eunoia
JUNIOR COLLEGE

2023 JC1 H2 CHEMISTRY (9729)
CORE IDEA 3 - TRANSFORMATION
Topic 5: CHEMICAL ENERGETICS - THERMOCHEMISTRY & THERMODYNAMICS

Name: ____ Civics Group: _________

Students 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; hydration; solution; neutralisation; atomisation
  - (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 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
- (g) explain and use the term *entropy*
- (h) discuss the effects on the entropy of a chemical system by the following:
  - (i) change in temperature
  - (ii) change in phase
  - (iii) change in the number of particles (especially for gaseous systems)
  - (iv) mixing of particles

  [quantitative treatment is **not** required]
- (i) predict whether the entropy change for a given process or reaction is positive or negative
- (j) state and use the equation involving *standard Gibbs free energy change of reaction,* $\Delta G^\ominus$: $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$

  [the calculation of standard entropy change, $\Delta S^\ominus$, for a reaction using standard entropies, $S^\ominus$, is **not** required]
- (k) state whether a reaction or process will be spontaneous by using the sign of $\Delta G^\ominus$
- (l) understand the limitations in the use of $\Delta G^\ominus$ to predict the spontaneity of a reaction
- (m) predict the effect of temperature change on the spontaneity of a reaction, given standard enthalpy and entropy changes

LECTURE CONTENT

REFERENCES

1. Peter Cann & Peter Hughes, *Cambridge international AS & A level Chemistry*, Hodder Education, Chapter 5 & 20

2. Martin S. Silberberg, *Chemistry: The Molecular Nature of Matter and Change*, 6th Edition, McGraw-Hill Higher Education, Chapter 6 & 20

1 Introduction

In our everyday lives, we observe some changes occurring by themselves (spontaneous), while others require a continuous input of energy to make them happen (non-spontaneous). For example, calcium carbonate reacts readily with hydrochloric acid to form calcium chloride, carbon dioxide, and water. However, if we were to mix calcium chloride, carbon dioxide, and water together, they do not react to form the calcium carbonate and hydrochloric acid.

In the topic of Chemical Energetics, we are trying to understand why chemical reactions and physical changes happen. We will examine both the heat change of a reaction, as well as the change in the degree of disorder in the reaction system.

The following questions will be answered when we complete this topic:

- What are the energy changes in a chemical or physical process?
- How can we measure or find out the energy change in a chemical or physical process?
- Why do some chemical or physical processes take place spontaneously?
- How can we predict if a process is spontaneous?

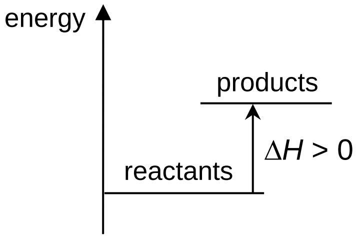
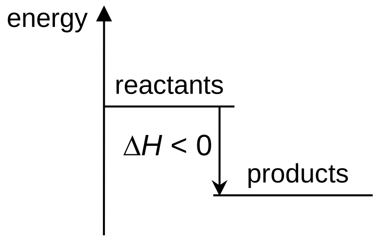
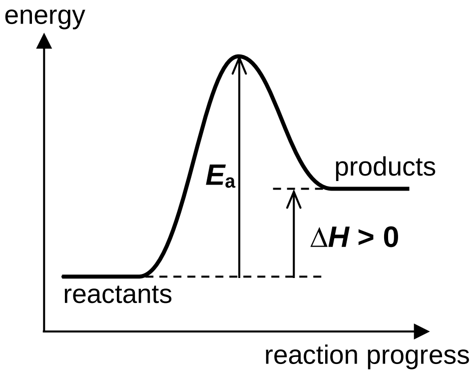
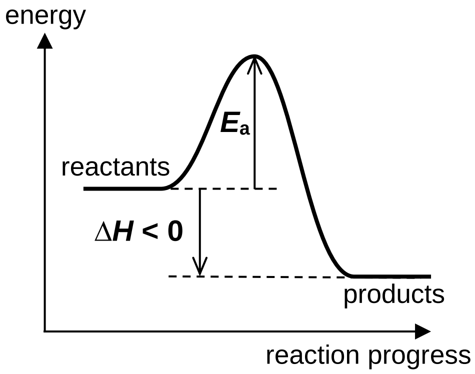
1.1 Enthalpy and enthalpy changes

Learning Outcome:
(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

The total chemical energy of a substance is called its **enthalpy** (or heat content), ***H***. Chemical energy consists of kinetic energy and potential energy. The potential energy, due to the electrostatic forces of attraction between particles, is usually the main component of the total chemical energy. The absolute enthalpy of a substance cannot be measured, but we can measure the changes in enthalpy accompanying a process.

During a chemical reaction at constant pressure, bonds are broken and new bonds are formed. The breaking of bonds requires energy while the formation of bonds releases energy. The energy change (the flow of thermal energy) that occurs is called the **enthalpy change**, ΔH. The units for ΔH are **kJ mol^{-1}** or **J mol^{-1}**.

Enthalpy changes may be exothermic or endothermic as illustrated below.

	endothermic reactions	**exothermic reactions**
enthalpy change, ΔH	ΔH is positive, $\Delta H > 0$	ΔH is negative, $\Delta H < 0$
heat transfer	The reaction **absorbs** heat from the surroundings.	The reaction **releases** heat to the surroundings.
temperature change	The temperature of the surroundings **decreases**	The temperature of the surroundings **increases**
energy level diagram	 - The products have **higher** energy content than the reactants. - The products are **energetically less stable** than the reactants.	 - The products have **lower** energy content than the reactants. - The products are **energetically more stable** than the reactants.
energy profile or reaction pathway diagram		
	The **activation energy** of a reaction (***E*$_a$**) is the minimum energy which the reacting particles must possess in order to form the products.	

Generally, exothermic reactions are more **energetically feasible** than endothermic reactions, and are thus **more likely to occur**.

1.2 Thermochemical equation

A thermochemical equation is a balanced equation that includes the enthalpy change of the reaction. The **state symbols** are included for **all** formulae given in a thermochemical equation since a change in state is accompanied by a change in energy.

E.g. $H_2(g) + ½O_2(g) \rightarrow H_2O(l)$ $\Delta H_r = –285.9 \text{ kJ mol}^{–1}$

The equation above indicates that 285.9 kJ of heat is released when 1 mole of H_2 gas reacts with 0.5 mole of O_2 gas to give 1 mole of liquid H_2O.

The magnitude of ΔH is directly proportional to the amount of reactant consumed in the process. If we multiply both sides of a thermochemical equation by a factor *n*, then ΔH must change by the same factor. For example, if we double the above equation, then $\Delta H_r = 2(–285.9) \text{ kJ mol}^{–1}$.

Example 1A

(a) Determine the enthalpy change of reaction for the following reactions by comparing with the equation on page 4:

(i) $H_2O(l) \rightarrow H_2(g) + ½O_2(g)$ $\Delta H_r =$

(ii) $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ $\Delta H_r =$

(b) $H_2(g) + ½O_2(g) \rightarrow H_2O(g)$ $\Delta H_r = –241.8 \text{ kJ mol}^{–1}$

Explain why the enthalpy change of the above reaction is less exothermic than $–285.9 \text{ kJ mol}^{–1}$ for $H_2(g) + ½O_2(g) \rightarrow H_2O(l)$.

ΔH_r is less exothermic as energy is **absorbed** to **convert liquid water to water vapour**. The difference (of $+44.1 \text{ kJ mol}^{–1}$) represents the **enthalpy change of vaporisation of water**.

1.3 Standard conditions and standard states

Learning Outcome:
(c) explain and use the terms:
 (i) *standard conditions*

Besides the physical state of the substances, the enthalpy change of a reaction is also affected by the physical conditions of temperature, concentration and pressure. Changes in enthalpy are normally reported for processes taking place under a set of standard conditions. In most of our discussions we shall consider the **standard enthalpy change**, represented by the symbol, $\boldsymbol{\Delta H^{\ominus}}$, with '$\ominus$' indicating the change in enthalpy for a process in which the initial and final substances are in their **standard states**:

The **standard state** of a substance at a **specified temperature** is its pure form at **1 bar** (=10^5 Pa)*, and **1 mol dm$^{–3}$** for solutions.

**Note: In 1982 IUPAC recommended the value 10^5 Pa (=1 bar), but prior to 1982 the value 101 325 Pa (= 1 atm) was usually used. The difference in thermodynamic values at 1 atm and 1 bar is usually insignificant.*

For example, the standard state of solid ethanol at 100 K is pure solid ethanol at 100 K and 1 bar; the standard state of liquid iron at 3000 K is pure liquid iron at 3000 K and 1 bar; the standard state of gaseous water at 550 K is pure steam at 550 K and 1 bar. For a given material or substance, the standard state is the **reference state** for the material's thermodynamic state properties such as enthalpy, entropy, Gibbs free energy.

Standard enthalpies may be reported for ***<u>any temperature</u>***. **<u>However</u>**, the ***<u>conventional temperature</u>*** for reporting thermodynamic data is **298 K** (corresponding to **25 ºC**). Unless otherwise mentioned, all thermodynamic data subsequently will refer to this conventional temperature.

The **standard enthalpy change of formation** for an **element** in its standard state (irrespective of temperature) is **zero**, and this convention allows a wide range of other thermodynamic quantities to be calculated and tabulated. The standard state of a substance *does not have to exist in nature*: for example, it is possible to calculate standard enthalpy change of formation values for steam at 298 K and 10^5 Pa, although steam does not exist (as a gas) under these conditions.

Checkpoints for Section 1

- To remember that:
  - endothermic reactions have positive enthalpy change and exothermic reactions have negative enthalpy change;
  - endothermic reaction absorbs heat from the surroundings while exothermic reaction releases heat to the surroundings;
  - how to draw the respective energy profile and energy level diagrams;
  - endothermic reaction results in products less energetically stable than reactants while for exothermic, the products are more energetically stable than reactants; and
  - write state symbols for thermochemical equations.
- To remember the standard conditions and standard states of common species. Note the difference from s.t.p. in The Gaseous State lecture (273 K [0 ºC], 10^5 Pa [1 bar]) and standard states.

2 Definitions of Enthalpy Changes of Reactions (Part I)

Learning Outcome:
(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)

2.1 Standard enthalpy change of formation, $\Delta H_f^\ominus$

The standard enthalpy change of formation, $\Delta H_f^\ominus$, is the **energy change** when **1 mole of a substance in its standard state** is formed from its **constituent elements in their standard states**, at a specified temperature, usually 298 K.

E.g. $\frac{1}{2}H_2(g) + \frac{1}{2}I_2(s) \rightarrow$ **$HI(g)$** $\Delta H_f^\ominus = +26.5\ \text{kJ mol}^{-1}$

$2C(s) + 3H_2(g) + \frac{1}{2}O_2(g) \rightarrow$ **$C_2H_5OH(l)$** $\Delta H_f^\ominus = -298\ \text{kJ mol}^{-1}$

The standard enthalpy change of formation of **elements** in their standard state (at 1 bar) is **zero**.

E.g. $Cl_2(g) \rightarrow Cl_2(g)$ $\Delta H_f^\ominus = 0$

$\Delta H_f^\ominus$ is a measure of the energetic stability of a substance relative to its constituent elements.

If $\Delta H_f^\ominus$ is **positive**,	If $\Delta H_f^\ominus$ is **negative**,
Compound is **less stable** than its constituent elements.	Compound is **more stable** than its constituent elements.

Example 2A

Write an equation to represent the standard enthalpy change of formation of $CaSO_4(s)$.

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

The standard enthalpy change of combustion, $\Delta H_c^\ominus$, is the **energy released** when **1 mole of a substance** is **completely burnt in excess oxygen**, with all reactants and products in their **standard states**, at a specified temperature, usually 298 K.

E.g. **$CH_4(g)$** $+ 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ $\Delta H_c^\ominus = -866\ \text{kJ mol}^{-1}$

$Mg(s)$ $+ \frac{1}{2}O_2(g) \rightarrow MgO(s)$ $\Delta H_c^\ominus = -601\ \text{kJ mol}^{-1}$

The enthalpy change of combustion is **always exothermic** *i.e.* heat is always evolved in combustion. $\Delta H_c^\ominus$ can be used to compare the energy values of fuels and food. The more exothermic the $\Delta H_c^\ominus$, the higher the energy value of the fuel or food.

Example 2B

State the type of enthalpy change(s) represented by the equation $H_2(g) + ½O_2(g) \rightarrow H_2O(l)$.

In some cases, $\Delta H_f^{\ominus}$ and $\Delta H_c^{\ominus}$ are equivalent. They have the same value and are represented by the same chemical equation.

2.3 Standard enthalpy change of neutralisation, $\Delta H_{neut}^{\ominus}$

The standard enthalpy change of neutralisation, $\Delta H_{neut}^{\ominus}$, is the **energy released** when **1 mole of water** is formed in the **neutralisation reaction between an acid and a base**, all in their **standard states**, at a specified temperature, usually 298 K.

Neutralisation is an **exothermic** reaction since it involves the **attraction** of H^+ and OH^- ions to form an O–H bond.

$H^+(aq) + OH^-(aq) \rightarrow \mathbf{H_2O(l)}$ $\qquad \Delta H_{neut}^{\ominus} = –57.0 \text{ kJ mol}^{-1}$

The enthalpy change of neutralisation of a strong acid with a strong base is **almost the same for all strong acids and bases** (–57.0 kJ mol^{-1}). This is because strong acids and strong bases **dissociate completely** in dilute aqueous solution. The reactions between them are effectively the reactions between aqueous H^+ ions and OH^- ions.

E.g. $KOH(aq) + HNO_3(aq) \rightarrow KNO_3(aq) + H_2O(l)$ $\qquad \Delta H_{neut}^{\ominus} = –57.0 \text{ kJ mol}^{-1}$

$NaOH(aq) + ½H_2SO_4(aq) \rightarrow ½Na_2SO_4(aq) + H_2O(l)$ $\qquad \Delta H_{neut}^{\ominus} = –57.0 \text{ kJ mol}^{-1}$

K^+, NO_3^-, Na^+ and Cl^- ions are essentially spectator ions in the above neutralisation reactions. Hence, the reactions are effectively the same: $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$.

The enthalpy change of neutralisation involving a **weak acid or weak base** may be **slightly less exothermic** than –57.0 kJ mol^{-1}. This is because weak acids and weak bases do not dissociate completely in dilute aqueous solution. During neutralisation, **energy is absorbed to dissociate the undissociated weak acid or weak base** to form H^+ or OH^- respectively. Thus, less energy is released and the resulting $\Delta H_{neut}^{\ominus}$ is less exothermic.

E.g. $OH^-(aq) + CH_3CO_2H(aq) \rightarrow CH_3CO_2^-(aq) + H_2O(l)$ $\qquad \Delta H_{neut}^{\ominus} = –55.2 \text{ kJ mol}^{-1}$

The difference of +1.8 kJ mol^{-1} compared to the enthalpy change of neutralisation of a strong acid with a strong base is due to the absorption of energy during the dissociation of the undissociated weak acid, $CH_3CO_2H(aq)$.

$CH_3CO_2H(aq) \rightleftharpoons CH_3CO_2^-(aq) + H^+(aq)$ $\qquad \Delta H^{\ominus} = +1.8 \text{ kJ mol}^{-1}$

2.4 Bond energy, BE

Bond energy is the **average energy required** to break **1 mole of a covalent bond** between two atoms in the **gaseous state**.

E.g. **$Cl–Cl$ (g)** → $2Cl$ (g) BE($Cl–Cl$) = +244 kJ $mol^{–1}$

CH_4 (g) → C (g) + 4H (g) 4 × BE(C–H) = 4 × (+410) kJ $mol^{–1}$

To break the covalent bond, energy is needed to pull the two atoms apart so bond energy is **always positive** (endothermic process). When the same bond is formed, the same amount of energy is released (exothermic process).

Bond energy is a measure of the strength of covalent bonds. The **stronger** the covalent bond, the **more endothermic** the bond energy.

Bond dissociation energy is the **energy required** to break **1 mole of a particular covalent bond** in a specific molecule in the gaseous state. Bond dissociation energy of the same type of bond in different molecules may differ, as the strength of a bond is influenced by neighbouring atoms. For these reasons we use **average bond energies** taken from a number of bonds of the same type but in different chemical environments.

The bond energy data below from the *Data Booklet* are **average values** derived from a large range of molecules containing that particular covalent bond. As the values may not be a true reflection of actual bond energies in a particular molecule, the enthalpy changes calculated using bond energies are thus only an **approximation.**

bond	energy / kJ $mol^{–1}$	bond	energy / kJ $mol^{–1}$
C–C	350	O–O	150
C=C	610	N–N	160
C≡C	840	C–N	305
C–H	410	C–O	360
C–F	485	C=O	740
C–Cl	340	C=O in CO_2	805

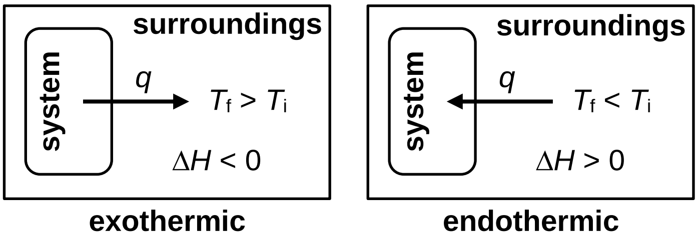
Checkpoints for Section 2

- To remember the definitions for *standard enthalpy change of formation*, *combustion*, *neutralisation* and *bond energy* and apply them accordingly by writing the relevant thermochemical equations.
- To know that thermochemical equations must be accompanied by state symbols.
- To infer that $\Delta H_f^{\ominus}$ of elements at standard state = 0; $\Delta H_c^{\ominus}(O_2(g)) = 0$; $\Delta H_c^{\ominus}(CO_2(g)) = 0$; $\Delta H_c^{\ominus}(H_2O(l)) = 0$; $\Delta H_c^{\ominus}(C(s)) = \Delta H_f^{\ominus}(CO_2(g))$ and $\Delta H_c^{\ominus}(H_2(g)) = \Delta H_f^{\ominus}(H_2O(l))$.
- To understand the factors that affect the enthalpy changes:
  - Weak acid or weak base can cause $\Delta H_{neut}^{\ominus}$ to be slightly more endothermic as energy is absorbed to dissociate the weak acid or weak bases.
  - The stronger the covalent bonds, the more endothermic the bond energy.

