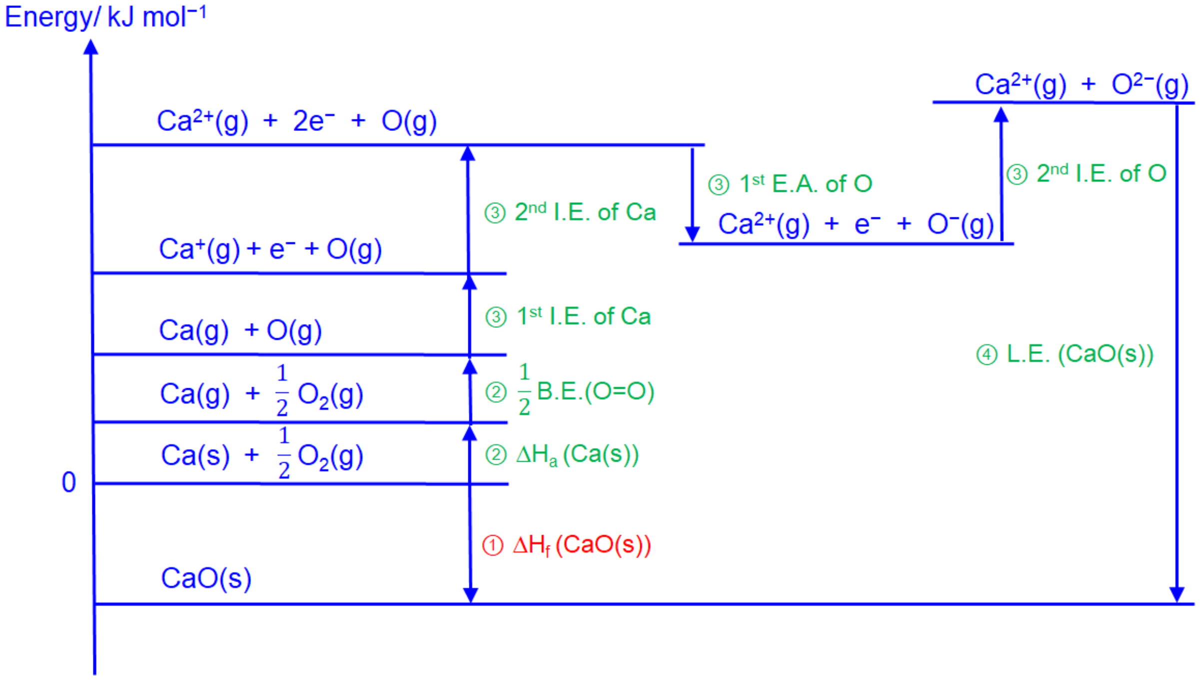
*L.E.* NaC*l*(s) = −789 kJ mol$^{-1}$

**_Worked Example 12_**

Use the following data and relevant data from the *Data Booklet*, construct a Born−Haber cycle to determine the standard enthalpy of formation of calcium oxide, CaO(s).

| | |
|---|---|
| enthalpy change of atomisation of calcium | $\Delta H_{at}$ = +178 kJ mol$^{-1}$ |
| ***BE*(O=O) (from *Data Booklet*)**<br>(recall: B.E. can be used in place of $\Delta H_{at}$ of diatomic non−metal, $\frac{1}{2}BE = \Delta H_{at}$) | *BE*(O=O) = +496 kJ mol$^{-1}$ |
| ***1st *I.E.* of calcium (from *Data Booklet*)** | 1st *I.E.* = +590 kJ mol$^{-1}$ |
| ***2nd *I.E.* of calcium (from *Data Booklet*)** | 2nd *I.E.* = +1150 kJ mol$^{-1}$ |
| 1st *E.A.* of oxygen | 1st *E.A.* = −141 kJ mol$^{-1}$ |
| 2nd *E.A.* of oxygen | 2nd *E.A.* = +790 kJ mol$^{-1}$ |
| Lattice energy of CaO(s) | *L.E.* = −3450 kJ mol$^{-1}$ |

Using the F−A−I−L approach,



**Note:** When drawing the steps ③ of the energy level diagram, recall that the correct number of electrons must be used to balance the equation to balance the charges.

