Chemical Energetics

Content

- Enthalpy changes (ΔH): ΔH of formation; combustion; neutralisation; bond energy; lattice energy
- Hess' Law

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

(c) explain and use the terms:

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

(ii) bond energy (ΔH positive, i.e. bond breaking)

(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 carry out calculations involving given simple energy cycles and relevant energy terms (restricted to enthalpy changes of formation, combustion and neutralisation), 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) average bond energies [construction of energy cycles is not required]

1 Introduction

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

1.1 Enthalpy Change, ΔH

Learning Objective:

Able to 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 (ΔH, negative)
- When there is a net absorption in energy, the reaction is endothermic (ΔH, positive).
- The sign in ΔH enable you to deduce whether the reactant or product is more stable (lower in enthalpy (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)

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

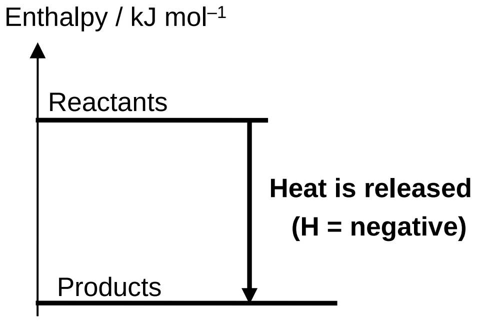
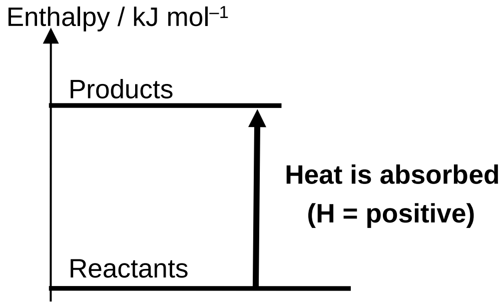
- ΔH is either determined experimentally by measuring the temperature change or via application of Hess' law.

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

Heat change, $q = \Delta H_r \times$ 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.
ΔH	$\Delta H < 0$ (−ve) H_{system} decrease	$\Delta H > 0$ (+ve) H_{system} increase
Relative energy levels of reactants and products **(Energy Level Diagram)**	- $E_{product} < E_{reactant}$ - Products energetically more stable than reactants.  	- $E_{product} > E_{reactant}$ - Products energetically less stable than reactants. 
Examples	$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$ $\Delta H = -57.3$ kJ mol^{-1} (neutralisation reaction)	$NH_4NO_3(s) + aq \rightarrow NH_4NO_3(aq)$ $\Delta H = +26.0$ kJ mol^{-1} (dissolving of aqueous ammonium nitrate)
More examples	Combustion, freezing, condensation, thermite reaction	Photosynthesis, melting, vapourisation

Note:

- 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:
ΔH 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:

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

Worked Example 1

Given the following reaction:

$Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 3CO_2(g)$ $\Delta H_r = -27$ 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 ΔH

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

- 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.

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

- 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 ΔH

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

- 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 ΔH:

(a) Amount of substance

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

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

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

(b) Physical states of reactants and products

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

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

(c) ΔH of forward and backward reactions

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

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

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

Checkpoint 1

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

Calculate ΔH for the reaction $HI\ (g) \longrightarrow \frac{1}{2}\,H_2(g) + \frac{1}{2}\,I_2(s)$ **[−26.48 kJ mol⁻¹]**

2 Definitions of Important Standard Enthalpy Changes

- Able to explain and use the terms, enthalpy change of reaction and standard conditions (298 K and 1 bar), with particular reference to: formation; combustion; neutralisation.
- Able to explain that bond energy is endothermic (Δ*H* positive) as it is defined as the amount of energy required to break one mole of covalent bond. (refer to chemical bonding notes)
- Able to explain that lattice energy of an ionic lattice is exothermic (ΔH negative) as it is a bond forming process where the gaseous ions of opposite charges attract each other electrostatically to form the solid lattice.
- Able to explain, in qualitative terms, the effect of ionic charge and ionic radius on the numerical magnitude of a lattice energy. i.e.
  $$|L.E| \propto \left|\frac{q_+ \times q_-}{r_+ + r_-}\right|.$$