3 Experimental Determination of Enthalpy Change (Calorimetry)

The **Law of Conservation of Energy** states that energy cannot be created or destroyed; it can only be converted from one form into another. Using this law, we can determine the enthalpy change of a reaction.

The **reaction** (part of the universe that is being studied) is defined as the **system**. The **environment of the reaction** (rest of the universe that is not part of the system) is known as the **surroundings**. For example, for a reaction carried out in a test tube, the surroundings can refer to the solvent; the air around the test tube, the test tube itself, and anything dipping into the test tube (*e.g.* a thermometer). The enthalpy change of a reaction at constant pressure appears as **heat**, which is transferred between the system and surroundings.



For example, in the following reaction,

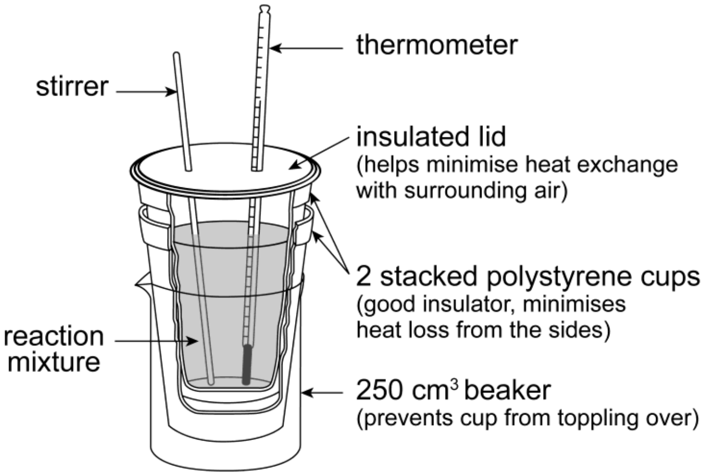
$$CuSO_4(aq) + Zn(s) \rightarrow ZnSO_4(aq) + Cu(s) \qquad \Delta H = -219 \text{ kJ mol}^{-1}$$

The system consists of the reactants ($CuSO_4$ and Zn) and the products ($ZnSO_4$ and Cu). The aqueous medium in which the reaction takes place is the surroundings. Since the reaction is exothermic (as ΔH is negative), heat is released by the reaction (system) and is transferred to the solution (surroundings). By measuring the amount of heat given out, we can determine the enthalpy change of the reaction.

3.1 A Simple Calorimeter

Depending on the nature of the reaction for which the enthalpy change is being measured, the experimental set-up will be different.

A simple **calorimeter** consisting of a polystyrene cup with a lid and a thermometer can be used to measure the heat change for **reactions involving solutions**.



3.2 Calculations using experimental results

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

The heat change, q, can be calculated using the following formula:

$\boldsymbol{q = -mc\Delta T}$	q = heat change (unit: J) positive (+) if heat is gained from the surroundings by the system negative (–) if heat is lost to the surroundings from the system m = mass of solution (unit: g) c = specific heat capacity of water (unit: J g^{-1} K^{-1}) ΔT = temperature change of solution (unit: K or ^{o}C) = **final** temperature of solution – **initial** temperature of solution

The **specific heat capacity**, ***c***, is defined as the amount of heat required to raise the temperature of 1 g of the substance by 1 K. The SI unit of specific heat capacity is **J g^{-1} K^{-1}**.

Sometimes, the heat capacity of the substance is given instead. The **heat capacity, C,** is defined as the amount of heat required to raise the temperature of a certain mass of the substance by 1 K (or 1 ^{o}C). The SI unit for heat capacity is **J K^{-1}**. To calculate the heat change, we use the following equation:

$\boldsymbol{q = -C\Delta T}$	q = heat change (unit: J) positive (+) if heat is gained from the surroundings by the system negative (–) if heat is lost to the surroundings from the system C = heat capacity of solution (unit: J K^{-1}) ΔT = temperature change of solution (unit: K or ^{o}C) = **final** temperature of solution – **initial** temperature of solution

Since we define enthalpy change of reaction (ΔH) for every one mole of the ***<u>limiting reagent or a specific substance</u>*** identified in the definition, we can calculate the **enthalpy change of reaction (ΔH)** by using the following equation:

$$\text{enthalpy change of reaction, } \Delta H_r = \frac{q}{n} = \frac{-mc\Delta T}{\text{amount of limiting reagent / specified substance}}$$

The sign of ΔH_r denotes whether the reaction is exothermic (*i.e.* energy lost to surroundings) or endothermic (*i.e.* energy gained from surroundings). If the reaction is exothermic, ΔH_r will be negative. If the reaction is endothermic, ΔH_r will be positive.

Assumptions in the calculations

To ensure accurate results, **all** the heat change of the reaction must be used to raise (or lower) the temperature of the solution. However, in practice, we cannot totally eliminate heat exchanges with the surrounding air or apparatus. Hence, we usually make the following assumptions in our calculations:

- **Negligible heat loss** to (or heat gain from) surrounding air
- **Negligible heat loss** to (or heat gain from) **calorimeter** (*i.e.* heat capacity of the calorimeter omitted)
- The **density** of the solution is the **same as that of water** (1.00 g cm^{-3}) since the solution is very dilute. In addition, it is more convenient to measure the volume of the solution to obtain the mass of the solution.

Example 3A – Reaction between two solutions

40.0 cm^3 of 2.0 mol dm^{-3} $HCl(aq)$ was added to 50.0 cm^3 of 2.0 mol dm^{-3} $NaOH(aq)$ in a polystyrene cup. The following results were obtained.

initial temperature of HCl (aq) / ºC	22.3
initial temperature of NaOH (aq) / ºC	22.5
highest temperature reached / ºC	34.6

Increase in temperature shows that reaction is **exothermic**.

Calculate the enthalpy change of neutralisation.

Recall definition of ΔH_{neut}: heat evolved when 1 mole of water is formed in the neutralisation reaction between acid and base.

Initial temperature of solutions = $\frac{40.0(22.3) + 50.0(22.5)}{40.0 + 50.0}$ = 22.4 ºC

This is the weighted average of the temperatures of the two solutions.

Heat change $= -mc\Delta T$

$= -(40.0 + 50.0) \times 1.00 \times 4.18 \times (34.6 - 22.4)$

$= -4586$ J

Assume ρ of solution = 1.00 g cm^{-3}

$\therefore m = 90.0 \times 1.00 = 90.0$ g

change in 1 ºC = change in 1 K

$HCl + NaOH \rightarrow NaCl + H_2O$

Amount of HCl reacted = $40.0 \times 10^{-3} \times 2.0 = 0.0800$ mol

Amount of NaOH reacted = $50.0 \times 10^{-3} \times 2.0 = 0.100$ mol

$\Rightarrow$ Amount of H_2O formed = 0.0800 mol (HCl is limiting)

□ΔH_r is **negative** since reaction is **exothermic.**

$\Delta H_{neut} = \frac{q}{n} = \frac{-4586}{0.08} = -57330$ J mol^{-1} = **-57.3 kJ mol^{-1}**

Self Check 3A

25.0 cm^3 of 2.0 mol dm^{-3} $H_2SO_4(aq)$ was added to 25.0 cm^3 of 2.0 mol dm^{-3} $NaOH(aq)$ in a polystyrene cup. The initial temperatures of the solutions were 30.0 ºC and 29.8 ºC respectively. When the solutions were mixed, the highest temperature reached was 43.6 ºC. Use the data to calculate a value for the enthalpy change of neutralisation. **[-57.3 kJ mol^{-1}]**

Example 3B – Reaction between a solid and aqueous solution

50.0 cm^3 of 0.10 mol dm^{-3} silver nitrate solution was placed in a polystyrene cup. A known mass of zinc powder was added and the following results were obtained.

mass of weighing bottle and Zn powder / g	4.310
mass of weighing bottle and residual Zn / g	3.510
mass of Zn added / g	0.800

initial temperature of solution / °C	21.1
highest temperature reached / °C	26.3
ΔT / °C	5.2

Calculate the enthalpy change for the reaction $Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$.

Heat change = $-mc\Delta T$

=

Adding a solid to a solution does not increase its volume, so **mass** of solution = **volume** of solution × **density** (assume density = 1.00 g cm^{-3})

Amount of Zn added = 0.8 ÷ 65.4 = 0.0122 mol

Amount of Ag^+ reacted = 0.10 × 50.0 ÷ 1000 = 0.00500 mol $\Rightarrow$ Ag^+ is the limiting reactant

ΔH_r (for one mole of Ag^+) =

"per mole of Ag^+"

$\therefore \Delta H_r$ (for two moles of Ag^+) =

"per mole of equation"

Note:
According to the written equation, you need to determine the enthalpy change when 1 mole of Zn reacts with **2 moles of Ag^+**, hence the '×2' in the calculations.

Temperature correction

In many experiments, the temperature may not immediately reach a maximum (or minimum), especially when the **reaction is slow**. In such reactions, heat loss to (or gain from) the surroundings becomes significant. To account for heat loss to (or gain from) the surroundings, a series of temperatures can be recorded before and after the mixing to give a **temperature–time graph**. Extrapolation is done to the point of mixing to obtain a more accurate maximum (or minimum) temperature.

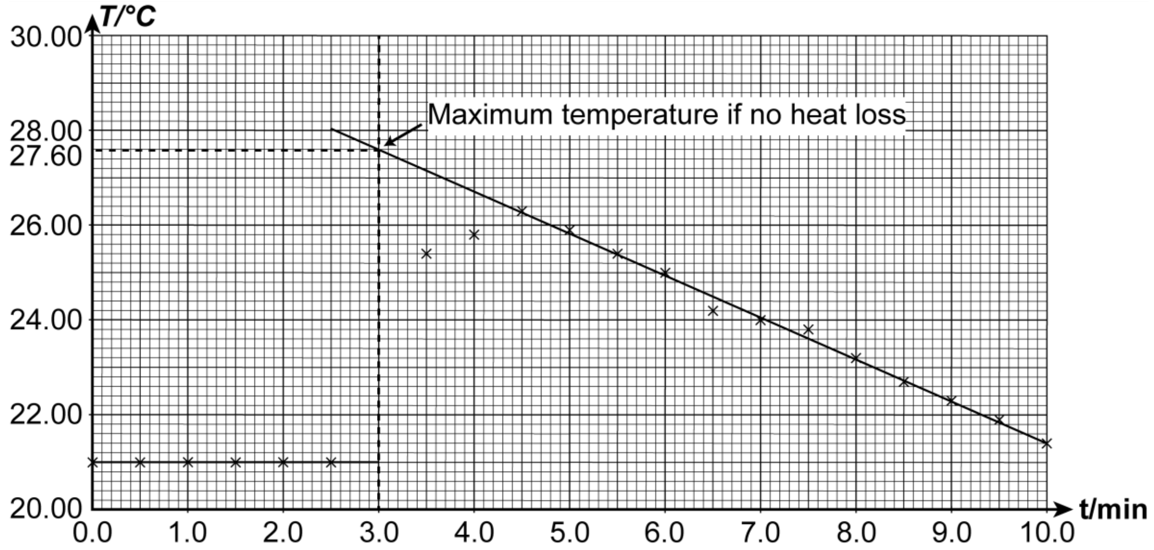
Example 3C

The experiment in **Example 3B** was repeated with the temperature being monitored continuously. Zinc powder was added when t = 3 min and the following results were obtained.

time, t / min	0.0	0.5	1.0	1.5	2.0	2.5	3.5	4.0	4.5	5.0
temperature, T / °c	21.1	21.1	21.1	21.1	21.1	21.1	25.4	25.8	26.3	25.9
time, t / min	5.5	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0
temperature, T / °c	25.4	25.0	24.2	24.0	23.8	23.2	22.7	22.3	21.9	21.4

Use the data to calculate the enthalpy change for the reaction

$$Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s).$$



Change in temperature = 27.6 – 21.1 = 6.5 °C

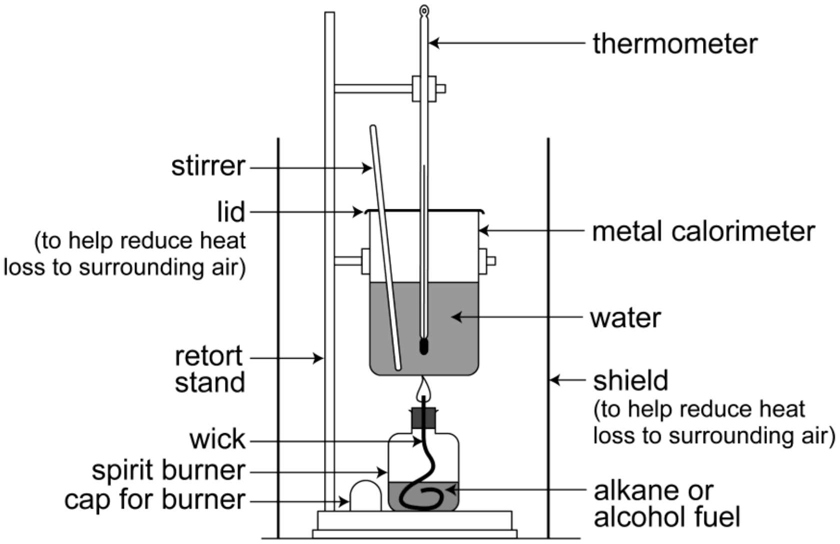
Heat change = $-mc\Delta T$
= –50.0 × 4.18 × 6.5
= –1359 J

$\Delta H_r = -\frac{-1359}{0.005} \times 2 = -543000 \text{ J mol}^{-1} = \underline{\mathbf{-543 \text{ kJ mol}^{-1}}}$

ΔH_r is **more negative** than that calculated in **Example 3B** as heat loss is accounted for.

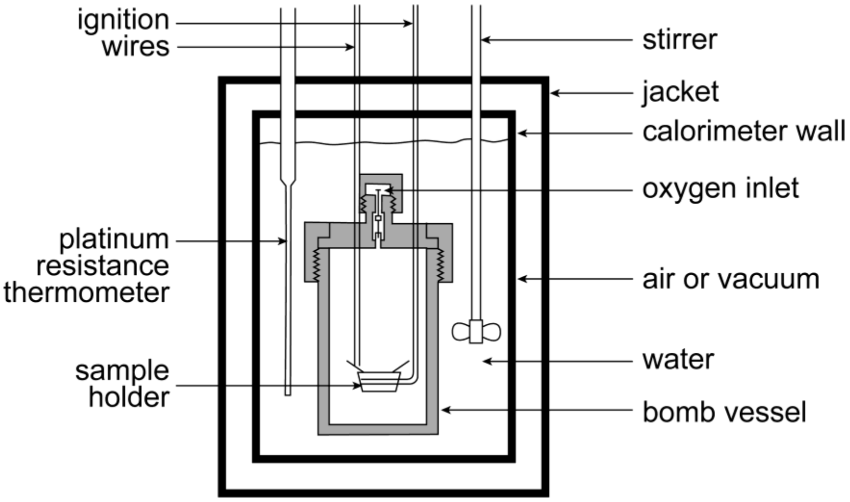
3.3 Calorimetry to determine enthalpy change of combustion

The following experimental set–up can be used to determine the $\Delta H_c^\ominus$ for a fuel such as ethanol. A known volume of water is placed in the metal (usually copper) calorimeter, and its initial temperature measured. The fuel is placed in the spirit burner and weighed. The spirit burner is then lit under the calorimeter, and the heat released during combustion heats up the water in the calorimeter. After some time, the combustion is stopped. The final temperature of the water is measured and the spirit burner is weighed again.



When highly accurate values of $\Delta H_c^\ominus$ such as the energy value of fuels and food is required, a **bomb calorimeter** can be used.

The bomb calorimeter works in a similar way as the set-up described above. A known mass of the substance whose $\Delta H_c^\ominus$ is to be determined is ignited in excess oxygen by heated ignition wires in a bomb calorimeter. The heat released from the combustion is transferred to a known mass of water in the calorimeter. The rise in temperature of the water is then measured, and the necessary calculations can be done. The bomb calorimeter is more accurate as the heat capacity of the bomb calorimeter and the heat evolved in burning the iron ignition wires used to ignite the substance can be taken into account.



Example 3D

In an experiment to determine $\Delta H_c^\ominus$ for ethanol, C_2H_5OH the following results were obtained.

mass of water in calorimeter / g	250.000
mass of burner and ethanol before combustion / g	16.200
mass of burner and ethanol after combustion / g	15.670
temperature of water before combustion / ºC	29.6
temperature of water after combustion / ºC	40.0

Calculate $\Delta H_c^\ominus$ for ethanol. Compare the experimental value with the literature value of –1368 kJ mol^{-1} and account for any difference.