By Hess' Law,

$\Delta H_f$ CaO(s) = $\Delta H_{at}$ Ca(s) + $\frac{1}{2}$ × *BE*(O=O) + 1st *I.E.* Ca + 2nd *I.E.* Ca + 1st *E.A.* O + 2nd *E.A.* O + *L.E.* CaO(s)

$\Delta H_f$ CaO(s) = (+178) + $\frac{1}{2}$ × (+496) + (+590) + (+1150) + (−141) + (+790) + (−3450)

= −635 kJ mol$^{-1}$

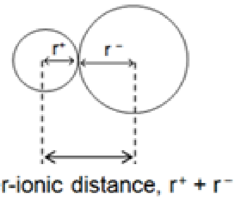
## 4.2 Magnitude of Lattice Energy

### 4.2.1 Factors affecting the magnitude of lattice energy

The magnitude of lattice energy is affected by:
(i) product of charge on the ions ($q_+ \times q_-$)
(ii) Interionic distance ($r_+ + r_-$) between the ions:

$$|L.E.| \propto \left|\frac{q_+ \times q_-}{r_+ + r_-}\right|$$

where, $q_+$ = charge of cation
$q_-$ = charge of anion
$r_+$ = radius of cation
$r_-$ = radius of anion



### 4.2.2 Comparison of theoretical and experimental values of lattice energy (***L.E.***)

- Theoretical values of lattice energy are calculated using the above formula.
- Experimental values of lattice energy are obtained using the Born−Haber cycle as **Δ***H* of the other stages in formation of the ionic solid can be experimentally determined.
- Generally, theoretical *L.E.* deviates experimental *L.E.*
- Reason:
  Theoretical *L.E.* is calculated using a model where ions are assumed to be spherical. (i.e. electron cloud of ions are evenly distributed.)
  However, this model is not entirely true for a real ionic lattice.
- Percentage difference between the theoretical *L.E.* and experimental *L.E.* therefore serve as reflection of the extent a polarised ionic bond deviates from the model of spherical ions.

| | Theoretical Lattice Energy / kJ mol$^{-1}$ | Experimental Lattice Energy / kJ mol$^{-1}$ |
|---|---|---|
| NaC*l* | −766 | −776 |
| NaBr | −731 | −742 |
| NaI | −686 | −699 |
| AgC*l* | −768 | −890 |
| AgBr | −759 | −877 |
| AgI | −736 | −867 |

- From NaC*l* to NaI, their theoretical and experimental lattice energy values of are within a difference of 1–2%.
- From AgC*l* to AgI, the magnitude of their experimental lattice energy values is 15% greater than that of their theoretical lattice energy values.
- This shows that ions in AgC*l* to AgI compounds deviates more significantly from the model of spherical ions compared to ions in group 1 metal halides.

Reason:
The silver ion is an ion of a d block element. Such ions have a **greater polarising power** compared to the main group metal cations of the same charge because their nuclei are poorly shielded by the d electrons (To be learnt in Transition Elements).

Therefore for the same halide anion, $Ag^+$ **distorts the electron cloud of the anion to a greater extent** compared to $Na^+$. Hence, the ions in silver halide deviate from the model of spherical ions by a larger extent.