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, ΔH_r^θ

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

E.g. $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$ $\Delta H_r^\theta = -92 \text{ kJ mol}^{-1}$

92 kJ of heat 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, ΔH_f^θ

The standard enthalpy change of formation is the heat 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. $Mg(s) + \frac{1}{2}O_2(g) \longrightarrow MgO(s)$ $\Delta H_f^\theta = -602 \text{ kJ mol}^{-1}$

602 kJ of heat 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) → Cu(s)

Explain why the value of ΔH_f° solid copper is 0 kJ mol^{-1}

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

More about ΔH_f°:

- ΔH_f° 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) $\longrightarrow$ C (graphite) ΔH_f° (graphite) = 0 kJ mol^{-1}

C (graphite) $\longrightarrow$ C (diamond) ΔH_f° (diamond) = +2 kJ mol^{-1}

2.3 Standard enthalpy change of combustion, ΔH_c°

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

E.g. $C(s) + O_2(g) \longrightarrow CO_2(g)$ ΔH_c° = –393 kJ mol^{-1}

393 kJ of heat 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. ΔH_c° is always negative.

Worked Example 3

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

Note:
ΔH_c° is per mole of fuel burnt in excess O_2 while ΔH_f° is per mole of product from elements in standard states.

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

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$ ΔH_c° (CH_4(g)) < 0

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

$C(s) + 2H_2(g) \longrightarrow CH_4(g)$ ΔH_f° (CH_4(g)) < 0

2.4 Standard enthalpy change of neutralisation, ΔH_n^o

The standard enthalpy change of neutralisation is the heat 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. $NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l)$ $\Delta H_n^o = -57.3 \text{ kJ mol}^{-1}$

57.3 kJ of heat 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:

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

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

  For example, for a weak acid HA,
  $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$ ΔH_1

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

Part of the heat released from $H^+(aq)$ reacting with $OH^-(aq)$, ΔH_2, is used to provide the energy to complete the dissociation of the weak acid or base, ΔH_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:
$NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l)$ $\Delta H_n^o = -57.3 \text{ kJ mol}^{-1}$

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

2.5 Bond Energy (*BE*)

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

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

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*.

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

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

Important Concept!
For diatomic gases, X_2: **$BE(X{-}X) = 2 \times \Delta H^{o}_{at}\ X_2(g)$**

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

$\frac{1}{2}F_2(g) \longrightarrow F(g)$ ΔH^{o}_{at} = +79 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}

2.6 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.* (NaCl) = −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

Checkpoint 2

Write thermochemical equations that represents the following standard enthalpy changes.

State whether ΔH 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

Learning Objective:

- Able to carry out an experiment to calculate enthalpy changes (J mol^{-1} or kJ mol^{-1}) and heat change (J or kJ) by measuring the change in temperature (ΔT) of the surroundings, using relationships such as:

$$\text{heat change (J or kJ)} = mc\Delta T \text{ , where } \Delta T = T_f - T_i$$

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

3.1 Direct method using Calorimetry

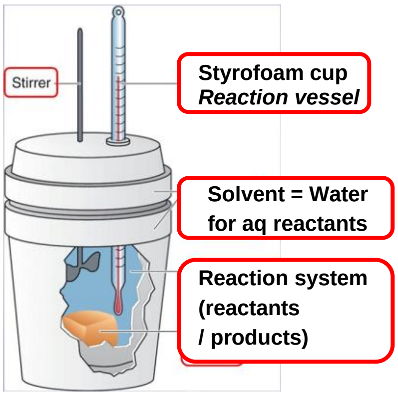
In order to determine the change in energy content of the reaction system experimentally, the principle of law of conservation of energy is used to derive a **relationship** between the heat energy change of the system and the surrounding.