Heat change = $-mc\Delta T$ = –250.00 × 4.18 × (40.0 – 29.6) = –10870 J = –10.87 kJ

Mass of ethanol burnt = 16.20 – 15.67 = 0.530 g

Amount of ethanol burnt = $\frac{0.53}{2 \times 12.0 + 6 \times 1.0 + 16.0}$ = 0.01152 mol

$\Delta H_c^\ominus = \frac{-10.87}{0.01152} = \underline{\mathbf{-943\ kJ\ mol^{-1}}}$

The value is **less exothermic** than the literature value as the **heat absorbed by the calorimeter is not accounted for / there is heat loss to surroundings / there is incomplete combustion**.

In Example 3D, the enthalpy change of combustion of ethanol determined experimentally is less exothermic than the theoretical value obtained from literature. This is because not all the heat evolved from the reaction has been transferred to the calorimeter and its contents – in this case, heating up the water and the container itself. In other words, the heat transfer is **not 100% efficient**.

To determine the efficiency of a combustion reaction, we can make use of the following equation:

$$q' = \frac{x}{100}q$$

where q' is the heat absorbed by the calorimeter (including its contents)
q is the total heat released from combustion
x is the efficiency of the combustion reaction

Example 3E

A 1.000 g sample of octane (C_8H_{18}) is burned in a bomb calorimeter containing 1200 g of water at an initial temperature of 26.7 ºC. After the reaction, the highest temperature of the water reached was 33.2 ºC. Given that the process is known to be only 80% efficient, calculate the heat of combustion of octane in kJ mol^{-1}. The heat capacity of the bomb calorimeter is 837 J K^{-1}.

Heat change of water =

Heat change of calorimeter =

$$q' = \frac{x}{100} q$$

Heat change of water + Heat change of calorimeter = × Heat change of combustion

= × Heat change of combustion

Heat change of combustion =

Amount of octane burnt = $\frac{1.000}{8 \times 12.0 + 18.0}$ = 0.008772 mol

$\Delta H_c^\ominus$ (octane) =

Checkpoints for Section 3

- To remember and know how to apply the following formula to calculate heat change.

$$\text{heat change, } q = -mc\Delta T = -mc(T_{\text{final}} - T_{\text{initial}}) = -C\Delta T = -C(T_{\text{final}} - T_{\text{initial}})$$

- To make use of given efficiency to calculate heat change, q.

$$q' = \frac{x}{100} q$$

where q' is the heat absorbed by the calorimeter (including its contents)
q is the total heat released from combustion
x is the efficiency of the combustion reaction

- To know the difference between heat change, q, and enthalpy change of reaction, ΔH, and how to calculate ΔH using

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

where n = amount of limiting reagent or specified substance

4 Theoretical Calculation of Enthalpy Change (Hess' Law)

Learning Outcome:

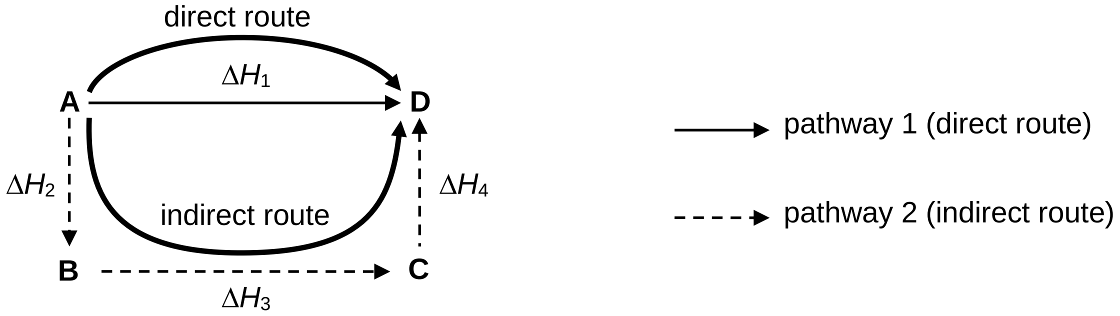
(f) apply Hess' Law to construct simple energy cycles, e.g. Born-Haber cycle, and carry out calculations involving such cycles and relevant energy terms (including ionisation energy and electron affinity), with particular reference to:
  - (i) determining enthalpy changes that cannot be found by direct experiment, e.g. an enthalpy change of formation from enthalpy changes of combustion
  - (iii) average bond energies

Some enthalpy changes can be easily calculated based on the necessary measurements obtained by conducting a calorimetry experiment.

However, some enthalpy changes of reaction are theoretical and cannot be determined directly by experiment. For example, C_2H_5OH cannot be formed by just reacting C, H_2 and O_2 together. For such reactions, we can find the enthalpy change indirectly by making use of Hess' Law to calculate the enthalpy changes of these reactions from other data such as enthalpy changes of combustion.

Hess' Law states that the enthalpy change (ΔH) of a reaction is determined only by the **initial and final states** and is **independent of the reaction pathway taken**.

In the figure below, the reactant **A** directly goes to form **D**. This is the direct route. In the indirect route, **A** is converted to **B**, followed by **C**, which then goes on to form **D**. The enthalpy change is the same for both the direct and indirect routes as both routes start with reactant **A** and end with product **D**.



By Hess' Law,

enthalpy change for direct route (pathway 1) = enthalpy change for indirect route (pathway 2)

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

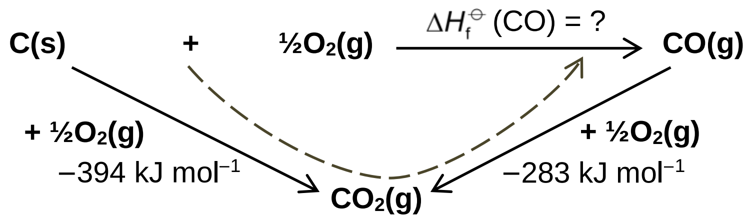
Example 4A

Calculate the standard enthalpy change of formation of carbon monoxide using the data given below.

$C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H_c^\ominus(C) = -394\ kJ\ mol^{-1}$

$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g) \quad \Delta H_c^\ominus(CO) = -283\ kJ\ mol^{-1}$

Method 1a: Energy cycle



By Hess' Law,

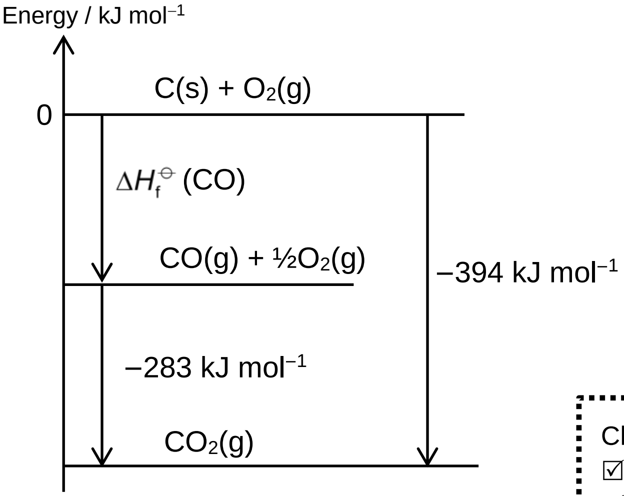
$\Delta H_f^\ominus(CO) = -394 - (-283)$

$= \underline{\mathbf{-111\ kJmol^{-1}}}$

When considering the **reverse** of a reaction i.e. product → reactant, the **sign of ΔH is reversed**.

Check!
☑ *Equations are balanced*
☑ *State symbols are correct*
☑ *Sign of ΔH is consistent with direction of arrow*

Method 1b: Energy level diagram



Energy level of an **element at standard state** is defined to be **0 kJ mol⁻¹**.

If ΔH is **negative** (exothermic reaction), we draw the arrow pointing **down** and vice versa.

By Hess' Law,

$\Delta H_f^\ominus(CO) = -394 - (-283)$

$= \underline{\mathbf{-111\ kJ\ mol^{-1}}}$

Check!
☑ *Axis is labelled*
☑ *Zero energy level is labelled if applicable*
☑ *Equations are balanced*
☑ *State symbols are correct*
☑ *Sign of ΔH is consistent with direction of arrow*

** **Note that construction of energy cycles and energy level diagrams are NOT required for H1 Chemistry.**

Example 4A (continued)

Calculate the standard enthalpy change of formation of carbon monoxide using the data given below.

$C(s) + O_2(g) \rightarrow CO_2(g)$ $\quad \Delta H_c^\ominus(C) = -394 \text{ kJ mol}^{-1}$

$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$ $\quad \Delta H_c^\ominus(CO) = -283 \text{ kJ mol}^{-1}$

Method 2: Algebraic method

$C(s) + O_2(g) \rightarrow CO_2(g)$ $\quad \Delta H = \Delta H_c^\ominus(C) = -394 \text{ kJ mol}^{-1}$

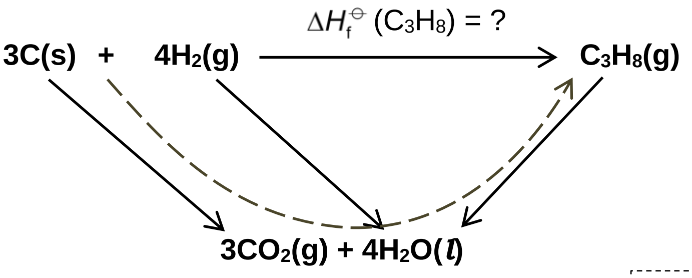
$CO_2(g) \rightarrow CO(g) + \frac{1}{2}O_2(g)$ $\quad \Delta H = -\Delta H_c^\ominus(CO) = +283 \text{ kJ mol}^{-1}$

$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$ $\quad (CO) = -394 + 283 = \underline{\mathbf{-111 \text{ kJ mol}^{-1}}}$

Example 4B

Calculate the standard enthalpy change of formation of propane, C_3H_8 using the combustion data provided.

substance	**$\Delta H_c^\ominus$ / kJ mol^{-1}**
graphite	–394
hydrogen	–286
propane	–2220



By Hess' Law, $\Delta H_f^\ominus$ (propane) =

Sign of ΔH is changed as the direction of the reaction is reversed.

Generally, for a given reaction, if we know the **combustion data** of all the reactants and products, we can find the enthalpy change of the reaction using the following formula:

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

where m, n = stoichiometric coefficients of the reactants and products in the given reaction.

Self Check 4A

Calculate the standard enthalpy change of formation of ethanol, C_2H_5OH using the combustion data provided.

substance	$\Delta H_c^{\ominus}$ / kJ mol^{-1}
graphite	–394
hydrogen	–286
ethanol	–1367

[–279 kJ mol^{-1}]

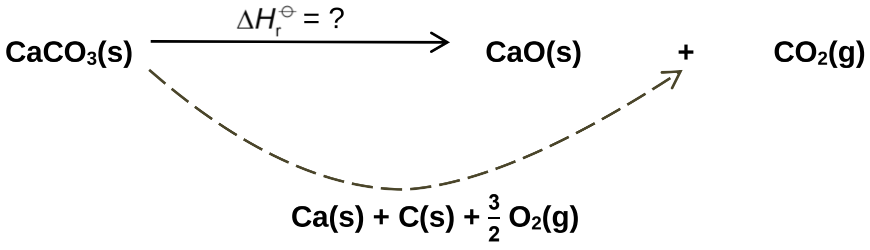
Example 4C

Calculate the standard enthalpy change for the reaction below using the data given.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

substance	$\Delta H_f^{\ominus}$ / kJ mol^{-1}
$CaCO_3(s)$	–1207
$CaO(s)$	–635
$CO_2(g)$	–394

Method 1: Energy cycle



By Hess' Law, $\Delta H_r^{\ominus}$ =

Method 2: Algebraic method

$CaCO_3(s) \rightarrow Ca(s) + C(s) + \frac{3}{2}O_2(g)$ $\quad \Delta H = -\Delta H_f^{\ominus}(CaCO_3) = +1207$ kJ mol^{-1}

$Ca(s) + \frac{1}{2}O_2(g) \rightarrow CaO(s)$ $\quad \Delta H = \Delta H_f^{\ominus}(CaO) = -635$ kJ mol^{-1}

$C(s) + O_2(g) \rightarrow CO_2(g)$ $\quad \Delta H = \Delta H_f^{\ominus}(CO_2) = -394$ kJ mol^{-1}

$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ $\quad \Delta H_r^{\ominus} = +1207 + (-635) + (-394)$

$= \underline{\textbf{+178 kJ mol}^{-1}}$

Generally, for a given reaction, if we know the **formation data** of all the reactants and products, we can find the enthalpy change of the reaction using the following formula:

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

where *m*, *n* = stoichiometric coefficients of the reactants and products in the given reaction.

Self Check 4B

Calculate the standard enthalpy of formation of solid ammonium chloride, $NH_4Cl(s)$, using the given data.

$$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s) \qquad \Delta H_r^\ominus = -176.0 \text{ kJ mol}^{-1}$$

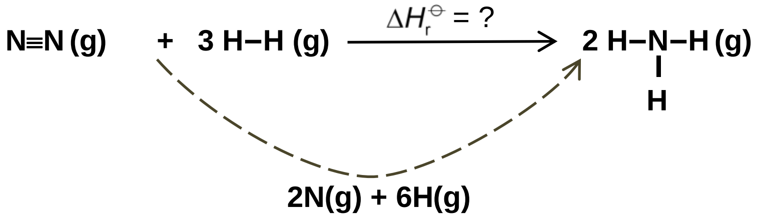
$$\Delta H_f^\ominus [NH_3(g)] = -46.1 \text{ kJ mol}^{-1}; \ \Delta H_f^\ominus [HCl(g)] = -92.3 \text{ kJ mol}^{-1}$$

[−314 kJ mol^{-1}]

Example 4D

Calculate the enthalpy change of reaction: $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ using the relevant bond energies.

bond	bond energy / kJ mol^{-1}
N≡N	944
H−H	436
N−H	390



By Hess' Law, $\Delta H_r^\ominus$ =

Generally, for reactions involving **covalent molecules**, if we know the **bond energies** of all the covalent bonds in the reactants and products, we can find the enthalpy change of the reaction using the following formula:

$$\boxed{\Delta H_r^\ominus = \sum \text{BE}(\text{bonds broken}) - \sum \text{BE}(\text{bonds formed})}$$

When using bond energy data to calculate the enthalpy change of reaction, we need to keep in mind that **bond energies in the *Data Booklet* are average values**, and not the actual amounts of energy required to break/form the specific bonds in the reaction. Hence, using them in calculations can result in **discrepancies** when compared to values obtained by other means *e.g.* from experiments or calculated from other enthalpy changes using Hess' Law.

Example 4E

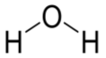
(a) Oxyacetylene torches, which operate at temperatures as high as 3300 °C, are fueled by the combustion of acetylene (i.e. ethyne), C_2H_2. The equation is given below:

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

Use bond energy values from the *Data Booklet* to calculate ΔH_r of the above reaction.

Draw out the structure of the reactants and products to determine the types of bonds between the atoms in the molecules.

$$\mathbf{2C_2H_2(g) \quad + \quad 5\ O_2(g) \quad \rightarrow \quad 4CO_2(g) \quad + \quad 2H_2O(g)}$$

2 H–C≡C–H   5 O=O   4 O=C=O   2 

bonds broken	BE / kJ mol^{-1}	bonds formed	BE / kJ mol^{-1}
4 × C–H	4(410) = 1640	8 × C=O	8(805) = 6440
2 × C≡C	2(840) = 1680	4 × O–H	4(460) = 1840
5 × O=O	5(496) = 2480		**$\sum$BE = 8280**
	$\sum$BE = 5800		

ΔH_r = $\sum$BE (bonds broken) **–** $\sum$BE (bonds formed)

=

(b) The ΔH_r of this reaction was calculated to be –2514 kJ mol^{-1} from enthalpy change of formation data. Suggest a reason for the difference in the values of ΔH_r obtained from **(a)** and the value above.

The bond energies given in the *Data Booklet* are the   bond energies of that particular covalent bond in different types of molecules. These values may not apply to the specific molecules in this reaction.

Self Check 4C

Sulfur hexafluoride can be made by reacting sulfur tetrafluoride with fluorine.

$$SF_4(g) + F_2(g) \rightarrow SF_6(g) \qquad \Delta H = -434 \text{ kJ mol}^{-1}$$

By considering the bonds broken and bonds formed during the reaction, calculate a value for the S−F bond energy. State any assumptions you have made. **[+296 kJ mol^{-1}]**

Checkpoints for Section 4

- To remember the definition of Hess' Law and apply accordingly when drawing energy cycle or energy level diagram.
- To make use of the following formulae and apply accordingly:

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

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

  (iii) $\Delta H_r^{\ominus} = \sum \text{BE}(\text{bonds broken}) - \sum \text{BE}(\text{bonds formed})$

- To explain why enthalpy change of reaction differs from the one derived from **(iii)** (for example: bond energies are average values)

5 Definitions of Enthalpy Changes of Reactions (Part II)

**** NOT IN H1 Chemistry Syllabus**

Learning Outcome:

(c) explain and use the terms:
  (i) *enthalpy change of reaction* and *standard conditions*, with particular reference to: atomisation
  (iii) *lattice energy* (ΔH negative, i.e. gaseous ions to solid lattice)

(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)

5.1 Standard enthalpy change of atomisation, $\Delta H^{\ominus}_{\text{at}}$

The standard enthalpy change of atomisation, $\Delta H^{\ominus}_{\text{at}}$, for an **element** is the **energy required** to form **1 mole of gaseous atoms** from the **element**, all in their **standard states**, at a specified temperature, usually 298 K.	The standard enthalpy change of atomisation, $\Delta H^{\ominus}_{\text{at}}$, for a **compound** is the **energy required** to form **gaseous atoms** from the **1 mole of the compound**, all in their **standard states**, at a specified temperature, usually 298 K.

E.g.