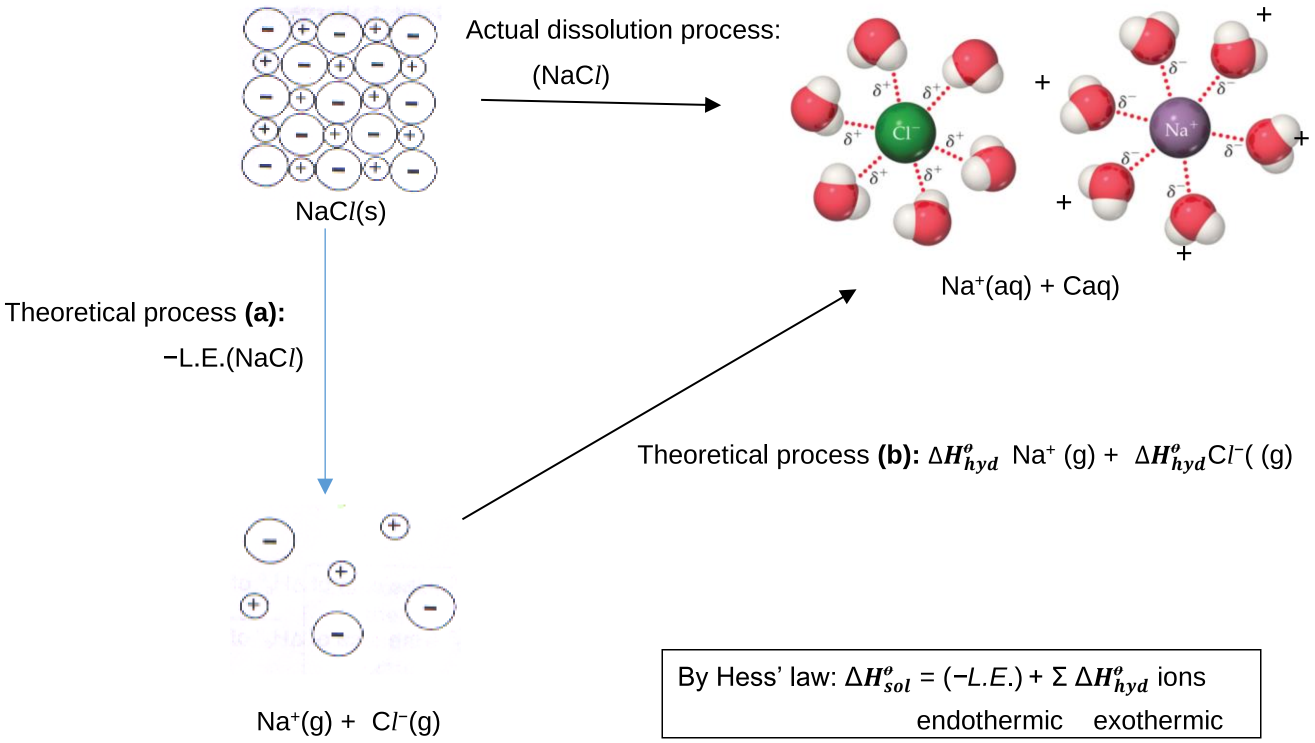
### 4.3 Enthalpy changes involved in dissolution of an ionic compound

The dissolution of an ionic compound (e.g. sodium chloride) is represented by the following equation:

$$\text{NaC}l\text{(s)} + \text{aq} \longrightarrow \text{Na}^{+}\text{(aq)} + \text{C}l^{-}\text{(aq)} \qquad \Delta \boldsymbol{H}^{\boldsymbol{o}}_{\boldsymbol{sol}} = +5.0 \text{ kJ mol}^{-1}$$

The following energy cycle shows an alternative route of dissolving ionic solid in water; a sequence of two theoretical processes where :

| Theoretical process | Description | Bonds |
|---|---|---|
| **(a)** | Solid giant ionic lattice is broken down into gaseous ions. | Ionic bonds in giant ionic lattice structure broken. |
| **(b)** | Gaseous ions hydrated in water to form aqueous ions. | Ion−dipole interactions formed between ions and water molecules |



By Hess' law: $\Delta \boldsymbol{H}^{\boldsymbol{o}}_{\boldsymbol{sol}} = (-L.E.) + \Sigma\, \Delta \boldsymbol{H}^{\boldsymbol{o}}_{\boldsymbol{hyd}}$ ions
endothermic exothermic

Therefore, the sign of $\Delta \boldsymbol{H}^{\boldsymbol{o}}_{\boldsymbol{sol}}$ depends on the relative magnitudes of lattice energy and hydration energy.