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**

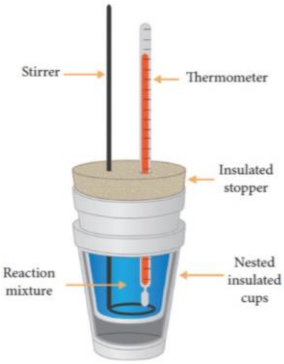
By rearranging the equation:

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

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

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

- units: J or kJ



Calorimetry is thus the measurement of ΔT 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.

General steps to determine enthalpy change of a reaction by calorimetry:

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, ΔT, of the reaction mixture is measured.
3. When the reaction is exothermic:

$\Delta H = -\text{ve}$ → heat is released by the reaction → temp ↑ ($\Delta T = +\text{ve}$) → heat change, $q = mc\Delta T$, is +ve

When the reaction is endothermic:

$\Delta H = +\text{ve}$ → heat is absorbed by the reaction → temp ↓ ($\Delta T = -\text{ve}$) → heat change, $q = mc\Delta T$, is −ve

Note:
1 °C change = 1 K change

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

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

where,

m	−	mass of solution in g (ignore mass of any solid added)
ΔT	−	temperature change (highest/lowest temp recorded – initial temp)
n	−	amount of specific substance (as per definition in Section 2) (e.g. For ΔH_c, n is the amount of substance burnt.) (e.g. For ΔH_n, n is the amount of water formed.
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:

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

- 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}.

3.1.1 Calculations of enthalpy changes using calorimetry

***Worked Example 4a: Determine enthalpy change of reaction,* ΔH_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 ΔH definition)

Step 2:
Determining limiting reagent, and hence the required n for the respective ΔH

Step 3:
Determine the unknown ΔH 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 8.563×10^{-3} mol Zn ≡ 1.713×10^{-2} mol HC*l*,

Hence, HC*l* is the limiting reagent.

Step 3:

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

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

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

Worked Example 4b: (Determine enthalpy change of neutralisation, ΔH_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 ΔH definition)

Step 2:
Determining limiting reagent, and hence the required n for the respective ΔH

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

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

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

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

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

$$= -56.4 \text{ kJ mol}^{-1} \text{ (exothermic)}$$

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 3

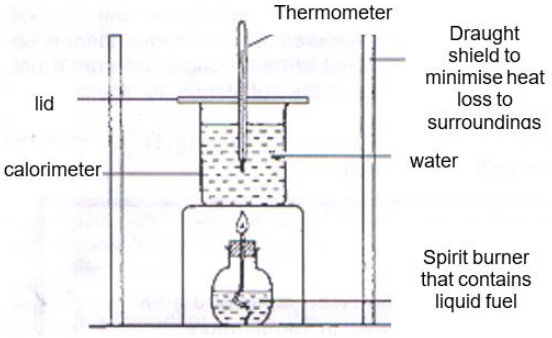
Zinc metal reacts with silver nitrate to give zinc nitrate and silver metal. 1.40 g of zinc powder was added to 50.0 cm^3 of 0.100 mol dm^{-3} $AgNO_3$ in a polystyrene cup. Initially the temperature was 21.1 °C and subsequently rose to 25.4 °C. Determine the enthalpy change of reaction for one mole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