$Na(s) \rightarrow$ **$Na(g)$** $\quad \Delta H^{\ominus}_{\text{at}} = +107\ \text{kJ mol}^{-1}$

$\frac{1}{2}Br_2(l) \rightarrow$ **$Br(g)$** $\quad \Delta H^{\ominus}_{\text{at}} = +112\ \text{kJ mol}^{-1}$

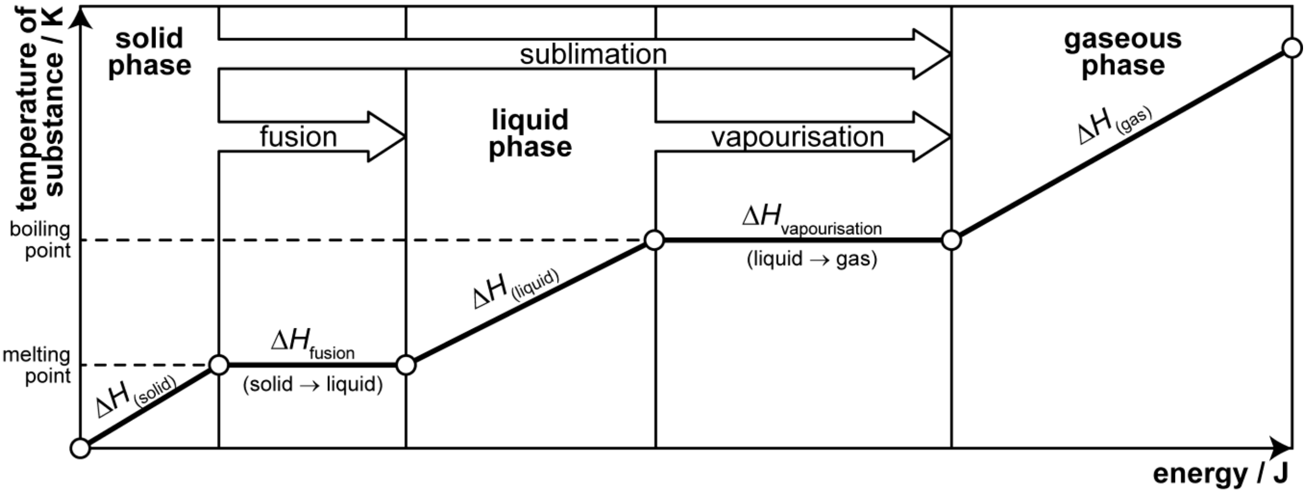
$\frac{1}{2}H_2(g) \rightarrow$ **$H(g)$** $\quad \Delta H^{\ominus}_{\text{at}} = +218\ \text{kJ mol}^{-1}$

E.g.

$CH_4(g) \rightarrow$ **$C(g)$** + **$4H(g)$** $\quad \Delta H^{\ominus}_{\text{at}} = +1661.5\ \text{kJ mol}^{-1}$

What are some elements with $\Delta H = 0\ \text{kJ mol}^{-1}$?

The enthalpy change of atomisation is always **positive**, as atomisation involves **bond breaking**.


sublimation versus fusion and vapourisation

If the standard state of an element is a monoatomic solid, atomisation will involve raising the temperature to melting point, the melting of the element $\left(\Delta H^{\ominus}_{\text{fus}}\right)$, raising of the temperature to boiling point, and then vaporisation $\left(\Delta H^{\ominus}_{\text{vap}}\right)$. For a monoatomic solid that undergoes sublimation, $\Delta H^{\ominus}_{\text{at}}$ is the same as the standard enthalpy change of sublimation $\left(\Delta H^{\ominus}_{\text{sub}}\right)$.

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

$$\Delta H^{\ominus}_{\text{at}} = \Delta H^{\ominus}_{\text{fus}} + \Delta H^{\ominus}_{\text{vap}} + c_{\text{m(solid)}}\Delta T + c_{\text{m(liquid)}}\Delta T$$

where c_{m} is the molar heat capacity

If the standard state of an element is a polyatomic solid, atomisation will involve the melting of the element $\left(\Delta H^{\ominus}_{\text{fus}}\right)$, evaporation $\left(\Delta H^{\ominus}_{\text{vap}}\right)$, and then breaking of the covalent bonds (BE).

E.g. $\frac{1}{2}I_2(s) \rightarrow I(g)$ $\quad \Delta H^{\ominus}_{\text{at}} = \frac{1}{2}\Delta H^{\ominus}_{\text{sub}} + \frac{1}{2}\text{BE}(\text{I—I})$ [Note: $I_2(s)$ sublimes to give $I_2(g)$]

$\frac{1}{4}P_4(s) \rightarrow P(g)$ $\quad \Delta H^{\ominus}_{\text{at}} = \frac{1}{4}\Delta H^{\ominus}_{\text{fus}} + \frac{1}{4}\Delta H^{\ominus}_{\text{vap}} + \frac{6}{4}\text{BE}(\text{P—P})$ [see **Example 5A**]

Note: Do not confuse atomisation with vaporisation!
Vaporisation is to bring an element or a compound from the liquid to the gaseous state (boiling). For substances with simple molecular structures, vaporisation does not break any covalent bonds, only overcome intermolecular forces of attraction.

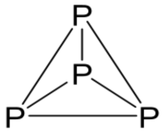
E.g. $Br_2(l) \rightarrow Br_2(g)$ $\quad \Delta H_{\text{vaporisation}}$

$\frac{1}{2}Br_2(l) \rightarrow Br(g)$ $\quad \Delta H_{\text{atomisation}}$

Compare the equations for the enthalpy change of atomisation of gaseous diatomic molecules such as Cl_2 and the bond energy of Cl_2. What is the relationship between the enthalpy changes?

Example 5A

Phosphorus exists as P_4 molecule with the following structure.



Use the following data to calculate the bond energy of P–P bond.

Standard enthalpy change of formation of $P_4(g)$ = +58.91 kJ mol^{-1}
Standard enthalpy change of atomisation of phosphorus = +314.4 kJ mol^{-1}

$$\begin{tikzcd}
P_4(s) \arrow[rr, "{4 \times \Delta H^{\ominus}_{\text{at}} = 4(+314.4)}"] \arrow[dr, dashed, dash] & & 4P(g) \\
& P_4(g) \arrow[ur, dashed] &
\end{tikzcd}$$

By Hess' Law,

$\therefore$ BE(P–P) =

5.2 Lattice Energy, LE

Lattice energy of an ionic compound is the **energy released** when **1 mole of solid ionic compound** is formed from its **constituent gaseous ions**.

E.g. $Na^+(g) + Br^-(g) \rightarrow \mathbf{NaBr(s)}$ LE = –742 kJ mol^{-1}
$Mg^{2+}(g) + 2Cl^-(g) \rightarrow \mathbf{MgCl_2(s)}$ LE = –2375 kJ mol^{-1}

Lattice energy is **always negative** as energy is released in **forming electrostatic forces of attraction** between oppositely charged ions (*i.e.* ionic bonds). The reverse of the above process, the breaking down of the solid crystal lattice to its gaseous ions is lattice dissociation energy and is always positive.

Lattice energy is a measure of the strength of ionic bonding and the stability of the ionic compounds. The **more exothermic** the lattice energy, the **stronger** the ionic bonding and the **more stable** the ionic compound.

5.2.1 Factors affecting lattice energy

The magnitude of lattice energy depends on:

- the **charges** on the ions
- the **sizes** of ions or inter–ionic distance

These two factors can be combined into the following expression.

$$\boxed{|\mathrm{LE}| \propto \left|\frac{q_+ \times q_-}{r_+ + r_-}\right|}$$

q^+ and q^- are the **charges** on the cation and anion respectively.

Note: This term is a *multiplication* of the charges.

$(r_+ + r_-)$ is the **inter-ionic distance** between the two ions in the lattice.

Note: This term is an *addition* of the two ionic radii.

compound	q_+	q_-	r_+ / nm	r_- / nm	LE / kJ mol^{-1}
NaCl	+1	–1	0.095	0.181	–776
NaBr	+1	–1	0.095	0.196	–742
MgCl_2	+2	–1	0.065	0.181	–2375

NaCl and NaBr have the **same cation**. The Br^- ion has the **same charge** but **larger ionic radius** than Cl^- ion. Since $|\mathbf{LE}| \propto \left|\frac{q_+ \times q_-}{r_+ + r_-}\right|$, LE of NaBr is **less exothermic** than that of NaCl.

MgCl_2 and NaCl have the **same anion**. Mg^{2+} has a **higher charge** and **smaller ionic radius** than Na^+. Since $|\mathbf{LE}| \propto \left|\frac{q_+ \times q_-}{r_+ + r_-}\right|$, LE of MgC$l_2$ is **more exothermic** than that of NaCl.

> ***Note:*** The terms ‘more or less exothermic/ endothermic’ or ‘magnitude of lattice energies increases /decreases’ should be used when comparing lattice energies of different compounds and NOT ‘larger / smaller’.

5.2.2 Experimental versus theoretical lattice energies

Lattice energies can be either determined from **experimental data** using the Born-Haber cycle (See Section 6) or calculated based on a **model** which assumes that the compound is **completely ionic**.

There is always a difference between the experimental and theoretical lattice energies, which suggests that no compound is completely ionic. A small difference shows that the compound is predominantly ionic, while a large difference shows that there is **covalent character in the ionic compound** (Refer to Section 6 of Chemical Bonding). This is most apparent when a cation with a high charge density (high polarising power) distorts an anion with a large electron cloud (high polarisability).

compound	theoretical LE / kJ mol^{-1}	experimental LE / kJ mol^{-1}
$CsCl$	–657	–659
$MgCl_2$	–2326	–2375
AgF	–953	–967
AgI	–808	–889

There is good agreement between the theoretical and experimental lattice energy for $CsCl$ but the discrepancy is greater for $MgCl_2$. Mg^{2+} has a **higher charge** and **smaller ionic radius** than Cs^+. Mg^{2+} thus has **higher charge density** and **greater polarising power** than Cs^+. Hence, Mg^{2+} distorts the electron cloud of Cl^- to a larger extent, resulting in **greater covalent character** in $MgCl_2$.

There is also close agreement between the theoretical and experimental lattice energy for AgF but not for AgI. This is because I^- has a **larger ionic radius** than F^- and is hence **more polarisable**. Thus Ag^+ polarises the electron cloud of I^- to a larger extent, resulting in **greater covalent character** in AgI.

In both cases of $MgCl_2$ and AgI, bonds are **strengthened** due to the covalent character in the ionic bond, hence the experimental lattice energy is **more exothermic** than the theoretical lattice energy.

5.3 Ionisation Energy, IE

The **first** ionisation energy is the **energy required** to remove **1 mole of electrons** from **1 mole of gaseous atoms** to form **1 mole of singly charged gaseous cations**.

E.g. First ionisation energy of magnesium:

$Mg(g) \rightarrow Mg^+(g) + e^-$ 1st IE (Mg) = +736 kJ mol^{-1}

The **second** ionisation energy is the **energy required** to remove **1 mole of electrons** from **1 mole of singly charged gaseous cations** to form **1 mole of doubly charged gaseous cations**.

E.g. Second ionisation energy of magnesium:

$Mg^+(g) \rightarrow Mg^{2+}(g) + e^-$ 2nd IE (Mg) = +1450 kJ mol^{-1}

IE is **always positive** since energy is required to remove an electron (endothermic process) which is being attracted by the nucleus.

The further removal of electrons requires more energy: There is a decrease in shielding effect as electrons are removed. Since nuclear charge remains the same, hence effective nuclear charge increases, leading to an increase in electrostatic forces of attraction between the nucleus and the remaining electrons. (Refer to Section 5 of Atomic Structure)

E.g. $\mathrm{A}\ell(\mathrm{g}) \rightarrow \mathrm{A}\ell^{+}(\mathrm{g}) + e^{-}$ 1st IE = +577 kJ mol^{-1}
$\mathrm{A}\ell^{+}(\mathrm{g}) \rightarrow \mathrm{A}\ell^{2+}(\mathrm{g}) + e^{-}$ 2nd IE = +1820 kJ mol^{-1}
$\mathrm{A}\ell^{2+}(\mathrm{g}) \rightarrow \mathrm{A}\ell^{3+}(\mathrm{g}) + e^{-}$ 3rd IE = +2740 kJ mol^{-1}

5.4 Electron Affinity, EA

**** NOT IN H1 Chemistry Syllabus**

The first electron affinity is the **energy change** when **1 mole of electrons** is added to **1 mole of gaseous atoms** to form **1 mole of singly charged gaseous anions**.

E.g. First electron affinity of oxygen:
$\mathrm{O}(\mathrm{g}) + e^{-} \rightarrow \mathrm{O}^{-}(\mathrm{g})$ 1st EA = –141 kJ mol^{-1}

1st EA is usually **exothermic** as more energy is released from the attraction between the nucleus and the electron added, than that required to overcome the repulsion between the electron added and those electrons already present in the atom.

The second electron affinity is the **energy change** when **1 mole of electrons** is added to **1 mole of singly charged gaseous anions** to form **1 mole of doubly charged gaseous anions**.

E.g. Second electron affinity of oxygen:
$\mathrm{O}^{-}(\mathrm{g}) + e^{-} \rightarrow \mathrm{O}^{2-}(\mathrm{g})$ 2nd EA = +844 kJ mol^{-1}

2nd EA, on the other hand, is usually **endothermic** as more energy is required to overcome repulsion between the added electron and the electrons that are already present in the monoanion, compared to the energy that is released from attraction between the nucleus and the electron added.

Example 5B

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

$$\mathrm{Na}(\mathrm{s}) \xrightarrow{\Delta H} \mathrm{Na}^{+}(\mathrm{g}) + e^{-}$$

is equal to

A the 1st IE of Na.

B the sum of the 1st IE and the EA of Na.

C the sum of the enthalpy change of atomisation and the 1st IE of Na.

D the sum of the enthalpy change of atomisation and the EA of Na.

Checkpoints for Section 5

- To remember the definitions for enthalpy change of *atomisation, lattice energy, ionisation energy* and electron affinity and apply them accordingly.
- To know how to calculate enthalpy change of *atomisation* of gaseous diatomic molecules such as O_2(g) using bond energy (*i.e.* $\Delta H^{\ominus}_{\text{at}}$ (X_2) = ½ B.E.(X–X))
- To know how to explain qualitatively the effect of charges and of ionic radii on the numerical magnitude of lattice energy $\left(i.e.\ |\text{LE}| \propto \left| \dfrac{q_+ \times q_-}{r_+ + r_-} \right| \right)$

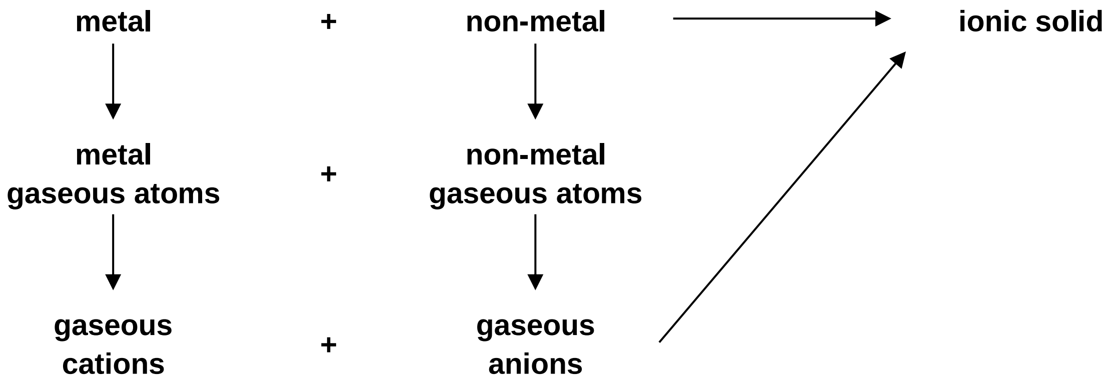
6 Born-Haber Cycle

**** NOT IN H1 Chemistry Syllabus**

Learning Outcome:
(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)
(ii) the formation of a simple ionic solid

Lattice energy cannot be determined directly as solid ionic compounds cannot be formed by reacting the constituent gaseous ions together. It can be obtained by calculation using other known enthalpy changes of reactions by the **Born-Haber cycle**. The cycle gives the relationship between the standard enthalpy change of formation of the ionic solid and the various enthalpy changes leading to its formation.