When $\Delta \boldsymbol{H}^{\boldsymbol{o}}_{\boldsymbol{sol}}$ of an ionic compound is **negative**, the compound is soluble in water. When $\Delta \boldsymbol{H}^{\boldsymbol{o}}_{\boldsymbol{sol}}$ of an ionic compound is **positive**, the compound can be soluble or insoluble in water. The ionic compound will be soluble if the $\Delta G < 0$ ($\Delta G = \Delta H - T\Delta S$). ($\Delta S$ and $\Delta G$ will be covered in *Thermodynamics*)

***Note:***
Generally when the $\Delta \boldsymbol{H}^{\boldsymbol{o}}_{\boldsymbol{sol}}$ is **more exothermic**, the **more soluble** is the compound.

***Worked Example 13:***

Using the following data, construct an energy cycle to calculate the standard enthalpy change of solution of calcium fluoride.

| | |
|---|---|
| Lattice energy of $CaF_2(s)$ / kJ $mol^{-1}$ | –2640 |
| Standard enthalpy change of hydration of calcium ion/ kJ $mol^{-1}$ | –1560 |
| Standard enthalpy change of hydration of fluoride ion/ kJ $mol^{-1}$ | –457 |

**Solution:**

$$\begin{tikzcd}
aq + CaF_2(s) \arrow[rr, "\Delta H^{\circ}_{sol}\ (CaF_2)"] \arrow[dr, swap, "\begin{array}{c} -L.E.CaF_2(s) \\ = -(-2640) \end{array}"] & & Ca^{2+}(aq) + 2F^-(aq) \\
& Ca^{2+}(g) + 2F^-(g) + aq \arrow[ur, swap, "\begin{array}{c} (Ca^{2+}) + 2 \times (F^-) \\ = -1560 + 2 \times (-457) \end{array}"] &
\end{tikzcd}$$

Using Hess' Law

$$\begin{aligned}
\Delta H^{\circ}_{sol}\ (CaF_2) &= -L.E.\ CaF_2(s) + \Delta H^{\circ}_{hyd}\ (Ca^{2+}) + 2 \times \Delta H^{\circ}_{hyd}\ (F^-) \\
&= -(-2640) + (-1560) + 2 \times (-457) \\
&= +166 \text{ kJ mol}^{-1}
\end{aligned}$$

**Checkpoint 6**

The lattice energy of lithium chloride is −848 kJ $mol^{-1}$ and that of sodium chloride is −776 kJ $mol^{-1}$.

**(a)** Define, using sodium chloride as an example, what is meant by the term *lattice energy*.

**(b)** Explain why the lattice energy of lithium chloride is more exothermic than that of sodium chloride.

**(c)** Some standard enthalpy changes of hydration are listed below.

| ions | $\Delta H^{o}_{hyd}$/ kJ mol$^{-1}$ |
|---|---|
| $Li^+$ | –499 |
| $Na^+$ | –390 |
| $Cl^-$ | –381 |

Draw two energy level diagrams using data in this question to determine the standard enthalpy change of solution, $\Delta H^{o}_{sol}$, for these two salts.

## Summary of formulae used for calculating $\Delta H_r^o$

Formula derived by applying Hess' law. Used when **question does not require energy cycle or energy level diagram** as part of the working.

| | |
|---|---|
| **1.** | **$\Delta H_r^o = \sum n \, \Delta H_f^o$ (products) – $\sum m \, \Delta H_f^o$ (reactants)**<br>Note: $\Delta H_f^o$ (element) = 0<br>Formula is used when $\Delta H_f^o$ values of all the reactants and the products are given.<br>Applicable to all kinds of reaction system. |
| **2.** | **$\Delta H_r^o = \sum n \, \Delta H_c^o$ (reactants) – $\sum m \, \Delta H_c^o$ (products)**<br>Formula is used when **$\Delta H_c^o$** values of all the reactants and the products are given.<br>Applicable to all kinds of reaction system. |
| **3.** | **$\Delta H_r^o = \sum$ *BE* of bonds broken (reactants) – $\sum$ *BE* of bonds formed (products)**<br>Only applicable to reactions involving gaseous covalent compounds.<br>Limitations:<br>(i) Bond energy values in the *Data Booklet* are average values.<br>(ii) Reactants and products should be in gaseous state. |
| **4.** | **$\Delta H_{sol}^o = -L.E. + \sum \Delta H_{hyd}^o$ (ions)**<br>Applicable to ionic solid only. |