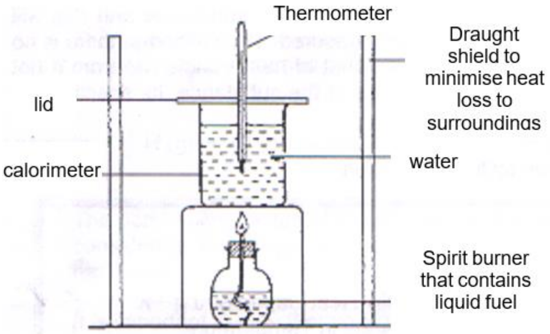
- A spirit burner containing liquid fuel is used. Weighing the spirit burner before and after burning gives the mass of fuel used for combustion.
- A known volume of water is placed in a copper calorimeter and its temperature taken.
- The wick is lighted and the water in the calorimeter is stirred with 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 ΔH_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. When inadequate oxygen is supplied, some methanol undergoes incomplete combustion to form carbon monoxide or carbon (soot). Thus, for the same mass of fuel burnt, less energy is released.	ΔT measured will be smaller than expected and thus the magnitude of ΔH_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. Significant amount of heat is lost to the surrounding air from the spirit lamp flame. 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. Evaporation of volatile methanol from the hot spirit burner cause additional loss in mass. Burning of wick can also cause additional mass loss after combustion.	Mass of methanol burnt recorded is larger than the actual mass burnt. Heat change is divided by a larger than expected amount of methanol, resulting in a smaller magnitude of ΔH_c calculated.

Worked Example 5

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*. Mass of the water heated up should be used. This is because heat released from the combustion is gained by the water. The temperature change recorded is that of the water, not the methanol.

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.

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

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

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

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

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

Worked Example 6

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.

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

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

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

$$\Delta H_c = -\frac{mc\Delta T}{n_{butane}} = -\frac{(500)(4.18)(44)}{5.862 \times 10^{-2}} = -1570 \text{ kJ mol}^{-1}$$

(iii) The true value of ΔH_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.

ΔT measured is lower than actual. ∴ΔH calculated is of smaller magnitude. (less exothermic)

Checkpoint 4

When 1.20 g of propan-1,2,3-triol (M_r = 92.0) was burnt, it was found that 100 g of water was heated from 25 °C to 67 °C. The process was known to be only 80% efficient.

Use these data and relevant information from the *Data Booklet* to calculate the enthalpy change of combustion of propan-1,2,3-triol.

A –1080 kJ mol^{-1}

B –1350 kJ mol^{-1}

C –1680 kJ mol^{-1}

D –1080 kJ mol^{-1}

3.2 Indirect methods of determining enthalpy changes

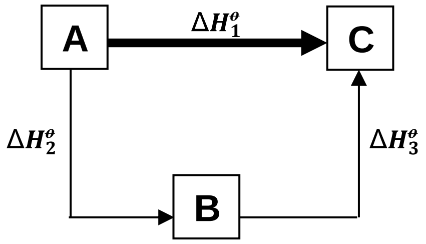
Learning Objectives

- Able to calculate the enthalpy change of a reaction by applying Hess' Law with or without an energy cycle.
- Able to calculate enthalpy change of reaction from enthalpy formation data. i.e. $\Delta \boldsymbol{H_r^\ominus} = \boldsymbol{\Sigma}\, n\, \Delta \boldsymbol{H_f^\ominus}$ (products) – $\boldsymbol{\Sigma}\, m\, \Delta \boldsymbol{H_f^\ominus}$ (reactants)
- Able to calculate enthalpy change of reaction involving simple covalent molecules using relevant bond energy data from Data Booklet. i.e. $\boldsymbol{H_r^\ominus} = \boldsymbol{\Sigma}$ *BE*(bonds broken) + $\boldsymbol{\Sigma}$ *BE*(bonds formed)

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.**

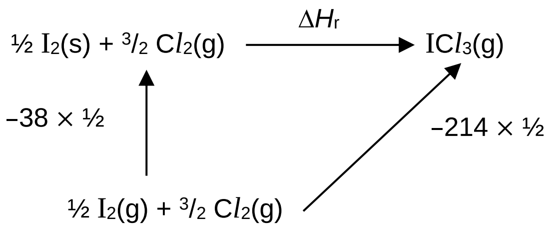


$$\boxed{\Delta \boldsymbol{H_1^\ominus} = \Delta \boldsymbol{H_2^\ominus} + \Delta \boldsymbol{H_3^\ominus}}$$

Worked Example 7

Given $I_2(g) + 3Cl_2(g) \longrightarrow 2ICl_3(g)$ $\Delta H^\ominus = -214$ kJ mol^{-1} and
$I_2(g) \longrightarrow I_2(s)$ $\Delta H^\ominus = -38$ kJ mol^{-1}.