A **Born-Haber cycle** involves the following stages:



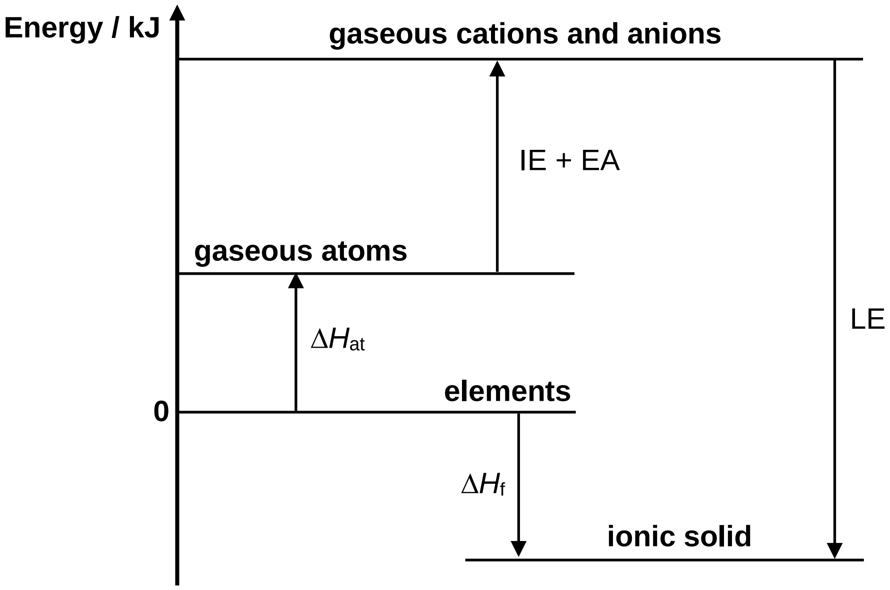
E.g. Formation of NaCl(s)

$$\begin{tikzcd}
\mathbf{Na(s)} \arrow[d, "\Delta H_1^\ominus"'] & + & \mathbf{\tfrac{1}{2}Cl_2(g)} \arrow[d, "\Delta H_2^\ominus"] \arrow[rr, "\Delta H_f^\ominus"] & & \mathbf{NaCl(s)} \\
Na(g) \arrow[d, "\Delta H_3^\ominus"'] & & Cl(g) \arrow[d, "\Delta H_4^\circ"] & & \\
Na^+(g) & + & Cl^-(g) \arrow[uurr, "\Delta H_5^\ominus\ (\text{lattice energy})"'] & &
\end{tikzcd}$$

By Hess' Law, $\Delta H_f^\ominus = \Delta H_1^\ominus + \Delta H_2^\ominus + \Delta H_3^\ominus + \Delta H_4^\ominus + \Delta H_5^\ominus$

where $\Delta H_1^\ominus$ = enthalpy change of atomisation of Na
$\Delta H_2^\ominus$ = enthalpy change of atomisation of Cl
$\Delta H_3^\ominus$ = first ionisation energy of Na
$\Delta H_4^\ominus$ = first electron affinity of Cl
$\Delta H_5^\ominus$ = lattice energy

A Born-Haber cycle is usually presented in the form of an **energy level diagram** where the 'zero enthalpy point' refers to the elements in the standard states.



How to draw a Born-Haber cycle

1. Anchor the Born-Haber cycle on two enthalpy change equations: **enthalpy change of formation** and **lattice energy** of the ionic compound.

   e.g. ΔH_f of **Na*Cl* (s)** & LE of **Na*Cl***

   ΔH_f of **Na*Cl* (s)**: $Na(s) + \frac{1}{2} Cl_2(g) \rightarrow$ **$NaCl(s)$**
   LE of **Na*Cl* (s)**: $Na^+(g) + Cl^-(g) \rightarrow$ **$NaCl(s)$**

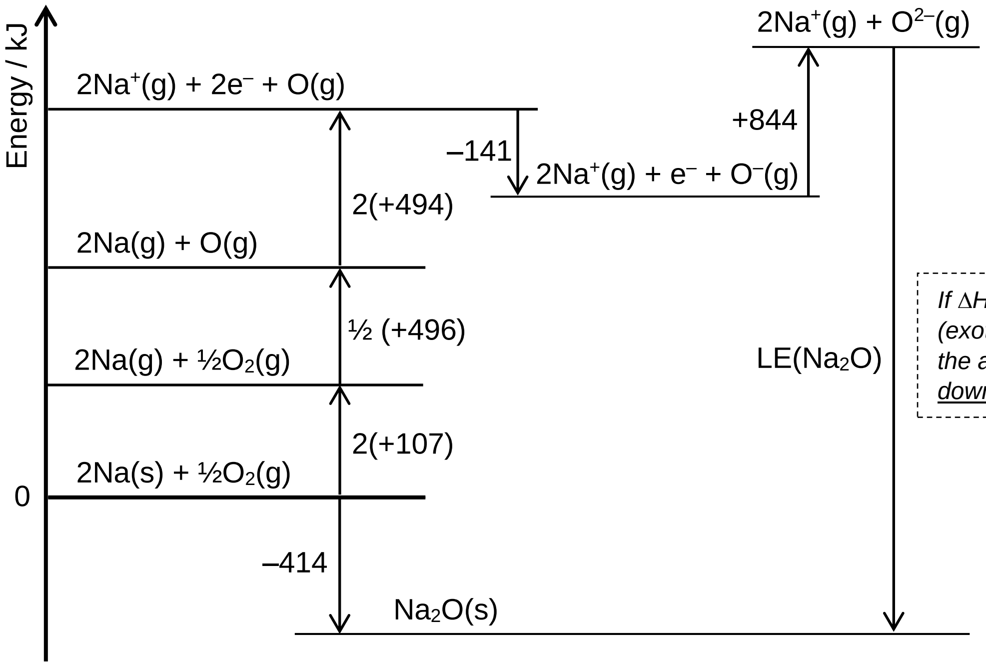
2. Construct the cycle, starting from the elements at the zero enthalpy point. Each level in the cycle should represent only **one** chemical change.
3. Complete the cycle by filling in the remaining ΔH (moving from elements → ionic compound).
4. Fill in the ΔH values from data given.
   Note: NOT all values may be given.
5. Apply Hess' Law to calculate ΔH of the unknown reaction.

Worked Example 6A

Construct a Born–Haber cycle for the formation of Na_2O from its elements and calculate the lattice energy of Na_2O from the following data and from the *Data Booklet*.

	ΔH / kJ mol^{-1}
enthalpy change of formation of $Na_2O(s)$	–414
enthalpy change of atomisation of sodium	+107
first electron affinity of oxygen	–141
second electron affinity of oxygen	+844

From the *Data Booklet*,
$\Delta H_{at}(O_2) = \frac{1}{2}BE(O{=}O)$
$= \frac{1}{2}(496)$ kJ mol^{-1}
1st IE of Na = +494 kJ mol^{-1}



If ΔH is negative (exothermic), we draw the arrow pointing down and vice versa.

By Hess' Law,

$-414 = 2(107) + \frac{1}{2}(496) + 2(494) + (-141) + 844 + LE(Na_2O)$

$-414 = 2153 + LE(Na_2O)$

$\therefore LE(Na_2O)$ **= <u>–2567 kJ mol^{-1}</u>**

LE is always **negative**.

Self Check 6A

Construct a Born–Haber cycle for the formation of $CaCl_2$ from its elements and calculate its lattice energy from the following data and relevant data from the *Data Booklet*.

ΔH_{at} of Ca = +178 kJ mol^{-1}; ΔH_f of $CaCl_2$ = –796 kJ mol^{-1}; 1st EA of Cl = –349 kJ mol^{-1};

[–2260 kJ mol^{-1}]

Checkpoints for Section 6

– To construct energy level diagram and energy cycle involving ionic compounds using the thermochemical equations derived from enthalpy changes covered in section 2 and 5.

– To apply Hess Law to calculate relevant enthalpy change.

7 Standard Enthalpy Changes of Hydration and Solution

**** NOT IN H1 Chemistry Syllabus**

Learning Outcome:
(c) explain and use the terms:
  (i) *enthalpy change of reaction* and *standard conditions*, with particular reference to: hydration; solution
(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)
  (ii) the formation of a simple ionic solid and of its aqueous solution

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

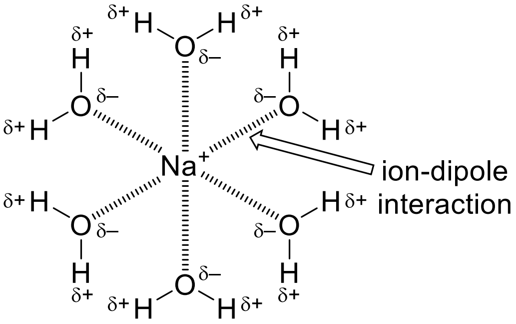
The standard enthalpy change of hydration, $\Delta H^{\ominus}_{\text{hyd}}$, of an ion is the **energy released** when **1 mole of free gaseous ions in its standard state** is **dissolved in water** to give a solution of **infinite dilution**, at a specified temperature, usually 298 K.

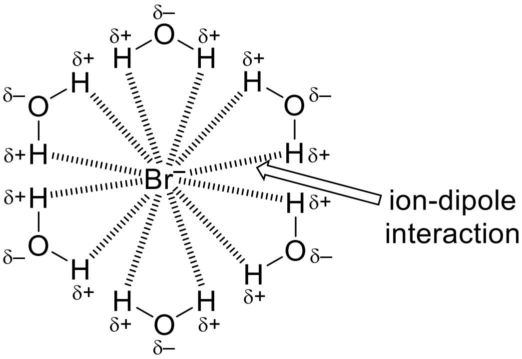
E.g. **Na^+(g)** + aq → Na^+(aq) $\Delta H^{\ominus}_{\text{hyd}} = -405$ kJ mol^{-1}

Br^-(g) + aq → Br^-(aq) $\Delta H^{\ominus}_{\text{hyd}} = -337$ kJ mol^{-1}

An infinitely dilute solution is one where there is a sufficiently large excess of water that adding any more does not cause any further heat to be absorbed or evolved.

$\Delta H^{\ominus}_{\text{hyd}}$ is always exothermic (regardless of anion or cation) as heat is evolved in forming ion–dipole interactions between the ions and the polar water molecules.





The magnitude of $\Delta H^{\ominus}_{\text{hyd}}$ of an ion depends on its **charge density**:

$\boxed{\left|\Delta H^{\ominus}_{\text{hyd}}\right| \propto \left|\frac{q}{r}\right|}$ where *q*: ionic charge and *r*: ionic radius

The **higher the charge density** of the ion, the **stronger the ion–dipole interaction** and $\Delta H^{\ominus}_{\text{hyd}}$ will be **more exothermic**.

E.g. Na^+(g) + aq → Na^+(aq) $\Delta H^{\ominus}_{\text{hyd}} = -405$ kJ mol^{-1} $r_{Na^+} = 0.095$ nm

Mg^{2+}(g) + aq → Mg^{2+}(aq) $\Delta H^{\ominus}_{\text{hyd}} = -1920$ kJ mol^{-1} $r_{Mg^{2+}} = 0.065$ nm

7.2 Standard enthalpy change of solution, $\Delta H^{\ominus}_{sol}$

The standard enthalpy change of solution, $\Delta H^{\ominus}_{sol}$, of a substance is the **energy change** when **1 mole of substance in its standard state** is **completely dissolved in a solvent** to give a solution of **infinite dilution**, at a specified temperature, usually 298 K.

E.g. **$NaCl(s)$** $\rightarrow Na^{+}(aq) + Cl^{-}(aq)$ $\Delta H^{\ominus}_{sol} = +3.9$ kJ mol^{-1}

$MgCl_2(s)$ $\rightarrow Mg^{2+}(aq) + 2Cl^{-}(aq)$ $\Delta H^{\ominus}_{sol} = -160$ kJ mol^{-1}

The solute is usually an **ionic compound** while the solvent is usually **water**.

$\Delta H^{\ominus}_{sol}$ can be **either positive or negative**.

If $\Delta H^{\ominus}_{sol}$ is highly positive, the salt is relatively insoluble in water.

E.g. AgC*l* $\Delta H^{\ominus}_{sol} = +65.7$kJ mol^{-1}

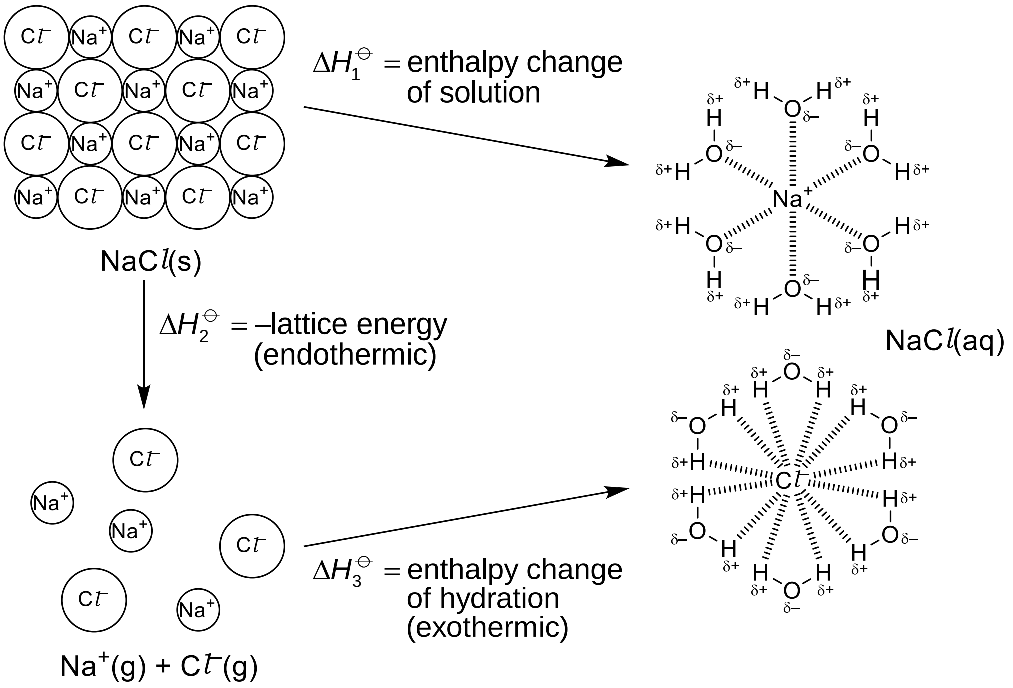
If $\Delta H^{\ominus}_{sol}$ is negative, the salt is likely to be soluble in water

E.g. NaBr $\Delta H^{\ominus}_{sol} = -0.6$ kJ mol^{-1}

However, there are salts with positive $\Delta H^{\ominus}_{sol}$ that are soluble e.g. NaC*l*, KC*l*, NH_4NO_3 due to positive entropy change (Refer to Section 9).

7.3 Relationship between lattice energy, enthalpy change of hydration and enthalpy change of solution

The dissolution of an ionic solid (e.g. NaC*l*) happens in two stages.



1) *Breaking up the solid ionic lattice to form isolated gaseous ions.* $\left(\Delta H_2^{\ominus}\right)$

Process is **endothermic** (overcoming ionic bonding) and the enthalpy change is '**–LE**'.

$MX(s) \rightarrow M^+(g) + X^-(g)$ $\Delta H_2^{\ominus} = -\text{LE}$ (lattice dissociation energy)

2) *Hydration of the gaseous ions.* $\left(\Delta H_3^{\ominus}\right)$

Process is **exothermic** (forming ion-dipole interactions between ion and water).

$M^+(g) + X^-(g) + aq \rightarrow M^+(aq) + X^-(aq)$ $\Delta H_3^{\ominus} = \Delta H_{\text{hyd}}^{\ominus}\left(M^+\right) + \Delta H_{\text{hyd}}^{\ominus}\left(X^-\right)$

The standard enthalpy change of solution can be obtained by calculation using standard enthalpy change of hydration and lattice energy.

By applying Hess' Law,

enthalpy change of solution = enthalpy changes of hydration − lattice energy

$$\boxed{\begin{aligned}\boldsymbol{\Delta H_{\text{sol}}^{\ominus}} &= \mathbf{-LE + \Delta H_{\text{hyd}}^{\ominus}(cation) + \Delta H_{\text{hyd}}^{\ominus}(anion)} \\ &= \mathbf{\left|LE\right| - \left|\Delta H_{\text{hyd}}^{\ominus}(cation) + \Delta H_{\text{hyd}}^{\ominus}(anion)\right|}\end{aligned}}$$

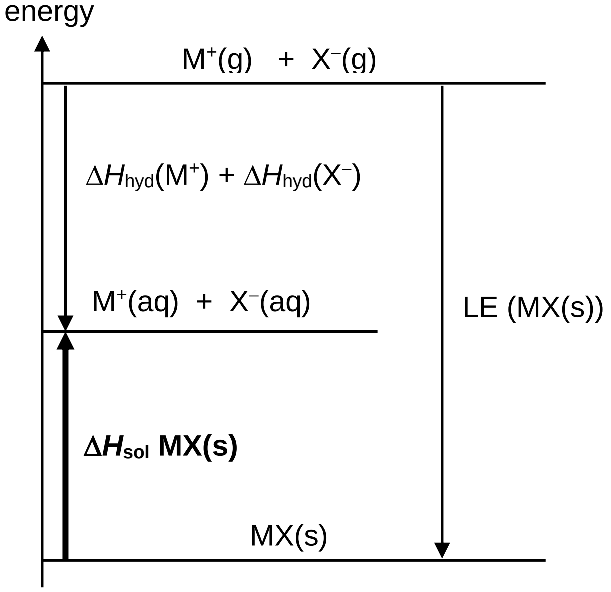
If $\left|\text{LE}\right| > \left|\Delta H_{\text{hyd}}^{\ominus}\right| \Rightarrow \Delta H_{\text{sol}}^{\ominus} > 0$ (endothermic)

If $\left|\text{LE}\right| < \left|\Delta H_{\text{hyd}}^{\ominus}\right| \Rightarrow \Delta H_{\text{sol}}^{\ominus} < 0$ (exothermic)

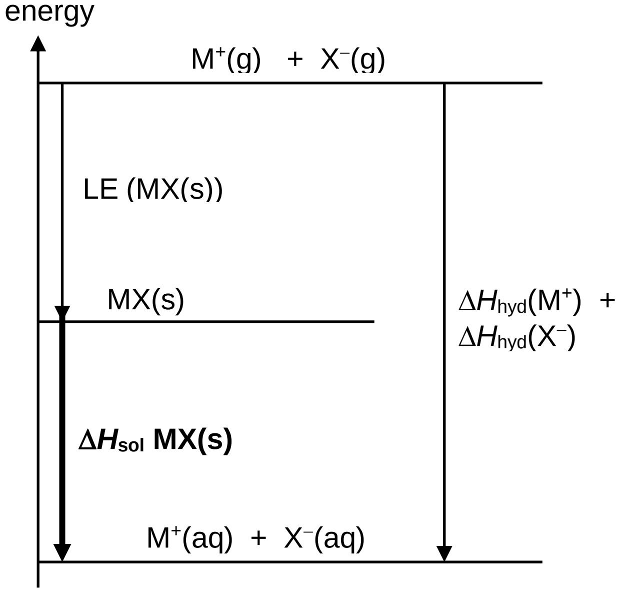
The relationship between lattice energy, enthalpy changes of hydration and enthalpy change of solution can also be represented using energy level diagrams.