When heat exchange with surrounding air and reaction vessel is assumed to be negligible,

| heat change, q = mc$\Delta$T or heat change, q = C$\Delta$T |
|---|
| $\Delta H = -\frac{heat\ change}{n}$ |

where,

| | | |
|---|---|---|
| m | = | mass of solution in g (ignore mass of any solid added) |
| $\Delta$T | = | temperature change (highest/lowest temp recorded – initial temp) |
| n | = | amt of specific substance (as per definition in Section 2)<br>(e.g. For $\Delta H_c$, n is the amount of substance burnt.)<br>(e.g. For $\Delta H_n$, n is the amount of water formed.)<br>(e.g. For $\Delta H_{sol}$, n is the amount of ionic compound dissolved.) |
| c | = | specific heat capacity of solution, defined as the amount of heat required to raise the temperature of 1g of solution by 1K. Unit is J $g^{-1}$ $K^{-1}$ or J $g^{-1}$ °$C^{-1}$. |
| C | = | heat capacity of the calorimeter, defined as the amount of heat required to raise the temperature of both the water and the reaction vessel by 1K. Unit is J $K^{-1}$ or J °$C^{-1}$.<br>$C_{calorimeter} = mc_{solution} + C_{container}$ |

The enthalpy change of reaction, which is dependent on the stoichiometry of the balanced equation, is determined using the following equations:

| heat change, q = mc$\Delta$T **or** heat change, q = C$\Delta$T |
|---|
| $\Delta H_r = -\frac{\mathrm{mc}\Delta \mathrm{T}}{\mathrm{n}_{\text{limiting reagent}}} \times \text{coefficient of limiting reagent}$ |

## Definitions in Chemical Energetics (Refer to Sections 2)

| | General definition | Thermochemical equation |
|---|---|---|
| 1 | **Standard enthalpy change of reaction, $\Delta H_r^o$**<br>The standard enthalpy change of reaction is the energy change when molar quantities of reactants as stated in the balanced stoichiometric equation react together at 298 K and 1 bar. | $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$ $\Delta H_r^o = -92$ kJ mol$^{-1}$ |
| 2 | **Standard enthalpy change of formation, $\Delta H_f^o$**<br>The standard enthalpy change of formation is the energy change when one mole of a substance is formed from its constituent elements in their standard states at 298 K and 1 bar. | $Mg(s) + \frac{1}{2}O_2(g) \longrightarrow \underline{MgO}(s)$ $\Delta H_f^o = -602$ kJ mol$^{-1}$ |
| 3 | **Standard enthalpy change of combustion, $\Delta H_c^o$**<br>The standard enthalpy change of combustion is the energy released when one mole of a substance is completely burnt in excess oxygen at 298 K and 1 bar. | $\underline{C(s)} + O_2(g) \longrightarrow CO_2(g)$ $\Delta H_c^o = -393$ kJ mol$^{-1}$ |
| 4 | **Standard enthalpy change of neutralisation, $\Delta H_n^o$**<br>The standard enthalpy change of neutralisation is the energy released when one mole of water is formed from the reaction between an acid and an alkali at 298 K and 1 bar. | $NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + \underline{H_2O(l)}$<br>$\Delta H_n^o = -57.3$ kJ mol$^{-1}$ |
| 5 | **Standard Enthalpy Change of atomisation, $\Delta H_{at}^o$**<br>The standard enthalpy change of atomisation is the energy absorbed when one mole of gaseous atoms is formed from its element in its standard state at 298 K and 1 bar. | $\frac{1}{2}F_2(g) \longrightarrow \underline{F(g)}$ $\Delta H_{at}^o = +79$ kJ mol$^{-1}$ |
| 6 | **Bond energy**<br>Bond energy is the energy absorbed to break one mole of covalent bonds between two atoms in gaseous molecules to form state to form gaseous atoms. | $\underline{N\equiv N(g)} \longrightarrow 2N(g)$ $BE(N\equiv N) = +944$ kJ mol$^{-1}$ |