Calculate the enthalpy change for the reaction, ΔHr, using the energy cycle below:



By Hess' law

$-38 \times \frac{1}{2} + \Delta H_r = (-214) \times \frac{1}{2}$

$\Delta H_r = (-214) \times \frac{1}{2} + 38 \times \frac{1}{2}$

$\Delta H_r = -88$ kJ mol^{-1}

Checkpoint 5

Given $2Fe(s) + {}^{3}/_{2}\ O_2(g) \longrightarrow Fe_2O_3(s)$ $\Delta H_1^{\ominus} = -822\ \text{kJ mol}^{-1}$
$C(s) + O_2(g) \longrightarrow CO_2(g)$ $\Delta H_2^{\ominus} = -394\ \text{kJ mol}^{-1}$
$CO(g) + \frac{1}{2}\ O_2(g) \longrightarrow CO_2(g)$ $\Delta H_3^{\ominus} = -284\ \text{kJ mol}^{-1}$

Calculate ΔH of the following reaction:

Calculate ΔH of the reaction:

$$\begin{tikzcd}
3O_2(g) + 3C(s) + Fe_2O_3(s) \arrow[rr, "\Delta H"] \arrow[dr] & & 3CO(g) + 2Fe(s) + 3O_2(g) \arrow[dl] \\
& 3CO_2(g) + Fe_2O_3(s) &
\end{tikzcd}$$

[+492 kJ mol^{-1}]

3.2.2 Using mathematical formulae to determine enthalpy change of reaction

1) When the values of **standard enthalpy change of formation** of the products and reactants are given, by Hess' law, the following formula is derived:

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

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

Note: $\Delta H_f^\ominus$ of all elements in standard states = 0 kJ mol^{-1}

2) When the values of **standard enthalpy change of combustion** of the products and reactants are given, by Hess' law, the following formula is derived:

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

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

3) 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:

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

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.

Worked Example 8

The equation for the combustion of ammonia to nitrogen monoxide and water is given below.

$$4\ NH_3\ (g) + 5\ O_2\ (g) \longrightarrow 4\ NO\ (g) + 6\ H_2O\ (l)$$

Using the following enthalpy changes of formation, calculate the enthalpy change of reaction for the combustion of ammonia.

$\Delta H_f(NH_3)$ = + 90.4 kJ mol^{-1}
$\Delta H_f(H_2O)$ = – 286 kJ mol^{-1}
ΔH_f (NO) = – 46.0 kJ mol^{-1}

$$\begin{aligned}\Delta H &= \sum n\, \Delta H_f \text{ (products)} - \sum m\, \Delta H_f \text{ (reactants)}\\ &= [4 \times \Delta H_f(NO) + 6 \times \Delta H_f(H_2O)] - [4 \times \Delta H_f(NH_3) + 5 \times \Delta H_f(O_2)]\\ &= [4 \times (-46.0) + 6 \times (-286)] - [4 \times (+90.4) + 0]\\ &= -2260 \text{ kJ mol}^{-1}\end{aligned}$$

Worked Example 9

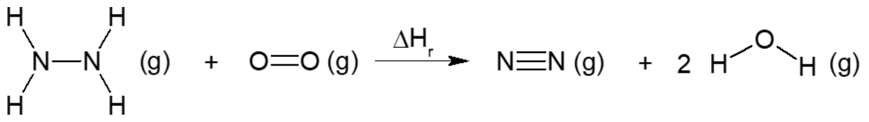
Hydrazine is often used as a rocket fuel and reacts with oxygen in an exothermic reaction. Using the bond energy values given below, calculate the enthalpy change of reaction when hydrazine reacts with oxygen.