E.g. For an ionic solid MX,

If $\boldsymbol{\Delta H_{\text{sol}}^{\ominus} > 0}$



If $\boldsymbol{\Delta H_{\text{sol}}^{\ominus} < 0}$



Example 7A

(a) By means of an appropriate energy cycle, calculate the enthalpy change of hydration of the chloride ion using the data provided.

enthalpy change of solution of $\mathrm{NaC}\mathit{l}(s)$	$+5$ kJ $\mathrm{mol^{-1}}$
enthalpy change of hydration of $\mathrm{Na^+}(aq)$	-390 kJ $\mathrm{mol^{-1}}$
lattice energy of $\mathrm{NaC}\mathit{l}(s)$	-776 kJ $\mathrm{mol^{-1}}$

$$\begin{tikzcd}
\mathrm{NaC}\mathit{l}(s) \arrow[rr] \arrow[dr, dashed] & & \mathrm{Na^+}(aq) + \mathrm{C}\mathit{l}^-(aq) \\
& \mathrm{Na^+}(g) + \mathrm{C}\mathit{l}^-(g) \arrow[ur, dashed] &
\end{tikzcd}$$

Since the question did not specific the type of energy cycle to be drawn, we can draw either an energy cycle or an energy level diagram.

By Hess' Law,

$\Delta H_{\mathrm{sol}} = -\mathrm{LE} + \Delta H_{\mathrm{hyd}}(\mathrm{Na^+}) + \Delta H_{\mathrm{hyd}}(\mathrm{C}\mathit{l}^-)$

$\Delta H_{\mathrm{hyd}}(\mathrm{C}\mathit{l}^-) =$

ΔH_{hyd} is always **negative**.

(b) The enthalpy change of hydration of iodide ion was found to be -308 kJ $\mathrm{mol^{-1}}$. Comment on the difference between this value and the value found in **(a)**.

$$\left|\Delta H^{\ominus}_{\mathrm{hyd}}\right| \propto \left|\frac{q}{r}\right|$$

$\mathrm{I^-}$ has the **<u>same charge</u>** but a **<u>larger ionic radius</u>** than $\mathrm{C}\mathit{l}^-$ so the **<u>ion–dipole attractions</u>** between $\mathrm{I^-}$ ion and the water molecules are **<u>weaker</u>**. Hence, enthalpy change of hydration of $\mathrm{I^-}$ is **<u>less exothermic</u>** than that of $\mathrm{C}\mathit{l}^-$.

Checkpoints for Section 7

- To remember the definitions for *enthalpy change of solution*, *hydration energy* and apply them accordingly.
- To construct energy cycle that involves enthalpy change of solution, hydration energy and lattice energy to derive the equation: $\Delta H^{\ominus}_{\mathrm{sol}} = -\mathrm{LE} + \Delta H^{\ominus}_{\mathrm{hyd}}(\text{cation}) + \Delta H^{\ominus}_{\mathrm{hyd}}(\text{anion})$.
- To explain qualitatively the effect of charges and ionic radii on the numerical magnitude of hydration energy $\left(\left|\Delta H^{\ominus}_{\mathrm{hyd}}\right| \propto \left|\frac{q}{r}\right|\right)$.

8 Entropy

**** NOT IN H1 Chemistry Syllabus**

Learning Outcome:
(g) explain and use the term entropy
(h) discuss the effects on the entropy of a chemical system by the following:
  (i) change in temperature
  (ii) change in phase
  (iii) change in the number of particles (especially for gaseous systems)
  (iv) mixing of particles
  [quantitative treatment is **not** required]
(i) predict whether entropy change for a given process or reaction is positive or negative

8.1 Spontaneous processes

From our experience, there are chemical reactions that take place on their own. For example, an iron nail rusts slowly when left to stand. Some physical processes also take place on their own, such as the diffusion of a drop of dye in a beaker of water to form a uniformly coloured solution. Such processes can be described as **spontaneous**. **A spontaneous process is one that takes place naturally in the direction stated.** The change occurs **without a need for continuous input of energy from outside the system**.

It is useful to predict if a reaction will occur spontaneously when reactants are brought together under a certain set of conditions. When we think of spontaneous process, many of the examples we have seen, such as combustion, are exothermic processes. However, there are endothermic reactions which are also spontaneous. For example, crystalline N_2O_5 is unstable and will explode spontaneously:

$$N_2O_5(s) \rightarrow 2NO_2(g) + \tfrac{1}{2}O_2(g) \qquad \Delta H = +109.5 \text{ kJ mol}^{-1}$$

Many soluble salts (e.g. $NaCl$, KCl, NH_4NO_3) dissolve endothermically and spontaneously.

$$KCl(s) \rightarrow KCl(aq) \qquad \Delta H = +25.7 \text{ kJ mol}^{-1}$$

The tendency of systems to move towards lower energy is not sufficient to predict whether a chemical change is spontaneous or not. Hence, **the sign of ΔH by itself does not predict if a reaction is spontaneous**.

If we examine the two examples above, they have one major feature in common: the chemical species (atoms, molecules, or ions) have more freedom of motion after the change. The particles have a **wider range of energy of motion** (kinetic energy) which means the **energy has become more dispersed or distributed**.

When solid N_2O_5 changes to gaseous NO_2 and O_2, the motion of the molecules in the solid state is restricted while the gaseous particles have more freedom of motion. Thus the energy of motion is more distributed after the change. Similarly, dissolving a salt separates the ions in the crystalline solid. The ions in the aqueous state have greater freedom of motion (or are more disordered) and their energy of motion is more distributed.

Hence, a change in the freedom of motion of particles in a system, that is, the distribution of their energy of motion, is one key factor affecting the direction of a spontaneous process. This factor is known as **entropy change**.

8.2 Entropy and entropy changes

Entropy, S, is a measure of the **randomness or disorder** in a system, reflected in the number of ways that the **energy** of a system can be distributed (or dispersed) through the motion of its particles. The unit for entropy is **J mol^{-1} K^{-1}**.

Many chemical reactions or physical processes are accompanied by a **change in entropy, ΔS**.

$$\Delta S = S_{\text{final}} \text{ (entropy of final state)} - S_{\text{initial}} \text{ (entropy of initial state)}$$

If a reaction or process results in **more ways to disperse or distribute the energy**, entropy **increases**, a **positive** entropy change occurs ($\Delta S > 0$).
If a reaction or process results in **fewer ways to disperse or distribute the energy**, entropy **decreases**, a **negative** entropy change occurs ($\Delta S < 0$).

Whether or not a reaction or process will be spontaneous is governed by the **Second Law of Thermodynamics** which states that the **entropy of the universe (system and surroundings) increases in a spontaneous change**.

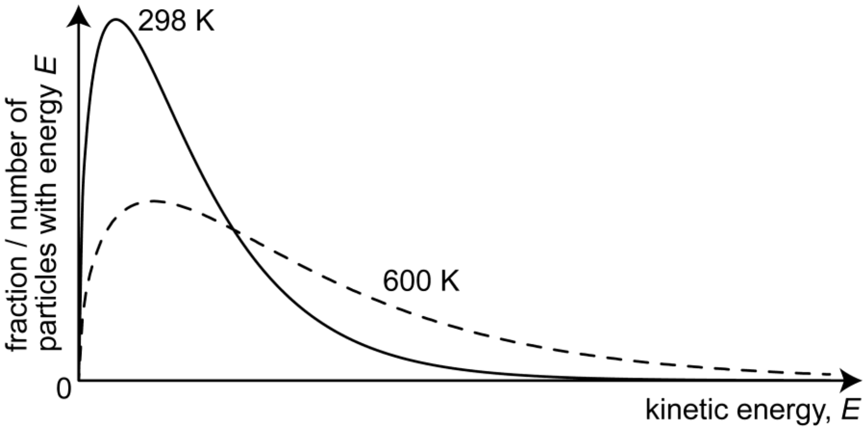
We shall first look at some factors that affect the change in entropy of a system before we consider how we can apply the Second Law of Thermodynamics to predict whether a given reaction or process is spontaneous.

8.2.1 Factors affecting Entropy of a Chemical System

(1) Change in temperature

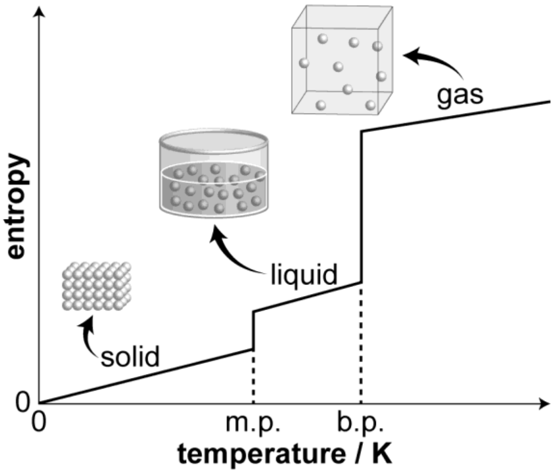
The Maxwell Boltzmann energy distribution curve shows how energy is distributed in a system for a particular temperature.

As temperature increases, the **average kinetic energy of the particles** and the **range of energies increase**. This is reflected in the broadening of the curve as the energy distribution of the particles becomes more spread out. There are thus **more ways in which the energy can be distributed among the particles** in the hotter system. Hence, **entropy increases** ($\Delta S > 0$).



*You will learn more about the Maxwell-Boltzmann distribution curve under **Topic 6: Reaction Kinetics**.*

(2) Change in phase



For the same amount of a substance, entropy of solid < liquid << gas

In a solid, the particles vibrate about their fixed positions. The energy is thus the least dispersed and the solid has the lowest entropy.

In a gas, the particles are the most randomly arranged and are able to move freely and possess a wide range of kinetic energy. There are many ways that the energy of the particles is distributed, thus it has the highest entropy.

When a solid melts or sublimes, or when a liquid vaporises, the particles in the final state **move more freely** and are **more disordered** than in the initial state. This **increases the number of ways that the particles and the energy can be distributed**. Hence, there is an **increase in entropy** ($\Delta S > 0$).

(3) Change in the number of particles (especially for gaseous systems)

When a chemical reaction results in an increase in the number of gas particles, **the number of ways that the particles and the energy can be distributed increases**. Hence, there is an **increase in entropy** ($\Delta S > 0$).

For example, many decomposition reactions result in an increase in the number of gas particles, hence an increase in entropy.

$N_2O(g) \rightarrow N_2(g) + ½O_2(g)$ no. of **gas** particles increase hence $\Delta S > 0$
$2NaN_3(s) \rightarrow 2Na(s) + 3N_2(g)$ no. of **gas** particles increase hence $\Delta S > 0$

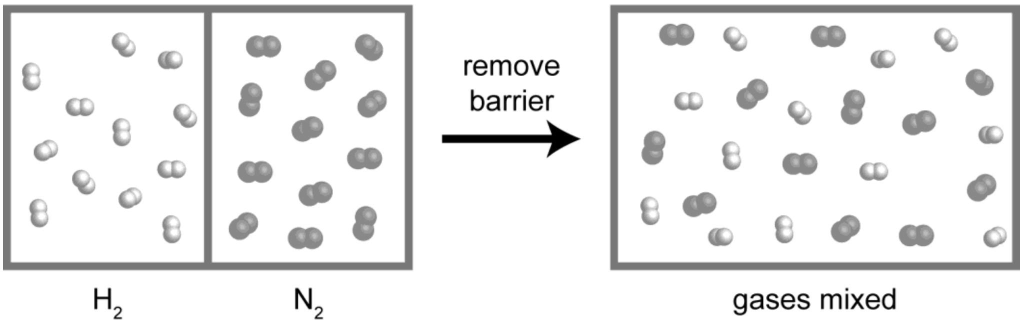
If there is **no change** in the number of gas particles, entropy may increase or decrease but the magnitude of ΔS will be relatively **small**. For example,

$N_2(g) + O_2(g) \rightarrow 2NO(g)$ $\Delta S \approx 0$

(4) Mixing of particles

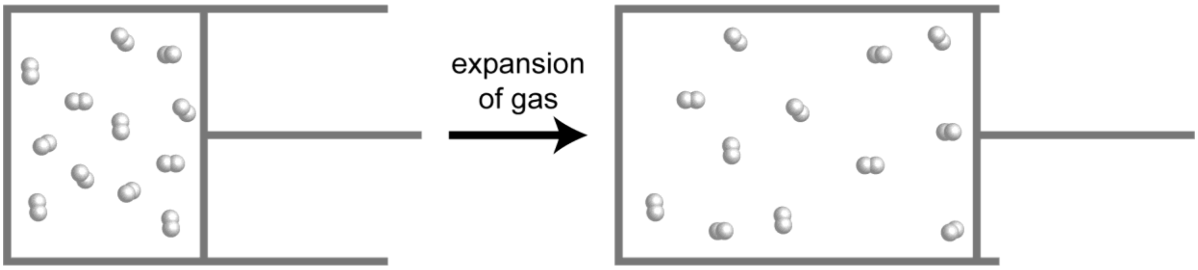
(a) Mixing of gas particles (assuming ideal gas behaviour)

Consider the mixing of equimolar H_2 gas and N_2 gas at **constant pressure** as shown below. Before mixing, each gas has the same volume and pressure. After the barrier is removed, each gas expands to occupy the whole container and hence the volume of each gas doubles. The partial pressure of each gas is reduced by half but total pressure remains constant.

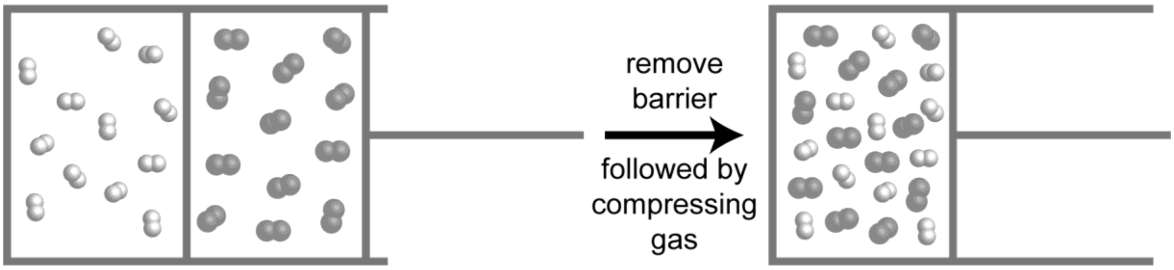


As the **volume available for each gas** (H_2 and N_2) **is increased**, there are **more ways to distribute the particles and their energy**. Thus, **entropy increases** ($\Delta S > 0$).

Similarly, when a gas **expands at constant pressure**, the **volume available for distribution of the particles increases**. **Entropy increases** as there are **more ways that the particles and the energy can be distributed**.



When gases are mixed at **constant volume**, the volume available to distribute the particles of each gas is the same. Hence the **entropy does not change** ($\Delta S = 0$).



(b) Mixing of liquid particles

When liquids with **similar polarities** (e.g. benzene and hexane) are mixed together, **entropy increases**. This is because **total volume increases** and hence there are **more ways to distribute the particles and their energy**.

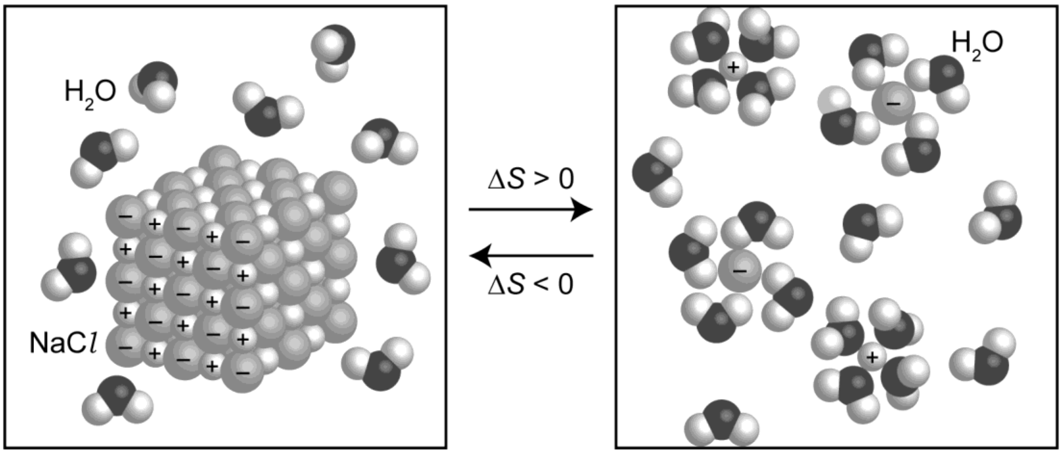
(c) Dissolution of an ionic solid

Two entropy terms operate when an ionic solid is dissolved in water:

- Entropy **increases** because the **ions in the solid** are **free to move in solution**.
- Entropy **decreases** because **water molecules** that were originally free to move become more **restricted in motion** as they **arrange themselves around the ions**.

If the first factor is more significant, the overall entropy change **is positive**.

E.g. $NaCl(s) + aq \rightarrow Na^+(aq) + Cl^-(aq)$ $\Delta S > 0$



The solubility of a compound depends on both the enthalpy and entropy change of dissolution.