| | Energetics associated with formation of ionic compounds (F−A−I−L) | Thermochemical equation |
|---|---|---|
| 7 | **First ionisation energy**<br>First ionisation energy (1st *I.E.*) of an element is the energy absorbed to remove one mole of valence electrons from one mole of gaseous atoms to form one mole of gaseous single positively charged cations. | $\text{Na(g)} \longrightarrow \text{Na}^{+}\text{(g)} + e^{-}$ 1st *I.E.* = +494 kJ mol$^{-1}$ |
| 8 | **First electron affinity**<br>First electron affinity (1st *E.A.*) of an element is the energy released when one mole of gaseous atoms gain one mole of electrons to form one mole of gaseous single negatively charged anions. | $\text{O(g)} + e^{-} \longrightarrow \text{O}^{-}\text{(g)}$ 1st *E.A.* = −142 kJ mol$^{-1}$ |
| 9 | **Second electron affinity**<br>Second electron affinity (2nd *E.A.*) of an element is the energy change when one mole of gaseous single negatively charged anions gain one mole of electrons to form one mole of gaseous double negatively charged anions. | $\text{O}^{-}\text{(g)} + e^{-} \longrightarrow \text{O}^{2-}\text{(g)}$ 2nd *E.A.*= +798 kJ mol$^{-1}$ |
| 10 | **Lattice Energy, *L.E.*, of an ionic compound**<br>Lattice energy (*L.E.*) of an ionic compound is the energy released when one mole of ionic solid is formed from its constituent gaseous ions. | $\text{Na}^{+}\text{(g)} + \text{C}l^{-}\text{(g)} \longrightarrow \text{NaC}l\text{(s)}$ *L.E.* = −776 kJ mol$^{-1}$ |
| | **Energetics associated with dissolution of ionic compounds** | **Thermochemical equation** |
| 11 | **Standard Enthalpy Change of hydration, $\Delta H^{o}_{hyd}$**<br>The standard enthalpy change of hydration is the energy released when one mole of gaseous ions is hydrated at 298 K and 1 bar. | $\text{Na}^{+}\text{(g)} + \text{aq} \longrightarrow \text{Na}^{+}\text{(aq)}$ $\Delta H^{o}_{hyd}$ = −390 kJ mol$^{-1}$<br>$\text{C}l^{-}\text{(g)} + \text{aq} \longrightarrow \text{C}l^{-}\text{(aq)}$ $\Delta H^{o}_{hyd}$ = −381 kJ mol$^{-1}$ |
| 12 | **Standard enthalpy change of solution, $\Delta H^{o}_{sol}$**<br>The standard enthalpy change of solution is the energy change when one mole of substance is completely dissolved in a solvent to form an infinitely dilute solution at 298 K and 1 bar. | $\text{NaC}l\text{(s)} + \text{aq} \longrightarrow \text{Na}^{+}\text{(aq)} + \text{C}l^{-}\text{(aq)}$<br>$\Delta H^{o}_{sol}$ = +5.0 kJ mol$^{-1}$ |