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

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*.



ΔH_r = **∑ BE of bonds broken in reactants – ∑ BE of bonds formed in products**

$= BE(\text{N−N}) + 4 \times BE(\text{N−H}) + BE(\text{O=O}) – [BE(\text{N≡N}) + 4 \times BE(\text{O−H})]$

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

Checkpoint 6

1) [N04P1Q8(modified)] Some enthalpy changes of combustion are given below.

	$\Delta H^\ominus_c$ / kJ mol^{-1}
$CO(g)$	–283
$H_2(g)$	–286
$CH_3OH(l)$	–715

What is the enthalpy change of the following reaction?

$$CO(g) + 2H_2(g) \rightarrow CH_3OH(l)$$

2) Given $\Delta H^\ominus_f$ ($CO_2(g)$) = –394 kJ mol^{-1}, $\Delta H^\ominus_f$ ($H_2O(l)$) = –286 kJ mol^{-1}, and $\Delta H^\ominus_c$ ($CH_4(g)$) = –890 kJ mol^{-1}, calculate $\Delta H^\ominus_f$ ($CH_4(g)$).

Definitions in Chemical Energetics (Refer to Sections 2)

	General definition	Thermochemical equation
1	**Standard enthalpy change of reaction, ΔH_r^o** 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.	$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$ $\Delta H_r^o = -92 \text{ kJ mol}^{-1}$
2	**Standard enthalpy change of formation, ΔH_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.	$Mg(s) + \frac{1}{2}O_2(g) \longrightarrow MgO(s)$ $\Delta H_f^o = -602 \text{ kJ mol}^{-1}$
3	**Standard enthalpy change of combustion, ΔH_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.	$C(s) + O_2(g) \longrightarrow CO_2(g)$ $\Delta H_c^o = -393 \text{ kJ mol}^{-1}$
4	**Standard enthalpy change of neutralisation, ΔH_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.	$NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l)$ $\Delta H_n^o = -57.3 \text{ kJ mol}^{-1}$
5	**Bond energy** 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.	$N{\equiv}N(g) \longrightarrow 2N(g)$ $BE(N{\equiv}N) = +944 \text{ kJ mol}^{-1}$
6	**Lattice Energy, *L.E.*, of an ionic compound** 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.	$Na^+(g) + Cl^-(g) \longrightarrow NaCl(s)$ $L.E. = -776 \text{ kJ mol}^{-1}$

	Success Criteria	**Check**
	I am able to:	
(a)	Define the following standard enthalpy change:	
	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) bond energy, *BE*	
	6) lattice energy, *L.E.*	
(b)	Calculate enthalpy change using direct calorimetry method using the equations: heat change = $mc\Delta T$ and $\Delta H = -\frac{mc\Delta T}{n}$	
	1) for reaction involving solid added to solutions	
	2) for reaction involving two solutions	
	3) for combustion reactions	
	4) for experiments with given percentage efficiency	
(c)	Calculate enthalpy change using indirect method by energy cycle	
(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)	
	2) $\Delta \boldsymbol{H_r^o} = \sum n\, \Delta \boldsymbol{H_c^o}$ (reactants) – $\sum m\, \Delta \boldsymbol{H_c^o}$ (products)	
	3) $\Delta \boldsymbol{H_r^o} = \sum$ *BE* of bonds broken (reactants) – $\sum$ *BE* of bonds formed (products)	
(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 $\lvert L.E.\rvert \propto \left\lvert \frac{q_+ \times q_-}{r_+ + r_-} \right\rvert$	
(f)	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	
(g)	Explain why the magnitude of enthalpy change calculated using bond energies data may deviate from the actual value due to:	
	1) bond energy from *Data Booklet* being average values, and	
	2) bonds involved in the reactions not in gaseous state.	