Checkpoints for Section 8

- To differentiate between a *spontaneous* reaction and a *non-spontaneous* reaction.
- To remember the definition for *entropy* (measurement of randomness or disorderliness in a system). Entropy increases when there are more ways in which the particles and their energies can be distributed.
- To predict whether entropy change, ΔS of a given reaction is positive (increase in disorderliness) or negative (decrease in disorderliness).
- To explain qualitatively the effect of ***temperature*** on entropy change, ΔS. For instance, when temperature increases, causing the energy content to increase, then entropy will increase because there is more energy to distribute and more ways to distribute the energy.
- To explain qualitatively effect of **change in phase** on entropy change, ΔS. For instance, entropy will increase from solid to liquid to gas because the level of disorderliness increases as gas particles are more randomly arranged than liquid and liquid particles are more randomly than solid particles.
- To explain qualitatively effect of **change in amount of gaseous particles** on entropy change, ΔS. If number of gaseous particles increase in the process, there are more gaseous particles and more ways to arrange the gaseous particles, level of disorderliness increases, hence, entropy increases.
- To explain qualitatively effect of **mixing** on entropy change, ΔS. For instance, when mixing of gaseous particles occurs with increase in volume to maintain constant pressure, then entropy will increase because there are more gaseous particles and more ways to arrange the gaseous particles, level of disorderliness increases, hence, entropy increases.

9 Gibbs Free Energy

**** NOT IN H1 Chemistry Syllabus**

Learning Outcome:

(j) state and use the equation involving *standard Gibbs free energy change of reaction,* $\Delta G^\ominus$: $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$
[the calculation of standard entropy change, $\Delta S^\ominus$, for a reaction using standard entropies, $S^\ominus$, is **not** required]

(k) state whether a reaction or process will be spontaneous by using the sign of $\Delta G^\ominus$

(l) understand the limitations in the use of $\Delta G^\ominus$ to predict the spontaneity of a reaction

(m) predict the effect of temperature change on the spontaneity of a reaction, given standard enthalpy and entropy changes

In thermodynamics, a **spontaneous** process is one that, *once started*, continues on its own *without* input of energy. A **non-spontaneous** process on the other hand, needs a *continual input* of energy.

This is somewhat different from the everyday usage of the term, in that a spontaneous process does not necessary *starts* on its own. For example, the combustion of petrol is a spontaneous process. However, in general, petrol does not catches fire and burn on its own in the presence of oxygen. This has to do with the **kinetics** aspect, *i.e.* the rate of a reaction, which you will learn under the topic of Chemical Kinetics later. A spark is required to ignite the petrol. However, once the petrol is ignited, it will carry on burning without the need for further input of energy.

We have seen earlier that both enthalpy and entropy changes have a part to play in determining whether a reaction will be spontaneous. To this end, the **Gibbs free energy**, G, is a useful concept that includes both enthalpy, H, and entropy, S, defined as $G = H – TS$.

A spontaneous process is one which results in a decrease, while a non-spontaneous process results in an increase, in the Gibbs free energy, G. In other words, the **Gibbs free energy change**, **ΔG**, is negative, for a spontaneous process, and *vice versa*. Therefore, one can use ΔG to determine the **spontaneity** of a process.

$$\boxed{\Delta G = \Delta H - T\Delta S}$$

Units of ΔG and ΔH : kJ mol^{-1} or J mol^{-1}
Units of ΔS : kJ mol^{-1} K^{-1} or J mol^{-1} K^{-1}
Units of T : K

$\Delta G < 0$ **(negative value)**	$\Delta G = 0$	$\Delta G > 0$ **(positive value)**
The reaction is **thermodynamically feasible** and said to be **spontaneous** or **exergonic**.	The system is at **equilibrium**. There is no net reaction in the forward or backward direction. *E.g.* $\Delta G = 0$ during melting and boiling at the melting point and boiling point, respectively	The reaction is **thermodynamically not feasible** and said to be **non-spontaneous** or **endergonic**. It is spontaneous in the **reverse** direction.

As a spontaneous process proceeds, the Gibbs free energy, G, decreases while the Gibbs free energy change, ΔG, becomes less negative, until equilibrium is established (*i.e.* ΔG becomes 0).

Similar to enthalpy and entropy changes, Gibbs free energy changes are frequently reported for substances under standard state (refer to section 1.3, page 5). The **standard Gibbs free energy change of reaction**, $\boldsymbol{\Delta G_r^\ominus}$, is the change in Gibbs free energy involved in a reaction, with all reactants and products in their **standard states**, at a specified temperature, usually at 298 K.

$$\boxed{\boldsymbol{\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus}}$$

$\boldsymbol{\Delta G_r^\ominus}$ can be used to predict the spontaneity of a reaction under **standard condition** (refer to section 9.1 below for a discussion on the limitations of the use of $\Delta G_r^\ominus$ to predict the spontaneity of a reaction).

More importantly, the **standard** Gibbs free energy change of reaction, $\Delta G_r^\ominus$, provides information on the **position of equilibrium** for the reaction, which you will learn under *Chemical Equilibria* later.

$\boldsymbol{\Delta G_r^\ominus < 0}$	$\boldsymbol{\Delta G_r^\ominus = 0}$	$\boldsymbol{\Delta G_r^\ominus > 0}$
The position of equilibrium lies to the side of the product, giving an equilibrium constant, $K_c > 1$.	The position of equilibrium does not favour either side, giving an equilibrium constant, $K_c = 1$.	The position of equilibrium lies to the side of the reactant, giving an equilibrium constant, $K_c < 1$.

9.1 Limitations in the use of $\Delta G^\ominus$ to predict spontaneity of a reaction

9.1.1 Standard states

Prediction on spontaneity using $\Delta G^\ominus$ is only valid assuming the reactants and products are in standard states. Although the *standard* Gibbs free energy change, $\Delta G^\ominus$, of a reaction may be positive, the Gibbs free energy change, ΔG, for the same reaction may become negative under non-standard conditions, and vice versa.

For example, consider the boiling of water : $H_2O(l) \rightarrow H_2O(g)$
$\Delta H^\ominus = +44.0$ kJ mol^{-1} and $\Delta S^\ominus = +118$ J K^{-1} mol^{-1}
At 298 K, $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus = +44.0\times10^3 - 298(+118) = +8.84$ kJ mol^{-1}
Hence water does not boil spontaneously under a pressure of 1 bar at 298 K. However, water can be made to boil at 298 K if the pressure is reduced sufficiently, such that ΔG becomes negative.

9.1.2 Temperature

From $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$, it can seen that the value of $\Delta G^\ominus$ changes with temperature, T. Using the same example of boiling water above, suppose we wish to boil water under standard condition,

$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus < 0$$

$$T > \frac{\Delta H^\ominus}{\Delta S^\ominus} = \frac{+44.0\times10^3}{+118} = 373 \text{ K}$$

Hence water can be made to boil under standard condition by heating it above 373 K (100 ºC).
Refer to section 9.4 on page 48 for more discussion on the effect of temperature on $\Delta G^\ominus$.

9.1.3 Kinetics considerations

The term **spontaneous** does **not** mean **instantaneous**. It is important to keep in mind that just because a reaction is spontaneous does not mean that it will occur at an observable rate.

While the Gibbs free energy change can be used to determine the spontaneity of a reaction, it does not take into account the **kinetics** of the reaction, that is, the **rate** at which the reaction takes place. The reacting species may have to overcome a large energy barrier (activation energy, E_a) before reaction can occur.

Some reactions are spontaneous (**thermodynamically favourable, ΔG** is negative) but happen very slowly (**kinetically unfavourable**). Examples of such reactions include rusting, and the conversion of diamond into graphite as shown below.

$$C(diamond) \rightarrow C(graphite)$$

Diamond is thermodynamically less stable (ΔG < 0) with respect to graphite. Hence, diamond can change to graphite without any need for extra energy to be supplied. However, due to the high activation energy for the reaction, diamond does not turn into graphite overnight. We say that diamond is kinetically stable.

9.2 Calculations involving standard Gibbs free energy change of reaction

Example 9A – Calculation of $\Delta G^\ominus$ from $\Delta H^\ominus$ and $\Delta S^\ominus$

Calculate the standard free energy change, $\Delta G^\ominus$, for the rusting of iron**.**

chemical reaction	**$\Delta H^\ominus$ / kJ mol^{-1}**	**$\Delta S^\ominus$ / J mol^{-1} K^{-1}**
$2Fe(s) + {}^{3}/_{2}O_2(g) \rightarrow Fe_2O_3(s)$	–825	–272

$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$$
$$= (-825) - 298(-\frac{272}{1000})$$
$$= \underline{\mathbf{-744\ kJ\ mol^{-1}}}$$

The units of $\Delta S^\ominus$ in **J mol^{-1} K^{-1}** must be converted to $\Delta S^\ominus$ in **kJ mol^{-1} K^{-1}**.

Temperature of standard free energy change when not specified, is **298 K** (25 ºC)

Since $\mathbf{\Delta G^\ominus < 0}$, the rusting of iron is **spontaneous** at 298 K (25 ºC) which is consistent with our observation.

Example 9B

Calculate the standard free energy change for the decomposition of **one mole** of sodium hydrogen carbonate.

chemical reaction	$\Delta H^\ominus$ **/ kJ mol^{-1}**	$\Delta S^\ominus$ **/ J mol^{-1} K^{-1}**
$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(g) + CO_2(g)$	+130	+335

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

$=$

For 1 mole of $NaHCO_3$, $\Delta G^\ominus =$

Since $\underline{\boldsymbol{\Delta G^\ominus > 0}}$, the decomposition of sodium hydrogencarbonate is **<u>non-spontaneous</u>** at 298 K (25 ºC). Based on our observation, we know that the decomposition will take place at **<u>higher temperature</u>**. At **<u>higher temperatures</u>** (in this case, T > 388 K such that $\Delta H^\ominus < T\Delta S^\ominus$), the magnitude of $T\Delta S^\ominus$ **<u>increases</u>**, making $\Delta G^\ominus$ **<u>negative</u>** and the reaction **<u>spontaneous</u>**.

Example 9C – Calculation of Δ*S* for phase change

Given the standard enthalpy change of fusion of ice (conversion of solid ice to liquid water) is +6.0 kJ mol^{-1}, calculate the standard entropy change which accompanies the melting of ice.

$$H_2O(s) \rightleftharpoons H_2O(l)$$

Since the freezing of water happens at equilibrium, $\Delta G^\ominus = 0$

$$\Delta H^\ominus - T\Delta S^\ominus = 0 \Rightarrow \quad \Delta S^\ominus_{\text{fus}} = \frac{\Delta H^\ominus_{\text{fus}}}{T_{\text{fus}}}$$

$$\Delta S^\ominus_{\text{fus}} = \frac{+6.0 \times 10^3}{273} = \underline{\mathbf{+22.0\ J\ mol^{-1}\ K^{-1}}}$$

$\Delta S^\ominus_{\text{fus}}$ is **<u>positive</u>**, which is expected when a solid melts to form a liquid since the particles is more disordered in the liquid state.

Self Check 9A

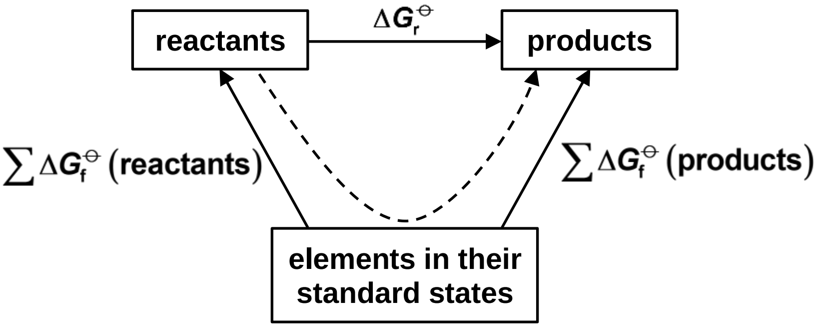
Given the standard enthalpy change of vapourisation of water is +44.0 kJ mol^{-1}, calculate the standard entropy change which accompanies the boiling of water: $H_2O(l) \rightleftharpoons H_2O(g)$
Comment on the difference in magnitude of $\Delta S^\ominus_{\text{vapourisation}}$ with $\Delta S^\ominus_{\text{fusion}}$ for water.

[+118 J mol^{-1} K^{-1}]

9.3 Calculations of $\Delta G_r^\ominus$ from $\Delta G_f^\ominus$

The **standard molar Gibbs free energy change of formation** is the free energy change that accompanies the formation of **one mole of a compound** from its elements in their standard state.

The **standard Gibbs free energy change of reaction** is the free energy change when the **amounts of the reactants shown in the stoichiometric equation** react under standard conditions to give products. The reactants and products must be in their **standard states**. The method of calculating Gibbs free energy change of reaction uses an energy cycle similar to the one used to calculate the enthalpy change of reaction.



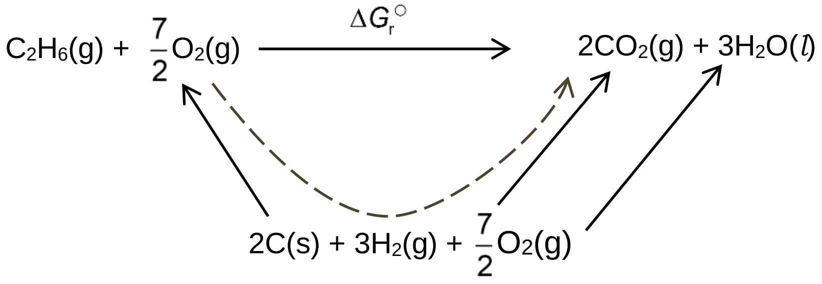
$$\Delta G_r^\ominus = \sum \Delta G_f^\ominus(\text{products}) - \sum \Delta G_f^\ominus(\text{reactants})$$

Example 9D

Calculate $\Delta G_r^\ominus$ for the reaction $C_2H_6(g) + 7/2\ O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$ using the data below.

$\Delta G_f^\ominus(C_2H_6(g)) = -32.9$ kJ mol^{-1}; $\Delta G_f^\ominus(CO_2(g)) = -394.4$ kJ mol^{-1};

$\Delta G_f^\ominus(H_2O(l)) = -237.2$ kJ mol^{-1}



$\Delta G_r^\ominus =$

9.4 Temperature dependence of $\Delta G^{\ominus}$

The term "$-T\Delta S^{\ominus}$" in the equation $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$ indicates that $\Delta G^{\ominus}$ is temperature-dependent. However, we can assume that **$\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ remain roughly constant** regardless of temperature and use them to calculate $\Delta G^{\ominus}$ at other temperatures.

This assumption is valid as shown in the following example involving reaction between hydrogen gas and chlorine gas at 298 K and 500 K.

	***T* / K**	**$\Delta H^{\ominus}$ / kJ mol^{-1}**	**$\Delta S^{\ominus}$ / J mol^{-1} K^{-1}**	**$T\Delta S^{\ominus}$ / kJ mol^{-1}**	**$\Delta G^{\ominus}$ / kJ mol^{-1}**
$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$	298	–184.6	+20.0	+6.0	–190.6
$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$	500	–185.6	+17.5	+8.8	–194.4

If we were to assume that $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ do not change with temperature, we can use the values of $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ at 298 K to calculate a value for $\Delta G^{\ominus}$ at 500 K as shown:

$$\begin{aligned}\Delta G^{\ominus}_{500\text{ K}} &\approx \Delta H^{\ominus}_{298\text{ K}} - 500 \times \Delta S^{\ominus}_{298\text{ K}} \\ &= -184.6 - 500 \times \frac{20.0}{1000} = -194.6 \text{ kJ mol}^{-1}\end{aligned}$$

This approximate value of $\Delta G^{\ominus}$ (–194.6 kJ mol^{-1}) is close to the actual value (–194.4 kJ mol^{-1}) obtained by using values of $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ at 500 K.

The assumption that $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ remain roughly constant is **not valid** if there is a **change in phase** of one of the reactants or products as the temperature is increased. Under these conditions, both $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ change significantly. For example, consider the synthesis of hydrogen iodide at 298 K and 500 K.

	***T* / K**	**$\Delta H^{\ominus}$ / kJ mol^{-1}**	**$\Delta S^{\ominus}$ / J mol^{-1} K^{-1}**	**$T\Delta S^{\ominus}$ / kJ mol^{-1}**	**$\Delta G^{\ominus}$ / kJ mol^{-1}**
$H_2(g) + I_2\mathbf{(s)} \rightarrow 2HI(g)$	298	+53.0	+166	+49.5	**+3.5**
$H_2(g) + I_2\mathbf{(g)} \rightarrow 2HI(g)$	500	–11.0	+18	+9.0	**–20.0**

As a result of the phase change in I_2 (from solid to gaseous), $\Delta G^{\ominus}$ changes from being slightly positive at 298 K to being very negative at 500 K. This means that the synthesis of HI is not spontaneous at room temperature but it becomes spontaneous if the temperature is raised above the boiling point of I_2.

Example 9E – Calculation of *T* at which a reaction becomes spontaneous

The standard enthalpy change of formation, $\Delta H_f^\ominus$, and the standard free energy change of formation, $\Delta G_f^\ominus$, of CO(g) and of CO_2(g) are as follows.

	CO(g)	CO_2(g)
$\Delta H_f^\ominus$ / kJ mol^{-1}	–110.5	–393.5
$\Delta G_f^\ominus$ / kJ mol^{-1}	–137.2	–394.4

(a) Calculate the standard entropy change of formation, $\Delta S_f^\ominus$, in J mol^{-1} K^{-1}, of CO(g) and of CO_2(g).

(b) Using the $\Delta H_f^\ominus$ values given and your answers in **(a)**, show that the reaction: $C(s) + CO_2(g) \rightarrow 2CO(g)$ is not spontaneous at 298 K and calculate the minimum temperature at which reaction becomes spontaneous.