| | Success Criteria | Relevant Tutorial Questions | What do you still struggle with? Write your queries here. |
|---|---|---|---|
| **(a)** | Define the following standard enthalpy change: | **1, 7a** | |
| | 1) standard enthalpy change of reaction, $\Delta\boldsymbol{H_r^o}$ | | |
| | 2) standard enthalpy change of formation, $\Delta\boldsymbol{H_f^o}$ | | |
| | 3) standard enthalpy change of combustion, $\Delta\boldsymbol{H_c^o}$ | | |
| | 4) standard enthalpy change of neutralisation, $\Delta\boldsymbol{H_n^o}$ | | |
| | 5) standard enthalpy change of atomisation, $\Delta\boldsymbol{H_{at}^o}$ | | |
| | 6) bond energy, *BE* | | |
| | 7) first ionisation energy, 1st *I.E.* | | |
| | 8) first electron affinity, 1st *E.A.* | | |
| | 9) second electron affinity, 2nd *E.A.* | | |
| | 10) lattice energy, *L.E.* | | |
| | 11) standard enthalpy change of hydration, $\Delta\boldsymbol{H_{hyd}^o}$ | | |
| | 12) standard enthalpy change of solution, $\Delta\boldsymbol{H_{sol}^o}$ | | |
| | | | |
| **(b)** | Calculate enthalpy change using direct calorimetry method using the equations:<br>heat change = $mc\Delta T$ and $\Delta H = -\frac{mc\Delta T}{n}$ or<br>heat change = $C\Delta T$ and $\Delta H = -\frac{C\Delta T}{n}$ | | |
| | 1) for reaction involving solid added to solutions | 9a | |
| | 2) for reaction involving two solutions | 2a | |
| | 3) for combustion reactions | 3,6a | |
| | 4) for experiments involving cooling curve | 2b | |
| | 5) for experiments with given percentage efficiency | 7a | |
| | | | |
| **(c)** | Calculate enthalpy change using indirect method by constructing: | | |
| | 1) energy cycle | 4,5,6d,8, 10b, 13a | |
| | 2) energy level diagram (including F−A−I−L) | 10a, 11a, 12 | |
| | | | |
| **(d)** | Calculate enthalpy change using indirect method by formula: | | |
| | 1) $\Delta\boldsymbol{H_r^o} = \sum n\ \Delta\boldsymbol{H_f^o}$ (products) – $\sum m\ \Delta\boldsymbol{H_f^o}$ (reactants) | 4 | |
| | 2) $\Delta\boldsymbol{H_r^o} = \sum n\ \Delta\boldsymbol{H_c^o}$ (reactants) – $\sum m\ \Delta\boldsymbol{H_c^o}$ (products) | 5 | |
| | 3) $\Delta\boldsymbol{H_r^o} = \sum$ *BE* of bonds broken (reactants) – $\sum$ *BE* of bonds formed (products) | 6b, 7b | |
| | 4) $\Delta\boldsymbol{H_{sol}^o} = -L.E. + \sum \Delta\boldsymbol{H_{hyd}^o}$ (ions) | 13c | |
| | | | |

| | Success Criteria | Relevant Tutorial Questions | What do you still struggle with? Write your queries here. |
|---|---|---|---|
| **(e)** | Explain, in qualitative terms, the factors affecting the magnitude of: | | |
| | 1) Standard enthalpy change of neutralisation according to the strength of the acid and alkali used. | | |
| | 2) lattice energy, according to $\|L.E.\| \propto \|\frac{q_{+} \times q_{-}}{r_{+} + r_{-}}\|$ | 11b | |
| | 3) standard enthalpy change of hydration, according to $\|\Delta H^{o}_{hyd}\| \propto \|\frac{charge\ of\ ion}{ionic\ radius}\|$ | 13b | |
| | | | |
| **(f)** | Explain why the magnitude of enthalpy change calculated using direct calorimetry method may deviate from that using indirect method due to: | 3b | |
| | 1) heat loss to surroundings or container | | |
| | 2) mass of substance burnt is lesser than expected (for $\Delta H^{o}_{c}$) | | |
| | | | |
| **(g)** | Explain why the magnitude of enthalpy change calculated using bond energies data may deviate from the actual value due to: | 6c, 7c | |
| | 1) bond energy from *Data Booklet* being average values, and | | |
| | 2) bonds involved in the reactions not in gaseous state. | | |
| | | | |
| **(h)** | Explain why the magnitude of theoretical lattice energy may deviate from experimental value due to: | 11c | |
| | 1) high polarising power of cation | | |
| | 2) high polarizability of anion | | |
| | | | |
| **(i)** | Predict the solubility of a compound in water using the sign of $\Delta H^{o}_{sol}$. | | |
| | | | |