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

$\Delta S_f^\ominus = [-110.5 - (-137.2)] \div 298 = +0.0896$ kJ mol^{-1} K^{-1} = **+89.6 J mol^{-1} K^{-1}**

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

$\Delta S_f^\ominus = [-393.5 - (-394.4)] \div 298 = +0.00302$ kJ mol^{-1} K^{-1} = **+3.02 J mol^{-1} K^{-1}**

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

$\Delta H_r^\ominus =$

$\Delta S_r^\ominus =$

At 298 K, $\Delta G_r^\ominus =$

Hence, reaction is

To be spontaneous, $\Delta G_r^\ominus < 0 \Rightarrow \Delta H_r^\ominus - T\Delta S_r^\ominus < 0$

$T > \Delta H_r^\ominus \div \Delta S_r^\ominus$

$T >$

Self Check 9B

1. The standard enthalpy and entropy changes for the thermal decomposition of sodium hydrogencarbonate are given below:

	$\Delta H^{\ominus}$ / kJ mol^{-1}	**$\Delta S^{\ominus}$ / J mol^{-1} K^{-1}**
$2NaHCO(s) \rightarrow Na_2CO_3(s) + H_2O(g) + CO_2(g)$	+130	+335

Calculate the temperature at which the decomposition becomes spontaneous. **[388 K]**

2. At temperatures below 13 ºC, shiny, ductile metallic tin, known as 'white tin' changes into a grey powder which is brittle.

	$\Delta H_f^{\ominus}$ /kJmol^{-1}	$S^{\ominus}$ / JK^{-1} mol^{-1}
white	0	51.4
grey	–2.09	44.1

What is $\Delta G^{\ominus}$, in J mol^{-1}, for the formation of grey tin from white tin at 12 ºC ?

[–9.50 J mol^{-1}]

9.5 Effect of Temperature on spontaneity of a reaction

For a reaction to be **spontaneous**, **ΔG** should be **negative**. We can use the equation $\Delta G = \Delta H - T\Delta S$ to predict the sign of ΔG (or $\Delta G^{\ominus}$, if under standard conditions) when temperature is varied (assuming ΔH and ΔS do not change with temperature)

There are four possibilities:

ΔH	**ΔS**	**ΔG (= $\Delta H - T\Delta S$)**	**reaction**
negative	positive	always negative (at all T)	spontaneous at **all** temperatures
positive	negative	always positive (at all T)	**non**-spontaneous at **all** temperatures
negative	negative	negative (at low T) if $\lvert\Delta H\rvert > \lvert T\Delta S\rvert$	spontaneous at **low** temperatures (reaction is enthalpy driven)
positive	positive	negative (at high T) if $\lvert\Delta H\rvert < \lvert T\Delta S\rvert$	spontaneous at **high** temperatures (reaction is entropy driven)

(1) ΔH negative and ΔS positive

These reactions are **spontaneous** (*i.e.* thermodynamically feasible) at **all temperatures** since $\Delta G < 0$ for all temperatures. A continuous input of energy from outside the system is not needed for such reactions.

type of reaction	example	$\Delta H^{\ominus}$ / kJ mol^{-1}	$\Delta S^{\ominus}$ / J mol^{-1} K^{-1}
organic combustion	$C_8H_{18}(l) + \frac{25}{2} O_2(g) \rightarrow 8CO_2(g) + 9H_2O(g)$	–5109	+238
decomposition of nitroglycerine	$2C_3H_5N_3O_9(s) \rightarrow 3N_2(g) + 6CO_2(g) + 5H_2O(g) + \frac{1}{2}O_2(g)$	–3617	+1840

(2) ΔH positive and ΔS negative

Reactions of this type are **non-spontaneous** (*i.e.* thermodynamically not feasible) and have to be driven as $\Delta G > 0$ for **all temperatures**. For example, energy (from the sun) must be continuously supplied for photosynthesis to take place.

type of reaction	example	$\Delta H^\ominus$ / kJ mol^{-1}	$\Delta S^\ominus$ / J mol^{-1} K^{-1}
photosynthesis	$6CO_2(g) + 6H_2O(l) \rightarrow C_6H_{12}O_6(s) + 6O_2(g)$	+2803	–225

(3) ΔH and ΔS both negative

These exothermic reactions are spontaneous at **low temperatures**.

When T is low, $|\Delta H| > |T\Delta S| \Rightarrow \Delta G\ (= \Delta H - T\Delta S) < 0$

type of reaction / process	example	$\Delta H^\ominus$ / kJ mol^{-1}	$\Delta S^\ominus$ / J mol^{-1} K^{-1}
precipitation	$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$	–65.5	–33.0
condensation	$H_2O(g) \rightarrow H_2O(l)$	–44.0	–118
freezing	$H_2O(l) \rightarrow H_2O(s)$	–6.0	–22.0

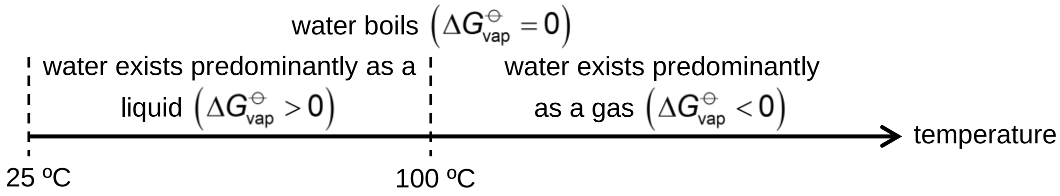
(4) ΔH and ΔS both positive

These endothermic reactions, which may not be spontaneous at room temperature, become spontaneous if the temperature is sufficiently **raised**.

When T is high, $|\Delta H| < |T\Delta S| \Rightarrow \Delta G\ (= \Delta H - T\Delta S) < 0$

type of reaction / process	example	$\Delta H^\ominus$ / kJ mol^{-1}	$\Delta S^\ominus$ / J mol^{-1} K^{-1}
melting	$H_2O(s) \rightarrow H_2O(l)$	+6.0	+22.0
boiling	$H_2O(l) \rightarrow H_2O(g)$	+44.0	+118
decomposition of Group 2 carbonate	$MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$	+100.3	+174
	$BaCO_3(s) \rightarrow BaO(s) + CO_2(g)$	+269.3	+172

At 25 ºC, $\Delta G^\ominus_{vap}(H_2O) = 44.0 - 298\ (118 \times 10^{-3}) = +8.84$ kJ mol^{-1} > 0. This means that boiling of water is non-spontaneous at room temperature which is consistent with our observation. When temperature is raised to 100 ºC, $\Delta G^\ominus_{vap} = 0$ which means liquid water and steam are in equilibrium. At temperatures above 100 ºC, $\Delta G^\ominus_{vap} < 0$ and hence the boiling of water is spontaneous.



Likewise, we observe that the decomposition of metal carbonate is non-spontaneous at room temperature but occurs at high temperatures. The decomposition of $MgCO_3$ is spontaneous above 576 K while the decomposition of $BaCO_3$ is spontaneous above 1566 K (Try to work out these temperatures using the data above). The difference in temperature at which decomposition occurs is due to $MgCO_3$ having less positive $\Delta H^\ominus$ than $BaCO_3$ while $\Delta S^\ominus$ is almost similar for both carbonates. Since decomposition becomes spontaneous when $\Delta G^\ominus < 0 \left(i.e.\ T > \frac{\Delta H}{\Delta S} \right)$, $MgCO_3$ has a lower decomposition temperature than $BaCO_3$.

By considering the bonding in the two compounds and the size of the cation, can you suggest a reason why ΔH of $MgCO_3$ is less positive than that of $BaCO_3$? *Hint: During decomposition, the covalent bond in the anion is weakened.*

Example 9F

For each of the following reactions, explain whether the reaction is spontaneous at all temperatures, at low temperature, at high temperature or non-spontaneous at all temperatures, **under standard conditions**. Predict how $\Delta G^\ominus$ will change with increasing temperature.

reaction	spontaneity of reaction under standard conditions	how $\Delta G^\ominus$ will change with increasing temperature
$2N_2O(g) + O_2(g) \rightarrow 4NO(g)$ $\Delta H^\ominus = +202.0\text{ kJ mol}^{-1}$	$\Delta S^\ominus$ is **positive** since there is an **increase** in number of moles of gas particles. Hence there are **more** ways to distribute the particles and their energies. $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$ $\Delta G^\ominus$ is **negative** when $\lvert \boldsymbol{T\Delta S^\ominus} \rvert > \lvert \boldsymbol{\Delta H^\ominus} \rvert$, *i.e.* when temperature is **high**. $\therefore$The reaction is **spontaneous** when temperature is **high**.	When temperature increases, $\boldsymbol{T\Delta S^\ominus}$ becomes **more positive**. $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$ Hence $\Delta G^\ominus$ becomes **more negative / less positive**.
$2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$ $\Delta H^\ominus = -196.1\text{ kJ mol}^{-1}$	$\Delta S^\ominus$ is __________ since there is an __________ in number of moles of gas particles. Hence there are _____ ways to distribute the particles and their energies. $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$ $\Delta G^\ominus$ is **negative** at ________________. $\therefore$The reaction is __________ at all temperatures.	When temperature increases, $\boldsymbol{T\Delta S^\ominus}$ becomes ______________________. $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$ Hence $\Delta G^\ominus$ becomes ______________________.
$3O_2(g) \rightarrow 2O_3(g)$ $\Delta H^\ominus = +285.3\text{ kJ mol}^{-1}$	$\Delta S^\ominus$ is __________ since there is a __________ in number of moles of gas particles. Hence there are _____ ways to distribute the particles and their energies. $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$ $\Delta G^\ominus$ is **positive** at ________________. $\therefore$The reaction is ________________ at all temperatures.	When temperature increases, $\boldsymbol{T\Delta S^\ominus}$ becomes ______________________. $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$ Hence $\Delta G^\ominus$ becomes ______________________.
$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ $\Delta H^\ominus = -197.8\text{ kJ mol}^{-1}$	$\Delta S^\ominus$ is __________ since there is a __________ in number of moles of gas particles. Hence there are _____ ways to distribute the particles and their energies. $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$ $\Delta G^\ominus$ is **negative** when $\lvert \boldsymbol{\Delta H^\ominus} \rvert > \lvert \boldsymbol{T\Delta S^\ominus} \rvert$, *i.e.* when the temperature is _____. $\therefore$The reaction is ___________ when temperature is _____.	When temperature increases, $\boldsymbol{T\Delta S^\ominus}$ becomes ______________________. $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$ Hence $\Delta G^\ominus$ becomes ______________________.

Checkpoints for Section 9

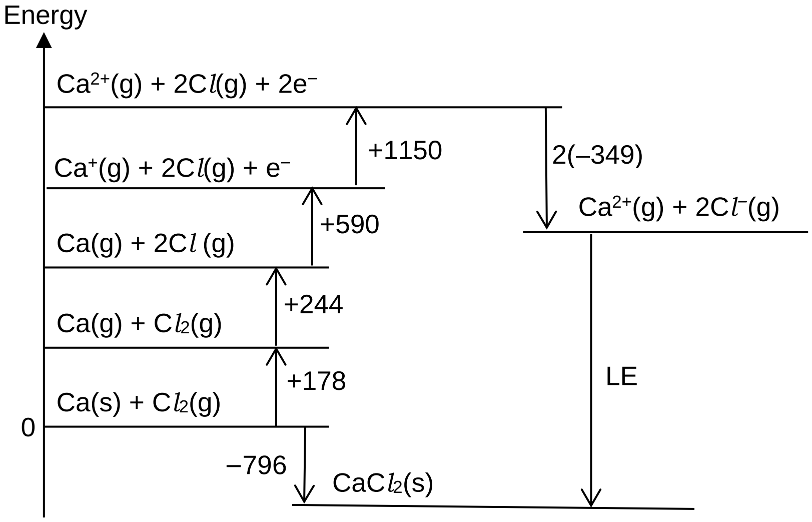
- Remember and know how to use the equation $\Delta G = \Delta H - T\Delta S$
- Know that negative sign for ΔG implies that the reaction/ process is spontaneous and vice versa.
- Know that $\Delta G^{\ominus}$ is a special case of ΔG, with all reactants and products in their **standard states**.
- Understand the limitations of $\Delta G^{\ominus}$ in predicting the spontaneity of a reaction, namely, standard states, temperature and kinetics considerations.
- Predict the effect of temperature changes on ΔG using the $\Delta G = \Delta H - T\Delta S$ equation assuming that ΔH and ΔS remains approximately constant over the range of temperature changes.

10 Summary Of Enthalpy Terms

standard enthalpy change, $\Delta H^{\ominus}$	**Definition** standard states: 1 bar (=10^5 Pa), 1 mol dm^{-3}	**exo / endo**
standard enthalpy change of reaction	the **energy** change when **molar quantities** of reactants as specified by the chemical equation react to form products, with all reactants and products in their **standard states**, at a specified temperature, usually 298 K.	exo / endo
standard enthalpy change of formation	the **energy change** when **1 mole of a substance in its standard state** is formed from its **constituent elements in their standard states**, at a specified temperature, usually 298 K.	exo / endo
standard enthalpy change of combustion	the **energy released** when **1 mole of a substance** is **completely burnt in excess oxygen**, with all reactants and products in their **standard states**, at a specified temperature, usually 298 K.	exo
standard enthalpy change of neutralisation	the **energy released** when **1 mole of water** is formed in the **neutralisation reaction between an acid and a base**, all in their **standard states**, at a specified temperature, usually 298 K.	exo
bond energy	bond energy is the **average energy required** to break **1 mole** of **a covalent bond** between two atoms in the **gaseous state**.	endo
standard enthalpy change of atomisation	(of element) the **energy required** to form **1 mole of gaseous atoms** from the **element**, all in their **standard states**, at a specified temperature, usually 298 K.	endo
	(of compound) the **energy required** to form **gaseous atoms** from the **1 mole of the compound**, all in their **standard states**, at a specified temperature, usually 298 K.	endo
lattice energy	the **energy released** when **1 mole of solid ionic compound** is formed from its **constituent gaseous ions**.	exo
(first) ionisation energy	the **first** ionisation energy is the **energy required** to remove **1 mole of electrons** from **1 mole of gaseous atoms** to form **1 mole** of **singly charged gaseous cations**.	endo
(first) electron affinity	the **first** electron affinity is the **energy change** when **1 mole of electrons** is added to **1 mole of gaseous atoms** to form **1 mole of singly charged gaseous anions**.	1st EA: exo 2nd EA onwards: endo
standard enthalpy change of hydration	the **energy released** when **1 mole of free gaseous ions in its standard state** is **dissolved in water** to give a solution of **infinite dilution**, at a specified temperature, usually 298 K.	exo
standard enthalpy change of solution	the **energy change** when **1 mole of substance in its standard state** is **completely dissolved in a solvent** to give a solution of **infinite dilution**, at a specified temperature, usually 298 K.	exo / endo

*Other enthalpy changes: enthalpy of fusion / enthalpy of vaporisation

ANSWERS TO SELF CHECK QUESTIONS

3A	Initial temperature = (25.0 × 30.0 + 25.0 × 29.8) / 50.0 = 29.9 °C $\Delta H_{\text{neut}} = -\frac{(25.0+25.0)\times 4.18\times(43.6-29.9)}{\frac{25.0}{1000}\times 2.0}$ = **-57.3 kJ mol^{-1}**
4A	$2C(s) + 3H_2(g) + \frac{1}{2}O_2(g) \rightarrow C_2H_5OH(l)$ $\Delta H_f^{\ominus}$ (ethanol) = 2(−394) + 3(−286) – (−1367) = **−279 kJ mol^{-1}**
4B	$\Delta H_f^{\ominus}$ (NH_4Cl) – (−46.1) – (−92.3) = −176.0 $\Delta H_f^{\ominus}$ (NH_4Cl) = **−314 kJ mol^{-1}**
4C	ΔH = BE (bonds broken) – BE (bonds formed) −434 = 4 BE(S−F) + 158 + (−6 BE(S−F)) BE(S−F) = **+296 kJ mol^{-1}** Assumption: All the S−F bonds (in SF_4 and SF_6) are equivalent.
6A	 LE = −2(−349) – 1140 – 590 – 244 – 178 −796 = **−2260 kJ mol^{-1}**
9A	Since the boiling of water happens at equilibrium, **$\Delta G^{\ominus} = 0$** $\Delta H^{\ominus} - T\Delta S^{\ominus} = 0 \Rightarrow \quad \Delta S^{\ominus}_{\text{vap}} = \frac{\Delta H^{\ominus}_{\text{vap}}}{T^{\ominus}_{\text{vap}}}$ $\Delta S^{\ominus}_{\text{vap}} = \frac{+44.0\times 10^3}{373}$ = **+118 J mol^{-1} K^{-1}** $\Delta S^{\ominus}_{\text{vaporisation}}$ is much more **positive** than $\Delta S^{\ominus}_{\text{fusion}}$ as the particles in the gaseous state is in a much more disordered state than in the liquid state. Hence there is a larger increase in the number of ways to distribute the particles and their energy when liquid water converts to steam.
9B	1. For the reaction to be spontaneous, $\Delta G < 0$ $\Delta H - T\Delta S < 0$ $130 - T(+335 \times 10^{-3}) < 0$ $T > \frac{130}{335\times 10^{-3}}$ = **338 K** Comment: Decomposition is favoured by high temperatures (T > 388 K). 2. $\Delta S^{\ominus}$ = 44.1 – 51.4 = −7.3 JK^{-1} mol^{-1} $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$ = −2.09 – (273 + 12) x (-0.0073) = −0.0095 kJ mol^{-1} = **−9.50 J mol^{-1}**